COMPARISON OF LABILITY OF SOIL-DERIVED DISSOLVED ORGANIC MATTER FROM HILLSLOPES OF CONTRASTING FORESTRY HISTORY IN A PACIFIC COASTAL FORESTED WATERSHED

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Abstract

Dissolved organic matter (DOM) is a key aspect of source water quality in forested headwaters and a subject of concern in drinking water treatment due to its potential for adverse chemical reactions. Forest soils contribute a substantial fraction of DOM entering freshwater systems and can be altered by land use practices such as forest harvest, with implications for water quality downstream. This study investigated the relationship between forest clear-cutting and the biodegradability of soil-derived DOM. The potential for water-extractable soil DOM to be metabolized was measured via in-laboratory incubation and quantified via two methods: loss of dissolved organic carbon (DOC) and changes in fluorescence and absorbance properties. Through comparison of clear-cut stands of differing histories with nearby forested hillslopes, a chronology of the extent of DOM alteration with time elapsed since harvest was established. Biodegradable DOC did not differ significantly between forested and clear-cut sites of any age, though the variability was greater for clear-cuts (forested: 9 ± 1% mean ± standard error; clear-cut: 8 ± 2%). DOM character was different in the most recent clear-cut (harvested in 2017), with a greater fraction of high molecular weight, plant-derived compounds resistant to biodegradation. Incubation did not affect forest and clear-cut DOM differently except for the 2017 sites, where the clear-cut sample showed reduced microbial metabolism and a greater degree of humification. These results may be attributable to the prevalence of woody debris at the more recent clear-cuts, a remnant of the logging process. Overall, DOM character pre- and post-incubation were similar, suggesting soil DOM is relatively refractory and may persist in aquatic systems. The higher fraction of terrestrial, refractory DOM, if sustained downstream, would increase coagulant demand during drinking water treatment, but observable differences in water quality are not projected to last beyond 10 years after harvest in regions similar to the study site.

Lay Summary

Dissolved organic matter (DOM) in source water from forested rivers can react adversely with disinfection chemicals when this water is treated for drinking use. The potential for harmful compounds to form depends on the type of DOM present. Forest soils contribute a substantial amount of DOM, and forestry activities can alter the characteristics of DOM that is transported from soils to streams and rivers. This thesis compares DOM (organic matter that is too small to be removed with a filter) in soils from clear-cut and forested sites at a research forest near Vancouver, Canada, in terms of how biodegradable the DOM is when introduced to stream microbes. Soil DOM characteristics were similar between most sites and contained significantly greater amounts of biodegradation-resistant compounds only at the most recently harvested clear-cut, which suggests forestry impacts soil DOM for a relatively short term in forests like this.

Preface

This thesis is original, unpublished, independent work by the author, Mengxi Wang.

The framework for this research is based on the objectives of the NSERC Network for Forested Drinking Water Source Protection Technologies (*for*Water), to which this project contributes. Mark Johnson and Suzanne Tank were involved in the research design.

Field work was conducted by Mengxi Wang, with assistance from Chunjie Ji, Kelcy Wang, and Trisa Ngo. Geographical data for the Malcolm Knapp Research Forest were provided by Ionut Aron (Research Coordinator, Malcolm Knapp Research Forest).

Laboratory analyses were conducted at the University of British Columbia. All data analyses were completed using R (ver. 4.1.1) and MATLAB (R2021a) by Mengxi Wang, with additional analytical approaches suggested by Mark Johnson and Suzanne Tank. Mark Johnson and Suzanne Tank contributed edits to the manuscript.

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List of Symbols

Symbol	Definition
±	Plus or minus
°C	Degrees Celsius
mg	Milligram, 10^{-3} grams
nm	Nanometer, 10^{-9} meters
Pg	Petagram, 10^{15} grams
μm	Micrometer, 10^{-6} meters

List of Abbreviations

Abbreviation	Definition
BDOC	Biodegradable dissolved organic carbon
BIX	Biological index
C	Carbon
CO2	Carbon dioxide
DBP	Disinfection by-product
DBP-FP	Disinfection by-product formation potential
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
E4/E6	Ratio of absorbance at 465 nanometers to absorbance at 665 nanometers wavelength of light
EEM	Excitation-emission matrix
Em	Emission wavelength
Ex	Excitation wavelength
FI	Fluorescence index
H	Hydrogen
HAA	Haloacetic acid
HCl	Hydrochloric acid
HIX	Humification index
IFE	Inner filter effect
KHP	Potassium hydrogen phthalate
L	Liter

m	meter
N	Nitrogen
NOM	natural organic matter
NPOC	Non-purgeable organic carbon
O	Oxygen
p	p-value
PARAFAC	Parallel factor analysis
r	Pearson correlation coefficient
RO	Reverse osmosis
SD	Standard deviation
SE	Standard error
SOM	Soil organic matter
SUVA	Specific ultraviolet absorbance
SWE	Soil water extract
THM	Trihalomethane
UKAS	United Kingdom Accreditation Service
WEOM	Water-extractable organic matter

Glossary

Term	Definition
Absorbance	Capacity to absorb light of a specified wavelength, caused by molecular interference with a beam of light (UV-VIS spectroscopy)
Allochthonous	(Of organic matter) originating outside a body of water and subsequently transported into the water body; typically terrestrially derived
Aromatic	(Of chemical molecular structure) containing conjugated pi-bonds with a ring structure, e.g. benzene, C6H6
Autochthonous	(Of organic matter) formed in place (i.e. in a body of water); typically formed by microbes
Chlorination	Addition of chlorine or chlorine-containing substances for oxidation and disinfection of water
Coagulant demand	Dose of chemical(s) required for effective removal of charges on particulate matter in raw source water, allowing particles to agglomerate and settle
Disinfection by-product	Halogenated organic compounds that form from undesired reactions during chlorination of drinking water
Dissolved organic matter	Organic matter operationally defined as being able to pass through a filter of 0.45 μm (threshold can range from 0.22 μm to 0.7 μm)
Fluorescence	Irradiation emitted as a result of incident radiation of a shorter wavelength (e.g. ultraviolet light)
Functional group	Group of atoms responsible for the characteristic reactions of a molecule
Headwater	Tributary stream of a river close to or forming part of its source
Humification	The process of changing organic matter (i.e. decaying plant matter) into humic substances
Hydrophilic	Tending to mix with, dissolve in, or be wetted by water

Hydrophobic	Tending to repel or resist mixing with water
Inner filter effect	(In fluorescence spectroscopy) attenuation of the emitted light signal caused by a high concentration of light-absorbing matter in the sample
Lability	Potential for organic matter to be broken down via decay or biological consumption
Natural organic matter	Carbon-based compounds found in natural and engineered environments.
Non-purgeable organic carbon	(For Shimadzu TOC-V CSN analyzer) instrument parameter to measure organic carbon where inorganic carbon is purged from the sample by lowering pH (thus converting it to carbon dioxide) and the remaining carbon is combusted to carbon dioxide and measured with a non-dispersive infrared gas analyzer
PARAFAC analysis	A multivariate analysis used to extract individual components from composite 3D data
Slash	(In forestry) woody debris generated during logging operations which are not harvested as timber
Watershed	A region bounded peripherally by a divide and draining ultimately into one body of water

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I have been privileged with the opportunity to work with so many wonderful people over the course of my research work. This thesis would not have been possible without all their support and assistance.

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1 Introduction

Surface waters supply about 50% of all drinking water in Canada, and almost 80% of municipal water in British Columbia is derived from forest watersheds (Pike et al., 2010). The safety of drinking water is a priority in nations worldwide and at all levels of government; safe, clean drinking water reduces infectious diseases and extends life expectancy (Ryan & Glasser, 2000). Treatment of source drinking water depends on the water needs and specific characteristics of each supply region, with treatment plans typically involving considerations toward costs as well as source water quality. Poor source water quality can increase the cost of treating water to make it drinkable (T. C. Brown, 2000). Proper land management practices are therefore crucial in ensuring source drinking water quality.

Forested watersheds naturally attenuate many common inorganic contaminants; however, forest source waters typically contain high natural organic matter (NOM) content due to interactions with forest soils (Dudley et al., 2003; Scatena, 2000). The concentration and chemical composition of NOM in streams draining naturally forested ecosystems are dependent on biogeochemical processes involving surface water, groundwater, biota, the atmosphere, and sediments, and can be affected by many natural and anthropogenic factors (Fegel et al., 2021; Fellman, Hood, D'Amore, et al., 2009; Fellman, Hood, Edwards, et al., 2009; Laudon et al., 2009; Mattsson et al., 2005; Ruhala & Zarnetske, 2017). Seasonal variations in biological activity can alter NOM entering forest headwaters, as can long-term changes in the environment. For instance, increased precipitation between 1983 and 2001 has been linked to increased color and organic acid content in Norwegian forest lakes (Hongve et al., 2004), and dissolved organic carbon in Alaskan rivers have been observed to decrease in summer and peak in spring (Holmes

et al., 2008). Disturbances such as timber management and fire have also been shown to impact source water quality (Burd et al., 2020; Olefeldt et al., 2013). Forestry activities disturb the soil surface and can lead to increased turbidity due to soil erosion, or expose small stream channels to direct solar radiation, altering stream temperatures and light intensities and thus the biological activity in the water (Stednick, 2000). Removal of timber impacts nutrient cycling and reallocates NOM pools within the ecosystem: compounds once taken up by trees may be absorbed instead by low-growing vegetation of different physiologies (Stednick, 2000), leading to shifts in nutrient cycling.

The presence of NOM in source water presents a challenge in drinking water treatment, as it can impact taste and color, and is also a precursor to potentially hazardous disinfection by-products (DBPs). Chlorination is a widely used practice in drinking water treatment to disinfect microbial contaminants (Henry, 2013); interactions between NOM and chlorine used in treatment create a variety of DBPs, of which the two main categories are trihalomethanes (THMs) and halo-acetic acids (HAAs). A subset of DBPs are regulated due to potential adverse health effects (Health Canada, 2020; Henry, 2013). The DBP formation potential (DBP-FP) of NOM is dependent on its specific chemical characteristics (Health Canada, 2020).

Dissolved organic matter (DOM) is a soluble mixture of compounds consisting of carbon, nitrogen, oxygen, hydrogen, and other trace elements (Moody & Worrall, 2017). Operationally, DOM is defined as the fraction of NOM that can pass through a filter with a specified pore size, typically ranging between 0.22 and 0.7 μm; the most commonly used threshold is 0.45 μm (Bruckner, 2021; Kolka et al., 2008; Nimptsch et al., 2014). Approximately 50% of DOM by mass is dissolved organic carbon (DOC; Moody & Worrall, 2017). Ubiquitous in soils and

natural waters, DOM plays an important role in the cycling of nutrients in terrestrial and aquatic ecosystems (Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009).

DOM represents a wide range of chemical compounds. The chemical structure of DOM varies based on its source: DOM of terrestrial origin (typically referred to as allochthonous DOM), such as soil and plant leachates, is typically rich in humic constituents and hydrophobic, while aquatic (autochthonous) DOM derived from microbial activity (e.g. photosynthesis and microbial exudates within the water column) tends to be low molecular weight, hydrophilic, and protein-rich (Health Canada, 2020; Kelso et al., 2020). DOM chemical composition is an important control in microbial metabolic processes and DOM decay (Kelso et al., 2020).

Soils contain the largest store of terrestrial carbon (Minasny et al., 2013): the global soil carbon budget is estimated at 12.97 Pg in the top 0-100 cm soil profile (Guo et al., 2020). DOC in forest headwaters is largely derived from the interaction of hydrological flowpaths with terrestrial C sources such as soil and plant matter. The flux of DOC from terrestrial sources to waters is a significant component of organic carbon cycling. As DOC is transported from soil to streams, it is transformed both by decay processes of the allochthonous material and by biological metabolic activities (Fellman et al., 2008). The lability, or biodegradability, of DOM depends on numerous factors. Marschner and Kalbitz (2003) classify these into three levels: 1) intrinsic DOM characteristics controlled by molecular structure, functional group content or molecule size; 2) soil properties that may affect the degradation process and thus the DOM chemical composition, such as nutrient availability and microbial community structure; 3) external factors such as vegetation and climate that may influence soil properties, which in turn can affect DOM molecular characteristics.

In terrestrial ecosystems, soil DOC is impacted by natural environmental factors such as vegetation (Bourbonniere & Creed, 2006; Lajtha et al., 2005) and seasonality (Burd et al., 2020; Fellman, Hood, D'Amore, et al., 2009), as well as anthropogenic land use practices, including forestry (Stednick, 2000). Soil DOC is derived from the decomposition and humification of microbial biomass, plant litter, and root exudates (Kalbitz et al., 2000); these sources and processes may be significantly impacted by forest management, leading to potential effects on the lability of DOC in affected soils and headwaters.

Research on soil DOM lability is complicated by the complex and interdependent nature of DOM (including DOC) processes in natural systems. A wide range of environmental controls have been found to impact soil DOM. Previous studies have shown that DOM chemical composition and lability in soil pore water may vary between ecosystems: Fellman et al. (2008) found greater DOM lability in wetland soils than forest soils, while Sebestyen et al. (2021) found similar biodegradability in peatland DOM and DOM from forested uplands. Seasonality can also impact DOM lability, though its influence can differ between ecosystems. For example, Wickland et al. (2007) found no seasonal variability in soil pore water from Alaskan boreal forests, whereas significantly higher lability was observed in the spring in coastal temperate rainforests (Fellman, Hood, D'Amore, et al., 2009) and in southwestern Northwest Territories taiga peatlands (Burd et al., 2020). Some detrital controls are correlated with changes in the chemical quality and lability of soil DOM (Bourbonniere & Creed, 2006; Hensgens et al., 2021; Lajtha et al., 2005; O'Donnell et al., 2016), and DOM lability can vary even between different fractions of soil pore water (Andreasson et al., 2009). Due to the multitude of environmental factors that play a role in DOM dynamics, detailed knowledge of site characteristics is necessary to predict DOM chemical processes and lability.

The flux of DOM from terrestrial to aquatic ecosystems means that downstream biogeochemical processes are often impacted to some extent on the characteristics of terrestrial DOM. It is therefore important to study soil DOM chemical quality and biodegradability in forest uplands, as it can be an indicator of its availability for metabolism in forest headwaters. Knowledge regarding terrestrial DOM lability and its responses to land use practices such as forestry can play a vital role in predicting downstream water quality and the subsequent treatability of forest source waters.

1.1 Methods for understanding dissolved organic matter characteristics and lability

1.1.1 DOC loss in soil water extract after incubation

The vast majority of NOM in soil is not extractable by water, with the water-extractable fraction typically constituting less than 1% of the total soil NOM pool (Hassouna et al., 2012). However, the NOM that is extracted/released into water is thought to play a substantial role in soil biogeochemical processes (Haynes, 2005). These compounds contribute to in-situ soil processes, such as the transfer and stabilization of soil organic matter (SOM) in deeper soil horizons (Hassouna et al., 2012), and also are transported to inland waters, where they may impact biological activity in aquatic ecosystems (Fellman, Hood, D'Amore, et al., 2009; Swanson et al., 2000). Water-soluble SOM compounds recoverable using predetermined laboratory procedures are referred to as water-extractable organic matter (WEOM), of which soil-derived DOC is a substantial fraction (Hassouna et al., 2012; Á. Zsolnay, 2003).

The terms "DOM" and "DOC" both encompass a wide range of chemical compounds with varying properties and dynamics in the environment. Characteristics such as molecular

structure and functional group content influence the reactivity of the compound (Marschner & Kalbitz, 2003) and thus control the biogeochemical processes in which it is involved. Detailed analysis of all the chemical constituents in a sample of DOM can be a complex endeavour, and it is not always possible to identify every component. However, the lability, or biodegradability, of DOC can be a useful indicator of its reactivity, e.g. its availability for microbial metabolism (Fellman et al., 2008; Wickland et al., 2007; Yano et al., 2000). Therefore, lability can help predict the behavior and transformation of DOC as it is transported through the environment.

Studies of DOC lability often report conflicting or ambiguous results. This is due partly to the complexity of DOC dynamics in the environment, but the lack of standardized methods is also a major obstacle to understanding controls on lability (Marschner & Kalbitz, 2003). Incubation duration, inoculum, temperature, and nutrient addition vary between studies, as do methods of quantifying lability. In incubation studies, biodegradability is typically reported in terms of DOC loss after incubation, though total organic carbon (TOC, i.e. analysis without filtration) loss has been used in some cases instead. Alternatively, researchers also use the production of CO2 during incubation as a metric for biodegradability. Yet another approach is to use flow-through bioreactors filled with microbial colonies and measure organic carbon content in the input and output solutions. This forgoes the incubation process altogether, as bioreactor residence times typically last 24 hours or less (Marschner & Kalbitz, 2003; McDowell et al., 2006). The variability in analysis techniques can greatly hinder comparisons between studies.

1.1.2 Optical characteristics of fluorophoric and chromophoric DOM

As DOM comprises a wide range of chemical compounds, the complexity of DOM chemical structures poses a challenge in the study of its role and significance in the environment. To quantify the overall composition and reactivity of DOM, many analytical approaches have been employed. In particular, techniques that quantify DOM optical properties, such as specific ultraviolet absorbance (SUVA) and fluorescence spectroscopy, have been useful not only in determining DOM concentrations and composition (Aiken, 2014; Spencer et al., 2008; Weishaar et al., 2003), but also (due to their ease of data collection and ability to be measured in situ) in better understanding the source influences and processes occurring within ecosystems (Downing et al., 2009; Saraceno et al., 2009).

Fluorescence spectroscopy employs the optically reactive molecular structures of DOM compounds to determine their character; various functional groups, such as -OH, -NH_2, and -COOH (Aiken, 2014), fluoresce differently, leading to unique DOM composition 'fingerprints'. DOM fractions that absorb light are chromophoric, while those that absorb and re-emit light are fluorophoric (Gabor et al., 2014).

The excitation-emission matrix (EEM) is a three-dimensional fluorescence spectroscopy scan typically comprising a range of excitation (Ex) wavelengths, a range of emission (Em) wavelengths, and the intensity of the fluorescence detected at each Ex/Em wavelength combination. EEMs typically contain intensity peaks characterized by the excitation-emission pairs at which they occur, which reveal information about the chemical properties of the DOM. For instance, humic molecules tend to fluoresce in the Ex 240-370 nm, Em 350-550 nm range (Gabor et al., 2014). Coble (1996) identified five major fluorescent compounds in marine water samples, each characterized by a unique EEM peak (Table 1). These are commonly referred to as

"Coble's peaks". Similar peaks (labelled 'D', 'E' and 'N') were defined by Stedmon et al. (2003). When numerous DOM samples are compared, parallel factor (PARAFAC) analysis can be used to distinguish the spectral features of multiple components and determine the contribution of each component to the overall EEM signature (Stedmon et al., 2003; Stedmon & Bro, 2008).

Table 1: Diagnostic EEM peak ranges

Peak	***Ex maximum***	***Em maximum***	***Characteristics***	***Source***
B	275	305	Tyrosine-like (protein-like)	(Coble, 1996)
T	275	340	Tryptophan-like (protein-like)	(Coble, 1996)
A	260	400-460	Humic-like	(Coble, 1996)
M	290-310	370-410	Marine humic-like	(Coble, 1996)
C	320-360	420-460	Humic-like	(Coble, 1996)
D	390	509	Soil fulvic acid	(Stedmon et al., 2003)
E	455	521	Soil fulvic acid	(Stedmon et al., 2003)
N	280	370	Plankton-derived	(Stedmon et al., 2003)

In addition to the identification of EEM peaks, the use of spectral indices is another approach to DOM spectral analysis. Spectral indices have been used to characterize organic matter for several decades, and can be generally defined as the ratio of absorbance or fluorescence intensity measured at two different regions in optical space (Gabor et al., 2014). Several indices have been developed that define various properties of DOM (Table 2).

The robustness of fluorescence spectroscopy makes it a useful tool for studying the source and chemical composition of organic matter, with a wide range of applications in water quality, from drinking water and wastewater treatment (Jutaporn et al., 2020; Lyon et al., 2014;

Raeke et al., 2017; Yadav et al., 2019) to environmental monitoring (Cincotta et al., 2019; M. S. Johnson et al., 2011; Santín et al., 2009).

Table 2: Common spectral indices for characterizing organic matter. Modified from Gabor et al. (2014) and Hansen et al. (2016).

Index	***Parameter***	***Property described***
Humification index (HIX) (Ohno, 2002; A. Zsolnay et al., 1999)	At Ex = 254 nm, ratio of total fluorescence at Em = 435-480 nm and Em = 300-340 nm	Degree of humification of soil extracts. Higher values indicate greater humification.
Freshness/biological index (BIX) (Huguet et al., 2009; Parlanti et al., 2000; Wilson & Xenopoulos, 2009)	At Ex = 310 nm, ratio of intensities at Em = 380 nm and 430 nm	Proportion of freshly produced DOM. A measure of microbial production.
Fluorescence index (FI) (Cory & McKnight, 2005; McKnight et al., 2001)	Ratio of fluorescence at Em = 450 nm and 500 nm, at Ex = 370	Source and aromaticity of DOM. Higher values are typically associated with microbial DOM, while lower values tend to be of terrestrial origin.
Peak T/Peak C ratio (Baker, 2001)	Ratio of maximum fluorescence intensity at peak T to maximum intensity at peak C (refer to Table 1 for Ex/Em ranges)	Biological oxygen demand relative to dissolved organic carbon.
E4/E6 (Y. Chen et al., 1977)	Ratio of absorbance at 465 nm to absorbance at 665 nm	Ratio of humic acid and fulvic acid in soil solutions. However, research has shown it is impacted by other factors such as pH, and more closely correlated with particle or molecular weight than humic acid/fulvic acid concentrations.
Slope ratio (Helms et al., 2008)	Ratio of absorbance in the 275-295 nm range to absorbance at 350-400 nm	Relative molecular weight. Higher values indicate overall lower molecular weight compounds.
$SUVA_{254}$ (Weishaar et al., 2003)	Ratio of absorbance at 254 nm to DOC concentration	Relative aromaticity. Higher values indicate greater fractions of aromatic content.

1.2 Research Objectives

This study aimed to evaluate the chemical composition and lability of water-extractable soil DOM in the headwaters of a forest in the Pacific Maritime ecozone. Two analytical approaches were used to qualify and quantify DOM chemical quality: DOC concentration and DOM optical properties such as fluorescence and absorbance. These parameters were assessed prior to and after a 7-day incubation in order to determine changes in DOC concentration and DOM character corresponding to the biodegradation of DOM.

This thesis will address the following research questions:

1. How does the composition of water-extractable DOM differ in soil from undisturbed forested landscapes compared to clear-cut forest landscapes?
2. Upon introduction into forest streams, to what extent does the lability of water-extractable soil DOC derived from forested and harvested areas differ?
3. To what extent do the differences in 1. and 2. depend on the time elapsed since the forest disturbance?
4. What implications do the potential impacts of forest management on the lability of soil-derived DOM have for the treatability of forest source drinking water?

2 Methodology

2.1 Site description

The study was conducted in the University of British Columbia's Malcolm Knapp Research Forest (MKRF), located at 49° 18' N and 122° 35' W, about 60 km east of Vancouver, Canada. The forest falls within the Coastal Western Hemlock biogeoclimatic zone (Haught & Meerveld, 2011). The elevation ranges from 10 meters above sea level (masl) to 1010 masl, with the mean elevation of the sampling sites being 360 masl.

Average precipitation at the Environment Canada climate station "Haney UBC RF Admin" (station number 1103332) is 2184 mm, of which snowfall typically comprises 5% at low elevations. 70% of precipitation typically falls between October and April due to Pacific frontal systems (Leach & Moore, 2015). The daily mean temperature at the Haney UBC RF Admin station for March 2021, when samples were collected, was 6.1°C. Snow cover was present in areas of high elevation. In general, forest cover consists primarily of western hemlock (*Tsuga heterophylla*), Douglas-fir (*Pseudotsuga menziesii*), and western red cedar (*Thuja plicata*) (Leach and Moore 2015), while the undergrowth is primarily salal (*Gaultheria shallon*), red huckleberry (*Vaccinium parvifolium*), and sword fern (*Polystichum munitum*) (Haught & Meerveld, 2011).

Soils at the forest are mostly coarse-textured humo-ferric podzols (Feller & Kimmins, 1979) and contain large amounts of woody debris. They exhibit large variability in depth, ranging up to 2 m, but are generally less than 1 m. On average, glacial till or granitic bedrock underlies the soil at 1 m depth. Due to the high permeability of the soils, almost all water reaching the ground surface infiltrates the soil and flows downslope in a saturated layer of soil

directly overlying the till or bedrock (Leach & Moore, 2015; Thompson & Moore, 1996). Many streams are ephemeral, drying up during the summer.

Four cut blocks of varying clear-cut histories were selected for sampling. For each cut block, a corresponding unharvested block on the same hillslope was paired for comparison to control for local variations in elevation, temperature, moisture and light intensity to the extent possible. A total of eight sites were sampled; the characteristics for each are described in Table 3.

Table 3: Characteristics of sampling sites at MKRF

Site ID	***Site description***	***Location***	***Transect length (m)***	***Average elevation (masl)***	***Dominant substrate***
2017H	2017 clear cut	49° 19’35” N, 122° 33’14” W	450	383	Woody debris; snow cover present
2017F	2017 paired undisturbed block	49° 19’00” N, 122° 33’15” W	260	354	Leaf litter
2014H	2014 clear cut	49° 18’47” N, 122° 33’13” W	290	348	Low-growing vegetation with woody debris
2014F	2014 paired undisturbed block	49° 18’30” N, 122° 33’09” W	300	358	Moss and leaf litter
2006H	2006 clear cut	49° 18’25” N, 122° 33’58” W	570	428	Leaf litter
2006F	2006 paired undisturbed block	49° 18’11” N, 122° 33’47” W; 49° 18’52” N, 122° 33’51” W*	290; 320	481; 432	Moss and ferns
2000H	2000 clear cut	49° 16’37” N, 122° 34’08” W	240	239	Leaf litter
2000F	2000 paired undisturbed block	49° 17’12” N, 122° 34’05” W	330	342	Moss and ferns

* A second block north of the harvested site was included in the sampling scheme due to the main block’s small size.

2.2 Sample collection

Soil samples were collected in a linear transect parallel to the road at each sampling site. This corresponded to the bottom of the slope at most cut blocks. To avoid potential effects from mass wasting or pollution from road runoff, samples were collected at least 2 m upslope from the road. The distance between individual sampling locations varied depending on the dimensions of the cut block; each transect was divided to accommodate 15 evenly spaced soil samples. Every cut block was divided into three subsections, from which five samples were obtained from each and homogenized to create three replicates for each cut block. Soil was removed with an auger from the organic layer, or top 0-5 cm where the organic layer extended deeper than 5 cm.

Samples from Sites 2017F, 2017H, 2014F and 2014H were collected on March 22, 2021, and Sites 2006F, 2006H, 2000F and 2000H were sampled on March 25, 2021. Due to time constraints, it was not possible to complete all sampling on the same day. Soil samples were stored fresh at 4°C following collection and were used within 7 days, following the sample preservation procedures outlined by the British Columbia Ministry of Environment and Climate Change (2019). All samples were processed in the laboratory on March 29, 2021.

2.3 Soil water extraction

Samples were sieved fresh at ¼ in (6.3 mm) to remove large debris and stones, then mixed with reverse osmosis (RO) water at approx. 30 g soil to 200 g water. The soil/water mixtures were shaken for 2 hours (Eberbach E6010 fixed speed reciprocal shaker, 180 osc/min) to produce soil water extracts. Leftover soil was dried at 105°C for 24 hours to determine the soil moisture content for each sample.

To facilitate filtration, the soil water extract was first centrifuged for 10 minutes at 4500 rpm (approx. 2000x *g*) and 10°C, based on extraction procedures described by Guigue et al. (2014). Low-speed centrifugation is sufficient to settle the sediments without pelleting organic molecules of potential interest. Samples were centrifuged a second time if sediments were found to be too loose for filtration after the first attempt. The resulting supernatant was then poured out for filtration.

Samples were filtered at 0.7 μm (Millipore AP4004705 glass fiber, Massachusetts, USA) and analyzed for DOC concentration. Prior to use, the glass fiber filters were combusted at 450°C for 2 hours to remove residual organic carbon.

2.4 Inoculation and incubation

The incubation parameters used in this study were chosen with consideration to its goal of investigating soil-stream DOM interactions to evaluate forest source drinking water treatability. Incubation duration and temperature were 7 days and 20°C, respectively, in adherence to the recommended method by McDowell et al. (2006) for analysis of relatively labile DOC. A standardized mixture of stream water grab samples collected in situ was used as the inoculum, and no nutrients were added. Lability is measured as the change in DOC concentration, a metric relevant to most drinking water treatment schemes.

Stream water grab samples were obtained at six locations (Table 4) and filtered at 1.6 μm (Millipore APFA04700 glass fiber, Massachusetts, USA) to remove microbial grazers. These were combined in equal parts to create a standardized inoculant, which was introduced to the soil water extracts at a 1% wt/wt ratio.

All previously prepared soil water extract samples were diluted with additional RO water to approx. 9 mg/L, the lowest concentration among the samples. Samples were then divided into two sets: one set was kept at room temperature (approx. 20°C), while the other was kept at 4°C. Air temperature was monitored using data loggers (Trutrack WT-HR, Australia). All samples were incubated for 7 days and stored in the dark in airtight, acid-washed glass vials, with a 5-10% headspace to allow for aerobic respiration. Sample vials were insulated from temperature fluctuations by submersion in water.

Table 4: Stream sampling sites at MKRF

Sample ID	***Sample description***	***Location***
SS-1	Within 2000F site	49° 17'18.68" N, 122° 34'4.8" W
SS-2	Within 2006H site	49° 18'15.18" N, 122° 33'55.20" W
SS-3	Within 2014F site	49° 18'31.32" N, 122° 33'3.60" W
SS-4	Within 2014H site	49° 18'48.53" N, 122° 33'9.40" W
SS-5	Approx. 400 m south of 2014F along the same hillslope	49° 18'19.80" N, 122° 32'56.65" W
SS-6	Clear cut block approx. 2 km south of 2014F, last harvested in 2016	49° 17'0.24" N, 122° 33'21.6" W

DOC concentration was determined using a Shimadzu TOC-V CSN total organic carbon analyzer, while fluorescence was analyzed with a Horiba Aqualog spectrofluorometer. All samples were filtered at 0.7 μm using glass fiber filters prior to analysis. Prior to use, filters were pre-combusted at 450°C for 2 hours to remove residual carbon.

2.5 DOC concentration analysis

DOC concentration was determined with a TOC-V CSN total organic carbon analyzer (Shimadzu Inc., Kyoto, Japan), using a non-purgeable organic carbon (NPOC) setting. Inorganic carbon and volatile organic carbon species are released from solution as CO_2 and not incorporated into the reported DOC concentration. The TOC-V analyzer was calibrated using solutions of potassium hydrogen phthalate ($C_8H_5KO_4$, abbreviated as KHP) prepared from dry solid. RO water was used as the blank solution. The calibration solutions ranged from 0 mg/L to 50 mg/L.

Aliquots of calibration solution were run as unknown samples to validate the calibration, and internal standards of KHP were used as further validation and to monitor for instrument drift throughout instrument operation. If the instrument was found to have drifted more than 10% from its original calibration during the analysis, the DOC concentrations were adjusted by the same factor by which the reported standard solution concentration deviated from its known value. In addition, randomly selected duplicate samples were run to confirm reproducibility, following the guidelines provided in Hansen et al. (2018).

Samples were manually acidified with 50 µL of 4 M hydrochloric acid (HCl) before analysis. This was to reduce the pH below 4, ensuring any inorganic carbon in the form of carbonates was volatilized as CO_2 (Zeebe & Wolf-Gladrow, 2001). pH was confirmed to be between 2-4 using Fisherbrand pH strips (Fisher Scientific, Massachusetts, USA).

Five injections were analyzed for each sample. For most samples, the DOC concentration was reported by default as the average of the three injections producing the lowest coefficient of variance (as determined by the TOC analyzer software). In cases where the maximum and

minimum injection values differed by over 25% of the minimum, the injections used to calculate the final concentration were selected based on injection peak shape and consistency, as well as coherence between duplicate samples and with other similar samples in the batch.

2.5.1 Biodegradable DOC

The percentage DOC loss, hereby referred to as biodegradable DOC (BDOC), was calculated as:

$$BDOC\ (\%) = \frac{[DOC]_{initial} - [DOC]_{final}}{[DOC]_{initial}} * 100$$

The mean BDOC was then calculated for each of the three replicate samples per cut block.

The change in percentage DOC concentration of clear-cut block samples relative to forested samples was calculated by averaging the BDOC for all the samples of each cut block and then subtracting the BDOC value for each forested site from that of its corresponding paired clear-cut site:

$$BDOC_{difference}\ (\%) = BDOC_{clear-cut} - BDOC_{forest}$$

For example, for a sample pair with 5% $BDOC_{forest}$ and 10% $BDOC_{clear\text{-}cut}$, the clear-cut sample would be expressed as having an additional 5% BDOC relative to its forested counterpart.

2.5.2 Soil moisture

Soil samples were dried at 105°C for 24 hours to obtain the dry weight. Gravimetric soil moisture content, SM_g, reported as a percentage of the dry soil weight, was calculated using the equation:

$$SM_g(\%) = \frac{m_{moist} - m_{dry}}{m_{dry}} * 100$$

where *m* is the mass of the soil.

2.6 Fluorescence and absorbance spectroscopy - EEM and absorbance acquisition

Soil water extract samples were filtered at 0.7 μm using pre-combusted glass fiber filters and analyzed using an Aqualog spectrofluorometer (HORIBA, Kyoto, Japan). Aliquots of sample were analyzed before and after incubation. Samples were kept at 4°C and out of direct light as much as possible when not being analyzed. The analysis spanned two days due to time constraints, and as a result some samples were analyzed at 8 days post-incubation rather than 7 days. Filtration was performed only immediately preceding analysis in order to minimize disturbance of the samples. On the second day, two randomly selected previously completed samples were also re-analyzed to assess any potential effects of the extra holding time. No samples were acidified for EEM analysis except for two "high floc" samples (see 4.4.2

Flocculation and sample heterogeneity due to acidification").

Samples were scanned at Ex 239-800 nm and Em 249.18-830.37 nm with a 3 nm and 2.39 nm interval between wavelengths, respectively, resulting in an EEM with a total of 188 × 237 Ex/Em points. The integration time was 2 seconds for each wavelength scanned. Absorbance

was obtained simultaneously on the HORIBA Aqualog for the same wavelengths as Ex values for the EEMs. A UKAS-certified ultrapure water standard (Starna Scientific Ltd., Ilford, United Kingdom) was used to confirm instrument operational quality and perform Raman correction. Samples were not diluted before scanning.

2.6.1 EEM correction and PARAFAC analysis

Raw EEMs were processed in batches based on the date of scanning. A combination of procedures using R statistical software and MATLAB R2021a (The MathWorks Inc., 2021) was used to correct the EEMs. First, the staRdom package (Pucher et al., 2019) was used to correct for inner filter effects (IFEs) and to subtract blanks. Where multiple blanks existed for one batch, an average of all the blanks was used. Then, the drEEM toolbox (Murphy et al., 2013) was used to remove Raman and Rayleigh scattering. drEEM was preferable over staRdom for this step due to its ability to adjust scattering removal band widths asymmetrically, preserving as much original EEM data as possible. Next, Raman normalization was performed using staRdom before the fully corrected batches of EEMs were combined into a single dataset and imported for PARAFAC analysis using drEEM. The same dataset was also used for PARAFAC analysis using staRdom to compare the outcomes of the two softwares. The models were validated using split-half analysis.

A total of 126 EEMs were processed, of which 80 were incubation samples, 6 were stream water samples, 38 were soil water extract samples scanned at various times throughout the sample preparation process, and 2 were acidified and re-filtered soil water extracts. Of these

EEMs, 120 were used for PARAFAC analysis; the stream water samples were omitted from the initial PARAFAC model due to their high leverage in the model.

The modelled components were uploaded to the OpenFluor online database (openfluor.org) for comparison to components identified in previous studies (Murphy et al., 2014). Similarity between components was evaluated based on a combination of the similarity score provided by OpenFluor, the range of wavelengths for which data is available, and a visual comparison between components using OpenFluor's Ex and Em comparison graphs.

2.6.2 Spectral indices

After performing all aforementioned EEM corrections, the humification index (HIX), biological index (BIX), fluorescence index (FI), and maximum intensities at Coble's (1996) B, T, A, M and C peaks were determined using built-in tools from the R package "eemR" (Massicotte, 2016), which calculates the values based on their respective specifications as described in the Introduction. Peak T/peak C ratio, E4/E6 and slope ratio were calculated manually using R according to their respective parameters. Linear interpolations were made for wavelengths for which data was not collected, where applicable.

2.6.3 Acidification of soil water extract sample with high floc formation

One soil water extract sample, notable for its high DOC concentration during initial analysis and its formation of substantial amounts of brown aggregate following the addition of HCl, was scanned before and after acidification to investigate changes in its composition

following acidification and 0.7 μm filtration to remove the floc. Two aliquots each of pre-acidification and post-acidification sample solution were scanned.

2.7 Statistical analysis

Statistical analyses were conducted using R statistical software (ver. 4.1.1). Data groups were checked for normal distribution using the Shapiro-Wilk test. As some metrics failed the normality check, non-parametric tests were used. Wilcoxon signed rank tests were carried out to check for significant differences before and after incubation, and Mann-Whitney tests were used to compare each set of paired clear-cut and forested sites.

Differences between sites were checked using the Kruskal-Willis test, and in cases where significant differences existed, a pairwise Mann-Whitney test with no p-value adjustment was used to identify the differing sites. The p-value threshold for Mann-Whitney and Wilcoxon signed rank tests, which were two-sided, was set at 0.1, while for other tests it was 0.05. General relationships between metrics were determined using Pearson linear correlation.

3 Results

3.1 Characteristics of soil water extracts

3.1.1 DOC concentration

Complications with the TOC analyzer at the time of initial analysis impeded precise acquisition of DOC concentrations for all the soil water extract samples within a 24-hour period. As a result, four samples had to be diluted based on estimated values from preliminary results. The soil water extract DOC concentration was back-calculated using the dilution factor for each respective sample and the DOC concentration immediately prior to incubation, which was successfully obtained within one instrument analysis sequence.

Prior to dilution, DOC concentrations ranged from 11.35 to 22.90 mg C/L for forested site samples, and 9.67 to 58.96 mg C/L for samples from the clear-cut blocks. Mean ± one standard error (SE) DOC concentration was 16 ± 1 mg C/L for forested sites and 19 ± 4mg C/L for clear-cut sites. The highest concentrations were derived from soils of the 2017 clear-cut, while the soils producing the lowest concentrations came from the 2000 and 2006 clear-cuts.

DOC concentrations were not significantly different between the four forested sites (Kruskal-Wallis test, $p > 0.05$). Some differences were found in harvested sites, with the 2017 clear-cut being most distinct from the others (Figure 1). DOC concentration was not found to correlate with soil moisture content or initial soil to water ratio (Pearson correlation, $|r| < 0.2$, $p > 0.05$ in both cases).

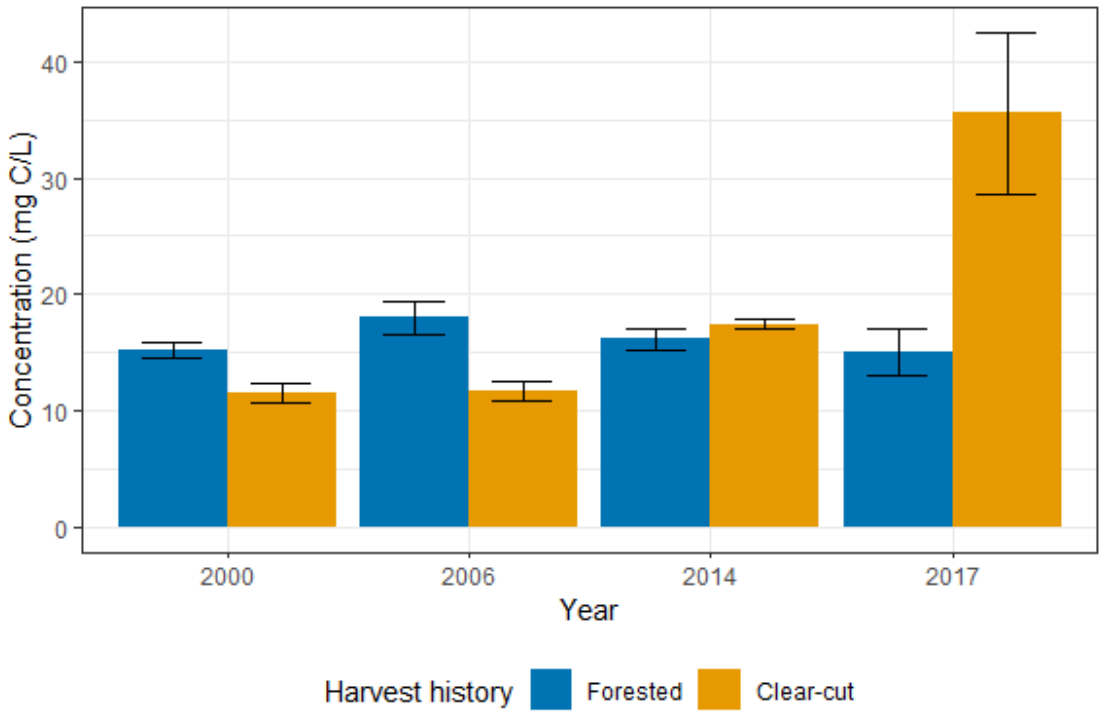

Figure 1: Dissolved organic carbon concentration of soil water extract prior to dilution. Error bars represent 1 standard error.

3.1.2 Spectral indices

3.1.2.1 Humification index (HIX)

Among the soil water extract samples, the HIX ranged from 0.71 to 0.92, with a mean ± 1 SE of 0.84 ± 0.01 for forested samples and 0.82 ± 0.01 for clear-cut samples. Overall, the mean HIX was 0.83 ± 0.04 standard deviation (SD), which is consistent with the IFE-corrected HIX values for soil DOM found by Ohno (2002), who reported a mean ± 1 SD HIX of 0.838 ± 0.006.

In general, the HIX of soil water extracts from clear-cut locations tended to be lower than that of their forested paired sites. Samples from more recent disturbances (2017, 2014) exhibited

a greater variation in HIX (Figure 2). HIX was not statistically different between sites (Table B, Appendix A).

3.1.2.2 Biological index (BIX)

The minimum BIX was 0.4, while the maximum was 0.54. Average BIX was 0.46 ± 0.04 (mean ± 1 SD). Overall, BIX tended to be higher in clear-cut samples, except for samples from the 2017 site, where this trend was reversed. Variation in BIX was greater in clear-cut samples (SD = 0.05) than forested (SD = 0.03), suggesting more stable conditions for microbial production at the sampled forested locations than at disturbed sample sites. However, BIX did not differ significantly between sites.

BIX was negatively correlated with HIX (Pearson correlation, $r = -0.71$, $p < 0.001$). This is consistent with previous findings that greater microbial production is associated with lower humification, as lower molecular weight DOM compounds are preferentially consumed and more humic compounds remain (Balser, 2005).

3.1.2.3 Fluorescence index (FI)

FI ranged from 0.94 to 1.1, indicating an overall more terrestrially-derived source (McKnight et al., 2001). Similar to BIX, FI values were generally higher at clear-cut sites than forested, with the exception of the 2017 clear-cut (Figure 2). Significant differences were found in FI between sites (Table B, Appendix A). The 2017 and 2014 clear-cuts differed from their paired forested sites, while the 2006 and 2000 sites were not statistically distinct.

FI values followed a similar pattern to BIX across sites. FI and BIX are positively correlated (Pearson correlation, $r = 0.73$, $p < 0.001$), confirming the relationship between microbial activity and the presence of 'freshly-produced' DOM.

3.1.2.4 Peak T/Peak C

Peak T/peak C ratios exhibited a strong positive correlation with BIX (Pearson correlation, $r = 0.91$, $p < 0.001$), consistent with expectations for greater biological oxygen demand under conditions of greater microbial production. Average peak T/peak C was 0.5 ± 0.2 (mean ± 1 SD). Differences in peak T/peak C ratio between sites were not statistically meaningful.

Increase in peak T/peak C ratio was strongly associated with a decrease in HIX (Pearson correlation, $r = -0.89$, $p < 0.001$).

3.1.2.5 E4/E6

E4/E6 values ranged from 2.57 to 3.33, with a mean ± standard deviation of 3.0 ± 0.2. These are lower than the values expected for humic acids extracted from podzolic soils, reported to be about 5.0 (Y. Chen et al., 1977; Kononova, 1966). However, due to the potential for other factors to affect the E4/E6 ratio, including humic and fulvic acid concentration, pH, and molecular weight, as well as differences in sample extraction and purification methods, a direct comparison with literature values may not reveal definitive information about the samples in this study. E4/E6 was not significantly different between sites.

3.1.2.6 Slope ratio

Average slope ratio was 0.87 ± 0.04 (mean ± SD), and ranged from 0.77 to 0.95. The slope ratio of clear-cut samples trended lower than that their corresponding forested samples except in the 2000 sample pair. Overall, the slope ratio of clear-cut sites increased with time elapsed since harvest, suggesting a decrease in molecular weight over time. The difference between forested and clear-cut slope ratio values was most defined in the 2017 paired samples (Figure 2).

Slope ratio correlated negatively with E4/E6 (Pearson correlation, $r = -0.62$, $p < 0.001$), supporting observations by Chen et al. (1977) of a partial dependency of the latter on molecular weight. Slope ratio differed significantly only for the 2017 paired sites.

3.1.2.7 SUVA

SUVA ranged between 3.10 to 5.59. Average SUVA of forested soil water samples was 4.03 ± 0.04 L/mg·m, while for clear-cut samples it was 4.34 ± 0.05 L/mg·m (mean ± SE). No significant differences between forested and clear-cut samples were found among the sites.

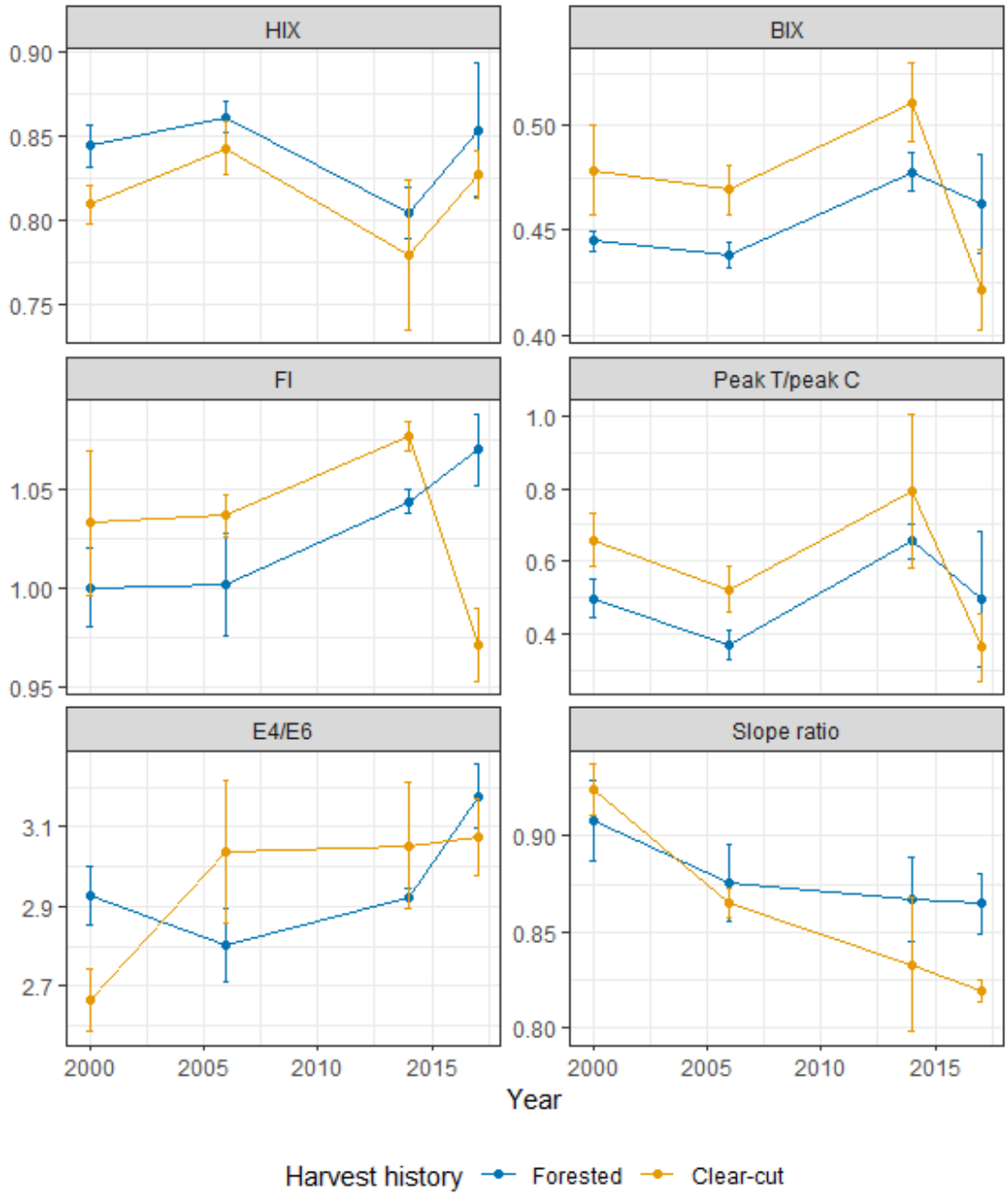

Figure 2: Mean spectral indices of soil water extracts. Error bars represent 1 standard error.

3.1.3 PARAFAC analysis

3.1.3.1 PARAFAC analysis using drEEM

PARAFAC analysis identified 4 different components, henceforth referred to as C1, C2, C3 and C4 (Figure 3). All the components were successfully matched to components reported in previous studies via the OpenFluor database, with varying similarity score thresholds. The four components are as described below:

Component 1 (C1) had a maximum peak at 239/441 nm Ex/Em, and was consistent with components from many previous studies in a variety of environments. It has been described as a "typical humic-like component found in water samples" (Derrien et al., 2019), and is of terrestrial origin. The EEM peak corresponds to Coble's (1996) A peak. Comparison of C1 yielded the greatest number of matches and the highest similarity score at which close matches were found (>0.98) to previously identified components (Derrien et al., 2019; Jutaporn et al., 2020; Lin & Guo, 2020; Wünsch & Murphy, 2021; Yamashita et al., 2010).

Component 2 (C2)'s maximum peak was at 368/457 nm Ex/Em, with a secondary peak at 275/457 nm Ex/Em. The maximum peak is close to the region defined by Coble's (1996) C peak. The best matches were obtained at a similarity score threshold of >0.94. Components like C2 are described as being of terrestrial origin, corresponding to "highly processed organic material that tends to be preserved in soils" (Panettieri et al., 2020)**.** This component is likely to be a product of the decomposition of leaf litter and compounds like tannin and lignin (Osburn et al., 2012; Panettieri et al., 2020; Wünsch et al., 2017).

Component 3 (C3) yielded the fewest matches on OpenFluor, with best matches found at a similarity score threshold of >0.93. This component has two peaks, a higher one at 401/521 nm

Ex/Em and a secondary peak at 275/521 nm Ex/Em. This type of component is characterized as soil fulvic acid (Chai et al., 2019; B. Chen et al., 2018; Hong et al., 2021), with the higher Em wavelength of the primary peak corresponding to the E peak described by Stedmon et al. (2003).

Component 4 (C4) appeared to exhibit three peaks, with (in order of intensity) a maximum peak at 278/327 nm Ex/Em, a secondary peak at <239 nm Ex of which less than 50% was captured, and a third peak at 278/491 nm Ex/Em. C4's maximum EEM intensity corresponded closely to the T peak, suggesting a tryptophan-like compound (Coble, 1996), and was consistent with other components from previous studies that have been described as protein-like and likely of microbial origin (Bianchi et al., 2014; Huang et al., 2022). Best matches for C4 on OpenFluor were found at a similarity score of >0.96.

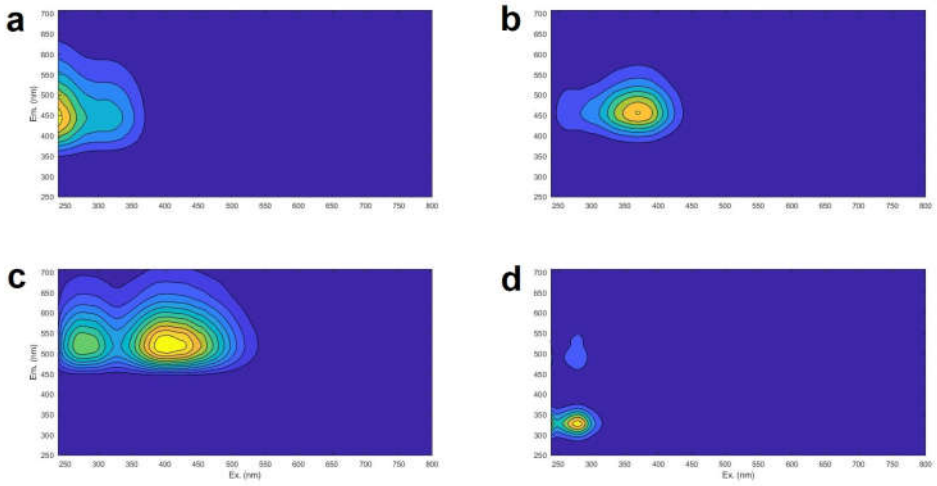

Figure 3: Components of PARAFAC analysis via drEEM: a) C1; b) C2; c) C3; d) C4.

3.1.3.2 PARAFAC analysis using staRdom

Analysis using the staRdom package in R identified four components similar to those found using drEEM. The characteristics of each are comparable to the drEEM components (Table 5, Figure 4).

Table 5: Components of PARAFAC analysis using staRdom

Component	***Maximum fluorescence(s) (nm Ex/Em)***	***Description***	***Corresponding drEEM component and peaks (nm Ex/Em)***
Comp. 1	239/441	Terrestrial, humic-like	C1 (239/441)
Comp. 2	386/513 (maximum), 278/513	Fulvic acid-like	C3 (401/521, 275/521)
Comp. 3	359/445 (maximum), 257/445	Humic-like, similar to lignin and tannin	C2 (368/457, 275/457)
Comp. 4	278/326 (maximum), <239/326	Tryptophan-like	C4 (278/327, <239/327, 278/491)

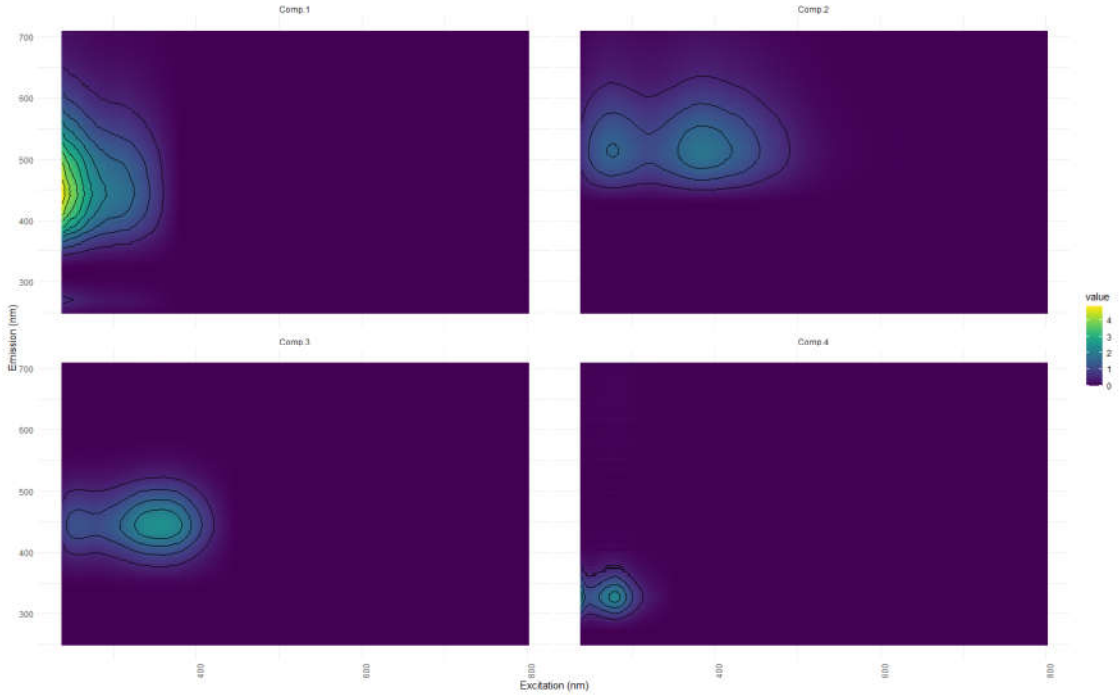

Figure 4: Components of PARAFAC analysis via staRdom.

3.1.3.3 Variability in relative abundance of PARAFAC-derived components

FDOM composition is generally similar between clear-cut and forested samples. The samples exhibiting the greatest difference are the 2017 clear-cut and forested pair: in the clear-cut sample, the proportion of C1 is significantly lower, while C2 and C3 are more abundant (Figure 5). While the differences in C2 and C3 were statistically insignificant, the lower amount of C1 distinguishes the 2017 clear-cut from all the other sites except the 2014 paired sites, where the difference was not found to be meaningful. The relative abundance of C4 was not statistically distinct at any sites.

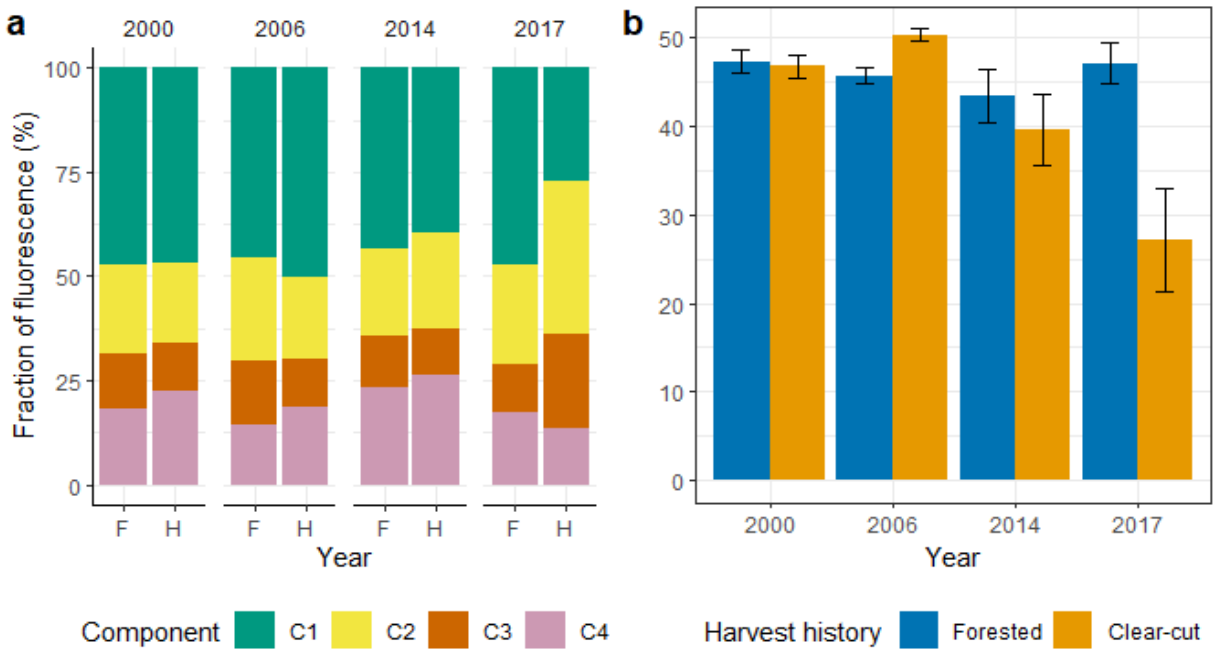

Figure 5: a) Relative contribution of all PARAFAC model components in soil water extract; b) Relative contribution of PARAFAC component C1, showing error bars (mean ± 1 SE).

The relative abundance of C4 was strongly correlated with an increase in BIX and decrease in HIX, supporting its characterization as a compound of microbial origin. Similarly, an

increasing proportion of C2 and C3, compounds which were identified as terrestrially-derived compounds, were negatively correlated with BIX, peak T/peak C ratio, and slope ratio. This suggests that they are of relatively high molecular weight and are less bioavailable. Finally, C1 abundance is correlated with a higher slope ratio, indicating that this component's molecular weight may be relatively low (Figure 10).

Based on the above, the differences in relative abundance of the PARAFAC model-derived components were consistent with the decreased biological activity and higher molecular weight composition observed via spectral indices in the 2017 clear-cut sample.

3.1.3.4 Effect of HCl addition to soil water extracts

Samples were acidified with HCl as part of the procedure for measuring DOC concentration. However, acidification of soil water extract caused aggregation and formation of brown particulates ("floc") in the sample (see 4.4.2 Flocculation and sample heterogeneity due to acidification"). To evaluate the impact on FDOM properties and identify the characteristics of the in the sample, a soil water extract sample was analyzed before and after adding acid.

Based on the changes in spectral indices and PARAFAC component proportions (Table 6), the floc may contain FDOM with a mixture of characteristics that do not adhere strictly to the general types previously discussed, i.e. greater biological activity typically corresponding with lower humification. For instance, the sample's BIX and HIX both increased. Assuming that a decrease in proportion would indicate the compound being filtered out or excluded from the soluble fraction, and an increase means the compound tends to remain in solution, it is postulated that the floc's constituents most resemble C2 and C3 and are least like C1.

Table 6: Spectral indices and PARAFAC components of soil water extract sample before and after removal of aggregate particles

Parameter	***Before***	***After acidification and filtration***
HIX	0.84	0.92
BIX	0.39	0.46
FI	0.96	1.05
Peak T/peak C	0.23	0.15
E4/E6	3.26	4.14
Slope ratio	0.83	0.81
C1	22%	58%
C2	43%	26%
C3	26%	11%
C4	9%	5%

3.2 Results of incubation

3.2.1 Biodegradable dissolved organic carbon (BDOC)

Both batches of incubation samples were processed and loaded for DOC analysis at the same time. However, time constraints and instrument complications led to a delay of up to 72 hours in analyzing the 4°C samples, which potentially affected analysis results due to unfavorable sample storage conditions (see 4.4.2 Flocculation and sample heterogeneity due to acidification"). Therefore, only BDOC results from the 20°C incubation will be presented and discussed. The 4°C incubation results are available in Appendix A.

The overall post-incubation decrease in DOC was statistically significant (Wilcoxon signed rank test, $p < 0.001$). Samples from forested cut blocks experienced a DOC loss of 9 ± 1% (mean ± SE) over the 7-day incubation, while those from clear-cut areas had a DOC loss of 8± 2%. In general, BDOC was lower in clear-cut samples (Figure 6).

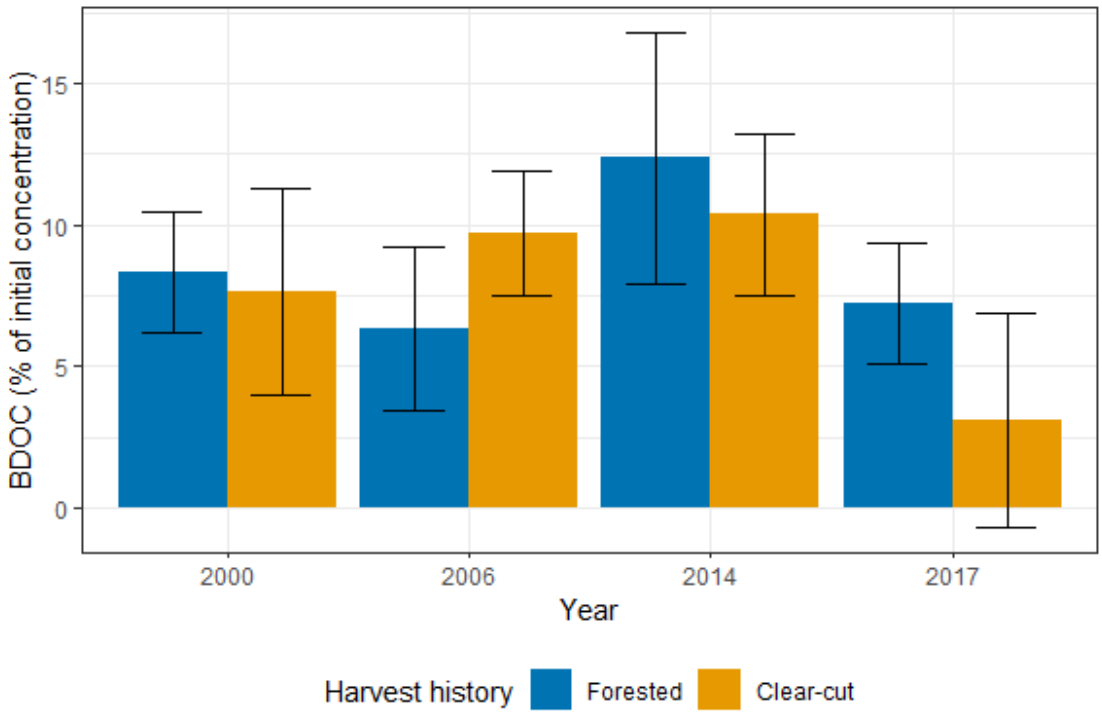

Figure 6: Mean ± 1 SE BDOC after 7-day incubation (20°C incubation).

Comparison of BDOC in clear-cut samples relative to forested ones showed a trend toward decreased BDOC at the 2017 and 2014 clear-cut sites (4 years and 7 years elapsed since harvest, respectively; Figure 7): for instance, the 2017 clear-cut had a BDOC content of 3.1%, which was 4% less than the BDOC content of its paired forested site (7.2%). For the 2000 paired forested and clear-cut sites, the fraction of BDOC was similar. However, the differences in BDOC between paired sites were not found to be significant (Kruskal-Wallis test, $p > 0.05$). Though the preliminary results appear to indicate that forestry activities may reduce overall DOC lability in forest soils in the short term (<10 years), further study is required to confirm this conclusion.

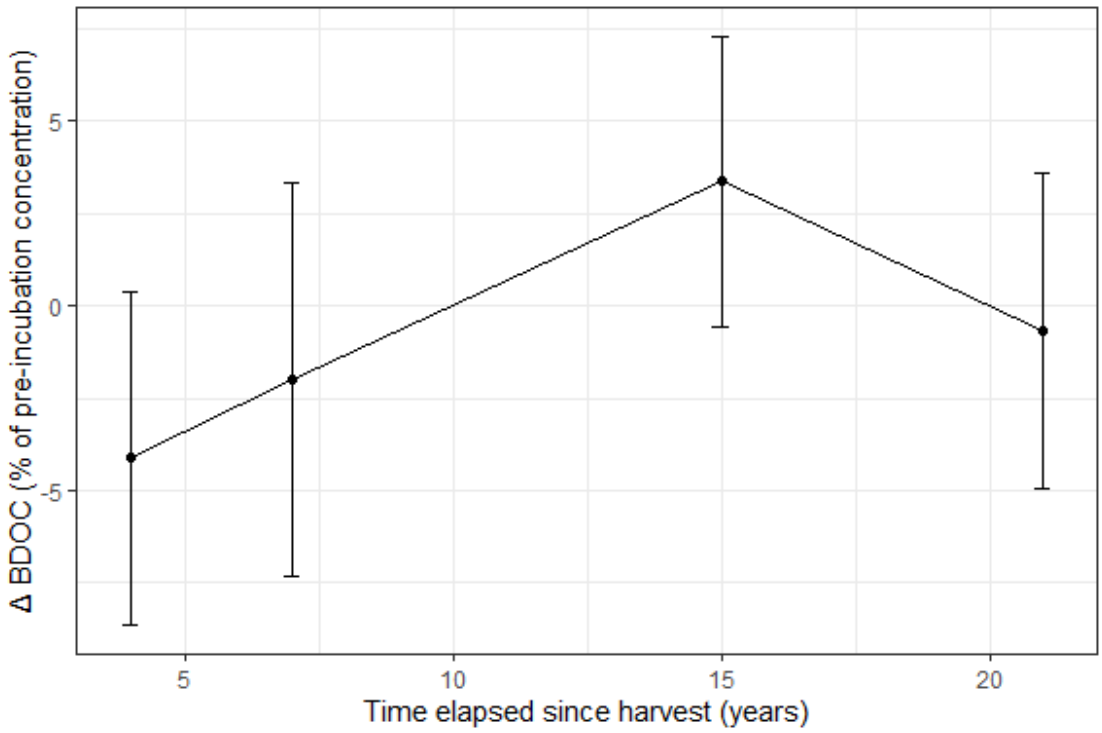

Figure 7: Mean ± 1 SE BDOC content of clear-cut soils relative to forests (20°C incubation).

3.2.2 Spectral indices

Some changes in spectral indices were observed after incubation. Table 7 shows the average post-incubation changes for each index value. The majority of index values shifted in the same direction for both the 4°C and 20°C incubations, and the magnitude of change was generally greater in the 20°C incubation. Mean BIX and FI were higher after incubation. Slope ratio decreased, which corresponded loosely with higher E4/E6 values. Peak T/peak C ratio increased in the 4°C incubation, but decreased at 20°C. This was reversed for HIX, which was lower at 4°C and higher at 20°C incubation. Mean SUVA was slightly higher after incubation.

SUVA values are only available for the 20°C batch, as the 4°C DOC concentration results were rejected, thus invalidating the post-incubation SUVA values.

In the 4°C incubation, statistically significant differences were found for HIX, BIX, FI, and peak T/peak C ratio, while for the 20°C set, all the measured indices except BIX differed significantly (Table A, Appendix).

The differences in index values between clear-cut samples and their corresponding forested sites averaged in the 10^{-3} - 10^{-2} range (10^{-2} - 10^{-1} for E4/E6, due to its intrinsically higher index values), generally within 10% of the original value (Figure 8). Most sites exhibited similar trends in index changes post-incubation. The greatest differences between clear-cut and forested sites were generally observed in the 2017 pair. Compared to its associated forested site, the 2017 clear-cut sample exhibited a higher HIX and a lower BIX and FI, which were found to be statistically meaningful (peak T/peak C, E4/E6, slope ratio, and SUVA were not significantly different). These characteristics suggest that soil FDOM at the 2017 clear-cut became more humified and hosted less biological activity (and therefore less microbial material) relative to its forested counterpart. At the other sites, this trend was reduced (HIX) or reversed (BIX and FI, Figure 8). However, no statistical significance was found in these trends, meaning that the 2014, 2006 and 2000 clear-cut sites generally resembled their forested counterparts in terms of DOM humification, biological activity, oxygen demand, relative molecular weight, and aromaticity after incubation.

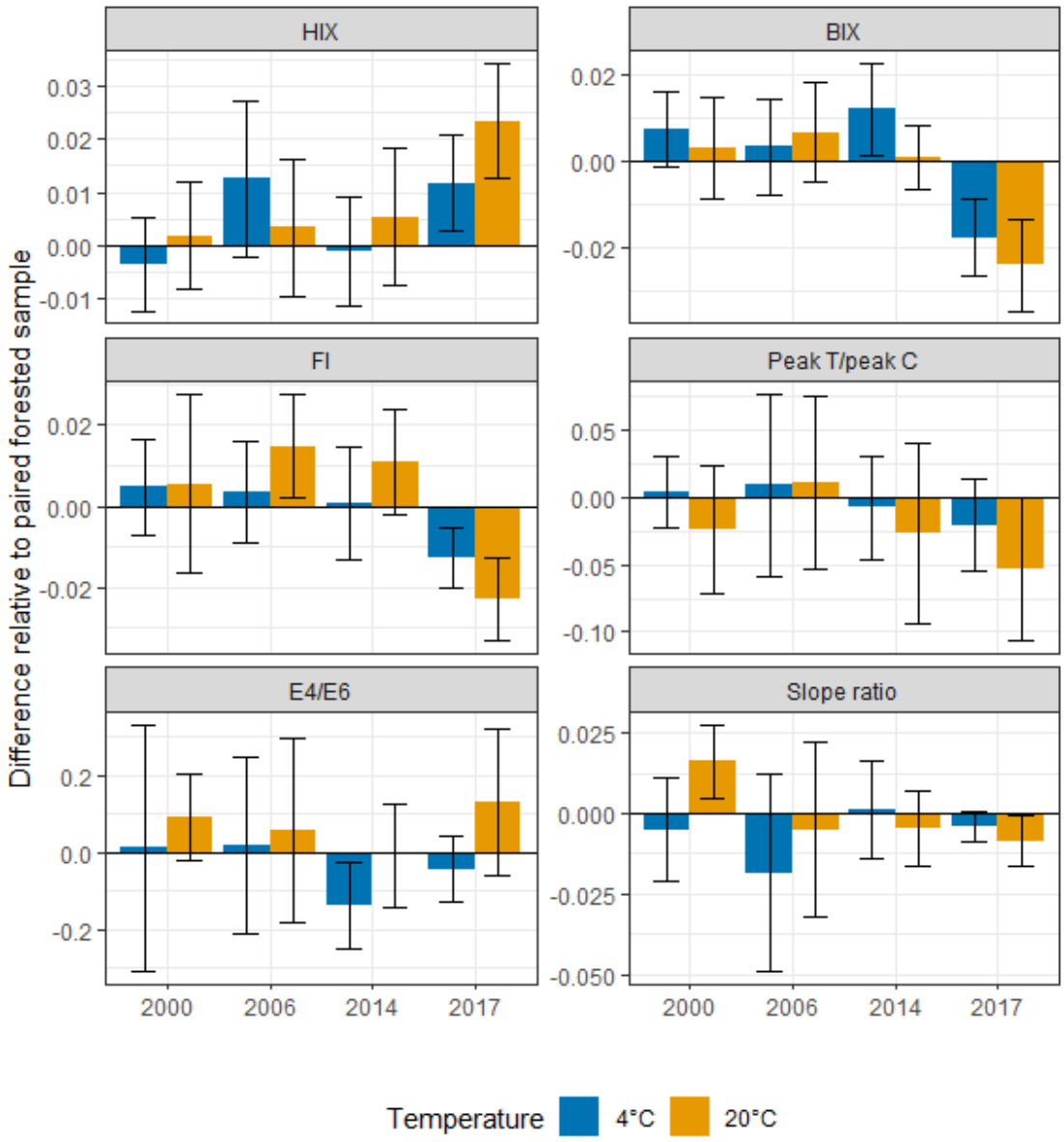

Figure 8: Mean difference in spectral indices of clear-cut site samples after 7-day incubation, relative to corresponding forested sites. Error bars represent 1 standard error.

Table 7: Mean ± standard deviation percentage change in spectral indices and PARAFAC component fractions after incubation

Index	***4°C***	***20°C***
HIX	-1 ± 1	1 ± 2
BIX	2 ± 2	1 ± 3
FI	1 ± 1	1 ± 2
Peak T/peak C ratio	7 ± 10	-7 ± 10
E4/E6	0 ± 7	2 ± 6
Slope ratio	0 ± 2	-2 ± 2
C1	-1 ± 1	2 ± 3
C2	0 ± 4	2 ± 4
C3	-5 ± 4	-2 ± 6
C4	7 ± 9	-4 ± 10
SUVA	NA	6 ± 7

3.2.3 PARAFAC model components

Significant changes were observed the in relative abundances of the four components, and were similar between clear-cut and forested samples. As with the spectral indices, these changes averaged within 10% of the pre-incubation value (Table 7). C2 generally increased in proportion after incubation, while C3 decreased. For C1 and C4, results were contradictory between the 4°C and 20°C incubations: C1 increased in the 20°C incubation and decreased at 4°C, while C4 abundance was higher after the 20°C incubation and lower at 4°C (Figure 9).

In general, clear-cut samples exhibit a slightly lower proportion of C2 and higher C1 compared to forested sites, which could indicate a preferential removal of higher molecular weight compounds from solution relative to forested samples. Increased prevalence of C1 also coincides with a decline in the abundance of C4. It is likely that lower biological activity is associated with higher levels of humic-like compounds. However, there is high variability in C1

and C4 for the 2017 samples incubated at 20°C. This was determined to be derived from the clear-cut samples rather than forested, suggesting a greater local variability at that site (assuming the sample was not compromised during processing).

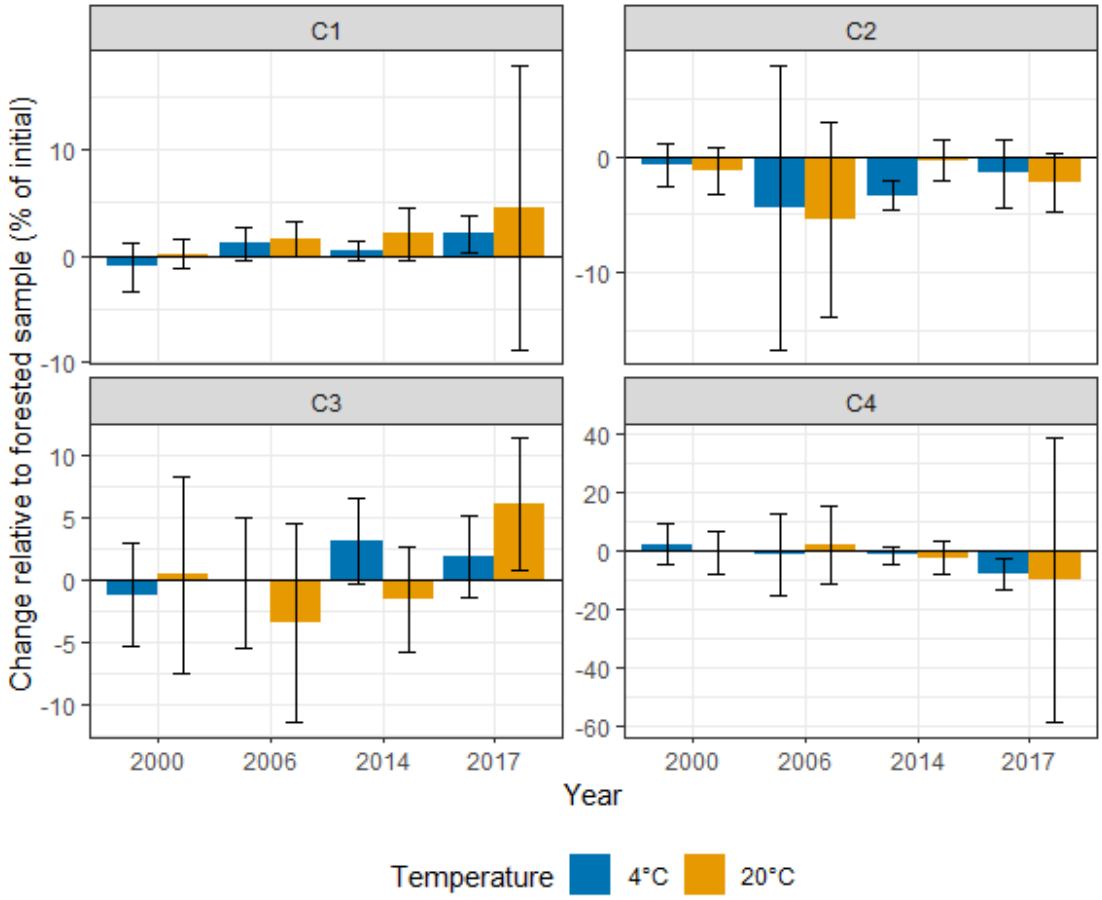

Figure 9: Change in relative contribution of PARAFAC components in clear-cut samples post-incubation. Error bars represent 1 SE.

Correlations between PARAFAC components and spectral indices differ slightly post-incubation compared to the undiluted soil water extract (Figure 10). The most notable changes occur with C1: the incubation data suggest its increased presence is associated with an increase in HIX, decrease in BIX, decrease in peak T/peak C ratio, and decrease in relative C4 abundance,

whereas these relationships were less apparent pre-incubation. These correlations likely characterize C1 as a product of humification that is less readily metabolized by microbes.

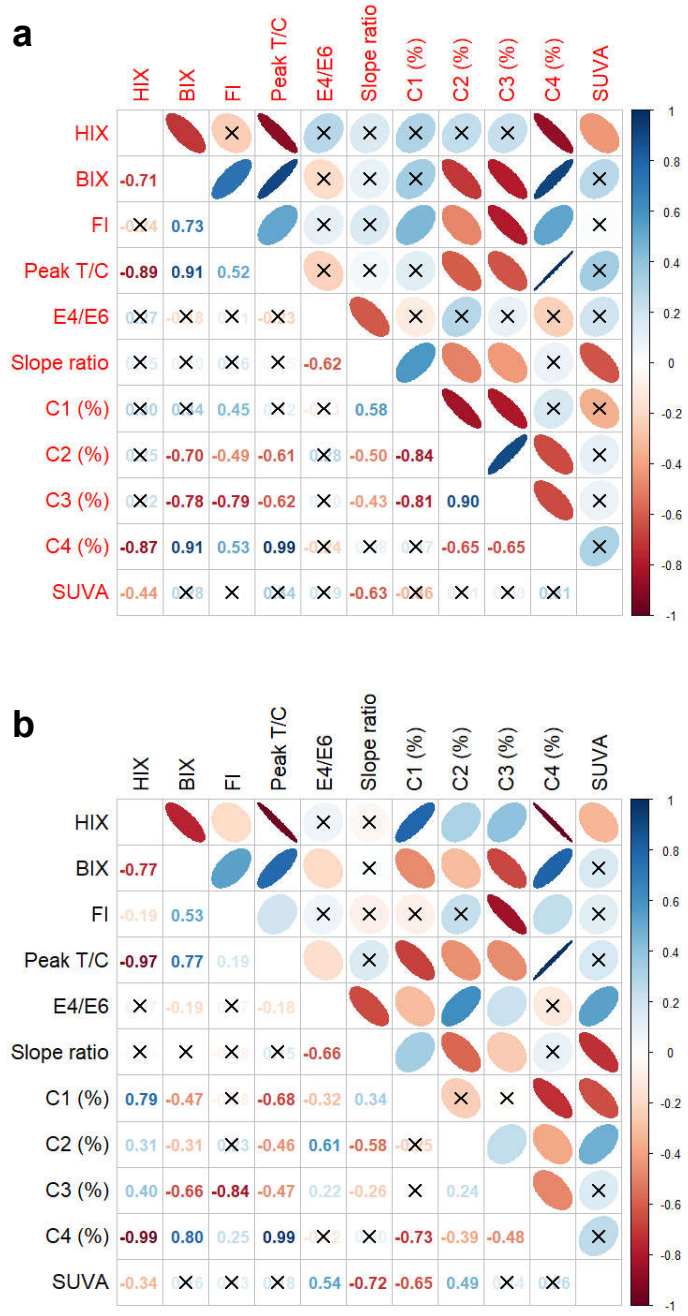

Figure 10: Correlograms showing Pearson correlation coefficients between spectral indices and PARAFAC components in: a) fresh soil water extract, showing relationships between DOM fractions; b) pre- and post-incubation samples, showing effects of biodegradation. R values with $p > 0.05$ are crossed out. "Peak T/C" refers to peak T/peak C ratio.

4 Discussion

4.1 Characteristics of soil water extracts

DOC concentrations in soil water samples were generally consistent with those previously reported for forested upland soils in a coastal temperate rainforest ecosystem (Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009). These amounts are typically low compared to that of peatland and wetland soil solutions (Burd et al., 2020; Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009; Hansen et al., 2016; Lajtha et al., 2005). Average DOC concentration at clear-cut sites was slightly higher than in forested sites, especially at the 2017 clear-cut, corroborating findings by Dai et al. (2001). This may be attributed to the tendency for OM loss and reduced OM storage in harvested hillslopes; OM is more readily lost from clear-cuts due to alterations to soil properties (Blanco, 2012; Dean et al., 2017; Nave et al., 2010).

DOC levels varied more in soils from clear-cut sites compared to their forested counterparts, possibly due to greater heterogeneity in ground cover at these locations. For instance, the 2017 and 2014 clear-cut blocks contained large piles of woody debris and tree stumps amid finer leaf litter and low-growing vegetation, some of which intersected with the sampling locations. In such cases, soil was sampled at the fringe of these obstructions. However, it is likely that these samples were heavily influenced by the nearby detritus. This was less problematic at the 2006 and 2000 clear-cuts, which exhibited a comparatively more uniform growth of vegetation over the soil. The presence of woody debris could be a contributing factor in the higher DOC content, as addition of woody debris over soil has been shown to significantly increase DOC levels in the organic soil horizon (Lajtha et al., 2005).

Though some spectral indices were similar to previous findings (HIX: Ohno, 2002; SUVA: Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009), overall FDOM characteristics at the study site did not fully match those found in other soil studies. In particular, average BIX and FI were considerably lower at this study site (Hansen et al., 2016; Strid et al., 2016), as was E4/E6 (Y. Chen et al., 1977; Kononova, 1966). Slope ratio was consistent with values previously found for peat soil pore water and stream water (Frey et al., 2016). In general, soils at this study site appeared to exhibit less biological activity and a smaller fraction of microbially-derived material than comparable soils in other studies. Comparison to optical properties of surface waters (Cincotta et al., 2019; Hansen et al., 2016; Huguet et al., 2009; Kusakabe et al., 2008; Mistick, 2019; Strid et al., 2016; Wilson & Xenopoulos, 2009) suggests that this may be typical of soil DOM, and as soil water is transported to headwaters, biological activity would be expected to increase (Frey et al., 2016).

General characteristics of the PARAFAC model components were determined via comparison to PARAFAC components described in previous studies, and confirmed by correlations with specific spectral indices. C1, a terrestrial humic-like component (Derrien et al., 2019; Jutaporn et al., 2020; Lin & Guo, 2020; Wünsch & Murphy, 2021; Yamashita et al., 2010), was loosely associated with low molecular weight (slope ratio). C2 and C3, described as organic matter resembling lignin and tannin (Osburn et al., 2012; Panettieri et al., 2020; Wünsch et al., 2017) and soil fulvic acid (Chai et al., 2019; B. Chen et al., 2018; Hong et al., 2021), respectively, were correlated with decreased microbially produced DOM (BIX), more terrestrially derived material (FI), less oxygen demand (peak T/peak C ratio), and greater molecular weight (slope ratio), which match the general characteristics of these compounds. C4 was strongly correlated with less humification and greater biological activity and oxygen

demand, corroborating its description as a tryptophan-like material of microbial origin (Bianchi et al., 2014; Huang et al., 2022).

Soils at the 2017 clear-cut exhibited a higher proportion of terrestrial, relatively high molecular weight FDOM and less material of microbial origin. Of the PARAFAC components determined in this study, the largest fraction found at this site is C2, which corresponds to constituents similar to lignin and tannin. Both compounds are derived from plant material: lignin is a component of cell walls (M. E. Brown & Chang, 2014), while tannin is a class of organic compound that can originate from root litter (Erktan et al., 2017). The prevalence of these materials can be explained by the presence of large amounts of woody debris at this site, which was likely a by-product of logging activities (Zon & Cunningham, 1931). Due to their resistance to biodegradation, they could contribute to reduced lability at this site.

Overall, soil water extracts exhibited similar characteristics between all sites except the 2017 clear-cut, where a greater proportion of high molecular weight FDOM components and reduced amount of microbial protein-like material was observed, corresponding with reduced biological activity and greater relative molecular weight as determined via spectral indices. These differences indicate a greater proportion of hydrophobic DOM, of which aromatic compounds form a fraction (Inamdar et al., 2012), and agree with previous results indicating higher aromatic content in soil solutions from clear-cuts than unharvested forest stands (Dai et al., 2001).

4.2 Lability of water-extractable soil DOM in clear-cut versus forested sites

BDOC was generally low compared to the results of other soil water incubation studies, which typically found losses of 20-40% in forest soils (Andreasson et al., 2009; Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009; McDowell et al., 2006; Yano et al., 2000), compared to an average of 10% in this study. However, it should be noted that other biodegradability incubation studies often use soil microbial inocula instead of a stream-derived one. In addition, variations in soil DOC extraction methods may not allow for a direct comparison of this study's results with others, as soil DOM characteristics have been found to vary depending on the method (Guigue et al., 2014). Of the previous studies compared, the method for soil DOC extraction described in Andreasson et al. (2009) is the most similar to this study's, but the reported DOC loss ranged from 37% to 42%, about 4 times that found in this study.

The BDOC results obtained in this study most closely resemble the findings described by Burd et al. (2020), in which pore water samples were inoculated with nearby stream water and returned BDOC fractions ranging from 2.8% to 25.6%. It is unclear whether lability is controlled by the microbial community available to metabolise DOC. Further incubations using inocula of various sources would be useful in evaluating the significance of this factor.

DOM characteristics were altered only minorly after incubation, with spectral index values typically shifting less than 10% relative to the original. These findings corroborate a 111-day incubation study carried out by Hansen et al. (2016), which found that soil DOM tends to resist changes in character, especially compared to other sources of DOM such as leaf leachate and algae: HIX, BIX, FI, and SUVA remained roughly consistent throughout the incubation. Based on this, and findings by McDowell et al. (2006) that the majority of DOC decay occurs

within 7 days of incubation, it is hypothesized that continued incubation would not alter DOM characteristics significantly beyond what was observed in this study. Therefore, overall changes in soil DOM character are expected to occur only on a small scale as SOM is transported to aquatic ecosystems.

Correlations between spectral indices suggest relationships between certain DOM characteristics and processes. Greater biological activity (measured by BIX) tends to correspond to an increased abundance of microbially-derived material (FI) and lower amounts of humification (HIX)–though FI and HIX themselves do not appear to be interrelated. HIX is also positively correlated with slope ratio, indicating that more microbial activity generally signifies compounds of lower molecular weight. The correlation between slope ratio and E4/E6 confirms previous findings that E4/E6 is partially controlled by molecular weight. Finally, the negative correlation of peak T/peak C ratio with HIX and slope ratio confirms the involvement of oxygen and microbial metabolism in the humification process (Balser, 2005; Flores, 2014). Similarly, the strong association of higher C1 levels with a drop in C4, higher HIX, and lower peak T/peak C ratio during incubation could point to C1 consisting of products of humification.

4.2.1 Duration of effects from forest management

Differences in BDOC between forested and clear-cut sites were not found to be statistically meaningful in this study, though DOC lability tended to be lower in soils obtained from clear-cut sites compared to forested sites. The greatest difference between clear-cut and forested sites was found in the 2017 pair.

Though BDOC was statistically the same, FDOM composition did vary significantly between the 2017 sites, with relatively low microbially-derived DOM and overall high molecular weight. Highly processed organic compounds, such as lignin, were more abundant, while the amount of humic material presumed to be of comparatively lower molecular weight and resulting directly from microbial humification processes was proportionately lower. While minor differences were observed for the 2014 and 2006 sites, the clear-cut/forested pairs were generally similar to each other, and the 2000 sites were statistically the same. Most of the notable characteristics observed at the clear-cuts are inferred to become indistinguishable from those of the forested sites sometime between 4 and 7 years after harvest. Therefore, the preliminary results of this study suggest that forestry practices alter water-extractable soil DOM only in the relatively short term. DOM compositional changes and DOC lability, if impacted, might be expected to resemble pre-harvest levels again within less than 7 years, and certainly in less than 10 years.

The duration of perceivable differences inferred from this study is relatively short compared to some findings from previous research on the effects of forest harvest. For example, Fegel et al. (2021) reported that DOM exported in headwaters from a second-growth forest that was clear-cut 32 years prior to the study was five times more reactive than that from an old-growth forest on the same hillslope, and DOC flux from the harvested site was lower. DOC fluxes were also found to differ between subtropical forest catchments of differing succession stages, with the youngest stand being 60-70 years old (Yan et al., 2015), and Dai et al. (2001) reported elevated DOC concentrations in soil solutions sampled from a clear-cut 15 years after harvest. Evidence shows that forestry may alter soil organic matter dynamics for decades (Dai et al., 2001; Nave et al., 2010) or even centuries (Blanco, 2012; Dean et al., 2017) after harvest.

While long-persisting effects of forestry on forest soils have been observed, site-specific changes are less well-defined. A meta-analysis (D. W. Johnson & Curtis, 2001) found that some studies reported higher C stocks in forest mineral soils following harvest, while for others it was lower; overall, the differences were minor (Yanai et al., 2003). Research on decomposition rates in the forest floor also returned highly variable results, which possibly depend on regional climate (Prescott et al., 2000). In a study by Prescott et al. (2000), decomposition rates of leaf litter were not found to vary between even recent clear-cuts (1 - 6 years) and forested sites except in the case of pine needles, where decomposition was slightly reduced in clear-cuts. Of the literature reviewed, the study sites of Prescott et al. (2000) are the most similar to the one used in this study, lending credence to the hypothesis that differences between clear-cuts and unharvested forests may be relatively small in ecosystems like this study's location.

However, changes in soil DOM do not always result in changes further downstream. Dai et al. (2001) found no significant difference in DOC chemistry between streams draining clear-cut regions versus forested, despite differences in soil solutions, and proposed that factors such as lower mineral soil processes, in-stream processes, and variations in hydrological flowpaths may influence the DOC chemistry of stream waters. Furthermore, Sebestyen et al. (2021) reported that DOM from upland temperate forests had negligible influence on DOM lability in downslope peatlands and downstream, with the most prominent effect simply being dilution of TOC levels by runoff. The complexity of DOM dynamics in forested catchments means that the effects of clear-cutting on water-extractable soil DOM are not always apparent, and efforts to predict the magnitude, nature, and duration of DOM alterations after forest harvest may depend heavily on a detailed understanding of site characteristics.

4.3 Implications for drinking water treatability

NOM in natural waters (of which DOM is a constituent) presents a number of challenges in the drinking water treatment process. It exerts coagulant and chemical disinfectant demands which can reduce the efficacy of pathogen removal procedures; it reacts with disinfectants to form potentially harmful DBPs; it also facilitates the development of biofilms in the water treatment system, which can harbour pathogens (Health Canada, 2020). The extent of NOM's effects on the treatment process is controlled by the amount and character of the NOM present.

NOM can be broadly categorized as hydrophobic and hydrophilic fractions. Hydrophobic compounds include humic and fulvic acids, phenols such as lignin, tannins, and aromatic molecules, while hydrophilic compounds include amino acids and sugars. Of the two groups, carbohydrates and proteins tend to be more biodegradable, and lignins and tannins are among the most recalcitrant compounds (Health Canada, 2020). A significant fraction of hydrophobic NOM can be removed via coagulation, a process in which DOM is converted into particulate matter that is then charge-neutralized so the particles aggregate during flocculation and can subsequently be removed via clarification or filtration (Croué et al., 1993; Health Canada, 2020). In waters with SUVA measurements above 4 L/mg·m, up to 80% removal of hydrophobic NOM is typically achievable (Health Canada, 2020). Hydrophilic compounds producing low SUVA have a low affinity for removal via coagulation (Edzwald & Tobiason, 1999; Health Canada, 2020), though biodegradation may be effective at eliminating certain species (Zhou et al., 2014).

In addition to other factors such as temperature, pH, and NOM concentration, DBP formation potential depends on the type of precursor compound available to react with chemical disinfectants. Humic and fulvic acids are the primary source of trihalomethanes (THMs) and haloacetic acids (HAAs), two major categories of DBPs (Bond et al., 2011, 2012). Some amino

acids, such as tryptophan, are also significant precursors to THM and HAA, as well as to nitrogen-containing DBPs (Health Canada, 2020). Hydrophilic matter of microbial origin (e.g. algal cells) have been proven to contribute to DBP-FP (Yang et al., 2011).

Given that the results of this study indicate a higher amount of terrestrial-origin humic compounds in water-extractable soil DOM from recently harvested hillslopes, and that such compounds have been shown to resist biodegradation by stream microbial communities, it stands to reason that a greater fraction of hydrophobic NOM may be expected downstream in forested catchments subjected to clear-cutting. Therefore, the coagulation demand for source drinking waters derived from such catchments may increase. The extent of additional coagulant required is also dependent on the specific compound type: for example, fulvic acid has been found to increase coagulant demand twofold compared to an equal amount of humic acid (Edzwald, 1993; Rigobello et al., 2011), possibly because a greater proportion of them are non-coagulable (Hall & Packham, 1965; Health Canada, 2020). At the same time, hydrophobic NOM tends to exert only a low level of chlorine demand compared to hydrophilic compounds (Health Canada, 2020; Hwang et al., 2001). This suggests that the bulk of the adjustments to water treatment required to accommodate an increase in terrestrial humic materials lies in the coagulation process.

Humic and fulvic acids may also contribute to color in in natural waters; these compounds range from yellow to black (Health Canada, 2020; Kononova, 1966). The soil water extract samples were observed to be a light yellow to tan color. Since coagulation has proven effective at removing a substantial portion of humic and fulvic acids, there is potential for it to simultaneously reduce issues with color.

4.4 Experimental footnotes

4.4.1 Reproducibility of DOC concentration analysis results

Assessment of TOC analyzer results from duplicate samples indicates that the duplicate's DOC concentration falls within 15% of the original result. In most cases, the duplicate analysis returned a lower DOC concentration than the original. Given that this margin sometimes exceeds the calculated BDOC fraction of the samples, further investigation into potential factors affecting sample reproducibility (holding time, photodegradation, sample heterogeneity, etc.) may be needed in order to obtain more reliable results.

4.4.2 Flocculation and sample heterogeneity due to acidification

Addition of HCl caused the formation of floc in a small portion of samples. If present, floc is typically visible within 24 hours after acidification, and may continue to settle within the sample as time passes. The extent of floc formation varies from sample to sample, with some particulates being mm-scale in size. This floc is hypothesized to result from aggregation of humic acid, which becomes insoluble below a pH of 2 (Young & von Wandruszka, 2001). During acidification, efforts were made to avoid lowering the pH of the sample past this threshold; however, the use of pH indicator strips did not allow for precise measurement of the pH, especially since they displayed similar colors in the 2-4 pH range.

The presence of floc creates heterogeneity in the sample, which may have affected the obtained DOC concentration values. Floc may be composed of organic carbon that is removed from the sample solution when the particles settle to the bottom of the vial, lowering the overall DOC concentration reported; it may also be drawn into the TOC analyzer, artificially increasing the detected concentration. In the 4°C incubation batch, it was observed that for vials that

contained floc, the sample immediately following it tended to yield disproportionately low concentrations when compared to expected values from similar samples in the 20°C incubation, which could suggest some extent of interference with the TOC analyzer caused by the floc. The 4°C samples were likely disproportionately affected due to the longer holding time, which would have allowed floc to settle.

EEM analysis of soil water extract before and after HCl addition confirmed that higher molecular weight material was preferentially removed from solution, presumably as floc, but it is unclear if this correponds directly to humic acid in the sample, as the components that coagulated the most are described as highly processed organic material (C2) and soil fulvic acid (C3). That a fulvic acid-like compound would coagulate is particularly unexpected, as fulvic acid is typically described as lower molecular weight and soluble regardless of pH; the solubility of fulvic acid after acidification is sometimes used as the defining factor in separating fulvic acids from humic acids (Kononova, 1966; Young & von Wandruszka, 2001). It is likely that PARAFAC analysis was unable to separate the components to enough of an extent that humic acids were completely excluded from the EEM signatures of C2 and C3.

5 Conclusion

Dissolved organic matter (DOM) is ubiquitous in natural waters, and while it is crucial for nutrient cycling in the environment, it can pose challenges in drinking water treatment (H. Chen et al., 2019; Health Canada, 2020; Lyon et al., 2014). Forestry practices in catchments where source drinking water is derived may alter DOM dynamics in forest soils (Blanco, 2012; Dean et al., 2017; Nave et al., 2010; Prescott et al., 2000; Stednick, 2000), with varying effects in aquatic systems downstream (Dai et al., 2001; Laudon et al., 2009; Schelker et al., 2012). Soil DOM processes are driven by a multitude of interrelated environmental factors that are not fully understood (Marschner & Kalbitz, 2003; Yanai et al., 2003), but the lability of DOM can be used to estimate its reactivity during transport. This thesis investigated the relationship between forest clear-cutting and the lability of water-extractable soil DOM in a Pacific coastal temperate rainforest near Vancouver, Canada, attempting to establish a chronology of how DOM lability changes with time elapsed since forest harvest.

Four clear-cut blocks of varying harvest history were each compared to nearby forest stands to evaluate differences in the characteristics and lability of their soil DOM. Soil from the topmost (organic) layer was mixed fresh with reverse osmosis water to obtain soil water extract (SWE). The potential for DOM biodegradation was determined via in-laboratory incubation of SWE samples, using stream water to simulate the introduction of soil DOM to headwaters. Lability was quantified using two types of parameters: 1) change in dissolved organic carbon (DOC) concentration; 2) changes in optical properties of fluorophoric DOM (FDOM).

DOC concentrations in fresh SWE were higher on average in clear-cut samples (19 ± 4mg C/L mean ± 1 standard error) than forested (16.1 ± 1 mg C/L), though also more variable.

The high variability in DOC from clear-cuts, especially the more recently harvested sites, is attributed to the heterogeneity of soil surface substrate (i.e. woody debris such as slash piles) at the site. Overall, DOC levels were similar to those reported by Fellman et al. (2008; 2009) for an Alaskan coastal temperate rainforest ecosystem, and low compared to soils of other ecosystem types (Burd et al., 2020; Hansen et al., 2016; Lajtha et al., 2005). The difference between clear-cut and forested sites was not statistically significant, but mimicked findings by Dai et al. (2001), where higher DOC concentrations were found in soil solutions from clear-cuts.

Analysis of FDOM fluorescence and absorbance properties revealed that some characteristics were generally low compared to literature values found (BIX and FI: Hansen et al., 2016; Strid et al., 2016 E4/E6: Y. Chen et al., 1977; Kononova, 1966), possibly indicating that the microbial fraction of DOM is particularly low at this study site. Other characteristics such as HIX (Ohno, 2002), slope ratio (Frey et al., 2016) and SUVA (Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009) were consistent with values expected for soil DOM. Parallel factors (PARAFAC) statistical analysis identified four FDOM components, of which three fractions are terrestrially-derived and one is of microbial origin. Terrestrial material was found to constitute over 75% of detectable FDOM at all sites. FDOM composition and optical properties were generally similar between clear-cut and forested blocks, with the exception of the most recent clear-cut, last harvested in 2017. For the cut-block harvested in 2017, significantly lower fractions of the terrestrial humic-like Component 1 (Derrien et al., 2019) were found, and FDOM was instead dominated by the higher molecular weight, lignin-/tannin-like Component 2 (Panettieri et al., 2020). FI and slope ratio were also significantly lower. These differences may be due to the prevalence of woody debris covering the soil, a remnant of logging at the site (Zon & Cunningham, 1931).

Biodegradable DOC (BDOC) fractions in SWE samples averaged 12 ± 9% (mean ± 1 standard deviation), lower than the 20 – 40% generally reported by other studies on forest soils (Andreasson et al., 2009; Fellman et al., 2008; Fellman, Hood, D'Amore, et al., 2009; McDowell et al., 2006; Yano et al., 2000). BDOC was not found to differ significantly between clear-cut and forested blocks, though it tended to be lower in the 2017 and 2014 clear-cut/forested site pairs. Optical properties shifted after incubation, pointing to increased microbial activity (BIX, FI) but also a higher proportion of high molecular weight (slope ratio), aromatic (SUVA) compounds. Correlations between optical properties and PARAFAC component abundance further hinted at their character: an increase in the humic-like Component 1 was strongly associated with a decline in microbially-derived Component 4, an increase in the proportion of humic-like material and inferred reduction in oxygen demand (peak T/peak C ratio), and an increase in humification (HIX), indicating Component 1 is a humic-like material that may be a more recent metabolic by-product compared to Components 2 and 3. No significant differences were found between clear-cut/forested sites except for the 2017 pair, where a higher degree of humification and reduced biological activity were observed for the clear-cut.

Significant differences in DOM character and lability were found between harvested and forested sites for the 2017 clear-cut/forested site pair, while these differences were generally not observed in the 2014, 2006 and 2000 pairs, suggesting that alterations to DOM lability persist for less than 10 years after harvest. This duration is shorter than observations from previous studies, which have reported significant differences in soil DOM for clear-cuts well over 10 years post-harvest (Dai et al., 2001; Fegel et al., 2021). Regional environmental variability may play a role in this inconsistency, as evidenced by the lack of major differences observed even in very recent clear-cuts at a nearby site in the same biogeoclimatic zone (Prescott et al., 2000).

Terrestrially-derived hydrophobic compounds, which were found in higher amounts in soil solutions from recent clear-cuts, are a primary source of two major classes of disinfection by-products (DBPs). As these fractions are resistant to biodegradation (M. E. Brown & Chang, 2014; Erktan et al., 2017; Health Canada, 2020), soil-derived DOM transported downstream from clear-cut areas can potentially increase DBP formation potential. Coagulation is effective at removing the majority of these substances, but a small fraction remains non-coagulable. Increasing coagulant demand is predicted to be the main impact of clear-cutting on forest source drinking water treatability.

Overall, this research indicated that alterations in water-extractable soil DOM caused by clear-cutting were small for the forested ecosystem studied, and suggests that observable changes may be relatively short-lived at this site compared to forests in other biogeoclimatic zones (Dai et al., 2001; Fegel et al., 2021; Prescott et al., 2000). These alterations carry minor implications for water treatment: soil DOM from clear-cuts did not exhibit significantly different lability from unharvested forests, but recent clear-cuts produced a higher portion of terrestrially-derived DOM that may persist downstream, potentially leading to increased coagulant demand during drinking water treatment. This study also contributes to a pool of varying results from previous soil DOM lability research, confirming the complexity of soil DOM dynamics and a need for greater understanding of unique regional characteristics in order to accurately predict soil DOM responses to forestry and subsequent downstream effects. A standardized methodology for soil water extractions and incubations is recommended for ease of comparison between studies.

5.1 Future research

Throughout this study, several knowledge gaps were identified that hindered the understanding of how soil DOM responds to clear-cutting. Investigation into the following areas would provide crucial insight into the relationship between forest harvesting and soil DOM lability in Pacific coastal temperate rainforests and the subsequent implications for drinking water treatability.

1. Effect of seasonality on DOM lability: Seasonal variations in DOM concentration and lability have been observed in both terrestrial and aquatic ecosystems; specific patterns of variation differ substantially across regions (Burd et al., 2020; Fellman, Hood, D'Amore, et al., 2009; Holmes et al., 2008; Sebestyen et al., 2021; Wickland et al., 2012). Research into seasonal effects in this biogeoclimatic zone would improve understanding of variations in soil DOM lability and assist in the engineering of more time-specific, targeted mitigation strategies to adapt to the changes in DOM dynamics caused by clear-cutting.

2. In-situ incubation: Laboratory incubations are effective at measuring the potential for DOM biodegradation, but their results may not reflect actual responses in-situ. Additional environmental factors such as photodegradation can affect biodegradation (Burd et al., 2020; Cory et al., 2015; Hansen et al., 2016) such that the resulting DOM pool actually entering headwaters is different from what may be expected. In-situ incubation of soil DOM would incorporate highly localized environmental factors that are difficult to control for, including temperature fluctuations, differences in light intensity, and

variations in stream biota, but may provide a better understanding of whether the differences observed in laboratory results are significant in a natural setting.

3. Downstream propagation of forestry effects: Due to the complexity of DOM dynamics, differences at the hillslope scale are not always observable downstream (Dai et al., 2001). Watershed-level study of DOM flux and character, e.g. à la Mattsson et al. (2005), would allow a better understanding of how small-scale disturbances interact with the environment and impact water quality at a scale relevant to drinking water treatment engineering.

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7 Appendices

Appendix A: Supplementary data

Table A: P-values of two-sided Wilcoxon signed rank test for significant changes in spectral indices and PARAFAC component fractions after incubation of diluted SWE samples

Index	***4°C***	***20°C***
HIX	0.000	0.079
BIX	0.008	0.107
FI	0.000	0.046
Peak T/peak C ratio	0.001	0.003
E4/E6	0.663	0.029
Slope ratio	0.877	0.000
C1	0.000	0.003
C2	0.684	0.001
C3	0.000	0.152
C4	0.000	0.014
SUVA	NA	0.000

Table B: P-values of two-sided Mann-Whitney test for significant differences in spectral indices and PARAFAC component fractions between each clear-cut/forested site pair, undiluted SWE samples

Index	***2017***	***2014***	***2006***	***2000***
HIX	0.860	0.663	0.383	0.383
BIX	0.112	0.190	0.081	0.190
FI	0.052	0.081	0.383	1.000
Peak T/peak C ratio	0.860	0.663	0.190	0.190
E4/E6	0.596	0.663	0.383	0.190
Slope ratio	0.052	0.663	1.000	1.000
C1	0.052	0.663	0.081	0.663
C2	0.112	0.383	0.383	0.663
C3	0.112	0.190	0.081	1.000
C4	0.860	0.663	0.190	0.383
SUVA	0.216	0.383	0.190	0.190

Table C: P-values of two-sided Mann-Whitney test for significant differences in post-incubation spectral index and PARAFAC component changes between each clear-cut/forested site pair

Index	***2017, 4°C***	***2017, 20°C***	***2014, 4°C***	***2014, 20°C***	***2006, 4°C***	***2006, 20°C***	***2000, 4°C***	***2000, 20°C***
HIX	0.663	0.081	1.000	1.000	0.383	1.000	0.663	1.000
BIX	0.190	0.081	0.190	0.663	0.663	1.000	1.000	1.000
FI	0.383	0.081	1.000	0.663	1.000	0.383	1.000	0.663
Peak T/peak C ratio	0.383	0.383	0.663	1.000	0.663	1.000	1.000	1.000
E4/E6	1.000	0.190	0.383	1.000	1.000	1.000	1.000	1.000
Slope ratio	0.663	0.190	1.000	1.000	1.000	1.000	1.000	0.383
C1	0.190	0.081	0.663	0.663	0.663	0.190	0.383	1.000
C2	0.663	0.383	0.081	1.000	1.000	1.000	0.663	0.663
C3	0.663	0.081	0.663	0.383	0.663	0.663	0.663	0.663
C4	0.383	0.383	0.383	0.663	1.000	1.000	0.663	0.663
SUVA	NA	0.383	NA	0.663	NA	1.000	NA	1.000

Table D: Initial (post-dilution) and post-incubation concentrations and BDOC of soil water extract samples

Sample ID	*Temperature (°C)*	*Year*	*Harvest history*	*Initial DOC concentration (mg/L)*	*Final DOC concentration (mg/L)*	*BDOC (%)*
1	20	2017	Clear-cut	12.28 ± 0.04	12.57 ± 0.06	-2.4
2	20	2017	Clear-cut	9.10 ± 0.08	8.98 ± 0.1	1.3
3	20	2017	Clear-cut	18.03 ± 0.2	16.17 ± 0.1	10.3
4	20	2017	Forested	9.98 ± 0.1	8.84 ± 0.02	11.4
5	20	2017	Forested	7.05 ± 0.05	6.73 ± 0.03	4.5
6	20	2017	Forested	7.14 ± 0.03	6.74 ± 0.03	5.7
7	20	2014	Clear-cut	18.22 ± 0.2	16.90 ± 0.1	7.3
8	20	2014	Clear-cut	9.31 ± 0.07	8.58 ± 0.2	7.8
9	20	2014	Clear-cut	9.26 ± 0.04	7.78 ± 0.01	16
10	20	2014	Forested	8.48 ± 0.08	7.93 ± 0.06	6.5
11	20	2014	Forested	11.30 ± 0.1	8.91 ± 0.05	21.1
12	20	2014	Forested	8.70 ± 0.06	7.87 ± 0.2	9.5
13	20	2006	Clear-cut	9.67 ± 0.05	8.79 ± 0.2	9.1
14	20	2006	Clear-cut	9.53 ± 1	8.22 ± 0.08	13.8
15	20	2006	Clear-cut	8.89 ± 0.1	8.35 ± 0.02	6.2
16	20	2006	Forested	8.84 ± 0.1	8.43 ± 0.08	4.7
17	20	2006	Forested	8.70 ± 0.2	8.49 ± 0.08	2.4
18	20	2006	Forested	10.37 ± 0.1	9.14 ± 0.05	11.9
19	20	2000	Clear-cut	8.39 ± 0.06	8.34 ± 0.05	0.5
20	20	2000	Clear-cut	8.93 ± 0.1	7.79 ± 0.008	12.8
21	20	2000	Clear-cut	9.74 ± 0.03	8.80 ± 0.03	9.7
22	20	2000	Forested	9.46 ± 0.1	8.72 ± 0.08	7.9
23	20	2000	Forested	9.19 ± 0.1	8.74 ± 0.05	4.9
24	20	2000	Forested	8.74 ± 0.3	7.67 ± 0.06	12.3

25	4	2017	Clear-cut	12.28 ± 0.04	11.11 ± 0.2	9.6
26	4	2017	Clear-cut	9.10 ± 0.08	8.61 ± 0.08	5.4
27	4	2017	Clear-cut	18.03 ± 0.2	17.16 ± 0.2	4.9
28	4	2017	Forested	9.98 ± 0.1	8.58 ± 0.1	14
29	4	2017	Forested	7.05 ± 0.05	5.58 ± 0.4	20.8
30	4	2017	Forested	7.14 ± 0.03	7.24 ± 0.06	-1.4
31	4	2014	Clear-cut	18.22 ± 0.2	16.71 ± 0.1	8.3
32	4	2014	Clear-cut	9.31 ± 0.07	8.31 ± 0.09	10.7
33	4	2014	Clear-cut	9.26 ± 0.04	8.19 ± 0.3	11.6
34	4	2014	Forested	8.48 ± 0.08	7.41 ± 0.2	12.7
35	4	2014	Forested	11.30 ± 0.1	7.77 ± 0.07	31.2
36	4	2014	Forested	8.70 ± 0.06	6.66 ± 0.1	23.4
37	4	2006	Clear-cut	9.67 ± 0.05	7.92 ± 0.6	18.1
38	4	2006	Clear-cut	9.53 ± 1	9.89 ± 0.1	-3.8
39	4	2006	Clear-cut	8.89 ± 0.1	5.65 ± 0.5	36.4
40	4	2006	Forested	8.84 ± 0.1	7.64 ± 0.02	13.6
41	4	2006	Forested	8.70 ± 0.2	6.69 ± 0.1	23.1
42	4	2006	Forested	10.37 ± 0.1	7.84 ± 0.3	24.4
43	4	2000	Clear-cut	8.39 ± 0.06	6.71 ± 0.03	20
44	4	2000	Clear-cut	8.93 ± 0.1	6.91 ± 0.6	22.6
45	4	2000	Clear-cut	9.74 ± 0.03	7.86 ± 0.03	19.3
46	4	2000	Forested	9.46 ± 0.1	7.76 ± 0	18
47	4	2000	Forested	9.19 ± 0.1	7.40 ± 0.05	19.5
48	4	2000	Forested	8.74 ± 0.3	7.00 ± 0.09	19.9

Table E: Spectral indices and PARAFAC component fractions of undiluted soil water extract samples

Year	*Harvest history*	*HIX*	*BIX*	*FI*	*Peak T/peak C ratio*	*E4/E6*	*Slope ratio*	*C1 (%)*	*C2 (%)*	*C3 (%)*	*C4 (%)*	*SUVA (mg•m/L)*
2017	Forested	0.858	0.486	1.103	0.461	3.077	0.891	51.39	21.83	9.91	16.88	3.878
2017	Forested	0.783	0.488	1.067	0.833	3.122	0.865	43.64	18.85	10.17	27.34	4.223
2017	Forested	0.922	0.415	1.040	0.192	3.334	0.837	46.16	31.73	14.75	7.36	3.934
2017	Clear-cut	0.835	0.396	0.946	0.240	3.086	0.815	17.59	44.95	28.22	9.24	4.040
2017	Clear-cut	0.813	0.398	0.942	0.270	2.830	0.822	17.37	44.02	28.44	10.17	4.087
2017	Clear-cut	0.865	0.415	0.978	0.306	3.298	0.808	32.13	35.21	20.82	11.84	5.260
2017	Clear-cut	0.798	0.477	1.021	0.641	3.077	0.833	41.31	22.98	13.10	22.60	4.663
2014	Forested	0.778	0.496	1.046	0.734	2.962	0.831	39.25	22.16	13.14	25.45	5.221
2014	Forested	0.807	0.471	1.053	0.664	2.927	0.863	41.74	22.56	12.50	23.20	4.215
2014	Forested	0.830	0.468	1.032	0.569	2.877	0.907	49.26	18.56	11.52	20.67	3.102
2014	Clear-cut	0.764	0.516	1.065	0.896	2.734	0.890	40.27	20.02	10.45	29.27	4.353
2014	Clear-cut	0.712	0.542	1.073	1.101	3.186	0.769	32.43	22.64	10.95	33.97	5.590
2014	Clear-cut	0.864	0.476	1.090	0.389	3.237	0.839	46.29	25.73	12.36	15.62	4.302
2006	Forested	0.863	0.435	1.017	0.335	2.622	0.909	43.87	28.18	15.00	12.95	3.914
2006	Forested	0.877	0.430	1.037	0.328	2.911	0.879	46.50	26.04	14.55	12.92	4.400
2006	Forested	0.845	0.449	0.952	0.451	2.881	0.838	46.72	19.84	16.42	17.02	4.218
2006	Clear-cut	0.858	0.455	1.016	0.447	3.288	0.862	51.60	20.35	11.93	16.12	3.806
2006	Clear-cut	0.813	0.492	1.045	0.645	2.689	0.853	49.42	17.45	10.83	22.30	4.174
2006	Clear-cut	0.860	0.461	1.049	0.478	3.139	0.880	49.82	20.76	12.10	17.33	3.596
2000	Forested	0.821	0.455	1.024	0.600	2.946	0.933	44.99	21.64	12.34	21.04	3.654
2000	Forested	0.851	0.438	0.961	0.455	2.793	0.925	47.48	20.40	15.15	16.96	3.584
2000	Forested	0.862	0.441	1.016	0.437	3.046	0.866	49.37	21.36	13.32	15.95	4.056
2000	Clear-cut	0.787	0.517	1.104	0.800	2.597	0.947	46.11	19.29	8.28	26.32	3.735
2000	Clear-cut	0.821	0.443	1.009	0.566	2.825	0.901	44.88	21.65	13.47	20.01	4.066
2000	Clear-cut	0.821	0.477	0.985	0.609	2.575	0.923	49.31	16.61	13.61	20.47	4.800

Table F: Spectral indices and PARAFAC component fractions before and after incubation

Year	*Harvest history*	*Temperature (°C)*	*Incubation*	*HIX*	*BIX*	*FI*	*Peak T/ peak C ratio*	*E4/E6*	*Slope ratio*	*C1 (%)*	*C2 (%)*	*C3 (%)*	*C4 (%)*	*SUVA (mg•m /L)*
2017	Forested	20	Before	0.918	0.440	1.052	0.222	3.340	0.802	57.09	22.25	11.93	8.74	3.780
2017	Forested	20	Before	0.865	0.492	1.097	0.433	3.165	0.868	56.82	18.21	8.96	16.00	3.574
2017	Forested	20	Before	0.775	0.505	1.074	0.853	3.242	0.852	48.28	15.64	8.13	27.95	3.972
2017	Forested	20	After	0.920	0.448	1.071	0.205	3.467	0.794	57.72	22.34	11.75	8.19	4.137
2017	Forested	20	After	0.857	0.509	1.105	0.444	3.025	0.848	56.69	18.52	8.26	16.53	3.748
2017	Forested	20	After	0.845	0.517	1.115	0.484	3.382	0.859	55.56	18.54	7.77	18.14	3.749
2017	Forested	20	After	0.778	0.528	1.109	0.750	3.200	0.855	48.71	16.73	8.01	26.55	4.232
2017	Forested	4	Before	0.918	0.440	1.052	0.222	3.340	0.802	57.09	22.25	11.93	8.74	NA
2017	Forested	4	Before	0.865	0.492	1.097	0.433	3.165	0.868	56.82	18.21	8.96	16.00	NA
2017	Forested	4	Before	0.775	0.505	1.074	0.853	3.242	0.852	48.28	15.64	8.13	27.95	NA
2017	Forested	4	After	0.908	0.452	1.061	0.243	3.391	0.810	56.82	22.03	11.62	9.52	NA
2017	Forested	4	After	0.843	0.506	1.117	0.499	3.248	0.879	55.18	18.23	8.19	18.40	NA
2017	Forested	4	After	0.757	0.528	1.106	0.898	3.164	0.865	46.66	16.07	7.60	29.68	NA
2017	Clear-cut	20	Before	0.853	0.451	1.005	0.384	3.603	0.796	44.59	24.83	15.42	15.16	4.727
2017	Clear-cut	20	Before	0.787	0.501	1.053	0.733	3.102	0.833	49.16	15.80	10.15	24.89	4.325
2017	Clear-cut	20	Before	0.749	0.496	1.005	0.834	3.179	0.870	43.70	16.84	11.64	27.83	4.479
2017	Clear-cut	20	After	0.871	0.444	1.015	0.315	3.700	0.781	46.68	24.81	15.59	12.92	5.042
2017	Clear-cut	20	After	0.798	0.509	1.050	0.694	3.361	0.814	50.23	16.01	10.05	23.71	4.152
2017	Clear-cut	20	After	0.782	0.475	0.995	0.694	3.341	0.859	47.03	17.04	12.15	23.78	4.031
2017	Clear-cut	4	Before	0.853	0.451	1.005	0.384	3.603	0.796	44.59	24.83	15.42	15.16	NA
2017	Clear-cut	4	Before	0.787	0.501	1.053	0.733	3.102	0.833	49.16	15.80	10.15	24.89	NA
2017	Clear-cut	4	Before	0.749	0.496	1.005	0.834	3.179	0.870	43.70	16.84	11.64	27.83	NA
2017	Clear-cut	4	After	0.860	0.437	1.007	0.373	3.606	0.794	45.11	25.00	15.32	14.57	NA
2017	Clear-cut	4	After	0.767	0.516	1.062	0.820	3.185	0.845	47.88	15.40	9.19	27.53	NA
2017	Clear-cut	4	After	0.748	0.491	1.017	0.831	3.020	0.879	44.16	16.74	11.41	27.69	NA
2014	Forested	20	Before	0.831	0.520	1.008	0.591	2.713	0.876	53.99	14.04	12.40	19.57	3.289

2014	Forested	20	Before	0.788	0.506	1.067	0.687	2.796	0.873	47.16	17.76	10.20	24.89	3.843
2014	Forested	20	Before	0.781	0.531	1.071	0.777	3.110	0.826	47.87	15.52	9.96	26.65	4.608
2014	Forested	20	After	0.828	0.518	0.998	0.586	2.765	0.850	54.38	14.03	11.88	19.71	3.601
2014	Forested	20	After	0.796	0.508	1.089	0.642	3.190	0.839	48.06	18.41	9.76	23.77	4.632
2014	Forested	20	After	0.797	0.532	1.057	0.646	3.114	0.812	49.60	16.20	10.22	23.98	4.733
2014	Forested	4	Before	0.831	0.520	1.008	0.591	2.713	0.876	53.99	14.04	12.40	19.57	NA
2014	Forested	4	Before	0.788	0.506	1.067	0.687	2.796	0.873	47.16	17.76	10.20	24.89	NA
2014	Forested	4	Before	0.781	0.531	1.071	0.777	3.110	0.826	47.87	15.52	9.96	26.65	NA
2014	Forested	4	After	0.813	0.519	1.028	0.640	2.770	0.884	52.94	14.37	11.13	21.56	NA
2014	Forested	4	After	0.783	0.508	1.073	0.727	3.121	0.854	46.86	18.00	9.38	25.76	NA
2014	Forested	4	After	0.767	0.543	1.093	0.773	3.230	0.813	48.00	16.03	8.46	27.51	NA
2014	Forested	4	After	0.770	0.518	1.053	0.830	3.098	0.804	46.76	15.72	9.97	27.55	NA
2014	Forested	4	After	0.750	0.527	1.083	0.891	3.089	0.820	45.38	15.57	9.29	29.76	NA
2014	Clear-cut	20	Before	0.845	0.513	1.093	0.458	3.191	0.850	52.71	19.63	9.60	18.06	4.125
2014	Clear-cut	20	Before	0.781	0.528	1.079	0.844	2.835	0.881	47.39	15.93	8.98	27.71	3.806
2014	Clear-cut	20	Before	0.752	0.537	1.085	0.831	3.531	0.757	38.13	22.64	10.69	28.55	4.767
2014	Clear-cut	20	After	0.850	0.506	1.101	0.442	3.370	0.801	53.86	19.84	9.16	17.14	4.267
2014	Clear-cut	20	After	0.785	0.528	1.083	0.627	3.569	0.737	41.48	23.58	10.92	24.02	4.844
2014	Clear-cut	20	After	0.789	0.534	1.088	0.642	3.569	0.739	41.32	23.72	10.92	24.03	4.841
2014	Clear-cut	20	After	0.778	0.542	1.100	0.794	3.046	0.862	48.18	16.15	8.23	27.44	4.262
2014	Clear-cut	4	Before	0.845	0.513	1.093	0.458	3.191	0.850	52.71	19.63	9.60	18.06	NA
2014	Clear-cut	4	Before	0.781	0.528	1.079	0.844	2.835	0.881	47.39	15.93	8.98	27.71	NA
2014	Clear-cut	4	Before	0.752	0.537	1.085	0.831	3.531	0.757	38.13	22.64	10.69	28.55	NA
2014	Clear-cut	4	After	0.837	0.512	1.099	0.481	3.262	0.822	52.79	19.26	9.42	18.53	NA
2014	Clear-cut	4	After	0.744	0.546	1.090	0.852	3.528	0.752	37.51	22.74	10.45	29.30	NA
2014	Clear-cut	4	After	0.751	0.553	1.100	0.919	2.767	0.893	46.41	15.40	7.89	30.30	NA
2006	Forested	20	Before	0.886	0.455	1.044	0.350	3.158	0.842	54.72	19.94	12.38	12.96	4.112
2006	Forested	20	Before	0.884	0.452	1.050	0.348	3.132	0.843	54.49	20.10	12.41	13.00	3.504
2006	Forested	20	Before	0.848	0.475	0.993	0.509	2.950	0.826	53.98	14.35	13.71	17.96	3.894
2006	Forested	20	After	0.886	0.453	1.057	0.324	3.423	0.823	55.06	20.05	12.34	12.55	4.164

2006	Forested	20	After	0.854	0.467	1.040	0.413	2.755	0.856	53.23	19.78	11.64	15.36	4.111
2006	Forested	20	After	0.848	0.490	0.987	0.495	3.047	0.798	52.78	15.91	14.02	17.28	4.008
2006	Forested	4	Before	0.886	0.455	1.044	0.350	3.158	0.842	54.72	19.94	12.38	12.96	NA
2006	Forested	4	Before	0.884	0.452	1.050	0.348	3.132	0.843	54.49	20.10	12.41	13.00	NA
2006	Forested	4	Before	0.848	0.475	0.993	0.509	2.950	0.826	53.98	14.35	13.71	17.96	NA
2006	Forested	4	After	0.875	0.452	1.049	0.361	3.353	0.847	54.44	19.47	12.30	13.79	NA
2006	Forested	4	After	0.836	0.478	1.066	0.455	2.626	0.888	52.18	19.57	11.12	17.13	NA
2006	Forested	4	After	0.837	0.489	0.986	0.523	2.989	0.804	52.35	15.78	13.56	18.31	NA
2006	Clear-cut	20	Before	0.854	0.464	1.024	0.416	2.729	0.879	53.66	19.14	11.83	15.38	3.963
2006	Clear-cut	20	Before	0.869	0.473	1.049	0.443	3.282	0.832	55.39	17.59	11.12	15.89	3.359
2006	Clear-cut	20	Before	0.855	0.469	1.043	0.449	3.211	0.837	54.06	18.93	10.72	16.29	3.730
2006	Clear-cut	20	After	0.874	0.476	1.052	0.395	3.049	0.842	56.22	17.94	11.18	14.67	3.864
2006	Clear-cut	20	After	0.852	0.479	1.047	0.422	3.452	0.842	54.41	19.09	10.48	16.01	3.914
2006	Clear-cut	20	After	0.832	0.499	1.058	0.550	2.877	0.814	52.96	17.33	10.28	19.43	3.991
2006	Clear-cut	4	Before	0.854	0.464	1.024	0.416	2.729	0.879	53.66	19.14	11.83	15.38	NA
2006	Clear-cut	4	Before	0.869	0.473	1.049	0.443	3.282	0.832	55.39	17.59	11.12	15.89	NA
2006	Clear-cut	4	Before	0.855	0.469	1.043	0.449	3.211	0.837	54.06	18.93	10.72	16.29	NA
2006	Clear-cut	4	After	0.870	0.477	1.056	0.430	3.189	0.848	55.23	17.98	11.10	15.68	NA
2006	Clear-cut	4	After	0.848	0.484	1.033	0.449	3.003	0.851	53.63	18.71	10.72	16.95	NA
2006	Clear-cut	4	After	0.828	0.492	1.050	0.590	2.817	0.822	51.90	17.37	10.33	20.40	NA
2000	Forested	20	Before	0.858	0.468	1.031	0.456	3.170	0.845	53.57	17.97	11.65	16.81	3.777
2000	Forested	20	Before	0.853	0.474	0.980	0.474	3.039	0.925	52.69	16.15	13.79	17.37	3.335
2000	Forested	20	Before	0.812	0.504	1.052	0.659	3.203	0.903	50.65	16.74	10.05	22.56	3.425
2000	Forested	20	After	0.869	0.468	1.027	0.387	3.030	0.815	55.10	18.45	11.96	14.50	4.271
2000	Forested	20	After	0.843	0.489	1.028	0.499	3.072	0.890	52.63	17.26	11.55	18.56	3.557
2000	Forested	20	After	0.838	0.483	1.039	0.526	3.214	0.854	52.68	17.59	10.92	18.80	3.522
2000	Forested	4	Before	0.858	0.468	1.031	0.456	3.170	0.845	53.57	17.97	11.65	16.81	NA
2000	Forested	4	Before	0.853	0.474	0.980	0.474	3.039	0.925	52.69	16.15	13.79	17.37	NA
2000	Forested	4	Before	0.812	0.504	1.052	0.659	3.203	0.903	50.65	16.74	10.05	22.56	NA
2000	Forested	4	After	0.856	0.477	1.049	0.456	3.733	0.835	53.64	18.27	11.38	16.70	NA

2000	Forested	4	After	0.832	0.472	1.004	0.526	3.065	0.900	51.86	16.50	12.23	19.42	NA
2000	Forested	4	After	0.819	0.502	1.044	0.624	2.706	0.925	50.89	17.26	10.25	21.59	NA
2000	Clear-cut	20	Before	0.838	0.468	1.033	0.538	3.148	0.856	51.98	17.62	11.08	19.32	3.870
2000	Clear-cut	20	Before	0.834	0.471	1.032	0.547	3.175	0.863	51.78	17.66	10.90	19.66	3.866
2000	Clear-cut	20	Before	0.821	0.483	1.021	0.597	2.886	0.880	51.10	17.14	11.64	20.11	3.834
2000	Clear-cut	20	Before	0.814	0.521	1.114	0.665	2.706	0.923	50.57	18.83	8.03	22.57	3.394
2000	Clear-cut	20	After	0.848	0.479	1.070	0.473	3.121	0.845	52.68	18.80	10.60	17.92	4.124
2000	Clear-cut	20	After	0.833	0.474	1.025	0.521	3.146	0.870	52.26	17.35	11.90	18.49	3.695
2000	Clear-cut	20	After	0.823	0.523	1.121	0.562	2.668	0.882	52.35	19.41	7.83	20.42	3.684
2000	Clear-cut	4	Before	0.838	0.468	1.033	0.538	3.148	0.856	51.98	17.62	11.08	19.32	NA
2000	Clear-cut	4	Before	0.834	0.471	1.032	0.547	3.175	0.863	51.78	17.66	10.90	19.66	NA
2000	Clear-cut	4	Before	0.821	0.483	1.021	0.597	2.886	0.880	51.10	17.14	11.64	20.11	NA
2000	Clear-cut	4	Before	0.814	0.521	1.114	0.665	2.706	0.923	50.57	18.83	8.03	22.57	NA
2000	Clear-cut	4	After	0.833	0.493	1.060	0.551	3.046	0.863	51.11	18.51	10.55	19.82	NA
2000	Clear-cut	4	After	0.815	0.479	1.031	0.595	3.106	0.856	51.00	16.98	11.04	20.97	NA
2000	Clear-cut	4	After	0.798	0.528	1.124	0.689	2.728	0.915	49.32	18.93	7.53	24.22	NA
NA	RO blank	20	Before	0.589	2.308	0.455	0.000	0.469	2.902	66.29	0.00	7.91	25.80	NA
NA	RO blank	20	After	0.643	0.857	0.655	1.009	1.136	1.248	61.93	2.35	0.00	35.72	NA
NA	RO blank	4	Before	0.589	2.308	0.455	0.000	0.469	2.902	66.29	0.00	7.91	25.80	NA
NA	RO blank	4	After	0.493	0.547	1.268	1.268	0.869	1.282	55.27	0.41	0.00	44.32	NA

Table G: Percentage change in spectral indices and PARAFAC component fractions after incubation (mean, SE)

Temp. (C)	*Year*	*Harvest history*	*BIX*	*E4/E6*	*FI*	*C1*	*C2*	*C3*	*C4*	*HIX*	*Peak T/C*	*Slope ratio*
20	2000	Forested	-0.3 ± 1	-1.0 ± 1	1.1 ± 1	2.2 ± 0.7	4.9 ± 0.7	-1.6 ± 4	-7.8 ± 4	1.1 ± 0.7	-10.0 ± 5	-4.2 ± 0.4
20	2000	Clear-cut	0.2 ± 0.6	2.1 ± 2	1.6 ± 0.6	2.4 ± 0.3	3.6 ± 0.9	-1.3 ± 1	-8.6 ± 0.3	1.3 ± 0.08	-13.7 ± 0.5	-2.4 ± 0.6
20	2006	Forested	2.0 ± 0.7	-0.1 ± 4	-0.1 ± 0.4	-1.3 ± 0.6	3.3 ± 2	-1.4 ± 1	3.7 ± 4	-1.1 ± 0.7	2.9 ± 5	-1.4 ± 0.8
20	2006	Clear-cut	3.4 ± 1	1.9 ± 3	1.3 ± 0.6	0.3 ± 0.5	-2.2 ± 2	-4.9 ± 2	5.6 ± 6	-0.8 ± 0.5	5.1 ± 8	-1.9 ± 2
20	2014	Forested	0.0 ± 0.1	5.4 ± 3	-0.1 ± 0.6	2.1 ± 0.5	2.7 ± 0.8	-2.0 ± 1	-4.6 ± 2	0.9 ± 0.4	-8.1 ± 3	-2.8 ± 0.4
20	2014	Clear-cut	0.1 ± 0.7	4.7 ± 1	0.9 ± 0.3	4.2 ± 1	2.3 ± 0.6	-3.6 ± 2	-7.3 ± 3	1.6 ± 0.9	-11.0 ± 4	-3.5 ± 0.7
20	2017	Forested	3.6 ± 0.5	1.2 ± 0.9	2.1 ± 0.4	0.3 ± 0.4	3.1 ± 1	-4.5 ± 2	-1.0 ± 3	-0.3 ± 0.4	-4.1 ± 3	-0.8 ± 0.3
20	2017	Clear-cut	-1.4 ± 1	5.4 ± 0.9	-0.1 ± 0.3	4.8 ± 0.9	0.8 ± 0.3	1.5 ± 0.9	-11.4 ± 2	2.7 ± 0.6	-13.4 ± 2	-1.8 ± 0.2
4	2000	Forested	0.4 ± 0.4	1.0 ± 6	1.1 ± 0.6	-0.3 ± 0.4	2.3 ± 0.3	-3.9 ± 2	2.3 ± 3	-0.6 ± 0.6	1.9 ± 3	-0.5 ± 0.9
4	2000	Clear-cut	1.8 ± 1	1.6 ± 2	1.5 ± 0.3	-1.4 ± 0.4	1.5 ± 1	-5.1 ± 0.4	4.4 ± 0.9	-1.0 ± 0.3	1.6 ± 0.7	-1.0 ± 0.5
4	2006	Forested	2.7 ± 1	-2.9 ± 4	0.4 ± 0.4	-2.6 ± 0.6	1.7 ± 2	-4.0 ± 2	13.4 ± 5	-2.6 ± 0.8	12.3 ± 5	1.1 ± 1
4	2006	Clear-cut	3.4 ± 0.9	-2.0 ± 2	0.8 ± 0.6	-1.5 ± 0.5	-2.7 ± 2	-4.3 ± 2	11.8 ± 6	-1.2 ± 0.6	12.9 ± 8	-1.0 ± 2
4	2014	Forested	-0.2 ± 0.1	4.9 ± 2	1.0 ± 0.3	-1.7 ± 0.3	1.8 ± 0.2	-8.5 ± 0.5	6.6 ± 1	-1.7 ± 0.3	7.0 ± 0.4	-1.0 ± 0.6
4	2014	Clear-cut	2.1 ± 0.8	-0.1 ± 0.8	1.0 ± 0.3	-1.2 ± 0.4	-1.6 ± 0.6	-5.4 ± 2	4.9 ± 1	-1.9 ± 0.5	5.5 ± 1	-0.9 ± 0.8
4	2017	Forested	3.4 ± 0.4	0.6 ± 0.9	1.9 ± 0.4	-2.2 ± 0.5	0.6 ± 0.6	-5.9 ± 1	10.0 ± 2	-2.0 ± 0.3	10.0 ± 2	1.2 ± 0.1
4	2017	Clear-cut	-0.4 ± 1	-0.8 ± 1	0.8 ± 0.2	-0.1 ± 0.7	-0.8 ± 0.5	-4.0 ± 2	2.1 ± 3	-0.6 ± 0.6	2.8 ± 3	0.7 ± 0.3

Table H: Soil moisture and initial (undiluted) DOC concentration in SWE

Year	*Harvest history*	*Initial DOC concentration (mg C/L)*	*Soil Moisture (% wt water/wt dry soil)*
2017	Forested	11.35	160.31
2017	Forested	11.60	261.56
2017	Forested	22.09	242.62
2017	Clear-cut	58.96	181.93
2017	Clear-cut	28.91	229.12
2017	Clear-cut	18.88	253.09
2014	Forested	17.10	158.28
2014	Forested	18.35	112.09
2014	Forested	13.14	169.30
2014	Clear-cut	15.94	160.18
2014	Clear-cut	18.22	265.53
2014	Clear-cut	18.01	178.57
2006	Forested	22.90	174.15
2006	Forested	16.06	142.37
2006	Forested	15.16	221.30
2006	Clear-cut	10.96	147.62
2006	Clear-cut	9.67	151.46
2006	Clear-cut	14.57	169.33
2000	Forested	16.74	167.91
2000	Forested	15.93	307.70
2000	Forested	12.87	189.96
2000	Clear-cut	10.18	218.51
2000	Clear-cut	14.66	222.21
2000	Clear-cut	9.74	242.49

Table I: Temperature logger data

Day	*Date & time, 4°C logger (dd/mm/yyyy hh:mm:ss)*	*Logger temperature (°C)*	*Date & time, 20°C logger (dd/mm/yyyy hh:mm:ss)*	*Logger temperature (°C)*
0	08/04/2021 00:26:48	5.4	08/04/2021 00:26:04	19.7
	08/04/2021 00:56:48	5.4	08/04/2021 00:56:04	19.6
	08/04/2021 01:26:48	5.3	08/04/2021 01:26:04	19.6
	08/04/2021 01:56:48	5.3	08/04/2021 01:56:04	19.6
	08/04/2021 02:26:48	5.3	08/04/2021 02:26:04	19.5
	08/04/2021 02:56:48	5.2	08/04/2021 02:56:04	19.5
	08/04/2021 03:26:48	5.2	08/04/2021 03:26:04	19.5
	08/04/2021 03:56:48	5.2	08/04/2021 03:56:04	19.4
	08/04/2021 04:26:48	5.3	08/04/2021 04:26:04	19.4
	08/04/2021 04:56:48	5.2	08/04/2021 04:56:04	19.4
	08/04/2021 05:26:48	5.2	08/04/2021 05:26:04	19.4
	08/04/2021 05:56:48	5.2	08/04/2021 05:56:04	19.4
	08/04/2021 06:26:48	5.2	08/04/2021 06:26:04	19.3
	08/04/2021 06:56:48	5.2	08/04/2021 06:56:04	19.3
	08/04/2021 07:26:48	5.2	08/04/2021 07:26:04	19.3
	08/04/2021 07:56:48	5.3	08/04/2021 07:56:04	19.3
	08/04/2021 08:26:48	5.3	08/04/2021 08:26:04	19.5
	08/04/2021 08:56:48	5.2	08/04/2021 08:56:04	20
	08/04/2021 09:26:48	5.2	08/04/2021 09:26:04	20.3
	08/04/2021 09:56:48	5.2	08/04/2021 09:56:04	20.3
	08/04/2021 10:26:48	5.2	08/04/2021 10:26:04	20.7
	08/04/2021 10:56:48	5.1	08/04/2021 10:56:04	20.8
	08/04/2021 11:26:48	5.1	08/04/2021 11:26:04	21
	08/04/2021 11:56:48	5.1	08/04/2021 11:56:04	21
	08/04/2021 12:26:48	5.2	08/04/2021 12:26:04	21.1
	08/04/2021 12:56:48	5.1	08/04/2021 12:56:04	21.2
	08/04/2021 13:26:48	5.1	08/04/2021 13:26:04	21.3

	08/04/2021 13:56:48	5.1	08/04/2021 13:56:04	21.4
	08/04/2021 14:26:48	5.1	08/04/2021 14:26:04	21.4
	08/04/2021 14:56:48	5.2	08/04/2021 14:56:04	21.4
	08/04/2021 15:26:48	5.2	08/04/2021 15:26:04	21.4
	08/04/2021 15:56:48	5.2	08/04/2021 15:56:04	21.5
	08/04/2021 16:26:48	5.2	08/04/2021 16:26:04	21.4
	08/04/2021 16:56:48	5.1	08/04/2021 16:56:04	21.4
	08/04/2021 17:26:48	5.1	08/04/2021 17:26:04	21.4
	08/04/2021 17:56:48	5.2	08/04/2021 17:56:04	21.4
	08/04/2021 18:26:48	5.1	08/04/2021 18:26:04	21.4
	08/04/2021 18:56:48	5.1	08/04/2021 18:56:04	21.3
	08/04/2021 19:26:48	5.1	08/04/2021 19:26:04	21.3
	08/04/2021 19:56:48	5.1	08/04/2021 19:56:04	21.3
	08/04/2021 20:26:48	5.1	08/04/2021 20:26:04	21.3
	08/04/2021 20:56:48	5.1	08/04/2021 20:56:04	21.3
	08/04/2021 21:26:48	5.1	08/04/2021 21:26:04	21.3
	08/04/2021 21:56:48	5.1	08/04/2021 21:56:04	21
	08/04/2021 22:26:48	5.1	08/04/2021 22:26:04	20.8
	08/04/2021 22:56:48	5.1	08/04/2021 22:56:04	20.7
	08/04/2021 23:26:48	5.1	08/04/2021 23:26:04	20.6
	08/04/2021 23:56:48	5.1	08/04/2021 23:56:04	20.5
1	09/04/2021 00:26:48	5	09/04/2021 00:26:04	20.3
	09/04/2021 00:56:48	5.1	09/04/2021 00:56:04	20.2
	09/04/2021 01:26:48	5.1	09/04/2021 01:26:04	20.1
	09/04/2021 01:56:48	5.1	09/04/2021 01:56:04	20
	09/04/2021 02:26:48	5.1	09/04/2021 02:26:04	19.9
	09/04/2021 02:56:48	5.1	09/04/2021 02:56:04	19.8
	09/04/2021 03:26:48	5.1	09/04/2021 03:26:04	19.8
	09/04/2021 03:56:48	5.1	09/04/2021 03:56:04	19.7

	09/04/2021 04:26:48	5	09/04/2021 04:26:04	19.7
	09/04/2021 04:56:48	5.1	09/04/2021 04:56:04	19.7
	09/04/2021 05:26:48	5.1	09/04/2021 05:26:04	19.6
	09/04/2021 05:56:48	5.1	09/04/2021 05:56:04	19.6
	09/04/2021 06:26:48	5.1	09/04/2021 06:26:04	19.6
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	14/04/2021 08:26:48	5.3	14/04/2021 08:26:04	20.5
	14/04/2021 08:56:48	5.3	14/04/2021 08:56:04	20.7
	14/04/2021 09:26:48	5.3	14/04/2021 09:26:04	20.9
	14/04/2021 09:56:48	5.3	14/04/2021 09:56:04	21.3
	14/04/2021 10:26:48	5.2	14/04/2021 10:26:04	21.5
	14/04/2021 10:56:48	5.2	14/04/2021 10:56:04	21.8
	14/04/2021 11:26:48	5.2	14/04/2021 11:26:04	22.1
	14/04/2021 11:56:48	5.2	14/04/2021 11:56:04	22.3
	14/04/2021 12:26:48	5.2	14/04/2021 12:26:04	22.3
	14/04/2021 12:56:48	5.2	14/04/2021 12:56:04	22.3
	14/04/2021 13:26:48	5.3	14/04/2021 13:26:04	22.3
	14/04/2021 13:56:48	5.3	14/04/2021 13:56:04	22.1
	14/04/2021 14:26:48	5.3	14/04/2021 14:26:04	21.9
	14/04/2021 14:56:48	5.3	14/04/2021 14:56:04	21.9
	14/04/2021 15:26:48	5.3	14/04/2021 15:26:04	21.9
	14/04/2021 15:56:48	5.3	14/04/2021 15:56:04	21.9
	14/04/2021 16:26:48	5.3	14/04/2021 16:26:04	21.9
	14/04/2021 16:56:48	5.3	14/04/2021 16:56:04	21.8

	14/04/2021 17:26:48	5.3	14/04/2021 17:26:04	21.8
	14/04/2021 17:56:48	5.3	14/04/2021 17:56:04	21.8
	14/04/2021 18:26:48	5.4	14/04/2021 18:26:04	21.9
	14/04/2021 18:56:48	5.3	14/04/2021 18:56:04	21.9
	14/04/2021 19:26:48	5.3	14/04/2021 19:26:04	22
	14/04/2021 19:56:48	5.3	14/04/2021 19:56:04	22
	14/04/2021 20:26:48	5.3	14/04/2021 20:26:04	22
	14/04/2021 20:56:48	5.3	14/04/2021 20:56:04	22
	14/04/2021 21:26:48	5.3	14/04/2021 21:26:04	21.9
	14/04/2021 21:56:48	5.3	14/04/2021 21:56:04	21.6
	14/04/2021 22:26:48	5.2	14/04/2021 22:26:04	21.5
	14/04/2021 22:56:48	5.3	14/04/2021 22:56:04	21.4
	14/04/2021 23:26:48	5.3	14/04/2021 23:26:04	21.3
	14/04/2021 23:56:48	5.2	14/04/2021 23:56:04	21.2
7	15/04/2021 00:26:48	5.2	15/04/2021 00:26:04	21.1
	15/04/2021 00:56:48	5.2	15/04/2021 00:56:04	21
	15/04/2021 01:26:48	5.2	15/04/2021 01:26:04	21
	15/04/2021 01:56:48	5.3	15/04/2021 01:56:04	20.9
	15/04/2021 02:26:48	5.2	15/04/2021 02:26:04	20.9
	15/04/2021 02:56:48	5.2	15/04/2021 02:56:04	20.8
	15/04/2021 03:26:48	5.2	15/04/2021 03:26:04	20.8
	15/04/2021 03:56:48	5.2	15/04/2021 03:56:04	20.8
	15/04/2021 04:26:48	5.2	15/04/2021 04:26:04	20.8
	15/04/2021 04:56:48	5.2	15/04/2021 04:56:04	20.7
	15/04/2021 05:26:48	5.2	15/04/2021 05:26:04	20.7
	15/04/2021 05:56:48	5.2	15/04/2021 05:56:04	20.7
	15/04/2021 06:26:48	5.2	15/04/2021 06:26:04	20.7
	15/04/2021 06:56:48	5.2	15/04/2021 06:56:04	20.7
	15/04/2021 07:26:48	5.1	15/04/2021 07:26:04	20.6

	15/04/2021 07:56:48	5.2	15/04/2021 07:56:04	20.6
	15/04/2021 08:26:48	5.3	15/04/2021 08:26:04	20.7
	15/04/2021 08:56:48	5.2	15/04/2021 08:56:04	20.8
	15/04/2021 09:26:48	5.2	15/04/2021 09:26:04	21.1
	15/04/2021 09:56:48	5.3	15/04/2021 09:56:04	21.3
	15/04/2021 10:26:48	5.3	15/04/2021 10:26:04	21.6
	15/04/2021 10:56:48	5.4	15/04/2021 10:56:04	21.8
	15/04/2021 11:26:48	5.4	15/04/2021 11:26:04	22
	15/04/2021 11:56:48	5.4	15/04/2021 11:56:04	22.2
	15/04/2021 12:26:48	5.4	15/04/2021 12:26:04	22.3
	15/04/2021 12:56:48	5.4	15/04/2021 12:56:04	22.4
	15/04/2021 13:26:48	5.4	15/04/2021 13:26:04	22.4
	15/04/2021 13:56:48	5.4	15/04/2021 13:56:04	22.4
	15/04/2021 14:26:48	5.4	15/04/2021 14:26:04	22.5
	15/04/2021 14:56:48	5.3	15/04/2021 14:56:04	22.5
	15/04/2021 15:26:48	5.3	15/04/2021 15:26:04	22.5
	15/04/2021 15:56:48	5.3	15/04/2021 15:56:04	22.5
	15/04/2021 16:26:48	5.3	15/04/2021 16:26:04	22.4
	15/04/2021 16:56:48	5.3	15/04/2021 16:56:04	22.5
	15/04/2021 17:26:48	5.3	15/04/2021 17:26:04	22.5
	15/04/2021 17:56:48	5.3	15/04/2021 17:56:04	22.5
	15/04/2021 18:26:48	5.3	15/04/2021 18:26:04	22.6
	15/04/2021 18:56:48	5.3	15/04/2021 18:56:04	22.6
	15/04/2021 19:26:48	5.2	15/04/2021 19:26:04	22.6
	15/04/2021 19:56:48	5.2	15/04/2021 19:56:04	22.6
	15/04/2021 20:26:48	5.3	15/04/2021 20:26:04	22.6
	15/04/2021 20:56:48	5.3	15/04/2021 20:56:04	22.6
	15/04/2021 21:26:48	5.2	15/04/2021 21:26:04	22.6
	15/04/2021 21:56:48	5.2	15/04/2021 21:56:04	22.5
	15/04/2021 22:26:48	5.2	15/04/2021 22:26:04	22.3

	15/04/2021 22:56:48	5.1	15/04/2021 22:56:04	22.2
	15/04/2021 23:26:48	5.2	15/04/2021 23:26:04	22
	15/04/2021 23:56:48	5.2	15/04/2021 23:56:04	21.8
8	16/04/2021 00:26:48	5.1	16/04/2021 00:26:04	21.6
	16/04/2021 00:56:48	5.1	16/04/2021 00:56:04	21.6
	16/04/2021 01:26:48	5.1	16/04/2021 01:26:04	21.6
	16/04/2021 01:56:48	5.1	16/04/2021 01:56:04	21.5
	16/04/2021 02:26:48	5.1	16/04/2021 02:26:04	21.5
	16/04/2021 02:56:48	5.1	16/04/2021 02:56:04	21.5
	16/04/2021 03:26:48	5.1	16/04/2021 03:26:04	21.4
	16/04/2021 03:56:48	5.1	16/04/2021 03:56:04	21.3
	16/04/2021 04:26:48	5.1	16/04/2021 04:26:04	21.3
	16/04/2021 04:56:48	5.1	16/04/2021 04:56:04	21.2
	16/04/2021 05:26:48	5.1	16/04/2021 05:26:04	21.2
	16/04/2021 05:56:48	5.2	16/04/2021 05:56:04	21.1
	16/04/2021 06:26:48	5.2	16/04/2021 06:26:04	21
	16/04/2021 06:56:48	5.2	16/04/2021 06:56:04	21
	16/04/2021 07:26:48	5.2	16/04/2021 07:26:04	20.9
	16/04/2021 07:56:48	5.3	16/04/2021 07:56:04	20.9
	16/04/2021 08:26:48	5.2	16/04/2021 08:26:04	21
	16/04/2021 08:56:48	5.2	16/04/2021 08:56:04	21.2
	16/04/2021 09:26:48	5.2	16/04/2021 09:26:04	21.4
	16/04/2021 09:56:48	5.2	16/04/2021 09:56:04	21.5
	16/04/2021 10:26:48	5.2	16/04/2021 10:26:04	21.6
	16/04/2021 10:56:48	5.2	16/04/2021 10:56:04	21.7
	16/04/2021 11:26:48	5.1	16/04/2021 11:26:04	21.9
	16/04/2021 11:56:48	5.1	16/04/2021 11:56:04	22.1
	16/04/2021 12:26:48	5.3	16/04/2021 12:26:04	22.2
	16/04/2021 12:56:48	5.3	16/04/2021 12:56:04	22.3

	16/04/2021 13:26:48	5.3	16/04/2021 13:26:04	22.3
	16/04/2021 13:56:48	5.4	16/04/2021 13:56:04	22.2
	16/04/2021 14:26:48	5.4	16/04/2021 14:26:04	22.1
	16/04/2021 14:56:48	22.3	16/04/2021 14:56:04	22.5
	16/04/2021 15:26:48	19.9	16/04/2021 15:26:04	20.2
	16/04/2021 15:56:48	17.7	16/04/2021 15:56:04	17.6
	16/04/2021 16:26:48	22.2	16/04/2021 16:26:04	21.6
	16/04/2021 16:56:48	27.6	16/04/2021 16:56:04	27.3
	16/04/2021 17:26:48	30.3	16/04/2021 17:26:04	30.1
	16/04/2021 17:56:48	31.2	16/04/2021 17:56:04	31.2
	16/04/2021 18:26:48	31.3	16/04/2021 18:26:04	31.4
	16/04/2021 18:56:48	29.9	16/04/2021 18:56:04	30
	16/04/2021 19:26:48	27.1	16/04/2021 19:26:04	27.3
	16/04/2021 19:56:48	23.7	16/04/2021 19:56:04	23.9
	16/04/2021 20:26:48	22.2	16/04/2021 20:26:04	22.2
	16/04/2021 20:56:48	21.9	16/04/2021 20:56:04	21.9
	16/04/2021 21:26:48	21.3	16/04/2021 21:26:04	21.3
	16/04/2021 21:56:48	20.7	16/04/2021 21:56:04	20.7
	16/04/2021 22:26:48	20.1	16/04/2021 22:26:04	20.1
	16/04/2021 22:56:48	22.4	16/04/2021 22:56:04	22.4
	16/04/2021 23:26:48	22.8	16/04/2021 23:26:04	22.7
	16/04/2021 23:56:48	23	16/04/2021 23:56:04	22.9
9	17/04/2021 00:26:48	23	17/04/2021 00:26:04	22.9
	17/04/2021 00:56:48	22.9	17/04/2021 00:56:04	22.8
	17/04/2021 01:26:48	22.7	17/04/2021 01:26:04	22.7
	17/04/2021 01:56:48	22.6	17/04/2021 01:56:04	22.5
	17/04/2021 02:26:48	22.4	17/04/2021 02:26:04	22.3
	17/04/2021 02:56:48	22.3	17/04/2021 02:56:04	22.2
	17/04/2021 03:26:48	22.1	17/04/2021 03:26:04	22.1

	17/04/2021 03:56:48	22	17/04/2021 03:56:04	21.9
	17/04/2021 04:26:48	21.8	17/04/2021 04:26:04	21.7
	17/04/2021 04:56:48	21.6	17/04/2021 04:56:04	21.6
	17/04/2021 05:26:48	21.5	17/04/2021 05:26:04	21.5
	17/04/2021 05:56:48	21.4	17/04/2021 05:56:04	21.3
	17/04/2021 06:26:48	21.3	17/04/2021 06:26:04	21.2
	17/04/2021 06:56:48	21.2	17/04/2021 06:56:04	21.1
	17/04/2021 07:26:48	21	17/04/2021 07:26:04	21
	17/04/2021 07:56:48	21	17/04/2021 07:56:04	20.9
	17/04/2021 08:26:48	20.9	17/04/2021 08:26:04	20.8
	17/04/2021 08:56:48	20.9	17/04/2021 08:56:04	20.8
	17/04/2021 09:26:48	20.9	17/04/2021 09:26:04	20.8
	17/04/2021 09:56:48	20.9	17/04/2021 09:56:04	20.9
	17/04/2021 10:26:48	21.3	17/04/2021 10:26:04	21.2
	17/04/2021 10:56:48	21.5	17/04/2021 10:56:04	21.5
	17/04/2021 11:26:48	21.8	17/04/2021 11:26:04	21.8
	17/04/2021 11:56:48	22.1	17/04/2021 11:56:04	22.1
	17/04/2021 12:26:48	22.3	17/04/2021 12:26:04	22.3
	17/04/2021 12:56:48	22.5	17/04/2021 12:56:04	22.5
	17/04/2021 13:26:48	22.6	17/04/2021 13:26:04	22.6
	17/04/2021 13:56:48	22.9	17/04/2021 13:56:04	22.8

Appendix B: About Malcolm Knapp Research Forest

Malcolm Knapp Research Forest (MKRF) was established in 1949. Previous to this, logging was the main activity in this region, with about 2800 hectares of old growth stands being harvested in between 1920 and 1931. Fire was another major disturbance in the forest, with large fires typically occurring every 300-500 years on average. The most recent major fire occurred in 1931 in the eastern part of the forest, which was incited by a spark from a logging operation. Since then, this part of the forest has regenerated naturally to second growth forest consisting primarily of western hemlock and western redcedar. In the western side of the forest, an accidental fire during the dry season burned most of the land in 1868. This region now contains 140-year-old forests with Douglas fir, western hemlock, and western redcedar, along with pockets of old growth. MKRF is interspersed with pockets of younger stands from more recent harvests.

More information on MKRF can be found at https://www.mkrf.forestry.ubc.ca/.

Appendix C: Sample code for EEM analysis

EEM import and PARAFAC analysis – staRdom

```
library(tidyverse)
library(dplyr)
library(eemR)
library(staRdom)
library(purrr)
library(plotly)
library(stringr)

setwd("~/forWater/Lab_analysis/Apr_INC_EEM")

# -------------------- BEGIN FUNCTION --------------------

batch_load <- function(curFolder, eemListName) {
  # collate Abs data - purrr
  Absfiles <- list.files(paste0(curFolder, "/Abs.samples"))
  abs_final <- data.frame("Wavelength" = as.character(seq(800, 239, by=-3)))

  for(i in Absfiles) {
    abs_temp <- read.delim(paste0(curFolder, "/Abs.samples/", i),
                           colClasses =c(NA, "NULL", "NULL", "NULL", "NULL",
"NULL", "NULL", "NULL", "NULL", NA, "NULL"),
                           col.names = c("Wavelength", NA, NA, NA, NA, NA, NA
, NA, NA, substr(i,1,nchar(i)-25), NA))
    abs_temp <- abs_temp[c(-1, -2),]
    abs_final <- abs_final %>% inner_join(abs_temp)
  }

  names(abs_final) <- names(abs_final) %>%
    str_replace_all("fblank", "fblk") %>%
    str_replace_all("RO", "blank")

  abs_final %>% write_csv(paste0(curFolder,"/abs_output.csv"))

  # Read EEM and Abs
  eem_samples <- eem_read(paste0(curFolder, "/EEMs.samples"), recursive = TRU
E, import_function = "aqualog")
  absorbance <- absorbance_read(paste0(curFolder,"/abs_output.csv"))

  # Assign 0 to all values above 1:1 line
  for (j in 1:(length(eem_samples))) {
    col_i <- 1
    for (i in 1:237) {
      while (eem_samples[j][[1]]$ex[col_i] < eem_samples[j][[1]]$em[i]) {
        col_i <- col_i + 1
```

```
      }
      eem_samples[j][[1]]$x[i, (col_i):188] <- 0
    }
  }

  # Trim wavelength range to match Abs range
  # eem_samples <- eem_samples %>%
  #   eem_cut(ex = c(801, 850), em = c(801, 850), exact = FALSE)
  eem_samples <- eem_samples %>%
    eem_range(ex = c(239, 800), em = c(239, 800))

  # Abs baseline correction
  #***** THIS STEP RESETS SAMPLE NAMES *****
  absorbance <- abs_blcor(absorbance,wlrange = c(680,700))

  # Rename samples to exclude "(01)"
  eem_samples <- eem_name_replace(eem_samples,c("\\(01\\)"),c(""))

  # Write metatable
  eem_metatemplate(eem_samples, absorbance) %>%
    write.csv(file="metatable.csv", row.names = FALSE)

  # Check data
  # eem_checkdata(eem_samples,absorbance,metacolumns = c("dilution"),error=FA
LSE)

  # Rename RO as blank
  eem_samples <- eem_name_replace(eem_samples,c("fblank"), c("fblk"))
  eem_samples <- eem_name_replace(eem_samples,c("RO"), c("blank"))

  # IFE correction
  eem_samples <- eem_ife_correction(eem_samples,absorbance, cuvl = 1, unit =
"absorbance")

  # Subtract blank(s)
  eem_samples <- eem_remove_blank(eem_samples)

  # Raman normalisation
  # **** THIS STEP RESETS SAMPLE NAMES *****
  # eem_samples <- eem_name_replace(eem_samples,c("fblank"), c("fblk"))
  # eem_samples <- eem_raman_normalisation2(eem_samples, blank = "blank")
  eem_samples <- eem_name_replace(eem_samples,c("fblank"), c("fblk"))
  # eem_samples <- eem_name_replace(eem_samples,c("\\(01\\)"),c(""))

  # Retain data in global env
  assign(eemListName, eem_samples, envir = globalenv())
}
# -------------------- END FUNCTION --------------------
```

```
# -------------------- BEGIN FUNCTION --------------------

matlab_load <- function(matFolder, matEEMname) {
  # Read in Matlab export
  eem_samples <- eem_read(paste0("Matlab_export/", matFolder), recursive = TR
UE, import_function = eem_csv)

  # Interpolate NaN after scatter removal
  eem_samples <- eem_interp(eem_samples, cores = 2, type = 1, extend = FALSE)

  # Raman normalization
  eem_samples <- eem_raman_normalisation2(eem_samples, blank = "blank")

  # Remove blanks
  eem_samples <- eem_extract(eem_samples, c("nano", "miliq", "milliq", "mq",
"blank"),ignore_case = TRUE)

  # Indices
  bix <- eem_biological_index(eem_samples)
  coble_peaks <- eem_coble_peaks(eem_samples)
  fi <- eem_fluorescence_index(eem_samples)
  hix <- eem_humification_index(eem_samples, scale = TRUE)

  indices_peaks <- bix %>%
    full_join(coble_peaks, by = "sample") %>%
    full_join(fi, by = "sample") %>%
    full_join(hix, by = "sample")

  # indices_peaks
  indices_peaks %>% write_csv(paste0(matFolder, "/indices_output.csv"))

  assign(matEEMname, eem_samples, envir = globalenv())
}

# --------------------- END FUNCTION ---------------------



# ------------------- EXPORT TO MATLAB -------------------

# Variables

# EEMs are stored in separate folders by scan date. List folders here and pro
cess each as a separate batch.
curFolder <- c("Apr7_T0", "Apr8_T0", "Apr8_T0_Raman2", "Apr15_EEM", "Apr16_EE
M", "Apr30_HCl", "Mar31_SWE_EEM")
eemListName <- paste0("samples_", seq(1, length(curFolder), 1))
```

```
outFolder <- "./EEMs.output/"
outListName <- paste0("EEM_export_", seq(1, length(curFolder), 1))

# Create eemlists, 1 per batch
walk2(curFolder, eemListName, ~ batch_load(.x, .y))

# Create output folder
dir.create(file.path(outFolder), showWarnings = FALSE)
# outListBatch <- list(samples_1, samples_2, samples_3, samples_4, samples_5,
samples_6, samples_7)
outListBatch <- eval(parse(text=paste0("list(", paste(eemListName,collapse =
", "), ")")))

# export as Matlab files, 1 per batch
walk2(outListName, outListBatch, ~ eem_export_matlab(paste0(outFolder, .x, ".
mat"), .y))


# Continue processing - Raman/Rayleigh scattering removal - using drEEM (MATL
AB). Return to staRdom after exporting completed MATLAB data. Batches remain
separated by scan date.


# ------------------ IMPORT FROM MATLAB ------------------

# re-import Matlab files
# walk
matFolder <- curFolder
matEEMname <- paste0("mat_", seq(1, length(curFolder), 1))

walk2(matFolder, matEEMname, ~ matlab_load(.x, .y))

# Combine into 1 dataset
mat_all <- eval(parse(text=paste0("eem_bind(", paste(matEEMname,collapse = ",
"), ")")))

# trim above Em > 710nm
mat_all <- mat_all %>%
  eem_cut(em = c(710, 800), exact = FALSE)

# export to MATLAB for PARAFAC analysis
eem_export_matlab(paste0("EEMs.output/EEMs.for.PARAFAC1.mat"), mat_all)


# ---------------------- PARAFAC ----------------------

# Reduce all samples to dimensions of smallest sample
mat_all <- mat_all %>% eem_red2smallest()
```

```r
# Parafac models
pf_out <- mat_all %>% eem_parafac(comps = c(3, 4, 5), verbose = TRUE)
```

Raman/Rayleigh scattering removal – drEEM

```
% 1. load data
% 2. reshape EEM
OriginalData.X =
permute(reshape(OriginalData.X,length(sample_names),237,188),[1,2,3]);

% 3. create dataset
dreemdata =
assembledataset(OriginalData.X,OriginalData.Ex,OriginalData.Em,'RU','site',sample_nam
es, [ ]);

% 4. set scattering band widths
eemreview(smootheem(dreemdata,[24 10],[4 26],[18 42],[10 2],[0 0 0
0],[],3382,0),'samples',[1:dreemdata.nSample]);

% 5. export to CSV
for i=1:dreemdata.nSample
    filename=dreemdata.site{i}; %this removes unwanted final characters from
filename, e.g. .xslx
    eem_i=squeeze(dreemdata.X(i,:,:)); %3D dataset => 2D matrix
    eem_i=[[NaN; dreemdata.Em] [dreemdata.Ex'; eem_i]]; % attach Ex and Em to the eem
    csvwrite([filename '_corr.csv'],eem_i) %write the eem to a csv file
end
```

PARAFAC analysis – drEEM

```
dreemdata_120 = subdataset(dreemdata, [34:39], [], []);
test1 = outliertest(dreemdata_120, 2:6);
[LSmodel,all,details]=randinitanal(dreemdata_120,3:5,10,'nonnegativity',1e-8);

S1=splitds(dreemdata_120,[],4,'alternating',{[1 2],[3 4],[1 3],[2 4],[1 4],[2 3]});
A1=splitanalysis(S1,3:5,'starts',10,'constraints','nonnegativity');
splitvalidation(A1,4,[1 2;3 4;5 6],{'AB','CD','AC','BD','AD','BC'});
val_results=splitvalidation(A1,4,[],[],LSmodel);
openfluor(LSmodel, 4, "openfluor_4comp_Sept22.txt");
```