

LOSSES OF CARBON FROM MINERAL-ASSOCIATED SOIL
ORGANIC MATTER POOLS IN PODZOLIC HORIZONS
FOLLOWING SOIL CLIMATIC CHANGES ASSOCIATED WITH
FOREST CLEAR-CUT HARVESTING

by

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I dedicate this thesis to my dearest: my light and my love.

Frodo: Go back, Sam! I'm going to Mordor alone.

Sam: Of course you are, and I'm coming with you!

J.R.R. Tolkein

*You have been beside me as I moved through the darkest and the
brightest moments of this journey. This becoming...*

...it begins and ends with you, my loves.

Table of Contents

List of Tables	viii
List of Figures	x
Abstract	xiv
List of Abbreviations and Symbols Used	xv
Acknowledgements	xvii
Chapter 1 Introduction	1
1.1 Why study carbon?	1
1.2 Soils	2
1.2.1 Pedogenesis and soil characterization	4
1.2.2 Podzols	4
1.2.3 Association of soil organic matter with minerals	6
1.3 Nature of SOM in mineral-associated organic matter pools	7
1.3.1 Soil organic matter - solid SOM pool	7
1.4 Dissolved organic matter - aqueous SOM pool	8
1.5 Soil organic matter destabilization	10
1.5.1 Challenging an old paradigm	10
1.6 Mineral control of SOM stability	12
1.7 Soil organic matter and land-use	13
1.8 Other biogeochemical impacts of forest harvesting disturbance	14
1.9 Potential mechanisms to explain mineral soil C losses	15
1.10 Analytical approaches to study SOM storage and stability	17
1.10.1 Natural abundance of stable isotopes of C in soil and DOC	17
1.10.2 Dissolved organic carbon chemistry - Indicators	18
1.10.3 Quantifying organic matter-mineral associations	18
1.11 Research objectives	20
1.12 Contributions of this thesis	20

1.13	Thesis structure	20
Chapter 2	Site description	24
2.1	Overview	24
2.2	Forests description	24
2.3	Climate	25
2.4	Soil descriptions	28
2.5	Geological description	31
2.5.1	Regional geological setting	31
2.5.2	Regional glacial geology	37
2.6	Similarity of the Mooseland sites	38
Chapter 3	Examining mineral-associated soil organic matter pools through depth in harvested forest soil profiles	40
3.1	Introduction	40
3.2	Methods	44
3.2.1	Site description	44
3.2.2	Soil forming factors	46
3.2.3	Soil sampling	48
3.2.4	Sequential selective dissolution mineral extraction methodology	49
3.2.5	Selective dissolution extracts: Elemental analysis (C, Fe and Al) and stable isotope signatures of C	50
3.2.6	Calculations and Data analysis - Contribution from each mineral pool to total C	51
3.2.7	Calculations and Data analysis - Carbon content and stable isotope ratio ($\delta^{13}\text{C}$)	51
3.2.8	Calculations and Data analysis - Metrics of SOM-mineral interactions	52
3.2.9	Statistical Analysis	53
3.3	Results	53
3.3.1	Description of soil profiles at Young and Mature sites	53
3.3.2	Distribution of mineral-associated organic matter pools	56
3.3.3	Comparing C in bulk soil and mineral pools in Young and Mature sites	56
3.3.4	Fe and Al content of mineral-associated OM pools	59
3.3.5	Mineral-SOM interaction metrics	61
3.3.6	$\delta^{13}\text{C}$ patterns within soil profiles	64

3.4	Discussion	64
3.4.1	C content and distribution of mineral-associated pools	64
3.4.2	Interaction between organic matter and minerals	67
3.4.3	Distinct character of organic matter in mineral-associated pools	68
3.4.4	Quantity and character of C in mineral soil considering its disturbance history	70
3.5	Conclusions	73
3.6	Supporting Information	73
Chapter 4	Evaluating the susceptibility of soil organic matter in mineral soil horizons to losses after climatic changes associated with forest clear-cut harvesting	74
4.1	Introduction	75
4.2	Methods and Materials	80
4.2.1	Site description	80
4.2.2	Soil sampling and sample preparation	82
4.2.3	Soil incubation experimental design	82
4.2.4	Bulk soil carbon and $\delta^{13}\text{C}$ analysis	86
4.2.5	Carbon and metal content of mineral pools	86
4.2.6	Soil incubation respiration measurements	87
4.2.7	Aqueous C pool	89
4.2.8	Data analysis	90
4.3	Results	90
4.3.1	Soil organic carbon and mineral pool carbon contents	90
4.3.2	Respired CO_2 through depth following incubation	93
4.3.3	Aqueous extract chemistry shifts before and following short-term incubations	97
4.3.4	$\delta^{13}\text{C}$ of respired CO_2 following incubation	103
4.3.5	Effects of extreme climatic change treatments on respiration and extracted DOC	107
4.4	Discussion	111
4.4.1	Soil respiration responses to microclimatic changes through depth indicate enhanced susceptibility to SOM loss	111
4.4.2	Connecting respiratory substrate and soil respiration through DOC_{ex} and chemistry of respired CO_2	113
4.4.3	Extreme climatic disturbances can enhance mobility of soil C in surface horizons and respiratory losses of soil C at depth	116
4.4.4	Conclusions	118

Chapter 5	Impacts of redox conditions and temperature on dissolved organic carbon and Fe losses from mineral soils through depth	119
5.1	Introduction	120
5.2	Materials and Methods	125
5.2.1	Experimental design	125
5.2.2	Description of Study Sites	126
5.2.3	Incubation experiment - Mooseland soils	130
5.2.4	Dissolved organic matter extraction	130
5.2.5	Stream sampling strategy - Abraham's Lake	131
5.2.6	Extracted dissolved organic carbon and stream water chemistry	132
5.2.7	Carbon and $\delta^{13}\text{C}$ of soil samples	133
5.2.8	Statistical analyses	133
5.3	Results	134
5.3.1	Initial soil elemental, isotopic and optical characteristics through depth	134
5.3.2	Changes in DOC_{ex} following anoxic and oxic incubations . . .	134
5.3.3	Soluble Fe in soil extracts	137
5.3.4	The ratio of DOC to Fe in soil extracts	137
5.3.5	pH changes following incubation	144
5.3.6	Elemental and stable isotopic analysis of incubated soil solids	144
5.3.7	Seasonal trends in rainfall and stream water chemistry	146
5.4	Discussion	148
5.4.1	Significant release of DOC and its coupling with Fe primarily occurred in surface mineral soils following anoxic conditions .	148
5.4.2	Loss of SOC in deeper horizons with temperature and redox changes are more decoupled from mobilization of Fe	152
5.4.3	Local stream water chemistry is consistent with mineral soil temperature and redox disturbances associated with forest harvesting	153
5.5	Conclusion	155
Chapter 6	Conclusion	156
6.1	Summary	157
6.1.1	Mineral-associated soil organic matter pools in clear-cut harvested soils	157
6.1.2	Soil C loss following climatic changes	158
6.1.3	Redox conditions and temperature effects on DOC and Fe mobilization	159

6.2	Insights	161
6.2.1	Destabilization of mineral-associated SOM pools following clear-cut harvesting	161
6.2.2	Susceptibility of mineral-associated SOM pools to climatic changes	161
6.2.3	Role of soil minerals in protection of SOM	162
6.2.4	Improving forest C modelling	163
6.2.5	Implications for experimental methodology	164
6.2.6	Pedogenesis	165
6.2.7	Forest harvesting policy	165
6.3	Next steps	166
Appendix A		168
Appendix B		170
Appendix C		172
Bibliography		174

List of Tables

Table 3.1	Soil horizon characteristics for podzol forest soil profiles for a Young (35 year old) and Mature (110 year old) red spruce forest sites, sampled to 50 cm.	45
Table 3.2	Results of sequential selective dissolution of podzol soils from two sites, Young and Mature, 35 and 110 years since clear-cutting, respectively.	55
Table 3.3	Results of residue analysis and proportion of mineral-associated C extracted mineral fractions following sequential separations for horizon-based samples from Young and Mature forest sites.	60
Table 4.1	Soil texture and chemical data for mineral horizons of podzol soil profiles at Young (35 year old) and Mature (110 year old) red spruce forest in Mooseland, Nova Scotia, Canada.	92
Table 4.2	Parameters and correlation coefficients for curve fits of 2-parameter exponential model of temperature sensitivity, Q_{10} (Equation 3.2), fit to specific cumulative respired C data for A_e , B_f and BC horizons from Mature and Young sites in Mooseland, Nova Scotia, Canada.	96
Table 4.3	Solution chemistry data for soil extracts from A_e , B_f and BC horizons of forest soils sampled from Young and Mature sites at Mooseland, Nova Scotia, Canada, following incubation at 5 and 25 °C under optimum conditions (OP) and under treatment conditions of rewetting (RW) and freeze-thaw (FT).	99
Table 4.4	Results of repeated measures ANOVA for log-transformed specific respiration rate (R_d) and $\delta^{13}\text{C-CO}_2$, with Incubation Day (repeated measurements) for the fixed effects of temperature or climatic extremes treatments with Site and Horizon as random errors, tested with scenarios that included interactions for Site and Horizon, for composite samples (n=9) of A_e , B_f and BC horizons from Mature and Young sites in Mooseland, NS.	101
Table 4.5	Generalized linear mixed model results, testing for the effect of temperature or treatment on DOC_{ex} , SUVA_{254} and spectral slope ratio (S_r) for incubated samples from Mature and Young sites in Mooseland, Nova Scotia, Canada.	105

Table 4.6	$\Delta^{13}\text{C}$ expressed as the difference in respired weighted monthly mean $\delta^{13}\text{C}\text{-CO}_2$ following incubation under optimum moisture at 5, 15 and 25 °C or after dry-rewetting (RW) or freeze-thaw at 25 °C compared to initial DOC_{ex} from incubated podzol horizons from a Young and Mature red spruce forest sites in Mooseland, NS.	106
Table 5.1	Initial soil physicochemical characteristics of soil sampled from Mooseland, Nova Scotia, Canada through depth in increments.	136
Table 5.2	Results from chemical analysis of soil extracts following Oxidic and Anoxic incubations for 1 month, and 4 months, at 5 °C. . .	139
Table 5.3	Results from chemical analysis of soil extracts following Oxidic and Anoxic incubations for 1 month, and 4 months, at 15 °C. .	140
Table 5.4	Stream chemical data for Disturbed (Twelve Mile Stream) and Intact (Bear Brook) watersheds at Abraham's Lake, Nova Scotia, Canada, sampled monthly during ice-free period (July-May 2011-2012).	147
Table 6.1	Supplementary Table 1. Results of sequential selective dissolution of podzol soils from two sites	169
Table 6.2	Supplementary Table 2. Particle size analysis and elemental and stable isotope analysis of separated textural fractions	171

List of Figures

Figure 1.1	Photograph of the mineral horizons of typical Orthic Humo-Ferric podzol from this area of central Nova Scotia, Canada.	5
Figure 1.2	Depth profiles of $\delta^{13}\text{C}$ in terms of soil organic matter (SOM, filled) and respired CO_2 (open).	9
Figure 2.1	Map of the locations of the soil sampling sites in Mooseland, central Nova Scotia, Eastern Canada (Inset).	26
Figure 2.2	Location of sampling sites in Abraham's Lake area in central Nova Scotia, Eastern Canada (Inset), with location of Intact and Disturbed water sampling sites in Abraham's Lake area (larger map).	27
Figure 2.3	Topographic map of Young and Mature soil sampling sites in Mooseland, central Nova Scotia, Canada.	29
Figure 2.4	Topographic map of Disturbed and Intact stream sampling sites at Abraham 's Lake, Nova Scotia, Canada.	30
Figure 2.5	Generalized bedrock geology of Maritime Canada, showing the main geological terrain boundaries and location of highland regions.	33
Figure 2.6	Bedrock and surficial geology map of Mooseland, central Nova Scotia, Canada, within Cambrian/Ordovician metasilstone regional geology.	34
Figure 2.7	Location of Mooseland in central Nova Scotia, Canada and regional geological setting.	35
Figure 2.8	Bedrock and surficial geology map of the south central Nova Scotia, Canada, at Abraham's Lake, Nova Scotia, Canada, within Cambrian-Ordovician metasilstone to slate regional geology.	36
Figure 3.1	Map of sampling sites in Mooseland in Nova Scotia, Eastern Canada.	47

Figure 3.2	Distribution of C in sequential selective dissolution extracts (WS = water soluble; OMC = organo-metal complexes; PCrys = poorly crystalline; and Crys = crystalline) through depth (0-50 cm) in depth increments for the Young and Mature site at Mooseland, Nova Scotia, Canada.	57
Figure 3.3	Carbon (mg g soil ⁻¹) from sequential selective dissolutions of soil from horizons of podzols at Young and Mature forests in Mooseland, Nova Scotia, Canada.	58
Figure 3.4	Plot of pedogenic ratios for Young (broken line) and Mature (solid line) through depth, which are indexes of a) soil weathering and b) organic complexation.	62
Figure 3.5	Relationship between a) %C and the sum of organo-metal Fe and Al and poorly-crystalline Fe and Al; b) % C in bulk soil and the content of Fe and Al in crystalline secondary mineral phases.	63
Figure 3.6	Results of stable isotopic analysis of carbon ($\delta^{13}\text{C}$) in genetic horizons through depth at Young and Mature forest sites following sequential selective dissolutions for water soluble (WS), organo-metal (OMC), and crystalline (Crys) fractions.	65
Figure 4.1	Map of Mooseland in Nova Scotia, Canada, with the location of the Young (Guzzle Forest), and Mature (Otter Ponds Demonstration Forest) sampling sites, located approximately 3 km apart (circles).	81
Figure 4.2	Conceptual diagram outlining the experiments in this study, designed to test the effects of temperature and episodic moisture changes on C cycling in A _e , B _f and BC horizons at Young and Mature forest sites that differ in their time since clearcutting (35 vs. 110 years).	85
Figure 4.3	Cumulative respired C at 5, 15 and 25 °C over the course of a 28 day incubation for Mature and Young sites sampled through depth in A _e , B _f and BC horizons at Mooseland, Nova Scotia, Canada.	94
Figure 4.4	Specific cumulative respired C, or bioreactivity, (mg C respired g soil C ⁻¹) for a 28 day incubation at three temperatures (5, 15 and 25 °C) for A _e , B _f and BC horizons of soil profiles sampled from Mooseland, Nova Scotia, Canada.	95

Figure 4.5	a-b) Bioreactivity (specific cumulative respired C), c-d) net change in DOC_{ex} , e-f) net change in CDOM and g-h) net change in S_r over incubation of 1 month of soil samples from A_e , B_f and BC horizons of Mature (left) and Young (right) forest podzols from Mooseland, Nova Scotia, Canada.	100
Figure 4.6	Comparison of the amounts of cumulative respired C (light bar) and as DOC_{ex} (dark bar) (mg g soil^{-1}) for Mature (left) and Young sites (right) at Mooseland, Nova Scotia, Canada. . . .	102
Figure 4.7	The $\delta^{13}\text{C}$ - CO_2 of weighted mean monthly respired CO_2 ($\delta^{13}\text{C}$ - CO_2 ; $n=3$ for each horizon) from A_e , B_f and BC soil horizons through depth (for samples, $n=9$ for each horizon) from a Mature (a) and Young (b) site from Mooseland, Nova Scotia, Canada incubated at 25 °C for 28 days.	104
Figure 4.8	Relationship between weighted mean $\delta^{13}\text{C}$ respired CO_2 and SUVA_{254} of DOM_{ex} for the 28-day incubation for incubation at 25 °C under Optimal conditions (OP solid line), rewetting (RW long dash) and freeze-thaw (FT short dashes).	108
Figure 4.9	Mean and SD of ^{13}C of respired CO_2 over the 28 day incubation for A_e (circles), B_f (triangles) and BC (squares) horizons in Mature (filled symbols) and Young (open symbols) at 3 temperatures: 5, 15 and 25 °C.	109
Figure 4.10	This diagram depicts the general soil characteristics and relative differences in chemistry through depth in the SOM, DOM and CO_2 as measured during the incubation of the genetic horizons in this study.	110
Figure 5.1	Location of Intact and Disturbed water sampling sites in Abraham's Lake area.	127
Figure 5.2	Topographic map of stream water sampling sites in the Abraham's Lake area in Nova Scotia, Eastern Canada.	129
Figure 5.3	Results of chemical analysis of extracts following incubation of composite field moist mineral soil sampled through depth (0-10, 10-20, 20-35 and 35-50 cm) incubated under oxic or anoxic conditions for 1 (a,c,e,g) or 4 (b,d,f,h) months at 5 and 15 °C.	138
Figure 5.4	Relationships between the DOC and soluble Fe, comparing the differences in concentration between oxic (circles) and anoxic (triangles) conditions at 5 (black) and 15 (red) °C for samples through depth after 1 month (left) and 4 months (right). . . .	141

Figure 5.5	Plots of mean molar DOC:Fe ratios for a) Soil extracts from laboratory experiment under oxic and anoxic conditions for the shallow soil horizon (0-10 cm) samples at 5 and 15 °C for 1 and 4 months, where molar DOC:Fe values are significantly different $p < 0.05$; b) Field stream samples from Intact (black bars) and Disturbed (grey bars) watersheds at baseflow and after storm events (refer to Table 5.4 for the dates).	142
Figure 5.6	Comparing soluble Fe and pH, after 1 month (left) and 4 months (right) comparing the differences in concentration between oxic (circles) and anoxic (triangles) conditions at 5 (black) and 15 (red) °C for samples through depth.	143
Figure 5.7	Variation in a) mean stable isotope ratio of C ($\delta^{13}\text{C}$) and b) molar DOC:Fe ratio through depth for soil solids from increments before (Initial) and after 4 month incubation under Oxic and Anoxic conditions at 15 °C.	145
Figure 5.8	Q-Q plots of the data distribution comparing quantiles of molar DOC:Fe for extracts from anoxic incubation (combining data from 1 and 4 months and 5 and 15 °C) and stream data at Abraham's Lake, Nova Scotia, Canada.	149
Figure 5.9	Stable isotopic composition ($\delta^{13}\text{C}$, ‰) of plotted against SUVA_{254} for stream DOC in disturbed and intact sites for baseflow (slope = -1.1) and stormflow (slope = -1.3).	150
Figure 6.1	Soil texture triangle for composite soils (n=9) from horizons through depth at Young and Mature sites in Mooseland, NS.	173

Abstract

Losses of soil organic matter (SOM) from mineral soils through depth have been documented following intensive forest harvesting practices such as clear-cut harvesting, and this has implications for global carbon cycling. SOM is thought to be primarily stabilized in mineral soils by binding with hydroxide minerals, although evidence has determined that SOM associated with particular pools of minerals can be destabilized. The observed losses likely result from soil climatic changes following clear-cutting, although specific mechanisms remain uncertain. In order to improve our mechanistic understanding, it is necessary to quantify and characterize the distribution of mineral-associated SOM pools in disturbed forest soils through depth, and to manipulate both biotic and abiotic factors to examine their impacts upon mineral soil C release. The distribution and character of mineral-associated SOM pools through depth from adjacent Mature (110 yr) and Young (35 yr) forests were measured, and short-term respiration responses and shifts in soil and dissolved organic carbon (DOC) chemistry were analysed to determine the effects of soil microclimate shifts on SOM decomposition. The impact of soil temperature and redox conditions on mineral soil carbon mobilization due to reductive dissolution was also investigated. Organo-metal complex (OMC) pools dominated the distribution of mineral SOM, with the highest content in illuvial horizons of the Mature compared to the Young site, which indicates that it is susceptible to loss following clear-cutting. Short-term incubations revealed that temperature sensitivity of soil respiration was highest in B_f horizons, which could account for enhanced SOM losses due to microbial decomposition. Enhanced DOM aromaticity was measured following incubation, especially after rewetting, and was also observed following incubation under anoxic conditions and in disturbed catchment streams. Chemical data suggest that reductive dissolution may account for the mobilization of surface OMC pools. Results from this research indicate that the mineral-associated pools that account for profile C storage could be susceptible to loss through decomposition and mobilization due to the changes in soil climatic conditions following forest clear-cut harvesting.

List of Abbreviations and Symbols Used

ANOVA analysis of variance

$\delta^{13}\text{C}$ stable isotope of carbon

Crys crystalline mineral-associated organic matter pool

CDOM chromophoric dissolved organic matter

DI deionized water

DOC dissolved organic carbon

DOM dissolved organic matter

DOM_{ex} extracted dissolved organic matter

FT freeze-thaw

GLMM generalized linear mixed model

HMW high molecular weight

LMW low molecular weight

MW molecular weight

OM organic matter

OMC organo-metal complexes

OP optimum moisture

Pcrys poorly-crystalline mineral-associated organic matter pool

Q₁₀ temperature sensitivity

R_s soil respiration

RW dry-rewet

SOM soil organic matter

SUVA₂₅₄ specific UV-Vis absorbance

S_r spectral slope ratio

WS water soluble mineral-associated organic matter pool

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Chapter 1

Introduction

“Humankind as a whole is a powerful geologic force.”

V.I. Verdansky

1.1 Why study carbon?

Carbon (C) is a central element of organic life on Earth, performing a range of biogeochemical roles, including metabolic and structural functions, but since the Industrial Revolution, anthropogenic activities have resulted in an increase of atmospheric C. This increase occurs through several processes: 1) the combustion of organic compounds, primarily a result of fossil fuel production processes and consumption, which has resulted in increased C emissions to the atmosphere; 2) cement production, which transforms mineral carbonates, and 3) land-use disturbance through agriculture and forestry, which redistributes C among components of the biosphere, with the concomitant emissions of C gases to the atmosphere (Schlesinger and Berhardt, 2013). Increased atmospheric carbon dioxide (CO₂) and other greenhouse gases directly influence global climate change through their tendency to absorb and re-release radiative energy, enhancing Earth's natural greenhouse effect. Global warming can further increase C emissions by increasing chemical reaction rates that destabilize stored C, which represents an important positive feedback to global climate change (IPCC, 2013).

The Anthropocene epoch has been recently proposed to mark the seminal influence of human activity on the transformation of Earth, especially notable in soils (Richter et al., 2015). As humans reshape the terrestrial landscape, soil organic matter (SOM) storage can be reduced. An examination of the global pools of C reveals that SOM is a globally important pool of C, with more than twice the amount of C stored in terrestrial compared to atmospheric pools and is a significant

component of terrestrial C budgets (Clemmensen et al., 2013). A large proportion (>50%) of soil C stock resides in the deeper mineral subsoil (Cerri et al., 2007; Clemmensen et al., 2013; Jobbagy and Jackson, 2000; Rumpel and Kogel-Knabner, 2010; Rumpel et al., 2015; Trumbore and Czimczik, 2008); however, evidence from several recent studies are suggesting that “stable” subsoil mineral soil C may be susceptible to destabilization (Bernal et al., 2016; Fontaine et al., 2007; Lawrence et al., 2015) as a consequence of land-use activities like forest harvesting (Basile-Doelsch et al., 2009; James and Harrison, 2016; Noormets et al., 2014). Since any alteration of this important store of soil C is likely to have serious consequences for C cycling, including enhanced greenhouse gas emissions, improving our understanding of the processes that alter soil C storage and stability through depth in forests, especially in the mineral soils of forests that have undergone routine clearcutting (Dean et al., 2016; Diochon et al., 2009; Prest et al., 2014; Zummo and Friedland, 2011), is central to this issue (Achat et al., 2015).

Any human impact on the destabilization of this important store of C is essential to accurately account for, especially in light of mounting pressure on reducing C emissions to mitigate climate change; therefore, there is an urgent need for the development of a mechanistic understanding of how land-use change can destabilize C. Uncertainty regarding the impacts of forest harvesting limits our ability to predict the impacts of forest management on global carbon cycling and the resulting feedbacks to climate change. Furthermore, accurate and relevant knowledge is necessary for policy makers as they make decisions about the sustainability of intensive forest harvesting practices, considering the broader impacts of anthropogenic activity upon soil health and terrestrial C cycling.

1.2 Soils

Biogeochemistry is the study of the chemical cycling of Earth's components through terrestrial and aquatic environments, mediated by organisms, and soil represents an interface where the dynamic interplay among Earth's subsystems - biosphere, geosphere, and hydrosphere - is brought to life. Soil is a complex material with a porous structure, consisting of minerals, organic matter, water and gases, and is teeming with life. Soils are critical to human existence, serving a multitude of key ecosystem

functions for humans, as a substrate for plant growth, providing mineral and organic nutrients, and regulating the flow of water through the landscape. Many have argued for the recognition of the special role soil plays in our human story as a critical resource; but as is typical, it is most often in times of scarcity or absence that we recognize its importance. At the height of the Great Depression's calamitous “dust-bowl”, F.D. Roosevelt astutely observed, “The nation that destroys its soil, destroys itself.”

The study of soils was formalized by Hans Jenny's “Factors of Soil Formation” (Jenny, 1941), a treatise, that alongside “The Biosphere” (1926) by Vladimir Ivanovich Verdansky (the “Father” of Biogeochemistry), advanced the science of modern pedology. It is only in recent history that the study of soil and its biogeochemical cycling has been contextualized within the pressures placed upon it through anthropogenic activity.

Soils occupy a niche that gives them a dynamic character and subtle memory. The organic content of surface soil can change rapidly (in as little as 10 to 100 years) in response to climatic or land management practices. In contrast, extensive weathering of a soil's mineral content requires much more time. Soils thus acquire their basic attributes at very different rates. They reflect both the present and the past, recording how they have changed in response to recent events while they document changes (like weathering), that have occurred over tens of thousands of years.

McSweeney and Norman, 1996

Soil carries the imprints of cycling at many scales, carrying a “pedomemory” of its formation, disturbance and recovery (Nauman et al., 2015). This makes it a complex and fascinating subject for study — soil's dynamic and responsive nature allows researchers to both investigate its functioning and predict the impact of future disturbances, all while considering its formative influences and historical context.

1.2.1 Pedogenesis and soil characterization

Pedogenesis is a continuing process of soil formation that ultimately begins with primary mineral weathering of parent material and that results in the development of a soil profile over time, developing a soil's characteristic horizons and colours. Jenny (1941) described the five main factors that interact and lead to the formation of soils: Time, Climate, Parent Material, Topography, and Organisms. The relative importance of each factor depends on the location, but an understanding of the formation and disturbance of any soil takes the contribution of each factor into account. Pedogenesis results in the formation of particular soil types depending on combinations of conditions that lead to the development of particular soil morphology, which can then be classified according to a taxonomic system.

1.2.2 Podzols

Podzols (Canadian Soil Classification) dominate many northern boreal and temperate landscapes (Sanborn et al., 2011), and these soils are known to be acidic and nutrient poor, and primarily covered by coniferous forests and ericaceous vegetation. Podzols are most often formed in sandy soils with ample rainfall for translocation of metals complexed with organic acids leached from surface organic layers. Globally, podzol soils (or spodosols in U.S.D.A. taxonomy) represent a coverage of 485 million Ha, storing 71 Ptg C world-wide, which accounts for 5% of the global C store, an estimate that includes the contribution from deeper mineral soils (below 10-20 cm) (Jobbágy and Jackson, 2000; Rumpel and Kögel-Knabner, 2010; Trumbore and Czimczik, 2008).

Variations in the character and quality of minerals and SOM through depth are particularly notable in podzols, resulting in a distinctive appearance and sequence of horizons (Figure 1.1). In addition to organic matter surface layers, these soils are characterized by the formation of leached eluvial (A_e) horizons and an illuvial (B) horizon, a brightly-coloured red to orange layer that accumulates weathering products as secondary minerals in the form of precipitates and coatings (Buurman and Jongmans, 2005). Often, SOM accumulates in association with Fe and Al across a range of geometries and forms, as a nanoparticulate colloidal mineral phase, a poorly-crystalline phase co-precipitated with ferrihydrite and/or adsorbed to hydroxylated



Figure 1.1: Photograph of the mineral horizons of typical Orthic Humo-ferric podzol from this area of central Nova Scotia, Canada. The first 4 white dots from the top indicate 10 cm increments through the mineral soil. The first dot from the top, below the dark brown organic (O) horizon, is at 0 cm. The ashy leached A_e horizon is variable in thickness but typically 5-10 cm thick, followed by reddish B_f horizons that extend down to at least 20 cm, followed by a 15 cm increment in the BC transition horizon. Photograph by Amanda Diochon, used with permission.

crystalline mineral surfaces (Eusterhues et al., 2011; Kögel-Knabner et al., 2008). Aromatic humic acids accumulate in dark coloured humic-rich B_h and bright Fe-rich B_f horizons, associated with Fe and Al minerals. These play a number of critical roles in soils, including electron shuttling and pH buffering (Lovley et al., 1996), soil aggregation, and as a nutrient source (Davies et al., 2001). Spodic B horizons in well-expressed podzols are responsible for a large C storage in soils (Fritsch et al., 2009); therefore, disturbances that alter the stability of mineral soil C are important to understand.

1.2.3 Association of soil organic matter with minerals

SOM in northern temperate forest soils is primarily associated with a suite of Fe and Al minerals, including a range of mineral structural forms that differ based on their crystallinity, an indicator of the structural order of repeating mineral crystal units. A range of Fe oxide minerals commonly exists in soils (from least crystalline to most crystalline):

1. Colloidal organo-metal complexes are prevalent in soils, association with organic matter through ligand exchange interacting with oxide groups of Fe minerals, especially ionic forms of Fe and Al.
2. Poorly crystalline minerals, such as ferrihydrite ($(\text{Fe(III)}_2\text{O}_3 \cdot 0.5\text{H}_2\text{O})$), a bright red mineral that characterizes spodic horizons, and imogolite ($\text{Al}_2\text{SiO}_3(\text{OH})_4$), an Al organo-mineral. Ferrihydrite, in particular, is a poorly-crystalline Fe-oxide mineral with indeterminate structure and composition of organic matter and iron co-precipitates, known to be of high surface area, microbially synthesized, and influenced by the amount of organic matter present (Kleber et al., 2005; Mikutta et al., 2006). Soils also contain appreciable amounts of Al, present as aluminosilicate clay minerals and imogolite, also thought to confer stability to precipitated OM (Scheel et al., 2007).
3. Goethite (FeO(OH)) and hematite (Fe_2O_3), are crystalline Fe oxides and hydroxides that dominate in subsoils where the organic matter content is lower. Surface adsorption to highly crystalline minerals such as Fe and Al hydroxides in podzol soils is said to account for lower organic matter turnover (Torn et al.,

1997). Over time, ferrihydrite can mature through Ostwald ripening, whereby more crystalline phases of Fe oxides such as goethite or hematite are formed, but the presence of organic matter inhibits this process (Parfitt, 2009).

Distinct organic matter interactions with minerals across a range of forms and geometries have been thought to confer varying stability to bound organic matter and therefore lead to the existence of multiple pools of SOM (Lawrence et al., 2015). For instance, an exchangeable and/or labile pool is dominated by ionic and ligand interactions with non-crystalline Al and Fe (ie. organo-metal interactions), whereas a stable pool with a longer turnover time is associated through covalently-bonded crystalline mineral phases (Dungait et al., 2012; Kleber et al., 2005, 2011).

1.3 Nature of SOM in mineral-associated organic matter pools

1.3.1 Soil organic matter - solid SOM pool

Soil organic matter is a complex heterogenous mixture of organic molecules derived from senescent vegetation, including aboveground litter and root structures, and microbial biomass. Its composition varies continuously in pace with inputs that vary seasonally with changes in aboveground vegetation, and is modified by the activity of soil microbes (Bradford and Crowther, 2013; Liang et al., 2017). SOM is composed of a continuum of organic compounds, from water-soluble, colloidal and hydrophobic organic compounds, assembled loosely into a “supramolecular assembly” (Kleber and Johnson, 2010), in association with soil minerals and mineral surfaces. Organic molecules and associated minerals are arranged zonally (Kleber et al., 2007), with the most strongly bonded associations close to the mineral surface, weakening in strength with increasing distance from the mineral surface.

While SOM content is high in surface organic soil layers and its concentration relative to mineral mass decreases through depth, its composition also varies. SOM is high in surface layers, as a result of recent litter inputs, and is transported to deeper layers through mechanical mixing or leaching of solubilized components from decaying litter in forest floor or organic layer solution (Kalbitz and Kaiser, 2008), to root litter and fungal mycelia in the rhizosphere (Clemmensen et al., 2013). In deeper mineral soil horizons, SOM is autochthonous, primarily composed of local microbial

compounds including microbial ectopolymeric substances (EPS), microbial necromass (Rumpel et al., 2015) and metabolites (Kallenbach et al., 2016; Kögel-Knabner, 2017; Li et al., 2015; Spence et al., 2011). Deeper profile SOM is distributed heterogeneously (Vögel et al., 2014), and has a low C concentration relative to mineral mass than SOM nearer the surface.

Through depth in soil profiles, an enrichment in $\delta^{13}\text{C}$ of bulk soil organic matter is typically observed (Figure 1.2). Some studies explain this trend through the microbially-mediated isotopic fractionation during respiration (Crow et al., 2006; Diachon et al., 2009; Nadelhoffer and Fry, 1988). Other research explains this enrichment through depth through an increasing contribution of microbially-processed SOM (Bostrom et al., 2007; Kohl et al., 2015; Clemmensen et al., 2013, 2015; Rumpel et al., 2015). Ultimately, the change in soil $\delta^{13}\text{C}$ likely reflects patterns in C turnover: ^{13}C in deeper soils has more local microbial recycling under conditions of C and nutrient scarcity, with uptake of ^{13}C -enriched inorganic C (i.e. CO_2) as a C source, thus keeping C tightly cycled (Ford et al., 2007). Kohl et al. (2015) demonstrated that $\delta^{13}\text{C}$ through depth reflected the varying contribution from a continuum of microbial groups: at the surface, SOM is fungal-dominated (with a relatively lower $\delta^{13}\text{C}$ value) progressing downwards to a bacterial-dominated microbiome (with a relatively higher $\delta^{13}\text{C}$ value) .

Some research has also documented that the character of SOM varies depending on the mineral crystallinity (Jones and Singh, 2014). For instance, aliphatic SOM is also associated with crystalline secondary minerals (Adhikari and Yang, 2015) as stable inner-sphere compounds, while aromatic SOM is preferentially associated through ligand exchange with organo-metal or poorly-crystalline minerals (Sanderman et al., 2014) and is stabilized through polyvalent metal-cation bridges. While these trends have been documented, an understanding of the controls on the nature of SOM stabilized with minerals still remains poorly understood.

1.4 Dissolved organic matter - aqueous SOM pool

Dissolved organic matter (DOM) is a dynamic and mobile pool of SOM. This dissolved phase of SOM in soils is in equilibrium with soil surfaces. This exchange process is described as "chromatographic" (Kalbitz and Kaiser, 2008; Shen et al., 2014), a

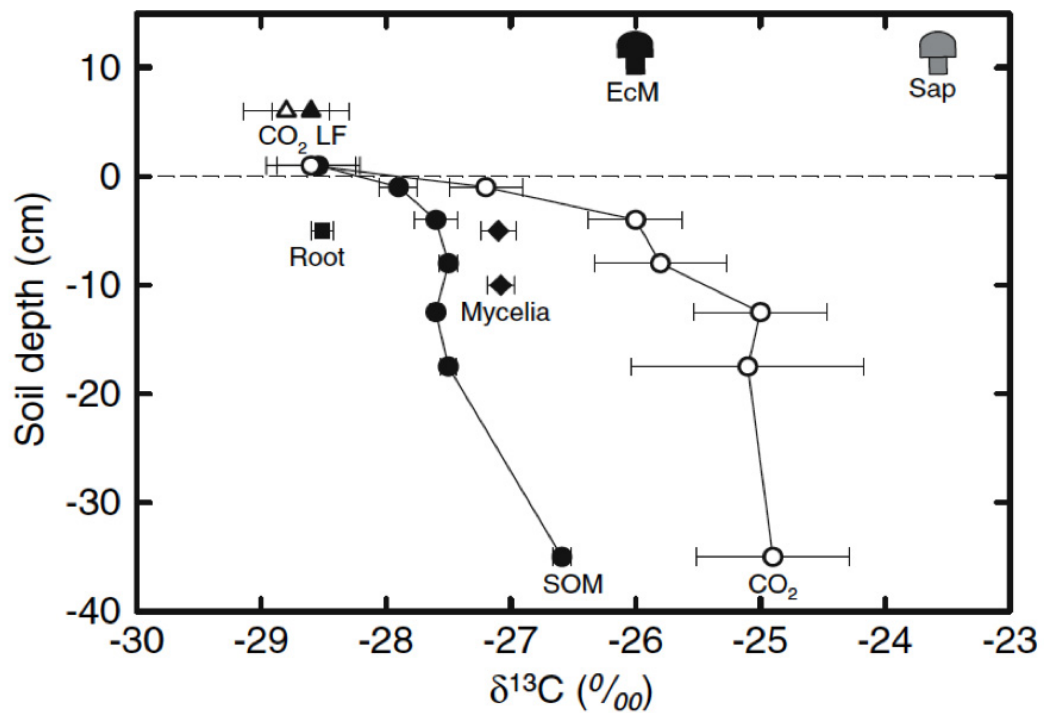


Figure 1.2: Depth profiles of $\delta^{13}\text{C}$ in terms of soil organic matter (SOM, filled) and respired CO_2 (open). The top of the mineral horizon is the 0 cm soil depth, above which are litterfall (LF) and litter layers. Roots (<2 mm) and fungal mycelia are also included. Mushrooms indicate the mean value for ectomycorrhizal (EcM, black) and saprotrophic (Sap, gray) sporocarps (Bostrom unpublished). Error bars indicate standard error. From Bostrom et al., (2007).

conceptual model that recognizes the role of mineral surfaces, hydrology, the chemical environment, and interaction with microbial activity (Shen et al., 2014) in controlling the selective binding, nature and mobility of organic compounds (Guggenberger and Kaiser, 2003; Heckman et al., 2012; Kalbitz and Kaiser, 2008; Rasmussen et al., 2005; Strahm et al., 2009), in particular, as the soil solution interacts with soil minerals, such as Fe and Al hydroxides (Sanderman et al., 2014). A longer residence time results in a higher degree of microbial processing.

Dissolved organic matter can be further modified as water transports organic matter throughout the soil, with alterations through inputs and shifts in redox conditions. Some have noted that a smaller portion of the DOM collected at a certain depth is from local SOM, estimated at up to 40% (Bengtson and Bengtsson, 2007), and that the remainder is transported, and produced by microbial activity (Chantigny, 2003). Recent evidence has found that microbes are important in this process, as they modify their local chemical environment and release mineral binding ligands, and can therefore simultaneously release OM from minerals (Clarholm et al., 2015), including the stable or “recalcitrant” mineral-stabilized fractions of SOM (Kleber, 2010).

While some DOM can be easily mobilized and transported to aquatic systems through groundwater or overland flow, some fractions of DOM, such as dissolved organic carbon (DOC) can be stabilized, associated with secondary minerals, and this contributes to long-term forest soil C storage (Fröberg et al., 2007; Kramer et al., 2012). The presence of Fe and Al poorly-crystalline mineral phases was identified as most important factor controlling the adsorption of DOC by soils by Kothawala and Moore (2009), due to the high surface area of these minerals and their affinity for aromatic carbon (Kramer et al., 2012; Sanderman et al., 2014), a large constituent of terrestrial SOM.

1.5 Soil organic matter destabilization

1.5.1 Challenging an old paradigm

Net accumulation of C in soils results from a balance between inputs and outputs, and C persistence results from protection against solubilization and microbial decomposition. Only organic matter that is stable can persist and be stored in soils. SOM is

ultimately stabilized in soils through conditions that protect against or limit oxidative activities such as decomposition and that determine reaction rates and dissociation constants, altering solubility (Sinsabaugh, 2010). A myriad of physical factors, which vary through depth in soil profiles and across landscapes, are recognized to play roles in SOM persistence, and are included as parameters in numerical modeling of soil organic matter dynamics. These include (not in order of relative importance): temperature, pH, moisture content, redox status, ionic strength, nutrient accessibility, and labile carbon availability, in addition to a consideration of a compound's biochemical complexity, clay and other soil mineral contents (Baldock and Skjemstad, 2000; Chenu and Plante, 2006; Conant et al., 2011; Davidson, 2015; Davidson et al., 2006; Doetterl et al., 2015; Heckman et al., 2009; Hicks Pries et al., 2016; Kleber et al., 2007; Lawrence et al., 2015; Torn et al., 1997; Wagai and Mayer, 2007). These factors together determine the turnover time of SOM, and therefore its persistence, in soil (von Lützow et al., 2006; Schmidt et al., 2011), although the relative importance of these factors remains uncertain.

The understanding of SOM persistence in soils over the past few decades has focused largely on biochemical controls on SOM decomposition, traditionally thought to be controlled in soils by the molecular complexity of plant litter compounds. However recent research challenges this view (Dungait et al., 2012; Kleber et al., 2011; Kleber, 2010; Lehmann and Kleber, 2015; Marschner et al., 2008; Mikutta et al., 2006). Subsoil SOM was traditionally assumed to be stable, as evidenced by its biochemical recalcitrance and older radiocarbon age (Trumbore and Czimczik, 2008). An assumption of stability based on chemical recalcitrance no longer holds, however, especially in soils subjected to disturbances that alter the physical, chemical and biological environment. Research demonstrates that SOM classified as recalcitrant can readily be decomposed. For instance, Fontaine et al. (2004) noticed that supply of fresh substrate stimulated the decomposition of recalcitrant C, which highlights the potential for SOM decomposition to proceed if particular environmental constraints are removed (Risk et al., 2008). However, a new understanding of SOM is evolving: one in which SOM is a highly-processed heterogeneous mixture of compounds modified by microbial activity, controlled by soil climate and nutrient availability, and

ultimately constrained by interactions with minerals (Kleber et al., 2011). This revised understanding of SOM highlights the central role of the physical protection of SOM as the primary constraint that explains its persistence.

1.6 Mineral control of SOM stability

SOM protection is offered through interaction with the mineral matrix through aggregation, occlusion within soil structure, especially fine pores, and direct sorption, which is connected to SOM binding and to soil aggregation, and which can impose spatial constraints (Davidson and Janssens, 2006; Marin-Spiotta et al., 2014; Risk et al., 2008; Schmidt et al., 2011). SOM accessibility for biodegradation is constrained by the interaction with the soil matrix (Davidson and Janssens, 2006; Gabriel and Kellman, 2014; Marin-Spiotta et al., 2014; Risk et al., 2008; Schmidt et al., 2011). The bioavailability of SOM has been linked with the content of Fe and Al hydroxides and the mineralogy of soil minerals (Andreasson et al., 2009; Gentsch et al., 2015; Heckman et al., 2009, 2011; Saïdy et al., 2015). Since minerals modulate SOM stability and DOM composition/dynamics, SOM storage is ultimately susceptible to disturbances that alter the physical, chemical and biological environment. Carbon in SOM can be destabilized as dissolved organic carbon as a result of the release from minerals (both abiotic and biotic) and in gaseous form as a result of microbial heterotrophic respiration (biotic).

Although the association between minerals and carbon storage has been long recognized (Torn et al., 1997), a complete understanding of the controls on its destabilization and its mineralization and mobilization is still lacking. Even worse, inaccurate parameterization of C turnover models leads to potential misunderstandings about the actual impacts of harvesting and other land-use strategies on mineral soil OM stability. For instance, many current forest harvesting models, which do account for soil C and N storage changes in soil as a result of harvesting, do not model soil deeper than 10 or 20 cm. The need for a more complete understanding of the role of soil minerals in SOM stability has pushed the scientific community to “dig deeper” and consider the role of mineral soil C more closely (Baisden and Parfitt, 2007; Diochon et al., 2009; Kleber et al., 2005; Rumpel and Kögel-Knabner, 2010; Rumpel et al., 2010; Salome et al., 2010; Sanaullah et al., 2011). Current research recognizes both

its importance as a substantial SOM store, and its vulnerability to disturbance.

1.7 Soil organic matter and land-use

Large terrestrial areas are susceptible to alterations in C cycling and storage processes from intensive forms of forest disturbance (Achat et al., 2015). In temperate and boreal coniferous forests of Canada, clearcutting accounts for a change in 0.2% of forest cover annually (Canadian Forest Service, 2013), and large areas of Nova Scotia in Eastern Canada have been heavily modified by this intensive form of forest harvesting. While extensive effort has been devoted to developing an understanding of the response of forest biomass and forest floor organic matter to harvesting disturbance, little is understood about how deeper mineral soil responds (i.e. below 10-20 cm), despite the fact that many studies have demonstrated that a large proportion of soil C stock resides in the deeper subsoil (Clemmensen et al., 2013; Jobbagy and Jackson, 2000; Rumpel et al., 2015; Rumpel and Kögel-Knabner, 2010; Trumbore and Czimczik, 2008).

Since mineral soil horizons play a significant role in terrestrial C budgets (Clemmensen et al., 2013), understanding the influence of anthropogenic disturbances such as forest harvesting on mineral soil C stability is critical to the development of a full picture of the impacts on C cycling. Forest harvesting-related alterations to soil organic matter (SOM) storage have been observed, notably in the mineral soil (Dean et al., 2016; Diochon and Kellman, 2008; Falsone et al., 2012; Grand and Lavkulich, 2011; Petrenko and Friedland, 2015; Prest et al., 2014; Zummo and Friedland, 2011). A minimum in SOM storage, which represents the greatest cumulative net disruption to the size of the C pools, has been observed to exist in the decades following forest clear-cutting in Northern temperate forests (Diochon and Kellman, 2008; Prest et al., 2014; Zummo and Friedland, 2011).

Although recent meta-analyses have documented that intensive forest harvesting (i.e. clear-cutting) threatens forest C storage (Achat et al., 2015; Kurz et al., 2014), a consensus on the impacts of forest harvesting on SOM storage is still lacking: consistent losses of soil C following harvesting are not universally observed (e.g. Johnson and Curtis, 2001; Nave et al., 2010; Thiffault et al., 2011; Wan et al., 2018). This may, in part, be due to inconsistencies amongst studies (Clark and Johnson, 2011;

Moinet et al., 2010; Pickett, 1989). Studies investigating soil C storage typically only sample the upper profile topsoil (0-10 cm or 0-20 cm), although many have noted that the largest C stocks are in subsoil (James and Harrison, 2016; Rumpel and Kögel-Knabner, 2010; Trumbore and Czimczik, 2008). Accurate and systematic efforts to investigate controls on SOM storage in mineral soils are rare (Marín-Spiotta et al., 2014), especially in subsoils (Trumbore and Czimczik, 2008). It is challenging to establish site differences using field sampling of bulk soil C due to issues of high spatial variability (Bekele et al., 2013) due to inconsistency among studies in sample collection protocols, including the decision as to whether to sample by depth increments or horizons (Moni et al., 2010). Among studies there are also issues with interpretation of site differences when using space-for-time substitution approaches such as chronosequence studies (Clark and Johnson, 2011; Pickett, 1989). Inconsistencies amongst studies, including sampling methodology and site selection, hinder the development of a clear understanding of how forest harvesting alters C storage in mineral soils and obfuscate clear interpretations.

1.8 Other biogeochemical impacts of forest harvesting disturbance

While forest harvesting-related alterations to SOM storage have been observed, notably in the mineral soil in the decades following harvesting, studies have documented other forestry-related impacts to C cycling. Enhanced greenhouse gas emissions have been measured from soils in the years following clear-cutting (Humphreys et al., 2006; Kellman et al., 2015; Kim, 2008; Lavoie et al., 2013), and increased export of dissolved organic matter and mineral cations to aquatic systems (Kreutzweiser et al., 2008; Moore et al., 2008; Oni et al., 2015; Qualls et al., 2000; Schelker et al., 2013) from harvested forest watersheds have been documented. Both soil C surface fluxes and soil C mobilization from terrestrial to aquatic systems can represent important losses of mineral SOM. Some studies report a short time frame for recovery (Glaz et al., 2015; Jewett et al., 1995) or no consistent impact on soil carbon fluxes (Pumpanen et al., 2004), although not all studies are consistent in the magnitude of disturbance and the length of time over which the system recovers, making it difficult to compare the impacts of forest harvesting across studies. Nevertheless, enhanced terrestrial export of DOC to aquatic systems following forest disturbance is important to consider,

regardless of the length of time over which it occurs, due to important impacts downstream from Fe, DOC, dissolved CO₂ and other dissolved nutrients and pollutants (Lapierre et al., 2013; Wallin et al., 2015; Weyhenmeyer et al., 2014).

1.9 Potential mechanisms to explain mineral soil C losses

Forest clearcutting leads to myriad physico-chemical changes at the landscape level that may explain observed SOM losses. Pedogenic processes involving SOM may be sensitive to environmental changes that result from the alteration of surface vegetation and soil climate, i.e. soil temperature and moisture (Basile-Doelsch et al., 2009; Hogberg and Read, 2006; Mossin et al., 2001). Disturbances that alter nutrient delivery to soils, especially labile C (Fontaine et al., 2007), that change the soil chemical environment through depth, or that redistribute or expose mineral surfaces can result in SOM destabilization (Doetterl et al., 2012). The removal of tree cover alters the radiative energy balance through reduced interception of solar radiation, exposing deeper mineral soil to a larger daily and seasonal amplitude than sites with intact forest cover (Bekele et al., 2007; Kellman et al., 2015). Since temperature exerts primary control on SOM decomposition (Gabriel and Kellman, 2014; Kellman et al., 2015), this increased heat leads to higher soil temperatures which increases microbial activity and reaction rates. Clear-cutting also results in a step change in soil moisture when tree cover is removed, with an increase in the frequency and severity of dry-rewetting events and freeze-thaw cycles, all to deeper depths than before vegetation removal and soil mixing. A dry-rewetting cycle can increase the water repellency (i.e. hydrophobic character) of OM on mineral surfaces, thus changing mineralization and DOM binding (Doerr and Thomas, 2000; Lamparter et al., 2009; Schimel et al., 2011). Freeze-thaw has been shown to also have impacts on SOM binding with minerals and decomposition rates (Foster et al., 2016; Herrmann and Witter, 2002; Yu et al., 2010), as well as soil structure itself. These disturbances both alter the soil architecture and lead to changes in organic matter and mineral binding, resulting in a suite of changes to the biogeochemical cycling of C and other elements such as Fe (Hobbie et al., 2000; Kim et al., 2010; Williams and Xia, 2009).

In addition to altered soil biogeochemistry following physical changes to the soil surface with the removal of tree cover, a rise in the water table may result. Tree

removal alters landscape hydrology, including discharge (Sanderman et al., 2008), creating periodic or seasonal flooding conditions that change the redox conditions (Buettner et al., 2014; Thompson et al., 2006) and pH of the soil. Soil organic matter can therefore be destabilized in flooded soils (Schelker et al., 2013) and then subsequently mobilized and transported to connected aquatic environments as a consequence of these changes in hydrology. Iron also has an important connection to C cycling (Davidson et al., 2003; Weyhenmeyer et al., 2014), and has been connected to organic matter decomposition (Cory et al., 2013; Emsens et al., 2016; Hall and Silver, 2013); therefore, an understanding of C dynamics across the terrestrial-aquatic interface requires an examination of Fe. Moreover, changes in the soil mineral assemblage as a consequence of these alterations may reduce the ability of podzolic soils to stabilize SOM (Diochon and Kellman, 2009; Grand and Lavkulich, 2011; Lacroix et al., 2016; Lawrence et al., 2015). Substrate availability is an important factor that can alter the apparent response to temperature (Davidson and Janssens, 2006), and so a better understanding of how minerals can alter both the magnitude and nature of the source of respiratory C would enhance efforts to predict changes in soil carbon storage following disturbance. Furthermore, the nature and amount of organic matter inputs change along with the vegetation sequence of secondary succession, resulting in a potential increase in SOM decomposition and mobilization.

When the soil physico-chemical environment is altered, the potential exists for a change in the binding of OM with minerals. In the Acadian Forest region of Nova Scotia, Canada, while studies have documented losses of mineral soil C from the soil profile (to 50 cm) following clear-cutting (Diochon and Kellman, Prest et al., 2014), knowledge about the specific mechanisms that are relevant to explain the observed losses are lacking. Furthermore, studies have not yet considered how changes in soil moisture and temperature - for example, increasing daily and seasonal amplitude of soil temperature, frequency of microclimatic extremes such as dry-rewet or freeze-thaw, and duration of soil flooding or drought - may influence the decomposition of SOM and the mobilization of DOC in these forest soils through depth.

1.10 Analytical approaches to study SOM storage and stability

Understanding how SOM chemistry varies through depth in soil relies on a combination of traditional analysis, including soil extractions, particle size distribution and elemental analysis, combined with new state-of-the-art analytical techniques, including the use of stable isotopes. Attempts to separate SOM into functional pools *ex situ* have relied on various extraction methods that isolate fractions of carbon by particle size, density characteristics, progressive disruption of soil structure, and mineral association (Lopez-Sangil and Rovira, 2013; von Lutzow et al., 2007; Redmile-Gordon et al., 2014; Six et al., 2001; Zakharova et al., 2014). The stability of SOM and the impact of particular environmental conditions on SOM decomposition has also been assessed through incubations (Andrews et al., 2000; Bernal et al., 2016; Crow et al., 2006; Fontaine et al., 2004; Gillabel et al., 2011; Dungait et al., 2012; Hartley and Ineson, 2018; Heckman et al., 2009; Hicks-Pries et al., 2016; Kalbitz et al., 2003; Kemmitt et al., 2008; Larionova et al., 2007; Moyano et al., 2012; Mueller et al., 2014; Ohm et al., 2007; Salome et al., 2010; Xu et al., 2014). Despite their limitations (Oburger and Jones, 2012; Risk et al., 2008), incubations confer many advantages; for instance, they allow for controlled testing of the impacts of one variable at a time.

1.10.1 Natural abundance of stable isotopes of C in soil and DOC

Stable isotope signatures of C ($\delta^{13}\text{C}$) are integrative measures of ecosystem processes (West et al., 2006), and have been used to reveal differences in pools of SOM (Billings and Richter, 2006; Bostrom et al., 2007) which vary in chemical character and turnover time through depth (Figure 1.2). The stable isotope signatures of respired CO_2 ($\delta^{13}\text{C-CO}_2$) collected during incubation experiments has been used to indicate sources of SOM for decomposition. The respired $\delta^{13}\text{C-CO}_2$ often differs from the stable isotope signature of the bulk soil C, and this difference may vary depending on biological and physical fractionation processes (Bowling et al., 2009). Difference the $\delta^{13}\text{C-CO}_2$ may provide information the impact of disturbance on soil C cycling (Trumbore, 2006; West et al., 2006; Zakharova et al., 2014). In addition, stable isotope ratios of DOC ($\delta^{13}\text{C-DOC}$) are not only integrative measures of ecosystem functioning (Billings and Richter, 2006), but also indicate the relative strength of

microbial vs. plant contribution to DOM quality (Cleveland et al., 2004; Sanderman et al., 2009).

1.10.2 Dissolved organic carbon chemistry - Indicators

Shifts in DOC chemistry can provide information about altered processes, mineral interactions and C cycling. Soluble OM pools such as extractable DOC have also been shown to act as indicators of disturbance (e.g. Ghani et al., 2003), and optical measures of DOC character have been widely used: indexes such as specific UV-Vis absorbance (SUVA) and spectral slope ratio (S_r) provide a proxy for relative aromaticity and the molecular weight of chromophoric DOM (CDOM), a fraction of DOM that is coloured (Helms et al., 2008; Weishaar et al., 2003). These serve as indicators of changes in DOM quality (Hood et al., 2006; O'Donnell et al., 2014). Stream DOC before and after storm events can provide information about hydrological flowpaths and the origin of DOC within the soil profile (Hood et al., 2006; Kothawala et al., 2014; Lambert et al., 2011; Malik and Gleixner, 2013; Sanderman et al., 2008). And the molar ratio of DOC to soluble Fe (DOC:Fe) provides information about the nature of metal-organic complexes, which varies with the chemical environment (Jansen et al., 2002; Mossin et al., 2001): soil solutions with low DOC:Fe ratios are associated with soluble DOC and Fe complexes (Riedel et al., 2013). Finally, since mineral phases can modify DOC composition due to preferential sorption of aromatic and phenolic compounds (Heckman et al., 2011; Kramer et al., 2012; Sanderman et al., 2008), DOC character can thus be an indicator of relevant mineral phases that stabilize OM in podzols (Kaiser and Kalbitz, 2012; Kalbitz et al., 2005). Measurement of the $\delta^{13}\text{C}$ of DOC and of respired CO_2 has been used to indicate the source of substrate for respiration and to indicate the impact of disturbance on soil C cycling (Bostrom et al., 2007; Trumbore, 2006; West et al., 2006; Zakharova et al., 2014).

1.10.3 Quantifying organic matter-mineral associations

Attempts to understand how minerals control C storage have generally relied on studies of soil textural fractions, especially clay (Kogel-Knabner et al., 2008), soil mineralogy (Heckman et al., 2009), and use of physical fractionations (Diochon and Kellman, 2009; Gregorich et al., 2009; Six et al., 2001). Selective dissolution of soils

with chemicals that target specific soil mineral fractions, are most often carried out using parallel treatments of separate samples (Grand and Lavkulich, 2011; McKeague and Day, 1966; Porras et al., 2017). The variation in C in soil profiles has been found to be highly correlated with the Al and Fe content of amorphous/poorly-crystalline mineral phases, which is typically extracted with oxalate or hydroxylamine (Grand and Lavkulich, 2011; Rasmussen et al., 2005). Sequential selective dissolutions, alternatively, have the advantage of effectively isolating separate SOM pools through the removal of SOM-associated phases from mineral surfaces/associations in order of increasing crystallinity from a single sample (Doetterl et al., 2015; Kaiser et al., 2016; Lacroix et al., 2016; Lawrence et al., 2015; Lopez-Sangil and Rovira, 2013). These SOM fractions, then, serve to isolate SOM pools based on the strength of mineral interactions. Podzolic soils are ideal for studying the relative importance of different mineral phases on C dynamics due to the stratified nature of their minerals and abrupt boundaries between horizons, which when sampled on a horizon basis, confers higher analytical resolution than when using depth increment samples where horizons may be blended.

A further level of resolution is achieved by sequential selective dissolution, an approach that has the advantage of effectively isolating separate SOM pools through the removal of SOM-associated phases from mineral surfaces/associations in order of increasing crystallinity from a single sample (Doetterl et al., 2015; Kaiser et al., 2016; Lacroix et al., 2016; Lawrence et al., 2015). Since sequential selective dissolutions separate minerals into a suite of phases of varying crystallinity (including organo-metal complexes and crystalline phases) (Heckman et al., 2018), they thus represent distinct functional pools of SOM (Kramer et al., 2012). Once isolated, these mineral-associated OM pools can be quantified and characterized for their chemical character, including stable isotope ratio, aromaticity, molecular weight and molar C to mineral ratios. Molar C to mineral ratios reveal information about the nature of the mineral-SOM associations: low ratios indicate coatings/adsorption on mineral surfaces, whereas higher C:mineral (Fe+Al) ratios indicate that SOM is co-precipitated (Grand and Lavkulich, 2011; Kleber et al., 2015; Wagai and Mayer, 2007). Particular ratios of minerals extracted with these selective dissolutions have also been used to comment on pedogenesis (Lawrence et al., 2015), which has been shown to be altered

in podzolic soils following clear-cutting (Bonifacio et al., 2013; Falsone et al., 2012; Hole, 1975; Schaetzl and Isard, 1996).

1.11 Research objectives

The overall objective of this thesis was to improve understanding of mineral-associated forest soil C pools through depth and their potential for destabilization following soil disturbance.

Several lines of inquiry were addressed:

1. Are there multiple pools of mineral-associated soil organic matter that confer different levels of protection, and are these chemically distinct?
2. How does soil organic matter decomposition respond to shifts in soil microclimatic conditions?
3. How do changes in soil microclimate following harvesting alter the mobilization of SOM and associated minerals from soils?

Due to the methodological challenges of quantifying SOM pools in situ, this research employed a variety of techniques to characterize and trace OM in ecosystems, based on incubations, extractions, solubility characteristics, and measurement of stable isotopes of C. A laboratory experimental approach was used to address questions about the mechanisms and processes responsible for the observed losses, and field sampling for measurement and confirmation of processes observed in vitro. Specifics of the appropriate methods will be explained in detail in each of the chapters.

1.12 Contributions of this thesis

Chapter 3 has been published in PLoS One on Nov. 19, 2018 - Vol. 13(11): e0206847. Chapters 4 and 5 are in final draft form for submission to peer-reviewed journals in the autumn of 2019.

1.13 Thesis structure

In order to address these more specific questions, this study was divided into 3 research studies that represent individual chapters of this thesis.

1. Manuscript 1 - Chapter 3

Examining mineral associated soil organic matter pools through depth in harvested forest soil profiles

Are there multiple pools of mineral-associated soil organic matter that confer different levels of protection, and are these chemically distinct?

Many temperate forest systems experience routine clear-cutting and as a consequence, may be susceptible to levels of mineral soil C loss that are significant from a forest management perspective. The objective of this research was to 1) describe and characterize organic matter-mineral interactions through depth in a typical temperate forest soil; and 2) how mineral-associated SOM is different in soils with contrasting land-use histories. This is accomplished by characterizing these mineral and mineral-associated C pools through depth in mineral soil at two sites, one clear-cut 35 years ago and another clear-cut 110 years ago, identified as representing maximum and minimum C storage for a forest clear-cut cycle (Prest et al., 2014) at a model temperate forest system in Eastern Canada. It was hypothesized that clear-cutting would result in a reduction in C storage due to the destabilization of SOM associated with mineral phases. This is, to our knowledge, the first study to document changes in C quality and quantity (content and $\delta^{13}\text{C}$) of SOM in a full suite of sequentially-extracted mineral fractions from horizons of harvested forest soils.

2. Manuscript 2 - Chapter 4

Evaluating the susceptibility of soil organic matter in mineral soil horizons to losses following climatic changes associated with forest clear-cut harvesting

How does soil organic matter decomposition respond to shifts in soil climatic conditions?

The objective of this research study was to determine the susceptibility of mineral SOM through depth subjected to changes in environmental conditions, including increases in temperature and extreme climatic events, associated with forest harvesting disturbances. Samples were collected from soils

sampled through depth by horizon at two forest sites differing in stand age. Incubations of minimally-disturbed samples (A_e , B_f and BC horizons) was carried out at three temperatures and following a dry-rewetting and a freeze-thaw cycle. To accomplish this objective, decomposition rates, bioreactivity and the temperature sensitivity of mineral SOM decomposition were determined along with changes in the chemistry of respired CO_2 and the net extractable dissolved organic carbon (DOC_{ex}), $\delta^{13}\text{C-CO}_2$, and SUVA and S_r of chromophoric DOM. The susceptibility of this mineral C to loss was examined through depth in horizons and between sites of contrasting time since disturbance. This was accomplished through measurement of these changes in DOC chemistry and respired CO_2 the susceptibility of this mineral C to loss through depth in horizons and between sites of contrasting time since disturbance.

3. Manuscript 3 - Chapter 5

Impacts of redox conditions and temperature on dissolved organic carbon and iron mobilization from mineral soils through depth

How do changes in soil microclimate following harvesting alter the mobilization of SOM and associated minerals from soils?

In order to better understand SOM mobilization in forest soils through depth in response to harvesting disturbance, the impacts of flooding and temperature on the quantity and chemistry of DOC from mineral soils through depth were examined. It was hypothesized that warmer and reducing conditions mobilize DOC and Fe from soils. Stream water chemistry was analysed to confirm whether the quantity and character of DOC were similar to DOC mobilized from controlled manipulations. The objectives were accomplished through analysis of extracts from lab experiments designed to simulate redox conditions and to test the impacts at two temperatures, and by comparing field samples that represent water draining intact and disturbed catchments. Field samples collected from contrasting streams under both baseflow and stormflow conditions provided information about the soil C mobilized as flowpaths change, since the flux and composition of DOC are linked to catchment hydrology. It is likely

that destabilization of C occurs via both decomposition of SOM and mobilization of DOC, controlled by temperature and as a result of the creation of anoxic conditions following flooding.

Chapter 2

Site description

2.1 Overview

The Otter Ponds Demonstration Forest, located east of the village of Mooseland, in central Nova Scotia, Canada (44°56'42.51"N, 62°47'39.53"W) (Figure 2.1), is a site that is typical of the Acadian Forest of Eastern Canada. Within the Otter Ponds Demonstration Forest at Mooseland (ML), there are two secondary regrowth coniferous forest sites (Mature, 110 years, and Young, 35 years, Guzzle Forest). These sites were previously characterized for soil C storage patterns through depth which showed a > 27% decline in mineral soil C storage following forest clear-cut harvesting (Prest et al., 2014). Abraham's Lake (AL) is a forest site located in the Governor Lake Ecodistrict in central Nova Scotia, eastern Canada (45°5'0" N 62°25'54" W) (Figure 2.2). In this forest area, a chronosequence was established (Diochon et al., 2008) that represents a range of stages of natural regrowth (1, 15, 45, 80, and 125 years since clearcutting). At the AL site, there are two distinct catchments that contrast in land-use (Intact and Disturbed).

2.2 Forests description

The forests are typical of the Acadian Forest Region, in the northern temperate zone (Mosseler et al., 2000), with forest structure influenced by land-use practices. At the Mature reference site, a second-growth stand of red spruce currently dominates the canopy, while at the Young site, the canopy is dominated by a mix of red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* (L.) Mill), eastern white pine (*Pinus strobus* L.), yellow birch (*Betula alleghaniensis* Britt.), and red maple (*Acer rubrum* L.) and is currently undergoing self-thinning (Prest et al., 2014). Both sites were cleared for lumber using axes and horses in 1900. As logging operations at that time happened exclusively in winter, there was likely little physical disturbance

to the forest floor and mineral soil. The Young site experienced a second clear-cut harvesting event in the summer of 1974 with chainsaws and skidders. At both sites, limbs and small to large diameter tops would have been left on-site as detritus.

The Abraham's Lake chronosequence is also dominated by red spruce (*Picea rubens* Sarg.) with balsam fir (*Abies balsamea* (L.) Mill.), eastern white pine (*Pinus strobus* L.), yellow birch (*Betula alleghaniensis* Britt.), and red maple (*Acer rubrum* L.), and encompassed a range of stages of forest secondary succession, from stand initiation (1-15 years), to stem exclusion (45 years), understory initiation (80 years) and a climax forest in the old growth forest (>125 years). The two oldest sites were located south of Abraham's Lake in a separate catchment east of the youngest sites, also located to the south of the lake. Within the Intact catchment flows Bear Brook, the main outflow of Abraham's Lake, a protected old-growth forest area managed by the Nature Conservancy of Canada. This site represents an intact site, free of anthropogenic activity, and serves as reference site to the Disturbed site. The other forest stands that reside within this catchment through which runs Twelve Mile Stream, a third-order stream that drains a catchment with forests that have experienced routine clear-cutting along the length of the stream at rates of approximately 25-50% land cover change over several decades.

The ground cover in the forested sites at ML and AL were dominated by mosses (*Bazzania tribolata* and *Pleurozium schreberi*). Forbs and shrubs common among the sites included lamb-kill (*Kalmia angustifolia*), creeping snowberry (*Gaultheria hispidula*), bunchberry (*Cornus canadensis*), blue-bead lily (*Clintonia borealis*), Canada mayflower (*Maianthemum canadense*), and wood sorrel (*Oxalis acetosella*). At AL, living ground cover was sparse in the recent clearcuts with trace amounts of seedlings (<1 m² area) and herbaceous species (<1%).

2.3 Climate

Central Nova Scotia, Canada, where the Mooseland (ML) and Abraham's Lake (AL) sites are located, receives 1300 mm of precipitation annually, and lies at approximately 100 m above sea level. Mean annual air temperature is 5.8 °C, with mean January and July temperatures 5.8 °C and 16.9 °C, respectively (Environment Canada climate normals as of 2018). These forest sites all have an undulating terrain, with slopes

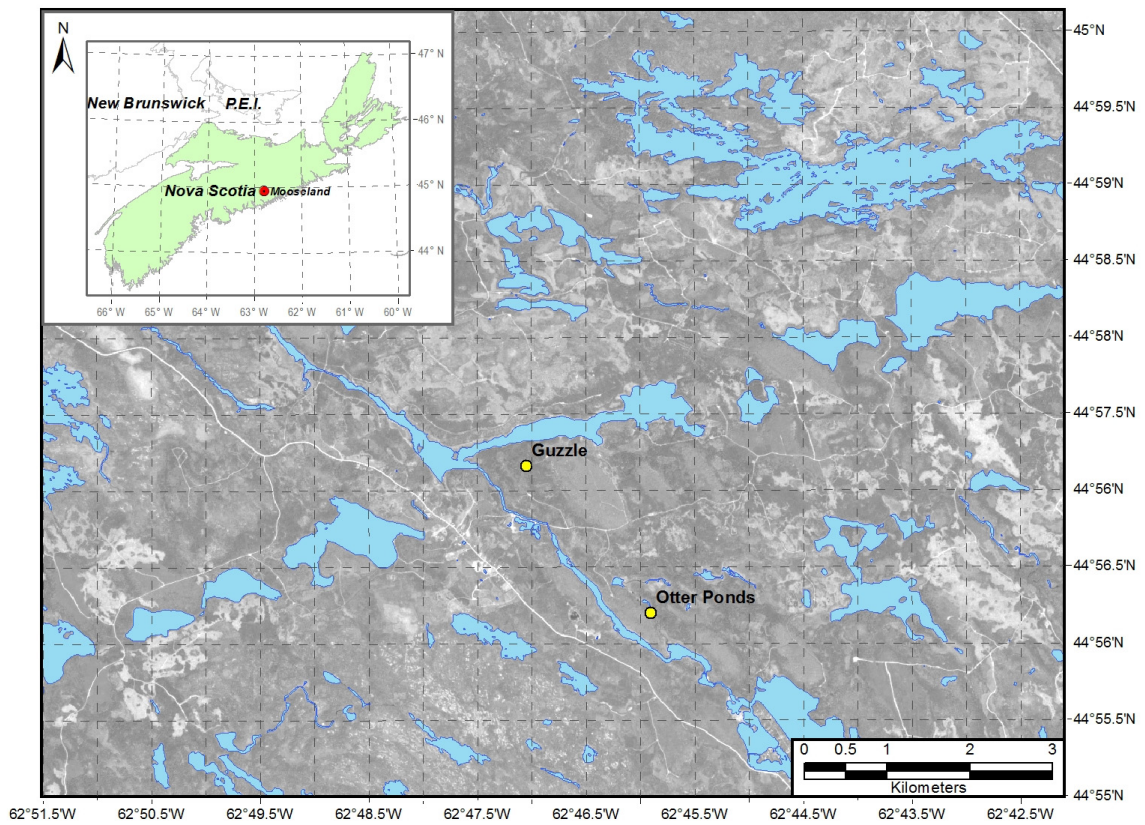


Figure 2.1: Map of the locations of the soil sampling sites in Mooseland, central Nova Scotia, Eastern Canada (Inset). At Guzzle, the Young forest (35 years since forest clear-cut harvesting) is located, while at Otter Ponds, the 110 year old forest (i.e. Mature) is located.

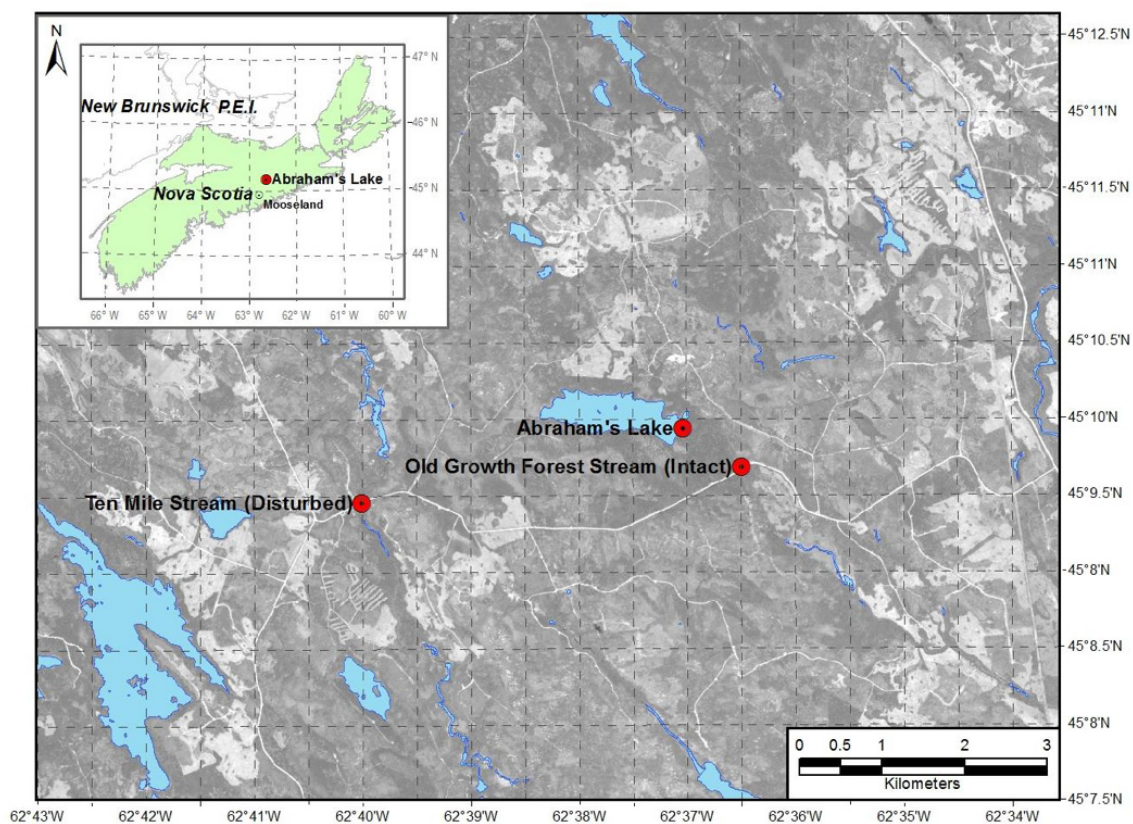


Figure 2.2: Location of sampling sites in Abraham's Lake area in Nova Scotia, Eastern Canada (Inset), with location of Intact and Disturbed water sampling sites in Abraham's Lake area (larger map). Soil samples were from Mooseland, NS, located approximately 30 km southwest of this site (inset). The water sampling site at Abraham's Lake is also indicated. Lighter-coloured patches show the alteration to forest cover associated with forest harvesting in the disturbed watershed.

between 2-15% (MacDougall et al., 1963) (Figures 2.3 and 2.4). The ML and AL sites are 30 km apart and have similar climate, vegetation type, soil type, and land-use. These two sites also experience similar positions geographically, and so the soil forming factors of slope and aspect affect the sites equally.

2.4 Soil descriptions

The soils at the ML and AL sites are Orthic Humo-ferric podzols (Canadian Soil System), are known to be acidic from extremely acidic (4.5) - to strongly acidic (5.5) through depth, and were developed from moderately coarse textured stony till, commonly gravelly, on moderately to well-drained sites of the Halifax series (MacDougall and Nowland, 1972) in the Eastern Ecoregion of Nova Scotia (Neily et al., 2003). These soils are characterized by well-developed A_e eluvial horizon, a brown sandy loam illuvial B_f horizon high in organic matter associated with Fe and Al, and an olive- to yellowish-brown sandy loam subsoil (Figure 1.1) (MacDougall et al., 1963). Organic horizons are on average 11.9 cm and 13.3 cm, respectively, for Young and Mature sites (Prest et al., 2014). The Halifax series soils are not suitable for agriculture due to acidity, infertility and stoniness, and are often forested (MacDougall and Nowland, 1972). In general, where the parent material (till) is thin (<50 cm), soil horizons are characterized by heavy oxidation, making it difficult to differentiate the boundary between B- and C-horizons based solely on colour (Goodwin et al., 2003).

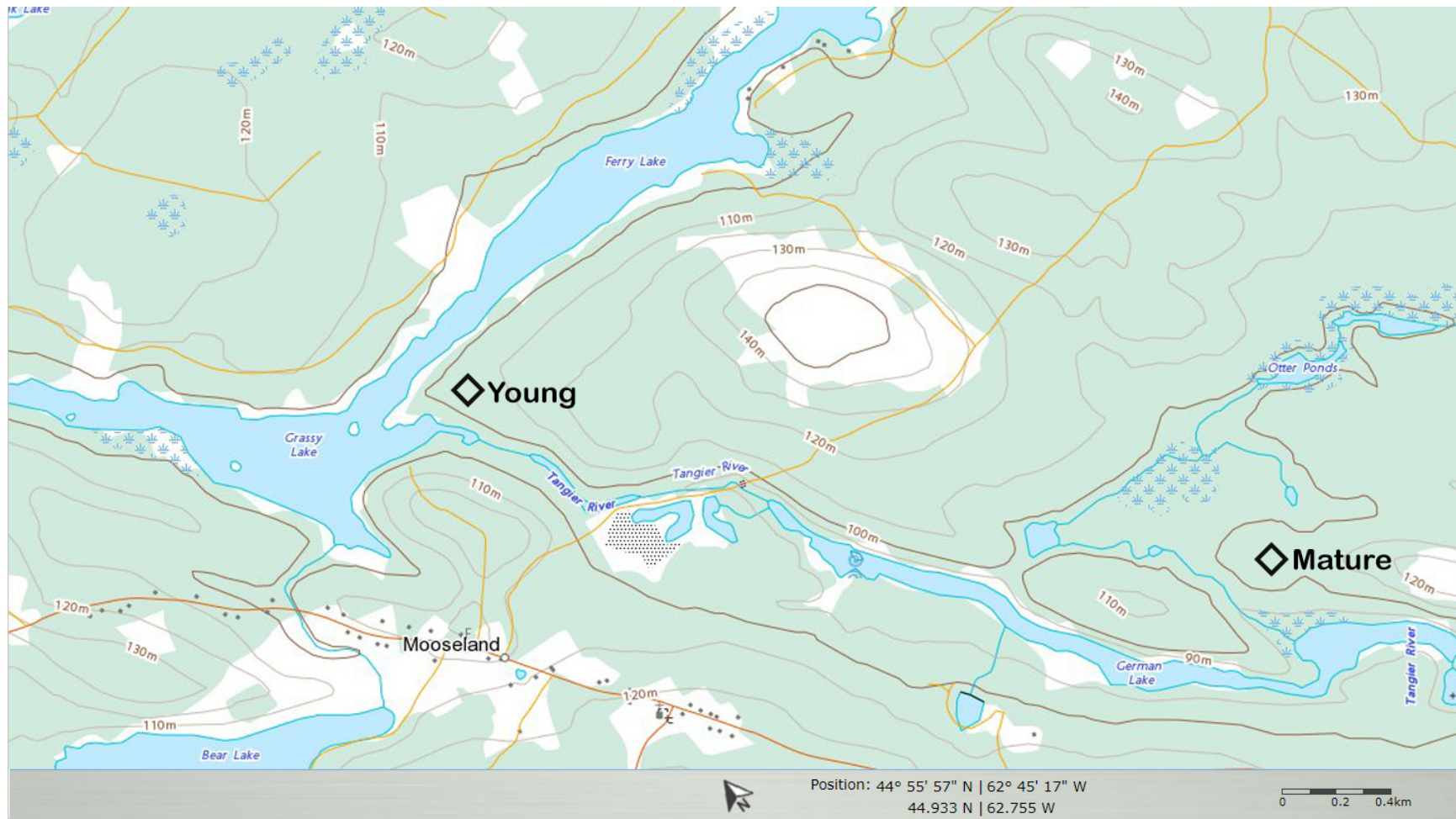


Figure 2.3: Topographic map of Young and Mature soil sampling sites in Mooseland, central Nova Scotia, Canada. Note that these sites are both northeast facing with similar altitude <100 m.

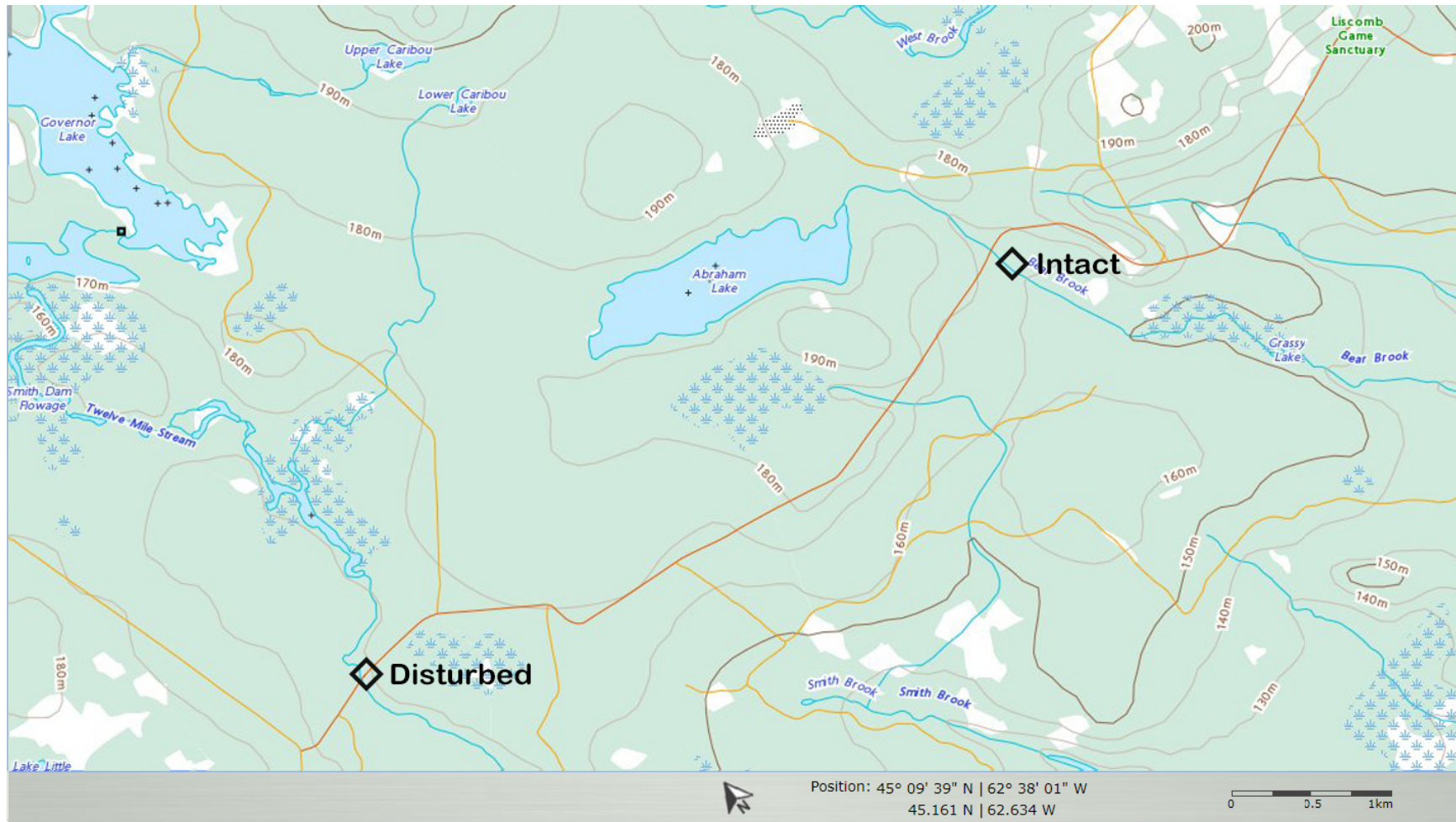


Figure 2.4: Topographic map of Disturbed and Intact stream sampling sites Abraham 's Lake, Nova Scotia, Canada. Sampling sites are located where the road crosses the streams in Abraham's Lake in central Nova Scotia, indicated by open diamonds.

2.5 Geological description

2.5.1 Regional geological setting

Nova Scotia is divided geologically into two distinct parts, the Avalon Terrane to the north and the Meguma Terrane to the south (Figure 2.5). The Cambrian-Ordovician Meguma Terrane (Supergroup) of Nova Scotia (White et al., 2008) was deformed into regional, east- to northeast-trending folds with well-developed axial planar cleavages and northeast- and southwest-plunging intersection lineations during the Middle Devonian to Early Carboniferous Neoacadian Orogeny (ca 400 Ma). The Meguma Supergroup consists of two main formations with a combined vertical thickness of at least 11 km (White, 2010): the basal metasandstone- to metasilstone-dominated Goldenville Group, and the younger slate and metasilstone (with minor metasandstone) of the Halifax Group (Ryan and Smith, 1998; White, 2010). The Goldenville Group is conformably overlain by the Halifax Group. These rocks were formed in a sedimentary marine environment most likely as a deep water turbidite sequence during the Cambrian-Ordovician. These rocks subsequently underwent deformation accompanied by greenschist-facies (chlorite-grade) metamorphism (Boyle, 1986; Taylor and Schiller, 1966).

All study sites are located in the eastern region of the Halifax Regional Municipality, Nova Scotia, on this Meguma Terrane. The bedrock units (Goldenville and Halifax Groups) are folded together and closely spatially distributed in this region (White, 2010), characterized by interbedded slates, metasilstones, and metasandstones (Boyle, 1986). The Mature site at ML is underlain by a tight east-west trending anticline, exposing the silty to sandy deep water turbidite sequences within Formations of the Goldenville Group. The Young site is at the southern edge of the Mooseland Property close to the axis of the syncline, exposing slates of the Halifax Formation (Figure 2.6 and 2.7). The Mooseland region contains gold-bearing facies, arsenic occurrences, and some units are susceptible to acid mine drainage (White and Goodwin, 2011). The Goldenville Group at Abraham's Lake (Figure 2.8) is composed of the lower metasandstone-dominated Governor Lake and Taylors Head Formations and overlying Beaverbank Formation, a coticule-bearing metasilstone. Units in the overlying Halifax Group include the slate-rich Cunard Formation and Glen Brook

Formation. These metasedimentary units are similar to those established elsewhere in the Meguma Terrane, and as is typical of this Terrane, vary mainly in the relative proportions of these units at a given location.

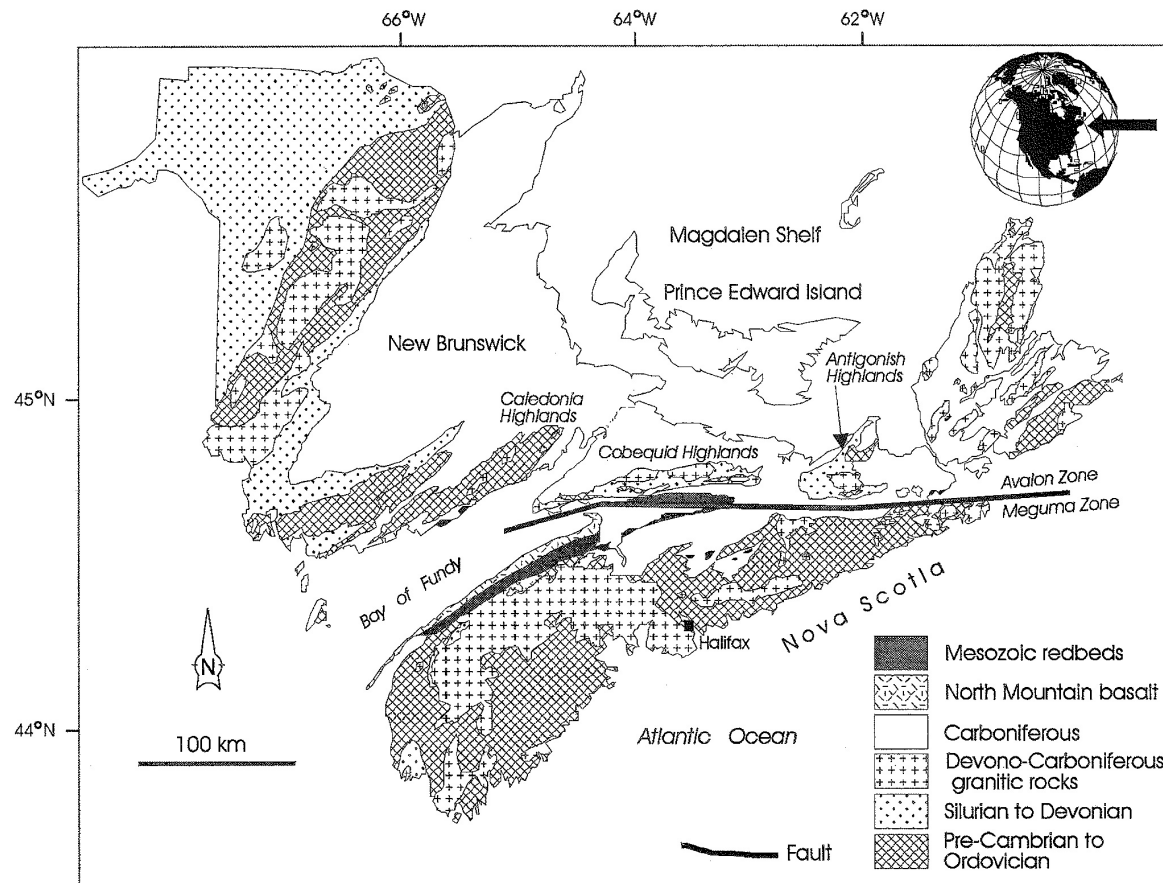


Figure 2.5: Generalized bedrock geology of Maritime Canada, showing the main geological terrain boundaries and location of highland regions. From Stea and Finck, 2001.

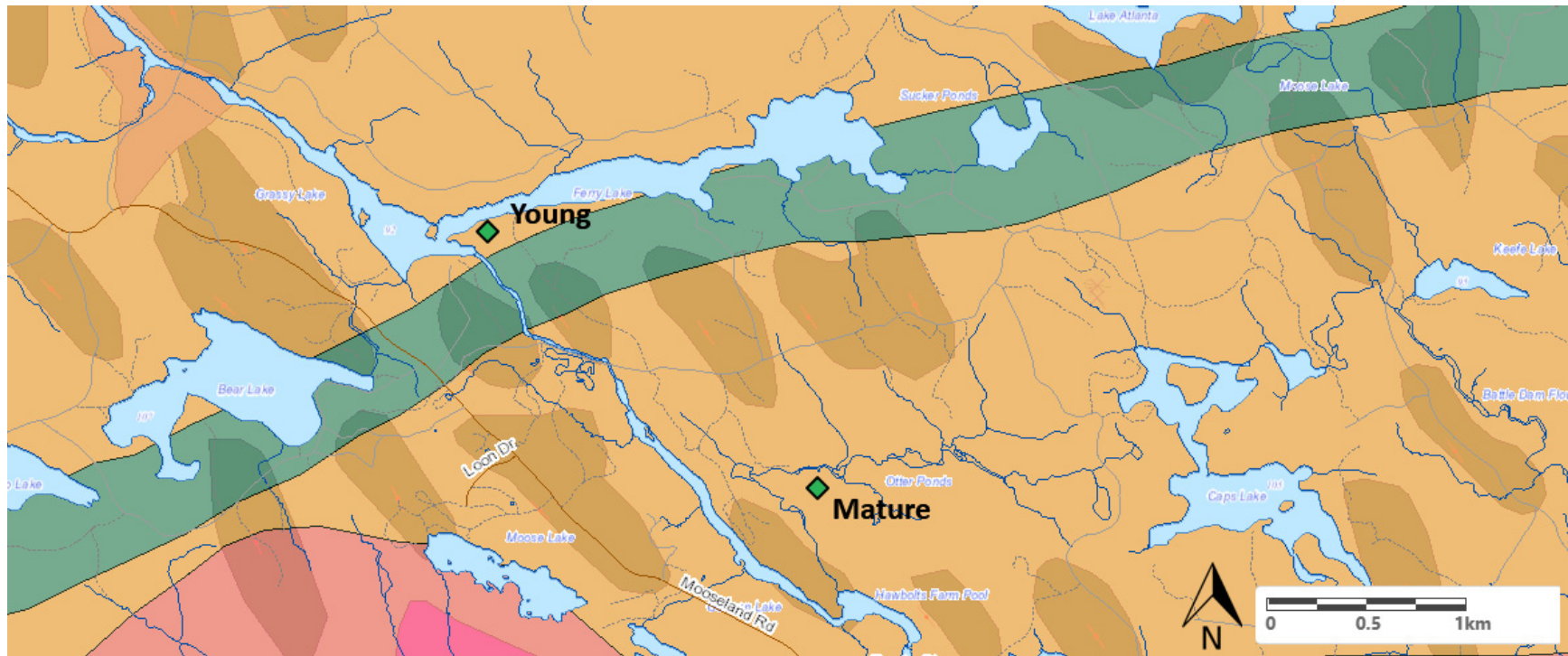


Figure 2.6: Bedrock and surficial geology map of Mooseland, central Nova Scotia, Canada, within Cambrian-Ordovician metasilstone regional geology. The light brown-coloured region that dominates this area is the Goldenville Formation, and the green-coloured band that stretches across the map is the Halifax Formation. The red and pink areas are granite and outside the area of study. Superimposed is a layer that indicates the locations of drumlins (darker shaded ovals are northwest-southeast trending). Redrawn from Keppie (2000).

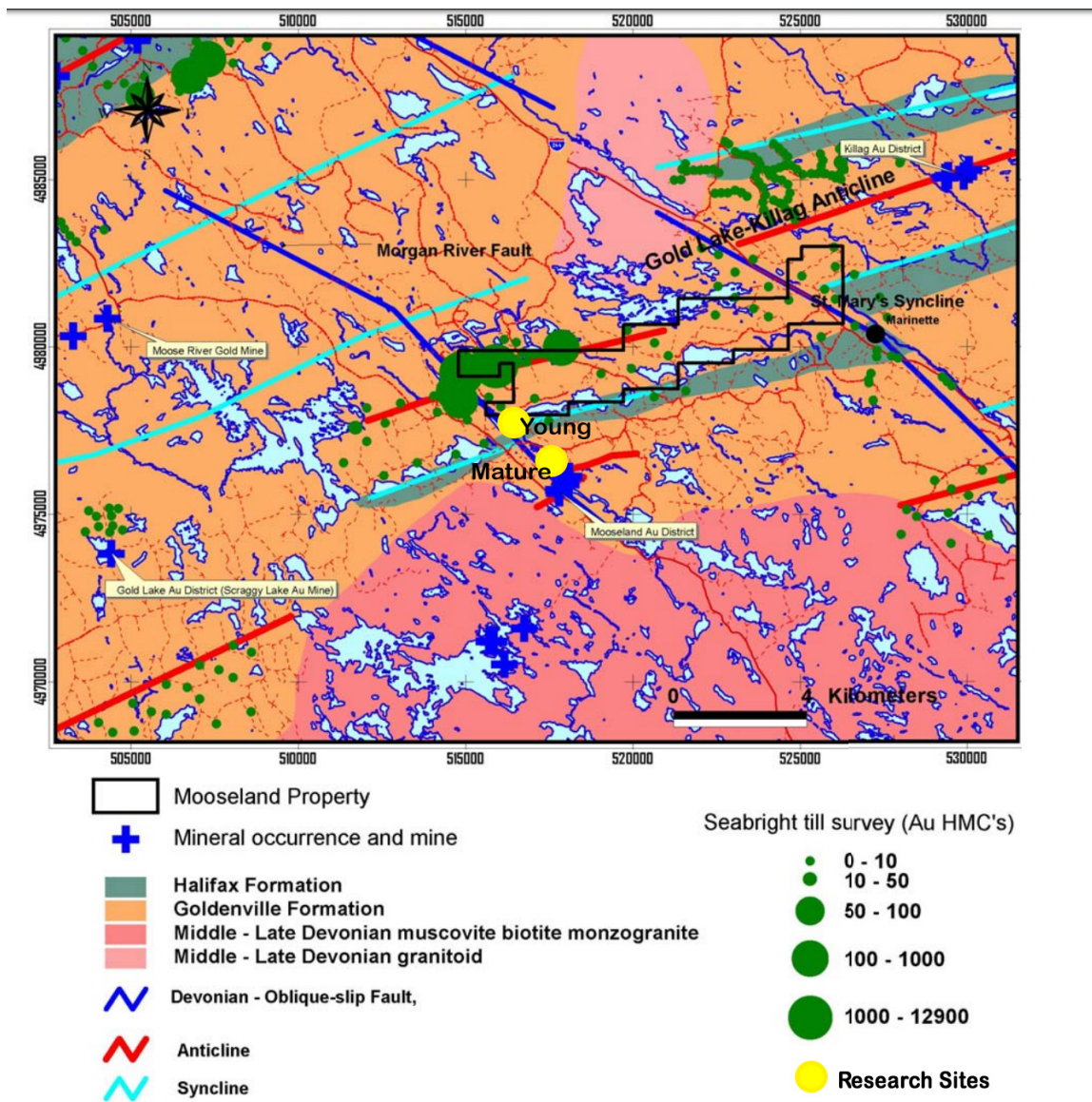


Figure 2.7: Location of Mooseland in central Nova Scotia, Canada and regional geological setting. Modified from Stea (2010). Young and Mature sites are located in the region indicated by the yellow circles.

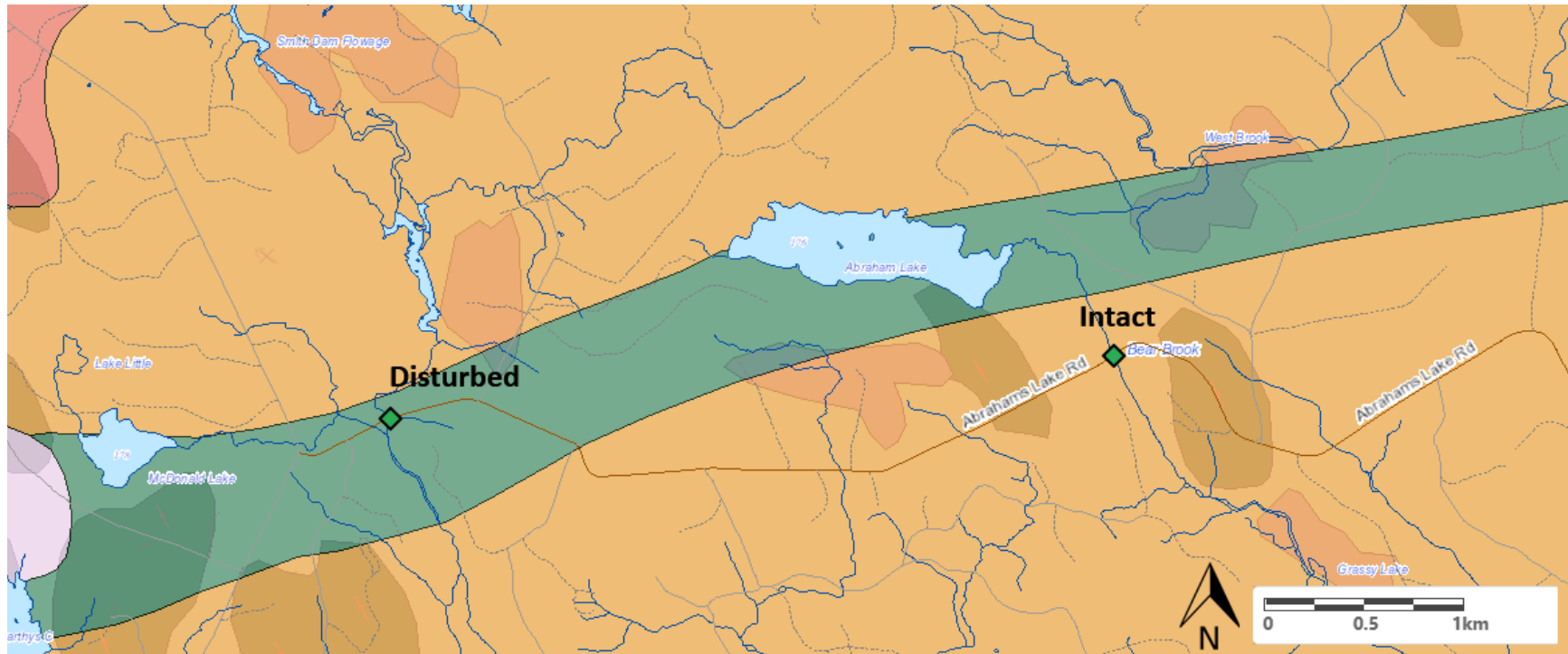


Figure 2.8: Bedrock and surficial geology map of the south central Nova Scotia, Canada, at Abraham 's Lake, Nova Scotia, Canada, within Cambrian-Ordovician metasiltstone regional geology. The Goldenville formation is in light brown and the band of the Halifax Formation stretches across the lake (in green). The red and pink areas are granite and outside the area of study. Superimposed is a layer that indicates the locations of drumlins (darker patches). Redrawn from Keppie (2000).

2.5.2 Regional glacial geology

Beaver River Till on the Stony Till plain is a short distance cold-based glacial till formed due to lodgement under glacial ice during the most recent (Wisconsinian) glaciation event (Stea and Finck, 2001). Beaver River Till is a stony, sandy-textured till which varies widely in thickness across Nova Scotia, between $< 1\text{-}5$ m in upland areas and >7 m in lower elevations (Stea and Finck, 2001). Its distribution is characterized by hummocky topography, commonly with large quartzite or granite boulders (Stea and Finck, 2001). This till is described as consisting of an olive-grey unsorted sediment, containing particles ranging in size from clay to boulders, suspended in a matrix of mud or sand, with a high percentage of angular-subangular cobbles and boulders (Stea and Fink, 2001). Beaver River Till has high permeability (O'Brien et al., 2011), which is also consistent with the soil textural classification and particle size distribution for the soils formed from this till (Tables 3.1 and 7.2).

In thin cold-based tills, clasts are often reflective of the immediate underlying bedrock, dominated by single local bedrock derived clast lithology (generally $>90\%$) (Goodwin et al., 2003; Stea and Finck, 2001). The local nature of the till is further demonstrated by the angularity of the clasts, the presence of large boulders and the compact nature of the till (Goodwin et al., 2003). Any lithological, chemical and grain size variability of this till that cause it to deviate from a truly locally derived cold-based till such as Beaver River Till (for instance, inclusion of clasts) is due to inheritance from the underlying Lawrencetown Till (Stea and Finck, 2001).

Clasts within the till are derived from the local low-grade metamorphic metasiltstone, slates and quartzites of the Goldenville Group in this region (Goodwin, 2002). The metasandstone facies in the Beaver River Till (formerly quartzite till of Stea and Fowler, 1981) is light bluish grey and contains loose, angular metasandstone and metasiltstone clasts which are derived from Goldenville Formation metasediment, largely cobble sized, set in a silt-sand matrix. The slate till facies of the Beaver River Till is derived from Halifax Formation slate (Stea and Fowler, 1981). At these Mooseland sites, a pebble count (<12 mm) indicated that the Young site pebble lithology is dominated by slate ($>80\%$) with lesser metasiltstone, while at the Mature site, it is a mix of metasiltstone to quartzite with minor slate ($<32\%$). The Young site contains a higher proportion of slate of <0.5 cm than the Mature site, which is consistent with

variability in the underlying bedrock units at these sites (Figure 2.6 and 2.7). In the Young site, the proportion of pebbles was 22.5% by weight, with median diameter of 12 mm. At the Mature site, the proportion of pebbles was 17.3 % by weight with a median diameter of 8 mm. These observations are consistent with findings from previous till surveys (Goodwin, 2003; Stea and O'Reilly, 1982; Stea and Fowler, 1979; White and Goodwin, 2011).

The primary rock-forming minerals in the metasedimentary host rocks of the Cambro-Ordovician Meguma Supergroup are fine sand- to silt-sized quartz, feldspar, illite and chlorite, with traces of vermiculite and kaolinite (Brydon, 1958; Goodwin et al., 2003). The slate of the Halifax Formation is high in reduced S (as pyrite or pyrrhotite and arsenopyrite), and Fe with Mn-rich horizons (coticules) (White et al., 2008). Carbonate and sulphide minerals occur in minor to trace amounts in lower units of the conformable sequence (Halifax to Goldenville transition), along with secondary minerals such as scorodite (Percival et al., 2013) and magnesite (Goodwin, 2002). Enrichment of gold and arsenic with lesser enrichment of copper, lead, zinc, tungsten, bismuth, tellurium and iron (plus other elements and minerals) characterize the gold deposits of the Meguma Terrane (Kontak and Smith, 1993), though these are likely to be of low contribution to the over chemistry.

2.6 Similarity of the Mooseland sites

The sites at Mooseland may be considered broadly similar, despite differences in parent material. In this area of Nova Scotia, the bedrock geology is relatively consistent. At both locations the tills consist of siliciclastic metasediment, dominated by varying proportions of slate and/or metasiltstones. From a mineralogical point of view, the Beaver River till at both sites are similar, varying only in relative proportion of the slate and metasiltstone components. Till in this region is internally consistent and thin to bedrock with no evidence of the presence of Lawrencetown Till. While grain size and detrital clay content of the two sites may vary, bulk mineralogy and minor mineral phases should be relatively homogenous and similar between the sites, dominated by SiO₂ with trace Al and Fe. This assertion is supported by findings from others: for instance, the clay at both sites was predominantly illite with traces of chlorite, vermiculite and kaolinite (Brydon, 1958). The underlying rocks in both

locations have high acid-producing potential (White and Goodwin, 2011). However, despite these differences in till lithology, there was little difference between the sites on the basis of particle size distribution (Appendix B), soil texture (Appendix C), drainage class (Canadian Soil System), and bulk density (Table 3.1).

In addition, it is important to consider whether any site differences in regards to geography, pH, and soil texture may have an influence on soil C content. The geographical characteristics (slope, aspect and climate) which influence soil formation were similar or the same at both sites at ML (Figure 2.6). These two sites are close in proximity, and so variations in regional climate would affect both sites equally; however, soil microclimate might be quite different for two proximal sites if forest disturbance altered water table level or increased incoming solar radiation due to differences in forest structure. It is also possible that the nature of the parent material can influence the amount of organic C in soil, exerted through the effect of lithology on soil pH (Catoni et al., 2016), on the proportion and nature of the clay present (Oades et al., 1997; Torn et al., 1988), and on soil texture (Heckman and Rasmussen, 2011). Despite differences in the pebble lithology of the Beaver River Till at the Young and Mature sites at Mooseland, the soil pH was the same at both sites. Soil pH was acidic (below 4.5) at both sites within the ML property, and not significantly different in equivalent horizons except for the A_e , where the soil pH was 3.5, and 4 for Young and Mature, respectively. Additionally, composites of soil from 9 pits within the Mature and Young sites were texturally similar through depth, lying within sandy loam classification (Appendix C), with similar amounts of clay. This would suggest that despite differences in till at the two sites the overall impact on the chemical characteristics of the soil itself appears to be minimal. Further work on the clays themselves would be needed to conclude otherwise.

Chapter 3

Examining mineral-associated soil organic matter pools through depth in harvested forest soil profiles

Preamble

Chapter 3 is the manuscript by C.E. Gabriel, L. Kellman and D. Prest, "Examining mineral-associated soil organic matter pools through depth in harvested forest soil profiles", published in Nov. 2018 in the Proceedings of the Library of Sciences (PLoS One).

As first author on this paper, C.E. Gabriel has undertaken all of the research and the writing of this paper, and has incorporated suggestions and recommendations from L. Kellman during the research and the writing phases of this study. D. Prest was primarily responsible for soil sampling and its methodology, site descriptions and initial analyses of bulk soil C storage.

The following represents the final published version of the document, outside of the single modification of the journal's referencing style. This is the first study to be presented in this thesis, as it forms the logical basis for the differences between the sites, and connects this study directly to previous observations of lower SOM in subsoil or younger sites in podzolic soils of Eastern Canada, as well as identifying and documenting the particular mineral-associations that govern mineral SOM storage.

3.1 Introduction

Soil organic matter (SOM) is a globally important pool of C, holding more than twice the amount of C stored in terrestrial compared to atmospheric pools (Batjes, 1996; IPCC, 2013). As a consequence, understanding SOM stability and the processes controlling carbon (C) storage in soils is required for assessing the broader impacts of human activity upon terrestrial C cycling. A large proportion (>50%) of soil C stock resides in the deeper mineral subsoil below 10-20 cm (Cerri et al., 2007; Clemmensen

et al., 2013; Jobbagy and Jackson, 2000; Rumpel et al., 2015; Rumpel and Kögel-Knabner, 2010; Trumbore and Czimczik, 2008); however, evidence from several recent studies is suggesting that mineral soil C may be less stable than previously assumed (Bernal et al., 2016; Fontaine et al., 2007; Lawrence et al., 2015) when exposed to disturbance from activities such as forest harvesting (Basile-Doelsch et al., 2009; Bellamy et al., 2005; James and Harrison, 2016; Noormets et al., 2014).

SOM is a complex, heterogeneous mixture of organic molecules derived from particulate, water-soluble and colloidal compounds from decaying above- and below-ground organic matter, including microbial biomass and their exudates. The storage of SOM results from a dynamic balance between above- and below-ground OM inputs and loss through mobilization and decomposition. SOM turnover depends on a soil's chemical and physical conditions, including pH, moisture content, temperature, nutrient availability, aggregation, and SOM molecular structure (Asner et al., 2001; Conant et al., 2011; Davidson, 2015; Davison et al., 2006; Fontaine et al., 2007; Hicks Pries et al., 2016; Keiluweit et al., 2017). Evidence suggests that mechanisms that lead to SOM stability are more complex than previously assumed (Lehmann and Kleber, 2015; Marin-Spiotta et al., 2014; Marschner et al., 2008; Schmidt et al., 2011) and that storage can be strongly mediated through interactions with the mineral soil matrix (Baldock and Skjemstad, 2000; Heckman et al., 2009; Kaiser and Guggenberger, 2000; Kleber et al., 2015; Lawrence et al., 2015; von Lutzow et al., 2008; Torn et al., 1997; Wagai and Mayer, 2007). Some studies suggest that over 75% of bulk SOM in podzols can be mineral-associated (e.g. Diochon and Kellman, 2009), with the majority of mineral C associated with organo-metal complexes (OMC)(Heckman et al., 2018).

The pedogenic weathering of primary minerals produces secondary minerals that interact with SOM. This mineral-associated organic matter can include a range of mineral structural forms: colloidal OMC (interacting with surfaces through ligand exchange); organic matter associated with a precipitated (and/or co-precipitated) amorphous poorly-crystalline secondary mineral phase characterized by a high surface area (Kleber et al., 2005; Mikutta et al., 2006); and surface adsorption to highly-ordered crystalline mineral surfaces (such as iron (Fe) and aluminum (Al) hydroxides in podzol soils). Often, SOM accumulates in association with Fe and Al across a range

of geometries and forms, varying in the relative proportions of C and minerals. The nature of SOM associated with these varying mineral phases has been characterized to some degree (Jones and Singh, 2014): for instance, short-chain hydrophobic SOM is found to interact with crystalline minerals (Adhikari and Yang, 2015) as stable inner-sphere complexes, while aromatic SOM like lignin is preferentially associated through ligand exchange with organo-metal or poorly-crystalline Fe and Al hydroxide minerals (Sanderman et al., 2014), and are stabilized through polyvalent metal-cation bridges.

Association with minerals is thought to confer C stability, but disturbances that alter the soil physical environment may disrupt these interactions. Studies investigating these processes suggest that not all organic matter-mineral pools are equally susceptible to disturbance. Mineral-associated organic matter pools from phases of lower crystallinity (i.e. OM associated through ionic bonds or ligand exchange) are bound more loosely to minerals, and are therefore more susceptible to microbial decomposition (Dungait et al., 2012) or to solubilization (Borke et al., 2011) with a faster turnover time than OM bound to crystalline secondary mineral phases (Heckman et al., 2018). In a study across an intensively managed forest harvesting chronosequence, Diochon et al. (2009) showed that up to 50% of SOM was lost from the mineral soil in the decades following harvesting and that this loss occurred mainly from the mineral-associated organic matter pools. While some studies have documented losses of mineral-associated OM following soil disturbance (Basile-Doelsch et al., 2009; Diochon et al., 2009; Mobley et al., 2015), only a few have explored SOM losses from specific mineral-associated C pools following forest harvesting disturbance (Falsone et al., 2012; Grand and Lavkulich, 2011; Lacroix et al., 2016; Petrenko and Friedland, 2015). A process-based understanding of C stability in mineral soils and its potential for loss following forest harvesting thus requires a more complete understanding of the stability of organic carbon across the full range of mineral-associated OM interactions than currently exists.

The processes that confer long-term stability to SOM in soils can be investigated using a combination of traditional and newer analytical approaches. Attempts to understand how minerals control C storage have generally relied on studies of soil textural fractions, especially clay (Kögel-Knabner et al., 2008), soil mineralogy (Heckman

et al., 2009), and using physical fractionation techniques, including density fractionation (Diochon and Kellman, 2009; Gregorich et al., 2009; Six et al., 2001). Selective dissolution of soil samples with chemicals targets specific soil mineral fractions and allows separate C pools to be isolated and quantified based on the strength of their interactions with minerals (Heckman et al., 2018; Wagai et al., 2013). If carried out sequentially, these extractions effectively isolate separate pools through the removal of SOM associated with minerals in order of increasing crystallinity from a single sample (Doetterl et al., 2015; Kaiser et al., 2016; Lacroix et al., 2016; Lawrence et al., 2015; Lopez-Sangil and Rovira, 2013). This allows for a detailed characterization of the mineral phases that control C storage.

Analysis of isolated mineral-associated OM pools can then provide information about the nature of mineral-organic matter interactions and the character of the organic matter stabilized in these distinct mineral-associated organic matter pools. Ratios of C to iron and aluminum (Fe + Al) of extracted mineral pools can be used to evaluate how much C is associated with these elements in mineral soil, providing an indicator of C-mineral associations or “loading” of C on mineral surfaces. Relative differences in C loading on soil minerals are important to understand in relation to C storage potential (Masiello et al., 2004), but analysis of the variation of molar C:(Fe+Al) ratios through depth and between sites can also provide information about pedogenic processes through depth. Low molar C to metal ratios of extracts indicate adsorption on mineral surfaces, whereas higher C: mineral ratios indicate that SOM is co-precipitated with Fe and/or Al (Grand and Lavkulich, 2011; Kleber et al., 2015; Wagai and Mayer, 2007). Stable isotope ratios of C ($\delta^{13}\text{C}$) are integrative measures of ecosystem processes (West et al., 2006), and can be used to reveal differences in pools of SOM (Billings and Richter, 2006) which vary in chemical character and turnover times. Analysis of sequential extracts for elemental C and $\delta^{13}\text{C}$ have the potential to reveal differences in the quantity and chemical character of C held in distinct mineral-associated SOM pools (Kayler et al., 2011). Enrichment in ^{13}C can also arise from kinetic fractionation as a result of increased microbial processing of SOM (Diochon and Kellman, 2008). Furthermore, plant-derived C has a lower value of $\delta^{13}\text{C}$ compared to microbially-derived SOM (Ehleringer et al., 2000) (Figure 1.2).

This research aims to contribute to an improved understanding of the nature and

distribution of mineral-associated C pools and their variability through depth in forest podzol soils. The objective of this research is to determine how the quantity of C in mineral-associated organic matter pools, distribution of mineral-associated pools of differing crystallinity, and $\delta^{13}\text{C}$ of SOM held in these pools vary through depth in soils subjected to harvesting disturbance. In order to accomplish this, we quantified and characterized the nature of OM-mineral interactions and $\delta^{13}\text{C}$ signatures in mineral pools isolated through sequential selective dissolution through depth at two sites representing contrasting forest stand ages (35 and 110+ year stands (Prest et al., 2014)) and C storage within a forest clearcut cycle in Eastern Canada. We hypothesized that the mineral pools' C quantity, Fe and Al – C interactions, and $\delta^{13}\text{C}$ signatures would vary through soil depth and as a function of disturbance history.

3.2 Methods

3.2.1 Site description

Soils were sampled through depth in genetic horizons sampled from two secondary regrowth coniferous forest sites east of the village of Mooseland, Nova Scotia, Canada ($44^{\circ}5642.51''\text{N}$, $62^{\circ}4739.53''\text{W}$). A Mature forest stand (110 years since cutting) is located within the Otter Ponds Demonstration Forest, and a Young (Guzzle) forest (harvested 110 and 35 years ago), is located 2.5 km north of Otter Ponds (Figure 3.1). Otter Ponds Demonstration Forest is operated by non-governmental organizations on Crown land, and the Guzzle forest site is currently owned and managed by Ecofor Management (Mooseland, NS). These sites were previously characterized for soil C storage patterns through depth in fixed increments to 50 cm (Prest et al., 2014), as depicted in Figure 1.1. Mineral soil carbon remained low for many years following clear-cutting, with 27% lower mineral soil C storage in mineral soils (0-50 cm) 35 years after forest clear-cut harvesting (Prest et al., 2014) (data summarized in Table 3.1).

Table 3.1: Soil horizon characteristics for podzol forest soil profiles for a Young (35 year old) and Mature (110 year old) red spruce forest sites, sampled to 50 cm. Numbers in brackets, when present, are 1 SD. Bulk density values were estimated based on depth increment bulk density values (Prest et al., 2014) and known horizon thicknesses.

Site	Horizon	Thickness (cm)	Color	C (%)	$\delta^{13}\text{C}$ bulk soil (‰)	C:N	Bulk density (g cm^{-3})
Young	A _e	6.4 (3.4)	10YR 5/1 Grey	3.19 (1.36)	-27.26 (0.64)	26.6 (9.3)	0.72
	B _f	11.0 (1.5)	10YR 4/4- 4/6 Dark Yellowish Brown	4.51 (1.32)	-26.03 (0.34)	24.3 (1.1)	0.66
	BC	27.5 (2.6)	2.5Y 4/3 Olive Brown	2.51 (2.35)	-25.45 (0.60)	21.7 (2.2)	1.16
Mature	A _e	8.9 (6.4)	10 YR 4/2 Dark Greyish Brown	1.95 (0.36)	-26.95 (0.33)	31.4 (8.9)	0.72
	B _h	1.0 (0.4)	5 YR 2.5/2 Dark Reddish Brown	8.49 (0.71)	-26.30 (0.29)	24.4 (0.3)	0.10
	B _f	19.5 (9.9)	7.5YR 3/3 - 10YR 3/6 Dark Brown - Yellowish Brown	6.54 (1.54)	-25.58 (0.46)	22.8 (3.4)	0.67
	BC	17.0 (4.4)	10YR 4/3 Brown	2.32 (0.24)	-24.96(0.21)	20.6 (6.7)	0.94

3.2.2 Soil forming factors

The soils at both sites are Orthic Humo-ferric podzols (Canadian Soil System) developed from stony, well-drained sites of the Halifax soil series (MacDougall et al., 1963) in the Eastern Ecoregion of Nova Scotia (Neily et al., 2003). They are characterized by strongly-developed A_e eluvial horizon, a brown sandy loam illuvial B_f horizon high in organic matter, and a olive- to yellowish-brown sandy loam subsoil (MacDougall et al., 1963). Organic horizons are on average 11.9 cm and 13.3 cm, respectively, for Young and Mature sites (Prest et al., 2014). Soils are acidic (MacDougall et al., 1963), with mean pH of 4.5.

The two forests sites in Mooseland, NS, are located in the eastern region of the Halifax Regional Municipality, Nova Scotia, where bedrock geology belongs to the Cambrian-Ordovician Meguma Terrane, which consists of the Goldenville Group dominated by meta-sandstone, overlain by the Halifax Group, which is dominated by slate (White, 2010). The parent material of these soils is Beaver River Till which is a glacial till with a sandy texture characterized by >90% local clast lithology (Stea and Finck, 2001) within the Meguma Terrane (Supergroup) of Nova Scotia (White et al., 2008). Clay at both Young and Mature sites was predominantly illite with traces of chlorite, vermiculite and kaolinite (Brydon, 1958). Mature and Young forest sites both have an undulating terrain, with slopes between 2-15%, and have similar positions geographically, and so the soil-forming factors of slope and aspect (Jenny, 1941) would affect both sites equally. This region in central Nova Scotia receives 1300 mm of precipitation annually, and lies at approximately 100 m above sea level. Mean annual air temperature is 5.8 °C, with mean January and July temperatures of 5.8 °C and 16.9 °C, respectively (Environment and Climate Change Canada climate normals for Halifax, Nova Scotia). These two sites are close in proximity (2.5 km), and so variations in regional climate are considered identical. Any observed characteristics that were different at the two forest sites are assumed to be a result of variations in the remaining soil-forming factors: time since harvest and biota.

The forest stands at the Young and Mature sites are both typical of the Acadian Forest Region of the northern temperate zone (Mosseler et al., 2000), dominated by red spruce (*Picea rubens* Sarg.) with some balsam fir (*Abies balsamea* (L.) Mill.), and a small component of eastern white pine (*Pinus strobus* L.), yellow birch (*Betula*

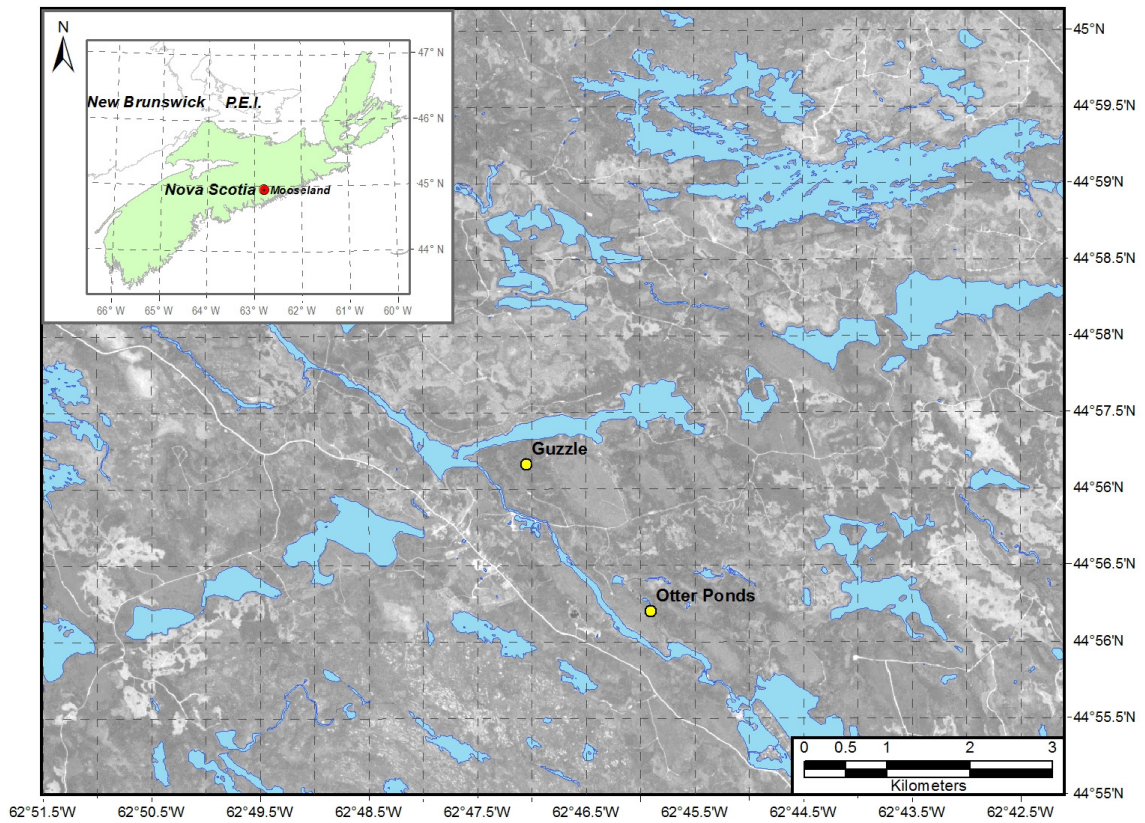


Figure 3.1: Map of sampling sites in Mooseland in Nova Scotia, Eastern Canada. The location of the Young (Guzzle Forest), and Mature (Otter Ponds Demonstration Forest) sampling sites are approximately 2.5 km apart and are indicated with circles. The location of Mooseland in Nova Scotia, Canada is indicated in the inset, top left.

alleghaniensis Britt.) and red maple (*Acer rubrum* L.). At the Mature site, a second-growth stand of red spruce currently dominates the canopy, with balsam fir, while at the Young site, the canopy is dominated by a mix of red spruce and balsam fir, and is currently undergoing self-thinning (Prest et al., 2014). Both sites were cleared for lumber using axes and horses in 1900. As logging operations at that time happened exclusively in winter, there was likely little physical disturbance to the forest floor and mineral soil. At both sites, limbs and small to large diameter tops would have been left on-site as detritus, and both forests regenerated naturally through secondary succession to mature forest stands. The Young site then experienced a second clear-cutting harvesting event in the summer of 1974 with chainsaws and skidders. This site regenerated naturally without site preparation, planting, fertilizers, pesticides or thinning. The only difference in forest management practices and general site and soil characteristics between the two sites is the clear-cutting that took place in 1974 at the Young site. These two forest sites in Mooseland, NS, are thus deemed comparable on the basis of parent material, soil texture/drainage class, soil type and morphology, as well as similar acidity (Catoni et al., 2016), regional climate and other geographical characteristics (slope and aspect).

3.2.3 Soil sampling

Three randomly selected sampling pits were established for bulk density measurements within a representative area at each forest site (Prest et al., 2014). At each of these bulk density sampling locations, two additional soil pits were dug within a 7 m distance from the bulk density sampling pit. At each forest sampling pit (n=9) mineral soils were sampled by genetic horizons (A_e , B_h , B_f and BC) according to the Canadian soil taxonomy (Soil Classification Working Group, 1998). The organic horizon was removed and the mineral soil was then excavated. Soil samples were carefully excavated by hand from each genetic horizon at both sites by combining a sample from each of the 4 walls of the pit, starting at the bottom layer to avoid cross-contamination. Samples were sieved to 12 mm in the field. The mean thicknesses of genetic horizons were measured in the middle of each of the 4 walls of each soil pit. Following sample collection, soil pits were backfilled. Sampled soils were kept cool immediately following sampling and were stored at 4°C until analysis.

Soil was processed in the laboratory by removing visible particulate organic matter, including root litter, and small rocks and pebbles that passed through a 12 mm sieve. As a result of methodological challenges arising from the high spatial variability in these soils (Bekele et al., 2013), soil samples from the nine pits were pooled in order to describe and comment on differences in the mineral pool structure in genetic horizons and not upon the inherent variability at the site level. Composite samples were created by thoroughly mixing equal amounts of sieved < 12 mm soil (by weight) from 9 sites. Soil color for genetic horizons was determined using fresh composite samples. Bulk density estimates were obtained from data on depth increments of soil sampled from this site (Prest et al., 2014) (Table 3.1).

3.2.4 Sequential selective dissolution mineral extraction methodology

Separation of four secondary mineral pools and associated C were carried out sequentially using selective dissolutions. The mineral pools extracted included: water-soluble minerals (extracted with deionized water); non-crystalline and/or amorphous organo-metal complexes (extracted with 0.1 M Na-pyrophosphate); poorly crystalline minerals, including ferrihydrite and imogolite (extracted with 0.1 M Na-hydroxylamine-HCl); and crystalline secondary minerals (extracted with Na-dithionite and HCl). The Na-pyrophosphate extraction is assumed to extract material from organo-metal complexes (OMC fraction), but may also dissolve allophane/imogolite and can promote limited dissolution of ferrihydrite and/or goethite (Kaiser and Zech, 1996). Hydroxylamine HCl extracts poorly-crystalline minerals (PCrys fraction) and is preferred to the traditionally-used oxalate in this study because it is a carbon-free analogue, and also because it represents a better extractant for poorly-crystalline phases as it has a higher specificity for ferrihydrite and other poorly-crystalline minerals (Chao and Zhou, 1983; Kostka and Luther, 1994). Dithionite HCl, a modified dithionite extractant (Wagai and Mayer, 2007), extracts the remainder of minerals from crystalline phases (Crys fraction) which are not removed by Na-pyrophosphate and hydroxylamine HCl, with dissolution of goethite, hematite, lepidocrocite, magnetite and gibbsite (McKeague and Day, 1966; Mehra and Jackson, 1960). The residual fraction left after these sequential extractions represented a SOC pool with slow turnover time and likely represents a stable or passive fraction of mineral-associated

SOC (Heckman et al., 2018). While there is limited understanding of this C pool, we assume it represents a pool that does not turn over on the timescales investigated in this study.

Briefly, triplicate 1.0 g sub-samples of air-dried composite was sieved to 2 mm, and then samples were shaken with 30 mL of extractant for 20 hours in 50 mL polypropylene centrifuge tubes, centrifuged at 10 000 RPM and decanted. Extraction residue underwent an additional wash stage where 20 mL (DI, pyrophosphate and hydroxylamine) or 20 mL 0.1 M HCl (dithionite) was added, and samples were shaken for a further 2 hours, centrifuged and decanted. Extracts from both stages were combined, filtered to 0.45 micrometers and kept at 4°C until analysis. Solids were dried, weighed and then homogenized before the next extraction. The final residue was dried and homogenized prior to elemental analysis (Heckman et al., 2018).

3.2.5 Selective dissolution extracts: Elemental analysis (C, Fe and Al) and stable isotope signatures of C

For bulk soil, C content (% C) and $\delta^{13}\text{C}$ of soils dried and milled soil solids were analyzed using continuous flow isotope ratio mass spectrometry (CF-IRMS) following combustion in an elemental analyzer (Eurovector EA-3028-HT, Manchester, UK) in line with a continuous flow isotope ratio mass spectrometer (Nu Horizon Isotope Ratio Mass Spectrometer, Wrexham, UK; and GV Isoprime Mass Spectrometer, Manchester, UK, carried out at St. Francis Xavier University).

Selective dissolution aqueous extracts were analyzed for C content (5050 Shimadzu TOC analyser - acidified samples, non-purgeable organic carbon combustion method, St. Francis Xavier University). Aqueous extracts were analyzed for $\delta^{13}\text{C}$ at the Memorial University Stable Isotope Laboratory (DeltaVPlus I interfaced using ConFlo III to a OI Analytical Aurora 1030W TOC Analyzer). Note that only one set of PCrys mineral pools (extracted with hydroxylamine HCl) was analyzed due to technical limitations.

Fe of selective dissolution extracts was determined using flame atomic absorption spectroscopy (Perkin Elmer AAnalyst 300, St. Francis Xavier University). A single set of soil horizon selective extracts was analyzed for Al with inductively coupled plasma mass spectrometry (ICP-MS) (Earth Sciences Department, Dalhousie

University). Matrix corrections were applied to all Fe and Al analyses.

3.2.6 Calculations and Data analysis - Contribution from each mineral pool to total C

Measured carbon content of solid soil samples and sequential selective dissolution extracts were expressed on a per mass basis (mg C g soil^{-1}). For each genetic horizon, the proportion of extractable C through the selective dissolution process was calculated from the sum of the amount of C extracted from all four selectively extracted mineral fractions (WS, OMC, PCrys, Crys) plus the C of the final solid residue remaining after extraction, and was compared to the C in the original soil horizon sample (i.e. bulk soil C), as follows in Equations 3.1 - 3.3:

$$\text{BulksoilC} = \text{Total}_{\text{extractableC}} + \text{ResidualC} \quad (3.1)$$

$$\text{ExtractableC} = \sum (C_{WS}, C_{OMC}, C_{PCrys}, C_{Crys}) \quad (3.2)$$

Experimental recovery of C was calculated as the difference between bulk soil C and the total measured C from extracts and residual C, as follows:

$$\text{ExperimentalRecovery} = \frac{\text{BulksoilC}}{\text{ExtractableC} + \text{ResidualC}} \quad (3.3)$$

We expect experimental recoveries to be lower than 100% due to the multiple steps involved in the methodology and potential for C loss during sample extraction processing, but note that it is possible for the recovery to be greater than 100% due to experimental and analytical error (Heckman et al., 2018).

3.2.7 Calculations and Data analysis - Carbon content and stable isotope ratio ($\delta^{13}\text{C}$)

Stable isotope ratios from isotopic abundances of ^{13}C and ^{12}C from aqueous extracts and soil solids were determined using the following relationship in equation 3.4:

$$\delta^{13}\text{C}(\text{‰}) = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] * 1000 \quad (3.4)$$

where R is the ratio of ^{13}C to ^{12}C , relative to PeeDee Belemnite.

3.2.8 Calculations and Data analysis - Metrics of SOM-mineral interactions

The Fe and Al content of extractable mineral pools along with the C content of each pool provides a measure of the minerals available for binding with C in each mineral-associated OM pool.

C:mineral ratio

The molar ratio of C to extracted minerals (Fe+Al) in each pool (WS, OMC, PCrys, Crys), was used as an indicator of the nature of the interaction of OM with minerals. Low ratios, such as those found at depth, indicate adsorption onto mineral surfaces (i.e. coatings), whereas higher ratios indicate mixed organic matter and mineral phases such as colloidal complexes and solid co-precipitates. (Fuss et al., 2011; Sauer et al., 2007).

Empirical relationship between C content and Fe+Al minerals

The relationship between the mass of Fe and Al in each pool extracted following sequential selective dissolutions (WS, OMC, PCrys and Crys pools) and the bulk C content, which provides a measure of the C sorption and binding potential, was evaluated using regression analysis for each horizon at the two sites. Note that the sum of sequentially extracted OMC and PCrys yields the total C associated with poorly-crystalline phases ($PCrys_T$) as isolated in other studies serially with oxalate or hydroxylamine (Courchesne and Tourmel, 2008). This was used to determine which mineral pools control the variation in C storage through depth.

Pedogenic ratios

The amount of Al in the organo-metal complexes pool relative to the $PCrys_{Totalpool}$ ($Al_{OMC} / Al_{OMC} + Al_{PCrys}$) indicates the proportion of non-crystalline mineral-organic matter interactions that are based on complexation reactions, and the ratios of $Fe_{PCrys} : Fe_{Crys}$ provide information on weathering and crystallinity of Fe phases (Lawrence et al., 2015), where a low Fe_{PCrys} to Fe_{Crys} ratio signifies that soil has a higher relative content of crystalline minerals and therefore has likely experienced a stronger degree of weathering (Courchesne and Tourmel, 2008). (Note that while in some disciplines, weathering may have other meanings, according to the convention of pedology, weathering indicates biotic- or climate-influenced breakdown of mineral structure.)

3.2.9 Statistical Analysis

In order to determine the significance in the difference of means (two-tailed) when comparing extracted pools through depth, one-way analysis of variance (ANOVA) at each site through depth and Student's T-tests were calculated. Generalized linear mixed models (GLMM) were used to assess the effect of site as a fixed categorical effect, with random error assigned for extracted pools and horizon on C, Fe+Al, C:Fe+Al ratio, and $\delta^{13}\text{C}$. Models that explained the effect of site were compared to null models through ANOVA analysis. The correlation of linear regressions between soil mineral pool measurements and C were also assessed. Regression was carried out using Sigmaplot (version 14.0). GLMM analysis and ANOVA to compare models used R package lme4 (lmer) under R version 3.3.1.

3.3 Results

3.3.1 Description of soil profiles at Young and Mature sites

Carbon in bulk soil samples at Mature and Young forest sites showed a distinct pattern through depth, with highest C content (mg C g soil^{-1}) for the B (B_h and/or B_f) horizons at both sites (Figure 3.2, and Supplementary data Appendix A). Samples of bulk soil also showed an enrichment in $\delta^{13}\text{C}$, an increase in bulk density, and a decrease in C:N ratio through depth (Table 3.1).

Soil samples belonged to the same textural class (primarily sandy loam) through depth, due to a similarity in particle size distribution (Supplementary data Appendix B), with the exception of an outlier: the thin B_h horizon, found only at the Mature site, which contained 30% clay. Other differences between the morphology of the soil at the two sites were apparent. The B_f horizon was almost twice as thick at the Mature site compared to the B_f at the Young site, with a darker value and redder hue (Table 3.1). Although the A_e horizon was characterized by a similar thickness at both the Young and Mature sites, the A_e horizon at the Mature site was lighter than the Young site and contained less C. One-way analysis of variance at each site indicated that the depth trends at each site for C content, $\delta^{13}\text{C}$, Fe, and Al were significant at $p < 0.05$.

Bulk C content (mg C g soil^{-1}) was 45% higher, 45% lower, and no different

for A_e , B_f , and BC horizons, respectively, when comparing Young and Mature sites (Table 3.1). Overall, the sum of C from all extracted pools through depth was more than double at the Mature site compared to the Young site (from Eq. 3.2: $\Sigma = 138.04$ mg C g soil⁻¹ (± 4.35) versus 61.80 (± 1.17) mg C g soil⁻¹, respectively). Results from GLMM analysis of C content in extraction pools from horizons indicated that between-site differences could explain the variation in C content between the sites, significant at $p < 0.1$ ($\chi^2 = 3.3708$, $p = 0.06636$).

Table 3.2: Results of sequential selective dissolution of podzol soils from two sites, Young and Mature, 35 and 110 years since clear-cutting, respectively. Numbers in brackets are ± 1 SD; n=3 for C and Fe, and n=1 for Al. Extractions are water soluble (WS), organo-metal complexes (OMC), poorly crystalline (PCrys), and crystalline (Crys) minerals. Note that analysis of $\delta^{13}\text{C}$ of PCrys was not possible due to technical limitations.

		YOUNG				MATURE			
Horizon	Mineral phase	Prop of total C (%)	Fe mg g soil ⁻¹	Al mg g soil ⁻¹	Molar C:Fe+Al	Prop of total C (%)	Fe mg g soil ⁻¹	Al mg g soil ⁻¹	Molar C:Fe+Al
A _e	WS	5.1	0.0019 (0.005)	0.010	0.13 (0.03)	4.8	0.004 (0.001)	0.009	0.34 (0.05)
	OMC	76.7	2.90 (0.09)	0.42	8.33 (1.07)	79.6	2.6 (0.1)	0.54	5.396 (0.003)
	PCrys	8.0	0.170 (0.001)	0.46	2.88 (0.44)	7.1	0.80 (0.02)	0.31	2.49 (0.22)
	Crys	10.2	1.3 (0.7)	0.23	2.50 (0.61)	8.5	0.7 (0.7)	0.36	1.17 (0.02)
B _h	WS					0.2	0.057 (0.007)	0.036	0.11 (0.05)
	OMC					88.6	26.4 (1.0)	3.50	7.43 (0.37)
	PCrys					5.4	1.6 (0.5)	1.43	2.61 (0.19)
	Crys					5.8	1.74 (1.00)	0.34	3.95 (1.74)
B _f	WS	0.8	0.13 (0.001)	0.033	0.11 (0.03)	0.5	0.001 (0.0004)	0.033	1.29 (0.32)
	OMC	92.8	11.0 (0.13)	6.02	5.68 (0.12)	94.9	11.7 (0.6)	10.11	6.78 (0.44)
	PCrys	4.0	2.30 (0.08)	2.35	0.80 (0.02)	3.1	2.3 (0.2)	3.31	0.79 (0.09)
	Crys	2.4	3.80 (2.60)	0.84	0.67 (0.21)	1.5	2.9 (1.0)	0.65	0.84 (0.14)
BC	WS	0.9	0.015 (0.002)	0.012	0.06 (0.01)	1.1	0.001 (0.001)	0.012	0.91 (0.52)
	OMC	89.5	5.2 (0.2)	4.93	5.26 (0.17)	89.2	5.0 (0.4)	4.61	5.46 (0.16)
	PCrys	5.9	1.4 (0.1)	2.94	0.71 (0.04)	6.3	1.51 (0.06)	4.37	0.53 (0.04)
	Crys	3.7	5.6 (3.0)	1.20	0.44 (0.08)	3.4	4.4 (0.5)	1.32	0.43 (0.05)

3.3.2 Distribution of mineral-associated organic matter pools

The sequential selective dissolution procedure extracted four C pools of increasing crystallinity from each soil horizon that varied in their individual contributions through depth at each site (Figure 3.3). The most abundant extracted mineral-associated OM pool was the organo-metal complexed (OMC) pool, which accounted for 77% to 80% of the total extracted in A_e horizons, over 93% to 95% of the C in B_f horizons, and 90% of the C in BC horizons at both sites (Figure 3.3). The water soluble pool at both sites made the lowest contribution to extracted pools, with 5% in A_e , and less than 1% in B_f and BC horizons (Figure 3.2 and 3.3). The combined contribution from PCrys and Crys fractions were similar in BC horizons between sites at approx. 6% and 3.5% of the total C, respectively (Figure 3.3). In A_e horizons, Crys and PCrys pools together represented 15%-18% of the total C, with a higher proportion of Crys pools than PCrys. In B_f horizons, these more crystalline pools represented a much smaller proportion of the total C (5-6.5%), where PCrys contributed a higher proportion than Crys (Figure 3.3).

3.3.3 Comparing C in bulk soil and mineral pools in Young and Mature sites

Organo-metal complexes accounted for 65% and 74% of bulk soil C in B_f horizons, and 66% and 72% of bulk soil C in BC horizons for Young and Mature sites respectively, while 32% and 25% of bulk soil C in A_e horizons of Young and Mature were associated with OMC (Figure 3.2). The other mineral-associated OM pools contributed less to bulk soil C storage than OMC; PCrys OM pool C was 2.5-5.0% of bulk soil C, and Crys mineral C pool ranged from approx. 1.0-3.5% of total bulk soil C. In each horizon at both sites, the WS pool accounted for the lowest proportion of total bulk soil C at 0.4-1.7% (Figure 3.3). When comparing sites, there was a consistent difference observed: A_e and B_f horizons of the Young site consistently had a lower proportion of OMC pools and a higher proportion of PCrys and Crys C pools than the Mature site (Figure 3.2 and 3.3). PCrys and Crys pools in the A_e horizon at the Young site had a higher C content compared to the Mature site (Figure 3.2 e-g and Figure 3.3), whereas C in pools from BC horizons had a similar C content at both sites (Figure 3.3).

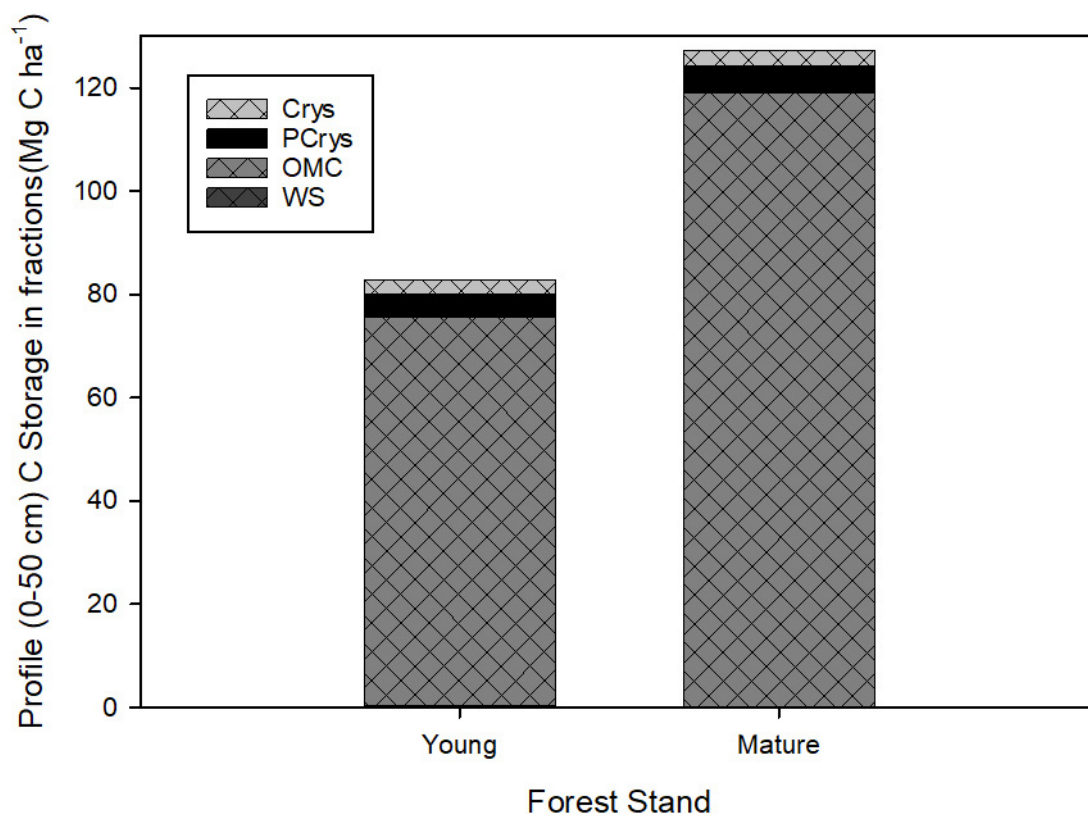


Figure 3.2: Distribution of C in sequential selective dissolution extracts (WS = water soluble; OMC = organo-metal complexes; PCrys = poorly crystalline; and Crys = crystalline) through depth (0-50 cm) in depth increments for the Young and Mature site at Mooseland, Nova Scotia, Canada. Note that the WS contribution to the total is less than 1% in both Young and Mature forest soils, and is therefore not visible in this graph.

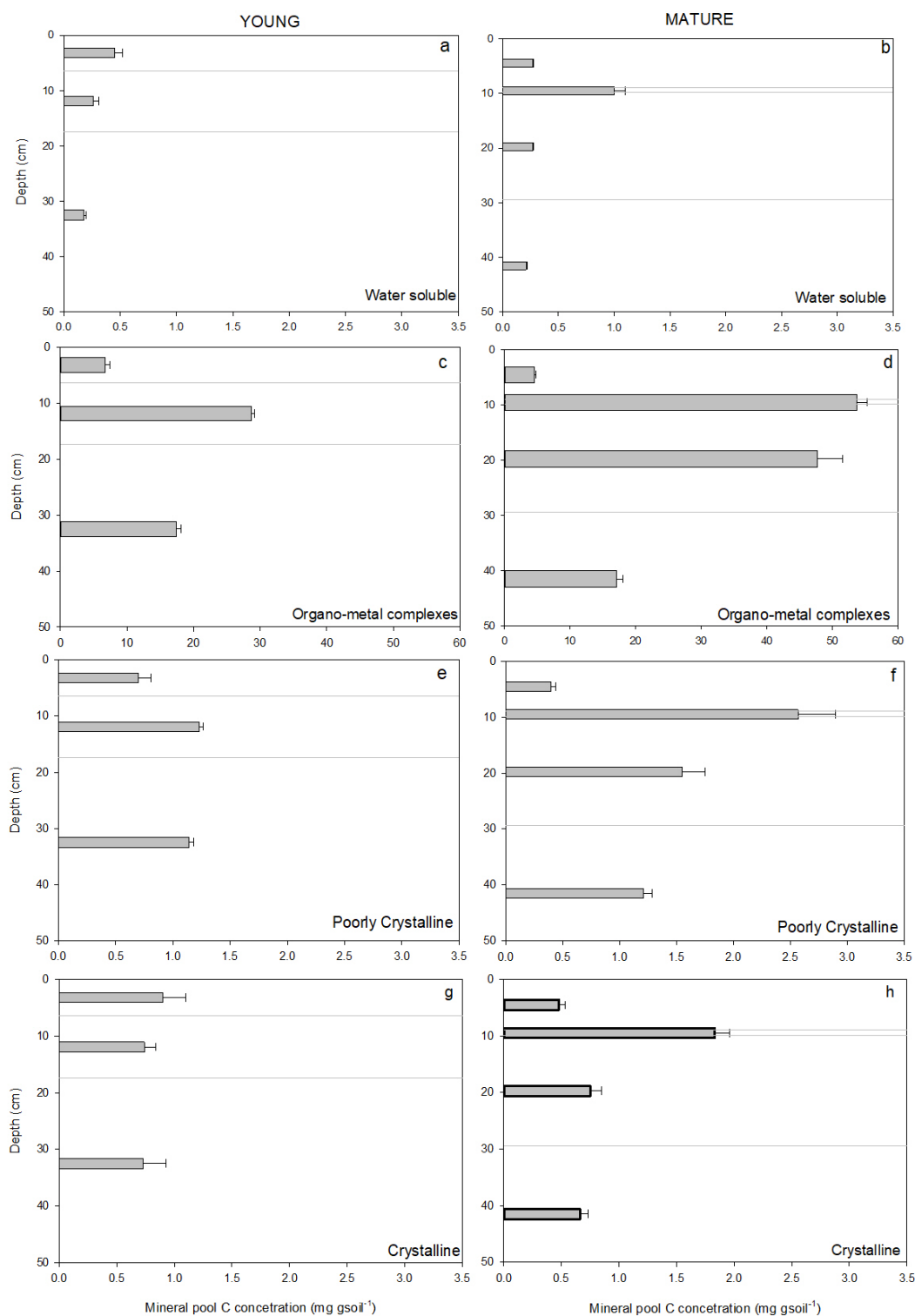


Figure 3.3: Carbon (mg g soil^{-1}) from sequential selective dissolutions of soil from horizons of podzols at Young and Mature forests in Mooseland, Nova Scotia, Canada. Grey lines indicate the position of A_e , B_h , B_f and BC horizons in sequence through depth for the Young and Mature sites. Note the large difference in scales for the C content for the following mineral fractions a) water soluble, b) organo-metal complexes and c) poorly crystalline and d) crystalline secondary minerals.

3.3.4 Fe and Al content of mineral-associated OM pools

Analysis of sequential selective dissolution extracts for minerals revealed differences in the content of Fe+Al minerals when comparing the suite of mineral-associated pools in soil horizons at the Mature and Young sites through depth. The amount of extractable Al and Fe minerals (per g soil) was lowest in A_e (eluvial) and highest in illuvial B horizons (where $B_h > B_f > BC$) (Table 3.2). Overall, total Fe and Al were 42% higher at the Mature site compared to the Young site through the profile. In the B_h horizon at the Mature site (note that this horizon was absent from the Young site), almost as much Fe was extracted in that one single horizon (29.85 mg g soil⁻¹) as that in the entire profile at the Young site (33.72 mg g soil⁻¹) (Table 3.2).

Overall, Fe+Al in the OMC pools made the largest contribution to all extractable minerals for all horizons at both sites (Table 3.2). Higher amounts of Fe and Al minerals (per g soil) were extracted from the Mature site in the WS (26% higher), OMC (58% higher) and PCrys (29% higher) pools, but a smaller proportion (8% lower) of Fe+Al in the Crys pool were extracted, compared to the Young site (Table 3.2). PCrys pools and Crys pools accounted for 8%-27% and 11%-32% of extractable soil minerals in each horizon (Table 3.2), respectively. A general increase in Crys pool Fe + Al was observed through depth, with a larger mineral content in Crys pools at the Young site (Table 3.2). Despite this, total Fe plus Al were not significantly different when comparing sites: the results of GLMM analysis indicated that site category did not explain differences in Fe plus Al content of extracted fractions from A, B and BC horizons ($\chi^2 = 0.7115$; $p = 0.3989$).

Between 65% and 74% of bulk soil C in B horizons (B_f and BC) was extracted through this sequential selective dissolution methodology. The proportion of mineral-associated C in A_e horizons at both sites was lower than in B horizons, with only 25% to 32% of bulk C bound in extractable mineral-associated OM pools (Table 3.3).

Table 3.3: Results of residue analysis and proportion of mineral-associated C extracted mineral fractions following sequential separations for horizon-based samples from Young and Mature forest sites. The results of analysis of final residue compared to summed fractions from water, pyrophosphate, hydroxylamine and dithionite extractions. The recovery was based on the difference between the bulk C (Table 3.1) and residue to generate an expected extracted amount compared to measured fractions. The proportion of bulk C that is associated with extractable secondary minerals. * Note: Calculation of recovery of C in A_e horizons involves comparison of extracted fraction to bulk soil with particulate organic matter.

	YOUNG					MATURE				
Horizon	Residue C %	Residue $\delta^{13}C$ ‰	Σ mineral C in extracted fractions (mgC g soil ⁻¹)	Recovery %	Prop. C Assoc. w Minerals %	Residue C %	Residue $\delta^{13}C$ ‰	Σ mineral C in extracted fractions (mgC g soil ⁻¹)	Recovery %	Prop. C Assoc. Minerals (%)
A _e	1.73 (0.02)	-27.72 (0.03)	0.88 (0.11)	60.1	27.6	0.82 (0.07)	-26.95 (0.12)	0.57 (0.04)	50.0	29.0
B _h						2.55 (0.20)	-26.64 (0.03)	5.91 (0.27)	99.6	69.7
B _f	1.27 (0.43)	-27.05 (0.22)	3.09 (0.08)	95.2	68.5	1.44 (0.13)	-26.37 (0.08)	5.03 (0.42)	98.5	76.8
BC	0.68 (0.01)	-26.98 (0.04)	1.95 (0.09)	106.1	77.5	0.45 (0.03)	-25.74 (0.12)	1.92 (0.11)	102.8	80.0

3.3.5 Mineral-SOM interaction metrics

The molar C:(Fe+Al) ratio of mineral-associated C pools generally declined through depth at both sites (Table 3.2). The OMC mineral-associated OM pools in each horizon at both sites had the highest values of molar C:(Fe+Al) compared to all other extracted mineral pools. High values in the B_f horizons (Table 3.2) indicates co-precipitation with C, whereas low ratios, observed in the WS, PCrys and Crys pools, are coatings of organic C on minerals. Molar C:(Fe+Al) ratios were different in Young and Mature sites for B_f and A_e horizons, and the effect of site found to explain differences in molar C:(Fe+Al) through GLMM analysis ($\chi^2 = 4.3631$; $p = 0.03672$). In the B_f horizon at the Mature site, higher molar C:(Fe+Al) ratios compared the Young site indicates higher loading of C with minerals in this mineral-associated pool, where higher molar C:(Fe+Al) ratios were calculated for the A_e horizon extracts from the Young site compared to the Mature site. Molar C:(Fe+Al) ratios for BC horizon C pools at the two sites were not different when comparing the two sites.

Using Fe and Al data for extracted fractions, calculated pedogenic ratios indicate that the two sites contrasted in regards to organic complexation and weathering. Organic complexation was higher for all horizons through depth at the Mature site, and especially notable in the B horizons (Figure 3.4a). Weathering was consistently higher for the Young site (Figure 3.4b), as indicated by consistently lower pedogenic ratios in each horizon.

The variation in bulk soil C was correlated with the variation in C and in Fe and Al of certain mineral pools. A positive linear relationship between bulk soil C and total of OMC pool was observed ($r^2 = 0.88$; Figure 3.5a). The extent to which this linear model described the relationship between soil C and mineral content was greatly improved when data from A_e horizons were removed from the analysis ($r^2 = 0.99$; $p < 0.05$). There was a strong but negative relationship between bulk soil C and the Fe ($r^2 = 0.89$) and Al ($r^2 = 0.97$) content of Crys fraction at both sites (Figure 3.5b) ($p < 0.05$).

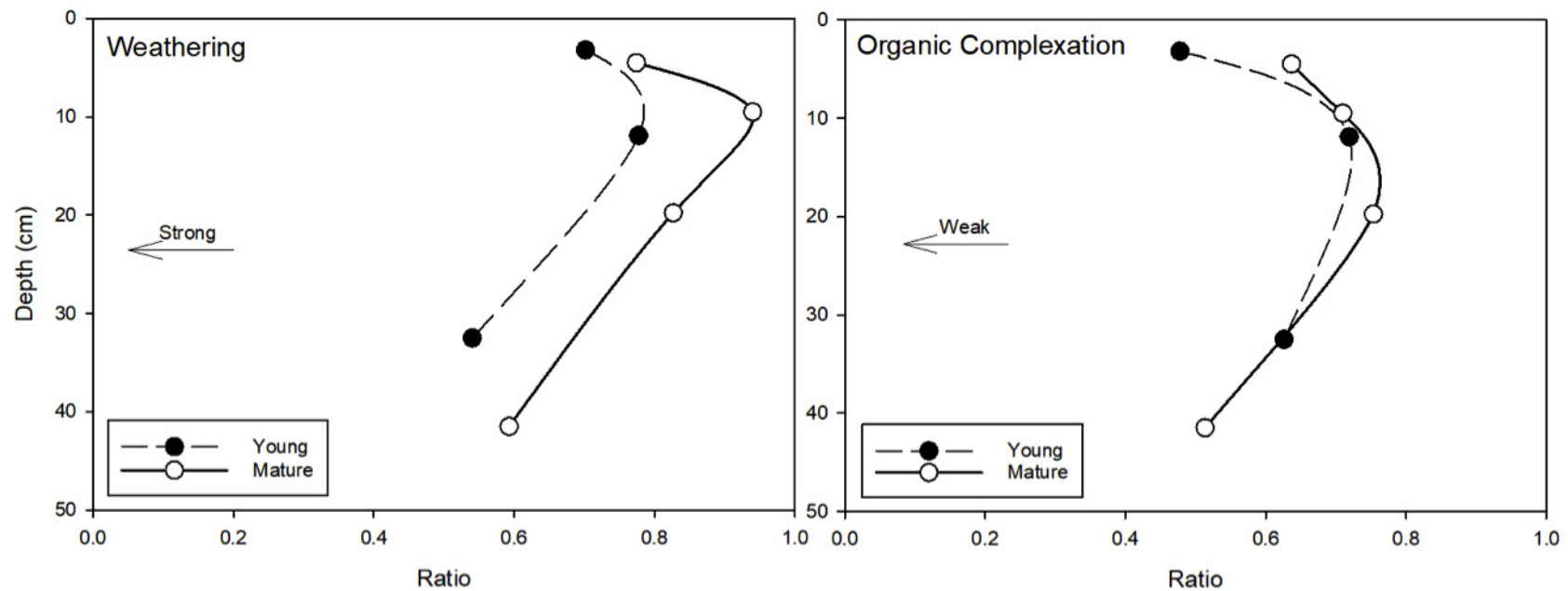


Figure 3.4: Plot of pedogenic ratios for Young (broken line) and Mature (solid line) through depth, which are indexes of a) soil weathering and b) organic complexation. Note that strong soil weathering is indicated by a low ratio in a). In both diagrams, the site with stronger complexation or soil weathering has a darker line.

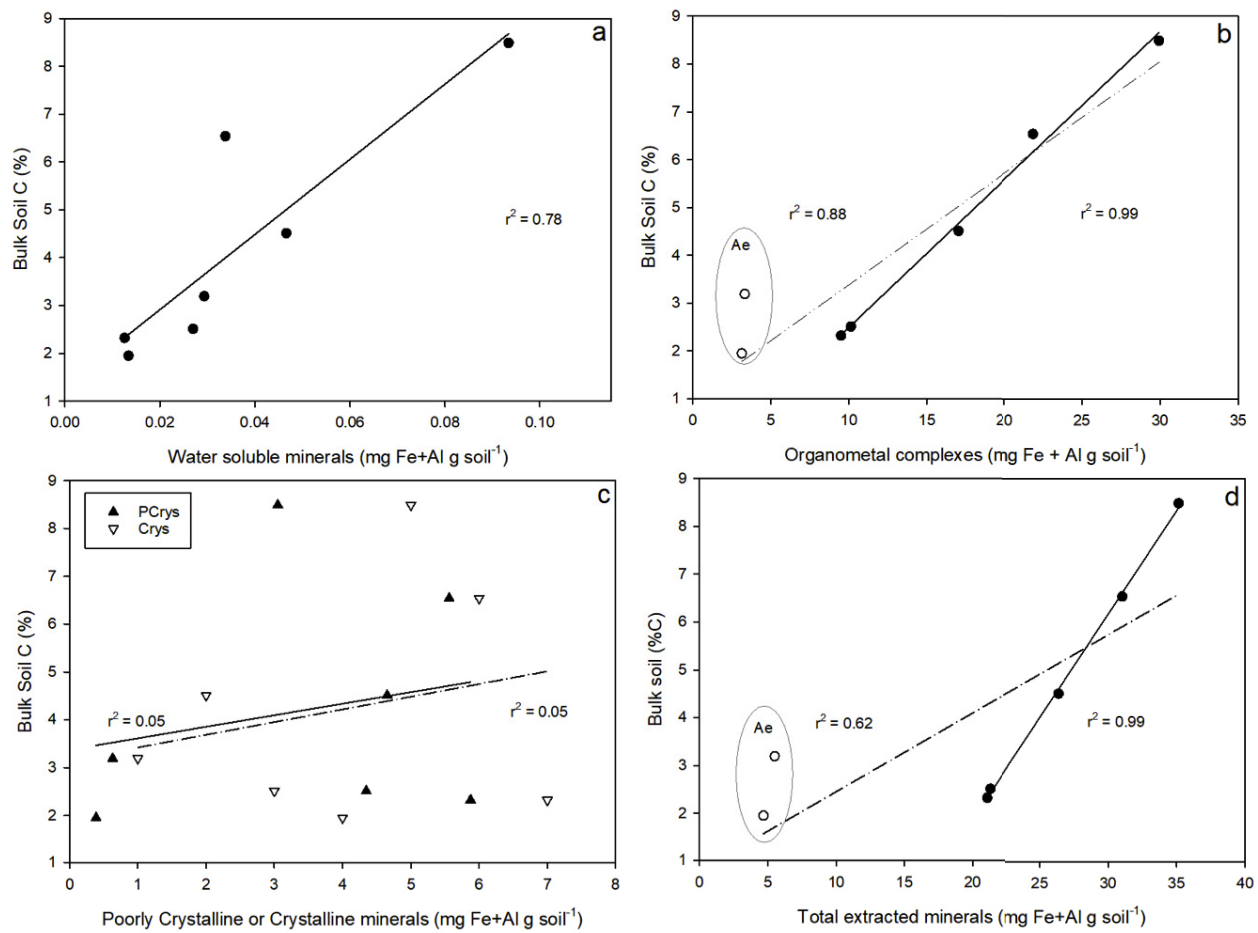


Figure 3.5: a) Relationship between a) %C and the sum of organo-metal Fe and Al and poorly-crystalline Fe and Al; b) % C in bulk soil and the content of Fe and Al in crystalline secondary mineral phases. Data for both Mature and Young sites are combined, and the difference between Al and Fe are highlighted with a broken(Al) or solid(Fe) regression line.

3.3.6 $\delta^{13}\text{C}$ patterns within soil profiles

Bulk soil had progressively higher values of $\delta^{13}\text{C}$ through depth at both sites, and this trend through depth was significant ($p < 0.05$). Stable isotope signatures of C in bulk soil horizons ranged from -27.0‰ in A_e to -25.0‰ in BC at the Mature site, and $\delta^{13}\text{C}$ values of bulk soil from -27.3 to -25.5‰ at the Young site in horizons through depth (Figure 3.6). The OMC C pool $\delta^{13}\text{C}$ isotope signatures most closely followed that of bulk soil C through depth (Figure 3.6) ranging from -27.7‰ in A_e to -25.3‰ in BC horizons. Water soluble extracts were the most ^{13}C -depleted mineral-associated SOM pool, and were more depleted than bulk soil (-29.0‰ (WS) compared to -26.5‰ (bulk soil)), while the most enriched stable isotope signatures of C were measured in the Crys pools at both sites, ranging from -13.4‰ to -16.4‰ (Figure 3.6). The stable isotope ratio of each of the mineral-associated OM pools was similar when comparing sites. The only difference in the $\delta^{13}\text{C}$ of mineral-associated OM pools between sites was in the A_e horizon, where the Young site was more depleted by 3‰ , although this difference is not significant according to one-way ANOVA at $p < 0.05$. GLMM analysis, on the other hand, determined that site was a significant explanatory factor in a model to explain $\delta^{13}\text{C}$ of extracted pools ($\chi^2 = 5.8603$; $p = 0.01549$).

3.4 Discussion

The results of this study demonstrated that soil C bound with a suite of mineral-associated pools vary in quantity and stable isotope ratio through depth in podzolic soils. The observed differences between sites of contrasting stand age suggest that disturbance history may influence these factors.

3.4.1 C content and distribution of mineral-associated pools

Sequential selective dissolution separated mineral-associated OM into pools of increasing crystallinity, from water soluble (WS), to non-crystalline colloidal organo-metal complexes (OMC), to poorly-crystalline organic matter and mineral co-precipitates (PCrys), and OM associated with crystalline minerals (Crys). Overall, the results demonstrated that the majority of C through depth in the soil profile was associated

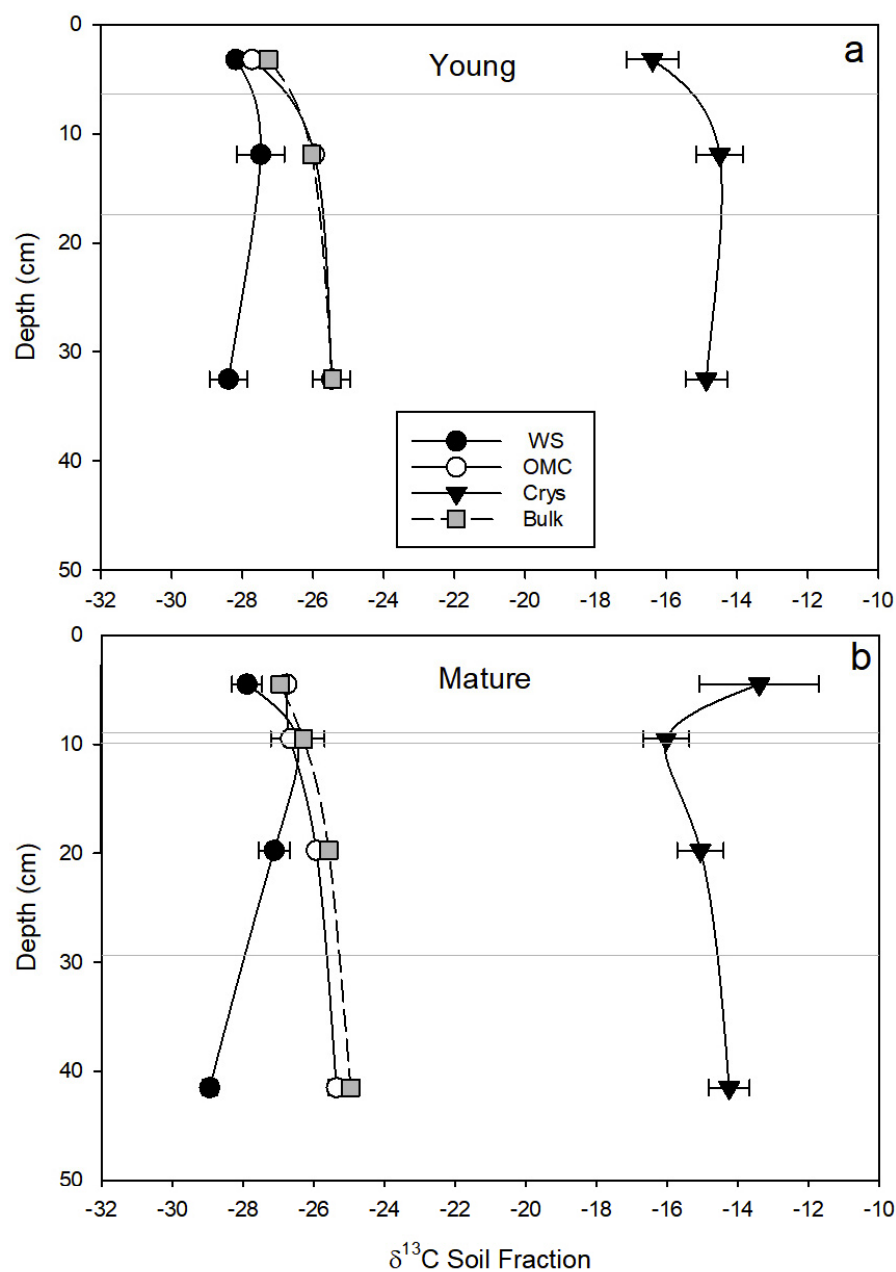


Figure 3.6: (a-d) Results of stable isotopic analysis of carbon ($\delta^{13}\text{C}$) in genetic horizons through depth at Young and Mature forest sites following sequential selective dissolutions for water soluble (WS), organo-metal (OMC), and crystalline (Crys) fractions. Grey lines indicate the position of A_e , B_h , B_e and BC horizons in sequence through depth for the Young and Mature sites. $\delta^{13}\text{C}$ bulk soil at both sites (white circles) are included for comparison. Note how closely the bulk soil $\delta^{13}\text{C}$ follows the trajectory of the organo-mineral fraction data.

with minerals in illuvial B_f and BC horizons (Table 3.3), and that this mineral-associated organic matter was primarily present as organo-metal complexes (Figures 3.2 and 3.3).

Organo-metal complexes had the highest C concentrations (mg C g soil^{-1}) of all mineral-associated pools (Figure 3.3), and accounted for more than 80% of the bulk soil C in all horizons (Table 2.3). The highest proportion of OMC was observed (>90%) in the B_f horizons at both sites and in the B_h horizon (found only at the Mature site) (Figures 3.2 and 3.3). Minor contributions to mineral-associated OM pools were made by PCrys and Crys pools, and together accounted for only 5-10% of mineral-associated C (Figure 3.2). A negligible contribution was made by WS minerals, whose C concentrations were an order of magnitude lower than the OMC pools, contributing approximately 1-5% of the total mineral-associated C (Figure 3.3). These findings are supported by Heckman et al. (2018), who, using the same sequential methodology, also concluded that the distribution of mineral pools is dominated by organo-metal complexes in a range of soil types through depth, with minor contributions from other mineral-associated OM pools.

Although most organic matter in B horizons was mineral-associated, in contrast, only a small proportion of the C in the eluvial A_e horizons was associated with minerals. The bulk C and the C and mineral content (Fe and Al) of the mineral-associated pools were lower in A_e than B horizons (Table 3.2), although they were still dominated by OMC pools, and had a relatively higher proportion of PCrys and Crys pools than B horizons (Figure 3.3). These trends are not surprising from a pedological standpoint: podzolic eluvial horizons are highly weathered and by their nature would contain an overall lower content of minerals for C binding, and a higher content of more weathered crystalline phases (Buurman and Jongmans, 2005; Lundstrom et al., 2000). The relatively low content of C associated with minerals in A_e horizons compared to B horizons is consistent with previous research. In density-separated soils from depth increments, Diochon and Kellman (2009) determined that the free organic matter fraction (including particulate SOM) ranged from 30-60% of the C in the top 5 cm, while the heavy density organo-mineral fraction below 5 cm was >60% of bulk soil C. Heckman et al. (2018) also found that C from a heavy density fraction of a podzolic eluvial (A_e) horizon was only partially extractable with the same suite

of extractants as this study. Thus, the C in A_e that is not associated with minerals but is measured in bulk soil C analysis was likely either particulate organic matter or a stabilized phase that was not extractable using this methodology (Heckman et al., 2018).

3.4.2 Interaction between organic matter and minerals

OMC pools extracted with (pyrophosphate) also contained the most Fe and Al in each horizon (per mass basis), and the C:(Fe+Al) ratio was higher in this pool than the other more crystalline pools (Table 3.2). In fact, a strong linear relationship was found to exist between bulk C content in horizons and the mineral (i.e. Fe + Al) content of OMC pools (Figure 3.5), highlighting the role of non-crystalline minerals in the variation in C storage through depth in soil profiles. Previous research has determined that bulk soil C storage is directly related to the content of pyrophosphate- and/or oxalate-extractable minerals (Heckman et al., 2009; Jimenez and Villar, 2017; Kaiser et al., 2012; Lawrence et al., 2015; Sanderman et al., 2014), which would correspond to the combination of the sequentially-extracted pyrophosphate (OMC) and hydroxylamine (PCrys) pools in this study. This combining of mineral pools (OMC + PCrys) is justified since Na-pyrophosphate can extract Al and Fe and associated organic matter from colloidal and from more crystalline forms of organo-mineral associations (Kaiser and Zech, 1996), and so there is likely some overlap between the OMC and PCrys pools.

Molar C:(Fe+Al) ratios were used to indicate the forms of mineral binding for each mineral pool. High C:(Fe+Al) ratios for OMC are consistent with co-precipitation of a mixed organic matter and mineral phase, consistent with known soil formation processes occurring in podzols, where the highly-coloured C-rich B horizons are characterized by precipitated Fe and Al hydroxide organo-mineral complexes (Buurman and Jongmans, 2005; Lundstrom et al., 2000; Sauer et al., 2007). Low C:(Fe+Al) ratios of PCrys and Crys suggest that the adsorption of organic molecules onto mineral surfaces is a dominant stabilization process for more crystalline minerals (Table 3.2). Water soluble OM had the highest C:(Fe+Al) ratios, and represents an ionic form of OM-mineral associations, although this mineral pool was found to be the lowest in abundance and generally also had the lowest C content.

In sharp contrast to the trends observed with OMC and PCrys pools, the quantity of Fe and Al in crystalline mineral pools were found to be negatively correlated with bulk C content (Figure 3.5b). This is counter-intuitive, since radiocarbon evidence indicates that OM associated with crystalline minerals turns over more slowly (Heckman et al., 2018), thus representing a more stable pool. Since mineral-OM interactions in the Crys pool are primarily through surface adsorption, it is possible that there is a limit to the storage potential of this pool, consistent with the concept of C saturation (Stewart et al., 2007). This could explain why the C content of this pool is relatively constant through depth (Table 3.2). Increasing C storage in soil profiles beyond the limits of the crystalline mineral pool would thus depend on increasing the size of the OMC pool. However, the presence of OMC has been demonstrated to prevent the formation of more crystalline secondary mineral phases (Lawrence et al., 2015; Parfitt et al., 2009), thus paradoxically limiting long-term storage. Studies have established that the effects of land-use on soil C stability and turnover are regulated by the content and crystallinity of Fe and Al oxide minerals (Lawrence et al., 2015; Lacroix et al., 2016; Doetterl et al., 2015; Li et al., 2012), so it is important for research to further resolve the relative importance and mechanistic understanding of the stability of OM associated with the suite of mineral phases of different crystallinity.

3.4.3 Distinct character of organic matter in mineral-associated pools

Isotopic trends have been used as informative integrative indicators of soil processes, especially in regards to changes in litter inputs and identification of functional SOM pools. In this study, analysis of $\delta^{13}\text{C}$ of mineral-associated OM pools were used to examine the chemical character of extracted mineral-associated OM pools and to compare the nature of C stabilized with minerals at both sites.

Analysis of natural abundance of $\delta^{13}\text{C}$ in sequential selective dissolution extracts revealed differences in the character of C associated with these mineral pools. Generally, mineral-associated OM pools became increasingly enriched in ^{13}C through depth in horizons, with an enrichment of 0.5 - 1‰, a trend observed in both the bulk soil and the mineral-associated OM pools from A_e , B_f and BC horizons. The $\delta^{13}\text{C}$ of the OM associated with the OMC was close to that of the bulk OM through depth, whereas

the WS and Crys pools were distinct: the WS pool had 1-3‰ lower and Crys had 9-15‰ higher values of $\delta^{13}\text{C}$ than bulk soil and OMC pools (Table 3.2, Figure 3.6). These results are in accordance with previous research studies that have analyzed trends in $\delta^{13}\text{C}$ of OM of isolated soil mineral pools (e.g. Adhikari and Yang, 2015; Kallenbach et al., 2016; Zhao et al., 2016). The $\delta^{13}\text{C}$ of OMC extracted in this study were found to be in the same range as the $\delta^{13}\text{C}$ signatures of pyrophosphate-extracted soil mineral-associated OM pools in similar soils (Kayler et al., 2011; Lawrence et al., 2015), and matches the range of $\delta^{13}\text{C}$ signatures observed for plants and associated soil microbes in C3 systems (James R. Ehleringer et al., 2000; Kohl et al., 2015; West et al., 2006). These results suggest that the source of OM in OMC is likely plant-derived, with a contribution from ^{13}C -depleted aromatic lignin and humic moieties (Kramer et al., 2012; Sanderman and Kramer, 2017; Watanabe and Takada, 2006).

Our results are also consistent with studies that have identified an isotopically-light water soluble pool (i.e. dissolved organic carbon) in mineral soil horizons that is more depleted in ^{13}C than the bulk soil (Ludwig et al., 2007; Mobley et al., 2015). The higher $\delta^{13}\text{C}$ values of OM associated with the Crys pool of this study are also in the range observed in other studies (e.g. (Adhikari and Yang, 2015)), and are also in accordance with research that has demonstrated that this SOM is characterized by an increasing proportion of aliphatic and microbially-derived C with depth (Bostrom et al., 2007; Etcheverra et al., 2009; Kelleher and Simpson, 2006; Kohl et al., 2015; Rumpel et al., 2015; Shen et al., 2014; Zhao et al., 2016). Radiocarbon measurements of sequentially-extracted mineral-associated organic matter pools support this: C in OMC was found to be relatively recent, and thus a pool with a faster turnover, and C in the Crys mineral-associated OM pool is older with a slow turnover time (Heckman et al., 2018), thus representing a more stable OM pool. Due to technical limitations due to the interference of hydroxylamine with the DOC analysis methodology, it was not possible to analyze the PCrys fraction for $\delta^{13}\text{C}$, but this information could help to resolve whether this pool was also distinct from OMC and Crys.

3.4.4 Quantity and character of C in mineral soil considering its disturbance history

Evidence from this study suggests that changes in the C content and proportions of mineral-associated OM pools through depth in soil profiles were a result of destabilization following harvesting, primarily driven by changes in the size and C content of the OMC pool. Since these two study sites only differ in their disturbance history, the reduction in the C quantity and the change in the nature of mineral associations at the Young (35 yr) compared to the Mature (110 yr) site through depth are assumed to be due to the more recent clear-cutting disturbance experienced by the Young site. The sites were selected based on a previous regional study (Diochon et al., 2009) that identified minimum soil C stores after approximately 3 decades when compared to sites > 100 years of age.

In B horizons, where the greatest differences in the soil C between sites was observed, bulk soil C and mineral-associated C of illuvial B_f horizons in the Young site were lower by 50% compared to the Mature site (Table 3.2 and Figure 3.2). Organo-metal complexes and PCryst mineral-associated OM pools showed the greatest change in C storage in response to recent forest harvesting disturbance, as suggested by differences in the C content of these pools between sites (Figure 3.3). Since B_f horizons occupy most of the soil profile down to >40 cm at both of these sites, changes to the mineral-associated OM content of illuvial horizons have important implications for profile C storage.

Although there was a lower amount of potential minerals for organic matter binding at the Young site (mg Fe+Al per g soil⁻¹; Table 3.2), lower C:(Fe+Al) ratios in B horizons at the Young site indicated that the minerals bound less C than an equivalent mass at the Mature site (Table 3.2). This suggests that there is a reduced loading of organic matter on available mineral surfaces and/or reduced binding of organic matter precipitated with minerals in B_f horizons at the Young site following harvesting. Information provided by pedogenic ratios suggests that the Young site has experienced a stronger degree of weathering (Figure 3.4b) and has a weaker degree of complexation (Figure 3.4a). This is also consistent with the larger observed proportion of crystalline mineral pools at this site (Table 3.2). In addition to the reduction in OMC C content in B_f horizons at the Young site, the loss of OMC pools

may also play a role in the thinner B_f horizon, the lack of a B_h horizon, the lower metal (Fe and Al) content, and the shift towards a lower $\delta^{13}\text{C}$ signature of SOM.

The results from this study are consistent with previous work at the same site in Mooseland, NS. Here, Prest et al. (2014) examined bulk soil C storage in depth increments, and documented C storage losses of 27% in mineral soils below 10 cm (down to 50 cm). At an adjacent red spruce forest harvest chronosequence, Diochon and Kellman (2009) determined that the observed 50% reduction in C storage approximately 3 decades post-harvest (compared to an intact old-growth reference site) was a result of changes in C storage in the organomineral fraction, which is equivalent to the total of the mineral-associated pools extracted in this study. Diochon et al. (2009) concluded that changes in mineral soil OM in depth increments below 20 cm (which directly corresponds to the B_f horizons here) were driving the pattern in soil C storage across a forest harvest chronosequence. Other studies investigating the effects of land-use on soil C storage in a range of systems and soil types have come to similar conclusions (Falsone et al., 2012; Kaiser and Kalbitz, 2012; Lawrence et al., 2015; Mikutta et al., 2006; Mobley et al., 2015; Porras et al., 2017).

The changes in soil morphology and chemistry suggest that the factors that have influenced soil development at these sites are a result of processes that exert their influence upon A_e and B_f horizons. No differences between the sites in regards to C, C:(Fe+Al), or $\delta^{13}\text{C}$ were observed when comparing BC transitional horizons at the two sites, which further confirms the comparability of these sites and indicates that soil-forming processes are operating similarly in deeper parts of the soil profile of both forests.

A mechanistic explanation for changes in the storage of mineral-associated OM is still lacking, especially in regards to harvesting-related destabilization, although several potential explanations exist. Organic matter bound in OMC may become vulnerable to microbial decomposition (Buchholz et al., 2014; Clarholm et al., 2015), which would be enhanced at higher post-harvest soil temperatures (e.g. Kellman et al., 2015), or through solubilization under anoxic conditions (Hartmann et al., 2012; Palviainen et al., 2015; Pan et al., 2016; Shah et al., 2016; Zhao et al., 2017). Destabilization of organo-metal complexes have been observed in other studies following changes in redox conditions with water table rise (Buettner et al., 2014; De-Campos et

al., 2009; Thompson et al., 2006). This highlights the potential for aqueous mobilization of organo-metal complexes after even short-term flooding conditions (Herndon et al., 2017). Furthermore, higher water infiltration rates as a result of lower foliar interception at clearcut sites would increase soil weathering rates, and increase the export of dissolved mineral-associated OM from the soil profile. In this study, physical changes to soil biogeochemistry occurred over a relatively short period (i.e. several decades) and multiple studies have suggested that changes to surface vegetation following forest clearing can alter podzol morphology over this shorter time scale instead of centuries (Barrett and Schaetzl, 1998; Falsone et al., 2012; Ferro-Vazquez et al., 2014; Hogberg and Read, 2006; Hole, 1975; Miles, 1985; Mossin et al., 2001; Nornberg et al., 1993; Vadeboncoeur et al., 2014).

At the same time we observed a lower C content in the illuvial (B_f) horizon at the Young site compared to the Mature site, there were also modest increases in C in the surface eluvial (A_e) horizon of the Young site. Gains in C have been reported in other similar studies following forest harvesting (Diochon et al., 2009; Prest et al., 2014). Mixing of surface soil layers from skidders and incorporation of particulate litter after clear-cutting may explain these trends in surface A_e horizons. These changes in C storage were also accompanied by an increase in weathering at the Young site as indicated by pedogenic ratios and a higher crystalline mineral-associated OM content, alongside a reduction (by 0.5 - 3 ‰) in the $\delta^{13}\text{C}$ signatures of mineral-associated OM pools at the Young site (Figure 2.6). Since OM quantity and quality influence the bulk $\delta^{13}\text{C}$ signature (Billings and Richter, 2006; Diochon and Kellman, 2008), shifts in litter inputs as a result of harvesting disturbance would alter the C content and $\delta^{13}\text{C}$ of mineral-associated OM, especially at the surface. This trend of shallow soil C increase was also observed in another study by Mobley et al. (2015), who noted surface gains and subsoil losses of C over a similar time frame to this study (40 years of forest development). Note that if only shallow mineral soils are sampled (to 10 cm) in efforts to quantify soil C dynamics (e.g. Nave et al., 2010), it may obscure the dynamics in the deeper soil profile that are contributing to important C storage changes.

3.5 Conclusions

This research contributes improved knowledge about the specific mineral-associated OM pools that are vulnerable to destabilization following intensive harvesting disturbance. Mineral-associated organic matter pools ranged from non-crystalline organo-metal complexes to highly crystalline C-mineral pools, and the organo-metal complexed pools dominate in size and in susceptibility to C losses following disturbance. The findings confirm the existence of distinct pools of mineral-associated OM that depend on mineral crystallinity.

Further experimental and modeling research should pay close attention to the effect of forest harvesting on soil biogeochemistry by considering the mechanisms for the alterations to C storage, especially with the recognition of the distinct nature of different soil mineral pools that vary in crystallinity, and therefore in their potential for OM storage and stability.

3.6 Supporting Information

Appendix Table 7.1. Results of sequential selective dissolution of podzol soils from two sites Young (35 years since clear-cutting) and Mature (110 years since clear-cutting), expressed as mg element per g soil for C, and storage in the depth increment as tonne of C per hectare. Numbers in brackets are ± 1 SD; $n=3$ for C and Fe. Extractions are water soluble (deionized water), organo-mineral (pyrophosphate), poorly crystalline (hydroxylamine), and crystalline (dithionite) minerals. Storage of C was calculated using bulk density for each increment as provided in Prest et al. (2014).

Appendix Table 7.2. Particle size analysis for composite soil from horizons of podzol soil profiles sampled at Young (35 yrs since harvest) and Mature (110 years since harvest) forests sites. Numbers in brackets are ± 1 SD. Soil texture at both sites is sandy loam, with clay loam only in Mature B_h. %C is on a per mass basis.

Chapter 4

Evaluating the susceptibility of soil organic matter in mineral soil horizons to losses after climatic changes associated with forest clear-cut harvesting

Preamble

This chapter represents the final draft stage of a manuscript by C.E. Gabriel, L. Kellman and S. Ziegler entitled, "Evaluating the susceptibility of soil organic matter in mineral soil horizons to losses after climatic changes associated with forest clear-cut harvesting" which is intended for submission to the journal *Soil Biology and Biochemistry*. C.E. Gabriel undertook all the research and writing of this manuscript. Suggestions from L.Kellman and S. Ziegler were incorporated into the preparation of this work, and particularly in the final stages of this draft. We also appreciate helpful comments from M. Lavigne and help with data analysis from L. Kohl and F. Po-drebarac.

Chapter 3 quantified and described the distribution of C associated with mineral pools, and had demonstrated that organo-metal pools dominate the contribution to soil C storage in all horizons (Section 3.6.1). Most importantly, research from Chapter 2 determined that the content of this organo-metal fraction is significantly lower at a site three decades following clear-cutting (Section 3.6.4). This research study was designed to document C losses from soil horizons through depth, and to confirm whether microbial decomposition following changes in soil climate following clearcutting could account for the observed losses of OM from organo-metal pools. Respired CO₂ and dissolved organic matter chemistry following short-term soil incubations indicate SOM losses from mineral soils have occurred following harvesting.

4.1 Introduction

Soil organic matter (SOM) represents a larger carbon (C) store than the biomass and atmosphere combined, and any destabilization of this important C reservoir can have important implications for our warming global climate (IPCC, 2013). A recent meta-analysis suggests that intensive forest clear-cut harvesting is responsible for significant losses of C from mineral soils (Achat et al., 2015), supporting research conducted in harvested coniferous forests in northeastern North America that has documented losses of SOM after clear-cutting, most notably from mineral subsoils (Dean et al., 2016; Diochon and Kellman, 2009; Lacroix et al., 2014; Mobley et al., 2015; Petrenko and Friedland, 2015; Prest et al., 2014; Zummo and Friedland, 2011). Despite field efforts to document C losses, a process-based understanding of the mechanisms to explain SOM destabilization from mineral soils following clear-cut harvesting is lacking.

SOM is a complex mixture of organic molecules derived from senescent vegetation and biota that varies in composition and content through soil depth and with forest succession. Net accumulation results from a balance between SOM inputs and outputs, and C persistence in soils results from conditions that reduce or limit losses. This C loss from minerals produces dissolved organic carbon (DOC), which in turn can be released as CO₂ via microbial decomposition (Sinsabaugh, 2010). Protection from destabilization is offered through interaction with the soil mineral matrix, via occlusion, such as aggregation and binding within fine pore structure, and as a result of insolubility and spatial separation (Davidson and Janssens, 2006; Marin-Spiotta et al., 2014; Risk et al., 2008; Schmidt et al., 2011).

Pools of mineral-associated SOM can be described across a spectrum that ranges from poorly to more highly crystalline minerals (Heckman et al., 2018), and as such, are variable in their chemical structure and degree of protection from microbial decomposition. Reactive soil minerals such as iron (Fe) and aluminum (Al) hydroxides, that bind C in the poorly-crystalline range of the spectrum, often as organo-metal complexes, have been thought to confer longer-term stability to particular fractions of SOM (Buchmann and Flanagan, 2016; Eusterhues et al., 2011; Heckman et al., 2009; Kalbitz et al., 2005; Kramer et al., 2012; Kramer and Chadwick, 2018; Rasmussen et al., 2006; Sanderman and Kramer, 2017; Sanderman et al., 2014; Torn

et al., 1997). Organo-metal pools dominate the distribution of mineral-associated SOM, especially in B_f horizons, where they accumulate and form the characteristic spodic horizons of podzolic soils (Sanborn et al., 2011). OM in these pools are highly coloured, plant-derived organic compounds with chromophoric aromatic ring structures such as phenols complexed with Fe and Al hydroxides (Ehleringer et al., 2000; Gabriel et al., 2018). Evidence suggests, however, that the pools of organic matter associated with minerals of low crystallinity such as organo-metal complexes (OMC), are decadally-cycling and are likely vulnerable to forest harvesting disturbance (Basile-Doelsch et al., 2009; Gabriel et al., 2018).

The mechanisms that increase the susceptibility of the mineral SOM pools to losses following forest clear-cut harvesting are largely thought to arise from changes in soil climate, but an understanding of the impacts of disturbance on SOM stability in mineral soils remains incomplete. It is well established that with the removal of trees, solar interception by foliage and transpiration are both reduced and as a result, soil thermal dynamics and hydrology are altered (Beltrami and Kellman, 2003; Kellman et al., 2015). The loss of ground cover exposes soil in forest clear-cuts to a larger diurnal and seasonal temperature amplitude that extends to deeper mineral soil depths, potentially increasing rates of temperature-driven C exchange processes, including decomposition and desorption from mineral surfaces. Studies have often documented enhanced greenhouse gas emissions from soils following clear-cut harvesting (Kellman et al., 2015; Lavoie et al., 2013; Risk et al., 2008), alongside increased export of SOM from terrestrial to aquatic systems (Jewett et al., 1995; Moore et al., 2008; Oni et al., 2015; Qualls et al., 2000; Schelker et al., 2013, 2014) from harvested forest watersheds. Despite these observations, many uncertainties exist regarding the extent to which these climatic conditions post-harvest may destabilize SOM in forest soils (Nave et al., 2010), including how the susceptibility of mineral SOM to loss changes through secondary succession.

Temperature and moisture are primary controls on SOM decomposition (Davidson et al., 1998; Davidson et al., 2012; Moyano et al., 2012 ; Gabriel and Kellman, 2014). Within an optimal soil moisture range, higher temperature directly modifies microbial enzyme kinetics, thus increasing SOM decomposition rates exponentially according to

Arrhenius function or the Michaelis-Menten model (Davidson et al., 2012). Desorption from minerals and microbial production of DOC are also temperature-sensitive processes (Kothawala et al., 2009; Moore et al., 2008).

The response of SOM decomposition to temperature, commonly expressed as its temperature sensitivity (Q_{10}), has been proposed to depend on the C quality (Agren and Bossatta, 2001). Soil organic matter with higher structural complexity would decompose more slowly, thus having a lower bioreactivity, which would require a larger activation energy, and thus would have a higher response to temperature compared to simple, labile substrates (i.e. the carbon quality-temperature (CQT) hypothesis) (Bossatta and Agren, 1999; Ballantyne and Billings, 2003; Davidson and Janssens, 2006).

Many recent studies have documented results that are contrary to the proposed CQT hypothesis, however, with other factors, including chemical and physical factors, modulating the temperature response (Davidson et al., 2006; Lehman and Kleber, 2015). These chemical and physical factors include substrate availability, mineral content, soil moisture and soil structure (Davidson and Janssens, 2006). Dissolved organic matter (DOM) is the source of substrate for microbial CO_2 respiration in soils (Bengtson and Bengtsson, 2007; Bolan et al., 2011), a soluble and mobile heterogenous pool of SOM that experiences continuous modification as it moves within soil profiles. Aromatic components of DOM sorb to reactive mineral surfaces, through binding to reactive Fe and Al hydroxide mineral surfaces (Guggenberger and Kaiser, 2003; Heckman et al., 2012; Kalbitz and Kaiser, 2008; Kramer et al., 2012; Rasmussen et al., 2005; Sanderman and Kramer, 2013). This sorption can lead to potential long-term storage, or to desorption with changes in pH and/or redox conditions (Thompson et al., 2006). DOM chemistry also changes over time with shifts in temperature, since more labile components are preferentially decomposed at higher rates when soil temperature is raised. Simultaneously, the microbial production of organic compounds and desorption from minerals both modify DOM chemistry through the increased release of organic compounds from SOM at higher temperatures. As such, DOM may be thought of as a dynamic intermediary pool, since its chemistry is the net result of several abiotic and biotic processes. Dissolved organic carbon (DOC) content is a proxy for DOM, and is likely controlled by multiple factors (Kögel-Knabner et

al., 2008) that affect its production and consumption (Moore et al., 2008), including the mineral pool distribution, DOM_{ex} chemistry itself, and dynamics of the active microbial community.

In addition to temperature increases, the vulnerability of soils to extreme shifts in soil moisture, such as freeze-thaw (FT) events and rewetting (RW) of dry soil have the potential to mobilize C through physical disruption of soil structure (Kim et al., 2012). Measured soil responses to RW and FT disturbances are not consistent across systems or through soil depth (Kim et al., 2012), however. Rewetting of dry soil is known to increase the release of DOM and to stimulate soil respiration through a well-documented process (i.e. the Birch effect) (Jarvis et al., 2007). Freeze-thaw effects on DOM are thought to result in the increased release of ^{13}C -enriched labile compounds such as sugars and amino acids from necromass (Skogland et al., 1988), but magnitudes of C release and respiration responses are often site-dependent (Kim et al., 2012; Song et al., 2017; Sorensen et al., 2018).

To date, efforts to understand the impacts of soil disturbance on SOM biogeochemistry have relied on analysis of samples from laboratory extractions and incubations of shallow depth increments, because these permit examination of soils under controlled conditions, and remain advantageous despite several drawbacks (Oburger and Jones, 2009). Few studies have been performed to include measurement of respired CO_2 collected over the course of short-term incubations of specific soil horizons, which provides an opportunity to determine the relative or specific respiration rates of SOM decomposition (i.e. the bioreactivity) (Agren and Bossata, 1988; Ballantyne and Billings, 2003), of functionally distinct units potentially affording higher analytical resolution. Using this information, we can calculate the temperature sensitivity, or Q_{10} of SOM decomposition (Davidson and Janssens, 2006) through depth. Chemical characterization through optical measures of DOM have been used as indicators of change in chemistry of aqueous pools. Indexes such as specific UV-Vis absorbance (SUVA) and spectral slope ratio (S_r) provide a measure of the aromatic organic matter content and the molecular weight of chromophoric (i.e. coloured) DOM (CDOM), respectively (Helms et al., 2008; Weishaar et al., 2003), and serve as indicators of DOM character (Hood et al., 2006), and of organic matter age (O'Donnell et al., 2014). Stable isotope ratios of carbon ($\delta^{13}\text{C}$) in bulk soil, mineral SOM pools, DOC

and respired CO_2 are not only integrative measures of ecosystem functioning (Billings and Richter, 2006), but can also be used as indicators of changes in soil C storage through enhanced decomposition (Diochon et al., 2008; 2009), substrate availability (Trumbore, 2006; West et al., 2006; Zakharova et al., 2014), and the relative strength of microbial vs. plant contribution to DOM quality (Cleveland et al., 2004; Sanderman et al., 2009). For instance, plant-derived SOM has lower values of $\delta^{13}\text{C}$ than SOM recycled by microbes (Ehleringer et al., 2000). Furthermore, the nature of $\delta^{13}\text{C}$ in separate crystalline mineral pools reveals distinct SOM pools (Chapter 3). For example, the organo-mineral complexes (OMC), characterized by low crystallinity, have lower $\delta^{13}\text{C}$ signature than crystalline (Crys) mineral fractions, thus suggesting distinct differences in SOM origin and processing. Together, these experimental observations can provide multiple lines of evidence to indicate the susceptibility of soil horizons to loss, and to identify which pools of SOM are most susceptible to C loss following the shifts in climate that occur in clear-cut forest soils.

This research aims to develop an improved mechanistic understanding of the susceptibility of mineral soil C to loss via aqueous (extracted DOC, or DOC_{ex}) and respired (CO_2) pathways through depth in harvested forest soil profiles. In order to accomplish this, we will determine the SOM bioreactivity and temperature sensitivity (Q_{10}) of decomposition through depth and between sites of contrasting stand age. This will also provide information about the relevant pools of SOM susceptible to loss as DOC and CO_2 under these treatment conditions. Specifically, the objectives of this study were to:

- document the variation in soil respiration rates through depth in horizons of soil profiles from two forests of contrasting forest age across a range of temperatures;
- investigate how the chemical composition of DOC, the pool considered available for decomposition, and the $\delta^{13}\text{C}$ of respired CO_2 , the product of respiratory substrate consumption, changes under these experimental conditions; and
- examine how $\delta^{13}\text{C}$ of respired CO_2 , DOC and CDOM changes in response to extreme events associated with harvesting and climate change impacts (rewetting and freeze-thaw);

We hypothesized that the bioreactivity of SOM would decline through depth in soil

profiles, with the highest relative rates of respiration at the surface, and that the Q_{10} of SOM decomposition would be similar through depth, consistent with known relationships (Gabriel and Kellman, 2014) in these soils. Furthermore, we expect that decomposition would result in shifts in DOM chemistry representing the net result of DOM production and consumption, and that this would be reflected in $\delta^{13}\text{C-CO}_2$ signatures. Finally, we expect that extreme events of rewetting and freeze-thaw would result in the enhanced release of C, and that the susceptibility to C loss would vary through depth and between forest sites.

4.2 Methods and Materials

4.2.1 Site description

Genetic soil horizons were sampled from two secondary regrowth forests: Mature (110 years, Otter Ponds Demonstration Forest) and Young, (35 years, Guzzle Forest) located 3 km apart, east of the village of Mooseland, Nova Scotia, Canada ($44^{\circ}5642.51''\text{N}$, $62^{\circ}4739.53''\text{W}$) (Figure 3.1). The region receives 1300mm of precipitation annually, and lies at approximately 100 m above sea level. Mean annual air temperature is 5.8°C , with mean January and July temperatures -5.8°C and 16.9°C , respectively (Environment Canada). The forest is typical of the Acadian Forest Region, a typical forest of the northern temperate zone (Mosseler et al., 2000), dominated by red spruce (*Picea rubens* Sarg.) with some balsam fir (*Abies balsamea* (L.) Mill.). These sites have an undulating terrain, with slopes between 2-15% and are acidic (MacDougall et al., 1963). These sites were previously characterized for soil C storage patterns which showed a 27% decline in soil C storage in depth increments in the 35 years following forest clear-cut harvesting (Prest et al., 2014).

The soils are Orthic Humo-ferric podzols from stony, well-drained sites of the Halifax soil series in the Eastern Ecoregion of Nova Scotia (Neily et al., 2003). They are characterized by a well-developed A_e eluvial horizon, a brown sandy loam illuvial B horizon high in organic matter, and a yellowish-brown sandy loam subsoil and are derived from an olive- to yellow-brown stony sandy loam till with a quartzite parent material (MacDougall et al., 1963). The clay mineralogy at both sites is predominantly illite with traces of chlorite, vermiculite and kaolinite (Brydon, 1958).

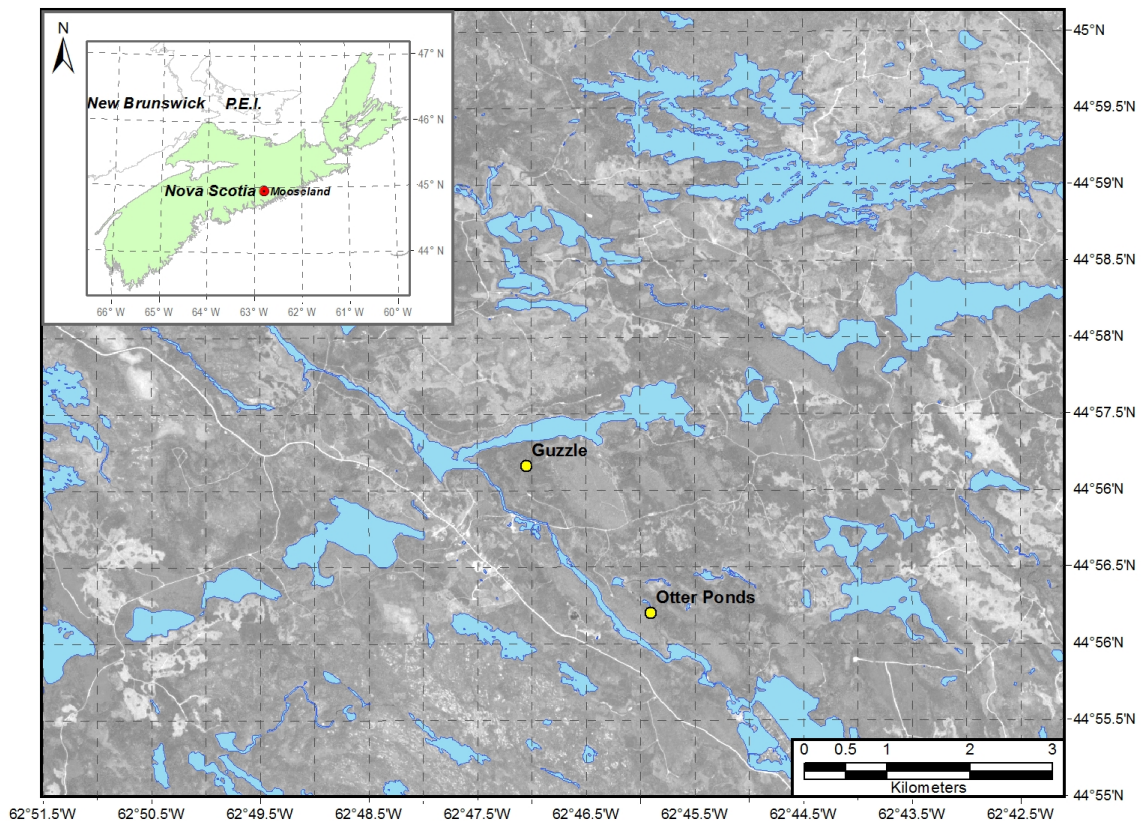


Figure 4.1: Map of Mooseland in Nova Scotia, Canada, with the location of the Young (Guzzle Forest), and Mature (Otter Ponds Demonstration Forest) sampling sites, located approximately 3 km apart (circles). The location of Mooseland in Nova Scotia, Eastern Canada is indicated on the inset map (top left).

4.2.2 Soil sampling and sample preparation

At each forest sampling pit (n=9 for each forest site) mineral soils were sampled by genetic horizons (A_e , B_f and BC) according to the Canadian soil taxonomy (Soil Classification Working Group, 1998). The organic horizon was removed and the mineral soil was then excavated. The mean thicknesses of genetic horizons were measured in the middle of each of the 4 walls of each soil pit. Soil samples were carefully excavated by hand from each genetic horizon at both sites. Sampled soils were kept cool immediately following sampling and were stored in sealed bags at 4 °C until analysis, ensuring maintenance of field moist conditions.

In order to mimic natural soil conditions, soils were sieved at a coarse scale (to 12 mm), and pre-incubated for 2 weeks prior to treatment to ensure that the respiration rate measured was not a result of disturbance or rewetting (Gabriel and Kellman, 2014). Samples were carefully prepared, removing visible root and particulate organic matter fragments, including fungal sporocarps. Composites were made from pit samples (n=9) by thoroughly mixing equal masses of each horizon. Bulk density estimates were obtained from data on depth increments of soil sampled from this site (Prest et al., 2014) (Table 4.1). Refer to Section 3.2.3 (Chapter 3) for full details of soil sampling and further details of composite sample preparation.

4.2.3 Soil incubation experimental design

The C content of mineral, aqueous and respired pools were measured for horizon-based samples in soils of the Mature and Young sites following treatments designed to simulate disturbance responses (Figure 4.2). At optimum moisture and after episodic disturbances of dry-rewet (RW) and freeze-thaw (FT) at 25 °C, soil respiration was measured for samples from each horizon of the Mature and Young sites. Aqueous extracts from a set of samples prior to incubation (Initial) and extracts from all samples after the 28-day incubation experiment (Final) to quantify C release as DOC_{ex} and CDOM optical properties following disturbance. Important information is likely gleaned from changes to DOC_{ex} chemistry, which would indicate the particular compounds that the microbial community accessed, combined with the $\delta^{13}\text{C-CO}_2$, which could in turn link the respiration to particular SOM pools.

The bulk soil C, and the $\delta^{13}\text{C}$, C and Fe+Al content of a full suite of mineral-associated organic matter pools of soil horizons, including organo-metal complexes (OMC) was determined (Chapter 3, Section 3.6) using composite samples that were dried at room temperature. All together, the information from solid, dissolved and gaseous pools was used to quantify the loss of soil C which could then be connected to particular mineral-associated OM pools arising from each of the experimental treatments (Figure 4.2).

To measure respired C losses in response to temperature, triplicate field-moist soil samples (equivalent to 2.5 g dry weight) for two sites and three horizons were placed in 12 ml Exetainers and incubated at 5, 15 and 25 °C (field moist conditions). Respired soil C (CO_2) and its stable carbon isotope composition ($\delta^{13}\text{C}$) were measured weekly over a 28-day period on a full set of soil samples in order to quantify cumulative respiration losses and to identify shifts in substrate sources of respired C. Previous research in this region has identified 0.2-0.6 water-filled pore space (WFPS) as the optimum moisture range for SOM decomposition, with rewetting effects negligible above 0.25 WFPS (Gabriel and Kellman, 2014). Soils were amended with 0.5 mL of deionized water (DI) on Day 0, and moisture was maintained by adding water if the Exetainer weight changed.

These constant incubation conditions represented the optimal moisture (OP) responses. Another full set of soil samples ($n=3$) were exposed to dry-rewetting (RW). Briefly, one set of samples was allowed to dry from field moist conditions at room temperature, until there were no further changes in moisture (weight). Samples were then rewet on Day 0 with the same amount of water to return it to initial moisture conditions. Another full set experienced freeze-thaw (FT) - samples were frozen while at field moisture (optimal range) at -15 °C for one month and then its incubation period began (Day 0) once removed from the freezer. The effects of RW and FT were assessed by comparing the results to the samples incubated under constant optimal moisture conditions at 25 °C. A parallel incubation of a full set of composite samples was carried out to monitor aqueous C (DOC_{ex}). Here, 25 g (dry weight) of composite was incubated in triplicate in 50 ml glass jars. Samples experienced identical conditions as the samples being monitored for respiration in Exetainers, including RW and FT conditions.

Results from all soil incubations must be interpreted with care, as they only represent potential respiration rates, even though steps were taken in this experiment to reduce physical disturbance and to minimize measurement of artifacts from disturbance. In addition to unrealistic stimulation of rates due to a departure from native conditions, soil structure and organic matter cycling, they are subject to physical disturbance as a result of sampling and processing (Berhe et al., 2017; Kaiser et al., 2015; Oburger and Jones, 2009; Risk et al., 2008). It is especially important to recognize this when attempting to compare relative differences between shallow and deep soil incubation respiration rates and when comparing these to in situ respiration rates.

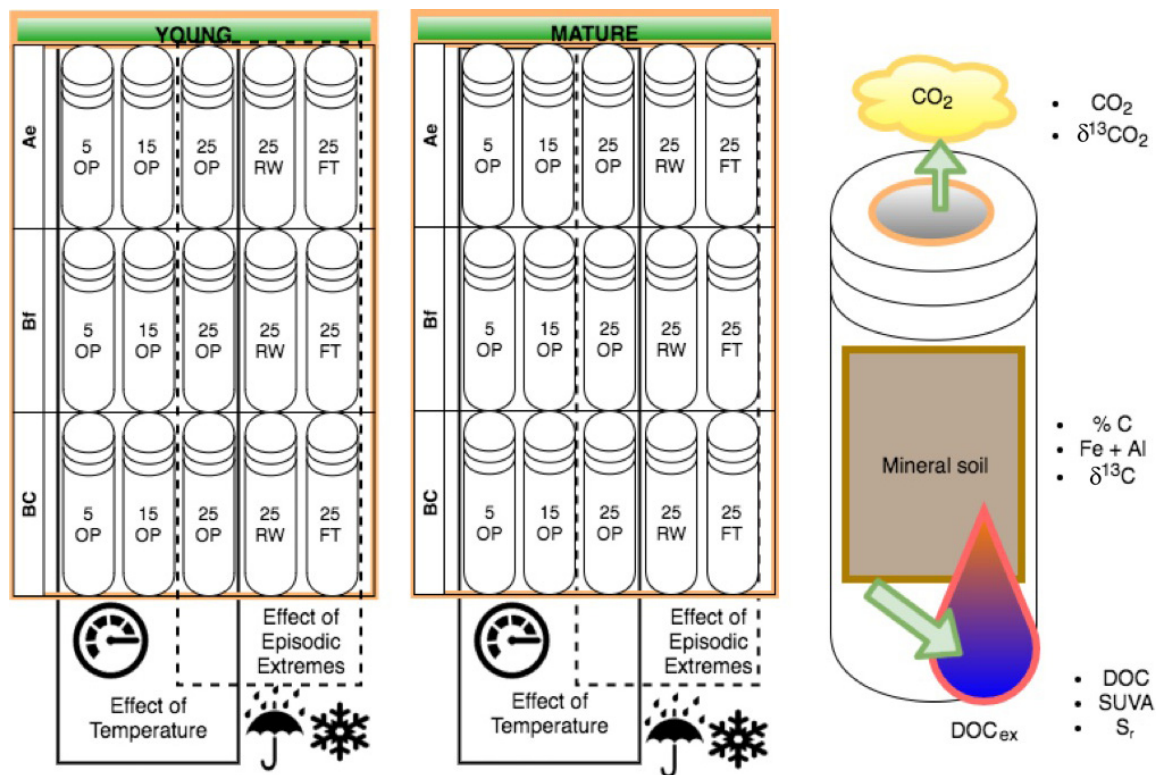


Figure 4.2: Conceptual diagram outlining the experiments in this study, designed to test the effects of temperature and episodic moisture changes on C cycling in A_e, B_f and BC horizons at Young (left column) and Mature (right column) forest sites that differ in their time since clearcutting (35 vs. 110 years). OP, RW and FT refer to treatments of optimum moisture, dry-rewetting, and freeze-thaw, respectively. Refer to section 4.2.3 of text for full details of sampling methodology.

4.2.4 Bulk soil carbon and $\delta^{13}\text{C}$ analysis

To determine the C content (% C) and $\delta^{13}\text{C}$ of bulk soil, combustion products from an elemental analyzer (Eurovector EA-3028-HT, Manchester, UK) were separated using a gas chromatograph and analyzed with a continuous flow isotope ratio mass spectrometer (Nu Horizon Isotope Ratio Mass spectrometer, Wrexham, UK; GV Isoprime Mass Spectrometer, Manchester, UK) carried out at St. Francis Xavier University.

4.2.5 Carbon and metal content of mineral pools

Sequential selective dissolutions were carried out for each depth horizon at Mature and Young sites to quantify soil C within mineral soil pools through depth of increasing crystallinity. These include non-crystalline organo-metal complexes (extracted with 0.1 M Na-pyrophosphate) and crystalline secondary minerals (extracted with Na-dithionite and HCl) (USGS, 2013). Pyrophosphate extraction is assumed to extract material from organo-metal complexes (OMC fraction). Poorly crystalline minerals (PCrys fraction), a minor pool (Refer to Ch. 2 for details) were removed using hydroxylamine HCl (Chao and Zhou, 1983; Kostka and Luther, 1994). Dithionite HCl extracts secondary minerals from crystalline phases (Crys fraction), especially goethite, with dissolution of hematite, lepidocrocite, magnetite and gibbsite (McKeague and Day, 1966; Mehra and Jackson, 1960).

Briefly, triplicate samples of 1.0 g composite samples (air dry, sieved to 2mm) were shaken with 30 mL of extractant for 20 hours, centrifuged at 10 000 RPM and decanted. Extraction residue underwent an additional wash stage where 20 mL DI (in the case of the pyrophosphate and hydroxylamine) or 20 mL 0.1 M HCl (dithionite) was added, and samples were shaken for a further 2 hours, centrifuged and decanted. Extracts from both stages were combined, filtered to 0.45 micrometers (mixed cellulose ester) and kept at 4 °C until analysis. Solids were dried and weighed before the next extraction (Heckman et al., 2018). Refer to Section 3.2.4 (Chapter 3) for full details.

Sequentially extracted mineral pools were analysed for Fe and Al and associated C and $\delta^{13}\text{C}$ of organo-metal (OMC) and crystalline (Crys) pools. Fe and Al were analysed by flame atomic absorption spectroscopy and inductively coupled plasma mass spectrometry, respectively. Selective dissolution aqueous extracts were analyzed for

C content (5050 Shimadzu TOC analyser - acidified samples, non-purgeable organic carbon combustion method, St. Francis Xavier University).

$\delta^{13}\text{C}$ of selectively extracted mineral pools and incubation soils DOM_{ex} were analyzed at the Memorial University Stable Isotope Laboratory (DeltaVPlus I interfaced using ConFlo III to a OI Analytical Aurora 1030W TOC Analyzer).

4.2.6 Soil incubation respiration measurements

Carbon dioxide concentration and $\delta^{13}\text{C}\text{-CO}_2$ was measured initially, immediately after amendment with DI (Day 0), at 3 days and then weekly (at 7, 14, 21 and 28 days) for 28 days using continuous flow isotope ratio mass spectroscopy (Nu Horizon Isotope Ratio Mass spectrometer, Wrexham, UK; GV Isoprime Mass Spectrometer, Manchester, UK). CO_2 was sampled with a dual inlet needle from the headspace of the 12 ml capped Exetainer vials fitted with rubber septa.

Respiration rates

Respiration rate ($\text{mg C g soil}^{-1}\text{s}^{-1}$) was calculated from incubation headspace CO_2 concentration data. The observation period started following flushing the headspace of the 12mL Exetainers with CO_2 -free air. The length of this observation period was optimized for each sampling date, according to the length of time that produced a headspace CO_2 concentration that fell within the linear range of the instrument. The length ranged from 2 minutes (B_f horizons at 25°C) to 48 hours (BC horizons at 5°C) and varied for each horizon depending on temperature and soil C content. The change in C concentration over the observation period was scaled to a daily rate. From this, specific decomposition rates (R_d) were calculated from R_{soil} (soil respiration rate) (mg C per day) divided by C_{soil} (soil carbon), which takes the C content (mg C per g soil) of the particular horizon into account (Equation 4.1).

$$R_d = \frac{R_{soil}}{C_{soil}} \quad (4.1)$$

Cumulative respiration was determined by taking the sum of the respired C, either measured (on days 0, 7, 14, 21 and 28), or modelled, where modelled rates were calculated by interpolation under an assumption of a linear rate of change in respiration over the days between sampling. The specific cumulative respiration (Equation

3.1) is a measure of the SOM bioreactivity in each incubated sample (Ballantyne and Billings, 2003). $\Delta^{13}\text{C}$ is the difference between the natural abundance of ^{13}C of respired CO_2 and $\delta^{13}\text{C}$ of substrate sources for decomposition (i.e. bulk soil, mineral pools, DOM_{ex}). Values of $\Delta^{13}\text{C}$ were expressed with permil (‰) notation and larger values indicate greater ^{13}C enrichment of respired CO_2 compared to substrate C source (Heckman et al., 2009).

Temperature sensitivity of SOM decomposition

Exponential relationships described the change in specific cumulative respiration (mg respired C per g C) at three temperatures and were modelled following Equation 3.2 using a modified van t' Hoff equation (2 component, exponential growth):

$$R_{cum} = ae^{bT} \quad (4.2)$$

where R is cumulative respired C (mg C g soil C^{-1}), T is temperature, e is an exponential function, and a and b are parameters derived from curve fitting (van't Hoff, 1884). Temperature sensitivity (Q_{10}) was then calculated following Equation 2 from the curve fitting parameter b (Kirschbaum, 1995) as follows:

$$Q_{10} = e^{10b} \quad (4.3)$$

Stable Isotope Ratio of C ($\delta^{13}\text{C}$)

The stable isotopic ratio of C ($^{13}\text{C} / ^{12}\text{C}$) is calculated as the relative difference between the sample and the C standard ((PeeDee Belemnite) in parts per thousand, or ‰), such that:

$$\delta^{13}\text{C} = \left(\frac{R_{sample}}{R_{standard}} - 1 \right) * 1000 \quad (4.4)$$

where R is equal to the ratio of the heavy to light isotope (i.e. $^{13}\text{C}/^{12}\text{C}$). Following the incubation, a weighted monthly mean $\delta^{13}\text{C}$ - CO_2 (WMM $\delta^{13}\text{C}$ - CO_2) was calculated that took the proportion of the daily respiration rate to the cumulative respired C into account for its contribution to a monthly mean stable isotope ratio, as follows:

$$\text{WMM}\delta^{13}\text{C} - \text{CO}_2 = \Sigma[(\text{Daily } C)x(\text{Daily } \delta^{13}\text{C} - \text{CO}_2)] \quad (4.5)$$

4.2.7 Aqueous C pool

Extraction of dissolved organic carbon (DOC_{ex})

Following the incubation period for all samples (Final), the dissolved fraction of organic carbon (DOC_{ex}) was extracted with a low ionic strength solution (1:2 g soil:ml solution ratio; 0.01 M CaCl_2) similar in ionic strength to rainwater, and vacuum filtered to 0.45 micrometers following Chantigny (2008). An initial pre-incubation set of samples (Initial) was also extracted for DOC_{ex} to provide a reference point for each horizon for assessing changes in C concentration and optical properties (net change from Initial).

Measurement of DOC_{ex} for C content and character

For each extract from each horizon, DOC_{ex} was determined. Acidified extracts were analyzed for carbon content (5050 Shimadzu TOC analyzer - non-purgeable organic carbon combustion method, St. Francis Xavier University) with potassium hydrogen phthalate (KHP) as a standard. The initial extracts were also analyzed for stable isotope ratio of carbon ($\delta^{13}\text{C}$) at Memorial University's Stable Isotope Laboratory (DeltaVPlus I interfaced using ConFlo III to a OI Analytical Aurora 1030W TOC Analyzer) following a wet chemical method (permanganate oxidation). In every run, a series of standards made up in each of the extractants used to obtain DOC pools were examined before, midway and at the end of every run to account for drift. The use of extractants for DOC standards was also to assess accuracy in the $\delta^{13}\text{C}$ of DOC measures of these solutions which contain solutes which compete with DOM for the oxidants used in converting DOC to CO_2 for the measurement. These analyses reported a mean of repeated TOC analysis ($3 < n < 5$), where $\text{SD} < 0.01 \text{ mg L}^{-1}$.

The specific UV-Vis absorbance (SUVA) at 254 nm was calculated from the ratio of UV-Vis absorbance at 254 nm (scanning spectrophotometer, Genysys) to DOC (mg L^{-1}) for each extract (Weishaar et al., 2003). Spectral analysis was performed on each extract to generate spectral slope (S_r) values, using the analysis outlined by Helms et al. (2008). The ratio is calculated from the ln transformed slopes of the absorbance for the spectral regions of 275-295 nm to 350-400 nm. S_r is an indicator of the molecular weight of the aromatic, or chromophoric dissolved organic matter (CDOM). Low

calculated S_r values indicate a high molecular weight (HMW) of CDOM compounds present in solution (Helms et al., 2008). All optical measurements across the entire spectra were corrected by subtracting the interference from Fe (Poulin et al., 2014).

4.2.8 Data analysis

Repeated measures ANOVA was used to assess the significance of multiple measurements of respiration rates for the weekly incubation data, with temperature (continuous) or treatment (categorical) as co-variates, and site and horizon as fixed errors. Respiration rate data across the dataset was non-normal, as determined using a heteroskedasticity test. This test was performed through Q-Q plots, which present the quantiles associated with two datasets' distributions to assess whether the two populations are from the same distribution. Due to non-normal distribution, respiration data was log-transformed before repeated measures ANOVA. Statistically significant differences in models was assessed at $\alpha < 0.05$.

Generalized linear mixed models (GLMM) were used to compare the effects of temperature or treatment on the modeling of the cumulative data (Cumulative respired C, $\delta^{13}\text{C-CO}_2$) or DOC_{ex} data ($\delta^{13}\text{C DOC}$, Soluble C, SUVA_{254} , S_r). Specifically, GLMM were used to assess the effect of temperature as a fixed continuous effect or treatment as a categorical fixed effect alongside soil mineral content (sum of soil organo-mineral and crystalline pools Fe+Al; Table 3.1) with random error assigned for site and horizon; following this, models that explained the treatment or effect were compared to null models through ANOVA analysis. Regression was carried out using Sigmaplot (version 14.0), the repeated measures ANOVA with the R package aov and GLMM analysis and ANOVA with the R package lme4 (lmer) under R version 3.3.1.

4.3 Results

4.3.1 Soil organic carbon and mineral pool carbon contents

Soil organic carbon (SOC) followed a typical trend among horizons for podzols at both sites through depth: low C concentrations in the A_e horizon, with highest C contents in the B_f in the Mature site horizons, then lower again in BC horizons, with low C at both sites. B_f horizons at the Mature site were thicker than the Young site

(Table 4.1). For both sites, the trend through depth in SOC concentrations generally followed that of the selectively dissolved reactive mineral assemblage through depth. The lowest mineral content and C was observed in the A_e horizon in the Mature site, however (Table 4.1). The B_f horizons at both sites had the highest total mineral (Fe+Al) contents in organo-metal and crystalline mineral pools (OMC + Crys mg g soil⁻¹). The A_e and BC horizons had a higher proportion of Fe+Al in crystalline (Crys) mineral phases than B_f horizons. In contrast to patterns for % C and OMC and Crys Fe+Al content, the $\delta^{13}\text{C}$ of bulk soil C increased monotonically through depth at both sites in the profile by approximately 1 ‰ (Table 4.1). However, similar to the pattern for %C OMC and Crys, the $\delta^{13}\text{C}$ of DOC_{ex} is lowest in A_e , and highest in B_f horizons.

The Young site had a lower % C in B_f and BC horizons than the Mature site, but had a higher % C in the A_e horizon compared to the Mature site (Table 4.1). The OMC Fe+Al was lower in B_f but similar in A_e and BC horizons, but the Crys fraction Fe+Al was higher in all horizons at the Young site compared to the Mature site (Table 4.1). Generally, bulk soil OM in each horizon was more ¹³C-depleted at the Young site than at the Mature site: the stable isotope ratios of C in bulk soil solids in the B_f and BC horizons were more ¹³C-depleted by approx. 0.5 ‰ at the Young site relative to the Mature site ($\delta^{13}\text{C}$ was -26.03 vs -25.58 ‰ for B_f and -25.45 vs. -24.96 ‰ in BC), while $\delta^{13}\text{C}$ in A_e horizons were near -27 ‰, with the Young site slightly (0.3 ‰) more depleted than the Mature site (Table 4.1). The $\delta^{13}\text{C}$ of the Crys pool was the most enriched in ¹³C (mean $\delta^{13}\text{C}$ = -14.6 ‰), compared to the $\delta^{13}\text{C}$ for the SOM in the water soluble fraction (mean $\delta^{13}\text{C}$ = -27.5 ‰), and the OMC fraction ($\delta^{13}\text{C}$ ranged from -25.3 ‰ to -27.0 ‰) (Table 4.1). GLMM analysis determined that site was a significant explanatory factor in a model to explain $\delta^{13}\text{C}$ of extracted pools ($\chi^2 = 5.8603$; $p = 0.01549$).

Table 4.1: Soil texture and mineralogical data for mineral horizons of podzol soil profiles at Young (35 year old) and Mature (110 year old) red spruce forest in Mooseland, Nova Scotia, Canada, n= 9 for each site. Numbers in brackets are 1 SD. Where there is no SD indicated, n=1, due to technical limitations. Soil texture is sandy loam. In the table, DOC_{ex} is dissolved organic carbon from extracts; OMC is organo-metal complexes; Crys is crystalline mineral pools.

Site	Horizon	Thickness (cm)	C %	$\delta^{13}\text{C}$ bulk soil ‰	$\delta^{13}\text{C}$ DOC _{ex} ‰	C:N	Fe+Al OMC (mg g soil ⁻¹)	$\delta^{13}\text{C}$ OMC ‰	Fe+Al Crys (mg g soil ⁻¹)	$\delta^{13}\text{C}$ Crys ‰
Young	A _e	6.4 (3.4)	3.19 (1.36)	-27.26 (0.64)	-27.70	26.6 (9.3)	3.32 (0.09)	-27.72	1.52 (0.73)	-16.39 (0.74)
	B _f	11.0 (1.5)	4.51 (1.32)	-26.03 (0.34)	-22.86	24.3 (1.1)	17.02 (0.13)	-25.95 (0.06)	4.64 (2.55)	-14.28 (0.66)
	BC	27.5 (2.6)	2.51 (2.25)	-25.45 (0.60)	-25.15	21.7 (2.2)	10.13 (0.15)	-25.47 (0.18)	6.80 (3.03)	-14.49 (0.59)
Mature	A _e	8.9 (6.4)	1.95 (0.36)	-26.94 (.0.33)	-25.66	31.4 (8.9)	3.14 (0.11)	-26.76 (0.06)	1.14 (0.18)	-13.40 (1.69)
	B _f	19.5 (9.9)	6.54 (1.54)	-25.58 (0.46)	-21.74	22.8 (3.4)	21.81 (0.55)	-25.93 (0.04)	3.58 (1.18)	-15.05 (0.66)
	BC	17.0 (4.5)	2.32 (0.24)	-24.96 (0.21)	-22.32	20.6 (6.7)	9.61 (0.35)	-25.36 (0.23)	5.70 (0.47)	-14.24 (0.58)

4.3.2 Respired CO₂ through depth following incubation

Temperature relationships

Generally, at a given temperature, the respiration rate of C was highest in A_e and B_f horizons and declined through depth for the optimum moisture (OP) treatment at both sites (Figure 4.3). Respiration rates (per g soil) were lower in the A_e horizon at the Young site than the Mature site, but the deeper horizons (B_f and BC) had higher respiration rates than in horizons of the Mature site. Cumulative respired CO₂ increased with increasing incubation temperature for all horizons at both sites, but was an order of magnitude lower in BC horizons compared to A_e and B_f horizons (Figure 4.3). Differences in respiration rates (per g soil) between sites were not significant (Table 4.4). However, when soil respiration rates are expressed relative to soil C (i.e. bioreactivity), the A_e and BC horizons at the Mature site respired significantly more and less, respectively, than their counterparts at the Young site (Figure 4.4) ($p < 0.05$). The temperature sensitivity (Q_{10}) was lowest in BC horizons (Figure 4.4), and Q_{10} values were higher at the Mature site than the Young site in horizon-by-horizon comparisons, with a significant difference between Q_{10} estimates for the B_f horizons for Mature and Young sites, respectively (Table 4.2).

Effects of climatic treatments

The impacts of RW and FT on bioreactivity (cumulative respired C per g soil C) of SOM in horizons differed through depth and between sites when compared to optimal conditions (OP) (Table 4.3 and Figure 4.5 a-b). There was a net reduction in bioreactivity following RW and FT treatments in A_e horizon soils compared to optimal conditions, with a notable reduction in rates in A_e at the Young site. However, large increases in bioreactivity in BC horizons at both sites were measured following RW and FT treatments, with the largest amount of C relative to SOC respired from soils following RW at both sites (Figure 4.5 a-b). Freeze-thaw and RW increased respiration rates in the B_f horizon of the Young site and decreased respiration rate in the A_e horizon of the Young site relative to OP, whereas RW and FT reduced respiration in A_e and B_f horizons at the Mature site. In BC at both sites, RW and FT respiration rates were higher than OP (Figure 4.5 a-b).

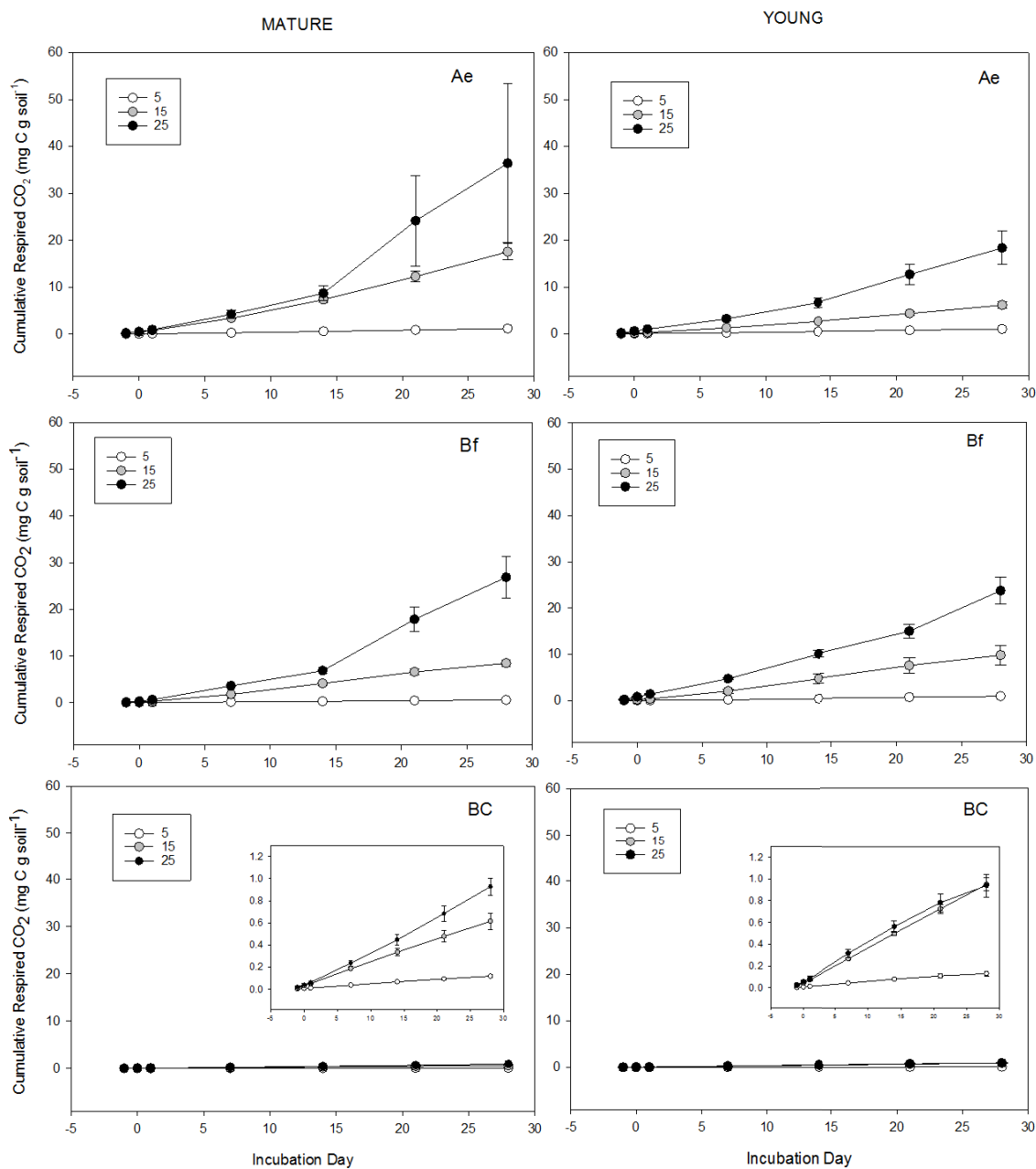


Figure 4.3: Cumulative respired C at 5, 15 and 25 °C over the course of a 28 day incubation for Mature and Young sites sampled through depth in A_e , B_f and BC horizons at Mooseland, Nova Scotia, Canada. In insets, the BC scale is expanded (0 to 1.6 mg C g soil⁻¹) to show the differences by temperature at these lower rates. Initial measurements following 2 week pre-incubation at field moist conditioned at the given temperature, denoted as day -1. On day zero, deionized water was applied that adjusted samples to 60 % volumetric water content.

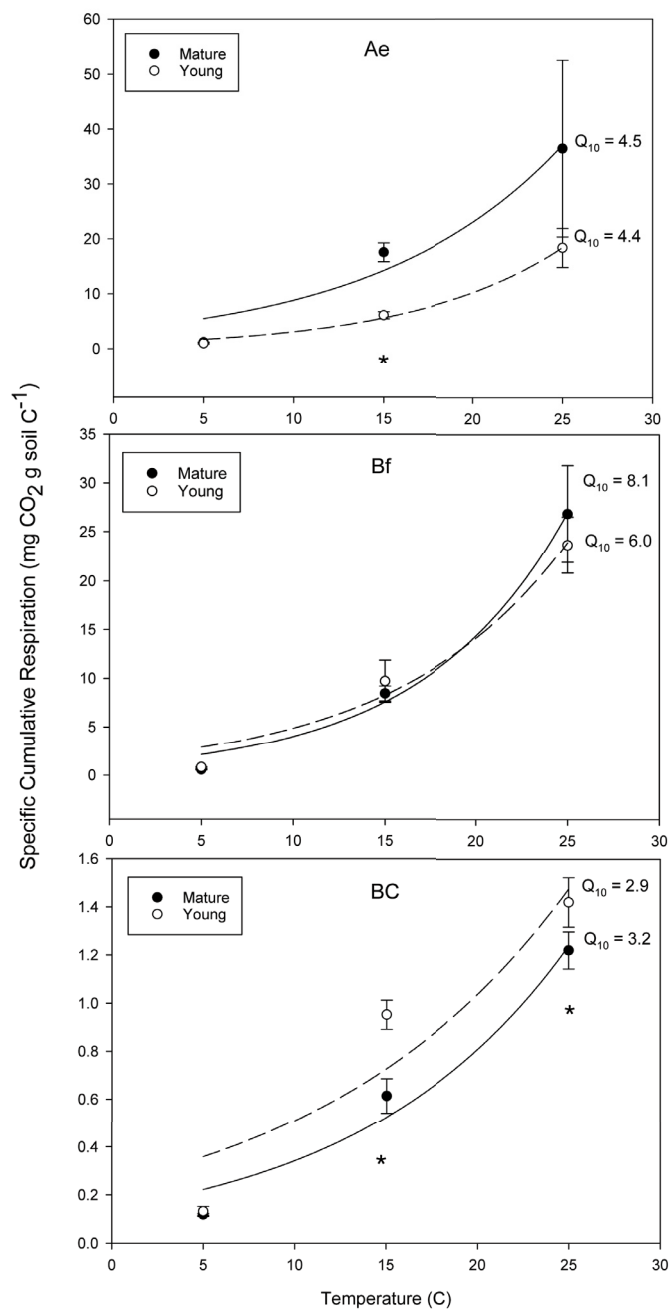


Figure 4.4: Specific cumulative respired C, or bioreactivity, (mg C respired g soil C⁻¹) for a 28 day incubation at three temperatures (5, 15 and 25 °C) for A_e, B_f and BC horizons of soil profiles sampled from Mooseland, Nova Scotia, Canada. Note that the scales for all horizons are different to highlight the dynamics within each horizon. Curves are fitted 2 parameter exponential growth models which were used to calculate Q₁₀, indicated at the right hand side of the graphs. Coefficients and fits are listed in Table 4.2. Mature (filled circles) and Young (open circles) sites respired at different rates across the temperature range. Q₁₀ values were still consistently higher in the Mature site horizons. Stars under data points in panels indicate a significant difference between Mature and Young sites at p < 0.05.

Table 4.2: Parameters and correlation coefficients for curve fits of 2-parameter exponential model of temperature sensitivity, Q_{10} (Equation 3.2), fit to specific cumulative respired C data for A_e , B_f and BC horizons from Mature and Young sites in Mooseland, Nova Scotia, Canada.

	Horizon	a	b	r^2	Q_{10}
Young	A_e	0.5161	0.1490	0.98217	4.4
	B_f	0.4203	0.1790	0.95413	6.0
	BC	0.1051	0.1063	0.80197	2.9
Mature	A_e	0.8383	0.1496	0.81958	4.5
	B_f	0.2516	0.2086	0.97521	8.1
	BC	0.0778	0.1166	0.94743	3.2

4.3.3 Aqueous extract chemistry shifts before and following short-term incubations

Dissolved organic carbon in soil extracts

Mean DOC_{ex} C concentrations (pre- and post-incubation) were highest in A_e horizons at both sites for all temperatures, and declined through depth in B_f and BC horizons (Table 4.3). Initial mean DOC_{ex} ranged from 0.0517-0.0869 mg g soil⁻¹ for the horizons through depth at both sites, and final (i.e. post-incubation) mean DOC_{ex} ranged from 0.0571-0.0996 mg g soil⁻¹ at 5 and 25 °C (Table 4.3).

Following incubation at different temperatures, there were no significant differences ($p < 0.05$) in DOC_{ex} extracted from A_e and BC horizons at the two sites. An exception to this trend was incubation at 5 °C, which resulted in significantly higher mean DOC_{ex} compared to Initial ($p < 0.05$) (Table 4.3). DOC_{ex} did not differ significantly between horizons of Young and Mature sites (Table 4.3, $p < 0.05$). Dissolved organic carbon extracted from the incubated B_f horizons at both sites declined by 33.3 and 30.1 %, respectively, following incubation at 25°C, but it did not decline following incubation at 5°C (Figure 4.5). Note that samples were not available for DOC_{ex} at 15°C.

In most samples, regardless of treatment (temperature (5 vs. 25°C), RW or FT), higher cumulative respiration rates were accompanied by lower extracted DOC (Figure 4.5 and Figure 4.6). Notable exceptions to this trend included the increase in DOC_{ex} following RW in A_e and B_f horizons at both sites (Table 4.3). For these samples, the specific cumulative respired C rates (bioreactivity) were also high. There was an increase in DOC_{ex} in the deepest horizon at both sites for BC samples after incubation at 5 °C, which also had the lowest respiration rates in samples of the experiment (Figure 4.5, and Figure 4.6). The cumulative respiration from B_f horizons vastly outweighed the contribution from C released in DOC_{ex} after 1 month, whereas in BC horizons, DOC_{ex} was a more important source of C (Figure 4.6).

Chemistry of DOM extracted from soils

The highest initial (i.e. pre-incubation) CDOM SUVA_{254} values were consistently observed in A_e horizons compared to B_f and BC horizons (Table 4.3). The CDOM

SUVA₂₅₄ in the B_f horizon was lower than in A_e, and similar to SUVA₂₅₄ in the BC horizon at both sites (Table 4.3). Furthermore, the highest S_r (i.e. lowest MW), was consistently observed in BC horizon extracts (Table 4.3). The δ¹³C of DOC_{ex} is lowest in A_e, and is highest in B_f horizons. Note that these trends in extract chemistry did not follow those of the horizon bulk soil C (Table 4.1).

Shifts in CDOM aromaticity also accompanied the changes in DOC_{ex} following incubation compared to pre-incubation extracts. Samples at both sites experienced an increase in SUVA₂₅₄ by generally between 0.5 to 1 unit (L mg⁻¹m⁻¹) (Figure 4.5 e and f) following incubation. In BC horizons, DOC_{ex} shifted such that a large increase in SUVA₂₅₄ was mirrored by an increase in HMW CDOM (decrease in S_r) (Figure 4.5 g and h). Between sites, a larger increase in SUVA₂₅₄ (Figure 4.5 f), and a larger change in LMW compounds was observed at the Young site (Figure 4.5 h).

Although DOC_{ex} often decreased following incubation (with the exception of RW), SUVA₂₅₄ always increased following incubation for all 3 horizons at both sites for all treatments and temperatures (Table 4.3 and Figure 4.5 e - f). In particular, while FT and RW resulted in an increase and a decrease, respectively, in DOC_{ex}, they both resulted in an increase in CDOM SUVA₂₅₄ for all horizons (Table 3.3). Overall, temperature and treatment (OP, RW or FT) both had significant effects on SUVA₂₅₄ when comparing effects within each horizon (p<0.05; Table 4.4). Only the effect of treatment was important in explaining changes to S_r on a horizon basis (p<0.001; Table 4.4).

While there was little difference after incubation at 5 compared to 25 °C in the DOC_{ex} concentration in extracts of samples from the Mature and Young sites, differences in the optical properties were apparent following incubation (Table 4.4). A significant increase in SUVA₂₅₄ was observed with higher temperature in DOC_{ex} (Figure 4.5 e-f). The greatest increase in SUVA₂₅₄ and decrease in S_r was observed in horizons of the Mature site (Table 4.3). Overall, OP, RW and FT treatments did not generate differences in DOC chemistry for a given temperature.

Table 4.3: Solution chemistry data for soil extracts from A_e , B_f and BC horizons of forest soils sampled from Young and Mature sites at Mooseland, Nova Scotia, Canada, following incubation at 5 and 25 °C under optimum conditions (OP) and under treatment conditions of rewetting (RW) and freeze-thaw (FT). DOC - extracted dissolved organic carbon and $SUVA_{254}$ is specific UV-Vis absorbance at 254 nm. Optical measurements were Fe corrected following Poulin et al. (2014).

				Young		Mature	
Horizon	Conditions	DOC _{ex} (mg C g soil ⁻¹)	SUVA ₂₅₄ (L mg ⁻¹ cm ⁻¹)	S _r	DOC _{ex} (mg C g soil ⁻¹)	SUVA ₂₅₄ (mg ⁻¹ cm ⁻¹)	S _r
A_e	Initial	0.0869 (0.0041)	0.69 (0.05)	0.87 (0.03)	0.0827 (0.0021)	0.68 (0.05)	0.89 (0.01)
	5 OP	0.0996 (0.0841)	1.08 (0.02)	0.95 (0.03)	0.0738 (0.0699)	0.99 (0.14)	0.97 (0.02)
	25 OP	0.0896 (0.0079)	1.61 (0.09)	0.84 (0.02)	0.0783 (0.0115)	1.14 (0.07)	0.90 (0.02)
	25 RW	0.1627 (0.0058)	1.21 (0.0757)	0.71 (0.01)	0.1174 (0.0068)	1.22 (0.03)	0.75 (0.002)
	25 FT	0.0757 (0.0027)	1.69 (0.0027)	0.90 (0.01)	0.0669 (0.0028)	1.37 (0.09)	0.83 (0.02)
B_f	Initial	0.0720 (0.0095)	0.14 (0.03)	0.72 (0.14)	0.0655 (0.0072)	0.43 (0.07)	0.70 (0.05)
	5 OP	0.0640 (0.0492)	0.13 (0.02)	1.95 (0.24)	0.0660 (0.0639)	0.30 (0.11)	1.25 (0.17)
	25 OP	0.0663 (0.0587)	0.25 (0.01)	0.49 (0.25)	0.0815 (0.0071)	0.51 (0.05)	0.48 (0.18)
	25 RW	0.5774 (0.0517)	0.87 (0.12)	0.76 (0.04)	0.1353 (0.0192)	0.67 (0.19)	0.83 (0.02)
	25 FT	0.0432 (0.0035)	0.27 (0.04)	2.65 (1.24)	0.0517 (0.0112)	0.70 (0.03)	0.98 (0.05)
BC	Initial	0.0670 (0.0179)	0.18 (0.04)	0.118 (0.004)	0.0997 (0.0133)	0.086 (0.002)	2.22 (0.08)
	5 OP	0.0812 (0.0873)	0.15 (0.04)	2.19 (0.36)	0.0571 (0.0027)	0.15 (0.02)	2.31 (0.37)
	25 OP	0.2593 (0.2449)	0.20 (0.05)	4.53 (0.20)	0.0666 (0.0731)	0.20 (0.05)	2.69 (0.48)
	25 RW	0.0569 (0.0037)	0.54 (0.02)	0.73 (0.06)	0.0453 (0.0001)	0.65 (0.08)	8.00 (2.22)
	25 FT	0.0361 (0.0024)	0.21 (0.01)	2.99 (0.54)	0.01319 (0.0025)	0.16 (0.03)	5.49(0.70)

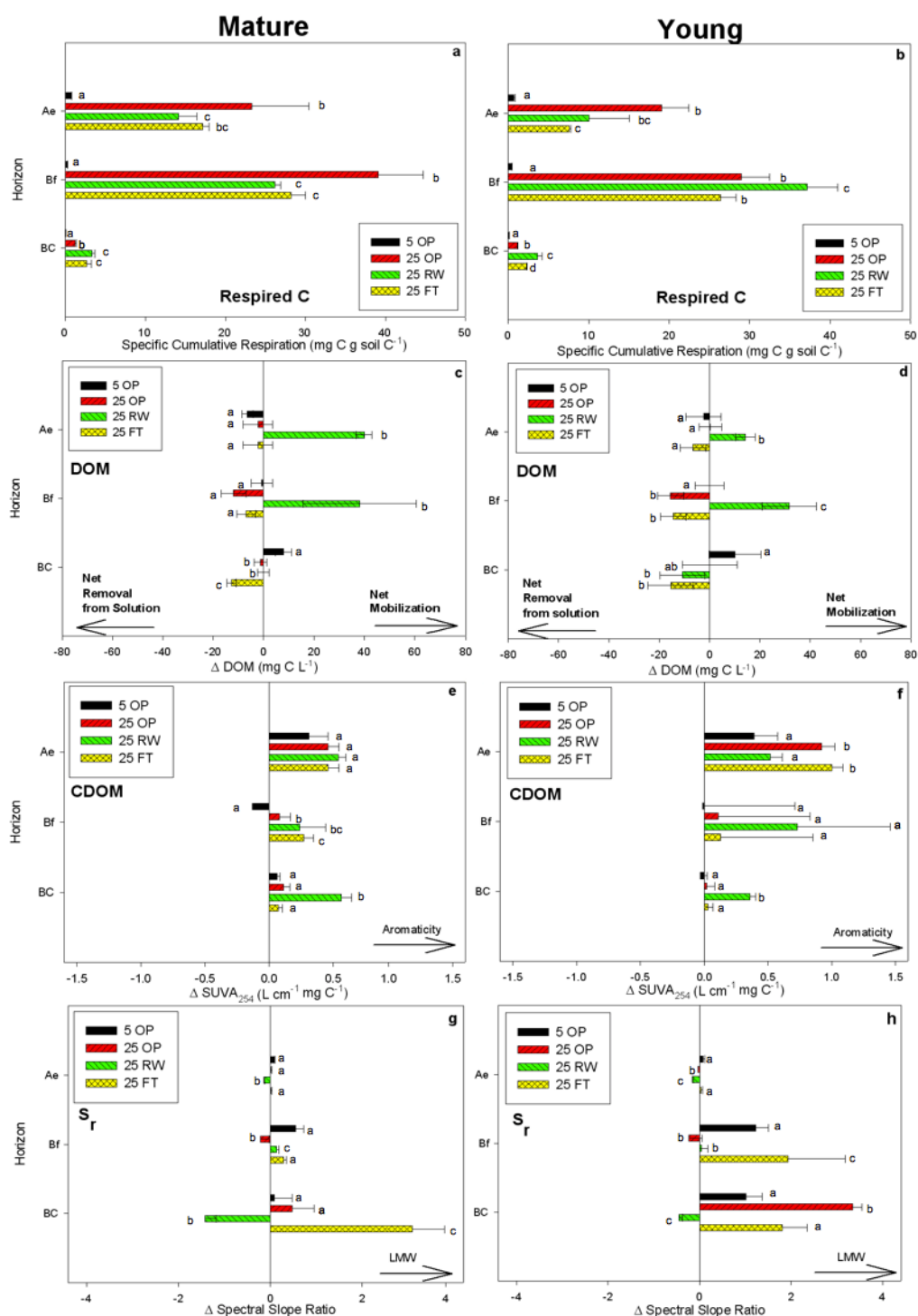


Figure 4.5: a-b) Bioreactivity (specific cumulative respired C), c-d) net change in DOC_{ex} , e-f) net change in Fe-corrected CDOM and g-h) net change in S_r over incubation of 1 month of soil samples from A_e , B_f and BC horizons of Mature (left) and Young (right) forest podzols from Mooseland, Nova Scotia, Canada. Soils were incubated with deionized water under optimal conditions (OP), or subjected to dry-rewetting (RW) or freeze-thaw (FT). Different lower case letters at the end of bars indicate significant differences ($p < 0.05$) among treatments.

Table 4.4: Results of repeated measures ANOVA for log-transformed specific respiration rate (R_d) and $\delta^{13}\text{C-CO}_2$, with Incubation Day (repeated measurements) for the fixed effects of temperature or climate extremes treatments with Site and Horizon as random errors, tested with scenarios that included interactions for Site and Horizon, for composite samples (n=9) of A_e , B_f and BC horizons from Mature and Young sites in Mooseland, NS. Significance codes: * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s. not significant.

		log Specific respiration rate		$\delta^{13}\text{C}$ bulk soil	
Fixed effect	Within (interactions)	F value	p	F value	p
Temperature	Temperature	439.259	$<2e^{-16}$ ***	6.589	0.0016 **
	Temperature:Site	0.220	n.s.	3.694	0.0261 *
	Temperature:Horizon	146.356	$<2e^{-16}$ ***	7.746	$6.27e^{-6}$ ***
	Temperature:Site:Horizon	0.134	n.s.	1.092	n.s.
Treatment	Treatment	51.796	$<2e^{-16}$ ***	125.628	$<2e^{-16}$ ***
	Treatment:Site	1.741	n.s.	7.126	0.00096 ***
	Treatment:Horizon	60.358	$<2e^{-16}$ ***	32.475	$6.27e^{-6}$ ***
	Treatment:Site:Horizon	0.482	n.s.	5.802	n.s.

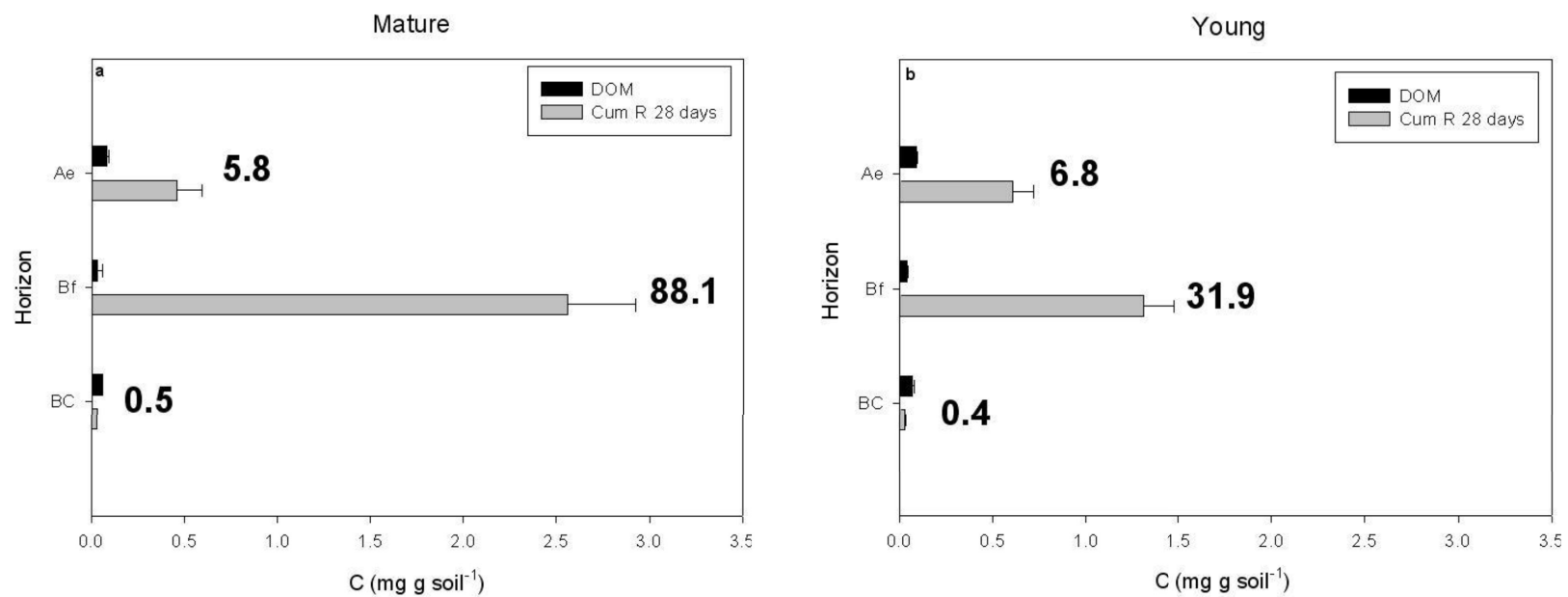


Figure 4.6: Comparison of the amounts of cumulative respired C (light bar) and as DOC_{ex} (dark bar) (mg g soil⁻¹) for Mature (left) and Young sites (right) at Mooseland, Nova Scotia, Canada. The number at the end of the horizontal bars is the ratio of respired C to DOC for each sample. In the BC, the DOC_{ex} pool was larger than the respired C.

4.3.4 $\delta^{13}\text{C}$ of respired CO_2 following incubation

Depth trends

A_e horizons respired CO_2 with a lower $\delta^{13}\text{C}$ signature (-26‰) than B_f and BC horizons (Figure 4.7). B_f and BC horizons maintained a respired $\delta^{13}\text{C}\text{-CO}_2$ signature at a mean of -21‰ (Figure 4.7). Note that the $\delta^{13}\text{C}$ of respired CO_2 for B_f and BC horizons decreased in ^{13}C over the period of the 28 day incubation (data not shown). Overall, site differences between weighted monthly mean respired $\delta^{13}\text{C}\text{-CO}_2$ were not significant (Table 4.4).

Carbon dioxide respired from horizons was generally more enriched in ^{13}C (i.e. higher) relative to ^{13}C of bulk soil $\delta^{13}\text{C}$, organo-metal complexes and water soluble pools (Table 4.6 and 4.1, and Figure 4.7). In contrast, $\delta^{13}\text{C}$ of respired CO_2 was lower in ^{13}C than C of OM in crystalline pools in each horizon at both sites. Under optimal moisture, stable isotope ratios of respired CO_2 were most similar to $\delta^{13}\text{C}$ of DOC_{ex} for all horizons (Table 4.3 and Figure 4.7). For each horizon, $\delta^{13}\text{C}$ of respired CO_2 was always higher relative to DOC_{ex} , and this difference varied up to 3.37‰ (Table 4.5). The $\delta^{13}\text{C}\text{-CO}_2$ and extract SUVA_{254} were highly correlated for all samples, with decreases in $^{13}\text{C}\text{-CO}_2$ as the SUVA_{254} of the soil extracts increased ($r^2 = 0.76$, $p < 0.0001$; Figure 4.8).

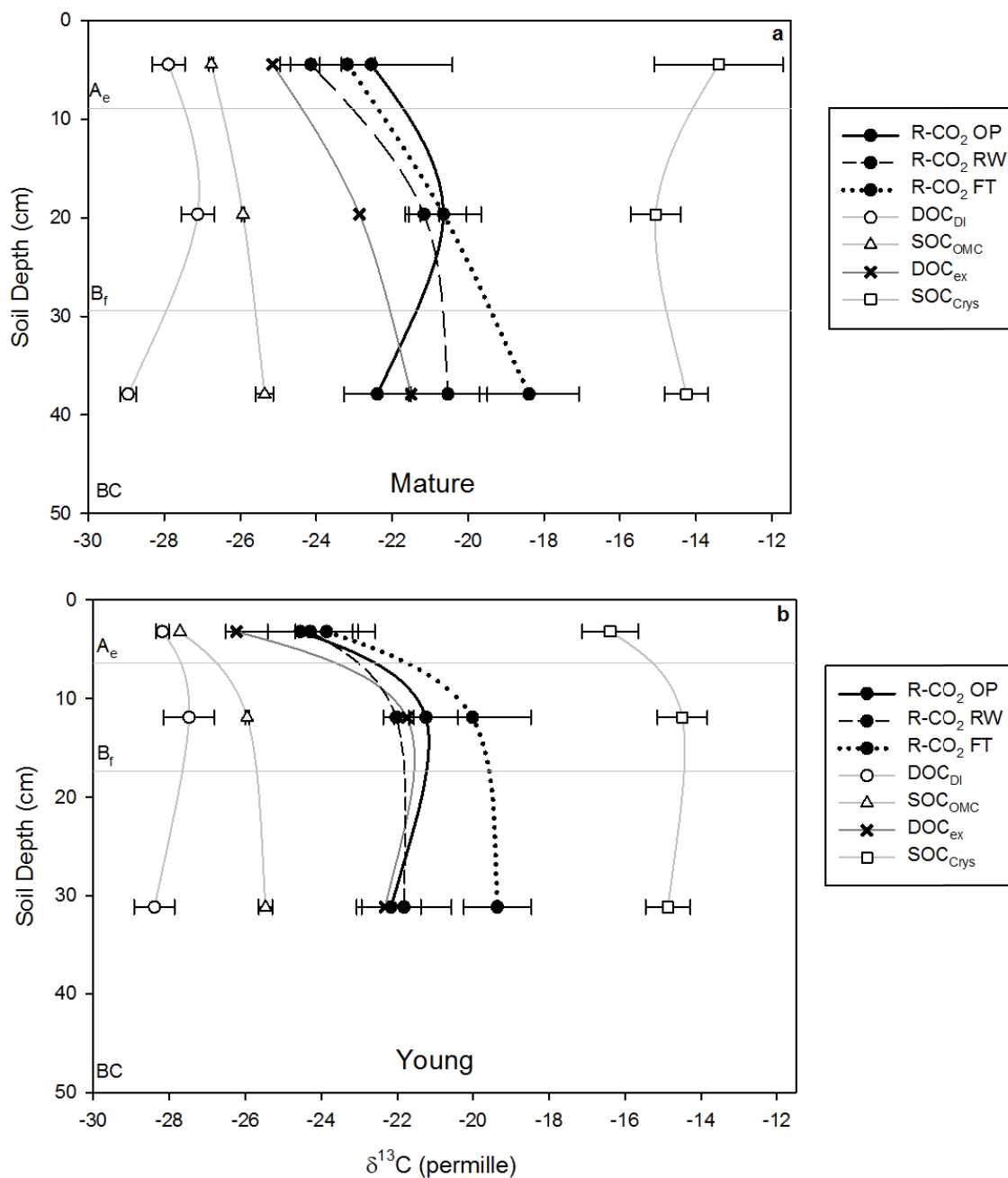


Figure 4.7: The $\delta^{13}\text{C}$ - CO_2 of weighted mean monthly respired CO_2 ($\delta^{13}\text{C}$ - CO_2 ; $n=3$ for each horizon) from a Mature (a) and Young (b) site from Mooseland, Nova Scotia, Canada incubated at 25 °C for 28 days. Incubated soils experienced Optimum conditions (OP - solid line), rewetted from dry (RW - broken line), or freeze-thaw (FT - dotted line). Error bars indicate 1 SD. For reference, the initial values of $\delta^{13}\text{C}$ of DOC_{ex} in mineral fractions are plotted, with DI (white circles), Organo-metal (white triangles), and Crystalline fraction (white squares). Horizons, indicated at left in each figure, are delineated with gray horizontal lines.

Table 4.5: Generalized linear mixed model results, testing for the effect of temperature or treatment on DOC_{ex} , SUVA_{254} and spectral slope ratio (S_r) for incubated samples from Mature and Young sites in Mooseland, Nova Scotia, Canada. Models were tested that included the effects of horizon, site and organo-metal complexes (OMC)and crystalline (Crys) mineral cotents. Significance codes: . $p < 0.1$; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$; n.s. not significant.

Covariate	Model comparisons	Temperature χ^2 value	p	Treatment χ^2 value	p
DOC_{ex}	Horizon	11.550	$6.775e^{-4}$ ***	28.567	$9.05e^{-08}$ ***
	Site	4.147	0.04171 *	0.0339	n.s.
	Mineral OMC	7.138	0.007547 **	1.286	n.s.
	Mineral Crys	6.205	0.01274 *	0.307	n.s.
SUVA_{254}	Horizon	10.916	$9.532e^{-4}$ ***	6.494	0.01802 *
	Site	0.1702	n.s.	0.0339	n.s.
	Mineral OMC	7.130	0.007598 **	2.951	0.08582 .
	Mineral Crys	11.479	$7.038e^{-4}$ ***	0.4177	n.s.
S_r	Horizon	0.496	n.s.	26.663	$2.42e^{-07}$ ***
	Site	2.3861	n.s.	0.1547	n.s.
	Mineral OMC	0.2733	n.s.	0.6032	n.s.
	Mineral Crys	7.287	0.006945 **	0.8697	n.s.

Table 4.6: $\Delta^{13}\text{C}$ expressed as the difference in respired weighted monthly mean $\delta^{13}\text{C}\text{-CO}_2$ following incubation under optimum moisture at 5, 15 and 25 °C or after dry-rewetting (RW) or freeze-thaw at 25 °C compared to initial DOC_{ex} from incubated podzol horizons from a Young and Mature red spruce forest sites in Mooseland, NS. Larger values indicate greater ^{13}C enrichment of CO_2 relative to the DOC_{ex} in particular horizon.

Site	Horizon	5	15	25	25 RW	25 FT
Mature	A_e	0.71	1.39	1.30	4.48	3.41
	B_f	0.14	0.56	-0.71	1.21	1.57
	BC	0.53	1.04	-0.84	2.81	4.41
Young	A_e	1.37	1.67	2.10	6.65	4.99
	B_f	1.86	1.15	0.05	1.83	2.27
	BC	2.78	3.37	1.23	5.99	6.03

Effect of temperature

Temperature could explain differences in $\delta^{13}\text{C-CO}_2$ between sites and when comparing horizons overall (repeated measures ANOVA $p < 0.05$; Table 4.5). In A_e horizons, increases in temperature were significantly correlated to an increase in $\delta^{13}\text{C-CO}_2$ ($r^2 = 0.995$; Figure 4.9 and Table 4.5). There were no observed changes in $\delta^{13}\text{C}$ of respired CO_2 with increasing incubation temperature in the B_f and BC horizons (Figure 4.9).

4.3.5 Effects of extreme climatic change treatments on respiration and extracted DOC

Although similar trends in respiration and bioreactivity in horizons at each site following RW and FT treatments were observed (Figure 4.5), there were differences in the responses of DOC_{ex} and respired $\delta^{13}\text{C-CO}_2$ to RW and FT disturbance treatments (Table 4.3 and Figure 4.7). Rewetting resulted in increases in DOC_{ex} released from A_e and B_f horizons, whereas FT resulted in decreases in DOC_{ex} released from these horizons (Table 4.6 and Figure 4.5 c-d); however, both of these climatic treatments generally resulted in decreases for BC horizons (Table 4.6 and Figure 4.5 c-d). The $\delta^{13}\text{C}$ of respired CO_2 was higher for all samples following RW or FT than OP conditions, with larger $\delta^{13}\text{C}$ of CO_2 compared to $\delta^{13}\text{C}$ of DOC_{ex} . Here, a notably large isotopic enrichment was observed following rewetting in A_e ($\delta^{13}\text{C} = 3.41 - 6.65 \text{ ‰}$), and following freeze-thaw in BC ($\delta^{13}\text{C} = 2.81 - 4.48 \text{ ‰}$). The $\delta^{13}\text{C-CO}_2$ following these climatic treatments in B_f horizons were not markedly different than OP (Table 4.6).

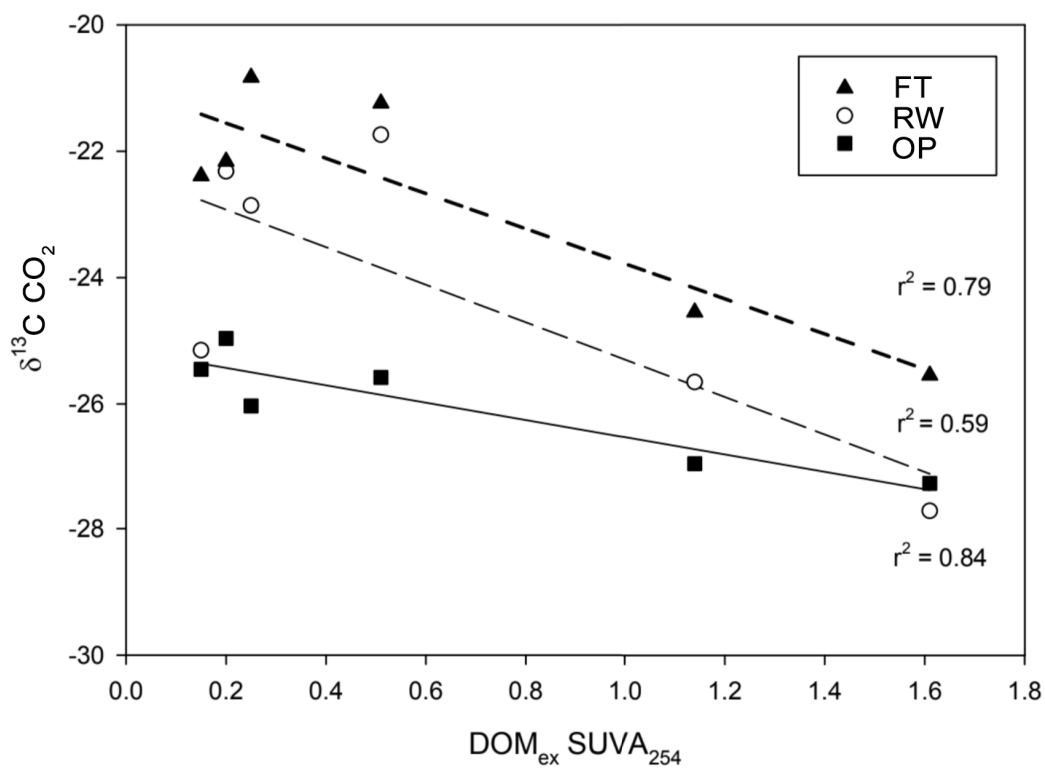


Figure 4.8: Relationship between weighted mean $\delta^{13}\text{C}$ respired CO_2 and SUVA_{254} of extract CDOM for the 28-day incubation for incubation at 25 °C under Optimal conditions (OP solid line), rewetting (RW long dash) and freeze-thaw (FT short dashes). Decreases in $\delta^{13}\text{C}$ respired CO_2 are highly correlated with the increases in SUVA_{254} ($r^2 = 0.76$, 0.89 and 0.95 for OP, RW and FT).

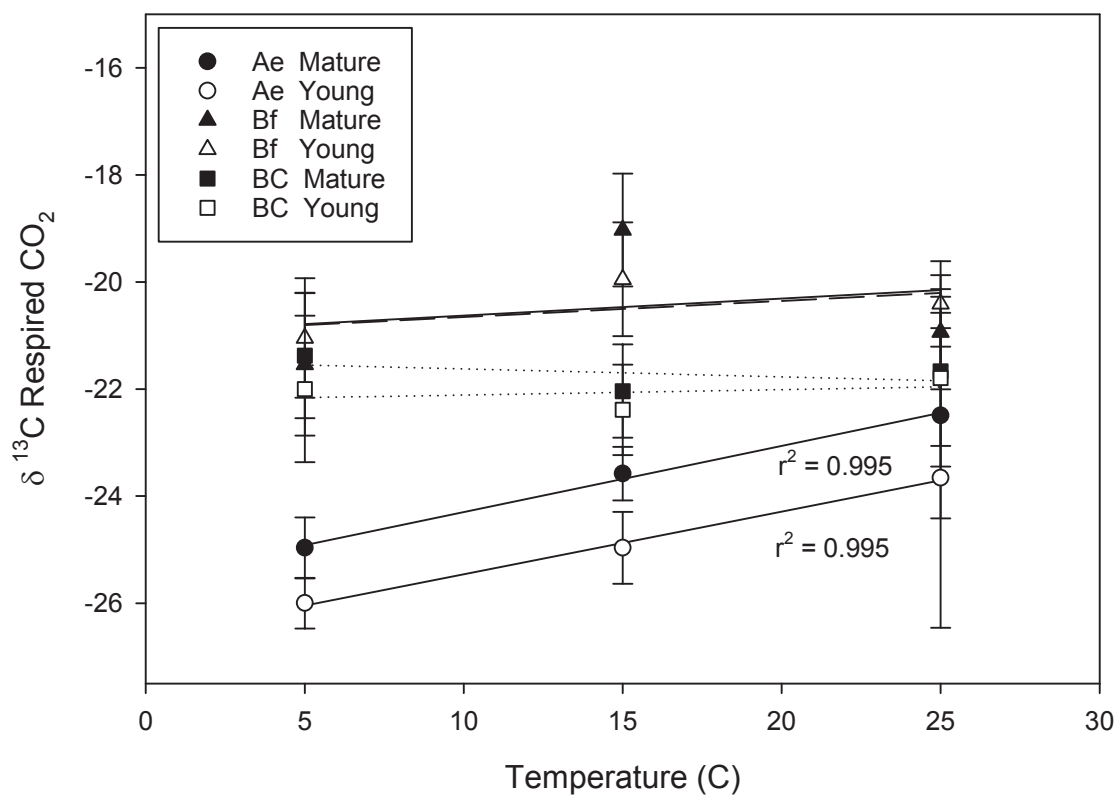


Figure 4.9: Mean and SD of $\delta^{13}\text{C}$ of respired CO_2 over the 28 day incubation for A_e (circles), B_f (triangles) and BC (squares) horizons in Mature (filled symbols) and Young (open symbols) at 3 temperatures: 5, 15 and 25 °C. Linear regression lines are shown for all horizons, but correlation coefficients are only shown for the relationships between $\delta^{13}\text{C}$ of respired CO_2 and temperature in Young and Mature A_e horizons ($p < 0.05$). $\delta^{13}\text{C}$ of respired CO_2 is consistently different between the sites, where for every 10 °C rise, the $\delta^{13}\text{C}$ of respired CO_2 increased by 1 ‰.

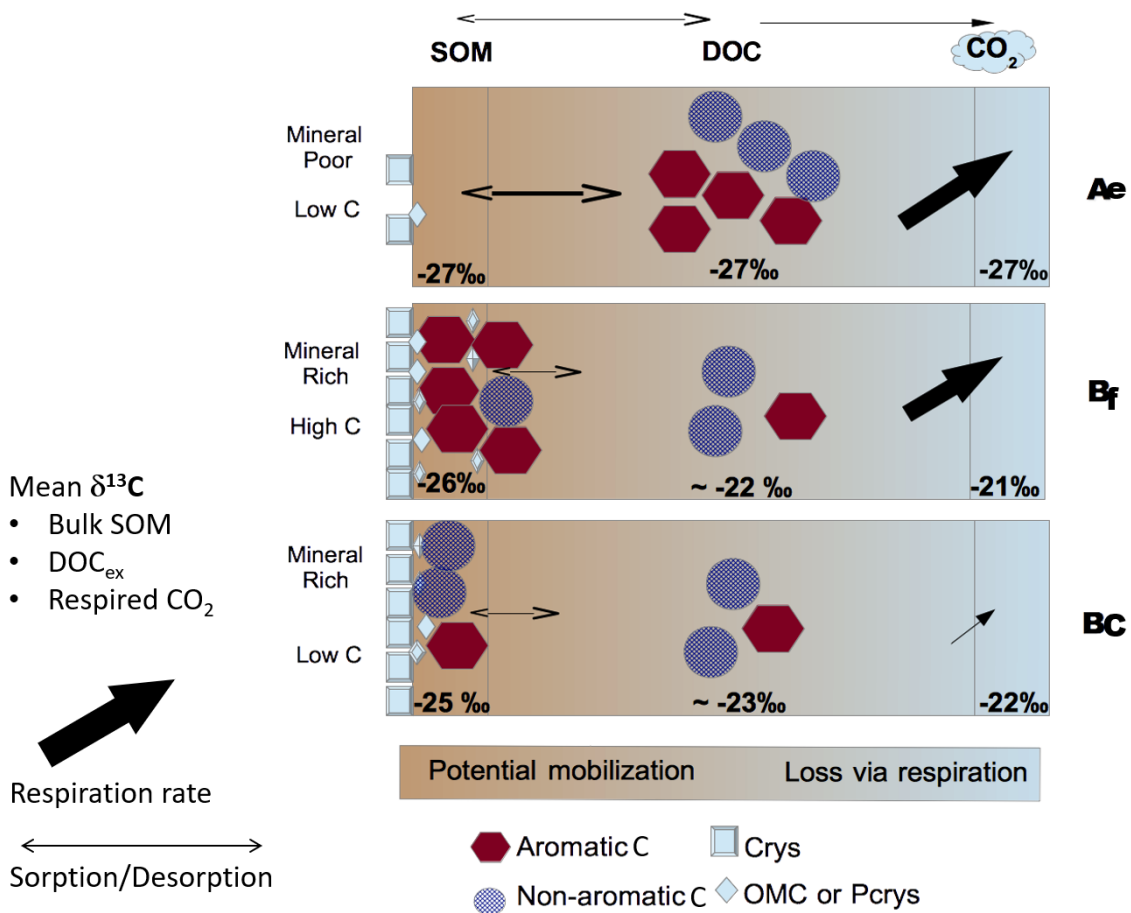


Figure 4.10: This diagram depicts the general soil characteristics and relative differences in chemistry through depth in genetic horizons. The $\delta^{13}\text{C}$ of solid C, DOC and CO₂ C is given at the bottom of each box. Note that all 3 genetic horizon boxes are the same size and do not depict the actual horizon thicknesses. The relative magnitude of bioreactivity is indicated by the size of the arrow. Aromatic C compounds are indicated by red hexagons, non-aromatic moieties by blue hatched circles, crystalline minerals by rectangles and organometal and poorly crystalline minerals by diamonds. Relative differences in the number of symbols in each horizon indicate their relative abundance.

4.4 Discussion

4.4.1 Soil respiration responses to microclimatic changes through depth indicate enhanced susceptibility to SOM loss

Surface horizons are highly susceptible to C loss with increases in temperature

The results of this study indicate that surface soil horizons, A_e and B_f , are highly susceptible to C loss via SOM decomposition (relative to DOC mobilization - Figure 4.6) when exposed to increased temperatures that may occur with harvesting disturbance. This is significant because these horizons occupy the greatest thickness within the soil profile in these shallow coniferous forest soils, store the greatest amount of C in soil profiles, and have been documented to experience the greatest losses through depth following forest clear-cut harvesting (Gabriel et al., 2018, Chapter 2; Prest et al., 2014). The results of this study are also consistent with other research studies that measured high respiration rates and bioreactivity in incubated surface soils (Gabriel and Kellman, 2014; Risk et al., 2008; Salome et al., 2009), and are consistent with the documented lower C storage in mineral soils of harvested compared to mature forest sites (Gabriel et al., 2018; Prest et al., 2014). These data further suggest that temperature shifts in forest soils can have significant impacts on the soil C balance. Furthermore, since thermal alteration of soil persists for years following forest clear-cut harvesting (Kellman et al., 2015), the higher mean temperature and physical disturbances arising from clear-cut harvesting present important challenges to recovery of soil C storage. The effects of altered soil climate would be expected to be persistent over timescales of forest recovery, at least until recovering ground vegetation and canopy closure resulted in a lower soil temperature and the stabilization of soil climate.

In the deeper soil horizons, we found that SOM was relatively resistant to decomposition, with lower rates of respiration and bioreactivity compared to surface horizons. Slower rates of respiration measured in the deeper soil horizons may be due to factors other than SOM molecular structure or C quality. Low nutrient availability limits SOM activity in deep soil (Fontaine et al., 2004; Rumpel et al., 2015; Salome et al., 2009). This limitation is due to a more heterogeneous distribution of deep SOM

(Chabbi et al., 2009), and higher physical protection of SOM by Fe and Al hydroxide minerals compared to surface soils (Almagro et al., 2009; Gentch et al., 2015; Moinet et al., 2018; Plante et al., 2009). Despite these factors at play in deeper mineral soils, C losses at depth can be stimulated if physically disturbed (Berhe et al., 2017; Kaiser et al., 2015; Oburger and Jones, 2009), or if particular environmental constraints are removed (Fontaine et al., 2007; Risk et al., 2008). Changes to soil physical conditions following harvesting disturbance may lead to enhanced losses, even at depth.

Trends in temperature sensitivity of SOM decomposition through depth

Elevated Q_{10} of soil respiration provides further evidence that SOM is more susceptible to decomposition with increased temperature in surface compared to deeper horizons (Table 4.2). Several studies have reported similar results to this study, with higher Q_{10} in shallow compared to deep soils (Berhe et al., 2017; Gillabel et al., 2010; Larionova et al., 2007; Reynolds et al., 2017; Risk et al., 2008; Salome et al., 2010; Xu et al., 2014). While these results are in direct contrast to the CQT hypothesis (Balantyne and Billings, 2003), they are in accordance with an emerging understanding of SOM whereby respiration responses are not necessarily dependent on the chemical composition of SOM alone (Lehmann and Kleber, 2015), but instead may be due to other physical factors that constrain decomposition. Respiratory substrate availability is modulated by a multitude of physical factors (Davidson et al., 2012), including microbial processes (Clarholm et al., 2012; Kemmitt et al., 2008; Kothawala et al., 2009) and mineral characteristics, such as mineral-organic matter interactions, that vary through depth (Lawrence et al., 2017; Reynolds et al., 2017). Physicochemical processes regulated by temperature can increase apparent temperature sensitivity relative to intrinsic responses (Davidson and Janssens, 2006; Davidson et al., 2012).

The observation of higher Q_{10} values of soil respiration observed in the B_f horizon of the Mature and Young sites is consistent with indications that this C-rich surface mineral horizon is susceptible to loss with an increase in temperature. Furthermore, the Mature site exhibited a higher Q_{10} of soil respiration relative to the Young site, likely due to larger SOC stocks relative to reactive mineral surfaces in the Mature forested site that haven't been subjected to disturbance. In B_f horizons, the ratio of C to minerals in the organo-mineral fraction was significantly higher in the Mature

site (C:Fe+Al of 6.78 (\pm 0.44)) compared to the Young site (C:Fe+Al of 5.68 (\pm 0.12)) (Table 4.2). The higher ratio likely indicates that this C that is less protected and more easily destabilized, consistent with the concept of C saturation (Stewart et al., 2008).

4.4.2 Connecting respiratory substrate and soil respiration through DOC_{ex} and chemistry of respired CO_2

Net shifts in soil DOC_{ex} and $\delta^{13}\text{C}$ of respiratory CO_2 consistent with susceptibility of surface horizons to loss with increased temperature

Reduced DOC_{ex} and increases in its aromaticity with temperature exposure within the surface horizons is consistent with greater respiratory C losses (Figure 4.10). These results are in accordance with other studies that have documented changes in DOC and aromaticity during soil incubation (Camino-Serrano et al., 2014; Heckman et al., 2011; Kalbitz and Kaiser, 2008; Kalbitz et al., 2003; Klotzbücher et al., 2013; Pan et al., 2016; Smolander et al., 2001). These shifts in soil solution chemistry could have resulted from a combination of processes that can occur simultaneously in soils: 1) preferential decomposition of labile and non-aromatic C compounds, like carbohydrates, amino acids and amino sugars, which would result in a higher SUVA_{254} as these compounds accumulate in solution; and, 2) production of DOC from the mobilization of smaller aromatic organic molecules from mineral-associated SOM pools with increases in temperature (Moore et al., 2008), and the microbial production of organic compound chelators (e.g. oxalate and citrate) (Clarholm et al., 2015) that would support respiration.

Despite the general association between increased soil respiration rates and reduced DOC_{ex} concentrations in A_e and B_f horizons, decoupling of these processes appeared to occur in the deeper BC horizon soils. In this experiment, extracted DOC and its aromaticity declined through depth, similar to data obtained by Heckman et al. (2009), who also noted differences in DOC chemistry through depth in surface and subsurface soils. BC horizon soils have a higher proportion of crystalline mineral-associated pools which have stronger sorption and higher stability (Lawrence et al., 2015), compared to surface horizons. Furthermore, following incubation, the potential mobilization of C as DOC was over twice as large as the cumulative respired

C pool (Figure 4.6) in the BC horizons at both sites, which suggests that despite the presence relatively high soluble C compounds, respiration in BC remained low. In subsoil horizons of these sites, respiratory substrate availability may be controlled by the nature of the minerals present, consistent with the Regulatory Gate Hypothesis, wherein the release of labile substrates to the soluble phase is a rate-limiting step that precedes decomposition (Kemmitt et al., 2008). At depth, nutrient limitations may also exacerbate potential respiration responses (Fontaine et al., 2007).

Similarity of the $\delta^{13}\text{C}$ of respiratory CO_2 and of DOC_{ex} supports the role of this aqueous C pool (i.e. DOC) in supporting the microbial activity that results in C losses in these soils. This similarity of $\delta^{13}\text{C}$ of respired CO_2 is consistent with DOC_{ex} as the source of respiratory substrate (Bengston and Bengsston, 2007). In B_f and BC horizons, the respired $\delta^{13}\text{C}\text{-CO}_2$ was higher than in A_e horizons, similar to the results of other studies that examined the $\delta^{13}\text{C}$ of respired CO_2 from soils (Bostrom et al., 2007) and from mineral SOM pools (Crow et al., 2006). Elevated $\delta^{13}\text{C}$ values of CO_2 relative to DOC_{ex} are consistent with fractionation between substrate and product. And these data also support a link between the CDOM aromaticity (i.e. SUVA_{254}) and the $\delta^{13}\text{C}\text{-CO}_2$. In samples through depth, when CDOM was more aromatic (e.g. A_e), the respired $\delta^{13}\text{C}\text{-CO}_2$ signature was also lower, in comparison to the higher $\delta^{13}\text{C}\text{-CO}_2$ values that were observed (e.g. B_f and BC horizons) when SUVA_{254} of DOC_{ex} was low (Figure 4.8). Increasingly higher values of $\delta^{13}\text{C}$ of CO_2 through depth follow bulk soil trends and suggest an increasingly ^{13}C -enriched SOC source which may be microbial-derived (Brunn et al., 2014; Ehleringer et al, 2000; Kohl et al., 2016), and may be associated with SOC pools of increasing crystallinity (Figure 4.7).

Trends through depth in the role of minerals in the control of access to respiratory substrate

The $\delta^{13}\text{C}\text{-CO}_2$ may provide information about the role of minerals on respiratory substrate availability through depth. In the A_e horizons, the similarity between the $\delta^{13}\text{C}$ of respired CO_2 with $\delta^{13}\text{C}$ of DOM_{ex} (Figure 4.7) is consistent with the lack of sorptive minerals (low Fe and Al OMC and Crys - Table 4.1) in A_e horizons. Thus, the nature of SOM in bulk soil is directly reflected in the DOC_{ex} of the A_e

horizon. Further evidence of this exists in the higher $\delta^{13}\text{C}$ of CO_2 and of soil C at the Mature compared to the Young site. A lower $\delta^{13}\text{C}$ signature of SOM in A_e relative to B horizons could be explained by mechanical mixing of surface litter following harvesting (Zummo and Friedland, 2011), although this would be expected in the upper profile.

In B horizons, however, the influence of the higher content of reactive soil minerals on substrate availability was more apparent than in A_e horizons. In B horizons, poorly crystalline Fe and Al hydroxide minerals preferentially bind aromatic fractions of DOC_{ex} in B horizons (Sanderman and Kramer, 2017). Large differences between the $\delta^{13}\text{C}$ of respired CO_2 compared to DOC_{ex} $\delta^{13}\text{C}$ of soil SOM pools were observed in the B horizons, similar to those of other studies that examined the $\delta^{13}\text{C}$ of respired CO_2 from soils (Bostrom et al., 2007) and from mineral SOM pools (Crow et al., 2006). These ^{13}C -enriched isotopic signatures are most similar to that of crystalline mineral pools in these soils which calls into question the protective or stabilizing nature of crystalline mineral associations, in particular.

Variation in temperature responses of $\delta^{13}\text{C}$ of respired CO_2 may signify differences in pools of SOM accessed with increased temperature and by horizon. In A_e horizons, increased temperature was associated with a higher $\delta^{13}\text{C}$ - CO_2 signature, potentially signifying shifts toward more microbial and/or mineral-protected C. This higher $\delta^{13}\text{C}$ of respired CO_2 may point to increased access to the C compounds in crystalline pools in these soils which were notably higher in ^{13}C than all other SOC pools (Figure 4.7). Little variation with temperature was observed in the $\delta^{13}\text{C}$ of respired CO_2 from B_f and BC horizons, however: these had consistently higher $\delta^{13}\text{C}$ than respired CO_2 of A_e across the temperature range. The reason for a lack of temperature response in $\delta^{13}\text{C}$ - CO_2 of B horizons was not clear, distinct differences exist in the communities of microbes through depth (Kohl et al., 2017) that exhibit different substrate preferences and responses to temperature (Andrews et al., 2000) and this may be a factor in the observed responses. These data also may be due to the presence of minerals in deeper horizons (B_f and BC), which are absent from the A_e horizon, which can confer a protective effect on particular SOM pools that is not temperature sensitive.

4.4.3 Extreme climatic disturbances can enhance mobility of soil C in surface horizons and respiratory losses of soil C at depth

Both RW and FT generally resulted in changes in soil respiration rates and bioreactivity compared to optimal conditions, with variation in responses depending on the site and specific horizon. In surface A_e horizons of both sites and the B_f horizon of the Mature site, bioreactivity was generally lower following RW and FT compared to optimal conditions (Figure 4.3.5), consistent with observations of shallow soils made by others (Jarvis et al., 2007; Kim et al., 2012; Sharma et al., 2006). Reduced decomposition rates of the RW and FT treatment samples may be a function of the following: 1) a longer lag time may be required for microbial communities to recover from drying or freezing; 2) the precipitation of Fe and CDOM mixed phases can occur following freezing, reducing substrate availability (Fellman et al., 2008). Meanwhile, the largest stimulation of respiration following RW and FT treatments was observed in the B_f horizon of the Young site, consistent with lower aggregate stability in recovering forests (Bronick and Lal, 2006; Degryze et al., 2004; Deneff et al. 2007), which would reduce SOM protection. The deeper BC horizons exhibited relatively greater potential losses via respiration following both RW and FT disturbances. Studies have documented priming of deep SOM decomposition with labile respiratory substrates (Fontaine et al., 2007), and since RW and FT conditions can result in the release of labile OM, these disturbances may present a particular risk for deep soils. Rewetting and FT events would be rare in situ for deep soils, even considering the loss of insulating ground cover following clear-cut harvesting, which exposes soils to repeated cycles of RW and FT that can lead to losses through erosion (Berhe et al., 2017). However, soils are often mixed during site preparation following clear-cut harvesting, thereby exposing deeper layers to this type of disturbance.

Rewetting conditions enhanced the net production of DOC_{ex} following incubation, signifying the potential for greater mobilization of soil C. Since we generally observed reduced respiration responses in surface soil horizons following RW compared to OP, the higher DOC in these samples this suggests that the processes governing DOC production and its uptake by microbes are not necessarily temporally connected following rewetting of dry soil. A lag time following rewetting of dry soil is required before microbial activity recovers (Kim et al., 2014). Furthermore, incubation following RW

treatment resulted in increases of CDOM aromaticity (Figure 4.5). This increase in the aromatic character and HMW compounds (S_r evidence) of DOC_{ex} following RW are in accordance with the observations from other studies (Campbell et al., 2014; Kim et al., 2012). DOC_{ex} chemistry shifts following RW disturbance have been explained by the disruption of soil structure, releasing aromatic compounds into soil solution, alongside microbial osmolytes and necromass (Berhe et al., 2017; Mueller et al., 2014; Salome et al., 2010). Reductive dissolution of Fe hydroxide mineral associations following the temporary flooding conditions upon RW of dry soil can also solubilize mineral-associated SOM (Keiluweit et al., 2017), which would also increase DOC aromaticity. While we did not measure soluble Fe in any soil extracts, this analysis could confirm whether this redox-sensitive process was relevant. In contrast, following FT treatment, others have observed an increased flush of labile non-aromatic compounds, which would decrease the aromaticity of extracted DOC (Campbell et al., 2014; Kim et al., 2012). While these effects were observed here, the impacts of RW and FT depend on the soil or ecosystem type in question (Kim et al., 2012).

Rewetting and freeze-thaw stimulated the use of more ^{13}C -enriched pools of soil C

Following RW and FT disturbance respiration rates were generally not enhanced compared to optimal conditions, but nevertheless DOM_{ex} chemistry shifted. This shift is likely due to increased consumption of ^{13}C -enriched compounds which leads to the relative enrichment of $\delta^{13}\text{C}\text{-CO}_2$ of up to 6-8 ‰ following the extreme climatic conditions of RW and FT. Therefore, the shift in DOC_{ex} chemistry following incubation might arise from the preferential decomposition of ^{13}C -enriched non-aromatic moieties from soil solution. This trend has been observed elsewhere following RW and FT disturbance (Bostrom et al., 2007; Heckman et al., 2011; Jarvis et al., 2007; Unger et al., 2012).

These results also highlight the potential temporal lag between the release of substrates and their use by microbes. This is important to consider in terms of the C balance in harvested ecosystems, because DOM can be mobilized to aquatic environments following clear-cut harvesting via lateral and overland flow (Bowering et al., submitted; Schelker et al., 2013). Extreme events can mobilize soil C (especially

from A_e and B_f horizons) and their impact on mobilization is likely dependent upon the frequency and depth of rewetting and freeze-thaw events. This underlines the need for greater tracking of extreme event-driven C mobilization in watersheds.

4.4.4 Conclusions

This study provides some insights into the susceptibility of surface A_e and B_f horizons in podzolic soils, where the greatest soil C stocks are often found in these forests, despite the purported protective effects of organo-mineral associations. Surface A_e and B_f horizons respired at rates an order of magnitude higher than deeper BC horizons and were highly sensitive to temperature, which indicates that SOM in surface horizons are susceptible to loss, providing a mechanism for observed in situ losses of soil C following clear-cut harvesting. Surface horizons were also susceptible to C loss via solute mobility following extreme climatic events. Decomposition in short-term incubations vastly outweighed the pool of C represented by dissolved organic carbon. Net production of DOC and shifts in aromaticity following incubation did not always result in an increase in respiration, but net shifts in DOC and its chemistry aligned with isotopic data, which were consistent with DOC as the source of respiratory substrate.

The results of this study can be extended to contributing knowledge about the impact of climate change on soil C losses, since extreme climatic events may result in greater mobilization of solutes within watersheds. The fate of soil C will likely depend upon the intensity, frequency and depth of disturbances. Associations with minerals in B_f horizons, which occupy the greatest thickness of the soil profile, do not necessarily protect SOM and are susceptible to C loss following climatic changes associated with forest clear-cut harvesting.

Chapter 5

Impacts of redox conditions and temperature on dissolved organic carbon and Fe losses from mineral soils through depth

Preamble This chapter represents the final draft stages of a manuscript by C.E. Gabriel, S. Ziegler, L. Kellman and A.M. Ryan entitled, "Impacts of redox conditions and temperature on dissolved organic carbon and Fe losses from mineral soils through depth" is intended for submission to the journal *Biogeochemistry*. C.E. Gabriel undertook all the research and writing of this manuscript. Suggestions from S. Ziegler and L. Kellman, and A.M. Ryan were incorporated into the preparation of this work, particularly in the final stages of the draft.

Chapter 3 identified that organo-metal pools dominate the distribution of soil C in all horizons (Section 3.5.1), and that the content (per g soil) of this pool is significantly lower in B_f horizons (Section 3.5.4) at a young forest site compared to a mature forest. Chapter 4 examined the potential for microbial decomposition to account for differences between sites. Although C lost via decomposition following short-term incubations vastly outweighed the pool DOC pool (Figure 4.6) especially in shallow soil horizons, the mobilization of DOC may nevertheless represent an important pathway to explain the loss of soil C. This chapter is therefore positioned to examine another potential mechanism for the lower C storage associated with forest harvesting disturbance by addressing the impact of low redox conditions and temperature rise that occurs following clear-cutting as factors responsible for dissolved organic carbon (DOC) and Fe release. These changes may alter reaction rates and soil redox state changes, which can result in the reductive dissolution of Fe minerals, thereby solubilizing organo-metal complexes. This process was examined through a combination of laboratory manipulations and of stream water surveys to assess potential for DOC and Fe mobilization in situ.

5.1 Introduction

Soil organic matter in mineral soils represents a significant component of terrestrial C budgets (Clemmensen et al., 2013), and accurate soil C accounting depends on a process-based understanding of how anthropogenic disturbances alter soil organic matter SOM storage through depth. SOM is a heterogeneous mixture of organic molecules that varies in composition through depth (Clemmensen et al., 2013; Rumpel et al., 2015), and is ultimately stabilized in soils through chemical conditions that reduce or limit oxidative activities, such as moisture content, temperature, pH, and ionic strength, among others; and through physical conditions including spatial inaccessibility and/or aggregate structure (Chenu and Plante, 2006) and occlusion due to interaction with soil mineral phases (Doetterl et al., 2015; Heckman et al., 2009, 2018; Kleber et al., 2005; Kogel-Knabner et al., 2008; Lawrence et al., 2015; Masiello et al., 2004; Sanderman et al., 2014; Torn et al., 1997).

Forest clear-cutting-related alterations to SOM storage have been observed, notably in the mineral soil, in the decades following harvesting (Achat et al., 2015; Dean et al., 2016; Diochon and Kellman, 2008; Falsone et al., 2012; Prest et al., 2014). In temperate and boreal coniferous forests of Canada, clear-cutting accounts for a change in 0.2% of forest cover (or 64 000 ha) every year (Canadian Forest Service, 2013) and across forests of North America, 6.1 million ha annually (Masek et al., 2011), making large terrestrial areas susceptible to alterations in C cycling and storage processes from this intensive form of forest disturbance (Achat et al., 2015). Significant changes to mineral soil carbon (C) storage in the decades following forest clear-cut harvesting in northern forests have been observed (Achat et al., 2015; Diochon et al., 2009; Gabriel et al., 2018; Grand and Lavkulich, 2011; Gross et al., 2018; James and Harrison, 2016; Petrenko and Friedland, 2015; Zummo and Friedland, 2011). Despite these observations, however, mineral soil C losses following forest clear-cutting are not consistent across all ecosystems (IPCC, 2019; Nave et al., 2010; Thiffault et al., 2011; Wan et al., 2018), and observations about C mobilization to aquatic systems are also inconsistent (Schelker et al., 2014 cf. Jewett et al., 1995). The mechanisms for C stability in mineral soil, including its mobilization as dissolved organic carbon (DOC) to aquatic systems, remain poorly understood.

The aqueous organic matter phase in soils is in equilibrium with minerals, and as

such, DOC and its character changes through depth in soils (Sanderman et al., 2008; Strahm et al., 2009). Some have described the exchange process as chromatographic in nature (Kalbitz and Kaiser, 2008; Shen et al., 2014), a conceptual model that recognizes the roles of mineral surfaces, chemical environment and hydrology or retention time (Shen et al., 2014) in controlling the sorption dynamics, microbial processing and thereby composition of DOC. The concentration and character of DOC is a result of a set of equilibrium exchange processes. Organic matter bonded with solid mineral phases (Kaiser and Kalbitz, 2012; Kothawala et al., 2008, 2009; Sanderman et al., 2014; Zsolnay, 2003), and the presence of Fe and Al poorly-crystalline mineral phases were identified as the most important factors controlling the adsorption of DOC by minerals. This is thought to be due to the presence of poorly crystalline minerals (Kothawala and Moore, 2009), whose high surface area can contribute to long-term forest soil mineral carbon storage (Froberg et al., 2007; Kramer et al., 2012). In addition, SOM may be modified by microbes, that can simultaneously decompose bioavailable fractions of SOM and release more DOC from minerals (Clarholm et al., 2015). The collective balance of these biotic and abiotic processes determines the nature and fate of DOC: the net export of DOC results from a greater release of SOM from both biotic and abiotic processes, compared to microbial decomposition. However, it is still unclear which factors are most important for controlling the release of SOM as DOC, especially in the context of soil disturbance associated with forest harvesting disturbance.

Organic matter associations with Fe and Al hydroxide minerals and their turnover time vary depending on mineral crystallinity, ranging from co-precipitated amorphous Fe and Al and organic matter phases, to binding with short-range order Fe and Al minerals, to sorption on crystalline surfaces (Heckman et al., 2018). The relative distribution of these organic matter-mineral pools varies through depth in soils (e.g. Gabriel et al., 2018). Several recent studies have linked changes in soil C storage with the content and nature of soil mineral phases. Density fractionations and sequential selective dissolutions of mineral phases of soils from sites representing a range of ages since clear-cutting have revealed that the quantity of mineral-associated organic matter held in soils may be reduced following harvesting (Diochon and Kellman, 2009; Gabriel et al., 2018), and that particular organo-mineral associations are more likely

to be altered following this disturbance (Gabriel et al., 2018; Grand et al., 2011; Lacroix et al., 2016, Petrenko and Friedland, 2015; Zummo and Friedland, 2011). Organo-metal complexes have been found to be responsible for C storage and are also susceptible to loss following harvesting (Gabriel et al., 2018). An improved understanding of the processes releasing SOM is therefore required to better account for losses from these large subsoil stores of C, and to provide accurate information about the impact of clear-cutting on soil C cycling.

The myriad of systemic changes following clear-cut harvesting alter multiple components of the soil environment: the removal of tree cover alters the radiative energy balance through reduced interception of solar radiation, exposing deeper mineral soil to a larger daily and seasonal temperature amplitude than sites with intact forest cover (Bekele et al., 2007; Kellman et al., 2015). In addition, a rise in the water table resulting from tree removal alters landscape hydrology, including an increase in soil moisture (Kellman et al., 2015) and discharge (Hood et al., 2006; Jewett et al., 1995; Sanderman et al., 2008), resulting in erosion (Yesilonis et al., 2016) and creating periodic or seasonal flooding that can shift soils towards more anoxic conditions (Buettner et al., 2014; Thompson et al., 2006). When the soil physico-chemical environment is altered through elevated temperature and anoxic conditions, the potential exists for a change in the nature of the binding of organic carbon with minerals. Studies have linked the flux and composition of DOC to catchment hydrological characteristics (Hood et al., 2006; Lambert et al., 2011). Following soil flooding, anoxic conditions can also affect the mobility of redox-sensitive minerals such as Mn and Fe hydroxide minerals. Because highly coloured (i.e. chromophoric) aromatic SOM is selectively bound (Sanderman et al., 2014) and retained by reactive minerals in soils such as secondary Fe(III) hydroxides (Kalbitz and Kaiser, 2008; Kramer et al., 2012), anoxic conditions have the potential to simultaneously solubilize Fe (as Fe(II)) and mobilize these dissolved organic molecules, resulting in their export to aquatic systems as DOC (Berhe et al., 2012; Buettner et al., 2014; Doetterl et al., 2012; Falsone et al., 2012; Fritsch et al., 2009; Schelker et al., 2013; Weyhenmeyer et al., 2014). The terrestrial export of chromophoric dissolved organic matter (CDOM) associated with Fe to waterways following forest disturbance can result in the translocation of Fe and associated SOM to downslope depositional environments and/or can become an

important downstream source of exported DOC and Fe, contributing to aquatic CO₂ emissions (Lapierre et al., 2013; Wallin et al., 2015; Weyhenmeyer et al., 2014).

Despite the need for a process-based understanding of C loss from mineral soils in disturbed environments, accurate and systematic efforts to investigate mechanistic controls on C storage in soils through depth are rare (Marín-Spiotta et al., 2014), especially in mineral soils (Trumbore and Czimczik, 2008). Studies investigating soil C storage typically only sample the upper soil profile topsoil (0-10 cm), even though the largest C stocks are typically found in the mineral soil (James and Harrison, 2016), specifically in the B horizons of podzolic soils (Rumpel and Kögel-Knabner, 2010; Trumbore and Czimczik, 2008). This is particularly significant given that it is from mineral horizons where some studies have documented the greatest SOM losses following forest clear-cutting (Achat et al., 2015; Buchholz et al., 2014; Dean et al., 2016; Diochon et al., 2009; Falsone et al., 2012; Lacroix et al., 2016; Petrenko and Friedland, 2015; Prest et al., 2014; Zummo and Friedland, 2011). Note that these results are not universally consistent, with the results of meta-analyses pointing to greatest losses from shallow mineral soils (Nave et al., 2010; Wan et al., 2018), and therefore, a better understanding of the controls on SOM stability in mineral soils is required.

Due to the methodological challenges inherent in quantifying soil C pools in situ and through depth, researchers employ a variety of techniques to characterize and trace SOM in ecosystems, based on extractions, solubility characteristics, optical properties and measurement of stable isotopes of C, among other indicators. The resulting quantity and chemical character of this released SOM varies as a function of specific land-use changes and soil characteristics (Butman et al., 2014; Cawley et al., 2014; Sanderman et al., 2009; Schelker et al., 2013), allowing it to be traced within soil profiles and between sites characterized by altered conditions. The widely-used index, specific UV-Vis absorbance (SUVA₂₅₄) provides a measure of the aromaticity of CDOM (Helms et al., 2008; Weishaar et al., 2003), serving as an indicator of changes in DOM character (Hood et al., 2006), and location of origin in the soil profile (O'Donnell et al., 2014). In addition, stable isotope ratios of carbon ($\delta^{13}\text{C}$) are integrative measures of ecosystem functioning (Billings and Richter, 2006) that can indicate the relative contribution of microbial vs. plant organic matter to SOM

quality (Cleveland et al., 2004; Sanderman et al., 2009) and can act as an indicator of soil C loss (Diochon and Kellman, 2008). Seasonal trends in optical properties ($SUVA_{254}$) and stable isotopes $\delta^{13}C$ of stream water are correlated (Sanderman et al., 2008) and reveal that CDOM chemistry varies seasonally due to factors such as shifts in temperature and rainfall (Hood et al., 2005). Evaluation of these OM characteristics can assist researchers in understanding the relative importance of soil factors and conditions that influence SOM stability and its release as DOC.

As DOM and soluble Fe moves through landscapes, their chemistry may be modified by biotic and abiotic factors as they pass through soil and to downstream depositional environments. While microbial activity may modify DOC, abiotic factors such as pH and redox state can change the speciation of Fe, altering its mobility. The acidity of the soil is a key controlling variable in soils (Brady and Weil, 2007), therefore its influence must be accounted for. For example, organic matter may be desorbed from soil minerals due to pH increases (Grybos et al., 2009; Pan et al., 2014; Thompson et al., 2006). Podzolic soils of Nova Scotia, Canada, are acidic with generally poor buffering capacity (MacDougall et al., 1963). At the pH range of these soils (4.0-5.0), the dominant form of redox-sensitive elements like Fe is in its dissociated state or complexed with organic ligands. At this pH, Fe(II) is soluble at low redox potentials or it can precipitate from solution as a solid as Fe(III) hydroxide at higher redox potentials. In addition, the effect of pH must also be accounted for when carrying out spectrophotometric measurements of organic compounds (Pace et al., 2012).

In an effort to understand the impacts of clear-cutting on soil C losses, a better understanding of the controls on soil organic matter release to aquatic systems in forest catchments is required. This involves manipulation of soil redox conditions and temperature in mineral soils through depth in order to isolate changes in SOM and DOC chemistry. By linking SOM studies and experiments to watershed observations of stream chemistry, we may be able to assess the potential for mechanisms uncovered in the experimental component of this study.

For instance, stream DOC measurements before and after storm events can provide information about the mobilization and origin of DOC within the soil profile (Hood et al., 2006; Kothawala et al., 2014; Lambert et al., 2011; Malik and Gleixner, 2013;

Sanderman et al., 2008), especially since the nature of the binding in mineral-organic complexes such as Fe and Al hydroxides varies with soil depth (Jansen et al., 2002; Mossin et al., 2001). Furthermore, the presence of soluble Fe may indicate reductive dissolution under anoxic conditions. Since the mobility of DOC can be connected with changes in Fe (Kritzberg et al., 2014), determination of molar DOC:Fe ratios can indicate the nature of the DOC-Fe associations, and can be an indicator of the redox conditions under which DOC was mobilized; low ratios are typical when anoxic conditions have released DOC and Fe (Masiello et al., 2004; Riedel et al., 2013), and higher ratios when Fe is reduced (i.e. a shift to Fe(III)).

This research seeks to examine the impacts of altered redox and temperature conditions that may accompany forest clear-cut harvesting on the susceptibility of mineral SOM and Fe export from soils. Our research was conducted to address knowledge gaps about how shifts in soil climate following clear-cut harvesting can result in the loss of SOM. The first objective of this research study was to evaluate, under controlled laboratory conditions, the potential for changes in redox and temperature to release DOC and Fe from mineral podzolic soils through depth. A second objective was to characterize the chemistry of DOC and Fe released under anoxic conditions from laboratory experiments and to compare this to measurements from streams in areas of contrasting forest harvesting history to assess possible in situ evidence for the experimental observations of this study. We hypothesized that higher temperature and anoxic conditions would increase mobilization of DOC and associated Fe from soils, and further assumed that longer exposures to these conditions would result in enhanced DOC and Fe release.

5.2 Materials and Methods

5.2.1 Experimental design

The laboratory experiments were designed to mimic the rise in temperature and soil flooding within the range of conditions experienced in situ by soils of temperate coniferous soils that have been clear-cut harvested. Mineral soil DOC chemistry and Fe release were examined in soil increments through depth to 50 cm at two temperatures (5 and 15 °C) over two incubation lengths (1 and 4 months). Soil samples were also

analyzed via dissolved organic matter (DOM) extraction following the incubation to measure changes in C quantity and chemical character. In addition to laboratory experiments, stream samples that represent water draining intact and disturbed catchments, collected over a field season under both baseflow and stormflow conditions, provided information about the DOC and Fe mobilized from soils of differing harvest history.

5.2.2 Description of Study Sites

For the laboratory experiment, soils were sampled from a mature forest site at Mooseland (ML), a 110 year old secondary regrowth temperate coniferous forest located within the Otter Ponds Demonstration Forest, east of the village of Mooseland, Nova Scotia, Canada (44°56'42.51" N, 62°47'39.53" W) (Figure 5.2). Streams and soils were sampled at Abraham's Lake (AL), a nearby forest chronosequence located in the Governor Lake Ecodistrict in central Nova Scotia, Canada (45°5'0" N 62°25'54" W), which has both a disturbed and reference catchment. AL and ML sites are 30 km apart and have broadly similar climate, geology, soil, vegetation type and land-use (Figure 4.2). They are both well-drained shallow (<1 m) soils dominated by red spruce (*Picea rubens* Sarg.) with balsam fir (*Abies balsamea* (L.) Mill.), eastern white pine (*Pinus strobus* L.), yellow birch (*Betula alleghaniensis* Britt.), and red maple (*Acer rubrum* L.). The forests at both sites are representative of the Acadian Forest Region, a typical forest of the northern temperate zone (Mosseler et al., 2000), where the majority of soils from both AL and ML sites were well-drained sandy loam Orthic Humo-ferric podzols on parent materials of the Goldenville and Halifax Formations overlain by glacial till (Beaver River Till), primarily quartzite and metasiltstone (Refer to Chapter 2, Section 2.2).

At AL, the two stream sampling sites reflecting contrasting land-use histories were established, identified throughout this study as Intact and Disturbed sampling sites. Due to the low relief (<10%) of this region, soils at both Intact and Disturbed sites at AL are highly connected to streams hydrologically, thus making it possible to connect changes in stream chemistry (DOM, SUVA₂₅₄, $\delta^{13}\text{C}$, S_r and pH) to soil processes and the impacts of land-use. The headwater for Bear Brook stream is Abraham's Lake, in the Intact watershed at AL drains primarily upland areas with no recent history

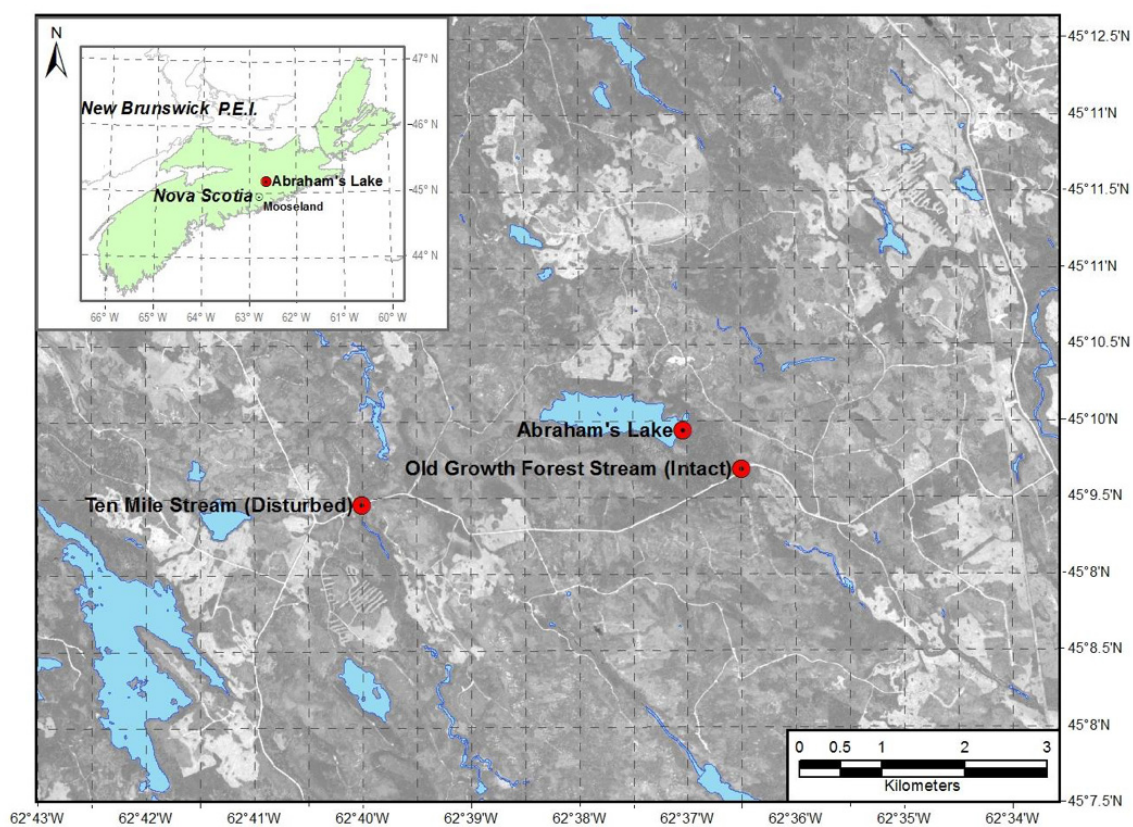


Figure 5.1: Location of Intact and Disturbed water sampling sites in Abraham's Lake area. Soil samples were from Mooseland, NS, located approximately 30 km southwest of this site (see inset). The water sampling site at Abraham 's Lake is also indicated. Lighter-coloured patches show the alteration to forest cover associated with forest harvesting in the Disturbed watershed.

of harvesting, including an old growth forest protected by the Nature Conservancy of Canada, and an 80 year old red spruce forest on crown land. Nearby, the Disturbed catchment along Twelve Mile Stream (Figure 5.1) drains a catchment with a larger contribution of riparian zone or saturated soils than the Intact site, which is lake-influenced (Figure 5.2). Forests in the Disturbed catchment have been harvested by clear-cutting at rates of approximately 25-50% land cover over several decades, where the forests along the length of a third-order stream represent various stages of regrowth, including recent harvesting (Figure 5.1).

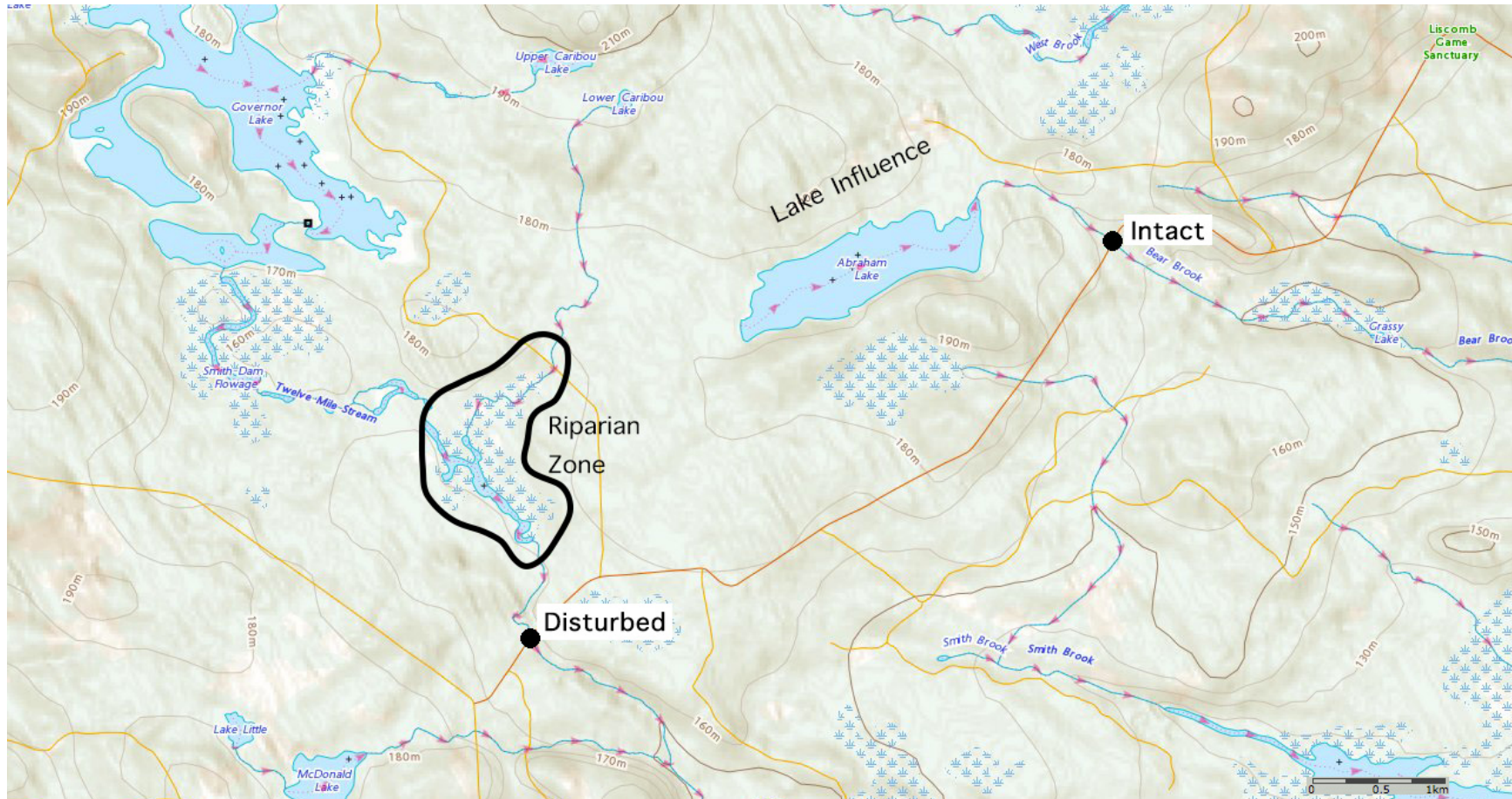


Figure 5.2: Topographic map of of stream water sampling sites in the Abraham's Lake area in Nova Scotia, Eastern Canada. Location of Intact and Disturbed water sampling sites are indicated by black dots, where the road meets the two watershed streams (Twelve Mile Stream, Disturbed, and Bear Brook outflow of Abraham's Lake, Intact). The direction of the flow of water (south) is indicated with red arrows. The encircled area on the left is the riparian zone that influences water chemistry in the Disturbed site.

5.2.3 Incubation experiment - Mooseland soils

For the controlled soil temperature and redox manipulations in this study, mineral soil samples were obtained from fixed soil strata sampled by depth (0-10, 10-20, 20-35 and 35-50 cm) from nine excavated soil pits (50 cm depth by 1 m² area) over a 250 m² area in Mooseland (ML) (Mature forest). The organic horizons were removed, and samples were sieved to 12 mm in the field. Composite samples (n=9) were made by combining field-moist samples of equal weight. Due to the stony nature of the soils, bulk density was measured according to Huntington et al. (1988). Soil from the shallowest layer (0-10 cm) incorporated soil from bleached A_e horizon and the dark brown humic B_h horizon. The 10-20 cm layer contained some B_h material, but primarily consisted of B_f horizon soil. The 20-35 cm increment was dominantly an illuvial B_f horizon, and 35-50 was a B-C transitional horizon. For further soil sampling details, see Prest et al. (2014). For additional information about the soil profile, refer to Chapter 2, Section 4 (Section 2.4).

Field-moist composite soils from ML (30 g dry weight) from each fixed depth stratum were incubated under oxic or anoxic conditions. Soils were incubated at 5 and at 15 °C in 100 mL glass jars in triplicate inside sealed 1 L Mason jars with a rubber septum inserted in the metal top of each jar. To create anoxic conditions, soils were flooded with 20 mL deionized water (DI), and the headspace of the incubation chamber flushed with N₂. This amount of water covered the soil surface with 0.5 cm of water, representing >100% WHC (soil:water ratio of 30 g:20 mL). Oxic treatment soils were held at optimum soil moistures (60-80% WHC for these soils (Gabriel and Kellman, 2014), moisture maintained gravimetrically), with the jar open to the atmosphere with a needle inserted into the rubber septum for gas exchange. These were held under these conditions continuously for 1 or 4 months.

5.2.4 Dissolved organic matter extraction

Following the incubation period, soil solution was extracted from depth increment samples following the addition of deionized water (DI), carried out via vacuum filtration using 0.45 micrometer filters. This soil solution extracted with DI was assumed to represent the DOM fraction. Oxic soils received 50 mL of DI, while the anoxic soils that were flooded received 30 mL DI so the total volume of water added equalled

that of the oxic treatment (refer to previous subsection for details).

5.2.5 Stream sampling strategy - Abraham's Lake

Two catchments at AL, Intact and Disturbed, represent contrasting harvesting histories. The Intact water sample site is located on a second-order reference stream, Bear Brook, that drains from Abraham's Lake, near the old growth forest and within the 80 year old forest site. This watershed is lake influenced and drains upland areas, free of anthropogenic impacts. The Disturbed water sampling site is on Twelve Mile Stream, a second-order stream located 2 km to the west of the Intact sample site (Figure 4.1 and Figure 4.2), and is wetland-influenced, with evidence of harvesting all along the length of the stream. Stream water was sampled from July 2011 to May 2012 at monthly intervals in the ice-free season from the Intact and Disturbed sites streams, >10 m upstream from the road-stream intersection (Figure 4.2). At the Intact catchment, samples were also collected from the shoreline at Abraham's Lake. Stream samples were collected monthly at the stream sampling sites and the timings of precipitation events prior to sampling were noted in order to identify differences in stream chemistry due to stormflow or baseflow conditions. Post-precipitation events were targeted in our field sampling strategy in order to capitalize on flushing of DOC and Fe from soils. If sampling was within 5 days of a precipitation event, it was considered stormflow, and samples were classified as baseflow if there was no precipitation (i.e. no events greater than those classified as trace (i.e. < 2mm)) prior to sampling for greater than 5 days. In the Intact site, stormflow samples represented a greater riparian influence than during baseflow which is dominated by lake processes. Samples in May 2012 represented freshet, i.e. the influx of snowmelt during spring thaw.

Stream water samples were collected in acid-washed Nalgene bottles. Temperature, pH and conductivity were measured immediately after sampling on a subsample using a handheld pH and conductivity meter (Oakton). Samples were kept on ice until vacuum filtration (Advantec, 0.45 micrometer pore size, mixed cellulose ester filter) in the lab within 24 hours of collection. Filtrates were analyzed for optical properties using a scanning UV-Vis spectrophotometer (quartz cuvettes, 10mm path length, Thermo Scientific Genysys 840-208100) within 24 hours, against blanks, with

remainder frozen until further analysis.

5.2.6 Extracted dissolved organic carbon and stream water chemistry

Extracted dissolved organic carbon (DOC) is used to quantify dissolved organic matter and was measured in extracts and stream water samples (Shimadzu TOC 5050 Analyser, KHP standard, high temperature combustion). The UV-Vis was measured at 254 nm (Thermo Scientific GENESYS 10S UV-Vis scanning spectrophotometer; quartz cuvette) and converted from an absorbance per cm (A) to decadal absorptivity using the decadal absorptivity coefficient 2.303, with a path length of 1 cm as defined by l , as follows in Eq. 5.1:

$$UV - Vis = \frac{2.303 * A}{l} \quad (5.1)$$

Specific UV-Vis absorbance (i.e. $SUVA_{254}$) was calculated from the ratio of UV-Vis absorbance at 254 nm to DOC concentration (Weishaar et al., 2003) in order to assess the aromatic character of dissolved organic matter (i.e. chromophoric DOM, or CDOM) following Eq. 5.2:

$$SUVA_{254} = \frac{UV - Vis_{254}}{DOC} \quad (5.2)$$

$SUVA_{254}$ was corrected for the estimated contribution to UV-Vis from dissolved Fe (III) following Poulin et al. (2014), using an extinction coefficient of 0.0687 (for 254 nm). This correction for soluble Fe interference was performed for all samples (experimental and field samples).

Extracted dissolved organic matter (DOM_{ex}) and stream water samples were analyzed for total dissolved Fe (Perkin Elmer AAnalyst 300 flame atomic absorption spectroscopy). Soluble Fe was assumed to be Fe(II) at these pH levels (4-5), although some Fe(III) could have been present in ionic form, associated with colloidal organo-metal complexes (i.e. with DOC).

The acidity (pH_{H_2O}) of soil extracts was measured (<2 mm fraction; 1:2 soil:water ratio) using a glass electrode (Oakton). The pH range of extracts was typically 4-5: in this range, the acidity would have a negligible effect on $SUVA_{254}$ (Pace et al., 2012).

Stream samples and selective dissolution extracts were analyzed for $\delta^{13}C$ -DOM via a wet chemical oxidation method (permanganate oxidation) for DOC interfaced

with a stable isotope ratio mass spectrophotometer (ConFlo II to a DeltaVPlus I) using a OI Analytical Aurora 1030W TOC/TIC analyzer, carried out at Memorial University, St. Johns, Newfoundland). Isotopic standards were prepared in the same extraction solutions as the selective dissolution extracts to ensure that interferences were properly accounted for.

Molar DOC:Fe was calculated for experimental samples and for stream water samples by dividing the molar mass of C and Fe. In this experiment, we calculate the net changes in concentrations of DOC, Fe, and SUVA₂₅₄ from initial and final measurements and will only consider the dissolved phase of DOC:Fe interactions. The presence of particulate DOM and Fe phases will be noted.

5.2.7 Carbon and $\delta^{13}\text{C}$ of soil samples

Post-extraction soils were retained for solids analysis and were allowed to dry at room temperature over several weeks prior to homogenization through crushing with a mortar and pestle, sieving to 2 mm and pulverisation on a roller mill. These solids were analyzed for the %C, and the stable isotope ratio of carbon ($\delta^{13}\text{C}$) of the soil solids (post-extraction solids and bulk soil) relative to PeeDee Belemnite was measured using elemental analysis (Eurovector EA-3028-HT, Manchester, UK) in line with a continuous flow isotope ratio mass spectrometer (Nu Horizon Isotope Ratio Mass Spectrometer, Wrexham, UK; and GV Isoprime Mass Spectrometer, Manchester, UK, carried out at St. Francis Xavier University).

5.2.8 Statistical analyses

In order to determine whether redox state and temperature had an impact on DOC and Fe release from mineral soils, the significance of differences in means of DOC, Fe, molar DOC:Fe, and SUVA₂₅₄ of experimental soil extracts were compared between oxic and anoxic soil treatments at 5 and 15 °C for each fixed depth soil increment using ANOVA ($p < 0.05$).

The stream and soil extract molar DOC:Fe from controlled manipulations and from monitoring data at two field sites was compared using Q-Q plots. Q-Q plots present the quantiles associated with the distributions of two datasets to assess whether these populations are from the same distribution. This then indicates the

level of similarity of the distribution of the data when comparing datasets with unequal variance, and the datapoints on a Q-Q plot follow a straight line if the two distributions are from the same populations. Statistics were carried out using Excel (Excel for Mac 2011), Sigmaplot (ver. 14) and R (ver. 3.1.0).

5.3 Results

5.3.1 Initial soil elemental, isotopic and optical characteristics through depth

Chemical properties of soils prior to treatment varied through depth for the fixed increment composite samples. Soil carbon content, C:N and DOC concentration declined through depth, while soil pH and bulk density increased, and bulk soil became more enriched in ^{13}C , resulting in a higher $\delta^{13}\text{C}$ signature (Table 5.1). Generally, DOC_{ex} from shallower horizons (0-10 and 10-20 cm depth increments) exhibited higher SUVA_{254} than deepest horizons; in the subsoil horizons (20-35 cm and 35-50 cm), DOC_{ex} had lower SUVA_{254} (Figure 5.3, e-f). These differences comparing increments were significant by depth ($p < 0.05$).

5.3.2 Changes in DOC_{ex} following anoxic and oxic incubations

In the 0-10 cm increment, there was a net release of DOC_{ex} under both oxic and anoxic incubation compared to initial. Higher DOC was measured in shallow soil extracts (i.e. 0-10 cm increment; $p < 0.05$) from samples incubated under anoxic compared to oxic conditions. Approximately 24-350% higher DOC concentrations was measured in leachates compared to initial conditions (in Table 5.1) after 1 and 4 months (Tables 5.2 and 5.3). The difference in DOC and Fe between anoxic and oxic incubations was greater after the longer 4 month incubation (Figure 5.3 a-b). Soils under anoxic conditions resulted in the net release of 55% and 262% more DOC after 1 month (at 5 and 15 °C, respectively) compared to oxic conditions (Figure 5.3). Seventy-seven% and 384% more C was extracted at 5 and 15 °C, respectively, after 4 months of anoxic compared to oxic conditions. DOC concentrations for soils incubated at 15 °C were significantly higher in the 0-10 cm increment samples compared to 5 °C ($p < 0.05$). Below 10 cm, lower net DOC (5-31% lower than initial) was extracted from soils

incubated under oxic and anoxic conditions at 5 and 15 °C compared to soils before the incubation (Figure 5.3).

The optical properties of DOC_{ex} were affected by redox state, temperature, and incubation time. Generally, higher temperatures and a longer period of anoxia (1 vs. 4 months) resulted in higher SUVA_{254} for CDOM extracted from soils above 10 cm (Figure 5.3 e-f). Interactive effects of temperature and redox state on CDOM were significant (ANOVA, $p > 0.05$) for 0-10 cm after 1 month and 4 months, and for all depths to 35 cm after 4 months (Figure 5.3 e-f). The largest increases in CDOM compared to initial soil extractions were observed under anoxic conditions at the higher incubation temperature (15 °C), and after a longer incubation time 4 months (Figure 5.3 b,d and Table 5.1 and 5.3). The DOC_{ex} from soils incubated under anoxic conditions generally had a higher mean SUVA_{254} than that from soils incubated under oxic conditions (Figure 5.3 a,c,e and Table 5.3). Differences in SUVA_{254} of DOC_{ex} between anoxic and oxic samples were significant at $p < 0.001$ for all depth increments after 1 month, but SUVA_{254} for oxic and anoxic incubations were not significantly different after 4 months.

Table 5.1: Initial soil physicochemical characteristics of soil sampled from Mooseland, Nova Scotia, Canada through depth in increments. Note that soils were sampled from 9 pits at one forest site (Mature) and bulked to make a composite. Reported numbers are means of several analytical replicates ($n \geq 3$). Numbers in brackets are ± 1 standard deviation. The influence of Fe on UV-Vis absorption was corrected (Poulin et al., 2014).

Depth Increment (cm)	Soil pH (H ₂ O)	Bulk Density (mg g ⁻¹)	Soil C (mg g ⁻¹)	C:N	$\delta^{13}\text{C}$ Bulk soil ‰	DOC (DI) (mg C g soil ⁻¹)	UV-Vis ₂₅₄ DOM _{ex} (cm ⁻¹)	SUVA ₂₅₄ DOM _{ex} (L cm ⁻¹ mg C ⁻¹)	Soluble Fe (mg L ⁻¹)	Molar DOC:Fe
0-10	4.29 (0.01)	0.72 (0.05)	54.11 (24.21)	26.1 (2.3)	-26.90 (0.17)	0.0599 (0.0061)	0.613 (0.088)	2.81 (0.24)	0.77 (0.16)	121.72 (12.84)
10-20	4.41 (0.01)	0.67 (0.04)	52.79 (19.93)	23.2 (1.6)	-26.65 (0.22)	0.0357 (0.0017)	0.124 (0.015)	0.97 (0.08)	0.13 (0.01)	420.46 (39.94)
20-35	4.56 (0.03)	0.74 (0.01)	36.24 (21.46)	20.8 (1.4)	-25.46 (0.06)	0.0242 (0.0008)	0.031 (0.002)	0.34 (0.04)	0.05 (0.03)	934.01 (664.83)
35-50	4.76 (0.03)	0.94 (0.01)	29.72 (10.17)	22.1 (1.9)	-25.32 (0.05)	0.0249 (0.0007)	0.025 (0.006)	0.29 (0.08)	0.02 (0.01)	2361.69 (1259.0)

5.3.3 Soluble Fe in soil extracts

The highest soluble Fe was measured in extracts from the shallowest (0-10 cm) increment and varied with redox conditions and temperature. Regardless of incubation length, soil increments released Fe in amounts larger than initially extracted except for the 1 and 4 month oxic incubation of 0-10 cm and 10-20 cm increments at 5 and 15 °C. Soluble Fe concentrations in soil increments incubated under anoxia were an order of magnitude higher than those incubated under oxic conditions ($p < 0.05$); (Table 5.2). Under anoxic conditions, an increase in incubation temperature from 5 to 15 °C generally resulted in a further increase in soluble Fe compared to oxic conditions (Figure 5.3 c-d and Table 5.2).

5.3.4 The ratio of DOC to Fe in soil extracts

Soluble Fe and DOC through depth were linearly related in all samples, at both 5 and 15°C, and at 1 and 4 months (Figure 5.4), such that an increase in Fe was related to an increase in DOC. Overall molar DOC:Fe ratios were lower under anoxic compared to oxic conditions: the mean molar DOC:Fe ratio was 179 for oxic samples, and mean molar DOC:Fe ratio was 50 for anoxic samples (Figure 5.3 and Table 5.2 and 5.3). Mean molar DOC:Fe values under oxic vs anoxic conditions were different ($p < 0.05$) at 1 and 4 months for 0-10 cm and 10-20 cm, and for all depth increments following 4 months incubation (Figure 5.5) (at $p < 0.05$). Molar DOC:Fe ratios of extracts generally decreased following incubation for soil horizons (Figure 5.3), and increased through depth (Figure 5.7b).

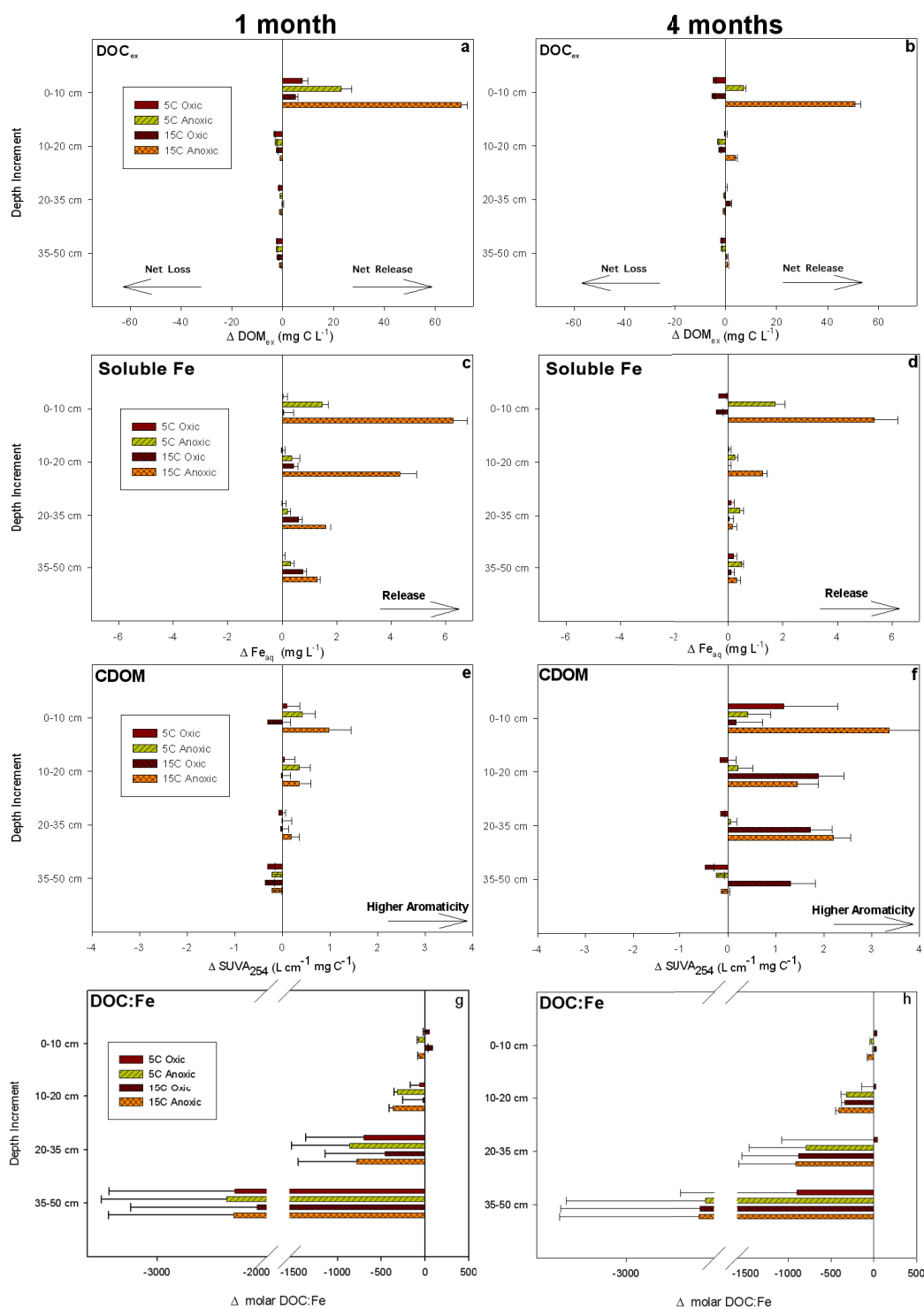


Figure 5.3: Results of chemical analysis of extracts following incubation of composite field moist mineral soil sampled through depth (0-10, 10-20, 20-35 and 35-50 cm) incubated under oxic or anoxic conditions for 1 (a,c,e,g) or 4 (b,d,f,h) months at 5 and 15 °C. Data presented are net shifts in DOC_{ex} , Fe, CDOM SUVA_{254} and molar DOC:Fe for final extracts compared to Initial extracts. Error bars indicate 1 SD.

Table 5.2: Results from chemical analysis of soil extracts following oxic and anoxic incubations for 1 month, and 4 months, at 5 °C. Numbers in brackets are 1 SD and for all reported means, n=3. Note: b.d. indicates below detection level of instrument.

Treatment	Increment (cm)	pH	DOC (mg C g soil ⁻¹)	UV-Vis ₂₅₄ (cm ⁻¹)	SUVA ₂₅₄ (L cm ⁻¹ mg C ⁻¹)	Soluble Fe (mg L ⁻¹)	Molar DOC:Fe
Oxic 1 month	0-10	4.58 (0.03)	0.5539 (0.0015)	0.690 (0.132)	2.98 (0.07)	0.80 (0.02)	160.4 (8.5)
	10-20	4.29 (0.03)	0.0167 (0.0008)	0.094 (0.012)	1.08 (0.06)	0.10 (0.04)	446.5 (166.2)
	20-35	4.36 (0.01)	0.0124 ()	0.003 (0.0007)	0.31 (0.04)	0.05 (0.03)	978.6 (910.1)
	35-50	4.63 (0.03)	0.0116 (0.0004)	b.d.	b.d.	0.02 (0.01)	890.3 (80.9)
Oxic 4 months	0-10	4.47 (0.16)	0.0302 (0.0060)	0.370 (0.045)	2.05 (0.20)	0.43 (0.11)	173.5 (67.8)
	10-20	4.15 (0.02)	0.0224 (0.0084)	0.093 (0.004)	0.88 (0.28)	0.15 (0.02)	355.7 (97.4)
	20-35	4.33 (0.01)	0.0164 (0.0019)	0.019 (0.001)	0.24 (0.01)	0.16 (0.01)	235.2 (16.0)
	35-50	4.68 (0.03)	0.0128 (0.0013)	b.d.	b.d.	0.22 (0.03)	140.2 (21.1)
Anoxic 1 month	0-10	4.48 (0.01)	0.0116 (0.0004)	3.617 (0.510)	3.15 (0.04)	2.24 (0.17)	89.2 (1.3)
	10-20	4.43 (0)	0.0178 (0.69)	0.153 (0.0014)	1.04 (0.22)	0.49 (0.23)	100.1 (48.1)
	20-35	4.57 (0.05)	0.0142 (0.0004)	0.038 (0.002)	0.16 (0.02)	0.24 (0.02)	139.1 (11.2)
	35-50	5.00 (0.04)	0.0113 (0.0016)	0.006 (0.004)	0.09 (0.06)	0.32 (0.04)	82.7 (21.4)
Anoxic 4 months	0-10	4.16 (0.01)	0.0536 (0.0024)	0.939 (0.157)	2.87 (0.43)	2.50 (0.22)	50.3 (4.9)
	10-20	4.24 (0.02)	0.0173 (0.0013)	0.110 (0.026)	0.97 (0.22)	0.38 (0.02)	105.0 (1.3)
	20-35	4.64 (0.03)	0.0146 (0.0014)	0.032 (0.002)	0.45 (0.03)	0.48 (0.03)	71.7 (8.1)
	35-50	4.88 (0.03)	0.0131 (0.0012)	0.005 (0.001)	0.07 (0.004)	0.51 (0.01)	59.2 (4.6)

Table 5.3: Results from chemical analysis of soil extracts following Oxidic and Anoxic incubations for 1 month, and 4 months, at 15 °C. Numbers in brackets are 1 SD and for all reported means, n=3. Note: b.d. indicates below detection level of instrument.

Treatment	Increment (cm)	pH	DOC (mg C g soil ⁻¹)	UV-Vis ₂₅₄ (cm ⁻¹)	SUVA ₂₅₄ (L cm ⁻¹ mg C ⁻¹)	Soluble Fe (mg L ⁻¹)	Molar DOC:Fe
Oxic 1 month	0-10	4.52 (0.06)	0.0497 (0.0024)	0.690 (0.132)	2.55 (0.36)	0.82 (0.26)	149.8 (39.4)
	10-20	4.26 (0.07)	0.0186 (0.0020)	0.094 (0.012)	0.63 (0.02)	0.54 (0.07)	80.4 (4.4)
	20-35	4.42 (0.10)	0.0153 (0.0028)	0.026 (0.007)	0.34 (0.07)	0.65 (0.03)	54.9 (11.3)
	35-50	4.59 (0.02)	0.0119 (0.0020)	b.d.	b.d.	0.77 (0.04)	36.2 (8.2)
Oxic 4 months	0-10	3.99 (0.01)	0.0291 (0.0042)	0.471 (0.111)	3.09 (0.67)	0.33 (0.03)	205.7 (48.2)
	10-20	4.08 (0.02)	0.0186 (0.0047)	0.205 (0.106)	2.00 (0.70)	0.12 (0.04)	396.9 (97.4)
	20-35	4.30 (0.01)	0.0200 (0.0006)	0.160 (0.073)	1.62 (0.78)	0.10 (0.03)	472.1 (126.6)
	35-50	4.51 (0.02)	0.0175 (0.0019)	0.141 (0.060)	1.53 (0.073)	0.12 (0.03)	365.4 (145.8)
Anoxic 1 month	0-10	4.53 (0.09)	0.1801 (0.0346)	3.617 (0.510)	3.53 (0.35)	7.04 (0.17)	59.2 (5.8)
	10-20	4.38 (0.03)	0.0218 (0.0024)	0.153 (0.019)	1.04 (0.22)	4.45 (0.23)	11.7 (48.1)
	20-35	4.54 (0.03)	0.0135 (0.0020)	0.038 (0.002)	0.57 (0.04)	1.66 (0.05)	18.9 (2.4)
	35-50	4.57 (0.02)	0.0140 (0.0015)	0.006 (0.004)	0.08 (0.06)	1.30 (0.02)	25.0 (2.6)
Anoxic 4 months	0-10	4.08 (0.10)	0.141 (0.0251)	4.439 (0.094)	5.87 (1.22)	6.14 (2.06)	56.0 (11.8)
	10-20	4.23 (0.10)	0.0316 (0.0027)	0.391 (0.044)	1.92 (0.41)	1.39 (0.07)	53.0 (6.4)
	20-35	4.38 (0.03)	0.0142 (0.0018)	0.146 (0.025)	1.49 (1.22)	0.22 (0.03)	150.3 (9.7)
	35-50	5.35 (0.25)	0.0181 (0.0006)	0.016 (0.001)	0.17 (0.02)	0.33 (0.05)	130.9 (19.5)

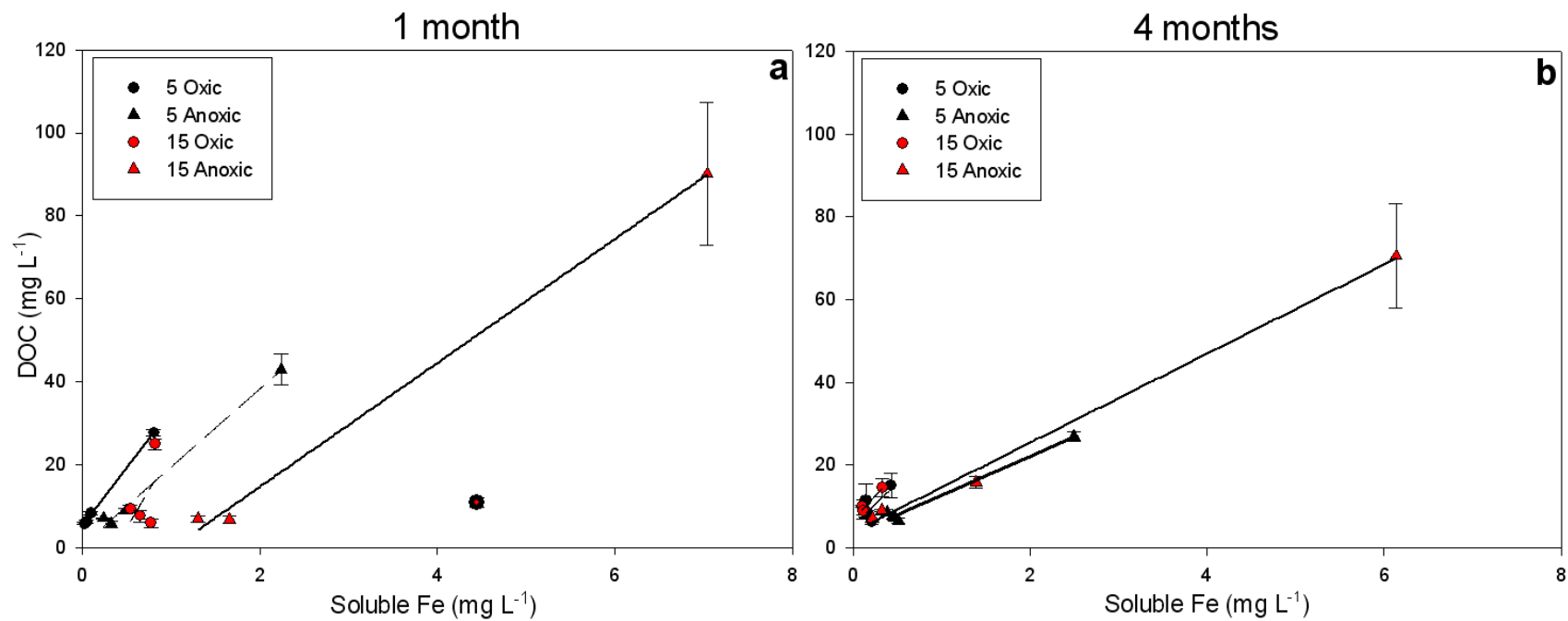


Figure 5.4: Relationships between the DOC and soluble Fe, comparing the differences in concentration between oxic (circles) and anoxic (triangles) conditions at 5 (black) and 15 (red) °C for samples through depth after a) 1 month and b) 4 months.

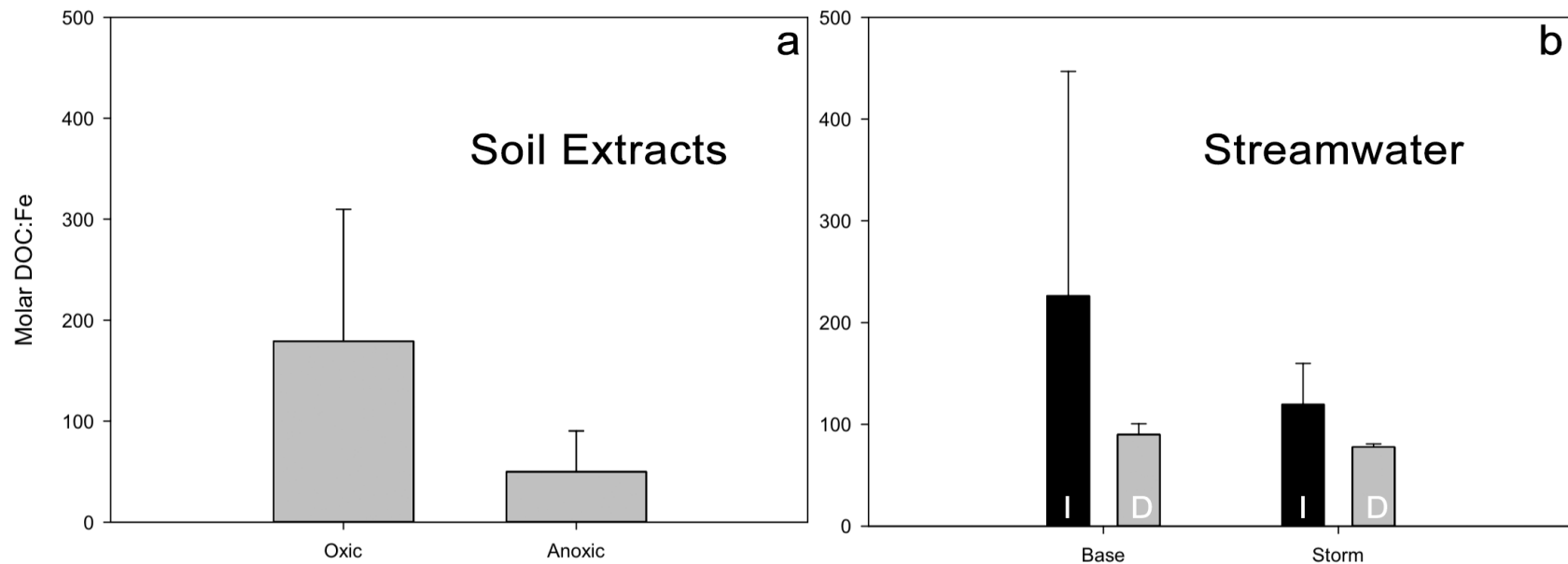


Figure 5.5: Plots of mean molar DOC:Fe ratio for a) Soil extracts from laboratory experiment under oxic and anoxic conditions for the shallow soil horizon (0-10 cm) samples at 5 and 15 °C for 1 and 4 months, where molar DOC:Fe values are significantly different $p < 0.05$ for these two treatment groups ; b) Field stream samples from Intact (black bars) and Disturbed (grey bars) watersheds at baseflow and after storm events (refer to Table 5.4 for the dates). The difference between molar DOC:Fe of Intact and Disturbed is significantly different for both base and storm at $p < 0.05$. Error bars are $1 \pm \text{SD}$.

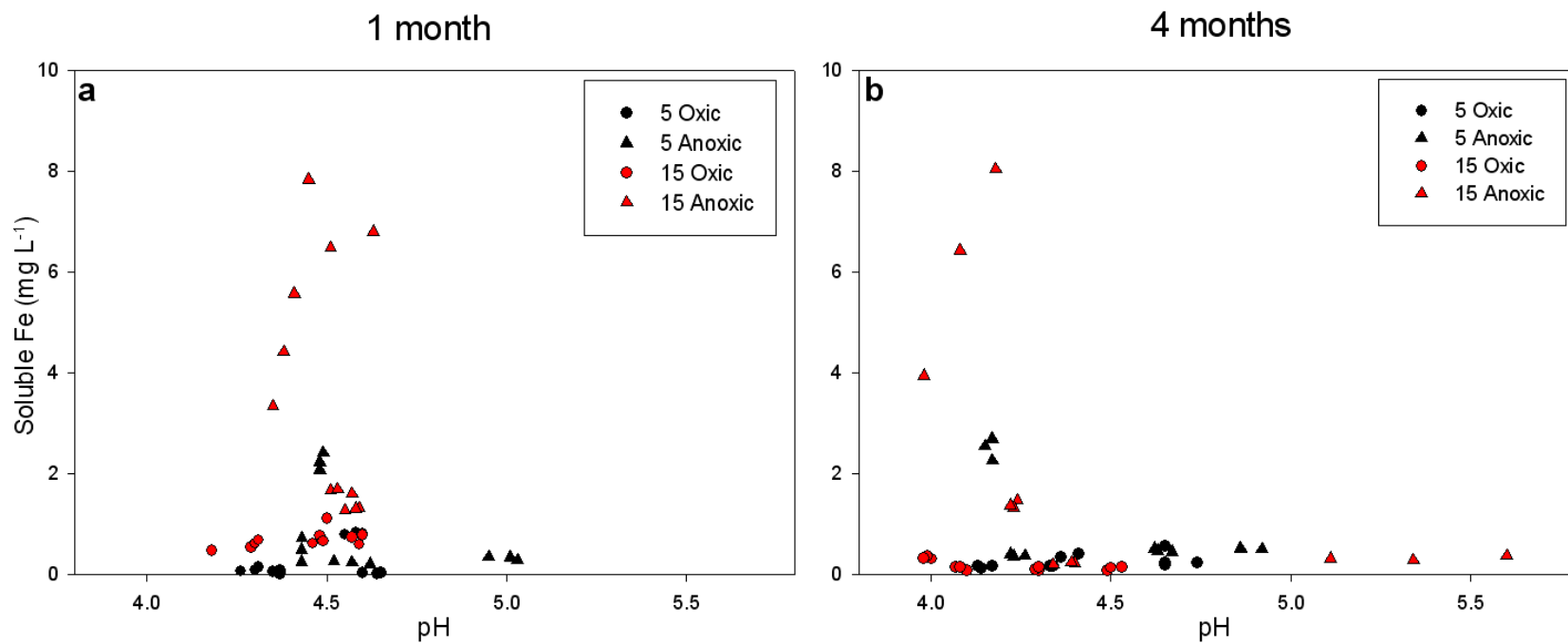


Figure 5.6: Comparing soluble Fe and pH, after 1 month (left) and 4 months (right) comparing the differences in concentration between oxic (circles) and anoxic (triangles) conditions at 5 (black) and 15 (red) °C for samples through depth.

5.3.5 pH changes following incubation

Solutions extracted from soils incubated under oxic conditions had a narrow pH range (4.2-5.0) through depth that decreased slightly (i.e. became more acidic) over time for most increments (Tables 5.2 and 5.3). Generally, the pH of the soil extracts were similar when comparing anoxic soils to oxic soils at both temperatures (no significant differences at $p < 0.05$) (Figure 5.6). One notable exception was the observation that the range of pH values increased over time (i.e. pH at 4 months $>$ 1 month) for the deepest (35-50 cm) increment, where the mean pH values increased from 4.8 to 5.3 following anoxic incubation for 4 months (difference significant at $p < 0.05$) (Figure 5.6). There was no clear relationship between Fe and pH (Figure 5.6).

5.3.6 Elemental and stable isotopic analysis of incubated soil solids

While elemental analysis of incubated soil solids after extraction showed no significant change in elemental C content from initial conditions (Table 5.1) after 4 months ($p < 0.05$), isotopic analysis of post-extraction solids revealed significant differences (at $p < 0.05$) as a result of incubation (Table 5.2 and Table 5.3). The $\delta^{13}\text{C}$ of soil solids ranged from approx. -27‰ at the surface to -25.5‰ at 35-50 cm depth (Figure 5.7). After 4 months of incubation under both oxic and anoxic treatments, soil solids were generally more enriched in ^{13}C compared to Initial bulk soil (Figure 5.7). The $\delta^{13}\text{C}$ of oxic treatment solids were not different from the stable isotope ratio of the initial bulk solids in 0-10 cm increment (at $p < 0.05$), whereas the anoxic treatment was enriched by approx. 1‰ compared to initial bulk solids; however, this difference between oxic and anoxic treatments was not present in the deepest increment, where soil solids were approximately 1.5‰ more enriched for both oxic and anoxic soils compared to initial bulk soil (Figure 5.7). Differences were significant at $p < 0.05$.

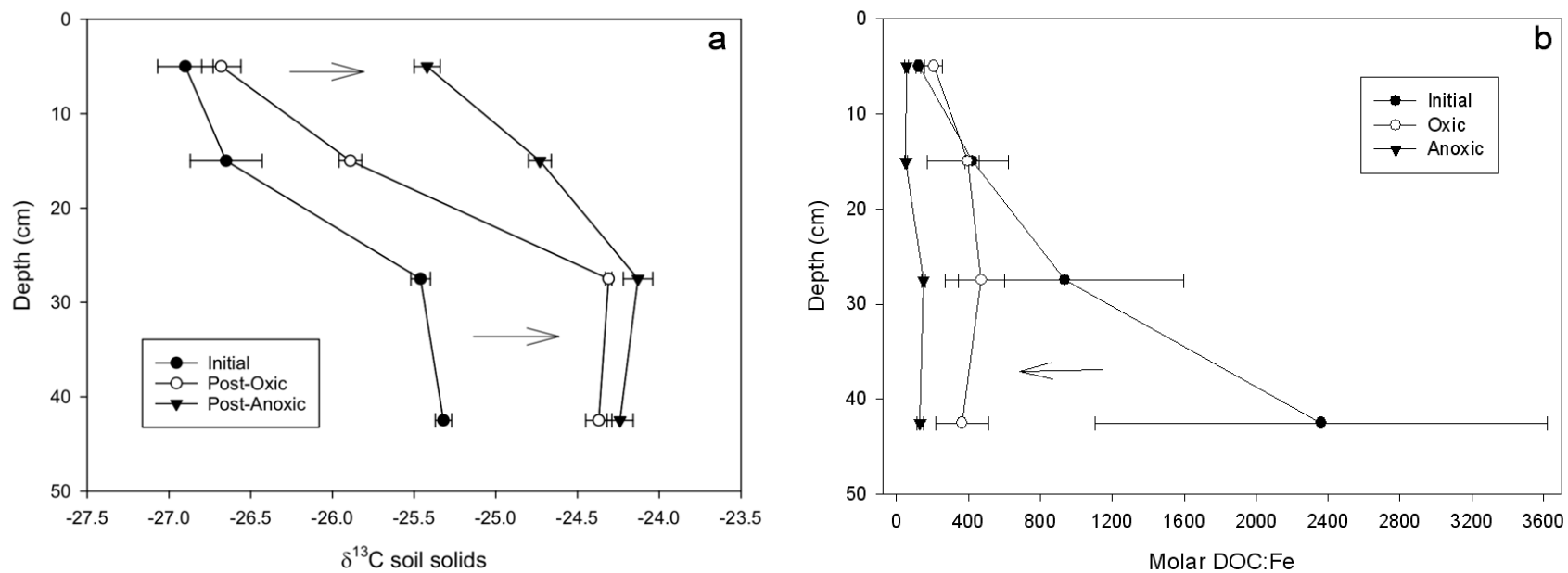


Figure 5.7: Variation in a) mean stable isotope ratio of C ($\delta^{13}\text{C}$) and b) molar DOC:Fe through depth for soil solids from increments before (Initial) and after 4 month incubation under oxic and anoxic conditions at 15 °C. Arrows indicate the notable enrichment in ^{13}C compared to initial conditions that has occurred for all anoxic incubation samples, and for oxic samples below 20 cm.

5.3.7 Seasonal trends in rainfall and stream water chemistry

Stormflow stream samples were sampled after rain events in August and October (low antecedent soil moisture conditions), and November 2011 (high antecedent soil moisture), and May 2012, with monthly rainfall totals at a nearby Environment Canada weather station (Halifax Stanfield Airport) of 64.4 mm, 104.4 mm, and 106.4 mm, respectively. In other months, there were no rainfall events (more than trace) for > 5 days before sampling, representing baseflow conditions.

At the Intact site, the concentration of stream DOC (seasonal mean = 2.50 mg L⁻¹) and soluble Fe (seasonal mean = 0.10 mg L⁻¹) were generally lower on each sampling date compared to those for the Disturbed site (6.05 mg L⁻¹ and 0.32 mg L⁻¹, for DOC and Fe, respectively), although the mean seasonal DOC and Fe were not significantly different between Intact and Disturbed sites at $p < 0.05$ (Table 5.4). Mean seasonal pH was higher at the Intact site (range 4.8-7.0) than at the Disturbed site (4.12-6.8), and was higher at each sampling date except for September (Table 5.4); however, the difference in mean seasonal pH of stream water at the sites was not significant ($p < 0.05$). DOC, Fe, and pH were responsive to storm events (stormflow > baseflow) in August and October, November, and May, and were always higher in the Disturbed system compared to the Intact system and the reference lake (Table 5.4).

Mean storm- and baseflow molar DOC:Fe at the Intact site were different ($p < 0.05$), with high values (mean = 226) during baseflow and a reduced value at stormflow (mean = 119) (Figure 5.5). Molar DOC:Fe at the Disturbed site was generally lower than that at the Intact site and had a similar value at both base- and stormflow (90 compared to 77, respectively) (Table 5.3).

Table 5.4: Stream chemical data for Disturbed and Intact watersheds at Abraham's Lake, Nova Scotia, Canada, sampled monthly during ice-free period (July-May 2011-2012).

Site	Month * = stormflow + = freshet	pH	$\delta^{13}\text{C-DOC}$ ‰	DOC (mg L ⁻¹)	UV-Vis ₂₅₄ (cm ⁻¹)	SUVA ₂₅₄ (L cm ⁻¹ mg C ⁻¹)	Soluble Fe (mg L ⁻¹)	Molar DOC:Fe
Disturbed	July	5.80	-26.55	2.99	1.73	5.79	0.29	48.36
	Aug *	4.92	-27.10	8.51	0.731	8.60	0.11	362.23
	Sept	5.42	-27.20	3.41	0.219	6.41	0.51	31.29
	Oct *	4.12	-27.30	9.29	0.837	9.01	0.09	464.31
	Nov *	4.48	-27.30	5.65	0.554	9.81	0.57	46.48
	May *+	4.84	-27.70	10.19	0.356	4.91	0.37	127.37
Intact	July	6.00	-25.29	1.44	0.064	4.44	0.01	670.28
	Aug *	5.90	-26.88	4.89	0.340	7.12	0.20	112.46
	Sept	5.66	-27.12	1.81	0.107	5.91	0.01	840.46
	Oct *	4.76	-26.62	3.21	0.246	7.65	0.16	95.81
	Nov *	4.81	-26.59	2.58	0.190	7.35	0.12	103.60
	May *+	5.23	-26.65	4.80	0.132	2.90	0.12	183.15
Abe's Lake	Sept	6.00	-27.12	2.92	0.070	2.40	0.17	57.01
	Nov *	4.94	n/a	2.83	0.155	5.48	0.08	136.58
	May *+	5.16	-27.30	2.64	0.082	3.11	0.03	559.60

SUVA₂₅₄ was highest at the Disturbed site on each sampling date (mean SUVA₂₅₄ = 7.42), compared to the Intact site (mean SUVA₂₅₄ = 5.90) and samples from Abraham's Lake (mean SUVA₂₅₄ = 3.66) (but were not different at $p < 0.01$) (Table 5.4), and the highest values in each dataset were on stormflow sampling dates. DOC was consistently more depleted in ¹³C at the Disturbed site compared to the Intact site, with a mean $\delta^{13}\text{C}$ from July to May of -27.20 ‰, compared to a mean of -26.53 ‰ at the Intact site stream (Table 5.4, which were different at $p < 0.05$). Q-Q plots of Molar DOC:Fe data for storm- and baseflow revealed that the data distributions were not from the same populations, and can be interpreted as evidence of their distinct chemistry (Figure 5.8).

Fe-corrected SUVA₂₅₄ and the $\delta^{13}\text{C}$ of DOC in stream water across the July 2011-May 2012 season at the Intact and Disturbed catchments of the Abraham's Lake site are negatively correlated (Figure 5.9: baseflow: $r^2 = 0.501$ and stormflow: $r^2 = 0.924$), and the relationships were different for storm- and baseflow. For both catchment streams, as the $\delta^{13}\text{C}$ DOC increased, SUVA₂₅₄ decreased. Higher SUVA₂₅₄ relative to $\delta^{13}\text{C}$ of DOC were observed during periods of higher flow after rain events, and their relationship was weaker, leading to higher variance for the stormflow data (Figure 5.9).

5.4 Discussion

5.4.1 Significant release of DOC and its coupling with Fe primarily occurred in surface mineral soils following anoxic conditions

In general, podzolic soils contain significant quantities of C held in organo-metal complexes (Sanborn et al., 2008) which could be vulnerable to reductive dissolution and release as DOM and Fe. Observations from previous studies conducted in mineral soils of this region (Diochon and Kellman, 2009) have documented that the organo-mineral pool is vulnerable to loss of stored C in the decades following harvesting. The results of Chapter 2 (Gabriel et al., 2018) also confirm that organo-metal complexes dominate the mineral-associated C pool, and that these pools may release C in the decades following harvesting disturbance.

In this study, the release of DOC under anoxic conditions was observed to be

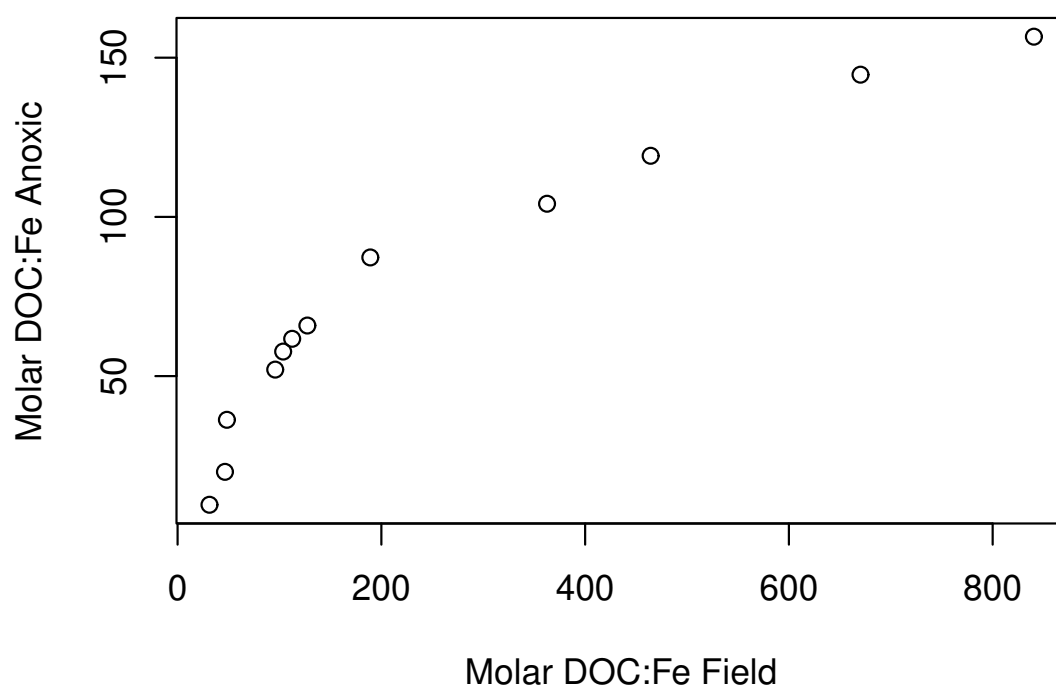


Figure 5.8: Q-Q plots of the data distribution comparing quantiles of molar DOC:Fe for extracts from anoxic incubation (combining data from 1 and 4 months and at 5 and 15 °C) and stream data at Abraham's Lake, Nova Scotia, Canada.

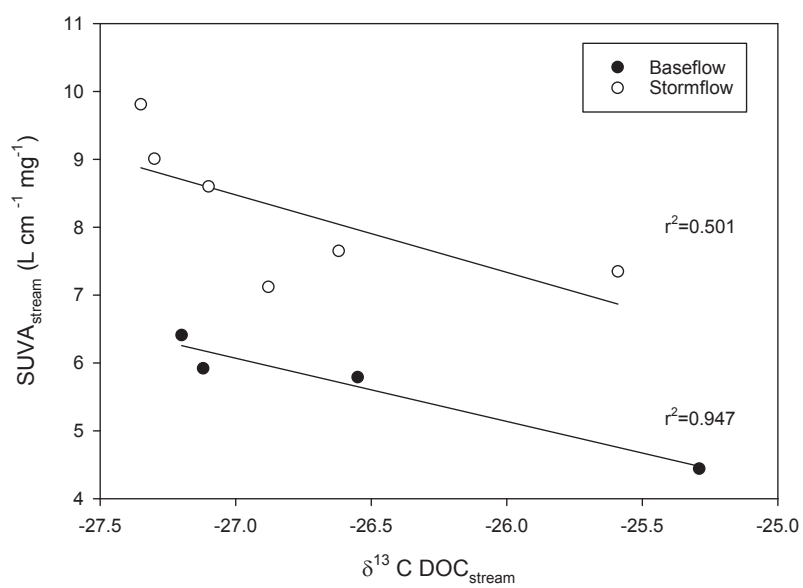


Figure 5.9: Stable isotope ratio ($\delta^{13}\text{C}$, ‰) of plotted against SUVA_{254} for stream DOC in disturbed and intact sites for baseflow (slope = -1.1) and stormflow (slope = -1.3).

significant in the 0-10 cm mineral soil increment (Figure 5.3; Table 5.2 and 5.3). The release of DOC was coupled to Fe, and was observed to increase with the length of time spent under anoxic conditions and with elevated temperatures (Figure 5.3; Table 5.2 and 5.3). These patterns are consistent with the reductive dissolution of redox-sensitive minerals containing Fe, and the subsequent release of the associated organic matter from mineral soils to the surrounding soil solution. The observed patterns are in accordance with results from other recent studies that examined the impacts of soil flooding on the release of DOM and Fe from soils (Hall et al., 2015; McNicol and Silver, 2014; Pan et al., 2016).

Further evidence to support the role of anoxic conditions and elevated temperatures in releasing DOC and Fe from shallow mineral soils can be drawn from the changes in extracted DOC chemistry observed following incubations. In the surface layer (0-10 cm), losses of ^{13}C -depleted aromatic DOC were facilitated by anoxia. These observations are in accordance with results from other studies that have determined that aromatic soil compounds have been found to be mobilized under flooded conditions (Chow et al., 2006; Christ and David, 1996; De-Campos et al., 2009; Kim et al., 2014). The preferential decomposition of labile non-aromatic DOC compounds may also leave aromatic compounds to constitute a larger proportion of the soil solution. Note that we assume that for Fe correction of SUVA_{254} , all Fe was present as Fe(III). Correction of SUVA by factoring in Fe(II) species which do not interfere with SUVA at 254 nm would result in an overestimation of the influence of Fe. We acknowledge that samples may have been anoxic when measured, therefore leading to an underestimation of SUVA_{254} .

This release of ^{13}C -depleted aromatic DOC from surface soils is consistent with ^{13}C enrichment of soils following anoxic conditions in the 0-10 cm increment. Isotopic analysis of post-extraction soil solids revealed an enhanced ^{13}C -enrichment following anoxia compared to oxic conditions, more prominent in soils incubated at higher temperatures (Figure 5.7 and Table 5.2).

DOC-Fe coupling in surface soils likely means anoxic conditions in surface soil layers is a determinant in where soil C mobilization occurs. For example, perhaps lower SOC stocks through depth following land-use disturbance is related to reduced

surface C sources mobilized to deeper soil. Hillslope hydrology could dictate the consequences of these soil C losses, mobilized to deeper horizons or laterally to streams.

5.4.2 Loss of SOC in deeper horizons with temperature and redox changes are more decoupled from mobilization of Fe

In contrast to the shallow (0-10 cm) mineral soil, little net change of DOC_{ex} was observed below 10 cm depth following anoxia and elevated temperatures in this study (Fig 5.5; Tables 5.2 and 5.3). This was unexpected given the previous observations of mineral-associated C loss in these soils which primarily occurred in deeper soil layers (Gabriel et al., 2018; Prest et al., 2014). Reductive dissolution may not always proceed in mineral soils through depth incubated under anoxic conditions (Angelico et al., 2014; Wagai and Mayer, 2007). The high quantity of mineral-bound organic matter in podzolic B_f (i.e. spodic) horizons may slow the reductive dissolution of Fe oxides (Eusterhues et al., 2014). However, a higher net release of soluble Fe was measured in all extracts through depth, suggesting reductive dissolution of Fe minerals in soil through depth below 10 cm may have still occurred. For instance, molar DOC:Fe ratios were distinctly different in deeper soil horizons compared to the 0-10 cm layer (Gabriel et al., 2018 and Figure 5.7b), driven by shifts in Fe. Thus, in contrast to the 0-10 cm increment, there is less coupling between C and Fe deeper in the soil profile.

While shifts in C cycling under different redox conditions were not detectable by assessing the net change in extractable DOC concentrations directly, analysis of DOC chemistry, including SUVA_{254} and pH of soil extracts, and $\delta^{13}\text{C}$ of remaining soil solids suggest that C cycling was altered in these deeper soils following incubation. An increase in the aromatic character of DOC extracted following incubation was observed in deep soils for both oxic and anoxic conditions, exacerbated over time and at higher temperatures (Figure 4.7). An increase in the aromatic character of DOC extracted from deeper mineral soils following incubation has also been observed by others under both oxic (Cleveland et al., 2004; Malik et al., 2013) and anoxic conditions (Hanke et al., 2014). In addition, higher acidity (lower pH) generally observed in soil extracts incubated under anoxic compared to oxic soil conditions was consistent with observations of the connection between anoxic conditions and changes

in pH documented in previous studies (Grybos et al., 2009; Herndon et al., 2015). Fe(II) oxidation coupled to DOC decomposition drove a decrease in solution pH in flooded soils (Hall and Silver, 2013). This decrease in pH could be a consequence of increased microbial decomposition leading to higher production of carbonic acid.

The increase in $\delta^{13}\text{C}$ of post-extraction soil solids in deeper increments is further evidence of changes to C cycling that resulted in the loss of ^{13}C -depleted compounds from soils after 4 months for both oxic and anoxic conditions (Figure 5.7). This change in cycling is important to note as it likely demonstrates that although DOC_{ex} was low, C still has the potential to be lost from soils through depth. Measurement of the rates of the production of gases (CO_2 , methane and nitrous oxide) from these samples could likely confirm these changes to C cycling. This evidence suggests that in deep soils, regardless of the redox conditions, shifts in C cycling occurred following incubation, more prominent under warmer conditions. It may be that several mechanisms of loss are at play, some of which are not redox-dependent (e.g. temperature-supported microbial decomposition).

Several processes might explain the observed pattern of an increase in soil solids $\delta^{13}\text{C}$ through depth following the 4 month incubation. First of all, this observation is in accordance of the mobilization of aromatic DOM following anoxic conditions, which has a lower $\delta^{13}\text{C}$; however, this mobilization was only observed in the surface 0-10 cm increment. These observations of a higher $\delta^{13}\text{C}$ through depth are also consistent with a signal arising from the effects of kinetic fractionation due to microbial decomposition (Diochon and Kellman, 2009), which would result in a higher $\delta^{13}\text{C}$ of soil C. Microbial discrimination and utilization of substrates with lower $\delta^{13}\text{C}$ would leave behind SOM with a higher $\delta^{13}\text{C}$, and this could explain the trends observed at greater depths; regardless, a more complete understanding of these processes would require further investigation.

5.4.3 Local stream water chemistry is consistent with mineral soil temperature and redox disturbances associated with forest harvesting

Monitoring of the Intact and Disturbed stream sites, watersheds that contrasted in their level of disturbance, was conducted to assess whether there is in situ evidence

for the experimental observations in this study. The Disturbed site was expected to experience more frequent episodes of anoxic conditions and higher soil temperatures (due to reduced radiative protection). The Disturbed site exhibited consistently higher DOC and Fe, ^{13}C -depleted DOC and higher SUVA_{254} compared to the Intact stream across the sampling period, in accordance with expectations since this site was under significant wetland influence, had the potential for large changes in temperature due to low forest cover, and was likely more consistently experiencing anoxic conditions. Our results are in agreement with observations from other studies that examined stream water chemistry in watersheds with harvesting influence (Hood et al., 2006; Schelker et al., 2016), where aromatic high molecular weight CDOM was mobilized from surface soils following warmer and anoxic conditions (Fellman et al., 2008; Hood et al., 2006; Sanderman et al., 2009; Stutter et al., 2012).

In contrast, the water chemistry of the upland Intact stream was variable across the sampling period. We expected that the water chemistry of Bear Brook would be characterized by lower DOC, CDOM and Fe, since it is dominantly influenced by lake processes, with intact canopy coverage and little wetland or riparian contribution within the watershed. During baseflow, the water chemistry was similar to extracts of soils incubated under oxic conditions. In particular, high molar DOC:Fe of Intact samples during baseflow (Table 5.4) were in a similar range as the oxic samples (Figure 5.5) and in deep soils (Table 5.2 and 5.3). However, following rain events, the water chemistry of the lake-fed Intact watershed stream became more similar in chemical character to the wetland-influenced Disturbed site (Table 5.4). This shift might reflect the inputs from surface soils when hydrologic connectivity of the system would be high, and is consistent with the chemistry of extracts from soils incubated under anoxic conditions.

The aquatic chemistry is variable in space and time in a manner that connects it to conditions experienced in upstream areas including soils. Forest clear-cut harvesting is associated with increases in the contribution of aromatic compounds as a result of surface water flowpaths (Hood et al., 2006; Schelker et al., 2014; Ussiri and Johnson, 2007). And although both DOC and Fe are associated in soils and are both potentially mobile, these data indicate that C and Fe can become decoupled when exposed to anoxic conditions and that this can be amplified at higher temperatures. Redox

shifts in situ can reduce Fe mobility through re-oxidation of Fe (II) to Fe(III), and consequential precipitation of Fe(III); however, DOC can remain mobile en route to streams. As such, the molar DOC:Fe ratios are likely a non-conservative indicator of redox conditions.

5.5 Conclusion

The results of this study have provided insight into the impacts of shifts in redox and temperature conditions experienced by mineral soils in harvested forest systems. Overall, these results suggest that the soil microclimatic conditions prevalent in the years following forest clear-cut harvesting can result in aromatic C and Fe release in situ, providing a plausible mechanism for the observed loss of mineral soil C from coniferous forests harvested by clear-cutting. While warmer and more prolonged anoxic soil conditions with water-table rise typical in the years following clear-cutting may explain documented losses of surface soil C, the results from this experiment suggest that at depth, biotic processes (i.e. microbial metabolism/decomposition) might explain the loss of C from mineral soils. Systems disturbed by land-use contribute to the release of C including aromatic compounds and Fe. Since differences in aquatic chemistry were observed with contrasting land-use, chemical indicators have a potential to be used as tools for connecting soils to aquatic systems.

Changes to C cycling are not necessarily detectable when only measured as changes in net DOC concentrations, which suggests that a full accounting of organic matter cycling, especially in regards to evolved CO₂ and methane, in this experiment would improve our understanding of the controls on C release, also including quantification of soil N. Quantification of other redox-sensitive minerals abundant in this soil series (e.g. Mn hydroxides) could also help to explain the effect of redox conditions and temperature on the stability of this significant store of soil C. We caution that these depth-specific conclusions may not be broadly applicable. Overall, it is essential to further elucidate how deeper soils are connected to surface soils or upslope sources of C, and this will improve knowledge about the controls on the stability of C stored in mineral soils.

Chapter 6

Conclusion

“The whole is greater than the sum of its parts.”

Aristotle

More carbon is stored in mineral soils than in all other terrestrial pools and the atmosphere combined, so any changes to mineral soil organic matter (SOM) storage could result in important shifts in global C cycling. Losses of soil C from mineral horizons of disturbed podzolic soils following clear-cut harvesting have been documented (Diochon et al., 2008; Prest et al., 2014). These losses are likely linked to shifts in climatic conditions of soils following landscape-level removal of vegetation and following soil disturbance from industrial machinery. A complete understanding of these mineral soil C losses, however, is challenged by the current gap in our knowledge about mineral soil C stability.

Accurate accounting of C storage changes following forest clear-cut harvesting requires an improved mechanistic understanding of the susceptibility of mineral soil C to shifts in soil climate (i.e. temperature and moisture). The overall objectives of my thesis, therefore, were to address the following questions: Are there multiple pools of mineral-associated soil organic matter that confer different levels of protection, and are these chemically distinct? How does soil organic matter decomposition respond to shifts in soil climatic conditions? How do changes in soil microclimate alter the mobilization of SOM and associated minerals? In order to address these questions, I quantified and characterized mineral-organic associations in podzolic mineral soil horizons in forests where losses attributed to clear-cut harvesting had been documented, and investigated mechanisms for the loss of mineral soil C through depth following forest clear-cut harvesting disturbance.

6.1 Summary

6.1.1 Mineral-associated soil organic matter pools in clear-cut harvested soils

Accurate forest C accounting requires improved knowledge about the distribution, chemical nature, and stability of mineral-associated soil C. My research furthered earlier work at two clear-cut harvested sites representing contrasting forest stand ages (35 and 110+ year stands) within a forest clear-cutting cycle in Eastern Canada that had documented a lower soil bulk C storage in the younger forest stand (Prest et al., 2014). The contribution from this work was to refine information about the distribution and nature of mineral-associated SOM and how it differed between these sites. This research was accomplished by determining the quantity of C, Fe and Al in mineral-associated OM pools of differing crystallinity isolated through sequential selective dissolution, and characterizing the $\delta^{13}\text{C}$ signatures of SOM held in these mineral-associated pools. Each step of the sequential dissolution procedure targets increasingly crystalline pools with a higher degree of structural order with each dissolving reactant: (from lowest to highest) water soluble, organo-metal complexes, poorly crystalline oxides, and likely hydroxides and oxy-hydroxide minerals, and crystalline oxides.

The distribution of C and Fe and Al in mineral pools varied through soil depth, consistent with soil formation processes in podzols, and differed as a function of disturbance history. A comparison of the distribution and C, Fe and Al content of these mineral-associated SOM pools from Young and Mature forest sites suggest that clear-cut harvesting reduces mineral soil C storage (Section 2.3.4). While pedogenic processes are thought to occur over hundreds to thousands of years (Jenny, 1941), forest clear-cut harvesting disturbance may have impacted soil formation on a decadal timescale (Section 2.3.5). My findings also confirm the existence of distinct pools of mineral-associated SOM that are linked to mineral crystallinity. I found that the organo-metal complex (OMC) pool dominated the distribution of mineral-associated SOM in all horizons, and was most significant in the spodic B_f horizons. Most importantly, the dynamics of the OMC pool drove the observed patterns of mineral soil C losses following disturbance through depth (Sections 2.3.1-2.3.3). My research

thereby contributes improved knowledge about the identity of the mineral-associated SOM pools that are vulnerable to destabilization following intensive harvesting disturbance. In addition, I noted that SOM with a lower $\delta^{13}\text{C}$ was associated with OMC pools, whereas SOM with a higher $\delta^{13}\text{C}$ was associated with mineral pools of higher crystallinity (Section 2.3.6). This is a key finding that refines our understanding about the distinct nature of soil organo-mineral interactions and about their relative susceptibility to destabilization.

6.1.2 Soil C loss following climatic changes

Increased subsurface temperatures and climatic extremes are more prevalent in temperate forests following clear-cut harvesting. Under these conditions, the loss of soil C may be exacerbated. This component of my thesis aimed to develop an improved mechanistic understanding of the susceptibility of mineral soil C to loss via mobilization (as dissolved organic carbon (DOC)) and respiration (CO_2) from mineral soil horizons of clear-cut harvested forest soils. Through my research, the potential susceptibility of soil C to decomposition and/or DOC mobilization with shifts in soil microclimate was evaluated. This was carried out through experimental manipulation of increased soil temperatures, and of extreme climatic events (dry-rewetting and freeze-thaw). My research also provided information about pools of C susceptible to loss as DOC and CO_2 under these treatment conditions, and how soil respiration rates varied through depth in A_e , B_f and BC horizons from two forests of contrasting forest age across a range of temperatures and extreme climatic conditions.

Carbon associated with minerals in horizons of podzol soils was found to be susceptible to loss following increases in temperature, with large differences between shallow (A_e and B_f) and deep (BC) mineral soils (Section 3.3.1). Carbon-rich B_f horizons were the most vulnerable to losses, with the highest respiration rates, bioreactivity and highest temperature sensitivity (Section 3.3.2). This is an important observation because these horizons store the most C, which suggests that temperature-enhanced decomposition is one mechanism for the observed losses from mineral soils in clear-cut harvested sites. In addition, temperature sensitivity and bioreactivity of SOM decomposition was higher in B_f horizons at the Mature site, consistent with previously documented observed in situ soil C losses at these sites. Bioreactivity and

respiration rates were found to be an order of magnitude lower in BC horizons than surface horizons (Section 3.3.2), and instead, SOM from BC horizons was primarily mobilized as DOC with temperature increases (Section 3.3.1).

Furthermore, it was expected that decomposition would result in shifts in DOC_{ex} chemistry representing the net result of DOC production and consumption (Section 3.3.3), and that this would be reflected in $\delta^{13}\text{C}$ - CO_2 signatures (Section 3.3.4). Congruent shifts in aromatic character of DOC_{ex} and $\delta^{13}\text{C}$ of respired CO_2 were observed, which indicated that certain components of DOC were the likely source of respiratory substrate (Section 3.3.3 and 3.3.4). In each horizon, DOC_{ex} likely represents a bioavailable pool of SOM because its $\delta^{13}\text{C}$ most closely resembles that of respired CO_2 (Section 3.3.4). In the mineral-poor A_e horizons, a lower value of $\delta^{13}\text{C}$ - CO_2 compared to B_f and BC horizons suggested that the aromatic CDOM pool was being utilized as the substrate for respiration. Contrary to expectations, in deeper soils, microbes preferred to use a substrate source with higher $\delta^{13}\text{C}$, which may indicate that the greater mineral content of B_f and BC horizons may be constraining access to the OMC pool (Section 3.3.3).

Extreme climatic disturbances of dry-rewetting (RW) and freeze-thaw (FT) can enhance mobility of soil C in surface horizons and respiratory losses of soil C at depth. Increases in DOC_{ex} and CDOM were observed following RW, resulting from a mobilization of aromatic CDOM from soil. Following exposure to RW and FT disturbance, C was lost from deeper soil (BC) horizons through enhanced decomposition, and in these horizons, microbes utilized substrates that were more highly enriched in ^{13}C compared to surface horizons (Section 3.3.5). These results suggest that the susceptibility to C loss from extreme climatic events can vary through depth in horizons, with the greatest impact on surface soils via mobilization following dry-rewetting.

6.1.3 Redox conditions and temperature effects on DOC and Fe mobilization

Development of a more complete understanding of DOC mobilization, coupled with Fe, following clear-cut harvesting in watersheds requires a consideration of the impacts of shifts in soil redox conditions and increased soil temperatures. The first objective of this component of my thesis was to evaluate, under controlled laboratory

conditions, the potential for changes in redox state and temperature in releasing DOC and Fe from mineral soils through depth. Soils were incubated at 5 and 15 °C under optimal (oxic) and flooded (anoxic) conditions and compared extracts before and after incubation periods of 1 and 4 months. I hypothesized that higher soil temperature and anoxic conditions, and longer exposures would increase mobilization of DOC and associated Fe from soils. Significant release of DOC and its coupling with Fe primarily occurred in surface mineral soils following anoxic conditions, which was increased after longer exposure (Section 4.3.2). A loss of SOC from deeper horizons with increased temperature was also observed, but here, redox changes were more decoupled from the mobilization of Fe (Sections 4.3.3-4.3.4). These alterations to the redox state of soils disturbed by harvesting may have the potential to release DOC, including organo-metal compounds, and Fe from surface layers to streams or downslope depositional environments (Section 4.4.1 and 4.4.2), but the impact of soil climatic changes depends on the depth, frequency and severity of climatic extremes.

The second objective of this component of the thesis was to characterize the chemistry of DOC and Fe released under anoxic conditions from laboratory experiments, and to compare these measurements with those from streams in areas of contrasting forest harvesting history to assess possible in situ evidence for the experimental results of this study. Chemical indicators ($SUVA_{254}$ and DOC:Fe) reveal differences between anoxic and oxic incubation conditions (Section 4.3.6). Local stream water chemistry is consistent with shifts in soil temperature and redox disturbances associated with forest harvesting (Section 4.3.7). Soil climatic conditions prevalent in the years following forest clear-cut harvesting may result in organo-metal C and Fe release in situ. This is one plausible mechanism explaining the observed loss of mineral soil C from coniferous forests harvested by clear-cutting. The results from these experiments suggest that warmer and more prolonged anoxic soil conditions typical in the years following clear-cutting may explain documented losses of soil C from the upper mineral soil through decomposition and mobilization. However, at depth in mineral soils, the losses of C under the conditions in these experiments were slower by an order of magnitude, largely due to SOM decomposition.

6.2 Insights

6.2.1 Destabilization of mineral-associated SOM pools following clear-cut harvesting

Knowledge about the role of minerals in controlling the persistence of soil organic matter is growing, at a time when soil C accounting is of national and international interest. This thesis contributes improved knowledge about the specific mechanisms that may explain C losses from mineral soils following clear-cut harvesting in typical forest soils of Nova Scotia, Canada. Through my research, I examined mineral-associated SOM pools in horizons of forests that have experienced clear-cut harvesting, and determined that mineral-associated SOM pools of forests of contrasting age since harvest are different. Mineral soil C was lower in Young compared to Mature forests, and these trends were driven by the lower content of the organo-metal (OMC) pool extracted with pyrophosphate-extractable SOM. From this, I conclude that the OMC mineral-associated SOM pool is both most the abundant pool in the horizons of these podzols and the most vulnerable to destabilization from intensive land-use.

6.2.2 Susceptibility of mineral-associated SOM pools to climatic changes

A key finding of this research was to investigate the susceptibility of C to loss in mineral horizons in podzolic soils. I determined that increased soil temperatures, anoxia, and extreme climatic conditions (dry-rewetting and freeze-thaw) can destabilize mineral-associated SOM from shallow soils (A_e , B_h and B_f horizons, equivalent to soil depths of 0-35 cm). Shallow soils also display the highest potential for C destabilization with increased soil temperatures, with loss as respired CO_2 , and following periods of anoxia, mobilized as aromatic DOC. I conclude from this that climatic changes due to forest clear-cutting might be a mechanism that explains documented losses from mineral soils. This is significant because forest soils disturbed by clear-cut harvesting in Nova Scotia experience increased subsurface soil temperatures and increased soil moisture (Kellman et al., 2015) compared to intact forests. This implies that these microclimate-induced losses of mineral soil C will be significant and continue to persist until soil climate stabilizes during secondary succession.

I assert that the fate of soil C will likely depend upon the intensity, frequency

and depth of disturbances. For example, the C-rich B_f horizons studied here are likely to lose more C via respiration with increased temperature and more C loss via solute mobility with freeze-thaw and dry-rewetting disturbances. In contrast, at depth, these disturbances may elicit increased respiration losses. And since extreme climatic events may result in greater SOM decomposition and mobilization of solutes within watersheds, the results of this study can also be extended to contributing knowledge about the impact of climatic extremes on soil C storage through depth in these podzolic forest soils due to climate change.

6.2.3 Role of soil minerals in protection of SOM

Association of SOM with minerals is assumed to provide protection against C loss (Torn et al., 1997). I expected that B_f horizons, the soil horizons with highest mineral content, especially in the deepest horizons, would have low respiration rates and bioreactivity, and would respond to temperature with high sensitivity (Q_{10}) due to the constraints imposed by mineral binding. Although the high Q_{10} observed in the B_f horizons supported these expectations, in contrast, the highest respiration rates and bioreactivity were observed in these horizons. In addition, the BC horizons, also rich in minerals, respired at rates an order of magnitude lower and with a lower temperature sensitivity. Interestingly, the A_e horizons, with the lowest mineral content, also displayed similar bioreactivity as the B_f horizons, with also higher Q_{10} values than the BC horizons. Surface soils were also most susceptible to reductive dissolution due to anoxic conditions, with an important release of DOC and Fe, exacerbated by higher temperatures. Therefore, the greatest potential for loss was demonstrated in surface A_e and B_f horizons, where the largest soil C stocks are often found in these forests, despite the presence or absence of mineral associations and their purported protective effects. I conclude from these observations that association with minerals does not necessarily protect soil C against loss.

Further knowledge about the mineral assemblage is necessary to determine the relative susceptibility of particular mineral pools to C loss. Recent research has demonstrated that binding with crystalline minerals are thought to be more stable (Lawrence et al., 2015). However, $\delta^{13}\text{C}$ evidence in this thesis points to the destabilization of crystalline mineral pools, especially with disturbance following dry-rewetting and

freeze-thaw. I conclude from this that there is more to understand about the relative susceptibility of each of these mineral-associated SOM pools to destabilization. While some preliminary exploration of these ideas were explored in this thesis, further work should explicitly consider how the content of particular mineral pools as defined by crystallinity controls both abiotic and biotic processes governing SOM stability. In addition, investigation into the possible impact of differences in parent material on soil C content between the two sites is required to more fully characterize soil C differences between sites. Research suggests that till lithology can exert control on C cycling (Caton et al., 2016; Heckman et al., 2009; Lawrence et al., 2014) and has an important influence on soil C storage (Yang et al., 2018). The impact of parent material is thought to be exerted through its impact on grain size and soil texture (Heckman and Rasmussen, 2011), and so the similarities in the soil texture between the Young and Mature sites allowed for preliminary comparison despite differences in the relative proportions of metasediment and slate rocks. However, in order to fully account for any potential influences from the parent material, further characterization (e.g. clay mineralogy) would be required.

6.2.4 Improving forest C modelling

Although mineral soils have historically lacked attention from researchers, the mounting evidence for soil C losses following intensive land-use disturbance justifies increasing attention to improving both modelling and accounting for C losses through soil depth. Most forest carbon models often inaccurately represent soil C dynamics following clear-cut harvesting disturbance and recovery during secondary succession (e.g. the carbon budget model of the Canadian Forest Service (CBM-CFS) (Kurtz et al., 2009)). Therefore, these models likely underestimate the impact of this intensive form of land-use on C stocks through depth.

I propose that further experimental and modelling research is necessary that will help to parameterize predictive relationships for soil C loss through depth across a full range of forest and soil types, including responses to subsurface temperature and moisture (Kellman et al., 2015), and to dry-rewetting and freeze-thaw events (Kim et al., 2014). In addition, while most soil models do include parameterizations for soil mineral content, they do not often parameterize for the dynamics of SOM pools based

on their mineral crystallinity. Since these soil mineral pools have distinct chemical natures and differences in their relative susceptibility to climatic changes, including knowledge about mineral properties could be used to trace shifts in biogeochemistry after disturbance and during secondary succession.

6.2.5 Implications for experimental methodology

Indicators

Several experimental indicators used in this research study were informative about biogeochemical processes. The content of OMC pools, extracted with Na-pyrophosphate, are vulnerable following land-use change such as clear-cutting and their content in soils should be explored for their potential to indicate soil C changes and soil health. The presence of aromatic DOC in streams also can indicate disturbance - CDOM $SUVA_{254}$ and $\delta^{13}C$ were important conservative indicators of DOC chemistry that spanned the soil-stream continuum. Molar DOC:Fe ratios were non-conservative as the relationship between DOC and Fe could become decoupled when redox shifts altered Fe speciation. Therefore, molar DOC:Fe ratios also provided important information about the redox conditions that may be impacting catchment biogeochemistry.

Sampling

If only shallow soils (i.e. top 10 cm) are sampled in efforts to quantify soil C, it may vastly underestimate soil C storage and obscure the dynamics in the deeper mineral soil profile. Researchers attempting to accurately quantify C should sample to a depth appropriate to measure changes in C in illuvial (B) horizons. Sampling by depth and by genetic horizon allows researchers to benefit from the added resolution when sampling by horizons (Goodwin, 2002), yet allows for calculation of C storage at a landscape scale. With regards to stream sampling, collection of samples throughout the year will provide more information as it will capture seasonal variations in hillslope hydrology. This will help to further elucidate how deeper soils are connected to surface soils or upslope sources of C, and will improve knowledge about the controls on the stability of C stored in mineral soils.

6.2.6 Pedogenesis

Evidence gleaned from my research suggests that the patterns in soil C loss following intensive forest harvesting is due to an alteration of podzolization (Section 2.4.4). Clear-cut harvesting results in a shift in surface vegetation (biota) and therefore alter local soil climatic conditions, which are two soil forming factors (Jenny, 1941). I observed a difference of podzolic features in the Young forest compared to the Mature forest that are not explained by other soil forming factors (parent material, slope, aspect, time). The B horizon of the Young site was thinner and stored less C than the B horizons at the Mature site, with greater mineral weathering, and the C-rich B_h horizon was completely absent in the Young site. Other researchers also report the loss of podzolic features (i.e. regressive podzolization) in the years following forest clearing (Barrett and Schaetzl, 1998; Falsone et al., 2012; Ferro-Vazquez et al., 2014; Hogberg and Read, 2006; Hole, 1975; Miles, 1985; Mossin et al., 2001; Nornberg et al., 1993; Vadeboncoeur et al., 2014). Changes to surface vegetation following forest clearing likely results in altered soil biogeochemistry over a decadal time scale which can alter podzol morphology. These results imply that a shift in pedogenesis and its direction occurred over a period of only several decades as a result of this disturbance. I suggest that revisiting theoretical assumptions about the timescale of soil formation is required.

6.2.7 Forest harvesting policy

The results from this thesis highlight the myriad impacts of clear-cut harvesting, practices that are already criticized for their reduction in aboveground C storage and harm to biological diversity. However, these impacts have been justified due to an assumption that over time frames of a harvest rotation (approximately 40 years), forest assemblages, including soil, recover. Our results show that for a typical forest stand in the Acadian region, soil C is released as CO_2 and as DOC to streams. Therefore, clear-cut harvesting for biomass energy production is not a sustainable practice, as some have suggested, especially given these relatively short harvest rotation lengths of 40 years. I assert that harvesting forests via clear-cutting for biomass energy production is not a carbon-neutral solution, and that harvesting forests for biomass should not be included in the Province of Nova Scotia's renewable energy strategy, especially

without the explicit recognition and accounting for these implications.

Soil organic matter decomposition and physical disturbance from climatic extremes are likely enhanced for decades as soil temperature and moisture fluctuate with the loss of the stabilizing influence of radiative cover. Soil carbon can only start to accumulate once inputs (net primary productivity) exceeds outputs (ecosystem respiration), so mineral soil C losses should be expected to endure until forest canopy closure, which occurs from 29-50 years into secondary succession following clear-cut harvesting of red spruce (Wu et al., 1999). This explains why mineral soil C storage was still low after 35 years following forest clear-cut harvesting in coniferous forests. The results of this research therefore suggest that efforts to establish stable soil climate is essential for the protection of mineral soil C stores.

Alternative methods of forest harvesting that are less destructive to soil physical structure, such as partial or selective harvesting methods and/or practices without the use of heavy machinery, may offer several benefits for soil C storage recovery. Furthermore, reducing or eliminating the use of herbicides (e.g. glyphosate) would help to re-establish ground cover (Freedman et al., 1993). These more ecologically-based and sustainable forest harvesting practices encourage the recovery of ground cover undergrowth and the forest canopy, and limit mobilization of C and other solutes into watersheds.

6.3 Next steps

The following investigations are suggested to provide further insight into mineral-associated organic matter dynamics:

1. An expansion of this study to include a full range of vegetation types, soil types, topography, climate and mineralogy would enhance the predictive power of forest C models, which will need to include these aspects to account for shifts in C cycling depending on soil mineral OM pools, temperature, and redox state.
2. An explicit incorporation of other soil minerals, in particular, Al and Mn hydroxides and oxy-hydroxides, would be necessary to fully clarify the role of the full suite of relevant secondary minerals. These minerals are redox and pH sensitive, and are therefore likely to respond to climatic changes following clear-cut

harvesting.

3. Further studies should explicitly examine the impact of mineral-SOM interactions in controlling substrate availability to microbes and how this impacts temperature sensitivity of SOM decomposition and bioreactivity, which would further highlight the susceptibility of particular pools to disturbance.
4. The experiments should be expanded to control for a range of soil moisture contents to consider key moisture thresholds; for instance, at lower and upper moisture limits, redox conditions switch and exert control over temperature dynamics.
5. The tracing of a ^{13}C labelled organic compounds through the soil system could allow for partitioning of SOM for a refined estimates of losses from particular mineral-associated SOM pools.
6. Longer incubations, with expanded efforts to characterize changes in solution chemistry and release of gases over time, would provide information about longer-term controls and dynamics.
7. Inclusion of quantification of net changes in limiting nutrients like nitrogen (DON and respired $\delta^{15}\text{N}$) and phosphate would improve understanding of the constraints which regulate C cycling in coniferous forest soils.

Appendix A

The following table in Appendix A are data that were included as supplementary information for the article published in PLoS One, Ch. 3 of this thesis.

Table 6.1: Supplementary Table 1. Results of sequential selective dissolution of podzol soils from two sites Young (35 years) and Mature (110 years since clear-cutting) from Mooseland, Nova Scotia, Canada, expressed as mg C g soil C⁻¹, and C storage of in extracted pools from depth increment as tonnes of C per hectare. Numbers in brackets are ± 1 SD; n=3. Extractions are water soluble (WS), organo-metal complexes (OMC), poorly crystalline (PCrys), and crystalline (Crys) minerals. Storage of C was calculated using bulk density estimates for each increment as provided in Prest et al. (2014).

		YOUNG		MATURE	
Depth Increment	Mineral phase	C (mg g soil ⁻¹)	C Storage (Mg C ha ⁻¹)	C mg g soil ⁻¹	C Storage Mg C ha ⁻¹
0-10 cm	WS	0.10 (0.01)	0.07 (0.01)	0.10 (0.01)	0.07 (0.01)
	OMC	12.15 (0.52)	8.7 (0.4)	32.1 (1.1)	23.1 (0.8)
	PCrys	1.00 (0.07)	0.72 (0.05)	1.13 (0.09)	0.81 (0.07)
	Crys	0.86 (0.41)	0.60 (0.30)	0.85 (0.30)	0.60 (0.20)
10-20 cm	WS	0.073 (0.005)	0.048 (0.003)	0.060 (0.003)	0.400 (0.002)
	OMC	23.65 (2.70)	15.6 (1.8)	30.68 (1.10)	20.6 (0.7)
	PCrys	0.98 (0.08)	0.65 (0.1)	1.30 (0.3)	0.9 (0.2)
	Crys	0.67 (0.16)	0.4 (0.1)	0.57 (0.10)	0.38 (0.06)
20-35 cm	WS	0.049 (0.007)	0.067 (0.009)	0.040 (0.001)	0.045 (0.002)
	OMC	17.65 (0.73)	24.4 (1.0)	32.1 (2.0)	35.6 (2.0)
	PCrys	0.98 (0.03)	1.4 (0.1)	1.40 (0.10)	1.5 (0.2)
	Crys	0.56 (0.16)	0.8 (0.2)	0.77 (0.30)	0.9 (0.3)
35-50 cm	WS	1.50 (0.08)	0.078 (0.004)	0.042 (0.001)	0.059 (0.002)
	OMC	15.35 (0.52)	26.7 (0.9)	28.1 (1.2)	39.6 (2.0)
	PCrys	0.98 (0.03)	1.70 (0.05)	1.4 (0.2)	2.0 (0.2)
	Crys	0.47 (0.14)	0.8 (0.2)	0.79 (0.05)	1.11 (0.07)

Appendix B

The following table in Appendix B are data that were included as supplementary information for the article published in PLoS One, Ch. 3 of this thesis.

Table 6.2: Supplementary Table 2. Particle size analysis and elemental and stable isotope analysis of separated textural fractions for composite soil samples of soil from podzol soil profiles sampled from Young (35 years) and Mature (110 years since clear-cutting) red spruce forests sites in Mooseland, NS, Canada. Numbers in brackets are ± 1 SD, and $n=3$ except for Mature clay sample of BC horizon, where $n=1$. Soil texture at both sites was sandy loam. % C is on a per mass basis.

		YOUNG				MATURE			
Horizon	Textural Fraction	Size %	C %	$\delta^{13}\text{C}$ ‰	C:N	Size %	C %	$\delta^{13}\text{C}$ ‰	C:N
A_e	Sand	66.2	5.36 (0.92)	-27.57 (0.18)	33.8 (5.4)	63.4	4.08 (0.44)	-27.13 (0.13)	39.2 (5.9)
	Silt	27.0	2.97 (0.05)	-27.47 (0.15)	23.7 (4.1)	27.7	2.22 (0.03)	-27.08 (0.05)	22.6 (5.1)
	Clay	6.8	7.46 (0.17)	-26.50 (0.16)	19.8 (1.6)	8.9	6.65 (0.29)	-26.01 (0.18)	18.2 (1.4)
B_h	Sand					56.0	16.59 (0.43)	-26.35 (0.22)	26.6 (3.2)
	Silt					13.8	11.35 (0.06)	-26.32 (0.16)	21.9 (1.1)
	Clay					30.2	19.70 (1.24)	-25.94 (0.21)	20.6 (0.1)
B_f	Sand	66.2	6.91 (0.08)	-26.40 (0.30)	27.7 (2.9)	78.7	11.11 (0.79)	-25.88 (0.31)	18.2 (2.9)
	Silt	22.4	5.86 (0.01)	-26.17 (0.15)	22.0 (1.7)	15.4	7.80 (0.02)	-25.46 (0.16)	19.2 (0.7)
	Clay	11.4	11.91 (0.47)	-25.29 (0.12)	20.8 (6.6)	5.9	18.48 (0.13)	-25.06 (0)	21.5 (0.6)
BC	Sand	58.2	2.97 (0.12)	-26.27 (0.48)	26.2 (4.9)	56.0	2.41 (0.32)	-25.47 (0.23)	18.2 (3.2)
	Silt	30.3	3.53 (0.04)	-25.43 (0.18)	18.7 (2.1)	35.6	3.29 (0.01)	-24.84 (0.14)	16.8 (3.2)
	Clay	11.5	8.82 (0.68)	-24.75 (0.08)	20.5 (1.7)	8.4	10.78 (-)	-24.62 (-)	20.8 (-)

Appendix C

The figure in Appendix C is a soil texture triangle that uses particle size information in Appendix B to calculate soil texture through depth for soil horizons at the Mooseland, NS sites.

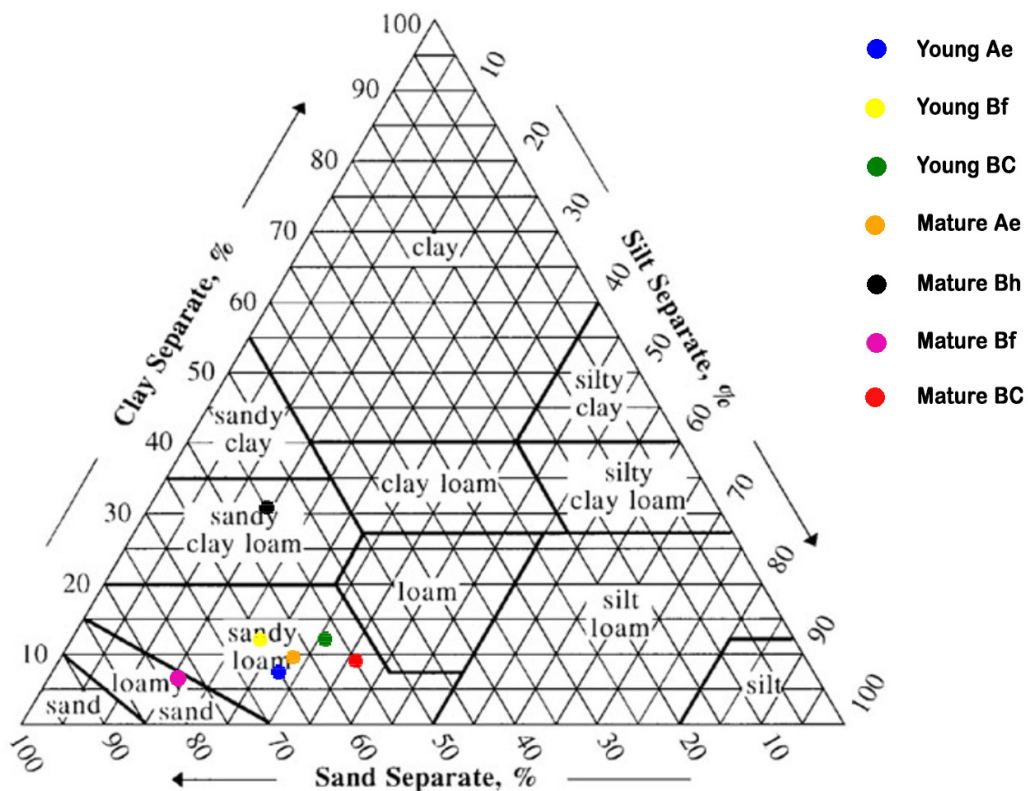


Figure 6.1: Soil texture triangle for composite soils from horizons through depth at Young and Mature sites in Mooseland, NS. Soil horizons are largely sandy loam for all samples at both sites, except for the thin B_h horizon at the Mature site. Note, that there was only one replicate of each of these particle size separates, and so the natural variability within each site was not likely adequately assessed. Further work could determine whether these were significantly different.

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