FROM STREAMS TO CITIZENS: A MULTI-LENS INVESTIGATION OF WATER QUALITY THROUGH CARBON CYCLES AND PARTICIPATION WITHIN WATER SCIENCE AND POLICY

by

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Abstract

Water management approaches that are scientifically sound and societally relevant are critical, given the myriad demands and threats posed to this resource and its necessity for environmental and human life. This thesis reflects the inherently complex and multifaceted nature of water management by investigating issues of water quality, as well as societal participation within science outlining the health of water resources, and policy that determines admissible human impacts.

First, the technical details of deploying in situ water quality monitoring networks are examined, given challenges of installing sensitive and costly sensors within remote and physically dynamic stream environments. A year of high frequency measurements explicates the necessity of measuring concentrations at adequate time intervals to accurately calculate fluxes of dissolved organic carbon (DOC).

Secondly, these spectrophotometric approaches were used to investigate how forest harvest affects in-stream DOC biogeochemistry within a small headwater stream on Vancouver Island, British Columbia. Forest harvest has a large impact on catchment biogeochemistry and hydrology. Harvest increases DOC concentration and flux within the stream. It also alters the chemical composition of DOC, signifying impacts on the catchment scale mechanisms by which DOC is created and transported.

Thirdly, the impacts of citizen participation on scientific data outcomes within the burgeoning field of citizen science are detailed. Six critical lessons learned were distilled from a citizen science water quality monitoring program (concerning DOC concentration and characteristics). Scientific data was used alongside qualitative vignettes to explicate the importance of citizen perspectives, contextual knowledge, and motivations for involvement on critical data outcomes.

Lastly, the process and outcomes of public participation through consultation in the creation of provincial-level water policy are discussed. The extensive public consultation process undertaken during the modernization of BC's Water Sustainability Act was used to examine what was expressed during consultation, and how this compared to the contents of the Act. Differences between consultation outcomes and Act contents (especially related to water allocation) bring to bear questions regarding the function of consultation within participatory policy processes, including how consultation was (and should be) used, and the possible influence of elite groups.

Preface

Chapter Two is based on work conducted on a long-term monitoring site initially designed by Dr. Mark Johnson, and implemented by Dr. Mark Johnson and collaborators, including significant technical and scientific contributions from Iain Hawthorne. From 2010-2014, I was responsible for the function and operation of sensors and sampling associated with the study of dissolved organic carbon (DOC). I was responsible for data analysis. Chapter 2 was primarily written and drafted by myself, with contributions from Iain Hawthorne and Dr. Johnson through subsequent revisions. A version of Chapter Two has been published as:

Jollymore, A., Johnson, M. S., and Hawthorne, I. 2012. "Submersible UV-Vis Spectroscopy for Quantifying Streamwater Organic Carbon Dynamics: Implementation and Challenges Before and After Forest Harvest in a Headwater Stream." Sensors, 12(4). 3798–3813. doi:10.3390/s120403798

Chapter 3 also draws on data collected from the field site discussed in Chapter 2. Laboratory analysis of water samples, including absorbance and fluorescence spectrophotometry as well as ion chromatography, was my primary responsibility. I was responsible for data analysis, as well as drafting and writing the chapter, with critical feedback from Dr. Johnson through drafting the chapter and subsequent drafts. Also connected to this chapter is Appendix C, regarding soil characteristics at the same site. I designed the research, and was primarily responsible for sample collection and analysis; I also analyzed data and wrote the corresponding section.

Chapter 4 is based on a citizen science project by Morgan Haines, Dr. Terre Satterfield, Dr. Mark S. Johnson, and myself. I was primarily responsible for research design, implementation and outreach, and sample analysis, with much contribution from Morgan Haines and Dr. Johnson. I was responsible for data analysis. I composed the initial chapter draft with Dr. Mark S. Johnson, Dr. Karen Bartlett, and Dr. Terre Satterfield, with comments through

subsequent drafts from Dr. Johnson, Morgan Haines, and Dr. Satterfield. A version of this manuscript has been submitted to the Journal of Environmental Management (January 2017) as:

Jollymore, A, Haines, M, Satterfield, T, and Johnson, M. S. 2017. Citizen science for water quality monitoring: Implications of citizen perspectives and context for data quality. Journal of Environmental Management (manuscript submitted, January 2017)

Chapter Five is based on a project done collaborative by myself, Kiely McFarland, and Dr. Leila Harris. This work was supported financially through the Water Economics Policy and Governance Network (SSHRC grant 895-2011-1029). Ms. McFarlane, Dr. Harris and myself collaboratively designed the research program. All data analysis was split between Ms. McFarland, and myself with contributions from Aisha Udman during the primary coding of submissions. Ms. McFarland and I wrote the chapter draft together, with much feedback from Dr. Harris upon composition and through subsequent drafts. A version of this chapter is accepted for publication (January 2017) in Critical Policy Studies as:

Jollymore, A., McFarland, K.,* and Harris, L. 2017 "Whose input counts? Evaluating the process and outcomes of public consultation through the BC Water Act Modernization" Critical Policy Studies. pp 1- 25 *Both authors contributed equally*

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List of Abbreviations

OM – Organic matter

DOC – Dissolved organic carbon

DIC – Dissolved inorganic carbon

TOC – Total organic carbon

DBPs – Disinfection by-products

EEMs – Excitation-emission matricies

PARAFAC - Parallel factor analysis

PCA – Principal component analysis

$SUVA_{254}$ – Specific absorbance at 254 nm normalized by DOC concentration

abs_{254} – Absorbance at 254 nm

SR – Slope ratio

FI – Fluorescence index

HIX – Humification index

FrI – Freshness index. Also called BIX (biological index)

RU – Raman units

IC – Ion chromatography

EC – Electrical conductivity

DO – Dissolved oxygen

ORP – Oxygen reduction potential

WSA – Water Sustainability Act (British Columbia)

WAM – Water Act Modernization process

BC – British Columbia

WSOM - Water-soluble organic matter

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I would firstly like to thank Dr. Mark Johnson for his supervision during my time as a student. I greatly appreciate his willingness to think outside the box, as well as the latitude that he gave me to pursue my meandering interests. I also owe a debt of gratitude to my committee, Dr. Terre Satterfield and Dr. Karen Bartlett for their time and invaluable feedback over the years. I also thank Dr. Troy Vassos for his time and contributions early within this process. I'm truly humbled by the insight and intelligence embodied within this committee, and am enormously grateful for the opportunity to learn and work closely with them all.

Being a student within the Institute for Resources, Environment and Sustainability (IRES) has been an incomparable opportunity to work within an exceptionally passionate, incredibly talented, and intelligent group of people (both within the student and professor populations). It's been an incredible experience. I'd also like to thank the IRES administration for their continual support. The opportunity to dedicate years necessary to this thesis would have been impossible without the financial support through NSERC, the Four Year Fellowship program, and Water Economics Policy and Governance Network (SSHRC grant 895-2011-1029). I'd like to thank members of the Ecohydrology group, both past and present, for their friendship, collaboration and camaraderie. I'd like to specifically mention Iain Hawthorne, Angela Eykelbosh, Laura Morillas, Alicia Speratti, Cam Webster, Ryan Davis, and Silja Hund; I'm grateful to have had the opportunity to work with you all.

I would also like to thank those that I've worked with directly beyond those mentioned above. Firstly, it was truly a pleasure and rare opportunity to work closely with Kiely McFarland and Dr. Leila Harris – I learned a great deal from their expertise and vast knowledge. I'd also like to thank Dr. Andy Black and the Biometeorology group at the University of British Columbia for

the opportunity to work at their HDF11 site. Thank you to Dr. Hongbin Li for the many lessons. Lastly, thank you to the many summer students and interns who have dedicated their time and energy within the various projects that I've been lucky to be a part of during my tenure as a PhD student.

I'd also like to thank the many people and organizations outside of the university environment that has made it possible to use the experience of research to engage with the community. This includes: Evergreen (Dana McDonald), Dr. Maureen Connelly (BCIT), the Resort Municipality of Whistler, the Pacific Streamkeepers Federation, the North Shore Wetland Partners, Silver Creek Streamkeepers, the City of Burnaby, the Municipality of Bowen Island, and the Galiano Conservancy Association (Ken Millard).

Lastly, I'd like to thank the amazing support network of friends and family I've relied on through this process. These people have given more in friendship and support than I can express or pay back, for which I am infinitely grateful. I promise that I'll be more fun now. I'd like to especially thank my family – my parents, my sister, as well as my truly wonderful extended Jollymore/Bichler family - for their continued support. Thank you for not only understanding the winding path that I've taken, but for helping me to see the joy in it. I'd also like to especially thank my Paul - I truly couldn't have made it through graduate school (either time) without your unwavering support, patience and understanding. Thanks for getting why this was so important to me.

Dedication

To my Paul, my parents and sister, and the Jollymores.

Chapter 1: Introduction

1.1 Thesis context and rational for interdisciplinary perspectives

Water is both a critical and unique resource, given that both environmental and human health is unassailably dependent on water of sufficient quantity and quality. Water quality describes the chemical, physical and biological characteristics of water; such features are an expression of the complex interplay between natural and human variables articulated over a wide range of spatial and temporal scales (Pike et al. 2010). This includes hydrologic, ecologic and anthropogenic factors that all contribute towards the availability and quality of surface water such as streams, rivers and lakes. Issues of water management and decision-making around water quality and quantity are multifaceted and complex. The complexity reflects the interplay between natural and anthropogenic cycles, as well as the uncompromising need for water of sufficient quality for human and environmental health. To this complexity are the tensions inherent within the sundry, sometimes conflicting demands for water. Human uses of water, as well as unintended impacts on natural water processes deriving from human activities, can have large and adverse affects on both water quality and quantity. Thus, the challenge within water resource management is to understand natural cycles driving water quality, how human activities impact such cycles, as well as societal dimensions of how to best manage such resources, given myriad human and environmental demands.

1.1.1 Water quality as an inherently interdisciplinary issue

Natural factors driving water quality include climate, ecology, plant cover and species, geology and hydrology (how water moves through a landscape). These natural dynamics act on scales varying from regionally to globally, and are ultimately expressed water availability and quantity within different contexts. Anthropogenic factors can alter these cycles through long-term, slow

moving factors (such as climate change), more directly through changes in land use and cover, and also directly, such as through impoundment and pollution. Outlining how complex natural cycles are manifest through water availability and quality is a key scientific challenge, and also critical for managerial approaches that ensure water of adequate quality and availability for both human and environmental well-being.

Scientific knowledge regarding water quality, including biogeochemical and hydrologic mechanisms, can and should inform a greater societal understanding of how to best plan and use such resources. This includes the link between societally acceptable uses, and how science can inform water-relevant policy. There is much opportunity within such intersections. This includes using natural science as a tool for societal engagement to underline the importance of anthropogenic impacts on aquatic environments, a view that is increasingly prevalent within scientific investigations across many types of environmental issues (Allen 2004; Brossard, Lewenstein, and Bonney 2005; Devictor, Whittaker, and Beltrame 2010). Such engagement can include aspirations for bringing scientific understanding regarding water resources to bear within relevant policy delineating water resources (Jepson and Canney 2001; Jepson and Canney 2003; Devictor, Whittaker, and Beltrame 2010).

Approaches that bridge multiple disciplines are thus necessary in order to undergird scientific knowledge with potential for societal impact, as well as better understand the complex natural and anthropogenic systems that drive water resources. The need for such interdisciplinary approaches is pervasive throughout the water management literature:

> *"Any analysis is an exercise in the drawing of boundaries, and the boundaries for some subjects – particularly environmental-related issues – are more porous and artificial than others. Most experts working on water issues… would agree that an integrated approach, although difficult, is absolutely necessary, given that water is*

a multi-purpose resource that is essential for life … linking complex social and technical systems." (Bakker et al., 2011)

This progression towards interdisciplinary approaches is apparent within a number of frameworks that merge and blur distinctions between scientific disciplines to provide a more comprehensive understanding of water quality impacts. The emergent discipline of ecohydrology is an example of the increased use of multi-disciplinary approach. This lens merges elements of ecology and hydrology to interactions between biota (including microbes, as well as flora and fauna) and water movement, availability and quality. Recent iterations of ecohydrology also integrate institutional and cultural demands and impacts on water resources, combining biophysical processes with anthropogenic needs and impacts; for example, Pataki et al. (2011) used socio-ecohydrology to outline hydrologic cycles within highly managed urban landscapes, including evapotranspiration of different planting and irrigation schemes. The proliferation of these multi-disciplinary attempts at evaluating issues of water allocation and quality reflect the complex, multidisciplinary nature of water issues.

1.1.2 Study objectives

This study uses a multi-disciplinary methodology to explore several key issues within water quality and management in British Columbia, Canada, based on the premise that scientific understandings regarding water require approaches that span water resource monitoring and greater societal engagement.

This thesis addresses four specific research questions within four experimental chapters:

1. What are the advantages and technical challenges of implementing in situ water monitoring networks?
2. How does forest harvest affect the concentration and general mechanisms driving dissolved organic carbon within small, headwater streams?

3. How do citizen perspectives affect data outcomes of a water quality monitoring program that uses citizen science to investigate in-stream DOC concentration and characteristics?
4. How is public participation garnered through consultation used within the formation of water policy, and what does this mean for consultation as a form of participatory democracy?

Two themes emerge from these research questions (Figure 1.1). The first theme regards how human activity (specifically, forest harvest) alters biogeochemical cycles of carbon within coupled terrestrial-aquatic systems, and how this is expressed through changes in water quality (questions 1, 2 and 3). The second theme concerns engagement and participation within water sciences and relevant policies that ultimately determine how humans interface with water resources within British Columbia (research questions 3 and 4).

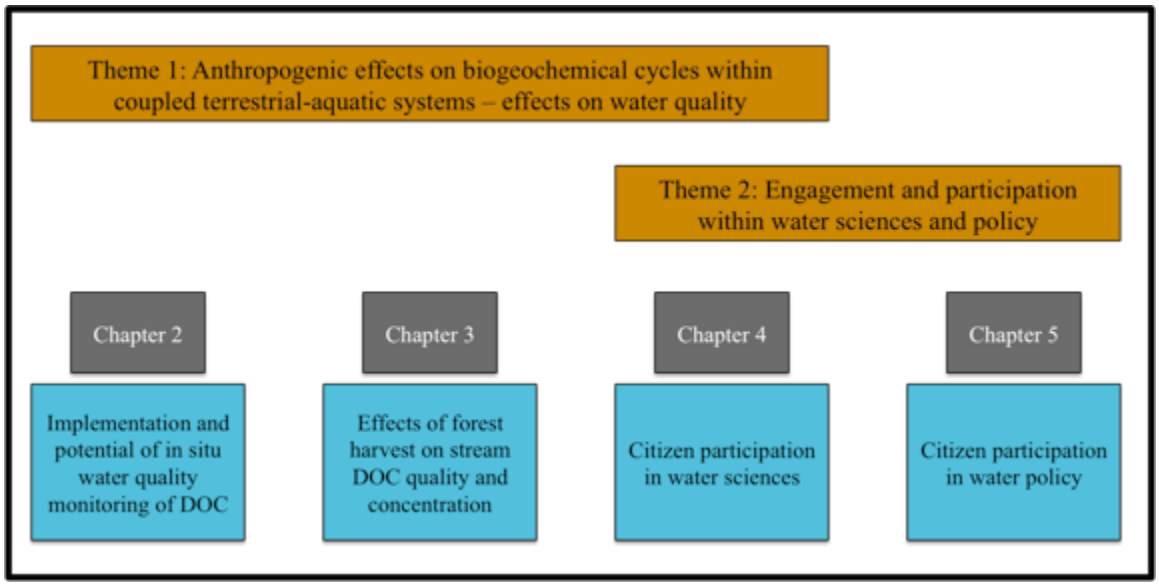

Figure 1.1 Thesis overview.

1.1.3 Introduction overview

This introduction provides background literature underpinning each of the research questions (Chapter 1.2). It begins with an overview of biogeochemical processes driving in-stream organic

matter quality that undergirds Chapters 2, 3 and 4, and ends with pertinent literature regarding engagement and participation within water sciences (relevant to Chapter 4) and policy (Chapter 5). Increased detail regarding biogeochemical processes driving in-stream organic matter is presented to provide necessary context regarding these complex mechanisms. The second portion of this introduction (Chapter 1.3) provides a detailed overview of each of the four research questions, as embodied within four experimental chapters.

1.2 Water quality as an expression of biogeochemical and hydrologic cycles - Chapters 2, 3 and 4

The impact of human activity on the biogeochemical cycling of carbon between terrestrial ecosystems (specifically the soil) and aquatic environments is the premise for Chapters 2 and 3, and the citizen science program discussed in Chapter 4. A generalized relationship between paired aquatic-terrestrial environments, as well as how such relationships are impacted by forest harvest, is thus presented as background for these chapters.

Carbon cycling refers to the recirculation of carbon between inorganic and organic forms across a variety of ecosystems and environments. These biogeochemical transformations can have large effects on freshwater quality, although much more attention is cast to the atmospheric component of carbon cycles, given climate change implications. Hydrologic cycles of water through groundwater, as well as surficial networks such as streams, rivers and lakes, serve to both transport and generate ecologically relevant, carbon-containing moieties. The portion of the carbon cycle relevant to freshwater quality begins when plants fix atmospheric carbon dioxide during photosynthesis. Plant biomass ultimately becomes a part of the soil, whereupon soil microbes begin to metabolize biomass carbon into volatile and stable forms. Stable types of

carbon (including recalcitrant forms of plant biomass, as well as microbial extrudates) can either remain within the soil, or be transported to aquatic environments through the movement of water. This process results in a global store of carbon within soils exceeding that within vegetation and the atmosphere combined, illustrating the importance of soil carbon dynamics in understanding global carbon cycles (Lehmann and Kleber 2015). Additionally, soils are also the dominant source of dissolved organic carbon (DOC) in surface waters within forested catchments (Richardson, Bilby, and Bondar 2005), the focus of water quality investigations in this thesis.

Soil characteristics important to freshwater carbon export include parent material features (such as mineral composition and porosity) that derive from factors such as geology, topography, and climate that act over long time scales. Biotic components, most critically the composition and intensity of vegetative cover, also impacts carbon-relevant soil characteristics. Within forested catchments, tree and sub-canopy biomass contributes organic matter to the soil through root extrudates, as well as through the support of complex mycorrhizal networks; such networks act as a subterranean support and communication network between trees. This dynamic soil matrix is also inhabited by a large variety of microbial species that add subsequent organic matter through activities including the breakdown of plant biomass. The composition and complexity of biological components within terrestrial systems - including microbial and plant communities - is ultimately dictated by climate; specifically, temperature, and the frequency, duration, form, and volume of precipitation.

The complex soil environment milieu results in the presence of a wide variety of carbon-containing forms of soil organic matter. Certain forms of soil organic matter may be subsequently transported to surface water sources by the movement of water through soil (depending on characteristics such as solubility). Surficial flows of water through the soil (water

that flows at or close to the surface of the soil) include surface and subsurface flows that pass through soil horizons typically enriched with organic matter. Deeper pathways include baseflow, which exhibit much longer residence times within the catchment relative to surficial flows. These various hydrologic pathways can transport elements – such as carbon and nutrients, as well as sediment and woody debris – from the soil and into surface water sources, depending on hydrologic connections. In addition to receiving soil carbon, aquatic environments can also act as sites of transformation for elements like carbon and nutrients. For example, soil organic matter from plant biomass, microbial metabolism, and root extrudates can be subsequently transformed through microbial degradation and growth of biomass within the aquatic environment.

Aqueous forms of organic matter are functionally compartmentalized according to size, solubility and biological availability (Figure 1.2). The distinction between dissolved and particular forms is made according to forms of organic matter that will pass through a 0.45 μm filter; that which passes through is referred to as the dissolved fraction. Many studies use 0.70 μm as an operational cut off due to the availability of carbon-free glass fibre filters at this pore size (cellulose filters are available at 0.45 μm, but are not carbon-free). This dissolved fraction is composed of both organic (DOC) and inorganic (DIC) forms. DIC includes CO_2, bicarbonates and carbonates within the aquatic environment. Alternatively, DOC describes a diverse range of carbon-containing chemicals that constitute an extensive range of biological lability. This heterogeneous DOC fraction is important to stream and ecosystem biogeochemistry, as it is the dominate form of organic matter within streams and rivers in the Pacific Northwest (Richardson, Bilby, and Bondar 2005), a primary measurement of total dissolved organic matter within natural waters (e.g., Thurman 2012), and a critical water quality component within forested catchments (Leenheer and Croué 2003; Cory, Boyer, and McKnight 2011).

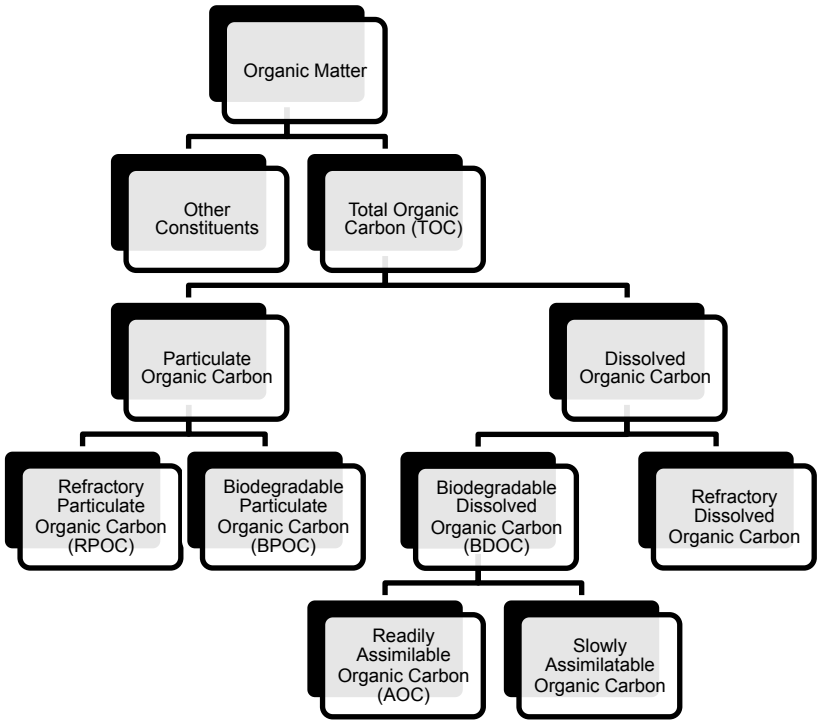

Figure 1.2 Classification of organic matter on the basis of physical properties. Organic matter is classified through physical properties including size and biological lability.

Dissolved organic matter plays multiple important roles within the ecology and energy balance of streams, rivers and lakes. Firstly, DOC represents a major portion of the carbon and energy cycled within forested catchments (Fisher and Likens 1973; Mulholland 1997). Chromophoric DOC forms, including humic DOC, can absorb visible and UV wavelengths within sunlight, thus controlling the amount of light and energy entering the aquatic environment. Sunlight can also spur the photochemical degradation of DOC to various end products (Scott et al. 2003; Porcal, Hejzlar, and Kopácek 2004; Cory et al. 2007; Yoshioka et al. 2007). Labile or bioavailable forms of DOC fuel microbial growth (Berggren, Laudon, and Jansson 2007; Pataki et al. 2011), which underpins the food web of aquatic ecosystems (Carpenter et al. 2005), and therefore the metabolism of streams in environments ranging from high latitude boreal forests (Naiman et al. 1987), to temperate rainforests (Roberts, Mulholland, and Hill 2007). Humic DOC

fractions can mobilize and transport potentially harmful trace metals and contaminants (such as mercury) by chelating and increasing the solubility of such substrates (McKnight et al. 1992; Haitzer et al. 2002; Ravichandran 2004). Humic DOC can also act as an electron shuttle, participating in aqueous redox reactions and energy transfer through hyporheic exchange (Miller, McKnight, and Cory 2006); such humic DOC forms can also contribute to stream acidity (McLaughlin and Liu 1996; Hruška et al. 2003).

In-stream DOC characteristics can also impact human health when water is used for drinking water, providing one of the central motivations for undertaking thesis research on this topic. Specifically, DOC can react with disinfection agents such as chlorine and DOC during municipal water treatment, resulting in the formation of potentially harmful disinfection by-products (DBPs). The pathogenic organisms that these disinfection agents remove from drinking water present a large and acute risk to human health; however, these disinfection processes also form DBPs that have the potential for adverse health impacts, especially given the potentially long period over which individuals are exposed.

DBPs describe a wide range of compounds comprised of organic matter in some combination with chlorine, chloroamine, chlorine dioxide or bromine. Currently, the concentration of DBPs in the water supply of most developed nations is controlled owing to concerns over the effect of these compounds on health. Exposure to different DBPs may occur through oral, dermal and inhalation routes. Most toxicological studies focus solely on exposure through water consumption, where epidemiology studies have suggested a causal link between injestion of DBPs within drinking water and certain types of cancers, predominantly bladder and colon cancers (King and Merrit 1996; Cantor et al. 1998; Villanueva and Cantor 2004; Villanueva et al. 2006; Bove et al. 2007; Rahman et al. 2010). Many species of DBPs (such as

chloroform) are volatile and likely to be quickly off-gassed from water, making it likely that such studies underestimate total exposure to DBPs. Indeed, inhalation of DBPs during activities such as bathing and showering are the predominant exposure route for most individuals within developed nations (Baker and Ashley 2000). Inhalation of DPBs has been linked to respiratory ailments such as asthma in studies that investigated exposure through use of chlorinated swimming pools, which produce high concentrations of airborne DBPs (Bernard et al. 2005; Li and Blatchley 2007; Glauner and Frimmel 2007; Richardson et al. 2010). Previous studies have also shown that pregnant woman may be particularly vulnerable to DBPs exposure, although the connections between exposure to these compounds and adverse reproductive outcomes (such as low birth weight, urinary tract anomalies and pregnancy loss) remains unclear (Nieuwenhuijsen et al. 2000; Graves et al. 2001; Savitz et al. 2006).

Assessing the risk that DBPs pose to health remains an active area of reseach. This includes analytical approaches for quantifying previously identified and emergent DBPs species, understanding connections between DOC precursors and DBPs formation (as well as formation kinetics within various treatment systems), as well as understanding risk of exposure, including toxicological profiles of different species and accurately quantifying total exposure over multiple exposure routes and time. This also includes understanding the role that source water quality plays within DBPs formation, and how natural processes determine the potential for DBPs formation in waters used for human consumption.

1.2.1 DOC transport from forest soils to aquatic systems

Most of the DOC within surface waters in forested catchments is transported from the soil into the aquatic system through hydrologic pathways, and is thus allochlonous in character (Degens and Kempe 1991). This connection between terrestrial and aquatic environments is particularly

evident within headwater streams (Kaushik and Hynes 1971; Hynes 1975; Kreutzweiser, Hazlett, and Gunn 2008). DOC transport into headwater streams is thought to be dominated by the 'transmissivity feedback' mechanism (Bishop, Seibert, and Köhler 2004). In this, soil DOC is transported from terrestrial to aquatic environments by the lateral flow of saturated soil water, which rises to superficial layers during high flow conditions (Kendall, Shanley, and McDonnell 1999; Bishop, Seibert, and Köhler 2004). Beyond this mechanism (which is driven by the position of the groundwater table), stream DOC is affected by both soil variables (Schelker, Grabs, et al. 2013) and air temperature (Boyer, Hornberger, and Bencala 1996; Sebestyen, Boyer, and Shanley 2008; Kohler et al. 2009). Aspects related to soil properties are particularly important to in-stream DOC concentrations and characteristics. Such factors including soil carbon concentrations, catchment slope, and drainage intensity (Ludwig, Probst, and Kempe 1996). Additionally, the presence and condition of wetland soils is particularly pertinent in determining in-stream DOC concentration, as riparian wetland soils tend to be enriched in DOC (Ågren et al. 2010; Haei et al. 2010; Lehmann and Kleber 2015). DOC can also be produced within the aquatic environment itself (autochthonous DOC). This processing can include the removal of labile DOC fractions, either through the direct uptake of DOC by stream biota through respiration (Berggren et al. 2007), or by processing within the hyporheic zone (Zarnetske and Haggerty 2011). Autochthonous processing of DOC within first-order streams typically constitutes a small overall percentage of the DOC fraction. However, in-stream processing – including losses of DOC through sedimentation (Cole, Carpenter, and Kitchell 2002; Ask, Karlsson, and Jansson 2012), and photosynthetic production within nutrient-rich, eutrophic environments (Henderson et al. 2008) – can significantly impact DOC biogeochemistry within downstream river and lake networks.

1.2.2 DOC is delivered to stream environments via a variety of flowpaths

Variables controlling catchment hydrology are critical in determining in-stream DOC conditions, given that DOC in forested streams is dominated by terrestrial (allochthonous) rather than aquatic (autochthonous) DOC. These hydrologic pathways are highly dynamic, and vary across different watershed ecosystems, as well as temporally within the same environment. Temporal variations in stream DOC within a particular catchment (including concentration and chemical composition), arise from hydrologic engagement with different soil types and horizons, which can vary widely across longitudinal, lateral and vertical dimensions within the terrestrial environment (Covino 2016). Hydrologic connectivity between different areas within a watershed and the stream are also sensitive to temporal perturbations depending on climatic conditions and watershed morphology; this results in changeable connections between landscape sources of DOC to surface waters (Hewlett and Hibbert 1967). These includes shallow subsurface hydrologic pathways integrating near-surface soil horizons that tend to have higher concentrations of organic matter and nutrients, such as DOC and nitrogen (Bishop, Lundström, and Giesler 1993; Hornberger, Bencala, and McKnight 1994; Boyer and Hornberger 1995; Creed and Band 1998; Pacific, Jencso, and McGlynn 2010). Catchment variables related to hydrologic connectivity and flow within a landscape – including slope and drainage intensity – thus have a strong relationship to DOC fluxes observed within surface waters (Ludwig et al. 1996). Biotic factors are also important to these hydrologic flowpaths; specifically, plant biomass is the ultimate source of terrestrial DOC, and plants can also alter hydrologic flowpaths such as through the evapotranspiration of groundwater. DOC dynamics within streams are thus an ecohydrologic reflection of terrestrial-aquatic systems coupled though hydrology, and highly influenced by

watershed-scale biological activity. These drivers and relationships are especially critical in the context of possible disruptions, such as forest harvest and other land use changes.

However, few studies have successfully extrapolated behaviour observed within one catchment to diverse ecosystems (Strohmeier et al. 2013), making it difficult to generalize such mechanisms between contexts.

1.2.3 Human effects on biogeochemical DOC cycles through changes in land use

Anthropogenic factors can affect how much and what types of carbon are present within water. Human activity can affect biogeoclimatic cycles by altering climate, vegetative cover, and movement of water through soil (for example, through changes to soil porosity and permeability characteristics). Changes in land use can have large impacts on the ecologic and hydrologic determinants of organic matter composition and concentration. Unlike degradation of water quality due to pollution, water quality impacts associated with land use are typically diffuse over a large geographical area (i.e., non-point source pollution). Understanding such impacts across wider spatial scales, while also compensating for the multiple uses and impacts typically present within a watershed, makes it challenging to characterize the cumulative impacts upon water quality. This complexity stems from spatial variability, geographical size and combinations of land uses, as well as the time period over which human and natural events can affect hydrologic mechanisms. However, changes in land use are particularly pertinent for investigating human effects on biogeochemical cycles and corresponding effects on water quality, given the prevalence and intensity of human activities within catchments globally.

1.2.4 Justification for examining forest harvest impacts to organic matter cycles

Forest harvest is a particularly pertinent form of land use/land cover change within British Columbia. Forests comprise the predominant physical geography of British Columbia. Almost

60% (55 million ha) of British Columbia's land base (95 million ha) is classified as forest, only 14% of which are located in protected areas (Ministry of Forests, 2010). The majority of forests in British Columbia (52 million ha) are crown land, only three million ha of which are privately held. Approximately 22 million hectares of crown forest is subject to forest management agreements, and thus considered the land base for timber harvest (Ministry of Forests, Lands and Natural Resource Operations, 2015). Yearly harvest has varied between 125,000 – 225,000 hectares since 1990 (Figure 1.3), the majority of which is harvested through clearcutting, rather than more selective (and less invasive) methods such as patch cutting, commercial thinning, or clearcutting with reserves (National Forestry Database 2015). Despite possible deleterious environment impacts associated with forestry, it is a vital activity with deep economic, recreational and cultural roots within British Columbia. Forestry has long been an economic driver for the province; even through its economic importance has waned, forestry still provided 4% of the total provincial economic activity, 30% of total exports, and some 7% of provincial jobs in 2009 (Ministry of Forests, Lands and Natural Resource Operations 2010). Understanding the impact that harvest has on water quality within the British Columbia context is also important given the diversity of uses present within catchments beyond forest harvest. For example, approximately 80% of water for municipalities in the province is drawn from forested watersheds (Parfitt 2000).

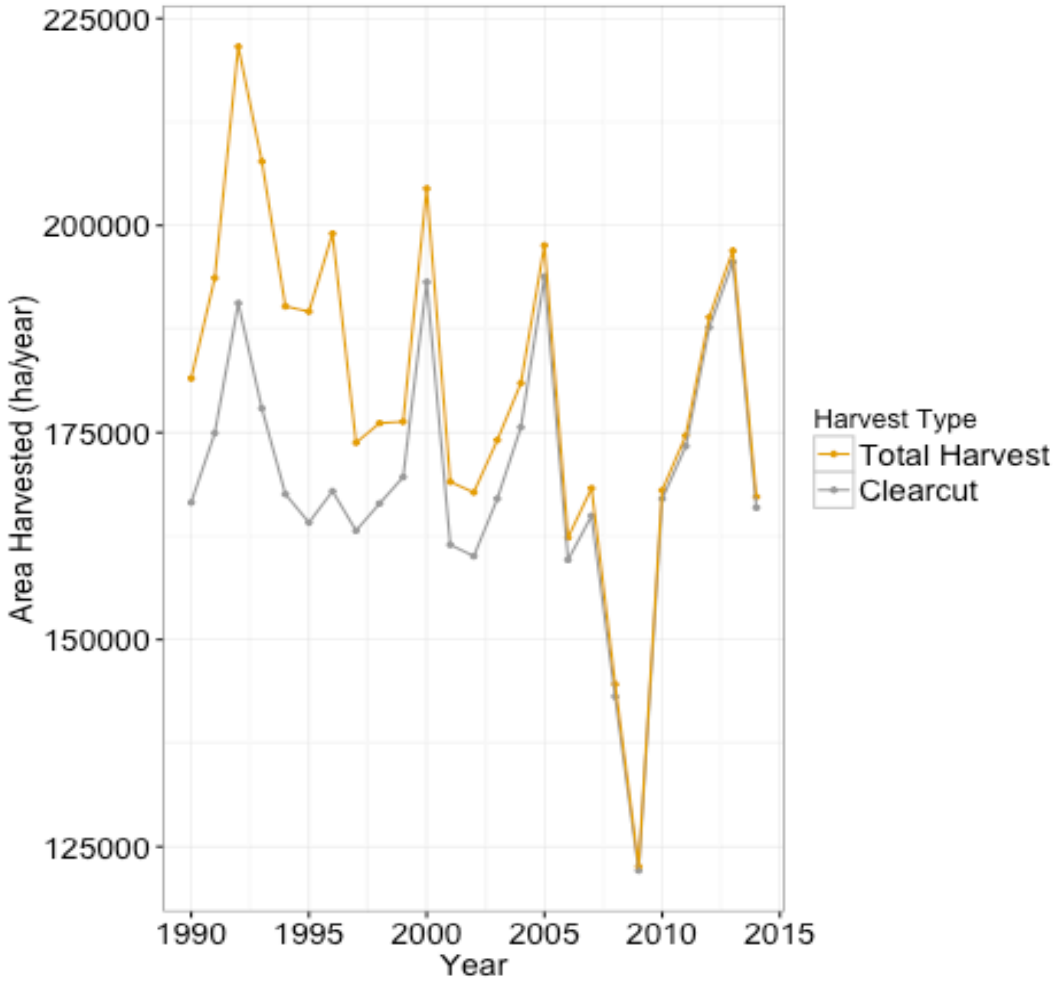

Figure 1.3 Extent of forest harvest (total and clearcut) in BC over 1990-2014. Data from National Forestry Database, 2015.

1.2.5 Effects of forest harvest on water quality – Chapter 3

Forests play a particularly critical role within the global carbon cycle, including ecological services such as carbon storage within soils and biota, carbon transformation (through terrestrial and aquatic removal of CO_2 through photosynthesis), as well as the provision of water for drinking, agriculture, and economic activities. Deforestation associated with forest harvest or land conversion thus risks diminishing such critical roles, and can have lasting detrimental ecological and hydrologic effects within a specific context. This includes, but is not limited to,

fragmentation of forested habitat, disruption of forest morphology (including species and age composition), increased sediment and nutrient loading in streams through erosion and land destabilization, and destruction of riparian habitat. More specifically, the effect of intensive logging practices and road building on water quality (including increases in turbidity due to erosion and flashier surficial flowpaths relative to slower subsurface flowpaths), are of particular concern in evaluating effects on water quality for human and natural uses. Forest harvest can increase stream temperature, which can alter stream metabolism, biological activity, and rate of decomposition, thus detrimentally impacting sensitive aquatic species (Pike et al. 2010). Harvest can also intensify runoff by influencing the microclimate of forests, including increasing snow accumulation (Murray and Buttle 2003; Sørensen et al. 2009), and decreasing evapotranspiration from plants (Hornbeck et al. 1993; Andréassian 2004; Schelker, Kuglerová, et al. 2013).

Forest harvest can also disturb biogeochemical cycles and fluxes between coupled terrestrial-aquatic systems. This involves altering forest vegetative cover and composition of the plant community, as well as impacting soil conditions including moisture and temperature, (Schelker et al. 2013), associated microbial activity, hydrologic flowpaths, and nutrient and matter leaching to surface waters (Kreutzweiser, Hazlett, and Gunn 2008; Glaz et al. 2015). In terms of effects of stream chemistry, forest harvest can affect biogeochemical soil processes and/or hydrologic transport mechanisms by which nutrients and other elements arrive within aquatic environments (Kreutzweiser, Hazlett, and Gunn 2008). Harvest can disrupt soil processes, which results in a short-term increase in soil nutrient availability (Tamm 1964; Kimmins 2004; Glaz et al. 2015). This is primarily associated with heightened microbial activity in upper soil layers (Bormann and Likens 1994; Kreutzweiser, Hazlett, and Gunn 2008), which converts nutrients into mobile forms that can be exported into surface waters through subsurface

hydrologic pathways (Buttle, Creed, and Moore 2005; Kreutzweiser, Hazlett, and Gunn 2008). However, predicting how forest harvest could impact water quality within a specific catchment is difficult. This is because catchment-specific conditions including stand type, hydrologic conductivity and connectivity, slope, soil texture, post-harvest weather patterns and geologic conditions – as well as details regarding the type and timing of harvest – can all shape the impact harvest has upon water resources (Kreutzweiser, Hazlett, and Gunn 2008).

Forest harvest, as well as associated activities like site preparation and road construction, can also significantly increase the export of organic matter through receiving waters (e.g., Evans et al. 2005; Kreutzweiser, Hazlett, and Gunn 2008; Williams et al. 2010; Schelker et al. 2014). Several mechanisms have been implicated with observed increases in in-stream DOC concentration upon harvest. First is the increased availability of transportable DOC within the soil; this derives from increased biomass inputs (such as surficial litter from harvest residue), as well as augmented microbial activity within surficial soil layers that liberates transportable DOC. Hydrologic shifts can also result in the transportation of more soil DOC into surface water. For example, the loss of plant evapotranspiration can cause groundwater levels to rise, improving hydrologic connectivity between DOC rich surficial soil layers and intensifying DOC export into receiving waters (Bishop, Seibert, and Köhler 2004; Kreutzweiser, Hazlett, and Gunn 2008; Schelker et al. 2012; Strohmeier et al. 2013).

Increased DOC concentrations within surface water, as well as shifts in the types of DOC present, can potentially affect both ecosystem and human health. Heightened stream DOC following forest harvest can increase mercury mobilization (Bishop et al 2009), and can alter pH balance in DOC rich boreal streams containing acid-sensitive fish. Recent studies have shown that aquatic DOC can have a significant contribution to greenhouse gas emissions (such as CO_2

and CH_4) when labile DOC fractions are metabolized by in-stream microbes (Cole et al. 2007; Battin et al. 2008; Butman and Raymond 2011; Schade and Bailio 2016). DOC can affect human health when water with elevated levels of DOC or labile DOC forms are used for drinking water; high concentrations of labile DOC can interfere with water treatment and form potentially carcinogenic disinfection by-products (DBPs) upon disinfection using chlorine or chloroamines (for example, Fujii et al. 1998; Bergamaschi et al. 1999).

Many of the keystone studies investigating forest harvest effects on DOC have been based either in high latitude boreal forests (e.g., Strohmeier et al. 2013), or cold-climate hardwood forests in the Northeast United States (e.g., Singh et al. 2014). However, the Pacific Northwest is unique in terms of climate, soil traits and plant communities when compared to these catchments; such characteristics may affect how watershed processes respond to harvest, and how such shifts are expressed through in-stream DOC characteristics. These questions are addressed in Chapter 3, which investigates how forest harvest affects DOC biogeochemistry within a small headwater catchment on Vancouver Island, British Columbia, Canada.

1.2.6 Advent and potential for in situ DOC monitoring – Chapter 2

Previous studies regarding in-stream DOC biogeochemistry emphasize their inherent temporal dynamism, where the advent of high frequency, in situ sensors has greatly improved the resolution with which such DOC dynamics may be observed. This temporal variability stems from hydrologic connectivity between different landscape elements that serve as DOC sources, as well as the interplay between flowpaths connecting groundwater to stream. Temporal variability is thus connected primarily to flow components contributing to stream discharge; specifically, the position of groundwater tables and surface flow from riparian wetland soils (McGlynn and McDonnell 2003; Hood, Gooseff, and Johnson 2006). Previous studies show the importance of

elucidating these cycles at a fine temporal resolution in order to illuminate biogeochemical DOC cycles. This includes diurnal cycles of streamwater DOC concentration (Spencer et al. 2007), as well as the significant contribution that extreme precipitation events can make to yearly DOC fluxes (Jeong, Bartsch, and Fleckenstein 2012). The ability to characterize the temporal variability of stream DOC concentrations and qualities, which can vary in scale from hours to seasons, is a predominant advantage in using in situ, high time frequency methods of DOC measurement. Such benefits of in situ monitoring are specified within Chapter 2. Data spanning a year of high frequency in situ measurements of DOC concentration shows that less frequent measurements underestimate calculations of DOC flux, and obscures fine timescale phenomena (Jollymore, Johnson, and Hawthorne 2012). This chapter also presents technical details regarding the implementation of high-tech, in situ monitoring networks, given challenging conditions within remote, physically rough stream environments. The spectrophotometric methods that compose such in situ approaches also enabled the citizen science program explored within Chapter 4, given their ease of use and economic cost per sample.

1.3 Participation and citizen engagement - Chapters 4 and 5

1.3.1 Societal engagement and citizen participation within water sciences and policy

Chapters 4 and 5 within this thesis concern citizen inclusion within aspects of water management spanning from science to policy. This reflects recognition within the natural sciences that public engagement and outreach is an increasingly important part of scientific research (Lasker 2003; Conrad and Daoust 2008), and the amplified call for societal participation within various faucets of resource management, especially within democratic contexts. Such calls for improving the interface between scientific institutions and society is evidenced by attention to further avenues of communication and engagement, such as the delivery of knowledge from scientists to society

(Couvet et al., 2008; Bonney, Cooper, et al. 2009; Bonney, Ballard, et al. 2009; Silvertown, 2009).

This study focuses on two forms of participation and societal engagement within water sciences and policy. We first focus on citizen science as a means of participation within the science of water quality monitoring (Chapter 4). This reflects the popularity of such approaches and their use as a means of engagement, vested at times with lofty goals for heightening societal concerns for environmental issues (Brossard et al. 2005). The second implementation of participation examined in this thesis concerns how public consultation contributes to the policy that legally frames acceptable uses of water resources within British Columbia (Chapter 5). Thus, participation within this study encompasses both the scientific monitoring of water resources, as well as decisions around policy that shape how these resources are used.

1.3.2 Participation in water sciences through citizen science – Chapter 4

The first iteration of participation examined in this thesis scrutinizes the use of citizen science as a means of participation and engagement within water-related sciences. Citizen science, which broadly defines activities that involve citizens within the scientific process, have become an increasingly popular approach for engaging the public within science. Citizen science programs include long-term, robust observations made by nonprofessional citizens within a vast range of scientific disciplines, such as watershed health assessments under various American programs since the 1972 Clean Water Act (Jalbert and Kinchy 2015). Citizen science has also been adopted by scientific actors within a range of different contexts, including universities and academic environments, government, private companies, not-for-profit organizations, and community organizations. Implementation of citizen science has been spurred by its potential to radically increase the breadth of data collection and analysis at a small fraction of the cost if such research

involved only professional scientists (Silvertown 2009). However, the justification and motivation for using citizen science approaches also includes the desire for engagement within the greater public, including the general elevation of scientific institutions within society. Aspirations for disseminating knowledge specifically regarding environmentally relevant issues can be coupled with engagement goals, with the aim of increasing societal concern and promoting potential action towards ameliorating such issues. The elevation of science concerning environmental issues though the engagement of citizens within the scientific process is particularly pertinent within democratic contexts, in which decision-making concerning both policy and scientific funding are made by government institutions that are held accountable to the public. Citizen sciences within resources such as water are thus accountable to the public through funding structures of the scientific program itself, as well as the relevancy of data garnered to policy decisions regarding resource management.

Despite enthusiasm around the potential of citizen science to increase societal education and engagement, as well as the potential to economically gather and analyze data at greater spatial and temporal scales (McKinley et al. 2015), questions remain regarding how to effectively and ethically engage citizens in science. First, questions regarding the scientific robustness of data collected by non-professionals, who lack training regarding the assumptions and machinations of the modern scientific process, threaten the acceptance of studies and conclusions based on citizen data (Riesch and Potter 2013). This includes the ultimate use of policy-relevant sciences within decision-making (Jepson and Canney 2001, 2003; McKinley et al. 2015). Additional uncertainties also remain regarding best practices for scientific actors engaging with citizens and citizen-lead groups, including the consideration of expectations, motivations and identity that can be expressed through participation through citizen science. Such considerations

are examined in Chapter 4, which presents our experience using citizen science to investigate water quality (specifically, how DOC quality and concentration is influenced by human land use). We present lessons learned regarding the experience of engaging with citizens and citizen-lead community groups, explicitly with regards to how citizens characteristics and identities (including motivations and contextual knowledge), as expressed through data outcomes.

1.3.3 Participation in water-relevant policy – Chapter 5

The second implementation of participation within this study concerns public engagement through consultation during the modernization of legislation regarding water allocation, use, and management within British Columbia. Chapter 5 examines public engagement and participation within the political rather than scientific realm (as embodied by participation through citizen sciences), offering a secondary embodiment of public participation within diverse and societally important issues surrounding water management. Examining public participation within policy also recognizes that policy (including legislation and associated regulations) ultimately dictates uses and acceptable impacts on resources within our context, whose far-ranging implications include water quality (such as parsed within Chapters 2, 3 and 4).

The notion that participation is key to good governance has lead to the increased use of consultation within public planning processes and policy-making in a variety of contexts (Shipley and Utz 2012). Public participation in Canadian policy has a long tradition, and is usually manifest through public hearings and citizen polls (Woodford and Preston 2013). More specifically, the requirement to consult the public regarding plans, regulations, and proposed activities concerning resource management decisions is embedded within Canadian legislation at all levels (Halseth and Booth 2003). An example of this duty to consult is present within The

Forest and Range Practices Act (2002), which regulates forest harvest activities in order to mitigate impacts on water, soil, wildlife and other environmental elements:

> *Public participation is an essential component of BC's sustainable forest management of our public forest lands. It begins with public involvement in the strategic land use plans and continues through to the operational plans of forest companies. Under the Forest and Range Practices Act before a Forest Stewardship Plan is approved by government, the license holder is required make the plan available for review and comment by other stakeholders, the public and First Nations. (From the Province of British Columbia – Sustainable Forest Management in British Columbia; The Forest and Range Practices Act 2002)*

Commonly cited reasons for public participation within policy decision-making processes include increasing public acceptance of resultant policy, procuring expertise within the public, as well as to generally solicit feedback, especially within western democracies (Kaehne and Taylor 2015). In response to the increasing institutionalization of public participation and consultation as part of the policy formation process, a corresponding literature has emerged that interrogates the process of participation. Fewer studies analyze policy outcomes relative to process itself, with only a few that specifically link policy outcomes to what was expressed within participation itself. Questions stemming from critical investigations of public participation within policy have increasingly interrogated how participation is used. A common critique and conclusion of such studies is that participation risks being tokenistic, where outcomes of the participation process, and what citizens desire out of policy, bears little resemblance to the policy that is ultimately decided upon (Arnstein 1969; Innes and Booher 2004). Such questions are especially relevant within water-related policies, given that water is critical to human health and hygiene, economic activities, as well as ecological functions.

Chapter 5 thus investigates the public participation process contributing to British Columbia's Water Sustainability Act (2014). This Act, passed in 2014, is the defining piece of provincial legislation governing allocation and use of water resources within British Columbia. It replaced legislation that had been in force (with periodic amendments) for some 100 years. This previous Water Act was passed in British Columbia's infancy; during this time, the primary concern facing the provincial government was assigning surface water rights to enable industrial development, rather than complex modern issues of scarcity, and the equitable and balanced allocation between multiple stakeholders and interests. A public engagement and participation process unprecedented in scale within the provincial context preceded the WSA, providing a unique opportunity to examine citizen participation as it pertains to water policy within British Columbia. Chapter 5 examines the outcomes of this public participation relative to the contents of the final Act as a means of examining participation within water-relevant policy.

1.4 Thesis overview

Chapters 2 and 3 present a multi-year monitoring study of DOC characteristics and concentrations within a small headwater stream located on the east side of Vancouver Island. This site was harvested during the midst of monitoring, providing the opportunity to observe the effects of such alteration as expressed through water flows and quality. Chapter 2 presents the technical implementation and challenges surrounding the installation of relatively nascent in situ DOC sensors within a remote, physically demanding stream environments. This chapter also explores the potential of such in situ approaches in observing high frequency dynamics of stream DOC concentrations and fluxes.

Chapter 3 examines results from this multi-year investigation, addressing how forest harvest affects 1) DOC concentrations and fluxes; 2) DOC characteristics (the chemical

components present in heterogeneous stream DOC), and 3) general biogeochemical drivers of stream DOC characteristics. This study reports the longest example to date of continuous, high frequency measurements of in situ DOC concentration. It is also one of the few studies focused on DOC dynamics within a temperature rainforest headwater catchment, as the majority of such studies have to date focused on boreal, northern latitude, or otherwise climatically different environments. Our temperate Pacific Northwest context differs in many regards to these existing studies that could affect DOC dynamics (Richardson, Bilby, and Bondar 2005), augmenting existing knowledge regarding DOC biogeochemical transformations within a unique biogeoclimatic ecosystem. Appendix C also contains details regarding DOC characteristics of riparian soils found at the site. Such information is necessary in order to understand the use of DOC characteristics as a fingerprint for alterations within hydrologic pathways and biogeochemical processes. However, it is presented as an appendix rather than a stand-alone chapter, given that investigating soil characteristics was secondary to the overarching theme present within the thesis, which concerns explicit human impacts to forested ecosystems.

Chapter 4 interrogates how citizen perspectives shape data outcomes using a citizen science case study that investigated anthropogenic effects on DOC characteristics and concentrations across an array of surface water ecosystems proximal to Vancouver, British Columbia, Canada. Much of the scientific protocols regarding water quality investigations, such as the parameters investigated and methods used, build on those used in Chapters 2 and 3. Chapter 4 specifically investigates lessons learned through implementing this citizen science water monitoring campaign by presenting data outcomes alongside qualitative vignettes explicating the context and citizen perspective of participation.

Chapter 5 investigates citizen participation within water policy by examining the public consultation process undertaken by the province as it formed the new Water Sustainability Act (2014). This chapter uses a mixed methods approach to detail both how stakeholders responded to policy options defined during consultation, as well as how this relates to policy contained within the final Act. This chapter is directly related to Chapter 4 through its themes of participation and citizen engagement, and relates to Chapters 2 and 3 more generally, given the importance of policy in dictating appropriate allocation and uses of water resources as manifest within these chapters.

Taken together, this work encompasses an investigation of water quality through a multitude of lenses, spanning both the scientific investigation of water quality to more general societal engagement within both policy and policy-relevant science. This societal context is explicitly presented alongside an in-depth investigation of the impact of human activities on water quality. Doing so emphasizes the importance of human activities on water quality, driven both by policy and more generally by societal attitudes. Presenting a study that encompasses a multitude of lenses is also an attempt to reflect the inherently interdisciplinary nature of issues within the broad realm of water resource management. The spectrum of perspectives also mirrors the nature of research within the interdisciplinary institution in which this thesis was produced; such institutions give the opportunity for collaboration between individuals with diverse academic backgrounds, allowing for the inclusion of multiple perspectives. The multifaceted nature of this thesis thus reflects both the complex nature of water resource issues, as well as the opportunities provided by the academic institution to consider such issues using multiple disciplines.

Chapter 2: Submersible UV-Vis spectroscopy for quantifying streamwater organic carbon dynamics: Implementation and challenges

2.1 Introduction

Organic matter within aquatic ecosystems constitutes a large range of compounds that play important ecosystem and biogeochemical roles. Organic carbon makes up a large portion of the total dissolved organic material within aquatic ecosystems, represented by both total and dissolved organic carbon (TOC and DOC, respectively). DOC represents organic carbon compounds in solution, while TOC refers to the entire organic carbon pool, constituted of both dissolved and particulate organic carbon phases. Both TOC and DOC are highly sensitive to catchment ecological conditions, originating either from soil or plant organic material of the surrounding catchment (allochthonous precursor material), or from in-stream production (autochthonous precursor material). Organic carbon in aquatic ecosystems is a key indicator of how the catchment functions in terms of biogeochemical nutrient and energy cycling (Fisher and Likens 1973; Mulholland 1997).

DOC is typically characterized as the organic fraction that remains in solution after filtering with a pore size of 0.7 μm or less. Much previous work has focused on quantifying DOC dynamics, including concentration and quality, between different ecosystems, such as forest streams (Jaffrain et al. 2007; Laudon et al. 2011), wetlands (Senga et al. 2011), and lakes (Rouillard et al. 2011). Additional work has focused on how land management changes affect the export and cycling of carbon through DOC, utilizing DOC concentration and quality changes as a means of quantifying the extent of ecosystem alteration (Kreutzweiser, Hazlett, and Gunn 2008; C. J. Williams et al. 2010; MacDonald et al. 2011). The motivation behind these studies partially stems from concerns over ecological and water quality effects, as well as from larger questions

concerning DOC within the context of the global carbon cycle (Battin et al. 2008). From an ecological perspective, DOC is implicated in a number of important processes in aquatic systems, including the transport and bioavailability of metals, the influence it has on acid-base chemistry, the attenuation of UV penetration (De Haan 1993), as well as microbial processing of DOC which acts to fuel the food web within aquatic systems (Carpenter et al. 2005). DOC can also have implications in terms of water quality for drinking water, as DOC can affect aesthetic qualities of water such as taste and colour; DOC can also form potentially carcinogenic disinfection by-products upon treatment (Fujii et al. 1998; Bergamaschi et al. 1999). Lastly, DOC plays an important role in terms of how energy and carbon are cycled through forest ecosystems, and has become an important means of monitoring how management and land use decisions, such as forest harvest, affect overall ecohydrologic productivity and biogeochemical nutrient cycling (Monteith et al. 2007; Wilson and Xenopoulos 2009).

Traditional means of quantifying DOC concentration typically involves grab sampling, followed by filtration and lab analysis, usually by wet oxidation or high temperature combustion methods. Despite their ubiquity, such methods require a good deal of time necessary for sample collection, preparation and analysis (Wang 1992). These drawbacks have lead to the development of spectroscopic methods towards the quantification of DOC concentration. This includes UV-Vis absorbance, which has been previously shown to provide an excellent proxy for DOC concentration and limited information regarding quality (specifically, the concentration of the aromatic fulvic acid fraction in DOC via absorbance at 254 nm) (Weishaar et al. 2003; Jaffrain et al. 2007). Spectroscopic methods hold a number of significant advantages over chemical analysis methods, owing to the savings in time and possibility for higher sample throughput, particularly when utilized in situ.

The recent development of commercial, field-deployable spectrophotometers has made it possible to introduce spectroscopic analysis in situ. The implementation of field-based spectrophotometers able to measure DOC concentration and quality holds many potential advantages, primarily stemming from the ability to track DOC dynamics over a much improved temporal scale than traditional grab sampling. Specific challenges arise with remote deployment of such instruments, which are intensified with the remoteness of the field site in general. This includes the ability to provide a steady and sufficient source of power, as well as the ability to know when the instrument requires maintenance.

This methodological case study investigates the deployment of a field UV-Vis spectrophotometer (spectro::lyzer, s::can, Austria) in a headwater catchment near Campbell River, British Columbia, Canada. First, the utility of high frequency measurement is investigated by comparing high frequency in situ measurements to dynamics observed at longer measurement intervals. Additionally, challenges surrounding field deployment are considered, including why data loss occurs, and the steps taken to minimize such data loss due to instrument failure. Given the potential for data loss, we also detail a wireless communication network able to transmit data as well as provide access to the instrument's software; this was implemented to help prevent long-term instances of data loss by identifying instances of equipment failure.

2.2 Experimental section

2.2.1 Description of study site

The study site (49°30'N-49°55'N, 124°50'W-125°30'W) is located on the eastern side of Vancouver Island, British Columbia, Canada near the city of Campbell River (Figure 2.1). This site is located in the coastal western hemlock biogeoclimate zone, an area that covers over three million hectares of the Pacific North American Coast. The study watershed is approximately 91

ha, ranging from 300 to 400 m above sea level. Previously, the site was a second growth stand, having been harvested and replanted in 1949 with Douglas-fir (80%) western red cedar (17%) and western hemlock (3%). The site has been referred to in the literature as DF49 (e.g., (Humphreys et al. 2006; Schwalm et al. 2006; Schwalm, Black, and Morgenstern 2007; Jassal et al. 2008; Hilker et al. 2010); the area is now referred to as HDF11 (Harvested Douglas-fir, planted in 2011). Preparation for another forest harvest began late in October, 2010 with the construction of new haul roads throughout the site. Harvest began in late December 2010, extending through late January 2011. Disturbance of the site occurred throughout 2011, including extensive traffic through the site due to timber hauling from January-March 2011, planting during the summer months, and slash burning in September.

The DF49/HDF11 site has been the focus of ongoing studies investigating CO_2, water vapour and energy exchange between the land and atmosphere from 1997 to present (Humphreys et al. 2006; Jassal et al. 2008; Hilker et al. 2010; Jassal et al. 2010; B. Chen et al. 2011). Additionally, an in situ water quality monitoring system has been operational since 2007, measuring parameters including dissolved oxygen and CO_2 (Johnson et al. 2010), pH, discharge, and electrical conductivity adjacent to a V-Notch weir located at the outlet of the catchment's headwaters. That the site has been extensively studied poses multiple advantages from the perspective of remotely deploying the UV-Vis spectrophotometer discussed within this case study, considering the prospect of adding information regarding aquatic carbon flux to measurements of atmospheric and forest carbon dynamics already underway.

2.2.2 Spectrophotometer deployment

Long-term goals of the study include an investigation of how forest harvest (including the management practices that accompany harvest), affect carbon dynamics and its export from the

catchment. In order to investigate water quality dynamics in this catchment, a study site was established in a headwater stream draining the watershed (Figure 2.1). This installation provides continuous monitoring of various water quality parameters on either a 10 or 30 min schedule, with parameters downloaded on a daily basis via remote connection to the site on a cell phone modem coupled to the data logger (model CR1000, Campbell Scientific, Logan Utah, USA).

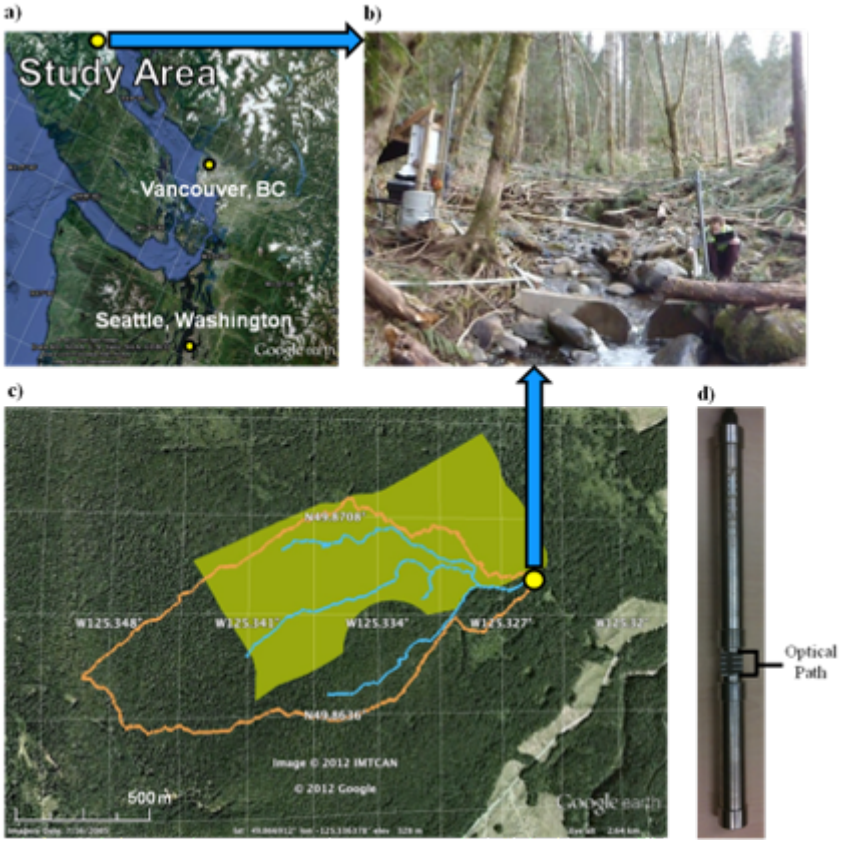

Figure 2.1 Study site details. (a) Location of the HDF11 site on Vancouver Island, British Columbia (©2012 Google, ©2012 TerraMetrics). (b) Water sampling site at HDF11, postharvest. (c) Map of the HDF11 site. The water sampling site (yellow dot) is located at the outlet of the watershed indicated by the orange boundary. The area clearcut in December 2010-January 2011 is indicated by the yellow rectangle (©2012 Google, ©2012 IMTCAN). (d) Photo of the field-deployable UV-Vis spectrophotometer (s::can, Austria). The perforated protective PVC housing for instrument as described in text is not shown in this photo.

Field-based measurement of stream absorbance using the UV-Vis spectrophotometer began in November 2009 (during the pre-logging period) with the intent that it be used to monitor changing dynamics in organic carbon occurring as a result of harvest related disturbance, particularly how disturbance affects export within the HDF11 catchment. The UV-Vis spectrophotometer was installed on the streambed of the shallow headwater stream in a protective, perforated PVC tube mid-channel approximately two meters upstream of the weir (Figure 2.1D). The spectrophotometer was installed such that streamwater flows parallel to the light path of the instrument, and was affixed to the center of the stream channel using rocks and a metal guide wire attached to the water site hut structure. An air compressor system was installed to clean the instrument's pathway of any accumulated debris prior to measurement. Initially, a tank of compressed air was used to provide timed bursts of air through a datalogger-controlled solenoid valve. This was replaced in 2010 with an automated air compressor cleaning system, which consists of a 12 V air compressor that builds 60 psi of pressure behind a solenoid valve before releasing the pressure as a burst of air to clean materials from the spectrophotometer windows. The datalogger system was programmed to provide six short bursts of air (one second bursts) twice a day, with additional bursts provided based on rapid changes in water depth.
The spectrophotometer utilized in this case study is a fully submersible, commercially available UV-Vis spectrophotometer manufactured specifically for field-based measurements of water quality. This spectrophotometer has found wide application in a number of industrial applications, such as the monitoring of municipal wastewater quality, pharmacology, and beer brewing. However, it has been less applied in the type of long-term ecohydrologic impact investigations such as that at the HDF11 site, except for a few notable exceptions (such as the study by Waterloo et al. (2006)). The spectrophotometer utilized throughout this study (spectro::lyzer

model UV-Vis, s::can, Austria) was composed of a stainless steel casing that houses a xenon flash lamp, and a 256 pixel array detector comprising a instrument pathlength of 30 mm.

In terms of installation, the spectrophotometer setup encompassing the date range discussed here was relatively autonomous from other sensors present at the HDF11 water site. The main intersection into the existing system was through the provision of power to the spectrophotometer. DC power to both the water quality monitoring station and the spectrophotometer was provided through a 12 V deep cycle battery recharged using an on-site methanol fuel cell (EFOY, SFC Energy Inc, Germany), where the spectrophotometer requires 11-15V DC or 100-230V AC in order to function (with a typical power consumption of 4.2 W). The maximum power use of the entire site, encompassing the whole suite of sensors at site as well as the spectrophotometer setup, was approximately 37 W while both the site's computer and spectrophotometer was on, and 24 W when only the spectrophotometer was on (without the computer).

2.2.3 The first two years: Investigating streamwater DOC November 2009 - 2011

The deployed spectrophotometer was programmed to measure the absorbance spectrum of flowing streamwater every 30 minutes, measuring streamwater absorbance from 200 to 720 nm in increments of 2.5 nm. To reduce overall power consumption, the instrument was switched on for five minutes every 30 minutes to take a measurement. Upon turning on the instrument, the instrument's xenon gas discharge lamp flashed six times to make a measurement (approximately 1 second between each flash) as the flash lamp does not require the warmup time of a conventional xenon arc lamp. After the lamp flashed, data processing took an additional minute to complete the measurement. Data was stored in the spectrophotometer's memory, and downloaded on a monthly basis (at the sample frequency indicated, the spectrophotometer

storage space lasted approximately one month). A blank measurement of distilled, deionized water was taken upon each data download, to manually determine whether window fouling by microbial growth or iron oxide had occurred. The instrument's sapphire windows was cleaned with a Q-tip, using the alkaline solution provided by the manufacture to clear off microbial growth, followed by a 3% HCl solution to clear any accumulated iron oxide. A second blank was subsequently taken to determine the extent of cleaning.

Water quality parameters, including turbidity, TOC, DOC, and absorbance at 254 nm were derived from the measured absorbance spectrum. Previous investigations have shown that DOC concentration correlates with absorbance over a wide range of wavelengths, where DOC absorbance decreases exponentially with increasing wavelength; such wavelengths of light at which DOC absorbs have been previously described by Stedmon and Markager (2001). DOC concentration was calculated from the absorbance spectra over 240-300 nm, based on derivative spectroscopy using proprietary algorithms that comprise a 'global calibration' file. These calibration equations have been optimized by the manufacturer for the determination of DOC within stream environments (s::can 'global calibration' files for streamwater). While local calibration files can be developed, we found the global calibration to be a good fit for the ionic strength and composition of the streamwater in the study site. Calculated concentrations of DOC were graded by the software on the basis of whether they were within range, as well as whether the instrument was experiencing issues arising from power loss during measurement. Only DOC concentrations that were determined as such to be free of both interferences were retained for further analysis. DOC values measured by the spectrophotometer and reported in this paper were blank corrected using DOC measurements of distilled, deionized water taken during monthly

field visits; DOC blanks did not deviate significantly month to month, indicating that fouling did not significantly affect DOC measurements over the 2010–2011 period.

2.2.4 Spectrophotometer calibration

Calibrating the response of the field-deployed spectrophotometer using a laboratory-based method is critical for ensuring that data reported by the instrument accurately reflects the DOC concentration, given the stream matrix. This was done in the manner as previously reported by Waterloo et al. (2006). To do so, aliquots of streamwater collected during November 2011 were filtered at 0.7 μm using pre-combusted glass fibre filters. These filtered samples were serially diluted, and the DOC concentration of these dilutions measured using the field-deployed UV-Vis spectrophotometer by placing a watertight cuff over the optical path of the spectrophotometer in Figure 2.1(D). These same diluted streamwater samples were then analyzed via high temperature combustion (Shimadzu Scientific Model TOC-V CSH/CSV). The relationship between concentrations measured by each method was strongly linear ($R^2 = 0.997$):

$$[DOC]_{lab} = 1.027 \times [DOC]_{spectro} - 0.200 \qquad \text{(Equation 2.1)}$$

This relationship was then used to correct raw measurements of DOC concentration made using the spectrophotometer, where $[DOC_{lab}]$ is the DOC concentration measured on the Shimadzu TOC analyzer, and $[DOC_{spectro}]$ is the blank corrected, spectrophotometer measured DOC concentration. DOC concentrations reported in this study are all laboratory corrected from spectrophotometer values using Equation (2.1).

2.3 Results

2.3.1 DOC dynamics in pre-harvest versus post-harvest periods

DOC concentrations from January 2010 to November 2011, measured using the remotely deployed spectrophotometer, are shown in Figure 2.2. The discharge over the same period, derived from stage measurements taken at the HDF11 weir site (model WT-VO, TruTrack Ltd.,

Christchurch, New Zealand), is shown on the same figure to reflect the stream conditions present at the time of DOC measurement. Breaks in the DOC time series data reflects data loss occurring due to some type of system failure (e.g., power loss, concentration over range, interference from excessive turbidity, or exceeding the memory of the spectrophotometer). Despite these breaks, Figure 2.2 demonstrates the ability of remote spectrophotometer deployment to garner a great deal of data with fine-scale temporal resolution, a distinct advantage considering long-term research aims centered around DOC dynamics.

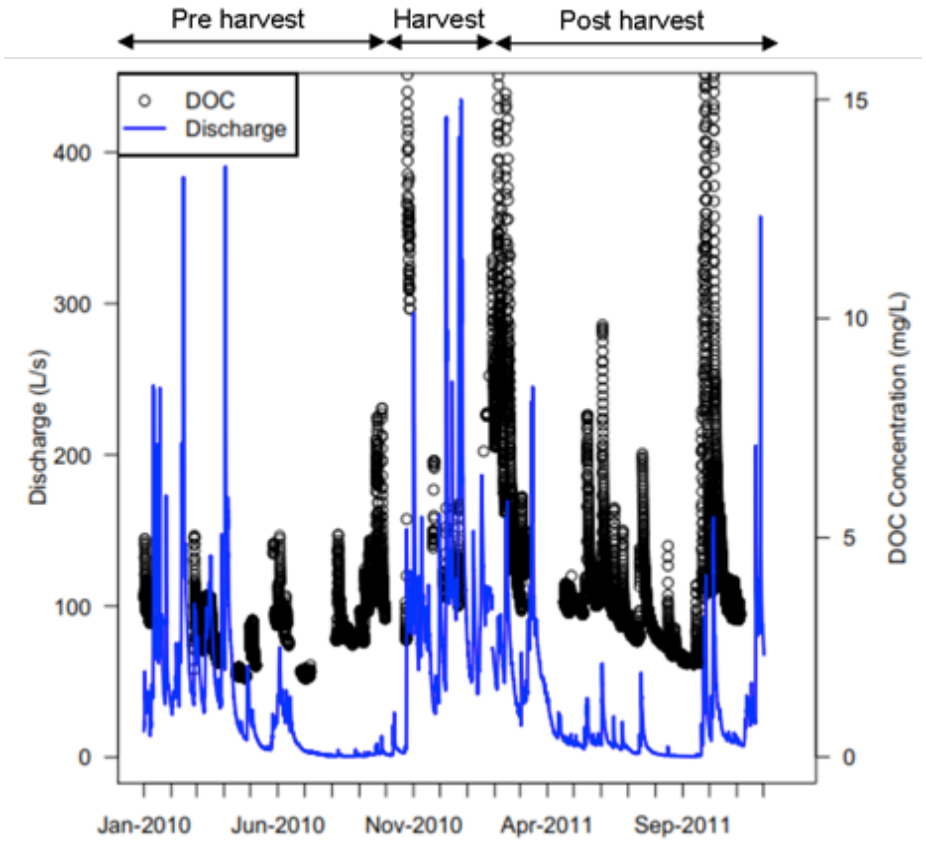

Figure 2.2 DOC concentration dynamics. Dynamics shown from January 2010 to November 2011 (in black); stream discharge, measured in L/s, over the same time period is also shown (blue line).

2.3.2 Examining the high temporal resolution of the field-deployed spectrophotometer

As previously discussed, DOC measurements are typically made using laboratory-based analysis of water samples taken at discrete time intervals. Much of the promise of field-deployed sensors, such as the UV-Vis spectrophotometer discussed here, lies in the ability to examine dynamics on much finer temporal scales. The influence of different measurement time scales on observable DOC dynamics is explored in Figure 2.3. DOC concentration changes for May-July 2011 were evaluated for different collection intervals by recasting the 30-min time series as a series of simulated time series with various time steps. This allowed us to compare the DOC dynamics calculated using a 30-min time interval with those that would have been obtained from grab samples at 1, 1.5 and 7-day intervals. It was assumed that daily samples were taken at 12:20 PM. How these sampling intervals affect the DOC time series is examined in Figure 2.3. It is notable that as the time between measurements increases, the ability to observe large peaks and minimums in DOC concentration becomes more restrictive, with more detail lost as the time between measurements increases (Table 2.1). This demonstrates the importance of using high frequency measurements, possible only with remote deployment of the spectrophotometer, to observe rapid changes in DOC concentration over time.

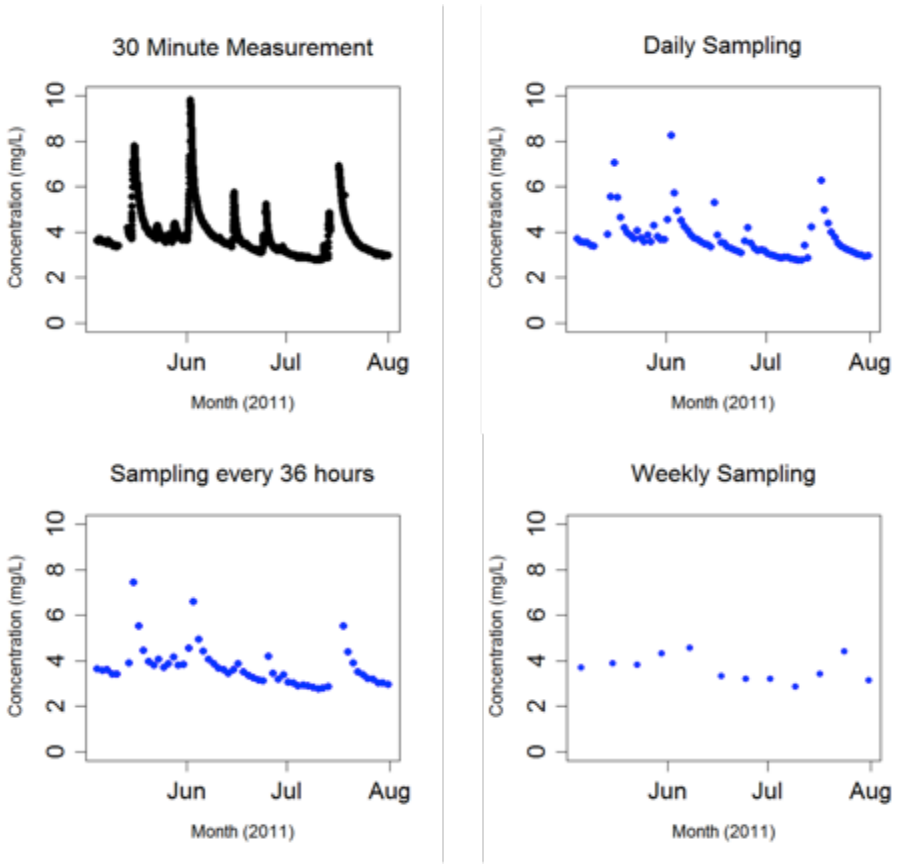

Figure 2.3 Effect of sampling frequency on DOC concentration. The frequency of DOC concentration measurements greatly affects the DOC concentration time series, predominantly by narrowing the range of DOC concentrations measured as well as reducing the observable dynamic detail present in the DOC concentration trace.

Increasing the time between measurements has uneven effects on monthly means depending on how measurement timing captures DOC concentration dynamics, which is a somewhat random process depending on when a measurement is taken (Table 2.1). However, the range between the observed maximum and minimum observed concentrations tends to decrease as measurement timing increases. This makes sense, considering the decreased probability in observing the less frequent high and low concentration events for decreasing temporal resolution. The effects of measurement frequency are more pronounced when DOC fluxes are considered.

Table 2.2 presents DOC export over the May-July 2011 period. DOC export was calculated according to Walling and Webb (1985) (Method #3 Walling and Webb 1985; Hope, Billett, and Cresser 1997).

	Monthly Median DOC Concentration (mg/L)				Monthly DOC Concentration Maximum (mg/L)				Monthly DOC Concentration Minimum (mg/L)			
	30 min	Daily	36 h	Weekly	30 min	Daily	36 h	Weekly	30 min	Daily	36 h	Weekly
May	3.78 ± 0.88	3.76 ± 0.85	3.83 ± 0.98	3.86 ± 0.26	7.79	7.04	7.43	4.30	3.35	3.38	3.40	3.69
June	3.59 ± 1.10	3.56 ± 1.05	3.61 ± 0.81	3.28 ± 0.64	9.80	8.25	6.60	4.52	3.08	3.10	3.12	3.20
July	3.03 ± 0.76	3.01 ± 0.78	3.01 ± 0.68	3.28 ± 0.65	6.93	6.28	5.51	4.38	2.76	2.77	2.78	2.87

Table 2.1 Effect of measurement frequency on descriptive statistics.

	DOC export						
	30 min Sampling	Daily Sampling		36 Hour Sampling		Weekly Sampling	
	DOC (10^5 g)	DOC (10^5 g)	Deviance from 30 min (%)	DOC (10^5 g)	Deviance from 30 min (%)	DOC (10^5 g)	Deviance from 30 min (%)
May	1.30	1.33	2.16	1.32	1.55	1.00	-22.96
June	1.51	1.43	-4.76	1.29	-14.55	1.00	-33.67
July	1.09	0.94	-13.76	0.54	-50.70	0.59	-46.03
	Mean deviance (%) (Mean ± 1 SE for n = 3 months)		-5.45 ± 4.61		-21.23 ± 15.45		-34.22 ± 6.66

Table 2.2 Effect of measurement frequency on calculated DOC export.

2.4 Discussion

2.4.1 Advantages of remote sensor deployment

Results from the first years of instrument implementation demonstrates the relative robustness of the instrument, including setup and field maintenance methodologies that encompass environmental conditions present over this time. This included fluctuating seasonal temperatures and increased sediment loadings in the stream due to winter precipitation and effects of harvest that, at times, exposed the instrument to high flows, rocks and abrasive sediments. The instrument performed well under widely variable conditions, providing data for the majority of the deployment period, demonstrating the potential using such remote sensors to monitor DOC dynamics. Remote deployment of a UV-Vis spectrophotometer capable of measuring DOC concentration at high frequency has provided the ability to see dynamic changes in concentration that would have been difficult to observe with traditional sampling and analysis methods. Results in Figure 2.3 and Table 2.1 further demonstrate that high frequency data provides a more complete picture of DOC dynamics. This is true both for short timescales, where high frequency data is able to show DOC changes that occur on diurnal and longer timescales, where high frequency data provides a more accurate representation within basic statistical treatments such as means, deviation, maximums and minimums (Table 2.1). The ability to measure discrete

concentrations on a much finer timescale through remote deployment presents a greater probability of observing concentration dynamics than previous sampling regimes.

As previously discussed, DOC concentration and export is one indicator for ecosystem function, showing how biogeochemical carbon cycling is occurring within a particular ecosystem. That the frequency of measurement has a large effect on the perception of DOC dynamics could thus be important in terms of resource management decisions concerning DOC. For example, it has been previously shown that forest harvest can result in an increase in DOC export, affecting the water quality and biological productivity of impacted aquatic environments. (Kreutzweiser, Hazlett, and Gunn 2008) Such measurements, made using traditional lab based analysis, may substantially underestimate the dynamic range of DOC, where the actual amount of DOC exported through the aquatic environment may be much greater than that calculated using methods that employ a low measurement frequency. Measurement frequency had a profound effect on calculated DOC flux, as shown in Table 2.2. Increasing sampling interval in order to emulate traditional means of grab sampling and laboratory-based analysis dramatically decreased the calculated DOC export over the May-July period. This underestimation of DOC export increased with sampling frequency, from -5.45 ± 4.61 % for daily measurements to -34.22 ± 6.66 % for weekly measurements (monthly mean percent error ± 1 SE for n = 3 months). Thus, it is important to consider the impact that sampling frequency has when considering and comparing calculated DOC export, noting that these values may be significantly underestimated depending on measurement regime.

Lastly, the time investment involved in obtaining high resolution field DOC measurements differs dramatically from that of traditional methods; the latter involves sampling, transporting, filtering, preserving and analyzing. Although field deployment requires

infrastructure such as a power source sufficient to power a field spectrophotometer, and time for deployment, field maintenance and periodic calibration, this time investment is less than that of traditional methods, especially considering the ratio of time invested to the data obtained and the advantages of higher frequency measurements.

2.4.2 Ongoing challenges - combating data loss

Despite the many advantages of remote spectrophotometer deployment for DOC measurements, several considerations remain. As noted in Figure 2.2, there are periods in which either no data was collected by the spectrophotometer, or the collected data was graded as poor. These scenarios can stem from a number of different issues, which could be loosely grouped into those concerned with operating conditions or power issues during measurement and data downloading. Data loss occurred when operating conditions were unfavourable, at which time data was marked as poor and discarded during data cleaning. Unfavourable conditions included when DOC concentrations were out of range, if sediment concentrations were high, or the velocity of the stream exceeded 3 m/s. The upper DOC concentration limit was generally 15 mg/L, but could be slightly higher based on absorbance characteristics related to the stream conditions at the time of measurement. These conditions tended to occur during the winter period, as evident in Figure 2.2, in which the largest amount of data loss occurred during the high discharge winter months. Additionally, data was marked as poor if the spectrophotometer was dislodged and no longer submerged, or if it was buried under sediments and rocks transported by the stream; the latter scenario occurred several times during the high discharge winter period. The most common cause of data lost was due to power disruptions that impeded the sensor's ability to take a measurement. Such power disruptions occurred for several reasons, including: if multiple power demands caused the battery to experience a large voltage drop (at which point the spectrophotometer could

not draw sufficient power to make a measurement); if the methanol supply to the fuel cell charging the battery ran out; if the battery aged to the point where it could not recharge sufficiently to provide power to all of the sensors (including the spectrophotometer); or if low temperatures sufficiently compromised battery performance. Data loss also occurred during data downloading if the memory of the spectrophotometer was exceeded, or if the performance of the battery was sufficiently compromised such that sufficient voltage could not be supplied to the spectrophotometer during the data download process. If sufficient voltage was not supplied to the spectrophotometer during downloading, the data download terminated before the entire data file could be downloaded. The remote nature of the site, and its location under a partial canopy even after harvest, narrowed the options available in providing power to the site. Locations without these constraints (for example, those with a ready supply of power, or those in which a range of power provision such as solar could augment or replace the use of fuel cells, which need to be replenished), may not encounter power-related issues to the same degree as discussed.

As field trips to maintain and check the instrument occurred on a monthly basis, the potential existed that up to an entire month of data was lost if the spectrophotometer operation was disrupted soon following a field visit. The first full year of implementation (2010) shows the largest periods of data loss, demonstrating the significant improvement in data coverage that has stemmed from progressive upgrades made to the system. This includes decreasing wire length and increasing wire gauge where possible to reduce voltage drops, insulating the box containing the fuel cell and battery during winter, ensuring that batteries are changed when their charge capacity begins to diminish, as well as timing data downloads such that data is not lost. Additionally, because of the importance in providing a steady 12 V supply to the spectrophotometer to ensure proper function, a 12 V-12 V converter was installed such that

power flows from the battery, through a fuse, and into the converter prior to the spectrophotometer. This converter ensures that voltage drops caused by demand upon the battery do not disrupt spectrophotometer measurement, and the spectrophotometer continues to receive the required steady 12 V supply every 30 minutes when measurements are taken and when the spectrophotometer is turned on in order to download data.

2.4.3 Setting up a wireless communication network

In terms of preventing data loss observed in the 2010 portion of Figure 2.2, it became obvious that the inability to see how the spectrophotometer was functioning between field trips resulted in loss of data, as it was impossible to observe whether maintenance was necessary prior to scheduled monthly visits. Additionally, the spectrophotometer contained sufficient memory to store only one month of data (when measuring every 30 min); this resulted in some data loss if visits were spaced longer than one month apart. Both of these issues were the motivation behind implementing a remote connection to the site, which was installed in Oct, 2011.

This remote connection is detailed in Figure 2.4. Briefly, it consists of two systems running in concert and communicating slightly different information with regards to the spectral measurements made. The first entails a modbus communication scheme that enables the ongoing transfer of parameters calculated from the UV-Vis spectrophotometer spectra to the datalogger, including DOC, TOC, turbidity, and absorbance at 254 nm. The spectrophotometer is connected to a CR1000 (Campbell Scientific) data logger through a RS232 modbus protocol, which is programmed to collect parameter data from the spectrophotometer every 30 min. This datalogger is connected to a cellphone modem, with a remote computer programmed to download data from the remote datalogger to a database located at the University of British Columbia each morning.

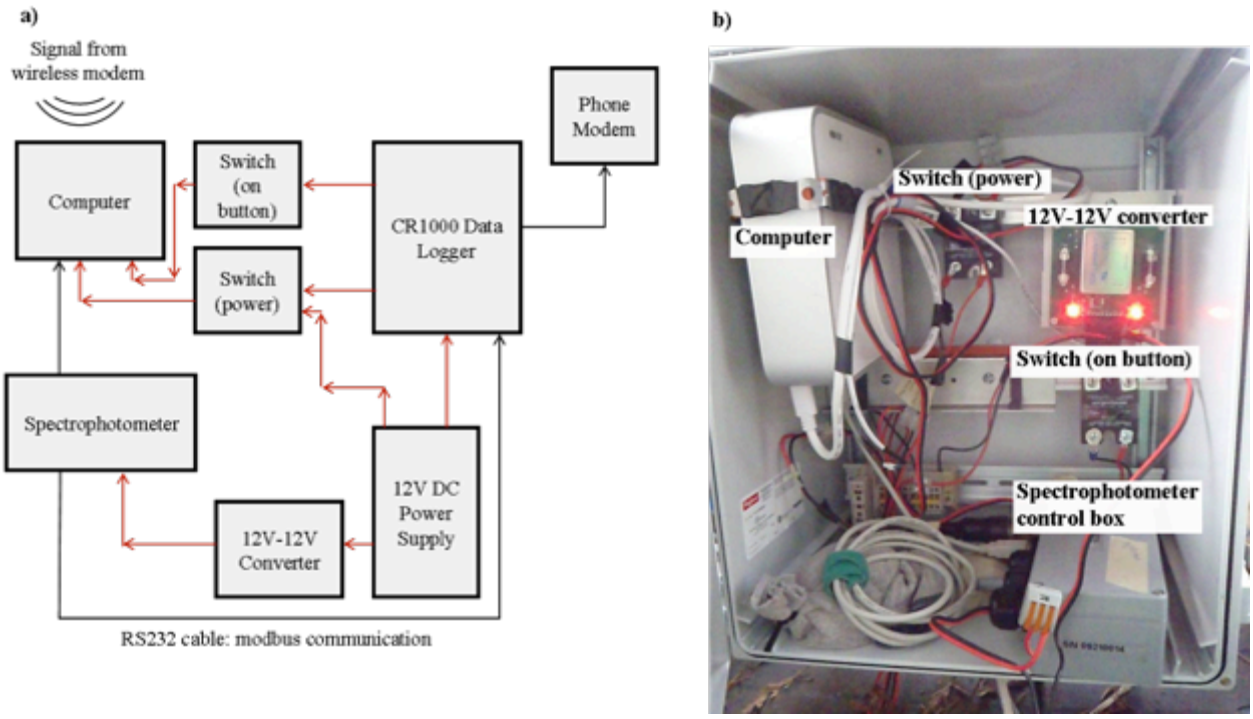

Figure 2.4(a) Schematic of spectrophotometer connection (both the modbus and wireless connection). Power connections are noted in red; connections that convey data in black. (b) Photo of current remote connection scheme, showing the 12 V-12 V converter, as well as the computer connection to the spectrophotometer. The CR1000 datalogger, and associated connections are located in an adjacent box, and are not shown. The computer is in the top left of the photo; the switches are the two black boxes; the 12 V-12 V converter is the board with the two lit LEDs; the spectrophotometer connection is represented by the grey box in the bottom right of the photo.

The second system allows for the remote download of raw absorbance spectra data, which cannot be transmitted through the modbus protocol due to incompatible file formatting. This network is composed of a field-deployed computer (MacMini, Apple) configured to run on 12 V power. The spectrophotometer was connected via USB to the computer; the computer was controlled via the CR1000 datalogger to permit remote activation of downloads from the spectrophotometer to the field computer. An internet connection to the field computer was achieved with a wireless Internet connection. Once the field computer was accessed using a

remote desktop application, spectral data was downloaded from the spectrophotometer to the field computer and uploaded through the modem into a cloud-based server. The implementation of a remote connection to the spectrophotometer provides numerous advantages, including the remote observation of spectrophotometer function, the ability to determine when field visits are necessary to prevent compromised and/or lost data, as well as preventing data loss due to exceeding the month-long spectrophotometer memory.

2.4.4 Extensibility to other aquatic environments

As previously discussed, investigations into DOC dynamics are instigated by a range of different research motivations, taking place within a wide variety of ecosystems. The remote deployment described above has proven to be robust considering the environmental conditions encountered in the headland stream located on the east coast of Vancouver Island, Canada. This particular instrument was chosen for a number of reasons, including its portability, ease of use, relative robustness, and its ability to measure a number of parameters including turbidity, NO_3^-, TOC and DOC. Whether the setup would also demonstrate the same resilience in other environments depends on a number of factors. This includes the ability to supply sufficient power to the spectrophotometer, either through the type of rechargeable DC supply discussed here, or an accessible AC supply. The spectrophotometer is able to operate within a broad water temperature range (from 0˚C to 45˚C); despite this range, extreme temperatures (and even temperatures within this operating range) could affect the operation of batteries commonly used to power instruments in off the grid contexts. As previously discussed, a decrease in battery performance due to low temperatures was one of the major contributing factors towards loss of data; thus, the effect of temperature extremes must be taken into account in order to prevent data loss. Environments in which the instrument is likely to encounter a large degree of physical contact or

jostling could also pose a problem. The spectrophotometer, though fairly robust, is more delicate and expensive relative to many field-deployed sensors.

Additionally, the spectrophotometer required regular field maintenance to ensure that it is still correctly installed, as well as to prevent lens fouling by chemical cleaning (to augment automated cleaning). Obstruction of the spectrophotometer window occurred through sedimentation build up (if the automated cleaning system failed or was overwhelmed), through the growth of biofilm, or the precipitation of iron oxide. We did not visually observe precipitation of iron oxides in the stream described in this paper; however, this could be a problem for aquatic environments where iron concentrations are more significant. Thus, field sites at which such spectrophotometers are deployed cannot be so remote such that periodic visits (e.g., monthly) are impossible, though remote connection strategies as discussed previously greatly alleviates many of the difficulties that accompany monitoring remote field sites. As discussed in section 4.2, data collected outside of the optimal operating conditions of the spectrophotometer were marked as poor and discarded during data cleaning (as observed in Figure 2.2). Thus, environments in which these conditions (such as instances of high turbidity or streamflow) are likely to be encountered frequently could result in significant and frequent loss of data.

Lastly, spectroscopic methods of DOC concentration determination may not be appropriate for all environments as high concentrations of NO_3^- and iron can co-aborb at wavelengths used for calculating DOC concentrations, causing an apparent increase in DOC concentration (e.g. Simonsson et al. 2005). In the past, studies assumed that the concentration of Fe and NO_3^- for most surface waters are between 0-0.6 mg L^{-1} (for iron) and <1.0 mg L^{-1} (for nitrate), representing an insignificant contribution to the absorbance within the range used to measure DOC concentration (Weishaar et al. 2003). Recent studies have begun to demonstrate

that such interferences can be significant even within surface waters that are not affected contamination or significant ground water contributions. While the in situ absorbance instrument measures and corrects for NO_3^-, it is more commonly accepted that best, scientifically rigorous practices for using absorbance spectrophotometry to monitor DOC includes correcting measurements for Fe concentrations (e.g., Weishaar et al. 2003; Poulin et al. 2014). In scenarios where Fe and NO_3^- are significant, it is necessary to correct for their presence within the absorbance spectra, or use laboratory-based means of DOC determination (that are not affected by interferences, such as previously discussed), with greater frequency to ensure that DOC concentration data is accurate.

2.5 Conclusions

High frequency, field-based measurements of DOC provide a means of gaining insight into dynamics at a temporal scale that is impossible to emulate through traditional means. The ability to resolve variations at small time scales provide an invaluable means of tracking DOC variations to its biogeochemical origins. Determining DOC at a high time resolution through field-based UV-Vis spectroscopy can also be used for the accurate observation of concentrations over longer time periods; this is exemplified by the data segment presented here, which spans DOC concentration dynamics before, during and directly following forest harvest within the study catchment. The ability to measure DOC at high frequency is critical towards accurately understanding DOC export, where decreasing measurement frequency leads to a large underestimation in DOC exports. The development of robust instruments able to perform over a wide range of conditions, the implementation of power networks able to support these instruments, and the creation of remote connection networks that allows for these instruments to

be monitored remotely, proves that remote deployment strategies are a very promising tool towards examining DOC transformations within aquatic ecosystems.

Chapter 3: Effect of forest harvest on stream DOC biogeochemistry – illuminating human impacts using DOC concentration and quality

This study investigates the effects of forest harvest on dissolved organic carbon (DOC) dynamics within a small headwater stream in the Pacific Northwest. It details scientific outcomes using the monitoring station described within the previous chapter, utilizing data procured at this site to investigate DOC biogeochemistry before and after forest harvest. The main goals of this multi-year study was to investigate the effect of forest harvest on: 1) DOC concentrations and fluxes; 2) DOC characteristics (the chemical components present in heterogeneous stream DOC), and 3) general biogeochemical drivers of stream DOC characteristics.

3.1 Introduction

3.1.1 The importance of investigating effects of forest harvest on DOC

The dissolved organic carbon (DOC) fraction of organic matter (OM) plays a number of critical biogeochemical and ecological roles within aquatic ecosystems, and has thus become an important focus of studies spanning biogeochemistry, hydrology and ecology. Such previous studies have shown the importance of DOC in diverse range of critical functions including controlling the food web structure in lakes, (Findlay and Sinsabaugh 2003) acting as a microbial substrate, (Berggren, Laudon, and Jansson 2007) mediating the penetration of solar radiation into aquatic ecosystems as an 'aquatic sunscreen' (Zhang et al. 2007), influencing aquatic acid-base chemistry, (Buffam et al. 2008) and altering the reactivity and transport of metals such as mercury (Grigal 2003; Dittman, Shanley, and Driscoll 2010) and aluminum (Cory et al. 2006). DOC within aquatic ecosystems plays an important role in the overall carbon cycle of forested catchments (Nilsson et al. 2008; Dinsmore, Billett, and Skiba 2010); this role is significant

enough to necessitate inclusion when evaluating the overall carbon budget of forest ecosystems (Cole et al. 2007; Kindler, Siemens, and Kaiser 2011). Particular attention to the effect that anthropogenic activities have on aquatic DOC has grow in recent years, owing to general concern regarding the effect of land uses (such as forest harvest) on DOC cycling from terrestrial to aquatic systems, as well as observation of increased DOC within surface waters across a range of biomes globally (Worrall, Burt, and Shedden 2003; Skjelkvåle et al. 2005; Roulet and Moore 2006; Monteith et al. 2007). Additionally, the generalized pathways that link DOC from terrestrial sinks within soil to surface water systems - as well as how such pathways are affected by climate, soil conditions, vegetation types, and anthropogenic activities - are still poorly understood, despite growing scholarship regarding carbon cycles within either soil or aquatic systems (Strohmeier et al. 2013).

Despite their small size, the biogeochemistry of DOC within headwater streams is particularly important and often overlooked within larger-scale carbon budgets (Bishop et al. 2008). This is because headwaters are the dominant site of transfer of DOC from terrestrial to aquatic environments (Temnerud et al. 2007; Bishop et al. 2008), and can thus be a large determinant of DOC conditions within the context of downstream ecosystems (Ågren, Buffam, and Jansson 2007; Laudon et al. 2011).

3.1.2 Effects of forest harvest on biogeochemical cycles

Anthropogenic activities can alter catchment biogeochemical cycling of carbon through many guises, including short-term (such as conversion of land to agriculture or urban areas) to long-term (such as climate change) impacts. Forest harvest is a major human alteration of forested catchments across the world, leading to numerous studies detailing the effect of forest harvest on

catchment processes including (but certainly not limited to) hydrology, soil biogeochemistry, and nutrient fluxes.

Forest harvest is known to have large effects on biogeochemical, climatic and hydrologic functions, significantly altering the ecology and biogeochemical behaviour of affected watersheds. Specifically, forest harvest (specifically, clear-cutting) has been shown to significantly increase in-stream DOC concentrations within boreal forest catchments (Nieminen 2004; Kreutzweiser, Hazlett, and Gunn 2008; Laudon et al. 2009; Schelker, Eklöf, and Bishop 2012). Three major mechanisms have been implicated in how forest harvest alters in-stream DOC concentrations and composition. Firstly, harvest can affect factors that determine concentrations of soluble DOC within the soil. Secondly, forest harvest can increase the overall flux of water through the soil, thereby enhancing DOC export (Kreutzweiser, Hazlett, and Gunn 2008). Thirdly, harvest can alter hydrologic pathways that connect terrestrial (soil) DOC sources to receiving waters. For example, harvest can increase water flow through surficial soil layers enriched in soluble DOC relative to deeper soil horizons, leading to an increase in stream DOC (Schelker et al. 2012).

The first mechanism altering DOC concentration relates to the increased availability of transportable DOC within the soil. The process of forest harvest typically results in a large accumulation of biomass residues (such as logging slash), accumulating litter inputs into the soil (Hyvönen et al. 2000). Forest harvest can also increase soil moisture and temperature, which can intensify microbial activity within surficial soil layers and facilitate the conversion of biomass to OM forms easily transported through hydrologic flowpaths (Kreutzweiser, Hazlett, and Gunn 2008). Indeed, accumulations of organic matter within forest litter upon harvest have been associated with heightened nutrient availability in soil nutrients (McLaughlin and Liu 1996), and

increased nutrient mobility and export into receiving waters (Lamontagne et al. 2000; Kreutzweiser, Hazlett, and Gunn 2008). Both mechanisms have been implicated in observed increases in stream DOC concentrations in northern latitude forests upon forest harvest (Zoltai and Martikainen 1994; Lamontagne et al. 2000; McHale et al. 2007; Laudon et al. 2009; Schelker et al. 2012; Glaz et al. 2015), as well as after site preparation for replanting (Mannerkoski et al. 2005; Piirainen et al. 2007; Schelker et al. 2012).

Both the second and third mechanism relate to alterations in hydrologic pathways that transport DOC from terrestrial (soil) to aquatic environments. These mechanisms are underpinned by the effect of forest harvest activities on catchment hydrology. Climatically, forest harvest has been associated with an increase in snow accumulation (Murray and Buttle 2003; Sørensen et al. 2009), and a decrease in evapotranspiration; both can cause groundwater levels to rise, and facilitate the transport of soil nutrients and DOC into runoff (Kreutzweiser, Hazlett, and Gunn 2008). In particular, decreases in evapotranspiration can increase runoff, especially in summer months following harvest when the loss of evapotranspiring biomass is most keenly felt (Hornbeck et al. 1993; Andréassian 2004; Sørensen et al. 2009; Schelker, Kuglerová, et al. 2013). Intensification of runoff suggests an overall increase in water flux moving through the soil, which also enhances the transportation of available DOC from soil to stream. In addition to altering how much water is moving through the soil, forest harvest can also alter where water is flowing. Specifically, the overall rise in water table and activation of superficial soil layers enriched in DOC relative to deeper soil layers (Bishop, Seibert, and Köhler 2004; Seibert et al. 2009), has been associated with increased DOC flux from forested catchments affected by harvest (Sebestyen, Boyer, and Shanley 2009).

DOC biogeochemical cycles are complex, and are further complicated by forest harvest. How forest harvest affects the three generalized mechanisms outlined above is in turn determined by factors related to the soil, climate, as well as how forest harvest and associated activities were executed within the specific context. DOC export is strongly influenced by landscape units, including the presence of uplands, wetlands and open water bodies (Ågren, Buffam, and Jansson 2007; Laudon et al. 2011; Schelker, Burns, and Weiler 2011). Thus, generalizing the effects of forestry on DOC from catchment to catchment, as well as extrapolating such effects from small, headwater catchments towards more comprehensive river networks, is difficult (Mallik and Teichert 2009; Lee and Lajtha 2016).

Despite such difficulties, furthering understandings in catchment DOC biogeochemistry are particularly important because DOC export through runoff can represent a significant proportion of a catchment's net carbon budget (Kindler, Siemens, and Kaiser 2011). However, flux calculations can be subject to errors when DOC concentrations are measured on a more infrequent timescale than discharge, necessitating data interpolation within flux deriving from DOC concentration and discharge. DOC concentrations are also highly dynamic, and can vary widely on timescales from minutes to seasons. Such dynamics can be missed by infrequent measurements, which can greatly affect the accuracy of flux measurements when interpolation is used to compensate for infrequent DOC measurements (Hinton, Schiff, and English 1997). The frequency of DOC measurements is critical as traditional approaches towards investigating in-stream DOC concentrations center on discrete measurements (i.e., grab sampling), often measured at daily-weekly frequencies as sampling at sub-daily intervals is laborious and impossible within remote sites. Studies comparing annual flux measurements using DOC concentration measurements at different time intervals have reported conflicting effects of DOC

measurement frequency on annual DOC flux calculations. For example, Koehler et al. (2009) reported insignificant differences in flux calculations derived from either 30 minute to daily measurements (Koehler et al. 2009). However, our own calculations show that interpolating data from daily to weekly time steps can underestimate DOC fluxes compared to data measured on an hourly basis (Jollymore, Johnson, and Hawthorne 2012). The sensitivity of DOC flux measurements to sampling frequency, due to the temporal variability inherent in DOC dynamics, contrasts with the behavior of more chemostatic water quality markers such as chloride, nitrate, and sulfate, where flux calculations are much less sensitive to sampling frequency (Alewell et al. 2004).

3.1.2.1 DOC quality as a fingerprint for carbon biogeochemistry

Shifts within the biogeochemical mechanisms that affect how much DOC is dissolved within a stream can also alter what kind of DOC is present – specifically, alterations within formation and transportation mechanisms due to forest harvest could also affect the chemical composition of DOC within surface waters. DOC describes a heterogeneous, structurally complex, and diverse array of chemical families, whose character reflects biogeochemical processing within both terrestrial and aquatic environments, and hydrologic connectivity between sources and receiving waters. Exploring in-stream DOC composition is important in terms of further understanding DOC biogeochemistry within linked terrestrial-aquatic systems, as well as comprehensively appreciating the impact of DOC on human and ecological health. Different forms of DOC have diverse biogeochemical roles, with consequences for water quality, human health, as well as general ecological processes (Driscoll and Fuller 1988; Morris and Hargreaves 1997; Seitzinger and Sanders 2002; Inamdar, Singh, et al. 2011). Specifically, the chemical composition of DOC determines its biochemical functionality within aquatic environments, including its mobility,

bioavailability and degradability (Jaffé et al. 2008; Fellman, Hood, and Edwards 2009; Fellman, Hood, and Spencer 2010). Distinct forms of DOC behave differently within the aquatic environment, in ways that impact their microbial lability, ability to bind and transport potentially harmful metals, and redox potential within biochemical cycles involving electron transfer. The mineralization of microbially labile DOC species is of particular interest within the context of carbon cycling, as such processes result in emission of greenhouse gases (such as carbon dioxide) to the atmosphere, and are thus a concern in terms of carbon accounting and climate change (Cole et al. 2007; Battin et al. 2008; Butman and Raymond 2011; Schade and Bailio 2016). Lastly, different categories of in-stream DOC have diverse reactivities to disinfectants used in drinking water treatment, where different DOC classes can yield potentially harmful disinfection by-products (for example: Chang et al. 2001).

In-stream DOC composition can be used a tracer for DOC sources and flowpaths, given that such composition is a reflection of DOC formation within the terrestrial environment, its transport through various flowpaths, and further processing within receiving waters (Hood, Gooseff, and Johnson 2006; Inamdar, Finger, et al. 2011; Inamdar, Singh, et al. 2011; Strohmeier et al. 2013; Singh et al. 2014). DOC 'fingerprinting' to identify DOC composition is possible both spatially (between different landscape units within a catchment, as well as within the soil column), and temporally (from diurnal to seasonal scales due to climatic variability and subsequent shifts in plant communities). Thus, the three mechanisms that drive DOC from terrestrial to aquatic ecosystems can also shift the composition of DOC itself, noting that changes in biogeochemical processing of organic matter within the soil, as well as hydrologic connectivity and transportation pathways, can all alter the composition of stream DOC. Variations within any of these mechanistic levers, including changes in climate, hydrology or

large-scale changes in biota such forest harvest, can therefore affect the production, consumption and transport of DOC, altering both how much, and what types, of DOC are present within aquatic systems (Frank et al. 2000; Kalbitz et al. 2000; Aitkenhead-Peterson and McDowell 2003; McDowell 2003; Fellman et al. 2009).

3.1.3 Spectrophotometric DOC characteristics as an indicator of hydrologic flowpaths

Despite the potential for using DOC concentration and composition (e.g. "quality") as a marker for the drivers and biogeochemical mechanisms by which DOC is formed, transported, and processed within terrestrial-aquatic ecosystems, several gaps need to be addressed. Firstly, the drivers and interactions between complex biogeochemical cycles and hydrologic pathways dominating the transfer of different sources of terrestrial DOC to aquatic systems are poorly understood (Strohmeier et al. 2013). Understanding these mechanisms within a broad range of ecosystems is critical towards using DOC characteristics as a hydrologic signal to illuminate DOC mechanistics, as well as to elucidate the impact of ecosystem alterations such as forest harvest. Traditional studies for parsing the chemical identity of in-stream DOC characteristics comprise analytical approaches involving intensive multi-stage separation and analysis methods, such as resin fractionation (Leenheer 1981; Chow et al. 2004; Soh et al. 2008), gel filtration chromatography (Helms et al. 2008), and high-performance size exclusion chromatography (HPSEC) (Her et al. 2002). While accurate, such methods are time intensive, costly, and mechanistically difficult. Critically, they can also alter DOC characteristics, making it difficult to relate back to DOC characteristics within the natural state (Schmidt et al. 2002). In recent years, spectrophotometric absorbance and fluorescence methods have emerged as a low-cost, high-sensitivity, and high throughput means of investigating aqueous DOC. The strength of these approaches is their ability to parse broad DOC characteristics (such as humic-like, fulvic-like,

and microbial-like fractions), with minimal sample interference. Given the ability to identify discrete classes of compounds occurring within the bulk DOC matrix, these methods have been used to investigate DOC origins, fate, transformations, and redox state in natural and anthropogenic environments (e.g., Coble et al. 1996; McKnight el at. 2001; Baker et al. 2004; Cory and McKnight 2005; Miller et al. 2006), and are particularly sensitive for signaling compartmental sources of DOC in runoff (Austnes et al. 2009; Fellman et al. 2009; Ishii and Boyer 2012; Strohmeier et al. 2013). Both absorbance and fluorescence spectra can be used to calculate optical proxies descriptive of broad chemical fractions within bulk DOC. To date, these indices relate to the degree of aromaticity ($SUVA_{254}$), age, degree of humification, and DOC molecular weight (more information regarding spectral indices in Appendix A). In addition to these commonly used spectral proxies, the fluorescence signature of stream DOC is particularly sensitive to the presence of different DOC fractions, and has proven a remarkably useful means of tracking DOC source (Strohmeier et al. 2013). Such fluorescence signatures are observed when spectra are collected over large ranges of paired excitation and emission wavelengths, creating a three-dimensional emission-excitation spectrum (EEMs) whose peaks are representative of diverse forms of organic matter. Applying chemometric techniques for parsing these spectra, including principal component analysis (PCA) and parallel factor analysis (PARAFAC), can distill quantitative information regarding DOC characteristics from complex spectral data (Cory and McKnight 2005). For example, Strohmeier at al. (2013) used a thirteen component PARAFAC model (Cory and McKnight 2005) to deconstruct bulk stream DOC characteristics according to whether it originated from deep groundwater, shallower groundwater from riparian soils, and runoff within a forested catchment in Germany (Strohmeier et al. 2013). Other studies have used spectrophotometric absorbance and fluorescence characteristics to

outline compartmental sources of DOC, temporal variability, as well as phenomena such as the effect of storms on sources and connectivity between terrestrial and stream environments (Inamdar, Finger, et al. 2011; Inamdar, Singh, et al. 2011; Jaffé, Cawley, and Yamashita 2014; Singh et al. 2014). The recent development of in situ sensors (integrating either absorbance and fluorescence spectrophotometers), also provides the opportunity to investigate dynamics in DOC concentration and characteristics at a near-continuous timescale, a vast improvement over traditional 'grab' sampling (Jollymore, Johnson, and Hawthorne 2012; Ruhala and Zarnetske 2016). This includes the observation of short timescale dynamics otherwise difficult to capture. For example, in situ measurements of streamwater absorbance were used to elucidate diurnal cycles in DOC characteristics, reflecting both photochemical and biologically-mediated processes in the stream and terrestrial DOC sources (Spencer et al. 2007).

Notwithstanding the potential of these approaches, there are relatively few studies of longer-term DOC dynamics spanning times in which significant land use changes (such forest harvest) have occurred. Additionally, only a few studies have paired in situ measurements (such as absorbance spectrophotometry) with highly sensitive fluorescence spectrophotometry to comprehensively elucidate catchment DOC dynamics.

3.1.4 Study overview

The overarching aim of this study is to investigate how forest harvest affects DOC cycling, specifically the concentration, flux and composition of DOC within a small headwater stream. This study does so by illustrating stream DOC characteristics over a long (~4 year) time period, parsed using both high temporal frequency in situ measurements of absorbance as well as high-sensitivity fluorescence spectra of discrete streamwater sampling, captured within three-dimensional EEMs. The specific questions leading towards this overarching aim are: 1) how does

forest harvest affect DOC concentration and DOC flux?; 2) how does forest harvest alter DOC characteristics?; and 3) what does this mean in terms of the effect that forest has on DOC biogeochemistry within linked terrestrial-aquatic systems? Collectively, these three questions attempt to evaluate the higher-level variations in hydrologic and biogeochemical mechanisms resulting from forest harvest.

3.2 Methods

3.2.1 Study site

This study site is located on the east coast of Vancouver Island, Canada (49°30′N–49°55′N, 124°50′W–125°30′W), south of Campbell River, British Columbia. The site comprises a first-order stream that drains a 91-hectare, second growth forest that ranges from 300-400 m above sea level (slope = 5-10 degrees). This site is located in the coastal western hemlock biogeoclimatic zone, which is characterized by a mild, coastally influenced climate that receives an abundance of precipitation as rain (despite the rain shadow cast by the mountainous center of the island, shielding the eastern coast from the brunt of storm systems received from the Pacific Ocean). The forest canopy was dominated by Douglas-fir (80%), western red cedar (17%) and western hemlock (3%), with a sparse understory composed of salal, vanilla-leaf deer foot, Oregon grape, and various species of ferns and mosses. This stand was composed of secondary growth, having been initially harvested in the late 1940's. Soils are distinguished by humo-ferric podzols, with a shallow organic horizon (2-10 cm deep), a deep Bf horizon (distinguished by an accumulation of iron and aluminum oxides), and an impermeable duric basal till layer. Further detail regarding soil characteristics is available in Appendix C, which investigates soil organic matter characteristics from the same study site.

3.2.2 Details of forest harvest

Forest harvest began in October 2010, with the improvement of an existing road system (Figure 2.1, Chapter 2). Timber harvest began in December 2010 and extended through late January, 2011. Harvest was accomplished via clearcutting and whole stem removal, without site preparation beyond road construction. Trees within a riparian setback of ~3 m adjacent to the stream were retained, noting that riparian setbacks occurred only within the immediate upstream reach of the study site (likely as the stream channels were less clear given the small size of the stream upstream of the study site). Continued disturbance to the site occurred throughout 2011, including timber hauling from January-March 2011, planting during summer 2011, and burning of harvest residues (i.e., slash) in September 2011.

3.2.3 Hydrometric and climatic monitoring

A hydrologic monitoring station was installed at the outlet of the watershed study area in 2007, and was the site of various water quality and discharge measurements at staggered time intervals from this time until June 2014. The site consists of a V-notch weir, at which in situ water quality parameters were measured. Measurements of stream depth were made between 2007 – June 2014 at a 30-minute time interval (WT-VO Water Height sensor, TruTrack, Christchurch, New Zealand), and stream discharge derived from depth through rating curves calculated using the salt dilution gauging method (Moore 2004).

Additional measurements of in situ water quality indices include the measurement of electrical conductivity (EC), stream and groundwater CO_2 (Johnson et al. 2009), dissolved oxygen (DO) concentration, pH, stream temperature, and oxygen reduction potential (ORP). Such measurements of streamwater quality were taken on an approximately 30 minute timescale, and spanned from ~2008 - June 2014 (depending on the measurement).

In addition to in situ measurements, an automated sampling system (6712 Portable Sampler, Teledyne ISCO, Lincoln, Nebraska, USA), collected water samples at regular time intervals (ranging from 36 to 60 hours, to capture diurnal cycles) for laboratory water quality analysis.

Data regarding climatic conditions (including air and soil temperature, precipitation, wind speed, and solar radiation) was recorded on an eddy covariance tower located within the middle of the clear-cut, some ~1 km west of the hydrometric stream site (for further details regarding the extensive activities at this climatology study site, see Jassel et al. 2008, 2010).

3.2.4 In situ water quality measurements – DOC concentration

In situ measurement of DOC concentration was accomplished by measuring the absorbance spectra of streamwater via an in-stream spectrophotometer (spectro:lyzer model, s::can, Austria). Further details regarding the deployment, setup and details regarding issues of instrument deployment (specifically within the stream context) is detailed within Jollymore et al (2012; Chapter 2 of this thesis). Briefly, measurements of DOC concentration were calculated from 30-minute measurements of stream absorbance spectra over 240-300 nm, based on derivative spectroscopy algorithms provided by the instrument manufacturer (further details in Jollymore, Johnson, and Hawthorne 2012). Spectrally-derived DOC concentration measurements were calibrated by comparison to concentrations determined using a high temperature combustion method (Shimadzu Scientific Model TOC-V CSH/CSV, Shimadzu Corporation, Kyoto, Japan), in a method pioneered by Waterloo et al. (2006) and further described in Jollymore et al. (2012). Specifically, calibrations were made according to a wet and dry season relationship between DOC measured via either absorbance or high temperature combustion methods. Additionally, instream measurements of DOC concentration made using in situ spectrophotometry were

compared to DOC measurements of automated grab samples made using high temperature combustion (Shimadzu Scientific Model TOC-V CSH/CSV, Shimadzu Corporation, Kyoto, Japan). Automated grab sampling of streamwater is described in more detail below (Section 3.2.5). Absorbance spectra were also corrected as per Green et al. (2008) and Helms et al. (2003) using custom scripts in R (Green and Blough 2003; Helms et al. 2008), as described further in Appendix A. Various absorbance indices were calculated from corrected streamwater absorbance spectra. Such indices offer proxies for organic matter composition, with further detail regarding their calculation and interpretation in Appendix A). Both calibration of DOC concentration, data cleaning and calculation of spectral indices were conducted using custom scripts in R (version 3.3.1; R Core Team 2016).

3.2.5 Water sampling and laboratory analyses

Stream water samples were taken using an automated sampler (6712 Portable Sampler, Teledyne ISCO, Lincoln, Nebraska, USA), which collected stream samples on 36-hour increments from 2008-2013 and increments of 60 hours from 2013- 2014. Samples were collected on a monthly basis, kept cool during transport, filtered at 0.7 μm (pre-combusted glass filters, EDM Millipore, Merk KGaA, Darmstadt, Germany) upon arrival in the laboratory, and kept at 4°C until analysis. Samples were analyzed for water quality parameters such as concentrations of anions including nitrate, phosphate, sulphate and chloride (via liquid ion chromatography; Advanced Compact IC, Metrohm AG, Herisau, Switzerland), DOC concentration via high temperature combustion (Shimadzu Scientific Model TOC-V CSH/CSV, Shimadzu Corporation, Kyoto, Japan), and DOC characteristics through fluorescence, as described below.

3.2.6 Fluorescence spectrophotometry

Measurements of excitation-emission matrices (EEMs) from filtered streamwater samples were conducted using an Aqualog spectrofluorometer (Horiba, New Jersey, United States) over an excitation range of 240-600 nm (2 nm increments), and an emission range of 249-620 nm (~1 nm increments). Strongly absorbing samples (O.D > 0.30 at a absorption wavelength of 254 nm) were diluted prior to EEM collection. Instrument corrected EEMs were blank corrected, corrected for inner filter effects (Ohno 2002), and normalized to the area under the Raman curve (e.g., Determann, Reuter, and Wagner 1994; Nieke et al. 1997; Stedmon, Markager, and Bro 2003). Additionally, second order Raleigh scatter, as well as Raman bands, were masked and replaced with interpolated values (bandpass = 12 nm) (Zepp, Sheldon, and Moran 2004;, Bahram, Bro, and Stedmon 2006), while first-order Raleigh scatter was excised at a bandwidth of 50 nm to prevent spectral artefacts (Bro 1997; Stedmon and Bro 2008). The dilution factor, if applicable, was applied to absorbance and fluorescence spectra in accordance with Beer's Law. All corrections steps were performed using custom scripts in R, and described in more detail in Appendix A (version 3.3.1, R Core Team 2016).

Corrected EEMs were used to calculate various fluorescence parameters, including fluorescence index (FI), humification index (HIX), freshness index (FrI), Peak A, Peak C Peak T, and overall fluorescence intensity (as described in more detail in Appendix A). The calculation of fluorescence indices was accomplished in R (version 3.3.1; R Core Team 2016). To obtain information regarding the quality of organic matter fractions described by the 3-D EEMs spectra, corrected spectra were fit to an established 13-component parallel factor analysis model (PARAFAC), from which the redox index and percent protein were calculated (Cory and McKnight 2005), as well as a custom 4 component model (Stedmon and Bro 2008; Murphy et al.

2013). All PARAFAC modelling was accomplished through established protocols using MATLAB (student version 7.14.0). The custom model was evaluated by split half analysis, as well as by minimizing the sum of square errors describing the fit between the model and the corrected spectra.

3.2.7 Statistical analysis

3.2.7.1 Flux calculations

All data analysis outside of PARAFAC modelling - including spectral corrections and statistical analysis - was done using R (version 3.3.1; R Core Team 2016). To calculate the monthly mean discharge (mm/month) to compare between the pre and post-harvest period, the specific discharge was calculated by dividing discharge measurements (L/s) taken every 30 minutes to the watershed area (91 hectares). To compensate for missing data within the 30-minute discharge time series, the daily average specific discharge (m^3/day) was calculated from 30-minute data, and missing data interpolated using linear interpolation. Monthly discharge (mm/month) was calculated by summing daily discharge by month, and the monthly mean discharge calculated for both the pre- and post-harvest periods (Table 3.2).

DOC flux was calculated as per Strohmeier et al. (2013). Briefly, 30 minute DOC concentrations (mg/L) were multiplied by corresponding 30-minute discharge measurements (L/s) to get DOC flux at 30-minute intervals (mg/s). Missing variables in the time series were interpolated via linear interpolation. To determine the DOC flux on a monthly basis, the mean daily DOC flux was calculated from 30-minute measurements to compensate for missing data. The monthly flux was then calculated by summing the mean daily DOC over the month time; missing values were compensated via linear interpolation. Flow duration analysis was done in R using the hydroTSM package in R (version 3.3.1; R Core Team 2016).

3.3 Results and discussion

This section (Chapter 3.3) presents both the results and brief discussion regarding the impact of forest harvest as observed within DOC biogeochemistry; for clarity, it is broken into three discrete sections. The first section (Chapter 3.3.1) investigates the effect of harvest on stream hydrology (given its importance to instream DOC dynamics). The second section of the results and discussion (Chapter 3.3.2) parses divergence in DOC concentration and flux between the pre and post-harvest periods. The third section (Chapter 3.3.3) investigates how forest harvest affects DOC characteristics observed within both absorbance and fluorescence spectral properties. Lastly, Chapter 3.4 presents further discussion regarding what the behaviour explicated within Chapter 3.3 means in terms of the biogeochemical consequences of forest harvest.

3.3.1 Part 1: Effect of forest harvest on hydrology

This study first outlines basic climatic conditions important to catchment hydrology, as well as investigating the effect of forest harvest on stream runoff and discharge. This is presented as a preamble to examining effects on DOC dynamics, given the importance of hydrologic pathways to DOC dynamics within coupled terrestrial-aquatic systems.

3.3.1.1 Site and climate characteristics

The climate at the site is characterised by a relatively wet winter period (October – March), and a drier summer period (April – Sept), where an average of 1230 mm of rain per year fell during the study period (ranging from ~870 mm in 2013 to 1830 mm in 2010). Approximately 80% of the yearly precipitation falls between the months of October to March, denoted here as the rainy, or 'wet', portion of the year; this period is shown as blue boxplots in Figure 3.1, and the drier period

as yellow (Figure 3.1). Temperatures at the site are relatively mild; during the rainy winter months, temperatures varied from ~3°C to ~8°C, only occasionally dipping below -5°C during the five year study period (Figure 3.1B). Likewise, summer or dry period temperatures were relatively mild (~8°C to ~18°C on average), and peaked in July (Figure 3.1B). Because of this, precipitation throughout the year fell mainly as rain. Snowpack dynamics, such as springtime snowmelt, thus did not dominate the hydrologic regime; snowfall occurring during the study period tended not to persist on the ground, where temperatures sufficiently cold to support snowfall and the lasting presence of a snowpack typically lasted only a few days.

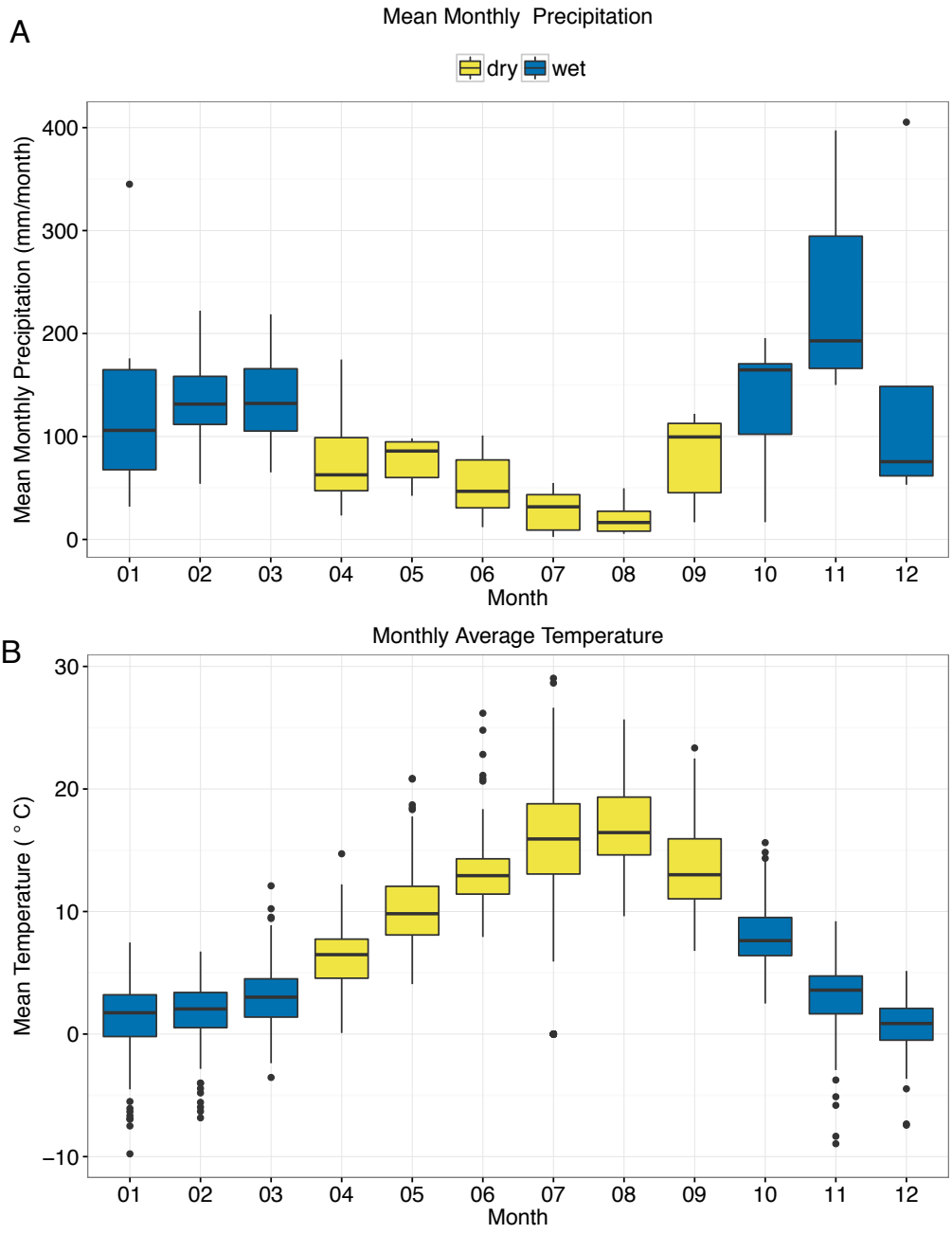

Figure 3.1 Mean monthly precipitation and temperature. The average monthly precipitation and rainfall calculated from climate data from January 2009 - December 2014 is shown. Boxplots present means as thick line within the box, where the upper and lower boundaries of the boxes correspond to the 75th and 25th percentile, respectively, and whiskers incorporate data 1.5 times the interquartile range.

3.3.1.2 Impacts of forest harvest on runoff

Given the importance of hydrologic pathways to DOC dynamics, we firstly investigated the effect of harvest on runoff within the stream. Figure 3.2 shows the monthly precipitation (mm/month), as well as 30-minute measurements of discharge (L/s), and the monthly runoff for the study period (~2008-2014). As noted in Figure 3.1 (trends in monthly precipitation), the wet winter months are the most hydrologically active. Indeed, some ~85% of total yearly runoff occurred within the 'wet' period of October – March (Table 3.2). During this time, stream discharge was highly dynamic (with sharp peaks in the hydrograph corresponding to the occurrence of precipitation events, demonstrating the responsiveness of stream discharge to precipitation). Correspondingly, the mean monthly runoff was greatest during this wet period, with less runoff occurring during the drier summer months.

Year	Total Runoff (mm/year)	Total DOC Flux (kg/ha*year)
2008	966	-
2009	744	-
2010	1390	50
2011	1359	76
2012	1624	75
2013	1151	49
2014	1483	-
Average	1206	63

Table 3.1 Total runoff and DOC flux by year.

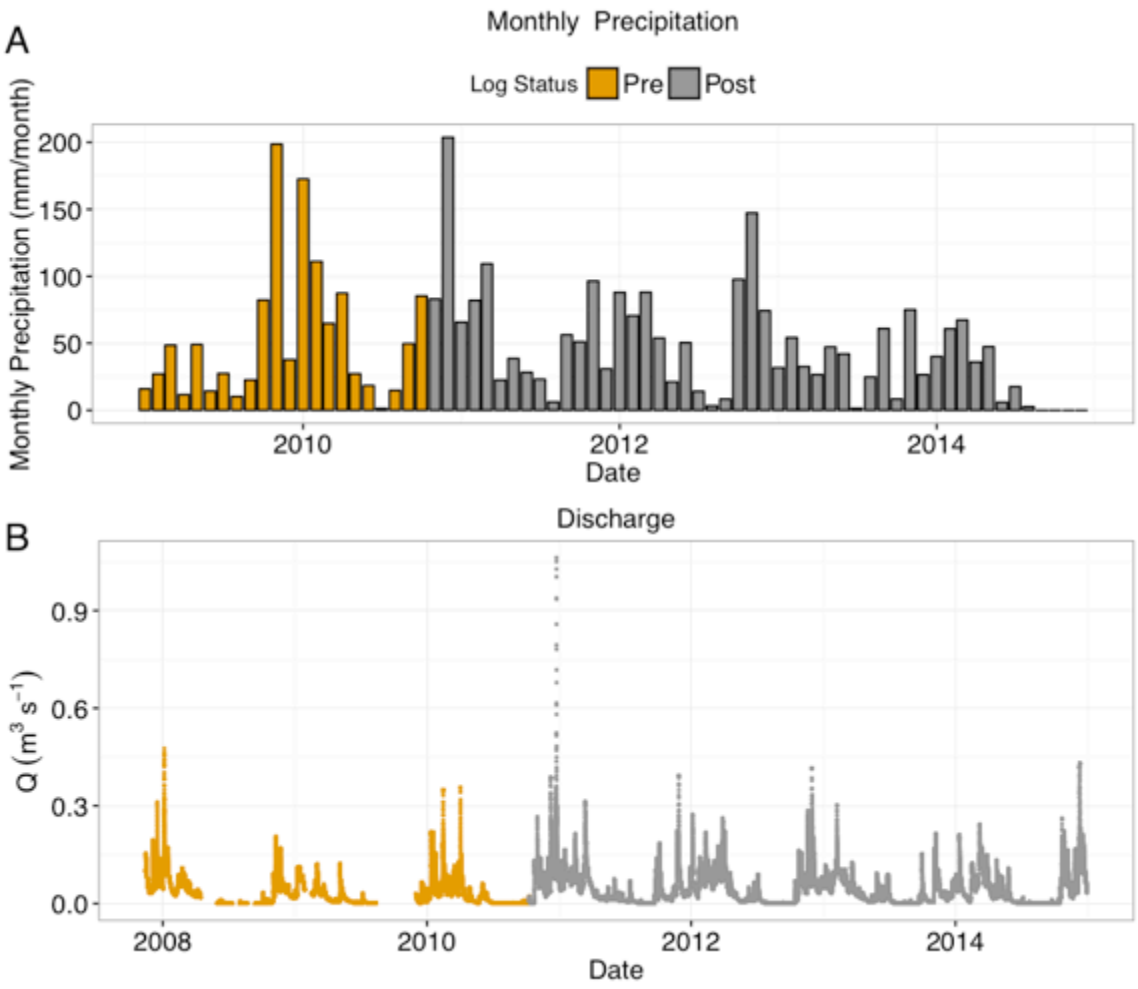

Figure 3.2 Precipitation and discharge for the study period. The pre-harvest period is noted in orange, and the post-harvest period in grey.

Two approaches were used to determine how forest harvest affects stream runoff. Firstly, flow duration analysis was used to investigate how discharge differs between the two periods, partitioned according to hydrologically distinct wet and dry seasons; secondly, the difference in runoff between the pre and post-harvest period was analyzed using percent difference in mean monthly runoff (mm/month).

3.3.1.3 Effect of forest harvest on discharge: Flow duration analysis

Flow duration curves, showing the percent of time that flow within a stream is likely to equal or exceed a specific discharge value, was performed using the mean daily discharge (m^3 day^{-1}). Discharge values were partitioned both according to hydrologic period (wet/dry), as well as whether it occurred within the pre or post logging period. The data was partitioned in this way to better show possible effects of forest harvest, given the stark differences in flow regimes between the wet and dry months. Mean daily discharge was used to improve the computational time of the analysis. These curves are shown in Figure 3.3; vertical dotted lines show the 20% and 70% probability of exceeding a specific value of daily discharge.

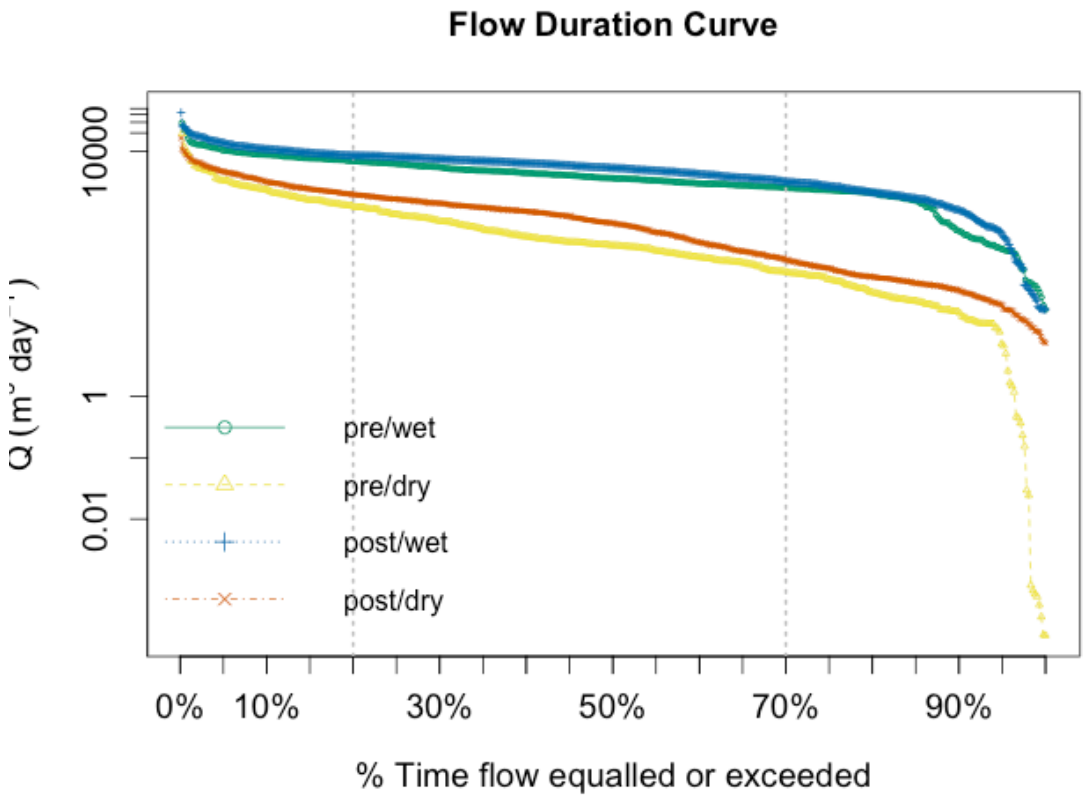

Figure 3.3 Effect of harvest on stream flow duration analysis. Values for mean daily discharge (m^3 day^{-1}) were partitioned according to both hydrologic period (wet/dry), as well as logging status (pre/post-harvest).

The division between 'wet' and 'dry' months is clear within flow duration curves. Dry months are characterized by lower daily Q values across all probabilities for exceedances when compared to the wet October – March period (which exhibit curves shifted to higher values of discharge for the sample probability). Additionally, probability curves show higher values of Q for the post-harvest period when compared to those of the same hydrologic period within the pre-logging period. This is especially true for the dry period, where the dry post-harvest period has little overlap with that of the dry pre-harvest period (except within the low probability of exceedance (<5%) region, when both curves converge).

3.3.1.4 Effect of forest harvest on runoff

Secondly, the mean runoff was compared between months in the pre-harvest period to that within the post-harvest period, following the method used by Sorensen et al. (2009). To do this, the mean monthly runoff (mm/month) was calculated for all months, and the mean calculated by month for either the pre or post-harvest period (shown in Table 3.2). The percent difference between the pre-harvest to post-harvest periods was then calculated (as per Sørensen et al. 2009):

$$\% \textbf{ change} = \frac{\textbf{(Post Runoff} - \textbf{Pre Runoff)}}{\textbf{Post Runoff}} * \textbf{100} \qquad \textbf{(Equation 3.1)}$$

As shown in in Table 2, the post-harvest mean monthly runoff was greater than pre-harvest for all months except for January. The percent difference between the two periods was greatest for July (77%), October (53%) and June (51%). Both June and July tend to have low precipitation (Figure 3.2), which results in less discharge and runoff (only ~3% and ~1% of yearly runoff occurs within these months). Thus, while the percent change in runoff is large, the absolute change in runoff is less than observed within wetter winter months.

Month	Pre-Harvest Runoff (mm/month)	Post-Harvest Runoff (mm/month)	% Runoff Change (mm/month) *(absolute change, mm/month*)		Average Percentage of Total Yearly Runoff (%)
January	214	199	-8	-15	17
February	148	214	31	66	15
March	135	257	47	121	17
April	73	103	29	30	7
May	41	57	29	16	4
June	24	48	51	24	3
July	5	22	77	17	1
August	4	4	2	0	0
September	11	18	37	7	1
October	45	95	53	51	6
November	122	195	38	73	14
December	134	234	43	100	16

Table 3.2 Percent difference in mean monthly runoff between the post and pre-harvest periods. Both the percent and absolute change (mm/month) are shown. Also shown is the average percentage of total yearly runoff that flows within each month (across the entire study period).

Many previous studies within various ecological contexts have noted increases in runoff upon the loss of vegetation through forest harvest, including runoff timing and volume (Andréassian 2004), annual runoff (Buttle, Creed, and Moore 2009), and peak flows (Guillemette, Plamondon, and Prévost 2005). Increased runoff has been attributed to decreases in evapotranspiration, as well as the increased accumulation of snow within open clearcuts (Pomeroy and Granger 1997). We found an increase in runoff during drier and warmer seasons for the post-harvest period relative to pre-harvest conditions, which was also observed by Sorensen et al. (2009) in their study within a northern latitude boreal forest. They noted that although the absolute change in runoff was lower within growing months, the relative change was greater, which they attributed to loss of plant transpiration (Sørensen et al. 2009). Given the

milder climate of our study, plant transpiration can potentially occur throughout the year, but likely peaks during the warmer summer months, potentially also driving changes in runoff within our study.

Statistically evaluating the significance of such differences is difficult, as runoff and discharge tends to be non-normally distributed (Sørensen et al. 2009). Climatic variables, such as precipitation, largely drive runoff generation. As climatic conditions can vary between years, it is also difficult to disentangle the effects of such inherent variability from that of specific impacts like forest harvest. This is especially true when comparing data collected over a limited span of time (where our study only encompassed some ~5 years). As such, increased data regarding year-to-year changeability in climatic drivers (especially within the pre-harvest period) would provide a better baseline regarding the effects of such variability relative to forest harvest. However, based on flow frequency analysis on discharge as well as percent changes in runoff, the post-harvest period appears to be characterized by increased discharge volume throughout the year, which translates into increased runoff when compared to the pre-harvest period.

3.3.2 Part 2: Effect of forest harvest on DOC concentration and flux

Given that forest harvest increased both the volume and total runoff of the small headwater stream within our study, we next aimed to scrutinize how forest harvest affects the instream concentration of DOC using high frequency, in situ monitoring.

3.3.2.1 Effect of forest harvest on in-stream DOC concentration

Figure 3.4 shows measurements of Q (m^3 s^{-1}) alongside in situ measurements of DOC concentration from 2009-2014. In-stream DOC concentrations were highly dynamic, as denoted by the many sharp peaks within the DOC concentration timeseries. However, the baseline DOC

concentration within the stream is relatively low (<5 mg/L), in line with previous studies investigating DOC characteristics within streams in the Pacific Northwest (Richardson, Bilby, and Bondar 2005). However, the presence of many sharp increases in DOC concentration demonstrate that although DOC concentrations are low (< 5 mg/L) the majority of the time, the stream experiences peaks in DOC concentration over short timescales, during which time DOC concentration can be much higher (8-17 mg/L). Such patterns are akin to hydrographs; peaks in concentration are quite sharp, and gradually decrease over a long time period, forming a distinctive tailing pattern. Previous studies have echoed such innate dynamism, and that behaviour in DOC exports are sensitive to catchment precipitation, tending to peak during storm events (Hinton, Schiff, and English 1997; Inamdar, O'Leary, and Mitchell 2006; Raymond and Saiers 2010; Inamdar, Singh, et al. 2011). The DOC concentrations timeseries in Figure 3.4 shows both the changeability of in-stream DOC concentrations, while also underscoring the importance of monitoring such changeable systems through high frequency methods. Figure 3.4 shows boxplots of DOC concentration measured at 30 minute intervals compiled by month over the 2009-2014 period. As observed, DOC concentrations are greatest (though not always significantly) within the rainy, hydrologically active winter months (October-March).

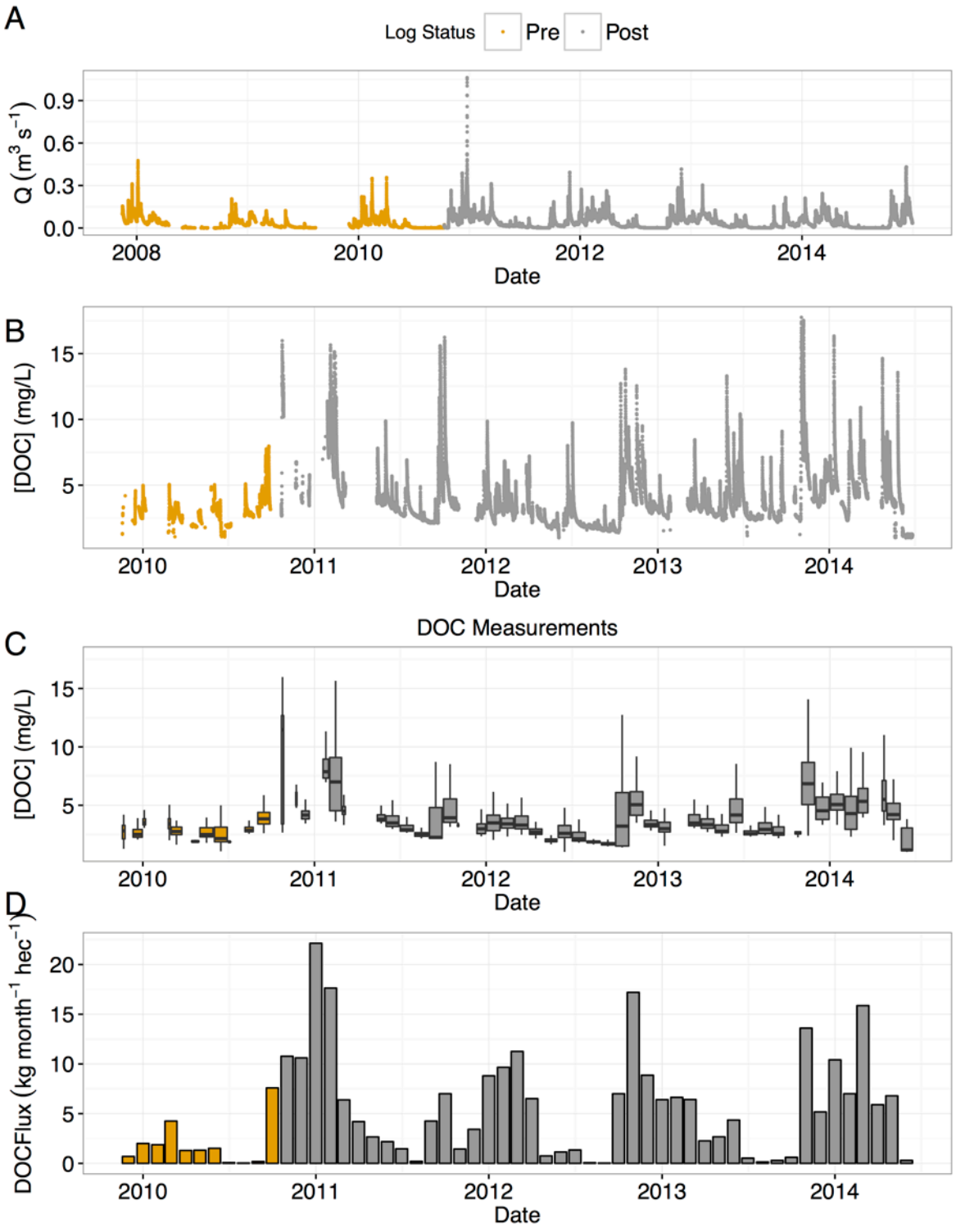

Figure 3.4 DOC concentration and flux over the study period (2009 - 2014), encompassing both the pre (orange) and post-harvest periods (grey). Panel A presents discharge, B the concentration measured at 30

minute intervals, C gives boxplots showing the mean and distribution of concentration measurements, and D shows monthly DOC fluxes.

We sought to determine whether forest harvest affects in-stream DOC concentrations by statistically comparing DOC concentrations for months in the pre- versus post-harvest period. We did this by calculating the mean month DOC concentration for all months within both the pre- and post-harvest period from 30-minute measurements. Daily mean DOC concentrations were segregated by month, such that the daily mean DOC concentrations were statistically compared by month between the pre-and post-harvest periods (resulting in the statistical comparison of mean daily DOC concentration by month). Month to month comparison was done in an attempt to evaluate according to conditions that would be the most climatically similar, noting that monthly precipitation and temperature can exhibit inter-annual variability (Figure 3.4). DOC data was non-normally distributed according to a Shapiro-Wilk test. Thus, a nonparametric Kruskal-Wallis one-way analysis of variance on ranks (ANOVA-R) was combined with Dunn's test to evaluate the statistical significance in differences within monthly mean DOC concentrations following harvest, as per Schelker et al. (2012). The percent and absolute change in mean monthly DOC concentrations were also calculated in the same manner as for runoff previously described (Table 3.5, Equation 3.1).

DOC concentrations within the post-harvest period were significantly greater for all months, except for August and September (which are the driest months of the year). In general, DOC concentrations are greater within months that also tend to be rainier (with lower concentrations within the drier summer months). More specifically, the largest change between the pre and post-harvest was observed in November, which also had the highest mean monthly DOC concentrations within the post-harvest period. November tends to be quite rainy (average

rainfall = 240 mm); this heightened period of rainfall follows the dry summer months of June – September (average rainfall = 181 mm over all four months). A peak in DOC concentration during November could thus arise from DOC that accumulates within surficial soil layers during the dry summer months, when such terrestrial DOC pools would be disconnected from the stream. The increased precipitation encountered within November could revive surficial flowpaths, resulting in increased concentrations of stream DOC as accumulated soil DOC is transported to the stream.

	DOC Concentration (mg L^{-1})					
	Pre - logging mean (± sd, mg/L)	**Post - logging mean (± sd, mg/L)**	**Percent Difference (%)**	**Absolute Difference (mg/L)**	**ANOVA-R Results chi**	**p**
January	3.62 ± 0.43	4.44 ± 2.04	18	0.81	23	$p < 0.05$
February	3.45 ± 0.69	5.11 ± 2.51	32	1.66	77	$p < 0.05$
March	2.80 ± 0.41	4.48 ± 1.39	37	1.67	1692	$p < 0.05$
April	2.02 ± 0.30	3.72 ± 1.56	46	1.70	1059	$p < 0.05$
May	2.74 ± 0.61	3.61 ± 1.79	24	0.88	95	$p < 0.05$
June	2.50 ± 0.82	3.26 ± 1.76	23	0.77	143	$p < 0.05$
July	1.87 ± 0.05	2.84 ± 0.92	34	0.97	733	$p < 0.05$
August	3.02 ± 0.48	2.47 ± 0.71	-22	-0.54	1047	$p < 0.05$
September	4.08 ± 1.09	2.92 ± 2.26	-40	-1.16	1440	$p < 0.05$
October	- -	4.41 ± 2.73	-	-	-	-
November	2.63 ± 0.85	6.28 ± 2.78	58	3.64	38	$p < 0.05$
December	2.65 ± 0.48	4.02 ± 1.16	34	1.37	1046	$p < 0.05$
Overall	3.01 ± 0.95	3.82 ± 2.10	21	0.82		

Figure 3.5 Mean DOC concentration: pre- and post-harvest. Mean monthly DOC concentrations (calculated from 30 minute data) are shown for months in the pre- and post-harvest periods. Details from significance testing through ANOVA-R are also shown.

There is a large degree of variability in DOC concentrations, even when comparing within the same months (noted within large standard deviations of 30 minute measurements compiled by month, Figure 3.4). This likely stems from the inherent variability within climatic drivers such as precipitation, which shape hydrologic factors that ultimately dictate DOC transport within forested ecosystems (Bishop, Seibert, and Köhler 2004; Laudon et al. 2011; Schelker et al. 2012). It was possible to collect only one year of data for the pre-harvest period, rather than approximately three for the post-harvest period.

To further explore the effect of forest harvest on DOC concentration, we also compared the mean monthly DOC concentration from each month within the post-harvest period to the corresponding month within the pre-harvest period. Given the non-normality of data, we again used ANOVA-R combined with Dunn's test to statistically compare mean monthly DOC concentrations pairwise between months in the pre-harvest period to those after harvest. Of the 40 total months in the post-harvest period, 53% have significantly higher mean DOC concentrations than the corresponding month in the pre-harvest period, while 70% of the months have greater (though not necessarily significant) DOC concentrations. Thus, only 8% of months in the post-harvest period have mean monthly DOC concentrations that were significantly less than the corresponding month in the pre-harvest period, while 30% of months in the post-harvest period shown lower (though not significantly) mean DOC concentrations within the corresponding month in the pre-harvest period.

Other studies from a variety of ecosystems mirror our findings that forest harvest generally increases in-stream DOC concentration. This includes studies in boreal forest catchments (Bishop, Seibert, and Köhler 2004; Laudon et al. 2011; Schelker et al. 2012), as well as across North American watersheds generally, which showed a 2-5 fold increase in DOC

concentration after harvest (Kreutzweiser, Hazlett, and Gunn 2008). DOC concentrations can be quite dynamic, where variations in hydrologic drivers (such as precipitation and snowfall), can have large effects on observed DOC concentration (Kreutzweiser, Hazlett, and Gunn 2008). Thus, increased stream DOC concentrations after harvest likely stem from the 'transmissivity feedback mechanism', where forest harvest drives increased lateral flow of water (especially during precipitation events), transporting DOC from riparian soils enriched with DOC relative to deeper soil horizons (Bishop, Seibert, and Köhler 2004). Given the wet, mild climate at the study site during the winter period (at which time in-stream DOC concentrations are heightened), such a mechanism likely plays a critical role in transporting DOC to the stream. Forest harvest can cause groundwater levels to increase due to the loss of plant biomass and associated evapotranspiration (Mannerkoski et al. 2005; Monteith et al. 2006). Such rising groundwater levels can connect DOC rich riparian soils to the stream, transporting DOC even during times of low or medium hydrologic flows (Schelker et al. 2012). This mechanism would be especially evident within the drier summer months (where baseflow is likely to contribute to a greater percentage of streamflow relative to rainy winter months). Thus, it is interesting that summer months in the post-harvest period show lower mean monthly DOC concentrations relative to summer months prior to harvest, given that increases within groundwater levels should link DOC rich soil horizons to the stream. This could be due to the lack of hydrologic connectivity during summer months that is re-established with the onset of the rainy period.

Increases in stream DOC upon harvest have also been linked to decomposition of residual biomass materials from forest harvest, resulting in more available soil OM. Previous studies within boreal catchments have also found that harvest increases soil temperature, intensifying microbial decomposition of biomass inputs; however, a definitive link to increased in-stream

DOC has not yet been elucidated (Schelker et al. 2012). Within our study, we note that the greatest change in DOC concentration between the pre- and post-harvest period occurred in the rainy month of November, where the post-harvest November also showed the highest mean monthly DOC concentration over all months (Table 3.5). DOC could accumulate within the soil during the dry summer months, and be subsequently transported to the stream when increased rainfall resurrects hydrologic flowpaths connecting landscape units within the catchment to the stream. Such an effect would be akin to increased concentrations of stream DOC observed after periods of drought (e.g., Sowerby et al. 2010), which could be exacerbated within our study through the increased contribution of logging residues to soil OM during dry summer conditions.

3.3.2.2 Effect of forest harvest on DOC flux

Given that forest harvest increases runoff and generally results in higher in stream DOC concentrations, we then sought to quantify how DOC flux out of the catchment was altered by forest harvest. The monthly flux of DOC through the stream is shown in Figure 3.4D; time series analysis of the monthly flux decomposed into seasonal, trend and residual components is shown in Appendix B. DOC flux is highly seasonal, peaking within the wet winter months (as observed within both Figure 3.4D and Appendix B), echoing trends within both runoff and stream DOC concentration discussed previously.

Yearly DOC fluxes were calculated for all years with a full year of measurement (four years total). Yearly values of DOC flux (calculated by summing monthly fluxes and normalizing by watershed area), ranged from 50-76 kg/ha*year over the period from 2010-2013 (Table 3.1). These values are similar to those found within other forested ecosystems. For example, Kindler et al (2011) observed an average DOC flux of 35 kg/ha*year over five forested European catchments, where DOC flux was quite variable between different sites. Strohmeier et al (2013)

found greater (84 kg/ha*year) DOC fluxes from a forested catchment in eastern Germany; they attributed these higher fluxes to the significant presence of riparian wetland soils throughout the catchment (Strohmeier et al. 2013). Additionally, Frank et al. (2000) observed even higher DOC fluxes (186 kg/ ha*year) from a gleysol dominated alpine forest.

The effect of forest harvest on DOC flux was approached in the same manner as per DOC concentration. Firstly, we calculated daily DOC flux by summing 30-minute flux derived from discharge and DOC concentration measurements; daily measurements were used to improve computational time and compensate for missing data. The mean daily DOC flux was calculated for each month within both the pre and post-harvest period (Table 3.6). However, the daily mean DOC flux was compiled by month for statistical comparison between the pre and post-harvest period (resulting in the statistical comparison of mean daily DOC flux by month). As per DOC concentrations, mean daily DOC fluxes were also non-normally distributed (according to a Shapiro-Wilcox test). Thus, we used ANOVA-R with Dunn's test to evaluate the statistical significance of differences between months in either the pre- or post-harvest period. This mirrors the approach used to evaluate differences within DOC concentrations, using the method initially suggested by Schelker et al. (2012). As noted in timeseries analysis of monthly DOC fluxes (Appendix B), the largest mean daily fluxes occur within the wet winter months (Table 3.6), which also showed the largest absolute differences in flux between the pre- and post-harvest periods.

	Mean Daily DOC Flux					
	Pre – Logging Mean ± sd (mg/s*ha)	Post – Logging Mean ± sd (mg/s*ha)	Percent Difference (%)	Absolute Difference (mg/s*ha)	Kruskal- Wallis Test for Significance	
					chi	p
January	1.07 ± 0.25	3.70 ± 3.64	71	2.63	10	$p < 0.05$
February	1.72 ± 1.08	4.67 ± 3.91	63	2.95	4	$p < 0.05$
March	1.78 ± 0.94	4.38 ± 3.66	59	2.60	19	$p < 0.05$
April	0.40 ± 0.25	1.78 ± 2.19	78	1.38	19	$p < 0.05$
May	0.54 ± 0.26	1.17 ± 1.88	54	0.63	0	$p > 0.05$
June	0.68 ± 0.68	0.83 ± 1.13	19	0.16	0	$p > 0.05$
July	0.04 ± 0.01	0.40 ± 0.73	90	0.36	13	$p < 0.05$
August	0.01 ± 0.02	0.05 ± 0.05	72	0.04	29	$p < 0.05$
September	0.07 ± 0.07	0.62 ± 2.33	89	0.55	3	$p > 0.05$
October	- -	2.70 ± 4.38	-	-	-	-
November	- -	5.63 ± 5.53	-	-	-	-
December	0.25 ± 0.26	2.45 ± 2.18	90	2.21	37	$p < 0.05$
Overall	0.60 ± 0.81	2.22 ± 3.39	73	1.62		

Table 3.3 Mean daily DOC flux: pre/post-harvest by month

Given issues around data availability within the pre-harvest period, we individually compared months in the post-harvest period to the corresponding month prior to harvest. Similar to trends in stream DOC concentration, 70% of the 40 months in the post-harvest period had greater mean daily DOC fluxes than the corresponding month prior to harvest (50% of which were significantly greater at a $p < 0.05$). Only 25% of the months in the post-harvest period had lower mean daily DOC fluxes than the corresponding month in the pre-harvest period (17.6% of which were significantly lower). Additionally, previous studies have highlighted the importance of discharge, rather than DOC concentrations, in regulating DOC flux. Specifically, such studies found that year-to-year variability in DOC fluxes are strongly controlled by variability in discharge, rather than in-stream DOC concentrations (Laudon, Kohler, and Buffam 2004; Ågren,

Buffam, and Jansson 2007; Nilsson et al. 2008; Schelker et al. 2012). This dependence was corroborated by our own study, where discharge explained ~79% of the variability observed within flux, and only ~10% of which was explained by variations in DOC concentration.

3.3.3 Part 3: Investigating drivers of in-stream DOC concentration

The third focus of this study concerns the effects that forest harvest has upon DOC characteristics – specifically, the chemical composition of DOC within the stream. This section integrates in situ as well as discrete measurements of spectrophotometric DOC characteristics, towards analyzing how forest harvest affects the composition of stream DOC, and thus biogeochemical and hydrologic mechanisms driving in-stream DOC. To help elucidate terrestrial sources of stream DOC (and to complement investigations of in-stream DOC characteristics), a study concerning soil DOC characteristics is presented in Appendix C.

3.3.3.1 General characteristics of stream DOC absorbance

The first section of this study parses general features of in-stream DOC characteristics as determined through in situ and discrete sampling, prior to analysis elucidating the effects of forest harvest on such DOC characteristics.

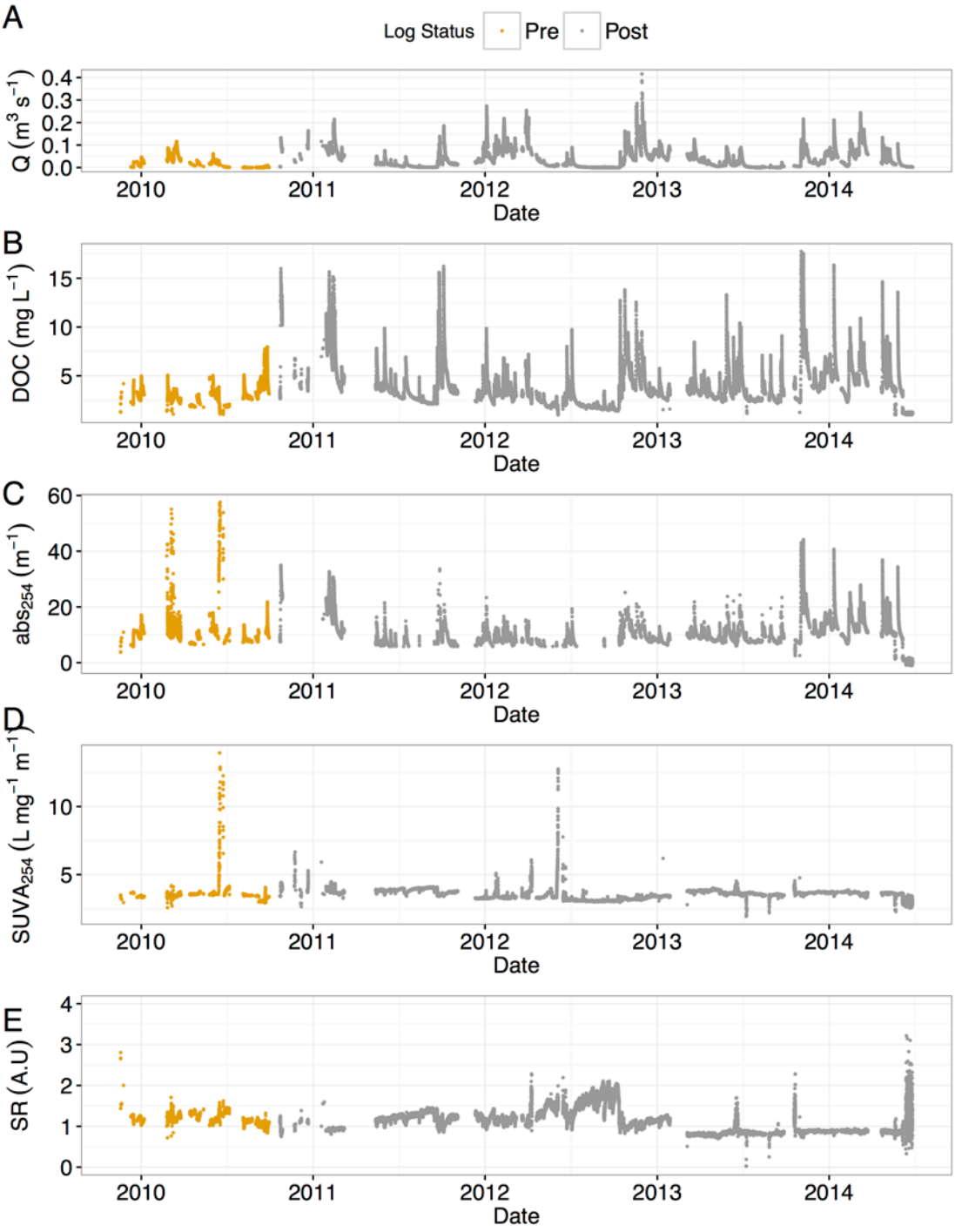

Figure 3.6 In situ data time series: Q, [DOC], abs_{254}, $SUVA_{254}$ and Slope Ratio. DOC concentration, abs_{254}, $SUVA_{254}$ and slope ratio are all calculated from measurements of stream absorbance taken at 30-minute increments (November 2009-June 2014). Missing data indicates times in which data collection failed (due mainly to power or connection failures).

Figure 3.6 shows stream characteristics – discharge and DOC concentration – alongside quality proxies calculated from in situ monitoring of stream absorbance. Both DOC concentration and discharge are presented as a point of comparison for spectral DOC characteristics, as they were discussed within the first part of this chapter. DOC quality parameters derived from absorbance spectra (including abs_{254}, $SUVA_{254}$ and slope ratio (SR)), are less dynamic than DOC concentration and discharge, with less defined peaks than present within the DOC concentration timeseries. Both the abs_{254} and SUVA traces contain large spikes that could indicate the presence of increased concentrations of aromatic carbon within the stream (Figure 3.6). However, both abs_{254} and $SUVA_{254}$ are affected by the co-absorbance of iron within near UV wavelengths (Weishaar et al. 2003). Such interference is difficult to correct for, given the difficulty of obtaining data regarding iron concentrations approaching the frequency of in situ DOC measurements. Thus, it is difficult to concretely relate values of either abs_{254} or $SUVA_{254}$ to the concentration of aromatic carbon within bulk stream DOC, the typical correlation for these proxies. Despite the likely co-absorbance of iron, the parameters are presented here for two reasons. Firstly, both parameters (especially $SUVA_{254}$) are widely reported within studies on spectral DOC characteristics, both corrected and uncorrected for the co-absorbance of iron. Secondly, given the promise and relative nascency of in situ monitoring, we also expect that developments regarding correcting high frequency data will be a key focus of future research.

Given this interference, we examined the slope ratio (SR), which is less affected by iron interference as it is calculated over a wider portion of the absorbance spectrum (beyond the near UV regions where iron absorbance is prominent) (Poulin et al 2014). Previous studies have suggested that the slope ratio is inversely related to DOC molecular weight, aromaticity, and

vascular plant inputs to DOC (Helms et al. 2008; Spencer et al. 2010; Osburn and Stedmon 2011; Spencer and Butler 2012). Values of the dimensionless SR generally varied between values of 1 and 2 over the duration of the study period, and did not exhibit the same dynamic nature as DOC concentration or abs_{254}. However, values of SR tended to decrease during times of high DOC (Figure 3.6), indicating that DOC absorbance increased within the UV region relative to longer wavelengths. This inverse relationship between DOC concentration and slope ratio suggests that the concentration of higher molecular weight, aromatic DOC also increased during periods when the DOC concentration was also high.

3.3.3.2 General characteristics of stream DOC fluorescence

In addition to in situ measurements of streamwater absorbance, fluorescence characteristics of discrete (i.e "grab") water samples were measured using three-dimensional excitation-emission (EEMs) fluorescence spectrophotometry. This analysis results in data-rich spectra resembling topographical maps that are descriptive of broad chemical constituents within the fluorescent DOC fraction. Corrected EEMs (n = 920, Figure 3.7) were fit to a custom 4-component PARAFAC model that parses complex EEMs into peaks representative of broad DOC classes (see Methods within this chapter for more detail). EEMs from streamwater samples were compartmentalized into three components previously correlated to humic-like fluorescence (C1, C3, and C4), and one component (C2) connected to protein-like fluorescence (Table 3.4) (Stedmon, Markager, and Bro 2003; Stedmon and Markager 2005; Coble 2007; Hudson, Baker, and Reynolds 2007). Humic-like fluorescence dominated features (~80% of the total fluorescence), where protein-like fluorescence tended to compose <20% of the overall DOC fluorescence. Such attributes parallel previous investigations of DOC characteristics of small and headwater streams within predominantly forested catchments (e.g., Strohmeier et al. 2013).

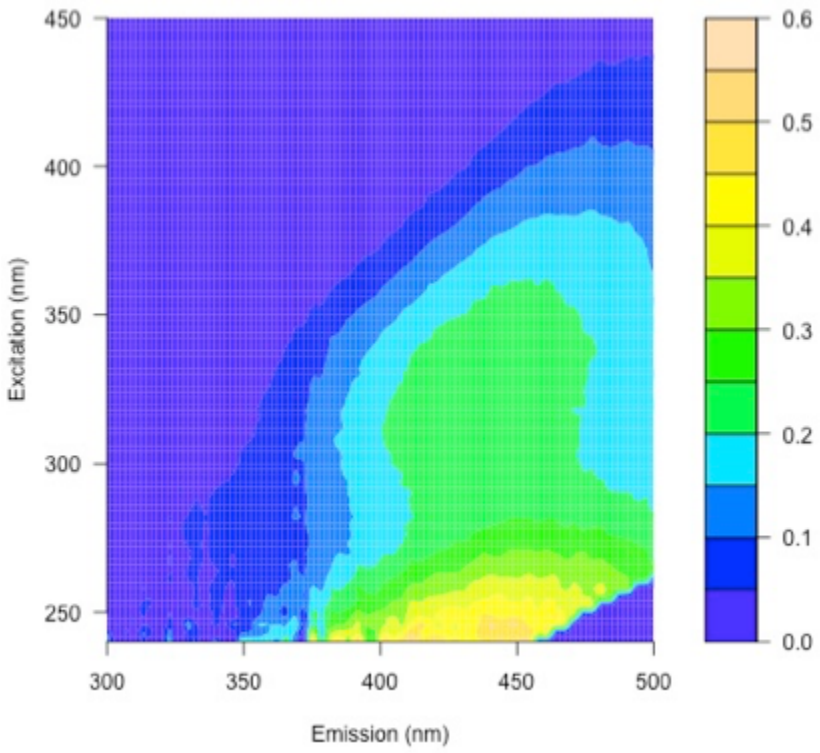

Figure 3.7 Representative streamwater EEM. EEMs from stream grab samples were fit to a 4-component parallel factor (PARAFAC) model (three humic-like peaks and one protein-like peak, Table 3.4). Fluorescence intensity is shown in Raman units (R.U, z-axis).

Component	Excitation Max (nm)	Emission Max (nm)	Description	References
C1	≤250 (broad to 350)	410	A Humic- like. Terrestrial humic fluorophore	Kraus et al. 2010; Stedmon et al. 2003; Stedmon et al 2005
C2	270 (broad to 450)	500 (350)	B – Protein-like fluorescence	Kraus et al. 2010; Stedmon et al. 2003
C3	1 = 250; 2 = 250	1 = 550; 2 = 450	C - Humic-like	Kraus et al. 2010; Stedmon et al. 2003; Stedmon et al. 2005
C4	250	480	A – Humic-like; Humic fluorophore group. Dominating the DOM exported from the natural catchments during the warmer months of the year. Also exported from agricultural catchments. Absent in wastewater DOM.	Stedmon et al. 2003; Stedmon et al 2005

Table 3.4 Description of PARAFAC components.

To show the behavior of PARAFAC components within the stream over time, Figure 3.8 shows both the F_{max} and percentage of fluorescence from each of the fluorescent components parsed from stream EEMs. F_{max} values varied between 0 and 1 (Raman units). The C1 component dominated other components across most of the study period, as shown within F_{max} values. This component, along with humic-like C4, comprised the bulk of DOC fluorescence, as shown in percent fluorescence across all samples (~30% of total fluorescence for each component, Figure 3.8). The balance in total fluorescence was comprised of humic-like C3 (~20%) and protein-like C2 (~20%). The compartmentalization of total sample fluorescence between the four components was relatively stable over the study period, save for a small period in the summer months of 2011, in which fluorescence shifted to humic-like C1 with a corresponding decline in humic-like

C3 (Figure 3.8). This apparent stability might relate to the timescale at which samples were collected. Discrete samples were obtained on relatively short timescales (intervals of 36-60 hours) in an attempt to elucidate possible diurnal cycles. As discussed in Appendix B, these timescales were insufficiently fine to capture short-term diurnal dynamics observed within indices calculated from in situ absorbance sensor measurements (discussed in Appendix B), and may contribute to this apparent stability.

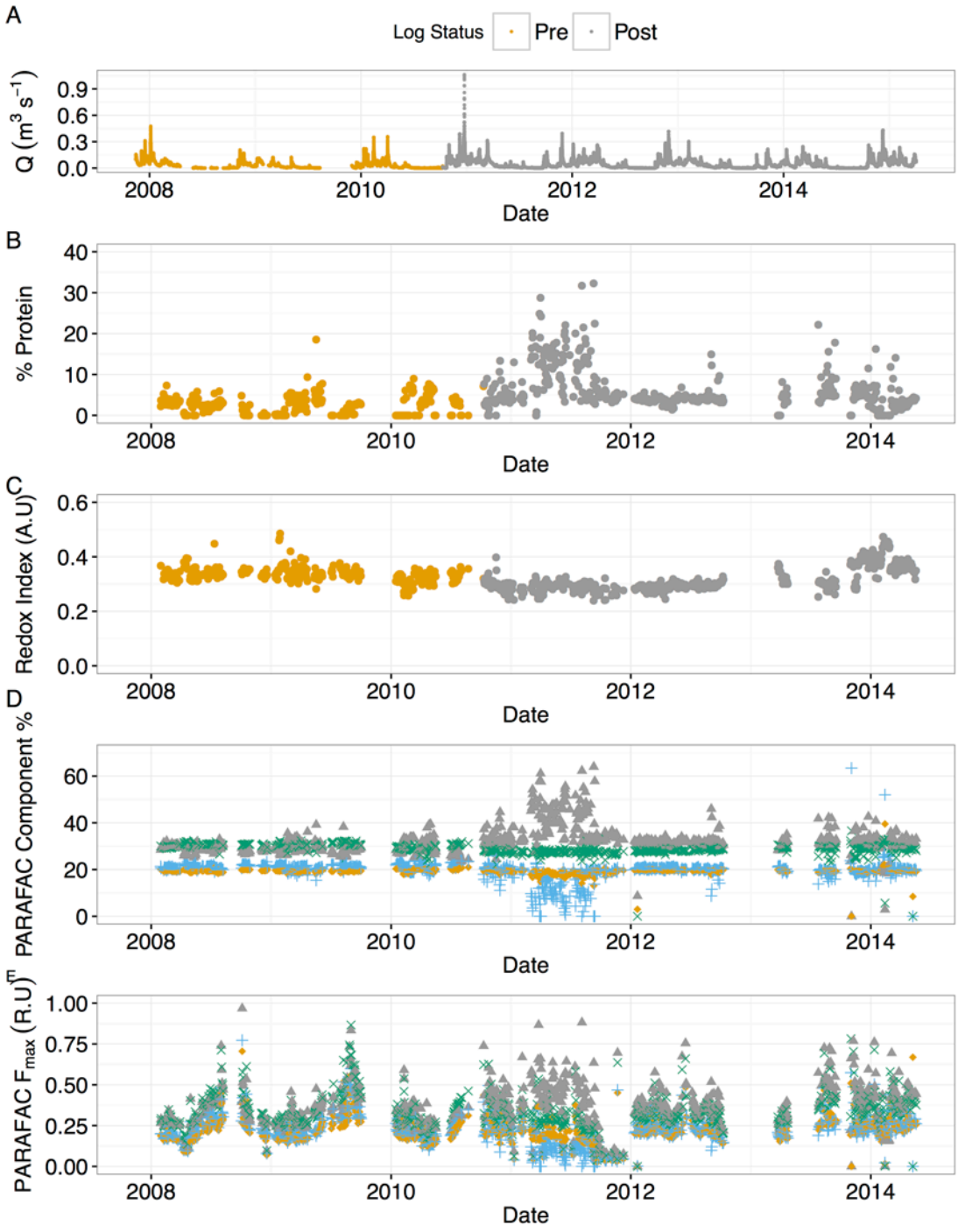

Figure 3.8 Time series of stream fluorescence characteristics. Figure 3.8 shows DOC characteristics calculated from fluorescence spectra from discrete stream samples (2008-2014) alongside discharge (Q) and DOC concentrations calculated from in situ stream absorbance. Redox Index and percent protein are calculated from a 13-component PARAFAC model described previously (Cory and McKnight 2005).

In addition to the custom 4-component PARAFAC model, streamwater EEMs were fit to the 13-component PARAFAC model established by Cory and McKnight (2005), denoted as CM-C1 – CM-C13. Both the redox index and percent protein were derived from this 13-component model to further illuminate stream DOC characteristics. The percent protein was low over the study period (<10% of total fluorescence), save for several periods in 2011 when the percent protein spiked above 10% (Figure 3.8). This percent protein parameter tended to be lower than protein-like fluorescence parsed through our custom four-component model, suggesting that the two indices could describe unique DOC fractions. Redox index (indicative of redox DOC characteristics), was also relatively stable through the study period, and tended to vary between 0.2-0.4 (dimensionless).

3.3.3.3 Effect of forest harvest on stream DOC characteristics

Given general characteristics of stream DOC (parsed through both in situ absorbance and discrete fluorescence measurements), we then sought to quantify the effect of forest harvest on DOC spectral characteristics, and further implications for DOC biogeochemistry and transport mechanisms. This was done by examining mean parameters over the entire pre- and post-harvest period, as well as looking specifically at how spectral proxies compare between months before and following harvest.

Mean values were calculated for spectral parameters over the entire pre- and post-harvest period, as shown alongside standard deviation, maximum and minimum values in Table 3.5. A Kruskal-Wallis test was used to assess the statistical significance of means within the pre- and post-harvest periods (Table 3.5). This test was chosen due to the non-normality of data distributions within each partition, as confirmed using a Shapiro-Wilk normality test ($p < 0.05$).

Non-normal distributions within spectral DOC characteristics data has also been found within previous studies (for example, Inamdar and Finger et al. 2011). Values of DOC, HIX, CM-C1 (%), CM-C12 (%), percent protein (%), and C1 (%) from the custom PARAFAC model were all significantly greater in the post-harvest period relative to the pre-harvest period. This indicates that in addition to altering the amount of DOC, harvest also altered the chemical composition of DOC present within the stream.

	Pre-Harvest				Post-Harvest				Kruskal- Wallis Test for Significance	
	Mean Value	Standard Deviation	Max	Min	Mean Value	Standard Deviation	Max	Min	chi-value	p - value
$SUVA_{254}$ ($L*m^{-1} mg^{-1}$)	3.52	0.63	16.38	2.57	3.59	0.63	17.82	1.93	750	$p < 0.05$
FI (A.U)	1.82	0.17	2.23	1.45	1.65	0.20	2.22	1.13	109	$p < 0.05$
HIX (A.U)	0.58	0.86	5.19	-5.11	0.72	0.29	1.98	-0.70	0	$p < 0.05$
FrI (A>U)	0.77	0.19	1.07	0.44	0.65	0.35	7.05	0.20	100	$p < 0.05$
CM-C1 (%)	8.98	1.03	13.59	5.55	10.02	3.25	77.36	0.00	160	$p < 0.05$
CM-C12 (%)	8.67	1.89	12.89	0.00	8.94	2.16	14.27	0.00	14	$p < 0.05$
Percent Protein (%)	2.29	2.25	18.58	0.00	6.19	6.14	86.49	0.00	226	$p < 0.05$
Redox Index (A.U)	0.34	0.03	0.49	0.26	0.31	0.06	1.00	0.24	184	$p < 0.05$
C1 %	29.25	2.43	39.50	23.60	34.25	7.23	91.53	0.00	316	$p < 0.05$
C2 %	19.59	0.55	20.99	17.96	19.22	1.79	39.52	0.00	17	$p < 0.05$
C3 %	21.08	1.18	23.79	15.40	18.37	6.18	88.33	0.00	243	$p < 0.05$
C4 %	30.09	1.26	32.43	22.50	28.16	2.48	36.58	0.00	348	$p < 0.05$

Table 3.5 Spectral proxies by month between the pre- and post-harvest period.

Given the possible seasonality to varying DOC composition, we compared monthly mean values for spectral characteristics after harvest to the corresponding month prior to harvest. Segregating means by month is thus an attempt to illustrate the effect of harvest, while compensating for such seasonality (as was done for DOC concentration and flux previously described). Thus, Figures 3.9-3.11 shows boxplots outlining the mean, 25% and 75% confidence

intervals for parameters parsed according to both month, as well as logging status. This was done for water quality parameters including discharge and electrical conductivity (EC, Figure 3.9), as well as spectral indices calculated from in situ absorbance (DOC and slope ratio, Figure 3.10), fluorescence indices (FI, HIX, and FrI, Figure 3.10), and parameters from both the custom 4 component (% C1-C4) and Cory and McKnight (2005) 13-component (% CM-C1 and CM-C12) PARAFAC models (Figure 3.11).

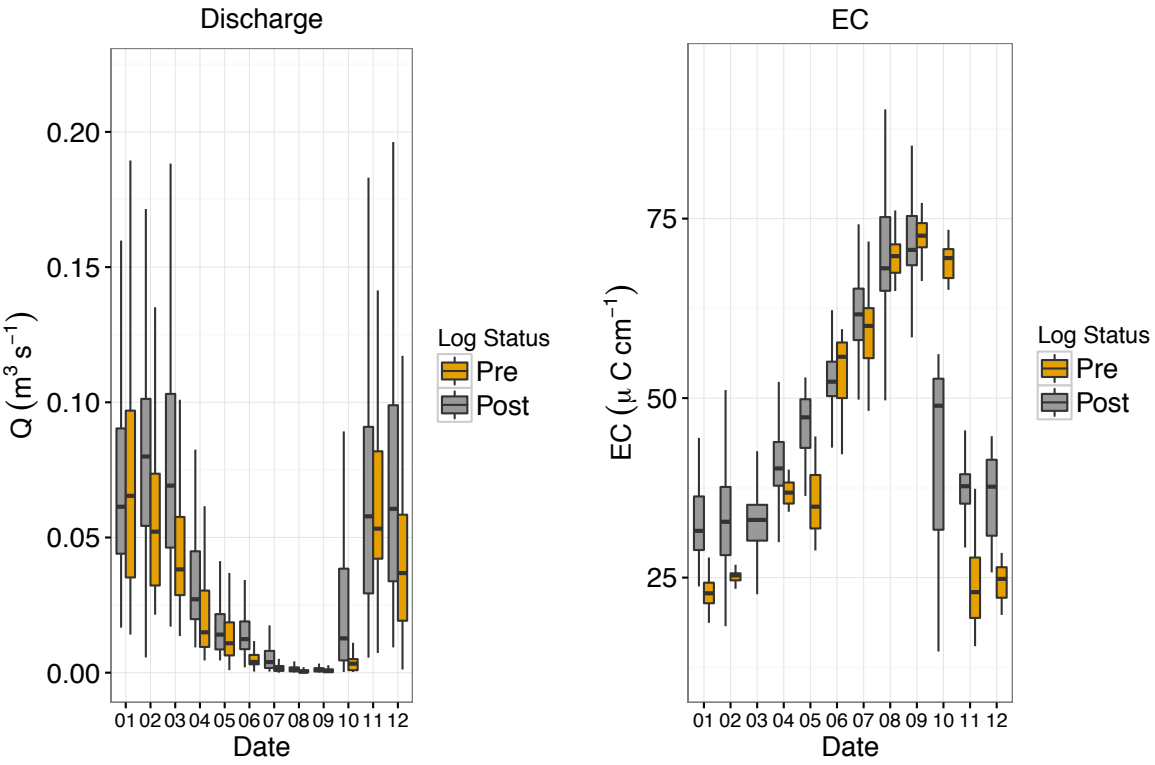

Figure 3.9 Mean streamwater qualities by month for both the pre (yellow) and post (grey) harvest period. Mean values are shown by the line within the box, which encompasses 50% of the data striation; whiskers indicate 1.5 times this reach.

Stream EC was included within this analysis to compare to trends within spectral DOC proxies, as it is a commonly used indicator for the relative contribution of baseflow to overall stream flow. Trends in stream EC (Figure 3.9) show a clear seasonality that opposes trends in

discharge, which peaks during the rainy winter months. This increase in EC during dry summer months suggests an upsurge in groundflow contribution to streamflow, as the EC in groundwater is typically enhanced by the increased contact to mineral soils relative to surficial flowpaths.

Indices calculated from absorbance (in situ) and fluorescence (water samples) spectra were partitioned by month and whether they fell within the pre- or post-harvest period (Figure 3.10). The mean $SUVA_{254}$ calculated from the entire post-harvest period was significantly greater than for the pre-harvest mean (Table 3.5), mirroring behavior in DOC concentration. Increased $SUVA_{254}$ within the post-harvest period was especially apparent within the wet winter months (Figure 3.10). As $SUVA_{254}$ values are likely affected by variable concentrations of iron within the stream, it is difficult to concretely associate trends in $SUVA_{254}$ to that of aromatic carbon concentrations, as per Weishaar et al. (2003). Effects of iron and other interferences are less pronounced within the slope ratio (SR), as it is calculated over a larger region of the absorbance spectra beyond near UV wavelengths. The mean SR was significantly less during the post-harvest period relative to pre-harvest (Table 3.5), a relationship that was most pronounced within the wet winter months. This suggests harvest increases the concentration of aromatic, high molecular weight DOC within the stream relative to the pre-harvest period, especially within hydrologically active winter months.

Three indices calculated from fluorescence spectra were also used to compare DOC characteristics by month between the post-harvest to pre-harvest period. The fluorescence index (FI) post-harvest is significantly less than pre-harvest (Table 3.5), a trend supported when individual months are compared (Figure 3.10). This suggests that the DOC within the stream following harvest is more terrestrial in nature (FI closer to 1.2), which mirrors trends towards increased aromaticity evident in the slope ratio. Similarly, HIX values were significantly greater

post-harvest, suggesting a higher degree of humification (and lower H-C ratio) relative to mean values pre-harvest. Converse to these trends, which appear to suggest a greater contribution of aromatic surficial DOC to the stream within the post-harvest period, the FrI post-harvest is significantly less than pre-harvest, a trend maintained through most months (Figure 3.10). However, this proxy is more commonly used within marine and estuary environments, and thus may be less indicative of DOC age within this context.

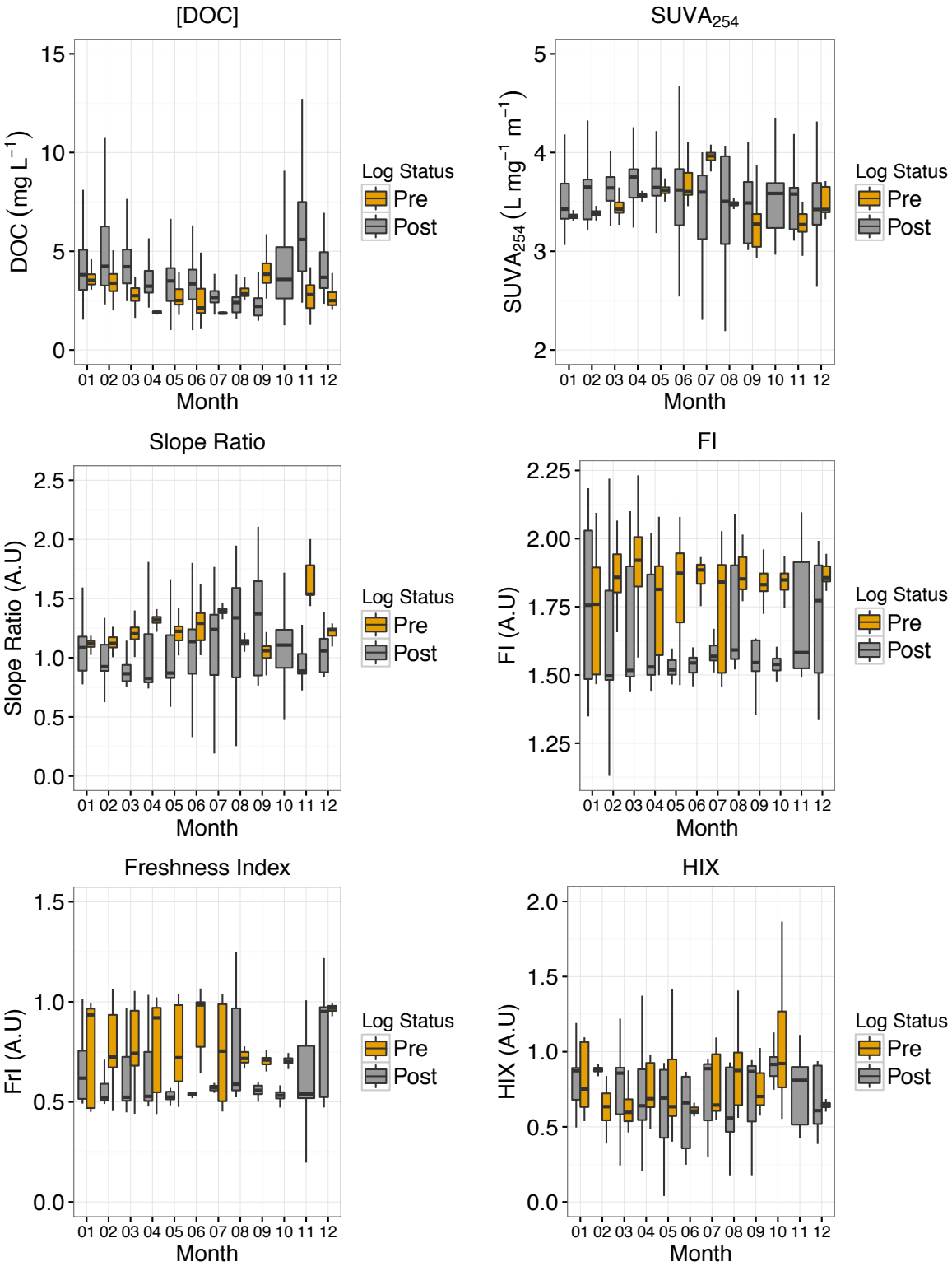

Figure 3.10 Trends in calculated parameters by month: pre and post-harvest. Spectral proxies (absorbance and fluorescence) for DOC characteristics by month for both the pre (yellow) and post (grey) harvest period.

Mean values are shown by the line within the box, which encompasses 50% of the data above and below the mean; whiskers indicate 1.5 times this reach.

Figure 3.11 shows indices from the 13 component Cory and McKnight model (CM-C1, CM-C12, redox index and percent protein), as well as the percent contribution of each of the four components from the custom 4-component PARAFAC model. CM-C1 (%) is the percent fluorescence arising from the first Cory McKnight component; this component is particularly interesting, as it has been correlated to the concentration of ketal or acetal carbon through ^{13}C NMR, and thus related to the contribution of DOC from riparian soils (Cory and McKnight 2005; Strohmeier et al. 2013). The % CM-C1 contribution to overall fluorescence is significantly greater post-harvest relative to before harvest (Table 3.5). Additionally, CM-C1 demonstrated little seasonality within either period (as observed within boxplots segregated by month), and varied from ~9-11% post-harvest, and ~7-11% pre-harvest period (Figure 3.11). We also examined the 12th component from this PARAFAC model (CM-C12). This is because the percent contribution of CM-C12 to fluorescence has previously been related to aliphatic carbon content, and used as a proxy for groundwater contribution as its refractory nature reflects DOC that is more processed due to longer soil residence time (Strohmeier et al. 2013). The % CM-C12 is greater within the post-harvest period (Table 3.5) by only a small margin (8.6% vs 8.9%). For both periods, CM-C12 is lowest in the late wet season/early dry season (March), and gradually increases over drier summer months (as shown post-harvest, Figure 3.11). This echoes trends within EC that suggest an increased contribution of groundwater to the stream during dry summer months. We also calculated the redox index by summing reduced quinine-like inputs over total quinone-like inputs from components in the Cory McKnight model. This proxy has been used to outline the redox behavior of DOC within aquatic environments – for example,

redox index decreased when microbial DOC within an alpine stream was exposed to sunlight (Miller, McKnight, and Chapra 2009). In general, the redox index in our study was lower post-harvest relative to before harvest (Figure 3.10). In particular, the redox index during the summer (dry) months was elevated in the pre-harvest period relative to the post-harvest period, indicating that quinone-like compounds were more reduced pre-harvest relative to after harvest. The second parameter calculated from the Cory McKnight model was the percent protein, which is the sum over all components corresponding to protein-like fluorescence. The mean percent protein post-harvest was greater than that pre-harvest (Table 3.5), a trend especially evident within the dry summer months (Figure 3.10).

In terms of components derived from the custom four-component PARAFAC model, C1 and C4 showed the greatest monthly differences between pre and post-harvest. Specifically, C1 (%) increased post-harvest relative to pre-harvest, especially during dry summer months. This shift was facilitated by a decrease in C4 fluorescence, relative to characteristics before harvest (Figure 3.11). Both C1 and C4 were identified as humic-like fluorescence, and were the most sensitive parameters to shifts in fluorescence upon harvest, suggesting that they may be the most responsive to alterations in hydrologic flowpaths and DOC origins caused by harvest. Although identified as a humic-like component, the behavior of C1 tracks closely with changes within protein-like fluorescence. The only protein-like component identified within the model was C2, which demonstrated behavior that differed from that of the percent protein parameter calculated from the Cory McKnight model (with increased mean values pre-harvest relative to post-harvest, especially with the dry summer period). Additionally, the C4 peak is similar to peaks that have been correlated to humic-like fluorophores that dominate the DOM characteristics of DOC within

natural catchments, especially within the summer months. Indeed, the percent contribution of the C4 peak was greatest within the warm, dry hydrologic period (Figure 3.11).

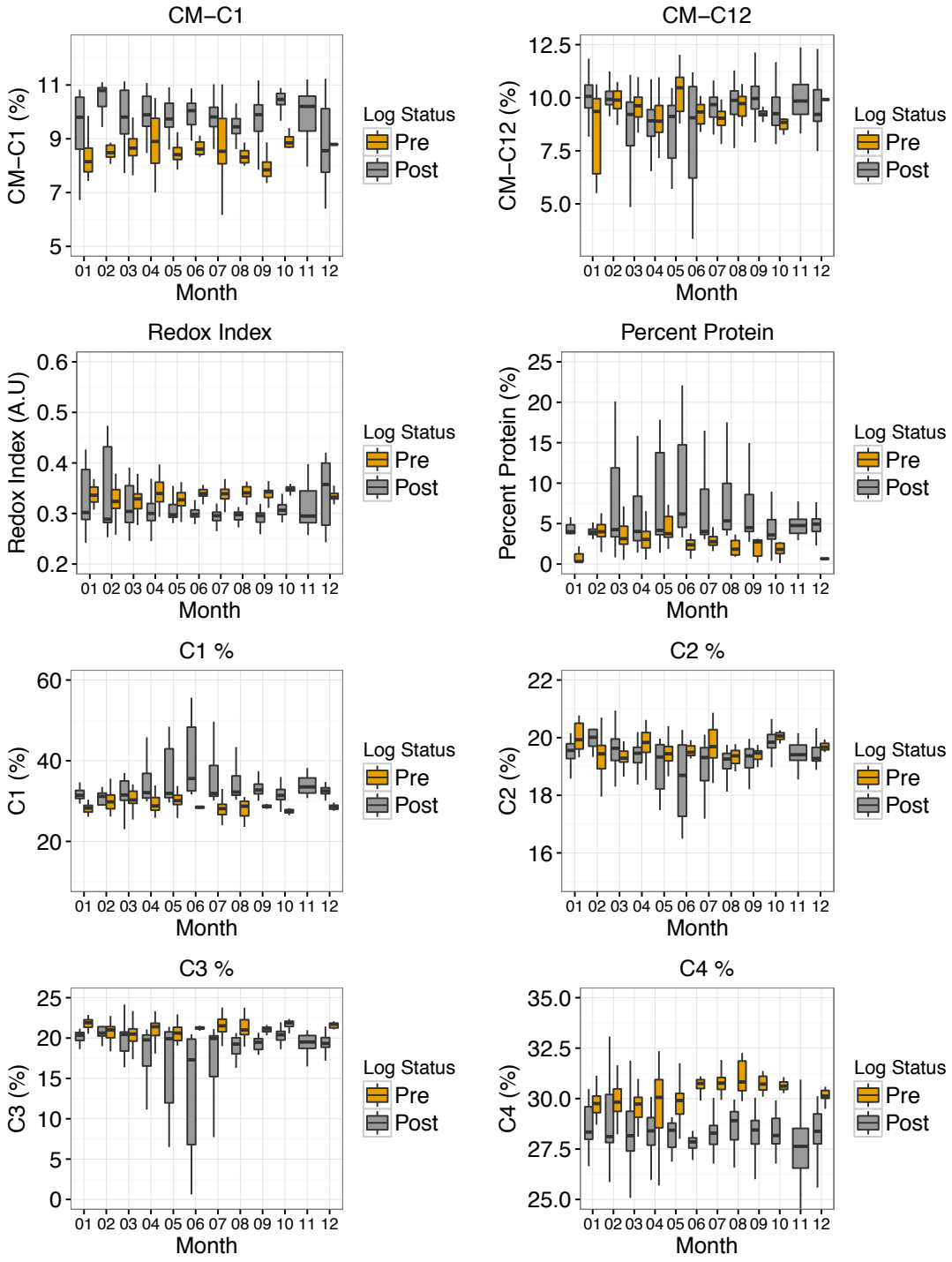

Figure 3.11 Fluorescence DOC characteristics (determined by PARAFAC model) parsed by month for both the pre (yellow) and post (grey) harvest period. Mean values are shown by the line within the box, which encompasses 50% of the data striation; whiskers indicate 1.5 times this reach.

3.3.3.4 Differentiating fluorescence characteristics by logging status

Previous studies have used several approaches to parse specific DOC characteristics between different sources and environmental conditions, including 1) principal component analysis to evaluate how DOC characteristics are altered according to seasonality and contributions of different flowpaths, such as quickflow versus baseflow, as per Singh et al. (2014); and 2) relationships between specific PARAFAC components. We used these approaches to investigate whether DOC characteristics were uniquely defined between the pre- and post-harvest periods. However, neither approach clearly separated pre- or post-harvest spectral characteristics; thus, trends from these analyses are briefly discussed below, and all figures shown within Appendix C.

Four combinations of PARAFAC components were used to investigate changes in DOC characteristics between the pre and post period. First, CM-C1 and CM-C12 were compared, as relative shifts within these components have successfully used to segregate stream characteristics based on DOC origin - specifically, groundwater, shallow groundwater from riparian soils, and runoff (Strohmeier et al. 2013). Supplemental Figure B.9 demonstrates four different combinations of comparisons between PARAFAC components in an attempt to demark characteristics of samples partitioned by both pre/post-harvest status as well as hydrologic time: CM-C1 versus CM-C12 (riparian DOC versus groundwater); C1 versus C4 (the two most prevalent components within the custom PARAFAC model), and C1 and C4 versus the protein-like C2 (Figure B.9). Ellipses throughout Supplemental Figure B.9 indicate 95% confidence intervals for each of the four partitions. None of these pairings provided a clear segregation in DOC characteristics, demonstrating that stream DOC characteristics are complex, and relatively stable in comparison to studies that specifically use these characteristics to fingerprint DOC origins. While no pairing provided complete separation (according to 95% confidence levels),

subtle shifts in DOC characteristics between the pre and post-harvest periods are apparent. For example, Supplemental Figures B.9 demonstrate a shift towards a greater percentage of fluorescence for humic-like C1 relative to humic-like C4 within the post-harvest period when compared to the pre-harvest period. Additionally, principal component analysis has also been successfully used to identify characteristics that separate DOC characteristics between different flowpaths, including quickflow versus baseflow pathways, as well as differentiating between DOC sources (Inamdar, Finger, et al. 2011; Singh et al. 2014). However, PCA on fluorescence characteristics also resulted in unclear separation between pre/post-harvest delineations (Supplemental Figure B.7 and B.8).

3.3.3.5 Behaviour in DOC characteristics: concentration-discharge relationships

Two approaches were used to investigate further behaviour in stream DOC characteristics to determine possible mechanisms by which DOC arrives within the stream, as well as how such mechanisms are altered by harvest. First, relationships between DOC quality proxies and discharge were investigated through concentration-discharge relationships. Linear relationship between select parameters and discharge (as well as 95% confidence intervals), partitioned according to logging status is shown in Figure 3.12. Increases in DOC, slope ratio, and CM-C1 (%) with discharge indicate that increases in parameters describe more surficial, quickflow pathways. Similarly, the inverse relationship between slope ratio and percent protein and discharge suggests that increased values of both parameters are correlated with DOC characteristics arising due to baseflow conditions. Thus, increased discharge shifts DOC sources towards riparian and surficial soil environments, which tend to be enriched within DOC (specifically, higher molecular weight, aromatic DOC) relative to deeper mineral soil layers

connected to baseflow hydrologic pathways. This shift towards quickflow pathways is also born out by trends within event EC, where event EC values tended to be lower than baseflow.

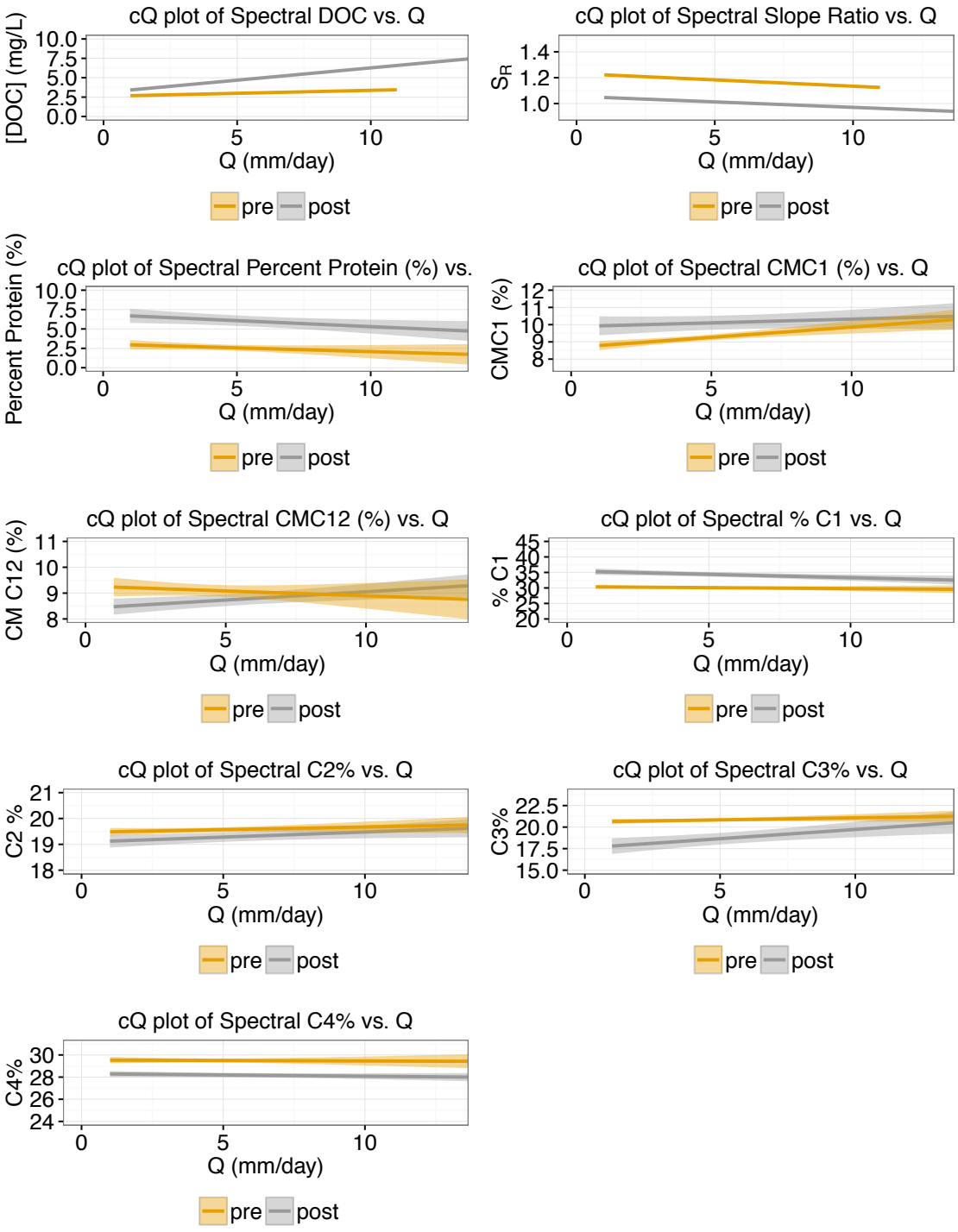

Figure 3.12 Concentration-discharge relationships. The relationship between concentration of various parameters and discharge can be used to describe characteristics of DOC arising during high flow periods, and low flow periods dominated by baseflow hydrologic pathways.

3.4 Further discussion

This section presents further discussion regarding what the alterations observed upon forest harvest (explored in Chapter 3.3) means in terms of shifts in biogeochemical functions and mechanisms driving instream DOC.

3.4.1 Linking trends in DOC concentration and characteristics: Identifying hydrologic and biogeochemical mechanisms

Both DOC concentration and characteristics exhibited significant variability on hourly and seasonal scales, highlighting the inherent dynamism of the biogeochemical cycles within coupled terrestrial-aquatic ecosystems. DOC concentrations were greatest within the wet winter months, driven especially by large spikes in stream concentration upon precipitation events. This suggests that during these months, the large amount of precipitation that falls as rain on the site activates surficial hydrologic networks. These hydrologic pathways connect riparian soils enriched in DOC to the stream, resulting in higher concentrations of in-stream DOC. In addition, there is much more water moving through the catchment during this time (shown by large increases in discharge and runoff during the wet rainy months), increasing both the DOC concentration and flux out of the catchment. Such a mechanism is supported by trends in transportable DOC within soil horizons. Previous studies have noted the enrichment of riparian soils in DOC, a trend confirmed in our study of transportable and extractable DOC from soils, where surficial soil layers were enhanced in DOC relative to deeper layers (Appendix C).

Investigating spectral DOC characteristics as a proxy for chemical composition is a means of examining biogeochemical mechanisms of DOC sources and hydrologic delivery. For example, in situ measurements of slope ratio in the post-harvest period (which is more resilient to

the effect of interfering species such as iron than $SUVA_{254}$), tended to peak within the dry summer months. As the slope ratio is inversely related to aromaticity and vascular plant inputs, this suggests that summertime stream DOC is less aromatic, with less inputs from terrestrial plants than during the wetter winter months. Slope ratio tended to decrease with increasing discharge, suggesting that baseflow pathways exhibit increased slope ratio values, lending more weight to evidence that shows an increased contribution of baseflow within the summer months. These trends are also mirrored within the percent protein calculated from fluorescence (as well as the % contribution from C1 of the custom PARAFAC model), which demonstrates a larger percentage of the overall fluorescence in the summer months relative to winter.

In terms of general characteristics of stream DOC, as well as correlating specific indices to different flowpaths, previous studies have highlighted that groundwater components tend to decrease with increasing discharge, and that components related to contributions of riparian soils (associated with more surficial flowpaths) tend to increase with discharge (Frei, Lischeid, and Fleckenstein 2010; Strohmeier et al. 2013). This suggests that slope ratio, percent protein, and C1 are particularly sensitive signals indicative of deeper flowpaths within our study. We also note that increases in stream DOC concentration within the wet winter months correspond to heightened occurrences of terrestrially derived, aromatic DOC. Previous studies connecting the characteristics of transportable DOC within the soil to stream characteristics have shown that riparian soils tend to be enriched in aromatic DOC (Strohmeier et al. 2013). Indeed, our own studies of soil qualities (both extractable and soil pore DOC) show that DOC concentrations and aromaticity decrease with soil depth. Additionally, we observed that DOC characteristics within deeper soil layers tend to be more protein-like and microbial-like relative to surficial soils (Appendix C). This provides further evidence for the mechanism by which increased

precipitation within the winter months drives a large flux of DOC out of the terrestrial environment due to hydrologic connectivity between surficial, aromatic DOC rich soil layers to the stream. During the drier summer months, the stream is mostly fed by baseflow, which is characterized by lower concentrations of DOC with protein-like characteristics, suggesting their derivation from soil microbes rather than plant biomass.

3.4.2 Effects of forest harvest on DOC biogeochemistry

A key extension of examining trends in in-stream DOC characteristics is to use spectral features to elucidate ecohydrologic change. In this case, we considered how forest harvest affects the biogeochemical and hydrological mechanisms driving in-stream DOC within paired terrestrial-aquatic ecosystems. We found that forest harvest significantly increased in-stream DOC concentrations for most months post-harvest relative to before harvest. This upsurge in stream DOC concentration, as well as the increase in runoff observed after harvest, also resulted in a significant upswing in the DOC flux exported from the catchment following harvest. This increase in flux was especially evident within the wet winter months. We also observed large increases in stream DOC concentration in November in both pre- and post-harvest periods. This could have arisen from the accumulation of DOC in surficial, hydrological disconnected parts of the catchment during the dry summer months, where heavy rains in November activate dormant hydrologic networks that export accumulated DOC to the stream. November also showed the largest change in DOC concentration upon harvest, which may be due to increased inputs of soil OM through biomass residues after forest harvest.

Harvest also changed the types of DOC present within the stream at different points of the year, suggesting that harvest alters the mechanisms by which DOC is generated or arrives within

the stream. For example, the slope ratio post-harvest was significantly lower than that prior to harvest for most months of the year (save August and September; Figure 3.10). This suggests that DOC within the stream after harvest tended to be more aromatic, with more contributions from vascular plant biomass (save for two dry summer months). The overall shift towards terrestrial, aromatic carbon post-harvest was also reflected in increased values of the fluorescence index. However, this overall shift towards more aromatic DOC in general after harvest (reflective of surficial riparian soil characteristics, according to soil DOC characteristics), was also accompanied by an increase in protein-like fluorescence within the drier summer months. This behaviour was evident within percent protein values derived from the 13-component Cory McKnight model (Cory and McKnight 2005), as well as the contribution of C1 from a custom 4-component PARAFAC model. This could reflect the increased contribution of water from deeper flowpaths to the stream within summer months following forest harvest. Soil within the catchment is characterized by a relatively impermeable basal till layer at shallow depths (~1 m deep). Thus, decreased evapotranspiration due to the loss of plant transpiration upon harvest could increase baseflow to the stream, given this relatively shallow soil column. This behaviour could also explain increases in stream discharge and runoff observed during the post-harvest summer months, relative to the pre-harvest period (Figure 3.2). Additionally, the increased contribution of baseflow to summer stream flow after harvest could also explain why DOC concentrations in summer months post-harvest months are lower than that observed prior to harvest; such deeper hydrologic flowpaths tend to be depleted in DOC, according to soil DOC trends observed in soil extracts and soil pore water (Appendix C). It is possible that stream DOC in the pre-harvest period is characteristic of episodic precipitation events, which would explain

differences within fluorescence characteristics relative to post-harvest (given the shorter timescale activation of more surficial flowpaths).

An overarching aim in examining spectral DOC characteristic is to concretely link such characteristics to DOC sources and mechanisms; this link is critical to identify basic hydrological functionality, as well as impact due to long or short-term disruptions to various biogeochemical components within an ecosystem. Specifically, our aim was to first link DOC characteristics to specific mechanisms within the three general processes by which in-stream DOC arises, and use this to inform a detailed model of DOC processes at the catchment scale. Indeed, several previous studies have begun conceptual models for catchment geochemical function under different climatic conditions using spectral indicators of DOC composition (for example: Inamdar, Finger, et al. 2011; Inamdar, Singh, et al. 2011; Singh et al. 2014; Strohmeier et al. 2013). These studies have elucidated general behaviors in DOC features. This includes the increase in fluorescence from protein-like DOC deeper within the soil column due to the preferential sorption and co-precipitation of humic and aromatic constituents to mineral soil in the upper soil column (McDowell and Likens 1988; Kaiser and Zech 1998; Kalbitz et al. 2000; Ussiri and Johnson 2003; Kaiser, Guggenberger, and Haumaier 2004; Singh et al. 2014). Sorbed DOC may be subject to microbial processing, increasing the proportion of microbially-derived and protein-like fluorescence deeper within the soil column (Kaiser and Kalbitz 2012). Such mechanisms could correspond to baseflow events observed within our study, which corresponded to more protein-like and microbial-like fluorescence. Characteristics of riparian DOC, implicated within surficial flowpaths during periods of high discharge, tend to reflect the DOC enriched, aromatic character of these soils (Strohmeier et al. 2013), a trend also observed in the present study.

Several characteristics of our site may contribute to differences from that observed in previous studies on DOC characteristics as markers or biogeochemical and hydrologic function. These include several notable studies that also used spectrophotometric characteristics to describe DOC biogeochemical processing. Most of these studies occurred within forested catchments that are much colder than our context, and are thus dominated by deciduous (rather than coniferous) tree species. For example, Singh et al. (2014) observed that DOC flux peaked within summer months within their eastern hardwood forest context, due to transport mechanisms as well as increased microbial production of DOC within the soil (Singh et al. 2014). They also observed the effects of spring leaf out (through the associated production of organic extrudates), as well as leaf litter inputs during the fall (Singh et al. 2014), both of which are not apparent within our temperate, coniferous tree-dominated context. Additionally, winter-time DOC in colder and snow-dominated catchments are affected by decreased movement of water through soil, due partially to the decrease in hydrologic conductivity of frozen soil, as well as the presence of a snowpack (which also insulates soil from extreme temperatures, allowing for the microbial production of DOC) (Singh et al. 2014). Soil characteristics at our site contain a relatively shallow organic layer (2-10 cm deep). Soils within our site are also relatively shallow overall, due to the presence of a impermeable basal till layer at a depth of ~ 1 m, and were thus much shallower and with a thinner organic layer compared to other studies. For example, Stroheimer et al. (2013) used groundwater wells from 3-15 m deep to describe DOC characteristics of 'deep' hydrologic flowpaths. Compared to this, shallower soil horizons within our context provided less opportunity for vertical movement of water, and thus less opportunity for DOC processing within the soil.

This difference in 'active' soil depth within our context versus other studies may have large implications for behavior in hydrologic flowpaths, including how such flowpaths are affected by climate and harvest. Our study catchment contains pockets of variably saturated areas scattered throughout the watershed area. It is thus possible that subsurface flows connecting variable small riparian source areas within the catchment contribute a significant degree to DOC stream characteristics, especially considering the relatively shallow nature of soil horizons. Given these features, alterations in flowpaths occurring throughout the year due to seasonal climate fluctuations (especially dynamics between the wet winter versus the dry summer months), may impact hydrological connectivity and be critical in laterally connecting variable source areas within the watershed, rather than vertically through the soil column. Such lateral connectivity is expressed through the transmissivity feedback mechanism, which has been used to describe exponential increases in DOC delivery upon increases in riparian groundwater levels. Increases in groundwater level act to create efficient flow networks by connecting source areas (surface depressions); these surficial networks tend to contain more DOC, as well as exhibit much improved hydraulic conductivity, creating effective drainage pathways for water as well as biogeochemical fluxes from the soil to the aquatic environment (Seibert et al. 2009; Frei, Lischeid, and Fleckenstein 2010). The presence of an impermeable basal till layer (at ~90 cm deep in the soil column), as well as the small, headwater nature of the catchment, likely enhances riparian groundwater responses, which may account for the reactive nature of DOC concentrations in the stream upon increased discharge.

In considering how forest harvest could affect this system, we observed an overall shift towards increased export of aromatic (surficial) DOC within the post-harvest period, perhaps signaling a shift towards these surficial, high transmissivity networks, especially within the

hydrologically active wet winter months. Activities connected to forest harvest, specifically the construction of transecting roads with associated culvert systems, have also been noted to 'cut' deeper hydrologic pathways, promoting surficial over baseflow hydrologic pathways, especially in the presence of relatively shallow impermeable soil horizons (Moore and Wondzell 2005). This could have contributed towards the responses observed in response to forest harvest for our study site, given that a disused road (constructed some ~50 year previous) that transects the watershed was significantly upgraded with drainage ditches and culverts prior to forest harvest. The presence of increased aromatic concentrations within wet winter months of the post-harvest period could also reflect such forest harvest site preparations, as baseflow is 'cut' by ditching and culverting.

3.5 Conclusion

This chapter presents the results of a multi-year research program describing changes to the ecohydrologic functioning of a watershed in response to forest harvest. The variety of methodology utilized includes in situ measurements of stream chemistry and DOC concentration through absorbance spectrophotometry, as well as discrete sampling to outline DOC characteristics using sensitive fluorescence spectrophotometry. Firstly, we used in situ measurement of the DOC concentration (via absorbance spectrophotometry) to gain a high temporal resolution understanding of how forest harvest affects DOC concentration and flux within a headwater catchment. The post-harvest period was characterized by higher concentrations of DOC within the stream than the pre-harvest period, where increases in runoff contributed to overall increases in DOC flux exported from the site through the stream. Secondly, we used both in situ measurements of DOC characteristics (from stream absorbance spectra) as

well as sensitive fluorescence measures of discrete streamwater samples to observe that this DOC tended to be more terrestrial and aromatic in nature after harvest. This suggests that surficial hydrologic networks were preferentially activated in the post-harvest period, efficiently transporting DOC derived from surficial soil organic matter to the stream when compared to the pre-harvest period. Stream DOC characteristics also show an increased contribution of groundwater to summer streamflows, possibly stemming from increases in summer groundwater flows due to a loss of plant evapotranspiration upon forest harvest. Lastly, we attempted to connect DOC characteristics within the stream to characteristics of DOC from soil extracts and analysis of soil pore water using lysimeters (detailed in Appendix C). The protein-like character of soil DOC increased with soil depth, consistent with the argument that percent protein in DOC can be used to signal hydrologic flows from deeper groundwater. This study is one of the first to apply spectrophotometric methods (especially in situ methods) towards investigating ecohydrologic impacts of large-scale alterations such as forest harvest. It also spans the longest time in which such methods have been used to investigate trends and dynamics of stream DOC. Spectrophotometric analysis of DOC has much potential, given its sensitivity to various types of DOC, as well as the possibility to use in situ. This study demonstrates the potential for spectral proxies to identify of DOC classes in longer-term monitoring programs, given their ease, accuracy and economy. The potential for such methods is especially pertinent towards further understanding and elucidating mechanisms driving the complex and dynamic flux of carbon connecting terrestrial and aquatic systems within landscapes. Such studies are especially necessary towards understanding the biogeochemical consequences of different approaches to land use and water resource management, and will be critical for understanding effects of

phenomena (such as climate change and land use alterations), towards further elucidating human effects on complex biogeochemical cycles and ecological functions.

Chapter 4: Citizen science for water quality monitoring: Implications of citizen perspectives and context for data quality

4.1 Introduction

4.1.1 Citizen science in environmental management

Citizen science has become increasingly popular across a variety of scientific disciplines in recent years, as indicated by the appearance of a number of peer reviewed publications and uptake by academics, governments, non-governmental and community organizations. Most citizen science relates to the practical implementation of citizen participation within the scientific process (Bonney, Cooper, et al. 2009), where a second definition envisions citizen science as the relationship between citizens and scientific institutions (Irwin 1995). 'Citizen science' thus describes a wide range of projects (Riesch and Potter, 2013), which are defined by approaches that span crowdsourcing through to explicit involvement and integration of citizens within the scientific process (Wiggins and Crowston 2011).

Citizen science has become particularly popular within ecology, biology, and environmental monitoring (Devictor et al. 2010; Greenwood 2007), including the rise of 'citizens-sensor-networks' (Carton and Ache, 2017). This includes water quality monitoring, such as volunteer contributions to watershed health assessments under various programs in the USA following the 1972 Clean Water Act (Jalbert and Kinchy 2015). Citizen science can dramatically expand data collection and analysis at a fraction of the cost of traditional scientific campaigns (Silvertown 2009). Citizen science can augment project scope across temporal and spatial scales (McKinley et al. 2015), improve the statistical power of data sets (Greenwood 2007; Schmeller et al. 2009), and facilitate the observation of otherwise difficult to quantify phenomena (Ricciardi et al. 2000). Other cited advantages driving the proliferation of citizen

science include goals for education, improving scientific literacy, and engaging with the public. Education is a fundamental motivator for pursuing citizen science, involving the transfer of knowledge regarding the frameworks, assumptions and machinations that constitute the modern scientific process from scientific actors to the public (Couvet et al. 2008; Bonney, Ballard, et al. 2009; Bonney, Cooper, et al. 2009; Silvertown 2009). The 'knowledge deficit' model typifies education within citizen science, where knowledge flows one-way from scientific to community actors (Irwin 1995). Citizen science within environmental realms can also be implicitly vested with public engagement goals (Lasker 2003; Conrad and Daoust 2008). These goals echo the dramatic upsurge in concern over environmental issues in the latter half of the 20th century, with a corresponding escalation in opportunities for citizen involvement within environmentally relevant policy and decision-making (Allen 2004). Goals of increasing environmental awareness, promoting pro-environmental attitudes, (Brossard, Lewenstein, and Bonney 2005) and reconnecting people to nature (Devictor, Whittaker, and Beltrame 2010), are often inherent within environmental citizen sciences (such as water quality monitoring), which have also been used to include citizens in policy-relevant science (Jepson and Canney 2001; Jepson and Canney 2003).

4.1.2 Mistrust of citizen data - Barriers to citizen science

Despite the potential for citizen science, empirical works based on citizen engagement with data collection are at present under-reported within the scientific literature, with concerns regarding data quality the most invoked barrier (Catlin-Groves 2012). Citizen inexperience around how to best collect scientific data can indeed bias or skew data, hindering data quality and reliability (Flanagin and Metzger 2008). Thus, the challenge of understanding how non-professionals operate within scientific programs, including the resultant effect on data quality, has necessitated

development of citizen science frameworks and best practices for practitioners (for example: C. T. Conrad and Daoust 2008; Bonney, Cooper, et al. 2009; Silvertown 2009). Such frameworks generally constrain experimental conditions to minimize the potential for citizens to bias or improperly collect data. Subsequent to this, a range of approaches for comparing and validating citizen data have been reported, including replication, expert review for identification and screening of outlier data (Wiggins et al. 2011; Bonter and Cooper 2012), as well as statistical tactics for validating hydrologic data (D. Walker et al. 2016).

Citizen data has and can mirror the quality of professionally collected data, a finding reported in numerous recent studies (for example, Delaney et al. 2007; Smith, Lynn, and Lintott 2013; Danielsen et al. 2014; Sullivan et al. 2014). Such examples are facilitated by the continued development of frameworks for identifying sampling bias, errors in detection, measurement and identification, and spatial clustering (Munson et al. 2010; Bird et al. 2014). Recent iterations of citizen science thus emphasize their scientific rigor, and that they be subject to the same assumptions and expectations as conventional science (McKinley et al., 2015). Despite evidence that citizen data can rival professional data, and a growing understanding of what constitutes 'good' citizen science, surveys of scientist perceptions show that concerns regarding data quality remains a significant barrier for trusting scientific conclusions deriving from citizen science data (Riesch and Potter 2013). Perhaps as a consequence of this, many citizen science projects are reported outside of peer-review (Conrad and Hilchey 2010). This mistrust is particularly concerning for policy-relevant science such as environmental research, where concerns regarding data quality can impede the use of findings derived from citizen data in high-level policy and decision-making (Conrad and Hilchey 2010; Jalbert and Kinchy 2015).

4.1.3 Citizen science from the citizen perspectives – why participate?

Despite growing scholarship regarding citizen science applied to scientific investigations, few studies investigate citizen science from the perspective of citizens. Instead, the tendency is to report only those case studies deemed 'successful' based only on data (Riesch and Potter 2013). Studies exploring perspectives beyond data outcomes include those investigating participant learning outcomes (Trumbull et al. 2000; Cronje et al. 2011; Jordan et al., 2011; Crall et al. 2013), the motivations behind and experience of participants (Raddick et al. 2009), and the public-expert relationship (Cornwell and Campbell 2012). Studies have also scrutinized whether participation increases knowledge metrics related to the topic and/or the scientific process, a critical outcome reflecting the importance of educational goals in many citizen science programs. These conclude, in general, that participation in citizen science does not always improve either scientific or subject-based knowledge, nor does it necessarily result in the adoption of pro-environmental attitudes (Brossard, Lewenstein, and Bonney 2005; Cronje et al. 2011; Druschke and Seltzer 2012). Further studies also question whether citizen science is an effective means of engaging citizens, such as within environmental policies or management controversies (Druschke and Seltzer 2012). Hindering the meaningful delivery of goals embedded in citizen science is the absence of two-way dialogue between scientists and citizen participants. Instead, transfer of information from scientist to citizen tends to be uni-directional, with the common assumption by scientific actors that communication be predicated on the public's 'knowledge deficit' (Jensen and Holliman 2009; Riesch and Potter 2013). This one-way knowledge flow impedes meaningful integration of contextual, traditional and local knowledges, a commonly cited benefit that has been absent from much citizen science reported to date (Couvet et al. 2008). In general, significantly less focus has been made to elements outside of data outcomes, including social

identity, questions of political power, and empowering citizen voices as a basic premise of environmental justice and democracy (Jalbert and Kinchy 2015). The focus on scientific outcomes (i.e., data) has also resulted in less opportunity to voice concerns, and consider the roles and experiences of both participants and scientist advisors (Riesch and Potter 2013). This also includes little discussion regarding how such citizen perspectives alter their participation within citizen science programs, and how this impacts data outcomes. Additionally, despite numerous implementations of citizen science programs within water management, there are few discussions of best practices, frameworks, and lessons learned regarding citizen participation specifically within hydrological sciences (Buytaert et al. 2014; Breuer et al. 2015).

4.1.4 Study overview

In this paper, we use our citizen science experience to interrogate the relationship between citizen perspectives (such as contextual knowledge and motivations for participation) on critical data outcomes. Our citizen science program involved citizens in the investigation of human impacts on water quality, and was motivated by the potential to increase research scope while also serving goals for community engagement and education. We employed a data validation method based on replication, using a 'split-sampling' approach to compare citizen data to that of professional scientists. Data collected are presented alongside qualitative information that arose from this project to investigate: 1) the nature of outliers when comparing and validating citizen against scientist data, and 2) the how and why behind data aberrations, and differences between how citizens versus scientists interpret results. Analysis of our experience resulted in six key lessons learned, which are presented as data vignettes. We also offer recommendations regarding the importance of citizen perspectives, motivations, and knowledge in undertaking citizen

science programs by presenting qualitative experiences alongside more commonly reported data outcomes.

4.2 Methods

4.2.1 Citizen science project overview

Our water quality monitoring citizen science campaign, "Waterlogged", was designed as a 'contributing' citizen science project (i.e., scientist-directed program encompassing participation) (Bonney, Ballard, et al. 2009). The aim was to investigate how human activities affect water quality, specifically around the concentration and types of organic matter within surface waters like streams and rivers. Given that organic matter is a lesser known water quality parameter among the public, information regarding organic matter (what it is, and why it is important environmental and human health metric), was made available through the project website (http://www.waterloggedubc.ca). This website also publicly presented all data produced within the project.

4.2.2 Participant procurement

Project participants were primarily solicited by advertising within the university community, and by approaching community leaders attached to municipalities and organizations concerned about watershed and water quality management. Additional participants were recruited through word of mouth, by advertising the project to the general public via social media, and through advertising within a local science museum. Procurement of citizen participants was thus accomplished through a mix of 'snowball sampling' techniques, in which participants passed on information through word of mouth (Atkinson and Flint 2001), in addition to network mapping, where suggestions regarding relevant participants were made to the researchers. The difficulty of advertising within the general public versus networks and word of mouth is perhaps reflected in

who participated, where the majority (~60%) of samples were collected by citizen groups already involved within community-based environmental monitoring around Metro Vancouver. This group included community organizations, not-for-profit organizations and regional governments. Citizen data was collected between June 2014 and July 2015.

4.2.3 Sampling protocol

Participants were given a sample kit, which consisted of an acid-washed brown polyethelene bottle in a sample kit bag. This sample kit bag consisted of a resealable bag with a pencil, a protocol for taking a sample and data sheet to be filled out (both printed on waterproof paper), and a freezer pack (to keep the sample cool). The sampling protocol was designed to be scientifically robust yet easy to follow, and included criteria for choosing a sample location (stipulating that sampling occur in actively flowing streams and rivers). This protocol also emphasized safety. Sampling timing and location were kept intentionally open over concerns that constraining these details would dissuade participation or increase citizen fatigue (Delaney et al. 2007), though such checks can prevent spatial or temporal data bias (Catlin-Groves 2012). Participants were instructed to rinse the bottle in the stream at least three times prior to taking a sample. They were also instructed to sample in a location that had not been disturbed, and given specific directions to reduce the likelihood of contamination. Participants were asked to note critical information on the sample collection sheet, including the date and time of collection, the GPS location (if possible, for example through a geo-tagged photo taken by smart-phone), and a brief description of the location. A sample description example was also included to help orient feedback. Participants were asked to take photos of the sampling location, including up stream, down stream, and lateral photos to provide information regarding sample surroundings and location. Upon collection, participants were instructed to prevent degradation by keeping the

sample cool, first using the provided ice pack and secondly by refrigeration until collection by the scientific team. Approximately 66% percent of sample kits distributed (145 out of 221) were returned with a water sample, a slightly greater return percentage than reported by Breuer et al. (2015) in their citizen grab sampling campaign.

4.2.4 Sample analysis

Samples were analyzed for various water quality parameters, including total suspended solids (TSS), nitrate (NO_3^-) concentration, dissolved organic carbon (DOC) concentration, and a range of indices calculated from absorbance and fluorescence spectra (Supplemental Table D.1). NO_3^- and DOC concentrations, as well as parameters related to DOC qualities, were measured using absorbance (spectro::lyzer model, s::can, Austria) and fluorescence (Aqualog, Horiba, New Jersey, United States) spectrophotometry through published methods (detail in Supplemental Information, Appendix D) (Cory and McKnight 2005).

4.2.5 Data validation: Split-sampling design

We employed a replication-based validation method we called 'split-sampling' to compare citizen data to that collected by researchers. Basically, this involved scientist re-sampling of sites citizens had sampled. Citizen sampling occurred over a range of sites and times that we could not fully reproduce, given that we gave broad specifications regarding where citizens could sample and were not present when they did so. This unpredictable geographical extent of citizen sampling has been observed in previous hydrologic studies that employed citizen science (Breuer et al. 2015). We instead attempted 'replication' of citizen data by sampling popular sampling locations to provide a snapshot of water quality characteristics (Wiggins et al. 2011). The citizen data pool comprised 145 samples, where researcher-collected data consisted of 104 samples (a 'split' data set). Samples collected by citizens were concentrated within urban areas

(Supplemental Table D.2), a bias observed in other citizen science programs (Catlin-Groves 2012). Previous studies have used Pearson correlation coefficients and bias calculations to compare citizen to scientist rainfall data, an approach that would be difficult to apply within our own instance given imperfect replication of temporal and geographical citizen sampling extent (Walker et al. 2016). Instead, independent (unpaired) t-tests were used to evaluate the statistical significance of differences between mean DOC and NO_3^- concentrations in citizen and scientist collected samples (Supplemental Table D.1). T-tests were performed on the scientist versus citizen data as a whole, rather than on a site-by-site basis.

4.3 Results

4.3.1 Comparing citizen to scientist data: Split-sampling design

Independent T-testing showed that the mean DOC concentration between citizen ([DOC] = 3.18 ± 0.30 mg/L) and scientist data ([DOC] = 2.94 ± 0.30 mg/L) was not significantly different ($p > 0.05$, Supplemental Table D.1). Specifically, the distribution of scientist DOC data was bi-modal (Figure 4.2A), where the lower DOC concentration peak is representative of many streams and rivers around the Metro Vancouver region and the second, higher DOC concentration peak arises from samples taken in the Gulf Islands. The distribution of citizen-collected data shows the presence of several high DOC concentration samples when compared to scientist data (Figure 4.1A). The mean NO_3^- concentration of citizen data ($[NO_3^-] = 0.44 \pm 0.05$ mg/L) was significantly (nearly three times) greater than scientist collected data (mean $[NO_3^-] = 0.16 \pm 0.07$ mg/L; Figure 4.2B).

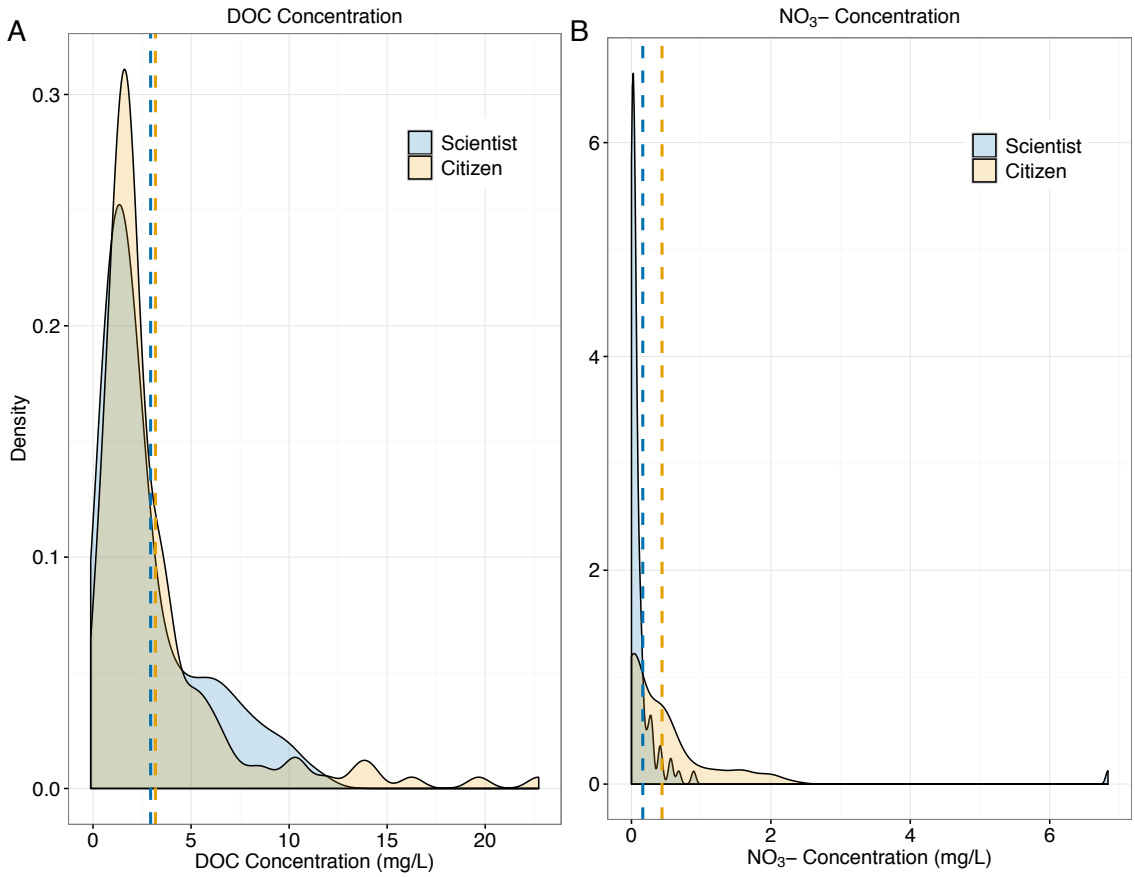

Figure 4.1 Distribution of citizen versus scientist data for DOC and NO_3^- concentrations. Figure 4.1A) DOC concentration distribution. Both the citizen (orange colour) and scientist data (blue colour) has statistically similar means, where citizen data (orange) contained higher concentration DOC samples than scientist data. Figure 4.1B shows distribution functions for NO_3^- concentrations for both citizen and scientist data sets. The mean NO_3^- concentration from citizen data (orange line) is significantly greater than the scientist data mean.

To illustrate the spread and frequency of data points within each data set, Figure 4.2 shows DOC and NO_3^- concentrations for both the citizen and scientist data. To display specific points within the context of the overall data set, the median (50% quartile, solid line), 25% quartile and 75% quartile (dotted lines, Figure 4.2) were calculated from DOC and NO_3^-

concentrations from both citizen and scientist data sets.

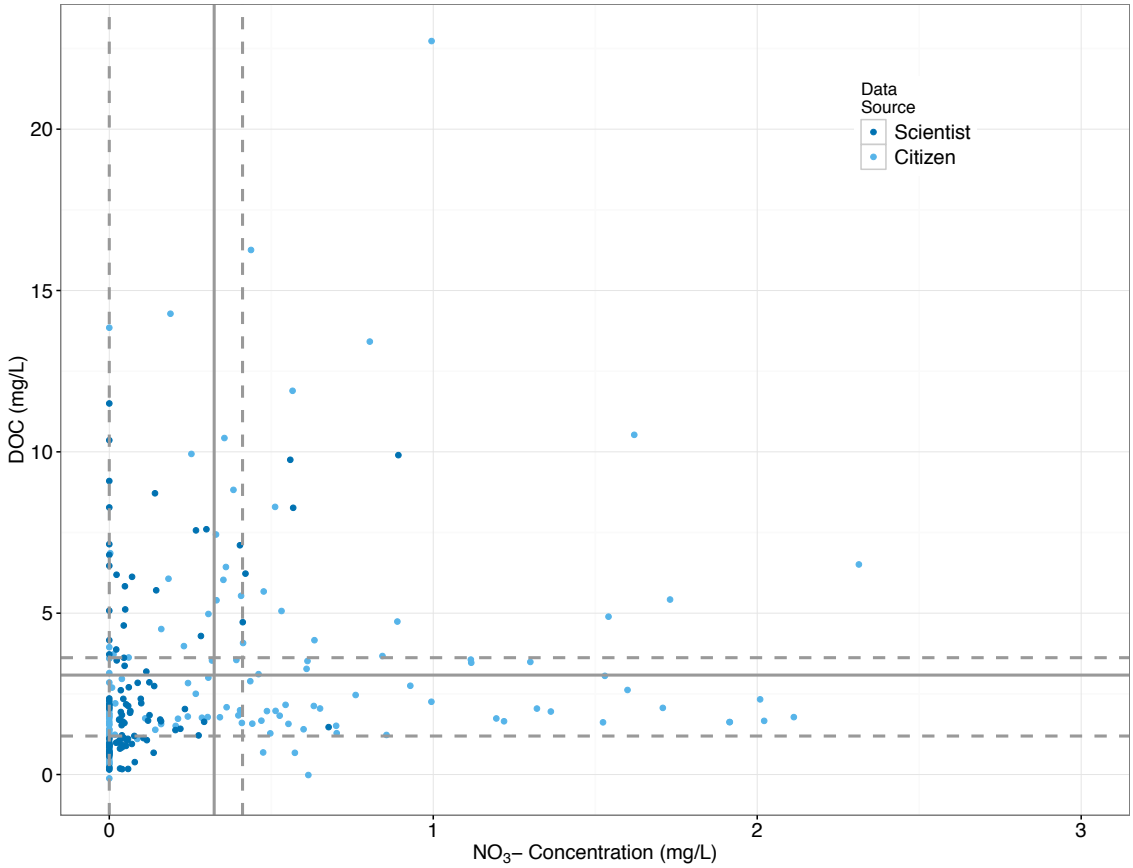

Figure 4.2 Citizen and scientist data for DOC and NO_3^- concentrations are shown alongside the median (solid grey lines), 25% quartile and 75% quartile (upper and lower dotted grey lines, respectively), calculated from pooled citizen and scientist data.

4.4 Sampling vignettes

Data points corresponding to specific narrated interpretations of explanations from participants and described below are shown superimposed on the median and quartile lines in Figure 4.3. This highlights data points within the overall data set, with a provided summation of these below and also depicted as lessons learned in Table 4.1.

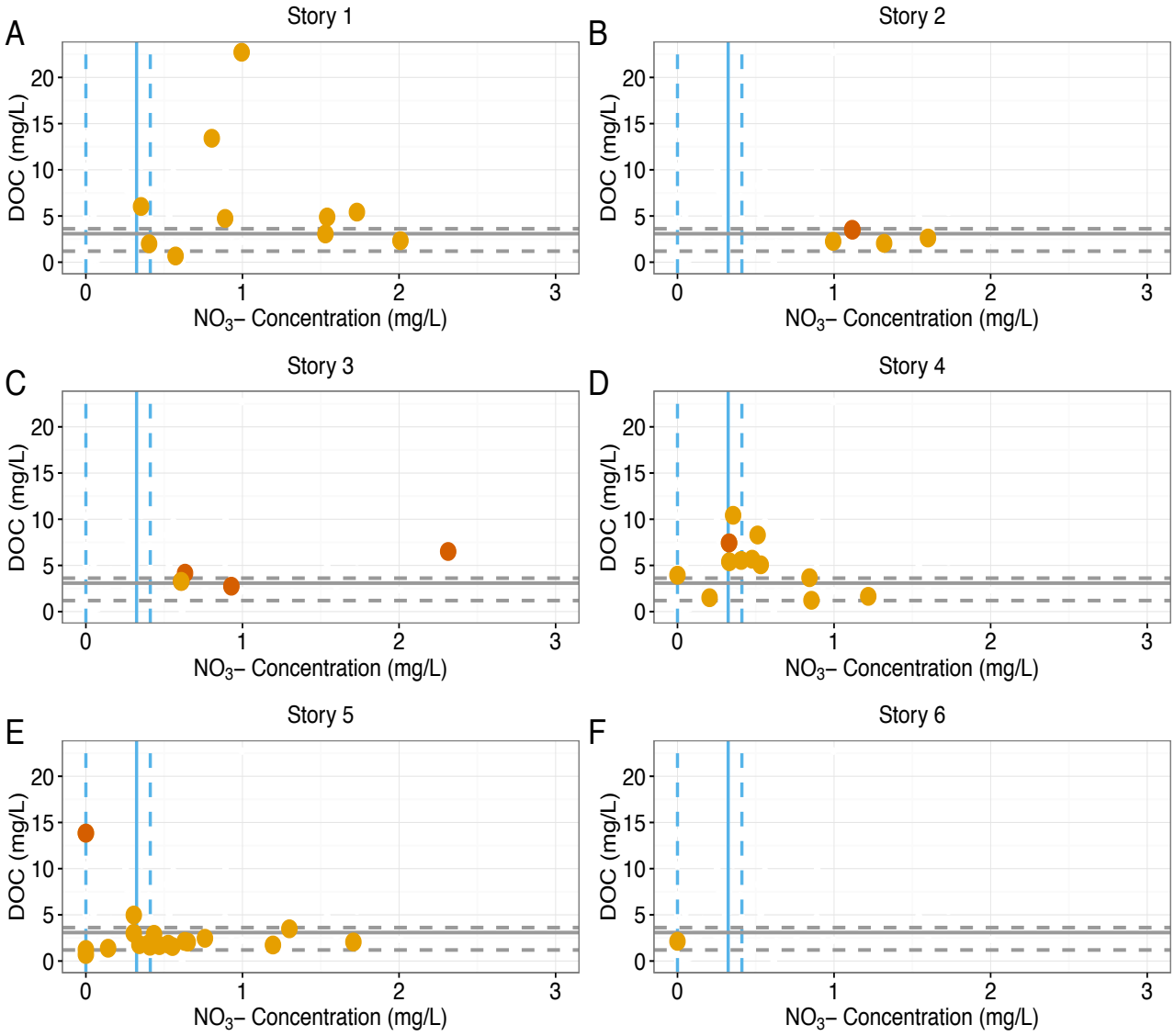

Figure 4.3 Scatter plots showing data from respective stories in the context of all data collected by citizens as well as professional scientists. The median, 25% and 75% quartiles calculated from the combined citizen and scientist data are shown as per Figure 4.2. Data for each story are shown in yellow and orange, where the median and quartile data is shown to contextualize data points within the overall (pooled) data set. Orange dots indicate samples discussed within data vignettes.

4.4.1 Story 1: Participation as education

Story 1 involves a national not-for-profit organization whose participation coincided with their citizen science project. This project involved citizens in the restoration, rehabilitation and monitoring of urban streams in Metro Vancouver, and focused primarily on community engagement and education. Program volunteers took 12 samples during their collaboration with our citizen science program. Upon analysis, samples tended to have high concentrations of DOC and NO_3^-, which could reflect the urban, highly impacted nature of sample sites (location details in Supplemental Table D.2), and the possible presence of storm water (Figure 4.3A). The highest DOC concentrations correspond to a man-made pond with significant eutrophication, especially during summer months when sampling occurred. These highly impacted urban watersheds are key sites for restoration central to long-term programs undertaken by this organization. Thus, sampling locations reflected their mandate of education and engagement, and their desire towards place-based sites relevant for urban citizens, rather than scientific goals of our own program (Table 4.1). This priority of contextually-relevant education and community capacity-building over scientific goals resulted in sampling biased towards highly impacted sites, visible as a cluster of high DOC and NO_3^- concentrations within the citizen dataset (Figure 4.3A).

4.4.2 Story 2: Interpreting data after a major event

The second vignette (Figure 4.3B) concerns Silver Creek, a small urban stream that flows through residential, wooded, and heavily industrial areas until it discharges into the Brunette River in Burnaby, British Columbia (location details in Supplemental Table D.2). A community-lead volunteer organization conducts monitoring, fish release and restoration activities within this small urban stream, which is home to various species of animals and fish. This creek was the site of a coal train derailment several months prior to sampling. During this event, high rains caused

the creek to breech a beaver dam upstream of the track; the creek then overflowed the track, derailing several cars and spilling 270 tonnes of metallurgical coal into the stream (5.5 m^3 of which remained in the stream after heavy rains transported 76 m^3 into a downstream lake). Subsequent cleanup and remediation efforts were considered to have removed the majority of the coal, and long-term risk posed to the aquatic environment deemed low (Gilron 2015). However, from communication with the participant organization, we understood that concern remained regarding effects on the long-term health of this already-impacted watershed. Participants took three samples upstream and two downstream of the derailment site in November 2014, approximately eight months following derailment. All samples demonstrated significantly higher than average NO_3^- concentrations (Figure 4.3B). In addition, samples upstream of the coal derailment (Figure 4.3B, yellow points) had slightly (though not significantly) lower DOC concentrations when compared to samples taken downstream of the derailment (Figure 4.3B, two orange dots).

Obtaining water quality data in the context of this event was the primary motivation for participation within our study, which was suggested by the local municipality due to lingering fears regarding effects from the coal train derailment. Other concerns regarding watershed-scale impacts on water quality were also communicated, including dominant industrial land use within the lower watershed, significant recent construction upstream of the derailment site, deforestation associated with a pipeline assessment, exposed peat within the channel, and creosote-soaked wooden ties in the stream at the site of the derailment. Such concerns certainly dominated the choice of sampling location (sampling transect), and could further contextualize interpretations of data provided as a means of 'compensating' participation. However, the significance of water quality differences is difficult to quantitatively assess. Although the need for further work was

communicated alongside evidence of potential impacts within the data, we acknowledge the potential that further interpretations be made given the organization's knowledge and concern about the watershed. Thus, there is the potential for mismatch between participant and scientific goals, which can affect the interpretation of data procured for specific outcomes desired by citizen participants when participation is spurred by particular concerns (Table 4.1). Mismatch in this instance resulted in indeterminate conclusions; although these results could spur further study regarding impacts, such ambiguity provided an unsatisfying outcome given the participant's interests and expectations.

4.4.3 Story 3: Assessing effects of development

The third story involves the participation of a local municipality, who were concerned about the aggregate effects of increased residential development and possible septic contamination into a small lake. Participation in our study was communicated as being a preliminary determination of such effects, towards establishing whether further monitoring would be necessary. Municipal staff took four samples in February, 2015 (Figure 4.3C). One sample, taken from the stream entering the lake, was meant to be a control (Figure 4.3C, yellow dot), and showed lower concentrations of both NO_3^- and DOC when compared to lake samples (Figure 4.3C, orange dots). In particular, a sample taken at the north side of the lake (which participants considered to be a likely candidate for septic contamination) had the highest NO_3^- concentrations of any sample analyzed within either the citizen or scientist data sets. Although sewage contamination can increase NO_3^- concentrations, other factors such as fertilizers from lawns and gardens can also increase NO_3^- concentration. Thus, participation within the project lent some gravity to concerns about septic field contamination, with the provision that the specific question posed by the municipality would be best answered using other analytic methods and a more in-depth sampling

regime. This speaks to the difficulty of reconciling motivations that citizens bring to sampling, as well as the possible dissonance between questions of interest to citizens versus scientists (Table 4.1).

4.4.4 Story 4: Reconciling water quality parameters to context

The fourth story concerns another volunteer-run community organization whose participation was spurred by a desire to augment existing water quality, ecosystem monitoring and restoration activities in several of the watersheds that drain Metro Vancouver's North Shore. This organization took twelve samples, nine of which exhibited higher than average DOC concentrations, and eight with higher than average NO_3^- concentrations (Figure 4.3D). Through data sheets, they expressed concerns that samples from one site suffered from unusually high concentrations of iron, and that the 'unusual' presence of iron derived from historic clear-cutting (Figure 4.3D, orange dot). Given that iron is a common to the iron-rich podzol that dominates much local soils, it would be difficult to link forest harvest to increased iron. High concentrations of iron impart a vivid orange hue to affected streams and rocks, which could serve as a dramatic visual cue that water quality is impaired, given the participant's knowledge of past disruption. This sample also had the third-greatest DOC concentration within the subset of samples taken by this organization, where concerns over water quality given the context could impart greater meaning to this result.

4.4.5 Story 5: Advantages of citizen place-centrism

The fifth story concerns sampling conducted by a citizen-run organization operating on the North Shore of Vancouver. This organization has a uniquely strong scientific background, having co-developed an in-depth scientific monitoring protocol used by many other stream-keeping organizations. This group monitors the health of several watersheds around North Vancouver

through community-based monitoring, with a specific focus on fish-bearing streams. An exceptional champion coordinates the extensive volunteer and citizen science activities undertaken by this organization, and also sampled for our program; such 'champions' are critical to robust and long-lived community monitoring organizations (Walker et al. 2016). Samples from this organization tended to have lower than average DOC concentrations, and slightly elevated NO_3^- concentrations. However, one high DOC concentration sample was particularly noteworthy (Figure 4.3E, orange point). This sample was taken downstream of a construction site during the course of routine monitoring. The participant observed a large sediment plume from a culvert leading from the construction site during storm runoff, and took an immediate sample of this short timescale event. This sample was opaque with suspended sediment, and had a DOC concentration of 13.67 mg/L - the fourth highest DOC measurement across all data (Figure 4.3E, orange dot). Thus, the capacity of citizen samplers, especially specific 'champions' exceptionally involved within their context, can garner data regarding events at a difficult to capture timescale. Additionally, given the high DOC concentration of the streamwater sample, it is likely that without data regarding sampling circumstances, it would be a likely outlier candidate (suspect of contamination or improper sampling, given the low DOC concentration of past sampling of the same and vicinal streams).

4.4.6 Story 6: Mt. Polley mining disaster - 'inliers' versus outliers

The sample taken furthest outside of the Metro Vancouver region was a sample collected from the Quesnel River three days after a major dam breech spilled mine effluent into the Quesnel Lake and River. A drinking water ban on these water sources was in place during sampling. The returned sample data sheet emphasizes this event, stating "three days after major environmental disaster at Mt. Polley Mountain Mine. Lake and surrounding water ways have floating debris +

government water ban." Data from this single sample did not appear to represent an outlier for either DOC or NO_3^- concentrations - indeed, it showed lower than average concentrations of both (Figure 4.3E, yellow dot). Sampling in this instance speaks to what motivations and interests underlie participation within water quality monitoring (Table 4.1). In this case, the occurrence of a major, well-publicized event spurred the participant to take a sample, despite the mismatch between our research goal of characterizing DOC and NO_3^- at the regional scale and the citizen's interest in water quality impacts from this major event. This sample also showcases the complexity of water quality monitoring itself, and the myriad analytical approaches that fall under this umbrella. Given all of the analytical approaches that can be taken within water quality assessments, determining the nature of an impact is also a matter of approach taken. In our research program that focused on characterization of dissolved organic matter, the sample from this event was unremarkable. However, this sample was taken only three days following an event that mine safety experts have called one of the largest in Canadian history. Subsequent water quality testing undertaken by the province in service of drinking water goals showed that samples met provincial drinking water guidelines, but exhibited elevated concentrations of metals including selenium, arsenic, copper, and vanadium within sediment, with unknown long-term environmental effects.[1] How water quality is investigated shapes the understanding regarding how a specific event impaired water quality. For example, the importance of how water quality is investigated is illustrated within this vignette, in which the exceptional circumstances under which this sample was collected was belied by its presence as an 'in-lier' within the data distribution.

[1]http://www.env.gov.bc.ca/epd/mount-polley/

4.5 Discussion

The first section of the discussion that follows links vignettes surrounding the context of data collection to their implications in the form of lessons. Such lessons apply to the specific context of our study, as well as other circumstances regarding public engagement in the practice and analyses of water quality data. Two additional points – what participants get out of citizen science, as well as the challenge of integrating citizen perspectives within science hierarchies – are also discussed.

4.5.1 Lessons learned

	Criteria for what is an outlier can be difficult to determine	Aberrations that are within normal distribution can be interpreted as more meaningful by citizens due to collection context	Citizens and citizen-lead community groups can insert their own interests into data collection	Questions of interest to scientists versus citizens may not coincide	Data might be primary for scientists, but secondary for citizens whose aim is education	Place-centrism in citizen science can have advantages
Story 1: Participation as education (Figure 4.3A)	×				×	
Story 2: Interpreting Data After a Major Event (Figure 4.3B)		×	×	×		
Story 3: Assessing Effects of Development (Figure 4.3C)			×			
Story 4: Reconciling Water Quality to Context (Figure 4.3D)		×	×			
Story 5: Citizen Place-Centrism (Figure 4.3E)	×					×
Story 6: Mining Disaster: 'Inliers' versus Outliers (Figure 4.3F)	×		×	×		×

Table 4.1 Lessons learned by data vignette. Each of the six specific lessons learned are juxtaposed along the vignette to which it applies

4.5.1.1 Lesson 1: Criteria for what is an outlier can be difficult to determine

Identification of outlier points has been used as one means of validating citizen-collected data; for example, as an automated, first-pass validation of electronically submitted data (Bonter and Cooper 2012). The difficulty in identifying data outliers was a reoccurring theme during our citizen science experience, and a major lesson learned in the context of critiques regarding the quality of citizen science data (Table 4.1). Identifying outlier data firstly involves the calculation of mean and data distributions, both of which depend on the quality of data collected. Specifically, we found that the mean and data distribution can vary between citizen and scientist collected data (our 'split-sampling' design). We statistically compared citizen to scientist data using unpaired-T tests, which was done in tandem with identifying specific citizen data outliers towards validating citizen versus scientist data. Mean nitrate concentrations, though not DOC concentrations, were statistically greater within the citizen dataset. A bias for statistically higher NO_3^- concentrations could derive from geographical differences in where citizens sampled (despite our attempts to emulate sampling locations), or possible issues within citizen samples (such as contamination). Constraining where citizens can sample within the experimental design would eliminate geographical bias. However, such constraints can depress participation, even as volunteer recruitment is difficult, time-intensive and costly (Conrad and Hilchey 2010). Additionally, the location and timing of sampling was in certain cases an expression of contextual knowledge or specific interests inserted into sampling (as discussed in Lessons 3 and 4). Thus, citizen data may contain inherent bias that could hinder the identification of potential outlier points.

Our initial assumption was that outliers far from the mean should be treated with a degree of suspicion, owing to uncertainty regarding whether the data point was 'valid' or not. However,

outliers identified within this study were typically explained through contextual information regarding sampling conditions, rather than potential issues in citizen collection, such as degradation or sample contamination. For example, high concentration DOC samples (outlined in Story 1, Figure 4.3A) occurred due to a highly impacted urban storm water lagoon. In this instance, selection of site locations was driven not by our research question, but by education and engagement goals central to organization involved. Story 5 (Figure 4.3E) highlights another 'outlier' point, in which high DOC was due to timely sampling of an erosion event caused by construction (Figure 4.3E, orange dot). Events occurring on such short timescales would be difficult to resample by scientists in order to verify their authenticity. An additional complication in using outliers to validate citizen data quality is that identification of low-concentration outliers (which could be caused by sample degradation due to improper storage) would be difficult, given the naturally low mean DOC and NO_3^- concentrations characteristic of many streams in our geographical context (Richardson et al. 2005). Examining outliers in this way is one method of validating citizen data, which also includes statistical metrics (for example, Walker et al. 2016). However, there is no current robust methodology for validating hydrologic and water resource data (Walker et al. 2016). This is important as citizen science data is subject to heightened critique regarding its quality, and is more likely than scientist collected data to be dismissed as faulty. This lack of trust around the quality of citizen-collected data may hinder truly revolutionary discoveries to be made from citizen science (Riesch and Potter 2013). This is especially precarious for policy-relevant data such as water quality, where such mistrust has already translated into instances where regulators disregard findings from citizen data owing to concerns regarding validity, alignment to acceptable standards, and the possible insertion of political motivations (Fowler et al. 2013; Jalbert and Kinchy 2015; Pfeffer and Wagenet 2007).

Validation approaches that are both scientifically robust and replicable across different studies are thus critical to improve confidence in citizen-collected data, and therefore acceptance within scientific and regulatory audiences.

4.5.1.2 Lesson 2: Aberrations that are within normal distribution can be interpreted as more meaningful by citizens due to collection context

Participants may attach meaning to data aberrations based on the context of collection. This speaks partially to issues related to data complexity and the difficulty of clearly communicating complex data and scientific certainties to non-scientific audiences. We observed this in the instance of samples collected within a creek affected by train derailment (Table 4.1), in which the samples downstream of the derailment were elevated in DOC relative to upstream samples, but were not high within the context of the overall data set (Story 2, Figure 4.3B, two orange dots). This was also encountered in Story 4 (Figure 4.3D), where knowledge of past disruption could impart greater meaning than scientifically provable to elevated DOC concentrations. Concepts of significance and variability can be difficult to communicate beyond a scientific audience, with the potential that participants insert their own interpretations into this knowledge gap. Clearly communicating data and data interpretation integrates elements of effective risk communication, and is the responsibility of the scientist directing the project, given issues regarding possible insertion of citizen interpretations.

4.5.1.3 Lesson 3: Citizens and citizen-lead community groups can insert their own interests into data collection

A third lesson learned is that citizens and citizen-led community groups can insert their own interests into data collection, with can be subsequently reflected in data outcomes. This is particularly relevant for water quality monitoring in our experience, given the prevalence of

community-based watershed monitoring activities. Participation within our project was enthusiastically received by these groups, and was generally perceived as a means of adding to activities already underway. Thus, each group brought to sampling their own knowledge and concerns about the specific watersheds in which they are already actively monitoring. In many cases, this translated into particular research questions that shaped their participation – for example, taking samples at specific locations to determine whether impacts such as a coal train derailment (Story 2, Figure 4.3B) or septic field contamination (Story 4.4, Figure 3D) was occurring. This 'nested' several context-specific research questions within our own research. Citizens also insert their own interests into where and when they sampled. For example, interest over the effects of a dam breach on the local water quality spurred a participant to take a sample (Story 6, Figure 4.3E). However, in this case the interests and concerns of community groups and municipalities that shaped sampling were often buttressed by a significant repository of knowledge born from (in some cases) years of place-based experience, potentially reflected in over-sampling within particular areas of concern. Constraining where, when and how citizens participate can reduce the potential for bias within citizen science data (Delaney et al. 2007). Given our experience, we add that such limitations could diminish the appeal of participating, especially for community groups for whom participation augments existing knowledge and activities (such as community-based monitoring). Thus, scientists themselves could benefit from a better understanding of human behavioural research behind the intuitions people use for when and why they sample in certain areas (Kraus, Malmfors, and Slovic 1992; Auyero and Swistun 2008).

4.5.1.4 Lesson 4: Questions of interest to scientists versus citizens may not coincide

Ultimately, the research questions that citizens and citizen-led community groups can bring through participation may contradict questions that matter to scientists. The potential that both sets of research interests could clash is particularly high, given the amorphous and broad nature of 'water quality monitoring'. This manifested at many points within our study, where citizens or citizen-led community groups were interested in questions beyond the purview of our own research - for example, searching for *E.Coli* contamination from septic field contamination in Story 3 (Figure 4.3C), for effects of mine tailings (Story 6, Figure 4.3E), or for the presence of coal residue following derailment (Story 2, Figure 4.3B). Initially, it was our assumption that these multiple research intents could exist in tandem, serving both our interests, as well as that of the citizens and citizen-led community groups (constituting a 'win-win' situation). However, the ways in which different objectives shaped the data outcomes within our citizen science campaign was surprising.

Explicitly reconciling research aims of the scientist with that of citizens and community-based monitoring groups may be difficult. Firstly, the research questions nested within our own experience were typically based within a very defined context (often within a specific watershed). The resultant diversity in research objectives would make it difficult to select one methodology or research question to satisfy all or even most interests if the research program was co-created (where research questions are decided upon collaboration between citizens and scientists) rather than contributory (scientist-directed) citizen science (Bonney et al. 2009). Indeed, the investigation of place-based questions has been previously invoked as a rational for citizen groups to pursue citizen science; because academic research is more likely to pursue research with a larger scope, place-based (and even event-based) questions may be a better fit for

citizen science projects lead by citizens themselves, rather than scientists (Miller-Rushing et al. 2012). Despite the potential for mismatch in research aims, there can be significant mutual benefit to collaboration between community organizations and scientists within citizen science. This includes sharing resources, contextual knowledge and technical expertise, as well as common interests towards environmental monitoring, management and protection. However**,** valuing specific goals and interests that citizens and citizen-lead organizations bring to participation is important for appreciating participant motivations, effect on involvement and data outcomes, and expectations for how participation can benefit all parties.

We encountered a number of citizen goals and research questions that shaped participation within our citizen science program, demonstrating the depth of activities around water and watershed conservation within our community. Such diversity may be unique to water and environmental monitoring for a number of reasons. Government capacity for environmental monitoring, assessment and remediation (especially related to water quality), has undergone a well-documented decrease within Canada (Conrad and Daoust 2008). Specifically, hydrologic monitoring networks critical to the accurate assessment and management of water resources have shrunk globally (Walker et al. 2016). This gap has increasingly been filled by volunteer led community organizations subsiding on minimal and/or highly provisional budgets (Day and Cantwell 1998; Savan, Morgan, and Gore 2003). Limited resources (including both money and expertise), can hamper the ability of such organizations to implement long-term monitoring programs, especially those involving sophisticated monitoring technologies (Jalbert and Kinchy 2015). In our experience, local community groups and representatives from municipalities enthusiastically greeted the prospective of participating (and obtaining water quality data) through our project. This was true even when the type of data aligned imperfectly with setting-

specific concerns and questions (the idea that any data offered for the price of participation is 'good' data). Many of the community-lead concerns we encountered were in response to specific events, such as previous forest clearing (Story 4, Figure 4.3D), coal train derailment (Story 2, Figure 4.3B), or mining tailings dam breach (Story 6, Figure 4.3F). The specificity of such worries arising from particular events within particular contexts mirror previously reported instances where community-lead investigations regarding environmental health risks have been instigated to demand accountability between regulators and those responsible for pollution (Overdevest and Mayer 2007; Jalbert and Kinchy 2015).

4.5.1.5 Lesson 5: Data might be primary for scientists, but secondary for citizens whose aim is education

Another element of interests that shape participation is the idea that data collection might be a primary goal for scientists, but could be secondary for citizens whose primary aim is education. Although many citizen science projects are undertaken with primary goals of education and/or engagement, progress in citizen science increasingly emphasizes scientific objectives, with the goal of producing data with sufficient rigor to pass peer-review (McKinley et al., 2015). The division between citizen science performed within an academic setting and that performed by citizen-lead community organizations with a central goal of education and engagement, has been little explored (other than to note the proliferation of citizen science activities outside of academic research) (Conrad and Hilchey 2010). Firstly, engaging with these organizations can provide a means of significantly improving the reach and participation within a citizen science program. Such collaboration must take into account the different agendas and objectives that other organizations (such as school groups) may have, which can reduce participation within a secondary citizen science program (Bonney, Cooper, et al. 2009). In reiterating these concerns,

we also add that collaboration may invert educational goals over that of data quality, which can be reflected in how, where, and the attention with which samples are collected (as observed in Story 1, Figure 4.3A).

4.5.1.6 Lesson 6: Place-centrism in citizen science can have advantages

The place-centrism of citizens is a lesson learned that emphasises the potential advantages of citizen science. This derives from the likelihood that citizens can be embedded within context in a much more accessible way than scientific teams, dramatically increasing their ability to respond to and observe short timescale events. This was illustrated within Story 5 (Figure 4.3E). A citizen participant sampled a high-sediment event within a stream that arose from an improperly armoured construction site, a short timescale event accessible only due to the participant's timely observation (Story 5, Figure 4.3E). This highly involved individual regularly visits stream sites during monitoring activities, dramatically increasing their likelihood of observing and capturing small time scale events when compared to a remote scientific team. Such place-centrism has been discussed for data collection when scientific personal have limited ability to reach inaccessible sites; this could enable monitoring during natural or human caused disasters, and has included monitoring flood risk from remote sites and reporting rainfall during times of famine (Bonney et al., 2014). As observed in both the sample taken after dam breech (Story 6, Figure 4.3F), as well as the construction-impacted sample (Story 5, Figure 4.3E), the advantages of place-centrism extends beyond programs designed to monitor risk within remote or broad geographical locations, and is especially relevant to water quality monitoring.

4.5.2 What do participants get out of citizen science?

Only recently have discussions begun to focus on what participants get out of the citizen science process, as opposed to scientific advantages. This includes the ethics surrounding data

ownership, and attribution of the unpaid effort offered by the public (Riesch and Potter 2013). Being cognizant of these concerns, and aware that direct feedback was found to facilitate participation within other projects (Sullivan et al. 2009), we posted all data on a Google Map on the project website to enable participants to look up sites they had sampled. Community organizations that contributed multiple samples were also provided with data regarding their sampling within a report format that also explained the project aims, methods and background information on the water quality parameters analyzed. In this way, it was our hope to create a 'win-win' situation, in which the time associated with participation would be 'paid' by data provided. Offering 'data as payment' is an approach taken by many citizen science studies, where scientific analysis of citizen-collected samples can contribute to engagement and education goals (Bonney, Cooper, et al. 2009), as well as increase participation by reducing civilian fatigue (Sullivan et al. 2009). However, our experience demonstrates that organizations and citizens often bring their own nested interests to participation, which can align poorly with research demands. These interests highlight the perspective of citizen science participants, and how this affects the data they collect. To date, there has been less discussion of citizen science from the perspective of participants, when compared to motivations and outcomes for scientists. Those that do exist highlight participant outcomes such as whether participation increased knowledge or altered attitudes, as well as the ethics of how participants should be compensated for their participation (Riesch and Potter 2013). There are few considerations of participant characteristics in the literature that include elements of social identity that shape motivations for participation, what they hope to gain from it, and what the expectations in general are of participation. In our experience, participants can bring context-specific concerns and questions that can be difficult to reconcile with scientific aims and the resultant data, and can thus create

ethical dilemmas around compensation for participation that is meaningful and useful. Does offering 'data as payment' for participation thus create an ethical onus for the researcher to ensure that data is useful beyond their own scientific goals?

One significant motivator for participation within citizen science projects that has been identified is the opportunity to contribute to scientific endeavours (Alender 2015). Thus, clearly communicating data outcomes to participants (how their participation contributed to a greater scientific goal) is critical to prevent participant disappointment. However, outcomes can be difficult to communicate to non-scientific audiences, given implicit concepts of uncertainty and significance nested within data, and underlying scientific assumptions within explanations and conclusions. Ambiguity created by poor communication creates the potential that citizens insert their own interpretations, especially if they have context-specific knowledge or perceptions regarding the environmental 'health' of where they chose to sample. Communication difficulty also scales directly with data complexity. In our study, data beyond DOC and nitrate concentration consisted partially of spectral indices that describe the composition and possible origin of DOC within the sample (Supplemental Table D.1). These indices are difficult to explain and contextualize in a meaningful and relevant manner; they describe water quality elements that are proxies for broad chemical classes, rather than a direct measure of concentration. However, spectrophotometric methods used to produce this complex data appear perfectly suited to citizen science, given their speed, ease of use, and low cost per sample. In our case, the relative simplicity of the analytical method contradicts the complexity of data produced, and corresponding challenge of clearly communicating results to a non-scientific audience.

4.5.3 Reversing the (knowledge) flow: The challenge of integrating citizen perspectives

An additional theme present within many of the lessons learned is the directionality of knowledge generation and flow. Given that much citizen science is predicated on the "knowledge defect" model of scientific understandings, it is unsurprising that knowledge flow directionality is from scientific actors to the public (Irwin 1995; Bonney, Cooper, et al. 2009). Discussions regarding the potential for citizen science seem to refute this linear directionality by pointing to the potential for implementing traditional or other contextual forms of knowledge upon engaging with the public. While there are few current examples of such integration, our experience highlights the significant capacity, scientific activities, and knowledge generation that can exist within the greater community. This is especially true for environmental monitoring such as that pertaining to water quality, where community groups are shouldering critical monitoring activities previously undertaken by government scientists (Conrad and Daoust 2008). Such community capacity could be an invaluable resource for citizen science projects. However, the question remains about how to encompass and make best scientific use of this capacity, while also understanding that contextual expertise can alter why, how and what is expected of participation within a 'exterior' citizen science campaign.

4.6 Conclusion

We utilized our experience undertaking a citizen science campaign regarding water quality to interrogate the nature of citizen-lead data collection as it compares to traditional science programs. We examined the nature of 'outliers' within citizen data, and question the presence and nature of data aberrations from a scientific perspective, as well as context imparted by non-scientist participants. Data from the project are presented alongside qualitative vignettes to provide background information regarding specific instances that occurred within our experience.

Six lessons learned were distilled from these vignettes: 1) criteria for what is an outlier can be difficult to determine; 2) aberrations that are within normal distribution can be interpreted as more meaningful by citizens due to collection context; 3) citizens and citizen-lead community groups can insert their own interests into data collection; 4) questions of interest to scientists versus citizens may not coincide (such as investigating long-term trends versus effects of a specific event); 5) that data might be primary for scientists, but secondary for citizens whose aim is education; and 6) the advantages of citizen place-centrism. These lessons illustrate the importance of citizen motivations, knowledge and expectations in shaping data outcomes, as well as possible difficulties in communicating and examining these outcomes versus traditional scientific approaches. They also illustrate the potential for inverting current uni-directional considerations of knowledge flow assumed within many current discussions around citizen science, and the possibility of considering other forms of knowledge generation. Furthermore, examinations of citizen science especially from perspectives that go beyond scientific motivations are critical if such participatory approaches are to fulfil both lofty scientific and societal goals.

Chapter 5: Whose input counts? Evaluating the process and outcomes of public consultation through the BC Water Act Modernization

5.1 Introduction

Public consultation has become an increasingly important feature of policy-making, intended to promote broad citizen participation and enhance democratic engagement by enabling citizens to influence the plans and policies that affect them (Patten 2000; Shipley and Utz 2012). This is particularly true for policy dealing with issues around resources such as water. While public consultation processes differ significantly in their format and outcomes, they are typically characterized by the solicitation of citizen feedback on decisions, plans, or policy proposals (Rowe and Frewer 2005), ultimately informing government decisions or revisions to a proposal under consideration. Consultation processes are advocated as an inclusive, efficient means of gaining insight into public values and perceptions, which are expected to improve the outcomes, equity, and legitimacy of government decisions while retaining the central role of professional policy experts (Shipley and Utz 2012). However, public consultation has not always lived up to its democratic ideals; studies show that consultation processes often align poorly with decision-making processes, lack transparency, and have little influence on policy and planning (Cheeseman and Smith 2001; J. Carr 2012; Monno and Khakee 2012). Arnstein's initial critique (1969) that consultation can be tokenistic, reproduce power hierarchies, and contribute to citizen disengagement, thus continues to resound (e.g., Innes and Booher 2004; Woodford and Preston 2013; Kaehne and Taylor 2015).

The institutionalization of consultation techniques by democratic governments therefore demands critical analysis of how consultation reproduces or disrupts power hierarchies, and

contributes to social (in)justices. According to Fischer (2016), critical policy analysis 'means not only to focus on problems, and the decisions designed to deal with them, but also to examine the normative assumptions upon which they are based.' In the context of public policy consultation, critical inquiry thus demands an engagement with the democratic assumptions underpinning consultation theory and practice (Patten 2000; Carvalho, Pinto-Coelho, and Seixas 2016).

Although a range of evaluative criteria and frameworks have been developed to assess public participation processes (e.g. Beierle and Cayford 2002; Rowe and Frewer 2000), many of these lack an explicitly critical orientation. Recent reviews have highlighted that evaluations tend to emphasize process criteria and participant satisfaction, to the relative neglect of outcomes (J. Carr 2012; Brown 2014). In particular, systematic analyses of how consultation influences policy/planning outcomes are rare, making it difficult to examine consultation's role in perpetuating existing societal inequalities (Gilens and Page 2014). More explicitly critical evaluations that exist tend to focus on more direct and deliberative participatory processes (e.g. J. Carr 2012), rather than large-scale submission-based consultation processes that have become common among state and national governments (Kaehne and Taylor 2015). Little is consequently known about how large-scale processes contribute towards democratizing government decision-making.

This study contributes to research on consultation evaluation through a detailed analysis of a recent large-scale, submission-based public consultation process. We develop a novel mixed methods approach to analyse both the consultation process and its policy outcomes with respect to principles of democracy inherent to consultation. Our use of mixed methods echoes arguments by Harris et al. (2016) that "it is useful to pursue qualitative and quantitative work in tandem – allowing the quantitative work to reveal patterns that can then be explained and understood with

more in-depth work." In this study, qualitative analysis was used to explore themes in submitters' perceptions of policy proposals and the consultation process, while quantitative analysis revealed patterns in how submitter input aligned with policy outcomes. A mixed methods approach thus allows us to critically examine the consultation process with respect to meaningful influence and equity dimensions – indicating possible instances of uneven influence on policy-making – to further interrogate democratic assumptions that are embedded in consultation.

Our case study, focused on British Columbia's Water Act Modernization (WAM) process, provides an example of an intensive, multi-stage consultation process that received significant public attention and government investment. The provincial government held three rounds of public consultation over five years, resulting in over 4000 submissions. These submissions were used to refine policies that comprise BC's new Water Sustainability Act (WSA 2014). The consultation process has generally been considered successful, based on the large number of submissions generated and sustained engagement over multiple stages. As such, it is likely to influence future consultation exercises in BC and elsewhere.

We begin this article by reviewing existing literature on the evaluation of public participation processes, identifying key criteria and approaches to evaluate process design and outcomes. Following a brief background on the BC WAM, we describe the methods used to analyze submissions and policy outcomes. Subsequent sections summarize key strengths and limitations of the consultation process, variability in policy preferences across submitter groups, and differential alignment between policy preferences and outcomes. Finally, we discuss the politics of 'democratic' consultation, and challenges towards providing accountability.

5.1.1 Evaluating participation: From process to outcomes

5.1.1.1 Participation in environmental policy-making

Public participation has been called a cornerstone of modern democracy, and is increasingly mandated in policy formation. This is especially evident within policy related to resource management, especially around issues of environment and sustainable development. The Aarhus convention highlights interactions between the public and governmental authorities as key to justice considerations, focusing on the need for public access to information as well as broad engagement in decision-making (UNECE 1998). Participation is also one of the four key principles related to water governance highlighted in the Dublin Principles (1992), while the Organization for Economic Co-operation and Development (OECD) states that: "Engaging citizens in policy-making… contributes to building public trust in government, raising the quality of democracy and strengthening civic capacity" (OECD 2001, 2011). Additional motivations for public participation include the inclusion of citizen knowledge and expertise, especially when institutional capacity is limited (Fischer 2000).

This focus on participatory engagement as key to good governance, and democracy broadly, has resulted in the institutionalization of consultation within public planning and policy-making (Shipley and Utz 2012); The advent of the internet has transformed consultation, generating electronic platforms that enable broad, low-cost engagement (Culver and Howe 2004). In Canada, participation in policy-making has a long history, and is traditionally operationalized through public hearings and citizen polls (Woodford and Preston 2013). In British Columbia, the requirement to consult the public regarding plans, regulations, and proposed activities is embedded within legislation (Halseth and Booth 2003). Specific

requirements to consult and accommodate First Nations are also embedded in federal and provincial legislation (Government of Canada 2011).

5.1.1.2 Evaluating participation

The increasing prevalence of participatory policy-making has inspired a growing literature on process evaluation, including criteria and frameworks that evaluate participation's effectiveness and inclusivity, and empirical accounts of specific processes. While some of this work is specific to consultation, the majority relates to public participation generally. In this section we outline key trends in existing research on participation evaluation, focusing first on criteria to evaluate process design, and then on assessments of participation outcomes. A significant finding of this review is that while a range of approaches have been developed for process evaluation, there are few systematic analyses of participation outcomes. This study thus presents a novel approach that addresses this gap by linking process evaluation to policy outcomes.

5.1.2 Process-based evaluations

Multiple studies have identified a wide-ranging list of process-based criteria to evaluate fair and effective participatory processes. Over the last 20 years, these criteria have been consolidated in a number of frameworks for evaluating public participation, the most well-cited of which is Rowe and Frewer's (2000) framework of process and acceptance criteria (where other examples include: Beierle and Cayford 2002; Buchy and Hoverman 2000; Blackstock, Kelly, and Horsey 2007; G. Carr, Blöschl, and Loucks 2012; Brown 2014). Common process criteria include early involvement, representativeness, inclusivity, adequate time and resources, access to information, clarity of objectives/agenda, and the ability of participants to provide input (Brown 2014). Criteria-based frameworks enable assessment of specific case studies, and comparison across processes (Rowe and Frewer 2004). The critique of such generalized check-list approaches is

that they can obscure power dynamics present within participation processes (Bickerstaff and Walker 2005). Other approaches include examining participatory processes through open-ended qualitative approaches, including participant observation, document analysis, and interviews (for example, Bickerstaff and Walker 2005; J. Carr 2012; Carvalho, Pinto-Coelho, and Seixas 2016). These methods have identified barriers to meaningful engagement (particularly amongst marginalized populations) (Morinville and Harris 2014), the politics driving process design (Cheeseman and Smith 2001), and how process design and implementation affects participation (Halseth and Booth 2003).

Analyses identify the inclusivity and representativeness of participation as key considerations for process design. Studies examine both who participates (or does not) and how particular perspectives are represented (Catt and Murphy 2003). Paramount concerns include participation by marginalized groups, elitism, and the legitimacy of relying upon 'representative' individuals (Cornwall 2008; Nissen 2014; Parkins and Sinclair 2014). Several authors have in fact argued that participatory processes act to construct publics and interest groups, rather than simply represent pre-existing groups (Braun and Schultz 2009; Eden and Bear 2012).

A related set of concerns focus on access to participation, typically assessed in terms of process timing, resourcing, method, and location (Brown 2014). Studies have highlighted that the selection of participation techniques, as well as the timing and format of participation, can promote or inhibit participation by certain groups (Cornwall 2004; Parkins and Sinclair 2014). Submission-based consultation (including online consultation) can be prone to self-selection biases, promoting participation by those who are already politically engaged and have the time, resources, and expertise to participate (Kaehne and Taylor 2015). Investigations specifically regarding online participation have shown that while such participation improves rates of

participation, participants tended to be older, better educated, and more politically engaged than the general population (Culver and Howe 2004). While limited access and familiarity with computers can inhibit online participation, such forums can provide engagement opportunities for marginalized groups who would be reluctant to participate in-person (for example, survivors of domestic violence) (Coleman 2004).

Finally, power dynamics are an important concern in evaluating participatory processes. Such dynamics are frequently observed in in-person processes (such as focus groups) due to pre-existing relationships, group identity politics, the presence of vested interests, and participants' differing abilities to make their concerns heard (Cornwall 2004). Evaluative frameworks examine whether process design creates a safe environment for participants to voice opinions, accommodates their differing capacities, and provides facilitation for a fair and respectful process (Blackstock, Kelly, and Horsey 2007; Brown 2014). Studies emphasize the potential for 'elite capture' of participatory processes (Parkins and Sinclair 2014), and the silencing of particular perspectives due to politics around participant identity and consensus-based processes (Bickerstaff and Walker 2005; Koch 2013).

5.1.3 Outcome-based evaluations

Despite the recent advance of evaluative frameworks, very few studies assess consultation's effectiveness in terms of policy, planning, and resource management outcomes (for one example, see Brown 2014). Assessing of process effectiveness and participant satisfaction are frequently used as proxies for outcome evaluation, despite evidence that good processes do not always lead to good outcomes (Rowe and Frewer 2004; G. Carr, Blöschl, and Loucks 2012). This lack of outcome assessment renders relationships between consultation and policy-making unclear,

providing few measures to ensure decision-maker accountability (Bickerstaff and Walker 2005; Emery, Mulder, and Frewer 2015).

Evaluation frameworks typically assess acceptance of process outcomes, transparency, and accountability (Rowe and Frewer 2000; G. Carr, Blöschl, and Loucks 2012; Brown 2014). Acceptance criteria gauge whether participants and government officials accept and/or are satisfied with participation outcomes based on the perceived legitimacy of the process (Rowe and Frewer 2000), established primarily through surveys (Rowe and Frewer 2004). In contrast, transparency and accountability are typically assessed using simple indicators, including whether decision-making is structured and clearly articulated, consultation results are made available, and outcomes communicated to participants (G. Carr, Blöschl, and Loucks 2012; Brown 2014). While evaluation frameworks often contain criteria such as 'participant inputs have a genuine impact on policy' (J. Carr 2012), there are few measures that actually measure participant impact on policy (Rowe and Frewer 2004; Emery, Mulder, and Frewer 2015).

Additionally, some evaluation frameworks highlight the tangible and intangible outcomes of participation. Intangible outcome criteria include participant empowerment, social learning, willingness to participate in the future, increased trust of government, and improved understanding of government processes (Abelson and Gauvin 2006; Brown 2014). Tangible outcomes assess the 'products' that emerge directly from participation, including decisions, reports, plans, policies, and new institutions or processes (G. Carr, Blöschl, and Loucks 2012; Brown 2014), although the nature and content of products is rarely analyzed. Intangible and tangible outcomes are typically evaluated using a combination of presence/absence criteria, document analysis, and participant surveys (Rowe and Frewer 2004).

Empirical analyses of consultation outcomes typically involve either observation or interview-based studies on how consultation impacts decisions (for example, Cheeseman and Smith 2001; J. Carr 2012; Monno and Khakee 2012), or quantitative analyses of participant satisfaction with outcomes (such as Culver and Howe 2004). Very few studies have systematically analyzed the policy/planning impact of consultation – in other words, the relationship between consultation outputs (e.g. submissions) and policy outcomes. One exception is a study by Gilens and Page (2014); their quantitative analysis of 1,779 public policy issues subject to public consultation in the US showed that 'when the preferences of economic elites and… organized interest groups are controlled for, the preferences of the average American appear to have only a minuscule, near-zero, statistically non-significant impact upon public policy' (Gilens and Page 2014). These results support other case studies that found that economic elites profoundly influence public policy-making (J. Carr 2012; Parkins and Sinclair 2014; Kaehne and Taylor 2015). Studies have also highlighted the role that government officials can play in limiting the policy impact of consultation (Cheeseman and Smith 2001; Carvalho, Pinto-Coelho, and Seixas 2016). Our study seeks to fill in the relative lack of systematic analyses around how consultation affects policy outcomes by quantitatively analyzing the relationship between public submissions and resultant legislation.

5.2 Case study background: The BC Water Sustainability Act (WSA)

This study examines the public consultation process undertaken as part of the modernization of BC's Water Sustainability Act (WSA 2014). This process was designed to update British Columbia's Water Act, which was established in 1909, and served as the primary legislation for managing the diversion and use of BC's water for over a century. Written for a settler state, it established a system of surface water property rights to enable the development of primary

industries in the province. Subsequent amendments to the Act only marginally expanded its original focus, despite increasing evidence of water scarcity and water use conflicts in recent decades.

In 2008, the BC Ministry of Environment released 'Living Water Smart: BC's Water Plan', which set out the government's new vision for water in BC (Ministry of Environment 2008). A key commitment of the plan was the modernization of BC's water laws to ensure the sustainability of water resources and the environment. The Water Act Modernization (WAM) project commenced in 2010 with an intensive public consultation process (Figure 5.1). Consultation took place over three stages and five years; each stage involved the release of a consultation document and solicitation of feedback on the policy information and options presented. The public were invited to submit comments via mail, fax, email, or the Living Water Smart blog. In addition, the government conducted 12 regional one-day workshops during the first phase of consultation, including three sessions specifically for First Nations.

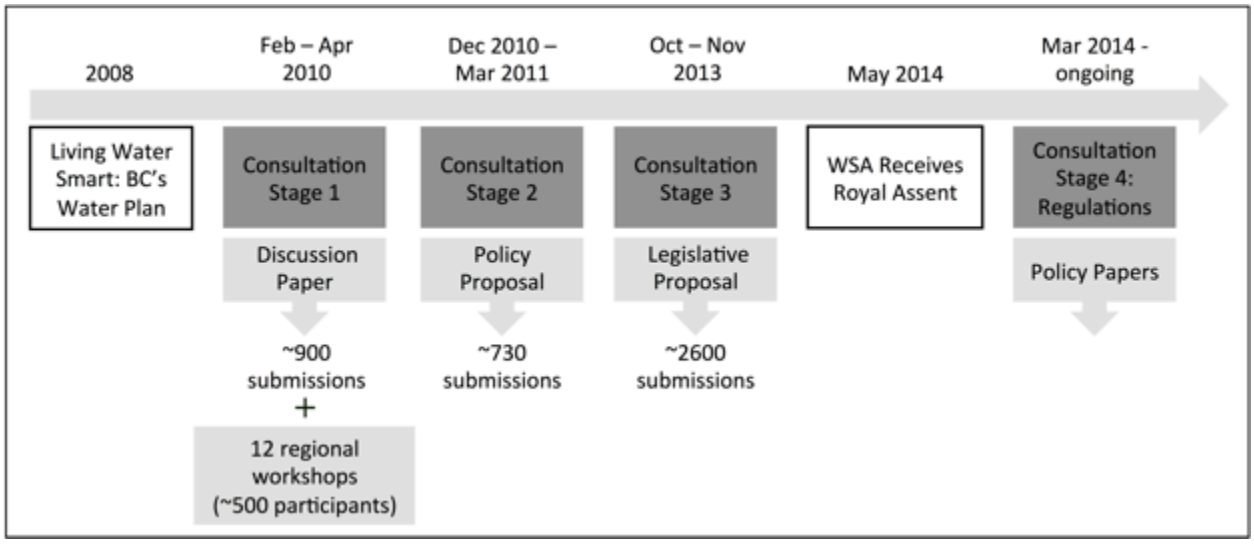

Figure 5.1 Water Act Modernization (WAM) process.

The WSA received royal assent in 2014, and came into force in February 2016 with the development of initial regulations. Over the coming years, further regulations will be developed in phases; the government has committed to continued public input on proposed regulations. Among the key policy revisions with the WSA are the introduction of groundwater licensing, the protection of environmental flows, and the ability to establish provincial water objectives, water sustainability plans for priority areas, and alternative governance arrangements.

5.3 Methods

5.3.1 Source material

Our analysis is based on submissions from the first three stages of consultation; the fourth stage had not been completed at the time of the analysis. Submissions were downloaded from the Ministry of Environment's website in May 2015.[2] Ministry officials classified all submissions according to submitter group and consultation stage, which we retained for our own analysis.

5.3.2 Submission analysis

All submissions were analyzed for 15 of the 16 submitter groups identified by the ministry. For the 16th group, comprised of 'individual'[3] submitters, 10% (482) of submissions were randomly selected from each stage for analysis due to the large number of submissions from individuals, and resources available for analysis. Form submissions, deriving from documents distributed through membership within community organizations, constituted the majority of individual submissions (Figure 5.2). Proprietary scripts were used to identify individual submissions that derived from forms (on the basis of similarity in both word count and frequency), in order to streamline analysis. In total, 867 submissions were analyzed across all 16 submitter groups

[2] https://engage.gov.bc.ca/watersustainabilityact/whatweheard/
[3] The 'individuals' submitter group includes form-based and freestyle (non-form) submissions from unaffiliated individuals

(Figure 5.2). The random selection of submissions, identification of form submissions, as well as quantitative analysis described below, was done using R (version 3.2.4, R Core Team 2016); all associated code is available at https://github.com/ashjolly/WSA_Analysis.

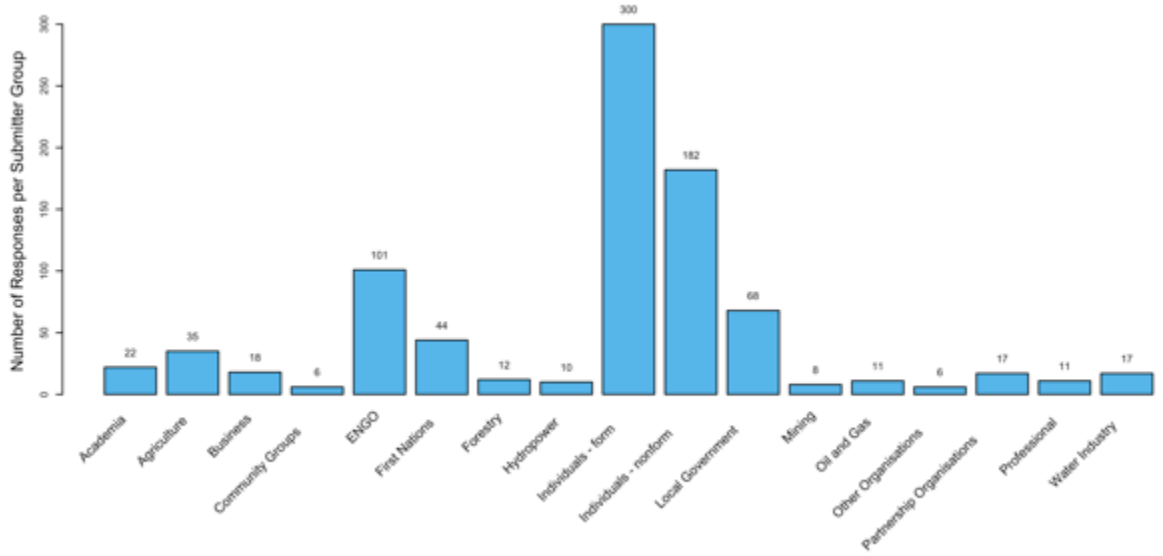

Figure 5.2 Number of submissions analyzed by submitter group (all consultation stages).

5.3.3 Qualitative analysis

Submissions were coded in NVivo (version 10.2.1, QSR International) using an iterative coding procedure focused on understanding how participants responded to the policy options raised during consultation. All statements that participants made in direct response to the policy options proposed in consultation documents were coded. The resulting codes were used to construct a coding rubric that reflects the range of policy areas (26 in total) contained within consultation documents (Figure 5.3). Within each policy area, responses were coded according to the level of legislative intervention advocated by participants; responses were categorized as advocating

either 1) a more transformative approach to water governance with stronger regulation, 2) a moderate degree of regulation, or 3) less or weakened regulation for that policy area.

In addition, submissions contained a large number of comments regarding the consultation process itself, revealing recurrent themes in submitter concerns and suggestions about the process. Such comments were coded as either positive or negative in tone, and according to themes in recommendations for the process. Many submissions also contained policy ideas or concerns outside the scope of consultation, and are therefore not included in this analysis.

Given the number of submissions, coding was split between three individuals. All team members analyzed several submissions at the beginning of the process and compared results to ensure consistency. All results were reviewed at the end of the process by a single team member to ensure proper identification and classification.

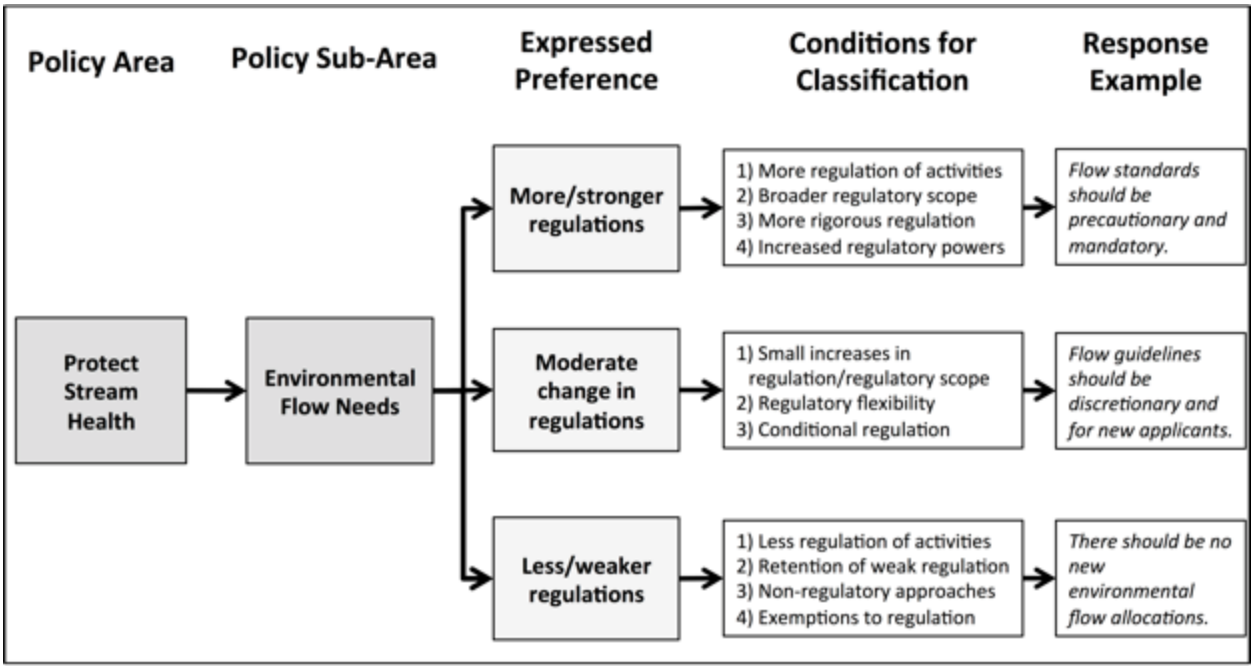

Figure 5.3 Method for coding submissions, based on policy areas and sub-categories contained in the WSA LP. Submissions were analyzed on stated preferences for more, moderate, or weaker regulation (as per example).

5.3.4 Quantitative analysis

To examine the relationship between submitter responses and final policy outcomes, a quantitative analysis of submitter responses to policy areas was then conducted using the coding rubric described previously. This analysis involved calculating two 'constructed metrics' (e.g., Satterfield et al. 2013) – a 'response factor', and 'alignment factor' – using R (v. 3.3.1, R Core Team 2016).

Firstly, 'Response Factors' were calculated to identify how each submitter group responded to a specific policy area, in terms of their desire for more, less, or moderate levels of regulation (Equation 5.1):

$$\textbf{Response Factor} = \left(\frac{\textbf{Number of submitters desiring increase}}{\sum \textbf{responses in policy area for submitter group}}\right) * \mathbf{101} + \left(\frac{\textbf{Number of submitters desiring moderate regulation}}{\sum \textbf{responses in policy area for submitter group}}\right) * \mathbf{51} + \left(\frac{\textbf{Number of submitters desiring decrease}}{\sum \textbf{responses in policy area for submitter group}}\right) * 1$$

(Equation 5.1)

The 'Response Factor' is the average number of submitters in a group that advocated a particular level of regulation, multiplied by a weighting factor, and summed across all regulation levels for a particular policy area. Weighting factors were chosen to ensure clear separation between groups advocating for more versus less regulation.

Secondly, 'Alignment Factors' were calculated to compare the level of regulation desired by submitters within specific policy areas (i.e. submitter group response factors) to the outcomes present within the WSA:

$$\textbf{Alignment Factor} = \textbf{Response Factor} - \textbf{WSA Factor} \qquad \textbf{(Equation 5.2)}$$

The 'WSA Factor' in this equation was calculated by coding the finalized WSA according to our rubric (Figure 5.3), which identifies whether the response advocated for strong, moderate, or weak regulation for the 26 policy areas in our analysis.

The 'Alignment Factor' measures the distance from the level of governance desired by a submitter group to the contents of the WSA. Thus, if the WSA contains the same level of regulation desired by a submitter group, the Alignment Factor will be close to 0; if the submitter group desired more regulation than contained in the WSA, the alignment factor will be closer to 100, and if submitters desired less regulation than the WSA, the alignment factor will be closer to -100.

In effect, both the Response and Alignment factors capture an operational average of the stated desire for legislation according to submitter group. As shown in Figure 5.2, the number of submissions analyzed by group varied widely, from <10 submissions (within Mining and Community groups) to hundreds (Individuals). Both constructed metrics have the impact of equalizing, or 'normalizing', the number of submissions into one factor for comparison across different groups. How to account for the different number of submissions across submitter groups was a concern within both our method, as well as one articulated by the Ministry of Environment within their own analysis. This also includes the issue of how to account for single submissions that purported to speak for many people through organizational submissions (with further discussion regarding the 'counting' of submissions present in Section 5.4.4). Thus, while

we realize that our analysis approach equalizes groups that represent vastly different levels of submissions and participation within this process, we content that the process of counting submissions is complex, and our analysis a best attempt at comparing responses across different submitter groups.

5.4 Results and discussion

5.4.1 Analysis of the WAM consultation process

Our analysis revealed that 182 submissions (21% of all submissions) included some form of comment on the consultation process, of which 70% were negative in tone (where only ~ 6% were positive), while 62% provided a recommendation on the process. The four most common recommendations were to provide more opportunities for input, to undertake meaningful consultation with First Nations, to extend the comment period, and to provide more information on proposed policies.

The most common recommendation among submitters was to provide more opportunities for public input. During the first stage of consultation, a discussion paper was released that invited the public to indicate their level of support for the proposed principles, objectives, and potential solutions outlined in the document. The discussion paper was necessarily very high-level, and the government did not indicate that they were considering further consultation. Submitters consequently argued that 'if this government is serious about democracy, there should be a broader public input process instead of an insufficient 10 day review process' (Individual, Stage 1). The government responded to the public's requests by providing two additional stages of consultation, each with an increasingly detailed policy proposal. This extension speaks to the government investment in public participation, and the influence of initial consultation on overall process design, resulting in a multi-stage process where

participants were involved from goal evaluation to policy analysis (such as advocated by Patten 2000).

Submitters criticized the government for their lack of meaningful engagement with BC First Nations. For example, the Union of BC Indian Chiefs (Stage 1) stated that:

> *UBCIC is deeply concerned that the submission process outlined in the Discussion Paper is highly problematic; it was designed without Indigenous involvement and treats Indigenous people as 'stakeholders' in the water policy process… There is no recognition of Indigenous jurisdiction or constitutionally-enshrined and judicially-recognized Aboriginal Title and Rights.*

Such critiques were re-stated throughout consultation. Indeed, First Nations' submissions had the highest rate of negative comments on the WAM consultation process; 66% of all First Nations' submissions were negative in tone, compared to 15% of all submissions across all submitter groups. While we are unable to provide detail here, it is clear that consultation fell short of the government's legal responsibilities,[4] let alone broader ethnical guidelines on what might constitute appropriate consultation.

Despite clear direction that the government has a specific responsibility to consult First Nations, the WAM consultation process was broadly framed in terms of public interest, and First Nations' input was incorporated as one among 16 'stakeholder' groups (rather than on a government-to-government basis). The creation of three (out of nine) workshops was the only attempt to specifically engage First Nations, and denounced as 'woefully inadequate' (First

[4] A series of Supreme Court of Canada decisions in 2004-2005 established the government's constitutional duty to consult and accommodate First Nations on decisions that might impact their aboriginal or treaty rights (Government of Canada 2011). Furthermore, the BC government entered into a 'New Relationship' with BC First Nations in 2005 to improve government-to-government relations. These two developments created legal and societal expectations that the BC government consult First Nations during the WAM, as it would affect aboriginal water use rights and watershed health within their territories.

Nations Leadership Council, Stage 2). Indeed, of 198 First Nations in the province, only 18 made formal submissions to the process.[5] This low response rate was likely due in part to the perception that public consultation was not an adequate replacement for the legal 'duty to consult' (Porten and de Loë 2014; Joe, Bakker, and Harris 2016). The Government's failure to fulfil their duty to consult, and dilution of First Nations' rights to those of 'stakeholders', has the potential to contribute to further mistrust, as well as disenfranchisement of First Nations (Porten and de Loë 2014; Joe, Bakker, and Harris 2016).

Submitter comments identified the duration of consultation as another constraint, repeatedly requesting that the government extend the deadline for submissions. The third consultation stage was criticized as particularly insufficient; submitters were given just four weeks to respond to a 127-page legislative proposal. The consequences of short timeframes are unevenly distributed; whereas industry groups, academia, and government organizations have time and resources to dedicate to responding to consultation documents (Kaehne and Taylor 2015), individual citizens, NGOs, and other under-resourced groups are significantly disadvantaged by short timeframes (Cornwall 2008). Local governments and First Nations noted especially that there was insufficient time to consult with their communities and governing boards before formulating a response.

> *Whereas many organizations have a governance Board who's meeting schedule does not accommodate such a short timeline… the Board of the Cowichan Valley Regional District formally request the Ministry of Environment to extend the timeline for public submissions (CVRD, stage 3)*

[5] Another 16 First Nations organizations and individuals also made submissions.

As such, consultation timing constrained the democratic potential of the process, and also undermined the democratic structure of contributing organizations, limiting their ability to submit a representative, well-informed response. The final concern raised by submitters was the limited policy information provided, with insufficient detail on proposed policies:

> *(W)hen it comes to legislation, the devil is in the details. Unfortunately, we will not know those details until the act is presented to the Legislative Assembly… For many of us the answer to these questions will affect the way we do our jobs and how we provide water to our residents. (Water Supply Association of BC, Stage 3)*

This stands in direct contrast to the government's stated 'interest in hearing about any possible unintended consequences that have not yet been considered' (Ministry of Environment 2013). The lack of policy information limited both submitters' ability to provide an informed response, and the utility of responses for policy-making; confusion over policy implications contributed to at times contradictory responses to certain policies. For example, the government's proposal to create a new 'oil and gas' water use purpose was met with strong opposition from both oil and gas submitters, and ENGOs, individuals, and First Nations. Oil and gas submitters worried that the new purpose "would provide another opportunity for interest groups to delay development" (Devon Canada, Stage 3), while others assumed it would provide this industry with "special and legally-protected rights to use water" (Fraser Riverkeeper Society, Stage 3).

Similar confusion was evident in submitters' responses to 'transfer of rights' and 'permitted uses' policies. This confusion remained despite significant investment on the part of government to provide informational resources for submitters, including informational workshops, an online blog to respond to questions, and a background report on options presented

in the discussion paper (Stage 1). The contrast between submitters concerns over the lack of detail and the government's efforts shows that information provision is a key challenge for enabling public participation in policy-making.

5.4.2 Submitter positions on WAM policy areas

This section describes how submitters responded to the policy options and proposals outlined in WAM consultation documents. First, we examined the number of submissions contributed by each submitter group across all consultation stages (Figure 5.2), which ere quite variable across different submitter groups. Individuals were by far the largest single contributing group, with the majority of individual submissions originating from forms (300 of the 482 individual submissions coded). Following individuals, ENGO, Local Government, and First Nations submitter groups contributed the greatest number of submissions, while many industry submitter groups contributed few submissions – for example, hydropower, oil and gas, forestry, and mining each had less than 15 submissions.

We then examined how submitter groups responded to the WAM policy areas. We did this by calculating a response factor (the average stated desire for strength of regulation) for each policy area a submitter group responded to. The response factor for each submitter group/policy area pair was compiled as a heat map (Figure 5.4). Response factors lie on a continuum from 1 to 101, where a response factor closer to 1 (grey) indicates a desire for less regulation, and that closer to 101 (dark blue) indicates a desire for stronger regulation. Additionally, submitter groups were clustered according to statistical similarity in response factors across all policy areas; these relationships are illustrated by the dendrogram to the left of Figure 5.4 (policy areas were also clustered; dendrogram not shown).

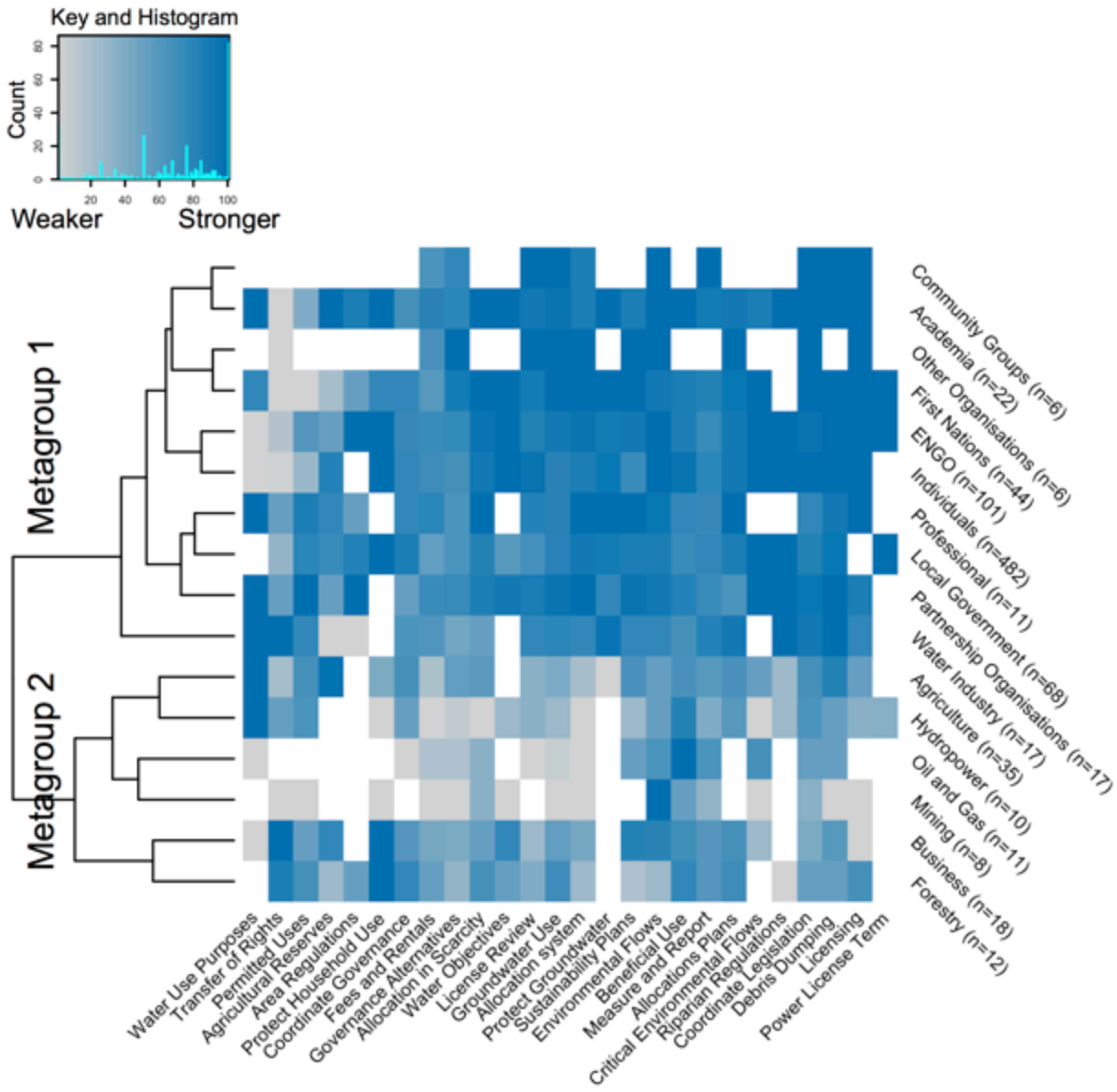

Figure 5.4 Response factors for each submitter group represented by heatmap pixels, clustered by similarities between submitters (rows) and policy area (columns).

The dendrogram identified two discrete submitter clusters – labelled Metagroups 1 and 2 (Figure 5.2). Statistical clustering based on response similarities resulted in a strong aggregation of

submitters best described as 'industrial'.[6] This 'industry' group (Metagroup 2) – consisting of Agriculture, Hydropower, Oil and Gas, Mining, Business and Forestry submitters - tended to favour less regulation, as shown by the predominance of grey and light blue squares. For example, industry responses to policy areas related to allocation, licensing, governance, and groundwater resulted in response factors close to or equal to 1, indicating a strong consensus within these groups towards less regulation overall.

Metagroup 2, comprised of 'non-industry' submitter groups (Community Groups, Academic, First Nations, ENGO, Individuals, Professionals, Local Government, Other Organizations, Partnership Organizations, and Water Industry[7]), is associated with higher response factors, signalling a desire for stronger overall regulation. This was especially true for policy areas enabling stronger environmental protections (e.g. Debris Dumping), improved governance (e.g. Coordinate Legislation), and stronger regulation of licensing (e.g. Licensing) – visible in the cluster of higher response factors at the top right of Figure 5.4. Submitters within this metagroup also exhibited a greater degree of internal similarity than submitters in Metagroup 2, as illustrated by colour variations in Figure 5.4.

The internal likeness of response factors within Metagroups 1 and 2, along with the differences separating them, suggests that similar interests and motivations drive both groups. This is substantiated by qualitative analysis; within the industry-dominated Metagroup 2, many submissions underlined the need for regulatory certainty and clarity regarding potential changes

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[6] Response and alignment factor clusters were determined through hierarchical cluster analysis using a complete linkage method without initial bias (number of clusters, composition, etc.).

[7] The 'Water Industry' submitter group incorporates a wide range of submitters, including provincial water associations and consultancies, water utility companies and commercial suppliers, and water retailers (e.g. Nestle Waters Canada). Because the category encompasses a diverse range of views, it does not fit neatly into Metagroup 1 or 2.

to water allocation systems. Further, submissions repeatedly emphasized the importance of protecting existing water rights to maintain industrial and economic activities:

> *(We are) able to optimize the water resources granted under its licences because of the certainty the current Water Act provides with respect to priority of allocation rights. A change … could amount to an expropriation, with significant implications for energy planning, electricity rates, and provincial revenue. (BC Hydro, Stage 1)*

In contrast, submissions in Metagroup 1 tended to emphasize other non-economic considerations, including respecting First Nations' rights, current and intergenerational equity, over-allocation, and improving environmental protection. Thus, these groups appear to be motivated to participate by a desire to change the existing system, rather than to protect existing rights for economic benefits.

5.4.3 Alignment of submitter positions with WSA policy outcomes

The results of the alignment factor analysis for the 26 policy areas are illustrated in Figure 5.5. Each square represents the degree of alignment between a particular submitter group's response and the WSA policy outcome for a particular policy area. How well submissions aligned to WSA legislation is indicated along a colour continuum. Alignment factors indicated in blue indicate that the majority of submitters desired a greater degree of regulation than delivered within the WSA. Mustard yellow indicates that the majority of submissions within a particular submitter category called for less or weaker regulation than is contained within the WSA. Grey squares indicate where submitter preferences were reflected by the WSA, and white squares show where no submissions were made regarding that policy area (no data). Within Figure 5.5, both submitter groups and policy areas are clustered according to alignment factor similarities; the dendrogram to the left illustrates similarities between submitter groups based on their alignment

factors. As observed in Figure 5.5, clustering of submitter groups according to alignment to the WSA results in the emergence of the same two broad submitter groups as observed when submitters are clustered according to their responses (Figure 5.4).

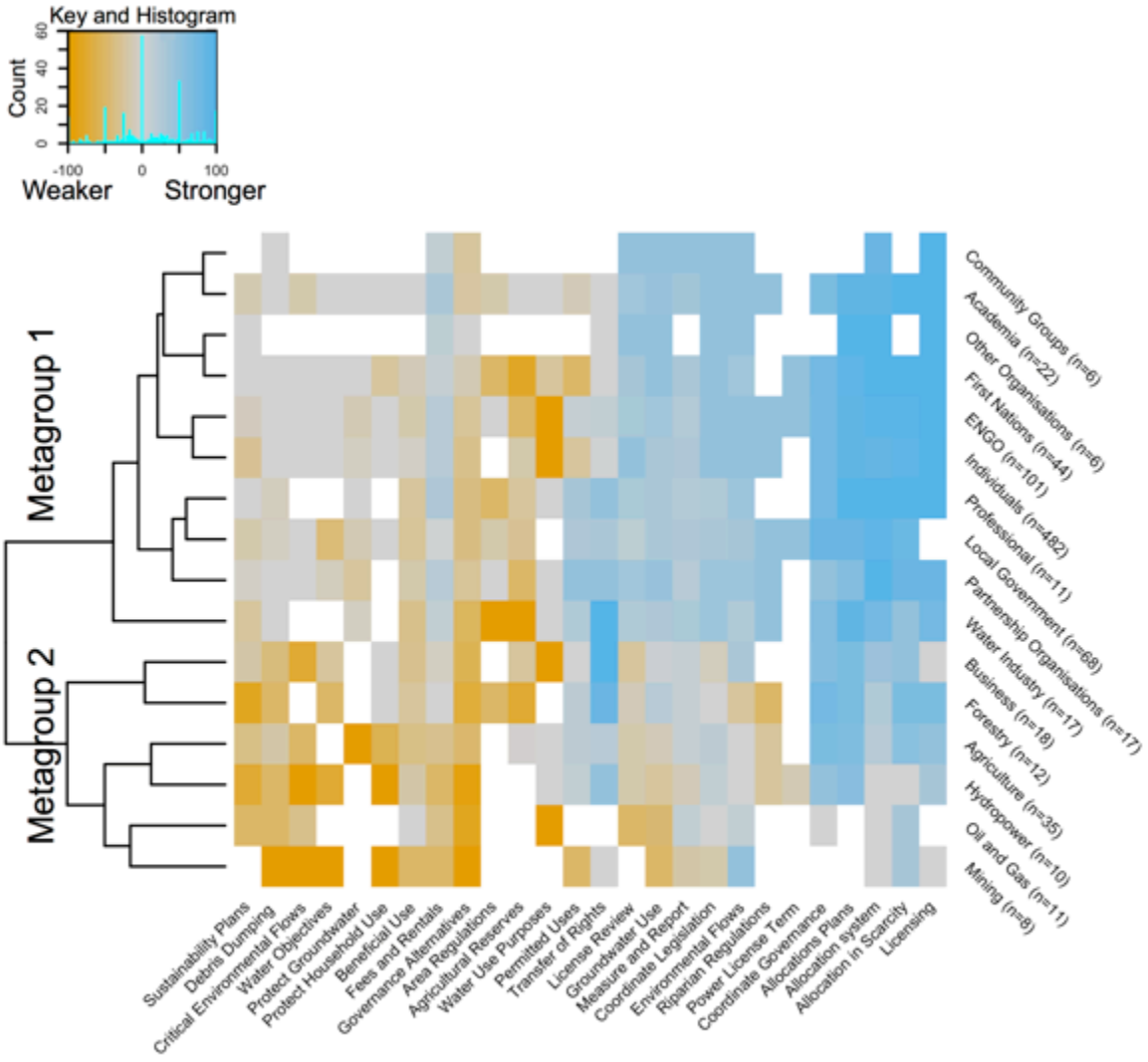

Figure 5.5 Alignment factors for each submitter group, describing the relationship between submitters' responses to consultation and WSA policy outcomes. Submitters (rows) and policy areas (columns) clustered by similarity.

The clustering of alignment values on the right of Figure 5.5 highlights a group of policy areas where the outcomes in the WSA aligned with the preferences of industry submitter groups (Metagroup 2). This cluster is comprised of policy areas related to water licencing and allocation, including 'allocation plans', 'allocation system', 'allocation in scarcity', and 'licensing'. Metagroup 2 advocated for weaker regulations that would maintain status quo approaches to licensing, ensuring the protection of existing water use rights. In contrast, Figure 5.5 shows a near-uniform desire among non-industry submitter groups (Metagroup 1) – who represent the majority of submitters – for more regulation of these policy areas than is contained within the WSA. Non-industry submitters tended to advocate for strong regulation to ensure the sustainability of water resources, protection of priority uses (e.g. household use), and instatement of more equitable systems of allocation. Allocating and regulating water resources, in effect outlining who gets water and how, is a core component of water policy – indeed, it was the impetus for the initial Act over 100 years ago. However, these policy areas are a critical site of conflict, shown by strong divisions between non-industry and industry submissions. The alignment between the licensing policies included in the WSA and Metagroup 2's policy preferences – rather than the majority of submitters – raises questions about how the consultation process fed into policy development, and thus the equity of policy outcomes.

To illustrate these possible divisions more clearly, we examined the response to the 'allocation system' policy area specifically across all submitter groups (Figure 5.6). This policy area captures submitter responses to the option to change the system of water allocation, raised during the first stage of consultation. Although the majority of submissions (82%) advocated to replace the existing 'First in Time, First in Right' (FITFIR) system of allocation (where water rights are based on historical precedence of licences), the WSA retained this contentious allocation

method. While the majority of submitters in industry groups[8] argued for the retention of FITFIR, submitters in non-industry groups tended to advocate for allocation systems based on water use priorities or proportional water licences, along with increased community involvement in water licensing decisions. First Nations and partnership/environmental organizations were particularly strong advocates for a change in allocation system, as FITFIR has not recognised the historical precedence of First Nation water uses, nor protected water for household and environmental uses. This strong divergence between the degree of regulation called for and observed thus speaks to the unequal rights and privileges held by different submitter groups. One interpretation of the decision to retain FITFIR within the WSA is therefore that consultation privileges the voices of existing rights holders (status quo), resulting in the entrenchment of existing rights and power relations, and the valuation of economic elite interests beyond those of the majority.

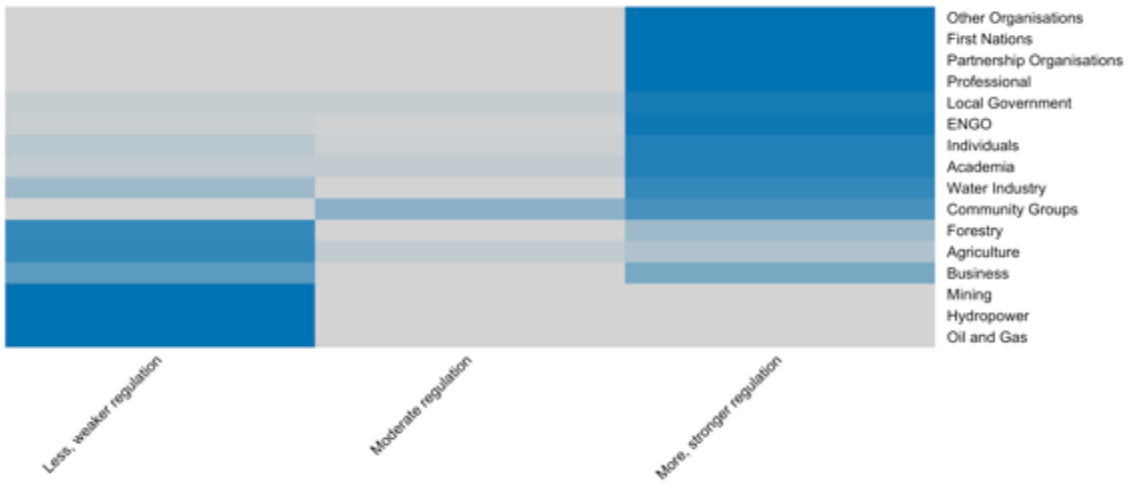

Figure 5.6 Percentage of submitter group advocating a particular level of regulation for the 'water allocation' policy area; dark blue = 100%, grey = 0%.

[8] Water Industry is a clear exception to this trend. As stated previously, this category represents a range of stakeholders with divergent perspectives.

Close examination of the alignment factors on the left of Figure 5.5 reveals a cluster of policy areas that were subject to strong regulation in the WSA, as was advocated by non-industry (Metagroup 1) submitters, and resisted by many industry (Metagroup 2) submitters. It is notable that several of these policies are conditional, only applying to certain (priority) areas or times when the ministry deems it necessary. For example, new policies enabling the protection of critical environmental flows and household uses will only protect minimal flows/use volumes when a significant water shortage has been declared. Similarly, a ministerial order is required to develop water sustainability plans for designated priority areas (e.g. areas of sustained scarcity), while alternative governance arrangements for specific areas must be negotiated with the ministry. Other policy areas that received strong regulation under the WSA (i.e. prohibition on debris dumping, groundwater protection) represent pre-existing regulations that have been strengthened with the WSA. In discussing these examples of 'strong' regulation in the WSA, we note that there is significant uncertainty regarding their final form, as this will be established through regulations currently under development.

In summary, our analysis of alignment factors illustrates that WSA policy outcomes align differently with perspectives of two primary groups: industry and non-industry submitters. While accounting for all elements that shaped the final contents of the WSA is beyond the scope of this paper, we do note that core elements of the WSA appear to align better with the level of regulation desired by a small subset of submitters (i.e. industry), particularly for critical policy areas that define water rights and allocation. In contrast, policy outcomes that align with non-industry preferences tend to be conditional and discretionary. The following section reflects further on these trends, discussing implications of public consultation processes in terms of aspirations for participatory democracy.

5.4.4 Assessing the impact of consultation

This chapter began by noting critiques of consultation's democratic potential, as well as the lack of systematic evaluation to assess consultation's democratic performance. In this study we sought to address this gap by quantitatively comparing participants' inputs with the policy outcomes of a submission-based consultation process. This section uses our analysis to address two questions: 1) does public consultation influence policymaking? and 2) whose input counts in policy?

In terms of broader considerations related to democracy, it is significant that the policy outcome aligned with the majority view for only half of the 26 policy areas addressed through the consultation. In this regard the policy impact of the consultation process is unclear. It appears that the majority public opinion shaped outcomes in only specific instances, while other considerations may have been paramount in other policy areas.

However, we note the large amount of government resources invested in consultation throughout the WAM, from the publication of submissions online, and the maintenance of an active blog, to the production of a summary of submissions highlighting controversial policy areas (Ministry of Environment 2010). Furthermore, policy documents published at each stage of the consultation process highlight that changes in policy did occur over the course of consultation. Most notably, the potential for transferring water rights and marketization approaches that appeared in initial policy proposals were removed in later iterations due to significant public opposition. As such, while our analysis does detail shortcomings, it would be difficult to discuss this process as merely tokenistic (Arnstein 1969; Innes and Booher 2004). Other evidence points against the idea that consultation served broader democratic aims of allowing the public input into decision-making. The retention of FITFIR as a system of licencing

is perhaps the most prominent instance where a contentious policy was retained despite strong opposition across the majority of submitters and submitter groups. We note that other motivations for governments to invest in consultation beyond 'informing policy' may be a factor within this context, including interests in informing the public, procuring broader knowledge, addressing conflicts, and promoting wider citizen participation (Fischer 2000). More critically, consultation in this instance may have served as a 'shadow referendum', allowing government to avoid policy change that might have spurred significant opposition from powerful (industry) groups (J. Carr 2012).

From our results, unexplained differences in alignment between submitter input and policy outcomes speak to opacity in the translation of public consultation into policy. Although motivations for undertaking public consultation were communicated at the outset, it is also the case that subsequent documents did not provide a clear account of how submissions were used to inform policy, or how other inputs shaped the ultimate composition of the Act. This lack of transparency regarding decision-making is a commonly noted issue in the literature (Halseth and Booth 2003). While governments may have good reasons for choosing particular policies over alternatives, the failure to clearly communicate policy rationales post-consultation reinforces perceptions that consultation is tokenistic, contributing to participation fatigue and citizen disengagement (Bickerstaff and Walker 2005; M. Murray, Fagan, and McCusker 2009). Systematic analyses of consultation outcomes, such as our own, may help to improve transparency and accountability by highlighting patterns of influence that warrant further explanation.

A key consideration we are only partially able to address is whether some submissions or submitters influenced policy outcomes more than others. Overall, our alignment factor analysis

suggests inequality in submitter leverage on policy outcomes. Specifically, the dominance of economic actors within submitter groups that aligned with contentious policy outcomes (especially key policies regarding water licensing, see Figures 5.5 and 5.6) lends weight to claims of elite access and influence on disputed policy developments. (J. Carr 2012; Gilens and Page 2014). Indeed, the suspicion that the final form of the WSA would favour elite interests was expressed in several submissions:

> *As much as the stated goals of the WSA include environmental protection, the industry-specific approach outlined in the WSA eases the approval of industrial water uses with potentially harmful social and environmental consequences. A dominant purpose of the WSA is to streamline water use and access by resource industries, such as mining and oil and gas. (Union of BC Indian Chiefs, Stage 3)*

As such, our analysis provides further evidence that economic elites can have greater influence on key policy development than the general public, even when an open participatory process is undertaken (Parkins and Sinclair 2014).

The indication of elite influence in our results raises yet other questions about how such influence occurs, especially when participatory processes are as heavily resourced and carefully undertaken as the WAM. We echo J. Carr (2012), where the socio-political context of consultation, its design, and strategies employed by interest groups can reinforce elite influence, even within an open consultation process. In particular, rights-based arguments made by industry submitters, which emphasized economic and legal rationales for protecting existing entitlements, served to embed existing power relations within consultation. Additionally, several submissions from prominent industry groups mentioned consultation beyond the process open to all citizens. For example, formal submissions from Nestle Waters Canada mention discussions with high-level members of the Ministry of Environment, suggesting that they were provided

additional spaces to voice their opinions. On this point, it is worth reiterating that submitter groups whose perspective aligned with controversial policy outcomes tended to have fewer submissions than those who argued for alternative policies (Figure 5.2). This could derive from perceptions among powerful stakeholders that their interests will be accounted for no matter their level of participation within open consultation, echoing broad concerns about the dominance of organized interests within participatory democratic processes (Gilens and Page 2014; Kaehne and Taylor 2015).

Our quantitative analysis of whose input 'counts' in public policy-making also shows that the practice of classification could influence how submitters' views are represented and accounted for. Consultation evaluations typically assess process representativeness according to socio-economic and interest group characteristics of participants, when compared to the general population (Rowe and Frewer 2000; Shipley and Utz 2012). However, our results highlight that representation is also a product of how participant views are made visible through the construction of submitter categories. As described by the Ministry of Environment (Ministry of Environment 2010, 2013) submissions were classified into categories based on 'submitters self-identifying as a representative of a particular group or organization'; submitters who did not self-identify were classified as 'individuals.' The Ministry then used these categories to quantitatively assess submitter responses to the objectives and policy options proposed (as we have also done). While there is nothing inherently wrong with this approach, the classification submissions by submitter categories is inherently political, and should include understandings of how this affects representation of minority versus majority interests.

By retaining the Ministry's classifications in our analysis, we highlight the limited alignment between submitter input and policy outcomes, revealing concerns about the WAM

classification and counting process. First, categories created by ministry officials to capture the diversity of submitters were somewhat arbitrary, and at times grouped submitters who would not necessarily have identified with specific categories. For example, a citizen who used his employer's address as a contact address was classified as a 'business' submission. In such cases, it was not clear whether the submitter intended to represent an organization, or had the authority to do so. Second, the creation of categories can obscure the diversity of views contained within the group by reducing them to a series of discrete perspectives. For example, the category 'water industry' represents a wide range of submitters, from provincial water associations (who favoured strong regulation to promote sustainable water use), to water retailers (who supported the retention of existing regulations). Neither perspective is clearly visible when such opposing views are combined within one category, which contributed to the weak relationship of 'water industry' to both metagroups (as is evident in Figures 5.4-5.6). Third, we noted significant variability in the number of submissions per category, from six submissions from 'community groups', to 300 'individual form submissions' (see Figure 5.2). This variability in submissions is hidden when submitter positions are compared across categories (such as in Figures 5.4 and 5.5). Thus, classification according to submitter group has the effect of equalizing inputs across each category, effectively undermining the significance of a large number of responses from a particular group. Given the previously mentioned low number of submissions from many industry groups, the category-based analysis may have elevated their influence on decision-making. Fourth, a related concern voiced by ministry analysts is how to weigh submissions representing organizations (where one submission professes to speak for many people, e.g. an NGO or entire First Nation) against those representing individuals (Ministry of Environment 2010). All of these concerns speak to the very political nature of classification and counting, and

the effects of representational choices, including those that affected our own study design and results.

5.5 Conclusion

As public consultation is increasingly ubiquitous and mandated, and given criticisms regarding the outcomes and transparency of consultation (Arnstein 1969; Innes and Booher 2004), it is critical to enrich frameworks that evaluate the equity and influence of consultation in policy-making. This study utilized a mixed methods approach to critically analyse both the process and outcomes of the multi-stage public consultation undertaken during British Columbia's WAM, according to principles of democracy. Our novel mixed methods approach enabled us to parse patterns of possible submitter influence by mapping submissions against policy outcomes, while also exploring how influence related to process design and the wider political-economic context. Our findings highlight the uncertain influence of consultation on policy-making, as well as the possibility of elite influence. We therefore argue that greater analysis of consultation alongside policy outcomes is necessary to both examine possible inequities within consultation, and to hold governments accountable for policy decisions. Such evaluations are especially necessary as consultation becomes increasingly institutionalized as a means of participatory democracy (Shipley and Utz 2012; Kaehne and Taylor 2015).

Our quantitative analysis of submissions on the WAM revealed two distinct clusters in submitter groups' policy preferences. Industry submitters were more likely than non-industry submitters to state a desire for less/weaker regulation – views that tended to align with WSA outcomes on contentious policy issues such as water allocation. The emergence of these clusters and related patterns in policy alignment raise questions about how submitter voices are

accounted within consultation, and whether such processes serve to counter or reinforce existing power dynamics. Qualitative analysis of submissions revealed that constraints in timing and resourcing of consultation, as well as limited policy information, served to constrain public input into the Act's development; this contrasted with access claimed by certain industry stakeholders in their submissions. In the Canadian context, the real or perceived entrenchment of certain interests over others is especially problematic given the government's constitutional responsibility to consult and accommodate First Nations, and the unresolved nature of their water rights.

In the spirit of reflexive critique, as outlined by Fischer (2016), our study draws attention to the assumptions and forms of democracy underlying the practice of consultation. Our analysis of whose input count raises the issue of whose input should count, and what form of democracy this embodies. Public participation processes are frequently undergirded by an assumption of majoritarian democracy, where the majority or 'consensus' view is expected to inform policy (e.g., Gilens and Page 2014; Parkins and Sinclair 2014). However, Catt and Murphy (2003), Cornwall (2004), Cornwall (2008), and Patten (2000) all highlight that majoritarian processes can both reinforce existing power dynamics and inequalities, and fail to address issues specific to minority and marginalized groups. Our study further demonstrates that diversity within interest groups (as enacted through the creation of stakeholder categories) can enhance the influence of economic elites at the expense of more marginalized interests (Gilens and Page 2014). There are lingering questions about how to engage such groups in consultation processes, how to address specific rights and inequalities, and whether in some instances marginalized groups should have greater influence on decision-making; such questions are particularly critical, given the clear failures with respect to the duty to consult and accommodate First Nations.

Furthermore, our study highlighted analytical practices as a key site of democracy and accountability within consultation. Specifically, practices of 'counting' submitter input were complicated by variability in submitter types, including organizations, individuals, and form submitters. It is clear that different approaches to counting and/or weighting these submissions would deliver different outcomes for interest groups' influence on decision-making. The post-hoc classification of submitters into interest groups further obscured quantification of majority and minority views by implicitly equalizing the input of these groups. These findings highlight the representational effects of our analytical practices; in this case, the question of whose input counts is tightly connected to how input is counted.

Our study indicates that evaluation of consultation must be informed by examination of the power relations implicit in participation. To the extent possible, it is important that studies of participatory democracy must be attentive to the outcomes of policy decisions for different groups, with particularly focus on whether outcomes address or reinforce existing inequalities (Cornwall 2008). This study makes a modest contribution towards such analysis by providing a way to parse submitter input and analyze its alignment with policy outcomes, revealing patterns that can then be interrogated through further research. Such analyses of 'outcome equality' are likely to be most effective when undertaken in conjunction with critical interpretative analysis of the consultation process within its wider socio-political context.

Chapter 6: Conclusion

This thesis presents an interdisciplinary examination of water quality in the context of societal participation in the science that characterizes anthropogenic impacts, as well as the policy that determines admissible human uses. It critically considers issues of water quality, science and policy through the effect of human impacts on the biogeochemical cycling of aquatic dissolved organic carbon (Chapters 2-4), and public participation in water quality monitoring and water-relevant policy (Chapters 4-5).

The first section of this concluding chapter presents specific findings, followed by implications for the state of knowledge referenced within each chapter. The second section draws on repercussions of this work more generally, parsing ramifications for future work related to each of the views present within this interdisciplinary examination of water management. Lastly, broader implications regarding such interdisciplinary work, especially dealing with critical and complex issues around the societally and ecologically ethical management of water resources, is discussed.

6.1 Summary of major findings and implications

Chapters 2 and 3 detail the implementation and results of a multi-year study regarding how forests harvest affects biogeochemical and hydrologic cycling within a small headwater catchment. Chapter 4 details the use of citizen science to investigate dissolved organic matter concentration and qualities within a broader span of catchments, describing broad lessons learned regarding the enactment of citizen science within water quality management. Chapter 5 examines citizen participation within the formation of the Water Sustainability Act (WSA, 2014), the defining piece of legislation defining water rights and uses within British Columbia,

relating to the second theme of citizen engagement. The main findings and implications for future research within each chapter are explored within this section.

Chapter 2 presented technical details regarding the deployment of in situ water quality monitoring within a remote, forested headwater catchment. This includes power and communication systems, challenges of setting up sophisticated sensors within remote locations, and how issues of communication and power provision can make data loss a continual challenge. Despite these concerns, this chapter also explores the potential for interconnected in situ sensor networks. As compared to traditional grab sampling campaigns for monitoring aspects of water chemistry, using in situ sensors (such as the absorbance sensor within our study), can provide data regarding water quality dynamics at a much greater time resolution. This time resolution allows for the observation of DOC dynamics that occur on a shorter timescales. Data gained at higher time resolution also enables the accurate calculation of DOC fluxes; increasing the time between measurements can miss key dynamics, can significantly underestimate the calculated flux of DOC exported through stream ecosystems.

Chapter 3 presents results gained from the monitoring station described in Chapter 2. The overarching research question regarding how forest harvest affects DOC quality and concentration was broken into three specific questions: 1) how forest harvest affects in-stream DOC concentration and flux; 2) the effect of forest harvest on DOC characteristics within the stream; and 3) what such changes mean in terms of mechanisms (biogeochemical and hydrologic) driving stream DOC. This study is one of the longest examples of in situ DOC monitoring currently reported, as well as one of the first to use this methodology towards investigating the effect of specific disturbances, such as forest harvest.

Firstly, forest harvest significantly increased DOC concentration and flux within the stream in the post-harvest period relative to the pre-harvest period. DOC concentrations within the stream were significantly greater for most months during the post-harvest period (save for the dry summer months), likely driven by increased connections between DOC rich surficial riparian soils to the stream during periods of high precipitation and discharge. This connection is also supported by changes in the type of DOC within the stream after harvest, which tended to be more aromatic and terrestrial-plant like post-harvest relative to before harvest (according to both in situ and discrete measurements of streamwater DOC absorbance and fluorescence). During the drier summer months, the stream within the post-harvest period exhibited lower concentrations of DOC relative to the pre-harvest period. DOC in the stream during the summertime in the post-harvest period also tended to be more protein-like in character, both of which suggests that flowpaths within deeper soil layers contribute to streamflow in the post-harvest summer period relative to the summer before harvest. Sources of terrestrial DOC were confirmed by examining trends in concentration and characteristics of both soil pore water and extractable DOC with riparian soil depth (Appendix C).

Chapter 4 examines the use of citizen science as a means of engaging the public in water quality research. Specifically, we used a citizen science campaign to gather data regarding how human activities affect DOC characteristics. This study used the same methods explored within Chapters 2 and 3 to investigate DOC concentration and characteristics, but within a wider range of catchments. Vignettes regarding the context of citizen collection were used to explore six specific lessons learned; these lessons included the identification, criteria and contextualization of 'outlier' data points, how citizens might interpret data given contextual knowledge, and the insertion of interests beyond primary research goals when involving citizens and citizen-led

community groups. This chapter highlights the necessity of considering the motivations, actions and outcomes for citizens involved in this promising form of societal engagement within water sciences.

Chapter 5 used a mixed methods approach to examine the citizen consultation process, and its relationship to resulting policy, using the reformation of British Columbia's Water Sustainability Act (WSA) as a case study. Quantitative analysis was used to parse what was expressed during the consultation process (specifically, the desire for more or less regulation, or the policy status quo), according to stakeholder group defined by the Province during its own process accounting. This was quantitatively compared to what was contained within the WSA in order to reveal policy areas in which other mechanisms, such as elite influence, could have had more leverage than public consultation. Qualitative analysis was used to elucidate main themes within the consultation process to further explore contentious policy areas identified by the quantitative analysis, as well as general response to the process itself. Two groups of stakeholders were identified through statistical clustering of submitter responses, both according to what stakeholders wanted, as well as alignment to the contents of the final Act. One of these clusters was composed predominately of industry-related stakeholder groups. The possibility for uneven influence of economic interest on policy outcomes was identified for contentious policy issues (such as those defining water allocation), in which the contents of the final Act appeared to align more strongly with these economic actors. Such work contributes to existing scholarship regarding consultative approaches by providing a mixed-method approach that spans both the process of consultation, as well as policy outcomes. Assessing outcomes alongside process allows for critical analyses of how consultation is used towards policy decisions. This helps define possibilities for uneven influence on decision-making, despite the aims for participatory

democracy that underlines commonly expressed motivations for implementing public participation within policy-making.

6.2 Implications

This section examines the broad implications uncovered within this work, - as well as connotations for future research - within the two themes that tie the work together. Finally, this thesis culminates by examining the utility of investigating complex issues, such as those around water sciences and intersections with society, through multiple lenses and disciplines.

6.2.1 Theme 1: Organic matter and biogeochemical cycling

The first theme pertains to how human activity and changes to land use affect biogeochemical cycles of carbon within coupled terrestrial-aquatic systems, specifically expressed through water quality. This theme is explored through both a detailed examination of how forest harvest affects DOC dynamics within a headwater stream (Chapters 2 and 3) as well as the use of citizen science to explore DOC conditions within a multitude of different catchments (Chapter 4). As human activities like forest harvest can impact the mechanisms and delivery of DOC to surface waters (as shown within our own work), this raises questions regarding what the ecological implications for such changes are. Lastly, the implications, potential, and critical areas for future research as regarding the use of spectrophotometric methods to outline DOC characteristics are discussed, including the promise of such methods within citizen science.

6.2.1.1 If stream DOC is increased upon forest harvest, what are the implications for stream health?

Ways of minimizing water quality impairments are critical to ecologically sustainable forest harvest operations, given their prevalence and economic importance at both the local and provincial scale within this particular context. The importance of water quality as a vital

ecosystem service has been widely investigated specifically within the boreal forest context, given the prevalence of forest harvest activities within this globally dominant and massive ecosystem. This includes managing stream DOC concentrations following harvest. The most sensitive managerial strategy towards managing DOC concentration is controlling harvest area. Previous studies have shown that catchments have a 'critical harvest area'; when this threshold is passed, downstream water quality may be threatened through heightened concentrations of DOC (Schelker et al. 2014). Managerial practices such as limiting harvest area are less widely encountered within the Pacific Northwest relative to measures such as riparian setbacks, which are meant to reduce sediment loading and erosion into streams. Such measures are likely to be less effective at mitigating effects on DOC, given the contribution of landscape units within the watershed that are hydrologically connected to the stream towards in-stream DOC conditions. Refining forest management practices to reduce the effects of harvest on DOC loading, including determining harvest area thresholds across different ecosystems, is critical given the important ecological roles that DOC plays within the aquatic environment. Additionally, future work could determine whether the timing of forest harvest operations affects stream DOC; this is given that most harvest within the Pacific Northwest occurs within the wet winter months when discharge and in-stream DOC concentrations also peak, due to fire hazard during the dry summer.

Given that forest harvest increases DOC concentrations within our context, future work should also address the persistence of such effects. Previous studies within the boreal forest suggest that harvest effects on DOC concentration can persist for at least 10 years (Schelker et al. 2014). Investigating the duration of such impacts requires long-term study, which can be difficult and expensive to implement and maintain (especially if using in situ sensors). To date, this study

presents the longest record of high frequency measurements of DOC measurements before and after forest harvest, demonstrating the need for continued study regarding long-term impacts.

6.2.1.2 Using spectrophotometric analysis of DOC characteristics: From scientists to citizens

Future research regarding impacts on DOC dynamics is aided by the continued progress in, and technical advancement of, spectrophotometric methods including in situ and discrete measurements of DOC absorbance and fluorescence (including evolving best practices regarding their deployment and long-term use). Despite their sensitivity and potential for in situ deployment, several questions remain regarding the future use of such methods to investigate DOC characteristics, catchment scale biogeochemical processes, and the impact of climatic and land use changes. Foremost are questions regarding the transferability of DOC metrics derived from absorbance and fluorescence between different catchments. All of the DOC compositional metrics calculated from absorbance and fluorescence spectra are proxies, rather than direct measurements of broad forms of DOC. Previous studies have questioned the direct molecular interpretation of PARAFAC components identified by Cory and McKnight (Macalady and Walton-Day 2009), demonstrating that it is difficult to concretely assign components from this model to specific forms of DOC (Strohmeier et al. 2013). Beyond the Cory McKnight model, components from site-specific models may change between sites. For example, fluorescence characteristics of the C1 component within our study was similar to previously identified humic-like components; the behaviour of this component within our study was more similar to protein-like fluorescence, making interpretation of fluorescence data complex. While PARAFAC components and indices continue to have worth as ‘statistical fingerprints’ (Strohmeier et al. 2013), the difficulty of concretely assigning characteristics to indices and components between

sites makes it necessary to investigate DOC sources from a variety of catchment-specific compartments. This significantly increases the complexity of monitoring studies using spectrophotometry. Omitting details regarding the chemical characteristics of proxies derived from fluorescence spectra also removes critical details regarding DOM character that are necessary to understand how catchment scale dynamics between biota, soil and hydrology are expressed within stream and river water quality.

In comparing the two spectrophotometric approaches, we echo previous studies that underline the sensitivity of fluorescence spectrophotometry, as well as the wealth of data and information regarding DOC quality present within the 3-D EEMs. Despite these advantages, the in situ nature of the absorbance probe used within this study provided high temporal resolution of DOC characteristics on timescales ranging from hourly to seasonal. In many cases, the ability of in situ monitoring to capture DOC dynamics on a short timescale offered insight into stream dynamics that was clearer than examining water samples using the more sensitive fluorescence technique. This included discrimination of diurnal cycles (Appendix B.1), as well as fine resolution of event dynamics ranging in time from hours to days (Chapter 3). Previous studies have attempted to capture such event-specific dynamics using automated sampling approaches that are triggered by rapid increases in discharge (for example, Inamdar et al. 2011). In contrast, we utilized a constant time sampling approach that providing less resolution regarding such dynamics. In our case, the higher time resolution of in situ absorbance appeared to offer clearer perspectives on DOC dynamics, belying the higher inherent sensitivity of data-rich fluorescence from discrete samples. This hints as to the potential of monitoring programs that integrate novel in situ fluorescence sensors that combine the sensitivity of this technique with the high temporal resolution necessary to capture the full dynamisms of in-stream DOC.

Despite the potential for in situ sensors, our experience shows that further work is necessary in order to provide methods that are robust enough to withstand the physical environment in which they must work, as well as to compensate for the complex streamwater matrix to provide accurate measurements. Firstly, in situ sensors must work within stream conditions that can be extreme – during times of high discharge, even small streams such as our own have ample power to transport large rocks, trees and other forms of detritus that can ruin expensive sensor systems. Sediment that is carried by streams outside of high discharge events can scour surfaces, which can obscure windows and have a large impact on light-based measurement methods (such as absorbance and fluorescence). Such windows can also be fouled by the growth of microbial films or by deposition of minerals, hampering measurement accuracy in a way that is difficult to correct for and requires regular maintenance (as described in Chapter 2). As discussed within Chapters 2 and 3, the co-absorbance of nitrate and metals such as iron and aluminum, which are prevalent within many catchments, can increase absorbance within the critical near UV range, inflating measurements of DOC proxies. Further work is necessary to develop robust methods of identifying and eventually correcting for instances in which such interferences are significant. Lastly, such systems must work within remote conditions, necessitating robust power and communication protocols that can be expensive and need regular maintenance; failures within such systems can lead to large periods of data loss, as we explored within Chapter 2. Thus, despite the potential of in situ systems, further work is necessary to ensure their accuracy and robustness within dynamic natural environments.

Another advantage related both to in situ as well as laboratory-based spectrophotometric methods is their speed, ease of use, and low cost per sample of analysis. These benefits make these methods uniquely suited for analysis associated with citizen science approaches, and

facilitated the implementation of our citizen science water quality monitoring program detailed in Chapter 4. However, we found that the ease of analysis belied the complexity of data produced. Indeed, even communicating the utility of exploring DOC dynamics from the perspective of both ecological and human health was necessary, as this is a less explored and thus more unfamiliar parameter for many groups and citizens interested or involved in water resource monitoring. Further explaining the outputs of these analyses – proxies that relate to broad classes of DOC, but are not a direct measure of concentration, with issues as previously described – was also a critical communication barrier for the project. This complexity emphasizes the need for well-designed information products alongside scientific protocols, to ensure that participants understand what is being examined, as well as how and what the scientific process will produce in terms of data outputs.

6.2.2 Theme 2: Participation within water sciences and related policy

The second theme within this work interrogates engagement and participation within water sciences and relevant policy that ultimately determines how humans impact water resources within British Columbia. The first iteration of participation involved an examination of citizen sciences as a means of engaging the public within water quality monitoring (Chapter 4). The second instance examined public consultation within policy defining water rights, allocation and uses in the province of British Columbia (Chapter 5).

Using citizen science within scientific monitoring and research (Chapter 4) is often motivated by benefits for the researcher (such as economically improving the breadth of data collection and analysis), as well as goals around engaging and educating citizens by direct inclusion within the scientific process. Much of the attention to date has rested on scientific

goals, primarily around the accuracy of citizen-collected data, with subsequent attention on societal engagement. However, much of the increased use of citizen science methods within policy-relevant sciences, such as environmental and water monitoring, springs specifically from the desire to increase engagement within scientific questions that pose a possible risk to society. However, as we found within our own experience of citizen science, participation within scientific questions is not always an inherently neutral activity for the participant. Specifically, we observed that citizens and citizen groups could both insert their own interests through their participation within an external science program, as well as interpret data arising from such programs in a way that reflects their own contextual experiences and knowledge. As much of the focus has been on the implementation and scientific validity of citizen science programs, the dimensions of social identity, and even whether participation can be a politically influenced act, warrants further investigation. This is especially true for scientific activities such as environmental monitoring campaigns, including water research, where the data produced could be relevant to downstream policy decisions.

Further research into the second iteration of participation, specifically investigating the use of consultation processes in relation to water-related policy, is also important, given that forms of consultation are increasingly institutionalized for decision-making around natural resources (such as water) within democratic contexts. This is partially motivated by benefits for decision-makers. This includes the potential to gain expertise from broad citizen involvement, especially when institutional capacity is limited, increasing the breadth of knowledge in a similar way as citizen science increases the breadth of data collection. Additional motivations for implementing such forms of participation within policy, including that related to natural resources like water, derives from aspirations for participatory democratic processes as a means

of equitable decision-making around potentially contentious and complex issues. Consultation can also thus be a means of improving the eventual acceptance of policy, derived from the notion that if people have the opportunity to have a say regarding policy, they will be more likely to accept it when implemented. However, common critiques of consultation in policy focus on whether such processes are tokenistic, in that they lack actual power over decision-making, and can thus lead to increased dissatisfaction with policy decisions and disenfranchisement with the political process. Our own work echoes certain of these critiques, finding that even well resourced processes can have significant potential for elite influence on key decisions, such as those related to water allocation.

What to make then of forays into engagement, specifically around water sciences and policy? Both are linked together by mirrored desired for increased engagement within the public, especially for issues related to resources such as water. These issues are complex, involve multiple stakeholders, and have the potential for controversy, given the importance of water to human and ecological life as well as economic activity. Is engagement in and opportunities for participation a 'good' thing? There is much potential for future research to explore such a multifaceted and complex question. Firstly, we note that in the case of citizen science, few studies have critically examined goals of engagement. Indeed, those studies that exist have shown that engagement through citizen science doesn't necessarily improve pro-environmental goals or knowledge regarding environmental issues. Within our own study, the majority of participation was from citizen groups already involved in community-based monitoring. Recruiting participants was a difficult and time consuming process, where it was challenging to reach beyond the small group of already educated, engaged citizens involved in groups involved in ecosystem monitoring. However, in terms of engaging the public in policy-making, we found

that such broad engagement doesn't necessarily result in transparently equitable policy outcomes. One example of this within the WSA context was the retention of First in Time, First in Right (FITFIR) as an allocation system, despite widespread opposition expressed within the consultation process. Certain of these broad issues with participation relate to improving the frameworks that support and determine best practices. Modern citizen science, for example, is a relatively nascent scientific concept, driven partially by demand for transparent scientific practices, and accountability to taxpayers for government-funded sciences. With increased use and acceptance of such practices will also come intensified focus on scientific protocols and statistical approaches for validating 'good data', alongside more emphasis on what citizen participants bring to scientific practices, and what they get (and should get) out of participation. In terms of policy, critical evaluations encompassing both the process and outcomes, such as our own, are necessary towards investigating the transparency and use of feedback gained in consultation directly alongside what is within the final policy. Such information can drive improved consultation methods, assumptions and practices, as well as provide a tangible means towards demanding increased transparency and accountability within policy decisions.

6.2.3 Interdisciplinary perspectives on water

This thesis presented a multi-lens investigation of several key aspects of water management, beginning by exploring water quality through the lens of biogeochemical carbon cycling, and broadening to examining how society intersects with the science and policy driving water issues through citizen science and consultation in public policy. Such an interdisciplinary approach reflects not only the complex and multifaceted nature of such issues, but also the specifically interdisciplinary academic environment in which this thesis is based. The opportunity afforded by such academic environments to pursue issues from a variety of lenses also provided the

opportunity to collaborate with people with diverse backgrounds. Such collaboration is key to supporting interdisciplinary work. Within this context, this included integrating societally relevant issues around participation alongside a very specific study of water quality. Integrating lenses of water quality and societal engagement provided the prospect of contextualizing water sciences in a way that is important towards understanding the societal relevance and utility of scientific research. Providing water monitoring alongside broader investigations of societal engagement, as well as the governance mechanisms responsible for determining uses, thus provides a means of examining the broad mechanisms needed to understand and confront some of the environmental challenges confronting water and water quality.

Bibliography

Abelson, J., Gauvin, F.P., 2006. *Assessing the impacts of public participation: Concepts, evidence and policy implications*. Ottawa: Canadian Policy Research Networks.

Aitkenhead-Peterson, J.A., McDowell, W.H., Neff, J.C., Stuart, E., Robert, L., 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters. *Aquatic ecosystems: interactivity of dissolved organic matter*, pp.26-70.

Akagi, J., Zsolnay, A., Bastida, F. 2007. Quantity and Spectroscopic Properties of Soil Dissolved Organic Matter (DOM) as a Function of Soil Sample Treatments: Air-Drying and Pre-Incubation. *Chemosphere, 69*(7): 1040–46. doi:10.1016/j.chemosphere.2007.04.036.

Alewell, C., Lischeid, G., Hell, U., Manderscheid, B., 2004. High Temporal Resolution of Ion Fluxes in Semi-Natural Ecosystems – Gain of Information or Waste of Resources? *Biogeochemist*ry, 69(1): 19–35. doi:10.1023/B:BIOG.0000031029.46798.7f.

Allen, J.L., 2004. The global environment: An emerging world view. *Environment*, *23*(1).

Andréassian, V., 2004. Waters and Forests: From Historical Controversy to Scientific Debate. *Journal of Hydrology*, *291*(1), pp.1-27.

Arnstein, S. R., 1969. A Ladder of Citizen Participation. *Journal of the American Institute of Planners*, *35*(4), pp.216-224. doi:10.1080/01944366908977225.

Ask, J., Karlsson, J., Jansson, M., 2012. Net Ecosystem Production in Clear-Water and Brown-Water Lakes. *Global Biogeochemical Cycles, 26*(1). doi:10.1029/2010GB003951/full.

Atkinson, R., Flint, J., 2001. Accessing Hidden and Hard-to-Reach Populations: Snowball Research Strategies. *Social Research Update,* 33.1: 1–4.

Austnes, K., Evans, C. D., Eliot-Laize, C., Naden, P. S., Old, G. S., 2009. Effects of Storm Events on Mobilisation and in-Stream Processing of Dissolved Organic Matter (DOM) in a Welsh Peatland Catchment. *Biogeochemistry*, 99(1-3): 157–73. doi:10.1007/s10533-009-9399-4.

Auyero, J., Swistun, D., 2008. The Social Production of Toxic Uncertainty. *American Sociological Review, 73*(3). SAGE Publications: 357–79. doi:10.1177/000312240807300301.

Ågren, A., Buffam, I., Jansson, M., 2007. Importance of Seasonality and Small Streams for the Landscape Regulation of Dissolved Organic Carbon Export. *Journal of Geophysical Research: Biogeosciences*, *112*(G3). doi:10.1029/2006JG000381/full.

Ågren, A., Haei, M., Kohler, S. J., Bishop, K., Laudon, H., 2010. Regulation of Stream Water Dissolved Organic Carbon (DOC) Concentrations During Snowmelt: the Role of Discharge, Winter Climate and Memory Effects. *Biogeosciences, 7*(9): 2901–13. doi:10.5194/bg-7-2901-2010.

Backer, L.C., Ashley, D.L., Bonin, M.A., Cardinali, F.L., KIESZAK, S.M., Wooten, J.V., 2000. Household exposures to drinking water disinfection by-products: whole blood trihalomethane levels. *Journal of Exposure Science and Environmental Epidemiology*, *10*(4), p.321.

Bahram, M., Bro, R., Stedmon, S., 2006. Handling of Rayleigh and Raman Scatter for PARAFAC Modeling of Fluorescence Data Using Interpolation. *Journal of Chemometric*s, 20(3-4), pp.99-105. doi:10.1002/cem.978/abstract.

Baker, A., 2001. Fluorescence Excitation−Emission Matrix Characterization of Some Sewage-Impacted Rivers. *Environmental Science & Technology, 35* (5): 948–53. doi:10.1021/es000177t.

Baker, A., Curry, M., 2004. Fluorescence of leachates from three contrasting landfills. *Water Research, 38,* 2605–2613

Bakker, K. ed., 2011. *Eau Canada: The future of Canada's water*. UBC Press. Vancouver, British Columbia, Canada

Bartlett, R., James, B., 1980. Studying Dried, Stored Soil Samples—Some Pitfalls. *Soil Science Society of America Journal, 44*(4), pp.721-724.

Battin, T.J., Kaplan, L.A., Findlay, S., Hopkinson, C.S., 2008. Biophysical Controls on Organic Carbon Fluxes in Fluvial Networks. *Nature Geoscience*, *1*(2), pp.95-100.

Beggs, K.M.H., Summers, R.S., 2011. Character and Chlorine Reactivity of Dissolved Organic Matter From a Mountain Pine Beetle Impacted Watershed. *Environmental Science & Technology 45*(13): 5717–24. doi:10.1021/es1042436.

Beierle, T.C., Cayford, J., 2002. *Democracy in Practice: Public Participation in Environmental Decisions. by Thomas C. Beierle and Jerry Cayford. Washington, DC: Resources for the Future Press, 2002.* Vol. 1. Washington, DC: Resources for the Future Press. doi:10.1017/S1537592703450159.

Bergamaschi, B.A., Fram, M.S., Kendall, C., Silva, S.R., 1999. Carbon Isotopic Constraints on the Contribution of Plant Material to the Natural Precursors of Trihalomethanes. *Organic Geochemistry*, *30*(8), pp.835-842.

Berggren, M., Laudon, H., Jansson, M., 2007. Landscape Regulation of Bacterial Growth Efficiency in Boreal Freshwaters. *Global Biogeochemical Cycles, 21*(4). doi:10.1029/2006GB002844.

Bernard, A., Carbonnelle, S., Nickmilder, M., de Burbure, C., 2005. Non-invasive biomarkers of pulmonary damage and inflammation: Application to children exposed to ozone and trichloramine. *Toxicology and Applied Pharmacology*, *206*(2), pp.185-190.

Bickerstaff, K., Walker, G., 2005. Shared Visions, Unholy Alliances: Power, Governance and Deliberative Processes in Local Transport Planning. *Urban Studie*s, *42*(12): 2123–44. doi:10.1080/00420980500332098.

Bieroza, M., Baker, A., Bridgeman, J., 2009. Relating Freshwater Organic Matter Fluorescence to Organic Carbon Removal Efficiency in Drinking Water Treatment.

Science of the Total Environment, 407(5): 1765–74. doi:10.1016/j.scitotenv.2008.11.013.

Bird, T.J., Bates, A.E., Lefcheck, J.S., Hill, N.A, Thomson, R.J, Edgar, G.J., Stuart-Smith, R.D., Pecl, G.T., 2014. Statistical Solutions for Error and Bias in Global Citizen Science Datasets. *Biological Conservation, 173*(May): 144–54. doi:10.1016/j.biocon.2013.07.037.

Bishop, K.H., Lundström, U.S., Giesler, R., 1993. Transfer of Organic C From Forest Soils to Surface Waters: Example From Northern Sweden. *Applied Geochemistry, 8*, pp.11-15.

Bishop, K., Buffam, I., Erlandsson, M., Fölster, J., 2008. Aqua Incognita: the Unknown Headwaters. *Hydrological Processes*, *22*(8), pp.1239-1242. doi:10.1002/hyp.7049/abstract.

Bishop, K., Seibert, J., Köhler, S., 2004. Resolving the Double Paradox of Rapidly Mobilized Old Water with Highly Variable Responses in Runoff Chemistry. *Hydrological Processes*, *18*(1), pp.185-189. doi:10.1002/hyp.5209/abstract.

Bishop, K., Allan, C., Bringmark, L., Garcia, E., Hellsten, S., Högbom, L., Johansson, K., Lomander, A., Meili, M., Munthe, J., Nilsson, M., 2009. The Effects of Forestry on Hg Bioaccumulation in Nemoral/Boreal Waters and Recommendations for Good Silvicultural Practice. *AMBIO: A Journal of the Human Environment*, *38*(7), pp.373-380.

Blackstock, K.L., Kelly, G.J., Horsey, B.L., 2007. Developing and Applying a Framework to Evaluate Participatory Research for Sustainability. *Ecological Economics*, *60*(4), pp.726-742.

Blough, N.V., Del Vecchio, R., 2002. Chromophoric DOM in the Coastal Environment-Chapter 10. doi:10.1029/2007JC004493/full.

Blough, N.V., Green, S.A., 1995. Spectroscopic characterization and remote sensing of non-living organic matter. *The Role of Non-living Organic Matter in the Earth's Carbon Cycle (RG Zepp and C. Sonntag, eds.), John Wiley & Sons Ltd*, pp.23-45.

Bonney, R., Ballard, H., Jordan, R., McCallie, E., Phillips, T., 2009. Public Participation in Scientific Research: Defining the Field and Assessing Its Potential for Informal Science Education. A CAISE Inquiry Group Report. *Online Submission*.

Bonney, R., Cooper, C.B., Dickinson, J., Kelling, S., Phillips, T., Rosenberg, K.V., Shirk, J., 2009. Citizen Science: a Developing Tool for Expanding Science Knowledge and Scientific Literacy. *BioScience,* 59(11). Oxford University Press: 977–84. doi:10.1525/bio.2009.59.11.9.

Bonter, D.N, Cooper, C.B., 2012. Data Validation in Citizen Science: a Case Study From Project FeederWatch. *Frontiers in Ecology and the Environment, 10*(6): 305–7. doi:10.1890/110273.

Bormann, F.H., Likens, G.E., 1994. *Pattern and Process in a Forested Ecosystem*. New York, New York: Springer-Verlag.

Bove, G.E., Rogerson, P.A., Vena, J.E., 2007. Case-control study of the effects of trihalomethanes on urinary bladder cancer risk. *Archives of Environmental & Occupational Health*, *62*(1), pp.39-47.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1995. Variation of dissolved organic carbon during snowmelt in soil and stream waters of two headwater catchments, Summit County, Colorado. *IAHS Publications-Series of Proceedings and Reports-Intern Assoc Hydrological Sciences*, *228*, pp.303-312.

Boyer, E.W., Hornberger, G.M., Bencala, K.E., 1996. Overview of a Simple Model Describing Variation of Dissolved Organic Carbon in an Upland Catchment. *Ecological Modelling*, *86*(2), pp.183-188

Boyer, J. N., Groffman, P.M., 1996. Bioavailability of Water Extractable Organic Carbon Fractions in Forest and Agricultural Soil Profiles. *Soil Biology and Biochemistry*, *28*(6), pp.783-790.

Braun, K., Schultz, S., 2009. '… A Certain Amount of Engineering Involved': Constructing the Public in Participatory Governance Arrangements. *Public Understanding of Science*. doi:10.1177/0963662509347814.

Breuer, L., Hiery, N., Kraft, P., Bach, M., Aubert, A.H., Frede, H.G., 2015. HydroCrowd: a Citizen Science Snapshot to Assess the Spatial Control of Nitrogen Solutes in Surface Waters. *Scientific Reports,* 5. Nature Publishing Group: 16503. doi:10.1038/srep16503.

Bro, R., 1997. PARAFAC. Tutorial and Applications. *Chemometrics and Intelligent Laboratory Systems*, *38*(2), pp.149-171.

Brossard, D., Lewenstein, B., Bonney, R., 2005. Scientific Knowledge and Attitude Change: the Impact of a Citizen Science Project. *International Journal of Science Education,* 27(9): 1099–1121. doi:10.1080/09500690500069483.

Brown, J., 2014. Evaluating Participatory Initiatives in South Africa. *SAGE Open*. doi:10.1177/2158244014531966.

Bu, X., Wang, L., Ma, W., Yu, X., McDowell, W. H., Ruan, H., 2010. Spectroscopic Characterization of Hot-Water Extractable Organic Matter From Soils Under Four Different Vegetation Types Along an Elevation Gradient in the Wuyi Mountains. *Geoderma*, *159*(1), pp.139-146.

Buchy, M., Hoverman, S., 2000. Understanding Public Participation in Forest Planning: a Review. *Forest Policy and Economics*, *1*(1), pp.15-25. doi:10.1016/S1389-9341(00)00006-X.

Buffam, I., Laudon, H., Seibert, J., Mörth, C.M., 2008. Spatial Heterogeneity of the Spring Flood Acid Pulse in a Boreal Stream Network. *Science of the Total Environment*, *407*(1), pp.708-722.

Burns, M.A., Barnard, H.R., Gabor, R.S., McKnight, D.M., Brooks, P.D., 2016. Dissolved Organic Matter Transport Reflects Hillslope to Stream Connectivity During Snowmelt in a Montane Catchment. *Water Resources Research,* 52(6): 4905–23. doi:10.1002/2015WR017878.

Buss, H.L., Bruns, M.A., Schultz, M.J., Moore, J., 2005. The Coupling of Biological Iron Cycling and Mineral Weathering During Saprolite Formation, Luquillo Mountains, Puerto Rico. *Geobiology*, *3*(4), pp.247-260. doi:10.1111/j.1472-4669.2006.00058.x/full.

Butman, D., Raymond, P.A., 2011. Significant Efflux of Carbon Dioxide From Streams and Rivers in the United States. *Nature Geoscience*, *4*(12), pp.839-842.

Buttle, J.M., Creed, I.F., Moore, R.D., 2005. Advances in Canadian Forest Hydrology, 1999-2003. *Hydrological Processes, 19*(1). John Wiley & Sons, Ltd.: 169–200. doi:10.1002/hyp.5773.

Buttle, J.M., Creed, I.F., Moore, R.D., 2009. Advances in Canadian Forest Hydrology, 2003-2007. *Canadian Water Resources Journal* 34 (2): 113–26. doi:10.4296/cwrj3402113.

Buytaert, W., Zulkafli, Z., Grainger, S., Acosta, L., Alemie, T.C., Bastiaensen, J., De Bièvre, B., Bhusal, J., Clark, J., Dewulf, A., Foggin, M., 2014. Citizen Science in Hydrology and Water Resources: Opportunities for Knowledge Generation, Ecosystem Service Management, and Sustainable Development. *Frontiers in Earth Science, 2*(26): 2–26.

Cantor, K.P., Lynch, C.F., Hildesheim, M., Dosemeci, M., Lubin, J., Alavanja, M., Craun, G., 1998. Drinking Water Source and Chlorination Byproducts I. Risk of Bladder Cancer. *Epidemiology*, *9*(1), pp.21-28.

Carpenter, S.R., Cole, J.J., Pace, M.L., Van de Bogert, M., Bade, D.L., Bastviken, D., Gille, C.M., Hodgson, J.R., Kitchell, J.F., Kritzberg, E.S., 2005. Ecosystem Subsidies: Terrestrial Support of Aquatic Food Webs From 13C Addition to Contrasting Lakes. *Ecology*, *86*(10), pp.2737-2750. doi:10.1890/04-1282/full.

Carr, G., Blöschl, G., Loucks, D.P., 2012. Evaluating Participation in Water Resource Management: A Review. *Water Resources Research 48*, no. W11401: 1-17. doi:10.1029/2011WR011662

Carr, J., 2012. Public Input/Elite Privilege: the Use of Participatory Planning to Reinforce Urban Geographies of Power in Seattle. *Urban Geography*, *33*(3), pp.420-441. doi:10.2747/0272-3638.33.3.420.

Carton, L., Ache, P., 2017. Citizen-sensor-networks to confront government decision-makers: Two lessons from the Netherlands. *Journal of Environmental Management, 196,* 234-251

Carvalho, A., Pinto-Coelho, Z., Seixas, E., 2016. Listening to the Public – Enacting Power: Citizen Access, Standing and Influence in Public Participation Discourses. *Journal of Environmental Policy & Planning*, March, 1–19. doi:10.1080/1523908X.2016.1149772.

Catlin-Groves, C.L. 2012. The Citizen Science Landscape: From Volunteers to Citizen Sensors and Beyond. *International Journal of Zoology,* 2012 (2). Hindawi Publishing Corporation: 1–14. doi:10.1155/2012/349630.

Catt, H., Murphy, M., 2003. What Voice for the People? Categorising Methods of Public Consultation. *Australian Journal of Political Science, 38*(3): 407–21.

Chang, E.E., Chiang, P.C., Ko, Y.W., Lan, W.H., 2001. Characteristics of Organic

Precursors and Their Relationship with Disinfection by-Products. *Chemosphere*, *44*(5), pp.1231-1236.

Chantigny, M.H., 2003. Dissolved and Water-Extractable Organic Matter in Soils: a Review on the Influence of Land Use and Management Practices. *Geoderma,* 113(3-4): 357–80. doi:10.1016/S0016-7061(02)00370-1.

Cheeseman, G., Smith, H., 2001. Public Consultation or Political Choreography? The Howard Government's Quest for Community Views on Defence Policy. *Australian Journal of International Affairs*, *55*(1), pp.83-100. doi:10.1080/10357710120055094.

Chen, B., Coops, N.C., Black, T.A., 2011. Modeling to Discern Nitrogen Fertilization Impacts on Carbon Sequestration in a Pacific Northwest Douglas-Fir Forest in the First-Postfertilization Year. *Global Change Biology*, *17*(3), pp.1442-1460. doi:10.1111/j.1365-2486.2010.02298.x/full.

Chen, Y, Senesi, N., Schnitzer, M., 1977. Information Provided on Humic Substances by E4/E6 Ratios. *Soil Science Cociety of America Journal*, *41*(2), pp.352-358.

Chow, C., Fabris, R. Drikas, M., 2004. A rapid fractionation technique to characterise natural organic matter for the optimisation of water treatment processes. *Journal of Water Supply Research and Technology-Aqua, 53*, 85–92

Coble, P.G., 1996. Characterization of Marine and Terrestrial DOM in Seawater Using Excitation-Emission Matrix Spectroscopy. *Marine Chemistry*, *51*(4), pp.325-346. doi:10.1016/0304-4203(95)00062-3.

Coble, P.G., 2007. Marine Optical Biogeochemistry: the Chemistry of Ocean Color. *Chemical Reviews*, *107*(2), pp.402-418 doi:10.1021/cr050350.

Cole, J.J., Carpenter, S.R., Kitchell, J.F., 2002. Pathways of Organic Carbon Utilization in Small Lakes: Results From a Whole-Lake 13C Addition and Coupled Model. *Limnology and Oceanography*, *47*(6), pp.1664-1675. doi:10.4319/lo.2002.47.6.1664/full.

Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., Melack, J., 2007. Plumbing the Global Carbon Cycle: Integrating Inland Waters Into the Terrestrial Carbon Budget. *Ecosystems, 10*(1): 172–85. doi:10.1007/s10021-006-9013-8.

Coleman, S., 2004. Connecting Parliament to the Public via the Internet: Two Case Studies of Online Consultations. *Information, Communication & Society*, *7*(1), pp.1-22. doi:10.1080/1369118042000208870.

Conrad, C.T, Daoust, T., 2008. Community-Based Monitoring Frameworks: Increasing the Effectiveness of Environmental Stewardship. *Environmental Management, 41*(3). Springer-Verlag: 358–66. doi:10.1007/s00267-007-9042-x.

Conrad, C.C., Hilchey, K.G., 2010. A Review of Citizen Science and Community-Based Environmental Monitoring: Issues and Opportunities. *Environmental Monitoring and Assessment, 176*(1-4): 273–91. doi:10.1007/s10661-010-1582-5.

Cornwall, A., 2004. Introduction: New Democratic Spaces? the Politics and Dynamics of

Institutionalised Participation. *iDS Bulletin*. doi:10.1111/j.1759-5436.2004.tb00115.x.

Cornwall, A., 2008. Unpacking 'Participation': Models, Meanings and Practices. *Community Development Journal*, *43*(3), pp.269-283. doi:10.1093/cdj/bsn010.

Cornwell, M.L., Campbell, L.M., 2012. Co-Producing Conservation and Knowledge: Citizen-Based Sea Turtle Monitoring in North Carolina, USA. *Social Studies of Science, 42*(1). SAGE Publications: 101–20. doi:10.1177/0306312711430440.

Corvasce, M., Zsolnay, A., D'Orazio, V., Lopez, R., Miano, T.M., 2006. Characterization of Water Extractable Organic Matter in a Deep Soil Profile. *Chemosphere, 62*(10): 1583–90. doi:10.1016/j.chemosphere.2005.07.065.

Cory, N., Buffam, I., Laudon, H., Köhler, S., Bishop, K., 2006. Landscape Control of Stream Water Aluminum in a Boreal Catchment During Spring Flood. *Environmental Science & Technology, 40*(11): 3494–3500. doi:10.1021/es0523183.

Cory, R.M., McKnight, D.M., 2005. Fluorescence Spectroscopy Reveals Ubiquitous Presence of Oxidized and Reduced Quinones in Dissolved Organic Matter. *Environmental Science & Technology, 39*(21): 8142–49. doi:10.1021/es0506962.

Cory, R.M., McKnight, D.M., Chin, Y.P., Miller, P., Jaros, C.L., 2007. Chemical Characteristics of Fulvic Acids From Arctic Surface Waters: Microbial Contributions and Photochemical Transformations. *Journal of Geophysical Research Biogeosciences, 112*(G4). doi:10.1029/2006JG000343.

Cory, R,M, Boyer, E.W., McKnight, D.M., 2011. Spectral Methods to Advance Understanding of Dissolved Organic Carbon Dynamics in Forested Catchments. In *Forest Hydrology and Biogeochemistry*, 216:117–35. Ecological Studies. Dordrecht: Springer Netherlands. doi:10.1007/978-94-007-1363-5_6.

Couvet, D., Jiguet, F., Julliard, R., Levrel, H., Teyssèdre, A., 2008. Enhancing Citizen Contributions to Biodiversity Science and Public Policy. *Interdisciplinary Science Reviews, 33*(1): 95–103. doi:10.1179/030801808X260031.

Covino, T., 2016. Hydrologic Connectivity as a Framework for Understanding Biogeochemical Flux Through Watersheds and Along Fluvial Networks. *Geomorphology*, September. doi:10.1016/j.geomorph.2016.09.030.

Crall, A.W., Jordan, R., Holfelder, K., Newman, G.J., Graham, J., Waller, D.M., 2013. The Impacts of an Invasive Species Citizen Science Training Program on Participant Attitudes, Behavior, and Science Literacy. *Public Understanding of Science, 22*(6). SAGE Publications: 745–64. doi:10.1177/0963662511434894.

Creed, I.F., Band, L.E., 1998. Export of Nitrogen From Catchments Within a Temperate Forest: Evidence for a Unifying Mechanism Regulated by Variable Source Area Dynamics. *Water Resources Research*, *34*(11), pp.3105-3120. doi:10.1029/98WR01924/full.

Cronje, R., Rohlinger, S., Crall, A., Newman, G., 2011. Does Participation in Citizen Science Improve Scientific Literacy? A Study to Compare Assessment Methods. *Applied Environmental Education & Communication, 10*(3): 135–45.

doi:10.1080/1533015X.2011.603611.

Culver, K., Howe, P., 2004. Calling All Citizens: the Challenges of Public Consultation. *Canadian Public Administration*, *47*(1), pp.52-75. doi:10.1111/j.1754-7121.2004.tb01970.x.

Cumberland, S.A, Baker, A., 2007. The Freshwater Dissolved Organic Matter Fluorescence–Total Organic Carbon Relationship. *Hydrological Processes, 21*(16). John Wiley & Sons, Ltd.: 2093–99. doi:10.1002/hyp.6371.

Danielsen, F., Jensen, P.M., Burgess, N.D., Altamirano, R., Alviola, P.A., Andrianandrasana, H., Brashares, J.S., Burton, A.C., Corpuz, N., Enghoff, M., Fjeldså, J., 2014. A Multicountry Assessment of Tropical Resource Monitoring by Local Communities. *BioScience, 64*(3). Oxford University Press: 236–51. doi:10.1093/biosci/biu001.

Day, J.C., Cantwell, M., 1998. Citizen Initiated River Basin Planning: the Salmon Watershed Example [Salmon River Watershed Round Table]. *Environments, 25.3*/3: 80.

De Haan, H., 1993. Solar UV-Light Penetration and Photodegradation of Humic Substances in Peaty Lake Water. *Limnology and Oceanography*, *38*(5), pp.1072-1076. doi:10.4319/lo.1993.38.5.1072/full.

De Haan, H., De Boer, T., 1987. Applicability of Light Absorbance and Fluorescence as Measures of Concentration and Molecular Size of Dissolved Organic Carbon in Humic Lake Tjeukemeer. *Water Research*, *21*(6), pp.731-734. doi:10.1016/0043-1354(87)90086-8.

Degens, E.T., Kempe, S., 1991. Biogeochemistry of Major World Rivers. SCOPE 42. *Scientific Committee on Problems of the Environment (SCOPE)*, p.356.

Del Vecchio, R., Blough, N.V., 2004. On the Origin of the Optical Properties of Humic Substances. *Environmental Science & Technology, 38*(14): 3885–91. doi:10.1021/es049912h.

Delaney, D.G., Sperling, C.D., Adams, C.S., Leung, B., 2007. Marine Invasive Species: Validation of Citizen Science and Implications for National Monitoring Networks. *Biological Invasions, 10*(1): 117–28. doi:10.1007/s10530-007-9114-0.

Determann, S., Reuter, R., Wagner, P., Willkomm, R., 1994. Fluorescent Matter in the Eastern Atlantic Ocean. Part 1: Method of Measurement and Near-Surface Distribution. *Deep Sea Research Part I: Oceanographic Research Papers*, *41*(4), pp.659-675

Devictor, V., Whittaker, R.J., Beltrame, C., 2010. Beyond Scarcity: Citizen Science Programmes as Useful Tools for Conservation Biogeography. *Diversity and Distributions, 16*(3). Blackwell Publishing Ltd: 354–62. doi:10.1111/j.1472-4642.2009.00615.x.

Dinsmore, K.J., Billett, M.F., Skiba, U.M., Rees, R.M., Drewer, J., Helfter, C., 2010. Role of the Aquatic Pathway in the Carbon and Greenhouse Gas Budgets of a Peatland Catchment. *Deep Sea Research Part I: Oceanographic Research Papers*, *41*(4), pp.659-675. doi:10.1111/j.1365-2486.2009.02119.x/full.

Dittman, J.A., Shanley, J.B., Driscoll, C.T., Aiken, G.R., Chalmers, A.T., Towse, J.E., Selvendiran, P., 2010. Mercury Dynamics in Relation to Dissolved Organic Carbon Concentration and Quality During High Flow Events in Three Northeastern US Streams. *Water Resources Research*, *46*(7). doi:10.1029/2009WR008351/full.

Driscoll, C.T., Fuller, R.D., 1988. Longitudinal Variations in Trace Metal Concentrations in a Northern Forested Ecosystem. *Journal of Environmental Quality*, *17*(1), pp.101-107.

Druschke, C.G., Seltzer, C.E., 2012. Failures of Engagement: Lessons Learned From a Citizen Science Pilot Study. *Applied Environmental Education & Communication, 11*(3-4): 178–88. doi:10.1080/1533015X.2012.777224.

"The Dublin Statement on Water and Sustainable Development." 1992. Paper presented at the International Conference on Water and the Environment, Dublin, January 31.

Eden, S., Bear, C., 2012. The Good, the Bad, and the Hands-on: Constructs of Public Participation, Anglers, and Lay Management of Water Environments. *Environment and Planning A*, *44*(5), pp.1200-1218. doi:10.1068/a4495.

Eilers, K.G., Debenport, S., Anderson, S., Fierer, N., 2012. Digging Deeper to Find Unique Microbial Communities: the Strong Effect of Depth on the Structure of Bacterial and Archaeal Communities in Soil. *Soil Biology and Biochemistry*, *50*, pp.58-65.

Emery, S.B., Mulder, H.A.J., Frewer, L.J., 2015. Maximizing the Policy Impacts of Public Engagement a European Study. *Science, Technology & Human Values*, *40*(3), pp.421-444. doi:10.1177/0162243914550319.

Evans, C.D., Monteith, D.T., Cooper, D.M., 2005. Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environmental Pollution, 137*, 55–71

Fellman, J.B., Hood, E., Edwards, R.T., 2009. Changes in the Concentration, Biodegradability, and Fluorescent Properties of Dissolved Organic Matter During Stormflows in Coastal Temperate Watersheds. *Journal of Geophysical Research: Biogeosciences*, *114*(G1). doi:10.1029/2008JG000790/full.

Fellman, J.B., Hood, E., Spencer, R.G., 2010. Fluorescence Spectroscopy Opens New Windows Into Dissolved Organic Matter Dynamics in Freshwater Ecosystems: a Review. *Limnology and Oceanography, 55*(6): 2452–62. doi:10.4319/lo.2010.55.6.2452.

Fellman, J.B., Hood, E., D'Amore, D.V., Edwards, R.T., White, D., 2009. Seasonal Changes in the Chemical Quality and Biodegradability of Dissolved Organic Matter Exported From Soils to Streams in Coastal Temperate Rainforest Watersheds. *Biogeochemistry, 95*(2-3): 277–93. doi:10.1007/s10533-009-9336-6.

Fest, E.P., Temminghoff, E.J.M., Comans, R.N.J., Van Riemsdijk, W.H., 2008. Partitioning of Organic Matter and Heavy Metals in a Sandy Soil: Effects of Extracting Solution, Solid to Liquid Ratio and pH. *Geoderma*, *146*(1), pp.66-74.

Findlay, S., Sinsabaugh, R.L., 2003. *Aquatic Ecosystems*. Academic Press.

Fischer, F., 2000. *Citizens, Experts, and the Environment: the Politics of Local Knowledge*.

Durham, North Carolina, USA: Duke University Press.

Fisher, S.G, Likens, G.E., 1973. Energy Flow in Bear Brook, New Hampshire: an Integrative Approach to Stream Ecosystem Metabolism. *Ecological Monographs*, *43*(4), pp.421-439. doi:10.2307/1942301/full.

Flanagin, A.J, Metzger, M.J., 2008. The Credibility of Volunteered Geographic Information. *GeoJournal,* 72 (3-4): 137–48. doi:10.1007/s10708-008-9188-y.

The Forest and Range Practices Act. 2002. S.B.C, ch. 69.

Fowler, A., Whyatt, J.D., Davies, G., Ellis, R., 2013. 2013. How Reliable Are Citizen-Derived Scientific Data? Assessing the Quality of Contrail Observations Made by the General Public. *Transactions in GIS,* 17.4: 488–506. doi:10.1111/tgis.12034.

Fischer, F., 2016. What Is Critical? Connecting the Policy Analysis to Political Critique. *Critical Policy Studies, 10*(1). Routledge: 95–98. doi:10.1080/19460171.2015.1129350.

Frank, H., Patrick, S., Peter, W., Hannes, F., 2000. Export of Dissolved Organic Carbon and Nitrogen From Gleysol Dominated Catchments–the Significance of Water Flow Paths. *Biogeochemistry, 50*(2): 137–61. doi:10.1023/A:1006398105953.

Frei, S., Lischeid, G., Fleckenstein, J.H., 2010. Effects of Micro-Topography on Surface–Subsurface Exchange and Runoff Generation in a Virtual Riparian Wetland—a Modeling Study. *Advances in Water Resources*, *33*(11), pp.1388-1401.

Fujii, Roger, Ranalli, A., Aiken, G.R., Bergamaschi, B.A., 1998. *Dissolved organic carbon concentrations and compositions, and trihalomethane formation potentials in waters from agricultural peat soils, Sacramento-San Joaquin Delta, California: Implications for drinking-water quality.* Water-Resources Investigations Report. U.S Geological Survey.

Gabor, R.S., Eilers, K., McKnight, D.M., Fierer, N., Anderson, S.P., 2014. From the Litter Layer to the Saprolite: Chemical Changes in Water-Soluble Soil Organic Matter and Their Correlation to Microbial Community Composition. *Soil Biology and Biochemistry*, *68*, pp.166-176.

Gabor, R.S., Burns, M.A., Lee, R.H., Elg, J.B., Kemper, C.J., Barnard, H.R., McKnight, D.M., 2015. Influence of Leaching Solution and Catchment Location on the Fluorescence of Water-Soluble Organic Matter. *Environmental Science & Technology*, *49*(7), pp.4425-4432. American Chemical Society. doi:10.1021/es504881t.

Gilens, M., Page, B.I., 2014. Testing Theories of American Politics: Elites, Interest Groups, and Average Citizens. *Perspectives on Politics, 12*(03). Cambridge University Press: 564–81. doi:10.1017/S1537592714001595.

Gilron, G., 2015. Aquatic Impact Assessment Burnaby Lake Coal Derailment Yale Subdivision Mile 122.7 Final Report. Prepared for CN Environmental.

Glaz, P., Gagné, J.P., Archambault, P., Sirois, P., Nozais, C., 2015. Impact of Forest Harvesting on Water Quality and Fluorescence Characteristics of Dissolved Organic Matter in Eastern Canadian Boreal Shield Lakes in Summer. *Biogeosciences, 12*(23).

Copernicus GmbH: 6999–7011. doi:10.5194/bg-12-6999-2015.

Government of Canada. 2011. *Aboriginal Consultation and Accommodation: Updated Guidelines for Federal Officials to Fulfill the Duty to Consult*. Ottawa: Department of Aboriginal Affairs and Northern Development Canada.

Graves, C.G., Matanoski, G.M., Tardiff, R.G., 2001. Weight of evidence for an association between adverse reproductive and developmental effects and exposure to disinfection by-products: a critical review. *Regulatory Toxicology and Pharmacology*, *34*(2), pp.103-124.

Green, S.A., Blough, N.V., 1994. Optical Absorption and Fluorescence Properties of Chromophoric Dissolved Organic Matter in Natural Waters. *Limnology and Oceanography, 39*(8): 1903–16. doi:10.4319/lo.1994.39.8.1903.

Greenwood, J.J.D., 2007. Citizens, Science and Bird Conservation. *Journal of Ornithology, 148*(1). Springer-Verlag: 77–124. doi:10.1007/s10336-007-0239-9.

Grigal, D.F., 2003. Mercury Sequestration in Forests and Peatlands: a Review. *Journal of Environment Quality, 32*(2): 393–405.

Guillemette, F., Plamondon, A.P., Prévost, M., Lévesque, D., 2005. Rainfall Generated Stormflow Response to Clearcutting a Boreal Forest: Peak Flow Comparison with 50 World-Wide Basin Studies. *Journal of Hydrology*, *302*(1), pp.137-153.

Haei, M., Öquist, M.G., Buffam, I., Ågren, A., Blomkvist, P., Bishop, K., Ottosson Löfvenius, M., Laudon, H., 2010. Cold Winter Soils Enhance Dissolved Organic Carbon Concentrations in Soil and Stream Water. *Geophysical Research Letters*, *37*(8). doi:10.1029/2010GL042821/full.

Haitzer, M., Aiken, G.R., Ryan, J.N., 2002. Binding of Mercury(II) to Dissolved Organic Matter: the Role of the Mercury-to-DOM Concentration Ratio. *Environmental Science & Technology, 36*(16). American Chemical Society: 3564–70. doi:10.1021/es025699i.

Halseth, G., Booth, A., 2003. What Works Well; What Needs Improvement: Lessons in Public Consultation From British Columbia's Resource Planning Processes. *Local Environment, 8*(4): 437–55. doi:10.1080/13549830306669.

Harris, L., Kleiber, D., Goldin, J., Darkwah, A., Morinville, C., 2016. Intersections of gender and water: comparative approaches to everyday gendered negotiations of water access in underserved areas of Accra, Ghana and Cape Town, South Africa. *Journal of Gender Studies*, 1-22. doi:10.1080/09589236.2016.1150819

Harrison, J.A., Matson, P.A., Fendorf, S.E., 2005. Effects of a Diel Oxygen Cycle on Nitrogen Transformations and Greenhouse Gas Emissions in a Eutrophied Subtropical Stream. *Aquatic Sciences, 67*(3): 308–15. doi:10.1007/s00027-005-0776-3.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., Mopper, K., 2008. Absorption Spectral Slopes and Slope Ratios as Indicators of Molecular Weight, Source, and Photobleaching of Chromophoric Dissolved Organic Matter. *Limnology and Oceanography, 53*(9): 955–69.

Henderson, R.K., Baker, A., Parsons, S.A., Jefferson, B., 2008. Characterisation of Algogenic Organic Matter Extracted From Cyanobacteria, Green Algae and Diatoms. *Water Research, 42*(13): 3435–45. doi:10.1016/j.watres.2007.10.032.

Her, N., Amy, G., Foss, D., Cho, J., 2002. Variations of molecular weight estimation by HP-size exclusion chromatography with UVA versus online DOC detection. *Environmental Science & Technology*, *36*(15), pp.3393-3399. doi:10.1021/es015649y

Hernes, P.J., Bergamaschi, B.A., Eckard, R.S., Spencer, R.G., 2009. Fluorescence-Based Proxies for Lignin in Freshwater Dissolved Organic Matter. *Journal of Geophysical Research: Biogeosciences*, *114*(G4). doi:10.1029/2009JG000938/full.

Hewlett, J.D., Hibbert, A.R., 1967. Factors Affecting the Response of Small Watersheds to Precipitation in Humid Areas. *Forest Hydrology*, *1*, pp.275-290.

Hilker, T., Hall, F.G., Coops, N.C., Lyapustin, A., Wang, Y., Nesic, Z., Grant, N., Black, T.A., Wulder, M.A., Kljun, N., Hopkinson, C., 2010. Remote Sensing of Photosynthetic Light-Use Efficiency Across Two Forested Biomes: Spatial Scaling. *Remote Sensing of Environment*, *114*(12), pp.2863-2874

Hinton, M.J., Schiff, S.L. and English, M.C., 1997. The Significance of Storms for the Concentration and Export of Dissolved Organic Carbon From Two Precambrian Shield Catchments. *Biogeochemistry, 36*(1): 67–88. doi:10.1023/A:1005779711821.

Hood, E., Williams, M.W., McKnight, D.M., 2005. Sources of Dissolved Organic Matter (DOM) in a Rocky Mountain Stream Using Chemical Fractionation and Stable Isotopes. *Biogeochemistry, 74*(2): 231–55. doi:10.1007/s10533-004-4322-5.

Hood, E., Gooseff, M.N., Johnson, S.L., 2006. Changes in the Character of Stream Water Dissolved Organic Carbon During Flushing in Three Small Watersheds, Oregon. *Journal of Geophysical Research, 111*(G1): G01007. doi:10.1029/2005JG000082.

Hope, D., Billett, M.F., Cresser, M.S., 1997. Exports of Organic Carbon in Two River Systems in NE Scotland. *Journal of Hydrology*, *193*(1), pp.61-82. doi:10.1016/S0022-1694(96)03150-2.

Hornbeck, J.W., Adams, M.B., Corbett, E.S., Verry, E.S., Lynch, J.A., 1993. Long-Term Impacts of Forest Treatments on Water Yield: a Summary for Northeastern USA. *Journal of Hydrology*, *150*(2), pp.323-344.

Hornberger, G.M., Bencala, K.E., McKnight, D.M., 1994. Hydrological Controls on Dissolved Organic Carbon During Snowmelt in the Snake River Near Montezuma, Colorado. *Biogeochemistry, 25*(3). Kluwer Academic Publishers: 147–65. doi:10.1007/BF00024390.

Hruška, J., Köhler, S., Laudon, H., Bishop, K., 2003. Is a Universal Model of Organic Acidity Possible: Comparison of the Acid/Base Properties of Dissolved Organic Carbon in the Boreal and Temperate Zones. *Environmental Science & Technology, 37*(9): 1726–30. doi:10.1021/es0201552.

Hu, C., Muller-Karger, F.E., Zepp, R.G., 2002. Absorbance, Absorption Coefficient, and Apparent Quantum Yield: a Comment on Common Ambiguity in the Use of These

Optical Concepts. *Limnology and Oceanography*, *47*(4), pp.1261-1267. doi:10.4319/lo.2002.47.4.1261.

Hudson, N., Baker, A., Reynolds, D., 2007. Fluorescence Analysis of Dissolved Organic Matter in Natural, Waste and Polluted Waters—a Review. *River Research and Applications*, *23*(6), John Wiley & Sons, Ltd.: 631–49. doi:10.1002/rra.1005.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J.M., Parlanti, E., 2009. Properties of Fluorescent Dissolved Organic Matter in the Gironde Estuary. *Organic Geochemistry*, *40*(6), pp.706-719. doi:10.1016/j.orggeochem.2009.03.002.

Humphreys, E.R., Black, T.A., Morgenstern, K., Cai, T., Drewitt, G.B., Nesic, Z., Trofymow, J.A., 2006. Carbon Dioxide Fluxes in Coastal Douglas-Fir Stands at Different Stages of Development After Clearcut Harvesting. *Agricultural and Forest Meteorology*, *140*(1), pp.6-22

Hynes, H.B.N., 1975. Edgardo Baldi Memorial Lecture. The Stream and Its Valley. *Verhandlungen der Internationalen Vereinigung fur theoretische und angewandte Limnologie*, *19*, pp.1-15.

Hyvönen, R., Olsson, B.A., Lundkvist, H., Staaf, H., 2000. Decomposition and Nutrient Release From Picea Abies (L.) Karst. and Pinus Sylvestris L. Logging Residues. *Forest Ecology and Management*, *126*(2), pp.97-112.

Inamdar, S.P., O'leary, N., Mitchell, M.J., Riley, J.T., 2006. The Impact of Storm Events on Solute Exports From a Glaciated Forested Watershed in Western New York, USA. *Hydrological Processes*, *20*(16), pp.3423-3439. doi:10.1002/hyp.6141/abstract.

Inamdar, S., Finger, N., Singh, S., Mitchell, M., Levia, D., Bais, H., Scott, D., McHale, P., 2011. Dissolved Organic Matter (DOM) Concentration and Quality in a Forested Mid-Atlantic Watershed, USA. *Biogeochemistry, 108*(1-3). Springer Netherlands: 55–76. doi:10.1007/s10533-011-9572-4.

Inamdar, S., Singh, S., Dutta, S., Levia, D., Mitchell, M., Scott, D., Bais, H., McHale, P., 2011. Fluorescence Characteristics and Sources of Dissolved Organic Matter for Stream Water During Storm Events in a Forested Mid-Atlantic Watershed. *Journal of Geophysical Research Biogeosciences, 116*(G3): G03043. doi:10.1029/2011JG001735.

Innes, J.E, Booher, D.E., 2004. Reframing Public Participation: Strategies for the 21st Century. *Planning Theory & Practice, 5*(4): 419–36. doi:10.1080/1464935042000293170.

Irwin, A., 1995. *Citizen Science: a Study of People, Expertise and Sustainable Development*. Psychology Press.

Ishii, S.K.L., Boyer, T.H., 2012. Behavior of Reoccurring PARAFAC Components in Fluorescent Dissolved Organic Matter in Natural and Engineered Systems: a Critical Review. *Environmental Science & Technology, 46*(4): 2006–17. doi:10.1021/es2043504.

Jaffé, R., McKnight, D., Maie, N., Cory, R., McDowell, W.H., Campbell, J.L., 2008. Spatial and Temporal Variations in DOM Composition in Ecosystems: the Importance of Long-Term Monitoring of Optical Properties. *Journal of Geophysical Research*

Biogeosciences, 113(G4): G04032. doi:10.1029/2008JG000683.

Jaffé, R, Cawley, K.M., Yamashita, Y., 2014. Applications of excitation emission matrix fluorescence with parallel factor analysis (EEM-PARAFAC) in assessing environmental dynamics of natural dissolved organic matter (DOM) in aquatic environments: a review. *Aquatic environments: a review. Advances in the physicochemical characterization of dissolved organic matter: impact on natural and engineered systems, Fernando Rosario-Ortiz, ed*, pp.27-73.

Jaffrain, J., Gérard, F., Meyer, M., Ranger, J., 2007. Assessing the Quality of Dissolved Organic Matter in Forest Soils Using Ultraviolet Absorption Spectrophotometry. *Soil Science Society of America Journal, 71*(6). Soil Science Society: 1851–58. doi:10.2136/sssaj2006.0202.

Jalbert, K., Kinchy, A.J., 2015. Sense and Influence: Environmental Monitoring Tools and the Power of Citizen Science. *Journal of Environmental Policy & Planning, 18*(3). Routledge: 379–97. doi:10.1080/1523908X.2015.1100985.

Jassal, R.S., Black, T.A., Chen, B., Roy, R., Nesic, Z., Spittlehouse, D.L., Trofymow, J.A., 2008. N_2O Emissions and Carbon Sequestration in a Nitrogen-Fertilized Douglas Fir Stand. *Journal of Geophysical Research: Biogeosciences*, *113*(G4). doi:10.1029/2008JG000764/full.

Jassal, R.S., Black, T.A., Cai, T., Ethier, G., Pepin, S., Brümmer, C., Nesic, Z., Spittlehouse, D.L., Trofymow, J.A., 2010. Impact of Nitrogen Fertilization on Carbon and Water Balances in a Chronosequence of Three Douglas-Fir Stands in the Pacific Northwest. *Agricultural and Forest Meteorology*, *150*(2), pp.208-218.

Jensen, E., Holliman, R., 2009. *Investigating Science Communication to Inform Science Outreach and Public Engagement*. Oxford University Press.

Jeong, J.J., Bartsch, S., Fleckenstein, J.H., Matzner, E., Tenhunen, J.D., Lee, S.D., Park, S.K., Park, J.H., 2012. Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements. *Journal of Geophysical Research: Biogeosciences*, *117*(G3). doi:10.1029/2012JG001999/full.

Jepson, P., Canney, S., 2001. Biodiversity Hotspots: Hot for What? *Global Ecology and Biogeography, 10*(3): 225–27. doi:10.1046/j.1466-822X.2001.00255.x.

Jepson, P., Canney, S., 2003. Values-Led Conservation. *Global Ecology and Biogeography, 12*(4). Blackwell Science Ltd: 271–74. doi:10.1046/j.1466-822X.2003.00019.x.

Joe, N., Bakker, K., Harris, L.M., 2016. Perspectives on the B.C. Water Sustainability Act: First Nations Respond to Water Governance Reform in British Columbia*. Program on Water Governance*. Vancouver.

Johnson, M.S., Billett, M.F., Dinsmore, K.J., Wallin, M., Dyson, K.E., Jassal, R.S., 2009. Direct and Continuous Measurement of Dissolved Carbon Dioxide in Freshwater Aquatic Systems-Method and Applications. *Ecohydrology, 3*(1). John Wiley & Sons, Ltd.: n/a–n/a. doi:10.1002/eco.95.

Jollymore, A., Johnson, M. S., Hawthorne, I., 2012. Submersible UV-Vis Spectroscopy for Quantifying Streamwater Organic Carbon Dynamics: Implementation and Challenges Before and After Forest Harvest in a Headwater Stream. *Sensors,* 12(4). 3798–3813. doi:10.3390/s120403798.

Jones, D. L., Willett, V.B., 2006. Experimental Evaluation of Methods to Quantify Dissolved Organic Nitrogen (DON) and Dissolved Organic Carbon (DOC) in Soil. *Soil Biology and Biochemistry*, *38*(5), pp.991-999.

Jordan, R.C., Gray, S.A., Howe, D.V., Brooks, W.R., Ehrenfeld, J.G., 2011. Knowledge gain and behavioral change in citizen-science programs. *Conservation Biology*, *25*(6), pp.1148-1154. doi: 10.1111/j.1523-1739.2011.01745.x

Kaehne, A, Taylor, H., 2015. Do Public Consultations Work? the Case of the Social Services and Well-Being (Wales) Bill. *Public Policy and Administration, 31*(1). SAGE Publications: 80–99. doi:10.1177/0952076715595676.

Kaiser, K, Kalbitz, K., 2012. Cycling Downwards–Dissolved Organic Matter in Soils. *Soil Biology and Biochemistry*, *52*, pp.29-32.

Kaiser, K, Zech, W., 1998. Soil Dissolved Organic Matter Sorption as Influenced by Organic and Sesquioxide Coatings and Sorbed Sulfate. *Soil Science Society of America Journal*, *62*(1), pp.129-136.

Kaiser, K., Kaupenjohann, M., Zech, W., 2001. Sorption of Dissolved Organic Carbon in Soils: Effects of Soil Sample Storage, Soil-to-Solution Ratio, and Temperature. *Geoderma*, *99*(3), pp.317-328.

Kaiser, K., Guggenberger, G., Haumaier, L., 2004. Changes in Dissolved Lignin-Derived Phenols, Neutral Sugars, Uronic Acids, and Amino Sugars with Depth in Forested Haplic Arenosols and Rendzic Leptosols. *Biogeochemistry, 70*(1): 135–51. doi:10.1023/B:BIOG.0000049340.77963.18.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the Dynamics of Dissolved Organic Matter in Soils: a Review. *Soil Science, 165*(4): 277.

Kalbitz, K., Geyer, W., Geyer, S., 1999. Spectroscopic Properties of Dissolved Humic Substances—a Reflection of Land Use History in a Fen Area. *Biogeochemistry*, *47*(2), pp.219-238. doi:10.1007/BF00994924.

Kaplan, L.A., Bott, T.L., 1982. Diel Fluctuations of DOC Generated by Algae in a Piedmont Stream. *Limnology and Oceanography*, *27*(6), pp.1091-1100. doi:10.4319/lo.1982.27.6.1091/full.

Kraus, T.E., Anderson, C.A., Morgenstern, K., Downing, B.D., Pellerin, B.A., Bergamaschi, B.A., 2010. Determining Sources of Dissolved Organic Carbon and Disinfection Byproduct Precursors to the McKenzie River, Oregon. *Journal of Environment Quality, 39*(6): 2100–2113. doi:10.2134/jeq2010.0030.

Kaushik, N.K.K., Hynes, H.B.N., 1971. Fate of the Dead Leaves That Fall Into Streams. *Archiv Fur Hydrobiologie*. Archiv fur Hydrobiologie.

Kendall, K.A., Shanley, J.B., McDonnell, J.J., 1999. A Hydrometric and Geochemical Approach to Test the Transmissivity Feedback Hypothesis During Snowmelt. *Journal of Hydrology*, *219*(3), pp.188-205.

Kindler, R., Siemens, J.A.N., Kaiser, K., Walmsley, D.C., Bernhofer, C., Buchmann, N., Cellier, P., Eugster, W., Gleixner, G., Grunwald, T., Heim, A., 2011. Dissolved Carbon Leaching From Soil Is a Crucial Component of the Net Ecosystem Carbon Balance. *Global Change Biology*, *17*(2), pp.1167-1185.

King, W.D., Marrett, L.D., 1996. Case-control study of bladder cancer and chlorination by-products in treated water (Ontario, Canada). *Cancer Causes & Control*, *7*(6), pp.596-604.

Kimmins, J.P., 2004. Forest ecology, a foundation for sustainable forest management and environmental ethics in forestry. 3rd ed. Prentice Hall, NJ.

Koch, N., 2013. Technologising the Opinion: Focus Groups, Performance and Free Speech. *Area, 45*(4): 411–18. doi:10.1111/area.12039.

Koehler, A.K., Murphy, K., Kiely, G., Sottocornola, M., 2009. Seasonal Variation of DOC Concentration and Annual Loss of DOC From an Atlantic Blanket Bog in South Western Ireland. *Biogeochemistry, 95*(2-3): 231–42. doi:10.1007/s10533-009-9333-9.

Köhler, S.J., Buffam, I., Seibert, J., Bishop, K.H., Laudon, H., 2009. Dynamics of Stream Water TOC Concentrations in a Boreal Headwater Catchment: Controlling Factors and Implications for Climate Scenarios. *Journal of Hydrology*, *373*(1), pp.44-56.

Kraus, N., Malmfors, T., Slovic, P., 1992. Intuitive Toxicology: Expert and Lay Judgments of Chemical Risks. *Risk Analysis, 12*(2) 215–32. doi:10.1111/j.1539-6924.1992.tb00669.x.

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*(NA): 157–79. doi:10.1139/A08-006.

Lamontagne, S., Carignan, R., D'Arcy, P., Prairie, Y.T., Paré, D., 2000. Element Export in Runoff From Eastern Canadian Boreal Shield Drainage Basins Following Forest Harvesting and Wildfires. *Canadian Journal of Fisheries and Aquatic Sciences, 57*, 118–28.

Larsen, L., Harvey, J., Skalak, K., Goodman, M., 2015. Fluorescence-Based Source Tracking of Organic Sediment in Restored and Unrestored Urban Streams. *Limnology and Oceanography*, *60*(4), pp.1439-1461. doi:10.1002/lno.10108/full.

Lasker, R D., 2003. Broadening Participation in Community Problem Solving: a Multidisciplinary Model to Support Collaborative Practice and Research. *Journal of Urban Health: Bulletin of the New York Academy of Medicine, 80*(1): 14–60. doi:10.1093/jurban/jtg014.

Laudon, H., Berggren, M., Ågren, A., Buffam, I., Bishop, K., Grabs, T., Jansson, M., Köhler, S., 2011. Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: the Role of Processes, Connectivity, and Scaling. *Ecosystems, 14*(6). Springer-

Verlag: 880–93. doi:10.1007/s10021-011-9452-8.

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): 381–86. doi:10.1579/0044-7447-38.7.381.

Laudon, H., Köhler, S., Buffam, I., 2004. Seasonal TOC Export From Seven Boreal Catchments in Northern Sweden. *Aquatic Sciences, 66*(2): 223–30. doi:10.1007/s00027-004-0700-2.

Lawaetz, A.J., Stedmon, C.A., 2009. Fluorescence Intensity Calibration Using the Raman Scatter Peak of Water. *Applied Spectroscopy, 63*(8): 936–40. doi:10.1366/000370209788964548.

Lee, B.S., Lajtha, K., 2016. Hydrologic and Forest Management Controls on Dissolved Organic Matter Characteristics in Headwater Streams of Old-Growth Forests in the Oregon Cascades. *Forest Ecology and Management*, *380*, pp.11-22. doi:10.1016/j.foreco.2016.08.029.

Leenheer, J A., 1981. Comprehensive Approach to Preparative Isolation and Fractionation of Dissolved Organic Carbon From Natural Waters and Wastewaters. *Environmental Science & Technology, 15*(5): 578–87. doi:10.1021/es00087a010.

Leenheer, J.A., Croué, J.P. 2003. Peer Reviewed: Characterizing Aquatic Dissolved Organic Matter. *Environmental Science & Technology, 37*(1). 18A–26A. doi:10.1021/es032333c.

Lehmann, J., Kleber, M., 2015. The Contentious Nature of Soil Organic Matter. *Nature*, November, 1–9. doi:10.1038/nature16069.

Li, J., Blatchley, E.I., 2007. Volatile disinfection byproduct formation resulting from chlorination of organic-nitrogen precursors in swimming pools. *Environmental Science and Technology-Columbus*, *41*(19), pp.6732-6739.

Ludwig, W., Probst, J.L., Kempe, S., 1996. Predicting the Oceanic Input of Organic Carbon by Continental Erosion. *Global Biogeochemical Cycles*, *10*(1), pp.23-41. doi:10.1029/95GB02925/full.

Macalady, D.L. and Walton-Day, K., 2009. New Light on a Dark Subject: on the Use of Fluorescence Data to Deduce Redox States of Natural Organic Matter (NOM). *Aquatic Sciences, 71*(2): 135–43. doi:10.1007/s00027-009-9174-6.

MacDonald, J.D., Chantigny, M.H., Angers, D.A., Rochette, P., Royer, I., Gasser, M.O., 2011. Soil Soluble Carbon Dynamics of Manured and Unmanured Grasslands Following Chemical Kill and Ploughing. *Geoderma, 164*(1-2). Elsevier B.V.: 64–72. doi:10.1016/j.geoderma.2011.05.011.

Maie, N., Scully, N.M., Pisani, O., Jaffé, R., 2007. Composition of a Protein-Like Fluorophore of Dissolved Organic Matter in Coastal Wetland and Estuarine Ecosystems. *Water Research, 41*(3): 563–70. doi:10.1016/j.watres.2006.11.006.

Mallik, A.U., Teichert, S., 2009. Effects of forest management on water resources in Canada: a research review. NCASI Tech. Bull. (969), 1–84.

Mannerkoski, H., Finér, L., Piirainen, S., Starr, M., 2005. Effect of Clear-Cutting and Site Preparation on the Level and Quality of Groundwater in Some Headwater Catchments in Eastern Finland. *Forest Ecology and Management*, *220*(1), pp.107-117.

Manny, B.A., Wetzel, R.G., 1973. Diurnal Changes in Dissolved Organic and Inorganic Carbon and Nitrogen in a Hardwater Stream. *Freshwater Biology*, *3*(1), pp.31-43. doi:10.1111/j.1365-2427.1973.tb00060.x/full.

McDowell, W.H., 2003. Dissolved Organic Matter in Soils—Future Directions and Unanswered Questions. *Geoderma*, *113*(3), pp.179-186.

McDowell, W.H, Likens, G.E., 1988. Origin, Composition, and Flux of Dissolved Organic Carbon in the Hubbard Brook Valley. *Ecological Monographs*, *58*(3), pp.177-195. doi:10.2307/2937024/full.

McDowell, W.H., Zsolnay, A., Aitkenhead-Peterson, J.A., Gregorich, E.G., Jones, D.L., Jödemann, D., Kalbitz, K., Marschner, B., Schwesig, D., 2006. A Comparison of Methods to Determine the Biodegradable Dissolved Organic Carbon From Different Terrestrial Sources. *Soil Biology and Biochemistry*, *38*(7), pp.1933-1942.

McGlynn, B.L., McDonnell, J.J., 2003. Role of Discrete Landscape Units in Controlling Catchment Dissolved Organic Carbon Dynamics. *Water Resources Research*, *39*(4). doi:10.1029/2002WR001525/full.

McHale, M.R., Burns, D.A., Lawrence, G.B., Murdoch, P.S., 2007. Factors Controlling Soil Water and Stream Water Aluminum Concentrations After a Clearcut in a Forested Watershed with Calcium-Poor Soils. *Biogeochemistry, 84*(3): 311–31. doi:10.1007/s10533-007-9124-0.

McKinley, D.C., Miller-Rushing, A.J., Ballard, H.L., Bonney, R., Brown, H., Evans, D.M., French, R.A., Parrish, J.K., Phillips, T.B., Ryan, S.F., Shanley, L.A., 2015. Investing in citizen science can improve natural resource management and environmental protection. *Issues in Ecology*, *19*.

McKnight, D.M., Bencala, K.E., Zellweger, G.W., Aiken, G.R., Feder, G.L., Thorn, K.A., 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. *Environmental Science & Technology*, *26*(7), pp.1388-1396.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., 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), pp.38-48. doi:10.4319/lo.2001.46.1.0038.

McLaughlin, J.W., Liu, G., 1996. Organic Carbon Characteristics in a Spruce Swamp Five Years After Harvesting. *Soil Science Society of America Journal*, *60*(4), pp.1228-1236.

Mertens, J., Diels, J., Feyen, J., Vanderborght, J., 2007. Numerical Analysis of Passive Capillary Wick Samplers Prior to Field Installation. *Soil Science Society of America Journal*, *71*(1), pp.35-42.

Miller, M.P., McKnight, D.M., 2010. Comparison of Seasonal Changes in Fluorescent

Dissolved Organic Matter Among Aquatic Lake and Stream Sites in the Green Lakes Valley. *Journal of Geophysical Research: Biogeosciences*, *115*(G1). doi:10.1029/2009JG000985/full.

Miller, M.P., McKnight, D.M., Cory, R.M., Williams, M.W., Runkel, R.L., 2006. Hyporheic Exchange and Fulvic Acid Redox Reactions in an Alpine Stream/Wetland Ecosystem, Colorado Front Range. *Environmental Science & Technology*, *40*(19), pp.5943-5949. doi:10.1021/es060635j.

Miller, M.P., McKnight, D.M., Chapra, S.C., Williams, M.W., 2009. A Model of Degradation and Production of Three Pools of Dissolved Organic Matter in an Alpine Lake. *Limnology and Oceanography*, *54*(6), p.2213.

Miller-Rushing, A., Primack, R., Bonney, R., 2012. The History of Public Participation in Ecological Research. *Frontiers in Ecology and the Environment, 10*(6): 285–90. doi:10.1890/110278.

Ministry of Environment. 2008. *Living Water Smart: British Columbia's Water Plan*. Victoria, BC: Government of British Columbia.

Ministry of Environment. 2010. *British Columbia's Water Act Modernization: Report on Engagement*. Victoria, BC: Government of British Columbia.

Ministry of Environment. 2013. *A Water Sustainability Act for B.C.: Legislative Proposal*. Victoria, BC: Government of British Columbia.

Ministry of Forests, Lands and Natural Resource Operations, 2010. The State of British Columbia's Forests: Third Edition. http://www.for.gov.bc.ca/hfp/sof/2010/SOF_2010_Web.pdf

Ministry of Forests, Lands and Natural Resource Operations 2015. http://www.sfmcanada.org/images/Publications/EN/BC_info_Province_and_territories_EN.pdf

Miró, M., Fitz, W.J., Swoboda, S., Wenzel, W.W., 2010. In-Situ Sampling of Soil Pore Water: Evaluation of Linear-Type Microdialysis Probes and Suction Cups at Varied Moisture Contents. *Environmental Chemistry, 7*(1). CSIRO Publishing: 123–31. doi:10.1071/EN09084.

Monno, V., Khakee, A., 2012. Tokenism or Political Activism? Some Reflections on Participatory Planning. *International Planning Studies, 17*(1). Routledge: 85–101. doi:10.1080/13563475.2011.638181.

Monteith, D.T., Stoddard, J.L., Evans, C.D., De Wit, H.A., Forsius, M., Høgåsen, T., Wilander, A., Skjelkvåle, B.L., Jeffries, D.S., Vuorenmaa, J., Keller, B., 2007. Dissolved Organic Carbon Trends Resulting From Changes in Atmospheric Deposition Chemistry. *Nature, 450*(7169): 537–40. doi:10.1038/nature06316.

Monteith, S.S., Buttle, J.M., Hazlett, P.W., Beall, F.D., Semkin, R.G., Jeffries, D.S., 2006. Paired-basin comparison of hydrologic response in harvested and undisturbed hardwood forests during snowmelt in central Ontario: II. Streamflow sources and groundwater residence times. *Hydrological Processes*, *20*(5), pp.1117-1136.

doi:10.1002/hyp.6073/abstract.

Moore, R.D., 2004. Introduction to Salt Dilution Gauging for Streamflow Measurement: Part 1. *Streamline Watershed Management Bulletin*, *7*(4), pp.20-23.

Moore, R.D, Wondzell, S.M., 2005. Physical Hydrology and the Effects of Forest Harvesting in the Pacific Northwest: a Review. *Journal of the American Water Resources Association*, *41*(4), p.763. doi:10.1111/j.1752-1688.2005.tb03770.x.

Morinville, C., Harris, L.M., 2014. Participation, Politics, and Panaceas: Exploring the Possibilities and Limits of Participatory Urban Water Governance in Accra, Ghana. *Ecology and Society*, *19*(3), p.36.

Morris, D.P, Hargreaves, B.R., 1997. The Role of Photochemical Degradation of Dissolved Organic Carbon in Regulating the UV Transparency of Three Lakes on the Pocono Plateau. *Limnology and Oceanography*, *42*(2), pp.239-249.

Mulholland, P.J., 1997. Dissolved Organic Matter Concentration and Flux in Streams. *Journal of the North American Benthological Society*, *16*(1), pp.131-141.

Munson, M.A., Caruana, R., Fink, D., Hochachka, W.M., Iliff, M., Rosenberg, K.V., Sheldon, D., Sullivan, B.L., Wood, C., Kelling, S., 2010. A Method for Measuring the Relative Information Content of Data From Different Monitoring Protocols. *Methods in Ecology and Evolution, 1*(3). Blackwell Publishing Ltd: 263–73. doi:10.1111/j.2041-210X.2010.00035.x.

Murphy, K.R., Stedmon, C.A., Graeber, D. and Bro, R., 2013. Fluorescence Spectroscopy and Multi-Way Techniques. PARAFAC. *Analytical Methods, 5*(23): 6557–11. doi:10.1039/c3ay41160e.

Murray, C.D., Buttle, J.M., 2003. Impacts of Clearcut Harvesting on Snow Accumulation and Melt in a Northern Hardwood Forest. *Journal of Hydrology*, *271*(1), pp.197-212.

Murray, M., Fagan, G., McCusker, P. 2009. Measuring Horizontal Governance: a Review of Public Consultation by the Northern Ireland Government Between 2000 and 2004. *Policy & Politics*, *37*(4), pp.553-571.

Naiman, R.J., Melillo, J.M., Lock, M.A., Ford, T.E., Reice, S.R., 1987. Longitudinal Patterns of Ecosystem Processes and Community Structure in a Subarctic River Continuum. *Ecology, 68*(5). Ecological Society of America: 1139–56. doi:10.2307/1939199.

National Forestry Database 2015. 6.1. Silvicultural Statistics by Province/Territory 1990-2015. http://nfdp.ccfm.org/data/compendium/html/comp_61e.html. Accessed on September 2016.

Nelson, P.N., Dictor, M.C., Soulas, G., 1994. Availability of Organic Carbon in Soluble and Particle-Size Fractions From a Soil Profile. *Soil Biology and Biochemistry*, *26*(11), pp.1549-1555.

Nguyen, H.V.M., Hur, J., Shin, H.S., 2010. Changes in Spectroscopic and Molecular Weight Characteristics of Dissolved Organic Matter in a River During a Storm Event. *Water, Air, & Soil Pollution, 212*(1-4): 395–406. doi:10.1007/s11270-010-0353-9.

Nieke, B., Reuter, R., Heuermann, R., Wang, H., Babin, M., Therriault, J.C., 1997. Light Absorption and Fluorescence Properties of Chromophoric Dissolved Organic Matter (CDOM), in the St. Lawrence Estuary (Case 2 Waters). *Continental Shelf Research*, *17*(3), pp.235-252.

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), pp.123-132.

Nieuwenhuijsen, M.J., Toledano, M.B., Eaton, N.E., Fawell, J., Elliott, P., 2000. Chlorination disinfection byproducts in water and their association with adverse reproductive outcomes: a review. *Occupational and Environmental Medicine*, *57*(2), pp.73-85.

Nilsson, M., Sagerfors, J., Buffam, I., Laudon, H., Eriksson, T., Grelle, A., Klemedtsson, L., Weslien, P.E.R., Lindroth, A., 2008. Contemporary Carbon Accumulation in a Boreal Oligotrophic Minerogenic Mire–a Significant Sink After Accounting for All C-Fluxes. *Global Change Biology*, *14*(10), pp.2317-2332. doi:10.1111/j.1365-2486.2008.01654.x/full.

Nissen, S., 2014. Who's in and Who's Out? Inclusion and Exclusion in Canterbury"s Freshwater Governance. *New Zealand Geographer*, *70*(1), pp.33-46. doi:10.1111/nzg.12038/full.

Organization for Economic Co-operation and Development (OECD). 2001. *Engaging Citizens in Policy-Making: Information, Consultation, and Public Participation*. Public Management Policy Brief No. 10. Paris: OECD Publishing.

Obernosterer, I., Benner, R., 2004. Competition Between Biological and Photochemical Processes in the Mineralization of Dissolved Organic Carbon. *Limnology and Oceanography*, *49*(1), pp.117-124. doi:10.4319/lo.2004.49.1.0117.

Ohno, T., 2002. Fluorescence Inner-Filtering Correction for Determining the Humification Index of Dissolved Organic Matter. *Environmental Science & Technology*, *36*(4), pp.742-746.doi:10.1021/es0155276.

Osburn, C.L., Stedmon, C.A., 2011. Linking the Chemical and Optical Properties of Dissolved Organic Matter in the Baltic–North Sea Transition Zone to Differentiate Three Allochthonous Inputs. *Marine Chemistry, 126*(1-4): 281–94. doi:10.1016/j.marchem.2011.06.007.

Overdevest, C., Mayer, B., 2007. Harnessing the Power of Information Through Community Monitoring: Insights From Social Science. *Tex L Rev, 86*: 1493.

Pacific, V.J., Jencso, K.G., McGlynn, B.L., 2010. Variable Flushing Mechanisms and Landscape Structure Control Stream DOC Export During Snowmelt in a Set of Nested Catchments. *Biogeochemistry, 99*(1-3): 193–211. doi:10.1007/s10533-009-9401-1.

Parfitt, B., 2000. *Muddied Waters: a Case for Protecting Water Sources in BC*. Sierra Legal Defence Fund. Retrieved February 2016, p.2005.

Parkins, J.R., Sinclair, A.J., 2014. Patterns of Elitism Within Participatory Environmental Governance. *Environment and Planning C: Government and Policy*, *32*(4), pp.746-761.

Parlanti, E., Wörz, K., Geoffroy, L., Lamotte, M., 2000. Dissolved Organic Matter Fluorescence Spectroscopy as a Tool to Estimate Biological Activity in a Coastal Zone Submitted to Anthropogenic Inputs. *Organic Geochemistry, 31*(12): 1765–81. doi:10.1016/S0146-6380(00)00124-8.

Pataki, D.E., Boone, C.G., Hogue, T.S., Jenerette, G.D., McFadden, J.P., Pincetl, S., 2011. 2011. Socio-Ecohydrology and the Urban Water Challenge. *Ecohydrology*, *4*(2), pp.341-347. doi:10.1002/eco.209/full.

Patten, S., 2000. Democratizing the Institutions of Policy-Making: Democratic Consultation and Participatory Administration. *Journal of Canadian Studies/Revue d'Études Canadiennes*, *35*(4), p.221.

Perdrial, J.N., Perdrial, N., Harpold, A., Gao, X., Gabor, R., LaSharr, K., Chorover, J.,2012. Impacts of Sampling Dissolved Organic Matter with Passive Capillary Wicks Versus Aqueous Soil Extraction. *Soil Science Society of America Journal, 76*(6). 2019–30. doi:10.2136/sssaj2012.0061.

Peters, A., Durner, W., 2009. Large Zero-Tension Plate Lysimeters for Soil Water and Solute Collection in Undisturbed Soils. *Hydrology and Earth System Sciences*, *13*(9), pp.1671-1683.

Peuravuori, J., Pihlaja, K., 1997. Molecular Size Distribution and Spectroscopic Properties of Aquatic Humic Substances. *Analytica Chimica Acta, 337*(2): 133–49. doi:10.1016/S0003-2670(96)00412-6.

Pfeffer, M.J, Wagenet, L.P., 2007. Volunteer Environmental Monitoring, Knowledge Creation and Citizen–Scientist Interaction. *The SAGE handbook of environment and society. Sage, London* (2007): 235-250.

Piirainen, S., Finér, L., Mannerkoski, H., Starr, M., 2007. Carbon, Nitrogen and Phosphorus Leaching After Site Preparation at a Boreal Forest Clear-Cut Area. *Forest Ecology and Management*, *243*(1), pp.10-18.

Pike, R.G., Feller, M.C., Stednick, J.D., Rieberger, K.J., Carver, M., 2010. Water quality and forest management. In *Compendium of forest hydrology and geomorphology in British Columbia. RG Pike, TE Redding, RD Moore, RD Winker, & KD Bladon (editors). BC Ministry of Forests and Range, Forest Science Program, Victoria, BC, and FORREX Forum for Research and Extension in Natural Resources, Kamloops, BC. Land Management Handbook* (Vol. 66).

Pomeroy, J.W., Granger, R.J., 1997. Sustainability of the Western Canadian Boreal Forest Under Changing Hydrological Conditions. I. Snow Accumulation and Ablation. *IAHS Publication*, *240*, pp.237-242.

Porcal, P., Hejzlar, J., Kopáček, J., 2004. Seasonal and Photochemical Changes of DOM in an Acidified Forest Lake and Its Tributaries. *Aquatic Sciences, 66*(2). Birkhäuser-Verlag: 211–22. doi:10.1007/s00027-004-0701-1.

von der Porten, S., de Loë, R.C., 2014. Water Policy Reform and Indigenous Governance. *Water Policy, 16*(2): 222–23. doi:10.2166/wp.2013.046.

Poulin, B.A., Ryan, J.N., Aiken, G.R.,2014. Effects of Iron on Optical Properties of Dissolved Organic Matter. *Environmental Science & Technology, 48*(17). American Chemical Society: 10098–106. doi:10.1021/es502670r.

Provenzano, M.R., Caricasole, P., Brunetti, G., Senesi, N., 2010. Dissolved Organic Matter Extracted with Water and a Saline Solution From Different Soil Profiles. *Soil Science, 175*(6): 255–62. doi:10.1097/SS.0b013e3181e457a6.

Provenzano, M.R., Cilenti, A., Gigliotti, G., Senesi, N., 2008. Spectroscopic Investigation on Hydrophobic and Hydrophilic Fractions of Dissolved Organic Matter Extracted From Soils at Different Salinities. *CLEAN – Soil, Air, Water, 36*(9). WILEY-VCH Verlag: 748–53. doi:10.1002/clen.200800033.

R Core Team. 2016. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.

Raddick, M.J., Bracey, G., Gay, P.L., Lintott, C.J., Murray, P., Schawinski, K., Szalay, A.S., Vandenberg, J., 2009. Galaxy Zoo: Exploring the Motivations of Citizen Science Volunteers. *arXiv.org*. doi:10.3847/AER2009036.

Rahman, M.B., Driscoll, T., Cowie, C., Armstrong, B.K., 2010. Disinfection by-products in drinking water and colorectal cancer: a meta-analysis. *International Journal of Epidemiology*, p.dyp371.

Ravichandran, M., 2004. Interactions Between Mercury and Dissolved Organic Matter—a Review. *Chemosphere, 55*(3): 319–31. doi:10.1016/j.chemosphere.2003.11.011.

Raymond, P.A., Saiers, J.E., 2010. Event Controlled DOC Export From Forested Watersheds. *Biogeochemistry, 100*(1-3): 197–209. doi:10.1007/s10533-010-9416-7.

Reemtsma, T., Bredow, A., 1999. The Nature and Kinetics of Organic Matter Release From Soil by Salt Solutions. *European Journal of Soil Science*, *50*(1), pp.53-64. doi:10.1046/j.1365-2389.1999.00212.x/full.

Rennert, T., Gockel, K.F., Mansfeldt, T., 2007. Extraction of Water-Soluble Organic Matter From Mineral Horizons of Forest Soils. *Journal of Plant Nutrition and Soil Science*, *170*(4), pp.514-521. doi:10.1002/jpln.200625099/full.

Ricciardi, A., Steiner, W.W., Mack, R.N., Simberloff, D., 2000. Toward a Global Information System for Invasive Species. *BioScience, 50*(3): 239–44. doi:10.1641/0006-3568(2000)050[0239:TAGISF]2.3.CO;2.

Richardson, J.S., Bilby, R.E., Bondar, C.A.,2005. Organic Matter Dynamics in Small Streams of the Pacific Northwest. *JAWRA Journal of the American Water Resources Association, 41*(4). Blackwell Publishing Ltd: 921–34. doi:10.1111/j.1752-1688.2005.tb03777.x.

Richardson, S.D., DeMarini, D.M., Kogevinas, M., Fernandez, P., Marco, E., Lourencetti, C., Ballesté, C., Heederik, D., Meliefste, K., McKague, A.B. Marcos, R., 2010. What's in the pool? A comprehensive identification of disinfection by-,products and assessment of mutagenicity of chlorinated and brominated swimming pool water. *Environmental Health Perspectives*, *118*(11), p.1523.

Riesch, H., Potter, C., 2013. Citizen Science as Seen by Scientists: Methodological, Epistemological and Ethical Dimensions. *Public Understanding of Science, 23*(1). SAGE Publications: 0963662513497324–120. doi:10.1177/0963662513497324.

Roberts, B.J., Mulholland, P.J., Hill, W.R., 2007. Multiple Scales of Temporal Variability in Ecosystem Metabolism Rates: Results From 2 Years of Continuous Monitoring in a Forested Headwater Stream. *Ecosystems, 10*(4). Springer-Verlag: 588–606. doi:10.1007/s10021-007-9059-2.

Rouillard, A., Rosén, P., Douglas, M.S., Pienitz, R., Smol, J.P., 2011. A Model for Inferring Dissolved Organic Carbon (DOC) in Lakewater From Visible-Near-Infrared Spectroscopy (VNIRS) Measures in Lake Sediment. *Journal of Paleolimnology, 46*(2). Springer Netherlands: 187–202. doi:10.1007/s10933-011-9527-8.

Roulet, N., Moore, T.R., 2006. Environmental Chemistry: Browning the Waters. *Nature, 444*(7117). Nature Publishing Group: 283–84. doi:10.1038/444283a.

Rowe, G., Frewer, L.J., 2000. Public Participation Methods: a Framework for Evaluation. *Science, Technology & Human Values*, *25*(1), pp.3-29. doi:10.1177/016224390002500101.

Rowe, G., Frewer, L.J., 2004. Evaluating Public-Participation Exercises: a Research Agenda. *Science, Technology & Human Values*, *29*(4), pp.512-556.doi:10.1177/0162243903259197.

Rowe, G., Frewer, L.J., 2005. A Typology of Public Engagement Mechanisms. *Science, Technology & Human Values, 30*(2). SAGE Publications: 251–90. doi:10.1177/0162243904271724.

Ruhala, S.S., Zarnetske, J.P., 2016. Using in-Situ Optical Sensors to Study Dissolved Organic Carbon Dynamics of Streams and Watersheds: a Review. *Science of the Total Environment*.

Ryder, E., de Eyto, E., Dillane, M., Poole, R., Jennings, E., 2014. Identifying the Role of Environmental Drivers in Organic Carbon Export From a Forested Peat Catchment. *The Science of the Total Environment, 490*(August): 28–36. doi:10.1016/j.scitotenv.2014.04.091.

Satterfield, T., Gregory, R., Klain, S., Roberts, M., Chan, K.M., 2013. Culture, Intangibles and Metrics in Environmental Management. *Journal of Environmental Management, 117*(C). Elsevier Ltd: 103–14. doi:10.1016/j.jenvman.2012.11.033.

Savan, B., Morgan, A.J., Gore, C., 2003. Volunteer Environmental Monitoring and the Role of the Universities: the Case of Citizens' Environment Watch. *Environmental Management, 31*(5): 561–68. doi:10.1007/s00267-002-2897-y.

Savitz, D.A., Singer, P.C., Herring, A.H., Hartmann, K.E., Weinberg, H.S., Makarushka, C., 2006. Exposure to drinking water disinfection by-products and pregnancy loss. *American Journal of Epidemiology*, *164*(11), pp.1043-1051.

Schade, J.D., Bailio, J., McDowell, W.H., 2016. Greenhouse Gas Flux From Headwater Streams in New Hampshire, USA: Patterns and Drivers. *Limnology and Oceanography*,

61(S1). doi:10.1002/lno.10337/full.

Schelker, J., Burns, D.A., Weiler, M., Laudon, H., 2011. Hydrological Mobilization of Mercury and Dissolved Organic Carbon in a Snow-Dominated, Forested Watershed: Conceptualization and Modeling. *Journal of Geophysical Research: Biogeosciences*, *116*(G1). doi:10.1029/2010JG001330/full.

Schelker, J., Eklöf, K., Bishop, K., Laudon, H., 2012. Effects of Forestry Operations on Dissolved Organic Carbon Concentrations and Export in Boreal First-Order Streams. *Journal of Geophysical Research: Biogeosciences*, *117*(G1). doi:10.1029/2011JG001827.

Schelker, J., Kuglerová, L., Eklöf, K., Bishop, K., Laudon, H., 2013. Hydrological Effects of Clear-Cutting in a Boreal Forest–Snowpack Dynamics, Snowmelt and Streamflow Responses. *Journal of Hydrology*, *484*, pp.105-114.

Schelker, J., Grabs, T., Bishop, K., Laudon, H., 2013. Drivers of Increased Organic Carbon Concentrations in Stream Water Following Forest Disturbance: Separating Effects of Changes in Flow Pathways and Soil Warming. *Journal of Geophysical Research Biogeosciences, 118*(4): 1814–27. doi:10.1002/2013JG002309.

Schelker, J., Öhman, K., Löfgren, S., Laudon, H., 2014. Scaling of Increased Dissolved Organic Carbon Inputs by Forest Clear-Cutting: What Arrives Downstream? *Journal of Hydrology, 508*(C). Elsevier B.V.: 299–306. doi:10.1016/j.jhydrol.2013.09.056.

Schmeller, D.S., HENRY, P.Y., Julliard, R., Gruber, B., Clobert, J., Dziock, F., Lengyel, S., Nowicki, P., Déri, E., Budrys, E., Kull, T., 2009. Advantages of Volunteer-Based Biodiversity Monitoring in Europe. *Conservation Biology : the Journal of the Society for Conservation Biology, 23*(2). Blackwell Publishing Inc: 307–16. doi:10.1111/j.1523-1739.2008.01125.x.

Schmit, K.H., Wells, M., 2002. Preferential adsorption of fluorescing fulvic and humic acid components on activated carbon using flow field-flow fractionation analysis. *Journal of Environmental Monitoring*, *4*(1), pp.75-84 doi:10.1039/B107167J

Schwalm, C R, T A Black, and K Morgenstern. 2007. A method for deriving net primary productivity and component respiratory fluxes from tower-based eddy covariance data: A case study using a 17-year data record from a Douglas-fir chronosequence. *Global Change Biology*, *13*(2), pp.370-385. doi:10.1111/j.1365-2486.2006.01298.x/full.

Schwalm, C.R., Black, T.A., Morgenstern, K., Humphreys, E.R., 2006. Photosynthetic Light Use Efficiency of Three Biomes Across an East–West Continental-Scale Transect in Canada. *Agricultural and Forest Meteorology*, *140*(1), pp.269-286.

Scott, D.T., Runkel, R.L., McKnight, D.M., Voelker, B.M., Kimball, B.A., Carraway, E.R., 2003. Transport and Cycling of Iron and Hydrogen Peroxide in a Freshwater Stream: Influence of Organic Acids. *Water Resources Research, 39*(11): n/a–n/a. doi:10.1029/2002WR001768.

Sebestyen, S.D., Boyer, E.W., Shanley, J.B., Kendall, C., Doctor, D.H., Aiken, G.R., Ohte, N., 2008. Sources, transformations, and hydrological processes that control stream

nitrate and dissolved organic matter concentrations during snowmelt in an upland forest. *Water Resources Research*, *44*(12) doi:10.1029/2008WR006983/full.

Sebestyen, S.D., Boyer, E.W., Shanley, J.B., 2009. Responses of Stream Nitrate and DOC Loadings to Hydrological Forcing and Climate Change in an Upland Forest of the Northeastern United States. *Journal of Geophysical Research Biogeosciences, 114*(G2): n/a–n/a. doi:10.1029/2008JG000778.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., Bishop, K., 2009. Linking Soil- and Stream-Water Chemistry Based on a Riparian Flow-Concentration Integration Model. *Hydrology and Earth System Sciences,* 13(12). Copernicus Publications: 2287–97.

Seitzinger, S.P., Sanders, R.W., Styles, R., 2002. Bioavailability of DON From Natural and Anthropogenic Sources to Estuarine Plankton. *Limnology and Oceanography*, *47*(2), pp.353-366. doi:10.4319/lo.2002.47.2.0353/full.

Senesi, N., Miano, T.M., Provenzano, M.R., Brunetti, G., 1989. Spectroscopic and Compositional Comparative Characterization of IHSS Reference and Standard Fulvic and Humic Acids of Various Origin. *Science of the Total Environment*, *81*, pp.143-156.

Senga, Y., Hiroki, M., Nakamura, Y., Watarai, Y., Watanabe, Y., Nohara, S., 2010. Vertical profiles of DIN, DOC, and microbial activities in the wetland soil of Kushiro Mire, Northeastern Japan. *Limnology, 12*, 17–23.

Shipley, R., Utz, S., 2012. Making It Count: a Review of the Value and Techniques for Public Consultation. *Journal of Planning Literature, 27*(1): 22–42. doi:10.1177/0885412211413133.

Silvertown, J., 2009. A New Dawn for Citizen Science. *Trends in Ecology & Evolution, 24*(9): 467–71. doi:10.1016/j.tree.2009.03.017.

Simonsson, M., Kaiser, K., Danielsson, R., Andreux, F., Ranger, J., 2005. Estimating Nitrate, Dissolved Organic Carbon and DOC Fractions in Forest Floor Leachates Using Ultraviolet Absorbance Spectra and Multivariate Analysis. *Geoderma*, *124*(1), pp.157-168.

Singh, S., Inamdar, S., Mitchell, M., McHale, P., 2014. Seasonal Pattern of Dissolved Organic Matter (DOM) in Watershed Sources: Influence of Hydrologic Flow Paths and Autumn Leaf Fall. *Biogeochemistry, 118*(1-3). Springer International Publishing: 321–37. doi:10.1007/s10533-013-9934-1.

Skjelkvåle, B.L., Stoddard, J.L., Jeffries, D.S., Tørseth, K., Høgåsen, T., Bowman, J., Mannio, J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., 2005. Regional Scale Evidence for Improvements in Surface Water Chemistry 1990–2001. *Environmental Pollution, 137*(1): 165–76. doi:10.1016/j.envpol.2004.12.023.

Smith, A., Lynn, S., Lintott, C.J., 2013. Human Computation and Crowdsourcing: Works in Progress and Demonstrations. Vol. 13. Palo Alto, CA: Association for the Advancement of Artificial Intelligence. doi:10.1111/j.2041-210X.2010.00035.x/full.

Soh, Y. C., Roddick, F., van Leeuwen, J., 2008. The impact of alum coagulation on the

character, biodegradability and disinfection by-product formation potential of reservoir natural organic matter (NOM) fractions. *Water Science & Technology, 58*, 1173–1179

Sowerby, A., Emmett, B.A., Williams, D., Beier, C., Evans, C.D., 2010. The Response of Dissolved Organic Carbon (DOC) and the Ecosystem Carbon Balance to Experimental Drought in a Temperate Shrubland. *European Journal of Soil Science, 61*(5). Blackwell Publishing Ltd: 697–709. doi:10.1111/j.1365-2389.2010.01276.x.

Spencer, R.G.M., Butler, K.D., 2012. Dissolved Organic Carbon and Chromophoric Dissolved Organic Matter Properties of Rivers in the USA. *Journal of Geophysical Research: Biogeosciences*, *117*(G3). doi:10.1029/2011JG001928/pdf.

Spencer, R.G., Pellerin, B.A., Bergamaschi, B.A., Downing, B.D., Kraus, T.E., Smart, D.R., Dahlgren, R.A., Hernes, P.J., 2007. Diurnal Variability in Riverine Dissolved Organic Matter Composition Determined by in Situ Optical Measurement in the San Joaquin River (California, USA). *Hydrological Processes, 21*(23). John Wiley & Sons, Ltd.: 3181–89. doi:10.1002/hyp.6887.

Spencer, R.G., Hernes, P.J., Ruf, R., Baker, A., Dyda, R.Y., Stubbins, A., Six, J., 2010. Temporal Controls on Dissolved Organic Matter and Lignin Biogeochemistry in a Pristine Tropical River, Democratic Republic of Congo. *Journal of Geophysical Research Biogeosciences, 115*(G3): G03013. doi:10.1029/2009JG001180.

Stedmon, C.A., Bro, R., 2008. Characterizing Dissolved Organic Matter Fluorescence with Parallel Factor Analysis: a Tutorial. *Limnology and Oceanography: Methods*, *6*(11), pp.572-579. doi:10.4319/lom.2008.6.572/abstract.

Stedmon, C.A., Markager, S., 2001. The Optics of Chromophoric Dissolved Organic Matter (CDOM) in the Greenland Sea: an Algorithm for Differentiation Between Marine and Terrestrially Derived Organic Matter. *Limnology and Oceanography, 46*(8): 2087–93. doi:10.4319/lo.2001.46.8.2087.

Stedmon, C.A., Markager, S., 2005. Resolving the Variability in Dissolved Organic Matter Fluorescence in a Temperate Estuary and Its Catchment Using PARAFAC Analysis. *Limnology and Oceanography*, *50*(2), pp.686-697.

Stedmon, C.A., Markager, S., Bro. R., 2003. Tracing Dissolved Organic Matter in Aquatic Environments Using a New Approach to Fluorescence Spectroscopy. *Marine Chemistry*, *82*(3-4): 239–54. doi:10.1016/S0304-4203(03)00072-0.

Strohmeier, S., Knorr, K.H., Reichert, M., Frei, S., Fleckenstein, J.H., Peiffer, S., Matzner, E., 2013. Concentrations and Fluxes of Dissolved Organic Carbon in Runoff From a Forested Catchment: Insights From High Frequency Measurements. *Biogeosciences, 10*(2): 905–16. doi:10.5194/bg-10-905-2013.

Sullivan, B.L., Wood, C.L., Iliff, M.J., Bonney, R.E., Fink, D., Kelling, S., 2009. eBird: a Citizen-Based Bird Observation Network in the Biological Sciences. *Biological Conservation, 142*(10): 2282–92. doi:10.1016/j.biocon.2009.05.006.

Sullivan, B.L., Aycrigg, J.L., Barry, J.H., Bonney, R.E., Bruns, N., Cooper, C.B., Damoulas, T., Dhondt, A.A., Dietterich, T., Farnsworth, A., Fink, D., 2014. The eBird Enterprise:

an Integrated Approach to Development and Application of Citizen Science. *Biological Conservation, 169*(January): 31–40. doi:10.1016/j.biocon.2013.11.003.

Sørensen, R., Ring, E., Meili, M., Högbom, L., Seibert, J., Grabs, T., Laudon, H., Bishop, K., 2009. Forest Harvest Increases Runoff Most During Low Flows in Two Boreal Streams. *AMBIO: a Journal of the Human Environment, 38*(7): 357–63. doi:10.1579/0044-7447-38.7.357.

Tamm, C.O., 1964. Determination of nutrient requirements of forest stands. *Int. Rev. For. Res.* 1: 115–170.

Temnerud, J., Seibert, J., Jansson, M., Bishop, K., 2007. Spatial Variation in Discharge and Concentrations of Organic Carbon in a Catchment Network of Boreal Streams in Northern Sweden. *Journal of Hydrology*, *342*(1), pp.72-87.

Thurman, E.M., 2012. *Organic geochemistry of natural waters* (Vol. 2). Springer Science & Business Media.

Traina, S.J., Novak, J., Smeck, N.E., 1990. An Ultraviolet Absorbance Method of Estimating the Percent Aromatic Carbon Content of Humic Acids. *Journal of Environment Quality* 19 (1). American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America: 151–53. doi:10.2134/jeq1990.00472425001900010023x.

Trumbull, D.J., Bonney, R., Bascom, D., Cabral, A., 2000. Thinking Scientifically During Participation in a Citizen-Science Project. *Science Education, 84*(2). John Wiley & Sons, Inc.: 265–75. doi:10.1002/(SICI)1098-237X(200003)84:2<265::AID-SCE7>3.0.CO;2-5.

Twardowski, M.S., Boss, E., Sullivan, J.M., Donaghay, P.L., 2004. Modeling the Spectral Shape of Absorption by Chromophoric Dissolved Organic Matter. *Marine Chemistry*, *89*(1), pp.69-88. doi:10.1016/j.marchem.2004.02.008.

UN. 2014. Resolution on Access to Information, Public Participation in Decision-Making and Access to Justice in Environmental Matters. In *The Aarhus Convention*, 179–82. United Nations. doi:10.18356/df79acf3-en.

UNECE (United Nations Economic Commission for Europe). 1998. *Convention on Access to Information, Public Participation in Decision-Making and Access to Justice in Environmental Matters, Signed 25 June 1998 at Aarhus, Denmark*. Geneva: UNECE.

Ussiri, D., Johnson, C.E., 2003. Characterization of Organic Matter in a Northern Hardwood Forest Soil by 13 C NMR Spectroscopy and Chemical Methods. *Geoderma*, *111*(1), pp.123-149.

van Verseveld, W.J., McDonnell, J.J., Lajtha, K., 2008. A Mechanistic Assessment of Nutrient Flushing at the Catchment Scale. *Journal of Hydrology*, *358*(3), pp.268-287.

Vergnoux, A., Di Rocco, R., Domeizel, M., Guiliano, M., Doumenq, P., Théraulaz, F., 2011. Effects of Forest Fires on Water Extractable Organic Matter and Humic Substances From Mediterranean Soils: UV–Vis and Fluorescence Spectroscopy Approaches. *Geoderma, 160*(3-4): 434–43. doi:10.1016/j.geoderma.2010.10.014.

Vidon, P., Wagner, L.E. and Soyeux, E., 2008. Changes in the Character of DOC in Streams

During Storms in Two Midwestern Watersheds with Contrasting Land Uses. *Biogeochemistry, 88*(3): 257–70. doi:10.1007/s10533-008-9207-6.

Villanueva, C.M., Cantor, K.P., Cordier, S., Jaakkola, J.J., King, W.D., Lynch, C.F., Porru, S., Kogevinas, M., 2004. Disinfection byproducts and bladder cancer: a pooled analysis. *Epidemiology*, *15*(3), pp.357-367.

Villanueva, C.M., Cantor, K.P., Grimalt, J.O., Malats, N., Silverman, D., Tardon, A., Garcia-Closas, R., Serra, C., Carrato, A., Castano-Vinyals, G., Marcos, R., 2007. Bladder cancer and exposure to water disinfection by-products through ingestion, bathing, showering, and swimming in pools. *American Journal of Epidemiology*, *165*(2), pp.148-156.

Walker, D., Forsythe, N., Parkin, G., Gowing, J., 2016. Filling the Observational Void: Scientific Value and Quantitative Validation of Hydrometeorological Data From a Community-Based Monitoring Programme. *Journal of Hydrology, 538*(July): 713–25. doi:10.1016/j.jhydrol.2016.04.062.

Walling, D.E., Webb, B.W., 1985. Estimating the Discharge of Contaminants to Coastal Waters by Rivers: Some Cautionary Comments. *Marine Pollution Bulletin*, *16*(12), pp.488-492.

Wang, X C., 1992. Comparison of High-Temperature and Persulfate Oxidation Methods for Determination of Dissolved Organic Carbon in Freshwaters. *Limnol. Oceanogr*, *14*, pp.799-801.

Water Sustainability Act. SBC 2014 c.5. British Columbia, Canada, May 29 2014.

Waterloo, M.J., Oliveira, S.M., Drucker, D.P., Nobre, A.D., Cuartas, L.A., Hodnett, M.G., Langedijk, I., Jans, W.W., Tomasella, J., De Araujo, A.C., Pimentel, T.P., 2006. Export of Organic Carbon in Run-Off From an Amazonian Rainforest Blackwater Catchment. *Hydrological Processes, 20*(12). John Wiley & Sons, Ltd.: 2581–97. doi:10.1002/hyp.6217.

Weihermüller, L., Kasteel, R., Vereecken, H., 2006. Soil Heterogeneity Effects on Solute Breakthrough Sampled with Suction Cups. *Vadose Zone Journal, 5*(3). Soil Science Society: 886–93. doi:10.2136/vzj2005.0105.

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): 4702–8. doi:10.1021/es030360x.

Wiggins, A., Crowston, K., 2011. From Conservation to Crowdsourcing: a Typology of Citizen Science. In, 1–10. IEEE. doi:10.1109/HICSS.2011.207.

Wiggins, A., Newman, G., Stevenson, R.D., Crowston, K., 2011. Mechanisms for Data Quality and Validation in Citizen Science. In, 14–19. IEEE. doi:10.1109/eScienceW.2011.27.

Williams, C.J., Yamashita, Y., Wilson, H.F., Jaffé, R., Xenopoulos, M.A., 2010. Unraveling the Role of Land Use and Microbial Activity in Shaping Dissolved Organic Matter Characteristics in Stream Ecosystems. *Limnology and Oceanography, 55*(3): 1159–71.

doi:10.4319/lo.2010.55.3.1159.

Wilson, H. F., Xenopoulos, M.A., 2008. Effects of Agricultural Land Use on the Composition of Fluvial Dissolved Organic Matter. *Nature Geoscience, 2*(1). Nature Publishing Group: 37–41. doi:10.1038/ngeo391.

Woodford, M.R., Preston, S., 2013. Strengthening Citizen Participation in Public Policy-Making: a Canadian Perspective. *Parliamentary Affairs*, *66*(2), pp.345-363. doi:10.1093/pa/gsr065.

Worrall, F., Burt, T., Shedden, R., 2003. Long Term Records of Riverine Dissolved Organic Matter. *Biogeochemistry* 64 (2). Kluwer Academic Publishers: 165–78. doi:10.1023/A:1024924216148.

Yoshioka, T., Mostofa, K.M., Konohira, E., Tanoue, E., Hayakawa, K., Takahashi, M., Ueda, S., Katsuyama, M., Khodzher, T., Bashenkhaeva, N., Korovyakova, I., 2007. Distribution and Characteristics of Molecular Size Fractions of Freshwater-Dissolved Organic Matter in Watershed Environments: Its Implication to Degradation. *Limnology, 8*(1). Springer-Verlag: 29–44. doi:10.1007/s10201-006-0194-9.

Zarnetske, J.P., Haggerty, R., 2011. Labile Dissolved Organic Carbon Supply Limits Hyporheic Denitrification. *Journal of Geophysical Research: Biogeosciences*, *116*(G4). doi:10.1029/2011JG001730/full.

Zepp, R.G., Sheldon, W.M., Moran, M.A., 2004. Dissolved Organic Fluorophores in Southeastern US Coastal Waters: Correction Method for Eliminating Rayleigh and Raman Scattering Peaks in Excitation–Emission Matrices. *Marine Chemistry*, *89*(1), pp.15-36.

Zhang, H., Jiuhui, Q.U., Huijuan, L.I.U., Dongbin, W.E.I., 2009. Characterization of Dissolved Organic Matter Fractions and Its Relationship with the Disinfection by-Product Formation. *Journal of Environmental Sciences*, *21*(1), pp.54-61. doi:10.1016/S1001-0742(09)60011-5.

Zoltai, S., Martikainen, P., 1994. Estimated extent of forested peatlands and their role in the global carbon cycle. In *Forest Ecosystems, Forest Management and the Global Carbon Cycle* (pp. 47-58). Springer Berlin Heidelberg.

Zsolnay, A., Görlitz, H., 1994. Water Extractable Organic Matter in Arable Soils: Effects of Drought and Long-Term Fertilization. *Soil Biology and Biochemistry*, *26*(9), pp.1257-1261.

Zwiener, C., Richardson, S.D., De Marini, D.M., Grummt, T., Glauner, T., Frimmel, F.H., 2007. Drowning in disinfection byproducts? Assessing swimming pool water. *Environmental Science & Technology*, *41*(2), pp.363-372.

Appendices

Appendix A: Spectral indices supplemental information

A.1 Absorbance and fluorescence spectral corrections

Prior to calculating indices from absorbance and fluorescence spectra, several correction steps were taken. Absorbance spectra were blank corrected by subtracting the average absorbance between 700-800 nm from all measurements (Green and Blough 1994). Observed absorbance ($A(\lambda)$, in O. D units) were converted to Naperian absorbance coefficients ($a(\lambda)$, in m^{-1}) according to:

$$a(\lambda) = \frac{2.303A(\lambda)}{l} \qquad \text{(Equation A.1)}$$

where l is the pathlength (in m^{-1}) (Hu, Muller-Karger, and Zepp 2002). Instrument corrected EEMs were also blank corrected, corrected for inner filter effects (Ohno 2002), and normalized to the area under the Raman curve (e.g., Determann, Reuter, and Wagner 1994, Nieke et al. 1997, Stedmon, Markager, and Bro 2003). Additionally, second order Raleigh scatter, as well as Raman bands, were masked and replaced with interpolated values (Zepp et al. 2004; Bahram, Bro, and Stedmon 2006), while first-order Raleigh scatter was excised at a bandwidth of 30 nm to prevent spectral artifacts (Bro 1997; Stedmon and Bro 2008). The dilution factor, if applicable, was applied to absorbance and fluorescence spectra in accordance with Beer's Law.

A.2 Calculation of absorbance and fluorescence indices

Optical proxies for DOC characteristics were calculated from absorbance and fluorescence spectra. DOC indices based on absorbance included $SUVA_{254}$, E2:E3, E4:E6, CDOM and the spectral slope ratio (SR). $SUVA_{254}$, calculated as the absorbance at 254 nm (abs_{254})

normalized by DOC concentration, varies in proportion to the concentration of aromatic DOC (Traina, Novak, and Smeck 1990; Weishaar et al. 2003). The ratio of absorption at 250 to 365 nm, called E2:E3, has been used to track relative changes in DOC molecular size, where a decrease in E2:E3 indicates a relative increase in high molecular weight DOC that absorbs more light at longer wavelengths (De Haan and De Boer 1987; Peuravuori and Pihlaja 1997; Helms et al. 2008). The ratio of absorbance at 465 to 665 nm (called E4:E6), has been used in recent years as a humification indicator (Helms et al. 2008), as it has been found to be better correlated to molecular size, O:C and C:N ratios, total acidity, and carboxyl content than to aromaticity (Y. Chen, Senesi, and Schnitzer 1977; Senesi, Miano, and Provenzano 1989). Spectral slope values (*S*), calculated over different sections of the absorbance spectra, have also been used to examine changes in DOC character (Blough and Vecchio 2002), including tracking DOC source, biological and photochemical alterations (Stedmon and Markager 2001; Obernosterer and Benner 2004; Osburn and Stedmon 2011), as well as molecular weight and aromaticity (Blough and Green 1995; Helms et al. 2008). Values of *S* are calculated using a non-linear fit of the absorbance spectra over ranges λ to λ_{ref} using the following exponential function:

$$a(\lambda) = a(\lambda_{ref})e^{-S(\lambda - \lambda_{ref})} \qquad \text{(Equation A.2)}$$

where a is the Naperian absorption coefficient (m^{-1}) at wavelengths λ and λ_{ref} (nm), over which the spectral slope (*S*) is calculated (e.g., Twardowski et al. 2004). The spectral regions of 275-295 nm ($S_{275\text{-}295}$) and 350-400 nm ($S_{350\text{-}400}$) within log-transformed spectra are typically used to calculate the slope ratio (SR), as the first derivative of the natural log spectra within these ranges previously showed the greatest sensitivity over an extensive range of aquatic ecosystems (Helms et al. 2008). These wavelength ranges were thus used to

calculate slope ratio as reported throughout this thesis. Previous studies have shown that S_r, calculated by the ratio of $S_{275-295}$ to $S_{350-400}$, is inversely related to DOC molecular weight, aromaticity, and vascular plant inputs to DOC (Helms et al. 2008; Spencer et al. 2010; Osburn and Stedmon 2011; Spencer and Butler 2012). Total chromophoric dissolved organic matter (CDOM) absorption was calculated as the integral of the absorbance spectra from 250 to 450 nm (Helms et al. 2008).

We also examined several indicators calculated from fluorescence spectra. The fluorescence index (FI) was calculated as the ratio between emission intensity at 470 nm and 530 nm at an excitation wavelength of 370 nm (McKnight et al. 2001; Cory and McKnight 2005). FI has been related to the concentration of aromatic DOC, as well as lignin carbon-normalized yields, where a higher FI value indicates DOC that is dominated by microbially-derived DOC. The humification index (HIX), quantifies the red shift that occurs in fluorescence emission upon increased humification of humic organic matter, thus describing the degree of humification. Several fluorescence regions have been proposed to calculate HIX (for example: Beggs and Summers 2011); here, we calculated HIX according to the method proposed by Ohno (2002) by calculating the area under the red-shifted part of the fluorescence spectra at an excitation of 254 nm (from an emission of 435 to 480 nm), and dividing this by the sum of the area under this red-shifted peak with a blue-shifted peak (spanning 300 to 354 nm at an excitation of 254 nm) (Ohno 2002). The Freshness Index (BIX) describes the proportion of DOC recently formed by biological activity, calculated as the ratio between the beta and alpha peaks within the fluorescence spectrum, where beta and alpha peaks correspond to fluorescence intensities at emissions of 380 nm and 430 nm, respectively, for an excitation wavelength of 310, with intensities normalized by the

maximum intensity occurring over emission wavelengths from 420 to 436 nm for excitation at 310 nm. The beta peak corresponds to recently formed DOC, and the alpha peak to older, more decomposed DOC forms (Parlanti et al. 2000; Huguet et al. 2009; Wilson and Xenopoulos 2009).

In addition to these indices, peak intensities within previously identified EEMs regions were employed to investigate DOC functional types of interest. Both peaks A and C have been previously correlated to humic-like fluorescence (Coble 1996). Peak A is the maximum fluorescence intensity at emission wavelengths of 380-470 nm resulting from excitation at 240-270 nm. Peak C was calculated as the max intensity occurring between an excitation range of 300 to 340 nm, and an emission range of 400-450 nm. Peak C has been associated with DOC aromaticity and hydrophobicity (Kalbitz, Geyer, and Geyer 1999), and used to differentiate between sources of DOC (where fresher DOC tends to fluoresce more). Cumberland and Baker (2007) correlated Peak C to THM formation potential (Bieroza, Baker, and Bridgeman 2009).

Peaks B (tyrosine-like fluorescence) and T (tryptophan-like fluorescence) (Coble 1996) have been used as indicators of protein-like compounds, as well as indicators of certain polyphenols, tannins and lignin (Maie et al. 2007; Hernes, Bergamaschi, and Eckard 2009; Beggs and Summers 2011). We calculated peak B by finding the max fluorescence intensity over an excitation range of 240-290 nm, and an emission range of 300-320 nm, while peak T was calculated as the maximum fluorescence intensity over an excitation range of 260-290 nm, and an emission range of 326-350. All four peaks were normalized to DOC concentration. Lastly, the ratio between peak T and peak C was calculated. Previous studies

have found that the T/C ratio is indicative of the biochemical oxygen demand relative to DOC, and has been used to track wastewater effluent within a stream (Baker 2001).

Appendix B: Chapter 3 supplemental information

B.1 Diurnal DOC dynamics

To investigate possible diurnal trends within DOC concentrations, stream DOC concentration was plotted for the two driest months (July and August) to focus on phenomena not connected to precipitation events. Figure B.1A ([DOC] concentration during this time) shows the importance of discharge in stream DOC dynamics, with peaks in discharge mirrored by stream DOC concentrations. Diurnal cycles within DOC concentration are apparent beyond the short timescale peaks. These diurnal cycles tended to peak during hours in the later afternoon, where minimal DOC concentration values tended to occur in during the night. These cycles tended to reflect diurnal cycles in discharge (Figure B.1B), which (when not influenced by precipitation events) tended to drop following increases in air temperature, likely spurred by increase in plant evapotranspiration spurred by increasing solar radiation during the warmest, sunniest parts of the day (Figure B.1C). DOC concentrations vary between the three years for which a complete DOC trace during the July-August period, where the difference between years is greater than the difference due to diurnal cycles (which tended to vary between 0.1 - 0.3 mg/L over a 24 hour time period).

Diurnal cycles within DOC concentration can be difficult to capture, given the high degree of temporal resolution needed (making high frequency or in situ sampling necessary). The amount by which DOC concentrations vary can be quite small (< 0.2 mg/L), and can be beyond the resolution of many analytical approaches (Spencer et al. 2007). Previous studies have thus shown conflicting evidence of diurnal DOC cycles. Studies by both Manny et al. (1973) and Spencer et al. (2007) showed little evidence of diurnal cycles within the resolution of their measurements; Spencer et al. did, however, show diurnal cycles within

absorbance parameters a_{350} and CDOM fluorescence (Manny and Wetzel 1973; Spencer et al. 2007). Other studies have suggested that DOC concentrations do undergo diurnal cycles, finding that DOC concentrations peak either during night time hours within a agricultural channel (Harrison et al. 2005), or during the late afternoon within a stream environment (which reflects the diurnal timing within summer month DOC dynamics in our own study) (Kaplan and Bott 1982).

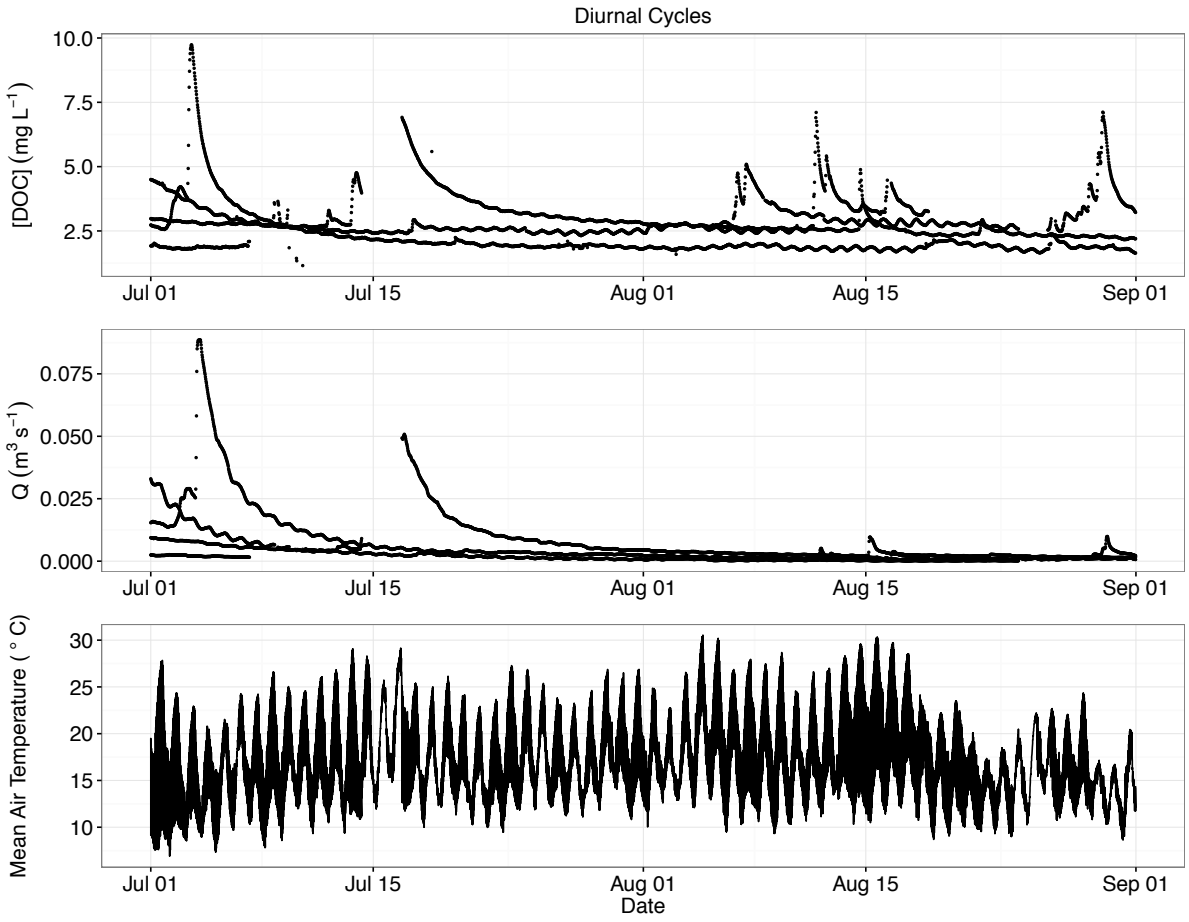

Figure B.1 Diurnal cycles in DOC mirror that of discharge (Q). Daily trace of DOC concentrations for dry months (July – August), alongside discharge (Q) and mean daily air temperature. Multiple traces within DOC and Q indicate measurements made within different years between July – August.

B.2 Characteristics of stream OM: Diurnal cycles in spectral proxies

We sought to investigate the presence of short-term dynamics (such as diurnal cycles within in situ parameters) within absorbance spectral parameters, as well as how relationships between different spectral parameters describe mechanisms occurring within the stream.

Figure B.2 shows abs_{254}, $SUVA_{254}$ and slope ratio for dry July and August months, in which DOC characteristics are least likely to be affected by precipitation events significantly altering hydrologic connectivity and delivery of DOC into the stream. As for DOC concentration (examined within the preceding section of this chapter), all three parameters exhibit prominent diurnal cycles. Measurements of abs_{254} tended to peak around 6:00 PM (later afternoon), with minimal concentrations during the early morning (around 4:00 in the morning), echoing DOC diurnal dynamics. Measurements of abs_{254} were more similar between years than either measurements of $SUVA_{254}$ or slope ratio. Diurnal cycles in $SUVA_{254}$ was less defined and showed inverse behavior when compared to abs_{254}, with minimum at early afternoon, and maximum during pre-dawn nighttime hours, indicating that aromatic carbon concentration within the stream peaks during the pre-dawn hours. Additionally, examining the $SUVA_{254}$ timeseries shows that $SUVA_{254}$ tends to decrease during times when DOC concentration and abs_{254} both increase, which may occur if the relative increase in DOC concentration is greater than the increase in absorbance at 254 nm (where DOC calculated over a larger spectral region by instrument manufacture). The slope ratio shows distinctive diurnal cycles that mirror abs_{254} and DOC concentrations, with minimums in the early morning (6:00 am), and maxima in later afternoon (5:00 PM), suggesting that concentrations of high molecular weight tends to peak when DOC, and aromatic DOC does. Similar trends in abs_{254} and slope ratio also show increased absorbance

of wavelengths closer to the UV region during the early afternoon, falling to an inflection point within the pre-dawn hours. These results echo diurnal behavior of stream DOC characteristics described by Spencer et al. (2007), who noted a diurnal cycles in abs_{350} nm which tended to peak in early evening, with lowest values around dawn (Spencer et al. 2007). Slope ratio tended to peak during the early evening/late afternoon, during which time $SUVA_{254}$ tended to reach a minimum, suggesting that stream aromaticity decreased through the day. This was noted within the dry summer months (less impacted by precipitation events that have a large impact on stream characteristics), where diurnal cycles in slope ratio were also noted within January (Figure B.2). Such diurnal trends suggest that the concentration of humic DOC decreases, which could indicate a larger contribution of baseflow to stream discharge during warmer hours of the day (which could mimic cycles in plant evapotranspiration on the site).

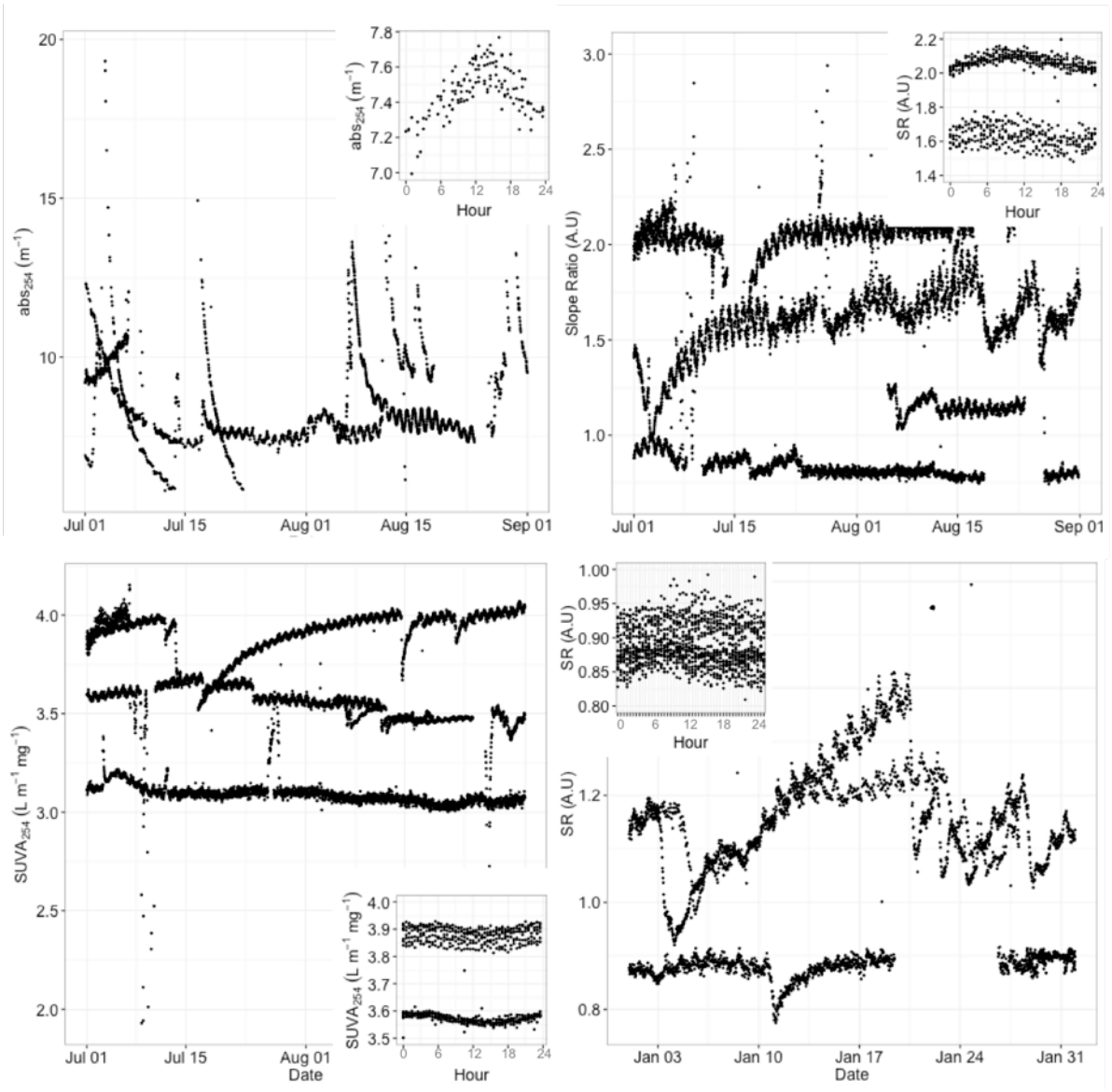

Figure B.2 Diurnal cycles in absorbance DOC characteristics. $SUVA_{254}$, abs_{254} and slope ratio all demonstrated diurnal cycles during dry, warm summer months, while slope ratio exhibited such cycles even during wet winter months (lower right). Large figures show measurement timeseries over the summer months, where multiple lines show measurements taken over different years. Inset figures show measurements compiled according to hour of the day at which it was collected, to illustrate peaks within diurnal cycles.

Although grab samples were taken on alternating day-night cycles (either at 12:00 PM or 12:00 AM), fluorescence characteristics (parsed also by hydrologic time period), did not show distinctive characteristics between samples taken at night versus day (as shown by boxplots showing mean, 25% and 75% intervals, Figure B.3). In situ absorbance indices tended to vary most between hours in the late afternoon and early morning (during the dry July-August period), thus it is possible that the sampling interval did not capture periods of greatest difference. Diurnal cycles represent alterations on a relatively small scale, and are thus difficult to capture without sampling at a high temporal scale. Diurnal cycles may thus exist within fluorescence parameters, where the sampling approach employed by this study may not be sufficient to capture sensitive perturbations (Figure B.3).

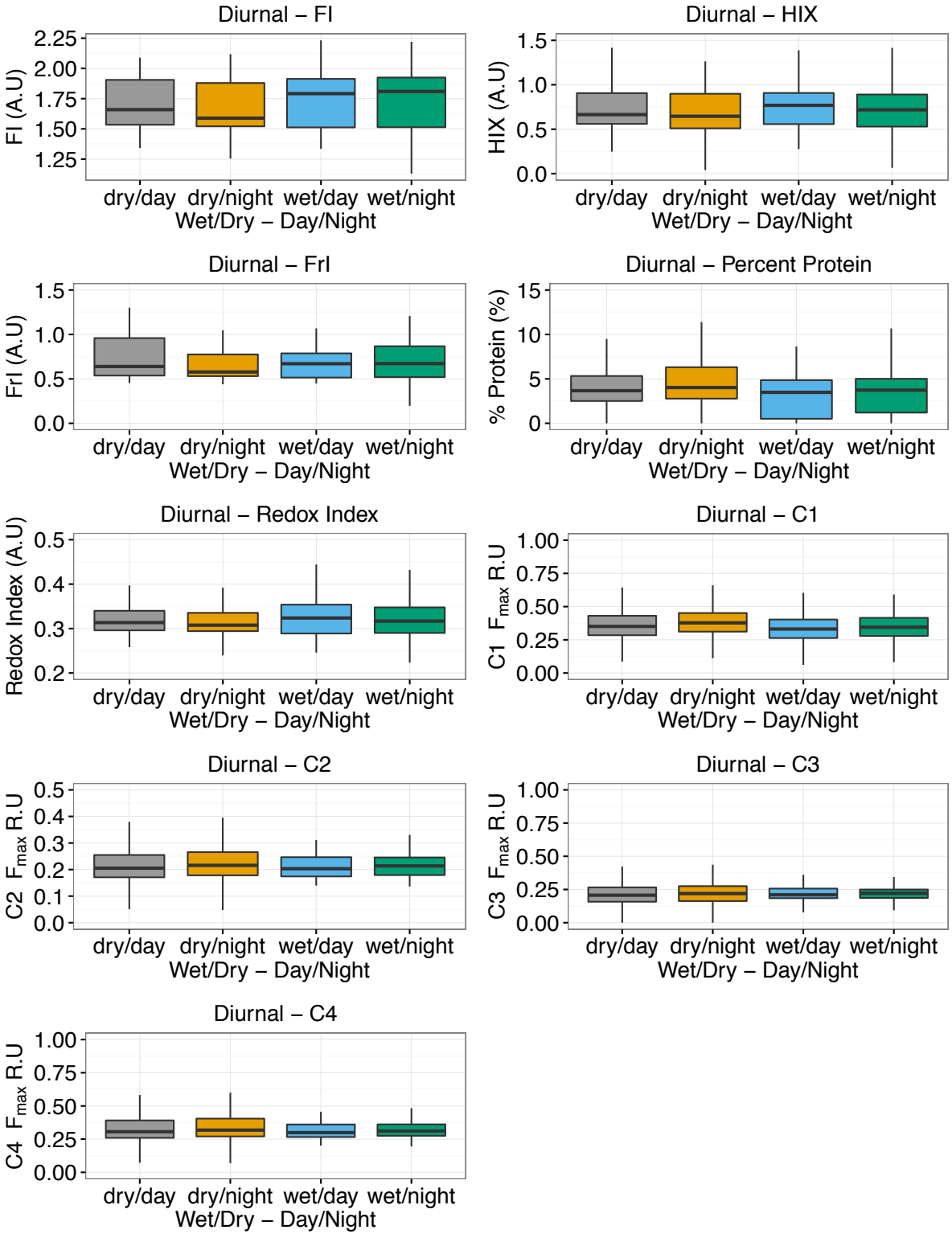

Figure B.3 Fluorescence characteristics parsed by whether they were collected during the day or night.

B.3 Timeseries analysis – discharge, DOC concentration and flux

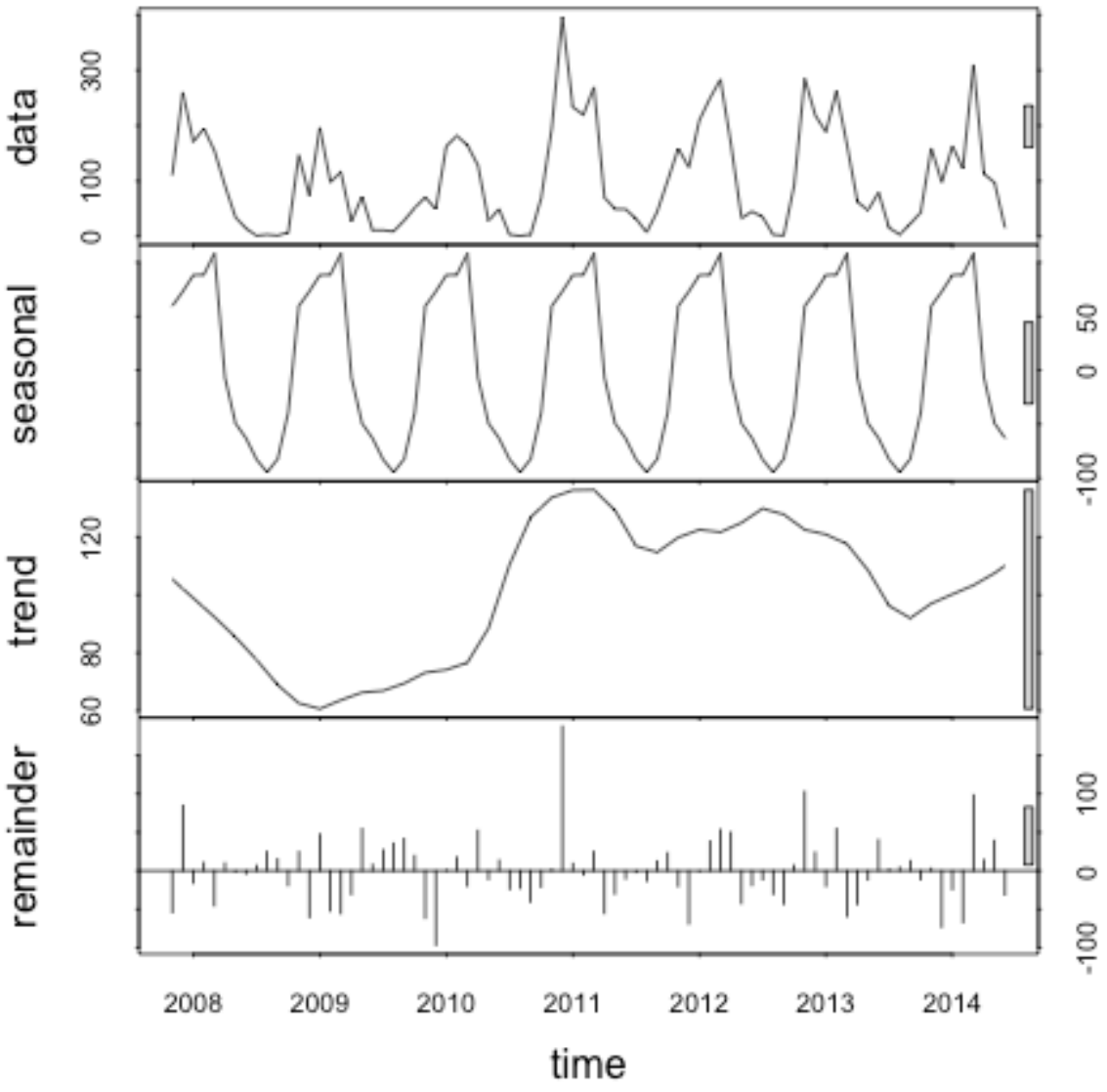

Figure B.4 Timeseries analysis of stream discharge. Stream discharge data (top; L s^{-1}) is broken down into seasonal, trend and residual components.

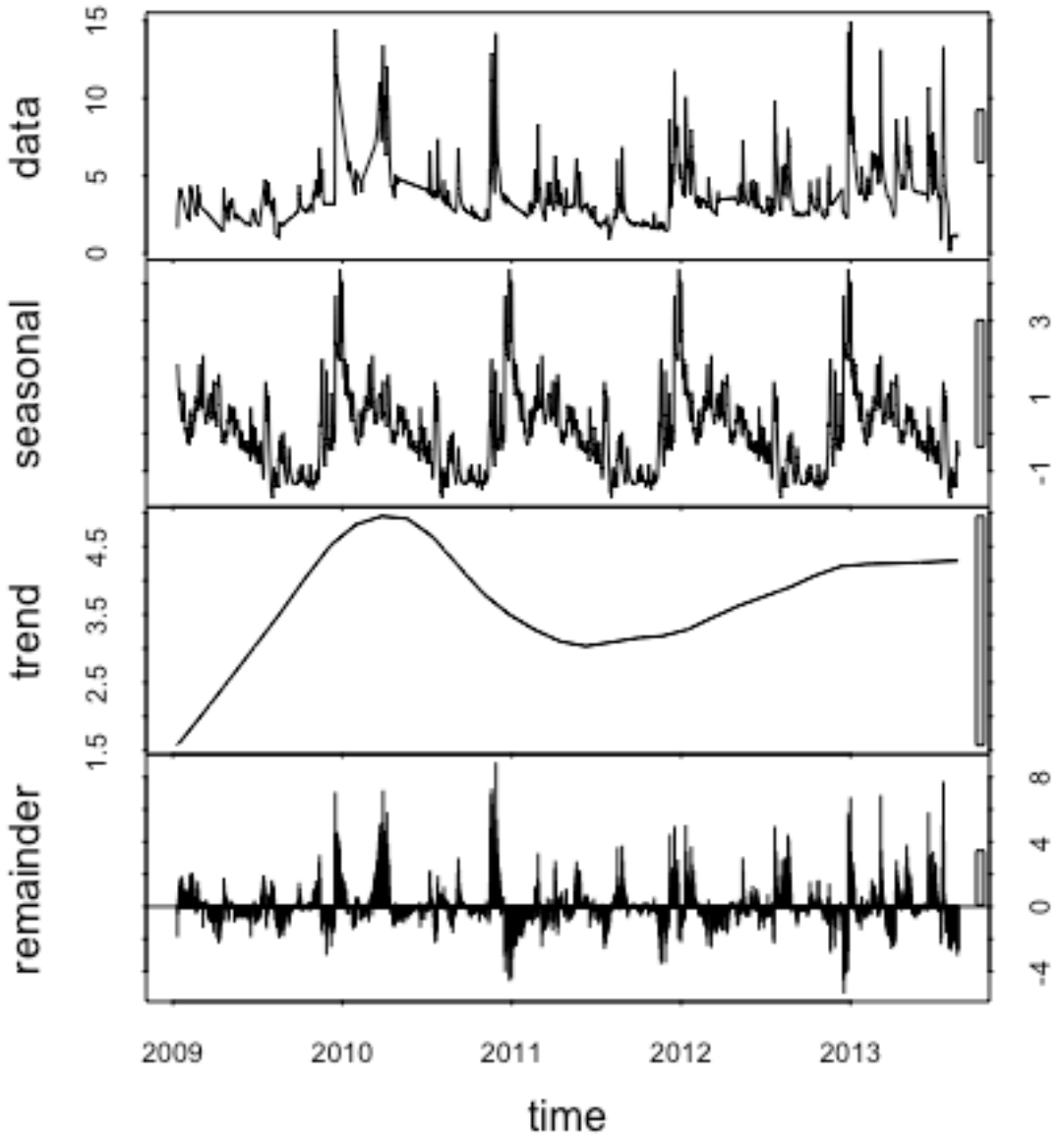

Figure B.5 Timeseries analysis of DOC concentration. DOC concentration data (top, in mg L^{-1}) is broken down into seasonal, trend and residual components.

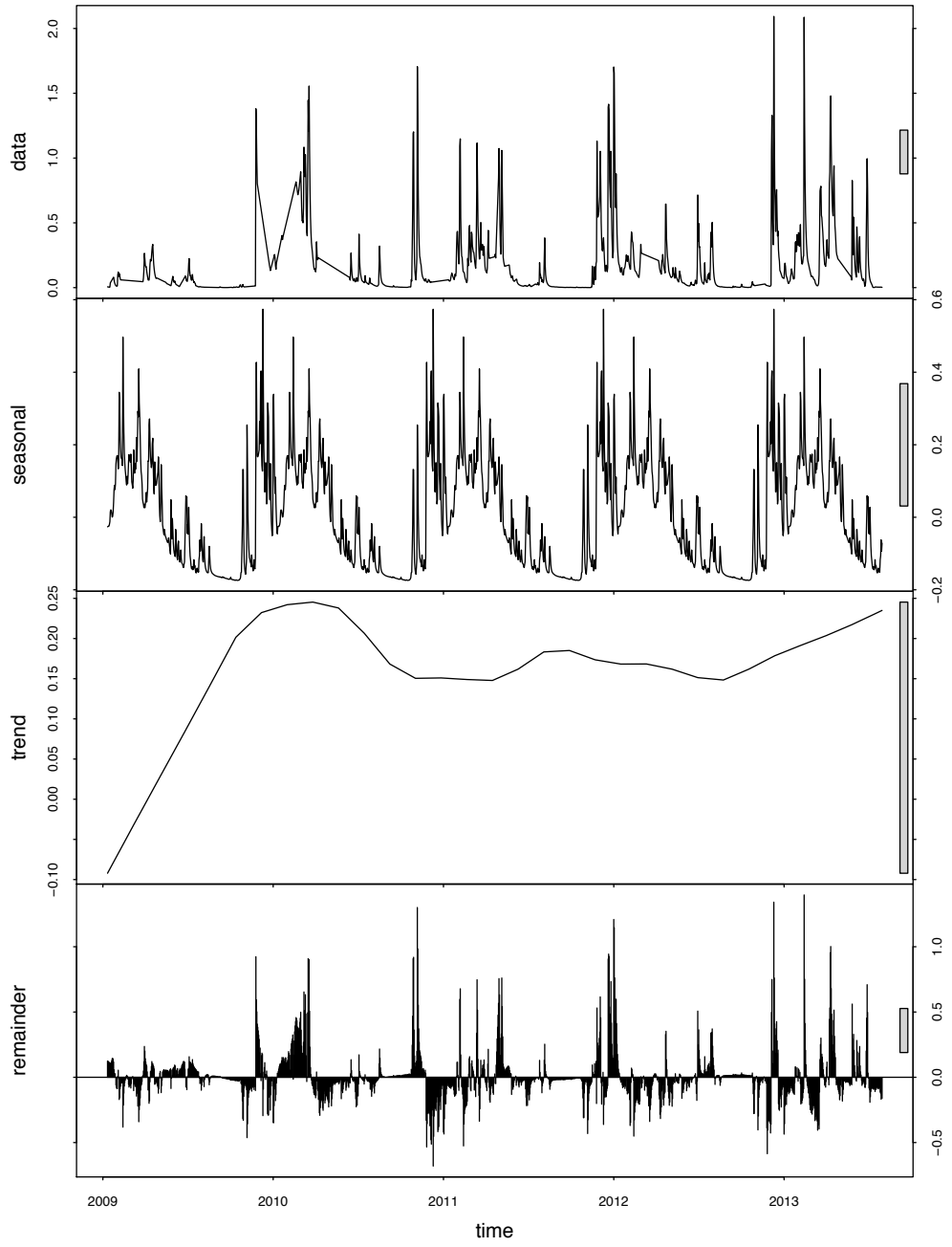

Figure B.6 Timeseries analysis of daily DOC flux. DOC flux data (top; kg*day^{-1}*ha^{-1}) is broken down into seasonal, trend and residual components.

B.4 Using spectral proxies to differentiate by pre/post-harvest

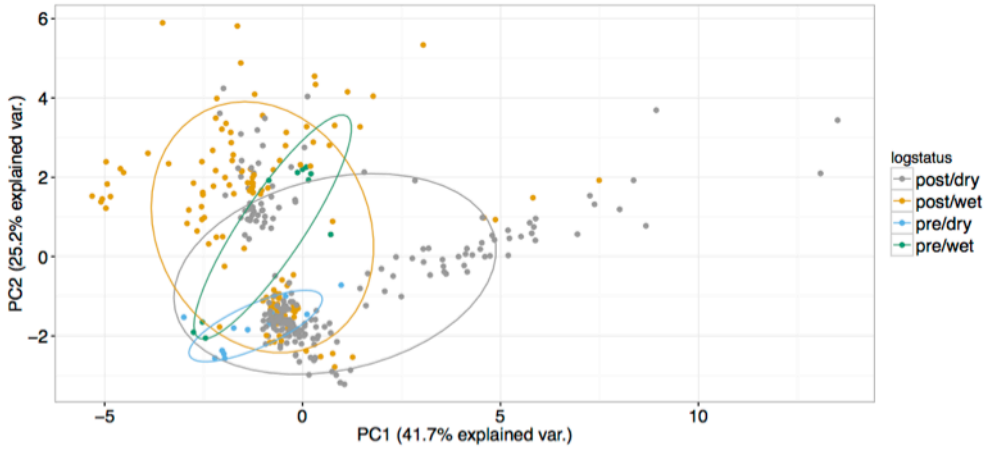

Figure B.7 PCA on absorbance and water quality (in situ), and fluorescence (discrete samples) parameters

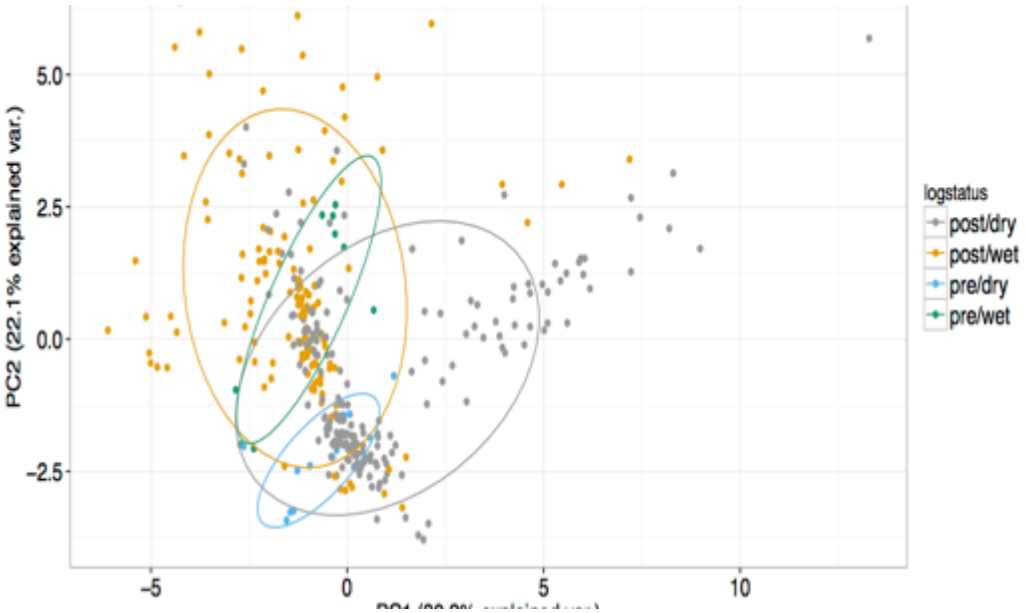

Figure B.8 PCA on fluorescence parameters (discrete samples only)

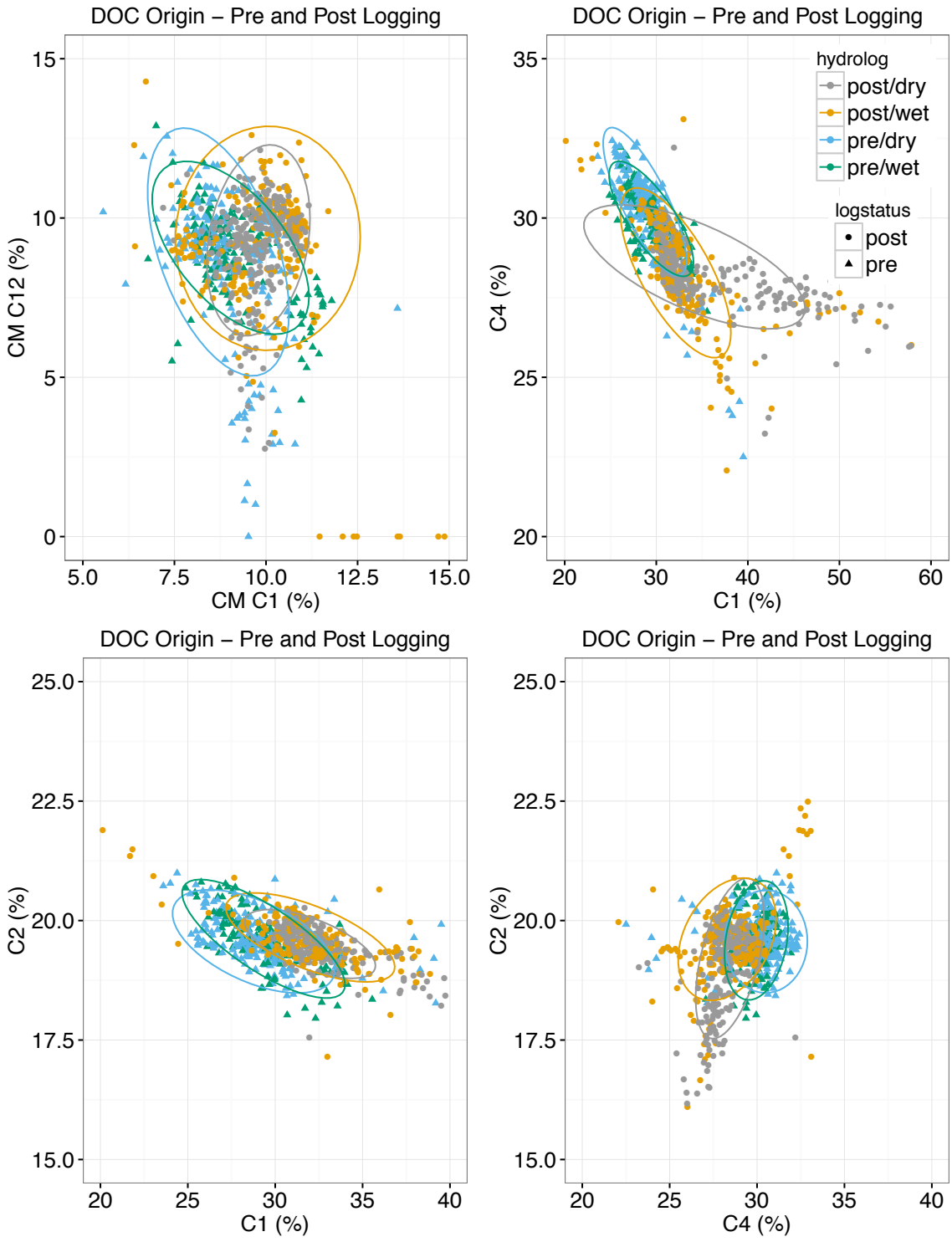

Figure B.9 Fluorescent DOC characteristics to differentiate on the basis of hydrologic time period as well as pre/post-harvest status.

Appendix C: Supplemental section - connecting terrestrial to stream organic matter by investigating soil organic matter

C.1 Introduction

Aquatic systems are often intrinsically linked to terrestrial systems through the hydrologic flow of water through soil. This flow of water links the biogeochemical of elements and nutrients such as carbon within terrestrial soil ecosystems to that within streams and other receiving waters. Given this connectivity, studies have begun to explicitly connect soil organic matter (including the quantity as well as characteristics of OM) to stream OM. Part of the impetus for this is to better understand terrestrial-aquatic feedback within biogeochemical cycling of carbon, as well as using OM stream characteristics to determine origins within streams dominated by terrestrial sources of OM, such as headwater streams (Temnerud et al. 2007; Bishop et al. 2008).

The fraction of organic matter of particular interest within the soil is the water-soluble fraction that can be transported via hydrologic flowpaths into receiving waters, which is a small part of the overall OM present within soil. Within soils, water-soluble organic matter (WSOM) exists within a dynamic equilibrium between particulate, mineral-bound and soil pore fractions (Chantigny 2003). This equilibrium and WSOM chemistry is influenced by environmental factors like aridity (Akagi, Zsolnay, and Bastida 2007), the occurrence of forest fires (Vergnoux et al. 2011), vegetation (Bu et al. 2010), and land uses (Chantigny 2003), as well as soil factors including salinity and acidity (Provenzano et al. 2008; Lui et al. 2009). WSOM can be flushed into receiving waters during precipitation events and increases in groundwater levels. Thus, factors such as land use change that affect soil OM chemistry can also have a corresponding effect on stream OM characteristics (Wilson and Xenopoulos 2008; Fellman, Hood, and Spencer

2010), demonstrating the linked nature of these ecosystems and large-scale effects of external controls on soil OM within a particular watershed.

Investigating WSOM Properties – Links to Stream Chemistry

The ease and sensitivity of spectrophotometric measurements have resulted in the evolution of their use parsing stream OM characteristics to infer hydrologic connectivity between terrestrial soil environments and receiving waters. Only a small proportion of soil OM is mobile (Boyer and Groffman 1996), where processes of mineralization and humification are key in determining soil OM mobility within the soil column (Nelson, Dictor, and Soulas 1994). Soils closer to the surface tend to be enriched in terrestrial organic matter that contains aromatic-rich compounds including tannins, lignins and polyphenols, which is depleted within deeper, mineral-rich horizons (Green and Blough 1995; Del Vecchio and Blough 2004). Such trends have been observed in extracted soil OM, where $SUVA_{254}$ has been observed to decrease with soil depth (Corvasce et al. 2006). Soil water OM is also a function of soil microbe activity, where depth and soil composition has been observed to have a smaller effect on soil microbe activity (Buss et al. 2005; Eilers et al. 2012; Gabor et al. 2014). Studies connecting the mobile fraction of soil OM to stream characteristics has found that different soil OM fractions have different mobility when the soil is saturated, and that such saturation events transport pulses of humic soil OM to waters within rain and snow-dominated catchments (Hornberger, Bencala, and McKnight 1994; Hood, Williams, and McKnight 2005; van Verseveld, McDonnell, and Lajtha 2008; Inamdar, Singh, et al. 2011; M. A. Burns et al. 2016). This has lead into much interest in using spectrophomeric OM signatures to trace hydrologic connectivity and streamflow generation sources between terrestrial and aquatic systems under different hydrologic conditions (Vidon, Wagner, and Soyeux 2008; Miller and McKnight 2010; Nguyen, Hur, and Shin 2010; Inamdar, Singh, et al. 2011; Larsen,

Harvey, and Skalak 2015). A recent study by Burns et al. (2016) successfully connected humic-like fluorescent soil OM fingerprints to stream OM characteristics, chemically demonstrating the soil water contribution to receiving waters during times of snowmelt (Burns et al. 2016).

Approaches for investigating soil OM

There are a variety of methods of determining soil OM, specifically the soil pore OM presumably available for transportation to receiving waters. This includes methods of determining soil extractable OM, as well as OM specifically within soil pore water. Common approaches for sampling soil pore water includes soil pore tension lysimeters as well as piezometers. Despite the application of both approaches, such in situ sampling of soil pore water can have a number of issues. Sampling via tension samplers can introduce artefacts such as preferential flow paths upon installation (Peters and Durner 2009; Miró et al. 2010), alter the distribution of water within soil (Mertens, Diels, and Feyen 2007), can change water chemistry depending on the inertness of the material that comes into contact with soil pore water (Perdrial et al. 2012), and may not produce a sample reflective of a site, depending on how heterogenous water flow paths and hydraulic conductivities are within a site (Weihermüller, Kasteel, and Vereecken 2006).

Extracting soil OM with a multitude of different solutions, and under different conditions, is likewise used to investigate the extractable fraction of soil OM (Jones and Willett 2006; McDowell and Zsolnay 2006; Perdrial et al. 2012). Common extraction solvents include distilled water, as well as K_2SO_4, KCl, NaH_2PO_4, $CaCl_2$ and $NaNO_3$, where extraction conditions (temperature, pH, shaking velocity, extraction time, soil to solvent ratio, sieved vs. unsieved soils, field moist vs. dried soils) can vary between studies (Zsolnay and Görlitz 1994; Reemtsma and Bredow 1999; Corvasce et al. 2006; Jones and Willett 2006; Rennert and Gockel 2007; Fest, Temminghoff, and Comans 2008; Bu et al. 2010). Firstly, these diverse approaches make it

difficult to compare results between studies. Different extraction conditions also alters the type of OM extracted from soil – this makes interpretation of soil extracted OM characteristics examined using spectrophotometric means difficult, given the complexity of the soil OM pool, and the added complexity posed as different extraction techniques extract diverse forms of OM. This includes the amount of WSOM extracted; previous studies showed that K_2SO_4 tends to extract the most WSOM, and $CaCl_2$ the least (Rennert and Gockel 2007; Provenzano et al. 2010; Gabor et al. 2015). WSOM spectrophotometric measurements also differ depending on extraction method; for example, water extracts often exhibit a high degree of scatter due to poorly flocculated silicon colloids and clays, resulting in higher measurements of absorbance (Gabor et al. 2015). This includes $SUVA_{254}$, a widely used proxy for aromatic carbon (Traina, Novak, and Smeck 1990; Weishaar et al. 2003). Extracts can also differ in terms of fluorescence intensity independent of the concentration WSOM extracted (Provenzano et al. 2010). In addition to complexity arising from the lack of a standard extraction method (Rennert and Gockel 2007; Provenzano et al. 2010), the act of collecting and analyzing soil samples can disrupt soil aggregates, and alter extractable DOC concentration and composition (Bartlett and James 1980; Kaiser, Kaupenjohann, and Zech 2001; Fest, Temminghoff, and Comans 2008).

C.2 Study overview

Given the potential drawbacks of either approach, we employed both soil extractions and soil pore water sampling using tension lysimeters towards investigating potentially hydrologically active fractions of soil OM. The overarching aim of this study is to investigate soil OM characteristics as a means of linking to stream characteristics, towards using spectrophotometric indices as an indicator of hydrologic connectivity and terrestrial origins. This study has three specific aims: 1) compare soil OM properties determined through both soil extraction and

sampling of soil pore water via lysimeters; 2) determine trends in soil OM characteristics with depth, and 3) how soil OM characteristics, and trends with depth, compare to stream OM characteristics within the same period.

C.3 Methods

Soil characteristics[9]

The study site located 10 km south-east of Campbell River on Vancouver Island, Canada (49°30′N–49°55′N, 124°50′W–125°30′W). Soil at the study site is characterized by a humo-ferric podzol with a gravelly sandy loam texture (soil order = podzol; great group = humo-ferric podzol; subgroup = duric humo-ferric podzol). A shallow forest litter layer (characterized by low decomposition of forest biomass) overlays a shallow surface organic layer that is on average three cm deep, but can range from 1 to 10 cm in-depth (Table C.1). Beneath this shallow organic layer is a deep BF mineral layer (approximately 10-80 cm deep), characterized by an accumulation of iron and aluminum oxides, which imparts a characteristic red colour to the soil (Table C.1). A transitional layer at the base of the BF layer is demonstrated by a change in colour from red to orange-yellow, denoting the transition from the deep BF layer to a dense, yellow basal till layer. The low permeability of this layer (depth ≥ 80 cm) is demonstrated by the presence of dark mottles at the top of the layer, showing where water accumulates creating oxidising conditions during periods of soil saturation. Previous studies have demonstrated that the total soil carbon content of these soils to 1 m was 11.5 kgC/m^2, 2.5 kgC/m^2 of which is contained within the surface organic layer.[10]

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[9] SOilx http://www.soilx.ca/site/?id=16

[10] ftp://daac.ornl.gov/data/fluxnet/fluxnet_canada/data/BC-DFir1949/Flux/BC-DF49_Flux_metadoc_final.txt

Soil Depth (cm)	Sampling	Horizon	Description
1 cm - 10 cm (average = 3 cm)	Soil Extract	Organic (AH)	Mineral horizon with organic enrichment from surficial forest litter layer
13 - 40 cm	Lysimeter; Soil Extract	BF	Thick mineral layer dominated by iron and aluminum oxide accumulation, giving reddish colour. Relatively low organic C content (0.5 -5%).
38 - 47 cm	Lysimeter, Soil Extract		
64 - 75 cm	Lysimeter; Soil Extract		
> 80 cm	-	Basal till (C horizon)	Dense, duric basal till layer with low permeability. Presence of mottles at the top indices oxidizing conditions due to water accumulation at the top during wet times of year.

Table C.1 Site soil characteristics by depth

Groundwater analysis

Lysimeter deployment and analysis

Ceramic suction lysimeters were installed at four depths (within the riparian zone adjacent to the stream). We utilized lysimeters (1900, SoilMoisture Equipment Corp, Santa Barbara, CA) that consisted of a PCV tube with a permeable ceramic cap a porous ceramic cup (2 bar air-entry). These lysimeters were installed by digging specific pits, taking care to disturb as little of the surrounding soil structure as possible to minimize introduction of sampling artefacts (preferential flow paths, etc). The vacuum within each lysimeter was set to 11 PSI using a hand pump. Samples were collected on a monthly basis over a year timespan (July 2013 – July 2014). Field collected samples were kept cool during transport, filtered at 0.7 μm (pre-combusted glass filters, Millipore, Merck KGaA, Darmstadt, Germany) and stored at 4°C until analysis. Samples were analysed for DOC and total nitrogen (TN) concentration using high temperature combustion (Shimadzu Scientific Model TOC-V CSH/CSV, Shimadzu Corporation, Kyoto, Japan), and for

quality proxies via absorbance and fluorescence spectroscopy as described for streamwater grab samples (described in Appendix A). Concentrations of anions including fluoride, chloride, bromide, nitrate, nitrite, phosphate and sulphate were determined using liquid ion chromatography (Advanced Compact IC, Metrohm AG, Herisau, Switzerland).

Soil extract experiment

To further investigate how spectrally-determined organic matter proxies change with soil depth, soil extracts of samples was used in combination with lysimeter data. Three soil pits were dug to a depth of 80 cm (coinciding with an impermeable basal till layer) along the northern slope of the stream (between the stream and clearcut). These pits were dug within a 10 m proximity to the north-facing lysimeters represented within the study. Soil samples were collected on January 22, 2014.

Soil samples were taken at four depths within each of the three pits (Table 1). Sieved soil was partitioned according soil horizon, and samples from each pit analyzed separately. Soil was air dried and sieved at 2 mm, and extracted as per methods outlined by Jones et al.; (Jones and Willett 2006) briefly, 1:5 soil-to-liquid solutions were made by adding samples to either distilled water, 0.5 M K_2SO_4 and 2 M KCl in PE bottles. Soil extract solutions were then shook at room temperature at 25°C for 1 hour. Soil extracts were then centrifuged, filtered (0.7 μm pre-combusted glass filters, Millipore, Merck KGaA, Darmstadt, Germany), and analyzed for DOC and total nitrogen (TN) via high temperature combustion (Shimadzu Scientific Model TOC-V CSH/CSV, Shimadzu Corporation, Kyoto, Japan). DOC quality was determined through fluorescence and absorbance spectrophotometry as previously described for streamwater samples.

Spectrophotomeric measurements

Measurements of excitation-emission matricies from filtered samples were made over an excitation range of 240-600 nm (2 nm increments), and an emission range of 249-620 nm (~2 nm increments) (Aqualog, Horiba, New Jersey, United States). Absorbance measurements were made simultaneously over a range of 240-800 nm, and an increment of 2 nm. Strongly absorbing samples were diluted on an optical density ≤ 0.2 O.D at 254 nm. Fluorescent EEMs were corrected for instrument response, inner filter effects, blank corrected, and Raman normalized (Lawaetz and Stedmon 2009). The first and second Raleigh peaks were removed (bandpass = 12 nm); the first band was replaced with 0's to reduce the introduction of artefacts, and the second peak replaced with interpolated values. Both the first and second Raman peaks removed and compensated by interpolation (Murphy et al. 2013). Corrected EEMs were used to calculate various fluorescence parameters, including fluorescence index (FI), humification index (HIX), freshness index (FrI), Peak A, Peak C Peak T, and overall fluorescence intensity (as described in more detail in Appendix A). EEMs corrections and calculation of fluorescence indices was accomplished in R (version 3.3.1, R Core Team 2016). To obtain information regarding the quality of organic matter fractions described by the 3-D EEMs spectra, corrected spectra were fit to a 13-component parallel factor analysis model (PARAFAC), from which the redox index and percent protein were calculated (Cory and McKnight 2005). Additionally, EEMs from both the lysimeter and soil extract samples were fit to a five-component PARAFAC model (Table C.2: description of PARAFAC peaks) (Stedmon et al. 2008; Murphy et al. 2013). This PARAFAC model was fit using non-negativity constraints, and all EEMs were normalized to the unit max prior to fitting the model. The appropriateness of the PARAFAC model was confirmed by minimizing the sum of square errors and by split half validation (Stedmon et al. 2008; Murphy et

al. 2013). All PARAFAC modelling was accomplished through established protocols using MATLAB (student version 2012a, 7.14.0).

Component Number	Ex positions (nm)	Em position (nm)	Peak Name	Description	References
C1	410	340	GG-PS	particle scatter	Gabor et al. 2015
C2	256 (320)	430	GG-SQ2	reduced semiquinone-like humic peak	Gabor et al. 2015
C3	286 (366)	520	GG-SQ1	reduced semiquinone-like humic peak	CM-C5 (reduced quinone-like), K-P3 (terrestrial humic) Gabor et al. 2015
C4	272	300	GG-P1	tyrosine-like protein peak	Gabor et al. 2015
C5	260	500	GG-SH	soil humic-like	Gabor et al. 2015

Table C.2 Characteristics of PARAFAC model fit to soil extract and lysimeter samples

C.4 Results and discussion

Comparing SWOM between lysimeters and soil extracts

Firstly, we set out to compare the two methods (extracts and soil pore water sampling) used to investigate soil OM. Although these methods sampling different fractions of soil OM (specifically, extractable OM versus soil pore OM), the lack of a standard method of examining soil OM characteristics makes careful comparison useful.

K_2SO_4 extracted the highest concentration of DOC when compared to either of the other extracts as well as the lysimeter samples (Figure C.1A, Table C.3). This has also been noted in previous spectrophotometric assessments of soil extracts, and has been attributed to the higher

divalent nature of the SO_4^{2-} ion, which results in a higher ionic strength solvent and greater extraction efficiency of OM bonded to mineral surfaces (Provenzano et al. 2010; Gabor et al. 2015). In comparing spectral characteristics between methods, it is apparent that extracts with distilled water show unique behaviour when compared to other approaches. Fluorescence signatures of water extracts are dominated by a PARAFAC component previously associated with scatter (Figure C.1, Table C.3, C1). Additionally, water extracts demonstrate significantly greater values for $SUVA_{254}$. Similar behaviour has been observed within previous studies, and scatter attributed to the presence of silicon colloids and clays that are difficult to remove via filtering and centrifugation. It has been suggested that salt solutions act to flocculate such colloids responsible, noting that scatter peaks are diminished within water extracts to which salt solutions have been added (Gabor et al. 2015). Indeed, this peak is much less evident within other extracts and lysimeter samples (<5% of overall fluorescence within K_2SO_4 and lysimeter samples; 12% of KCl extracts), suggesting that such colloids are present at a much lower concentration within these samples.

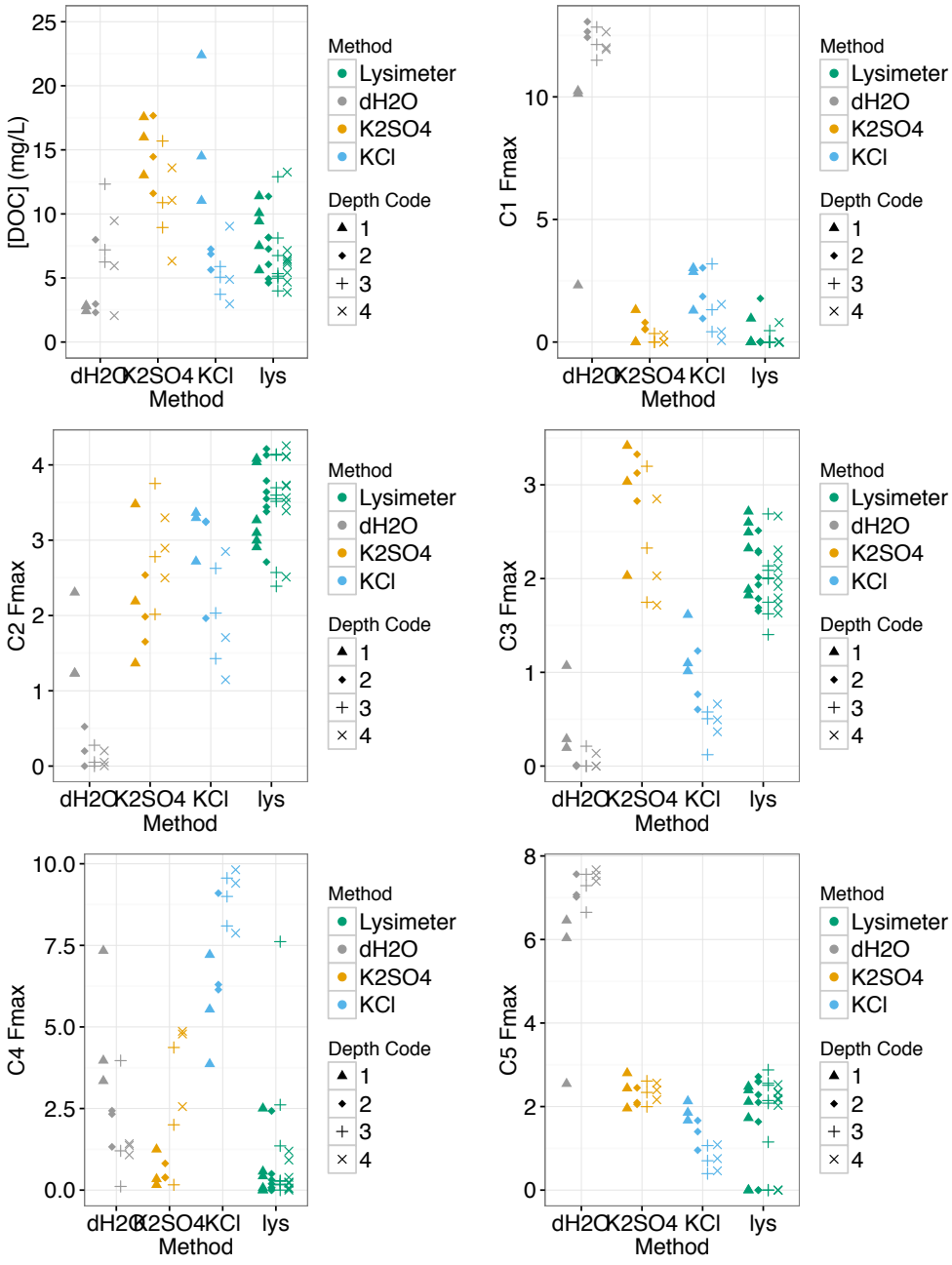

Figure C.1 Comparing characteristics between soil OM methods. OM characteristics as determined using three types of soil extraction methods and lysimeters. Depth codes for lyimsters 1 = 40 cm, 2 = 43 cm, 3 = 50 cm, 4 = 80 cm. Depth codes for soil extracts: 1 = 2-8 cm; 2 = 13-40 cm; 3 38 – 47 cm, 4 =64 – 75 cm.

Lysimeter fluorescence characteristics were dominated by reduced semi-quinone humic-like peaks (C2 and C3); F_{max} values were similar between salt extracts and lysimeters (Figure C.1), noting that C2 has a greater percentage of the overall fluorescent signature for lysimeter samples than for either salt (45% for lysimeter; 26% for K_2S0_4, 18% for KCl; Table C.3). A prominent tyrosine-like protein peak (C4) was most apparent within KCl extracted samples, suggesting that this type of extraction method resulted in the largest release of proteinous OM from soil OM when compared to K_2S0_4 or pore water samples. The increase prevalence of protein-like fluorescent OM within KCl samples is also demonstrated by increased values of percent protein, and elevated fluorescence indices (indicating a greater fraction of microbial OM relative to biomass OM).

Of the soil extraction methods, the fluorescence characteristics of K_2S0_4 extracts appear most similar to that of lysimeter samples (where K_2S0_4 extracts a significantly greater amount of DOC when compared to lysimeter samples). Even in this case, soil extract and lysimeter samples demonstrated unique characteristics in terms of fluorescence intensity and characteristics, echoing previous studies comparing soil extract to lysimeter properties (Perdrial et al. 2012; Gabor et al. 2015). Unlike results found by Gabor et al. (2015), a soil humic peak (C5) was present within both soil extract and soil lysimeter samples, perhaps indicating a greater degree of similarity between the type of OM present within soil extracts (especially K_2SO_4 samples) when compared with soil lysimeter samples. Theoretically, soil pore water sampling should be the more applicable method of examining the mobile fraction of soil OM relevant for examining linked terrestrial-stream OM cycles. As lysimeter deployment is not always possible (if soil pore water is limited, for example), and can have other issues including disruption of soil flowpaths, and difficulty in sampling the heterogeneity of soil characteristics within a particular context,

using extracting soil OM using K_2SO_4 within our specific context may provide the best comparison to the OM characteristics present within soil pore water.

	Soil Extracts			
	dH_2O (mean ± sd)	K_2SO_4 (mean ± sd)	KCl (mean ± sd)	Lysimeter (mean ± sd)
DOC (mg/L)	5.38 ± 3.36	13.07 ± 3.47	8.27 ± 5.50	7.20 ± 2.60
Total Nitrogen (mg/L)	0.38 ± 0.17	1.50 ± 1.00	1.83 ± 1.46	0.85 ± 1.34
abs_{254} (A.U)	90.80 ± 53.94	54.69 ± 28.87	0.75 ± 0.21	3.11 ± 1.00
$SUVA_{254}$ (L mg^{-1} m^{-1})	18.82 ± 12.23	4.09 ± 1.62	1.44 ± 0.40	3.11 ± 1.00
abs_{272} (A.U)	84.85 ± 50.38	45.25 ± 23.68	10.28 ± 7.46	18.61 ± 9.84
E2E3 (A.U)	1.99 ± 0.51	6.38 ± 0.33	5.55 ± 1.33	5.96 ± 0.86
E4E6 (A.U)	6.83 ± 1.46	6.83 ± 1.46	5.19 ± 1.80	47.59 ± 187.21
Slope Ratio (A.U)	0.68 ± 0.11	0.66 ± 0.01	0.72 ± 0.02	0.64 ± 0.03
Fluorescence Index (A.U)	1.33 ± 0.16	1.03 ± 0.27	1.68 ± 0.12	0.99 ± 0.60
HIX (A.U)	0.60 ± 0.06	0.85 ± 0.08	0.51 ± 0.11	0.69 ± 0.38
FrI (A.U)	1.49 ± 0.39	0.61 ± 0.07	0.87 ± 0.11	0.40 ± 0.29
Peak A	0.86 ± 0.38	1.89 ± 0.63	0.69 ± 0.34	186.13 ± 318.86
Peak C	0.08 ± 0.03	1.52 ± 0.77	0.39 ± 0.22	0.54 ± 0.35
Peak B	0.50 ± 0.18	1.28 ± 1.16	2.32 ± 1.64	0.48 ± 1.01
Peak T	0.23 ± 0.04	0.83 ± 0.51	1.34 ± 0.68	0.36 ± 0.52
OFI	4208.06 ± 1757.77	24,093.92 ± 11,368.40	7,550.71 ± 3,190.75	92,387.15 ± 141,082.95
C1 (%)	52.19 ± 12.62	3.76 ± 5.05	11.74 ± 7.66	1.26 ± 3.66
C2 (%)	2.68 ± 4.34	26.25 ± 6.53	17.75 ± 4.93	45.43 ± 11.74
C3 (%)	0.91 ± 1.94	28.79 ± 10.49	5.45 ± 2.89	26.21 ± 5.32
C4 (%)	12.54 ± 12.18	16.71 ± 14.94	56.58 ± 16.72	7.80 ± 12.26
C5 (%)	31.69 ± 5.69	24.50 ± 3.76	8.48 ± 3.83	19.30 ± 13.66
Percent Protein (%)	5.16 ± 4.55	4.92 ± 1.86	17.89 ± 3.24	4.26 ± 2.74
Redox Index (A.U)	0.86 ± 0.13	0.55 ± 0.04	0.46 ± 0.03	0.41 ± 0.09
CM C1 (%)	0.98 ± 2.05	10.43 ± 2.18	6.87 ± 0.94	10.20 ± 0.96
CM C2 (%)	10.02 ± 3.67	21.06 ± 1.04	19.10 ± 1.98	21.95 ± 0.77
CM C3 (%)	5.34 ± 0.73	6.81 ± 1.78	6.81 ± 1.78	5.88 ± 1.87
CM C4 (%)	71.52 ± 16.32	12.68 ± 5.27	15.61 ± 1.38	10.62 ± 7.50
CM C5 (%)	0.34 ± 1.05	12.11 ± 5.67	2.03 ± 1.00	6.21 ± 1.28
CM C6 (%)	0.00 ± 0.00	1.78 ± 1.96	0.17 ± 0.41	3.16 ± 1.82
CM C7 (%)	0.66 ± 1.30	9.41 ± 1.81	7.18 ± 1.22	8.35 ± 0.82
CM C8 (%)	4.20 ± 2.24	3.64 ± 1.01	10.85 ± 4.18	2.62 ± 1.39
CM C9 (%)	3.85 ± 1.10	6.08 ± 1.46	5.34 ± 1.14	4.40 ± 0.74
CM C10 (%)	0.30 ± 1.04	2.61 ± 1.13	1.49 ± 0.81	5.04 ± 0.60

	Soil Extracts			
	dH_2O (mean ± sd)	K_2SO_4 (mean ± sd)	KCl (mean ± sd)	Lysimeter (mean ± sd)
CM C11 (%)	0.81 ± 2.80	5.99 ± 3.06	7.80 ± 1.95	11.96 ± 2.68
CM C12 (%)	1.05 ± 2.18	6.12 ± 1.16	8.93 ± 1.43	7.97 ± 3.58
CM C13 (%)	0.96 ± 3.33	1.28 ± 1.40	7.04 ± 3.56	1.64 ± 1.96

Table C.3 Mean indices – by soil OM analysis method. Mean values for parameters associated with OM characteristics for soil extract and lysimeter samples

How do soil characteristics change with depth?

To investigate how extractable DOC characteristics change within soil depth, we investigated the effect of soil depth on soil extractable DOC within using both soil extracts as well as soil lysimeters. Both approaches were used, given the diversity of methods used to determine the fraction of soil OM most likely to be transported to the stream, either due to precipitation effects or alterations in groundwater level due to forest harvest.

Soil extracts – trends with soil depth

Extracts of soil organic matter was done using three commonly used solutions – distilled water (dH_2O), KCl and K_2SO_4 (Jones and Willett 2006). As previously discussed, although the three solvents are commonly used (given the lack of standard extraction protocol), extract approach can alter the type of soil OM extracted. Thus, results from all three extracts are presented.

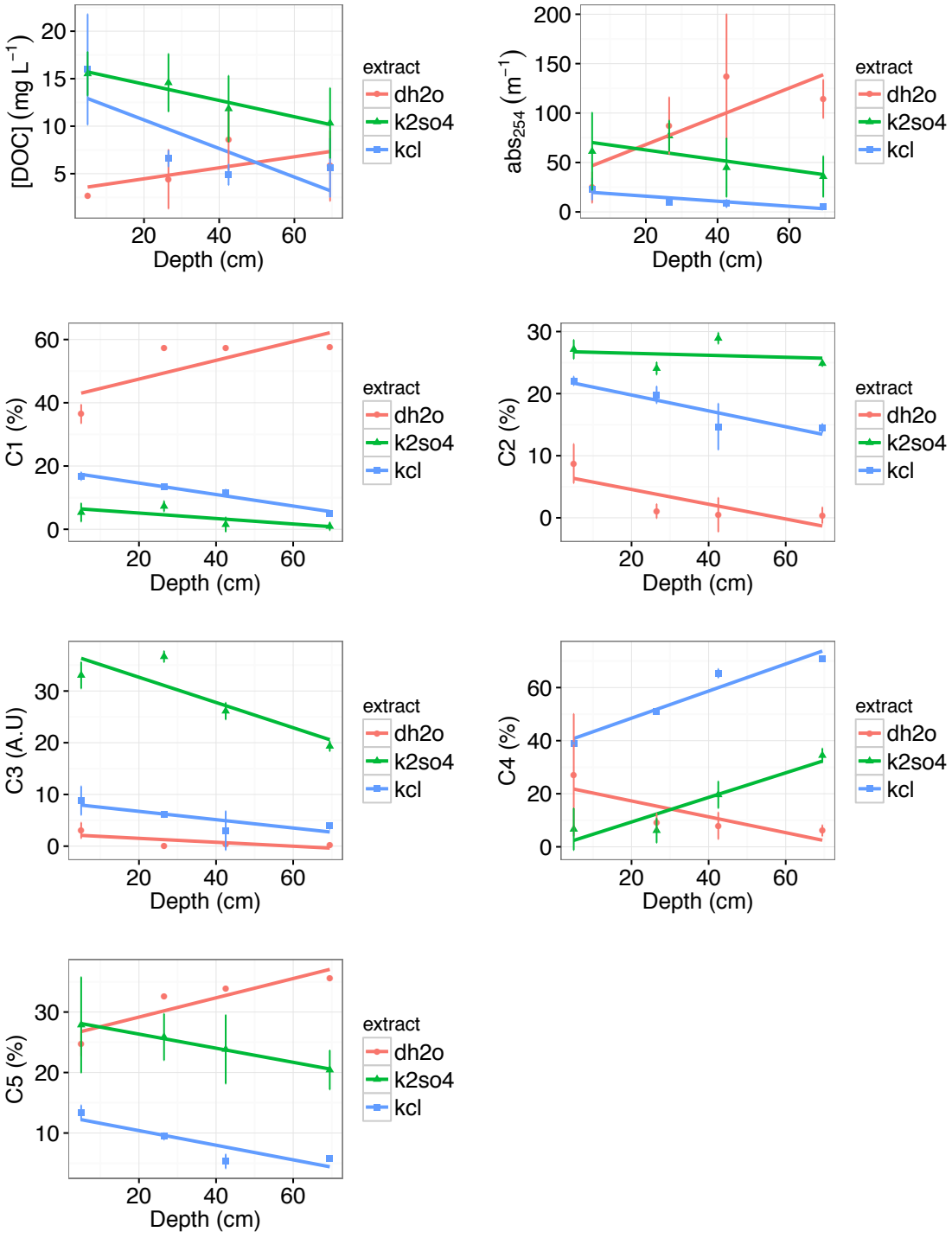

Figure C.2 Soil extract characteristics shown as a function of soil depth. The relationship between extracts made using all three solvents (water, KCl and K_2SO_4), are shown, despite the contrary behaviour of water extracts (possibly linked to the presence of colloids). DOC and abs_{254} decrease with soil depth. Additionally,

fluorescence characteristics are increasingly dominated by tyrosine-like fluorescence (C4) rather than humic-like fluorescence (C2, C3) with increasing depth for both salt extracts.

Table C.4 shows fit coefficients for linear relationships describing the changes in various WSOM characteristics within increasing soil sampling depth, and Figure C.2 shows trends in DOC concentration and PARAFAC components with increasing depth. Characteristics of samples extracted using water show behaviour contrary to that of salt extracts, in terms of general trends in parameters with depth. As previously discussed, it is likely that the presence of unflocculated colloids and clays within water extracted samples disrupt spectrophotometric measurements due to scatter, which has been observed within other studies (Gabor et al. 2015). However, trends in DOC and TN concentration (determined using high temperature combustion methods), were also counter to other extracts. Specifically, concentrations of both DOC and TN increased with depth for water extracted samples, which is also counterintuitive to commonly held understandings regarding soil processes (Bishop, Seibert, and Köhler 2004; Seibert et al. 2009). This discussion thus focuses on trends observed within salt extracted samples, where data from water extracted samples is provided given the ubiquity of this type of soil extraction approach.

For both salt extracts, DOC and TN concentrations decrease with increasing soil depth, as indicated by negative slopes within linear relationships for both approaches (Figure C.2A and Table C.4). The overall contribution of fluorescent characteristics related to humic OM signatures (PARAFAC fits C2 and C3) also decrease with depth (Figure C.2, Table C.4), as does a peak identified as a soil humic peak (C5). Correspondingly, the percentage of fluorescence from the tyrosine-like protein peak C4 increased with increasing depth. Thus, as soil depth

increases, the fluorescence OM signature is increasingly dominated by microbial OM, rather than humic OM (which tends to dominate within shallower soil horizons). These trends are similar between both KCl and K_2SO_4 extraction methods, noting a larger negative slope with depth of the C3 reduced semiquinone-like humic peak within K_2SO_4 relative to KCl. It is interesting that these trends with depth are not observed within commonly used fluorescence indices, including FI, Fr and BIX, which were all insensitive to soil depth relative o PARAFAC components (Table C.4). This perhaps suggests that using PARAFAC to parse fluorescence signatures is more sensitive to subtle changes within spectral fingerprints, relative to indices that encompass a smaller spectral range.

In terms of trends in absorbance, both abs_{254} and abs_{272} decreased with depth. However, these trends were not born out within $SUVA_{254}$, which showed little dependence with depth (Table 4). Previously, Corvasce et al. showed that $SUVA_{254}$ decreased with depth in samples extracted using $CaCl_2$ (Corvasce et al. 2006). $SUVA_{254}$ has been correlated to the concentration of aromatic carbon (Traina, Novak, and Smeck 1990; Weishaar et al. 2003), suggesting that the aromaticity of soil OM decreases with depth (Corvasce et al. 2006). This relationship is complicated by the presence of interfering species such as iron, aluminum and nitrate, which show strong absorbance within the regions used to calculate abs_{254} and $SUVA_{254}$. Given the likely presence of iron an aluminum oxides within podzols, especially within the characteristic Bf horizon, it is likely that both parameters suffer from interference, which likely differs significantly as oxide concentration changes within the soil column. Thus, it is likely difficult to concretely assign trends within either parameters to aromatic carbon within our context.

Soil lysimeters – trends with soil depth

As with soil extracts, the characteristics of soil pore water extracted using lysimeters at different depths is shown in in Figure C.3. As with soil extracts, soil lysimeters were installed at various depths. However, lysimeter depth is less well distributed than soil extract depths, given the difficulty of accurate depth placement within heterogenous soil characteristics. Linear relationships between parameters and soil depth were fit as for the extracts (fit parameters within Table C.4), noting the bias towards shallower lysimeter placement than soil extracts. Additionally, sampling soil pore water within the organic layer was impossible due both to its narrow width within the soil column (~3 cm, on average), as well as the highly episodic nature of soil pore water within these narrow layers available for tension sampling.

As for soil extracts, DOC concentrations tended to decrease with increasing soil depth over both lysimeter locations (Figure C.3A). Total nitrogen also decreased with depth, though this relationship was also true for total nitrogen concentrations (Table C.4). As with soil extracts, the absorbance at 254 nm decreased with soil depth (Figure C.3B), a relationship that was not observed within $SUVA_{254}$ values calculated from absorbance at this wavelength (Table C.4). Interferences from iron and aluminum oxides are also likely within both parameters, given the accumulation of iron and aluminum oxides at different concentrations through the Bf horizon (in which all lysimeters were placed). Fluorescent characteristics of lysimeter samples were generally dominated by humic-like fluorescence, as represented either by soil humic peak (C5) or the two reduced semi-quinone-like peaks (C2 and C3 derived from PARAFAC fitting of EEMs (Figure C.3). In particular, samples from lsyimeters on the north side of the stream had a higher percentage of fluorescence as the C3 reduced semiquinone-like humic peak. The percentage of total fluorescence as this peak tended to decrease with depth over both locations (Figure C.3).

The percentage of fluorescence from the tyrosine-like protein peak (C4) tended to increase with depth in samples from this location.

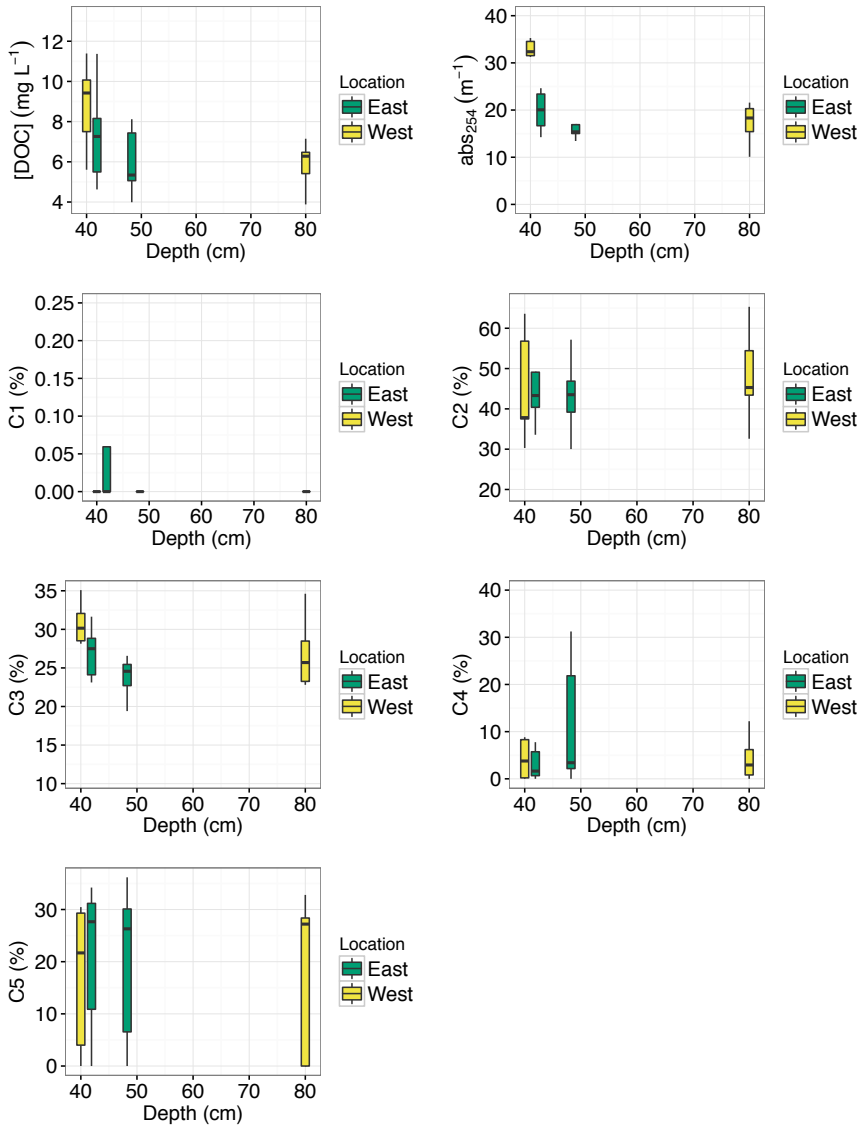

Figure C.3 Changes in lysimeter characteristics with soil depth. Lysimeter characteristics from four lysimeters at different depths are shown as boxplots. Mean values are shown as the line within the box, where the box encompasses 50% of the data distribution, and the whiskers indicate the last observation within 1.5 times the box range. DOC concentration tends to decrease with depth, as does abs_{254}. Fluorescence characteristics are dominated by humic-like fluorescence (C2 and C3), with a greater contribution of tyrosine-like protein with increasing depth.

	K_2SO_4			KCl			Distilled H_2O			Soil Lysimeter		
	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2
DOC (mg/L)	16.14	-0.09	0.37	13.66	-0.15	0.45	3.30	0.06	0.18	8.73	-0.03	0.03
Total Nitrogen (mg/L)	2.19	-0.02	0.23	3.19	-0.04	0.41	0.31	0.00	0.07	1.14	-0.01	0.00
abs_{254} (m^{-1})	72.71	-0.50	0.18	21.00	-0.25	0.52	39.58	1.43	0.42	34.07	-0.21	0.09
$SUVA_{254}$ ($L*mg^{-1}m^{-1}$)	0.29	0.00	0.18	0.63	0.00	0.52	0.14	0.00	0.42	0.14	0.00	0.42
abs_{272} (A.U)	59.60	-0.40	0.17	17.94	-0.21	0.49	37.12	1.33	0.42	28.09	-0.17	0.09
E2E3 (A.U)	6.18	0.01	0.17	5.35	0.01	0.01	2.22	-0.01	0.10	6.30	-0.01	0.02
E4E6 (A.U)	-15.35	0.50	0.14	6.91	-0.05	0.44	6.10	0.02	0.11	151.16	-1.91	0.03
Slope Ratio (A.U)	0.88	0.00	0.51	1.34	0.01	0.54	0.81	0.00	0.57	0.73	0.00	0.03
Fluorescence Index (A.U)	0.88	0.00	0.14	1.56	0.00	0.48	1.47	0.00	0.36	0.74	0.00	0.02
HIX (A.U)	0.94	0.00	0.56	0.62	0.00	0.49	0.54	0.00	0.42	0.59	0.00	0.01
FrI (A.U)	0.57	0.00	0.24	0.79	0.00	0.22	1.08	0.01	0.51	0.36	0.00	0.00
Peak A	2.15	-0.01	0.08	0.99	-0.01	0.35	0.46	0.01	0.49	246.93	-1.12	0.00
Peak C	1.95	-0.01	0.14	0.57	-0.01	0.32	0.06	0.00	0.32	0.68	0.00	0.02
Peak B	0.19	0.03	0.42	1.43	0.02	0.14	0.30	0.01	0.62	0.93	-0.01	0.02
Peak T	0.41	0.01	0.32	1.21	0.00	0.02	0.20	0.00	0.27	0.65	-0.01	0.03
OFI	29780.92	-158.52	0.12	10092.54	-70.85	0.30	2173.71	56.71	0.63	124224.56	-587.06	0.01
C1 (%)	6.86	-0.09	0.18	18.26	-0.18	0.34	41.56	0.30	0.33	1.71	-0.01	0.00
C2 (%)	26.82	-0.02	0.00	22.33	-0.13	0.41	6.94	-0.12	0.45	40.57	0.09	0.02
C3 (%)	37.54	-0.24	0.33	8.34	-0.08	0.47	2.27	-0.04	0.23	26.32	0.00	0.00
C4 (%)	0.10	0.46	0.58	38.25	0.51	0.56	23.25	-0.30	0.36	11.46	-0.07	0.01
C5 (%)	28.68	-0.12	0.58	12.81	-0.12	0.60	25.98	0.16	0.47	19.93	-0.01	0.00
Percent Protein (%)	3.56	0.04	0.25	17.31	0.02	0.02	9.39	-0.12	0.41	4.62	-0.01	0.00
Redox Index (A.U)	0.57	0.00	0.14	0.47	0.00	0.05	0.75	0.00	0.33	0.43	0.00	0.01
CM C1 (%)	12.16	-0.05	0.30	7.59	-0.02	0.27	2.79	-0.05	0.36	10.21	0.00	0.00
CM C2 (%)	21.79	-0.02	0.24	20.06	-0.03	0.11	13.63	-0.10	0.45	21.30	0.01	0.07
CM C3 (%)	7.39	-0.02	0.05	7.03	0.02	0.03	5.15	0.01	0.03	6.21	-0.01	0.00
CM C4 (%)	9.32	0.09	0.19	15.27	0.01	0.03	56.64	0.41	0.39	10.89	0.00	0.00
CM C5 (%)	15.99	-0.11	0.22	2.78	-0.02	0.27	1.01	-0.02	0.19	7.23	-0.02	0.06

	K_2SO_4			KCl			Distilled H_2O			Soil Lysimeter		
	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2	Intercept	Slope	R^2
CM C6 (%)	1.40	0.01	0.02	0.22	0.00	0.01	0.00	0.00	NA	2.70	0.01	0.01
CM C7 (%)	10.29	-0.02	0.11	7.81	-0.02	0.13	1.91	-0.03	0.44	8.32	0.00	0.00
CM C8 (%)	2.81	0.02	0.31	7.37	0.10	0.33	6.51	-0.06	0.50	2.96	-0.01	0.01
CM C9 (%)	6.45	-0.01	0.03	5.12	0.01	0.02	3.08	0.02	0.23	4.38	0.00	0.00
CM C10 (%)	1.89	0.02	0.19	1.51	0.00	0.00	0.90	-0.02	0.16	5.57	-0.01	0.08
CM C11 (%)	4.28	0.05	0.15	7.73	0.00	0.00	2.42	-0.05	0.16	10.94	0.02	0.01
CM C12 (%)	5.47	0.02	0.15	7.57	0.04	0.42	3.08	-0.06	0.41	7.63	0.01	0.00
CM C13 (%)	0.74	0.02	0.07	9.94	-0.08	0.31	2.88	-0.05	0.16	1.67	0.00	0.00
[Cl] (mg/L)										1.99	-0.01	0.02
[NO3] (mg/L)										0.50	0.00	0.00
[SO4] (mg/L)										0.60	0.00	0.04

Table C.4 Linear relationships: Soil extract characteristics with depth. Linear regression parameters describing how soil OM parameters change with increasing depth.

Comparing SWOM to Stream DOC Characteristics

Lastly, we set out to compare characteristics of soil OM determined through lysimeter and soil extracts to streamwater OM characteristics over the same period. Figure C.4 shows the discharge, DOC concentration, as well as abs_{254} and $SUVA_{254}$ calculated from in situ monitoring, and PARAFAC components from grab samples taken during the year period during which soil sampling occurred. DOC concentrations were exceptionally sensitive to the occurrence of precipitation events, where peaks in stream DOC concentrations tended to occur during times of peak discharge caused by precipitation events (Figure C.4 A and B). Trends in abs_{254} were similar to that of DOC concentration, peaking during times of high discharge (especially within the wet winter period). $SUVA_{254}$ was less dynamic than DOC and abs_{254}, likely reflecting the linked nature of these parameters (given than in-stream DOC is calculated from absorbance spectra over the 254 nm absorbance range). $SUVA_{254}$ does exhibit small 'dips' during times of high discharge (Figure C.4), when both abs_{254} and DOC concentrations spike. This may indicate less aromatic carbon received by the stream. However, given the potential for interfering specifies such as iron and aluminum, it may mean also mean that concentrations of these species within the stream are decreased during times of high discharge. Such an occurrence would mean that the increase in abs_{254} would be less than the relative increase in DOC during times of high discharge, which could also result in decreased $SUVA_{254}$ values.

As observed within soil extract and lysimeter trends, PARAFAC components were more sensitive to changes in soil depth than absorbance or fluorescence indices. Stream grab samples were fit to a 4-component PARAFAC model (see Chapter 3), three peaks of which correspond to humic-like fluorescence (C1, C3 and C4), and one (C2) corresponding to protein-like fluorescence. Fluorescence characteristics show less variability with events, possibly reflecting

the timescale at which they are collected, and the increased resolution available within in situ measurements. Overall fluorescence characteristics suggests that humic characteristics arise from surficial flow paths, whereas DOC from deeper groundwater is more protein-like in character. These trends, derived from concentration-discharge relationships within Chapter 3, especially echo characteristics observed, especially within soil extracts.

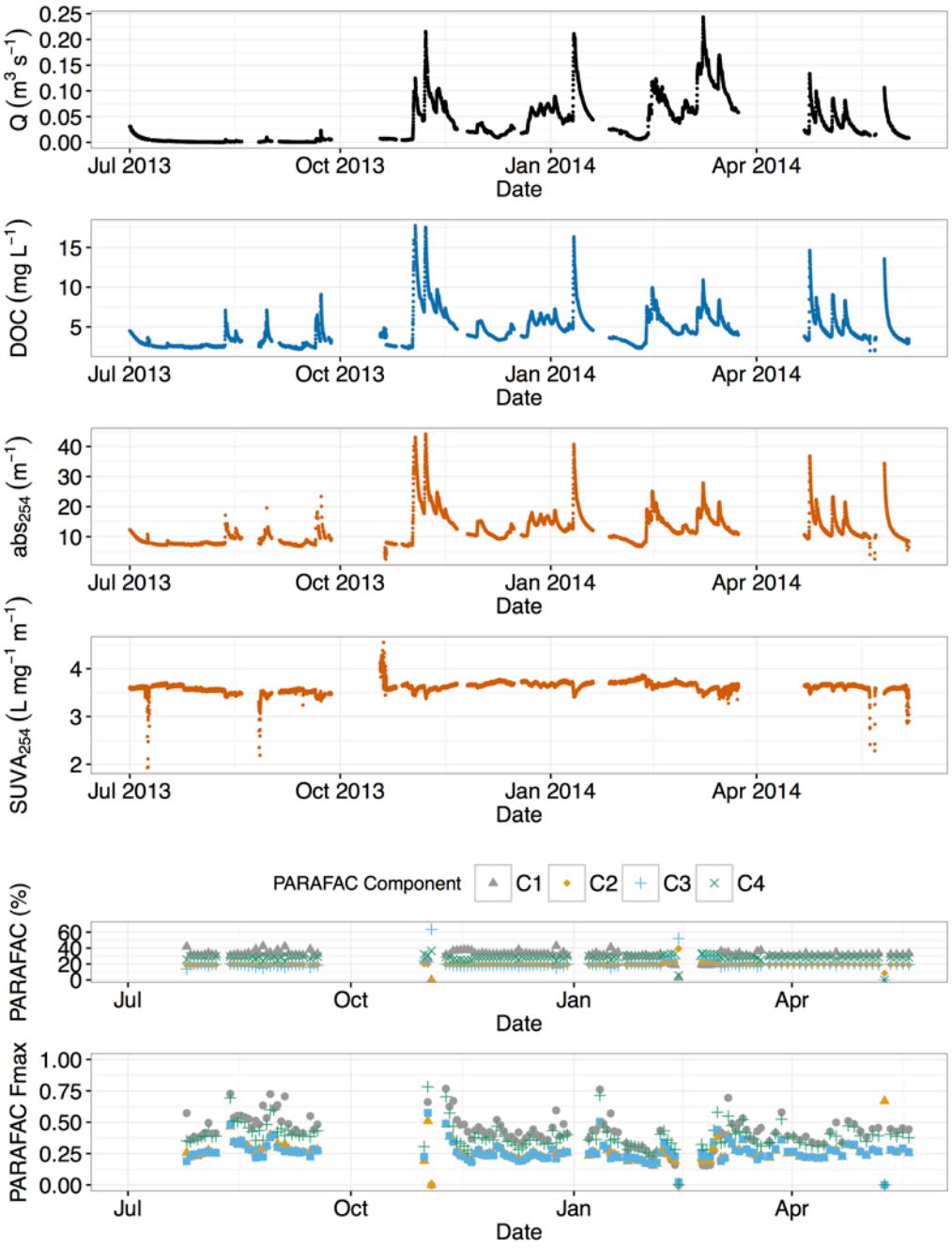

Figure C.4 Stream characteristics during soil sampling. Characteristics include discharge, as well as in situ determinations of DOC concentration, abs_{254} and $SUVA_{254}$. Additionally, F_{max} and percentage of overall fluorescence is shown for the four-component PARAFAC model fit to stream grab samples during the same time.

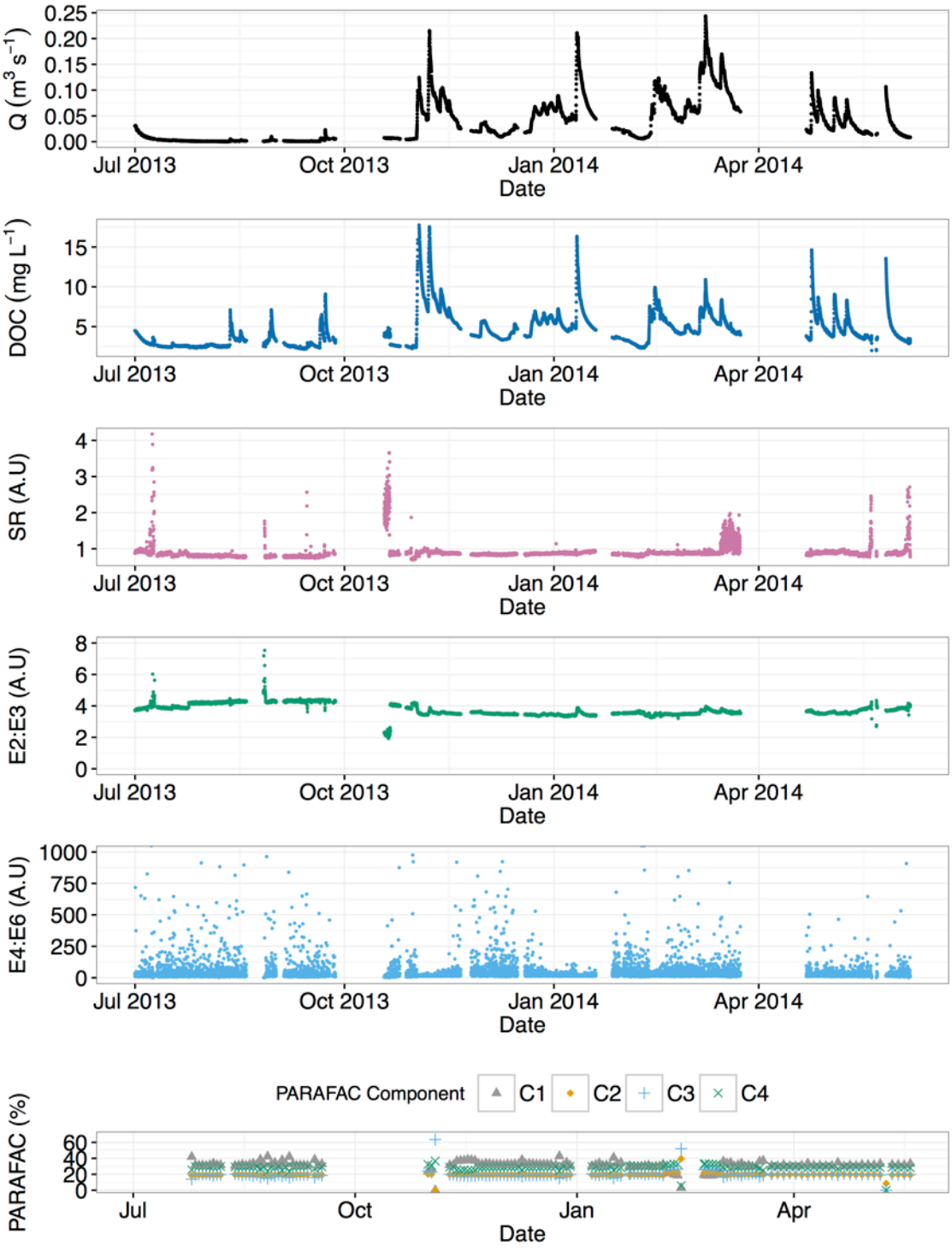

Figure C.5 Absorbance indices (slope ratio (SR), E2E3 and E4E6) calculated from in sit monitoring of stream absorbance for the soil sampling time period.

Appendix D: Chapter 4 supplemental information

D.1 Details of spectrophotometric measurements

Two forms of spectrophotometry were used to measure DOC and NO_3^- concentrations, as well as a range of indices that relate to the composition of the DOC fraction (what types of chemicals make up the bulk DOC measurement). DOC and NO_3^- concentrations were calculated from the absorbance spectra of samples (using instrument-proprietary algorithms). Indices describing DOC characteristics, including $SUVA_{254}$, E2:E3, and E4:E6 were also calculated from absorbance spectra (Supplemental Table 1). Fluorescence spectra of all samples were taken as excitation-emission wavelength pairs spanning a large range of excitation and emission spectra; the resultant excitation-emission matrix (EEMs) contains information regarding the fluorescence characteristics of the sample over a large range of excitation and emission wavelengths. Resultant EEMs, which resembles a topographic map, contains information regarding the types of fluorescent dissolved organic matter present within the sample, based on the location and intensity of fluorescence peaks. A variety of proxies related to the identity of different types of DOC groups (Supplemental Table 1) are calculated from EEMs spectra, including fluorescence index (FI), humification index (HIX), freshness index (BIX), peaks A, B, T and C, redox index and percent protein (for more information, see Cory, Boyer, and McKnight 2011). Given the light-based nature of these measurements, all samples were filtered using a pre-combusted 0.7 μm glass filter (Millipore, Merck KGaA, Darmstadt, Germany); highly absorbing samples were diluted to an optical density ≤ 0.3 at 254 nm prior to taking a measurement.

D.2 Supplemental tables

Water Quality Parameter	Citizen Mean (± standard error)	Scientist Mean (± standard error)	p value
DOC (mg/L)	3.18 ± 0.30	2.90 ± 0.30	**> 0.05**
NO_3^- (mg/L)	0.44 ± 0.05	0.16 ± 0.07	≤ 0.05
$SUVA_{254}$	2.64 ± 0.01	3.1 ± 0.2	≤ 0.05
E2E3	4.53 ± 0.06	5.3 ± 0.1	≤ 0.05
E4E6	4.7 ± 0.2	10.4 ± 2.5	≤ 0.05
FI	1.54 ± 0.01	1.422 ± 0.01	≤ 0.05
HIX	0.82 ± 0.01	0.90 ± 0.01	≤ 0.05
BIX	0.65 ± 0.01	0.54 ± 0.02	≤ 0.05
Peak A	2.1 ± 0.2	0.68 ± 0.08	≤ 0.05
Peak C	1.0 ± 0.1	0.32 ± 0.04	≤ 0.05
Peak T	0.10 ± 0.03	0.24 ± 0.01	≤ 0.05
Peak B	0.25 ± 0.03	0.076 ± 0.007	≤ 0.05
Redox Index	0.405 ± 0.007	0.421 ± 0.008	**> 0.05**
Percent Protein (%)	6.5 ± 0.5	4.79 ± 0.7	**> 0.05**

Table D.1 Mean (± standard error) of water quality parameters from citizen and scientist data sets. Significant differences were evaluated through independent (unpaired) t-tests, and significance evaluated at 95% confidence. Instances where means between the two groups was not significant at this confidence interval are shown in bold.

Story	Sampling Date	Sampling Location (Lat/Long; decimal degrees)	DOC Concentration (mg/L)	NO_3^- Concentration (mg/L)	Name of Stream
Story 1: Participation as education (Figure 3A)	August 28, 2014	49.271120, -123.194671	19.34	ADL*	Jericho Pond
	August 10, 2014	49.271120, -123.194671	13.26	0.80	Jericho Pond
	August 23, 2014	49.18335, -122.77326	1.77	0.57	Serpentine River
	August 11, 2014	49.322318, -123.086518	2.28	0.40	Wagg Creek
	August 28, 2014	49.26338, -123.013487	4.81	0.89	Chubb Creek
	August 8, 2014	49.265004, -123.013058	5.47	1.73	Chubb Creek
	August 28, 2014	49.250776, -123.042755	3.17	1.53	Still Creek
	August 13, 2014	49.250776, -123.042755	4.96	1.54	Still Creek
	September 10, 2014	49.250776, -123.042755	2.26	1.36	Still Creek
	September 14, 2014	49.23728, -122.89171	6.07	0.35	Brunette River
Story 2: Interpreting Data After a Major Event (Figure 3B)	November 2, 2014	49.26881, -122.91898	2.75	1.60	Silver Creek - upstream
	November 2, 2014	49.26494, -122.91988	2.18	1.32	Silver Creek - upstream
	November 2, 2014	49.25766, -122.92018	2.39	0.99	Silver Creek - upstream
	November 2, 2014	49.25064, -122.91911	3.57	1.60	Silver Creek - downstream
	November 2, 2014	49.24808, -122.92001	3.66	1.12	Silver Creek - downstream
Story 3: Assessing	February 2, 2015	49.38273, -123.33548	2.75	0.93	Bowen Island

Story	Sampling Date	Sampling Location (Lat/Long; decimal degrees)	DOC Concentration (mg/L)	NO_3^- Concentration (mg/L)	Name of Stream
Effects of Development (Figure 3C)	February 2, 2015	49.38185, -123.33554	4.16	0.63	Bowen Island
	February 2, 2015	49.38272, -123.33809	6.51	2.31	Bowen Island
	February 2, 2015	49.38441, -123.3402	3.28	0.61	Bowen Island - Control
Story 4: Reconciling Water Quality Parameters to Context (Figure 3D)	August 18, 2014	49.39554, -123.2031	7.44	0.33	Cypress Creek
Story 5: Advantages of Citizen Place-Centrism (Figure 3E)	April 23, 2015	49.338, -123.039	13.67	0.00	Hastings Creek
Story 6: Mt Polley Mining Disaster: 'Inliers' versus Outliers (Figure 3F)	August 7, 2014	52.60951, -121.5505	2.27	0.00	Quesnel River

Table D.2 Location, date, DOC and NO_3^- concentrations for specific data points discussed within the vignettes, shown by story number and title

*ADL = Above detection limit