Effect of Heating Temperature on the Magnitude and Solubility of Dissolvable Constituents from Soil and Litter Material in the Colorado Front Range

by

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Effect of Heating Temperature on Dissolvable Constituents from Soil and Litter Material in the Colorado Front Range

Thesis directed by Professor Fernando L. Rosario-Ortiz

Wildfires are a natural and ubiquitous phenomenon that leave behind a perturbed hydrologic environment. Post-fire landscapes become susceptible to erosion, decreased infiltration capacity, and soil hydrophobicity, which facilitate transport of post-fire residue into surface waters serving potable water sources. The risks posed by post-fire residue deposition to raw water sources and subsequent impairment of water quality are difficult to understand due to the complex nature of wildfire effects. Research indicates that soil organic matter (SOM) and plant material undergo chemical and structural changes following heating. As a result, water extractable organic matter from forest floor material altered by heat may be significantly different from that of unaltered material in quantity and quality. To address the impacts of ash on water quality, surface soils and litter were progressively heated to a range of temperatures (150 to 550°C) and subsequently leached in water to evaluate changes in the release of dissolvable constituents as a function of burn temperature. Water quality parameters assessed include dissolved organic carbon (DOC), dissolved organic nitrogen (DON), dissolved inorganic nitrogen (DIN), fractions of water extractable organic carbon and nitrogen (WEOC and WEON), and soluble elements. The quality of dissolved organic matter (DOM) from unaffected and heat-impacted soil and litter was assessed using ultraviolet absorbance at 254 nm (SUVA254). Following heating, the quantity and solubility of DOC and DON from soil were enhanced at 250°C to 350°C while the litter decreased drastically

after material was heated above 150°C. DOC contributions from litter across all temperatures exceeded that from soil while DON contributions for both materials were comparable. Soluble element trends varied; however, litter concentrations were magnitudes higher than soil for all except for Al and Mn, which were comparable. For both soil and litter leachates, SUVA<sub>254</sub> increased with increasing temperature, indicating a higher concentration of aromatic moieties for leachates of heat-impacted material. Findings contribute to the growing understanding of impacts wildfires have on water quality and helps identify major contributors (soil or litter) to water quality risk based on fire severity.

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## **List of Acronyms**

- CBI Composite Burn Index
- DBP Disinfection Byproduct
- DOC Dissolved Organic Carbon
- DIN Dissolved Inorganic Nitrogen
- DOM Dissolved Organic Material
- DON Dissolved Organic Nitrogen
- EPA Environmental Protection Agency
- FLG Flagstaff
- GROSS Gross Reservoir
- HAA Haloacetic Acid
- HAN4 Haloacetonitriles, sum of concentration of dichloroacetonitriles, bromochloroacetonitriles, dibromoacetonitriles, and trichloroacetonitriles.
- N-DBP Nitrogenous Disinfection Byproduct
- NED Nederland
- NOAA National Oceanic and Atmospheric Administration
- NOM Natural Organic Matter
- LEGS Laboratory for Environmental and Geological Sciences
- TDN Total Dissolved Nitrogen
- TN Total Nitrogen
- TP Total Phosphorous
- TTHM Total Trihalomethane
- WEOC Water Extractable Organic Carbon
- WEON Water Extractable Organic Nitrogen
- SABS Suspended and Bedded Sediments

SOM – Soil Organic Matter

 $SUVA_{\rm 254}-Specific \ Ultra-Violet \ Absorbance \ at \ 254 \ nm$ 

WHO – World Health Organization

## **1** Introduction

Wildfires are a natural and nearly-ubiquitous phenomenon that can have drastic effects on forested landscapes and wildland ecosystems. Conditions for the pervasiveness of wildfire have become exacerbated by climate change (Fried, Torn, and Mills 2004; Westerling 2006), changes in land use, and the over-densification of forests through prolonged wildfire prevention management (Sexton 2006). Fires are anticipated to persist or worsen in the next century. Within the last year alone, nearly 71,500 fires have consumed over 10,000,000 acres of forested land in the United States (National Interagency Fire Center, 2018). While forest fires have played an integral role in ecological productivity and health for millennia in forested areas (Reneau et al. 2007; Kondolf et al. 2014), many wildfire events can jeopardize public health and safety as well as urban infrastructures as the proximity of homes to wildland areas becomes more common. In addition to the destruction of property and homes, the subsequent and indirect impacts of wildfires pose human safety and health concerns; namely, degraded water quality, poor air quality, and exposure to the effects of increased erosion including debris flows and landslides. Marked increases in the frequency and season length of forest wildfires in the last 40 years (Westerling 2006) are the impetus for a large push in the research community towards understanding the impacts and implications of these perturbations.

Many water quality risks are introduced by the advent of wildfire in forested water catchments including aesthetic concerns (taste, appearance, odor, etc.), elevated turbidity levels, elevated nutrient levels, shifts in stream water chemistry, reduced reservoir capacity from sedimentation, impediments to the treatability of raw water, and the introduction of material that could render finished water toxic through disinfection byproduct yields. Previous work has suggested that the perturbed hydrologic environment coupled with storm-induced introductions of post-fire residue, including ash, into the aquatic environment contribute greatly to these risks (Smith et al. 2011; Santín et al. 2015; Rhoades, Entwistle, and Butler 2011; Murphy et al. 2015; Bladon et al. 2014). The introduction of ash, a mixture of charred organic and inorganic material (Bodí et al. 2015), into surface waters after a fire has been identified as contributing to elevated dissolved constituents in water bodies. The specific impact of ash on water quality in forest catchments is difficult characterize because rarely is ash decoupled from mineral soil as they are both delivered into streams and water bodies following a post-fire storm event (Santín et al. 2015). Moreover, the composite nature of ash further complicates distinguishing what type of material is contributing how much of a specific constituent.

## 1.1 Wildfire dynamics and classification

Changes in carbon and nutrient dynamics of forest floor litter and soil during a wildfire depend greatly on the extent and duration in which energy from the fire is propagated through the forest floor (DeBano et al., 1998). There are several interconnected factors that contribute to the extent to which heat is propagated through the forest floor matrix during a wildfire, including antecedent soil moisture, type and density of vegetative ground cover, wildfire duration, terrain relief, wind speeds, the surface microenvironment, and fire regime. Furthermore, ground temperatures can vary continuously both temporally and spatially within a single burn perimeter (Janzen and Tobin-Janzen 2008). Fire severity, often used interchangeably with burn severity, is operationally defined by the change or loss of above and belowground organic matter due to the fire (Keeley 2009) and depends on the rate at which thermal energy is produced, or fire intensity (DeBano et al., 1998). Because the extent to which thermal energy can be transmitted to the soil is limited by the soil's thermal properties, the most significant factor that controls soil heating is wildfire duration and maximum temperature reached (Neary et al. 1999). Slow-burning fires, sometimes categorized as "smoldering" or "ground" fires, will have a more extensive impact on litter and soil organic matter

(SOM) than fast-burning crown fires (Janzen and Tobin-Janzen 2008; González-Pérez et al. 2004). Several measures have been used to classify fire severity from the perspective of a fire's impact on the soil environment. Each takes a different number or combination of factors into consideration. Ryan and Noste (1985) developed a two-dimensional fire severity matrix, which uses both surface fire behavior and depth of burn characteristics to encompass the overall severity of a wildfire (Neary et al. 2005). The aboveground heat pulse, from flaming combustion, and the belowground heat pulse, from smoldering combustion, are the two defining components in this matrix. Wells et al. (1979) classified fire severity based on the areal ratio of spatial severities within the burn perimeter. For example, a low severity burn would be characterized as having less than 2 percent of the area severely burned, less than 15 percent of the area moderately burned, while the remaining area is either unburned or burned at a low severity. Although largely arbitrary, Wells' classification technique was aimed at capturing the spatial dissimilarities due to inherent variation in the burn environment. Later, in 2005, Key and Benson developed a ranking system using fieldbased visual observations and satellite imagery, which they called the Composite Burn Index (CBI). Other models venture to include impacts of fires on other systems beyond just organic matter consumption. Hydrologic impacts have been linked to fire severity, as soil burn depth is a significant factor of concern to wildfire impacts on water resources (Neary et al. 2005; Parson et al. 2010). Conceptually, as both fire severity and hydrologic event magnitude increase, so does the severity of the watershed response by way of water quality degradation and soil instability. Figure 1-1 depicts such a conceptual model describing fire severity, which was proposed by Neary et al. (2005). It encompasses these environmental factors including fire behavior, soil burning depth, microenvironment characteristics, and climatic factors.

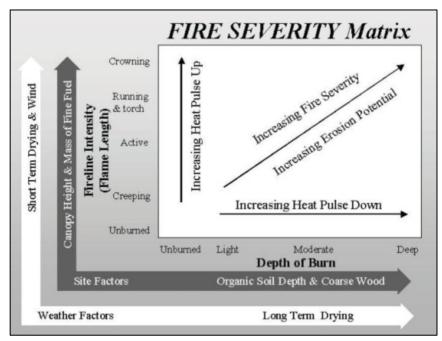


Figure 1-1: Conceptual model of fire severity (Neary et al. 2005).

With so many system components contributing to wildfire dynamics, this conceptual model endeavors to encompass the chief criteria that contribute to fire severity.

The forest floor can experience heat pulses at a wide range of temperatures and durations ranging from 50°C to over 1500°C over time scales of seconds (instantaneous) to hours (smoldering) (Neary et al. 1999). Typical maximum temperatures range from 200°C to 300°C; however, under conditions where heavy fuel loads are present, temperatures have been recorded up to 700°C (Neary et al. 1999). For fires having low severity effects, the forest floor temperature up to 5 cm in depth generally does not exceed 150°C. Fires of medium and high severities can reach temperatures up to 400°C and above 675°C respectively (Janzen and Tobin-Janzen 2008). To understand better some of the processes that are impacted by wildfire, many studies have used laboratory-based heating simulations (Malmström 2008; Ebel 2012; Savage 2002; Almendros and González-Vila 2012; Knicker et al. 1996; González-Vila and Almendros 2003).

## 1.2 Wildfire impacts on forested landscapes

Fire has been observed to have drastic impacts on the functionality of a forest landscape, including the physical, chemical, and biological properties of the forest floor. Part of that impact translates to dramatic changes in watershed hydrology, brought on by multiple impacted factors including changes in bulk density (Moody and Martin 2001), strength and persistence of soil water repellency (Huffman, MacDonald, and Stednick 2001), and homogenization of soil-water retention (Ebel 2012) and a decrease in the hydraulic capacity of soil. Post-fire hydrologic responses are often more intense, causing higher and quicker peak-flows, enhanced overland runoff, mobilization of fire-impacted forest floor material, and a quicker watershed response to rainfall (Neary, Gottfried, and Ffolliott 2003). With all these processes occurring in concert, post-fire water quality deterioration has become a concern for water managers and ecologists immediately following a storm event (Hohner et al. 2016; Writer et al. 2014) and even persistently over many years (Rhoades, Entwistle, and Butler 2011).

The magnitude of wildfire perturbation on the environment is confounded by multiple processes occurring simultaneously, including the loss of forest floor structure. Forest fires typically cause radical changes to the integrity of the forest floor, many times impacting the organic-rich soil layer while simultaneously experiencing an additional carbon-rich input from charred overstory vegetation, which then is incorporated into the soil profile (Santín et al. 2016; Knicker et al. 2005). For high fire severities, most of the forest floor biomass is consumed and this layer of particulate residue that remains is called 'ash' (Parson et al. 2010). Although the term 'ash' has been defined in multiple ways by many disciplines, i.e. ecology, geomorphology, wildfire science, etc., 'ash' here is composed of mineral materials and charred organic material possessing different chemical and physical properties than its parent material (Bodí et al. 2014). The sources of ash, although varying by ecosystem, are typically dominated by fine surface fuels, including

duff layers and litter, as well as freed detritus from trees and surficial understory vegetation. Following a wildfire, much of what is most readily entrained and mobilized by overland runoff after a storm event is ash. The production and persistence of ash in a watershed landscape can have long-term water quality impacts especially when compounded by post-fire forest conditions including reduced soil infiltration (Neary, Gottfried, and Ffolliott 2003; Doerr, Shakesby, and MacDonald 2006), soil matrix instability due to vegetative loss, and enhancement of runoff transport capacity to move material. The composite nature of ash presents a unique challenge when trying to quantify the impacts of post-fire material on water quality, as constituent solubility of charred plant material versus charred soil material are innately different.

## 1.3 Wildfire impacts on water quality

Wildfire is of particular concern for water managers due to the widespread susceptibility of forested catchments to fire, which often serve as imperative sources of potable water to communities around the globe (Smith et al. 2011; Martin 2016). Several potential water quality concerns are brought about from post-fire watershed conditions. Following a wildfire, ash that is mobilized into surface water systems can increase stream and lake concentrations of nutrients, trace elements, and total suspended solids for which the implications for drinking water quality impairment can be great (Smith et al. 2011). Currently, no standards for ash characterization exist, and it is almost impossible to determine the proportions of constituents contributed by plant material or soil material after the ash and incorporated soil are eroded and transported. Profiling the dissolvable constituents brought on by ash deposition into streamflow and waterbodies is difficult to assess due to the variability in ash composition, which is controlled by the degree of combustion, vegetation type, part of the vegetation that was impacted, climate, soil type, and climate conditions. Notwithstanding, there have been many field reports of elevated concentrations of trace elements (Fe, Mn, Al, Pb, Zn, etc.), various ions including Na<sup>+</sup>, NH3/NH4<sup>+</sup>, NO3<sup>-</sup>, and

SO<sub>4</sub><sup>2-</sup>, and dissolved organic carbon both immediately after the fire and for months and years following (Rhoades, Entwistle, and Butler 2011).

One of the most frequently reported constituents befalling fire-impacted watersheds is suspended sediment loads in streams and reservoirs (Silins et al. 2009; Lane, Sheridan, and Noske 2006; Ryan, Dwire, and Dixon 2011, Chessman, 1986). Expanded upon and defined by the Environmental Protection Agency (EPA) as suspended and bedded sediments (SABS), the impact of elevated suspended solids in an aquatic system has consequences for water treatment efficacy and act as a major stressor to aquatic ecosystems. From a water quality and treatment perspective, elevated SABS can obstruct the detection of viral and bacterial species (Templeton, Andrews, and Hofmann 2008), support outbreaks of microbial blooms due to heightened nutrient adsorption to sediment, and substantially raise water treatment cost and lower treatment efficacy, and reduce the capacity of reservoirs.

Trace element contamination of streams and reservoirs can be problematic for aesthetic and public health reasons. Although post-fire concentrations of many trace elements are illdocumented, some cases caused serious water quality issues. Ambient concentrations of Fe and Mn became elevated by factors of 3 and 5 times respectively in Bendora reservoir in SE Australia (White et al. 2015) and were compounded by an additional release from lakebed sediments, which was trigged by a heightened water temperature. Continued exceedances of Fe have also been reported up to 6 weeks after a wildfire, in some cases surpassing World Health Organization (WHO) guidelines by 100 times (Smith et al. 2011). After the Cerro Grande wildfire in 2000, 40 ephemeral streams were sampled and analyzed for a large range of water quality parameters, including trace elements (Gallaher et al. 2002). Iron, Mn, and Zn were found to exceed WHO guidelines by 1870, 255, and 1.2 times, respectively. Cation, such as Ca, Mg, and K, and anion concentrations have also been reported to increase in magnitude beyond baseline responses during discharge following the Hayman Fire in Colorado both immediately and up to 4 months after the event (Rhoades, Entwistle, and Butler 2011). There is certainly a scarcity in information regarding the prevalence of elevated trace element stream and lake concentrations following a wildfire event and what information does exist is difficult to compare due to differences in sampling duration, technique, and location (Murphy et al. 2015). However, further investigation is warranted.

Nutrients are typically delivered to water bodies via overland flow and have been reported to increase N and P levels between 5 and 60 times background levels following a wildfire (Spencer and Hauer 1991). Elevated exports of nutrients can cause issues for managers of water supply catchments because N and P are limiting nutrients for the proliferation of aquatic flora and cyanobacterial communities. Eutrophication sets the stage for algal blooms, which can stress the functionality of aquatic ecosystems through anoxia and trigger taste, odor, and color issues in finished water (Drewry 2006). Rarely have reports of elevated species of inorganic nitrogen, like  $NO_x$  and  $NH_3/NH_4^+$ , exceeded guidelines for drinking water; however, they often exceed guidelines for aquatic health by up to 1640 times in both tributaries of subalpine coniferous catchments and in lakes and reservoirs (Bladon et al. 2008; Chessman 1986; Leak et al. 2003). Elevated stream and reservoir levels of bulk nutrients, both total nitrogen (TN) and total phosphorous (TP), have been reported in multiple studies representing a 0.3 to 431-fold increased from baseline levels (Smith et al. 2011). Cases where enhanced exports of nutrients reach reservoirs can be problematic for water managers in the form of eutrophication-induced algal blooms leading to decreased consumer confidence from subsequent taste and odor issues. Postwildfire rain events can also facilitate an elevated export of organic nitrogen.

Although not explicitly regulated, dissolved organic matter (DOM) is also of concern due to its role in the potential formation of carbonaceous and nitrogenous disinfection byproducts (N-DBPs) upon chlorination of finished water. Disinfection Byproducts (DBPs) arise from the reactions between DOM in raw water and commonly used disinfectants such as chlorine and chloramines. Since the discovery of trihalomethanes (THMs) in 1974, over 60 epidemiological studies have associated adverse reproductive outcomes, colon and rectal cancers, and urinary bladder cancer with DBPs via either dermal contact or inhalation (Hrudey 2009; EPA 2006; Richardson, 2007). Among the most commonly-formed halogenated DBPs, THMs and haloacetic acids (HAAs) are currently regulated at by United States EPA at 80 and 60 µg/L, respectively (EPA 2006). Furthermore, the formation of nitrogenous DBPs (N-DBPs) from dissolved organic nitrogen (DON) is of increasing interest as N-DBPs are several orders of magnitude more carcinogenic, cytotoxic, and genotoxic than the regulated THMs and HAAs and thus may pose greater health concern over long-term exposure (Shah 2011; Plewa 2008)). Although background watershed sources of DOM impedes an understanding in how wildfire-induced changes to DOM contributes directly increased N-DBP formation potential, bench scale experiments suggest elevated concentrations of four haloacetonitriles (HAN4) and chloropicrin from extracts of heatimpacted soils (Hohner et al. 2016; Cawley et al. 2017). Concerns about an increased export of dissolved organic carbon (DOC) following a wildfire are mirrored by those presented by DON due to the formation potential of regulated carbon-containing DBPs. While enhanced DOC exports are typically an acute watershed response associated with post-fire rainfall/discharge events (Murphy et al. 2015; Writer et al. 2014), they can cause complications for water treatment facilities that do not have the resources to appropriately respond to acute anomalies from incoming water sources. While scarce, likely due to the absence of DOC as a regulated water quality parameter in source waters, reports of elevated post-fire DOC exports exist (Hohner et al. 2016), ranging from 2 to 4 times the baseline TOC stream levels, which represents concentrations well beyond those that affect water treatment (Murphy et al. 2015). And while the magnitude of DOC exports can correlate with higher yields of DBPs, the quality of DOC also plays a significant role in the

reactivity of fire-impacted DBP precursors. Some field studies have touched on the prevalence of DBP precursor reactivity. Elevated DBP yields following wildfires burning as little as 10% of the Cash la Poudre watershed suggest that material flushed into waterways contributed significantly to DBP precursor material (Writer et al. 2014). The complexity of the system compounded by the difficulty of profiling a complex perturbation like wildfire makes it very hard to directly correlate DBP formation with enhanced quantity and shifts in quality of fire-impacted DOC. As a result, these investigations lend themselves more readily to bench-scale experiments. Hohner et al. (2017) investigated DBP yields from sediments of the Cache la Poudre catchment after the High Park wildfire, revealing elevated TTHM and HAA5 formation from treated water (Hohner et al. 2017). Understanding the implications of wildfires for enhanced and more extensive production of DBPs is pressing in order to then understand how the impacts can be properly mitigated. Studies from Hohner et al. (2017) suggest that something as simple as a higher coagulant dose can help to fully mitigate these challenges.

Forest fires can severely alter several components of forest biomass, including vegetation, fallen litter, organic matter, soil, etc., that facilitate the movement and storage of water in forested catchments. Therefore, water quality is inextricably impacted by the post-fire landscape. Previous work has demonstrated increases in DOC and nutrients on a basin-scale (Hohner et al. 2016; Writer 2012; Jardine, Wilson, and McCarthy 1990; Revchuk and Suffet 2014). Notwithstanding, to fully understand the mobility of DOM and potential contaminants on a watershed scale, a fundamental understanding of processes that drive their mobility must be established. While studies on soil have established pivotal shifts in the chemical structure of SOM due to heating that lead to enhanced carbon and nitrogen release (Santos, Russell, and Berhe 2016; Cawley et al. 2017), this thesis adds to the growing knowledge by including the contribution of litter to the discussion.

#### 1.4 Research objectives

Watershed-scale constituent exports are highly variable between studies, as are export estimates following wildfire events. It is evident that the complexity of this system is confounded by several processes operating simultaneously on a heterogeneous mix of forest materials. There is a necessity for a clear and fundamental study regarding the capacity for litter and soil that are wildfire-impacted to release ecology-altering and water quality-threatening constituents into the environment. The innate complexity of the system and differing techniques in sampling designation and regimes makes it difficult to deconstruct what processes are at play. This research introduces a highly controlled, systematic, and deconstructed study to attempt to decouple the impacts of heat-impacted litter and soil on water quality separately.

The purpose of this study is to examine the impacts of burn temperature on the emergence of water quality parameters that may be of concern. Specifically, the objectives are to:

- Investigate changes in solubility of dissolved constituents originating from forest floor material, namely soil and plant matter, as a function of fire severity parameterized by maximum temperature reached.
- 2. Compare dissolution behavior between soil and plant matter as a function of fire severity parameterized by maximum temperature reached.
- 3. Compare resulting water quality parameter changes from lab-simulated wildfire through heating to those resulting from field-based, prescribed wildfire events in Spain and Australia.

Results of this analysis will contribute to the growing understanding regarding the impacts of wildfires on water quality in general, help identify major contributors (soil or litter) to water quality risk based on fire severity, and softly assess the applicability and context of lab-simulated heating experiments.

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## 2 Materials and Methods

Soil and litter samples were collected in the Colorado Front Range at three locations in the Boulder Creek Watershed, which encompasses 6 major cities. Materials were dried and heated to five temperatures using a muffle furnace. Changes in the properties of the heated material were assessed, including total C and total N. Heated material was then leached in ultra-pure water and the resulting leachates were analyzed for the following parameters: DOC, DON, dissolved inorganic nitrogen (DIN), water extractable organic carbon and organic nitrogen (WEOC and WEON), soluble bio- and lithogenic elements, and SUVA254. Three soil replicate samples were collected at three different geographical locations within the Colorado Front Range, totaling nine samples. One composite litter sample was collected at each location, totaling three samples. A general research flow chart can be visualized by Figure 2-1.

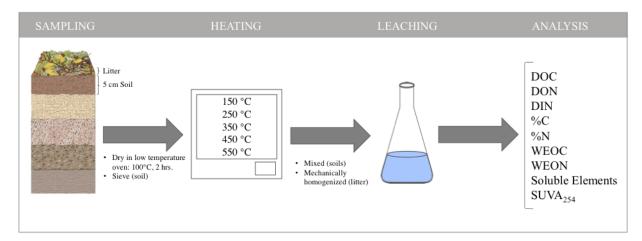


Figure 2-1: Research flow chart.

Ash and soil samples from a prescribed fire in SE Australia were supplied by Dr. Cristina Santín from Swansea University. Data for total C and total N, and temperature profiling were analyzed and provided by Santín's lab while all other analyses of parameters listed above were performed by our lab.

## 2.1 Site description

The Boulder Creek Watershed, located East of the Continental Divide within the Front Range of the Colorado Rocky Mountains, spans approximately 1160 square kilometers and comprises headwater regions that supply water for over 300,000 residents (U.S. Census Bureau, 2017). Elevations in the Boulder Creek Watershed range from 1480 meters to 4120 meters above sea level, encapsulating several climatic and vegetal zones including plains, foothills, montane, subalpine, and alpine (Murphy 2000). The watershed spans two physiographically distinct regions. The upper basin, described by steeply sloping valleys and mountainous terrain (Murphy 2000) is part of the Southern Rocky Mountain Province. The lower basin, described by gentle sloping terrain to the east, is encompassed by the Southern Rocky Mountain Province. The mountainous regions receive precipitation mainly in the form of snow in the winter and spring months; however this area also experiences episodic high-intensity convective storm events during summer months, which is one of the major drivers contributing to post-fire water quality impairment (Murphy et al. 2015). Summer convective storms are known to produce rainfall intensities greater than 10 mm h<sup>-</sup> <sup>1</sup>, eliciting substantial runoff responses in fire-impacted Colorado watersheds. Wildfire represents one of many factors that produce variation in water quality within the Boulder Creek Watershed and the increasing prevalence, size, and severity of fires are compelling reasons to gain more information about how they impact raw water sources.

## 2.2 Sampling

#### 2.2.1 Soil sampling

Sampling took place in a sub-basin of the South Platte River Watershed a sub-catchment of the greater Mississippi River Watershed, Boulder Creek Watershed (Figure 2-2).

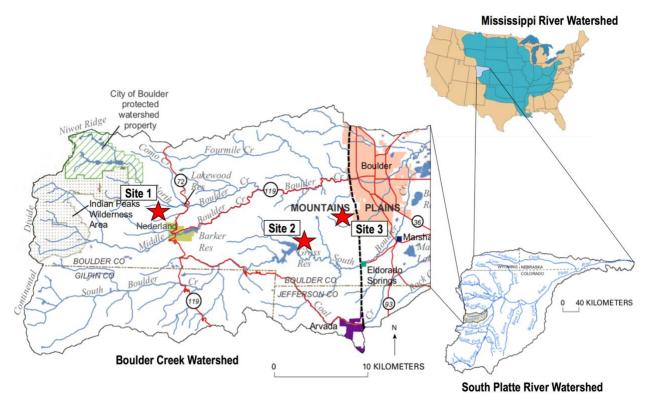


Figure 2-2: Sampling locations (indicated by red stars in the boulder Creek Watershed). Images from Murphy et al. 2006.

Sampling locations were chosen based on their proximity to one Denver-owned and one Boulderowned water storage reservoir. Three geographical locations are shown as red stars in Figure 2-2. Site 1 is located close to Lakewood Reservoir, which is one of two reservoirs that supply 40 percent of the city of Boulder's water supply and is diverted to Betasso Water Treatment Plant through the Lakewood Pipeline. Site 2 is proximal to Gross Reservoir, which serves as a combined storage and water regulating facility for water that flows under the continental divide and diverts water to the Denver Metropolitan area through Moffat Tunnel. Site 3 was chosen as an intermediate site representing an area of lower elevation. Sites 1 and 2 are located in the upper basin while Site 3 was meant to represent the lower basin. At the time of sampling in September 2016, Boulder, CO had a recorded mean monthly precipitation of 114 mm and a mean annual precipitation of 1724 cm in 2016 (NOAA). The mean monthly temperature was 18.3°C with a low of 6.1°C and a high of 27.3°C in September 2016 and a mean annual temperature of 11.1°C. Three soil subsamples were collected at each location to account for the considerable spatial heterogeneity of soil environments that occur over even small distances. Triplicate samples were taken within 10 m from one another from locations of varying canopy coverage. Soils A, B, and C were collected north of Nederland, Colorado (39°58'52"N 105°31'07"W, 39°58'52"N 105°31'05"W, 39°58"52'N 105°31'10"W; 2601 m elevation). This sampling area had no closed canopy with understory vegetation characterized by blue grama grass (*Bouteloua gracilis*), needle-and-thread grass (*Hesperostipa comate*), and western wheatgrass (*Pascopyrum smithii*). The Nederland soil series is moderately permeable and well-drained, characterized by a cobbly sandy loam.

Soils D, E, and F were collected near the summit of Flagstaff Mountain outside of Boulder, CO (39°59'51"N 105°18'33"W, 39°59'52"N 105°18'31"W, 39°59'53"N 105°18'32"W; 1849 m elevation). All three sampling replicates were taken under closed canopy, which was characterized by coniferous forest stands comprised of ponderosa pine, Douglas-fir, and subalpine fir-Engelmann spruce (*Picea engelmanni, Abies lasiocarpa*). There was no prominent understory vegetation; however, a layer of fallen litter consisting chiefly of pine needles was present and was removed prior to soil excavation.

Soils G, H, and I were collected south of Gross Reservoir in Boulder Country, Colorado (39°56'51.7"N 105°21'14.9"W, 39°56'51.7"N 105°21'14.2"W, 39°56'51.3"N 105°21'14.1"W; elevation 2,222 m). Soil G had no overstory canopy, Soil H had 30% canopy coverage, while Soil I had a closed canopy. The surrounding overhead vegetation varied in density comprising of four main coniferous tree species: ponderosa pine, lodgepole pine (*Pinus contorta*), limber pine, and Douglas-fir. Understory vegetation for the sampling area include a mix of grasses, forbs, and shrubs; largely dominated by cheatgrass (*Bromus* spp.) and Canada thistle (*Cirsium arvense*).

For the remainder of this document, Nederland, Flagstaff, and Gross Reservoir will be referred to as NED, FLG, and GROSS.

## 2.2.2 *Litter sampling*

Litter samples were obtained in December of 2017. Forest floor material, referred to as 'litter' here, is the uppermost layer of organic debris on the ground, including some vegetation, and is highly susceptible to consumption and combustion during a wildfire. Because understory vegetation litter was relatively spatially homogenous, one large composite sample was taken at each site. For NED, where there was minimal overhead canopy cover and the understory was dominated by grass that was still intact during the fall and winter months, litter sampling included some grass, pine needles, pine cones, and small twigs. Litter contents at both FLG and GROSS were relatively similar, comprised of mostly pine needles, pine cones, pollen cones, and small twigs.

## 2.2.3 Soil processing

All soil samples were processed immediately after sampling. Soils were distributed on metal trays to a depth of approximately 1 cm and oven-dried at 100°C for two hours to eliminate moisture and to suppress the survival of microbial communities present in the soil (Dunn, Barro, and Poth 1985) that may compromise sample integrity during storage and to avoid any impacts of antecedent soil moisture. Soil was then passed through both a 2 mm (No. 10) stainless steel sieve to remove large rocks and plant matter and through a 0.841mm (No. 20) sieve to remove smaller plant matter before storage.

## 2.2.4 Litter processing

All litter samples were also processed immediately after sampling. Drying took place similarly to that of the soil where litter was uniformly and of minimal density distributed over metal trays and dried for two hours at temperature of 100°C. The purpose of drying litter was twofold: first, to achieve an even level of dryness between litter materials to allow the material to later be heated as consistently as possible and second, to optimize sample integrity for storage.

#### 2.3 Heating process

The extensive variability associated with fire behavior during wildland fires exacerbates the complex changes that forest floor material undergoes because of such environmental perturbations. The range of temperatures chosen for this experiment is meant to encompass the thermally variant temperatures that topsoil may be exposed to during a wildfire, notwithstanding other metrics commonly used to characterize wildfire behavior or effects (i.e. fuel loads, flame length and flame front depth, burn duration, heat flux, ecological damage, etc.). Topsoil can experience temperatures between 50 and 700°C (Janzen and Tobin-Janzen 2008).

Soils were heated in an electric muffle to temperatures of 150, 250, 350, 450, and 550°C in 90-mL porcelain dish crucibles using a Lindberg/Blue Box Furnace Model BF51442C with a Lindberg Furnace Power Supply Controller Model 59344. Litter was heated to temperatures of 150, 250, 350, and 450°C in loaf pans using the same furnace. Results for 550 °C were excluded due to limited sample volume, as litter heated to this temperature had significant mass loss as well as anticipated negligible levels of mobilized carbon and nitrogen. For this experiment, CTRL/150°C, 250/350°C, and 450/550°C were considered to encompass three respective burn classes: Unburned/Low, Modern, and High severity.

All batches of samples were held at each temperature in aerobic conditions for 2 hours and once cooled, stored in either amber glass 40 mL vials (soils) or half-pint glass jars (litter) at room temperature. To ensure uniformity in soil heating, 10 g soil per crucible (approximately 0.5 cm high) was heated in batches of 10 crucibles. In-tact litter was loosely placed in the loaf pans to ensure uniform litter heating. After heating, the litter samples were mechanically ground using an

8150 Enclosed Shatterbox for 15 seconds, producing a fine powder (Figure 2-3) and immediately stored in sterilized mason jars.



Figure 2-3: Burned litter before (left) and after (right) mechanical homogenization for 15 seconds.

The purpose of grinding the litter material was to homogenize the samples, which maximized the reproducibility and visibility of trends resulting from leaching tests, which are driven by mass. Because litter parent material is so heterogeneous in both composition and density, homogenization was required.

## 2.4 Soil and litter leaching

Two experiments were conducted for sites A, B, D, and E (soils) and NED and GROSS (litter) to determine an optimal leaching duration and leaching concentration (solid-to-solution ratio) as well as to investigate the leaching capacity of forest floor material. A kinetics test was performed to determine an optimal leaching time for the subsequent experiments (Appendix III). Processed soil samples were leached in 100 mL of ultra-pure Milli-Q water separately for a contact time of 1, 2, 4, 6, 8, 10, 24 and 48 hours (DOC and total dissolved nitrogen (TDN) dissolution curves can be viewed in Figures III-4 and III-5) while being agitated on a VWR Standard Analog Shaker table. A fixed concentration of 5 g soil/L water was used throughout all the kinetics experiments so that both the DOC and TDN concentrations at the end of the reaction would not exceed the maximum detection thresholds of the total carbon and nitrogen analyzer. Processed

litter samples were leached in the same way; however, contact times were 1, 2, 4, 6, 8, and 24 hours and a fixed concentration of 2 g litter/L water was used (Figures III-1, III-2, III-3). The linearity of solubility behavior was tested to ensure appropriate scaling in which 0.1, 0.25, 0.5, 1.0, 2.5, 5.0, 10, and 15 g of each soil and 0.1, 0.25, 0.5, 1.0, 2.5 and 5.0 g of litter was leached separately under the same conditions as the kinetics test at a fixed contact time of 6 hours. All data and plots for linearity and kinetics can be seen in Appendix III.

All leachates were passed through a 25-mm, 0.45-micron Whatman Puradisc Polyethersulfone syringe filter. Each filter was prewashed with 500 mL of Milli-Q water and field rinsed with 100 mL of leachate solution in order to saturate adsorption sites on the filter and avoid potential loss of dissolved organic matter through filtration (Karanfil, Erdogan, and Schlautman 2003). Leachates were filtered directly into 20-mL glass vials for immediate analysis. The same leaching procedure was then scaled up, using a soil mass of 5.0 g of soil or 0.2 g of homogenized litter material leached in 1 L of ultra-pure Milli-Q water. These masses were chosen based on targeted DOC and TDN concentrations, which reflect commonly observed levels in surface waters. Because a larger volume of leachate was being filtered, large scale filtration was done through a 47-mm, 0.50-micron EMD Millipore Express PLUS Membrane disc filter using a pre-washed glass vacuum filtration apparatus. The discrepancy in filter pore size was accepted in order to keep the filtration material constant, as it was not possible to acquire this size filter in a 0.45-micron pore size. Leachates for these experiments were stored at 4°C in 1-L amber Wheaton bottles. All containers used for any experiments and storage had been Liquinox-soaked, acid washed, and prefurnaced to prevent contamination.

## 2.5 Analyses of leachates

#### 2.5.1 Elemental Analysis

Carbon and nitrogen fractions in the soil were determined using a Thermo Scientific Flash EA1112 Nitrogen and Carbon Analyzer, which employs the Flash Dynamic Combustion method. These analyses were done in replicates of two. Total carbon percentage was assumed to be total organic carbon content. These data were reported in two ways. First, as percent organic carbon (OC) or organic nitrogen remaining as a function of heating temperature using the following equation:

%OC or %ON Remaining = 
$$\frac{\left[1000 \text{ mg}_{\text{solid}, T} \times \left(1-\%M_{\text{loss}, T}\right) \times \%OC_{T} \text{ or } \%ON_{T}\right]}{1000 \text{ mg}_{\text{solid}}} \times 100 \quad (1)$$

where  $mg_{solid,T}$  is a theoretical mass of the starting material at temperature, T,  $\% M_{loss,T}$  is the percent mass loss due to heating at temperature, T, calculated using the difference between the original sample mass and the sample mass after burning, and the  $\% OC_T$  or  $\% ON_T$  is the carbon or nitrogen content at temperature, T. This equation allowed for a successive tracking of OC or ON degradation as a function of heating temperature.

The second way the data was reported is a direct output of the CHN analyzer, which is a percent value of carbon or nitrogen content within the solid material (%OC<sub>T</sub> or %ON<sub>T</sub>). This parameter is an intrinsic value to the material being analyzed and does not take into consideration the mass loss at each successive temperature step.

### 2.5.2 Dissolved organic carbon and total dissolved nitrogen

Both DOC and TDN concentrations in the resulting leachates were determined using a Shimadzu TOC-V CSN Total Organic Carbon Analyzer with a TN unit in replicates of four. DOC was determined as non-purgeable organic carbon (NPOC), detected as CO<sub>2</sub> by a nondispersive

infrared detector (NDIR). TraceMetal<sup>TM</sup> Grade hydrochloric acid was used as used as the purging agent, which was added to each sample manually.

#### 2.5.3 DON Calculation

DON was calculated by subtraction of DIN from TDN using the following equations:

$$DON = TDN - DIN$$
(2)

$$DIN = (NO_{2}^{-}N) + (NO_{3}^{-}N) + (NH_{3}^{+}N)$$
(3)

Nitrate and nitrite were measured together using a Lachat QuikChem 8500 Flow Injection Module where nitrate is quantified as reduced nitrite by passage through a copperized cadmium column. Nitrite (reduced nitrate plus pre-existing nitrite) was then quantified calorimetrically (Arikaree Environmental Laboratory, INSTAAR, CU Boulder). Nitrate was then back-calculated through subtraction of nitrite values. Ammonium was measured calorimetrically using a BioTek Synergy 2 Multi-Detection Microplate Reader (Arikaree Environmental Laboratory, INSTAAR, CU Boulder). Both analyses were done in replicates of four.

## 2.5.4 Fraction of water extractable carbon and nitrogen

With both total carbon and nitrogen compositions in the soil and total dissolved concentrations of carbon and nitrogen characterized for each soil, the respective fractions of water extractable organic carbon and organic nitrogen (WEOC and WEON) SOM were calculated using the following equation:

WEOC or WEON = 
$$\frac{\text{DOC}_{\text{T}} \text{ or } \text{DON}_{\text{T}} (\text{mg } \text{L}^{-1}) \times \text{V}_{\text{leachate}} (\text{L})}{\text{M}_{\text{solid leached}} (\text{mg}) \times \% \text{OC}_{\text{T}} \text{ or } \% \text{ON}_{\text{T}}}$$
(4)

where  $DOC_T$  and  $DON_T$  are the leachate OC and ON concentrations resulting from the solid burned at temperature, T, V<sub>leachate</sub> is the leaching volume, M<sub>solid leached</sub> is the mass of either soil or litter that was leached, and %OC<sub>T</sub> or %ON<sub>T</sub> is the carbon or nitrogen content at temperature, T.

## 2.5.5 Soluble elements

All soluble element concentrations were determined using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Thermo Finnigan Element2 magnetic sector inductively-coupled plasma mass spectrometer by Fredrick Luiszer at the Laboratory for Environmental and Geological Sciences (LEGS), CU Boulder. Soil and litter leachate samples were prepared in replicates of 4 for soil and 2 for litter and acidified (pH < 1.5) using TraceMetal<sup>TM</sup> Grade nitric acid before analysis. This analysis was conducted for soil samples from NED and FLG and for litter samples from all sites.

## 2.5.6 Specific absorbance at 254 nm (SUVA<sub>254</sub>)

Without employing more specific analytical techniques, molecular-level and functional transformations that SOM may have undergone cannot be defined in this study; however, the specific absorbance at 254 nm (SUVA<sub>254</sub>) can act as a surrogate for defining specific bonding arrangements in the samples. Studies have long established correlations between SUVA<sub>254</sub> and aromatic carbon content determined by liquid state <sup>13</sup>C Nuclear Magnetic Resonance (NMR) (Weishaar et al. 2003; Traina et al. 1990; Chin et al. 1994) for typical DOC in whole water samples. SUVA<sub>254</sub> is calculated by dividing UV absorbance at 254 nm (m<sup>-1</sup>) by DOC (mgc L<sup>-1</sup>) using the following equation:

$$SUVA_{254} = \frac{UV_{254}(m^{-1})}{DOC (mg_C L^{-1})}$$
(5)

UV-Vis absorbance was measured using a UV-vis spectrophotometer (Cary 100, Agilent Technologies) using a 1-cm path length quartz cuvette for temperatures up to 350°C and a 5-cm path length quartz cuvette for 450°C and 550°C from 200-800 nm. Sample replicates of two and instrumental replicates of three were used.

## 2.5.7 Statistical Analysis

Statistical analysis was conducted using the open source programming language, R. All values are reported as the arithmetic mean of 4 replicates  $\pm$  one standard deviation, unless otherwise indicated. For calculated parameters, standard deviation is represented as a propagated error using the following equation

Addition or subtraction:

$$Q = a + b + \dots + c - (x + y + \dots + z)$$
(6a)

$$\delta Q = \sqrt{(\delta a)^2 + (\delta b)^2 + \dots + (\delta c)^2 + (\delta x)^2 + (\delta y)^2 + \dots + (\delta z)^2}$$
(6b)

Multiplication or division:

$$Q = \frac{ab\cdots c}{xy\cdots z}$$
(7a)

$$\delta Q = |Q| \sqrt{\left(\frac{\delta a}{a}\right)^2 + \left(\frac{\delta b}{b}\right)^2 + \dots + \left(\frac{\delta c}{c}\right)^2 + \left(\frac{\delta x}{x}\right)^2 + \left(\frac{\delta y}{y}\right)^2 + \dots + \left(\frac{\delta z}{z}\right)^2}$$
(7b)

where a, b, c, ... are measured quantities with uncertainties  $\delta a$ ,  $\delta b$ ,  $\delta c$ , ... and Q is the calculated parameter.

Statistically significant differences between heating temperature and sites were assessed using a 2-tailed, 2-sample *t*-test with a Satterthwaite approximation of degrees of freedom. Each parameter was compared for each temperature to the control (e.g. CTRL-150, CTRL-250, CTRL-350, CTRL-450, CTRL-550). The linearity of desorption behavior for increasing soil leaching concentrations were established by linear regression.

### 3 Results

This section outlines the results from analyses on both soil and litter. Because soil was subsampled in triplicate, all figures depicting results from soil leachates represent an average of three subsamples at each site, i.e. results from subsamples A, B, C were averaged to represent NED; results from subsamples D, E, F were averaged to represent FLG, etc. Due to the inherent and vast spatial heterogeneity of the soil matrix, even over small distances, error bars for averaged soil data are relatively large. However, the trends among each subsample are consistent. All discretized data for all parameters can be found in Appendix I while plots showing data between subsamples can be found in Appendix IV.

## 3.1 Carbon and nitrogen content

The top panels of Figure 3-1 and Figure 3-2 show total carbon and nitrogen content as percentages.

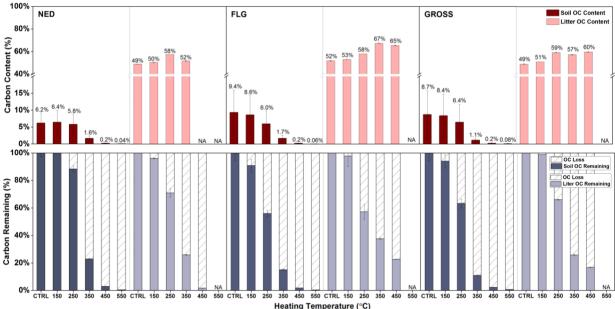


Figure 3-1: Thermal impacts on carbon content. Upper panel is carbon content of soil (left) and litter (right). Lower panel is carbon remaining as a function of temperature for soil (left) and litter (right).

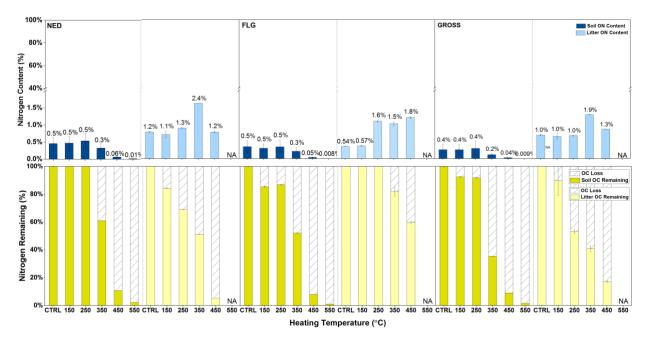


Figure 3-2: Thermal impacts on nitrogen content. Upper panel is organic nitrogen content of soil (left) and litter (right). Lower panel is organic nitrogen remaining as a function of temperature for soil (left) and litter (right).

Carbon and nitrogen remaining from initial carbon and nitrogen percentage for both soil and litter can be visualized on the bottom panels of Figure 3-1 and Figure 3-2. This parameter was calculated

by tracking the progressive carbon or nitrogen loss as a function of temperature. This representation, which accounts for mass loss during burning, is often more intuitive.

Results show average carbon and nitrogen composition in sampled soils to be 6.2 - 9.4% and 0.4 - 0.5% respectively for all three samples. For litter, typical carbon and nitrogen compositions were much higher than for soil (48.8 - 67.8% and 0.5 - 1.2% respectively). In contrast to soil, whose carbon and nitrogen contents are derived from degraded plant material, microbial necromass, and microbial metabolites that are adhered to the mineral surface, the backbone of litter plant material is comprised of carbonaceous biomacromolecules and can therefore be reduced into condensed forms of carbon- and nitrogen content results, shown in the upper panels of Figure 3-1 and Figure 3-2, where there is no observed degradation of carbon and nitrogen content. Instead, for both the carbon and nitrogen content of litter, percentages remain stable and even increase in the case of FLG and GROSS.

All soils experienced complete loss of organic carbon, beginning at a nearly zero loss for CTRL to below detection limit at 550°C. At 250°C, soils from all three sites lost about 30 - 40% of organic carbon. At 350°C, all soils experienced an 80% organic carbon loss with an almost-complete loss (>95%) at higher temperatures. A similar trend was observed for carbon remaining in litter material for temperatures up to 250°C, showing only a 1 - 4% loss at 150°C and a 30 - 40% loss at 250°C. Above 350°C, litter organic carbon proved to be more thermally resistant than that of soil, with consistently lower carbon loss at 350°C (twice as little loss than that of soil) and 450°C (about ten times as little loss than that of soil) for the FLG and GROSS. For NED, carbon loss was only slightly less (by 1%) at 350°C and the same for 450°C.

Generally, soil organic nitrogen proved to be more thermally resistant than organic carbon at moderate and high temperatures. While soils experienced a similar carbon loss trend at 250°C (0 to 15% loss), soils heated to 350°C only experienced a 40 to 60% loss. At 450°C, 90% of soil nitrogen was lost and a near 100% loss was observed at 550°C. Litter-derived organic nitrogen for NED and GROSS experienced a step-wise loss starting from a 10 - 15% loss at 150°C and ending in an 85 - 95% loss. FLG litter behaved slightly differently, experiencing much less nitrogen loss than the other two sites. Nitrogen depletion began at a higher temperature, 350°C, with an 80% total loss. The highest temperature burned for litter, 450°C, yielded only a 40% loss of organic nitrogen.

In general, carbon content data indicates that the material becomes more carbon-rich with increasing temperature. The marked increase of C content in litter after 150°C could be the result of a loss of readily-combusted functional groups with a simultaneous mineralization into aromatic carbon (Knicker et al. 1996). A loss of mass from readily-volatilized functional groups at temperatures above 150°C (the temperature at which lignin and hemicellulose begin to degrade (Knicker 2007)) coupled with a concurrent preservation of aromatic structures that typically do not suffer C-loss and carbohydrate conversion into additional cyclic compounds will result in a higher carbon content by mass for higher temperatures. This supports the classical observation that alkyl carbon is more thermally vulnerable than aromatic material (van Krevelen, 1950). As heating temperature progressively increases, polymolecular units are exposed to continual reordering.

For N content in litter, a similar concept can be applied; however bio macromolecular amide functional groups have been proven to be very stable and resistant toward thermal degradation compared to carbonaceous functional groups (Knicker et al. 1996). Additionally, the simultaneous condensation process that produces heterocyclic nitrogen compounds could explain the near two-fold increase of nitrogen content between CTRL and 350°C for all sites. Remaining carbon and nitrogen (bottom panel, Figures 3-1 and 3-2), where carbon and nitrogen content is normalized by the loss of mass of the bulk material, successively decreases with increasing

temperature. Litter displayed less loss for both carbon and nitrogen than soil at higher temperatures. This is likely due to differences between the carbon-based structure of plant material throughout compared to soil-bound organic matter, which is adhered to a mineral surface. The rate at which the two thermally degrade is likely different.

Both litter derived organic material and SOM experience very little impact at temperatures below 200°C (Araya, Fogel, and Berhe 2017; Knicker et al. 1996), which could explain the similar behavior at 150°C and 250°C. At higher temperatures, the behavior of SOM and litter organic matter begin to diverge, where SOM experiences significant charring and much of the nutrients are volatilized (Araya, Fogel, and Berhe 2017) and lignocellulose becomes condensed and more C and N enriched.

## 3.2 Dissolved organic carbon

Dissolution of organic carbon from soil showed nearly the same trend between site subsamples (Figure 3-3), and consequently between averaged sites (Figure 3-4) with DOC increasing to reach a maximum at 250°C and subsequently decreasing rapidly.

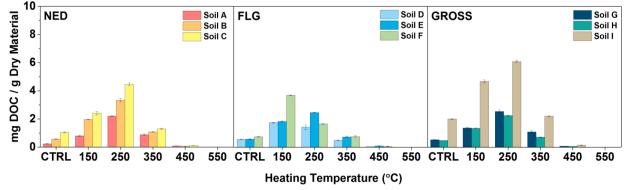


Figure 3-3: Discretized DOC data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 standard deviation (n=3).

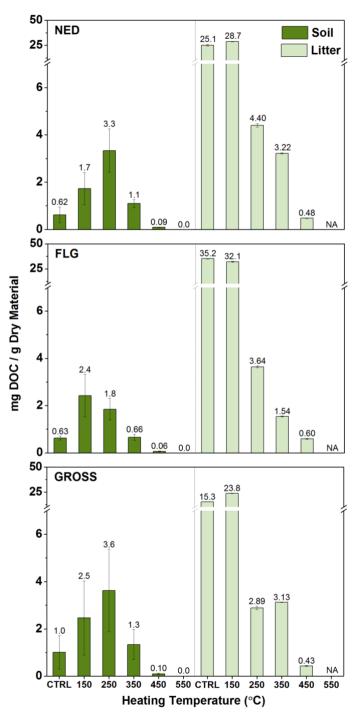


Figure 3-4: DOC concentration with heating for soil (left) and litter (right). Error bars for soil represent a site-averaged standard deviation where n=12 i.e. four sample replicates of three spatial replicates. For litter, error bars represent one standard deviation (n=4).

FLG was the exception, whose average peak came at 150°C instead of 250°C with a two-fold increase from soil heated to 150°C compared to the control. Two FLG subsamples D followed this

same trend while subsamples D and E reached a maximum at 150°C, skewing the site average. For NED and GROSS, averaged DOC increased 3-fold for soils heated to 250°C compared to the CTRL soil. There was at least a 2.5-fold increase of DOC originating from soil alone at this temperature point.

DOC concentrations for litter far exceeded that of soil by nearly one order of magnitude in all sampling sites. DOC originating from litter also had consistent trends between all three sites, showing relatively high DOC concentrations  $(15 - 35 \text{ mgc L}^{-1})$  for litter heated up to 150°C and a subsequent, sharp, and step-wise decrease with increasing burn temperatures to levels below 1 mgc L<sup>-1</sup>. At the 250°C threshold, there was a DOC decrease between 7 - 10 times less than that of the CTRL and 150°C.

In general, organic carbon originating from litter contributes successively less DOC with increasing maximum burn temperature while soil contributes more DOC up to a moderate maximum burn temperature (350°C) and subsequently decreases at higher temperatures.

## 3.3 Total dissolved nitrogen and nitrogen speciation

Discretized data for TDN had far clearer and universal trends between subsamples for all sites. Plots can be reviewed in Appendix V, Figure V-3. TDN profiles for soil and litter looked very similar to the DOC profiles, with a clear peak for soils that had been heated to 250°C and a sharp decrease after 150°C for litter (Figure 3-5).

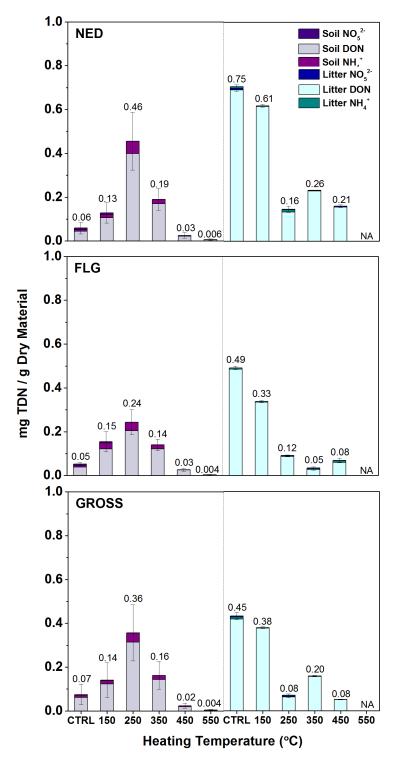


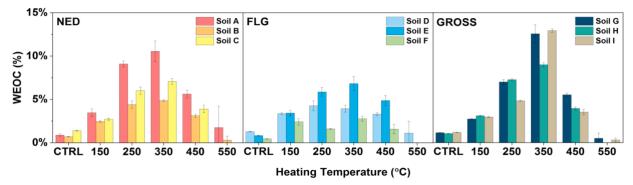
Figure 3-5: Nitrogen speciation for heated soil (left) and litter (right) leachates. Error bars for soil represent the average of the calculated error propagation of each nitrogen species, each having one standard deviation where n=4. Error bars for litter represents the calculated error propagation of each nitrogen species, which are represent one standard deviation with n=2 for nitrate/nitrite and n=4 for ammonium. Discretized soil and litter TDN data are available in Appendix I and Appendix II.

Soil leachates from 250°C yielded 4.5 - 7.5 times more TDN than leachates from CTRL while litter leachates from 250°C yielded 4 - 4.5 times less TDN than leachates from CTRL. Unlike DOC, there was no marked discrepancy between soil and litter for TDN throughout the entire temperature range. While the profiles or trends looked similar to those observed for DOC, the magnitude of release of DON was much smaller and more comparable between the two materials. They both yielded between 0 and 1 mg<sub>N</sub> L<sup>-1</sup>.

For both soil and litter, the majority of TDN was comprised of organic nitrogen. No other inorganic nitrogen species (NO<sub>5</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) showed statistically significant change from the CTRL leachate for either material, except for ammonium for soil samples. Ammonium increased 4 - 7 times for leachates of soil heated to 250°C for NED, FLG, and GROSS. Soil and litter nitrate/nitrate levels were almost negligible.

## 3.4 WEOC/WEON

The solubility of soil organic carbon (SOC) significantly increased with increasing burn temperature up to 350°C for most sites. Trends for WEOC in soil subsamples, shown in Figure 3-6, demonstrate a near-universal maximum solubility of organic carbon occurring at 350°C.





Exceptions include subsamples D and F (middle panel of Figure 3-6), which did not show statistically significant differences between 150°C, 250°C, and 350°C; however, WEOC did increase significantly compared to CTRL upon heating.

On average, maximum carbon solubility was reached at a burn temperature of 350°C (between 4.5% and 11.5%) across all samples (Figure 3-8), which was approximately one order of magnitude higher than the solubility of thermally unaltered SOC from unburnt soils (ranging from 5.3 to 10.5 times higher than CTRL).

Similarly, soil heating led to the solubility of soil organic nitrogen (SON), which is plotted in Figure 3-7, to increase compared to CTRL.

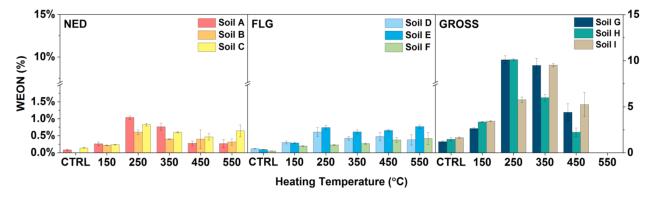


Figure 3-7: Discretized WEOC data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent propagated error between TDN (n=3) and %C (n=2).

NED subsamples (A, B, and C) observed a maximum in SON solubility (between 3.75 and 10 times WEON of CTRL) at a slightly lower temperature than for SOC at 250°C (Figure 3-6). Subsamples for FLG and GROSS varied slightly. Although a statistically significant increase was observed upon heating for D, E, and F (Figure 3-7; middle panel) SON solubilities peaked at 250°C and remained steady and temperatures above that. Subsamples from GROSS peaked at either 250°C or 350°C (250°C for G and H and 350°C for I); however, maximums represented nearly 10-fold increases in the fraction of solubilized SON between samples heated to either 250°C or 350°C and CTRL.

Site-averaged soil carbon and nitrogen solubility data juxtaposed with that of litter is shown in Figure 3-8.

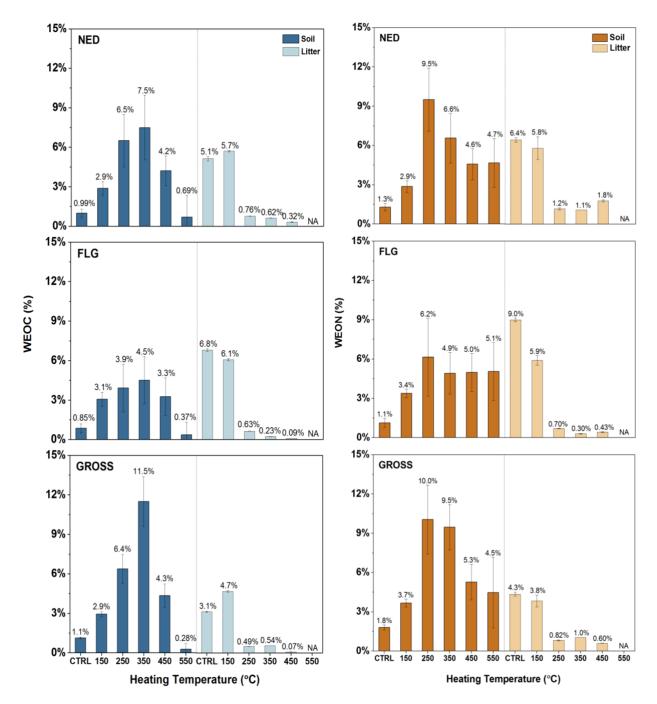


Figure 3-8: Water extractable carbon (blue) and nitrogen (orange) where error is represented by propagated error between C/N (n=2) and DOC/DON (n=3,4). Soil results are on the left panel (darker color) and litter results are on the right panel (lighter color). Litter error is represented by one standard deviation (n=4).

In general, the highest solubility was observed at relatively lower burn temperature (i.e., 250°C) compared to SOC; however, solubilities were higher on average for each respective temperature and experienced a slightly smaller range of change in solubility between peak solubilities and

CTRL. Solubilities from soil heated to 250°C ranged from 5.5 to 7.5 times higher than from CTRL samples. This suggests that heat-impacted SOM, in general, is much more water soluble than organic matter that is originally present in soils, which may be one of the reasons that enhanced DOC and TDN mobility following some wildfires has been observed.

The solubility of litter-derived carbon remained relatively stable for CTRL and 150°C (between 3.1 and 5.7%) until a sharp decrease (<1%) at 250°C. This is likely due to the condensation of plant-derived carbon into a more aromatic-rich structure at temperatures higher than 150°C (Knicker 2007). This trend indicates that litter-derived nitrogen from non-impacted plant material is much higher than the solubility of thermally-altered litter. Nitrogen solubility from unheated litter was slightly (~1%) higher compared to that of soil and then subsequently shows a similar trend with a sharp drop from 3 to 5% within the temperature range of 150 to 250°C. Litter WEON was much lower than soil WEON for temperatures above 250°C.

## 3.5 Soluble elements

Results for NED are shown below in Figure 3-9 and soluble elements for materials from FLG can be found in Appendix VII, Figure VII-5.

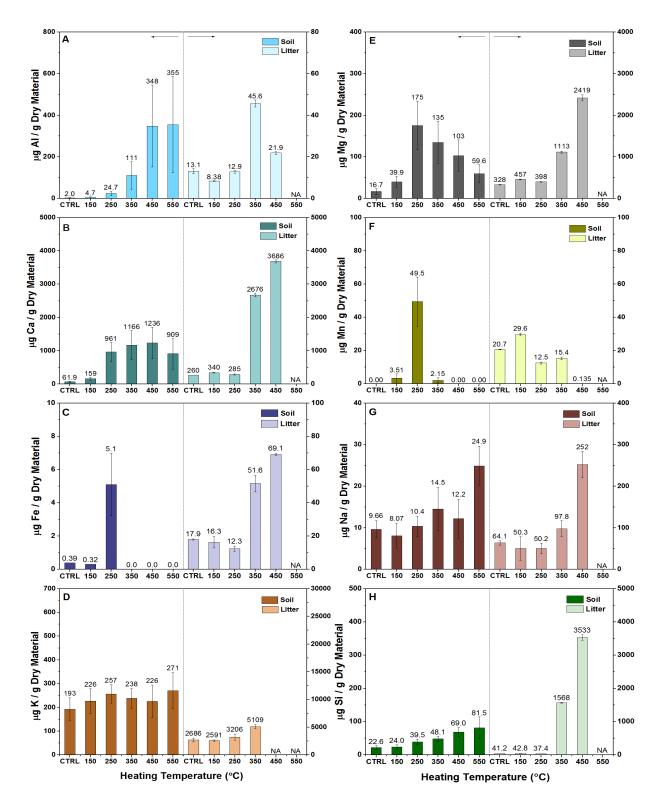


Figure 3-9: Water soluble elements for soil (left panel) and litter (right panel) for NED. Values for soil are represented by the average of each site for each respective temperature (n=3) and the average of their standard deviations. Litter values represent the average of two analytical duplicates and two sample duplicates (n=4) with one standard deviation.

Discretized data for soil subsamples A, B, and C (NED) and D, E, F (FLG) are plotted in Appendix VI, Figures VI-1 and VI-2. Data itself can be seen in Appendix I. All but two soluble element species differed by orders of magnitude in concentration and by trend with respect to temperature between soil and litter.

- Al Soil exhibited a much higher (10x) release than litter, with the highest concentrations occurring at higher temperatures (nearly 350 μg g<sup>-1</sup><sub>Dry Material</sub> at 450°C and 550°C). Litter released a maximum of 45.6 μg g<sup>-1</sup><sub>Dry Material</sub> at 350°C.
- Ca There was a 30-fold release of Ca from litter at 450°C compared to the maximum release of soil, which also occurred at 450°C. Ca became mobile in litter starting at 350°C (2676 μg g<sup>-1</sup><sub>Dry Material</sub>) whereas Ca in soil became mobile starting at 250°C and sustained a relatively constant release for subsequent temperatures (961 1236 μg g<sup>-1</sup><sub>Dry Material</sub>).
- *Fe* Almost no Fe was mobilized from soil, except for at 250°C (5.1 μg g<sup>-1</sup><sub>Dry Material</sub>). Litterderived Fe peaked at 350 and 450°C (51.6 and 69.1 μg g<sup>-1</sup><sub>Dry Material</sub>). Fe release from lower temperatures, including CTRL, was stable (between 12.3 and 16.3 μg g<sup>-1</sup><sub>Dry Material</sub>).
- *K* Litter released nearly 20x more K than did soil, with a peak at 5109  $\mu$ g g<sup>-1</sup><sub>Dry Material</sub> at 350°C. Concentrations from soil remained relatively stable from CTRL to 550°C, ranging between 193 and 271  $\mu$ g g<sup>-1</sup><sub>Dry Material</sub>. Litter had similar trend, which remained constant at a notably higher concentration compared to soil across all temperatures. Data from 450°C was unusable; therefore, it was excluded. For FLG (Figure VII-5), peak K concentrations occurred at 450°C and was 4383  $\mu$ g g<sup>-1</sup><sub>Dry Material</sub>.
- *Mg* Litter released almost 14x more Mg at its peak (2419 μg g<sup>-1</sup><sub>Dry Material</sub> at 450°C) than that of soil (175 μg g<sup>-1</sup><sub>Dry Material</sub> at 250°C). Mg release from soil was relatively constant until a sharp increase at 250°C and then a slower, step-wise decrease from 250 to 550°C. Litter remained

constant at CTRL, 150°C, and 250°C (ranging in concentration from 328 to 398  $\mu$ g g<sup>-1</sup><sub>Dry</sub> <sub>Material</sub>) and experienced a notable increase for subsequent temperatures.

- *Mn* There was no large difference between Mn dissolution from soil compared to that of litter. Mn concentration spiked to about 50  $\mu$ g g<sup>-1</sup><sub>Dry Material</sub> at 250°C, but was otherwise negligible for all other temperatures. Litter showed higher Mn concentrations for CTRL and 150°C (20.7 – 29.6  $\mu$ g g<sup>-1</sup><sub>Dry Material</sub>) relative to 250°C and 350°C 12.5 – 15.4  $\mu$ g g<sup>-1</sup><sub>Dry Material</sub>).
- Na Na dissolution from litter was a full order of magnitude higher than soil for all temperatures, except for 250°C and 350°C, where concentrations were 5 and 6.5 times higher. Trends for both types of material were similar with relatively stable concentrations until a spike at 550°C for soil and 450°C for litter.
- Si Concentrations up to 250°C for both littler and soil were comparable ranging from  $22.6 39.5 \ \mu g g^{-1}_{Dry Material}$  for soil and  $41.2 37.4 \ \mu g g^{-1}_{Dry Material}$  for litter. Si dissolution from litter far exceeded that of soil, showing a 32- and 51-fold concentration compared to soils heated to  $350^{\circ}$ C and  $450^{\circ}$ C.

### 3.6 SUVA254

Soil extracts followed almost the exact same trend for all sites except for GROSS (Figure 3-10), which did not experience the same dip in SUVA<sub>254</sub> at higher temperatures.

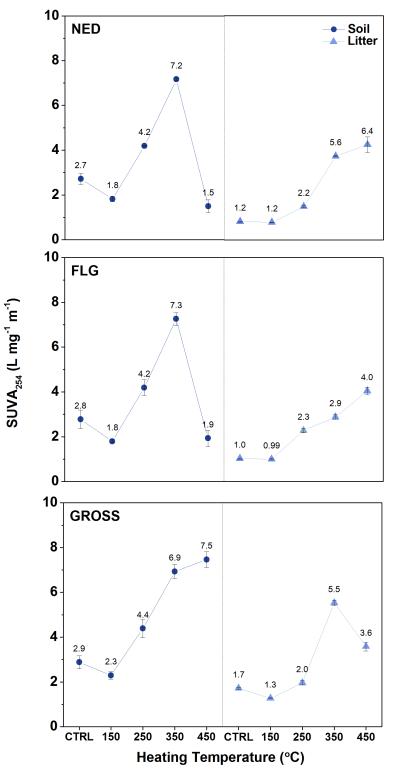


Figure 3-10: Specific UV at 254 nm (SUVA<sub>254</sub>) for soil (left) and litter (right). For soil, values represent an average of three subsamples plus/minus one standard deviation (n=3). For litter, values represent a calculated SUVA between an averaged UV measurement at 254 in replicates of 3 normalized by an averaged DOC in replicates of 2. Standard deviation for litter SUVA<sub>254</sub> values are calculated error propagations.

For 150°C leachates there is a decrease of 1 L mg<sup>-1</sup>m<sup>-1</sup> from the CTRL. SUVA<sub>254</sub> increases drastically peaking at 7.2 L mg<sup>-1</sup>m<sup>-1</sup> at 350°C indicating an enrichment in aromatic carbon structures. At 450°C, SUVA<sub>254</sub> decreases to below 2 L mg<sup>-1</sup>m<sup>-1</sup>. GROSS was the exception here, experiencing an increase (+0.6 L mg<sup>-1</sup>m<sup>-1</sup>), instead of the very drastic decrease observed for all other sites. There is very little variation between SUVA<sub>254</sub> at different sites for each respective temperature, indicating a global consistency in DOC character.

Litter extracts followed almost the exact same trend for all sites, except for GROSS. There was no significant difference between CTRL and 150°C for all sites, remaining steady between 1.0 and 1.7 L mg<sup>-1</sup>m<sup>-1</sup> with a 2-fold jump at 250°C (ranging from 2.0 to 2.3 L mg<sup>-1</sup>m<sup>-1</sup> between sites). Trends for NED and FLG continue to increase by 1 L mg<sup>-1</sup>m<sup>-1</sup> from 350°C to 450°C; however, leachates from GROSS showed a decrease in SUVA (from 5.5 to 3.6 L mg<sup>-1</sup>m<sup>-1</sup>) and a consequent change in character from aromatic to more aliphatic structure in general.

#### 4 Case study for fire-impacted forest floor material from Australian prescribed burn

Results presented above revealed a distinct increase of carbon and nitrogen dissolution in both magnitude and extent of solubility and an increase in aromatic moieties at moderate temperatures from leachates of thermally-impacted soil and litter material. The precision and reproducibility afforded by finely controlled conditions of laboratory soil heating are useful to capture a resolution that can expose some of the specific micro processes at play. However, not only does simulated soil and litter heating fail to fully capture the complexity of a wildfire, such experiments are often typified by use of samples that have been drastically altered from their original structure. This motivated us to investigate the impacts of prescribed forest fire on the magnitude and solubility of many of the same water quality parameters from field samples. This case study was made possible by Dr. Cristina Santín of Swansea University, UK who provided soil, organic material, and ash from a prescribed fire in a forested catchment in SE Australia.

#### 4.1 Study background

The prescribed fire for this study took place west of Sydney in a dry eucalypt forest, which encompasses part of Greater Sydney's water supply catchments. Vegetative cover is dominated by a dry sclerophyllous forest overstory; the study area was chosen for the homogeneity of fuel type. Understory vegetation can be characterized as shrubby and dense, populated by rapid-recovery species that are fire-adapted. Post-fire assessments documented this fire as low to moderate severity in general where the majority of the ground and understory fuel were burned leaving the over story canopy unaffected. Plots where the experiment and sampling took place did achieve what can be classified as a high severity class of wildfire where the canopy was impacted and scorched. Maximum temperatures and their respective durations, shown in Table 4-1, were recorded using imbedded thermocouples, which were placed within the litter layer.

Transect	Sampling Point	T <sub>max</sub> (°C)	Duration > 300°C (s)	Duration > 500°C (s)	Duration > 700°C (s)
1	1	550	110	40	0
2	1	498	240	0	0
2	3	794	140	100	60
3	4	476	80	0	0

Table 4-1: Maximum temperature and durations during the prescribed fire in the litter layer. Sampling point designation can be found in Figure 4-1.

# 4.2 Sampling regime

Five transects were delineated, each 15 m away from each other; samples were collected along each transect every 3 m (Figure 4-1).

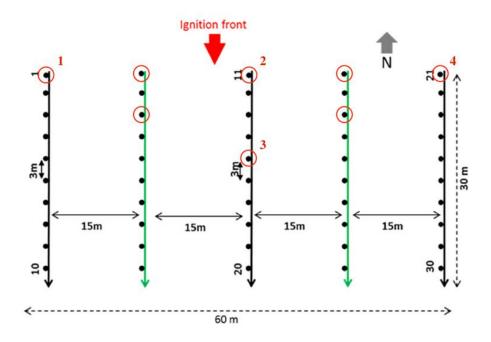


Figure 4-1: Sampling regime (Santín et al. 2018); transects used as control samples are pictured in green while post-fire sampling transects are shown in black (transects 1, 2, and 3 from left to right). Samples provided to us are circled in red.

Sampling plots (represented by black dots in Figure 4-1) measured 20 x 20 cm where the litter layer, the uppermost surface soil layer, and mineral soil were sampled and stored separately before fire ignition. After the fire, ash samples were taken at each sampling plot. The ash layer was comprised of a mix of charred residues and burnt organic-rich soil. The mineral soil layer after the

prescribed burn was also sampled (0-2 cm in depth). Our lab was sent a total of 16 sample classes; 4 control mineral soil samples, 4 control organic-rich soil samples, 4 post-fire mineral soil samples, and 4 ash samples. Samples from the plots that were sent to our lab are circled in red in Figure 4-1.

## 4.3 Analyses of material and lab conditions

Soil and ash provided by Dr. Santín were leached as-is according to the protocol outlined in Section 2.4 using a solids concentration of 5 g of solid material per 1-L of ultra-pure Milli-Q water for a shaken contact time of 6 hours. Solid material was already characterized, including %C and %N, which were used in the calculations for WEOC and WEON. Leachates were analyzed for DOC, TDN, NO<sub>2</sub>/NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>-</sup>, and UV-Vis absorbance. DON, WEOC/WEON and SUVA<sub>254</sub> were calculated in the same way they were for lab data.

Results from the same sampling class (i.e. mineral soil, organic soil, ash) were averaged. For example, parameters values (DOC, TDN, etc.) from leachates from all 4 ash samples were each averaged together.

## 4.4 Results

No change was observed between DOC release from the mineral soil layer for pre- and post-fire conditions (Figure 4-2).

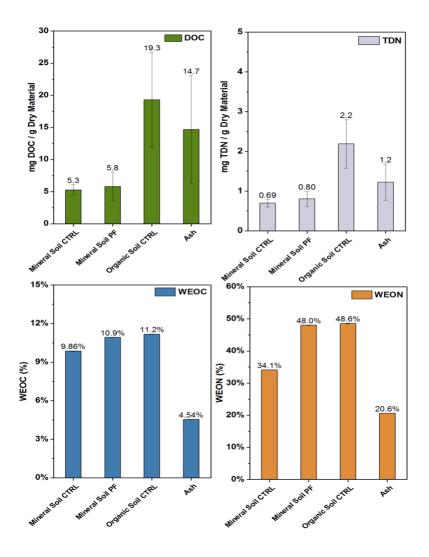


Figure 4-2: DOC, TDN, WEOC, and WEON results for field samples. Error bars represent one standard deviation (n=4).

Both averages remained between 5 and 6 mg DOC per g of solid material. Max temperatures reached for all sampling points were above 450°C and experienced heat pulses much more erratically and in shorter spurts (Table 4-1) in general than did our lab simulation, which held material at a constant temperature for 2 hours. That said, it is possible that the soil organic matter in the field samples remained intact and unaffected by the surface heating of the prescribed fire, explaining a lack of change in DOC release between control and heat-impacted soils. In our experiment, DOC yields from material heated to 350°C was comparable to that of CTRL; it may

be possible that field samples surpassed the process of enhanced solubility (around 250°C in lab samples) during higher intensities of heating. The organic soil layer put off almost four times as much DOC than did mineral soil, as expected. DOC from ash, which is a composite mixture of partially consumed litter and the organic soil collapsed into the same layer, decreased slightly.

The percentage of WEOC remained constant between pre- and post-fire mineral soil. WEOC decreased slightly between organic soil and ash (~1%), which is consistent with the trends we observed with low and high temperature litter material (Figure 3-8). Shifts in WEOC indicate shifts in SOM chemical properties; however, trends are harder to detect with so coarse a profiling of heating temperature.

Like DOC, no change was observed between TDN release from the mineral soil layer for pre- and post-fire conditions; both remained below 1 mg TDN per g of solid material. Unburned organic soil released the highest amount of TDN around 2 mg TDN per g solid on average. TDN released from ash decreased by almost half. The majority of TDN was comprised of organic nitrogen, with negligible contributions from inorganic species investigated, namely  $NO_2^{-7}/NO_3^{-7}$  and  $NH_4^+$ .

The fraction of WEON for all samples far exceeded those from the lab samples. WEON increased slightly by approximately 0.1% between pre- and post-fire mineral soil layer. WEON decreased by almost half between the organic soil layer and ash.

Figure 4-3 depicts SUVA<sub>254</sub> for leachates of field material.

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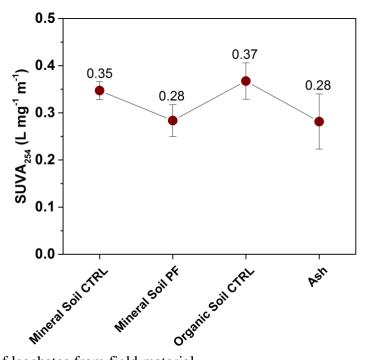


Figure 4-3: SUVA of leachates from field material.

SUVA<sub>254</sub> values between unburned samples were nearly identical (0.35 L mg<sup>-1</sup>m<sup>-1</sup> for mineral soil and 0.37 for organic soil layer) and between both burned samples (0. L mg<sup>-1</sup>m<sup>-1</sup> for both post fire mineral soil and ash). This suggests that the DOM character for each class of samples remained unchanged between leachates of unburned and burned samples. In general, all SUVA<sub>254</sub> values were far lower than what we observed for soil and litter from the Front Range, which could be a function of geographic and ecological differences.

### 5 Discussion

The findings of this research demonstrate that heat-altered soil and litter exhibit very different dissolution trends for nearly all dissolved parameters investigated. This could indicate that each component will contribute different magnitudes of constituents based on their respective combustion temperatures, assuming that both are mobilized to the same degree during a post-fire precipitation event. Findings reveal that, depending on maximum temperature reached, expected increases in litter-derived organic matter and soil-derived organic matter may be coarsely scaled and predicted. Exploring a field-based case study helped to contextualize the role of laboratory-based simulations in understanding impacts of fires on forest floor material. The results of these experiments together can contribute to the ongoing exploration of ash by the wildfire community with respect to its impact on water quality parameters of concern.

## 5.1 Laboratory experiments

In the laboratory-based study, the most notable changes in magnitude of release of carbon and nitrogen occurred at 250°C, representing here a low-/moderate- severity fire, for both soil and litter. For carbon, you might expect a much higher DOC contribution from litter than soil up to  $150^{\circ}$ C if the debris is mobilized to a waterbody or stream. Despite the drastic change in DOC concentrations between temperatures for soil alone, soil was a much weaker contributor of DOC than that of litter for all temperatures, with maximum concentrations having one order of magnitude less DOC than from litter. In general, litter contribution to DOC dominates for unburned to low severity fires while for a higher intensity fire, there will be a smaller (< 6 mgc L<sup>-1</sup>), composite soil/litter contribution to DOC export.

While soil and litter DON had similar dissolution profiles to DOC, concentrations across both materials and across all temperatures never exceeded 1.0 mg<sub>N</sub> L<sup>-1</sup>. As with DOC, litter contributions to DON dominate for unburned to low severity fires. For moderately severe fires (corresponding to 250/350°C maximum surface temperatures), contributions to DON export are dominated by soil, as concentrations for soil leachates exceed that of litter by a factor of two. Nearzero concentrations for leachates from soil and litter alike were found at high-severity temperatures (450/550°C). As for nitrogen speciation, a slight increase of NH4<sup>+</sup> was observed for soil only at 250°C. Negligible levels of NO<sub>3</sub> and NO<sub>2</sub> were detected from both soil and litter leachates, which came as a surprise because elevated nitrate and nitrite stream and lake levels have often been reported both immediately after and for months to years following wildfires (Chessman1986; Carignan et al. 2000; Rhoades, Entwistle, and Butler 2011). In our experiments, soil and litter leachates were not significant exporters of inorganic nitrogen species; however, elevated stream levels observed in field studies may be caused by a less straightforward mechanism as ash and soil leaching i.e. stream solute dynamics, seasonality, plant root uptake, and nitrogen metabolism of stream biota (Betts and Jones 2009).

Solubility of soil- and litter-derived organic carbon and nitrogen was expressed as the percentage of total organic carbon or nitrogen that is water soluble. Litter-derived organic carbon solubility dominates at CTRL and 150°C peaking at 6.8% while soil-derived organic carbon solubility dominates at moderate and higher temperatures (250-450°C) peaking at almost 12% at 350°C. It has been shown that heating soils is connected to severe changes in the solubility of SOM; however, much of the literature poses a decrease in solubility for SOM heated up to 350°C due to the detection of loss of functional groups that would facilitate solubility behavior (Knicker 2007; Fernandez, Cabaneiro, and González-Prieto 2004). Litter is much more susceptible to loss of solubility-enhancing functional groups than soil. The mineral surface, with which SOM is bonded to, has been theorized to provide protection due to its low heat conductivity or by the

strength of the its bond to SOM (Knicker 2007). This could explain the difference in solubilities between soil and litter organic matter at 350°C, as organic matter originating from litter is much more vulnerable to combustion at relatively lower temperatures. The solubility of nitrogen tells a similar story, with litter-derived organic nitrogen peaking at CTRL and 150°C and dipping below 1% for all higher temperatures. For soil, nitrogen solubility peaks at 250°C (up to 10%) and decreases gradually for higher temperatures. In general, carbon and nitrogen solubility from litter dominates only at very low burn temperatures, while carbon and nitrogen solubility from soil dominates at mid- to high-temperatures.

Peak soluble element release from litter far exceeded peak releases from soil by at least an order of magnitude for all species investigated across almost all temperatures, except for Al and Mn, whose release was dominated by soil. Calcium, Fe, Mg, Na and Si concentrations from litter peaked at moderate to high temperatures (350 or 450°C). Trends from soil different among elements for the most part, showing increasing concentrations with temperature for Al, Ca, Na, and Si. Ron and Mn experienced peak concentrations at 250°C while K experienced no significant change across temperatures. Collectively, concentrations yielded by either soil or litter were far higher than reported concentrations found in field samples of ash. For example, Santín et al. (2015) reported concentrations less than 100  $\mu$ g g<sup>-1</sup> across all severity classes (low, high, and extreme) for Ca, K, Mg, Na, Al, Fe, and Si. In this study, Mn is the only trace element that yielded lower concentrations than concentrations from field-based ash in either soil or litter. Campos et al. (2016) reported Mn concentrations of up to 500  $\mu$ g g<sup>-1</sup> in ash and 150  $\mu$ g g<sup>-1</sup> in fire-impacted mineral soils compared to a peak of 49.5  $\mu$ g g<sup>-1</sup> for soil (at 250°C) and 29.6  $\mu$ g g<sup>-1</sup> for litter (at 150°C). It is important to note that seeking correlations between wildfires and the solubility of trace elements is confounded by the fact that solubility is largely driven by the pH of the solution, which can be

different depending on geographic location. While there may not be ubiquitous trends expected with fire severity, trends seen in this study are clearer between temperatures when the conditions are held constant. Generally, litter dominates in solubility of most investigated trace elements across all temperatures, and especially at moderate to high temperatures of 350°C and 450°C except for Al and Mn when soil is either comparable (Mn) or exceeds release from litter entirely (Al). The results of this study indicate that exports of many trace elements following a wildfire originate from the portion of ash that is derived from plant material with soil playing a less significant role.

Water extractable soil leachates experienced a much more drastic change in character across temperatures than did litter. For two of the three sites, SUVA254 of leachates from soil heated only slightly at 150°C declined, increased continually up to 350°C, and dipped drastically at 450°C. This spike at 350°C indicates a significant change in DOC character from soil extracts, which corroborates with the observed heightened solubility observed at the same temperature. This is also consistent with Santos et al. (2017), whose results demonstrated a greater abundance of conjugated C-structure through liquid-state <sup>1</sup>H NMR spectroscopy. Litter remained relatively constant in SUVA<sub>254</sub> up to 250°C and increased continually up to 450°C for two of the three sites. Aromaticity from litter leachates increased by a greater factor than did soil leachates with SUVA254 values increasing between 3 and 4 times the CTRL at 350°C; however, SUVA<sub>254</sub> values for soil at the same temperature peaked at a higher value (between 6.9 and 7.3 for soil versus 2.9 and 5.6 for litter). Leachates from both materials experienced an increase in SUVA254 relative to their respective controls, which is consistent with other studies that observe an increase in both C- and N-containing aromatic structure from SOM and plant material (Knicker et al. 2005; Knicker et al. 1996) through solid-state <sup>13</sup>C-NMR and <sup>15</sup>N-NMR.

## 5.2 Case study

The complexity in determining water quality trends influenced by wildfire made it difficult to correlate field samples from the case study with lab samples. Organic carbon and nitrogen dissolution (DOC and TDN) from the mineral soil layer experienced no change post-fire; whereas dissolution from lab soil samples was significantly different at moderate temperatures compared to the control. This is may be due to the difference in both heating sources and heating duration. It could have been possible that heat from the prescribed fire did not reach the mineral soil; therefore, it remained relatively un-impacted. However, Santín et al. (2018) reported notable differences in other properties due to the fire, like solution pH and water-soluble Ca. Notwithstanding, WEOC and WEON both demonstrated an increase in solubility between the control and post-fire mineral soil (+1% for WEOC and +14% for WEON), which is consistent with what was observed in lab samples.

A slight decrease in average DOC and TDN occurred between the unperturbed organic soil and post-fire ash. The relationship here is difficult to parse, as the resulting ash is comprised of partially-consumed and charred litter material, which is incorporated into the organic soil layer. Furthermore, upon burning, the organic layer completely lost its structure and was mostly consumed (Santín et al. 2018). Considering the high combustion temperatures reached during the prescribed burn (Table 4-1), much of the organic matter may have been consumed or made insoluble through mineralization. Without data on the litter layer, not many correlations can be drawn here; however, WEOC and WEON experienced a decrease between the layer of organic soil and ash (-6.7% for WEON and -28% for WEON), which could partially explain the decrease in corresponding DOC and TDN.

SUVA<sub>254</sub> across all field samples were much lower (below 1 L mg<sup>-1</sup>m<sup>-1</sup>) than the lowest value for lab samples (above L mg<sup>-1</sup>m<sup>-1</sup> for both soil and litter CTRL samples). Post-fire SUVA<sub>254</sub>

remained unchanged, indicating a more alkyl-dominant character of DOC whereas heat-impacted lab samples demonstrated a significant increase in SUVA<sub>254</sub> and were generally more aromatic in character across all temperatures.

#### 6 Summary and Conclusion

This thesis explored the respective contributions of heat-impacted soil and litter to dissolvable constituents that may impair water quality in the Boulder Creek Watershed and investigated a case study to help contextualize lab-based burn simulations in the wildfire community.

Findings of this study demonstrate that dissolution behavior across burn severities differ between soil and litter material. The most critical temperature for soil-derived organic carbon and organic nitrogen release magnitude and solubility profile was 250°C and 350°C, showing a peak of DOC at 250°C and a peak of solubility at 350°C. For litter, peaks occurred for CTRL and 150°C and dropped sharply for all subsequent temperatures. Litter is the chief contributor of most constituents across all temperatures, with the exception of two of the investigated soluble elements and DON, suggesting that charred and combusted plant material poses a greater threat to water quality impairment following a wildfire with regard to the magnitude of DOC and soluble element exported. SUVA<sub>254</sub> showed a dramatic increase for soil extracts at 350°C, suggesting a dominance of aromatic DOC, and decreases again at 450°C. This detail, together with the peak of solubility at 350°C may suggest a critical molecular transformation mechanism that renders wildfireimpacted soil dissolved organic matter a-typical in structure and therefore chemical behavior that warrants further investigation. SUVA<sub>254</sub> values for litter extracts increased gradually with temperature.

The clear trends of this laboratory study did not corroborate completely with the case study. This highlights the need for field studies to compliment laboratory experiments from the beginning, especially if investigations into the impacts of fire continue to be explored in laboratory environments. It is possible that temperature and duration alone as factors simulating wildfires is inadequate while other factors, like heating type, heating rate, and the magnitude of energy pulse play a more significant role than accounted for during most laboratory experiments.

Soil and litter are not decoupled in natural systems following a wildfire; so, the contributions of their respective dissolved constituents will obviously be combined. You would expect different dissolution behavior between them because soil organic matter and organic matter from 'fresh' plant material are fundamentally different in structure; therefore, mechanisms driving their solubilities are not the same. Additionally, their fate, capacity to be metabolized, and the reactivity of the dissolved constituents from either soil or plant matter impacted by wildfire will likely be different. Notwithstanding, trends across parameters for soil and litter showed very consistent respective patterns, making it potentially feasible to estimate water quality impacts under different burning conditions if maximum temperatures can be elucidated and further, if maximum temperature reached can be solidly related to wildfire severity. This research revealed that land and water managers can expect contributions of dissolved constituents from both litter and soil material following a wildfire with contributions from each differing in magnitude depending on the severity and thermal regime of the wildfire event.

# References

- Almendros, G, and F J González-Vila. 2012. "Wildfires, Soil Carbon Balance and Resilient Organic Matter in Mediterranean Ecosystems. a Review Los Incendios Forestales, El Balance De Carbono en El Suelo Y La ...." Spanish Journal of Soil .... doi:10.3232/SJSS.2012.V2.N2.01.
- Araya, Samuel N, Marilyn L Fogel, and Asmeret Asefaw Berhe. 2017. "Thermal Alteration of Soil Organic Matter Properties: a Systematic Study to Infer Response of Sierra Nevada Climosequence Soils to Forest Fires." Soil 3 (1): 31–44. doi:10.5194/soil-3-31-2017.
- Betts, Emma F, and Jeremy B Jones Jr. 2009. "Impact of Wildfire on Stream Nutrient Chemistry and Ecosystem Metabolism in Boreal Forest Catchments of Interior Alaska." *Arctic, Antarctic, and Alpine Research* 41 (4): 407–17. doi:10.1657/1938-4246-41.4.407.
- Bladon, Kevin D, Monica B Emelko, Uldis Silins, and Micheal Stone. 2014. "Wildfire and the Future of Water Supply." *Environmental Science & Technology* 48 (16): 8936–43. doi:10.1021/es500130g.
- Bodí, Merche B, Deborah A Martin, Victoria N Balfour, Cristina Santín, Stefan H Doerr, Paulo Pereira, Artemi Cerdà, and Jorge Mataix-Solera. 2014. "Wildland Fire Ash: Production, Composition and Eco-Hydro-Geomorphic Effects." *Earth Science Reviews* 130 (C). Elsevier B.V.: 103–27. doi:10.1016/j.earscirev.2013.12.007.
- Carignan, R. and Steedman, R.J., 2000. Impacts of major watershed perturbations on aquatic ecosystems. Canadian Journal of Fisheries and Aquatic Sciences, 57(S2), pp.1-4.
- Cawley, Kaelin M, Amanda K Hohner, David C Podgorski, William T Cooper, Julie A Korak, and Fernando L Rosario-Ortiz. 2017. "Molecular and Spectroscopic Characterization of Water Extractable Organic Matter From Thermally Altered Soils Reveal Insight Into Disinfection Byproduct Precursors." *Environmental Science & Technology* 51 (2): 771–79. doi:10.1021/acs.est.6b05126.
- Chessman, B.C., 1986. Impact of the 1983 wildfires on river water quality in East Gippsland, Victoria. Marine and Freshwater Research, 37(3), pp.399-420.
- Chin, Y.P., Aiken, G. and O'Loughlin, E., 1994. Molecular weight, polydispersity, and spectroscopic properties of aquatic humic substances. Environmental science & technology, 28(11), pp.1853-1858.
- Doerr, Stefan H, Richard A Shakesby, and Lee H MacDonald. 2006. "Soil Water Repellency: a Key Factor in Post-Fire Erosion?." *Fire Effects on Soils and Restoration Strategies*, December, 1–29.
- Dunn, P H, S C Barro, and M Poth. 1985. "Soil-Moisture Affects Survival of Microorganisms in Heated Chaparral Soil." Soil Biology and Biochemistry 17 (2): 143–48. doi:10.1016/0038-0717(85)90105-1.

- Ebel, Brian A. 2012. "Wildfire Impacts on Soil-Water Retention in the Colorado Front Range, United States." *Water Resources Research* 48 (12): 1128–12. doi:10.1029/2012WR012362.
- Fernandez, Irene, Ana Cabaneiro, and Serafín J González-Prieto. 2004. "Use of13C to Monitor Soil Organic Matter Transformations Caused by a Simulated Forest Fire." *Rapid Communications in Mass Spectrometry* 18 (4). Wiley-Blackwell: 435–42. doi:10.1002/rcm.1345.
- Fried, Jeremy S, Margaret S Torn, and Even Mills. 2004. "The Impact of Climate Change on Wildfire Severity: a Regional Forecast for Northern California." *Climatic Change*, April, 169–91.
- González-Pérez, José A, Francisco J González-Vila, Gonzalo Almendros, and Heike Knicker.
  2004. "The Effect of Fire on Soil Organic Matter—a Review." *Environment International* 30 (6): 855–70. doi:10.1016/j.envint.2004.02.003.
- González-Vila F J and G Almendros 2003. 2003. "Thermal Transformation of Soil Organic Matter by Natural Fires and Laboratory-Controlled Heatings." In *Natural and Laboratory-Simulated Thermal Geochemical Processes*, 153–200. Dordrecht: Springer, Dordrecht. doi:10.1007/978-94-017-0111-2\_4.
- Hohner, Amanda K, Kaelin Cawley, Jill Oropeza, R Scott Summers, and Fernando L Rosario-Ortiz. 2016. "Drinking Water Treatment Response Following a Colorado Wildfire." Water Research 105 (C). Elsevier Ltd: 187–98. doi:10.1016/j.watres.2016.08.034.
- Hohner, Amanda K, Leigh G Terry, Eli B Townsend, R Scott Summers, and Fernando L Rosario-Ortiz. 2017. "Water Treatment Process Evaluation of Wildfire-Affected Sediment Leachates." *Environmental Science: Water Research & Technology* 3 (2). Royal Society of Chemistry: 352–65. doi:10.1039/C6EW00247A.
- Huffman, Edward L, Lee H MacDonald, and John D Stednick. 2001. "Strength and Persistence of Fire-Induced Soil Hydrophobicity Under Ponderosa and Lodgepole Pine, Colorado Front Range." *Hydrological Processes* 15 (15). Wiley-Blackwell: 2877–92. doi:10.1002/hyp.379.
- Janzen C., Tobin-Janzen T. (2008) Microbial Communities in Fire-Affected Soils. In: Dion P., Nautiyal C.S. (eds) Microbiology of Extreme Soils. Soil Biology, vol 13. Springer, Berlin, Heidelberg, p. 299-316.
- Jardine, P M, G V Wilson, and J F McCarthy. 1990. "Hydrogeochemical Processes Controlling the Transport of Dissolved Organic Carbon Through a Forested Hillslope." *Journal of Contaminant* ... 6 (1): 3–19. doi:10.1016/0169-7722(90)90008-5.
- Karanfil, Tanju, Ilke Erdogan, and Mark A Schlautman. 2003. "Selecting Filter Membranes for Measuring DOC and UV 254." *American Water Works Association*, January, 1–16.
- Keeley, Jon E. 2009. "Fire Intensity, Fire Severity and Burn Severity: a Brief Review and Suggested Usage." *International Journal of Wildland Fire* 18 (1). CSIRO PUBLISHING: 116–11. doi:10.1071/WF07049.

- Key, C.H. and Benson, N.C., 2005. Landscape assessment: remote sensing of severity, the normalized burn ratio and ground measure of severity, the composite burn index. FIREMON: Fire effects monitoring and inventory system Ogden, Utah: USDA Forest Service, Rocky Mountain Res. Station.
- Knicker, H, F González-Vila, O Polvillo, J González, and G Almendros. 2005. "Fire-Induced Transformation of C- and N- Forms in Different Organic Soil Fractions From a Dystric Cambisol Under a Mediterranean Pine Forest ()." Soil Biology and Biochemistry 37 (4): 701–18. doi:10.1016/j.soilbio.2004.09.008.
- Knicker, H, G Almendros, F J GonzalezVila, F Martin, and H D Ludemann. 1996. "C-13- and N-15-NMR Spectroscopic Examination of the Transformation of Organic Nitrogen in Plant Biomass During Thermal Treatment." *Soil Biology and Biochemistry* 28 (8): 1053–60. doi:10.1016/0038-0717(96)00078-8.
- Knicker, Heike. 2007. "How Does Fire Affect the Nature and Stability of Soil Organic Nitrogen and Carbon? a Review." *Biogeochemistry* 85 (1). Kluwer Academic Publishers: 91–118. doi:10.1007/s10533-007-9104-4.
- Kondolf, G. M. et al. (2014), Sustainable sediment management in reservoirs and regulated rivers: Experiences from five continents, *Earth's Future*, 2, doi: 10.1002/2013EF000184.
- Lane, Patrick N J, Gary J Sheridan, and Philip J Noske. 2006. "Changes in Sediment Loads and Discharge From Small Mountain Catchments Following Wildfire in South Eastern Australia." *Journal of Hydrology* 331 (3-4): 495–510. doi:10.1016/j.jhydrol.2006.05.035.
- Leak, M., Passuello, R. and Tyler, B., 2003. I've seen fire. I've seen rain. I've seen muddy waters that I thought would never clear again. Waterworks, 6, pp.38-44.
- Martin, Deborah A., 2016. At the nexus of fire, water and society. Phil. Trans. R. Soc. B 371: 20150172. http://dx.doi.org/10.1098/rstb.2015.0172
- Malmström, Anna. 2008. "Temperature Tolerance in Soil Microarthropods: Simulation of Forest-Fire Heating in the Laboratory." *Pedobiologia* 51 (5-6): 419–26. doi:10.1016/j.pedobi.2008.01.001.
- Moody, John A, and Deborah A Martin. 2001. "Initial Hydrologic and Geomorphic Response Following a Wildfire in the Colorado Front Range." *Earth Surface Processes and Landforms* 26 (10). John Wiley & Sons, Ltd.: 1049–70. doi:10.1002/esp.253.
- Murphy, S.F., Barber, L.B., Verplanck, P.L. and Kinner, D.A., 2000. Environmental setting and hydrology of the Boulder Creek Watershed, Colorado. Comprehensive water quality of the Boulder Creek watershed, Colorado, during high-flow and low-flow conditions: US Geological Survey, pp.5-26.
- Murphy, S.F., 2006. State of the watershed: water quality of Boulder Creek, Colorado. US Department of the Interior, US Geological Survey.

- Murphy, Sheila F, Jeffrey H Writer, R Blaine McCleskey, and Deborah A Martin. 2015. "The Role of Precipitation Type, Intensity, and Spatial Distribution in Source Water Quality After Wildfire." *Environmental Research Letters* 10 (8). IOP Publishing: 084007–15. doi:10.1088/1748-9326/10/8/084007.
- National Interagency Figure Center 2018. "National Report of Wildland Fires an dAcres Burned by State, viewed 21 July 2018, <a href="https://www.predictiveservices.nifc.gov/intelligence/2017\_statssumm/fires\_acres17.pdf">https://www.predictiveservices.nifc.gov/intelligence/2017\_statssumm/fires\_acres17.pdf</a>
- Neary, D G, C C Klopatek, L F DeBano, and P F Ffolliott. 1999. "Fire Effects on Belowground Sustainability: a Review and Synthesis." *Journal of the North American Benthological Society* 122 (1-2): 51–71. doi:10.1016/S0378-1127(99)00032-8.
- Neary, Daniel G, Gerald J Gottfried, and Peter F Ffolliott. 2003. "Post-Wildfire Watershed Flood Responses ." Edited by Proceedings of the nd International Fire Ecology Conference. *American Meteorological Society* 65982 (August). Orlando: 1–8.
- Neary, Daniel G.; Ryan, Kevin C.; DeBano, Leonard F., eds. 2005. (revised 2008). Wildland fire in ecosystems: effects of fire on soils and water. Gen. Tech. Rep. RMRS-GTR-42-vol.4. Ogden, UT: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station. 250 p.
- Parson, Annette; Robichaud, Peter R.; Lewis, Sarah A.; Napper, Carolyn; Clark, Jess T. 2010. Field guide for mapping post-fire soil burn severity. Gen. Tech. Rep. RMRS-GTR-243. Fort Collins, CO: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station. 49 p.
- Reneau, Steven L, Danny Katzman, Gregory A Kuyumjian, Alexis Lavine, and Daniel V Malmon. 2007. "Sediment Delivery After a Wildfire." *Geology* 35 (2). GeoScienceWorld: 151–54. doi:10.1130/G23288A.1.
- Revchuk, Alex D, and I H Mel Suffet. 2014. "Effect of Wildfires on Physicochemical Changes of Watershed Dissolved Organic Matter." *Water Environment Research* 86 (4): 372–81. doi:10.2175/106143013X13736496909671.
- Rhoades, Charles C, Deborah Entwistle, and Dana Butler. 2011. "The Influence of Wildfire Extent and Severity on Streamwater Chemistry, Sediment and Temperature Following the Hayman Fire, Colorado." *International Journal of Wildland Fire* 20 (3). CSIRO PUBLISHING: 430–13. doi:10.1071/WF09086.
- Ryan, Sandra E, Kathleen A Dwire, and Mark K Dixon. 2011. "Impacts of Wildfire on Runoff and Sediment Loads at Little Granite Creek, Western Wyoming." *Geomorphology* 129 (1-2). Elsevier B.V.: 113–30. doi:10.1016/j.geomorph.2011.01.017.
- Santín, Cristina, Stefan H Doerr, Agustín Merino, Robert Bryant, and Neil J Loader. 2016. "Forest Floor Chemical Transformations in a Boreal Forest Fire and Their Correlations with Temperature and Heating Duration." *Geoderma* 264 (Part A). Elsevier B.V.: 71–80. doi:10.1016/j.geoderma.2015.09.021.

- Santín, Cristina, Stefan H Doerr, Xose L Otero, and Chris J Chafer. 2015. "Quantity, Composition and Water Contamination Potential of Ash Produced Under Different Wildfire Severities." *Environmental Research* 142 (October): 297–308. doi:10.1016/j.envres.2015.06.041.
- Santín, Cristina, Xose L Otero, Stefan H Doerr, and Chris J Chafer. 2018. "Impact of a Moderate/High-Severity Prescribed Eucalypt Forest Fire on Soil Phosphorous Stocks and Partitioning." *Science of the Total Environment* 621 (April): 1103–14. doi:10.1016/j.scitotenv.2017.10.116.
- Santos, Fernanda, David Russell, and Asmeret Asefaw Berhe. 2016. "Thermal Alteration of Water Extractable Organic Matter in Climosequence Soils From the Sierra Nevada, California." *Journal of Geophysical Research: Biogeosciences* 121 (11): 2877–85. doi:10.1002/2016JG003597.
- Savage, S M. 2002. "(1974) Mechanism of Fire-Induced Water Repellency in Soil," March, 1-6.
- Silins, Uldis, Micheal Stone, Monica B Emelko, and Kevin D Bladon. 2009. "Sediment Production Following Severe Wildfire and Post-Fire Salvage Logging in the Rocky Mountain Headwaters of the Oldman River Basin, Alberta." *Catena* 79 (3). Elsevier B.V.: 189–97. doi:10.1016/j.catena.2009.04.001.
- Smith, Hugh G, Gary J Sheridan, Patrick N J Lane, Petter Nyman, and Shane Haydon. 2011.
  "Wildfire Effects on Water Quality in Forest Catchments: a Review with Implications for Water Supply." *Journal of Hydrology* 396 (1-2): 170–92. doi:10.1016/j.jhydrol.2010.10.043.
- Spencer, Craig N, and F Richard Hauer. 1991. "Phosphorus and Nitrogen Dynamics in Streams During a Wildfire." *Journal of the North American Benthological Society* 10 (1): 24–30. doi:10.1016/S0378-1127(03)00058-6.
- Sexton, Tim. 2006. U.S. Federal Fuel Management Programs: Reducing Risk to Communities and Increasing Ecosystem Resilience and Sustainability. In: Andrews, Patricia L.; Butler, Bret W., comps. 2006. Fuels Management-How to Measure Success: Conference Proceedings. 28-30 March 2006; Portland, OR. Proceedings RMRS-P-41. Fort Collins, CO: U.S. Department of Agriculture, Forest Service, Rocky Mountain Research Station. p. 9-12.
- Templeton, Michael R, Robert C Andrews, and Ron Hofmann. 2008. "Particle-Associated Viruses in Water: Impacts on Disinfection Processes." *Critical Reviews in Environmental Science and Technology* 38 (3): 137–64. doi:10.1080/10643380601174764.
- Traina, S.J., Novak, J. and Smeck, N.E., 1990. An ultraviolet absorbance method of estimating the percent aromatic carbon content of humic acids. *Journal of environmental quality*, *19*(1), pp.151-153.
- Van Krevelen, D.W., 1950. Graphical-statistical method for the study of structure and reaction processes of coal. Fuel, 29, pp.269-284.

Weishaar, James L, George R Aiken, Brian A Bergamaschi, Miranda S Fram, Roger Fujii, and

Kenneth Mopper. 2003. "Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon." *Environmental Science & Technology* 37 (20): 4702–8. doi:10.1021/es030360x.

- Wells, C.G., Campbell, R.E.; DeBano, L.F.; Lewis, C.E.; Fredrickson, R.L.; Franklin, E.C.;
  Froelich, R.C.; Dunn, P.H. 1979. Effects of fire on soil: a state-of-the-knowledge review.
  Gen. Tech. Rep. WO- 7. Washington, DC: U.S. Department of Agriculture, Forest Service. 34 p.
- Westerling, A L. 2006. "Warming and Earlier Spring Increase Western U.S. Forest Wildfire Activity." *Science* 313 (5789). American Association for the Advancement of Science: 940– 43. doi:10.1126/science.1128834.
- White, Ian, Alan Wade, Martin Worthy, Norm Mueller, Trevor Daniell, and Robert Wasson. 2015. "The Vulnerability of Water Supply Catchments to Bushfires: Impacts of the January 2003 Wildfires on the Australian Capital Territory." *Australasian Journal of Water Resources* 10 (2): 179–94. doi:10.1080/13241583.2006.11465291.

Writer, Jeffrey H. 2012. Wildfire Effects on Source-Water Quality.

Writer, Jeffrey H, Amanda Hohner, Jill Oropeza, Amanda Schmidt, Kaelin Cawley, and Fernando L Rosario-Ortiz. 2014. "Water Treatment Implications After the High Park Wildfire, Colorado." *Journal - American Water Works Association* 106 (4). American Water Works Association: E189–99. doi:10.5942/jawwa.2014.106.0055.

## APPENDIX I: Summary of analyzed soil data

Subsample ID	Temperature (°C)	DOC (mg L <sup>-1</sup> )	DOC (mgoc g <sup>-1</sup> dry material)	Carbon Content (%)	Mass Loss (%)	OC Remaining (%)	WEOC (%)
А	CTRL	1.2 (0.1)	0.2 (0)	2.7 (0.4)	DL	100 (0.4)	0.8 (0.2)
А	150	4.0 (0.2)	0.8 (0)	2.3 (0.3)	1.0 (0.2)	83.7 (1.9)	3.5 (0.5)
А	250	11.0 (0.1)	2.2 (0)	2.4 (0.1)	2.9 (0.4)	86.4 (0.5)	9.1 (0.4)
А	350	4.4 (0.3)	0.9 (0.1)	0.8 (0.1)	5.1 (0.2)	29.2 (0.9)	10.5 (1.3)
А	450	0.4 (0)	0.9 (0)	0.2 (0)	6.5 (0.4)	5.4 (0.1)	5.6 (0.5)
А	550	DL	DL	0.1 (0)	7.6 (0.2)	0.5 (0.5)	1.8 (3.2)
В	CTRL	2.8 (0.1)	0.6 (0)	8.2 (0.2)	DL	100 (0.2)	0.7 (0)
В	150	9.9 (0.1)	2.0 (0)	8.0 (0.4)	0.6 (0.1)	97 (1.1)	2.5 (0.1)
В	250	16.7 (0.6)	3.3 (0.1)	7.6 (0.7)	6.2 (1.2)	86.5 (2.2)	4.4 (0.5)
В	350	5.4 (0.1)	1.1 (0)	2.2 (0)	14.6 (1.0)	23.3 (0.1)	4.9 (0.1)
В	450	0.3 (0)	0.1 (0)	0.2 (0)	16.5 (0.4)	2.2 (0.2)	3.1 (0.2)
В	550	DL	DL	DL	17.5 (0.5)	0.4 (0.4)	0.3 (0.6)
С	CTRL	5.3 (0.2)	1.1 (0)	7.6 (0.3)	DL	100 (0.3)	1.4 (0.1)
С	150	12.1 (0.7)	2.4 (0.1)	8.9 (0.1)	1.2 (0.2)	116.2 (1.3)	2.7 (0.2)
С	250	22.3 (0.6)	4.5 (0.1)	7.4 (0.5)	7.2 (0.6)	91.1 (1)	6.0 (0.5)
С	350	6.5 (0.2)	1.3 (0)	1.9 (0.1)	16.8 (0.3)	20.3 (0.2)	7.1 (0.4)
С	450	0.6 (0)	0.1 (0)	0.3 (0)	19.3 (0.4)	3 (1.1)	3.9 (0.5)
С	550	DL	DL	0.1 (0)	21.2 (0.9)	0.6 (2.7)	DL
D	CTRL	2.8 (0)	0.6 (0)	4.3 (0)	DL	100 (0)	1.3 (0)
D	150	8.7 (0.1)	1.7 (0)	5.2 (0.1)	1.0 (0.1)	119.2 (0.5)	3.4 (0.1)
D	250	7.1 (0.8)	1.4 (0.2)	3.3 (0.2)	4.2 (0.7)	73.8 (0.9)	4.3 (0.6)
D	350	2.4 (0.1)	0.5 (0)	1.2 (0.1)	9.7 (1.4)	26 (1.0)	3.9 (0.4)

Table I-1: Carbon-based parameters for discretized soil subsamples. Mean values of analysis and standard errors in brackets.

Subsample ID	Temperature (°C)	DOC (mg L <sup>-1</sup> )	$\frac{DOC}{(mg_{OC}\ g^{-1}_{dry\ material})}$	Carbon Content (%)	Mass Loss (%)	OC Remaining (%)	WEOC (%)
D	450	0.2 (0)	DL	0.1 (0)	10.9 (0.4)	2.8 (0)	3.3 (0.2)
D	550	DL	DL	DL	11.8 (0.3)	0.5 (0)	1.1 (1.7)
Е	CTRL	2.9 (0.1)	0.6 (0)	6.9 (0.3)	DL	100 (0.3)	0.8 (0)
Е	150	9.2 (0.2)	1.8 (0)	5.4 (0.5)	0.4 (0.1)	77.0 (2.0)	3.4 (0.3)
Е	250	12.3 (0.1)	2.5 (0)	4.2 (0.4)	4.5 (0.7)	58.0 (1.4)	5.9 (0.5)
Е	350	3.7 (0.2)	0.7 (0)	1.1 (0.1)	10.0 (0.4)	14.0 (1.2)	6.8 (0.8)
Е	450	0.4 (0.1)	0.1 (0)	0.2 (0)	12.3 (1.0)	2.3 (0.6)	4.9 (1.0)
Е	550	DL	DL	DL	13.0 (0.9)	0.5 (0)	DL
F	CTRL	3.7 (0.1)	0.7 (0)	16.8 (0.7)	DL	100 (0.7)	0.4 (0)
F	150	18.5 (0.1)	3.7 (0)	15.3 (2.3)	1.8 (0.2)	89.3 (4.3)	2.4 (0.2)
F	250	8.3 (0.2)	1.7 (0)	10.4 (0.2)	18.0 (1.0)	50.6 (0.5)	1.6 (0.1)
F	350	3.8 (0.3)	0.8 (0)	2.7 (0.1)	20.8 (1.4)	12.8 (0.4)	2.8 (0.3)
F	450	0.3 (0.1)	0.1 (0)	0.4 (0)	34.4 (3.5)	1.4 (1.8)	1.6 (0.6)
F	550	DL	DL	0.1 (0)	33.5 (2.6)	0.4 (4.1)	DL
G	CTRL	2.7 (0)	0.5 (0)	4.6 (0)	DL	100 (0)	1.2 (0)
G	150	6.9 (0.2)	1.4 (0)	5.0 (0)	0.8 (0.2)	107.4 (1.0)	2.7 (0.1)
G	250	12.7 (0.5)	2.5 (0.1)	3.6 (0)	4.0 (0.6)	75.3 (0.5)	7.0 (0.3)
G	350	5.5 (0.5)	1.1 (0.1)	0.9 (0)	8.5 (0.4)	17.2 (0)	12.6 (1.1)
G	450	0.4 (0)	0.1 (0)	0.1 (0)	9.7 (0.2)	2.8 (0)	5.5 (0.2)
G	550	DL	DL	DL	9.9 (0.2)	0.7 (0)	0.5 (0.1)
Н	CTRL	2.4 (0)	0.5 (0)	4.6 (0.1)	DL	100 (0.1)	1.0 (0)
Н	150	6.7 (0.1)	1.3 (0)	4.3 (0.1)	0.9 (0.1)	92.3 (0.4)	3.1 (0.1)
Н	250	11.2 (0.2)	2.2 (0)	3.1 (0)	4.2 (0.4)	63.9 (0.2)	7.3 (0.1)
Н	350	3.6 (0.1)	0.7 (0)	0.8 (0)	8.1 (0.3)	15.8 (0.1)	9.0 (0.3)
Н	450	0.3 (0)	0.1 (0)	0.2 (0)	12.6 (0.6)	3.1 (0.1)	4.0 (0.2)

Table I-1 cont'd

Table I-1 cont'd

Subsample ID	Temperature (°C)	DOC (mg L <sup>-1</sup> )	$\begin{array}{c} DOC \\ (mg_{OC} \ g^{-1}_{dry \ material}) \end{array}$	Carbon Content (%)	Mass Loss (%)	OC Remaining (%)	WEOC (%)
Н	550	DL	DL	DL	13.3 (0.4)	0.9 (0)	DL
Ι	CTRL	10.0 (0.1)	2.0 (0)	16.9 (0.1)	DL	100 (0.1)	1.2 (0)
Ι	150	23.4 (0.5)	4.7 (0.1)	15.8 (0)	2.7 (0.3)	90.9 (1.4)	3.0 (0.1)
Ι	250	30.4 (0.4)	6.1 (0.1)	12.6 (0.1)	19.7 (4.1)	59.8 (2.1)	4.8 (0.1)
Ι	350	11.0 (0.2)	2.2 (0)	1.7 (0)	21.1 (1.0)	8 (0.1)	12.9 (0.2)
Ι	450	0.7 (0.1)	0.1 (0)	0.4 (0)	23.6 (0.6)	1.9 (0)	3.5 (0.4)
Ι	550	DL	DL	0.2 (0)	25.2 (0.7)	0.8 (0)	0.3 (0)

Table I-2: Carbon-based parameters for site-averaged soil data. Mean values of analysis and standard errors in brackets (where n=3)

Site	Temperature (°C)	DOC (mg L <sup>-1</sup> )	DOC (mgoc g <sup>-1</sup> dry material)	Carbon Content (%)	OC Remaining (%)	WEOC (%)
NED	CTRL	3.1 (1.7)	0.6 (0.3)	6.2 (2.5)	100 (39.7)	1.0 (0.3)
NED	150	8.6 (3.4)	1.7 (0.7)	6.4 (2.9)	102.9 (46.9)	2.9 (0.5)
NED	250	16.7 (4.6)	3.3 (0.9)	5.8 (2.4)	88.4 (35.5)	6.5 (2.0)
NED	350	5.5 (0.9)	1.1 (0.2)	1.6 (0.6)	22.9 (7.5)	7.5 (2.5)
NED	450	0.4 (0.1)	0.1 (0)	0.2 (0.1)	3.0 (0.6)	4.2 (1.1)
NED	550	DL	DL	DL	0.5 (0.2)	0.7 (2.0)
FLG	CTRL	3.1 (0.4)	0.6 (0.1)	9.4 (6.6)	151.4 (87)	0.9 (0.3)
FLG	150	12.1 (4.5)	2.4 (0.9)	8.6 (5.8)	137.6 (74.5)	3.1 (0.5)
FLG	250	9.2 (2.2)	1.8 (0.4)	6.0 (3.8)	84.8 (37.8)	3.9 (1.8)
FLG	350	3.3 (0.6)	0.7 (0.1)	1.7 (0.9)	22.9 (8.5)	4.5 (1.8)
FLG	450	0.3 (0.1)	0.1 (0.0)	0.2 (0.1)	2.8 (0.7)	3.3 (1.5)
FLG	550	DL	DL	0.1 (0)	0.7 (0.3)	0.4 (1.1)

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Table	1-1	cont'd
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Site	Temperature (°C)	DOC (mg L <sup>-1</sup> )	$\frac{DOC}{(mg_{OC}\ g^{-1}_{dry\ material})}$	Carbon Content (%)	OC Remaining (%)	WEOC (%)
GROSS	CTRL	5.0 (3.5)	1.0 (0.7)	8.7 (7.1)	141.1 (93.5)	1.1 (0.1)
GROSS	150	12.3 (7.8)	2.5 (1.6)	8.4 (6.4)	132.8 (82)	2.9 (0.2)
GROSS	250	18.1 (8.7)	3.6 (1.7)	6.4 (5.3)	89.3 (52.7)	6.4 (1.1)
GROSS	350	6.7 (3.2)	1.3 (0.6)	1.1 (0.5)	15.5 (4.4)	11.5 (1.9)
GROSS	450	0.5 (0.2)	0.1 (0)	0.2 (0.2)	3.2 (1.4)	4.3 (0.9)
GROSS	550	DL	DL	0.1 (0.1)	1.1 (0.7)	0.3 (0.6)

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Subsample ID	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> + NO <sub>2</sub> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mgon g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	٨	CTDI	0.12	0.02	0.02	0.08	0.02	0.19	100	0.08
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	A	CIKL	(0.02)	(0)	(0)	(0.01)	(0)	(0.02)	(0.02)	(0.02)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	٨	150	0.27	0.05	0.01	0.22	0.04	0.17	87.4	0.26
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Λ	150	· /	(0.01)	(0)	· /	· /	· /	· · · ·	(0.06)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	٨	250	1.37	0.25	וח	1.14	0.23	0.22 (	109.8	1.04
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	A	230	(0.05)	(0)	DL	(0.05)	(0.01)	0)	(0.03)	(0.05)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	٨	350	0.63	0.09	וח	0.55	0.11	0.14	69.8	0.77
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	A	330	(0.04)	(0.01)	DL	(0.04)	(0.01)	(0.02)	(0.02)	(0.1)
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	٨	450	0.07	0.01	וח	0.06	0.01	0.04	21.0	0.28
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Λ	430	(0.01)	(0.01)	DL	(0.02)	(0)	(0)	(0)	(0.07)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	٨	550	0.02	0.01	וח	0.01	DI	0.01	4.4 (	0.27
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	A	550	(0.01)	(0)	DL	(0.01)	DL	(0)	0)	(0.12)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	D	CTDI	0.31	0.04	0.08	0.2	0.04	0.61	100	0.06
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	D	CIKL	(0.01)	(0)	(0)	(0.02)	(0)	(0.02)	(0.02)	(0.01)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	D	150	0.82	0.09	0.08	0.66	0.13	0.59	96.9	0.22
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	D	150		(0)	(0)		(0)	(0.01)	· /	(0.01)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	B	250	2.42	0.28	וח		0.43	0.71	109.7	0.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	D	230	(0.08)	(0.01)	DL		(0.02)	(0.08)	(0.14)	(0.07)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	B	350	0.98	0.11	וח	0.88	0.18	0.44	61.7	0.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	D	550	(0.01)	(0)	DL	(0.01)	. ,	(0.01)	(0.03)	(0.01)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	B	450			וח					0.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	D	430	(0.01)	(0.01)	DL		(0.01)	(0)	(0)	(0.27)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	B	550	0.03	וח	וח	0.02	DI	0.01	1.9	0.32
	D	550	· · · ·						. /	(0.09)
(0.01) $(0.01)$ $(0.01)$ $(0.02)$ $(0.02)$ $(0.02)$ $(0.02)$ $(0.02)$	C	CTRI								0.14
	C	CIKL	(0.01)	(0.01)	(0)	(0.02)	(0)	(0.02)	(0.02)	(0.01)
	C	150								0.23
(0.04) $(0)$ $(0)$ $(0.04)$ $(0.01)$ $(0)$ $(0.09)$ $(0)$	C	150	(0.04)	(0)	(0)	(0.04)	(0.01)	(0)	(0.09)	(0.01)

Table I-3: Nitrogen-based parameters for discretized soil subsamples. Mean values of analysis and standard errors in brackets.

Table I-3 cont'd

Subsample ID	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> + NO <sub>2</sub> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mg <sub>ON</sub> g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
С	250	3.04	0.32	DL	2.72	0.54	0.66	108.8	0.82
C	230	(0.09)	(0.01)	DL	(0.09)	(0.02)	(0.02)	(0.06)	(0.04)
С	350	1.25	0.11	DL	1.16	0.23	0.39	57.0	0.6
C	330	(0.02)	(0.01)	DL	(0.02)	(0)	(0.01)	(0.01)	(0.02)
С	450	0.18	0.01	DL	0.18	0.04	0.08	10.9	0.47
C	450	(0.03)	(0.01)	DL	(0.03)	(0.01)	(0.01)	(0)	(0.09)
С	550	0.05	DL	DL	0.05	0.01	0.01	2.0	0.65
C	550	(0.01)			(0.01)	(0)	(0)	(0)	(0.17)
D	CTRL	0.21	0.05	0.02	0.16	0.03	0.27	100	0.12
D	CIKL	(0.01)	(0.01)	(0)	(0)	(0)	(0)	(0)	(0)
D	150	0.55	0.08	0.02	0.47	0.09	0.31	113.5	0.3
D	150	(0.05)	(0.01)	(0)	(0.05)	(0.01)	(0.03)	(0.04)	(0.04)
D	250	0.99	0.19	DL	0.79	0.16	0.26	91.7	0.61
D	230	(0.16)	(0.02)	DL	(0.15)	(0.03)	(0.02)	(0.05)	(0.13)
D	350	0.54	0.1	DL	0.44	0.09	0.21	70.4	0.42
D	550	(0.05)	(0.01)	DL	(0.04)	(0.01)	(0.02)	(0.03)	(0.05)
D	450	0.09	DL	DL	0.09	0.02	0.04	12.9	0.48
D	450	(0.02)		DL	(0.02)	(0)	(0)	(0)	(0.12)
D	550	0.01	DL	DL	0.01	DL	0.01	2.3	0.38
D	550	(0.01)			(0.01)		(0)	(0)	(0.15)
Е	CTRL	0.23	0.03	0.01	0.2	0.04	0.44	100	0.09
L	CIRL	(0.01)	(0)	(0)	(0.01)	(0)	(0.01)	(0.01)	(0.01)
Е	150	0.55	0.07	0.01	0.48	0.1	0.34	77.3	0.29
Ľ	150	(0.02)	(0.01)	(0)	(0.03)	(0.01)	(0.02)	(0.08)	(0.02)
Е	250	1.64	0.24	DL	1.41	0.28	0.38	83.4	0.74
Ľ	230	(0.04)	(0.01)		(0.03)	(0.01)	(0.03)	(0.07)	(0.07)
Е	350	0.72	0.06	DL	0.67	0.13	0.22	44.9	0.61
Ľ	550	(0.01)	(0)		(0.01)	(0)	(0.02)	(0.02)	(0.06)
Е	450	0.16	DL	DL	0.16	0.03	0.05	9.6	0.65
Ľ	150	(0.01)			(0)	(0)	(0)	(0)	(0.03)

Table I-3 cont'd

Subsample ID	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO5 <sup>2-</sup> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mg <sub>ON</sub> g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
Е	550	0.03	DL	DL	0.03	0.01	0.01	1.5	0.77
Ľ	550	(0.00)	DL	DL	(0)	(0)	(0)	(0)	(0.05)
F	CTRL	0.32	0.05	0.04	0.23	0.05	0.88	100	0.05
1	CIKL	(0.01)	(0)	(0)	(0)	(0)	(0.02)	(0.02)	(0)
F	150	1.22	0.27	0.05	0.72	0.14	0.72	80.8	0.2
1	150	(0.03)	(0.01)	(0)	(0.04)	(0.01)	(0.01)	(0.1)	(0.01)
F	250	1.04	0.15	DL	1.07	0.21	0.94	87.2	0.23
1	230	(0.06)	(0.01)	DL	(0.05)	(0.01)	(0.02)	(0.05)	(0.01)
F	350	0.83	0.1	DL	0.74	0.15	0.56	50.2	0.27
1	550	(0.05)	(0.01)	DL	(0.04)	(0.01)	(0.03)	(0.04)	(0.02)
F	450	0.14	DL	DL	0.14	0.03	0.08	5.7	0.38
1	430	(0.01)	DL	DL	(0.01)	(0)	(0.01)	(0.01)	(0.07)
F	550	0.02	DL	DL	0.02	DL	0.01	0.7	0.42
1	550	(0.01)	DL	DL	(0.01)	DL	(0)	(0)	(0.18)
G	CTRL	0.18	0.02	0.02	0.13	0.03	0.22	100	1.2
U	CIKL	(0.01)	(0)	(0)	(0.01)	(0)	(0)	(0)	(0.1)
G	150	0.4	0.05	0.02	0.32	0.06	0.24	109.2	2.64
U	150	(0.01)	(0)	(0.01)	(0.01)	(0)	(0)	(0.05)	(0.12)
G	250	1.39	0.2	0.01	1.18	0.24	0.23	101.4	10.11
U	230	(0.05)	(0)	(0)	(0.05)	(0.01)	(0)	(0.03)	(0.43)
G	350	0.71	0.08	DL	0.63	0.13	0.13	55.2	9.49
U	330	(0.05)	(0)	DL	(0.05)	(0.01)	(0)	(0.01)	(0.77)
G	450	0.09	0.02	DL	0.07	0.01	0.03	13.3	4.4
U	430	(0.01)	(0.01)	DL	(0.01)	(0)	(0)	(0)	(0.92)
G	550	0.01	0.01	0.01	DL	DL	0.01	2.8	0.0
U	550	(0.01)	(0)	(0.01)	DL	DL	(0)	(0)	0.0
Н	CTRL	0.2	0.03	0.01	0.16	0.03	0.22	100	1.47
11	UIKL	(0.03)	(0.01)	(0)	(0.02)	(0)	(0.01)	(0.01)	(0.2)
Н	150	0.41	0.06	0.01	0.35	0.07	0.21	95.4	3.35
11	150	(0.01)	(0)	(0)	(0)	(0)	(0)	(0.02)	(0.04)

Tab	le I-3	cont'd	

Subsample ID	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> + NO <sub>2</sub> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mgon g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
Н	250	1.25	0.18		1.06	0.21	0.21	91.8	10.12
п	250	(0.01)	(0.01)	DL	(0.01)	(0)	(0)	(0.02)	(0.09)
Н	350	0.46	0.07	DL	0.38	0.08	0.13	53.9	5.99
П	550	(0.02)	(0)	DL	(0.02)	(0)	(0)	(0.01)	(0.36)
Н	450	0.07	0.03	DI	0.04	0.01	0.04	14.5	2.23
П	430	(0.01)	(0.01)	DL	(0.01)	(0)	(0)	(0)	(0.45)
Н	550	0.03	0.01	DL	0.01	DL	0.01	3.1	0
п	550	(0.01)	(0.01)	DL	(0)	DL	(0)	(0)	0
Ι	CTRL	0.74	0.1	0.01	0.63	0.13	0.77	100	1.64
1	CIKL	(0.03)	(0)	(0)	(0.03)	(0.01)	(0)	(0)	(0.08)
Ι	150	1.3	0.11	0.01	1.18	0.24	0.69	86.9	3.43
1	150	(0.02)	(0.01)	(0)	(0.01)	(0)	(0.01)	(0.06)	(0.05)
Ι	250	2.71	0.24	0.01	2.47	0.49	0.86	89.2	5.77
1	230	(1.51)	(0.01)	(0)	(0.12)	(0.02)	(0.02)	(0.14)	(0.3)
Ι	350	1.27	0.13	DL	1.14	0.23	0.24	24.5	9.53
1	330	(0)	(0)	DL	(0.02)	(0)	(0)	(0.01)	(0.19)
Ι	450	0.19	0.03	DL	0.17	0.03	0.06	6.3	5.24
1	450	(0)	(0)	DL	(0.04)	(0.01)	(0)	(0)	(1.31)
Ι	550	0.01	0.02	DL	DL	DL	0.01	1.1	0
1	550	(0)	(0)	DL	DL	DL	(0)	(0)	0

Site	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> + NO <sub>2</sub> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mgon g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
NED	CTRL	0.3	0.3	0.04	0.22	0.04	0.46	100.0	0.1
NED	CIKL	(0.14)	(0.14)	(0.04)	(0.13)	(0.03)	(0.19)	(0.19)	(0.03)
NED	150	0.64	0.07	0.04	0.53	0.11	0.47	101.6	0.24
NED	150	(0.26)	(0.03)	(0.03)	(0.23)	(0.05)	(0.21)	(0.21)	(0.02)
NED	250	2.28	0.28	DL	1.99	0.4	0.53	109.35	0.82
NED	230	(0.69)	(0.03)	DL	(0.66)	(0.13)	(0.22)	(0.2)	(0.22)
NED	350	0.95	0.1	DL	0.85	0.17	0.32	60.95	0.59
NED	330	(0.25)	(0.01)	DL	(0.25)	(0.05)	(0.13)	(0.1)	(0.18)
NED	450	0.14	0.02	DL	0.11	0.02	0.06	10.83	0.38
NED	430	(0.05)	(0.01)	DL	(0.06)	(0.01)	(0.01)	(0.01)	(0.1)
NED	550	0.03	DL	DL	0.03	0.01	0.01	2.3	0.41
NED	550	(0.01)	DL		(0.02)	(0)	(0)	(0)	(0.21)
FLG	CTRL	0.26	0.04	0.02	0.19	0.04	0.53	100.0	0.09
TLU	CIKL	(0.05)	(0.01)	(0.02)	(0.03)	(0.01)	(0.26)	(0.26)	(0.03)
FLG	150	0.77	0.14	0.03	0.61	0.12	0.46	85.4	0.26
TLU	150	(0.31)	(0.11)	(0.02)	(0.2)	(0.04)	(0.19)	(0.18)	(0.06)
FLG	250	1.22	0.19	DL	1.02	0.2	0.53	86.94	0.53
TLU	250	(0.3)	(0.04)	DL	(0.29)	(0.06)	(0.29)	(0.22)	(0.27)
FLG	350	0.7	0.09	DL	0.61	0.12	0.33	52.14	0.43
TLU	330	(0.12)	(0.02)	DL	(0.13)	(0.03)	(0.16)	(0.12)	(0.17)
FLG	450	0.13	DL	DL	0.13	0.03	0.05	8.02	0.5
TLU	430	(0.03)	DL	DL	(0.03)	(0.01)	(0.02)	(0.01)	(0.14)
FLG	550	0.02	DL	DL	0.02	DL	0.01	1.17	0.52
I'LU	550	(0.01)			(0.01)		(0)	(0)	(0.21)
GROSS	CTRL	0.37	0.05	0.01	0.31	0.06	0.38	100.0	1.44
010055	UINL	(0.26)	(0.03)	(0.01)	(0.23)	(0.05)	(0.22)	(0.26)	(0.22)

Table I-4: Nitrogen-based parameters for site-averaged soil data. Mean values of analysis and standard errors in brackets (where n=3)

Site	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO <sub>3</sub> + NO <sub>2</sub> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mgon g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
GROSS	150	0.7	0.07	0.01	0.62	0.12	0.38	92.52	3.14
01055	150	(0.42)	(0.03)	(0.01)	(0.40)	(0.08)	(0.22)	(0.21)	(0.44)
GROSS	250	1.78	0.21	0.01	1.57	0.31	0.43	91.9	8.66
OROSS		(0.66)	(0.02)	(0)	(0.64)	(0.13)	(0.3)	(0.22)	(2.51)
GROSS	350	0.81	0.09	DL	0.72	0.14	0.17	35.41	8.34
UKUSS	550	(0.34)	(0.03)	DL	(0.32)	(0.06)	(0.05)	(0.03)	(2.04)
GROSS	450	0.12	0.03	DL	0.09	0.02	0.04	9.03	3.96
GROSS	450	(0.05)	(0.01)	DL	(0.06)	(0.01)	(0.01)	(0.01)	(1.55)
GROSS	550	0.02	0.01	DL	DL	DL	0.01	1.75	0.74
01(055	550	(0.01)	(0.01)	DL	DL	DL	(0)	(0)	(1.29)

Table I-4 cont'd

Subsample ID	Temperature (°C)	Al	Ca	Fe	K	Mg	Mn	Na	Si
А	CTRL	DL	39.7	DL	163.1	10.7	DL	9.3	23.8
			(3.0)		(35.8)	(0.5)		(2.3)	(6.3)
А	150	DL	95.8	DL	172.1	24.4	DL	8.6	30.6
			(4.4)		(51.1)	(1.5)		(4.5)	(5.3)
А	250	10.1	584.6	3.2	209.7	115.4	30.2	19.5	50.9
		(0.5)	(4.9)	(0.5)	(45.3)	(2.8)	(1.4)	(16.3)	(4.3)
А	350	21.0	577.2	DL	201.9	76.7	2.8	8.7	48.4
		(0.6)	(46.4)		(23.9)	(4.9)	(0.4)	(2.9)	(2.6)
А	450	90.7	563.6	DL	146.6	50.9	DL	16.1	55.2
		(3.3)	(11.6)		(27.0)	(1.3)		(5.3)	(1.2)
А	550	76.5	302.7	DL	175.9	31.6	DL	19.4	69.0
		(4.1)	(8.5)		(48.9)	(1.5)		(3.4)	(2.8)
В	CTRL	3.9	351.7	0.6	226.4	12.2	DL	12.5	15.8
	-	(0.6)	(585.5)	(1.1)	(70.3)	(0.7)		(7.9)	(4.6)
В	150	6.2	180.4	DL	247.0	38.0	5.6	4.9	16.5
_		(0.4)	(2.5)		(16.3)	(0.9)	(0.2)	(1.0)	(4.3)
В	250	28.1	1023.9	4.7	276.8	156.6	65.8	9.3	32.1
		(0.8)	(46.8)	(0)	(28.1)	(7.2)	(2.1)	(2.2)	(1.2)
В	350	134.5	1293.7	DL	262.7	128.3	3.6	15.2	38.2
		(6.7)	(12.0)		(53.9)	(2.9)	(0.1)	(1.6)	(1.3)
В	450	569.2	1585.3	DL	302.0	120.5	DL	13.2	64.6
		(18.2)	(82.5)		(29.3)	(2.8)		(2.1)	(11.3)
В	550	618.8	1288.5	DL	327.0	76.0	DL	28.6	78.7
		(18.3)	(41.4)		(81.0)	(2.3)		(1.2)	(19.3)
С	CTRL	4.7	86.4	0.6	189.2	25.9	DL	11.9	24.6
		(2.5)	(1.1)	(1.2)	(22.0)	(0.9)		(1.3)	(3.3)
С	150	7.9	201.7	0.9	312.8	57.2	4.9	9.1	24.9
		(1.7)	(7.0)	(1.1)	(87.3)	(1.2)	(0.6)	(0.9)	(1.5)

Table I-5: Discretized soluble elements data (expressed in  $\mu$ g element per g of soil) for subsamples A, B, and C (NED), D, E, and F (FLG). Mean values of analysis and standard deviation (n=4) in brackets.

Table I-5 cont'd

Subsample ID	Temperature (°C)	Al	Ca	Fe	K	Mg	Mn	Na	Si
С	250	35.9 (1.1)	1275.9 (46.6)	7.5 (1.1)	271.6 (19.8)	254.2 (10.9)	52.5 (3.3)	10.6 (3.2)	35.6
С	350	(1.1) 176.1 (13.0)	(40.0) 1628.6 (99.2)	(1.1) DL	(19.8) 234.7 (40.7)	(10.9) 199.6 (10.2)	(3.3) DL	(3.2) 19.8 (3.6)	(1.7) 57.7 (3.0)
С	450	384.6 (4.8)	(559.4 (14.4)	DL	228.0 (38.7)	137.5 (1.9)	DL	7.3 (1.4)	87 (4.4)
С	550	374.5 (14.7)	921.8 (579.3)	DL	220.7 (70.1)	59.3 (31.7)	DL	21.9 (11)	87.9 (5.1)
D	CTRL	4.4 (0.5)	24.7 (2.0)	0.5 (0.9)	144.7 (34.4)	7.5 (0.3)	DL	6.8 (1.1)	5.5 (3.7)
D	150	8.5 (2.4)	101.2 (2.3)	DL	211.1 (43.9)	27.3 (0.8)	7.5 (0.6)	8.5 (2.5)	12.7 (2.6)
D	250	19.2 (2.9)	275.8 (33.5)	6.4 (1.6)	144.1 (9.2)	58.3 (8.2)	27.0 (3.3)	12.3 (1.5)	17.0 (6.4)
D	350	4.8 (1.0)	298.9 (18.5)	DL	137.4 (27.6)	45.3 (3.6)	9.6 (0.2)	14.1 (2.4)	36.2 (8.5)
D	450	221.5 (4.1)	535.6 (5.3)	DL	106.7 (24.4)	52.3 (1)	1.4 (1.0)	11.7 (1.0)	50.8 (6.1)
D	550	288.7 (6.7)	527.4 (6.5)	DL	113.6 (18.6)	51.7 (1.6)	DL	12.9 (2.8)	67.6 (3.2)
Ε	CTRL	4.8 (1.6)	59.6 (1.3)	DL	110.5 (50.7)	13.1 (0.2)	DL	2.0 (4.0)	11.6 (3.2)
Ε	150	8.5 (0.5)	196 (8.2)	DL	143.1 (25.8)	40.8 (1.9)	4.2 (0.1)	10.1 (2)	12.6 (4.7)
Ε	250	31.2 (2.8)	668.9 (8)	9.6 (1.9)	167.2 (408.8)	99.1 (2.9)	25.1 (0.8)	16.6 (7.9)	18.2 (6.0)
Ε	350	198.8 (6.0)	928.2 (30.2)	DL	124.2 (34.6)	79.1 (3.5)	DL	10.8 (1.9)	38.5 (1.5)

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Table	1-2	cont'd
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Subsample ID	Temperature (°C)	Al	Ca	Fe	К	Mg	Mn	Na	Si
Е	450	517	1146.8	DL	DL	75.8	DL	9.1	66.0
-	100	(2.1)	(18.6)	(18.6)		(2.4)	22	(2.6)	(2.0)
Е	550	527.1	1028.7	DL	292.8	59.4	DL	11.9	92.0
Ľ	550	(7.9)	(4.7)	DL	(368.8)	(0.7)	DL	(1.8)	(7.0)
F	CTRL	5.5	48.4	DI	142.9	11.4	1.6	5.6	10.5
Г	CIKL	(0.4)	(0.5)	DL	(35.9)	(0.4)	(1.0)	(1.4)	(2.5)
F	150	14.3	277.1	3.2	206.8	63.1	20.6	7.4	12.0
Г	150	(0.9)	(5.2)	(2.2)	(21)	(1.8)	(0.9)	(2.1)	(3.2)
Б	250	12.8	717.5	1.0	198.8	122.3	37.9	12.7	36.6
F	250	(1.1)	(21.8)	(2.0)	(19.5)	(4.4)	(0.6)	(0.2)	(8.2)
F	250	234.3	1524.3	DI	205.2	153.3	4.1	17.0	71.3
Г	350	(11.6)	(96.5)	DL	(24.8)	(9.8)	(0.2)	(1.2)	(2.7)
Б	450	845.1	2161.9	DI	178.6	121.5	DI	18.0	104
F	450	(39.0)	(115.6)	DL	(19.3)	(4.8)	DL	(2.4)	(3.5)
	~ ~ ~	815.4	1809.1	DI	173.7	70.5	DI	24.5	128.4
F	550	(36.5)	(113.5)	DL	(58.8)	(1.5)	DL	(3.2)	(23.3)

Temperature (°C)	Al	Ca	Fe	K	Mg	Mn	Na	Si
CTRI	2.0	61.9	וח	192.9	16.7	וח	9.7	22.6
CIRL	(2.3)	(20.1)	DL	(48.5)	(7)	DL	(2.1)	(5.4)
150	4.7	159.3	וח	226.3	39.9	3.5	8.1	24.0
150	(3.5)	(45.9)	DL	(52.3)	(13.5)	(2.5)	(3.0)	(6.8)
250	24.7	961.5	5.1	256.6	175.4	49.5	10.4	39.5
250	(10.8)	(287.6)	(1.9)	(39)	(58.6)	(14.8)	(2.4)	(8.5)
350	110.5	1166.5	DI	238.4	134.9	2.2	14.5	48.1
550	(65.9)	(442.0)	DL	(41.7)	(50.7)	(1.6)	(5.2)	(8.2)
450	348.2	1236.1	DI	225.5	103.0	DI	12.2	69
-50	(197.3)	` '	DL	` '	(37.5)	DL	· /	(14.7)
550	355.0	908.8	DI	270.8	59.6	DI	24.9	81.5
550	` '	` '		· /	. ,		· /	(32.7)
CTRI								21.9
CIRL	(1.0)	(14.6)	(0.5)	(35.4)	(2.4)	(0.9)	(1.3)	(5.6)
150			1.5		43.8			12.5
150	. ,	` '	(2.4)	. ,	(14.8)	. ,	. ,	(3.8)
250			5.7					23.9
250		` '	(3.9)	` '	· /	· /	· /	(10.8)
350	170.5	917.1	DI	164.6	92.6	4.5	14.0	48.7
550	(90.4)	(503.0)	DL	(38.2)	(45.4)	(3.9)	(3.0)	(16.6)
450	527.9	1281.5	וח	95.1	83.2	0.5	13	73.6
+50	(255.5)	(673.3)	DL	(75)	(28.9)	(0.8)	(4.2)	(22.7)
550	543.7	1121.7	DI	132.2	60.5	Ы	16.4	91.9
550	(216.2)	(530.4)	DL	(42.6)	(7.8)	DL	(6.2)	(23.7)
	-	$\begin{array}{c c} (^{\circ}C) & AI \\ \hline CTRL & 2.0 \\ (2.3) \\ 150 & 4.7 \\ (3.5) \\ 250 & 24.7 \\ (10.8) \\ 350 & 110.5 \\ (65.9) \\ 450 & 348.2 \\ (197.3) \\ 550 & 231.8 \\ CTRL & 4.9 \\ (1.0) \\ 150 & 10.5 \\ (3.0) \\ 250 & 21.1 \\ (7.9) \\ 350 & 170.5 \\ (90.4) \\ 450 & 527.9 \\ (255.5) \\ 550 & 543.7 \\ \end{array}$	$\begin{array}{c c} \mathbf{(^{\circ}C)} & \mathbf{AI} & \mathbf{Ca} \\ \hline \mathbf{CTRL} & 2.0 & 61.9 \\ (2.3) & (20.1) \\ 150 & 4.7 & 159.3 \\ (3.5) & (45.9) \\ 250 & 24.7 & 961.5 \\ (10.8) & (287.6) \\ 350 & 110.5 & 1166.5 \\ (65.9) & (442.0) \\ 450 & 348.2 & 1236.1 \\ (197.3) & (475.7) \\ 550 & 355.0 & 908.8 \\ (231.8) & (460.3) \\ \mathbf{CTRL} & 4.9 & 44.3 \\ (1.0) & (14.6) \\ 150 & 10.5 & 502.2 \\ (3.0) & (435.8) \\ 250 & 21.1 & 554.1 \\ (7.9) & (198.8) \\ 350 & 170.5 & 917.1 \\ (90.4) & (503.0) \\ 450 & 527.9 & 1281.5 \\ (255.5) & (673.3) \\ 550 & 543.7 & 1121.7 \\ \end{array}$	$(^{\circ}C)$ AICaFeCTRL $2.0$ $61.9$ $(2.3)$ DL150 $4.7$ $159.3$ $(3.5)$ DL250 $24.7$ $(10.8)$ $961.5$ $5.1$ $(10.8)$ 250 $24.7$ 	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$(^{\circ}C)$ AICaFeKMgMnCTRL $2.0$ $61.9$ $(2.3)$ DL $192.9$ $16.7$ $(48.5)$ DL150 $4.7$ $159.3$ $(3.5)$ $45.9$ DL $226.3$ $39.9$ $3.5$ 250 $24.7$ $961.5$ $5.1$ $256.6$ $175.4$ $49.5$ $(10.8)$ $(287.6)$ $(1.9)$ $(39)$ $(58.6)$ $(14.8)$ $350$ $110.5$ $1166.5$ $(65.9)$ $442.0$ $0L$ $(41.7)$ $(50.7)$ $(1.6)$ $450$ $348.2$ $1236.1$ $(197.3)$ $0L$ $225.5$ $103.0$ $(69.3)$ $0L$ $231.4$ $550$ $355.0$ $(231.8)$ $908.8$ $(460.3)$ $DL$ $270.8$ $59.6$ $(231.8)$ $0.2$ $10.7$ $CTRL$ $4.9$ $(1.0)$ $44.3$ $0.2$ $127.0$ $10.7$ $0.5$ $(21.3)$ $0L$ $150$ $355.0$ $(231.8)$ $(460.3)$ $DL$ $(76.5)$ $(21.3)$ $DL$ $150$ $10.5$ $(3.0)$ $(435.8)$ $(2.4)$ $(42)$ $(14.8)$ $(7.1)$ $250$ $(7.9)$ $(198.8)$ $(3.9)$ $(27.4)$ $(26.9)$ $(5.9)$ $350$ $170.5$ $(7.9)$ $1281.5$ $(90.4)$ $527.9$ $1281.5$ $(255.5)$ $673.3)$ $DL$ $60.5$ $450$ $527.9$ $(255.5)$ $673.3$ $DL$ $95.1$ $83.2$ $0.5$ $550$ $543.7$ $1121.7$ $(255.5)$ $132.2$ $60.5$ $DL$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table I-6: Site-averaged soluble element data (expressed as ug per g of soil) for sites NED and FLG. Mean value of analysis and 1 standard deviation (n=3) in brackets.

## APPENDIX II: Summary of analyzed litter data

Site	Temperature (°C)	DOC (mg L <sup>-1</sup> )	DOC (mgOC g <sup>-1</sup> Dry Material)	%C	Mass Loss (%)	OC Remaining (%)	WEOC (%)
NED	CTRL	50.1 (1.6)	25.1 (0.8)	48.9 (0.1)	0	100.0 (0)	5.1 (0.3)
NED	150	57.4 (0.4)	28.7 (0.2)	50.4 (0.2)	6.8 (0)	96.1 (0.2)	5.7 (0.1)
NED	250	8.8 (0.2)	4.4 (0.1)	57.5 (0)	39.7 (3.6)	70.9 (3.1)	0.8 (0)
NED	350	6.4 (0)	3.2 (0)	51.6 (0.1)	75.5 (2.8)	25.9 (0.5)	0.6 (0)
NED	450	1.0 (0)	0.5 (0)	15.1 (0.6)	94.7 (0.6)	1.6 (0)	0.3 (0)
FLG	CTRL	70.4 (0.9)	35.2 (0.4)	51.8 (0.4)	0	100.0 (0)	6.8 (0.2)
FLG	150	64.3 (0.9)	32.1 (0.5)	53 (0.1)	4.6 (0.7)	97.7 (7.6)	5.7 (0.4)
FLG	250	7.3 (0.1)	3.6 (0)	57.9 (0)	48.9 (9.0)	57.2 (5.5)	0.8 (0)
FLG	350	3.1 (0)	1.5 (0)	67.4 (0.2)	71.1 (2.8)	37.6 (0.8)	0.4 (0.2)
FLG	450	1.2 (0)	0.6 (0)	65.4 (0.3)	82.1 (0)	22.6 (0.1)	0.1 (0)
GROSS	CTRL	30.5 (0.2)	15.3 (0.1)	48.8 (0.3)	0	100.0 (0)	3.1 (0.1)
GROSS	150	47.6 (0.5)	23.8 (0.3)	50.9 (0)	5.3 (0)	98.8 (0)	4.7 (0.1)
GROSS	250	5.8 (0.2)	2.9 (0.1)	59.2 (0.2)	45.5 (0.6)	66 (0.5)	0.5 (0)
GROSS	350	6.3 (0)	3.1 (0)	57.4 (0.5)	78.1 (3.8)	25.7 (0.6)	0.5 (0)
GROSS	450	0.9 (0)	0.4 (0)	59.7 (0.2)	86.4 (3.8)	16.7 (0.4)	0.1 (0)

Table II-1: Carbon-based parameters for litter material. Mean values of analysis and standard errors in brackets (where n=3)

Site	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO5 <sup>2-</sup> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mgon g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
NED	CTRL	1.5	0.12	DL	1.38	0.69	1.17	100.0	5.91
NED	CIKL	(0.01)	(0.02)	DL	(0.02)	(0.02)	(0.03)	(0)	(0.17)
NED	150	1.23	DL	DL	1.23	0.61	1.06	84.51	5.8
NED	150	(0.01)	DL	DL	(0.01)	(0.01)	(0.16)	(0.15)	(0.86)
NED	250	0.31	0.05	DL	0.27	0.13	1.34	69.23	1.0
NLD	250	(0.02)	(0)		(0.02)	(0.01)	(0.03)	(0.07)	(0.08)
NED	350	0.53	0.07	DL	0.46	0.23	2.44	51.17	0.94
NLD	550	(0)	(0)		(0)	(0)	(0)	(0.02)	(0.01)
NED	450	0.42	0.1	DL	0.31	0.16	1.17	5.3	1.34
NED	450	(0)	(0.01)		(0.01)	(0.01)	(0.05)	(0)	(0.07)
FLG	CTRL	0.97	DL	DL	0.97	0.49	0.54	100.0	8.99
TLO	CIKL	(0.01)			(0.01)	(0.01)	(0.01)	(0)	(0.15)
FLG	150	0.67	DL	DL	0.67	0.33	0.57	100.05	5.9
TLO	150	(0.01)			(0.01)	(0.01)	(0.03)	(0.09)	(0.37)
FLG	250	0.23	0.06	DL	0.17	0.09	1.65	155.92	0.53
TLO	250	(0)	(0.01)		(0.01)	(0)	(0.05)	(0.16)	(0.02)
FLG	350	0.09	0.04	DL	0.05	0.03	1.53	82.02	0.18
TLO	550	(0.01)	(0.01)		(0.01)	(0.01)	(0.1)	(0.03)	(0.04)
FLG	450	0.15	0.03	DL	0.12	0.06	1.81	59.82	0.33
TLO	-50	(0.02)	(0)	DL	(0.02)	(0.01)	(0.05)	(0.01)	(0.04)
GROSS	CTRL	0.9	0.07	DL	0.84	0.42	1.04	100	4.03
ORODD	CIRE	(0.02)	(0.01)		(0.02)	(0.02)	(0.03)	(0)	(0.15)
GROSS	150	0.75	DL	DL	0.75	0.38	0.98	89.94	3.82
01(055	150	(0.01)			(0.01)	(0)	(0.11)	(0.11)	(0.45)

Table II-2: Nitrogen-based parameters for litter material. Mean values of analysis and standard errors in brackets (where n=3).

Table II-2 cont'd

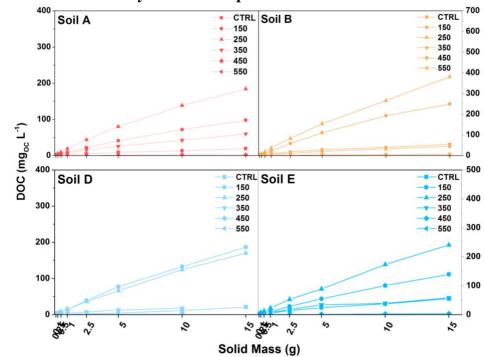
Site	Temperature (°C)	TDN (mg L <sup>-1</sup> )	NH4 <sup>+</sup> (mg L <sup>-1</sup> )	NO5 <sup>2-</sup> (mg L <sup>-1</sup> )	DON (mg L <sup>-1</sup> )	DON (mgon g <sup>-1</sup> Dry Material)	Nitrogen Content (%)	ON Remaining (%)	WEON (%)
GROSS	250	0.17 (0.01)	0.04	DL	0.13 (0.01)	0.06	1.02 (0.02)	53.4 (0.02)	0.62
		(0.01)	(0.01) 0.09		0.31	(0.01) 0.16	(0.02) 1.94	(0.02) 40.95	(0.06) 0.81
GROSS	350	(0)	(0)	DL	(0)	(0)	(0.01)	(0.02)	(0.01)
GROSS	450	0.16	0.05	DL	0.1	0.05	1.3	17.1	0.39
	430	(0)	(0)	DL	(0)	(0)	(0)	(0.01)	(0.01)

Site	Temperature (°C)	Al	Ca	Fe	K	Mg	Mn	Na	Si
NED	CTRL	13.1	260.5	17.9	2685.7	328.3	20.7	64.1	41.2
NED	CIKL	(1.2)	(1.1)	(0.3)	(329.4)	(7.6)	(0.1)	(5.5)	(0.1)
NED	150	8.4	340.3	16.3	2591.4	456.8	29.6	50.3	42.8
NLD	150	(0.2)	(13.5)	(3.5)	(122)	(8.8)	(0.8)	(28.7)	(3.1)
NED	250	12.9	285.2	12.3	3205.6	397.8	12.5	50.2	37.4
NLD	230	(0.7)	(15.2)	(1.6)	(547)	(9.9)	(0.6)	(13.1)	(1.3)
NED	350	45.6	2675.7	51.6	5108.7	1112.8	15.4	97.8	1568.2
NLD	550	(1.7)	(54.5)	(5.0)	(349.9)	(24.0)	(0.7)	(19.3)	(17.7)
NED	450	21.9	3686.4	69.1	23508.9	2418.7	0.1	252.3	3532.9
NLD	-30	(0.7)	(43.6)	(0.7)	(32.4)	(69.6)	(0)	(31.8)	(81.4)
FLG	CTRL	54.7	237.1	13.0	3070.4	346.1	43.6	41.7	38.8
I LO	CIRL	(0)	(0.7)	(3.6)	(487.9)	(9.5)	(0.1)	(0.1)	(1.8)
FLG	150	66.6	264.6	15.1	2082.7	402.1	57	74.4	33.4
I LO	150	(3.1)	(2.4)	(4.1)	(59.7)	(1.5)	(2.2)	(59)	(0.8)
FLG	250	53.5	1179.9	30.2	1801.9	427.0	35.1	78.6	40.8
I LO	230	(2.0)	(84.1)	(1.2)	(146.7)	(20.4)	(1.2)	(21.0)	(3.0)
FLG	350	12.0	1550.7	36.0	2412.6	663.6	28.9	77.2	174.8
TLO	550	(0.3)	(2.6)	(1.0)	(36.3)	(13.7)	(2.6)	(0.9)	(1.1)
FLG	450	557.1	2544.3	55.5	4382.7	988.3	5.4	106.4	570.7
I LO	450	(5.5)	(34.2)	(9.1)	(549.5)	(4.9)	(0.4)	(20.5)	(15)
GROSS	CTRL	9.5	214.9	11.2	4919.8	161.3	18.3	38.8	22.8
ORODD	CIAL	(0)	(1.4)	(0)	(2575.1)	(3.5)	(0)	(0)	(1.3)
GROSS	150	16.7	372	15.7	3634.4	305.5	36.2	47.6	30.6
UKObb	150	(0.5)	(7.5)	(0.9)	(585.5)	(4.9)	(0.5)	(24.5)	(0.9)
GROSS	250	18.3	367.3	18.5	1941.4	234.7	19.5	35.5	20.0
UKOSS	230	(0.1)	(4.0)	(2.4)	(31.4)	(2.2)	(0.3)	(10.6)	(0.6)
GROSS	350	15.6	3288.6	61.5	2951	846.1	36.9	77.8	493.2
01(000	550	(0.3)	(69.3)	(1.2)	(66.8)	(3.4)	(0)	(0.5)	(16.1)

Table II-3: Soluble element data for litter material, sites NED and FLG. Mean values of analysis and standard errors in brackets (where n=4).

Tabl	le I	I-3	cont'	d

Site	Temperature (°C)	Al	Ca	Fe	К	Mg	Mn	Na	Si
GROSS	450	365.6 (12.4)	2527.7 (75.9)		4212.5 (833.5)		2.2 (0)	80.8 (17.3)	988.2 (98.1)



**APPENDIX III:** Linearity and kinetics plots for soil and litter

Figure III-1: DOC linearity plots for soils, subsamples A, B, D, and E. Soil masses of 0.1, 0.25, 0.5, 1.0, 2.5, 5.0, 10, and 15 g per 100 mL of ultra-pure Milli-Q water were used for all temperatures.

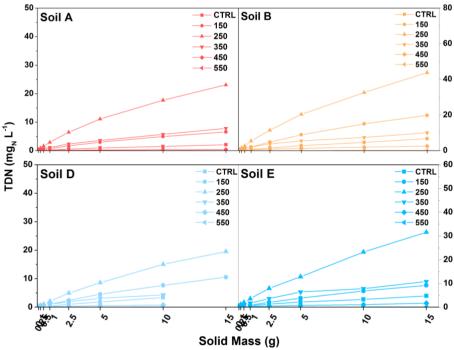


Figure III-2: TDN linearity plots for soils, subsamples A, B, D, and E. Soil masses of 0.1, 0.25, 0.5, 1.0, 2.5, 5.0, 10, and 15 g per 100 mL of ultra-pure Milli-Q water were used for all temperatures.

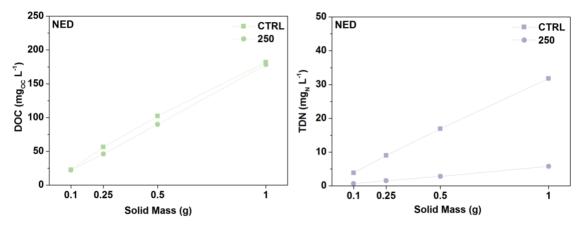


Figure III-3: DOC (left) and TDN (right) linearity for litter from sampling site, NED. Due to limited material, masses of 0.1, 0.25, 0.5, and 1.0 g per 100 mL of ultra-pure Millie-Q water were used for CTRL and 250°C only.

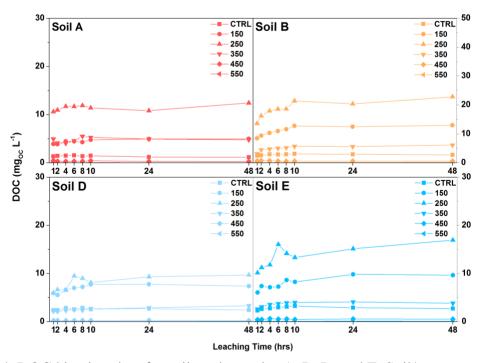


Figure III-4: DOC kinetics plots for soils, subsamples A, B, D, and E. Soil/water contact times of 1, 2, 4, 6, 8, 10, 24, and 48 hours with a soil concentration of 0.5 g soil per 100 mL of ultra-pure Milli-Q water were used for all temperatures.

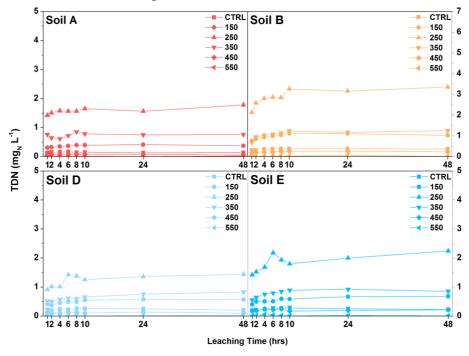


Figure III-5: TDN kinetics plots for soils, subsamples A, B, D, and E. Soil/water contact times of 1, 2, 4, 6, 8, 10, 24, and 48 hours with a soil concentration of 0.5 g soil per 100 mL of ultra-pure Milli-Q water were used for all temperatures.

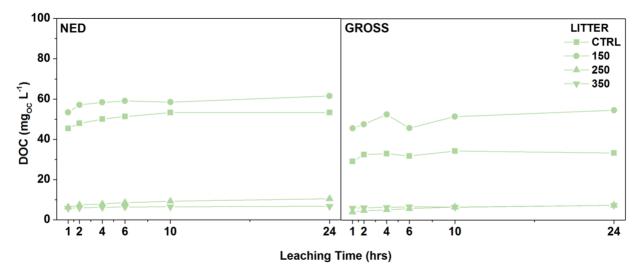


Figure III-6: DOC kinetics plots for litter, sites NED (left) and GROSS (right). Due to limited material, litter/water contact times of 1, 2, 4, 6, 10, and 24 with a litter concentration of 0.2 soil per 100 mL of ultra-pure Milli-Q water were used for temperatures up to 350°C.

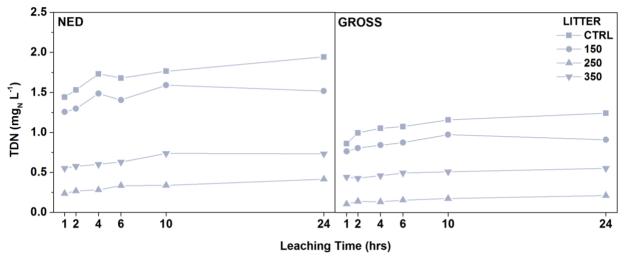
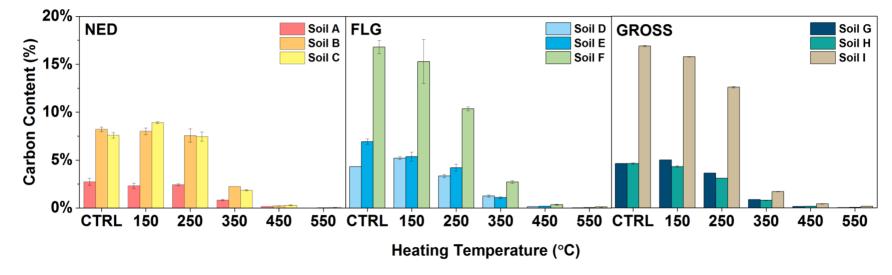


Figure III-7: DOC kinetics plots for litter, sites NED (left) and GROSS (right). Due to limited material, litter/water contact times of 1, 2, 4, 6, 10, and 24 with a litter concentration of 0.2 soil per 100 mL of ultra-pure Milli-Q water were used for temperatures up to 350°C.



**APPENDIX IV:** Carbon-based discretized soil data – C Content, C Remaining, DOC, WEOC

Figure IV-1: Discretized %C data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 standard deviation (n=2).

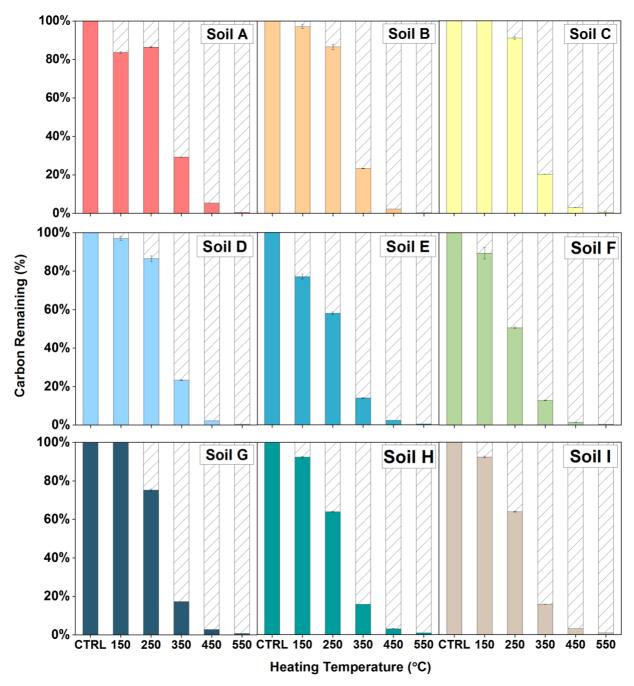


Figure IV-2: Discretized C remaining data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 propagated error between %C (n=2) and percent mass loss (n=10).

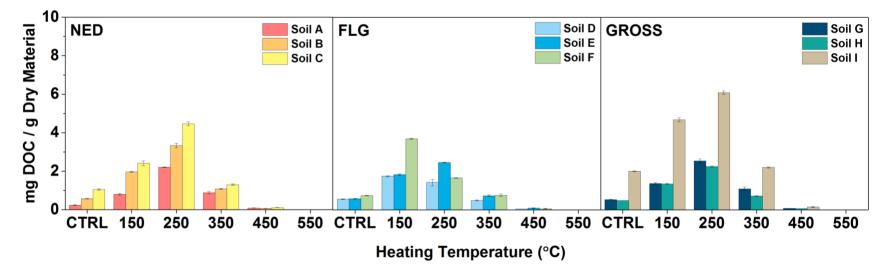


Figure IV-3: Discretized DOC data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 standard deviation (n=4).

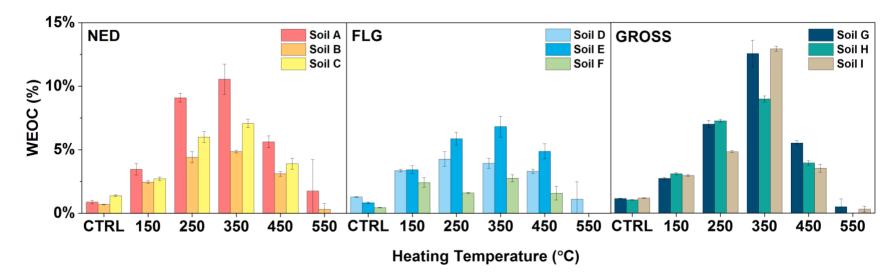
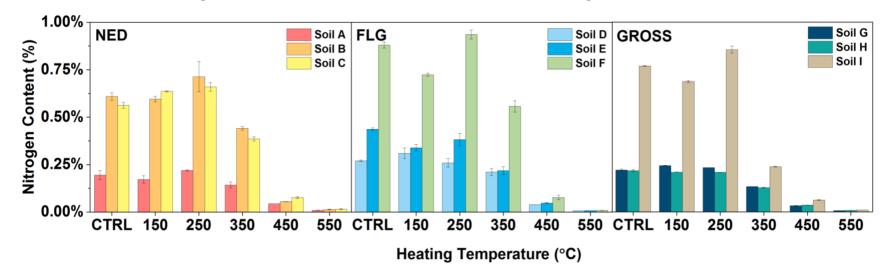


Figure IV-4: Discretized WEOC data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent propagated error between DOC (n=4) and %C (n=2).



APPENDIX V: Nitrogen-based discretized soil data - N Content, N Remaining, TDN, WEON

Figure V-1: Discretized %N data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 standard deviation (n=2).

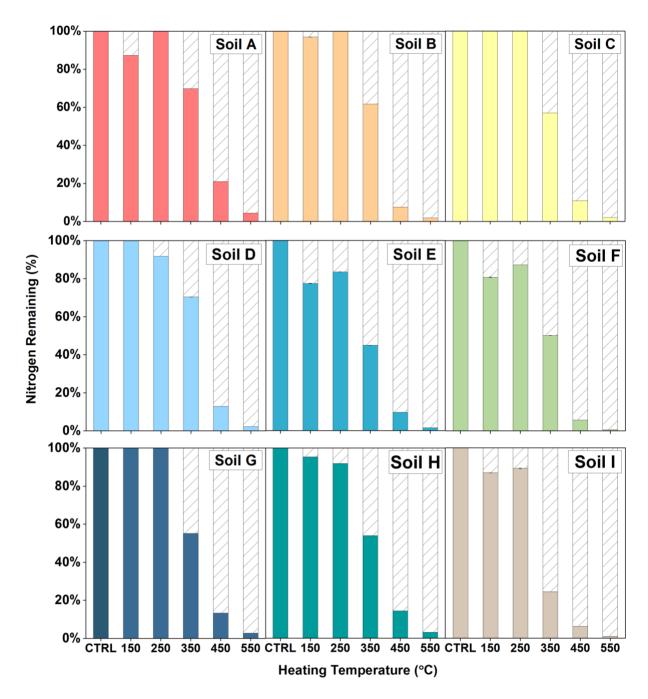


Figure V-2: Discretized N remaining data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 propagated error between %N (n=2) and percent mass loss (n=10).

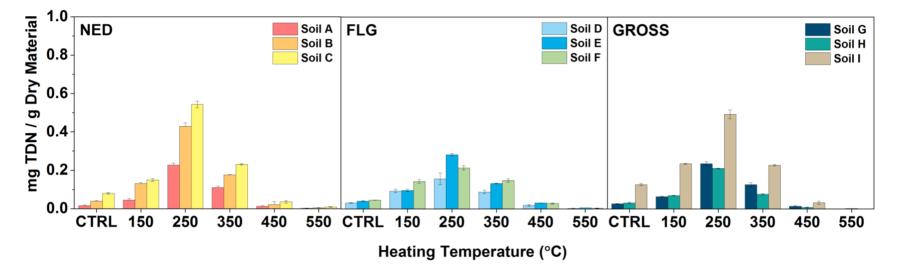


Figure V-3: Discretized TDN data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent 1 standard deviation (n=3).

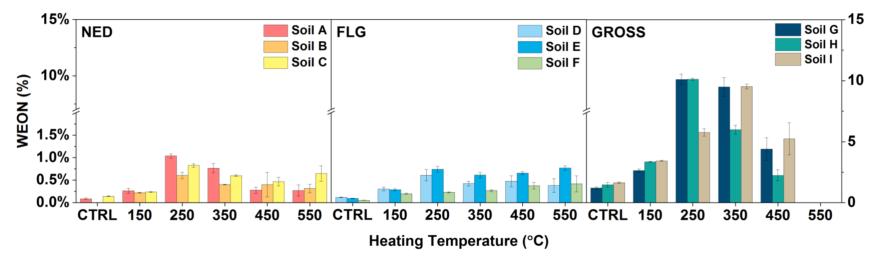
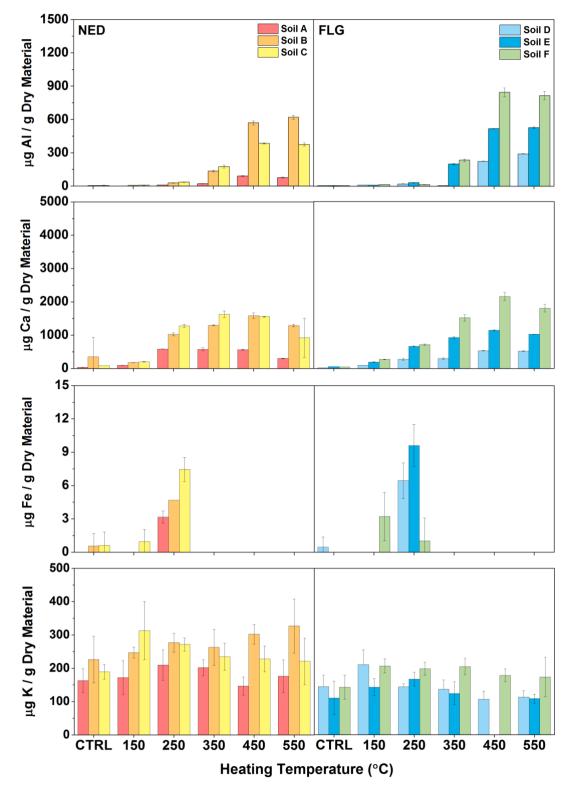


Figure V-4: Discretized WEOC data for NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent propagated error between TDN (n=3) and %C (n=2).



APPENDIX VI: Discretized soluble elements from soil for sub samples A, B, and C (NED) and D, E, and F (FLG).

Figure VI-1: Discretized soil data for Al, Ca, Fe, and K (top to bottom), sites NED (left panels) and FLG (right panels). Error bars represent 1 standard deviation (n=4).

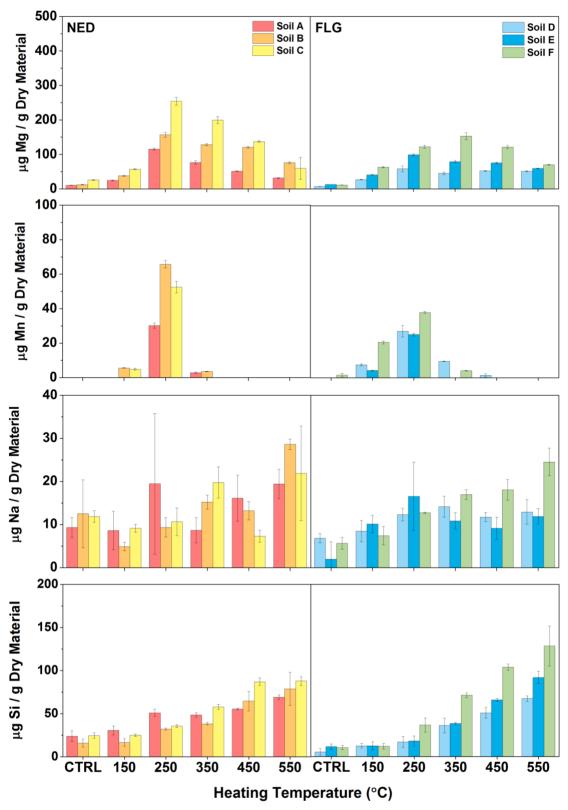
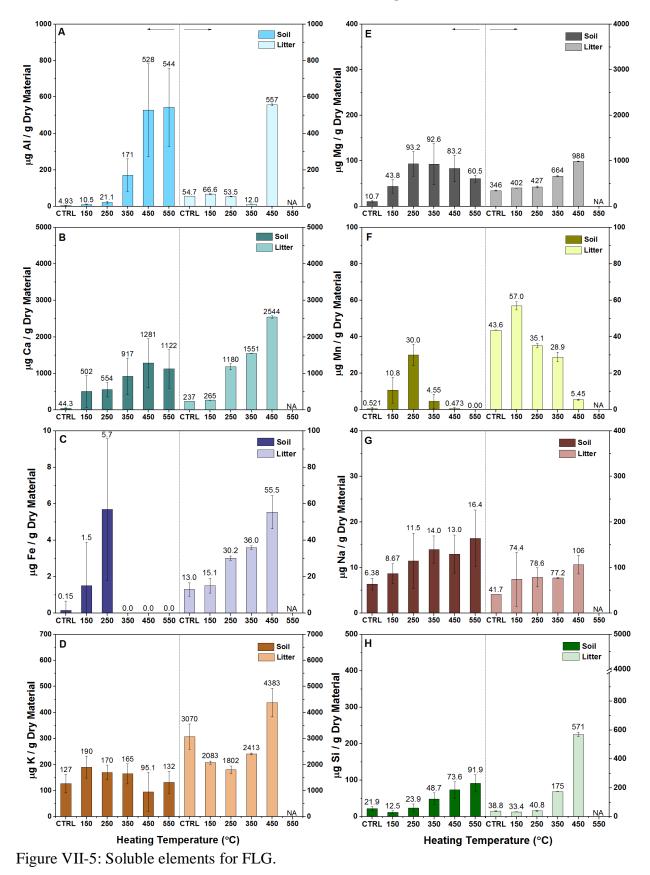


Figure VI-2: Discretized soil data for Mg, Mn, Na, and Si (top to bottom), sites NED (left panels) and FLG (right panels). Error bars represent 1 standard deviation (n=4).



APPENDIX VII: Soluble elements for FLG - site averaged soil and litter

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APPENDIX VIII: Discretized SUVA254 data for soil

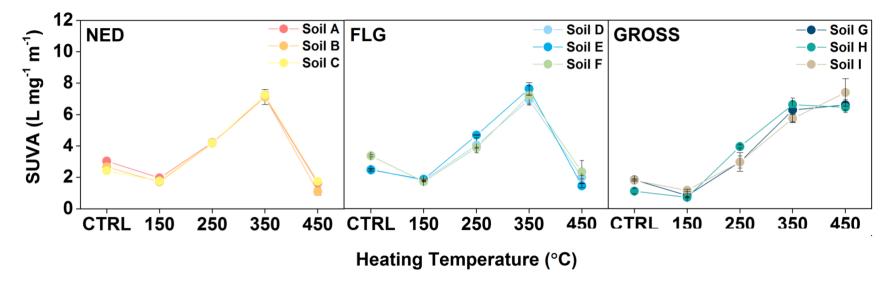


Figure VIII-1: Discretized SUVA values for soil sites NED (ABC), FLG (DEF), and GROSS (GHI). Error bars represent propagated error between  $UV_{254}$  (n=3) and DOC (n=4).

Sample ID	Class	Carbon Content (%)	DOC (mgoc g <sup>-1</sup> Material)	WEOC (%)	Nitrogen Content (%)	TDN (mg <sub>N</sub> g <sup>-1</sup> Material)	WEON (%)	SUVA254 (L mg <sup>-1</sup> m <sup>-1</sup> )
Wa_1_Mineral Soil	CTRL	6.40	4	0.06	0.20	0.6	0.3	0.3
			(0)	(0)		(0)	(0.03)	(0)
Wa_3_Mineral Soil	CTRL	6.20	5.1	0.08	0.20	0.8	0.42	0.3
			(0.2)	(0)		(0.2)	(0.09)	(0)
Wb_1_Mineral Soil	CTRL	4.90	6.1	0.12	0.20	0.7	0.35	0.4
			(0.2)	(0)		(0.1)	(0.03)	(0)
Wb_3_Mineral Soil	CTRL	4.70	5.9	0.13	0.20	0.6	0.3	0.4
			(0.1)	(0)		(0.1)	(0.09)	(0)
Wa_1_Organic Soil	CTRL	17.20	22.0	0.13	0.50	2.0	0.39	0.3
			(3.6)	(0.02)		(0.3)	(0.05)	(0.1)
Wa_3_Organic Soil	CTRL	12.70	8.2	0.06	0.30	1.3	0.42	0.4
0			(0.3)	(0)		(0.4)	(0.14)	(0)
Wb_1_Organic Soil	CTRL	13.60	18.5	0.14	0.40	2.8	0.68	0.4
-			(3.6)	(0.03)		(0.5) 2.7	(0.02) 0.45	(0.1)
Wb_3_Organic Soil	CTRL	26.60	28.6 (0.4)	0.11 (0)	0.60	(0.2)	(0.03)	0.4 (0)
			5.1	0.12		0.5	0.53	0.2
W1_1_Mineral Soil	Post Fire	4.30	(0.6)	(0.01)	0.10	(0)	(0.27)	(0)
			2.6	(0.01)		0.4	(0.27)	0.3
W2_1_Mineral Soil	Post Fire	-	(0.1)	-	-	(0)	-	(0)
W2_5_Mineral Soil	Post Fire	7.50	8.5	0.11	0.20	0.9	0.46	0.3
			(0.3)	(0)		(0)	(0.03)	(0)
W3_1_Mineral Soil	Post Fire	7.60	7.1	0.09	0.20	0.9	0.46	0.3
			(0.4)	(0.01)		(0.1)	(0.09)	(0)
W1_1_Ash	Post Fire	35.30	21.1 (0.4)	0.06 (0)	0.70	1.8 (0.1)	0.25 (0.01)	0.3 (0)

Table IX-1: Summary of analyzed data for Australia case study. Corresponding locations for Sample ID's can be viewed in Figure 4-1.

APPENDIX IX: Summary of analyzed data for Case Study

Table IX-1 cont'd

Sample ID	Class	Carbon Content (%)	DOC (mg <sub>OC</sub> g <sup>-1</sup> <sub>Material</sub> )	WEOC (%)	Nitrogen Content (%)	TDN (mg <sub>N</sub> g <sup>-1</sup> Material)	WEON (%)	SUVA254 (L mg <sup>-1</sup> m <sup>-1</sup> )
W2_1_Ash	Post Fire	-	6.3 (0.6)	-	0.30	0.8 (0.1)	0.25 (0.06)	0.3 (0)
W2_5_Ash	Post Fire	18.20	6.5 (0.3)	0.04 (0)	0.50	0.8 (0)	0.15 (0.01)	0.4 (0)
W3_1_Ash	Post Fire	44.40	24.8 (1.2)	0.06 (0)	0.90	1.6 (0.1)	0.17 (0.02)	0.2 (0)