

PR	OPOS	AL NO
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ISSUE DATE

#### REQUEST FOR PROPOSAL (RFP) COVER SHEET

PROPOSAL TITLE:		
SUBMISSION DEADLINE:	on	
SUBMIT PROPOSAL TO:	City Clerk's Office 11701 Community Center Dr Northglenn CO 80233 or rfp@northglenn.org	
CONTACT:		
EMAIL:		
PHONE:		
Bidding instructions and d https://w	rawings are available at the Rocky N ww.northglenn.org/government/bids_	lountain E-Purchasing website or at: _with_the_city.php
MANDATORY PREBID CONFERENCE:		
DATE & TIME:		at
LOCATION:		

The undersigned hereby affirms that (1) they are a duly authorized agent of the vendor, (2) they have read all terms and conditions, requirements, and instructions of this bid as stated or implied, (3) the vendor warrants that they are familiar with all provisions of the contract documents and technical specifications which were made available in conjunction with this solicitation and fully understands and accepts them unless specific variations have been expressly listed in their offer, (4) that the offer is being submitted on behalf of the vendor in accordance with any terms and conditions set forth in this document, and (5) that the vendor listed on the bid submission must match all contract and insurance documents submitted upon award.

#### PRINT OR TYPE YOUR INFORMATION

Company	Fax Number	
Address	City, State Zip	
Contact Person	Title	
Email	Phone	
Signature		
Print name		

#### **INSTRUCTIONS TO BIDDERS**

- 1. PROPOSAL NO: \_\_\_\_\_
- 2. PROPOSAL TITLE: \_\_\_\_\_
- 3. PURPOSE OF SOLICITATION:

4. SCHEDULE OF ACTIVITIES: The following schedule of activities delineates the timing of the solicitation and the estimated project schedule. These dates may be subject to change at the City's discretion.


- 5. INTERPRETATION OF DOCUMENTS AND SPECIFICATIONS: Wherever the word "contract" appears, it shall be held to include all the documents as listed. No less than all of the parts of the contract documents shall constitute the formal contract. If any person contemplating submitting a proposal for the proposed contract is in doubt as to the true meaning of any part of specifications, schedules, or information sheets or the proposed contract documents, they may submit to the project manager a written request for an interpretation thereof. The person submitting the request will be responsible for its prompt and actual delivery. Any interpretation of such documents will be made only by an addendum duly issued, and a copy of such addendum will be mailed or delivered to each person receiving a set of such documents. The City will not be responsible for any explanation or interpretation of such documents which anyone presumes to make on behalf of the City.
- 6. TERMS AND CONDITIONS: As set forth in the contract agreements and any supplemental, the following terms and conditions will apply to this Request for Proposal, each vendor's proposal and to the negotiations, if any, of any said contract. The City will consider specific recommended changes that clarify the intent of the agreement. <u>The City will not consider contract changes that have not been specifically identified in your proposal response.</u> A general statement suggesting that, if selected you reserve the right to discuss contract issues at a later date will not be accepted and will be grounds for disqualification. Submission of a proposal in response to this RFP indicates the vendor's acceptance of the terms and conditions contained in this document and the contract.
- 7. **BIDDER EXPENSES:** The City of Northglenn will not be responsible for any expenses incurred by any vendor in preparing and submitting an offer.

- 8. WITHDRAWAL: A vendor may withdraw their proposal at any time prior to the expiration of the final date and time set for receipt of bids. Withdrawal notification must be in written form, and must be received in the Offices of the City Clerk prior to the closing date and time.
- 9. IRREVOCABILITY: Following the time of closing, all bids will become irrevocable offers to the City and will remain as such until 90 days from date of submission. By submission of a bid, the vendor agrees to enter into a contract. In addition all quoted prices will be firm and valid up to 90 days from date of submission The City may, in its sole discretion, release any proposal and return any bonds if applicable prior to the 90 days.
- 10. LATE PROPOSALS: Any proposal received after the Final date and time for receipt of proposal will not be accepted and will be unopened and discarded without being considered.
- 11. SIGNATURES OF VENDORS: Each vendor shall sign their proposal, using their legal signature and giving their full business address. The person signing the proposal must be an officer of the company or partnership. Bids by partnerships shall be signed with the partnership name by one of the members of the partnership or by an authorized representative, followed by the signature and designation of the President, Secretary, or other persons authorized to bind it in the matter. The names of all persons signing should also be printed below the signature. A proposal by a person who affixes to their signature the word, "President", "Secretary", "Agent" or other designation without disclosing their principal, may be held to be a proposal of the individual signing. When requested by the City, satisfactory evidence of the authority of the officer signing in behalf of the corporation shall be furnished. Bids submitted electronically are to be typed in lieu of written signature (see the cover letter).
- 12. OPEN RECORDS ACT: Notwithstanding any language contained in a proposal to the contrary, all proposals submitted to the City become the property of the City. Any information considered proprietary should be marked by the vendor and as such and will be kept confidential to the extent provided by law.
- **13. SALES TAX:** Vendors shall not include federal, state, or local excise, sales or use taxes in prices offered, as the City is exempt from payment of such taxes.
- 14. MISTAKES IN BIDDING INSTRUCTIONS: If the City makes a mistake in drafting the bidding instructions or any other contract documents, the City reserves the right to reject any or all bids, or to require that vendors submit an alternate proposal with adjustments made to correct the error(s). Such errors will be set forth in an addendum. If the vendor has already been selected and has started performing work under the contract, and the City then discovers a mistake in the contract documents for which the City is responsible, the City may opt to reform the contract. If the mistake causes the vendor to receive compensation for materials not used in the work or for labor that would not be required for the work, the contract price shall be decreased proportionally. If the mistake causes the vendor to fail to bid on work which must be performed in order to properly complete the contract, the City may increase the contract price to equal the proportionate increase in the cost of required materials and labor caused to the vendor. In the alternative, the City may solicit bids for such additional work, or the City may reassign such additional work to another vendor, as the City deems appropriate. Nothing in this provision shall apply to mistakes made by the vendor in completing the proposal form or in performing the contract.
- 15. ACCEPTANCE OF PROPOSAL: It is expressly understood and agreed that the City reserves the right to reject any or all bids, to waive formalities, and accept the proposal which appears to be in the City's best interest.
- 16. APPEAL OF AWARD: Solicitations will be awarded based on multiple criteria, price being just one of the conditions. Vendors can review the solicitation's special terms and conditions for information on evaluation criteria. Vendors may appeal the award decision by submitting, in writing, to the City of Northglenn, a request for reconsideration within 7 calendar days after the posting of the Notice of Intent to Award, provided that the appeal is sought by the vendor prior to the City finalizing a contract with the selected vendor. Vendors who were deemed non- responsive are ineligible to participate in the appeal process.

- 17. DEFENSE OF SUITS: In case any action at law or suit in equity is brought against the City, any officer, employee, or agent thereof, for or on account of the failure, omission, or neglect of the vendor to do and perform any of the covenants, acts, matters, or things by this contract undertaken to be done or performed, or for the injury or damage caused by the negligence of the vendor or their subcontractors or their agents, or in connection with any claim or claims based on the lawful demands of subcontractors, workmen, material, men or suppliers or machinery and parts thereof, equipment, power tools and supplies incurred in the fulfillment of the contract, the vendor shall indemnify and save harmless the City, officers, employees, and agents of the City, of and from all losses, damages, costs (including attorney's fees), expenses, judgments, or decrees whatever arising out of such action of suit that may be brought as aforesaid.
- 18. CONTRACT NEGOTIATIONS: If the City decides to proceed and to negotiate a contract, the City intends to provide written notification to the vendor whose proposal is deemed by the City to be in the best interests of the City and the City will attempt to negotiate a contract with the selected vendor(s) on terms and conditions stated in this RFP or in the successful vendor's bid, but shall also include terms and conditions later negotiated. If the City and the successful vendor are unable to execute a contract and the vendor has been notified that it is the successful vendor then the City may cease all discussions with the (first) successful vendor without any further obligation to that vendor and select another (second) vendor as the successful vendor as per the terms above, then the City, without any further obligation to that vendor as the successful vendor and so on, or the City reserves the right to reject all proposals and re-bid.
- 19. OPENING OF PROPOSALS: The City reserves the right to open Proposals received in response to this RFP, privately and unannounced, after the closing date and time.
- 20. EXTENSION OF TIME: No time extensions are being considered at this time; however, should the City extend this proposal, all vendors will be given the same considerations.

City of Northglenn 11701 Community Center Drive Northglenn, Colorado 80233-8061

PROPOSAL: Pursuant to the "advertisement for proposal" for the above named project, and being familiar with all contractual requirements therefore, the undersigned bidder hereby proposes to furnish all labor, materials, tools, supplies, equipment, transportation, services and all other things necessary for the completion of the contractual work, and perform the work in accordance with the requirements and intent of the contract documents, within the time of completion set forth herein, for, and in consideration of the following prices.

Proposal o f	(hereinafter	called	BIDDER) organized
a n d existing under the laws of the State of	_doing business as_		*. To
the CITY OF NORTHGLENN (hereinafter called CITY). In	compliance with your	advertis	sement for bids, <b>BIDDER</b>
hereby proposes to perform WORK on			

in strict conformance with the **CONTRACT DOCUMENTS**, within the time set forth therein, and at the prices stated below.

By submission of this **BID**, each **BIDDER** certifies, and in case of a joint bidder each party thereto certifies as to their own organization that this **BID** has been arrived at independently, without consultation, communication, or agreement as to any matter relating to this **BID** with any other **BIDDER** or with any competitor.

**BIDDER** hereby agrees to commence **WORK** under this contract on or before a date to be specified in the **NOTICE TO PROCEED** and to fully complete the **PROJECT** as indicated in the General Conditions.

BIDDER acknowledges receipt of the following ADDENDUM:

\*Insert "a corporation", "a partnership", or "an individual" as applicable.

Sub-contractors (if any): Work they will perform:

1	Email:
2	Email:
3	Email:
Please provide a complete and accu	rate list of at least three references and contact phone numbers:
1	Phone:
Email:	
2	Phone:
Email:	
3	Phone:
Email:	
	Respectfully submitted,
(Seal, if Proposal is by a	Signature
Corporation)	Address
	Title
Attest	Date
	License Number (If Applicable Signature)

Phone Number



Public Works 2350 W. 112th Avenue Northglenn, CO 80234 P: 303-451-1289 F: 303-450-4044 northglenn.org

## **SCOPE OF WORK**

#### INTRODUCTION

The City of Northglenn is seeking a consultant to assist with treatment options to address water quality impacts from wildfire to both raw water as well as changes to water quality in the distribution system should a fire within city limits occur. The study should build upon WRF Project #4482 and recent experience and mitigation strategies of other utilities. Impacts shall be estimated at Standley Lake with any treatment/mitigation that can be achieved at the Standley Lake intake, raw water pipeline, terminal reservoir, and the NGWTP. Any treatment to take place at Standley lakes intake structure, and Standley Lake Pipeline (SLPL) would require both Northglenn and Thornton consent as we share those assets. The consultant shall study and quantify the potential impacts of a grassland fire around SL, the delivery system, terminal reservoir, and treatment plant and make recommendations for mitigation. Special attention should be given to how water can be delivered and treated in the event of damage to the raw water pipeline from SL to the NGWTP. Treatment options, parameters addressed by each of the options, and treatment location in the operation process to be identified. Prioritization and cost estimates for each option and operational implications to be identified. Permitting and other regulatory considerations required. A generalized cost estimate, low, medium, high, and time to complete individual options required. The City of Northglenn is considering an aquifer storage and recovery program. Consultant should identify water quality concerns of blended water, ASR + wildfire impacted Standley Lake water on treatment options. Recommendations to be presented in a workshop prior to finalizing the report. Northglenn staff will provide water quality data upon request.

This contract is for calendar year 2023. All work to be completed within the year.

#### **GENERAL INFORMATION**

The City of Northglenn (Northglenn) serves a population of approximately 50,000 with drinking water from a single source, Standley Lake. Northglenn is considering the use of aquifer storage and recovery to extend supply. The Northglenn water treatment plant is a 14 MGD conventional surface water treatment plant producing a free chlorine residual. Water delivery from Standley Lake is through a 6.5 mile pipeline. Water can be delivered directly to the treatment plant or stored in a 40 million-gallon terminal reservoir. In case of emergency, water can also be delivered via the Farmers High Line Ditch.

Mandatory Prebid attendance and tour will be required.

#### DELIVERABLES

1. Completed study to encompass all tasks identified under the Introduction section, above.

#### ATTACHMENTS

- Map of delivery ditches from Clear Creek to Standley Lake
- Standley Lake Pipeline mapSchematic of Northglenn water treatment plant

- https://www.clearcreekpartnership.org/wildfire-planning, under Map Tips, UCCWA Pre wildfire planning study





PROJECT NO.		
4590		

# Wildfire Impacts on Drinking Water Treatment Process Performance: Development of Evaluation Protocols and Management Practices

## Wildfire Impacts on Drinking Water Treatment Process Performance: Development of Evaluation Protocols and Management Practices

Prepared by:

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> William Becker Hazen and Sawyer

> **Co-sponsored by:**

**City of Westminster** 

**Denver Water** 

New York City Department of Environmental Protection

San Francisco Public Utilities Commission

**Truckee Meadows Water Authority** 

## 2018



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Prepared by University of Colorado Boulder and Hazen and Sawyer.

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- City of Northglenn, CO
- City of Thornton, CO
- San Francisco Public Utilities Commission, CA
- New York City Department of Environmental Protection, NY
- Truckee Meadows Water Authority, NV
- Metropolitan Water District of Southern California, CA

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#### **EXECUTIVE SUMMARY**

#### **KEY FINDINGS**

- Post-fire water quality was simulated by heating soil and litter samples in a furnace. Following heating, the samples were leached in low-carbon tap water and the character of the dissolved organic matter was assessed. Bench-scale treatment tests were performed to evaluate the treatability of the leachates.
- Soil and litter released different quantities and qualities of dissolved constituents following heating. In general, low temperatures resulted in enhanced mobilization of carbon from soils, and lower for litter. At higher temperatures, both soils and litter released less carbon.
- The leachates consistently exhibited an overall poor response to coagulation and, even at high coagulant doses, often marginal dissolved organic carbon removal was achieved. Utilities should plan for higher coagulant doses, and the subsequent solids handling implications on downstream processes. Coagulant doses will likely be case specific depending on the wildfire- and watershed-specific factors, and post-fire flow events.

#### BACKGROUND

The frequency and intensity of wildfires has increased in recent decades, and this trend is expected to continue in the near future, especially in areas where climate change is predicted to result in warmer, drier conditions. In particular, the western United States has observed an increase in the frequency, duration, and amount of burned area from wildfires. Extreme droughts, higher temperatures, earlier snowmelt, and changes in precipitation patterns can all contribute to the likelihood of wildfires. Other factors influencing wildfire occurrence include land use changes, such as livestock grazing and fire suppression. Consequently, wildfires are of increasing concern, and their resulting impacts on the environment must be further investigated.

As wildfire frequency increases, the potential effects on forested watersheds, which commonly serve as high-quality drinking water sources for many communities, become a concern. Drinking water utilities that rely on these water sources are considering the potential impacts of wildfires in their watersheds. These impacts include water quantity and availability, source water quality, and the ability to effectively treat and provide the high-quality water that the public demands. Currently, there are a limited number of reported case studies where post-wildfire water quality and treatability were monitored at drinking water utilities. Therefore, there is a need to better understand the effects of wildfires on source water quality and treatability, while also considering the effects on treatment plant operations and costs.

#### **OBJECTIVES**

The overarching objective of this project was to expand the knowledge base regarding the effects of wildfire on drinking water quality, treatment, plant performance, and operations. In order to meet this objective, this project focused on three main aspects. First, in order to evaluate the effects of a wildfire on a particular treatment operation, an approach to simulate the effects of a wildfire on water quality was developed. Second, simulated post-fire runoff was treated using

mostly conventional processes. Lastly, an evaluation of the best treatment practices to deal with wildfire-impacted source waters was conducted. An additional objective of this project was to extend the post-fire water quality monitoring at a water intake in a burned watershed.

This project included the collaboration and support from the following utilities:

- Denver Water (DW)
- City of Westminster, CO (WM)
- City of Northglenn, CO
- City of Thornton, CO
- San Francisco Public Utilities Commission (SFPUC)
- New York City Department of Environmental Protection (NYCDEP)
- Truckee Meadows Water Authority
- Metropolitan Water District of Southern California

#### APPROACH

To complete this project, the team first collected surface soil and litter samples from watersheds serving four water utilities (DW, WM, SFPUC, NYCDEP). The samples were collected from multiple sites in the different source watersheds for the utilities. The samples were transported to the University of Colorado Boulder (CU Boulder) for processing. At CU Boulder, the samples were air dried and heated at a temperature of 225°C for two hours in a muffle furnace. This temperature was selected as the amount of dissolved organic carbon (DOC) released into solution was greatest compared to other temperatures (350°C and 500°C). Therefore, for this study, heating soils and litter materials at 225°C represents worst-case scenario conditions for disinfection byproduct (DBP) precursors.

After the samples were heated, they were leached into water, followed by an evaluation of the water quality and treatability by coagulation. Unheated (control) soil/litter leachates were also characterized and evaluated with bench-scale treatment studies and compared to the heated leachates.

#### **RESULTS/CONCLUSIONS**

Soil and litter samples released different quantities and qualities of dissolved constituents following heating. Litter tended to release more dissolved organic matter (DOM) following heating compared to soil. The release of anions and cations was altered following heating. Anion release into solution showed strong heating dependence, but was not consistent among the measured species. Sulfate concentrations demonstrated the most consistent behavior, increasing with heating of each material, especially litter, which was shown to release nearly ten times more sulfate than soil following heating. Nitrate concentrations generally decreased following heating of both litter and soil. Phosphate release was not constant among the soils, but phosphate release from litter increased after heating at 225°C. Iron and manganese showed similar trends and demonstrated greater release after heating.

Generally, the trends observed for the four utilities were consistent and aid in understanding the effects of heating on water soluble compounds, raw water quality, and the associated treatment challenges. Marginal increases in pH and alkalinity were observed for the heated samples, which may be attributed to the denaturing of organic acids upon heating, with residual alkaline components remaining. An observed decrease in the quantity of DOC leached per gram of material for the heated leachates is consistent with other work indicating partial combustion of soluble organic carbon compounds at 225°C. Alternatively, organic nitrogen has been shown to volatilize at higher temperatures, supporting the observed enrichment of dissolved organic nitrogen (DON) relative to DOC following heating. SFPUC leachates did not follow the same trend as the other utilities, and the DOC leached per gram of soil increased after heating. Only soils were leached for the SFPUC samples (litter samples were not available), and perhaps different organic precursor materials of soils and litter may help explain the difference. Clear and measurable alterations to the soluble DOM character was indicated by increased specific UV absorbance at 254 nm (SUVA<sub>254</sub>). Iron concentrations of the heated leachates were low (< 0.005 mg/L) and did not significantly interfere with absorbance measurements. Consistently higher SUVA<sub>254</sub> for the heated samples indicates enhanced aromaticity of soluble compounds upon heating, supported by previous soil organic matter studies.

For raw water (not coagulated) carbonaceous DBP (C-DBP) yields, the changes following heating at 225°C varied for total trihalomethane (TTHM) and haloacetic acid (HAA) precursors, but C-DBP yields were often lower following heating. However, this trend was not consistent for all samples. Bromide concentrations were low (< 0.003 mg/L), and primarily chlorinated DBP species were formed. It should be noted that the similar or lower TTHM and HAA precursor reactivity of the heated leachates compared to the control (unheated) samples may not be representative of the precursor load a water treatment facility might receive in its influent supply post-wildfire. Enhanced erosion of terrestrial DOM following a wildfire can significantly increase DOC levels and DBP formation, as observed in field-based studies. Haloacetonitrile (HAN) precursor reactivity of the raw waters also varied following heating. Alternatively, the chloropicrin precursor reactivity was generally higher for the heated leachates, which may be associated with the enrichment of DON relative to DOC, or elevated inorganic nitrogen levels. While the DOC:DON ratio decreased upon heating, and chloropicrin formation and precursor reactivity per unit of carbon increased, HAN4 precursors did not appear consistently altered by heating at 225°C. Previous studies have associated elevated HAN4 reactivity with wildfire.

Following heating of soil and litter, the leachates consistently exhibited an overall poor response to coagulation and, even at high coagulant doses (e.g., > 80 mg/L alum), often marginal DOC removal was achieved (e.g., <30%). The treatability findings are consistent with the results from a field-based post-fire watershed monitoring study when rainstorms transported substantial sediments and debris downstream to a water intake. The adverse effect of heating on the treatability of the leachates might be explained by a lower molecular weight DOM composition. Despite the higher SUVA254, a change in DOM quality, such as a shift towards lower molecular weight compounds, may have adversely affected coagulation treatment, resulting in elevated settled water turbidity levels and minimal DOC removal. Further, finished water quality was negatively influenced, including the exceedance of DBP maximum contaminant levels (MCLs) and high chloropicrin concentrations. Heat-induced changes to particle size and characteristics were not explored in this study, but may have negatively affected coagulation processes, possibly due to the presence of finer materials. Following treatment, most heated leachates exceeded DBP MCLs, whereas all control samples were below MCLs. Treated water nitrogenous DBP formation was also higher for the heated leachates, specifically chloropicrin. While findings suggest an altered DOM character, utilities may also experience an increase in influent DOC concentrations coupled with higher, or even extreme, sediment loads, resulting in compounding effects on water treatment.

Lastly, recommendations were made regarding the design and operation of treatment systems for utilities under the threat of wildfire. The following recommendations are presented with the assumption that sufficient space is available.

- 1. Pre-sedimentation basin
  - a. May be required/useful if raw water turbidity exceeds 100 NTU for long periods (i.e., days or weeks)
  - b. Include the ability to bypass under normal conditions or potential addition of an oxidant
- 2. Coagulation
  - a. Ensure chemical storage and feed pumps can deliver the higher chemical doses that may be needed after a wildfire
  - b. Consider polymer feed facilities that may be needed to treat waters with ash content
  - c. Develop operational protocols and install equipment such as streaming current monitors or zeta potential analyzers to help determine optimum coagulant dosages
- 3. Flocculation
  - a. Install a means of removing silty solids that may settle out in flocculation tanks under high turbidity conditions
- 4. Sedimentation
  - a. Use large conventional sedimentation basins if possible to handle large amounts of solids; if not practical, consider the use of lamella plate settlers
  - b. Ensure solids can be easily removed from basins via mechanical sludge removal equipment
  - c. If in an area where it is not likely that high turbidity will reach the intake, and there is concern that algal blooms could occur, consider dissolved air flotation (e.g., where ash or soil-related turbidity from a watershed after a fire is likely to settle out in an upstream reservoir, but nutrients could be transported to downstream reservoirs)
- 5. Filtration
  - a. Consider the use of deep bed dual-media filters with larger media that can store more solids than conventional filters
  - b. Consider granular activated carbon (GAC) in place of anthracite to help with taste and odor
  - c. Provide enough backwash water and waste backwash storage so multiple filters can be backwashed at once
- 6. Membranes
  - a. Membrane-based treatment systems should not be used if the raw water will be subject to the impact of firefighting foams that could foul membranes
- 7. Disinfection
  - a. Higher levels of NOM may lead to DBP compliance issues
  - b. Attention should be given to maximizing removal of NOM or relying on the use of alternative disinfectants including UV and ozone
- 8. Advanced treatment
  - a. Smoky taste and odor could occur after a fire

- b. Nutrient release from wildfires could result in long-term eutrophication and increased algal growth in downstream reservoirs leading to algal toxins and taste and odor issues
- c. The installation of powdered activated carbon or post filter GAC contactors should be considered to handle these events
- d. The installation of ozone/biofiltration should also be considered when possible

#### APPLICATIONS/RECOMMENDATIONS

It is recommended that utilities under the threat of wildfires consider the treatment implications of this perturbation in their watersheds. The results from this study indicate that higher coagulant doses will likely be required, with implications for operations and residual handling. If extreme post-fire erosion conditions occur, coagulation alone may not be effective for meeting turbidity and TOC removal requirements. Expanding water storage capacity and diversifying water sources is also recommended to handle worst-case scenario runoff conditions. In addition, a robust water quality monitoring plan is needed to ascertain the specific effects following wildfire and to rapidly and effectively adjust and respond to water quality changes. Utilities should have the capacity to conduct simple treatment evaluation tests in-house to address site-specific effects of post-fire runoff on treatment operations.

#### **RELATED WRF RESEARCH**

- An Integrated Modeling and Decision Framework to Evaluate Adaptation Strategies for Sustainable Drinking Water Utility Management Under Drought and Climate Change (project 4636)
- Effects of Wildfire on Drinking Water Utilities and Best Practices for Wildfire Risk Reduction and Mitigation (project 4482)
- Impact of Wildfires on Source Water Quality and Implications for Water Treatment and Finished Water Quality (project 4524)
- Utility Guidance for Mitigating Catastrophic Vegetation Change in Watersheds (project 4009)
- Wildfire Impacts on Water Supplies and Potential for Mitigation: Workshop Report (project 4529)

#### CHAPTER 1 INTRODUCTION

#### **INTRODUCTION**

Climate change and population growth continue to stress water resources, resulting in heightened pressures on drinking water supplies. Concurrently, natural and anthropogenic watershed disturbances are rising, potentially impacting the integrity of watersheds and the water quality of potable sources. These disturbances include wildfires, droughts, and floods. Addressing the effects of watershed disturbances on drinking water treatment presents a critical challenge for ensuring delivery of safe and sustainable drinking water.

The frequency and intensity of wildfires has increased in recent decades, and this trend is expected to continue in the near future especially in areas where climate change is predicted to result in warmer, drier conditions (Smith et al. 2011). Globally, many regions are experiencing a marked rise in wildfire activity as a consequence of climate change, increased fuel loads, and drought (Figure 1.1) (Flannigan et al. 2013, 2009; McKenzie et al. 2004; Westerling et al. 2006). In particular, in the Western United States, there has been an increase in the frequency, duration and amount of burned area from wildfires (Brown et al. 2004, Westerling et al. 2006, Flannigan et al. 2009). This increase can be partially attributed to consequences of climate change (Brown et al. 2004, Westerling et al. 2006). Extreme droughts, higher temperatures, earlier snowmelt, and changes in precipitation patterns can all contribute to the likelihood of wildfires. Other factors influencing wildfire occurrence include land-use changes, such as livestock grazing, and fire suppression (Savage and Swetnam 1990, Belsky and Blumenthal 1997). Consequently, wildfires are of increasing concern and the resulting impacts on the environment must be further investigated.



*Source:* Reprinted (adapted) with permission from Bladon et al. 2014. Copyright 2014 American Chemical Society.

The red dashed line indicates the rolling 5-year average area burned. Figure 1.1 Annual area burned in the United States from 1960-2013

The increased likelihood of wildfire has created concerns among downstream water utilities regarding the integrity and resiliency of their water systems, including source water watersheds (Sham et al. 2013). While the ecological, forestry, and watershed science communities have investigated wildfires extensively, post-wildfire drinking water effects are relatively unexplored (Emelko et al. 2011, Hohner et al. 2016, Revchuk and Suffet 2014, Writer et al. 2014). A thorough investigation of post-fire treatment challenges is needed to help utilities make informed management decisions and develop mitigation approaches. The vulnerability of watersheds, infrastructure, and process performance must be assessed to provide water utilities with recommendations to effectively prepare for a wildfire.

In recent years, several major wildfires have impacted water treatment systems (WTS) in the Western United States (Sham et al. 2013). In 2002, the Hayman Fire of Colorado burned the forested area of the Upper South Platte River. This watershed serves as the drinking water supply for the City of Denver. The 2012 High Park Fire burned sections of the Cache la Poudre (CLP) watershed, which serves as a drinking water source for three northern Colorado communities, including the City of Fort Collins. Also in 2012, the Waldo Canyon Fire burned Pike National Forest threatening the City of Colorado Springs' drinking water supply. The Rim Fire of 2013 in California burned within four miles of the Hetch Hetchy Reservoir, which serves the City of San Francisco. Other regions of the contiguous United States that have received extensive wildfire damage in the last decade include: Arizona, Montana, Wyoming, and New Mexico. Internationally, wildfires are also a concern in different regions of the world, including Canada, Spain, and Australia.

#### Wildfire Effects on Soils

Water quantity and quality are inextricably linked to forest soil properties (Neary et al. 2005), and wildfire changes to soils are critical to understanding watershed effects of fire. Research has shown the development of a hydrophobic layer following wildfire (DeBano 2000a, 2000b) that can increase surface-runoff upon rainfall (Neary et al. 2009). Nutrient cycling in soils may also be affected by wildfires. Carbon and nitrogen losses in the organic layer vary depending on fire severity, fuel type, pre-fire conditions (Homann et al. 2011), and time since the disturbance (Prieto-Fernandez 1998). However, several studies have shown an increase in forest floor carbon and nitrogen content following a low or moderate severity fire as a result of partly charred biomass accumulation and integration into the soil (Almendros et al. 1990, 1988; Knicker et al. 2005).

The effects of wildfires on soil organic matter (SOM) have been more extensively studied than DOM and were reviewed by Knicker (2007). Wildfire induced changes to SOM quantity and quality will likely affect the DOM of nearby waters based on soil biogeochemical processes that govern DOM fluxes in watersheds and the hydrologic connectivity through the landscape (Cawley et al. 2018, Cawley et al. 2017, Dick et al. 2014, Sanderman et al. 2009). Specifically, research suggests the importance of rainstorms in the transport of terrestrial debris and SOM to surface waters in unburned (Clark et al. 2007, Inamdar et al. 2012, Inamdar and Mitchell 2007) and burned watersheds (Murphy et al. 2015, Mast et al. 2016).

#### Wildfire Impacts to Water Quality

There are numerous concerns regarding the impact of a wildfire on source water quality and water treatment systems (WTS) operations. These concerns include water quantity and availability, as well as the impact on source water quality and the ability of WTS to effectively treat and provide high quality water that the public demands (Sham et al. 2013). Currently, there are a limited number of reported studies that have monitored post-fire water quality and treatability at drinking water utilities.

Many confounding and seasonally varying watershed factors, as well as wildfire specific factors, such as burn severity, forest type, location and extent, influence post-fire water quantity and quality responses (Hohner et al. 2016, Neary et al. 2005, Rhoades et al. 2011, Smith et al. 2011). Combined these factors make it challenging to elucidate impacts specifically related to wildfire (Neary et al. 2005). Wide ranges of post-fire responses have been observed and are highly dependent on the timing and magnitude of precipitation in the burned area. Current research shows the primary influences of wildfire on surface water quality are enhanced erosion, increased sediment loads, elevated nutrient concentrations (i.e., nitrogen and phosphorus), and generally more variable water quality (Smith et al. 2011). The potential changes in water quality pose significant challenges to water utilities, however previous work mostly speculates regarding post-fire treatment challenges, lacking a direct evaluation.

The most apparent influence of wildfires on watersheds is an altered hydrologic regime characterized by flashy events and subsequent sediment transport. Effects can include increased total runoff volume, increased peak flow, flooding, and increased sediment mobilization (Sham et al. 2013). A wildfire can result in loss of vegetation, decreased soil infiltration (higher soil hydrophobicity), and decreased evapotranspiration, all contributing to the effects listed above. Consequently, erosion and sediment mobilization can be elevated post-fire, particularly during

storm events and when discharge is greatest in the first year following a wildfire (Silins et al. 2009).

From a water supply and treatment perspective, these changes can greatly influence total suspended solids (TSS) and turbidity levels. Rhoades et al. (2011) found turbidity levels were four times higher in a basin with high severity burn compared to basins that were not burned as severely. Other research has shown elevated turbidity levels in wildfire impacted waters can reach extreme values under specific hydrological conditions (e.g., heavy rainfall, rapid snowmelt) (Emelko et al. 2011, Writer et al. 2012). The elevated level of TSS is a concern to utilities, which are restricted regarding the turbidity levels that are permitted for potable water. It has been shown that the enhanced turbidity associated with a rain event following a wildfire can be effectively coagulated, however the required coagulant doses are, as expected, higher (Hohner et al. 2016). The higher coagulant doses may be beyond what a WTS could handle and will also result in increased costs for disposal of material.

Regarding the specific impacts on water quality, the observed changes depend greatly on different parameters including fire intensity, severity, and duration, as well as forest terrain slope, the frequency and intensity of rain storm events, and snowmelt patterns (Landsberg and Tiedeman 2000, Neary et al. 2005). The effects are all driven by the extent of perturbation by the wildfire (e.g., localized low intensity fire versus mixed severity, large size, and location near a water intake). For instance, a high severity fire burns the overstory and understory vegetation and consumes most surface organic matter (Keeley 2009).

Perhaps one of the most studied parameters regarding the effect of wildfire on water quality is the mobilization of nutrients (nitrogen and phosphorous). In general, previous work has shown that nutrient concentrations increased in watersheds after a wildfire. Ranalli (2004) showed that nitrogen levels increased and then eventually stabilized once vegetation regrowth was established. Studies in the Rocky Mountains of Alberta also reported increased nitrogen and phosphorus levels (Bladon et al. 2008, Silins et al. 2009). Other studies found nitrate levels were increased in burned watersheds (Mast and Clow 2008, Writer et al. 2012). Research by Rhoades et al. (2011) found that high severity burns increase nitrate and turbidity levels, whereas a lower intensity fire had less of an effect on water quality. Nutrient levels in streams can also be affected by inputs from atmospheric deposition as well as hillslope soil erosion and transport from burned areas (Smith et al. 2011). Wildfires are also known to enhance the mobilization of metals, including iron, manganese, and mercury (Sham et al. 2013), although the specific mechanisms by which this happens are subject of ongoing research.

#### **Dissolved Organic Matter and Disinfection Byproducts**

One large research gap regarding the short and long-term effects of a wildfire on water quality is in the effect on the mobilization and changes to the chemical properties of dissolved organic matter (DOM) after a wildfire. DOM is generally quantified as dissolved organic carbon (DOC). DOM is ubiquitous in the aquatic environment, composed of a complex, heterogeneous mixture of aromatic and aliphatic structures that contain many functional groups (Leenheer and Croué 2003). Terrestrial sources of DOM include plant debris and soil organics flushed into surface waters by rainfall, commonly referred to as allochthonous organic matter. Terrestrially derived DOM is generally more aromatic with higher humic content, and well removed by conventional treatment processes (Edzwald 1993). Autochthonous, or aquatically derived, DOM originates from algal and microbial productivity within a water body. Autochthonous DOM is

commonly characterized by higher nitrogen content and a more aliphatic and hydrophilic composition (Leenheer and Croué 2003, Westerhoff and Mash 2002).

There have been numerous studies regarding the mobilization of DOM in watersheds. The background DOM observed in a watershed is from leaching of soils in surface and groundwater (this is for watersheds that do not contain significant proportions of wetlands, peats, or bogs). During baseflow conditions, the DOM is mostly from groundwater and the DOC levels are lower because mineral soils contain less SOM (Thurman 1985). During higher flow (surface) events, including snowmelt and storms, surface SOM is mobilized which typically has higher aromaticity (quantified by WTS as SUVA<sub>254</sub>) (Weishaar et al. 2003).

Wildfire changes to the landscape and forest floor may alter the quantity and quality of DOM in source waters. There are several studies regarding the fate of SOM after a wildfire (Knicker 2007, Lopez-Martin et al. 2016), however there are limited studies on the mobilization to surface waters (Majidzadeh et al. 2015, Tsai et al. 2015, Wang et al. 2015a, Wang et al. 2015b). It has been reported by different groups that, at temperatures associated with low intensity fires, DOM mobilization can increase (Cawley et al. 2017). Alternatively, other studies have concluded minimal effects on DOC levels in burned areas compared to unburned (Lamontagne et al. 2000, Mast and Clow 2008). These seemly contradictory findings highlight the need for further research to address the complexity of wildfire characteristics, environmental influences, and hydrologic effects following wildfires on water quality.

Elevated DOM levels, commonly quantified as dissolved organic carbon (DOC - mgc/L), following wildfires have been documented (Emelko et al. 2011, Hohner et al. 2016, McEachern et al. 2000, Minshall et al. 2001), while others found minimal effects on DOC (Mast and Clow 2008). It is suggested that background DOC concentrations may dampen the contributions from wildfire (Smith et al. 2011), emphasizing the importance of local hydrology, burn severity, and extent, when interpreting effects on water quality.

Although DOM is naturally occurring, it poses a concern in source water supplies because it can react with disinfectants (e.g., chlorine, chloramines) to form disinfection byproducts (DBPs) as an unintended consequence of water treatment (Christman et al. 1983, Rook 1977, Stevens et al. 1976). DBP exposure has been linked to cancer risks and reproductive developmental effects (Muellner et al. 2007; Plewa et al. 2004; Richardson et al. 2007; Villanueva et al. 2004, 2006). The United States Environmental Protection Agency (EPA) regulates certain DBP species in drinking water, including total trihalomethanes (TTHM) and the sum of five haloacetic acids (HAA5) (EPA 2011). The regulated TTHM and HAA5 maximum contaminant levels (MCLs) under the Stage 2 Disinfectant/Disinfectant Byproduct Rule are 80 µg/L and 60 µg/L, respectively.

Nitrogenous disinfection byproducts (N-DBPs), such as haloacetonitriles (HAN), halonitromethanes (e.g., chloropicrin), and nitrosamines are not currently regulated, but are of interest as they may be more of a health concern than TTHM and HAA5, even at lower concentrations (Muellner et al. 2007; Plewa et al. 2004, 2008). Minimal information is available regarding the effects of wildfire on DBP formation (Wang et al. 2015b, Writer et al. 2014) and water treatment processes (Emelko et al. 2011). Current research suggests material burned in wildfires may constitute a terrestrial source of N-DBP precursors (Cawley et al. 2017, Wang et al. 2015b). Understanding the sources, characteristics, and reactivity of DOM is essential to control DBP formation in potable water supplies.

#### Water Treatment Unit Processes

There are limited reports on the effects of wildfires on source water quality coupled with the water treatment process performance (Emelko et al. 2011, Hohner et al. 2016, Hohner et al. 2017, Majidzadeh et al. 2015, Tsai et al. 2015, Wang et al. 2015a, Wang et al. 2015b, Writer et al. 2014). Several lab-based leaching studies of material burned in wildfires have been conducted to assess the effects on DOM and drinking water treatment (Revchuk and Suffet 2014, Wang et al. 2015a). In a leaching study of material burned in California wildfires, a 10-fold increase in the concentration of DOC leached was observed when compared to unburned material (Revchuk and Suffet 2014). A study evaluating water extractable material of burned detritus from the Rim Fire revealed elevated N-DBP reactivity (HAN and NDMA) compared to unburned detritus (Wang et al. 2015b). Other work has shown that waters impacted by wildfire could be effectively treated by coagulation (Emelko et al. 2011).

Our group has conducted detailed treatment studies on wildfire-impacted source waters. Initially, we coagulated water samples collected from the CLP River after the 2012 High Park wildfire in Colorado. The results indicated that post-fire samples required on average a 10 mg/L higher coagulant dose during baseflow and spring snowmelt conditions when compared to water collected from an unburned reference site (Hohner et al. 2016). In a follow up study, post-fire source water quality was simulated using field sediments impacted by the High Park wildfire (Hohner et al. 2017). Sediments were collected from four sites (A-D) along the banks of the CLP River after the wildfire. The sediments were then leached in the laboratory for 24 hours with baseline source water (SW) collected from two utilities. Sediments A-D were also leached in City of Boulder tap water treated with granular activated carbon (GAC) to minimize background DOC (< 0.2 mgc/L), referred to as low carbon tap-water (LCT). In this previous study, multiple unit processes were evaluated: coagulation, enhanced coagulation, powdered activated carbon (PAC), biofiltration and pre-oxidation with chlorine dioxide or ozone. The different treatment processes were evaluated for DBP precursor removal.

Figure 1.2 shows the coagulation dose response curves for baseline waters, SW leachates and LCT leachates. The baseline samples represent the source waters for the two participating utilities with no sediment added. The baseline waters were effectively treated with 25 mg/L of aluminum sulfate. For the SW leachates, which includes the baseline waters with the addition of sediments, the waters were more difficult to treat, demonstrated by higher finished water turbidity and DOC levels. When the sediments were leached in LCT water, the dose responses were similar to the baseline waters.



*Source:* Hohner et al. 2017. Reproduced by permission of The Royal Society of Chemistry. An alum dose of 25 mg/L was used for conventional treatment and 50 mg/L for enhanced coagulation.

## Figure 1.2 Raw and coagulated turbidity and DOC values of baseline waters, source water leachates, and low carbon water (LCT) leachates

Table 1.1 presents results from the treatability evaluation of multiple unit processes for baseline waters, SW leachates, and LCT leachates. TTHM and HAA5 MCL values (80 and 60  $\mu$ g/L, respectively) were divided by the corresponding carbon normalized DBP yield ( $\mu$ g/mgc) determined from the bench scale chlorination tests to calculate *DOC thresholds* (mgc/L). DOC thresholds represent the required DOC concentration at the point of chlorination to meet TTHM and HAA5 regulations for each water sample and treatment process. In each case, the more

restrictive DBP yield (TTHM or HAA5) was used. The DBP yield and *DOC* threshold approach allows for a comparison of all samples, independent of raw water DOC concentrations. As shown in Table 1.1, pre-ozonation was most often the best treatment option (highest DOC threshold) for the sediment leachates to minimize DBP formation and meet DBP MCLs. Refer to Hohner et al. (2017) for further detail on the previous study.

		MCL DOC Threshold (mgc/L)							
	Sample Name	Conventional Treatment	Enhanced Coagulation	РАС	Chlorine Dioxide	Pre-ozonation	Biofiltration	Pre- ozonation/ Biofiltration	Best Treatment Option
Baseline Waters	Fort Collins (FC)	2.6	2.8	2.3	2.6	2.7	2.6	3.0	Pre-ozonation/ Biofiltration
	Denver Water (DW)	3.1	3.3	2.8	4.8	3.0	2.7	3.3	Chlorine Dioxide
Average increase in DOC thresho			0.2	-0.3	0.8	0.0	-0.2	0.3	
Source Water Leachates	A- FC	2.0	2.0	1.8	1.8	2.4	1.4	2.2	Pre-ozonation
	B- DW	1.7	2.1	1.8	1.8	3.0	1.6	2.6	Pre-ozonation
	C- DW	2.1	2.8	2.1	2.1	2.8	2.4	2.1	Enhanced Coag & Pre-ozonation
	D- FC	1.8	2.4	1.3	2.0	2.4	1.8	2.3	Enhanced Coag & Pre-ozonation
LCT Leachates	A- LCT	2.0	2.3	1.8	2.1	2.6	1.6	2.4	Pre-ozonation
	B- LCT	1.6	2.1	2.0	2.0	1.7	1.7	2.1	Enhanced Coagulation Pre-ozonation/ Biofiltration
	C-LCT	1.4	1.9	2.1	1.7	3.0	1.5	2.1	Pre-ozonation
	D- LCT	2.1	2.0	1.8	2.2	2.7	1.6	2.5	Pre-ozonation
Average increase in DOC threshold			0.4	0.0	0.1	0.7	-0.1	0.5	Pre-ozonation

 Table 1.1

 DOC values required at the point of chlorination to meet DBP MCLs (DOC thresholds) determined from treated water

 TTHM and HAA5 yields and DBP MCLs for the range of unit processes evaluated

Source: Hohner et al. 2017. Reproduced by permission of The Royal Society of Chemistry.

#### **Project Motivation**

The work discussed so far offers insight into the potential effects of a wildfire on water quality and treatment processes. However, published literature is primarily based on field samples collected after a select number of wildfires, and it is unknown whether these results apply to other utilities with different treatment processes, or located in different geographical regions. In this regard, there is a need to develop a framework for utilities to evaluate the potential local effects of a wildfire on water quality and treatment performance. Essentially, there is a need to develop an approach to simulate the effects of a wildfire, which presents many challenges and lacks an ideal solution. As part of a previous Water Research Foundation project (WRF 4524), our team conducted preliminary experiments to evaluate lab-based heating experiments to simulate postfire effects on water quality (Cawley et al. 2017). For this project (WRF 4590), the team continued the development of the laboratory heating approach to simulate post-fire effects on water quality and treatment for four utilities. Soil and litter samples from different watersheds were collected and processed in the lab. In consultation with the participating utilities, samples were heated to 225°C and then leached in LCT water at CU Boulder. The leached samples were evaluated for water quality parameters. In addition, in consultation with the participating utilities, bench-scale treatment tests were developed and conducted. The following sections contain a discussion of the project results.

The following utilities participated in this project:

- Denver Water (DW)
- City of Westminster (WM)
- City of Northglenn, CO
- City of Thornton, CO
- San Francisco Public Utilities Commission (SFPUC)
- New York City Department of Environmental Protection (NYCDEP)
- Truckee Meadows Water Authority
- Metropolitan Water District of Southern California

Further, this project also funded an extension of previous work addressing the changes in CLP River water quality after the High Park fire of 2012. The intent was to expand the monitoring work done as part of previously funded work by both The Water Research Foundation and the Colorado Department of Public Health and Environment. This work is discussed in Chapter 2.

#### CHAPTER 2 CONTINUED MONITORING OF THE CACHE LA POUDRE WATERSHED FOLLOWING THE HIGH PARK WILDFIRE

In 2012, the High Park wildfire burned approximately 87,284 acres of the Cache la Poudre (CLP) watershed located in northern Colorado. The CLP watershed supplies potable water to three water districts in Colorado, including the City of Fort Collins, serving over 300,000 customers. The immediate and future impacts of the High Park wildfire on source water quality of the CLP River presented a high concern for the local water utilities.

Two previous WRF projects (#4282 and #4524) were conducted by the research team to monitor the water quality and treatability of the CLP River prior to the wildfire (2008 - 2009) (Summers et al. 2013) and for the first year following the wildfire (2012 - 2013) (Writer et al. 2014). As part of this project, to further address post-fire water quality effects, the CLP River monitoring campaign was extended. The CLP watershed was sampled April-October 2015, biweekly during spring snowmelt and monthly during baseflow conditions. Samples were collected from the City of Fort Collins water intake located within the burned area, and from an upstream reference site (Figure 2.1). Water quality analysis, chlorination tests and DBP analysis of the monitoring samples were completed following established methods (Hohner et al. 2016). Pre-fire data collected from the CLP River at the water intake (downstream of burned area) and a reference site (upstream of burned area) were used for comparison (Beggs 2010, Summers et al. 2013).


*Source:* Hohner et al. 2016. Reprinted from *Water Research*, vol. 105, Drinking Water Treatment Response Following a Colorado Wildfire. Copyright 2016 with permission from Elsevier.

# Figure 2.1 CLP River sampling sites include the City of Fort Collins drinking water intake within the High Park fire burn area, and the reference site, upstream and outside of the burned area

Table 2.1 shows the water quality concentrations for the water intake and reference site including pre-fire years (2008 – 2011), and two post-fire years, 2013 and 2015. Samples collected in 2012 were previously published in Writer et al. 2014 as part of preliminary effort to capture immediate post-fire runoff. The data and text related to the pre-fire and 2013 data sets were taken from Hohner et al. 2016 (Hohner et al. 2016). Unfortunately, samples were not collected during 2014 due to budget constraints and a delayed project start date. A paired data analysis approach was used. For each sampling date the difference ( $\Delta$ ) in water quality concentrations between the water intake and reference site was determined to assess whether any differences occurred following the wildfire. Further, the post-fire spatial differences between the sites were compared to the pre-fire differences.

Pre-fire paired spatial differences are presented in Table 2.1 (pre-fire p values not shown) and reveal the water quality concentrations of the two sampling sites were similar before the wildfire. Total nitrogen (TN) and total organic carbon (TOC) levels were not statistically different (p > 0.05) for the two sampling sites before the fire (median  $\Delta$ : < 0.01 mg<sub>N</sub>/L and - 0.12 mg<sub>C</sub>/L, respectively). Spatial differences for total phosphorus (TP) were statistically significant (p < 0.05). The mean and median TP concentrations for both sites were very close to the reporting limit (0.01 mg<sub>P</sub>/L) and the median difference was < 0.001 mg<sub>P</sub>/L, therefore TP was assumed reasonably similar between the sites prior to the wildfire. The upstream site was chosen as a reasonable

reference location for comparison to the water intake due to the minimal differences in pre-fire water quality, which reflect the influence of basin differences (e.g., drainages, elevation) that could impact water quality.

The 2013 post-fire spatial differences for TP and TN were at least an order of magnitude greater than before the fire (p < 0.01). In 2015, total dissolved phosphorus (TDP) and total dissolved nitrogen (TDN) were higher at the water intake compared to the reference site. Note that samples collected in 2015 were analyzed as the dissolved fraction, rather than total nutrients (particulate plus dissolved). The 2013 post-fire TOC spatial differences were significantly greater than before the fire (Table 2.1) and showed more variability, likely indicating an increased watershed input of organic matter to the river after the wildfire. In 2015 the spatial differences in nutrients between sites were elevated compared to pre-fire years, but were lower than observed in 2013, suggesting the post-fire effects had mostly dissipated, however the 2015 samples only included the dissolved fraction, which may have influenced the comparison to 2013 nutrient levels. The elevated post-fire TN, TP, and TOC in 2013 likely reflect increased erosion and sediment transport to the stream channel. Whereas, by 2015 most of the fire-impacted materials had been washed downstream by rainfall and snowmelt.

Pre- and post-fire water quality for the CLP River are shown. The water intake is located downstream of the burned area and the reference site is located upstream and outside of the burned area. Samples collected in 2015 were analyzed as the dissolved fraction for TDP. TDN. and DOC.

Table 2.1

Water Quality Parameter			Pre-fire	e		Post-f	ire		Post-fire						
			(2008 – 2011)				2013				2015				
		Concentration		Δ		Concentration		Δ		Concentration		Δ			
		Water Intake	Reference	(intake - reference)	n	Water Intake	Reference	(intake - reference)	n	Water Intake	Reference	(intake - reference)	n		
	Mean	0.018	0.014	+0.004		0.058	0.013	+0.046		0.010	0.006	+0.004	9		
TP/TDP (mgp/L)	Median	0.013	0.012	+0.000	44	0.023	0.011	+0.013	11	0.007	0.004	+0.002			
(ingr/L)	Stdev	0.014	0.007	0.008		0.077	0.004	0.077		0.008	0.007	0.005			
	Mean	0.29	0.27	+0.02		0.66	0.27	+0.4		0.28	0.19	+0.09			
TN/TDN (mgn/L)	Median	0.25	0.24	+0.00	20	0.34	0.28	+0.16	11	0.21	0.16	+0.02	9		
(ingivit)	Stdev	0.2	0.18	0.11		0.69	0.1	0.7		0.19	0.08	0.19			
TOCIDOC	Mean	4.8	4.8	+0.01		4.9	4.2	+0.71		5.3	5.1	+0.19	9		
TOC/DOC (mgc/L)	Median	3.5	3.9	-0.12	43	4.6	4.2	+0.47	10	4.6	5.1	+0.22			
	Stdev	2.8	2.7	0.8		1.9	1.9	0.91		2.4	2.6	0.62			

*Source:* Hohner et al. 2016. Reprinted from *Water Research*, vol. 105, Drinking Water Treatment Response Following a Colorado Wildfire. Copyright 2016 with permission from Elsevier.

In 2013 and 2015, SUVA<sub>254</sub> values at the water intake were higher than pre-fire values (Table 2.2). However, post-fire pairwise comparison of the water intake to the reference site indicated SUVA<sub>254</sub> was statistically the same, suggesting during baseflow and snowmelt conditions the aromaticity of the DOM was not significantly altered by the wildfire. Pre-fire SUVA<sub>254</sub> data were not available for the reference site, and therefore a pre- to post-fire spatial analysis was not possible.

Carbon-normalized DBP formation yields (DBP concentration/DOC concentration) were used to understand the reactivity of DOM on a per unit carbon basis ( $\mu$ g/mgc). TTHM yields at the water intake were similar pre- and post-fire (2013 and 2015), whereas HAA5 yields were considerably higher in both 2013 and 2015, compared to 2009 (Table 2.2). However, the 2013 TTHM and HAA5 yields were similar between the water intake and reference sites, suggesting wildfire impacts on C-DBP reactivity were minimal for this watershed and wildfire. Further, in 2015 HAA5 yields measured at the reference site were higher than the intake. The higher HAA5 reactivity observed in 2013 and 2015 compared to 2009 may be attributed to temporal variability resulting in a shift in the watershed HAA5 precursor material independent of the wildfire, such as increased primary productivity in the late summer, and would likely also be observed for the reference site. Pre-fire data were only available for the water intake, so a pairwise statistical analysis was not possible before the fire, limiting further conclusions. In 2013 paired analysis showed the HAN4 yields were higher at the water intake (median  $\Delta = 0.12 \mu$ g/mgc), while in 2015 the spatial difference was minimal (median  $\Delta = -0.04 \mu$ g/mgc). Chloropicrin yields at the two sites were similar in both 2013 and 2015. Pre-fire N-DBP data were not available.

		Pre-fire (2008 - 2009	9)		Post-fire (2013)			Post-fire (2015)				
DOM Parameter		Water Intal	Water Intake		ike Reference		Δ	Water Intake	Reference		Δ	
		Value	n	Va	lue	n	(intake - reference)	Value			(intake - reference)	
SUVA254	Mean	2.7		3.3	3.3		+0.01	3.2	3.3		-0.08	
(L/mg <sub>C</sub> -m)	Median	2.9	22	3.4	3.4	12	-0.02	3.3	3.3	9	-0.08	
	Stdev	0.5		0.7	0.8		0.21	0.4	0.4		0.12	
TTHM	Mean	46.5		52.4	56.6		-4.3	57.7	51.6		+1.1	
Yield (ug/mgc)	Median	47.1	6	50.1	56.4	12	-5.7	55.3	57.4	9	-0.9	
(µg/mgc)	Stdev	17.3		15.5	15.8		5	12.5	14.4		11.1	
HAA5 Yield	Mean	26.7		50	53.7		-3.7	58.6	69.6		-16.4	
(µg/mg <sub>C</sub> )	Median	20.3	6	52.2	54.2	12	-1.1	51.3	58.5	9	-7.5	
	Stdev	14.3		17.2	18.4		8.0	15.0	33.7		22.2	
HAN4 Yield	Mean			1.7	1.6		+0.12	1.33	1.36		+0.06	
(µg/mg <sub>C</sub> )	Median	NA		1.7	1.5	12	+0.09	1.37	1.32	9	-0.04	
	Stdev			0.32	0.2		0.21	0.28	0.29		0.20	
Chloropicrin	Mean			1.1	1.2		-0.09	1.04	1.02		+0.01	
Yield	Median	NA		1.1	1.1	12	-0.09	1.00	1.00	9	-0.01	
(µg/mg <sub>C</sub> )	Stdev			0.32	0.42		0.23	0.16	0.22		0.19	

Pre- and post-fire DOM properties for the CLP River are shown. The water intake is located downstream of the burned area and the reference site is located upstream and outside of the burned area.

Table 2.2

*Source:* Hohner et al. 2016. Reprinted from *Water Research*, vol. 105, Drinking Water Treatment Response Following a Colorado Wildfire. Copyright 2016 with permission from Elsevier.

Following the High Park wildfire, the City of Fort Collins was forced to shut down the water intake along the CLP River due to high sediment loads that posed a threat to water conveyance infrastructure. Fort Collins relied solely on an alternate water supply for 100 consecutive days. Previous work conducted immediately following the wildfire showed evident post-fire effects on CLP water quality (turbidity, TP, TN, TOC) (Writer et al. 2014). Post-fire changes in source water quality were most pronounced following rainstorms in the fire-affected area of the watershed. Post-rainstorm samples not presented in Tables 2.1 and 2.2 due to the lack of samples from the reference site. Please refer to Hohner et al. 2016 for post-rainstorm results. Smaller changes in water quality were observed during baseflow and spring snowmelt conditions in 2013, and to a certain extent in 2015. However, by 2015 post-fire effects likely had been washed away. It should be noted that monitoring samples were not collected following rainstorms in 2015, which would likely have captured any erosion of remaining sediments and debris burned in the wildfire. An in-depth study of the post-fire treatability in the CLP watershed is available in previous reports and publications (Hohner et al. 2016, Hohner et al. 2017, Writer et al. 2014).

### CHAPTER 3 SAMPLING SITES FOR TREATMENT STUDIES

#### SOIL SAMPLING AND WATERSHED DESCRIPTIONS

As discussed in Chapter 1, to complete the evaluation of the potential impacts of wildfire on water quality and treatment (Chapters 4 and 5), surface soil and litter samples were collected from the participating utilities. Soil (mostly O-horizon) and litter samples were collected in the watersheds of four municipal water providers including New York City's (NYC) Kensico, Ashokan, Neversink, and Rondout watersheds; San Francisco's (CA) Hetch-Hetchy Reservoir, East Bay Watershed and San Antonio Reservoir; Denver's (CO) Gross Reservoir and Westminster's (CO) Clear Creek watershed. For each watershed or reservoir, a series of sampling locations were selected in consultation with the utilities. Specific locations were sampled using a 0.5 by 0.5 m plot to generate sufficient material for a composite sample for each site. Soil and litter samples from the plot were collected using a clean trowel or large shovel. Large rocks and nonsoil materials were removed from the samples in the field. Litter was defined as material that still retains the shape of its precursor material, e.g., pine needles, partially decayed leaves, and sticks. Surface soil was defined as the top 5-cm below the litter. The samples were transported back to the laboratory in gallon sized plastic freezer bags or large trash bags (unscented plain plastic, double bagged). For samples that required shipping, the collected materials were dried first at room temperature for two days prior to transport to the laboratory. Additional methods are described as appropriate in the following chapters.

Denver Water (DW) provides drinking water to 1.4 million consumers in the metropolitan area, relying heavily on high quality water from forested watersheds. The Buffalo Creek fire (1996) and Hayman fire (2002) burned areas which provide water for the region, significantly impacting the sediment load to Denver Water supply reservoirs. Gross Reservoir is part of Denver's water system, located at an elevation of 2202 m in Roosevelt National Forest, northwest of Denver, Colorado. Three soil/litter sites surrounding Gross Reservoir were included in the study. The drainage area is primarily composed of granite bedrock with deposition of some metals, which generated historical mining activity (Murphy 2006). The watershed is a mountainous forested area, consisting of ponderosa and lodgepole pines and mixed confiners, and has been significantly affected by the mountain pine beetle infestation since the late 1990s. South Boulder Creek serves as a channel for transferring water from the western slope of the continental divide to Gross Reservoir, and the City of Denver water treatment facility.

The City of Westminster (WM) relies on the Clear Creek watershed for its water supply. Clear Creek eventually drains to Stanley Lake which provides drinking water to over 250,000 consumers. The Clear Creek headwaters begin near the continental divide, west of Denver, and ultimately meet the South Platte River near Golden, CO. Three soil/litter sampling sites along the upper basin of Clear Creek were sampled for this study. The sites were selected from a wildfire hazard ranking assessment of areas in the watershed (JW Associates 2013). The Clear Creek watershed is steep and mountainous, also located in Colorado's Roosevelt National forest. The geology is made up of crystalline rocks, including granite and gneiss, with quartz and pyrite minerals, among others, and the clay content of soils is 12% (Butler et al. 2009).

The New York City (NYC) water system encompasses 5180 km<sup>2</sup>, contains nineteen reservoirs and three controlled lakes, and supplies potable water to half the population of New York State. The West-of-Hudson (WOH) portion of the NYC system is located in the Catskill

Mountains ~160 km northwest of NYC, west of the Hudson River. Three watersheds in the WOH System were included in this study: Ashokan (NYC-EA), Neversink (NYC-NN), and Rondout (NYC-RR). A fourth sample site, Kensico (NYC-KEN), is part of NYC's East-of-Hudson (EOH) District, located east of the Hudson River ~ 24 kilometers due north of NYC. The Kensico watershed is very small (25.5 km<sup>2</sup>) compared to the WOH watersheds (227.2-1329 km<sup>2</sup>) and the terrain much less mountainous. From each of the studied watersheds five soil/litter samples were collected and composited to provide good representation of each watershed and sufficient material for testing. The geology of the WOH region is characterized by sedimentary bedrock of sandstone and shale, of which  $\sim 30\%$  is exposed, while glacial till (60%) and alluvial deposition (10%) make up the remaining surface geology (Mehaffey et al. 2005). In the EOH region, surficial geology is mostly glacial till interspersed with kame deposits. Bedrock is mostly made up of metamorphic gneiss and schist which contain abundant marble formations resulting in soils with higher carbonate content than the WOH soils. Annual precipitation for the NYC water system region ranges from 500-1650 mm, with most rainfall occurring in spring and fall (Mehaffey et al. 2005). All watersheds in the NYC water system are predominantly deciduous although conifers are more prevalent at the higher elevations of the WOH watersheds. Tree species include northern hardwood trees such as maple, oak and birch, and conifers such as white pine and hemlock.

The City of San Francisco (SF) and the greater surrounding Bay Area relies on the Hetch Hetchy (HH) watershed located in Yosemite National Park for its primary source of drinking water. The snowmelt from the Sierra Nevada Mountains supplies water to the Tuolumne River which then drains to Hetch Hetchy Reservoir. The Hetch Hetchy water system is supported by the Alameda and Peninsula watersheds, which provide approximately 15% of water supplies to SF. Together, the SF water system supplies water to 2.6 million customers. Soil samples were collected from three sites within the SF water system: near Hetch Hetchy Reservoir, San Antonio Reservoir located within the Alameda watershed in the East Bay, and San Andreas Reservoir located within the Peninsula watershed in the West Bay. Litter samples were not collected for the SF watersheds. The area surrounding Hetch Hetchy Reservoir was burned in the Rim Fire of 2013, and the HH soil sample was collected in 2015 from the burned area.

### CHAPTER 4 EXAMINATION OF CARBON, NUTRIENT, AND METAL RELEASES FROM LABORATORY HEATED FOREST SOILS AND LITTERS

#### **OVERVIEW**

The objective of this portion of the project was to investigate the role of heating on the release of DOM, nutrients, and metals from soil and litter into aqueous solution. DOM from the soil and litter samples was measured and these data were analyzed for trends that could help predict DOM release. In a set of sub-experiments designed to evaluate release of dissolved constituents subject to heating, we used samples collected from two watersheds that broadly represent the coniferous forests of the West, and deciduous forests of the East: (1) Kensico watershed in New York City's watershed and (2) Clear Creek watershed in Colorado (referred to as deciduous and coniferous sites, respectively, in results). The soils were characterized for organic matter content, major element composition, and mineralogy. The soil and litter fractions collected from each site were leached independently to examine the source of DOM released. Each of the materials (soil and litter) from the two sites were heated at temperatures of a) 225°C and b) 350°C for two hours. The heated leachates were compared to leachates from unheated material to evaluate the role of heating on the release of dissolved constituents. The authors recognize that the results may not be universally representative of conditions observed in the specific watersheds, but were used as an indication of expected effects.

The analysis of the aqueous release of carbon from the soil and litter was important for understanding the leachates used for the treatment tests (see Chapter 5). The parent terrestrial materials vary such that the organic matter leached into solution was predicted to be different. The litter material is freshly deposited and only minimally decomposed, while soils contain extensively degraded organic matter that can interact with mineral and organic surfaces. These differences were predicted to result in very different responses to heating and leaching.

The temperatures used are in the range that promote browning, but do not cause major mass losses. For example, exposure of conifer litter (pine and fir needles) to 225°C did not produce ash, instead the needles were lightly charred and retained their original structure. At the 350°C, the litter material was degraded such that about 50% of the material lost its initial form and structure, which was observed by the production of dark ash in the samples. In addition to DOM, the aqueous releases of nitrate, iron, and manganese were evaluated to assess the relative effects of heating on commonly measured constituents of interest for water quality.

Lastly, an experiment was conducted to evaluate the effects of solution pH on leaching by examining release of DOM under acidic and basic conditions. We predicted that pH would likely alter the release of DOM as higher pH promotes the release of soil organic matter (SOM) molecules. The effects of pH on the release of DOM from heated and unheated soils were evaluated on a subset of soils only, but provides insight into the character of DOM released. It was hypothesized that heating would alter the size and reactivity of the molecules. Specifically, at low temperature heating (225°C) molecules will be smaller and partially oxidized and high temps (350°C) molecules will be increasingly condensed and less soluble. Size exclusion chromatography was used to evaluate the role of heating on molecular size, an important characteristic for treatment and DOM reactivity.

#### PROCEDURE

#### **Sample Processing**

To generate composite samples, soils from each location were mixed by equal mass and litters were mixed by equal mass, resulting in a composite soil sample and a composite litter sample for each site. In total, approximately 115 individual samples were processed. These were condensed into 14 composite soil and 14 composite litter samples. For this analysis, seven Colorado and four New York State watershed samples were used to evaluate general leaching trends across forest types. Beyond the general analysis, one Colorado site and one New York site were chosen randomly to be investigated in greater details for comparison between coniferous and deciduous forest types and soil characteristics. Soil samples were collected by water utilities and/or by the University of Colorado team and transported or shipped to the University. Once received, soil samples were sifted through 6.25 mm mesh to remove rock and large forest material, then sifted through a #20 sieve. For soils, material that passed the fine sieve was retained for experiments. For litter, the material retained by the fine sieve was used for experiments. The sieved soils were dried at room temperature while being frequently stirred and weighed to determine moisture loss in ambient air.

Heating of soil and litter was carried out in muffle furnace where materials were spread in the bottom of foil boats (or crucibles) to produce evenly distributed heating. Soils were heated for 2 hours at 225°C, a temperature that produces light charring and some structural changes in organic matter. In this section, a subset of samples was also heated at 350°C to examine the role of increased temperature on soil and litter leachates.

#### Soil and Litter Characterization

Soil and litter samples collected form the deciduous and coniferous sites were characterized for organic content by performing loss on ignition measurements. Each material was weighed in a pre-tared crucible and then heated at 550°C for 4 h. Following cooling in a desiccator, the material was again weighed. The mass difference represents the organic matter that is lost to thermal oxidation and represents the organic matter content of the material (Dean 1974). Soil elemental analysis (Fe, Al, Si, Mn, Na, K, Mg, Ca) was determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) after perchloric acid digestion following the methods of Farrell et al. (1980). Soil minerology was determined by quantitative XRD. Samples were prepared for XRD using a method based on Eberl (2003). Samples were analyzed using a Siemens D500 X-ray diffractometer from 5 to 65 degrees two theta using Cu Ka X-ray radiation, with a step size of 0.02 degrees and a dwell time of 2 seconds per step. Quantitative mineralogy was calculated using the USGS software, RockJock (Eberl 2003). Molecular size distribution in solution was determined using size exclusion chromatography (SEC) with a high-liquid chromatograph (HPLC) equipped with a protein-pak column (Waters) and UV detector (280 nm) and calibrated using polystyrene sulfonate standards (PSS, 210, 1000, 4300, 6800, and 17000 Da). A 5 mM sodium sulfate and phosphate buffer solution (pH 6.8) was used as the mobile phase at a flow rate of 0.7 mL/minute. Values are reported as weight averaged molecular weight estimates relative to the PSS standards.

#### **Leaching Procedure and Analysis**

Leaching experiments were conducted using the soil and litter collected from each site to assess DOM release. Leaching experiments were conducted on soil and litter independently and also soil and litter mixtures. Leaching tests were performed by adding 1.25 g soil or litter to 100 mL of high purity (18.2 M $\Omega$ ) laboratory water. Soil to water ratios were varied to evaluate concentration effects on the release of DOM; none were detected. Solids were allowed to equilibrate for 24 h and were then filtered through 0.7  $\mu$ m Whatman glass fiber filters. A small subset of samples was filtered with 0.2  $\mu$ m polyethersulfone (Supor®, Pall Life Science) membranes for a comparison of organic matter size fractions during the experiments evaluating solution pH on DOM release. The filtered samples were transferred to amber glass vials (40 mL, I-chem<sup>TM</sup>, Fisher Scientific, USA) and refrigerated prior to analysis.

Leachates were characterized by UV absorbance and DOC measurements. UV<sub>254</sub> was measured using a UV-Vis spectrophotometer (Cary 100, Agilent Technologies) and a 1 cm quartz cuvette. A Siever's 5310 C analyzer (GE Analytical Instruments) was used for DOC measurements. Solution pH was measured using a pH electrode that was calibrated daily using buffers of pH 4, 7, and 10. Samples for metal and ion analyses were stored in low-density polyethylene bottles. Nitrate was quantified by ion chromatography (IC; Dionex IonPac® AS14A column). Total iron and manganese concentrations were determined for filtered samples following acidification using ICP-OES. Select samples filtered through 0.2  $\mu$ m membranes were characterized for size distribution using size exclusion chromatography.

#### **RESULTS AND DISCUSSION**

Figure 4.1 presents the DOC release per mass of soil for the two types of sites evaluated. Soils varied markedly in organic content. The soils had a mean organic content of  $13 \pm 9.0\%$  and litter contain a mean organic content of  $79 \pm 11.8\%$ . The release of DOC per unit soil was similar for both coniferous and deciduous sites (approximately 0.015-0.02 mg DOC per g of soil). In the case of the coniferous soil, this increased after heating whereas for deciduous materials there was a slight decrease.

The difference in DOM release behavior between the coniferous and deciduous sites may be related to the difference in the SOM content of the soils; the deciduous materials had a higher SOM content. There was no discernable trend between the litter organic matter (OM) content and the release of DOM (data not shown). It is assumed that non-degraded organic structures, such as pine needles or leaves, will release DOM from the surface of the material only and therefore much of the organic mass measured is part of the physical structure and unlikely to result in massdependent leaching. Conversely, soils have much greater surface area per unit mass and less of the organic material is associated with the physical structure of needles and leaves.

There was no discernable relationship between initial organic content of soil and release of DOM after heating. In general, the heated coniferous soils (collected from Colorado) released more organic carbon into solution compared to the respective unheated samples (Figure 4.1). Release of DOM from soils following heating was not consistent across the sites. The deciduous soils (collected from New York City) generally behaved opposite of the coniferous site, releasing less DOM into solution following heating. Whereas, litter from both sites behaved similarly by releasing considerably less DOM following heating. One possible explanation for the lower release of DOM after heating an alteration in the oxygen functionality content of the SOM molecules. It has been shown that organic matter begins to lose carboxylic acids and oxygen functionality

around 225°C (Knicker 2007). The results here indicate that deciduous sites generally contained greater organic material, so it is possible that soil release followed the organic-organic interactions similar to litter materials, while the low organic content coniferous soil DOM release was controlled by organic-mineral interactions. Current literature lacks an explanation for this observation, and further research is recommended.



Release from heated material is plotted against the organic content of the unheated material. The coniferous site is from Colorado (Clear Creek Watershed) and the deciduous site from New York City (Kensico).

## Figure 4.1 Dissolved organic matter (measured as DOC) released per gram of material as a function of soil and litter organic content

#### **Optical Properties of Soil and Litter Leachate**

In addition to quantifying DOM release, the UV absorbance at 254 nm was measured on leachates to optically characterize the DOM (Figure 4.2). Note that regression lines were not added for clarity. In general, there was a relationship between the amount of carbon in solution and the UV absorbance; greater DOM release resulted in greater absorbance by the solution. The absorbance at 254 nm is often normalized to the carbon content of the solution to obtain a SUVA<sub>254</sub> value, which is an indication of the aromatic content of the DOM (Weishaar et al. 2003). Using absorbance data from soil leachates has resulted in unreliable data in previous studies (Gabor et

al. 2015) yielding SUVA<sub>254</sub> greater than values commonly observed for DOM (i.e., 5.0 L/mg-m). Similarly, in this study SUVA<sub>254</sub> for several heated leachates was higher than typical values. The general absorbance trends suggest the DOM became more aromatic with heating, which is consistent with the visual indications of darkening of the materials. Average unheated soil leachate SUVA<sub>254</sub> was 3.4 L/mg-m and average SUVA<sub>254</sub> of the unheated litter leachates was 2.8 L/mg-m. Following heating the average SUVA<sub>254</sub> values increased to 4.7 L/mg-m for both soil and litter leachates. The relatively low DOC concentrations measured in soil leachates appeared to lead to elevated (>5 L/mg-m) SUVA<sub>254</sub> values, and it is likely the increasing colloid-to-DOC ratio causes the overestimation. The increase in aromatic content of DOM with heating is consistent with previous studies showing heating of biomass causes breakdown of woody material and produces carbon gases that mix with O<sub>2</sub> and cause combustion; if the heating stops prior to combustion the material is charred (charcoal; Scott 2010). Charring results in loss of O-alkyl and di-O-alkyl structures that dominate woody materials and an increase in aromatics (Certini 2005, Gonzalez-Perez et al. 2004), which supports the observed results.



The coniferous site is from Colorado (Clear Creek Watershed) and the deciduous site from New York City (Kensico).



#### In-depth Analysis of a Coniferous and Deciduous Site

In this section, an investigation of two sites broadly representing the deciduous and coniferous types were evaluated for differences in leachate characteristics. The parent soil material was considered due to the possibility of DOM-mineral interactions causing leaching characteristics beyond changes attributable to solely forest types or thermal alterations. The major elemental composition of the soils and litter from the coniferous and deciduous sites are presented in Table 4.1. The elemental composition and clay content did not differ greatly between the two sites examined, as shown in Table 4.2. The results did not provide evidence to explain difference in DOM release behavior between the two soils. It has been demonstrated previously that DOM export from terrestrial environments is governed by interactions between DOM and soil material, primarily mineral surfaces (Sollins et al. 1996, Kaiser and Guggenberger 2003, Feng et al. 2005).

The extent of DOM sorption depends on the character of soil and DOM, as well as solution chemistry (Tipping 1981, Feng et al. 2005, Gabor et al. 2015). The sorption of DOM is primarily due to carboxyl and hydroxyl functional groups of DOM interacting with oxide surfaces in the mineral soil, specifically under acidic or slightly acidic conditions (Gu et al. 1994, Feng et al. 2005). In this study, the influence of soil clay content on DOM release following heating was not clear, and requires further exploration.

Table 4.1

Major constituents of coniferous and deciduous soils and litters													
	OM	Si	Al	Fe	Ca	Mg	Na	Κ	Ti	Mn	Р		
						%							
Coniferous Soil	5.6	28.2	7.4	6.4	2.6	2.2	2.4	1.5	0.5	0.1	0.1		
Coniferous Litter	87.4	4.3	1.1	1.0	1.5	0.3	0.4	0.3	0.1	0.1	0.1		
Deciduous Soil	9.5	29.4	6.4	3.9	1.3	0.9	1.4	1.3	0.4	0.1	0.1		
Deciduous Litter	75	3.9	0.7	0.3	1.3	0.2	0.2	0.3	0.0	0.1	0.1		

Table Mineralogy of coniferou	4.2 is and deciduo	us soils
<u> </u>	Coniferous Soil	Deciduous Soil
Mineral	Weight %	Weight %
NON-CLAYS		
Quartz	15.7	40.2
Kspar (intermediate microcline)	7.0	6.8
Kspar (anorthoclase)	6.0	10.9
Plagioclase (albite, var. cleavelandite)	8.3	3.8
Plagioclase (oligoclase; Norway)	13.1	14.0
Plagioclase (anorthite)	5.6	1.5
Amphibole (ferrotschermakite)	2.5	0.0
Amphibole (actinolite)	30.4	10.3
Total non-clays	88.6	87.6
CLAYS		
Kaolinite (disordered)	5.0	6.8
Illite (1M; RM30)	6.4	5.6
Total clays	11.4	12.4

#### Nutrient and Metal Release into Solution

Analysis of unheated and heated deciduous and coniferous soil and litter leachates (unheated, 225°C, 350°C; 12 leachates total) revealed a wide range of anions and metals in solution (Table 4.3). Sulfate showed the strongest dependence on heating and sulfate concentrations were found to increase markedly with heating. The litter showed a different response, and after heating at 350°C, litter from both the deciduous and conifer forest types released nearly 10 times the

amount of sulfate in comparison to the respective unheated litters. The release of sulfate from the forest material is likely a result of organic sulfur oxidation as nearly all sulfur exists in organic form in forest soils (Solomon et al. 2003). Phosphate release from the materials was not as consistent as sulfate. For instance, phosphate release from the coniferous soil was similar to sulfate release, but phosphate release from coniferous litter differed. The release of phosphate from coniferous litter increased following heating at 225°C, but decreased markedly in the litter exposed to 350°C. The leaching response of both litters was similar: phosphate release increased following heating at 225°C with respect to unheated samples, but samples heated at 350°C showed lower phosphate release than either the unheated or 225°C heated litters. Phosphate release could be a result of organic phosphorous oxidation, similar to sulfate. Nitrate release generally decreased following heating. There was one exception to this pattern; deciduous litter released a greater amount of nitrate into solution following heating. It is not clear what caused the general decreases of nitrate following heating. Nitrogen is a common component of organic matter and is likely oxidized when exposed to heating.

The concentration of iron and manganese, measured as total Fe and total Mn, showed similar trends and both metals tended to follow the general trends observed for DOM release (Table 4.3). Heating increased the release of iron and manganese from soils, but only caused minimal release from litter. Further, when heated at 350°C, there was no measurable release of iron and greatly diminished release of manganese. It is unclear exactly what drives this behavior, while the close parallel with DOM release suggest the thermal changes that influence carbon release may be closely tied to metal release.

		NO <sub>3</sub> -	PO4 <sup>3-</sup>	<b>SO</b> <sub>4</sub> <sup>2-</sup>	Mn	Fe
			ppm		pp	ob
<b>Coniferous Soil</b>	Unheated	0.3	0.3	0.1	19	17
	225°C	0.1	0.6	0.8	180	33
	350°C	DL	0.9	3.3	9.9	DL
<b>Coniferous Litter</b>	Unheated	0.2	2.4	0.4	92	23
	225°C	0.1	5.0	9.3	120	19
	350°C	0.1	0.9	30	DL	DL
<b>Deciduous Soil</b>	Unheated	0.3	0.3	0.2	22	31
	225°C	DL	DL	1.8	960	220
	350°C	DL	DL	3.6	440	DL
<b>Deciduous</b> Litter	Unheated	0.2	2.3	0.1	270	22
	225°C	DL	2.5	7.1	830	24
	350°C	0.5	1.4	25	5.9	DL
Duplicates						
<b>Coniferous Soil</b>	Unheated	0.5	0.3	0.2	15	21
<b>Coniferous</b> Litter	350°C	0.1	0.8	30		
<b>Deciduous</b> Litter	350°C	0.5	0.3	20	4.9	DL

Table 4.3Release of anions and total iron and manganese from unheated and heated materials. DLindicates below detection limit

#### Effects of pH on Heated and Unheated Soil DOM Release

To examine the influence of pH on DOM release, we leached the coniferous soils at multiple pH levels. Leaching of the coniferous soils revealed that the pH of solution, at the extremes of pH 3 and pH 11, will alter the release, but does not explain the trends of DOM release following heating (Figure 4.3). Note that in Figure 4.3 two filter sizes were used, 0.2 and 0.7 um. The amount of DOM released from unheated soil nearly doubled when leached in a basic solution compared to an acidic solution. The release of DOM from soil heated at 225°C was less sensitive to the change in pH compared to the unheated soil. Wildfires can cause changes in soil solution chemistry, including pH shifts, which can influence DOM mobilization (Molina et al. 2007, Quill et al. 2010, Periera et al. 2012). Increases in pH have been correlated with increasing burn severity due to organic acid denaturation and formation of K and Na oxides, hydroxides, and carbonates (Vega et al. 2013, Revchuck and Suffet 2014, Bodi et al. 2014). The increase in acid extractable DOM following heating and the decrease in sensitivity to base extraction following heating suggests that the molecules available for release into solution tend to be more soluble and smaller. These types of organic acids are referred to as fulvic acids, and are not removed from solution during acidification. From these experiments, it appears the majority of extractable OM is less sensitive to low pH and not greatly increased by basic extraction.

Leachates from the pH experiments were evaluated with size exclusion chromatography (SEC) (Table 4.4), which revealed that heating decreased the average molecular weight (MW) of the released DOM. These results are in agreement with the pH release data and together they provide evidence that heating results in smaller and increasingly homogenous DOM structures. The SEC results also support the results of the pH experiments; the smaller molecules are likely to be increasingly soluble. The effects of base extraction would tend to favor mobilization of larger molecules.



Acidic samples were leached at pH 3 and basic samples were leached at pH 11. Experiments were conducted for the coniferous soil, in triplicate. Bars represent mean concentrations and error bars represent the standard deviation.

#### Figure 4.3 DOC release for different pH conditions

Table 4.4
Size exclusion chromatography results of dissolved organic matter released from
coniferous soil at pH 3 and pH 11. Samples were filtered at 0.2 microns.

	Temperature	MW
рН	°C	(Da)
3		2087
3	225	1633
3	350	1434
11		2521
11	225	1889
11	350	1528

#### SUMMARY

The findings of this chapter demonstrate that soil and litter release different quantities and qualities of dissolved constituents following heating. Litter released more carbon compared to soils, and the effect of heating on soils varied. Experiments examining the effects of pH suggest a loss of acid-base functionality during heating that decreased pH effects on DOC release. In additional to decreases in acid-base functional group content, heating produced smaller, more homogenous molecules. The loss of oxygen containing functional groups, particularly carboxylic acids, may explain the decrease in DOM release from heated litter and organic rich materials, while the same loss of oxygen containing functional groups could explain the greater release of DOM from mineral-dominated soils. The loss of carboxylic acid functionality is also supported by the trends in pH dependent release from soil, where loss of acidic functional groups would make the release of DOM less pH dependent.

The release of anions and metals was altered following heating. Anion release into solution showed strong heating dependence, but was not consistent for the measured species. Sulfate demonstrated the most consistent behavior of the anions, increasing with increased heating for all materials. Specifically, the litter released nearly ten times more sulfate than the soils following heating. Nitrate generally decreased following heating for soils and litter. Phosphate release was not consistent for the soils, but phosphate release from litter increased after heating at 225°C and decreased, with respect to the release from unheated material, after heating at 350°C. The metals, iron, and manganese, had similar release of either metal was measured following heating at 350°C.

#### CHAPTER 5 TREATMENT PROCESS PERFORMANCE EVALUATION OF LABORATORY LEACHATES

#### **INTRODUCTION**

To isolate the fundamental effects of heating during wildfire on drinking water treatment, surface soil and litter samples were heated in a furnace and leached in the laboratory. The majority of literature studying laboratory-based heat alterations to forest material is focused in the biogeochemical community, while the impact on water treatment has yet to be fully explored (Wang et al. 2015a). Water providers are concerned about the effects of increased DOM, potentially of altered character, following wildfire. The objective of this work was to address the removal efficacy of heat-altered DOM by conventional treatment and additional processes. The raw and finished water DBP levels were also evaluated. Unheated (control) and heated leachates were coagulated and characterized for water quality, optical properties, TTHM, HAA5, haloacetonitrile (HAN4), and chloropicrin formation before and after treatment.

A laboratory-based approach was used to investigate the effects of forest floor heating during wildfire on drinking water treatment and finished water quality for utilities. Surface soil and litter samples from four watersheds (Denver, New York, Westminster, and San Francisco; described in Chapter 3) were heated in a furnace at 225°C and leached to evaluate changes to water-soluble compounds, and the subsequent treatment process implications. Pairwise data analysis was used to understand the changes in water quality likely associated with heating. Paired differences ( $\Delta$ ) between the heated and control samples (heated – control) were calculated for each site, and the respective parameter analyzed.

#### **LEACHING METHODS**

The soil and litter samples collected as described in Chapter 3 were placed in ceramic evaporating dishes or aluminum pans in a pre-heated (225 °C) muffle furnace for two hours under oxic conditions. The soil and litter samples were added to low-carbon tap (LCT) water (treated with granular activated carbon) and manually mixed. The samples were leached in the dark at room temperature to evaluate water-soluble compounds. LCT water was used to maintain a representative inorganic water quality matrix for treatment tests (DOC  $< 0.3 \text{ mgcL}^{-1}$ ; pH = 7.1; alkalinity = 50 mg CaCO<sub>3</sub>L<sup>-1</sup>; conductivity = 100  $\mu$ S). Following 24-h the leachates were passed through a 2 mm sieve, decanted, and refrigerated at 4 °C. A previous study showed after 6 hours, 75-99% of the 24-h DOC was leached into solution (Cawley et al. 2017). Soil and litter were leached together for treatment tests, representative of a mixture likely to enter a treatment facility. Soil and litter were added in equal amounts by weight, and diluted with LCT water to a DOC concentration of  $5.0 \pm 1 \text{ mgcL}^{-1}$ . San Francisco leachates contained only soil (litter samples were not collected) and were diluted to a DOC concentration of 2.5± 0.5 mgcL<sup>-1</sup>. Subsamples of the leachates were filtered through 0.45 µm polyethersulfone membrane filters (pre-rinsed) for optical property measurements and DOC analysis, and glass fiber filters (GF/F- combusted 3 h at 550°C) for chlorination experiments and DBP analyses.

#### **ANALYTICAL METHODS**

For the leachates, turbidity was measured with a HACH 2100 N turbidimeter. A Siever's 5310 C analyzer (GE Analytical Instruments) was used for DOC measurements. Analysis of total dissolved nitrogen (TDN) was performed with a TOC-V analyzer (Shimadzu Corp., Japan). Ultraviolet absorbance was measured with a 1-cm path length quartz cuvette and a Cary 100 UV-Vis spectrophotometer (Agilent Technologies). Specific ultraviolet absorption (SUVA254) was calculated by normalizing UV<sub>254</sub> absorbance by the DOC concentration and absorbance path length (Weishaar et al. 2003). Nitrate and nitrite were measured with an analytical flow solution IV spectrophotometric analyzer (OI Analytical, USA). Ammonium was analyzed with a BioTek Synergy 2 Microplate Reader. Dissolved organic nitrogen (DON) was calculated from the difference between TDN and inorganic nitrogen. For several samples the inorganic N concentration was high (> 60% of TDN), and the DON calculation may be less accurate (Lee and Westerhoff 2005). EPA Method 551.1 (1995) was followed for the analysis of total trihalomethanes (TTHMs) and haloacetonitriles (HANs). HAN4 analysis included: dichloroacetonitrile (DCAN), tri-chloroacetonitrile (TCAN), di-bromoacetonitrile (DBAN), and bromo-chloroacetonitrile (BCAN). EPA method 552.2 was used for analysis of haloacetic acids (HAAs) and reported as the five-regulated species (HAA5). An Agilent 6890 Gas Chromatography system with an electron capture detector was used.

#### **TREATMENT METHODS**

#### **Denver Water and New York City**

Jar tests were performed using a 6-jar programmable jar tester (Phipps &Bird model 7790-901) with 2-liter B-KER<sup>2</sup> jars. Aluminum sulfate (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>18H<sub>2</sub>O, Mallinckrodt Chemicals, 3208-04) was applied at doses ranging from 20-120 mgL<sup>-1</sup>. The alum doses were selected from preliminary alum dose vs. DOC response curves. Generally, point of diminishing returns (PODR) criteria were used to select the final alum dose (White et al. 1997). Mixing conditions included a rapid mix phase (1 minute at 290 rpm), two flocculation phases (10 minutes at 55 rpm and 10 minutes at 20 rpm) and a 30-minute sedimentation period. Following sedimentation, pH and turbidity were measured and filtered samples were analyzed for DOC and UV<sub>254</sub>, and chlorinated for DBP analysis.

#### Westminster

Westminster leachates were treated with ferric chloride and pH adjusted with caustic either pre- or post- mixing and settling. Mixing conditions included a rapid mix phase (1 minute at 290 rpm), flocculation (4 minutes at 50 rpm), and a 1-minute sedimentation period. Four coagulation tests were performed on each leachate (45 and 90 mg/L, pre- and post pH adjustment). Raw and treated samples were filtered and chlorinated following uniform formation conditions (UFC) (Summers et al. 1996) and analyzed for C- and N-DBPs. Treated samples were also analyzed for turbidity, DOC, and UV<sub>254</sub>.

#### **Chlorination Conditions**

DBP formation was evaluated for all samples with bench scale chlorination following uniform formation conditions (UFC), representative of a typical water treatment plant (Summers

et al. 1996). Samples were chlorinated with a buffered sodium hypochlorite dosing solution (pH 8) at 20 °C. Borate buffer was added to samples to maintain a pH of  $8.0 \pm 0.3$ , as necessary. Preliminary chlorine demand curves were used to determine doses required for a 24-hour free chlorine residual of  $1.0 \pm 0.4$  mg/L. Chlorine residuals were measured with the DPD (N,N-diethyl-p-phenylenediamine) colorimetric method (SM4500-Cl G) and quenched with ammonium chloride immediately following 24 hours.

#### **San Francisco Treatment Tests**

San Francisco leachates (soils only) were treated to simulate treatment plant operations for three facilities: East Bay (EB), West Bay (WB), and Hetch Hetchy (HH). Bench-scale treatment of Hetch Hetchy leachates included pre-chlorination (dose = 1.8 mg/L; pH = 8.0; contact time = 16 hours), coagulation (15 mg/L alum and 0.3 mg/L polymer; pH = 6.8), followed by flocculation/sedimentation/filtration. Samples were chloraminated (chlorine = 1.8 mg/L and ammonia = 0.6 mg/L; pH = 9.6) and held for 24 hours prior to quenching with sodium thiosulfate and DBP analysis. Treatment of the East Bay leachates included pre-chlorination (dose = 2.5 mg/L; contact time = 6 hours), coagulation (35 mg/L alum and 1.2 mg/L polymer; pH = 7.0), followed by flocculation/sedimentation/filtration. Samples were chlorinated (chlorine dose = 1.0 mg/L; contact time = 30 minutes) and chloraminated (chlorine dose = 1.8 mg/L and ammonia dose = 0.6 $mg_N/L$ ; pH = 8.8) and held for 24 hours prior to quenching with sodium thiosulfate and DBP analysis. Treatment of the West Bay leachates included pre-ozonation (dose = 1.5 mg/L; contact time = 10 minutes) coagulation (1.5 mg/L ferric chloride and 3.0 mg/L polymer), flocculation/sedimentation/filtration. Samples were chloraminated (chlorine dose = 2.8 mg/L and ammonia dose = 0.6 mg/L; pH = 9.0) and held for 24 hours prior to quenching with sodium thiosulfate and DBP analysis. Polymer was provided by SFPUC.

#### DENVER WATER TREATMENT PROCESS PERFORMANCE

DW control and heated samples were generated following heating and leaching, and analyzed for water quality. As shown in Table 5.1, following heating the pH and alkalinity of the leachates increased compared to the control samples (mean  $\Delta = +0.2$  and +6.6 mgCaCO<sub>3</sub>/L). Turbidity levels, inorganic nitrogen, DON, and DOC concentrations are presented, but reflect the amount of material (soil and litter) leached, rather than the effects of heating. Therefore, where appropriate, the sample results were normalized by the concentration of DOC, or the total mass of litter and soil leached. Soil and litter samples were mixed together, leached, and diluted to a DOC concentration of 5.0 ± 1.0 mgc/L for better comparison of the samples at a realistic DOC concentration. The DOC:DON ratios imply the heated leachates were enriched in organic nitrogen compared to control samples (mean  $\Delta = -20.8 \text{ mgc/mN}$ ). DOC leached per gram of solid material was lower after heating (mean  $\Delta = -1.3 \text{ mgc/g}$ ). SUVA<sub>254</sub> was consistently higher for the heated samples compared to the control leachates (mean  $\Delta = +0.6 \text{ L/mg-m}$ ).

								<u> </u>			
Denver Water	Alkalinity (mgCaCO <sub>3</sub> /L)	рН	Turbidity (ntu)	TDN (mg <sub>N</sub> /L)	NO <sub>3</sub> +NO <sub>2</sub> (mg <sub>N</sub> /L)	NH4 <sup>+</sup> (mg <sub>N</sub> /L)	DON (mg <sub>N</sub> /L)	DOC (mg <sub>C</sub> /L)	DOC Leached (mg <sub>C</sub> /g)	DOC:DON (mg <sub>C</sub> /mg <sub>N)</sub>	SUVA <sub>254</sub> (L/mg-m)
DW1 Control	39	7.6	15.2	0.24	0.105	0.042	0.09	4.8	3.6	54.4	2.7
DW1 Heated	44	7.7	9.9	0.25	0.007	0.020	0.23	5.3	1.6	23.3	3.2
DW2 Control	31	7.4	10.7	0.10	< 0.001	0.082	NA	4.9	2.1	NA	2.6
DW2 Heated	45	7.5	11.7	0.29	< 0.001	0.071	0.22	5.3	1.1	24.5	3.2
DW3 Control	50	7.5	10.8	0.28	0.069	0.014	0.20	5.7	2.8	29.2	2.6
DW3 Heated	52	7.8	19.2	0.37	< 0.001	0.079	0.29	5.5	2.0	18.8	3.5
Average $\Delta$ (heated – control)	+6.6	+0.2	+1.4	+0.10	-0.06	+0.01	+0.12	+0.2	-1.3	-20.8	+0.6
Stdev Δ	6.4	0.1	6.8	0.09	0.05	0.05	0.03	0.4	0.6	14.6	0.2

 Table 5.1

 Raw water quality for Denver Water control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from three different sites within the DW system.

Raw leachates were chlorinated and analyzed for DBP formation to address changes to DBP precursors following heating (Table 5.2). TTHM formation showed variable responses to heating, increasing for one sample and decreasing for two samples, compared to the controls (mean  $\Delta = +2.2 \ \mu g/L$ ). HAA5 formation of the heated leachates was on average lower than the control samples (mean  $\Delta = -35.3 \ \mu g/L$ ), but DW2 showed an increase in HAA5 formation following heating. HAN4 formation of the control and heated leachates was variable, both increasing and decreasing following heating (mean  $\Delta = +0.1 \ \mu g/L$ ). However, chloropicrin formation was consistently elevated following heating (mean  $\Delta = +6.9 \ \mu g/L$ ). Although samples were diluted to similar DOC concentrations, carbon normalized DBP yields allow for a better comparison of the DBP precursor reactivity of the control and heated samples (Table 5.2). Following heating, on average TTHM yields slightly decreased (mean  $\Delta = -0.7 \ \mu g/mgc$ ), while mean HAA5 yields showed a larger decrease (mean  $\Delta = -7.9 \ \mu g/mgc$ ). HAN4 yields showed varied responses for the control and heated samples, and on average showed minimal difference (mean  $\Delta = 0.0 \ \mu g/mgc$ ), whereas chloropicrin yields increased following heating (mean  $\Delta = +1.3 \ \mu g/mgc$ ).

Denver Water	Chlorine Dose (mg/L)	TTHM (μg/L)	TTHM Yield (µg/mg <sub>C)</sub>	HAA5 (µg/L)	HAA5 Yield (µg/mg <sub>C)</sub>	HAN4 (µg/L)	HAN4 Yield (µg/mg <sub>C)</sub>	Chloropicrin (µg/L)	Chloropicrin Yield (µg/mg <sub>C)</sub>
DW1 Control	5.5	181.8	37.9	234.9	48.9	4.2	0.9	4.3	0.9
DW1 Heated	5.4	149.4	28.3	197.1	37.4	6.3	1.2	11.4	2.2
DW2 Control	4.6	93.1	19.1	92.4	19.0	5.4	1.1	1.9	0.4
DW2 Heated	6.1	192.4	36.1	130.2	24.4	3.1	0.6	14.0	2.6
DW3 Control	6.8	186.3	32.7	256.0	44.9	5.9	1.0	6.5	1.1
DW3 Heated	6.0	125.9	23.0	150.0	27.4	6.6	1.2	7.9	1.4
Average ∆ (heated – control)	NA	+2.2	-0.7	-35.3	-7.9	+0.1	0.0	+6.9	+1.3
Stdev <b>A</b>	NA	85.3	15.3	71.9	11.9	2.3	0.5	5.3	1.0

Raw water DBP formation and carbon normalized DBP yields for Denver Water control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from three different sites within the DW system.

Table 5.2

The DW leachates were coagulated to address the effects of heating on conventional treatment processes. Preliminary jar tests were conducted to select the optimal alum dose for DOC removal. Distinct differences in the coagulation response for the control and heated samples were apparent (Figure 5.1). In most cases, turbidity of the heated leachates remained elevated compared to the control leachates for alum doses ranging from 20-60 mg/L. At doses greater than 60 mg/L particles commonly re-stabilized due to a decrease in pH, and turbidity increased relative to lower doses. The control leachates showed typical DOC dose responses (Figure 5.1), with considerable removal occurring at the lowest applied dose (20-30 mg/L). For the control samples the treated water DOC concentrations were generally <3.0 mg/L at doses ranging from 20-40 mg/L, and showed only marginal removal (<20%). Although the heated leachate DOC concentration continued to decrease with increasing alum dose, the DOC remained near 4.0 mg/L following treatment with 80–120 mg/L alum. The raw water UV<sub>254</sub> absorbance of the heated samples was initially higher than the control leachates, despite having similar DOC concentrations. As such, the UV<sub>254</sub> of the heated samples remained higher than the control leachates, despite having similar DOC concentrations.



DOC<sub>0</sub> = initial DOC concentration. Figure 5.1 Alum dose-response for Denver Water control and heated leachates

Following preliminary jar tests, leachates were coagulated at a final dose, filtered, and chlorinated to characterize the DBP levels likely to enter a distribution system. The required alum dose was on average 13.3 mg/L higher for the heated leachates compared to the control samples (Table 5.3). Even at a higher alum dose, the settled water turbidity levels were on average 1.3 ntu greater for heated samples, and treated water DOC concentrations remained higher compared to the control leachates (mean  $\Delta = 2.1 \text{ mgc/L}$ ). Treated water heated samples showed higher SUVA<sub>254</sub> values, indicating considerable aromatic material still remained compared to control leachates (mean  $\Delta = +1.1 \text{ L/mgc-m}$ ). The poor DOC removal for the heated samples resulted in elevated TTHM, HAA5, and chloropicrin levels compared to the control samples, following coagulation treatment. HAN4 formation was similar for the control and heated samples following treatment. As expected from the poor treatability of the heated leachates, the percent decrease for all parameters was lower following conventional treatment. For the heated leachates the percent decrease of DOC (mean  $\Delta = -13\%$ ), SUVA<sub>254</sub> (mean  $\Delta = -7\%$ ), C-DBPs (TTHM mean  $\Delta = -18\%$ ; HAA5 mean  $\Delta = -22\%$ ), and N-DBPs (HAN mean  $\Delta = -9\%$ ; chloropicrin mean  $\Delta = -16\%$ ) were lower than the control samples (Table 5.4).

The lower DOC removal, and consequently poor removal of DBP precursors for the heated samples impacted the finished water DBP concentrations likely to enter a distribution system. As demonstrated in Figure 5.2, treated water DOC concentrations of the heated DW samples ranged from 3.9-4.5 mgc/L, whereas the control leachate DOC levels were consistently below 2.5 mgc/L. Accordingly, following treatment all heated leachates exceeded both TTHM and HAA5 maximum contaminant levels (MCLs), 80 and 60  $\mu$ g/L, respectively, whereas all control samples were below MCLs. Chloropicrin concentrations of the heated samples (6.6-10.4  $\mu$ g/L) were also higher than finished water control leachates (1.1-2.0  $\mu$ g/L). Alternatively, following treatment, HAN4 concentrations were on average lower for the heated samples (mean  $\Delta = -1.1 \mu$ g/L).

Denver Water	Alum Dose (mg/L)	Treated Turbidity (ntu)	Treated pH	Treated DOC (mg <sub>C</sub> /L)	Treated SUVA <sub>254</sub> (L/mg <sub>C</sub> -m)	Treated TTHM (μg/L)	Treated HAA5 (μg/L)	Treated HAN4 (μg/L)	Treated Chloropicrin (µg/L)
DW1 Control	40	0.3	6.5	1.6	1.7	35.6	27.4	4.1	1.1
DW1 Heated	45	1.3	6.6	4.1	2.8	107.2	82.2	3.6	8.1
DW2 Control	30	0.1	7.1	2.1	1.4	37.8	30.0	4.7	1.3
DW2 Heated	45	1.7	6.6	3.9	2.6	112.4	94.5	3.6	10.4
DW3 Control	30	0.1	7.0	2.4	1.8	48.7	41.0	8.3	2.0
DW3 Heated	50	1.4	6.8	4.5	2.9	100.9	110.0	6.4	6.6
Average ∆ (heated – control)	+13.3	+1.3	-0.2	+2.1	+1.1	+66.1	+62.7	-1.1	+6.9
Stdev ∆ (heated – control)	7.6	0.3	0.3	0.4	0.0	12.2	7.3	0.7	2.3

Treated water quality and DBP formation for Denver Water control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from three different sites within the DW system.

Table 5.3

Denver Water	% Decrease Turbidity	% Decrease DOC	% Decrease SUVA <sub>254</sub>	% Decrease TTHM	% Decrease HAA5	%Decrease HAN4	% Decrease Chloropicrin
DW1 Control	98	67	38	80	88	3	74
DW1 Heated	87	22	12	28	58	42	29
DW2 Control	99	56	45	59	68	14	31
DW2 Heated	89	27	18	26	24	-24	26
DW3 Control	99	57	32	74	84	-39	68
DW3 Heated	93	18	18	20	27	3	16
Average $\Delta$ (heated – control)	-3	-13	-7	-18	-22	-9	-16
Stdev $\Delta$ (heated – control)	5	42	35	30	34	22	28

 Table 5.4

 Percent removal following conventional treatment for Denver Water control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from three different sites within the DW system.



Figure 5.2 Treated water DOC and DBP formation for Denver Water control and heated samples

#### NEW YORK CITY TREATMENT PROCESS PERFORMANCE

NYC control and heated samples were generated following the heating and leaching methods presented above, and analyzed for water quality. As shown in Table 5.5, following heating the pH and alkalinity increased compared to the control samples (mean  $\Delta = +0.2$  and +18.1 mgCaCO<sub>3</sub>/L). Turbidity levels, inorganic nitrogen, DON, and DOC concentrations are presented, but reflect the amount of material (soil and litter) leached, rather than isolating the effects of heating. Therefore, where appropriate, the sample results were normalized by the concentration of DOC, or the total mass of litter and soil leached. Soil and litter samples were mixed together, leached, and diluted to a DOC concentration of 5.0 ± 1.0 mgc/L for better comparison of the samples at a realistic DOC concentration. The DOC:DON ratios imply the heated leachates were enriched in organic nitrogen compared to control samples (mean  $\Delta = -4.9 \text{ mgc/m}$ ). DOC leached per gram of solid material was lower after heating (mean  $\Delta = -2.2 \text{ mgc/g}$ ). SUVA<sub>254</sub> was consistently higher for the heated samples compared to the control leachates (mean  $\Delta = +1.2 \text{ L/mg-m}$ ).
New York City	Alkalinity (mgCaCO <sub>3</sub> /L)	рН	Turbidity (ntu)	TDN (mg <sub>N</sub> /L)	NO <sub>3</sub> +NO <sub>2</sub> (mg <sub>N</sub> /L)	NH4 <sup>+</sup> (mg <sub>N</sub> /L)	DON (mg <sub>N</sub> /L)	DOC (mg <sub>C</sub> /L)	DOC Leached (mg <sub>C</sub> /g)	DOC:DON (mg <sub>C</sub> /mg <sub>N)</sub>	SUVA <sub>254</sub> (L/mg <sub>C</sub> -m)
NYC-EA Control	41	7.3	8.2	0.59	0.036	0.377	0.18	4.6	3.8	26.2	2.6
NYC-EA Heated	69	7.8	18.7	0.52	0.009	0.289	0.23	5.1	1.2	22.7	3.6
NYC-NN Control	35	7.4	5.7	1.13	0.068	0.877	0.19	5.8	3.4	30.9	3.4
NYC-NN Heated	56	7.6	33.9	0.63	0.009	0.282	0.34	4.3	0.7	12.9	5.0
NYC-RR Control	45	7.6	5.3	0.58	0.037	0.371	0.17	4.3	4.2	24.8	3.1
NYC-RR Heated	60	7.6	33.7	0.66	0.013	0.304	0.34	4.1	0.8	12.1	5.4
NYC-KEN Control	40	7.3	7.4	0.46	0.067	0.141	0.25	5.5	3.0	21.9	3.3
NYC-KEN Heated	48	7.4	6.9	0.24	0.003	0.087	0.15	5.4	3.1	36.4	3.2
Average ∆ (heated – control)	+18.1	+0.2	+16.7	-0.18	-0.04	-0.20	+0.07	-0.3	-2.2	-4.9	+1.2
Stdev $\Delta$ (heated – control)	8.6	0.2	14.2	0.25	0.02	0.26	0.13	0.8	1.5	14.3	1.0

 Table 5.5

 Raw water quality for New York City control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the NYC system.

NYC raw water leachates were chlorinated and analyzed for DBP formation to address changes to DBP precursors following heating (Table 5.6). As stated in the methods section, chlorine residuals were 1 mg/L ( $\pm$  0.4). Following heating, TTHM and HAA5 formation were on average considerably lower compared to the control samples for three of the sites (TTHM mean  $\Delta$ = -72.2  $\mu$ g/L; HAA5 mean  $\Delta$  = -40.9  $\mu$ g/L). However, for NYC-EA the TTHM formation was higher for the heated leachate compared to the control sample (TTHM  $\Delta = +29.3 \ \mu g/L$ ). For HAA5s NYC-RR showed higher formation in the heated sample (HAA5  $\Delta$  = +18.1µg/L), whereas the other three heated samples showed lower HAA5s compared to respective controls. HAN4 formation of the heated leachates was also generally lower (mean  $\Delta = -1.0 \ \mu g/L$ ), with one exception (NYC-RR  $\Delta = +1.8 \mu g/L$ ). The different trends may be explained by the variability of the litter material that was leached in solution and may contain substantially different precursor material between sample collection sites. Alternatively, chloropicrin formation was consistently elevated following heating (mean  $\Delta = +5.9 \,\mu\text{g/L}$ ). Although samples were diluted to similar DOC concentrations, carbon normalized DBP yields allow for a better comparison of the DBP precursor reactivity of the control and heated samples (Table 5.6). Following heating, TTHM yields and HAA5 yields were similar to control samples or decreased. NYC-RR was the only sample that showed an increase in HAA5 yield ( $\Delta = +2.0 \,\mu\text{g/mgc}$ ), which was relatively small. HAN4 yields both increased and decreased, whereas chloropicrin yields of the NYC heated leachates were higher compared to control samples (mean  $\Delta = +1.2 \,\mu g/mg_c$ ).

New York City	Chlorine Dose (mg/L)	TTHM (µg/L)	TTHM Yield (µg/mg <sub>C)</sub>	HAA5 (µg/L)	HAA5 Yield (µg/mg <sub>C)</sub>	HAN4 (µg/L)	HAN4 Yield (µg/mg <sub>C</sub> )	Chloropicrin (µg/L)	Chloropicrin Yield (µg/mg <sub>C</sub> )
NYC-EA Control	7.7	130.4	29.3	161.2	36.2	5.3	1.2	4.5	1.0
NYC-EA Heated	7.5	159.7	30.2	123.7	23.4	3.5	0.7	10.5	2.0
NYC-NN Control	14.8	279.5	48.3	248.5	42.9	7.8	1.4	7.8	1.4
NYC-NN Heated	7.3	167.6	35.6	179.6	38.1	4.3	0.9	14.3	3.0
NYC-RR Control	8.1	161.7	37.1	166.5	38.2	4.2	1.0	4.1	0.9
NYC-RR Heated	7.3	137.3	29.9	184.6	40.2	6.0	1.3	10.0	2.2
NYC-KEN Control	9.0	316.5	54.5	237.9	40.9	6.9	1.2	5.5	0.9
NYC-KEN Heated	5.9	134.8	25.0	162.8	30.2	6.4	1.2	10.8	2.0
Average ∆ (heated – control)	NA	-72.2	-12.1	-40.9	-6.6	-1.0	-0.15	+5.9	+1.2
Stdev Δ (heated – control)	NA	93.3	12.9	42.6	6.7	2.2	0.4	0.5	0.3

 Table 5.6

 Raw water DBP formation and carbon normalized DBP yields for New York City control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the NYC system.

The NYC leachates were coagulated to address the effects of heating on conventional treatment processes. Preliminary jar tests were conducted to select the optimal alum dose for DOC removal, following methods described previously. Distinct differences in the coagulation response for the control and heated NYC samples were apparent (Figure 5.3). In most cases, turbidity of the heated leachates remained elevated compared to the control leachates for alum doses ranging from 20-60 mg/L, and particles re-stabilized at 120 mg/L. The control leachates showed typical DOC dose responses (Figure 5.3), with considerable removal occurring at alum doses between 20 and 30 mg/L. For the control samples the treated water DOC concentrations were generally <3.0 mgc/L at doses of 30 mg/L. However, the DOC of the heated leachates remained high >3.9 mgc/L at doses of 30 mg/L, and showed only marginal removal (<20%). Although the heated leachate DOC concentration continued to decrease with increasing alum dose, the DOC remained near 3.0 mgc/L following treatment with up to 90 mg/L alum. The raw water UV<sub>254</sub> absorbance of the heated samples was generally higher than the control leachates, despite having similar DOC concentrations. As such, the UV<sub>254</sub> of the heated samples remained higher than the control samples, following treatment at a range of alum doses.



DOC<sub>0</sub> = initial DOC concentration. Figure 5.3 Alum dose-response for New York City control and heated leachates

Following preliminary jar tests, the NYC leachates were coagulated at a final dose, filtered, and chlorinated to characterize DBP levels likely to enter a distribution system. The required alum dose was on average 21.3 mg/L higher for the heated leachates compared to the control samples (Table 5.7). Even at a higher alum dose, the settled water turbidity levels were on average 2.0 ntu greater for heated samples, and treated water DOC concentrations were higher compared to the control leachates (mean  $\Delta = +1.2 \text{ mgc/L}$ ). NYC treated water heated samples showed higher SUVA<sub>254</sub> values (mean  $\Delta = +2.2 \text{ L/mg-m}$ ), indicating considerable aromatic material still remained compared to control leachates. The poor DOC removal for the heated samples resulted in elevated TTHM, HAA5, and chloropicrin levels compared to the control samples, following coagulation treatment. HAN4 formation was similar for the control and heated samples following treatment. As expected from the poor treatability of the heated leachates, the percent decrease for all parameters was lower following conventional treatment. For the heated leachates the percent decrease of DOC (mean  $\Delta = -29\%$ ), SUVA<sub>254</sub> (mean  $\Delta = -35\%$ ), C-DBPs (TTHM mean  $\Delta = -52\%$ ; HAA5 mean  $\Delta = -40\%$ ), and N-DBPs (HAN mean  $\Delta = -17\%$ ; chloropicrin mean  $\Delta = -45\%$ ) were lower than the control samples (Table 5.8).

The lower DOC removal, and consequently poor removal of DBP precursors for the heated samples impacted the finished water DBP concentrations likely to enter a distribution system. As demonstrated in Figure 5.4, treated water DOC concentrations of the heated NYC samples ranged from 3.0-3.9 mgc/L, whereas the control leachate DOC levels were consistently below 2.7 mgc/L. Accordingly, following treatment all heated leachates exceeded TTHM and HAA5 MCLs, whereas all control samples were below MCLs. Chloropicrin concentrations of the heated samples (8.1-10.8  $\mu$ g/L) were considerably higher than finished water NYC control leachates (0.8-2.3  $\mu$ g/L). Following treatment HAN4 concentrations were similar for control and heated NYC samples.

New York City	Alum Dose (mg/L)	Treated Turbidity (ntu)	Treated pH	Treated DOC (mg <sub>C</sub> /L)	Treated SUVA <sub>254</sub> (L/mg-m)	Treated TTHM (mg/L)	Treated HAA5 (mg/L)	Treated HAN4 (mg/L)	Treated Chloropicrin (mg/L)
NYC-EA Control	25	0.3	6.8	2.0	1.7	30.9	27.8	6.3	1.7
NYC-EA Heated	45	2.5	6.8	3.9	3.4	109.9	70.2	3.9	8.1
NYC-NN Control	30	0.2	6.9	2.3	2.0	28.1	26.7	3.6	0.8
NYC-NN Heated	50	2.8	7.1	3.2	4.9	115.6	106.1	4.9	10.8
NYC-RR Control	35	0.2	7.0	2.0	1.8	44.2	34.3	3.4	2.3
NYC-RR Heated	60	2.7	6.7	3.0	4.7	94.9	102.5	6.2	9.0
NYC-KEN Control	30	0.1	6.9	2.7	1.5	69.2	57.2	6.8	2.3
NYC-KEN Heated	50	0.8	6.8	3.8	2.7	110.8	97.5	5.7	8.8
Average ∆ (heated – control)	+21.3	+2.0	-0.1	+1.2	+2.2	+64.7	+57.6	+0.1	+7.4
Stdev $\Delta$ (heated – control)	2.5	0.9	0.2	0.4	0.8	22.0	19.3	2.3	1.7

Treated water quality and DBP formation for New York City control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the NYC system.

% Decrease % Decrease % Decrease % Decrease % Decrease %Decrease % Decrease **New York City** TTHM Turbidity SUVA<sub>254</sub> Chloropicrin DOC HAA5 HAN4 NYC-EA Control 97 56 83 63 37 76 -20 87 24 5 31 43 -13 22 NYC-EA Heated 54 NYC-NN Control 97 60 90 89 90 41 NYC-NN Heated 92 25 2 31 41 -12 24 19 96 52 73 79 45 NYC-RR Control 41 92 27 31 45 -2 9 NYC-RR Heated 12 98 51 53 78 76 0.7 58 NYC-KEN Control 88 28 14 40 12 18 NYC-KEN Heated 18 Average  $\Delta$ -52 -7 -29 -35 -40 -17 -45 (heated – control) Stdev ∆ 3 5 5 9 6 36 14 (heated – control)

 Table 5.8

 Percent removal following conventional treatment for New York City control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the NYC system.



Figure 5.4 Treated water DOC and DBP formation for New York City control and heated leachates

## WESTMINSTER TREATMENT PROCESS PERFORMANCE

WM control and heated samples were generated following the heating and leaching methods presented previously, and analyzed for raw water quality. As shown in Table 5.9, following heating the pH and alkalinity increased compared to the control samples (mean  $\Delta = +0.19$  and +8.2 mgCaCO<sub>3</sub>/L). Turbidity levels, inorganic nitrogen, DON, and DOC concentrations are presented, but reflect the amount of material (soil and litter) leached, rather than the effects of heating. Therefore, where appropriate, the sample results were normalized by the concentration of DOC, or the total mass of litter and soil leached. Soil and litter samples were mixed together, leached, and diluted to a DOC concentration of 5.0 ± 1.0 mgc/L for better comparison of the samples at a realistic DOC concentration. The DOC:DON ratios imply the heated leachates were enriched in organic nitrogen compared to control samples (mean  $\Delta = -4.9 \text{ mgc/m}$ ). DOC leached per gram of solid material was lower after heating (mean  $\Delta = -1.4 \text{ mgc/g}$ ). SUVA<sub>254</sub> was consistently higher for the WM heated samples compared to the control leachates (mean  $\Delta = +1.2 \text{ L/mgc-m}$ ).

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Westminster	Alkalinity (mgCaCO <sub>3</sub> /L)	рН	Turbidity (ntu)	TDN (mg <sub>N</sub> /L)	NO <sub>3</sub> +NO <sub>2</sub> (mg <sub>N</sub> /L)	NH4 <sup>+</sup> (mg <sub>N</sub> /L)	DON (mg <sub>N</sub> /L)	DOC (mg <sub>C</sub> /L)	DOC Leached (mg <sub>C</sub> /g)	DOC:DON (mg <sub>C</sub> /mg <sub>N</sub> )	SUVA <sub>254</sub> (L/mg-m)	
WM35 Control	51	7.8	8.9	0.07	< 0.001	0.033	NA	4.0	3.1	NA	2.3	
WM35 Heated	55	7.8	21.8	0.38	0.029	0.121	0.23	5.6	1.2	24.3	4.3	
WM40 Control	48	7.5	11.3	0.39	0.004	0.178	0.21	4.4	3.3	21.0	1.9	
WM40 Heated	54	7.5	8.5	0.17	< 0.001	0.023	0.15	5.5	2.0	37.0	2.5	
WM49 Control	33	7.3	19	0.18	0.023	0.020	0.14	4.5	2.3	31.9	2.8	
WM49 Heated	48	7.7	15.0	0.36	0.003	0.119	0.23	5.4	1.9	23.1	2.9	
WM50 Control	37	7.4	10.1	0.10	< 0.001	0.002	0.10	4.5	4.5	46.6	2.0	
WM50 Heated	45	7.7	9.7	0.27	< 0.001	0.049	0.22	5.5	2.5	24.7	3.1	
Average ∆ (heated – control)	+8.2	+0.19	+1.4	+0.11	0.00	+0.02	+0.05	+1.0	-1.4	-4.9	+1.2	
Stdev Δ	4.9	0.2	7.8	0.23	0.02	0.12	0.10	0.5	0.7	19.3	1.0	

 Table 5.9

 Raw water quality for Westminster control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the WM system.

WM raw leachates were chlorinated and analyzed for DBP formation to address changes to DBP precursors following heating (Table 5.10). On average DBP formation increased following heating (TTHM mean  $\Delta = +11.8 \ \mu g/L$ ; HAA5 mean  $\Delta = +25.5 \ \mu g/L$ ; HAN4 mean  $\Delta = +1.2 \ \mu g/L$ ; chloropicrin mean  $\Delta = 8.0 \ \mu g/L$ ). However considerable variability was observed and for several samples DBP formation was lower for the heated leachates. TTHM formation was lower for the heated leachates, WM49 and WM50, and HAA5 formation was lower for WM49 following heating. HAN4 formation decreased for two of the leachates (WM35 and WM50) following heating. Chloropicrin formation consistently increased for all heated leachates. Although samples were diluted to similar DOC concentrations, carbon normalized DBP yields allow for a better comparison of the DBP precursor reactivity of the control and heated samples (Table 5.10). Following heating, TTHM and HAA5 yields on average decreased slightly (TTHM yield mean  $\Delta$ = -3.3 µg/mgc; HAA5 yield mean  $\Delta$  = -0.7 µg/mgc), again variability following heating was observed. The WM40 heated leachates showed higher TTHM yield compared to the control, and WM35 and WM40 showed higher HAA5 yields compared to unheated samples. HAN4 yields for the heated and control samples varied, both increasing and decreasing following heating (mean  $\Delta$  $= +0.01 \,\mu g/mg_{\rm C}$ ), whereas chloropicrin yields of the WM heated leachates were consistently higher compared to control samples (mean  $\Delta = +1.3 \ \mu g/mg_C$ ).

Westminster	Chlorine Dose (mg/L)	TTHM (µg/L)	TTHM Yield (μg/mg <sub>C</sub> )	HAA5 (µg/L)	HAA5 Yield (µg/mg <sub>C</sub> )	HAN4 (µg/L)	HAN4 Yield (µg/mg <sub>C</sub> )	Chloropicrin (µg/L)	Chloropicrin Yield (µg/mg <sub>C</sub> )
WM35 Control	4.3	121.3	30.1	118.7	29.4	7.1	1.8	2.3	0.6
WM35 Heated	6.5	157.5	28.3	189.7	34.1	6.0	1.1	8.8	1.6
WM40 Control	5.6	149.8	25.2	131.7	22.1	6.2	1.0	5.1	0.9
WM40 Heated	5.5	220.2	39.7	196.1	35.4	10.4	1.9	15.5	2.8
WM49 Control	6.1	226.0	49.9	237.6	52.5	7.4	1.6	9.3	2.0
WM49 Heated	6.6	194.4	36.7	192.7	36.4	9.2	1.7	18.9	3.6
WM50 Control	4.8	175.9	39.4	150.3	33.7	3.9	0.9	4.0	0.9
WM50 Heated	6.4	148.0	26.7	161.3	29.1	3.7	0.7	9.4	1.7
Average ∆ (heated – control)	NA	+11.8	-3.3	+25.4	-0.7	+1.2	+0.01	+8.0	+1.3
Stdev Δ	NA	49.9	13.0	54.0	12.6	2.3	0.64	2.4	0.5

 Table 5.10

 Raw water DBP formation and carbon normalized DBP yields for Westminster control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the WM system.

WM control and heated leachates were coagulated with ferric chloride at two doses (45 and 90 mg/L) and pH adjusted with caustic either pre- or post-mixing and settling. Dose response curves for the four sample collection sites (WM 35, 40, 49, and 50) are presented in Figures 5.5-5.8. No clear trends for turbidity were observed. The settling time was limited to 1 minute and as a consequence turbidity levels were high for both WM control and heated samples. Control and heated samples showed similar DOC dose-response curves, however the WM heated samples had higher raw water DOC concentrations (mean  $\Delta = +1.0$  mg/L) and also showed higher treated water DOC concentrations at ferric doses of 45 and 90 mg/L, and for both pH adjustment conditions. UV<sub>254</sub> showed a similar dose-response, with heated samples having considerably higher raw and finished water UV<sub>254</sub>.

Control and heated leachate finished water quality parameters under all treatment conditions are reported in Table 5.11. Minimal differences were observed for different pH adjustment conditions. Treated water DOC concentrations for control samples ranged from 1.3–1.9 mgc/L (ferric dose = 45 mg/L) and 1.5–1.8 mgc/L (ferric dose = 90 mg/L), suggesting that the higher ferric chloride dose did not provide additional DOC removal. For the heated leachates treated water DOC concentrations ranged from 3.3-3.8 mgc/L (ferric = 45 mg/L) and 2.5-3.3 mgc/L (ferric dose = 90 mg/L), with the higher ferric dose providing better DOC removal. Similar trends were observed for finished water SUVA<sub>254</sub>. The control samples showed SUVA<sub>254</sub> values of 1.5-2.4 L/mgc-m (ferric dose = 45 mg/L) and 1.4–2.4 L/mgc-m (ferric dose = 90 mg/L). Again, these results indicate the higher ferric dose did not improve the finished water quality of the control samples. WM heated leachate SUVA<sub>254</sub> values were 2.4- 4.5 L/mgc-m (ferric dose = 45 mg/L) and 2.4 – 3.9 (ferric dose = 90 mg/L), demonstrating improved finished water quality at the higher ferric chloride dose for heated leachates.

Overall, the heated leachates showed a poorer response to ferric chloride coagulation than control samples. On average the treated water turbidity was 1.2 ntu higher than WM control samples, DOC was 1.6 mg<sub>C</sub>/L higher and SUVA<sub>254</sub> was 1.2 L/mg-m higher (Table 5.11). Treated water C-DBP formation followed similar trends for the control and heated leachates (Table 5.11) with consistently higher DBP levels following heating (TTHM mean  $\Delta = +49.9 \ \mu g/L$ ; HAA5 mean  $\Delta = +56.1 \ \mu g/L$ ). N-DBP formation following ferric chloride treatment was also elevated for the heated samples (HAN4 mean  $\Delta = +2.0 \ \mu g/L$ ; chloropicrin mean  $\Delta = +6.4 \ \mu g/L$ ).

As expected from the poorer treatability of the heated leachates, the percent decrease for all parameters was lower following treatment compared to WM control samples. For the heated leachates the percent decrease of DOC (mean  $\Delta = -21\%$ ), SUVA<sub>254</sub> (mean  $\Delta = -15\%$ ), C-DBPs (TTHM mean  $\Delta = -27\%$ ; HAA5 mean  $\Delta = -28\%$ ), and N-DBPs (HAN mean  $\Delta = -30\%$ ; chloropicrin mean  $\Delta = -21\%$ ) were lower than the control samples (Table 5.12).

The lower DOC removal, and consequently poor removal of DBP precursors for the heated samples impacted the finished water DBP concentrations. As demonstrated in Figure 5.9, treated water DOC concentrations of the heated WM samples ranged from 2.5-3.8 mg<sub>C</sub>/L, whereas the control leachate DOC levels were consistently below 2.0 mg<sub>C</sub>/L. Accordingly, following treatment all except one of the heated leachates exceeded TTHM and HAA5 MCLs, whereas most control samples were below MCLs. HAN4 and chloropicrin concentrations of the heated samples were also higher than finished water WM control leachates (Figure 5.9).



Samples were pH adjusted prior to mixing and settling (PRE) or after mixing and settling (POST). DOC<sub>0</sub> = initial DOC concentration of raw leachate.

Figure 5.5 Dose response curves for WM35 control and heated samples



Samples were pH adjusted prior to mixing and settling (PRE) or after mixing and settling (POST). DOC<sub>0</sub> = initial DOC concentration of raw leachate.

Figure 5.6 Dose response curves for WM40 control and heated samples



Samples were pH adjusted prior to mixing and settling (PRE) or after mixing and settling (POST).  $DOC^0$  = initial DOC concentration of raw leachate.

Figure 5.7 Dose response curves for WM49 control and heated samples



Samples were pH adjusted prior to mixing and settling (PRE) or after mixing and settling (POST). DOC<sub>0</sub> = initial DOC concentration of raw leachate.

Figure 5.8 Dose response curves for WM50 control and heated samples

# Treated water quality and DBP formation for Westminster control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the WM system.

Westminster	Ferric Chloride Dose	pH Adjustment	Treated Turbidity (ntu)	Treated DOC (mg <sub>C</sub> /L)	Treated SUVA254 (L/mg <sub>C</sub> -m)	Treated TTHM (μg/L)	Treated HAA5 (μg/L)	Treated HAN4 (µg/L)	Treated Chloropicrin (µg/L)
	45	PRE	12.4	1.8	1.6	40.3	24.5	3.8	1.7
WM25 Control	45	POST	11.7	1.8	1.7	38.4	26.2	3.9	1.1
wiviss Control	90	PRE	0.6	1.8	1.4	33.7	21.6	2.7	1.3
	90	POST	12.1	1.7	1.6	29.1	17.5	4.3	1.1
	45	PRE	22	3.8	4.5	106.6	112.4	5.2	7.3
WM25 Hostad	45	POST	19.6	3.5	4.2	99.3	98.2	5.1	5.1
www.soneateu	90	PRE	11	3.3	3.9	88.2	81.5	5.2	4.9
	90	POST	1.58	2.5	3.4	61.9	55.8	4.7	3.9
	45	PRE	14.9	1.8	1.6	42.7	30.6	4.0	1.7
WM40 Control	45	POST	11.0	1.7	1.5	22.6	26.5	3.3	2.1
W WI40 CONTO	90	PRE	1.7	1.6	1.5	35.8	20.0	3.1	1.6
	90	POST	6.0	1.6	1.7	36.2	27.4	3.9	1.2
	45	PRE	9.6	3.4	2.5	114.0	70.2	5.08	8.22
WM40 Heated	45	POST	10.8	3.4	2.4	100.9	67.7	4.93	8.91
WM40 Healed	90	PRE	6.9	3.2	2.5	88.2	108.1	4.81	8.91
	90	POST	8.3	3.1	2.4	97.8	64.8	5.17	7.83
	45	PRE	12.8	1.6	2.4	84.0	49.9	4.5	5.1
WM49 Control	45	POST	9.19	1.3	2.1	59.3	29.1	4.5	4.3
w w149 Control	90	PRE	7.23	1.5	2.4	66.5	42.9	3.9	4.0
	90	POST	11.1	1.5	2.1	63.5	40.6	3.9	3.9
_	45	PRE	13.1	3.3	3.0	138.9	113.8	6.5	15.6
WM40 Heated	45	POST	13.4	3.4	3.1	138.6	108.5	6.5	13.0
wivi49 ficated	90	PRE	8.8	2.9	2.8	115.1	100.6	7.1	13.4
	90	POST	8.3	2.9	2.8	122.1	81.8	5.1	11.9
-	45	PRE	8.1	1.9	2.1	75.0	40.5	2.5	1.7
WM50 Control	45	POST	7.3	1.7	1.6	60.0	35.3	2.4	1.6
www.so.control	90	PRE	6.3	1.8	1.7	66.3	32.7	2.5	1.5
	90	POST	11.0	1.8	1.5	93.0	28.9	2.1	1.5
-	45	PRE	9.0	3.8	3.0	107.5	104.1	5.0	6.1
WM50 Heated	45	POST	9.4	3.5	2.6	93.9	85.7	5.7	7.4
Wiso Heated	90	PRE	4.7	3.1	2.7	84.7	68.5	4.8	7.6
	90 POST		8.7	3.3	2.7	86.8	70.5	6.1	7.2
A	Average $\Delta$ (heated – control)		+1.4	+1.6	+1.2	+49.9	+56.1	+2.0	+6.4
	Stdev <b>Δ</b>		5.4	0.3	0.8	22.8	18.3	1.0	2.1

Percent removals following ferric chloride treatment for Westminster control and heated samples. Samples are leached mixtures of soil and litter. Soil and litter samples were collected from four different sites within the WM system.

Westminster	Ferric Chloride Dose (mg/L)	pH Adjustment	% Decrease Turbidity	% Decrease DOC	% Decrease SUVA254	% Decrease TTHM	% Decrease HAA5	%Decrease HAN4	% Decrease Chloropicrin
	45	PRE	-39	55	31	67	79	47	24
WM25 Control	45	POST	-31	54	26	68	78	45	51
wws5 Control	90	PRE	93	55	40	72	82	62	44
	90	POST	-36	58	32	76	85	40	53
	45	PRE	-1	32	-5	32	41	12	17
WM35 Heated	45	POST	10	37	2	37	48	14	42
www.wiss ficated	90	PRE	50	42	10	44	57	14	44
	90	POST	93	56	20	61	71	22	55
	45	PRE	-32	59	15	72	77	35	66
WM40 Control	45	POST	3	61	20	85	80	46	59
WWWWWWW	90	PRE	85	64	23	76	85	50	69
	90	POST	47	64	10	76	79	37	77
	45	PRE	-13	38	2	48	64	51	47
WM40 Heated	45	POST	-28	38	6	54	65	53	43
w M40 Heated	90	PRE	19	43	2	60	45	54	43
	90	POST	2	43	4	56	67	50	49
	45	PRE	33	64	14	63	79	40	45
WM40 Control	45	POST	52	70	25	74	88	40	54
www.wi49.Control	90	PRE	62	67	16	71	82	48	56
	90	POST	42	66	24	72	83	47	58
	45	PRE	13	39	-3	29	41	29	17
WM40 Heated	45	POST	11	37	-4	29	44	29	31
w w149 mealeu	90	PRE	42	46	4	41	48	23	29
	90	POST	45	47	6	37	58	45	37
	45	PRE	20	59	-7	57	73	36	57
WM50 Control	45	POST	28	61	20	66	76	38	59
WWI90 Control	90	PRE	38	60	15	62	78	36	62
	90	POST	-9	60	25	47	81	45	62
	45	PRE	7	30	4	27	35	-34	35
WM50 Heated	45	POST	3	36	14	37	47	-52	21
WM50 Heated	90	PRE	51	43	11	43	58	-28	19
90 POST		10	41	12	41	56	-64	23	
Average $\Delta$ (heated – control)		-3	-21	-15	-27	-28	-30	-21	
Stdev <b>A</b>		47	7	12	10	11	37	13	



Figure 5.9 Treated water DOC and DBP formation for Westminster control and heated samples

## SAN FRANCISCO TREATMENT PROCESS PERFORMANCE

San Francisco (SF) control and heated samples were generated following the heating and leaching methods presented above, and analyzed for water quality. Note that the SF-HH (Hetch Hetchy) sample was collected in 2015 from an area burned in the Rim Fire (2013) and was not heated in the laboratory or included in the calculation of differences between heated and control samples ( $\Delta$ ). However, the soil sample was collected two years after the fire and may have been subject to pre-leaching due to rainstorms. As shown in Table 5.13, following heating of the SF-WB sample, the pH and alkalinity slightly increased compared to the control sample, whereas the SF-EB sample showed minimal change in pH and alkalinity. Turbidity levels, inorganic nitrogen, DON, and DOC concentrations are presented, but reflect the amount of soil leached, rather than the effects of heating. Therefore, where appropriate, the sample results were normalized by the concentration of DOC, or the mass of soil leached. Due to the lack of SF litter samples (only soils were collected). DOC concentrations of the leachates were lower than leachates for the other utilities (DW, NYC, WM), and only soils were used for heating and leaching experiments. The DOC leached per gram of SF soil was higher after heating for EB and WB samples, which differs from the trend observed for the three other watersheds when soils and litter were composited and leached, suggesting different behavior between soils and litter samples upon heating. The SF-HH sample leached the lowest DOC per gram of soil, compared to all other SF samples. The DOC:DON ratios for the EB and WB samples imply the heated leachates were enriched in organic nitrogen compared to respective control samples. The DOC:DON ratio for SF-HH was within the range of the SF-EB and SF-WB heated and SF control leachates. SUVA<sub>254</sub> was consistently higher for SF-EB and SF-WB heated samples compared to the control leachates. For SF-HH, the SUVA<sub>254</sub> was between the values for the two SF heated leachates (EB and WB).

within the Sr system. Sr-fift was impacted by the Kin fife and not neated in the laboratory.												
San Francisco	Alkalinity (mgCaCO <sub>3</sub> /L)	рН	Turbidity (ntu)	TDN (mg <sub>N</sub> /L)	NO <sub>3</sub> +NO <sub>2</sub> (mg <sub>N</sub> /L)	NH4 <sup>+</sup> (mg <sub>N</sub> /L)	DON (mg <sub>N</sub> /L)	DOC (mg <sub>C</sub> /L)	DOC Leached (mg <sub>C</sub> /g)	DOC:DON (mg <sub>C</sub> /mg <sub>N</sub> )	SUVA <sub>254</sub> (L/mg <sub>C</sub> -m)	
SF-EB Control	46	7.7	17.3	0.51	0.357	0.034	0.12	2.8	0.4	23.0	2.4	
SF-EB Heated	46	7.6	1.3	0.36	0.001	0.189	0.17	3.0	3.2	17.9	3.2	
SF-WB Control	46	7.6	5.7	0.27	0.013	0.119	0.13	2.5	0.8	18.3	3.1	
SF-WB Heated	54	7.8	3.3	0.62	0.003	0.350	0.27	2.9	1.3	11.0	4.5	
SF-HH	58	7.6	98.2	0.14	0.001	0.022	0.11	2.2	0.1	18.7	3.7	

Raw water quality for San Francisco control and heated soil samples (leachates). Soils were collected from three different sites within the SF system. SF-HH was impacted by the Rim fire and not heated in the laboratory.

SF raw leachates were chloraminated and analyzed for DBP formation to address changes to DBP precursors following heating (Table 5.14). Following heating DBP formation generally increased for EB and WB samples. DBP formation for the SF-HH leachate was relatively low, which may be attributed to pre-leaching of the soil organic matter during rainfall, prior to sample collection. However, the HAN4 formation of the SF-HH leachate was higher than both the control and heated samples for the other SF sites. Although the leachates were diluted to similar DOC concentrations, carbon normalized DBP yields allow for a better comparison of the DBP precursor reactivity of the control and heated samples (Table 5.14). Following heating, TTHM and HAA5 yields increased for the EB and WB leachates. For SF-HH, TTHM and HAA5 yields were within the range of the control leachates for SF-EB and SF-WB (Table 5.14), and were lower than the heated leachates. HAN4 yields showed minimal differences for the heated and control samples, increasing slightly for SF-EB and decreasing slightly for SF-EB heated leachate was higher than the control sample, while SF-WB control was below the detection limit for chloropicrin. The chloropicrin yield for SF-HH was also low (chloropicrin yield = 0.1  $\mu$ g/mgc).

Raw water DBP formation and carbon normalized DBP yields for San Francisco control and heated soil samples (leachates). Soils were collected from three different sites within the SF system. SF-HH was impacted by the Rim fire and not heated in the

San Francisco	TTHM (µg/L)	TTHM Yield (µg/mg <sub>C</sub> )	HAA5 (µg/L)	HAA5 Yield (µg/mg <sub>C</sub> )	HAN4 (µg/L)	HAN4 Yield (µg/mg <sub>C</sub> )	Chloropicrin (µg/L)	Chloropicrin Yield (µg/mg <sub>C</sub> )
SF-EB Control	5.2	1.9	5.9	2.1	1.1	0.4	1.1	0.4
SF-EB Heated	22.4	7.5	26.3	8.8	1.5	0.5	4.4	1.5
SF-WB Control	12.4	5.0	15.7	6.4	1.4	0.6	<dl< td=""><td>NA</td></dl<>	NA
SF-WB Heated	16.3	5.5	31.9	10.9	1.4	0.5	3.3	1.1
SF-HH	6.5	3.0	8.1	3.8	1.8	0.9	0.2	0.1

The SF leachates were treated following the conditions described previously. The samples were filtered and chloraminated to characterize the DBP levels likely to enter a distribution system. The settled water turbidity levels for SF-EB and SF-WB were lower for heated samples compared to the control samples from respective sites (Table 5.15). Following heating, the treated water DOC concentrations for EB and WB samples remained higher compared to the control leachates. For SF-HH, the treated water DOC was the lowest (1.7 mgc/L; Table 5.16: 22% removal) compared to SF-EB and SF-WB samples, however the raw water DOC was also the lowest (2.2 mgc/L). The SF-WB heated treated water sample had a slightly higher SUVA<sub>254</sub> value than the respective control sample, and the SF-EB heated leachate also showed a greater treated water SUVA254 than the control. For SF-HH the treated water SUVA254 was higher than all other SF samples, suggesting this soil was enriched in more aromatic soluble organic matter. The poorer DOC removal for the EB and WB heated samples resulted in elevated TTHM, HAA5, HAN4, and chloropicrin levels compared to the control samples following treatment. Treated water C-DBP formation for SF-HH was relatively high compared to the other SF samples (second highest overall). SF-HH treated water HAN4 formation was the lowest, while chloropicrin formation was higher than most SF samples. Turbidity and SUVA254 consistently decreased following treatment for the control and heated leachates, however DOC and DBP formation showed considerable variability, poor removal, and often increased following treatment (Table 5.16). For instance, DOC decreased for the EB and WB control samples, but increased for the EB and WB heated samples, after treatment. For all samples except SF-WB control, TTHM formation increased following treatment. For the SF-EB samples and SF-HH, HAA5 formation increased after treatment. For all SF-EB and SF-WB samples HAN4 formation increased following treatment. For SF-HH HAN4 formation decreased after treatment (41%), while chloropicrin formation increased substantially. Overall, a wide range of treatment responses and variability in DBP formation were observed for SF samples. This observation is likely attributed to pre-chlorination or the use of an organic polymer, both of which were not used for DW, NYC, and WM treatment tests (treatment with aluminum sulfate or ferric chloride).

Despite the general increase in DBP formation following treatment of the SF control and heated leachates, DBP MCLs were not exceeded for any treated water samples (Figure 5.10), although SF-EB heated was very close to the MCLs. The SF-EB heated sample formed high HAN4 (2.7  $\mu$ g/L) and chloropicrin (14.1  $\mu$ g/L) compared to the control samples, SF-HH, and SF-WB heated.

San Francisco	Treated Turbidity (ntu)	Treated pH	Treated DOC (mg <sub>C</sub> /L)	Treated SUVA <sub>254</sub> (L/mg <sub>C</sub> -m)	Treated TTHM (μg/L)	Treated HAA5 (μg/L)	Treated HAN4 (μg/L)	Treated Chloropicrin (μg/L)
SF-EB Control	4.8	6.9	2.1	1.3	15.4	22.4	1.7	1.5
SF-EB Heated	0.2	6.8	3.5	1.9	68.6	57.4	2.7	14.1
SF-WB Control	3.5	7.5	2.4	2.3	7.3	7.5	1.4	0.2
SF-WB Heated	2.6	7.6	3.3	2.4	17.2	24.7	1.5	1.7
SF-HH	2.3	7.4	1.7	2.6	25.3	45.3	1.1	2.3

Treated water quality and DBP formation for San Francisco control and heated soil samples (leachates). Soils were collected from three different sites within the SF system. SF-HH was impacted by the Rim fire and not heated in the laboratory.

 Table 5.16

 Percent removal following treatment for San Francisco control and heated soil samples. Soils were collected from three different sites within the SF system. SF-HH was impacted by the Rim fire and not heated in the laboratory.

San Francisco	% Decrease Turbidity	% Decrease DOC	% Decrease SUVA <sub>254</sub>	% Decrease TTHM	% Decrease HAA5	%Decrease HAN4	% Decrease Chloropicrin
SF-EB Control	72	23	44	-194	-280	-50	-32
SF-EB Heated	82	-15	41	-206	-118	-85	-217
SF-WB Control	39	1	24	41	52	-1	NA
SF-WB Heated	21	-13	46	-5	23	-1	48
SF-HH	98	22	31	-286	-458	41	-1263



Red indicates the samples were heated prior to leaching. Figure 5.10 Treated water DOC and DBP formation for San Francisco control and heated soil samples

#### DISCUSSION

Generally, the trends observed for the four utilities were consistent and aid in understanding the effects of heating on water soluble compounds and the associated treatment challenges. The marginal increase in pH and alkalinity observed for the laboratory heated samples may be attributed to the denaturing of organic acids upon heating, with residual alkaline components remaining (Ulery and Graham 1993). The decrease in DOC leached per gram of material for the heated leachates is consistent with other work indicating partial combustion of soluble organic carbon compounds at 225°C, whereas organic nitrogen has been shown to volatilize at higher temperatures (Hogue and Inglett 2012), supporting the observed enrichment of DON relative to DOC, following heating. SF-EB and SF-WB leachates did not follow the same trend, and the DOC leached per gram of soil increased after heating. SF-HH was burned in the Rim fire, was not subject to laboratory heating, and the DOC leached per gram of soil was very low. SF litter samples (not available) were not leached with the soils, and perhaps different organic precursor materials of soils and litter may help explain the difference. Consistently higher SUVA254 for the heated samples indicates enhanced aromaticity of soluble compounds upon heating, supported by soil organic matter studies (González-Pérez et al. 2004, Knicker 2007). Iron concentrations of the heated leachates were low (<0.005 mg/L) and did not significantly interfere with absorbance measurements.

Generally, for raw water C-DBP yields, the changes associated with heating were inconsistent, both increasing and decreasing compared to paired control samples. These findings suggest variable alterations in TTHM and HAA5 precursors at 225 °C. Bromide concentrations were low (< 0.003 mg/L), and primarily chlorinated DBP species were formed. An overall decrease in C-DBP reactivity was observed by others (Wang et al. 2015a), and suggests destruction of TTHM and HAA5 water-soluble precursors during heating, despite the observed increase in SUVA<sub>254</sub>, which generally correlates with C-DBP precursor reactivity (Archer and Singer 2006, White et al. 1997). It should be noted, the similar or on average lower TTHM, HAA5, and HAN4 precursor reactivity of the heated leachates compared to the control samples may not be representative of the precursor load a water treatment facility might receive in their influent supply, post-wildfire. Enhanced erosion of terrestrial DOM following wildfire can significantly increase DOC levels and DBP formation, as observed in field-based studies (Hohner et al. 2016, Writer et al. 2014).

The increase in chloropicrin precursor reactivity following heating may be associated with the enrichment of DON relative to DOC, or elevated inorganic nitrogen levels. Studies have identified 2- and 3-nitrophenol (Merlet et al. 1985, Thibaud et al. 1987) as well as glycine (Mitch et al. 2009) as chloropicrin precursors. While the DOC:DON ratio decreased upon heating, and chloropicrin formation and precursor reactivity per unit carbon increased, HAN4 precursors did not appear altered by heating. Previous studies have associated elevated HAN4 reactivity with wildfire (Hohner et al. 2016, Wang et al. 2015b). Enhanced post-fire erosion and mobilization of HAN4 precursors may have been more significant than heat-induced alterations to terrestrial organic matter. Perhaps water-soluble chloropicrin precursors formed at 225 °C, whereas HAN4 precursors may form at a different temperature, or under different conditions existing in the natural environment. A lab-controlled study showed different trends for HAN4 reactivity based on oxygen conditions during heating (Wang et al. 2015a).

Previous work by Cawley et al. showed a consistent increase in HAN4 yields of heated soils (225°C) relative to unheated soils (Cawley et al. 2017), however litter materials were not

included in the experiments, possibly explaining the disconnect with the results of this study. Further, the Cawley et al. study suggests a shift upon heating in the composition of soils, towards more N-containing compounds indicated by high resolution mass spectroscopy. Alternatively for the current study, heated litter, the dominant source of DOM in the mixed leachates, may not contribute substantial HAN4 precursors relative to unheated litter, potentially implying heating alters HAN4 precursors in soils and litter differently. Other research showed for plant biomass, the maximum extractable DON occurred from heating at 350°C (Hogue and Inglett 2012), higher than the temperature used for the treatment tests.

The adverse effect of heating on the overall treatability of the leachates might be explained by a lower-molecular weight DOM composition, as smaller compounds are generally less amenable to removal by coagulation (Quang et al. 2015). Further, although small, the increase in raw water pH and alkalinity of the heated leachates may have decreased the efficacy of coagulation. pH adjustment was not optimized in this study, but may have improved process performance of the heated leachates by lowering the pH for more effective turbidity or DOM removal. The raw water turbidity levels of the heated leachates were low relative to the range of observed post-fire particle loads (e.g., > 200 ntu) (Hohner et al. 2016, Writer et al. 2014). The changes heating imparted on particle characteristics (e.g., size, surface charge, density, adsorptive properties) were not explored, but may have also influenced the coagulation response. As expected, the lower DOC removal and consequently poor removal of DBP precursors for the heated samples significantly impacted the finished water DBP concentrations likely to enter a distribution system. Heating appeared to alter the DOM composition, resulting in poor removal of C-DBP precursors and negative implications for finished water quality, despite the generally lower raw water TTHM and HAA5 yields.

The negligible removal of HAN4 precursors by coagulation for the heated leachates, and better, although low, removal for the control leachates is likely attributed to low molecular weight and low anionic charge of N-DBP precursors, resulting in relatively ineffective removal (Bond et al. 2012). Overall, the results suggest chloropicrin precursors are more amenable to coagulation than HAN4 precursors, consistent with previous work (Hohner et al. 2016). Nitrosamines were not considered in this study, however an increase in reactivity was observed from chloramination of wildfire-affected detritus extracts (Wang et al. 2015b).

## CONCLUSIONS

Controlled laboratory heating at 225°C of soil and litter samples from varying geographic regions resulted in clear and measurable alterations to the soluble DOM character, indicated by increased SUVA<sub>254</sub>. Despite the higher SUVA<sub>254</sub>, a change in DOM quality, such as shifts towards lower molecular weight compounds, may have adversely affected coagulation treatment, resulting in elevated settled water turbidity and minimal DOC removal. Further, finished water quality was negatively influenced, including the exceedance of DBP MCLs and high chloropicrin concentrations. Heat-induced changes to particle size and characteristics were not explored in this study, but may have negatively affected coagulation processes possibly due to the presence of finer materials.

While the results from this study provide insight into the potential alterations that may occur during a wildfire, important considerations must be noted. Natural fires will likely result in patchiness across the burned landscape and a heterogeneous mixture of post-fire residues, unburned soils, and vegetation. Similarly, wildfire specific factors such as oxygen availability, temperature, and fuel moisture may result in different alterations to terrestrial sources of DOM than observed in this laboratory study. Further, environmental transformations (e.g., photolysis, biodegradation) of soils and litter are possible, but were not considered in the laboratory experiments. Temporal variation in wildfire-burned detritus characteristics have been observed following cumulative rainfall events (Wang et al. 2016). Of particular importance for interpreting post-fire watershed responses is the timing and magnitude of rainfall, and proximity and extent of the burned area relative to drinking water intakes, ultimately influencing the mobilization of post-fire forest floor detritus to source waters.

Both the enrichment of N-DBP precursors and the poor response to coagulation observed in this controlled laboratory study are supported by findings from a post-wildfire field-based study where debris and sediments were mobilized to the CLP river following rainstorms (Hohner et al. 2016). Water providers should be informed that post-wildfire runoff might contain an altered DOM composition significantly less amenable to coagulation than the background watershed DOM. Increased coagulant doses will likely be necessary, and pH may need to be lowered to optimize DOM removal, impacting solids handling processes and filter run times. While findings from this study suggest an altered DOM character, utilities may also experience an increase in influent DOC concentrations coupled with higher, or even extreme, sediment loads, resulting in compounding effects on water treatment due to substantial challenges from high turbidity levels. Exploring alternate water supplies, expanding storage capacity, adding a pre-sedimentation basin, and increasing upstream water quality monitoring with early warning systems are avenues utilities should take into consideration when preparing for, or coping with, wildfire. Additional recommendations for managing post-fire runoff and treatment challenges are discussed in Chapter 6.

# CHAPTER 6 THE IMPACT OF WILDFIRES ON TREATMENT PLANT OPERATIONS AND DESIGN

Wildfires and other extreme weather events present great challenges and risks to water utilities throughout the United States. In many cases, such events have caused treatment plants to either shut down, reduce flow, or deliver water that was of inferior quality or failed to meet regulations. These risks are due to changes in the frequency, duration, magnitude, and speed of raw water quality changes, specifically increases in turbidity and NOM. As presented in previous chapters, wildfires often result in increased solids loadings to plants in terms of ash content and runoff from soils due to loss of groundcover, and increased transport of terrestrial NOM of altered character. These two parameters – turbidity and NOM – drive the design and operation of water treatment plants. Other water quality parameters that can influence process selection and plant operations after a wildfire include algae, iron, manganese, and taste and odors.

The purpose of this chapter is to provide guidance to utilities on the impact of wildfires on treatment plant operations and to develop design recommendations to increase treatment resiliency and reliability. Utility managers need to know what new processes or additional facilities they need to install to protect against future water quality excursions. The approach to this chapter is to first describe a conventional water treatment plant, followed by other common plant configurations. Once the major unit processes are described, limitations to each process in terms of water quality and loading rates will be presented. The chapter will conclude with design recommendations for increasing plant resiliency to better address post-wildfire water quality issues.

Treatment challenges expected from wildfires include both short term and long-term issues. Short term issues that may occur in the weeks and months after an event are mostly due to increased turbidity due to ash from post-fire erosion, spikes in NOM, and pH and alkalinity changes. Longer term issues that can occur over several years include:

- Increased turbidity from soils due to loss of vegetation this can continue for years
- Increased NOM
- Changed character of NOM
- Algal growth and associated byproducts: algal toxins and taste and odors that result from release of nutrients after a fire and warmer temperatures due to loss of shade cover
- Iron and manganese

The first focus of this chapter is on the primary initial impacts caused by turbidity and NOM on each unit process. A discussion of treatment challenges expected from wildfires due to other potential secondary impacts is also included.

## **DESCRIPTION OF MAIN TYPES OF TREATMENT SYSTEMS**

## **Conventional and High-Rate Sedimentation**

A conventional treatment plant (Figure 6.1) consists of coagulant addition followed by flocculation, clarification via gravity sedimentation in large rectangular or circular sedimentation basins, and rapid rate granular media filters. Note that high-rate plate and tube sedimentation

processes are considered as conventional sedimentation in this discussion as they are governed by the same sedimentation theory as rectangular basins. Coagulant is needed to destabilize particles and to provide metal hydroxide floc for adsorption or co-precipitation of NOM. Since new particles are formed by precipitation, it is important to note that these new particles need to be removed along with particles present in the source water during the sedimentation and filtration processes. Coagulant addition also influences solids handling and disposal practices. It is important that chemical coagulation dosing and pH conditions be controlled such that the removal of both particles and NOM is optimized. Flocculation (slow mixing) is needed to promote particle growth through particle-particle contacts. The goal of flocculation in a conventional treatment plant is to make "settleable" floc, i.e., floc that can be readily be removed in a sedimentation basin. The surface loading (or overflow) rate for conventional sedimentation is in the range of 0.5 to 1 gpm/ft<sup>2</sup>, depending on the type of sedimentation process, nature of the raw water turbidity (mineral or nonmineral) and water temperature. Addition of plates or tubes to sedimentation basins will reduce the footprint of the treatment process by providing additional sedimentation surface area which allows for higher hydraulic loading rates, in the range of 2 to 5 gpm/ft<sup>2</sup>. Granular media filtration follows sedimentation to remove any remaining particles. Filters typically consist of dual-media (anthracite or GAC over sand) with loading rates of 4 to 8 gpm/ft<sup>2</sup>. Filtered water is then collected in a clearwell, where disinfectants and corrosion control chemicals are added, and the water is stored prior to delivery to customers.



*Source:* Becker et al. 2018. **Figure 6.1 Schematic of a conventional water treatment plant** 

## **Dissolved Air Flotation**

A dissolved air flotation (DAF) plant is similar to a conventional sedimentation plant except flocculated particles are removed by attachment to microscopic air bubbles and floating to the water surface (see Figure 6.2). Coagulant addition and flocculation are still used, but the goal of flocculation in this case is to produce a small floc that can be removed by attachment to air bubbles. Flocculation times needed for DAF facilities are on the order of 5-10 minutes (for example, 5 min for the New York City Croton Water Treatment Plant. Two-stage flocculation is commonly used. The typical design surface loading rate of the DAF process usually varies between 6 to 8 gpm/ft<sup>2</sup> -- significantly higher than the loading rate on a conventional sedimentation basin and higher than the footprint loading rates for high-rate plate and tube sedimentation processes. In addition, high-rate DAF processes have recently been developed at rates of 8 to 16 gpm/ft<sup>2</sup>. DAF is ideal for treating low turbidity waters and waters with high levels of algae and/or NOM.



*Source:* Becker et al. 2018. **Figure 6.2 Schematic of a DAF plant** 

# **Contact Clarification**

Contact clarification is a category used for a variety of processes that includes solidsblanket clarification, ballasted-sand clarification, and contact adsorption clarification. Although each of these specific processes is different from a mechanical perspective, they all work by enhancing particle removal via particle–particle or particle–media contacts. Of these, contact adsorption clarification is limited to low turbidity waters with low to moderate TOC levels. Higher turbidity and TOC (and higher coagulant dosages) result in excessive clarifier flushes and reduced plant production. Solids blanket and ballasted-sand clarifiers often have difficulty with algae, but can treat high turbidity source waters.

## **Direct Filtration**

Direct filtration plants are similar to conventional or DAF plants without a sedimentation/clarification step. Flocculation may or may not be included. If flocculation is not included the plant is often referred to as an in-line filtration plant. If flocculation is included, shorter times on the order of 10-15 minutes are normally practiced. A schematic of a direct filtration plant is included in Figure 6.3. Because the filters are the only means of removing solids, direct filtration is limited to very high-quality source waters with low turbidity and low levels of NOM and algae.



*Source:* Becker et al. 2018. **Figure 6.3 Schematic of a direct filtration plant**
#### IMPACT OF POST-WILDFIRE WATER QUALITY CHANGES ON UNIT PROCESSES

After a wildfire, the range of source water turbidity levels can be quite significant compared to normal operations. For example, in several studies, there have been measurements of turbidities on the order of >>100 NTU (citation needed). Treating these extreme turbidities is unrealistic, and under these conditions, the utility should close down the intake if possible to avoid numerous treatment issues and the possibility of producing unsafe water, contaminating the distribution system. For the sake of discussion, we will examine the case of a plant that needs to treat water at an upper source water turbidity value of 50-100 NTU.

The plant descriptions and unit process loading rates discussed above are applicable to water treatment plants under "normal" source water quality conditions. The performance of each unit process in a plant is dependent on the water quality it experiences and the hydraulic loading rate. In general, poorer water quality requires a decrease in the loading rate to produce acceptable treated water quality, and in severe cases, plants need to shutdown altogether. Since the performance of each unit process is dependent on the performance of prior unit processes, the following begins with a discussion of the impact of raw water quality excursions on coagulation/rapid mix and follows through the plant – flocculation, clarification, filtration, and disinfection. This discussion is presented with the aim of continuously meeting targeted finished water quality goals and regulatory requirements.

#### Coagulation

The performance of all downstream processes and the quality of finished drinking water is dependent on proper coagulation. Optimum coagulant conditions are a function of the required coagulant dose needed to neutralize the charge on NOM and particles, pH, and the presence of enough alkalinity so hydroxide floc can form. Under- and overdoses of coagulant can result in poor flocculation, high settled water turbidity, high filtered water turbidity and inadequate disinfection (due to pathogen shielding). Likewise, high pH adversely affects coagulation by decreasing the charge on alum and can also lead to high filtered water aluminum levels. Low alkalinity can result in poor floc formation, but very high alkalinity impacts the ability to decrease pH by coagulant or acid addition. Changes in raw water quality due to wildfires can stress the ability of any plant to ensure optimum coagulation.

The impact of increased solids or NOM as a result of a wildfire on coagulation depends on what parameter is driving the optimum coagulant dose. In most cases, NOM is the master variable that dictates optimum coagulant dosing strategies, so increases in turbidity generally have minimal impact, however, there are exceptions. For very high-quality waters treated by direct filtration or adsorption clarifiers, the coagulant dose is often controlled by turbidity. In these cases, post-fire increases in turbidity will likely lead to significant increases in the required coagulant dose. In addition to increased coagulant cost and residuals production, increased turbidity and coagulant doses will lead to shorter filters runs as noted below. For very high-quality waters treated by conventional treatment, an increase in turbidity may enhance the flocculation/sedimentation process such that a decrease in coagulant dose may be feasible. This is because when conventional sedimentation is used on high quality raw waters there are not enough particles for effective flocculation. Higher coagulant doses are often practiced to make enough metal hydroxide precipitate such that flocculation occurs.

Increases in raw water NOM concentrations following a forest fire will almost always require an increase in coagulant dose which equates to increased particulate loading to downstream

processes. Failure to use the optimal coagulant dose would result in higher settled water turbidity, and adverse impacts on the filtration process.

Wildfires can also impact raw water pH and alkalinity – both of which affect coagulation. Results from a WRF study that examined the effect of extreme weather events on water quality showed that in some cases heavy rain can result in an increase in alkalinity (when soils were high in limestone content) while in other instances alkalinity decreased (where it was just a dilution impact with no added alkalinity). pH and alkalinity are important parameters to monitor and can be controlled through chemical addition if available.

The following practices are recommended for coagulation:

- 1. Train utility staff to conduct jar testing on-site in order to support decision making and action during extreme weather events. Research has noted that utilities that were able to perform jar testing on-site were better able to responds to extreme turbidity and water quality excursions and avoid consequences such as turbidity breakthrough and potential boil water advisories.
- 2. Pay close attention to assure the optimum coagulant dose and pH conditions are maintained. A wildfire that leads to water quality changes will likely lead to increased coagulant requirements in most cases.
- 3. It may be necessary to increase the frequency of coagulant delivery during or after a wildfire.
- 4. It may also be necessary to install chemical feed pumps with a higher capacity. Similarly, feed systems to adjust pH and/or add alkalinity may be needed to better respond to turbidity events.

## Flocculation

Increased solids loading to a filtration plant will not impact the design or operation of the flocculation process. As mentioned above, with more particles, the flocculation process may improve in some cases – especially when the process is limited by contact opportunities (low turbidity waters). If the raw water turbidity increases dramatically then solids may settle out in the flocculation basin and would have to be periodically removed.

The following practices are recommended for flocculation:

- 1. Consider installing a means of removing silt that may settle in the bottom of the floc tanks.
- 2. Evaluate the impact of increased solids production on residuals handling capacity and plan for how to handle additional solids loads during high turbidity events.

## Sedimentation

Sedimentation basins remove approximately 90 to 98% of the applied turbidity under typical loading conditions. In order for the filters to function properly, settled water turbidity levels should be less than 2 NTU for dual media filters and less than 3 NTU for deep bed filters. Higher turbidity values will result in higher head loss and shorter filter runs. As an example, if a plant normally achieves 48-hour filter runs at a settled water turbidity of 1 NTU, it is not unrealistic to assume that the filter run length would decrease to 24 hours at 2 NTU and to only 18 hours at 3 NTU, at the same flow rate. Given the typical performance of conventional sedimentation

(including plate settlers), raw water turbidity levels of 50 to 100 NTU can be adequately treated without causing downstream filtration issues. Note that increases in coagulant doses due to changes in raw water turbidity or NOM add to the solids loading that must be removed in sedimentation and ultimately handled and disposed of. Also note that post-fire increases in turbidity would require more frequent solids removal from the basins, so automated sludge removal systems should be installed. For example, assuming a turbidity: TSS ratio of 2:1, the following mass loadings of solids are produced as a function of raw water turbidity for a 10 mgd plant. As shown in Table 6.1, increases in raw water turbidity can result in thousands of pounds per day of solids that must be removed, collected, processed, and disposed of.

 Table 6.1

 Solids produced due to turbidity for a 10 mgd water treatment plant. The numbers shown do not include solids produced from coagulant addition.

Turbidity (NTU)	Mass Loading (lbs/day)	
2	83	
10	830	
100	4200	
200	8300	

Source: Becker et al. 2018

Recommendations as a function of the type of clarification process are provided below.

- 1. Conventional sedimentation (including plate settlers)
  - a. Conventional sedimentation basins can adequately treat raw waters with turbidity values in the 50 100 NTU range. If turbidity is consistently above 100 NTU then a pre-sedimentation basin should be installed.
  - b. It should be noted that the maximum turbidity levels that can be treated are a function of the type of turbidity. That is, inorganic clay turbidity settles more readily than turbidity caused by algae or other lighter density material. Elevated levels of non-organic turbidity (i.e., particles) may require an alternative clarification process such at dissolved air flotation (DAF).
- 2. High-rate clarification
  - a. DAF
    - i. DAF can treat inorganic turbidities up to 10 NTU for extended periods of time.
    - ii. No upper limit for algal based turbidity.
  - iii. If (inorganic) turbidities exceed 10 NTU then consideration should be given to installation of a pre-sedimentation basin or converting the plant to conventional settling.
  - b. Adsorption clarifier
    - i. Limited to 10 NTU or less (regardless of type of turbidity).
    - ii. If turbidities exceed 10 NTU then consideration should be given to installation of a pre-sedimentation basin or converting the plant to conventional settling.
  - c. Sludge blanket clarifiers
    - i. Can handle more than 100 NTU of inorganic turbidity.
    - ii. Sludge blanket clarifiers can have difficulty with algae.
  - d. Ballasted flocculation

- i. Can handle very high raw water turbidities greater than 100 NTU.
- ii. Ballasted flocculation clarifiers can have difficulty with algae.
- 3. Enhance solids removal in all cases, elevated turbidity levels will increase solids production.
- 4. If turbidity is greater than 100 NTU, consider a pre-sedimentation basin.

#### Filtration

Granular media filters are the final particle removal process in drinking water treatment plants. As particles are removed in a granular media filter head loss accumulates and eventually the filter needs to be backwashed. If the time between backwashes is too short, then the plant cannot produce enough water to meet demands. In addition, more wasted backwash water will be produced than can be adequately handled.

Historically, rapid granular media filters consisted of monomedia sand, typically 24 inches of 0.5 mm effective size (ES). These filters were designed to operate at a maximum loading rate of 2 gpm/ft<sup>2</sup>. They have given way over the years to dual media filters that typically consist of 20 to 24 inches of 1 - 1.1 mm ES anthracite over 10 to 12 inches of 0.5 mm ES sand. Because of the larger media diameter and greater bed depth, these filters can store more particles and can therefore operate at high loading rates – 4 to 6 gpm/ft<sup>2</sup>. Deep bed filters, those with 5 to 6 feet of anthracite, an even larger ES (maybe 1.4 mm) and over 12 inches of sand typically operate at loading rates of 8-12 gpm/ft<sup>2</sup>.

The effectiveness of any of these filter media designs is predicated on effective coagulation and the applied turbidity. Effective coagulation is needed to destabilize particles so that they can be removed by sedimentation and filtration. Particles not removed in sedimentation enter the filters, where they are removed and contribute to head loss. From an operations perspective, a useful parameter for evaluating filter production is the unit filter run volume (UFRV). The UFRV is the volume of water produced per square foot of filter area over the course of a filter run. The UFRV should average at least 7,500 gallons per square foot under normal water quality conditions when the settled water turbidity is less than 2 NTU for filters operating at a common filtration rate of 4 gpm/ft<sup>2</sup>. This means that 7,500 gallons of water are produced per square foot of filter area between backwashes. This equates to roughly 30 hour filter run lengths at a filtration rate of 4 gpm/ft<sup>2</sup>. The minimum desired UFRV is greater than 5,000 gallons per square foot under challenging conditions which equates to roughly 20 hour filter runs at 4 gpm/ft<sup>2</sup>. Values lower than this result in excessive waste backwater production and frequent backwashing that makes it difficult for the plant to meet its production goals when producing filtered water with less than 0.1 NTU. Table 6.2 shows UFRV values as a function of filtration rate for a 24-hour period.

	UFRV (gallons/ft <sup>2</sup> )					
Filtration Rate (gpm/ft <sup>2</sup> )	20 hours	24 hours	36 hours	48 hours	72 hours	
2	2,400	2,880	4,320	5,760	8,640	
4	4,800	5,760	8,640	11,520	17,280	
6	7,200	8,400	12,960	17,280	25,920	
8	9,600	11,520	17,280	23,040	34,560	

Table 6.2UFRV as a function of filtration rate for a 24-hour filter run

An increase in raw water NOM following a forest fire would require an increase in coagulant dosage, which equates to increasing particulate loading to downstream processes. Failure to use the optimal coagulant dose would result in higher settled water turbidity. This would result in higher filter head loss and shorter filter runs and hence more backwash water. In addition, inadequate coagulant dose can lead to poor particle removal in filters, and as a result high effluent turbidity and early turbidity breakthrough.

These operational constraints suggest the following for filter media designs:

- 1. Filtered water turbidity should always be < 0.1 NTU.
- 2. Maximum applied turbidity to filters to meet these criteria:
  - a. Monomedia filter:
    - i. Loading rate: 2 gpm/ft<sup>2</sup>
    - ii. UFRV  $\geq$  3,000 gal/ ft<sup>2</sup> under extended water quality excursions
  - iii. Maximum applied turbidity: 1 NTU
  - b. Dual-media filter:
    - i. Loading rate:  $4-6 \text{ gpm/ft}^2$
    - ii. UFRV  $\geq$  5,000 gal/ ft<sup>2</sup> under extended water quality excursions
  - iii. Maximum applied turbidity: 1-2 NTU
  - c. Deep bed dual-media:
    - i. Loading rate up to  $12 \text{ gpm/ft}^2$
    - ii. UFRV  $\geq$  12,000 gal/ ft<sup>2</sup> under extended water quality excursions
  - iii. Maximum applied turbidity: 2-3 NTU
- 3. Recommendations to increase robustness:
  - a. Consider deeper bed, larger diameter media filters to increase solids storage.
  - b. Address media size depending on pilot testing or state regulations.
  - c. Inspect current filters and conduct a filter surveillance to ensure media is in good condition (e.g., right size, no mudballs, etc.).

## Membranes

Membranes (microfiltration or ultrafiltration) are commonly used in place of granular media filters at utilities throughout the country and the use is increasing. Particle removal in membrane systems is by straining – not by transport and attachment mechanisms that work in granular media filters. If the particulate loading is too high, the membrane flux declines which can impact plant production. This leads to increase flushes to remove the particulate matter which impacts residuals handling. Finished water quality is not normally affected since the membranes are absolute barriers. NOM also affects the rate of membrane fouling. When membranes become

fouled, they need to be chemically cleaned. Post-fire water quality changes can overwhelm membrane plants, especially when sedimentation is not practiced. Increases in turbidity and NOM can result in flux declines and increased fouling. In addition, firefighting foams can sorb to membrane surfaces and cause excessive fouling.

# DESIGN RECOMMENDATIONS FOR UTILITIES UNDER THE THREAT OF WILDFIRES

In addition to the raw water quality, the selection of the optimum treatment processes for any given plant is also a function of site-specific conditions (e.g., space limitations) and operational philosophy of the utility. The following recommendations are presented with the assumption sufficient space is available.

- 1. Pre-sedimentation basin
  - a. May be required/useful if raw water turbidity exceeds 100 NTU for long periods (i.e., days)
  - b. Include ability to bypass under normal conditions
- 2. Coagulation
  - a. Ensure chemical storage and feed pumps can deliver the higher chemical doses that may be needed after a wildfire
  - b. Consider polymer feed facilities that may be needed to treat waters with ash content
  - c. Develop operational protocols and install equipment such as streaming current monitors or zeta potential analyzers to help determine optimum coagulant dosages.
- 3. Flocculation
  - a. Install a means of removing silty solids that may settle out in flocculation tank under high turbidity conditions
- 4. Sedimentation
  - a. Use large conventional sedimentation basins if possible to handle large amounts of solids. If not practical, consider the use of plate settlers.
  - b. Ensure solids can be easily removed from basins via mechanical sludge removal equipment.
  - c. If in an area where it is not likely that high turbidity will reach the intake, and there is concern that algal blooms could occur, consider dissolved air flotation.
- 5. Filtration
  - a. Consider the use of deep bed dual-media filters with larger media that can store more solids than conventional filters.
  - b. Consider GAC in place of anthracite to help with taste and odors.
  - c. Provide enough backwash water and waste backwash storage so multiple filters can be backwashed at once.
- 6. Membranes
  - a. Membrane-based treatment systems should not be used if the raw water will be subject to the impact of firefighting foams that could foul membranes.
- 7. Disinfection
  - a. Higher levels of NOM may lead to DBP compliance issues.
  - b. Attention should be given to maximizing removal of NOM or relying on the use of alternative disinfectants including UV and ozone.
- 8. Advanced treatment

- a. Smoky taste and odors could occur after a fire.
- b. Nutrient release from wildfires could result in long-term eutrophication and increased algal growth in downstream reservoirs leading to taste and odors and algal toxins.
- c. The installation of powdered activated carbon or post filter GAC contactors should be considered to handle these events.
- d. The installation of ozone/biofiltration should also be considered.

## CHAPTER 7 CONCLUSIONS

This project focused on developing a framework for utilities to assess the impacts of a wildfire on water quality and treatment. To do so, post-fire water quality was simulated by heating soil and litter samples collected from the participating utilities in a furnace. Following heating, the samples were leached in low-carbon tap (LCT) water and the character of the DOM was assessed. In addition, bench-scale treatment tests were performed to evaluate the treatability of the leachates, focusing on turbidity, DOC, and DBP precursor removal. Lastly, utility surveys and interviews were conducted to better understand concerns, challenges, and experiences following wildfires and extreme weather events.

Soil and litter samples released different quantities and qualities of dissolved constituents following heating. The release of anions and cation quantity was altered following heating. Anion release into solution showed strong heating dependence, but was not consistent among the measured species. Sulfate concentrations demonstrated the most constant behavior, increasing with heating of each material, especially litter, which was shown to release nearly ten times that of the soil following heating. Nitrate concentrations generally decreased following heating of both litter and soil. Phosphate release was not constant among the soils, but phosphate release from litter increased after heating at 225°C. Iron and manganese had similar trends that generally demonstrated greater release after heating.

Generally, the trends observed for the four utilities were consistent and aid in understanding the effects of heating on water soluble compounds, raw water quality, and the associated treatment challenges. The marginal increase in pH and alkalinity observed for the heated samples may be attributed to the denaturing of organic acids upon heating, with residual alkaline components remaining (Ulery and Graham 1993). An observed decrease in the quantity of DOC leached per gram of material for the heated leachates is consistent with other work indicating partial combustion of soluble organic carbon compounds at 225°C. Alternatively, organic nitrogen has been shown to volatilize at higher temperatures (Hogue and Inglett 2012), supporting the observed enrichment of DON relative to DOC, following heating. SFPUC leachates did not follow the same trend, and the DOC leached per gram of soil increased after heating. SFPUC litter samples were not leached with the soils, and perhaps different organic precursor materials of soils and litter may help explain the difference. Clear and measurable alterations to the soluble DOM character was indicated by increased specific UV absorbance at 254 nm (SUVA254). Iron concentrations of the heated leachates were low (< 0.005 mg/L) and did not significantly interfere with absorbance measurements. Consistently higher SUVA254 for the heated samples indicates enhanced aromaticity of soluble compounds upon heating, supported by previous soil organic matter studies (González-Pérez et al. 2004, Knicker 2007).

During a natural wildfire, the litter layer is generally consumed leaving behind an ash layer. Ash can take on many different physical characteristics depending on the temperature and duration of heating as well as the parent material, which was not evaluated in these experiments. Therefore, the temperatures and heating durations used for this study are intended to mimic wildfirewatershed responses, but we cannot claim that the results accurately reflect environmental wildfire conditions and post-fire water quality responses. There are currently no rigorous studies examining the quantities and origins of DOM released from recently burned soils and litters. Future studies should examine the release of DOM from recently burned watershed materials to explore the potential shifts in DOM sources that may occur following fire.

#### **TREATMENT STUDIES**

For raw water (not coagulated) carbonaceous DBP yields, generally the changes associated with heating were minimal and suggest relatively small and variable alterations in total trihalomethane (TTHM) and haloacetic acid (HAA) precursors at 225°C. Bromide concentrations were low (< 0.003 mg/L), and primarily chlorinated DBP species were formed. An overall decrease in C-DBP reactivity was observed by others (Wang et al. 2015a), and suggests destruction of TTHM and HAA5 water-soluble precursors during heating, despite the observed increase in SUVA254, which generally correlates with C-DBP precursor reactivity (Archer and Singer 2006, White et al. 1997). It should be noted, the similar or lower TTHM, HAA5, and haloacetonitrile (HAN) precursor reactivity of the heated leachates compared to the control (unheated) samples may not be representative of the precursor load a water treatment facility might receive in their influent supply, post-wildfire. Enhanced erosion of terrestrial DOM following wildfire can significantly increase DOC levels and DBP formation, as observed in field-based studies (Hohner et al. 2016, Writer et al. 2014). Alternatively, the increase in chloropicrin precursor reactivity following heating may be associated with the enrichment of DON relative to DOC, or elevated inorganic nitrogen levels. Studies have identified 2- and 3-nitrophenol (Merlet et al. 1985, Thibaud et al. 1987) as well as glycine (Mitch et al. 2009) as chloropicrin precursors. While the DOC:DON ratio decreased upon heating, and chloropicrin formation and precursor reactivity per unit carbon increased, HAN4 precursors did not appear altered by heating. Previous studies have associated elevated HAN4 reactivity with wildfire.

Following heating of soil and litter, the leachates consistently exhibited an overall poor response to coagulation and even at high coagulant doses (e.g., > 80 mg/L alum) often marginal DOC removal was achieved (e.g., <30%). The treatability findings are consistent with the results from a field-based post-fire watershed monitoring study when rainstorms transported substantial sediments and debris downstream to the water intake (Hohner et al. 2016). Despite the higher SUVA<sub>254</sub>, a change in DOM quality, such as shifts towards lower molecular weight compounds, may have adversely affected coagulation treatment, resulting in elevated settled water turbidity and minimal DOC removal. Further, finished water quality was negatively influenced, including the exceedance of DBP maximum contaminant levels (MCLs) and high chloropicrin concentrations for the heated leachates compared to control samples. Heat-induced changes to particle size and characteristics were not explored in this study, but may have negatively affected coagulation processes possibly due to the presence of finer materials and should be considered in future work. Treated water nitrogenous DBP formation was also higher for the heated leachates, specifically chloropicrin.

Overall the heated leachates were more difficult to coagulate, requiring higher coagulant doses, consistent with previous work evaluating post-fire river samples collected following the High Park fire (Hohner et al. 2016). Consequently, utilities should plan for higher coagulant doses, and the subsequent solids handling implications on downstream processes. Coagulant doses will likely be case study specific depending on the wildfire (e.g., burned area size, proximity) and watershed (e.g., slopes, hydrology) specific factors, and post-fire flow events (e.g., rainstorm intensity and location). While findings from this study suggest an altered DOM character, utilities may also experience an increase in influent DOC concentrations coupled with higher, or even extreme, sediment loads, resulting in compounding effects on water treatment due to substantial

challenges from high turbidity levels. Exploring alternate water supplies, expanding storage capacity, adding a pre-sedimentation basin, and increasing upstream water quality monitoring with early warning systems are avenues utilities should take into consideration when preparing for, or coping with, wildfire.

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## **ABBREVIATIONS**

BCAN	bromo-chloroacetonitrile
CLP	Cache la Poudre
DAF DBAN DBP DCAN DOC DOM DON DW	dissolved air flotation di-bromoacetonitrile disinfection byproduct di-chloroacetonitrile dissolved organic carbon dissolved organic matter dissolved organic nitrogen Denver Water
EOH ES	East-of- Hudson effective size
GAC	granular activated carbon
HAA HAN HH HPLC	haloacetic acid Haloacetonitrile Hetch Hetchy high-liquid chromatograph
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
LCT	low carbon tap-water
MCL	maximum contaminant level
N-DBP NYC NYCDEP	Nitrogenous disinfection byproduct New York City New York City Department of Environmental Protection
OM	organic matter
PAC	powdered activated carbon
SEC SFPUC SOM SUVA254 SW	size exclusion chromatography San Francisco Public Utilities Commission soil organic matter specific UV absorbance at 254 nm surface water
TCAN	tri-chloroacetonitrile

TDN	total dissolved nitrogen
TDP	total dissolved phosphorus
TN	total nitrogen
TOC	total organic carbon
ТР	total phosphorus
TSS	total suspended solids
TTHM	total trihalomethane
UFRV	unit filter run volume
WM	City of Westminster
WOH	West-of-Hudson
WTS	water treatment systems















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#### AGREEMENT FOR PROFESSIONAL SERVICES

THIS AGREEMENT is made and entered into this \_\_\_\_\_ day of \_\_\_\_\_ 20\_\_\_\_ by and between the City of Northglenn, State of Colorado (hereinafter referred to as the "City") and (hereinafter referred to as "Consultant").

## RECITALS:

A. The City requires professional services.

B. Consultant has held itself out to the City as having the requisite expertise and experience to perform the required work for the Project.

NOW, THEREFORE, it is hereby agreed for the consideration hereinafter set forth, that Consultant shall provide to the City, professional consulting services for the Project.

## I. <u>SCOPE OF SERVICES</u>

Consultant shall furnish all labor and materials to perform the work and services required for the complete and prompt execution and performance of all duties, obligations, and responsibilities for the Project which are described or reasonably implied from **Exhibit A** which is attached hereto and incorporated herein by this reference.

## II. THE CITY'S OBLIGATIONS/CONFIDENTIALITY

The City shall provide Consultant with reports and such other data as may be available to the City and reasonably required by Consultant to perform hereunder. No project information shall be disclosed by Consultant to third parties without prior written consent of the City or pursuant to a lawful court order directing such disclosure. All documents provided by the City to Consultant shall be returned to the City. Consultant is authorized by the City to retain copies of such data and materials at Consultant's expense.

## III. OWNERSHIP OF WORK PRODUCT

The City acknowledges that the Consultant's work product is an instrument of professional service. Nevertheless, the products prepared under this Agreement shall become the property of the City upon completion of the work.

## IV. <u>COMPENSATION</u>

A. In consideration for the completion of the services specified herein by Consultant, the City shall pay Consultant an amount not to exceed (\$ ). Payment shall be made in accordance with the schedule of charges in **Exhibit B** which is attached hereto and incorporated herein by this reference. Invoices will be itemized and include hourly breakdown for all personnel and other charges. The maximum fee specified herein shall include all fees and expenses incurred by Consultant in performing all services hereunder.

B. Consultant may submit monthly or periodic statements requesting payment. Such request shall be based upon the amount and value of the work and services performed by Consultant under this Agreement except as otherwise supplemented or accompanied by such supporting data as may be required by the City.

1. All invoices, including Consultant's verified payment request, shall be submitted by Consultant to the City no later than the twenty-fourth (24th) day of each month for payment pursuant to the terms of this Agreement. In the event Consultant fails to submit any invoice on or before the

twenty-fourth (24th) day of any given month, Consultant defers its right to payment pursuant to said late invoice until the twenty-fourth (24th) day of the following month.

2. Progress payments may be claimed on a monthly basis for reimbursable costs actually incurred to date as supported by detailed statements, including hourly breakdowns for all personnel and other charges. The amounts of all such monthly payments shall be paid within thirty (30) days after the timely receipt of invoice as provided by this Agreement.

C. The City has the right to ask for clarification on any Consultant invoice after receipt of the invoice by the City.

D. In the event payment for services rendered has not been made within forty-five (45) days from the receipt of the invoice for any uncontested billing, interest will accrue at the legal rate of interest. In the event payment has not been made within ninety (90) days from the receipt of the invoice for any uncontested billing, Consultant may, after giving seven (7) days written notice and without penalty or liability of any nature, suspend all work on all authorized services specified herein. In the event payment in full is not received within thirty (30) days of giving the seven (7) days written notice, Consultant may terminate this Agreement. Upon receipt of payment in full for services rendered, Consultant will continue with all authorized services.

E. Final payment shall be made within sixty (60) calendar days after all data and reports (which are suitable for reproduction and distribution by the City) required by this Agreement have been turned over to and approved by the City and upon receipt by the City of Consultant's certification that services required herein by Consultant have been fully completed in accordance with this Agreement and all data and reports for the Project.

## V. COMMENCEMENT AND COMPLETION OF WORK

Within seven (7) days of receipt from the City of a Notice to Proceed, Consultant shall commence work on all its obligations as set forth in the Scope of Services or that portion of such obligations as is specified in said Notice. Except as may be changed in writing by the City, the Project shall be complete, and Consultant shall furnish the City the specified deliverables as provided in **Exhibit A**.

## VI. <u>CHANGES IN SCOPE OF SERVICES</u>

A change in the Scope of Services shall constitute any material change or amendment of services or work which is different from or additional to the Scope of Services specified in Section I of this Agreement. No such change, including any additional compensation, shall be effective, or paid unless authorized by written amendment executed by the City. If Consultant proceeds without such written authorization, then Consultant shall be deemed to have waived any claim for additional compensation, including a claim based on the theory of unjust enrichment, quantum merit or implied contract. Except as expressly provided herein, no agent, employee, or representative of the City shall have the authority to enter into any changes or modifications, either directly or implied by a course of action, relating to the terms and scope of this Agreement.

## VII. PROFESSIONAL RESPONSIBILITY

A. Consultant hereby warrants that it is qualified to assume the responsibilities and render the services described herein and has all requisite corporate authority and professional licenses in good standing, required by law.

B. The work performed by Consultant shall be in accordance with generally accepted professional practices and the level of competency presently maintained by other practicing professional firms in the same or similar type of work in the applicable community.

C. Consultant shall be responsible for the professional quality, technical accuracy, timely completion, and the coordination of all designs, drawings, specifications, reports, and other services furnished by Consultant under this Agreement. Consultant shall, without additional compensation, correct or resolve any errors or deficiencies in his designs, drawings, specifications, reports, and other services, which fall below the standard of professional practice, and reimburse the City for construction costs caused by errors and omissions which fall below the standard of professional practice.

D. Approval by the City of drawings, designs, specifications, reports, and incidental work or materials furnished hereunder shall not in any way relieve Consultant of responsibility for technical adequacy of the work. Neither the City's review, approval or acceptance of, nor payment for, any of the services shall be construed to operate as a waiver of any rights under this Agreement or of any cause of action arising out of the performance of this Agreement, and Consultant shall be and remain liable in accordance with applicable performance of any of the services furnished under this Agreement.

E. The rights and remedies of the City provided for under this Agreement are in addition to any other rights and remedies provided by law.

## VIII. INDEMNIFICATION

A. INDEMNIFICATION – GENERAL: The City cannot and by this Agreement does not agree to indemnify, hold harmless, exonerate or assume the defense of the Consultant or any other person or entity whatsoever, for any purpose whatsoever. Provided that the claims, demands, suits, actions or proceedings of any kind are not the result of professional negligence, the Consultant, to the fullest extent permitted by law, shall defend, indemnify and hold harmless the City, its Council members, officials, officers, directors, agents and employees from any and all claims, demands, suits, actions or proceedings of any kind or nature whatsoever, including worker's compensation claims, in any way resulting from or arising from the services rendered by Consultant, its employees, agents or subconsultants, or others for whom the Consultant is legally liable, under this Agreement; provided, however, that the Consultant need not indemnify or save harmless the City, its Council members, its officers, agents and employees from damages resulting from the negligence of the Council members, officials, officers, agents and employees.

B. INDEMNIFICATION FOR PROFESSIONAL NEGLIGENCE: The Consultant shall, to the fullest extent permitted by law, defend, indemnify and hold harmless the City, its Council members, and any of its officials, officers, directors, and employees from and against damages, liability, losses, costs and expenses, including reasonable attorneys fees, but only to the extent caused by or arising out of the negligent acts, errors or omissions of the Consultant, its employees, agents or subconsultants, or others for whom the Consultant is legally liable, in the performance of professional services under this Agreement. The Consultant is not obligated under this subparagraph IX.B. to indemnify the City for the negligent acts of the City, its Council members, or any of its officials, officers, directors, agents and employees.

C. INDEMNIFICATION – COSTS: Consultant shall, to the fullest extent permitted by law, defend, investigate, handle, respond to, and provide defense for and defend against, any such liability, claims or demands at the sole expense of Consultant or, at the option of the City, agrees to pay the City or reimburse the City for the defense costs incurred by the City in connection with any such liability, claims or demands. Consultant shall, to the fullest extent permitted by law, defend and bear all other costs and expenses related thereto, including court costs and attorney fees, whether or not any such liability, claims or demands alleged are groundless, false or fraudulent. If it is determined by the final judgment of a court of any competent jurisdiction that such injury, loss or damage was caused in whole or in part by the act, omission or other fault of the City, its Council members, officials, officers, directors, agents and employees, the City shall reimburse Consultant for the portion of the judgment attributable to such act, omission or other fault of the City, its Council members, officials, officers, directors, agents and employees.

D. To the extent this Agreement is subject to C.R.S. § 13-50.5-102(8), Contractor's liability under this provision shall be to the fullest extent of, but shall not exceed, that amount represented by the degree or percentage of negligence or fault attributable to Contractor, any subcontractor of Contractor, or any officer, employee, representative, or agent of Contractor or of any subcontractor of Contractor. If Contractor is providing architectural, engineering, surveying or other design services under this Agreement, the extent of Contractor's obligation to defend, indemnify and hold harmless the City may be determined only after Contractor's liability or fault has been determined by adjudication, alternative dispute resolution or otherwise resolved by mutual agreement of the Parties, as provided by C.R.S. § 13-50.5-102(8)(c).

#### IX. INSURANCE

A. Consultant agrees to procure and maintain, at its own cost, a policy or policies of insurance sufficient to insure against all liability, claims, demands, and other obligations assumed by Consultant pursuant to Section IX, above. Such insurance shall be in addition to any other insurance requirements imposed by this Agreement or by law. Consultant shall not be relieved of any liability, claims, demands, or other obligations assumed pursuant to Section IX, above, by reason of its failure to procure or maintain insurance, or by reason of its failure to procure or maintain insurance in sufficient amounts, durations, or types.

B. Consultant shall procure and maintain and shall cause any subcontractor of Consultant to procure and maintain, the minimum insurance coverages listed below. Such coverages shall be procured and maintained with forms and insurers acceptable to the City. All coverages shall be continuously maintained to cover all liability, claims, demands, and other obligations assumed by Consultant pursuant to Section IX, above. In the case of any claims-made policy, the necessary retroactive dates and extended reporting periods shall be procured to maintain such continuous coverage.

1. Worker's Compensation Insurance to cover obligations imposed by applicable laws for any employee engaged in the performance of work under this Contract, and Employer's Liability Insurance with minimum limits of five hundred thousand dollars (\$500,000) each incident, five hundred thousand dollars (\$500,000) disease - policy limit, and five hundred thousand dollars (\$500,000) disease - each employee.

2. Commercial general liability insurance with minimum combined single limits of one million dollars (\$1,000,000) each occurrence and two million dollars (\$2,000,000) general aggregate. The policy shall be applicable to all premises and operations. The policy shall include coverage for bodily injury, broad form property damage (including completed operations), personal injury (including coverage for contractual and employee acts), blanket contractual, products, and completed operations. The policy shall contain a severability of interests provision.

3. Professional liability insurance with minimum limits of six hundred thousand dollars (\$600,000) each claim and one million dollars (\$1,000,000) general aggregate.

C. The policy required by paragraph 2. above shall be endorsed to include the City and the City's officers, employees, and consultants as additional insureds. Every policy required above shall be primary insurance, and any insurance carried by the City, its officers, its employees, or its consultants shall be excess and not contributory insurance to that provided by Consultant. No additional insured endorsement to the policy required by paragraph 1. above shall contain any exclusion for bodily injury or property damage arising from completed operations. Consultant shall be solely responsible for any deductible losses under any policy required above.

D. The certificate of insurance provided for the City shall be completed by Consultant's insurance agent as evidence that policies providing the required coverages, conditions, and minimum limits are in full force and effect, and shall be reviewed and approved by the City prior to commencement of the Agreement. No other form of certificate shall be used. If the City is named as an additional insured on any policy which does not allow for the automatic addition of additional insureds, the Consultant's

#### Contract #XXXX-XXX

insurance agent shall also provide a copy of all accompanying endorsements recognizing the City as an additional insured. The certificate shall identify this Agreement and shall provide that the coverages afforded under the policies shall not be cancelled, terminated or materially changed until at least thirty (30) days prior written notice has been given to the City. The completed certificate of insurance shall be sent to:

City of Northglenn Attn: Kathy Kvasnicka 11701 Community Center Drive Northglenn, Colorado 80233-8061

E. Failure on the part of Consultant to procure or maintain policies providing the required coverages, conditions, and minimum limits shall constitute a material breach of agreement upon which the City may immediately terminate this Agreement, or at its discretion, the City may procure or renew any such policy or any extended reporting period thereto and may pay any and all premiums in connection therewith, and all monies so paid by the City shall be repaid by Consultant to the City upon demand, or the City may offset the cost of the premiums against any monies due to Consultant from the City.

F. The City reserves the right to request and receive a certified copy of any policy and any endorsement thereto.

G. The parties hereto understand and agree that the City, its officers, and its employees, are relying on, and do not waive or intend to waive by any provision of this Agreement, the monetary limitations (presently three hundred fifty thousand dollars (\$350,000) per person and nine hundred ninety thousand dollars (\$990,000) per occurrence) or any other rights, immunities, and protections provided by the Colorado Governmental Immunity Act, Colo. Rev. Stat.,§§ 24-10-101, et seq., as from time to time amended, or otherwise available to the City, its officers, or its employees.

#### X. <u>NON-ASSIGNABILITY</u>

Neither this Agreement, nor any of the rights or obligations of the parties hereto, shall be assigned by either party without the written consent of the other.

## XI. <u>TERMINATION</u>

This Agreement shall terminate at such time as the work in Section I is completed and the requirements of this Agreement are satisfied, or upon the City's providing Consultant with seven (7) days advance written notice, whichever occurs first. In the event the Agreement is terminated by the City's issuance of said written notice of intent to terminate, the City shall pay Consultant for all work previously authorized and completed prior to the date of termination. If, however, Consultant has substantially or materially breached the standards and terms of this Agreement, the City shall have any remedy or right of set-off available at law and equity. If the Agreement is terminated for any reason other than cause prior to completion of the Project, any use of documents by the City thereafter shall be at the City's sole risk, unless otherwise consented to by Consultant.

#### XII. CONFLICT OF INTEREST

The Consultant shall disclose any personal or private interest related to property or business within the City. Upon disclosure of any such personal or private interest, the City shall determine if the interest constitutes a conflict of interest. If the City determines that a conflict of interest exists, the City may treat such conflict of interest as a default and terminate this Agreement.

#### XIII. <u>VENUE</u>

This Agreement shall be governed by the laws of the State of Colorado, and any legal action concerning the provisions hereof shall be brought in the County of Adams, State of Colorado.

#### XIV. INDEPENDENT CONTRACTOR

Consultant is an independent contractor. Notwithstanding any provision appearing in this Agreement, all personnel assigned by Consultant to perform work under the terms of this Agreement shall be, and remain at all times, employees or agents of Consultant for all purposes. Consultant shall make no representation that it is the employee of the City for any purposes.

#### XV. <u>NO WAIVER</u>

Delays in enforcement or the waiver of any one or more defaults or breaches of this Agreement by the City shall not constitute a waiver of any of the other terms or obligation of this Agreement.

#### XVI. ENTIRE AGREEMENT

This Agreement and the attached **Exhibits A and B** is the entire Agreement between Consultant and the City, superseding all prior oral or written communications. None of the provisions of this Agreement may be amended, modified, or changed, except as specified herein.

#### XVII. SUBJECT TO ANNUAL APPROPRIATION

Consistent with Article X, Section 20 of the Colorado Constitution, any financial obligations of the City not to be performed during the current fiscal year are subject to annual appropriation, and thus any obligations of the City hereunder shall extend only to monies currently appropriated.

#### XVIII. NOTICE

Any notice or communication between Consultant and the City which may be required, or which may be given, under the terms of this Agreement shall be in writing, and shall be deemed to have been sufficiently given when directly presented or sent pre-paid, first class United States Mail, addressed as follows:

The City: City of Northglenn 11701 Community Center Drive Northglenn, Colorado 80233-8061

Consultant:

IN WITNESS WHEREOF, the parties hereto each herewith subscribe the same in duplicate.

## **CITY OF NORTHGLENN, COLORADO**

	By	/:	
ATTEST:		Drint Manua	
		Print Name	
Johanna Small, CMC City Clerk	Date	Title	Date
APPROVED AS TO FORM:			
Corey Y. Hoffmann City Attorney	Date		
		CONSULTANT:	
	Ву	<u>r</u>	
ATTEST:		Print Name	
Ву:		Fint Name	
		Title	Date
Print Name			
Title	Date		

Attach Exhibit A "SCOPE OF SERVICES" and Exhibit B "AMOUNT OF COMPENSATION"

Indicate on the bottom of each page

EXHIBIT A – Page 1 of ? EXHIBIT B

- Page 1 of ?

Then discard this page