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Water Impact Statement

Conventional drinking water treatment plants are not designed to remove many trace organic contaminants (TOrC). This study demonstrates that biofiltration, particularly when granular activated carbon media is employed, can achieve consistent TOrC removal under variable water quality conditions. These findings can help water utilities assess the reliability of biofiltration, which requires minimal energy and material inputs, for TOrC control.

Biodegradation and attenuation of MIB and 2,4-D in drinking water biologically active sand and activated carbon filters

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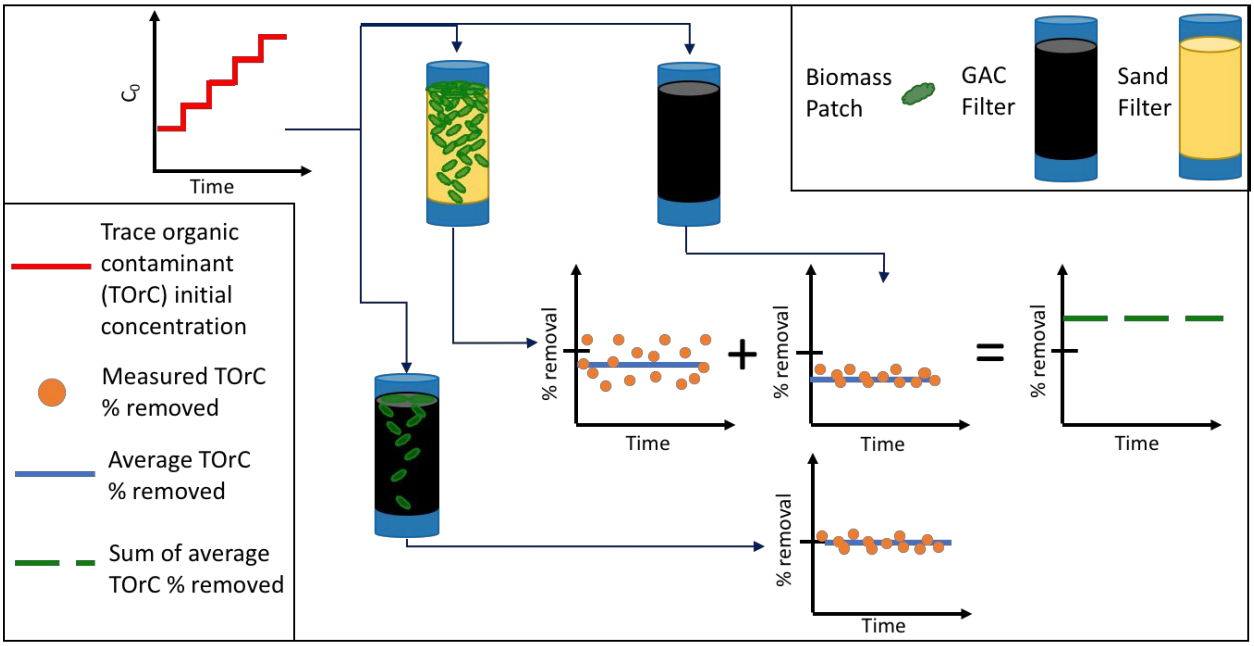
Biologically acclimated sand and granular activated carbon (GAC) filter performance for trace organic contaminant control is compared under variable water quality and operational conditions.



Abstract

Biofiltration for the control of two trace organic contaminants (TOrCs), 2-methylisoborneol (MIB) and 2,4-dichlorphenoxyacetic acid (2,4-D), in the presence of background dissolved organic matter (DOM) was examined. TOrC removal was monitored in biologically acclimated sand and granular activated carbon (GAC) filters and non-acclimated sand and GAC filters. TOrC biodegradation followed pseudo-first-order behavior as removal on a percentage basis remained constant when TOrC influent concentrations increased from 100 and 500 ng L^{-1} and greater removals were observed at longer empty bed contact times. Biomass concentrations on a bed volume basis in the acclimated sand filter were twice that found in the acclimated GAC filter, as the sand particles provided more external specific surface area for biomass attachment. When accounting for differences in biomass concentrations, greater TOrC biodegradation occurred in the acclimated sand filter, indicating that synergistic interactions between biodegradation and adsorption did not occur in the acclimated GAC filter. Equivalent amounts of TOrCs desorbed from the acclimated and non-acclimated GAC filters when TOrCs were no longer spiked into the influent. Thus, acclimated and non-acclimated GAC filters adsorbed similar amounts of TOrCs and biodegradation of adsorbed or desorbed TOrCs was negligible. After switching the primary substrate from non-ozonated to ozonated DOM, total organic carbon removal in the acclimated sand filter increased, but TOrC removal initially declined and then recovered over several days. TOrC removal in the acclimated GAC filter remained relatively constant before, during, and after DOM pre-ozonation, potentially because the residual adsorption capacity in the GAC attenuated fluctuations in TOrC biodegradation.

Keywords

Biofiltration; adsorption; ozone; micropollutant; taste and odor; BAC

1 Introduction

Trace organic contaminants (TOrCs) (i.e., organic contaminants occurring at low- to sub-part per billion concentrations) of natural and anthropogenic origin are frequently detected in drinking water sources.[1] Conventional drinking water treatment plants are not effective in removing most TOrCs, and advanced treatment processes can be expensive, resource intensive, and produce waste residuals.[2] Biologically active filtration (biofiltration) can be a more sustainable alternative for controlling TOrCs in drinking water because it requires minimal energy and material inputs and is simple to implement and operate.[2] In the absence of a disinfectant residual, a more robust population of source water microorganisms can attach to filter media surfaces and degrade TOrCs. Thus, drinking water treatment utilities can promote TOrC removal by eliminating disinfectant residuals through filters while incurring minimal capital and O&M costs. However, effective operation of theses biofilters for pathogenic microorganism removal is paramount.

Despite economic, and environmental advantages, questions remain surrounding biofilter performance for TOrC control during variable influent water quality and operational conditions.[2] These are critical factors to understand because TOrCs do not occur at constant concentrations in the environment,[3,4] and drinking water treatment facilities seldom operate under uniform conditions. For example, seasonal variation in demand flow impacts the hydraulic loading rate resulting in changes to empty bed contact times (EBCTs).

Because TOrCs are present at low concentrations and cannot support primary cellular processes, background dissolved organic matter (DOM) is utilized as the primary substrate in drinking water sources, and TOrCs can be cometabolized or directly catabolized as secondary substrates.[5,6] Secondary substrate utilization occurs when TOrCs are catabolized by specific

enzymes and used as carbon and energy sources, which can be associated with an acclimation phase.[5-8] Cometabolism arises when nonspecific enzymes generated by the primary substrate metabolism fortuitously degrade TOrCs and energy or elemental constituents produced from TOrC degradation reactions are not utilized by cells.[5,9] As a result, TOrC biodegradation rates increase as DOM degradation rates increase. Thus, the concentration and character of DOM can be one of the key water quality parameters that determines the abundance and microbial composition of biomass and, consequently, the ability of a biofilter to biodegrade TOrCs.[10,11] While biomass often requires an acclimation phase to develop the ability to degrade TOrCs,[5,6] the impact of DOM concentration and character on TOrC acclimation and degradation in biofilters is poorly understood.[12]

One approach to increase the resilience of biofilter performance to influent fluctuations and operational changes is to use granular activated carbon (GAC) as the biomass attachment media because biologically active GAC (BAC) removes TOrCs by adsorption and biodegradation.[11, 13, 14] It is conceivable that the ability of BAC filters to adsorb TOrCs and decrease their mobility may provide additional time for biomass to acclimate and recover from water quality perturbations. Also, it has been hypothesized that bio-regeneration of adsorption sites can occur and lead to synergistic TOrC removal by biodegradation and adsorption.[15]

The primary objectives of this study are to (i) investigate the influence of changes to influent TOrC concentration, background DOM concentration and character, and EBCT on TOrC biodegradation performance and acclimation in biofilters, and (ii) evaluate if BAC media enhances biofiltration performance relative to that with non-adsorptive sand media. These objectives were achieved by monitoring the removal of 2-methylisoborneol (MIB) and

2,4-dichlorophenoxyacetic acid (2,4-D) in biologically acclimated sand and GAC filters and in non-acclimated sand and GAC laboratory-scale filters. TOrC influent concentrations were varied by a factor five and influent DOM concentrations and EBCTs were increased by a factor of two. The DOM was preozonated to modify its character for part of this study.

MIB was selected as it is a taste and odor nuisance for many drinking water utilities because it leads to complaints by consumers. MIB is also a cyanobacteria metabolite and can be produced at high levels in cyanobacteria blooms. MIB is recalcitrant to conventional drinking water treatment,[3] but has been shown to biodegrade in drinking water biofilters after biomass acclimation.[6, 16-19] 2,4-D was selected because it is a drinking water contaminant regulated by the U.S. Environmental Protection Agency and it is one of the most widely detected herbicides in drinking water sources.[20] It is commonly applied to agricultural lands in the United States and can enter drinking water sources through stormwater runoff.[4] 2,4-D has also been shown to biodegrade in drinking water biofilters.[6,19, 21]

2 Material and methods

2.1 Filter design, operation, and media treatment history

The biological sand and BAC media used in this study were sampled from full-scale drinking water biofilters. The sand media was collected from the Richard Miller Treatment Plant at the Great Cincinnati (Ohio) Water Works where it had been used for >7 years. The BAC media was collected from the North Bay Regional Water Treatment Plant in Vacaville, CA, were it had been in use for over 2 years without reactivation or "topping" off of filter media. Both Ohio River and Sacramento-San Joaquin River Delta waters treated by biofilters containing the sand and BAC media, respectively, were impacted by domestic and industrial

wastewater as well as agricultural runoff. After media was sampled, it was saturated in filter influent water and shipped in coolers at ambient temperature to the laboratory.

Once media was received in the laboratory it underwent an "acclimation" phase where it was exposed to 34 TOrCs at constant influent concentrations between 10 and 1,000 ng L^{-1} for >1 year.[6] Two of these TOrCs were MIB and 2,4-D that can exhibit steady-state biodegradation after an acclimation phase.[6,19] Their influent concentrations during the acclimation phase are provided in Table 1. Background DOM was also present at 3 mg-C L^{-1} using a DOM isolate described in section 2.2.

Table 1. Average Influent Concentrations with ±95% CI for Each Phase of the Study

phase	experimental description	duration (days)	n	TOrC concentration (ng L^{-1})		TOC concentration (mg-C L^{-1})
				MIB	2,4-D	
acclimation	pre-baseline (sand)	432	4-23	84 ± 35	171 ± 57	3.1 ± 0.3
	pre-baseline (BAC)	432	4-23	98 ± 12	142 ± 33	3.1 ± 0.3
I – influent concentration	baseline 1 (100 ng L^{-1})	3	3	133 ± 77	104 ± 8	2.5
	200 ng L^{-1}	3	5	197 ± 55	188 ± 26	2.4 ± 0.1
	300 ng L^{-1}	8	10	317 ± 4	292 ± 35	2.7 ± 0.2
	500 ng L^{-1}	13	6	525 ± 47	511 ± 42	2.9 ± 0.2
	desorption	3	6	0	0	2.8 ± 0.1
II – primary substrate	baseline 2	5	5	117 ± 4	94 ± 5	2.6 ± 0.1
	2x increased TOC	6	7	138 ± 17	96 ± 4	5.7 ± 1.0
	ozonated DOM	4	5	138 ± 27	106 ± 17	2.7 ± 0.5
III – EBCT	baseline 3	18	13	112 ± 8	127 ± 23	2.3 ± 0.1
	2x increased EBCT	14	8	88 ± 7	113 ± 7	2.2 ± 0.2

After the acclimation phase, a portion of sand and BAC were autoclaved to produce abiotic media. Media was autoclaved at 121°C and 100 kPa for 20 min in feedwater (see Section 2.2) that contained 3 mg-C L^{-1} of total organic carbon (TOC) and 100 ng L^{-1} of MIB and 2,4-D to limit desorption and modifications to the media surfaces.[22] Four glass columns

were filled with (i) autoclaved sand, (ii) biologically-active sand, (iii) autoclaved BAC, and (iv) BAC (Table 2 and Supplementary Information (SI) Figure S1). Sand media with an effective particle size of 0.45 mm was packed into glass columns with an inner diameter of 11 mm (ACE Glass 5820-12) to a height of 32 cm with 8 cm of support media (2 mm glass beads). "Abiotic" and biological sand filters are hereafter referred to as Sand A and Sand B, respectively. GAC media with an effective particle size of 1.1 mm was packed into glass columns with an inner diameter of 15 mm (ACE Glass 5820-20) to the same height as the sand columns. "Abiotic" and biological GAC filters are hereafter referred to as GAC A and BAC, respectively. The GAC A filter was considered an adsorption-only filter and the Sand A filter was used as a control to assess any TOrC losses not caused by biodegradation or adsorption. "Abiotic" filters were expected to become biologically active within a few days of operation as they were colonized by microorganisms in the feedwater. However, "abiotic" filters were not expected to acclimate and biodegrade MIB or 2,4-D in the 11-week study based on previous research with MIB and 2,4-D using a similar setup, and are thus referred to as non-acclimated biofilters.[6, 19, 23]

Table 2. Filter Design and Removal Mechanisms

			Removal Mechanism	
Filter	**"Abiotic"**	**Media Type**	**Biological**	**Adsorption**
Sand A	Yes	Sand	No	No
Sand B	No	Sand	Yes	No
GAC A	Yes	GAC	No	Yes
BAC	No	GAC	Yes	Yes

Filters were gravity-fed from 52 L polyethylene barrels through Teflon-lined plastic 64 mm tubing. Feed tanks were connected to a volatilization trap to limit MIB losses. Target loading rates were 2.4 m hr^{-1} (1 gal/ft^2·min) and 1.2 m hr^{-1} to achieve EBCTs of

approximately 7.5 and 15 min, respectively. Tubing and columns were covered to limit the growth of photosynthesizing microorganisms.

2.2 Feedwater

Feedwater was composed of dechlorinated City of Boulder, CO tap water, which was spiked with a DOM isolate that was concentrated using reverse osmosis from a mountain lake in Big Elk Meadows, CO. Tap water was dechlorinated using GAC.

2.3 TOrC

Radiolabeled MIB and 2,4-D were purchased from American Radiolabeled Chemicals Inc. (St. Louis, MO). Radiolabeled MIB and 2,4-D stocks were prepared in nanopure water. MIB was ^{14}C-ring labeled and 2,4-D was ^{3}H labeled. Unlabeled 2,4-D from Arcos Organics (Geel, Belgium) was mixed with ^{3}H 2,4-D to target a specific activity of 41.1 mCi mmol^{-1}. The ^{14}C MIB stock had a specific activity of 55 mCi mmol^{-1} that was not modified. All of the stocks were free of organic solvents to minimize easily biodegradable primary substrates in the feed.

2.4 Study phases

During the acclimation phase and Phase I, DOM was dosed into tap water to target a concentration of 3.0 mg-C L^{-1}. MIB and 2,4-D were spiked at 100 ng L^{-1} stepped increases from 100 to 500 ng L^{-1} over the course of 27 days as shown in Table 1. For three days thereafter, MIB and 2,4-D were not spiked into the feed to assess their desorption.

In Phase II, primary substrate conditions were modified by increasing the target TOC concentration to 6 mg-C L^{-1}. After six days at the higher TOC the dose was returned to 3 mg-C L^{-1} but the biodegradable fraction in the DOM was increased by ozonating it at a ratio of

1 mg O_3 to 1 mg TOC. Ozone dissipated overnight to ensure no ozone remained before spiking MIB and 2,4-D.

In Phase III, the hydraulic loading rate decreased 2-fold to increase the EBCT from 7.5 min to 15 min. Between Phases I, II, and III, the filters were exposed to baseline conditions that had a target TOC concentration of 3 mg-C L^{-1} and target MIB and 2,4-D concentrations of 100 ng L^{-1} (Table 1). During each phase, Damköhler number II values were determined to be <0.1 according to Terry et al. (2019), indicating that TOrC removal was not external mass transfer limited.[24] Therefore, results from this study are scalable to full-scale biofilters where external mass transfer resistance is also negligible.[24]

2.5 Filter sampling and analysis

The filter influent and effluent were sampled simultaneously for TOC, MIB, and 2,4-D. A single influent sample was collected because the same feedwater was used in all four filters (SI Figure S1). TOC was analyzed by a Sievers 800 TOC Analyzer with an inorganic carbon removal unit in accordance with Standard Method 5310 C.[25] MIB and 2,4-D concentrations were analyzed by a solid-phase extraction/liquid scintillation counting (SPE-LSC) method detailed in Zearley and Summers (2015).[19] This method differentiates parent compounds and transformation products that would be retained on the SPE cartridge from radiolabeled constituents that would pass through the cartridge (e.g., $^{3}H_2O$, dissolved $^{14}CO_2$) as described in Zearley and Summers (2015).[19] The radiolabeled MIB and 2,4-D detection limits were ~10 ng L^{-1}. The coefficient of variance (CV) of the LSC analysis was less than 10% and 12% for MIB and 2,4-D, respectively. Phospholipid biomass concentrations were analyzed at the beginning of the study, after the desorption phase (operation day 30), and after

the third baseline (operation day 49) for all four filters according to the method detailed in Wang et al (1995),[26] which was developed for anthracite, BAC, and sand biofilters.

2.6 Data analysis and modeling

A locally weighted scatter plot smoothing (LOWESS) function with a span window of eight was used to smooth the removal data to determine trends.[27] All statistical analysis was performed with MATLAB 2012a Statistical Package (Natick, MA).

3 Results and discussion

3.1 Non-acclimated sand and GAC filters

Within six days of operation, TOC removal began in the Sand A filter, indicating that there was biological activity (SI Figure S2a). MIB and 2,4-D removal was negligible throughout the 11-week study, suggesting that the biomass never acclimated to MIB and 2,4-D (SI Figure S2b). Acclimation to TOrCs most likely did not occur because the study period was short and/or there was a lack of microorganisms capable of degrading these compounds in the feed. This lack of acclimation is consistent with studies that have examined biomass acclimation to MIB and other organics on fresh media.[28-30] It was assumed that the GAC A filter also acclimated to background DOM because it achieved similar TOC removal as the Sand A filter (SI Figure S2a), but that it did not acclimate to MIB and 2,4-D based on the Sand A filter results.

3.2 Biologically acclimated results

3.2.1 Increasing influent concentration (Phase I)

In Phase I, influent MIB and 2,4-D concentrations increased in 100 ng L^{-1} increments from 100 to 500 ng L^{-1} over the course of 27 days (Table 1). Effluent concentrations from each filter rose after each increase in influent concentration as shown in Figure 1a and SI Figure S3. Removal by biodegradation in the BAC filter was estimated by subtracting the removal in the GAC A filter from the total removal in the BAC filter. TOrC removal expressed on a percentage basis did not systematically change in Sand B, GAC A, and BAC filters as influent concentrations increased (Figure 1b, SI Figure S3b, and Figure 2) and was not statistically different at the different TOrC concentrations tested. During Phase I, the average removals with ±95% CIs across the Sand B filter were 67 ± 4.1% (n = 27) for MIB and 37 ± 4.6% (n = 27) for 2,4-D. TOrC biodegradation in the Sand B and BAC filters exhibited pseudo-first-order removal behavior because the percent removal appeared to be independent of TOrC influent concentrations. Eqn. 1 shown below describes pseudo-first-order kinetics and shows that the percent removed is independent of concentration:

$$\%\ Removal = 100 \times (1 - exp\left(-k' \times EBCT\right)) \qquad (1)$$

where k' is the pseudo-first-order rate constant.

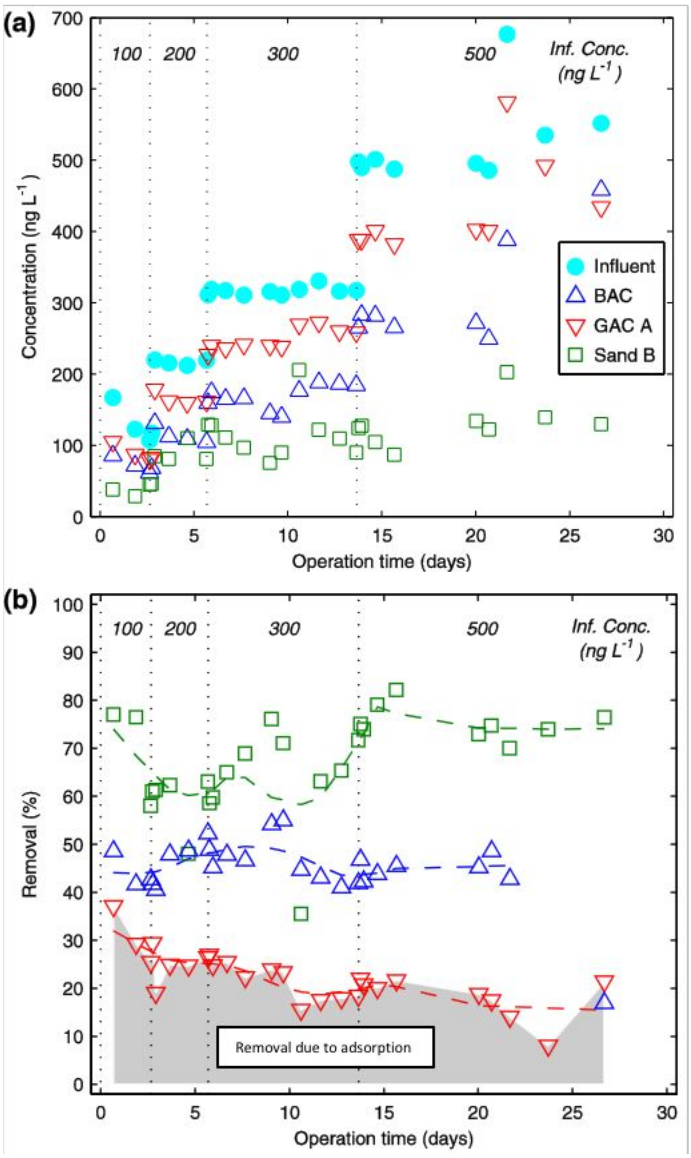


Figure 1. MIB influent (solid) and effluent (open) concentrations (a) and percent removals (b) in the BAC, GAC A, and Sand B filters when influent concentrations were increased from 100 to 500 ng L^{-1} over the 27-day period during Phase I.

TOC removal in Sand B and BAC media was at steady state throughout Phase I. Because the BAC adsorption capacity was effectively exhausted for background DOM, as exhibited by the steady-state TOC removal across the non-acclimated GAC filter that matched TOC removal in the Sand A filter (SI Figure S2), TOC removal in the BAC filter can be attributed to biodegradation. Average TOC removal is represented by data points at the

bottom of each bar indicating MIB removal in Figure 2. Average TOC removals were within the range previously observed for BAC and biologically active sand when operating under similar conditions and when the sand media was in full-scale filters.[6, 31, 32]

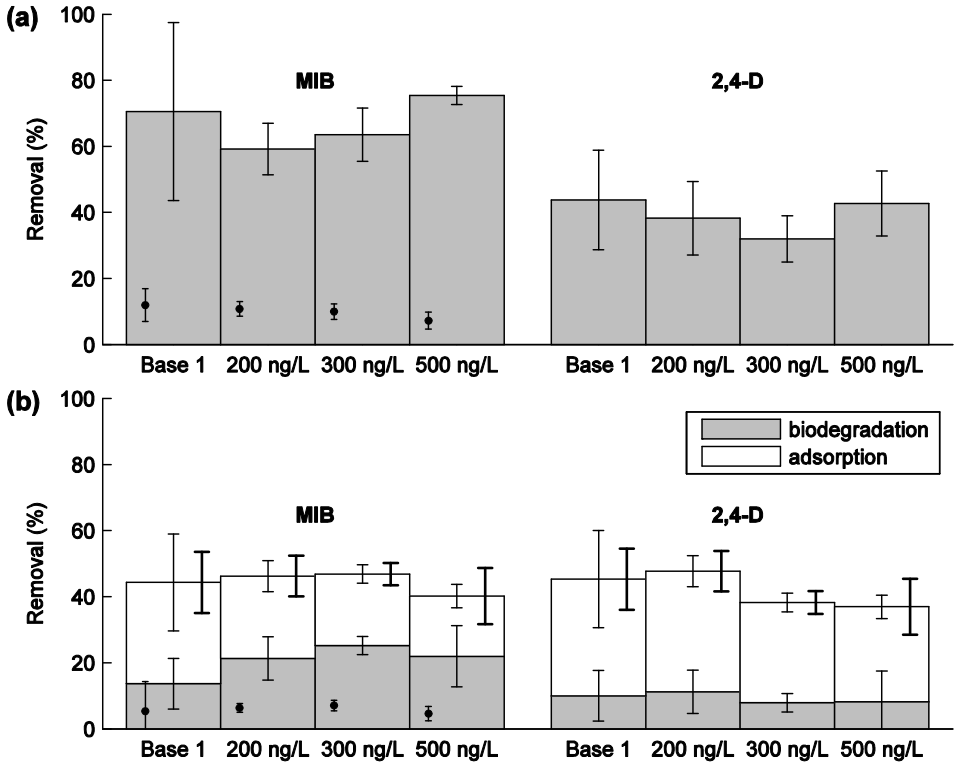


Figure 2. MIB and 2,4-D average removal in the Sand B (a) and BAC filters (b) during Phase I. Errors bars represent ±95% CIs. TOC removal is depicted by circular data points shown towards the bottom of the bars. Removal by biodegradation and adsorption mechanisms in the BAC filter is shown. Thicker error bars are for total BAC removal.

3.2.2 Increased EBCT (Phase III)

In Phase III, the EBCT was increased from ~7.5 to ~15 min by decreasing the hydraulic loading rate in each filter. Figure 3 shows MIB and 2,4-D removal increased across both Sand B and BAC filters when the EBCT increased. Removal due to biodegradation for the ~15 min EBCT was predicted (dashed lines in Figure 3) using the pseudo-first-order model (Eqn. 1) where k' values, shown in Table 3, were calculated using removals by biodegradation at a ~7.5 min EBCT. On average, observed MIB and 2,4-D biodegradation

was lower than predicted in the BAC filter whereas MIB and 2,4-D removal was less than and greater than predicted, respectively, in the Sand B filter (Figure 3). Nonetheless, observed removals by biodegradation at the ~15 min EBCT were not statistically different at a 95% confidence level from predicted removals for both TOrCs. Since the filters were only operated at the increased EBCT for 14 days, the lower observed removal relative to the predicted removal for three of the four filter-TOrC combinations may have been caused by the biomass not being fully developed in the filters. It is possible that if the biofilters were run longer at the ~15 min EBCT, the biomass concentration could have increased further and lead to additional removal.[31]

Table 3. Sand B and BAC filter pseudo-first-order biodegradation rate constants, *k′*, determined with Phase I results.

	***k″* (min)$^{-1}$**	
	MIB	**2,4-D**
Sand B	$1.2 \pm 0.1 \times 10^{-1}$[(a)]	$5.2 \pm 0.8 \times 10^{-2}$[(a)]
BAC	$7.7 \pm 4.7 \times 10^{-2}$[(b)]	$1.4 \pm 0.4 \times 10^{-2}$[(b)]

[a]95% CI, [b]Propagated error

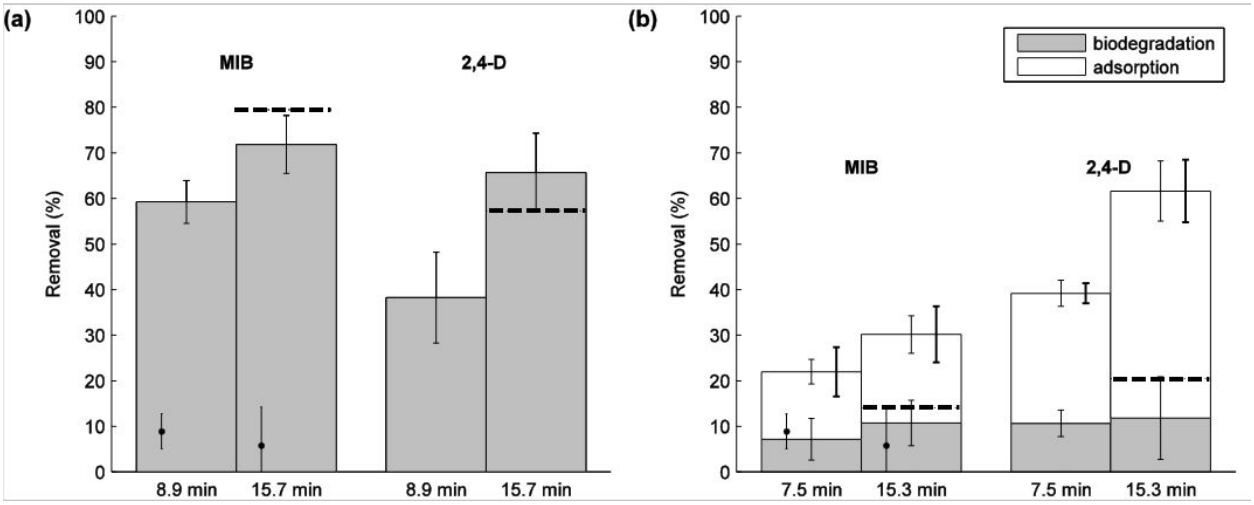


Figure 3. Average TOrC removal by biodegradation across the Sand B filter at 8.9 min and 15.7 min EBCTs (a) and the BAC filter at 7.5 min and 15.3 min EBCTs (b) with ±95% CIs. Predicted TOrC biodegradation removal at the higher EBCT (dashed line) along with the average TOC removals (data points near bottom of bars) are shown. Removals at the shorter and longer EBCTs were determined during Phase I and Phase III, respectively.

3.3 Adsorption and biological removal interactions in BAC

MIB removal across the non-acclimated GAC A filter slightly declined over time as shown in Figure 1b. TOrC removal by GAC adsorption expressed on a percentage basis is independent of TOrC initial concentration when background DOM is present.[33] Thus, the decrease in removal is a result of adsorption sites becoming exhausted as throughput increased. This behavior was also observed for 2,4-D, but was less pronounced most likely because it is more strongly adsorbed relative to MIB and additional throughput was needed to exhaust adsorption sites.[34] When adsorption breakthrough curves approach complete breakthrough an adsorption "tail", characterized by a gradual decrease in removal as throughput increases, can develop.[35] Since MIB and 2,4-D adsorption curves in the GAC A filter were approaching complete breakthrough, it is difficult to discern from this data if adsorption had plateaued or was continuing to decrease. TOC and TOrC removal by adsorption were expected to be relatively small because the GAC was in service at a drinking

water treatment plant for over two years where background DOM continuously fouled the GAC and TOrCs potentially exhausted adsorption sites. TOrC adsorption capacity was further decreased by an additional year of exposure to DOM, MIB, and 2,4-D in the laboratory (Table 1).

TOrC removal occurred in the BAC filter by biodegradation and adsorption (Table 2). Since each filter was operated at the same EBCT and fed by the same influent matrix, removal due to adsorption in the BAC filter was assumed to be the same as removal observed in the GAC A filter. This assumption was supported by desorption tests, discussed further in section 3.4 "Desorption", that showed the same amounts of TOrCs desorbed from the BAC and GAC A filters.

The estimated contributions of biodegradation and adsorption to overall removal are shown in Figure 2-4. During Phase I, the average (± 95% CI) removal across the BAC filter was 44 ± 2.8% for MIB and approximately half of the removal was attributed to biodegradation (Figure 1b & Figure 2b). For 2,4-D, the removal was 40 ± 3.0% and approximately a quarter of the removal was attributed to biodegradation (Figure 2b).

Although greater micropollutant removal would be expected in the BAC filter compared to the Sand B filter because BAC removes contaminants by biodegradation and adsorption, greater MIB removal was observed in the Sand B filter (Figure 2). One reason could be because the effective particle size of the sand media (0.45 mm) is less than half that of the GAC media (1.1 mm) and could provide more external surface area for biomass attachment. Assuming that sand and GAC particles are uniform and spherical, their external surface area to volume ratios (i.e., specific surface areas) would be 5.45 and 13.3 mm^{-1}, respectively, and sand media would provide roughly 2.4-times as much outer surface area as

the GAC media for biomass attachment for a given volume. Biomass concentrations in the Sand B and BAC filters were 183 ± 18 nmol PO_4 (mL bed)$^{-1}$ and 80 ± 9 nmol PO_4 (mL bed)$^{-1}$, respectively, which is similar to biomass concentrations reported elsewhere in drinking water filters.[36,37] There was also 2.3 ± 0.3 times as much biomass in the Sand B filter relative to the BAC filter.

Because the relative differences between the Sand B and BAC biomass concentrations and external specific surface areas were similar (Table 4), these results suggest that the availability of external surface area governs biomass attachment. This finding is in agreement with studies that have found biomass covers a small percentage of available surface area on GAC media and mainly attaches to external surface area possibly because of the limited availability of biodegradable compounds in macropores.[38,39] Other research has found higher biomass concentrations in GAC media relative to inert media, which could indicate that internal surface area increases biomass attachment.[40] One explanation for the discrepancy could involve differences in the bioavailability of adsorbed primary substrate. Higher biomass levels have been found in BAC relative to inert media when the solid-phase primary substrate was bioavailable.[40, 41] Before reaching a steady-state, biomass concentrations have been shown to peak and then decline soon after primary substrate adsorption capacities are exhausted in BAC filters.[22,37,42] Whether studies sampled before, during, or after the biomass concentration peaked could also lead to discrepancies.

Biomass-normalized pseudo-first-order biodegradation rate constants, k'', are provided in Table 4. k'' was calculated by using the pseudo-first-order relationship in Eqn. 1 and replacing the pseudo-first-order rate constant, k', with $k''{\cdot}X$, where X is the biomass concentration. The Sand B k'' value was approximately 1.5-times the BAC k'' value for both

MIB and 2,4-D. Therefore, even when accounting for the effect of biomass concentration on biodegradation rates, it appears that the biomass in Sand B was more efficient at biodegrading MIB and 2,4-D. This finding contrasts with previous reports that observed additive removal or even synergistic interactions between biodegradation and adsorption when adsorbed or desorbed organics were biodegraded.[13,15] However, in these studies the organic contaminants were present at high concentrations and served as primary substrates. Biodegradation of adsorbed and desorbed TOrC could have been limited here because the organic contaminants were present at low concentrations and adsorbed to high energy adsorption sites that could be difficult to regenerate.[35] In addition, when DOM is present it can foul pores and limit TOrC desorption.[43]

Table 4. Sand B and BAC media specific surface areas (i.e., outer surface area to volume ratios), biomass concentrations, and biomass-normalized pseudo-first-order biodegradation rate constants, k'', determined with Phase I results.

	Specific Surface Area (mm^{-1})	Biomass ($nmol\text{-}PO_4$ (mL bed)$^{-1}$)	k'' MIB (mL bed (nmol-PO_4 • min)$^{-1}$)	k'' 2,4-D (mL bed (nmol-PO_4 • min)$^{-1}$)
Sand B	13.3	183 ± 18[(b)]	$6.84 \pm 0.8\times10^{-4}$[(c)]	$2.85 \pm 0.5\times10^{-4}$[(c)]
BAC	5.5	80 ± 9[(b)]	$4.14 \pm 0.3\times10^{-4}$[(c)]	$1.76 \pm 0.5\times10^{-4}$[(c)]
Sand B:BAC	2.4[(a)]	2.3 ± 0.3[(a),(c)]		

[a]Unitless, [b]95% CI, [c]Propagated error.

Because these filters were not external mass transfer limited (see Section 2.4), differences in external mass transfer limitations were likely negligible despite differences in sand and GAC particle sizes.[24] Since the Sand B and BAC media had been exposed at full-scale to different water qualities and TOrCs, it is conceivable that the Sand B filter had additional time to acclimate to MIB and 2,4-D and, as a result, was capable of higher biodegradation rates. However, both medias acclimated to the same water that contained MIB

and 2,4-D for ~1.2 years prior to these experiments (Table 1), and acclimation to these TOrCs has occurred in less than half this time when biofilters were operated under similar conditions.[6,19] Another possibility is that if TOrC biodegradation and adsorption behaved like competitive reactions, adsorption and biodegradation could be antagonistic processes. As discussed in the following section, equivalent TOrC masses desorbed from the BAC and GAC A filters, suggesting the same amounts were adsorbed. It should be noted that GAC A filter also supported biomass (see Section 3.1), and any TOrC adsorption fouling by biomass would have affected both filters. Also, the presence of biomass does not typically limit TOrC adsorption in drinking water biofilters.[44] Since TOrC biodegradation most likely did not limit adsorption, it is possible that TOrC adsorption may have limited biodegradation. One reason could be because adsorption is an instantaneous process once TOrCs diffuse through the stagnant film layer whereas biodegradation requires several steps (e.g., TOrC attachment to the cell envelope, transport through the cell envelope, complexation with an enzyme, etc.).[35,40,45]

Although TOrC removal in the BAC filter was less than the sum of removals observed in the GAC A and Sand B filters, the BAC filter was more efficient than the GAC A filter at removing both TOrCs as shown in Figure 1 and SI Figure S3. This finding is consistent with numerous studies that have found biological activity increases the service life of GAC.[11,13,14] In addition, it is possible that the TOrC removal in the BAC media could have been even more efficient if the particle sizes and biomass concentrations were more similar to that of the Sand B media.

An advantage of using BAC filters rather than the biological sand filters is that BAC filters can be more resilient against water quality perturbations. For example, Figure 2b shows

that when TOrC initial concentrations increased, MIB and 2,4-D removal by the BAC filter remained relatively constant whereas removal in the Sand B filter was more variable ($p<0.05$). Similar results can be found in the literature for the removal of organic compounds that served as the primary substrate.[14,15,46] TOrC percent removal by the GAC A filter also stayed stable, which was expected because TOrC removal is independent of its initial concentration and the initial concentration of other TOrCs when background DOM is present.[33,47] Consistent TOrC removal by adsorption in the BAC filter is likely one reason why the overall TOrC removal remained more stable. It is also possible that the residual adsorption capacity in the BAC decreased TOrC mobility and provided additional time for biomass to acclimate and attenuate increases in influent concentrations.

The cumulative MIB and 2,4-D masses removed by the Sand B and BAC filters normalized by mass and volume of filter media during Phase I are provided in Table 5. Approximately 40% and 36% of the MIB and 2,4-D, respectively, that was loaded onto the BAC filter was removed. The biodegradation to adsorption ratio for the BAC filter was 1.2 for MIB and 0.3 for 2,4-D. This shows that biodegradation and adsorption played near equal roles in MIB removal and adsorption was the dominant 2,4-D removal mechanism in the BAC filter as illustrated in Figure 2b. When the EBCT increased in the BAC filter, the MIB biodegradation to adsorption ratio remained the same. However, for 2,4-D the biodegradation to adsorption ratio decreased at the larger EBCT, indicating that most of the increased removal was associated with adsorption (Figure 3). The adsorption-biodegradation ratio was expected to change with an increase in EBCT since adsorption is not exponentially affected by changes in EBCT as is biodegradation (Eqn. 1).[34] The adsorption ratio at the 15.3 and 7.5 min EBCTs for MIB was 1.3 and for 2,4-D it was 1.8. These results suggest that adsorption

will play a more significant role at higher EBCTs for more strongly adsorbed compounds. Adsorption increased at longer EBCTs because adsorption in GAC adsorbers is controlled, in part, by adsorption kinetics and increasing the EBCT provided additional time for TOrC adsorption.[35]

3.4 Desorption

At the end of Phase I, TOrC addition to the filter influent was discontinued for a period of three days. No desorption was detected from the Sand B filter, which supports the assumption that biodegradation was the only TOrC removal mechanism. In the GAC A and BAC filters the effluent MIB concentration at the beginning of the desorption phase was initially 100 ng L^{-1} and decreased by ~25% each day. For 2,4-D, the initial desorption effluent concentration was 35 ng L^{-1} and decreased by ~50% each day. Beyond 3 days MIB and 2,4-D concentrations in the filter effluent were below detection and the BAC and GAC A filters desorbed similar amounts of MIB and 2,4-D as shown in Table 5. These results suggest that they also adsorbed similar masses of each TOrC and that adsorbed MIB and 2,4-D were not bioavailable and did not biodegrade after they were desorbed. Of the cumulative mass adsorbed, ~11% of the MIB and ~2.0% of the 2,4-D desorbed from each filter during the desorption period (Table 5). Little TOrC desorption was expected because adsorbed DOM blocks pores and can hinder back diffusion and desorption of TOrCs.[43] Higher MIB desorption compared to 2,4-D was expected since MIB is more weakly adsorbed relative to 2,4-D.[34]

Table 5. Cumulative Mass Removed by Biodegradation and Adsorption over 27 days during the Increasing Contaminant Concentration Phase (n=28) and Desorption for 3 days (n=6) of MIB and 2,4-D in BAC and Sand B filters

	MIB			2,4-D		
	Mass ($\mu g\ g^{-1}$ bed)	Mass ($\mu g\ mL^{-1}$ bed)	(%)	Mass ($\mu g\ g^{-1}$ bed)	Mass ($\mu g\ mL^{-1}$ bed)	(%)
BAC						
loaded	4.2	1.9	--	4.0	3.3	--
removed	1.7	0.76	40	1.5	1.22	36
biodegraded	0.91	0.41	54	0.32	0.27	22
adsorbed[1]	0.78	0.35	46	1.13	0.95	78
Desorbed[2]	0.09	0.04	11	0.023	0.019	2.0
Sand B						
loaded	1.1	1.8	--	1.0	1.7	--
removed	0.77	1.3	71	0.45	0.73	43

[1]Measured in the GAC A filter and assumed to be the same in the BAC filter, [2]Measured in both the BAC and GAC A filters.

3.5 Primary substrate conditions (Phase II)

After the desorption phase, the filters were run under baseline conditions for 5 days (Table 1) and then the influent TOC concentration increased ~2-fold to 5.7 ± 1.0 mg-C L^{-1} for the next six days. Average MIB and 2,4-D removal did not significantly change compared to baseline removal for each filter as illustrated in Figure 4. The average TOC percent removal decreased slightly when the TOC influent concentration was increased, but the difference was not statistically significant at a 95% confidence level in the Sand B and BAC filters. While it was anticipated that an increase in the primary substrate would yield more biomass and subsequently increase the degradation of MIB and 2,4-D, the six days of operation under the higher TOC loading may have been inadequate for biomass growth that would result in a quantifiable difference in degradation.

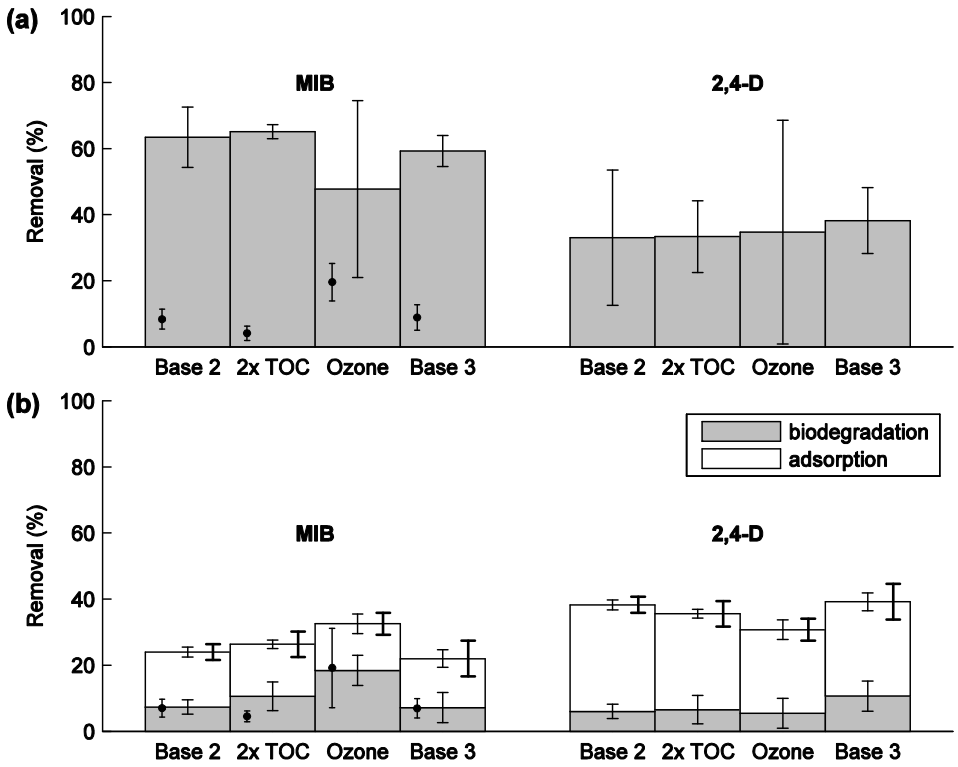


Figure 4. MIB and 2,4-D average removals with ±95% CI during increased influent TOC concentration and preozonated TOC phase for (a) Sand B filter and (b) BAC. Thicker error bars are for the total BAC removal, and baseline conditions are given as Base 2 and Base 3.

When DOM was preozonated, the average TOC percent removal increased by a factor of ~2.5 compared to baseline conditions for the Sand B and BAC filters as shown in Figure 4. Increased TOC removal was expected since ozonation increases the portion of easily biodegradable DOM.[5,48] Greater TOC removal was likely associated with an increase in biomass concentration because the headloss significantly increased in Sand B, causing the hydraulic loading rate to decrease and the EBCT to increase to ~25 min in the Sand B filter. To account for changes in removal caused by the increase in EBCT, removal was normalized using Eqn. 2 to match the 8.1 min EBCT measured in the BAC filter during ozonation according to the approach detailed in Zearley and Summers (2015):[19]

$$\text{EBCT Normalized Removal} = 1 - \exp\left(\ln\left(\frac{C_{Eff}}{C_{Inf}} \right) \frac{EBCT_{norm.}}{EBCT_{sampling}} \right) \quad (2)$$

The normalized removals of MIB and 2,4-D by the Sand B filter are shown in Figure 5. Removals dropped significantly 1 hr after exposure to preozonated DOM and then recovered over the next few days. However, MIB removal did not fully recover and remained lower than baseline removals throughout the preozonated DOM phase whereas 2,4-D removal recovered to slightly above average baseline removals. Removals of the contaminants quickly (<2 days) returned to baseline removals once preozonation ceased. Likewise, headloss decreased and the EBCT returned to baseline conditions within 1 day.

If TOrCs were removed by cometabolism, greater TOrC removal would have been expected with the greater TOC removal. Thus, the temporary decrease in removal supports utilization of MIB and 2,4-D as secondary substrates. However, it is also possible preozonated DOM selected for microorganisms that were less capable of biodegrading these TOrCs via cometabolism.[5]

Ozonated DOM may have selected for MIB degraders that took several days to increase in abundance until reaching a steady-state. The activity of other MIB degraders may have decreased rapidly if a portion of their primary substrate was destroyed by ozonation. Such a scenario could explain the sharp decline followed by a slow increase in MIB removal. This hypothesis could also explain the observed changes in 2,4-D removal, except 2,4-D degrading bacteria selected by ozonated and non-ozonated DOM might degrade 2,4-D at similar rates. Speitel et al (1989) put forth a similar theory after decreased 2,4-dichlorophenol removal was observed when preozonation was performed.[11]

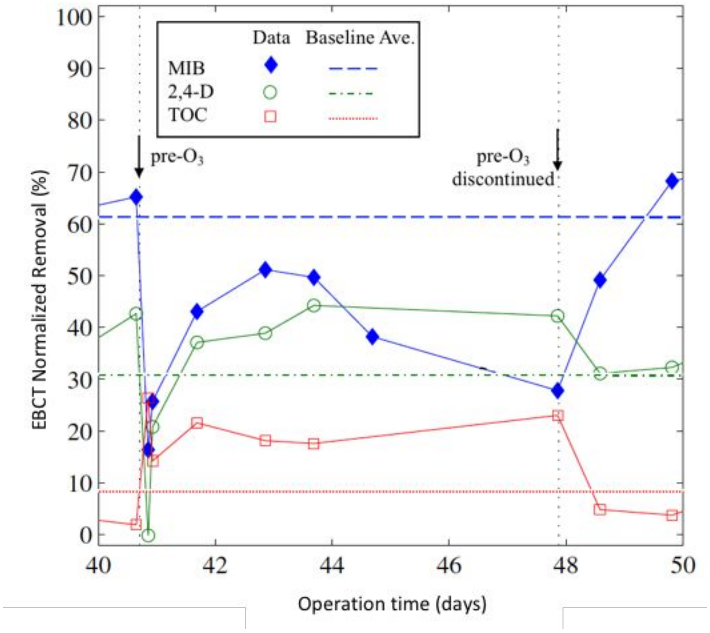


Figure 5. MIB, 2,4-D, and TOC removal by the Sand B filter normalized to a 8.1 min EBCT during the preozonated DOM phase (between dashed vertical lines). Average removals at baseline conditions are indicated by horizontal lines.

MIB and 2,4-D removal by the GAC A and BAC filters did not significantly change when ozonated DOM was present (Figure 6). These results show that the BAC filter was more resilient to changes in DOM character compared to the sand filter. One reason is because TOrC removal by adsorption did not decline, except for one data point, in the presence of ozonated DOM (Figure 6). The more constant removal could have also been associated with the GAC media potentially adsorbing and desorbing ozonated and non-ozonated DOM that may have slowed the transition in primary substrate surrounding attached biomass.[48]

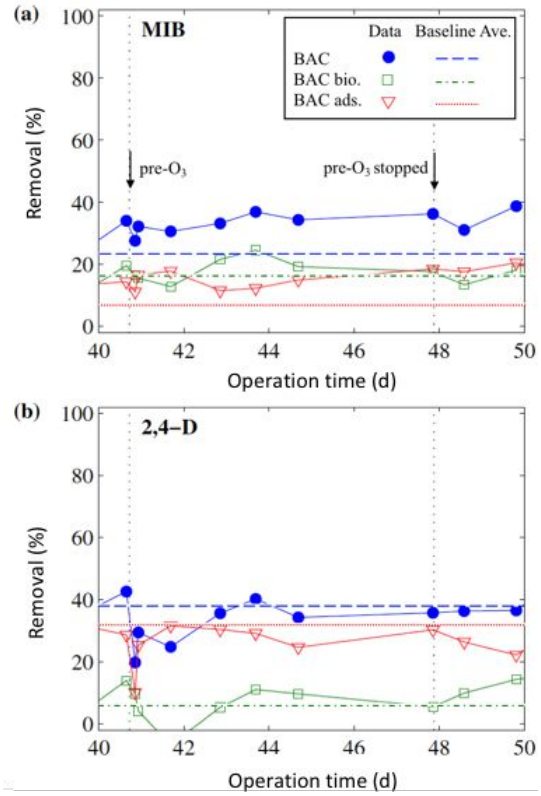


Figure 6. MIB (a) and 2,4-D (b) removal by the BAC filter before, during, and after the preozonated DOM phase. Average removals determined under baseline conditions are depicted by dashed lines.

4 Conclusions

- Varying influent TOrC concentrations between 100 and 500 ng L^{-1} did not influence the percent removal of MIB and 2,4-D. Greater removal was observed at longer EBCTs in the acclimated sand and BAC filters. These results suggest that TOrC biodegradation followed pseudo-first-order kinetics.
- Biomass concentrations were higher in the acclimated sand filter relative to the BAC filter, likely because of the smaller diameter of the sand particles that would provide more external surface area for biomass attachment.

- The BAC filter achieved less TOrC removal than the acclimated sand filters, even when accounting for differences in biomass concentrations.
- The BAC filter achieved higher MIB and 2,4-D removal relative to the non-acclimated GAC filter.
- Equivalent TOrC masses desorbed from the BAC and non-acclimated GAC filters when the influent TOrC feed was temporarily halted, suggesting that the BAC and GAC filters adsorbed similar amounts of TOrCs. These results show that biodegradation of adsorbed and desorbed TOrCs was negligible.
- When pre-ozonated DOM was utilized, TOrC removal rapidly declined and then recovered over several days in the acclimated sand filter. Because TOC removal increased after pre-ozonation was performed, TOrC biodegradation likely occurred by secondary substrate utilization instead of cometabolism. This removal behavior could also suggest that ozonated DOM selected for different TOrC degrading bacteria.
- TOrC removal remained relatively constant in the GAC and BAC filters compared to the acclimated sand filter throughout this 11-week study, including when pre-ozonation was performed. The more resilient performance under variable influent conditions can likely be attributed to the residual adsorption capacity in the BAC media.

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