# FIRE HISTORY EFFECTS ON ORGANIC MATTER PROCESSING FROM HILLSLOPES TO STREAMS

A THESIS

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# TABLE OF CONTENTS

# ABSTRACT

Climate change impacts temperature and precipitation regimes which can shift species composition and induce state changes. Disturbance events, which alter the productive capacity of ecosystems, may also shift pre-disturbance stable states to entirely new, alternative stable states. Under scenarios of increased frequency and intensity of disturbances predicted with climate change, state shifts are likely to become more common. In the Intermountain West, interactions between climate change and severe wildfires may decrease forest resilience through forest ecosystem conversion to different tree species assemblages, shrubland or grassland states. Our findings support the notion that current shifts from forest to non-forested vegetation may be underway and that these changes are likely expedited by wildfire disturbance. Results indicate that severe wildfire has markedly altered soil OM pools such that burned sites are not only storing significantly less SOM (burned soils contained 77% less C than reference soils) but retaining a significantly smaller fraction of SOM than unburned sites (burned soils retain 4% less DOC, 3.4% less TDN and 3.7% less DON than unburned soils export to the subsurface). Transformation of flow paths in burned landscapes also had cascading effects on nutrient concentrations in streams: DOC and DON concentrations were 50% to 80% higher in burned streams relative to unburned streams. This study shows that even fifteen years postfire, C accumulation, sequestration and transport remain altered, providing further evidence that Ponderosa pine forests in the Intermountain West may transform into a decadal-scale C source under a more frequent and severe disturbance regime.

# INTRODUCTION

## Setting

Average temperatures in 2017 were the warmest reported on Earth for the third consecutive year (NOAA). During this period, record-breaking wildfires burned an estimated 4 million hectares across the United States resulting in the burning of an unprecedented 60 hectares per fire (NOAA). Increased wildfire activity over recent decades reflects responses to changes in climate, namely reduced winter precipitation and earlier spring snowmelt (Westerling et al. 2006; Christensen 2007). Warmer springs have led to earlier snow melt and thus a longer summer dry season, prompting a longer fire season (Westerling et al. 2006). Projections indicate that these trends will continue into the coming decades across the United States but will likely be even more pronounced within the Rocky Mountain region (Westerling et al. 2006). Consequently, increases in the average length and intensity of summer droughts in the Intermountain West will accentuate conditions favorable to the occurrence of severe, stand-replacing wildfires (e.g. Flannigan et al. 2000; Savage and Mast 2005; Smithwick et al 2005; Turner 2010; Buma et al. 2014; Abella and Fornwalt 2015).

For at least 300–500 years prior to the late 19th century, a regime of high-frequency, low-intensity fires characterized the semiarid forests of the Intermountain West (Savage and Mast 2005). However, over a century of fire suppression and heavy livestock grazing eliminated this disturbance regime from most forests (Dore et al. 2008; Rhoades et al. 2011; Abella and Fornwalt 2015). Under high stand densities and an abundance of fine fuels created by decades of fire exclusion, continuous horizontal and vertical fuel structure generated a large-scale shift to high-intensity crown fires (Dore et al. 2008; Rhoades et al. 2011; Abella and Fornwalt 2015). In conjunction with changing temperature and precipitation patterns, these fires are becoming unprecedented in size and severity (Savage and Mast 2005; Rhoades et al. 2011; Abella and Fornwalt 2015). As a result, dry coniferous forests of the Intermountain West are being transformed at a rapid pace – since 1986 annual area burned has increased more than sixfold over previous decades (Westerling et al. 2006; Abella and Fornwalt 2015).

Current estimates indicate that western Ponderosa pine forests account for 20 to 40% of the total carbon (C) sequestration of the United States (Westerling et al. 2006). Projected regional warming and an increase in the frequency and intensity of wildfires across the Intermountain West threaten to shift this terrestrial carbon sink to a source (e.g. Law et al. 2001; Westerling et al. 2006; Dore et al. 2008; Dore et al. 2012; Stevens-Rumann et al. 2018). Even under a relatively modest temperature-increase scenario, drier conditions incite biomass burning which will inhibit short-term C storage (e.g. Law et al. 2001; Savage and Mast 2005; Dore et al. 2008; Dore et al. 2012; Stevens-Rumann et al. 2018). The extent to which long-term C storage is inhibited is dependent upon the resiliency of these forests and their subsequent recovery trajectories (e.g. Buma et al. 2014; McLauchlan et al. 2014; Stevens-Rumann et al. 2018).

## Recovery Trajectories

In the absence of change in the disturbance regime, terrestrial C storage is constrained by rates of accumulation (e.g. photosynthesis and burial) and degradation (e.g. respiration and decomposition) (Dore et al. 2012; McLauchlan et al. 2014). Under this scheme, ecosystem C balance can be considered relatively stable as C lost during a disturbance event is largely recovered before the next disturbance (McLauchlan et al.

2014). As follows, changes in the disturbance regime may drive a system away from C balance (Law et al. 2001; Savage and Mast 2005; Dore et al. 2008; Dore et al. 2012; McLauchlan et al. 2014). Increased disturbance severity has the potential to exceed the ecological resilience of a system by triggering changes in species composition and vegetation-soil feedbacks (Reiners 1983; Gunderson 2000; McLauchlan et al. 2014; Stevens-Rumann et al. 2018). The capacity of an ecosystem to resist this shift is thus highly dependent on ecological resilience and disturbance severity (Gunderson 2000; McLauchlan et al. 2014).

In the Intermountain West forest resilience is determined by sufficient tree regeneration (Johnstone et al. 2016; Stevens-Rumann et al. 2018). Interactions between climate change and severe wildfires decrease forest resilience through a reduction in tree densities and an alteration of species assemblages (Stevens-Rumann et al. 2018). If these changes persist, conversion from Ponderosa pine forest to shrub or grassland ecosystems is expected (Bell et al.2014; Stevens-Rumann et al. 2018). The question remains as to whether Rocky Mountain forests will support an altered productive capacity or an entirely new, alternative stable state following fire (Reiners 1983; Bell et al.2014; Stevens-Rumann et al. 2018). Evidence suggests that the degree to which severe wildfire alters montane ecosystem processes will be catastrophic to overstory recovery (e.g. Law et al. 2001; Savage and Mast; Roccaforte et al. 2012; Abella and Fornwalt 2015).

## Impact of Fire on Ecosystem Processes

Fire affects ecosystem processes by altering the physical, chemical and biological properties of soil (e.g. González-Pérez et al. et al. 2004; Beyers et al. 2005; Certini 2005; Knicker 2007). The most intuitive change that ecosystems experience during burning is the loss of organic matter (OM); high-intensity fires cause a near total reduction in litter and organic layers (e.g. Beyers et al. 2005; Knicker 2007). Soil organic matter (SOM) that is not fully combusted undergoes heat-induced changes in structure and composition, affecting its C storage potential (e.g. González-Pérez et al. 2004; Certini 2005; Knicker 2007). Effects of fire on soil water storage further influences this storage potential (e.g. Beyers et al. 2005; Betts and Jones 2009; Raymond and Saiers 2010).

### *Soil*

Soil heating can destroy soil structure, a change which significantly alters the physical properties of soil (Beyers et al. 2005). During fire, organic matter that served as a binding agent in the soil structure is destroyed, increasing soil density (Beyers et al. 2000). Upon the collapse of soil structure, soil porosity is reduced, such that pores become partially or totally sealed during precipitation events (Beyers et al. 2000). After being compacted by raindrops, the soil surface becomes impenetrable, reducing infiltration rates and increasing erosion rates (Beyers et al. 2000). Postfire runoff and erosion are accentuated when vaporized (i.e. hydrophobic) SOM moves downward into the soil profile and forms a water-repellent layer below the soil surface (Beyers et al. 2000). The duration of this water-repellency is highly dependent on fire severity and ecosystem characteristics (Certini 2005). Wieting et al. (2017) found that soils burned at very high temperatures became more homogeneous with depth in respect to OM and bulk density which enabled water to infiltrate deeper into the soil. Accordingly, water repellency at high temperatures appeared to be reduced relative to low temperatures. Cerdà (1998), who examined the influence of ecosystem recovery on runoff, observed that the infiltration capacity of soil increased every year postfire. From this observation

Cerdà (1998) deduced that runoff and infiltration changes are primarily determined by vegetation recovery. Hence, the relationship between runoff and vegetation cover changes throughout the recovery period.

The primary chemical soil properties affected by fire is OM quantity and quality which play key roles in nutrient cycling, cation exchange, and water retention (Beyers et al. 2000). When SOM is combusted, stored nutrients are either volatilized or are changed into highly available forms (e.g. $NH_4^+$) and readily utilized by microorganisms and vegetation (Beyers et al. 2000). Nutrients that are not immobilized are easily lost by leaching and erosion (Beyers et al. 2000). Nitrogen (N) is often considered the most important nutrient affected by fire as it is volatilized at relatively low temperatures (Certini 2005). The amount of total N that is volatilized during combustion is directly proportional to the amount of organic matter destroyed (Beyers et al. 2000). It has been estimated that ~99% of the volatilized N is converted to $N_2$ (Beyers et al. 2000). The portion that is not completely volatilized either remains as part of the unburned fuels or is converted into bioavailable ammonium (Beyers et al. 2000). Higher concentrations of inorganic N immediately following fire lead to higher rates of nitrification which results in increased lateral N exports to streams (Rhoades et al. 2011). N loss postfire is of particular concern given that it can only be replaced by N-fixing organisms which are also impacted by fire (Beyers et al. 2000). Consequently, postfire soil processes and vegetation regrowth can be markedly inhibited (Rhoades 2011).

In addition to impacting SOM quantity, fire also affects SOM quality (Marschner and Kalbitz 2003; González-Pérez et al. 2004; Knicker 2007). Burning tends to decrease biodegradability of SOM via alteration of SOM chemical structure (Marschner and

Kalbitz 2003; González-Pérez et al. 2004; Knicker 2007). Extreme heating induced by fire causes a decrease in the atomic hydrogen to carbon ratios (H:C) and oxygen to carbon ratios (O:C), indicating an increase in SOM aromaticity and a decrease in SOM solubility (Marschner and Kalbitz 2003; González-Pérez et al. 2004; Knicker 2007). Bioavailability and biodegradability of these pyrogenic C-enriched aromatic compounds are low given that they are extremely recalcitrant (Marschner and Kalbitz 2003; González-Pérez et al. 2004; Knicker 2007). Consideration of SOM quality during recovery is important as it influences microbial respiration rates and subsequent ecosystem C balance (Hart et al. 2005; Dooley and Treseder 2012).

The effect of heating on microorganisms is another way that fire alters C cycling (Hart et al. 2005; Dooley and Treseder 2012). Microorganisms play a major role in nutrient cycling processes by decomposing organic material and producing a labile pool of nutrients (Hart et al. 2005; Dooley and Treseder 2012). Fire impacts soil organisms directly by killing or injuring the organisms, and indirectly by altering SOM, microclimates and plant succession (Hart et al. 2005; Dooley and Treseder 2012). By destroying organic matter, fire changes soil temperature and moisture regimes, and in turn, rates of organic matter accumulation and the postfire vegetative community (Hart et al. 2005; Dooley and Treseder 2012). Most studies show recovery of microbial populations to prefire levels within a few years after wildfire, however, reduced microbial biomass has been reported for as many as 11 years after fire (Beyers et al. 2000). When the microbial community will fully recolonize and how the community composition will change depends on ecosystem recovery. Thus, ecosystem C balance following fire is highly dependent on the regrowth of vegetation, as well as the quantity and quality of OM that was not fully combusted.

### *Hydrology*

Fires can have substantial effects on soil water storage and streamflow regimes (Beyers et al. 2000). As noted above, burned soils often display increased bulk density, decreased water-holding capacity (WHC) and increased infiltration rates due to the loss of SOM (Certini 2005). In addition to these factors, reduced canopy interception and evapotranspiration following fire alter hydrologic pathways (Shakesby and Doerr 2006). Alteration of flow paths both reduces soil water storage and augments baseflows, water yields and peak flows (Beyers et al. 2000). Such hydrologic changes are likely to enhance nutrient transport, potentially leading to substantial losses of C, N, and base cations. Indeed, recent studies illustrate that the lateral export of C from terrestrial ecosystems is not negligible relative to net terrestrial ecosystem production (e.g. Tranvik et al. 2007; Raymond et al. 2013; Hotchkiss et al. 2015). Rather, gaseous $CO_2$ losses from riparian ecosystems represent a significant C source on the global scale, releasing an estimated 1.8 Pg C annually (Raymond et al. 2013). DOM export from terrestrial ecosystems is thus critical to examine when considering the impact of fire on ecosystem C cycling.

## **Scope**

Terrestrial ecosystems strongly influence the global carbon cycle – forest ecosystems cover approximately 4.1 billion hectares globally and sequester an estimated 12240 Pg of C (Lal 2005; Dore et al. 2008, 2012; Buma et al. 2014). As much as two-thirds of this C storage occurs in soils (Lal 2005). An increase in the frequency and intensity of wildfires due to climate change thus has drastic implications for the long-term C cycling trajectory of these ecosystems (McLauchlan et al. 2014).

In the United States, forests dominated by Ponderosa pine constitute a carbon sink (e.g. Dore et al. 2008, 2012). Severe wildfire has the ability to shift terrestrial carbon balance from a sink to a source for decades (Law et al. 2001; Savage and Mast 2005; Dore et al. 2008, 2012; Roccaforte et al. 2012). Estimates from mesic Ponderosa forests demonstrate that a period of 10 to 20 years is necessary to shift the ecosystem from a C source to a C sink while a period of 50 to 100 years is required to replace the C lost by a wildfire disturbance (Law et al. 2001; Dore et al. 2008, 2012). In southwestern Ponderosa pine forests where a drier climate appears to slow postfire recovery, effects of wildfire are more prominent (Savage and Mast 2005; Dore et al. 2008, 2012; Roccaforte et al. 2012). Dore et al. (2012) found that due to a decrease in aboveground biomass and OM, C sequestration of a burned Ponderosa forest was 60% less than that of an undisturbed Ponderosa forest 10 years postfire. Similarly, Savage and Mast (2005) and Roccaforte et al. (2012) noted that postfire biomass regeneration was lacking in burned Ponderosa forests indicating a shift from forest to grass- or shrublands for extended periods.

If recovery of C stocks cannot keep pace with losses from increased fire frequency and intensity, forests in the Intermountain West may transform into a decadal-scale C source, further exacerbating excess atmospheric $CO_2$ via the creation of a positive feedback. It is therefore pivotal to understand the mechanisms which determine both the recovery and resilience of montane ecosystems and their soil C stocks.

## Research Questions

While various studies have quantified aboveground C fluxes (e.g. Law et al. 2001; Savage and Mast 2005; Dore et al. 2008, 2012; Roccaforte et al. 2012), few have examined lateral C fluxes (e.g. Tranvik et al. 2007; Raymond et al. 2013; Hotchkiss et al. 2015) and even fewer have evaluated the transformation and transport of C from hillslopes to streams. This study aims to improve our understanding of the long-term dynamics of C cycling in forest ecosystems after severe fire, focusing on C retention between surface soils, subsurface soils and streams. By investigating C stocks and C retention at the terrestrial-aquatic ecosystem interface this research aims to addresses the questions below.

- How is the carbon storage potential of montane Ponderosa pine ecosystems altered by fire?
    - What do the recovery and C sequestration trajectories of these forests look like?
- What are the mechanisms that inhibit or promote postfire C sequestration in these forests?
    - Why might burned systems sequester less C?
    - How will more frequent drought impact postfire C sequestration?
- What are the implications of C retention for the postfire recovery of montane ecosystems and their C stocks?

# METHODS

## Site Descriptions

Sampling sites were distributed between five montane first and second order watersheds within the Colorado Front Range near Decker's, CO (**Figure 1**). Three watersheds – Pine, Wigwam and Fourmile – were severely burned in 2002 (Hayman and Schoonover fires) while Rainbow Falls and Painted Rocks watersheds which have not burned in over a century, act as reference sites. The Hayman and Schoonover burn scars were of particular interest given their duration and severity. Considered stand-replacing (i.e. severe) fires, the Hayman and Schoonover burns resulted in the loss of at least 80 percent of aboveground biomass (Beyers et al. 2000). The Schoonover wildfire began two weeks prior to the Hayman fire and burned nearly 4,000 acres of land including the Fourmile watershed (Robichaud and MacDonald 2009). The Hayman fire burned for nearly five months (8 June 2002 to 30 October 2002) and impacted approximately 560 $km^2$ including the Pine and Wigwam watersheds; it was marked as the largest Colorado fire recorded in history (Rhoades 2011; Robichaud and MacDonald 2009).

All sites are characterized as relatively dry montane forests dominated by Ponderosa Pine (*Pinus ponderosa*) and Douglas Fir (*Pseudotsuga menziesii*) (Stevens 2013). Forest soils are classified as Typic Ustorthents and Typic Cryorthents (i.e. well-drained sandy loams) and are located above Pikes Peak batholith, a course-grained biotite granite (Stevens 2013). Mean annual temperature is 9.4ºC while mean annual precipitation is approximately 60 cm (Stevens 2013). However, precipitation during sample collection was notably low, averaging between 0.1 cm and 0.3 cm per day (Intellicast). Burned sites exhibit little forest regrowth; vegetation covers an estimated

40% of the landscape (Wolf 2016) with predominate vegetation comprised of ruderal species including grasses and forbs. Reference sites contain significantly higher amounts of vegetation ($p<0.05$); forest ground cover was estimated at nearly 90% (Wolf 2016) and is comprised of grasses and forbs in addition to coniferous trees.

## Sample Collection

### *Soil*

Within each watershed, a total of three 15x15m plots were created along a geomorphic gradient (i.e. at the crest, mid-slope and toe slope positions) adjacent to the stream. Soil samples were collected between June and July 2017 in addition to previous surface soil samples collected in June 2016 (Wolf 2016). Collection of soil in each plot included taking three surface soil samples and two subsurface soil samples at random (i.e. 9 soil samples and 6 soil cores per watershed). Samples of surface soil (top ~10 cm) were taken using a hand bulb planter (7cm diameter) while subsurface soil samples (top ~30 cm) were taken using an AMS soil corer (3.5 cm diameter). Soil cores (20-30 cm) represented the entire soil column, with core depth determined by depth to saprolite.

### *Water*

Stream samples were collected weekly from June 2017 through August 2017 (excluding the last week of June and the first week of July). Prior to collecting samples, stream temperature, pH, percent dissolved oxygen, dissolved gases and discharge measurements were taken and recorded using a YSI Pro1020 while channel characteristics (e.g. stream cross sectional area) and stream velocity were measured. During each sampling effort, two liters of stream water were obtained and used for carbon, nitrogen and major ion analyses.

## Soil Chemistry

During the 2017 collection period three surface soil samples were collected in each plot and kept cool in sealed bags until processed. Processing included determination of coarse and fine materials, soil moisture, water extractable nutrients and ions, and elemental (C and N) analysis. Sample analyses conducted by Wolf in 2016 (for ten surface samples in each plot) were utilized to (1) make comparisons of C and N dynamics between years and (2) compile a multi-year dataset.

### *Coarse and Fine Fractions*

All surface soil samples (n=9 per watershed x 5 watersheds = 45), were sieved through 2 mm mesh to differentiate between coarse (>2 mm) and fine (<2 mm) fractions. Upon separation, each fraction was weighed and its subsequent "wet weight" was recorded. Subsamples ~5 to 8 g from each "wet" fraction were taken and mixed together to produce two sets of surface soil samples (n=45 samples x 2 sets = 90). The mixing of subsamples was done to randomly obtain representative samples of the top 10 cm of soil to be used for further analyses (described below). This method was not used in previous studies (Wolf 2016), however, it was used in this study as a means to best replicate water-soil interactions as they occur in the environment.

Remaining soil was oven dried at ~60ºC for 24 hours and weighed. After recording weights, soil was either further processed for elemental analysis (described below) or inventoried for future studies.

### *Soil Moisture*

Percent moisture was calculated for the coarse and fine fractions of all samples in addition to a set of top 10 cm soils. Percent moisture was calculated as the mass difference between the wet and dry soil weights, divided by the wet soil weight. Between 5 to 10 g of soil was oven dried at ~60ºC for 36 hours prior to calculations.

### *Carbon and Nitrogen*

After being oven dried and weighed, portions of organic matter from coarse and fine fractions from all soils were ground into powder using a Certiprep 8000 Mixer/Mill soil grinder. To determine %C and %N for each powdered sample (n=45 total soil samples x 2 fractions= 90) samples were run on an elemental analyzer. Masses of analyzed samples ranged from 15 to 20 mg of soil. With each set of samples, six standards (0.5, 1, 2, 3, 6, and 8 mg) of atropine (4.84% N, 70.56% C) were analyzed to generate a calibration curve. Replicate samples indicated a standard deviation of 0.17% for the determination of percent C and a standard deviation of 0.071% for percent N.

## Solute Analyses

Analysis of solutes included ion chromatography, combustion-oxidation, UV/VIS spectroscopy, and fluorometry.

### *Soil Extractions*

Solute was extracted from top 10 cm soil samples (n=45) after combining ~10–15 g of undried soil with ~100-150 mL MilliQ water in a beaker and agitating the mixture on a shaker table for ~24 hours. The resulting mixture was then filtered through both a pre-combusted 0.7 µm glass microfiber filter (Whatmann GF/F) and a 0.45 µm syringe filter. Extracted liquid was stored at ~0ºC for ion analysis and ~5ºC for dissolved organic matter analyses.

### *Column Experiments*

Prior to experimentation materials were weighed and recorded to calculate masses of soil and column eluent. Immediately after collection, masses of columns and heights of soil in columns were measured and recorded. Heights of soil in columns ranged from 21.0 cm to 26.6 cm; henceforth soil in columns will be referred to as subsurface (top 30 cm) soil given that they characterize the soil profile to depth of saprolite.

Before performing soil-column experiments, 30 mL MilliQ water per column was measured as well as the dry weight (i.e. weight before addition of MQ) of each column. Addition of 30 mL (~26 mm storm) of water was used to simulate a storm falling at the higher end of the for the common convective summer storm in the Front Range, 2 to 22 mm $hr^{-1}$ with max $I_{30}$ of 36 mm $hr^{-1}$ reported in the region (Gary 1975; Moody and Martin 2001). Upon addition of MQ, columns were covered with tin foil (**Figure 2**). After ~8 hours, the wet weight (i.e. weight after addition of MilliQ) and eluent mass were measured and recorded for each column.

To better understand how prolonged periods of drying impact water, C, and N transport and processing, this procedure was repeated for three different antecedent moisture conditions: moist, dry, and very dry (**Table 1**). Field conditions were considered "very dry" given that soil columns had the smallest mass on the day of collection. After collection, field soils underwent three consecutive storm simulations (i.e. addition of 90 mL MillQ) and allowed to dry for five days, after which soils were considered "moist." Moist soils underwent one storm simulation and allowed to dry for twelve days after which they were considered "dry." Dry soils underwent two consecutive storm simulations and were then stored at ~5ºC.

For each antecedent moisture condition eluent was collected, massed, filtered through a 0.45 µm syringe filter and diluted (usually by a factor of 1 to 40 so that UV absorbance at 254 nm was <0.2 L $mg^{-1}$ $m^{-1}$). Eluent was stored at ~0ºC for ion analysis and ~5ºC for all other analyses.

*Stream Samples*

Stream samples were taken weekly (sites were located using a Trimble GPS unit). After recording temperature, pH, and percent dissolved oxygen, discharge was calculated by 1) measuring stream width and depth 2) determining velocity using ping pong ball. Post collection, water was immediately filtered through a pre-combusted 0.7 µm glass microfiber filter (Whatman GF/F) and a 0.45 µm syringe filter. Filtered samples were stored at ~0ºC until ion analysis and at ~5ºC until all other analyses.

*Dissolved Organic Matter (DOM)*

Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured on a Shimadzu TOC-L/TNM-L unit. Standards were made from KHP, $KNO_3$ (0.5, 1, 2.5, 5, 10 mg/L C and N). Prior to analysis column eluents and soil extracts were typically diluted (gravimetrically) by a factor of 1 to 20. Replicate samples indicate good precision, with a coefficient of variation of 2.5% and 0.8% for DOC and TDN, respectively.

*Anions and Cations*

Major ions were measured for all stream samples, column eluent, and soil extracts using a Dionex ICS-5000 ion chromatograph. Samples were analyzed for $NO_2^-$, $NO_3^-$, $Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$. Prior to analysis, column eluents and soil extracts were typically diluted by a factor of 1 to 20 (all dilutions were done gravimetrically). Samples were thawed completely and well mixed before analysis. Replicate sample analyses indicate good precision, with error of less than 2% for most measurements (coefficient of variation of 0.7% for $NO_2^-$, 2.3% for $NO_3^-$, 0.4% for $Na^+$, 2.1% for $NH_4^+$, 2.0% for $K^+$, 2.0% $Mg^{2+}$ and 0.2% for $Ca^{2+}$).

### *UV Absorbance*

Ultraviolet-Visible absorbance of dissolved organic matter (DOM) and water extractable organic matter (WEOM) were measured with an Agilent 8453 UV/VIS spectrometer. UV-Vis absorbance measurements were taken from 190 nm to 1100 nm for all samples. Specific UV absorbance ($SUVA_{254}$) – a proxy for DOC aromaticity – was calculated by dividing the absorbance at 254 nm by the DOC concentration (L $mg^{-1}$ $m^{-1}$) (Weishaar et al. 2003). The absorption ratio E3:E3 – a proxy for the relative size of DOM molecules (De Haan and De Boer 1987) – was calculated from measurements at 250 nm and 350 nm. Prior to analysis, the 1 cm quartz cuvette was rinsed three times with Milli-Q water and run with MilliQ blanks (typically 5 to 10) until a non-biased absorbance spectrum was produced. During analysis the cuvette was rinsed three times with MilliQ and once with sample before measurement.

### *Fluorescence*

Fluorescence spectra of DOM and WEOM were measured using an Aqualog fluorometer at the U.S. Geological Survey's Laboratories in Boulder, CO. The quartz cuvette (stored in methanol) was rinsed copiously with MilliQ before a contamination check, daily prior to analyses. In addition, a daily water blank was run (to correct for Raman scatter). Sample fluorescence intensities were corrected on a daily basis (instrument and water correction factors change frequently) using Matlab. Matlab software was also used to determine fluorescence intensities (A, B, C, M, N, T; e.g. Coble 1996), the maximum intensity, as well as to calculate the fluorescence index (FI) which provides information about the source of the DOM (McKnight et al. 2001).

Differences in the intensity and position of the fluorescence peaks A, B, C, M, N and T are proxies for sources of DOM (Cory and McKnight 2005). According to Cory and Kaplan (2012) peak M (250 nm: 420 nm) indicates new, biological production of humic substances, peak A (250 nm: 500 nm) and peak C (250 nm: 466 nm) indicate terrestrial sources of DOM while peak T (285 nm: 344 nm) and peak B (275 nm: 324 nm) designate that DOM is composed of protein-like material (i.e. amino acids). The contribution of each peak to the total fluorescing dissolved organic matter (FDOM) pool was calculated as the fluorescence peak relative to its maximum intensity. The biologically labile portion of the FDOM pool was considered the sum of the contribution of fluorescence peaks B, N and T (Cory and Kaplan 2012).

## Data Analysis

### *Normalization*

Concentrations of soil extracts and column eluent were normalized to dry weight of soil to make comparisons between the different solute types. Determination of transport and transformation of DOM was done through the normalization of each watershed to the mass of soil in the top 30 cm of the soil profile (i.e. mass of soil above saprolite). Estimation of these values were obtained by determining the average dry column weight for each watershed and multiplying this mass by the watershed area. Comparisons between soil, extracts, eluent, and stream samples were also done through the calculation of ratios (e.g. DOC:TDN, DOC:DON) or qualitative measurements of the DOM pool (i.e. SUVA and fluorescence peaks).

*Calculations*

Data presented for surface soil (top 10 cm) are either averages of coarse and fine fractions per treatment (burned n= 54; unburned n= 36) or per watershed (n= 18). Values for soil extractions are averages per treatment (burned n= 27; unburned n=18) or per watershed (n=9) while values for column eluent are averages per treatment (burned n= 54; unburned n= 36), per watershed (n=18) or per antecedent moisture (moist, dry and very dry n= 30). Material retention was calculated as differences between surface and subsurface soils and is presented as an average extract value per hillslope position minus an average eluent value of each column (e.g. SE – $CE_{PineCrest=}$ average extract $[solute]_{PineCrest}$ – average eluent $[solute]_{column1PineCrest}$) per treatment (burned n=18; unburned n=12) or per watershed (n=6). Differences are also presented as the fraction of material retained, calculated as the average difference between surface and subsurface values divided by the plot average surface value (e.g. Retention= $SE_{PineCrest}$ – $CE_{PineCrest}$/ $SE_{PineCrest}$).

*Statistics*

Minitab 17 was used for all statistical analyses. Comparisons between fire histories (burned versus unburned), watersheds, soil depth (coarse versus fine fractions), antecedent moisture (moist versus dry versus very dry) and hillslope position (crest versus mid-slope versus toe slope) were conducted using t-tests with a Tukey Family Comparison. Data that was not normally distributed was transformed via a log or square root function, prior to parametric statistical tests. Reported means and standard deviations were calculated from non-transformed data while reported p-values were calculated from comparisons performed on transformed data, when applicable. Statistical significance was defined as $p<0.05$. Statistical tests were not conducted on stream data for Rainbow Falls given that samples could only be obtained from 5 June 2017 to 20 June 2017, after which the stream went dry and remained so (5 July 2017 to 10 August 2017). Furthermore, unless noted otherwise, hillslope position did not significantly influence variation in the physical or chemical properties observed in this study.

## RESULTS

### Soil

Severe fire significantly impacted soil characteristics including the percentage of coarse and fine materials, soil moisture, and elemental carbon (**Figure 3**) and nitrogen (**Figure 4**) contents.

*Coarse and Fine Fractions*

Burned soils contained coarser materials (%CF = 52 ± 8.0) such as pebbles and granules while reference soils were comprised primarily of fine materials (%FF = 57 ± 12) such as clay and silt ($p=0.004$). Comparisons across all watersheds showed that Pine soils were largely composed of coarse materials (56 ± 4.5%) while Rainbow Falls soils were mostly composed of fine materials (59 ± 15%). Further, Wolf's measurements (2016) illustrated that burned soils had higher bulk densities than reference soils on average ($p<0.05$).

*Soil Moisture*

Soil moisture both within and between fractions were higher in reference plots ($p<0.0001$), with unburned soils containing 4.4 ± 3.4% moisture in the coarse fraction and 6.0 ± 3.6% moisture in the fine fraction (average soil moisture in the top 10 cm = 5.9 ± 3.4% ). Conversely, burned soils contained only 0.07 ± 0.12% moisture in the coarse fraction, 1.2 ± 0.65% moisture in the fine fraction, resulting in an average combined moisture content of the top 10 cm of 1.2 ± 0.67%.

Looking at the soil moisture in the top 10 cm and fine fractions of all watersheds showed that the reference soils of Painted Rocks and Rainbow Falls were similarly moist and significantly different to the dry soils of Pine, Wigwam and Fourmile ($p<0.0001$).

However, in the coarse fraction of soils, soil moisture was highest in Rainbow Falls (5.9 ± 3.9%), relatively low in Painted Rocks (2.9 ± 3.1%) and Pine soils (0.21 ± 0.13%) and negligible in Wigwam and Fourmile soils.

### *Soil Elemental Analysis*

Given the coarser composition of burned soils, it is not unexpected that concentrations of carbon and nitrogen were significantly lower in burned plots than in reference plots ($p<0.0001$). Reference soils contained over four times the amount of total carbon (9.0 ± 10% versus 2.0 ± 3.7%) and three times the amount of total nitrogen (0.19 ± 0.22% versus 0.06 ± 0.13%) of burned soils (**Figures 3** and **4**). This discrepancy was consistent throughout fractions, with unburned soils containing nearly five times the amount of carbon (12 ± 13% versus 2.5 ± 5.2%) and three times the amount of nitrogen (0.24 ± 0.26% versus 0.07 ± 0.18%) in the coarse fraction and nearly four times as much carbon (5.6 ± 6.2% versus 1.6 ± 0.87%) and nitrogen (0.15 ± 0.15% versus 0.04 ± 0.03%) in the fine fraction.

Relating all watershed soils in terms of C and N, the burned soils of Pine, Wigwam and Fourmile contained the least percent carbon (<3%) and the least percent nitrogen (<1%) while Painted Rocks contained less percent carbon and nitrogen than Rainbow Falls soils (7.4 ± 7.5% C versus 10.6 ± 12.5% C and 0.17 ± 0.17% N versus 0.22 ± 0.26% N). When normalizing %C to %N, values did not significantly differ across watersheds likely due to large amounts of heterogeneity, with average C:N ranging from 33 in Wigwam to 68 in Rainbow Falls ($p=0.057$). C and N were typically impacted by fraction ($p=0.021$ for %N versus soil fraction and $p=0.001$ for C:N versus soil fraction).

Subsequently, direct comparisons of soil carbon to nitrogen show that reference plots generally had higher C:N than burned plots. Within the top 10 cm and coarse fraction of soil, C:N of burned plots (coarse fraction= 30 ± 47; top 10 cm= 37 ± 34 and 30 ± 47) were significantly lower ($p<0.01$) than those in reference plots (coarse fraction=69 ± 31; top 10 cm= 56 ± 25). However, within the fine fraction of soil, the C:N between burned (44 ± 10) and unburned plots (43 ± 6) did not significantly differ ($p=0.6$).

## Soil Extractions

Fire significantly influenced concentrations of WEOM and base cations in the top 10 cm of soil (**Figures 5**–**8**) but did not significantly impact the quality of the OM pool.

### *Water Extractable Organic Matter (WEOM)*

Concentrations of water extractable carbon and nitrogen constituents were significantly higher in unburned soils than burned soils ($p<0.0001$) (**Figures 5**–**7**). On average, concentrations of WEOM were fifteen to twenty times higher in reference soil. Mean DOC, TDN and DON concentrations of unburned extracts were 1.07 ± 2.19 mg DOC $g^{-1}$, 0.156 ± 0.281 mg TDN $g^{-1}$ and 0.106 ± 0.191 mg DON $g^{-1}$ respectively.

Comparisons of average WEOM concentrations in each watershed showed that Rainbow Falls had markedly more WEOM than all other sites ($p<0.05$). Painted Rocks had similar mean concentrations of DOC and TDN as burned sites ($p>0.05$) but had notably higher mean concentrations of DON than Pine and Fourmile (0.022 ± 0.025 mg $g^{-1}$ versus 0.005 ± 0.001 mg $g^{-1}$ and 0.005 ± 0.001 mg $g^{-1}$). Mean WEOM concentrations of Fourmile extracts were among the lowest of all sites; in particular, mean DON concentration of Fourmile extracts was significantly lower than those of the reference sites ($p<0.05$).

Although concentrations of carbon and nitrogen differed between watersheds, C:N of WEOM did not ($p>0.2$). Average DOC:DON in reference extracts were 8.4 ± 3.9 whereas in burned extracts they were 9.3 ± 3.4. Interestingly, while Rainbow Falls had the highest average ratio (7.0 ± 1.5), Painted Rocks had the lowest (3.9 ± 1.6).

*Base Cations*

The sum of water extractable base cations $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ in the top 10 cm of soil was significantly lower in burned soils ($p<0.0001$) (**Figure 8**). The average concentration of base cations in unburned soils was 0.029 ± 0.053 meq $g^{-1}$, a value approximately fifteen times higher than the average concentration of base cations in burned soils (0.002 ± 0.001 meq $g^{-1}$). Extracts from Rainbow Falls had the highest concentration of base cations (0.055 ± 0.067 meq $g^{-1}$) while all other extracts had a mean base cation concentration of approximately 0.002 meq $g^{-1}$. The DOC: base cations was not significantly different between burned and unburned soils ($p=0.111$). In all extracts, ratios ranged from 2 to 3, with the lowest mean DOC: base cations of 2.4 ± 0.9 in Wigwam and the highest mean DOC: base cations of 3.0 ± 1.6 in Rainbow Falls.

*UV Absorbance*

Mean SUVA values did not vary between burned and unburned extracts ($p=0.112$). Reference extracts had a marginally higher mean SUVA values; with mean SUVA values of 3.9 ± 0.7 L $mg^{-1}$ $m^{-1}$ compared to 3.3 ± 1.2 L $mg^{-1}$ $m^{-1}$, for unburned and burned respectively. The highest mean SUVA value was seen in Wigwam extracts (4.1 ± 0.6 L $mg^{-1}$ $m^{-1}$) however, mean SUVA values in extracts from Painted Rocks and Rainbow Falls were also quite high (3.9 ± 1.1 L $mg^{-1}$ $m^{-1}$ and 3.9 ± 0.5 L $mg^{-1}$ $m^{-1}$).

Absorbance ratios (E2:E3) did not statistically vary with landscape fire history (p=0.162). Unburned extracts had a mean absorbance ratio of 3.6 ± 0.3 which was quite similar to burned extracts with a mean absorbance ratio of 3.5 ± 0.2. Across watersheds, ratios ranged between 3.4 ± 0.3 in Wigwam and 3.7 ± 0.3 in Painted Rocks. The highest mean absorbance ratios were typically located in the crest of hillslopes and the lowest in the toe slope however hillslope position was not a significant factor (p=0.052).

### *Fluorescence*

The average contribution of various fluorophores (represented by A, B, C, N and T peaks) did not vary with fire history (p>0.155). Burned extracts had slightly higher average contributions of A, B, C and N peaks than reference extracts and a minimally lower average T peak contribution. Pine extracts had the highest average A, B and C peak contributions, Wigwam extracts had the highest average N peak contribution and Painted Rocks extracts had the highest average T peak contribution. Lowest average contributions were typically seen in Rainbow Falls extracts (N and T peaks) or Wigwam extracts (B and C peaks).

The fraction of FDOM contributed by the M peak was significantly greater in burned than unburned extracts (0.296 ± 0.027% than unburned 0.277 ± 0.025%, p=0.024) with the highest average contribution in Wigwam extracts (0.306 ± 0.009%) and the lowest average contribution in Painted Rocks extracts (0.275 ± 0.031%).

The biologically labile portions of the fluorescence pool (the sum of the contribution of the B, N and T peaks) did not significantly differ between burned and unburned extracts (p=0.758).

### Column Eluent

Fire significantly altered concentrations of DOM (**Figures 9–11**) and water throughput in the subsurface soil (20-30 cm depth) but did not significantly impact concentration of base cations (**Figure 12**) or the quality of OM within this soil depth.

#### *Throughput*

Water output relative to water input was significantly higher in burned soils, with fire affected soils discharging 64 ± 21% of added water versus 49 ± 25% in reference soils ($p=0.002$). Comparisons of throughput on a watershed basis show that Fourmile retained the least amount of water with 67 ± 18% loss while Rainbow Falls retained the greatest amount of water, losing an average of 41 ± 24%. Antecedent moisture conditions were a significant factor in water retention with moist soils releasing notably more water than dry soils ($p<0.0001$). Moist soils discharged 84 ± 16% of the water added to them while dry soils released 46 ± 13% and very dry soils only released 42 ± 14%.

#### *Dissolved Organic Matter (DOM)*

Concentrations of carbon and nitrogen constituents in burned eluent were one-third to one-fourth those in reference eluent ($p<0.001$) (**Figures 9 –11**). Average TDN and DON concentrations in burned eluent were $0.001 \pm 0$ mg $g^{-1}$ and $0.0003 \pm 0$ mg $g^{-1}$, respectively; whereas reference eluent concentrations were $0.001 \pm 0.001$ mg $g^{-1}$ and $0.001 \pm 0$ mg $g^{-1}$, respectively. Mean DOC concentration in burned eluent was $0.004 \pm 0.002$ mg $g^{-1}$ while reference eluent concentration was $0.009 \pm 0.009$ mg $g^{-1}$. Average DOM concentrations were highest in Rainbow Falls eluent and lowest in Wigwam or Fourmile eluent. Variation in antecedent moisture conditions explained a significant amount of variation in DOM concentrations ($p<0.04$). Moist soils produced the lowest average DOM concentrations while dry and very dry soils produced relatively high DOM concentrations. Unlike other DON and TDN, DOC concentrations varied with hillslope; the highest DOC concentrations were observed in mid-slope column eluent, while the lowest were seen in the toe slope ($p=0.02$)

Although average soil C:N did not significantly differ with fire history ($p>0.285$), eluent produced by columns from burned watersheds had higher C:N values. Mean DOC:DON of 17.0 ± 17.9 was produced in burned eluent while 16.2 ± 11.3 was produced in reference eluent. Burned soils showed the greatest variability in column eluent C:N, with both the highest and lowest values (10.9 ± 4.0 to 23.3 ± 16.3). Eluent from the reference sites, Rainbow Falls and Painted Rocks, produced DOC:TDN and DOC:DON ratios of ~9 and ~16 respectively. Both moisture and hillslope were factors in ratio differences ($p<0.0.01$) with dry conditions and mid-slope position resulting in the largest average C:N values.

### *Base Cations*

The sum of base cations did not significantly differ with burn history ($p=0.083$) (**Figure 12**). Average concentrations were very low in both burned and unburned soils. The highest concentrations of base cations were present in Rainbow Falls (0.0002 ± 0.0001 meq $g^{-1}$) and the lowest in Wigwam (~0 meq $g^{-1}$). Average concentrations of base cations in Pine, Painted Rocks and Fourmile eluent were ~0.001 meq $g^{-1}$. Moisture and hillslope significantly impacted base cation concentrations ($p<0.03$), as the highest base cation concentrations were present in very dry soils and soils located at the crest of hillslopes.

The ratio of DOC: base cations did significantly differ between fire histories ($p=0.005$), with reference eluent producing an average ratio of 4.6 ± 3.6 and burned eluent producing an average ratio of 2.9 ± 2.0. DOC: base cations was lowest in Pine eluent (2.1 ± 0.9) and highest in Painted Rocks eluent (5.6 ± 4.3). Antecedent soil moisture was a significant determinant ($p<0.0001$) of in ratio differences (dry soils produced the greatest DOC: base cation values).

### *Spectral Characterization of DOM*

SUVA values were significantly different between burned and unburned eluent ($p<0.0001$). The mean SUVA value for reference eluent was 2.6 ± 0.8 L mg$^{-1}$ m$^{-1}$ and 1.8 ± 1.1 L mg$^{-1}$ m$^{-1}$ in burned eluent. Painted Rocks eluent produced the largest average SUVA value of 2.9 ± 0.6 L mg$^{-1}$ m$^{-1}$ which was similar to the average SUVA value of Pine eluent (2.8 ± 1.0 L mg$^{-1}$ m$^{-1}$) but markedly higher than the average SUVA value of Wigwam eluent (1.3 ± 0.7 L mg$^{-1}$ m$^{-1}$).

Average absorbance ratios did not significantly differ between fire histories or watersheds ($p=0.766$); both burned and unburned eluent had an average approximate ratio of 4. Wigwam had the highest mean absorbance ratio (5.8 ± 8.8) while Pine had the lowest (2.8 ± 0.2) with reference ratios of ~3.8.

Antecedent moisture conditions did not significantly impact the aromaticity of exported DOM ($p=0.292$) with all soil conditions producing eluent with mean SUVA values of 2 L mg$^{-1}$ m$^{-1}$. Antecedent moisture did not significantly impact absorbance ratios ($p>0.136$).

The average contribution of fluorophores A, B, M, N and T in column eluent were not significantly different between burned and unburned sites ($p>0.45$). Mean peak A contributions were notably low in Pine eluent (0.423 ± 0.210%) but nearly equivalent to 0.6% in all other watershed eluents. Mean peak B contributions were highest in Painted Rocks eluent (0.286 ± 0.237%) and lowest in Fourmile eluent (0.145 ± 0.084%). Mean peak M contributions were markedly high in Fourmile eluent (0.371 ± 0.075%) and markedly low in Pine eluent (0.214 ± 0.095%) while Painted Rocks and Rainbow Falls had similar mean peak contributions of 0.3%. Mean peak N contributions were highest in Wigwam eluent 0.219 ± 0.034%) and lowest in Pine eluent (0.160 ± 0.060%). Mean peak T contributions were highest in Painted Rocks eluent (0.189 ± 0.081%) and lowest was in Pine eluent (0.152 ± 0.067%). Antecedent moisture did significantly impact the mean contribution of the fluorophores ($p=0.008$). Mean contributions by B, N and T peaks were significantly impacted by moisture ($p<0.05$); very dry soils had the highest mean contributions.

Mean contributions of C peaks did significantly differ between fire histories ($p=0.008$). Burned eluent had a mean C peak contribution of 0.338 ± 0.103% while unburned eluent had a mean peak C contribution of 0.388 ± 0.044%. Antecedent moisture was not a significant determinant of C peak contributions ($p>0.42$). Rainbow Falls eluent had the highest mean peak C contribution (0.394 ± 0.029%) whereas Pine eluent had notably low peak C contributions (0.245 ± 0.126%).

The sum of the average contributions of fluorophores B, N and T did not significantly differ between burned and unburned eluent ($p=0.631$). Eluent from Painted Rocks had the highest portion of biologically labile material (0.677 ± 0.349%) while Rainbow Falls eluent contained the least amount of labile material (0.525 ± 0.363%).

## Material Retention

Fire significantly influenced the retention of OM and base cations between surface and subsurface soils. Burned soils retained a significantly lower fraction of OM and base cations than unburned soils (**Figures 13 –16**).

### *Organic Matter*

Absolute differences between carbon and nitrogen constituents present in soil extracts and column eluent were over 15 times higher in reference soils than burned soils ($p<0.0001$). Average DOC, TDN and DON concentrations retained in reference soils were 1.06 ± 1.77 mg $g^{-1}$, 0.155 ± 0.222 mg $g^{-1}$ and 0.106 ± 0.152 mg $g^{-1}$ respectively whereas average concentrations in burned soils were 0.0438 ± 0.022 mg $g^{-1}$, 0.010 ± 0.004 mg $g^{-1}$ and 0.006 ± 0.003 mg $g^{-1}$ respectively. Rainbow Falls retained significantly more DOC, TDN and DON than all other sites ($p<0.05$) while Painted Rocks retained less carbon and nitrogen than Rainbow Falls soils but more than burned soils.

DOC:TDN was higher in column eluent than soil extracts. This discrepancy was smaller in reference soils than burned soils with mean DOC:TDN values varying less between surface and subsurface soils in unburned sites (3.2 ± 4.8) than those in burned soils (3.9 ± 7.5). When DOC:TDN between surface and subsurface soil extracts was significantly different, the subsurface always exported solutes with lower C:N values. On average, Pine extracts had higher DOC:TDN values than columns (difference =1.9 ± 1.0) while Rainbow Falls extracts had slightly lower DOC:TDN values than eluent (difference =0.7 ± 3.1). Wigwam extracts had much lower mean DOC:TDN values than eluent (difference =8.9 ± 10.9).

DOC:DON was higher in column eluent; in burned soils this discrepancy was smaller with mean differences of DOC:DON between extracts and eluent equaling 7.0 ± 11.9 in burned soils and 7.8 ± 9.4 in unburned soils (i.e. the DOM pool C:N changed more in unburned soils). On average, Pine extracts differed the least from eluent in terms of DOC:DON (0.19 ± 2.3) while Wigwam differed the most (16.2 ± 16.9).

The fraction of carbon and nitrogen constituents retained between burned and unburned soils was significantly different (p=0.044; **Figures 13** –**15**). Burned soils retained 91.5 ± 5.1% of DOC, 94.4 ± 2.0% of TDN and 94.6 ± 2.7% of DON while unburned soils retained 95.5 ± 5.2% of DOC, 97.8 ± 2.0% of TDN and 98.3 ± 1.4% of DON. Rainbow Falls retained the most material (99.3 ± 0.3%; 99.2 ± 0.6%; 99.3 ± 0.5%) while Wigwam retained the least DOC (89.5 ± 7.5%) and Fourmile retained the least TDN and DON (94.0 ± 2.7%; 92.7 ± 2.7%).

*Base Cations*

The sum of base cations was significantly different between fire histories (p<0.0001) (**Figure 16**). Base cation concentrations were higher in extracts than columns. Unburned extract soils contained 0.03 ± 0.04 meq $g^{-1}$ more base cations than eluent while burned extracts contained only 0.002 ± 0 meq $g^{-1}$ more base cations than eluent. Soils from Rainbow Falls had the largest difference between extract and column base cation concentrations (0.05 ± 0.04 meq $g^{-1}$) whereas Pine soils had the smallest difference (0.002 ± 0 mEq $g^{-1}$).

Retention of base cations was significantly different between burned and unburned soils (p=0.001). Reference soils retained 97.2 ± 2.7% while burned soils retained 94.0 ± 2.2%. Rainbow Falls retained notably more base cations (99.3 ± 0.5%) while Fourmile retained the least (93.5 ± 0.03%).

The ratio of DOC to the sum of base cations did not significantly vary between burned and unburned soils ($p=0.088$). Mean unburned extract ratios were 1.9 ± 2.2 lower than eluent  while burned mean extract ratios were 0.7 ± 1.6 lower than eluent (i.e. on net DOC was preferentially retained or base cations were preferentially leached). Difference in ratios were largest in Painted Rocks (3.2 ± 2.3) and smallest in Pine (0.6 ± 0.8), reflecting the retention of materials in the subsurface.

### *UV Absorbance*

Differences in SUVA between extracts and eluent were not significantly different between burned and unburned sites ($p=.071$). In general, extracts had higher SUVA values than eluent with burned extracts having 1.7 ± 1.2 L $mg^{-1}$ $m^{-1}$ higher average SUVA values than eluent versus unburned extracts having 0.7 ± 1.7 L $mg^{-1}$ $m^{-1}$ higher average SUVA values than eluent. Wigwam soil had the largest mean difference in SUVA values with a difference of 2.8 ± 0.7 L $mg^{-1}$ $m^{-1}$ compared to Painted Rocks soil which had a mean difference of 0.3 ± 1.9 L $mg^{-1}$ $m^{-1}$.

Burning did not significantly influence differences in absorption ratios ($p=0.572$). On average, columns had higher absorbance ratios than extracts (burned difference= 0.7 ± 3.3 while unburned difference= 0.2 ± 0.8). Differences in absorbance ratios were largest in Wigwam soils (2.4 ± 5.3) and smallest in Painted Rocks soils (0.1 ± 0.6).

### *Fluorescence*

Differences in the average contribution of various fluorophores between extracts and eluent were not significantly impacted by fire ($p>0.10$). However, average differences were generally larger in unburned soils (contributions of B, M, N and T and biologically labile material). Average differences in the fluorescence contributions from A and C were notably large in Pine soils (0.306 ± 0.154% and 0.181 ± 0.080%), very small in Painted Rocks soils (0.016 ± 0.074% and 0.001 ± 0.047%) and small in other sites (e.g. Fourmile mean contribution of A= 0.025 ± 0.052% and mean contribution of C= 0.018 ± 0.030%). Differences in mean contributions of B and N were negative which indicates that eluent from all watersheds had higher B and N contributions than extracts. Average differences in M contributions were notably large in Pine soils (0.111 ± 0.070%) very small in Wigwam, Painted Rocks and Rainbow Falls soils (~0.02%) and small in Fourmile soils (0.082 ± 0.041%). Differences in average N contributions were high in Pine soils (0.044 ± 0.049%), negligible in Painted Rocks and Wigwam soils (~0%) and small in Rainbow Falls and Fourmile soils (~0.03%).

Given the lack of significant differences in average contributions of B, N, and T, the amount of biologically labile material available between burned and unburned extracts and eluent did not significantly differ (p=0.191). The average difference in the amount labile material between extracts and eluent was 0.137 ± 0.172% in burned soils and 0.225 ± 0.186% in unburned soils. The largest average difference was present in Painted Rocks soils (0.236 ± 0.219%) while the smallest difference was in Pine soils (0.080 ± 0.114%).

### Streams

Comparisons of water quality measures across watersheds show that stream pH and conductivity did not significantly differ between individual streams ($p>0.05$) but stream temperature, DO and water yield did significantly differ ($p<0.05$). Concentrations of

DOM and base cations varied among streams with DOM yields and the sum of base cations differing significantly ($p<0.05$). Furthermore, both the quantity and quality of OM were distinctly different when comparing individual streams ($p<0.05$).

*Stream Characteristics*

Stream pH and conductivity did not significantly differ among watersheds ($p>0.05$). Average pH values ranged from 6.97 ± 0.41 in Wigwam to 7.33 ± 0.31 in Painted Rocks indicating neutral conditions across streams. Mean conductivity values ranged from 70.8 ± 11.6 µS in Wigwam Creek to 176.9 ± 53.6 µS in Painted Rocks. Average conductivity values in Fourmile Creek (154.8 ± 159.2 µS) and Pine Creek (148.80 ± 15.69 µS) were similar to that observed in Painted Rocks.

Stream temperatures and dissolved oxygen (DO) varied notably across watersheds ($p<0.05$). The average water temperature range between streams was 4.38°C with the highest temperatures observed in Fourmile Creek (18.3 ± 2.1°C) and the lowest temperatures observed in Pine Creek (13.9 ± 1.1°C). The highest average DO concentrations observed in Fourmile Creek (78.1 ± 2.8%) and Pine Creek (77.2 ± 6.7%) were significantly different from the lowest DO concentrations present in Painted Rocks (62.0 ± 19.8) ($p<0.05$).

Water yield varied significantly across watersheds, with burned landscapes producing greater water yields than unburned sites. Water yield was highest in Fourmile Creek with an average of 0.23 ± 0.1 m $yr^{-1}$. This yield was very similar to the average yield of observed in Wigwam Creek (0.22 ± 0.2 m $yr^{-1}$) but was notably higher than the average yields of Pine (0.11 ± 0.08 m $yr^{-1}$) and Painted Rocks (0.03 ± 0.03 m $yr^{-1}$). The lowest average yield observed in Painted Rocks was significantly lower than those observed in Fourmile and Wigwam ($p<0.05$).

*Dissolved Organic Matter (DOM)*

Highest average TDN and DON concentrations were observed in Fourmile Creek while the highest average DOC concentration was present in Painted Rocks. Lowest average TDN and DON concentrations were observed in Pine while the lowest average DOC concentration was observed in Fourmile. Comparisons of average DOM yields in each watershed showed that Fourmile and Wigwam had higher yields on average than Pine and Painted Rocks. Highest mean DOC yield was observed in Wigwam Creek (0.93 ±1.3 g $m^{-2}$ $yr^{-1}$) while highest mean DON and TDN yields were observed in Fourmile Creek (0.13 ± 0.1 g $m^{-2}$ $yr^{-1}$ and 0.22 ± 0.2 g $m^{-2}$ $yr^{-1}$). Mean DOM yields of Painted Rocks were the lowest among all sites. Average DOC and TDN yields in Painted Rocks (0.24 ± 0.3 g $m^{-2}$ $yr^{-1}$ and 0.02 ± 0.02 g $m^{-2}$ $yr^{-1}$) significantly differed from the largest values observed ($p<0.05$).

Although DOM yields significantly differed between watersheds, DOC:DON did not ($p>0.05$). Average DOC:DON were typically between 10 and 30 with the lowest ratios observed in Fourmile (9.8 ± 15) and the highest ratios observed in Wigwam (62 ± 100). Conversely, DOC:TDN did significantly differ among streams ($p<0.05$). The highest average DOC:TDN observed in Painted Rocks (9.8 ± 3.7) was significantly larger than the similar average ratios observed in Wigwam (5.8 ± 2.8) and Pine (4.9 ± 2.1) as well as the smallest average ratio observed in Fourmile (3.0 ± 1.2) ($p<0.05$).

### *Base Cations*

The sum of base cations significantly differed among individual streams ($p<0.05$). The lowest concentration of base cations observed in Wigwam (1.1 ± 0.43 meq $L^{-1}$) was significantly less than the highest concentration of base cations observed in Painted Rocks (2.4 ± 0.85 meq $L^{-1}$) ($p<0.05$). Concentrations of base cations observed in Pine and Wigwam were similar; both streams contained ~1.5 meq $L^{-1}$ on average.

DOC: base cations did not significantly differ among streams ($p>0.05$). Given the relatively small DOC concentrations observed in each stream DOC: base cations were all less than 0.5. The lowest average ratio of 0.12 ± 0.03 was observed in Fourmile while the highest average ratio of 0.31 ± 0.36 was observed in Painted Rocks.

### *UV Absorbance*

Mean SUVA values varied across watersheds. The highest mean SUVA value observed was in Wigwam Creek (3.5 ± 0.57 L $mg^{-1}$ $m^{-1}$); however, mean SUVA from Painted Rocks was also quite high (3.4 ± 0.92 L $mg^{-1}$ $m^{-1}$). Mean SUVA values observed in Fourmile (2.5 ± 0.45 L $mg^{-1}$ $m^{-1}$) and Pine (2.45 ± 0.35 L $mg^{-1}$ $m^{-1}$) were significantly smaller than the average SUVA observed in Wigwam ($p<0.05$).

UV absorbance ratios (E2:E3) also varied across watersheds. Among individual streams ratios ranged from 2.5 ± 1.7 in Fourmile to 5.1 ± 1.1in Pine. The difference observed between these two watersheds was statistically significant ($p<0.05$).

### *Fluorescence*

The average contribution of various fluorophores to the FDOM pool significantly differed between streams. Highest average contributions were observed in Painted Rocks (A contribution = 0.7 ± 0.01%), Fourmile (B contribution = 0.2 ± 0.06%; N contribution

= 0.3 ± 0.06%; T contribution = 0.2 ± 0.07%), and Pine (C contribution = 0.4 ± 0.01%; M contribution = 0.3 ± 0.008%) values. Lowest average contributions were typically observed in Fourmile (A contribution = 0.6 ± 0.1%; C contribution = 0.3 ± 0.06%; M contribution = 0.3 ± 0.06%) or Painted Rocks (B contribution = 0.04 ± 0.02%; N contribution = 0.2 ± 0.01%; T contribution = 0.1 ± 0.03%). Differences among average contributions were statistically significant ($p<0.05$) for all fluorophores except for M. The average contribution of M in all stream water was ~0.32%.

The sum of the average contributions of B, N and T significantly differed among individual streams. Stream water from Fourmile had significantly more biologically labile material in its FDOM pool than all other streams (0.7 ± 0.2%) ($p<0.05$). Pine Creek and Wigwam Creek contained similar amounts of biologically labile material (0.46 ± 0.09% and 0.47 ± 0.08%). Stream water from Painted Rocks contained significantly less biologically labile material than all other streams (0.34 ± 0.05%) ($p<0.05$).

## DISCUSSION

Fifteen years post-disturbance, landscapes burned by the Hayman and Schoonover fires exhibit little recovery. In these systems, wildfire has markedly altered soil OM pools such that burned sites are not only storing significantly less SOM but retaining a significantly smaller fraction of SOM than unburned sites. Reduced SOM storage is attributed to the substantial loss (>80%) of aboveground biomass that resulted from these stand-replacing fires (Law et al. 2001; Certini 2005; Dore et al. 2008). Biomass loss prompted both a reduction in pre-fire OM inputs and a reduction and alteration of post-fire OM inputs which led to a subsequent decrease in soil C and N. Reduced SOM retention appears to be driven by changes in infiltration, SOM quality and microbial community composition induced by fire. Given that study sites exhibit transport limitation (**Figure 17**), increased infiltration due to decreased canopy interception, litter accumulation and evapotranspiration (Beyers et al. 2005; Stoof et al. 2014) generates additional pathways for DOM transport (Bundt et al. 2001a; Bundt et al. 2001b). Changes in vegetative community structure following fire (particularly the relative abundance of N-rich plants observed in the burn scars) alters SOM quality through the addition of low-lignin, high-N herbaceous litter (Covington et al. 1997; Hart et al. 2005). Consequently, composition of microbial community changes both as a result of the selective effect of fire on certain groups of microorganisms and shifts in vegetation (Certini 2005; Hart et al. 2005). In these ways fire alters SOM processing rates and in turn reduces SOM retention. The effect of reduced SOM retention in the terrestrial landscape is to increase DOM export to streams, making C evasion more likely (Tranvik et al. 2007; Betts and Jones 2009).

## Alteration of SOM Storage

Severe fire inhibited SOM storage by reducing OM inputs, altering species assemblages and accelerating nutrient processing.

### *Reduced OM Inputs*

Soil C stocks in burned sites were significantly smaller than those in unburned sites: burned soils contained 77% less C than reference soils. This finding is supported by Wolf (2016) who found that montane soils impacted by fire had on average 52% less total carbon than unburned soils. This reduction is due in large part to the lack of aboveground biomass present in the Hayman and Schoonover burn scars. In burned sites aboveground biomass was estimated between <0.1 Mg C $ha^{-1}$ and 37.3 ± 46.8 Mg C $ha^{-1}$ values which are equivalent to an approximate 80% decrease relative to unburned sites (Wolf 2016). This postulation is further supported by Rhoades et al. (2011) and Roccaforte et al. (2012) who investigated the regeneration dynamics of Ponderosa pine following severe fires. Rhoades et al. (2011) observed that four years after the Hayman burn, zero Ponderosa Pine seedlings were found in high severity plots compared to seedlings being present in 52% and 37% of plots located in low and moderate severity burn areas respectively. Similarly, Roccaforte et al. (2012) found that overstory regeneration was completely lacking in 57% of study sites. As follows, fire reduced aboveground biomass (pre-fire OM inputs) and future OM inputs (post-fire OM inputs) which decreased SOM storage (Roccaforte et al. 2012).

### *Altered Species Assemblages*

In addition to a reduction in biomass, C storage was also inhibited by shifts in the vegetative community structure. Predominant vegetation in the Hayman and Schoonover burn scars is comprised of grasses and forbs which produce litter with notably lower C:N than pine litter (**Table 2**). Direct comparisons of soil carbon to nitrogen confirm that burned plots generally had lower C:N ratios than unburned plots; within the coarse fraction and top 10 cm of soil, this difference was statistically significant. A similar finding was described by Wolf (2016) who identified shifts in OM inputs as the predominate driver of significantly lower C:N in soils burned by the Hayman.

Observations made by Fornwalt et al. (2018) and Abella and Fornwalt (2014) who studied the overstory structure and surface cover dynamics in the decade following the Hayman fire provide further evidence of decreased C concentrations relative to N. Fornwalt et al. (2018) recount that prior to the Hayman fire, pine litter and duff blanketed most of the ground surface at their study sites. However, post-fire, nearly all litter, duff, and needles in tree crowns had been consumed such that litter and duff cover did not change in the subsequent ten years. This change, in addition to herb cover more than doubling relative to pre-fire levels as observed by Fornwalt et al. (2018), highlight how fire can alter species assemblages. Species alteration was likewise documented by Abella and Fornwalt (2014) who found that the post-Hayman vegetative assembly consisted of both short- and long-lived forbs, graminoids and shrubs. Taken together these studies show how the relative abundance of N-rich plants following fire can decrease soil C:N and in turn, reduce C storage.

### *Accelerated Nutrient Processing*

Vegetation shifts may promote accelerated nutrient processing (Hart et al. 2005; Rhoades et al. 2011; Olefeldt et al. 2013) which is another way that C storage can be inhibited by wildfire. In Ponderosa pine dominated forests, where there is an abundance of pine and other conifer litter inputs compared to herbaceous litter inputs, the vegetation structure is considered “lignified” (Hart et al. 2005). Namely, a greater proportion of the OM input is high-lignin, low-N pine litter as opposed to low-lignin, high-N herbaceous litter (Hart et al. 2005). Under this OM scheme litter quality is low and N cycling rates are reduced (Hart et al. 2005). Alternatively, under a higher quality OM scheme, as is observed in our study systems post-fire, N cycling rates may increase (Hart et al. 2005). Evidence for accelerated N cycling post-fire can be seen in the reduction of available soil N in burned sites: on average, burned soils contained 68% lower N content, 72% less water extractable DON in the top 10 cm and 41% less water extractable DON in the soil column to reference soils. These discrepancies are comparable to the 47% reduction in soil N and 28% reduction in extractable TDN in burned soils observed by Wolf (2016).

Olefeldt et al. (2013) and Rhoades et al. (2011) support these findings and provide further evidence for increased N processing following fire. Olefeldt et al. (2013), who assessed the impacts of wildfire on DOM production, composition and reactivity, found that soil DOC/TN decreased following fire. This result indicated that post-fire, N became relatively more mobile and was in turn, processed faster (Olefeldt et al. (2013). Rhoades et al. (2011) documented a similar acceleration in N processing after the Hayman fire. This acceleration was attributed to the combined influence of reduced plant N demand and stimulated N mineralization and nitrification due to increased soil temperature and pH induced by fire. Given that higher rates of N cycling are associated with higher rates of decomposition (Dooley and Treseder 2012) shifts to herbaceous cover in burned sites would tend to further reduce C stocks. Moreover, since nutrient processing is strongly influenced by flow paths (Bundt et al. 2001a; Bundt et al. 2001b; Cheng et al. 2014) fire induced changes to soil-water interactions likely reinforce a reduction in C storage (discussed below).

## Alteration of SOM Retention

In addition to storing significantly less SOM, burned sites also retain a significantly smaller fraction of SOM than unburned sites. Comparisons of surface and subsurface OM pools revealed that burned soils retain 4% less DOC, 3.4% less TDN and 3.7% less DON than unburned soils export to the subsurface. On the ecosystem scale these values may seem inconsequential but given that Ponderosa pine forests cover nearly fifteen million hectares across the United States (Allred 2015), reduced SOM retention has the potential to considerably impact regional and global C budgets. It is therefore crucial to elucidate the factors influencing SOM retention including changes in infiltration, SOM quality and microbial community composition caused by fire.

### *Changes in Infiltration*

Increased infiltration following fire is most commonly attributed to decreased canopy interception and evapotranspiration (Beyers et al. 2005; Stoof et al. 2014), however another key factor causing increased infiltration is flow instability (Stoof et al. 2014). This factor – defined as inhomogeneous flow across a wetting front – is initiated by differences in water content, trapped air, water repellency or textural surfaces and is thus more likely to occur after fire (Bundt 2000; Stoof et al. 2014). It is a key factor to consider when discussing infiltration as it is a primary mechanism causing preferential flow – the rapid movement of water through the soil profile (Bundt 2000). As such, an increase in its propensity generates an increase in preferential flow. Since much of this flow will bypass the soil matrix, nutrient transport is accelerated in these pathways

(Bundt 2000; Bundt et al. 2001a, 2001b). Acceleration of nutrient transport is further enhanced by preferential flow with its tendency to create multiple pathways in dry soils (Stoof et el. 2014).

The impact that increased infiltration and its initiation of preferential flow has on SOM transport was investigated by Stoof et al. (2014) and Bundt et al. (2001a, 2001b). Stoof et al. (2014) found that preferential paths in burned soil were more distinct and wetter than those in unburned soil. While preferential flow in unburned soil was restricted to one wide path, burned soil exhibited finger flow by producing three narrow paths (Stoof et al. 2014). Given that narrower fingers develop greater finger front velocities, water moved much more quickly down these paths, such that infiltration was roughly five times deeper in burned soil than unburned soil (Stoof et al. 2014). Consequently, soil nutrients in these pathways may be transported much farther than anticipated, reducing the likelihood that they are retained (Bundt 2001a, 2001b). Validation of this occurrence is provided by Bundt et al. (2001a, 2001b) who observed that SOM was much more mobile in preferential pathways. In one study, SOC concentrations were 10% to 70% higher in preferential flow paths (Bundt et al. 2001b) while in the other study, SOC and total N were 15% to 75% higher in preferential pathways (Bundt et al. 2001a). These findings suggest that not only is SOM more mobile in preferential flow paths, but more abundant, demonstrating that retention of SOM is much less likely to occur in these paths (Bundt et al. 2001a, 2001b).

Preferential flow has the potential to be a key factor inhibiting SOM retention in burned sites, especially when considering that our systems are transport limited (**Figure 17**). Evidence for the presence of preferential flow in burned plots include decreased soil moisture, increased throughput, increased water yield and higher DOM concentrations in streams relative to soils in burned plots. Soil moisture both within and between fractions was significantly lower in burned soils such that water output relative to water input in drier, burned soils was notably higher than reference soils. Consistent with the theory of preferential flow in burned sites, water moving much more quickly in drier soil would result in higher water yields which was observed in both this study and the study completed by Wolf (2016). While average water yield in burned sites was nearly 84% higher than that in unburned sites in this study, it was nearly 94% higher than reference sites in Wolf's study (2016). Moreover, Wolf (2016) found that the fraction of precipitation exported, (calculated as stream discharge normalized to watershed area and divided by precipitation) was more than twenty times higher in the Hayman burned sites relative to unburned sites (Wolf 2016). Also consistent with the theory of preferential flow in burned sites would be the indication that SOM is more mobile and but more abundant in burned sites. Indeed, it seems that when looking at differences in concentrations of mg DOM $g^{-1}$ soil between soils, subsurface soils and streams, preferential flow may be a driver influencing trends (**Table 3**). Concentrations of average DON in both Wigwam Creek and Fourmile Creek were higher than those observed in subsurface soil but less than those observed in surface soils, a trend that was not present in either reference watershed. Furthermore, average stream TDN concentration in Fourmile Creek was higher than that observed in the subsurface soil but less than that observed in the surface soil. Preferential flow is one way to describe this discrepancy via rapid transport of SOM from the surface to streams with little adsorption occurring in the subsurface (Bundt et al. 2001a, 2001b). Together, hydrologic characteristics and concentrations of stream DOM demonstrate that retention of SOM is much less likely to occur in burned soils.

The influence of preferential flow on SOM retention may persist for decades (Stoof et al. 2014). Since increased infiltration via finger flow develops in dry substrates, drier soils will exhibit frequent preferential flow (Stoof et al. 2014). Consistently drier soils following fire indicate that the increased propensity for preferential flow may last as long as it takes for the vegetation to regenerate to the point that the drying out of the topsoil ends (Stoof et al. 2014). In our study sites, burned plots still contain drier soils than unburned plots fifteen years postfire; this pattern will likely continue for many more years given the lack of overstory regeneration in burned watersheds.

### *Changes in SOM Quality*

Shifts in the quality of OM inputs is cited as one of the most influential mechanisms driving postfire microbial community dynamics (Hart et al. 2005; Knicker 2007). Changes in vegetative community structure following fire alters relative nutrient concentrations (Certini 2005; Knicker 2007), which not only impacts the amount of SOM stored but the fraction of SOM retained. In addition to reducing C storage via decreasing C:N and accelerating nutrient cycling, the relative abundance of N-rich plants in the burn scars may reduce SOM retention by increasing SOM quality (Covington et al. 1997; Hart et al. 2005).

Characteristics of high SOM quality include low C to nutrient ratios, low concentrations of secondary metabolites and low levels of structural carbohydrates (Marschner and Kalbitz 2003; Hart et al. 2005). Accordingly, high quality SOM pools tend to be more bioavailable (Marschner and Kalbitz 2003). In burned sites where there is has been a shift from high-lignin, low-N pine litter to low-lignin, high-N herbaceous litter, one would expect high bioavailability and biodegradability of SOM. Wolf (2016) confirmed this expectation with the finding that the rate of $CO_2$ production per g soil C (a proxy for relative bioavailability) was approximately 44% higher in burned plots compared to unburned plots. This expectation is also supported by the differences in the specific UV absorbance ($SUVA_{254}$) – a proxy for DOC aromaticity – observed between burned and unburned soils in this study. On average, SUVA values were between 0.6 L $mg^{-1}$ $m^{-1}$ and 0.8 L $mg^{-1}$ $m^{-1}$ lower in burned solutes than reference solutes, a finding which suggests that OM is less aromatic in the burned soils of the Hayman and Schoonover burn scars. Such an outcome is contrary to the typical finding of an increase in the proportion of aromatic structures following fire (González-Pérez et al. 2004; Certini 2005; Knicker 2007; Certini et al. 2011; Santos et al. 2016) but is easily explained by the prevalence of herbaceous vegetation in burn scars. Where the relative abundance of N-rich herbaceous cover has increased in the fifteen years postfire, C:N ratios of OM inputs have decreased and in turn, SOM quality has increased (Sun et al. 1997; Hunt et al. 2000; Wiegner et al. 2010). Consequently, the transfer of C from burned watersheds to the atmosphere via the decomposition of organic material has likely increased and in turn, the likelihood that SOM will be retained is reduced.

### *Changes in Microbial Community Composition*

Wildfire affects the composition of microbial communities through both direct and indirect mechanisms (Certini 2005; Hart et al. 2005; Dooley and Teseder 2012). Heat transfer to soils during fire may directly reduce microbial populations through heat-induced microbial mortality while transformation of the physical and chemical properties of soil and successive plant community-induced changes in the soil environment following fire indirectly impact microbial community composition (Wardle 2002; Certini 2005; Hart et al. 2005; Dooley and Teseder 2012). Being that distinct microbe communities mediate C feedbacks between terrestrial ecosystems and the atmosphere differently, changes in microbial composition following fire may notably alter SOM retention (Certini 2005; Hart et al. 2005; Dooley and Teseder 2012).

Taking into account the postfire interval (fifteen years), one can assume that the extent to which heat-induced mortality continues to impact microbial composition is minimal (Certini 2005; Hart et al. 2005; Dooley and Teseder 2012). However, given the strong links between plant assemblages and microbial communities, change in the vegetative community structure in the years following fire has the potential to be a dominant driver of microbial community composition (Hart et al. 2005). Given that vegetation samples collected from study sites show that C:N of pine litter is 70 whereas C:N of grasses and forbs are 47 and 44 respectively (**Table 2,** Wolf 2016) microbial communities in burned plots likely differ considerably from those in unburned plots.

Evidence for postfire microbial community structure change in response to altered species assemblages is provided by Hamman et al. (2007) and Covington et al. (1997). Hamman et al. (2007) found that microbial communities in both low and high severity burn sites were structurally different from populations in unburned sites (Hamman et al. 2007), a finding which suggests that SOM processing among these sites also varied. Variation in SOM processing among altered sites was substantiated by Covington et al. (1997) who found that when C to N ratios of litter decreased, the chemoautotrophic nitrifier population size increased by 60% (Covington et al. 1997). Ongoing studies suggest that differences in the quality of SOM continue to widen between burned and unburned sites and are expected to continue to alter microbial community structure (Covington et al. 1997). These studies show how fire can change the composition of microbial communities in burned sites and in kind influence SOM retention.

## Alteration of Stream DOM

Given that terrestrial and aquatic systems within watersheds are connected via hydrologic pathways, transformation of flow paths in burned landscapes can have cascading effects on nutrient concentrations in streams. Findings from our systems demonstrate rapid transport of OM from surface soils to streams with little adsorption occurring along the way in burned areas. Although absolute DOM concentrations in mg $L^{-1}$ were generally lower in the burned streams, when normalized to the mass of soil in the watershed ($\mu g\ g^{-1}$), DOC and DON concentrations were 50% to 80% higher in burned streams relative to unburned streams (**Table 3**). Ergo, burned streams produced the highest average DOC and DON yields ($g\ m^{-2}\ yr^{-1}$). Other studies conducted in the Hayman burn also support the notion that elevated DOM in burned streams is driven by the more rapid movement of water through soils impacted by fire (Wolf 2016; Rhoades et al. 2011, 2016). Wolf (2016) determined that the average yields of C and N ($g\ m^{-2}\ yr^{-1}$) from burned watershed was ~89% higher than from reference watersheds. Similarly, Rhoades et al. documented that five years postfire stream nitrate concentrations and export in burned streams were twofold higher than reference streams (2011) while fourteen years postfire stream nitrate remained an order of magnitude higher in burned watersheds compared to unburned watersheds (2016).

Together these studies speak to the influence that slow vegetation recovery has on OM transport in the drier, burned soils. Following the Hayman and Schoonover fires, reduced vegetation increased insolation to burned soils such that they are consistently drier and so, continue to have an increased propensity for preferential flow. Consequently, little adsorption of OM is occurring in these terrestrial landscapes, increasing DOM concentrations and biological labile material in streams. As a result, these streams will like exhibit greater respiration rates (Betts and Jones 2009). If this occurrence persists, not only will the terrestrial carbon balance shift, the carbon balance of the inland waters draining these landscapes will shift (Tranvik et al. 2007). Despite the small area that they occupy, this shift would have an impact on the regional C budget as the amounts of C received from the terrestrial environment is disproportional to their spatial extent (Tranvik et al. 2007; Raymond et al. 2013). Approximately 70% of the $CO_2$ evaded from streams covers only ~20% of the earth's surface (Raymond et al. 2013).

## Impacts of Drought

Investigation of varying antecedent moisture conditions indicate that the consequences of wildfire on OM accumulation, storage and retention are likely to be more pronounced under a reduced precipitation regime. Variation in antecedent moisture conditions explained a significant amount of variation in DOM concentrations: very dry soils exported 53% more DOC, 44% more TDN and 40% more DON than moist soils. As follows, drier soils exported solutes with notably higher contributions of biologically labile material than moist soils. Antecedent moisture has been noted to be an important factor in DOC levels in soil solutions and streams (Raymond and Saiers 2010; Xu and Saiers 2010; Stacy et al. 2015); these results validate that the transformation of hydrologic pathways remains an essential mechanism altering SOM transport and retention. Other authors' observations of the selective transport of OM-rich material during low precipitation suggests that surficial OM will be preferentially transported during drought (Raymond and Saiers 2010; Xu and Saiers 2010; Stacy et al. 2015). These studies indicate that during low precipitation years OM-poor material from deeper in the soil profile remains attached to the soil matrix while in years with high precipitation, increased infiltration detaches OM-poor material and transports it through the soil profile (Raymond and Saiers 2010; Xu and Saiers 2010; Stacy et al. 2015). As a result, one can expect OM transport to streams and subsequent DOM concentrations to increase with drought. This expectation in conjunction with the projection that net $CO_2$ uptake will decline under drier conditions (Sacks et al. 2007) emphasize the reduction in C storage via reduced SOM accumulation and retention that will likely occur in the future.

## Implications

Previous studies demonstrate that severe wildfire has the ability to shift montane C balance from a sink to a source for decades (Law et al. 2001; Savage and Mast 2005; Dore et al. 2008, 2012; Roccaforte et al. 2012). This study provides further evidence that Ponderosa pine forests in the Intermountain West may transform into a decadal-scale C source under a more frequent and severe disturbance regime. Due to slow vegetation recovery and minimal tree regeneration, montane Ponderosa pine forest C stock recovery is estimated to take twice as long as that of a more mesic Lodgepole pine forest (Wolf 2016). This difference is attributed to phenological, biogeochemical and climatic factors. Unlike Lodgepole pine, Ponderosa pine lack cone serotiny which means that following severe fires Ponderosa seed reserves are destroyed and tree recolonization is inhibited

(Rhoades 2011; Chambers et al. 2016). Another potential barrier to postfire tree recolonization is the lack of available soil N in burned sites. Given that Ponderosa pine forests tend to be N limited (Covington et al. 1992), a reduction in N following fire in addition to accelerated N cycling could further limit N and hinder regrowth.

Although phenological and biogeochemical factors will influence montane ecosystem recovery, recent studies demonstrate that climate will be the key driver influencing postfire regeneration (Rother et al. 2017; Stevens-Rumann et al. 2018). Ponderosa pine establishment primarily occurs in years with above-average moisture availability (Rother et al. 2017; Stevens-Rumann et al. 2018). However, trends of increasing temperature and associated water stress suggest that postfire periods with suitable climate for tree seedling establishment and survival will occur less frequently in upcoming decades (Rother et al. 2017; Stevens-Rumann et al. 2018). Projections indicate that across a broad region and multiple forest types within the Intermountain West, periods of wetter climate that have favored tree regeneration in the past may not occur frequently enough to facilitate tree regeneration in the future (Rother et al. 2017; Stevens-Rumann et al. 2018). As a consequence, shifts to lower density forest or non-forested states are likely (Chambers et al. 2016; Rother et al. 2017; Stevens-Rumann et al. 2018).

Despite the fact that western forests have historically exhibited high resiliency to fire – in that they resist transformation into alternative states such as grasslands or shrublands – mounting evidence suggests a trend toward lower resiliency. Given that the Ponderosa pine is the most widely distributed pine in North America (Allred 2015), this potential change has drastic implications for regional and global C budgets. Future studies should aim to further understand the mechanisms that inhibit C sequestration so that positive feedbacks like the ones identified in this study may be minimized.

TABLES AND FIGURES

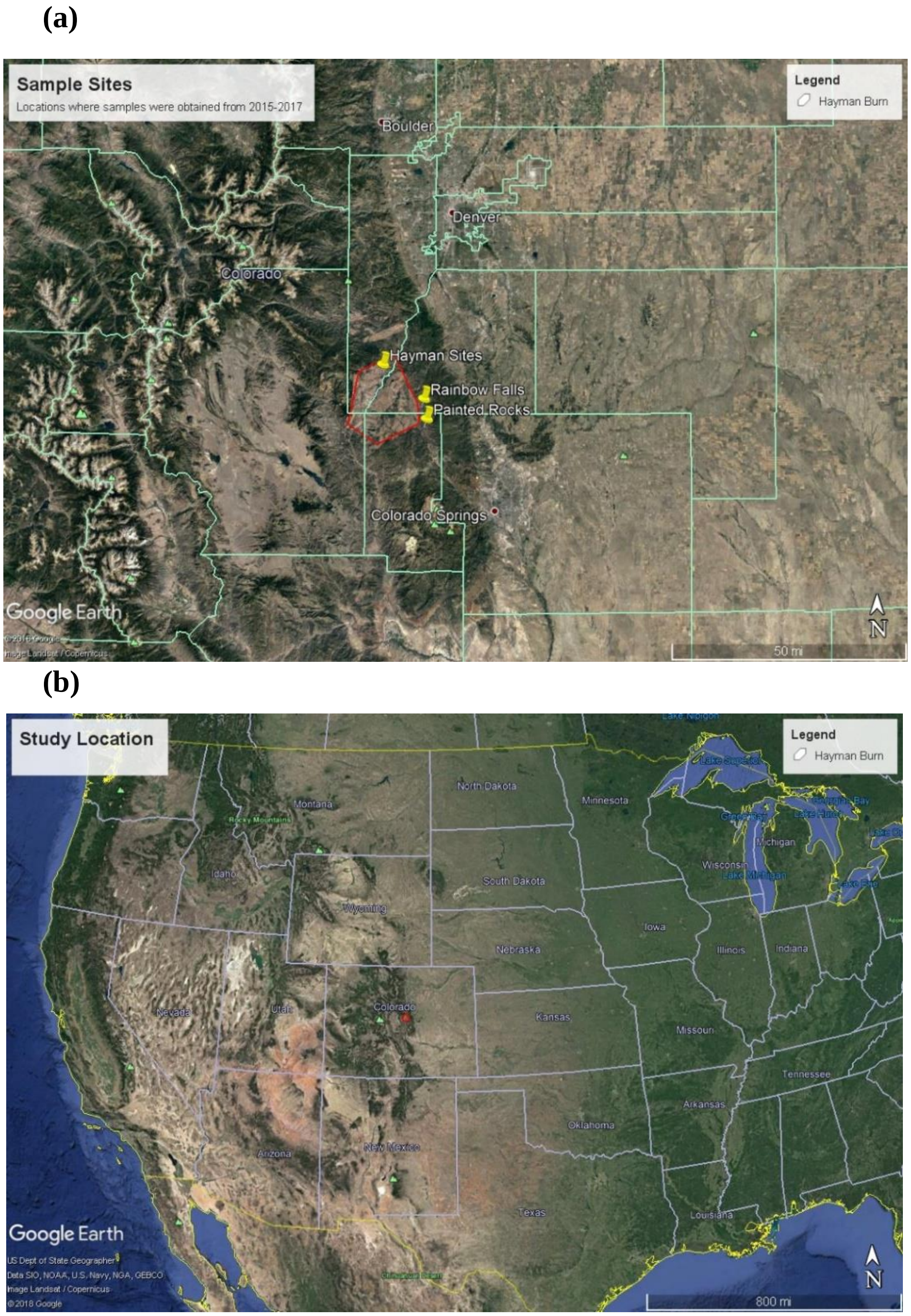

**Figure 1**

**(a)** Approximate location of the Hayman burn sites (Pine, Wigwam and Fourmile) and the reference sites Painted Rocks and Fourmile

**(b):** Location of study sites in reference to the United States

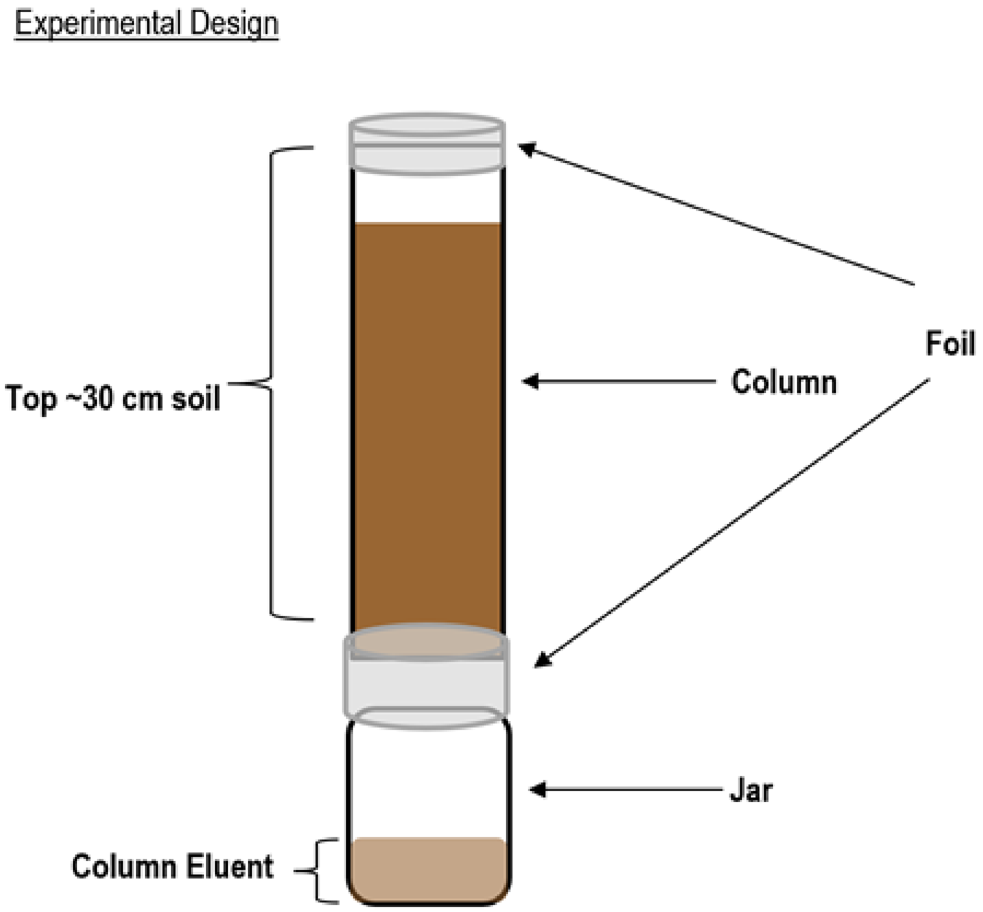

**Figure 2:** Diagram depicting the set-up for column experiments

**Experiment Timeline**

| Day | Antecedent Moisture Condition | Treatment | Amount of MQ added (mL) |
|---|---|---|---|
| 1 thru 3 | Very dry | 1 storm simulation per day | 90 |
| 4 thru 7 | Very dry | Exposed to air | |
| 8 | Moist | 1 storm simulation | 30 |
| 9 thru 19 | Moist | Exposed to air | |
| 20 and 21 | Dry | 1 storm simulation per day | 60 |
| | | | **180** |

**Table 1:** Description of experiment timeline

| | Pine Litter | Grass | Forb | Shrub Leaves | Shrub Branches |
|---|---|---|---|---|---|
| **%N** | 0.808 | 1.077 | 1.227 | 2.969 | 1.062 |
| **%C** | 48.43 | 43.51 | 45.87 | 49.11 | 47.78 |
| **C:N** | 69.91 | 47.13 | 43.62 | 19.53 | 62.87 |

**Table 2:** %N, %C, and C:N of vegetation samples collected from Hayman watersheds. Shrubs include leaf and branch samples from Mountain mahogany and Gambel Oak (Wolf 2016).

**Pine Watershed**

| **Location** | **µg DOC/g soil** | **µg TDN/g soil** | **µg DON/g soil** |
|---|---|---|---|
| Surface Soil | 48 ± 8.7 | 8.7 ± 0.8 | 5.3 ± 0.6 |
| Subsurface Soil | 2.3 ± 0.7 | 0.56 ± 0.3 | 0.30 ± 0.2 |
| Stream | 0.90 ± 0.8 | 0.24 ± 0.2 | 0.24 ± 0.2 |

**Painted Rocks Watershed**

| **Location** | **µg DOC/g soil** | **µg TDN/g soil** | **µg DON/g soil** |
|---|---|---|---|
| Surface Soil | 85 ± 39 | 30 ± 26.1 | 22 ± 19.1 |
| Subsurface Soil | 8.0 ± 6.6 | 0.85 ± 0.5 | 0.51 ± 0.4 |
| Stream | 0.71 ± 0.8 | 0.075 ± 0.1 | 0.067 ± 0.1 |

**Wigwam Watershed**

| **Location** | **µg DOC/g soil** | **µg TDN/g soil** | **µg DON/g soil** |
|---|---|---|---|
| Surface Soil | 49 ± 41 | 12 ± 7.5 | 8.2 ± 6.3 |
| Subsurface Soil | 3.3 ± 1.1 | 0.49 ± 0.1 | 0.23 ± 0.1 |
| Stream | 2.6 ± 3.7 | 0.46 ± 0.4 | 0.46 ± 0.4 |

**Fourmile Watershed**

| **Location** | **µg DOC/g soil** | **µg TDN/g soil** | **µg DON/g soil** |
|---|---|---|---|
| Surface Soil | 44 ± 14.5 | 10 ± 1.6 | 5.2 ± 0.4 |
| Subsurface Soil | 4.4 ± 1.3 | 0.62 ± 0.2 | 0.37 ± 0.1 |
| Stream | 1.8 ± 1.2 | 0.77 ± 0.6 | 0.77 ± 0.6 |

**Rainbow Falls Watershed**

| **Location** | **µg DOC/g soil** | **µg TDN/g soil** | **µg DON/g soil** |
|---|---|---|---|
| Surface Soil | 686 ± 244 | 282 ± 28.7 | 190 ± 17.2 |
| Subsurface Soil | 9.8 ± 8.3 | 1.4 ± 0.8 | 0.90 ± 0.6 |
| Stream | 0.63 ± 0.9 | 0.03 ± 0.04 | 0.03 ± 0.04 |

**Table 3**: Comparisons of DOM across watersheds normalized to watershed area. Rainbow Falls was excluded from analysis given lack of replicate samples.

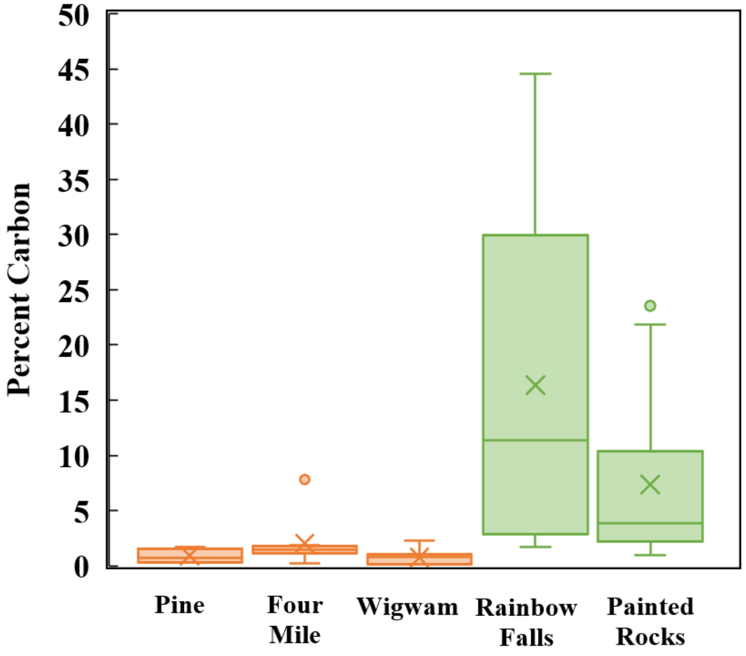

**Figure 1**: Comparison of soil percent carbon between burned sites (orange) and unburned sites (green).

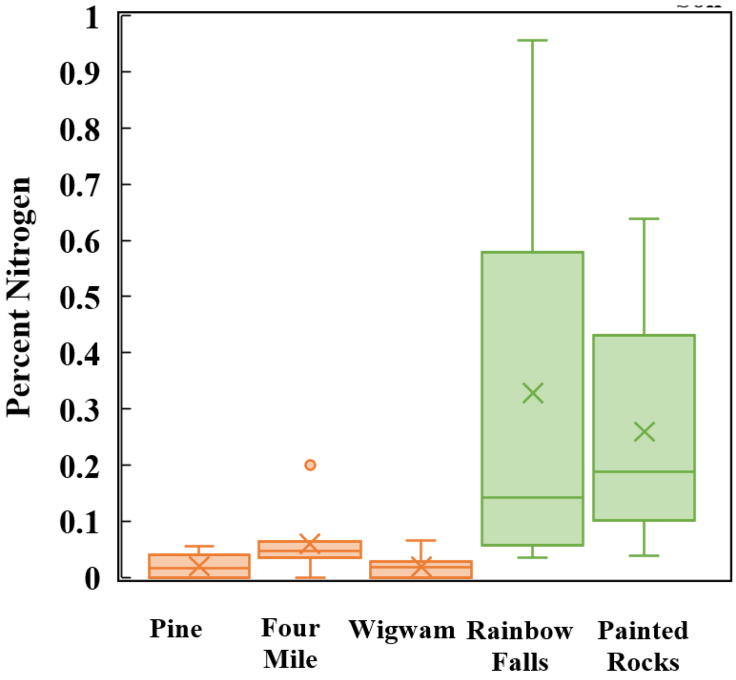

**Figure 2**: Comparison of soil percent nitrogen between burned sites (orange) and unburned sites (green).

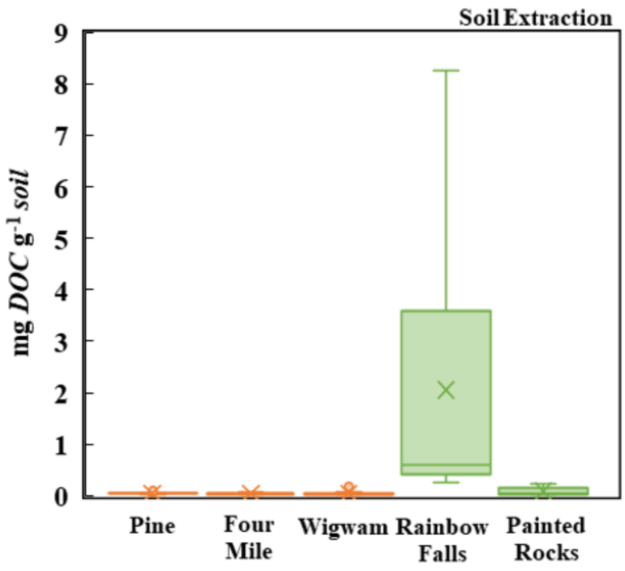

**Figure 5**: Soil Extraction DOC for burned sites (orange) and unburned sites (green).

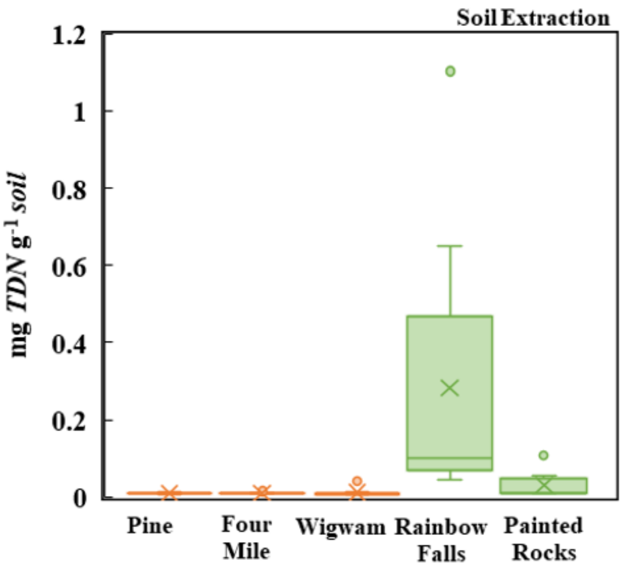

**Figure 6**: Soil Extraction TDN for burned sites (orange) and unburned sites (green).

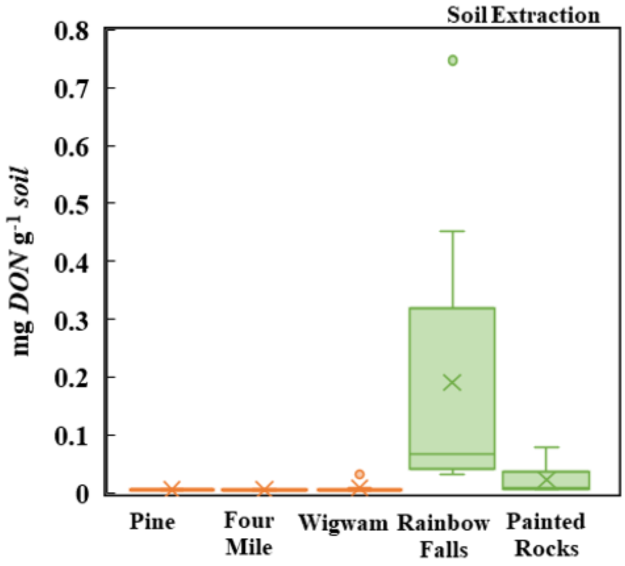

**Figure 7**: Soil Extraction DON for burned sites (orange) and unburned sites (green).

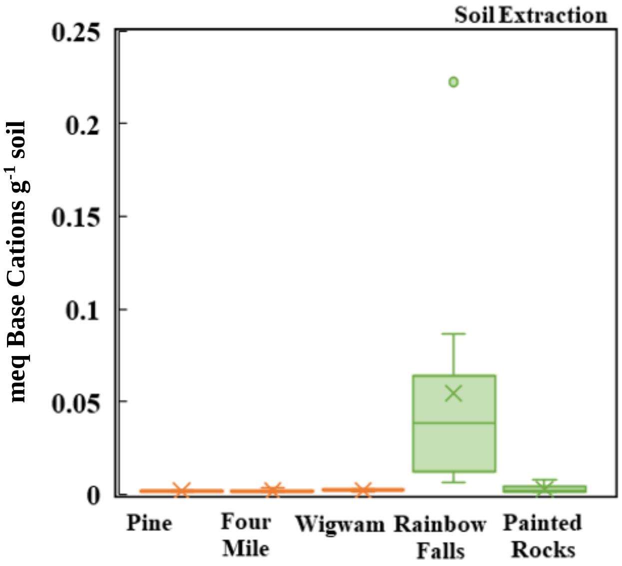

**Figure 8**: Soil Extraction Base Cations for burned sites (orange) and unburned sites (green).

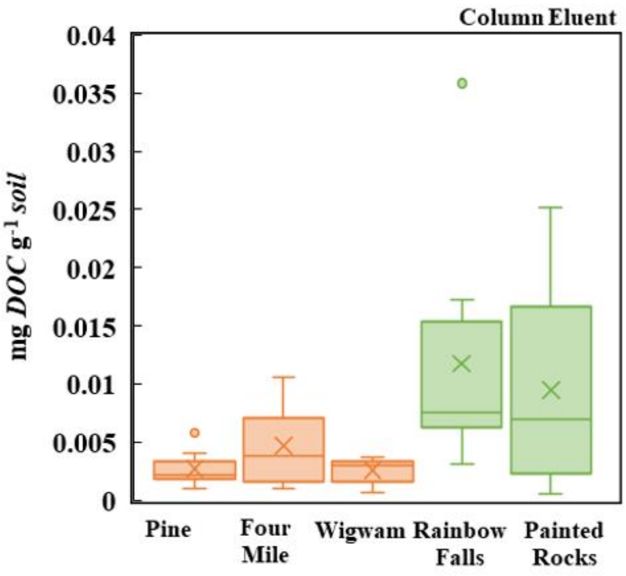

**Figure 9**: Column Eluent DOC for burned sites (orange) and unburned sites (green).

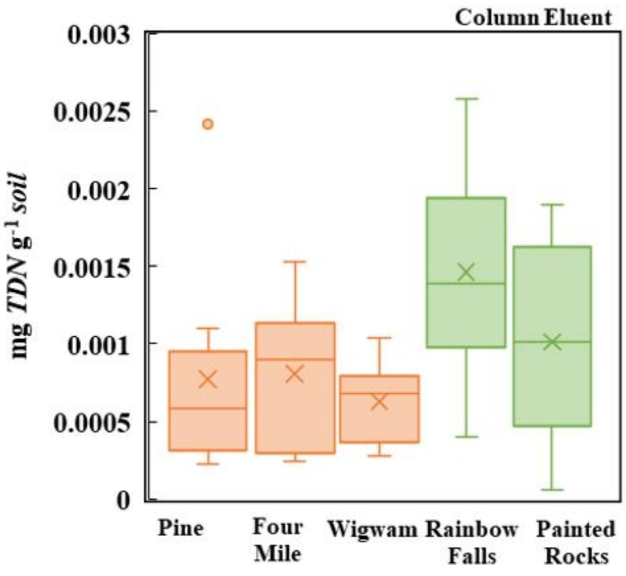

**Figure 10**: Column Eluent TDN for burned sites (orange) and unburned sites (green).

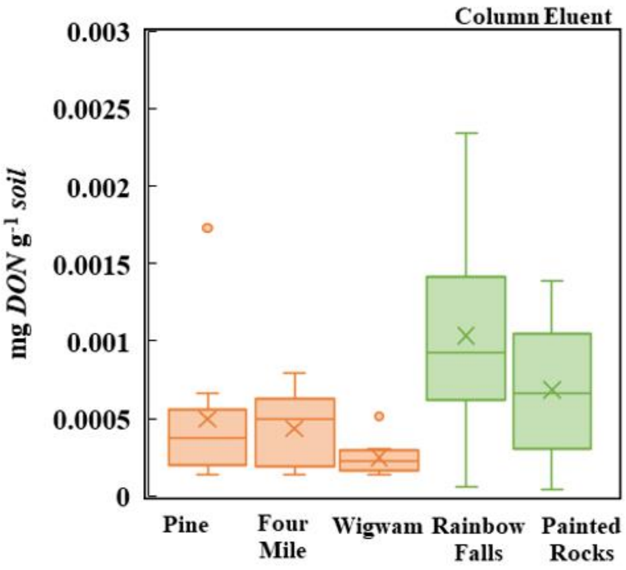

**Figure 11**: Column Eluent DON for burned sites (orange) and unburned sites (green).

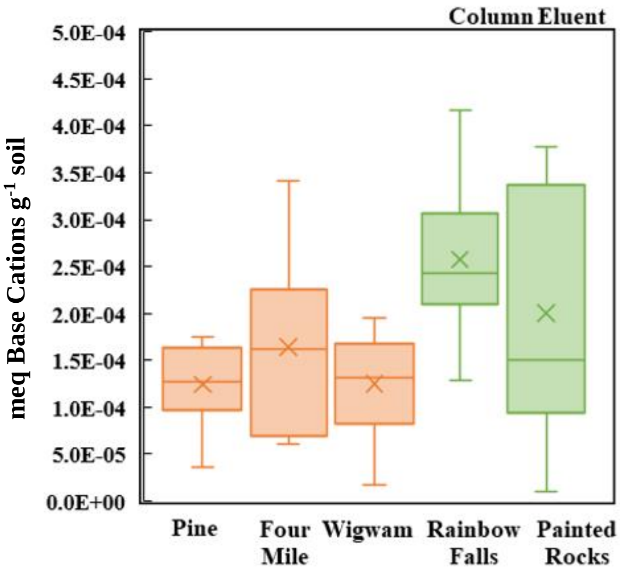

**Figure 12**: Column Eluent Base Cations for burned sites (orange) and unburned sites (green).

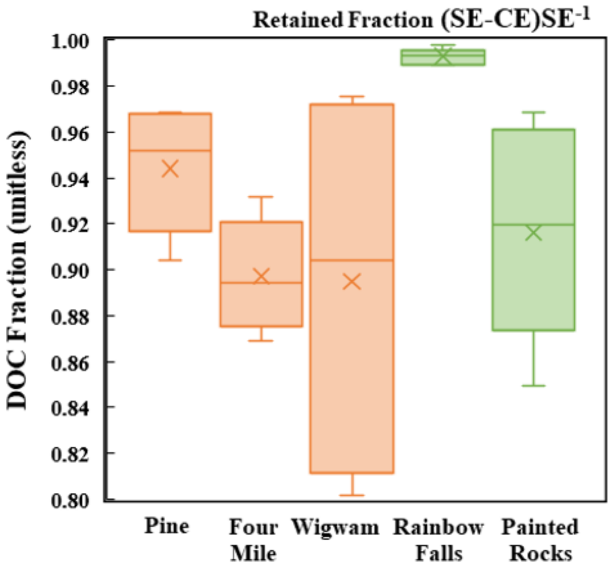

**Figure 13**: Retained Fraction DOC for burned sites (orange) and unburned sites (green).

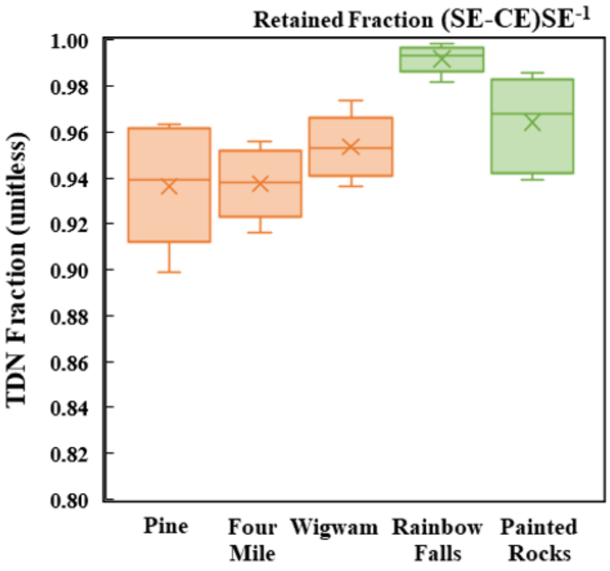

**Figure 14**: Retained Fraction TDN for burned sites (orange) and unburned sites (green).

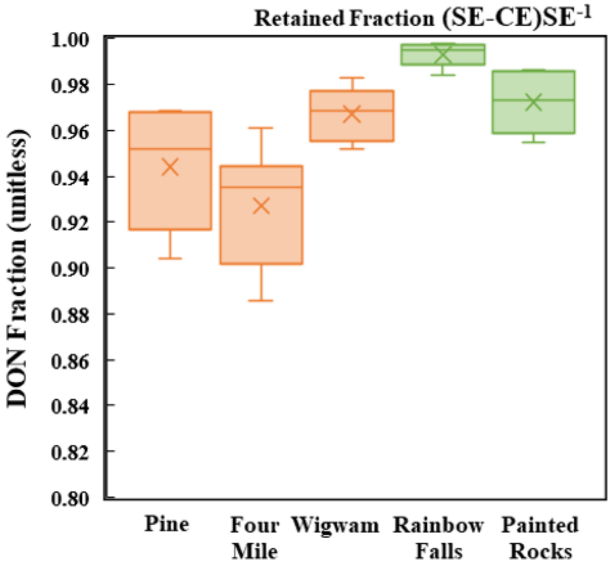

**Figure 15**: Retained Fraction DON for burned sites (orange) and unburned sites (green).

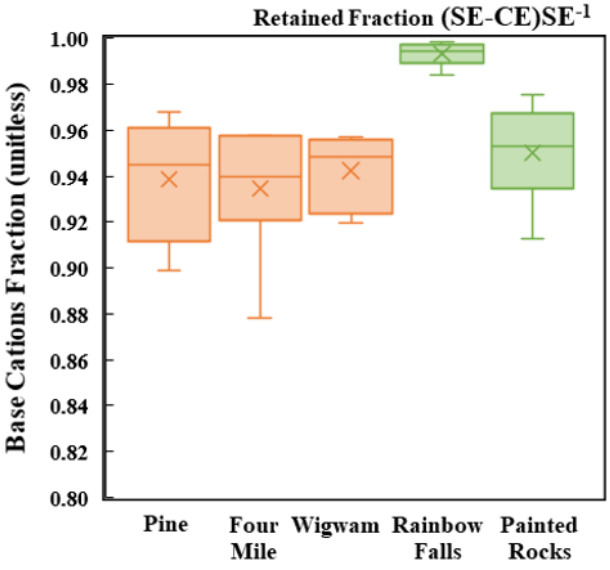

**Figure 16**: Retained Fraction Base Cations for burned sites (orange) and unburned sites (green).

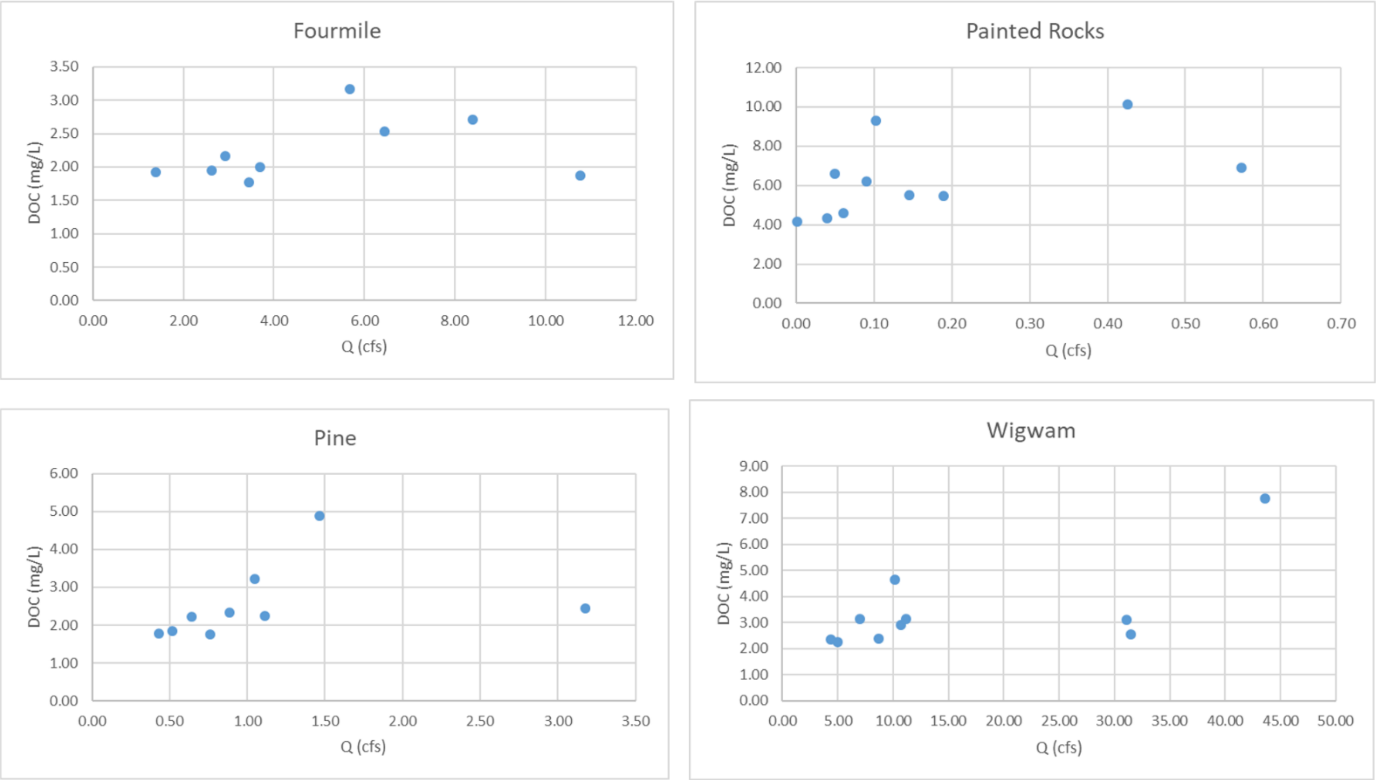

**Figure 17**: Given that DOC increases with discharge, we can assume that the study sites are transport limited and not source limited.

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