

Short-Term Wildfire Impacts in a Rocky Mountain Catchment: Searching for Evidence of
Riverine Black Carbon Transport after the Cold Springs Wildfire

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ABSTRACT

Black Carbon (BC) is a long-lasting and ubiquitous product of combustion. It is found nearly everywhere on the Earth's surface, oceans, and atmosphere. It was originally considered to be very stable in soils, but is now understood to be mobile in terrestrial and aquatic environments. The magnitude of BC flux into oceans via riverine transport has been established, but the exact conditions under which transport occurs are unknown. This research monitored surface water sites to determine if a pulse of BC could be identified from a recently burned forested area in the Colorado Rocky Mountains. BC was shown to vary more highly in concentration at lower stream order, however, short-term trends in concentration demonstrated no signal of recent fire activity in dissolved BC. Instead, surface waters exhibited evidence of a stable pool of dissolved BC being released to streams from the watershed.

INTRODUCTION

Black carbon (BC) is a complex molecular product of combustion, and is found in both the atmosphere and biosphere. During a wildfire most carbon is released in the form of carbon dioxide, but a small amount of biomass is not completely combusted and becomes black carbon, an example of which is soot or charcoal (Baldock & Smernik, 2002). These are components of pyrogenic carbon (PyC), which is a more general term for organic matter that has been thermochemically altered. The purpose of this thesis is to analyze surface water of three streams in the Boulder Creek watershed for evidence of black carbon mobilization from soil following the Cold Springs fire, which occurred near Nederland, CO in July 2016.

Rivers reflect the watershed that they are connected to, and the chemical conditions in streams and rivers provide insight into the ecosystems they interact with. Streams occupy only a fraction of the watershed land area, but they are the lowest geographic point and therefore act to concentrate terrestrial inputs and represent watershed processes. Other studies have analyzed surface waters and soils for BC in the years or decades following a fire (Boot et al., 2014; Ding et al., 2013; Dittmar, 2008; Wagner, 2015). This project is unique in investigating surface waters within days of a wildfire for evidence of BC mobilization.

The main questions that I am studying are: (1) How does the in-stream concentration of black carbon change in the weeks following the Cold Springs fire? (2) How do hydrologic processes impact black carbon (BC) transport in the Boulder Creek Watershed? (3) What changes in stream water chemistry associated with BC will appear in the ancillary data? I expect my results to illuminate the spatial and temporal variation of BC across the sampling transect. I

also seek to show what conditions are associated with BC transport, specifically as convective thunderstorms move solutes from soil to the lacustrine environment.

Purpose and Benefits of This Thesis

Carbon is the core building block of all living tissue, and is ubiquitous on the Earth in many different forms. Black carbon is a small component of the carbon budget, but it is an important link between the short-term (biospheric) carbon cycle, and the long-term (geologic) carbon cycle. Until the 1990's, BC in soils was considered a carbon sink, and was thought to be persistent for thousands of years. This research will investigate short-term transport processes within the watershed for evidence of mobility and underlying mechanisms. Furthering knowledge on soil organic carbon fluxes will improve our ability to develop strategies for mitigating global climate change in the future.

Studying water quality impacts of wildfires is crucial to better manage water resources. Wildfires in mountain forests have direct water quality impacts for downstream communities, and can make water treatment more expensive. Rivers in the Colorado Rockies supply drinking water for millions of people. Population growth in the American West has already stressed this limited resource, and climate change will further exacerbate these challenges in the coming decades. The Cold Springs Fire burned upstream from the Betasso Water Treatment plant. Predicting a possible pulse of dissolved or particulate BC in the source water could offer the treatment plant a cost or resource saving opportunity. In the future, advanced climate models incorporating carbon cycling can be made more accurate by including the transport of black carbon from terrestrial environments to the ocean. Organic carbon in soils is a significant carbon sink, so research into BC mobilization could help model the function of this major sink.

Location

This research maps BC transport in North Boulder Creek immediately after the Cold Springs fire, which occurred in July 2016 and burned 2.02 km² (528 acres). The sampling area includes five sites upstream and downstream of the burn area. We utilized a weekly sampling regime beginning on July 15th, 2016 and ending November 28th 2016. The center of the Cold Springs fire was approximately 2.5 kilometers Northeast of Nederland, CO. This area is a montane forest ranging in elevation of from 2,500 m to 2,700 m. The forest of the burn area was composed of Ponderosa Pine, Douglas Fir, and Lodgepole. The watershed is fed by two streams, Sherwood Creek and Delonde Creek, which empty into North Boulder Creek (NBC) and then Middle Boulder Creek. Small headwaters catchments present an excellent laboratory for the study of BC export. North Boulder Creek is an ideal location to study black carbon mobilization because lower stream order systems are more representative of the landscape immediately surrounding the stream. At lower stream orders, there is more spatial and temporal variation among riverine solutes (Vannote et al., 1980).

Hypothesis

There will be a pulse of dissolved black carbon (DBC) from the freshly burned biomass, detected in surface waters within weeks of the Cold Springs wildfire. I expect to see higher concentrations of DBC in the lower stream order sampling sites because the ratio of burned to unburned land area is smaller (the signal is a great percentage of the total drainage). In higher stream order sites, more unburned land area is integrated into the drainage area, thus the wildfire induced BC pulse signal will be much weaker, because it includes BC from sources higher up in the watershed.

BACKGROUND

Linking Black Carbon Sources and Sinks

Streams connect terrestrial and aquatic ecosystems by facilitating the movement of energy and nutrients through trophic levels and space. The River Continuum Concept (Vannote et al., 1980) describes how stream ecosystems change from their headwaters to the rivers and lakes they drain into. This concept illustrates how the energy base of a stream changes from allochthonous (external) sources like forest litter in the first and second order streams of forested watersheds to the increasing influence of in-stream primary production in the open waters of rivers and lakes. In small streams the influence of the watershed is more significant. Allochthonous organic matter from the catchment represents a significant energy source in streams (Fisher & Likens, 1972). Thinking of streams as a mechanism of concentrating, transporting, and transforming organic matter is key to understanding how solutes can move from the terrestrial to the lacustrine environment.

It is useful to consider how black carbon fits into the terrestrial carbon cycle. Forest soils hold 73% of the planet's soil carbon (Sedjo, 1993). Soil organic matter (SOM), which is mostly carbon (~58%), exists as a labile and a resistant fraction (Jain et al., 1997). The labile material, consisting of freshly dead plant material, is relatively quick to breakdown and is easily eroded into waterways (Gregorich et al., 1994). This labile fraction is readily bioavailable, and represents a significant energy source. In comparison, the thermochemical alteration of biomass creates a resistant form of carbon that does not degrade easily. This refractory component represents only a fraction of the total soil organic carbon (SOC). It is this component where charcoal—a form of pyrogenic carbon—is identified in almost all soils (Masiello, 2004). A small

fraction is subject to erosion into waterways in the form of black carbon, in both particulate and dissolved phases.

The relationship between discharge and solute concentration is not always intuitive. During a precipitation event, water can runoff into streams and dilute solute concentrations by displacing stream water with precipitated water. In other cases, depending on the solute, streams can become more enriched by the flushing of groundwater, or other more concentrated sources, into streams (Evans & Davies, 1998). Interestingly, the concentration can remain nearly constant in a behavior called chemostasis. This concept dictates that the biogeochemical processes that facilitate solute transfer into streams act in tandem to minimize variation in concentration as discharge fluctuates (Godsey et al., 2009). Changing source water does not solely account for the tendency of catchments to exhibit chemostatic behavior, and chemical reactions along the pathway of water are suggested to play a role as well. Unsaturated zones can release more solutes when preferential flow patterns shift and they become saturated. Dissolved organic matter (DOM) concentration has been demonstrated to show less variability and more chemostatic behavior at higher stream order (Creed et al., 2015).

Strahler stream order clarifies how the stream interacts with the surrounding landscape (Strahler, 1957). Stream order is an organizing principle of waterways based on the integration of different channels, for example, a 1st order stream has no tributaries, and would be considered a headwater stream. Low-order streams show much more variability because they are dominated by processes occurring outside of the stream, in the catchment landscape (Vannote et al., 1980). This variability is caused partly by the large ratio of catchment land area to stream size. Therefore, low order streams are more likely to exhibit non-chemostatic behavior. On the opposite side of the spectrum, higher order rivers tend to behave chemostatically because greater

dominance of in-stream processes balances variable hydrologic processes. This is due in part to the greater availability of sunlight in rivers compared to streams. Wildfires act as a perturbation that disrupts the normal functioning of the catchment, and may change the equilibrium state of terrestrial solute inputs.



Figure 1. Cold Springs wildfire, sampling locations, and streams. White text indicates sampling location. Image taken August 8th, 2016. Textured mesh representation. Google Earth (2016).

Catchment Characteristics

The hydrologic regime of this study site is dominated by snow, having the highest annual discharge during the spring. This dominance by snowmelt is important in understanding the surface water characteristics, and must be considered when thinking about changes to the stream during the summer and fall. The Cold Springs wildfire burned during the summer, on the descending limb of the seasonal hydrograph (Figure 4). This period is characterized by declining discharge, with convective storms offering the greatest source of discharge variability. These precipitation events change the stream from being dominated by groundwater and snowmelt, to surface and soil runoff dominated. It is during this source-water transition that I want to identify changes in the mobility of black carbon after wildfire. In similar sub-alpine environments, soil water in snow-melt driven catchments has been shown to be the greatest driver of increasing dissolved organic carbon (DOC) concentrations in surface water during high discharge events. (Burns et al., 2016). In this way DOC, like other terrestrial inputs, is transported from soil into streams and carried downstream.

The sampling transect for this study was designed to take advantage of the low stream order and proximity to the burned area. Because the Cold Springs fire burned in a relatively small area, the containment efforts by fire crews utilized both NBC and Boulder Creek as Northern and Southern boundaries. As result, the burn was limited to the area between these two streams. The fire did not burn through the littoral zone of any stream in this study. The closest proximity site was Fire_2, located approximately 20 meters from the burn edge on Sherwood Creek, a first order stream. Fire_2 is located approximately 100 meters downstream of two consecutive beaver bonds. Upstream of the burn area, a control site was sampled above the influence of the burned area (NBC_B1). The next sites—moving lower in the catchment—were

CS_3, and Boulder Falls (all sampled from NBC, adjacent to the fire). Middle Boulder Creek was sampled 4 km above the outlet of the canyon, representing the lowest point in the watershed (BC_SW_4).

Wildfire Impacts

Wildfires are a significant perturbation that can change the flux of nutrients between soils, vegetation, and water (Johnson et al., 2007). The effects of wildfires on surface water are highly variable and differ based on many conditions. The aftermath of a fire can alter forest ecosystems on a scale of hours to years (Rhoades et al., 2011). Burning releases nutrients and other constituents from trees, vegetation, and forest litter (Richter et al., 1982). After a wildfire, excess nutrients in water runoff can lead to eutrophication downstream, posing a challenge for treatment of drinking water (Rhoades et al., 2011). Each site will undergo differing rates of erosion based on the intensity of the burn, the aspect, steepness of the slope, and precipitation patterns. Previous research has established that wildfire activity on the Colorado Front Range increases erosion rates and sediment load of streams in the burn area (Moody & Martin, 2001). Wildfires change the morphology of stream channels, leading to both increased discharge (Loáiciga et al., 2001) and higher sediment loading (Reneau et al., 2007).

The combustion of surface litter creates hot gases that infiltrate soil, following the extreme temperature gradient (Letey, 2001). When these gases cool, they condense onto soil particles and leave a film. This process creates hydrophobic soils that resist wetting and infiltration, leading to more surface runoff. However, this sequence does not occur after every wildfire—the forest litter must be thick and burn at a high temperature. Slow moving fires are the best candidates to cause hydrophobicity. The Cold Springs area contained limited understory, characterized as a *closed timber litter* fuel model (Scott & Burgan, 2005). Fire behavior in this model is dominated by slow burning surface fires with low flame heights. Based on this

behavior, some degree of hydrophobicity is likely to have occurred after the Cold Springs wildfire.

The range of wildfire impacts that have been observed across many studies include higher turbidity (cloudiness), pH, and higher concentrations of nutrients, organic carbon, nitrogen, and sulfate (SO₄) (Mast et al., 2016). Higher concentrations of total suspended solids (TSS) present a number of concerns for watersheds. TSSs increase the difficulty of water treatment by allowing certain microorganisms to be shielded from disinfection processes within heterogeneous particulates (Weiss, 2007). Additionally, some pollutants collect in soils, which are then transported and accumulated downstream. In some cases there is an almost immediate increase in total nitrogen concentrations after a wildfire, on the order of 5 to 60 times greater than background levels, within just a few days of a wildfire (Hauer & Spencer, 1998). All of these wildfire effects represent a departure from the pre-fire state. The volume and complexity of known watershed impacts demonstrate the dynamic character of wildfires.

	Slightly charred biomass	Char	Charcoal	Spheroidal carbonaceous particles (SCP)	Soot
Formation T	low				high
Size	mm and larger	mm to μm		μm	nm
Composition and formation	residue of burnt material (biomass and coals)			residue of fossil fuel combustion	combustion condensate
Plant or fuel structures	abundant	significant presence	few	few	none
Reactivity	high				low
Drift range	short (m)	short (m to km)		intermediate (km to 1000s of km)	long (up to several 1000s of km)

Figure 2. The black carbon combustion continuum (Hedges et al., 2000).

Black Carbon in the Terrestrial and Aquatic Environment

Although BC exists along a continuum of size and components, black carbon is most commonly identified as a polycondensed aromatic compound that is produced by the combustion of biomass. BC has been studied in atmospheric sciences for decades as a pollutant and contributor to climate change, as well as a source of paleoenvironmental data. BC is now under scrutiny for its role in biogeochemical pools that influence carbon cycling. BC has research implications pertaining to oceanography, limnology, soil sciences, and aquatic chemistry.

Part of the difficulty in understanding how BC moves throughout landscapes is the relative heterogeneity of BC molecules. In 1999, the idea of BC as part of a combustion continuum was presented by John I. Hedges, making sense of the wide range of combustion products (Figure 2). The continuum ranges from biomass that has been partially burned, to soot that is highly condensed and thermally refractory (Hedges et al., 2000). Each step along the combustion continuum contains products that are aromatic, and chemically heterogeneous. Aromaticity describes organic molecules that are cyclic and planar—essentially flat rings that are more stable (less reactive) than other atomic arrangements. Aromaticity can be thought of as the chemical potential energy of a substance; highly aromatic molecules are inert and don't react or degrade easily. The aromaticity of BC is proportional to the charring temperature of the biomass being combusted. Baldock and Smernik (2002) documented this phenomenon using ^{13}C NMR spectroscopy to identify the changing chemical structure as a sample of pine wood was charred, moving further along the combustion continuum. In this way, the charring temperature of biomass determines the structure and its stability in the environment. Low temperature chars are not as condensed, and break down on a scale of tens or hundreds of years. High charring

temperature produces very resistant graphite-like structures that are among the most refractory forms of carbon found on Earth.

The combustion continuum is relevant for the airborne transport distance of BC. On the large end of the size continuum, particles of charcoal are only apparent in sediments within a local range of the burn. Millimeter sized particles drop out of the atmosphere within 100 m of the fire (Clark and Patterson, 1997), while soot particles in the submicron size range may remain suspended in the atmosphere for months. This creates a bifurcated chemical signal of wildfire activity in sediments. Only larger particles can be associated with recent wildfire activity, while the smaller components are more closely related to background atmospheric deposition than wildfire activity. One study in the Santa Monica Basin found that charcoal particles in sediment could only be correlated with local wildfire activity if they were greater than 60 nanometers in size (Mensing et al., 1999). In this way, the size of the particles influences the initial reservoir that BC exists in. This is an important concept for this research—it illustrates how the range of BC compounds are subject to different transport processes at each step of their lifecycle. BC varies in reactivity along the combustion continuum, Masiello (2002) demonstrated in a laboratory setting that charcoal oxidized faster than soot when exposed to certain chemicals. In-situ experiments have suggested that the lability (how readily it is modified and broken-down) of charcoal changes based on the soil conditions, including microbial decay and photo-oxidation (Bird et al., 1999).

As part of a combustion continuum model, there are many forms of BC. In the dissolved phase, BC has been highly correlated with dissolved organic carbon (DOC) in rivers (Jaffe et al., 2013a). The study incorporated samples from twenty-seven different rivers to establish this correlation. DOC transport in mountain streams is controlled largely by discharge events and

snowmelt, and it is estimated that such events compromise 86% of DOC export (Raymond & Saiers, 2010). The link between DOC and DBC is an intriguing and mostly unknown component of BC transport, and helps to understand the role of flushing in the BC lifecycle. The existing research on DBC export in streams is limited; this thesis will help understand the conditions in which mobilization can occur.

Understanding the relationship between BC fluxes and pools is an ongoing process. In 1973, Smith et al. determined that elemental carbon was present in deep ocean sediment, thereby suggesting a highly refractory role of pyrogenic carbon (PyC, resisting breakdown in the environment). This view of PyC having a very long environmental life span has given way to a more nuanced understanding of PyC as part of a continuum. For example—if BC is indeed highly refractory—it should account for over 25% of total soil organic carbon after thousands of years of biomass burning (Masiello, 2004; Masiello & Druffel, 2003). This percentage does not match with the composition of soil present today, thus indicating that there are other means of BC removal that are unaccounted for (Major et al., 2010). It has been well established that BC is subject to erosion and degradation processes (Singh et al., 2012). This process may be altered by transport conditions in soils. Studies have shown that a large portion of BC is deposited near the burn site, and it tends to accumulate in geographic low areas (Chaplot et al., 2005). In a seminal paper Jaffe et al. (2013a) identified DBC in many global rivers, in concentrations ranging from 1.94×10^{-3} to 2.77 mg carbon per liter. Additionally, the authors posit that the global flux of BC in rivers may be as high as 26.5 ± 1.8 MMT of carbon per year.

More recent research has shown that in-stream particulate black carbon (PBC), unlike DBC, is affected by recent wildfire activity, suggesting that there are different mechanisms controlling the flux of DBC (Ding et al., 2013). This indicates that burn events have less

influence on in-stream DBC than the processes that control DOC export. Ding (2013) suggests that the lack of correlation between recent burning and DBC transport may be because of greater export during high stream discharge. Boot et al. (2014) analyzed the top 15cm of soil after a Colorado wildfire and found that BC content was not correlated to slope angle. They reported that none of the BC deposited on the soil surface had been incorporated into any subsurface layers at the time of sampling, approximately four months after the wildfire. Based on the lower than expected BC soil stocks compared to similar forests, the authors suggest that BC transport via erosion occurred during this period.

Wagner et al. (2015) posit that BC may need to undergo oxidation processes in soil, before it can enter the dissolved phase. The same study also quantified PBC and DBC transport in the Poudre River in CO after the High Park wildfire. They found that summer storm activity increased the flux of PBC at a rate up to sixteen times greater than that of DBC. Interestingly, during peak seasonal discharge DBC is the dominant form of BC export, and is seven times greater than PBC. In total, they found that the total BC flux for the period of March through August was four times greater for PBC than DBC, one year after the fire. It should be noted that while this study is a relevant comparison for this project, it did not include samples from the immediate post-fire period. It has been shown that freshly deposited bio char leaches a small amount DBC (Abiven et al., 2011) and this may lead to a pulse of DBC in surface water during the days or weeks immediately following a burn event. These prior studies indicate that both significant fluxes of DBC and PBC are moving from their source location, and this transport occurs in streams, but the exact circumstances are still unknown. Such results inspire more critical study of the relationship between black carbon mobility and fluvial transport.

METHODS

Field Sampling

This project includes six different sites where we sampled two liters of water on a weekly basis. The first sampling occurred on the day that Cold Springs Drive was re-opened to the public. We used one HDPE bottle and one pre-combusted glass amber bottle at each site. In addition we recorded field parameters using a YSI-Professional Plus pH meter. These included pH, air temperature, water temperature, and specific conductivity. In the neighboring Gordon Gulch, approximately 2.5km to the northeast, I setup an ISCO automated water sampler with a liquid level actuator to trigger an hourly sampling regime at the onset of increasing discharge from a precipitation event.

Studying the effects of wildfire in a watershed presents several practical issues, outlined in detail by Murphy (2015). Gathering data on in-stream chemical changes requires a high temporal resolution sampling regime, limiting the usefulness of weekly water samples. Precipitation events can mobilize soil water in fire effected areas very rapidly. Capturing this chemical signal necessitates sampling during the rising limb of the hydrograph, which we accomplished by using an ISCO, triggered by a liquid-level actuator. When the discharge begins to rise, the sampler is kicked on. The ISCO sampler was located in Gordon Gulch, approximately three kilometers Northeast from the wildfire.

The rates of erosion after a wildfire are much higher. Wildfires lead to more frequent instances of overland flow—they lower the precipitation intensity required to initiate overland flow. A 5-year storm in an area that has previously burned can produce the same runoff as an unburned area would during a 30-year storm (Wondzell & King, 2003). This makes event-based samples very important to understanding pyrogenic changes in streams. ISCO data were not available in time to be included with the following results, but will be included in any future

publication. The area of this study has multiple sites with precipitation gauges in close proximity operated by the Boulder Creek Critical Zone Observatory (CZO). Additional sites are operated by the USGS along Boulder Creek, including the Orodell gauging station located 4km from the mouth of Boulder Canyon. Discharge for North Boulder Creek was not available, but it can be approximated based on the outlet of Martinelli basin in Green Lakes Valley (the headwaters of North Boulder Creek) and the USGS stream gauge at the Orodell.

Black Carbon Analytical Process

The samples were filtered using combusted Whatman glass fiber filters and then acidified to pH 2 with 12M hydrochloric acid (HCL) to prepare for analysis. I conducted a solid phase extraction (SPE) process to isolate BC using Bond Elut PPL cartridges. We allocated 60 cartridges to be split between water samples from our close proximity burn sites, and the automated (ISCO) water samples. These commercially manufactured cartridges allow for high extraction efficiency of BC. The cartridges were prepared by rinsing with 2-3 cartridges volumes of methanol (MeOH), followed by 30 mL of 0.01M HCL (diluted from 12M) to protonate the cartridge sorbent so that it will readily form bonds with dissolved organic matter (DOM) in the water. The sample was then passed through the PPL cartridge using Teflon tubing to siphon water out of the 1L amber glass, placed directly above the cartridge. After the sample passed through the cartridge and into a new 1L amber glass, it was weighed for later use in determining concentration. The PPL cartridges were dried on a manifold using high-purity nitrogen gas (N₂). Next, the cartridges were eluted with 10mL of MeOH into amber vials. The vials were evaporated with a stream of N₂ gas to concentrate the MeOH-DOM solution to about 3mL. Just before the oxidation step, the vials were further evaporated leaving only the solid phase DOM. For the trial run, nitric acid (HN0₃) was added, and then the samples were transferred to glass

ampules and sealed closed with a propane torch. Unfortunately, the pressure difference in the microwave digester caused the ampules to implode, so the oxidation process was done inside the Teflon reaction vessels without the glass ampules. The nitric acid acts to oxidize polyaromatic hydrocarbons into benzenepolycarboxylic acids (BPCAs). BPCAs then act as molecular markers for black carbon via chromatography. The microwave digester heats and pressurizes the sample, allowing the nitric acid to be more effective for oxidation. This step is necessary to release the BPCA molecular markers from the DOM. The initial run included four standards, containing known quantities of carbon. The standards were precisely weighed and mobilized in nitric acid prior to the digestion.

The samples were again evaporated under a stream of N₂ to remove the nitric acid, and then re-dissolved in the mobile-phase solution. The HPLC measures black carbon based on the retention time of the BPCAs in the chromatography column, which is based on molecular polarity. The HPLC column used was a Sunfire C18 reverse-phased column. The reverse phase designation indicates that the mobile phase is more polar than the stationary phase. For clarity, the structure of functional groups determines the polarity of an organic molecule. For example, in water molecules the difference in electronegativity from the H and C covalent bonds causes it to exhibit polarity. The poly-condensed aromatics that constitute black carbon are highly non-polar, and can be differentiated based on their retention times in the column. Because of the high sensitivity, care must be taken when preparing the analyte to avoid under- or over-saturating the detector. BC concentration can later be determined stoichiometrically, based upon an estimation of carbon atoms contained in each polyaromatic hydrocarbon molecule (Koch & Dittmar, 2006).

TOC & SUVA₂₅₄

125 mL of each sample was poured off in an amber bottle before the samples were acidified and used to determine the absorbance, using the specific UV absorbance value at

254nm (SUVA₂₅₄). SUVA is a measure of the aromatic content of a water sample, normalized for the organic carbon content. In the ultraviolet spectrum (200-400nm), conjugated groups (alternating single and double bonds) have a greater absorptivity. These alternating conjugate bonds delineate the structure of polycyclic aromatic hydrocarbons (PAHs) that compromise black carbon. SUVA is not an exact measurement, but serves as a useful parameter for estimating the dissolved aromatic carbon content of water samples. A complementary measurement to SUVA is ¹³C NMR spectroscopy to quantify the aromatic carbon content, which requires more extensive sample processing and resources. The determination of absorbance at 254nm was conducted on an Agilent 8453 UV-visible Spectroscopy System. SUVA₂₅₄ was calculated by dividing the absorbance value (in cm⁻¹) by the DOC content (in mg/L) and then multiplying by 100.

Before the SPE process, 125 mL of each sample was poured off to be analyzed for dissolved organic carbon (DOC) and total nitrogen (TN) using a Shimadzu TOC-5000, using the non-purgeable organic carbon (NPOC) method. This method is a measure of the organic carbon left in the sample after it has been purged with gas to remove inorganic carbon (carbon derived from rock weathering). The PPL cartridge effluent samples were also run as a comparison to the filtered samples so the extraction efficiency of the PPL cartridges could be determined.

Total suspended solids (TSS) were determined by pre-weighing the GFF filter and passing a known sample volume through the filter. Before weighing, the filters were freeze-dried for approximately 5 days to remove all moisture. The concentration of TSS was determined by dividing the filter mass by the sample volume. The filter contents were stored for future analysis of PBC via BPCA analysis.

The BPCA method represents a simpler process than other BC extraction techniques. Using benzene polycarboxylic acids as indicators for black carbon was first derived by Dittmar et al. (2008). The heterogeneity of BC makes it difficult to detect throughout the entire combustion continuum. In most cases the method used results in either under- or over-detection of BC. There are several approaches to quantifying black carbon, differing principally in their detection range within the combustion continuum of BC (Masiello, 2004). Microscopic techniques are limited to large particles, and thermal methods can char organic compounds and lead to over-detection (Lim & Cachier, 1996). In at least one case, using ^{13}C NMR spectroscopy has led to unintentional detection of non-pyrogenic organic compounds (Almendros et al., 2003), and requires more extensive sample processing. There is some difficulty in comparing BC measurements made using differing analytical methods, but BPCA provides the widest detection range. Given these limitations, the BPCA method is the best choice for this project. Most recent studies on black carbon have utilized the BPCA method, as developed by Dittmar (2008). Considering the difficulty and inconsistency of comparing BC measured from different techniques, using this method allows the results to be more easily compared with future research. Once all of the data were collected, determination of statistical relevance was done in R-Studio using linear regression analysis to compare r^2 values between discharge and concentration.

RESULTS

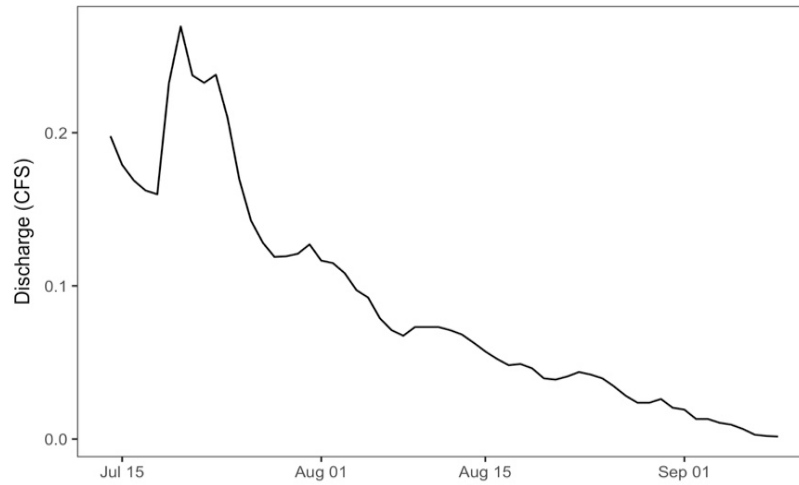


Figure 3. Discharge from Martinelli Basin outlet, unit is cubic feet per second.

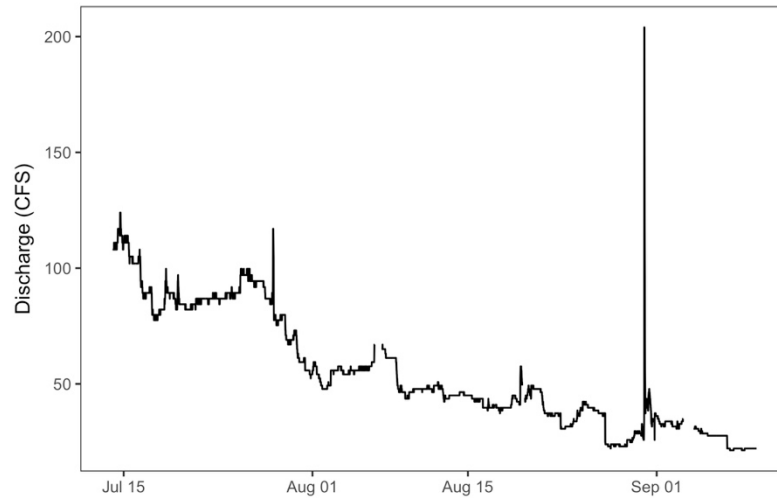


Figure 4. Boulder Creek Discharge at Orodell, 4km from the mouth of Boulder Canyon. This is the lowest site in the watershed.

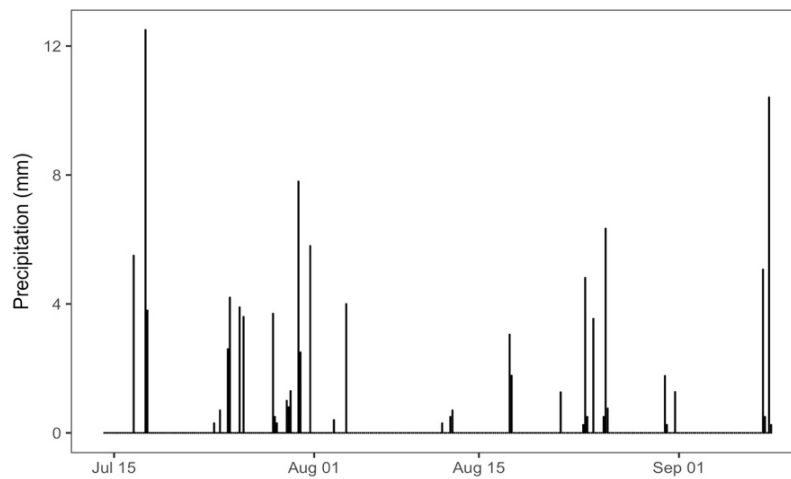


Figure 5. Four-hour precipitation accumulation. Recorded via tipping-bucket in Gordon Gulch, 2.3 km from the Cold Springs burn.

Discharge and Precipitation

The Martinelli outlet discharge shows a signal of snowmelt, as expected during this time period. This is the very top of the watershed, far above Cold Springs, but this gives a general impression of the flow regime at the beginning of North Boulder Creek. The Boulder Creek discharge at Orodell shows declining flow and one very significant pulse flow. Boulder Creek experienced an unusually high discharge event near the end of August. This highly localized storm-derived pulse flow occurred near Betasso Preserve, below the Cold Springs area, and therefore did not influence the burn area. The Gordon Gulch tipping bucket data (Figure 5.) displays the recorded precipitation through the sampling period, summed into four hour intervals. The precipitation for this date at Gordon Gulch is very little, only amounting to ~1.5 mm. The similarity between these two hydrographs, located above and below the burn area, establish a basis for assuming similar flow conditions on North Boulder Creek

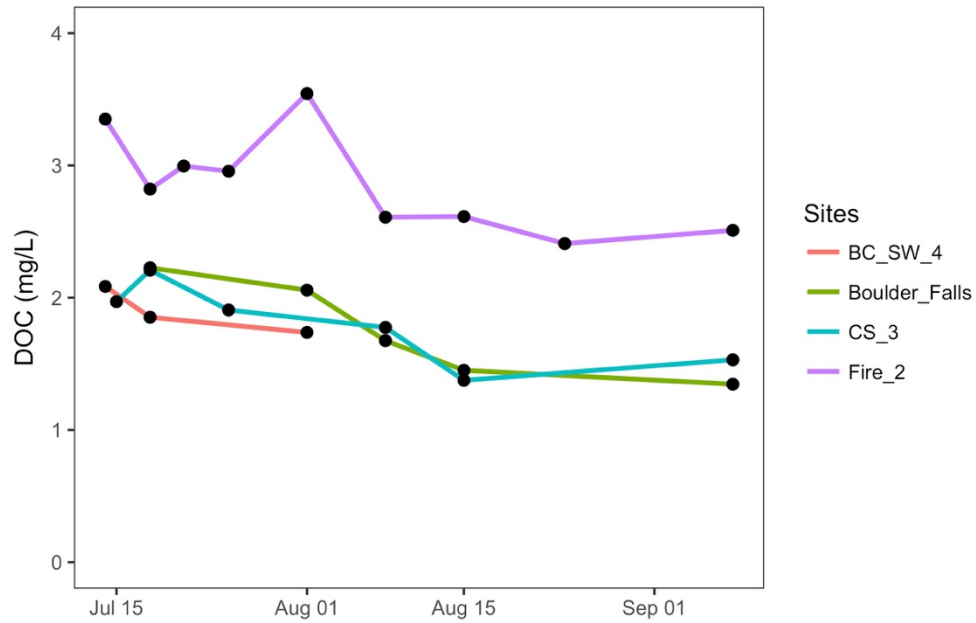


Figure 6. Dissolved organic carbon concentrations.

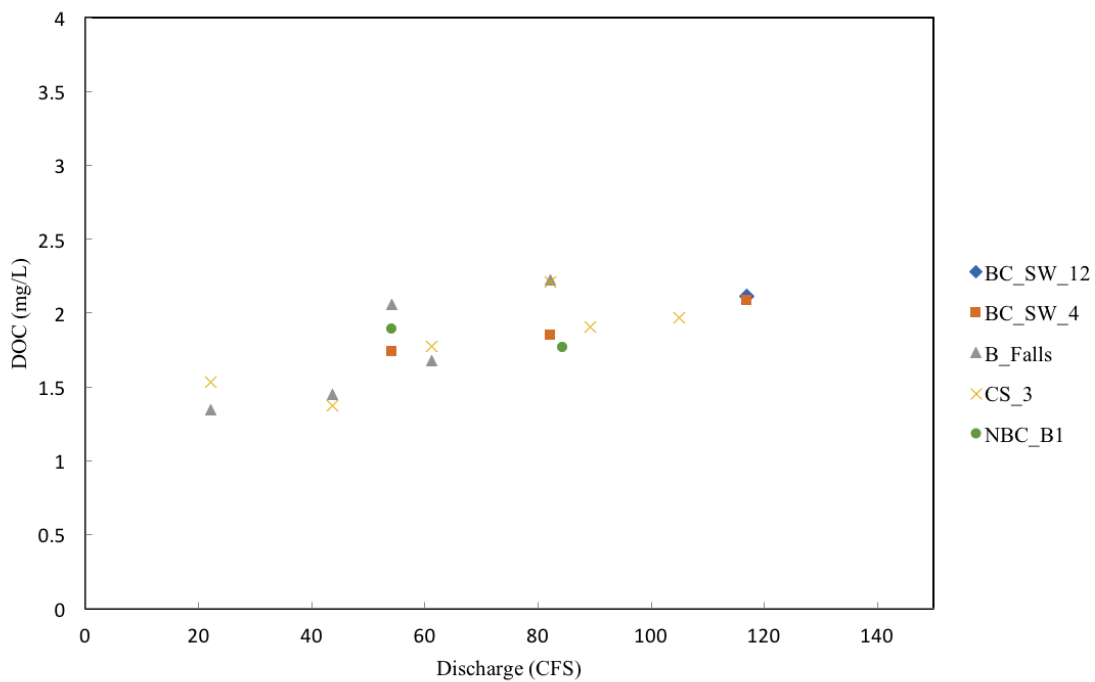


Figure 7. DOC concentration and discharge (in cubic feet per second) for sites on North Boulder Creek, and Boulder Creek (CQ). Sherwood Creek (Fire_2) excluded because discharge was not available for that site. $R^2 = .29$, $p < 0.05$

DOC Concentration

Overall, DOC concentrations were higher in the lower order stream sites, and lower at higher stream order. In all sampling sites the DOC concentration fell throughout the sampling period. The DOC concentration was highest at the Fire_2 site, with a noteworthy spike of 3.54 mg/L seen on August 1st. This spike occurred within 16 hours of a precipitation event that occurred over the Cold Springs area. This event produced 9 mm of recorded rain in Nederland, and 5 mm on the north facing slope of Gordon Gulch. These meteorological sites are both 2.3 kilometers NE and SW of the burn, respectively. Despite the short sampling period and limited sample size, the change in DOC was correlated to discharge ($r^2 = .29$, $p < 0.05$), demonstrating the well-established relationship between these two parameters.

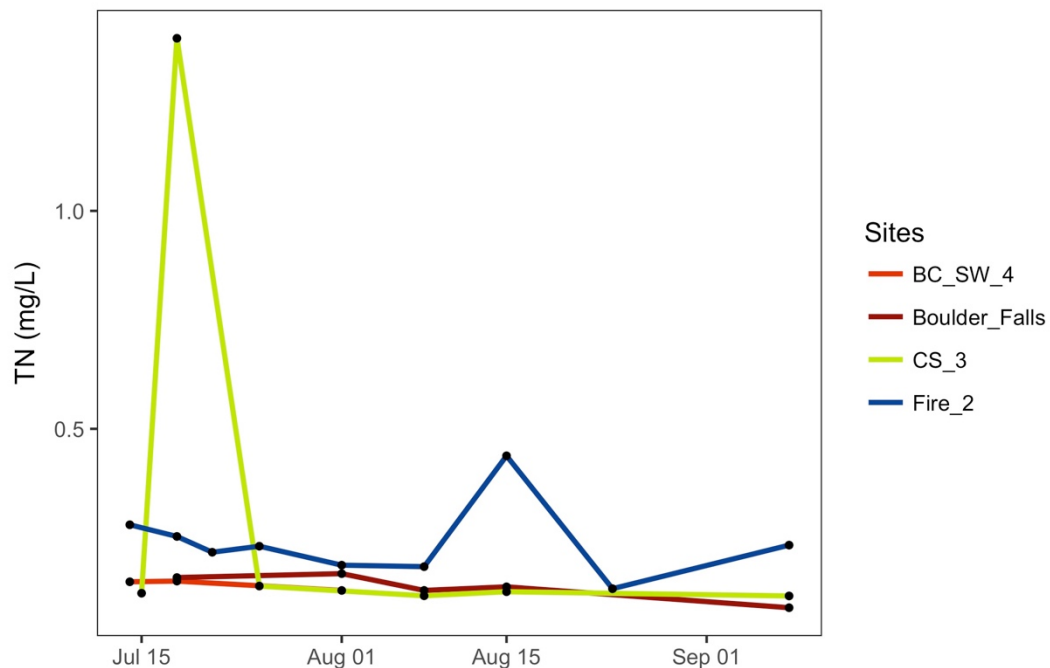


Figure 8. Total Nitrogen.

Total Nitrogen

Nitrogen concentration in most sites stayed relatively stable. The TN concentration at B_Falls and BC_SW_4 varied only from 0.13 to 0.17 mg/L. The most significant deviation occurred at the CS_3 site, showing an increase on June 18th of nearly eleven times the base level, from 0.13 to 1.39 mg/L. This high nitrogen value was not observed upstream at Fire_2 or at any downstream site. Fire_2 concentrations doubled on August 15th to 0.44 mg/L, before dropping down again to 0.13 mg/L. Similar to the previous peak, this increase was not seen in any other downstream sampling site. The August 1st precipitation event did not mobilize nitrogen in detectable levels.

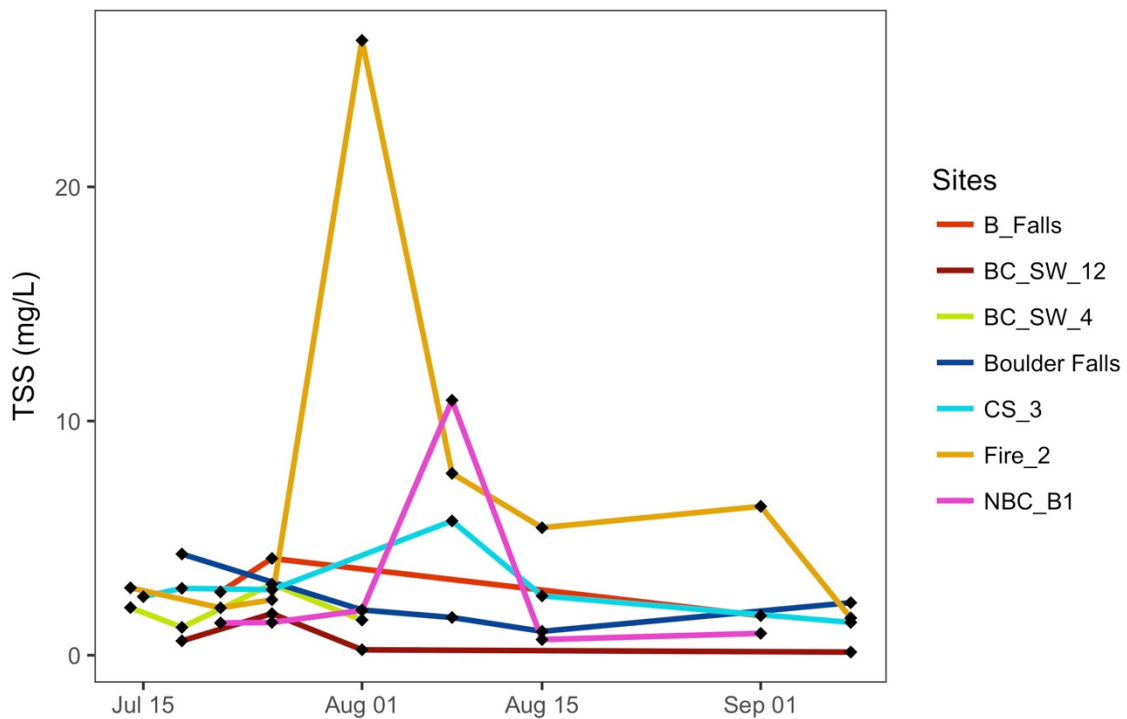


Figure 9. Total Suspended Solids.

TSS concentrations

From July 14th, through the 18th, the TSS load in all sampling sites was very similar (~3 mg/L). On August 1st, the Fire_2 site shows a sharp increase from 2.36 to 26.26 mg/L, over ten times greater than the base conditions. This peak was short lived, but the site retained high TSS through September 1st. This spike was not seen in any other sampling location that day. This peak also occurred within 16 hours of the previously described precipitation event on August 1st. NBC_B1 showed a similar peak on August 15th from 1.40 to 10.89 mg/L, although less than the magnitude observed at Fire_2. This signal was visible downstream, at the nearby CS_3, approximately 0.5km downstream, though not as apparent. This peak was not observed at Boulder Falls, approximately 3 km downstream, and returned to the base level on the next sampling date.

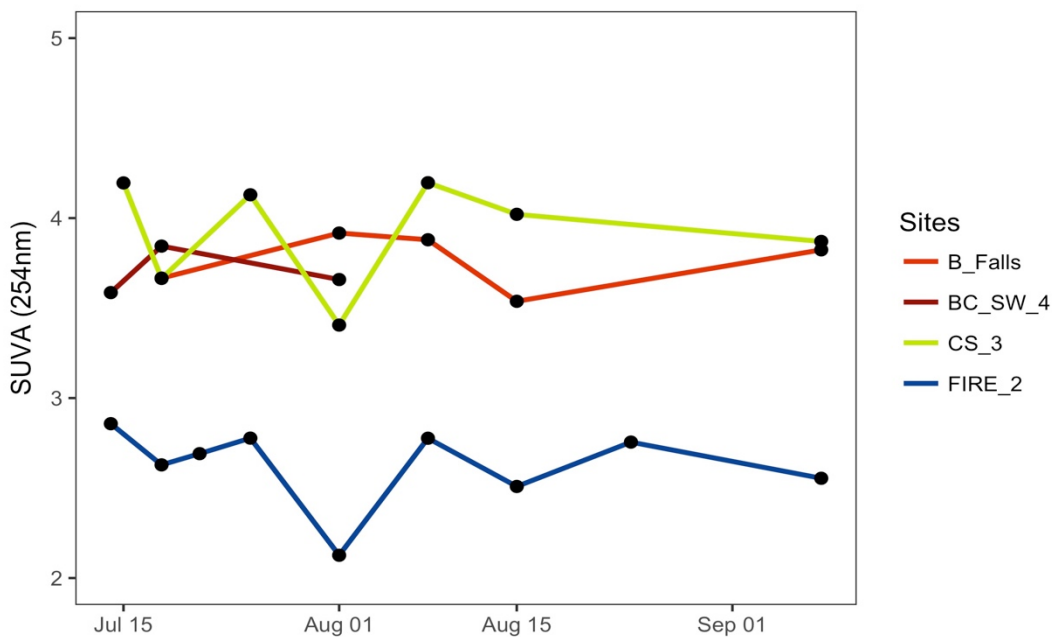


Figure 10. Specific UV absorbance at 254 nm.

$$SUVA_{254}$$

The most striking feature of the SUVA values was the difference in SUVA between Fire_2 and all other sampling locations. Surprisingly, the Fire_2 values were consistently below three, while CS_3 and B_Falls stayed consistently near four. This demonstrates the difference between Sherwood Creek (low discharge, first stream order) and North Boulder Creek (higher discharge, second stream order). Both Fire_2 and CS_3 demonstrated similar variation in their temporal response. This similarity between the two upper sites was not shared downstream at B_Falls or BC_SW_4. As with other parameters, B_Falls and BC_SW_4 demonstrated little variation throughout the sampling period.

Sample	Date	DOC Extraction Efficiency
B_Falls	7/18/16	0.231
B_Falls	8/1/16	0.602
B_Falls	8/8/16	0.475
B_Falls	8/15/16	0.463
B_Falls	9/8/16	0.578
BC_SW_12	7/14/16	0.603
BC_SW_4	7/18/16	0.441
BC_SW_4	8/1/16	0.362
BC_SW_4	7/14/16	0.458
CS_2	7/18/16	0.265
CS_2	8/1/16	0.694
CS_3	7/15/16	0.284
CS_3	7/18/16	0.435
CS_3	7/25/16	0.451
CS_3	8/8/16	0.277
CS_3	8/15/16	0.290
CS_3	9/8/16	0.528
Fire_2	7/14/16	0.618
Fire_2	7/18/16	0.626
Fire_2	7/21/16	0.611
Fire_2	7/25/16	0.519
Fire_2	8/1/16	0.204
Fire_2	8/8/16	0.582
Fire_2	8/15/16	0.313
Fire_2	8/24/16	0.523
NBC_B1	7/21/16	0.601
NBC_B1	8/1/16	0.609

Figure 11. Extraction efficiency of DOC, determined from DOC concentration before and after solid phase extraction.

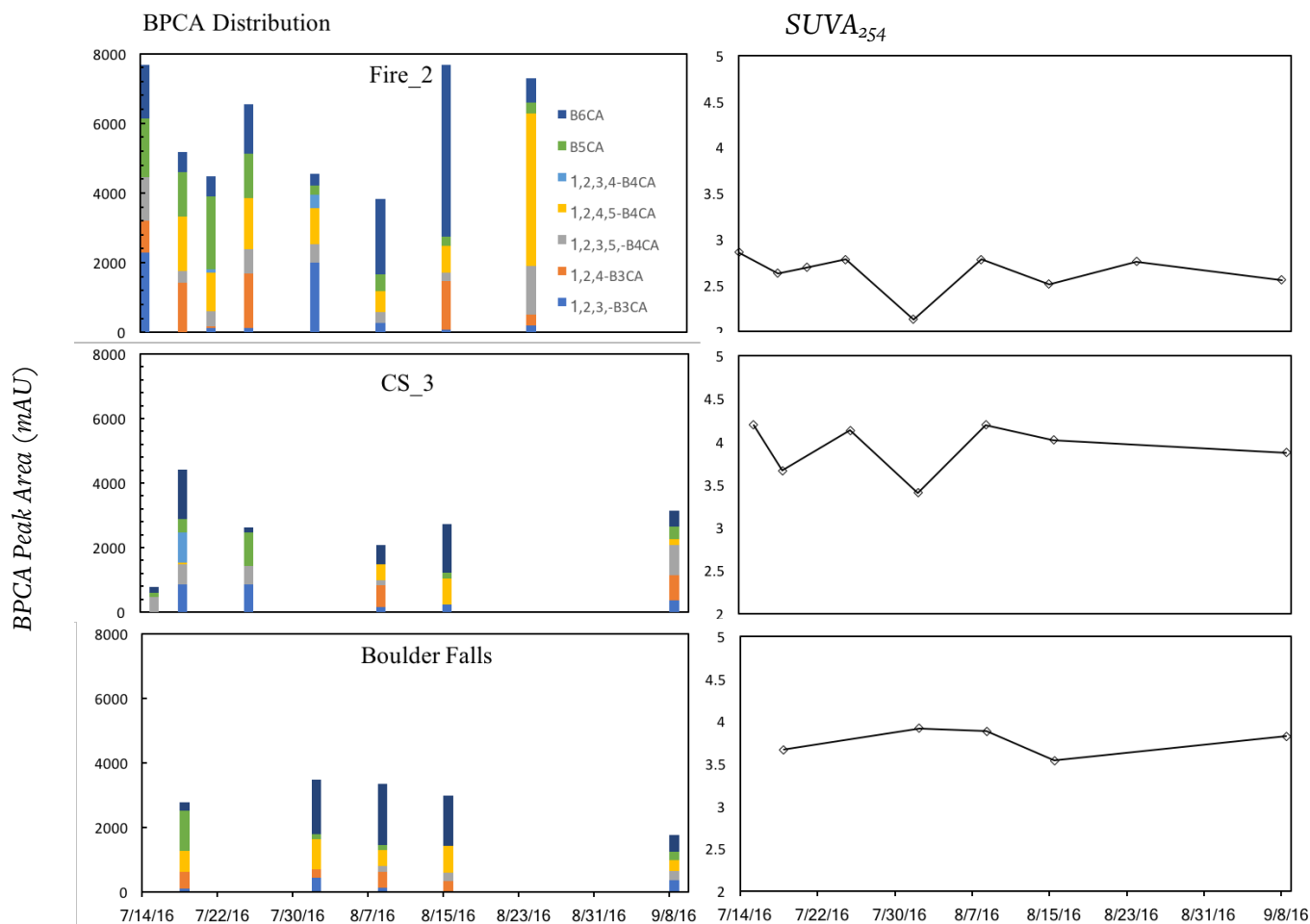


Figure 12. BPCA distribution and SUVA. NBC_B1 and BC_SW_4 did not have consistently identifiable peaks.

Black Carbon

Several samples were lost during the BPCA preparation process, one due to a cartridge sorbent failure, and five due to glass ampules imploding during the pressurization ramp of the microwave digester. The average extraction efficiency for DOC was 46.8% (Figure 11). This is similar to the efficiency reported by Dittmar (2008) for freshwater samples. The HPLC data displayed poor differentiation among peaks in both runs. The peaks had a variation of up to 4

minutes in the lower retention-time peaks. The peaks near the end of the run had slightly more reliability, and were observed within one minute. This inconsistency among retention times made identifying BPCA markers difficult and imprecise. This limitation made stoichiometric determination of BC concentration unlikely to be accurate. Despite this, the relative changes in the area of BPCA peaks and distribution of BPCAs illustrates the change in BC amounts throughout the catchment (Figure 12). B6CA represents the most poly-condensed black carbon (higher char temperature) and 1,2,3-B3CA represents the least (lower char temperature).

Fire_2 demonstrated the highest peak areas (as identified by HPLC) overall, followed by CS_3 and B_Falls. BC_SW_4 was also examined, but the low sampling frequency and highly inconsistent peak identification yielded inconclusive determination of BPCAs. The remaining two sites in Figure 12 show that relative concentration was lower in both sites downstream from the burn area. In addition, variability is diminished at B_Falls. SUVA at Fire_2 appeared to follow the BC concentration, but this behavior was not consistent among the other sites. B_Falls showed the lowest variation in both BC and SUVA. At all three sites B5CA was present initially, then decreased or disappeared throughout the sampling period, while B6CA was always present.

DISCUSSION

DOC

Pyrogenic changes to streams were evident in the watershed throughout spatial and temporal scales. Stream order explained the overall solute variability between sites well. As expected, Fire_2 generally exhibited the highest level of variability followed by CS_3, both being the lowest stream order and closest to the Cold Springs burn. Sherwood Creek is a first order stream, and therefore had the lowest discharge. This enabled a higher sensitivity to changing allochthonous inputs. Overall, descending DOC concentration was the only consistent

trend exhibited throughout the entire sampling period. The DOC pulse seen on August 1st illustrates how quickly precipitation events can change surface water composition, and how fleeting these changes may be. This sampling date had the closest temporal proximity to any precipitation event throughout the sampling period.

DOC at Fire_2 was consistently elevated from the other sites, likely because Sherwood Creek is hydrologically unique from the other sites. The lower discharge, and proximity to several beaver ponds contribute to the long residence time of water at this sampling location. It is known that during base flow, lake outlet flows contain higher DOC concentrations than the inlet flow (Goodman et al., 2011). The differences between the DOC concentration at low- and high-stream order sites demonstrate the heterogeneity of DOC export throughout the watershed.

Total Nitrogen

TN stayed near base levels, with the exception of two dramatic and short-lived peaks. The first nitrogen spike on August 18th, occurred after a significant precipitation event of ~12mm rainfall (within 24 hours), but did not occur alongside a rise in TSS or DOC. This short-lived signal was not detected downstream at Boulder Falls, perhaps because of the addition of another second order stream just before the sampling site. The lack of consistently elevated levels indicates that nitrogen is only mobilized under specific conditions. Elevated release of nitrogen from burned biomass has been shown after wildfires, but it is highly dependent on both the burn severity and extent (Rhoades et al., 2011). Because of the low extent of the Cold Springs Fire, this impact was not detected. It may have become apparent after this sampling period had ended. This disconnection between timing in peaks is likely because of the two different drainages that lead towards the CS_3 and Fire_2 locations. Another explanation for the spikes in TN is the contribution from flame retardants dropped by aircraft during the burn. Nearly all modern

airborne fire retardants contain ammonium, and slurry was used extensively on the Cold Springs fire perimeter. The retardant also contains thickening chemicals specifically to prevent erosion (Kalabokidis & Kostas, 2000). Despite this, it may have been present in streams after the burn.

Changing Solute Concentrations

Precipitation was not linked to solute concentrations in any predictable way. Rain events did not consistently mobilize all solutes—this is likely because of two factors: (1) Convective thunderstorms behave in complicated ways in mountainous landscapes. Rainfall is not consistent over even modest spatial scales, such as the 2.03 km² burn area. (2) The landscape of the Cold Springs area does not drain into one stream. The burn occurred on steep terrain near a geographical high point known as Hurricane Hill, this area drains into both Boulder Creek on the south facing slopes, and channels into two separate drainages on the North Boulder Creek facing slopes. This explains some of the variation in timing of pulses in TSS as well as TN between the Fire_2 and CS_3. Fire_2 drains the northern aspects and CS_3 represents the eastern drainage of the Hurricane Hill area. Precipitation that occurred over the eastern drainage area would not cause erosion into Sherwood Creek, and therefore would not be detectable at Fire_2.

SUVA₂₅₄

Interestingly, SUVA was consistently lower at Fire_2 than at any other site. This suggests that BC is not strongly influencing the overall aromatic content of the surface water, likely because of its relatively low concentrations. DBC only contributes to a small percentage of DOM (Wagner, 2015). During the period of highest DOC concentration at Fire_2, the SUVA value dropped, as did total BC peak area. This is surprising given the existing literature reporting an increase in the aromatic fraction of DOC during flushing events (Hood et al., 2006). One explanation for this behavior is greater incorporation of autochthonous (in-stream) DOC at Fire_2. Upstream of Fire_2 on Sherwood creek is a series of multiple beaver ponds, which may

have altered the character of downstream DOC. This would explain why DOC concentration was higher, but less aromatic. The temporal pattern in SUVA was connected between Fire_2 and CS_3 despite the different drainage areas. This indicates that both of these sites have the same pool of DOM that is being represented by SUVA. This interpretation is consistent with their close physical proximity and position within the watershed.

Total Suspended Solids

Higher overall TSS concentration at Fire_2 show the expected result of ash produced by the fire, and the increased sensitivity of the landscape to erosion after a wildfire. This pool of coarse and fine particulate organic matter contains PBC and is known to carry higher loads of PBC after a recent burn. This component will be analyzed with the BPCA method in the future by removing particulate material from the filters for each sample.

Black Carbon

The poorly differentiated BPCA peaks from both HPLC runs were likely a result of the slightly modified digestion process, or an issue within the column itself. Because of the inability of the glass ampules to withstand the digestion pressurization, we opted for an open digestion within the Teflon reaction vessels themselves. For future analysis, this process will include glass ampules, more closely replicating the original method.

A change in spatial distribution of BC was detected throughout the catchment. This study established that BC is present in higher concentrations in Sherwood Creek than elsewhere in the study area, including downstream sites on both North Boulder Creek and Boulder Creek. The variability in BC composition is diminished at higher stream order. The consistency of B6CA indicates that highly aromatic BC is present across all sites, but it is not clear if this is related to the fire. The lack of response to changes in precipitation or discharge show that the transport of DBC is disconnected from the export of other solutes.

Moreover, these data do not show evidence of the correlation between DOC and DBC that has been previously observed. As DOC concentration decreases throughout summer, DBC peak area remains consistent. The stability of DBC during the declining discharge also indicates that the flux is decreasing. The existence of a mostly stable pool of DBC is consistent with previous literature. Wagner et al. (2015) demonstrated slight seasonal changes in concentration, but over a range of 1800 cfs on the Poudre River (before and after spring melt), compared to 100 cfs on Boulder Creek (after spring melt) during this sampling period. This indicates that the connection between DBC and DOC may only be apparent over longer time scales. However, the greater concentration and variability of BC at Fire_2 implies that stream order, and therefore terrestrial connectivity, plays a role in determining BC concentration. In addition, the greater abundance of DBC at Fire_2 may also be connected to the longer residence time of surface water at Fire_2.

The water in this watershed is all coming from the continental divide, and therefore has relatively little contact with soils, which act a major pool of BC. This may have had a dilution effect on the water incorporated into North Boulder Creek from Sherwood Creek. This would explain why BC was very difficult to detect in North Boulder Creek, and further down in Boulder Creek. The coarse temporal resolution of weekly sampling events makes illustrating changes based on hydrologic factors difficult. Having only an approximate knowledge of discharge at North Boulder Creek further challenged the interpretation. One explanation for the overall lack of expected solute changes is the size of the watershed relative to the burn area. The Cold Springs fire only burned 2.02 km² of the 1,160 km² catchment, meaning at the lowest point (at BC_SW_4 on Boulder Creek) fire derived solutes were only a fraction of the total landscape being incorporated into surface waters.

Further Research:

To more fully understand the mobility of black carbon after wildfire, there is more work to be done. Firstly, because of the small sample volume required for HPLC work, all previously run samples can be re-run with the fittings recommended by Sunfire for use with the C18 column—clearly defining DBC concentration at all sites is crucial. The next step is comparing the particulate phase of BC to the dissolved. This will highlight differences in transport between both reservoirs of BC. The next phase of this research includes analyzing the ISCO samples associated with precipitation events, to better determine the relationship of BC and discharge after the wildfire. One of the strengths of this dataset is that sampling began within four days of the fire. Even so, more frequent sampling would have illuminated some of the rapid changes that occurred in Sherwood Creek and North Boulder Creek. Tracking solutes throughout the changing hydrograph during a rain event would more clearly determine the ability of precipitation to initiate transport of BC.

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Appendix:

