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Biological Filtration is Resilient to Wildfire Ash-Associated Organic Carbon Threats to Drinking Water Treatment

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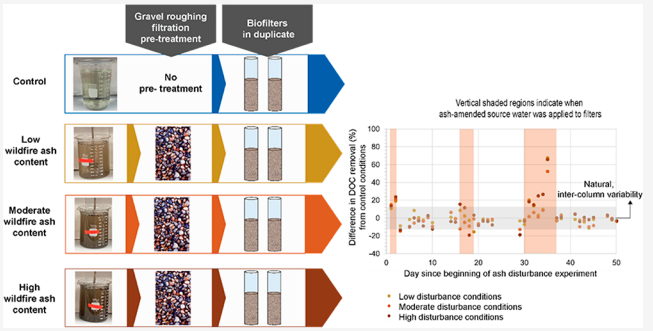
ABSTRACT: Elevated/altered levels of dissolved organic matter (DOM) in water can be challenging to treat after wildfire. Biologically mediated treatment removes some DOM; here, its ability to remove elevated/altered postfire dissolved organic carbon (DOC) resulting from wildfire ash was investigated for the first time. Treatment of wildfire ash-amended (low, moderate, high) source waters by bench-scale biofilters was evaluated in duplicate. Turbidity and DOC were typically well-removed (effluent turbidity ≤0.3 NTU; average DOC removal ~20%) in all biofilters during periods of stable source water quality. Daily DOC removal across all biofilters (ash-amended and controls) was generally consistent, suggesting that (i) the biofilter DOC biodegradation capacity was not deleteriously impacted by the ash and (ii) the biofilters buffered the ash-associated increases in water extractable organic matter. DOM fractionation indicates this was because the biodegradable low molecular weight neutral fractions of DOM, which increased with ash addition, were reduced by biofiltration while humic substances were largely recalcitrant. Thus, biological filtration was resilient to wildfire ash-associated DOM threats to drinking water treatment, but operational resilience may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, as was observed during brief periods herein.



KEYWORDS: *biofiltration, slow sand filtration, natural disturbance, climate change adaptation, NOM, WEOM, LC-OCD*

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 and the proliferation of algae,[10] including cyanobacteria, that can produce toxins of human health concern[17]—these effects are magnified when they converge with those from anthropogenic landscape disturbances.[18] 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.[9,19]

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.[20,21] Although DOC is not a regulated "contaminant", elevated source water DOC increases coagulant demand[9,22] and is a precursor for potentially harmful disinfection byproducts.[23,24] The occurrence of smaller, more aromatic, and thus more difficult to coagulate postfire DOC has been suggested.[9,14,25] More aromatic DOC also tends to lead to greater formation of regulated disinfection byproducts.[26,27] These DOC-associated postfire treatment concerns emphasize the need for water supply and treatment resilience, potentially in the form of techno-ecological nature-based solutions such as biofiltration, to mitigate these respective threats at the source and/or in treatment plants.[28,29]

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 pretreatment by chemical coagulants for effective operation even when source water

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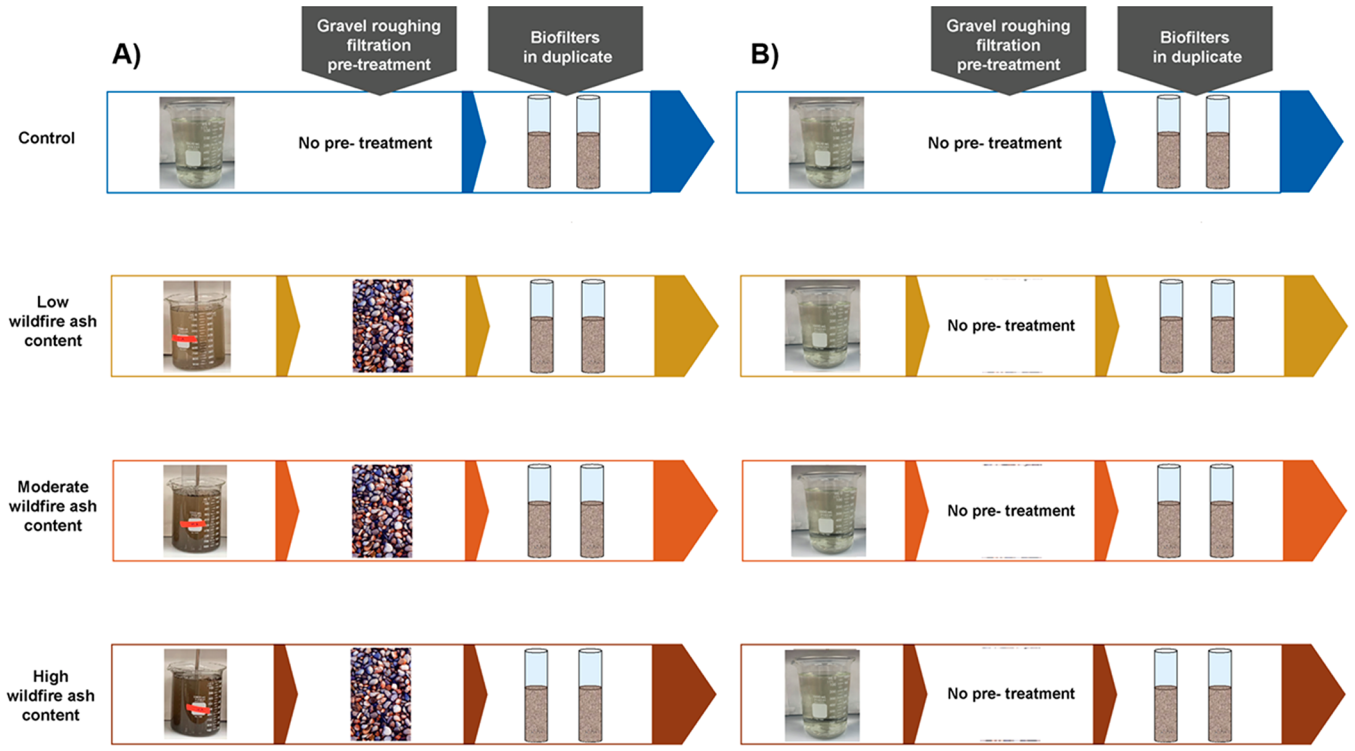

Figure 1. Operational conditions during the bench-scale evaluations (Days 1−50, eight biofilters) of biofilter treatment resilience in (A) buffering elevated aquatic WEOM resulting from low, moderate, and high wildfire ash content (for 2-, 4-, and 7-days periods), followed by a (B) return to baseline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

quality is high,[30] biological filtration offers additional treatment benefits, including reductions of taste and odor compounds and NOM (and therefore regulated disinfection byproducts).[31−34] Biological filtration also improves the biological stability of drinking water in distribution systems.[35] Particle, pathogen, and DOC removal by biological filtration depends on biofilm formation and biodegradation.[33,34] Biological filtration processes range from classical—biofiltration in an otherwise conventional treatment plant (i.e., preceded by coagulation/flocculation/clarification and sometimes advanced oxidation processes such as ozonation)[33]—to slow sand filtration (SSF) that is typically operated without chemical or other pretreatment.[29,33,34] Thus, while biofilters may utilize physicochemical filtration mechanisms that rely on synergies between particle size, media depth, media size, particle destabilization by coagulation, and media roughness,[36−39] additional mechanisms of 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;[32,40,41] thus, lab- and pilot-scale assessments remain essential to demonstrating biological treatment capabilities.

Biological filtration may be considered for the management of wildfire ash-associated organic carbon threats to the provision of safe drinking water because it preferentially removes low molecular weight (LMW) compounds[42,43] that may be present in wildfire ash-impacted source waters. Its ability to offer treatment resilience in buffering elevated source water DOM after wildfire has not been demonstrated, however. An SSF-like approach is a logical starting point for such investigation 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.[44−46] Low hydraulic loading rates (HLRs) and extended contact times (relative to classical biofiltration) promote biodegradation of DOC, even without chemical or energy-intensive pretreatments such as coagulation or ozonation.[47,48] Thus, biological filtration with relatively long contact times is the design configuration most likely to provide resilience in buffering elevated source water DOM resulting from wildfire ash by biologically mediated treatment in absence of pretreatment. This is because kinetic limitation is practically precluded. If elevated and/or altered postfire source water DOM cannot be buffered by biological filtration with long contact times, it is unlikely that it would be buffered by biological filtration mechanisms in operational configurations with shorter contact times. A novel proof-of-concept evaluation of this resilience was the focus of this investigation. Specifically, the resilience of biological filtration processes to achieve biologically mediated reductions of postfire ash-derived water extractable organic matter (WEOM) was investigated. To the authors' knowledge, this is the first study to investigate biodegradability of ash-derived WEOM and its specific fractions (based on size exclusion chromatography) by drinking water treatment processes.

METHODOLOGY AND 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.[49] This water was pretreated by roughing

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filtration to remove suspended solids to a level (<5 NTU)[46] appropriate for subsequent treatment by biological filtration. Given that altered NOM (measured as DOC concentrations and/or character) results in some of the most significant treatment challenges commonly observed after wildland fire,[9] DOC removal was investigated here. Two-, four-, and seven-day disturbances were investigated because they are consistent with or longer than most observations of episodically altered source water DOC after wildfire.[9,16,50−54] Each DOC pulse was followed by a one-week return to "baseline" source water quality without ash amendment. Figure 1 depicts the operational conditions during the bench-scale evaluations.

"Baseline" Source Water and Preparation of Wildfire Ash-Amended Source Water. Baseline source water was 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 one to seven days before being (i) fed to the biofilters in batches or (ii) used to prepare the wildfire ash-amended source water. DOC concentration did not decrease by more than 5% during the storage period.

Wildfire ash-amended 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).[55] Ash-amended 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). Each wildfire ash-amended source water matrix was freshly prepared immediately prior to use. To ensure WEOM was adequately leached from the ash, each ash matrix was mixed for 18 h at a rate of 200 rpm for 2 h, followed by mixing for 16 h at a rate of 180 rpm (Phipps & Bird, PB-900 Series Programmable 6-Paddle Jar Tester). Following mixing and a subsequent 3 h settling period to reduce turbidity, the settled water quality was analyzed (Table S1) and the water was immediately used.

Biofilter Design. The study was not designed to mimic operational aspects of pilot- or full-scale biological filtration. Rather, bench-scale, SSF-like biofilters with low HLRs and extended contact times (relative to classical biofiltration) were used because maximal biodegradation of DOC would be expected at these conditions.[47,48] 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 biodegradable contaminants is generally understood[56−58] and has gained renewed interest in recent years.[59,60] 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.[61] 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.[60] 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 designs (Supporting Information, Section S3). Nonadsorptive filter media were used to ensure that only biotic DOC removal 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.[46] 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.[62] 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 filter influent stream was prepared and applied in batches, in which influent water quality remained consistent for approximately 1 week before a new batch was required. The filters were operated at room temperature (19−22 °C) with an extended EBCT of approximately 10 h (corresponding HLR of 0.07 m/h), which represents the upper ranges of previously reported EBCTs in full-scale SSF.[47,63] They were covered in aluminum foil to prevent photosynthesis. The filters were acclimatized until stabilization of DOC removal (i.e., plateau) was observed; this occurred after 103 days of continuous operation. When the water level reached the height of the column, indicating that maximum headloss was reached, the filters were maintained by scraping the schmutzdecke so that the underlying filter media were visible.[46] This was done immediately prior to each period of ash disturbance so that biofilter performance and treatment resilience were evaluated when performance might be vulnerable due to reduced biomass on the filter surface.[46,64]

Pretreatment of ash-amended water was limited to settling (described above) 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 repacked after no more than 24 h of run-time. Roughing filter effluent water quality was analyzed as described below.

Water Quality Analyses. Standard Methods[65] 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 end point of 4.5), DOC concentration (filtration through prerinsed 0.45 μm Nylaflo membranes, Pall, Port Washington, NY; Method 5310B; Shimadzu TOC-V CPH analyzer, Kyoto, Japan) with a reporting limit of 0.2 mg/L, and ultraviolet absorbance at 254 nm (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.[69]

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.[66] Samples were first filtered through a prerinsed 0.45 μm polyether sulfone membrane (Millipore Express PLUS; Merck Millipore, Burlington, MA). Chromatographic separation was completed using a weak cationic exchange column (Toyopearl, TSK HW 50S, Tosoh, Japan).

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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 follow a roughly normal distribution and (2) the variance between the two data sets is approximately equal. These assumptions were evaluated using normal scores plots for the differences between the matched pairs. Additionally, a heteroscedastic t test examining the difference between the mean percent DOC removals in the control and disturbance impacted filters was also conducted. Two-tailed tests were conducted. All assumptions, normal scores plots, and t test details are presented in Supporting Information Section S2.

RESULTS AND 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 (Figures S17−S32). Thus, filter performance met or exceeded performance expectations.[46,67] DOC removal varied considerably throughout the 50-day experimental period, ranging from slightly negative to approximately 40% removal; and, in most cases, differences in daily DOC removal between control biofilters receiving baseline source water and biofilters treating ash amended water were within the range of natural, intercolumn variability calculated as three times the standard deviation of the mean difference in DOC removal between the two control biofilters (Figure 2A). DOC concentrations typically decreased significantly from influent to effluent across all biofilters ($p \leq 0.026$ for all filters; Supporting Information, Section S2) and were consistent with those reported for various types of biological filtration. For example, Collins et al.[47] reported 12−33% removal of DOC in several full-scale SSF plants with EBCTs ranging from 3.8 to 21.9 h, while Vines and Terry[68] reported only 7−8% DOC removal in bench-scale anthracite biofilters (EBCTs of 5−30 min). DOC removals of 12−38% by classical biological activated carbon filtration (i.e., preceded by coagulation/flocculation/clarification) with preozonation also have been reported.[43] 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.[32] Here, the use of an SSF-like approach that did not include adsorptive filter media or pretreatment to remove or enhance the removal of more hydrophobic DOM (i.e., coagulation) or more recalcitrant DOM (i.e., postclarification 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 ($p \leq 1.16 \times 10^{-05}$, average change in daily UVA_{254} measurements <0.012 cm^{-1}; Figure 3). The observation of limited capacity to reduce UVA_{254} is consistent with other reports of biological filtration performance[43,68] and a common

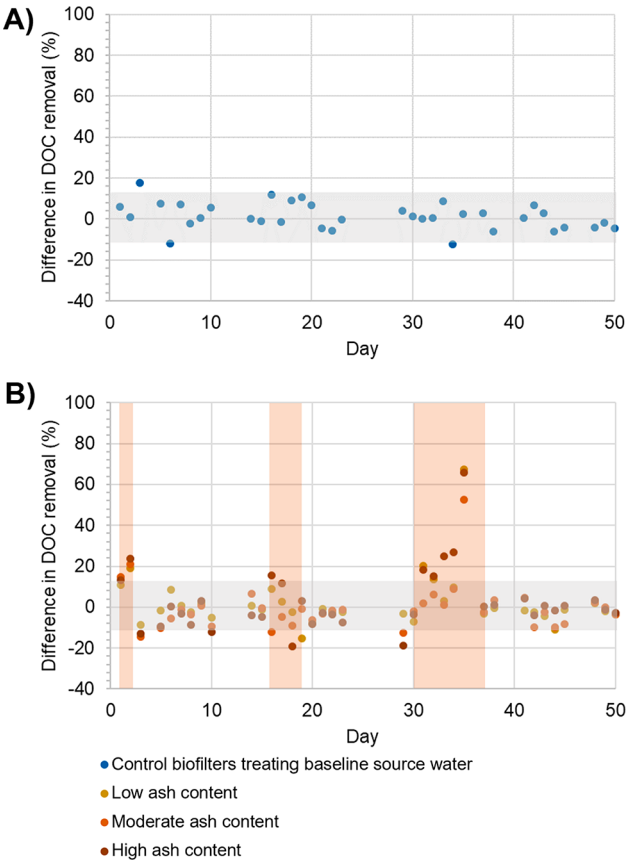

Figure 2. Daily difference in DOC removal (%) between (A) replicate control biofilters and (B) control biofilters and biofilters receiving wildfire ash-amended source waters. Horizontal gray-shaded regions indicate natural, intercolumn variability (i.e., three times the standard deviation of the mean difference in DOC removal between the two control biofilters). Vertical shaded regions indicate when ash-amended source water was introduced to the biofilters. Biofilters were acclimated for 103 days prior to start of 50-day experiment (i.e., experimental day 0 was day 104 of filter operation).

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,[69] (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.[42,43,70] 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). Nonetheless, the biofilter DOC and UVA_{254} removal data collectively demonstrate that the bench-scale biofilters provided a reasonable indication of biologically mediated reductions in DOM, which were consistent with those that have been previously reported. While the bench-scale biofilter design was suitable for evaluating DOM removal by biological filtration processes and the potential for treatment resilience in buffering elevated source water DOM resulting from wildfire ash, the biofilters were not designed to mimic all aspects of full-scale biofiltration (especially not operational aspects). Operational investigations were not a focus of the present investigation and associated performance (e.g., headloss accumulation) was not evaluated; such investigations would be best conducted at pilot-scale.

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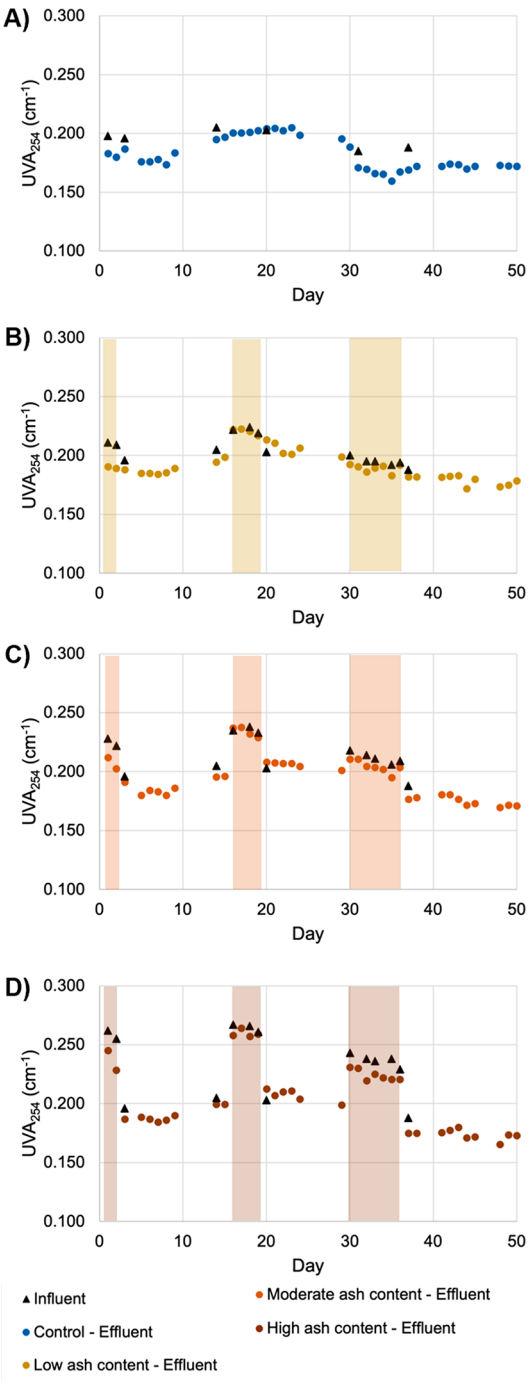

Figure 3. Daily change in UVA254 across biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content source water. Vertical shaded regions indicate when ash-amended source water was fed to the biofilters.

Impact of Wildfire Ash on DOC Removal by Biofilters. DOC removals by the control biofilters and those treating wildfire ash-amended source waters were generally within the range of natural, intercolumn variability; thus, significant differences in overall DOC removal between the biofilters were not observed ($p \geq 0.489$ in all cases; Figure 2B). Although no differences in overall DOC removal over time were observed between the control biofilters and those periodically treating wildfire ash-amended water, it should be noted that for brief periods, DOC removal (on both a mass and percentage basis) was significantly lower in the biofilters treating high ash content-amended water. These brief periods (~2 days) occurred immediately after the return to baseline source water after the two-day and four-day periods of ash amendment ($p \leq 0.0271$; Figure 2B). This type of performance difference was not observed after the other experiments involving ash addition to the source water, however ($p \geq 0.146$; Figure 2B). These data may suggest that biofilters adjusting from high levels of readily bioavailable nutrients (i.e., LMW neutral fractions of DOC) to levels of lower availability may release some DOC while microbial communities adjust to these shifts. Moona et al.[71] 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 could not be elucidated mechanistically herein, they underscore the need to better understand DOC removal mechanisms (e.g., adsorption, biodegradation, bioregeneration) in biological filtration processes.

In drinking water treatment, 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.[72] It is for this reason that regulatory compliance monitoring for demonstrating well-operated treatment relies on synoptic sampling (e.g., EPA[73]) and 95th percentile water quality performance thresholds (e.g., EPA[74]) rather than imposing absolute criteria. Here, duplicate biofilters promptly and consistently 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. In fact, some level of enhanced DOC removal was observed in biofilters treating wildfire ash-amended water relative to control biofilters treating baseline source water. For example, average DOC removal during the two-day ash disturbance period was significantly higher in each of the biofilters treating wildfire ash-amended water relative to the control biofilters (Figure 2B; p = 0.0044, 0.0012, and 0.0012 for biofilters receiving low, moderate, and high ash content-amended water, respectively). Following the 7-day ash disturbance period, all biofilters regardless of ash amendment achieved especially high DOC removal (~30%). Collectively, 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, 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 between the control biofilters and those treating wildfire ash-amended water were not observed.

DOC fractionation by size exclusion chromatography with LC-OCD revealed that the enhanced DOC removal (on a percentage basis) in the biofilters treating wildfire ash-amended water relative to control biofilters treating baseline source water during the two-day disturbance period was likely attributable to the greater proportion of LMW neutrals comprising WEOM in wildfire ash-amended filter influent streams compared to control biofilters treating only baseline source water (Figure 4A,B). LMW neutrals accounted for the majority of DOC added with ash-amended waters, despite some differences in amounts of DOC leached due to natural

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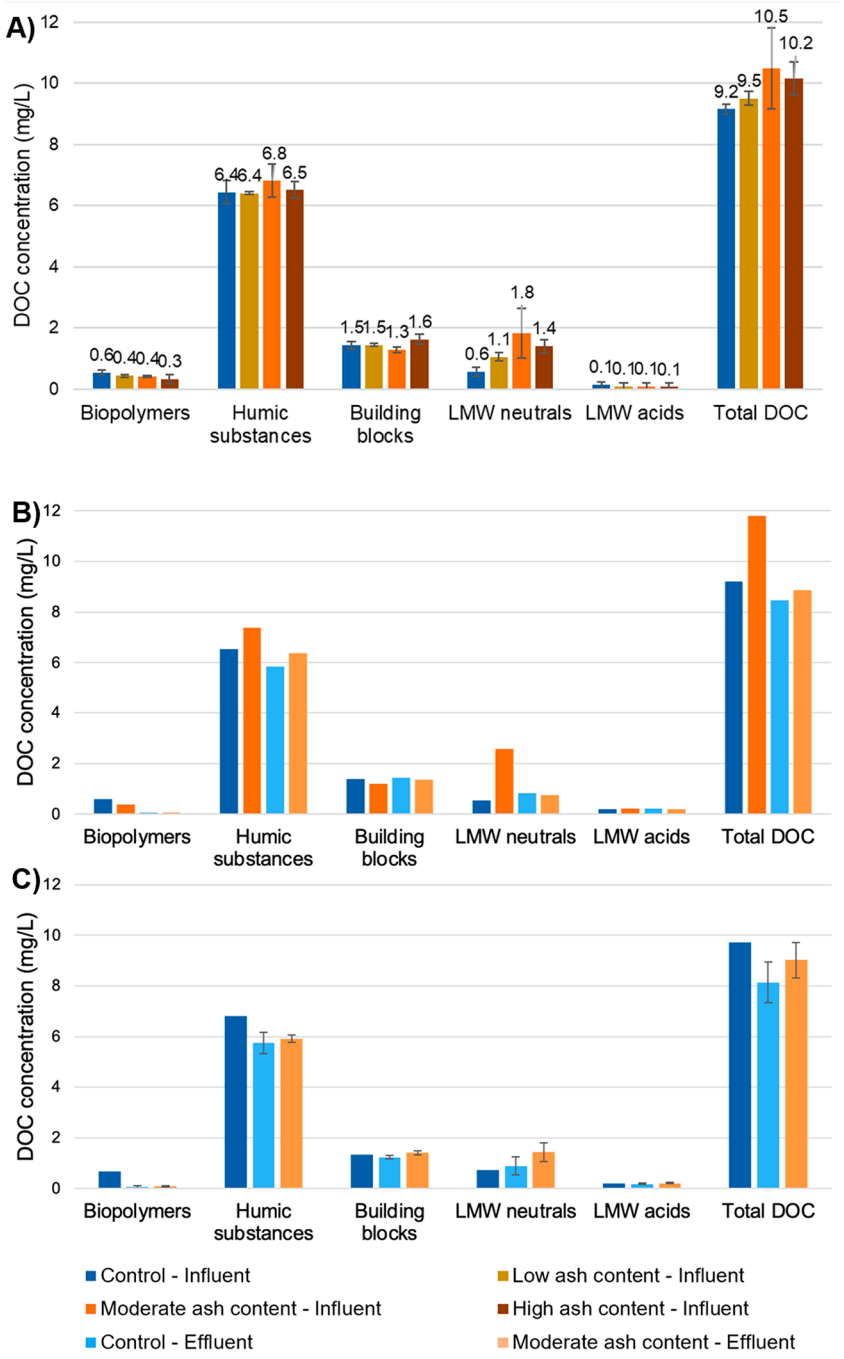

Figure 4. Dissolved organic carbon fractions (mean ± standard deviation) in (A) influent streams of control biofilters and biofilters treating wildfire ash-amended water during ash trials (n = 3), (B) influent and effluent streams of biofilters treating control and moderate ash content water during two-day ash trial (days 1 and 2), and (C) influent and effluent streams of control biofilters and biofilters treating moderate ash content water during return to baseline period following two-day ash trial (days 3−15; n = 4).

variability of ash (Figure 4A; Figures S33 and S34). On average, LMW neutrals accounted for approximately 83%, 67%, and 53% of the total DOC added in the low, moderate, and high disturbance waters, respectively. While humic substances only accounted for approximately 22% and less than 10% on average of the total DOC added to the moderate and high disturbance waters, on average they were similar in the baseline source and low disturbance waters. The sum of the differences between LC-OCD fractions of the baseline and ash-amended waters and their respective total DOC values remained within 87% (100% in 7 samples, 90% in one sample, and 87% in one sample), indicating good mass balance during ash amendment. Although the observed small increase or lack of change in humic substances in ash-amended waters is somewhat inconsistent with previous wildfire studies[21]—and likely due to natural heterogeneity of the ash material—the observed increase in LMW compounds as a result of ash amendment is consistent with other studies.[14,21] LMW neutrals are readily biodegradable, and their removal during biofiltration has been well-documented;[43,78,80] they tend to be removed even more effectively in biofiltration preceded by ozonation.[43,78] This behavior was observed again in biofilters

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Table 1. Raw Grand River Water Dissolved Organic Carbon Fractions in Summer and Fall 2021[a]

date of sampling	day of application to biofilters	total DOC (mg/L)	biopolymers (mg/L)	humic substances (mg/L)	building blocks (mg/L)	LMW neutrals (mg/L)	LMW acids (mg/L)
September 2	Day −41	6.5	0.7	4.3	1.0	0.5	<0.044
September 14	Day −32	9.5	0.6	3.8	1.1	4.0	<0.044
October 14	Day 1	9.2	0.6	6.5	1.4	0.5	0.20
October 20	Day 3	9.7	0.7	6.8	1.3	0.7	0.20
October 29	Day 14	9.4	0.5	6.8	1.4	0.5	0.20
November 4	Day 20	9.9	0.2	7.1	1.7	0.9	<0.044
November 16	Day 31	8.9	0.6	6.0	1.6	0.7	<0.044
November 24	Day 37	13	0.9	9.3	2.0	0.9	0.10

[a]Note: Samples taken during the 103-day acclimation period prior to the 50-day experimental period are indicated with a minus (−) sign, indicating the day before which the experimental period began.

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 and 1.19 mg/L, respectively; Table S4). In contrast, enhanced DOC removal in biofilters treating ash-amended source water was not observed during the four-day ash disturbance period (p > 0.344 for all cases)—this was likely because of the shift in baseline source water quality during that experiment, discussed below. DOC fractionation also revealed that biopolymers were most effectively removed by biofilters compared to other carbon fractions (Figure 4B,C), consistent with some other studies.[75−80] It should be noted, however, that So et al.[43] 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 that study was in the context of otherwise conventional treatment with preozonation, which can impact biodegradability of DOC.[40] Even during periods of impaired DOC removal, such as the week following the two-day ash disturbance period, biopolymers were typically well-removed, while LMW neutrals increased from the influent to the effluent, indicating transformation or incomplete degradation (Figure 4C). Collectively, these results underscore that the extent of DOC removal that can be achieved by biofiltration depends on its character and associated bioavailability. However, it would be expected that the humic substance fractions of DOM that are poorly removed by biofiltration would be more readily removed with coagulation, as coagulation preferentially removes humic substances that are aromatic and have high molecular weight.[22,25]

As indicated above, while DOC removal across experimental conditions was generally consistent, it did vary over the course of the study. Seasonal water quality changes, including those in DOM, in the Grand River have been well-documented. In the summer, primary productivity is at its highest and discharge is at its lowest. During the fall, nutrient and dissolved oxygen concentrations shift.[41,81,82] 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 during the present study (Table 1), and substantial increases in humic-like fluorescence/DOC and larger sizes of DOC molecules that have been observed in other investigations.[83] Higher DOC/dissolved organic nitrogen (DON) ratios and lower protein content consistent with more allochthonous organic matter have also been observed during this period.[83] Accordingly, it is not surprising that DOC removal by the biofilters fluctuated during these brief periods because a greater proportion of DOC is known to be less biodegradable during these transitional periods (Table 1).[41,82,83] It is also not surprising that relatively high DOC removal was observed in all biofilters during the end of the experiment (∼30% removal), given that higher amounts of readily biodegradable DOC (i.e., biopolymers and LMW neutrals) were present in this batch of raw Grand River water fed to the biofilters compared to batches collected in October (Table 1). Aside from this observation, no significant changes in bulk water quality were observed in the discrete batches of water used during the present study; however, historical data and accounts including full-scale plant data corroborate reduced biological filtration performance during the fall "transitional" period.[32,84]

Although biomass was not quantified herein because it is not directly indicative of biological activity,[32,40,41] break-through of biopolymers during the four-day ash disturbance period and return to baseline period following the four-day ash disturbance period (Tables S2 and S3) 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 3), despite inconsistent increases in DOC with sequentially higher ash content (Figure 4A). 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.[21,85] As discussed above, LC-OCD analyses revealed that LMW neutrals and smaller amounts of humic substances by mass were added to source water with ash-amendment (Figure 4A; Figures S33 and S34). Since LMW neutrals do not contribute to UVA_{254}

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absorbance,[66] the observed increase in UVA_{254} in ash-amended source waters is likely driven by the relatively small addition of humic substances. Humic substances are not typically well-removed by biofiltration[77,79,86] since they are not readily biodegradable;[42,87] thus, it is not surprising that average daily change in UVA_{254} absorbance throughout the 50-day experiment was significantly lower in all biofilters treating ash-amended water relative to control biofilters ($p < 0.034$) and thus emphasizes the insights obtained from DOC characterization by fractionation. Other treatment processes such as coagulation and especially enhanced coagulation, however, are recognized as best-available technologies for removing DOC (particularly the humic substances fraction) from water.[73]

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,[32,88] 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 time scales (i.e., minutes).[88] 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,[43,70,89] regardless of contact time. Notably, the extended contact time of 10 h 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 to 30 min).[43,78,88] 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 advisible 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 ozonation for increased biodegradability (and subsequent removal by biofiltration). Additionally, source water quality fluctuations that were observed herein underscore that source water DOM can fluctuate in biodegradability.[41,82,83] 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[9,90] and possibly inhibit biological activity,[91] 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 postfire DOC resulting from wildfire ash. To the authors' knowledge, this is the first study to investigate biodegradability of wildfire ash-derived WEOM as it pertains to drinking water treatment. UVA_{254} measurements and DOC fractionation revealed that WEOM derived from ash resulted in increased relative mass of LMW neutrals and, to a lesser degree, humic substances fractions in ash-amended source waters. There was evidence of increased DOC removal in biofilters treating wildfire ash-amended water relative to the control biofilters during the two-day and some evidence during the 7-day ash disturbance periods, but not the four-day disturbance period. DOC fractionation revealed that the enhanced DOC removal was likely attributable to the greater proportion of readily biodegradable LMW neutrals comprising WEOM in wildfire ash-amended filter influent streams compared to control biofilters treating only baseline source water. UVA_{254} measurements and DOC fractionation revealed that humic substances, which are a main driver of UVA_{254} absorbance,[66] 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.[26,27] While they also suggest that resilience of biological filtration may be compromised if the balance between readily removed and recalcitrant fractions of DOM change, this may be mitigated if biological filtration is preceded by coagulation to remove less biodegradable DOM fractions such as humic substances.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.2c00209.

Tables of water quality of ash-amended water and baseline raw Grand River water, LC-OCD results during the four-day ash disturbance period, LC-OCD results during the return to baseline period, LC-OCD results during 7-day ash disturbance period, paired comparison tests, p-values of one-tailed heteroscedastic t-tests for differences in overall average daily change, and calculated values for Damkohler number II estimation, figures of influent and effluent turbidity, influent and effluent SUVA, influent and effluent pH, influent and effluent alkalinity, LC-OCD results for influent, and normal scores plots, discussions of statistical analyses and Damkohler number II estimation (PDF)

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Author Contributions

The manuscript was written through contributions of all authors and all authors have given approval to the final version of the manuscript. CRediT: **Emma A. J. Blackburn** conceptualization (equal), formal analysis (equal), investigation (lead), methodology (lead), visualization (equal), writing-original draft (lead), writing-review & editing (equal); **Sarah E. Dickson-Anderson** conceptualization (equal), formal analysis (equal), funding acquisition (supporting), methodology (supporting), supervision (equal), visualization (equal), writing-review & editing (equal); **William B Anderson** formal analysis (equal), methodology (supporting), visualization (equal), writing-review & editing (equal); **Monica B. Emelko** conceptualization (equal), formal analysis (equal), funding acquisition (lead), methodology (supporting), resources (lead), supervision (equal), visualization (equal), writing-review & editing (equal).

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Notes

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