

FINAL REPORT

Title: The Long-term Legacy of the
2002 Hayman Fire on Stream Water
Quality and Treatability

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ABSTRACT

Forested watersheds supply drinking water for millions of people in the United States. The increased frequency and severity of wildfires during recent decades have elevated public concern regarding source water protection. Large, high-severity wildfires alter the physical and biological conditions that determine how watersheds retain and release nutrients and regulate stream water quality. The short-term water quality impacts of severe wildfire are often dramatic, but little is known about whether significant post-fire changes persist and what such changes mean for post-wildfire watershed resilience, sustained delivery of clean water from headwater catchments and challenges for water treatment.

Our overall objective was to assess the effects of the largest fire in recorded Colorado history, the 2002 Hayman Fire, on stream water quality. Specifically, we set out to 1) examine stream nitrogen (N) and carbon (C) concentrations and export, 2) quantify the abundance and composition of precursors of potentially hazardous byproducts of treatment water chlorination (e.g., disinfection-by-products, DBPs) including trihalomethanes (THMs), haloacetonitrile (HANs), chloral hydrate (CHD) and halo ketone (HKT) and 3) evaluate the chemical composition of C contained in soil organic matter. We sampled stream water and soils in burned and unburned catchments during 2015 and 2016, nearly 15 years after the wildfire. For stream nutrients, sediment and stream temperature we were able to compare current conditions with those found 1-5 years after the fire, and with pre-fire conditions. We analyzed soil C using pyrolysis Gas Chromatography / Mass Spectrometry (PyGCMS) and developed an automated data management and analysis pipeline to process and interpret large volume of chemical analytical information.

The headwaters of the Upper South Platte River have yet to recover from the 2002 Hayman Fire. We found that stream nitrate, total dissolved N (DTN) and C (DOC) all remained elevated in burned catchments. The extent of a catchment that burned or that burned at high severity had a strong effect both on stream N and C. Nitrate-N was more than an order of magnitude higher in streams draining extensively-burned catchments (>60% of their area) compared to unburned catchments. In contrast to unburned catchments that retain more than 95% of atmospheric N inputs, extensively-burned catchments release more than half of N inputs. Conversely, DOC was higher in streams with moderate wildfire extent. Accordingly, DBP formation was generally greater in these catchments compared to unburned ones. Importantly, precursors of US EPA-regulated THMs (a group of potential carcinogens) were almost double in moderately burned compared to unburned catchments. We found that soil organic matter in burned landscapes had higher percentages of stable aromatic hydrocarbon and nitrogen-containing compounds but lower percentages of lignin compounds and phenol compounds than unburned soils.

The slow return of forest vegetation is likely to contribute to the lasting stream and soil biogeochemical responses to the Hayman Fire. Annual, remotely-sensed estimates of vegetation cover and field trials both suggest that it will take several more decades before forest canopy cover, and expected nutrient demand, return to pre-fire levels. High stream N coupled with low dissolved organic C in burned catchments suggests that C may have replaced N as the primary limitation to in-stream production. Though the persistent stream N increases we report are below human health, drinking water thresholds, they exceed ecoregional reference stream concentrations and demonstrate that extensively-burned headwater catchments no longer function as strong sinks for atmospheric N in the Upper South Platte drainage.

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KEYWORDS

Ponderosa pine forests, water quality, watershed biogeochemistry, nitrogen cycling, water treatment, black carbon, disinfection byproducts, wildfire effects, fire severity, stream nutrients.

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BACKGROUND

Wildfires are natural disturbance events that shape the composition, structure and function of most North American forest ecosystems (Turner, 2010). However, during recent decades increased fire frequency, size and severity (Westerling, 2016) has prompted questions about the capacity of burned catchments to sustain delivery of clean water and other ecosystem services. Forest biomass and organic soil layer combustion causes dramatic short-term nutrient and carbon (C) losses (Bormann et al., 2008; Homann et al., 2011), but it also exposes catchments to post-fire erosion. Wildfires influence stream water quality and nutrient export by reducing plant demand and increasing soil availability in upland and riparian environments (Certini, 2005; Turner et al., 2007; Wan et al., 2001). Post-fire hillslope and stream reconfiguration alters hydrologic connectivity and transport from uplands to stream channels (Hallema et al., 2017; Wagner et al., 2014) as well as the in-stream processes that regulate nutrient retention and release.

Similar to other disturbances, the impacts of wildfires increase with their relative extent and severity within burned catchments (Rhoades et al., 2011; Riggan et al., 1994). High-severity wildfires consume virtually all vegetation and surface organic layers, exposing mineral soils to greater sediment, nutrient and C losses, relative to moderate-severity fires that consume and expose significantly less (Keeley, 2009). Stream water nitrate and sediment export, for example, were higher and more variable in catchments affected by extensive, high-severity burning during Colorado's 2002 Hayman Fire (Rhoades et al., 2011). High-severity wildfires are not uncommon in the dry conifer forests typical of this region (Sherriff and Veblen, 2008; Sherriff et al., 2006). However, if the frequency of such fires increases, vegetation composition, catchment nutrient retention and drinking water supply are all likely to change as well.

The dramatic short-term effects of wildfire on water quality are well-characterized, yet less is known about their long-term consequences or about related factors that control post-fire watershed dynamics (Silins et al., 2014). It is the persistent changes that determine how wildfires impact drinking water sources and water treatment utilities (Bladon et al., 2014; Martin, 2016) for many years and have implications for populations that rely on forested watersheds of the western US (Hutson et al., 2004). The effect of small, low-severity wildfires or those burning in forest ecosystems that regrow rapidly are often short-lived (Mast and Clow, 2008; Mast et al., 2016). Dry conifer ecosystems, in contrast, recover over multiple decades (Abella and Fornwalt, 2015; Fornwalt and Kaufmann, 2014). If as some predict, temperature and drought related shifts in wildfire frequency and behavior cause lasting change in forest composition (Millar and Stephenson, 2015; Trumbore et al., 2015; Westerling et al., 2011) the consequences of the disturbance on watershed nutrient retention could be both lasting and significant (Schlesinger et al., 2015).

Dissolved organic matter (DOM) is a great concern for water utilities because it is a source of precursors of carcinogenic and mutagenic disinfection byproducts (DBPs), including trihalomethanes (THMs) and haloacetonitriles (HANs), formed during drinking water chlorination. Soil organic matter and plant tissues naturally release DBP precursors to source water seasonally (Chow et al., 2008; Hohner et al., 2016). Wildfires have dramatic, lasting effects on plant composition, soil conditions and watershed hydrology (Hallema et al., 2016) that also influence soil C and DOM production, though their effects on DBP precursors are unknown.

Pyrolysis Gas Chromatography / Mass Spectrometry (PyGCMS) can provide a molecular fingerprint of complex organic matter (OM) such as SOM (Smits et al., 2016). Pyrolysis breaks

large molecules down through thermal decomposition in the absence of oxygen (Gonzalez-Perez et al., 2014). GC separates analytes based on their relative affinity for the column stationary phase, and MS detects the mass-to-charge ratios of the ionized fragments. PyGCMS analysis commonly yields hundreds of products from wildfire-induced soils (Faria et al., 2015; Jimenez-Morillo et al., 2016). The time and labor intensive nature of manual peak identification and quantification (Liu et al., 2011) has prevented analysis of well-replicated sampling required to adequately evaluate the effects of wildfires or other land use changes. A fast, reproducible analysis pipeline is necessary in order to process mass chromatographs from PyGCMS (Wehrens et al., 2014).

OBJECTIVES

Public and land management concerns about post-fire watersheds typically recede once notable episodes of soil erosion cease. However, the linked processes that influence ecosystem and soil productivity, nutrient retention and release, and stream water quality and aquatic health continue to respond for years after a fire. Given expectations that changing climate and human-caused ignitions will increase wildfire frequency (Balch et al., 2017; Dennison et al., 2014; Harvey, 2016; Schoennagel et al., 2017), managers responsible for sustaining ecosystem productivity, watershed conditions and clean water supply will require greater understanding of post-fire changes that control stream nutrient and C retention and loss. Owing to the scarcity of pre-fire data and long-term post-fire monitoring, there are few opportunities to characterize the sustained effect of high-severity wildfires on stream water quality and nutrient and C losses. In this project, we revisit streams sampled for five years after the Hayman Fire (Rhoades et al., 2011), including several where sampling began prior to the Fire, to evaluate if that fire's effects persist for more than a decade. We sampled ten burned and four unburned headwater catchments to assess the effect of wildfire extent, burn severity and status of upland and riparian vegetation on water quality 13 and 14 years after the fire.

Working hypothesis – based on our earlier study we expected to find that magnitude of catchment-scale effects will be related to the extent of wildfire or the extent of severe wildfire in a catchment.

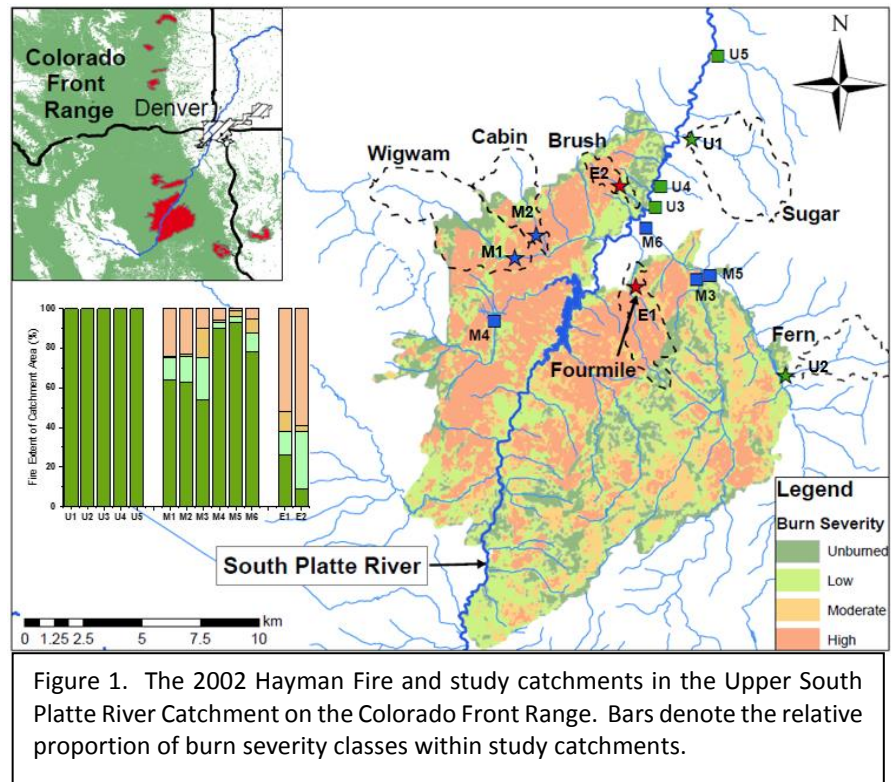
MATERIALS AND METHODS

Study Site

The Hayman Fire burned tributaries of the Upper South Platte River drainage, about 50km southwest of Denver, Colorado (Figure 1). This water source supplies most of the drinking water to the Denver metropolitan area as well as to agricultural and industrial users. The fire burned in the lower montane zone (1980–2750 m) of Colorado's Front Range, in forests comprised primarily of Ponderosa pine (*Pinus ponderosa* Dougl. ex Laws) and Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco). Annual precipitation averages 41 cm (WRDC, 2017) with equal contribution of summer rain and snow fall. The majority of the burn is underlain by the Pikes Peak batholith, a coarse-grained biotite and hornblende-biotite granite (Bryant et al., 1981). Soils are weakly-developed (Typic Ustorthents), excessively-drained, coarse sandy loams (Cipra et al., 2003). Depth to bedrock ranges from 25 to 50 cm and coarse fragments represent 25–50% of the soil volume.

This study included fourteen first and second order tributaries that span from 4 to 40 km² (Figure 1; Table 1). We sampled four unburned streams adjacent to the Burn and ten streams in catchments with 33 to 100% wildfire extent. As a whole, the Hayman Fire burned 25-62% of the uplands and 32-96% of riparian zones in similar headwater catchments (Kershner et al., 2003). Crown and ground cover consumption estimates derived from satellite imagery and ground-based observations, respectively, were used to

determine that 35 and 16% of the Hayman Fire burned at high and moderate severity (Robichaud et al., 2003). Though a recent survey revised the total coverage of high and moderate severity burning within the fire perimeter to 52% and 18 % (Wang and Zhang, 2017), we used the initial post-fire estimates to allow comparison with earlier work (Rhoades et al., 2011).



Sampling and Stream Nutrient Analysis

Streamwater samples were collected and analyzed for dissolved nitrogen and carbon, turbidity and suspended sediment. Stream water was sampled monthly throughout 2015 and 2016 to evaluate seasonal patterns and to estimate nutrient and C export (Figure 1). Discharge was measured concurrent with monthly sampling to flow-weight streamwater concentrations and calculate watershed export. Stream chemistry was analyzed monthly, seasonally and annually; seasonal divisions correspond to the rising limb (Feb-May), falling limb (June – Sept) and base flow (Oct-Jan) of the streamflow hydrograph. Water temperature was measured at 20 minute intervals in these streams using Hobo Water Temp Pro v2 data loggers (U22-001; OnSet Corp, Bourne, MA).

Stream water nitrate (NO₃-N) and ammonium (NH₄-N) concentrations were determined by ion chromatography and electrical conductivity detection, using a AS12A Anion-Exchange column and AG12A guard column for NO₃-N (Dionex Corp, Sunnyvale, CA) and a IC-Pak Cation M/D column for NH₄-N (Waters, Co., Millford) (APHA, 1998a). Dissolved total N (DTN) and organic C (DOC) and was determined by high-temperature combustion catalytic oxidation using a Shimadzu TOC-V_{CPN} total organic carbon analyzer (Shimadzu Corporation Columbia, MD). Dissolved organic N (DON) was calculated as the difference of DTN and DIN (dissolved inorganic

N = nitrate plus ammonium). Turbidity was measured in the 1-L samples using the nephelometric method (APHA, 1998c) (Hach Scientific, Loveland, CO).

Stream Carbon and Disinfection Byproduct Analysis

Filtered water samples were scanned from 200-700 nm using UV-VIS spectrometry (Shimadzu UV-1800), and specific UV absorbance at 254 nm ($SUVA_{254}$, L/mg/m), a surrogate for aromaticity, was calculated by normalizing UV absorbance at 254 nm to DOC concentration. The E2/E3 ratio, correlated with molecular weight of dissolved organic matter, is the absorbance measured at 254 nm divided by the absorbance at 365 nm.

The procedures and methodology for DBP formation tests have been described in our previous publications (Wang et al., 2015; Tsai et al., 2017). Briefly, stream water samples were buffered to pH 8.0 using a $H_3BO_3/NaOH$ solution and chlorinated with $NaOCl/H_3BO_3$ solution (pH 8.0) for 24 hours in the dark at 25 °C. The chlorine concentration added to the sample was calculated according to the equation $[Cl_2] = [3 \times (DOC) + 7.6 \times (TDN)]$, where all concentrations are expressed in mg/L. The residual chlorine was quenched by a 10% Na_2SO_3 solution and DBPs were extracted and quantified by GC-ECD (Agilent 7890) following EPA method 551.1. We quantified trihalomethanes (THMs; trichloro-, dichlorobromo-, dibromochloro-, and tribromo-methanes), haloacetonitriles (HANs; trichloro-, dichloro-, bromochloro-, and dibromo-acetonitriles), chloral hydrate (CHD), and haloketones (HKs; 1,1-dichloro-2-, 1,1,1-trichloro-2-, 1,2,3-trichloro- propanones). The DOM reactivity in forming DBPs was expressed as specific DBP-FP (SDBP-FP, $\mu g\text{-DBP}/mg\text{-DOC}$), which was calculated by dividing the DBP concentration by the initial DOC concentration.

Soil C and Black Carbon Quantification

Total soil C was analyzed by Dumas dry combustion (LECO CHN 2000; St. Joseph, MI). Black carbon (BC) in organic soil layers was quantified using Benzene Polycarboxylic Acid (BPICA) Analysis. We focused analysis on the sum of benzene pentacarboxylic acid (B5CA) and mellitic acid (B6CA). We analyzed soil C composition with the PyGCMS method (Song and Peng, 2010). An automated identification and quantification pipeline was used to extract, identify and categorize into nine classes (*i.e.*, aromatic hydrocarbon (ArH), carbohydrate (Carb), halogen containing compound (Hal), lignin compounds (LgC), nitrogen containing compound (Ntg), polyaromatic hydrocarbon (PAH), phenol compounds (PhC), saturated hydrocarbon (SaH), and unsaturated hydrocarbon (UnSaH) according to degree of chemical similarity.

RESULTS

Stream Nitrogen and Carbon

The effects of the Hayman Fire on stream N have persisted for nearly 15 years. Across fourteen headwater catchments, we found that wildfire extent and severity remained good predictors of stream nitrate and DTN concentrations (Fig 2). The extent of a catchment burned explained 75 and 56% of variation in nitrate and DTN among streams, respectively. The portion of a catchment affected by high severity wildfire explained only slightly less variation. Both N forms increased exponentially with wildfire extent and severity; compared to unburned catchments, stream nitrate

was roughly 10-times higher where > 60% of a catchment burned or > 40% burned at high severity. Stream ammonium concentrations did not differ between burned and unburned catchments.

Mean nitrogen concentrations were higher in burned compared to unburned catchments (Fig 3), throughout this study. Extensively-burned catchments had 16-times more nitrate and 5-times more DTN than unburned catchments, and both N forms were significantly higher than catchments with moderate amounts of wildfire. Ammonium concentrations were unaffected by burning and averaged 0.04 mg L^{-1} overall. Nitrate comprised 33% of DTN on averaged across seasons in unburned watersheds but 61 and 89% in moderate and extensively-burned catchments. Further, in unburned catchments, DIN was split evenly between nitrate and ammonium. In contrast, in moderate and extensively-burned catchments, nitrate comprised 84 and 94% of DIN, respectively.

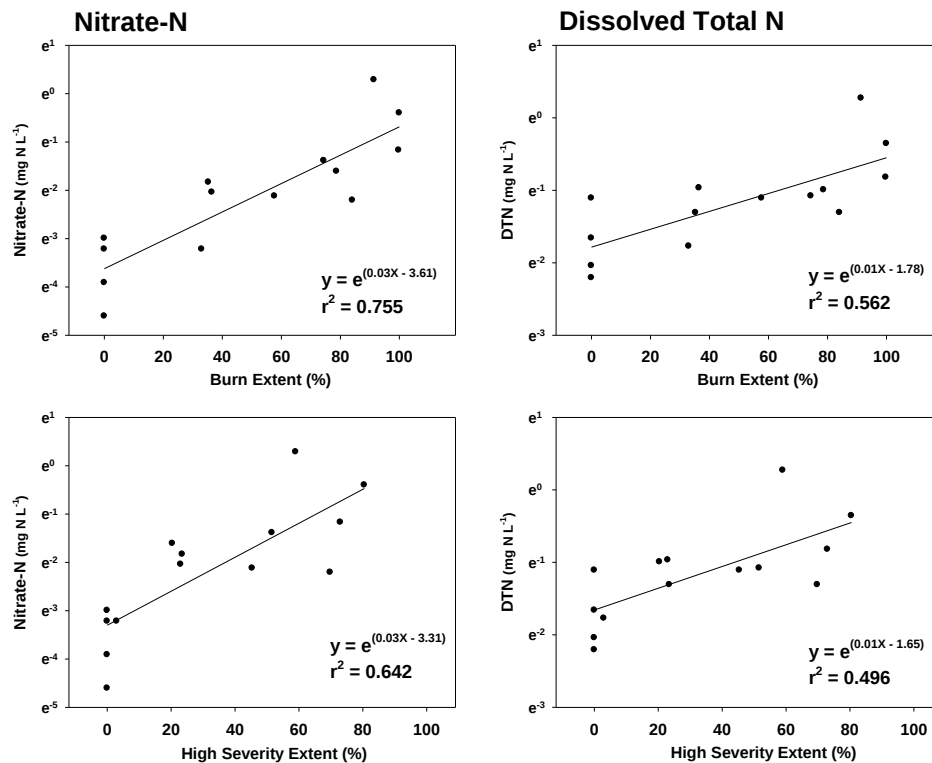


Figure 2. Relations between total wildfire extent within a catchment and the combined extent of high severity wildfire with stream a) nitrate-N and b) dissolved total N.

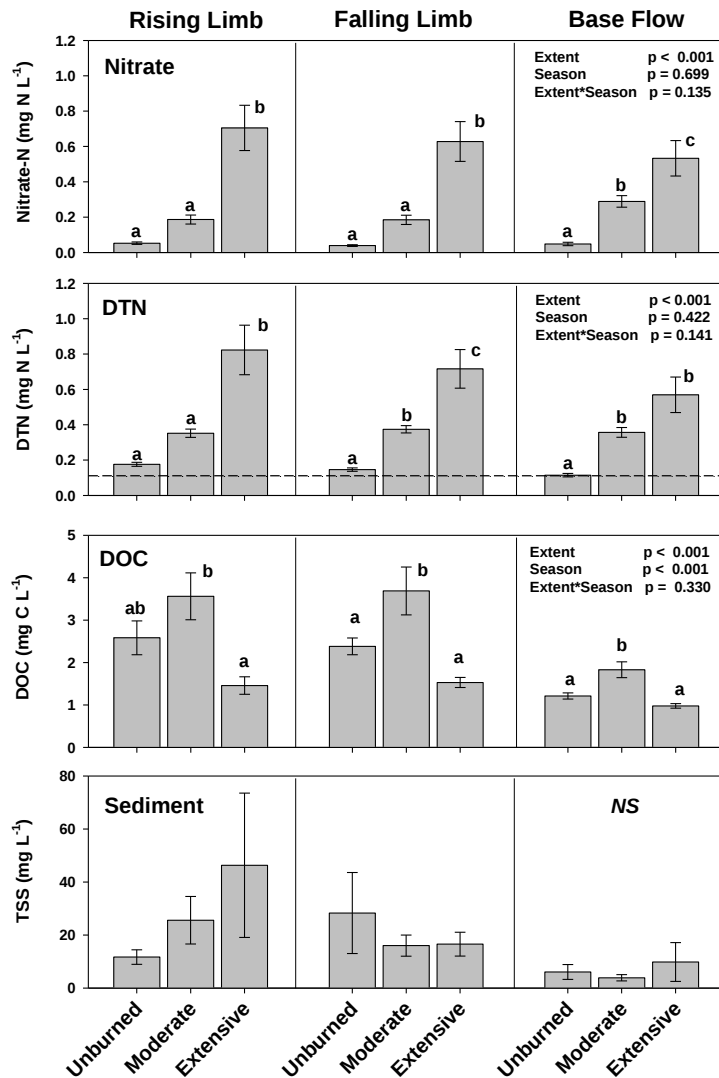


Figure 3 Seasonal mean nitrogen, carbon and total suspended sediment (TSS) concentrations from catchments burned and adjacent to the 2002 Hayman Fire sampled during 2015 and 2016. The dashed line on the DTN panel denotes the proposed TN threshold for least-impaired reference streams in the Western Forest Region of North America (US EPA 2000).

N and C Export

During our resampling, annual DTN export from unburned catchments averaged 0.12 kg N ha⁻¹ compared to 0.44 and 0.65 kg N ha⁻¹ from moderate and extensively-burned catchments (Fig 4). Nitrate-N averaged 0.03, 0.18 and 0.56 kg N ha⁻¹, across the burn severity gradient. Annual nitrate export from extensively-burned catchments was 20- and 3-times higher than unburned and moderately burned catchments. Nitrate represented an increasing proportion of DTN across the burn severity gradient, averaging 21, 44, and 85% of DTN in unburned, moderate and extensively

Dissolved organic C (Fig 3) and N (DON; not shown) concentrations were both highest in catchments with moderate wildfire extent and on average were 1.5 to 2 times higher than unburned or extensively-burned catchments. Stream DOC varied with the stream hydrograph, with lowest average concentrations during base flow relative to the rising and falling limbs. Averaged across seasons, DON comprised 35% of DTN in unburned catchments compared to 6% in extensively-burned catchments. The ratio of stream water C to N (e.g., DOC to DTN) differed among unburned and extensively-burned catchments, as did the relation to stream nitrate-N (Fig 3). Average C:N was 18 in unburned catchments (range: 13-27) and 8 in extensively-burned catchments (range: 1-16). The observed pattern of high stream N and low C in burned streams may result from a shift in nutrient demand and declining N limitation, relative to undisturbed streams.

burned catchments, respectively. Monthly N export peaked in May along with streamflow; May export comprised 30-35% of annual N losses.

Both DOC (Fig 4) and DON export (not shown) were about 3-times higher in moderately-burned catchments compared to unburned and extensively-burned catchments. While DON comprised about half of the DTN exported from unburned and moderately-burned catchments, it was only 11% of DTN lost from the extensively-burned catchments. Sediment losses were 4 and 5-times higher in the moderate and extensively-burned catchments compared to unburned catchments, and 71 and 84% of those losses occurring during peak streamflow in May.

Stream DOC, SUVA₂₅₄, and DBP-FP

The effects of the Hayman Fire on stream DOC and C composition were also still evident after almost 15 years (Table 1). Mean annual DOC concentrations differed among unburned, moderately burned, and highly burned watersheds and were 1.88 ± 1.17 , 3.30 ± 1.81 , and 1.32 ± 0.60 mg/L, respectively. Moderately burned catchments had large variation in DOC (1.17 - 9.55 mg/L). The range of DOC concentration in unburned watersheds fell between two fire severities (0.58 - 5.83 mg/L). The lowest mean DOC and concentration range in extensively burned catchments is consistent with the loss of nearly all vegetation and organic soil cover during severe wildfire and limited forest recovery. In contrast, catchments with moderate extent of wildfire support mixtures of live, partially-combusted and fully-combusted vegetation, soil organic matter layers, and downed wood.

We observed similar patterns among burn severity classes for both DOC and SUVA₂₅₄, a surrogate of C aromaticity. The average SUVA₂₅₄ in the unburned, moderately burned, and highly burned catchments were 2.38 ± 0.57 , 2.98 ± 0.66 , and 2.12 ± 0.61 L/mg/m, respectively, with ranges of 2.93 (1.15-4.08), 3.53 (1.53-5.06), and 2.32 (1.23-3.55) L/mg/m. It is notable that these field data closely matched our previous laboratory experiments (Wang et al., 2015) that found detritus burned at moderate temperature (i.e., ~ 250 °C) produce more aromatic DOC than material burned at higher temperature. Furthermore, other studies found distinct DOC concentrations in burned compared to unburned catchments (Emelko et al., 2011; Hohner, 2016; Writer, 2014) within 1-2 years after wildfire. Our work provides the first evidence that wildfire can influence DOC export for longer than a decade.

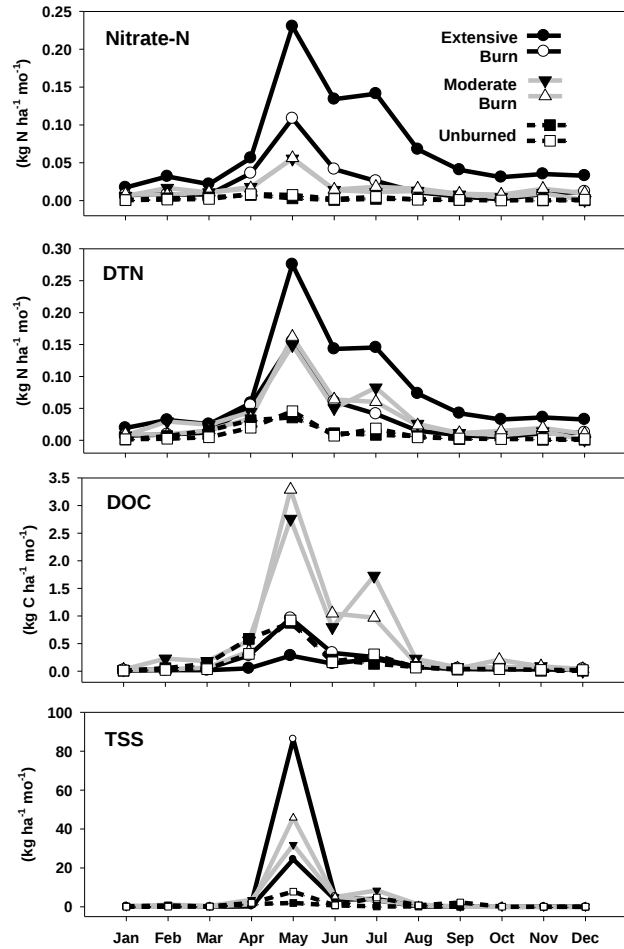


Figure 4 Nitrogen, carbon and TSS export from catchments burned and adjacent to the 2002 Hayman Fire sampled during 2015 and 2016.

To evaluate the potential impacts of wildfire on drinking water treatment we examined DBP formation potential in stream water. THM was the major DBP species in all streams, regardless of fire severity. Similar to DOC, the highest THM formation potential (FP) and widest concentration range occurred in moderately burned watersheds. The lowest THM-FP was observed in highly burned catchments. The differences among the three classes of fire severity were statistically significant ($p < 0.05$). Similar patterns were observed for HAN-FP and CHD-FP. Overall, these results demonstrate that streams draining moderately burned catchments have higher DOC concentration, aromaticity, and DBP formation potential compared to streams in unburned and extensively burned catchments.

Soil Black C

Wildfire decreases the content of total C, but increases the BC content of soil organic layers. The sum of B5CA and B6CA estimated using a 2.27 conversion factor (Guggenberger et al., 2008) was 0.1 ± 0.1 %, 0.1 ± 0.0 %, and 0.6 ± 0.6 % in unburned, moderate-severity and high severity burned landscapes, respectively ($p = 0.12$) (Figure 1b). The amount of B6CA-BC in soil C significantly was sensitive to burn severity ($p = 0.04$). The B5CA to B6CA ratios were 1.0 ± 0.3 , 0.2 ± 0.1 , and 0.3 ± 0.1 in unburned, moderately and highly burned sites, respectively ($p = 0.002$) (Figure 5c). Combustion temperature is known to decrease the B5CA/B6CA ratio (Wolf et al., 2013). In increasing proportion of B5CA and B6CA in total BPCAs (Figure 5d), suggests that burn severity has an influence on the degree of aromatic condensation.

Though BC is persistent to chemical degradation, because of its low density it is highly susceptible to export in post-fire erosion. Elsewhere in Colorado, shortly after the 2012 High Park Fire total BPCA-BCs in organic soil layers were 0.0 %, 1.9 %, and 4.0 % in unburned, moderate- and high severity landscapes (Boot et al., 2015). We also found a small amount of BC remaining in the surface organic layers 14 years after the Hayman Fire. In both cases, post-fire erosion is likely responsible for substantial BC losses.

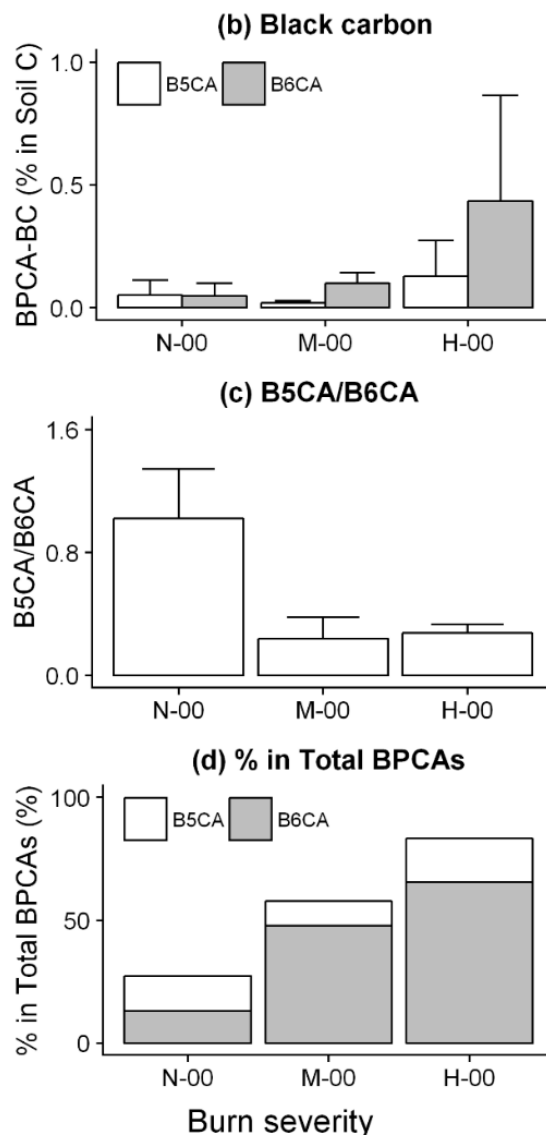


Figure 5. Black carbon per soil C in organic soils sampled 14 years after the Hayman Fire (b); (c) the ratios of B5CA to B6CA in surface soils; and (d) percentages of B5CA and B6CA in total BPCAs. N-00, M-00, and H-00 identify soils in unburned landscapes and moderate-severity and high-severity burned landscapes.

Table 1. Stream DOC and DBP formation potential in Upper South Platte River tributaries during 2015 and 2016. Means with different superscripts differ statistically among burn severity classes (one-way ANOVA; Tukey test, $p \leq 0.05$).

<u>Site ID</u>	<u>Catchment Area</u>		<u>DOC</u>			<u>DBP Formation Potential</u>				
	Total (km ²)	Burned (%)	Conc. (mg/L)	SUVA (L m/ mg)	E2/E3	THM	HAN	CHD	HKT	BSF (%)
						----- (ug/L) -----				
Sugar (U1)	34.3	0	1.8 ± 0.3	3.0 ± 0.2	5.3 ± 0.2	94 ± 17	5.1 ± 0.9	5.2 ± 0.9	8.0 ± 2.0	11.5 ± 1.0
Fern (U2)	18.6	0	2.4 ± 0.4	3.5 ± 0.5	5.6 ± 0.2	186 ± 39	9.7 ± 2.0	8.6 ± 1.8	8.7 ± 2.4	8.5 ± 1.1
No name (U3)	3.8	0	0.9 ± 0.1	2.1 ± 0.3	7.5 ± 0.7	41 ± 5	3.6 ± 0.8	2.4 ± 0.2	6.4 ± 1.6	24.3 ± 2.4
Jenny (U4)	4.6	0	1.5 ± 0.2	2.4 ± 0.3	8.0 ± 0.7	64 ± 10	4.4 ± 1.0	3.4 ± 0.5	7.0 ± 2.1	13.9 ± 1.3
Pine (U5)	35.2	0	2.5 ± 0.3	2.9 ± 0.3	5.6 ± 0.1	149 ± 22	8.6 ± 2.4	6.7 ± 1.0	7.2 ± 1.8	11.0 ± 1.0
Wigwam (M1)	43.3	36	2.2 ± 0.3	3.0 ± 0.1	5.6 ± 0.1	151 ± 24	6.1 ± 1.1	6.9 ± 1.1	8.9 ± 2.2	7.5 ± 0.9
Cabin (M2)	19.8	37	4.0 ± 0.6	4.2 ± 0.5	4.7 ± 0.1	308 ± 54	13.1 ± 3.8	17.6 ± 4.9	8.3 ± 2.0	6.6 ± 0.9
West (M3)	178.6	46	2.6 ± 0.3	3.4 ± 0.3	4.9 ± 0.2	155 ± 18	7.7 ± 1.1	7.8 ± 1.4	9.1 ± 2.1	11.7 ± 1.1
Goose (M4)	215.3	10	3.6 ± 0.5	4.1 ± 0.4	4.8 ± 0.1	286 ± 46	9.5 ± 1.7	15.1 ± 2.3	9.9 ± 2.2	3.5 ± 0.6
Trout (M5)	325.9	7	3.9 ± 0.4	2.3 ± 0.1	6.1 ± 0.1	229 ± 25	10.6 ± 2.4	11.5 ± 2.2	8.5 ± 1.9	15.5 ± 1.5
Horse (M6)	529.8	22	2.9 ± 0.3	2.9 ± 0.2	5.4 ± 0.1	167 ± 21	8.4 ± 1.5	8.0 ± 1.4	7.6 ± 1.8	16.1 ± 1.7
Fourmile (E1)	20.6	74	1.5 ± 0.1	3.0 ± 0.3	5.7 ± 0.2	79 ± 11	5.7 ± 1.1	4.0 ± 0.4	8.0 ± 2.1	13.3 ± 1.1
Brush (E2)	5.9	91	1.0 ± 0.1	1.6 ± 0.1	7.5 ± 0.6	41 ± 3	3.8 ± 0.7	2.5 ± 0.1	6.7 ± 1.9	17.8 ± 0.9
Unburned Watersheds			1.8 ± 0.2 ^A	3.0 ± 0.2 ^A	5.4 ± 0.1 ^A	114 ± 17 ^A	6.2 ± 0.9 ^{AB}	5.8 ± 0.8 ^A	8.1 ± 1.3 ^A	14.5 ± 1.7 ^A
Moderately Burned Watersheds			2.9 ± 0.3 ^B	3.4 ± 0.2 ^A	5.2 ± 0.1 ^A	203 ± 26 ^B	8.6 ± 1.6 ^A	10.6 ± 2.0 ^B	8.9 ± 1.4 ^A	8.1 ± 0.7 ^B
Extensively Burned Watersheds			1.3 ± 0.1 ^A	2.3 ± 0.2 ^B	6.5 ± 0.4 ^B	60 ± 6 ^A	4.7 ± 0.7 ^B	3.2 ± 0.2 ^A	7.3 ± 1.4 ^A	15.5 ± 0.8 ^A

CONCLUSIONS

Post-Fire Water Quality

The persistent stream nutrient and C changes we report here indicate that the Hayman Fire altered how headwater catchments retain and release N. Prior to the Hayman Fire, average annual nitrate export from headwater tributaries of the Upper South Platte River was $0.03 \text{ kg N ha}^{-1}$ (Fig 4). This low level of N release is the net result of 98% retention of atmospheric N inputs (e.g., $1.9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; NADP Site CO21, 2017). During the current study, nitrate export averaged $0.56 \text{ kg N ha}^{-1}$ annually from extensively-burned catchments (Fig 4). This represents only 48 and 70% retention of atmospheric nitrate and total inorganic N input, respectively, in these catchments. Since the fire we estimate that nitrate and DTN export from extensively-burned catchments totaled 7.8 and 9.1 kg N ha^{-1} , respectively, compared to 0.4 and 1.4 kg N ha^{-1} lost from unburned catchments. Owing to logistical limitations, we were unable to sample individual storm events and therefore missed large nutrient export events; as such these are conservative estimates. Nonetheless, our study demonstrates that extensively-burned headwater catchments no longer function as strong sinks for atmospheric N in the Upper South Platte drainage.

Average stream nitrate-N concentrations in catchments with moderate and extensive wildfire were 6- and 16-times above pre-fire levels (Table 2). The mean and maximum nitrate concentrations in burned catchments fell well below the national drinking water standard for nitrate-N (e.g., 10 mg N L^{-1} ; USEPA, 2003). However, we were unable to sample storm-related peak concentrations that likely exceeded that water quality threshold. Storms with rainfall intensities sufficient to generate runoff, increase streamflow and spike nitrate concentrations (Larsen and MacDonald, 2007; Rhoades et al., 2011) occur several times per summer in the Upper South Platte area (WRDC, 2017).

Though post-fire stream nitrate concentrations do not pose a threat to human health, they raise questions about sustaining desired aquatic resources in the Upper South Platte. Prior to the Hayman Fire, stream temperature and sediment were identified as water quality concerns in Upper South Platte tributaries (Colorado, 2002) that have specific relevance to sport fisheries and other aquatic resources. The water quality of Upper South Platte tributaries has become a larger issue since the Hayman Fire, and burned catchments are listed on Colorado's 303d list (Colorado, 2016b) for dissolved oxygen, temperature, reactive iron, and threats to aquatic life. Stream temperature increased after the fire and remained elevated through our current study (Fig 5). In burned catchments, we found that stream nitrate and DTN frequently exceeded concentration thresholds that were established to signal concerns regarding public water supply, aquatic life, and other beneficial uses in Colorado's cold rivers and streams (e.g., $1.25 \text{ mg TN L}^{-1}$; (Colorado, 2016a)). Further, in both moderate and extensively-burned catchments, nitrate and DTN concentrations greatly exceeded N concentrations representative of 'least-disturbed' reference streams of the Western Forest Region (e.g., $0.12 \text{ mg TN L}^{-1}$ and $0.014 \text{ mg nitrate-N L}^{-1}$; (USEPA, 2000)). We found that elevated DOC in catchments with moderate burning contribute chemical precursors that react during water treatment chlorination to form potentially hazardous disinfection by-products (Table 1; Tsai et al., 2017). Interestingly, as opposed to lingering stream nutrient and C responses, sediment problems have abated for a number of Upper South Platte tributaries that have subsequently been delisted since the time of the fire (Colorado, 2016b).

Recovery Processes

Almost 15 years after the Hayman Fire, we found little indication that elevated nutrient concentrations and export from extensively-burned catchments were returning to pre-fire levels. The lasting shift reflects combined changes in vegetation, soils and ecosystem nutrient and C cycling. Post-fire increases in soil nutrient availability commonly persist for several years (Rhoades et al., 2015; Turner et al., 2007; Wan et al., 2001), though the precise duration of this effect is less certain (Jiménez-Esquilín et al., 2008). After the Hayman Fire, herbaceous plant cover increased rapidly and surpassed pre-fire levels within about five years (Abella and Fornwalt, 2015; Fornwalt and Kaufmann, 2014). This post-fire increase in herbaceous plant cover would increase infiltration, reduce overland flow (Pannkuk and Robichaud, 2003) is likely to explain the decline in stream sediment we observed. The persistent post-fire stream nutrient response, in contrast, may be the consequence of the extremely slow pace of forest recovery into the burn (Fig 6; Chambers et al., 2016; Wang and Zhang, 2017). Tree establishment has been rare within high-severity burn patches, both for the Hayman Fire and other Colorado fires in ponderosa pine forests (Chambers et al., 2016). Our estimate that forest recovery to pre-fire conditions may require 34 years (Fig 6) agrees with these field observations and is within the timeframe proposed by others for the Hayman Fire (e.g., 20-50 yrs (Wang and Zhang, 2017).

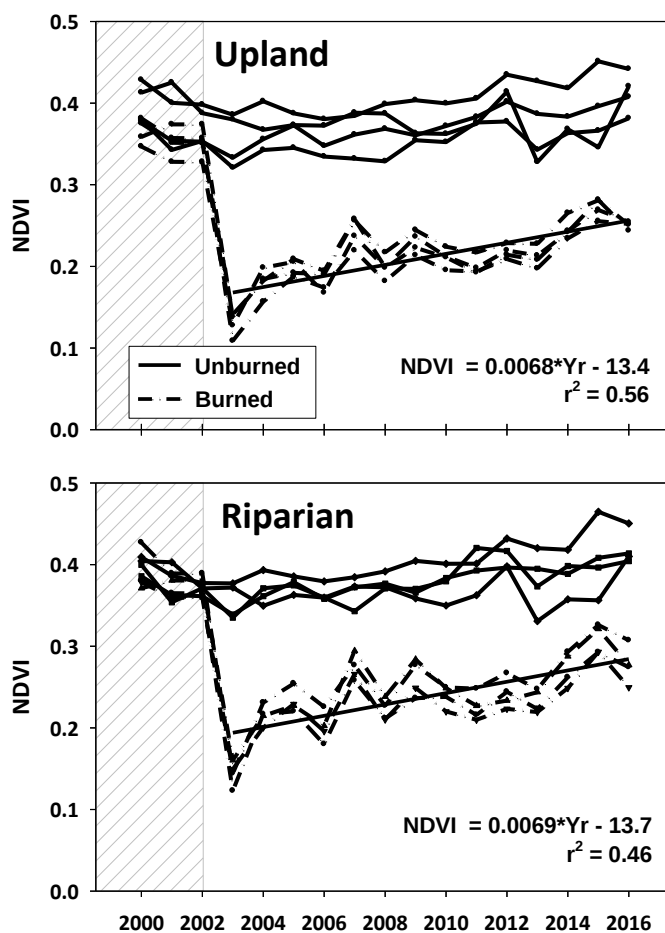


Fig 6 Growing season (May-July) normalized difference vegetation index (NDVI) for riparian and upland landscapes in four catchments burned by the June 2002 Hayman Fire and four unburned catchments.

Catchment-scale nutrient demand is expected to remain depressed for another two decades until upland and riparian vegetation regain pre-fire canopy cover and aboveground biomass. In addition to reduced soil nutrient uptake, the slow recovery of riparian vegetation has long-term implications for stream light, temperature and organic matter inputs and subsequent effects on in-stream metabolism and nutrient demand. We found, for example, much lower stream C:N and higher inorganic N in severely-burned catchments. Low stream DOC in burned catchments may be the lasting effect of organic matter losses during the wildfire compounded by limited allochthonous inputs from upland and especially riparian zones. The high inorganic N and low DOC we measured in these catchments may indicate that severe wildfire generates a switch from the N-

limited conditions typical of pristine catchments to C-limited in-stream production. On-going tracer additions have measured lower stream N uptake in burned compared to unburned Colorado catchments, providing preliminary evidence that wildfires alter nutrient limitation and in-stream retention processes.

Land Management Implications

Elevated post-fire N and C export from headwater catchments have obvious consequences for drinking water supply, municipal water treatment and aquatic habitat, yet they also underscore the prolonged response to severe wildfire. It is unknown if the continued nutrient losses in catchments burned by the Hayman Fire are the consequence of lasting changes in soil nutrient availability and leaching (Certini, 2005; Jiménez-Esquilín et al., 2008; Turner et al., 2007), or merely because nutrient supply remains higher than plant demand. On-going upland reforestation will compensate for slow tree establishment in severely-burned areas (Chambers et al., 2016) and facilitate recovery of numerous ecosystem processes and conditions. Our findings suggest that targeting planting activities at exposed headwater riparian zones may accelerate the return to pre-fire stream nutrient levels.

The Hayman Fire, the largest wildfire in Colorado's recorded history, is an example of the impacts of changing climate on forest watersheds, and of the effects of long-term land use practices on wildfire behavior. It has become a motivation to increase the pace of hazardous fuel reduction treatments in Front Range forests. The fire had a relatively large proportion of high-severity combustion, resulting from extreme drought and fuel accumulated during decades of fire suppression (Chambers et al., 2016; Sherriff et al., 2006). The persistent post-fire stream nutrients and C changes we report here, offer an example of how a 'megadisturbance' (*sensu* Millar and Stephenson, 2015) may alter ecosystem structure (Westerling et al., 2011) and processes such as nutrient retention in dry conifer forests. Forests of the Colorado Front Range, like elsewhere in the continental US, are subject to increased amounts of N deposition associated with urban growth, agricultural production and other factors (Fenn et al., 2003; Galloway et al., 2003; Vitousek et al., 1997). Chronic, elevated nutrient inputs coupled with increasing frequency and severity of forest disturbances (Abatzoglou and Williams, 2016; Westerling, 2016) are a serious challenge for sustained delivery of clean water from headwater forests (Bladon et al., 2014; Brown and Froemke, 2012; Emelko et al., 2011).

Remaining Gaps & Future Considerations

We were able to meet and surpass the proposed study objectives and advance general understanding of the long-term effects of wildfires on forest watershed processes, post-fire stream water quality and potential concerns for post-fire drinking water treatment. Our work provides new evidence for the persistent effects of extensive, high-severity wildfire on stream nutrients. It also demonstrates that even watersheds burned to a moderate extent have lasting stream water N and C responses. Further, we show that the increase in DOC and disinfection byproduct precursors exported from burned catchments is a consideration for drinking water treatment and may be a source of additional treatment costs. We were able to leverage support JFSP to expand studies into the High Park fire, another Colorado Front Range Fire, and to establish new research collaboration and outreach partnerships.

In spite of these advances, the processes that regulate in-stream N retention remain poorly understood. Further work is needed to evaluate whether soil N turnover and leaching from upland and riparian areas is a significant contributor to stream nutrient losses. It is possible that the observed high inorganic N and low stream DOC in extensively-burned catchments signals a reduction in N-limitation that typifies pristine forest catchments. The potential that N demand has been saturated in burned catchments has been confirmed by initial trials that show minor N uptake following experimental stream injections. Coupled with high N concentrations, the low stream DOC in extensively-burned streams may represent the lasting effect of organic matter losses during the wildfire compounded by low allocthonous inputs from uplands or riparian zones. Work, conducted at multiple catchment scales, burn severities and times since fire will be required to adequately understand how wildfire alters N and C stoichiometry and regulates stream N and C release.

The Hayman Fire is often considered ‘extreme’ owing to its size, extent of severe fire behavior, historic drought conditions at the time of ignition, hazardous pre-fire fuel loads, erosive nature of the soils and slow forest recovery. Continued work at Hayman and on wildfires elsewhere is needed to determine how representative these findings are of long-term watershed responses to large, high-severity wildfires.

Source Water Protection & Advancing Watershed Restoration

Forests and watersheds disturbed by severe wildfire represent a testbed to advance knowledge of ecosystem resilience. The “megafires” of the past decades underscore limitations of current understanding about recovery of water quality and nutrient retention to pre-fire conditions. There is additional need to examine the effectiveness of upland and riparian plantings aimed at restoring post-fire nutrient retention. Such work will help broaden thinking about source water protection and watershed restoration to include ecosystem resilience, forest recovery and nutrient retention. Future efforts to involve monitoring by trained citizen scientists will expand our project’s capacity to survey water quality, aquatic biota, stream channel and watershed condition more extensively and will strengthen local involvement.

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APPENDIX A- Contact Information

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Proposed Deliverables and Science Delivery Products

Deliverable Type	Description	Delivery Dates
Master's thesis	Clemson University MSc student project	Summer 2017
Presentations	AGU, Fire Ecology Association	Fall 2017
Field demonstrations/tour	Field trip for local land managers, researchers, and others	Summer 2017
Refereed publication	Long term effects and watershed conditions	Winter 2017
Refereed publication	DBPs	Winter 2017
Non-refereed publication	(FMT) BMP recommendations for managers for distributing fuels into piles to minimize plant and soil impacts	Winter 2017

APPENDIX B- Completed Deliverables

Deliverable Type	Description	Delivery Dates
PhD Dissertation	Kuo-Pei Tsai - Clemson University, Forestry and Environmental Conservation Dept. ‘Alterations of disinfection byproduct formation following exposures algae to wildfire ash solutions and copper algaecide (jointly supported by JFSP and other funds).	Spring 2017
Presentations Organized Special Sessions	Session Title: B025. Challenges of Wildland Fire on Water Quality and Drinking Water Supply; Session ID: 13514; 2016 American Geophysical Union Fall Meeting; Co-convenors: C. Rhoades, USFS; A. Chow, Clemson U.; T. Covino, CSU. Section/Focus Group: Biogeosciences Session Title: Forests to Flames to Faucets: The Influence of Wildfire on Watershed Processes; Fire Continuum Conference, Assoc for Fire Ecology and Int’l Assoc of Wildland Fire; Missoula, MT; Co-convenors: C. Rhoades, USFS; S. Doerr, U Swansea; U. Silins, U. of Alberta	December 2016 May 2018
Invited Presentations	Colorado Watershed Wildfire Protection Group. ‘The Legacy of Severe Wildfire on Front Range Water Quality.’ National Forest Foundation Collaborative Restoration Workshop ‘Targeting Post-Wildfire Watershed Restoration at Source Water Protection.’ Watershed Effects of Wildfire Research Findings Workshop; Coalition for the Poudre River Watershed. CO-WY, Soc of Am Foresters, Casper, WY. ‘Changing Forest Conditions - Implications for Colorado and Wyoming Watersheds.’ Denver Water Monthly Lecture Series; ‘Biogeochemical Effects of Wildfire - Implications for Watersheds and Water Supply.’	4/8/16 4/27/16 11/15/16 5/12/17 7/20/17
Professional Meetings	Soil Science Society of America Annual Meeting, Phoenix, AZ; ‘Linking Soil Nitrogen & Carbon to Post-Wildfire Water Quality.’ American Geophysical Union Fall Meeting ‘Persistent Influences of the 2002 Hayman Fire on Stream Nitrate and Dissolved Organic Carbon’ ‘A Tracer Approach to Quantify Post-Wildfire Stream Nitrogen Retention’ ‘The Lasting Effect of Wildfire and Fire Extent on the Chlorine Reactivity of Dissolved Organic Matter after the 2002 Hayman Fire, Colorado’ Western South Dakota Hydrology Meeting. ‘Drought-Related Disturbances - Implications on Forest Water Quality.’ European Geophysical Union, Annual Meeting, Vienna, Austria; ‘Filling Gaps in Biogeochemical; Understanding of Wildfire Effects on Watersheds & Water Quality.’	11/16 December 2016 4/5/17 4/25/17

University Lectures	‘Implications of Wildfire for Forest Soils and Watersheds.’ Foundations of Soil Science (SOCR 571); Soil and Crops Dept, CSU. (30 March 2015).	3/30/15
	‘Implications of Wildfire For N Biogeochemistry.’ Dept of Atmospheric Sciences, CSU.	12/8/15
	‘Biogeochemical Water Quality Implications of Front Range Wildfires.’ Environmental Engineering, CU.	2/24/17
	‘Water Quality Implications of Front Range Wildfires.’ Dept Forest, Range, Watershed, CSU.	11/16 & 11/17
Field demonstrations/tour	Riparian restoration options in severely burned catchments, Green Forests Work, LLC; Pike San Isabell NF.	6/16
	Residual black carbon implications for catchments and soil mapping; Hayman Fire, NRCS, CSU, U. Clemson.	7/16
	Watershed considerations for expanding prescribed fire and managed wildfires in Front Range forests; Northern Colorado FireShed Network; Southern Rockies Fire Science Exchange	8/17
Refereed publications	The Long-Term Effects of a Severe Wildfire on Stream Nitrogen and Carbon in Headwater Catchments	In Review – Ecosystems (10/17)
	The Lasting Effect of Wildfire on Disinfection Byproduct Precursors in Forested Watersheds	In Review – ES&T (10/17)
	Molecular Characterization of Soil Organic Matter 14 Years after Wildfire using Pyrolysis GC/MS	In Review – ES&T (10/17)
Non-refereed publications	Stream Water Quality Concerns Linger Long After the Smoke Clears - Learning from Front Range Wildfires. Special Issues on Forests; Colorado Water; March/April 2017.	March 2017
	Learn from the Burn: The High Park Fire 5 Years Later, US Forest Service, Rocky Mountain Research Station; Science You Can Use Bulletin; May / June 2017 Issue 25	June 2017
	Forest Management to Protect Colorado’s Water Resources - A Synthesis Report to Support House Bill 16-1255, Colorado State Forest Service; CO Water Conservation Board June 2017	June 2017
Computer Program	An automated identification and quantification pipeline was developed in the RStudio Desktop version 1.0.44 (Boston, MA, USA) for extracting the pyrolysis products’ information from PyGCMS data. All identified pyrolysis products were automatically categorized into nine chemical classes according to degree of chemical similarity. This program will be freely available upon request.	Spring 2018