Spring 1-1-2012

Biodegradation and Attenuation of Trace Organic Contaminants in Biological Drinking Water Filters

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by

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A thesis submitted to the
Faculty of the Graduate School of the
University of Colorado in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
Department of Civil, Environmental, and Architectural Engineering
2012

This thesis entitled:
Biodegradation and attenuation of trace organic contaminants in biological drinking water filters

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November 28th, 2012

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above-mentioned discipline.

ABSTRACT

Zearley, Thomas L. (Ph.D. Civil Engineering)

Biodegradation and attenuation of trace organic contaminants in biological drinking water filters

Thesis directed by R. Scott Summers, Professor, Department of Civil, Environmental, and Architectural Engineering, University of Colorado at Boulder

The occurrence of trace organic contaminants in drinking water sources concerns utilities since the human health risk is often unknown for many of the contaminants and their occurrence in mixtures complicates the health risk uncertainty. Drinking water treatment facilities are looking for technologies that remove trace organic contaminants to lower this potential risk. Biological filtration (biofiltration) can be an effective treatment process to reduce trace organic contaminants at little extra cost to most surface water treatment plants.

The objectives of this thesis were to evaluate and model the effects of biological filter (biofilter) design and operation on trace organic contaminant removal. The long-term removals of 34 trace organic contaminants were evaluated at a constant influent concentration. The contaminants included pesticides, pharmaceuticals, and personal care products, some of which are endocrine disrupting chemicals, and represented a wide range of uses, chemical structures, adsorbabilities, and biodegradabilities. Contaminant removal ranged from no measurable removal to near-complete removal with effluent concentrations below the detection limit. Contaminant removals followed one of four trends: steady state removal throughout, increasing removal to steady state (acclimation), deceasing removal, and no removal (recalcitrant).

Acclimation occurred at different rates depending on the contaminant and the community structure of the biofilter. Contaminant removals followed pseudo-first-order kinetics in drinking water biofilters and were modeled using a biomass based pseudo-first-order rate constant model. When a biofilter was intermittently exposed to a trace organic contaminant, the biofilter retained its biodegradation capacity for non-exposure events less than five months. Granular activated carbon (GAC) biofilters provided more stable removals under variable influent conditions (attenuation) as compared to a non-adsorptive media. The performance of trace organic contaminant removal in biological GAC (BAC) was a function of the adsorption affinity and biodegradability of a contaminant and the acclimation state of the biofilter. The framework for a biofiltration treatment technique for the control of trace organic contaminants was developed from the models and behaviors observed.

DEDICATION

I dedicate this thesis to my father who shared with me his love of water.

ACKNOWLEDGMENTS

I would like to thank everyone that supported and helped me completed this thesis. First on this list is my advisor, Scott Summers, with his steady guidance and mentoring allowed me to expand my knowledge and experience in the water sector for which I will forever be thankful. Additionally, the discussions and advice from JoAnn Silverstein, Fernando Rosario-Ortiz, Kevin McCabe, and Robin Collins were much appreciated.

A portion of this research was funded by the Solano County Water Agency, California Department of Water Resources, California Department of Public Health through the state of California Proposition 50 and MWH, Inc.

I would like to acknowledge the Department of Civil, Environmental, and Architectural Engineering at CU, the National Water Research Institute (NWRI), Malcolm Pirnie, Inc., and the U.S. EPA for providing fellowships for my study and research. The U.S. EPA fellowship was through the Science To Achieve Results (STAR) program (No. 9173000). This thesis has not been formally reviewed by the EPA. The views expressed in this thesis are solely those of the author and the EPA does not endorse any products or commercial services mentioned in this thesis.

I would like to thank the Greater Cincinnati Water Works and Debbie Metz, Bruce Whitteberry, and Jeff Vogt for providing the sand media, data, and always supporting our research goals; the North Bay Regional Water Treatment Plant for providing the GAC media; and Deflef Knappe's laboratory at North Carolina State for providing GC analysis. Special

thanks go to Imma Ferrer and Michael Thurman for providing the LC/MS-MS analysis along with stimulating conversation and the occasional winter skiing hut trip.

Thanks to all of my past and present lab mates and colleagues that helped out with my experiments and made it a joy to go to the lab every day. I would especially like to thank Kate Dowdell and Kyle Shimabuku for collecting the data in Chapter 5; and Janet Cardenas, Anthony Kennedy, and Chris Corwin for collecting adsorption data used in this research and teaching me how adsorption works. Thank you to Erin Fletcher who taught statistical analysis to an engineer. Thank you to Ali Ling and Matt Haggerty for their friendship, support, and entertaining escapes to the mountains.

I would like to thank my family and friends who has always supported my ambitions and dreams. I would especially like to thank my wife Amelia who is the reason I am still sane by giving me daily encouragement and always making me laugh.

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Chapter 1
Introduction

1.1 MOTIVATION

Trace organic contaminants, defined herein as organic compounds of interest occurring at low- to sub- parts per billion (ppb) concentrations, can be either anthropogenic or naturally derived. Trace organic contaminants are being detected more frequently in surface waters which are used as drinking water sources (Kolpin et al., 2002; Coupe & Blomquist, 2004; Benotti et al., 2008; Focazio et al., 2008) and in treated drinking water (Coupe & Blomquist, 2004; Benotti et al., 2008; Wang et al., 2011; Delgado et al., 2012). The increased frequency of detection is a function of both the increased use of organic chemicals and of improved analytical capabilities. The human health risk is generally unknown for trace organic contaminants at these low concentrations (Fawell, 2008), and their occurrence in mixtures complicates the human health risk uncertainty.

The current constraints in the Safe Drinking Water Act (SDWA) require the U.S. Environmental Protection Agency (EPA) to regulate contaminants individually. Another regulatory approach suggested by USEPA Administrator Jackson is to address contaminates as groups (USEPA, 2010). There is recently support for this regulatory approach as the USEPA announced plans to regulate carcinogenic volatile organic compounds (VOCs) as a group (USEPA, 2011), and the European Union has regulated pesticides as a group (EU, 1998). A technology approach to the treatment of these groups can be to define a "treatment technique" that controls the trace organic contaminants, e.g. membranes, activated carbon, advanced

oxidation, or biotreatment. Such an approach is used with the Long-term Enhance Surface Water Treatment Rule (LTESWTR) for pathogenic microorganisms; filtration and disinfection.

This research lays a foundation for the development of a biological filtration treatment technology that could serve as a regulatory defined "treatment technique" for the control of trace organic contaminants.

1.2 DRINKING WATER BIOLOGICAL FILTERS

Biological filtration is a viable drinking water treatment technology, with widespread use in Europe, but limited use in the United States. Most granular media filters can be converted into biological filters (biofilters) simply by not carrying a disinfection residual through the filter (Servais et al., 2005), thus allowing naturally occurring microorganisms in the source water to attach to the media surface and develop a biofilm (Hozalski & Bouwer, 1998; Servais et al., 2005). The biomass in biofilters grows and maintains itself on the biodegradable fraction of the dissolved organic matter (DOM) which serves as the primary substrate. The DOM is comprised of a heterogeneous mixture of organic compounds, both natural and anthropogenic in nature, which vary from location to location.

A wide range of media types are used for biofilters, the most common materials are silica sand, anthracite, or granular activated carbon (GAC). When GAC filters are operated in a biological mode, they are often referred to as biological GAC (BAC). BAC usually out performs inert media because of simultaneously biodegrades and adsorbs organic. Biofilters are usually operated in a similar manner as traditional media filters including backwash cycles. Backwashing does not cause a significant loss of the attached microorganisms from the media, although chlorine-free backwash water leads to increased biomass concentrations and is preferred (Servais et al., 2005).

1.2.1 Organic Compound Removal

Organic compounds are biodegraded in biofilters either by direct catabolism or cometabolism (Alexander, 1999). Primary and secondary substrates are directly catabolized by specific enzymes and used as carbon and energy sources for the microorganisms. A secondary substrate is defined as a compound at a concentration below the threshold concentration (S_{min}) needed to support primary cellular processes without another substrate present (Stratton et al., 1983; Rittmann & McCarty, 2001). Typical S_{min} concentrations range from 40 to 800 μg L^{-1} (Stratton et al., 1983). Cometabolized compounds are biodegraded by nonspecific enzymes generated by the primary substrate metabolism and any energy or constituent elements gained from this reaction are not used by the cell (Alexander, 1967).

The primary substrate in most drinking water biofilters is the biodegradable fraction of the dissolved organic matter (DOM), which consists of a range of natural and, in some cases, anthropogenic compounds that occur at concentrations above a S_{min}, either singularly or collectively (Rittmann & McCarty, 2001; Koudjonou et al., 2005). Trace organic contaminants are removed by secondary substrate utilization or cometabolism because of their low concentrations. An acclimation period (sometimes called an adaptation period) lasting for days to months can occur for trace organic contaminants biodegradation (Alexander, 1999). Possible explanations for the observation of an acclimation period include the proliferation of small microbial populations and genetic adaptations within the microbial population through mutations or transfer of genetic information (Alexander, 1999; Rittmann & McCarty, 2001).

Drinking water biofilters have been shown to biodegrade algal metabolites, such as 2-methylisoborneol (MIB), geosmin, and microcystins (Westerhoff et al., 2005b; Elhadi et al., 2006; Ho et al., 2006; McDowall et al., 2007). Biofilters have also been shown to biodegrade

endocrine disrupting compounds (EDCs) and pharmaceuticals at trace contaminant concentrations (Snyder et al., 2007; Zuehlke et al., 2007; Halle, 2010; Meffe et al., 2010). Some EDCs, pharmaceuticals, and herbicides are removed in bank filtration and the main removal mechanism is attributed to biodegradation (Verstraeten et al., 2002; Hoppe-Jones et al., 2010; Maeng et al., 2011). However, other than for ozonation by-products and algal metabolites, there is little trace contaminant removal data available under controlled conditions in which the impact of design and operation parameters and biomass behavior have been systematically evaluated for a range of trace organic contaminants (Servais et al., 2005).

1.3 RESEARCH OBJECTIVES AND HYPOTHESES

The objective of this research was to evaluate and model the effects of biofilter design and operation and biomass behavior on trace organic contaminant biodegradation by attached microorganisms under drinking water conditions. In addition, the results were outlined to form a foundation for the development of a biofiltration "treatment technique" for the control of biodegradable trace organic contaminants (Figure 1.1). These objectives were achieved by testing three hypotheses.

Hypothesis 1: Incomplete removal of a trace organic contaminant is caused by lack of exposure to adapted biomass and can be predicted using first-order kinetics. Longer empty bed contact times (EBCTs) will increase removal of trace organic contaminants because of the increased exposure to adapted biomass.

Hypothesis 2: Attached microorganisms in biofilters retain the capacity to re-acclimate in less than a day to degrade trace organic contaminants during intermittent exposure.

Hypothesis 3: The use of GAC media will improve removal of trace organic contaminants in biofilters.

Hypothesis 3a: GAC biofilter media attenuates trace organic contaminant removals during variable influent conditions.

Hypothesis 3b: Adsorption and biodegradation are significant trace organic contaminant removal mechanisms in BAC. Removal behaviors can be predicted by using the trace organic contaminant biodegradation potential, adsorption potential, and the degree of DOM fouling on the GAC.

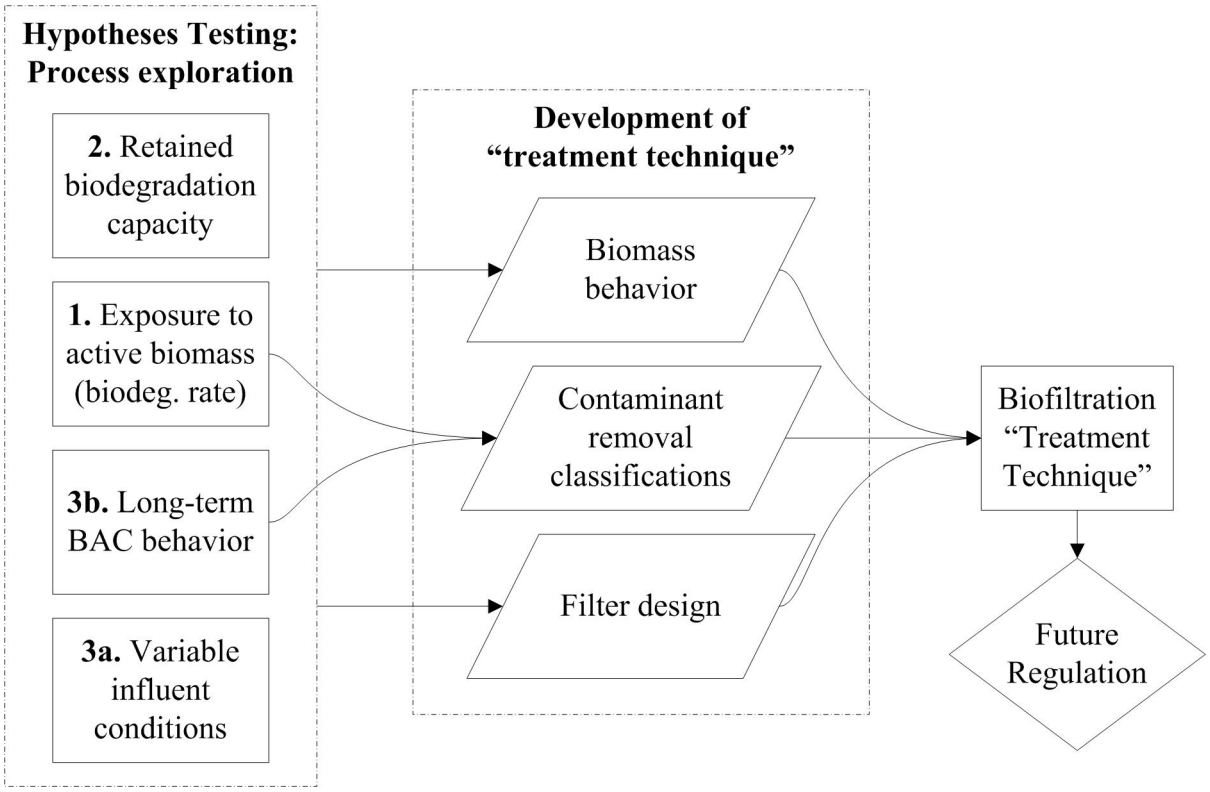

Figure 1.1. Flowchart of research.

1.4 SCOPE

This research was limited to the study of bench-scale biofilters with media from full-scale drinking water facilities. The trace organic contaminants were at environmentally relevant concentrations and chosen as a representative sample of contaminants likely to occur in drinking water sources. The representative trace organic contaminants had a wide range of biodegradability and adsorbability.

1.5 THESIS ORGANIZATION

This thesis is divided into seven chapters to address the objectives and hypotheses. Chapter 2 outlines the materials and methods used throughout this research. Chapter 3 evaluates and models the impact that exposure to adapted biomass has on trace contaminant removal by determining trace organic contaminant biodegradation rates. Chapter 4 investigates the retained biodegradation capacity of biofilters during episodic exposure events. Chapter 5 investigates the attenuation capacity of GAC biofilter media to variable trace organic contaminant influent conditions. Chapter 6 evaluates the long-term removal behavior of trace organic contaminants in BAC filters and includes a foundation for a future regulatory "treatment technique". Lastly, Chapter 7 summarizes the findings of this research.

Chapter 2
Material and Methods

2.1 EXPERIMENTAL DESIGN AND OPERATION

2.1.1 Media Type and Origin

Unless noted, biologically active media from full-scale biological filters was used for all experiments. The sand and GAC media came from different drinking water facilities.

Biologically active sand media from a full-scale filter, which was in operation for over seven years in the Richard Miller Plant at Greater Cincinnati Water Works, was sampled three times (August 2009, January 2010, and April 2010) and shipped to the University of Colorado. The sand media had an effective size of 0.45 mm and an approximate uniformity coefficient of 1.3. The source water, the Ohio River, was impacted by upstream anthropogenic activity including municipal and industrial wastewater treatment discharges, as well as agricultural and urban runoff. Previous sampling of the Ohio River water has shown occurrence of a range of trace organic contaminants (Metz et al., 2009).

The GAC media was sampled in April 2010 from the North Bay Regional Water Treatment Plant in Vacaville, CA. Three media ages were sampled from three filters that had been in service for 2, 6, and 15 years without the media being replaced or reactivated. The GAC media was wet sieved in chlorine free water to a Standard Mesh size of 10 x 16 before packing the columns. The source water, the North Bay Aqueduct, was impacted by similar discharges and runoff as the Ohio River but to a lesser degree (CADWR, 2011). The North Bay Aqueduct pulls water from the northern end of the Sacramento-San Joaquin River Delta.

2.1.2 Biofilter and Feed System Design

The biofilters were packed into laboratory glass columns with Teflon end caps and 316L stainless steel fittings. All of the filters had the same design except for the slow sand filter (SSF) and Biofilter G1. The design parameters of all the filters are shown in Table 2.1. Every filter had a layer of support media (2 mm glass beads) below the filter media. The support media was not included in the calculation of the EBCT. The sand filters were packed into 11 mm inner diameter glass columns (ACE Glass 5820-12), and the GAC filters were packed into 25 mm inner diameter glass columns (ACE Glass 5820-37). A needle valve after each column was used to control flow. Sampling ports were located immediately before and after each column to assess the removal associated directly with the filter.

Table 2.1. Biofilter Design Parameters

Biofilter	media type	experiment	target EBCT (min)	media height (cm)	inner diameter (mm)	support media height (cm)
1a	sand	BR, VIC	7.5	31	11	8
1b	sand	BR	7.5	31	11	8
2	sand	BR, LTB	7.5	31	11	8
SSF	sand	BR	5.25 hr	46	50	5
R1	sand	RBC	7.5	31	11	8
R2	sand	RBC	7.5	31	11	8
R3	sand	RBC	7.5	31	11	8
R4	sand	RBC	7.5	31	11	8
R5	sand	RBC	7.5	31	11	8
R6	sand	RBC	7.5	31	11	8
R7	sand	RBC	7.5	31	11	8
G1	GAC (fresh)	LTB	7.5	61	25	8
G2	GAC (2 yr)	LTB, VIC	7.5	31	25/15	8
G3	GAC (6 yr)	LTB	7.5	31	25	8
G4	GAC (15 yr)	LTB	7.5	31	25	8

BR: biodegradation rate
RBC: retained biodegradation capacity
VIC: variable influent conditions
LTB: long-term behavior in BAC

The SSF was run parallel to Biofilter 1 with the same feedwater (Figure 2.1). The SSF consisted of one 50 mm inner diameter glass column (ACE Glass 5820-55) with 46 cm of sand

media and 5 cm of support media (2 mm glass beads). The sand media in the SSF was 40.6% Richard Miller Plant sand and 59.4% Standard Mesh size 20 x 60 Quikrete play sand.

The biofilters were gravity fed from multiple polyethylene (PE) feed barrels 2 to 3 m above the biofilters. The feed barrels were refilled as needed, usually every two to three days. Teflon coated PE tubing connected the feed barrels to the biofilters. The biofilter columns and tubing were covered to minimize photosynthesizing microorganisms from growing in the filters. A feed system schematic for all of the experiments is present in Figure 2.1, Figure 2.2, and Figure 5.1.

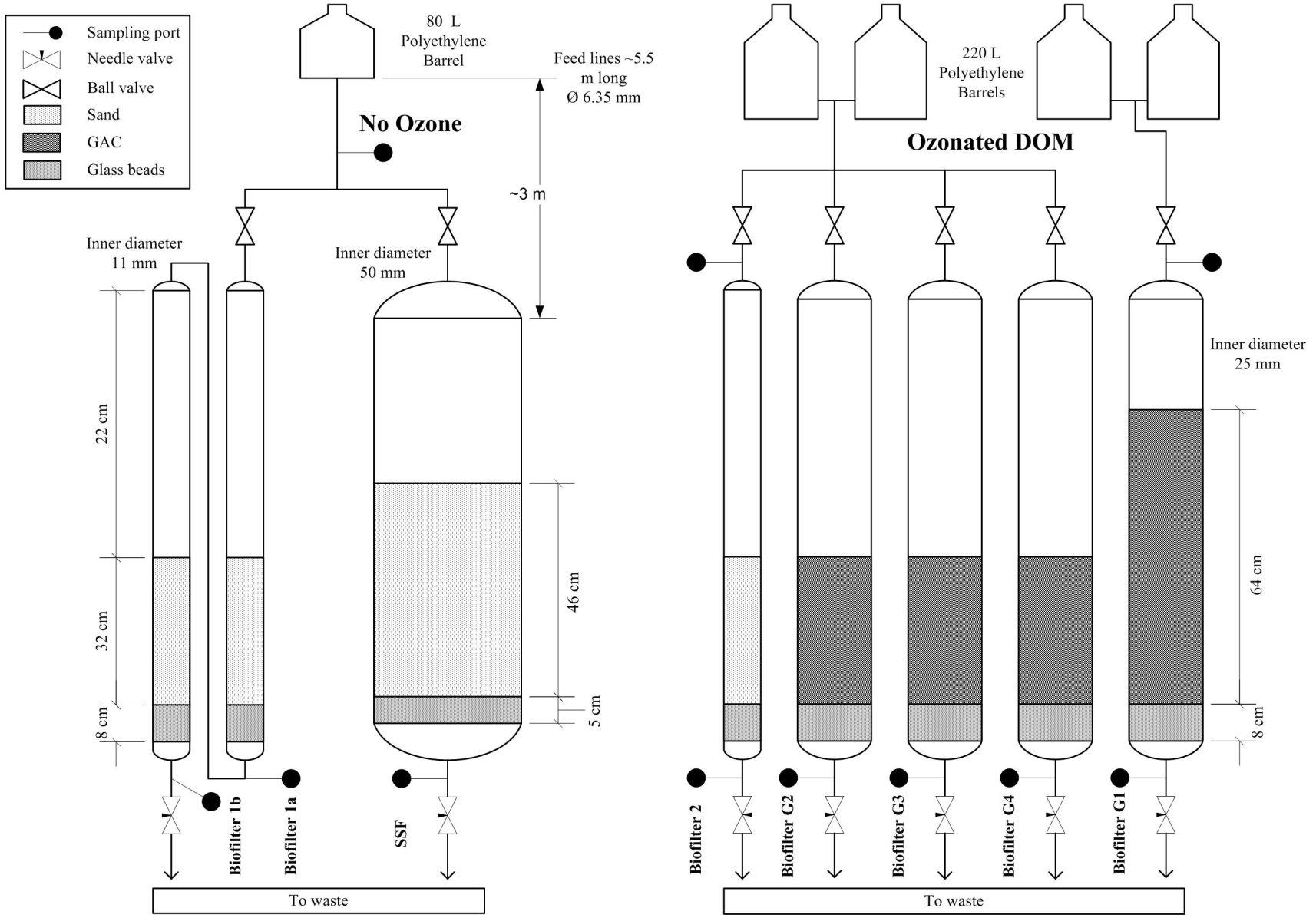

Figure 2.1. Experimental setup of biofilters and feed system for biodegradation rates and long-term behavior in BAC experiments.

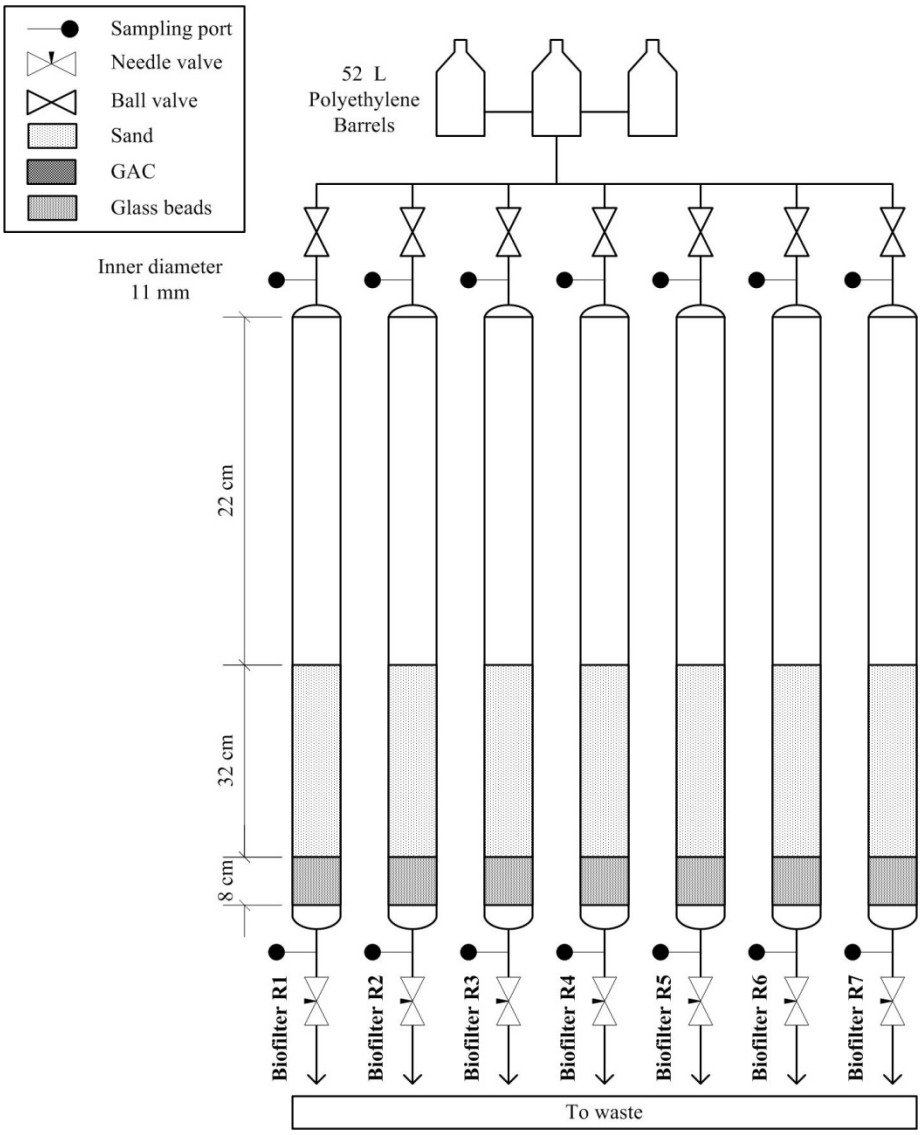

Figure 2.2. Experimental setup of biofilters and feed system for retained biodegradation capacity experiment.

2.1.3 Operation

The biofilters were operated in parallel as a one-pass system to simulate full-scale operation. The target hydraulic loading rate (HLR) for all of the filters except for Biofilter G1 and SSF was 2.4 m hr^{-1} (1 gal/ft^2·min) to achieve a target EBCT of 7.5 min. Biofilter G1 was operated at a target HLR of 4.9 m hr^{-1} (2 gal/ft^2·min) and 7.5 min EBCT. SSF was operated at a target HLR of 0.09 m hr^{-1} (0.04 gal/ft^2·min) and 5.25 h (315 min) EBCT. While these loading rates are on the low end of filter operation rates, they facilitated the operation of the filters as

they decreased the required volume of water. The Damköhler number was calculated to be <0.1 for all of the filters, thus external mass transfer was thought not to be limiting and DOM and trace organic contaminant removals would not be affected at these loading rate. Each biofilter consisted of one column except for Biofilter 1 which was operated as two columns in series with a target EBCT of 15 min. All of the systems were operated at lab temperature (20 ± 2 °C) which is within the range of temperatures that, depending on geographic location, most water treatment facilities experience.

The flow varied due to biomass and particle buildup within the filter and was measured every 2 to 3 days and adjusted as needed. The change in hydraulic head due to the water level decreasing in the feed tanks did not cause a measurable change in the biofilter flow rate. The flow was monitored by measuring the amount of water collected in a graduated cylinder in 1 min and the flow was adjusted by a needle valve immediately after the biofilter.

2.1.3.1 Backwashing

All of the filters except the SSF were backwashed as needed to reduce pressure build-up (approximately every 2 months). The filters were backwashed without air scour with dechlorinated feedwater and to ~50% bed expansion until the backwash effluent was clear (~10 min). The SSF was not backwashed; after 102 and 208 days of operation, the top 2 cm of media was removed, washed with dechlorinated tap water, and placed back in the top of the filter.

2.2 BIOFILTER FEEDWATER

The feedwater for the biofilters was dechlorinated City of Boulder, CO tap water supplemented with DOM to a target TOC concentration of 3 mg L^{-1}. The biofilter feedwater was

dechlorinated overnight by allowing the supplemental DOM to react with the free chlorine in the tap water and allowing the temperature to stabilize. The absence of free chlorine was confirmed before trace organic contaminants were spiked. Trace organic contaminant stocks were added and mechanically mixed just before the feedwater was added to the feed barrels

The feedwaters for all of the experiments had an average influent pH of 7.7, alkalinity of 40 mg L^{-1} as $CaCO_3$, ammonia concentration of <0.015 mg NH_3-N L^{-1}, nitrate concentration of <0.23 mg NO_3-N L^{-1}, and phosphate concentration of ~0.06 mg PO_4^{3-} L^{-1}.

2.2.1 DOM Concentrates

Two different DOM concentrates were used in this research. Big Elk Meadows (BEM) concentrate was used in all of the experiments except for the retained biodegradation capacity study, in which Manatee Lake Concentrate was used.

2.2.1.1 Big Elk Meadows (BEM) Concentrate

Big Elk Meadows (BEM) concentrate was concentrated from a very low alkalinity mountain lake in Big Elk Meadows, CO, utilizing a reverse osmosis membrane (DOW FILMTEC LE-4040). It was concentrated to an average TOC concentration of 180 mg L^{-1} and stored at 4°C in 225 L barrels.

2.2.1.2 Manatee Lake Concentrate

Manatee Lake concentrate was concentrated from Manatee Lake, FL using reverse osmosis to a TOC concentration of 100 mg L^{-1} and stored at 4°C in 225 L barrels.

2.2.2 Ozonation

For Biofilters 2 and G1-G4, the BEM concentrate was ozonated before it was added to the mixing barrels. Prior to ozonation the BEM concentrate was diluted 1:1 (v/v) to a TOC concentration less than 100 mg L^{-1}. The diluted BEM concentrate was continuously mixed in a 20 L glass carboy with a diffuser plate and directly ozonated to concentration ratio of 1 mg O_3 to 1 mg TOC. Since the ozone reacts quickly with DOM, direct measurement of ozone was not possible and the change in ultraviolet absorbance at 254 nm (UVA) was monitored instead. Based on small batch studies, a 1:1 O_3/TOC resulted in a 60% reduction in UVA of the diluted BEM concentrate. After ozonation the ozonated concentrate was stored in a 20 L PE carboy at 4°C until use. The ozonated concentrate was used within a week of production.

2.3 TRACE ORGANIC CONTAMINANT SELECTION

The trace organic contaminants were selected based on a suite of analytical methods that were considered to be industry standard at the time of development (base list was USGS Method 2) and are presented in Table 2.2. These trace organic contaminants are chemicals of emerging concern that have either been previously detected in surface water used as drinking water (Kolpin et al., 2002; Batt et al., 2007; Donald et al., 2007; Focazio et al., 2008) or expected to be present in many sources due to upstream runoff and wastewater impacts. The trace organic contaminants selected included pesticides, pharmaceuticals, EDCs, and personal care products and represent a wide range of uses, chemical structures, adsorbabilities, and biodegradabilities (Arnot et al., 2005; Gao et al., 2010). The target trace organic contaminant influent concentrations used (Table 2.2) were based on environmental occurrence concentrations (Kolpin et al., 2002; Batt et al., 2007; Donald et al., 2007; Focazio et al., 2008) and analytical detection limits.

Table 2.2. Trace Organic Contaminants with Target Influent Concentration

contaminant	CAS	molecular weight (Da)	target inf. conc. (ng/L)	use
2,4-dichlorophenoxyacetic acid (2,4–D)	94-75-7	221.04	100	herbicide
acetaminophen	103-90-2	151.17	200	pharmaceutical
acetochlor	34256-82-1	269.77	200	herbicide
aldicarb	116-06-3	190.26	200	insecticide
atrazine	1912-24-9	215.69	10	herbicide
bisphenol A (BPA)	80-05-7	228.29	500	manufacturing additive
caffeine	58-08-2	194.19	100	personal care product
carbamazepine	298-46-4	236.28	100	pharmaceutical
carbaryl	63-25-2	201.23	200	insecticide
chlorpyrifos	2921-88-2	350.59	500	insecticide
clofibric acid	882-09-7	214.65	200	pharmaceutical
cotinine	486-56-6	176.22	100	personal care product
diazinon	333-41-5	304.35	10	insecticide
diclofenac	15307-86-5	296.148	200	pharmaceutical
dimethoate	60-51-5	229.25	100	insecticide
diuron	330-54-1	233.1	100	herbicide
erythromycin	114-07-8	733.93	100	antibiotic
17α-ethinyl estradiol (EE2)	57-63-6	296.41	500	artificial hormone
gemfibrozil	25812-30-0	250.34	200	pharmaceutical
ibuprofen	15687-27-1	206.29	500	pharmaceutical
iopromide	73334-07-3	791.12	500	pharmaceutical
malaoxon	1634-78-2	314.29	200	insecticide
methomyl	16752-77-5	162.21	200	insecticide
metolachlor	51218-45-2	283.793	200	herbicide
2-methylisoborneol (MIB)	2371-42-8	168.28	500	algal metabolite
molinate	2212-67-1	187.3	200	herbicide
naproxen	22204-53-1	230.27	200	pharmaceutical
prometon	1610-18-0	225.29	100	herbicide
simazine	122-34-9	201.66	50	herbicide
sulfamethoxazole	723-46-6	253.28	200	antibiotic
tributyl phosphate	126-73-8	266.32	100	manufacturing additive
triclosan	3380-34-5	289.55	500	antimicrobial
trimethoprim	738-70-5	290.32	100	antibiotic
warfarin	81-81-2	308.34	100	pharmaceutical

CAS: chemical abstract number

For the biodegradation rates (Chapter 3) and long-term behavior in BAC (Chapter 6) experiments, all of the trace organic contaminants were analyzed by high performance liquid or gas chromatography. For the retained biodegradation capacity (Chapter 4) and variable influent conditions (Chapter 5) experiments radiolabeled MIB and 2,4-D was used and analyzed by a liquid scintillation counting (LSC).

2.3.1 Trace Organic Contaminant Stock Preparation

The unlabeled trace organic contaminants were all purchased from Sigma-Aldrich (St. Louis, MO), with three exceptions. 2,4-D was purchased from Acros Organics (New Jersey, US), iopromide was purchased from U.S. Pharmacopa (Rockvill, MD), and simazine was purchased from Alfa Aesar (Ward Hill, MA).

Since many of the trace organic contaminants can be difficult to dissolve directly in water, each trace organic contaminant was first dissolved in methanol except bisphenol A, caffeine, ethinyl estradiol, MIB, and triclosan. The concentration of the methanol-based stocks ranged 1-50 g L^{-1} depending on the solubility of the contaminant. An aliquot from each methanol stock was put into a clean and empty 1 L amber glass bottle with a tight fitting lid. More than one bottle was used so that the total amount of methanol did not exceed 2 mL. This meant there were 5 water-based stock bottles. The final concentration of the water-based stocks was 10,000 times greater than the target influent concentrations (Table 2.2) expect chlorpyrifos which was 2,000 greater. The glass bottles were slowly rotated on their sides for the next 4 to 8 hours until the all of the methanol had completely evaporated. Rotating the bottle spread the methanol stock along interior surface of the glass allowing the trace organic contaminants to form an amorphous solid on the surface of the bottle after the methanol evaporated. This amorphous solid required less energy and dissolved faster into water than the crystalline solid would have. The bottle was

then left open without a cap overnight to ensure that all of the methanol had evaporated. The following morning, 1 L of nanopure water was added to the bottle with a magnetic stir bar and capped. The solution was then slowly heated on a magnetic stir plate to 37 °C, and once reaching 37 °C the bottle was moved to another stir plate and allowed to cool.

Bisphenol A, ethinyl estradiol, and triclosan were each dissolved directly into 1 L of pH 10 water at a concentration of 1.5 mg L^{-1}. The methanol stock method could not be used because of trace contaminant volatilization. The higher pH water increased the solubility of the trace organic contaminants allowing for easy dissolving.

The high water solubility of MIB and caffeine allowed the trace organic contaminants to be directly dissolved in neutral pH water. Multiple small bottles of MIB stock at a concentration of 1 mg L^{-1} were prepared, reducing the potential for volatilization each time a bottle was opened.

The methanol- and water-based stocks were stored at 4 °C. The methanol stocks remained stable for approximately six months, except the organophosphate trace organic contaminants, which degraded within a few months time and were remade every three months. The water-based trace organic contaminant stocks were made fresh at least every two months. All of the water-based trace organic contaminant stocks were organic solvent-free to minimize the addition of an easily biodegradable substrate.

2.3.2 Radiolabeled Trace Organic Contaminant Stocks

For the retained biodegradation capacity (Chapter 4) and variable influent conditions (Chapter 5) experiments, radiolabeled MIB and 2,4-D were used. Both radiolabeled trace organic contaminants were purchased from American Radiolabeled Chemicals, Inc. (St. Louis, MO). The radiolabeled stock preparation is explained in Section 4.2.2.

2.3.3 Trace Organic Contaminant Spiking

All of the trace organic contaminants were spiked into the dechlorinated tap water and mechanically mixed at the influent concentrations listed in Table 2.2 except MIB which was spiked at 20% higher than the target influent concentration to allow for volatilization in the feed barrel (Kim, 2006). The spiked feedwater was added to the feed barrels connected directly to the biofilters. For Biofilters 1-2, G2-G4 and SSF, the trace organic contaminants were divided into five water-based stock solutions outlined in Table A.2. Because of analytical and laboratory constraints, each of the five trace organic contaminant stocks was started at different times ranging from a few days to 31 weeks after the start of biofilter operation as shown in Table A.3. Once a trace organic contaminant was added to the feed it was continued for the remainder of the study. Biofilters 1-2, G2-G4 and SSF were exposed to all of the trace organic contaminants for at least 6 months except for MIB which was only added for the last 4 months. For this reason, removals are reported in relation to the trace organic contaminant exposure time and not in biofilter operation time unless noted. Biofilter G1 was exposed to all of the trace organic contaminants for its entire operation.

2.4 BIOFILTER SAMPLING

Influent samples were collected from sampling ports immediately before each filter and effluent samples were collected from ports immediately after each column (Figure 2.1 and Figure 2.2). By placing sampling ports immediately before and after the columns, the removal measured was attributable only to the processes within the filter. Influent and effluent samples were collected for trace organic contaminants and TOC analysis in amber glassware that had been cleaned with distilled water and baked at 400 °C for 3 hours.

2.5 WATER QUALITY ANALYSIS

Water quality analysis was conducted regularly on influent and effluent samples from the biofilters. Table 2.3 contains the water quality parameters, the instrument used, and analysis method.

Table 2.3. Water Quality Analysis Instruments and Methods

analyte	measuring units	method detection limit	equipment / procedure	reference method
pH	n/a	n/a	Corning Model 430 Meter and Probe	SM 4500-H^+
TOC / DOC	mg/L	0.05	Sievers 800 Total Organic Carbon Analyzer with Auto-sampler	SM 5310 C
UVA	cm^{-1}	0.001	Hach DR 4000 UV-Visible Recording Spectrophotometer	SM 5910 B
alkalinity	mg/L as $CaCO_3$	2	Hach Digital Titrator Model 16900-01	SM 2320 B
free chlorine	mg/L as Cl_2	0.02	Hach Pocket Colorimeter/ Hach Method 8021	SM 4500-Cl G
NH_3	mg/L NH_3-N	0.015	Hach DR 5000 UV-Visible Recording Spectrophotometer/ Hach Method 10205	
NO_3	mg/L NO_3-N	0.23	Hach DR 5000 UV-Visible Recording Spectrophotometer/ Hach Method 10206	
NO_2	mg/L NO_2-N	0.015	Hach DR 5000 UV-Visible Recording Spectrophotometer/ Hach Method 10207	EPA Method 354.1
orthophosphorus	mg L^{-1} PO_4^{3-}	0.045	Hach DR 4000 UV-Visible Recording Spectrophotometer/ Method 8048	SM 4500-P E

SM: Standard Methods for the Examination of Water and Wastewater (APHA et al., 2005)

2.6 PHOSPHOLIPID BIOMASS

Viable biomass concentrations were measured by the phospholipid method (Wang et al. (1995) in quadruplicate using 0.2 g of filter media. Sample blanks were analyzed with each sample run. Phospholipid biomass concentrations were reported on a volumetric basis using a packed bed density of 1.63 kg L^{-1} for sand, and 0.45 kg L^{-1} for GAC filters. The biofilter packed

bed density was measured by wet packing a 100 mL graduated cylinder and measuring the mass after drying at 105 °C overnight.

2.7 TRACE ORGANIC CONTAMINANT ANALYSIS

2.7.1 High Performance Gas Chromatography

The trace organic contaminants bisphenol A, ethinyl estradiol, and triclosan were analyzed by immersion solid-phase microextraction (SPME) preconcentration (CombiPAL autosampler, Carrboro, NC) followed by gas chromatographic separation and tandem mass spectrometry using chemical ionization (Model 3800GC, 2000MS/MS, Varian Inc., Santa Clara, CA) at Dr. Detlef Knappe's laboratory at North Carolina State University (Mastropole, 2011). The method quantification limit for these three contaminants was 100 ng L^{-1}. The relative standard deviation (RSD) for bisphenol A, ethinyl estradiol, and triclosan was 7.7%, 10%, and 1.3%, respectively (Mastropole, 2011).

Aqueous-phase concentrations of MIB were analyzed with a gas chromatograph (GC) (Varian 3800, Palo Alto, CA) equipped with a split/splitless injector, a 30-m column (Factor Four VF-5ms low bleed, I.D. 0.25 mm, film thickness 0.25 μm, Palo Alto, CA), and a mass spectrometer (MS) (Varian Saturn 2200, Palo Alto, CA) that was used in the chemical ionization tandem mass spectrometry (MS/MS) mode (Knappe et al., 2010). The method quantification limit for MIB was 1 ng/L.

2.7.2 High Performance Liquid Chromatography

The remaining trace organic contaminants were analyzed at University of Colorado Center for Environmental Mass Spectroscopy (CEMS) by off-line solid phase extraction followed by high performance liquid chromatography (HPLC) (Agilent Series 1290, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C_{18} analytical column of

50 mm x 2.1 mm and 1.8 μm particle size (Zorbax Eclipse Plus). This HPLC system was connected to a triple quadrupole mass spectrometer Model 6460 (Agilent Technologies, Santa Clara, CA, USA) equipped with electrospray Jet Stream technology operating in positive and negative ion mode. Some of the influent and effluent samples were analyzed at CEMS by LC-Time of Flight Mass Spectroscopy (LC/TOF-MS) (Agilent Model 6220) for the presence of biotransformation products. The method detection limits for the trace organic contaminant analyses are reported in Table A.2. The RSDs for the LC analyzed trace organic contaminants were all less than 11% (Ferrer et al., 2010).

2.7.3 Trace Organic Contaminant Removal Calculation

For the non-radiolabeled trace organic contaminants, removal was defined as the loss of the parent compound through the biofilter rather than complete mineralization of the compound. Removals of the GC-measured trace organic contaminants (bisphenol A, ethinyl estradiol, MIB, and triclosan) were calculated using paired influent and effluent concentrations. For the trace organic contaminants analyzed by LC, the influent concentration was measured up to three times during the study. The breakthrough of the LC trace organic contaminants was quantified by dividing the signal intensity of the effluent by the signal intensity of the influent sample for each trace organic contaminant. Concentrations or signal intensities less than the detection limit were reported as one-half of the detection limit. Any removals less than zero were reported at zero.

For radiolabeled MIB and 2,4-D, removal was defined as complete mineralization (Section 2.7.4.3).

2.7.4 Solid Phase Extraction - Liquid Scintillation Counting (SPE-LSC) Method

Radiolabeled trace organic contaminants were analyzed by LSC before and after passing through a solid phase extraction (SPE) cartridge. The SPE step was necessary because ^{3}H-labled 2,4-D mineralizes into tritiated water ($^{3}H_2O$) in a biofilter which is indistinguishable in the liquid scintillation counter from the radiolabeled parent compound. While the majority of the $^{14}CO_2$ from ^{14}C-labeled MIB mineralization could offgas in the biofilter, any dissolved $^{14}CO_2$ would be indistinguishable from the radiolabeled MIB. The SPE-LSC method developed allows for quick and inexpensive analysis of two radiolabeled trace organic contaminants (^{14}C and ^{3}H) in one-pass biodegradation column experiments.

2.7.4.1 Procedure

Each sample was prepared by acidifying with phosphoric acid to a pH less than 2.0 as to protonate the 2,4-D (pK_a=2.73) allowing it to better adsorb to the SPE cartridge. After acidification, the samples were analyzed by LSC before and after passing through a SPE cartridge (AccuBond^{II} C18 500mg/6mL). The difference between the unextracted sample and the effluent of the SPE cartridge was the concentration of MIB and 2,4-D and unminerzlized compounds, as the parent compounds and biotransformation products with similar molecular characteristics were retained on the SPE cartridge. Extraction and sampling for LSC was completed within 10 min of acidification to minimize acid hydrolysis of MIB. Each SPE cartridge was preconditioned before use by passing 5 mL of methanol followed by 10 mL of distilled water. A vacuum manifold was used for the SPE extraction with a flow rate through the cartridge of approximately 5 mL min^{-1}. A large SPE cartridge (6 mL) was used which allowed for a quicker extraction rate to reduce potential MIB volatilization.

A Packard Tri Carb 2300 liquid scintillation analyzer was used to determine MIB and 2,4-D concentrations according to the method by Corwin and Summers (2010).

2.7.4.2 Method Efficiency

The addition of phosphoric acid did not affect the concentration measurements of MIB or 2,4-D. The SPE cartridge retained >99.6% of MIB and >99.4% of 2,4-D under this method as shown in Table 2.4. By analyzing a paired influent sample under the same method as the effluent sample, the extent of biodegradation or hydrolysis occurring in the feed barrel or lines was able to be determined.

Table 2.4. Average Retention on the SPE Cartridge with 95% CI

	retention (%)		
run	**MIB**	**2,4-D**	**n**
1	99.6 ± 0.2	99.4 ± 0.5	23
2	99.9 ± 0.1	99.8 ± 0.3	7
3	99.9 ± 0.2	99.4 ± 0.6	7

2.7.4.3 Mineralization/Ultimate Biodegradation

The SPE-LSC method measured mineralization or ultimate biodegradation of the parent compounds. The method did not measure the formation of biotransformation products, since many labeled biotransformation products of MIB (Eaton & Sandusky, 2009) and 2,4-D (Evans et al., 1971) are retained on the SPE cartridge just as the parent compounds are. Mineralization studies with radiolabeled trace organic contaminants often measure $^{14}CO_2$, but this was not possible because the experimental setup was a one-pass flow through system.

The removal as measured with and without the SPE step was compared for MIB and shown in Figure 2.3. The additional removal measured with the SPE step was likely a measure of the dissolved $^{14}CO_2$ or radiolabeled biotransformation products. There was a strong linear relationship between the two measurements for MIB (Figure 2.3). Using this relationship,

comparisons were made to removals from previous biofilter experiments using radiolabeled MIB but measured without the SPE step (Chae et al., 2006).

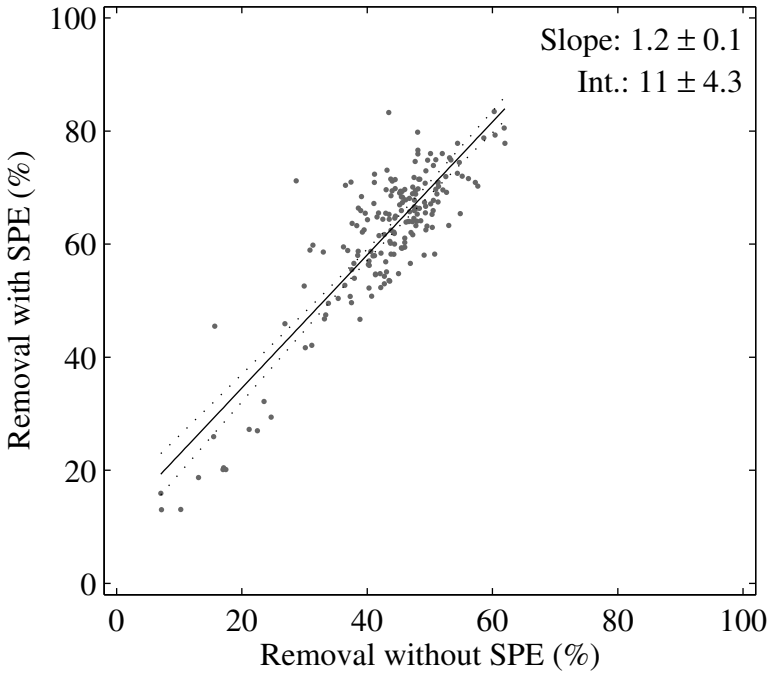

Figure 2.3. MIB removal measured using and not using solid phase extraction (SPE) for all of the samples in this research (n = 187). The linear regression is given (solid line) with 95% confidence bounds (dotted lines).

2.8 DATA ANALYSIS

All statistical analysis was performed with MATLAB 2012a Statistical Package (MathWorks, 2012). A locally weighted scatter plot smoothing (LOWESS) function with a span window of 8 was used to smooth the removal data to determine trends over time (Cleveland, 1979).

Chapter 3
Modeling Biodegradation of Trace Organic Contaminants in Drinking Water Biological Sand Filters

A significant portion of this chapter was adapted with permission from Zearley, T.L. and Summers, R.S. (2012) Removal of Trace Organic Micropollutants by Drinking Water Biological Filters.. *Environmental Science and Technology 46*(17): 9412-9419.

3.1 INTRODUCTION

A key component to understanding trace organic contaminant removal behavior in drinking water biofilters is determining what factors affect the biodegradability of each contaminant. These factors include but are not limited to the biodegradability of a contaminant, the acclimation state of the biomass, contact time with biomass, and influent conditions. A few of these factors, such as EBCT have been evaluated under controlled conditions. However, the research has primarily focused on ozonation by-products and algal metabolites. There is little data available regarding trace organic contaminant removal under controlled conditions in which the impact of design and operation parameters and biomass behavior have been systematically evaluated for a range of trace organic contaminants (Servais et al., 2005). The impacts of EBCT, temperature, and contaminant concentration on atrazine, carbamazepine, ibuprofen, and naproxen removal have been studied by one researcher (Halle, 2010), and similar operational impacts have been studied for MIB (Westerhoff et al., 2005b; Elhadi et al., 2006). There are models to predict primary substrate utilization in drinking water biofilters but very few for trace

organic contaminants. A biomass based pseudo-first-order rate model was proposed by Meyer (2005) to predict MIB and geosmin removal in drinking water biofilters and was expanded to 33 other trace organic contaminants in this research.

The objective of this study was to evaluate and model the long-term performance of biofilters for the control of trace organic contaminants. The removal of 34 trace organic contaminants across two biofilters with sand media and a slow sand filter were monitored for a year. To model contaminant removals, a pseudo-first-order rate equation with a rate constant, average biomass concentration, and EBCT was used. The model was verified with data from other biofilters operated at different influent conditions and previously published pilot- and full-scale data.

3.2 MATERIAL AND METHODS

For this experiment, Biofilters 1 and 2 along with the SSF were used to determine and verify trace organic contaminant biodegradation rate constants. The contaminants investigated are shown in Table 2.2 and were spiked according to Section 2.3.3.

3.2.1 Biofilter Sampling

Influent and effluent samples were collected from sampling ports immediately before and after each biofilter (Figure 2.1). The day prior to sampling, the flow was measured, and if required, adjusted to the target hydraulic loading rate. The flow was rechecked, and adjusted as needed, prior to sampling. If adjusted, a minimum of 10 bed volumes were allowed to pass before samples were taken. The average EBCTs for the sampling events are reported in Table 3.1.

Table 3.1. Average Biofilter EBCTs at Sampling, and TOC Concentrations and Removal

	Biofilter			
	1a	**1b**	**2**	**SSF**
EBCT (min)	7.9 ± 0.8 (8) [a]	7.9 ± 0.8 (8)	7.6 ± 0.6 (8)	354 ± 99 (8)
TOC Influent (mg L^{-1})	3.1 ± 0.3 (23)	2.7 ± 0.3 (7)	2.6 ± 0.3 (22)	3.1 ± 0.3 (23)
TOC Removal (%)	7.2 ± 2.8 (7)	2.6 ± 1.7 (7)	6.5 ± 2.9 (7)	21 ± 6.6 (7)

[a] avg. ± SD (n)

The biofilters were sampled for contaminants approximately every 6 weeks for the first 8 months of operation and then approximately every 10 weeks for a total of 8 sampling events to capture acclimation and steady state removal behavior (Table A.3). Paired influent and effluent samples were taken at all times. Samples for TOC were taken during all but the first contaminant sampling event. Additional influent TOC samples were collected to monitor TOC influent concentration more closely.

3.3 THEORETICAL MODEL DEVELOPMENT

3.3.1 Trace Organic Contaminant Utilization

Trace organic contaminant concentrations are below S_{min}, and under these conditions, saturating kinetics describe the utilization of a contaminant in a cell (Schmidt et al., 1985). This can be expressed as a Michaelis-Menten relationship. The reaction rate, r, for contaminant utilization in biofilters was described as:

$$r = -\frac{dC}{dt_{BF}} = \frac{V_{\max} \cdot X \cdot C}{K_m + C} \qquad 3.1$$

where C is the contaminant concentration [ng L^{-1}], t_{BF} is the contact time in the biofilter [min], V_{max} is the maximum reaction rate [ng (min·nmol PO_4)$^{-1}$], X is the biomass concentration or density [nmol PO_4 mL^{-1}], and K_m is the Michaelis constant [ng L^{-1}]. When the contaminant

concentration is very low compared to the Michaelis constant ($C \ll K_m$), Eqn. 3.1 can be simplified into a pseudo-first-order rate (Schmidt et al., 1985).

$$r = -\frac{dC}{dt_{BF}} = k'' \cdot X \cdot C \qquad 3.2$$

where k'' is the contaminant utilization rate constant [mL (min·nmol PO_4)$^{-1}$] ($k'' = V_{max}/K_m$). If t_{BF} is approximated by the EBCT and Eqn. 3.2 is integrated by t_{BF} from 0 to EBCT and by C from C_{Inf} to C_{Eff} results in Eqn. 3.3.

$$\frac{C_{Eff}}{C_{Inf}} = \exp\left(-k'' \cdot X \cdot EBCT\right) \qquad 3.3$$

where C_{Inf} to C_{Eff} are the influent and effluent concentrations of the contaminant. The contaminant utilization rate constant and biomass can be represented by a pseudo-first-order rate constant, k' [min^{-1}].

$$k' = k'' \cdot X \qquad 3.4$$

By using Eqn. 3.4, Eqn. 3.3 simplifies to:

$$\frac{C_{Eff}}{C_{Inf}} = \exp\left(-k' \cdot EBCT\right) \qquad 3.5$$

3.3.1.1 Temperature Correction

If the operating temperature was not at 20 °C, the k'' value was temperature corrected using the van 't Hoff-Arrhenius relationship:

$$k''_2 = k''_1 \cdot \theta^{(T_2 - T_1)} \qquad 3.6$$

where θ is the temperature activity coefficient, T is the temperature, and the subscripts represent the two different temperature conditions. A temperature activity coefficient, θ, of 1.07 was used for all temperature conversions in this research (Rittmann & McCarty, 2001).

3.3.1.2 EBCT Normalized Removal

The trace organic contaminant removals were normalized to the same EBCT for some comparisons in this research. When this was done, first the "instantaneous" pseudo-first-order rate constant, k', was calculated using Eqn. 3.5, the observed removal and the EBCT at sampling. The calculated k' was then plugged into Eqn. 3.5 with the normalized EBCT to calculate the normalized removal (Eqn. 3.7).

$$\text{Norm. Removal} = 1 - \exp\left(\frac{\ln\left(\frac{C_{Eff}}{C_{Inf}} \right)}{EBCT_{sampling}} \cdot EBCT_{norm.} \right) \quad 3.7$$

3.3.2 Biomass Distribution

In biofilters with a developed microbial community, the biomass concentration is higher at the top of the filter than the bottom, because higher concentrations of primary substrate are available at the top of the filter and can sustain higher levels of microorganisms (Wang et al., 1995). This biomass distribution can be approximated by an exponential decay where the depth of the filter is represented by the EBCT (Carlson & Amy, 1998). When the depth of the filter is represented by the EBCT, the biomass distribution is independent of the loading rate (Wang et al., 1995).

$$-\frac{dX}{dEBCT} = \beta \cdot X \quad 3.8$$

where β is the biomass distribution coefficient. Eqn. 3.8 can be solved to determine the biomass concentration, X, at any EBCT:

$$X(EBCT) = X_{top} \exp(-\beta \cdot EBCT) \quad 3.9$$

where X_{top} is the biomass concentration at the top of the filter. The total biomass in a filter at can be determined by integrating Eqn. 3.9 with respect to EBCT.

$$X_{Total} = \frac{X_{top}}{\beta}\left(1 - \exp\left(-\beta \cdot EBCT_{Total}\right)\right) \quad 3.10$$

The average biomass concentration is the total biomass divided by media volume.

$$X_{avg} = \frac{\frac{X_{top}}{\beta}\left(1 - \exp\left(-\beta \cdot EBCT_{Total}\right)\right)}{EBCT_{Total}} \quad 3.11$$

Eqn. 3.11 was used to calculate the average biomass concentration for the external datasets where the biomass profile was known.

3.4 RESULTS AND DISCUSSION

3.4.1 Primary Substrate Utilization

Primary substrate utilization was represented by TOC removal across the filters since biodegradation is the only significant removal mechanism of DOM with non-adsorptive sand media. The average influent TOC concentrations and removals for Biofilters 1, 2 and SSF are shown in Table 3.1. The TOC removal in Biofilters 1 and 2 were at steady state. This was expected as the media had been in full-scale use for several years prior to the laboratory study. Minor variability in TOC removals can be attributed to small level of removals, EBCT differences, and changing laboratory temperatures over the one-year study. The TOC removal of Biofilter 1a and 2 was not statistically different at a 95% confidence level. Higher TOC removal was expected in Biofilter 2 as it was fed ozonated DOM and ozone increases the biodegradable DOM fraction (Goel et al., 1995; Carlson & Amy, 2001). However, the influent sample was taken at the top of the biofilter and much of the easily biodegraded DOM fraction was likely

biodegraded in the feed barrel and line which resulted in a lower than targeted influent TOC concentration and a similar percentage of the DOM that was biodegradable.

3.4.2 Viable Biomass

The biomass concentration was measured when the media was placed into the filter columns. Biofilter 1 and 2 had an initial phospholipid biomass concentration of 84 ± 7.3 nmol PO_4 (mL dry sand)$^{-1}$ (51 ± 4.5 nmol PO_4 (g dry sand)$^{-1}$) and the SSF had an initial biomass concentration of 34 ± 2.9 nmol PO_4 (mL dry sand)$^{-1}$ (21 ± 1.8 nmol PO_4 (g dry sand)$^{-1}$). The biomass was not measured immediately after the end of this study in Biofilter 1 and 2 as the media was used in other experiments. The SSF biofilter biomass profile after 1.2 years of operation is shown in Figure 3.1. After 1.2 years of operation, the SSF had an average biomass concentration of 71 nmol PO_4 (mL dry sand)$^{-1}$ when calculated using Eqn. 3.11.

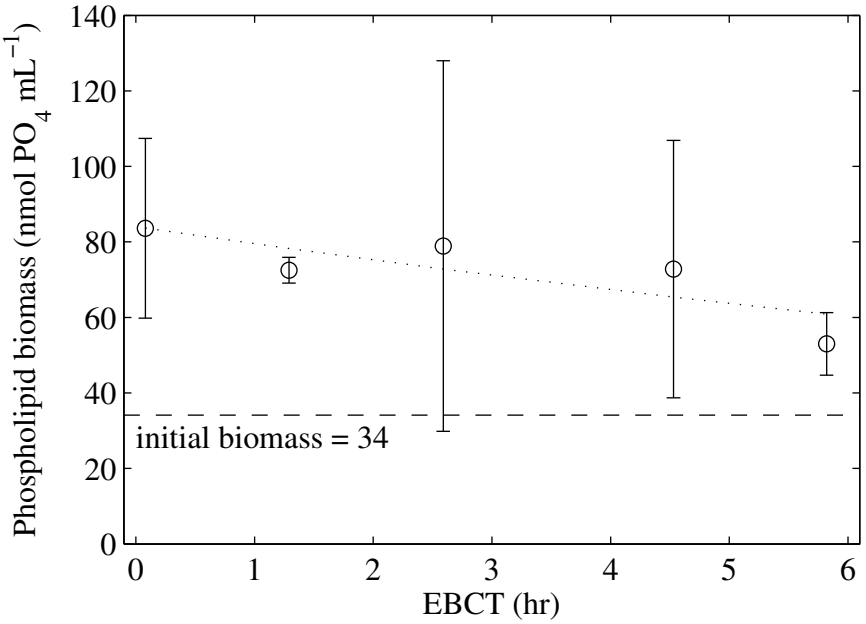

Figure 3.1. Phospholipid biomass profile initially and after 1.2 years of operation for the slow sand filter (SSF) with exponential regression (short dotted line). Error bars are ±1 SD (n=4).

3.4.3 Trace Organic Contaminant Removal

A wide range of biodegradation and acclimation behavior was observed. The contaminant influent concentrations and steady state removals for Biofilter 1 are reported in Table 3.2 and varied over the course of the study. The contaminants that had the highest influent concentration coefficient of variance (CV) were contaminants likely to degrade by hydrolysis in the stock bottles or feed barrels, for example the organophosphate contaminants (chlorpyrifos, diazinon, dimethoate, malaoxon, and tributyl phosphate). While biodegradation possibly occurred in the stock and feed system, it was most likely not a significant source of variability since there was no relationship between the CV and the biodegradation rates. The feed barrels and lines were cleaned and disinfected approximately every 2 months to minimize the buildup of biofilms acclimated to biodegrading the contaminants. However, unadapted biofilms redeveloped after cleaning, utilizing the DOM primary substrate.

Table 3.2. Steady State Removal of Trace Organic Contaminants in Biofilter 1.

		Biofilter 1a		Biofilter 1		
	EBCT	*7.9 min*		*15.8 min*		
contaminant	**influent conc. [a] (ng/L)**	**removal (%)**	**n**	**removal (%)**	**n**	**acclimation behavior**
2,4–D	171 ± 57 (3)	68 ± 11	4 [e]	77 ± 13	7	increase
acetaminophen	306 ± 142 (3)	59 ± 11	6	79 ± 11	7	steady state
acetochlor	266 ± 93 (2)	8 ± 11	5	17 ± 8.2	5	recalcitrant
aldicarb	31 (1) [c]	49 ± 8.2	3 [e]	72 ± 6.9	4	increase
atrazine	9 ± 2 (3)	0.2 ± 0.4	6	3 ± 3.6	7	recalcitrant
bisphenol A [b]	311 ± 285 (3) [c]	64 ± 29 [d]	3	>64	3	increase
caffeine	188 ± 147 (3)	67 ± 18	3 [e]	80 ± 13	4 [e]	steady state to decrease
carbamazepine	85 ± 49 (3)	0.4 ± 1.1	6	1.6 ± 3.5	7	recalcitrant
carbaryl	96 (1) [c]	3.3 ± 5.2	4	17 ± 14	4	recalcitrant
chlorpyrifos	385 ± 335 (2) [c]	63 ± 20	2	83 ± 15 [d]	3	steady state
clofibric acid	263 ± 70 (2)	35 ± 5.9	3 [e]	52 ± 8	3 [e]	increase
cotinine	92 ± 32 (3)	23 ± 21	6	39 ± 36	7	steady state
diazinon	4 ± 3 (3)	12 ± 12	5	40 ± 14	6	recalcitrant
diclofenac	252 ± 90 (2)	21 ± 2.1	3	28 ± 8.1	3	steady state
dimethoate	38 (1) [c]	75 ± 2.7	2 [e]	81 ± 6.9	4	increase
diuron	92 ± 13 (3)	0.3 ± 0.8	6	7.8 ± 8.1	7	recalcitrant
erythromycin [b]	104 ± 77 (2)	15 ± 27	3	22 ± 38	3	decrease
ethinyl estradiol	316 ± 193 (4)	12 ± 14	4	22 ± 17	4	recalcitrant
gemfibrozil	228 ± 49 (2) [c]	70 ± 7	5	94 ± 3.4 [d]	6	steady state
ibuprofen	276 ± 176 (2) [c]	95 ± 3.3 [d]	3	>95	4	steady state
iopromide	556 ± 168 (3)	13 ± 18	4	3 ± 5.6	6	recalcitrant
malaoxon	132 (1) [c]	16 ± 9.1	3	49 ± 8.9	3	steady state
methomyl	179 ± 86 (3)	12 ± 11	6	5.3 ± 6.9	7	recalcitrant
metolachlor	284 ± 117 (2)	6.6 ± 11	3	8.7 ± 4	3	recalcitrant
MIB	84 ± 35 (3)	93 ± 1.3	3	99 ± 1.1 [d]	3	steady state
molinate	205 ± 95 (2) [c]	85 ± 6.7	5	97 ± 0.66 [d]	6	steady state
naproxen	170 ± 101 (2)	72 ± 2	3 [e]	86 ± 8.2	5	increase
prometon	132 ± 28 (2)	2.5 ± 2.2	3	0	3	recalcitrant
simazine	52 ± 11 (3)	6.8 ± 9.4	6	8.2 ± 9.5	7	recalcitrant
sulfamethoxazole	230 ± 33 (3)	2.4 ± 4.1	6	4.1 ± 6.3	7	recalcitrant
tributyl phosphate	149 ± 44 (2)	16 ± 12	5	24 ± 8.5	5	steady state
triclosan	190 ± 42 (2) [c]	90 ± 0 [d]	2	>90	2	steady state
trimethoprim	175 ± 98 (3)	83 ± 13	3 [e]	92 ± 7.4 [d]	4 [e]	steady state to decrease
warfarin	268 ± 24 (2)	39 ± 11	5	68 ± 9.3	5	steady state

[a] Avg. ± 1 SD (n).
[b] Removal not at steady state, reported average of all samples.
[c] At least one influent sample below MDL and not used to calculate average.
[d] Percent removal limited by MDL in at least one sample.
[e] Non-steady state removals not used to calculate average.

Based on the steady-state removal after 7.9 min of EBCT (Biofilter 1a), the contaminants were classified as follows: 13 contaminants had removals less than 15% and were classified as

recalcitrant to biodegradation, 7 contaminants had removals between 15 and 50% and were classified as having slow or low biodegradation rates, 8 contaminants had removals between 50 and 85% and were classified as having fast or high biodegradation rates, and 4 contaminants had removals greater than 85% and were classified as having very fast or very high biodegradation rates. While removal of bisphenol A and erythromycin was observed, steady state removal was not achieved during the study, and they were not included in the above classification. As expected, more removal occurred after 15.8 min of EBCT (Biofilter 1) compared to that at 7.9 min (Biofilter 1a) except for iopromide, methomyl, and prometon. These three contaminants were classified as recalcitrant and any removals were not statistically significant at a 95% confidence level. Bisphenol A, ibuprofen, and triclosan were removed to below detection limits in the top 7.9 min of EBCT, thus it was not possible to quantify the removal in the bottom 7.9 min of EBCT. When ranking the contaminants by biodegradability, the rankings were similar to results observed in wastewater biofilters (Nakada et al., 2007; Gerrity et al., 2011; Reungoat et al., 2011).

3.4.3.1 Adsorption and Biotransformation Products

Adsorption to the sand media was not a significant source of contaminant removal since the contaminant removals did not correlate with adsorption potential as measured by the octanol-water distribution coefficient and confirmed by other researchers (Ternes et al., 2002). Adsorption of contaminants to the biomass was also not significant since the maximum biomass sorption capacity was reached within 2 h of operation for all of the contaminants. The maximum biomass sorption capacity was estimated by the procedure of Stratton et al. (1983)

No biotransformation products were discovered by LC/TOF-MS in the influent or effluent samples from Biofilter 1. These products may have been present in the effluent samples,

but at concentrations below the detection limit of the instrument; because of this, the extent of complete mineralization could not be assessed for this experiment.

3.4.4 Acclimation Behavior

Biofilter acclimation behavior followed one of four trends over the one-year study period: steady state removal throughout the study, increasing removal to steady state (acclimation), no removal, or decreasing removal. These are illustrated in Figure 3.2 for five example contaminants.

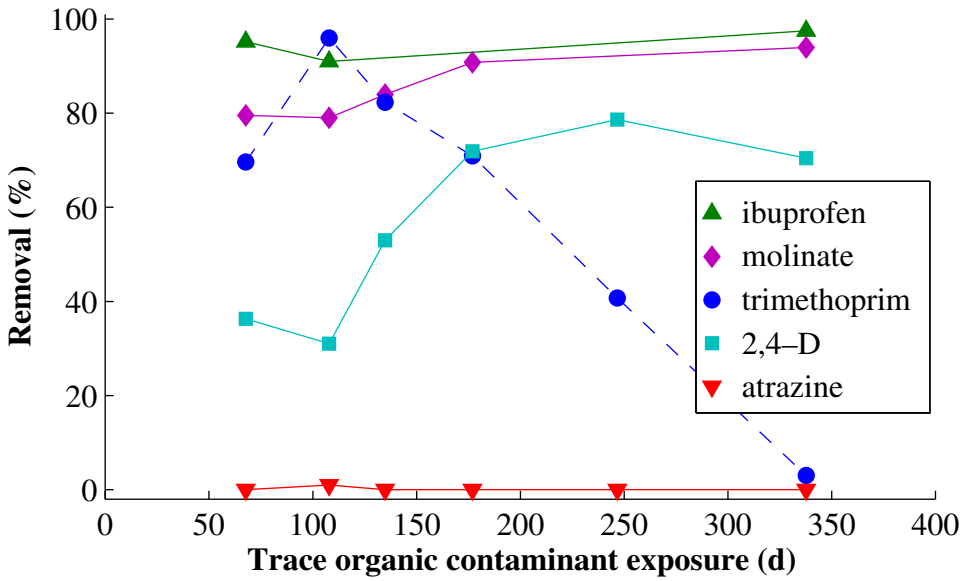

Figure 3.2. Contaminant removal after 7.9 min of EBCT at the top of Biofilter 1a.

3.4.4.1 Steady State Behavior

As noted in Table 3.2, 12 of the contaminants displayed steady state removal throughout the study; removals did not change by more than 20 percentage points, as illustrated in Figure 3.2 by ibuprofen and molinate. Many of these contaminants have been identified in the Ohio River and others may be there at concentrations below the detection limit, thus the biomass likely had been previously acclimated over the seven years of use at the full-scale (Metz et al., 2009; Metz,

2012), or these contaminants were cometabolized via nonspecific enzymes generated by the primary substrate metabolism.

3.4.4.2 Increasing to Steady State Behavior

Six of the contaminants displayed at least a 20 percentage point increase in removal, defined as acclimation, across Biofilter 1a (EBCT 7.9 min) from the first sample to steady state removal (Table 3.2). This behavior is illustrated in Figure 3.2 by 2,4-D and for all four contaminants at an EBCT of 7.9 min in Figure 3.3. Removals for 2,4-D, aldicarb, clofibric acid, dimethoate, and naproxen plateaued at steady state within 3 months of contaminant exposure. Bisphenol A displayed increasing removal throughout the study with >80% removal after 180 days. The long-term behavior after 15.8 min of EBCT, for 4 of these 6 contaminants was found to be at steady state as opposed to increasing removal as was found in the top 7.9 min of EBCT. This is illustrated in Figure 3.3 by steady state removal of aldicarb, dimethoate, and naproxen. For clofibric acid and bisphenol A (not shown), acclimation was observed at both EBCTs. An acclimation period of 60 days was observed by Halle (2010) for naproxen in a drinking water biofilter at 5 min of EBCT compared to 90 days in this study. Microorganism acclimation to 2,4-D in soil and sequencing batch reactors has been observed (Smith & Aubin, 1994; Celis et al., 2008), as has acclimation to aldicarb in soil (Bromilow et al., 1996). The increasing removal with time found with these 6 contaminants is an indication of secondary substrate utilization, or the growth of microorganisms not originally present that are capable of biodegrading these contaminants through cometabolism. The growth of microorganisms not originally present at significant numbers in the biofilter could be attributed to the different primary substrate character and influent microorganisms present in the feedwater, relative to the Ohio River water. The steady-state behavior of 4 of these 6 contaminants in the bottom of the

filter may be associated with the lower level of primary substrate and the likely difference in community structure at this depth (Moll et al., 1998).

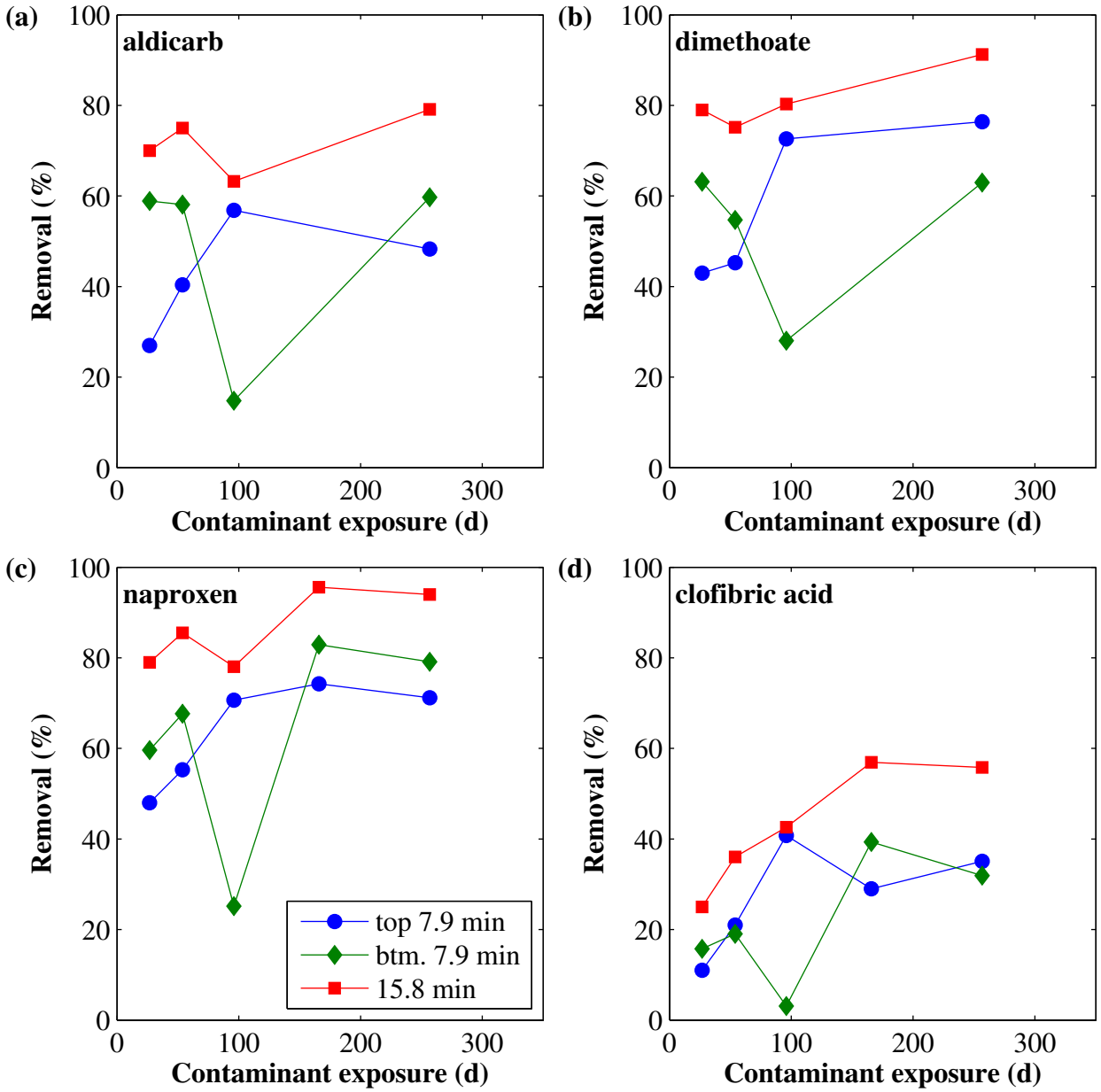

Figure 3.3. Contaminant removal for increasing to steady state contaminants in the top and bottom 7.9 minutes of EBCT in Biofilter 1 and after 15.8 minutes of EBCT for (a) aldicarb, (b) dimethoate, (c) naproxen, and (d) clofibric acid.

3.4.4.3 Decreasing Removal Behavior

Three of the contaminants displayed decreased removal over time at some point in the study. Trimethoprim and caffeine were well removed (>50%) during the first 150 days of exposure and appeared to be at steady state as shown in Figure 3.4. These removals are similar to those reported in the literature (Nakada et al., 2007; Metz et al., 2009). This was followed by a steady decline in removal to <10% removal at 340 days of exposure after 7.9 min of EBCT. Erythromycin removal was initially around 50% at 10 days of exposure and decreased immediately. No removal was measured at the next sampling event 70 days later. The same trends occurred in Biofilter 1b (data not shown) and Biofilter 2 (Figure 3.4). The decreasing trend in caffeine and trimethoprim removal did not begin until after the addition of erythromycin to the feedwater as is shown in Figure 3.4. Note the data in Figure 3.4 is reported in biofilter operation time and not contaminant exposure time. A likely hypothesis is the loss of adapted biomass after the erythromycin addition, as erythromycin is known to affect certain microbial communities in natural biofilms at subinhibitory concentrations (Yergeau et al., 2012). The lack of microorganisms with erythromycin resistance genes in the laboratory feedwater could contribute to the decline in adapted biomass since there would be few microorganisms capable of deactivation of the antibiotic (Fan & He, 2011). The rate of decrease for all three contaminants was approximately the same. The microbial community responsible for biodegradation of these three contaminants appears not to be responsible for the biodegradation of other contaminants since their removals did not change after the erythromycin addition. The adapted biomass was not lost due to backwashing, since the decreasing trend was observed between backwashes. While not well documented, sustained biodegradation of these three contaminants has been observed in pilot- and full-scale drinking water filters operating under similar conditions (Snyder

et al., 2007; Metz et al., 2009; Metz, 2012), indicating microorganisms present in full-scale feedwater allowed for replacement of biofilter microorganisms capable of continued removal of trimethoprim, erythromycin, and caffeine.

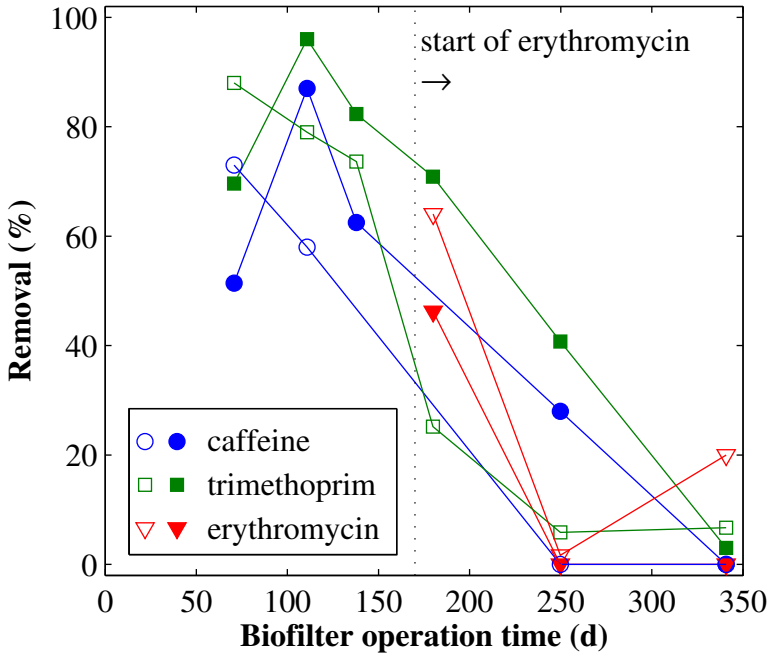

Figure 3.4. Decrease in contaminant removal after erythromycin addition for Biofilter 1a (close symbols) and Biofilter 2 (open symbols).

3.4.4.4 Non-Biodegradable Contaminants

Thirteen of the contaminants were classified as recalcitrant, with <15 % removal, and no acclimation occurred (Table 3.2), as illustrated in Figure 3.2 for atrazine. Previous research has shown atrazine, carbamazepine, and simazine to be recalcitrant to biodegradation in drinking water biofilters (Chowdhury et al., 2010; Halle, 2010). A cutoff of 15% was used to determine if a contaminant was recalcitrant because the RSD of the contaminant analysis was as high as 11% for some of the contaminants and average removals below the cutoff were not statistically significant at a 95% confidence level.

3.4.5 Modeling Contaminant Biodegradation

Figure 3.5 shows a comparison of the average percent removal in Biofilter 1 after the top 7.9 min of EBCT (Biofilter 1a) to that in the bottom 7.9 min of EBCT (Biofilter 1b). Bisphenol A, ibuprofen, and triclosan were not included in Figure 3.5 since their removal in the bottom of the filter could not be quantified. Regression of the data in Figure 3.5 shows a near 1:1% removal relationship. The slope of the regression was not significantly different from one and the intercept was not significantly different from zero at a 95% confidence level. These results are supportive of a first-order removal behavior where the percent removal is independent of the influent concentration. However, the removal across the bottom half of the filter was expected to be lower than the top half since the average biomass should be lower in the bottom half (Eqn. 3.3).

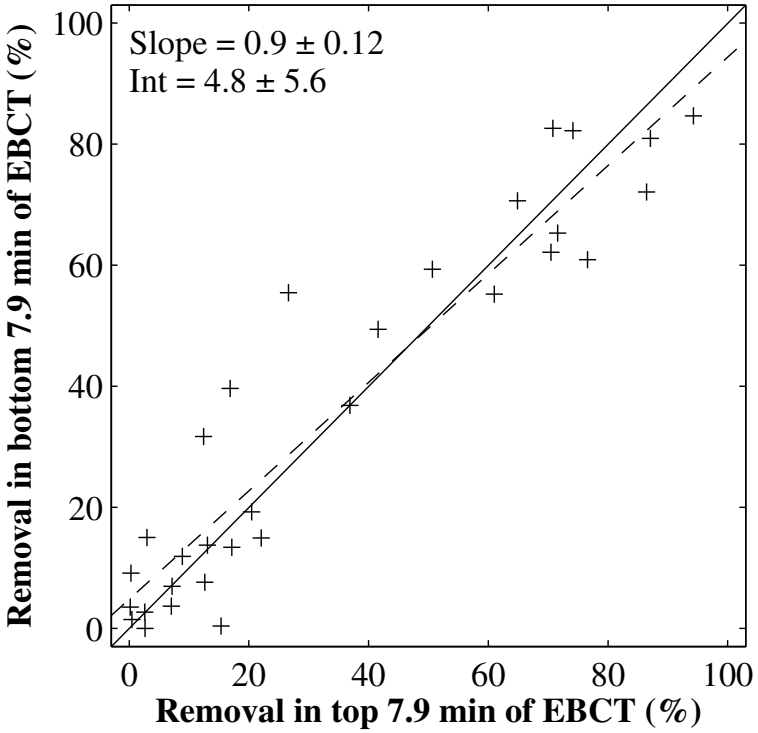

Figure 3.5. Steady state removal in top and bottom halves of Biofilter 1 for 31 contaminants with 1:1 ratio line (solid line), linear regression (dashed line), and regression coefficients and their 95% CI.

For the 32 contaminants that displayed steady-state behavior in Biofilter 1a, average pseudo-first-order rate constants, k', were calculated from the removal and EBCT using Eqn. 3.5 at each sampling event and then averaged and reported in Table 3.3. Assuming a biomass concentration of 84 ± 7 nmol PO_4 (mL bed)$^{-1}$, the contaminant utilization rate constants were calculated using Eqn. 3.4.

Table 3.3. Trace Organic Contaminant Utilization Rate Constants with Comparison to US EPA BIOWIN Model Predictions

				Probability Model		Expert Survey		MITI Model	
contaminant	**k' (min^{-1})**	**k'' [a] × 1000**	**classification this study**	**BIOWIN 1 (linear)**	**BIOWIN 2 (non-linear)**	**BIOWIN 3 (ultimate)**	**BIOWIN 4 (primary)**	**BIOWIN 5 (linear)**	**BIOWIN 6 (non-linear)**
2,4–D	0.16	1.9	fast	slow	slow	weeks-months	days-weeks	fast	slow
acetaminophen	0.12	1.4	fast	fast	fast	weeks	days	slow	fast
acetochlor	0.012	0.14	recalcitrant	slow	slow	months	days-weeks	slow	slow
aldicarb	0.089	1.1	slow	slow	slow	weeks-months	days-weeks	slow	slow
atrazine	0.0002	0.003	recalcitrant	slow	slow	months	weeks	slow	slow
bisphenol A [b]	>0.020	>2.3	very fast	fast	slow	weeks-months	days-weeks	slow	slow
caffeine	0.154	1.8	fast	fast	fast	weeks	days-weeks	slow	slow
carbamazepine	0.001	0.007	recalcitrant	fast	slow	weeks-months	days-weeks	slow	slow
carbaryl	0.004	0.045	recalcitrant	fast	fast	weeks-months	days	slow	slow
chlorpyrifos	0.13	1.6	fast	slow	fast	recalcitrant	days-weeks	slow	slow
clofibric acid	0.058	0.69	slow	slow	slow	weeks-months	days-weeks	fast	slow
cotinine	0.039	0.47	slow	fast	fast	weeks-months	days	slow	slow
diazinon	0.017	0.20	recalcitrant	fast	fast	weeks-months	days-weeks	slow	slow
diclofenac	0.032	0.38	slow	slow	slow	weeks-months	days-weeks	slow	slow
dimethoate	0.18	2.2	fast	fast	fast	weeks	days	slow	slow
diuron	0.0004	0.004	recalcitrant	slow	slow	weeks-months	weeks	slow	slow
erythromycin [b]	--	--	--	slow	slow	recalcitrant	weeks-months	slow	slow
ethinyl estradiol	0.018	0.21	recalcitrant	slow	slow	months	weeks	slow	slow
gemfibrozil	0.16	1.9	fast	fast	fast	weeks-months	days-weeks	fast	fast
ibuprofen	0.37	4.4	very fast	fast	fast	weeks	days	slow	slow
iopromide	0.021	0.25	recalcitrant	slow	slow	months	days-weeks	slow	slow
malaoxon	0.023	0.28	slow	fast	fast	weeks	hours-days	fast	fast
methomyl	0.017	0.20	recalcitrant	fast	fast	weeks	days-weeks	slow	slow
metolachlor	0.009	0.11	recalcitrant	slow	slow	months	days-weeks	slow	slow
MIB	0.36	4.3	very fast	slow	slow	months	weeks	slow	slow
molinate	0.26	3.1	very fast	fast	fast	weeks-months	days	slow	slow
naproxen	0.17	2.0	fast	fast	fast	weeks	days	slow	slow
prometon	0.003	0.041	recalcitrant	slow	slow	months	days-weeks	slow	slow
simazine	0.009	0.11	recalcitrant	slow	slow	months	weeks	slow	slow
sulfamethoxazole	0.003	0.040	recalcitrant	slow	slow	weeks-months	days-weeks	slow	slow
tributyl phosphate	0.024	0.28	slow	fast	fast	days-weeks	hours-days	fast	slow
triclosan	0.31	3.7	very fast	slow	slow	months	weeks	slow	slow
trimethoprim	0.25	3.0	very fast	fast	fast	months	days-weeks	slow	slow
warfarin	0.07	0.81	slow	fast	fast	weeks-months	days-weeks	fast	slow
			Similar Rate	***67%***	***70%***			***55%***	***61%***

[a] $k'' = k'/X$ [mL/ (min · nmol PO_4)] where X = 84 nmol PO_4 $(mL)^{-1}$. [b] Removal not at steady state, reported average of all samples. -- n/a.

The pseudo-first-order-rate constants were classified into four categories based on three natural breaks at 15%, 50% and 85% steady state removals at 7.9 min of EBCT. The rate constants were classified as: recalcitrant ($k' < 0.022$ min^{-1}), slow (0.022 min^{-1} < k' < 0.093 min^{-1}), fast (0.093 min^{-1} < k' < 0.248 min^{-1}), and very fast ($k' > 0.248$ min^{-1}), which under the biomass conditions of this study corresponds to contaminant utilization rate cutoffs of 0.17×10^{-3}, 1.1×10^{-3}, and 3.0×10^{-3} mL bed (min·nmol PO_4)$^{-1}$.

These classified biodegradation rates were compared to the first six (aerobic models) prediction models of the Biodegradation Probability Program for Windows (BIOWIN) in the EPA Estimation Program Interface (EPI) Suite v4.10 (USEPA, 2012). Descriptions of the EPA-BIOWIN models can be found in (Boethling et al., 2003). BIOWIN 1, 2, 5, and 6 models had an output of either fast or slow; the very fast and fast biodegradation rates of this study were considered fast, and slow and recalcitrant biodegradation rates were considered slow for comparison to the EPA-BIOWIN models. The rates measured in this study were the same as the EPA-BIOWIN models for >55% the contaminants (Table 3.3), with BIOWIN 2 having the highest agreement at 70%.

3.4.6 Model Verification

Using the calculated pseudo-first-order rate constants, the model was then used to predict removals in Biofilter 1 at EBCTs of 7.9 and 15.8 min after the influent concentration was increased by a factor of 2 and in Biofilter 2 with an EBCT of 7.6 min (Figure 3.6). The average influent concentrations and steady state removals for Biofilter 2 are shown in Table 6.2. The two cotinine results at the higher influent concentration were 2 to 4 times higher than expected and not included in the figure. The model predicts the high and low observed removals well, but

there was more variation between the model and observed removals in the midremovals region. This variation may be because there was only one sampling event for Biofilter 1 after doubling the influent concentration, especially considering many of these contaminants in this range had a standard deviation around 10% when sampled at steady state. These variations appear to be random since the residuals are approximately normally distributed (Figure 3.6b). The model had a root-mean-square error (RMSE) of 11%, and 79% of the data was predicted to be within 10% of the observed values for the 29 contaminants modeled in the top 7.9 min of EBCT, suggesting biofilter contaminant removals follow pseudo-first-order kinetics. The RMSE for the bottom 7.9 min of EBCT (Biofilter 1b) was 13% for the 27 contaminants modeled and 48% of the data was predicted to be within 10% of the observed values.

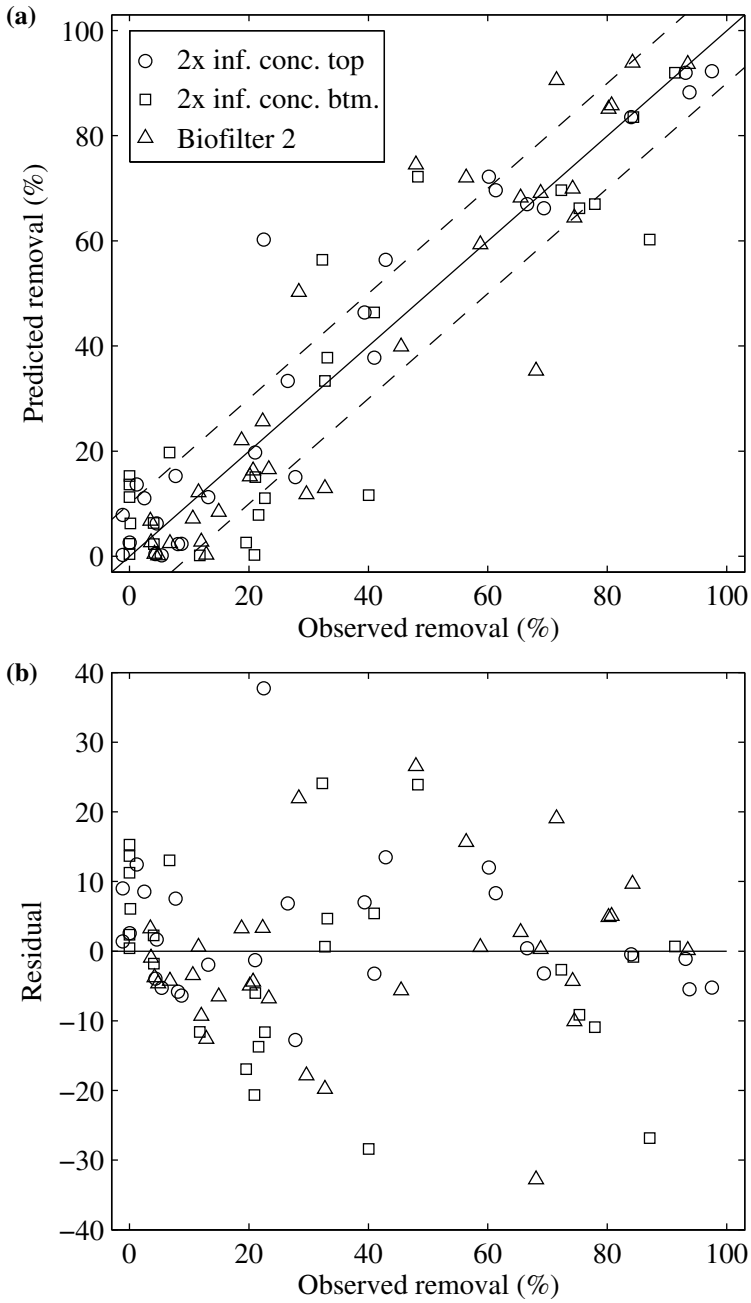

Figure 3.6. Modeled and observed contaminant removals in biofilters with different influent concentrations and EBCTs with 1:1 ratio (solid line) and ±10% of 1:1 ratio (dashed line) with (b) residual of model fit.

Also shown in Figure 3.6 is a comparison of predicted and average steady state observed removals from Biofilter 2. Biofilter 2 was fed ozonated DOM, but it yielded the same average TOC removal as Biofilter 1a (Table 3.1), indicating the two different waters had the same

amount of easily biodegradable DOM that could be biodegraded in 7.9 min of EBCT. The RMSE of the modeled data to the measured data was 12%, and 72% of the predicted data fell within 10% of the observed values, indicating a good prediction of the bioremoval of the 32 contaminants.

3.4.6.1 External Data

The model and calculated contaminant utilization rate constants were also applied to field- (full- or pilot-) scale biofilter removal data from five previously published studies (Snyder et al., 2007; Metz et al., 2009; Chowdhury et al., 2010; Halle, 2010; Metz, 2012). The operational parameters of the external datasets are in Table 3.4. The contaminant influent concentrations in all datasets were below 5 μg L^{-1}. All of the filters were operated for eight months or longer and were assumed to be at steady state. Since the field-scale biofilters were not operated at the same temperature as the laboratory setting, 20 ± 2 °C, the utilization rate constants were temperature corrected using Eqn. 3.6.

Table 3.4. Operational Parameters of Field-Scale Biofilters Datasets used as External Model Verification with Root Mean Square Error of Model

dataset	number contaminants (no. of samples)	media	EBCT (min)	temp. (°C)	avg. biomass conc. (nmol PO_4 mL^{-1})	RMSE (%)	source
Predictive Mode							
1	4 (36)	Anthracite	5/14	1 - 22	126/65	15	Halle (2010)
2	3 (3)	Anthracite	7.1	20	30	3.1	Chowdhury et al. (2010)
Simulation Mode							
3	9 (9)	Sand	6.8	16	160 [b]	15	Metz (2012)
4	5 (5)	Sand	5.6	14	87 [b]	10	Metz et al. (2009)
5	16 (16)	Anthracite	2	15 [a]	56 [b]	9.0	Snyder et al. (2007)

[a] Estimated.
[b] Average biomass was calculated.

The observed and model results from these five external datasets are shown in Figure 3.7. The contaminants in the external datasets included both recalcitrant and biodegradable

contaminants. Biomass distributions with filter depth were used to calculate the average biomass concentration (Eqn. 3.11) for datasets 1-2, which allowed the model to be used in a predictive mode; the RMSE was below 16% for these two data sets. Biomass data was not reported for datasets 3-5 and the average biomass concentration for each of these datasets was calculated by least squares of Eqn. 3.3 for all of the removal data points in each dataset. Thus, the model was used in a simulation mode. Contaminant removals in the calculated biomass datasets were in a similar relative order as the contaminant utilization constants.

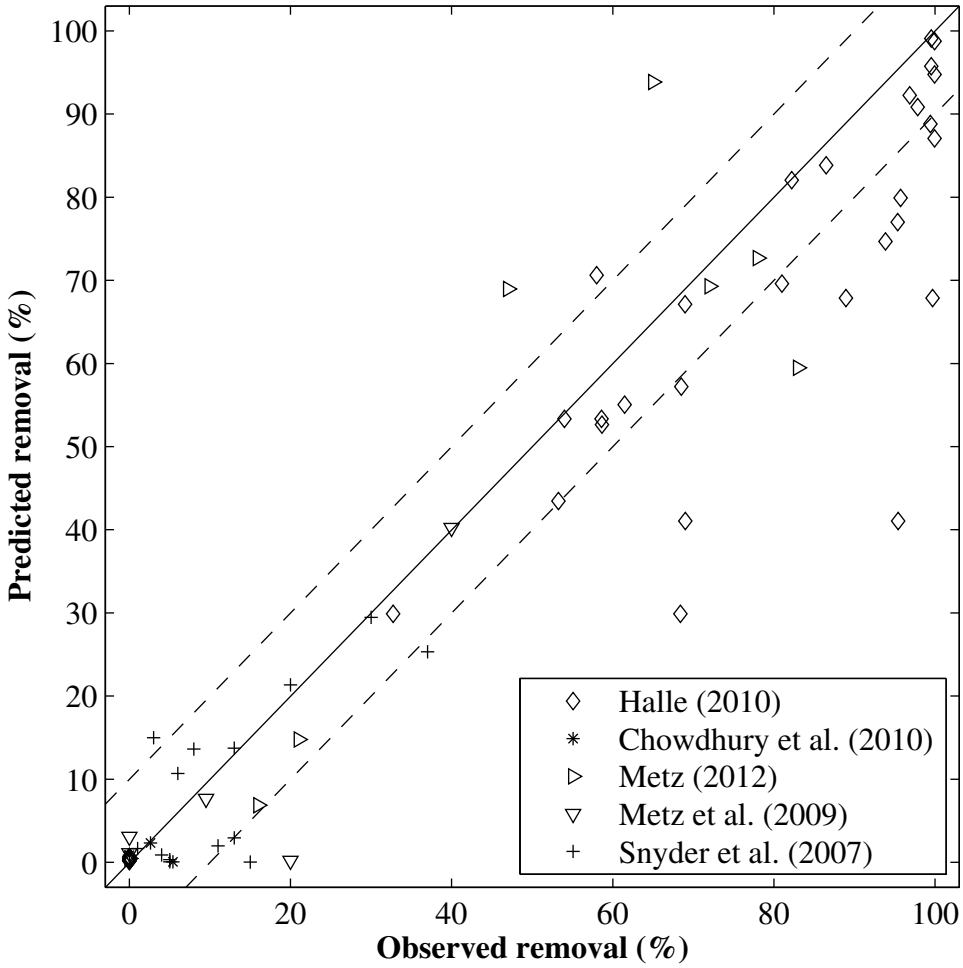

Figure 3.7. Modeled and observed contaminant removals of external datasets with 1:1 ratio (solid line) and ±10% of 1:1 ratio (dashed line).

The RMSE of the combined external model verification datasets, was 13%, 68% of the predicted data fell within 10% of the measured values and the slope of a least squares linear regression was 0.87 ± 0.07 (95% confidence limits). The combined external model verification datasets were also modeled using a non-biomass based model (Eqn. 3.5) and the temperature corrected pseudo first order rate constants which resulted in a poorer fit compared to the biomass based model ($F = 21.0$, $p < 0.001$). This supports the use of biomass concentration based model for the modeling biological drinking water filters.

3.4.6.2 Model Limitations

The pseudo-first-order contaminant removal model requires the biofilter to be acclimated and operating at steady state. When phospholipid biomass concentrations are not available, other biomass measures can be converted into phospholipid biomass using known conversions (Findlay et al., 1989). Additional studies need to be conducted covering a wide range of trace organic contaminants under a variety of operating conditions including a range of biomass concentrations, temperatures, and acclimation levels to fully develop the model.

3.4.7 Trace Organic Contaminant Removal in the Slow Sand Filter (SSF)

A majority, 59% (20/34), of the contaminants were removed to below detection limits in the SSF (Table 3.5). 5 contaminants (atrazine, carbamazepine, diuron, prometon, simazine) had removals less than 15% in the SSF and are likely recalcitrant to biodegradation even at extend contact times in drinking water. Other researchers have found little removal of carbamazepine (Heberer et al., 2004; Hoppe-Jones et al., 2010; Maeng et al., 2011) and simazine (Verstraeten et al., 2002; Kuster et al., 2010) in bank filtration and aquifer recharge systems. Steady state removal was observed for all of the contaminants except bisphenol A, ethinyl estradiol, and

erythromycin at the first sampling event. Bisphenol A and ethinyl estradiol removals increased throughout the study, and after 180 days of exposure, the effluent concentrations were below detection limits. Erythromycin removal was near 100% after 10 days of exposure and decreased to 24% after 170 days of exposure. The rate of loss of biodegradation capacity for erythromycin was the same as observed in Biofilter 1 (EBCT = 7.9/15.8 min). Decreased removal of caffeine and trimethoprim was not observed in the SSF as it was in Biofilters 1 and 2. The sustained removal of caffeine and trimethoprim in the SSF was likely due to the increased contact with active biomass ($EBCT \times X_{avg}$) or a different community structure than Biofilters 1 and 2.

Table 3.5. Steady State Contaminant Removals in Slow Sand Filter (SSF)

	EBCT: 5.9 hr		
contaminant	**removal (%) [a]**	**n**	**predicted removal (%)**
2,4–D	>98 [c]	6	100
acetaminophen	>97 [c]	6	100
acetochlor	66 ± 3.8	5	97
aldicarb	>98 [c]	4	100
atrazine	5.9 ± 5.2	6	6
bisphenol A [b]	>79 [c]	3	--
caffeine	95 ± 1.5	3	100
carbamazepine	0.8 ± 1.1	6	16
carbaryl	40 ± 13	4	68
chlorpyrifos	>89 [c]	2	100
clofibric acid	>95 [c]	5	100
cotinine	>98 [c]	6	100
diazinon	>92 [c]	5	99
diclofenac	89 ± 4.9	3	100
dimethoate	>98 [c]	4	100
diuron	9.5 ± 4.8	6	10
erythromycin [b]	77 ± 18 [c]	3	--
ethinyl estradiol [b]	>84 [c]	4	100
gemfibrozil	>99 [c]	5	100
ibuprofen	>98 [c]	3	100
iopromide	38 ± 18	5	100
malaoxon	>98 [c]	3	100
methomyl	28 ± 15	6	99
metolachlor	24 ± 9.3	3	94
MIB	>99 [c]	3	100
molinate	>98 [c]	5	100
naproxen	>95 [c]	5	100
prometon	6.1 ± 9.5	3	64
simazine	9.4 ± 10	6	94
sulfamethoxazole	18 ± 5.3	6	63
tributyl phosphate	63 ± 13	5	100
triclosan	>90 [c]	2	100
trimethoprim	>98 [c]	3	100
warfarin	>97 [c]	5	100

[a] Avg. ± 1 St. Dev. (n).
[b] Removal not at steady state, reported average of all samples.
[c] Percent removal limited by method reporting limit in at least one sample.

The SSF results were modeled using an average biomass concentration of 71 nmol PO_4 $(mL\ bed)^{-1}$ (Section 3.4.2). The model correctly (difference <20 percentage points) predicted 72 % (23/32) of the contaminant removals in the SSF. For remainder of the contaminants, the model significantly over predicted removals. The contaminants that were over predicted were all

recalcitrant contaminants except for tributyl phosphate. However, tributyl phosphate was just above the 15% threshold defining recalcitrant contaminants. Since the RSD of detection was around 11%, removals <15% at 7.9 min of EBCT may not be accurate enough to correctly calculate contaminant utilization rates for the recalcitrant contaminants. Future studies at longer EBCTs are needed to further refine contaminant utilization rates of the recalcitrant contaminants.

3.5 CONCLUSIONS

Trace organic contaminant removal ranged between no measurable removal (<15%) at an EBCT of 7.9 min for 13 contaminants and removal to effluent concentrations below the detection limit. Contaminant removals followed one of four trends over the one year study period: steady state removal throughout, increasing removal to steady state (acclimation), decreasing removal, or no removal (recalcitrant). Removals for all 19 nonrecalcitrant contaminants followed pseudo-first-order kinetics when at steady state with increased removal at longer EBCTs. Pseudo-first-order rate constants, k', were calculated, 0.02 to 0.37 min^{-1}, and contaminant utilization rates, k'', were calculated, 0.0003 to 0.04 mL (min·nmol PO_4) for each contaminant. Using these contaminant utilization rates a pseudo-first-order rate biomass based model was able to predict removals in laboratory biofilters at a different EBCTs and influent conditions. The model also predicted contaminant removal in previous field-scale research. Drinking water biofiltration has the potential to be an effective process for the control of many trace organic contaminants and a pseudo-first-order biomass based model can serve as an appropriate method for approximating performance.

Chapter 4
Retained Biodegradation Capacity of Biofilters for 2,4-D and MIB during Intermittent Exposure

4.1 INTRODUCTION

Many trace organic contaminants found in drinking water sources have episodic occurrence with long periods between exposures. Oftentimes these episodes occur seasonally. An example of two seasonally episodic contaminants are the naturally occurring algae metabolic 2-methylisoborneol (MIB) and the anthropogenic herbicide 2,4-dichlorphenoxyacetic acid (2,4-D). While MIB does not pose a public health risk, it can cause an earthy/musty odor in water and has an odor threshold of 5 to10 ng L^{-1} (Young et al., 1996). MIB occurrence is related to increased cyanobacteria activity and varies seasonally with the highest concentrations typically occurring during the warmest months of the year (Westerhoff et al., 2005a). MIB concentrations of up to 1,700 ng L^{-1} have been reported by water utilities (Graham et al., 2000). Various researchers have proven biofiltration to be an effective removal technology of MIB (Rittmann et al., 1995; Westerhoff et al., 2005b; Elhadi et al., 2006; McDowall et al., 2007). Research by Meyer (2005) has shown that an acclimation period of several months is needed for MIB biodegradation when starting new biofilters. Other researchers have found MIB removal was unaffected by a non-exposure periods less than 2 weeks (Chae et al., 2006; Elhadi et al., 2006; Ho et al., 2007). The herbicide 2,4-D is applied to control broadleaf weeds and has an episodic occurrence tied to runoff (Thurman et al., 1991). Surface water concentrations over 1800 ng L^{-1} have been reported (Donald et al., 2007; Ignatowicz, 2009). Researchers have found

2,4-D acclimation behavior to occur in drinking water biofilters (Zearley & Summers, 2012), sequencing batch reactors (Celis et al., 2008), and soil (Smith & Aubin, 1994).

Given the episodic nature of these two contaminants, the effectiveness of drinking water biofilters may be impacted. Little research has been conducted in controlled studies assessing how long biodegradation capacity can be sustained without constant exposure to either MIB or 2,4-D.

The objective of this study was to evaluate the impact of intermittent exposure of MIB and 2,4-D on biofilter removal. Additionally, the reproducibility of parallel laboratory biofilter columns was determined along with long-term acclimation behavior of 2,4-D.

4.2 MATERIAL AND METHODS

For this experiment, Biofilters R1-R7 with sand were used to evaluate the retained biodegradation capacity of MIB and 2,4-D removal during intermittent exposure periods.

4.2.1 Feedwater and Trace Organic Contaminant Spiking

The feedwater used in this experiment is described in Section 2.2. Radiolabeled MIB and 2,4-D were the trace organic contaminants investigated. Contaminant spiking occurred in two phases to evaluate: 1) the reproducibility of parallel biofilters, and 2) the impact of intermittent contaminant exposure on contaminant removal. For the reproducibility phase, Biofilters R2-5 were not exposed (NE) to MIB and 2,4-D for 43 days followed by a constant contaminant exposure for 60-96 days depending on the biofilter and contaminant. For the second phase of the experiment, Biofilters R1-R6 were systematically not exposed (NE) for anywhere between 0-263 days and then re-exposed to contaminants for 23-66 days as shown in Table 4.1. During the second phase an identical control biofilter with a constant contaminant feed was run in parallel

with the NE biofilters. To account for fluctuations in laboratory temperature and water quality, simultaneous paired sampling of the NE biofilters and the control biofilter was conducted. When comparisons were made between a NE biofilter and the control, only the paired samples with the control were used. The biofilters were spiked with contaminants, with target MIB and 2,4-D influent concentrations of 100 ng L^{-1}. During the non-exposure periods, the biofilters were operated only with dechlorinated tap water with supplemental DOM but no contaminants.

Table 4.1. Biofilter Days of Non-Exposure and Exposure with Average EBCT at Sampling with 95% CI for the Impact of Intermittent Trace Organic Contaminant Exposure Phase

Biofilter	days of non-exposure	days of exposure	EBCT (min)	n	media extraction data
R1	0	66	8.6 ± 1.1	20	April 2010
R2	36	31	8.2 ± 1.3	9	January 2010
R3	47/83 [a]	49	8.4 ± 1.1	12	January 2010
R4	83	43	8.0 ± 1.3	12	January 2010
R5	113/149 [a]	23	7.9 ± 1.2	8	January 2010
R6	263	66	10.7 ± 1.7	20	August 2009
R7 (control)	--	232	8.8 ± 0.7	51	January 2010

[a] MIB/2,4-D

4.2.2 Radiolabeled Contaminant Stocks

Radiolabeled MIB and 2,4-D stocks were prepared in nanopure water. The radiolabeled MIB stock consisted of pure ^{14}C-ring labeled MIB. The 2,4-D stock was 0.18% ^{3}H-acetic acid labeled 2,4-D, and the remaining was unlabeled 2,4-D. The specific activities of the MIB and 2,4-D stocks were 55 mCi $mmol^{-1}$ and 38.8 mCi $mmol^{-1}$, respectively. The detection limits for radiolabeled MIB and 2,4-D were 34 ng L^{-1} and 18 ng L^{-1}, respectively. All of the stocks were free of organic solvents to minimize easily biodegradable primary substrates in the feed. MIB and 2,4-D concentrations were analyzed by the solid-phase extraction/liquid scintillation counting (SPE-LSC) method (Section 2.7.4). Since radiolabeled contaminants were used, the removals reported in this chapter are a measure of complete mineralization.

4.2.3 Steady State Determination

Trace organic contaminant removal was determined to be at steady state when there was no significant correlation (α>0.05) between the removal rates and contaminant exposure time. This was determined statistically using the method proposed by Yum and Peirce (1997).

4.3 RESULTS AND DISCUSSION

4.3.1 Organic Compounds Removal

The average EBCTs at sampling are reported in Table 4.1. The average influent TOC concentration was 2.9 ± 0.1 mg L^{-1} and did not significantly change throughout the study. The average influent MIB and 2,4-D concentrations were 97 ± 4.2 ng L^{-1} and 87 ± 7.6 ng L^{-1}, respectively.

4.3.1.1 Trace Organic Contaminants Removal in the Control Biofilter (Biofilter R7)

The average MIB removal for the control biofilter was 68 ± 2.1% (Figure 4.1a). There appeared to be no acclimation period for MIB with this media. This was most likely because the full-scale media had low-level MIB exposure year-round (Metz et al., 2006).

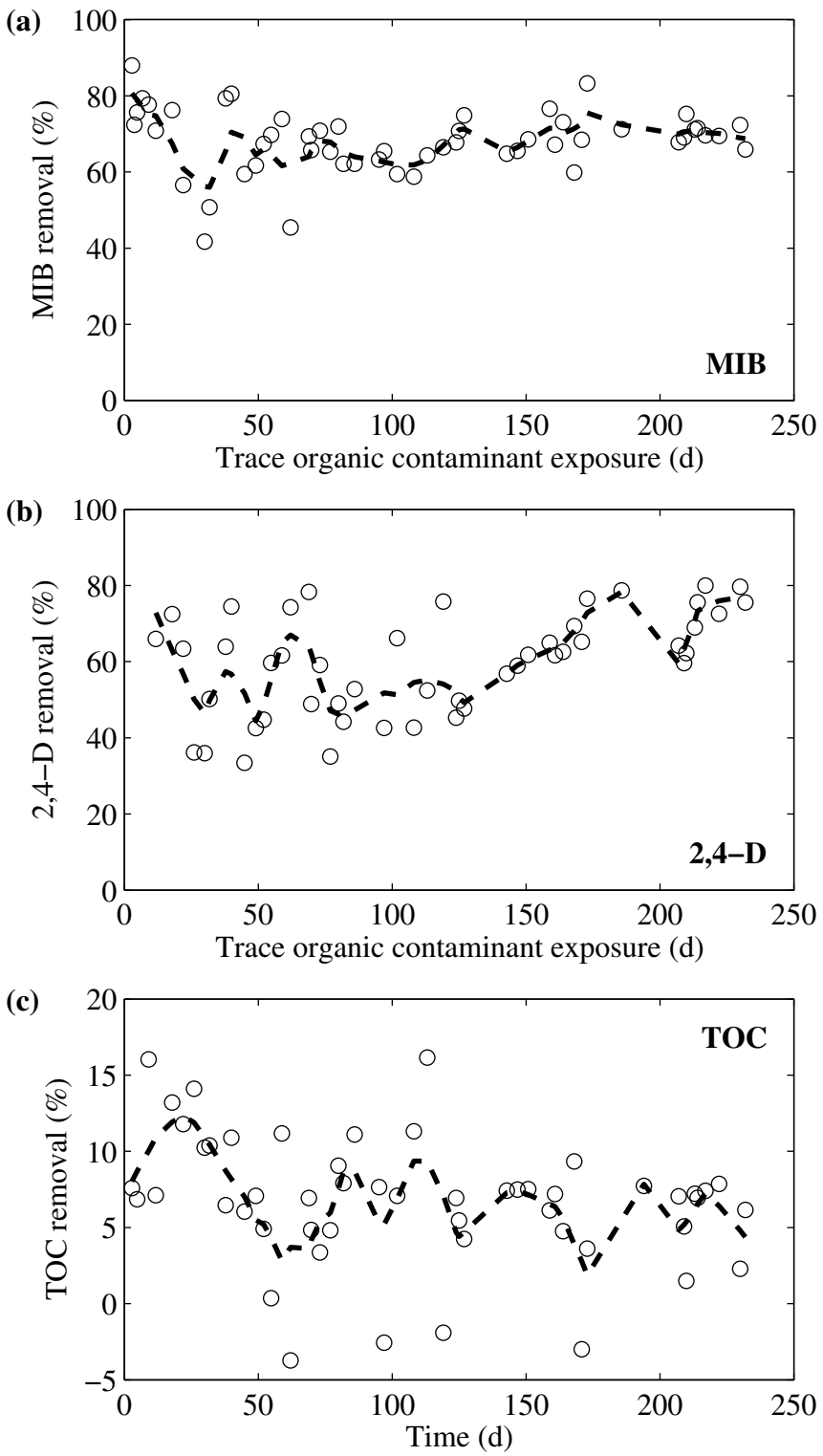

Figure 4.1. Removal of (a) MIB, (b) 2,4-D, and (c) TOC in the control biofilter with smoothing line (dashed line).

2,4-D removals fluctuated for the first 130 days of exposure, after which 2,4-D removals started to increase for the next 30 days indicating an acclimation period (Figure 4.1b). After approximately 160 days of exposure, 2,4-D removal was at steady state with 70 ± 4.0% removal. Similar acclimation behavior to 2,4-D has been observed in drinking water biofilters (Chapter 3; Zearley and Summers, 2012), sequencing batch reactors (Celis et al., 2008), and soil (Smith & Aubin, 1994).

The control had an average TOC removal of 7.6 ± 0.9% (Figure 4.1c). The TOC removal was similar to full-scale removals observed at the plant where the media originated (Metz et al., 2006). Trace organic contaminant removals did not correlate with TOC removal when comparing paired TOC and trace organic contaminant samples. The lack of correlation between trace organic contaminant and TOC removals indicates that MIB and 2,4-D are used as secondary substrates and not being cometabolized in the biofilter since cometabolism rates are directly related to the primary substrate utilization.

4.3.2 Reproducibility in Parallel Biofilters

The experimental reproducibility was assessed using 4 parallel biofilters (Biofilters R2-5). Much of the variability was accounted for with changes in the EBCT and temperature. There was a first-order relationship following Eqn. 3.5 between trace organic contaminant removals and EBCT for both contaminants as shown in Figure 4.2. There was additional scatter above and below the first-order fit line which was likely due to different temperatures at sampling affecting the biodegradation rates. There was evidence from the control biofilter that 2,4-D was not at steady state removal during this phase (Section 4.3.1.1), so any k' values calculated from this first-order relationship may not represent steady state k' values.

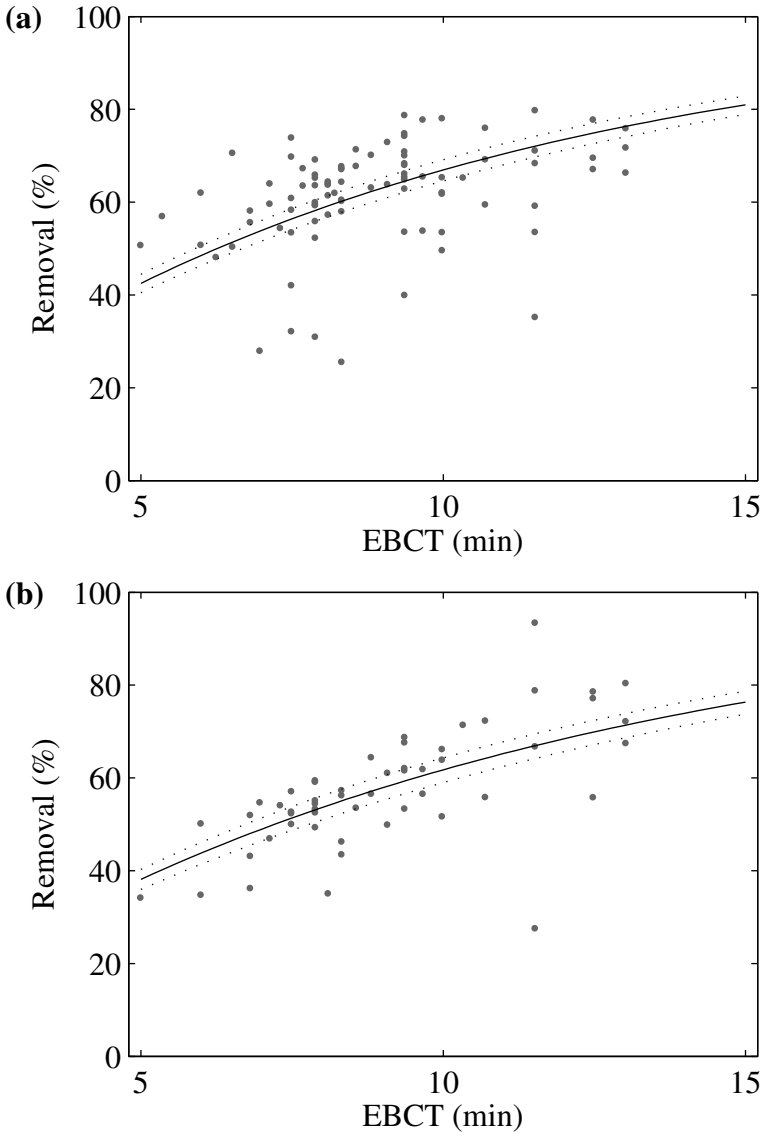

Figure 4.2. Removal by EBCT for (a) MIB and (b) 2,4-D with fitted first-order line (solid line) and 95% CI (dashed lines) for Biofilters R2-5 during the reproducibility phase.

The average removal with ±1 SD for the four biofilters at each sampling event is shown in Figure 4.3. At each sampling event a coefficient of variance (CV) was calculated, and the average CVs for MIB and 2,4-D are shown in Table 4.2. The impacts of different EBCTs between biofilters at sampling were evaluated by normalizing the removals to the same EBCT of 7.5 min (Eqn. 3.7), and by comparing the CVs from the normalized removal data to the original CVs. The average CV of the normalized data decreased for 2,4-D (Table 4.2). This indicated that

a portion of the variability in removal between biofilters was attributable to different EBCTs. A decrease in average CV was not observed for MIB.

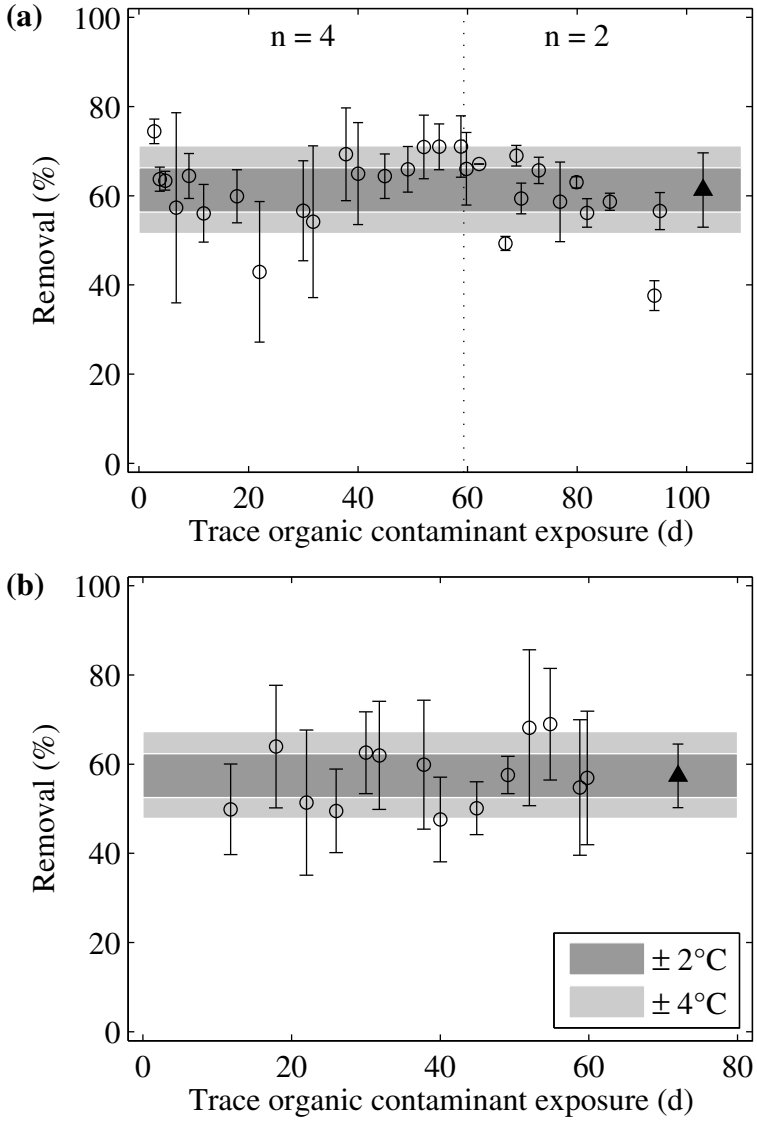

Figure 4.3. Average removal for Biofilters R2-R5 with ±1 SD error bars for (a) MIB and (b) 2,4-D (n=4). Overall average and ±1 SD are represented by a solid triangle.

Table 4.2. Average Coefficient of Variance (CV) for Observed and Normalized to EBCT Removal Data Across Biofilters R2-R5 Operated in Parallel

	average CV (%)	
		EBCT
	observed	**normalized**
MIB	11	11
2,4-D	21	14

The overall average removals for the reproducibility phase of the study are represented by a solid triangle in Figure 4.3. The trace organic contaminant removals varied between sampling events. This variability was could have been caused by changes in laboratory temperature. Since there was no systematic increase in removal, the observed variability between sampling events was unlikely due to acclimation. Since the temperature was not measured at each sample event, the impacts of temperature changes were estimated by temperature correcting the average pseudo-first-order rate constants, k', using the van 't Hoff equation (Eqn. 3.6). The dark and light bands in Figure 4.3 represent the range of removals within ±2 °C and ±4 °C change in temperature from 20 °C. A ±4 °C temperature change accounts for most of the variation between sampling events observed. The laboratory did experience temperature fluctuations of this magnitude during this experiment. MIB removal variability due to temperature changes is higher than 2,4-D because MIB had a higher k' value.

The TOC removal was at steady state with an average removal of 9.6 ± 1.0% for Biofilters R2-R5 in the reproducibility phase of the study.

4.3.3 Impact of Non-Exposure Periods

Generally, MIB removal was not significantly affected by non-exposure periods less than 113 days, however, after 263 days of non-exposure, MIB removal was 29% lower than the control biofilter as shown in Figure 4.4. There was a significant difference between the NE and the control biofilters at 47 and 83 days of non-exposure, but the difference was small (<13 percentage points). These results indicate that non-exposure periods less than 4 months have no impact on MIB removal. It is likely that the adapted microorganisms remained abundant enough to significantly biodegrade MIB during non-exposure periods less than 4 months (Alexander, 1999; Rittmann & McCarty, 2001). TOC removals were at steady state for all the biofilters

throughout this study and are shown near the bottom of the bars in Figure 4.4 and Figure 4.5. There was no significant difference between the TOC removals of the NE biofilters and the paired control TOC removal data at a 95% confidence level.

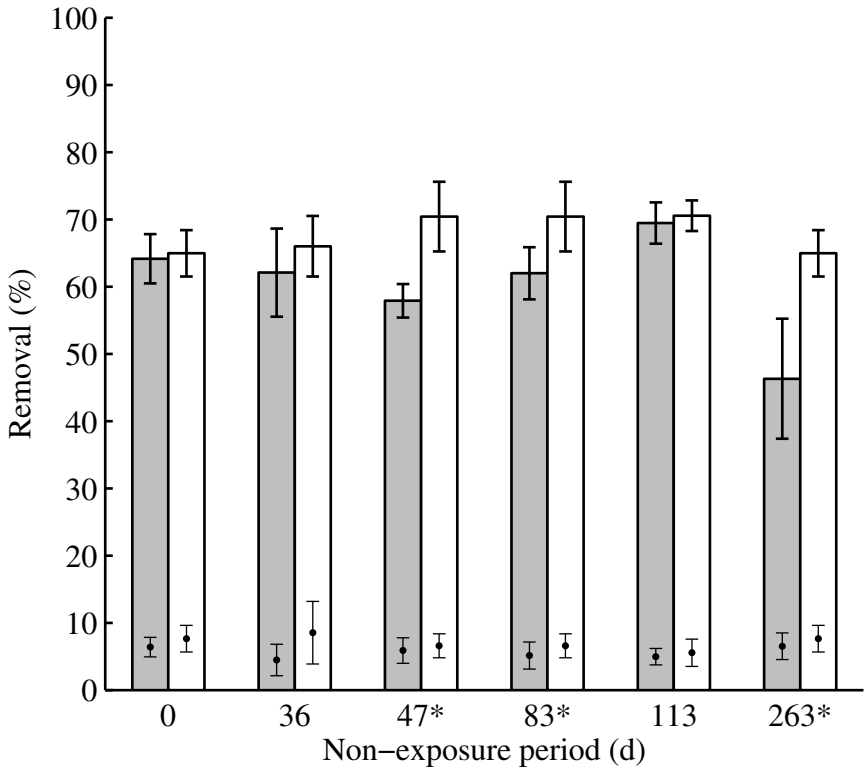

Figure 4.4. Impact of non-exposure periods on average MIB removal with ±95% CI error bars for NE biofilters (gray bars) and control biofilter (white bars). TOC removal is shown as dots near the bottom of the bars. *MIB removals statistically different at a 95% confidence level.

The NE biofilters had lower 2,4-D removals compared to the control for all of the non-exposure periods except after 149 days of non-exposure as shown in Figure 4.5. Acclimation to 2,4-D was observed in the NE biofilters in addition to the control biofilter. Since the control biofilter had been exposed to 2,4-D longer than the NE biofilters, the removals were higher in the control than the NE biofilters. At 149 days of non-exposure, the removal in the NE biofilter was the same as the control that had been constantly exposed to 2,4-D for 209 days. Since acclimation occurred in the NE biofilters during non-exposure periods, constant exposure to 2,4-D was not necessary for acclimation. Microorganisms capable of 2,4-D degradation likely

grew on the primary substrate during the absence of 2,4-D. When re-exposed to 2,4-D, the adapted microorganisms immediately utilized 2,4-D as they had before the non-exposure period. Ho et al. (2007) observed acclimation without constant exposure for MIB in sand biofilters. However after 263 days of non-exposure, 2,4-D removal in the NE biofilter (Biofilter R6) was 59% lower than the control. Biofilter R6 (non-exposure = 263 days) did not acclimate during the non-exposure period as was seen in the other biofilters.

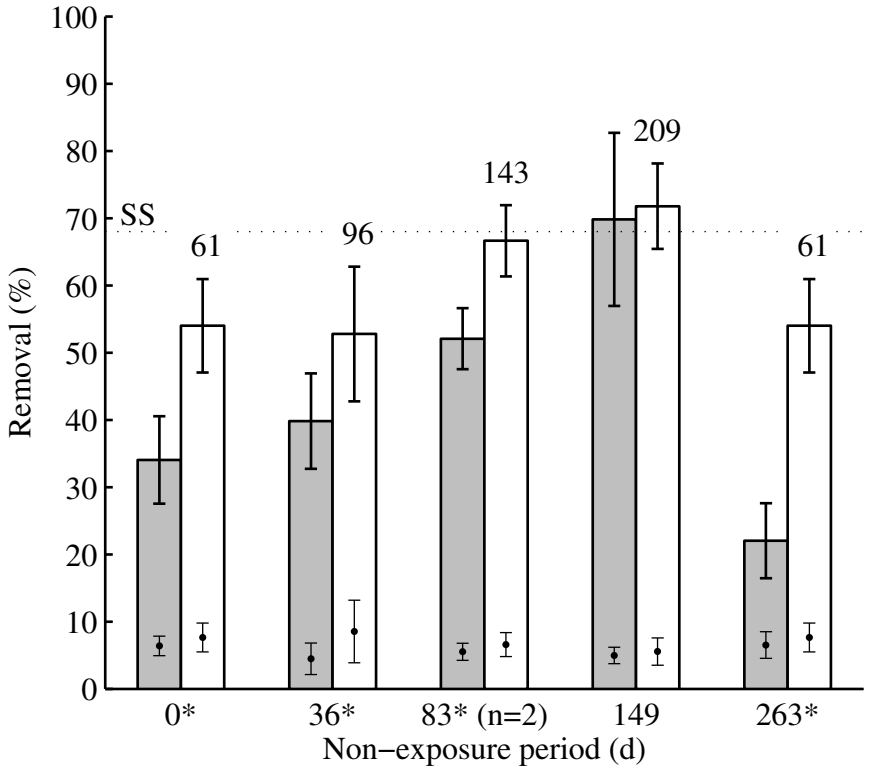

Figure 4.5. Impact of non-exposure periods on average 2,4-D removal with ±95% CI error bars for NE biofilters (gray bars) and control biofilter (white bars). Prior days of 2,4-D exposure for the control are labeled above each control bar, TOC removal is shown as dots near the bottom of the bars, and the steady state removal of the control is given (dashed line). *2,4-D removals statistically different at a 95% confidence level.

4.3.4 Acclimation after Non-Exposure Periods

After each non-exposure period, MIB removal immediately returned to steady state removal after re-exposure (Figure 4.6a) except for Biofilter R6 (263 days of non-exposure)

which showed acclimation behavior after ~10 days. MIB removal was initially around 13% and climbed to over 60% after 20 days of exposure as shown in Figure 4.6b.

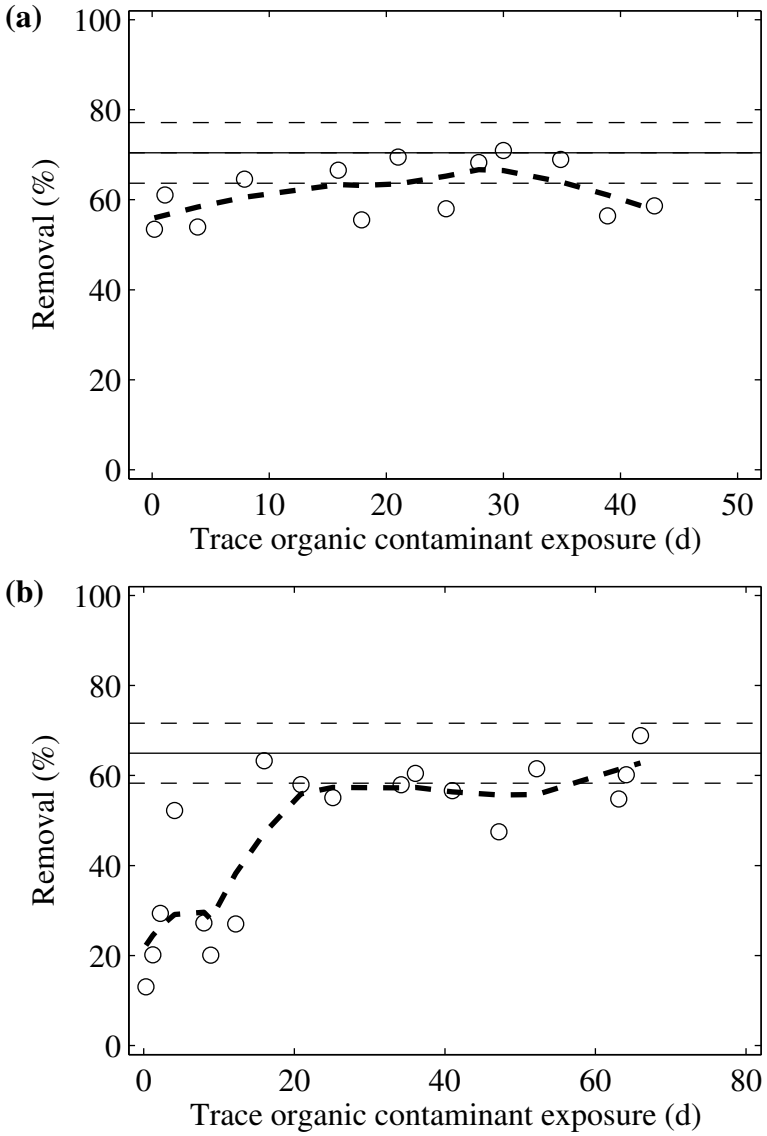

Figure 4.6. MIB removal after (a) 83 days and (b) 263 days of non-exposure with a smoothing line (bold dashed line). The average removal (solid line) and ±1 SD (dashed lines) of the control are given for reference.

Like MIB, after each non-exposure period, 2,4-D removal appeared to be at steady-state after re-exposure (Figure 4.7a) except for Biofilter R6 (263 days of non-exposure) which showed weak acclimation behavior. 2,4-D removal was initially around 20% and continued to increase

for the 66 days of exposure as shown in Figure 4.7b. The onset of acclimation occurred much sooner in the Biofilter R6 (~40 days) than the control (130 days). 2,4-D acclimation in Biofilter R6 also occurred at a greater rate than in the control. The observed acclimation phase in the Biofilter R6 (263 days of non-exposure) was likely due to adapted microorganisms increasing either through enzyme induction, gene transfer, or proliferation of a microbial community that was caused by the re-exposure to MIB and 2,4-D (Alexander, 1999).

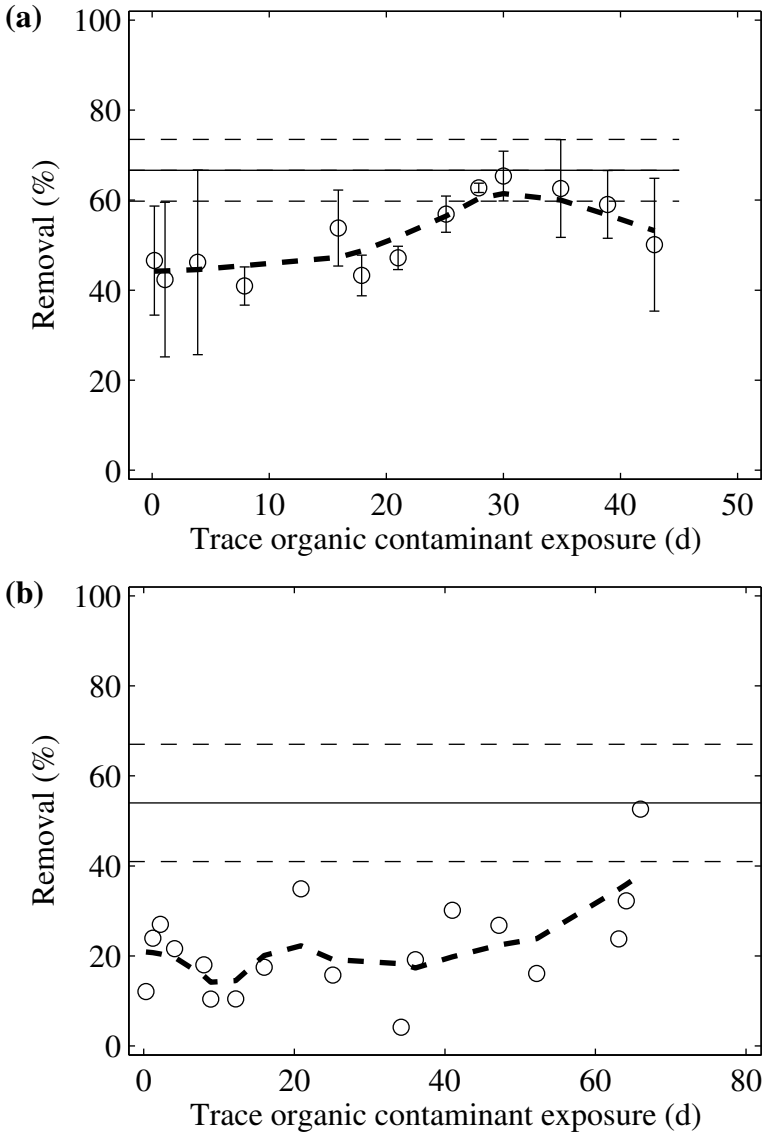

Figure 4.7. Acclimation of 2,4-D removal after (a) 83 days (n = 2) and (b) 263 days of non-exposure with a smoothing line (bold dashed line). The average removal (solid line) and ±1 SD (dashed lines) of the control are given for reference.

4.3.5 Applications for Treatment Facilities

Once adapted biomass was present in a biofilter, non-exposure events less than 5 months did not impact MIB or 2,4-D removal in drinking water biofilters. For a non-exposure period of 9 months, a biofilter needs time to re-acclimate which occurs on the order of a few weeks for MIB and months for 2,4-D but possibly at a great rate than the initial acclimation. If using an inert media such as sand, temporary control measures such as powder activated carbon (PAC) could be used during the re-acclimation phase. The low removals during re-acclimation would likely be diminished for adsorptive media such as GAC since there would be continued removal due to adsorption.

4.4 CONCLUSIONS

There was a first-order relationship between trace organic contaminant removal and EBCT. Within each sampling event of identical parallel biofilters, the variability was partially attributable to differences in the EBCT at sampling of each biofilter. Removals for the parallel biofilters also showed variation between each sampling event but the magnitude of this variability was of the same magnitude as predicted removals due to a ±4 °C in temperature. Additionally, long-term acclimation to 2,4-D was observed in the control biofilter, reaching steady state removal after 160 days of exposure.

Adapted microorganisms in drinking water biofilters retained the capacity to biodegrade MIB and 2,4-D after non-exposure periods less than 5 months. After 9 months of non-exposure, the biofilter removals were significantly lower than the control biofilter although the biofilters began to acclimate to the trace organic contaminants.

Chapter 5
MIB and 2,4-D Removal in Drinking Water Biofilters with Variable Influent Conditions

5.1 INTRODUCTION

Trace organic contaminants rarely occur at constant concentrations in the environment (Thurman et al., 1991; Westerhoff et al., 2005a). In addition, drinking water treatment facilities do not operate under constant operation conditions. It is important to understand the how changes to the influent trace organic contaminant concentration, water quality, and flow rate affects biofilter operation. MIB and 2,4-D are naturally occurring and synthetic trace organic contaminants, respectively, that are associated with seasonal concentration fluctuations and were chosen as to evaluate these impacts. Chae et al. (2006) investigated the impacts of changing influent concentrations on MIB and geosmin removal in sand, BAC, and anthracite biofilters. Part of this evaluation was to determine if GAC media provided more stable trace organic contaminant removal during fluctuating influent conditions.

This study explored the impacts of three varying influent scenarios on MIB and 2,4-D removals in biological drinking water filters: varying trace organic contaminant concentration with desorption, varying primary substrate conditions, and decreasing hydraulic loading rates, i.e. increasing EBCTs.

5.2 MATERIAL AND METHODS

5.2.1 Filter Setup and Operation

After the conclusion of the biodegradation rates (Chapter 3) experiments and long-term behavior in BAC (Chapter 6) experiments, Biofilters 1a and G2 were used for evaluating the impacts of variable influent conditions on trace organic contaminant removal. Biofilter 1a was used as is and was called "Sand B" for this experiment. Biofilter G2 was unpacked and a portion of the GAC was packed into a glass column with an inner diameter of 15 mm (ACE Glass 5820-20) to the same heights as described in Section 2.1.2 and was referred to as "BAC". The remaining portion of GAC from Biofilter G2 was autoclaved to inactivate the attached microorganisms and was packed to the same specifications as the BAC filter, this filter was called "GAC A". The media was autoclaved at 121°C, 100 kPa for 20 min in feedwater with 3 mg L^{-1} of TOC, 100 ng L^{-1} of MIB, and 2,4-D in order to reduce the desorption of the trace organic contaminants. A fourth column was packed with sterile sand to the same specifications as Sand B and was called "Sand A". The experimental setup is shown in Figure 5.1. The filters with inactivated or no microorganisms were referred to as "abiotic" filters. The "abiotic" GAC (GAC A) filter represented trace organic contaminant removal by adsorption-only and the "abiotic" sand (Sand A) media was a control with no biological or adsorption removal of trace organic contaminants. The "abiotic" filters were expected to become biologically active within a few days of operation as they were colonized by microorganisms in the feedwater, however the "abiotic" filters were not expected to acclimate and biodegrade MIB or 2,4-D in the 11 week study based on previous MIB research by Meyer (2005) using a similar setup.

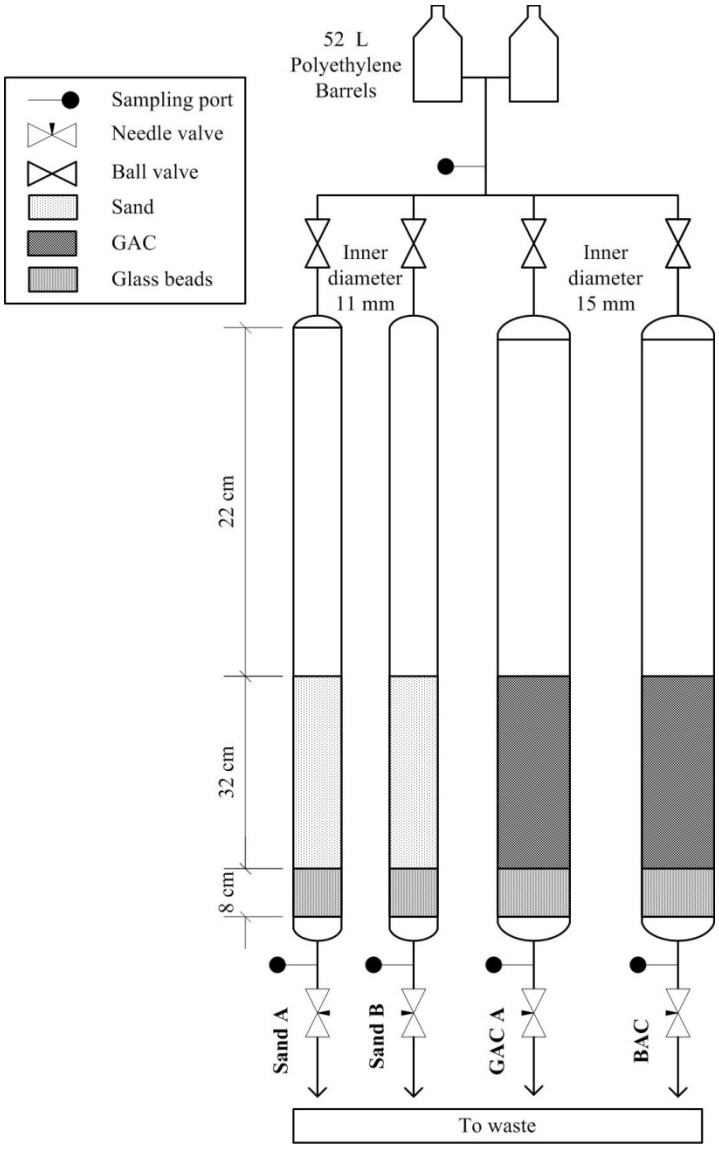

Figure 5.1. Setup for variable influent conditions experiment.

5.2.2 Feedwater with Varying Influent Conditions

The feedwater was the same as described earlier (Section 2.2). The first phase of the study consisted of stepped increases in trace organic contaminant influent concentrations from 100 to 500 ng L^{-1} over the course of 27 days as seen in Table 5.1. It was then followed by three days where the trace organic contaminant was not spiked into the feed and desorption was assessed. During the desorption portion of the study, the target influent TOC concentration was constant at 3 mg L^{-1}. In the second phase, the primary substrate changed. First, the TOC

concentration was increased by a factor of two. Second the easily biodegradable fraction of the TOC was increased by ozonating the DOM as described in Section 2.2.2. When the DOM was ozonated, the ozone was allowed to dissipate overnight so that no ozone remained in the influent water before trace organic contaminants were spiked. In the third phase of the study, the loading rate was decreased which increased the EBCT. Between each significant phase of the study, the filters were exposed to baseline conditions that had a target TOC concentration of 3 mg L^{-1} and MIB and 2,4-D target concentrations of 100 ng L^{-1}.

Table 5.1. Average Influent Concentrations with ±95% CI for Each Phase of the Study

phase	experimental description	duration (days)	n	contaminant concentration (ng L^{-1})		TOC concentration (mg L^{-1})
				MIB	2,4-D	
influent concentration	baseline 1	3	3	133 ± 77	104 ± 8	2.5
	200 ng/L	3	5	197 ± 55	188 ± 26	2.4 ± 0.1
	300 ng/L	8	10	317 ± 4	292 ± 35	2.7 ± 0.2
	500 ng/L	13	6	525 ± 47	511 ± 42	2.9 ± 0.2
	desorption	3	6	0	0	2.8 ± 0.1
primary substrate	baseline 2	5	5	117 ± 4	94 ± 5	2.6 ± 0.1
	increased TOC	6	7	138 ± 17	96 ± 4	5.7 ± 1.0
	ozonated DOM	4	5	138 ± 27	106 ± 17	2.7 ± 0.5
EBCT	baseline 3	18	13	112 ± 8	127 ± 23	2.3 ± 0.1
	2x EBCT	14	8	88 ± 7	113 ± 7	2.2 ± 0.2

5.2.3 Radiolabeled Contaminant Stocks

The radiolabeled MIB stock was 100% ^{14}C-ring labeled, and the 2,4-D stock was 0.18% ^{3}H-acetic acid labeled. The specific activities of the MIB and 2,4-D stocks were 55 mCi $mmol^{-1}$ and 41.07 mCi $mmol^{-1}$, respectively. The detection limits for radiolabeled MIB and 2,4-D were 20 ng L^{-1} and 33 ng L^{-1}, respectively.

5.2.4 Filter Sampling

The filters were regularly monitored for TOC, MIB, and 2,4-D. A single influent sample was used as the influent for all four filters. Viable biomass concentrations were taken at the beginning of the study, after the desorption phase (operation day 30), and after the third baseline (operation day 49) for all of the filters. MIB and 2,4-D concentrations were analyzed by the solid-phase extraction/liquid scintillation counting (SPE-LSC) method (Section 2.7.4). The removals reported in this chapter are for complete mineralization.

5.2.5 Removal Calculation in the Biological GAC (BAC)

Trace organic contaminant removal occurred in the biological GAC (BAC) filter by both biodegradation and adsorption. The removal due to adsorption in the BAC filter was approximated by the removal in the GAC A filter as illustrated by the shaded area in Figure 5.3. At each sampling event, the biological removal in the BAC was calculated by subtracting the removal in GAC A from the removal in BAC, since the influents were identical and each was operated at approximately the same EBCT. Both BAC removal mechanisms are shown on the bar graphs as the fraction of the removal due to biodegradation and adsorption.

5.3 RESULTS AND DISCUSSION

5.3.1 "Abiotic" Sand Control

Sand A had very little removal (<5%) of MIB and no removal of 2,4-D throughout the 11 week study. Some MIB removal was likely due to volatilization within the filter or during sampling since the removal remained constant throughout the study. No removal of 2,4-D and very low constant MIB removal indicated that there was no significant adsorption of the trace organic contaminants to the experimental apparatus, media, or biofilm. Within 6 days of

operation, TOC removal started to occur indicating the filter became biologically active. While the Sand A filter did not truly remain abiotic, it never acclimated to biodegrade MIB and 2,4-D. The lack of acclimation was due to the short study period and the low concentration of adapted microorganisms in the laboratory feed water compared to full-scale filters. This is consistent with other acclimation studies using fresh media (Namkung & Rittmann, 1987; Meyer, 2005; McDowall et al., 2007). Acclimation was assumed to not have occurred in the GAC A filter based on the Sand A results.

5.3.2 First-Order Kinetics

5.3.2.1 Increasing Influent Concentration

Influent MIB and 2,4-D concentrations were increased from 100 to 500 ng L^{-1} over the course of 27 days (Figure 5.2). The effluent concentrations of each filter increased after each increase of the influent concentration as shown in Figure 5.2 for both contaminants. However, when the removals are plotted over the same time period (Figure 5.3 & Figure 5.4), the removals were at steady state across the biological sand (Sand B) and BAC filters for both contaminants. The biological removal was not significantly different in a systematic way as the contaminant influent concentrations increased, which supports contaminant utilization by first-order kinetics since first-order kinetics removals are independent of the influent concentration (Eqn. 5.1).

$$\frac{C_{Eff}}{C_{Inf}} = \exp\left(-k' \cdot EBCT\right) \qquad 5.1$$

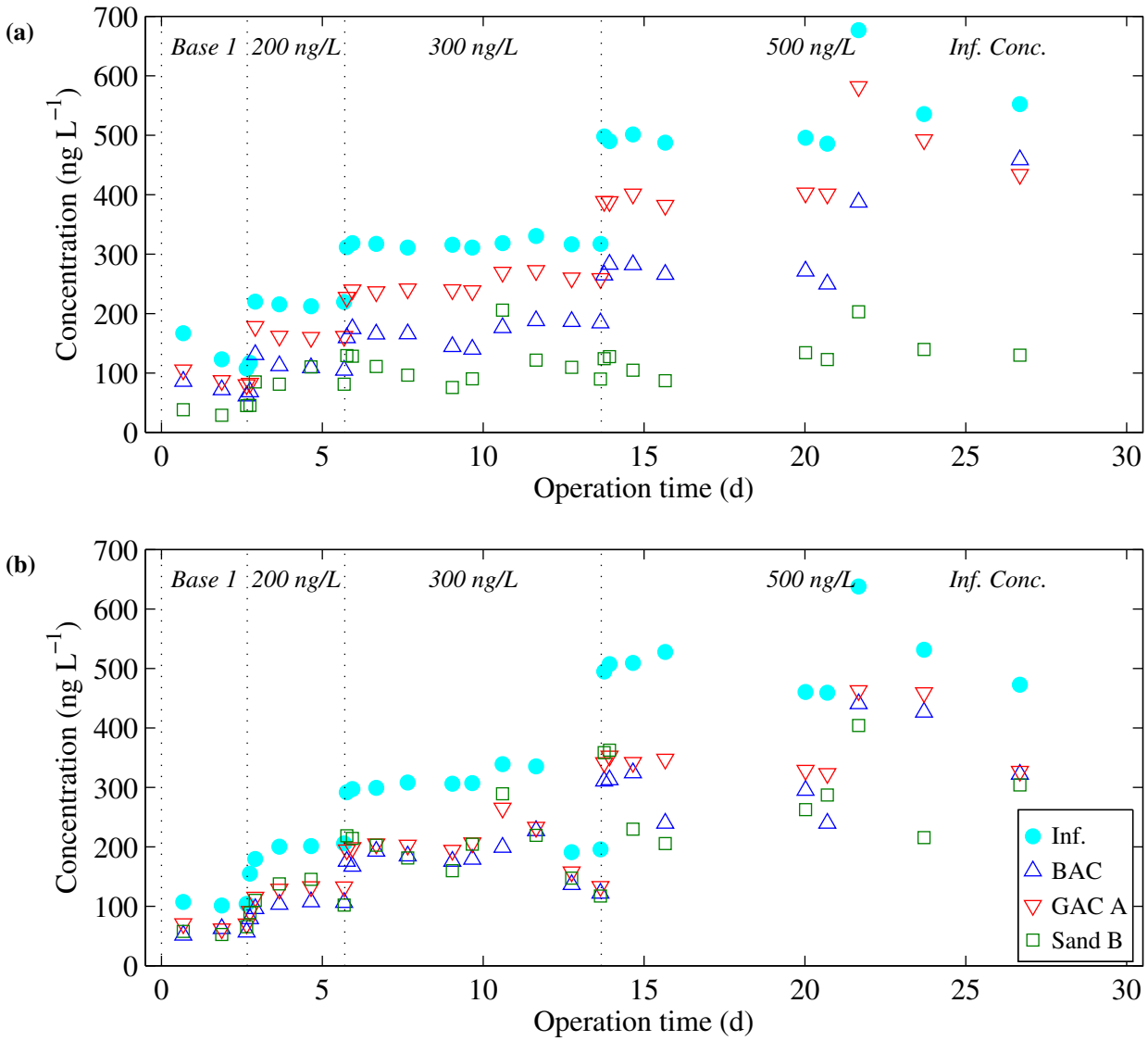

Figure 5.2. Influent and effluent (a) MIB and (b) 2,4-D concentrations in biological sand (Sand B), biological GAC (BAC), and "abiotic" GAC (GAC A) during increasing influent concentrations.

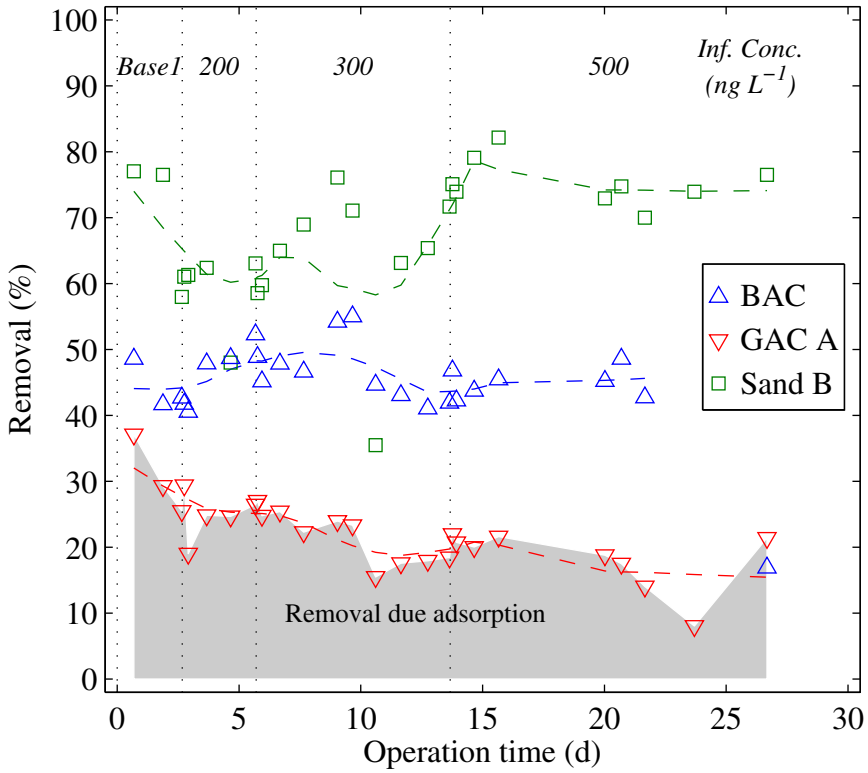

Figure 5.3. MIB biodegradation and adsorption in biological sand (Sand B), biological GAC (BAC), and "abiotic" GAC (GAC A) with smoothing lines during increasing MIB influent concentrations.

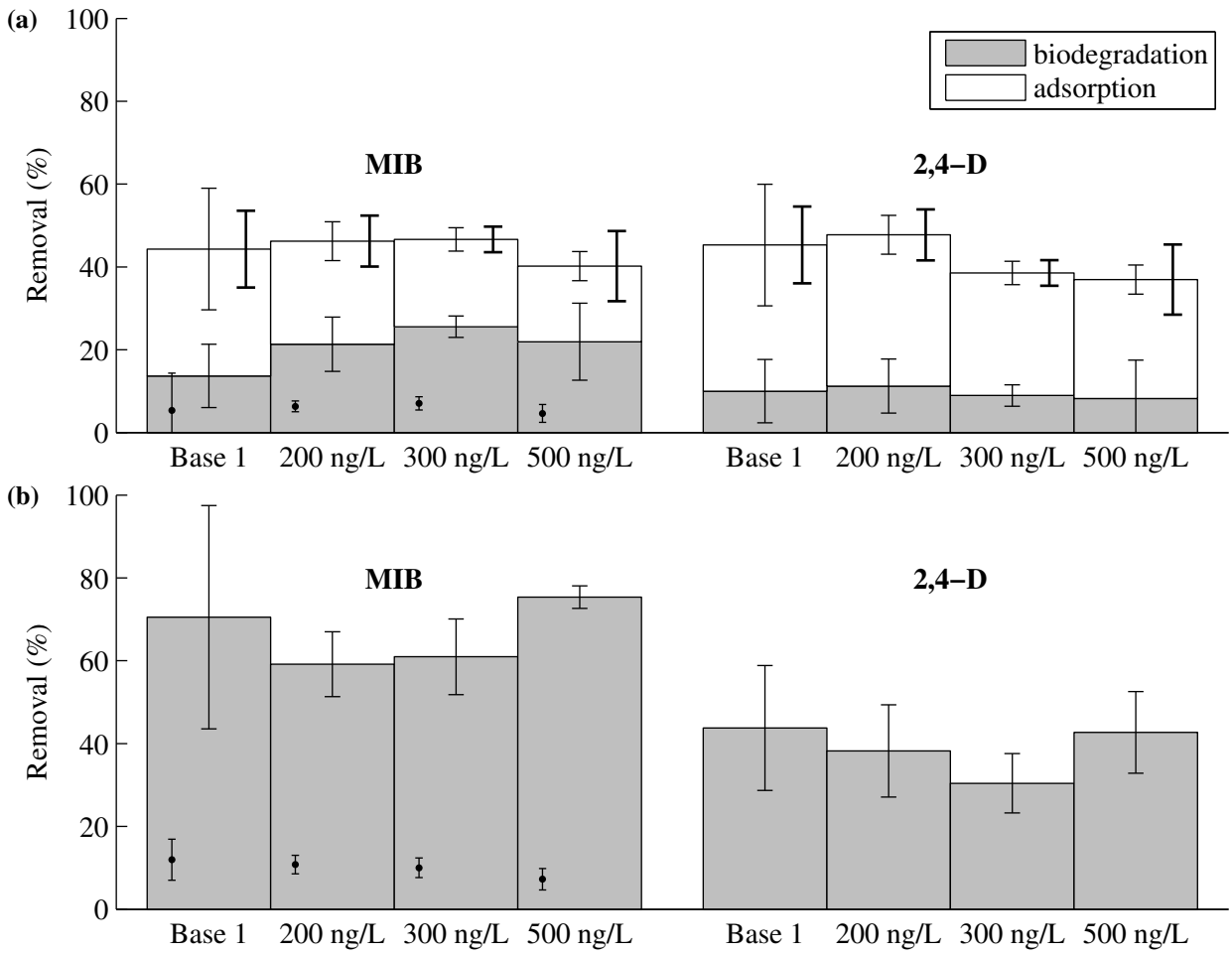

Figure 5.4. MIB and 2,4-D average removal in (a) BAC and (b) Sand B filters with ±95% CI. TOC removal is given by small dots towards the bottom of the bars. Removal by biodegradation and adsorption mechanisms in the BAC filter is shown. Thicker error bars are for total BAC removal, and baseline conditions are given as Base 1

Average steady state removal across Sand B was 66 ± 4.5% for MIB and 37 ± 4.6% for 2,4-D. MIB removal was lower in the BAC filter compared to Sand B (Figure 5.3). Lower removal in the BAC was likely due to a lower biomass concentration than Sand B. The biomass concentration of the BAC filter (80 ± 9 nmol PO_4 (mL bed)$^{-1}$) was 56% lower than Sand B (183 ± 18 nmol PO_4 (mL bed)$^{-1}$).

TOC removals in the biological media were at steady state throughout study except for Phase II where the DOM concentration and character were changed. Average TOC removal is represented by dots at the bottom of each bar in Figure 5.4. The average TOC removals were

within the range of removals previously observed for this media operating under similar conditions (Chapter 3 & Chapter 6) and were within the range of removals observed when the media was in operation at full-scale. Both GAC medias did not display any TOC breakthrough behavior and were considered DOM-exhausted.

5.3.2.2 Increased EBCT

At the end of the study, the filter loading rate was decreased by 50%, thus increasing the EBCT by a factor of two to a target EBCT of 15 min for 8 days. Figure 5.5 shows the removals for both contaminants increased when the EBCT was doubled for the biological medias. The removal due to biodegradation for the increased EBCT was predicted using a pseudo-first-model (Eqn. 3.5) where the k' values were calculated from the biological removal at the lower EBCT (Figure 5.5). While the observed biodegradation at the increased EBCT was not statistically different ($\alpha = 0.05$) from the predicted removals, the observed biodegradation was lower than predicted. The lower observed removal to predicted removal was likely due to the biomass not being fully developed at the increased EBCT since it was only operated at increased EBCT for 14 days. If the biofilters had been run at the increased EBCT for longer, then the average biomass concentration would be higher leading to increased removal due to biodegradation. Once removal due to biodegradation was at steady state under the increased EBCT conditions, the removals would be expected to more closely match the predicted values.

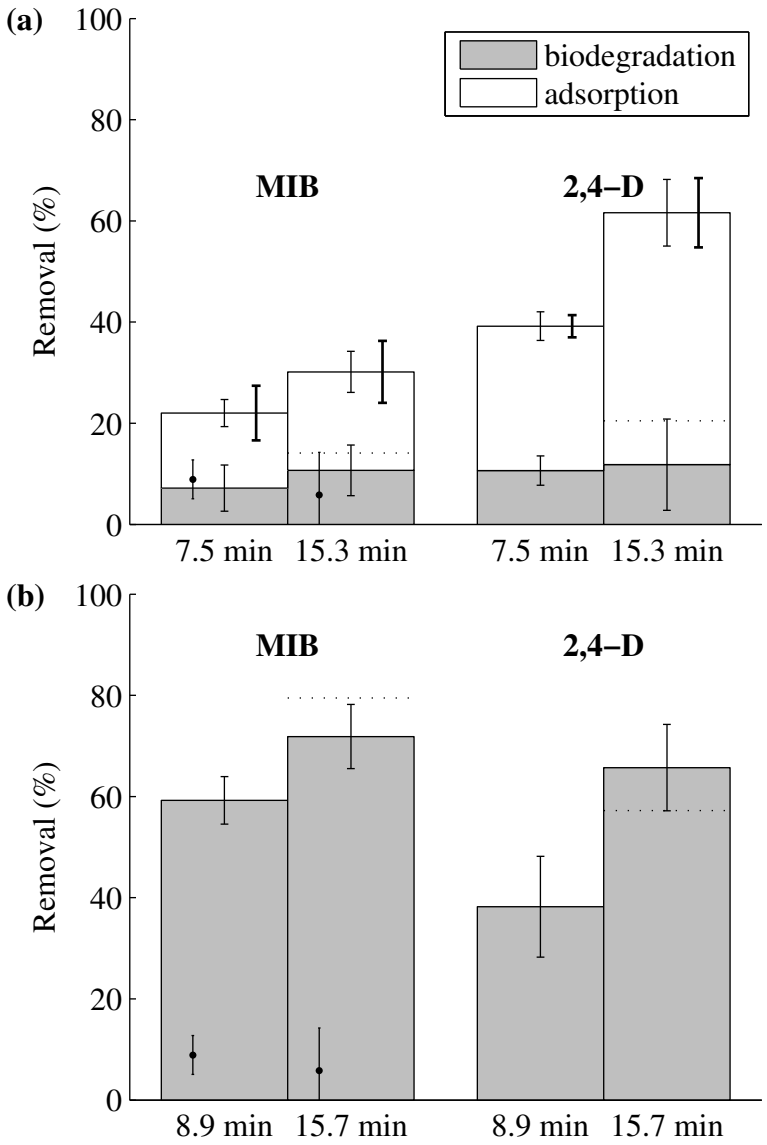

Figure 5.5. Average trace organic contaminant removal across (a) BAC at 7.5 min and 15.3 min of EBCT (b) Sand B filters at 8.9 min and 15.7 min of EBCT with ±95% CI. Predicted trace organic contaminant biodegradation removal at the higher EBCT (dashed line) along with the average TOC removals (dots near bottom of bars) are shown.

5.3.3 Benefits of Adsorption

MIB removal across the abiotic GAC A filter decreased over time following adsorption breakthrough behavior as shown in Figure 5.3. This behavior was also observed for 2,4-D but was less pronounced than for MIB because MIB is weaker adsorbing than 2,4-D (Corwin & Summers, 2012). Initially, the GAC A filter removed 37% of MIB and 34% of 2,4-D. After

loading the filter for 27 days, removal rates were around 18% and 29% for MIB and 2,4-D, respectively. Low initial adsorption removal rates were expected since the media had been in full-scale service for over two years during which the GAC surface became fouled with DOM, reducing the adsorption capacity (Sontheimer et al., 1988). Contaminant adsorption capacity was further reduced by an additional year of laboratory exposure to MIB and 2,4-D at 100 ng L^{-1} and TOC at 3 mg L^{-1} prior to this study (Chapter 3 & Chapter 6).

Figure 5.3 and Figure 5.4 show the overall removal by the BAC filter did not significantly change during the increasing contaminant concentration phase of the study. Since the removal due to adsorption decreased over time, there was a corresponding rise in the biodegradation rate. Figure 5.3 also shows the removal rates in the Sand B filter was more variable than in the BAC ($p<0.05$) for both contaminants. More consistent removal by the BAC was likely due to the remaining adsorption capacity being able to attenuate changes in the influent contaminant concentration.

Cumulative mass removal of MIB and 2,4-D by the Sand B and BAC filters are reported on a mass and volume of filter media basis in Table 5.2. The BAC filter removed 40% and 36% of the MIB and 2,4-D loaded. The biodegradation to adsorption ratio for the BAC filter was 1.2 for MIB and 0.3 for 2,4-D. This meant that biodegradation and adsorption played near equal roles in MIB removal, and the BAC filter was adsorption dominant for 2,4-D removal, this is also seen in Figure 5.4 and Figure 5.5. When the EBCT was increased in the BAC, the adsorption-biodegradation ratio remained the same for MIB, but not for 2,4-D where most of the increased removal was associated with adsorption. This was most likely due to the strong adsorption affinity of 2,4-D. The adsorption-biodegradation ratio was expected to change with

increased EBCT since adsorption is not exponentially affected by changes in EBCT (Corwin & Summers, 2012) as biodegradation is.

Table 5.2. Cumulative Mass Removed by Biodegradation and Adsorption for 27 days During the Increasing Contaminant Concentration Phase (n=28) and Desorption for 3 days (n=6) of MIB and 2,4-D in Sand B and BAC filters

	MIB			2,4-D		
	Mass (µg/g bed)	**Mass (µg/mL bed)**	**(%)**	**Mass (µg/g bed)**	**Mass (µg/mL bed)**	**(%)**
BAC						
loaded	4.2	1.9	--	4.0	3.3	--
removed	1.7	0.76	40	1.5	1.2	36
biodegraded	0.91	0.41	54	0.32	0.27	22
adsorbed	0.78	0.35	46	1.13	0.95	78
desorbed	0.088	0.039	11	0.023	0.019	2.0
Sand B						
loaded	1.1	1.8	--	1.0	1.7	--
removed	0.77	1.3	71	0.44	0.72	43

5.3.4 Desorption

Of the cumulative mass adsorbed to the BAC filter, 11% of the MIB and 2.0% of the 2,4-D desorbed in 3 days of no contaminant exposure (Table 5.2). Higher MIB desorption compared to 2,4-D was expected since MIB is weaker adsorbing than 2,4-D. The effluent MIB concentration at the beginning of the desorption phase was initially 100 ng L^{-1} and decreased by about 20% each day. For 2,4-D, the initial desorption effluent concentration was 35 ng L^{-1} and decreased by about 50% each day. Low level desorption would have likely continued if this portion of the study had been extended. Even if low levels continued to desorb at these rates, this would not account for the total mass initially adsorbed. The difference between the total adsorbed and desorbed mass was likely attributable to the trace organic contaminant being biodegraded by attached microorganism after initial adsorption (Aktas & Cecen, 2007) and/or pore blockage hindered back diffusion and desorption of the trace organic contaminants (Corwin & Summers, 2011).

5.3.5 Primary Substrate Conditions

5.3.5.1 Increased TOC Concentrations

After the desorption phase, the filters were run with baseline conditions for 5 days. When the influent TOC concentration was increased by a factor two to 5.7 ± 1.0 mg L^{-1}, average MIB and 2,4-D removals did not significantly change when compared to the baseline for any of the filters as seen in Figure 5.6. Average TOC removal decreased slightly when the TOC influent concentration was increased but the difference was not significantly at a 95% confidence level.

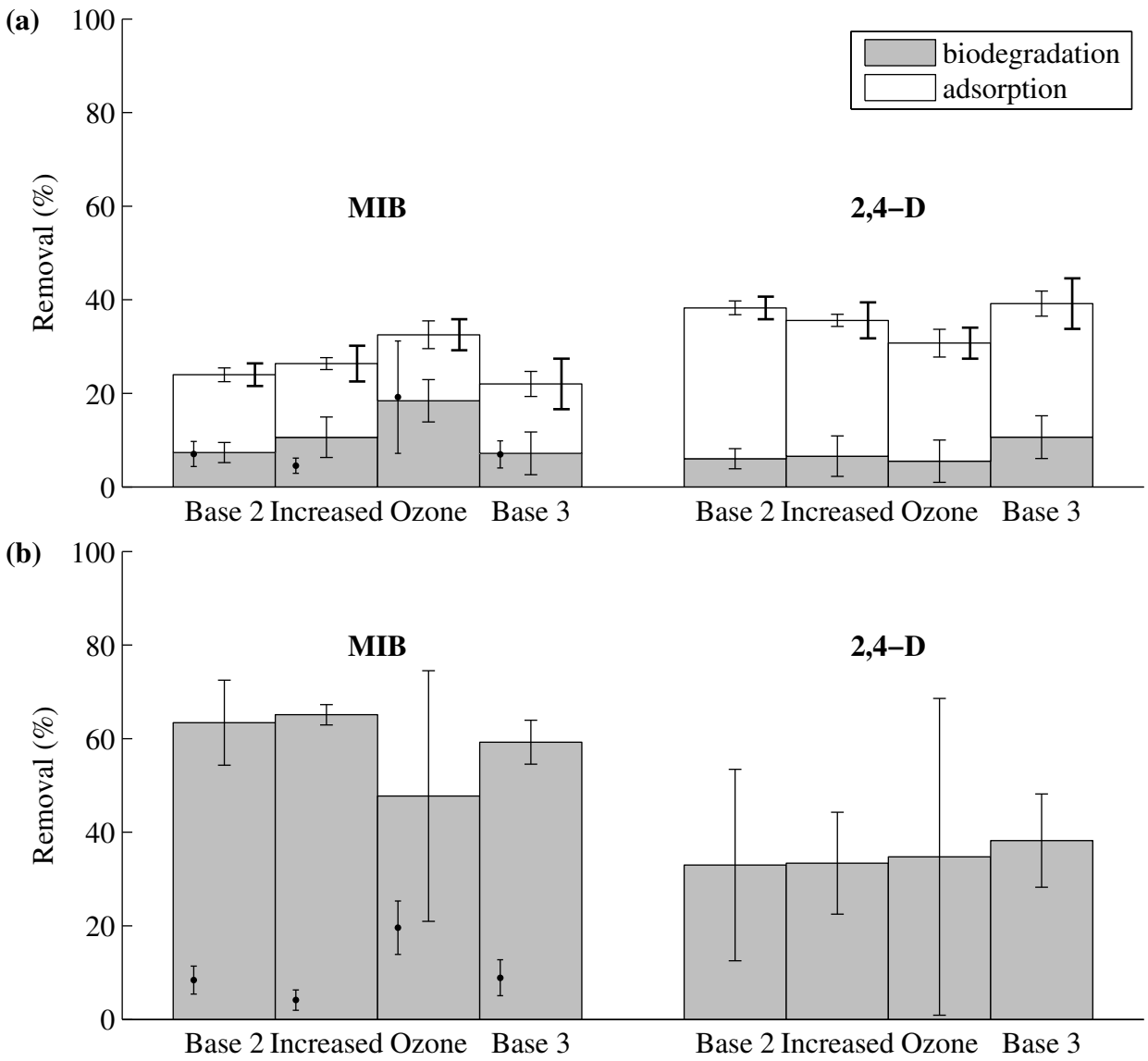

Figure 5.6. MIB and 2,4-D average removals with ±95% CI during increased influent TOC concentration and preozonated TOC phases for (a) BAC and (b) Sand B filters. Thicker error bars are for total BAC removal, and baseline conditions are given as Base 2 and Base 3.

5.3.5.2 Ozonated DOM

When the supplemented DOM was ozonated, the average TOC removal increased by 2.5 times as compared to baseline conditions for all the filters as seen in Figure 5.6. Increased TOC removal was expected since ozonation increases the easily biodegradable organic matter (Goel et al., 1995; Carlson & Amy, 2001). The average MIB removal due to biodegradation in the BAC filter increased when operated on pre-ozonated water (Figure 5.6). During all portions of the

varying primary substrate phase of the study, the MIB removal by adsorption in the BAC did not significantly change. Biodegradation of 2,4-D in the BAC filter did not change, but removal due to adsorption slightly decreased with pre-ozonated DOM as compared to the baseline conditions.

The observed MIB and 2,4-D removals in the Sand B filter dropped significantly after exposure to pre-ozonated influent DOM but recovered to at least baseline removals after two days for MIB and less a day for 2,4-D (Figure 5.7). The temporary decrease in removal was observed in the other filters except the Sand A filter but to a lesser extent, indicating that adsorption by the GAC media attenuated contaminant removal while the filter microorganisms adapted to the change in their primary substrate (Figure 5.8).

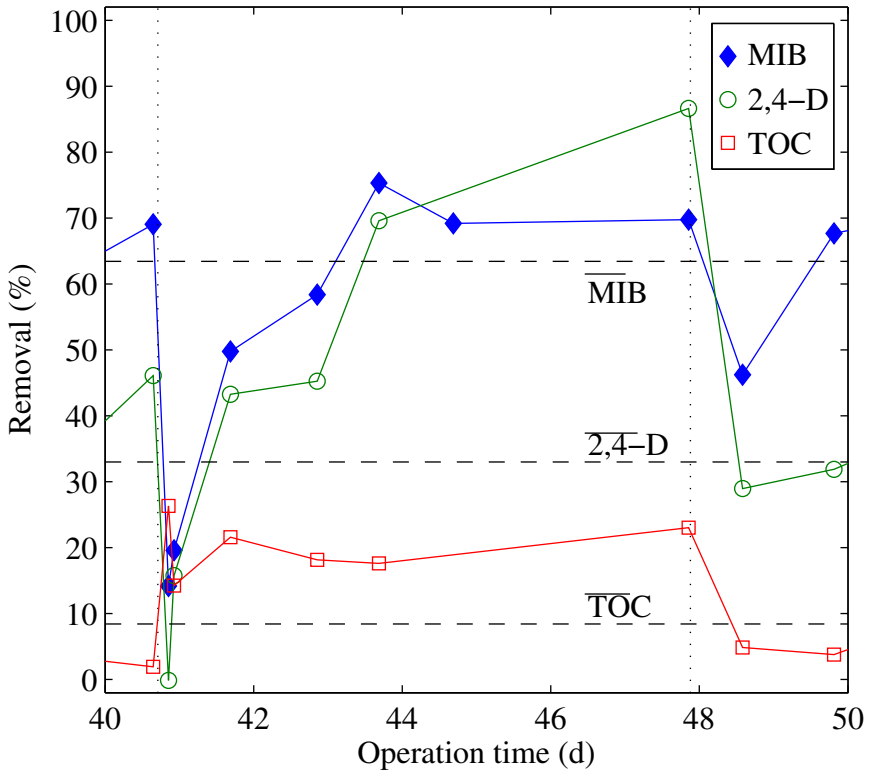

Figure 5.7. Observed MIB, 2,4-D and TOC removal during preozonated DOM phase (between vertical dashed vertical lines) with average removals at baseline conditions.

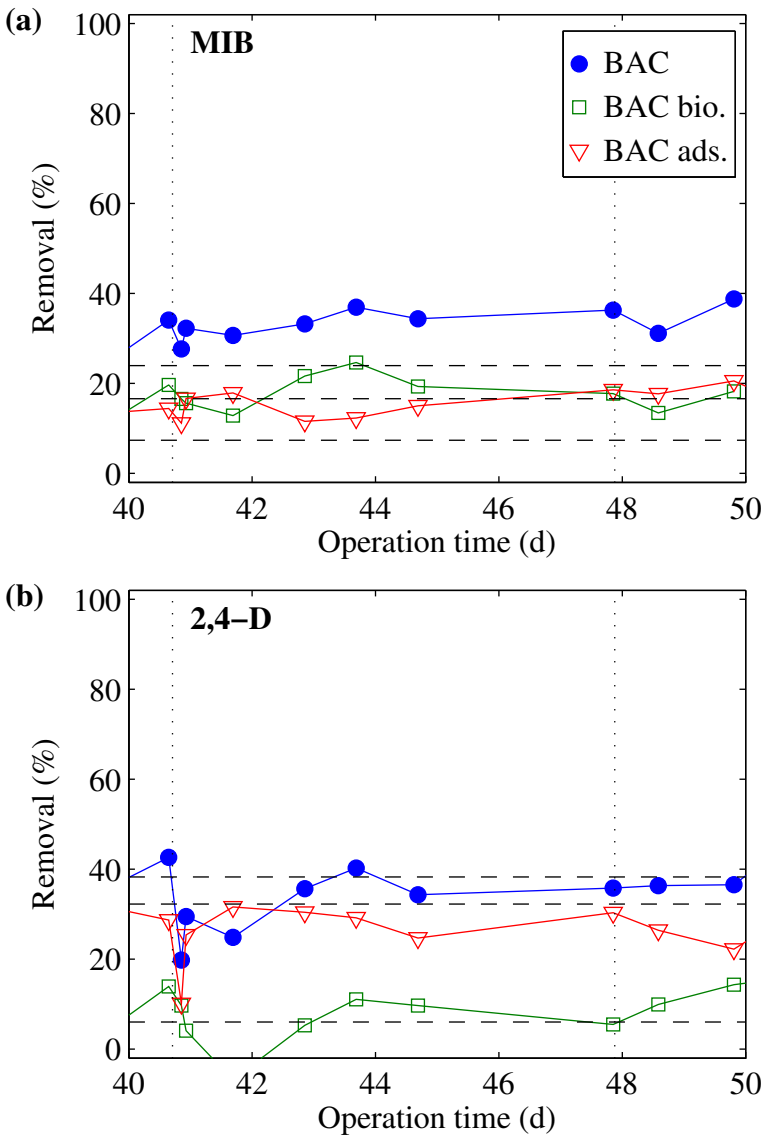

Figure 5.8. Removal in BAC of (a) MIB and (b) 2,4-D during preozonated DOM phase (between vertical dashed vertical lines) with average removals at baseline conditions.

During the ozonated phase of the study, the EBCT dramatically increased only for Sand B up to an EBCT of 25 min which increased the removal. To account for changes due to EBCT, the removals were normalized to the same EBCT of 7.5 min using Eqn. 3.7 and are presented in Figure 5.9. When looking at the same data on a normalized basis, both contaminants removals temporary dipped and recovered. MIB removal did not fully recover and remained lower than baseline removals throughout the preozonated DOM phase. 2,4-D removal recovered

with a day and was slightly above baseline removals. Both contaminants quickly (<2 days) returned to baseline removals once the preozonated DOM was stopped. The temporary drop in removal supports utilization of trace organic contaminant as a secondary substrate rather than as a cometabolite since increased trace organic contaminant removal would be expected with cometabolism because of the increased primary substrate utilization.

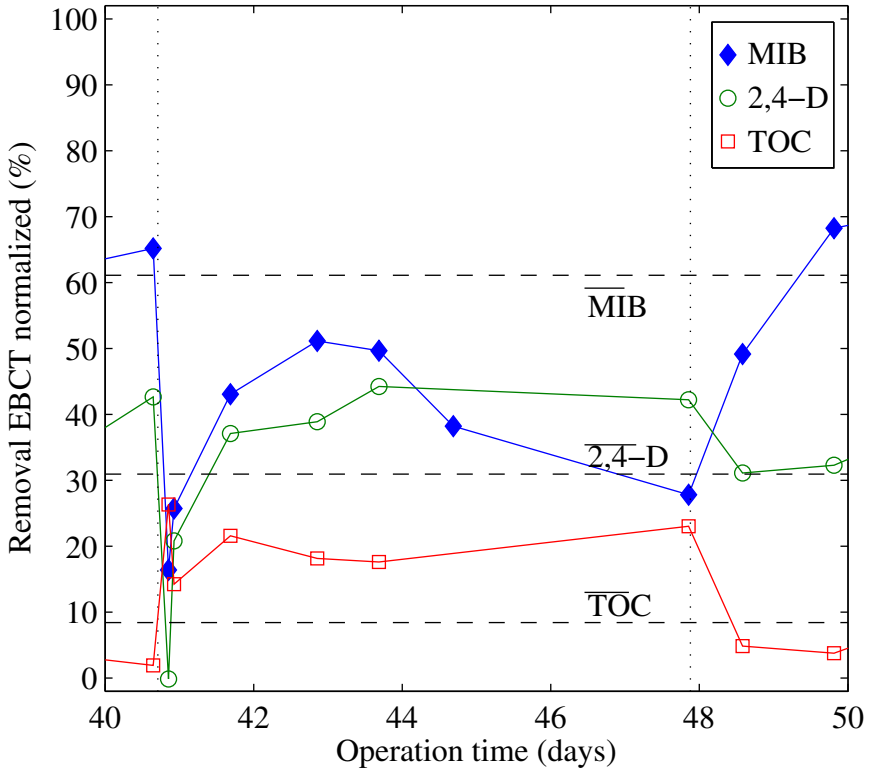

Figure 5.9. MIB, 2,4-D and TOC removal normalized to a 7.5 min EBCT during preozonated DOM phase (between dashed vertical lines) with average removals at baseline conditions.

5.4 CONCLUSIONS

The dual removal mechanisms of adsorption and biodegradation in the BAC filter provided more stable removal of MIB and 2,4-D during varying influent conditions than in the biologically active Sand B filter. Both contaminant removals followed first-order kinetics in respect to both increased influent concentrations and increased EBCTs. When there was no contaminant present in the influent, <11% of the MIB and <2% of the previously loaded mass

desorbed from the BAC in 3 days. When the primary substrate was increased by ozonating the DOM, MIB removals decreased and 2,4-D removal temporarily decreased but recovered within a day. MIB removals returned to baseline removals after the use of pre-ozonated DOM was stopped.

Chapter 6
Long-Term Trace Organic Contaminant Removal in Biological Activated Carbon and the Development of a Biofiltration "Treatment Technique"

6.1 INTRODUCTION

Granular activated carbon (GAC) utilized in a filter-adsorber mode is the most common application of GAC in drinking water treatment. While a wide range of organic compounds can be removed by filter adsorbers, historically it was most commonly applied to control trace organic compounds like pesticides and those that cause taste and odor. More recently it has been used to remove dissolved organic matter (DOM) for disinfection by-product control. Often the GAC is not frequently replaced and the main mode of removal for many non-strongly adsorbing compounds is biodegradation. When GAC filters become colonized by microorganisms, the biologically-active GAC (BAC) is able to biodegrade and adsorb organic compounds of both natural and anthropogenic origin (Kim et al., 1997; Rittmann & McCarty, 2001; Bonne et al., 2002). Trace contaminant removal in BAC filters is dependent on adsorption affinity of the contaminant to the media and the biodegradability of the contaminant by attached microorganisms. Adsorption and biodegradation removal mechanisms in BAC filters act semi-independently of each other, but they can have a synergistic relationship. BAC media can also be bio-regenerated, allowing a quasi-steady state adsorption capacity (Aktas & Cecen, 2007).

Contaminant adsorption affinity depends on the: a) the characteristics and age of the activated GAC, b) type and concentration of other adsorbing compounds including DOM, and c) the chemical characteristics of the trace organic contaminant (Summers et al., 2010). Influent concentration normalized adsorption affinity has been found to be independent of influent

concentrations in the low parts per billion range (Corwin & Summers, 2012). The surface of GAC becomes fouled over time with DOM, reducing its adsorption capacity for trace organic contaminants (Sontheimer et al., 1988). However, even when the DOM adsorption capacity of GAC is completely exhausted, it can retain adsorption capacity for smaller molecular weight organic contaminants.

Biodegradation of a trace organic contaminant in BAC filters is determined by the biodegradation potential of a compound, the acclimation state of the attached microbial community, and active biomass concentration. The level of acclimation is important because attached microorganisms may lack the necessary enzymes to readily degrade new substrates leading to a lag period where little biodegradation occurs (Alexander, 1999). Easily biodegradable trace organic contaminants can be removed quickly after initial exposure with no acclimation phase if the attached microorganisms have been previously acclimated to it or a similar compound.

A treatment technique is a specific treatment method used to control a contaminant or group of contaminants in drinking water treatment. Treatment techniques are often used when it is infeasible and uneconomical for utilities to measure the concentration of a contaminant.

The objectives of this study were to evaluate and model the long-term trace organic contaminant removal in BAC drinking water filters and to develop a biofiltration treatment technique for the control of trace organic contaminants. The approach taken was to run four BAC filters with different levels of adsorption capacity represented by the years in full-scale operation from fresh to 15 years. Additionally, results from non-adsorptive sand and rapid small-scale column tests (RSSCTs) were used to determine biodegradation and adsorption

potentials. The foundation of a biofiltration treatment technique was developed using the results from all of the chapters of this thesis.

6.2 MATERIAL AND METHODS

6.2.1 Biofilter Operation and Sampling

For this experiment, Biofilters 2 (sand media) and G1 through G4 (GAC media) were used to evaluate the long-term removal behavior of trace contaminants in partially exhausted BAC. The contaminants investigated are shown in Table 2.2 and were spiked according to Section 2.3.3.

Samples were collected as described in Section 3.2.1. The average EBCTs for the sampling events are reported in Table 6.1 for the GACs with different use ages.

Table 6.1. Average Biofilter EBCTs at Contaminant Sampling with TOC Removal

	Biofilter				
	2*	**G1**	**G2**	**G3**	**G4**
GAC age (yr)	--	0	2	6	15
EBCT (min)	7.6 ± 0.6 (8) [a]	7.5 ± 0.4 (5)	7.4 ± 0.4 (8)	7.4 ± 0.2 (8)	7.5 ± 0.4 (8)
TOC influent (mg L^{-1})	3.1 ± 0.3 (23)	2.8 ± 0.3 (26)	Same as Biofilter 2		
TOC removal (%)	7.2 ± 2.8 (7)	n/a	5.9 ± 3.0 (7)	4.7 ± 3.1 (7)	5.7 ± 2.8 (7)

* sand media.
[a] avg. ± SD (n).
n/a – not applicable, see Figure 6.1.

6.3 RESULTS AND DISCUSSION

Qualitative classifications of biodegradation potential and adsorption potential for each contaminant were determined. Biodegradation potential was determined by a sand biofilter run in parallel (Biofilter 2) with the GAC media filters (G1-G4), and adsorption potential was determined by RSSCTs run with fresh GAC.

6.3.1 Biodegradation Potential

Biofilter 2 was used to determine biodegradation potential of each contaminant, since there is no adsorption in the sand biofilter. The average steady state contaminant removal across Biofilter 2 is shown in Table 6.2 along with the biodegradation potential and acclimation behavior. The same biodegradation definitions were used as described in Section 3.4.5. The biodegradation potential and acclimation behavior were nearly identical to Biofilter 1 (Table 3.3). The average contaminant influent concentrations for Biofilters 2 and G1-G4 are shown in Table 6.2.

Table 6.2. Steady State Removal of Trace Contaminants in Biofilter 2

contaminant	influent conc. [a] (ng/L)	removal (%)	n	biodegradation potential	acclimation behavior
2,4–D	142 ± 33 (3)	74 ± 2.4	3 [e]	fast	increase
acetaminophen	251 ± 71 (3)	59 ± 17	6	fast	steady state
acetochlor	184 ± 15 (2)	15 ± 4.1	5	recalcitrant	recalcitrant
aldicarb	58 ± 65 (2)	28 ± 10	4	slow	steady state
atrazine	9 ± 3 (3)	4.8 ± 3.5	6	recalcitrant	recalcitrant
bisphenol A [b]	203 ± 81 (3) [c]	37 ± 27	2	fast	increase
caffeine	91 ± 14 (3)	66 ± 11	2 [e]	fast	steady state to decrease
carbamazepine	77 ± 50 (3)	4.2 ± 4.7	6	recalcitrant	recalcitrant
carbaryl	72 ± 35 (2) [c]	12 ± 10	5	recalcitrant	recalcitrant
chlorpyrifos	439 ± 253 (3)	74 ± 12 [d]	5	fast	steady state
clofibric acid	211 ± 67 (2)	68 ± 8.1	2 [e]	fast	increase
cotinine	85 ± 43 (3)	22 ± 13	6	slow	steady state
diazinon	4 ± 3 (3)	30 ± 2.1	4	slow	steady state
diclofenac	167 ± 6 (2)	19 ± 3.5	3	slow	steady state
dimethoate	53 ± 21 (2)	48 ± 19	5	fast	steady state
diuron	87 ± 24 (3)	13 ± 14	6	recalcitrant	recalcitrant
erythromycin [b]	72 ± 25 (2)	29 ± 32	3	--	decrease
ethinyl estradiol	261 ± 112 (3) [c]	33 ± 18	3	slow	steady state
gemfibrozil	192 ± 65 (3)	69 ± 9.7	6	fast	steady state
ibuprofen	281 ± 118 (3)	93 ± 6.3 [d]	6	very fast	steady state
iopromide	501 ± 182 (3)	20 ± 18	5	slow	steady state
malaoxon	70 ± 47 (2)	23 ± 2.8	3	slow	steady state
methomyl	171 ± 43 (3)	12 ± 12	6	recalcitrant	recalcitrant
metolachlor	188 ± 5 (2)	11 ± 9.2	3	recalcitrant	recalcitrant
MIB	98 ± 12 (3)	84 ± 11	3	very fast	steady state
molinate	160 ± 98 (3)	81 ± 10	6	fast	steady state
naproxen	154 ± 5 (2)	56 ± 7.1	5	fast	steady state
prometon	100 ± 23 (2)	3.6 ± 6.2	3	recalcitrant	recalcitrant
simazine	44 ± 14 (3)	3.5 ± 5.4	6	recalcitrant	recalcitrant
sulfamethoxazole	172 ± 42 (3)	6.8 ± 3.8	6	recalcitrant	recalcitrant
tributyl phosphate	91 ± 2 (2)	21 ± 12	5	slow	steady state
triclosan	145 ± 21 (2) [c]	72 ± 26 [d]	2	fast	steady state
trimethoprim	122 ± 66 (3)	80 ± 7.3	3 [e]	fast	steady state to decrease
warfarin	154 ± 50 (2)	45 ± 21	5	slow	steady state

[a] Avg. ± 1 SD (n). [b] Removal not at steady state, reported average of all samples. [c] At least one sample below MDL and not used to calculate average. [d] Percent removal limited by MDL in at least one sample. [e] Non-steady state removals not used to calculate average.

6.3.2 Trace Contaminant Removal Behavior in New GAC Media

6.3.2.1 Contaminant Adsorption Potential (RSSCT)

Adsorption potential was determined by RSSCTs in another study by Cardenas (2011). The RSSCTs used filtered influent water and ran for less than 2 months to minimize the

likelihood of biodegradation. The RSSCTs represented removal due to adsorption-only. The adsorption potential of each contaminant was classified into three categories: weak, moderate, and strong as defined by Cardenas (2011) and shown in Table 6.3. The adsorption potentials were also ranked with respect to each other.

Table 6.3. Adsorption Potential with Rank from Cardenas (2011) with Dominant Removal Mechanism.

contaminant	biodegradation potential	adsorption potential	adsorption rank [a]	adsorption dominant
2,4–D	fast	moderate	16	y
acetaminophen	fast	strong	27	y
acetochlor	recalcitrant	moderate	14	y
aldicarb	slow	moderate	11	y
atrazine	recalcitrant	moderate	18	y
bisphenol A	fast	weak	2	n
caffeine	fast	moderate	22	y
carbamazepine	recalcitrant	strong	26	y
carbaryl	recalcitrant	strong	27	y
chlorpyrifos	fast	strong	27	n
clofibric acid	fast	weak	4	y
cotinine	slow	weak	7	n
diazinon	slow	strong	24	y
diclofenac	slow	moderate	13	y
dimethoate	fast	moderate	17	y
diuron	recalcitrant	strong	27	y
erythromycin	--	moderate	20	n
ethinyl estradiol	slow	strong	27	n
gemfibrozil	fast	moderate	12	y
ibuprofen	very fast	weak	5	n
iopromide	slow	weak	1	n
malaoxon	slow	moderate	19	y
methomyl	recalcitrant	strong	24	y
metolachlor	recalcitrant	moderate	10	y
MIB	very fast [b]	weak	3	n
molinate	fast	moderate	23	y
naproxen	fast	moderate	21	y
prometon	recalcitrant	moderate	9	y
simazine	recalcitrant	strong	27	y
sulfamethoxazole	recalcitrant	weak	8	y
tributyl phosphate	slow	moderate	15	n
triclosan	fast [b]	strong	27	n
trimethoprim	fast	strong	27	y
warfarin	slow	weak	6	n

[a] weakest to strongest. [b] From Corwin (2010). y – yes, n – no.

6.3.2.2 Fresh GAC at Pilot-Scale (Biofilter G1)

TOC removal in Biofilter G1 followed GAC breakthrough behavior as shown in Figure 6.1. After about 75 days of operation, the TOC removal leveled off at around 25%.

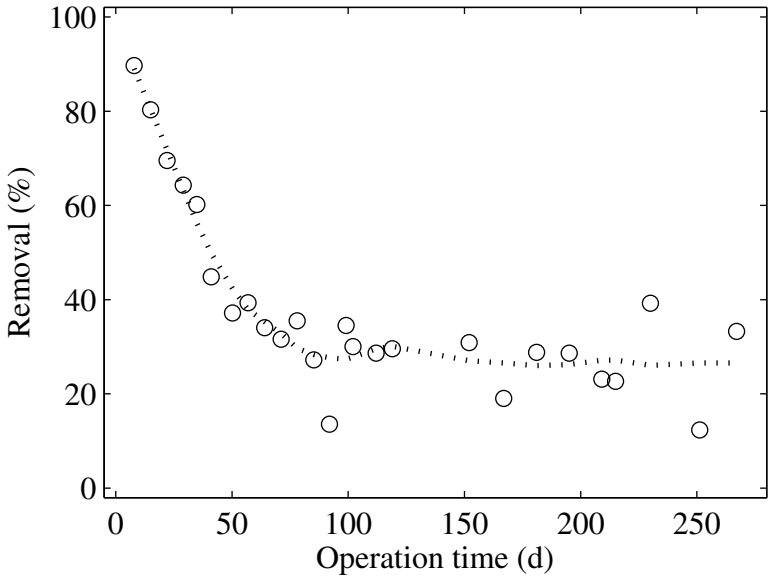

Figure 6.1. TOC removal across Biofilter G1 with smoothing line.

The trace contaminant removal behavior of the fresh GAC (Biofilter G1) was plotted into three bins: initial (<70 days of exposure), intermediate term (70-150 days of exposure), and long-term (>150 days of exposure) as shown in Figure 6.2. In Figure 6.2, each trace contaminant is plotted with respect to its biodegradation and adsorption potential and the color of the dot represents the average removal observed at each time interval. A smoothed surface using LOWESS was fitted to all of the data points to show trends. The weakly adsorbing contaminants started to breakthrough after 70 days of exposure. This was expected since the adsorption capacity for trace contaminants decreases over time due to adsorption sites being inaccessible due to DOM fouling or contaminants already occupying the sites. After 150 days of exposure, all but a few strongly adsorbing contaminants start to breakthrough. However, the contaminants

with higher biodegradation potentials show sustained high removals regardless of adsorption potential indicating biodegradation is a more important removal mechanism.

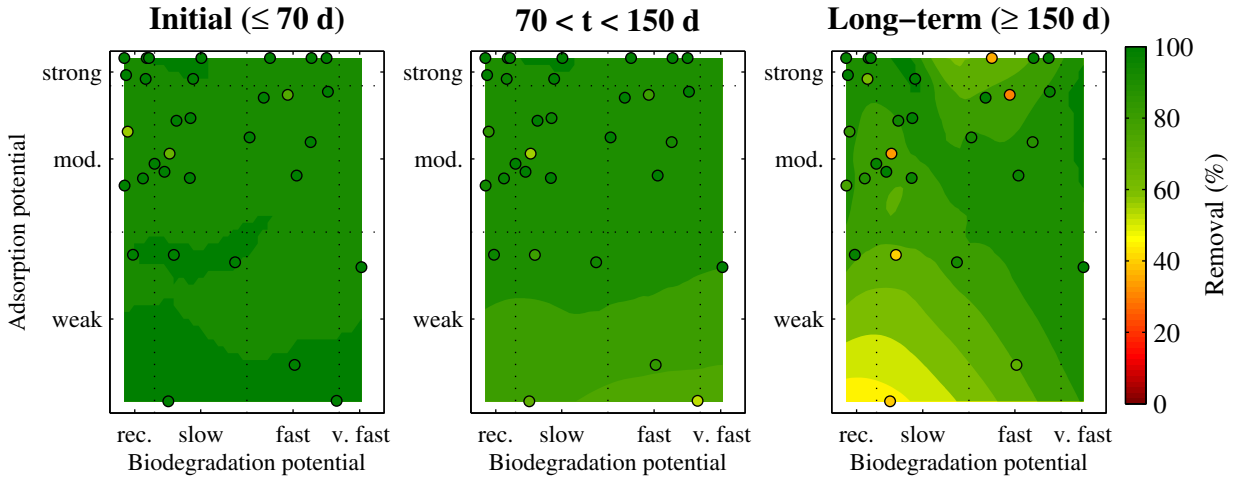

Figure 6.2. Trace contaminant removals (colored dots) in fresh GAC (Biofilter G1) for exposure periods <70 days, 70-150 days, and >150 days. Removal behavior trends are shown by a smoothed (LOWESS) contour plot with 10% removal intervals.

6.3.3 Long-Term Behavior in Partially Exhausted BAC

The TOC removal rates remained constant at less than 6% for the three aged GAC biofilters (Biofilters G2-G4) throughout the one year of laboratory exposure as shown in Table 6.1. The TOC removal rates were similar to the parallel sand biofilter (Biofilter 2). These results indicate that with respect to DOM the aged GAC was exhausted and operating at biological steady state.

Trace contaminant removal in aged GAC was found to be a function of adsorption affinity and biodegradation potential as shown in Figure 6.3 for nine representative contaminants. The adsorption affinity was a function of GAC age (representing the degree of DOM fouling) and the adsorption potential as measured by RSSCTs. Higher contaminant removals occurred for the younger GAC indicating more adsorption sites were available and the surface was less fouled with DOM (Sontheimer et al., 1988). The impact of adsorption on

removal was minimal for weakly adsorbing contaminants, such as clofibric acid, cotinine, ibuprofen, iopromide, MIB, and warfarin, as expected. The removal behavior for each contaminant group followed similar trends shown for the nine representative contaminants in Figure 6.3.

Contaminants with higher biodegradation potential had higher removals than lower biodegradation potential contaminants (Figure 6.3). This behavior was observed for each adsorption potential category. All of the very fast biodegrading contaminants (ibuprofen and MIB) were also weakly adsorbing, so the impacts of easily biodegraded contaminants could not be assessed for the other adsorption potentials.

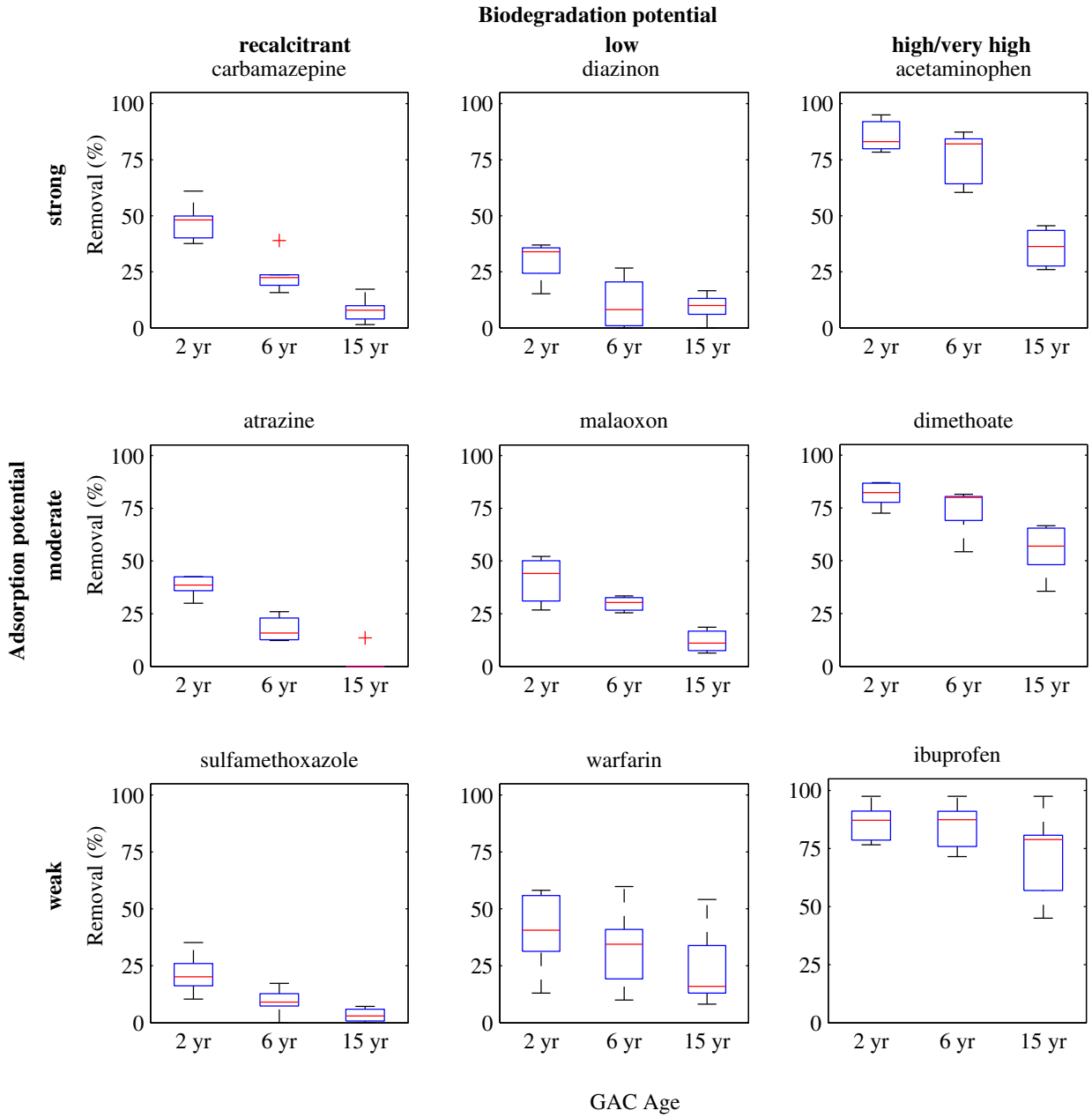

Figure 6.3. Trace contaminant removal behavior in aged GAC grouped by adsorption and biodegradation potential. The median removals with 25-75% quartile boxes, 5-95% whiskers, and outliers are shown.

6.3.3.1 Adsorption Dominant Removal

For 23 contaminants, adsorption was the dominant removal mechanism with biodegradation playing a role for some biodegradable contaminants (Table 6.3). The dominant removal mechanism was determined for each contaminant by performing a one-way analysis of

variance test (ANOVA) comparing the overall removal means of the three ages of GAC. When the means were different at a 95% confidence level then it was classified as adsorption dominant.

All of the recalcitrant contaminants were adsorption dominant, which was expected since biodegradation should be minimal (Table 6.3). The general trend with a few exceptions (bisphenol A, chlorpyrifos, ethinyl estradiol, tributyl phosphate, and triclosan) was that strongly and moderately adsorbing contaminants were adsorption dominant and the weakly adsorbing contaminants were not adsorption dominant.

6.3.4 Biofilter Acclimation

6.3.4.1 Initial Laboratory performance

Since the aged GAC media had been in a full-scale biological filter prior to being brought into the laboratory, the attached organisms were acclimated to the DOM and any contaminants in the source water. Acclimation levels were assessed by measuring the initial laboratory removal rates (any sample less than 70 days) after first laboratory exposure to a contaminant. The 15-year old GAC (Biofilter G4) initially had nine contaminants with removals greater than 15% (Table 6.4 & Table 6.5). The recalcitrant contaminants metolachlor and simazine had initial removals greater than 15% in the 15-year old GAC indicating there was still adsorption capacity for strongly to moderately adsorbing contaminants in GAC that had been in service for 15 years. The 2-year old (Biofilter G2) and 6-year old (Biofilter G3) GAC had 29 and 19 contaminants with removals over 15%, respectively. The removals are shown with respect to their biodegradation and adsorption potential in Figure 6.4. A smoothed surface was fitted to the removals in the same manner as Figure 6.2.

Table 6.4. Adsorption Dominant Contaminant Initial (<70 days of exposure) and Long-Term (>150 days of exposure) Removals for Different Ages of GAC. Removals are given as avg. ± SD (n).

dominant removal mechanism	acclimation behavior	contaminant	2 yr (Biofilter G2)		6 yr (Biofilter G3)		15 yr (Biofilter G4)	
			initial	long-term	initial	long-term	initial	long-term
adsorption	increase	molinate	54 (1)	75 ± 4.2 (3)	36 (1)	61 ± 12 (3)	17 ± 5.2 (2)	35 ± 5.3 (3)
		trimethoprim	43 (1)	61 ± 13 (3)	14 (1)	43 ± 21 (3)	9.1 ± 0.1 (2)	14 ± 3.2 (3)
		2,4–D	23 (1)	49 ± 18 (3)	0 (1)	30 ± 13 (3)	6.7 ± 5.3 (2)	16 ± 24 (3)
		gemfibrozil	15 (1)	46 ± 11 (3)	2.2 (1)	33 ± 16 (3)	3.4 ± 4.8 (2)	19 ± 21 (3)
	none	clofibric acid	24 ± 6.4 (2)	28 ± 8.1 (2)	14 ± 3.1 (2)	9.2 ± 8.3 (2)	9.8 ± 1.1 (2)	6.7 ± 9.4 (2)
		caffeine	50 (1)	58 ± 22 (2)	12 (1)	40 ± 6.7 (2)	4.3 ± 0.9 (2)	4.1 ± 5.8 (2)
		acetaminophen	85 (1)	85 ± 8.8 (3)	64 (1)	77 ± 15 (3)	28 ± 3.5 (2)	36 ± 9.2 (3)
		naproxen	34 ± 1.2 (2)	38 ± 4.9 (2)	16 ± 4.5 (2)	26 ± 6.2 (2)	11 ± 1 (2)	8.7 ± 2.3 (2)
		dimethoate	87 ± 0.3 (2)	81 ± 2.1 (2)	77 ± 4.2 (2)	81 ± 1.0 (2)	66 ± 1.1 (2)	55 ± 3.3 (2)
		diazinon	15 (1)	34 ± 0.7 (2)	1.9 (1)	20 ± 8.7 (2)	9 ± 1.4 (2)	8.3 ± 12 (2)
		aldicarb	86 (1)	48 ± 8.1 (2)	0 (1)	41 ± 1.7 (2)	0 (1)	13 ± 12 (2)
		malaoxon	27 (1)	48 ± 5.7 (2)	33 (1)	28 ± 3.4 (2)	11 (1)	12 ± 8.7 (2)
		diclofenac	30 (1)	38 (1)	17 (1)	22 (1)	14 (1)	4.5 (1)
		acetochlor	24 ± 0.9 (2)	34 ± 1.5 (2)	9.9 ± 7 (2)	12 ± 0.22 (2)	7.9 ± 1.3 (2)	2.3 ± 3.2 (2)
		diuron	73 (1)	75 ± 13 (3)	40 (1)	60 ± 12 (3)	7.8 ± 2.5 (2)	19 ± 18 (3)
		carbaryl	69 (1)	67 ± 17 (2)	39 (1)	55 ± 20 (2)	9.3 (1)	8 ± 5 (2)
		methomyl	59 (1)	59 ± 11 (3)	23 (1)	36 ± 15 (3)	8.2 ± 1.8 (2)	4.5 ± 5.2 (3)
		metolachlor	30 (1)	34 (1)	17 (1)	8.6 (1)	18 (1)	0 (1)
		sulfamethoxazole	10 (1)	24 ± 10 (3)	0 (1)	12 ± 5 (3)	2 ± 1.5 (2)	4.3 ± 3.8 (3)
		atrazine	36 (1)	38 ± 7.3 (3)	23 (1)	17 ± 7.8 (3)	0 (2)	4.5 ± 7.8 (3)
		carbamazepine	38 (1)	50 ± 10 (3)	16 (1)	28 ± 9.6 (3)	4.9 ± 2.7 (2)	8.9 ± 7.9 (3)
		prometon	30 (1)	39 (1)	14 (1)	21 (1)	8.5 (1)	0 (1)
		simazine	43 (1)	54 ± 12 (3)	15 (1)	32 ± 14 (3)	18 ± 0.39 (2)	3.3 ± 5.8 (3)
No. contaminants within removal ranges		0 – 15%	1	0	11	4	18	17
		15 – 50%	14	13	10	14	4	5
		50 - 100%	8	10	2	5	1	1

Table 6.5. Non-Adsorption Dominant Contaminant Initial (<70 days of exposure) and Long-Term (>150 days of exposure) Removals for Different Ages of GAC. Removals are given as avg. ± SD (n).

dominant removal mechanism	acclimation behavior	contaminant	2 yr (Biofilter G2)		6 yr (Biofilter G3)		15 yr (Biofilter G4)	
			initial	long-term	initial	long-term	initial	long-term
no adsorption	decrease	triclosan	n/a	62 (1)	n/a	46 (1)	n/a	46 (1)
		erythromycin	72 (1)	29 (1)	50 (1)	32 (1)	38 (1)	14 (1)
	increase	ibuprofen	79 (1)	88 ± 11 (3)	76 (1)	87 ± 14 (3)	58 ± 19 (2)	77 ± 23 (3)
		bisphenol A	49 (1)	n/a	40 (1)	n/a	7.3 (1)	n/a
		chlorpyrifos	37 (1)	72 ± 16 (3)	25 (1)	64 ± 20 (3)	0 ± 0 (2)	49 ± 34 (3)
		warfarin	34 ± 30 (2)	48 ± 15 (2)	16 ± 8.7 (2)	47 ± 18 (2)	12 ± 5.6 (2)	34 ± 28 (2)
		cotinine	13 (1)	36 ± 9.6 (3)	2.1 (1)	14 ± 16 (3)	2.5 ± 3.5 (2)	1.7 ± 3 (3)
		tributyl phosphate	13 ± 3.2 (2)	43 ± 8.3 (2)	2.4 ± 0.5 (2)	21 ± 17 (2)	2.5 ± 3.5 (2)	9.2 ± 1.8 (2)
	none	MIB	54 (1)	n/a	95 (1)	n/a	93 (1)	n/a
		ethinyl estradiol	50 (1)	50 (1)	54 (1)	6 (1)	54 (1)	29 (1)
		iopromide	0 (1)	14 ± 18 (3)	0 (1)	0.9 ± 1.3 (3)	0 (2)	0.1 ± 0.2 (3)
No. contaminants within removal ranges		0 – 15%	3	1	3	3	6	4
		15 – 50%	4	4	4	4	1	4
		50 - 100%	3	4	3	2	3	1

n/a – not available.

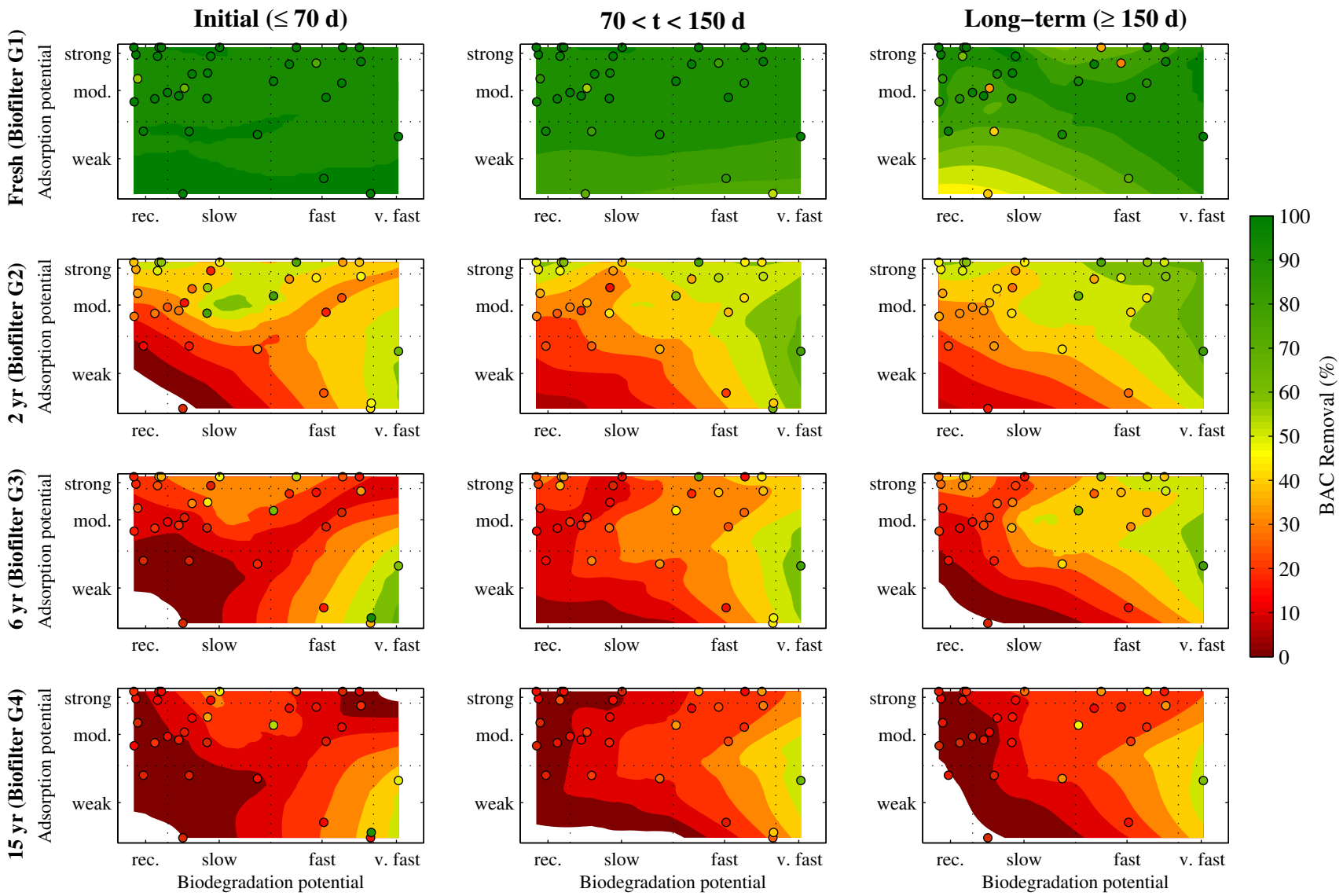

Figure 6.4. Contaminant removals (colored dots) in BAC biofilters for exposure periods <70 days, 70-150 days, and >150 days by GAC age. Removal behavior trends are shown by a smoothed (LOWESS) contour plot with 10% removal intervals.

6.3.4.2 Long-Term Removal

All of the contaminants reached steady state removal behavior after 5 months, which agrees with results from the sand biofilters (Biofilter 1 and 2). The initial removals (<70 days of exposure) and long-term removals (>150 days of exposure) were compared to determine if acclimation occurred in the aged GAC. The acclimation behavior was classified by the general trend of all three GAC ages. Contaminant removal increased over time for 10 contaminants, did not change for 22 contaminants, and decreased for two contaminants (Table 6.4 & Table 6.5). The contaminants in Table 6.4 and Table 6.5 are grouped by acclimation behavior and sorted by biodegradation potential within each group. Biodegradation acclimation was evident in all three GAC ages, as seen in Figure 6.4, where there was an increase in removal over time for the fast and very fast biodegradation potential contaminants. Erythromycin and triclosan removals significantly decreased over time. This was likely due to loss of biodegradation capacity, since the decreasing removal behavior was similar to Biofilter 1 and 2 (Section 3.4.4.3). A decrease in removal due to adsorption-only breakthrough was not systematically observed in the aged GACs over the 1-year study. If the study had been operated longer, it would be expected breakthrough behavior to become evident for the recalcitrant contaminants.

6.4 BIOFILTRATION "TREATMENT TECHNIQUE"

The increased use and detection of many unregulated trace organic contaminants in drinking water sources is likely to lead to additional drinking water regulations on trace organic contaminants. Regardless of the regulatory outcome, drinking water utilities are looking for ways to bolster consumer confidence by removing trace organic contaminants since the public health

risks are often unknown for many trace organic contaminants. These drivers support the development of treatment techniques to control trace organic contaminants.

A treatment technique is a specific treatment method used to control a contaminant or group of contaminants in drinking water treatment. The Safe Water Drinking Act (SWDA) states "a treatment technique [can be used] in lieu of establishing a maximum contaminant level, if … it is not economically or technologically feasible to ascertain the level of the contaminant" (42 U.S.C. § 300(g)(1)(b)(3)(C)(ii)). For many utilities it is cost prohibitive to regularly monitor for a wide range of trace organic contaminants, particularly at sub parts per billion concentration range, which highlights the need for the development of treatment techniques for the control of trace organic contaminants. While there are many potential treatment techniques available (membranes, activated carbon, ion exchange, advanced oxidation), this research focused on biofiltration.

The major benefit of biofiltration is the relative low cost of implementation and operation in conventional surface water treatment facilities. There is little additional infrastructure costs associated with biological filtration since most surface water treatment facilities already employ granular media filtration to meet the requirements of the Long-Term 2 Enhanced Surface Water Treatment Rule (LTESWTR). While in most plants eliminating chlorine in the filter feed will convert a conventional filter into a biofilter, attention must be given to maintain primary inactivation and the operation of the filters to meet turbidity standards. By converting conventional filtration into biological filtration, another removal mechanism is added to the already existing treatment train with little extra cost to the utilities. A further side benefit of biofiltration, is additional TOC removal by biodegradation and biologically stable water in the distribution system (Urfer et al., 1997; Volk & LeChevallier, 2000). An extension and

enhancement of the biofiltration treatment technique can be made with the use of BAC, as removal of strongly adsorbing compounds can occur for long run times; years.

This section focuses on a preliminary approach to a biofiltration treatment technique for trace organic contaminant removal and identifies future research needs to support the development of a biofiltration treatment technique.

6.4.1 Controlling Factors and Limitations

The primary controlling factors for biofiltration of trace organic contaminants appear to be twofold: (1) the biodegradability of the contaminant, (2) the acclimation state of the biomass, and (3) the contact with adapted biomass. The biodegradability of the contaminant is mostly dependent on the chemical structure of the compound (Alexander, 1999). The acclimation state is function of the exposure of the biomass to the target compound. The contact with adapted biomass can be approximated by the product of the biomass concentration and the contact time (or EBCT) of the filter. Biofiltration of trace organic contaminants with non-adsorptive media is not effective in removing recalcitrant contaminants.

6.4.1.1 Trace Organic Contaminant Biodegradability

Trace organic contaminant biodegradation rates in drinking water biofilters vary greatly (Chapter 3). The theoretical maximum rate (V_{max}) at which a microorganism can biodegrade a compound can provide insight to biodegradation potential. By determining removal rates in a wide range of mixed community aerobic drinking water biofilters, the maximum biodegradation rate of each contaminant can be approximated. The biodegradation potentials were calculated in Chapter 3 (Table 3.3).

It is not necessary to determine biodegradation rates for every individual contaminant as models can predict biodegradation rates. This research showed that biodegradation rates can be estimated using existing models such as the EPA-BIOWIN model (Table 3.3). While the EPA-BIOWIN model correctly predicted biodegradation rates for 55-70% the contaminants, a more refined model needs to be developed specifically for the oligotrophic conditions of biological drinking water treatment.

6.4.1.2 Acclimation State

The acclimation state of the biomass is a key component to biodegradation, as the biomass has to be at least partially acclimated to a contaminant in order for biodegradation to occur. The acclimation state depends on how the contaminant is utilized by the microorganism (secondary substrate or cometabolite). This often depends on the previous exposure to a contaminant or a similar compound(s) (Alexander, 1999). An example of the assessment of acclimation state was developed from the results in Chapter 3, 4, and 6 and is shown in Figure 6.5. The key parameters analyzed were: the occurrence behavior of the contaminant, the operation time of the biofilter, t_{op}, and the duration of non-exposure, t_{NE}, if the contaminant has an intermittent occurrence. This assessment identified several "critical" time values that need to be experimentally determined to complete the assessment such as time to full acclimation, t_{acc}, and retained biodegradation capacity time, t_{RBC}.

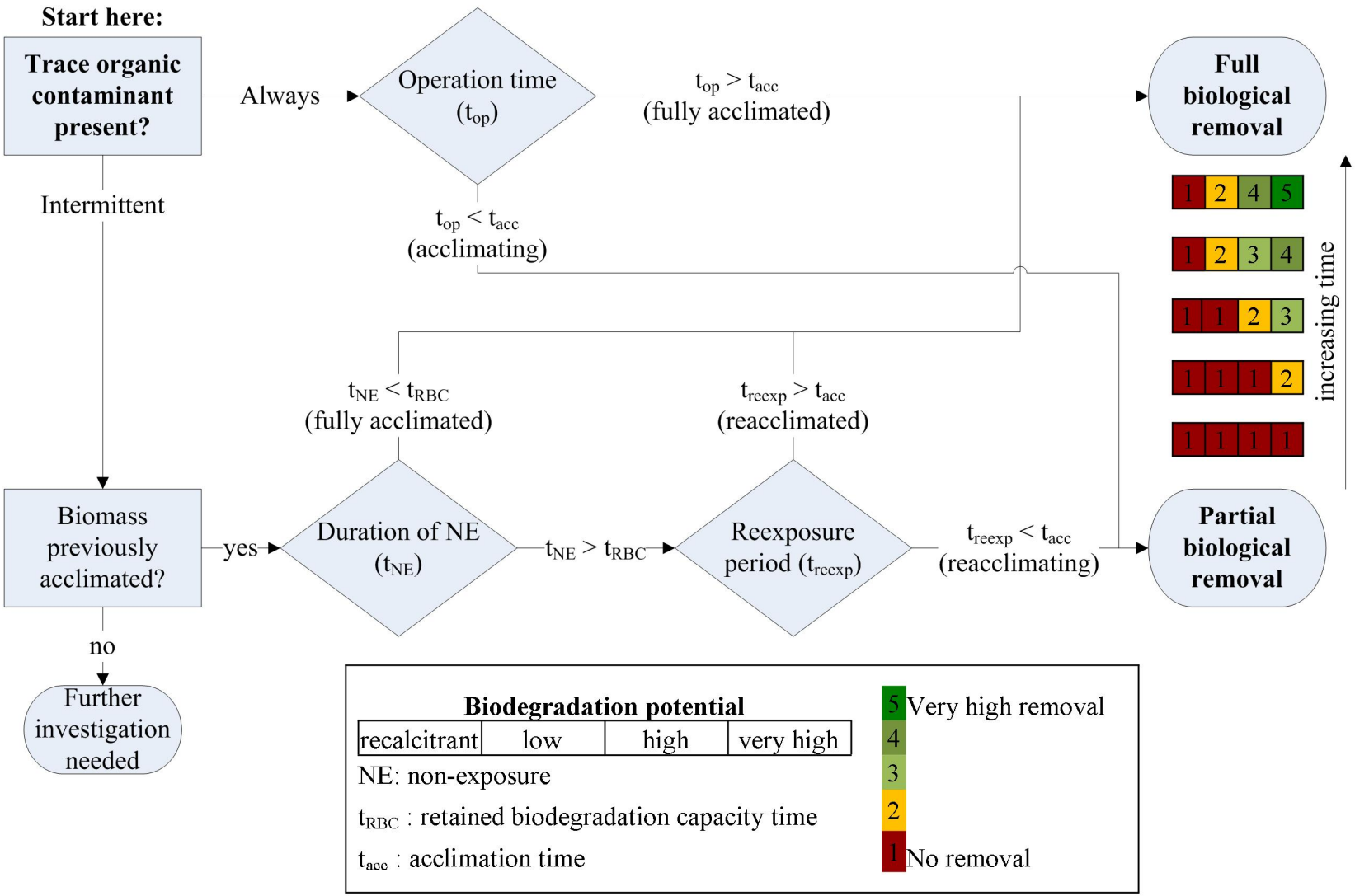

Figure 6.5. Example of an acclimation assessment of non-adsorbable media.

The results from Chapter 3 and 6 suggest acclimation times were less than 6 months for most of the trace organic contaminants in media that was already biologically active. The time to steady state behavior in both medias used in this research is shown in Table 6.6. For new media, acclimation times maybe longer (Meyer, 2005; McDowall et al., 2007). The retained biodegradation capacity time was between 5-9 months for MIB and 2,4-D (Chapter 4).

Table 6.6. Time in Days to Steady State Removal Behavior by the Full-Scale Water Source.

	time to steady state removal (days)	
	Biofilter 1	**Biofilters G2-G4**
full-scale water source	*Ohio River*	*Sacramento-San Joaquin River Delta*
contaminant		
2,4–D	135-177	68-108
aldicarb	54-96	--
bisphenol A	>180	>147
chlorpyrifos	--	135-177
clofibric acid	54-96	--
cotinine	--	135-177
dimethoate	54-96	--
gemfibrozil	--	68-108
ibuprofen	--	177-247
molinate	--	135-247
naproxen	54-96	--
tributyl phosphate	--	54-96
trimethoprim	--	68-108
warfarin	--	27-96

6.4.1.3 Total Biomass

The product of the adapted biomass concentration and EBCT represents the total biomass in the biofilter. The concept of total biomass is similar to CT (concentration × time) in disinfection. Just as certain CT values pertain to a specific level of inactivation, certain levels of total biomass (biomass concentration [X_{avg}] × EBCT) pertain to specific levels of removals of trace organic contaminants. If the biomass depth distribution is known, the total biomass can be

directly calculated, if not the average biomass concentration can be approximated using Eqn. 3.11. An example of how total biomass will affect biodegradation of trace organic contaminants is shown in Figure 6.6 for each of the four biodegradation rate levels defined in Section 3.4.5.; the cutoff values of k'' were 0.17×10^{-3}, 1.1×10^{-3}, and 3.0×10^{-3} mL bed $(\text{min}\cdot\text{nmol PO}_4)^{-1}$.

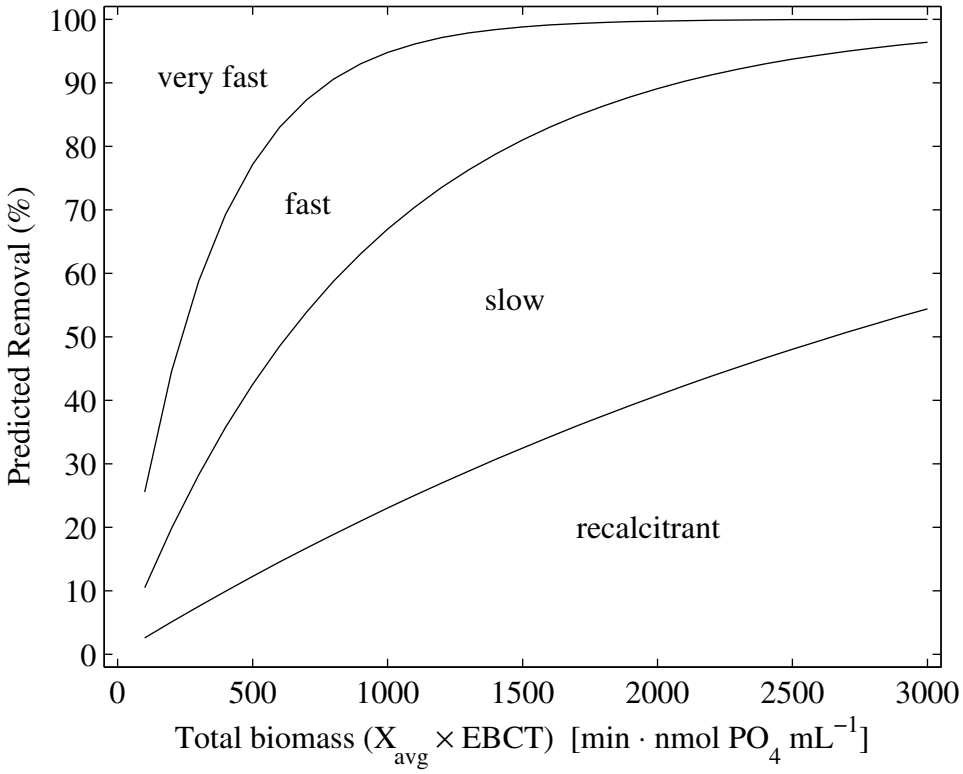

Figure 6.6. Predicted trace organic contaminant removal at 20 °C by total biomass for different biodegradation rates where X_{avg} is the average biomass concentration.

In order for a treatment technique to be acceptable, it will also need to take into account the operating temperature of the biofilter. The level of removal can be predicted at different temperatures for the same trace organic contaminant, as shown for acetaminophen in Figure 6.7.

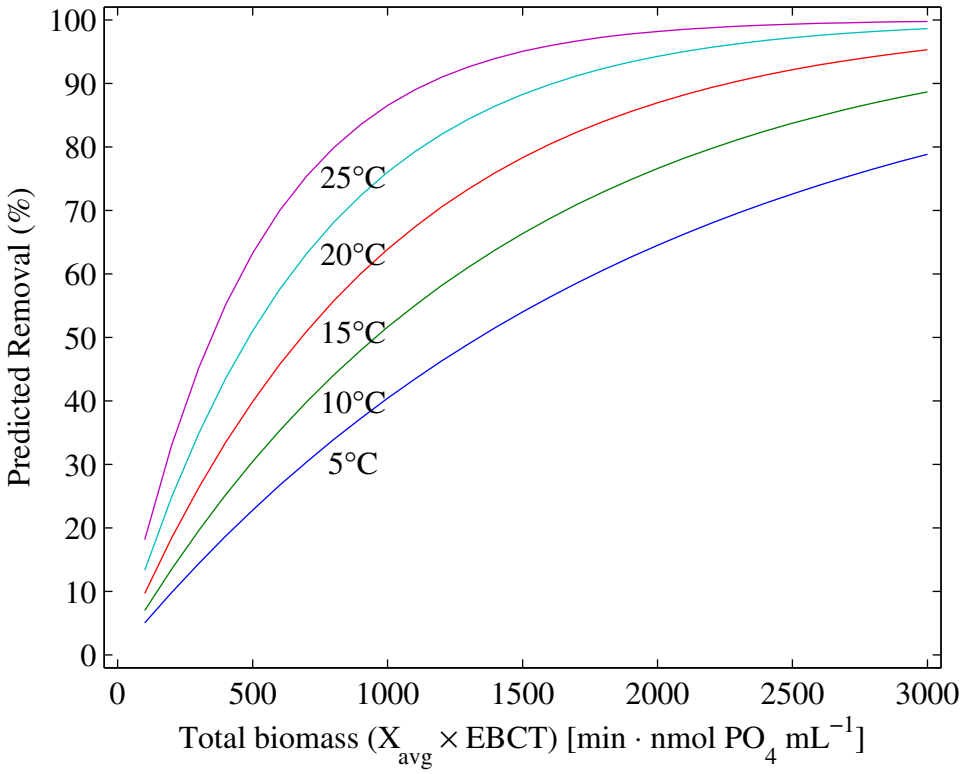

Figure 6.7. The impact of temperature on removal of acetaminophen (k'' = 0.0014 mL bed (min·nmol PO_4)$^{-1}$) over a range of total biomass values where X_{avg} is the average biomass concentration.

6.4.1.4 Limitations

The primary limitation of biofiltration for trace organic contaminant control is the lack of removal of recalcitrant contaminants or low removals of less biodegradable contaminants. While it might be possible to increase removal by increasing the total biomass by dramatically increasing the EBCT (as is the case with slow sand filtration), it is unrealistic for most treatment facilities to use SSF because of the large footprint it requires. Additionally, non-adsorptive media may not provide stable removal rates when there are influent perturbations (Chapter 5). Further, if there are daughter products or biotransformation products that are more toxic than the parent compound, other treatment techniques should be investigated.

6.4.1.5 Monitoring

As biofiltration is a dynamic process until the filter reaches steady state, quick, easy, and inexpensive biomass monitoring needs to be developed to accurately assess the state of the level of acclimation and the total biomass. Measurements of adenosine triphosphate (ATP) have shown promise as a surrogate for biomass concentration which is quick and easy (Dowdell, 2012). Monitoring the production and concentration of enzymes could be an important step to developing a biofiltration treatment technique. However, the relevant enzymes need to be first identified and cost of analysis needs to decrease before monitoring enzyme levels could be implemented in treatment facilities. A possible monitoring tool would be to identify and monitor an "indicator" compound(s) or enzyme(s). An ideal indicator compound would be inexpensive and easy to monitor with a common co-occurrence with other trace organic contaminants. Additionally, an indicator compound or enzyme could be used to monitor the level of biological treatment.

6.4.2 Biological Granular Activated Carbon

All of the controlling factors of biological filtration also pertain to BAC filters, however, there are additional benefits of BAC over a non-adsorptive media. The benefits stem from the adsorption capacity of the BAC; the adsorption capacity can increase performance under varying influent conditions (attenuation) (Chapter 5), remove some recalcitrant contaminants (Chapter 6), and remove by products that are adsorbable.

BAC trace organic contaminant removal performance can be predicted using the adsorption affinity, as well as the acclimation state and biodegradation potential of a trace organic contaminant. The adsorption affinity is affected by the availability of adsorption sites where GAC age can serve as an approximation, and the adsorption potential of a trace organic

contaminant to a specific GAC type, estimated with RSSCTs. Performance charts similar to Figure 6.4 could be used to predict removal behavior in BAC over time.

6.4.3 Research Needs

This thesis identified research areas that need further study to fully develop a biofiltration treatment technique for trace organic contaminant removal. A partial list of these needs is given below.

6.4.3.1 Evaluate Additional Trace Organic Contaminants

More trace organic contaminants need to be evaluated under a variety of operating conditions. In particular, additional contaminants that are in very fast biodegradation potential category will expand this dataset. Evaluating the behavior of weakly adsorbing contaminants would also strengthen the BAC removal behavior data. By evaluating additional trace organic contaminants, one could develop a drinking water specific biodegradation rate model, two likely model types have been proposed: structure–activity relationship (SAR) analysis (Raymond et al., 2001) and artificial intelligence based models (Baker et al., 2004). Additional focus should be placed on the formation of biotransformation products in biofilters and if there is any increased toxicity.

6.4.3.2 Acclimation State

Acclimation behavior of a variety of trace organic contaminants using a variety of source waters is needed to be able to accurately generalize acclimation behavior. These source waters should include domestic and/or industrial wastewater impacted, runoff impacted, preozonated, and pristine conditions from protected mountain watersheds. A possible outcome of this could be

the identification of "indicator" microorganisms or enzymes that could be used for monitoring the acclimation state of biofilters.

6.4.3.3 Design and Operation Criteria

The final step would be to develop design and operation criteria which have easy to implement monitoring tools associated with them. The development of these criteria would likely be facilitated by models that could predict the behavior of many trace organic contaminants. A treatment technique would likely include tables and figures similar to the ones presented here on the treatability of a range of trace organic contaminants.

6.5 CONCLUSIONS

The long-term removal behavior of trace organic contaminants in BAC filters was characterized by using adsorption affinity in addition to the acclimation state and biodegradation potential of a trace organic contaminant. The biodegradation potential was determined using a parallel non-adsorptive sand biofilter, and adsorption potential was estimated by RSSCTs. The time the BAC was in operation had a significant impact on trace organic contaminant removals. For fresh media, trace organic contaminant removals were very high (>90%) for the first 150 days of operation as adsorption was the primary removal process. After 150 days, the weaker adsorbing contaminants started to breakthrough but removal remained high for contaminants with very fast biodegradation rates as the biofilter acclimated to the biodegradable contaminants. Similar behavior was observed in the "aged" GAC but the initial removal was low (<50%) due to reduced adsorption capacity from DOM fouling. In the "aged" GAC (≥ 2 yrs), 23 of 34 trace organic contaminants removals were adsorption dominated. The dominant removal mechanisms strongly correlated with the adsorption potential as determined by RSSCTs.

Regardless of GAC age, the BAC filters acclimated to 10 of the trace organic contaminants. The remainder of the contaminants were either recalcitrant or at steady state removal. After 150 days of exposure, 14 contaminants, 7 contaminants, and 2 contaminants were removed above 50% for the 2-year old, 6-year old, and 15-year old BAC, respectively.

Control of trace organic contaminants through biofiltration appears to be a possible treatment technique to simultaneously control a wide range of trace organic contaminants. However, the scope of research needs to expand from the preliminary research of this thesis in order to fully characterize a biofiltration treatment technique

Chapter 7
Conclusions

Hypothesis 1: Incomplete removal of a trace organic contaminant is caused by lack of exposure to adapted biomass and can be predicted using first-order kinetics. Longer empty bed contact times (EBCTs) will increase removal of trace organic contaminants because of the increased exposure to adapted biomass. Trace organic contaminants followed first-order removal kinetics in drinking water biofilters with EBCT as a measure of contact time and trace organic contaminant influent concentration not affecting normalized to influent concentration removal (Chapters 3, 4 and 5). Trace organic contaminant removal increased as the biofilter microbial community acclimated which increased the number of adapted microorganism in the biofilter (Chapters 3, 4, and 6). A pseudo-first order rate steady-state model was developed in Chapter 3 with an accompanying classification scheme. The classification grouped contaminants by similar biodegradation rates (recalcitrant, slow, fast, and very fast).

Hypothesis 2: Attached microorganisms in biofilters retain the capacity to re-acclimate in less than a day to degrade trace organic contaminants during intermittent exposure. Results in Chapter 4 showed that non-exposure periods of less than 5 months did not affect trace organic contaminant removals after re-exposure. After 9 months of non-exposure, the trace organic contaminant removals were significantly lower than the control although acclimation began within 10-40 days of contaminant exposure. Changes in temperature likely attributed to some variability between sampling events when acclimation could be ruled out.

Hypothesis 3: The use of GAC media will improve removal of trace organic contaminants in biofilters. The benefits of GAC biofilter media was evaluated in two parts:

Hypothesis 3a: GAC biofilter media attenuates trace organic contaminant removals during variable influent conditions. Results in Chapter 5 showed the dual removal mechanisms of adsorption and biodegradation in BAC provided more stable removal of trace organic contaminants during varying influent conditions when compared to non-adsorptive media. This was observed when the easily biodegradable primary substrate was increased and the trace organic contaminant influent concentration was also increased. When the trace organic contaminant influent concentration is reduced to zero, desorption of a trace organic contaminant from BAC occurs at a level related to its adsorbability.

Hypothesis 3b: Adsorption and biodegradation are significant trace organic contaminant removal mechanisms in BAC. Removal behaviors can be predicted by using the trace organic contaminant biodegradation potential, adsorption potential, and the degree of DOM fouling on the GAC. Results in Chapter 6 showed the long-term removal behavior of trace organic contaminants in BAC filters is a function of adsorption affinity and biodegradation potential of a trace contaminant in addition to the acclimation state of the biofilter. Biodegradation potential was predicted using non-adsorptive media biofilters and adsorption affinity was predicted by the adsorption potential determined by RSSCTs and the age of GAC. The primary removal mechanism was closely related to the adsorption potential of the trace organic contaminant.

Treatment technique: The use of biofiltration as a treatment technology appears to be feasible for the simultaneous control of many trace organic contaminants, especially when GAC media is used. The research produced a few examples of how some of the design and operational

criteria may look for a future biofiltration treatment technique. It also identified further research needs to fully implement a biofiltration treatment technique (Section 6.4.3).

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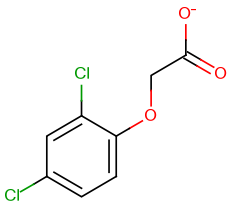
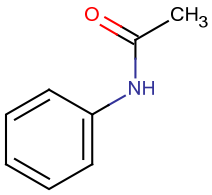
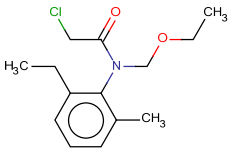
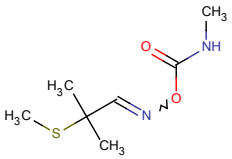
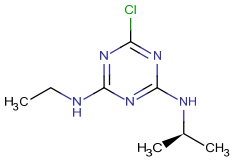
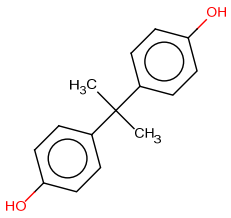
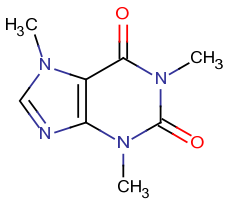
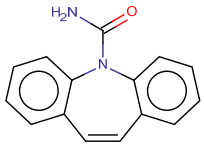
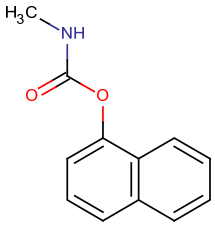
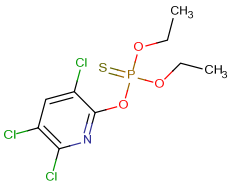
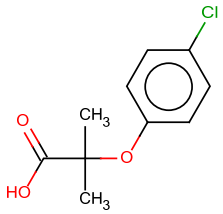
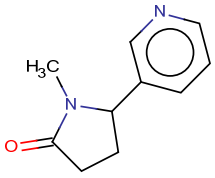
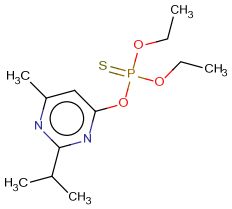
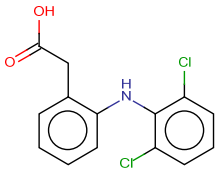
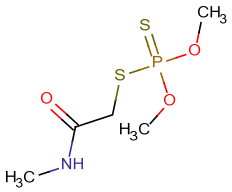
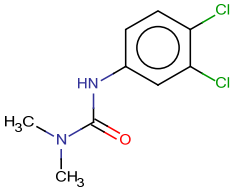
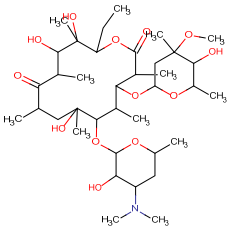
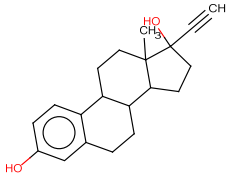
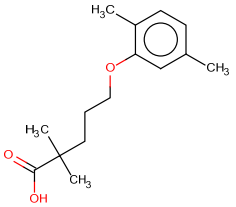
Appendix A
Trace Organic Contaminants

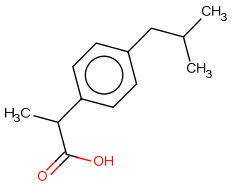
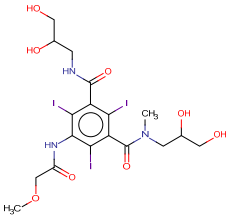
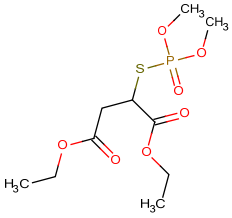
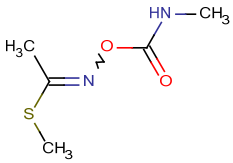
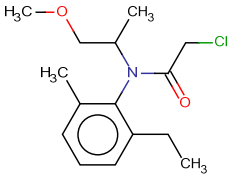
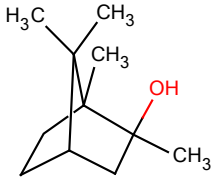
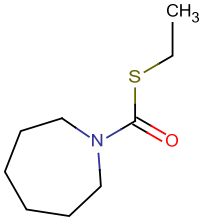
A.1 TRACE ORGANIC CONTAMINANT PROPERTIES

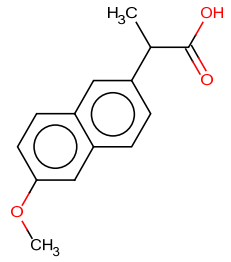
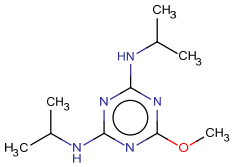
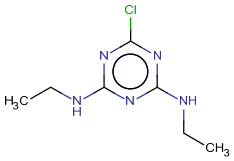
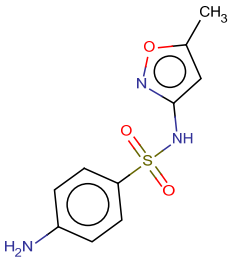
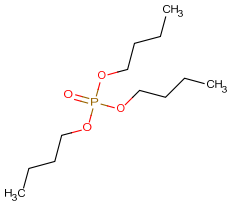
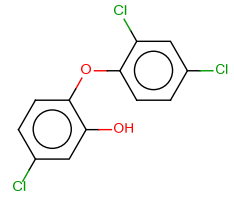
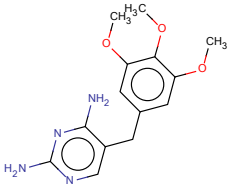
Table A.1. Trace Organic Contaminant Chemical Properties and Structures

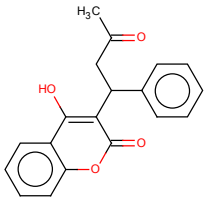
contaminant **CAS**	**properties** [a]	**structure**
2,4–D 94-75-7	$C_8H_6Cl_2O_3$ MW: 221.04 Log K_{ow}: 2.81	
acetaminophen 103-90-2	$C_8H_9NO_2$ MW: 151.17 Log K_{ow}: 0.46	
acetochlor 34256-82-1	$C_{14}H_{20}ClNO_2$ MW: 269.77 Log K_{ow}: 3.03	
aldicarb 116-06-3	$C_7H_{14}N_2O_2S$ MW: 190.26 Log K_{ow}: 1.13	
atrazine 1912-24-9	$C_8H_{14}ClN_5$ MW: 215.69 Log K_{ow}: 2.61	

contaminant CAS	properties [a]	structure
bisphenol A 80-05-7	$C_{15}H_{16}O_2$ MW: 228.29 Log K_{ow}: 3.32	
caffeine 58-08-2	$C_8H_{10}N_4O_2$ MW: 194.19 Log K_{ow}: -0.07	
carbamazepine 298-46-4	$C_{15}H_{12}N_2O$ MW: 236.28 Log K_{ow}: 2.45	
carbaryl 63-25-2	$C_{12}H_{11}NO_2$ MW: 201.23 Log K_{ow}: 2.36	
chlorpyrifos 2921-88-2	$C_9H_{11}Cl_3NO_3PS$ MW: 350.59 Log K_{ow}: 4.96	
clofibric acid 882-09-7	$C_{10}H_{11}ClO_3$ MW: 214.65 Log K_{ow}: 2.57	
cotinine 486-56-6	$C_{10}H_{12}N_2O$ MW: 176.22 Log K_{ow}: 0.07	

contaminant **CAS**	**properties** [a]	**structure**
diazinon 333-41-5	$C_{12}H_{21}N_2O_3PS$ MW: 304.35 Log K_{ow}: 3.81	
diclofenac 15307-86-5	$C_{14}H_{10}Cl_2NNaO_2$ MW: 296.15 Log K_{ow}: 4.51	
dimethoate 60-51-5	$C_5H_{12}NO_3PS_2$ MW: 229.25 Log K_{ow}: 0.78	
diuron 330-54-1	$C_9H_{10}Cl_2N_2O$ MW: 233.1 Log K_{ow}: 2.68	
erythromycin 114-07-8	$C_{37}H_{67}NO_{13}$ MW: 733.95 Log K_{ow}: 3.06	
ethinyl estradiol 57-63-6	$C_{20}H_{24}O_2$ MW: 296.41 Log K_{ow}: 3.67	
gemfibrozil 25812-30-0	$C_{15}H_{22}O_3$ MW: 250.34 Log K_{ow}: n/a[#]	

contaminant **CAS**	**properties** [a]	**structure**
ibuprofen 15687-27-1	$C_{13}H_{18}O_2$ MW: 206.29 Log K_{ow}: 3.97	
iopromide 73334-07-3	$C_{18}H_{24}I_3N_3O_8$ MW: 791.12 Log K_{ow}: -2.05	
malaoxon 1634-78-2	$C_{10}H_{19}O_7PS$ MW: 314.29 Log K_{ow}: n/a	
methomyl 16752-77-5	$C_5H_{10}N_2O_2S$ MW: 162.21 Log K_{ow}: 0.6	
metolachlor 51218-45-2	$C_{15}H_{22}ClNO_2$ MW: 283.8 Log K_{ow}: 3.13	
MIB 2371-42-8	$C_{11}H_{20}O$ MW: 168.28 Log K_{ow}: 3.31	
molinate 2212-67-1	$C_9H_{17}NOS$ MW: 187.3 Log K_{ow}: 3.21	

contaminant **CAS**	**properties** [a]	**structure**
naproxen 22204-53-1	$C_{14}H_{14}O_3$ MW: 230.27 Log K_{ow}: 3.18	
prometon 1610-18-0	$C_{10}H_{19}N_5O$ MW: 225.3 Log K_{ow}: 2.99	
simazine 122-34-9	$C_7H_{12}ClN_5$ MW: 201.66 Log K_{ow}: 2.18	
sulfamethoxazole 723-46-6	$C_{10}H_{11}N_3O_3S$ MW: 253.28 Log K_{ow}: 0.89	
tributyl phosphate 126-73-8	$C_{12}H_{27}O_4P$ MW: 266.32 Log K_{ow}: 4	
triclosan 3380-34-5	$C_{12}H_7Cl_3O_2$ MW: 289.55 Log K_{ow}: 4.76	
trimethoprim 738-70-5	$C_{14}H_{18}N_4O_3$ MW: 290.32 Log K_{ow}: 0.91	

contaminant **CAS**	**properties** [a]	**structure**
warfarin 81-81-2	$C_{19}H_{16}O_4$ MW: 308.34 Log K_{ow}: 2.7	

[a] Chemical properties from ChemIdPlus

A.2 TRACE ORGANIC CONTAMINANT SPIKING

Table A.2. Analytical Methods with Detection Limit, Trace Organic Contaminants Stock Group, and Total Exposure Time

micropollutant	CAS	contaminant group	total exposure (days)	method	method detection limit (ng L^{-1})
2,4–D	94-75-7	1	338	LC	5
acetaminophen	103-90-2	1	338	LC	10
acetochlor	34256-82-1	2	257	LC	10
aldicarb	116-06-3	2	257	LC	10
atrazine	1912-24-9	1	338	LC	1
bisphenol A	80-05-7	3	181	GC	100
caffeine	58-08-2	1	338	LC	10
carbamazepine	298-46-4	1	338	LC	5
carbaryl	63-25-2	1	338	LC	10
chlorpyrifos	2921-88-2	1	338	LC	100
clofibric acid	882-09-7	2	257	LC	5
cotinine	486-56-6	1	338	LC	5
diazinon	333-41-5	1	338	LC	1
diclofenac	15307-86-5	4	171	LC	10
dimethoate	60-51-5	2	257	LC	5
diuron	330-54-1	1	338	LC	5
erythromycin	114-07-8	4	171	LC	10
ethinyl estradiol	57-63-6	3	181	GC	100
gemfibrozil	25812-30-0	1	338	LC	5
ibuprofen	15687-27-1	1	338	LC	25
iopromide	73334-07-3	1	338	LC	25
malaoxon	1634-78-2	2	257	LC	10
methomyl	16752-77-5	1	338	LC	5
metolachlor	51218-45-2	4	171	LC	10
MIB	2371-42-8	5	123	GC	1
molinate	2212-67-1	1	338	LC	10
naproxen	22204-53-1	2	257	LC	10
prometon	1610-18-0	4	171	LC	1
simazine	122-34-9	1	338	LC	5
sulfamethoxazole	723-46-6	1	338	LC	5
tributyl phosphate	126-73-8	2	257	LC	5
triclosan	3380-34-5	3	181	GC	100
trimethoprim	738-70-5	1	338	LC	5
warfarin	81-81-2	2	257	LC	5

Table A.3. Trace Organic Sampling Schedule for Biofilters 1-2, G2-G4, and SSF.

		trace organic contaminant group [a]				
		group 1	**group 2**	**group 3**	**group 4**	**group 5**
	Start Date:	*5/9/10*	*7/29/10*	*10/13/10*	*10/23/10*	*12/10/10*
sample date	**TOC**					
5/17/2010	--	Biofilter 1, G4	--	--	--	--
7/16/2010	All	All	--	--	--	--
8/25/2010	All	All	All	--	--	--
9/21/2010	All	All	All	--	--	--
11/2/2010	All	All	All	All	All	--
1/11/2011	All	All	All	All	All	All
3/9/2011	All	--	--	All	--	All
4/12/2011	All	All	All	All	All	All
4/20/2011 (2x MP Inf.)	Biofilter 1	Biofilter 1	Biofilter 1	Biofilter 1	Biofilter 1	Biofilter 1

[a] Defined in Table A.2.
-- not sampled.

Appendix B
Trace Organic Contaminant Removal Data

B.1 BIOFILTER 1 AND SLOW SAND FILTER

Table B.1. Trace Organic Contaminant Removal for Biofilter 1 and Slow Sand Filter

contaminant	sample date	inf. conc. (ng L^{-1})	removal (%) Biofilter 1a	Biofilter 1b	SSF
2,4–D	5/17/2010	121	--	59	--
	7/16/2010	164 [a]	36	82	100
	8/25/2010	160 [a]	31	65	100
	9/21/2010	172 [a]	53	85	100
	11/2/2010	221 [a]	72	82	100
	1/11/2011	158	79	96	100
	4/12/2011	233	70	72	100
	4/20/2011	375	67	93	--
acetaminophen	5/17/2010	267	--	90	--
	7/16/2010	453 [a]	48	90	100
	8/25/2010	77 [a]	78	92	100
	9/21/2010	209 [a]	62	64	100
	11/2/2010	355 [a]	56	76	100
	1/11/2011	187	50	69	96
	4/12/2011	464	60	74	100
	4/20/2011	1156	43	61	--
acetochlor	8/25/2010	151 [a]	0 [b]	14	72
	9/21/2010	54 [a]	0 [b]	10	62
	11/2/2010	137 [a]	7	9	64
	1/11/2011	200	6	23	67
	4/12/2011	332	27	27	65
	4/20/2011	557	0 [b]	21	--
aldicarb	8/25/2010	325 [a]	27	70	100
	9/21/2010	163 [a]	40	75	100
	11/2/2010	546 [a]	57	63	100
	4/12/2011	31	48	79	100
	4/20/2011	340	39	64	--
atrazine	5/17/2010	8	--	0	--
	7/16/2010	4 [a]	0 [b]	0 [b]	0 [b]
	8/25/2010	9 [a]	1	5	11
	9/21/2010	4 [a]	0 [b]	10	11
	11/2/2010	6 [a]	0 [b]	4	4
	1/11/2011	11	0 [b]	0 [b]	0 [b]
	4/12/2011	8	0 [b]	2	9
	4/20/2011	30	5	17	--
bisphenol A	11/2/2010	133	32	32	58
	3/9/2011	640	70	84	98
	4/12/2011	160	78	97	100
	4/20/2011	65	30	100	--
caffeine	5/17/2010	99	--	74	--

contaminant	sample date	inf. conc. (ng L^{-1})	removal (%) Biofilter 1a	1b	SSF
	7/16/2010	46 [a]	51	85	96
	8/25/2010	11 [a]	87	95	95
	9/21/2010	12 [a]	63	64	93
	11/2/2010	5 [a]	14	8	62
	1/11/2011	108	28	44	93
	4/12/2011	357	0 [b]	4	93
	4/20/2011	100	19	19	--
carbamazepine	5/17/2010	132	--	0	--
	7/16/2010	50 [a]	0 [b]	0 [b]	0 [b]
	8/25/2010	39 [a]	0 [b]	0	0 [b]
	9/21/2010	38 [a]	0 [b]	2	1
	11/2/2010	40 [a]	0 [b]	0 [b]	0 [b]
	1/11/2011	35	0 [b]	0 [b]	1
	4/12/2011	88	3	9	3
	4/20/2011	341	4	0 [b]	--
carbaryl	5/17/2010	n/a	--	1	--
	7/16/2010	83 [a]	11	20	55
	8/25/2010	56 [a]	0 [b]	14	43
	9/21/2010	32 [a]	0 [b]	0 [b]	23
	4/12/2011	96	2	35	39
	4/20/2011	476	0	20	--
chlorpyrifos	5/17/2010	148	--	66	--
	7/16/2010	355 [a]	49	93	88
	8/25/2010	55 [a]	66	93	100
	9/21/2010	81 [a]	20	100	100
	11/2/2010	48 [a]	100	100	100
	4/12/2011	622	78	100	100
	4/20/2011	528	23	100	--
clofibric acid	8/25/2010	99 [a]	11	25	95
	9/21/2010	76 [a]	21	36	92
	11/2/2010	292 [a]	41	43	95
	1/11/2011	213	29	57	100
	4/12/2011	312	35	56	93
	4/20/2011	450	27	51	--
cotinine	5/17/2010	110	--	6	--
	7/16/2010	266 [a]	10	46	100
	8/25/2010	44 [a]	62	80	100
	9/21/2010	154 [a]	31	7	100
	11/2/2010	352 [a]	12	26	100
	1/11/2011	110	7	15	100
	4/12/2011	55	18	94	100
	4/20/2011	396	60	100	--
diazinon	5/17/2010	7	--	38	--
	7/16/2010	1 [a]	18	62	100
	8/25/2010	1 [a]	0 [b]	19	85
	9/21/2010	1 [a]	0 [b]	35	93
	11/2/2010	1 [a]	30	27	100

contaminant	sample date	inf. conc. (ng L^{-1})	removal (%) Biofilter 1a	1b	SSF
	1/11/2011	2	13	41	100
	4/12/2011	4	29	43	90
	4/20/2011	14	2	25	--
diclofenac	11/2/2010	199 [a]	20	24	86
	1/11/2011	188	19	38	94
	4/12/2011	316	23	23	85
	4/20/2011	385	21	26	--
dimethoate	8/25/2010	98 [a]	43	79	100
	9/21/2010	43 [a]	45	75	100
	11/2/2010	21 [a]	73	80	100
	4/12/2011	38	76	91	100
	4/20/2011	130	60	79	--
diuron	5/17/2010	107	--	0	--
	7/16/2010	71 [a]	2	8	3
	8/25/2010	60 [a]	0 [b]	13	14
	9/21/2010	69 [a]	0 [b]	2	11
	11/2/2010	34 [a]	0 [b]	0 [b]	9
	1/11/2011	82	0 [b]	9	5
	4/12/2011	87	0 [b]	22	15
	4/20/2011	312	0 [b]	20	--
erythromycin	11/2/2010	67 [a]	46	65	100
	1/11/2011	49	0 [b]	0 [b]	75
	4/12/2011	159	0 [b]	15	60
	4/20/2011	513	41	36	--
ethinyl estradiol	11/2/2010	109	11	27	72
	1/11/2011	195	0 [b]	0 [b]	100
	3/9/2011	480	4	23	85
	4/12/2011	480	31	40	100
	4/20/2011	1300	0 [b]	31	--
gemfibrozil	5/17/2010	263	--	93	--
	7/16/2010	132 [a]	72	100	100
	8/25/2010	84 [a]	64	93	100
	9/21/2010	47 [a]	62	94	100
	11/2/2010	71 [a]	77	89	100
	4/12/2011	194	76	96	100
	4/20/2011	216	69	92	--
ibuprofen	5/17/2010	400	--	99	--
	7/16/2010	204 [a]	95	100	100
	8/25/2010	97 [a]	91	100	100
	9/21/2010	6 [a]	100	100	100
	4/12/2011	152	100	100	100
	4/20/2011	210	100	100	--
iopromide	5/17/2010	369	--	0	--
	7/16/2010	1014 [a]	0 [b]	0 [b]	25
	8/25/2010	15 [a]	0	5	5
	9/21/2010	156 [a]	59	4	70
	11/2/2010	1192 [a]	13	14	31

contaminant	sample date	inf. conc. (ng L^{-1})	removal (%) Biofilter 1a	1b	SSF
	1/11/2011	694	38	0 [b]	27
	4/12/2011	604	0 [b]	0 [b]	34
	4/20/2011	2474	1	0 [b]	--
malaoxon	8/25/2010	11 [a]	10	46	100
	9/21/2010	18 [a]	12	42	100
	4/12/2011	132	27	59	100
	4/20/2011	270	28	43	--
methomyl	5/17/2010	216	--	1	--
	7/16/2010	116 [a]	1	3	51
	8/25/2010	17 [a]	5	16	12
	9/21/2010	58 [a]	27	0 [b]	15
	11/2/2010	142 [a]	7	15	19
	1/11/2011	81	23	2	38
	4/12/2011	240	7	0 [b]	34
	4/20/2011	539	13	2	--
metolachlor	11/2/2010	131 [a]	0 [b]	6	18
	1/11/2011	201	0 [b]	7	19
	4/12/2011	366	20	13	35
	4/20/2011	476	0 [b]	1	--
MIB	1/11/2011	54	93	97	100
	3/9/2011	76	92	100	100
	4/12/2011	122	95	99	99
	4/20/2011	320	93	99	--
molinate	5/17/2010	272	--	96	--
	7/16/2010	113 [a]	80	100	100
	8/25/2010	42 [a]	79	100	100
	9/21/2010	40 [a]	84	100	100
	11/2/2010	35 [a]	91	98	100
	4/12/2011	138	94	100	100
	4/20/2011	336	84	100	--
naproxen	8/25/2010	172 [a]	48	79	100
	9/21/2010	112 [a]	55	86	85
	11/2/2010	188 [a]	71	78	100
	1/11/2011	99	74	96	100
	4/12/2011	242	71	94	100
	4/20/2011	461	61	89	--
prometon	11/2/2010	93 [a]	4	0 [b]	0 [b]
	1/11/2011	112	0 [b]	0 [b]	1
	4/12/2011	152	3	0 [b]	17
	4/20/2011	255	9	3	--
simazine	5/17/2010	60	--	0	--
	7/16/2010	28 [a]	10	14	5
	8/25/2010	29 [a]	0	6	4
	9/21/2010	22 [a]	25	27	27
	11/2/2010	39 [a]	2	4	0 [b]
	1/11/2011	39	1	0 [b]	5
	4/12/2011	58	3	7	15

contaminant	sample date	inf. conc. (ng L^{-1})	removal (%) Biofilter 1a	Biofilter 1b	SSF
	4/20/2011	156	5	5	--
sulfamethoxazole	5/17/2010	221	--	0	--
	7/16/2010	160 [a]	0 [b]	0 [b]	17
	8/25/2010	59 [a]	0 [b]	1	20
	9/21/2010	39 [a]	10	13	27
	11/2/2010	132 [a]	5	13	19
	1/11/2011	203	0 [b]	1	11
	4/12/2011	267	0 [b]	0 [b]	15
	4/20/2011	948	8	12	--
tributyl phosphate	8/25/2010	209 [a]	14	34	57
	9/21/2010	156 [a]	10	14	43
	11/2/2010	106 [a]	22	26	74
	1/11/2011	118	0 [b]	18	73
	4/12/2011	180	33	30	68
	4/20/2011	250	8	2	--
triclosan	3/9/2011	220	95	100	100
	4/12/2011	160	100	100	100
	4/20/2011	160	94	100	--
trimethoprim	5/17/2010	187	--	91	--
	7/16/2010	68 [a]	70	100	100
	8/25/2010	3 [a]	96	100	100
	9/21/2010	11 [a]	82	82	100
	11/2/2010	87 [a]	71	82	100
	1/11/2011	72	41	46	100
	4/12/2011	267	3	19	100
	4/20/2011	335	8	9	--
warfarin	8/25/2010	112 [a]	25	63	100
	9/21/2010	143 [a]	39	76	94
	11/2/2010	491 [a]	51	75	98
	1/11/2011	251	49	72	98
	4/12/2011	286	33	54	95
	4/20/2011	237	41	61	--

[a] estimated influent concentration.
[b] removal less than zero.
-- not sampled

B.2 BIOFILTERS R1-R7

Table B.2. MIB and 2,4-D Removal for Biofilters R1-R7

	MIB Removal (%) Biofilter							2,4-D Removal (%) Biofilter							EBCT (min) Biofilter						
sample time	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**
3/8/2010 9:05	--	74	74	71	78	--	88	--	--	--	--	--	--	--	--	9.4	7.5	8.6	10.0	--	8.3
3/9/2010 8:55	--	67	61	64	63	--	72	--	--	--	--	--	--	--	--	8.3	7.5	7.9	9.4	--	7.9
3/10/2010 8:30	--	62	62	64	66	--	76	--	--	--	--	--	--	--	--	8.1	8.2	8.1	9.4	--	8.3
3/12/2010 8:10	--	26	64	68	71	--	79	--	--	--	--	--	--	--	--	8.3	8.1	9.4	11.5	--	9.4
3/14/2010 15:45	--	60	61	68	69	--	78	--	--	--	--	--	--	--	--	7.1	8.3	9.4	10.7	--	8.6
3/17/2010 9:35	--	54	65	51	53	--	71	--	54	53	35	57	--	66	--	7.3	9.4	6.0	7.5	--	8.8
3/23/2010 10:55	--	56	60	56	68	--	76	--	53	72	52	79	--	72	--	7.9	10.7	6.8	11.5	--	10.7
3/27/2010 13:10	--	31	54	28	59	--	57	--	59	64	55	28	--	63	--	7.9	10.0	7.0	11.5	--	10.0
3/31/2010 13:20	--	20	19	26	16	--	13	--	57	36	55	50	--	36	--	8.3	6.8	7.9	9.1	--	6.0
4/4/2010 13:10	--	65	42	66	54	--	42	--	71	50	62	67	--	36	--	10.3	7.5	9.7	11.5	--	6.8
4/6/2010 9:05	--	70	32	65	50	--	51	--	77	53	66	52	--	50	--	12.5	7.5	10.0	10.0	--	7.1
4/12/2010 9:00	--	58	79	71	83	--	79	--	43	68	69	86	--	64	--	6.8	9.4	9.4	21.4	--	9.1
4/14/2010 12:35	--	69	62	51	78	--	81	--	49	50	34	57	--	74	--	7.9	6.0	5.0	9.7	--	9.4
4/19/2010 10:30	--	70	64	58	65	--	59	--	57	47	44	53	--	33	--	8.8	7.1	8.3	7.9	--	5.8
4/23/2010 15:15	--	70	70	59	64	--	62	--	62	52	59	56	--	43	--	9.4	7.5	7.9	8.3	--	5.5
4/26/2010 14:00	--	80	73	63	68	--	67	--	93	61	64	54	--	45	--	11.5	9.1	8.8	8.6	--	6.2
4/27/2010 14:30	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	6.8	--	--
4/29/2010 9:50	--	76	75	67	66	--	70	--	80	62	79	55	--	60	--	13.0	9.4	12.5	7.9	--	7.5
5/3/2010 10:05	--	78	76	66	64	--	74	--	56	56	72	35	--	62	--	12.5	10.7	13.0	8.1	--	10.0
5/4/2010 8:20	--	72	--	60	--	--	--	--	67	--	46	--	--	--	--	13.0	11.5	8.3	8.3	--	10.7
5/5/2010 16:45	47	--	--	--	--	13	--	27	--	--	--	--	12	--	6.2	--	--	--	--	7.5	--
5/6/2010 15:55	52	83	--	67	--	20	45	29	--	--	--	--	24	74	6.5	24.9	10.0	8.3	10.0	8.8	10.7
5/7/2010 15:15	59	--	--	--	--	29	--	44	--	--	--	--	27	--	7.5	10.0	10.7	9.4	10.0	10.0	11.5
5/9/2010 13:35	74	--	--	--	--	52	--	34	--	--	--	--	22	--	8.3	13.6	10.0	10.7	10.7	10.7	11.5
5/11/2010 11:10	70	50	--	48	--	67	71	52	--	--	--	--	33	88	10.3	6.5	13.6	6.2	4.4	16.6	16.6
5/13/2010 11:20	71	71	--	67	--	27	69	44	--	--	--	--	18	78	8.3	6.5	15.0	7.7	8.3	6.2	11.5
5/14/2010 9:00	69	57	--	62	--	20	66	38	--	--	--	--	10	49	8.6	5.3	6.0	10.0	7.1	5.2	7.5
5/17/2010 14:30	66	68	--	64	--	27	71	37	--	--	--	--	10	59	7.5	8.3	6.0	7.7	10.0	6.0	7.9
5/21/2010 11:20	62	65	--	52	--	63	65	19	--	--	--	--	17	35	7.1	9.4	9.4	7.9	8.8	10.7	6.5
5/24/2010 10:10	76	64	--	62	--	70	72	81	--	--	--	--	48	49	21.4	9.1	21.4	10.0	10.0	49.9	11.5

	MIB Removal (%)							2,4-D Removal (%)							EBCT (min)						
	Biofilter							Biofilter							Biofilter						
sample time	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**
5/26/2010 7:55	65	58	--	54	--	58	62	28	--	--	--	--	35	44	7.5	7.5	6.5	9.7	9.4	15.0	7.5
5/30/2010 13:30	64	60	--	57	--	55	62	29	--	--	--	--	16	53	7.3	7.9	7.9	8.1	7.1	8.3	7.5
6/7/2010 15:30	--	40	--	35	--	--	--	--	--	--	--	--	--	--	--	9.4	10.0	11.5	10.7	11.5	10.7
6/8/2010 15:00	65	60	--	54	--	58	63	5	--	--	--	--	4	14	8.3	7.9	5.8	9.4	6.0	10.7	9.4
6/10/2010 13:40	65	--	62	--	--	60	65	18	--	33	--	--	19	43	7.7	8.8	7.5	9.4	7.9	10.0	8.3
6/13/2010 13:10	--	--	70	--	--	--	--	--	--	54	--	--	--	--	15.8	7.1	12.0	10.0	10.0	21.4	13.6
6/15/2010 10:20	66	--	47	--	--	57	59	49	--	37	--	--	30	66	12.0	6.4	8.3	10.7	10.7	15.0	10.0
6/21/2010 16:10	53	--	50	--	--	47	59	31	--	36	--	--	27	43	6.5	8.3	7.0	12.5	13.6	9.4	7.9
6/26/2010 15:45	59	--	67	--	--	61	64	17	--	37	--	--	16	52	7.9	9.4	7.5	13.6	18.7	12.5	9.4
7/2/2010 15:30	70	--	70	--	--	74	66	81	--	56	--	--	72	76	16.6	15.0	10.0	12.5	7.1	18.7	11.5
7/7/2010 12:25	64	--	58	--	--	55	68	41	--	30	--	--	24	45	8.3	13.6	6.5	14.3	7.7	7.9	7.5
7/8/2010 14:10	73	--	67	--	--	60	71	50	--	41	--	--	32	50	8.8	10.0	7.5	9.4	8.8	10.0	7.5
7/10/2010 11:20	75	--	67	--	--	69	75	55	--	35	--	--	53	48	11.5	10.7	7.5	7.9	10.7	15.0	8.3
7/13/2010 14:30	--	--	64	--	--	--	--	--	--	44	--	--	--	--	--	13.6	7.9	7.1	10.0	--	8.8
7/22/2010 9:55	--	--	46	--	--	--	--	--	--	52	--	--	--	--	--	7.3	10.0	7.9	6.8	--	7.1
7/26/2010 9:50	--	--	63	--	--	--	65	--	--	67	--	--	--	57	--	7.5	11.1	8.3	7.1	--	8.1
7/26/2010 15:30	--	--	--	63	53	--	--	--	--	--	55	38	--	--	--	--	--	8.8	7.1	--	--
7/27/2010 12:15	--	--	--	63	61	--	--	--	--	--	55	30	--	--	--	7.7	11.5	8.8	6.8	--	7.9
7/30/2010 8:30	--	--	68	54	54	--	66	--	--	69	61	32	--	59	--	9.7	11.5	9.7	6.8	--	7.9
8/3/2010 8:20	--	--	59	55	65	--	69	--	--	40	38	44	--	62	--	6.1	6.5	6.4	8.3	--	8.8
8/11/2010 9:10	--	--	68	63	67	--	77	--	--	62	60	48	--	65	--	8.3	7.9	7.1	6.4	--	7.9
8/13/2010 9:00	--	--	71	57	56	--	67	--	--	64	46	40	--	62	--	8.6	8.3	7.1	6.5	--	7.9
8/16/2010 10:00	--	--	71	55	69	--	73	--	--	73	49	45	--	63	--	10.7	9.1	7.3	7.5	--	7.5
8/20/2010 14:00	--	--	64	57	58	--	60	--	--	71	60	54	--	69	--	14.0	12.0	8.3	8.3	--	10.0
8/23/2010 9:10	--	--	--	60	68	--	68	--	--	--	62	63	--	65	--	11.5	--	8.3	8.8	--	10.0
8/25/2010 10:25	--	--	--	56	71	--	83	--	--	--	69	61	--	77	--	5.8	--	8.8	10.0	--	12.5
8/30/2010 8:15	--	--	--	62	69	--	70	--	--	--	70	55	--	83	--	6.2	--	13.0	13.6	--	16.6
9/3/2010 8:30	--	--	--	50	56	--	53	--	--	--	64	54	--	89	--	7.5	--	7.5	6.0	--	16.6
9/7/2010 7:30	--	--	--	59	59	--	71	--	--	--	61	40	--	79	--	7.5	--	7.9	7.1	--	12.5
9/15/2010 12:45	--	--	--	53	--	--	58	--	--	--	44	--	--	38	--	9.4	--	7.1	--	--	6.0
9/17/2010 13:30	--	--	--	55	--	--	--	--	--	--	54	--	--	--	--	9.1	--	7.5	--	--	5.2
9/28/2010 13:50	--	--	--	69	--	--	68	--	--	--	78	--	--	64	--	7.5	--	8.3	--	--	7.5
9/30/2010 13:30	--	72	--	57	--	--	69	--	46	--	73	--	--	60	--	6.5	--	8.8	--	--	6.2

	MIB Removal (%) Biofilter							2,4-D Removal (%) Biofilter							EBCT (min) Biofilter						
sample time	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**	**R1**	**R2**	**R3**	**R4**	**R5**	**R6**	**R7**
10/1/2010 12:00	--	72	--	--	--	--	75	--	60	--	--	--	--	62	--	6.8	--	8.8	--	--	6.5
10/4/2010 13:50	--	66	--	--	--	--	71	--	59	--	--	--	--	69	--	6.5	--	10.0	--	--	9.4
10/5/2010 15:30	--	64	--	64	--	--	72	--	62	--	86	--	--	76	--	7.1	--	10.7	--	--	7.5
10/8/2010 14:30	--	71	--	--	--	--	70	--	76	--	--	--	--	80	--	7.5	--	12.0	--	--	8.1
10/13/2010 15:15	--	66	--	58	--	--	69	--	79	--	68	--	--	73	--	8.6	--	6.2	--	--	7.3
10/21/2010 14:20	--	70	--	--	--	--	72	--	91	--	--	--	--	80	--	10.0	--	--	--	--	15.0
10/23/2010 10:20	--	75	--	--	--	--	66	--	85	--	--	--	--	76	--	10.0	--	--	--	--	8.6

-- not sampled

B.3 BIOFILTERS FROM VARIABLE INFLUENT CONDITIONS EXPERIMENT

Table B.3. MIB and 2,4-D Removal for Biofilters from Variable Influent Conditions Experiment

	MIB Removal (%) Biofilter				2,4-D Removal (%) Biofilter				EBCT (min) Biofilter			
sample time	**GAC A**	**BAC**	**Sand A**	**Sand B**	**GAC A**	**BAC**	**Sand A**	**Sand B**	**GAC A**	**BAC**	**Sand A**	**Sand B**
7/13/2011 9:20	37	49	10	77	34	52	4	46	8.1	8.4	8.3	8.3
7/14/2011 14:00	29	42	4	77	39	38	4	48	7.7	8.7	6.5	9.4
7/15/2011 8:30	25	43	6	58	33	45	8	37	7.6	7.5	5.8	6.5
7/15/2011 11:00	29	42	10	61	41	49	-3	43	7.6	7.5	5.8	6.5
7/15/2011 15:00	19	41	1	61	36	46	2	39	7.6	7.5	5.8	6.5
7/16/2011 9:00	25	48	1	62	36	48	9	31	8.4	8.7	7.0	11.5
7/17/2011 8:40	25	49	0	48	34	47	0	28	9.0	8.7	7.0	5.8
7/18/2011 9:15	26	52	9	63	36	48	12	50	9.9	9.6	9.1	6.8
7/18/2011 11:15	27	49	5	59	33	40	0	25	8.6	8.4	7.5	6.5
7/18/2011 15:30	25	45	6	60	33	44	-2	28	7.2	7.0	7.7	7.3
7/19/2011 9:15	25	48	5	65	32	36	5	32	8.3	7.3	8.8	7.9
7/20/2011 8:45	22	47	1	69	34	40	6	41	7.3	8.0	7.0	8.1
7/21/2011 18:00	24	54	1	76	37	43	3	48	7.0	8.4	7.3	9.4
7/22/2011 8:50	23	55	3	71	33	42	2	33	8.2	9.1	7.1	9.7
7/23/2011 7:30	15	45	-1	35	22	41	-8	15	7.3	8.4	6.5	8.3
7/24/2011 8:30	18	43	3	63	31	32	8	35	8.0	7.5	7.9	8.1
7/25/2011 11:00	18	41	3	65	17	28	-8	23	7.7	8.0	7.9	7.9
7/26/2011 8:30	18	42	1	72	32	38	7	40	8.4	8.2	7.9	8.1
7/26/2011 11:15	22	47	5	75	31	37	-5	28	8.4	8.2	7.9	8.1

7/26/2011 15:15	21	42	0	74	30	38	-3	28	8.4	8.2	7.9	8.1
7/27/2011 8:40	20	44	3	79	33	36	0	55	8.2	8.0	7.9	7.9
7/28/2011 8:50	22	45	4	82	34	55	2	61	9.0	8.1	11.5	9.7
8/1/2011 17:30	19	45	8	73	29	36	1	43	7.1	8.0	6.1	7.5
8/2/2011 9:45	18	49	6	75	30	48	1	37	7.3	8.7	6.8	7.9
8/3/2011 9:00	14	43	6	70	28	31	6	37	7.0	8.0	6.7	7.9
8/5/2011 9:45	8	--	0	74	20	14	4	59	7.5	7.5	8.3	9.4
8/8/2011 9:15	21	17	16	76	31	32	-4	36	9.6	9.0	10.7	9.1
8/8/2011 12:00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.2	7.7	5.3	7.9
8/8/2011 14:00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.2	7.7	5.3	7.9
8/8/2011 16:00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.2	7.7	5.3	7.9
8/9/2011 10:10	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.2	7.5	8.8	8.3
8/10/2011 11:00	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.4	8.0	10.0	8.8
8/11/2011 8:30	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8.4	8.0	10.0	8.8
8/12/2011 9:15	16	21	-1	51	31	31	3	15	7.3	7.6	6.6	6.9
8/13/2011 9:30	16	24	5	63	36	38	4	26	8.5	8.1	7.9	7.6
8/14/2011 10:20	19	25	5	70	35	36	-5	38	8.9	8.6	9.2	8.6
8/15/2011 9:45	16	24	8	66	27	28	-10	27	8.3	7.9	8.3	8.3
8/16/2011 8:30	17	26	9	67	32	57	-2	59	8.8	7.9	8.6	8.6
8/16/2011 12:15	15	23	5	66	21	35	-7	43	7.6	7.1	6.6	8.1
8/16/2011 14:30	17	23	5	66	34	32	-2	29	7.6	6.8	7.2	8.6
8/17/2011 9:30	16	22	7	62	29	27	-3	41	8.1	7.3	8.1	8.6
8/18/2011 8:45	17	28	9	64	22	28	-5	13	7.7	7.9	8.6	8.6
8/19/2011 8:20	17	28	10	64	37	47	5	25	8.3	8.0	9.2	6.9
8/21/2011 12:30	14	26	5	64	31	37	0	37	8.6	8.6	7.9	7.6
8/22/2011 8:30	14	34	1	69	29	43	-2	46	8.6	9.2	7.6	8.3
8/22/2011 13:30	11	28	2	14	10	20	-11	0	7.6	7.6	6.0	6.4
8/22/2011 15:15	17	32	1	20	25	29	2	16	7.7	6.8	5.7	5.5
8/23/2011 9:30	18	31	1	50	32	25	-1	43	8.6	8.1	6.9	9.2
8/24/2011 13:30	12	33	-6	58	30	36	-8	45	7.9	8.5	6.9	9.2
8/25/2011 9:30	12	37	3	75	29	40	3	70	7.9	8.5	8.6	15.3
8/26/2011 9:30	15	34	3	69	25	34	-8	--	9.1	8.9	9.5	18.3
8/29/2011 13:30	19	36	12	70	30	36	0	87	7.9	6.8	6.9	27.5
8/30/2011 7:00	18	31	4	46	26	36	-1	29	8.3	7.0	7.1	6.9
8/31/2011 12:30	21	39	15	68	22	37	-3	32	8.5	6.6	7.4	7.4
9/1/2011 8:00	16	-7	7	69	29	45	1	36	8.5	6.6	7.4	7.4

9/2/2011 9:00	18	17	5	58	25	40	3	23	7.6	7.9	7.0	8.4
9/4/2011 13:00	19	17	4	53	38	42	7	26	7.8	7.6	7.0	6.4
9/5/2011 8:30	18	17	5	51	38	41	12	38	8.5	7.8	7.0	6.4
9/6/2011 10:00	11	16	2	50	25	40	-1	29	6.7	7.5	7.0	6.4
9/7/2011 15:00	16	21	4	61	28	41	1	46	7.1	7.5	7.4	7.2
9/8/2011 8:00	11	15	-1	64	29	40	3	43	7.9	8.3	7.8	8.4
9/9/2011 8:00	12	18	0	66	26	44	3	44	7.3	7.8	7.6	8.4
9/12/2011 13:45	8	15	3	56	25	33	-18	24	9.1	8.5	8.1	10.0
9/13/2011 7:00	7	21	-1	57	28	35	-2	41	6.9	7.4	5.5	5.3
9/13/2011 10:00	18	23	12	74	51	52	-2	56	16.5	14.6	11.4	12.6
9/14/2011 17:45	23	32	13	64	61	67	12	52	20.5	17.1	13.9	15.7
9/15/2011 10:15	14	29	4	65	52	58	1	69	23.3	17.1	14.8	16.7
9/16/2011 16:20	15	19	-4	78	48	56	-9	65	16.5	12.8	15.7	13.2
9/19/2011 17:30	25	34	1	67	57	64	-1	78	18.3	14.2	15.7	15.7
9/21/2011 12:15	27	37	5	82	50	74	5	79	19.7	16.0	16.7	16.7
9/23/2011 8:15	18	41	0	71	35	69	-5	71	15.0	17.6	25.1	25.1
9/27/2011 17:45	16	26	0	12	44	53	-6	57	13.1	13.1	10.0	10.0

n/a not applicable (desorption phase).
-- not sampled.

B.4 BIOFILTER G1

Table B.4. Trace Organic Contaminant Removal for Biofilter G1 (Fresh Media)

	removal (%) sample date				
contaminant	**3/9/2011**	**5/9/2011**	**6/28/2011**	**8/30/2011**	**11/18/2011**
2,4–D	100	95	95	90	94
acetaminophen	100	100	100	0	77
acetochlor	100	100	100	100	96
aldicarb	100	100	100	97	98
atrazine	71	85	96	89	90
bisphenol A	100	65	--	--	--
caffeine	84	84	92	4	59
carbamazepine	100	100	100	100	100
carbaryl	100	100	100	100	100
chlorpyrifos	100	100	100	100	100
clofibric acid	100	90	90	73	92
cotinine	100	90	87	31	59
diazinon	100	100	100	100	100
diclofenac	100	100	100	100	100
dimethoate	100	100	100	95	95
diuron	100	100	100	100	100
erythromycin	100	97	97	100	100
ethinyl estradiol	100	100	100	--	--
gemfibrozil	100	98	100	97	97
ibuprofen	100	100	100	100	100
iopromide	100	84	79	32	55
malaoxon	100	100	100	96	96
methomyl	100	100	94	84	69
metolachlor	100	98	97	98	89
MIB	--	--	--	--	--
molinate	100	100	100	97	100
naproxen	100	100	100	100	100
progesterone	--	--	--	--	--
prometon	100	97	95	89	83
simazine	100	100	100	100	95
sulfamethoxazole	100	97	97	97	100
tributyl phosphate	80	54	87	54	19
triclosan	100	100	100	--	--
trimethoprim	100	100	100	100	100
warfarin	100	96	97	95	96

-- not sampled.

B.5 BIOFILTERS 2 AND G2-G4

Table B.5. Trace Organic Contaminant Removal for Biofilters 2 and G2-G4

contaminant	sample date	inf. conc. (ng L^{-1})	Removal (%) Biofilter 2	G2	G3	G4
2,4–D	5/17/2010	121	--	--	--	3
	7/16/2010	147 [a]	49	23	0 [b]	10
	8/25/2010	139 [a]	40	47	22	14
	9/21/2010	119 [a]	73	48	31	18
	11/2/2010	190 [a]	35	41	15	2
	1/11/2011	180	77	70	38	44
	4/12/2011	124	73	37	38	3
acetaminophen	5/17/2010	267	--	--	--	26
	7/16/2010	366 [a]	71	85	64	31
	8/25/2010	50 [a]	57	92	81	39
	9/21/2010	87 [a]	58	80	83	46
	11/2/2010	347 [a]	30	78	60	27
	1/11/2011	174	55	95	84	45
	4/12/2011	313	81	81	87	36
acetochlor	8/25/2010	121 [a]	17	23	5	7
	9/21/2010	48 [a]	9	24	15	9
	11/2/2010	98 [a]	20	32	19	12
	1/11/2011	195	13	33	12	5
	4/12/2011	174	15	35	11	0 [b]
aldicarb	8/25/2010	7 [a]	32	27	0 [b]	10
	9/21/2010	15 [a]	22	86	0 [b]	0 [b]
	11/2/2010	647 [a]	19	49	29	15
	1/11/2011	104	42	54	40	22
	4/12/2011	12	30	43	43	4
atrazine	5/17/2010	8	--	--	--	0
	7/16/2010	5 [a]	5	36	23	0 [b]
	8/25/2010	9 [a]	7	37	16	0
	9/21/2010	3 [a]	0 [b]	40	16	0 [b]
	11/2/2010	4 [a]	9	43	13	14
	1/11/2011	12	1	42	12	0 [b]
	4/12/2011	6	7	30	26	0 [b]
bisphenol A	11/2/2010	226	18	49	40	7
	3/9/2011	270	56	78	50	26
	4/12/2011	25	80	60	0	20
caffeine	5/17/2010	99	--	--	--	5
	7/16/2010	38 [a]	73	50	12	4
	8/25/2010	10 [a]	58	67	42	23

contaminant	sample date	inf. conc. (ng L^{-1})	Removal (%) Biofilter 2	G2	G3	G4
	9/21/2010	7 [a]	33	34	32	13
	1/11/2011	100	0 [b]	74	35	8
	4/12/2011	74	0 [b]	42	45	0 [b]
carbamazepine	5/17/2010	132	--	--	--	3
	7/16/2010	51 [a]	7	38	16	7
	8/25/2010	38 [a]	5	47	19	10
	9/21/2010	36 [a]	0 [b]	49	24	10
	11/2/2010	28 [a]	12	50	22	17
	1/11/2011	35	0 [b]	61	23	8
	4/12/2011	64	1	40	39	1
carbaryl	7/16/2010	100 [a]	11	69	39	9
	8/25/2010	68 [a]	24	68	34	8
	9/21/2010	46 [a]	4	71	45	12
	1/11/2011	47	1	79	41	4
	4/12/2011	96	21	55	70	12
chlorpyrifos	5/17/2010	148	--	--	--	0
	7/16/2010	279 [a]	82	37	25	0 [b]
	8/25/2010	57 [a]	78	69	42	68
	9/21/2010	101 [a]	64	50	11	10
	11/2/2010	189 [a]	100	100	86	86
	1/11/2011	565	74	68	50	41
	4/12/2011	603	62	59	55	19
clofibric acid	8/25/2010	88 [a]	20	29	12	9
	9/21/2010	67 [a]	27	20	16	11
	11/2/2010	278 [a]	25	20	5	4
	1/11/2011	258	74	22	15	13
	4/12/2011	163	62	33	3	0 [b]
cotinine	5/17/2010	110	--	--	--	5
	7/16/2010	188 [a]	20	13	2	0 [b]
	8/25/2010	49 [a]	34	51	39	27
	9/21/2010	125 [a]	15	0 [b]	26	13
	11/2/2010	288 [a]	0 [b]	30	4	5
	1/11/2011	109	31	31	4	0 [b]
	4/12/2011	35	33	47	32	0 [b]
diazinon	5/17/2010	7	--	--	--	10
	7/16/2010	1 [a]	28	15	2	8
	8/25/2010	1 [a]	32	37	0	12
	9/21/2010	1 [a]	8	29	13	2
	11/2/2010	0 [a]	54	57	41	34

contaminant	sample date	inf. conc. (ng L^{-1})	Removal (%) Biofilter 2	G2	G3	G4
	1/11/2011	2	28	34	27	17
	4/12/2011	3	31	33	14	0 [b]
diclofenac	11/2/2010	193 [a]	20	30	17	14
	1/11/2011	171	21	18	16	10
	4/12/2011	163	15	38	22	4
dimethoate	8/25/2010	100 [a]	58	87	74	65
	9/21/2010	37 [a]	35	87	80	67
	11/2/2010	46 [a]	23	73	54	36
	1/11/2011	68	51	82	81	57
	4/12/2011	38	73	79	80	52
diuron	5/17/2010	107	--	--	--	6
	7/16/2010	78 [a]	3	73	40	10
	8/25/2010	40 [a]	10	75	38	14
	9/21/2010	56 [a]	0 [b]	76	41	0 [b]
	11/2/2010	26 [a]	38	76	49	40
	1/11/2011	93	7	88	57	14
	4/12/2011	60	19	62	74	5
erythromycin	11/2/2010	56 [a]	64	72	50	38
	1/11/2011	54	2	6	11	8
	4/12/2011	90	20	29	32	14
ethinyl estradiol	11/2/2010	133	47	50	54	54
	3/9/2011	310	13	39	6	0 [b]
	4/12/2011	340	38	50	6	29
gemfibrozil	5/17/2010	263	--	--	--	0
	7/16/2010	139 [a]	81	15	2	7
	8/25/2010	80 [a]	60	37	15	22
	9/21/2010	93 [a]	71	44	32	22
	11/2/2010	214 [a]	55	37	21	15
	1/11/2011	176	73	59	51	42
	4/12/2011	136	73	43	27	0 [b]
ibuprofen	5/17/2010	400	--	--	--	45
	7/16/2010	219 [a]	100	79	76	71
	8/25/2010	128 [a]	92	88	87	80
	9/21/2010	42 [a]	95	86	88	79
	11/2/2010	262 [a]	82	77	72	52
	1/11/2011	280	100	100	100	100
	4/12/2011	163	100	91	91	81
iopromide	5/17/2010	369	--	--	--	0
	7/16/2010	712 [a]	20	0 [b]	0 [b]	0 [b]

contaminant	sample date	inf. conc. (ng L^{-1})	Removal (%) Biofilter			
			2	G2	G3	G4
	8/25/2010	24 [a]	29	42	13	15
	9/21/2010	108 [a]	39	0 [b]	41	45
	11/2/2010	930 [a]	5	7	2	0
	1/11/2011	708	0 [b]	1	0	0 [b]
	4/12/2011	425	38	34	0 [b]	0 [b]
malaoxon	8/25/2010	8 [a]	17	30	11	6
	9/21/2010	30 [a]	20	27	33	11
	1/11/2011	37	26	52	25	19
	4/12/2011	103	24	44	30	6
methomyl	5/17/2010	216	--	--	--	7
	7/16/2010	101 [a]	6	59	23	9
	8/25/2010	18 [a]	30	72	42	26
	9/21/2010	40 [a]	20	37	43	19
	11/2/2010	119 [a]	14	58	28	10
	1/11/2011	165	0 [b]	71	27	3
	4/12/2011	131	0 [b]	49	54	0
metolachlor	11/2/2010	103 [a]	20	30	17	18
	1/11/2011	192	2	25	10	6
	4/12/2011	185	9	34	9	0 [b]
MIB	1/11/2011	103	91	54	95	93
	3/9/2011	84	72	--	--	--
	4/12/2011	106	90	44	56	44
molinate	5/17/2010	272	--	--	--	13
	7/16/2010	105 [a]	92	54	36	20
	8/25/2010	38 [a]	78	70	46	43
	9/21/2010	29 [a]	72	61	39	20
	11/2/2010	51 [a]	67	73	47	29
	1/11/2011	91	86	80	68	39
	4/12/2011	118	90	72	67	37
naproxen	8/25/2010	141 [a]	51	33	13	10
	9/21/2010	84 [a]	58	35	19	11
	11/2/2010	231 [a]	47	38	16	10
	1/11/2011	157	61	34	22	10
	4/12/2011	150	64	41	30	7
prometon	11/2/2010	70 [a]	11	30	14	9
	1/11/2011	116	0 [b]	33	11	1
	4/12/2011	84	0 [b]	39	21	0 [b]
simazine	5/17/2010	60	--	--	--	18
	7/16/2010	31 [a]	0 [b]	43	15	19

contaminant	sample date	inf. conc. (ng L^{-1})	Removal (%) Biofilter 2	G2	G3	G4
	8/25/2010	30 [a]	10	61	25	9
	9/21/2010	20 [a]	0 [b]	56	23	2
	11/2/2010	30 [a]	11	49	24	10
	1/11/2011	40	0 [b]	67	23	0 [b]
	4/12/2011	34	0	45	48	0 [b]
sulfamethoxazole	5/17/2010	221	--	--	--	3
	7/16/2010	146 [a]	9	10	0 [b]	1
	8/25/2010	44 [a]	12	26	9	6
	9/21/2010	15 [a]	3	20	9	1
	11/2/2010	110 [a]	7	20	7	6
	1/11/2011	153	8	16	13	7
	4/12/2011	143	2	35	17	0 [b]
tributyl phosphate	8/25/2010	179 [a]	31	15	2	5
	9/21/2010	139 [a]	10	11	3	0 [b]
	11/2/2010	87 [a]	34	42	24	19
	1/11/2011	92	19	38	33	10
	4/12/2011	90	8	49	9	8
triclosan	3/9/2011	160	100	100	100	72
	4/12/2011	130	53	62	46	46
trimethoprim	5/17/2010	187	--	--	--	9
	7/16/2010	54 [a]	88	43	14	9
	8/25/2010	3 [a]	79	76	53	42
	9/21/2010	6 [a]	74	22	48	31
	11/2/2010	58 [a]	25	51	25	17
	1/11/2011	55	6	75	39	12
	4/12/2011	125	7	58	66	12
warfarin	8/25/2010	50 [a]	30	13	10	16
	9/21/2010	12 [a]	66	55	22	8
	11/2/2010	558 [a]	22	41	35	27
	1/11/2011	189	67	38	60	54
	4/12/2011	118	43	58	35	15

[a] estimated influent concentration.
[b] removal less than zero.
-- not sampled