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

AUTHOR NAMES. Emma A. J. Blackburn†, Sarah E. Dickson-Anderson‡, William B. Anderson†, Monica B. Emelko†*

†Water Science, Technology & Policy Group, Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, Ontario, Canada.

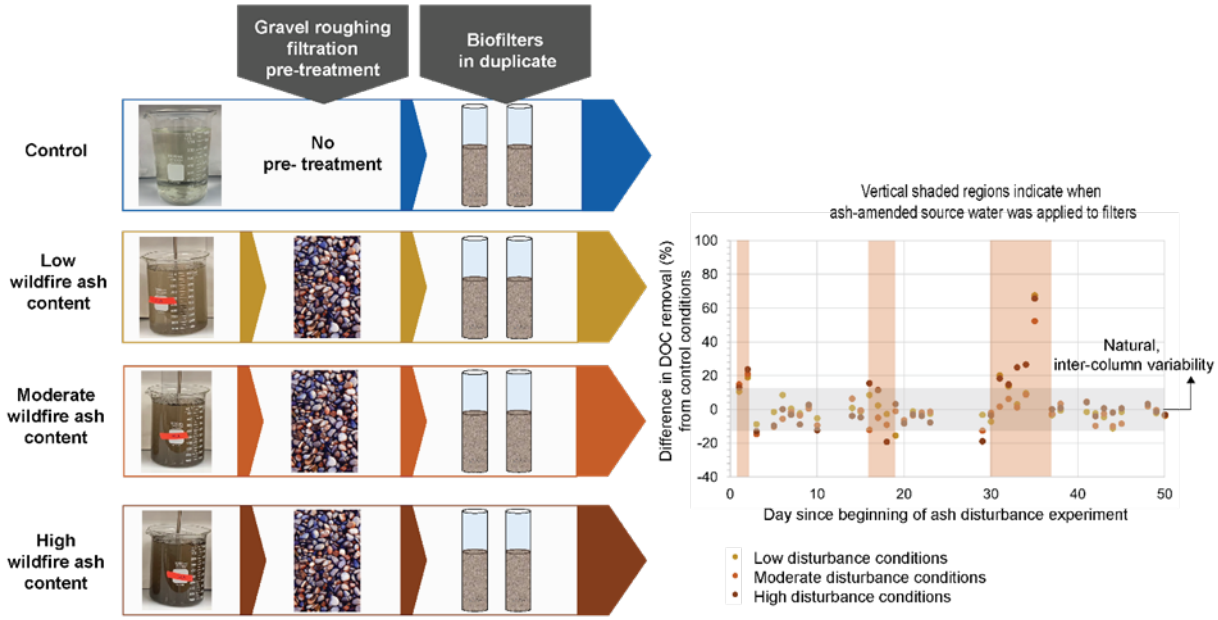
‡Department of Civil Engineering, McMaster University, Hamilton, Ontario, Canada.

KEYWORDS. Biofiltration, slow sand filtration, natural disturbance, climate change adaptation, NOM, WEOM, LC-OCD.

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 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.

SYNOPSIS. Biological filtration can increase drinking water treatment resilience to threats from wildfire ash-associated changes in dissolved organic carbon concentration and character.

GRAPHIC FOR TABLE OF CONTENTS.



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 by-products.[23,24] Smaller, more aromatic, and thus more difficult to coagulate post-fire DOC has been suggested.[9,14,25] More aromatic DOC also tends to lead to greater formation of regulated disinfection by-products.[26,27] These DOC-associated post-fire 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 pre-treatment by chemical coagulants for effective operation even when source water quality is high,[30] biological filtration offers additional treatment benefits, including reductions of taste and odor compounds and NOM (and therefore regulated disinfection by-products).[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 pre-treatment.[29,33,34] Thus, while biofilters may utilize physico-chemical 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 pre-treatments 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 pre-treatment. This is because kinetic limitation is practically precluded. If elevated and/or altered post-fire 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 post-fire 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 & 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 pre-treated by roughing filtration to removed 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.

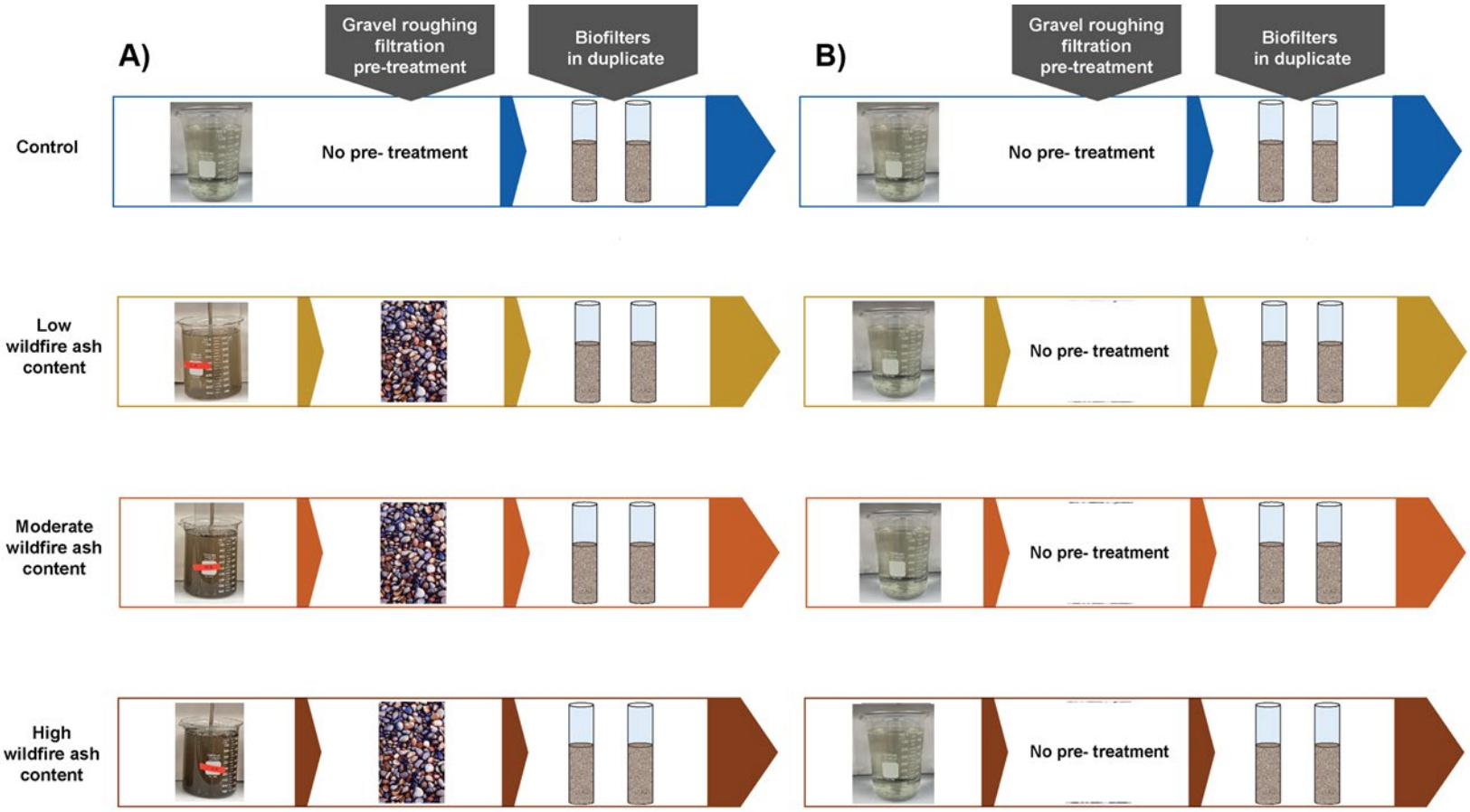


Figure 1. Operational conditions during the bench-scale evaluations (Days 1 to 50, 8 biofilters) of biofilter treatment resilience in (A) buffering elevated aquatic WEOM resulting from low, moderate, and high wildfire ash content (for 2-, 4-, and 7-days periods), followed by a (B) return to baseline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

"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 between one to 7 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 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-hour settling period to reduce turbidity, settled water quality was analyzed (Table S1) and the water was immediately used.

Biofilter design. The study herein 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, S3). Non-adsorptive 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 one week before a new batch was required. 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.[47,63] They were covered in aluminum foil to prevent photosynthesis. The filters were acclimatized until stabilization of DOC removal (i.e., plateau) after 103 days. When the water level reached the maximal 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]

Pre-treatment 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 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[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 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) 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]

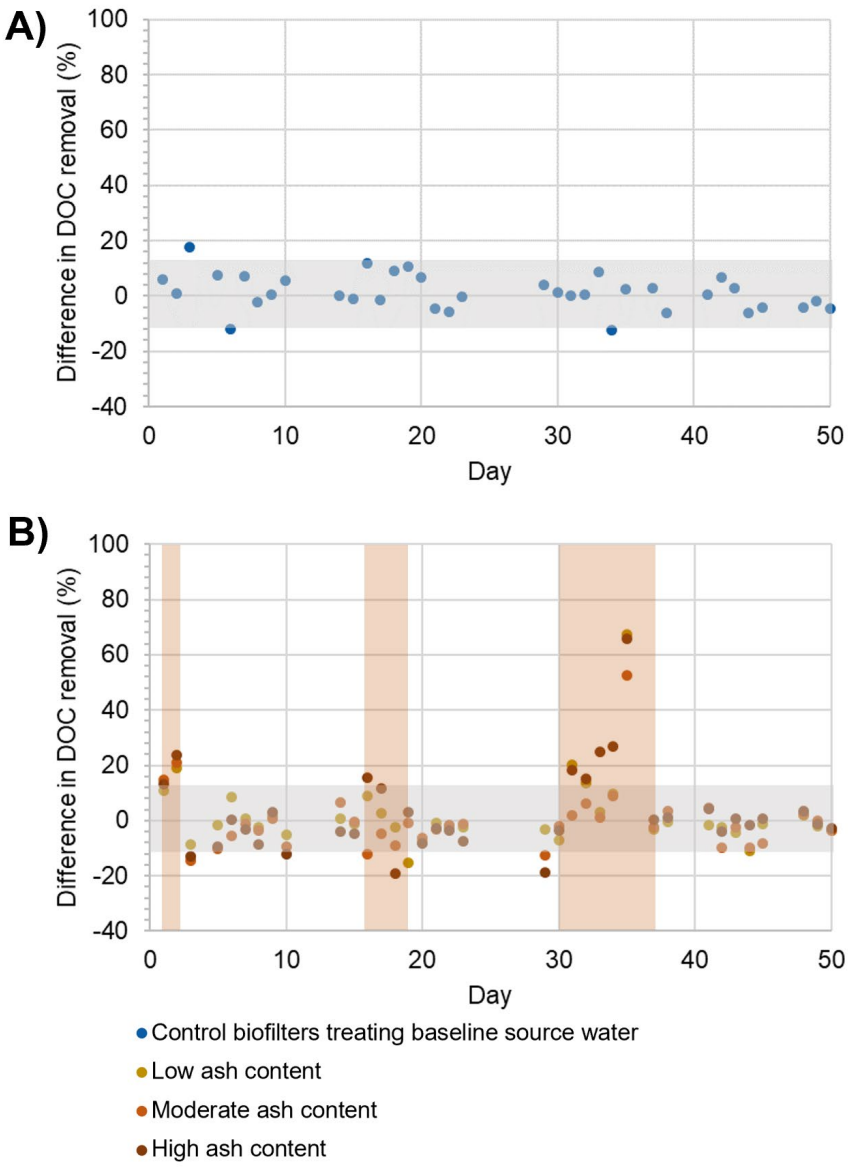
Liquid chromatography in combination with organic carbon detection (LC-OCD) was used to fractionate DOC (as biopolymers [BPs], humic substances [HS], building blocks [BB], low molecular-weight [LMW] neutrals, LMW acids) as described in Huber et al.[66] Samples were first filtered through a pre-rinsed 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. 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.[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, inter-column 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, 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 hours, while Vines & Terry[68] 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.[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-based approach that did not include adsorptive 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.



195

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

203

204

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}; Figure 3). The observation of limited capacity to reduce UVA_{254} is consistent with other reports of biological filtration performance[43,68] 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,[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

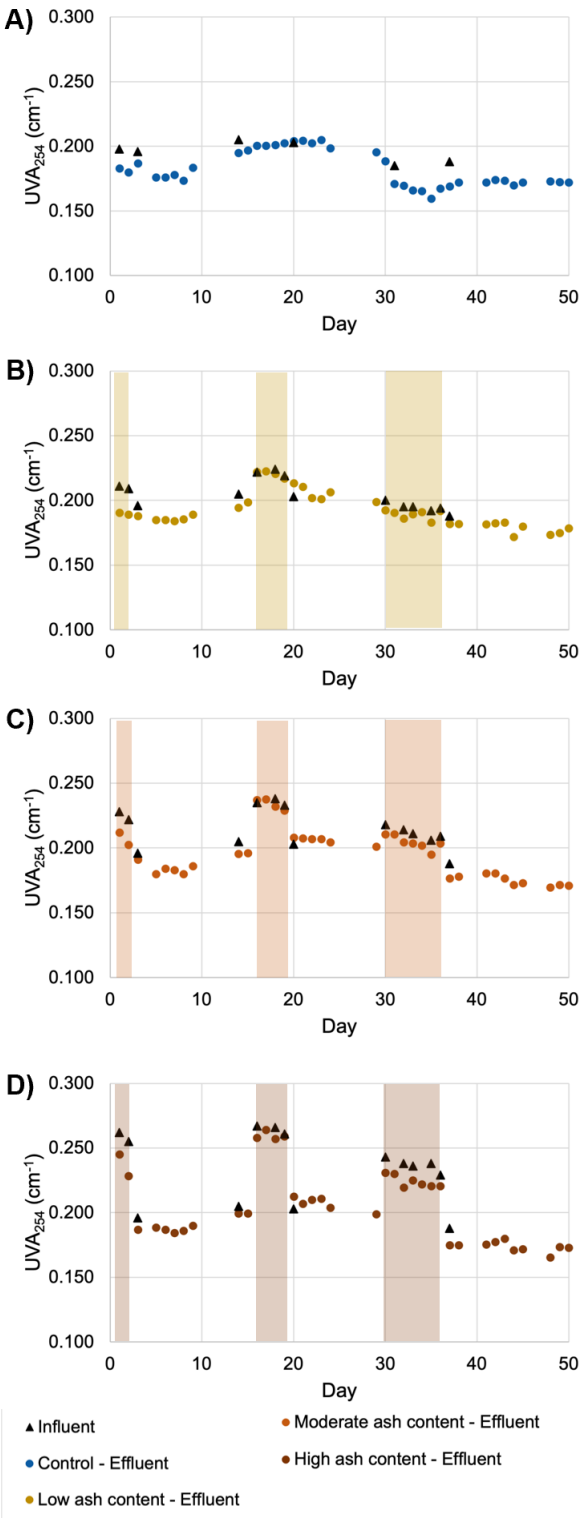


Figure 3. Daily change in UVA_{254} across biofilters treating (A) control and (B) low, (C) moderate, and (D) high wildfire ash content source water. Vertical shaded regions indicate when ash-amended source water was fed to the biofilters.

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) were not evaluated; such investigations would be best conducted at pilot-scale.

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, inter-column 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 DOC removal (on both a mass and percentage basis) was significantly lower in the biofilters treating high ash content-amended water for brief periods (~2 days) 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 while the biofilters are adjusting from high levels of readily bioavailable nutrients (i.e., LMW neutral fractions of DOC) to lower availability, biofilters 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

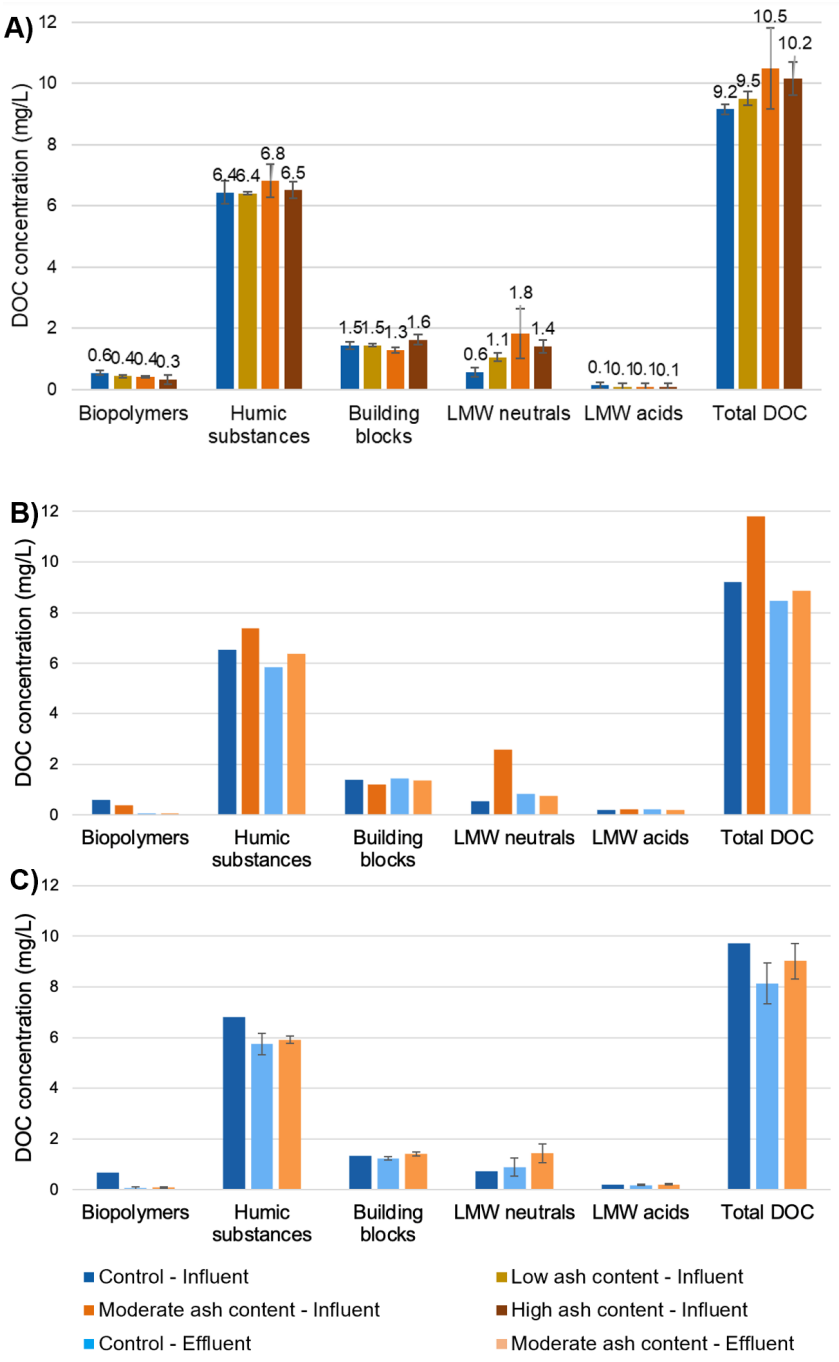
observations to organic matter desorption from filter media. While these brief periods of performance difference cannot be elucidated mechanistically herein, they underscore the need to better understand DOC removal mechanisms (e.g., adsorption, biodegradation, bioregeneration) in biological filtration processes.

Within the drinking water profession, 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 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 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-amended water and the control biofilters 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 4 A and 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 variability of the ash material (Figure 4 A; Figures S33-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, they remained unchanged on average from the baseline source water to the low disturbance water. 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]—likely due to natural heterogeneity of the ash material—the increase in LMW compounds post-fire 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 behaviour was observed again in biofilters receiving source

296 water amended with high ash content during the 7-day ash disturbance period ($p = 0.0187$),
297 where LMW neutrals were elevated in the ash-amended source water relative to the control (0.74
298 mg/L and 1.19 mg/L, respectively; Table S4). In contrast, enhanced DOC removal in biofilters
299 treating ash-amended source water was not observed during the four-day ash disturbance period
300 ($p > 0.344$ for all cases)—this was likely because of the shift in baseline source water quality
301 during this period, discussed below. DOC fractionation also revealed that biopolymers were most
302 effectively removed by biofilters compared to other LC-OCD components (Figure 4 B and C),
303 consistent with other studies.[75-80] In contrast, So et al.[43] reported that building blocks and LMW
304 neutrals were removed more efficiently than biopolymers and humic substances. A possible
305 explanation for divergent observation could be that biofiltration in this study was in the context
306 of otherwise conventional treatment with pre-ozonation, which can impact biodegradability of
307 DOC.[40] Even during periods of impaired DOC removal, such as in the week following the two-
308 day ash disturbance period, biopolymers were typically still well removed, while LMW neutrals
309 increased from the influent to the effluent, indicating transformation or incomplete degradation
310 (Figure 4 C). Collectively, these results underscore that the extent of DOC removal that can be
311 achieved by biofiltration depends on its character and associated bioavailability. However, it
312 would be expected that the humic substance fractions of DOM that are poorly removed by
313 biofiltration would be more readily removed with coagulation, as coagulation preferentially
314 removes humic substances that are aromatic and have high molecular weights.[22,25]
315



316

317 **Figure 4.** LC-OCD fractionation of (A) influent streams of control biofilters and biofilters
318 treating wildfire ash-amended water during ash trials (n=3), (B) influent and effluent streams of
319 biofilters treating control and moderate ash content water during two-day ash trial (day 1 and 2),
320 (C) influent and effluent streams of control biofilters and biofilters treating moderate ash content
321 water during return to baseline period following two-day ash trial (days 3 to 15; n=4). Error bars
322 indicate standard deviations where mean LC-OCD results are presented.

323

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 production 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 analyses by LC-OCD during the present study (Table 1), and substantial increases in humic-like fluorescence/DOC and larger sizes of DOC molecules observed in other investigations.[83] Higher DOC/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] Conversely, 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]

Table 1. LC-OCD results for raw Grand River water samples from summer and fall 2021

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

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.

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-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 4 A). 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] 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 4 A; Figures S33-S34). Since LMW neutrals do not contribute to UVA_{254} 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 treating DOC (particularly the humic substances fraction).[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 timescales (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 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).[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 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 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 post-fire 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 LC-OCD analyses 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. 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-amended filter influent streams compared to control biofilters treating only baseline source water. UVA_{254} measurements and LC-OCD analyses 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 on the ACS Publications website.

Supporting Information (PDF) containing:

- S1: Additional water quality analyses (Figures S1-S34, Tables S1-S4)
- S2: Statistical analyses (Equations S1-S4, Figures S35-S36, Tables S5-S8)
- S3: Damkohler number II estimation (Equations S5-S20, Table S9)

AUTHOR INFORMATION

Corresponding Author

*Monica B. Emelko – Water Science, Technology & Policy Group, Department of Civil and Environmental Engineering, University of Waterloo, Waterloo, Ontario, Canada.

Email: mbemelko@uwaterloo.ca

Author Contributions

The manuscript was written through contributions of all authors and all authors have given approval to the final version of the manuscript.

Funding Sources

We acknowledge the support of NSERC (Natural Science and Engineering Research Council of Canada), specifically through the *forWater* NSERC Network for Forested Drinking Water Source Protection Technologies (NETGP-494312-16) and a collaborative research and

448 development grant (CRDPJ 484588-15), and Alberta Innovates (3360-E086). This research was
449 undertaken, in part, thanks to funding from the Canada Research Chairs Program (ME; Canada
450 Research Chair in Water Science, Technology & Policy).

451 Notes

452 The authors declare no conflicts of interest.

453 **ACKNOWLEDGMENT**

454 The laboratory assistance of Dr. Fariba Amiri, Steven Ngo, Theadora Taylor, and Lauren
455 McGregor is appreciated.

REFERENCES

1. Robinne, F.-N., Bladon, K. D., Silins, U., Emelko, M. B., Flannigan, M. D., Parisien, M.-A., Wang, X., Kienzle, S. W., & Dupont, D. P. (2019). A regional-scale index for assessing the exposure of drinking-water sources to wildfires. *Forests, 10*(5), 384. https://doi.org/10.3390/f10050384.

2. Robinne, F.-N., Miller, C., Parisien, M.-A., Emelko, M., Bladon, K., Silins, U., & Flannigan, M. (2016). A global index for mapping the exposure of water resources to wildfire. *Forests, 7*(12), 22. https://doi.org/10.3390/f7010022.

3. Mishra, A., Alnahit, A., & Campbell, B. (2021). Impact of land uses, drought, flood, wildfire, and cascading events on water quality and microbial communities: A review and analysis. *Journal of Hydrology, 596,* 125707. https://doi.org/10.1016/j.jhydrol.2020.125707.

4. Williams, C. H., Silins, U., Spencer, S. A., Wagner, M. J., Stone, M., & Emelko, M. B. (2019). Net precipitation in burned and unburned subalpine forest stands after wildfire in the northern Rocky Mountains. *International Journal of Wildland Fire, 28*(10), 750. https://doi.org/10.1071/wf18181.

5. Silins, U., Stone, M., Emelko, M. B., & Bladon, K. D. (2009). Sediment production following severe wildfire and post-fire salvage logging in the Rocky Mountain headwaters of the Oldman River Basin, Alberta. *CATENA, 79*(3), 189–197. https://doi.org/10.1016/j.catena.2009.04.001.

6. Alessio, P., Dunne, T., & Morell, K. (2021). Post-wildfire generation of debris-flow slurry by rill erosion on colluvial hillslopes. J*ournal of Geophysical Research: Earth Surface, 126*(11). https://doi.org/10.1002/essoar.10506263.1.

7. Emmerton, C. A., Cooke, C. A., Hustins, S., Silins, U., Emelko, M. B., Lewis, T., Kruk, M. K., Taube, N., Zhu, D., Jackson, B., Stone, M., Kerr, J. G., & Orwin, J. F. (2020). Severe Western Canadian wildfire affects water quality even at large basin scales. *Water Research, 183,* 116071. https://doi.org/10.1016/j.watres.2020.116071.

8. Abraham, J., Dowling, K., & Florentine, S. (2017). Risk of post-fire metal mobilization into surface water resources: A review. *Science of The Total Environment, 599-600*, 1740–1755. https://doi.org/10.1016/j.scitotenv.2017.05.096.

9. Emelko, M. B., Silins, U., Bladon, K. D. & Stone, M. (2011). Implications of land disturbance on drinking water treatability in a changing climate: Demonstrating the need for 'source water supply and protection' strategies. *Water Research 45*(2), 461–472. https://doi.org/10.1016/j.watres.2010.08.051.

10. Silins, U., Bladon, K. D., Kelly, E. N., Esch, E., Spence, J. R., Stone, M., Emelko, M. B., Boon, S., Wagner, M. J., Williams, C. H., & Tichkowsky, I. (2014). Five-year legacy of wildfire and salvage logging impacts on nutrient runoff and aquatic plant, invertebrate, and fish productivity. *Ecohydrology, 7*(6), 1508–1523. https://doi.org/10.1002/eco.1474.

11. Gustine, R. N., Hanan, E. J., Robichaud, P. R., & Elliot, W. J. (2021). From burned slopes to streams: How wildfire affects nitrogen cycling and retention in forests and fire-prone watersheds. *Biogeochemistry, 157*(1), 51–68. https://doi.org/10.1007/s10533-021-00861-0.

12. Crouch, R. L., Timmenga, H. J., Barber, T. R., & Fuchsman, P. C. (2006). Post-fire surface water quality: Comparison of fire retardant versus wildfire-related effects. *Chemosphere, 62*(6), 874- 889. https://doi.org/10.1016/j.chemosphere.

13. Mansilha, C., Duarte, C. G., Melo, A., Ribeiro, J., Flores, D., & Marques, J. E. (2017). Impact of wildfire on water quality in Caramulo Mountain Ridge (Central Portugal). *Sustainable Water Resources Management, 5*(1), 319–331. https://doi.org/10.1007/s40899-017-0171-y.

14. Hohner, A. K., Cawley, K., Oropeza, J., Summers, R. S., & Rosario-Ortiz, F. L. (2016). Drinking water treatment response following a Colorado wildfire. *Water Research,* 105, 187–198. https://doi.org/10.1016/j.watres.2016.08.034

15. Stone, M., Collins, A. L., Silins, U., Emelko, M. B., & Zhang, Y. S. (2014). The use of composite fingerprints to quantify sediment sources in a wildfire impacted landscape, Alberta, Canada. *Science of The Total Environment, 473-474*, 642–650. https://doi.org/10.1016/j.scitotenv.2013.12.052.

16. Emelko, M. B., Stone, M., Silins, U., Allin, D., Collins, A. L., Williams, C. H., Martens, A. M., & Bladon, K. D. (2016). Sediment-phosphorus dynamics can shift aquatic ecology and cause downstream legacy effects after wildfire in large river systems. *Global Change Biology, 22*(3), 1168–1184. https://doi.org/10.1111/gcb.13073

17. Carmichael, W. W. (2001). Health effects of toxin-producing cyanobacteria: "The CyanoHABs." *Human and Ecological Risk Assessment: An International Journal, 7*(5), 1393–1407. https://doi.org/10.1080/20018091095087

18. Watt, C., Emelko, M. B., Silins, U., Collins, A. L., & Stone, M. (2021). Anthropogenic and climate-exacerbated land-scape disturbances converge to alter phosphorus bioavailability in an oligotrophic river. *Water, 13*(22), 3151. https://doi.org/10.3390/w13223151.

19. Price, J. I., Renzetti, S., Dupont, D., Adamowicz, W., & Emelko, M. B. (2017). Production costs, inefficiency, and source water quality: A stochastic cost frontier analysis of Canadian water utilities. *Land Economics, 93*(1), 1–11. https://doi.org/10.3368/le.93.1.1.

20. Kundert, K., Emelko, M.B., Mielke, L., Elford, T., & Deng, J.F. (2014). Alberta flood 2013 – City of Calgary water treatment system resiliency. 16th National Conference on Drinking Water, Gatineau, QC, Canada, October 26-29, 2014.

21. Skwaruk, J., Emelko M.B., Silins, U., Stone, M. (2022). Treatment of severely-deteriorated post-fire runoff: A comparison of conventional and high-rate clarification to demonstrate key drinking water treatment capabilities and challenges. https:// doi.org/10.26434/chemrxiv.13350785.v1.

22. Sharp, E. L., Parsons, S. A., & Jefferson, B. (2006). Seasonal variations in natural organic matter and its impact on coagulation in water treatment. *Science of The Total Environment, 363*(1-3), 183–194. https://doi.org/10.1016/j.scitotenv.2005.05.032.

23. Kitis, M., Karanfil, T., Wigton, A., & Kilduff, J. E. (2002). Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. *Water Research, 36*(15), 3834–3848. https://doi.org/10.1016/s0043-1354(02)00094-5.

24. Kraus, T. E., Anderson, C. A., Morgenstern, K., Downing, B. D., Pellerin, B. A., & Bergamaschi, B. A. (2010). Determining sources of dissolved organic carbon and disinfection by-product precursors to the McKenzie River, Oregon. *Journal of Environmental Quality, 39*(6), 2100–2112. https://doi.org/10.2134/jeq2010.0030.

25. Chow, C., van Leeuwen, J. A., Drikas, M., Fabris, R., Spark, K. M., & Page, D. W. (1999). The impact of the character of natural organic matter in conventional treatment with alum. *Water Sci. Technol, 40*, 97−104. https://doi.org/10.1016/S0273-1223(99)00645-9.

26. Singer, P. C. (1999). Humic substances as precursors for potentially harmful disinfection by-products. *Water Science and Technology, 40*(9), 25–30. https://doi.org/10.2166/wst.1999.0434.

27. Hua, G., Reckhow, D. A., & Abusallout, I. (2015). Correlation between SUVA and DBP formation during chlorination and chloramination of NOM fractions from different sources. *Chemosphere, 130,* 82–89. https://doi.org/10.1016/j.chemosphere.2015.03.039.

28. Emelko, M. B. & Sham, C.H. (2014). Wildfire impacts on water supplies and the potential for mitigation. Water Research Foundation and Canadian Water Network, Web Report #4529.

29. Blackburn, E. A., Emelko, M. B., Dickson-Anderson, S., & Stone, M. (2021). Advancing on the promises of techno-ecological nature-based solutions: A framework for green technology in water supply and treatment. *Blue-Green Systems, 3*(1), 81–94. https://doi.org/10.2166/bgs.2021.008.

30. Lee, K.M., Ballantyne, L., Vattukkalathil, R., Scott, D., Anderson, W.B., Emelko, M.B. (2018). Appropriate coagulation of *Cryptosporidium* oocyst seed suspensions is critical during filter performance demonstrations. AWWA Water Quality Technology Conference (WQTC), Toronto, ON, Canada, November 11-15, 2018.

31. Bouwer, E. J., & Crowe, P. B. (1988). Biological processes in drinking water treatment. *Journal - American Water Works Association, 80*(9), 82–93. https://doi.org/10.1002/j.1551-8833.1988.tb03103.x.

32. Emelko, M. B., Huck, P. M., Coffey, B. M., & Smith, E. F. (2006). Effects of media, backwash, and temperature on full-scale biological filtration. *Journal - American Water Works Association, 98*(12), 61–73. https://doi.org/10.1002/j.1551-8833.2006.tb07824.x

33. Kirisits, M. J., Emelko, M. B. & Pinto, A. J. (2019). Applying biotechnology for drinking water biofiltration: Advancing science and practice. *Current Opinion in Biotechnology, 57*, 197–204. https://doi.org/10.1016/j.copbio.2019.05.009.

34. Brown J, Upadhyaya G, Nyfennegger J, Pope G, Bassett S, Evans A, Carter J, Nystrom V, Black S, Alito C, Lauderdale C. (2020). Biofiltration guidance manual for drinking water acilities. American Water Works Association Research Foundation (Project no. 4719). Denver, CO, 194 pp. ISBN 978-1-60573-516-0.

35. Brown, J., Summers, R. S., LeChevallier, M., Collins, H., Roberson, J. A., Hubbs, S. & Dickenson, E. (2015). Biological drinking water treatment? Naturally. *Journal – American Water Works Association, 107*(12), 20–30. https://doi.org/10.5942/jawwa.2015.107.0183.

36. Tobiason, J. E., & O'Melia, C. R. (1988). Physicochemical aspects of particle removal in depth filtration. *Journal - American Water Works Association, 80*(12), 54–64. https://doi.org/10.1002/j.1551-8833.1988.tb03150.x.

37. Pernitsky, D. J., & Edzwald, J. K. (2006). Selection of alum and polyaluminum coagulants: Principles and applications. *Journal of Water Supply: Research and Technology - Aqua, 55*(2), 121–141. https://doi.org/10.2166/aqua.2006.062.

38. Jin, C., Glawdel, T., Ren, C. L., & Emelko, M. B. (2015). Non-linear, non-monotonic effect of nano-scale roughness on particle deposition in absence of an energy barrier: Experiments and modeling. *Scientific Reports, 5*(1). https://doi.org/10.1038/srep17747.

39. Jin, C., Zhao, W., Normani, S. D., Zhao, P., & Emelko, M. B. (2017). Synergies of media surface roughness and ionic strength on particle deposition during filtration. *Water Research, 114*, 286–295. https://doi.org/10.1016/j.watres.2017.02.010.

40. Urfer, D., Huck, P. M., Booth, S. D. J., & Coffey, B. M. (1997). Biological filtration for BOM and particle removal: A critical review. *Journal - American Water Works Association, 89*(12), 83–98. https://doi.org/10.1002/j.1551-8833.1997.tb08342.x.

41. Huck, P.M., B.M. Coffey, A. Amirtharajah, & E.J. Bower. (2000). Optimizing filtration in biological filters (Report No. 252). AWWA Research Foundation, Denver, CO.

42. Shin, H.-S., Lim, K.-H. (1996). Spectroscopic and elemental investigation of microbial decomposition of aquatic fulvic acid in biological process of drinking water treatment. *Biodegradation, 7*(4), 287–295. https://doi.org/10.1007/bf00115742.

43. So, S. H., Choi, I. H., Kim, H. C., & Maeng, S. K. (2017). Seasonally related effects on natural organic matter characteristics from source to tap in Korea. *Science of The Total Environment, 592*, 584–592. https://doi.org/10.1016/j.scitotenv.2017.03.063.

44. Fox, K. R., Miltner, R. J., Logsdon, G. S., Dicks, D. L., & Drolet, L. F. (1984). Pilot-plant studies of slow-rate filtration. *Journal - American Water Works Association, 76*(12), 62-68. doi:10.1002/j.1551-8833.1984.tb05457.x.

45. Bellamy, W. D., Hendricks, D. W., & Logsdon, G. S. (1985). Slow sand filtration: Influences of selected process variables. *Journal - American Water Works Association, 77*(12), 62-66. https://doi.org/10.1002/j.1551-8833.1985.tb05659.x.

46. Barrett, J. M., Bryck, J., Collins, M. R., Janonis, B. A., & Logsdon, G. S. (1991). Manual of design for slow sand filtration. Denver, CO: AWWA Research Foundation.

47. Collins, M. R., Eighmy, T. T., Jr., J. M., & Spanos, S. K. (1996). Using granular media amendments to enhance NOM removal. *Journal - American Water Works Association, 88*(12), 48-61. https://doi.org/10.1002/j.1551-8833.1996.tb06661.x.

48. Logsdon, G. S., Kohne, R., Abel, S., & LaBonde, S. (2002). Slow sand filtration for small water systems. *Journal of Environmental Engineering and Science, 1*(5), 339-348. https://doi.org/10.1139/S02-025.

49. GRCA (Grand River Conservation Authority). (2021). Update on water quality in the Grand River. Report Number GM-01-21-04.

50. Lyon, J. P., & O'Connor, J. P. (2008). Smoke on the water: Can riverine fish populations recover following a catastrophic fire-related sediment slug? *Austral Ecology, 33*(6), 794–806. https://doi.org/10.1111/j.1442-9993.2008.01851.x.

51. Writer, J. H. & Murphy, S. F. (2012). Wildfire effects on source-water quality: Lessons from Fourmile Canyon Fire, Colorado, and implications for drinking water treatment. US Department of the Interior, US Geological Survey.

52. Dahm, C. N., Candelaria-Ley, R. I., Reale, C. S., Reale, J. K., & Van Horn, D. J. (2015). Extreme water quality degradation following a catastrophic forest fire. Freshwater *Biology, 60*(12), 2584–2599. https://doi.org/10.1111/fwb.12548

53. Murphy, S. F., Writer, J. H., McCleskey, R. B., & Martin, D. A. (2015). The role of precipitation type, intensity, and spatial distribution in source water quality after wildfire. *Environmental Research Letters, 10*(8), 084007. https://doi.org/10.1088/1748-9326/10/8/084007.

54. Mast, M. A., Murphy, S. F., Clow, D. W., Penn, C. A., & Sexstone, G. A. (2016). Water quality response to a high-elevation wildfire in the Colorado front range. *Hydrological Processes, 30*(12), 1811-1823. https://doi.org/10.1002/hyp.10755.

55. BC Wildfire Service (2022, March 28). Wildfire season summary. Province of British Columbia. Retrieved May 11, 2022, from https://www2.gov.bc.ca/gov/content/safety/wildfire-status/about-bcws/wildfire-history/wildfire-season-summary

56. Manem, J. A., & Rittmann, B. E. (1990). Scaling procedure for biofilm processes. *Water Science and Technology, 22*(1-2), 329–346. https://doi.org/10.2166/wst.1990.0158.

57. Huck, P. M., Kenefick, S. L., Hrudey, S. E., & Zhang, S. (1995). Bench-scale determination of the removal of odour compounds with biological treatment. *Water Science and Technology, 31*(11), 203–209. https://doi.org/10.2166/wst.1995.0436.

638 58. Liu, X., Huck, P. M., & Slawson, R. M. (2001). Factors affecting drinking water
639 biofiltration. *Journal - American Water Works Association, 93*(12), 90–101.
640 https://doi.org/10.1002/j.1551-8833.2001.tb09358.x.

641 59. McKie, M. J., Ziv-El, M. C., Taylor-Edmonds, L., Andrews, R. C., & Kirisits, M. J.
642 (2019). Biofilter scaling procedures for organics removal: A potential alternative to piloting.
643 *Water Research, 151*, 87–97. https://doi.org/10.1016/j.watres.2018.12.006.

644 60. Terry, L. G., Pruisner, P., Peterson, E., Dickenson, E., Wang, J., & Summers, R. S.
645 (2019). Scale-up methodology for biological filtration removal of dissolved organic matter.
646 *Environmental Engineering Science, 36*(4), 405–412. https://doi.org/10.1089/ees.2018.0316.

647 61. Bear, J. (1972). *Dynamics of fluids in porous media*. American Elsevier.

648 62. Crittenden, J. C., Trussell, R. R., Hand, D. W., Howe, K. J. & Tchobanoglous, G. (2012).
649 MWH's Water Treatment: Principles and Design. John Wiley & Sons, Hoboken, NJ.

650 63. Rachwal, A., Rodman, D., West, J., Zabel, T. (1986). Uprating and upgrading slow sand
651 filters by pre-ozonation. *Effluent + Water Treatment Journal., 26*(5-6), 143–149.

652 64. Arora, Hemant. (2018). Optimising the Ripening Period of Slow Sand Filters (thesis).
653 Delft University of Technology. http://resolver.tudelft.nl/uuid:a586cde7-38dd-467c-89d2-
654 ee70900aa06c).

655 65. Baird, R., & Bridgewater, L. (2017). Standard methods for the examination of water and
656 wastewater. 23rd edition. Washington, D.C.: American Public Health Association.

657 66. Huber, S. A., Balz, A., Abert, M., & Pronk, W. (2011). Characterisation of aquatic humic
658 and non-humic matter with size-exclusion chromatography – organic carbon detection – organic

659 nitrogen detection (LC-OCD-OND). *Water Research, 45*(2), 879–885.
660 https://doi.org/10.1016/j.watres.2010.09.023

661 67. Health Canada. (2017). Guidelines for Canadian Drinking Water Quality - Summary
662 Table. Retrieved April 11, 2022, from https://www.canada.ca/en/health-
663 canada/services/environmental-workplace-health/reports-publications/water-quality/guidelines-
664 canadian-drinking-water-quality-summary-table.html#t2.

665 68. Vines, M., & Terry, L. G. (2020). Evaluation of the biodegradability of fluorescent
666 dissolved organic matter via biological filtration. *AWWA Water Science, 2*(5).
667 https://doi.org/10.1002/aws2.1201.

668 69. Weishaar, J. L., Aiken, G. R., Bergamaschi, B. A., Fram, M. S., Fujii, R., & Mopper, K.
669 (2003). Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition
670 and reactivity of dissolved organic carbon. *Environmental Science & Technology, 37*(20), 4702–
671 4708. https://doi.org/10.1021/es030360x.

672 70. Hozalski, R. M., Bouwer, E. J., & Goel, S. (1999). Removal of natural organic matter
673 (NOM) from drinking water supplies by ozone-biofiltration. *Water Science and Technology,*
674 *40*(9), 157–163. https://doi.org/10.2166/wst.1999.0466.

675 71. Moona, N., Wünsch, U. J., Bondelind, M., Bergstedt, O., Sapmaz, T., Pettersson, T. J., &
676 Murphy, K. R. (2019). Temperature-dependent mechanisms of DOM removal by biological
677 activated carbon filters. Environmental Science: *Water Research & Technology, 5*(12), 2232–
678 2241. https://doi.org/10.1039/c9ew00620f.

72. Emelko, M. B., & Huck, P. M. (2004). Microspheres as surrogates for cryptosporidium filtration. *Journal - American Water Works Association, 96*(3), 94–105. https://doi.org/10.1002/j.1551-8833.2004.tb10577.x.

73. EPA (U.S. Environmental Protection Agency). (2003). National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule. Federal Register, 68 FR 49548-4968.

74. EPA (U.S. Environmental Protection Agency). (1998). National Primary Drinking Water Regulations: Interim Enhanced Surface Water Treatment; Final Rule. Federal Register, 63:69478-521.

75. Halle, C., Huck, P. M., Peldszus, S., Haberkamp, J., & Jekel, M. (2009). Assessing the performance of biological filtration as pretreatment to low pressure membranes for drinking water. *Environmental Science & Technology, 43*(10), 3878–3884. https://doi.org/10.1021/es803615g.

76. Huang, G., Meng, F., Zheng, X., Wang, Y., Wang, Z., Liu, H., & Jekel, M. (2011). Biodegradation behavior of natural organic matter (NOM) in a biological aerated filter (BAF) as a pretreatment for ultrafiltration (UF) of river water. *Applied Microbiology and Biotechnology, 90*(5), 1795–1803. https://doi.org/10.1007/s00253-011-3251-1.

77. Pramanik, B. K., Roddick, F. A., & Fan, L. (2014). Effect of biological activated carbon pre-treatment to control organic fouling in the microfiltration of biologically treated secondary effluent. *Water Research, 63*, 147–157. https://doi.org/10.1016/j.watres.2014.06.014.

699 78. Pharand, L., Van Dyke, M. I., Anderson, W. B., Yohannes, Y., & Huck, P. M. (2015).
700 Full-scale ozone-biofiltration: Seasonally related effects on NOM removal. *Journal - American*
701 *Water Works Association, 107*(8). https://doi.org/10.5942/jawwa.2015.107.0121.

702 79. Chen, F., Peldszus, S., Elhadidy, A. M., Legge, R. L., Van Dyke, M. I., & Huck, P. M.
703 (2016). Kinetics of natural organic matter (NOM) removal during drinking water biofiltration
704 using different NOM characterization approaches. *Water Research, 104*, 361–370.
705 https://doi.org/10.1016/j.watres.2016.08.028.

706 80. Elsayed, E. H. A. M. (2016). Performance of biological filters for drinking water
707 treatment and their use for high pressure membrane biofouling control (dissertation). University
708 of Waterloo. http://hdl.handle.net/10012/10146

709 81. GRCA. (2021). Dissolved oxygen. Water quality dissolved oxygen. Retrieved May 8,
710 2022, from https://apps.grandriver.ca/waterdata/kiwischarts/wq_dissolvedoxygen.aspx

711 82. Cummings, T. F. (2015). Assessment of nitrate export in agricultural sub-catchments of
712 the Grand River watershed: An isotope approach (thesis). University of Waterloo.
713 http://hdl.handle.net/10012/9188

714 83. Hutchins, R.H. (2011). Dissolved organic matter in the anthropogenically impacted
715 Grand River and natural Burnt River watersheds (thesis). University of Waterloo.
716 http://hdl.handle.net/10012/6428

717 84. Camper, A.C., P. Butterfield, B. Ellis, W.L. Jones, W.B. Anderson, P.M. Huck, C. Volk,
718 N. Welch and M.W. LeChevallier. (2000). Investigation of the biological stability of water

719 treatment plants and distribution systems. American Water Works Association Research
720 Foundation (Report no. 90794), Denver, CO, 468 pp. ISBN 1-58321-072-5.

721 85. Skwaruk, J. (2021). Drinking water treatment technology resilience for management of
722 severely deteriorated water after wildfire (dissertation). University of Waterloo.
723 http://hdl.handle.net/10012/17585.

724 86. Peleato, N. M., Sidhu, B. S., Legge, R. L., & Andrews, R. C. (2017). Investigation of
725 ozone and peroxone impacts on natural organic matter character and biofiltration performance
726 using fluorescence spectroscopy. *Chemosphere, 172*, 225–233.
727 https://doi.org/10.1016/j.chemosphere.2016.12.118.

728 87. Namour, P., & Müller, M. C. (1998). Fractionation of organic matter from wastewater
729 treatment plants before and after a 21-day biodegradability test: A physical-chemical method for
730 measurement of the refractory part of effluents. *Water Research, 32*(7), 2224–2231.
731 https://doi.org/10.1016/s0043-1354(97)00428-4.

732 88. Basu, O. D., Dhawan, S. & Black, K. (2016). Applications of biofiltration in drinking
733 water treatment – a review. *Journal of Chemical Technology & Biotechnology, 91*(3), 585–595.
734 https://doi-org.proxy.lib.uwaterloo.ca/10.1002/jctb.4860.

735 89. Leenheer, J. A., & Croué, J.-P. (2003). Characterizing aquatic dissolved organic matter.
736 *Environmental Science & Technology, 37*(1). https://doi.org/10.1021/es032333c.

737 90. Kelly, E. N., Schindler, D. W., St. Louis, V. L., Donald, D. B., & Vladicka, K. E. (2006).
738 Forest fire increases mercury accumulation by fishes via food web restructuring and increased

739 mercury inputs. *Proceedings of the National Academy of Sciences, 103*(51), 19380–19385.
740 https://doi.org/10.1073/pnas.0609798104.

741 91. Sadler, W. R., & Trudinger, P. A. (1967). The inhibition of microorganisms by heavy
742 metals. *Mineralium Deposita, 2*(3). https://doi.org/10.1007/bf00201912.