FINAL REPORT

Title: Forest fire alters disinfection byproduct precursor exports from forested watersheds

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ABSTRACT

Detritus material in forested watersheds is the major terrestrial source of dissolved organic carbon (DOC) and disinfection byproduct (DBP) precursors in source waters. Carcinogenic DBPs, such as trihalomethanes (THMs), are formed when DOC reacts with disinfectants such as chlorine during drinking water treatment. Many studies have examined DBP precursor exported from forested watersheds; however, DOC leaching from pyrogenic organic matter, could have different treatability and reactivity in DBP formation compared to the DOC leaching from unburned detritus layer. Also, fire intensity is an important factor governing the yields and speciation of pyrogenic organic matter in forest floor and eventually affects the quantity and quality of DOC exported from the burned watersheds.

Here, we conducted controlled-field and watershed-monitoring studies to evaluate prescribed burning practices and landscape processes on the formation and exports of DOC and DBP precursors from forested watersheds. Detritus materials were collected from experimental plots with different burning schedules and frequency (including periodic and annual dormant season burn and annual growing season burn) and were incubated under field conditions. Water collected from different management practices at different times were characterized and tested for their water treatability, including propensities in DBP formation and removal efficiencies in coagulation-flocculation processes. In addition, an unmanaged and a regularly prescribed burned watersheds at the Santee Experimental Forest, South Carolina were monitored monthly for DOC exports in 2014. Water exported from several wildfires in California were also collected for DBP formation test.

Our experiments demonstrated the prescribed fire management practices could reduce the terrestrial sources of DBP precursors within watersheds, consequently improving water treatability in terms of lowering DOC concentration and THM-FP. Importantly, the prescribed burn only reduce concentrations of DOC and DBP precursors in source water but not affect the characteristics of DOC or its treatability. In contrast, our field investigation showed that wildfire deteriorated water quality in particular on sediment loads. Water utilities may need a greater dosage of coagulants to process the source water from wildfire burned watersheds. Finally, based on the field observation and controlled studies, we developed a box model to illustrate the impacts of wildfire and prescribed fire on surface water quality and treatability.

KEYWORDS

Box model; chemical composition; dissolved organic carbon; disinfection byproduct; forest management practices; forest floor; optical characterization; prescribed fire; water quality; water treatability;

LIST OF ABBREVIATION

BIF: bromine incorporation factor; C-DBP: carbonaceous DBP; CAA: chloro-acetic acid; DBP: disinfection byproduct; DCAA: dibromo-acetic acid; DOC: dissolved organic carbon; DON: dissolved organic nitrogen; EC: electoral conductivity; E_2/E_3: ratio of UV absorption at 250 to 365 nm; EEMs: fluorescence excitation-emission matrices; FI: fluorescence index; FRI: fluorescence regional integration; HAAs: haloacetic acids; HANs: haloacetonitriles; HIX: humification index; PAHs: polycyclic aromatic hydrocarbons; POC: particulate organic carbon; STHM-FP: specific THM-FP; SHAA-FP: specific HAA-FP; SHAN -FP: specific HAN-FP; SMB: soluble microbial byproduct; SUVA: UVA_{254}/DOC; TCM: trihalomethane; THM: trihalomethanes; TDN: total dissolved nitrogen; TDS: total dissolved solid; TSS: total suspended solid; TCAA: trichloro-acetic acid; UVA_{254}: specific ultraviolet absorbance at 254nm; VSS: volatile suspended solid; WEOC: water extractable carbon; WETN: water extractable total nitrogen.

ACKNOWLEDGEMENTS

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PROJECT OVERVIEW

Prescribed fire is a common forest management practice implemented in southern pine forests. Forest fires modify the chemical composition of the detritus layer on the forest floor, converting lignin and polysaccharide rich and relatively degradable carbon pools to polycyclic aromatic and charcoal rich and recalcitrant black carbon. The mass of these carbon pools is affected by the schedule and frequency of prescribed burning, and corresponding forest management practices applied on the forest ecosystems. Importantly, detritus material in forested watersheds is the major terrestrial source of dissolved organic carbon (DOC) and disinfection byproduct (DBP) precursors in source waters. Accordingly, forest management practices could affect the quantity and quality of DOC and DBP precursor export, eventually affecting the treatment processes in water facilities and the formation of DBPs in finished waters.

The study addressed two important research questions related to forest fire and drinking water quality: 1. Can we control DBP precursor production and export through effective fuel treatment and prescribed burn practices? 2. Are the treatability and DBP reactivity of DOC exported from prescribed burned watersheds different from those exported from unburned forested watersheds or severe wildfire burned watersheds? To provide scientific supports to answer these questions, we included three components in these works: 1) Management Practices, 2) Landscape Processes, and 3) Wildfire Investigation.

1) MANAGEMENT PRACTICES

A. Objective

The objective of this section is to evaluate different forest management practices on the production and characteristics of DOC and DBP precursors.

Specific Hypothesis: Annual dormant season prescribed burning at low severity produces heavier and more hydrophobic DBP precursors when compared to periodic growing season burning at high severity.

B. Background

Prescribed burning, widely used fuel reduction technique especially in southeastern United States, is one of the essential forest management practice to reduce the susceptibility of forests to wildfire by altering the thickness and composition of forest detritus and understory vegetation. Few, if any, other treatments have been developed that can compete with prescribed fire for its combination of economy and effectiveness. In 2011 alone, over 2.6 million hectares were burned by prescription for forestry purposes in the 13 southern states (Waldrop & Goodrick, 2012). The O Horizon of forest soils, comprised of the litter and duff, serves as a critical source of organic materials (Binkley & Fisher, 2013). This litter and duff, referred to in this publication as forest ground litter, contributes to dissolved organic matter in forested watersheds and subsequently impacts water quality (Bladon *et al.*, 2014). Wildfire causes considerable removal or the O Horizon, increases variability of stream DOC, increases suspended sediment and particulate organic carbon (POC) downstream, and increases soil pH (Smith *et al.*, 2011, Stephens *et al.*, 2004). Low intensity prescribed burn on the other hand, can have little to no effect on water quality

parameters, or as some reports similar effect to those of wildfire events if management consistently (Arkle & Pilliod, 2010, Brown *et al*., 2015, Douglas *et al*., 2015). As prescribed fire is supposed to be applied with high moisture content in the duff layer to ensure an organic layer remain after burn (Waldrop & Goodrick, 2012), if conducted properly in the lower Coastal Plains like our site, it should not necessarily increase soil erosion.

C. Materials and Methods

a. Study Sites

The source ground litter materials for this incubation was collected at the Tom Yawkey Wildlife Center in Georgetown, South Carolina, USA. Part of the forest on this site has been managed with prescribed fire since 1978 and the predominant overstory tree species are longleaf pine (Pinus palustris Miller), loblolly pine (Pinus taeda L.), turkey oak (Quercus laevis Walter), and sweetgum (Liquidambar styraciflua L.) (Coates, 2017). With a mild subtropical climate, the annual average precipitation (1981-2010) was around 55 inches, and air temperature around 18 °C in the area. At the time of this study in 2016, managed part of the forest has been burned 16-20 times since 1978, while the unmanaged part of the forest has not received any form of applications since this property was gifted to South Carolina Department of Natural Resources in 1976.

b. Field Observations

Prior to burning, one 1m × 1m destructive sample of live vegetation was obtained at each of six sampling plots within each treatment unit. We measured the height of this vegetation prior to collection with a 1 m ruler. Common understory species included common bracken fern (*Pteridium aquilinum*), sweetgum (*Liquidambary styraciflua*), gallberry (*Ilex glabra*), switch cane (*Arundinaria gigantea*), highbush blueberry (*Vaccinium corymbosum*), and a variety of grasses. None of these was wiregrass (*Aristida stricta*), however, which is commonly associated with longleaf pine forests. This island property lies within the wiregrass gap (Walker *et al*., 2006). Brown's Planar Intercept Method (Brown, 1974) was used to tally down and dead woody debris in all of our stands prior to and after burning. We specifically followed the specifications of this technique using the methods of Stottlemyer. (2004). Brown's Planar Intercept Method produces estimates of 1-, 10-, 100-, and 1000-hr fuel loads; we obtained these estimates in both the long-term unburned and frequently burned stands. 1000-hr fuels have been excluded from our results and discussion because they were not consumed as a result of these low intensity, low severity burns. Estimates of down and dead woody debris height, litter (Oi) depth, and duff (Oe+Oa) depth (when present) were obtained in nine locations per plot prior to fire along the transects.

c. Tray Study

To test the effect of prescribed burning, ground litter materials were collected at three units from the unmanaged site of the forest, and three units from the annual prescribed burned forest before and after a dormant seasonal prescribed fire in 2015. To test the effect of different burn practices, ground litter materials were also collected from 3 units burned during the growing season of 2015. Collection of ground litter materials was conducted immediately after containment of the fires. All burns were head-fires and mean flame lengths in each of the annual burns were mostly 0.3-1 m, and fire temperatures were recorded using in-situ thermocouples. The averaged peak burning temperatures were between 200-315 °C (Coates, 2017). Destructive sampling of ground litter was conducted with a 1 m x 1 m sampling frame, along a transect every 50 meters at each unit of the forest we conducted the study on. Mixture of burned (ash and charred), fine (live

vegetation and woody [only 1, 10, 100 hrs. ignited]) and detrital (litter and duff) materials were collected. Collected materials were dried in oven at 70 ˚C for 48 hours and kept in desiccators until start of the incubation experiment on Jan 11, 2016.

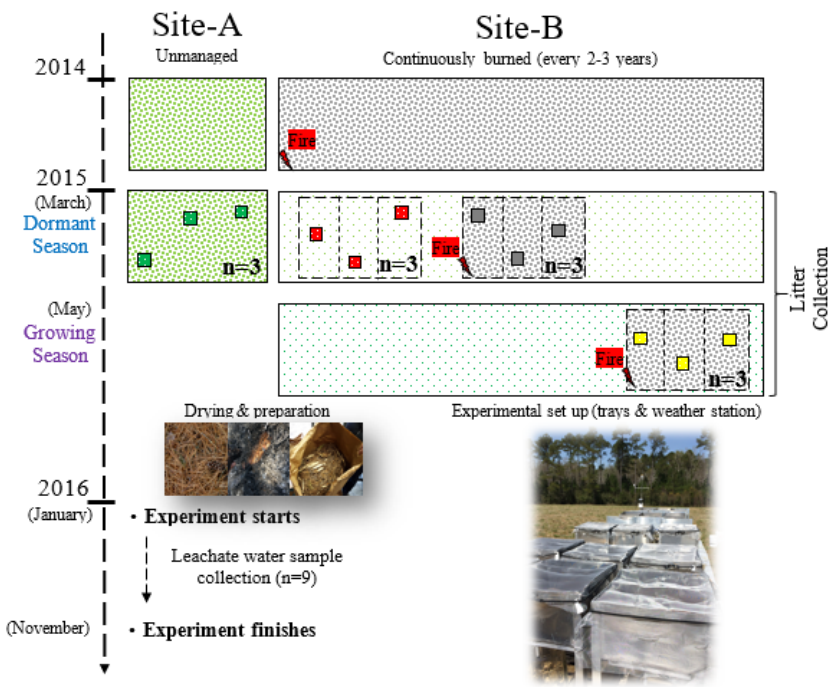

Figure 1. Scheme for the forest management strategy and experimental design. Sites-A and B show unmanaged and managed (i.e., managed pre-burnt, after dormant and growing season burns), respectively. Site A has not been burned or harvested since 1978, while the latest burning was performed for site B in 2014. Green, red, blue and purple rectangles show unmanaged, pre-burnt, after dormant and after growing season burned plots (n=3 for each), respectively.

One kilogram of collected litter material from each sample was placed in custom-made open top aluminum trays (2ft x 2ft x 1 ft) (Figure 1), and three trays were assigned to each treatment group (unmanaged, managed pre-burn, growing seasonal burned, and dormant seasonal burned). In addition to the sample trays, three blank controls for rain water (empty trays) were also placed on an open field at Hobcaw Barony, a privately-owned research preserve located on the coast near Georgetown, South Carolina. A weather station (Campbell Scientific CR800) was located next to the trays which recorded precipitation, air temperature, air pressure, radiation, humidity and wind speed every 15 minutes. This incubation experiment lasted one year, during precipitation events, rainwater saturates the litter material in trays and drains through a tubular opening at tray bottom, leachate was collected in 34L marked glass carboys connected underneath. Total volume of water collected by each tray was recorded for every rain event. When enough water (>2 L) was collected in carboys, we would transfer the samples into 1L amber glass bottles and keep them refrigerated at 4˚C until analysis. Depending on the frequency of precipitation and measurement difficulties, we measured different amounts of water quality parameters on selected samples. Basic water quality parameters including pH, electoral conductivity (EC), total suspended solid (TSS) and volatile suspended solid (VSS), DOC, total dissolved nitrogen (TDN), and orthophosphate concentrations. Spectroscopic properties including specific ultraviolet absorbance at 254nm (UVA_{254}), ratio of UV absorption at 250 to 365 nm (E_2/E_3), fluorescence excitation-emission matrices (EEMs) (categorized into regions I: tyrosine-like, II: tryptophan-like, III: fulvic acid-like, IV: soluble microbial byproduct (SMB)-like and V: humic acid-like (Chen *et al.*, 2003). Total weight loss for each tray was also calculated at the end of experiment as a measurement of how much total carbon were lost during the incubation.

d. THM-FP tests.

FP tests were conducted to determine the maximum precursor concentration levels in the samples. Initially, before addition of oxidants into the samples, water pH was maintained at 7.8 with 10 mM borate buffer. To measure THM-FP, samples were oxidized with excess Cl2, and initial oxidant doses were calculated for each samples using following formula: 3 x DOC + 7.6 x NH_4^+ + 10 (Majidzadeh *et al.*, 2017). After five days of incubation at room temperature (21-22 oC) in headspace free 125 mL pre-cleaned amber bottles, the residual Cl2 was measured and quenched with slightly excess (more than stoichiometric requirement) ascorbic acid. Detailed descriptions for sample extraction & analysis and minimum reporting levels (MRLs) used for quantification of DBPs were presented elsewhere. Student's t-test was used to detect statistically significant differences between measurements.

D. Results and Discussion

a. Field Observations

The primary contributor to pre-fire fuel loading in all treatments was forest detritus (Figure 2a). Total fuel loading was highest in the long-term unburned control ($p<0.01$). Post-fire fuel loading in our burned stands was composed of both woody debris and burned detritus. Live fuels were essentially consumed by the fires. Detrital mass post-fire was significantly greater in the annual growing treatment units ($p<0.01$) but did not differ between the annual and biennial dormant units. Results for pre-burn fuel structure did not mirror the results for pre-burn fuel loading; total pre-burn fuel height was greatest in the annual growing burns ($p=0.04$), due in large part to much higher totals for live fuel height (Figure 2b). Down and dead woody debris height was significantly more in the long-term unburned stand than in the burned units (ANOVA $p=0.01$; linear contrast $p=0.04$). Detrital depth was highest in the long-term unburned stand as well (ANOVA $p<0.01$; linear contrast $p<0.01$). Total post-burn fuel height did not differ among the burn treatments ($p=0.07$), despite differences in post-burn down and dead woody debris height ($p=0.04$) and charred depth ($p<0.01$). Charred depth was significantly greater in the biennial dormant burns ($p<0.01$).

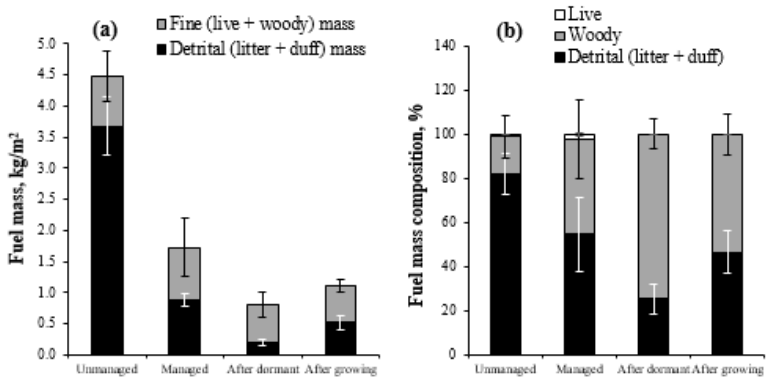

Figure 2. Fuel loading a) and fuel structure b) pre- and post-fire at treatment units on the Tom Yawkey Wildlife Center.

Pyrolysis results of only detritus materials showed that the phenolic compounds, (i.e., lignin like) constitutes ~60-80% of all functional groups independent from the management which can be related with incomplete combustion of the materials (Coates et al., 2017). In contrast with the significant decrease in detritus mass, prescribed burning did not significantly change the chemical functional groups (proteins [nitrogen compounds], carbohydrates [oxygen compounds], and lipids [aliphatic compounds] in the NOM structure of detritus materials (Figure 3). The Aromatic (1-ring) compounds have shown some degree higher concentration in unmanaged samples. This can be related to higher level of toluene concentration in unmanaged samples compared to burnt

samples (Coates, 2017). Controversial observations were reported on the formation and fate of polycyclic aromatic hydrocarbons (PAHs) after burning. While some researchers reported elevated level of PAH formation which survived and remained for long period of time (Forbes *et al.*, 2006), some others indicated that PAHs can be easily degraded and several months later its level usually returns back to original (Kim *et al.*, 2003). In this study, PAHs constituted only 2-3% of the total biomass regardless of the treatment. This indicates that the effect of prescribed burning on the formation of PAH is minimal possibly due to incomplete, low intensity and severity burning of some of the detritus materials (Coates, 2017). These findings suggest that low intensity prescribed burning does not significantly alter structure or functional groups attached on the NOM significantly.

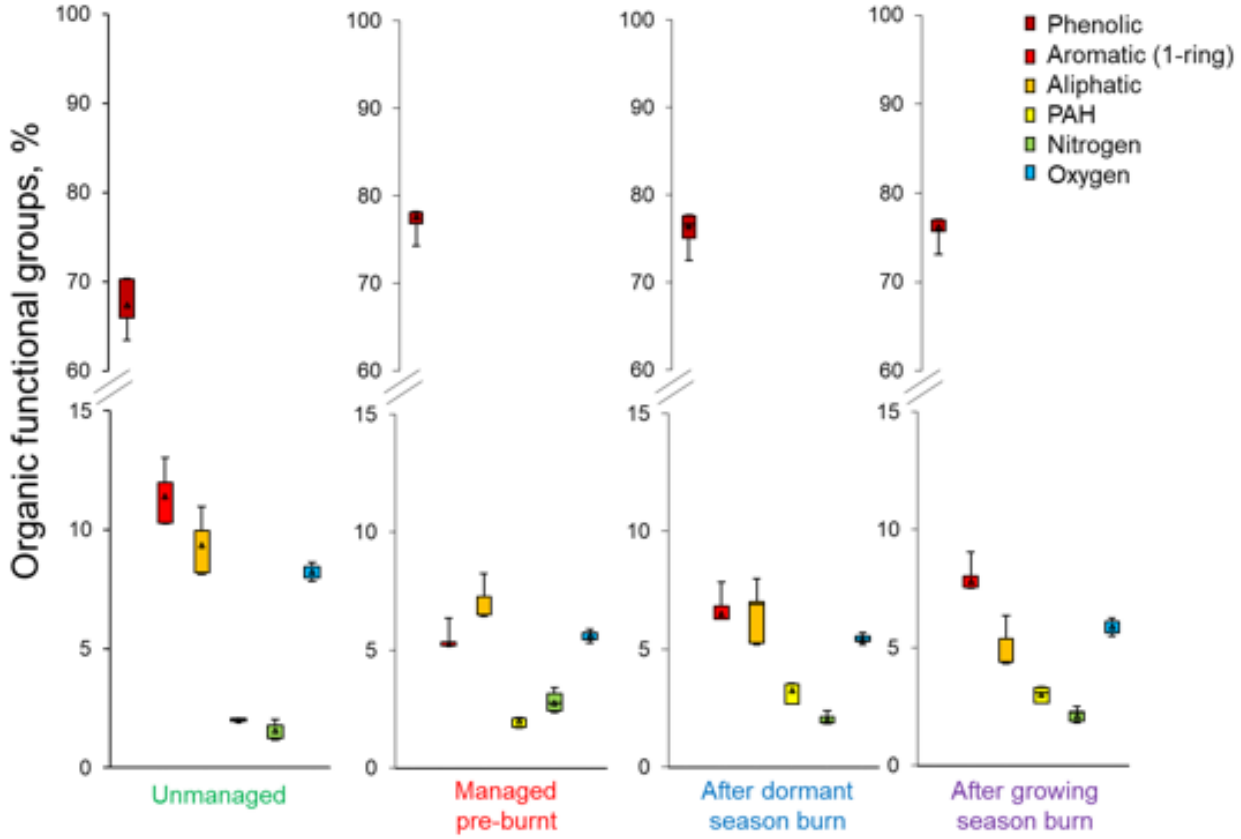

Figure 3. Composition of functional groups in detrital materials collected from unmanaged and managed sites.

b. Tray Study

Typical weather conditions for burned forests and our incubation field was dominated by mild winters, hot and humid summer (Zhang, 2017). Several times rainy periods were observed, but only two relatively dry periods (averaged precipitate < historical averaged precipitation) were recorded (March 15 – May 30, and Oct. 2016). A total of 38 rain event observed but water samples were collected and detailed measurements were conducted in nine selected samples (initial three flushes [1/15, 1/23, 2/5], three during relatively dry period [3/15, 3/28, 5/14], the first major flush after dry period [5/31], one of the selected sample during the relatively wet period [8/12], and the

last one for the experiment [11/14]). Since trays were open-top, rarely we observed some bird feces in trays and those were cleaned immediately once detected.

Even though, previous studies indicated a little effect of low intensity fires on DOC (Battle & Golladay, 2003, Minshall *et al.*, 2001), our study showed quite opposite trends. Averaged DOC value was 1.6 mg/L (n=9) for rain water collected in control trays. This averaged concentration was significantly lower ($p<0.05$) than averaged DOC values (n=9) measured in different leachate (unmanaged [41.3 mg/L], managed pre-burnt [23.7 mg/L], after dormant [22.5 mg/L] and growing season burn [23.5 mg/L]) water samples. As shown in Figure 3a, during the initial seven samples (initial flushes [n=3], dry period [n=3] and the very first flush after dry period [n=1]), DOC releases from unmanaged samples (45, 48, 53 mg/L) were significantly ($p<0.05$) higher than DOC release from other treatments (24-28, 26-28, 21-27 mg/L for managed pre-bunt, after dormant and growing season burns, respectively).

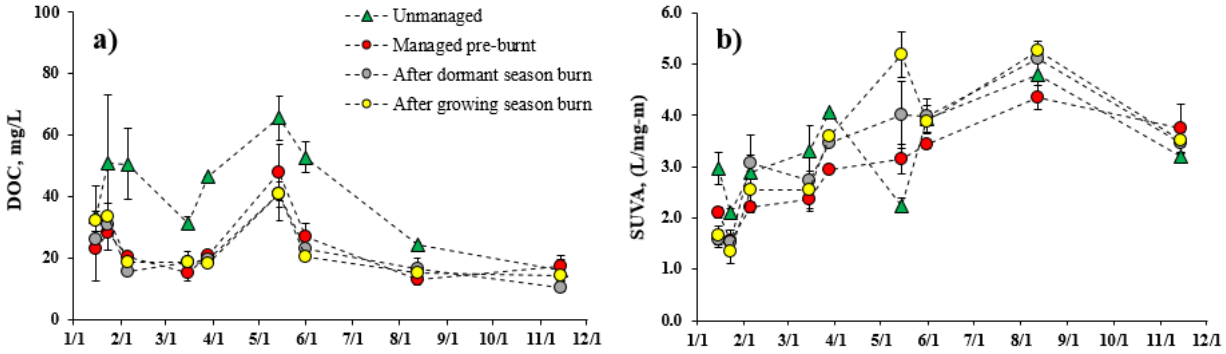

Figure 4. Water quality parameters of the leachate water for unmanaged and managed site samples DOC (a), SUVA (b). Effect of control samples (rain water) have been subtracted from the numbers. Error bars show standard deviation between three replicates.

In all cases, continued trends (increasing or decreasing) were observed in leachate water DOC concentrations collected during initial three flushes (average temperature = 8 ^{o}C), and dry periods (average temperature = 16 ^{o}C), respectively. DOC leaching trends during initial flushes in relatively colder periods indicate decreasing leaching capacity of material for all treatment (Figure 4a). However, opposite (increasing) trends indicates a microbial activity and consequently increased DOC concentration during relatively warmer periods. Lower DOC concentration observed in DOC concentrations (unmanaged: 24 mg/L, and others 13-17 mg/L) during the relatively wet period samples, and finally the levels were similar for the very last samples (11-17 mg/L) regardless of management. Overall, this indicates that long term prescribed burning practice can decrease DOC leaching capacity of forest litter and burning season does not affect leaching process significantly. This might be due to loss of organic matter (Vergnoux *et al.*, 2011), and consumption of materials that have relatively higher potential of DOC leaching (i.e. detritus materials) (Zhang, 2017).

During the experiment, averaged SUVA values for all samples (n=9) were comparable (2.9-3.3 L/mg-m) for all samples regardless of the treatment (Figure 4b). This indicates low intensity wildfire does not change overall hydrophobicity of the leachate water from litter materials. However, in general, higher SUVA values were observed as time progressed. This indicates that leaching speed of hydrophilic compounds are faster than hydrophobic ones regardless of management. An exact opposite trend for the samples collected after long dry period (between 3/28 and 5/14) from unmanaged (decrease) vs. managed (continued increasing trend) leachate

water were measured in the samples collected in the day of 5/14. Like indicated before, this period was dry, and the air temperature was relatively high (18 ^{o}C), and more than 70% of the litter composed from phenolic compounds. This indicates that newly formed phenolic group compounds (Figure 3) and PAHs in the managed samples breakdown and/or decompose slowly during the microbial activity. However, like indicated before, decomposition of these compounds are related to charring intensity and fuel source (Baldock & Smernik, 2002, Coates, 2017, Czimczik *et al.*, 2003, Masiello *et al.*, 2002).

c. Properties of DOC

It has been shown that EEM regions and fluorescence indices can provide useful information about DOM (Fellman *et al.*, 2010), and fires can cause changes in these parameters (Revchuk & Suffet, 2014). Despite the interference of iron reported before (Hohner *et al.*, 2016, Homann *et al.*, 2011), the effect of iron interferences are expected to be minimal in our samples due low levels <0.11 mg/L (includes effect of rain water [background]). During the experiment, we selected six dates for sample collection (1/15, 1/23, 5/14, 5/31, 8/12 and 11/14), and measured EEM regions and fluorescence indices of DOM in leachate waters. The data (Table 1) indicated that continuous burning practice can decrease fluorescence intensities particularly Soluble Microbial Byproduct (SMB)- and Humic-like DOC-eq. (calculated by: percent [%] volume of the region/100 x DOC [mg/L]) regions and consumes particularly humic substances in DOM leached from forest materials. These indicate a higher microbial activity (related with higher nutrient and carbon existence) and support higher DOC concentrations in unmanaged leachate water samples compared to managed-pre-burnt samples.

Furthermore, data showed that freshly burning (regardless of season) can cause further decreases in all EEM regions and consume particularly humic substances that has longer wavelength. However, neither FI nor β/α is affected from low intensity fires indicating the source (mostly terrestrial (Fellman *et al.*, 2010)) and decomposition rates of DOM in leachate waters are mostly similar regardless of management. Right after dry period, all EEM regions of DOM increased in unmanaged and managed pre-burnt leachate samples which might be related with the microbial activity in trays. In seasonal burned leachate waters, however, increases in only SMB- and humic-like components indicates limited microbial activity in these samples. Finally, a substantial reduction in all regions were observed during the wet period. This pattern was obvious in all samples but particularly noticeable in unmanaged and managed-pre-burnt samples indicating the decreased leaching potential of the materials.

Table 1. Comparison of EEM regions of leachate waters for unmanaged and managed site samples. DOC-eq. (equivalence) calculated by: (percent [%] volume of the region/100) x DOC (mg/L) of the sample.

Treatments	EEM Regions			
	I + II (Protein-like)	III (Fulvic-like)	IV (SMB-like)	V (Humic-like)
Unmanaged	7.58 ± 3.89	6.55 ± 2.79	10.67 ± 6.11	11.91 ± 6.22
Managed pre-burnt	7.72 ± 4.12	7.06 ± 3.62	7.66 ± 4.16	8.88 ± 3.65
Dormant season burn	5.67 ± 3.01	4.84 ± 2.36	7.00 ± 3.72	7.74 ± 3.77
Growing season burn	5.50 ± 2.50	4.91 ± 1.85	6.67 ± 3.80	7.35 ± 3.59

d. Treatability of DOC and DBP precursors

During the experiment, four times (1/15, 1/23, 3/15 and 5/31) 20 L of leachate waters were collected for unmanaged and managed samples, and treatability tests (coagulation + flocculation

+ settling) were conducted as explained in SI. DOC concentrations were mostly different in each sample. Therefore, we have adjusted DOC concentrations with distilled deionized water to bring organic carbon content to comparable levels (~4.2 mg-C/L) in different samples. Table 2 shows averaged water quality parameters for adjusted raw waters for each sample. This approach enabled us to apply coagulants into different leachate waters having similar organic carbon content and make better comparisons in terms of treatability of these waters.

Table 2. Comparison of diluted raw water quality parameters of leachate waters for unmanaged and managed site. Ferric chloride ($FeCl_3$).

Treatments	DOC (mg/L)	SUVA (L/mg-m)	THM-FP (µg/L)	Optimum Ferric dose (mg/L)
Unmanaged	4.4 ± 0.5	4.10 ± 0.79	441 ± 58	15 ± 0
Managed pre-burnt	4.0 ± 0.4	3.74 ± 1.05	379 ± 66	15 ± 0
Dormant season burn	4.2 ± 0.4	3.96 ± 1.23	399 ± 123	15 ± 0
Growing season burn	4.2 ± 0.7	3.62 ± 0.94	384 ± 103	15 ± 0

Results showed that coagulant demand (mg coagulant for mg removed DOC) for optimum DOC removals were not affected significantly from fire application. To reach optimum removal conditions, applied coagulant doses as 15 mg/L ferric were similar for unmanaged and managed samples regardless of burning season (Table 2). The averaged DOC removal for unmanaged and managed pre-burnt samples were similar with about 57%. However, 7-18 % lower DOC removals observed in seasonally burned samples. This difference can be related to relatively lower fulvic acid-like content (Table 1) in these samples. Nonetheless, in general, results showed that prescribed burning does not cause significant changes on treatability of DOC. Similarly, we have evaluated the treatability of THM (trihalomethanes) precursors in similar waters. A previous study indicated that trichloromethane can be formed from precursors which are more aromatic and hydrophobic (Bond *et al.*, 2012). Thus, higher removals for THM-FPs were expected. THM-FP removals were comparable and averaged removals were between 67 and 72 %.

E. Summary

Despite changes in fuel loading and fuel structure as a result of short-term alterations in fire frequency and fire season in longleaf pine stands, long-term, frequent prescribed fire does not appear to significantly alter forest detrital chemical composition. From the results of this one-year field incubation study, frequent prescribed fire management have similar effect on chemical properties of the ground litter leachate, regardless of the frequency or season of fire application. It has been summarized by previous researches at this forest that low-intensity prescribed fire effectively reduces the thickness of the forest O-horizon and decomposition rate that happens within, without qualitative impact on the chemical composition of the ground detritus (Coates, 2017). Regarding general water quality of the leachates in this controlled incubation system, managed forest litter leachate is less acidic, less nutritious, and have considerably lower total carbon output than the unmanaged control leachate. Increased runoff and erosion has been commonly observed and regarded as one of the biggest threat to water quality following wildfire and some prescribed fire events (Certini, 2005). However, with the same dry mass of detritus materials, managed sites litters were not as volatile as we expected, and significantly less litter mass was lost during the incubation period comparing to the unmanaged control litter. Quantitative differences of general water chemistry of the leachate between treatment groups and controls were

significantly reduced during the late part of incubation when compared to the beginning. Certain parameters of the leachate such as pH and molecular weight of the DOC may still be different after one year of field incubation, but for most water quality parameters concerning the general aquatic biota, prescribed burning in the southern pine forest does not seem to have a long-term direct impact on their habitat quality, and some of the short-term effects such as shifts in DOC and nutrient concentrations are reduced and recoverable within one-year period. These results indicate that forest management does not need to be overly concerned about the differences fire management frequency and season of application can have on the water chemistry of the watershed. Managing large forested watershed will indeed impact the downstream water quality both quantitatively and qualitatively, but most of the impacts are recoverable within several months after application. Aquatic ecosystem and habitat quality should not be affected chemically by low-intensity fire.

Our findings one more time confirmed that prescribed fires can decrease the amount of detrital material (fuel for the fire) and reduce the risk of wildfires. But, chemical functional groups in the detritus materials were not significantly changed. *Importantly, our study demonstrated that prescribed fire in either dormant or gowning season helped to reduce export of THM precursors without changing carbon normalized yields (DBP-FP/DOC) and removal efficiency of DOC and precursors of THMs during similar (i.e., organic carbon content, coagulant dose) ferric treatment.* Therefore, landowners and authorizes can feel confident that the low intensity fires do not change the chemical characteristics of the litter, decreases the release of DOC, and does not required additional treatment upon arrival of fire produced materials in source waters. This study did not consider effect of soil and hydrological conditions exist in natural forest environment. Therefore, additional study evaluating the effect of prescribed fire in real systems is required.

2) LANDSCAPE PROCESSES

A. Objective

The specific objective of this section is to understand the temporal variations of DOC and DBP precursors exported from managed forested watersheds.

Specific Hypothesis: Repeated burning reduces the biomass of the dead wood and forest floor layer, resulting in lower and less reactive DBP precursor export compared to unmanaged watersheds.

B. Background

Riverine DOC not only been linked to ecosystem function and global carbon cycle but also is a drinking water constituent of concern due to formation of regulated and unregulated disinfection by-products (DBPs) (Inamdar *et al.*, 2011, Linkhorst *et al.*, 2017, Majidzadeh *et al.*, 2017, Seitzinger *et al.*, 2002). Regulated DBPs such THMs and HAAs, and unregulated DBPs such as nitrogenous DBPs are carcinogenetic and can have adverse impacts on human health (Pereira *et al.*, 2012, Zeng *et al.*, 2016). Under the appropriate conditions, prescribed fires reduce excessive fuel loads and maintain a more open forest cover. Prescribed fires, in contrast to wildfires, are expected to minimally impact forest floor and water quality because fire intensity and fire severity remain low. However, short and long-term impacts of prescribed burnings on detritus layer composition and water quality is not clear. When fire intensity and fire severity are high, as is the

case in wildfires, the duff layer is generally altered, reduced, or completely consumed. Thus, surface runoff and erosion increase, sediments, heavy metals, and pollutants may be added to forested waters in this scenario (Pereira *et al.*, 2012), leading to a host of well-documented, detrimental effects. The effects of forest harvesting on water quality are similar to the effects of prescribed fire. As the intensity of harvesting disturbance increases, more detrimental effects are actualized to forest floor and forested waters. These effects may include increased water temperatures, sediment, and heavy metal loads as well as alterations in aquatic habitat (Emelko *et al.*, 2011). It is a concern for water resources that influence the voluntary or mandatory implementation of best management practices in forestry operations throughout the United States. Although immediate impacts of forest management practices such as prescribed burning on water quality have been studied (Wang *et al.*, 2015b), there is a paucity of data concerning the long-term impacts of forest management on detritus layer and water quality especially regarding the formation of DBPs.

C. Materials and Methods

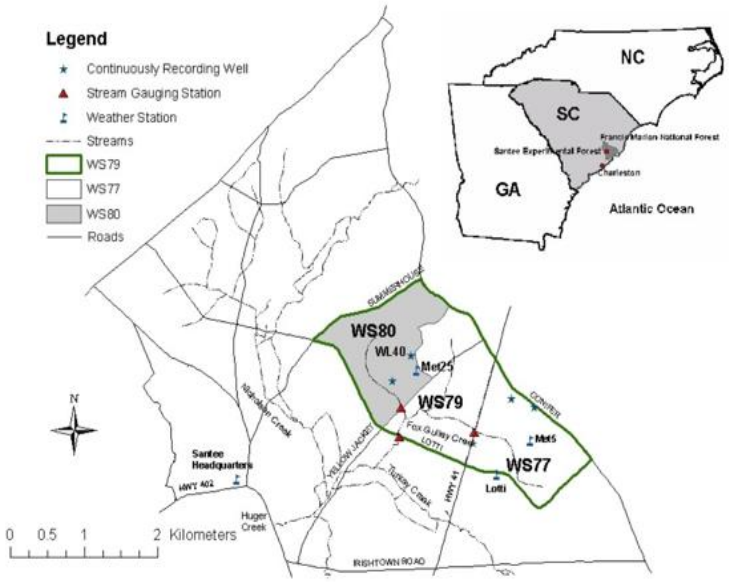

Figure 5. Location of the Santee Experimental Watersheds (WS77 and WS80) at South Carolina

Two experimental, coastal, first-order watersheds within the Santee Experimental Forest of the Francis Marion National Forest in Cordesville, South Carolina were utilized for this study (Figure 5). Lands comprising this forest have been used for agricultural and forestry purposes since the early 1700s (Amatya et al., 2007). The control watershed, Watershed 80, is a 160-ha watershed that has not been subjected to active forest management practices since 1968 and serves as a control site for the USDA Forest Service Southern Research Station Center for Forested Wetlands Research. The managed watershed, Watershed 77, is a 160-ha watershed that has been actively managed by a host of silvicultural practices since 1963, including prescribed fire, thinning, and mastication. One large natural disturbance of note affecting both watersheds in 1989 was Hurricane Hugo; approximately 80 percent of the dominant trees in the area were broken or uprooted. No post-hurricane debris was removed from the control watershed, and no silvicultural practices were utilized for stand recovery. The managed watershed was salvage-harvested in 1990.Since 2003, this watershed has been burned every 2-4 years. The dominant trees on both watersheds are loblolly pine (*Pinus taeda*), sweetgum (*Liquidambar syraciflua*), and many oaks (*Quercus spp.*). Basal area is currently greater in the control watershed (46.35 m^2/ha) than in the managed watershed (33.72 m^2/ha). Pines account for eighty-one percent of the basal area in the managed watershed and forty-one percent of the basal area in the control watershed. The soils have

developed in marine sediments and have drainage varying from very poorly drained in the riparian zones to moderately well drained in the uplands. They are defined as aquic Alfisols or Ultisols, containing argillic horizons (Jayakaran *et al.*, 2014). A randomized sampling grid was established for each watershed. Twenty locations were established approximately 300 m apart in each watershed. During January–February 2015, three 0.30 x 0.30 m (1 ft x 1 ft) destructive samples of forest detritus were taken approximately 1 m apart at each location. Each of these samples was brought back to the lab and oven-dried at 70^{o}C for not less than 48 hrs. These samples were then ground using a Wiley mill (2 mm sieve). To obtain the terrestrial DOC, 2 g of litter and duff samples were mixed with 200mL of Milli-Q water in a 250 mL Erlenmeyer flask for 1 hour. Monthly water samples were collected for a year from January 2015 to December 2015 at the upstream of each watershed. Samples were filtered through 0.45 □m membrane filters and were analyzed for DOC as described in the material and method sections above. In addition to THM, we also examined haloacetonitrile (HAN) formation in the study. Samples were oxidized with excess Cl_2, and initial oxidant doses were calculated for each sample using following formula: 3 x DOC + 7.6 x TDN. The pH of water sample was maintained at 7.8 with 10 mM borate buffer. After 24 hours of incubation at room temperature with headspace free pre-cleaned amber bottles, the residual Cl_2 was measured and quenched with slightly excess sodium sulfite. Detailed procedure can be found in Wang *et al.* (2015b).

D. Results and Discussion

Results from the field study showed that overall control watershed had higher DOC concentration than managed watershed and only in three months DOC was higher in the managed watershed than control watershed (Figure 6a). Higher or similar DOC concentration in managed watershed compared with control watershed was observed between May and September, which can be attributed to water flow paths. During this period due to reduced precipitation, flow significantly decreases and was mainly limited to contributions from baseflow. Management practices can reduce the evapotranspiration and thus the contribution of baseflow was higher at the managed watershed. However, in other months with contributions of surface flow, forest floor (litter and duff layers) served as the major source of organic matter which increases the DOC concentration more pronouncedly at the control watershed with a thicker layer of litter and duff than managed watershed. The TDN also followed the DOC pattern and was similar to linked to detritus layer, precipitation, and flow patterns (Figure 6b). DOC aromaticity, in terms of SUVA, was significantly higher in managed watershed than control watershed in 8 months out of the 12 sampled months ($p < 0.01$, Figure 6c). Higher DOC aromaticity may be due to (1) leach of more aromatic compounds from burned litter and duff or (2) higher contribution of subsurface flow in managed watershed which flushes aromatic organic matter from organic-rich soil horizons at riparian zones into the streams. The further assumption was highlighted considering that even during dry months of the year with no storm events and sole contributor of subsurface flow, SUVA was higher at the control watershed. Laboratory extraction study also confirmed this hypothesis and showed that the aromaticity of DOC leaching from vegetation was not significant between two watersheds (Table 3). This in accordance with previous studies suggesting that low intensity prescribed burnings may not change the DOC composition significantly and only high-intensity burnings results in an increase DOC aromaticity (Wang *et al.*, 2015b).

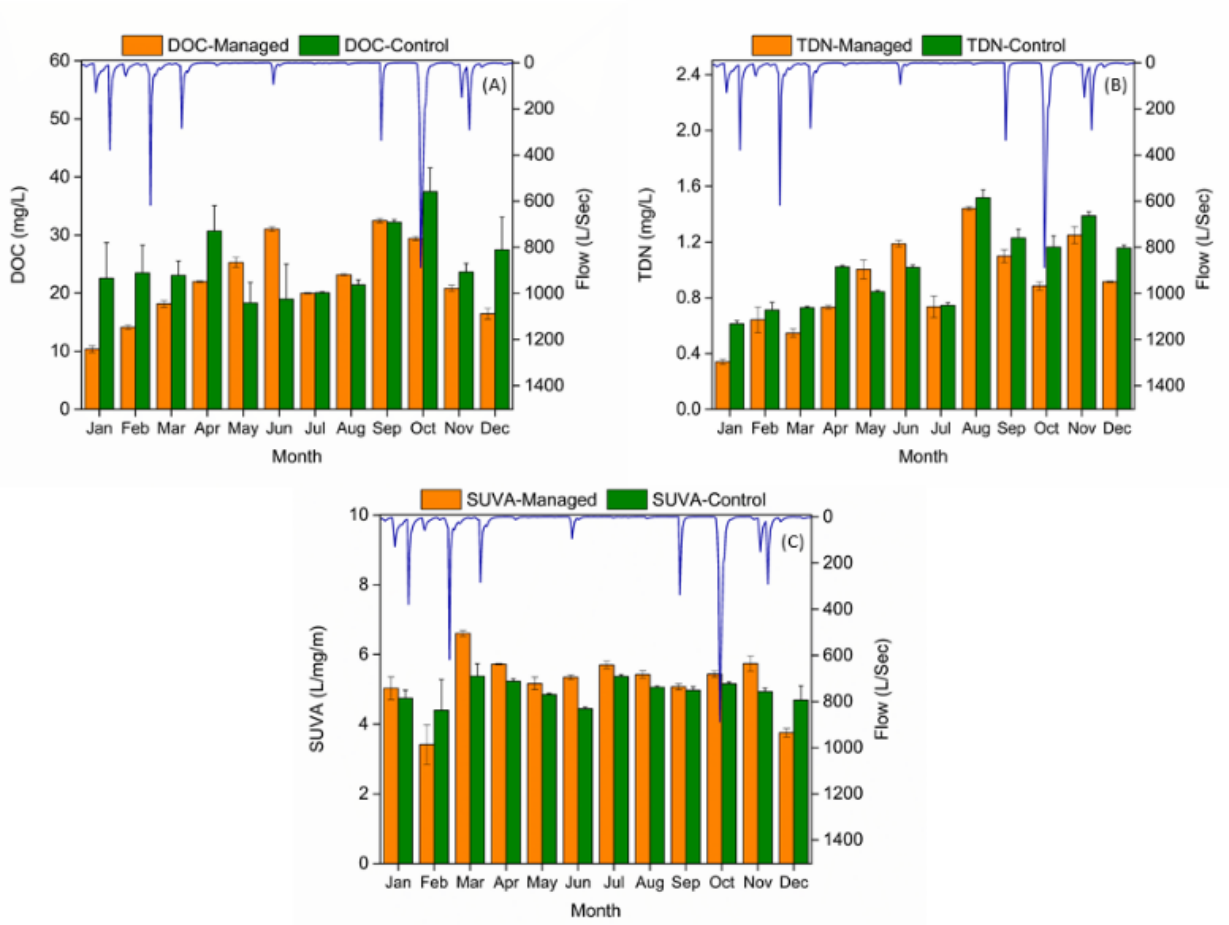

Figure 6. DOC (a), TDN (b), and SUVA (c) pattern during one year of sampling. The blue line represents the flow pattern at the control watershed.

Table 3. Characteristics along with formation potential and specific formation potential of THM and HAN of water extracts from litter and duff layer collected from managed and control watershed (n=5/treatment)

Parameter	Managed Watershed		Controlled Watershed	
	Leaf Litter	Duff	Leaf Litter	Duff
WEOC (mg/g detritus)	14.0 ± 0.4	6.4 ± 0.9	14.4 ± 2.4	8.1 ± 0.9
WETN (mg/g detritus)	0.18 ± 0.02	0.15 ± 0.04	0.25 ± 0.09	0.21 ± 0.04
NH_4^+-N (mg/g detritus)	0.07 ± 0.04	0.06 ± 0.02	0.10 ± 0.03	0.14 ± 0.04
NO_3^--N (mg/g detritus)	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.00
SUVA (L/mg-C/m)	8.5 ± 0.9	10.7 ± 1.0	8.5 ± 1.6	9.0 ± 2.7
HIX	1.10 ± 0.31	0.88 ± 0.20	1.37 ± 0.36	1.06 ± 0.30
FI	1.48 ± 0.03	1.51 ± 0.03	1.45 ± 0.04	1.47 ± 0.02
FRI	0.47 ± 0.06	0.51 ± 0.04	0.42 ± 0.05	0.45 ± 0.02
THM-FP (µg/ L)	5748 ± 1162	2941 ± 650	4710 ± 426	3242 ± 189
STHM-FP (µg/mg-C)	40.9 ± 7.6	42.8 ± 9.1	34.7 ± 3.1	42.7 ± 5.5
HAN-FP (µg/ L)	926 ± 103	361 ± 116	991 ± 206	588 ± 61
SHAN-FP (µg/mg-C)	6.6 ± 0.9	6.3 ± 0.7	7.2 ± 0.4	7.4 ± 1.4

Overall, water extractable carbon (WEOC) from litter layer was similar between two watersheds, however, at duff layer export of WEOC was higher at control watershed than managed watershed (Table 3). Water extractable total nitrogen (WETN) was higher at control watershed at both litter and duff layers. Optical properties such as SUVA, EEMs, and HIX did not show any change in chemical composition of extractable organic matter from the litter and duff layer due to management practices (Table 3). WEOC from leaf litter layer was 53.9% (± 6.6%, $p < 0.001$) and 42.4% (± 10.6%, $p = 0.002$) higher than that of at duff layer in managed and control watersheds respectively. WEOC from leaf layer was similar between two watersheds whereas WEOC from duff layer was significantly higher at controlled watershed (8.1 ± 0.8 mg/g detritus) compared with managed watershed (6.4 ± 0.7 mg/g detritus, $p = 0.04$). However, these values are based on a lab study which has used same amount of litter and duff for each treatment. Different management practices at these two watersheds have resulted in greater forest floor depth at control watershed, especially at duff layer (Coates, 2017). While litter mass was similar between managed and control watershed, duff layer mass at control watershed was 80.3% higher at control watershed. Normalizing the WEOC data with the duff mass, the export of WEOC from duff layer would be 85.1 ± 8.41 kg/ha, and 37.3 ± 4.08 kg/ha from control and managed watershed respectively assuming that during the storm events, precipitation is not a limiting factor. WEOC export from litter layer would be similar between two watersheds with 177.7 ± 29.6 and 175.4 ± 5.1 kg/ha from control and managed watershed respectively. Average WETN was higher at both layers of control watershed (0.23 ± 0.03 mg/g detritus) compared with managed watershed (0.17 ± 0.02 mg/g detritus, $p = 0.03$) and followed the order of $litter_{Control}$, $Duff_{Control}$, $Litter_{Managed,}$ and $Duff_{Managed}$ (Table 3). While highest concentrations of extractable ammonium were observed at $Duff_{Control}$, $Duff_{managed}$ had lowest concentration of extractable ammonium suggesting different decomposition pathways in managed and control watersheds. Extractable ammonium levels were similar between the two watersheds at leaf litter layer. In contrast to ammonium, nitrate concentrations were similar at both watersheds and layers. WEOC: WETN ratio (mol/mol) patterns were similar to WEOC and were higher at leaf litter layer compared with duff layer following the order of $Litter_{Managed}$ (88.1 ± 9.7) ≈ $Litter_{Control}$ (70.2 ± 14.1) > $Duff_{Managed}$ (52.8 ± 10.4) ≈ $Duff_{Control}$ (45.6 ± 14.6) suggesting that WEOC composition is not significantly different in two watersheds. Optical properties further confirmed this as no significant difference in aromaticity (SUVA), abundance of humic substances (HIX), and five EEMs region were observed between managed and controlled watersheds (Table 2). The aforementioned parameters can stay elevated for years after a wildfire (Wang *et al.*, 2015b). However, the results of this study suggest that low intensity, low severity prescribed burnings in the southeastern United States does not alert chemical composition of DOC significantly.

Monthly water samples were collected from two watersheds as well as water extracts from litter and duff layers were tested for THMs and HANs formation as two common carbonous and nitrogenous DBPs. In samples that were collected monthly, THM formation patterns were similar to DOC patterns and was higher at the control watershed than managed watershed except for four months with low precipitation (May-August, Figure 7) which can be attributed to positive relation between THM-FP and DOC concentration at both watersheds ($p < 0.001$, $r^2 = 0.82$). Moreover, organic matter reactivity in forming THM, termed as specific THM-FP (STHM-FP), which calculated by normalizing THM formation by DOC concentration was similar between managed and control watersheds further confirming that THM formation mostly impacted by DOC quantity rather than quality (Chow *et al.*, 2011, Majidzadeh *et al.*, 2017, Ruecker *et al.*, 2017). HAN formation was also higher at control watershed compared with managed watershed. However, it was statistically significant only in January, February, April, November, and December (Figure

7). DOC reactivity in forming termed as specific HAN-FP (SHAN-FP), was similar between two watersheds except for May, June, and July with higher relativities in the control watershed.

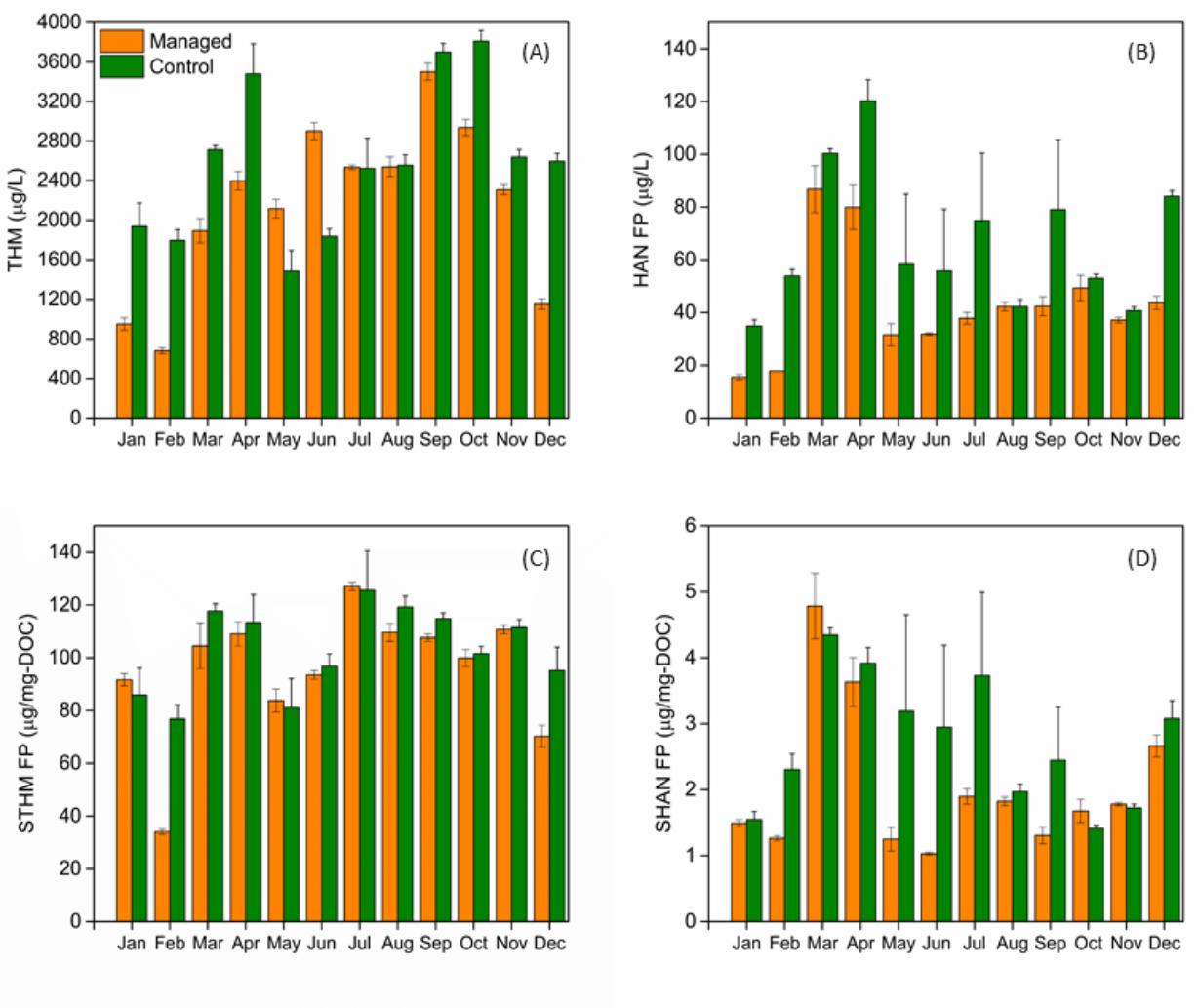

Figure 7. THM-FP (a), HAN-FP (b), and formation potentials normalized by DOC as STHM-FP (c) and SHAN-FP (c) pattern during one year of sampling.

This pattern can be attributed to the higher aromaticity of DOC during these months at control watershed. Multivariate regression analysis showed that SHAN-FP was positively linked to SUVA (p = 0.008). In addition, higher HAN concentration and activity at the control watershed can be linked to the Py-GS-MS findings that the duff layer at the control watershed exports more nitrogenous-aromatic compounds than managed watershed. This hypothesis further confirmed through the laboratory extraction study, separating HAN and THM formation at litter and duff layer. Laboratory study showed that HAN-FP at duff layer was not similar between two watersheds and controlled watershed (588 ± 38 µg/L) had significantly higher HAN-FP than managed watershed (428 ± 29 µg/L, p = 0.008). Reactivity of DOM forming HAN (SHAN-FP) was also higher (marginal significant at p = 0.07) at controlled watershed compared with managed watershed (Table 3). Average HAN-FP at litter layer was similar between two watersheds, however, was 83% (± 6.7) higher (954 ± 66 µg/L) than duff layer (519 ± 46 µg/L, p < 0.001). THM-FP and DOM reactivity in the formation of THM (STHM-FP) were not statistically different

between the controlled and managed watersheds (Table 3). Comparing the litter and duff layer THM-FP was significantly higher at litter layers (5303.1 ± 425.8 µg/L) compared with duff layer (3216.9 ± 301.1 µg/L, $p < 0.001$) which is probably due to higher WEOC. Normalizing THM-FP by DOC showed reactivity of DOM forming THM was similar at duff and litter layers (Table 3).

E. Summary

The field study showed that overall control watershed had higher DOC concentration than managed watershed and only in three months DOC was higher in the managed watershed than control watershed. DOC aromaticity (SUVA) was significantly higher in managed watershed than control watershed in 8 months out of the 12 sampled months ($p < 0.01$). Overall, water extractable carbon (WEOC) from litter layer was similar between two watersheds; however, at duff layer export of WEOC was higher at control watershed than managed watershed. Water extractable total nitrogen (WETN) was higher at control watershed at both litter and duff layers. Optical properties such as SUVA, EEMs, and HIX did not show any change in chemical composition of extractable organic matter from the litter and duff layer due to management practices. THM formation patterns were similar to DOC patterns and was higher at the control watershed than managed watershed except for four months with low precipitation (May-August) which can be attributed to positive relation between THM FP and DOC concentration at both watersheds ($p < 0.001$, $r^2 = 0.82$). Moreover, organic matter reactivity in forming THM which calculated by normalizing THM formation by DOC concentration was similar between managed and control watersheds further confirming that THM formation mostly impacted by DOC quantity rather than quality. HAN formation was also higher at control watershed compared with managed watershed. However, it was statistically significant only in January, February, April, November, and December. DOC reactivity in forming HAN (SHAN-FP) was similar between two watersheds except for May, June, and July with higher relativities in the control watershed. Therefore, *water exported from managed watershed had lower DOC concentration and lower formation potentials of THMs and HANs, indicating the prescribed fire favors the reduction of DBP precursors in source water.*

3) WILDFIRE INVESTIGATION

A. Objective

The objective of this section is to evaluate the impacts of wildfire on surface water quality and its treatability

Specific Hypothesis: DOC leaching from severe burned watersheds contains a greater number of aromatic and nitrogen moieties than that of naturally decomposed detritus materials, exhibiting greater reactivity in DBP formation.

B. Background

Ash material, consist of organics and inorganics (Bento-Goncalves *et al.*, 2012), is produces by fire (Abraham *et al.*, 2017). It is mainly composed of particulate carbon, oxides, hydroxides, silica, phosphorus, nutrients, metals, elements (Pereira *et al.*, 2015), and high calcite ($CaCO_3$) content (Abraham *et al.*, 2017, Goforth *et al.*, 2005). After wildfires, due to deposition of ash materials repellency of soil increases especially in dense forests, and the effect can persist for long

time (Goforth *et al.*, 2005). As a result, increased water yields, peak and fast discharges are possible with post-fire precipitation (Abraham *et al.*, 2017). As a natural consequence, these conditions increase soil erosions which pose a great potential to change water quality parameters (e.g., excess sediment, particulate matter, nutrients, organic matter, metals loads and etc.) at downstream points of burned areas (Bladon *et al.*, 2014, Emelko *et al.*, 2011). Previously, significant increases in turbidity (Writer *et al.*, 2014, Hohner *et al.*, 2016), and total suspended solid (TSS) (Murphy *et al.*, 2015, Writer *et al.*, 2014), concentrations were measured during post-fire run-offs. Increases in phosphorus (P), nutrients, water conductivity, metals, elements, total dissolved solid (TDS) concentrations were also reported (Writer *et al.*, 2014, Mast *et al.*, 2016). Due to quick responses, especially, low elevation fires have shown to impact downstream water quality more than high elevation fires (Mast *et al.*, 2016). In these systems, during the initial flushes, DOC leaching can be elevated (Revchuk & Suffet, 2014, Hohner *et al.*, 2016). This can be related with allochthonous contribution of post-fire run-offs (Shakesby, 2011), increased mobility (Hohner *et al.*, 2016, Clark *et al.*, 2007), and quick loss of DOM due to quick flushes (Revchuk & Suffet, 2014). Depends on intensity and oxygen availability of the fire especially terrestrial derived DOM quality and quantity can be affected (Hohner *et al.*, 2016, Wang *et al.*, 2015a). As a result, structure and the release of forest derived materials are expected to change from burned areas (Son *et al.*, 2015, Wang *et al.*, 2015b).

C. Materials and Methods

a. Site Information

In July-August 2015, Wragg and Rocky Fires consumed about ~8,000 (watershed burned completely [~99%]) and ~69,000 (watershed burned partially [~13%]) acres in Cold and Cache Creek Watersheds located in Napa, Solano and Lake County, California, respectively. Almost a year later, Cold Fire burned ~5,700 (watershed burned completely [~99%]) acres in repeatedly-burned (Monticello Fire burned around 6,500 acres in July, 2014) Bray Creek Watershed located adjacent to the Cold Creek Watershed, These incidences classified as high severity fires which typically result in complete consumption of surface detritus materials (e.g., live, woody, litter, duff and etc.) and damage or death of the trees. Vegetation was a mixture of oak savanna and woodlands (blue oak [*Quercus douglasii*], interior live oak [*Quercus wislizenii*], scrub oak [*Quercus dumosa*], buck brush [*Ceanothus cuneatus*]), chaparral (*chamise [Adenostoma fasciculatum*], California buckeye [*Aesculus californica*]), toyon (*Heteromeles arbutifolia*), manzanita (*Arctostaphylos manzanita*) and annual grasslands in the area. Adjacent Mill Canyon Watershed was selected as a Reference due to the similarity in vegetation, hydrology, geology and soils with burned watersheds. A Mediterranean climate, characterized by dry summers and mild, rainy winters, was the typical weather conditions in the area where major precipitations usually occur between November and March during the year. The mean annual air temperatures are close (in the range of 13-17 ^{o}C) within the watersheds.

b. Water Sample Collection

Grab water samples were collected from selected points of downstream of creeks which pass through from studied Watersheds. The Cache Creek receives water from upstream reservoir only throughout the year. Cold (Wragg Fire), Bray (Cold Fire), and Mill Canyon Creeks (Reference) are dried out during the year except rainy seasons. Similarly, after July-August 2015 fires, the study area did not receive sufficient rain to generate surface flow in any of the studied watersheds until January 2016. However, between January 5 and April 10, 2016, the area received ~20 inch

(Berryessa Station – BER and Knoxville Creek Station - KNO) of total rain. During this season, two liter grab samples were collected from selected points of burned watersheds (Cold Creek [n=17] and Cache Creek [n=16]) and the Reference (Mill Canyon Creek [n=6]) watersheds, when sufficient surface flow was generated. After dry period (May-Dec. 2016), the area entered the second post-fire rainy season (~38 inch of total rain) between December 15, 2016 and March 31, 2017. Grab samples were collected once again from same sampling points for Cold Creek (n=17), Cache Creek (n=16), and Mill Canyon Watersheds (n=16) during this season. In addition, to test the effect of wildfire in pre-burned watershed, grab samples were collected from Bray Creek (n=15) during the second post fire (Rocky and Cold Fires) rainy season. In all cases, we monitored weather conditions in the area closely, and performed carefully planned sampling campaign to collect water samples during all major flushes after wildfires. Stream flow for the Cache Creek sampling site was obtained for 2016 and 2017 rainy periods from United States Gaige Station (USGS) (11454000) located on the Cache Creek. Discharge for Cold Creek was approximated by subtracting upstream reservoir outflows from the USGS station located on Putah Creek for the first year of sampling campaign. However, the non-quantified release of water from the overflow spillway in the second year prevented estimates of stream flow contributions from both Cold (Wragg Fire) and Bray (Cold Fire) Creeks.

C. Water quality analysis and DOM characterization.

Water samples were collected with pre-cleaned amber bottles (1000 mL), filtered with pre-conditioned glass filters (Whatman 934-AH, ~0.7 µm pore sized) immediately, and kept in refrigerator (4 ^{o}C) until analysis. Turbidity and apparent color were measured with Hach 2100 IS laboratory turbidity meter and DR 900 Colorimeter following Hach Method 8025 (if necessary, samples were diluted with distilled deionized water and the results were corrected accordingly), respectively. Free chlorine (Cl_2) and chloramines (as Cl_2) concentrations were determined following Standard Method 4500-Cl (APHA/AWWA/WEF, 2012). For general water qualities (i.e., DOC, TDN, ammonia [NH_4^+], nitrate, nitrite [NO_2^-], DON [calculated] (Lee & Westerhoff, 2005), and bromide [Br^-]) samples were filtered with pre-washed membrane (Pall Supor, ~0.45 µm pore sized) filters. Total suspended solid (TSS) measurements were performed (with un-filtered samples [50-250 ml]) by following the Standard Method 2540 D. Measurement methods for spectroscopic properties (i.e., UV_{254}, humification index [HIX], fluorescence index [FI], and freshness index [β:α]), fluorescence excitation-emission matrices (EEMs) ([I: tyrosine-like, II: tryptophan-like, III: fulvic acid-like, IV: soluble microbial byproduct-like and V: humic acid-like] were measured as described in a previous studies (Ruecker *et al.*, 2017, Wang *et al.*, 2015a).

d. DBP FP tests.

FP tests were conducted to determine the maximum precursor concentration levels in the samples. Initially, before addition of oxidants into the samples, water pH was maintained at 7.8 with 10 mM borate buffer. To measure THMs and HAAs, samples were oxidized with excess Cl_2, and initial oxidant doses were calculated for each samples using following formula: 3 x DOC + 7.6 x NH_4^+ + 10 (Majidzadeh *et al.*, 2017). After five days of incubation at room temperature (21-22 ^{o}C) in headspace free 125 mL pre-cleaned amber bottles, the residual Cl_2 was measured and quenched with slightly excess (more than stoichiometric requirement) ascorbic acid. Detailed descriptions for sample extraction & analysis and minimum reporting levels (MRLs) used for

quantification of DBPs were presented elsewhere (Ruecker *et al.*, 2017, Uzun *et al.*, 2015). Student's t-test was used to detect statistically significant differences between measurements.

D. Results and Discussions

a. Water quality changes in burned watersheds: Short- vs long-term

In this study, selection of sample collection days was driven by weather conditions, and sampling campaigns were conducted carefully to capture all major post-fire flushes including initial ones. It is noted that the first post-fire rainy season consisted from two consecutive temporal rainy periods (i.e., January 5-22, 2016 and March 5-April 10, 2016). We defined these two periods as an "initial flushes" and "subsequent flushes" for the first post-fire rainy season. However, during the second post-fire rainy season, there were no distinct periods in terms of precipitation regimes.

Turbidity, apparent color, and TSS.

Results showed that intense post-fire rainstorms can result in high amount of particle release from burned areas. During the first post-fire rainy (~20 inch total rain) seasonal (Jan.1, Apr.10, 2016), averaged turbidity, apparent color and TSS values were 36 NTU, 362 Pt-co and 96 mg/L in the Reference samples, respectively. However, these constituents were significantly higher ($p<0.05$) during the initial flush, but dwindling trends during subsequent flushes in burned watershed samples, especially in Cold Creek (Figure 8a, b and c). More variability was observed, and averaged values were 1104 and 1026 NTU, 6268 and 5944 Pt-co and 840 and 1324 mg/L in Cache and Cold Creek, respectively. Also, TSS vs. turbidity and apparent color have shown strong positive linear correlation for each group of samples collected from these sources. These results indicate a significant release of burned watershed generated particles (non-settle able, light scattering or absorbing) which constituted most (>90%) of the suspended solids in Cache and Cold Creek samples during the first rainy season. Then, due to limited precipitation, studied watersheds did not generate surface run-off between Apr. 10 and Dec. 15, 2016.

During the second post-fire rainy season (~38 inch total rain), however, measured values for all three constituents increased significantly ($p<0.05$) in Reference samples. This might be due to increased transportation of particles to Mill Canyon Creek as a result of increased surface flow and erosion during this time period. In Cache River, values were similar for both seasons; however, significantly lower values (similar with Reference) were measured in Cold Creek samples. As stated before, in terms of the burned area coverage, Cache Creek and Cold Creek watersheds burned ~13% and ~99%, respectively, and the flow in Cache Creek was partially controlled by an upstream reservoir. Considering the effect of burned area coverage, these results show that i) as a result of fire, mobility of particles causing turbidity, color and TSS increases significantly, and most of them are flush out from burned areas quickly with initial flushes, and ii) upstream reservoir behaves as an equalization or a dilution basin for these three constituents in Cache Creek system.

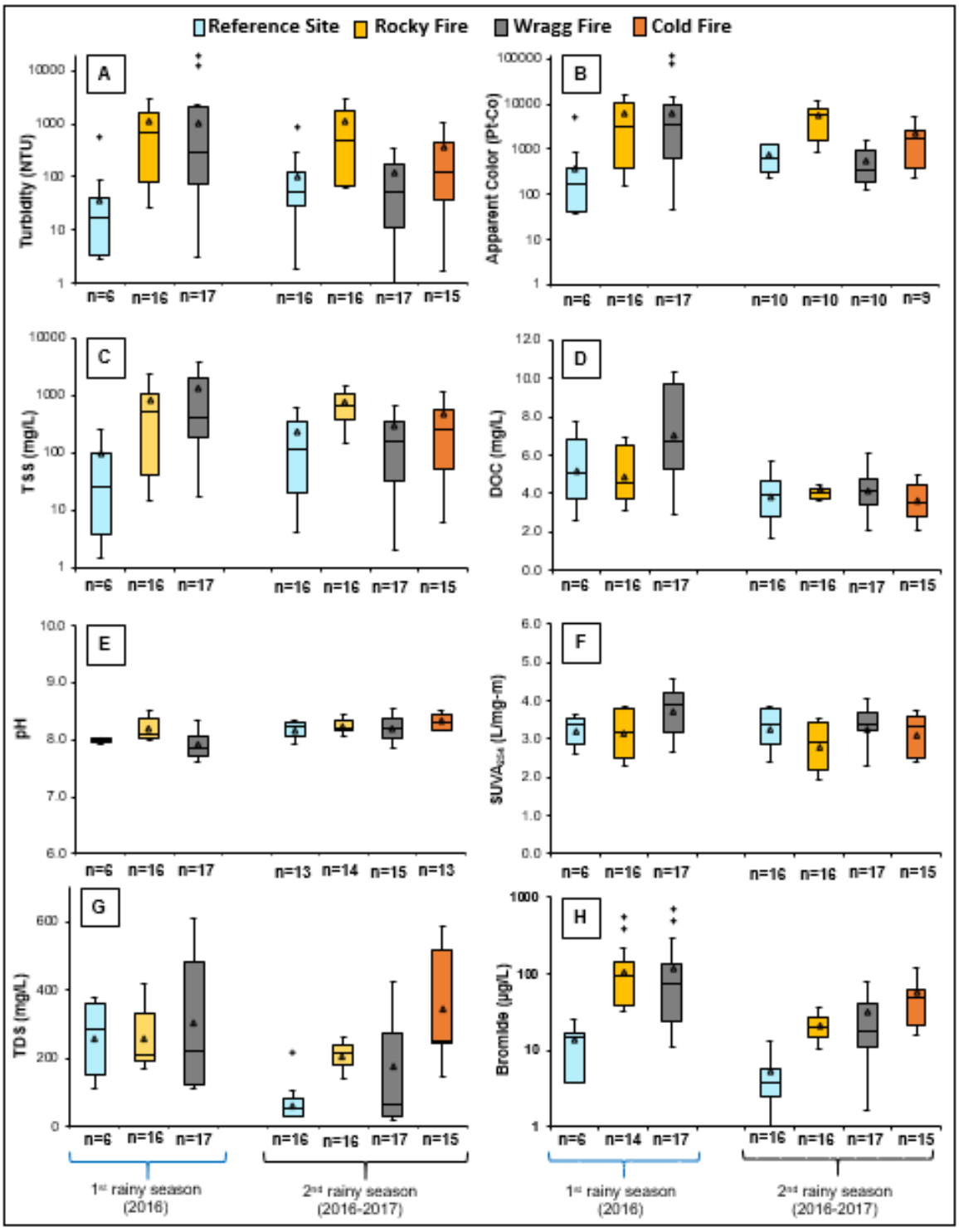

Figure 8. General comparison for water quality parameters for 1st (2016) and 2nd (2016-2017) rainy periods after wildfires. Turbidity (A), apparent color (B), TSS (C), DOC (D), pH (E), SUVA(F), TDS (G), and Bromide (H). Burned area coverage: ~13%, ~99%, ~99% in Cache, Cold and Bray Creek Watersheds, respectively. n: indicates the number of data used for calculations.

Similarly, averaged values of Bray Creek samples were significantly higher ($p<0.05$) (turbidity: 366 NTU, apparent color: 2259 Pt-co and TSS: 457 mg/L) compared to Reference (turbidity: 99 NTU, apparent color: 761 Pt-co and TSS: 231 mg/L). This further supports that the wildfires can enhance the mobility of particles. Therefore, turbidity (Writer *et al.*, 2014, Hohner *et al.*, 2016), apparent color, and TSS (Emelko *et al.*, 2011, Murphy *et al.*, 2015) values increased significantly in sources, especially during the initial major post-fire flushes (Mast *et al.*, 2016). In addition, TSS vs. turbidity and apparent color correlations were weaker in all group of samples during the second year of sampling. This shows that most of the particles composed of settable solids were probably set in motion by increased erosion rates and transported rapidly to creeks during the second rainy season.

Dissolved vs. suspended solids.

During the first post-fire rainy seasonal, averaged TDS values and their variability were comparable (260-300 mg/L) in all Creeks and lower than EPA`s secondary drinking water standards (500 mg/L). TDS vs. conductivity showed a positive linear correlation ($R^2 \geq 0.7$) in all creeks (data not shown). The TSS/TS ratio in Cache (76%) and Cold (90%) Creek sample were significantly higher ($p<0.05$) than Reference (27%). As indicated before, this can be related with the generation of external suspended solids in addition to typical principal dissolved constituents with wildfires.

During the second post-fire rainy season, however, averaged TDS values decreased in all Creeks. But, TSS/TS ration in Reference (76%) was higher compared to Cache (57%) and Cold Creek (63%) samples. In Reference samples, this might be due to release of external particulate matter and dilution of dissolved forms with intense precipitation. In burned Watersheds, however, it can be related with accelerated flush of bulk part of particulate matter from system during the first rainy season. These indicate that TSS/TS ratio can increase in the samples collected from burned watersheds during the initial flushes, and slowly decreases with subsequent flushes. In addition, averaged TDS value in Bray Creek ~343 mg/L and TSS/TS (79%) ratio was similar with the Reference. Considering the effect of external weather conditions, these results suggest that the true effect of fire on the release of dissolved matter from this site was masked.

DOC, water pH and SUVA.

During the first post-fire rainy season, DOC concentrations in Reference and Cache Creek samples were comparable with average values of 5.1 and 4.9 mg/L, respectively. Previously, it was indicated that the contribution of particulate matter on DOC was minimal (Mast *et al.*, 2016, Hohner *et al.*, 2016). In Cold Creek samples, however, significantly higher DOC release (averaged contribution was ~80%) was observed during the initial flushes (January 1-22, 2016)), and the values decreased with subsequent flushes over time. Considering the percent burned area coverage in Cache (~13%) and Cold Creek (~99%) watersheds, this indicates that high intensity fires can cause increased DOC release from burned areas, but the degree of influence on surface waters is related to the ratio of burned area over total watershed coverage. Therefore, DOC release from partially burned watersheds is not expected to change significantly.

During the second post-fire rainy season, however, averaged DOC values decreased to 3.8-4.2 mg/L range in each group of samples. This indicates that high intensity fires can generate external but more mobile DOC sources which can be flush out quickly from the systems with major post-fire run-offs (Murphy *et al.*, 2015). This is consistent with a previous study where recently burned ash had 10 times higher DOC leaching potential than weathered ash, and burned watershed DOC leaching was diluted during the second years of sampling (Revchuk & Suffet,

2014), A similar increasing DOC trend would be expected at Bray Creek site. However, averaged DOC concentration in Bray Creek samples was comparable and overlapped with DOC concentration in Reference samples (Figures 8). This might be related with earlier consumption of some of the DOC sources during previous incidence (Monticello Fire occurred at same area in July, 2014).

It has been indicated that soil pH can increase with increasing burned severity due to the mineralization and the release of acid volatiles (Wang *et al.*, 2016, 2015b), production of Ca, Mg, K and Na oxides, hydroxides and carbonates especially in newly burned organic matter (Revchuk & Suffet, 2014), therefore, post-fire run-off may increase water pH in downstream surface waters (Son *et al.*, 2015). However, some of the previous studies have revealed contradicted results on the change of pH where the recovery took years (Granged *et al.*, 2011, Wang *et al.*, 2015b), and did not persist for a long period (Certini, 2005, Oliver *et al.*, 2012). In any group of samples collected both seasons, however, averaged pH values were not significantly different ($p>0.05$) (in the range of 7.91-8.33) in this study. Considering previous studies and observation from this study, it can be inferred that several factors (e.g., burning intensity, mobility of DOC, mass of burned materials, soil properties and organic matter content, weather conditions, and etc.) may play a role on burned forest generated water pH.

Averaged UV absorbance measured at 254 nm, known as SUVA (an aromaticity indicator of DOC (Wang *et al.*, 2015b)), did not change significantly, and overlapped for all group of samples during each particular seasons. The values were 3.21 and 3.13 L/mg-m for Reference and Cache Creek samples, respectively. In contrast, Cold Creek samples had ~30% higher averaged SUVA values (Figure 8f) during the initial flushes, and the values decreased with subsequent rainstorms. Previously it was indicated that several polycondensed aromatic hydrocarbon (structures can be formed (Vila-Escale *et al.*, 2007) as a result of fires, and Cold Creek measurements were consistent with previous findings where concentrations of these newly generated compounds are expected to reach peak levels especially in recently burned sites (Tsibart *et al.*, 2014), and decreased over time with precipitation and time (Vila-Escale *et al.*, 2007, Olivella *et al.*, 2006). Similar with DOC, this observation once again showed that the increased burned area coverage augments the effects of fire. In terms of the two rainy seasons, average Reference values were similar. During the second rainy season, however, ~10% lower values were measured in Cache and Cold Creek samples compared to the first year in contrast to some of the previous studies (Revchuk & Suffet, 2014, Wang *et al.*, 2016). Also, in a previous study SUVA values from water extracts of ash followed the order of white ash > unburned detritus > black ash (Wang *et al.*, 2015b). Therefore, decrease in SUVA values during the subsequent flushes (only in Cold Creek), and second season can be related with the quick removal of PAHs with post-fire run-offs and/or formation of black and white ash mixture during the fires.

b. General DBP FP Trends.

Analysis for THM and HAA were conducted under excess chlorination conditions. During the first post-fire rainy season, average concentrations of THM and HAA in Reference and Cache River samples were 540, 355, 73 µg/L and 504, 360, 45 µg/L, respectively. As indicated before these increases can be associated with increased DOC concentration (~40%) in Cold Creek samples. Also, correlations for DOC vs. THM and HAA FP were strong positive ($R^2 \geq 0.7$). To present the reactivity of DBP precursors, DOC normalized concentrations were analyzed. Results have showed that carbon normalized averaged reactivity and variability of THM and HAA

precursors were within the comparable range for all samples (THM FP/DOC: ~100 µg/mg-C, HAA FP/DOC: 65-75 µg/mg-C). These results confirm that the carbon normalized reactivity of C-DBP precursors are not significantly changed with high intensity fires (Writer *et al.*, 2014, Hohner *et al.*, 2016). Therefore, increases in concentrations of carbonaceous DBP (C-DBP) precursors (Revchuk & Suffet, 2014, Cawley *et al.*, 2018) might be related with the enhanced mobility of DOC especially during initial post-fire flushes. During the second post-fire rainy season, significant decreases were observed in THM and HAA FP levels, but the carbon normalized reactivity did not change significantly and overlapped. Considering DOC trends and liner correlations between DOCs vs. C-DBPs, these observations can be related with decreased DOC levels in this rainy season.

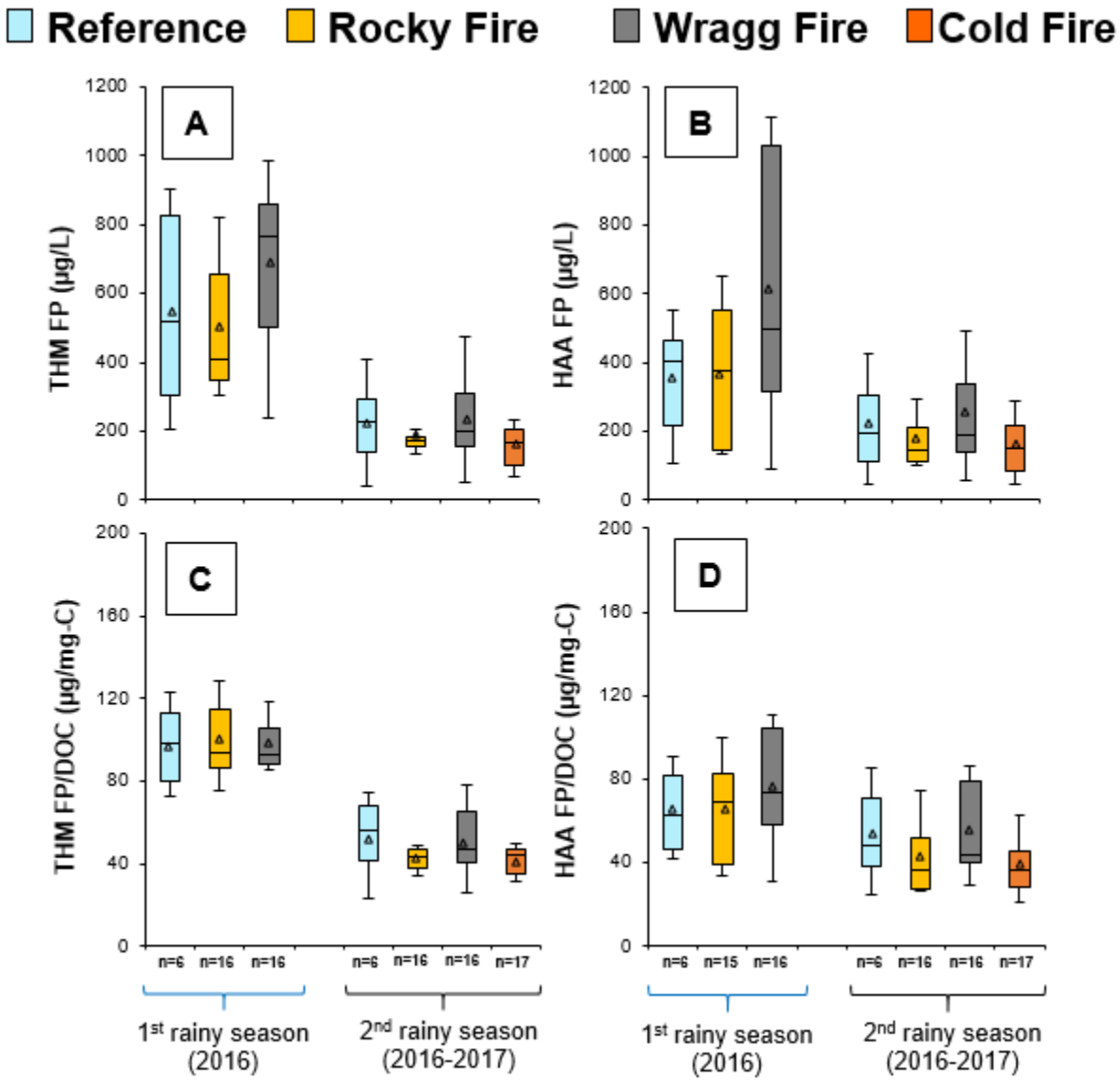

Figure 9. FPs of disinfection byproducts for the first (2016) and second (2016-2017) rainy seasons after wildfires. General trends and DOC normalized reactivity for THM-FP (A), HAA-FP (B), THM-FP/DOC (C), and HAA-FP/DOC (D). Burned area coverage: ~13%, ~99%, ~99% in Cache, Cold and Bray Creek Watersheds, respectively. n: indicates the number of samples used for calculation

c. Brominated THMs and HAAs in burned watershed samples.

As indicated before inorganic bromide can be released from ash materials by combustion (Wang *et al.*, 2015b), and this study showed for the first time that bromide release can be elevated from burned watersheds with post-fire runoff. Although we presented overall and carbon normalized DBP FP trends, formation of brominated C-DBP species were favored in some samples collected from burned watersheds.

During the first post-fire rainy season, trihalomethane (TCM) and chlorinated HAAs species [chloro-acetic acid (CAA), trichloro-acetic acid (TCAA), and dibromo-acetic acid (DCAA)] consisted >95% (molar based) of total THM_4 and HAA_9 FPs in Reference samples. And, an averaged THM_4 FP/HAA_9 FP, TCM FP/TCAA FP, and TCM FP/DCAA FP values were 1.98, 3.40 and 4.02, respectively. In Cache Creek, for initial vs. subsequent flushes, TCM and chlorinated HAAs species consisted of 72 vs. 89% and 89 vs. 94% of total THM_4 and HAA_9 FPs samples, respectively. In addition, THM_4 FP/HAA_9 FP, TCM FP/TCAA FP, and TCM FP/DCAA FP values were 1.42 vs. 2.35, 2.95 vs. 6.06, and 2.69 vs. 4.54, respectively. Similarly, in Cold Creek samples, TCM and chlorinated HAAs species consisted of 83 vs. 89% and 88 vs. 94% of total THM_4 and HAA_9 FPs samples, and THM_4 FP/HAA_9 FP, TCM FP/TCAA FP, and TCM FP/DCAA FP values were 1.23 vs. 2.37, 2.98 vs. 5.63, and 2.45 vs. 4.57 for initial and subsequent flushes, respectively. These results indicate that the brominated species were formed especially during initial flushes of the first rainy season, and TCM/DCAA and TCM/TCAA ratios were transformed similarly in burned watershed samples.

To present the reactivity of DBP species, DOC normalized molar DBP and Br^-concentrations were analyzed over time. Brominated species were lower than 4 and 2% of THM_4 and HAA_9 in Reference samples, respectively. In Cache Creek, for initial vs. subsequent flushes, carbon normalized brominated species consisted 28 vs. 11% and 11 vs. 7% of total THM_4 and HAA_9 FPs samples, respectively. Similar brominated specie ratios were observed in Cold Creek (18 vs. 11% and 12 vs. 6% for initial vs. subsequent flushes of total THM_4 and HAA_9 FPs, respectively). During the second post-fire rainy season, TCM and chlorinated HAAs species consisted >90% of total THM_4 and HAA_9 FPs in all samples except Bray Creek samples where brominated species for THMs and HAAs consisted 23 and 6%, respectively.

As expected, bromine incorporation factors (BIF), increased in Cache and particularly Cold Creek samples for both THM and HAA FPs. BIF, as defined bromine incorporation factor (Chow et al., 2007), for Reference, Cache Creek and Cold Creek were 0.04, 0.12, 0.15 and 0.02, 0.06, 0.11 for THMs and HAAs, respectively. During the second post fire rainy season, BIF values were still higher compared to reference samples including Bray Creek samples where BIF values were 0.14 and 0.12 for THMs and HAAs, respectively. These results showed that BIF can increase with increased burned area coverage such in burning intensity (Wang *et al.*, 2015b), and effect can persist for a long time. However, further research is needed to better understand BIF changes for different burning intensities and area coverage.

E. Summary

This study examines the impacts of three independent (i.e., partially burned, completely burned, and repeatedly-burned) low elevation California Wildfires on surface water quality, DOC characteristics, and precursors of DBPs. The first impact of post-fire run-off was elevated levels of turbidity, color and suspended solids in the water samples collected from burned watersheds. In

the completely burned (~99%) watersheds, DOC (~40%), SUVA (~30%), TDN (up to 600%), DON (up to 500%), and ammonium ion (NH_4^+) (up to 400%) concentrations increased significantly in the initial post-fire runoff (6-8 flushes) but declined with subsequent rain events. These are related with increased mobility of DOM, enriched organic content of soil particularly from vegetation, and increased charred sediment loads. Nitrate (NO_3^-) concentration increased (up to 400%) during the second and following rainy seasons indicating changed nitrogen (N) cycling and delayed nitrification in soils of the burned area. Changes in DOC optical properties indicated that high intensity fires can consume most of the terrestrial DOC sources. The elevated bromide concentrations in the burned watershed increased the concentration of brominated THMs, HAAs and BIF. *These field studies demonstrated that the first post-fire runoff contained a greater portion of aromatic and nitrogen compounds but DOC normalized THM and HAA FP values did not show significant differences among unburned partially, completely, and repeatedly burned watersheds.*

IMPLICATIONS FOR MANAGEMENT AND FUTURE RESEARCH

Wildfire on Water Quality

Based on the field observation and controlled studies, we developed a box model (Figure 9) to illustrate the impacts of wildfire and prescribed fire on surface water quality and treatability. First of all, the impacts of wildfire on water quality and treatability depend on fire extent and severity. The highest turbidity and TSS were observed in a completely burned watershed because of enhanced erosion. This resulted higher DOC values (up to 12 mg/L) and a lower coagulation removal efficiency (30% on DOC removal and 50% on THM-FP removal). Water of a partially burned watershed also contained a high sediment load, but the differences between unburned and partially burned watersheds in DOC and THM-FP were insignificant. Results showed that wildfire can deteriorate water quality in particular on sediment loads even from small-scale wildfire within a larger watershed. Water utilities using the water from wildfire burned watershed may need a greater dosage of coagulants to process the source water.

Prescribed Fire on Water Quality

One of the benefits of prescribed fire practice is to reduce the fuel loading in forest floor and the risk of wildfire. Results from our experimental plots with different management practices confirmed that the detritus biomass ($W_{detritus}$) was significantly reduced, and the extent could depend on the frequency and season of the prescribed fire practice. Specifically, the $W_{detritus}$ values were 8.9 ± 1.0, 2.0 ± 0.5, and 5.1 ± 1.1 Mg/ha when using periodic dormant, annual dormant, and annual growing season burns, respectively, all of which were much lower than 36.7 ± 4.6 from unmanaged area. The reduction of detritus biomass also reduced the DOC and THM-FP in surface water. Our experimental setting showed up to 40-50% reductions in DOC and THM-FP. Regarding the treatability and characterization of DBP precursors, there were no differences among unmanaged and managed watersheds. In other words, the prescribed burn only reduce DOC and DBP precursors but not affect the characteristics of DOC or its treatability.

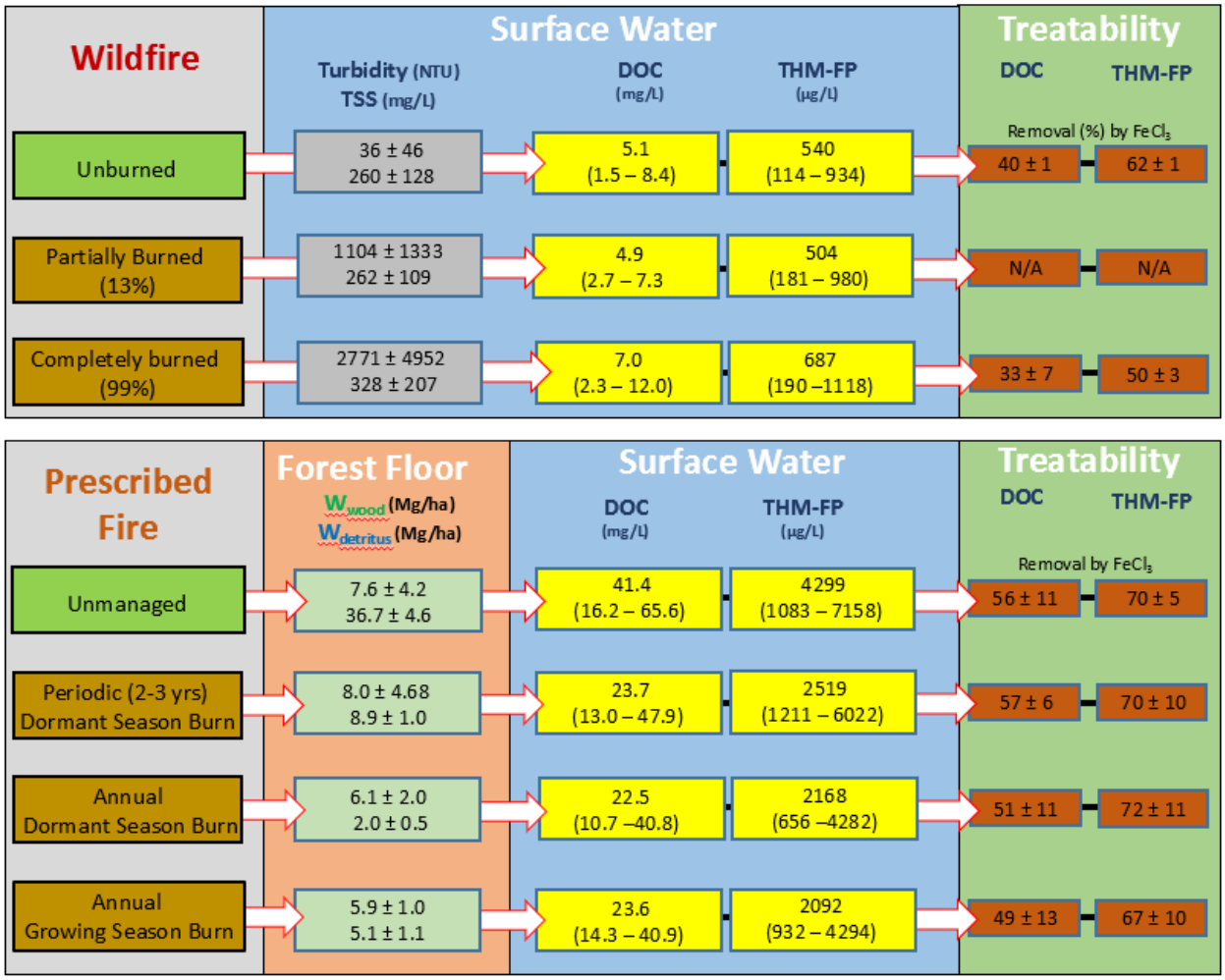

Figure 10. Box model developed from this project on the effect of wildfire and prescribed fire on the surface water quality along with their treatability.

Our experiments demonstrated the prescribed fire management practices could reduce the terrestrial sources of DBP precursors within watersheds, consequently improving water treatability in terms of lowering DOC concentration and THM-FP. However, the extent of reduction could be site specific and the values generated in this study may not be applied elsewhere. Other factors such as hydrology, soil types, vegetation composition, as well as weather pattern could also affect water quality and treatability. Water utilities shall collaborate with land mangers or foresters to examine the benefits on these fuel reduction techniques in their source waters.

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APPENDIX A – CONTACT INFORMATION

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APPENDIX B – COMPLETED DELIVERABLES

Deliverable Type	Description	Delivery Dates
Book Chapters in Compiled Works	Forest fire alters DOM and DBP precursors exports from forest watersheds - Part I. Lab Study	August 2015
	Forest fire alters DOM and DBP precursors exports from forest watersheds - Part II. Field Study	August 2015
Post-doc Scholar Training	Huan Chen – Project / Research Focus: using pyrolysis GC/MS to characterize the composition changes of organic carbon	August 2017 – August 2018
	Hamed Majidzadeh – Project / Research Focus: evaluating the temporal variations of DOC and DBP precursors exported from managed forested watersheds	January 2017 – June 2018
Ph.D. Dissertation	Thomas Adam Coates - Clemson University, Forestry and Environmental Conservation Dept. 'Forest Management in Coastal Pine Forests: An Investigation of Prescribed Fire Behavior, Detrital Chemical Composition, and Potential Water Quality Impacts'	Spring 2017
	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'	Spring 2017
	Jun-jian Wang - Clemson University, Forestry and Environmental Conservation Dept. 'Disinfection Byproduct Precursors in Detritus Materials of Fire-Affected Watersheds'	Spring 2015
MS Thesis	Richard Pepple - Clemson University, Biological Sciences Dept. 'Effect of Controlled Burns on the Bacterial Communities Composition over Time at Four Sites in the Yawkey Wildlife Center, Georgetown, SC'	Spring 2018
	Wen-bo Zhang - Clemson University, Forestry and Environmental Conservation Dept. 'Effects of Prescribed Forest Fire on Water Quality and Aquatic Biota in the Southeastern United States'	Fall 2017
Undergraduate student training	The undergraduate students of Luke Hatfield and Morgan Edwards were working on this project for field surveying.	Summer 2018
	The undergraduate students of Joseph Carr and Hunter Robinson were working on this project for field surveying.	Summer 2017
Journal Article	Thermocouple probe orientation affects prescribed fire behavior estimation	JEQ 2018
	Dynamic changes of disinfection byproduct precursors following exposures of *Microcystis aeruginosa* to wildfire ash solutions	ES&T 2017

	Frequent prescribed burning as a long-term practice in longleaf pine forests does not affect detrital chemical composition	JEQ 2017
	Temporal variations of disinfection byproduct precursors in wildfire detritus	WR 2016
	Growing algae alter spectroscopic characteristics and chlorine reactivity of dissolved organic matter from thermally-altered forest litters	ES&T 2016
	Wildfire altering terrestrial precursors of disinfection byproducts in forest detritus	ES&T 2015
	Controlled burning of forest detritus altering spectroscopic characteristics and chlorine reactivity of dissolved organic matter: effects of temperature and oxygen availability	ES&T 2015
Presentations Organized Special Sessions	Session Title: Disinfection By-Products: What Have We Learned about Dissolved Organic Matter Precursors? 252nd ACS National Meeting; Cosponsor: Michael Gonsior; Olya Keen; Julie Korak; Lee Blaney; Alex Chow	August 2016
Professional Meetings	Fire Continuum Conference, Missoula MT Forest Fire Alters Dissolved Organic Matter from Forested Watersheds: Impacts on Water Quality & treatability; Forest management improves water quality by altering detrital chemical composition.	May 2018
	AGU Fall Meeting, San Francisco CA Challenges of Wildland Fire on Water Quality and Drinking Water Supply	December 2016
	5th International Fire Behavior and Fuels Conference, Portland, OR Black Carbon Production and Storage as a Result of Differing Fire Frequencies in Longleaf Pine Forests	April 2016
	International Water Association Specialist Conference on NOM, Malmo, Sweden Effects of prescribed fire on dissolved organic matter in coastal plain forested watersheds; Impacts of wildfire on dissolved organic matter and disinfection byproduct precursors in forested watersheds.	September 2015
Field Days	Karanfil T and Chow AT, Sustainable Forested Watershed. Presented at South Carolina Environmental Conference, Myrtle Beach, SC	March 2018
	Chow AT. Presented in the field day at the fifth Interagency Conferences on Research in Watersheds in Charleston SC	March 2015

	Chow et al. Organized a field Day for students in Forestry Management Technology program in Horry Georgetown Technological College, Georgetown SC	April 2015
	Chow AT. Presented at the Coastal Fire Program, Georgetown, SC	October 2014
	Chow AT. Presented at Waccamaw Water Quality Data Conference, Conway, SC	September 2014