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MEASURING THE INFLUENCE OF ENVIRONMENTAL CONDITIONS ON
DISSOLVED ORGANIC MATTER BIODEGRADABILITY AND OPTICAL
PROPERTIES: A COMBINED FIELD AND LABORATORY STUDY

A Thesis Presented

by

Maxwell Landsman-Gerjoi

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfillment of the Requirements
for the Degree of Master of Science
Specializing in Geology

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ABSTRACT

Dissolved organic matter (DOM) plays a vital role in biogeochemical processes and can flux CO₂ to the atmosphere when labile fractions are degraded, hence DOM degradation is increasingly studied. Some studies have suggested that fluorescence-derived substrate characteristics are useful metrics for estimating bioavailability (as prerequisite condition for biodegradability), however, recent findings on soil organic matter emphasize the importance of ecosystem scale factors such as physical separation of substrate from soil microbial communities and soil physiochemical cycles driving organic matter stability. I extend this principle to soil derived DOM and hypothesize that such environmental conditions, covariant with season, land use and landscape position, impact the composition of soil DOM and activity and abundance of the microbial community, which together govern DOM biodegradability. As a result, DOM bioavailability may not reliably be predicted using substrate characteristics alone. To test these hypotheses, I assessed aqueous soil extracts for water extractable organic carbon (WEOC) content, biodegradability, microbial biomass and fluorescence spectroscopy on water extractable organic matter (WEOM) across a range of environmental conditions in northern Vermont, USA. My results indicate that changes in environmental conditions affect composition, quantity, and biodegradability of DOM. WEOC concentrations were highest in the fall and lowest in the summer, while no significant differences were found between land covers or landscape position, however, DOM biodegradability was significantly higher in the agricultural (AG) site across seasons. Despite a shift in utilized substrate from less aromatic DOM in summer to more aromatic DOM in winter, biodegradability was similar for all seasons. The only exception were cold temperature incubations where microbial activity was depressed, and processing was halted. These results indicate that bioavailability cannot be reliably predicted based on fluorescence-based metric alone, rather, my core findings illustrate a complex picture of how environmental conditions, landscape characteristics, and substrate composition interact to drive the biodegradability of labile carbon pools in the soil environment.

This thesis includes i) a background and comprehensive review of literature to inform the reader of any relevant topics, ii) a paper submitted for publication to Biogeochemistry (Chapter 2), and iii) supplemental information containing figures and tables pertinent to the paper.

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CHAPTER 1: COMPREHENSIVE LITERATURE REVIEW

1.1 The Role of Carbon in Soil Systems

Carbon (C) is a ubiquitous component in all ecosystem and the cycling of C (Fig. 1-1) within these systems is responsible for providing energy and nutrients used in most aspects of the biosphere (Meyer et al., 1998). The C cycle itself is a collection of the complex processes during which C is transformed back and forth between its inorganic and organic forms (Smith et al., 1993). Soils represent a significant component in this cycle and contain C-based molecules that originate from plant production including fresh plant litter, partially decomposed plants and animals, as well as microbially transformed C (e.g., waste products excreted by these organisms) (Bade et al., 2007).

Soil C storage is as high as 3000 Pg within the first meter of the soil profile (Heinze et al., 2018; Scharlemann et al., 2014) but the top layers are especially at risk to become a C source especially if affected by land use or climate change (Heinze et al., 2018; Moritz et al., 2009; Salomé et al., 2010). These surface horizons are also subject to flushing during hydrologic events soil C can be readily transported as dissolved organic carbon (DOC) through the soil profile and into streams and rivers (Wickland et al., 2007).

1.2 Dissolved Organic Matter Pool Dynamics

Labile DOC moving through soil water and other natural water systems is much more readily subjected to microbial and photolytic degradation than soil organic matter. Since degradation results in the production of carbon dioxide (CO₂), one of the principal drivers

of climate change (Cole et al., 2007; IPCC, 2013; Osterman, 2018; Sparks, 2003), DOC dynamics are carefully monitored.

One important aspect driving the magnitude of these fluxes are the characteristics and quantity of the larger dissolved organic matter (DOM) pool, of which DOC represents approximately 50% (Marschner and Kalbitz, 2003; Weishaar et al., 2003). DOM is a heterogeneous mixture of organic compounds that reflects its provenance from terrestrial or aquatic environments such bacterial, algal, or higher plant organic matter (Cory and McKnight, 2005; Fellman et al., 2008). Typical DOM fractions include amino acids, carbonyl compounds, fatty acids, lipids, proteins, and sugars as well as humic substances (D'Andrilli et al., 2013; Yulai et al., 2015) and are operationally defined to pass through a 0.45 or 0.7 μm filter (Anderson et al., 2015; Massicotte et al., 2017).

Because DOM substrates represent a crucial source of DOC for utilization by soil microbial communities (Fig. 1-2; Marschner and Kalbitz, 2003), the characteristics of DOM substrate play a significant role. In turn, assessing the characteristics of the DOM substrate illuminates mechanisms through which the DOM pool is processed, transformed, and exported (Lønborg et al., 2015; Nebbioso and Piccolo, 2013; Wickland et al., 2007; Wilson and Xenopoulos, 2008).

In addition to DOM composition and characteristics, environmental conditions and ecosystem scale variables control C fluxes (Marín-Spiotta et al., 2014; Nebbioso and Piccolo, 2013; Schmidt et al., 2011), either directly or by impacting microbial communities (O'Connell et al., 2000). For example, increased agricultural practices tend to decrease the

complexity of DOM and can increase microbial processing and ultimately CO₂ flux (Wilson and Xenopoulos, 2008).

1.2.1 Dissolved Organic Matter Bioavailability and Biodegradability

Bioavailability is the potential of a substance to be microbially processed whereas biodegradability is the utilization of organic compounds by microbial communities (Marschner and Kalbitz, 2003). Biodegradability has been thought to dependent on the chemical composition of the substrate and various DOM sources have been investigated. For example, biodegradability values of soil solution DOM have been reported anywhere from 10-44% (Fellman et al., 2008; Kalbitz et al., 2003; Sachse et al., 2001), while the biodegradability of leaf litter was generally found to be higher (52-75%) and riverine DOM biodegradability was found lower (2-35%) (Balcarczyk et al., 2009; Hongve et al., 2008; Wiegner and Tubal, 2010). Generally, low molecular weight, non-aromatic DOM was found to be more labile and more bioavailable to microorganisms, thus DOM sources abundant in non-aromatic DOM should be more biodegradable (Fellman et al., 2009b; Kalbitz et al., 2003; Marschner and Kalbitz, 2003; Wei et al., 2014). However, a study by Schmidt et al., (2011) suggests the molecular properties of a compound do not alone determine bioavailability and that soil C dynamics are the result of environmental factors as well. This concept was further investigated for aquatic C forms (Marín-Spiotta et al., 2014), but has not been investigated for soil derived DOM specifically.

1.3 Assessing DOM Characteristics and Measuring Biodegradability

Fluorescence spectroscopy is a fast and reliable method to assess carbon characteristics in natural waters. The analysis is based on the interaction between organic molecules and light (Osburn et al., 2012; Pellerin et al., 2011; Stedmon et al., 2003b; Xie et al., 2017b), is quick and now often routinely performed. The optical properties of the subgroup of DOM known as fluorescent dissolved organic matter (FDOM) have been shown to correlate with the biogeochemical characteristics of the larger pool (Fellman et al., 2010; Inamdar et al., 2012; Stedmon et al., 2003a). For example, studies by Blondel et al. (2012) and Liu et al. (2018) reported that FDOM served as good tracers for DOM in larger systems, especially tracking and monitoring of humic-acids.

With recent advances in fluorescence technology, new parameters have been established that are tested for insight into the biodegradability of a sample (Fellman et al., 2010; McDowell et al., 2006; Xie et al., 2017a). The fluorescence-based datasets created using these techniques produce maps showing the relationship between the light excitation wavelengths and the intensity of the light emitted from the sample being analyzed. These so-called Excitation-Emission Matrices (EEMs) provide qualitative information on the characteristics of the sample. EEMs can be used to calculate fluorescence indices such as Fluorescence Index (FI), a metric for assessing if a sample is microbial or terrestrially sourced (McKnight et al., 2001), or Humification Index (HIX), which provides insight into the polycondensation and molecular weight of a sample (Ohno, 2002). Lastly, entire EEMs can be analyzed using parallel factor analysis (PARAFAC), a powerful statistical tool that deconstructs EEMs and identifies intensity peaks associated with fluorophores such as fluvic-like, humic-like, and protein-like molecules (Fellman et al., 2009b). Fluorescence

analysis has been used to assess the degree of bioavailability of DOM in some studies with varying levels of success (Fellman et al., 2009b; Stedmon et al., 2003b).

A more direct measurement of the biodegradable fraction of C from DOM is accomplished through incubation experiments that track the loss of DOM *in situ* or in isolated laboratory settings (Fellman et al., 2008; Kalbitz et al., 2003; McDowell et al., 2006; Saadi et al., 2006). Incubation experiments can provide measured C losses to microbial decomposition by the disappearance of DOM or the production of CO₂ (Marschner and Kalbitz, 2003). This approach provides reliable data, but is laborious, time consuming, and not standardized (McDowell et al., 2006; Xie et al., 2017a). Often, the duration of the incubation, chosen extraction method, and chosen metric for measuring loss of C will result in different values for biodegradable dissolved organic matter (BDOM). Incubation time is one of the more crucial components to this process. While longer incubations measuring CO₂ production will account for the majority of the C pool (including more recalcitrant compounds), a shorter incubation focusing on the DOC concentrations will reflect the immediate release of large amounts of labile C from the C pool (McDowell et al., 2006).

Microbial biomass is another measure linked to bioavailability and can be assessed prior to incubations to determine the extent of the microbial population in the sample (Fierer, 2003). The presence of a microbial community is a prerequisite for microbial decomposition in soils and therefore quantifying the biomass present can give insights into how the soil communities will function, however it does not indicate microbial metabolic rates (Blume et al., 2002). More microbial biomass should coincide with higher levels of

respiration and therefore larger losses of C. Microbial communities can also contribute low molecular weight organic molecules that can be readily processed by other microbes, increasing soil respiration rates and CO₂ production (Fig. 1-2; Feghel et al., 2019).

1.4 Environmental Controls on DOM Bioavailability

Environmental conditions change seasonally through the influence of temperature, soil moisture/precipitation events, and changing of substrate and biotic productivity and can impact bioavailability (Miller and McKnight, 2010; Singh et al., 2013). For example, in temperate regions, seasonal changes in substrate availability and productivity range from scarcity and low productivity in winter to abundance and high productivity in fall (Arain et al., 2002). Seasonal changes in temperature play an important role in controlling productivity. For example, the capacity for microbial respiration is highly temperature dependent (Blume et al., 2002). Lower levels of DOM production during the colder seasons coincides with lower levels of microbial respiration rates, leading to DOM accumulation over winter (Contosta et al., 2011; Singh et al., 2013). In turn, summer processes might lead to more C breakdown to DOM, however this process might be counteracted by microbial mineralization and photodegradation and overall less DOM accumulation in soils (Singh et al., 2013).

Additionally, seasonal changes in hydrologic regime can significantly affect the characteristics and composition of the substrate, which could again potentially affect its bioavailability (Jaffé et al., 2008; Miller and McKnight, 2010). Flushing of the dissolved phase via subsurface and surface flow can bring in or remove sources of DOM causing a shift in the DOM pool bioavailability (Fellman et al., 2009a). Seasonal changes in

precipitation can affect the water content of the soils, which hinders DOM mobility as well as microbial capacity to interact with the substrate (Blume et al., 2002).

1.5 Land Cover Effects on DOM Bioavailability

Land cover has been shown to influence many of the variables that ultimately affect substrate bioavailability (Fellman et al., 2009a; Van Leeuwen et al., 2017). Different land cover types have been associated with changes in DOM concentrations and characteristics as well as the capacity for microbial respiration (Graeber et al., 2015; Williams et al., 2016). For instance, a study by Asmala et al. (2013) found that areas dominated by more agricultural land had higher levels of DOM degradation rates compared to lands dominated by forest cover. Different rates of biodegradation under changing land covers were also found by (Fellman et al., 2009c) in a study that assessed differing rates DOM degradation rates for substrate of different origin from different land covers across several seasons. However, land cover effects become difficult to assess in systems with seasonally changing hydrologic regimes (Lee et al., 2018).

1.6 Topographic Location Effect on DOM Bioavailability

Elevation and topographic position have also been shown to affect the composition of the DOM substrate and in part, the bioavailability (Fellman et al., 2009a; Jaffé et al., 2008). DOM concentrations have been shown to decrease significantly down a hillslope and positions located down slope (lower topographic position) typically have higher soil temperatures as well as higher potential for microbial activity (Whittinghill et al., 2014).

Processing of DOM within a hillslope can potentially decrease terminal inputs to the DOM pool, especially for labile DOM in these systems (Whittinghill et al., 2014).

Lateral transport of the dissolved phase through surface and near surface waters introduces continually changing substrate to new microbial communities allowing for the continual processing of DOM and the accumulation of microbial DOM across topographic changes (Jaffé et al., 2008; Whittinghill et al., 2014). Differential accumulation of the DOM pool based on topographic position has also been shown in several studies, which highlights the importance of assessing landscape position on bioavailability (Balcarczyk et al., 2009; Fellman et al., 2009a; Frey et al., 2016; Jaffé et al., 2008). Possible explanations for the differential accumulation and lateral transport include changing hydrological flow paths which would alter accessibility to labile DOM of soil microbial communities (Boyer et al., 1997). However, while changes in the composition of the DOM pool has been reflected across topographic position, DOM characteristics has not been shown to follow such trends. A study by Whittinghill et al. (2014) showed that DOM characteristics across different hillslope positions was relatively consistent, as was DOM decomposition loss from these sites.

1.7 Antecedent Conditions

DOM fluxes within a system can be assessed on an event, seasonal, or annual timescale and everywhere in between. Determining a timescale to properly assess the antecedent conditions can be variable with ranges up to two weeks for monitoring soil conditions before a sampling (Khamis et al., 2018). Antecedent soil conditions are typically used to

ensure consistent conditions prior to a sampling, or to see how far back the site's previous conditions will affect the substrate and subsequent analysis.

1.8 Figures

Figure 1-1. Schematic of the carbon cycle through terrestrial and aquatic ecosystems. Numbers in yellow refer to flows of carbon between reservoirs expressed in gigatons of carbon per year (GtC/y). Arrow size is roughly proportional to the size of the flux from each reservoir. White numbers indicate reservoir size and red numbers indicate alterations to the carbon size as the result of human activity (Bleam, 2012).

Figure 1-2. Schematic of the various origins of dissolved organic matter (DOM) that are expressed over the stages of decomposition or processing. In this example fresh substrate is exemplified as leaf litter transitioning from unprocessed, and relatively fresh to a state of increased decomposition to the final, well-processed substrate that might accumulate in the organic horizons that this study focused on (1-2a). Introduction of the substrate to the microbial communities (1-2b) will cause decomposition to increase resulting in the breakdown of the substrate and increase in microbial community size. Active microbial communities will produce DOM in the form of exudates used for decomposition as well as dead microbial biomass accruing in the soil that can be respired.

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CHAPTER 2: Article for Submission to Biogeochemistry

Measuring the Influence of Environmental Conditions on Dissolved Organic Matter Biodegradability and Optical Properties: A Combined Field and Laboratory Study

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Abstract

Dissolved organic matter (DOM) plays a vital role in biogeochemical processes in both terrestrial and aquatic ecosystems. Some studies have suggested that fluorescence-derived substrate characteristics are useful metrics for estimating bioavailability (as prerequisite condition for biodegradability), however, recent findings on soil organic matter emphasize the importance of ecosystem-scale factors, such as physical separation of substrate from soil microbial communities and soil physiochemical cycles driving organic matter stability. We apply this principle to soil derived DOM and hypothesize that such environmental conditions, covariant with season, land use and landscape position, impact the composition of soil DOM and activity and abundance of the microbial community. As a result, DOM bioavailability cannot reliably be predicted using substrate characteristics alone. To test this overarching hypothesis, we assessed aqueous soil extracts for water extractable organic carbon (WEOC) content, biodegradability, microbial biomass and fluorescence spectroscopy on water extractable organic matter (WEOM) across a range of environmental conditions in northern Vermont, USA. Our results indicate that changes in environmental conditions affect composition, quantity, and biodegradability of DOM. WEOC concentrations were highest in the fall and lowest in the summer, while no significant differences were found between land covers or landscape position, however, DOM biodegradability was significantly higher in the agricultural site across seasons. Despite a shift in utilized substrate from less aromatic DOM in summer to more aromatic DOM in winter, biodegradability was similar for all seasons. The only exception were cold temperature incubations where microbial activity was depressed, and processing was halted. These results agree with our hypothesis that bioavailability cannot be predicted based on fluorescence-based metric alone, rather, our core findings illustrate a complex picture of how environmental conditions, landscape characteristics, and substrate composition interact to drive the biodegradability of labile carbon pools in the soil environment.

Keywords: fluorescence spectroscopy, dissolved organic matter, bioavailability, biodegradability, PARAFAC.

2.1 Introduction

Dissolved organic matter (DOM) provides a significant energy source to microbial communities across ecosystems, and labile fractions are readily degraded through microbial and photolytic processes. Because DOM degradation can result in the production of the greenhouse gas carbon dioxide (CO₂) (Cole et al., 2007; IPCC, 2013; Osterman, 2018; Sparks, 2003), factors that govern DOM dynamics, such as characteristics and quantity of the DOM pool, and environmental conditions, are increasingly studied (Khamis et al., 2018; Marschner and Kalbitz, 2003; Weishaar et al., 2003). It is also becoming increasingly clear that the processing and production of DOM by microbial communities is a prerequisite for long term storage in soil organic matter (SOM), an important source of DOM, and is therefore important to include when monitoring soil carbon dynamics (Kallenbach et al., 2016). Despite the large body of research accumulating on the subject, it is still unclear how drivers for DOM transformations and mobilization interact with each other.

DOM characteristics vary greatly as a function of composition (e.g. sugars, amino acids, proteins, carbonyl compounds, fatty acids, lipids, and humic substances) (D'Andrilli et al., 2013; Yulai et al., 2015), which is partially dictated by substrate origin (Cory and McKnight, 2005; Fellman et al., 2008). Assessing DOM characteristics is important to understand the mechanisms through which DOM is processed, transformed, and exported (Lønborg et al., 2015; Nebbioso and Piccolo, 2013; Wickland et al., 2007; Wilson and Xenopoulos, 2008). Characterizing DOM based on its optical properties has been shown to be a valuable tool for gathering qualitative information and linking chemical composition (aromaticity, provenance, molecular weight, and degree of humification) (Cory et al., 2011; Cory and McKnight, 2005; Ohno, 2002; Wymore et al., 2015) and concentration to substrate origins (Cory et al., 2011; Hansen et al., 2016; Wymore et al., 2015).

The fate of DOM in the environment is controlled by two chief attributes: bioavailability (potential to be microbially processed) and the biodegradability (actual microbial utilization) of the substrate (Marschner and Kalbitz, 2003). Biodegradability varies greatly based on the substrate characteristics and composition, but is generally high for fresh leaf litter (Hongve et al., 2008; Wiegner and Tubal, 2010) and lower for soil carbon (10-44%; Fellman et al., 2008; Kalbitz et al., 2003; Sachse et al., 2001). Biodegradability can be directly assessed using incubation studies that provide data on either the loss of DOM or the production of CO₂ (Marschner and Kalbitz, 2003), however the approach is laborious and not standardized (McDowell et al., 2006; Xie et al., 2017a).

Indirect measurements of biodegradability include assessing microbial biomass present in the soil, which can be assessed prior to incubations to determine the size of the microbial population in the sample (Fierer, 2003). The presence of a microbial community is a

prerequisite for microbial decomposition in soils and therefore quantifying biomass can give insights into how the soil communities will function, however it does not indicate microbial metabolic rates (Blume et al., 2002). Another indirect method to infer biodegradability includes the characterization of DOM optical properties via fluorescence spectroscopy (Fellman et al., 2010; McDowell et al., 2006; Xie et al., 2017a). For example, low molecular weight, non-aromatic DOM, as determined using ^{13}C -NMR analysis by McKnight et al. (2001), (i.e. low fluorescence index [FI] and high specific ultra-violet absorbance [SUVA] values) is considered more labile and biodegradable to microorganisms, (Fellman et al., 2009b; Kalbitz et al., 2003; Marschner and Kalbitz, 2003; Wei et al., 2014). Parallel Factor Analysis (PARAFAC) is a tool that has been increasingly used to better assess optical data compiled from fluorescence spectroscopy (Murphy et al., 2013). This multivariate statistical analysis deconstructs fluorescence derived excitation emission matrices (EEMs) to build a model of the most prevalent components, which can be connected to classes of DOM (i.e. fulvic-like). Different DOM components have been linked to varying degrees of biodegradability (Fellman et al., 2008; Stedmon et al., 2003a).

However, while fluorescence derived metrics are used to make inferences on DOM composition and substrate lability, other factors might influence the potential for microbes to interact and utilize DOM. These factors include environmental conditions, such as soil moisture, temperature, nutrient status, or microbial community characteristics, e.g. Marín-Spiotta et al. (2014) and Schmidt et al. (2011) who both suggest that SOM dynamics are a function of the much larger ecosystem context and environmental factors, instead of molecular properties alone.

Environmental factors strongly impact DOM supply, composition, transport and microbial mineralization (Miller and McKnight, 2010; Singh et al., 2013; Stielstra et al., 2015) and often vary seasonally. For example, in temperate systems, fall foliage supplies fresh leaf litter and labile carbon is leached into the soils. During wet and warm conditions, microbial processing of DOM is promoted, however, during the colder seasons, DOM production and processing is halted (Contosta et al., 2011; Singh et al., 2013). Another important factor controlling substrate and environmental conditions is land cover and landscape position. For example, agricultural lands have been associated with changes in ecosystem productivity as well as increased capacity for soil microbial respiration (Lai et al., 2012) and thus can control biodegradability (Fellman et al., 2009a; Van Leeuwen et al., 2017). Differential accumulation of the DOM pool based on topographic position (Balcarczyk et al., 2009; Fellman et al., 2009a; Frey et al., 2016; Jaffé et al., 2008) and variable conditions of soil moisture and temperature (Whittinghill et al., 2014) between hilltop and toeslope areas further suggest that microbial processing can vary significantly.

The objective of this study is to assess how environmental conditions, specifically soil moisture, soil temperature, and substrate characteristics affect the biodegradability of DOM. We hypothesize that i) these environmental conditions (covariant with season, land cover, and landscape position) strongly impact the amount and type of soil DOM and that, as a result, ii) DOM biodegradability is controlled by ensuing substrate composition and

microbial abundance. Accordingly, DOM biodegradability might not be predicted reliably by using substrate characteristics, such as fluorescence derived parameters, alone.

To test these hypotheses, we investigated DOM dynamics using i) a leaf litter incubation experiment as simple system with a known, terrestrial carbon source and ii) aqueous soil extracts (ASE) from soils collected across four seasons, in two distinct land covers and landscape positions at well-studied sites in Vermont, USA. Leaf litter and soil extracts were analyzed for water extractable carbon (WEOC) concentrations, water extractable organic matter (WEOM) composition using fluorescence spectroscopy and incubated to monitor WEOC loss (biodegradability). For soil extracts we also assessed microbial biomass and we monitored field environmental conditions using an extensive *in-situ* soil sensor network at these sites and compare the variability of collected DOM parameters to variations in environmental conditions.

2.2 Materials and Methods

2.2.1 Field Sites

The study sites are located in the Lake Champlain Basin in Vermont in the Northeastern United States (Fig. 2-1) and are part of a larger soil monitoring network. This network comprises extensive above and below ground instrumentation in an agricultural and forested setting (hereafter referred to as AG and FOR, respectively, [Fig. 1]) that probe soil physical and chemical conditions at a 15cm depth in several locations along transects spanning from the far stream upland, through a riparian wetland and to near stream riparian areas. Soil volumetric water content (VWC) and temperature (T) are monitored using Decagon 5TE sensors (Decagon, Pullman, WA) at 15-minute intervals. Soil gas (carbon dioxide) concentration is monitored using Vaisala GMT221 probes at the same interval (Vaisala, Boulder, CO; 15 minute intervals). A weather station for each site (AG and FOR) provides information for mean annual ambient temperature and precipitation (MAT and MAP, HOBO, Bourne, MA).

The AG site is an agricultural catchment typical of the Champlain Valley and includes 5 instrumented locations spanning from a pasture field (Agricultural-Hilltop; AG-HT) through a riparian wetland (Agricultural-Hillslope; AG-HS) to the near stream riparian area of Hungerford Brook (Agricultural-Riparian Zone; AG-RZ, Fig. 2-1c) (Vaughan et al., 2017). The elevation range of this site spans from 101 to 106 m above sea level (a.s.l) and experiences a temperate climate with four distinct seasons with snow-rich winters, a distinct snow melt, temperate summers with occasional rains, and fall season dominated by foliage. MAT at this site is 7.15 °C, MAP is 872 mm with approximately 22% falling as snow. The site is subjected to seasonal anthropogenic interference from farming and residential activity. Vegetation includes American beech (*Fagus grandifolia*) trees, species of fern (group *Pteridophytes*) and nettles (*Urtica dioica*). Soils are Inceptisols (Aquic Dystric Eutrudepts, AG-HT, Fig. 2-1) and Entisols from glaciolacustrine, glaciofluvial and fluvial material respectively (i.e. Aquic Udipsamments at AG-HT end and Fluvaquentic Dystrudepts at AG-HS/RZ) (Ross, 2019; Soil Survey Staff, 2019).

The FOR site includes two transects are located approximately 7 km north of Montgomery, Vermont (Fig. 2-1b). The site includes 11 instrumented locations spanning from an upland terrace (Forested-Hilltop; FOR-HT), hillslope (Forested-Hillslope; FOR-HS), through a wetland (Forested-Hillslope/Riparian Zone; FOR-HS/RZ) to the near stream riparian area of Wade Brook (Forested-Riparian Zone; FOR-RZ, Fig. 2-1e).

Like the AG site the FOR site experiences a temperate climate with four distinct seasons but is higher in elevation (350-365m a.s.l.), has a lower MAT (5.8°C) and higher MAP (1080 mm) of which approximately 24% falls as snow forming a seasonal snowpack from December to April. Anthropogenic interferences of the predominately forested (95%) catchment are minimal. Vegetation is typical of a secondary growth northern hardwood forest and includes sugar maple (*Acer saccharum*), yellow birch (*Betula alleghaniensis*), white ash (*Fraxinus Americana*) and red spruce (*Picea rubens*). Soils are Spodosols (Haplorthods, FOR-HT/HS) and Inceptisols (Fluvaquentic Dystrudepts, FOR-HS/RZ; Fluvaquentic Endoaquepts, FOR-RZ) (Ross, 2019; Soil Survey Staff, 2019).

2.2.2 Sample Collection

To assess the effect different environmental conditions associated with change of seasons, land cover, and landscape position on soil DOM characteristics, we took composite samples for each season (spring [June 2018], summer [August 2018], fall [October 2018], and winter [December 2017 and February 2019]) and site collocated with transect instrumentation at 0-15cm depths. Collecting composite samples entailed taking 6 replicate core samples were taken per sampling locations using an AMS 7/8" x 24" SST Soil Recovery Probe with clean, removable liners, combining them in a sample bag, and shaking until homogenized (Tan, 2005). From these homogenized composite samples, we took duplicate samples to represent each location.

2.2.3 Microbial Biomass Extractions

To determine the microbial biomass in soil samples by season and sampling location, we performed microbial biomass extractions on soil using a modified chloroform extraction method (Fierer, 2003; Setia et al., 2012). To express microbial biomass in terms of g/dry soil we determined gravimetric soil moisture content on field fresh samples prior to analysis. All samples were treated with 0.5 M potassium sulfate in 70 ml glass culture tubes (including experimental blanks). Samples from each location were divided into a chloroform treatment group (receiving 0.5 ml of chloroform to lyse microbial cells) and a corresponding untreated control group. The tubes were sealed and set to shake (150 rpm) for 1 hour. In order to minimize chloroform contamination after shaking, solutions were allowed to settle out, giving the denser chloroform a chance to sink away from the supernatant. The supernatant was gravity-filtered using Whatman No. 1 (Buckinghamshire, United Kingdom), filtrate was collected and then bubbled vigorously for 20 minutes using an air pump to encourage the volatilization of any residual chloroform before analyses for DOC and TDN. Extractable microbial biomass C and N were calculated as the difference in total dissolved C and N between the chloroform exposed subsample and the control subsample, expressed as μm chloroform extractable biomass C or N/g dry soil. Extractable

biomass using this technique accounts for approximately 20-40% of the total biomass and so a conversion factor of 0.33 was used to determine total microbial biomass (Tate et al., 1988).

2.2.4 Aqueous Soil Extractions and Leaf Litter Leachate

To determine the composition and characteristics of water-soluble organic matter, aqueous soil extracts (ASE; analogue for well processed substrate and mobile soil solution) and leaf litter leachate extractions (leaf litter leachate; analogue for relatively unprocessed substrate) for all locations and seasons were performed on duplicate samples to recover WEOM using established methods (Cincotta et al., in review; Perdrial et al., 2012b; Swift, 1996). All ASE were created from field moist soils (taking into account existing water content) by combining soil and Nanopure water (resistivity $18 \text{ M}\Omega \text{ cm}^{-1}$) in combusted amber glass bottles at a 1:5 ratio and setting them to shake on a reciprocal shaker (Eberbach, Ann Arbor, MI, USA) for 1 hour (Perdrial et al., 2012a). The solutions were then centrifuged (3000 rpm, 30 min.) to separate the dissolved from the colloidal phase. Leaf litter leachates were created by combining 5g of air-dried litter samples from sugar maple, yellow birch, and white ash in Nanopure water in the same method as ASE. Supernatant solutions from both ASE and leaf litter leachates were then filtered through $0.7 \mu\text{m}$ glass fiber filters (Whatman GF/F, Buckinghamshire, UK). Splits of the filtrate were transferred into combusted glass vials for immediate analyses of DOC and TDN, fluorescence spectroscopy and incubations.

2.2.5 Incubations

We performed two types of incubations to 1) monitor how fluorescence characteristics change progressively in a relatively unprocessed substrate (leaf litter leachate) as microbial processing occurs and 2) assess the biodegradability of the WEOC and associated changes in fluorescence patterns in ASE from field samples by season. Aliquots of filtered leachate were inoculated with microbes in a slurry of unfiltered extract from the sampling location from which the litter had been taken (i.e. AG litter extracts were inoculated with unfiltered AG litter slurry) and incubated in combusted mason jars at 25°C on a reciprocal shaker for 5 weeks. Production of CO_2 was monitored using a Licor automated CO_2 flux monitoring system (LI-8100a, Lincoln, Nebraska, USA). To determine how substrate characteristics and biodegradability changed over the course of incubations, samples at selected time intervals (every day for week one, twice a week for week two and three, and once per week for week four and five) were taken, analyzed for DOC and TDN as well as fluorescence parameters.

For the soil extract incubation, filtered ASE aliquots were inoculated as described above and incubated for 7 days at 25°C for 2017 and 2018 samples and at 4°C for winter 2019 samples (henceforth referred to as winter II). The latter incubation temperature was chosen to more closely resemble conditions of an intermittent thaw event over winter. For these ASE incubations we did not track CO_2 evolution but determined loss of DOC and TDN and reported the difference as biodegradable water extractable organic carbon (BWEOC).

2.2.6 Analytical Procedures

All aqueous samples (microbial biomass assays, ASE, and leaf litter leachate) were measured for concentrations of DOC and TDN via combustion using a Total Organic Carbon Analyzer (TOC-L, Shimadzu, Columbia, MD, USA). The results were normalized to the amount of solution and soil used to the extractions and expressed as mg/kg dry soil.

Spectral characteristics of WEOM (from leaf litter leachate and ASE) were determined using the Aqualog Fluorescence and Absorbance Spectrometer (Horiba, Irvine, CA, USA). Excitation wavelengths ranged from 240-600 nm and emission wavelengths ranged from 212-600 nm. All resulting excitation-emission matrices (EEMs) were blank-subtracted (Nanopure water), corrected for inner filter effects based on the corresponding UV-vis values, and Raman normalized. Filtered, undiluted sample splits were used to measure absorbance at 254 nm and to calculate the specific ultra-violet absorbance at 254nm (SUVA), which is the absorbance at 254 nm normalized to DOC concentration (Weishaar et al., 2003). Two other indices were calculated using filtered, diluted samples including FI, calculated as the intensity at Emission 470 nm divided by the intensity at Emission 520 nm for Excitation 370 nm (McKnight et al. 2001), and HIX, calculated as the ratio of the area under Emission 435-480 nm divided by the quantity of both areas under Emission 300-345 nm and Emission 435-480 nm, at Excitation 254 nm (Ohno, 2002).

Parallel Factor Analysis (PARAFAC) was performed using *Matlab R2018b* and the *drEEM_4_0_(Ext.)* toolbox (Murphy et al., 2013) to validate a 4-component model and identify PARAFAC components that can be linked to DOM characteristics and used to generalize about the DOM composition (Bro, 1997). The four components found, which are in agreement with most studies published (Ishii and Boyer, 2012), are terrestrial humic-like (C1), terrestrial fulvic-like (C2-3), and microbial protein-like (C4, Table s-3).

2.2.7 Statistical Analysis

Statistical analyses were performed using JMP Pro 14.0.0 software by SAS (JMP, 2018) and R-Studio (R Core Team, 2017). An Analysis of Variance (ANOVA) and the Tukey's Paired Test were performed to determine the significance of variations in substrate characteristics (including fluorescence parameters) for each season, land cover, and landscape position but did not include interactions between these three variables. Two-way ANOVA was used to determine significance of differences between landcovers for each season. Bivariate regression was used to assess the correlations between fluorescence derived parameters and biodegradability. These results were compared to published literature to determine the variability between models. Significance of environmental conditions were determined based on linear regressions using F-tests conducted in JMP. An alpha level of 0.05 was set for all significance tests.

2.3 Results

2.3.1 Water Extractable Carbon Composition by Season, Land Cover, and Landscape Position

The amount of WEOC (in mg/kg) extracted from soils varied significantly by season and by land cover for selected seasons (Fig. 2-2a). WEOC amount was lowest and least variable in summer, ranging from 47 mg/kg dry soil to 1280 mg/kg dry soil (mean of 307 mg/kg dry soil). Highest and most variable values were measured for fall, ranging from 664 mg/kg dry soil to 11600 mg/kg dry soil (Fig 2-2a; mean of 4060 mg/kg dry soil) while winter and spring WEOC showed intermediate values for amount (and variability; means of 1930 mg/kg dry soil and 2590 mg/kg dry soil, respectively).

Differences in WEOC concentrations between land cover were only significant for the spring and fall season. In spring, WEOC concentrations were significantly higher in FOR (a difference of ~1200 g/kg) and in fall concentrations were higher in AG (a difference of ~3000 mg/kg, Table s2-2). No significant differences were found between WEOC concentrations and landscape position.

WETN concentrations were highest in the summer for both AG and FOR ranging from 6-68 mg/kg dry soil (Fig 2-2b). Lowest and least variable concentrations were found at both sites in the spring ranging from 2-6 mg/kg dry soil. The FOR site showed low WETN values for both the winter and fall, while the AG site showed intermediate to high WETN concentrations (5-20 mg/kg dry soil) in the fall and winter, respectively. Landscape position did not significantly impact WETN concentrations (Table s2-2).

FI in the AG site was highest in fall (Fig. 2-2c) and generally FI decreased from hilltop positions to riparian zone (from 1.56 ± 0.15 to 1.45 ± 0.08 , Fig. 2-2d). FI in the FOR site was less variable over the year and average FI values significantly increased with proximity to the stream (from 1.44 ± 0.08 at hilltop to 1.51 ± 0.04 in the riparian zone, Fig. 2-2d, p-value < 0.003). Values for HIX generally showed the opposite trend with increasing proximity to the stream, showing increasing values for the AG site (from 4.79 ± 1.95 to 5.34 ± 1.61) and decreasing values for the FOR site (6.50 ± 3.97 at the hilltop and 5.35 ± 2.42 at the riparian zone, Table s2-2). However, the difference in HIX values by landscape position was not significant for most seasons except spring (Fig. s2-1).

2.3.2 Water Extractable Organic Carbon Biodegradability and Microbial Biomass

The biodegradability of the WEOC was significantly different between the two land covers for most seasons, especially spring, with highest BWEOC in the agricultural site across most seasons (Fig. 2-3a, 2-way ANOVA p-values < 0.008 and < 0.0005 for site and season, respectively). For example, means of spring BWEOC were 32% higher in the AG vs. FOR land covers and means of summer BWEOC were almost 18% higher in AG vs. FOR sites (Fig. 2-3a). During fall, the AG site had overall higher average levels of BWEOC although the FOR site BWEOC values were less variable. The WEOC of the winter II soils showed

little to no biodegradability with increases in WEOC values for the majority of samples post-incubation (Table s2-2).

Soil microbial biomass varied significantly by season (Fig. 2-3b) but not by land cover or landscape position (Table s2-2). The largest amount of biomass was found in winter at both the AG and FOR sites (ranging from 11840 to 63450 mg chloroform extractable C/kg dry soil and 2830 to 11900 mg chloroform extractable C/kg dry soil for AG and FOR), respectively. Microbial biomass summer samples were lowest for both land covers (mean of 200 mg chloroform extractable C/kg dry soil for both land covers). Increases in soil microbial biomass correlated with DOM biodegradability, however not significantly (table s2-2).

2.3.3 Significant Correlations between Environmental Conditions and Water Extractable Organic Carbon Characteristics

Field measured soil moisture and temperature (averaged over 5 days prior to sampling), showed a strong correlation with BWEOC for some, but not all seasons (Fig. 2-4). For example, the correlation between %BWEOC and soil moisture was positive and statistically significant for spring (F-test, P-value <0.007) and negative and significant for fall (F-test, P-value <0.02, Fig. 2-4a), but not significant for either winter or summer (F-test, P-value >0.3, Fig. s2-2). Soil temperature correlated positively with %BWEOC for all seasons (Fig. 2-4b), however these trends were only significant for winter trends (F-test, P-value <0.03).

Field-measured CO₂ concentration measured *in situ* at a depth of 15cm prior to soil sampling was lowest for winter and fall soils (ranging from 290 ppm to 3900 ppm and 90 ppm to 6200 ppm, respectively). Spring showed intermediate CO₂ production levels, ranging from 530 ppm to over 10,000 ppm, while highest CO₂ levels were found in the summer (ranging from 1220 ppm to almost 13,000 ppm). CO₂ production in the field significantly correlated to increases in soil temperatures (Fig. 2-4d).

2.3.4 Significant Correlations between Fluorescence Parameters and Biodegradability

FI and HIX values showed moderate correlations with biodegradability for some seasons but not others. For example, FI showed negative correlations with biodegradability for the spring sampling and positive correlations for the summer sampling with r^2 values of 0.189 and 0.193, respectively but correlations were not significant (p-values <0.075 and <0.065 respectively; Fig. 2-5a). These trends were the same for both AG and FOR sites during the respective season. Biodegradability correlated most significantly with FI in the FOR site during the summer ($r^2=0.528$, p-value <0.02). Humification index showed negative correlations with biodegradability for both AG and FOR during both the summer and spring seasons, although only the summer trends were statistically significant (Fig. 2-5b).

Relative abundance of PARAFAC components correlated with BWEOC for specific seasons and specific land covers and exhibited the same directionality for trends with the

exception of C1 (Humic-like). For example, C1 showed a positive correlation with BWEOC for the fall FOR samples and a statistically significant, negative correlation for spring FOR samples (F-test, p -value<0.05, Fig. 2-5c). The correlations between C2 (Fulvic-like) and BWEOC for the summer, winter, and fall AG site samples and for the fall FOR site samples were positive and significant (Fig. 2-5d). BWEOC showed positive correlations with component 3 (C3, Fulvic-like) during the fall for both sites and in the winter AG site (Fig 2-5e). BWEOC showed negative correlations with component 4 (C4, protein-like) during the fall for both AG and FOR and during the winter at the AG site (Fig. 2-5f).

2.3.5 Experimental Results from Leaf Litter Leachate Incubations

To monitor the progressive change in fluorescence parameters from a source of fresh, unprocessed organic matter, we incubated leaf litter extracts over a four-week incubation. Average concentrations of WEOC progressively decreased from 876 mg/L to 52 mg/L during the entire incubation period, with the majority of WEOC having been lost within the first week (Fig. 2-6a). Synchronous CO₂ analyses indicated that this WEOC was lost through microbial respiration (Fig. s2-4).

Our fluorescence analysis of the WEOM indicated a drop in FI from 1.32 to below 1.16 over the first days followed by a progressive increase in to over 1.43. HIX value generally increased over the course of the first week from below 1 to over 5 and stabilized around 5.5 towards the end of the experiment (Fig 2-6b).

2.4 Discussion

2.4.1 Soil Water Extractable Organic Matter, a Function of Season, Land Cover and Landscape Position?

Our results show that DOM substrate is variable based on our previously defined drivers (season, land cover, and landscape position). Because substrate variability by season (e.g. less aromatic, low molecular weight compounds vs. larger, more aromatic compounds; Fellman et al., 2008; Miller and McKnight, 2010) and by the dominant land cover characteristics and landscape position (Lambert et al., 2017; Parr et al., 2015) have been previously reported, we hypothesized that the environmental conditions, covariant with these drivers strongly impact amount and type of water extractable organic matter from soil. Our results highlight a strong seasonal driver that was modulated by land use in many cases. For example, fall samples at both sites had highest WEOC concentrations (Fig. 2-1a), reflecting the introduction of important amounts of carbon from foliage during leaf fall (Meyer et al., 1998). High FI values at both sites suggested less aromatic compounds primarily contributing to the substrate (Fig. 2-2c, Cory and McKnight, 2005; Wymore et al., 2015), which may indicate active processing (Johnson et al. (2011). Interestingly, highest WEOC values were obtained from AG samples, which might be due to reduced *in-situ* processing, leaving organic materials for our extractions, or a different source of DOM, potentially yielding higher WEOC values.

Summer samples at both sites had the lowest WEOC amounts (Fig. 2-1a), which might be the result of extensive microbial processing during the warm season. CO₂ concentration, a measure of soil respiration (i.e. microbial and plant respiration) increased with temperature and was highest in summer (Fig. 2-3d), suggesting the potential for significant flux of C to the atmosphere during these times (Bond-Lamberty et al., 2016). In addition, both land uses had their highest respective amounts of WETN in summer, suggesting that microbial processes were not nutrient limited (Fig. 2-1b). The spectral results indicate higher FI values compared to other seasons (Fig. 2-2c), which suggests the microbial communities were actively processing the substrate. However, summer microbial biomass was found to be the lowest of all seasons (Fig. 2-3b), which is counterintuitive because the presence of microorganisms is an important prerequisite for microbial processing. In this case, the size of the microbial community was not reflective of their metabolic activity or efficiency, which was also observed by Blume et al. (2002).

Microbial community dynamics were dependent on the physical conditions of the soil as well as the nature of the substrate. Winter and spring WEOC concentrations were intermediate and generally higher for the AG sites (Fig. 2-1a). Interestingly, winter soil extracts had the highest microbial biomass, similarly found in Blume et al. (2002), and WETN values (Fig. 2-2b) which suggests that microbial presence and substrate for microbial processing were good, but other critical soil environmental conditions (i.e. the soil temperatures) were not conducive for increased levels of microbial metabolic activity (Blume et al., 2002). The low FI winter values (Fig. 2-2c) indicate that the substrate was of higher aromaticity, typical for sources that had not been processed. Spring samples in contrast showed both low biomass and very low WETN values (Fig. 2-2b), despite the fact that snow melt flushes shallow soils, releasing DOM from soils and nutrients from snow packs (Estop-Aragonés et al., 2018; Phillips and Nickerson, 2015). One reason for the low aqueous nitrogen concentrations could be the competition between soil microbial communities and vegetation (Hodge et al., 2000; Kuzyakov and Xu, 2013).

In addition to season and land cover, landscape position impacted WEOC fluorescence metrics but was highly site specific. For example, irrespective of the season, FI values for the AG sites were significantly higher (accordingly HIX was lower) in hilltop locations versus riparian toeslope positions (Fig. 2-2d). This pattern suggests a transition from microbially sourced or low aromaticity DOM near the hilltop position by the field to more terrestrial, high aromaticity materials near the stream (Burns et al., 2016). The AG site receives less fresh substrate at the edge of field likely due to limited vegetative cover, while the stream riparian locations might be impacted by periodic flooding, resulting in accumulations of more aromatic DOM. In contrast, WEOC from FOR sites had low FI values (lower aromaticity) at hilltop and high FI values in riparian toeslope locations, suggesting a downslope progression towards more microbial and well-processed substrate (Fig. 2-2d). These results paint a complex picture of the role of landscape position on DOM characteristics and reflects the variability found in other studies, where landscape position was found to have little effect as seen in a study by Whittinghill et al. (2014), versus

significant effects on DOM compositions as seen in Cincotta et al. (in prep) and Fellman et al. (2009c).

2.4.2 Water Extractable Organic Carbon Biodegradability a Function of Substrate Composition and Microbial Abundance?

DOC biodegradability is a measure for the utilization of organic matter by microorganisms in soils and depends both on intrinsic (i.e. molecular composition) and extrinsic factors (i.e. soil moisture content) (Marschner and Kalbitz, 2003). We hypothesized that WEOC biodegradability is determined by substrate composition and microbial abundance and, because both parameters vary by season, we expected seasonal variation in biodegradability.

Results of our lab incubation studies on WEOC biodegradability were highly variable for most seasons (Fig. 2-2a) and spring WEOC had some of the highest % of respired carbon. Especially in AG samples, spring biodegradability was high and negatively correlated with FI, suggesting that low FI material (i.e. terrestrial, high aromaticity organic matter) was used as substrate (Fig. 2-5a). In the case of FOR, spring biodegradability was negatively correlated with HIX and % humic-like fluorescence (Fig. 2-5b and 2-5c), indicating that fresh (i.e. unprocessed) organic matter was used (Fig. 2-5b). While biodegradability was correlated with specific substrate compositions, the relationship was variable, likely the result of other external factors associated with site and seasonal specific controls, such as changes to the microbial community and resulting preference for the dominant types of DOM present (Li et al., 2018; Mellado-Vázquez et al., 2019).

Summer WEOC was more biodegradable and (in contrast to spring) positively correlated with FI (and with fulvic acid like fluorescence for AG, Fig. 2-5d-e), suggesting that at this time microbially derived, low aromaticity organic matter was utilized (Miller and McKnight, 2010; Wong and Williams, 2010). Overall this represents a significant shift in utilized carbon source. While fall WEOC biodegradability was variable, winter WEOC biodegradability was zero at low incubation temperature (4 degrees C, Table s-2) and consistently high at 25 degrees C (Fig. 2-2a). Both fall and winter biodegradability correlate positively with fulvic-like fluorescence (Fig. 2-5d-e) and negatively with protein-like fluorescence (Fig. 2-5f) suggesting that carbon utilization shifted away from microbial sources to low aromaticity organic matter. The very high biodegradability values at 25 degrees C indicated that winter substrate composition was ideal to fuel microbial processing, possibly representing leftover fall substrate (Blume et al., 2002; Kim et al., 2017; LeClerc et al., 2014). This has important implications for carbon dynamics during winter thaw events and spring times, suggesting that decomposition of soil C may be high during these times (Matzner and Borken, 2008; Panneer Selvam et al., 2017). Changes to the climate system has already led to significant warming in high latitude environments (IPCC, 2014), hence, if the number of days with warm winter temperatures increases, annual carbon efflux will increase accordingly (Wipf et al., 2015).

Overall our results suggest that WEOC biodegradability is highly complex: utilized carbon sources shifted throughout the seasons and neither microbial biomass abundance nor substrate availability seemed to significantly limit biodegradability. The only factor that substantially reduced biodegradation was low incubation temperatures which prevented microbial processing and is in agreement with other studies (Kim et al., 2017).

2.4.3 How Can We Better Predict Biodegradability with Fluorescence Spectroscopy?

Several studies have attempted to use fluorescence parameters to predict biodegradability of DOM, but results have varied greatly between studies (Fellman et al., 2008; Johnson et al., 2011; Wymore et al., 2015). For instance, Johnson et al. (2011) showed that FI values were positively associated with more biodegradable DOM from bulk water samples, whereas a study by Wymore et al. (2015) found that FI values were negatively with respiration due to amendments from leaf litter leachate. The same study by Wymore et al. (2015) also showed that aromaticity determined by absorbance analysis (i.e. SUVA₂₅₄) correlated positively with respiration contrary to soil water by Fellman et al. (2008) and bulk water McDowell et al. (2006).

We posit that these results are not inconsistent but rather demonstrate how substrate utilization varies differentially with substrate composition and environmental conditions. To exemplify changes in biodegradability and fluorescence-based characteristics we conducted a simple incubation experiment using leaf-litter as purely terrestrial and unprocessed substrate. At the beginning of the incubation study, low HIX and FI reflect the fresh and terrestrial nature of this substrate (Fig. 2-6b). With prolonged microbial processing both HIX and FI increased, indicating the presence of more humified, typically polycondensed DOM on the one hand, and microbial, low aromaticity material on the other hand. Biodegradability was highest at the beginning and hence correlates negatively with FI and HIX in this case.

We can trace these progressive changes in an experiment because the starting point and substrate composition is known, however, the natural soil environment is more complex and complex substrate sources and trajectories are largely unknown. Soil DOM fluorescence characteristics therefore should reflect the combined signal of various stages of decomposition (e.g. fresh leaf litter, previously processes litter, humified soil material) and given this complexity, the carbon source for microbial utilization likely varies. Our field results reflect this dynamic where fluorescence parameters correlated differentially with biodegradability dependent on season and land cover (Section 2.4.2). For example, biodegradability of the summer substrate at both landcovers was negatively correlated with humified-terrestrial DOM (Fig 2-5, similarly found in Miller and McKnight, 2010) but in all other seasons this trend was negative or non-existent (Fig. s2-3). Relatedly, the humic-like PARAFAC component C-1 correlated positively with biodegradability for FOR samples in fall but negatively in spring (Fig. 2-5c). This is contrary to several studies published that show larger humic-components to be less biodegradable (Fellman et al., 2008; Fellman et al., 2009b; Inamdar et al., 2012; Stedmon et al., 2003a).

These results underline that substrate utilization is varied and the connection between fluorescence characteristics and biodegradability can change for the same site by season or for the same season by site. We therefore conclude that variations in fluorescence based WEOC characteristics provide important information on substrate characteristics, however DOM bioavailability (i.e. the possibility for microorganisms to interact with WEOC) is driven by the combination of substrate characteristics, microbial presence and activity that vary with environmental conditions that could be predicted with more dynamic fluorescence spectroscopic based models (Fig. 2-7). To fully investigate the complexity of DOM degradation, additional parameters will need to be assessed in further studies. For example, tracing shifts in microbial community structure, possibly covariant with environmental conditions, or priming effects will likely provide further valuable insights in how, when and by whom DOM is degraded and will improve our capabilities of predicting the fate of DOM in a changing environment.

2.5 Figures

Figure 2-1. Schematic of the field sites in northern Vermont (2-1a). The agricultural transect (AG) and forested transect (FOR; 2-1b) accompanying aerial photographs of the transect (2-1c, 2-1e) as well as photographs from the Hilltop (HT) positions looking down towards the riparian zones at AG-HT (2-1d) and FOR-HT (2-1f). Transects are ordered from HT (yellow), Hillslope (HS; grey), and riparian zone (RZ; blue) ending in a near stream position.

Figure 2-2. Amounts of water extractable organic carbon (WEOC) for all seasons and sampling locations (2-2a). Treatments with different letters indicate statistically different means, letters in italics located on the top left of the box plots represent AG, bolded letters located on the top right of the box plots represent FOR ($n=18$, ANOVA p -value <0.001). Amounts of water extractable total nitrogen (WETN) for all seasons and sampling locations (2-2b). Fluorescence Index (FI) for all seasons and sampling locations (2-2c). FI for all seasons compared against hillslope position for both AG and FOR sites (2-2d).

Figure 2-3. % biodegradable water extractable organic carbon (BWEOC) for the agricultural land cover (AG) and forested (FOR, 2-3a). Microbial biomass expressed as mg chloroform extractable C/kg dry soil for both AG and FOR across all seasons and 2-3b). Different letters indicate significant differences between treatments ($n=11$, ANOVA p -value <0.005), letters in italics located on the top left of the box plots represent AG, bolded letters located on the top left of the box plots represent FOR.

Figure 2-4. Selected correlations for all sampling locations between biodegradable water extractable organic carbon (BWEOC) and 5-day average of soil moisture from *in situ* sensors (expressed as volumetric water content, $\text{VWC m}^3 \text{m}^{-3}$) for fall (2-4a) and spring (2-4b). Correlations between 5-day average temperature and field measured CO_2 production (2-4d) and average percent bioavailable water extractable organic carbon (BWEOC, 2-4c) for all sample locations. Triangles indicate the directionality of statistically significant trends. Grey dashed lines indicate FOR sites and black dashed lines indicate AG sites.

Figure 2-5. Selected correlations for both sites (AG and FOR) between biodegradable water extractable organic carbon (BWEOC, %) and fluorescence index (FI, Fig 2-5a) and humification index (HIX, Fig 2-5b). Triangles indicate identity and directionality of statistically significant trends. Grey trend lines in 2-5a-b indicate summer samples and black trend lines indicate spring samples. Selected correlations for both sites (AG and FOR) between bioavailable water extractable organic carbon (BWEOC, %) and relative abundance of parallel factor components (PARAFAC) for C1 (Humic-like, Fig. 2-5c), C2 (Fulvic-like, Fig. 2-5d), C3 (Fulvic-like, Fig. 2-5e), and C4 (protein-like, Fig. 2-5f). Triangles indicate directionality of statistically significant trends.

Figure 2-6. Water extractable organic carbon (WEOC) concentrations expressed in mg/L, over a period of 4 week during the incubation experiment (2-6a). Each daily WEOC assessment has an associated humification index value (HIX) and fluorescence index (FI) value (2-6b).

Figure 2-7. *Conceptual model for potential bioavailability determined by the interactions between environmental conditions, type and accessibility of the substrate, and any interactions with microbial communities.*

2.6 Supplementary Materials

Supplementary Table 2-1. Full dataset all substrate characteristics for each season, site, and landscape position. Bolded text refers to Winter sampling and text within parenthesis refers to Winter II sampling data. Values shown are water extractable organic carbon (WEOC) and water extractable total nitrogen (WETN) expressed as mg/kg dry soil, Fluorescence index (FI), Humification index (HIX), biodegradable water extractable organic carbon (%), microbial biomass expressed in mg/kg dry soil, and parallel factor analysis (PARAFAC) components (C1-4) expressed as relative abundance (%)

	WEOC mg/kg dry soil	WETN mg/kg dry soil	FI	HIX	BWEO C [%]	Microbial Biomass mg/kg dry soil	C1 [%]	C2 [%]	C3 [%]	C4 [%]
Spring	2594±1799	3±1	1.46±0.06	5.18±1.87	58±20	3891±4410	14±1	14±1	47±4	24±6
AG	1922±1414	3±2	1.44±0.06	5.59±1.6	72±18	3040±2338	14±1	14±1	48±4	24±6
HT	2162±1727	5±1	1.52±0.03	4.51±1.44	71±6	1166±1235	14±1	14±1	49±3	23±3
HS	1800±65	2±1	1.4±0.01	5.13±1.2	93±4	3152±919	13	13	46	28
RZ	1843±2104	2±1	1.43±0.02	6.62±1.71	58±15	4213±3101	14±2	14±1	48±5	24±9
FOR	3022±1945	3±1	1.48±0.06	4.92±2.06	49±15	4433±5381	14±1	15±2	47±5	25±6
HT	4929±3310	4±2	1.44±0.14	3.17±1.36	65±7	3163±2173	12±1	14±2	42±2	32±3
HS	3361±860	3±1	1.48±0.05	4.39±2.13	46±17	4542±4812	14±1	16±1	51±2	20±4
RZ	1645±1681	2±1	1.5±0.04	6.48±1.32	44±12	4932±7914	15±1	13±2	45±4	26±5
Summer	307±328	21±15	1.48±0.04	5.69±2.45	50±17	205±123	15±2	14±2	47±6	24±9
AG	262±348	19±8	1.47±0.03	5.03±1.52	56±16	159±141	14±1	13±1	48±3	25±5
HT	108±7	10±1	1.49±0.04	6.16±1.57	59±8	323±NA	15±1	14±1	51±2	20±3
HS	705±415	21±8	1.47±0.04	3.06±0.04	75±9	141±163	13±1	14±1	47±1	26±1
RZ	69±32	24±8	1.45±0.02	5.58±0.21	42±5	117±141	14±1	12±1	45±4	29±7
FOR	335±328	23±18	1.49±0.04	6.11±2.88	46±17	233±109	15±2	15±2	47±7	24±10
HT	231±252	17±17	1.45±0.05	7.92±5.53	29±5	246±175	16±2	17±2	52±4	15±9
HS	434±473	29±25	1.5±0.04	5.18±3.02	49±10	214±109	14±3	14±2	45±8	27±12
RZ	264±95	18±8	1.5±0.02	6.37±1.28	52±23	245±113	16±1	14±2	46±6	25±8
Fall	4062±2961	8±7	1.54±0.13	4.6±2.4	54±16	5533±5363	14±2	13±3	40±9	33±13
AG	5888±2998	11±6	1.64±0.13	3.43±1.36	58±23	6113±5521	14±2	10±2	35±8	41±11
HT	5485±1488	10±2	1.79±0.15	2.59±0.12	53±16	10017	16±1	10±1	29±3	45±2
HS	8118±4928	7±3	1.63±0.03	3.86±1.67	47±13	2209	14±1	10±2	41±3	35±4
RZ	4670±2519	15±7	1.54±0.08	3.7±1.7	69±32	NA	12±2	10±3	34±12	44±17
FOR	2901±2387	5±6	1.47±0.07	5.35±2.67	52±9	5404±5661	14±2	15±3	44±7	26±11
HT	3275±879	10±4	1.41±0.13	5.5±0.6	54±8	11195±6914	14±1	16±1	46±3	24±2
HS	3057±3205	6±8	1.46±0.05	6.09±2.44	48±12	5195±5652	14±2	14±3	43±9	29±13
RZ	2518±2171	2±3	1.51±0.07	4.35±3.66	56±6	1822±1867	15±1	15±5	46±8	24±12
Winter	1933±1352	13±5 (12±5)	1.43±0.08	5.5±2.8	72±7 (0)	20263±17641	15±4	13±2	41±8	31±11
AG	1868±1023 (700±418) (1074±217)	16±4 (14±6)	1.38±0.08	4.94±1.86	72±10 (0)	25642±19473	16±5	14±2	46±4	24±4
HT	2733±192 (986±294)	12±1 (10±4)	1.46±0.02	6.26±2.03	70±4 (3±8)	18245±9059	14±1	14±2	47±2	25±4
HS	2267±1161 (1025±23)	14±1 (10±3)	1.3±0.03	2.84±0.66	67±2 (0)	27856±12934	NA	NA	NA	NA
RZ	1026±689 (1211±301)	19±4 (21±2)	1.39±0.07	5.47±1.22	78±14 (0)	29099±30585	17±7	14±2	45±5	24±6
FOR	1974±1574 (496±355)	11±5 (11±5)	1.47±0.06	5.85±3.31	72±5 (0)	12733±12864	13±2	12±3	36±9	38±12

Supplementary Table 2-2 *Soil sensor data measured at 15cm and averaged over a 5-day period for free Carbon dioxide (CO₂), volumetric water content (VWC), and temperature for each season and land cover.*

		Season							
		Spring		Summer		Fall		Winter	
		<i>AG</i>	<i>FOR</i>	<i>AG</i>	<i>FOR</i>	<i>AG</i>	<i>FOR</i>	<i>AG</i>	<i>FOR</i>
CO ₂ (PPM)	Average	6670	4054	5153	6135	2996	2581	2104	3109
	Standard Deviation	2408	2710	3449	4287	2593	2178	1414	1166
VWC (m ³ m ⁻³)	Average	0.32	0.32	0.25	0.29	0.36	0.31	0.45	0.36
	Standard Deviation	0.08	0.15	0.09	0.15	0.07	0.11	0.14	0.13
Temperature (°C)	Average	16	1	20	17	7	6	4	3
	Standard Deviation	0.9	0.7	2	0.5	0.8	0.7	0.3	0.6

Supplementary Table 2-3. *Components identified from Parallel Factor Analysis (PARAFAC) paired with other citations in the literature and respective designation.*

Component	Repetition in the literature	Designation
C1: Terrestrial, humic-like (EX: 250-325 nm; EM: 340-500 nm)	Singh et al., (2013) (FH1) Fellman et al., (2009) (C1) Wang et al., (2015) (C3)	Humic-like Humic-like Humic-like
C2-3: Terrestrial, fulvic-like (EX: 241-300 nm; EM: 425-575 nm)	Singh et al., (2013) (FH3) Fellman et al., (2008) (C1) Wang et al., (2015) (C3)	Fulvic-like Fulvic-like Fulvic-like
C4: Microbial, protein-like (EX: 280 nm; EM: 300-420 nm)	Singh et al., (2013) (FH5) Fellman et al., (2008) (C8)	Protein-like Protein-like (Tryptophan-like)

Supplementary Figure 2-1. *Humification Index (HIX) for spring samples compared against hillslope position for both agricultural (closed circles) and forested (open circles) sites. Treatments with different letters indicate statistically different means, (n=6, ANOVA p-value <0.001).*

Supplementary Figure 2-2. Soil sensor data measured at 15cm and averaged over a 5-day period for volumetric water content (VWC) for both land covers during summer (correlations displayed in grey) and winter (correlations displayed in black).

Supplementary Figure 2-3. Fluorescence index (FI) values compared against % biodegradable water extractable organic carbon (BWEOC) for spring (s2-3a), fall (s2-3b), summer (s2-3c), and winter (s2-3d). Humification index (HIX) values compared against %BWEOC for spring (s2-3e), fall (s2-3f), summer (s2-3g), and winter (s2-3h). Triangles indicated directionality of statistically significant trends.

Supplementary Figure 2-4. Carbon dioxide (CO₂) production in parts per million (ppm) over time during the leaf litter incubation experiment (Fig. s2-4a) and the subsequent loss of dissolved organic carbon (DOC) in parts per million (ppm; Fig. s2-4)

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