Examining mineral-associated soil organic carbon pool dynamics following clearcut harvesting in a temperate red spruce forest chronosequence

by

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Abstract

Clearcut forest harvesting is a common practice in temperate forests. Whereas the mineral soil contains a substantial proportion of total forest carbon (C), little is known about the effects of harvesting disturbance on the quantity and character of mineral-associated C pools. This thesis documents changes in the size and chemical character of four pools (water soluble, organo-metal, poorly crystalline, and crystalline) within the organo-mineral fraction through 50 cm mineral soil depth (0-5, 5-10, 10-15, 15-20, 20-35, and 35-50 cm) profiles from a chronosequence of Podzol soils representing important stages of forest development (1yr, 15yr, 45yr, 80yr post harvest and a 125+yr reference stand). At all sites, the dominant C pool was the organo-metal complexed, and significant losses were documented following disturbance, particularly in the deeper (>20 cm) mineral soil. Trends of decreasing C concentration, along with chemical character and isotopic data support the hypothesis that increased microbial processing is responsible for C losses following disturbance. These findings suggest that soil C associated with minerals can become destabilized with a change in soil environmental conditions, and that this can increase susceptibility to microbial decomposition. The sheer size of the mineral C pool, as well as the observation that deeper soil dynamics appear to drive trends at these sites, warrants further investigation.

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1.0. Introduction

1.1. General background

Carbon (C) is the basic building block of life on Earth and soil organic matter is the basis of healthy soils; however, while crucial in maintaining healthy ecosystems, human induced shifts in the natural C cycle have generated serious environmental problems (McDonough, 2016). The concentrations of carbon dioxide (CO_2) and other greenhouse gases in the atmosphere have significantly increased since the Industrial Revolution (IPCC, 2014), with current CO_2 levels surpassing 400 ppm (NOAA, 2017).

Soils play an essential role in C sequestration and atmospheric CO_2 level regulation. As the largest terrestrial pool of organic C, soils store more than three times as much C as the atmosphere or terrestrial vegetation, and are a significant component of the global C (Schmidt et al., 2011). Within forest ecosystems, soil and peat deposits hold more than two thirds of global soil C, and the mineral soil can represent more than 50% of a forest C budget (Jobbágy & Jackson, 2000). Forests are also important in regulating the hydrologic cycle, influencing climate by exchanging chemical species with the atmosphere, as well as sequestering large quantities of C annually (Bonan, 2008). However, deforestation can drastically alter patterns of C sequestration, possibly turning what is normally a sink for C into a future C source (Dixon et al., 1994). Disturbance of old growth forests, which accumulate and contain significant amounts of C, is expected to result in the transfer of C back to the atmosphere (Luyssaert et al., 2008). When decomposition surpasses inputs of C to the soil (either a consequence of anthropogenic activities, such as clearing forests, or increased decomposition rates, possibly related to global warming), the outcome is a soil C source (Trumbore, 1997).

Photosynthesis and respiration are the foremost processes responsible for exchanging C between soil and the atmosphere. These processes are carried out by autotrophic organisms (including plants and photosynthetic bacteria) that utilize inorganic C as their main C source and use external energy sources to synthesize biochemical constituents, as well as by heterotrophic organisms (such as fungi, animals, and some bacteria) that derive energy from the decomposition of organic compounds (Heimann and Reichstein, 2008; Hanson et al., 2000). Photosynthesis by autotrophic organisms removes CO_2 from the atmosphere via carbon fixation and synthesizes it into organic material, which cycles through plant tissues, litter, and soil (Gougoulias et al., 2014). A number of different pathways, including both autotrophic respiration (release of CO_2 by plants, live roots and stems) and heterotrophic respiration (mainly from microbial decomposition of OM) (Trumbore, 2006), are responsible for returning fixed C to the atmosphere (Du et al., 2014). Soil microbial and animal respiration, as well as plant respiration, release CO_2 back into the atmosphere, while a significant volume of terrestrial C is transported from soils to rivers and lakes as dissolved organic carbon (DOC), where a fraction is outgassed to the atmosphere as CO_2 (Ciais et al., 2013; Kreutzweiser et al., 2008).

1.2. Podzolic soil profiles

Variation in the abundance and composition of soil organic matter (SOM) can have significant impacts on C cycling processes (Batjes, 1996). Composed of OM, along with macro- and micronutrients needed by living organisms (Batille-Aguilar et al., 2011), soils are complex, dynamic systems organized into layers that develop over time (Jenny, 1994). These layers, or horizons, comprise the soil profile, and the development of this profile is influenced by climatic conditions (Schlesinger and Bernhardt, 2013). Development of the soil profile involves many

biogeochemical processes, and depends on the interactions of climate, living organisms, topography, parent material, and time (Jenny, 1994).

The influence of climate in Podzol development can be seen in the spatial distribution of this soil type, and is broken down into sub-factors mainly based on two variables: temperature and moisture (Jenny, 1994). Podzols mainly develop in cool and wet climates, particularly in the boreal zone, and thus are commonly found in Canada (Sauer et al., 2007). Not only do temperature and moisture directly affect soil development, but the influence of climate plays a role in the distribution of vegetation, with temperate forests covering mid-latitude regions (Lal, 2005). These soils are often covered by coniferous vegetation, which favours Podzol development (Lundström et al., 2000) as the acidic litterfall decomposes relatively slowly but produces organic acids that contributes to the podzolization process (Van Miegroet et al., 2005). Podzols typically occur on parent material that is coarsely textured (e.g. sandy deposits), often underlain by granitic or gneissic rock (Jenny, 1994).

Generally, Podzol forest soils can be divided into two broad categories, consisting first of a surficial organic horizon, and an underlying mineral soil, which can be further divided into horizons; the mineral soil is dominated by mineral matter, but can contain abundant organic matter (Currie, 1999). In the upper soil horizons, decomposition of SOM by microorganisms, as well as root exudation, produce various organic acids (Strobel, 2000). Humic, fulvic, and low molecular weight (LMW) acids within the soil solution contribute to mineral weathering and the formation of an eluvial horizon (Lundström et al., 2000). The hydrophilic nature of LMW organic acids and some organic material facilitates their solubility in water and, therefore, their mobility in soils by diffusion (Kleber and Johnson, 2010).

The organic layer or "O" horizon formed, by the microbial decomposition of surface litter, comprises the forest floor. Beneath the O horizon is the mineral soil, with the uppermost mineral layer designated as the A horizon. Chemical weathering of soil minerals within the A horizon is dominated by organic acids carried by percolating soil water (Schlesinger and Bernhardt, 2013). As fulvic and LMW organic acids move through the soil from the forest floor, iron (Fe) and aluminum (Al) complexes are mobilized and mineral components are removed from the A horizon (Fuss et al., 2011) in a process known as eluviation (Schlesinger and Bernhardt, 2013). The downward movement of these organic-metal complexes (chelation of Fe and Al with organic acids) and deposition into the underlying B horizon represents a zone of illuviation, and is known as podzolization (Fuss et al., 2011; Buurman and Jongmans, 2005), the central soil forming process in soils classified as Podzols (Dai et al., 2001). Within the B horizon, precipitation of Fe and Al oxides and hydroxides occurs, and these typically form crystalline oxides (Fuss et al., 2011; Schlesinger and Bernhardt, 2013). The translocation and accumulation of organo-mineral complexes deeper in the soil profile is evident by the presence of a dark spodic horizon rich in Fe and OM, which is characteristic of soils classified as Podzols (Schlesinger and Bernhardt, 2013). The C horizon, which shows minimal signs of soil formation, is found beneath the B horizon (Lundström et al., 2000) and may show similar mineralogy to the underlying parent rock if the soil developed on local material.

Soil formation operates on timescales of millennia, and development is linked to evolution in biogeochemical properties, including soil mineralogical composition, which shifts with chemical weathering reactions (Lawrence et al., 2015). Because they are inextricably linked, a framework of soil development is required to understand the dynamics of terrestrial C stocks below ground.

1.3. Forest dynamics

As both an economically and ecologically important resource in northeast North America, particularly as an economic driver in the Maritimes, forests provide a wealth of ecological services ranging from C sequestration and clean air, to economic sources of building materials and energy (MacLean et al., 2010).

Forests cycle over time through natural successional stages, moving from an unstable state undergoing constant changes to a steadier state, which reaches and remains in equilibrium until a disturbance (such as fire, wind throw, or clearcut harvesting) occurs, and so the successional cycle begins again (Mosseler et al., 2003). In the absence of disturbance, forests develop into a stage of old growth; following a disturbance, natural forests normally cycle through four developmental stages: stand initiation, where new seedlings begin growth following disturbance; stem exclusion, where competition for resources (e.g. light following crown closure) becomes limiting and new stems cannot be established; understory initiation, involving growth of understory herbaceous and woody plants; intact, mature old growth, with a multi-aged stand structures and dead and dying trees in various stages of decay (Oliver, 1980; Mosseler et al., 2003). However, the intervals within which forest harvesting occurs tend to be far shorter than natural disturbances, and so soils may not have enough time to re-accumulate C stores to pre-disturbance levels. While many temperate forests, including the Acadian Forest Region are intensively managed, studies of the effect of different types of harvesting on the mineral soil C pool are lacking.

1.4. Links between forest dynamics and mineral soil carbon stability

In terrestrial ecosystems, environmental and biotic controls that influence primary producer and microbial activity largely regulate the biogeochemical cycling of C (Fahey et al.,

2005). Following forest harvesting, the soil environment experiences significant physical and chemical changes that affect the ecosystem in a number of ways (Vario et al., 2014).

As residues from vegetation fall onto the forest floor, this litter can become altered by physical fragmentation, interactions with fauna and microflora, as well as mineralization (Batjes, 1996; Kreutzweiser et al., 2008). Plant organic C can enter the soil system via two pathways: aboveground litter and leachates (including DOC) can be transferred into the soil with infiltrating water; or the transfer of C-containing compounds can occur from belowground root litter and exudates to the soil through rhizodeposition (Gougoulias et al., 2014). In temperate coniferous forests, where litterfall is rich in organic acids and decomposition rates are slower, large quantities of organic acids can percolate to the underlying A horizon from the forest floor (Schlesinger and Bernhardt, 2013). Different enzymes are produced depending on the microbial population, although all C degrading enzymes produced by microorganisms are essential in the breakdown of litter and SOM (Waldrop and Firestone, 2004).

Stabilization, influenced by environmental and biotic controls, refers to the reduced potential for loss of SOM by respiration, erosion, or leaching (Sollins et al., 1996); essentially, processes that prolong soil turnover times and protect OM from mineralization (von Lützow et al., 2006). Factors controlling SOC pools can be classified in different ways, ranging from physical (aggregation, occlusion/isolation), to chemical (sorption, association with minerals, redox reactions) and biological (exudation, biodegradability) (Six et al., 2002; von Lützow et al., 2006; Sollins et al., 1996; Wagai and Mayer, 2007); it is the interplay of these processes that result in either the stabilization or destabilization of SOC (Schmidt et al., 2011; Lehmann and Kleber, 2015).

Organo-mineral interactions have been identified as imposing a strong effect on the bioavailability of SOM (Lacroix et al., 2016). Bioavailability is a prerequisite for decomposition. Operating on the premise that OM bound strongly to minerals is less bioavailable to microbes (for respiration), and weakly bound SOM is more available for microbial respiration (resulting in soil CO_2 production), sequential chemical extractions offer an approach for measuring the strength of SOM- mineral associations (Lacroix et al., 2016; Lopez-Sangil and Rovira, 2013). This approach allows SOC associated with mineral pools of increasing crystallinity, including water soluble minerals, organo-metal complexes, poorly crystalline, and crystalline pools to be extracted in soils. These mineral-associated pools can then be quantified and their chemical character examined to investigate changes in C storage and character through depth and/or time following forest disturbance. By examining changes in the amount and chemical character of the SOC, insight can be gained regarding the degree of microbial processing (Sanderman et al., 2008). Additional information regarding these concepts can be found in the introductory sections of chapters 2 and 3.

Despite the complexity of soil C cycles and the inter-related spatial and temporal scales SOC cycling operates within, the ability to detect shifts in SOC is crucial for determining responses to scientific and societal consequences of a rapidly changing environment (Harden et al., 2017). Significant advances in the conceptual framework for understanding SOC stability have been made in recent years (Lehmann and Kleber, 2015; Schmidt et al., 2011), subsequently motivating scientists to more closely examine and test these emerging paradigms.

1.5. Research problem and objectives

The impact of human disturbance on soils and biogeochemical cycling is significant in a variety of disciplines, and is a major topic of current research. There exists a need to know more

about the cycling of C in various physical and chemical fractions in soils to better predict the behaviour of soil C with respect to land use and climate change. The overall goal of this research is to investigate the links between forest harvesting and C released from soil profiles through changes in the stability of the mineral soil C pool of northern temperate forests.

In order to accomplish this, the specific objectives of this study to be addressed are:

1. To quantify (changes in) C storage within soil mineral pools of increasing crystallinity following forest harvesting in a temperate forest soil.

2. To determine whether the chemical character of C stored within dominant mineral pool(s) changes following harvesting disturbance.

In an effort to explore these questions and meet the specific research objectives, this thesis examines the quantity and character of mineral-associated C pools of mineral soils from managed red spruce forests located in the Abrahams Lake region of Nova Scotia.

1.6. Thesis structure

This thesis is divided into four chapters, including two chapters formatted for publication as peer-reviewed journal articles. Chapter 1 has outlined the broader background information regarding this research topic. In Chapter 2, the design and results of SOC mineral pool separation experiments are presented along with discussion of overall changes in C pools through depth and time. Chapter 3 focuses on the investigation and discussion of C chemical character from these disturbed soils through time and depth, focusing on the aromatic character of C within the organo-metal complexed pool. Finally, Chapter 4 summarizes general conclusions and recommendations for future work related to this study.

2.0. Investigation of mineral-associated soil organic carbon pool losses following clearcut harvesting

Preamble

This research manuscript is intended for publication in a journal that focuses on the impacts of forest management on soil C. I performed the lab work, data analysis, and statistical analysis. This study was conceived by my supervisor, Dr. Lisa Kellman, using methods tested and developed by Carrie-Ellen Gabriel. Soil samples used in this research were collected and archived by Dr. Amanda Diochon. Sections of this research were presented in the form of a poster at the American Geophysical Union Conference, December 12-16, 2016, in San Francisco, CA, titled "Changes in mineral-associated soil organic carbon pools across a harvested temperate forest chronosequence", co-authored by myself and L. Kellman, C.-E. Gabriel, and A. Diochon.

Abstract

Due to their substantial pool size, changes in mineral soil carbon (C) stores have the potential to generate significant changes in forest soil C budgets. Harvesting represents a significant land use disturbance that can alter atmospheric carbon dioxide (CO_2) concentrations and reduce soil organic carbon (SOC) stores. However, little is known about how the distribution of SOC changes amongst mineral-associated pools of differing crystallinity following a disturbance. The objective of this study was to quantify and examine changes in mineral-associated SOC pool sizes through depth and time for Podzol soils (mineral soil depths of 0-5, 5-10, 10-15, 15-20, 20-35, and 35-50 cm) of a harvested temperate red spruce forest chronosequence (representing stand ages of 1 yr, 15 yr, 45 yr, 80 yr, and 125+ yr) in Nova Scotia, Canada. Samples were subjected to a four-step sequential chemical dissolution to selectively extract C from mineral pools of increasing crystallinity: soluble minerals (deionized water), organo-metal complexes (Na-

pyrophosphate), poorly crystalline minerals (hydroxylamine), and crystalline minerals (Na-dithionite HCl). Carbon concentrations were calculated for the solutions acquired during each stage of the selective dissolution process, providing a sequence of changes in mineral-associated C through depth and time following harvesting. The greatest losses of SOC were observed within the organo-metal complexed pool following clearcut harvesting, particularly in the deeper mineral soil (20-50 cm). Whereas the water soluble, poorly crystalline, and crystalline pools (representing ~3-6%, ~8-21%, and ~4-16% of total deep mineral-associated C, respectively) also experienced some loss, they are minimal in comparison to the organo-metal pool (representing ~59-85% of total deep mineral-associated C). This study provides a useful model system for understanding how harvesting disturbance alters mineral pool SOM dynamics in temperate forest ecosystems.

2.1. Introduction

Soils are the largest terrestrial pool of organic carbon (C), storing more than three times as much C as the atmosphere or terrestrial vegetation (Schmidt et al., 2011). Involved in the rapid exchange of carbon dioxide (CO_2) and a fundamental terrestrial nutrient reserve, soil organic matter (SOM) is the largest terrestrial reservoir of C actively exchanging with the atmosphere (Torn et al., 2009; Wagai et al., 2013). In forest ecosystems, it is estimated that more than two thirds of the C is held within soils (Dixon et al., 1994), with the deeper mineral soil capable of representing more than 50% of a forest C budget (Jobbágy & Jackson, 2000). Despite this fact, there is limited scientific information regarding C dynamics associated with the mineral soil component and how it is affected by forest harvesting activities. Forest harvesting removes overstory trees and woody biomass, often disturbing surface soil layers, root structures (Yanai et al., 2003), and altering soil climate (Kellman et al., 2015; McVicar and Kellman, 2014), which, in

turn may, alter SOM stability through changes in nutrient availability, soil water content, and physicochemical interactions (Kellman et al., 2015).

While forest harvesting has occurred for centuries in eastern North America (Diochon et al., 2009) and continues to thrive as a widespread practice, development of a better understanding of C storage and stabilization mechanisms associated with disturbance and SOM in mineral soils represents a critical area of research, as the release of even a small proportion of SOM as gaseous C (CO_2) can result in significant changes in atmospheric greenhouse gas concentrations (Lehmann and Kleber, 2015; Petrenko and Friedland, 2015). In an effort to mitigate climate change, a potential increase in forest carbon sinks and subsequent offset from the forestry sector is expected as part of Canada's action plan to reduce carbon emissions (Bernier et al., 2012). An important consideration for sustainable forest management involves understanding how C cycling through SOM will be affected by biomass removal during forest harvesting.

The majority of the focus in research conducted to date in relation to forest soils and harvesting disturbance has been upon bulk C cycling within the forest floor and shallow mineral soil (usually the top 10-20 cm), generally within a decade of harvesting (Diochon et al., 2009). The rationale for this emphasis has been the assumption that this C has a long residence time, and that deeper mineral soil C is stable over harvesting cycles (Prest et al., 2014; Davidson and Janssens, 2006). Only recently have studies started to confirm that deep soil C may be lost following intensive forest harvesting (Achat et al., 2015) and to demonstrate that the mineral soil, including the deeper mineral soil, may be particularly sensitive to this disturbance (Diochon et al., 2009; Prest et al., 2014).

Our current understanding views the nature of SOM as a continuum of organic compounds in various stages of decomposition (Lehmann and Kleber, 2015) that vary in physical and chemical

properties as well as age (Eglin et al., 2010). Soil organic C, the primary constituent of SOM, is composed of a mixture of organic compounds organized through interactions with particulate surfaces and other molecules (Trumbore and Czimczik, 2008), and includes partially degraded litter, microorganisms (both living and dead), organics attached to mineral surfaces, as well as organo-metal complexes and precipitates (Kleber and Johnson, 2010). The recent shift in our understanding of factors that control SOM stability emphasizes that physicochemical and biological factors control accessibility of SOM to microbial decomposition, rather than an inherent chemical recalcitrance (Schmidt et al., 2011; Lehmann and Kleber, 2015; Dungait et al., 2012). Thus, SOM stabilization arises from interactions between SOM and the soil microenvironment, including association with reactive mineral surfaces, climate, and microbial activity (Schmidt et al., 2011; Davidson and Janssens, 2006). Interest in examining processes controlling deeper mineral SOM previously thought to be stable (Buchholz et al., 2014; Schmidt et al., 2011) has increased in efforts to understand whether changes in landuse and climate may destabilize this C fraction. While C stabilization mechanisms are not fully understood, the amount of C stored in soils is fundamentally controlled by inputs from plant production, and outputs from decomposition and leaching (von Lützow et al., 2006).

In mineral soils, organo-mineral interactions, in particular, have been identified as imposing a strong control on the stability of SOM (Lacroix et al., 2016; Diochon and Kellman, 2009). Bioavailability of SOM is a prerequisite for decomposition, as OM bound strongly to minerals is less available for microbial decomposition. This also represents a mechanism that stabilizes SOM, as bioavailability may vary as a function of bonding strength.

Methods used to distinguish different pools of carbon within soil systems include classifications based on turnover time (Trumbore, 2000), chemical fractionation (McKeague,

1967), as well as physical fractionation (typically based on density or particle size) (Sohi et al., 2001; Parker et al., 2002; Diochon and Kellman, 2009). While the use of chemical fractionation is not a new practice, modifications and improvements from previous methods have been introduced, with these newly designed protocols aimed at providing a better description of mineral-associated SOM (Lopez-Sangil and Rovira, 2013). For example, chemical fractionation studies have shown that SOM stabilization in mineral soils is influenced by the presence of iron (Fe) and aluminum (Al) oxides, hydroxides, and oxyhydroxides, as the surfaces of these compounds are extensive and reactive, and allow for organic matter sorption and stabilization (Grand and Lavkulich, 2011; Wagai and Mayer, 2007). Strong correlations between pyrophosphate extractable Al and Fe (representing organo-metal complexes) and SOC in the mineral soil have been found, suggesting organically bound Fe and Al promote the stabilization and accumulation of OM (Grand and Lavkulich, 2011).

Stabilization of SOM is largely dependent on interactions with soil minerals, which include a variety of mineral linkages with different strengths (Lawrence et al., 2015). Physical fractionation to separate OM based on density has previously demonstrated large losses in the organo-mineral fraction following harvesting (Diochon et al., 2009; Diochon and Kellman, 2009). On its own, however, physical fractionation cannot resolve the specific nature of the interaction between the mineral and organic components (Lopez-Sangril and Rovira, 2013). In order to evaluate the importance of the organo-mineral matrix for SOM stabilization, sequential chemical extractions can be used to quantify different mechanisms through which organic compounds and the mineral matrix are bound. The organo-mineral fraction can be systematically broken down into sub-fractions based on mineral classes of increasing crystallinity, including water soluble minerals, organo-metal complexes formed by the precipitation of dissolved Fe and Al cations with organics

(Heckman et al., 2018), and poorly crystalline phases (such as ferrihydrite and imogolite) and crystalline mineral (including goethite and hematite) surfaces involved in sorption of OM (Kleber et al., 2005; Lawrence et al., 2015).

These separate pools were isolated because they somehow function differently, and so interpretation of the pools extracted during selective dissolution procedures may provide insight into the stability of mineral-associated SOM pools, including SOM bioavailability. If the mineral-associated C pools change through soil depth and on decadal time scales following soil surface disturbances such as clearcut harvesting, this may provide further evidence that specific mineral soil C pools are susceptible to destabilization. Possible changes that could destabilize these pools include increased soil temperature, which can increase microbial activity and decomposition processes (Keiluweit et al., 2015; Kreutzweiser et al., 2008), and could result in the decomplexation, dissolution, or desorption of organo-mineral associations (Sollins et al., 1996). Also, changes in moisture, pH and redox conditions can promote the mobilization of C protected by Fe minerals phases (Huang and Hall, 2017).

In order to evaluate changes in SOM as a function of forest succession, which fluctuates on decadal timescales, a chronosequence approach (space for time substitution where sites of different ages are studied at the same time to infer changes over time) is often used. In the context of evaluating the impact of a forest harvesting disturbance on soil C stability, this technique involves identifying a series of soils representing different forest cover ages. This allows one to infer temporal trends (Pickett, 1989), assuming that sites chosen are similar in parent material, topography, tree species, and soil texture to minimize error (if sites differ in aspects other than age) and random variation (Yanai et al., 2003).

The objective of this study was to quantify changes in mineral-associated SOC pool sizes through depth and time for Podzol soils of a temperate harvest forest chronosequence that included an old growth reference site (>125+ years) with no history of harvesting. It builds upon previous research that documented losses from the organo-mineral SOM pool using a density fractionation approach (Diochon and Kellman, 2009) from the same sites. Through comparisons of concentrations (mg g $soil^{-1}$) and storage (Mg ha^{-1}) of C within separate mineral pools (soluble minerals, organo-metal complexes, poorly-crystalline minerals, and crystalline minerals), this study aims to contribute to developing a better understanding of whether specific mineral-associated SOM pools are susceptible to destabilization following forest harvesting disturbance.

2.2. Methods

2.2.1. Site description

This research was carried out in the Abrahams Lake region of the Liscomb Game Sanctuary, Nova Scotia, Canada (45 10°N 62 38°W). The area contains one of the Acadian Forest Region's last remaining virgin old growth red spruce forests (Diochon et al., 2009). Sites are located on soils from the Halifax series, which consists of sandy loam textured Orthic Humo-Ferric Podzols, chiefly derived from quartzite (Diochon and Kellman, 2008). Climatic conditions of the area include a mean annual air temperature of 5.8°C, with January and July having mean temperatures of -5.8°C and 16.9°C, respectively. The area receives approximately 1300 mm of precipitation annually, and is located 185-200 m above sea level, with a rolling topography (<10°) (Diochon et al., 2009). The typical vegetation cover is red spruce (*Picea rubens* Sarg.) forests of the Acadian Forest Region, which is typical of forests in the northern temperate zone (Mosseler et al., 2003).

Red spruce forests are of significant commercial importance to Nova Scotia, and because of intensive forest management, silvicultural activities within the province have increased in recent decades (Taylor et al., 2007). Forest management, using selective cutting, began in the early 1900s (Diochon and Kellman, 2008), and harvesting via clearcutting with branches and foliage left on site began around 1940; following harvesting, there is no scarification, planting or fertilizing (Diochon et al., 2009). Rotations of approximately 60 years are currently used to manage the forest in the study area.

A chronosequence consisting of 5 sites (1yr, 15yr, 45yr, 80yr, and 125+yr) that represent important stages of forest development (recent clearcut, stand initiation, stem exclusion, understory initiation, and intact, mature old growth, respectively) were established (Diochon and Kellman, 2008; Mosseler et al., 2003). To minimize between-site variability, sites are within 5 km of each other, with the same elevation, parent material, soil texture, as well as topography, so that the primary difference between sites is the time since harvesting (Diochon and Kellman, 2009). The last date of intervention of the >125+ year old growth stand is unknown, however trees within the stand are more than 200 years old (Mosseler et al., 2003); the other sites are naturally regenerating from first rotation clearcut harvesting (1-, 15-, and 45-year old sites) and partial harvest (80-year old site) (Diochon and Kellman, 2009).

Because of the Maritime provinces' long history of forest harvesting and clearing land for agricultural use, most older forests and previously unharvested (virgin) forests of the Acadian Forest Region have been eliminated, and so small, isolated stands of old growth that were protected or inaccessible to harvesting are typically all that remain (Mosseler et al., 2003). The lack of old growth reference stands makes it difficult to infer the effects of harvesting on soil C stores (Diochon et al., 2009).

2.2.2. Sample collection and preparation

Samples were collected at a chronosequence established in 2005 (Diochon et al., 2009). Three soil pits measuring 71cm x 71cm x 50 cm deep were randomly determined and hand excavated in a 400 m^2 area representative of the stand at each site. The organic horizons were removed and sieved through a 6.25 mm sieve in the field. The mineral soil was excavated by depth, rather than horizon, using sampling depths of 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-35 cm, and 35-50 cm. After excavation, all soil was sieved to 12 mm and weighed in the field. Representative samples were brought back to the laboratory, oven dried to constant weight, sieved to 2 mm, and reweighed to determine the <2 mm fraction. This soil fraction was then homogenized by grinding the sample on a roller mill. Excess soil samples have been sieved to <2 mm and archived. Composite samples were used in triplicate for this study. Further details of sample collection and preparation can be found in Diochon et al. (2009).

2.2.3. Sequential soil extractions and analyses

Archived samples were subjected to a four-stage sequential chemical dissolution to selectively extract C from mineral pools of increasing crystallinity. Extraction methods were based on the procedures outlined by the USGS (2013). Three 1 g samples of each soil sample were weighed into separate 50 mL polypropylene centrifuge tubes, and 30 mL of deionized water was added to each. Samples were shaken for approximately 16 h on a wrist-action shaker, and then centrifuged at room temperature for 20 min at approximately 7500 rpm. After centrifuging, the supernatant was decanted into 50 mL tubes, filtered through a 0.45µm filter, stored in acid washed plastic Nalgene bottles, and refrigerated at ~4°C until analysis. The residual solid sample was then dried overnight at ~60°C. After drying and reweighing, the residual soils were further extracted with 30 mL of tetrasodium pyrophosphate reagent (0.1M). Following a similar procedure to the

first extraction stage, samples were shaken overnight, centrifuged for 20 min, and the supernatant decanted. The remaining sediment then underwent a wash stage, in which 20 mL of deionized water was added and shaken for at least 2 h before undergoing 20 min centrifugation. The supernatants from this step were combined, filtered, and refrigerated until analyses. Once the residual solid sample was dried overnight, this process was repeated using hydroxylamine solution. The final extraction step involved the addition of sodium dithionite (0.049M) following a similar procedure, except the wash stage used 20 mL of HCl reagent (0.05M) shaken for 1 h prior to centrifugation.

The extraction procedure targeted organo-mineral associated pools sequentially, with more strongly bound SOC removed with each successive extraction. The first phase of the dissolution involved using deionized water to extract water soluble minerals. Deionized water extracts dissolved organic carbon, and water soluble amorphous minerals (D'Angelo et al., 2009). Organo-metal mineral complexes were targeted using sodium pyrophosphate ($Na_4P_2O_7$), which extracts complexed iron, aluminum, organic carbon, and manganese associated with soil organic matter (McKeague, 1967; Ross and Wang, 1993). Poorly crystalline minerals (e.g. ferrihydrite, imogolite) were extracted using hydroxylamine-HCl, which targets non-crystalline inorganic iron, aluminum, and organic carbon (Ross and Wang, 1993). Hydroxylamine (NH_2OH) is also a carbon free extractant with a greater specificity for poorly crystalline minerals compared to oxalate (Kostka and Luther, 1994), and solutions are more easily analyzed by atomic absorption spectroscopy (AAS) than the traditionally used oxalate (Ross et al., 1985; Wang et al., 1987). The final stage of the dissolution focuses on crystalline minerals, and uses sodium dithionite ($Na_2S_2O_4$) and HCl, which acts as a strong reducing agent, to extract crystalline iron oxyhydroxides such as goethite and hematite (Wagai and Mayer, 2007).

2.2.4. Calculations and analyses

The extracted solutions (DOC) were diluted to appropriate concentrations, and the dilutions were analyzed on a Shimadzu TOC-L Total Organic Carbon Analyzer for determination of C concentration (repeatability of the instrument for NPOC is ±50 µg/L).

For each site (1-, 15-, 45-, 80-, and 125+yr), triplicates of composite samples were analyzed through 50 cm mineral soil depth in increments of 0-5, 5-10, 10-15, 15-20, 20-35, and 35-50 cm.

2.3. Results

2.3.1. Carbon concentration

Carbon concentrations for each depth interval and mineral pool across the chronosequence are shown in Table 1. Overall, the organo-metal complexed pool dominated, representing the largest pool at all sites and depth increments, ranging from approximately 3-23 mg C g soil^{-1}. Overall C concentrations in the water soluble, poorly crystalline, and crystalline pools were generally low in comparison, holding <4.1, <2.5, and <5.4 mg C g soil^{-1}, respectively (Table 1).

Changes in the carbon concentration through depth for each mineral-associated pool are shown for each site across the chronosequence (Fig. 1). Total mineral-associated SOC concentrations (mg C g^{-1} soil) were variable across the chronosequence in the shallow mineral soil with no clear temporal trend evident. Carbon concentrations in the organo-metal pool represented ~67-81% of the C within the shallow mineral soil. Water soluble C represented less than 12% of the mineral bound C pool in shallow mineral soils, with the 15-year and 125+-year sites documenting the lowest and highest concentrations, respectively. Carbon associated with poorly crystalline minerals held ~5-10% of total mineral bound C in the top 20 cm of mineral soil. Within

the crystalline pool representing ~4-15% of the total mineral bound C, the old growth site (125+-years) had the highest C concentrations, nearly three times as much as the recent clearcut (1-year).

A clear temporal trend of C loss was observed in the deeper mineral soil across the chronosequence (Fig. 1). In the organo-metal complexed pool (representing ~59-85% of total mineral bound C), significant differences between C concentrations were observed between the 125+-year site and the 15-, 45-, and 80-year sites for both depth intervals (20-35 and 35-50 cm). Water soluble C represented less than 6% of the mineral bound C pool in deep mineral soils. Carbon associated with poorly crystalline minerals accounted for ~7-21% of total deep soil C. In the crystalline pool representing ~4-16% of the total mineral bound C, C concentrations were highest in the 125+-year site and lowest in the 45-year site (Table 1).

2.3.2. Total soil carbon storage

Soil C storage (from the combined organo-mineral pools) across the chronosequence shows total C content was highest in the old growth stand (124.8 Mg C ha^{-1}) and lowest in the 15-year-old clearcut (56 Mg C ha^{-1}) (Fig. 2). These values are within similar ranges found by Diochon and Kellman's (2009) investigation of the sites. There is no apparent age-related variation in C storage within the shallow mineral soil (0-20 cm). However, in the 15-20 cm strata, storage is low and relatively constant at the 1-year, 15-year, 45-year, and 80-year sites (~7-8 Mg C ha^{-1}), and slightly higher at the 125+-year old growth site (~12 Mg C ha^{-1}). Within the deeper mineral soil (20-50 cm), there are notable age-related variations in storage. In the 20-35 cm strata, C storage is similarly greatest in the 1-year and 125+-year stands (~37 Mg C ha^{-1}); storage increases throughout the other sites in the chronosequence from a minimum of ~17 Mg C ha^{-1} in the 15-year site, to 21 Mg C ha^{-1} in the 45-year site, and 28.5 Mg C ha^{-1} in the 80-year site. A similar pattern over time is found in the 35-50 cm depth strata. The 1-year and 125+-year sites have the highest C storage

(~35 and 53 Mg C ha^{-1}, respectively), while storage increases with time in the 15-year (~12 Mg C ha^{-1}), 45-year (~15 Mg C ha^{-1}), and 80-year (~35 Mg C ha^{-1}) stands (Fig. 2).

2.4. Discussion

2.4.1. Using sequential chemical extractions to measure SOC mineral-associations

Studies using similar chemical fractionation approaches have documented significant correlations of SOC content with organo-metal complexes (as extracted using sodium pyrophosphate), suggesting a connection between organo-metal complexation and long-term C storage (Lawrence et al., 2015). Recent research in temperate soils to measure the distribution of C within organo-metal, short range order minerals, and crystalline mineral surfaces using a similar sequential dissolution process as described here (sodium pyrophosphate, hydroxylamine, and dithionite-HCl, respectively) also found that the organo-metal complexed pool accounted for the largest pool of stabilized C, while the other pools were generally small (Heckman et al., 2018).

2.4.2. Trends in mineral soil carbon quantity following forest harvesting

Clearcut forest harvesting is a routine practice in northeastern North American forests, however the impacts these activities have on SOC dynamics remains a source of uncertainty in efforts to quantify changes in forest C storage (Diochon et al., 2009). The amount of C stored in soil is dynamic, and is fundamentally a balance of inputs from plant litter and outputs from decomposition and leaching (von Lützow et al., 2006). When a forest harvest occurs, the quantity, quality, and age of plant matter entering the soil is altered. Changes to the relative rates of inputs and outputs (e.g. resulting from altered environmental conditions or management regimes) will have an effect on the amount of C stored in the soil (Ellert et al., 2007). While the change in inputs can be deciphered relatively simply (patterns of vegetation regeneration can be identified and quantified), it is more challenging to isolate the processes responsible for changes in outputs and

to quantify their magnitude, as collectively, the alterations are numerous and influence one another. These inter-related consequences include increased solar radiation and decreased interception and transpiration from canopy removal (Dai et al., 2001), mechanical mixing from logging machinery (Yanai et al., 2003), changes in nutrient dynamics (Kellman et al., 2015), and increases in microbial and enzymatic activity (Sollins et al., 1996).

Soil organic matter that accumulates as a result of protection mechanisms (i.e. inaccessibility to microorganisms), or in an environment with low biological activity, may be more vulnerable to destabilization following disturbance, or environmental change (such as rising temperature) (Kallenbach et al., 2016; Kleber et al., 2010; Davidson and Janssens, 2006). The largest components of mineral soil OC have been related to the formation of organo-mineral associations (Ma et al., 2016). Organic matter in deeper soil layers has been found to be less decomposable and have a greater association with minerals, suggesting that deep soil profile environmental conditions inhibit OM decomposition (Rasse et al., 2006). This means that changes in conditions that reverse this OM protection (or increase OM bioavailability) make the SOM pool susceptible to destabilization and loss.

At all sites within the chronosequence, association with the mineral matrix is clearly important in SOC stability within these soils, with greatest C storage (~125 Mg C ha^{-1}) at the old growth reference site (Fig. 2). Storage declined through time following disturbance with minimum C storage observed at the 15 year site (56 Mg C ha^{-1}), and while it appears this C pool increases (Diochon identified ~30 years as the minimum C stock point relative to 125+yr point), it does not achieve full recovery to pre-harvest levels after 80 years (~88 Mg C ha^{-1}) (Fig. 2). This has implications in terms of forest sustainability and soil C pool recovery, as rotations of 60 years are

used at these sites (Diochon et al., 2009). This pattern has been identified using a separate set of soil samples as a trend for soil N levels at these sites as well (Kellman et al., 2014).

In the shallow mineral soil (0-20 cm), C concentrations were variable across the chronosequence. While no clear patterns through time were observed, the organo-metal complexed pool still represented the dominant pool at all sites (~67-81%) as compared to the water soluble, poorly crystalline, and crystalline pools (comprising ~9-12%, ~5-10%, and ~4-15% of shallow mineral-associated C, respectively). The lack of relationship within the upper part of the mineral soil profile suggests a decreased sensitivity of mineral-associated SOC to disturbance-driven destabilization as compared to the deeper mineral soil on the timescales investigated here.

Organo-metal complexed C dominated mineral-associated C pools and drove temporal trends in the deep mineral soil (20-50 cm) (Fig.1). For the deeper mineral soils at these sites, the most important mineral-associated organic C pools as a percentage of the total organic C (mg g^{-1} soil) were (in decreasing order of importance): organo-metal complexed (~59-85%) > poorly crystalline (~8-21%) > crystalline (~4-16%) > water soluble (~3-6%). This pattern demonstrates that the formation of organo-mineral complexes within these soils reduces the susceptibility of SOC to mineralization by microbes for undisturbed intact forest sites (125+yr reference site) (von Lützow et al., 2008). However, the relationship observed here (Fig.1) suggests that SOC stabilized within organo-metal complexed pools, when disturbed by forest harvesting activities, have the potential to release substantial amounts of C. This is particularly relevant as it represents a C pool previously considered stable (Buchholz et al., 2014; Clarholm et al., 2015) particularly on the time scales of harvesting disturbance.

It is worth noting the significance of data gained from examining deeper components of the soil profile. By looking only at the shallow depth strata, there are no clear patterns of loss or

gain, and one may misleadingly conclude that harvesting had a minimal overall effect on mineral soil C. However, when the deeper mineral soil is accounted for, a strong pattern emerges showing significant decreases in C concentration (Fig. 1), highlighting the importance of incorporating deeper mineral soil measurements into studies examining forest soil C dynamics (Prest et al., 2014).

The observations found here are significant in that they demonstrate the potential instability of a large proportion of the soil C pool, with stores deeper in the soil profile being sensitive to changes resulting from disturbance. From this, we suggest that once destabilized, this C is readily bioavailable and potentially decomposed. This is consistent with recent advances in the understanding of SOM bioavailability as controlled by inaccessibility rather than chemical recalcitrance. Because of its magnitude and potential feedback to the climate system, there has been considerable discussion regarding the sensitivity of the deeper C pool to alterations of the physical environment (Davidson and Janssens, 2006; Schmidt et al., 2011). By demonstrating significant changes in soil C stores in the decades following clearcut harvesting in this study, we emphasize the necessity for expanding our understanding of soil C dynamics on successional timescales for sites experiencing routine disturbances such as clearcut harvesting.

2.4.3. Implications for forest management

The findings of this study provide further evidence for specific mineral-associated C pools experiencing loss of C from the deeper mineral soil in the decades following clearcut harvesting. Ideally, knowledge gained from this research will help to inform policy makers and private woodlot owners, as well as lead to improvements in forest management practices to maintain forest soil C. Recommendations for improving forest management include reducing clearcut harvesting by shifting to forestry practices that value ecosystem services, (such as harvesting only what is

sustainable, and finding the best use for the harvested materials). Also, with research, including that shown here suggesting that C losses in clearcut soils take decades to recover (Diochon et al., 2009; Zummo and Friedland, 2011), it is important to ensure that harvest rotation lengths are sufficient to allow soil C losses in these vulnerable mineral-associated pools to recover to pre-harvest levels.

With efforts to replace fossil fuels with renewable sources that create lower greenhouse gas emissions, the use of forest biomass could undermine efforts to reduce C emissions. This study illustrates that the consequences to C storage within the mineral SOM pool are potentially large in magnitude and may last for many decades following harvesting. As a result, errors in emissions accounting can wrongly deem wood obtained from biomass harvesting as a carbon-neutral fuel (Searchinger et al., 2009), and may result in elevated C emissions (Cornwall, 2017).

2.5. Conclusions

Despite the importance and influence it exerts on climate and productivity, we still have a very limited understanding of the complex and interactive dynamics of C stored within the mineral soil. When investigating the C sequestration capability of a soil, arguably one of the most important properties to consider is the stability of different functional pools of SOM, and the amount of C each pool holds. Taking this into account, along with the recent shift in understanding of factors governing mineral SOM dynamics, this study focused on delineating SOC pools based upon differences in stability rather than the historical view solely of molecular structure and inherent chemical recalcitrance.

Decomposition of organic matter is typically greater in surface soils, partly because environmental conditions are more favourable than in subsurface soils. However, the potential for

increased decomposition rates, and subsequent losses of soil C deeper in the soil may arise if optimal environmental conditions occur as a consequence of disturbance. Used as a standard management practice in temperate red spruce forests, clearcut harvesting alters inputs and outputs of OM, and causes changes in soil climatic and biological factors that have the potential to reduce mineral soil C stores. This research suggests that SOC in specific mineral associations are vulnerable to destabilization following disturbance, and provides evidence for significant losses of organo-metal mineral-associated C concentrations and storage from disturbed sites in the decades following harvesting, as compared to an old growth reference stand. Replication of this type of study should be included in future research, along with further investigations of forest mineral soil OC destabilization processes following harvesting.

Table 1. Mean and standard error (in parenthesis) of the bulk density, carbon concentration for each pool and the total mineral soil (sum of all 4 extractions), and C-to-N ratio for each depth strata and site in the chronosequence. Bulk density and bulk soil C-to-N ratios from Diochon et al. (2009).

Depth (cm)	Stand Age (years)	Bulk Density (g cm^{-3})	Water Soluble (mg C g $soil^{-1}$)	Organo-metal (mg C g $soil^{-1}$)	Poorly Crystalline (mg C g $soil^{-1}$)	Crystalline (mg C g $soil^{-1}$)	Total Mineral C (mg C g $soil^{-1}$)	C:N
0-5	1	0.79 (0.10)	3.20 (0.17)	22.78 (0.56)	1.49 (0.06)	1.19 (0.05)	28.65	33.3 (3.2)
	15	0.97 (0.08)	2.33 (0.07)	6.97 (0.44)	1.17 (0.06)	3.01 (0.16)	13.48	33.4 (1.9)
	45	0.80 (0.17)	3.50 (0.19)	16.89 (0.09)	1.20 (0.04)	1.64 (0.10)	23.23	32.6 (2.1)
	80	0.69 (0.11)	2.52 (0.07)	8.14 (0.62)	1.04 (0.01)	2.58 (0.22)	14.27	35.7 (7.8)
	125+	0.79 (0.23)	4.09 (0.38)	11.90 (0.33)	1.95 (0.04)	5.39 (0.81)	23.33	38.2 (1.9)
5-10	1	1.11 (0.19)	1.62 (0.19)	11.84 (0.04)	0.83 (0.03)	0.79 (0.02)	15.09	25.2 (4.0)
	15	0.89 (0.06)	0.80 (0.03)	9.62 (0.14)	0.91 (0.02)	0.87 (0.03)	12.19	25.6 (1.5)
	45	0.95 (0.02)	2.71 (0.27)	18.39 (0.29)	1.18 (0.04)	1.09 (0.05)	23.36	22.4 (1.9)
	80	0.81 (0.10)	1.39 (0.05)	10.28 (0.15)	0.55 (0.01)	0.80 (0.06)	13.01	33.9 (5.0)
	125+	0.67 (0.21)	1.76 (0.01)	8.74 (0.05)	0.96 (0.02)	0.82 (0.02)	12.28	27.4 (1.8)
10-15	1	1.08 (0.26)	1.32 (0.06)	11.82 (0.21)	0.81 (0.003)	0.73 (0.05)	14.67	25.7 (0.5)
	15	1.20 (0.11)	0.69 (0.02)	8.93 (0.64)	0.98 (0.04)	0.83 (0.01)	11.43	23.3 (3.7)
	45	0.82 (0.10)	2.04 (0.03)	22.87 (0.34)	1.84 (0.01)	0.95 (0.07)	27.70	20.3 (5.0)
	80	0.94 (0.02)	1.30 (0.05)	11.39 (0.26)	0.60 (0.03)	0.70 (0.05)	13.98	31.4 (3.4)
	125+	0.95 (0.04)	1.65 (0.04)	15.27 (0.20)	1.36 (0.35)	0.71 (0.07)	18.99	24.2 (1.7)
15-20	1	0.96 (0.30)	0.81 (0.01)	12.79 (0.47)	0.68 (0.03)	0.56 (0.03)	14.85	20.2 (3.0)
	15	1.16 (0.10)	0.63 (0.08)	8.82 (0.29)	2.21 (0.41)	2.81 (0.06)	14.47	23.2 (3.1)
	45	1.05	0.91 (0.03)	11.60 (0.15)	1.45 (0.04)	0.98 (0.04)	14.95	22.6
	80	0.98 (0.03)	0.76 (0.17)	12.62 (0.47)	1.25 (0.05)	2.32 (0.11)	16.95	29.9 (2.8)
	125+	0.92 (0.05)	1.91 (0.04)	18.96 (0.49)	1.46 (0.07)	2.94 (0.12)	25.28	24.2 (1.0)
20-35	1	0.96 (0.26)	1.16 (0.09)	22.50 (0.55)	1.33 (0.03)	0.90 (0.08)	25.89	27.0 (0.5)
	15	0.96 (0.10)	0.45 (0.03)	8.05 (0.14)	2.47 (0.03)	0.77 (0.01)	11.74	23.5 (3.3)
	45	1.45	0.50 (0.03)	7.15 (0.14)	1.33 (0.06)	0.70 (0.07)	9.68	21
	80	1.24 (0.04)	0.80 (0.02)	13.07 (0.05)	0.85 (0.05)	0.61 (0.06)	15.32	26.0 (0.4)
	125+	1.02 (0.09)	0.93 (0.05)	21.17 (0.10)	1.57 (0.01)	0.74 (0.04)	24.41	22.4 (1.3)
35-50	1	1.13 (0.02)	0.73 (0.05)	16.84 (1.1)	2.36 (0.16)	0.73 (0.06)	20.66	23.1 (0.0)
	15	1.03 (0.09)	0.36 (0.02)	3.38 (0.41)	1.63 (0.08)	2.30 (0.20)	7.68	21.6 (5.5)
	45	1.23	0.50 (0.03)	5.56 (0.08)	1.09 (0.02)	0.91 (0.03)	8.06	22.3
	80	1.39 (0.11)	0.56 (0.05)	12.47 (0.75)	1.56 (0.02)	2.13 (0.05)	16.72	24.3 (0.3)
	125+	1.69 (0.30)	0.52 (0.02)	15.85 (0.42)	2.04 (0.09)	2.70 (0.28)	21.11	22.3 (0.4)

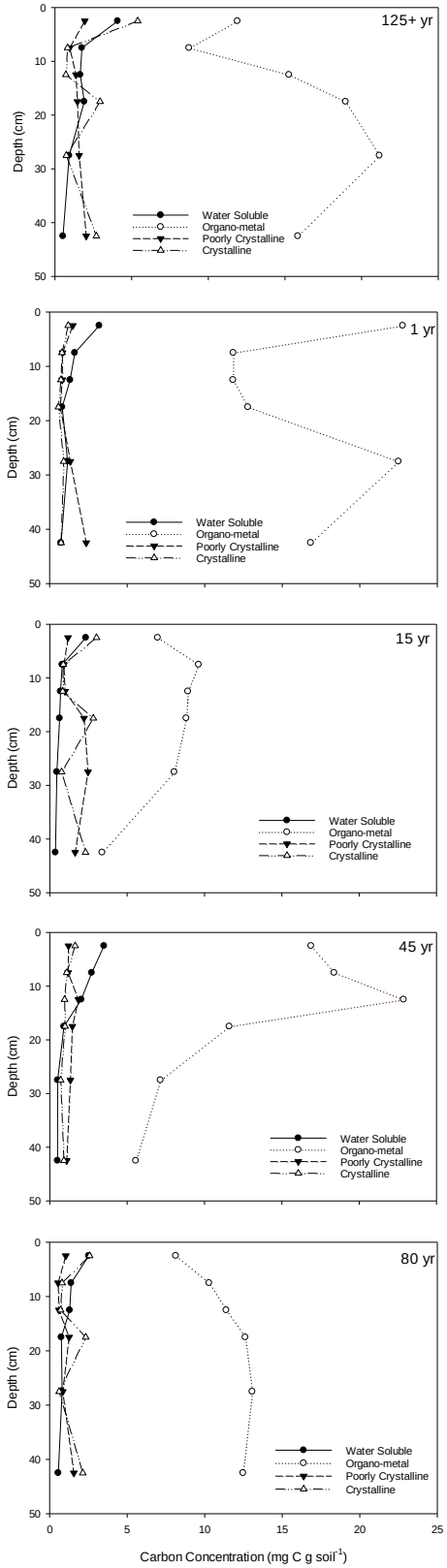

Figure 1: Changes in carbon concentration (mg C g soil^{-1}) for each organo-mineral pool through depth at each chronosequence site.

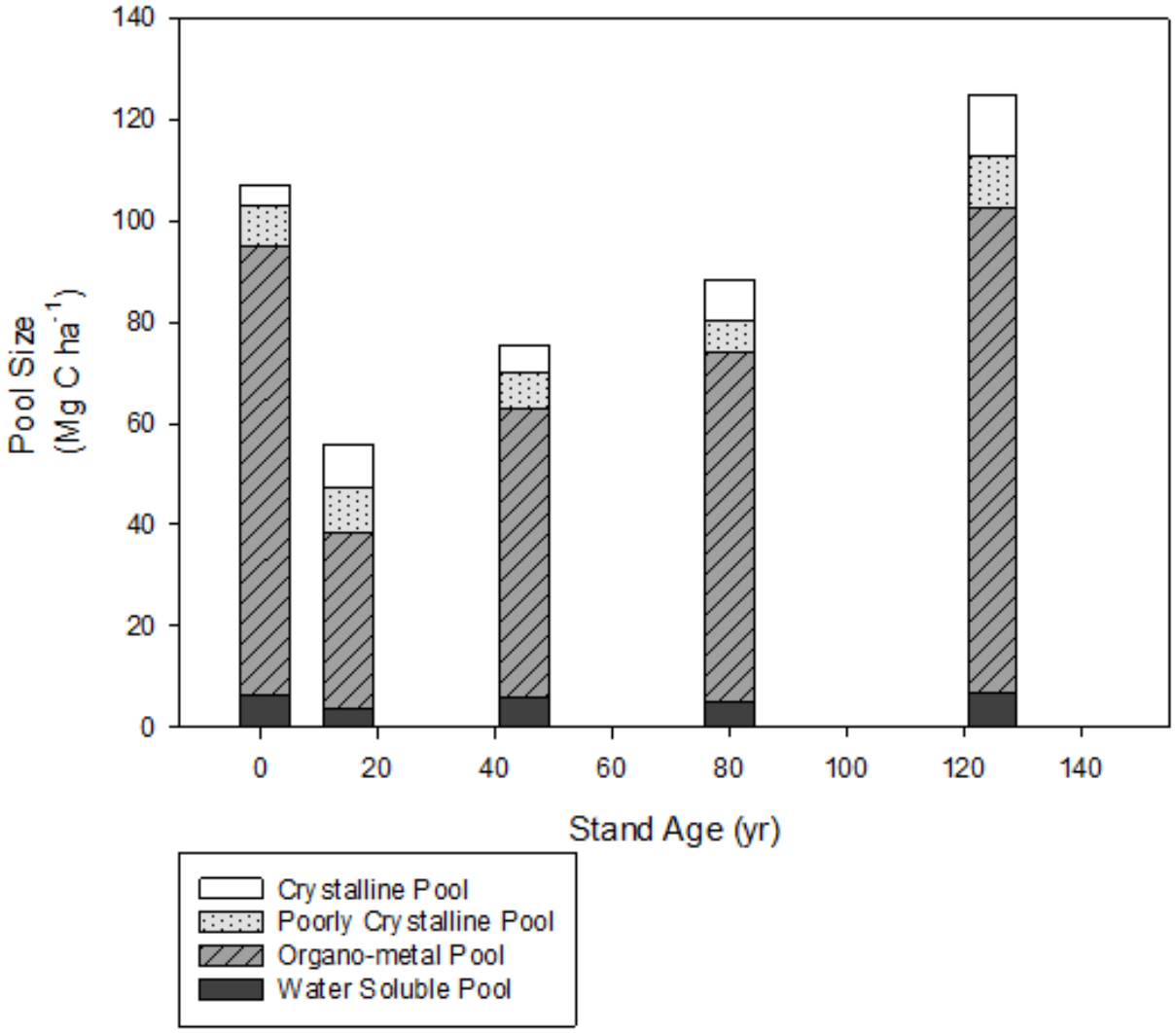

Figure 2: Total carbon storage in each mineral-associated pool across the chronosequence.

3.0. Changes in the chemical character of mineral-associated soil carbon following forest harvesting

Preamble

This research manuscript is intended for publication in a journal examining changes in C character following forest soil disturbance. I performed the lab work, as well as data and statistical analysis. This study was conceived by Dr. Lisa Kellman and Carrie-Ellen Gabriel. Dr. Amanda Diochon collected and archived soil samples used in this research, and also determined $\delta^{13}C$ values (see Diochon and Kellman, 2009).

Abstract

Although the mineral soil represents a globally important store of C, little is known about the mechanisms that are responsible for observed mineral soil C losses, and how the chemical character of soil C held as part of mineral associations changes through time and depth following forest harvesting disturbance. Chemical indicators are useful, as they can provide evidence of C sources and changes in cycling processes that may support field observations of reduced bulk soil C storage. Changes in signatures of stable isotopes of soil C ($\delta^{13}C$) and a reduced aromatic character of soil C through depth and time can provide an indication of increased alteration of a soil C pool. The objective of this study was to investigate whether changes in a common chemical indicator, the aromaticity of soil C, were observed in important mineral soil C pools through a forest harvest cycle. The aromatic character of Podzol soils of a harvested red spruce forest chronosequence in Nova Scotia, Canada (1 yr, 15 yr, 45 yr, and 80 yrs of age) along with an old growth reference stand (125+ yr), was examined through mineral soil depth (0-5, 5-10, 10-15, 15-20, 20-35, and 35-50 cm). Carbon extracted from the dominant organo-mineral C pool was analyzed for C concentration and aromaticity (specific UV absorbance: $SUVA_{254}$), and examined

alongside C-isotope ($\delta^{13}C$) patterns already established for these sites. Aromatic patterns through depth showed: i) a decreased aromaticity with lower C content across all sites within the deep mineral soil (20-50 cm), ii) minimum aromaticity at 15 and 45 yr sites at depth, and iii), strong regressions between SUVA and $\delta^{13}C$ for all samples and sites. Overall, the observed patterns provide further support for the hypothesis that at these chronosequence sites, increased decomposition following harvesting is responsible for mineral soil C losses. The findings of this study suggest that SUVA may provide a useful, low-cost tool for supporting observations of enhanced soil organic matter decomposition in similar temperate forest ecosystems.

3.1. Introduction

A significant component of the global carbon (C) cycle and the largest terrestrial pool of organic C, soils store more than three times as much C as the atmosphere or terrestrial vegetation (Schmidt et al., 2011). Within forest ecosystems, it is estimated that soils can hold more than two thirds of this C (Dixon et al., 1994), and the mineral soil can represent more than 50% of a forest C budget (Jobbágy & Jackson, 2000). Despite being a fundamental resource supporting terrestrial ecosystems, soil organic matter (SOM), and its main constituent of soil organic carbon (SOC), are vulnerable to changes in both climate and land use (Haddix et al., 2016).

The need to develop a better understanding of the processes controlling the turnover of soil C are gaining attention as areas of active investigation (Schmidt et al., 2011), with increased recognition that inaccessibility of OM to decomposition due to mineral associations, rather than chemical recalcitrance, may play a primary role in driving stabilization of SOC. The majority of past studies examining C cycling in harvested forests have focused on the upper portion of the soil profile (mainly the forest floor and top 10-20 cm of mineral soil), despite the fact that deeper mineral soil holds a significant proportion of total soil C (Jobbágy and Jackson, 2000). Justification

for this practice includes easier sampling of shallower soil as opposed to the labour-intensive process of excavating deep soil pits (Diochon et al., 2009), along with assumptions that the deeper mineral soil is stable and cycles on greater timescales than SOM held in upper soil horizons (Davidson and Janssens, 2006). This emphasis on sampling shallower soil depths has hindered the scientific development of understanding mineral soil C pool stability. However, because of the sheer size of the deeper soil C pool (typically storing 50% of total soil C below 20 cm depth (Jobbágy and Jackson, 2000)), mineral soil at depth needs to be included when examining potential C pool disturbances, including those resulting from forest harvesting activities (Zummo and Friedland, 2011).

Forest harvesting has occurred for centuries in eastern North America (Diochon et al., 2009) and continues as a standard management practice in many temperate forest systems. This practice generates a step change in environmental conditions resulting in physical disturbances, as well as changes in nutrient dynamics, soil chemistry and the thermal and moisture regime of soils. Recovery from soil nitrogen losses may lag behind that of soil C over harvesting timescales in temperate forest sites, suggesting long-term implications for soil fertility that may extend beyond a typical harvest cycle (Kellman et al., 2014). As well, clearcut harvesting has been shown to increase soil temperatures up to 1 meter depth in soils by 1-2 ^{o}C annually, and up to 4 ^{o}C during the growing season in comparison to intact forest sites (Kellman et al., 2015). These changes to the soil environment can increase SOM degradation rates by contributing to destabilization of mineral-associated SOM (Xu and Saiers, 2010; Diochon and Kellman, 2009), as well as increasing microbial and enzymatic activity and access to substrates (Sollins et al., 1996; Six et al., 2002). The carbon that is mobilized from soil systems can be lost in dissolved form as dissolved organic

carbon (DOC), or in gaseous form through respiration of carbon dioxide as SOM is decomposed (Eglin et al., 2010).

Recent studies have suggested that the vulnerability of soil C pools to changes in environmental conditions is greater than previously thought. A meta-analysis by Achat et al. (2015) has helped to establish that the size of the C pool in the mineral soil does change with intensive forest harvesting. Significant losses of SOM following forest harvesting have been observed in bulk soil (Zummo and Friedland, 2011; Diochon et al., 2009) as well as within the organo-mineral pool of disturbed forest soils in the decades following harvesting (Diochon and Kellman, 2009), a pool that has previously been considered stable. By improving our understanding of the vulnerability of soil C to destabilization in mineral soils, we can better predict how this C pool will respond to varying landuse and climate change scenarios (Fontaine et al., 2007).

Historically, it has been considered that OM persisted in soils because its chemical composition and structure made microbial decomposition difficult, thereby resulting in its long residence time (Schmidt et al., 2011; Kleber and Johnson, 2010; von Lützow et al., 2006). However, recent research has emphasized that factors controlling OM accessibility to microbes, rather than inherent chemical recalcitrance, are fundamentally responsible for the persistence of SOM (Lehmann and Kleber, 2015; Schmidt et al., 2011). This alters our previous understanding of SOM stability, and points to the need to develop a clearer understanding of mineral soil C susceptibility to loss, particularly in the deeper mineral soil where mineral stabilization of OM exerts a dominant control on microbial accessibility (Jackson et al., 2017). In shallower soils, the role of minerals in C stabilization can be less important because fresh litter and root inputs constantly replenish OM for biological activity, and there are fewer mineral associations.

In a typical, stable soil profile, a general shift from fresh to more altered OM occurs through depth, coincident with increased microbial processing (Sanderman et al., 2008). The transport of dissolved organic carbon (DOC) through depth in the mineral soil has been shown to be highly dynamic and complex in fine grained mineral soils, with continuous exchanges between the soil solution and SOM associated with mineral surfaces (Sanderman et al., 2008). The aromatic nature of SOM can provide some clues about the origins of this material in soils. Aromatic compounds, derived mainly from plant matter, including lignin (Adhikari and Yang, 2015), represent a SOM pool considered fairly resistant to decomposition (Kalbitz et al., 2003). Aromatic SOM may also be preferentially adsorbed to minerals, forming strong complexes with Al and Fe oxides in acid subsoils (Kaiser and Guggenberger, 2000; Kalbitz et al., 2000; Kaiser and Zech, 2000). Microbial communities in soils are proficient at decomposing and hence altering a wide range of OM substrates (Kallenbach et al., 2016), including following changes in environmental conditions (Biasi et al., 2005; Lehmann and Kleber, 2015; Schmidt et al., 2011). The aromatic nature of SOM can provide an indicator of relative changes in the degree of decomposition OM has undergone within the soil profile, with more highly altered SOM showing a decrease in aromatic content.

Specific UV absorbance (SUVA), measured at certain wavelengths (e.g. 254 nm; $SUVA_{254}$) is positively correlated with, and can be used as a low-cost and simple indicator of, the aromatic compounds in DOC (Weishaar et al., 2003). While SUVA has been applied in the context of studying DOC in freshwater and marine systems (Strid et al., 2016), it has not been widely used to examine SOM. In soils, mineral bound SOC can be mobilized (naturally or using chemical extractions), quantified, and characterized as dissolved organic carbon (DOC). Corrections need to be applied when analyzing DOC using SUVA in soil extractions, as iron has been found to influence measurements (Poulin et al., 2014; Doane and Horwath, 2010).

Analyses of stable isotopes of C provide an integrated measure of SOC biogeochemical processes, and have been widely used to provide insight into SOM dynamics (Ehleringer et al., 2000; Billings and Richter, 2006), including for studies examining disturbance-induced changes in SOC stores in forest ecosystems (Trumbore et al., 2000; Diochon and Kellman, 2008; Diochon et al., 2009; Zummo and Friedland, 2011). Typically, $\delta^{13}C$ values increase with depth in soil profiles, consistent with increased alteration of SOM (Ehleringer et al., 2000). The $\delta^{13}C$ enrichment depth trend has traditionally been explained by mixing and/or kinetic fractionation during SOM decomposition (Diochon and Kellman, 2008), whereby microbes preferentially respire ^{12}C, while ^{13}C accumulates in the residual SOM and becomes enriched relative to the initial substrate (Wynn et al., 2005). Combined trends in chemical indicators of DOC leaching, including SUVA and $\delta^{13}C$, through undisturbed soil profiles have shown a corresponding decrease in SUVA with increases in $\delta^{13}C$ through soil depth arising from mineral exchanges (Sanderman et al., 2008), illustrating the dynamic nature of exchanges between soil mineral surfaces and the soil solution.

Recent efforts to examine mineral-associated C pool stability following clearcut harvesting at sites in Nova Scotia, Canada, have identified the organo-mineral fraction as the largest and most dynamic fraction experiencing C loss following disturbance (Diochon and Kellman, 2009). These losses have been hypothesized to arise from increased decomposition due to harvesting disturbance based on changes in soil C storage and patterns of SOC- $\delta^{13}C$ (Diochon et al., 2009; Diochon and Kellman, 2008; 2009). Further investigation of this organo-mineral fraction at these sites (Chapter 2), has quantified the amount of C held by mineral associations in the water soluble, organo-metal complexed, poorly crystalline, and crystalline pools, and demonstrated that all pools are susceptible to some degree of destabilization in soils following forest harvesting. The water soluble pool represented a small pool, albeit one that is readily accessible, while poorly crystalline and

crystalline pools experienced minor loss following disturbance; however, it was the organo-metal complexed pool that represented the largest pool, and one that is most susceptible to significant C losses following harvesting (Chapter 2).

The objective of this research is to investigate whether SUVA provides a chemical indicator of increased decomposition following harvesting disturbance in mineral-associated SOM. This is investigated by examining relationships between C storage, $\delta^{13}C$, and SUVA within the dominant mineral-associated SOM pool through depth and time following forest harvesting disturbance. We expect that SUVA should show patterns consistent with increased alteration (decreasing SUVA through depth) as the C pool size decreases and $\delta^{13}C$ increases following harvesting if losses were incurred due to alteration arising from enhanced microbial decomposition. It is also expected that there would be an amplification of stable profile trends with a heightened degree of microbial processing.

3.2. Methods

3.2.1. Site description

This research was carried out in the Abrahams Lake region of the Liscomb Game Sanctuary, Nova Scotia, Canada (45 10°N 62 38°W). The area contains one of the Acadian Forest Region's last remaining virgin old growth red spruce forests (Diochon et al., 2009). Sites are located on soils from the Halifax series, which consists of sandy loam textured Orthic Humo-Ferric Podzols, chiefly derived from quartzite (Diochon and Kellman, 2008). Climatic conditions of the area include a mean annual air temperature of 5.8 °C, with January and July having mean temperatures of -5.8 °C and 16.9 °C, respectively. The area receives approximately 1300 mm of precipitation annually, and is located 185-200 m above sea level, with a rolling topography (<10°) (Diochon et al., 2009). The typical vegetation cover is red spruce (*Picea rubens* Sarg.) forests of

the Acadian Forest Region, which is typical of forests in the northern temperate zone (Mosseler et al., 2003).

Red spruce forests are of significant commercial importance to Nova Scotia, and intensive forest management has resulted in increased silvicultural activities within the province in recent decades (Taylor et al., 2007). Forest management, using selective cutting, began in the early 1900s (Diochon and Kellman, 2008), and harvesting via clearcutting with branches and foliage left on site began around 1940; following harvesting, there is no scarification, planting or fertilizing (Diochon et al., 2009). Rotations of approximately 60 years are currently used to manage the forest in the study area.

A chronosequence consisting of 5 sites (1yr, 15yr, 45yr, 80yr, and 125+yr) that represent succession of important stages of forest development (recent clearcut, stand initiation, stem exclusion, understory initiation, and intact, mature old growth, respectively) were established (Diochon and Kellman, 2008; Mosseler et al., 2003). To minimize between-site variability, sites are within 5 km of each other, with the same elevation, parent material, soil texture, as well as topography, so that the primary difference between sites is the time since harvesting (Diochon and Kellman, 2009). The last date of intervention of the 125+ year old growth stand is unknown, however trees within the stand are more than 200 years old (Mosseler et al., 2003); the other sites are naturally regenerating from first rotation clearcut harvesting (1-, 15-, and 45-year old sites) and partial harvest (80-year old site) (Diochon and Kellman, 2009). The 125+ year old growth stand is used to represent the undisturbed soil profile chemical state.

The Maritime provinces' have a long history of forest harvesting and clearing land for agricultural use, and so most older forests and previously unharvested (virgin) forests of the Acadian Forest Region have been eliminated, leaving only small, isolated stands of old growth

that were protected or inaccessible to harvesting (Mosseler et al., 2003). The lack of old growth reference stands therefore makes it difficult to infer harvesting effects on soil C stores (Diochon et al., 2009).

3.2.2. Sample collection and preparation

Samples were collected at a chronosequence established in 2005 (Diochon et al., 2009). Three soil pits measuring 71 cm x 71 cm x 50 cm deep were randomly determined and hand excavated in a 400 m^2 area representative of the stand at each site. The organic horizons were removed and sieved through a 6.25 mm sieve in the field. The mineral soil was excavated by depth, rather than horizon, using sampling depths of 0-5 cm, 5-10 cm, 10-15 cm, 15-20 cm, 20-35 cm, and 35-50 cm. After excavation, all soil was sieved to 12 mm and weighed in the field. Representative samples were brought back to the laboratory, oven dried to constant weight, sieved to 2 mm, and reweighed to determine the <2 mm fraction. This soil fraction was then homogenized by grinding the sample on a roller mill. Excess soil samples have been sieved to <2 mm and archived. Composite samples were used in triplicate for this study. Further details of sample collection and preparation can be found in Diochon et al. (2009).

3.2.3. Sequential soil extractions

Sequential chemical dissolutions were carried out on archived soil samples to selectively extract C from mineral pools of increasing crystallinity. These pools include water soluble minerals (extracted using deionized water (DI)); organo-metal complexes (extracted using 0.1 M Na- pyrophosphate); poorly crystalline minerals (extracted using 0.1 M hydroxylamine-HCl); and crystalline minerals (extracted using Na-dithionite and HCl) (USGS, 2013).

Briefly, triplicate 1 g sub-samples of each soil sample composite were added to separate 50 mL polypropylene centrifuge tubes, shaken with 30 mL of extractant for approximately 16 hours on a

wrist-action shaker, centrifuged at room temperature for 20 minutes at 7500 rpm, and the supernatant decanted. The residual solid sample underwent a wash stage where 20 mL of DI (pyrophosphate and hydroxylamine residues) or 0.05 M HCl (dithionite residue) was added, samples shaken for an additional 2 hours (1 hour for HCl), centrifuged, and decanted. Supernatants from the original extraction and wash stage were combined, filtered through a 0.45µm mixed cellulose ester membrane filter, stored in acid washed plastic Nalgene bottles, and refrigerated at ~4 °C until analysis. The residual solid samples were dried overnight at ~60 °C and weighed prior to the next stage of extraction.

3.2.4. UV-Vis Spectroscopy

The chemical character of the dissolved organic carbon was determined using ultraviolet-visible (UV-vis) spectrophotometry. Absorbance spectra of soil extract samples were determined using a dual-beam Genesys 10S UV-Vis spectrophotometer (Thermo Scientific) and 1 cm path length quartz cuvettes, with deionized water used as the blank.

Spectroscopic analysis of DOM can be affected because of iron interference (Poulin et al., 2014; Weishaar et al., 2003), and so absorbance values were corrected for absorption contributions of iron. Concentrations of iron in each selective dissolution soil extract were determined using flame atomic absorption spectroscopy (Perkin Elmer AAnalyte 300). The extinction coefficient for 254 nm (ε_{254}) was found in Poulin et al. (2014). Absorbance correction for Fe was calculated by

$$abs_{cor} = abs_{\lambda} - \left[\varepsilon_{\lambda,Fe-DOM} \times [Fe]\right]$$

where abs_{cor} is the corrected absorbance, abs_{λ} is the measured absorbance, $\varepsilon_{\lambda,\text{ Fe-DOM}}$ is the Fe extinction coefficient (L mg^{-1} cm^{-1}) and $[Fe]$ is the concentration of iron in the sample (mg L^{-1}).

$SUVA_{254}$ values were calculated by dividing the Fe corrected absorbance at 254 nm by the DOC concentration, and is reported in units of L mgC^{-1} m^{-1} as a measure of aromaticity (Weishaar et al., 2003).

$$SUVA_{254} = \frac{abs_{cor,254}\ (m^{-1})}{[DOC](mg\ L^{-1})}$$

3.2.5. Calculations and analysis

Changes in the chemical character of organo-metal extracts for all soil depths and sites were explored for changes in aromaticity (SUVA). Because clear patterns of C loss were seen in the deeper mineral soil (Chapter 2), we expected to see greater changes in the chemical character of C in the deeper (20-50 cm) mineral soil than the shallow (0-20 cm) mineral soil following disturbance. Therefore, upper (shallow) and lower (deep) mineral soil relationships in chemical character were observed for all sites by examining relationships between SUVA and C storage. The chemical character of SOC through depth and across the individual chronosequence soils is documented for changes in SUVA. Relationships between SUVA and $\delta^{13}C$ are explored to determine if a pattern of increased chemical alteration that coincides with enrichment in ^{13}C is evident.

The extracted solutions were diluted to appropriate concentrations, and the dilutions were analyzed on a Shimadzu TOC-L Total Organic Carbon Analyzer for determination of C concentration. Total mineral soil C storage was calculated using bulk density values from Diochon et al. (2009) (Table 1). Values of $\delta^{13}C$ for the organo-mineral fraction were from Diochon and Kellman (2009).

All analyses were completed using SigmaPlot 13.0 (Systat Software Inc., San Jose, CA, USA). Significance was assessed at α = 0.05.

3.3. Results

3.3.1. Mineral-associated carbon pools

The pool sizes of the group of mineral-associated C fractions (water soluble, organo-metal, poorly crystalline and crystalline) for the top 50 cm of mineral soil across the chronosequence shows that the organo-metal pool dominates as the largest of all fractions at all stand ages, with this pool experiencing substantial losses following harvesting (Fig. 1). Storage is highest in this organo-metal pool at the old growth 125+ yr site (96 Mg C ha^{-1}) and lowest at the 15-year-old site (35 Mg C ha^{-1}) (Fig. 1.). Changes in the poorly crystalline and crystalline pools also demonstrate losses, as shown in Figure 1, however these pools are minimal in size compared to organo-metal complexed pool losses. Because it represents the largest pool and the one most susceptible to change over the timescales of a forest harvest cycle, the subsequent chemical character analyses for these soils are examined for the organo-metal pool only.

3.3.2. Carbon chemical character (SUVA)

The chemical character of SOC measured in this study, aromaticity, was examined in relation to mineral-associated C quantity (Fig. 2). Measures of Fe-corrected $SUVA_{254}$ plotted against C storage within the organo-metal complexed pool show that no significant patterns are evident in the shallow mineral soil (P=0.193; Fig. 2a); within the deeper mineral soil (Fig. 2b), a significant positive relationship was found between SUVA and C storage (P<0.001). The variability is high, but also represents a broad group of sites that represent different times since disturbance (1 yr, 15 yr, 45 yr, 80 yr), or no history of disturbance (125+).

At individual sites, a strong relationship between aromaticity (SUVA) and depth was observed across the chronosequence. SUVA decreased through depth for all sites in the organo-metal pool (Fig. 3). At the 125+yr reference site, SUVA ranges from approximately 5.5 L mgC^{-1}

m^{-1} in the shallow mineral soil to 3.8 L mgC^{-1} m^{-1} in the deep soil. At the 1-yr site, SUVA ranges from 6.2 L mgC^{-1} m^{-1} in the shallow soil to 4.0 L mgC^{-1} m^{-1} in the deep soil. The pattern of decreasing aromaticity with depth is enhanced at the 15- and 45-yr site relative to the reference site, with SUVA ranging from 6.0 L mgC^{-1} m^{-1} (shallow) to 2.7 L mgC^{-1} m^{-1} (deep) and 5.6 L mgC^{-1} m^{-1} (shallow) to 3.2 L mgC^{-1} m^{-1} (deep) respectively. At the 80-yr site, SUVA decreases from 6.0 L mgC^{-1} m^{-1} at the top of the mineral soil to 4.5 L mgC^{-1} m^{-1} in the deep soil. The linear trend describing the SUVA-depth relationship changed systematically over time following harvesting (Fig. 3), with all sites showing an increase in the predicted range of measured SUVA through the profile compared to the 125+ yr reference site (this range is evident in the changing slope of the relationship). The greatest changes were observed at the 15 yr site. While gradual recovery of the SUVA-depth relationship was documented after 15 yrs, a full recovery to that documented for the 125+ yr site was not observed at the 80 yr site.

3.3.3. Relationships between SUVA and $\delta^{13}C$

Relationships between SUVA and $\delta^{13}C$ for the organo-metal complexed pool shows a significant relationship ($P<0.001$), demonstrating that across the group of chronosequence sites, as SUVA (aromaticity) decreases, SOC becomes enriched in $\delta^{13}C$ (Fig. 4). To examine if this pattern holds across the chronosequence sites, this relationship is further broken down by site (Fig. 5). At individual sites strong regressions were observed between SUVA and $\delta^{13}C$. The linear relationship for the reference 125+ yr site reflected the tighter range of SUVA- $\delta^{13}C$ values compared to the disturbed sites. Across the disturbed sites, this steady state trend (Fig. 5) of enrichment in $\delta^{13}C$ with decreasing aromaticity (SUVA) changes significantly ($P<0.05$) through time since harvest before returning to values similar to the reference site at 80 yrs.

3.4. Discussion

3.4.1. Changes in the chemical character of SOC following harvesting

With the traditional view of SOM stability through chemical recalcitrance being challenged and replaced with the concept that accessibility to decomposition controls the persistence of SOM (Schmidt et al., 2011; Lehmann and Kleber, 2015), there is a renewed need to both determine the susceptibility of soil C to environmental changes, and to identify mechanisms driving soil C loss in the mineral soil. While SOC can be protected from microbial access and stabilized through mineral associations (von Lützow et al., 2006), changing soil conditions as a consequence of forest harvesting can destabilize this large C pool, increasing microbial access to organic substrates (Rasmussen et al., 2006; Keiluweit et al., 2015; Conant et al., 2011). This has the potential to increase SOM losses, including through decomposition. While measurement of soil C storage provides one tool for establishing disturbance driven changes in soil C (Grand and Lavkulich, 2012; Clarke et al., 2015), confidence in data documenting losses can be increased if there are mechanistic observations that further support them. To date, stable isotopes have provided one option for supporting field observations (Wynn et al., 2005).

The size of the organo-metal pool compared to the water soluble, poorly crystalline, and crystalline pools, shows that at the sites investigated in this study, association with organo-metal complexes represents an important stabilization mechanism within the mineral SOM pool (Fig. 1). Losses observed from this pool also suggest that with soil surface disturbances (such as forest harvesting), C previously thought to be stable in the mineral soil can become destabilized and mobilized. As forest harvesting activities dominate many forest landscapes, the cumulative effects over large areas may have serious implications for C cycling and greenhouse gas emissions (Dean et al., 2017).

In this study we test whether the chemical character of SOC undergoes distinct changes following disturbance, as evidenced through changes in the aromatic nature of mineral-bound SOC. Through examination of SUVA, we test whether it has the potential to provide a simple and cost-effective indicator of qualitative changes arising from mineral SOC destabilization. While previous studies have used SUVA to demonstrate increased DOC exchange with mineral-bound C in undisturbed soil profiles (Sanderman et al., 2008) and the nature of DOC transported in aquatic systems (Helms et al., 2008; Inamdar et al., 2011), this study explores its use as an indicator of increased alteration following disturbance in mineral-bound C over forest harvest timescales.

The patterns of C aromaticity in DOC extracted from the organo-metal complexed pool (as indicated by $SUVA_{254}$) show that links between C storage and aromaticity vary between the shallow and deep soil profile (Fig. 2). No relationship was found between aromaticity (SUVA) and C storage in the shallow soil (0-20 cm) at these sites, while a significant relationship ($P<0.001$) was found between SUVA and C storage in the deeper soil (20-50 cm). At individual sites, these patterns suggest that as the SOC pool size is reduced following harvesting, the chemical character of SOC held within the dominant mineral-associated C pool changes, exhibiting a less aromatic character. The lack of a relationship between these variables within the shallow soil would suggest that there is a lower sensitivity of C in the upper mineral soil profile to disturbance-driven destabilization of mineral associated SOC over the harvesting timescales considered here. It is possible that net changes in the chemical character of this pool are either quantitatively unimportant, or are obscured by shorter-term dynamics associated with changes in soil surface vegetation; deeper soils likely filter out some of the shorter term variability in the C dynamics. Observation of patterns through depth across individual sites show changes that are best described by a linear model (Fig. 3). Patterns of decreasing aromaticity are expected with depth in a stable

soil profile as a function of increased processing of OM (Sanderman et al., 2008). In a profile where disturbance may have destabilized mineral-associated C pools, we would expect the changes to be enhanced if there is greater alteration of this C pool. The pattern observed across these sites (Fig. 3) is consistent with increased alteration of this mineral-associated C pool in the decades following disturbance, with the greatest profile differences through soil depth observed at the 15 and 45 yr sites.

3.4.2. Links between SUVA and $\delta^{13}C$

A number of hypotheses have been used to explain the soil profile trends of C isotopic enrichment with depth, including mixing of above- and below-ground biomass sources, and kinetic fractionation (Ehleringer et al., 2000; Wynn et al., 2005). Previous investigation of the soils studied here determined that mixing was a poor fit and therefore likely not the dominant process for observed enrichment trends, which instead were better explained by kinetic fractionation (Diochon and Kellman, 2008). The kinetic fractionation enrichment pattern provided evidence for observed soil C losses arising from increased decomposition of this C pool. These trends in $\delta^{13}C$ reported at these sites (Diochon and Kellman, 2009) show strong regressions with the aromaticity measurements conducted in this study (SUVA) for all depths and sites (Fig. 4); when $\delta^{13}C$ increases, aromaticity decreases.

At the 125+ yr reference site, the depth-dependent relationships between SUVA and $\delta^{13}C$ are consistent with shifts in SOM properties with depth observed in stable soil profiles that have been attributed to a shift from fresh plant material (high SUVA, low $\delta^{13}C$) to highly altered OM (low SUVA, high $\delta^{13}C$) (Sanderman et al., 2008; Wynn et al., 2005). In comparison to the reference 125+ yr site, changes in SUVA became more pronounced with depth 15 and 45 years following

disturbance (Fig. 5), with C in the deeper soil exhibiting a less aromatic character (lower SUVA) compared to the C at the old growth site at the same depth.

The $\delta^{13}C$ patterns linked with SUVA measurements described here provide further support for the hypothesis that decomposition is likely the dominant mechanism driving C losses following forest harvesting at these chronosequence sites. This may be a full or partial consequence of increased soil temperatures experienced following the removal of the canopy cover. As such, sustainable forest management practices should attempt to maintain the protective micro-environment (temperature and moisture conditions) created by structural attributes (including a layered forest canopy) characteristic of natural old growth forests (Mosseler et al., 2003).

The SUVA chemical character analyses also help to bolster trends in C storage by providing a mechanism for verifying that changes in the organo-mineral pool are not simply a function of natural variability in soil C storage between locations, but rather indicative of a shift in the dynamics that control C storage. SUVA provides an additional tool that is more cost effective than stable isotope analyses for examining qualitative changes arising from disturbance that complement efforts to document soil C storage.

3.5. Conclusions

This study has documented extensive losses from mineral-associated soil C pools under temperate forests that have undergone clearcut harvesting, with chemical character indicators (SUVA and $\delta^{13}C$) supporting the explanation that C losses at these sites are the result of increased microbial decomposition. These findings also highlight the importance of incorporating the deeper mineral soil (>20 cm) in future investigations of C dynamics at forested sites, and point to the use of SUVA as an inexpensive tool for supporting observations of enhanced SOM degradation in

similar forest ecosystems. Examining soils that differ only in the time since harvest allows for an investigation into the effects of forest management and the resulting response of C character, acting as a model system that could improve our ability to predict the effects of management and climate change in forest ecosystems.

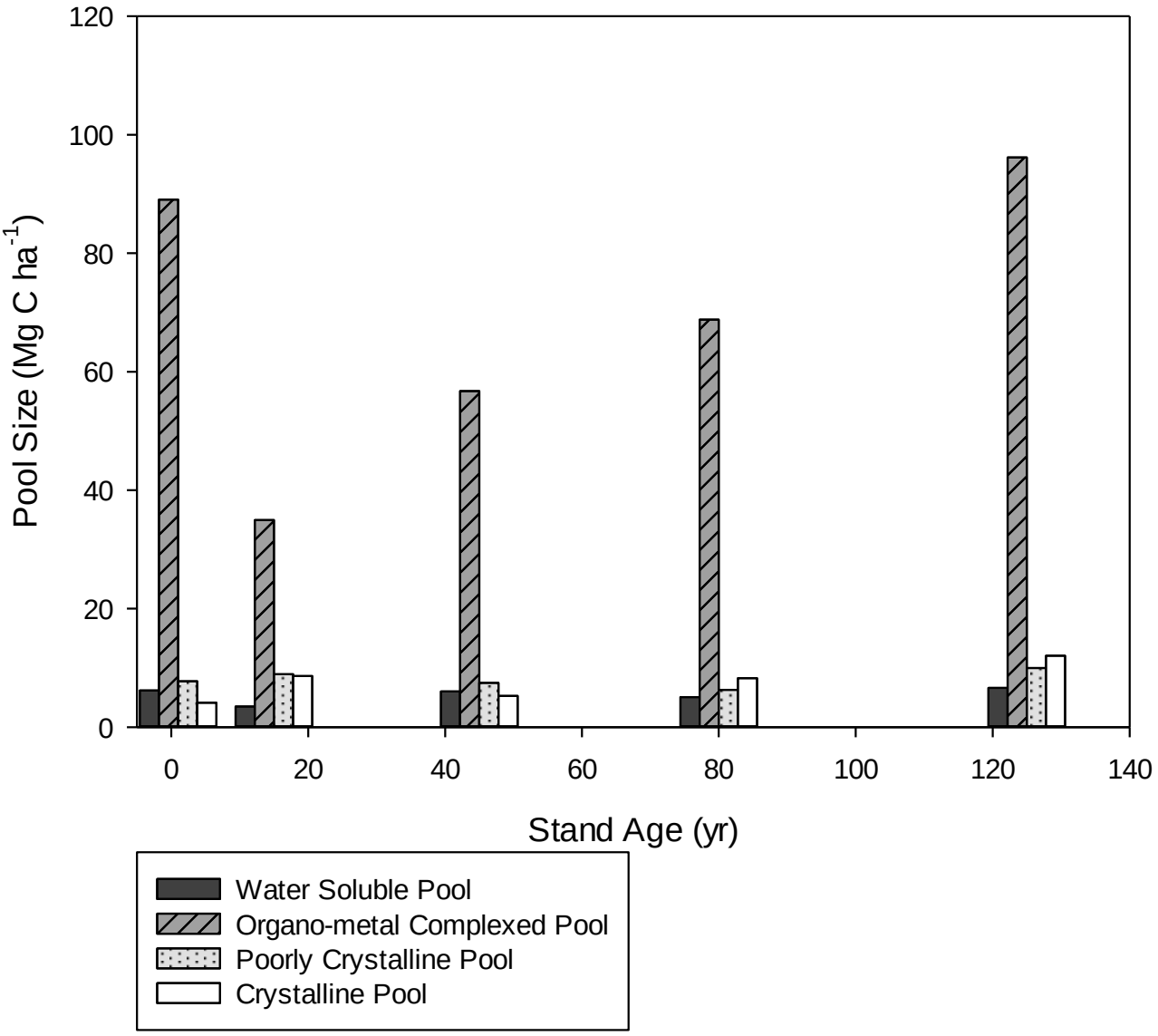

Figure 1: Carbon held in mineral-associated pools through the top 50 cm of mineral soil at a red spruce forest chronosequence ranging in time since harvest (1-, 15-, 45-, 80-yrs, and 125+ yr reference stand).

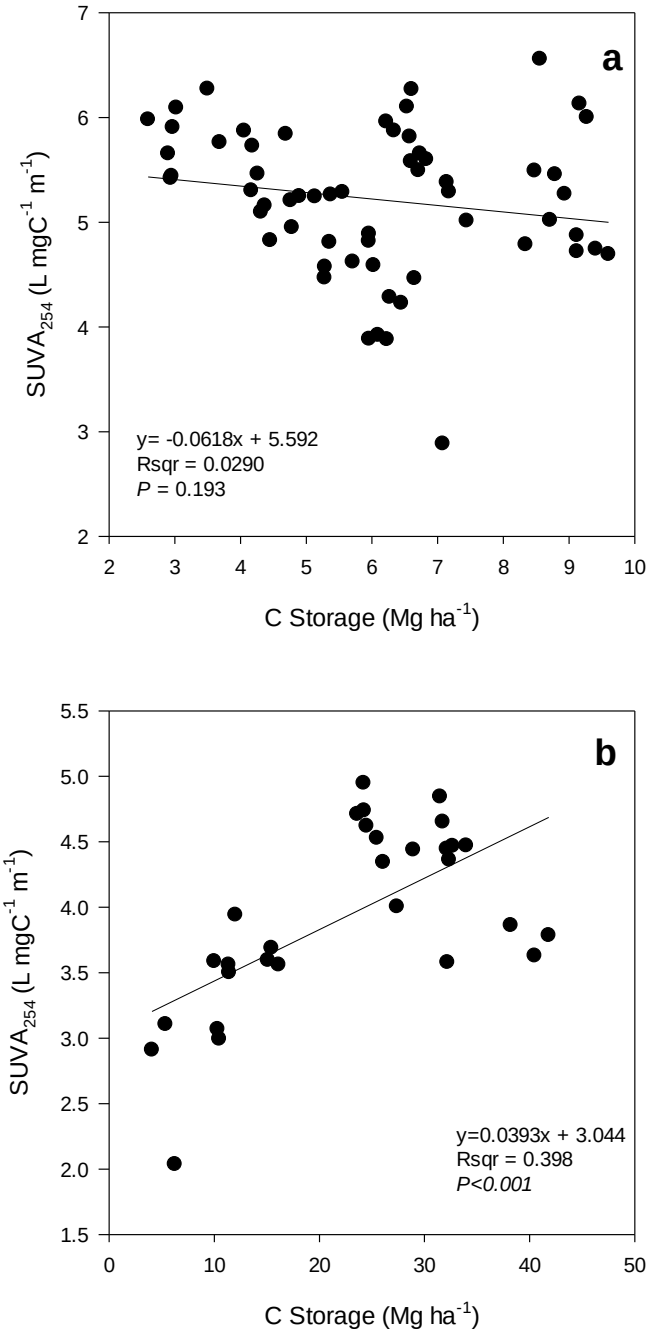

Figure 2: SUVA vs C storage in the organo-metal complexed pool for **(a)** shallow (0-20 cm) and **(b)** deep (20-50 cm) depth intervals.

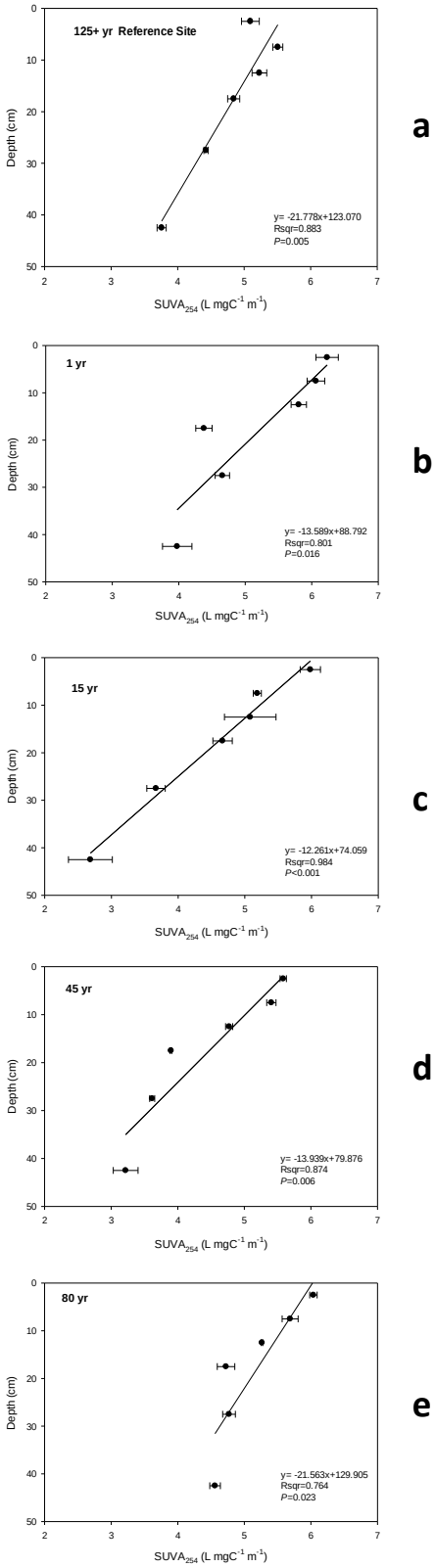

Figure 3: SUVA vs depth for each site in the organo-metal complexed pool. Panels represent the **(a)** 125+yrs, **(b)** 1 yr, **(c)** 15 yrs, **(d)** 45 yrs, and **(e)** 80 yrs. Error bars represent 1 SE.

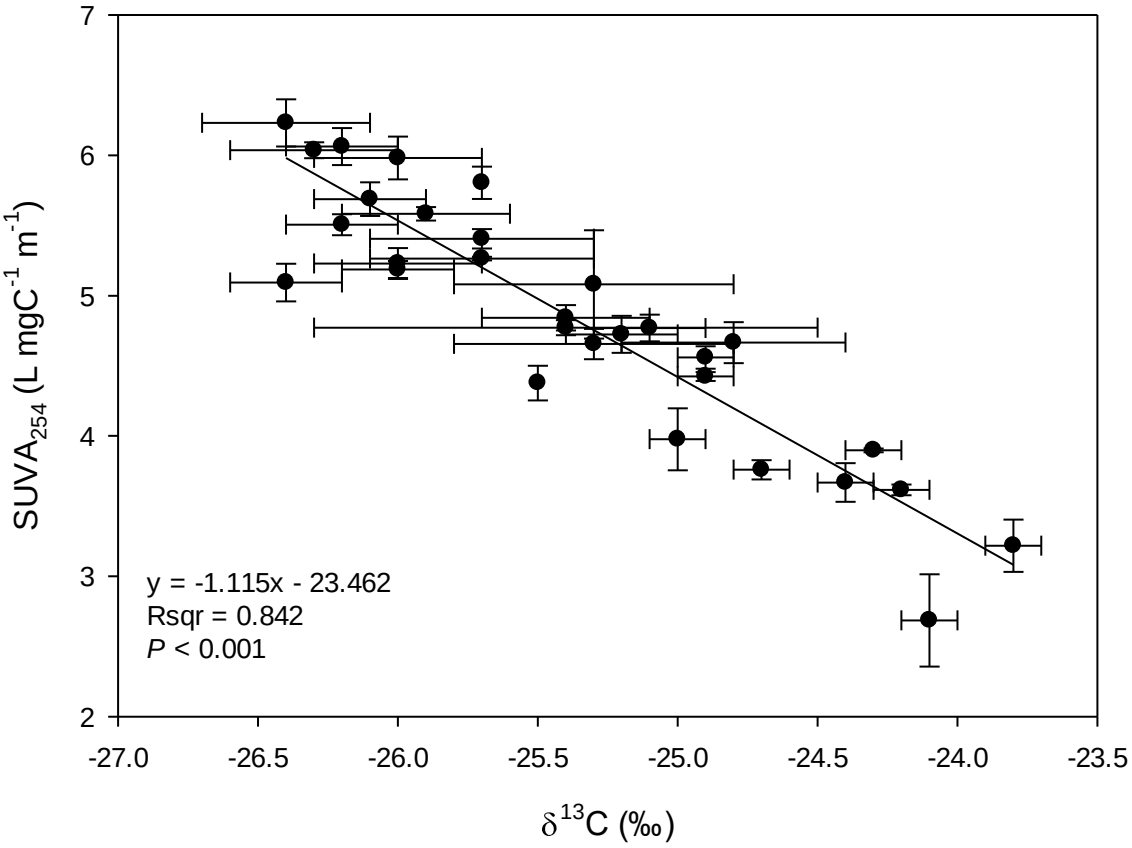

Figure 4: Carbon chemical character indicators for the top 50 cm of mineral soil in the organo-metal complexed pool. Error bars represent 1 SE.

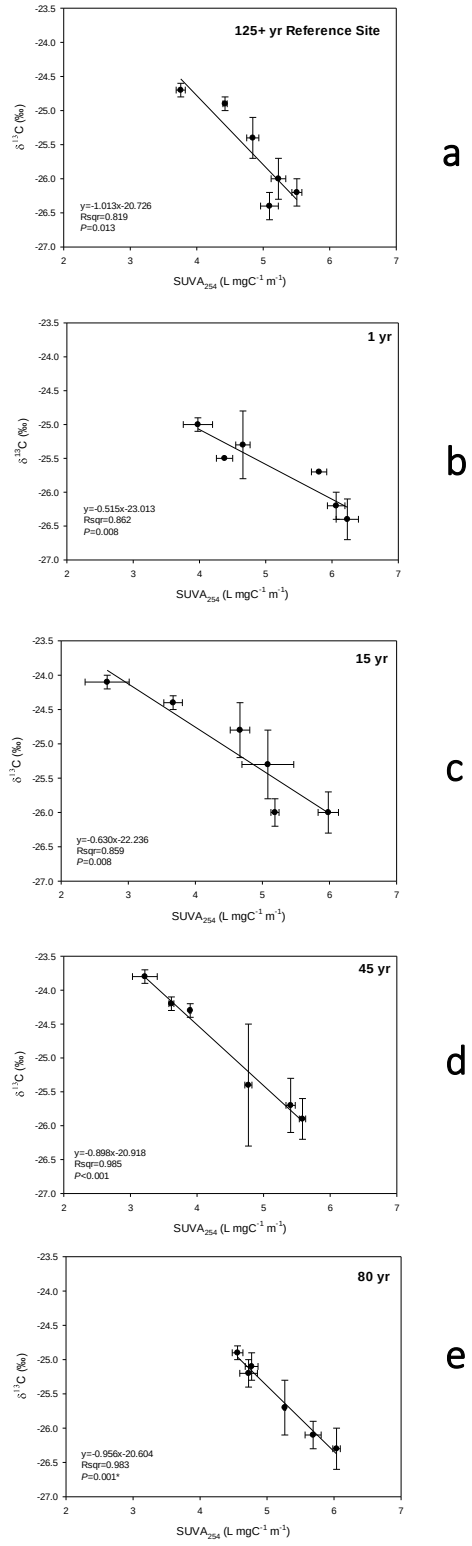

Figure 5: Overall look at SUVA vs $\delta^{13}C$ for the organo-metal complexed pool at each site. Panels represent the **(a)** 125+yrs, **(b)** 1 yr, **(c)** 15 yrs, **(d)** 45 yrs, and **(e)** 80 yrs. Error bars represent 1 SE. *Normality test failed.

4.0. Conclusions and Future Work

The aim of this research was to quantify the amount of, and determine the chemical character of, C held within mineral-associated pools of increasing crystallinity following forest harvesting. This thesis has shown that the effects of harvesting on the underlying mineral soil involve destabilization of a pool that has generally been assumed to be stable. While some loss was observed in the water soluble, poorly crystalline, and crystalline pools, no clear patterns were evident, and absolute losses from these pools were relatively minimal in comparison to the sheer size of the organo-metal complexed pool. Further examination of the organo-mineral pool has shown that C held in organo-metal complexes is the dominant pool at all sites investigated here, and that this pool is most susceptible to destabilization. Specifically, clear temporal trends of C loss following disturbance from the organo-metal complexed pool were observed in the deeper mineral soil (20-50 cm) at the sites investigated here. We infer that changes in soil environmental conditions associated with forest harvesting activities have increased susceptibility to SOC destabilization. Based on shifts in the chemical character (aromaticity) of the C held in the organo-metal complexed pool, the main mechanism of C loss for these disturbed soils points to increased microbial processing. These results highlight the need for better datasets that incorporate measurements deeper into the soil profile and that characterize different mineral-associated soil C pools.

Chemical analyses of SOC have been shown to be useful in providing insight into ecosystem processes and the biogeochemical mechanisms governing SOM dynamics (Billings and Richter, 2006). Environmental processes related to disturbance can accelerate decomposition by liberating C from protective mineral phases (Keiluweit et al., 2015). The coupling of SUVA and $\delta^{13}C$ measurements provides a potentially new approach to determine the degree of microbial

processing of SOC. While aromatic compounds in soils have historically been considered recalcitrant, they can ultimately be broken down and decomposed by a broad suite of organisms (Grandy and Neff, 2008), and can even turn over more quickly than bulk SOM (Schmidt et al., 2011). Patterns of $\delta^{13}C$ and aromaticity (SUVA) established in a stable soil profile (Sanderman et al., 2008) provide a baseline against which we can compare disturbed soils, potentially providing an indication of increased microbial alteration.

It has generally been found that there is a reduction in total amounts of SOC with increasing temperature (Kirschbaum, 2000). As temperature increases, soil respiration also increases, and so while additional C may be added to soils from increased plant growth, a large portion is expected to be returned to the atmosphere as CO_2 (Schlesinger and Andrews, 2000). Changes in the size of soil carbon reservoirs can significantly affect atmospheric concentrations of CO_2, and so increased rates of CO_2 production by soils can provide a positive feedback to global warming (Raich and Potter, 1995). Soil C storage was found to be lowest overall in the 15-yr stand, with lowest C concentrations in the deeper mineral soil (20-50 cm) at the 45-yr site.

Despite re-accrual of C in these soils occurring after about 30 years (Diochon et al., 2009), they do not completely recover to pre-harvest (intact forest) levels until around 100 years. These sites are currently managed on rotations of approximately 60 years. In order to sustainably manage forests for its resources, it is recommended that harvest rotation times be lengthened to allow for SOM pools to regenerate to ranges observed in reference systems, and ensure that C lost to the atmosphere is returned to the soils. Also, because intensive harvests have been shown to negatively impact SOC stocks (Achat et al., 2015), it is recommended that clearcutting be reduced in favour of less-intensive harvesting practices, such as selective cutting.

Sustainable management of forests (and the many resources they provide) in the short term and for generations to come is crucial from both a global environmental perspective and for the well-being of Canada's economy. Efforts that aim to reduce atmospheric CO_2 through C sequestration in soils offer opportunities for climate regulation, if the soil systems are managed responsibly (Harden et al., 2017). Scientific knowledge regarding C storage in Atlantic Canadian forest soils will contribute to negotiating landuse policies that minimize disruptions to natural system processes, sustain the forest industry for years to come, as well as support an improved understanding of the role of forests in climate change. By looking at how human activities alter the biogeochemical cycling of C in these disturbed systems, we will be better prepared to make predictions and employ mitigation strategies to protect stores of mineral soil C.

Because changes in SOC vary both spatially and temporally and are influenced by an assortment of factors (including climate, land use, and vegetation, among many others), it is becoming increasingly clear that the mechanisms underlying destabilization of SOC require further investigation. Understanding factors associated with both the stabilization and destabilization of SOC are critical to developing a prognostic view of soil C dynamics that can inform policy and be implemented in practice, as it is these mechanisms help determine SOC susceptibility to loss as CO_2 emissions or opportunities for sequestration (Harden et al., 2017).

Currently, there are a multitude of techniques used for partitioning SOM into operationally separate fractions, yet there is no clear, standard procedure that suitably describes functional pools. While the continuum of carbon pools may never be clearly organized into functionally discrete fractions, continued efforts to untangle the interwoven factors influencing SOC stability could better inform models used to predict soil responses to disturbance and climate change. The results

presented here are aimed at systematically isolating and quantifying stable soil C fractions via different mineral interactions.

The dissolution procedure used here is aimed at separating out pools within the organo-mineral fraction, and therefore does not consider non-mineral-associated OM. The concentration of C in the unextractable residual fraction (the C remaining in the pellet following the four extraction stages) was not measured in this research, but could be an important consideration in future studies (Heckman et al. (2018) found that this residual C accounted for a sizeable fraction of total C).

Potential sources of error can arise during interpretation of the pools extracted. While the extractants used target specific mineral associations, the specificity for dissolution has been challenged, with potential overlap in the interpretation of extracted minerals. Because of the sequential nature of the selective dissolution methodology used for this research, if an issue arises during subsequent stages, the process (which is also time consuming), must be started again from the beginning (Heckman et al., 2018). However, the combination and sequential application of traditionally separate protocols, along with the use of C free extractants, aims to provide an integrated fractionation procedure that better quantifies soil organo-mineral associations. Therefore, this method acts as a useful and promising tool for comparing distinct organo-mineral associations within SOM.

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Appendices

A. Carbon, iron, and spectral raw data

Table A.2. Carbon, iron (drift corrected), and spectral data for the water soluble pool. OG, CC, 15N, 45yr, and 80yr represent the 125+, 1-, 15-, 45-, and 80-yr sites, respectively.

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})	Fe Corrected SUVA (L mgC^{-1} m^{-1})	Fe Corrected S_R
OG 0-5cm 1.	4.601	1.817	1.460	1.322	0.652
OG 0-5cm 2.	3.357	1.326	1.204	1.757	0.933
OG 0-5cm 3.	4.305	1.701	1.189	1.329	0.646
OG 5-10cm 1.	1.776	0.595	4.966	2.042	0.811
OG 5-10cm 2.	1.769	0.593	5.959	2.266	0.886
OG 5-10cm 3.	1.736	0.581	3.585	2.531	0.823
OG 10-15cm 1.	1.598	0.759	5.373	1.626	0.580
OG 10-15cm 2.	1.617	0.768	5.554	1.624	0.633
OG 10-15cm 3.	1.729	0.821	5.053	1.491	0.485
OG 15-20cm 1.	1.862	0.857	2.830	0.939	0.352
OG 15-20cm 2.	1.893	0.871	2.827	0.931	0.437
OG 15-20cm 3.	1.988	0.914	3.024	0.922	0.608
OG 20-35cm 1.	0.846	1.295	1.084	1.250	1.168
OG 20-35cm 2.	0.907	1.387	1.201	1.036	0.646
OG 20-35cm 3.	1.028	1.573	1.455	0.945	0.346
OG 35-50cm 1.	0.525	1.331	0.203	1.061	1.599
OG 35-50cm 2.	0.493	1.250	0.020	0.868	1.531
OG 35-50cm 3.	0.547	1.386	0.067	1.056	1.450
CC 0-5cm 1.	3.051	1.205	4.013	3.725	0.745
CC 0-5cm 2.	3.000	1.185	3.312	3.741	0.799
CC 0-5cm 3.	3.545	1.400	3.807	3.155	0.723
CC 5-10cm 1.	1.238	0.687	3.256	3.177	0.717
CC 5-10cm 2.	1.849	1.026	4.301	2.137	0.700
CC 5-10cm 3.	1.783	0.990	4.255	2.301	0.723
CC 10-15cm 1.	1.431	0.773	2.874	1.840	0.629
CC 10-15cm 2.	1.239	0.669	2.492	2.252	0.772
CC 10-15cm 3.	1.279	0.691	2.119	2.345	0.783
CC 15-20cm 1.	0.789	0.379	1.070	2.030	0.846
CC 15-20cm 2.	0.833	0.400	0.959	1.834	0.807
CC 15-20cm 3.	0.804	0.386	0.790	1.783	0.860
CC 20-35cm 1.	1.257	1.810	1.603	1.026	0.426
CC 20-35cm 2.	1.244	1.791	1.710	1.048	0.526
CC 20-35cm 3.	0.973	1.402	1.421	1.309	0.917
CC 35-50cm 1.	0.803	1.361	0.489	1.074	0.776
CC 35-50cm 2.	0.646	1.095	0.383	1.480	1.166
CC 35-50cm 3.	0.745	1.263	0.171	1.066	1.235

Table A.1. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})	Fe Corrected SUVA (L mgC^{-1} m^{-1})	Fe Corrected S_R
15N 0-5cm 1.	2.432	1.179	3.116	1.531	0.878
15N 0-5cm 2.	2.340	1.135	3.523	1.542	0.858
15N 0-5cm 3.	2.206	1.070	3.466	1.621	0.871
15N 5-10cm 1.	0.815	0.363	1.097	2.025	0.863
15N 5-10cm 2.	0.831	0.370	0.913	1.954	0.840
15N 5-10cm 3.	0.744	0.331	0.564	1.696	0.804
15N 10-15cm 1.	0.728	0.437	0.333	1.171	0.818
15N 10-15cm 2.	0.655	0.393	0.307	1.279	0.984
15N 10-15cm 3.	0.700	0.420	0.471	1.537	0.893
15N 15-20cm 1.	0.779	0.452	0.346	0.976	0.890
15N 15-20cm 2.	0.617	0.358	0.394	1.067	1.368
15N 15-20cm 3.	0.501	0.290	0.235	0.988	1.621
15N 20-35cm 1.	0.470	0.676	0.446	0.637	0.653
15N 20-35cm 2.	0.403	0.581	0.447	0.778	0.780
15N 20-35cm 3.	0.483	0.696	0.468	0.623	n.d.
15N 35-50cm 1.	0.321	0.495	0.116	0.720	1.612
15N 35-50cm 2.	0.376	0.582	0.207	0.652	3.921
15N 35-50cm 3.	0.394	0.609	0.288	0.740	3.504
45yr 0-5cm 1.	3.872	1.549	5.960	2.026	0.837
45yr 0-5cm 2.	3.243	1.297	4.416	2.207	0.883
45yr 0-5cm 3.	3.387	1.355	5.277	2.253	0.893
45yr 5-10cm 1.	2.166	1.029	5.660	2.318	1.265
45yr 5-10cm 2.	2.977	1.414	5.455	1.883	0.649
45yr 5-10cm 3.	2.985	1.418	4.580	1.881	0.660
45yr 10-15cm 1.	1.984	0.813	3.423	1.117	0.245
45yr 10-15cm 2.	2.075	0.851	3.533	1.085	0.209
45yr 10-15cm 3.	2.045	0.839	3.405	1.086	0.250
45yr 15-20cm 1.	0.851	0.447	0.559	0.845	0.516
45yr 15-20cm 2.	0.962	0.505	0.187	0.823	0.737
45yr 15-20cm 3.	0.928	0.487	0.260	0.826	0.740
45yr 20-35cm 1.	0.562	1.223	0.346	0.643	0.803
45yr 20-35cm 2.	0.489	1.064	0.385	0.678	0.816
45yr 20-35cm 3.	0.454	0.987	0.386	0.739	0.727
45yr 35-50cm 1.	0.474	0.875	0.151	0.734	0.837
45yr 35-50cm 2.	0.468	0.863	0.249	0.678	0.727
45yr 35-50cm 3.	0.549	1.013	0.195	0.674	1.085

Table A.1. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})	Fe Corrected SUVA (L mgC^{-1} m^{-1})	Fe Corrected S_R
80yr 0-5cm 1.	2.418	0.834	3.444	1.488	1.180
80yr 0-5cm 2.	2.666	0.920	4.105	1.334	0.842
80yr 0-5cm 3.	2.483	0.857	3.720	1.410	0.901
80yr 5-10cm 1.	1.292	0.523	2.922	2.037	0.931
80yr 5-10cm 2.	1.415	0.573	2.422	2.088	0.934
80yr 5-10cm 3.	1.457	0.590	2.886	2.076	0.831
80yr 10-15cm 1.	1.359	0.639	0.552	1.940	0.732
80yr 10-15cm 2.	1.318	0.619	1.069	1.614	0.821
80yr 10-15cm 3.	1.207	0.567	0.950	1.801	0.777
80yr 15-20cm 1.	1.085	0.532	0.541	1.453	0.825
80yr 15-20cm 2.	0.582	0.285	0.914	1.978	1.397
80yr 15-20cm 3.	0.598	0.293	0.564	1.435	1.041
80yr 20-35cm 1.	0.811	1.508	0.153	1.540	1.142
80yr 20-35cm 2.	0.773	1.438	0.146	1.545	1.127
80yr 20-35cm 3.	0.828	1.540	0.306	1.448	1.091
80yr 35-50cm 1.	0.606	1.264	0.146	1.243	1.597
80yr 35-50cm 2.	0.467	0.973	0.175	1.313	1.733
80yr 35-50cm 3.	0.599	1.248	1.136	1.293	2.860
80yr Ae 1.	0.420	n.d.	n.d.	n.d.	n.d.
80yr Ae 2.	0.448	n.d.	n.d.	n.d.	n.d.
80yr Ae 3.	0.436	n.d.	n.d.	n.d.	n.d.
80yr Bfh 2.	0.354	n.d.	n.d.	n.d.	n.d.
80yr Bfh 3.	0.344	n.d.	n.d.	n.d.	n.d.
80yr C 1.	0.651	n.d.	n.d.	n.d.	n.d.
80yr C 2.	0.593	n.d.	n.d.	n.d.	n.d.
80yr C 3.	0.615	n.d.	n.d.	n.d.	n.d.

Table A.2. Carbon, iron, and spectral data for samples extracted from the organo-metal complexed pool. Iron concentrations represent the drift corrected concentration. OG represents the old growth reference site, CC represents the 1 yr clearcut, and 15N, 45yr, and 80yr represents the 15-, 45-, and 80-yr sites, respectively.

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})	Fe Corrected SUVA (L mgC^{-1} m^{-1})	Fe Corrected S_R
OG 0-5cm 1.	11.266	4.450	0.460	4.827	0.777
OG 0-5cm 2.	12.053	4.761	0.454	5.209	0.797
OG 0-5cm 3.	12.388	4.893	0.519	5.247	0.772
OG 5-10cm 1.	8.812	2.952	1.950	5.441	0.436
OG 5-10cm 2.	8.766	2.937	1.951	5.421	0.526
OG 5-10cm 3.	8.649	2.897	1.839	5.655	0.537
OG 10-15cm 1.	15.030	7.139	4.569	5.382	0.183
OG 10-15cm 2.	15.671	7.444	4.755	5.014	0.269
OG 10-15cm 3.	15.103	7.174	4.558	5.290	0.139
OG 15-20cm 1.	19.826	9.120	3.796	4.722	0.258
OG 15-20cm 2.	18.128	8.339	3.504	4.788	0.425
OG 15-20cm 3.	18.938	8.712	4.036	5.021	0.330
OG 20-35cm 1.	21.360	32.680	2.771	4.468	0.684
OG 20-35cm 2.	20.999	32.129	2.746	4.446	0.626
OG 20-35cm 3.	21.148	32.357	2.772	4.363	0.601
OG 35-50cm 1.	15.968	40.478	1.746	3.630	0.425
OG 35-50cm 2.	15.075	38.215	1.744	3.862	0.476
OG 35-50cm 3.	16.500	41.828	1.947	3.786	0.332
CC 0-5cm 1.	21.664	8.557	1.321	6.559	0.698
CC 0-5cm 2.	23.190	9.160	1.332	6.132	0.718
CC 0-5cm 3.	23.471	9.271	1.325	6.002	0.705
CC 5-10cm 1.	11.777	6.536	1.835	6.102	0.791
CC 5-10cm 2.	11.850	6.577	1.830	5.817	0.734
CC 5-10cm 3.	11.901	6.605	1.814	6.269	0.785
CC 10-15cm 1.	11.733	6.336	2.113	5.875	0.729
CC 10-15cm 2.	12.211	6.594	2.140	5.581	0.693
CC 10-15cm 3.	11.518	6.220	2.158	5.960	0.677
CC 15-20cm 1.	13.430	6.446	2.003	4.229	0.484
CC 15-20cm 2.	11.888	5.706	1.943	4.623	0.494
CC 15-20cm 3.	13.063	6.270	1.920	4.283	0.503
CC 20-35cm 1.	21.872	31.496	3.734	4.845	0.521
CC 20-35cm 2.	23.590	33.970	3.709	4.471	0.508
CC 20-35cm 3.	22.045	31.744	3.517	4.653	0.536
CC 35-50cm 1.	18.989	32.186	1.782	3.580	0.587
CC 35-50cm 2.	15.381	26.070	1.826	4.344	0.588
CC 35-50cm 3.	16.156	27.384	1.692	4.005	0.614

Table A.2. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})	Fe Corrected SUVA (L mgC^{-1} m^{-1})	Fe Corrected S_R
15N 0-5cm 1.	6.118	2.967	0.834	5.908	0.737
15N 0-5cm 2.	7.590	3.681	0.670	5.763	0.632
15N 0-5cm 3.	7.209	3.496	0.794	6.274	0.761
15N 5-10cm 1.	9.813	4.367	1.588	5.160	0.565
15N 5-10cm 2.	9.357	4.164	1.521	5.302	0.547
15N 5-10cm 3.	9.687	4.311	1.578	5.098	0.555
15N 10-15cm 1.	8.921	5.352	1.424	4.811	0.528
15N 10-15cm 2.	7.813	4.688	1.398	5.842	0.557
15N 10-15cm 3.	10.046	6.027	1.504	4.589	0.570
15N 15-20cm 1.	9.103	5.280	1.313	4.471	0.582
15N 15-20cm 2.	9.112	5.285	1.298	4.575	0.619
15N 15-20cm 3.	8.244	4.782	1.452	4.952	0.516
15N 20-35cm 1.	7.924	11.411	0.849	3.502	0.533
15N 20-35cm 2.	7.892	11.364	0.824	3.561	0.531
15N 20-35cm 3.	8.332	11.998	0.834	3.942	0.746
15N 35-50cm 1.	2.637	4.075	0.289	2.911	0.822
15N 35-50cm 2.	3.464	5.353	0.361	3.106	0.767
15N 35-50cm 3.	4.043	6.247	0.426	2.037	0.779
45yr 0-5cm 1.	16.830	6.732	1.556	5.656	0.699
45yr 0-5cm 2.	17.072	6.829	1.604	5.600	0.690
45yr 0-5cm 3.	16.771	6.708	1.512	5.494	0.667
45yr 5-10cm 1.	17.845	8.476	2.284	5.493	0.688
45yr 5-10cm 2.	18.503	8.789	2.331	5.457	0.687
45yr 5-10cm 3.	18.813	8.936	2.371	5.269	0.640
45yr 10-15cm 1.	22.243	9.120	1.763	4.875	0.723
45yr 10-15cm 2.	23.421	9.602	1.910	4.694	0.727
45yr 10-15cm 3.	22.946	9.408	1.916	4.746	0.728
45yr 15-20cm 1.	11.864	6.229	1.326	3.882	0.628
45yr 15-20cm 2.	11.343	5.955	1.302	3.887	0.648
45yr 15-20cm 3.	11.606	6.093	1.365	3.923	0.641
45yr 20-35cm 1.	7.407	16.110	1.076	3.561	0.380
45yr 20-35cm 2.	7.096	15.434	0.945	3.688	0.428
45yr 20-35cm 3.	6.938	15.091	0.925	3.596	0.141
45yr 35-50cm 1.	5.418	9.997	0.757	3.587	0.620
45yr 35-50cm 2.	5.586	10.306	0.737	3.068	0.500
45yr 35-50cm 3.	5.673	10.466	0.663	2.995	0.531

Table A.2. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})	Fe Corrected SUVA (L mgC^{-1} m^{-1})	Fe Corrected S_R
80yr 0-5cm 1.	8.756	3.021	1.154	6.093	0.790
80yr 0-5cm 2.	7.513	2.592	0.950	5.981	0.867
80yr 0-5cm 3.	20.518*	7.079	0.990	2.885	0.830
80yr 5-10cm 1.	10.322	4.180	2.341	5.730	0.561
80yr 5-10cm 2.	10.010	4.054	2.299	5.873	0.535
80yr 5-10cm 3.	10.515	4.258	2.254	5.463	0.531
80yr 10-15cm 1.	11.428	5.371	2.011	5.264	0.694
80yr 10-15cm 2.	11.812	5.552	1.929	5.287	0.630
80yr 10-15cm 3.	10.917	5.131	2.003	5.245	0.619
80yr 15-20cm 1.	12.149	5.953	1.928	4.821	0.469
80yr 15-20cm 2.	12.152	5.954	1.978	4.889	0.602
80yr 15-20cm 3.	13.567	6.648	2.115	4.464	0.606
80yr 20-35cm 1.	13.033	24.242	1.890	4.739	0.589
80yr 20-35cm 2.	13.012	24.202	1.830	4.949	0.615
80yr 20-35cm 3.	13.158	24.475	1.929	4.621	0.564
80yr 35-50cm 1.	12.223	25.485	1.215	4.529	0.713
80yr 35-50cm 2.	11.313	23.588	1.209	4.711	0.755
80yr 35-50cm 3.	13.880	28.940	1.520	4.439	0.711
80yr Ae 1.	2.763	n.d.	n.d.	n.d.	n.d.
80yr Ae 2.	3.177	n.d.	n.d.	n.d.	n.d.
80yr Ae 3.	n.d.	n.d.	n.d.	n.d.	n.d.
80yr Bfh 2.	10.612	n.d.	n.d.	n.d.	n.d.
80yr Bfh 3.	n.d.	n.d.	n.d.	n.d.	n.d.
80yr C 1.	38.502	n.d.	n.d.	n.d.	n.d.
80yr C 2.	35.005	n.d.	n.d.	n.d.	n.d.
80yr C 3.	35.743	n.d.	n.d.	n.d.	n.d.

Table A.3. Carbon and iron data for samples extracted from the poorly crystalline pool. Iron concentrations represent the drift corrected concentration. Spectral properties are not shown because values were below detection after correction for iron. OG represents the old growth reference site, CC represents the 1 yr clearcut, and 15N, 45yr, and 80yr represents the 15-, 45-, and 80-yr sites, respectively.

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})
OG 0-5cm 1.	1.982	0.783	0.456
OG 0-5cm 2.	7.338	2.898	0.521
OG 0-5cm 3.	1.909	0.754	1.308
OG 5-10cm 1.	0.959	0.321	1.949
OG 5-10cm 2.	0.918	0.307	1.876
OG 5-10cm 3.	0.997	0.334	1.819
OG 10-15cm 1.	1.015	0.482	4.079
OG 10-15cm 2.	2.071	0.984	4.310
OG 10-15cm 3.	1.005	0.478	4.803
OG 15-20cm 1.	1.564	0.719	2.944
OG 15-20cm 2.	1.499	0.689	3.622
OG 15-20cm 3.	1.328	0.611	3.819
OG 20-35cm 1.	1.554	2.378	5.941
OG 20-35cm 2.	1.576	2.412	5.916
OG 20-35cm 3.	1.587	2.429	5.450
OG 35-50cm 1.	1.918	4.862	3.224
OG 35-50cm 2.	1.981	5.022	3.145
OG 35-50cm 3.	2.217	5.620	3.061
CC 0-5cm 1.	1.369	0.541	1.965
CC 0-5cm 2.	1.534	0.606	1.815
CC 0-5cm 3.	1.558	0.615	2.026
CC 5-10cm 1.	0.790	0.439	2.816
CC 5-10cm 2.	0.820	0.455	2.674
CC 5-10cm 3.	0.875	0.486	2.690
CC 10-15cm 1.	0.803	0.434	3.461
CC 10-15cm 2.	0.813	0.439	3.695
CC 10-15cm 3.	0.812	0.439	3.758
CC 15-20cm 1.	0.737	0.354	3.874
CC 15-20cm 2.	0.658	0.316	4.302
CC 15-20cm 3.	0.658	0.316	4.546
CC 20-35cm 1.	1.310	1.886	5.219
CC 20-35cm 2.	1.286	1.852	5.044
CC 20-35cm 3.	1.396	2.010	5.977
CC 35-50cm 1.	2.571	4.358	5.592
CC 35-50cm 2.	2.465	4.179	5.320
CC 35-50cm 3.	2.034	3.448	5.018

Table A.3. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})
15N 0-5cm 1.	1.286	0.624	1.290
15N 0-5cm 2.	1.143	0.555	1.414
15N 0-5cm 3.	1.087	0.527	1.395
15N 5-10cm 1.	0.862	0.384	1.345
15N 5-10cm 2.	0.930	0.414	1.563
15N 5-10cm 3.	0.936	0.416	1.273
15N 10-15cm 1.	1.065	0.639	1.932
15N 10-15cm 2.	0.917	0.550	2.061
15N 10-15cm 3.	0.958	0.575	2.200
15N 15-20cm 1.	1.874	1.087	4.948
15N 15-20cm 2.	1.739	1.009	4.602
15N 15-20cm 3.	3.017	1.750	4.318
15N 20-35cm 1.	2.422	3.487	3.984
15N 20-35cm 2.	2.459	3.541	3.959
15N 20-35cm 3.	2.530	3.643	4.074
15N 35-50cm 1.	1.775	2.743	4.973
15N 35-50cm 2.	1.631	2.520	5.337
15N 35-50cm 3.	1.485	2.295	4.140
45yr 0-5cm 1.	1.221	0.489	1.520
45yr 0-5cm 2.	1.125	0.450	1.426
45yr 0-5cm 3.	1.266	0.506	1.453
45yr 5-10cm 1.	1.159	0.551	2.059
45yr 5-10cm 2.	1.257	0.597	2.132
45yr 5-10cm 3.	1.118	0.531	2.266
45yr 10-15cm 1.	1.862	0.763	4.763
45yr 10-15cm 2.	1.830	0.750	4.239
45yr 10-15cm 3.	1.836	0.753	4.252
45yr 15-20cm 1.	1.430	0.751	4.921
45yr 15-20cm 2.	1.521	0.799	5.184
45yr 15-20cm 3.	1.400	0.735	4.464
45yr 20-35cm 1.	1.451	3.155	3.466
45yr 20-35cm 2.	1.241	2.698	3.259
45yr 20-35cm 3.	1.296	2.819	3.384
45yr 35-50cm 1.	1.046	1.930	4.955
45yr 35-50cm 2.	1.127	2.080	5.626
45yr 35-50cm 3.	1.096	2.022	5.663

Table A.3. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})
80yr 0-5cm 1.	1.061	0.366	1.715
80yr 0-5cm 2.	1.014	0.350	1.523
80yr 0-5cm 3.	1.040	0.359	1.654
80yr 5-10cm 1.	0.566	0.229	1.968
80yr 5-10cm 2.	0.533	0.216	1.940
80yr 5-10cm 3.	0.537	0.218	2.255
80yr 10-15cm 1.	0.585	0.275	3.330
80yr 10-15cm 2.	0.657	0.309	3.225
80yr 10-15cm 3.	0.548	0.258	2.551
80yr 15-20cm 1.	1.215	0.595	4.845
80yr 15-20cm 2.	1.179	0.578	5.321
80yr 15-20cm 3.	1.357	0.665	4.300
80yr 20-35cm 1.	0.895	1.665	4.384
80yr 20-35cm 2.	0.895	1.664	4.272
80yr 20-35cm 3.	0.746	1.387	3.739
80yr 35-50cm 1.	1.578	3.289	5.431
80yr 35-50cm 2.	1.589	3.312	5.765
80yr 35-50cm 3.	1.510	3.149	5.755
80yr Ae 1.	0.683	n.d.	n.d.
80yr Ae 2.	1.342	n.d.	n.d.
80yr Ae 3.	n.d.	n.d.	n.d.
80yr Bfh 2.	1.282	n.d.	n.d.
80yr Bfh 3.	n.d.	n.d.	n.d.
80yr C 1.	3.554	n.d.	n.d.
80yr C 2.	3.323	n.d.	n.d.
80yr C 3.	3.147	n.d.	n.d.

Table A.4. Carbon and iron data for samples extracted from the crystalline pool. Iron concentrations represent the drift corrected concentration. Spectral properties are not shown because values were below detection after correction for iron. OG represents the old growth reference site, CC represents the 1 yr clearcut, and 15N, 45yr, and 80yr represents the 15-, 45-, and 80-yr sites, respectively.

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})
OG 0-5cm 1.	7.939	2.448	0.073
OG 0-5cm 2.	13.386	4.202	0.469
OG 0-5cm 3.	5.511	1.811	0.566
OG 5-10cm 1.	1.657	0.261	0.614
OG 5-10cm 2.	1.765	0.284	0.510
OG 5-10cm 3.	1.730	0.275	0.500
OG 10-15cm 1.	1.753	0.382	0.697
OG 10-15cm 2.	1.696	0.353	0.735
OG 10-15cm 3.	1.493	0.271	0.671
OG 15-20cm 1.	4.126	1.458	1.337
OG 15-20cm 2.	3.812	1.307	0.838
OG 15-20cm 3.	3.783	1.290	0.812
OG 20-35cm 1.	1.751	1.211	0.682
OG 20-35cm 2.	1.734	1.182	0.618
OG 20-35cm 3.	1.608	0.995	0.660
OG 35-50cm 1.	3.334	6.051	0.811
OG 35-50cm 2.	3.395	6.194	0.788
OG 35-50cm 3.	4.227	8.259	1.148
CC 0-5cm 1.	2.068	0.455	0.922
CC 0-5cm 2.	2.206	0.508	0.816
CC 0-5cm 3.	2.045	0.449	1.128
CC 5-10cm 1.	1.699	0.428	1.556
CC 5-10cm 2.	1.678	0.431	1.882
CC 5-10cm 3.	1.731	0.460	1.953
CC 10-15cm 1.	1.738	0.448	1.938
CC 10-15cm 2.	1.565	0.363	1.867
CC 10-15cm 3.	1.574	0.368	1.844
CC 15-20cm 1.	1.512	0.291	1.058
CC 15-20cm 2.	1.459	0.271	0.782
CC 15-20cm 3.	1.401	0.247	0.848
CC 20-35cm 1.	1.704	1.083	2.207
CC 20-35cm 2.	1.958	1.447	1.995
CC 20-35cm 3.	1.919	1.373	2.202
CC 35-50cm 1.	1.662	1.208	1.551
CC 35-50cm 2.	1.797	1.445	2.073
CC 35-50cm 3.	1.582	1.071	1.418

Table A.4. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})
15N 0-5cm 1.	3.731	1.387	1.103
15N 0-5cm 2.	3.717	1.378	3.491
15N 0-5cm 3.	4.231	1.620	3.963
15N 5-10cm 1.	1.766	0.387	0.787
15N 5-10cm 2.	1.803	0.404	0.739
15N 5-10cm 3.	1.705	0.365	0.839
15N 10-15cm 1.	1.726	0.500	0.844
15N 10-15cm 2.	1.707	0.488	0.702
15N 10-15cm 3.	1.738	0.503	0.747
15N 15-20cm 1.	3.810	1.687	4.367
15N 15-20cm 2.	3.902	1.632	0.468
15N 15-20cm 3.	3.634	1.570	0.223
15N 20-35cm 1.	1.691	1.123	0.887
15N 20-35cm 2.	1.706	1.093	n.d.
15N 20-35cm 3.	1.674	1.090	1.074
15N 35-50cm 1.	3.048	3.309	0.372
15N 35-50cm 2.	2.970	3.188	0.179
15N 35-50cm 3.	3.649	4.178	2.373
45yr 0-5cm 1.	2.368	0.586	0.903
45yr 0-5cm 2.	2.731	0.725	0.913
45yr 0-5cm 3.	2.529	0.651	0.887
45yr 5-10cm 1.	1.976	0.499	0.641
45yr 5-10cm 2.	2.114	0.565	0.825
45yr 5-10cm 3.	1.963	0.485	0.777
45yr 10-15cm 1.	1.999	0.430	1.210
45yr 10-15cm 2.	1.945	0.406	0.923
45yr 10-15cm 3.	1.773	0.336	1.020
45yr 15-20cm 1.	1.833	0.477	1.606
45yr 15-20cm 2.	1.912	0.525	1.386
45yr 15-20cm 3.	1.934	0.538	1.682
45yr 20-35cm 1.	1.726	1.819	1.166
45yr 20-35cm 2.	1.541	1.438	1.194
45yr 20-35cm 3.	1.491	1.313	1.018
45yr 35-50cm 1.	1.838	1.763	1.411
45yr 35-50cm 2.	1.808	1.689	1.122
45yr 35-50cm 3.	1.744	1.582	1.215

Table A.4. continued

Sample	DOC (mg C g soil^{-1})	C Storage (Mg C ha^{-1})	Fe (mg L^{-1})
80yr 0-5cm 1.	3.036	0.738	0.862
80yr 0-5cm 2.	3.689	0.956	0.658
80yr 0-5cm 3.	3.742	0.971	0.386
80yr 5-10cm 1.	1.589	0.286	0.794
80yr 5-10cm 2.	1.814	0.373	0.759
80yr 5-10cm 3.	1.645	0.310	0.867
80yr 10-15cm 1.	1.603	0.334	0.860
80yr 10-15cm 2.	1.679	0.368	1.253
80yr 10-15cm 3.	1.511	0.291	1.420
80yr 15-20cm 1.	3.074	1.035	1.325
80yr 15-20cm 2.	3.315	1.167	0.735
80yr 15-20cm 3.	3.595	1.214	1.316
80yr 20-35cm 1.	1.589	1.256	0.937
80yr 20-35cm 2.	1.396	0.911	1.996
80yr 20-35cm 3.	1.566	1.213	1.131
80yr 35-50cm 1.	3.052	4.417	0.793
80yr 35-50cm 2.	3.153	4.639	1.079
80yr 35-50cm 3.	2.976	4.270	0.675
80yr Ae 1.	2.623	n.d.	n.d.
80yr Ae 2.	2.850	n.d.	n.d.
80yr Ae 3.	3.218	n.d.	n.d.
80yr Bfh 2.	3.067	n.d.	n.d.
80yr Bfh 3.	3.513	n.d.	n.d.
80yr C 1.	3.859	n.d.	n.d.
80yr C 2.	4.154	n.d.	n.d.
80yr C 3.	3.681	n.d.	n.d.

Table A.5. Percentage of C representing each pool for depth strata and site in the chronosequence. Percentages calculated from C concentrations (mg C g soil^{-1}).

Depth Interval (cm)	Stand Age (years)	Water Soluble (%)	Organo-metal (%)	Poorly Crystalline (%)	Crystalline (%)
Shallow (0-20)	1	9.48	80.85	5.20	4.47
	15	8.63	66.57	10.22	14.58
	45	10.26	78.16	6.36	5.21
	80	10.24	72.88	5.89	10.99
	125+	11.78	68.71	7.17	12.34
Deep (20-50)	1	4.06	84.51	7.92	3.51
	15	4.20	58.87	21.12	15.80
	45	5.63	71.65	13.64	9.07
	80	4.25	79.71	7.50	8.54
	125+	3.18	81.33	7.93	7.54
Total (0-50)	1	7.37	82.27	6.26	4.10
	15	7.42	64.47	13.20	14.91
	45	9.50	77.08	7.57	5.85
	80	8.11	75.30	6.46	10.12
	125+	8.66	73.29	7.45	10.60

B. Spectroscopic data and methods

The use of absorption spectral slope ratios (S_R) is a newer approach that has allowed further insight into characterizing DOM (Helms et al., 2008). Using the ratio of two distinct ln transformed spectral slope regions (275-295 nm and 350-400 nm), S_R has been characterized as a good proxy for determining molecular weight (MW) of dissolved organic matter, displaying an inverse relationship between MW and S_R (Helms et al., 2008).

Spectroscopic analysis of DOM can be affected because of iron interference (Poulin et al., 2014; Weishaar et al., 2003), and so absorbance values were corrected for absorption contributions of iron. Concentrations of iron in each selective dissolution soil extract were determined using flame atomic absorption spectroscopy (Perkin Elmer AAnalyte 300). Extinction coefficients for wavelengths ranging from 275-295 nm and 350-400nm were provided by A. Morgan; the extinction coefficient for 254 nm (ε_{254}) was found in Poulin et al. (2014). Absorbance correction for Fe was calculated by

$$abs_{cor} = abs_{\lambda} - \left[\varepsilon_{\lambda,Fe-DOM} \times [Fe]\right]$$

where abs_{cor} is the corrected absorbance, abs_{λ} is the measured absorbance, $\varepsilon_{\lambda,\text{ Fe-DOM}}$ is the Fe extinction coefficient (L mg^{-1} cm^{-1}) and $[Fe]$ is the concentration of iron in the sample (mg L^{-1}).

UV-vis absorption measurements can be used to determine several spectral parameters, including slope ratio and $SUVA_{254}$. Defined as the ratio of two distinct ln transformed spectral slope regions (shorter wavelength: 275-295 nm, and longer wavelength: 350-400 nm), S_R has been characterized as a good proxy for determining molecular weight (MW) of dissolved organic matter (Helms et al., 2008).

Absorption spectra were transformed as shown in the following:

$$\ln(a) = \frac{2.303 abs_{cor}}{l}$$

where a is the Napierian absorption coefficient (m^{-1}), abs_{cor} is the Fe corrected absorbance, and l is the path length (m) (Helms et al., 2008; Poulin et al., 2014). Linear regression of the natural log transformed absorption spectra was calculated over the specified wavelengths (275-295 nm and 350-400 nm), and the slope ratio (dimensionless) was determined by dividing $S_{275\text{-}295}$ (the slope of the shorter wavelength interval) by $S_{350\text{-}400}$ (the slope of the longer wavelength interval). Slope ratio and MW are inversely related, with low S_R values indicating dissolved organic matter with high MW, and vice versa (Helms et al., 2008).

Table B.3. Iron extinction coefficients for DOM used for absorption correction of spectroscopy data, and provided by Alex Morgan and Dr. Susan Ziegler of Memorial University.

Wavelength (nm)	$\varepsilon_{\lambda, Fe\text{-}DOM}$	SD	% RSD
275	0.061091	0.001905	3.117943
276	0.06086	0.001902	3.125899
277	0.060681	0.001822	3.00238
278	0.060512	0.0018	2.974996
279	0.06034	0.001792	2.970201
280	0.060199	0.001811	3.007734
281	0.060023	0.001796	2.991773
282	0.059795	0.001777	2.972187
283	0.059566	0.001713	2.875749
284	0.059365	0.001683	2.834676
285	0.059158	0.001686	2.849598
286	0.058928	0.001696	2.8783
287	0.058684	0.001604	2.733355
288	0.058516	0.001597	2.728347
289	0.058334	0.001642	2.814294
290	0.058116	0.00155	2.666906
291	0.05791	0.001507	2.602102
292	0.057718	0.001455	2.520715
293	0.057563	0.001489	2.587151
294	0.057337	0.001435	2.502175
295	0.057153	0.001354	2.369757
350	0.045335	0.002733	6.027692
351	0.045135	0.002787	6.175762
352	0.044829	0.002857	6.373866
353	0.044562	0.00281	6.305413
354	0.044213	0.002979	6.738981
355	0.04389	0.002949	6.718428
356	0.043505	0.003062	7.038716
357	0.043156	0.003049	7.065772
358	0.04281	0.003129	7.308027
359	0.042437	0.003165	7.458146
360	0.041973	0.003221	7.67302
361	0.041591	0.00328	7.887497
362	0.041086	0.003375	8.214682
363	0.040663	0.003352	8.242926
364	0.040159	0.003501	8.717984
365	0.039707	0.003486	8.779347
366	0.039215	0.003522	8.980306
367	0.038654	0.003526	9.122798

Table B.1. continued

Wavelength (nm)	$\varepsilon_{\lambda,\ Fe\text{-}DOM}$	SD	% RSD
368	0.038234	0.003652	9.552887
369	0.037666	0.003645	9.678232
370	0.037051	0.003682	9.939002
371	0.036505	0.003699	10.13231
372	0.035994	0.003856	10.71176
373	0.035373	0.003597	10.16823
374	0.034711	0.003782	10.89432
375	0.034166	0.003623	10.60356
376	0.033671	0.003851	11.43761
377	0.033042	0.003561	10.77731
378	0.032235	0.003846	11.93038
379	0.03192	0.003627	11.36344
380	0.031294	0.004817	15.39187
381	0.030753	0.003291	10.70184
382	0.029896	0.004063	13.5913
383	0.029505	0.003478	11.78628
384	0.028895	0.003557	12.30862
385	0.028362	0.003734	13.16537
386	0.027872	0.003553	12.74814
387	0.027257	0.00368	13.50057
388	0.026802	0.003508	13.08706
389	0.026231	0.003607	13.75248
390	0.02579	0.003462	13.42225
391	0.025225	0.003542	14.04074
392	0.0248	0.003347	13.49497
393	0.024321	0.0035	14.38917
394	0.023918	0.003344	13.98139
395	0.023432	0.003459	14.7609
396	0.023023	0.003285	14.26921
397	0.022605	0.003403	15.05576
398	0.022294	0.003352	15.03361
399	0.021894	0.003435	15.69049
400	0.021583	0.003317	15.36984

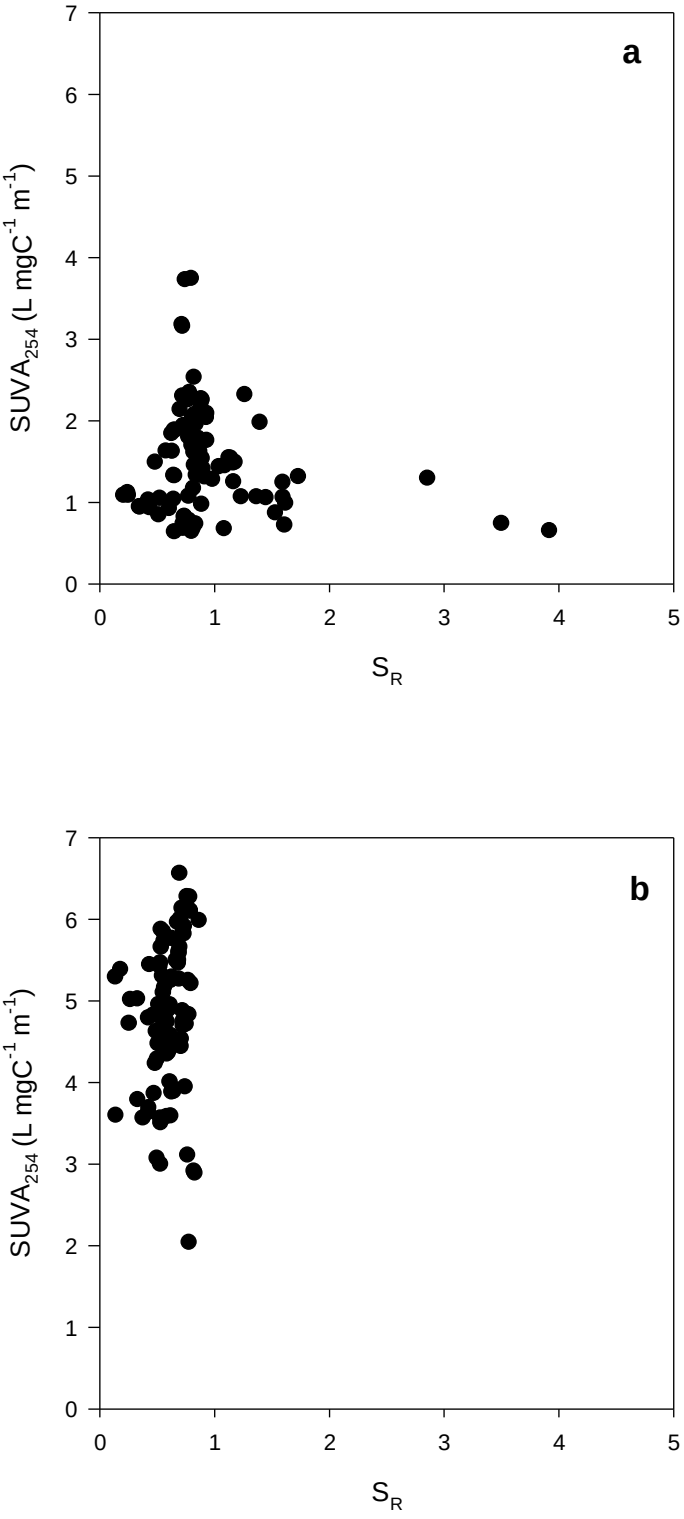

Figure B.2. Iron corrected SUVA vs slope ratio (S_R) for the top 50 cm of mineral soil for the (**a**) water soluble and (**b**) organo-metal complexed pools.