TITLE. Biological filtration is resilient to wildfire ash-associated organic carbon threats to drinking water treatment

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ABSTRACT: Elevated/altered levels of dissolved organic matter (DOM) in water can be challenging to treat after wildfire. Biologically-mediated treatment removes some DOM; its ability to remove elevated/altered post-fire dissolved organic carbon (DOC) resulting from wildfire ash was therefore investigated. The treatment of low, medium, and high wildfire ash-amended source waters by bench-scale biofilters was evaluated in duplicate. Turbidity and DOC were typically well-removed during periods of stable operation (effluent turbidity ≤ 0.3 NTU in 93% of samples, average DOC removal ~20% in all biofilters during periods of non-impaired DOC removal). Daily DOC removal across all biofilters was generally consistent, suggesting that the wildfire ash and associated water extractable organic matter did not reduce the DOC biodegradation capacity of the biofilters. DOM fractionation indicated that this was because the low molecular weight neutral (which are known to be readily biodegradable) and biopolymer fractions of DOM were reduced; however, humics were largely recalcitrant. Thus, biological filtration may be resilient to wildfire ash-associated DOM threats to drinking water treatment. However, operational resilience may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, as was observed when baseline source water quality fluctuated for brief periods during the investigation.

INTRODUCTION.

Wildfire threats to water supplies are recognized globally.[1-3] After wildland fire, vegetation is reduced or absent and more precipitation reaches the land surface,[4] leading to increased erosion and solids runoff;[5,6] even at large basin scales in systems with already deteriorated water quality.[7] Accordingly, solid-associated metals,[8] nutrients,[9-11] and other contaminants[12,13] also can be elevated—or transformed in the case of natural organic matter (NOM)—in wildfire-impacted waters.[14] Longer-term releases of bioavailable phosphorus from sediments to the water column also have been observed in some areas.[15,16] They promote primary productivity[10] and the proliferation of algae that can produce toxins of human health concern—these effects are magnified when they converge with those from anthropogenic landscape disturbances.[17] Collectively, these impacts underscore that wildfires can challenge treatment plants beyond their operational capacity, ultimately resulting in increased infrastructure and operating costs, service disruptions, or outages.[9,18]

While elevated turbidity can be treated with conventional technologies, elevated/altered NOM can be challenging. It is typically described by characterization of dissolved organic carbon (DOC) concentrations and aromaticity that can challenge treatment, especially when rapidly fluctuating.[19,20] Although DOC is not a regulated "contaminant", elevated source water DOC increases coagulant demand[21] and is a precursor for potentially harmful disinfection by-products.[22,23] Moreover, smaller, more aromatic, and thus more difficult to coagulate post-fire DOC has been suggested;[9,14,24] more aromatic DOC also tends to lead to greater formation of regulated disinfection by-products.[25,26] These DOC-associated post-fire treatment concerns emphasize the need for water supply and treatment resilience, potentially in the form of techno-ecological approaches, to respectively mitigate these threats at the source and/or in treatment plants.[27,28]

Biologically-mediated drinking water treatment technologies may offer treatment resilience in buffering altered aquatic DOC concentrations and character after wildfire. While conventional filtration focuses solely on achieving particle and pathogen removal and requires pre-treatment by chemical coagulants for effective operation even when source water quality is high,[29] biological filtration offers additional treatment benefits, including reductions of taste and odor compounds, NOM, and therefore regulated disinfection by-products.[30-33] Biological filtration also improves the biological stability of drinking water in distribution systems.[34] Particle, pathogen, and DOC removal by biological filtration depends on biofilm formation and biodegradation.[32,33] Biological filtration processes range from classical—biofiltration in an otherwise conventional treatment plant (i.e., preceded by coagula-

tion/flocculation/clarification and sometimes advanced oxidation processes such as pre-ozonation)—to slow sand filtration (SSF) that is typically operated without chemical or other types of pre-treatments.[28,32] Thus, while they may include physico-chemical filtration that relies on synergies between particle size, media depth, media size, particle destabilization by coagulation, and media roughness,[35-38] biodegradation, biotransformation, adsorption, and bioregeneration may also contribute to treatment. Critically, however, biological filtration performance is not directly proportional to the amount of biomass present;[31,39,40] thus, lab- and pilot-scale assessments remain critical to demonstrating biological treatment capabilities.

Biological filtration preferentially removes low molecular weight (LMW) compounds[41,42] that may be present in wildfire-impacted source waters.[14] Accordingly, it may offer treatment resilience in buffering elevated source water DOM after wildfire. Thus, biological treatment is a reasonable option for the management of wildfire ash-associated organic carbon threats to the provision of safe drinking water. Treatment by SSF is a logical starting point because it is differentiated from other types of biological filtration in that particles and dissolved constituents are predominantly removed in a layer of biologically active material associated with and atop the filter media, called the schmutzdecke, rather than throughout the depth of the filter.[43-45] Low hydraulic loading rates (HLRs) and extended contact times (relative to classical biofiltration) promote biodegradation of DOC, even without chemical or energy-intensive pre-treatments such as coagulation or pre-ozonation.[46,47] Thus, biological filtration with relatively long contact times is the most likely design configuration to enable demonstration of treatment resilience in buffering elevated source water DOM resulting from wildfire ash because kinetic limitation is practically precluded—a proof-of-concept evaluation was the focus of this investigation. Specifically, the resilience of biological filtration treatment in reducing elevated/altered post-fire DOC resulting from wildfire ash was investigated.

METHODOLOGY & METHODS.

Experimental approach. Bench-scale biological filtration experiments were conducted using wildfire ash-amended source water (in duplicate at three levels: low, medium, and high ash content) from an agriculturally- and municipally-impacted watershed.[48] This water was pre-treated by roughing filtration to removed suspended solids to a level ($\leq$ 5 NTU)[45] appropriate for subsequent treatment by biological filtration. Given that altered NOM (measured as DOC concentrations and/or character that are episodically altered) results in some of the most significant treatment challenges commonly observed after wildland fire, DOC removal was investigated here. Two-, four-, and seven-day disturbances were investigated because they are consistent with or longer than many observations of episodically elevated DOC after wildfire.[9,16,49-53] Each DOC pulse was followed by a one-week return to "baseline" source water without ash amendment. Figure 1 depicts the operational conditions during bench-scale experimental evaluations.

"Baseline" source water and preparation of ash disturbance-impacted source water. Baseline source water samples were collected from flowing Grand River water approximately five feet from shore, directly below water surface, every 7-10 days in Kitchener, Ontario (43°25'21.8"N 80°24'48.1"W). Water quality was subsequently characterized (as described below). Raw water was acclimatized to room temperature for a period of between one to 7 days before being fed to the biofilters or used to prepare the disturbance-impacted source water as described below.

Wildfire ash-impacted source water was created by amending the river water with ash collected on September 22, 2020, from the 2020 Doctor Creek wildfire (N21257, high burn severity) in British Columbia, Canada (50°05'00.2"N 116°03'52.6"W).[54] Disturbance-impacted source waters were created at three levels of ash content intended to correspond to disturbance "severity" and associated source water quality deterioration: low (0.25 g of ash/L of Grand River source water), moderate (0.50 g of ash/L of Grand River source water), and high (1.00 g of ash/L of Grand River source water; detailed water quality in Table S1). To ensure water extractable organic matter (WEOM) was adequately leached from the ash, each ash matrix was mixed for 18 hours at a rate of 200 RPM for two hours, followed by mixing for 16 hours at a rate of 180 RPM (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester). Following mixing and a subsequent three hours settling period to reduce turbidity, settled water quality was analyzed (Table S1).

Bench-scale filter design and operation. Bench-scale SSF-like biofilters with low HLRs and extended contact times (relative to classical biofiltration) were used because they represent operational scenarios in which maximal biodegradation of DOC would be expected.[46,47] The suitability of using bench-scale biofilters to reasonably represent aspects of pilot- and full-scale biological filtration performance such as the ability to remove dissolved contaminants is generally understood[55-57] and has gained renewed interest in recent years.[58,59] Thus, this approach was used here and enabled duplicate evaluation of several source water quality ash content scenarios and disturbance periods.

The biofilters were designed to ensure that porosity oscillations caused by small column diameter relative to grain size—wall effects—were negligible.[60] (Bear, 1972). Consideration of mass transfer dynamics was also incorporated. Lower HLRs at a given empty bed contact time (EBCT) may result in lower DOC removal if external mass transfer—rather than the reaction rate—is rate-limiting.[59] To confirm that the reaction rate is rate-limiting, the Damkohler number II (i.e., the ratio of reaction rate to mass transfer rate) was estimated for the bench-scale biofilter design specifications (Supporting Information, S3). Non-adsorptive filter media were used to ensure that only biotic DOC removal in the biofilters was evaluated.

Eight bench-scale filters were used. They had an inner diameter of 26 mm and a bed depth of 70 cm, which is in the recommended range of filter depths for SSF.[45] The filter media consisted of clean quartz sand with an effective size of 0.20 mm and uniformity coefficient of 1.5, which are also consistent with typical SSF design.[61] The filters were continuously operated in down-flow mode for approximately five months, with 103 days of acclimation and a 50-day experimental period. The filters were operated at room temperature (19-22°C) with an extended EBCT of approximately 10 hours (corresponding HLR of 0.07 m/h), which represents the upper ranges of previously reported EBCTs in full-scale SSF.[46,62] They were covered in aluminum foil to prevent photosynthesis. When maximum headloss was reached, they were maintained by scraping the schmutzdecke so that the underlying filter

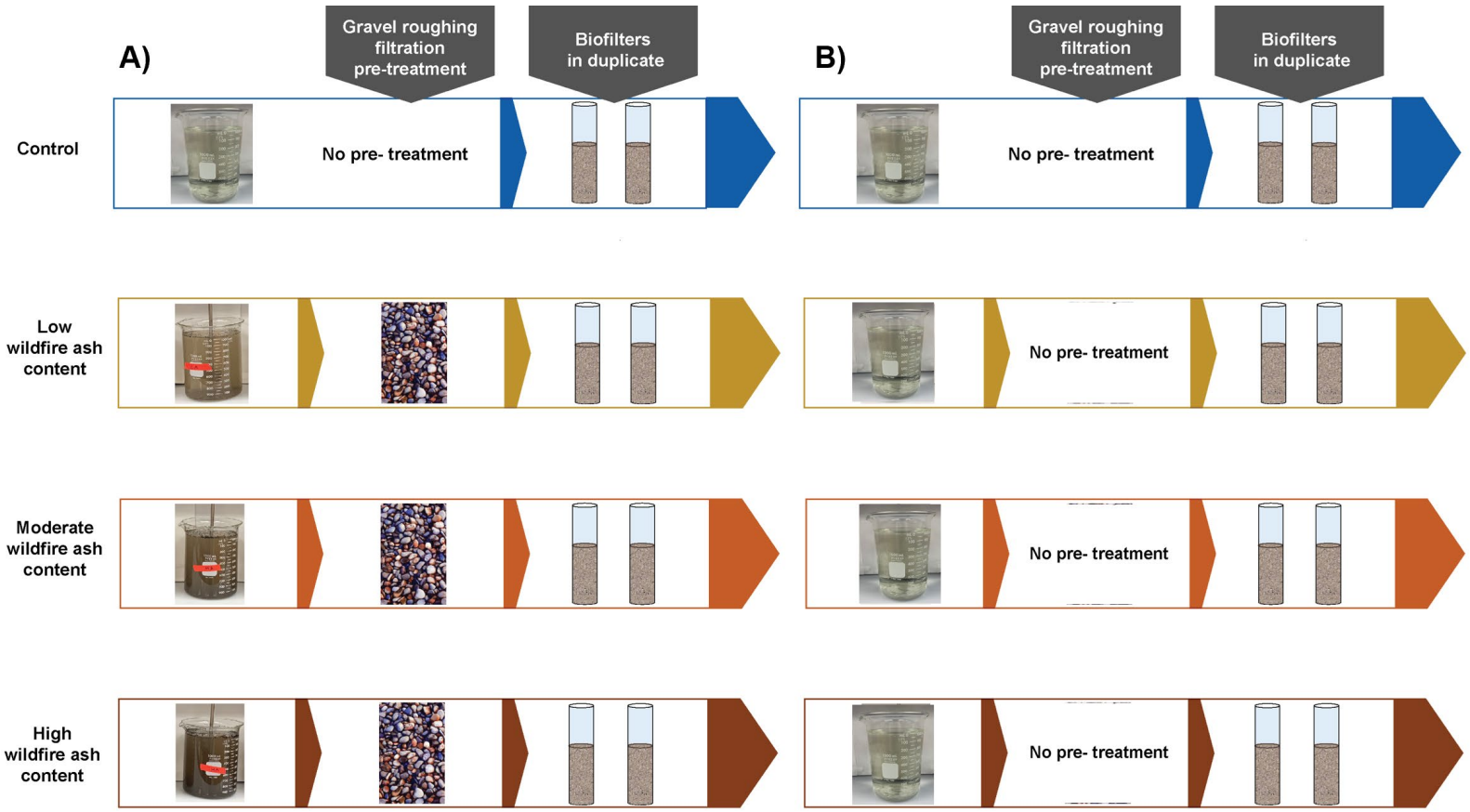

Figure 1. Operational conditions during the bench-scale experimental evaluation (Days 1 to 50, 8 biofilters) of biofilter treatment resilience in (A) buffering elevated aquatic NOM resulting from low, moderate, and high wildfire ash content (for 2-, 4-, and 7-days periods), followed by a (B) return to baseline source water quality conditions for approximate one week after each disturbance. Biofilters were acclimatized for 103 days prior to start of 50-day experiments.

media were visible.[45] This was done immediately prior to each period of ash disturbance so that biofilter performance and treatment resilience were evaluated during filter ripening when performance is most vulnerable.[45,63]

Pre-treatment of disturbance-impacted water was limited to settling (described below) and gravel roughing filtration to target an influent turbidity of ≤ 5 NTU to prevent filter clogging and shortened run times. The roughing filters had an inner diameter of 5 cm and a bed depth of 30 cm; they were operated intermittently at an HLR of 0.31 m/h. To ensure that DOC removal only within the biofilters was evaluated, the gravel media within the roughing filters were rinsed and the filters were re-packed after no more than 24 hours of run-time. Roughing filter effluent water quality was analyzed as described below.

Water quality analyses. Standard methods[64] were used to evaluate turbidity (Method 2130B; Hach 2100 N turbidimeter, Loveland, CO), pH (4500-H+B Electrometric method; Orion 720A pH meter, Thermo Fisher Scientific, Waltham, MA), alkalinity (Method 2320; titration method with pH endpoint of 4.5), DOC concentration (filtration through pre-rinsed 0.45 µm Nylaflo membranes, Pall, Port Washington, NY; Method 5310B; Shimadzu TOC-V CPH analyzer, Kyoto, Japan), and ultraviolet absorbance (UVA_{254}; Method 5910B; 1 cm quartz cell; Hach DR 5000 Spectrophotometer, Loveland, CO). Specific ultraviolet absorbance at 254 nm (SUVA) was calculated by dividing UVA_{254} absorbance by the DOC concentration (Weishaar et al., 2003).

Liquid chromatography in combination with organic carbon detection (LC-OCD) was used to fractionate DOC (as biopolymers [BPs], humic substances [HS], building blocks [BB], low molecular-weight [LMW] neutrals, LMW acids) as described in Huber et al.[65] Samples were first filtered through a pre-rinsed 0.45 µm polyethersulfone membrane (Millipore Express® PLUS; Merck Millipore, Burlington, MA). Chromatographic separation was completed using a weak cationic exchange column (Toyopearl, TSK HW 50S, Tosoh, Japan).

Statistical analyses. A paired-samples t-test was conducted to compare the influent and effluent DOC concentrations and UVA_{254} measurements between all filters throughout the experimental period. The assumptions of a paired t-test are that (1) the differences between the matched pairs follows a roughly normal distribution and (2) that the variance between the two data sets is approximately equal. These assumptions were tested by visually inspecting normal scores plots for the differences between the matched pairs. Additionally, a heteroscedastic t-test for the difference between the means of control and disturbance severity conditions with respect to DOC % removal was also conducted. Two-tailed tests were conducted using the p-value approach. All assumptions, normal scores plots, and t-test equations are presented in Supporting Information S2.

RESULTS & DISCUSSION.

Performance of bench-scale biofilters. Turbidity was effectively reduced in all biofilters (effluent turbidity ≤ 0.3 NTU in 93% of samples throughout 153 days of filter operation, never exceeding 1.0 NTU) (Figures S1-S8) and pH and alkalinity remained stable through the biofilters (Figures S17-S32). Thus, filter performance met or exceeded performance expectations.[45,66] DOC removal varied considerably throughout the 50-day experimental period, ranging from negative to approximately 40% removal. DOC concentrations typically decreased significantly from influent to effluent across all biofilters ($p \leq 0.026$ for all filters; Supporting Information, S2) and were consistent with those reported for various types of biological filtration. For example, Collins et al.[46] reported 12-33% removal of DOC in several full-scale SSF plants with EBCTs ranging from 3.8 to 21.9 hours, while Vines & Terry[67] reported only 7-8% DOC removal in bench-scale anthracite biofilters (EBCTs of 5 to 30 minutes). DOC removals of 12-38% by classical biological activated carbon filtration (i.e., preceded by coagulation/flocculation/clarification) with pre-ozonation also have been reported.[42] Full-scale classical biofiltration treating Grand River water achieved average total organic carbon removals of 14% with anthracite filter media and 23% with granular activated carbon filter media.[31] Here, the use of an SSF-based approach that did not include absorptive filter media or pre-treatment to remove or enhance the removal of more hydrophobic DOM (i.e., coagulation) or more recalcitrant DOM (i.e., post-clarification ozonation) resulted in DOC removals that were generally consistent with previous reports describing both classical biofiltration and SSF performance. It should be highlighted that despite the average to high overall extent of DOC removal observed herein, episodic impairment of DOC removal was also observed in all biofilters (regardless of wildfire ash amendment) in association with seasonal changes in source water quality that are known to occur during the fall. These periods are discussed below.

A small but significant decrease in UVA_{254} from biofilter influent to effluent was observed across all experimental conditions ($p \leq 1.16E\text{-}05$, average change in daily UVA_{254} measurements ≤ 0.012 cm^{-1}). The observation of limited capacity to reduce UVA_{254} is consistent with other reports of biological filtration performance[42,67] and common understanding of associated treatment mechanisms. Substantial reductions in UVA_{254} across the biofilters were not expected because (i) UVA_{254} reflects both DOC concentration and aromaticity,[68] (ii) WEOM is typically more aromatic when an impact of wildland fire on source water DOM is observed,[14] and (iii) aromatic DOC is less biodegradable than more aliphatic DOC.[41,42,69] Thus, while the biofilters were able to reduce UVA_{254} somewhat, the extent of removal diminished as more of the influent UVA_{254} was derived from wildfire ash addition (i.e., higher ash content). Importantly, the biofilter DOC, UVA_{254}, and LC-OCD removal data collectively demonstrate that while the biofilters were not designed to mimic all aspects of full-scale biofiltration (especially not operational aspects such as headloss accumulation), they provided representative and therefore reasonable indication of the biodegradation capabilities of biological filtration processes. Thus, the bench-scale biofilter design was suitable for evaluating DOM removal by biological filtration and the potential for treatment resilience in buffering elevated source water DOM resulting from wildfire ash.

Impact of wildfire ash on DOC removal by biofilters. DOC removal across all biofilters was generally consistent (Figures 2 and 3); significant differences in average DOC removals were not observed between biofilters treating baseline or ash-amended waters during the study ($p \geq 0.489$ in all cases). Moreover, DOC removal in biofilters treating ash-amended source water remained consistent with that in the control biofilters. For a brief period immediately after the return to baseline source water after the two-day period of ash amendment, DOC removal was significantly lower in the biofilters treating high ash content-impacted water than in control

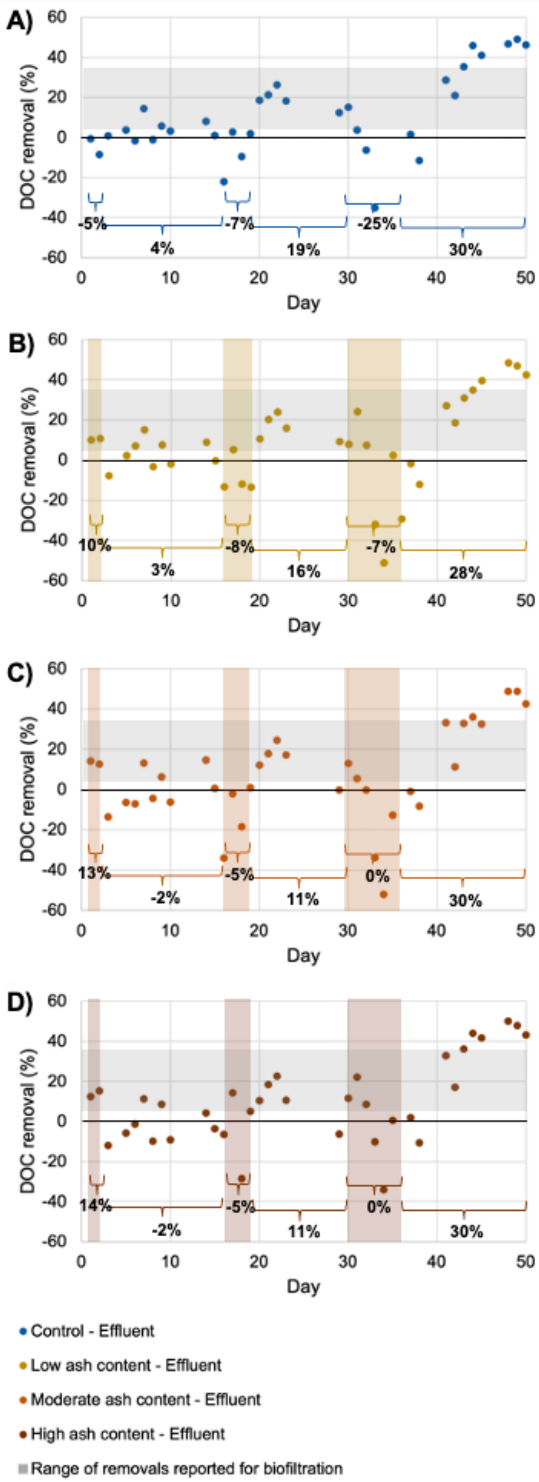

Figure 2 Daily DOC removal (%) by biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content Grand River water. Vertical shaded regions indicate when ash-amended source water entered filters, and braces correspond to average DOC removals for the periods indicated. Biofilters were acclimated for 103 days prior to start of 50-day ash experiments.

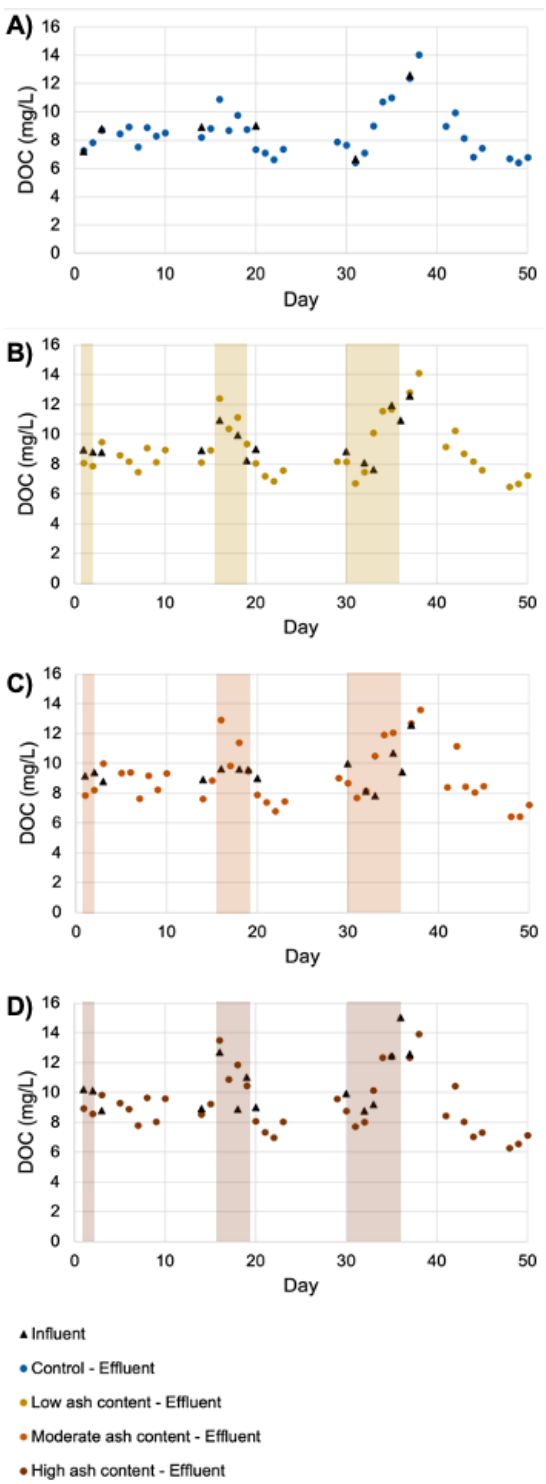

Figure 3 Daily change in DOC concentrations across biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content source water. Vertical shaded regions indicate when ash-amended source water was fed to filters. Biofilters were acclimated for 103 days prior to start of 50-day ash experiments.

biofilters ($p \leq 0.0271$)—this type of performance difference was not observed after the other experiments involving ash addition to the source water ($p \geq 0.146$) (Figure 2). These data may suggest that while the biofilters are adjusting from high nutrient (i.e., LMW neutral DOC) availability to lower availability, biofilters may release some DOC while communities adjust to these shifts. Moona et al.[70] suggested such shifts when periods of low biological activity coincided with negative concentration gradients and attributed their observations to organic matter desorption from filter media. While these brief periods of performance difference cannot be elucidated mechanistically herein, they underscore the need to better understand DOC removal mechanisms (e.g., adsorption, biodegradation, bioregeneration) in biological filtration processes.

In the water industry, it is widely recognized that brief periods of treated water quality fluctuation occur regularly (e.g., filter ripening, hydraulic surges) but are not necessarily indicative of process failure.[71] It is for this reason that regulatory compliance monitoring for demonstrating well-operated treatment relies on synoptic sampling (e.g., EPA[72]) and 95th percentile water quality performance thresholds (e.g., EPA[73]) rather than imposing absolute criteria. Here, despite brief periods of performance difference in some cases, the biofilters promptly recovered from "shock loads" associated with wildland fire ash delivery to source water and did not exhibit long-lasting DOC removal performance deterioration as a result of the rapid change in source water quality (including increased influent DOC concentrations) relative to baseline source water quality. Thus, these data indicate that biological filtration processes such as SSF offer resilience in buffering elevated source water DOM after wildfire. They also suggest that the wildfire ash and associated WEOM and any other materials that the ash released to the water matrix did not reduce/inhibit the DOC biodegradation capacity of the biofilters because differences in DOC removal by the biofilters treating wildfire ash-impacted water and the control biofilters were not observed.

Interestingly, the present investigation suggests enhanced DOC removal (on a per cent basis) in biofilters treating wildfire ash-impacted water relative to control biofilters treating baseline source water. Average DOC removal during the two-day ash disturbance period was significantly higher in each of biofilters treating wildfire ash-impacted water relative to the control biofilters ($p = 0.0044$, 0.0012, and 0.0012 for biofilters receiving low, moderate, and high ash content-amended water, respectively). DOC fractionation by size exclusion chromatography (i.e., LC-OCD analysis) revealed that biopolymers were most effectively removed by biofilters compared to other LC-OCD components (Figure 4), consistent with other studies.[74-79] In contrast, So et al.[42] reported that building blocks and LMW neutrals were removed more efficiently than biopolymers and humic substances. A possible explanation for divergent observation could be that biofiltration in this study was in the context of otherwise conventional treatment with pre-ozonation, which can impact biodegradability of DOC.[39] Even during periods of impaired DOC removal, such as in the week

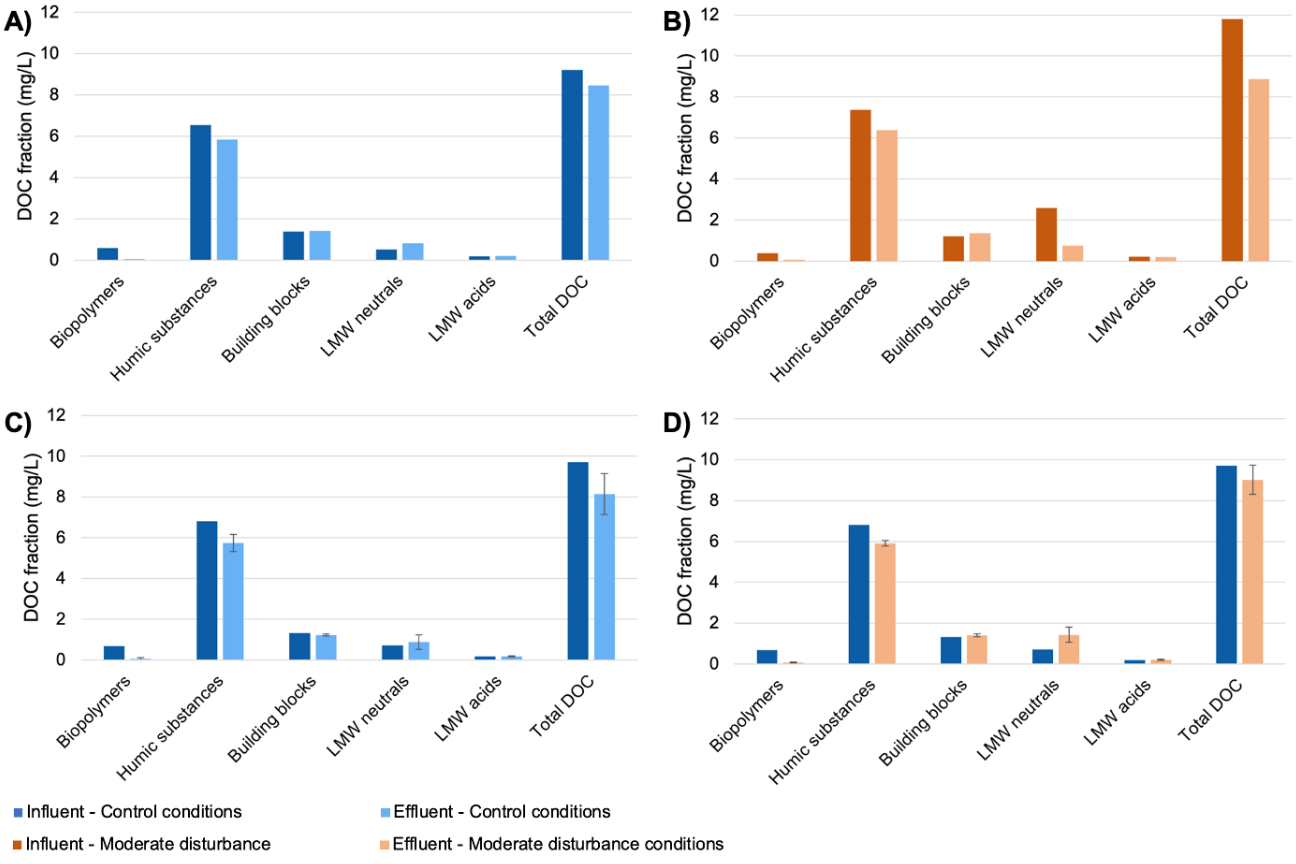

Figure 4 LC-OCD fractionation of influent and effluent DOC in (A) control biofilters during two-day ash trial (day 1 and 2), (B) biofilters treating moderate ash content water during two-day ash trial (day 1 and 2), (C) control biofilters during return to baseline period following two-day ash trial (days 3 to 15; n=4), and (D) biofilters treating moderate ash content water during return to baseline source water following two-day ash trial (days 3 to 15; n=4). Error bars indicate standard deviations where mean LC-OCD results are presented.

following the two-day ash disturbance period, biopolymers were typically still well removed, while LMW neutrals increased from the influent to the effluent, indicating transformation or incomplete degradation (Figure 4 C vs D).

DOC fractionation also revealed that the enhanced DOC removal was likely attributable to the greater proportion of LMW neutrals comprising WEOM in wildfire ash-impacted filter influent streams compared to control biofilters treating only baseline source water (Figure 4 A vs B). LMW neutrals are readily biodegradable, and their removal during biofiltration has been well-documented;[42,77,79] they tend to be removed even more effectively in biofiltration preceded by ozonation.[42,77] This behaviour was observed again in biofilters receiving source water amended with high ash content during the 7-day ash disturbance period ($p = 0.0187$), where LMW neutrals were elevated in the ash-amended source water relative to the control (0.74 mg/L and 1.19 mg/L, respectively; Table S5). In contrast, enhanced DOC removal in biofilters treating ash-amended source water was not observed during the four-day ash disturbance period ($p \geq 0.344$ for all cases)—this was likely because of the shift in baseline source water quality during this period, discussed below. Collectively, these results underscore that the extent of DOC removal that can be achieved by biofiltration depends on its character and associated bioavailability.

As indicated above, while DOC removal across experimental conditions was generally consistent, it did vary over the course of the study. All of the biofilters (regardless of ash amendment to the baseline source water) exhibited a few brief periods of biofilter performance decline, likely in association with seasonal fluctuations in source water quality (Figures 2-4). Seasonal water quality changes, including those in DOM, in the Grand River have been well documented. In the summer, primary production is at its highest and discharge is at its lowest. During the fall, nutrient and dissolved oxygen concentrations shift.[40,80,81] For a relatively brief period, DOM in the Grand River is more allochthonous in the fall than in the summer, as indicated by DOC fractionation analyses by LC-OCD during the present study (Table S2), and substantial increases in humic-like fluorescence/DOC and larger sizes of DOC molecules observed in other investigations.[82] Higher DOC/DON ratios and lower protein content consistent with more allochthonous organic matter have also been observed during this period.[82] Accordingly, it is not surprising that DOC removal by the biofilters was severely reduced during these brief periods (Figures 2-4) because a greater proportion of DOC is known to be less biodegradable during these transitional periods (Table S2).[40,81,82] Although no significant changes in bulk water quality were observed during the present study, historical data and accounts including full-scale plant data corroborate reduced biological filtration performance during the fall "transitional" period.[31,83] Although biomass was not quantified herein because it is not directly indicative of biological activity,[31,39,40] breakthrough of biopolymers during the four-day ash disturbance period and return to baseline period following the four-day ash disturbance period (Tables S3-S4) suggests the passage of extracellular polymeric substances from stressed or dead bacterial cells. Further evaluation of the source water quality and ecohydrological factors contributing to these periods of biofilter performance decline merits investigation but was beyond the scope of the present investigation. While these periods of biofilter performance decline did not preclude demonstration of biofilter resilience in buffering elevated source water DOM after wildfire, they did underscore the need to (i) further evaluate biofilter resilience during a variety of operational conditions, including periods of seasonal change in source water quality and (ii) develop watershed monitoring programs to better understand how shifts in source water quality affect drinking water treatability, especially in a changing climate.

UVA_{254} measurements complement LC-OCD analyses to provide additional insight into biodegradability of WEOM derived from wildfire ash used in the present study. UVA_{254} of the ash-amended source water consistently increased with higher contents of ash added (i.e., from low to high ash content, Figure 5), despite inconsistent increases in DOC with sequentially higher ash content (Figure 3). Relatively lower influent UVA_{254} during the 7-day ash disturbance relative to other ash-disturbance periods was expected given the lower baseline source water UVA_{254}. This good correlation of wildfire ash content with UVA_{254} (rather than DOC concentration) is consistent with previous wildfire ash studies.[20] As discussed above, LC-OCD analyses revealed that LMW neutrals and smaller amounts of humics by mass were added to source water with ash-amendment (Figure 4 A vs B; Table S5). Since LMW neutrals do not contribute to UVA_{254},[65] the observed increase in UVA_{254} in ash-amended source waters is likely driven by the relatively small addition of humics. Humics are not typically well-removed by biofiltration[76,78,85] since they are not readily biodegradable;[41,86] thus, it is not surprising that average daily change in UVA_{254} measurements throughout the 50-day experiment was significantly lower in all biofilters treating ash-amended water relative to control biofilters ($p \leq 0.034$) and thus emphasizes the insights obtained from DOC characterization by fractionation.

Collectively, the UVA_{254} and the DOC concentration and fractionation data provide a proof-of-concept demonstration that is supported by mechanistic insights regarding wildland fire ash-associated changes to DOM character that enable reductions in DOM by biofiltration. These results can likely be extended beyond SSF configurations (i.e., those with extended contact times) to other biological filtration processes with shorter contact times because it has been widely shown that most removal of DOC occurs at the top of the filter media,[31,87] corresponding to shorter contact times. The importance of contact time (typically reflected as EBCT) for DOC removal in biological filtration processes has been well-documented at relatively short timescales (i.e., minutes).[87] It is unlikely that extended contact times would result in enhanced DOC removal, as less readily biodegradable DOC is also less likely to be removed by biofiltration,[42,69,88] regardless of contact time. Notably, the extended contact time of 10 hours employed herein did not improve removal of aromatic or humic substances relative to their removal in more typical biofiltration configurations (with contact times ranging from 10-30 minutes).[42,77,87] Increased EBCT is not likely to further enhance DOC removal of elevated, wildfire ash-associated WEOM because (i) only the biodegradable fractions of DOC are removed by biological filtration and (ii) it is the removal of those fractions that was reflected in biofilter buffering of elevated source water DOM leached from wildland fire ash. Thus, this work suggests that implementation of biological filtration processes for enhanced NOM removal or as climate change adaptation strategies is not advisable in situations where NOM is especially aromatic or largely comprised of humic substances unless it is preceded by coagulation optimized for NOM removal or oxidation by

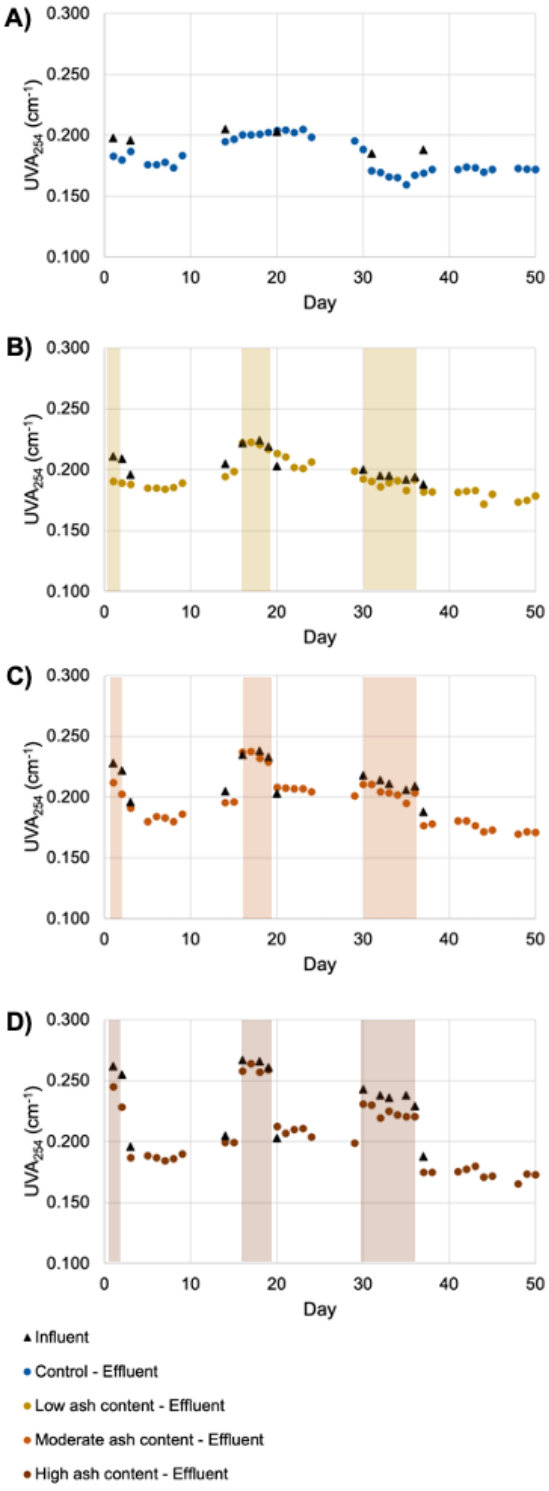

Figure 5 Daily change in UVA_{254} measurements across biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content source water. Vertical shaded regions indicate when ash-amended source water was fed to filters.

ozonation for increased biodegradability (and subsequent removal by biofiltation). Additionally, the brief periods of biofilter performance decline that were observed herein underscore that source water DOM can fluctuate in biodegradability.[40,81,82] Overall, this work underscores the need for improved aquatic carbon characterization in response to increasing climate-exacerbated landscape disturbances and integration of that understanding into treatment prioritization and design. Further research is also needed to evaluate treatment by biological filtration of source water impacted by ash rich in heavy metals such as mercury that may lead to elevated concentrations in impacted receiving waters[9,89] and possibly inhibit biological activity,[90] thereby compromising biofilter performance. Such evaluation was beyond the scope of the present investigation.

CONCLUSIONS.

Overall, this investigation demonstrated that biological filtration processes offer resilience in buffering elevated source water DOM after wildfire. Notably, all of the biofilters (regardless of ash amendment to the baseline source water) exhibited brief periods of biofilter performance decline, likely in association with seasonal fluctuations in source water quality, not ash delivery to the source water matrix. While these periods of biofilter performance decline did not preclude demonstration of biofilter resilience in buffering elevated source water DOM after wildfire, they did underscore the need to (i) further evaluate biofilter resilience during a variety of operational conditions, including periods of seasonal change in source water quality and (ii) develop watershed monitoring programs to better understand how shifts in source water quality affect drinking water treatability, especially in a changing climate.

UVA_{254} measurements and LC-OCD analyses revealed that WEOM derived from ash resulted in increased relative mass of LMW neutrals and, to a lesser degree, humics fractions in ash-amended source waters. There was evidence of increased DOC removal in biofilters treating wildfire ash-impacted water relative to the control biofilters during the two-day ash disturbance period, although this observation was weak or absent during other disturbance periods when DOC removal was impaired in all biofilters. LC-OCD analyses revealed that the enhanced DOC removal was likely attributable to the greater proportion of readily biodegradable LMW neutrals comprising WEOM in wildfire ash-impacted filter influent streams compared to control biofilters treating only baseline source water. UVA_{254} measurements and LC-OCD analyses revealed that humics, which are a main driver of UVA_{254},[65] were less effectively removed by biofilters treating ash-amended water relative to control biofilters. These observations highlight the importance of DOC characterization when evaluating biological filtration resilience in buffering elevated source water DOM, especially given that more aromatic DOM tends to result in greater formation of regulated DBPs.[25,26] They also suggest that resilience of biological filtration may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, as was observed when baseline source water quality fluctuated for brief periods during the investigation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Supporting Information (PDF) containing:

- S1: Additional water quality analyses (Figures S1-S32, Tables S1-S5)
- S2: Statistical analyses (Equations S1-S4, Figures S33-S34, Tables S6-S9)

- S3: Damkoher number II estimation (Equations S5-S20, Table S10)

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Notes

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SYNOPSIS TOC. Biological filtration can offer resilience to wildfire ash-associated organic carbon threats to drinking water treatment—but other water quality considerations compromise resilience.