Fire Intensity and Prescribed Fire Effects on Soil Organic Matter

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Abstract

Fire Intensity and Prescribed Fire Effects on
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Soil organic matter (SOM) in forested systems is affected by fire intensity and severity which has consequences on soil processes. Low-intensity prescribed fire is used to restore ponderosa pine (*Pinus ponderosa* Laws.) forests of the Pacific Northwest to their historical environment. This study investigated the changes in SOM composition by controlling fire intensity of laboratory burns on reconstructed soil profiles (O, A1 (0-1 cm), and A2 (1-2 cm)) and by controlling prescribed fire severity in the field. Soil profiles were burned at varying intensity by changing fuel moisture content and air temperature. Incubations were conducted to examine the decomposition characteristics of each soil horizon. In the O horizon, increasing fire intensity was associated with increased consumption of C and N and a higher proportion of recalcitrant SOM that depressed C mineralization rates. Mineral soil C content was unaffected by burning; however, composition shifted to more labile forms with burn intensity leading to an increase in short-term C mineralization rates. After incubation, O horizon SOM composition remained different from the control; however, mineral soil SOM composition returned to control characteristics. The effect of prescribed-fire severity was examined by applying one or two moderate-to high-severity fall burns and low-to moderate-severity spring burns. Fall burning decreased C and N capital of the soil by 22-25%, and decreased recalcitrant C content by 15 and 30% after one or two burns, respectively. Prescribed burning in either season did not have an effect on the labile SOM. Fall burning in fire-suppressed stands may be too severe to preserve soil C, N, and

recalcitrant SOM content, but may replicate the natural fire regime. Spring burning reduces the fuel load while having little impact on SOM and may be used to prepare a site for fall burning. Overall, prescribed fire examined in these studies showed that the major impacts to SOM occurred to the O horizon and that any fire-caused changes occurring in the mineral soil were not persistent. Recalcitrant forms of C produced by burning O horizons, *e.g.* charcoal, may accumulate in the soil if this material is not reburned.

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DEDICATION

To my parents

Al and Kandy Hatten

for giving me the opportunity to achieve my goals

and my soon to be wife

Reyna Starling Maestas

for giving me purpose.

Chapter 1
Introduction

Fire is a regularly occurring natural event that shapes ponderosa pine (*Pinus ponderosa* Laws.) forests of the Pacific Northwest. Historically these forests had a low-severity fire regime, with frequent fires that leave most trees alive. However, high-severity wildfires are occurring more frequently due to altered stand structure and accumulation of fuels caused by decades of fire suppression, recent climate trends, timber harvesting, road building, and historical overgrazing (Agee 1994, Everett *et al.* 2000, Tiedemann *et al*. 2000). Low-intensity prescribed fires are being used to reduce the threat of high-severity wildfires and return these forests to their historical stand structure and fire-return interval. The effect of fire on soils is largely through the alteration and combustion of soil organic matter (SOM). Soil organic matter plays a prominent role in regulating nutrient availability to plants. Further, SOM serves as an important reservoir of C containing 2344 Pg of global C (Jobbagy and Jackson 2000). Understanding the effect of fire intensity on SOM is important for natural resource managers if they are to protect and sustain ecosystem health.

Fire severity and intensity

Fire severity has been defined as the qualitative impact that fire has on the soil and water system, atmosphere, and society and has been used to describe individual fires and fire regimes (Simard 1991, Agee 1993, Neary *et al.* 1999). The broad definition of fire severity often leads to multiple interpretations of the term, even within the same discipline. Fire intensity has been more narrowly defined as the rate of energy released by an individual fire or the temperature of the burning environment (White and Pickett 1985, Neary *et al.* 1999). Further, the amount of material consumed and nutrients lost from the soil through volatilization have been found to be largely dependent on temperature (Raison *et al.* 1984a). Severity and intensity are not perfectly related in that the interaction of intensity and duration that a fire burns is important in determining the

total impacts to soil (DeBano *et al.* 1998). A high-intensity fire in the forest canopy may not cause high-severity changes to the soil, while a smoldering log (low intensity) can produce heat for a long period of time affecting the soil many centimeters deep. Additionally, the interaction of fire effects with site characteristics, such as topographic features and rainfall, is important in determining the severity of secondary effects of fire on soil and SOM.

For this dissertation fire intensity will be used to describe the energy released and temperatures achieved at a specific point (*e.g.*, maximum temperature). Fire severity will be defined as the impact that burning has on the soil system, including total energy released into the soil, and will be used when access to fire intensity was unavailable.

Fire volatilizes and combusts organic material, which results in losses of carbon and nutrients from the soil (Raison *et al.* 1984a and 1984b). Fire can also mineralize organically-bound elements such as N, P, and base cations, which are then available for uptake by plants or leaching from the soil (DeBano *et al.* 1998). Low-severity burns are likely to occur when there is a low-level of fuel, or fuels are moist, so that temperatures remain below 100°C in the mineral soil and unburned material is left as a residue (Neary *et al.* 1999). The temperatures achieved at the surface of the mineral soil would be high enough to kill most organisms, and begin destructive distillation of C (Figure 1.1). Moderate-severity burns alter the majority of O horizon through charring and achieve temperatures between 100 and 250°C in the mineral soil. Charring and combustion of N begin in these temperature ranges. High-intensity fires occur where temperatures in the mineral soil are >250°C; all O horizon material is consumed and more mineral soil material is altered by the heat. Nitrogen and sulfur are combusted at these temperatures and at higher temperatures clays can be altered while even higher temperatures result in combustion of phosphorus-containing compounds.

Fire severity varies across temporal and spatial scales and can be influenced by management decisions. Prescribed fires and wildfires in ponderosa pine ecosystems are patchy across the spatial extent of each fire occurrence. Further, fire intensity is dependent on the climate which is reliant on short- and long-term trends (Savage *et al.*

1996, Wright and Agee 2004). Fire severity and intensity may determine the degree to which soil and SOM are impacted by burning.

Soil organic matter

Soil organic matter includes both humic and non-humic substances (Figure 1.2). Non-humic substances are generally materials that can be identified and therefore classified in known groups of compounds. Humic substances are refractory, dark colored, heterogeneous, organic compounds, produced as byproducts of microbial metabolism (Stevenson 1994). Soil organic matter provides much of the soil's CEC; the CEC of SOM is dependent on the oxygen content, specifically the carboxylic group content (Stevenson 1994). The solubility of SOM is inversely related to molecular size, while solubility and CEC are positively related to oxygen content (Almendros *et al.* 1990, Stevenson 1994). Soil organic matter also serves as a reservoir of available nutrients that can eventually be mineralized by microorganisms. The availability and accessibility of SOM to microorganisms is dependent on its nutrient content, chemical structure, and physical protection within the soil (Baldock and Skjemstad 2000, Baldock and Smernik 2002, Kelleher *et al.* 2006). Lignin, waxes, and highly-condensed and aromatic substances, *e.g.*, charcoal, are less bioavailable (Shneour 1966, Baldock and Skjemstad 2000, Kelleher *et al.* 2006).

Classes of SOM have been defined based on an alkaline extraction and subsequent solubility in an acidic environment. Humin is often associated with mineral surfaces, is very stable in the soil, and is not soluble in an alkaline solution (Stevenson 1994). The humin fraction is composed of the largest molecules that have the greatest degree of aromaticity and the lowest concentration of oxygen (Figure 1.2). Non-soluble (NS) materials in O horizons, analogous to humin in the mineral soil, are usually made up of cellulose and lignin or charcoal in a burned soil. Humic acid (HA) is soluble in alkaline conditions but precipitates when the pH is lowered and is relatively immobile in soils. The fulvic acid fraction is extracted under alkaline conditions and remains soluble once the solution is acidified.

Fulvic acid (FA) is purified from the fulvic acid fraction through the use of an XAD-8 resin (Malcolm 1990, Swift 1996). Hydrophobic substances absorb to the XAD-8 resin while hydrophilic substances do not (Leenheer 1981, Thurman 1985). The hydrophilic soluble non-humic substances (NH) do not absorb to the XAD-8 resin. The NH fraction may include the hydrophilic acid, base, and neutral fractions defined by Leenheer (1981) which encompass sugars, amino acids, and low molecular weight acids. Fulvic acid absorbs in acidic conditions but elutes with 0.1 N NaOH (Swift 1996). Other hydrophobic materials (HO) in the fulvic acid fraction absorb to XAD-8 resin but do not elute with 0.1 N NaOH. The HO fraction may encompass Leenheer's (1981) hydrophobic-neutral and base fractions, and probably consists of hydrophobic-neutral materials since these solutions are extracted from the soil under basic conditions. Hydrophobic-neutral substances have less than 1 carboxylic acid group for every 12 C atoms (Thurman 1985). The portion of humic and fulvic acid fractions that does not elute from XAD-8 resin after 0.1 N NaOH elution have been shown to be high in aliphatic functional groups (Yonebayashi and Hattori 1990, Dai *et al.* 2006).

Black carbon (BC) is another component of SOM that often gets included into the insoluble humin fraction. Black carbon is the heterogeneous, aromatic and carbon-rich residue of biomass burning and fossil-fuel combustion, and includes charcoal, soot, and graphite (Goldberg 1985). Black carbon is a continuum of materials that increases in aromaticity, condensation, C:H, and C:O so that charcoal < soot < graphite (Figure 1.2). Charcoal is often part of the ash and residue remaining after biomass burning. Soot particles form in the gaseous phase and are easily transported from a fire site by wind. Graphite is usually geologically formed and inherited by soil.

Fire and soil organic matter

In general the chemical changes that occur in OM and SOM after heating and combustion are an increase in aromatic structures and a disproportionate loss of H and O relative to C (Almendros *et al.* 1990, Baldock and Smernick 2002, Almendros *et al.* 2003, Gonzalez-Vila and Almendros 2003, Gonzalez- Perez *et al.* 2004, Knicker *et al.*

2005). Heat-induced polymerization of labile material such as FA has been shown to decrease their solubility through the reduction of O containing functional groups and polymerization reactions as shown in Figure 1.2 (Almendros *et al.* 1990, Fernandez *et al.* 1997 and 2001, Gonzalez-Vila and Almendros 2003, Gonzalez-Perez *et al.* 2004). Most research regarding the effect of fire on SOM is based on individual wildfires and prescribed fires with little or no replication. Studies of the effect of fire severity on SOM have been achieved through the comparison of case studies and simulating fire intensity using heating in an oven. Very few studies have examined the effect of varying fire intensity on SOM.

Increased heating severity of organic matter leads to decreasing whole soil C, FA, and HA, and increasing proportions of humin and BC (Almendros *et al.* 1990, Czimczik *et al.* 2003). Isolated FA and HA samples were heated in an oven to 350 ^{o}C for a varying amount of time (0-150 seconds) simulating an increase in fire severity, resulting in O and H being increasingly lost from each fraction (Almendros *et al.* 1990). The researchers attributed this to a selective loss of O containing functional groups and carbohydrates, and an increase in aromaticity of the remaining SOM. The changes to the atomic makeup of FA and HA led to reduced solubility of each fraction. Similarly, water-soluble organic C decreased after heating wiregrass and longleaf pine needles to 340 ^{o}C in a muffle furnace for 1 hour (Battle and Golladay 2003).

When whole mineral soils are heated there is a release of soluble organic material with increasing severity up to a threshold (which appears to be dependent on the soil type, temperature, and duration) at which point soluble materials decrease rapidly. Blank *et al.* (1994) found that maximum amounts of oxalate, acetate, formate, and glycolate (all of which would be part of the NH fraction) were extracted after mineral soils were heated between 150 and 350 ^{o}C (depending on the compound); peak concentration of organic anions occurred at 300 ^{o}C, when heated for 5 minutes. When soils were heated 30 minutes, the peak concentration of total organic anions occurred at 250°C, at which point the concentration drops off very rapidly with higher temperatures. Serrasolsas and Khanna (1995) noted increases in dissolved organic N after heating

mineral soil to 120 ^{o}C. Water-soluble C has been seen to increase after heating mineral soil up to 500 ^{o}C, above this temperature there were sharp reductions (Guerrero *et al.* 2005, Battle and Golladay 2003). Fernanadez *et al.* (1997, 2004) found a reduction in water-soluble C and FA when mineral soils were heated above 220 ^{o}C for 30 minutes or 385 ^{o}C for 10 minutes. These researchers have attributed increases of water-soluble C and N to the destructive distillation of humic materials and the destruction of microbial cells releasing cell contents into the soil; reductions in soluble C were ascribed to reduced oxygen content, and increased aromaticity of SOM. None of these researchers attempted to account for all SOM fractions while varying fire severity, limiting the conclusions about the source of soluble C. The decrease in soluble C and N appears to occur at relatively high heating or fire severity, which is where most research regarding fire severity and whole soil has occurred. There has been very little research that has characterized SOM behavior after low- to moderate-intensity fire.

The release of soluble C and N by fire may increase the short-term N availability but reduce the C content of the soil by raising mineralization rates (Bauhus *et al.* 1993, Choromanska and DeLuca 2002). Monleon and Cromack (1996) found that after an initial increase, N availability decreased below control levels after prescribed burning which they attributed to a decrease in N capital, but may have been caused by a change in residual substrate quality. Guinto *et al.* (1999) showed that N mineralization and available N were depressed for a year after prescribed burning due to a lower availability of C.

Fire and C mineralization

The aforementioned recalcitrant C, *e.g.*, humin and BC that is produced when O horizons and SOM are heated, has been shown to reduce C mineralization and slow its decomposition (Baldock and Smernik 2002). The production of soluble toxic compounds during the heating and burning of the O horizon may also reduce microbial activity (Fritze *et al.* 1998). Lower decomposition rates of fire-affected SOM may be a process by which C can be sequestered into the soil (Kuhlbusch and Crutzen 1995).

Mineral soil C mineralization response to fire has been shown to be more complex and appears to be dependent on soil type, fire/heating temperature, fire/heating duration, and post-fire litterfall. The increase in C mineralization was attributed to the previously discussed release of labile organic materials from microbial biomass or destructive distillation of humic materials. Guerrero *et al.* (2005) showed that total CO_2-C mineralized from heated soils was increased above an unheated soil as the soils were heated up to 500 ^{o}C.

When mineral soils are exposed to higher-severity heating or wildfire there is a reduction in C mineralization. In the previously mentioned study by Guerrero *et al.* (2005) soils heated to temperatures above 500 ^{o}C had decreased C mineralized on a per C basis due to a reduction of total C and the production of recalcitrant forms of C. Carbon mineralized on a soil basis (g CO_2-C kg^{-1} soil) from soils burned by high severity wildfire has been shown to decrease due to a reduction in total soil C (Fernandez *et al.* 1997, 1999, 2004). It appears that there is a threshold severity. Below this threshold C becomes more labile while above it C becomes more recalcitrant.

Long-term effects of fire on soil organic matter

Changes to SOM fractions caused by high-severity wildfire may be long lasting. Knicker *et al.* (2005) found a decrease in HA and an increase in humin 5 years after a high-severity wildfire. However, Knicker *et al.* (2005) studied only one composite sample each from a burned and unburned area, limiting the conclusions that could be made. Soils collected long periods after fire have been shown to have lower levels of labile materials, which may be due to leaching or consumption of labile materials by microorganisms (Hernandez *et al.* 1997).

Fernandez *et al.* (2004) examined the decomposition products of heated SOM. They found that soil heated at 385°C had a greater proportion of humin and HA after heating and a greater proportion of each after incubation, however they did not examine an unburned control. Additionally, these researchers did not examine the effects of fire severity nor did they examine the effect of low heating severity which has been shown to

increase C mineralization and could result in different conclusions regarding post-fire and incubation SOM quality. The production of decomposition-resistant SOM may lead to a build-up of this material in soils where fire plays a prominent role.

Researchers have found accumulations of BC incorporated into the top 10 cm of grassland soils (Glaser and Amelung 2003); this increased as a proportion of total C with depth in a savanna soil (Dai *et al.* 2005). However, these materials are very susceptible to erosion when left at the soil surface, likewise BC at the surface and may be combusted if the site is reburned. Dai *et al.* (2005) found that repeated burning did not significantly affect BC in soils collected from a savanna treated with prescribed burning. Czimiczik *et al.* (2005) found that BC was non-existent in Scots pine (*Pinus sylvestris* L.) forests where the last fire was high severity. The charred material may have been present prior to burning; however, it was consumed by the high-intensity fire and not able to accumulate. They also found a very low rate of surface-soil mixing, so that BC was not able to be protected by the mineral soil through incorporation.

Objectives

Few studies have been conducted on the effect of fire intensity or severity on recalcitrant and labile forms of SOM by burning organic matter or using prescribed fire. Further, studying the immediate and long-term response of organic and mineral soil horizons to fire intensity while in their natural sequence has rarely been conducted. The following guiding research question was developed from these perceived research needs:

Main research question: What are the immediate and long-term effects of prescribed burning at different intensities on SOM composition of organic and mineral soil horizons in their natural sequence?

Laboratory burns that simulate prescribed fire will be used to investigate the role that fire intensity plays in altering SOM composition and C mineralization, where all variables except fire intensity will be held constant. These results will then be compared with the effects of fire severity on SOM from a field study where fire severity is

controlled by burning in the fall or spring. Based on the research question four objectives were developed to guide specific aspects of the research within this dissertation.

Objective 1: To determine the effect of fire intensity on SOM composition as measured by a fractionation of an alkaline extraction of organic and mineral soil horizons.

Chapter 2 investigates the role that fire intensity plays in transforming and consuming SOM while attempting to keep soil type and fuel loading constant. Burns were conducted in the laboratory to represent the fire intensity in the understory of a ponderosa pine forest. The fuel for each burn (O horizon) was placed on top of the mineral soil (A horizon) to replicate the natural sequence of soil horizonation. The SOM fractionation method used accounts for all SOM to examine the C sources and sinks of fire caused SOM transformations.

Objective 2: To determine the effect of fire intensity on C mineralization rates of organic and mineral soil horizons.

The effect of fire intensity on SOM from both organic and mineral horizons is assessed in Chapter 3 by examining the short- and long-term C mineralization characteristics of the burned soils during a laboratory incubation. The CO_2-C mineralized is compared to the C lost due to combustion to evaluate the use of fire as a process of sequestering C through production of decomposition-resistant materials.

Objective 3: To determine long-term effects of fire intensity on organic and A horizon SOM by examining post-incubation SOM composition of fire-treated soils.

Chapter 3 investigates the potential long-term effect of fire intensity on SOM by examining the SOM composition after a laboratory burning and incubation. Burned soils will be compared to unburned controls to separate the effects of incubation from the effects of burning. The propensities for recalcitrant fractions of SOM to accumulate in the soil will be assessed in this chapter.

Objective 4: To assess SOM composition as measured by a fractionation of an alkaline extraction of soils from single and multiple treatments of prescribed burns of differing severities due to season of application in a ponderosa pine forest.

Chapter 4 applies the knowledge gained from Chapters 2 and 3 to a field setting in which fire severity was varied through the use of prescribed fires applied in the fall or spring. Management recommendations regarding the use of prescribed fire in ponderosa pine forests will be developed which preserve soil C and N, protect soil processes, and sustain soil quality.

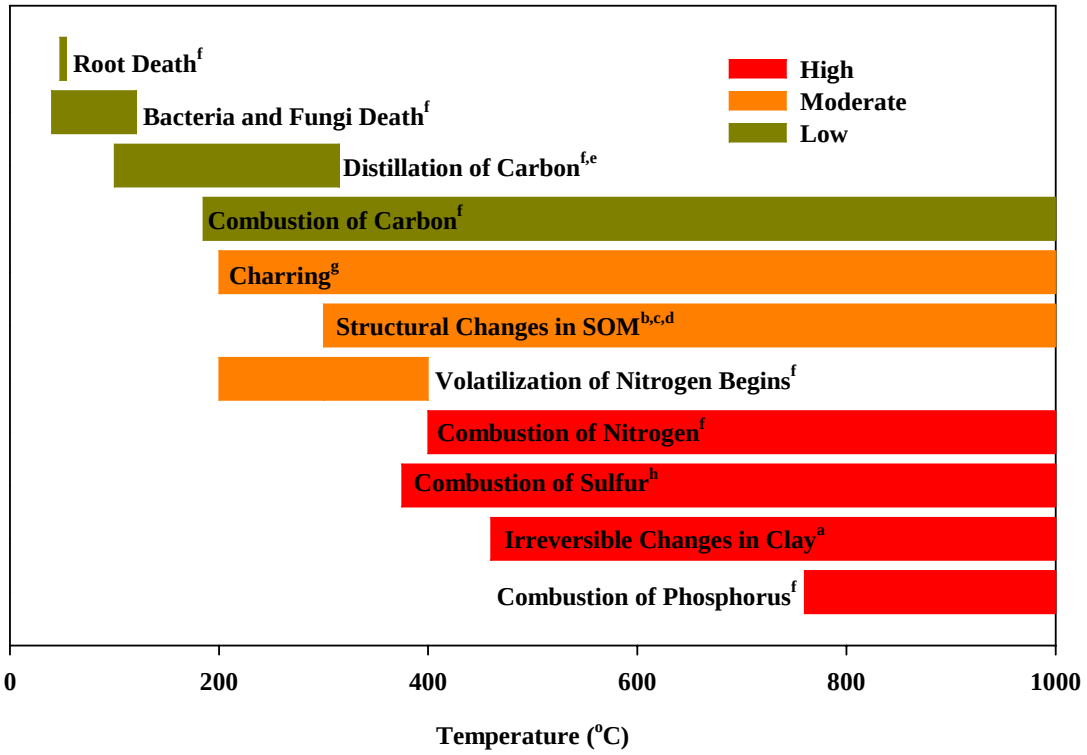


Figure 1.1 Temperature zones at which important biological processes occur. Intensity designations are based on the maximum temperature reached at the surface of the mineral soil as defined by DeBano *et al.* (1998). Each process is categorized into an intensity class by the lowest temperature at which it has been reported to occur. ([a]Giovannini *et al.* 1988, [b]Almendros *et al.* 1990, [c]Almendros *et al.* 1992, [d]Knicker *et al.* 1996, [e]Giovannini and Lucchesi 1997, [f]Neary *et al.* 1999, [g]Gonzalez-Perez *et al.* 2004, [h]Lide 2007)

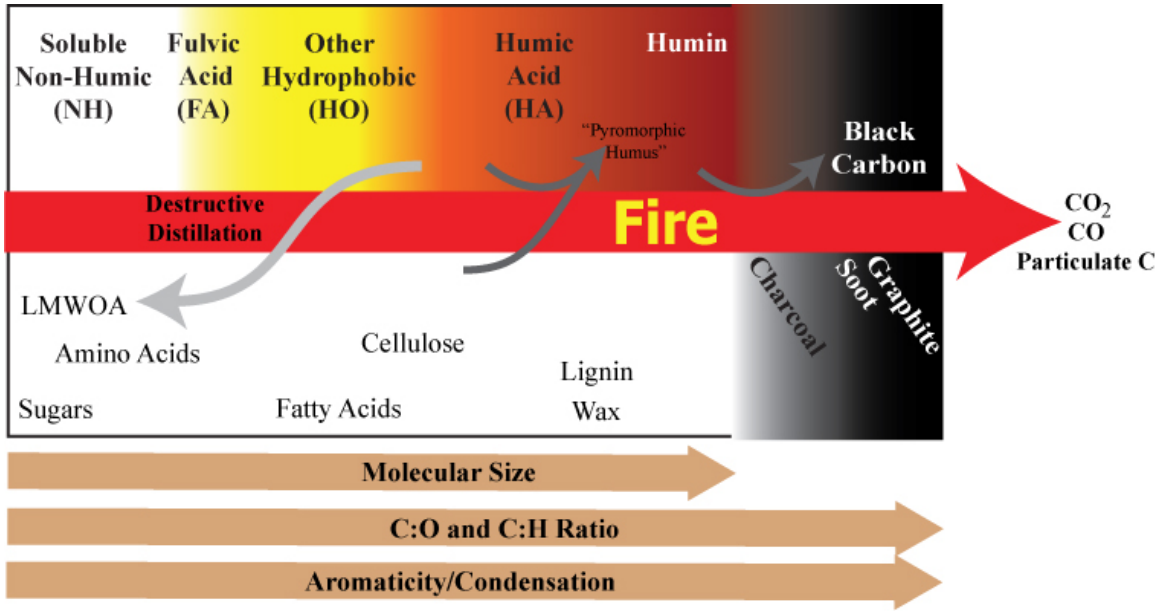


Figure 1.2 Humic and non-humic substances in soil and transformations of these materials caused by fire. The greatest effect on SOM caused by fire is combustion and the production of gaseous and particulate forms of C. Fire reduces the O and H content of SOM through "browning" or Maillard reactions (Maillard 1916), polymerization, and condensation reactions. The most extreme product of fire-caused transformation reactions of both humic and non-humic compounds is black carbon (BC). Additionally, labile substances, *e.g.*, low molecular weight organic acids (LMWOA) may be produced through destructive distillation of humic materials or through the destruction of microbial cells (Blank *et al.* 1994, and Guerrero *et al.* 2005).

Chapter 2
Fire Intensity Effects on Soil Organic Matter

Introduction

Ponderosa pine (*Pinus ponderosa* Laws.) forests of the Pacific Northwest historically had a low-severity fire regime (most trees survive each fire occurrence). However, high-severity wildfires are now occurring more frequently due to altered stand structure and accumulation of fuels caused by decades of fire suppression, timber harvesting, road building, and historical overgrazing (Agee 1994, Everett *et al.* 2000, Tiedemann *et al.* 2000). Low-intensity prescribed fires are being used to reduce the threat of high-severity wildfires and return these forests to their historical stand structure and fire-return interval. The effect of fire on soils is largely through the alteration and combustion of soil organic matter (SOM), which can provide much of a soil's CEC and contains a majority of soil N capital. In general, fire consumes C and fire altered SOM is more recalcitrant than unburned SOM, so that burning may be a mechanism by which soil can accumulate recalcitrant forms of C (Kuhlbusch and Crutzen 1995). However, these recalcitrant materials could limit nutrients to organisms (Guinto *et al.* 1999). The impact of prescribed fire on ecosystem components is dependent on fire intensity, which is likely controlling the alterations to SOM.

Soil organic matter includes both humic and non-humic substances associated with soil. Non-humic substances are generally materials that can still be identified as plant or animal, while humic substances are refractory, dark colored, heterogeneous, organic compounds, produced as byproducts of microbial metabolism (Stevenson 1994). Soil organic matter can be responsible for 20-70% of soil CEC which is related to oxygen content, specifically carboxylic group content (Stevenson 1994). The solubility is inversely related to molecular size, while solubility and CEC are positively related to oxygen content (Almendros *et al.* 1990, Stevenson 1994). Soil organic matter also serves as a reservoir of available nutrients, particularly N, which can be mineralized by microorganisms. The availability and accessibility of SOM to microorganisms is

dependent on its nutrient content, chemical structure, and physical protection within the soil (Baldock and Smernik 2000, Baldock and Skjemstad 2002, Kelleher *et al.* 2006). Lignin, waxes, and highly-condensed and aromatic substances such as charcoal are less bioavailable (Shneour 1966, Baldock and Skjemstad 2002, Kelleher *et al.* 2006).

Operational definitions have been developed to define classes of SOM based upon an alkaline extraction and subsequent solubility when subjected to an acidic solution. The fulvic acid fraction contains those substances that are extracted by an alkaline solution and remain in solution after the pH is acidified (Stevenson 1994). Fulvic acid (FA) is often purified from the fulvic acid fraction through the use of a nonionic XAD-8 resin (Malcolm 1990, Swift 1996). The nonionic XAD-8 resin separates dissolved organic matter based on its surface properties and hydrophobicity (Leenheer 1981, Thurman 1985). Soluble non-humic materials (NH), such as saccharides, low molecular weight organic acids, and inorganic salts do not adsorb to the XAD-8 resin, while FA adsorbs to the resin at a pH of 1 (Leenheer 1981). Fulvic acid is removed from the resin by eluting with 0.1N NaOH and other hydrophobic compounds (HO) remain adsorbed to the column. Humic acid (HA) is soluble in an alkaline extract but precipitates in a subsequent acidic condition and is relatively immobile in soils. Humin is composed of the largest molecules that have the greatest degree of aromaticity and the lowest concentration of oxygen (Stevensen 1994). Humin is often associated with mineral surfaces, is very stable in the soil, and is not extracted by an alkaline solution.

Black carbon (BC) is composed of organic compounds that often get included within the insoluble humin fraction. Black carbon has been defined as the heterogeneous, aromatic and carbon-rich residue of biomass-burning and fossil-fuel combustion following a continuum from charcoal, soot, to graphite (Goldberg 1985). Black carbon is itself also a continuum of materials with a gradient of aromaticity, condensation, C:H, and C:O so that charcoal < soot < graphite. Charcoal is often part of the ash and residue remaining after burning, while soot forms in the gaseous phase and is easily transported from a fire site by wind. Graphite is usually geologically formed and not formed by fire. It can be inherited by soil from parent materials.

Fire effects on soil organic matter

Fire consumes and alters OM at the surface of the soil through the process of combustion which results in volatilized C and other nutrients. A fraction of the energy produced from burning is able to penetrate into the soil and alter mineral SOM. Organically-bound elements such as N, P, and base cations can be mineralized and become available for uptake by plants or leached from the soil (DeBano *et al.* 1998). In general the chemical changes that occur in SOM after heating and combustion are an increase in aromatic structures and a disproportionate loss of H and O relative to C (Almendros 1990, Baldock and Smernick 2002, Almendros *et al.* 2003, Gonzalez-Vila and Almendros 2003, Gonzalez- Perez *et al.* 2004, Knicker *et al.* 2005). Reducing the oxygen content of the SOM has the effect of converting FA and HA fractions to humin and BC (Almendros *et al.* 1990, Fernandez *et al.* 1997, 2001, and 2004, Hernandez *et al.* 1997). In contrast, soluble C has been seen to increase after heating mineral soil up to 500 ^{o}C (Blank *et al.* 1994, Battle and Golladay 2003, Guerrero *et al.* 2005). These researchers attributed elevated levels of soluble C to destructive distillation of humic materials and destruction of microbial cells. Much of the research regarding the effects of fire intensity on SOM are from heating experiments or case studies of wildfires and prescribed fires. Very little research has examined fire intensity or severity on SOM.

To determine the effect of fire intensity on SOM, controlled burns were conducted in the laboratory on columns of soil assembled from homogenized samples collected from a ponderosa pine forest. Treated soils were analyzed for soil characteristics and quality of SOM to determine the effect of fire intensity on SOM. Understanding the effect of fire intensity on SOM will help natural resource managers utilize prescribed burning to preserve soil C and maintain benefits of SOM to soils.

Materials and Methods

Laboratory burning

Laboratory burns were designed to represent prescribed fire in the understory of a ponderosa pine forest. Clay-loam textured soil samples were collected from the

Dinkelman soil series (Vitrandic Haploxeroll) beneath a ponderosa pine tree in a Douglas-fir (*Pseudotsuga menziesii* (Mirbel) Franco)/ponderosa pine forest located near Cashmere, Washington on the east side of the Cascade Mountain Range (47°27'00"N/ 120°37'54"W; 1070 m elevation). O and A horizons were collected and air dried. After drying, pine cones, large pieces of wood, and other large materials were removed to create a more homogeneous substrate. O horizons were separated into Oi (litter) and Oe (duff). Mineral soil (A horizon) was sieved to 2 mm, homogenized, and stored in air-tight containers.

A cylindrical form (36 cm diameter) was used to reassemble four replicated soil profiles per fire intensity treatment. Sieved A horizon material was added to a depth of 2 cm and tamped to a bulk density of 0.8 g cm^{-3}. Air-dried Oe horizon was placed on top of the mineral material to a depth of 4 cm at a bulk density of 0.09 g cm^{-3}. Air-dried Oi horizon was placed on top of the Oe material to a depth of approximately 2 cm at a bulk density of 0.03 g cm^{-3}. These depths and bulk densities were similar to the soil at the collection site. This O horizon fuel represents much of a ponderosa pine forest's fuels as litter and duff represent about 25-80% of the mass of downed, dead fuels in ponderosa pine forests of Oregon and Washington (Page-Dumroese and Jurgensen 2006, McIver and Ottmar 2007).

Fire intensity was controlled by adjusting fuel moisture and applying heated air. An O horizon with 18% moisture content was used for the low-intensity treatments. To achieve the moderate- and high-intensity levels the fuels needed to be dried (using a convection oven at 40 °C) to a <9% fuel moisture content. For the high-intensity burns a heat gun was positioned 30 cm above the surface of the O horizon and aimed at the center of the circular form. The heated air increased the amount of oxygen reaching the combustion area, thereby increasing the intensity and temperature of burning. Heated air was supplied until completion of flaming combustion (approximately 30 minutes).

A heat-resistant, insulated circular form was used to stabilize and insulate the soil and fuelbed during burning. The temperature of the burns was monitored with three thermocouples connected to a datalogger that recorded temperature once every minute.

The thermocouples were placed on the surface of the O horizon at the interface of the O horizon and mineral soil (0 cm) and 2 cm into the mineral soil. The increase in heat content of the mineral soil profile was calculated by methods described in Raison *et al.* (1986). After burning, the soil columns were disassembled into O, A1 (0-1 cm) and A2 (1-2 cm). To control for additions of OM from the O horizon into the A horizon, control columns were also assembled, but not burned, and then dissassembled similarly to the burn treatments.

Soil analysis

The pH of all samples was measured using the saturated-paste method (Van Meigroet *et al.* 1994). Water repellency or hydrophobicity of each horizon was determined by measuring the amount of time that a 0.5 ml drop of water took to completely infiltrate the soil (Krammes and DeBano 1965). Subsamples of each horizon were ground and analyzed for C, H, and N concentration using a Perkin Elmer 2400 CHN analyzer. Carbon, H, and N concentrations were corrected for moisture content present in the air-dry samples. Whole soil samples were also measured for OM concentration by loss on ignition (LOI) in a muffle furnace (6 hours at 550 ^{o}C).

Soil organic matter was extracted pre- and post-incubation from each horizon (O, A1 and A2) using a method modified from Schnitzer (1982). Ten grams of mineral and 1 g of organic soil were extracted with 100 ml of 0.1 N NaOH under N_2. The solution was separated from the non-soluble residue using a centrifuge at a force of 6635*g* for 10 minutes. The residue contained humin and mineral material from the A horizons and non-soluble (NS) organic material, *e.g.,* lignin and cellulose, from the O horizons. The supernatant solution and one rinse containing the fulvic acid fraction and humic acid (HA) were collected for further processing. The residue which included humin and NS fractions was dried in a convection oven at 50 ^{o}C, weighed and prepared for loss on ignition (LOI; 550 ^{o}C for 6 hours) and C, H, and N analysis.

The supernatant containing the fulvic and humic acid fractions was acidified to pH 1 using 6N HCl and allowed to stand overnight to precipitate HA. The fulvic acid

fraction was also separated from HA by centrifuging at a force of 6635*g* for 10 minutes. Humic acid was freeze dried in a benchtop lypholizer, weighed, and stored in a light-protected dessicator.

Schnitzer (1982) defines the fulvic acid fraction as those materials that remain soluble after base extraction of soils and subsequent acidification. This fraction can contain a large component of materials that may not be classified as fulvic acid (FA) and could be affected by fire intensity. Fulvic acid was purified of salts and non-humic substances using a non-ionic resin (Malcolm 1990, Swift 1996). The solution containing the fulvic acid fraction was passed through a column containing 60 mL of DAX-8 resin (Supelco Supelite^{TM} DAX-8; methyl methacrylate ester). Fulvic acid adsorbs to the resin at a pH of 1. The soluble non-humic fraction (NH) was passed through the column along with 3 bed-volumes of deionized H_2O as a rinse, and was collected. Fulvic acid was desorbed by eluting the resin with 2 bed-volumes of 0.1 N NaOH; this material is identified as FA. Other hydrophobic materials (HO) remain adsorbed to the column after elution with 0.1 N NaOH The eluate containing FA was collected and passed over a column containing Dowex H^+ exchange resin to remove Na^+. The salt- and acid-free solution of FA was freeze dried, weighed, and stored in a light-protected dessicator. Prior to C, H, and N analysis, FA and HA samples were placed in pre-weighed tins and dried at 50° C for 48 hours. Humic acid and FA subsamples were analyzed for C, H, and N concentration.

Soluble non-humic materials and HO were not analyzed until a possible treatment effect on these fractions was determined during sample analysis. Therefore only one sample from each horizon and intensity level (12 samples) was collected and analyzed for NH and HO fractions. The solution containing NH materials was analyzed on a Shimadzu TOC/TN total organic carbon/nitrogen analyzer. The content of HO C and N was determined by difference using the following equation:

$$HO = T - R - HA - FA - NH \qquad (1)$$

where *HO* is the amount of other hydrophobic C or N that does not desorb from the DAX-8 resin column, *T* is the total soil C or N, *R* is C or N in the humin fraction (mineral soil) or non-soluble fraction (O horizon), *HA* is C or N from humic acid, *FA* is C or N from fulvic acid that desorbed from the DAX-8 resin column upon elution with 0.1 N NaOH, and NH is C or N from the soluble non-humic fraction. The other hydrophobic compounds (HO) that remain adsorbed to a DAX-8 resin column after elution with 0.1 N NaOH have been shown to have a large content of aliphatic groups and may be somewhat hydrophobic (Dai *et al.* 2006).

O and A horizons were analyzed for BC using a procedure adapted from the CTO375 method outlined by Gustafsson *et al.* (1997). This method uses the ability of BC to resist thermal oxidation at 375 ^{o}C. One gram or 0.1 g of A and O horizon, respectively, were weighed to 0.1 mg, placed in ceramic crucibles, and put into a preheated muffle furnace (375 ^{o}C). After 20 hours the samples were removed and weighed. Samples were subsequently returned to a preheated (550 ^{o}C) muffle furnace for loss on ignition to determine the amount of $LOI_{375\text{-}550}$ which would contain BC and black nitrogen (BN) using the formula:

$$\frac{LOI_{375-550}(g)}{S_i(kg)} = \left(\frac{A_{375}(g) - A_{550}(g)}{S_i(g)}\right) * \frac{1000g}{kg} \qquad (2)$$

where *A* is ash or residue after heating at 375 or 550 ^{o}C, and S_i is the initial amount of soil.

Nelson and Sommers (1982) recommend using a factor of 50% to convert SOM content of surface soils to C content. This ratio was confirmed by testing C and N on four O and four A1 horizon replicates from the high-intensity burn treatments after 20 hours in the muffle furnace at 375 ^{o}C. No significant difference ($p>0.05$), was found by t-test, between the ratios calculated from O and A1 horizons separately, so data from both horizons were pooled to develop one conversion rate. About half (50±17% (95% CI)) of $LOI_{375\text{-}550}$ was found to be BC, which agrees well with Nelson and Sommers (1982).

Black nitrogen accounted for 2±1% (95% CI) of $LOI_{375-550}$. The mass lost between muffle-furnace temperatures of 375 and 550 ^{o}C had a significant relationship ($p<0.05$) with BC and BN with r^2 values of 0.88 and 0.77, respectively. All samples were analyzed for $LOI_{375-550}$ so these data were used to assess statistical differences in this thermal-oxidation resistant fraction among the 3 burn treatments and unburned control. The mass lost between 375 and 550 ^{o}C converted to BC or BN was compared to other research regarding BC and BN.

Using this method, Vertisol and Mollisol BC standards from Australia were both found to have a BC concentration of 8 and 5 g kg^{-1} soil, respectively. During the BC Ring Trial conducted by the Black Carbon Steering Committee these soils were found to have very low BC concentrations of 0.1-1.3 g kg^{-1} soil and 0.2-1.6 g kg^{-1} soil for the Vertisol and Mollisol, respectively, when tested by the CTO375 method (Karen Hammes, unpublished data). The adapted method overestimated the BC concentration for the mineral-soil standards. Black carbon concentration was determined to be 2 g kg^{-1} when C analysis is conducted directly on the mineral-soil standards heated to 375 ^{o}C, which agrees well with the results from the BC Steering Committee. The significant linear relationship described above (r^2=0.88) suggests that the conversion rate between $LOI_{375-550}$ and BC is dependent on soil type. Charred-grass and wood standards prepared according to Hammes *et al.* (2006) were found to have BC concentrations of 6 and 1 g kg^{-1} sample, respectively, using the method described above. During the BC Ring Trial, these organic samples were found to have concentrations of 2.5-21 g BC kg^{-1} soil and 0.0 g BC kg^{-1} soil for the grass and wood samples, respectively (Karen Hammes, unpublished data). Thus, the adapted method agreed well with the results obtained for the organic samples.

Statistical analysis

O horizon and burn characteristics from four replicated burns and controls were tested with a one-factor ANOVA using burn intensity as the independent factor. Tukey's test for HSD was used to delineate homogeneous subsets.

A two-factor ANOVA was used to test the effect of burn intensity level and A horizon depth on soil characteristics. Burn intensity and horizon (A1 or A2) were the independent factors. If intensity was found to be a factor that was significantly different, then Tukey's HSD was used to define homogeneous subsets. If there was a significant interaction between horizon depth and intensity level, then the interaction was decomposed using pairwise contrasts. Pairwise contrasts were made on data between each depth at every burn intensity level (4 contrasts) and each intensity level at each depth (12 contrasts). Bonferrroni's procedure was used to reduce the chance of making a type I error below the α value of 0.05 when making simultaneous multiple comparisons.

O horizon residue mixed into the A1 horizon was determined by assuming that O horizon was incorporated at the same rate across all treatments. The average amount of O horizon incorporated into the A1 horizon of the unburned control (which would represent a maximum amount of O horizon incorporation) was calculated using:

$$O_{Ad} = \frac{OM_{A1} - OM_{A2}}{OM_{OC}} \tag{3}$$

where O_{Ad} is the average mass of unburned O horizon added to the A1 horizon (g O horizon kg^{-1} A1 horizon), $(OM_{A1}-OM_{A2})$ is the difference in OM content between the A1 and A2 horizon and is assumed to be the amount of OM added to the A1horizon (g OM kg^{-1} soil), and OM_{OC} is the average organic matter concentration of the unburned O horizon (g OM g^{-1} soil). This level of O horizon addition was assumed to be equal across all treatments and only the quality of the O horizon changed with treatment. To determine the average amount of C or N added the following formula was used:

$$C\,or\,N_{Ad} = C\,or\,N_{OT} * O_{Ad} \tag{4}$$

where $C\ or\ N_{Ad}$ is the average amount of C or N added to the surface A1 horizon due to O horizon incorporation (g C or N kg^{-1} A1 horizon) and $C\ or\ N_{OT}$ is the average C or N

concentration of O horizon at each intensity level (g C or N kg^{-1} O horizon). T-tests between the original concentrations and recalculated concentrations were conducted to determine if O horizon additions significantly increased C or N content of the A1 horizon. To be sure that statistical differences are captured, a higher rate of type I error was accepted by increasing the alpha value to 0.10 for these t-tests.

Results and Discussion

Laboratory burning

The three burn intensities showed increasing maximum temperature at the surface of the O and A1 horizon, and at 2 cm depth in the A2 horizon (Figure 2.1). The moisture content of the low intensity burn treatments caused the fires to burn cooler and extinguish on their own faster than the moderate- and high-intensity burn treatments. Heated air applied to the high-intensity burn treatments caused higher maximum temperatures, but it also consumed fuel (O horizon) faster than the moderate-intensity treatment. Each of the moderate-intensity burns smoldered for a long period of time, reaching high temperatures at varying points resulting in an inconsistent temperature profile. The average maximum temperature of the mineral soil did not exceed 300 ^{o}C, a temperature threshold at which structural changes to SOM take place (Gonzalez-Perez *et al.* 2004).

The mass of O horizon consumed increased with burn intensity so that nearly 80% was consumed by the high-intensity burn treatments (Table 2.1). Burning at moderate- and high-intensity levels caused the mineral soil to be darkened by ash and char that was incorporated into the soil and also by changes to the soil and SOM (Table 2.2). The release of energy by consumption of O horizon led to an increase in heat content of the top 2 cm of mineral soil, which was estimated to be 200 kJ m^{-2}, 600 kJ m^{-2} and 1000 kJ m^{-2} for the low-, moderate-, and high-intensity burns, respectively.

Post-fire assessments of fire severity are commonly made using qualitative guides such as the Composite Burn Index (CBI) (Key and Bensen 2006) and the classification system defined by Neary *et al.* (1999). Using both of these systems, the low- and moderate-intensity burns would be classified as low- and moderate-severity. Both

methods would classify the highest-intensity treatment between a moderate- and high-severity burn. If the mineral soil had been reddened and oxidized then both methods would have classified the high-intensity fire as a high-severity burn. Based on temperature and duration data these laboratory burns simulated fire severities and intensities of prescribed burns that would be typical in the understory of a ponderosa pine forest where there are few shrubs or coarse woody debris (*e.g.,* not under a slash pile or under a smoldering log) at low, moderate, and high-moderate severity levels.

O horizon

Carbon volatilizes and is combusted at lower temperatures than organic forms of N; therefore at lower fire intensities C will be preferentially consumed relative to N (DeBano *et al.* 1998, Baldock and Smernik 2002). As expected, the C:N ratio of the material combusted at low and moderate intensity was higher than the unburned O horizon (Table 2.1 and 2.2). The C:N ratio of material consumed at high intensity was not significantly different from the C:N ratio of the unburned O horizon, suggesting that C and N were consumed at the same rate during the high-intensity burns. Accordingly, the N content increased and C:N ratio of O horizons decreased with increasing fire intensity up to the moderate fire intensity (Table 2.2). Maximum temperature at the mineral-soil surface was significantly correlated with the C:N ratio of combusted O horizon material (R=-0.950, $p \leq 0.05$).

The SOM of the O horizon is dominated by non-soluble (NS) forms of C and N, which increases with increasing fire intensity (Figure 2.2). The total amount of C in the NS fraction of the O horizon decreased with burn intensity as a result of combustion (Table 2.3). Conversely, the proportion of NS C increased with burn intensity due to both an increase in C concentration within the NS fraction ($p_i=0.001$) and subsequent decrease in the proportion of the other SOM fractions. The reduction of FA and HA C concentration of the O horizon is about equal with each step in intensity, suggesting that combustion and transformation reactions did not discriminate between FA and HA. By

and large, the O horizon was primarily consumed and the remaining materials were converted to recalcitrant non-soluble materials, *e.g.*, charcoal.

Humic acid remaining may be made less bioavailable, while FA may be more bioavailable after burning. The C:H ratio of HA increased while the C:H ratio of FA was unaffected by burning (Table 2.4). Higher C:H ratios are associated with a higher degree of aromaticity and condensation, which may ultimately lead to lower bioavailability of HA. The C:N ratio of HA was unaffected by burning, while FA C:N decreased at moderate and high intensity. Changes in SOM quality may cause decomposer microbes to be more reliant upon FA with burning.

The soluble non-humic fraction (NH) C of the O horizon decreased with soil C concentration so that the proportion of NH C was not affected by burn intensity (Figure 2.2). Soluble organic carbon of wiregrass and longleaf pine needles was also shown to decrease with heating to 340 ^{o}C in a muffle furnace for 1 hour (Battle and Golladay 2003). The conversion of SOM to NS fractions may decrease the long-term availability of C while short-term C availability, on a per carbon basis, may remain unchanged due to the lack of effect on NH C as a proportion of total soil C.

The proportion of N as NS increased with burn intensity ($p=0.006$) probably as a result of preferential consumption of C relative to N, which leads to a decrease in the C:N ratio (Figure 2.2 and Table 2.4). Fulvic acid N is slightly more resistant to burning compared to HA N. At moderate and high intensity 78 and 94% of the HA N was consumed respectively while only 42 and 83% of the FA N was consumed. As a result C:N of HA was unaffected by burn intensity while FA C:N decreased (Table 2.4). This is similar to the results of Almendros *et al.* (1990) who found that at heating times below 1 minute at 350 ^{o}C HA was more susceptible to transformations affecting its solubility.

The increase in the proportion of recalcitrant forms of C and N, such as NS, with increasing fire intensity may allow recalcitrant materials to accumulate in the soil. Recalcitrant forms of C produced by fire may contribute to C sequestration (Kuhlbusch and Crutzen 1995) while recalcitrant forms of N may limit N availability (Guinto *et al.* 1999).

A horizon

Average O horizon incorporation into the A1 horizon of the control was 9 g O horizon kg^{-1} A1 horizon (Table 2.5). This rate of incorporation was assumed to be equal across all treatments. Only A1 horizons from control soils were significantly affected; nonetheless, there was always a small increase in nearly all C and N fractions for each treatment.

The incorporation of O horizon materials may be influencing pH and hydrophobicity of the A1 horizon even though there was not a significant rate of incorporation for the burn treatments. The pH of burned O horizons was higher than all A horizons while all O horizons had very high hydrophobicity that was always higher than A horizons (Table 2.2).

A horizon depth and intensity interacted significantly to affect soil pH. The A1 horizon showed an increase in pH with burn intensity especially at moderate and high intensity that could be due to incorporation of extremely alkaline materials from the burned O horizons or oxidation of organic matter neither of which appeared to occur in the A2 horizon (Table 2.2). Additionally, these soils were never exposed to precipitation so that the Na and K hydroxides that have been shown to be responsible for the exceedingly high pH in ash immediately after burning would still be present at the time of measurement (Ulery *et al.* 1993).

The water repellency of the soil, as measured by the amount of time it took for a drop of water to infiltrate the soil, was not affected by fire intensity in either the A1 or A2 horizon. However, the water repellency of the A1 was significantly higher than the A2 across all burn treatments. The incorporation of a small amount of very hydrophobic O horizon material into the surface mineral horizon occurred at all treatment levels. Furthermore, it is possible that there was some condensation of organic materials that may have increased the hydrophobicity of the A1 horizon during the moderate- and high-intensity burns.

The C concentration of both A horizons was unaffected by intensity of burn (Table 2.2). This suggests that any changes occurring to SOM composition in the mineral horizons will be due to SOM transformations and not consumption of C containing materials.

A horizon depth and burn intensity interacted significantly to affect N concentration and C:N ratio of both A1 and A2 horizons (Table 2.2). After the moderate- and high-intensity burn treatments there was a significant decrease in N concentration of the A2 horizon and a corresponding, but insignificant, increase in N concentration of the A1 horizons in those treatments. This is contradictory to the view that N is generally lost from mineral soils when heated or burned, after additions from the O horizon and litterfall are accounted for (DeBano *et al.* 1998, Neary *et al.*1999, Certini 2005). During the moderate- and high-intensity burns, the surface A horizon cooled faster than the lower A horizon, leaving the lower A horizon at a higher temperature than the upper A horizon for some portion of each burn after O horizon combustion had ceased (Figure 2.1). Nitrogen from the A2 horizon may have migrated into the A1 horizon in the form of volatile materials during the period of time that the temperature in the A2 horizon was higher than in the A1.

The proportion and total HO C increased with increasing intensity while humin C decreased ($p_i=0.119$) (Table 2.4 and Figure 2.2). The A1 horizon HA C and N content of the high-intensity burn also decreased while the A2 horizon remained unaffected causing a significant interaction with intensity and depth ($p_{i*d}=0.002$). Increasing fire intensity decreased the amount and proportion of humin C in both A1 and A2 horizons and the proportion of HA C and N of the A1 horizon of the high-intensity burn. This occurred despite a small amount of humin and HA C from the O horizon being mixed into the A1 horizon; humin C increases due to O horizon incorporation were only statistically significant at the control level. It appears as if SOM of the A1 horizon is becoming more labile at the expense of the more recalcitrant SOM fractions, HA and humin.

The increased HO may be due to thermal fragmentation, or destructive distillation, of long-chain aliphatic compounds which may be fractionated as HA or

humin in an unburned soil. Almendros *et al.* (1988) reports that there was a decrease in lipid chain length after wildfire. Fulvic and humic acids that remain adsorbed to a column of DAX-8 resin after elution with 0.1 N NaOH have been shown to have a large content of aliphatic groups and may be somewhat hydrophobic (Yonebayashi and Hattori 1990, and Dai *et al.* 2006). These fragmented aliphatic molecules may be colloidal sized and able to be extracted from the soil by 0.1 N NaOH and hydrophobic so that they are removed from the fulvic acid fraction by DAX-8 resin. Dai *et al.* (2006) also found that these substances had a clear amide presence in the FT-IR spectra which corresponds with the current study's finding that these substances provide a major proportion (10-34%) of total soil N (Figure 2.3).

The N containing HO substances in the A2 horizon appear to be most susceptible to losses, possibly by volatilization, which are then accumulating in the A1 horizon. These translocated HO materials may be raising the water repellency of the A1 horizon and increasing the N content of the A1 horizons at both the moderate- and high-intensity treatments. Water repellency of the A horizons was slightly correlated with the proportion of total soil C in the HO fraction (R=0.638, $p=0.089$). These HO compounds may be similar to the hydrophobic-neutral compounds defined by Lenheer (1981). Nitrogen containing hydrophobic-neutral compounds that may also be hydrophobic include chlorophyll and humic substances with <1 carboxylic group per 13 C atoms; however, it is not known whether any of these substances are volatile when heated (Thurman 1985, Qualls and Haines 1991, Doerr *et al.* 2000). In addition to thermal fragmentation and destructive distillation of humin and HA these labile substances may also have been derived from lysed microbe cells (*e.g.,* cell walls and nucleic acids) as suggested by Serrasolsas and Khanna (1995).

During SOM extraction microbes may be included in the humin and HA fractions and therefore could be the source for the increasing proportion of HO and decreasing humin and HA. If microbes remain associated with mineral surfaces during SOM extraction then they would be included in the humin fraction; if they are extracted by 0.1 N NaOH it is likely that they would precipitate with HA due to their electrostatic charge.

In the current study, the HO C increase in the high-intensity A1 horizon would account for 10% of the total soil carbon in the control. However, microbial C has been shown to account for 1 to 4% of the total C of forest soils in a Mediterranean environment (Hernandez *et al.* 1997, Prieto-Fernandez 1998); thus microbial biomass may only account for a small portion of the HO C released.

An additional hypothesis is that the mineralogy of the soil particles changed due to heating, thereby reducing the attraction of humin to mineral surfaces. Low fire severity has been shown to affect the mineralogy of tropical soils (Ketterings *et al.* 2000); however, it is unclear whether these changes would affect SOM attraction to mineral surfaces. It is possible that HO C is being derived from a combination of destructive distillation of humin or HA, microbial biomass, and change in mineralogy affecting SOM attraction to soil mineral surfaces.

Labile compounds may cause a flush of C and N mineralization from mineral soils as has been observed after fire (Fernandez *et al.* 1999, Choromanska and DeLuca 2002). Serrasolsas and Khanna (1995) report increased dissolved organic N (which may encompass HO N) after heating a soil to 120 ^{o}C. Soluble C (which may include HO C) has been seen to increase after heating mineral soil up to 500 ^{o}C (Battle and Golladay 2003, Guerrero *et al.* 2005). These authors attribute the release of soluble C and N to the release of microbial cell contents and destructive distillation of humic materials caused by heating (Serrasolsas and Khanna 1995, Battle and Golladay 2003, Guerrero *et al.* 2005). The increase in labile C at the expense of humin and HA may increase post-fire mineralization and reduce soil C content.

The amount of FA C decreased with increasing fire intensity which may have been caused by consumption and transformation reactions. Heat induced polymerization of labile materials such as FA has been shown to decrease their solubility through the reduction of O containing functional groups and ring formation (Almendros *et al.* 1990, Fernandez *et al.* 1997 and 2001, Gonzalez-Vila and Almendros 2003, Gonzalez-Perez *et al.* 2004). However, it is usually followed by an increase in HA or humin. Compared to the current study, previous research has used very severe heating or wildfire conditions.

Prescribed burning at low- to moderate-intensity levels may not be high enough intensity to cause reactions that create recalcitrant materials. There may be a threshold fire severity, above the severity achieved during the current study, at which mineral SOM is predominantly being altered by polymerization reactions and combustion.

Humin C:N ratio was significantly affected by depth due to O horizon additions in the A1 of the control while decreasing the C:N ratio of the A1 horizon from the moderate- and high-severity burns occurring as a result of fire intensity. The HA remaining after moderate- and high-intensity burning is less bioavailable due to a higher C:N and degree of aromaticity as measured by C:H. On the other hand, either N was converted to FA or FA was able to preserve N, which appears to have decreased its C:N ratio and improved its quality as a substrate for microbe growth. Similar to Almendros *et al.* (1990), FA C and N appear to be more resistant to fire intensity than humin and HA C and N in A horizons**.**

Higher burn intensity appears to be associated with an increase in labile materials that may increase post-fire mineralization and further reduce C storage in the soil. Fulvic acid appears to be more bioavailable after moderate- and high-intensity burning through a decrease in C:N ratio with burn intensity. The higher bioavailability of FA may cause a higher rate of post-burn C mineralization that would lower the C content of the soil further, and lead to higher nutrient availability.

Black carbon

The $LOI_{375\text{-}550}$ content of the O horizons increased with burn intensity and was positively correlated with the mass of O horizon consumed (R=0.800; $p \leq 0.05$) (Table 2.6). The $LOI_{375\text{-}550}$ was not affected by burning or depth of A horizon. The mineral soil, including control, has an average BC content of 6 g BC kg^{-1} soil and a BN content of 0.2 g kg^{-1} soil. Materials were converted to BC or BN in the O horizon but not in the A horizon, likely as the result of higher temperatures in the O horizon during burning.

The low and moderate intensity burns produced BC at a rate of 21 and 9 kg ha^{-1}, respectively; high intensity burns consumed much of the O horizon, and had an

undetectable production of BC in the entire profile. The production of BC in this study is much lower than that reported for a range of fire types, 61 to >20,000 kg BC ha^{-1} (as compiled by Preston and Schmidt 2006). This is in part due to the low fire intensity of these laboratory burns relative to fire intensities experienced during wildfires or slash burns. There was also very little woody material burned during this experiment which may be the principle source of most BC (Preston and Schmidt 2006).

Conclusions

The effects of fire on SOM and soil are dependent on fire intensity which varies across the landscape and seasons in ponderosa pine forests. Fires at varying intensity were reproduced in the laboratory and represented low- to moderate-severity level prescribed burns in the understory of a ponderosa pine stand. Increasing fire intensity increased the proportion of recalcitrant materials, *e.g.* charcoal, in the O horizon concurrent with other findings in the literature. The A horizon content of humin and HA decreased while HO content increased. Additionally, FA from the A horizons appears to be more bioavilable as the C:N ratio is lower. These results contrast with those of other studies that have examined high-severity heating or wildfire effects on SOM as most observed an increase in recalcitrant materials. Other studies used high-severity treatments that may have crossed a threshold at which mineral SOM is predominantly being altered by polymerization reactions and combustion. The intensity that these laboratory burns experienced may have changed the attraction of SOM to mineral surfaces, destructively distilled mineral soil humic materials, or released the contents of microbial cells. Polymerization reactions that could convert labile materials to more recalcitrant fractions did not dominate due to the low- to moderate-intensity fires. The increase in labile C and higher bioavailable SOM may be the source of increased C and N mineralization rates of the mineral soil often seen after fire. However, elevated levels of recalcitrant materials may protect the remaining C from decomposition.

Table 2.1 Proportion and C:N of organic matter combusted in the O horizon (mean±standard deviation) at three levels of fire intensity (n=4). p_i values are from a one-factor ANOVA (intensity as factor); significant values are in bold (α=0.05). Letters indicate similar subsets (columns) as determined by Tukey's HSD.

	Mass of O Horizon	Carbon	Nitrogen	C:N
	g g^{-1} initial soil			
Low	0.32 ± *0.13* [a]	0.37 ± *0.15* [a]	0.27 ± *0.19* [a]	99 ± *35*
Moderate	0.67 ± *0.08* [b]	0.78 ± *0.07* [b]	0.62 ± *0.12* [b]	76 ± *8*
High	0.80 ± *0.04* [b]	0.93 ± *0.00* [b]	0.88 ± *0.03* [c]	63 ± *2*
p_i	***0.000***	***0.000***	***0.000***	*0.090*

Table 2.2 Selected physical and chemical characteristics of O and A horizons (mean±standard deviation) from three levels of fire intensity and an unburned control (n=4). *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_d and p_{i*d})) factor ANOVA; significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*e,f,g* for A1 and *m,n* for A2). An * indicates A1 was significantly different from A2 at that treatment level. Hyd. indicates hydrophobicity.

O Horizon

	Control	Low	Moderate	High	p_i
Color (Moist)	5YR 4/4	5YR 3/2	10YR 2/1	N 3/	
Hyd. (sec)	1486 ± *626* ^{ab}	1901 ± *242* ^{a}	905 ± *93* ^{bc}	433 ± *316* ^{b}	***0.001***
pH	4.9 ± *0.4* ^{a}	7.2 ± *1.3* ^{b}	9.7 ± *0.2* ^{c}	10.5 ± *0.4* ^{c}	***0.000***
g C kg^{-1} soil	407 ± *5.5* ^{a}	414 ± *14* ^{a}	376 ± *16* ^{a}	226 ± *61* ^{b}	***0.000***
g N kg^{-1} soil	6.9 ± *0.5* ^{a}	8.1 ± *0.6* ^{a}	11 ± *0.7* ^{b}	6.5 ± *2.1* ^{a}	***0.001***
C:H	0.9 ± *0.3*	0.8 ± *0.2*	1.1 ± *0.3*	1.1 ± *0.1*	*0.324*
C:N	69 ± *6* ^{a}	60 ± *3* ^{a}	40 ± *2* ^{b}	42 ± *7* ^{b}	***0.000***

A Horizon

		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
Color (Moist)	A1	10YR 5/2	10YR 4/1.5	10YR 4/1	10YR 4/1			
	A2	10YR 5/2	10YR 5/2	10YR 5/2	10YR 5/2			
Hyd. (sec)	A1	45 ± *55* *	32 ± *32* *	21 ± *6* *	88 ± *106* *	*0.418*	***0.046***	*0.527*
	A2	17 ± *13* *	13 ± *12* *	10 ± *1* *	15 ± *16* *			
pH	A1	6.3 ± *0.2* ^{e}	6.5 ± *0.2* ^{f}	6.6 ± *0.1* ^{f*}	6.9 ± *0.1* ^{g*}	*0.001*	*0.000*	***0.000***
	A2	6.4 ± *0.1*	6.4 ± *0.1*	6.2 ± *0.0* *	6.4 ± *0.2* *			
g C kg^{-1} soil	A1	52 ± *3*	53 ± *7*	47 ± *4*	50 ± *4*	*0.454*	*0.438*	*0.740*
	A2	46 ± *3*	48 ± *8*	47 ± *5*	50 ± *5*			
g N kg^{-1} soil	A1	2.7 ± *0.2*	2.6 ± *0.2*	2.9 ± *0.2* *	2.9 ± *0.2* *	*0.887*	*0.089*	***0.003***
	A2	2.9 ± *0.0* ^{m}	2.7 ± *0.5* ^{mn}	2.4 ± *0.2* ^{n*}	2.4 ± *0.1* ^{n*}			
C:N	A1	23 ± *0* ^{ef*}	24 ± *2* ^{e}	19 ± *1* ^{f*}	20 ± *1* ^{f*}	*0.106*	*0.289*	***0.000***
	A2	19 ± *1* ^{m*}	21 ± *5* ^{mn}	23 ± *1* ^{n*}	24 ± *2* ^{n*}			

Table 2.3 Total soil C and N concentration of each SOM fraction (mean±standard deviation) from three levels of fire intensity and an unburned control (n=4 unless NH or HO then n=1). *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_d and p_{i*d})) factor ANOVA; significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b,c,d*) or pairwise contrasts (*e,f* for A1). An * indicates A1 was significantly different from A2 at that treatment level. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

O Horizon

	Control	Low	Moderate	High	p_i
g NS C kg^{-1} soil	300 ± *15* [a]	328 ± *33* [a]	332 ± *25* [a]	183 ± *44* [b]	***0.000***
g HA C kg^{-1} soil	62.6 ± *9.4* [a]	45.7 ± *11* [b]	14.7 ± *4.4* [c]	2.9 ± *3.2* [c]	***0.000***
g FA C kg^{-1} soil	18.2 ± *1.7* [a]	13.9 ± *2.1* [b]	4.8 ± *0.8* [c]	1.1 ± *0.8* [d]	***0.000***
g HO C kg^{-1} soil	ND	ND	ND	24	
g NH C kg^{-1} soil	43	32	29	15	
g NS N kg^{-1} soil	4.2 ± *0.8* [a]	5.7 ± *0.7* [a]	9.2 ± *0.7* [b]	5.2 ± *1.5* [a]	***0.000***
mg HA N kg^{-1} soil	2020 ± *445* [a]	1490 ± *629* [a]	453 ± *68* [b]	118 ± *161* [b]	***0.000***
mg FA N kg^{-1} soil	180 ± *50* [a]	171 ± *55* [a]	105 ± *15* [b]	26 ± *17* [b]	***0.000***
mg HO N kg^{-1} soil	ND	ND	72	690	
mg NH N kg^{-1} soil	1149	752	1333	469	

Table 2.3 is continued on the next page.

Table 2.3 Continued

		A Horizon						
		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
g Humin C	A1	35.5 ± *3.1* ^{ab*}	36.5 ± *4.3* ^{a*}	28.8 ± *1.8* ^{b*}	28.8 ± *5.0* ^{ab*}	***0.016***	***0.054***	*0.447*
kg^{-1} soil	A2	32.1 ± *2.6*	32.1 ± *3.8*	29.7 ± *2.2*	29.4 ± *2.8*			
g HA C	A1	7.2 ± *1.1* ^{e}	7.1 ± *1.2* ^{e}	6.8 ± *0.9* ^{e}	4.4 ± *1.0* ^{f*}	*0.028*	*0.192*	***0.001***
kg^{-1} soil	A2	6.2 ± *1.1*	6.7 ± *0.4*	7.2 ± *0.4*	7.1 ± *0.3* *			
g FA C	A1	1.3 ± *0.2* *	1.4 ± *0.4* *	1.3 ± *0.2* *	1.1 ± *0.1* *	*0.108*	***0.002***	*0.528*
kg^{-1} soil	A2	1.0 ± *0.1* *	1.0 ± *0.1* *	1.1 ± *0.1* *	1.0 ± *0.2* *			
g HO C kg^{-1} soil	A1	5	4	9	10			
	A2	1	2	6	10			
g NH C	A1	3	4	1	2			
kg^{-1} soil	A2	5	6	3	3			
g Humin N	A1	1.2 ± *0.1*	1.3 ± *0.2*	1.2 ± *0.2*	1.3 ± *0.1*	*0.417*	*0.303*	*0.855*
kg^{-1} soil	A2	1.4 ± *0.3*	1.4 ± *0.1*	1.2 ± *0.1*	1.4 ± *0.2*			
mg HA N	A1	437 ± *44* ^{e}	425 ± *77* ^{e}	406 ± *69* ^{e}	256 ± *64* ^{f*}	*0.016*	*0.063*	***0.002***
kg^{-1} soil	A2	385 ± *66*	419 ± *29*	440 ± *25*	428 ± *23* *			
mg FA N	A1	36.3 ± *6.6* ^{a}	36.2 ± *11* ^{ab}	47.3 ± *7.3* ^{ab}	41.3 ± *4.0* ^{b}	***0.006***	*0.383*	*0.629*
kg^{-1} soil	A2	29.2 ± *4.8*	29.1 ± *2.3*	32.5 ± *1.8*	36.4 ± *15*			
mg HO N	A1	810	580	930	1000			
kg^{-1} soil	A2	930	600	470	230			
mg NH N	A1	189	191	335	292			
kg^{-1} soil	A2	135	244	196	348			

Table 2.4 Ratios of C:N and C:H of SOM fractions (mean±standard deviation) from three levels of fire intensity and an unburned control (n=4 unless NH or HO then n=1). *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_d and p_{i*d})) factor ANOVA; significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b*) or pairwise contrasts (*e,f* for A1). An * indicates a significant difference between the two A horizons at that burn intensity. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

O Horizon

	Control	Low	Moderate	High	p_i
C:H NS	0.8 ± *0.1*	0.8 ± *0.1*	0.8 ± *0.0*	0.9 ± *0.1*	*0.294*
C:N NS	86 ± *17* ^{a}	68 ± *9* ^{a}	42 ± *3* ^{b}	42 ± *6* ^{b}	***0.000***
C:H HA	0.8 ± *0.0* ^{a}	0.9 ± *0.2* ^{a}	1.0 ± *0.1* ^{a}	1.9 ± *0.6* ^{b}	***0.002***
C:N HA	37 ± *5*	38 ± *7*	37 ± *6*	39 ± *22*	*0.990*
C:H FA	0.9 ± *0.0*	0.9 ± *0.1*	1.0 ± *0.1*	0.9 ± *0.1*	*0.206*
C:N FA	123 ± *23* ^{a}	99 ± *19* ^{a}	54 ± *8* ^{b}	44 ± *13* ^{b}	***0.000***
C:N HO	0	0	0	35	
C:N NH	38	43	21	33	

A Horizon

		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
C:N Humin	A1	34 ± *4* *	32 ± *1* *	28 ± *5* *	28 ± *2* *	*0.123*	***0.005***	*0.198*
	A2	28 ± *4* *	27 ± *3* *	28 ± *1* *	26 ± *3* *			
C:H HA	A1	0.8 ± *0.0* ^{e}	0.8 ± *0.1* ^{e}	1.0 ± *0.0* ^{f*}	1.0 ± *0.0* ^{f*}	*0.000*	*0.000*	***0.002***
	A2	0.8 ± *0.1*	0.8 ± *0.1*	0.8 ± *0.0* *	0.8 ± *0.1* *			
C:N HA	A1	19.2 ± *1.0* *	19.6 ± *0.3* *	19.7 ± *0.8* *	20.0 ± *0.5* *	*0.075*	***0.004***	*0.949*
	A2	18.6 ± *0.3* *	18.8 ± *0.5* *	19.1 ± *0.3* *	19.4 ± *0.3* *			
C:H FA	A1	1.0 ± *0.1*	1.0 ± *0.1*	1.0 ± *0.1*	1.0 ± *0.1*	*0.673*	*0.908*	*0.064*
	A2	1.0 ± *0.1*	1.1 ± *0.1*	0.9 ± *0.0*	1.0 ± *0.1*			
C:N FA	A1	42 ± *3* ^{a}	44 ± *6* ^{a}	33 ± *2* ^{ab}	30 ± *2* ^{b}	***0.000***	*0.196*	*0.222*
	A2	42 ± *5*	42 ± *2*	40 ± *1*	35 ± *10*			
C:N HO	A1	6	8	10	10			
	A2	1	3	13	42			
C:N NH	A1	17	19	2	7			
	A2	40	26	15	8			

Table 2.5 Carbon and N additions to A1 horizons by incorporation of O horizon residue at three levels of fire intensity and an unburned control (Equations 3 and 4). A1 horizons with and without O horizon (calculated by difference) additions were tested (t-test) against one another to determine if additions significantly increased the C or N content; significant differences are in bold (α=0.10). Only the control soils were affected by O horizon incorporation. Little significant effect from O horizon incorporation was experienced by the A1 horizon of burn treatments as a result of combustion. Abbreviations are: HA=humic acid and FA=fulvic acid.

	Control	Low	Moderate	High
	----------	g O Horizon C or N kg^{-1} A1 Horizon		----------
Carbon	**3.8**	3.9	3.5	2.1
Humin C	**2.8**	3.1	3.1	1.7
HA C	0.6	0.4	0.1	ND
FA C	**0.2**	0.1	ND	ND
Nitrogen	0.1	0.1	0.1	0.1
Humin N	ND	0.1	0.1	ND
	----------	mg O Horizon N kg^{-1} A1 Horizon		----------
HA N	19	14	4.2	1.1
FA N	1.7	1.6	1.0	ND

Table 2.6 Mass lost between muffle-furnace temperatures of 375 and 550 ^{o}C ($LOI_{375-550}$) for O and A horizons (mean±standard deviation) treated to three levels of fire intensity and an unburned control (n=4). These values have been converted to black carbon (BC) and black nitrogen (BN) by multiplying $LOI_{375-550}$ by 0.50 g BC g^{-1} $LOI_{375-550}$ and 0.02 g BN g^{-1} $LOI_{375-550}$, respectively. *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_d and p_{i*d})) factor ANOVA, significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b,c*).

		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
g $LOI_{375-550}$ kg^{-1} soil	O	2 ± *1* [a]	5 ± *2* [b]	9 ± *0* [c]	10 ± *1* [c]	***0.000***		
	A1	14 ± *3*	11 ± *2*	13 ± *1*	12 ± *2*	*0.474*	*0.899*	*0.946*
	A2	12 ± *2*	11 ± *2*	13 ± *1*	12 ± *2*			
g BC kg^{-1} soil	O	0.9	2.6	4.7	5.0			
	A1	7.2	5.7	6.3	6.0			
	A2	5.9	5.5	6.3	5.9			
g BN kg^{-1} soil	O	0.0	0.1	0.2	0.2			
	A1	0.3	0.2	0.3	0.2			
	A2	0.2	0.2	0.3	0.2			

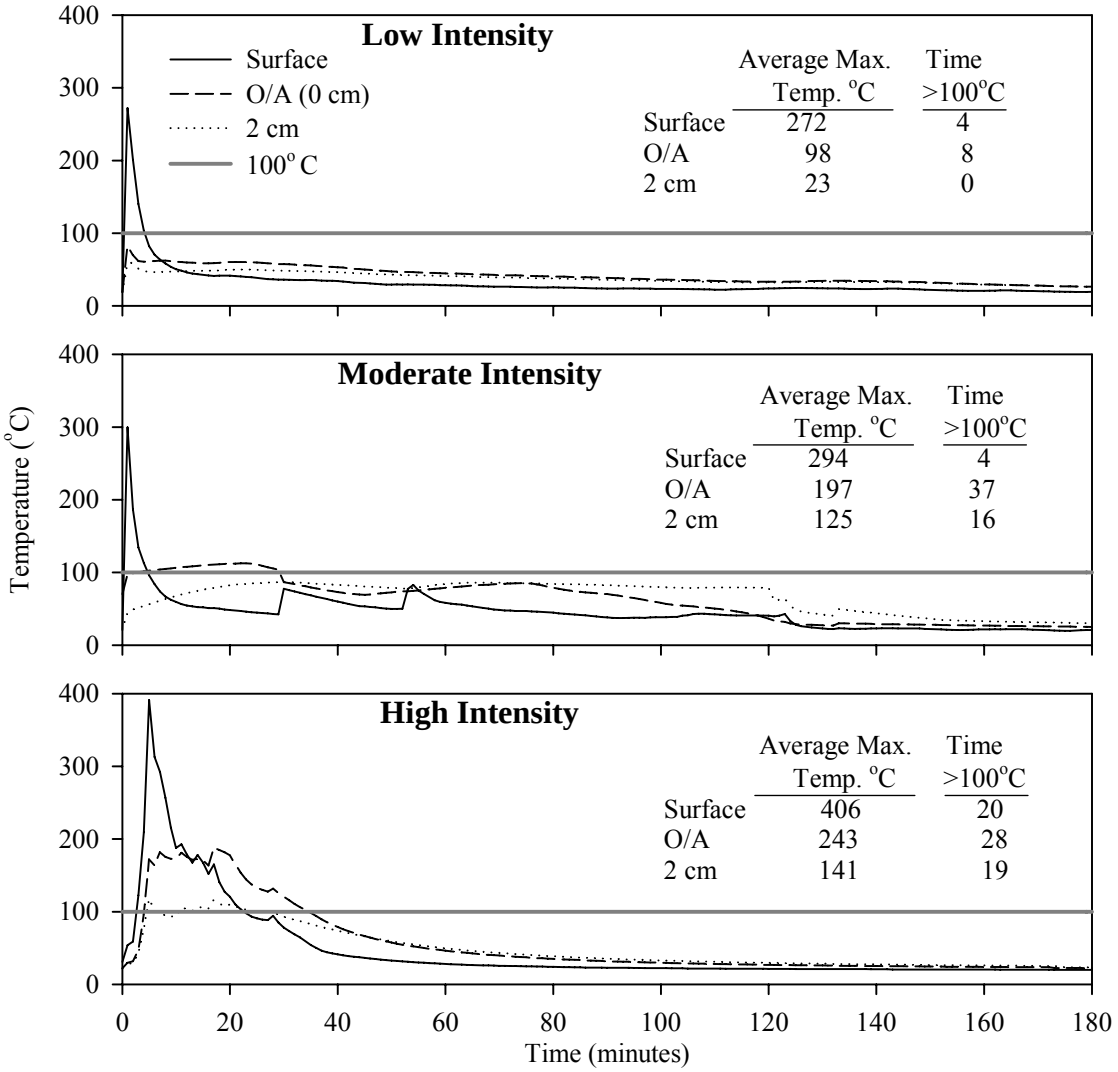


Figure 2.1 Temperature profiles of soils burned at low, moderate, and high intensity in the laboratory. Profiles are average values calculated at each time step (1 minute) from 4 replicated burns at each intensity. Temperatures were measured at the surface of the O horizon (O), interface of the O and A horizons (O/A) and 2 cm into the A horizon. The moderate-intensity burns smoldered for the longest leading to the inconsistent temperature readings during the later stages of burning as compared with the low- and high-intensity burns.

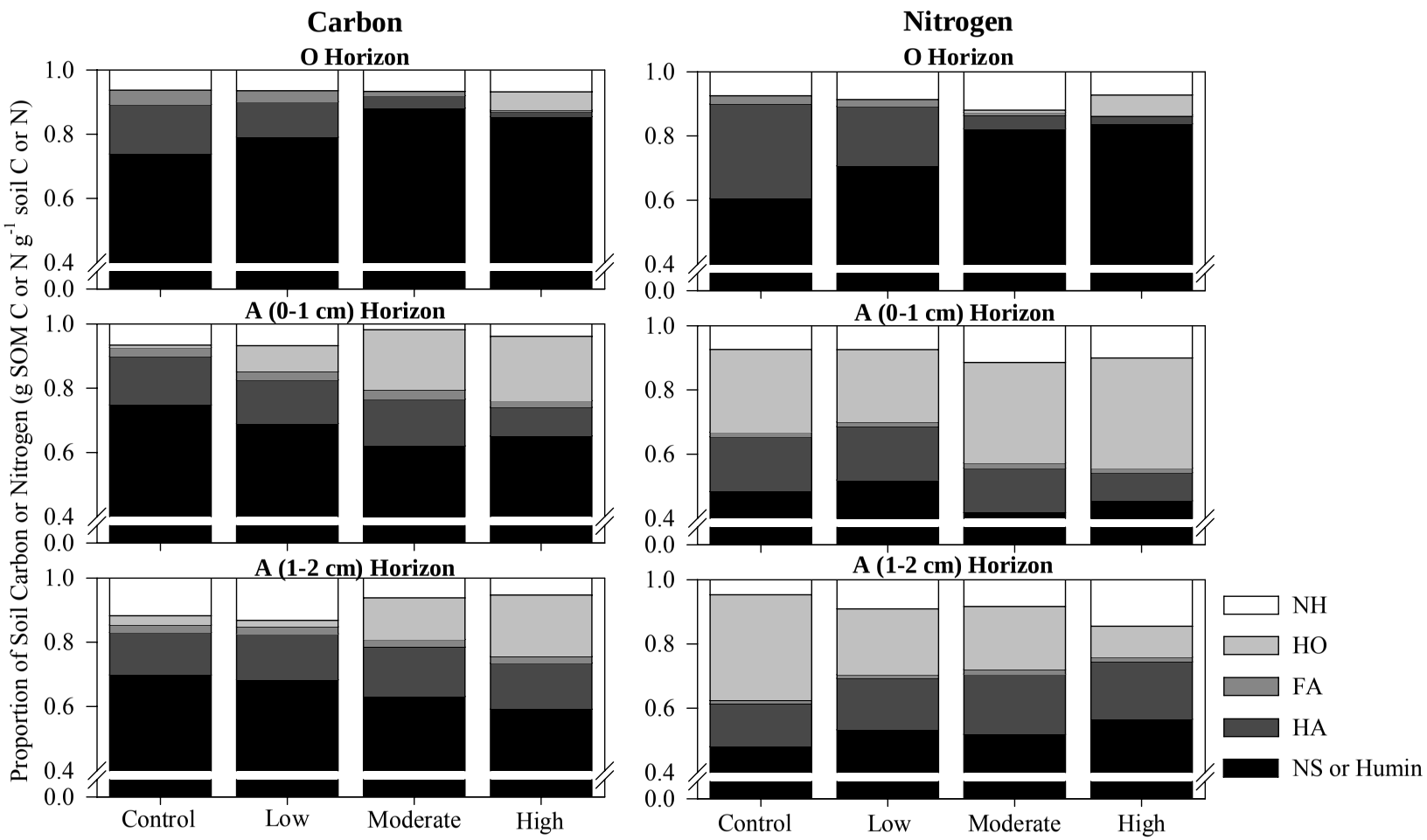


Figure 2.2 Proportion of SOM C or N of O and A horizon C or N with 3 levels of burn intensity and an unburned control (n=4). Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

Chapter 3
Fire Intensity Effects on Soil Carbon Mineralization and Products of Decomposition

Introduction

Soil organic matter (SOM) is one of the largest pools of carbon (C) on the Earth's surface accounting for 2344 Pg of global C (Jobbagy and Jackson 2000). Fire is a naturally occurring process that alters terrestrial C cycling. The direct effect of fire on the soil is a loss of C as combustion products. A portion of the SOM remaining after fire is often transformed to forms which are chemically and biologically recalcitrant, *e.g.,* black carbon (BC), and may contribute to long-term C storage in soils (Kuhlbusch and Crutzen 1995). The magnitude of transformations occurring to SOM is dependent on fire intensity.

Fire intensity has been defined as the rate of energy released by an individual fire or the temperature of the burning environment (White and Pickett 1985, Neary *et al.* 1999). The amount of material consumed and nutrients lost from soil through volatilization is dependent on temperature (Raison *et al.* 1984a). Therefore, the effect that fire has on soils and SOM is largely dependent on fire intensity. A related term, fire severity, has been broadly defined as the qualitative impact of fire on the soil and water system, atmosphere, and society and has been used to describe individual fires and fire regimes (Simard 1991, Agee 1993, Neary *et al.* 1999).

Soil organic matter includes both humic and non-humic organic substances associated with organic and mineral soil. Non-humic substances are generally any materials that can be identified and classified. Humic substances are refractory, dark colored, heterogenous organic compounds, produced as byproducts of microbial metabolism (Stevenson 1994). The function of SOM is largely dependent on its molecular size and oxygen content. While SOM solubility is inversely related to molecular size, solubility and CEC are positively related to oxygen content.

Operational definitions have been developed to define classes of SOM based upon an alkaline extraction and subsequent solubility in an acidic solution. Of these classes, humin is composed of the largest molecules and has the greatest degree of aromaticity and the lowest concentration of oxygen (Stevenson 1994). Humic acid (HA) is extracted by an alkaline extractant but precipitates when the solution pH is lowered to 1 and is relatively immobile in soils. The fulvic acid fraction is extracted by an alkaline solution and soluble in a subsequent acidic condition. Fulvic acids are often purified from saccharides, low molecular weight organic acids, and inorganic salts through the use of a nonionic XAD-8 resin (Malcolm 1990 and Swift 1996). Soluble non-humic (NH) materials do not adsorb to the XAD-8 resin, while fulvic acids adsorb to the resin at a pH of 1 (Leenheer 1981).

Black carbon (BC) is composed of organic compounds that often get included into the insoluble humin fraction. Black carbon is the heterogeneous, aromatic and carbon-rich residue of biomass burning and fossil-fuel combustion following a continuum from charcoal, soot, to graphite (Goldberg 1985). The continuum of BC materials increases in aromaticity, condensation, C:H, and C:O with charcoal < soot < graphite. Charcoal is often part of the ash and residue remaining after burning. Soot forms in the gaseous phase and is easily transported from a fire site by wind. Graphite is usually geologically formed and not created by fire.

Soil organic matter is responsible for nutrient retention in soils including CEC (Stevenson 1994). Additionally, it is also a reservoir of available nutrients that are ready to be mineralized by microorganisms. The availability and accessibility of SOM to microorganisms is dependent on its nutrient content, chemical structure, and physical protection within the soil (Baldock and Skjemstad 2000, Baldock and Smernik 2002, Kelleher *et al.* 2006). Lignin, waxes, and highly condensed and aromatic substances such as charcoal are less bioavailable (Shneour 1966, Baldock and Skjemstad 2000, Kelleher *et al.* 2006).

Fire effects on carbon mineralization

In large part, the effects of fire on soil properties and processes are the result of direct changes in the quantity and quality of SOM. Fire consumes and alters organic matter (OM) at the surface through the processes of combustion. Consumption of OM by fire is often incomplete and BC is produced. A portion of the energy produced from the burning of OM penetrates the mineral soil and may alter SOM. In general the chemical changes that occur in SOM after heating and combustion are increases in aromatic structures and disproportionate losses of H and O relative to C (Almendros 1990, Baldock and Smernick 2002, Almendros *et al.* 2003, Gonzalez-Vila and Almendros 2003, Gonzalez- Perez *et al.* 2004, Knicker *et al.* 2005). Increased heating of soil has been shown to decrease the oxygen content of the SOM, thereby reducing fulvic acid and HA fractions while increasing humin content and aromaticity, indicating greater recalcitrance and lower bioavailability (Almendros *et al.* 1990, Fernandez *et al.* 1997, 2001, and 2004). Additionally, Fritze *et al.* (1998) demonstrated a possible toxic effect of dissolved organic C extracted from burned humus on C mineralization. Due to the changes in decomposition rates of fire-affected SOM, fire may be a process by which C can be sequestered into the soil (Kuhlbusch and Crutzen 1995).

Mineral soil C decomposition after fire has been shown to be more complex. Some authors have noted that there is a flush of C and N mineralization after burning, but that over time less C is mineralized from burned soils (Bauhus *et al.* 1993, Fernandez *et al.* 1999, Choromanska and DeLuca 2002). The flush of C mineralization has been attributed to the release of soluble organics from microbial biomass (Choromanska and DeLuca 2002). Carbon mineralized on a mass basis (g CO_2-C kg^{-1} soil) has been shown to decrease after burning due to a reduction of total soil C (Fernandez *et al.* 1997, 1999, and 2004). When adjusted for C lost through burning, remaining C appears to be more labile with burned soil C mineralization increasing after burning (Fernandez *et al.* 1997, 1999). Soils collected from the field have shown increases in C mineralization due to incorporation of fire-induced litter fall (Almendros *et al.* 1990, Fernandez *et al.* 1999). Guerrero *et al.* (2005) showed that as mineral soils are heated to 500 ^{o}C the proportion of

C mineralized increases. The increase in C mineralization was attributed to a release of labile organic materials from microbial biomass while the downturn in mineralization that occurred above 500 ^{o}C was caused by decreased total C and the production of recalcitrant materials. Decreases in C mineralization appear to occur at relatively high heating or fire severity, which is where most research regarding fire severity and whole soil has occurred. There has been very little research characterizing SOM behavior after low- to moderate-intensity fire.

This study examined the effect of increasing fire intensity on C mineralization and SOM forms by incubating soils treated to escalating fire intensity. The objective was to determine how fire intensity affects mineralization rates of both organic and surface mineral soils. Results are presented in conjunction with pre-incubation SOM quality data to examine factors controlling C mineralization rates of fire-affected organic and mineral soils.

Materials and Methods

Laboratory burning

Laboratory burns were designed to represent prescribed fire in the understory of a ponderosa pine forest and are described in Chapter 2. Clay-loam textured soil samples were collected from the Dinkelman soil series (Vitrandic Haploxeroll) beneath a ponderosa pine (*Pinus ponderosa* Laws.) tree in a Douglas-fir (*Pseudotsuga menziesii* (Mirbel) Franco)/ ponderosa pine forest located near Cashmere, Washington on the east side of the Cascade Mountain Range (47°27’00”N/ 120°37’54”W; 1070 m elevation). O and A horizons were collected, air-dried, and homogenized.

Soil columns were assembled into O (6 cm), A1 (0-1 cm) and A2 (1-2 cm) horizons at bulk densities that were similar to the soil at the collection site. Fire intensity was controlled by adjusting fuel moisture and applying heated air to the surface of the O horizon. O horizon with an 18% moisture content was used during the low-intensity treatments while 9% moisture content was used for moderate- and high-intensity treatments. To achieve the highest-intensity burns a heat gun was positioned 30 cm

above the surface of the O horizon. The temperature of the burns was monitored with three thermocouples positioned at the surface of the O and A1 and 2 cm into the A2 horizon. Thermocouples were connected to a datalogger that recorded temperature once every minute. Pre-incubation laboratory burn conditions and soil characteristics are summarized in Tables 3.1 and 3.2.

Incubation

Following laboratory burns O and A horizons were incubated at 24 ^{o}C for 180 days to determine the effect of burn intensity on the decomposition characteristics of SOM present after burning. One hundred grams of air-dried mineral soil or 10 g of organic soil was placed into a 2 L canning jar. Inoculating solution was produced by shaking 400 g of soil with 4 L of deionized water for 24 hours. The solution was separated from the residual soil using qualitative filter paper with a vacuum applied to a Buchner funnel. A horizons were moistened with enough inoculating solution to bring the moisture content to 35% gravimetric moisture content (*ca.* 85% of field capacity) while the O horizons were moistened with solution to achieve 100% gravimetric moisture content. Approximately 35 ml and 10 ml of inoculant were added to organic and mineral soils respectively.

Carbon mineralization was analyzed using soda-lime traps as described by Zibilske (1994). A pre-weighed 50 ml beaker filled with 30 g of oven-dried soda-lime was placed onto a stand elevated above the sample. The 2 L canning jar was capped with an air-tight lid. At the end of each measurement period soda-lime traps were removed, oven dried, and weighed to determine the amount of CO_2 adsorbed. For the first four weeks, soda-lime traps were analyzed and replaced weekly. Gasses in the incubation vessel were renewed by removing the lid for at least 15 minutes and allowing a fan to circulate air over the chambers. At the time of gas exchange, soil gravimetric moisture content was brought up to 35 and 100% for mineral and organic horizons, respectively, using deionized water. The frequency of trap exchange lengthened to two weeks and eventually to four weeks. However, gas exchange always occurred at least every two

weeks. A blank jar and soda-lime trap was used to determine the quantity of CO_2 absorbed from the atmosphere while conducting the experiment. Soda-lime traps were replaced once any trap increased its initial mass by 6% (mean of 2.4% across all traps). The adjusted weight gain of each soda-lime trap was multiplied by 1.69 moles CO_2 mole^{-1} $CaCO_3$ to correct for $CaCO_3$ produced and H_2O evaporated during drying (Grogan, 1998). The CO_2 absorbed was converted to CO_2-C by multiplying CO_2 absorbed by 0.273 g C g^{-1} CO_2 using the following formula:

$$\frac{CO_2 - C}{Soil} = W_{SL} * 1.69 * 0.273 \qquad (1)$$

where *CO_2-C/ Soil* is the blank corrected carbon adsorbed as CO_2 to a soda-lime trap as a proportion of soil mass and W_{SL} is weight gained by the soda-lime trap. And to calculate CO_2-C as a proportion of total soil C the following formula was used:

$$\frac{CO_2 - C}{C_S} = \frac{W_{SL} * 1.69 * 0.273}{C_S} \qquad (2)$$

where *CO_2-C/ C_S* is the blank corrected carbon adsorbed as CO_2 to a soda-lime trap as a proportion of total soil C and C_S is total soil C. Average cumulative CO_2-C on a per soil basis released over time for each horizon at each severity was fitted to a double-exponential model proposed by Andren and Paustian (1987):

$$\frac{CO_2 - C}{Soil} = C_L(1 - e^{-k_L t}) + (C_S - C_L)(1 - e^{-k_R t}) \qquad (3)$$

where C_L is the initial amount of total C as labile C in the substrate, k_L is the rate constant for labile C, *(1-C_L)* is the amount of C in a recalcitrant pool, k_R is the rate constant for the recalcitrant pool and t is time in days.

The following equation was used to model cumulative CO_2-C released over time as a proportion of total soil C:

$$\frac{CO_2 - C}{C_S} = \frac{C_L}{C_S}(1 - e^{-k_L t}) + (1 - \frac{C_L}{C_S})(1 - e^{-k_R t}) \quad (4)$$

where $(1\text{-}C_L/C_S)$ is the proportion of total soil C in a recalcitrant pool. The double-exponential model allows the comparison of a system with materials that decompose at 2 different rates, providing a labile and a recalcitrant pool. Since fire and heat may be converting labile material into recalcitrant forms this model has been found to be more appropriate than the single-compartment first-order model which would imply that all components of the substrate decompose at one average rate (Fernandez *et al.* 1997, 2004, Rasmussen *et al.* 2006). For comparison the cumulative CO_2-C mineralized as a proportion of soil C will be fitted to a single-parameter model:

$$\frac{C_T}{C_S} = 1 - e^{-k\,t} \quad (5)$$

where k is a single-pool decomposition constant.

To compare the proportion of C remaining after burning and incubation the proportion of initial C remaining in the entire profile (O, A1, and A2 horizons) was fit to the following double-exponential model adapted from Andren and Paustian (1987):

$$\frac{C\,remaining}{C_S} = 1 - \left(\frac{C_L}{C_S}(1 - e^{-k_L t}) + (1 - \frac{C_L}{C_S})(1 - e^{-k_R t}) \right) \quad (6)$$

The proportion of initial C remaining after burning and incubation in the entire profile from each treatment was fit to this model to determine if slower decomposition rates of fire-produced SOM can overcome C lost to combustion.

Non-linear parameter estimation by each intensity, horizon, and replicate (n=4 for each combination of intensity and horizon) was determined using SPSS 10.1.3. The Levenberg-Marquardt procedure of parameter estimation was used. Convergence was obtained by the iterative minimization of the residual sum of squares to within the absolute value of $1x10^{-8}$. Initial parameter values for k_L and k_R were 0.1 and 0.0001 while C_L was initialized at the maximum CO_2-C mineralized for the particular treatment. To avoid errors due to convergence on local minima, parameter estimates were used after they were found to converge on the same values given initialization values 50% above and below (Updegraff *et al.* 1995). The r^2 values of the single-parameter model and double-exponential model were used to compare the fit of each to the cumulative CO_2-C data. The above procedure was used to estimate the parameters for each replicate in order to calculate means and standard deviations by treatment and horizon.

The mean residence times of the labile and recalcitrant pools were calculated using the following equation:

$$\tau = \frac{1}{k_L \; or \; k_R} \tag{7}$$

where τ is the mean residence time. The mean lifetime of the labile pool will be used to determine the period of time that the labile or recalcitrant materials dominate C mineralization. Short-term C mineralization will be defined as the period of time from the initiation of incubation (day 0) to the end of the period of time equal to the calculated mean residence time of the labile pool. Long-term C mineralization will be designated as the remainder of the incubation period.

Soil analysis

Soil pH of all samples was measured prior to incubation using the saturated paste method (Van Meigroet *et al.* 1994). Water repellency or hydrophobicity of each horizon pre-incubation was determined by measuring the amount of time that a 0.5 ml drop of

water took to completely infiltrate the soil (Krammes and DeBano 1965). Subsamples of each horizon from pre- and post-incubation were ground and analyzed for C, H, and N concentration using a Perkin Elmer 2400 CHN analyzer. Carbon, H, and N concentrations were adjusted for moisture content present in the air-dry samples.

Soil organic matter was extracted pre- and post-incubation from each horizon (O, A1 and A2) using a method modified from Schnitzer (1982). Ten grams of mineral and 1 g of organic soil were extracted with 100 ml of 0.1 N NaOH under N_2. The solution was separated from the non-soluble residue using a centrifuge at a force of 6635*g* for 10 minutes. The residue contained humin and mineral material from the A horizons and non-soluble (NS) organic material, *e.g.,* lignin and cellulose, from the O horizons. The supernatant solution and one rinse containing the fulvic acid fraction and humic acid (HA) were collected for further processing. The residue, that included the humin and NS fractions, was dried in a convection oven at 50 ^{o}C, weighed and prepared for loss on ignition (LOI; 550 ^{o}C for 6 hours) and C, H, and N analysis.

The supernatant containing the fulvic acid fraction and HA was acidified to pH 1 using 6N HCl and allowed to stand overnight to precipitate HA. The fulvic acid fraction was separated from HA by centrifuging at a force of 6635*g* for 10 minutes. Humic acid was freeze dried in a benchtop lypholizer, weighed, and stored in a light-protected dessicator.

Schnitzer (1982) defines the fulvic acid fraction as those materials that remain soluble after base extraction of soils and subsequent acidification. This fraction can contain a large component of materials that may not be classified as fulvic acid (FA) and could be affected by fire intensity. Fulvic acid was purified of salts and non-humic substances using a non-ionic resin (Malcolm 1990, Swift 1996). The solution containing the fulvic acid fraction was passed through a column containing 60 mL of DAX-8 resin (Supelco Supelite^{TM} DAX-8; methyl methacrylate ester). Fulvic acid adsorbs to the resin at a pH of 1 while the soluble non-humic fraction (NH) passed through. The column was rinsed with 3 bed-volumes of deionized H_2O which was combined with the NH fraction. Fulvic acid was desorbed by eluting the resin with 2 bed-volumes of 0.1 N NaOH; this

material is identified as FA. Other hydrophobic materials (HO) remain adsorbed to the column after elution with 0.1 N NaOH The eluate containing FA was collected and passed over a column containing Dowex H^+ exchange resin to remove Na^+. The salt- and acid-free solution of FA was freeze dried, weighed, and stored in a light-protected dessicator. Prior to C, H, and N analysis, FA and HA samples were placed in pre-weighed tins and dried at 50° C for 48 hours. Humic acid and FA subsamples were analyzed for C, H, and N concentration.

The solution containing NH was analyzed on a Shimadzu TOC/TN total organic carbon/nitrogen analyzer. The content of HO C and N was determined by difference using the following equation:

$$HO = T - R - HA - FA - NH \tag{8}$$

where *HO* is the amount of other hydrophobic C or N that does not desorb from the DAX-8 resin column, *T* is the total soil C or N, *R* is C or N in the humin fraction (mineral soil) or non-soluble fraction (O horizon), *HA* is C or N from the humic acid fraction, *FA* is C or N from the fulvic acid that desorbed from the DAX-8 resin column upon elution with 0.1 N NaOH, and NH is C or N from the soluble non-humic fraction. The other hydrophobic compounds (HO) that remain adsorbed to a column DAX-8 resin after elution with 0.1 N NaOH have been shown to have a large content of aliphatic groups and may be somewhat hydrophobic (Dai *et al.* 2006).

O and A horizons were analyzed for BC using a method adapted from the CTO375 method outlined by Gustafsson *et al.* (1997). This method uses the ability of BC to resist thermal oxidation at 375° C. One gram or 0.1 g of A and O horizon, respectively, were weighed to 0.1 mg, placed in ceramic crucibles, and put into a preheated muffle furnace (375 ^{o}C). After 20 hours the samples were removed and weighed. Samples were subsequently returned to a preheated (550 ^{o}C) muffle furnace for loss on ignition to determine the amount of $LOI_{375\text{-}550}$ which would contain BC and black nitrogen (BN).

$$\frac{LOI_{375-550}(g)}{S_i(kg)} = \left(\frac{A_{375}(g) - A_{550}(g)}{S_i(g)}\right) * \frac{1000g}{kg} \tag{9}$$

Where A is ash or residue after heating at 375 or 550 ^{o}C, and S_i is the initial amount of soil.

A ratio was developed to convert $LOI_{375-550}$ to BC or BN. Carbon and N analysis was conducted on four replicates of each O and A1 horizons after heating to 375° C. The mass lost between muffle-furnace temperatures of 375 and 550 ^{o}C had a significant linear relationship ($p<0.05$) with BC and BN with r^2 values of 0.88 and 0.77, respectively. About half (50±17% (95% CI)) of $LOI_{375-550}$ was found to be BC. This ratio agrees with the recommendation by Nelson and Sommers (1982) to use a factor of 50% to convert SOM content of surface soils to C content. Black nitrogen accounted for 2±1% (95% CI) of $LOI_{375-550}$. All samples and horizons were analyzed for $LOI_{375-550}$ so these data were used to assess statistical differences among the burn treatments. The mass lost between 375 and 550 ^{o}C converted to BC or BN was compared to other research examining BC and BN.

Statistical Analysis

To determine the effect of incubation on soil and SOM composition the difference between pre- and post-incubation values were calculated. Treatment effect on O horizon soil characteristics and differences were tested using a one-factor ANOVA. Tukey's test for HSD was used to delineate significantly different homogeneous subsets among different intensities (α=0.05).

A two-factor ANOVA was used to test the effect of burn intensity level and A horizon depth on soil characteristics and differences. If intensity was significant at $p\leq0.05$, then Tukey's HSD was used to define homogeneous subsets. If the interaction between horizon depth and intensity was significant at $p\leq0.05$, then the interaction was decomposed using pairwise contrasts. Pairwise contrasts were used to determine

differences between intensity levels at each depth (12 contrasts) and both A horizons at each intensity level (4 contrasts). The chance of making a type I error increases beyond the established value when making simultaneous multiple comparisons; Bonferrroni's procedure was used to reduce this chance to an α value of 0.05.

Results and Discussion

The double-exponential model (Equation 4) always provided a better fit to the cumulative CO_2-C data compared to the single-parameter model (Equation 5) as shown by higher r^2 values (Table 3.3). These results are similar to Updegraff *et al.* (1995) who found that the double-exponential model fit cumulative C mineralization data from humified organic soils better than a single-parameter model. The r^2 of the single-parameter model was closer to the double-exponential model for unburned or low fire intensity treated O horizons. Because of the greatly improved fit, only the double-exponential model will be utilized.

Incorporation of some O horizon into the A1 horizon could change C mineralization of the control A1 compared to the A2 horizons. The control A1 horizons were found to have incorporated about 9 g O horizon kg^{-1} A1 horizon as determined by LOI (see Chapter 2 for full description). This amount of O horizon would have added approximately 4 g of C kg^{-1} A1 horizon in the control. Only the control had a statistically significant increase in total soil C or N. C mineralization of A1 horizons from low-, moderate- and high-fire intensity are likely not affected by incorporation of O horizon materials.

O horizon

The total amount of C mineralized (on a mass basis) at 8 and 180 days decreased significantly after moderate-intensity burning of the O horizon (Table 3.4). Low-intensity burning left a large portion of the O horizon unburned, leading to more C being mineralized relative to the highly-charred O horizons from the moderate- and high-

intensity burns. The difference in the amount of C mineralized among the different intensities was due to changes in the decomposition rates.

The mineralization curves of the O horizon have distinctive slopes resulting in different decomposition constants (Figure 3.1). However, these differences were not statistically significant (Table 3.5). The decomposition rate of the labile pool (k_L) increased with increasing fire intensity while the amount of labile C (C_L) decreased. The labile pool will be depleted quicker after a moderate- and high-intensity burn as this O horizon fraction had a mean residence time of 11 and 7 days, respectively, while the control and low-intensity burn O horizons had mean life times of 32 and 25 days, respectively. However, once the C_L pool is depleted the long-term mineralization rate of these materials will be controlled by the recalcitrant SOM decomposition rate (k_R), which decreased with increasing fire intensity. Increasing the mean residence time of the recalcitrant pool of C may be a means by which recalcitrant forms of C can accumulate in the soil as suggested by Kuhlbusch and Crutzen (1995).

During a ponderosa pine litter decomposition study Hart *et al.* (1992) found k values (0.07-0.15 day^{-1} from a single exponential model) larger than the k_L values calculated for the double-exponential model used in this study. Mass loss through fragmentation and leaching are means by which material could be lost from a litter bag in addition to mineralized C. The current study examined only C mineralization and would therefore have calculated smaller k_L values. Additionally, litter bag studies traditionally utilize needles that are beginning to decompose while the current study used O horizon material which includes humified material that could decompose more slowly than material used in needle decomposition studies. Since the *k* values calculated by Hart *et al.* (1992) are at least 2 times higher than k_L values calculated for unburned O horizons in this study, suggesting that fragmentation and leaching may account for greater than half of the mass loss of needle decomposition.

Altered SOM composition caused by burning appears to be controlling the C mineralization rates of the O horizon. The concentration of all SOM fractions was reduced while $LOI_{375\text{-}550}$, which encompasses BC and BN, was increased by burning at

higher intensities (Table 3.1 and 3.2). Carbon mineralized after 8 days was positively correlated with NH, FA, and HA C concentration and negatively correlated with $LOI_{375-550}$ in the pre-incubation samples (Table 3.6). After 180 days the quantity of NH C was no longer significantly correlated with C mineralized, suggesting that it is only important for short-term C mineralization rates. Carbon mineralized after 180 days was negatively correlated with the quantity of $LOI_{375-550}$ and C:H of HA suggesting that the presence of fire-altered SOM is still causing a depression in C mineralization rates. Short-term mineralization appears to be controlled by the quantity of the most labile fractions NH, FA, and HA while long-term mineralization appears to be controlled by the quantity of FA and HA C and quality of HA.

Labile forms of C seem to be the source of C mineralized throughout the entire 180-day incubation of O horizons. Incubation reduced the amount of FA C of the control and low intensity treated soils by an average of 13% (Table 3.7). There was a significant relationship between C mineralized at 180 days with a decrease in FA C from pre- to post-incubation (R=-0.564; $p<0.05$). There was also a 32% reduction in NH C across all treatments. Recalcitrant forms of C, such as NS and $LOI_{375-550}$, do not appear to be major sources of C as they did not decrease due to incubation (Table 3.7 and 3.8). The FA fraction appears to be a major C source for short- and long-term C mineralization and, as previously mentioned, NH C may provide C during the early stages of C mineralization.

Humification is occurring concurrently and was related to C mineralization. Humic acid C, HA N and NS N increased significantly after incubating the control and low intensity soils, but not with moderate- or high-intensity treatments (Table 3.7). Carbon mineralized after 180 days was significantly correlated with the increase in O horizon HA C content (R=0.802; $p>0.05$). Qualls (2004) found that humic acid extracted from decomposed birch leaves decomposed more slowly than other SOM fractions, which is supported by the results from this current study. The increase in HA C with C mineralization also suggests that HA C is not a primary source of C for C mineralization in the O horizon, further supporting the assertion that the primary sources of mineralized C are FA and NH C fractions.

Baldock and Smernik (2002) found that when *Pinus resinosa* wood was heated to higher temperatures it had a lower bioavailability as measured by the amount of C mineralized after 120-day incubation. During the incubation they found that unaltered wood lost 20% of its initial C, and wood heated to 150° C reduced this C loss to 13%. Carbon loss due to mineralization was less than 2% when the wood was heated above 200 ^{o}C. They attributed this reduction in available C to a reduction of cellulose and hemicellulose which occurred mostly when the wood was heated to 200 ^{o}C as determined by NMR.

The effect of fire on the O horizon C mineralization is not necessarily entirely due to temperature, but may be more dependent on the amount of material that was consumed. In the current study the O horizons were not heated evenly through the profile, they simulated real conditions during combustion of the O horizon. There was a temperature gradient which was hottest where the material was burning, and coolest near the surface of the mineral soil; this gradient would only be partly represented by the maximum temperature of the O horizon. Maximum temperature and O horizon consumed were both similarly correlated with short-term C mineralization (Table 3.6). After 180 days of incubation there was only a significant correlation between the amount of O horizon consumed and C mineralized and no significant correlation with maximum temperature. Temperature may control alterations to SOM at a small scale (fuel particle); however the effect of fire on the whole O horizon is dependent on larger-scale phenomena, such as the proportion of O horizon consumed.

Figure 3.2 shows the difference in the proportion of each SOM fraction relative to the control, pre- and post-incubation. The SOM composition remained unchanged relative to the control after incubation of the O horizon. Only HO C and N are elevated relative to the control after burning at moderate and high intensity following incubation. These materials did not occur in the pre- or post-incubation control soil. The HO materials may be created through the decomposition of fire-altered SOM. The HO fraction may be more mobile in soil, as they were extracted from the soil along with FA,

and leach out of the O horizon and into the mineral soil where it could be mineralized or complexed with mineral surfaces.

The high rate of HA formation in the control caused the proportion of HA C of burned O horizons to be reduced relative to the control after incubation (Figure 3.2). Slow mineralization rates of the moderate- and high-intensity soils are keeping the distribution of C and N relatively static. Recalcitrant materials produced by burning may accumulate relative to unburned material over time since they are slower to decompose. However, the production of slower decomposing materials through humification in the unburned O horizon may offset slower decomposition by BC and sequester a similar amount of C over time.

A horizon

The quantity of C mineralized from both A horizons after 8 days was dependent on both fire intensity and A horizon depth (Table 3.4). Carbon mineralized from both A1 and A2 horizons at 8 days increased with fire intensity up to the moderate-intensity treatment. However, C mineralized from moderate-intensity burned A horizons was not significantly different from the high-intensity burned A horizons. Low-intensity burning did not have a significant effect on C mineralized from the A1 or A2 horizon compared to the control. Differences caused by burning at varying intensity disappeared over the course of the incubation, so that by the end of the incubation experiment (180 days) only the A1 and A2 horizons were significantly different from one another. Incorporation of O horizon significantly increased the amount of C of the control (Chapter 2) and likely elevated the amount of C mineralized at 8 and 180 days from the A1 over the A2 horizon of the control. The higher temperatures achieved during burning in the A1 horizon caused a significant increase in C mineralized over the A2 horizon of the low, moderate, and high fire intensity treated soils.

Differences in total C mineralized are due to changes in the recalcitrant pool decomposition rate (k_R) and the size of the labile pool (C_L) (Table 3.5). The labile pool was larger and recalcitrant materials decomposed at a significantly faster rate in the A1

horizon compared to the A2 horizon. The elevated C_L contributed to the short-term increase in C mineralized (8 days) while over the long-term (180 days) the elevated k_R of the control and low-intensity treated soil erased differences caused by burning at higher intensity. O horizons from the control soils have higher C_L and k_R than the mineral soils from those treatments, thereby elevating these parameters of the A1 when O horizon is incorporated into the mineral soil. Fire intensity significantly increased the short-term C mineralized and C mineralization rates of the moderate- and high-intensity treated soils while long-term mineralization was not affected.

It appears that short-term C mineralization increased with fire intensity due to an improved quality of substrate for microbial growth and a possible increase in labile compounds. Carbon mineralized from A1 horizons after 8 and 180 days was negatively correlated with the C:N of humin and FA. Mineralization at 8 days was negatively correlated with the quantity of FA in the A1 horizon suggesting that the quality of this fraction is more important than quantity in determining C mineralization. Soluble non-humic C concentration of the pre-incubated soils and C mineralized at 8 days were strongly negatively correlated. Fritze *et al.* (1998) showed that water-soluble materials, such as NH, may contain microbial growth inhibitors. The HO C was not significantly correlated with short-term mineralization, but the correlation coefficient was high (Table 3.6). Only four pre-incubation samples (one per treatment and horizon) were able to be analyzed for HO substances, more samples analyzed may have produced a significant result.

The mineralization of C from moderate and high intensity A1 horizons is similar to the results of Fernandez *et al.* (1997) who studied mineral soil after high-intensity wildfires. They saw an increased rate of C mineralization (on a total C basis) in burned soils compared to an associated unburned control soil. They attributed the increase in C mineralization results to an increase in labile compounds after burning. In another study of fire effects on C mineralization Fernandez *et al.* (2004) found that a soil heated to 385 ^{o}C for 10 minutes had a slightly lower rate of C mineralization than its unheated counterpart. High temperatures in the A1 horizons of the current study were associated

with higher rates of short-term mineralization (Table 3.6). In the current study the average maximum temperature of the surface A horizon was 197 and 243 ^{o}C for the moderate- and high-intensity burns, much lower than the temperatures used by Fernandez *et al.* (2004)(Figure 3.1). There may be a point in which fire intensity is high enough to convert all SOM to recalcitrant forms. This threshold would appear to be greater than 243 ^{o}C.

Of all SOM fractions FA was most consistently lowered in all treatments and both A horizons after incubation (Table 3.7). The decrease in FA is likely due to mineralization as suggested by the significant relationship with FA C:N and short-term mineralization rates (Table 3.6). There was an average of 61 and 38% reduction of A1 and A2 horizon FA C concentration, respectively, caused by incubation. The FA fraction may be preferentially used as a C source in the mineral soil.

Soluble non-humic C increased with incubation of the A2 horizon by an average of 60%; the increase was higher with decreasing fire intensity (Table 3.7). As mentioned, the NH C fraction of the mineral soil may contain microbial growth inhibitors that limit mineralization rates of the A horizons. Pre-incubation NH C concentrations were highest in the A2 horizons and are correlated to the increase in NH C caused by incubation ($R=0.736$; $p<0.05$). The NH C fraction of the A1 horizon was relatively unaffected by incubation, except the moderate-intensity burn which decreased with incubation. The lower mineralization rates possibly caused by the presence of NH C materials could have caused NH C in the control and low intensity A2 horizon to accumulate. The higher severity experienced by the A1 horizon during burning may have reduced the source or production of microbial growth inhibitors.

The transformations of C and N from humin, HA, and FA fractions into HO may be inhibited by the unburned NH fraction (Table 3.7). The NH fraction may represent inhibitory compounds that were volatilized from the A1 horizon during burning causing a shift in microbial activity as suggested by White (1991, 1994). The NH fraction in the fire-protected A2 horizon may still contain these inhibitory compounds, which allow them to accumulate and inhibit transformations of other fractions to HO compounds. The

higher temperatures achieved in the A1 horizon may have volatilized these inhibitory compound, thereby allowing the transformations from humin, HA, and FA to HO to occur. These transformations of C are leading to a return to control proportions of SOM fractions.

Figure 3.3 shows the difference in proportion of SOM of each treatment from the control. Generally, the result of burning and incubation on the proportion of total soil C and N as SOM fractions was a return to control proportions except at the low-intensity burn. Moderate- and high-intensity treated soils were more different than controls prior to incubation; however, the faster mineralization rates of these soils reduced these differences. The proportion of total C and N as humin, HA, and NH was reduced to nearly control levels after incubation of both A horizons. The production of HO C and N were the main differences caused by incubation between control and soils burned at moderate and high intensity; this may be caused by higher microbial biomass of decomposition products of fire affected SOM. The low-intensity treated A horizons are still reflecting the pre-incubation SOM C and N composition as seen by comparable incubation-caused changes as the control. Further, the resulting SOM C and N content of the low-intensity treated A horizons of any fraction was never significantly different from the control after incubation ($p>0.05$). In general, there does not appear to be a major long-term affect of prescribed burning on the composition of SOM.

The material lost on ignition after heating to muffle-furnace temperatures of 375 ^{o}C ($LOI_{375\text{-}550}$) of the A horizons treated to burning appears to be more robust against biological oxidation during incubation of the burned soils. $LOI_{375\text{-}550}$ decreased significantly in the control soil but was unaffected or increased in mineral soils treated to fire (Table 3.8). The resistance to oxidation may allow BC and BN to accumulate in soil over time.

Guerrero *et al.* (2005) found that unheated soils and soils heated at temperatures less than 300 ^{o}C had similar extractable C pre- and post-incubation. The current study supports these findings in that none of the mineral soil achieved a temperature greater than 300 ^{o}C and the most labile forms of C and N (the sum of FA_D, NH, and FA_A) were

not significantly different among the intensities after incubation ($p_i=0.906$ and $p_i=0.960$ for C and N respectively).

Fernandez *et al.* (2004) found an increase in the proportion of HA and humin after an 84 day incubation of a soil heated to 385 ^{o}C. That level of soil heating was more severe than the burn treatments in the current study and likely combusted or transformed the majority of labile C and N. Additionally, they did not use a control soil to determine how SOM from an unheated soil would respond to incubation. A higher-intensity fire on the soils of the current study may have produced similar results to those results by Fernandez *et al.* (2004).

Total carbon and nitrogen

Figures 3.3 and 3.4 show the total C and N lost from the entire soil profile from combustion at each of the intensity levels and from incubation. Combustion of the O horizon dominates the C losses across burn treatments. Nitrogen was lost predominantly through volatilization of N during incubation of A horizons from the control and low-intensity treated soils and combustion of the O horizon in the moderate- and high-intensity treatments. Volatilization of NH_4^+ as NH_3 may have occurred throughout the A horizon since it can occur at pH values (6.2-6.9) similar to these soils (He *et al.* 1999). The control O and A horizons mineralized nearly as much C as was lost through combustion in the low-intensity burn.

Total recalcitrant-non-soluble materials (humin and NS) C and N decreased with increasing fire intensity ($p_i=0.000$ for both C and N) (Figures 3.3 and 3.4). The proportion of total C and N that was in a recalcitrant form accounted for 72-75% and 58-63%, respectively, which were not significantly different between fire intensities ($p_i>0.05$). Fire does not appear to have affected the proportion of recalcitrant non-soluble materials.

The total content of $LOI_{375\text{-}550}$, which includes BC and BN, was not significantly affected by burn intensity ($p_i=0.119$) but as the total C and N decreased, the proportion of these very recalcitrant materials increased ($p_i=0.000$). The total soil C as BC increased

from 38 g BC kg^{-1} soil C to 64, 108, and 139 g BC kg^{-1} soil C after burning at low, moderate, and high intensity, respectively. Carbon sequestration through the production of BC comes with a high production rate of recalcitrant forms of N, which would have also increased in proportion. Recalcitrant forms of N have been shown to affect N mineralization rates and available N and may limit forest productivity over time (Guinto *et al.* 1999).

Figure 3.5 shows the average proportion of initial C remaining in the entire profile (O and A horizons) after burning and incubation. If these soils were allowed to incubate for a long period of time, then the moderate- and high-intensity burned soil profiles would overcome the C lost through burning and preserve C relative to the control after approximately 7 and 10 years of incubation. Soil profiles burned at low intensity may never preserve C relative to the controls. This study did not take into account the burning or decomposition characteristics of coarse woody debris, which would likely affect C storage and sequestration in a fire-prone forest. Clearly more long-term research would be needed to confirm if C could be sequestered by producing slower decomposing forms of C with burning of organic matter, but it shows the possibility that moderate- severity prescribed fire may have the ability to sequester C over a long period of time by slowing the decomposition rates of the remaining SOM if the fire-produced SOM is not burned by another fire.

Black carbon and charcoal may accumulate in the soil if it is protected from burning by a succeeding fire. Researchers have found accumulations of BC incorporated in the top 10 cm of grassland soils (Glaser and Amelung 2003) and as a proportion of total C with depth in a savanna soil (Dai *et al.* 2005). If left at the surface these materials are susceptible to erosion or may be combusted if the site is reburned. Dai *et al.* (2005) found that repeated burning did not significantly increase BC in soils collected from a savanna soil treated with prescribed burning. Czimczik *et al.* (2005) suggest that BC was not different among Scots Pine (*Pinus sylvestris* L.) stands burned at differing frequencies and severities due to consumption of BC by high-intensity wildfire. Depending on field conditions and fire-return interval, prescribed burning may allow

recalcitrant forms of C to accumulate in the soil if it is able to be protected from reburning through mixing into the mineral soil.

Conclusions

Fire intensity significantly reduced the C mineralization rate of O horizons. The decrease in C mineralized from the O horizon with increasing fire intensity appeared to be caused by fire-induced reductions of FA and NH C. Short-term C mineralization of A horizons increased with fire intensity while long-term C mineralization was not significantly affected by burning. It appears that short-term C mineralization of mineral soils increased with fire intensity due to an improved quality of substrate for microbial growth and a possible increase in labile compounds. After burning, the SOM composition of burned A horizons returned to control levels while the SOM composition of O horizons remained different from control. Exacerbating differences in O horizon HA content among the treatments was the positive correlation between the production of HA and C mineralization rates. In general, burning had little effect on the SOM quality of the A horizon after incubation, suggesting that there will be little long-term impact to SOM composition caused by burning. Total content of recalcitrant (humin and NS) C and N decreased with increasing fire intensity while BC and BN were unaffected by fire intensity. Production of recalcitrant materials through fire has been suggested as a way in which C may be sequestered in soils. It may take a long-period of time for recalcitrant materials to build up in a burned soil relative to an unburned soil due to C combustion; however, the role of coarse woody debris in these ecosystems was not examined. When coarse woody debris is excluded, prescribed fires at moderate and moderate-high intensity may have the greatest ability to sequester C through production of recalcitrant materials that decompose more slowly than unburned materials.

Table 3.1 Laboratory burn characteristics and soil chemical attributes of O and A horizons including $LOI_{375\text{-}550}$ (mean±standard deviation) after three levels of fire intensity and an unburned control (n=4). *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_d and p_{i*d})) factor ANOVA, significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b,c*) or pairwise contrasts (*e,f,g* for A1 and *m,n* for A2). An * indicates A1 was significantly different from A2 at that fire-intensity level. Max Temp. is the average maximum temperature at the surface of the O (O), surface of the mineral soil (0 cm), and at 2 cm depth in the A2 horizon.

		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
Max. Temp. (^oC)	O		272	294	406			
	0 cm		98	120	125			
	2 cm		23	53	66			
% Mass O Horizon burned		-	32 ± 13 ^{a}	67 ± 8 ^{b}	80 ± 4 ^{b}	***0.000***		
pH	O	4.9 ± *0.4* ^{a}	7.2 ± *1.3* ^{b}	9.7 ± *0.2* ^{c}	10.5 ± *0.4* ^{c}	***0.000***		
	A1	6.3 ± *0.2* ^{e}	6.5 ± *0.2* ^{f}	6.6 ± *0.1* ^{f*}	6.9 ± *0.1* ^{g*}	*0.001*	*0.000*	***0.000***
	A2	6.4 ± *0.1*	6.4 ± *0.1*	6.2 ± *0.0* *	6.4 ± *0.2* *			
g C kg^{-1} soil	O	407 ± *5* ^{a}	414 ± *14* ^{a}	376 ± *16* ^{a}	226 ± *61* ^{b}	***0.000***		
	A1	52 ± *3*	53 ± *7*	47 ± *4*	50 ± *4*	*0.454*	*0.438*	*0.740*
	A2	46 ± *3*	48 ± *8*	47 ± *5*	50 ± *5*			
g N kg^{-1} soil	O	6.9 ± *0.5* ^{a}	8.1 ± *0.6* ^{a}	11.1 ± *0.7* ^{b}	6.5 ± *2.1* ^{a}	***0.001***		
	A1	2.7 ± *0.2*	2.6 ± *0.2*	2.9 ± *0.2* *	2.9 ± *0.2* *	*0.887*	*0.089*	***0.003***
	A2	2.9 ± *0.0* ^{m}	2.7 ± *0.5* ^{mn}	2.4 ± *0.2* ^{n*}	2.4 ± *0.1* ^{n*}			
C:N	O	69 ± *5.9* ^{a}	60 ± *3.4* ^{a}	40 ± *1.6* ^{b}	42 ± *6.8* ^{b}	***0.000***		
	A1	23 ± *0.0* ^{ef*}	24 ± *2.2* ^{e}	19 ± *0.8* ^{f*}	20 ± *1.1* ^{f*}	*0.106*	*0.289*	***0.000***
	A2	19 ± *1.0* ^{m*}	21 ± *4.7* ^{mn}	23 ± *0.6* ^{n*}	24 ± *1.8* ^{n*}			
g $LOI_{375\text{-}550}$ kg^{-1} soil	O	2 ± *1* ^{a}	5 ± *2* ^{b}	9 ± *0* ^{c}	10 ± *1* ^{c}	***0.000***		
	A1	14 ± *3*	11 ± *2*	13 ± *1*	12 ± *2*	*0.474*	*0.899*	***0.946***
	A2	12 ± *2*	11 ± *2*	13 ± *1*	12 ± *2*			

Table 3.2 Soil C and N concentrations and C:N ratio of SOM fractions in O and A horizons (mean±standard deviation) after three levels of fire intensity and an unburned control (n=4 unless NH or HO then n=1). *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_i, p_d and p_{i*d})) factor ANOVA; significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b,c*) or pairwise contrasts (*e,f* for A1). An * indicates A1 was significantly different from A2 at that fire-intensity level. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
g Humin /NS C kg^{-1} soil	O	300 ± *15* ^{a}	328 ± *33* ^{a}	332 ± *25* ^{a}	183 ± *44* ^{b}	***0.000***		
	A1	35.5 ± *3.1* ^{ab*}	36.5 ± *4.3* ^{a*}	28.8 ± *1.8* ^{b*}	28.8 ± *5.0* ^{ab*}	***0.016***	***0.054***	*0.447*
	A2	32.1 ± *2.6*	32.1 ± *3.8*	29.7 ± *2.2*	29.4 ± *2.8*			
g HA C kg^{-1} soil	O	62.6 ± *9.4* ^{a}	45.7 ± *11* ^{b}	14.7 ± *4.4* ^{c}	2.92 ± *3.2* ^{c}	***0.000***		
	A1	7.21 ± *1.1* ^{e}	7.15 ± *1.2* ^{e}	6.83 ± *0.9* ^{e}	4.36 ± *1.0* ^{f*}	*0.028*	*0.192*	***0.001***
	A2	6.16 ± *1.1*	6.75 ± *0.4*	7.19 ± *0.4*	7.11 ± *0.3* *			
g FA C kg^{-1} soil	O	18.2 ± *1.7* ^{a}	13.9 ± *2.1* ^{b}	4.82 ± *0.8* ^{c}	1.08 ± *0.8* ^{d}	***0.000***		
	A1	1.32 ± *0.2* *	1.36 ± *0.4* *	1.34 ± *0.2* *	1.05 ± *0.1* *	*0.108*	***0.002***	*0.528*
	A2	1.04 ± *0.1* *	1.05 ± *0.1* *	1.12 ± *0.1* *	0.99 ± *0.2* *			
g HO C kg^{-1} soil	O	ND	ND	ND	24			
	A1	5	4	9	10			
	A2	1	2	6	10			
g NH C kg^{-1} soil	O	43	32	29	15			
	A1	3	4	1	2			
	A2	5	6	3	3			
C:N Humin /NS	O	86 ± *17* ^{a}	68 ± *9* ^{a}	42 ± *3* ^{b}	42 ± *6* ^{b}	***0.000***		
	A1	34 ± *4* *	32 ± *1* *	28 ± *5* *	28 ± *2* *	*0.123*	***0.005***	*0.198*
	A2	28 ± *4* *	27 ± *3* *	28 ± *1* *	26 ± *3* *			
C:N HA	O	37 ± *5*	38 ± *7*	37 ± *6*	39 ± *22*	*0.990*		
	A1	19 ± *1.0* *	20 ± *0.3* *	20 ± *0.8* *	20 ± *0.5* *	*0.075*	***0.004***	*0.949*
	A2	19 ± *0.3* *	19 ± *0.5* *	19 ± *0.3* *	19 ± *0.3* *			
C:N FA	O	123 ± *23* ^{a}	99 ± *19* ^{a}	54 ± *8.2* ^{b}	44 ± *13* ^{b}	***0.000***		
	A1	42 ± *3* ^{a}	44 ± *6* ^{a}	33 ± *2* ^{ab}	30 ± *2* ^{b}	***0.000***	*0.196*	*0.222*
	A2	42 ± *5*	42 ± *2*	40 ± *1*	35 ± *10*			
C:N HO	O	0	0	0	35			
	A1	6	8	10	10			
	A2	1	3	13	42			
C:N NH	O	38	43	21	33			
	A1	17	19	2	7			
	A2	40	26	15	8			

Table 3.3 A comparison of models fit to cumulative CO_2-C data from three levels of fire intensity and an unburned control**.** Data presented are r^2 values from non-linear regressions using a single-parameter (Equation 5) and double-exponential models (Equation 3 and 4) **(**Andren and Paustian 1987). In all cases the double-exponential model fit the cumulative CO_2-C mineralized data better.

O Horizon

	Single Parameter	Double Exponential
Control	0.91	0.96
Low	0.86	0.89
Moderate	0.60	0.86
High	0.52	0.79

A Horizon

		Single Parameter	Double Exponential
Control	A1	0.64	0.95
	A2	0.64	0.86
Low	A1	0.46	0.68
	A2	0.57	0.81
Moderate	A1	0.13	0.98
	A2	0.42	0.92
High	A1	0.27	0.86
	A2	0.41	0.87

Table 3.4 Total C mineralized after 8 and 180 days of incubation (mean±standard deviation) after three levels of fire intensity and an unburned control (n=4). *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_i, p_d and p_{i*d})) factor ANOVA; significant values are in bold (α=0.05). Letters indicate similar subsets (columns) as determined by Tukey's HSD (*a,b,c*) or pairwise contrasts (*e,f* for A1 and *m,n* for A2). An * indicates that A1 and A2 are significantly different at that fire-intensity level.

O Horizon

		Cumulative CO_2 Respired (8 days)		Cumulative CO_2 Respired (180 days)	
		mg CO_2-C g^{-1} soil	mg CO_2-C g^{-1} soil C	mg CO_2-C g^{-1} soil	mg CO_2-C g^{-1} soil C
Control		9.49 ± *1.8* ^{a}	23.4 ± *4.5*	96.8 ± *10* ^{a}	238.4 ± *27.7* ^{a}
Low		6.20 ± *1.5* ^{b}	15.0 ± *4.0*	68.7 ± *11* ^{b}	166.7 ± *30.7* ^{b}
Moderate		6.28 ± *0.7* ^{b}	16.6 ± *1.4*	30.1 ± *8.0* ^{c}	79.6 ± *19.0* ^{c}
High		3.51 ± *0.9* ^{b}	16.3 ± *6.5*	18.8 ± *2.5* ^{c}	85.8 ± *14.4* ^{c}
	p_i	***0.000***	*0.114*	***0.000***	***0.000***

A Horizon

		Cumulative CO_2 Respired (8 days)		Cumulative CO_2 Respired (180 days)	
		mg CO_2-C g^{-1} soil	mg CO_2-C g^{-1} soil C	mg CO_2-C $(g\ soil)^{-1}$	mg CO_2-C $(g\ C)^{-1}$
Control	A1	1.13 ± *0.2* ^{e*}	21.7 ± *3.5* ^{e}	5.38 ± *0.99* *	103.5 ± *18.4* *
	A2	0.83 ± *0.3* ^{m*}	18.3 ± *6.9*	3.94 ± *0.53* *	86.8 ± *16.9* *
Low	A1	1.14 ± *0.2* ^{e}	22.2 ± *6.3* ^{e}	5.18 ± *1.3* *	100.4 ± *35.1* *
	A2	0.97 ± *0.2* ^{mn}	20.6 ± *3.8*	4.02 ± *0.29* *	86.1 ± *20.7* *
Moderate	A1	1.97 ± *0.1* ^{f*}	42.1 ± *2.5* ^{f*}	5.41 ± *0.44* *	115.7 ± *3.4* *
	A2	1.24 ± *0.1* ^{n*}	26.5 ± *2.3* *	4.29 ± *0.25* *	91.8 ± *12.4* *
High	A1	1.69 ± *0.1* ^{f*}	34.2 ± *3.5* ^{f*}	5.08 ± *0.71* *	103.0 ± *18.0* *
	A2	1.16 ± *0.4* ^{n*}	23.2 ± *7.1* *	4.27 ± *0.72* *	85.5 ± *11.5* *
	p_i	*0.000*	*0.000*	*0.891*	*0.585*
	p_d	*0.000*	*0.000*	***0.000***	***0.003***
	p_{i*d}	***0.028***	***0.029***	*0.931*	*0.926*

Table 3.5 Labile pool and decomposition constants of C mineralization over a 180-day incubation (mean±standard deviation) fit to double-exponential model in equations 3 and 4 (n=4) after 3 levels of fire intensity and an unburned control. *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_i, p_d and p_{i*d})) factor ANOVA; significant values are in bold (α=0.05). An * indicates that A1 and A2 are significantly different at that fire-intensity level. C_L is the initial amount of labile C, k_L is the rate constant for the labile pool, k_R is the rate constant for the recalcitrant pool, and τ is the average residence time calculated as the inverse of the mineralization constant (k_L or k_R).

O Horizon

	C_L		k_L		k_R	
	mg CO_2-C g^{-1} soil	mg CO_2-C g^{-1} soil C	day^{-1}	τ (d)	day^{-1} x 10^4	τ (yrs)
Control	77.3 ± *71*	180 ± *162*	0.03 ± *0.03*	32	6.0 ± *6.2*	5
Low	73.5 ± *45*	103 ± *107*	0.04 ± *0.06*	25	2.9 ± *4.5*	10
Moderate	12.6 ± *4.3*	33.2 ± *10.8*	0.09 ± *0.08*	11	2.8 ± *1.4*	10
High	9.7 ± *4.8*	41.5 ± *20.5*	0.15 ± *0.20*	7	2.4 ± *1.6*	11
p_i	*0.066*	*0.179*	*0.473*		*0.476*	

Table 3.5 is continued on the next page.

Table 3.5 Continued

A Horizon

		C_L		k_L		k_R	
		mg CO_2-C g^{-1} soil	mg CO_2-C g^{-1} soil C	day^{-1}	τ (d)	day^{-1} x 10^4	τ (yrs)
Control	A1	2.3 ± *0.8* *	47.7 ± *11.0* *	0.08 ± *0.06*	12	3.9 ± *0.5* *	7
	A2	1.4 ± *0.4* *	29.9 ± *8.3* *	0.09 ± *0.05*	11	3.3 ± *0.8* *	8
Low	A1	2.2 ± *0.8* *	42.4 ± *18.2* *	0.09 ± *0.07*	11	3.5 ± *0.9* *	8
	A2	1.5 ± *0.3* *	34.5 ± *11.7* *	0.12 ± *0.11*	8	3.2 ± *0.2* *	8
Moderate	A1	2.9 ± *0.3* *	61.8 ± *4.4* *	0.11 ± *0.02*	9	3.4 ± *0.2* *	8
	A2	2.0 ± *0.4* *	42.2 ± *10.1* *	0.11 ± *0.06*	9	3.0 ± *0.2* *	9
High	A1	2.6 ± *0.5* *	51.9 ± *11.4* *	0.10 ± *0.03*	10	3.2 ± *0.3* *	9
	A2	2.2 ± *0.5* *	42.9 ± *7.6* *	0.07 ± *0.02*	15	2.6 ± *0.4* *	11
	p_i	*0.056*	*0.054*	*0.756*		*0.067*	
	p_d	***0.001***	***0.002***	*0.886*		***0.018***	
	p_{i*d}	*0.711*	*0.623*	*0.725*		*0.878*	

Table 3.6 Pearson correlation coefficients of O and A horizon CO_2-C evolved at 8 and 180 days (on a soil basis) with soil and pre-incubation SOM characteristics. Significant values are in bold ($p \leq 0.05$). Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

	Mass O Consm.	Max Temp. of Horizon	Time Temp >100°C O/A	Humin			HA			FA			NH	HO	$LOI_{375-550}$
				C	C:N	C:H	C	C:N	C:H	C	C:N	C:H	C (n=4)	C (n=4)	
Total C mineralized after 8 days (dry soil basis)															
O	**-0.622**	**-0.677**	-0.200	0.431	**0.616**	-0.319	**0.827**	-0.094	**-0.663**	**0.813**	**0.606**	-0.278	**0.983**	-0.736	**-0.797**
A1	**0.775**	**0.744**	**0.936**	**-0.686**	**-0.533**	-0.038	-0.401	0.215	**0.819**	**-0.794**	**-0.798**	0.198	**-0.999**	0.736	-0.132
A2	0.357	0.469	0.349	-0.081	0.170	-0.294	0.206	0.136	-0.056	-0.123	-0.319	-0.392	-0.507	0.692	0.347
Total C mineralized after 180 days (dry soil basis)															
O	**-0.890**	-0.544	**-0.617**	0.429	**0.806**	-0.201	**0.841**	-0.086	**-0.628**	**0.873**	**0.839**	-0.392	0.576	-0.752	**-0.841**
A1	-0.231	0.002	0.087	0.024	0.349	-0.020	0.178	0.284	0.013	0.399	0.158	-0.136	-0.171	-0.436	0.010
A2	0.087	0.146	0.191	0.075	-0.078	0.065	-0.074	-0.212	0.294	-0.353	**-0.521**	-0.384	-0.797	0.948	-0.022

Table 3.7 Change in each SOM fraction C and N concentration of O and A horizons (mean±standard deviation) from pre incubation to post incubation after three levels of fire intensity and an unburned control (n=4). Differences significantly different from zero, and therefore affected by incubation, are in bold. *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_i, p_d and p_{i*d})) factor ANOVA; significant p values are in bold. Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b,c*) or pairwise contrasts (*e,f for* A1and *m,n,o,p* for A2). An * indicates that A1 and A2 are significantly different at that fire-intensity level. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

O Horizon

	Control		Low		Moderate		High		p_i
g NS C kg^{-1} soil	-8.5 ± *16*	*a*	-9.5 ± *13*	*a*	-11 ± *15*	*a*	67 ± *66*	*b*	***0.008***
g HA C kg^{-1} soil	**22 ± *8.4***	*a*	**11 ± *6.2***	*ab*	-5.1 ± *7.7*	*bc*	2.3 ± *0.7*	*c*	***0.000***
g FA C kg^{-1} soil	**-2.6 ± *2.0***	*a*	**-1.5 ± *1.0***	*ab*	**0.5 ± *0.3***	*b*	0.0 ± *0.7*	*b*	***0.012***
g HO C kg^{-1} soil	ND		-6 ± *11*		-12 ± *25*		7 ± *20*		*0.428*
g NH C kg^{-1} soil	-11 ± *37*		-9 ± *41*		-28 ± *34*		4 ± *17*		*0.616*
mg NS N kg^{-1} soil	**746 ± *740***		**1196 ± *648***		105 ± *1138*		447 ± *932*		*0.389*
mg HA N kg^{-1} soil	**671 ± *508***	*a*	**513 ± *199***	*ab*	-104 ± *211*	*b*	22 ± *83*	*b*	***0.008***
mg FA N kg^{-1} soil	4.7 ± *18*	*a*	12 ± *26*	*a*	31 ± *25*	*a*	-7.1 ± *23*	*b*	***0.000***
mg HO N kg^{-1} soil	ND	*a*	-83 ± *167*	*a*	-977 ± *634*	*b*	410 ± *353*	*a*	***0.001***
mg NH N kg^{-1} soil	-0.11 ± *0.11*	*ab*	-0.03 ± *0.11*	*a*	-0.11 ± *0.08*	*b*	0.05 ± *0.06*	*a*	***0.009***

Table 3.7 is continued on the next page.

Table 3.7 Continued

		A Horizon																	
		Control			Low			Moderate			High			p_i	p_d	p_{i*d}
g Humin C	A1	**-1.8 ± 0.9**			**-5.7 ± 4.7**			-1.2 ± 4.6			-2.6 ± 4.1			*0.826*	*0.704*	*0.251*
kg^{-1} soil	A2	-2.5 ± 3.3			-0.8 ± 4.6			**-2.6 ± 1.5**			**-3.5 ± 1.8**					
g HA C	A1	0.0 ± 2.0			-0.7 ± 1.6			-0.7 ± 0.8			0.4 ± 1.4			*0.425*	*0.141*	*0.135*
kg^{-1} soil	A2	0.0 ± 0.9			**-0.6 ± 0.5**			**-1.1 ± 0.3**			**-1.9 ± 0.2**					
g FA C	A1	**-0.6 ± 0.2**		*	**-0.7 ± 0.3**		*	**-1.0 ± 0.2**		*	**-0.7 ± 0.2**		*	*0.107*	***0.000***	*0.520*
kg^{-1} soil	A2	**-0.4 ± 0.1**		*	**-0.3 ± 0.1**		*	**-0.5 ± 0.2**		*	**-0.4 ± 0.2**		*			
g HO C	A1	**4.9 ± 0.0**		*	0.3 ± 6.3		*	**6.7 ± 4.7**		*	**6.7 ± 3.8**		*	*0.137*	***0.034***	*0.377*
kg^{-1} soil	A2	4.6 ± 9.2		*	0.1 ± 3.4		*	1.6 ± 6.5		*	4.2 ± 4.6		*			
g NH C	A1	-0.9 ± 2.4		*	-0.1 ± 0.5		*	**-1.1 ± 1.1**		*	-0.8 ± 2.9		*	***0.029***	***0.000***	*0.138*
kg^{-1} soil	A2	**4.2 ± 0.4**		*	**4.0 ± 1.0**		*	**1.0 ± 0.5**		*	**1.3 ± 0.3**		*			
g Humin N	A1	0.1 ± 0.1		*	-0.1 ± 0.3		*	0.1 ± 0.3		*	0.1 ± 0.1		*	*0.866*	*0.036*	*0.363*
kg^{-1} soil	A2	-0.1 ± 0.3		*	-0.1 ± 0.2		*	**-0.1 ± 0.0**		*	-0.2 ± 0.3		*			
mg HA N	A1	-2.7 ± 3.0		*	**-4.1 ± 3.6**		*	**-5.5 ± 1.5**		*	**-3.9 ± 2.8**		*	*0.430*	*0.035*	*0.115*
kg^{-1} soil	A2	**-8.0 ± 1.4**		*	**-7.4 ± 3.1**		*	**-10 ± 1.1**		*	**-8.7 ± 2.1**		*			
mg FA N	A1	**-20 ± 8.5**	*ab*		**-19 ± 8.7**	*a*		**-35 ± 6.0**	*ab*		**-31 ± 10**	*b*		***0.015***	*0.752*	*0.972*
kg^{-1} soil	A2	**-10 ± 4.5**			**-6.5 ± 5.8**			**-16 ± 4.1**			**-21 ± 14**					
mg HO	A1	**721 ± 102**	*ef*		272 ± 332	*e*		**762 ± 169**	*ef**		**898 ± 107**	*f**		*0.096*	*0.001*	***0.000***
kg^{-1} soil	A2	**670 ± 483**	*m*		**557 ± 86**	*m*		**253 ± 227**	*mn**		-89 ± 195	*n**				
mg NH N	A1	**-89 ± 30**	*e**		**-131 ± 37**	*e**		-15 ± 31	*f**		-13 ± 24	*f**		*0.000*	*0.288*	***0.000***
kg^{-1} soil	A2	**-152 ± 8**	*m**		**-34 ± 20**	*n**		**-96 ± 19**	*o**		**75 ± 33**	*p**				

Table 3.8 Mass lost between 375° C and 550° C ($LOI_{375-550}$) and change in $LOI_{375-550}$ due to incubation (mean±standard deviation) after three levels of fire intensity and an unburned control. This material was found to include 50±17% black carbon (BC) and 2±1% black nitrogen (BN). Differences significantly different from zero, and therefore affected by incubation, are in bold. *p* values are from a one- (*intensity* (p_i)) or two- (*intensity* by *depth* (p_d and p_{i*d})) factor ANOVA, significant values are in bold (α=0.05). Letters indicate similar subsets (rows) as determined by Tukey's HSD (*a,b,c*) or pairwise contrasts (*e,f* for A1). An * indicates that A1 and A2 are significantly different at that fire-intensity level.

		Control	Low	Moderate	High	p_i	p_d	p_{i*d}
		----------	$LOI_{375-550}$ (g kg^{-1} soil)		----------			
Post-Incubation	O	ND [a]	1.1 ± 2.09 [ab]	7.7 ± 4.15 [bc]	12.8 ± 2.03 [c]	***0.001***		
	A1	11.2 ± 2.02	12.9 ± 1.67	12.7 ± 0.69	12.8 ± 1.97	*0.383*	*0.732*	*0.755*
	A2	12.1 ± 1.52	12.1 ± 2.28	12.7 ± 0.97	13.4 ± 1.56			
Difference (Post-Pre)	O	-4.3 ± 4.7	-4.0 ± 3.6	-1.7 ± 3.7	2.8 ± 2.5	*0.152*		
	A1	**-3.18 ± 2.48** [e*]	**1.47 ± 0.83** [f]	0.14 ± 1.34 [f]	**0.85 ± 0.24** [f]	*0.000*	*0.030*	***0.009***
	A2	0.37 ± 0.71 [*]	**1.06 ± 0.58**	0.09 ± 0.88	**1.54 ± 0.55**			

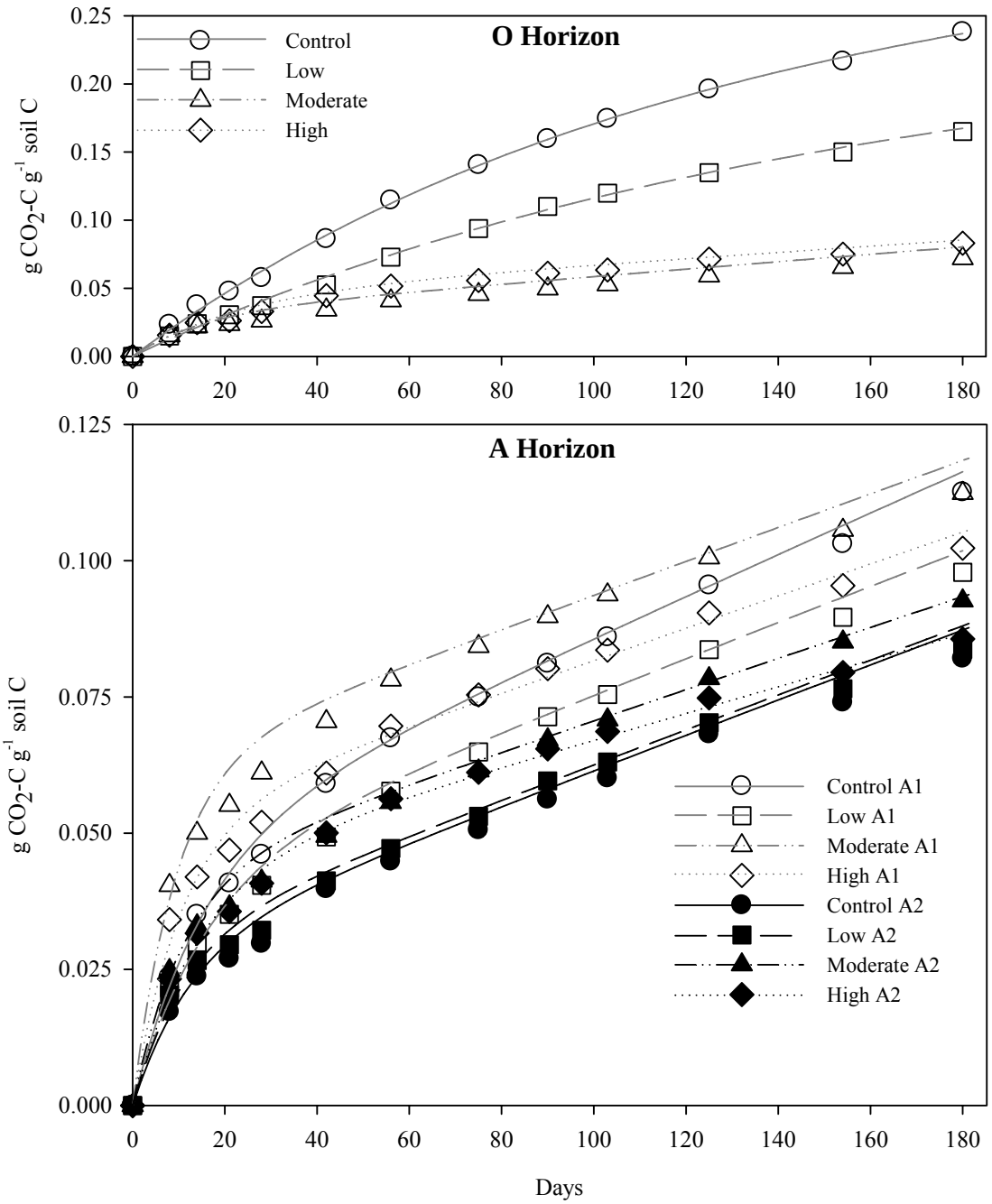


Figure 3.1 Cumulative C mineralized over 180 days from O and A horizons after burning at three levels of fire intensity and an unburned control. Points displayed are the mean of four replicates; lines are double-exponential model fit to cumulative CO_2-C data (Equation 4).

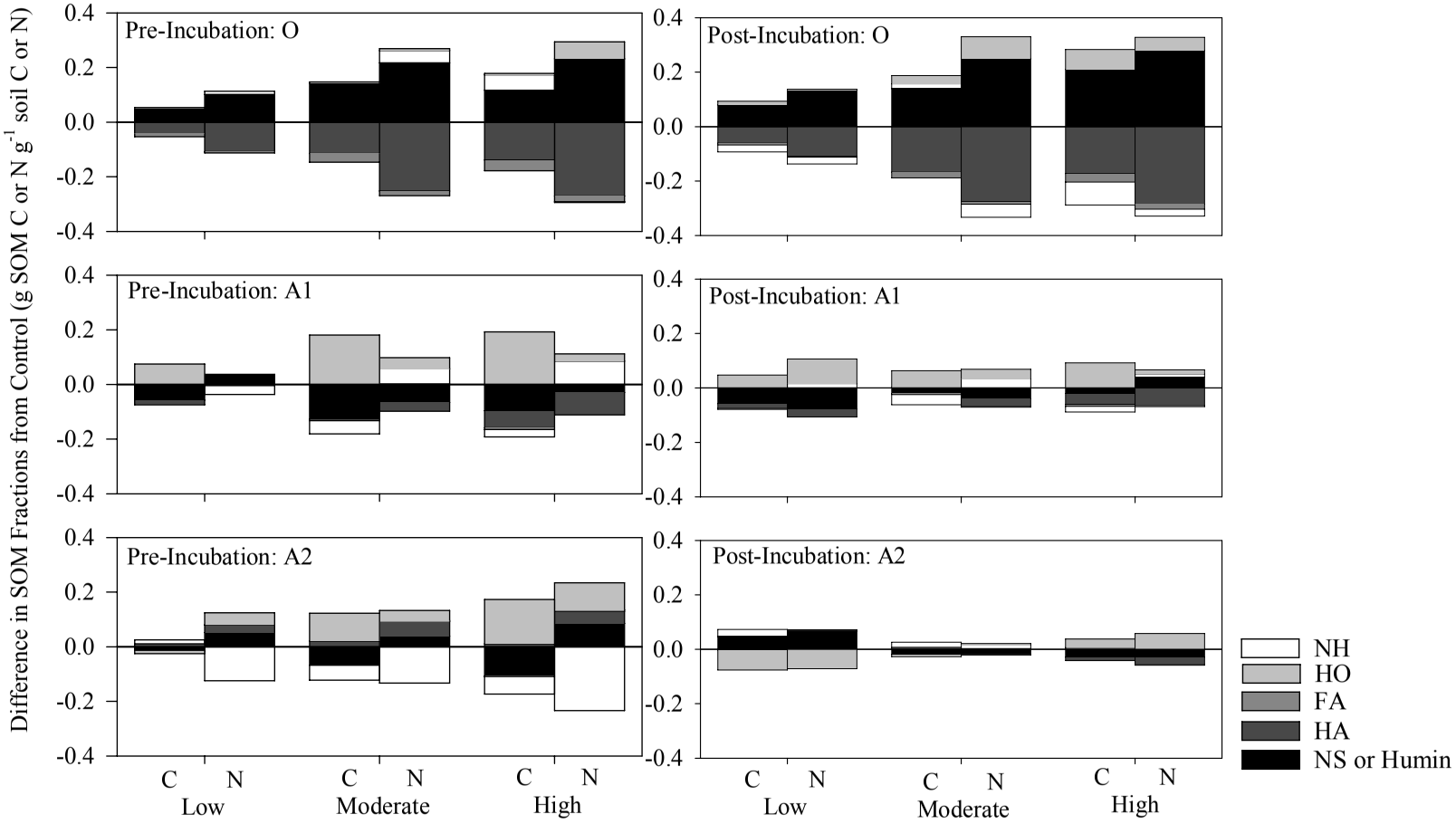


Figure 3.2 Difference in proportion of C and N content of each fraction at three burn intensities from an unburned control. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic. SOM fractions of mineral soils became similar to control while O horizons were altered by burning and remain different from control.

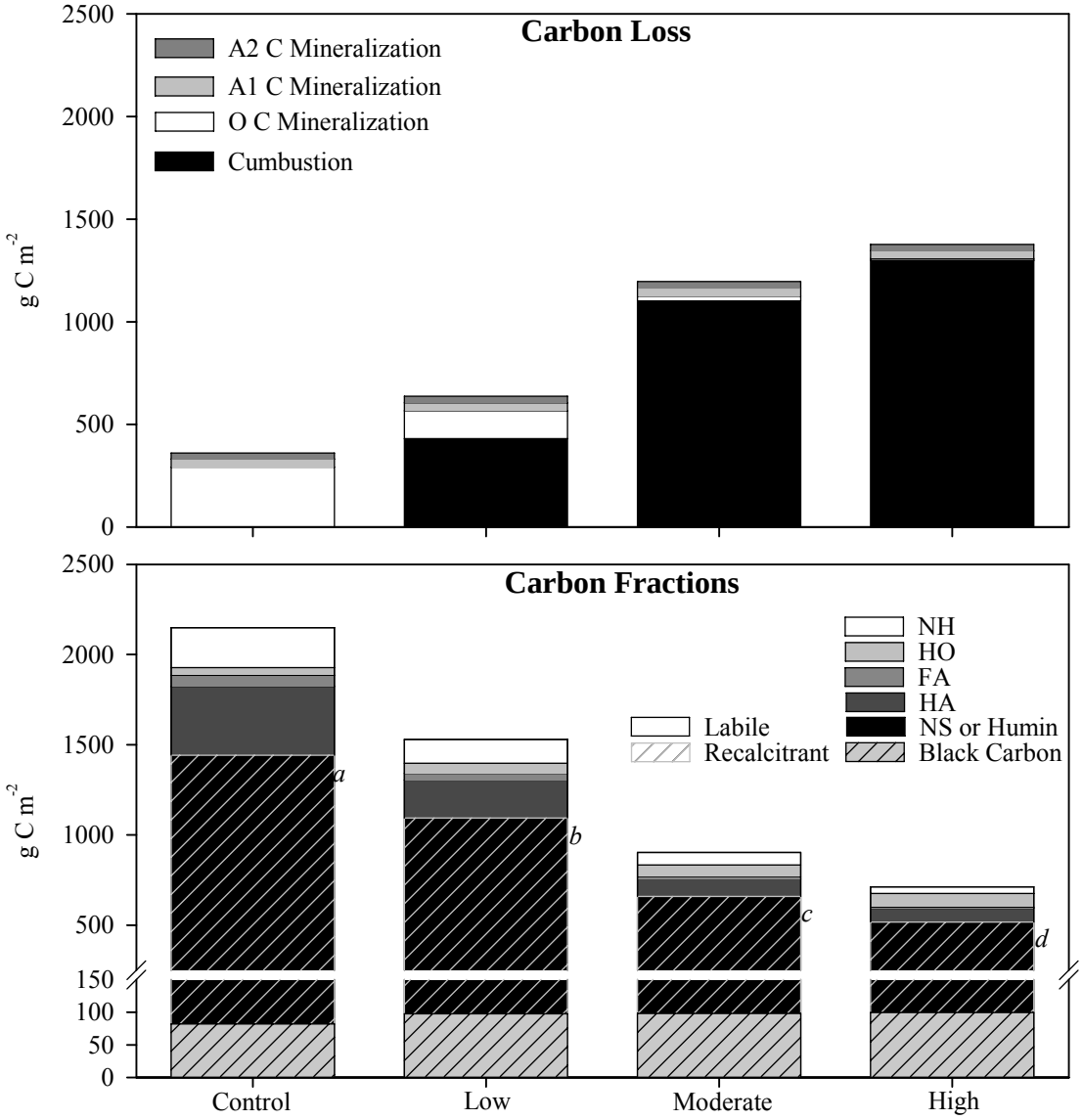


Figure 3.3 Total C lost and quantity of C fractions remaining after burning and incubation. Both O and A horizons from an unburned control and three levels of fire-intensity treatments were incubated for 180 days. Initial C content of the entire profile was 2500 g m^{-2} prior to burning or incubation. Total C losses are dominated by O horizon combustion, especially at moderate and high intensity. Total non-soluble C decreased with increasing fire intensity (*p=0.000*). Letters indicate statistically different humin+non-soluble material content as tested by Tukey's HSD. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

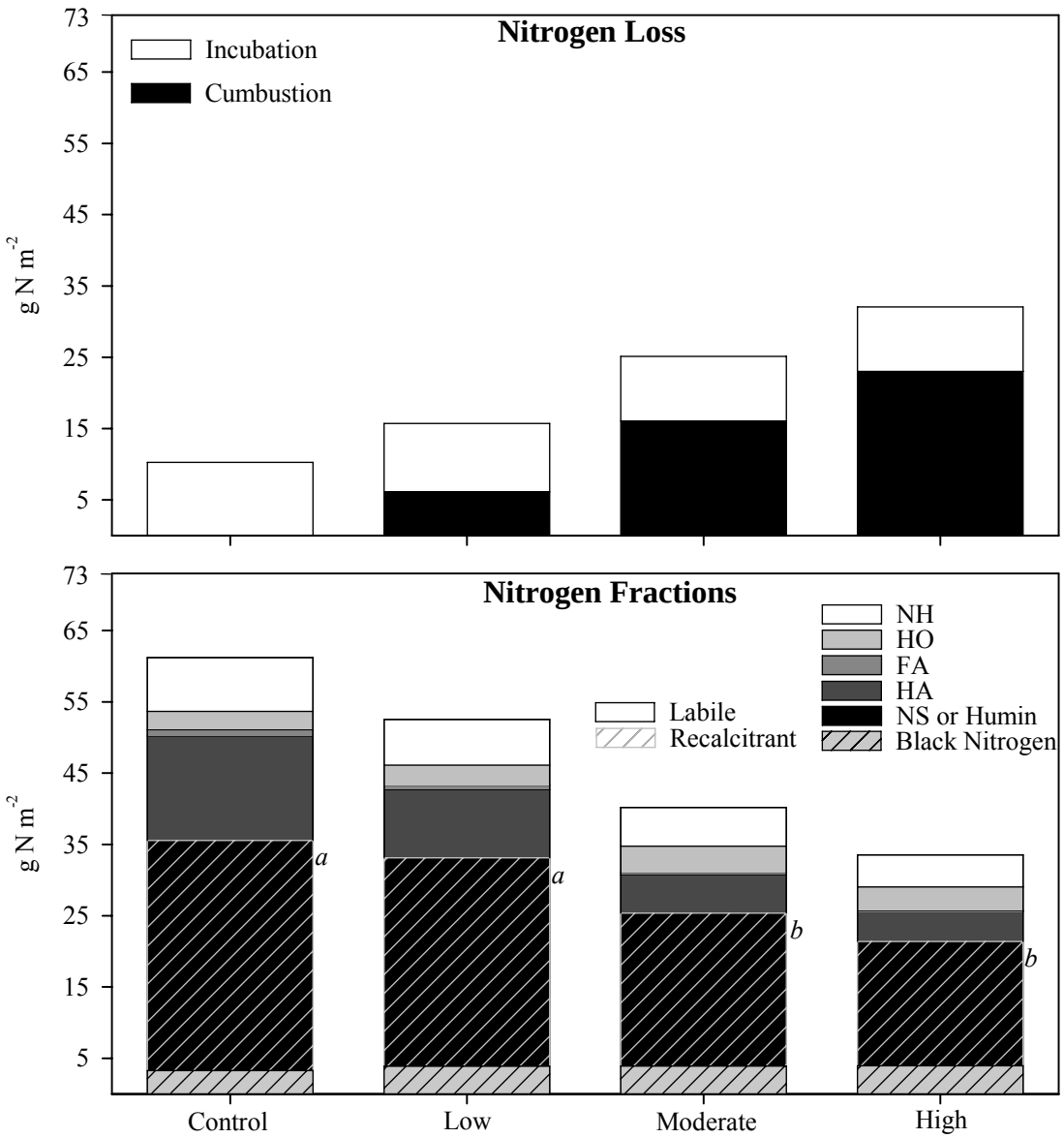


Figure 3.4 Total N lost through combustion and volatilization and quantity of N fractions remaining after burning and incubation. Both O and A horizons from an unburned control and three levels of fire-intensity treatments were incubated for 180 days. Initial N content of the entire profile was 73 g m^{-2} prior to burning or incubation. The total non-soluble N decreased with burning (*p=0.000*). Letters indicate statistically different humin+non-soluble material content as tested by Tukey's HSD. Abbreviations are: NS=non-soluble (O horizon), HA=humic acid, FA=fulvic acid, HO=other hydrophobic materials, and NH=soluble non-humic.

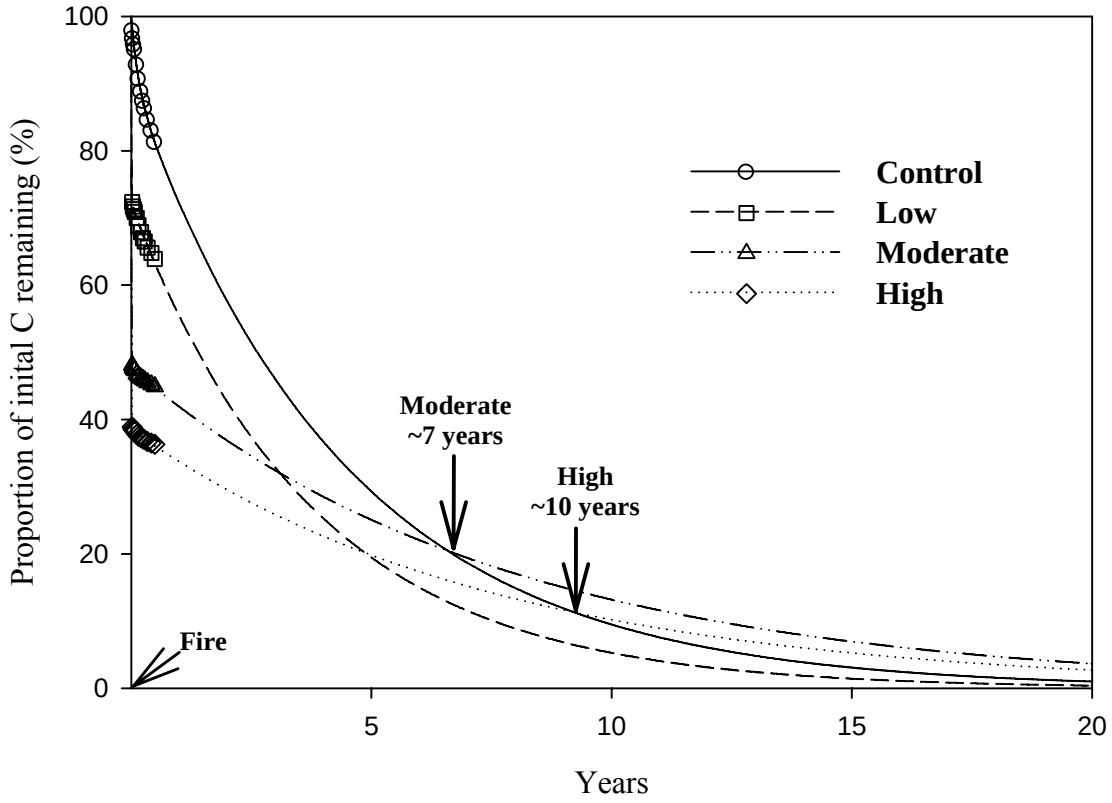


Figure 3.5 Proportion of C remaining after burning and incubation. Both O and A horizons (to 2 cm depth) from an unburned control and three levels of fire intensity treatments were incubated for 180 days. Curves were fit to a double-exponential model (Equation 6). Data on C mineralized after burning were collected for 6 months. Slower decomposition rates of fire produced SOM from soil profiles burned at moderate and high fire intensity allowed C to be preserved relative to the control after 7 and 10 years respectively. Soil profiles burned at low fire intensity may not be able to increase C relative to the control profiles.

Chapter 4
Soil Organic Matter in a Ponderosa Pine Forest with Varying Season and Interval of Burn

Introduction

Ponderosa pine (*Pinus ponderosa* Dougl. Ex Laws) forests in the inland Wetern U.S. are fire adapted with fire-return intervals ranging from 11 to 24 years. Fire exclusion and timber harvesting practices over the last 100 years have caused fuel loads to increase and changed the vegetative community. With recent climate trends this has resulted in frequent catastrophic wildfire (Tiedemann *et al.* 2000, Wright and Agee 2004). To avoid such wildfires managers use prescribed burning to reduce fuel loads and return ecosystem structure and function to a historical setpoint. The impact to the ecosystem caused by this restoration process is dependent on the severity of the prescribed fire, which is primarily managed by burning in either the fall or spring.

Historically, fires burned through these forests during the summer when fuels were dry, but frequent burning limited fuels resulting in low-severity fires (Agee 1993). Prescribed fires in ponderosa pine forests are frequently ignited during the spring when fuel moisture is high and fire behavior is controllable. Fall burning can be of moderate to high intensity since the fuels have dried during the summer months and may represent the natural fire severity better than the low-severity spring burn. The higher severity of fall burning would have a larger impact on accumulated fuels, but the current high fuel load may result in higher fire severity, which may be detrimental to management goals of preserving and restoring vegetation or soil processes. Very few studies have characterized the difference between spring and fall burning on ecosystem components, especially soils.

Multiple treatments of prescribed fire may be necessary to obtain the desired forest conditions especially if the burn applications are low severity. The frequency with which fires are applied will determine if fire-induced changes accumulate or if the forest

is able to recover between burn applications. The interaction of frequency and intensity may achieve some desired outcomes such as fuel reduction, but may cause cumulative impacts on soil nutrients and soil organic matter (SOM), potentially impacting forest productivity.

Soil organic matter includes both humic and non-humic organic substances associated with organic and mineral soil. Non-humic substances are generally any materials that can be identified and classified. Humic substances are refractory, dark colored, heterogeneous, organic compounds, produced as byproducts of microbial metabolism (Stevenson 1994).

Classes of SOM have been operationally defined by an alkaline extraction and subsequent solubility under acidic conditions. Humin is composed of the largest molecules that have the greatest degree of aromaticity and the lowest concentration of oxygen (Stevenson 1994). Humin is often associated with mineral surfaces, is very stable in the soil, and is not alkaline extractable. Non-soluble (NS) materials in O horizons, analogous to humin in the mineral soil, are usually made up of recognizable cellulose and lignin. Humic acid (HA) is soluble in alkaline conditions but precipitates in subsequent acidic solution and is relatively immobile in soils. Fulvic acid (FA) is soluble in both alkaline extract and in a subsequent acidic solution.

Black carbon (BC) is another component of SOM that often gets included into the insoluble humin fraction of both O and mineral soil horizons. Black carbon is the heterogeneous, aromatic, and carbon-rich residue of biomass burning and fossil-fuel combustion; it includes charcoal, soot, and graphite (Goldberg 1985). Charcoal is often part of the ash and residue remaining after biomass burning. Soot particles form in the gaseous phase and are easily transported from a fire site in the smoke plume. Graphite is usually geologically formed and inherited by soil. Black carbon decomposes at a much slower rate than uncharred material and has been suggested as a form of C useful for sequestering C in soil (Shneour 1966, Kuhlbusch and Crutzen 1995).

Fire consumes and alters SOM, mineralizes nutrients making them available for plant uptake, and raises pH (Neary *et al.* 1999). In general the chemical changes that

occur in SOM after heating and combustion are increases in aromatic structures with disproportionate losses of H and O relative to C (Almendros 1990, Baldock and Smernick 2002, Almendros *et al.* 2003, Gonzalez-Vila and Almendros 2003, Gonzalez- Perez *et al.* 2004, Knicker *et al.* 2005). Increasing heating severity on SOM has been shown to decrease the oxygen content, thereby reducing FA and HA fractions while increasing humin content and aromaticity (Almendros *et al.* 1990, Fernandez *et al.* 1997, 2001, and 2004). Few studies have examined the effect of varying fire severity in a natural setting on soils and SOM, especially in terms of season of prescribed burning.

A season of burn and burn interval study was begun in the southern Blue Mountains of eastern Oregon in 1997. This study provided an opportunity to examine prescribed burn severity (season) and repeated burn effects on soil and SOM. The objectives of this study were to: 1) determine the changes that are occurring to soil chemical characteristics, including SOM quality, as a result of different types and number of prescribed burns and 2) quantify changes to total soil C and N capitals. This research is important to clarify processes that are controlling SOM quantity and quality and develop management recommendations for prescribed fire that protect soil quality.

Materials and Methods

Site characteristics

The study site was located within the Malheur National Forest of the southern Blue Mountains of eastern Oregon (43°52’41”N/ 118°46’19”W). Elevation ranged from 1585-1815 m (5200-5955 ft). Ponderosa pine is the dominant tree with some western juniper (*Juniperus occidentalis* Hook.) and mountain mahogany (*Cercocarpus ledifolius* Nutt.) in drier areas that have shallow soils. The ponderosa pine trees are predominantly between 80 and 100 years old; the sites were thinned in either 1994 or 1995. Kerns *et al.* (2006) found that grasses and sedges that dominate the understory include Idaho fescue (*Festuca idahoensis* Elmer), bluebunch wheatgrass (*Agropyron spicatum* (Pursh)), sedges (*Carex* spp.), bottlebrush squirreltail (*Sitanion hystrix* (Nutt.)), Great Basin wild rye (*Elymus cinereus* Scribn. & Merr.), California Brome (*Bromus carinatus* H. & A.), and

western needlegrass (*Stipa occidentalis* Thurb.). Herbaceous cover consists of parsnipflower buckwheat (*Eriogonum heracleoides* Nuttall.), and large flowered collimia (*Collomia grandiflora* Douglas Ex Lindl.). Shrub cover is dominated by sage brush (*Artemesia tridentate* Nutt.), Oregon grape (*Berberis repens* Lindl.), and rabbitbrush (*Chrysothamnus* Nutt. Spp.).

Parent materials of the study sites consist of basalt, andesite, rhyolite, tuffaceous interflow, altered tuffs, and breccia (Carlson 1974). In addition, the soil has received ash from pre-historic eruptions of ancient Mount Mazama and other volcanos in the Cascade Mountains to the west (Powers and Wilcox 1964). Carlson (1974) found Lithic Argixerolls, Lithic Haploxerolls, and Vertic Argixerolls within the research sites, which were confirmed during this study. Alfisols and Inceptisols were also found during the soil sampling phase of the study.

At the Rock Spring SNOTEL station, about 25 km WNW of the study site, annual precipitation averages 46 cm with 80% falling as snow between November and April (NRCS 2007). Summers are dry and hot (17 ^{o}C mean air temperature in July-August) with cold winters (-3 ^{o}C mean air temperature in December-February).

Experimental design and treatment description

Six replicate study blocks were established and divided into 3 plots of similar stand type, aspect, slope, and parent materials (described by Thies *et al.* 2006a). Plot boundaries were established along roads and topographic features to control the prescribed burns. Each plot was randomly assigned as control, fall, or spring burn treatment. A burn interval of 5 or 15 years was assigned to a randomly designated half of each season's plot. The 5 treatment plots were of similar size (ranging from 6 to13 ha) within each block.

Fires were ignited by hand-carried drip torches using a multiple-strip head-fire pattern. Flame lengths were maintained at 60 cm during all burns. Fall burns were initiated in October 1997 and reburned in 2002. Spring burns were initiated in June 1998 and reburned in 2003. Temperature, humidity, and wind speed and direction were similar

during the application of all burns. At the time of soil sampling (summer of 2004), the 5-year-interval plots had burned twice with 1-2 years of recovery while the 15-year interval plots had burned only once with 6-7 years of recovery.

Soil Sampling

A transect of 8 points with 50 or 100 m spacing (depending on size of the particular plot) was established in each plot. Starting points and bearing were randomly chosen. Aspect, slope, and geomorphic shape were recorded at each point. Canopy cover was measured by estimating the amount of sky reflected off of a convex mirror held at chest level. A 4 m^2 plot was used to characterize vegetative and bare ground coverage at each sample point. Ground cover estimates of coarse woody debris (CWD), bare ground, grass, forbs, shrubs, and eroded soil were made. Burn severity was classified as low, moderate, or high at each point by examining char height on trees, tree mortality, organic matter consumption, and presence of char. A low-severity fire would produce char heights less than 2 m on a tree bole and consumed little of the O horizon. Moderate-severity fires produce char heights higher than 2 m and left a thin layer of char on the surface of the soil. High-severity fire was designated when tree mortality was high and little O horizon remained.

Representative soils were sampled from every major genetic horizon to a depth of 30 cm at each sampling point. Bulk density samples of each mineral soil horizon were collected using a hammer corer or, when soils were rocky, by water displacement. Mineral soil bulk density samples were brought back to the lab and oven dried at 105 ^{o}C until constant weight was achieved. O horizon bulk densities were sampled by removing a known area (207 cm^2), and averaging depth at 4 locations to obtain a volume. O horizon bulk density samples were oven dried at 70 ^{o}C until a constant weight was achieved. Hydrophobicity at the surface of the mineral soil was measured in the field by dropping 0.5 ml water and measuring the amount of time needed for the droplet to completely infiltrate the soil (Krammes and DeBano 1965).

Soil Analysis

Soil samples were air-dried, weighed, and mineral horizons were separated into coarse and fine fractions with a 2 mm sieve. Coarse fractions were weighed to determine gravel and rock content. Subsamples from each air-dried mineral and O horizon were analyzed for pH using the saturated-paste method (Van Miegroet *et al.* 1994). Each O horizon sample and each fine fraction of every mineral soil sample was ground using a mortar and pestle for analysis of C and N on a Perkin Elmer 2400 CHN analyzer. Total soil C and N content were calculated on a per hectare basis for all horizons to a depth of 30 cm using C and N concentrations and total amount of coarse-content-free soil (<2 mm).

Samples were combined by horizon across grid points so that there was one composite O and A horizon per plot. Composite samples were analyzed for SOM composition, C, N, cation exchange capacity (CEC), and base saturation. Subsamples of each composite were homogenized using a small coffee grinder. Base cations were extracted from a 5 g subsample of each composite A horizon samples using 50 ml of 1 M unbuffered NH_4Cl and extracted using a syringe extractor for 12 hours (Skinner *et al.* 2001). Extract solution cation concentrations were determined using an ICP. Cation exchange capacity was calculated using the sum of exchangeable Al, Ca, Fe, H, K, Mg, and Na cations (meq 100 g^{-1} soil).

Soil organic matter was extracted from both O and A horizon composites using a method adapted from Schnitzer (1982). The extraction consisted of 100 ml of 0.1 N NaOH solution and either 10 g of mineral or 1 g of O horizon under N_2. Soil and extractant were placed into a 250 ml centrifuge bottle and shaken for 16 hours on a reciprocal shaker. The solution was separated from the residue using a centrifuge at a force of 6635*g* for 10 minutes. The residue contained either humin and mineral material from the A horizons or non-soluble (NS) organic material, (*e.g.,* lignin and cellulose) from the O horizons. The supernatant solution and one rinse containing fulvic acid (FA) and humic acid (HA) fractions were collected for further processing. Humin or NS

fractions were dried in a convection oven at 50 ^{o}C, weighed, prepared for loss on ignition (LOI; heated to 550 ^{o}C for 6 hours in a muffle furnace), and C, H, and N analysis.

The supernatant containing FA and HA was acidified to pH 1 using 6 N HCl and allowed to stand overnight to precipitate HA. Fulvic acid was separated from HA by centrifugation at a force of 6635*g* for 10 minutes. Humic acid was freeze dried in a benchtop lypholizer, weighed, and stored in a light-protected dessicator.

The samples containing FA were purified to remove base-extracted acid-soluble non-humic materials and salts using a method adapted from Swift (1996). The solution containing FA was passed through a column containing 60 mL of DAX-8 resin (Supelco Supelite^{TM} DAX-8; methyl methacrylate ester). The column was rinsed with 2 bed-volumes of deionized H_2O, and then eluted with 2 bed-volumes of 0.1 N NaOH. The eluate containing FA was collected and passed over a column containing Dowex H^+ exchange resin to remove Na^+. The solution containing FA was freeze dried, weighed, and stored in a light-protected dessicator. Prior to C, H, and N analysis, FA and HA samples were placed in pre-weighed tins and dried at 50 ^{o}C for 48 hours. Fulvic acid and HA subsamples were analyzed for C, H, and N concentration.

Black Carbon

Composited O and A horizons were analyzed for BC using a method adapted from the CTO375 method outlined by Gustafsson *et al.* (1997). This method uses the ability of BC to resist thermal oxidation at 375° C. One gram or 0.1 g of A and O horizon, respectively, were weighed to 0.1mg, placed in ceramic crucibles, and then into a preheated muffle furnace (375 ^{o}C). After 20 hours the samples were removed and weighed. Samples were placed into a muffle furnace preheated to 550 ^{o}C for loss on ignition to determine the amount of $LOI_{375\text{-}550}$ which would potentially contain BC and black nitrogen (BN) using the following equation:

$$\frac{LOI_{375-550}(g)}{S_i(kg)} = \left(\frac{A_{375}(g) - A_{550}(g)}{S_i(g)}\right) * \frac{1000g}{kg} \qquad (1)$$

where A is ash or residue after heating at 375 or 550 ^{o}C, and S_i is the initial amount of soil.

The mass lost between muffle-furnace temperatures of 375 and 550 ^{o}C had a significant relationship ($p<0.05$) with BC and BN with r^2 values of 0.88 and 0.77, respectively (Chapter 2). About half (50±17% (95% CI)) of $LOI_{375-550}$ was found to be BC. This ratio agrees with the recommendation by Nelson and Sommers (1982) to use a factor of 50% to convert SOM content of surface soils to C content. Black nitrogen accounted for 2±1% (95% CI) of $LOI_{375-550}$. All samples were analyzed for $LOI_{375-550}$ so these data were used to assess statistical differences among the burn treatments. The mass lost between 375 and 550 ^{o}C converted to BC or BN was compared to other research regarding BC and BN.

Statistical Analysis

Average values for each horizon were calculated for each treatment within each study block (6 replicates), N=30 for each horizon. The experimental design was treated as a completely randomized block 2 by 2 factorial (season and interval of burn) with an augmented control. Differences between the soil and site characteristics from the control, 2 fall burns, 1 fall burn, 2 spring burns, and 1 spring burn were tested using a one factor ANOVA. Tukey's HSD was used to delineate significant homogenous subsets among the 5 treatments. Orthogonal contrasts were conducted to determine if season, number of burns, or the interaction of the two created significant differences within the 2 by 2 factorial of season and interval of burn. A significance level of α=0.10 was used for all statistical tests.

Results and Discussion

Site and soil characteristics

Prescribed fire applied in the fall imparted a slightly higher estimated severity than spring burns (Table 4.1). Canopy cover was lowest on the fall burn plots partly as a

result of higher tree mortality after the initial burn as reported by Thies *et al.* (2005 and 2006b). Additionally, Thies *et al.* (2006a) found that after the second fall and spring burn woody fuels were reduced by 85 and 75%, respectively, relative to the control. The greatest reduction in woody fuels was caused by fall burning and highest tree mortality occurred after the initial fall burn, suggesting that the initial fall burns were the most severe.

It appears that burn severity is affecting the understory species composition. Plots burned twice have reduced grass coverage relative to both controls and plots burned once. Fall burns had a slightly elevated coverage of forb species relative to spring burning ($p=0.058$). Similarly, Kerns *et al.* (2006) found reduced grass cover after the initial spring burn and increased forb coverage after the initial fall burn.

Repeated burning can decrease O horizon coverage and with reductions in grass cover can expose the mineral soil surface to erosion. Percent bare ground increased after burning in the fall and spring and was highest on plots burned twice. This indicates increased erosion risk and there was a small significant ($p=0.089$) increase in the percent of bare eroded soil on plots treated with 2 burns relative to plots with one burn (7% and 4% respectively). However, the increased incidence of erosion could be reflecting a higher coverage of bare ground, allowing the evidence of erosion to be observed.

Hydrophobicity was lowest on fall burn treatments and significantly negatively correlated with bare ground coverage ($R=-0.612$; $p<0.05$). Unobserved erosion occurring after the initial fall burn could have removed fire-produced hydrophobic materials from the surface of the A horizon. Hydrophobic O horizon materials were removed by fire, thereby reducing inputs of hydrophobic materials into the mineral soil. Further, mycelia of fungi have been shown to promote hydrophobicity along with litter of certain plants (Doerr *et al.* 2000). Smith *et al.* (2004) found that the initial fall burns of these sites had significantly reduced live ectomycorrhizal root biomass and ectomycorrhizal fungi species richness in the surface 10 cm. The high-severity initial fall burn may have caused a decrease in hydrophobic compounds in both the O and A horizons and reduced the populations of fungal species that produce hydrophobic materials.

O and A horizon pH values were slightly elevated by burning with the more recent higher-severity fall burns (Table 4.2). Ash produced by burning contains hydroxides and carbonates which raised soil pH (Ulery *et al.* 1993). There was a significant interaction between season and number of burns on the A horizon pH. Soil pH from plots with two spring burns may be influenced by a reduction in understory grass and grass litter. Additionally, a recent influx of fresh litter containing organic acids from fire-induced litterfall could have lowered the pH. The mineral soil pH of the control burns may be lower than historical levels due to the lack of fire for the last 100 years. If fall burning replicates the severity of fires that historically burned these forests, then pH may have returned to pre-fire suppression levels on these plots.

Two fall burns significantly lowered O horizon thickness 65% below the control (Table 4.2). The one fall and two spring burns reduced O horizon thicknesses by approximately 30% from the control but this reduction was not significantly different from the control. Similar to the current study, forest floor reduction caused by spring and fall prescribed burns was found to be 42% (Choromanska and DeLuca 2001) and 51% (Covington and Sackett 1984), respectively. Fall burning at 5-year intervals may keep O horizon thickness thin and patchy, exposing mineral soil to erosion and reducing organic matter inputs to the mineral soil.

O horizon thickness from plots treated to only one spring burn was not significantly different from the control. The lower severity of the spring burns removed a smaller portion of O horizon and time since burning (6-7 years) has allowed O horizon depth to recover. Approximately 2.4 cm of O horizon has accumulated since the initial fall and spring burns, when O horizons were measured by Smith *et al.* (2004). O horizon thickness of the plots with one spring burn appear to have completely recovered sooner than plots with one fall burn, implying that it remained and has protected the mineral soil from erosion. Additionally, organic matter and nutrient inputs from the O horizon to the mineral soil are being maintained on the plots with one spring burn.

Burning usually decreases the C and N concentration of O horizons due to combustion and production of ash (Neary *et al.* 1999). Fall burn treatments had a lower

O horizon C and N concentration than the spring burns, likely as a result of SOM consumption and higher ash content (Table 4.2). The difference in C and N concentration may be statistically significant, but the differences may be too small to cause noteworthy effects on ecosystem processes.

Increasing fire frequency has been shown to decrease the concentration of C and N of the upper 5 cm of A horizon in an Arizona ponderosa pine forest (Neary *et al.* 2003). Neither the season nor interval of burn-treatments had a significant effect on A or B horizon C or N concentrations. The intensity of the prescribed burns may be too low to cause significant differences in C concentration, or the number of repeated burn applications is too low for changes to have accumulated.

Average A horizon C and N concentration was 49 g C kg^{-1} soil and 2.7 g N kg^{-1} soil with B horizon concentrations averaging 25 g C kg^{-1} and 1.3 g N kg^{-1} soil. Ponderosa pine stands in eastern Washington, eastern Oregon, and western Montana averaged 8-56 g C kg^{-1} soil and 7-13 g C kg^{-1} soil for A and B horizons, respectively (Monleon *et al.* 1997, Baird *et al.* 1999, DeLuca and Zouhar 2000, Hatten *et al.* 2005). Nitrogen concentrations in these forests averaged 1.3-2.0 g N kg^{-1} soil and 0.7-1.8 g N kg^{-1} soil for A and B horizons, respectively. The highest values of C and N occurred under ponderosa pine stands in central Oregon (Monleon *et al.* 1997) and this study (eastern Oregon). Andic materials in both eastern and central Oregon sites may be promoting C and N accumulation in the soil through complexation of organic matter with allophanic mineral materials (Zunino *et al.* 1982a, 1982b). Additionally, understory vegetation of both of these forests is dominated by grasses which could have increased the amount C and N through the incorporation of fine roots into the upper soil horizons.

Summing O horizon and mineral soil total C to a 30 cm depth shows that fall burns reduced C by 22-25% relative to the spring and control treatments, while total N was reduced 13-19% (Figure 4.1). Carbon loss with fall burning was driven by consumption of C from the O and A horizons, which were reduced by 62 and 11%, respectively, relative to the control. Additionally, there is a reduction in C and N of the B horizons of plots burned 6-7 years ago which may be the result of a change in vegetative

community or due to the random placement of the treatment plots onto soil types with B horizons that have less SOM.

Baird *et al.* (1999) found a total C content of 48 Mg ha^{-1} in the upper 30 cm, including the O horizon, of an unburned ponderosa pine forest in eastern Washington. A high intensity wildfire reduced C content to 30 Mg ha^{-1} (a 37% reduction from control). Of the 18 Mg C ha^{-1} lost due to wildfire 61% of the loss was caused by consumption of C directly from the A horizon, while B horizons were unaffected by burning. In the current study only 17% of the 26 Mg ha^{-1} difference between the control and fall burns was due to reduced A horizon C content, with most C reduction caused by consumption of O horizon. The lower severity of fall prescribed burning relative to wildfire is helping to preserve C in the A horizon. Further, the high C content of the A horizon (44 Mg C ha^{-1} in control A horizon) relative to Baird *et al.* (1999) (23 Mg ha^{-1} in control A horizon) reduces the magnitude of change. Relative to wildfire even the higher severity fall burning may protect soil C.

The initial fall burns may have had the largest impact to the soil; however, it does not appear to have had a significant impact to soil processes or long-term productivity. There was no significant effect to CEC and %BS and only minor changes to soil pH. Additionally, Ogden (2005) did not find a significant effect on tree growth or available N between the treatments. The high OM content of these soils may be imparting resilience to these soils. A lower-productivity soil with less OM may not have as much capacity to resist change as well. Using fall burning to reintroduce fire to a forest with a lower quality soil could impact soil productivity by removing a greater percent of total of C and N.

Soil organic matter characteristics

Both O and A horizon total C was dominated by NS or humin materials (49 and 57%, respectively). The NS fraction of the O horizon had a much higher C:N ratio than the humin fraction of the A horizon, probably as a result of a higher concentration of unhumified and N-free materials such as cellulose and lignin (Table 4.3). There was

significantly higher NS C in the O horizons treated to two burns, which is probably due to an increase in charcoal. Charring may be increasing the NS C:H ratio of the plots with the most recent burns having a C:H ratio above 2.0. Baldock and Smernik (2002) found that wood (C:H = 0.7) heated to temperatures above 250° C had C:H ratios greater than 2.0 and Almendros *et al.* (2003) observed a similar response to the C:H ratio of heated peat. Chapter 3 showed that NS C in the O horizon subjected to moderate- or high-intensity prescribed fire did not change after decomposition, suggesting that this charred material does not readily decompose. If charred NS C is not consumed by wildfire or another prescribed fire, then it may accumulate in the soil due to slower decomposition.

Fulvic acid was concentrated equally across both O and A horizons (3% of total C). The C:N ratio of FA from O horizons was very high (Table 4.3) suggesting that there was a large quantity of N-free tannins or lignin decomposition products (*e.g.,* vanillin) which may be included in the FA fraction (Qualls and Haines 1991). Humic acid content of the A horizon was higher than the O horizon (23 and 9%, respectively) likely as a result of a higher degree of SOM humification. The HA:FA ratio of the A horizon was unaffected by burning but is remarkably high (HA:FA=11) for a forest soil as compared to HA:FA data presented by Kononova (1966). Fulvic acid preparation using DAX-8 resin may have reduced FA content and elevated the HA:FA ratio as reported by Kuwatsuka et al. (1992). If the portion of C removed by DAX-8 purification of FA is added to the FA fraction, the HA:FA ratio is 1.3 which is similar to the HA:FA ratio of other Mollisol soils (Kononova 1966).

Total humified materials (humin, HA, and FA) accounted for 60 and 83% of the C from O and A horizons, respectively. The remaining 40% and 17% may include soluble non-humic materials, which would have been discarded during FA purification, or organic material not desorbed from the DAX-8 column during FA purification (Chapter 2 and 3). These fractions were shown to be influenced by fire intensity in Chapters 2 and 3. No significant ($p>0.10$) treatment effect was detected on the proportion of unaccounted C, suggesting that they had not been affected by burning or had recovered since burning.

Knicker *et al.* (2005) found a decrease in HA and an increase in humin concentration 5 years after severe wildfire. High-severity wildfire may increase the recalcitrant C within the SOM pool for an extended period of time. However, Knicker *et al.* (2005) studied only one composite sample each from a burned and unburned area, which limits the conclusions from that study. The intensity of the prescribed fires in the current study may not have been high enough to cause lasting changes to SOM. While low- and moderate- severity fires have been shown to affect SOM composition (Chapter 2), these changes do not persist through incubation, suggesting that spring and fall prescribed burning will not have long-lasting effect on SOM composition (Chapter 3). High-severity fire, such as that studied by Knicker *et al.* (2005), may cause a long-term change to SOM composition by exceeding a threshold severity where the chemical reactions which create recalcitrant materials dominate.

The consumption of O horizon is having the greatest effect on the FA and HA C and N content of the soils (Table 4.4). The non-soluble materials, NS and humin, appear to be accumulating in the O and A horizons of the treatment with one spring burn while being consumed by multiple fall burns. Treatments with one spring burn are 6% higher than the control and 49% higher than plots with 2 fall burns. Repeated fall burning may be consuming material that contributes to humin and NS substances in both A and O horizons. The consumption of O horizon may be the most important factor regulating the quantity of long-term fire-affected SOM after repeated low-intensity prescribed fire.

Although not significant, one low-intensity spring burn may have produced the greatest quantity of non-soluble BC in the O horizon (Table 4.5). Czimczik *et al.* (2003) found that BC was non-existent in Scots pine (*Pinus sylvestris* L.) forests where the most recent fire was high severity. The charred material may have been present prior to burning; however, it was consumed by the high-intensity fire. They also found a low rate of surface soil mixing, so that BC was not able to be protected by the mineral soil through incorporation. At the current study site, burrowing animals are prevalent and have been observed to mix mineral and organic horizons. Also, cattle are sometimes present in these forests and are able to churn organic material into the mineral soil. Mixing of

charred NS material from the O horizon into the A horizon may increase total humin C content of the A horizon, which could protect it from low- to moderate-severity fires in the future.

Non-soluble materials such as charcoal may be providing soils under fire-prone forests with materials which contribute to the total soil CEC. Liang *et al.* (2006) showed that charcoal incorporated into mineral soil can impart a higher CEC over time. Charcoal may be combining with slightly higher pH in the A horizon of the plots with one spring burn to result in high CEC (Table 4.2).

The reduction of non-soluble materials caused by the fall burning at a 5-year interval may be further reduced with future repeated burning and could affect soil processes such as CEC in addition to available nutrients and understory species reestablishment. Charcoal has been shown to reduce the inhibitory effect of allelopathic compounds on seedling establishment and nitrification (Zackrisson *et al.* 1996, Wardle *et al.* 1998, DeLuca *et al.* 2002, 2006). If the understory species of ponderosa pine forests are adapted to the presence of charcoal at the time of understory reestablishment after low-intensity fire, then a fire regime that allows charcoal to accumulate may provide the most robust soil conditions for native plant restoration. The initial fall burn has caused a higher cover of non-native understory species (Kerns *et al.* 2006). If non-soluble materials in this study are dominated by charcoal then the higher-severity fall burning at 5-year intervals may reduce the success of understory native species reestablishment through the consumption of charcoal. The initial fall burn and fall burns at 5-year intervals may be consuming charcoal and other non-soluble materials that are important for soil processes, ecosystem function and C sequestration. High-severity fall burns applied every 5 years may not restore understory species composition to the historical structure.

Reinitiating fire into a fire-suppressed forest achieves management goals of fuel reduction whether the burns are applied in the fall or spring. However, increased SOM consumption of the fall burns may lead to significant changes to soil processes in these stands in the future. It is possible that the high SOM content of these soils gives them the

capacity to resist major changes caused by the initial fall burning that a lower quality soil may yield. Using fall burns initially to reduce fuel loads may need to be avoided in order to preserve soil health and sequester C in fire-suppressed stands.

Conclusions

The reintroduction of fire after 100 years of suppression has had the intended result of reducing fuels in the form of O horizon and coarse woody debris (CWD). Burning was associated with elevated pH of both O and A horizons while fall burning decreased the hydrophobicity at the surface of the A. If fall burning replicates the severity of fires that historically burned these forests, then pH and hydrophobicity may be returning to pre-fire suppression levels. Higher-severity fall burns decreased the C and N capital of the O and A horizons while the spring burns did not significantly affect the total C and N content of the soil. Generally, the prescribed fire treatments had few effects on SOM composition. O horizon SOM was largely consumed by the prescribed fires, which was reflected in reduced FA and HA content. Recalcitrant materials appear to be accumulating in the O and A horizons of the treatment with one spring burn while being consumed by multiple fall burns with most of the impact appearing to have been caused by the initial fall burn. Reinitiating fire into a fire-suppressed forest using fall burning may reduce soil C and N and impact soil processes. Spring burning at longer than 5-year intervals may cause little to no impact to the soil with repeated burns. Therefore, an initial lower-severity spring burn could be used to reduce fuels and forest structure before applying fall burns which may simulate the natural fire regime.

Table 4.1 Surface cover (mean ± standard deviation) of plots treated to 1 or 2 fall and spring burns. Significant (α=0.1) differences are in bold as determined by a one-factor ANOVA (*p*) and orthogonal contrasts for season (p_s) and number of burns ($p_{\#}$). Interaction between season and number of burns was not significant. Letters indicate similar subsets (rows) using Tukey's HSD. CWD indicates coarse woody debris surface cover.

	Control	Fall		Spring		p	p_s	$p_{\#}$
		2	1	2	1			
Burn Intensity	-	Low-Mod.	Low-Mod.	Low	Low			
CWD (%)	13 ± 6 ^{a}	5 ± 3 ^{b}	7 ± 3 ^{b}	7 ± 2 ^{b}	10 ± 2 ^{ab}	***0.014***	*0.205*	*0.124*
Bare Ground (%)	11 ± 7 ^{a}	28 ± 9 ^{b}	21 ± 9 ^{ab}	22 ± 12 ^{ab}	13 ± 10 ^{a}	***0.012***	***0.043***	***0.031***
Grass (%)	11 ± 8 ^{ab}	8 ± 2 ^{ab}	14 ± 8 ^{b}	5 ± 3 ^{a}	11 ± 7 ^{ab}	***0.099***	*0.156*	***0.019***
Canopy (%)	37 ± 9 ^{bc}	24 ± 8 ^{a}	25 ± 9 ^{ab}	33 ± 6 ^{abc}	41 ± 8 ^{c}	***0.006***	***0.001***	*0.142*

Table 4.2 Soil characteristics (mean ± standard deviation) of O and A horizons in plots treated with 1 or 2 fall or spring burns (n=6). Significant (α=0.1) *p*-values are in bold as determined by a one-factor ANOVA (*p*) and orthogonal contrasts for season (p_s), number of burns ($p_\#$), and interaction of season and number of burns ($p_{s*\#}$). Letters indicate similar subsets (rows) using Tukey's HSD. Abbreviations are: CEC=cation exchange capacity and BS=base saturation.

O Horizon																
	Control		Fall				Spring				p	p_s	$p_\#$	$p_{s*\#}$
			2		1		2		1					
Thickness (cm)	3.7 ± 1.2	a	1.3 ± 0.4	b	2.6 ± 1.3	ab	2.7 ± 0.9	ab	3.9 ± 0.8	a	***0.001***	***0.002***	***0.005***	*0.992*
pH	5.0 ± 0.4	ab	5.3 ± 0.3	c	5.3 ± 0.2	bc	4.9 ± 0.3	a	5.1 ± 0.2	abc	***0.004***	***0.001***	*0.657*	*0.151*
C (g kg^{-1} soil)	456 ± 53	abc	444 ± 39	ab	438 ± 48	a	484 ± 34	bc	488 ± 55	c	***0.010***	***0.000***	*0.981*	*0.649*
N (g kg^{-1} soil)	11 ± 2.0	ab	9.9 ± 1.1	a	10 ± 1.2	a	11 ± 1.8	b	12 ± 1.8	b	***0.042***	***0.003***	*0.546*	*0.706*
C:N	53 ± 8.6		57 ± 8.2		56 ± 8.5		55 ± 13		53 ± 9.8		*0.684*	*0.286*	*0.471*	*0.857*

A Horizon														
	Control		Fall				Spring				p	p_s	$p_\#$	$p_{s*\#}$
			2		1		2		1					
Hydrophobicity (sec)	44 ± 18	a	12 ± 5	b	17 ± 10	ab	40 ± 26	a	38 ± 32	ab	***0.016***	***0.003***	*0.779*	*0.645*
pH	6.0 ± 0.2	ab	6.3 ± 0.2	b	6.1 ± 0.3	ab	5.9 ± 0.2	a	6.2 ± 0.1	ab	***0.047***	*0.047*	*0.350*	***0.029***
C (g kg^{-1} soil)	47.4 ± 17		47.2 ± 15		44.9 ± 18		50.1 ± 22		54.9 ± 18		*0.635*	*0.191*	*0.801*	*0.457*
N (g kg^{-1} soil)	2.8 ± 1.1		2.6 ± 0.9		2.5 ± 0.9		2.6 ± 1.2		3.0 ± 1.0		*0.698*	*0.361*	*0.663*	*0.340*
C:N	21 ± 4.2		22 ± 3.0		22 ± 3.4		24 ± 6.4		23 ± 4.2		*0.375*	*0.182*	*0.314*	*0.611*
CEC (meq 100g^{-1} soil)	22 ± 5.7		22 ± 3.3		20 ± 6.2		21 ± 5.2		24 ± 4.4		*0.522*	*0.506*	*0.921*	*0.114*
BS (%)	98 ± 0.9		98 ± 0.4		98 ± 0.6		98 ± 0.7		98 ± 0.6		*0.721*	*0.544*	*0.849*	*0.226*
Ca (mg kg^{-1} soil)	3371 ± 1032		3336 ± 596		3022 ± 1000		3112 ± 912		3551 ± 812		*0.563*	*0.537*	*0.799*	*0.137*

Table 4.3 Soil organic matter characteristics (mean ± standard deviation) of O and A horizons in plots treated with 1 or 2 fall and spring burns (n=6). Significant (α=0.1) *p*-values are in bold as determined by a one-factor ANOVA (*p*) and orthogonal contrasts for season (p_s), number of burns ($p_\#$), and interaction of season and number of burns ($p_{s*\#}$). Letters indicate similar subsets (rows) using Tukey's HSD. Abbreviations are: NS=non-soluble (O horizon), Hu=humin (A horizon), HA=humic acid, and FA=fulvic acid. Humin C:H ratio not shown due to the inherited H content from mineral material.

O Horizon										
		Control	Fall		Spring		p	p_s	$p_\#$	$p_{s*\#}$
			2	1	2	1				
C (g kg^{-1} soil)	NS	222 ± 35.8	232 ± 39.5	213 ± 59.7	234 ± 33.6	225 ± 37.2	*0.396*	*0.427*	***0.100***	*0.529*
	HA	40 ± 7.3 ^{ab}	36 ± 10.4 ^{a}	36 ± 9.1 ^{a}	42 ± 13.7 ^{ab}	50 ± 11.6 ^{b}	***0.065***	***0.010***	*0.311*	*0.254*
	FA	13 ± 2.4	13 ± 3.9	10 ± 3.7	11 ± 2.1	12 ± 2.3	*0.156*	*0.864*	*0.251*	***0.078***
N (g kg^{-1} soil)	NS	5.5 ± 0.91	5.2 ± 0.86	4.8 ± 1.36	5.6 ± 1.65	5.6 ± 1.63	*0.651*	*0.188*	*0.651*	*0.592*
	HA	1.2 ± 0.32 ^{ab}	1.0 ± 0.29 ^{a}	1.1 ± 0.20 ^{ab}	1.3 ± 0.31 ^{ab}	1.6 ± 0.55 ^{b}	***0.084***	***0.012***	*0.308*	*0.367*
	FA	0.17 ± 0.13	0.14 ± 0.12	0.10 ± 0.07	0.14 ± 0.04	0.12 ± 0.09	*0.148*	*0.602*	*0.189*	*0.494*
C:N	NS	51.0 ± 5.6	56.1 ± 10	56.5 ± 13	55.7 ± 15	53.7 ± 16	*0.843*	*0.685*	*0.836*	*0.769*
	HA	11.5 ± 1.5	11.4 ± 1.8	11.3 ± 2.0	11.8 ± 1.9	11.3 ± 1.0	*0.946*	*0.650*	*0.742*	*0.557*
	FA	160 ± 127	238 ± 280	157 ± 98.2	103.9 ± 35.9	193 ± 176	*0.318*	*0.282*	*0.930*	***0.067***
C:H	NS	2.1 ± 0.46	2.1 ± 0.9	1.8 ± 0.67	2.5 ± 1.6	1.5 ± 0.24	*0.458*	*0.944*	***0.099***	*0.391*
	HA	2.8 ± 0.5	2.9 ± 0.6	2.8 ± 0.6	2.8 ± 0.5	2.8 ± 0.6	*0.419*	*0.369*	*0.207*	*0.234*
	FA	0.89 ± 0.04 ^{ab}	0.94 ± 0.10 ^{a}	0.93 ± 0.10 ^{ab}	0.87 ± 0.09 ^{ab}	0.84 ± 0.07 ^{b}	***0.061***	***0.005***	*0.527*	*0.608*

Table 4.3 is continued on the next page.

Table 4.3 Continued

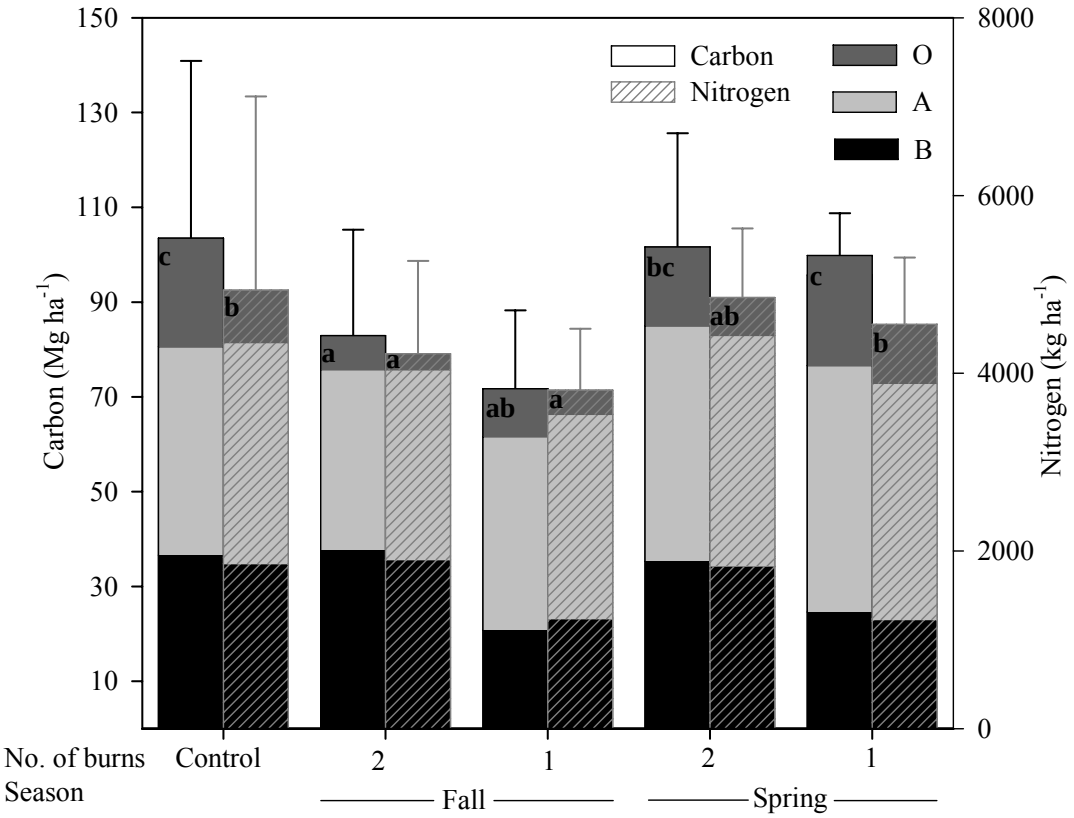
A Horizon										
		Control	Fall		Spring		p	p_s	$p_\#$	$p_{s*\#}$
			2	1	2	1				
C (g kg^{-1} soil)	Hu	25 ± 7.6	26 ± 5.9	26 ± 10.1	27 ± 10.9	30 ± 6.9	*0.592*	*0.303*	*0.472*	*0.513*
	HA	12 ± 4.7	11 ± 3.5	10 ± 4.7	11 ± 3.2	12 ± 4	*0.769*	*0.522*	*0.706*	*0.323*
	FA	1.1 ± 0.3	1.3 ± 0.4	1.1 ± 0.4	1.0 ± 0.3	1.3 ± 0.6	*0.364*	*0.871*	*0.518*	***0.060***
N (g kg^{-1} soil)	Hu	1.5 ± 0.72	1.4 ± 0.50	1.5 ± 0.63	1.4 ± 0.63	1.6 ± 0.56	*0.879*	*0.654*	*0.442*	*0.565*
	HA	0.7 ± 0.29	0.6 ± 0.20	0.6 ± 0.23	0.6 ± 0.21	0.7 ± 0.23	*0.617*	*0.499*	*0.923*	*0.406*
	FA	0.04 ± 0.02	0.04 ± 0.02	0.03 ± 0.02	0.03 ± 0.01	0.04 ± 0.02	*0.555*	*0.713*	*0.409*	*0.241*
C:N	Hu	23.4 ± 10.2	23.1 ± 8.15	22.4 ± 5.51	25.2 ± 9.47	24.4 ± 7.99	*0.788*	*0.240*	*0.662*	*0.970*
	HA	13.9 ± 1.46	13.8 ± 1.10	13.7 ± 2.67	13.9 ± 1.68	13.5 ± 1.79	*0.668*	*0.671*	*0.940*	*0.595*
	FA	39.0 ± 13.8	44.4 ± 13.8	35.4 ± 6.9	42.3 ± 11.7	41.9 ± 8.33	*0.622*	*0.676*	*0.584*	*0.677*
C:H	HA	1.44 ± 0.19	1.51 ± 0.18	1.53 ± 0.18	1.56 ± 0.33	1.53 ± 0.19	*0.984*	*0.918*	*0.644*	*0.828*
	FA	1.01 ± 0.04 [a]	1.05 ± 0.06 [ab]	1.14 ± 0.12 [b]	1.01 ± 0.09 [a]	1.05 ± 0.09 [ab]	***0.030***	***0.037***	***0.041***	*0.292*

Table 4.4 Total C and N by each soil organic matter fraction (mean ± standard deviation) of O and A horizons in plots treated with 1 or 2 fall or spring burns (n=6). Significant (α=0.1) differences are in bold as determined by a one-factor ANOVA (*p*) and orthogonal contrasts for season (p_s), and number of burns ($p_\#$). Letters indicate similar subsets (rows) using Tukey's HSD. Interaction between season and number of burns was not significant. Sum of HA and FA C and all fractions of N were not significantly different between the treatments.

		Control	Fall 2	Fall 1	Spring 2	Spring 1	p	p_s	$p_\#$
		Mg Carbon ha^{-1}							
NS Humin	O	13.8 ± 6.5	4.3 ± 1.0	7.1 ± 3.0	9.4 ± 3.1	14.3 ± 6.4	*0.148*	***0.067***	*0.183*
	A	25.0 ± 9.4	22.9 ± 4.2	25.9 ± 11.2	28.7 ± 11.0	26.3 ± 5.1	*0.787*	*0.341*	*0.926*
	Sum	38.8 ± 14 ^{ab}	27.3 ± 4 ^{a}	33.0 ± 11 ^{ab}	38.0 ± 11 ^{ab}	40.6 ± 9 ^{b}	***0.081***	***0.016***	*0.244*
Humic Acid	O	2.6 ± 1.4 ^{ab}	0.7 ± 0.2 ^{a}	1.2 ± 0.5 ^{a}	1.7 ± 0.7 ^{ab}	3.1 ± 1.2 ^{b}	***0.023***	***0.014***	***0.061***
	A	11.8 ± 5.3	9.7 ± 2.6	10.2 ± 4.8	11.4 ± 3.8	10.4 ± 2.8	*0.805*	*0.496*	*0.859*
Fulvic Acid	O	0.8 ± 0.4 ^{bc}	0.2 ± 0.1 ^{a}	0.3 ± 0.1 ^{ab}	0.4 ± 0.1 ^{abc}	0.7 ± 0.2 ^{c}	***0.014***	***0.024***	*0.105*
	A	1.1 ± 0.4	1.1 ± 0.4	1.1 ± 0.4	1.1 ± 0.5	1.2 ± 0.6	*0.991*	*0.833*	*0.960*
		kg Nitrogen ha^{-1}							
NS Humin	O	355 ± 195 ^{ab}	99 ± 32 ^{a}	171 ± 93 ^{ab}	230 ± 114 ^{ab}	358 ± 152 ^{b}	***0.051***	***0.028***	*0.140*
	A	1520 ± 783	1271 ± 434	1467 ± 720	1527 ± 599	1413 ± 501	*0.830*	*0.568*	*0.816*
Humic Acid	O	82 ± 51	20 ± 9	36 ± 16	51 ± 20	97 ± 46	*0.760*	*0.424*	*0.503*
	A	709 ± 318	547 ± 162	562 ± 252	635 ± 168	572 ± 144	*0.546*	*0.525*	*0.757*
Fulvic Acid	O	8.9 ± 6.9 ^{a}	2.8 ± 2.8 ^{b}	3.2 ± 2.0 ^{b}	5.2 ± 1.6 ^{ab}	7.2 ± 5.8 ^{a}	***0.004***	***0.008***	*0.444*
	A	38 ± 18	34 ± 18	30 ± 26	32 ± 12	34 ± 19	*0.903*	*0.864*	*0.918*

Table 4.5 Mass lost between muffle-furnace temperatures of 375 and 550°C ($LOI_{375-550}$) for (mean ± standard deviation) O and A horizons in plots treated with 1 or 2 fall or spring burns (n=6). These values have been converted to black carbon (BC) and black nitrogen (BN) by multiplying $LOI_{375-550}$ by 0.50 g BC g^{-1} $LOI_{375-550}$ and 0.02 g BN g^{-1} $LOI_{375-550}$, respectively. Significant (α=0.1) *p*-values are in bold as determined by a one-factor ANOVA (*p*) and orthogonal contrasts for season (p_s), and number of burns ($p_\#$). Interaction of season and number of burns was not significant. Letters indicate similar subsets (rows) using Tukey's HSD.

		Control	Fall 2	Fall 1	Spring 2	Spring 1	p	p_s	$p_\#$
		Mg ha^{-1}							
$LOI_{375-550}$	O	0.23 ± 0.21 [b]	0.07 ± 0.04 [a]	0.14 ± 0.09 [ab]	0.16 ± 0.1 [ab]	0.25 ± 0.18 [b]	***0.049***	***0.029***	***0.074***
	A	21 ± 6	21 ± 12	21 ± 10	23 ± 11	20 ± 8	*0.953*	*0.786*	*0.589*
Black Carbon	O	0.12	0.03	0.07	0.08	0.13			
	A	10	10	10	11	10			
		kg ha^{-1}							
Black Nitrogen	O	4.6	1.4	2.8	3.2	5.1			
	A	415	413	412	456	398			



	p	p_s	$p_\#$
Carbon			
O	***0.000***	***0.000***	***0.059***
A	*0.218*	***0.024***	*0.593*
B	*0.112*	*0.603*	***0.027***
Total	***0.077***	***0.021***	*0.330*
Nitrogen			
O	***0.001***	***0.000***	***0.040***
A	*0.714*	*0.183*	*0.703*
B	*0.332*	*0.918*	***0.062***
Total	*0.349*	*0.188*	*0.298*

Figure 4.1 Total carbon and nitrogen content in the top 30 cm of soil and O horizon after 1 or 2 fall and spring burns. Error bars are 1 standard deviation from the mean total soil C or N content. Significant (α=0.1) *p*-values are in bold as determined by a one-factor ANOVA (*p*) and orthogonal contrasts for season (p_s), number of burns ($p_\#$). Interaction between season and number of burns was not significant. Letters indicate similar groups of O horizon C or N content using Tukey's HSD.

Chapter 5
Conclusions

This dissertation comprises three papers which were written to clarify the effects of prescribed-fire intensity on soil organic matter (SOM) and to develop forest management recommendations for prescribed burning that protect soil quality in ponderosa pine forests. The main research concern addressed the immediate and long-term effects of burning at different intensities on SOM composition of O and A horizons. Five objectives were developed to deal with this concern.

Objective 1 was developed to determine the effect of prescribed fire intensity on SOM composition of O and A horizons. Fires that reproduce prescribed burns in a ponderosa pine forest understory were conducted in the laboratory. These fires and their effects on SOM are described in Chapter 2. These fires mimicked prescribed burns of low, moderate, and high-moderate severity on O and A horizons in their natural sequence. Maximum mineral soil temperatures did not achieve 300 ^{o}C, a suggested temperature threshold at which structural changes to SOM occur (Gonzalez-Perez *et al.* 2004). Increasing fire intensity increased the proportion of recalcitrant non-soluble (NS) materials in the O horizon which included lignin, cellulose, and charcoal. In the A horizons reduced humin and humic acid (HA) content coincided with increased hydrophobic material (HO) content. This result contrasted with other studies that observed a higher proportion of recalcitrant materials after high-severity heating or wildfire where mineral soil temperatures may have exceeded the aforementioned 300° C threshold. The increase in HO content at low to moderate intensity may have been derived from destructively distilled humic materials or lysed microbial cells. The C:N ratio of A horizon humin and fulvic acid (FA) decreased as a result of increasing fire intensity. The shift towards more labile materials may cause the flush of C and N mineralization observed in mineral soils after fire (Bauhus *et al.* 1993, Choromanska and DeLuca 2002).

Chapter 3 examined the effect of fire intensity on C mineralization rates of O and A horizons (*Objective 2*). Fire intensity significantly reduced the C mineralization rates of O horizons. The reduction in mineralization rates was mostly due to increased consumption of labile materials by burning. Short-term C mineralization of mineral horizons increased with fire intensity while long-term C mineralization rates were not significantly affected by burning. Increasing the quality of SOM as a substrate for microbial growth and decreased C:N ratios of FA and humin appeared to be more important in increasing C mineralization rates in the A horizon. The contrasting decomposition rates in O and A horizons lead to differing effects on the residual SOM composition.

Objective 3 examined the decomposition characteristics and extended effects of fire intensity on O and A horizon SOM, and were also considered in Chapter 3. Incubation caused the form of C and N in SOM of burned A horizons to return to control composition, while SOM composition of O horizons remained different from control. Combustion during moderate- and high-intensity fires reduced the total recalcitrant (NS and humin) C and N content of the total soil profile. However, the C remaining after moderate intensity prescribed fire decomposes so slowly that given enough time a burned soil could accumulate recalcitrant C relative to an unburned soil. Burning at moderate intensity may have the greatest ability to produce decomposition-resistant materials. However, before a strong conclusion could be made, further research would need to be conducted regarding the effect of course woody debris and priming from post-fire litterfall on the long-term decomposition characteristics of fire-altered SOM

Objective 4 considered a field study of fire severity using fall and spring prescribed burns at 5- and 15-year intervals as described in Chapter 4. Soil organic matter composition was examined using similar methods to the laboratory experiments so that the results of these studies could be compared. The reintroduction of fire after 100 years of suppression was found to reduce fuels in the form of O horizon depth and coarse woody debris. Higher-severity fall burns decreased the C and N capital of the O and A horizons while the lower-severity spring burns had little effect on soil C and N content.

Total C from fall burns was reduced by 22-25% relative to the control treatments, while total N was reduced 13-19%. Carbon loss with fall burning was driven by reductions of C from the O and A horizons. Generally, labile SOM quality was not significantly different across the prescribed fire treatments partly due to the high C content of these soils, relatively low fire severity, and time since last burn. The recalcitrant C content in the combined O and A horizon was much lower in both fall burn treatments relative to the control. Charcoal could be a significant component of the recalcitrant C pool which has been shown to reduce allelopathic chemicals and promote N mineralization in ponderosa pine forests (Zackrisson *et al.* 1996, Wardle *et al.* 1998, DeLuca *et al.* 2002, 2006). More research regarding the role of fire-altered SOM on ecosystem restoration is needed, but the implication may be that the consumption of charcoal by higher-severity fall burns may hamper forest restoration efforts.

Most of the impact of fall burning appears to have been caused by the initial burn, suggesting that reinitiating fire into a fire-suppressed forest using fall burns may be too severe to preserve soil health. Treatments with one spring burn caused little to no impact to the soil, suggesting that applying spring burns at an interval longer than 5 years may preserve soil C and N. Woody fuels appear to be effectively reduced by both fall and spring burns. The prescribed fire interval necessary to reduce fuels and preserve soil C and N may be dependent on the length of time it takes for O horizon to accumulate to pre-fire levels. In this way hazardous fire conditions will have been reduced and soil processes may be preserved.

The prescribed fire intensity and severity examined in both the laboratory burn experiments and the field study show that the largest and most persistent changes occurred to the O horizon while the A horizon SOM composition and content appear to be unaffected over the long-term. This suggests that long-term changes to SOM content and composition will be driven by combustion and transformation of O horizon material. Alteration of the quantity and quality of inputs from a burned O to an A horizon could affect SOM content and composition of the A horizon in the future, and these changes in amount and composition of SOM inputs from the O horizon to the mineral soil may

affect soil processes in the future. The altered SOM inputs to the mineral soil could hamper or enhance ecosystem restoration and C sequestration depending on prescribed fire severity and frequency.

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