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ABSTRACT

BIOLOGICALLY ACTIVE FILTERS: AN ADVANCED TREATMENT PROCESS FOR PHARMACEUTICALS AND PERSONAL CARE PRODUCTS

by
Shuangyi Zhang

With the increasing concern of pharmaceuticals and personal care products (PPCPs) in source water, this study examines the hypothesis that existing filters and adsorbents in water treatment plants can be converted to biologically active filters (BAFs) to treat these compounds. Removals through bench-scale BAFs are evaluated as a function of media, granular activated carbon (GAC) and dual-media, empty bed contact time (EBCT), and pre-ozonation. For GAC BAFs, greater oxygen consumption, increased pH drop, and greater DOC removal normalized to adenosine triphosphate (ATP) are observed indicating a different microbial community compared to dual-media BAFs. ATP concentrations in the upper portion of the BAFs are as much as four times greater than the middle and lower portions. Sixteen PPCPs are spiked in the source water. At an EBCT of 18 min, GAC BAFs are highly effective with overall removals greater than 80% without pre-ozonation; exceptions include tri(2-chloroethyl) phosphate (TCEP) and iopromide with removals at 76% and 59%, respectively. With the application of pre-ozonation, all indicator compounds are removed at greater than 75%. Reducing the EBCT to 10 min, the degree of PPCP removal is reduced with less than half of the compounds removed at greater than 80%. The dual-media BAFs show limited PPCP removal with only four compounds removed at greater than 80%, and 10 compounds are reduced by less than 50% with either EBCT. To further improve the removals, the application of pre-ozonation is needed and compounds removed at greater than 75% increase to 11 for the

10 min EBCT and 9 for the 18 min EBCT. DOC removal normalized to ATP is an important indicator for BAF performance. With DOC removals ranging from 200 to 600 mg/g ATP in BAFs, GAC shows significant removal efficiency (>80%) for PPCPs. On the other hand, with DOC removals of 100 to 200 mg/g ATP in dual media BAFs, limited removals are observed. *Proteobacteria* and *Planctomycetes* phyla are dominant in both GAC and dual-media BAF. In the filter influent and effluent the dominant phylum is *Proteobacteria*. Based on a factorial analysis, media type significantly affects the abundance of five bacterial phyla and ten bacterial classes. EBCT impacts the abundance of the dominant bacteria phylum *Proteobacteria*. The effect of pre-ozonation is observed at class level. This study demonstrates that GAC BAFs are an effective and advanced technology for treating emerging contaminants. On the other hand, pre-ozonation is needed for dual media BAFs to remove PPCPs.

BIOLOGICALLY ACTIVE FILTERS: AN ADVANCED TREATMENT PROCESS FOR PHARMACEUTICALS AND PERSONAL CARE PRODUCTS

by
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APPROVAL PAGE

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CHAPTER 1

INTRODUCTION

In the last decade, pharmaceuticals and personal care products (PPCPs) have been reported throughout the water cycle (Barnes et al., 2008; Batt et al., 2008; Blair et al., 2013; Daughton et al., 1999; Farré et al., 2001; Kolpin et al., 2002; Kostich et al., 2013; Writer et al., 2013), in wastewater treatment plant influents and effluents (Batt et al., 2008; Glassmeyer et al., 2005; Kolpin et al., 2002; Spongberg and Witter, 2008; Vanderford and Snyder, 2006), surface water (Bartelt-Hunt et al., 2009; Benotti et al., 2009; Conley et al., 2008; Ferrell and Grimes, 2014; Tabe et al., 2009), and even in drinking water treatment and distribution systems (Benotti et al., 2009; Focazio et al., 2008; Huerta-Fontela et al., 2011). As these unregulated contaminants make their way into source water for drinking water treatment systems, tracking their fate, transport, and removal becomes increasingly important. Although PPCPs were observed with concentrations ranging from nanograms per liter (ng/L) to micrograms per liter (μg/L), the consequence of environmental exposure is of upmost importance and cannot be ignored as these compounds have been design to be bioactive (Reungoat et al., 2011).

Several treatment technologies have been studied in treating PPCPs, including ozonation (Hollender et al., 2009; Nakada et al., 2007; Ternes et al., 2003; Wert et al., 2009), granular activated carbon (GAC) adsorption (Kennedy et al., 2015; Snyder et al., 2007b; Ternes et al., 2002), and ultraviolet light/hydrogen peroxide (UV/H_2O_2) (Pereira et al., 2007; Rosario-Ortiz et al., 2010). However, ozonation may result in by-products through incomplete oxidation at economically feasible ozone concentrations (Snyder et

al., 2006). Although GAC has been shown to be effective for some PPCPs, breakthrough and regeneration need to be considered (Snyder et al., 2007b). Treating PPCPs with UV/H_2O_2 also has drawbacks as the energy investment is significant; the process has showed limited efficacy (generally less than 50%) with intensities less than 300 mJ/cm^2 (Rosario-Ortiz et al., 2010). Disinfection by-products need to be considered as well (Metz et al., 2011).

Biologically active filters (BAFs) have been gaining more attention as a water treatment process in removing biodegradable natural organic matter (NOM) (Hozalski et al., 1999; Vahala et al., 1998), disinfection by-products (Griffini et al., 1999; Wobma et al., 2000), geosmin and 2-methylisoborneol (MIB) (Elhadi et al., 2004; Persson et al., 2007), and manganese (Burger et al., 2008; Cerrato et al., 2010). Recently, a number of studies have been conducted using BAFs to treat PPCPs (Hallé et al., 2015; Lee et al., 2012b; McKie et al., 2016; Reungoat et al., 2012; Zearley and Summers, 2012). With the presence of PPCPs becoming an increasing concern for utilities, the development of cost-effective treatment processes is of great importance.

Next-generation sequencing (NGS) (e.g., 454-sequencing, Illumina MiSeq, and Illumina HiSeq) has been useful in resolving microbial structures in water and wastewater treatment plants (Cai and Zhang, 2013; Chao et al., 2013; Huang et al., 2014; Newton et al., 2015; Ye and Zhang, 2011), surface water (Steffen et al., 2014), and filter media (Liao et al., 2013; Lin et al., 2014; Pinto et al., 2012; Wang et al., 2013). Recently, Illumina MiSeq has gained increasing attention becoming a more widely used platform for analysis of environmental samples. The method has high detection sensitivity, low false positive detection, and good sequencing depth (Tan et al., 2015). Therefore, this

sequencing technology was applied to identify microbial communities in BAF influents, effluents, and media.

In this research, the overarching hypothesis is that filters used in water treatment plants can be turned into advanced treatment processes for the additional purpose of treating PPCPs. While biofiltration has been gaining more attention in removing biodegradable organics in water treatment, the presence of PPCPs has become an increasing concern for utilities. The use of ozonation before biofiltration was studied and is expected to further enhance the removal and biodegradation of the more recalcitrant PPCP compounds. This work is important in evaluating potentially effective treatment processes and advanced BAFs to a new level. Two media were compared, GAC and anthracite/sand, and obtained from existing water treatment plants. Over the course of 14 months, this research addressed the following: the effectiveness in removing PPCPs with and without pre-ozonation, the relationship between biomass and BAF performance, BAF media performance in treating emerging organic contaminants found in drinking water supplies, the effect of empty bed contact time (EBCT), and the overall BAF process robustness through a long term study. Microbial activities and performance of BAFs were continuously monitored during the biomass ripening period as well as once steady state conditions were achieved. Indicator compounds were spiked in the source water with relevant concentrations observed in the water cycle. The microbial community was investigated in both BAF media and the filter influents and effluents with next generation sequencing technology. Through a factorial study, the impact of operational conditions (i.e., media type, EBCT, and pre-ozonation) on the resulting microbial composition in BAFs was addressed. The potential metabolic pathways were summarized based on

literature.

The following chapters include Chapter 2, a literature review of PPCP usage, occurrence, properties, treatment efficacy, and adverse effects for the identification of indicator compounds; Chapter 3, the operational conditions (i.e., organic carbon requirement, pretreatment, support media, and EBCT) affecting the performance, the formation of biomass, and PPCP removal in BAFs; Chapter 4, objectives and hypotheses; Chapter 5, experimental methods; Chapter 6, results and discussion; Chapter 7, conclusions; and, Chapter 8, future work.

CHAPTER 2

INDICATOR COMPOUNDS

PPCPs refer, in general, to any product used by individuals for personal health or cosmetic reasons or used in the agricultural industry to enhance plant or animal growth and health. PPCPs comprise a diverse collection of thousands of chemical substances, including prescription and over-the-counter therapeutic drugs, veterinary drugs, fragrances, and cosmetics. In a previous R+i project (EST 1001), a literature review (Zhang et al., 2016a) was conducted that resulted in criteria for selecting indicator compounds. These criteria included usage, occurrence, resistance to treatment, persistence, and properties. The Global Water Research Coalition (De Voogt et al., 2008) also developed a list of representative and priority compounds recommended for future studies and those identified were based on analytical detection, occurrence, treatability, and exposure. Relevant criteria applied in their effort are consistent with those selected in this study. In the following sections, the usage of PPCPs in the United States and their occurrence in the environment are reviewed first. PPCP properties are then discussed based on classes, followed by a review of the efficacy of the treatment technologies and the adverse effects of the environmental exposure. Based on these criteria, the indicator compounds are then identified.

2.1 Usage of PPCPs in the United States

The large usage of PPCPs has a potential impact on the occurrence of PPCPs in aquatic environments. Drug sales in the U.S. grew by 3.2% from $319.1 billion to $329.2 billion

between 2012 and 2013 (IMS Institute, 2014). The growth rate of drug sales in the United States has dropped below 5% only three times in the last 50 years (Pharmacy Times, 2010). The number of prescriptions dispensed from retail channels grew roughly 1.7% from 2012 to 2013 and 2.9% between 2011 and 2012. A total of 4.21 billion prescriptions were dispensed in 2013. Among the classes of pharmaceuticals, lipid regulators, antidepressants, codeine, β-blockers, antibiotics, and antiepileptics are the most frequently detected in aquatic environments (Batt et al., 2008; Vanderford and Snyder, 2006). Clearly, the large usage of pharmaceuticals has a potentially significant impact when excreted and not removed in wastewater treatment plants. In addition, pesticides applied totaled approximately 1.1 billion pounds in both 2006 and 2007 in the U.S. (U.S. EPA 2011). This estimate includes groups of pesticides classified as conventional (generally synthetic chemicals used predominately to kill insects, weeds, and fungi) (U.S. EPA, 2010), wood preservatives, specialty biocides, and chlorine/hypochlorite pesticides. Among the top used conventional pesticides, atrazine and metolachlor were most frequently detected in the water cycle (Glassmeyer et al., 2005; Kolpin et al., 2002; Oller et al., 2001). Because of the significant use and sources of PPCPs, they have likely been present in water and the environment for as long as humans have been using them (Daughton, 2007). In the next section, the occurrence of the PPCPs in the environment is reviewed.

2.2 Occurrence of PPCPs in the Environment

As a result of the usage, PPCPs in the water cycle (Barnes et al., 2008; Daughton et al., 1999; Farré et al., 2001; Focazio et al., 2008; Ternes et al., 2001) have raised concern,

because they have been found in the influents and effluents of wastewater treatment plants (Batt et al., 2008; Glassmeyer et al., 2005; Kolpin et al., 2002; Rivera-Utrilla et al., 2013 Vanderford and Snyder, 2006), surface water (Bartelt-Hunt et al., 2009; Benotti et al., 2009; Conley et al., 2008; Tabe et al., 2009; Writer et al., 2013), and even in drinking water treatment systems (Benotti et al., 2009; Focazio et al., 2008; Huerta-Fontela et al., 2011). The study conducted by the U.S. Geological Survey (USGS) in 2002 (Kolpin et al., 2002) was the first reconnaissance investigation to demonstrate the plethora of pharmaceuticals, steroid hormones, and other non-regulated organic compounds in the environment. The presence of these emerging contaminants has led to a number of studies to better understand their fate, transport, and removal. While the consequence of environmental exposure is of upmost importance, it has received less attention. Nevertheless, studies have demonstrated occurrences in aquatic systems all over the world, for example, in Europe (Babić et al., 2007; Koutsouba et al., 2003; Rabiet et al., 2006), in Asia (Bu et al., 2013; Han et al., 2006; Zhao et al., 2009), and in North America (Batt et al., 2008; Gagné et al., 2006). These studies reveal observations of many classes of PPCPs with concentrations ranging from ng/L to µg/L.

Kostich et al. (2013) measured concentrations of 56 active pharmaceuticals in effluent samples from 50 large wastewater treatment plants (WWTPs) across the United States. Metoprolol, atenolol, and carbamazepine were detected in over 90% of the samples collected. Valsartan, a drug to alleviate hypertension, was found to have the greatest average concentration of 1,600 ng/L across all the 50 samples. Seventeen neuro-active pharmaceuticals and their major metabolites were detected in surface waters receiving treated wastewater from 24 locations in Minnesota (Writer et al., 2013).

Although detection in ng/L levels may appear to be relatively low, environmental exposure cannot be ignored. Benner et al. (2013) reviewed studies conducted on the occurrence of emerging contaminants detected in drinking water sources and in the finished distribution system as well. Data from 27 sampling efforts revealed reports of 133 emerging contaminants. Atrazine, N,N-diethyl-meta-toluamide (DEET), diuron, metolachlor, simazine, and terbuthylazine were the most frequently detected pesticides in both source water and finished drinking water. The detection frequencies ranged from 10 to 100%, while maximum concentrations were found to be 5.5 to 4,200 ng/L in source water and 0.3 to 1,900 ng/L in finished drinking water. On the other hand, acetaminophen, bezafibrate, carbamazepine, diazepam, gemfibrozil, ibuprofen, naproxen, salicyclic acid, and sulfamethoxazole were the most frequently observed pharmaceuticals in source and finished water with detection frequencies up to 100%. The maximum concentrations ranged from 0.47 to 900 ng/L in source water and 0.33 to 601 ng/L in finished drinking water. The observed results indicate that these emerging contaminants are indeed present in both raw and finished drinking water.

In summary, PPCPs most frequently detected in WWTP influents and effluents include acetaminophen, ibuprofen, ketoprofen, and naproxen (analgesics); sulfamethoxazole and trimethoprim (antibiotics); amitriptyline and diazepam (antidepressants); carbamazepine (antiepileptic); atenolol and propranolol (beta-blockers); and, clofibrate, clofibric acid, and gemfibrozil (lipid regulators). The majority of WWTPs studied use conventional biological treatment processes. Furthermore, advanced processes, such as ozone and UV disinfection, were found to enhance the removals of the compounds ibuprofen, ketoprofen, clofibric acid, trimethoprim, and propranolol from

analgesics, lipid regulators, antibiotics, and beta-blockers are less resistant to treatment, demonstrating the necessity of advanced technologies in treating PPCPs.

PPCPs most frequently detected in surface water include caffeine (a stimulant), DEET (an insect repellent), carbamazepine (an antiepileptic), naproxen (an analgesic), sulfamethoxazole and trimethoprim (two antibiotics), tri(2-chloroethyl) phosphate (TCEP) (a fire retardant), and gemfibrozil (a lipid regulator). The frequency of detection demonstrates that these compounds are persistent in surface water that may ultimately serve as source water for drinking water treatment systems, indicating a potential risk for exposure.

PPCPs most frequently detected in drinking water treatment systems are herbicides (atrazine, and metolachlor), a nicotine metabolite (cotinine), antiepileptics (carbamazepine), antibiotics (sulfamethoxazole, and trimethoprim), lipid regulators (gemfibrozil), flame retardants (TCEP), plasticizer (bisphenol A), antidepressants (meprobamate), insect repellents (DEET), and analgesics (ibuprofen and naproxen). Studies demonstrated ineffective treatment for a number of frequently detected PPCPs, specifically, atrazine, carbamazepine, TCEP, DEEP, ibuprofen, gemfibrozil, sulfamethoxazole, and trimethoprim. To better understand why a compound is resistant to treatment and persistent in aquatic environments, the properties of these compounds by classes are discussed in the next section.

2.3 PPCP Classes

Many PPCPs (acetaminophen, diclofenac, sufamethoxazole, gemfibrozil, atenolol, carbamazeipne) move through WWTPs and enter surface water, which increases the

potential threat to aquatic organisms and human health through exposure. PPCPs have been found in source water for drinking water treatment facilities, where for example a number of compounds have been observed including acetaminophen, caffeine, and carbamazepine (e.g., Rabiet et al., 2006). Furthermore, subsequent drinking water treatment processes ineffective in removing these compounds have resulted in their presence in the finished drinking water (e.g., Snyder et al., 2007a). Studying the structure of these PPCPs by classes is useful in addressing treatment efficacy. To better understand persistence, degradability, and removal, this section reviews physical and chemical properties of groups of PPCPs routinely found in systems studied. In the following section, 11 groups of compounds are reviewed, including analgesics, antibiotics, antiepileptics, β-blockers, blood lipid regulators, steroids, flame retardants, metabolites, pesticides, psychomotor stimulants, and x-ray contrast agents.

2.3.1 Analgesics

Analgesics are widely detected in influents and effluents of WWTPs and even in drinking water treatment facilities (Snyder et al., 2007a, Rabiet et al., 2006). Most frequently detected analgesics are acetaminophen, diclofenac, ibuprofen, ketoprofen, naproxen, and paracetamol (Table 2.1). Acetaminophen, diclofenac, ibuprofen, and ketoprofen were detected in samples from WWTPs (influent and effluent) in Spain and Croatia (Petrovic et al., 2006). Among these analgesics, acetaminophen and ibuprofen, were found in hundred μg/L concentrations, ranging from 5.5 to 143 μg/L in influent samples and 0.02 to 15.8 μg/L in effluent. Diclofenac, ketoprofen, and naproxen were detected in lower levels ranging from 0.033 to 11.4 μg/L in influent samples and 0.002 to 11.0 μg/L in

Table 2.1 Concentration Range of PPCP Classes That Are Frequently Detected

Classes	PPCPs	WWTP Influent ng/L	WWTP Effluent ng/L	SW ng/L	DW ng/L	References
Analgesic	acetaminophen (paracetamol)	5529-84000	20-10300	nd-298	1.1-211	Batt et al. (2008); Bartelt-Hunt et al. (2009); Benner et al. (2013); Conley et al. (2008); Gros et al. (2006); Han et al. (2006); Kostich et al. (2013); Koutsouba et al. (2003); Lavén et al. (2009); Petrovic et al. (2006); Rabiet et al. (2006); Roberts et al. (2006); Snyder et al. (2007a); Ternes et al. (2001)
	diclofenac	nd-9870	nd-10960	nd-390	nd-2.5	Batt et al. (2008); Gros et al. (2006); Han et al. (2006); Koutsouba et al. (2003); Petrovic et al. (2006); Rabiet et al. (2006); Roberts et al. (2006); Wu et al. (2009); Zhao et al. (2009)
	ibuprofen	nd-143000	nd-15778	nd-2796	nd-32	Batt et al. (2008); Benner et al. (2013); Han et al. (2006); Gagné et al. (2006); Gros et al. (2006); Kostich et al. (2013); Lavén et al. (2009); Petrovic et al. (2006); Rabiet et al. (2006); Roberts et al. (2006); Santos et al. (2005); Snyder et al. (2007a); Wu et al. (2009); Zhao et al. (2009)
	ketoprofen	150-2100	1.5-1760	nd-620	nd-7	Benner et al. (2013); Gros et al. (2006); Lavén et al. (2009); Petrovic et al. (2006); Rabiet et al. (2006); Santos et al. (2005); Tixier et al. (2003)
	naproxen	33-11400	42-3120	nd-810	nd-44	Benner et al. (2013); Gagné et al. (2006); Gros et al. (2006); Lavén et al. (2009); Rabiet et al. (2006); Santos et al. (2005); Snyder et al. (2007a, 2008); Tixier et al. (2003); Zhao et al. (2009)
Antibiotic	erythromycin	71-250	100-290	nd-438	1-155	Benner et al. (2013); Gros et al. (2006); Petrovic et al. (2006); Roberts et al. (2006); Snyder et al. (2007a); Tixier et al. (2003); Wu et al. (2009);

Table 2.1 Concentration Range of PPCP Classes That Are Frequently Detected (Continued)

Classes	PPCPs	WWTP Influent ng/L	WWTP Effluent ng/L	SW ng/L	DW ng/L	References
Antibiotic	sulfamethoxazole	150-960	nd-2900	nd-820	0.39-173	Bartelt-Hunt et al. (2009); Batt et al. (2008); Benner et al. (2013); Gagné et al. (2006); Gros et al. (2006); Kostich et al. (2013); Petrovic et al. (2006); Snyder et al.(2007a,2008); Wu et al.(2009)
	trimethoprim	40-650	4-414	nd-310	1-19	Batt et al. (2008); Benner et al. (2013); Gagné et al. (2006); Gros et al. (2006); Kostich et al. (2013); Lavén et al. (2009); Petrovic et al. (2006); Roberts et al. (2006); Snyder et al. (2007a, 2008); Wu et al. (2009)
Antidepressant	Diazepam			nd-33	<RL-0.9	Benotti et al. (2009); Benner et al. (2013); Kolpin et al. (2002); Ternes et al. (2001)
	fluoxetine		<RL-76	nd-<18	0.64-3.0	Batt et al. (2008); Benner et al. (2013); Benotti et al. (2009); Glassmeyer et al. (2005); Kostich et al. (2013); Writer et al. (2013)
	meprobamate			<1.0-73	<1.0-73	Benner et al. (2013); Benotti et al. (2009); Snyder et al. (2007a, 2008)
	paroxetine		nd-13	nd-90		Batt et al. (2008); Wu et al. (2009)
	sertraline		21-87	nd-12	nd	Batt et al. (2008); Benner et al. (2013); Kostich et al. (2013)
Antiepileptic	carbamazepine	nd-9420	nd-1300	nd-1238	nd-601	Bartelt-Hunt et al. (2009); Batt et al. (2008); Benner et al. (2013); Gros et al. (2006); Han et al. (2006); Kostich et al. (2013); Lavén et al. (2009); Petrovic et al. (2006); Rabiet et al. (2006); Writer et al. (2013); Wu et al. (2009)

Table 2.1 Concentration Range of PPCP Classes That Are Frequently Detected (Continued)

Classes	PPCPs	WWTP Influent ng/L	WWTP Effluent ng/L	SW ng/L	DW ng/L	References
β-blocker	atenolol	50-1400	50-3000	nd-1150	2.8-48	Batt et al. (2008); Benner et al. (2013); Gros et al. (2006); Kostich et al. (2013); Lavén et al. (2009); Petrovic et al. (2006); Snyder et al. (2008)
	propranolol	60-380	15-520	nd-470	/	Batt et al. (2008); Benner et al. (2013); Gros et al. (2006); Kostich et al. (2013); Lavén et al. (2009); Petrovic et al. (2006); Roberts et al. (2006); Tixier et al. (2003)
Blood Lipid Regulator	clofibric acid	nd-4380	nd-740	nd-30	/	Gros et al. (2006); Han et al. (2006); Koutsouba et al. (2003); Roberts et al. (2006); Tixier et al. (2003); Wu et al. (2009); Zhao et al. (2009)
	gemfibrozil	nd-360	nd-2300	nd-320	0.8-34	Batt et al. (2008); Benner et al. (2013); Han et al. (2006); Gagné et al. (2006); Gros et al. (2006); Kostich et al. (2013); Lavén et al. (2009); Rabiet et al. (2006); Roberts et al. (2006); Snyder et al. (2007a, 2008); Ternes et al. (2001); Wu et al. (2009); Zhao et al. (2009)
Fire Retardent	TECP	/	/	100-540	<RL-720	Benotti et al. (2009); Focazio et al. (2008); Glassmeyer et al. (2005); Kolpin et al. (2002); Snyder et al. (2007a)
Steroid	Estradiol (Steroid Hormone)			nd-200	<RL-17	Benner et al. (2013); Benotti et al. (2009); Kolpin et al. (2002); Zhao et al. (2009);
	Estrone (Steroid Hormone)	/	0.4-12	2-112	<RL-2.3	Benotti et al. (2009); Kolpin et al. (2002); Snyder et al. (2007a); Tabe et al. (2009)
	Progesterone (Steroid Hormone)	/	/	110-199	<MRL-3.1	Benotti et al. (2009); Kolpin et al. (2002); Snyder et al. (2007a)

Table 2.1 Concentration Range of PPCP Classes That Are Frequently Detected (Continued)

Classes	PPCPs	WWTP Influent ng/L	WWTP Effluent ng/L	SW ng/L	DW ng/L	References
Steroid	Cholesterol (Sterol)	/	/	830-8700	UC	Focazio et al. (2008); Glassmeyer et al. (2005); Kolpin et al. (2002)
	Coprostanol (Sterol)	/	/	88-9800	<RL	Focazio et al. (2008); Glassmeyer et al. (2005); Kolpin et al. (2002)
Metabolite	Cotinine	/	/	21-1030	nd-100	Benner et al. (2013); Focazio et al. (2008); Glassmeyer et al. (2005); Kolpin et al. (2002)
Pesticide	Atrazine	/	/	nd-4200	1.3-1900	Benner et al. (2013); Benotti et al. (2009); Glassmeyer et al. (2005); Snyder et al. (2007a)
	Metolachlor	/	/	<RL-97	11-670	Benotti et al. (2009); Focazio et al. (2008); Glassmeyer et al. (2005); Snyder et al. (2007a)
	DEET	/	/	97-2100	<RL-110	Focazio et al. (2008); Glassmeyer et al. (2005); Snyder et al. (2007a)
Stimulant	Caffeine	2700-16300	72-4520	<RL-7990	nd-270	Benner et al. (2013); Focazio et al. (2008); Glassmeyer et al. (2005); Kolpin et al. (2002); Rabiet et al. (2006); Santos et al. (2005); Snyder et al. (2007a); Ternes et al. (2001)
X-ray Contrast Media	Iopromide			1.1-120	<1.0-40	Benner et al. (2013); Snyder et al. (2007a)

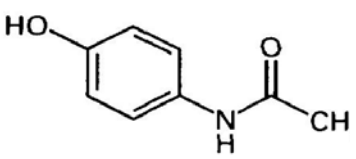
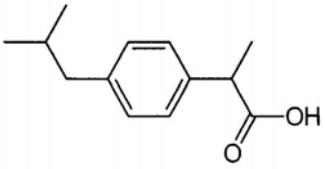
nd – not detected; RL – reporting level; UC – unquantified concentration; / - data not available; SW – surface water; DW – drinking water;

TCEP – Tri(2-chloroethyl)phosphate; DEET – N,N-Diethyl-meta-toluamide

effluent samples. Tracking the compounds through the plant revealed reductions from 0 to 61%. River samples in Spain were also tested for the possible occurrence of these analgesics in surface water. Samples were collected along the Ebro river basin in Spain (Gros et al., 2006) where acetaminophen, diclofenac, ibuprofen, ketoprofen, and naproxen were all detected. Although the concentration of compounds observed rarely exceeded 100 ng/L, with average concentrations (for 10 samples collected along the river) in the single ng/L range, the occurrence of analgesics in surface water was demonstrated. Acetaminophen, diclofenac, ibuprofen, and naproxen were detected in surface water in the U.S. as well (Wu et al., 2009; Conley et al., 2008; Bartelt-Hunt et al., 2009; Snyder et al., 2007a; Glassmeyer et al., 2005).

Because ibuprofen, ketoprofen, naproxen, and diclofenac have similar structural features (aromatic rings and carboxylic acid), they exhibit similar properties (Table 2.2), such as $LogK_{ow}$ values (3.97, 3.12, 3.18, and 4.51, respectively) and pKa values (4.91, 4.45, 4.15, and 4.14, respectively) (Gros et al., 2006; Schwab et al., 2005). K_{ow}, the octanol/water partition coefficient, is defined as the ratio of the compound concentration in the octanol phase to its concentration in the aqueous phase of a two-phase octanol/water system. K_{ow} has become a key parameter in studies of environmental fate of organic chemicals. Comparatively, compounds with low K_{ow} values (< 10) may be considered relatively hydrophilic, with lower soil/sediment adsorption coefficients, and greater solubilities in contrast to compounds with large K_{ow} values ($> 10^4$) that are very hydrophobic (Lyman et al., 1990). All of these analgesics have large K_{ow} values, indicating the hydrophobicity which is consistent with their limited aqueous solubilities. The K_{ow} values and solubilities suggest that biological treatment may not be highly

Table 2.2 Properties of Analgesics

Analgesics	Acetaminophen	Ibuprofen
Structure[6,7]		
Chemical Name	N-(4-hydroxyphenyl)-acetamide	α-methyl-4-(2-methylpropyl)-benzeneacetic acid
Molecular Formula[2]	$C_8H_9NO_2$	$C_{13}H_{18}O_2$
Aqueous Solubility[1,4,5]	Value: 1.4 $\times 10^4$ mg/L Temp: 25 ºC	Value: 21 mg/L Temp: 25 ºC
Boiling Point[8]	387.8±25.0 ºC	319.6±11.0 ºC
Molecular Weight[2]	151.17	206.23
Vapor Pressure[8]	1.43×10^{-6} Torr Temp: 25 ºC	1.39×10^{-4} Torr Temp: 25 ºC
Log K_{ow}[3]	0.46	3.97
pK_a[2,3]	9.38	4.91
k_{O3}[9,10,12]	2.70×10^5 $M^{-1}s^{-1}$ (pH 7)	9.6 (±1) $M^{-1}s^{-1}$ (pH 7, 20ºC)
K_{OH}[9,10,11]	–	6.5×10^9-7.4 (±1.2)$\times10^9$ $M^{-1}s^{-1}$ (pH 7, 25ºC)
K_{oc}[13, 14]	170-1300 mL·g C^{-1}	18-155 mL·g C^{-1}
Structural Features[1]	Phenol, amide	Aromatic ring, carboxylic acid

Source: [1] Snyder et al. (2007a); [2] Gros et al. (2006); [3] Schwab et al. (2005); [4] Khazaeinia et al. (2003); [5] DrugBank (2016); [6] Daughton (1999); [7] Tixier et al. (2003); [8] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [9] Huber et al. (2003); [10] Huber et al. (2005); [11] Nanaboina et al. (2010); [12] Javier Rivas et al. (2010); [13] Yamamoto et al., 2009; [14] Scheytt et al., 2005.

effective treatment for analgesics. In contrast, acetaminophen has relatively low Log K_{ow} value, suggesting a greater biodegradability.

K_{oc} is a partition coefficient reflecting the distribution of an organic compound between solid organic carbon and the aqueous phase (Lyman et al., 1990). Therefore, compounds with larger K_{oc} are more likely to be removed by adsorption. Acetaminophen has relatively greater K_{oc} (170-1,300 mL·g C^{-1}) than ibuprofen (18-155 mL·g C^{-1}) (Scheytt et al., 2005; Yamamoto et al., 2009), suggesting GAC may be effective in removing acetaminophen. Furthermore, acetaminophen has an aromatic ring with a phenolic moiety, suggesting O_3 is relatively effective (Wert et al., 2009; Westerhoff et al., 2005). Ibuprofen with a carboxylic group on its aromatic ring is an electron- withdrawing functional group that reduces the reactivity of the aromatic ring with ozone (Nakada et al., 2007; Westerhoff et al., 2005). The ozone rate constant (k_{O3}) for ibuprofen is 9.6 $M^{-1}s^{-1}$ (Table 2.2), indicating a relatively slow reaction with ozone. In contrast, acetaminophen with a greater rate constant (2.70×10^5 $M^{-1}s^{-1}$), would achieve improved removal through ozonation. With their varying degree of reactivity with ozone and different Log K_{ow}, acetaminophen and ibuprofen were selected to represent the group of analgesics (Table 2.2).

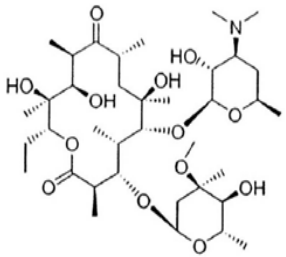
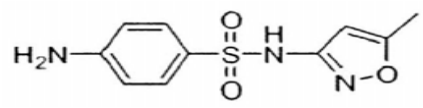
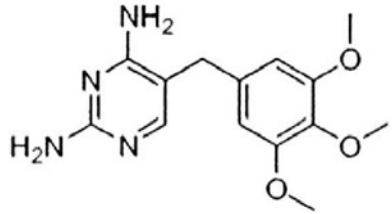
2.3.2 Antibiotics

Antibiotics are widely used in human, veterinary, and animal husbandry. The extensive use of antibiotics increases the likelihood of their release into the environment. Erythromycin, sulfamethoxazole, and trimethoprim are three of the most frequently detected antibiotics. These antibiotics have been observed in influents and effluents of

wastewater treatment plants as well as surface water samples. Properties of the more frequently detected antibiotics are considered (Table 2.3). K_{ow} values of erythromycin, sulfamethoxazole, and trimethoprim are $10^{3.06}$, $10^{0.89}$, and $10^{0.91}$, respectively. From K_{ow} values, erythromycin tends to be more hydrophobic, while sulfamethoxazole and trimethoprim are relatively hydrophilic. The results are consistent with the aqueous solubilities of these three antibiotics, where the solubility of erythromycin is much less than that those of sulfamethoxazole and trimethoprim.

Compounds with a large K_{oc} have lower mobility in the aqueous phase and tend to be more effectively adsorbed by GAC. Therefore, erythromycin with K_{oc} of 570 mL·g C^{-1} may be more efficiently removed by GAC than sulfamethoxazole (K_{oc} = 72 mL·g C^{-1}) and trimethoprim (K_{oc} = 75 mL·g C^{-1}) (Hazardous Substances Data Bank, 2016). Solubility affects the fate and transport of organic chemicals in the environment. Highly soluble compounds are easily and quickly distributed in the hydrologic cycle, and tend to be more readily biodegradable by microorganisms in wastewater treatment plants and surface water. On the other hand, compounds with low solubilities are less biodegradable (Lyman et al., 1990). Therefore, although erythromycin may be more difficult to biodegrade than the other two antibiotics, all have been frequently detected in the water cycle, suggesting a lower degradability. On the other hand, the ozonation rate constants for sulfamethoxazole and trimethoprim (Table 2.3) demonstrate the viability of ozonation. Structures with electron donors are amenable to ozonation (Nakada et al., 2007). Highly reactive compounds include activated aromatic structures (amine functionalities) (Hollender et al., 2009; Westerhoff et al., 2005). The three selected antibiotics have either primary, secondary, or a tertiary amines, suggesting possible locations for ozone to react.

Table 2.3 Properties of Antibiotics

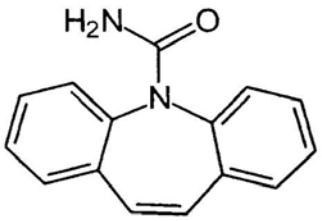
Antibiotics	Erythromycin	Sulfamethoxazole	Trimethoprim
Structure[4]			
Chemical Name	Erythromycin	4-amino-N-(5-methyl-3-isoxazolyl)-benzenesulfonamide	5-[(3,4,5-trimethoxyphenyl)methyl]-2,4-Pyrimidinediamine
Molecular Formula[1]	$C_{37}H_{67}O_{13}$	$C_{10}H_{11}N_3O_3S$	$C_{14}H_{18}N_4O_3$
Aqueous Solubility[1]	Value: 1.44 mg/L Temp: 25 ºC	Value: 610 mg/L Temp: 37 ºC	Value: 400 mg/L Temp: 25 ºC
Boiling Point[5]	818.4±65.0 ºC	482.1±55.0 ºC	526.0±60.0 ºC
Molecular Weight[4]	733.93 g/mol	253.28 g/mol	290.32 g/mol
Vapor Pressure[5]	4.94×10^{-31} Torr Temp: 25 ºC	1.89×10^{-9} Torr Temp: 25 ºC	3.74×10^{-11} Torr Temp: 25 ºC
Log K_{ow}[2]	3.06	0.89	0.91
pK_a[3]	8.8	6.0	7.12
k_{O3}[6,7,8]	–	5.5×10^5-2.5×10^6 $M^{-1}s^{-1}$ (pH 7, 20ºC)	2.7×10^5 $M^{-1}s^{-1}$ (pH 7, 20ºC)
K_{OH}[6,7]	–	5.5 (±0.7)×10^9 $M^{-1}s^{-1}$ (pH 7, 25ºC)	6.9 (±0.2)×10^9 $M^{-1}s^{-1}$ (pH 7, 25ºC)
K_{oc}[9]	570 mL·g C^{-1}	72 mL·g C^{-1}	75 mL·g C^{-1}
Structural Features[1]	Complex aliphatic structure, ketone, alcohols, ester, ethers, tertiary amine, heterocyclic rings	Sulfone, primary amine, secondary amine, aromatic ring, isoxazole ring	Aromatic ring, pyrimidine ring, primary amines, methoxy groups

Source: [1] Snyder et al. (2007a); [2] Schwab et al. (2005); [3] Gros et al. (2006); [4] Yargeau et al. (2008); [5] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [6] Huber et al. (2003); [7] Huber et al. (2005); [8] Dodd et al. (2006); [9] Hazardous Substances Data Bank (2016).

2.3.3 Antiepileptics

Antiepileptics are a class of drugs that work in preventing rapid, repetitive, stimulation of the brain that causes seizure activity. Carbamazepine was the most frequently observed antiepileptic where it was found in WWTP effluents, surface water, and drinking water systems in the US (Batt et al., 2008; Wu et al., 2009; Conley et al., 2008; Bartelt-Hunt et al., 2009; Snyder et al., 2007a; Glassmeyer et al., 2005). Carbamazepine was also the most frequently found antiepileptic in Germany where it was detected in WWTPs and receiving waters, with a maximum concentration of 6.3 µg/L (Ternes, 1998). This drug has not been effectively removed by conventional activated sludge, MBR, or even ozone with a dosage of 15 mg/L (Lavén et al., 2009). Interestingly, carbamazepine concentrations were 1.5 times greater in the activated sludge effluent than influent and 1.3 times greater in the MBR treated effluent as compared to the influent. Carbamazepine was only partially removed by ozone with a removal efficiency of 60%. As a result, antiepileptics are ubiquitous and persistent because of poor WWTP removal. This result may be related to the structure of carbamazepine (Table 2.4) with its aromatic rings and amide. Amide is not as reactive with ozone because of its electron-drawing nature, causing lower removal efficiencies (Westerhoff et al., 2005). However, carbamazepine has a relatively high rate constant ($k_{O3} = 3\times10^5\ M^{-1}s^{-1}$), demonstrating that it is a reactive compound with ozone. This high reactivity of carbamazepine can be attributed to the reactivity of ozone with the (electron donor) double bond that connects the two phenyl moieties (Huber et al., 2003). The poor removal observed in WWTPs with conventional activated sludge and MBR may be due to poor biodegradability of carbamazepine, which is reflected by the relatively large K_{ow} and lower aqueous solubility. Other than ozonation,

Table 2.4 Properties of Antiepileptic

Antiepileptic	Carbamazepine
Structure	
Chemical Name	5H-dibenzazepine-5-carboxamide
Molecular Formula[2]	$C_{15}H_{12}N_2O$
Aqueous Solubility[1]	Value: 17.7 mg/L Temp: 25 ºC
Boiling Point[4]	411.0±48.0 ºC
Molecular Weight[2]	236.27 g/mol
Vapor Pressure[4]	5.78×10^{-7} Torr Temp: 25 ºC
Log K_{ow}[2]	2.47
pK_a[2]	7
k_{O3}[5,6]	3×10^5 $M^{-1}s^{-1}$ (pH 7, 20 ºC)
K_{OH}[5,6]	$8.8\ (\pm1.2)\times10^9$ $M^{-1}s^{-1}$ (pH 7, 25 ºC)
K_{oc}[7]	510 mL·g C^{-1}
Structural Features	Aromatic rings, heterocyclic ring, amide

Source: [1] Snyder et al. (2007a); [2] Gros et al. (2006); [3] Tixier et al. (2003); [4] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [5] Huber et al. (2003); [6] Huber et al. (2005); [7] Hazardous Substances Data Bank (2016).

GAC may be a possible removal process for carbamazepine, because it has a K_{oc} of 510 mL·g C^{-1} (Hazardous Substances Data Bank, 2016).

2.3.4 β-Blockers

Beta blockers are used in managing cardiac arrhythmias, cardioprotection after heart attack, and hypertension. The most frequently detected β-blockers have been atenolol, metoprolol, and propranolol and were found in both WWTPs influent and effluent in Sweden (Lavén et al., 2009). While the influent was treated with conventional activated sludge followed by sand filtration, subsequent treatment comparing ozone to MBR was investigated. Atenolol was determined to be only partially removed through activated sludge and was detected at concentrations greater than half the influent concentrations. However, ozone and MBR treated effluents showed a significant decrease in the concentration of atenolol, indicating an increased treatment efficiency of these two processes. Metoprolol and propranolol were the most persistent compounds, where conventional activated sludge was ineffective. Furthermore, MBR was ineffective for propranolol yet ozone achieved 83% removal. Metoprolol could be treated with either process where ozone reduced the concentration 96% and MBR reduced it by 57%.

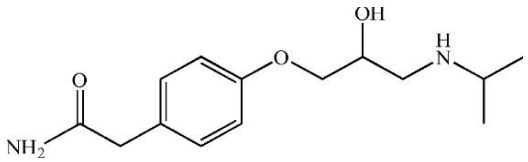
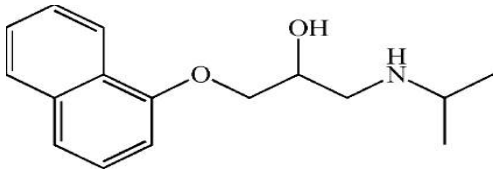
Atenolol and propranolol were also found in WWTP effluents and surface water in the US (Batt et al., 2008). Samples from seven different WWTPs in New Mexico and a surface water sample from the East Fork River in Cincinnati, Ohio were analyzed. The concentration of atenolol and propranolol detected in seven WWTP effleunts ranged from 120 to 960 ng/L and 32 to 77 ng/L, respectively. Atenolol (35 ng/L) and propranolol (23 mg/L) were found in samples collected from the river as well (Batt et al., 2008). These β-

blockers have similar structures (with an aromatic ring, carboxylic acid, ether, and amines); they also have similar properties (Table 2.5). Amine functionalities are structural components of β-blockers that render the compounds highly reactive with respect to ozone (Vieno et al., 2007). Atenolol has k_{O3} of 1.7×10^{3} $M^{-1}s^{-1}$, suggesting a moderate reaction rate with ozonation. The rate constant for propranolol with ozonation is 1.0×10^{5} $M^{-1}s^{-1}$, two orders of magnitude greater than that for atenolol, suggesting an increased rate of reaction with ozone. However, the Log K_{ow} ranges from 0.16 to 3.48 (Table 2.5) with varying aqueous solubility as well indicating potentially unique behavior. Moreover, atenolol has a reported K_{oc} ranging from 148 to 1,700 mL·g C^{-1} (Yamamoto et al., 2009), indicating potentially significant removal through GAC. Initially atenolol and propranolol were selected to represent the β-blockers group, but propranolol was not within the analyzable compounds for the selected lab. Therefore, atenolol was investigated in this study.

2.3.5 Blood Lipid Regulators

Blood lipid regulators have been detected worldwide in waterways (Table 2.1). Large volumes of usage are one reason for their wide release into aquatic environments. Both clofibric acid and gemfibrozil were detected in wastewater and surface water samples (Gros et al., 2006; Han et al., 2006; Koutsouba et al., 2003; Roberts et al., 2006; Snyder et al., 2007a; Ternes et al., 2001; Tixier et al., 2003; Zhao et al., 2009), which indicates possible environmental exposure. Tixier et al. (2003) also observed clofibric acid in samples from two lakes that receive treated wastewater from four WWTPs in Switzerland. Treatment processes included mechanical clarification, biological treatment, and

Table 2.5 Properties of β-Blockers

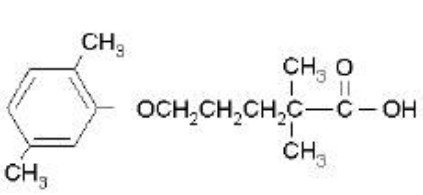
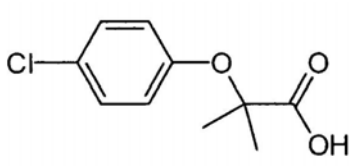
Beta Blockers	Atenolol	Propranolol
Structure[5]		
Chemical Name	4-[2-hydroxy-3-[(1-methylethyl)amino]propoxy]-benzeneacetamide	1-[(1-methylethyl)amino]-3-(1-naphthalenyloxy)- 2-propanol
Molecular Formula[1]	$C_{14}H_{22}N_2O_3$	$C_{16}H_{21}NO_2$
Aqueous Solubility[3,4]	26.7 mg/L	70 mg/L
Boiling Point[6]	508.0±50.0 ºC	434.9±30.0 ºC
Molecular Weight[1]	266.34	259.80
Vapor Pressure[6]	3.82×10^{-11} Torr Temp: 25 ºC	2.48×10^{-8} Torr Temp: 25 ºC
Log K_{ow}[1,2]	0.16	3.48
pK_a[1,2]	9.6	9.58
k_{O3}[7,8]	1.7 (±0.4)×10^3 $M^{-1}s^{-1}$ (pH 7, 20-22 ºC)	1.0×10^5 $M^{-1}s^{-1}$
K_{OH}[7,8]	8.0 (±0.5)×10^9 $M^{-1}s^{-1}$ (pH 7, 20-22 ºC)	1.0×10^{10} $M^{-1}s^{-1}$
K_{oc}[9]	148-1700 mL·g C^{-1}	–
Structural Features	Aromatic ring, carboxylic acid, ether, amine	Aromatic ring, carboxylic acid, ether, amine

Source: [1] Gros et al. (2006); [2] De Ridder et al. (2009); [3] Hatem et al. (1996); [4] DrugBank (2016); [5] Laven et al. (2009); [6] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [7] Hollender et al. (2009); [8] Reungoat et al. (2010); [9] Yamamoto et al., 2009; [10] Drori et al., 2005.

flocculation/filtration.

Clofibric acid and gemfibrozil are two of the most frequently reported PPCPs in studies; they are found in WWTP effluent, surface water, and even in drinking water systems in the US (Batt et al., 2008; Glassmeyer et al., 2005; Snyder et al., 2007a; Wu et al., 2009). Batt et al. (2008) reported occurrence of gemfibrozil in WWTP effluents where concentrations ranged from 47 to 1,220 ng/L. Gemfibrozil and clofibric acid were detected in untreated and treated samples at a water treatment plant as well (Snyder et al., 2007a). Zhao et al. (2009) reported gemfibrozil, ranging from 7.0 to 19.8 ng/L, in one river in China used as a drinking water source for Guangzhou city and the surrounding towns. Clofibric acid was also detected in both influent and effluent of wastewater samples in Korea (Han et al., 2006), where samples were collected during periods of routine operation. WWTPs in four cities were selected because of high population density and the resulting significant discharges of PPCPs expected. Treatment processes included primary clarification, an aeration tank, and final clarification. In addition, one WWTP had used advanced technology for phosphate removal and denitrification, and one was equipped with sand filtration followed by ultraviolet disinfection. Concentrations of clofibric acid ranged from 0.03 to 4.38 µg/L in influent samples to 0.31 to 0.74 µg/L in effluent samples. Results suggest biological treatment along with UV disinfection was insufficient in treating this blood lipid regulator. For blood lipid regulators, the K_{ow} varies with clofibric acid ($10^{2.88}$) and gemfibrozil ($10^{4.77}$), respectively (Gros et al., 2006; Snyder et al., 2007a), indicating hydrophobicity (Table 2.6). Compared to clofibric acid, gemfibrozil has a relatively lower solubility (19 mg/L), suggesting poor biodegradability. Therefore, gemfibrozil was selected as an indicator compound. Gemfibrozil with a K_{oc} of

Table 2.6 Properties of Blood Lipid Regulators

Blood Lipid Regulators	Gemfibrozil	Clofibric Acid
Structure[1, 3]		
Chemical Name[2]	5-(2,5-dimethylphenoxy)-2,2-dimethyl-Pentanoic acid	2-(4-chlorophenoxy)-2-methyl-propanoic acid
Molecular Formula[1, 4]	$C_{15}H_{22}O_3$	$C_{10}H_{11}O_3Cl$
Aqueous Solubility[1]	19 mg/L	Value: 583 mg/L Temp: 25 ºC
Boiling Point[2]	394.7±30.0 ºC	324.1±17.0 ºC
Molecular Weight[1, 4]	250.16	214.5
Vapor Pressure[2]	6.13×10^{-7} Torr Temp: 25 ºC	1.03×10^{-4} Torr Temp: 25 ºC
Log K_{ow}[1, 4, 5]	4.77	2.88
pK_a[1]	4.42	3.2
k_{O3}[3, 5]	2.0×10^{3} $M^{-1}s^{-1}$	20 $M^{-1}s^{-1}$
K_{OH}[3]	1.0×10^{10} $M^{-1}s^{-1}$	4.7×10^{9} $M^{-1}s^{-1}$
K_{oc}[4]	430 mL·g C^{-1}	-
Bioconcentration Factor[2]	1100-6.39 (1≤pH≤7, 25°C); 1 (8≤pH≤10, 25°C)	40.7-5.44 (1≤pH≤4, 25°C); 1 (5≤pH≤10, 25°C)
Structural Features[1]	Aromatic ring, carboxylic acid, ether	Aromatic ring, carboxylic acid, ether

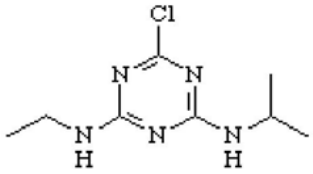
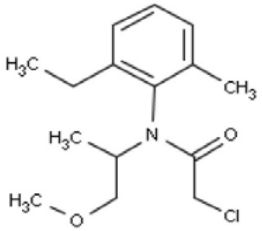
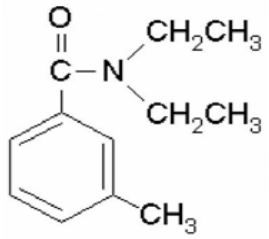
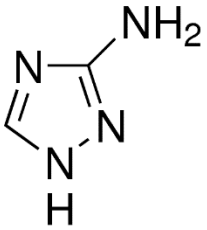
Source: [1] Snyder et al. (2007a); [2] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [3] Nanaboina et al. (2010); [4] Hazardous Substances Data Bank (2016); [5] Huber et al. (2005).

430 mL·g C^{-1} (Hazardous Substances Data Bank, 2016) may be easily removed through GAC. Gemfibrozil has structural features, including an aromatic ring, a carboxyl group, and ether (Table 2.6). The carboxyl group is an electron-withdrawing functional group indicative of potentially a lower efficiency with ozonation (Nakada et al., 2007). The rate constant for gemfibrozil is 2.0×10^3 $M^{-1}s^{-1}$ (Table 2.6), moderately reactive with ozone (Westerhoff et al., 2005)

2.3.6 Pesticides

Atrazine, metolachlor, DEET, aminotriazole were the most frequently detected pesticides in effluent of WWTPs, surface water, raw drinking water, and even in finished drinking water and tap water (Benotti et al., 2009; Focazio et al., 2008; Glassmeyer et al., 2005; Kolpin et al., 2002; Snyder et al., 2007a; Zgheib et al., 2012). DEET is an insect repellent which is widely used in the U.S. with an annual usage in excess of 1.8 million kg (Costanzo et al., 2007). Atrazine and metolachlor are widely used pesticides in the U.S. as well. The large usage of these three pesticides is one of the reasons why they are detected with great frequency in aquatic environments. The properties of these pesticides are the second most important reason (Table 2.7). Atrazine and aminotriazole both have a triazine ring, but atrazine does not has aromatic moieties (electron donors), indicating a slower reaction with ozone as seen with the rate constant (k_{O3} = 6.0-7.9 $M^{-1}s^{-1}$) (Table 2.7). Furthermore, amide moieties are not reactive with ozone (Nakada et al., 2007). Both metolachlor and DEET have amide on their aromatic rings, suggesting that they may be difficult to break down with ozone. Atrazine has a large K_{ow} and low aqueous solubility, which demonstrates its hydrophobicity and relatively low biodegradability. On the other

Table 2.7 Properties of Pesticides

Pesticides	Atrazine	Metolachlor	DEET	Aminotriazole
Structure[1]				
Chemical Name	6-chloro-N-2-ethyl-N4-(1-methylethyl)-1,3,5-triazine-2,4-diamine	2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)-acetamide	N,N-diethyl-3-methyl-benzamide	3-amino-1,2,4-triazole
Molecular Formula[1]	$C_8H_{14}ClN_5$	$C_{15}H_{22}ClNO_2$	$C_{12}H_{17}NO$	$C_2H_4N_4$
Aqueous Solubility[1,2,11]	Value: 34.7 mg/L Temp: 26 ºC	Value: 530 mg/L Temp: 20 ºC	Value: 912 mg/L Temp: 25 ºC	Values: 280,000 mg/L Temp: 25 ºC
Boiling Point[3]	368.5±25.0 ºC	406.8±45.0 ºC	297.5±0.0 ºC	347.2±25.0 °C
Molecular Weight[1]	215.1 g/mol	283.8 g/mol	191.13 g/mol	84.08 g/mol
Vapor Pressure[3]	1.27×10^{-5} Torr Temp: 25 ºC	7.91×10^{-7} Torr Temp: 25 ºC	1.53×10^{-3} Torr Temp: 25 ºC	5.45×10^{-5} Torr Temp: 25 ºC
Log K_{ow}[1,11]	2.61	3.13	2.18	-0.97
pK_a[1,3]	1.7	-1.34	0.67	11.14
k_{O3}[4,6,7]	6.0-7.9 $M^{-1}s^{-1}$	3.0 $M^{-1}s^{-1}$	1.0 $M^{-1}s^{-1}$	–
K_{OH}[4,5,6,7]	2.4×10^{9}-3.0×10^{9} $M^{-1}s^{-1}$	–	5.0×10^{9} $M^{-1}s^{-1}$	–
K_{oc}[8,9,10]	23-101 mL·g C^{-1}	–	300 mL·g C^{-1}	–
Structural Features[1]	Triazine ring, secondary amines, chlorine	Aromatic ring, amide, methoxy, chlorine	Aromatic ring, amide	Triazine ring, amines

Source: [1] Snyder et al. (2007a); [2] Rivard (2003); [3] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [4] Hollender et al. (2009); [5] Huber et al. (2003); [6] Westerhoff et al. (2005); [7] Acero et al. (2000); [8] Nkedi-Kizza et al. (2006); [9] Drori et al. (2005); [10] Hazardous Substances Data Bank (2016); [11] Fontecha-Cámara et al. (2007).

hand, though metolachlor and DEET have relatively greater aqueous solubilities than atrazine, their K_{ow} values are still very large, suggesting the poor biodegradability. Moreover, atrazine has a K_{oc} ranging from 23 to 101 mL·g C^{-1} lower than the K_{oc} reported for DEET (300 mL·g C^{-1}) (Drori et al., 2005; Hazardous Substances Data Bank, 2016; Nkedi-Kizza et al., 2006), suggesting lower removal through GAC. Metolachlor could not be analyzed by the selected lab. Therefore, atrazine, aminotriazole and DEET were studied in this research.

2.3.7 Steroids

In this study, steroids include sterols (steroid alchohols) and steroid hormones. Cholesterol and coprostanol are the most frequently detected natural sterols in the aquatic environment (Focazio et al., 2008; Kolpin et al., 2002; Glassmeyer et al., 2005). Cholesterol was detected in WWTP effluents (Glassmeyer et al., 2005) and surface water samples (Koplin et al., 2002) with great frequency, approximately 90% and 84%, respectively. It was also found in raw drinking water with a frequency of 42% (Focazio et al., 2008). Coprostanol has been observed frequently as well in WWTP effluents (60%) (Glassmeyer et al., 2005), surface water (86%) (Koplin et al., 2002), and in raw drinking water (18%) (Focazio et al., 2008).

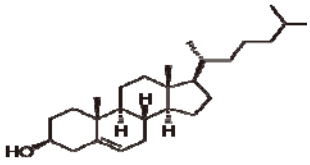
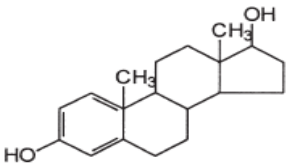
17β-Estradiol and progesterone are two steroid hormones that have been detected in surface water and drinking water as well, although the frequency of detection was not as great as the others above, approximately 7% (Kolpin et al., 2002; Tabe et al., 2009; Snyder et al., 2007a; Benotti et al., 2009). Because cholesterol and coprostanol have similar structures (aliphatic rings), and 17β-estradiol and progesterone have similar

structures (aliphatic rings), cholesterol and 17β-estradiol were selected to be representive of groups of steroids. The properties of cholesterol and 17β-estradiol reveal both have aliphatic moieties, expected to react with molecular ozone with large rate constants (Reungoat et al., 2010) (Table 2.8). Both steroid hormones and natural steroids have high K_{ow} values, indicating hydrophobicity. The aqueous solubilities of these two steroids are also relatively low, suggesting resistance to biodegradability. These properties demonstrate resistance to biological treatment and persistence in water systems. Compared to other compounds studied in this work, 17β-estradiol has a relatively high K_{oc} (3700-10,000 mL·g C^{-1}) (Yamamoto et al., 2005; Carballa et al., 2008; Karnjanapiboonwong et al., 2010), suggesting potentially significant removal through GAC. Cholesterol however cannot be detected by the selected lab. As a result, 17β-estradiol was studied.

2.3.8 Others

Some other PPCPs, though not always selected as the target compounds for analysis, also need to be considered because of their high frequency of detection. TCEP is a flame retardant that has been frequently observed in wastewater effluents, surface water, and drinking water systems (Snyder et al., 2007a; Benotti et al., 2009; Focazio et al., 2008; Kolpin et al., 2002; Glassmeyer et al., 2005). TCEP is a synthetic, phosphate-based chemical added to plastics, fabrics, and foams to reduce their flammability. TCEP production in 1975 was estimated to be more than 908 kg (2001 lbs) and is currently in the range of 500,000 to 1,000,000 pounds annually (U.S. Department of Health and Human Services, 2009). The significant production is one of the reasons why TCEP has

Table 2.8 Properties of Steroids

Steroids	Cholesterol	17β-estradiol
Structure[6]		
Chemical Name	(3β)-cholest-5-en-3-ol	(17β)- Estra-1,3,5(10)-triene-3,17-diol
Molecular Formula	$C_{27}H_{46}O$	$C_{18}H_{24}O_2$
Aqueous Solubility[1,4,8]	Value: 0.095 mg/L Temp: 30 º C	Value: 3.6 mg/L
Boiling Point[7]	480.6±14.0 º C	445.9±45.0 ºC
Molecular Weight	386.65 g/mol	272.38g/mol
Vapor Pressure[7]	2.95×10^{-11} Torr Temp: 25 ºC	9.82×10^{-9} Torr Temp: 25 ºC
Log K_{ow}[2,3,5,6]	8.74	4.01
pK_a[3,7]	15.03	10.4
k_{O3}[9]	–	1.0×10^{6} $M^{-1}s^{-1}$ (20 ºC)
K_{OH}[9]	–	1.41×10^{10} $M^{-1}s^{-1}$
K_{oc}[10,11,12]	–	3700-10000 mL·g C^{-1}
Structural Features[6]	Aliphatic rings	Phenol, alcohol, aliphatic rings

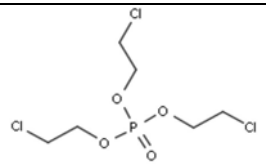
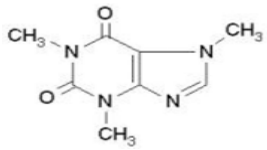
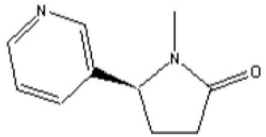
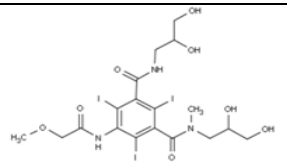
Source: [1] Human Metabolome Database (2016); [2] Elkins and Mullis (2006); [3] Nghiem et al. (2004); [4] DrugBank (2016); [5] Yoon et al. (2007); [6] Snyder et al. (2007a); [7] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [8] Hakk et al. (2005); [9] Broséus et al. (2009); [10] Yamamoto et al. (2005); [11] Carballa et al. (2008); [12] Karnjanapiboonwong et al. (2010).

been frequently detected. The most significant detection was 40% of the 15 tap water samples studied by Benotti et al. (2009) resulting in a potential risk to human health. Thus TCEP is already banned or restricted by several states in the US. During the 2011 legislative session, New York became the first state to prohibit the sale and products containing TCEP intended for use by a child under three years of age (New York Bill A6195-2011). The ban begins December 1, 2013, and violators are subject to civil penalties. Washington State requires manufacturers to report to the State, beginning August 2012, any children's product that contains intentionally added TCEP (Chapter 173-334 WAC, Children's Safe Product - Reporting Rule).

Caffeine is a stimulant widely consumed in the U.S., with sources from coffee, tea, chocolate, soft drinks, as well as others. This usage may be the most critical reason why caffeine was frequently detected in wastewater effluents, surface water, and finished drinking water systems (Glassmeyer et al., 2005; Kolpin et al., 2002; Snyder et al., 2007a). The detection frequency of caffeine in finished drinking water is 60% (Snyder et al, 2007a). Cotinine, a metabolite of nicotine, was detected in wastewater effluents, surface water, and drinking water resources with frequencies of 92.5%, 38.1%, and 35.1, respectively (Focazio et al., 2008; Glassmeyer et al., 2005; Kolpin et al., 2002). Iopromide is an x-ray contrast agent, which was detected in both raw and finished drinking water, with frequencies of 70% and 65%, respectively (Snyder et al., 2007a), indicating a large threat that iopromide may pose to the environment.

TCEP, caffeine, and cotinine have small K_{ow} values (Table 2.9), are hydrophilic compounds, and yet they are frequently detected in water systems, which may result from their large usage. Interestingly, iopromide has a relatively small K_{ow} value, high

Table 2.9 Properties of Other PPCPs

Compounds	TCEP	Caffeine	Cotinine	Iopromide
Structure[1]				
Chemical Name	2-chloro-phosphate (3:1) ethanol	3,7-dihydro-1,3,7-trimethyl-1H-Purine-2,6-dione	1-methyl-5-(3-pyridinyl)-, (5S)-2-Pyrrolidinone	N1,N3-bis(2,3-dihydroxypropyl)-2,4,6-triiodo-5-[(2-methoxyacetyl)amino]-N1-methyl-1,3-Benzenedicarboxamide
Molecular Formula[1]	$C_6H_{12}Cl_3O_4P$	$C_8H_{10}N_4O_2$	$C_{10}H_{12}N_2O$	$C_{18}H_{24}I_3N_3O_8$
Aqueous Solubility[1,3,4]	Value: 7,000 mg/L	Value: 2.16×10^4mg/L Temp: 25 º C	Value: 1.17×10^5 mg/L	Value: 23.8 mg/L Temp: 25 ºC
Boiling Point[6]	347.4±0.0 º C	416.8±37.0 ºC	316.0±0.0 º C	840.9±65.0 ºC
Molecular Weight[1]	285.5 g/mol	194.1 g/mol	176.1 g/mol	791.11 g/mol
Vapor Pressure[6]	1.08×10^{-4} Torr Temp: 25 º C	3.72×10^{-7} Torr Temp: 25 º C	4.21×10^{-4} Torr Temp: 25 º C	5.00×10^{-30} Torr Temp: 25 ºC
Log K_{ow}[1,4]	1.44	-0.07	0.04	-2.05
pK_a[1,2,4]	7.6	10.4	4.72	-2.60
k_{O3}[7,8,9,11]	–	$6.50\ (\pm0.2)\times10^2\ M^{-1}s^{-1}$ (20 ºC)	–	$< 0.8\ M^{-1}s^{-1}$ (pH 7, 20ºC)
K_{OH}[7,8,9,10,11,12]	$5.60\ (\pm0.21)\times10^8\ M^{-1}s^{-1}$	5.9×10^9-$6.9\times10^9\ M^{-1}s^{-1}$	–	$3.3\ (\pm0.6)\times10^9\ M^{-1}s^{-1}$ (pH 7, 25ºC)
K_{oc}[13,14]	67 mL·g C^{-1}	22 mL·g C^{-1}	130 mL·g C^{-1}	0.005 mL·g C^{-1}
Structural Features[1]	Phosphate, chlorines, aliphatic structure	Xanthine ring	Ketone, pyridine ring	Aromatic ring, iodines, alcohols, methoxy, amides

Source: [1] Snyder et al. (2007a); [2] Dmitrenko et al. (2007); [3] Trenholm et al. (2006); [4] Cone and Huestis (2007); [5] Human Metabolome Database (2016); [6] Calculated using Advanced Chemistry Development (ACD/Labs) Software V11.02 (© 1994-2016 ACD/Labs); [7] Hollender et al. (2009); [8] Huber et al. (2003); [9] Huber et al. (2005); [10] Westerhoff et al. (2005); [11] Broséus et al. (2009); [12] Watts and Linden (2009); [13] Hazardous Substances Data Bank (2016); [14] Carballa et al., 2008.

solubility, and was always detected when analyzed. These four compounds have relatively low K_{oc} values (Table 2.9). The K_{oc} for TCEP, caffeine, and cotinine are 67 mL·g C^{-1}, 22 mL·g C^{-1}, and 130 mL·g C^{-1}, respectively. Iopromide has a reported K_{oc} as low as 0.005 mL·g C^{-1} (Carballa et al., 2008; Hazardous Substances Data Bank, 2011). Therefore, GAC may not be an effective treatment process for these four compounds. TCEP has an aliphatic structure with chlorine functional groups, which are polar. TCEP has been shown to be resistant to oxidation using chlorine or ozone (Westerhoff et al., 2005). Caffeine has a k_{O3} of a 6.4×10^{2} $M^{-1}s^{-1}$ (Table 2.9), indicating a relatively slower reaction with ozone. Caffeine has purine base (xanthine ring), alkyl groups, and C=C double bond. C=C double bond and alkyl are electron donors, which are amenable to ozonation (Nakada et al., 2007). Cotinine has ketone and a pyridine ring. The k_{O3} of iopromide is relatively small, less than 0.8 $M^{-1}s^{-1}$. Therefore, the reaction of ozone with iopromide is very slow. Iopromide exhibits three nitrogen atoms as amides, which have a very low reactivity to ozone (Huber et al., 2003).

2.3.9 Summary

Eleven classes of PPCPs were reviewed in this section. Their general physicochemical properties were considered including aqueous solubility, K_{ow}, K_{oc}, ozone rate constant k_{O3}, and structure. Aqueous solubility and K_{ow} reflect properties that are related to biodegradability as well as mobility. The greater the K_{ow}, the more resistant the compound is to biodegradation. K_{oc} is a partition coefficient reflecting the distribution of an organic compound between the solid organic carbon and the aqueous phase. Compounds with larger K_{oc} values are more likely to be adsorbed. Similarly, compounds

with larger ozone rate constants are relatively fast-reacting compounds with ozone and more likely to be removed by ozonation. In contrast, compounds with smaller ozone rate constants have relatively less removal efficiencies by ozonation. The structure is an important factor when determining removal efficiency. The compounds with electron donors in their structure are more reactive with ozone, suggesting possible removal by ozonation.

Usage and properties by classes are two important factors that can determine whether a PPCP can be degraded through wastewater treatment processes or in natural aquatic environments. Significant usage has been found to be directly related to occurrence of a number of PPCPs, such as antibiotics (sulfamethoxazole, and erythromycin), stimulants (caffeine), and pesticides. The physicochemical properties are important when considering the potential behavior of PPCPs in the environment and in treatment systems with respect to resistance to treatment, persistence, and biodegradability. The structure is a key factor that affects the removal efficacy of the treatment processes. Occurrence is the basis for whether a PPCP can be found in water cycle resulting in environmental exposure. Therefore, usage, occurrence, and properties were critical factors considered as criteria for establishing indicator compounds in this work. In the following section, the efficacy of treatment processes is reviewed.

2.4 Efficacy of Treatment Technologies

Conventional and advanced treatment processes need to be evaluated for their effectiveness in removing diverse groups of PPCPs, as occurrences in the drinking water distribution systems have been observed (Benotti et al., 2009). Conventional treatment

processes include coagulation, chemical softening, flocculation, filtration, and disinfection. Advanced processes often involve GAC adsorption, nanofiltration, ozonation, UV irradiation, advanced oxidation (ozone/H_2O_2 or UV/H_2O_2) and biological degradation. Snyder et al. (2007a) determined the degree to which conventional and advanced water treatment processes were capable of removing PPCPs. The efficacy was (Tables 2.10 and 2.11) examined to some degree through bench and pilot scale treatment studies as well as in considering occurrence and removal of target analytes in full-scale drinking water and water reuse facilities. Atrazine (herbicide), iopromide (contrast medium), lindane (insecticide), meprobamate (antidepressant), trimethoprim (antibiotic), and TCEP (fire retardant) proved to be the more recalcitrant of the compounds evaluated (Tables 2.10 and 2.11).

For example, powdered activated carbon and ozonation plus H_2O_2 are the only two processes that were relatively effective (50-80% removed – medium to high level) for atrazine. Lindane (an insecticide) was only removed to a medium-high level by powdered activated carbon, while other treatment processes resulted in a low removal rate (<20%, or 20% to 50% removed). UV disinfection with a dosage of 40 mJ/cm^2 (millijoules per square centimeter) provides the least PPCP removal (<20% removed for all target compounds). However, the application of higher UV doses (439 mJ/cm^2) greatly increased the removal of majority target compounds, with only six compounds (TCEP, musk ketone, DEET, metolachlor, and caffeine) poorly removed (<20% removed). UV with H_2O_2 provides better PPCP removal compared to high UV dosage, only TCEP and lindane were poorly removed (20% removed). Magnetic ion-exchange media (MIEX) provide minimal target compound removal. Triclosan and diclofenac were

Table 2.10 Summary of Percent Removal by Coagulation, Chlorine Oxidation, Membrane, and Magnetic Ion-exchange (Snyder et al., 2007a)

Compounds	Coagulation	PAC	Cl_2 3mg/L	NH_2Cl 3mg/L	Membrane		MIEX
	With Alum or Ferric Chloride		Ambient pH		UF	NF	
Analgesics							
Acetaminophen	<20%	50-80%	>80%	>80%	<20%	20-50%	<20%
Diclofenac	<20%	20-50%	>80%	50-80%	<20%	50-80%	>80%
Hydrocodone	<20%	50-80%	>80%	20-50%	<20%	50-80%	<20%
Ibuprofen	<20%	<20%	<20%	<20%	<20%	50-80%	20-50%
Naproxen	<20%	20-50%	>80%	<20%	<20%	20-50%	50-80%
Antibiotics							
Erythromycin	<20%	20-50%	>80%	<20%	20-50%	>80%	20-50%
Sulfamethoxazole	<20%	20-50%	>80%	<20%	20-50%	50-80%	20-50%
Trimethoprim	<20%	50-80%	>80%	<20%	<20%	50-80%	<20%
Antiepileptic							
Carbamazepine	<20%	50-80%	<20%	<20%	<20%	50-80%	<20%
Dilantin	<20%	20-50%	<20%	<20%	<20%	50-80%	20-50%
Antidepressants							
Diazepam	<20%	50-80%	20-50%	<20%	20-50%	50-80%	<20%
Fluoxetine	<20%	>80%	<20%	<20%	>80%	>80%	<20%
Meprobamate	<20%	20-50%	<20%	<20%	<20%	50-80%	<20%
Antifungal							
Triclosan	<20%	>80%	>80%	>80%	>80%	>80%	>80%
Contrasts Media							
Iopromide	<20%	<20%	<20%	<20%	<20%	>80%	<20%
Fire Retardant							
TCEP	<20%	20-50%	<20%	<20%	<20%	50-80%	<20%
Hemorrheologic Agent							
Pentoxifylline	<20%	50-80%	20-50%	<20%	<20%	50-80%	<20%
Lipid Regulators							
Gemfibrozil	<20%	20-50%	50-80%	<20%	<20%	50-80%	20-50%

Table 2.10 Summary of Percent Removal by Coagulation, Chlorine Oxidation, Membrane, and Magnetic Ion-exchange (Snyder et al., 2007a) (Continued)

Compounds	Coagulation	PAC	Cl_2 3mg/L	NH_2Cl 3mg/L	Membrane		MIEX
	With Alum or Ferric Chloride		Ambient pH		UF	NF	
Musk							
Galaxolide	<20%	50-80%	20-50%	20-50%	20-50%	50-80%	20-50%
Musk Ketone	<20%	50-80%	>80%	<20%	20-50%	>80%	50-80%
PAH							
Benzo(a)pyrene	50-80%	>80%	>80%	50-80%	>80%	>80%	<20%
Fluorene	<20%	>80%	<20%	<20%	>80%	>80%	20-50%
Pesticides							
Atrazine	<20%	50-80%	<20%	<20%	<20%	50-80%	<20%
DDT	20-50%	50-80%	<20%	<20%	>80%	>80%	<20%
DEET	<20%	20-50%	<20%	<20%	<20%	50-80%	<20%
Lindane	<20%	50-80%	<20%	<20%	20-50%	50-80%	<20%
Metolachlor	<20%	20-50%	<20%	<20%	20-50%	50-80%	<20%
Steroids							
Androstenedione	<20%	50-80%	<20%	<20%	20-50%	50-80%	<20%
Estradiol	<20%	50-80%	>80%	>80%	20-50%	50-80%	20-50%
Estriol	<20%	20-50%	>80%	>80%	<20%	50-80%	<20%
Steroids							
Estrone	<20%	50-80%	>80%	>80%	20-50%	50-80%	<20%
Ethynyl Estradiol	<20%	50-80%	>80%	>80%	20-50%	50-80%	20-50%
Progesterone	<20%	>80%	<20%	<20%	50-80%	50-80%	<20%
Testosterone	<20%	50-80%	<20%	<20%	20-50%	50-80%	<20%
Stimulant							
Caffeine	<20%	50-80%	<20%	<20%	<20%	50-80%	<20%
Sunscreens							
Oxybenzone	<20%	>80%	>80%	50-80%	50-80%	>80%	20-50%

PAH - Polycyclic aromatic hydrocarbons

PAC – Powered activated carbon

UF – Ultrafiltration

MF – Microfiltration

MIEX – magnetic ion-exchange media

Table 2.11 Summary of Percent Removal by Ozone and Ultraviolet/Hydrogen Peroxide Oxidation in Other Studies

Compounds	O_3 [1] 3mg/L	TOC: 6.6 to 10.3 mg/L			UV [1] 40mJ/cm^2	UV [1] 439mJ/cm^2	UV/H_2O_2 [1] 372mJ/cm^2-5mg/L
		O_3/TOC[2] 0.2	O_3/TOC[2] 0.6	O_3/TOC[2] 1.0			
Analgesics							
Acetaminophen	>95%				20-50%	>80%	>80%
Diclofenac	>95%	20-95%	>99%	>99%	50-80%	>80%	>80%
Hydrocodone	>95%				<20%	>80%	>80%
Ibuprofen	50-80%	10-20%	50-99%	90-95%	<20%	20-50%	>80%
Naproxen	>95%	20-99%	>99%	>99%	<20%	>80%	>80%
Antibiotics							
Erythromycin	>95%				<20%	50-80%	50-80%
Sulfamethoxazole	>95%	25-90%	>95%	>99%	50-80%	>80%	>80%
Trimethoprim	>95%	50-99%	>99%	>99%	<20%	20-50%	>80%
Anticonvulsant							
Dilantin		0-55%	50-85%	90-95%			
Primidone		0-45%	40-70%	85-95%			
Antiepileptic							
Carbamazepine	>95%	50-99%	>99%	>99%	<20%	20-50%	>80%
Dilantin	50-80%				<20%	50-80%	>80%
Antidepressants							
Diazepam	50-80%	20-30%	65-75%	90-99%	<20%	<20%	50-80%
Fluoxetine	>95%	25-60%	90-99%	>99%	<20%	>80%	>80%
Meprobamate	20-50%	10-25%	35-55%	60-80%	<20%	<20%	20-50%
Antifungal							
Triclosan	>95%	45-95%	>95%	>95%	50-80%	>80%	>80%
β-blocker							
Atenolol		20-50%	80-99%	>99%			
Contrasts Media							
Iopromide	20-50%	5-15%	20-40%	60-80%	<20%	50-80%	50-80%
Fire Retardant							
TCEP	<20%	5-10%	0-10%	10%	<20%	<20%	<20%
TCPP		0-15%	0-15%	0-20%			
Hemorrheologic Agent							
Pentoxifylline	>80%				<20%	20-50%	50-80%

Table 2.11 Summary of Percent Removal by Ozone and Ultraviolet/Hydrogen Peroxide Oxidation in Other Studies (Continued)

Compounds	O_3 [1] 3mg/L	TOC: 6.6 to 10.3 mg/L			UV [1] 40mJ/cm^2	UV [1] 439mJ/cm^2	UV/H_2O_2 [1] 372mJ/cm^2-5mg/L
		O_3/TOC[2] 0.2	O_3/TOC[2] 0.6	O_3/TOC[2] 1.0			
Hemorrheologic Agent							
Pentoxifylline	>80%				<20%	20-50%	50-80%
Lipid Regulators							
Gemfibrozil	>95%	30-90%	>99%	>99%	<20%	20-50%	>80%
Musk							
Galaxolide	>80%				<20%	20-50%	50-80%
Musk Ketone	20-50%				<20%	<20%	50-80%
PAH							
Benzo(a)pyrene	>80%				<20%	50-80%	50-80%
Fluorene	>80%				<20%	50-80%	20-50%
Pesticides							
Atrazine	20-50%	5-25%	25-50%	60-99%	<20%	50-80%	50-80%
DDT	20-50%				<20%	20-50%	>80%
DEET	50-80%	20-50%	50-75%	85-95%	<20%	<20%	50-80%
Lindane	<20%				<20%	20-50%	<20%
Metolachlor	>80%				<20%	<20%	50-80%
Steroids							
Androstenedione	>80%				<20%	<20%	50-80%
Estradiol	>80%				<20%	>80%	>80%
Estriol	>95%				<20%	>80%	>80%
Estrone	>95%	65-99%	>99%	>99%	<20%	>80%	>80%
Ethynyl Estradiol	>95%				<20%	>80%	>80%
Progesterone	>80%				<20%	20-50%	>80%
Testosterone	>80%				<20%	20-50%	>80%
Stimulant							
Caffeine	>80%	20-55%	77-99%	>99%	<20%	<20%	50-80%
Sunscreens							
Benzophenone		0-25%	35-65%	75-99%			
Oxybenzone	>95%				<20%	>80%	>80%

PAH - Polycyclic aromatic hydrocarbons; mJ/cm^2 – millijoules per square centimeter;

Source: [1] Synder et al. (2007b); [2] Wert et al. (2009).

the only two compounds removed by over 80%, while the majority of the compounds showed less than 20% removal. Furthermore, TCEP (a fire retardant) was poorly removed through all the treatment processes considered, with a maximum of 50% removed, and a minimum of less than 20%. Comparing all the processes evaluated, UV and UV plus H_2O_2 were effective in achieving some of the greatest removal efficiencies. Almost all the target compounds tested could be removed to some degree by these treatment technologies, with the exception of lindane (an insecticide), TCEP (a fire retardant), and musk ketone (a fragrance).

Increased removals were observed with increasing ozone dosage (Wert et al., 2009) (Table 2.10). Wert et al. (2009) investigated three ozone dosages: 0.2 mg O_3/mg TOC, 0.6 mg O_3/mg TOC, and 1.0 mg O_3/mg TOC at in a pilot plant study where tertiary-treated effluent from three WWTPs with TOC ranging from 6.6 to 10.3 mg/L were tested. Removals of 23 PPCPs through ozonation were evaluated. The most recalcitrant compounds were atrazine, iopromide, tri(1-chloro-2-propyl) phosphate (TCPP), and TCEP with removals less than 60% even at the greatest ozone dosage of 9.27±2.31 mg/L. Thirteen compounds were removed at greater than 80% with two of the ozone dosages of 5.87±1.63 mg O_3/L and 9.27±2.31 mg O_3/L, while all 23 compounds were removed at less than 80% for the lowest ozone dosage of 2.27±0.49 mg O_3/L. As emerging contaminants show resistance to water treatment processes, they are released to the environment and cause potential risk to the aquatic environment and human health. In the next section the adverse effects of the PPCPs are reviewed.

2.5 Adverse Effects of PPCPs

While there are hundreds of emerging contaminants observed throughout the water cycle and the extent of studies is increasing, more work is needed in assessing effects of the low concentrations found for the compounds as well as the effect of mixtures on human health and the aquatic environment. Again, little is known about the potential effect of mixtures especially with sensitive populations. Nevertheless, a number of studies have been conducted that focus on PPCPs (Table 2.12). Many researchers have investigated the effect of the wastewater treatment processes on the prevalence of antibiotic resistant bacteria in the plants and receiving waters (Guardabassi et al., 2002; Silva et al., 2006, 2007). A number of stream surveys documented the significant prevalence of native bacteria that display resistance to a wide array of antibiotics including vancomycin (Ash et al., 1999). Bacteria isolated from wild populations of resident Canada Geese near Chicago, Illinois, are reported to be resistant to ampicillin, tetracycline, penicillin, and erythromycin (Eichorst et al., 1999). Lateef (2004) examined 25 bacterial strains isolated from a pharmaceutical company's effluent and their resistance to commonly used antibiotics. About 80% of the isolates were resistant to amoxicillin, 76% to nitrofurantoin, 64% to cotrimoxazole, and 12% to gentamicin. The effluents contaminate streams, food on the farms (using streams for irrigation), and inadvertently reach humans. WWTPs are important reservoirs of bacteria in which antibiotic resistant organisms persist and may be released to the environment. As environmental compartments are interconnected, including municipal sewage and surface water, WWTPs may facilitate the spread of antibiotics, antibiotic resistance genes, and antibiotic resistant bacteria (Zhang et al., 2009). Zhang et al. (2009) found the frequency of antibiotic resistant bacteria to rifampin,

Table 2.12 Adverse Effects from Exposure to Trace PPCPs

Adverse Effects	Group of Compounds Studied	References
Antibiotic Resistance	Antibiotics	[1] – [7]
Intersex in Fish	Endocrine Disrupting Chemicals: synthetic estrogen	[8] – [11]
Hyperglycemia and Hepatic Histological Abnormalities	Analgesics, Antibiotics, Antiepileptic, Nicotine Metabolite, and Psychomotor Stimulant	[12]

Source: [1] Czekalski et al., 2012; [2] Eichorst et al., 1999; [3] Guardabassi et al., 2002; [4] Lateef et al., 2004; [5] Silva et al., 2006; [6] Silva et al., 2007; [7] Young et al., 2013; [8] Hinck et al., 2009; [9] Kidd et al., 2007; [10]; Orlando et al., 2004; [11] Tetreault et al., 2011; [12] Buron et al., 2016.

chloramphenicol, amoxicillin/clavulanic acid, was greater downstream than upstream in the river receiving a wastewater effluent discharge. Such effluents likely contribute to the dissemination of antibiotic resistance in the aquatic environment. These reports suggest that the occurrence of antibiotic resistant bacteria is much greater than expected where uncontrolled release of antibiotics into the environment may prompt the increase in resistance. Excluding the significance of antibiotics themselves in the environment, their occurrence implicates the presence of other PPCPs and suggests further adverse effects on humans including resistance resulting in ineffective antibiotics and the formation of superbugs.

During the last decade, a significant amount of research has helped clarify the potential risk of exposure to endocrine-disrupting chemicals (EDCs) (Hinck et al., 2009; Jobling et al., 1998, 2002, 2009; Kidd et al., 2007). Adverse effects on fish populations have been frequently recorded downstream of sources of aquatic contamination. Masculinization of female fish was one of the first recorded effects, when mosquito fish downstream of a pulp and paper mill were found to have male secondary sexual characteristics (Howell et al., 1980). The converse effect has been frequently reported as well in freshwaters downstream of wastewater treatment plants, where feminization of male fish and mollusks through estrogen contamination in the effluent has a pronounced effect. Feminization of reproductive ducts in male fish, appearance of oocytes in male gonads, and the characteristic production of the female egg protein vitellin in male fish exposed to wastewater from sewage treatment plants has been recorded (Rodgers-Gray et al., 2001). Feminization of fish in English rivers is widespread, attributed to estrogen in sewage effluent (Jobling et al., 1998). Jobling et al. were the first to document an

example of a widespread sexual disruption in wild populations of any vertebrate demonstrating that reproductive and developmental effects do result from exposure to ambient levels of chemicals present in rivers. A 7-year, lake experiment was conducted in northwestern Ontario, Canada (Kidd et al., 2007), for determining the adverse impact of chronic exposure to a complex mixture of compounds containing estrogens and estrogen mimicking compounds on fish populations. The results showed that chronic exposure of fathead minnows to low concentrations (5-6 ng/L) of 17-α-ethynylestradiol led to feminization of males. Impacts on gonadal development as evidenced by intersex in males and altered oogenesis in females, and, ultimately, a near extinction of this species from the lake, demonstrated that what is considered low concentrations of estrogen and estrogen mimicking compounds may have profound developmental effects on wild fish populations. Hinck et al. (2009) found that intersex occurred in 3% of freshwater fish evaluated in nine river basins in the US. Intersex was most prevalent in large mouth bass (8-91% per site) and small mouth bass (14-73% per site). The authors hypothesized that the prevalence of intersex may be related to the season, the age of fish, and the endocrine active compounds in the environment.

Recently, the responses of mice with chronic and low exposure of pharmaceuticals were investigated (Buron et al., 2016). Hyperglycemia and hepatic histological abnormalities in mice were observed after 4 months of exposure to low dosages (10 to 1,000 µg/L) of eleven pharmaceuticals including carbamazepine, cotinine, erythromycin, and ibuprofen. These results suggested that PPCPs, even with low concentrations ranging from ng/L to µg/L, could pose a chronic adverse effects to the environment and human health. Based on the above studies, in the next section, criteria

that reflect how representative a compound or group of compounds are as indicator compounds for the PPCPs are reviewed. These criteria include usage, occurrence, resistance to treatment, persistence, and properties.

2.6 Indicator Compounds Studied: Criteria and List

Given the relatively lower concentrations as compared to typical regulated compounds, the indicator compounds are ones that need to be analyzable and that are detected frequently in water samples. Indicator compounds are also ones that would not necessarily be removed through conventional wastewater treatment processes. Additionally, these compounds represent PPCPs that are resistant to treatment and used in significant volume. For example, acetaminophen is a widely used analgesic ranked 3rd in the U.S. (in 2008) by prescriptions dispensed. In our earlier work (EST 1001) (Zhang et al., 2016a), PPCPs were refined based on their persistence in wastewater treatment effluents, surface water, and drinking water treatment systems. From the usage, occurrence, persistence, resistance to treatment, and properties, a list of indicator compounds was obtained (Tables 2.13 and 2.14). Compounds with similar physical and chemical properties were eliminated from the list, as these compounds are expected to behave similarly in treatment processes. For example, natural sterols cholesterol and coprostanol have similar structures; they were also detected at relatively consistent frequencies (Focazio et al., 2008; Glassmeyer et al., 2005; Kolpin et al., 2002). Therefore, coprostanol was eliminated from the list. Other compounds removed included diclofenac, ketoprofen, and naproxen (analgesics); gemfibrozil (blood lipid regulator), and progesterone (steroid hormone). Because atenolol has been routinely observed at much

Table 2.13 Concentration Range of Indicator Compounds Detected in Influent and Effluent of WWTP, SW, DW

Classes	Compounds	WWTP Inf. ng/L	WWTP Effluent ng/L	SW ng/L	DW ng/L	References
Analgesics	Acetaminophen	ND-19500	ND-6200	ND-250	1.1-9.5	[1],[2],[3],[4],[5],[6],[7],[8],[9]
	Ibuprofen	ND-143000	ND-15778	ND-2796	ND-32	[1],[2],[3],[4],[7],[10],[11],[12],[13],[14],[15],[16]
Antibiotics	Erythromycin	71-250	100-290	ND-438	1-3.5	[3],[4],[7],[13],[15],[17]
	Sulfamethoxazole	150-960	ND-2200	ND-820	0.39-173	[1],[3],[4],[7],[8],[11],[15][18]
	Trimethoprim	40-650	4-414	ND-310	1-19	[1],[3],[4],[7],[11],[12],[13][15],[18]
Antiepileptic	Carbamazepine	ND-9420	ND-970	ND-1238	ND-43.2	[1],[2],[3],[4],[8],[10][12],[15]
Beta-Blockers	Atenolol	50-1400	50-1200	ND-1150	2.8-48	[1],[3],[4],[12],[18]
Blood Lipid Regulators	Gemfibrozil	ND-360	ND-1220	ND-320	1.2-34	[1],[2],[4],[5],[7],[10],[11],[12],[13],[14],[15],[18]
Fire Retardant	Tri(2-chloroethyl)phosphate	–	–	100-540	<RL-720	[7],[19],[20],[21],[22]
Nicotine Metabolite	Cotinine	–	–	21-1030	100	[19],[21],[22]
Pesticides	Aminotriazole	–	–	30-3,250	–	[24]
	Atrazine	–	–	<RL-460	1.3-930	[7],[19],[21]
	N,N-Diethyl-meta-toluamide	–	–	97-2100	<RL-110	[7],[19],[21]
Steroids	17β-Estradiol	33-<100	<1	ND-93	<RL	[7],[14],[20],[22]
Psychomotor Stimulant	Caffeine	2700-16300	72-4520	<RL-7990	1.5-270	[5],[7],[10],[16],[19],[21],[22],
X-ray Contrast Agent	Iopromide	17-564	<1-79	NA-120	NA-86	[7],[23]

WWTP – wastewater treatment plant; Inf – influent; SW – surface water; DW – drinking water; ND – not detected; RL – reporting limit.

Source: [1]Batt et al. (2008); [2] Han et al. (2006); [3] Petrovic et al. (2006); [4] Gros et al. (2006); [5] Ternes et al. (2001); [6] Koutsouba et al. (2003); [7] Snyder et al. (2007a); [8] Bartelt-Hunt et al. (2009); [9] Conley et al. (2008); [10] Rabiet et al. (2006); [11] Gagné et al. (2006); [12] Lavén et al. (2009); [13] Roberts et al. (2006); [14] Zhao et al. (2009); [15] Wu et al. (2009); [16] Santos et al. (2005); [17] Tixier et al. (2003); [18] Snyder et al. (2008); [19] Glassmeyer et al. (2005); [20] Benotti et al. (2009); [21] Focazio et al. (2008); [22] Kolpin et al. (2002); [23] Benner et al., 2013; [24] Zgheib et al. (2012).

Table 2.14 Summary of Properties for the Indicator Compounds

Classes	Compounds	MF	MW g/mol	Log K_{ow}	k_{O3} $M^{-1}s^{-1}$	k_{OH} $M^{-1}s^{-1}$	Koc $mL \cdot g\ C^{-1}$
Analgesics	Acetaminophen	$C_8H_9NO_2$	151.17	0.46	2.70×10^5	-	170-1300
	Ibuprofen	$C_{13}H_{18}O_2$	206.23	3.97	9.6 (±1)	6.5×10^9-$7.4\ (\pm1.2)\times10^9$	18-155
Antibiotics	Erythromycin	$C_{37}H_{67}O_{13}$	733.93	3.06	-	-	570
	Sulfamethoxazole	$C_{10}H_{11}N_3O_3S$	253.28	0.89	5.5×10^5-2.5×10^6	$5.5\ (\pm0.7)\times10^9$	72
	Trimethoprim	$C_{14}H_{18}N_4O_3$	290.32	0.91	2.7×10^5	$6.9\ (\pm0.2)\times10^9$	75
Antiepileptic	Carbamazepine	$C_{15}H_{12}\ N_2O$	236.27	2.47	3×10^5	$8.8\ (\pm1.2)\times10^9$	510
Beta-Blockers	Atenolol	$C_{14}H_{22}N_2O_3$	266.34	0.16	$1.7\ (\pm0.4)\times10^3$	$8.0\ (\pm0.5)\times10^9$	148-1700
Blood Lipid Regulators	Gemfibrozil	$C_{15}H_{22}O_3$	250.16	4.77	2.0×10^3	1.0×10^{10}	430
Fire Retardant	Tri(2-chloroethyl)phosphate	$C_6H_{12}Cl_3O_4P$	285.5	1.44	-	$5.60\ (\pm0.21)\times10^8$	67
Nicotine Metabolite	Cotinine	$C_{10}H_{12}N_2O$	176.1	0.04	-	-	130
Pesticides	Aminotriazole	$C_2H_4N_4$	84.08	-0.97	-	-	-
	Atrazine	$C_8H_{14}ClN_5$	215.1	2.61	6.0-7.9	2.4×10^9-3.0×10^9	23-101
	N,N-Diethyl-meta-toluamide	$C_{12}H_{17}NO$	191.13	2.18	1.0	5.0×10^9	300
Steroids	17β-Estradiol	$C_{18}H_{24}O_2$	386.65	8.74	-	-	-
Psychomotor Stimulant	Caffeine	$C_8H_{10}N_4O_2$	194.1	-0.07	$6.50\ (\pm0.2)\times10^2$	5.9×10^9-6.9×10^9	22
X-ray Contrast Agent	Iopromide	$C_{18}H_{24}I_3N_3O_8$	791.11	-2.05	< 0.8	$3.3\ (\pm0.6)\times10^9$	0.005

MF – molecular formula; MW – molecular weight.

higher concentrations than propranolol, it was included. Lastly, the feasibility in analyzing compounds at environmentally relevant concentrations was considered. In total, 16 PPCPs belonging to 11 classes were identified as priority indicator compounds (Tables 2.13 and 2.14). These compounds include acetaminophen and ibuprofen (analgesics); erythromycin, sulfamethoxazole, and trimethoprim (antibiotics); carbamazepine (antiepileptic); atenolol (beta-blocker); gemfibrozil (blood lipid regulator); tris(2-chloroethyl)phosphate (TCEP) (fire retardant); cotinine (nicotine metabolite); aminotriazole, atrazine, and DEET (pesticides); 17β-estradiol (steroid); caffeine (psychomotor stimulant); and, iopromide (x-ray contrast agent).

The indicator compounds selected were widely used, observed at great frequency in aqueous systems, resistant to treatment, persistent in the environment, and representative of classes of organics. Although the selected indicator compounds were observed in low concentrations (in ng/L or μg/L) in the water cycle, their effects on the environment cannot be neglected. Therefore, efficient removal of PPCPs is very important. In our early pilot plant study (Zhang et al., 2016b), the effectiveness of using treatment trains to treat PPCPs was investigated. Using conventional and advanced treatment processes, 11 to 15 indicator compounds were reduced by over 90%. These treatment trains that achieved the greatest removals involved 1. DAF followed by intermediate ozonation, dual media filtration, and virgin GAC; 2. pre-ozonation followed by DAF, dual media filtration, and virgin GAC; and, 3. DAF (with either pre- or intermediate oxidation) followed by dual media filtration and UV/H_2O_2. However, in that pilot plant study, the used GAC (in service for 3 to 4 years) was inefficient for PPCP removal as biological activity was not sufficiently developed given an inadequate period

(8 hrs) for acclimation that prevented microbial ripening. As a result, this process (i.e., BAF) was not discussed, but became an area of future work and was investigated in the current bench-scale studies.

2.7 Summary

This chapter reviews the criteria for the identification of the indicator compounds. The usage of PPCPs in the U.S.; occurrences in wastewater, surface water, and drinking water systems; physiochemical properties; adverse effects from PPCPs; and, the effectiveness of treatment processes were considered. From the sales and dispensed prescriptions in the U.S, blood lipid regulators, antidepressants, antibiotics, analgesics, beta-blockers, and antiepileptics are among the pharmaceutical classes at the top of the lists. Not surprisingly, among pharmaceuticals these groups are also the most frequently detected ones in aquatic environments, indicating a relationship between usage and occurrence. A similar relationship was found for pesticides.

PPCPs most frequently detected include acetaminophen, ibuprofen, ketoprofen, and naproxen (analgesics); erythromycin, sulfamethoxazole and trimethoprim (antibiotics); fluoxetine and diazepam (antidepressants), carbamazepine (antiepileptic); atenolol and propranolol (beta-blockers); and, clofibrate, clofibric acid, and gemfibrozil (blood lipid regulators). The frequent detection of these PPCPs demonstrates their resistance to treatment processes studied. Similar results were found for occurrence in surface water; the most frequently detected include caffeine (a nervous system stimulant); DEET (an insect repellent); carbamazepine (an antiepileptic); naproxen (an analgesic); sulfamethoxazole and trimethoprim (two antibiotics); TCEP (a fire retardant); estrone,

progesterone, cholesterol, and coprostanol (four steroids); and, gemfibrozil (a lipid regulator). Most of these PPCPs are also frequently detected in WWTP effluents, indicating not only their resistance to the treatment processes, but also the persistence in the surface water. Finally, the most important is the ultimate occurrence of PPCPs in drinking water systems, which will have a potentially direct effect on human health. Those most frequently detected in drinking water systems were herbicides (atrazine, and metolachlor), nicotine metabolite (cotinine), antiepileptics (carbamazepine), antibiotics (sulfamethoxazole and trimethoprim), lipid regulator (gemfibrozil), fire retardant (TCEP), plasticizer (bisphenol A), steroids (estrone, progesterone, cholesterol, and coprostanol), antidepressants (meprobamate), insect repellent (DEET), and analgesics (ibuprofen and naproxen). The frequent detection demonstrates ineffective treatment for these PPHCPs, especially for atrazine, carbamazepine, TCEP, DEEP, ibuprofen, gemfibrozil, sulfamethoxazole, and trimethoprim. Occurrences in the water cycle reflect important classes of PPCPs that are ubiquitous and recalcitrant, useful in the establishment of indicator compounds.

The physicochemical properties of each class of PPCPs are reviewed as well. These properties are indicators for the behavior and directly impact the efficiency of treatment processes. Eleven classes of PPCPs were reviewed (analgesics, antibiotics, antiepileptic, blood lipid regulators, β-blockers, fire retardant, nicotine metabolite, pesticides, psychomotor stimulants, steroids, and x-ray contrast agent), based on those frequently detected in wastewater, surface water, and drinking water systems. Most of these PPCPs have large K_{ow} values and lower solubilities, which reflects their hydrophobicity.

Based on the criteria, usage, occurrence, physicochemical properties, persistence in aquatic environments, and resistance to treatment, the resulting PPCPs include a list of 16 priority indicator compounds belonging to 11 classes (Table 2.14). These compounds are erythromycin, sulfamethoxazole, and trimethoprim (antibiotics); acetaminophen and ibuprofen (analgesics); gemfibrozil (a blood lipid regulator); atenolol (an beta-blocker); carbamazepine (an antiepileptic); 17β-estradiol (a steriod); TCEP (a fire retardant); cotinine (a nicotine metabolite); aminotriazole, atrazine, and DEET (pesticides); caffeine (a psychomotor stimulant); and, iopromide (an x-ray contrast agent). In the following chapter, BAFs are reviewed with the operational conditions (e.g., organic requirement, support media, pre-ozonation, EBCT, and temprature) and their performance on PPCP removals.

CHAPTER 3

BIOLOGICALLY ACTIVE FILTERS (BAFS)

Biological processes have been used for decades in drinking water treatment (Zhu et al., 2010), but have only recently attracted more attention (Emelko et al., 2006; Hammes et al., 2008; Yang et al., 2011). Slow sand filters (SSFs) were the earliest application of a biological process in drinking water treatment with natural organic matter (NOM) removals down to 15±5 mg/L (Collins et al., 1992). Riverbank filtration (RBF) is another biofiltration application with total organic carbon (TOC) removals of 33 to 86% (Partinoudi and Collins, 2007). Biologically active filters (BAFs) have been demonstrated in treating biodegradable organic matter (BOM) (Carlson and Amy, 1998), total organic carbon (TOC) and dissolved organic carbon (DOC) (Moll et al., 1999; Velten et al., 2011; Yapsakli et al., 2010), assimilable organic carbon (AOC) (Chien et al., 2008; Yang et al., 2011), and PPCPs (Hallé et al., 2015; Hofmann et al., 2011; Lee et al., 2012b; McKie et al., 2016; Reungoat et al., 2011, 2012; Zearley and Summers, 2012). In the following sections, BAFs are reviewed along with organic carbon requirements, pre-treatment, support media and EBCT, biomass formation and factors impacting its development, and PPCP removal.

3.1 Performance, Organic Carbon Requirements, Pre-treatment, Support Media, and EBCT for BAFs

A number of parameters have been used to evaluate the performance of BAFs and demonstrate the organic carbon requirements. Studies have involved using total organic carbon (TOC) (Hozalski et al., 1995; Moll et al., 1999; Yapsakli et al., 2010), DOC

(Carlson and Amy, 1998; Ko et al., 2007; Velten et al., 2011), AOC (Chien et al., 2008; Liu 2002; Yang et al., 2011), turbidity (Simon et al., 2013), pre-ozonation (Reungoat et al., 2012), and EBCT (Seredyńska-Sobecka et al., 2005; Zearley and Summers, 2012). In this section, studies are reviewed on BAF performance, organic carbon requirements, pre-treatment, and EBCT.

3.1.1 TOC and DOC

DOC removal with biofiltration has been studied as a function of hydraulic loading rate (Carlson and Amy, 1998; Ko et al., 2007). Carlson and Amy (1998), for example, studied the removal of DOC through biofiltration (Table 3.1). In their work, a pilot plant study was conducted using anthracite BAFs with a pre-ozonated (3 mg/L) influent. Hydraulic loading rates (HLRs) from 5.0 m/h (2.0 gpm/sf) to 17.5 m/h (7.2 gpm/sf) were evaluated and the source water had a relatively constant DOC concentration of 3.51±0.26 mg/L. DOC removal was studied for 60 days after the BAF reached steady state. DOC removal increased from 6% to 9% as HLR decreased from 17.5 m/h to 9.7 m/h, both with an EBCT of 5 min. At an HLR of 9.7 m/h or less, removal plateaued. A similar trend was observed by Ko et al. (2007) as well where 31% of DOC removal was observed at a HLR of 6 m/h (2.5 gpm/sf), 26% at 12 m/h (5 gpm/sf), and 19% at 24 m/h (10 gpm/sf).

In a pilot plant study, Velten et al. (2011) evaluated the GAC BAF performance based on DOC. The GAC BAF was fed with ozonated surface water (ozone dosage not specified). With an influent DOC concentration of 1.1±0.04 mg/L, effluent concentrations increased from 0.25 mg/L to a steady state condition of 0.85 mg/L with 22% of removal (Table 3.1). In the start-up phase when the BAF was not fully developed,

Table 3.1 Parameters Used to Evaluate the Performance of BAFs and Demonstrate Organic Carbon Requirements

Study Scale	Media	Pre-O_3 (mg/L)	Parameter Studied	Influent Conc.	Removal %
Full[1]	GAC	1.5-5	DOC	2.3-8.1 mg/L	O_3+GAC: 17-48
Bench[2]	Sand	-	TOC	2.6-3.1 mg/L	Sand: 6.5-9.8
Pilot[3]	Anthracite	2	DOC	3.51±0.26 mg/L	Anthracite: 5-9
Pilot[4]	GAC/sand	1.7	DOC	1.28-4.11 mg/L	Dual: 19-31
Pilot[5]	GAC	NS	DOC	1.1±0.04 mg/L	GAC: 22
Pilot[6]	GAC and anthracite/sand	NS	AOC	88 µg acetate-C/L	GAC: 82 Dual: 70
Full[7]	GAC	-	AOC	42-135 µg acetate-C/L	O_3+GAC: 75-96
Bench[8]	Clay	10	TOC	9-13 mg/L	O_3: 15 O_3+Clay: 25
Bench[9]	Anthracite	1 and 4	TOC	-	Anthracite: 37-49
Bench[10]	Sand	9.2-14.4	TOC	2.34-6.24 mg/L	Sand: 16-33
Bench[11]	Sand	5.2	DOC	4.0±0.3 mg/L	Sand: 15-24
			BDOC	1.6±0.2 mg/L	Sand: 38-60
			AOC	1,400±180 µg/L	Sand: 43-57
Bench[12]	GAC	9	TOC	5.47 mg/L	GAC: 24-39
Bench[13]	GAC	6.3-6.7	DOC	3.14-3.35 mg/L	GAC: 34-48 O_3+GAC: 64-72
Full[14]	GAC and anthracite/sand	-	BOM：Oxalate	9 µg/L	GAC:60-90 Dual: 0-90
Pilot[15]	GAC and filtralite	-	DOC	4.29±0.32 mg/L	GAC: 12 Filtralite: 3-5
			BDOC	1.06±0.25 mg/L	GAC: 34 Filtralite: 28-30
			AOC	44±14 µg/L	GAC: 22 Filtralite: 35-41

Table 3.1 Parameters Used to Evaluate the Performance of BAFs and Demonstrate Organic Carbon Requirements (Continued)

Study Scale	Media	Pre-O_3 (mg/L)	Parameter Studied	Influent Conc.	Removal %
Pilot[16]	GAC, sand, and anthracite/sand	0.9-1.8	TOC	1.1-2.2 mg/L	GAC: 21-29 Sand: 20 Dual: 16
Pilot[17]	Anthracite/sand	0.9-1.8	TOC	1.1-2.2 mg/L	Dual: 16-21
Pilot[18]	GAC	NS	DOC	1.1-5.5 mg/L	GAC: 33
Bench[19]	GAC/sand and anthracite/sand	-	BOM	30-400 µg/L	GAC: 70-99 Anthracite: 50-95
Pilot[20]	sand	2.2-6.6	DOC	1.7-5.1 mg/L	15 (no O_3) 25 (with O_3)

GAC – Granular Activated Carbon; NS – Not Specified; PPCP – Pharmaceuticals and Personal Care Product; TOC – Total Organic Carbon; DOC – Dissolved Organic Carbon; AOC – Assimilable Organic Carbon; BDOC – Biodegradable Dissolved Organic Carbon; BOM – Biodegradable Organic Matter.

Source: [1] Reungoat et al., 2012; [2] Zearley and Summers, 2012; [3] Carlson and Amy, 1998; [4] Ko et al., 2007; [5] Velten et al., 2011; [6] Yang et al., 2011; [7] Chien et al., 2008; [8] Wang et al., 2008; [9] Lin, 2012; [10] Hozalski et al., 1995; [11] Moll et al., 1999; [12] Seredyńska-Sobecka et al., 2006; [13] Yapsakli et al., 2010; [14] Emelko et al., 2006; [15] Persson et al., 2006; [16] Wang et al., 1995; [17] Miltner et al., 1995; [18] Gibert et al., 2013; [19] Liu et al., 2001; [20] Fonseca et al., 2001.

DOC removal was attributed to the adsorption capacity of the GAC substrate. The increasing effluent concentration is the direct result of the decreasing adsorption capacity of the GAC. With DOC removal approaching steady state and with the development of biomass, the adsorption capacity of GAC was exhausted, and further removal was dominated by biodegradation.

TOC and DOC are the most studied parameters in evaluating BAFs (Hozalski et al., 1995; Moll et al., 1999; Seredyńska-Sobecka et al., 2006; Yapsakli et al., 2010) (Table 3.1). Hozalski et al. (1995) used lab-scale biologically active sand filters to evaluate the removal of TOC with influent concentration of 4.18 to 6.24 mg/L. Removals ranged from 16 to 33%. Sand BAFs were studied by Moll et al. (1999) as well. BAFs were operated in parallel at 5, 29 and 35 °C where DOC (4.0±0.3 mg/L) removal ranged between 15 and 24%. GAC filters were studied by Seredyńska-Sobecka et al. (2006) with TOC (5.47 mg/L) removal of 24 to 39% and by Yapsakli et al. (2010) with DOC (3.5 to 5.8 mg/L) removal ranging from 47% to 72%.

3.1.2 AOC

AOC is an important parameter for assessing the ability of organic matter to support heterotrophic bacterial growth as well as evaluate the bacterial growth potential in drinking water distribution systems. AOC is the part of DOC that can be easily assimilated by bacteria and converted to cell mass. The lower the AOC concentration in the finished water, the less likely bacteria will grow. Therefore, AOC is a controlling factor in microbial growth (Liu et al., 2002). Recent work (Yang et al., 2011; Chien et al., 2008) has included studying the effect of substrate and season (i.e., organic carbon

concentration) on AOC removal (Table 3.1). In a pilot-scale study, the efficiency of biofiltration on removal of AOC was evaluated as a function of a GAC substrate versus a dual media (Yang et al., 2011). GAC and dual media columns with an EBCT of 6.6 min were fed with ozonated water from a full-scale water treatment plant. Removals of 82% for the GAC-based substrate and 70% for the dual media system were observed with an effluent AOC concentration of 16 and 25 μg acetate-C/L, respectively. Although both columns observed significant AOC removals, the GAC BAF achieved greater removals as compared to dual media filters (Table 3.1).

Chien et al. (2008) took advantage of a full-scale water treatment plant study on AOC removal through biological activated carbon filters (Table 3.1). The influent AOC concentration varied as a function of season with the peak concentration of 135 μg acetate-C/L in the summer, moderate concentrations of 50 μg acetate-C/L in spring and fall, and the lowest concentration of 42 μg acetate-C/L in winter. An average AOC removal of 95% was achieved during spring, fall, and winter. During summer, with the increased influent AOC concentrations, a lower removal (75%) was observed. Therefore, seasonal variations reflect changes in organic carbon concentrations, which will impact the performance of BAFs on the removal efficiency of AOC.

3.1.3 Turbidity

Turbidity can be used to evaluate the BAF performance as well, but is often used to determine the time to address backwashing (Emelko et al., 2006). Simon et al. (2013) found turbidity removal of 38 to 75% through a pilot biofilter. The system operated for one year where expanded clay was used as the substrate. Results showed that turbidity

was reduced from 1 NTU in the influent to between 0.26 and 0.41 NTU in the effluent. Emelko et al. (2006) found that effluent turbidity of four parallel BAFs was less than 0.1 NTU with the influent turbidity ranging from 0.9 to 13.7 NTU. Backwashing was conducted when turbidity breakthrough was observed.

3.1.4 Pre-Ozonation

A number of studies (Carlson and Amy, 1998; Lin, 2012; Reungoat et al. 2012; Rodríguez et al., 2011; Treguer et al., 2010; Wang et al., 2008; Zearley et al., 2013) have demonstrated that pre-ozonation increases the fraction of NOM that can be biodegraded due to a decrease in aromatic character and an increase in carboxylic acid functionality and AOC (Table 3.2). A bench-scale study was conducted to evaluate the combination of pre-ozonation with biofiltration for the treatment of a secondary effluent from a domestic WWTP (Wang et al., 2008). The system involved a pre-ozonation contactor followed by two parallel BAFs with clay-based media. Filtered secondary effluent from a domestic WWTP served as the source water for this system. The ozone dosage applied was 10 mg O_3/L with an influent TOC ranging from 9 to 13 mg/L. The sludge from a secondary settling tank of a WWTP was used as the inoculant. The biomass concentration at a filter depth of 15 cm was stable at an average concentration of 63 nmol PO_4/g media after 14 days. TOC removal improved from 15% removal with ozonation alone to 25% with the ozonation/biofiltration system. Biodegradable dissolved organic carbon (BDOC) was determined before and after ozonation to investigate the effects of pre-ozonation. BDOC values increased from 0.8-1.1 mg/L to 2.0-2.7 mg/L after the ozone contactor where the biodegradability of the organic carbon improved. The molecular size distribution was

Table 3.2 Impact of Pre-ozonation on TOC and DOC Removal through BAFs

Study Scale	Source Water	Media	Parameter Studied	Influent Conc. (mg/L)	Pre-O_3 Dosage (mg/L)	Removal %
Bench[1]	Treated effluent from WWTPs	GAC	DOC	5.8-6.6	1.5	20
				4.2-5.8	2.2	50
				6.5-8.1	5.0	30
Bench[2]	Filtered secondary effluent from WWTP	Clay	TOC	9-13	10.0	25
Bench[3]	Synthetic raw water	Anthracite	TOC	-	1.0	28
					4.0	55
Bench[4]	Filtered raw water	GAC	DOC	3.14-3.35	No O_3 addition	41-53
					6.3-6.7	56-61
Pilot[5]	Untreated raw water	Sand	DOC	1.7-5.1	No O_3 addition	15
					2.2-6.6	25

WWTP – Wastewater Treatment Plant.
Source: [1] Reungoat et al., 2012; [2] Wang et al., 2008; [3] Lin, 2012; [4] Yapsakli et al., 2010; [5] Fonseca et al., 2001.

examined before and after pre-ozonation as well. The dissolved organic carbon in the influent was broken down by the pre-ozonation where dissolved organics with a size less than 1 kDa increased from 52.86% to 72.73% after ozonation. Overall BDOC concentration and molecular size distribution explained the improved removal efficacy of biofiltration.

Similar results were observed by Lin (2012) where the change in molecular weight distribution of organic matter via ozonation was investigated (Table 3.2). With a pre-ozonation dosage of 1.0 mg O_3/L, the molecular weight shifted from 303-7,031 g/mol to less than 303 g/mol by breaking down functional groups C═C in phenolic and C-O in alcohol compounds. Rodríguez et al. (2011) and Treguer et al. (2010) both found that pre-ozonation increased the fraction of BDOC, reduced the aromaticity of the DOC, and resulted in reduced molecular sizes. Ozone with dosages ranging from 0.1 to 0.8 mg O_3/mg DOC (0.3 to 2.1 mg O_3/L) were able to break down large molecules and increase biodegradability in the following biofiltration process. Improved TOC/DOC removal through BAF was observed with the application of pre-ozonation or with increasing dosages (Table 3.2). With a pre-ozonation dosage of 2 to 6 mg O_3/L, TOC and DOC removals were approximately 50% in GAC BAFs (Reungoat et al., 2012; Yapsakli et al., 2010). On the other hand, when sand was used as the support media, removals were less than 25% (Fonseca et al., 2001). A TOC removal of 55% was achieved in an anthracite BAF when a pre-ozonation dosage of 4 mg/L was used (Lin, 2012). For a clay substrate, TOC removal was less than 25% even with a 10 mg/L pre-ozonation dosage (Wang et al., 2008).

3.1.5 EBCT

Increased removal of TOC/DOC was observed with increasing EBCT (Table 3.3). In a lab-scale ozonation/biofiltration process (Seredyńska-Sobecka et al., 2005) the EBCT of a GAC BAF was studied over 2.4 minutes to 24 minutes, resulting in a range of flow rates from 8 mL/min to 80 mL/min. TOC removal increased from 24 to 39% with increasing EBCT. Other studies focused on EBCTs over the range of 5 min to 45 min and demonstrated an increased TOC or DOC removal at longer EBCTs on various filter media (Carlson and Amy, 1998; Ko et al., 2007; Zearley and Summers, 2012). EBCTs of 10 min to 18 min were observed to be the optimal range for TOC/DOC removal through BAFs. Further increasing the EBCT does not markedly improve the performance of the BAFs.

3.1.6 Summary

TOC and DOC, AOC, and to a lesser extent turbidity (Table 3.1) can be used to evaluate BAF performance. AOC (42 to 1,400 µg acetate-C/L) provides bacterial regrowth potential while TOC (1.1 to 13 mg/L) and DOC (1.1 to 8.1 mg/L) are used to correlate uptake. AOC is critical in controlling the growth of heterotrophic bacteria. Turbidity has been used for addressing the need for backwashing. Compared to TOC, DOC, and turbidity, AOC requires a three-day incubation. Removal of TOC generally is consistent with DOC removal. Therefore, for routine analysis, DOC is recommended, although AOC is an important parameter to monitor. With pre-ozonation dosages of 2 to 6 mg O_3/L, TOC and DOC removals of approximately 50% were achieved in GAC BAFs (Table 3.2). Sand substrates were not as effective with removals less than 25%. TOC

Table 3.3 Impact of EBCT on TOC and DOC Removal

Study Scale	Source Water	Media	Parameter Studied	Pre-O_3 (mg/L)	Influent Conc. (mg/L)	EBCT (min)	Removal (%)
Bench[1]	Dechlorinated tap water	Sand	TOC	no	2.6-3.1	7.9	6.5
						15.8	9.8
Pilot[2]	Treated effluent from WWTPs	GAC	DOC	1.5-5	5.8-6.6	9	20
					6.5-8.1	18	30
					4.2-5.8	45	50
Pilot[3]	Ozonated raw water	Anthracite	DOC	2	3.51±0.26	7	7
						10.8	9
						24.8	9
Pilot[4]	Settled raw water	GAC/Sand	DOC	1.7	1.28-4.11	5	19
						10	26
						20	31
Bench[5]	Filtered raw water	GAC	TOC	9	7.76-11.62	2.4	24
						11.2	34
						24.0	39

WWTP – Waterwater Treatment Plant;
Source: [1] Zearley and Summers, 2012; [2] Reungoat et al., 2012; [3] Carlson and Amy, 1998; [4] Ko et al., 2007; [5] Seredyńska-Sobecka et al., 2005.

removals of 28% were achieved in an anthracite BAF with a pre-ozonation dosage of 1 mg/L (Lin, 2012), and with a clay substrate, TOC removal was less than 25% even with a 10 mg/L pre-ozonation dosage. The studies have also shown that GAC exhibited superior substrate performance with greater 1.5 to 3 times TOC and DOC removed (Fonseca et al., 2001; Persson et al., 2006; Reungoat et al., 2012; Wang et al., 1995; Wang et al., 2008; Yapsakli et al., 2010) and 1.2 to 2.2 times AOC removed (Chien et al., 2008; Moll et al., 1999; Yang et al., 2011), EBCTs of 10 to 18 min were observed to be the optimal range for TOC/DOC removals through BAFs (Table 3.3). Further increasing of the EBCT has not been shown to improve the performance of the BAFs. In the following section the factors that impacted the formation of biomass in the BAFs are reviewed.

3.2 Biomass Formation and Impact Factors

A number of factors affect the development of a viable biomass: source water (Seredyńska-Sobecka et al., 2006; Velten et al., 2011), support media (Liu et al., 2001; Persson et al., 2006; Wang et al., 1995), backwashing (Miltner et al., 1995), EBCT (Carlson and Amy, 1998; Ko et al., 2007), temperature (Emelko et al., 2006; Moll et al., 1999; Urfer et al., 1997), and pre-ozonation (Zearley and Summers, 2012). In this section, studies on how these factors affect biomass formation are reviewed.

3.2.1 Source Water

Source water quality impact biomass concentration in BAFs (Table 3.4). In a 6 month pilot-plant study, the growth of biomass on a GAC filter was monitored by quantifying the biomass concentration using the ATP method (Velten et al., 2011). Ozonated surface

Table 3.4 Biomass Formation and Impact Factors

Study Scale	Source Water	Media with Seeding or Existing Biomass	Nutrient and OM Amendment	Water Quality	T (°C)	EBCT (min)	Biomass Conc. in Upper portion	Time to Reach Steady State	BW
Bench[1]	Dechorinated water	Sand with existing biomass	DOM solution target TOC of 3 mg/L	TOC: 2.6-3.1 mg/L	20	-	51±4 nmol PO_4/g sand	-	N
Pilot[2]	Ozonated raw water	Virgin anthracite without seeding	-	DOC: 3.51±0.26 mg/L pH: 7.3±0.2 Turbidity: 2.6±0.4 NTU	10.2±1.1	10.8	55 nmol PO_4/g anthracite	60 days	Y
						24.8	120 nmol PO_4/g anthracite		
Pilot[3]	Settled raw water	Virgin GAC/Sand without seeding	-	DOC: 1.28-4.11 mg/L pH: 6.62-7.67 Turbidity: 0.22-3.28 NTU	18.0-28.3	5	95 nmol PO_4/g GAC	7 months	Y
						10	120 nmol PO_4/g GAC		
						20	135 nmol PO_4/g GAC		
Pilot[4]	Ozonated surface water	Virgin GAC without seeding	-	DOC: 1.1±0.04 mg/L pH: 7.79±0.14	7.05±0.7	15.76	1.17×19^{-6} g ATP/g GAC	3 months	N
Bench[5]	Filtered secondary effluent from WWTP	Clay seeded with sludge from WWTP	-	TOC: 9-13 mg/L NH_4^+: 10-20 mg/L BOD: 11-15 mg/L TN: 20-25 mg/L	-	-	64 nmol PO_4/g clay	14 days	Y
Bench[6]	NOM solution	Sand seeded by soaking in settled raw water	-	DOC: 4.0±0.3 mg/L BDOC: 1.6±0.2 mg/L AOC: 1,400±180 µg/L	5	7	150 nmol PO_4/g sand	4 weeks	Y
					20		225 nmol PO_4/g sand		
					35		175 nmol PO_4/g sand		

Table 3.4 Biomass Formation and Impact Factors (Continued)

Study Scale	Source Water	Media with Seeding or Existing Biomass	Nutrient and OM Amendment	Water Quality	T (°C)	EBCT (min)	Biomass Conc. in Upper portion	Time to Reach Steady State	BW
Bench[7]	Filtered raw water	Virgin GAC without seeding	-	TOC: 7.76-11.62 mg/L NO_3^-: 0.01-0.40 mgN/L PO_4: 0.01-0.45 mgP/L	-	24	70 nmolPO_4/g GAC	8 months	Y
Full[8]	Ozonated raw water	Virgin GAC without seeding	-	DOC: 5-7 mg/L pH: 7.9-8.4 Turbidity: 0.9-13.7 NTU	1-3 21-25	17-36	5 nmolPO_4/g GAC 15-20 nmolPO_4/g GAC	-	Y
Pilot[9]	Untreated surface water	Virgin GAC and Filtralite without seeding	-	DOC: 4.29±0.32 mg/L pH: 6.9-7. 3 Turbidity: 0.6-1.2 NTU	-	31	175 nmolPO_4/cm^3 GAC 125 nmolPO_4/cm^3 anthracite	3 months	Y
Pilot[10]	Ozonated raw water treated by coagulation, flocculation and settlement	Virgin GAC, sand, and anthracite/sand without seeding	-	TOC: 1.1-2.2 mg/L pH: 6.9-7.7 Turbidity: 1-3 NTU	-	-	384 nmolPO_4/g GAC 55 nmolPO_4/g dual media 99 nmolPO_4/g sand	5 months	N
Bench[11]	Dechlorinated tap water	Virgin GAC/sand and Anthracite/sand without seeding	C:N:P (w/w/w) =15:5:1 Kaolinite: 1.5 mg/L $Al_2(SO_4)_2 18H_2O$: 3 mg/L BOM Solution	Particle Conc.: 1-4 mg/L	5 20	5.6	6×10^4 nmolPO_4/GAC filter 1×10^4 nmolPO_4/anthracite filter 7×10^4 nmolPO_4/GAC filter 4×10^4 nmolPO_4/anthracite filter	40 days	Y

OM – Organic Matter; DOM – Dissolved Organic Matter; TOC – Total Organic Carbon; DOC – Dissolved Organic Carbon; BW – Backwash; Y – Yes; N – No; WWTP – Wastewater Treatment Plant; TN – Total Nitrogen; NOM – Natural Organic Matter.

Source: [1] Zearley and Summers, 2012; [2] Carlson and Amy, 1998; [3] Ko et al., 2007; [4] Velten et al., 2011; [5] Wang et al., 2008; [6] Moll et al., 1999; [7] Seredyńska-Sobecka et al., 2006; [8] Emelko et al., 2006; [9] Persson et al., 2006; [10] Wang et al., 1995; [11] Liu et al., 2001.

water with a DOC of 1.1 ± 0.04 mg/L and no additional seeding was used as the source water for the BAF. Biomass accumulation was observed during the first 3 months of operation increasing from 10^{-8} g ATP/g GAC to 10^{-6} g ATP/g GAC. Biomass became stable at 91 days with a concentration of approximately 10^{-6} g ATP/g GAC. DOC removal reached 22% when the biomass approached the steady state. Therefore, the DOC data may be used as an indicator of achieving steady state conditions (Table 3.4). Seredyńska-Sobecka et al. (2006) found an 8 month period was needed for stabilizing a GAC BAF with a biomass concentration of approximately 70 nmol lipid P/gram of media based on phospholipids analysis. Ten liters of surface water were collected from a river once per week and filtered to remove the suspended solids prior to biofiltration. Because of seasonal variations, the filtered source water varied in TOC (7.76 to 11.62 mg/L), nutrient levels (NO_3-N: 0.01 to 0.40 mg/L and PO_4-P: 0.01 to 0.45 mg/L), and dissolved oxygen (6.0 to 8.0 mg/L). The authors found that 8 months were required to achieve a biologically active GAC due to the low concentrations of both biodegradable substances and nutrients in the source water (Table 3.4).

The biomass concentration in two parallel filters supported by GAC and filtralite was studied by Persson et al. (2006). Untreated surface water with a DOC of 4.29±0.31 mg/L served as the source water. Biomass concentration was evaluated using phospholipid analysis. The biomass concentration in the upper portion of the two BAFs was stable at 175 nmol/cm^3 of GAC and 125 nmol/cm^3 of filtralite after 3 months of operation (Table 3.4).

3.2.2 Support Media

BAF substrates vary with respect to surface properties, morphology, and surface area, and impact the formation of biomass (Tables 3.4 and 3.5). In a pilot plant study, sand, anthracite-sand, and GAC in parallel columns were evaluated for biomass growth (Wang et al., 1995). Ozonated river water was subsequently treated by alum coagulation, flocculation, and sedimentation prior to biofiltration. Biomass continuously accumulated for the first 5 months before reaching steady state. With a larger surface area per unit volume, GAC was found to retain a greater concentration of biomass than sand or dual media. Media samples collected from the upper portion of each filter were analyzed for phospholipids. GAC with an average biomass concentration of 384 nmol lipid-P/gram of media held approximately 3 to 7 times more biomass than dual media (55 nmol lipid-P/gram of media) or sand media (99.6 nmol lipid-P/gram of media). Similar results were observed by Liu et al. (2001), where biomass concentrations were 2 to 6 times greater in GAC filters than in anthracite-sand dual media filters with similar source water and operating conditions. Persson et al. (2006) investigated the biomass in parallel operated GAC and filtralite filters. Untreated surface water with a TOC of 4.29±0.32 mg/L was served as the source water. The biomass concentration in GAC filter (175 nmol PO_4/cm^3 GAC) was observed 1.4 greater than in the filtralite filter (125 nmol PO_4/cm^3 filtralite). Compared to sand, filtralite, and anthracite-sand dual media, GAC is porous with a larger surface area per unit volume for biomass attachment (Tables 3.4 and 3.5).

3.2.3 Backwashing

Excess biomass can cause clogging and significant head loss; consequently converting

Table 3.5 Impact of Support Media on Biomass Formation

Study Scale	Source Water	Media	Water Quality and Nutrient Amendment	Biomass Conc. in Upper portion
Pilot[1]	Untreated surface water	GAC and Filtralite	DOC: 4.29±0.32 mg/L pH: 6.9-7. 3 Turbidity: 0.6-1.2 NTU	175 nmol PO_4/cm^3 GAC 125 nmol PO_4/cm^3 filtralite
Pilot[2]	Ozonated raw water treated by coagulation, flocculation and settlement	GAC, sand, and anthracite/sand	TOC: 1.1-2.2 mg/L pH: 6.9-7.7 Turbidity: 1-3 NTU	384 nmol PO_4/g GAC 55 nmol PO_4/g dual media 99 nmolPO_4/g sand
Bench[3]	Dechlorinated tap water	GAC/sand and Anthracite/sand	C:N:P (w/w/w) =15:5:1 Kaolinite: 1.5 mg/L $Al_2(SO_4)_218H_2O$: 3 mg/L BOM Solution Particle Conc.: 1-4 mg/L	6×10^4-7×10^4 nmol PO_4/GAC filter 1×10^4-4×10^4 nmol PO_4/anthracite filter

Source: [1] Persson et al., 2006; [2] Wang et al., 1995; [3] Liu et al., 2001.

aerobic BAFs into anaerobic ones. Therefore, an appropriate backwashing strategy is necessary for long-term performance of BAFs. Miltner et al. (1995) examined the impact of chlorinated versus non-chlorinated backwashing on biomass concentration with anthracite-sand dual media in the same pilot plant study conducted by Wang et al. (1995). The ozonated water with TOC ranging from 1.1 to 2.2 mg/L and turbidity from 1 to 3 NTU was used as the source water. Filters were backwashed for 10 min with 50 percent bed expansion when the head loss exceeded 60 in. The free chlorine residual in the backwash water was approximately 1.0 mg/L. Chlorinated backwash resulted in an average loss of 22% by weight of biomass. This change in biomass concentration was immediate and required another 40 hours of operation to recover to the pre-backwash concentrations. Concurrent with the biomass loss, the removal of TOC and disinfection by-product (DBP) precursors dropped as well from 15%-30% to no observed removal. Removal efficiencies returned to pre-backwashing conditions after the biomass was recovered. On the other hand, no apparent loss of biomass was observed during non-chlorinated backwashing. The TOC and DBP precursor removals were also not affected. Therefore, backwashing with non-chlorinated water was conducted in the bench-scale study. The dissolved oxygen in BAF effluents was monitored to ensure aerobic conditions in the filters and backwashing was routinely conducted as well.

3.2.4 EBCT

EBCT is another impact factor on biomass formation (Table 3.6). Carlson and Amy (1998) investigated biomass concentration in anthracite filters with EBCT of 10.8 min and 24.8 min. Ozonated raw water with a DOC of 3.51±0.26 mg/L served as the source

Table 3.6 Impact of EBCT on Biomass Formation

Study Scale	Source Water	Media	Water Quality and Nutrient Amendment	EBCT (min)	Biomass Conc. in Upper portion
Pilot[1]	Ozonated raw water	Anthracite	DOC: 3.51±0.26 mg/L pH: 7.3±0.2 Turbidity: 2.6±0.4 NTU	10.8	55 nmol PO_4/g anthracite
				24.8	120 nmol PO_4/g anthracite
Pilot[2]	Settled raw water	GAC/Sand	DOC: 1.28-4.11 mg/L pH: 6.62-7.67 Turbidity: 0.22-3.28 NTU	5	95 nmol PO_4/g GAC
				10	120 nmol PO_4/g GAC
				20	135 nmol PO_4/g GAC

Source: [1] Carlson and Amy, 1998; [2] Ko 2007.

water. With an EBCT of 24.8 min, a biomass concentration of 120 nmol PO_4/g anthracite was observed in the upper portion of the anthracite filter, while less biomass concentration (55 nmol PO_4/g anthracite) in the filter was found with a shorter EBCT (10.8 min). Biomass concentration in GAC filters with various EBCTs (5, 10, and 20 min) was studied as well (Ko et al., 2007). Similar trends were observed where biomass concentration increased from 95 nmol PO_4/g GAC to 135 nmol PO_4/g GAC with EBCTs ranging from 5 to 20 min.

3.2.5 Temperature

Seasonal variability in source water temperature may impact biomass formation and performance of BAFs (Emelko et al., 2006; Moll et al., 1999; Urfer et al., 1997) (Table 3.7). Moll et al. (1999) studied the impact of temperature on sand BAFs. Bench-scale sand BAFs were operated in parallel at 5, 20, and 35 °C. Biomass was quantified based on phospholipid analysis. The virgin sand medium was seeded by soaking in settled river water for one month prior to packing the media into the filter column. After the BAFs reached steady state, average biomass concentrations in the upper portion of the column were analyzed. At both 5 and 35 °C, lower biomass concentrations (150 to 175 nmol PO_4/g sand) were observed as compared to 20 °C (225 nmol PO_4/g sand). The lower biomass concentration observed at 5 °C may result from slower metabolism at low temperatures which could decrease the utilization of nutrients and stress the microbial growth. While reduced growth at 35 °C may be due to the inability of the microbial community to function at this higher temperature (Moll et al., 1999). Low and high temperature extremes have been observed to inhibit the biomass growth in other studies

Table 3.7 Impact of Temperature on Biomass Formation

Study Scale	Source Water	Media with Seeding or Existing Biomass	Water Quality and Nutrient Amendment	T (°C)	Biomass Conc. in Upper portion
Bench[1]	NOM solution	Sand seeded by soaking in settled raw water	DOC: 4.0±0.3 mg/L BDOC: 1.6±0.2 mg/L AOC: 1,400±180 µg/L	5	150 nmol PO_4/g sand
				20	225 nmol PO_4/g sand
				35	175 nmol PO_4/g sand
Bench[2]	Dechlorinated tap water	GAC/sand and Anthracite/sand	C:N:P (w/w/w) =15:5:1 Kaolinite: 1.5 mg/L $Al_2(SO_4)_218H_2O$: 3 mg/L BOM Solution Particle Conc.: 1-4 mg/L	5	6×10^4 nmol PO_4/GAC filter 1×10^4 nmol PO_4/anthracite filter
				20	7×10^4 nmol PO_4/GAC filter 4×10^4 nmolPO_4/anthracite filter
Full[3]	Ozonated raw water	GAC	DOC: 5-7 mg/L pH: 7.9-8.4 Turbidity: 0.9-13.7 NTU	1-3	5 nmol PO_4/g GAC
				21-25	15-20 nmol PO_4/g GAC

Source: [1] Moll et al., 1999; [2] Liu et al., 2001; [3] Emelko et al., 2006.

as well. Emelko et al. (2006) investigated the effect of water temperature on the biomass concentrations in full-scale biological filters. Four parallel filters, two GAC and two anthracite-sand dual media based substrates, were fed ozonated water. Biomass was determined using the phospholipid method. Compared to higher temperatures (21 to 25 °C), filters formed significantly less biomass in the upper portion of the column as compared to lower temperature conditions (1 to 3 °C), where biomass decreased from 15-20 nmol P/cm^3 media at 25 °C to 5 nmol P/cm^3 media at 3 °C. Temperature is important and can significantly affect the biomass concentration in BAFs. Carboxylic acid oxalate was used to assess biodegradable organic matter (BOM) removal during cold and warm seasons. Water temperature significantly affected oxalate removal, which decreased from 90% to 60% as temperature decreased (from 21-25 to 1-3 °C) in the GAC filters to no observed removal in the anthracite-sand dual media filters. Although seasonal affects will need to be accounted for, moderate temperatures are preferable for biomass formation as well as the BAF performance (Table 3.7).

3.2.6 Pre-Ozonation

In a pilot plant study, the impact of pre-ozonation on biomass formation in sand filters was investigated (Fonseca et al., 2001) (Table 3.8). Sand filters were fed with ozonated and non-ozonated raw water that had a DOC of 3.4±1.7 mg/L. A pre-ozone dosage of 1.3 mg O_3/mg DOC was applied. Sand filters with ozonated source water held approximately two times more biomass (20-120 nmol PO_4/g sand) than filters fed with non-ozonated influent (18-70 nmol PO_4/g sand). Pre-ozonation breaks down organic carbon to more biodegradable forms that can enhance biomass formation.

Table 3.8. Impact of Pre-ozonation on Biomass Formation

Study Scale	Source Water	Media	Water Quality and Nutrient Amendment	Pre-O_3 Dosage	Biomass Conc. in Upper portion
Bench[1]	Dechlorinated tap water	Anthracite/sand	C:N:P (w/w/w) =15:5:1 BOM solution BDOC: 0.28 mg/L	0.15 mg O_3/L with and without H_2O_2 H_2O_2 dosage NS	BRP: (mg O_2/L per cm^3 of media) 0.15-0.23 (no O_3;no H_2O_2) 0.18-0.23 (O_3 alone) 0.22-0.43 (O_3+H_2O_2)
Pilot[2]	Untreated raw water	sand	DOC: 1.7-5.1 mg/L pH: 7±0.3 Turbidity: 0.6-4 NTU	1.3 mg O_3/mg DOC	Phospholipids: 18-70 nmol PO_4/g sand (no O_3) 20-120 nmol PO_4/g sand (with O_3) INT reduction: 0.2-0.8 Abs 490 nm/g sand (no O_3) 0.2-1.6 Abs 490 nm/g sand (with O_3)

BRP – Biomass Respiration Potential; NS – Not Specified.
Source: [1] Urfer et al., 2001; [2] Fonseca et al., 2001.

3.2.7 Summary

Several factors including source water (Table 3.4), support media (Table 3.5), backwashing (Table 3.4), EBCT (Table 3.6), temperature (Table 3.7), and pre-ozonation (Table 3.8) affect the biomass concentration developed on BAF substrates. Therefore, in studies with a sufficient acclimation (2 to 4 weeks when seeded and 3 to 8 months with settled or treated raw water), optimal support media, backwashing, EBCT, temperature, and pre-ozone dosage were investigated over relevant ranges (Tables 3.4 to 3.8). Specifically, bench-scale studies involved support media of GAC and anthracite/sand dual media, 10 and 18 min of EBCT, temperature of 23±2 °C, an ozone dosage between 2 mg/L and 6 mg/L, and non-chlorinated backwashing. Source water was collected from the existing water treatment plant. With the operational conditions determined in this section, the next section provides a literature review on the studies on PPCP removal in BAFs.

3.3 Studies on PPCP Removal in BAFs

A number of studies have been conducted using BAFs to remove BOM, TOC and DOC, and AOC (Boon et al., 2011; Carlson and Amy, 1998; Chien et al., 2008; Moll et al., 1999; Reungoat et al., 2012; Velten et al., 2011; Yang et al., 2011; Yapsakli et al., 2010). However, limited studies have focused on assessing PPCP removal through BAFs. In this section, studies on PPCP removal in BAFs are reviewed.

Zearley and Summers (2012) studied the removal of 34 PPCPs using BAFs in bench-scale experiments with a sand substrate. The BAFs were from a system that had been in operation for over 7 years at a water treatment plant with a viable biomass

concentration of 51±4 nmol PO_4/gram of sand. River water served as the source water for the BAF. The study was conducted with a hydraulic loading rate of 2.4 m/h (1 gpm/sf) and an EBCT of 7.9 min to 15.8 min. Over the course of the 1 year study and without pretreatment (an EBCT of 7.9 min and influent PPCP concentration from 4 to 556 ng/L), removals were less than 15% for 13 compounds including atrazine, carbamazepine, iopromide, and sulfamethoxazole. Increased removals between 15 and 50% were observed for seven compounds including cotinine and ethinyl estradiol. Fifty to 80% removal was found for eight compounds that included acetaminophen and caffeine while greater than 85% removal was reported for gemfibrozil and trimethoprim. Removal efficiencies increased by as much as 25 times at a 15.8 min EBCT with the exception of iopromide, methomyl, and prometon.

In addition to bench-scale studies, several pilot-scale efforts have been conducted to evaluate biofiltration with varying source water, support media, and pre-ozonation (Hofmann et al., 2010; Lee et al., 2012b; Reungoat et al., 2011). Hofmann et al. (2011) conducted a pilot-scale study at Bollman Water Treatment Plant in California to explore methods to enhance removal of PPCPs in the source water. Eleven compounds including atenolol, caffeine, carbamazepine, ibuprofen, gemfibrozil, iopromide, sulfamethoxazole, and atrazine were spiked at 500 to 1,000 ng/L. Processes in the plant included pre-chlorination, pH adjustment, alum coagulation and flocculation, conventional sedimentation, ozonation, GAC biofiltration, and chloramination. The effluent from conventional sedimentation was directed to the pilot system, which involved pre-ozone and GAC biofiltration processes. Ozone dosages of 0.5 mg/L and 1.0 mg/L were applied to evaluate the effect of ozone concentration. The GAC used in the pilot study was

obtained from the full-scale GAC BAFs that had more than 6 years of service. Five of the spiked compounds including 4-nonylphenol, triclosan, carbamazepine, gemfibrozil, and sulfamethoxazole were efficiently removed at greater than 90% for both ozone dosages. However, compared to 1 mg/L ozone dosage where 90% removal was achieved for atenolol, caffeine, and bisphenol A, removals of 20% to 50% were observed at the lower 0.5 mg/L dosage for atenolol, caffeine, bisphenol A, iopromide, ibupforen, and atrazine. Although removals for atenolol, caffeine, and bisphenol A were low at the lower dosage of ozone, additional removal (20 to 40%) was significant through the following GAC BAFs. Therefore, pre-ozonation followed by biofiltration is a combination of processes that have potential for achieving desirable removals for PPCPs.

In a pilot-scale study at a wastewater treatment facility, Lee et al. (2012b) compared the removal of PPCPs by ozone followed by biofiltration using anthracite media versus reverse osmosis. The 83 PPCPs in the wastewater ranged between 5.5 ng/L to 43,000 ng/L. Three ozone dosages, 2 mg/L, 4 mg/L, and 8 mg/L were studied. At 2 mg/L, while amoxicillin and carbamazepine with influent concentrations from 17 to 34 ng/L were removed at approximately 95%, over half the compounds were reduced less than 50%. PPCP removal increased with increasing ozone dosages, with 27 compounds (66%) being removed to below detectable limits. However, even at an ozone dose of 8 mg/L, compounds such as iopromide and TCEP with influent concentrations from 94 to 2,500 ng/L were found to be relatively resistant to ozonation. The BAF substrate anthracite was seeded with mixed liquor from a membrane bioreactor (MBR). Over the course of 1 week, filter ripening was promoted with this MBR effluent. Biomass concentration and efficiency were not evaluated. Removals were reported as insignificant

through the BAF. One possible reason may be due to insufficient development of biomass using an anthracite substrate.

Pilot plant studies were also conducted evaluating PPCP removal through biofiltration at the South Caboolture Water Reclamation Plant (Reungoat et al., 2011). Subsequent to denitrification, pre-ozonation, dissolved air flotation, and filtration in the reclamation plant, the effluent was directed into non-ozonated GAC BAFs where PPCP removal was evaluated. The biomass concentration was not studied and only compounds with a median concentration of at least 10 times the limit of quantification were evaluated. Through this BAF, caffeine, carbamazepine, diclofenac, erythromycin, metoprolol, roxithromycin, sulfamethoxazole, and trimethoprim were removed by more than 90% based on the influent to the filter. On the other hand, the biological sand filter showed limited removals. Only paracetamol was removed to a significant level (85%). Other compounds including atenolol, caffeine, carbamazepine, erythromycin, gemfibrozil, sulfamethoxazole, and trimethoprim were removed at less than 55%. In this work, Reungoat et al. demonstrate the importance of the GAC BAF over the sand-based substrate.

Reungoat et al. (2012) investigated the fate of PPCPs in three full-scale reclamation plants using ozonation followed by biological activated carbon filtration to treat wastewater treatment plant effluents. Ozone dosages of 1.5, 2.2, and 5 mg O_3/L were applied at the three plants. The combination of ozonation followed by a GAC-BAF resulted in removals of 80% to greater than 90% independent of the ozone dose for diclofenac, sulfamethoxazole, trimethoprim, propranolol, naproxen, carbamazepine, roxithromycin, and erythromycin. Because of their electron rich functional groups as well

as the ozone rate constant (>10^4 $M^{-1}s^{-1}$), the removals observed are expected. On the other hand, atenolol, hydrochlorothiazide, diuron, metroprolol, 2,4-D, and caffeine with rate constants less than 10^2 $M^{-1}s^{-1}$ were observed to result in lower removals from 20% to 40% with ozone dosages of 1.5 mg O_3/L. In our earlier work (Zhang et al., 2016b), we found similar results where compounds with a k_{O3} greater than 10^5 $M^{-1}s^{-1}$ were observed to achieve removals greater than 90% through ozonation, while most compounds with k_{O3} less than 2×10^3 M^{-1} s^{-1} resulted in removals less than 75%. The impact of pre-ozonation dosage on PPCP removal through BAFs was summarized in Table 3.9. Reungoat et al. (2012) also studied EBCTs of 9, 18, and 45 where PPCP removal increased from 9 to 18 minutes of contact time, although there was no significant difference between 18 and 45 minutes. Therefore, continuously increasing the EBCT does not necessarily improve PPCP removals.

Hallé et al. (2015) evaluated the influence of temperature (0-10 ºC and 1-20 ºC), influent PPCP concentration (500 ng/L and 5,000 ng/L), and EBCT (5 min and 14 min) on PPCP removal in pilot-scale anthracite/sand dual media BAFs. Removals were not observed for carbamazepine and atrazine. For DEET, naproxen, and ibuprofen, removals decreased as the temperature was lowered and increased with increasing EBCTs; reduced removals were observed at greater influent concentrations. DOC removal was continuously analyzed and a 4-month acclimation period was required.

In an effort to improve removal, McKie et al. (2016) studied the effectiveness of pre-treating with coagulation in pilot-scale anthracite/sand BAFs with an alum coagulant and GAC/sand BAFs with polyaluminum hydroxychloride (PACl). Although alum addition showed no significant improvement in anthracite/sand BAFs, PACl addition at

Table 3.9 Compounds Removed through BAFs with Pre-ozonation

Study Scale	Media	Influent Conc. (ng/L)	Pre-O_3 (mg/L)	Recalcitrant (Removal < 50%)	Moderately Biodegradable (Removal: 50-75%)	Readily Biodegradable (Removal > 75%)
Pilot[1]	GAC	10-695	0.5	Atrazine Ibuprofen Iopromide SMX	-	4-NP Atenolol BPA Caffeine CBZ Gemfibrozil Triclosan
			1.0	BPA Gemfibrozil Iopromide	Atrazine Caffeine Ibuprofen	4-NP Atenolol Triclosan CBZ SMX
Pilot[2]	Anthracite	5.5-43,000	2	Atenolol Caffeine DEET Dilantin Iopromide Meprobamate Primidone TCEP	Butalbital SMX	Amoxicillin CBZ Naproxen
			4	Iopromide Sucralose TCEP	Dilantin Iohexal Primidone	Amoxicillin Atenolol Butalbital Caffeine CBZ DEET Meprobamate Naproxen SMX
			8	Iohexal	Sucralose	Amoxicillin Atenolol Butalbital Caffeine CBZ DEET Dilantin Iopromide Meprobamate Naproxen Primidone SMX

4-NP – 4-Nonylphenol; BPA – Bisphenol A; CBZ – Carbamazepine; SMX – Sulfamethoxazole.
Source: [1] Hofmann et al., 2011; [2] Lee et al., 2012b.

0.8 mg/L, resulted in average removals of nine PPCPs increasing from 39% to 70% in GAC/sand BAFs. DOC removals ranging from 6.5% to 18% were observed. Greater media ATP concentrations (1,080 to 1,800 ng/g media) were found in filters receiving influent with higher nutrient and organic carbon concentrations.

In summary, studies have considered the impact of pre-ozonation (Table 3.9), EBCT (Table 3.10), filter media (sand, anthracite, and GAC) (Table 3.11), and source water (tap water, WWTP effluent, and treated river water) (Table 3.11) on the effectiveness of biofiltration. GAC based BAFs were observed to be the most effective substrate for removing PPCPs. The studies have shown that GAC exhibited superior substrate performance with approximately 1.5 to 3 times more PPCP removals (Table 3.11) (Hofmann et al., 2011; Reungoat et al., 2011). Moreover, more than 60% of the PPCPs have been removed at greater than 75% in GAC BAFs with pre-ozonation dosages of 2 to 6 mg/L and EBCTs of greater than 10 min (Tables 3.9 and 3.10). While in anthracite BAFs, similar PPCP removals were not achieved unless a pre-ozonation dosage of greater 4 mg/L was applied. Pre-ozonation improved PPCP removal in biofiltration processes and dosages from 2 to 6 mg/L were observed to be the optimal range. The EBCT is an important parameter affecting removal through BAFs. EBCTs of 10 to 18 min were observed to be the optimal range for PPCP removals through BAFs (Table 3.10). Further increasing of the EBCT has not been shown to improve the performance of the BAFs.

Studies on the effectiveness of BAFs for treating PPCPs have focused for the most part on a select process and the variables that may affect the performance, including pretreatment (ozonation or coagulation), EBCT, temperature, or influent PPCP

Table 3.10 Compounds Removed through BAFs as a Function of EBCT

Study Scale	Media	Influent Conc. (ng/L)	EBCT (min)	Recalcitrant (Removal < 50%)		Moderately Biodegradable (Removal: 50-75%)	Readily Biodegradable (Removal > 75%)	
Full[1]	GAC	NS	9	Caffeine Diuron Perindopril Roxithromycin Triclopyr		Atenolol HCT Metoprolol Venlafaxine	Citalopram Doxylamine Gemfibrozil Sertraline Tramadol	
			18	Furosemide Perindopril Triclopyr		2,4-D Caffeine Erythromycin SMX	Acetaminophen Atenolol Citalopram Diazinon Diuron Doxylamine	HCT Metoprolol Phenytoin Sertraline Tramadol Venlafaxine
			45	Perindopril		Phenytoin	Atenolol Caffeine Citalopram Diuron Doxylamine Erythromycin Gemfibrozil	HCT Metoprolol Roxithromycin Sertraline Tramadol Venlafaxine
Bench[2]	Sand	4-556	7.9	Acetochlor Aldicarb Atrazine CBZ Carbaryl Clofibric Acid Cotinine Diazinon Diclofenac Diuron Erythromycin	EE Iopromide Malaoxon Methomyl Metolachlor Prometon Simazine SMX TBP Warfarin	2,4-D Acetaminophen Bisphenol A Caffeine Chlorpyrifos Dimethoate Gemfibrozil Naproxen	Ibuprofen MIB Molinate Triclosan Trimethoprim	
			15.8	Acetochlor Atrazine CBZ Carbaryl Cotinine Diazinon Diclofenac Diuron Erythromycin	EE Iopromide Malaoxon Methomyl Metolachlor Prometon Simazine SMX TBP	Aldicarb Clofibric Acid Warfarin	2,4-D Acetaminophen Caffeine Chlorpyrifos Dimethoate Gemfibrozil	Ibuprofen MIB Molinate Naproxen Triclosan Trimethoprim
Bench[3]	Anthracite /Sand		5	DEET		Ibuprofen		
			14			DEET	Ibuprofen	

Table 3.10 Compounds Removed through BAFs as a Function of EBCT (Continued)

Study Scale	Media	Influent Conc. (ng/L)	EBCT (min)	Recalcitrant (Removal < 50%)		Moderately Biodegradable (Removal: 50-75%)	Readily Biodegradable (Removal > 75%)	
Pilot[4]	Sand	50-3,400	120	Atenolol	Metoprolol	Gemfibrozil	Paracetamol	
				Caffeine	Oxazepam	Roxithromycin		
				Diclofenac	Phenytoin			
				Doxylamine	Ranitidine			
				Erythromycin	Temazepam			
				Furosemide	Tramadol			
				Gabapentin	Trimethoprim			
				HCT	Venlafaxine			
Pilot[4]	GAC	50-3,400	120				Atenolol	Oxazepam
							Caffeine	Paracetamol
							Diclofenac	Phenytoin
							Doxylamine	Ranitidine
							Erythromycin	Roxithromycin
							Furosemide	Temazepam
							Gabapentin	Tramadol
							Gemfibrozil	Trimethoprim
							HCT	Venlafaxine
							Metoprolol	

NS – Not Specified; HCT – Hydrochlorothiazide; 2,4-D – 2,4-Dichlorophenoxyacetic Acid; SMX – Sulfamethoxazole; MIB – 2-Methylisoborneol; CBZ – Carbamazepine; EE – Ethinyl Estradiol; TBP – Tributyl Phosphate.
Source: [1] Reungoat et al., 2012; [2] Zearley and Summers, 2012; [3] Hallé et al., 2015; [4] Reungoat et al., 2011.

Table 3.11. Impact of Source Water and Support Media on Removal of PPCP through BAFs

Study Scale	Source Water	Media with Seeding or Existing Biomass	Water Quality	Pre-O_3 Dosage (mg/L)	EBCT (min)	Influent Conc. (ng/L)	Compounds Investigated	Removal <50%	Removal 50-75%	Removal >75%
Full[1]	Treated effluent from WWTPs	GAC	Temperature: 22.0-28.5 °C DOC: 4.2-8.1 mg/L PO_4: <0.02-2.00 mgP/L NH_4^+: <0.03-1.36 mgN/L NO_2^-: <0.02-0.06 mgN/L NO_3^-: <0.02-1.14 mgN/L pH: 6.6-7.1	1.5	9	NS	14	Caffeine Diuron Perindopril Roxithromycin Triclopyr	Atenolol HCT Metoprolol Venlafaxine	Citalopram Doxylamine Gemfibrozil Sertraline Tramadol
Full[1]	Treated effluent from WWTPs	GAC	Temperature: 22.0-28.5 °C DOC: 4.2-8.1 mg/L PO_4: <0.02-2.00 mgP/L NH_4^+: <0.03-1.36 mgN/L NO_2^-: <0.02-0.06 mgN/L NO_3^-: <0.02-1.14 mgN/L pH: 6.6-7.1	2.2	45	NS	15	Perindopril	Phenytoin	Atenolol Caffeine Citalopram Diuron Doxylamine Erythromycin Gemfibrozil HCT Metoprolol Roxithromycin Sertraline Tramadol Venlafaxine
Full[1]	Treated effluent from WWTPs	GAC	Temperature: 22.0-28.5 °C DOC: 4.2-8.1 mg/L PO_4: <0.02-2.00 mgP/L NH_4^+: <0.03-1.36 mgN/L NO_2^-: <0.02-0.06 mgN/L NO_3^-: <0.02-1.14 mgN/L pH: 6.6-7.1	5	18	NS	19	Furosemide Perindopril Triclopyr	2,4-D Caffeine Erythromycin SMX	Acetaminophen Atenolol Citalopram Diazinon Diuron Doxylamine HCT Metoprolol Roxithromycin Sertraline Tramadol Venlafaxine
Pilot[2]	Water treated with coagulation and conventional sedimentation in WTP	GAC/sand with existing biomass	-	1.0	7.4	10-695	11	BPA Gemfibrozil Iopromide	Atrazine Caffeine Ibuprofen	4-NP Atenolol Triclosan CBZ SMX

Table 3.11 Impact of Source Water and Support Media on Removal of PPCP through BAFs (Continued)

Study Scale	Source Water	Media with Seeding or Existing Biomass	Water Quality	Pre-O_3 Dosage (mg/L)	EBCT (min)	Influent Conc. (ng/L)	Compounds Investigated	Removal <50%	Removal 50-75%	Removal >75%
Bench[3]	Dechlorinated Tap Water	Sand with existing biomass	Temperature: 20±2 °C TOC: 2.6-3.1 mg/L	-	7.9	4-556	34	Acetochlor Aldicarb Atrazine CBZ Carbaryl Clofibric Acid Cotinine Diazinon Diclofenac Diuron Erythromycin EE Iopromide Malaoxon Methomyl Metolachlor Prometon Simazine SMX TBP Warfarin	2,4-D Acetaminophen Bisphenol A Caffeine Chlorpyrifos Dimethoate Gemfibrozil Naproxen	Ibuprofen MIB Molinate Triclosan Trimethoprim
Pilot[4]	Settled WW from the primary clarifiers	Anthracite seeded with mixed liquor from the MBR	Temperature: 12-22 °C TOC: 3.2-4.7 mg/L pH: 6.0-7.2 Turbidity: 0.2-0.6 NTU	2.0	20	5.5-43,000	13	Atenolol Caffeine DEET Dilantin Iopromide Meprobamate Primidone TCEP	Butalbital SMX	Amoxicillin CBZ Naproxen

WWTP – Wastewater Treatment Plant; WTP – Water Treatment Plant; WW – Wastewater; MBR – Membrane Bioreactor; NS – Not Specified; HCT – Hydrochlorothiazide; BPA – Bisphenol A; 4-NP – 4-Nonylphenol; CBZ – Carbamazepine; SMX – Sulfamethoxazole; MIB – 2-Methylisoborneol; 2,4-D – 2,4-Dichlorophenoxyacetic Acid; EE – Ethinyl Estradiol; TBP – Tributyl Phosphate.
Source: [1] Reungoat et al., 2012; [2] Hofmann et al., 2011; [3] Zearley and Summers, 2012; [4] Lee et al., 2012b.

concentration. There has been little focus on comparing BAF media substrates as well as the effect of pre-ozonation and EBCT. Moreover, the microbial activities, biomass concentration, and filter performance have not been continuously monitored during the course of past studies. Furthermore, these studies (Hallé et al., 2015; Lee et al., 2012b; McKie et al., 2016; Reungoat et al., 2012; Zearley and Summers, 2012) that investigated PPCP removals did not consider nutrient concentrations in the source water yet nutrients play a critical role in biomass development and biodegradation of PPCPs.

3.4 Summary

GAC-based substrates have been shown to exhibit improved performance: 1.5 to 3 times more efficient in removing TOC, DOC, and PPCPs than dual media. Biomass ripening is related to source water quality. To enhance the growth of biomass, nutrient and carbon amendment are needed. The time to reach steady state may require 2 to 4 weeks when seeded, while with settled or treated water biomass ripening may involve 3 to 8 months. Improved PPCP removals were observed with increased EBCT. However, EBCTs of 10 to 18 min were observed to be the optimal range for PPCP and TOC/DOC removal through BAFs. Further increasing the EBCT does not markedly improve the performance of the BAFs. Pre-ozonation breaks down the PPCPs to more biodegradable forms that results in greater removals through BAFs. The optimal ozone dosage ranged from 2 to 6 mg/L for PPCP removal. TOC, DOC, and AOC can be used as the parameters to evaluate the performance of the BAFs before the spiking with the selected indicator compounds. In contrast to chlorinated water, loss of biomass was not observed and TOC removal was also not affected when BAFs were backwashed with dechlorinated water. Atrazine,

iopromide, and TCEP were found to be the most recalcitrant compounds through biofiltration. H_2O_2 enhanced pre-ozonation (Huber et al., 2005; Wert et al., 2009) could improve the PPCP removal, because hydroxyl radicals derived from the addition of H_2O_2 reacts less selectively than ozone and may provide oxidation of compounds recalcitrant to ozone. Based on the review in this chapter, the experimental methods for the bench-scale studies are developed. The objectives of this research and the hypotheses that were tested are described in the following chapter.

CHAPTER 4

OBJECTIVES AND HYPOTHESES

The presence of PPCPs has led to a number of studies to better understand their fate, transport, and removal. Studies have demonstrated occurrences in aquatic systems all over the world. Indicator compounds representative of PPCPs with extensive usage, occurrence, persistence, range of chemical and physical properties, and resistance to treatment can be used to assess and optimize treatment process efficiency. BAFs have been gaining more attention in removing biodegradable organics in water treatment. The purpose of this research is to evaluate whether existing filters in water treatment plant can be turned into BAFs as advanced treatment processes for the additional purpose of removing PPCPs.

The objectives of this research bench-scale study are to:

- Develop biomass on the GAC and dual media substrates and monitor their formation and relationship with BAF performance.
- Understand the treatability of the indicator compounds in BAFs.
- Compare the removal efficiency in GAC and dual media BAFs.
- Evaluate the impact of EBCT on the BAF performance
- Assess PPCP treatment in the BAFs with and without pre-ozonation and investigate the effect of H_2O_2 enhanced pre-ozonation.
- Characterize the microbial community structure in the BAFs.

- Conduct a systematic analysis on the impact of operating conditions (i.e., media type, EBCT, and pre-ozonation) on the resulting microbial community structure in BAFs.

The following hypotheses are tested:

- Existing filters and adsorbents in water treatment plants can be converted to BAFs to treat PPCPs.
- GAC-based BAFs are expected to exhibit improved efficiency in removing PPCPs over dual media.
- PPCP removals are expected to increase with increasing EBCT for BAFs over 10 to 18 minutes.
- Pre-ozonation can break down the PPCPs to more biodegradable forms resulting in greater PPCP removal through BAFs.
- Microbial community structure is expected to be impacted by the operational conditions, such as media type, EBCT, and ozonation.

The following chapter describes the methods for testing the hypotheses and achieving the objectives. The approach involves bench-scale studies, spiking of indicator compounds, monitoring of microbial activities and BAF performance, and characterization of the microbial communities.

CHAPTER 5

BENCH-SCALE BAF SETUP AND ANALYTICAL METHODS

In this study, evaluating and optimizing BAFs included studying: biomass and BAF ripening, EBCT, pre-treatment ozonation, nutrient concentrations and amendments, DOC, UV_{254}, water chemistry, treatment processes in column experiments, and PPCP removals. Substrates including used GAC and dual-media were studied as BAFs in both bench-scale experiments for characterization and process optimization. Operating parameters were evaluated to optimize the BAF as well as apply pre-ozonation with and without the addition of H_2O_2. To study the relationship between biomass and BAF performance, the biomass concentrations were monitored throughout a 14-month study. Furthermore, the microbial community in BAF influents, effluents, and media was analyzed. The impact of operational conditions (i.e., media type, EBCT, and pre-ozonation) on the resulting microbial composition in BAFs was assessed. In the following sections, the experimental methods are described including bench-scale BAF design and operation, spiking of indicator compounds, monitoring of microbial activities and BAF performance, and the characterization of microbial community.

5.1 Bench-scale BAF Design and Operation

The GAC media (Calgon Filtrasorb 820; diameter at 1.0-1.2 mm) was collected from the Passaic Valley Water Commission (PVWC) water treatment plant in New Jersey, and the anthracite/sand dual media (diameter of anthracite at 0.9-1.6 mm and sand at 0.55-0.65 mm, respectively) was obtained from SUEZ North America's (SUEZ NA) Jersey City

water treatment facilities in New Jersey (Table 5.1). Both media were approximately 2 years old when collected. Eight columns were setup to evaluate PPCP removal in the BAFs with four columns dedicated to an individual BAF media: two with pre-ozonation and two without (each column run in duplicate) (Figure 5.1). The filter columns had an internal diameter of 37.5 mm and overall media depth of 400 mm; the aspect ratio was greater than 10 to prevent wall effects of media packing (Knappe et al., 1999). The depth ratio of anthracite to sand was 3:2 and is consistent with the full-scale dual media filters in the Jersey City Plant. Sampling ports for media collection were located in the upper (37.50 cm from the bottom), middle (21.25 cm from the bottom), and lower (5.00 cm from the bottom) portions of the columns. Allowing for 20 to 50% expansion of the filter bed during backwash and allowances for headloss, the overall column height was 700 mm. Filters were operated at flow rates of 25 and 44 mL/min to achieve two target EBCTs of 18 min and 10 min, respectively. Columns were covered to reduce the effect of light on biomass growth. The bench scale was designed to provide gravity flow across the individual unit processes. Peristaltic pumps were applied for source water injection and backwashing. Backwash was conducted weekly. Intermediate storage was provided to allow for overflow in the event the filters became clogged.

Pre-ozonation was conducted using an A2Z® MP-3000 multi-purpose ozone generator with a capacity of up to 3 g O_3/hr. Source water was collected from the PVWC Plant after coagulation and clarification and was maintained at 23±2 °C (Figure 5.2). Carbon, nitrogen, and phosphorous were added at a mass ratio of 15:5:1 (Liu et al., 2011) based on their concentrations in the source water to avoid any nutrient being a limiting factor for bacteria growth and control extracellular polymeric substances production

Table 5.1 Properties of Media Used in the Study

Proporties	GAC[1]	Dual Media[2]	
		Anthracite	Sand
Source	PVWC	SUEZ NA's Jersey City Water Treatment Facility	
Age of Bed When Collected	2 years	2 years	2 years
Use	Actiflo	Partical Removal	Particle Removal
Initial ATP Conc. (ng ATP/cm^3)	5 – 62	158 – 359	-
Vendor	Calgon Filtrasorb	-	-
Diameter Range (mm)	1.0 – 1.2	0.9 – 1.6	0.55-0.65
Maximum Uniformity Coefficient[3]	1.50	-	-
Density (g/cm^3)	1.5449	1.5593	2.3267
Bed Porosity	0.608	0.5	0.4
Minimum Iodine Number[4] (mg/g)	900	-	-
Surface Area (m^2/g)	900[5]	107[6]	0.302[7]

PVWC – Passaic Valley Water Commission.
[1]porous media with a larger surface area per unit volume for biomass attachment
[2]Conventional drinking water treatment process
[3]Uniformity Coefficient (CU) = d_{60}/d_{10}, when CU ≤ 4 particles were considered uniform (Adeyeri, 2015).
[4]Milligrams of iodine adsorbed by one gram of carbon when the iodine concentration in the residual filtrate is 0.02 normal, typical ranging from 500 to 1200 mg/g.
Source: [5] Klasson et al., 2009; [6] Davidson et al., 1996; [7] Tizaoui et al., 2012.

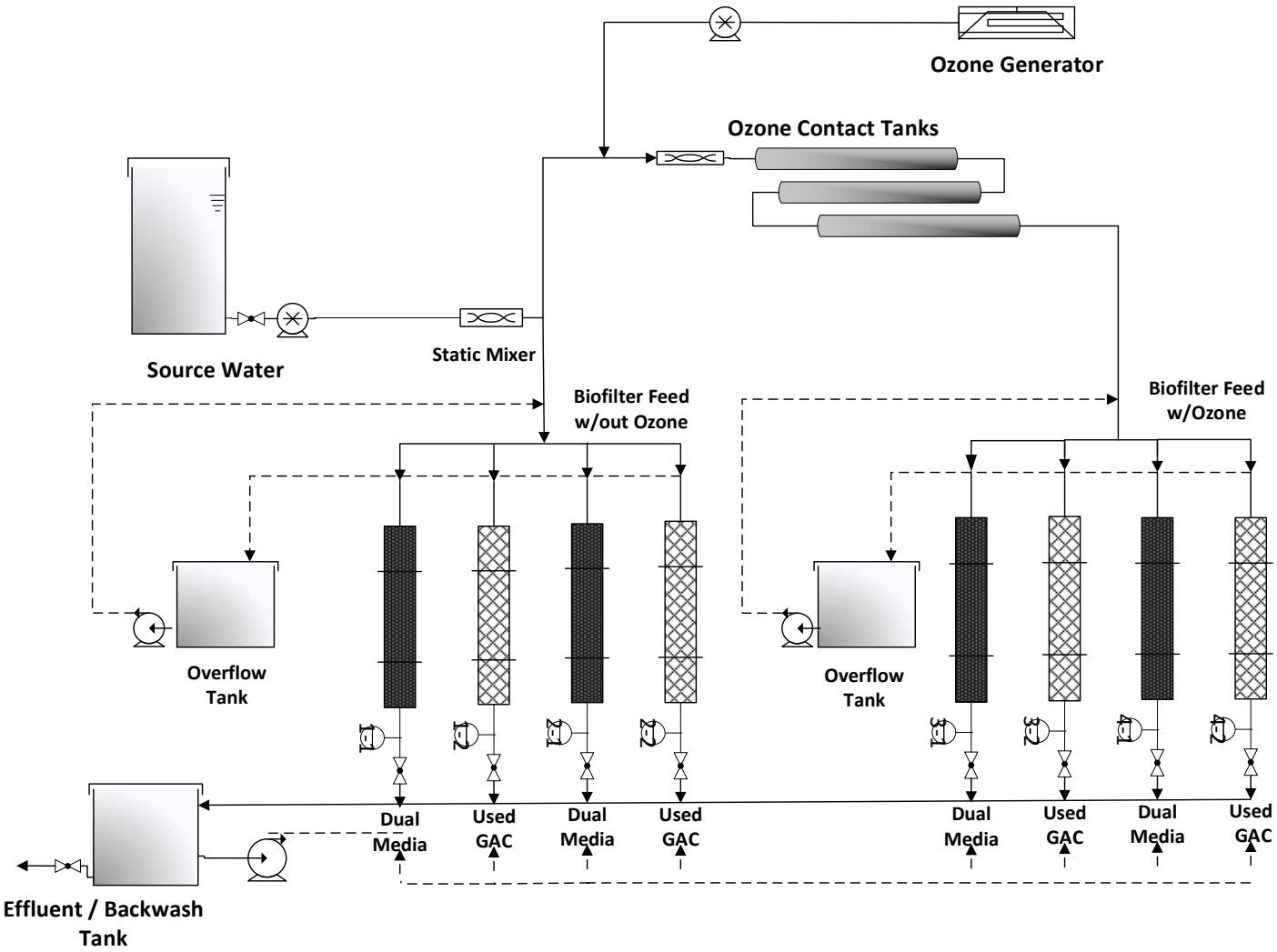


Figure 5.1 Bench-scale BAF schematic. GAC and dual media BAFs were tested in duplicate with four columns with pre-ozonation and four without pre-ozonation.

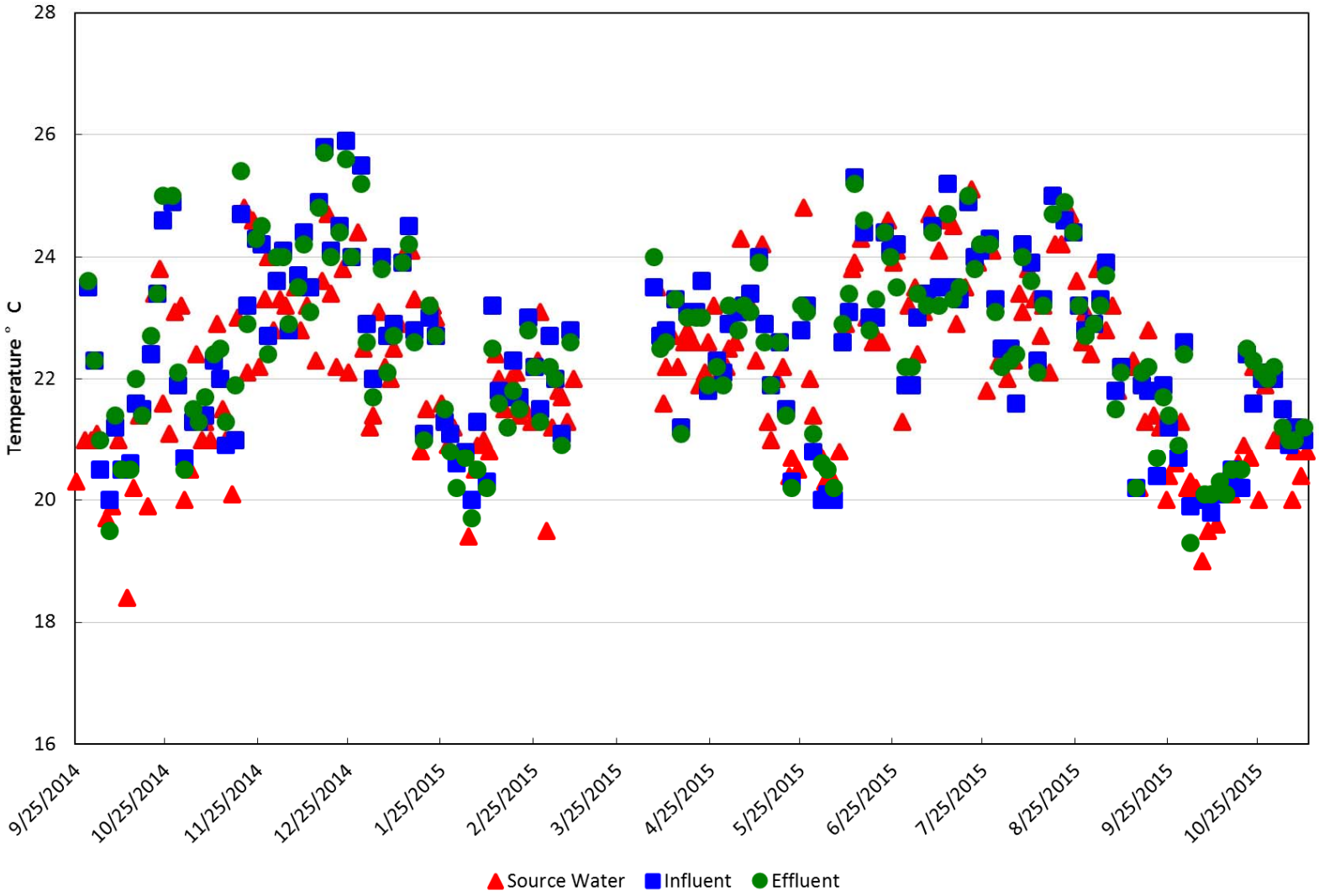


Figure 5.2 Temperature of source water (red symbols), influent (blue symbols), and effluent (green symbols) of the BAFs.

(Lauderdale et al., 2011) (Figure 5.3). Nutrients (ammonia, nitrate, nitrite, and phosphate) were analyzed using a HACH® DR 2700™ portable spectrophotometer. Potassium phosphate was used for phosphorous addition. Nitrogen amendments were not required given source water concentrations (average 2.38±1.08 mg N/L). Biodegradable organic matter (BOM) amendment before pre-ozonation included formaldehyde (100 µg/L), glyoxal (30 µg/L), formate (400 µg/L), and acetate (300 µg/L) as carbon sources to enhance the filter ripening (Urfer and Huck, 2001).

The influence of EBCT and pre-ozonation were studied with and without H_2O_2 (Table 5.2). Two ozone dosages, 3 mg/L (O_3:DOC = 0.6:1) and 4 mg/L (O_3:DOC = 0.8:1), were selected based on an ozone demand test (Figure 5.4) (NF, 2010); a minimum ozone demand of 3 mg/L was observed which included the demand for the TOC in source water and PPCPs dissolved in methanol from spiking. The dosage of 4 mg/L was selected based on the operational range of ozone dosages at PVWC and SUEZ NA treatment plants. Ozone with the addition of H_2O_2 was investigated at an optimized mass ratio of 0.2 for H_2O_2:O_3 (Snyder et al., 2006).

5.2 Indicator Compounds and Spiking Procedure

Sixteen PPCPs belonging to 11 groups were selected as priority indicator compounds reported with different levels of biodegradability (readily biodegradable, moderately biodegradable, and recalcitrant) (Tables 3.9 and 3.10): acetaminophen and ibuprofen (analgesics); erythromycin, sulfamethoxazole, and trimethoprim (antibiotics); carbamazepine (antiepileptic); atenolol (β-blocker); gemfibrozil (blood lipid regulator); TCEP (fire retardant); cotinine (nicotine metabolite); aminotriazole, atrazine, and DEET

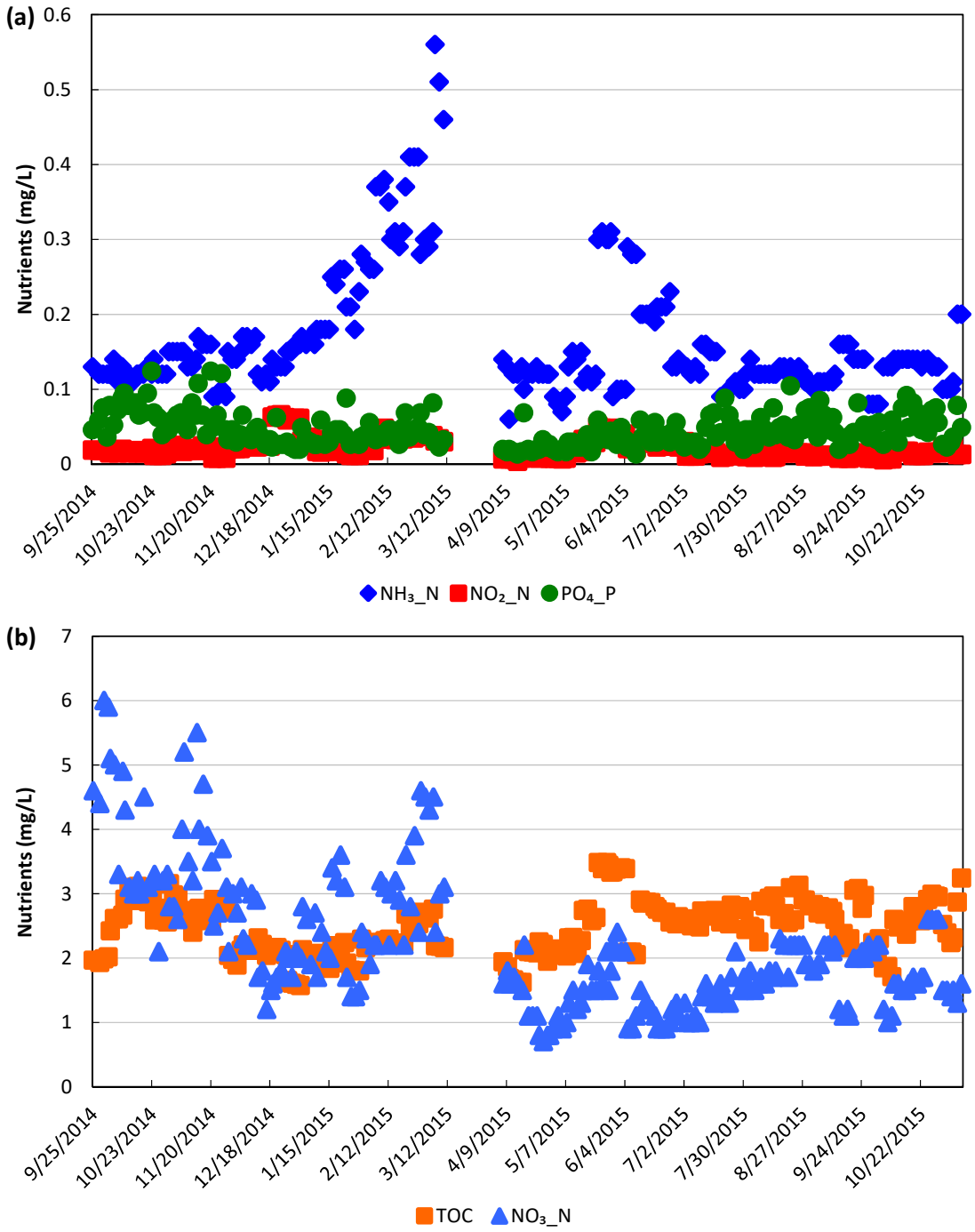


Figure 5.3 Nutrient and total organic carbon (TOC) concentrations in the source water: a) concentration of ammonia, nitrite, and phosphate; and b) concentration of TOC and nitrate.

Table 5.2 Ozone Dosage and EBCT Applied in the Bench-scale Test

Runs	**O_3 Dosage (mg/L)**	**EBCT (min)**
Run 1	3 mg O_3/L	18
Run 2	3 mg O_3/L + 0.6 mg H_2O_2/L	18
Run 3	4 mg O_3/L	18
Run 4	4 mg O_3/L + 0.8 mg H_2O_2/L	18
Run 5	3 mg O_3/L	10
Run 6	4 mg O_3/L	10
Run 7	4 mg O_3/L + 0.8 mg H_2O_2/L	10

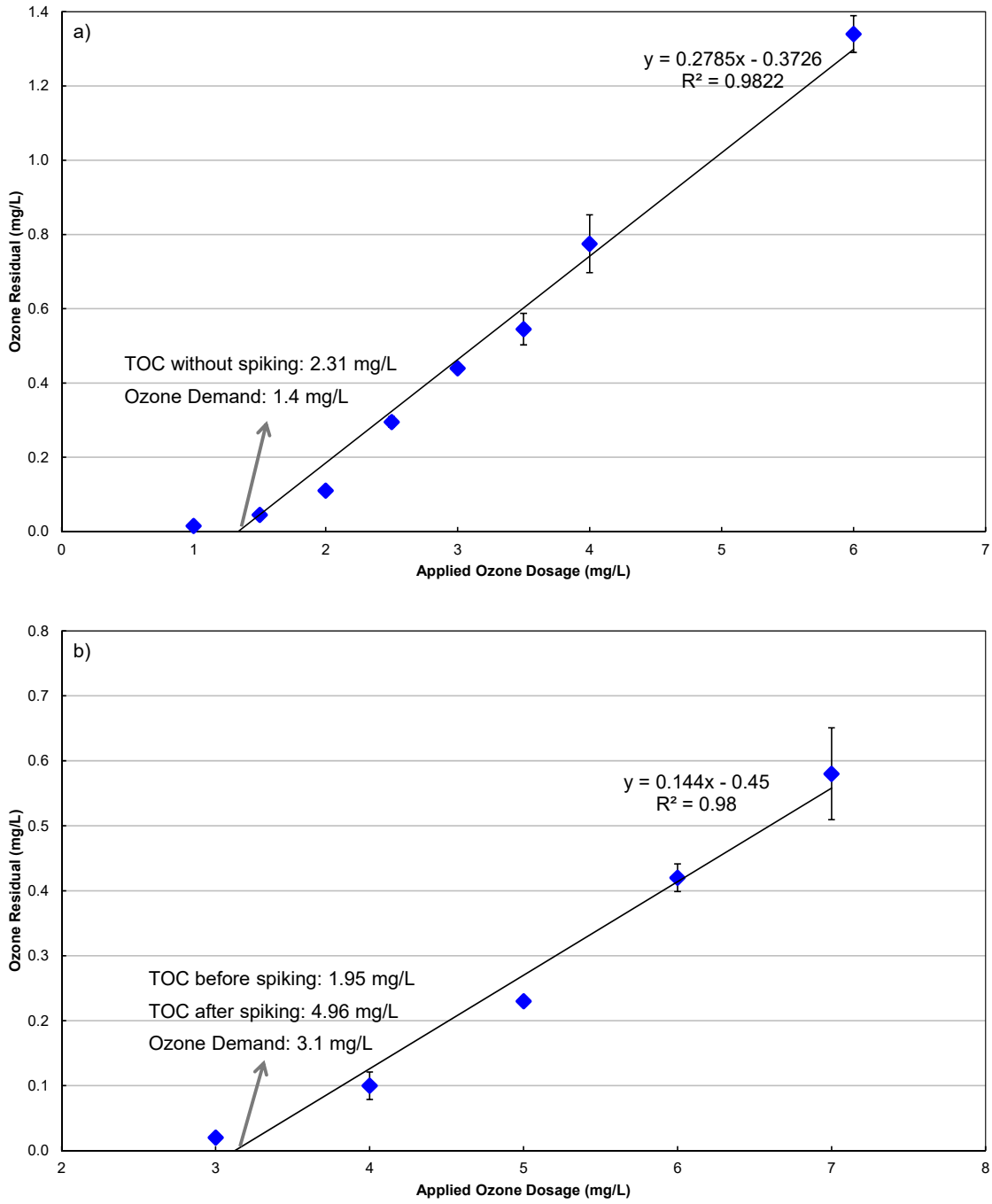


Figure 5.4 Ozone demand test. A minimum pre-ozone demand of 1.4 mg/L was observed before PPCP spiking and 3.1 mg/L was observed after spiking which accounted for TOC, PPCP, and methanol in source water.

(pesticides); caffeine (psychomotor stimulant); 17β-estradiol (steroid); and, iopromide (x-ray contrast agent). Spiked concentrations in the source water were based on environmentally relevant concentrations and their reported removal in treatment processes (Table 5.3) (Zhang et al., 2016b). Selected indicator compounds represent PPCPs widely used, detected with significant frequency in the water cycle, persistent in the environment, recalcitrant to treatment, and representative of the vast array of emerging compounds with respect to the chemical properties. All chemicals were of analytical standard quality or were labeled that they met the United States Pharmacopeia (USP) testing specifications with purity greater than 98%. A stock solution of indicator compounds was prepared in methanol (Vieno et al., 2006) and spiked in the source water during each sampling event. Removals through the BAFs were calculated based on PPCP influent and effluent concentrations. Transformation products produced from biodegradation were not evaluated in this study, although they may be more persistent and exhibit greater toxicity than the parent compounds. For example, nonylphenol ethoxylates and nonylphenol, the major biodegradation products of alkylphenol ethoxylates, are more persistent than the parent compound in aquatic environments and exhibit estrogenic properties (Farré et al., 2008). PPCP samples were sent to Eurofins Eaton Analytical and analyzed using a fully automated on-line solid phase extraction, high performance liquid chromatography, tandem mass spectrometry(SPE-HPLC-MS/MS) (Oppenheimer et al., 2011; Zhang et al., 2016b). Sodium omadine was added to prevent biological degradation of the PPCPs and a quenching agent (ascorbic acid) was preloaded for residual oxidants.

Powderless nitrile laboratory gloves were used during sampling and processing to

Table 5.3 Summary of PPCP analysis in Eurofins Eaton Analytical

Classes	Compounds	MRL ng/L	Concentration in BAF Influent ng/L
Analgesics	Acetaminophen	5	1,261
	Ibuprofen	10	1,270
Antibiotics	Erythromycin	10	1,711
	Sulfamethoxazole	5	2,471
	Trimethoprim	5	681
Antiepileptic	Carbamazepine	5	920
Beta-Blocker	Atenolol	5	389
Blood Lipid Regulators	Gemfibrozil	5	529
Fire Retardant	TCEP	5	601
Nicotine Metabolite	Cotinine	10	949
Pesticides	Aminotriazole	100	6,357
	Atrazine	5	344
	DEET	2	1,100
Psychomotor Stimulant	Caffeine	5	6,443
Steroid	17β-Estradiol	5	227
X-ray Contrast Agent	Iopromide	5	869

MRL – minimum reporting limits based on Eurofin Eaton Analytical Method.

protect against direct contact preventing contamination of the samples. Gloves were disposed and new gloves were used after collecting each sample (U.S. EPA 1669; USGS, 1999). Samples were filled to the neck of the sample bottles without overfilling or addition of air bubbles. The sample bottles were tightly sealed and chilled to 4 °C or less until receipt at the Eurofin Eaton Analytical (U.S. EPA 1669; USGS, 1999). Samples collected for analysis of PPCPs are susceptible to contamination because they are ubiquitous in daily use. To ensure sample integrity, it is important to avoid contact with or consumption of products that contain the indicator compounds (USGS, 1999). Many steps were taken to prevent contamination including maintaining distance from clothing, vicinity of material, and other possible sources of PPCPs. Clean hands/dirty hands techniques were used for water-quality sampling (USGS, 1999).

5.3 Monitoring of Microbial Activities and BAF Performance

A number of parameters were monitored over the course of this study (14 months) (Table 5.4). Oxygen consumption and pH change in the filters were investigated based on dissolved oxygen (DO) and pH measurements. Dissolved organic carbon (DOC) removal and UV_{254} reduction were monitored to evaluate BAF performance and ensure steady state conditions. Prior to analysis, samples were filtered through a 0.45 μm glass fiber filter (APHA et al., 2005). DOC was measured using a GE® Sievers 900 portable TOC analyzer (Thinnes, 2010) and UV_{254} was analyzed by an Agilent® model 8453 spectrophotometer. Monitoring of assimilable organic carbon (AOC) removal in BAFs was conducted to evaluate BAF performance as well as the effect of pre-ozonation and EBCT. Growth of bioluminescent bacteria *Pseudomonas fluorescens* P-17 and *Spirillum*

Table 5.4 Analyses and Frequency of Monitoring

Monitoring Tool	Influent	Effluent	Source Water	Media	Analysis Frequency
pH	√	√	√		Every two days
Temperature	√	√	√		Every two days
Alkalinity			√		Weekly
Hardness			√		Weekly
TOC			√		Every two days
DOC	√	√			Weekly
UV_{254}	√	√			Every two days
DO	√	√	√		Every two days
Turbidity	√	√			Every two days
Nutrients			√		Every two days
ATP				√	Every two weeks
PPCP	√	√			Seven runs
AOC	√	√			Seven runs
Illumina MiSeq sequencing	√	√		√	Two runs

sp. strain was measured during assimilation of organic carbon with a luminometer (Weinrich et al., 2009) and related to the AOC concentration. Ascorbic acid was added to quench residual oxidants.

ATP concentrations in the upper, middle, and lower portions of each BAF were analyzed once every two weeks to quantify the biomass in filter media. The method for ATP analysis was adapted from Velten et al. (2007) (Figure 5.5): 200 mg media wet weight (WW) was loaded into a centrifuge tube with 100 µL of phosphate buffer. The tube was then placed in a water bath at 30 °C. Simultaneously, 300 µL of BacTiter-Glo™ reagent (Promega Corporation, Madison, WI, USA) was transferred to a second centrifuge tube and was incubated at 30 °C for 3 min as well. After 3 min of incubation the BacTiter-Glo™ reagent was added to the media sample. After gentle mixing for 5 s, the sample container was then placed for 1.5 min into a water bath at 30 °C. The centrifuge tube was mixed gently once every 30 s to enable optimal contact between the media and the BacTiter-Glo™ reagent. Subsequently, the tube was removed from the water bath and 200 µL of the supernatant was transferred into an unused centrifuge tube. Exactly 30 s later, the relative light units (RLUs) was measured and converted to an ATP concentration using a calibration curve constructed with a pure ATP standard (Promega Corporation, Madison, WI, USA). RLUs were measured in a GloMax®-Multi Jr Single-Tube luminometer (Glomax, Turner Biosystems, Sunnyvale, CA, USA). DOC removal in the BAFs was normalized to the ATP concentration measured at the upper portion of the filters to compare the DOC removal efficiency of the microorganisms in the GAC and dual media BAFs. Influent and effluent turbidity was measured using a HF® Scientific DRT-15CE portable turbidimeter to ensure an NTU less than 0.1 (Figure 5.6), otherwise

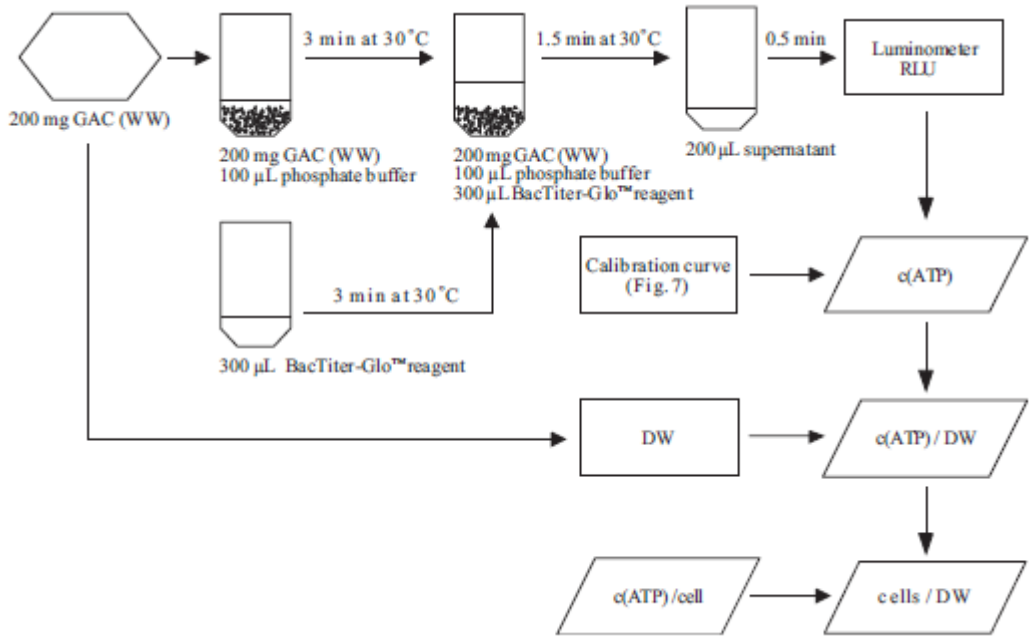


Figure 5.5 Schematic layout of the direct ATP measurement (Velten et al., 2007).

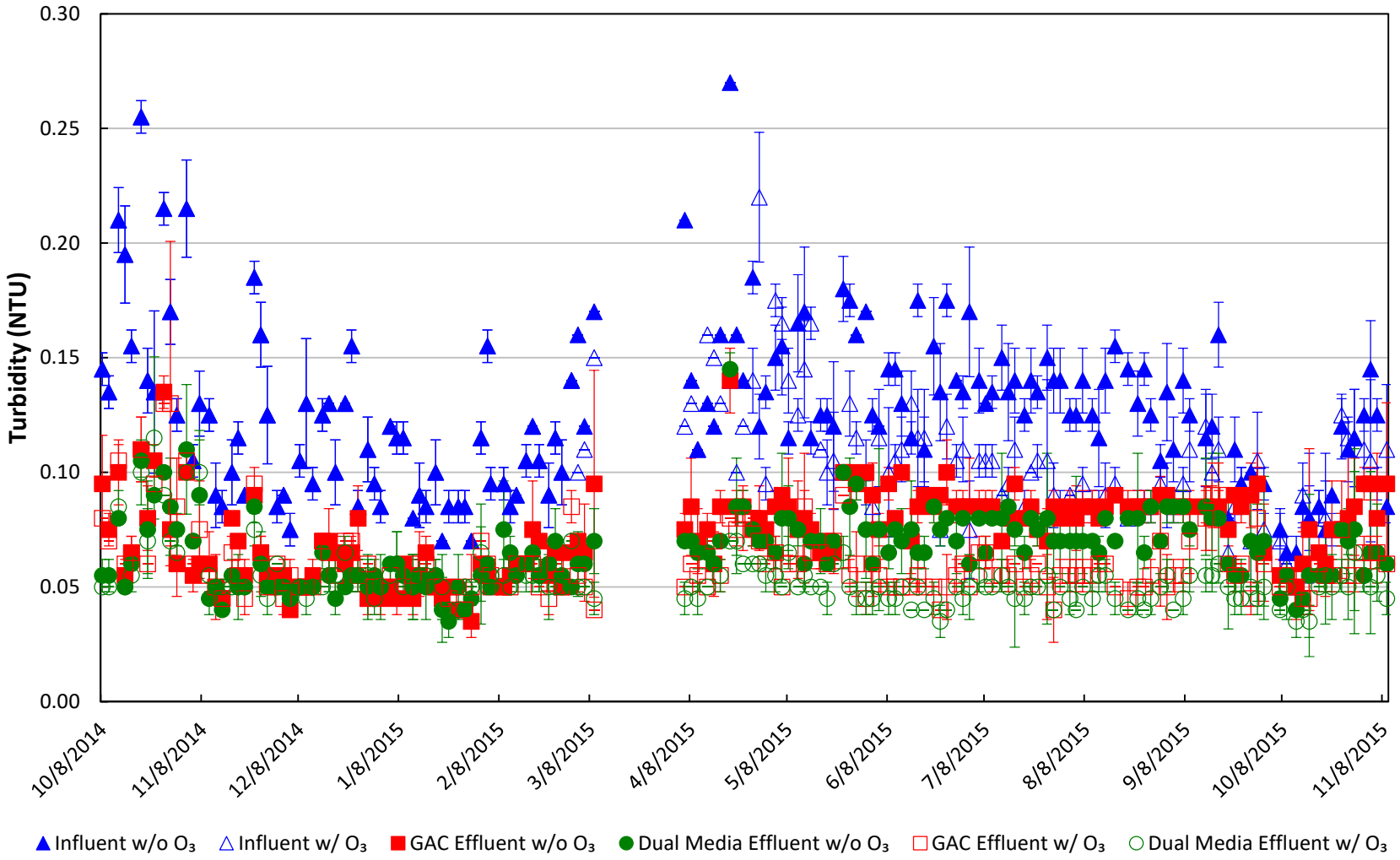


Figure 5.6 Turbidity in filter influents (blue symbols), GAC BAF effluents (red symbols), and dual media BAF effluents (green symbols) with and without ozonation.

the filters would be backwashed. Microbial community structure in media and filter influent and effluent were studied as well by Next-generation sequencing (Illumina MiSeq).

5.4 Microbial Community

The microbial community structure was studied after reaching steady state conditions. Samples were collected from the BAF influent, effluent, and media as a function of EBCT (18 min and 10 min), media (GAC and dual media), and application of pre-ozonation (4 mg/L). For filter influents and effluents, 500 mL of water was filtered through a sterile 0.22 μm polycarbonate membrane filter (47 mm diameter, Millipore, USA) (Pinto et al., 2012). Media samples (1 gram) were collected from the upper portion of the BAFs (2.5 cm from the top of the bed) using a sterile spatula. The filter sheets and media samples were transferred and secured into sterile 15 mL polypropylene centrifuge tubes with caps. All samples were frozen and shipped on dry ice at -20 ºC to Microsynth AG (Switzerland) for sequencing.

DNA extraction was conducted using FastDNA® SPIN Kit (MP Biomedicals, Solon, OH, USA) following the instruction manual of the manufacturer (Camarinha-Silva et al., 2014). Polymerase chain reaction (PCR) amplicon libraries for 16S rRNA gene sequences were constructed applying universal bacterial primers 341F (5'-CCTACGGGNGGCWGCAG-3') and 802R (5'-TACNVGGGTATCTAATCC-3'). The PCR used in this study amplifies the region V3 and V4 of the 16S rRNA gene with the primer pair proposed by Klindworth et al. (2013) and amplifies the majority of the known bacterial species (Lee et al., 2012a).

PCR products were purified and prepared for sequencing using Nextera XT library kit (Illumina, USA). Samples were indexed and pooled in single runs of Illumina MiSeq sequencing (De Vrieze et al., 2016). FLASH (Fast Length Adjustment of SHort reads) (Magoč and Salzberg, 2011) was used to join two paired-end reads (R1 and R2) on the overlapping ends. QIIME (Quantitative Insights Into Microbial Ecology) (Caporaso et al., 2010) was applied for metagenomic data analysis and sequence quality filtering with 75% consecutive high-quality base calls (p), the maximum number of consecutive low-quality base calls (r) of 3, the maximum number of ambiguous bases (n) of 0, and the minimum Phred quality score (q) of 3 (Navas-Molina et al., 2013). Sequences that passed the quality filtering were clustered into operational taxonomic units (OTUs) using Uclust (Edgar, 2010) at 97% of sequence similarity. The taxonomy was assigned to the OTUs based on the Green-Genes database (DeSantis et al., 2006; McDonald et al., 2012) and Ribosomal Database Project (RDP) classifier (Cole et al., 2007).

Microbial diversity and evenness were evaluated based on Shannon diversity index and Shannon's equitability, respectively (Shannon, 1948). The Heat map was implemented using WallGene (Genostar, 2015) and the Z-score for each sample was calculated. PPCP removal is related to the microbial community structure in the BAFs. To evaluate the impact of operational conditions on the microbial community structure, a factorial analysis was conducted (e.g., Xu and Axe, 2005). The factors considered included media type (GAC and dual media), EBCT (18 min and 10 min), and pre-ozonation. The impact of a factor on the abundance of bacteria was considered significant when the p-value was less than 0.05 with a 95% confidence interval. Principal component analysis (PCA) was conducted as well to reduce the dimensionality of the data (Shu et al.,

2015). In this study, PCA was applied to understand variables (i.e., abundance of bacteria class) that showed significant responses in GAC or dual media BAF media when ozone was applied or EBCT was changed.

5.5 Summary

The removal of 16 indicator compounds through BAFs is evaluated in this bench-scale study (Table 5.3). Support media involved GAC and anthracite/sand dual media (Table 5.5). Source water was collected from PVWC after clarification process with a carbon, nitrogen, and phosphorous ratio of 15:5:1. The impact of pre-ozonation was studied. The pre-ozonation dosage was based on the ozone demand tests. EBCT ranging from 10 to 18 min was tested. BAF effluents was used for backwashing. Water quality including pH, temperature, DO, turbidity, alkalinity, and hardness was monitored (Table 5.4). Nutrients in source water including ammonia, nitrate, nitrite, and phosphate and TOC were evaluated for carbon and nutrient amendments. DOC and UV_{254} in influent and effluent from the BAFs was analyzed to assess the BAF performance. The biomass concentration in upper, middle, and lower portion of the BAFs was analyzed as a function of time. Microbial community were characterized in BAF influents, effluents, and media samples. Through a factorial study, the impact of operational conditions (i.e., media type, EBCT, and pre-ozonation) on the resulting microbial composition in BAFs was addressed. The potential metabolic pathways were summarized based on literature. The results of this study are discussed in the following chapter.

Table 5.5 Source Water and Operating Conditions

Source Water	**Media**	**Nutrient and Carbon Amendment**	**Column**	**EBCT (min)**	**HLR gpm/sf**	**Pre-O_3 (mg/L)**	**Backwashing**
Water after Clarification	GAC and Anthracite/Sand	C:N:P (w/w/w) = 15:5:1	ID: 37.5 mm MD: 400 mm	10 to 18	0.55 to 0.98	Determined by ozone demand tests	BAF effluent

CHAPTER 6

RESULTS AND DISCUSSION

In this chapter, the results for the biomass ripening and microbial activites are discussed with ATP concentration, DO, and pH in the BAFs. The performance of the BAFs is then presented basd on DOC removal, UV_{254} reduction, and AOC removal through the BAFs. Removal of PPCP in the BAFs is compared as a function of media, EBCT, and pre-ozonation. The chapter continues with the diversity and composition of the microbial community in the BAF media, influents, and effluents as well as the impact of the operational conditions on the resulting community structure in the media. The abundance of the pathogens observed in the influent, effluent, and media samples is discussed along with the operational conditions. Moreover, the potential pathways of PPCP biodegradation is summarized based on literature.

6.1 Biomass Ripening and Microbial Activities

Biomass acclimation required a period of 6 months to reach steady state (Figure 6.1). Initial ATP concentrations in GAC (5 to 62 ng ATP/cm^3) were less than that in the dual media BAFs (158 to 359 ng ATP/cm^3); this difference was also observed after the steady state and may be due to the use of prechlorination at PVWC where the GAC was obtained (chlorine residual 0.5 mg/L) (Ahmad et al., 1998; Butterfield et al., 2002; Miltner et al., 1995; Stoddart and Gagnon, 2015). ATP concentrations were observed to be greatest in the upper portion of the columns where concentrations were approximately 350 ng ATP/cm^3 for GAC BAF and 800 ng ATP/cm^3 for dual media BAF, as much as

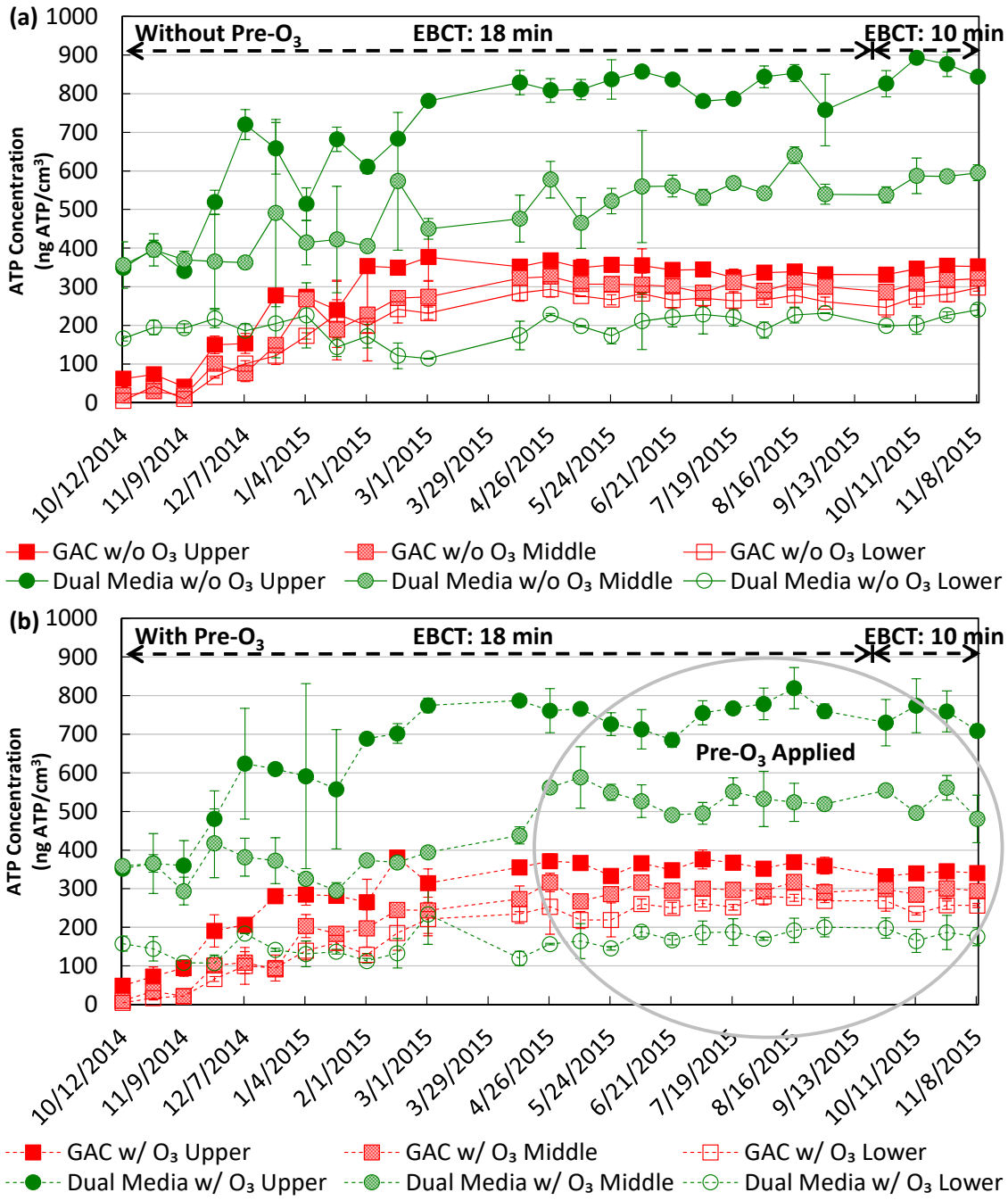


Figure 6.1 ATP concentration in upper, middle, and lower portions of the GAC (red symbols) and dual media (green symbols) BAFs with and without pre-ozonation. Empty bed contact time was switched from 18 min to 10 min for PPCP test. Solid, dotted, and hollow symbols indicate upper, middle, and lower portions of the BAFs, respectively. Solid line and dash line indicate results without and with pre-ozonation, respectively (a) ATP concentration in BAFs without pre-ozonation; and (b) ATP concentration in BAFs with pre-ozonation.

four times greater than the middle and lower portions. Influence of pre-ozonation and EBCT on the ATP concentration was insignificant. As the biomass growth reached steady state, the change in ATP concentrations as a function of EBCT and pre-ozonation was less than 5%.

Influent DO concentrations varied as a function of the season with approximately 4.5 to 6 mg/L from May to October and 5.5 to 7.5 mg/L from September to April (Figure 6.2). GAC BAFs revealed greater oxygen consumption than dual media. At an EBCT of 18 min, the GAC BAF consumed an average of 0.84±0.17 mg/L oxygen compared to dual media where 0.43±0.08 mg/L oxygen consumption was observed. At an EBCT of 10 min, oxygen consumption dropped by approximately 40% to 0.50±0.06 mg/L for GAC BAFs and 0.26±0.03 mg/L for dual media.

Similar trends were observed for pH changes across the columns (Figure 6.3). Source water pH was adjusted to 7.39±0.12 before use which is consistent with the pH (7.4±0.23) of the source water in PVWC. On average, pH from the GAC BAF effluents decreased by approximately 0.34±2% pH units at an EBCT of 18 min and 0.16±2% at an EBCT of 10 min. In dual media BAFs, the pH drop was less with 0.20±2% at an 18 min EBCT and 0.10±2% at a 10 min EBCT. The pH change across the dual media BAFs suggests reduced respiration or CO_2 production compared to the GAC BAFs, which is consistent with oxygen consumption. Decreased contact time resulted in a reduction in pH change across the columns as well. Overall, the greater oxygen consumption and increased CO_2 production (with a drop in pH) across the GAC BAFs suggest a different microbial community structure compared to dual media.

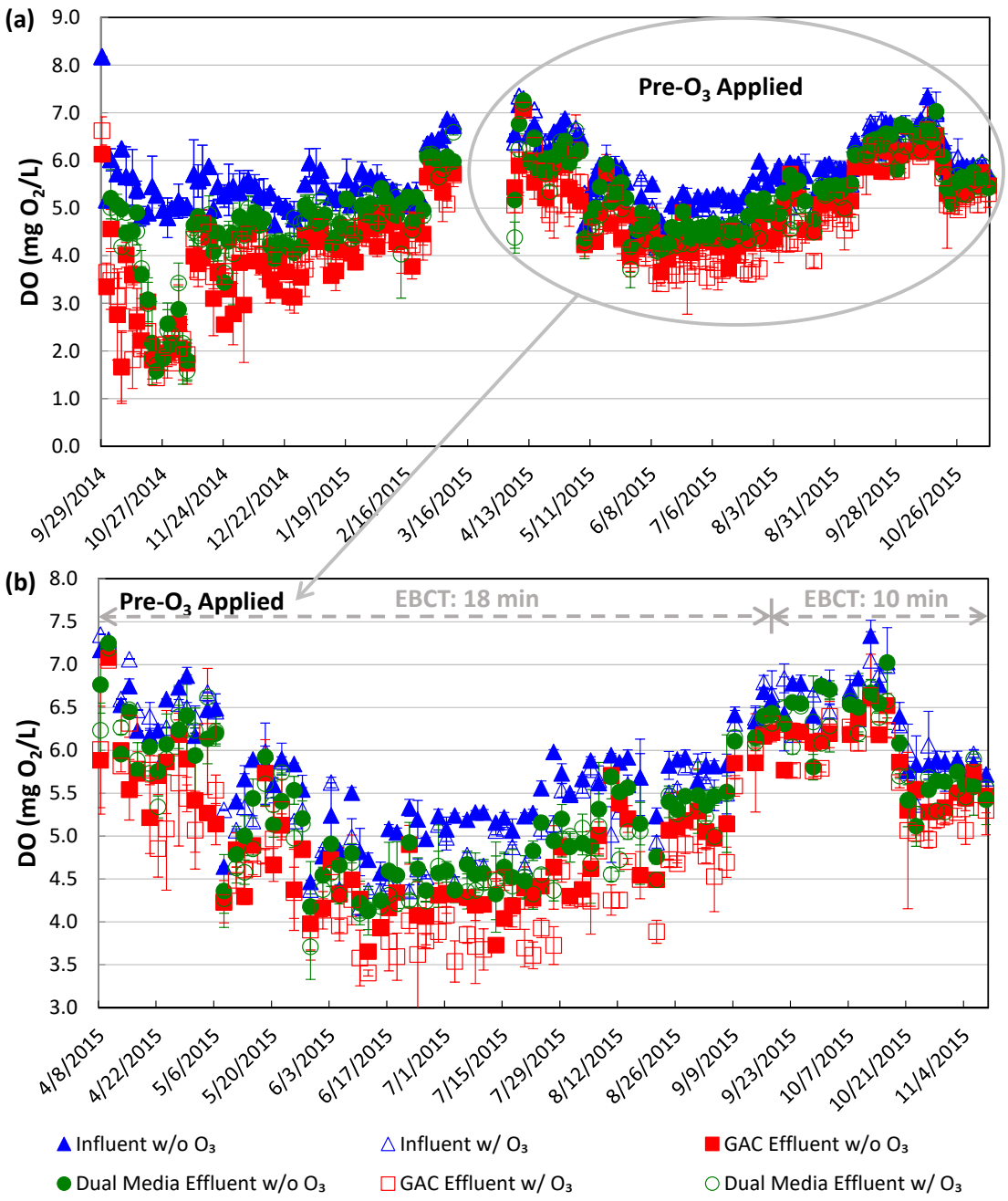


Figure 6.2 Dissolved oxygen consumption in BAFs with and without pre-ozonation. BAFs started up without pre-ozonation for all columns for biomass ripening. Pre-ozonation was applied to half of the BAFs after steady state was reached. Empty bed contact time was switched from 18 min to 10 min for PPCP test. (a) All DO data during this study; and (b) DO data after pre-ozonation was applied; solid symbols indicate columns without pre-ozonation and hollow symbols indicate columns with pre-ozonation.

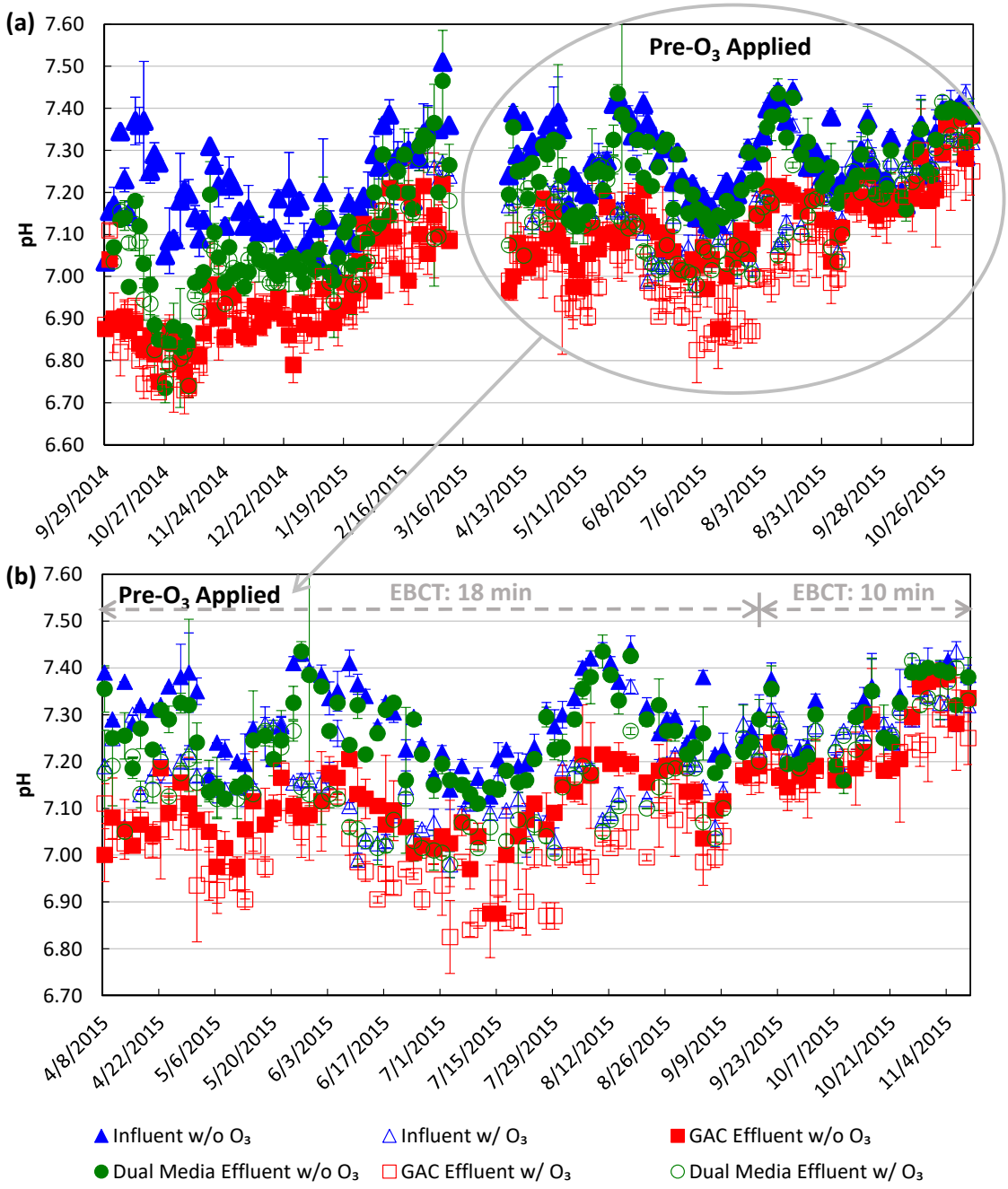


Figure 6.3 pH in BAF influents and effluents with and without pre-ozonation. BAFs started up without pre-ozonation for all columns for biomass ripening. Pre-ozonation was applied to half of the BAFs after steady state was reached. Empty bed contact time was switched from 18 min to 10 min for PPCP test. (a) All pH data during this study; and (b) pH data after pre-ozonation was applied; solid symbols indicate columns without pre-ozonation and hollow symbols indicate columns with pre-ozonation.

6.2 Performance of BAFs

Consistent with ATP results, steady state conditions were observed after 6 months of operation where DOC removal plateaued at 3% to 10% (median: 5.2%) for GAC BAFs and 5% to 15% (median: 7.6%) for dual media BAFs (Figure 6.4). Based on the ozone demand, pre-ozonation (3 mg/L) was applied for two GAC and two dual media columns after achieving steady state conditions. Influent DOC was reduced by approximately 12% (from 1.7±0.2 mg/L to 1.5±0.1 mg/L) through ozonation (Figure 6.4b). The impact of pre-ozonation on DOC removal in the subsequent GAC BAFs ($p = 0.277$, based on t-test at 95% confidence interval) and dual media BAFs ($p = 0.317$) was statistically insignificant. On the other hand, EBCT played a critical role on DOC removals. When the EBCT was reduced from 18 min to 10 min, DOC removal dropped by approximately 50% (Figure 6.4b). DOC removal normalized to ATP at the upper portion of the BAFs reveals significantly greater DOC removal efficiency of the microorganisms in the GAC BAFs than in dual media BAFs (Figure 6.5). Generally, DOC removals ranged from 200 to 600 mg/g ATP in GAC BAFs at an 18 min EBCT and is consistent with Velten et al. (2011) and Lautenschlager et al. (2014) (Table 6.1). On the other hand, for the dual media BAFs, removals were less than half (100 to 200 mg/g ATP) than that observed for the GAC BAFs. These results are consistent with oxygen consumption and pH drops across the beds, again indicating a potentially unique microbial community structure in GAC BAFs. This same trend was also observed at an EBCT of 10 min as well.

Reduction in UV_{254} absorbance is consistent with DOC removals (Figures 6.4 and 6.6); the carbon-carbon double bonds in organic molecules contribute to UV absorbance (Carey, 1996). At steady state, UV_{254} reduction plateaued at 3% to 10% (median: 7.9%)

Table 6.1 Comparison between Literautre Results and Our Study – DOC Removal Normalized to the ATP Concentration in the Upper Portion of the BAFs

Media	EBCT (min)	Pre-O_3 (mg/L)	ATP (ng ATP/cm^3)	DOC removed (mg/L)	(mg/DOC)/(g ATP)
GAC[1]	8-22	1.1	220 ± 77	0.21	580
Sand[1]	19-56	1.1	79 ± 7.4	0.072	550
GAC[2]	16	Not specified	538 ± 0.092	0.24	270
Our Study					
GAC	10	1.5-2.5	360 ± 16	0.08	360±171
	18	1.5-2.5	360 ± 16	0.11	433±237
Anthracite	10	1.5-2.5	749 ± 41	0.11	98±29
	18	1.5-2.5	749 ± 41	0.15	150±44

Source: [1] Lautenschlager et al., 2014 – Influent DOC: 0.96±0.07 mg/L; [2] Velten et al., 2011 – Influent DOC: 1.1±0.04 mg/L.

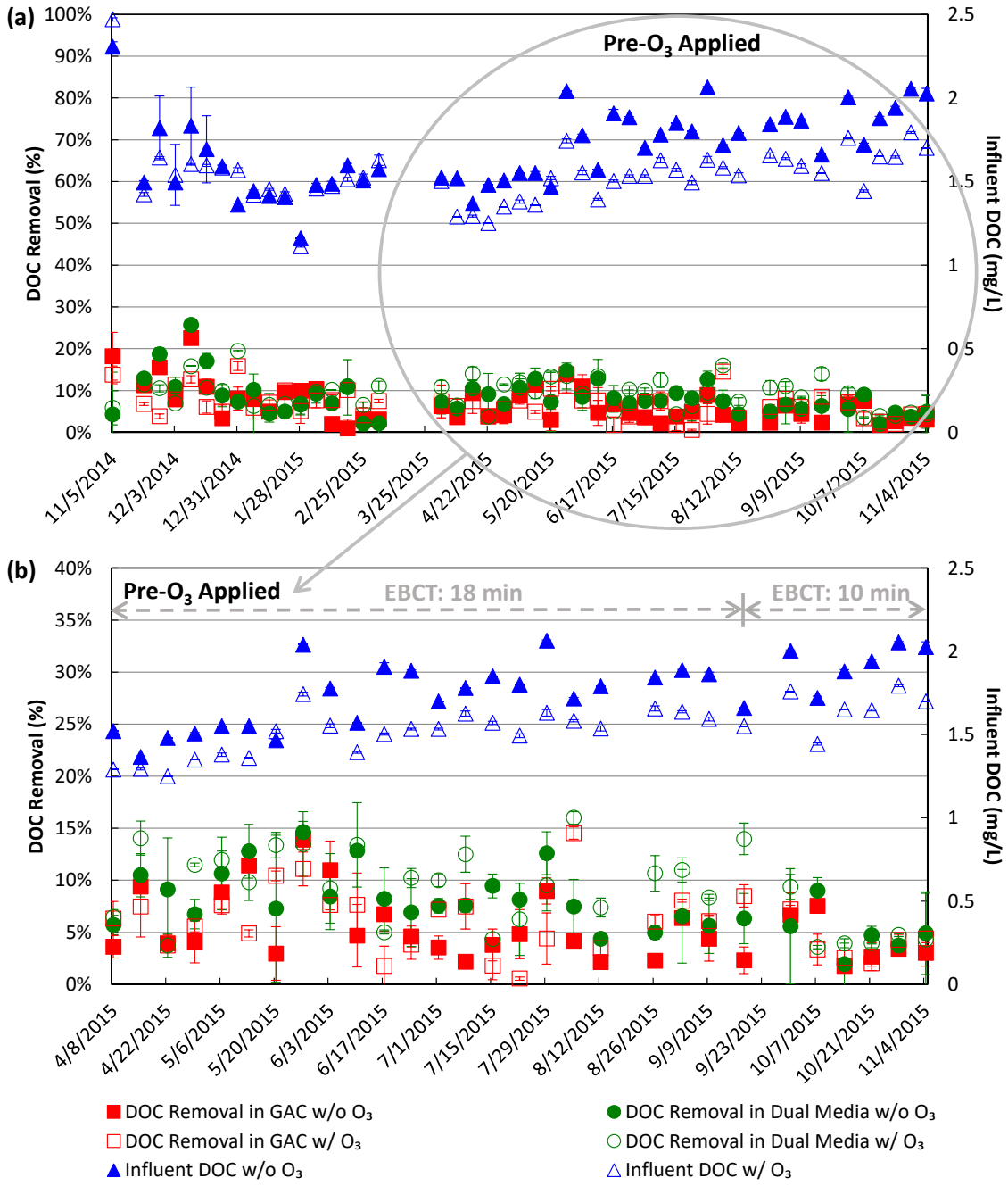


Figure 6.4 Influent DOC (triangle symbols) and its removal (square and circle symbols) in BAFs with and without pre-ozonation. BAFs started up without pre-ozonation for all columns for biomass ripening. Pre-ozonation was applied to half of the BAFs after steady state was reached. Empty bed contact time was switched from 18 min to 10 min for PPCP test. Solid and hollow symbols indicate data without and with pre-ozonation, respectively: (a) all data during this study; and (b) data after pre-ozonation was applied.

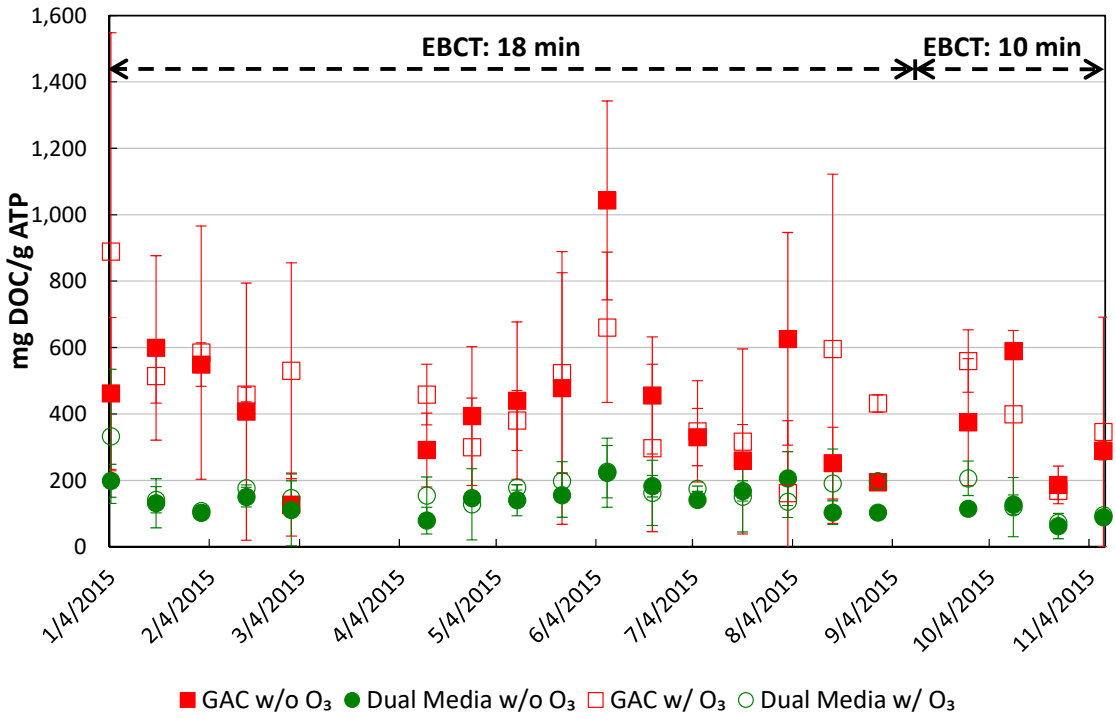


Figure 6.5 Comparison of microbial activities based on DOC removal per gram of ATP. BAFs started up without pre-ozonation for all columns for biomass ripening. Pre-ozonation was applied to four columns of the BAFs after steady state was reached (April 4, 2015). Empty bed contact time was switched from 18 min to 10 min for PPCP test. Solid and hollow symbols indicate data without and with pre-ozonation, respectively.

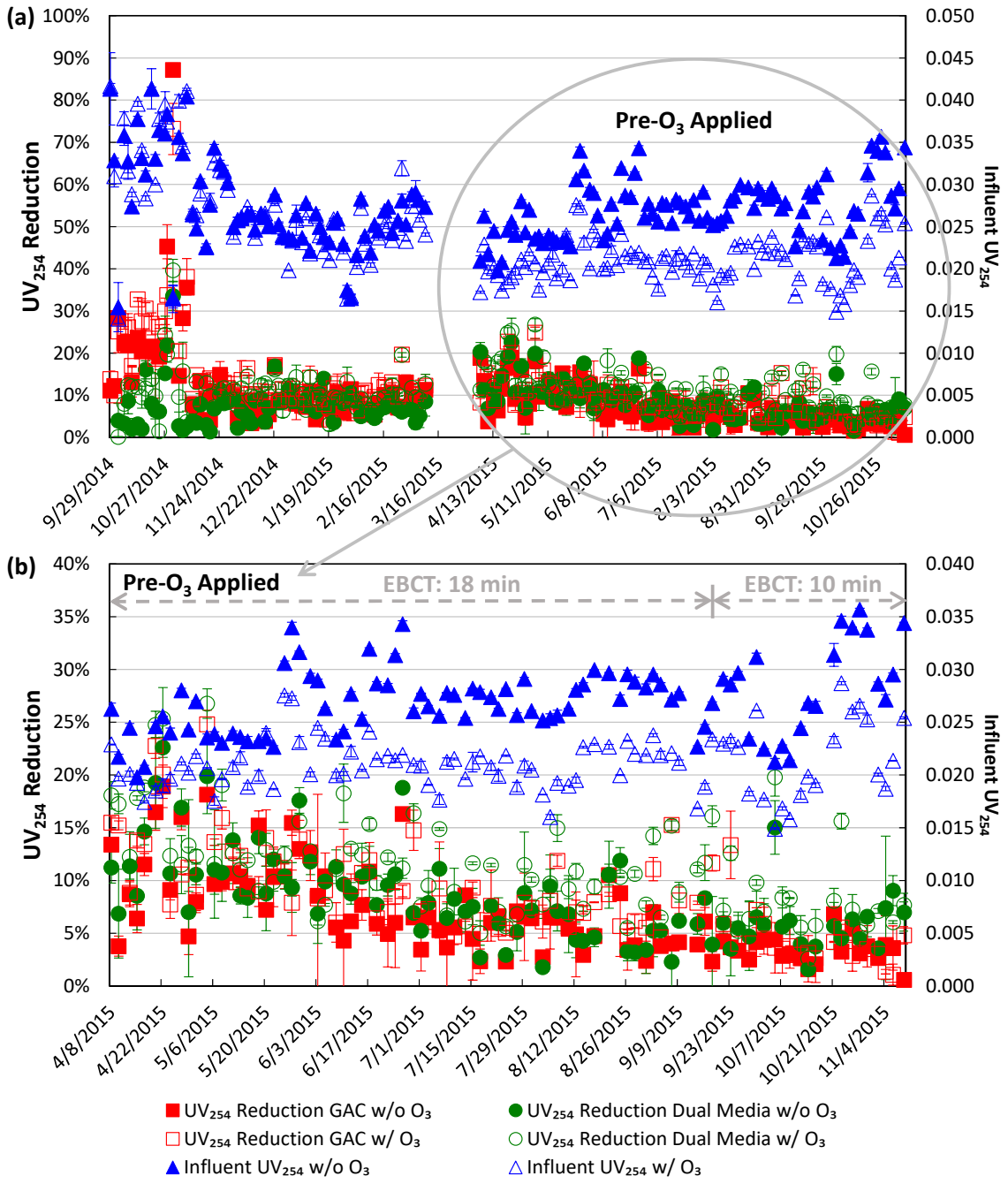


Figure 6.6 Influent UV_{254} (triangle symbols) and its reduction (square and circle symbols) in BAFs with and without pre-ozonation. BAFs started up without pre-ozonation for all columns for biomass ripening. Pre-ozonation was applied to half of the BAFs after steady state was reached. Empty bed contact time was switched from 18 min to 10 min for PPCP test. Solid and hollow symbols indicate data without and with pre-ozonation, respectively: (a) all data during this study; and (b) data after pre-ozonation was applied.

for GAC BAFs and 5% to 15% (median: 10.2%) for dual media BAFs; this reduction dropped by approximately 50% with reduced EBCT. Pre-ozonation decreased influent UV_{254} by 20% as ozone breaks down the carbon-carbon double bonds. Consistent reduction of UV_{254} throughout the study suggests that removal may be attributed to biodegradation in the BAFs.

AOC is generally used to assess the potential for microbial growth in drinking water treatment systems as it represents less complex NOM that is easily biodegradable (Evans et al., 2013; LeChevallier et al., 1992; Liu et al., 2002). In this study, AOC was used to evaluate BAF performance as well as the effect of pre-ozonation and EBCT (Figure 6.7). AOC concentrations increased by up to a factor of three when pre-ozonation was applied; oxidation increased influent AOC by breaking down DOC to more easily assimilated organic carbon for bacteria to consume (Pharand et al., 2015; Thayanukul et al., 2013). As a result, AOC removal in the BAFs increased by more than 50% (Figure 6.7). No significant difference was observed between the AOC removals in GAC and dual media BAFs ($p = 0.05$); this result further corroborates that adsorption is insignificant as AOC removal through GAC by adsorption would be significantly greater than through dual-media. A reduction in AOC removal was observed when the EBCT was reduced from 18 min to 10 min decreasing the time for bacteria to consume organic carbon. Influent AOC was less than 10 µg/L when H_2O_2 was applied (Figure 6.7); this result is consistent with others (Bazri et al., 2012) where in the AOC analysis H_2O_2 inhibits the growth of the microorganisms and leads to an underestimate of AOC.

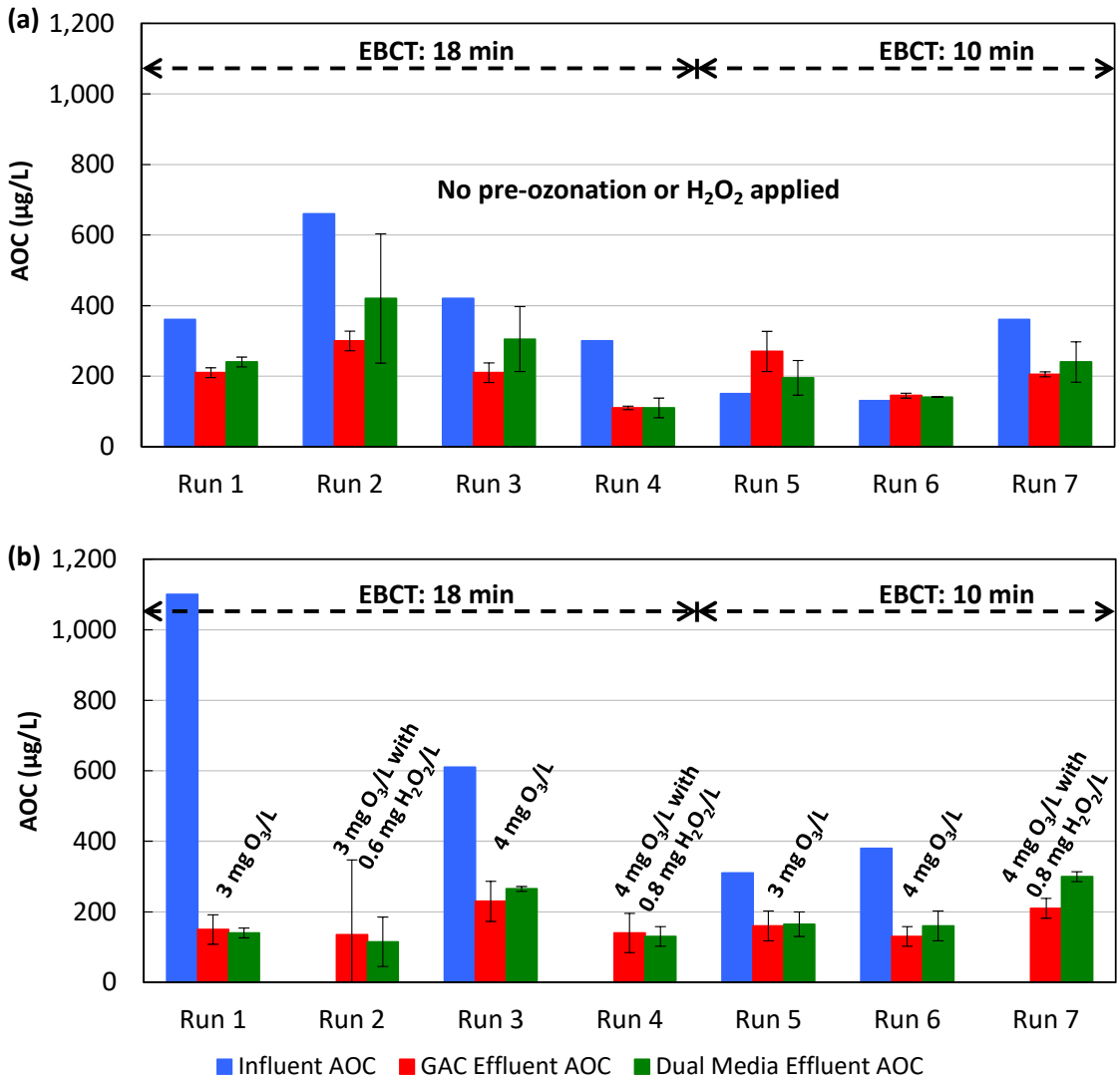


Figure 6.7 AOC concentration in influent (blue symbol), GAC BAF effluent (red symbol), and dual media BAF effluent (green symbol) (a) without pre-ozonation; and (b) with pre-ozonation with or without H_2O_2.

6.3 Removal of PPCPs in GAC and Dual Media BAFs

GAC BAFs without pre-ozonation showed significant PPCP removal (Figure 6.8). At an EBCT of 18 min (Runs 1-4), all compounds were removed by greater than 80% with the exception of TCEP (average 76% removal) and iopromide (average 59% removal). This significant as well as consistent removal was observed over the entire four-month sampling period for the PPCPs (June, 2015 to September, 2015). Given the GAC and dual-media were over 2 years old at the onset of the study with organic carbon and PPCPs in the source water (Table 6.2), removals observed with these exhausted media along with the performance of the beds (i.e., AOC, ATP concentration, DOC removal, UV_{254} reduction, and the pH and DO drops) are consistent with biodegradation. Dual media BAFs, showed limited PPCP removal for the same EBCT. Acetaminophen, ibuprofen, trimethoprim, and 17β estradiol were the only PPCPs that were consistently removed by greater than 80%. Ibuprofen and atenolol were removed by greater than 75%. All the other compounds were removed by less than 50%. The most recalcitrant compounds were carbamazepine, TCEP, cotinine, aminotriazole, atrazine, DEET, and iopromide with removals generally less than 30%. These observations are consistent with other studies where acetaminophen, ibuprofen, and trimethoprim were reported to be readily biodegradable (removal > 75%) in dual media or sand BAFs with an EBCT greater than 14 min (Hallé et al., 2015; Reungoat et al., 2012; Zearley and Summers, 2012), while TCEP, cotinine, atrazine, DEET, and iopromide were moderately biodegradable (removal: 50%-75%) or recalcitrant (removal < 50%) (Hallé et al., 2015; Hofmann et al., 2011; Lee et al., 2012b; Zearley and Summers, 2012) (Table 3.10). Compared to dual media BAFs, GAC BAFs at an EBCT of 18 min achieved consistent

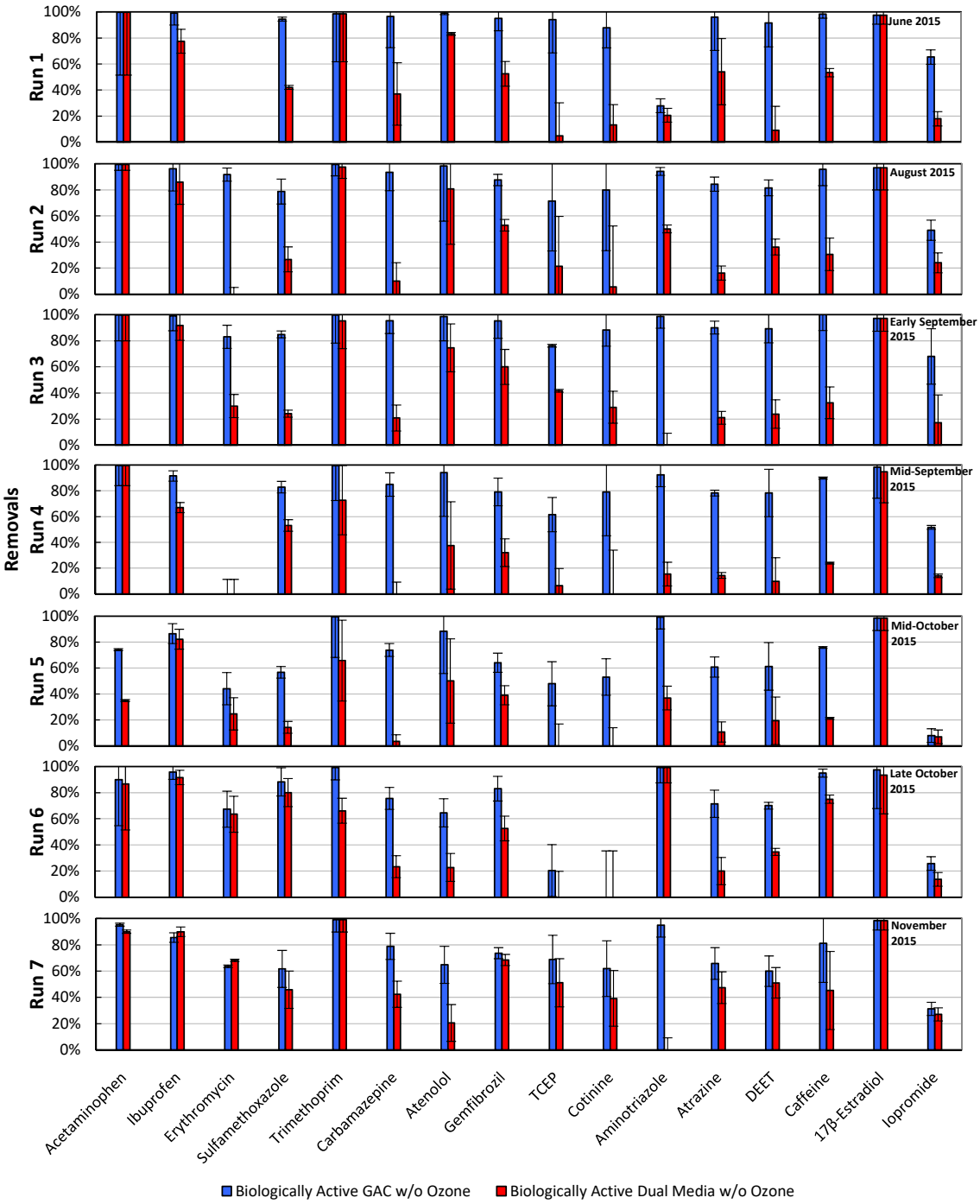


Figure 6.8 PPCP removal without ozonation. Runs 1 to 4 operated at an EBCT of 18 min; Runs 5 to 7 operated at an EBCT of 10 min.

Table 6.2 Water Quality of the Raw Water in Passaic Valley Water Commission

Parameters	**PVWC***
pH	6.9-8.2
Temperature (°C)	20.6-28.0
Turbidity (NTU)	3.2-5.4
TOC (mg/L)	3.6-6.9
UV@254 (nm)	0.092-0.157
Caffeine (ng/L)	61-130
Carbamazepine (ng/L)	57
Cotinine (ng/L)	18-19
DEET (ng/L)	62-100
Sulfamethoxazole (ng/L)	14
TCEP (ng/L)	74-120

Source: *Spencer et al., 2013.

and significant removals needed for a sustainable treatment process. The greater PPCP removals observed in GAC BAFs compared to dual media BAFs may result from different microbial community structure developed in the two media. This hypothesis was tested by characterizing the microbial community structure in media samples using Illumina MiSeq sequencing (Ji et al., 2015).

6.4 Impact of EBCT on PPCP Removals

With the reduced EBCT of 10 min without pre-ozonation (Figures 6.8 and 6.9), GAC BAFs revealed that less than half of the compounds were removed at greater than 80%. Specifically, acetaminophen, ibuprofen, trimethoprim, aminotriazole, and 17β-estradiol were consistently removed at greater than 80%, despite the reduced EBCT. The most significant impact in reducing the EBCT from 18 to 10 min was found for TCEP, cotinine, and iopromide, where the average removal dropped from 76% to 46% for TCEP, 84% to 38% for cotinine, and 59% to 22% for iopromide. All the other compounds were generally removed by greater than 60% with a 10 min EBCT. Similar trends were reported in other studies (Reungoat et al., 2012; Zearley and Summers, 2012), as EBCT is a critical design parameter. For example, Hallé et al. (2015) found that dual media BAFs with a reduced EBCT showed decreased removals. In our study, for dual media BAFs, ibuprofen and 17β-estradiol were the only PPCPs that were removed by greater than 80%. For acetaminophen and trimethoprim, the removals were reduced to 71% and 77%, respectively, in reducing the EBCT from 18 to 10 min; the remaining compounds were removed by less than 55%. For the most recalcitrant compounds, carbamazepine, TCEP, cotinine, aminotriazole, atrazine, DEET, and iopromide, removals

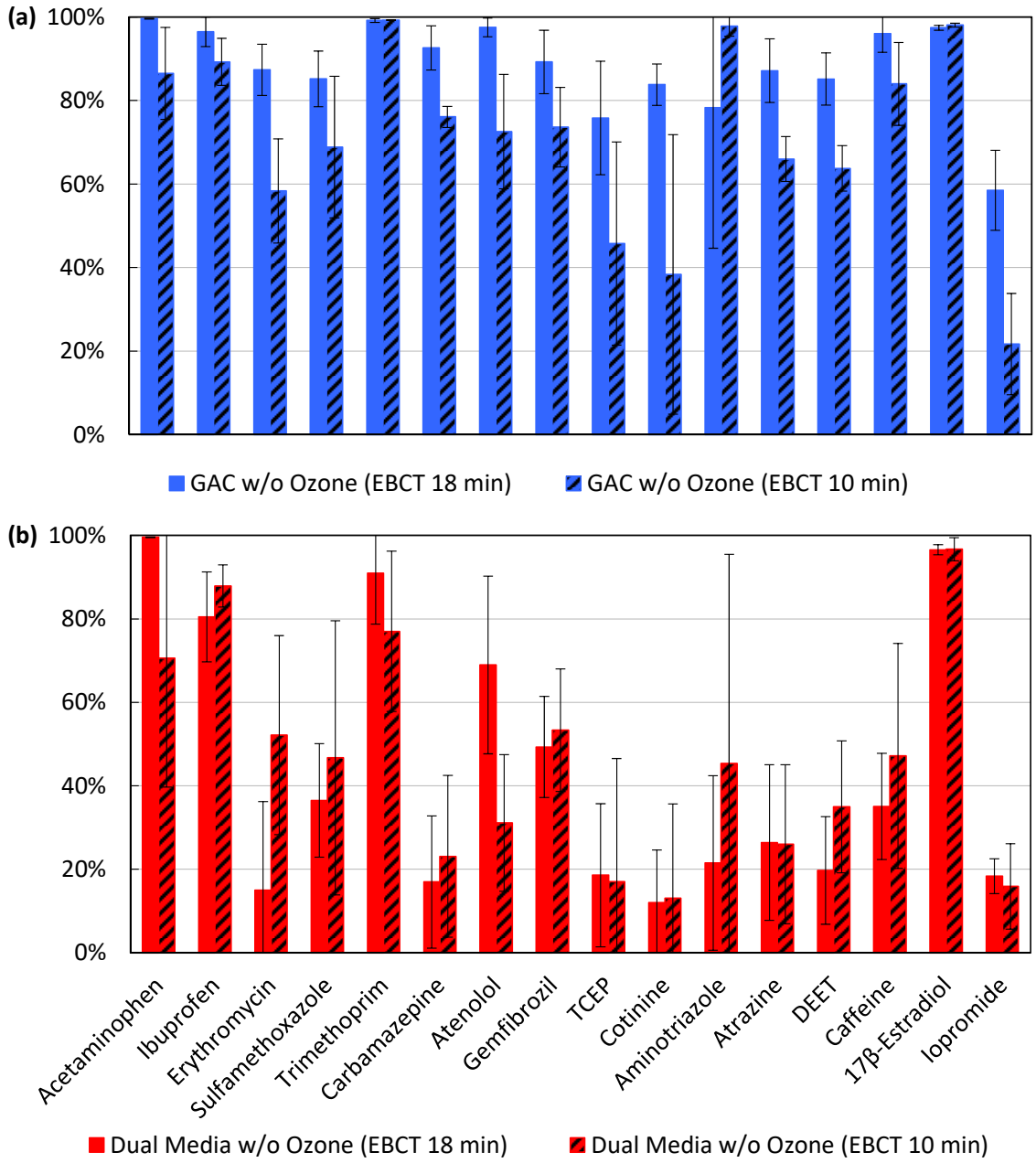


Figure 6.9 Impact of EBCT on removal of PPCP in a) GAC BAFs, and b) dual media BAFs.

were generally less than 30%. A greater impact of EBCT was observed for GAC BAFs than dual media as the latter showed limited PPCP removal for either EBCT. Further increases in the EBCT (i.e., > 18 min) for the dual media BAF may be required to achieve improved PPCP removals; however, for existing filters in water treatment plants, increasing the EBCT may not be feasible. The purpose of this study was to examine if existing filters in water treatment plants can be converted into advanced treatment processes for the removal of PPCPs. GAC BAFs has been demonstrated to be a viable and sustainable treatment process for PPCPs. At an EBCT of 18 min, GAC BAFs were effective in functioning as a sustainable treatment process for PPCPs with removals greater than 75%; the exception was iopromide with removals at 59% (Figure 6.9). Reducing the EBCT to 10 min, seven PPCPs were removed by greater than 75%. As a result, reducing the EBCT to less than 10 min is expected to result in little to no removal of the PPCPs.

6.5 Impact of Pre-Ozonation on PPCP Removals

The impact of ozonation with and without H_2O_2 in BAFs was investigated with ozone dosages of 3 mg/L and 4 mg/L and a H_2O_2 to O_3 mass ratio of 0.2 (Figures 6.10 and 6.11). Because of the significant removals observed using pretreatment, recalcitrant compounds are highlighted (Figure 6.10). Overall, GAC BAFs showed greater PPCP removal efficiencies than dual media BAFs with or without pre-ozonation. The impact of pre-ozonation and H_2O_2 was greater with an EBCT of 10 min than 18 min for GAC BAFs, as the latter bed without pretreatment achieves significant removals (Figure 6.10a). For recalcitrant compounds, TCEP and iopromide removals increased to 79.5% and 98%,

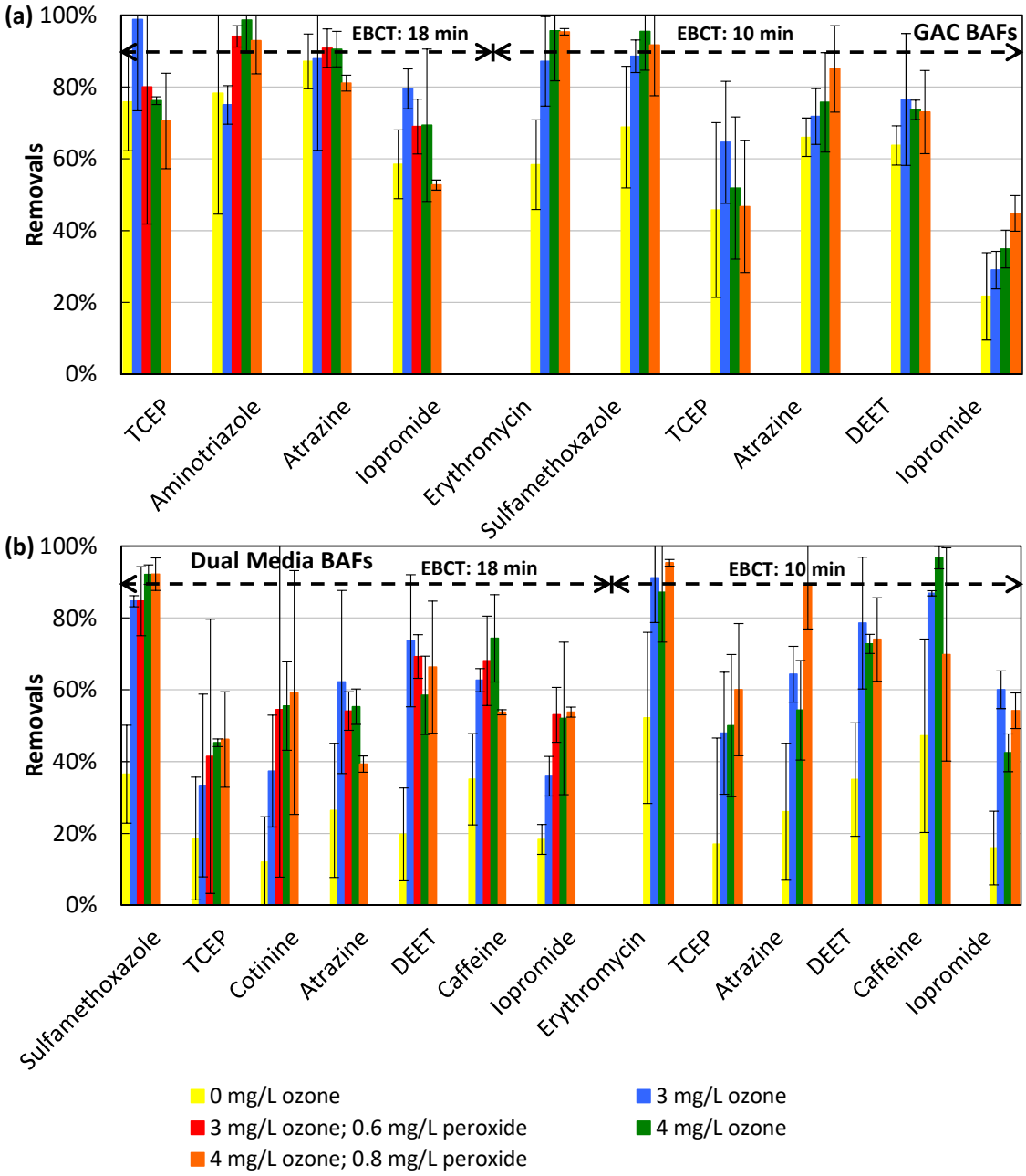


Figure 6.10 Impact of pre-ozonation with and without H_2O_2 on removal of PPCPs in GAC and dual media BAFs. EBCT tested were 18 min and 10 min. Removal was considered across the ozone/BAF process. Compounds showed in this figure were the most recalcitrant compounds. (a) PPCP removal in GAC BAFs; and (b) PPCP removal in dual media BAFs.

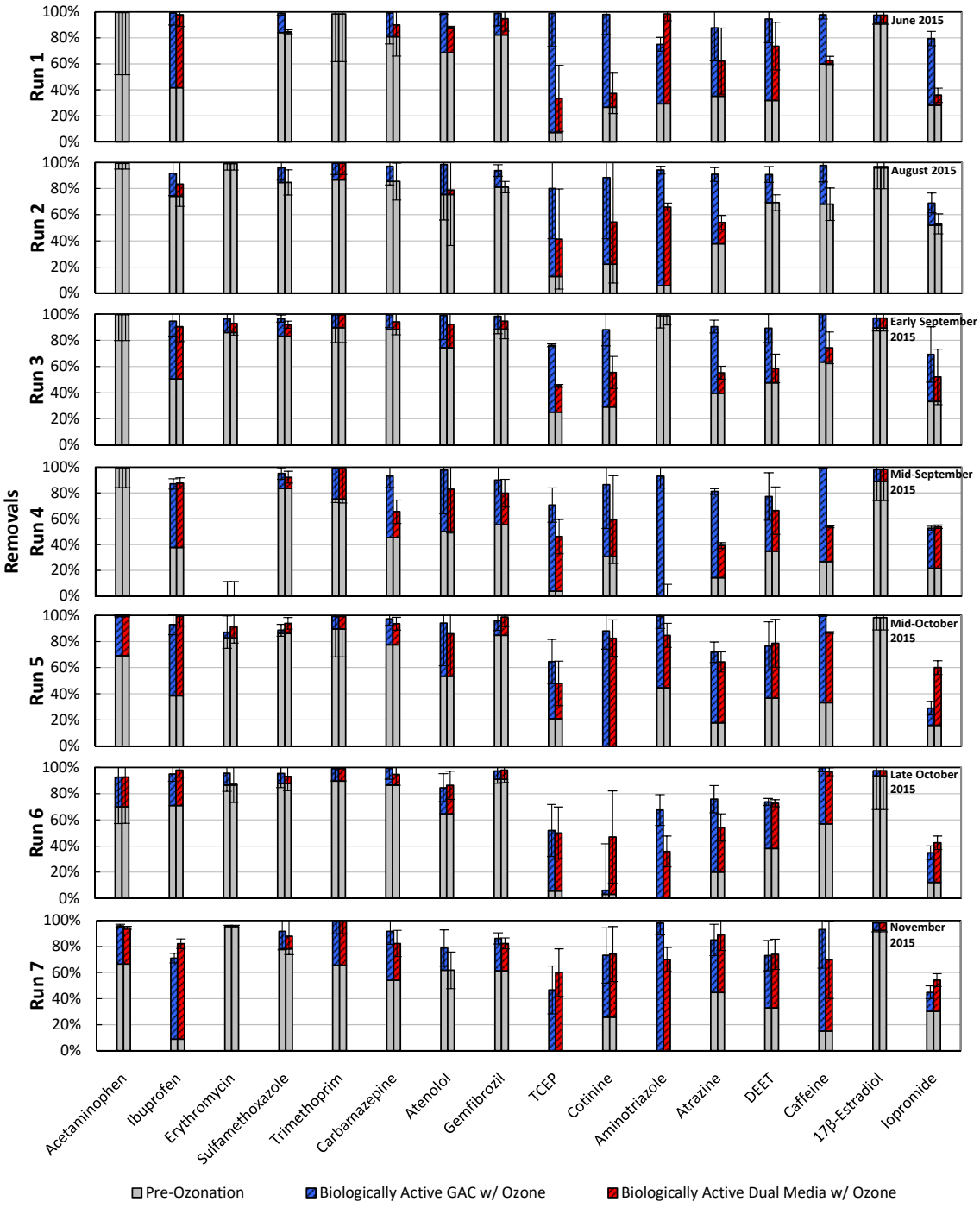


Figure 6.11 PPCP removal with pre-ozonation. Runs 1 to 4 operated at an EBCT of 18 min; Runs 5 to 7 operated at an EBCT of 10 min. The dosage of pre-ozonation in Runs 1 and 5 was 3 mg/L; the dosage of pre-ozonation in Runs 3 and 6 was 4 mg/L; Run 2 operated with pre-ozonation and H_2O_2 at dosage of 3 mg O_3/L and 0.6 mg H_2O_2/L, respectively; Runs 4 and 7 operated with pre-ozonation and H_2O_2 at dosages of 4 mg O_3/L with 0.8 mg H_2O_2/L.

respectively, with pre-ozonation (3 mg/L). As a result, all PPCPs studied were removed by greater than 75% at an EBCT of 18 min with a pre-ozonation dosage of 3 mg/L. Further increasing the ozone dosage or adding H_2O_2 did not result in improvement. At an EBCT of 10 min, the improvement of using pretreatment was significant. Erythromycin and sulfamethoxazole (ozone rate constants k_{O3}: 5.5×10^5 to 2.5×10^6 $M^{-1}s^{-1}$ (Dodd et al., 2006; Huber et al., 2005)) removals improved by 29% and 20%, respectively, with an ozone dosage of 3 mg/L. PPCPs with low ozone rate constants such as TCEP (<10 $M^{-1}s^{-1}$), atrazine (6.0 to 7.9 $M^{-1}s^{-1}$), DEET (10 $M^{-1}s^{-1}$), and iopromide (<0.8 $M^{-1}s^{-1}$) (Acero et al., 2000; Broséus et al., 2009; Huber et al., 2003; Nanaboina and Korshin, 2010; Reungoat et al., 2010; Westerhoff et al., 2005) did not benefit to the same degree with increased removals of 6% to 19%. Increasing the ozone dosage to 4 mg/L or adding H_2O_2 showed limited improvement for these more recalcitrant compounds TCEP, DEET, and iopromide. Especially for TCEP and iopromide, removals were still less than 65%. TCEP and iopromide were the most recalcitrant PPCPs in GAC BAFs with or without pre-ozonation at the 10 min EBCT.

Compared to GAC BAFs, dual media BAFs were much less effective (Figure 6.10b). At 18 min EBCT, only sulfamethoxazole removal improved to greater than 80% with pre-ozonation with or without H_2O_2 due to its relatively large ozone rate constant. All other compounds were more resistant to a greater degree with removals less than 60%; the two exceptions were DEET (up to 74%) and caffeine (up to 74%). The most significant improvement was observed at an ozone dosage of 3 mg/L with removals increasing by 28% to 54% for atrazine, DEET, and caffeine. Adding H_2O_2 or increasing the ozone dosage, however, further improved removals of TCEP, cotinine, and iopromide

(up to 18%), yet comparatively these compounds were still recalcitrant (< 60% removal). Similar trends were found at reduced EBCTs. Pre-ozonation with a dosage of 3 mg/L showed the most significant impact on PPCP removal with removals improved by up to 44%. Nevertheless, at an EBCT of 10 min, PPCPs were generally removed by less than 80% with the exception of erythromycin (up to 95%) and caffeine (up to 97%). TCEP and iopromide were removed by less than 60% with or without pre-ozonation. Overall, dual media BAFs with or without pre-ozonation demonstrated limited efficiency with half of the PPCPs removed at less than 80%.

6.6 Microbial Community Diversity

On average, QIIME quality filtering assigned 96.24% of sequence reads for media samples and 95.07% for water samples (Table 6.3). A total of 81,180 to 164,433 bacterial 16S rRNA gene sequences with an average length of 450 bp were recovered from media samples. In contrast, less sequences were obtained from water samples. With an average length of 459 bp, 103,401 to 105,716 sequences were recovered from influents and 40,334 to 109,320 sequences from effluents. The Shannon diversity index, calculated for all samples at the same rarefaction depth (36,890 sequence reads), in media samples was 8.81±0.07 and dropped to 7.67±0.11 in influents and 8.18±0.73 in effluents (Figure 6.12a). The most significant evenness was found in media samples with the Shannon's equitability at 0.76±0.01 (Figure 6.12b). The equitability was reduced to 0.67±0.01 for influent sample and 0.70±0.05 for effluent sample.

Shannon diversity index is a commonly used community diversity index (Shannon, 1948, Wang et al., 2013); a greater value indicates greater biodiversity. The

Table 6.3 Sequence Quality and Assignment Results from Illumina Miseq Sequencing

Sample		Number of reads after trimming	Median read length (bp)	Numbers of assigned reads	Percentage of assigned reads (%)
Media	GAC w/o O_3 09-15-15	164,433	452	158,241	96.23
	GAC w/o O_3 11-10-15	122,313	451	117,812	96.32
	GAC w/ O_3 09-15-15	116,025	448	111,885	96.43
	GAC w/ O_3 11-10-15	81,180	448	78,414	96.59
	Dual Media w/o O_3 09-15-15	88,432	452	85,230	96.38
	Dual Media w/o O_3 11-10-15	110,708	451	105,155	94.98
	Dual Media w/ O_3 09-15-15	114,968	449	110,812	96.39
	Dual Media w/ O_3 11-10-15	87,168	448	84,192	96.59
Influents	Influent 09-03-15	105,716	447	100,669	95.23
	Influent 10-29-15	103,401	463	98,568	95.33
Effluents	GAC w/o O_3 09-03-15	54,093	449	50,990	94.26
	GAC w/o O_3 10-29-15	79,829	449	76,108	95.34
	GAC w/ O_3 09-03-15	87,067	467	84,044	96.53
	GAC w/ O_3 10-29-15	59,585	452	56,340	94.55
	Dual Media w/o O_3 09-03-15	59,137	462	56,849	96.13
	Dual Media w/o O_3 10-29-15	40,334	462	36,895	91.47
	Dual Media w/ O_3 09-03-15	109,320	466	105,907	96.88
	Dual Media w/ O_3 10-29-15	73,315	464	69,920	95.37

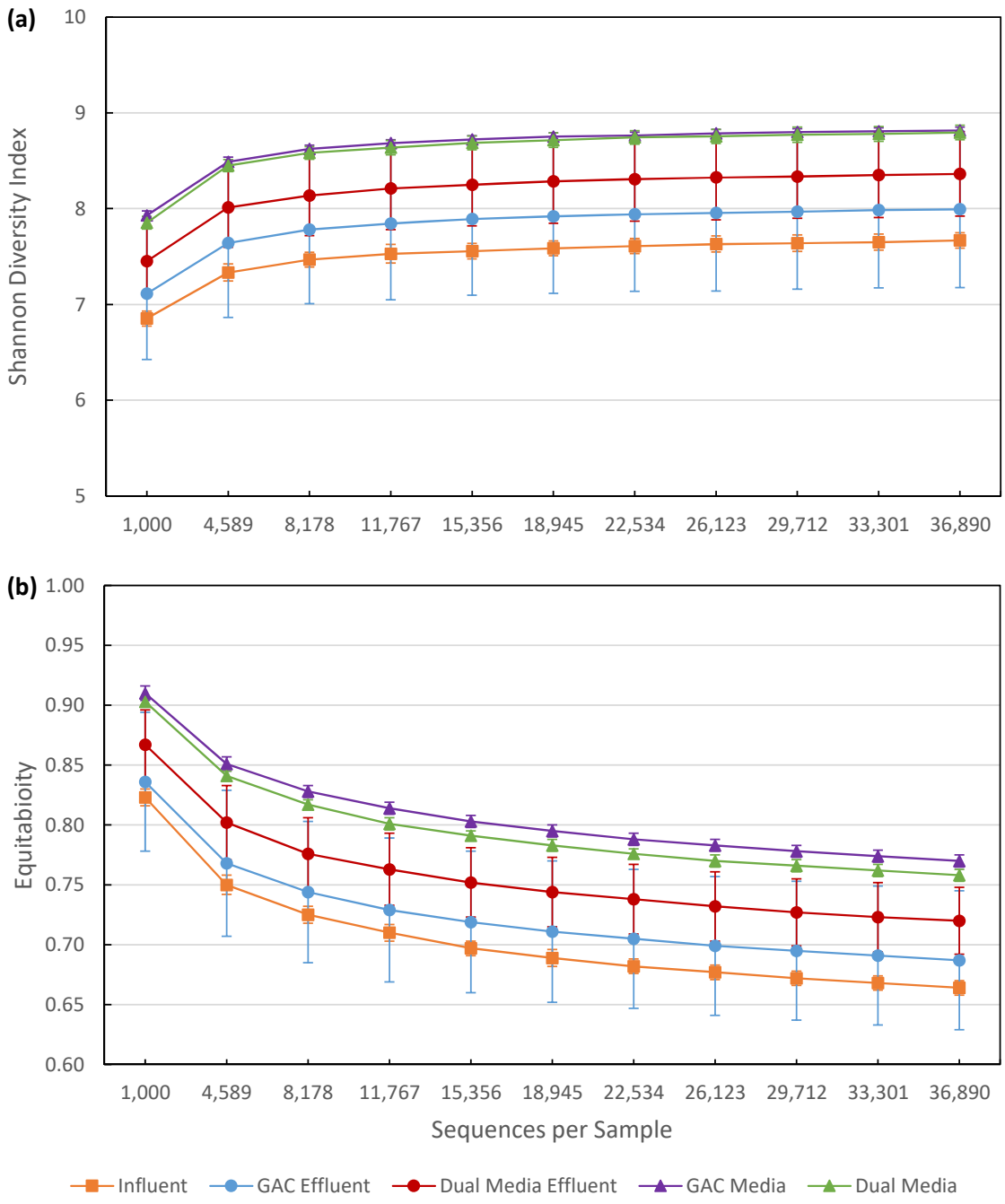


Figure 6.12 Diversity indices of the microbial community in influent, effluent from GAC and dual media BAFs, and media from GAC and dual media BAFs. (a) Shannon diversity index, and (b) equitability.

Shannon's equitability index has a value between 0 to 1 that signifies the dominance of one species or complete evenness. Based on the Shannon diversity index value, greater diversity was observed in media samples than in water samples (influents and effluents). For the Shannon's equitability index, a greater value was found in media samples compared to the water samples indicating less evenness in influent and effluent samples. Consistent with other studies (e.g., Pinto et al., 2012), water samples exhibited less stability as compared to media samples suggesting a more stable bacterial community in BAF media.

6.7 Composition of Microbial Community

Nineteen bacterial phyla were classified from both media and water samples (Figure 6.13). *Proteobacteria* were the most dominant phyla in all samples. In media, the relative abundance of *Proteobacteria* ranged from 31.7% to 45.3% followed by *Planctomycetes* (29.9% to 44.0%) and *Acidobacteria* (5.0% to 12.4%) (Figure 6.13a). On the other hand, in influent and effluent samples *Proteobacteria* (42.3% to 63.4%), *Actinobacteria* (6.4% to 31.8%), and *Chlamydiae* (1.2% to 19.1%) were the most dominant bacterial phyla. Furthermore, differences were observed between the two BAF media as well. For GAC BAFs, 3.6% to 7.6% of *Chloroflexi* and 1.2% to 2.0% of *Gemmatimonadetes* were observed while for dual media BAFs their relative abundance dropped to 0.7% to 2.5% and 0.4% to 1.2%, respectively. Additionally, greater *Acidobacteria* were observed in dual media BAFs (10.8% to 12.4%) and were reduced by as much as 50% in GAC BAFs (5.0% to 7.5%) (Figure 6.13a).

Similar trends were observed in the bacterial classes (Figure 6.14). Both GAC and

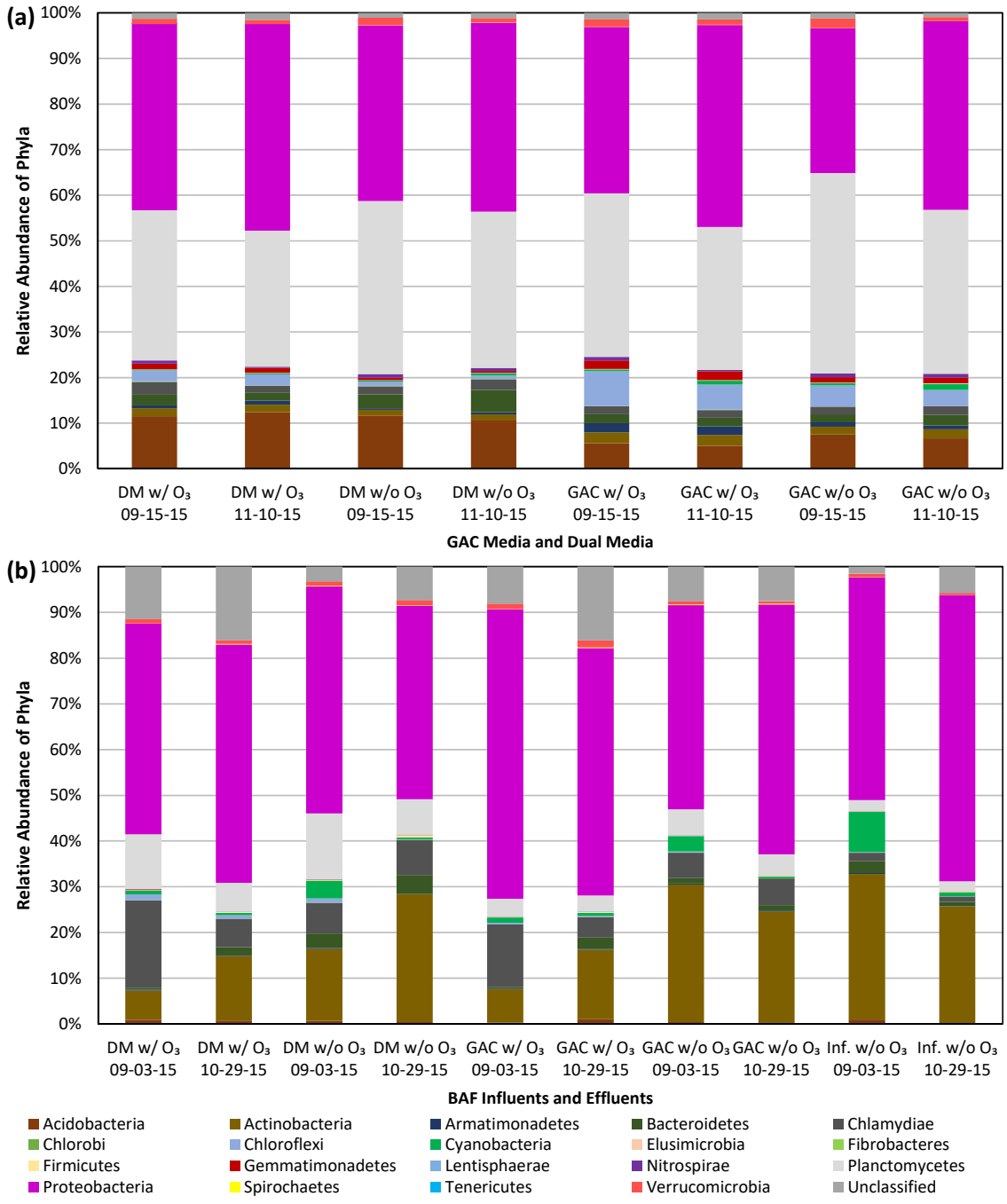


Figure 6.13 Relative abundance of phyla in (a) GAC and dual media (DM) BAF media samples with and without pre-ozonation, and in (b) BAF influent (inf.), GAC BAF effluent, and DM BAF effluent samples.

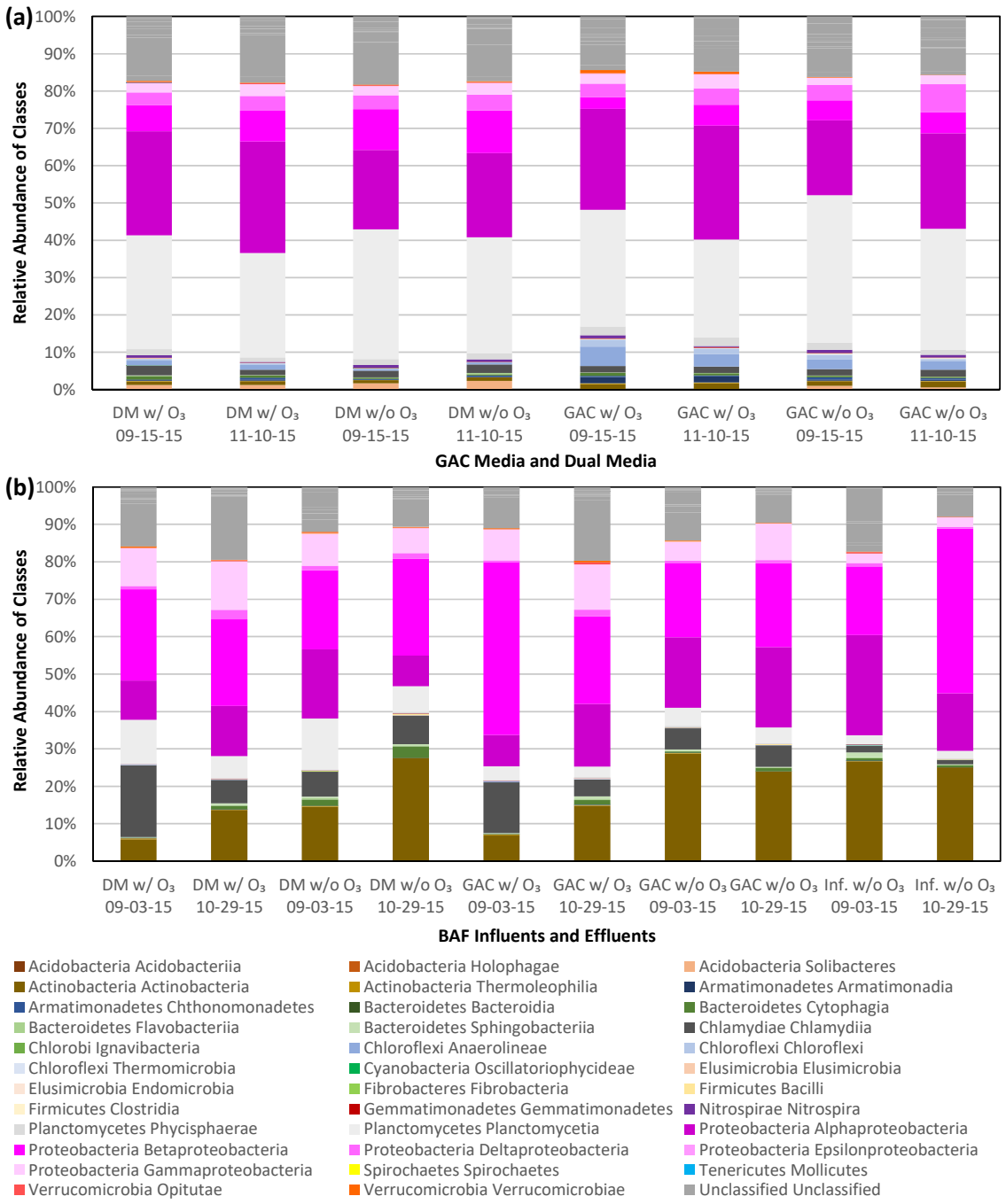


Figure 6.14 Relative abundance of classes in (a) GAC and dual media (DM) BAF media samples with and without pre-ozonation, and in (b) BAF influent (inf.), GAC BAF effluent, and DM BAF effluent samples.

dual media samples had a greater proportion of *α-Proteobacteria* class from *Proteobacteria* and *Planctomycetia* class from *Planctomycetes* with relative abundances at greater than 20% for both classes (Figure 6.14a). In influent ant effluent samples, classes *α-Proteobacteria*, *β-Proteobacteria*, and *Actinobacteria* were dominant consisting of more than 40% of the total abundance of the bacterial classes (Figure 6.14b). Differences in bacterial classes between media samples collected from GAC and dual media BAFs were detected and consistent with the results observed in bacterial phyla. GAC BAFs had approximately four times more *Anaerolineae* (belonging to *Chloroflexi* phylum) than dual media BAFs, while 1.2% to 2.3% *Solibacteres* (belonging to *Acidobacteria* phylum) were detected in dual media BAFs and dropped by 75% in GAC BAFs. Overall, bacterial classes belonging to *Proteobacteria* were dominant in all samples (media, influents, and effluents) (Figure 6.14a). Specifically, media samples were mainly comprised of *α-Proteobacteria*, *β-Proteobacteria*, *δ-Proteobacteria*, and *γ-Proteobacteria* with a total relative abundance at up to 41.4%, while influent and effluent samples revealed *α-Proteobacteria*, *β-Proteobacteria*, and *γ-Proteobacteria* up to 62.7% of the total abundance at the class level. For these media samples at the order level, the most abundant bacteria found were *Rhizobiales* (6.8% to 13.4%), *Rhodobacterales* (3.2% to 11%), and *Sphingomonadales* (3.8% to 7.8%) from *α-Proteobacteria*, *Burkholderiales* (1.8% to 6.2%) from *β-Proteobacteria*, *Legionellales* (0.9% to 2.3%) from *γ-Proteobacteria*, and *Myxococcales* (1.6% to 5.2%) from *δ-Proteobacteria* (Figure 6.15). For influent and effluent samples, the dominant *Proteobacteria* orders were *Rhizobiales* (1.5% to 9.9%), *Sphingomonadales* (2.1% to 13.0%), *Burkholderiales* (12.6% to 44.7%), and *Legionellales* (1.5% to 10.2%).

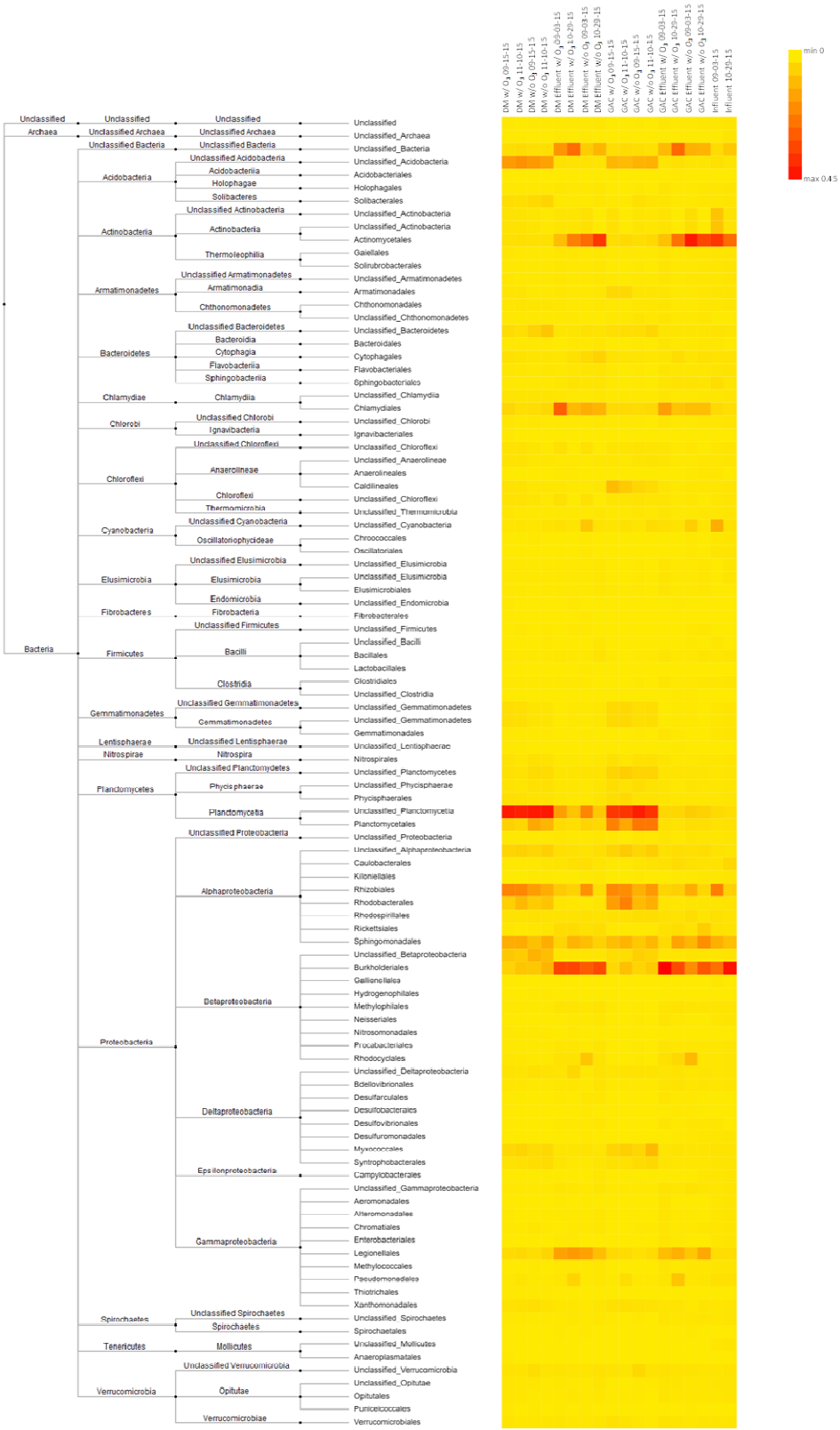


Figure 6.15 Heat map shows the abundance of the bacterial orders in water and media samples with yellow and red representing the minimum and maximum abundance, respectively. Sample type was shown on the top of this figure.

For bacterial orders, *Actinomycetales*, *Chlamydiales*, *Planctomycetales*, *Rhizobiales*, *Rhodobacterales*, *Sphingomonadales*, *Burkholderiales*, *Myxococcales*, *Syntrophobacterales*, and *Legionellales* were the ten most prevalent in systems based on heat maps (Figure 6.15). Among these orders, *Actinomycetales*, *Chlamydiales*, *Burkholderiales*, and *Legionellales* were more abundant in BAF effluents while *Planctomycetales*, *Rhizobiales*, *Rhodobacterales*, *Myxococcales*, and *Syntrophobacterales* were mostly detected in media samples. *Syntrophobacterales* were dominant in media, influent, and effluent samples (Figure 6.15).

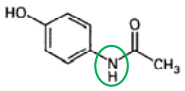
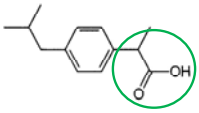
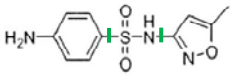
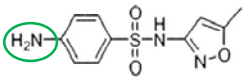
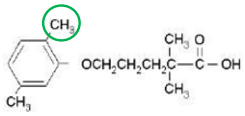
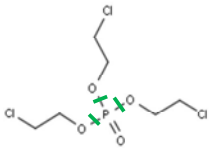
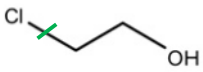
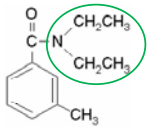
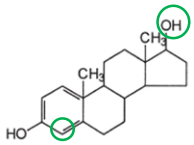
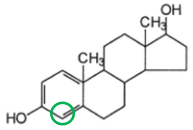
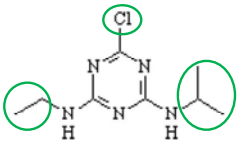
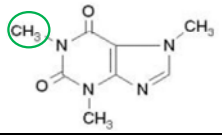
The abundance of bacteria belonging to *Proteobacteria*, *Planctomycetes*, *Acidobacteria*, *Actinobacteria*, and *Chloroflexi* was also reported in other studies (Lautenschlager et al., 2014; Pinto et al., 2012; Wang et al., 2013), as these bacteria are observed in fresh water environments (Newton et al., 2011) as well as drinking water systems (Lin et al., 2014; Wang et al., 2013). The detection of the most dominant bacteria *Proteobacteria* was expected (Figure 6.13). Similar observations were reported in studies on water treatment plants where *Proteobacteria* were the most abundant bacteria in filter media (Feng et al., 2013; Liao et al., 2013), filter influents (Pinto et al., 2012), and effluents (Wang et al., 2013). Consistent with other studies (e.g., Lin et al., 2014), different dominant bacteria were observed between the biomass and water samples (BAF influents and effluents). The microbial community developed in the media samples does not simply depend on the community in the source water, but is also affected by the surrounding environment (e.g., nutrient concentration, organic carbon level, and dissolved oxygen) (Henne et al., 2012; Lin et al. 2014). In this study, the emerging contaminants that were spiked may impact biomass assembly in media as well resulting

in unique microbial compositions between media and water samples (influents and effluents). For example, greater abundance of *α-Proteobacteria* was observed in BAF media than in influents. *Pesudomonas* sp. and *Sphingomonas* sp. belonging to *α-Proteobacteria* have been reported as PPCP degraders (Table 6.4). Therefore, the emerging contaminants spiked in the source water may result in the greater abundance of the PPCP degrading bacteria in BAF media.

6.8 Impact of Operational Conditions on the Microbial Community Structure in Media Samples

Based on the factorial analysis, media type and EBCT significantly affected the abundance of bacterial phyla, while media type and the application of pre-ozonation affected the abundance of bacterial classes (Figure 6.16). The greatest PPCP removals were observed in GAC BAFs with pre-ozonation at an EBCT of 18 min; under this condition, the microbial community structure was affected accordingly. Statistically significant greater abundance of bacterial phyla *Chloroflexi*, *Gemmatimonadetes*, *Actinobacteria*, and *Armatimonadetes* in GAC BAFs than in dual media BAFs may result in the greater PPCP removals. At the class level, 10 bacteria were affected by the media type. Consistent with bacterial phyla, the abundance of bacterial classes *Anaerolineae* and *Chloroflexi* (belonging to *Chloroflexi* phylum), *Actinobacteria* and *Thermoleophilia* (belonging to *Actinobacteria* phylum), and *Gemmatimonadetes* (belonging to *Gemmatimonadetes* phylum) was significantly greater in GAC BAFs. When the EBCT increased from 10 min to 18 min, the abundance of *Proteobacteria* decreased from 43% to 37%. Reduced abundance of *Proteobacteria* phylum at an EBCT of 18 min suggests that the abundance of other bacteria may improve PPCP removal. Applying ozonation

Table 6.4 Biodegradation of PPCPs and Their Potential Pathways

Compounds	Bacteria	Structure	Pathway
Acetaminophen[1,2]	*Pseudomonas putida* (phyla *Proteobacteria*)		Replace the amino group by a hydroxyl group for further ortho- or meta cleavage
Ibuprofen[3]	*Sphingomonas* sp. (phyla *Proteobacteria*)		Remove the prophionic acid moiety on ibuprofen resulting in the dioxygenation of the ring
Sulfamethoxazole[4,5]	*Pseudomonas* sp. (phyla *Proteobacteria*)		Involve cleavage of N-C and S-N bond
	Rhodococcus sp. (phyla *Actinobacteria*)		Replace the amine group on the ring by a hydroxyl group
Gemfibrozil[6]	Bacillus sp. (phyla Firmicutes)		Oxidize the methyl group on the aromatic ring to a carboxylic acid
TCEP[7]	Sphingomonas sp. (phyla Proteobacteria)		Break down the phosphotriester bonds
	Xanthobacter autotrophicus (phyla Proteobacteria)		Degrade 2-chloroethanol to glycolic acid
DEET[8]	Pseudomonas putida (phyla Proteobacteria)		Hydrolyze the amide bond
17β-Estradiol[9]	Rhodococcus sp. (phyla Actinobacteria)		Degrade to estrone first and hydroxylated to 4-hydroxyestrone
	Sphingomonas sp. (phyla Proteobacteria)		Direct hydroxylated to 4-hydroxyestradiol
Atrazine[10]	Rhodococcus sp. (phyla Actinobacteria)		Replace chlorine by a hydroxyl group during hydroxylation and remove alkyl groups
Caffeine[11]	Pseudomonas sp. (phyla Proteobacteria)		Remove methyl group

Source: [1] Wu et al., 2012; [2] Zhang et al., 2013; [3] Murdoch and Hay, 2005; [4] Jiang et al., 2014; [5] Gauthier et al., 2010; [6] Kjeldal et al., 2016; [7] Takahashi et al., 2012; [8] Rivera-Cancel et al., 2007; [9] Kurisu et al., 2010; [10] Kolekar et al., 2014; [11] Gummadi et al., 2012.

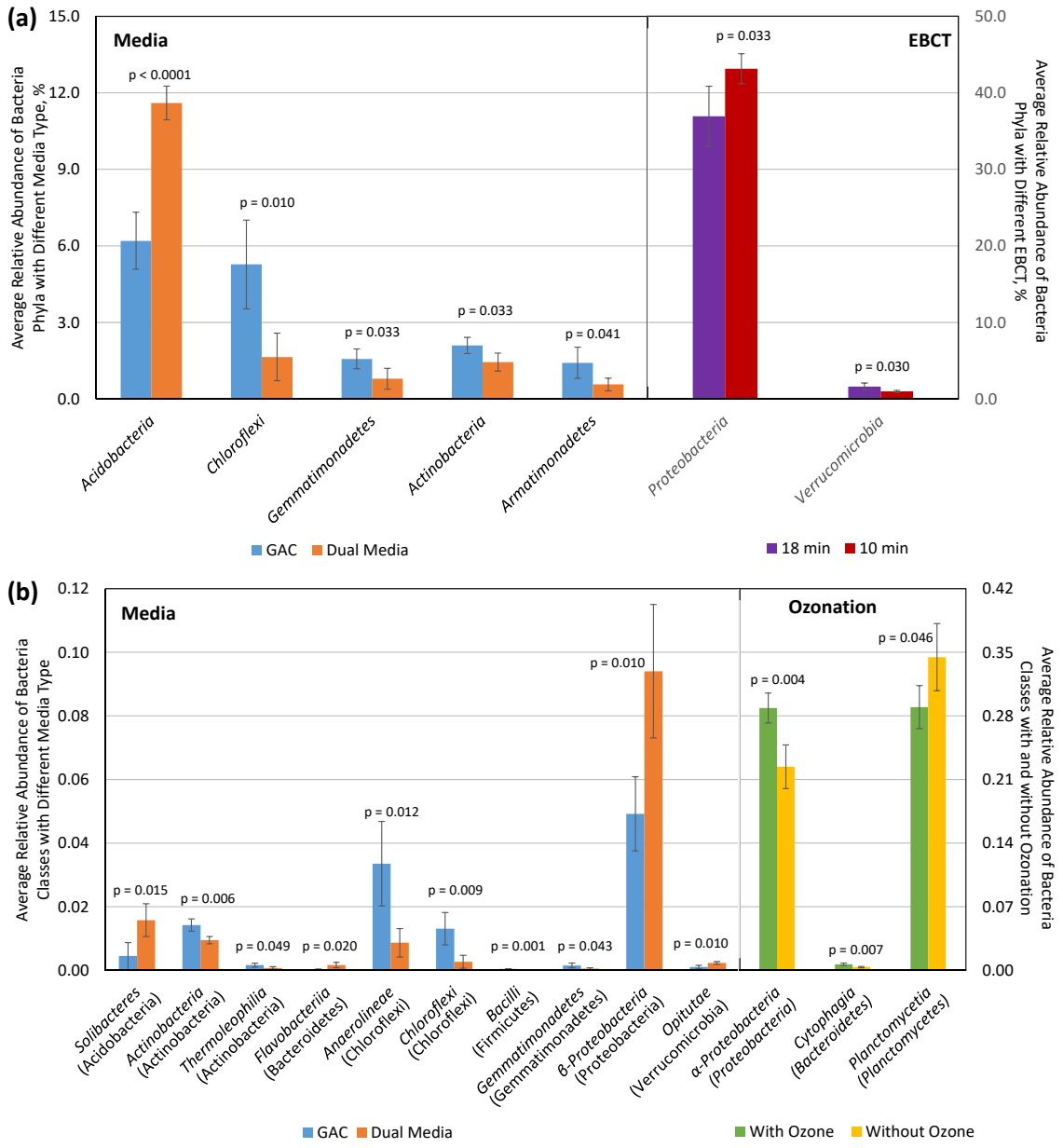


Figure 6.16 The factorial analysis on (a) bacterial phyla and (b) bacterial classes that were significantly affected by the operational parameters including media type (GAC and dual media), EBCT (18 min and 10 min), and the application of pre-ozonation.

statistically impacts the abundance of the two dominant bacterial classes: *α-Proteobacteria* increased from 22% to 29% and *Planctomycetia* decreased from 34% to 29%. As bacteria belonging to *Proteobacteria* were reported to degrade a number of the PPCPs studied (e.g., acetaminophen, ibupfrofen, sulfamethoxazole, TCEP, DEET, 17β-estradiol, and caffeine) (Table 6.4), the application of ozonation may not only break down the organic carbon in source water, but also increases the abundance of the PPCP degrading bacteria. Therefore, the microbial community structure was statistically significantly impacted by the operational conditions: media type, EBCT, and pre-ozonation.

6.9 Principal Component Analysis

A principal component analysis on the abundance of bacterial classes in both GAC and dual media BAFs showed three principal components that together explain 99% of the total data variance (Tables 6.5 and 6.6). The first principal component (PC) reveals a strong relationship with pre-ozonation in both GAC and dual media BAFs (Tables 6.5 and 6.6). The bacterial classes with positive values demonstrate an increasing abundance with pre-ozonation (i.e., *Thermoleophilia*, *Armatimonadia*, *Cytophagia*, *Anaerolineae*, *Chloroflexi*, *Gemmatimonadetes*, *Phycisphaerae*, *Opitutae*, and *Verrucomicrobiae* in GAC BAFs and *Holophagae*, *Thermoleophilia*, *Armatimonadia*, *Bacteroidia*, *Cytophagia*, *Ignavibacteria*, *Anaerolineae*, *Chloroflexi*, *Thermomicrobia*, *Endomicrobia*, *Clostridia* and *Gemmatimonadetes, α-Proteobacteria*, *Mollicutes*, and *Opitutae* in dual media BAFs). In contrast, the abundance of the bacterial classes decreased with the application of pre-ozonation when the value was negative (i.e., *Solibacteres*, *Chthonomonadetes*, and

Table 6.5 Principal Component Analysis on the Abundance of Bacterial Classes in GAC BAFs

Bacteria Phylum	Variables (Abundance of Bacterial Classes)	Principal Component (PC) 1	PC 2	PC 3
Acidobacteria	*Holophagae*	.606	.625	.492
	Solibacteres	**-.891**	.347	-.293
Actinobacteria	*Actinobacteria*	.024	**-.986**	.166
	Thermoleophilia	**.940**	.301	.159
Armatimonadetes	*Armatimonadia*	**.996**	-.084	.017
	Chthonomonadetes	**-.861**	.476	-.178
Bacteroidetes	*Bacteroidia*	.044	**.958**	.285
	Cytophagia	**.920**	.388	.057
	Flavobacteriia	.689	-.530	.495
	Sphingobacteriia	.456	**.832**	.316
Chlamydiae	*Chlamydiia*	-.322	-.206	**.924**
Chloroflexi	*Anaerolineae*	**.863**	.441	.247
	Chloroflexi	**.812**	.551	-.194
	Thermomicrobia	**-.998**	.043	-.045
Elusimicrobia	*Elusimicrobia*	.337	.786	-.518
Firmicutes	*Bacilli*	-.385	.641	.664
	Clostridia	-.266	**.883**	-.387
Gemmatimonadetes	*Gemmatimonadetes*	**.924**	-.124	-.361
Nitrospirae	*Nitrospira*	-.524	.709	.472
Planctomycetes	*Phycisphaerae*	**.869**	.279	-.410
	Planctomycetia	-.719	.680	-.144
Proteobacteria	*Alphaproteobacteria*	.747	-.642	.171
	Betaproteobacteria	-.594	-.645	-.481
	Deltaproteobacteria	-.649	-.601	.466
	Gammaproteobacteria	.766	-.631	-.123
Verrucomicrobia	*Opitutae*	**.969**	-.159	-.191
	Verrucomicrobiae	**.976**	.197	.094
	% of Variance	53.1	33.0	13.8

*Absolute value of correlation greater than 0.8 is bolded for each PC. Three components together explaining 99% of the data variance.

The first PC related to pre-ozonation represented 53% of the total variability. Bacterial classes with absolute value of correlation greater than 0.8 reveal a strong relationship with pre-ozonation.

The 2nd PC reveals EBCT represented 33% of the total variability. Bacterial classes with absolute value of correlation greater than 0.8 signifies those attributed to the change in EBCT.

The 3rd PC represented 14% of the total variability in GAC BAFs where bacteria with absolute value of correlation greater than 0.8 were strongly associated with the change of pre-ozonation and EBCT at the same time.

Table 6.6 Principal Component Analysis on the Abundance of Bacterial Classes in Dual Media BAFs

Bacteria Phylum	Variables (Abundance of Bacterial Classes)	PC 1	PC 2	PC 3
Acidobacteria	*Holophagae*	**.824**	.515	.236
	Solibacteres	-.794	.203	.572
Actinobacteria	*Actinobacteria*	.372	-.790	.487
	Thermoleophilia	**.867**	.110	-.486
Armatimonadetes	*Armatimonadia*	**.822**	-.537	-.188
	Chthonomonadetes	-.320	**-.927**	.195
Bacteroidetes	*Bacteroidia*	**.855**	.404	.324
	Cytophagia	**.978**	.144	.150
	Flavobacteriia	-.144	-.089	**.986**
	Sphingobacteriia	.704	-.218	.676
Chlamydiae	*Chlamydiia*	.374	.749	.546
	Ignavibacteria	**.827**	.557	.070
Chloroflexi	*Anaerolineae*	**.947**	-.305	-.099
	Chloroflexi	**.930**	-.236	-.283
	Thermomicrobia	**.965**	.208	-.159
Cyanobacteria	*Oscillatoriophycideae*	-.598	.378	-.707
Elusimicrobia	*Elusimicrobia*	-.540	**.814**	-.217
	Endomicrobia	**.827**	.557	.070
Firmicutes	*Bacilli*	.636	.649	.418
	Clostridia	**.911**	-.412	.003
Gemmatimonadetes	*Gemmatimonadetes*	**.874**	-.125	-.470
Nitrospirae	*Nitrospira*	-.351	**.935**	.054
Planctomycetes	*Phycisphaerae*	-.106	**.958**	.266
	Planctomycetia	-.618	.716	-.325
Proteobacteria	*Alphaproteobacteria*	**.848**	-.527	-.054
	Betaproteobacteria	**-.981**	.084	.177
	Deltaproteobacteria	-.684	-.565	.462
	Gammaproteobacteria	-.136	**-.818**	.560
Tenericutes	*Mollicutes*	**.827**	.557	.070
Verrucomicrobia	*Opitutae*	**.996**	-.061	.069
	Verrucomicrobiae	.118	.687	.717
	% of Variance	52.9	30.5	16.5

*Absolute value of correlation greater than 0.8 is bolded for each PC. Three components together explaining 99% of the data variance.

The first PC related to pre-ozonation represented 53% of the total variability. Bacterial classes with absolute value of correlation greater than 0.8 reveal a strong relationship with pre-ozonation.

The 2nd PC reveals EBCT represented 30% of the total variability. Bacterial classes with absolute value of correlation greater than 0.8 signifies those attributed to the change in EBCT.

The 3rd PC represented 17% of the total variability where bacteria with absolute value of correlation greater than 0.8 were strongly associated with the change of pre-ozonation and EBCT at the same time.

Thermomicrobia in GAC BAFs and *β-Proteobacteria* in dual media BAFs). The second PC signifies the bacterial classes that attributed to the change in EBCT (Tables 6.5 and 6.6). Bacterial classes with positive values (i.e., *Bacteroidia*, *Sphingobacteriia*, and *Clostridia* in GAC BAFs and *Elusimicrobia*, *Nitrospira*, and *Phycisphaerae* in dual media BAFs) were correlated to longer EBCT (18 min) where the abundance increased with greater EBCT. With negative values, reduced abundance was observed with a greater EBCT of *Actinobacteria* in GAC BAFs as well as *Chthonomonadetes* and *γ-Proteobacteria* in dual media BAFs. The third PC is strongly associated with the change of pre-ozonation and EBCT at the same time (Tables 6.5 and 6.6). For example, the abundance of bacterial class *Chlamydiia* in the GAC BAF increased at a lower EBCT (10 min) and without pre-ozonation. The same trend was observed for the bacterial class *Flavobacteriia* in the dual media BAF. Bacteria belonging to phyla *Proteobacteria*, *Actinobacteria*, *Firmicutes*, and *Bacteroidetes* were reported to be potentially degrading bacteria for the emerging contaminants (Table 6.4); based on the PCA analysis, these bacteria were significantly associated with the change of pre-ozonation and EBCT (Tables 6.5 and 6.6). Greater PPCP removal observed at greater EBCT or with the application of pre-ozonation may result not only from longer contact times or pre-oxidation of emerging contaminants, but also from a greater abundance of PPCP degrading bacteria.

6.10 Potential Pathogens

Potential pathogens that were detected in influent, effluent, and media samples included *Mycobacterium gordonae*, *Chlamydia pneumoniae*, *Staphylococcus aureus*, *Bacillus*

cereus, *Plesiomonas shigelloides*, and *Legionella pneumophila* (Table 6.7). Total abundance of potential pathogens ranged from 0.01% to 0.09% in water samples and 0.001% to 0.05% in media samples. *L. pneumophila* was the most dominant pathogen that was detected in all samples and made up to 50% to 95% of the total pathogens in effluents and 71% to 100% of the total pathogens in media samples. *M. gordonae* was the second most detected pathogen that accounted for up to 17% of the total pathogen in BAF effluents and up to 24% of the total pathogen in BAF media. The observations of pathogens in filter media and effluents were consistent with other studies where *L. pneumophila* and *M. gordonae* were detected most frequently (Lin et al., 2014; Wang et al., 2013). In our study, although pathogens were detected to a greater degree in effluents from dual media BAFs compared to GAC BAFs, the abundance was as low as 8.13×10^{-5} for *L. pneumophila* and 1.43×10^{-5} for *M. gordonae*. The application of pre-ozonation impacted the presence of these two most detected pathogen species (Figure 6.17). The abundance increased from 4.51×10^{-6} to 5.62×10^{-5} for *M. gordonae* and from 4.89×10^{-5} to 2.92×10^{-4} for *L. pneumophila* when pre-ozonation was applied. Ozone breaks down organic carbon in the source water making it more available for bacteria to consume, which may result in not only greater abundance of the potential pathogens but also other bacteria (e.g., PPCP degrading bacteria α-*Proteobacteria*).

6.11 Implications: Biodegradation of Emerging Contaminants and Their Potential Pathways

A number of studies have reported that bacteria associated with phyla *Proteobacteria*, *Actinobacteria*, *Firmicutes*, and *Bacteroidetes* were capable of degrading emerging contaminants (Bouju et al., 2012; Marchlewicz et al., 2016; Yu et al., 2007) (Table 6.4);

Table 6.7 Potential Pathogens in BAF in Influents, Effluents, and Media

(a) BAF influents and effluents

Species	**Influent**		**GAC Effluent w/o O_3**		**GAC Effluent w/ O_3**		**Dual Effluent w/o O_3**		**Dual Effluent w/ O_3**	
Date	09-03-15	10-29-15	09-03-15	10-29-15	09-03-15	10-29-15	09-03-15	10-29-15	09-03-15	10-29-15
Mycobacterium gordonae	10	3	0	1	3	1	1	1	5	1
Chlamydia pneumoniae	0	0	0	1	0	0	3	0	3	4
Staphylococcus aureus	0	0	0	0	0	0	0	1	0	0
Bacillus cereus	0	1	1	1	0	0	0	1	0	4
Plesiomonas shigelloides	2	0	0	0	0	0	0	0	0	0
Legionella pneumophila	12	12	6	15	27	20	6	3	87	56
Total species	24	16	7	18	30	21	10	6	95	65
Total Sequence Number	100,699	98,568	50,900	76,108	84,044	56,340	56,849	36,895	105,907	69,920
Pathogen %	0.02%	0.02%	0.01%	0.02%	0.04%	0.04%	0.02%	0.02%	0.09%	0.09%

(b) BAF media

Species	**GAC Media w/o O_3**		**GAC Media w/ O_3**		**Dual Media w/o O_3**		**Dual Media w/ O_3**	
Date	09-15-15	11-10-15	09-15-15	11-10-15	09-15-15	11-10-15	09-15-15	11-10-15
Mycobacterium gordonae	1	0	4	5	1	0	6	6
Chlamydia pneumoniae	0	0	0	0	0	0	0	0
Staphylococcus aureus	0	0	0	1	0	0	0	0
Bacillus cereus	1	0	0	0	0	0	0	0
Plesiomonas shigelloides	0	0	0	0	0	0	0	0
Legionella pneumophila	6	5	22	15	9	1	51	27
Total species	8	5	26	21	10	1	57	33
Total Sequence Number	158,241	117,812	111,885	78,414	85,230	105,155	110,812	84,192
Pathogen %	0.005%	0.004%	0.020%	0.030%	0.010%	0.001%	0.05%	0.04%

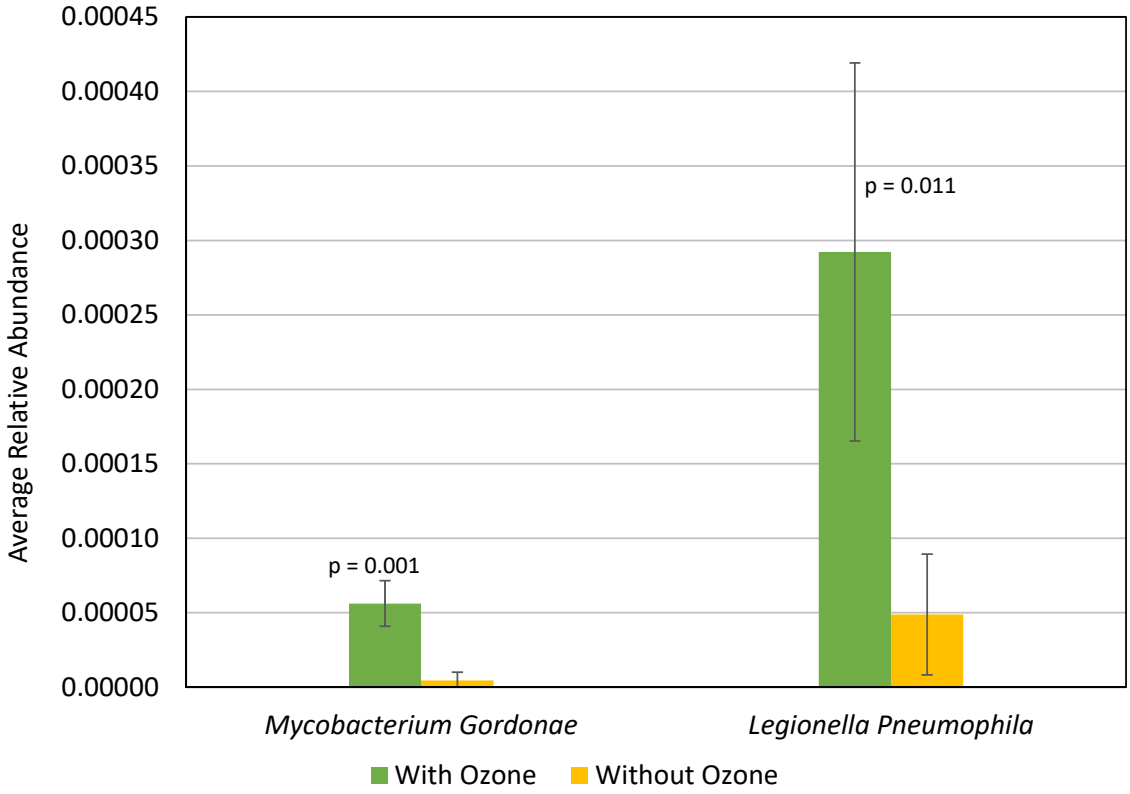


Figure 6.17 Potential pathogen species that were affected by the application of pre-ozonaiton.

these bacteria were observed to be abundant in our BAF media samples (Figures 6.13, 6.14, and 6.15). As these bacteria are aerobic, facultative anaerobic, or anaerobic, O_2, NO_3^-, Fe^{3+}, or S were reported as the electron acceptors (Table 6.8). Specifically, Wu et al. (2012) and Zhang et al. (2013) proposed a metabolic pathway for acetaminophen where bacteria *Pseudomonas putida* (phyla *Proteobacteria*) produced an intermediate product, protocatechuate, which replaced the amino group by a hydroxyl group. Protocatechuate has been hypothesized to be a precursor of carboxylic acids formed through ortho- or meta-cleavage. *P. putida* was also observed to utilize DEET as a sole carbon source (Rivera-Cancel et al., 2007) where 3-methylbenzoate and diethylamine were produced through hydrolysis of the amide bond. 3-Methylbenzoate was then degraded to 3-methylcatechol and with meta cleavage the ring structure was further metabolized to 2-hydoxy-6-oxo-hepta-2,4-dienoate.

Sphingomonas sp. and *Variovorax* sp. belonging to phyla *Proteobacteria* and *Bacillus* sp. belonging to phyla *Firmicutes* were reported as ibuprofen degraders (Marchlewicz et al., 2016; Murdoch and Hay, 2005, 2015). Murdoch and Hay (2005, 2015) hypothesized the metabolism of ibuprofen occurred through two pathways: 1) *Sphingomonas* sp. removed the propionic acid moiety on ibuprofen which resulted in the deoxygenation of the ring and production of isobutylcatechol, which is further metabolized via meta-cleavage; and, 2) *Variovorax* sp. metabolized ibuprofen via a trihydroxyibuprofen meta ring-fission pathway where ring-trihydroxylated ibuprofen (three hydroxyl groups on the ring structure of ibuprofen) was detected as a metabolic intermediate.

Pseudomonas sp. (phyla *Proteobacteria*) (Jiang et al., 2014; Lin et al., 2015),

Table 6.8 Electron Acceptors and Type of the PPCP Degrading Bacteria

Bacteria	Type	Electron Acceptor	Reference
Pseudomonas sp. (phylum *Proteobacteria*)	Facultative anaerobic bacteria	O_2 or NO_3^-	[1], [4]
Sphingomonas sp. (phylum *Proteobacteria*)	Mostly strictly aerobic bacteria Some anaerobic bacteria	O_2 NO_3^-, Fe^{3+}, or S	[2]
Xanthobacter autotrophicus (phylum *Proteobacteria*)	Aerobic bacteria	O_2	[3]
Rhodococcus sp. (phylum *Actinobacteria*)	Aerobic bacteria	O_2	[5]
Bacillus sp. (phylum *Firmicutes*)	Aerobic bacteria or facultative anaerobic bacteria	O_2, Fe^{3+}, or NO_3^-	[5], [6], [7]

Source: [1] Wenderoth et al., 2003; [2] Fredrickson et al., 1999; [3] Munro et al., 2016; [4] Li et al., 2014; [5] van Agteren et al., 2013; [6] Soudi et al., 2009; [7] Li et al., 2012.

Rhodococcus sp. (phyla *Actinobacteria*) (Bouju et al., 2012; Larcher and Yargeau, 2011), and *Variovorax* sp. (Herzog et al., 2013) have exhibited the ability to degrade sulfamethoxazole. Specifically, Jiang et al. (2014) proposed two potential pathway for the biodegradation of sulfamethoxazole by *Pseudomonas* sp. involving the cleavage of N-C bond and S-N bond. N-C bond cleavage may result in the formation of sulfanilamide while the S-N bond cleavage may form 3-amino-5-methylisoxazole. Gauthier et al. (2010) reported that *Rhodococcus* sp. acted on the amine functional group of the aromatic ring of sulfamethoxazole and replaced it by a hydroxyl group. Atrazine was found to be degraded by *Pseudomonas* sp. (Mandelbaum et al., 1995; Wenk et al., 1998), *Rhodococcus* sp. (Kolekar et al., 2014), and *Variovorax* sp. (Douglass et al., 2016) as well. Mandelbaum indicated that *Pseudomonas* sp. utilized nitrogen in atrazine and the ring was cleaved with carbon being liberated as CO_2. Kolekar et al. (2014) proposed hydroxylation and dealkylation as the two key processes for atrazine biodegradation by *Rhodococcus* sp.. During hydroxylation, hydroxyatrazine was formed through hydrolysis while deethylatrazine and deisopropylatrazine were produced from dealkylation. Moreover, *Pseudomonas* sp. and *Rhodococcus* sp. were also shown to be the caffeine-degrading bacteria (Gummadi et al., 2012). Gummadiet al. (2012) reported that with *Pseudomonas* sp. caffeine was dealkylated to theobromine or paraxanthine which was then degraded to dimethyluric acid while *Rhodococcus* sp. directly degraded caffeine to trimethyluric acid.

Kjeldal et al. (2016) reported *Bacillus* sp. as the gemfibrozil-degrading bacteria (Kjeldal et al., 2016) where methyl group on the aromatic ring of gemfibrozil was hydroxylated and oxidized to a carboxylic acid. Further degradation was through side-

chain cleavage to form 2-hydroxy-4-methylbenzoic acid and cleavage of the aromatic ring degrading the ring structure to 2-hydroxymuconate semialdehyde. Takahashi et al. (2012) reported the metabolic pathway for TCEP involved *Sphingomonas* sp. and *Xanthobacter autotrophicus* both belonging to phyla *Proteobacteria*. Once *Sphingomonas* sp. broke down the phosphotriester bonds in TCEP and formed 2-chloroethanol, *X. autotrophicus* further degraded 2-chloroethanol to the low toxic product – glycolic acid. Several bacteria genera were reported to be capable of degrading 17β-estradiol including *Pseudomonas* sp., *Sphingomonas* sp., *Rhodococcus* sp., and *Flavobacterium* sp. (phyla *Bacteroidetes*) (Kurisu et al., 2010; Roh and Chu et al., 2010; Yu et al., 2007; Zhou et al., 2013). Kurisu et al. (2010) proposed two potential pathways for 17β-estradiol: 1) oxidized to estrone and then hydroxylated to 4-hydroxyestrone followed by meta cleavage on the aromatic ring; and, 2) hydroxylated to 4-hydroxyestradiol followed by double bond cleavage on the aromatic ring. In the next chapter, the conclusions of this study are summarized.

CHAPTER 7

CONCLUSIONS

Converting existing dual media and GAC filters into BAFs is an advanced technology that can achieve PPCP removals. Results revealed limited PPCP removals in dual media BAFs when pre-ozonation was not applied. At 10 min of EBCT, three compounds (ibuprofen, trimethoprim, and 17β-estradiol) were removed by greater than 75%. With the EBCT increased to 18 min, the removal of acetaminophen was improved to greater than 75% (Figure 6.18). The application of pre-ozonation improved the removals at both EBCTs. With pre-ozonation, 11 indicator compounds were removed at greater than 75% with a 10 min EBCT and nine with an EBCT of 18 min; the difference between two EBCTs was not significant. The recalcitrant compounds were TCEP, cotinine, aminotriazole, atrazine and iopromide. In this study, the most cost effective operating conditions for dual media BAFs were a 10 min EBCT with the application of pre-ozonation.

To further improve the removal, converting GAC filters to BAFs is recommended. With GAC absorbents at an EBCT of 10 min, seven PPCPs were removed by greater than 75% (Figure 6.19). After the application of pre-ozonation, the indicator compounds removed at greater than 75% significantly increased to 12 with exceptions of TCEP, cotinine, DEET, and iopromide. Increasing the EBCT to 18 min, GAC BAFs even without pre-ozonation became effective in functioning as a sustainable treatment process for PPCPs with removals greater than 75%; the exception was iopromide with removals at 59%. To removal the recalcitrant compound iopromide, the application of pre-

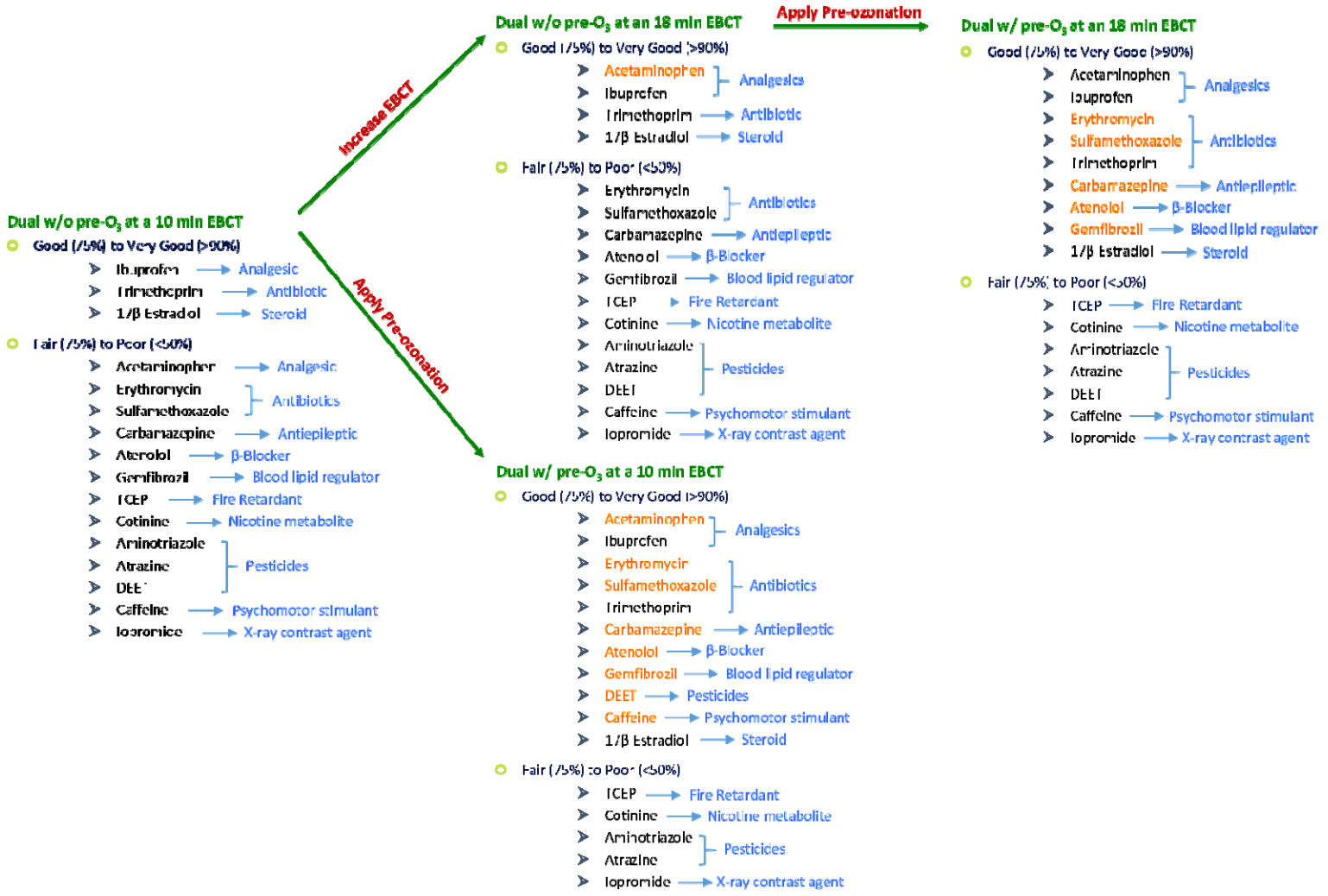


Figure 6.18 Treatablity of the indicator compounds in dual media BAFs. The improvements achieved by increasing EBCT and pre-ozonation application were summarized. Compounds with improved removals were highlighted with orange color.

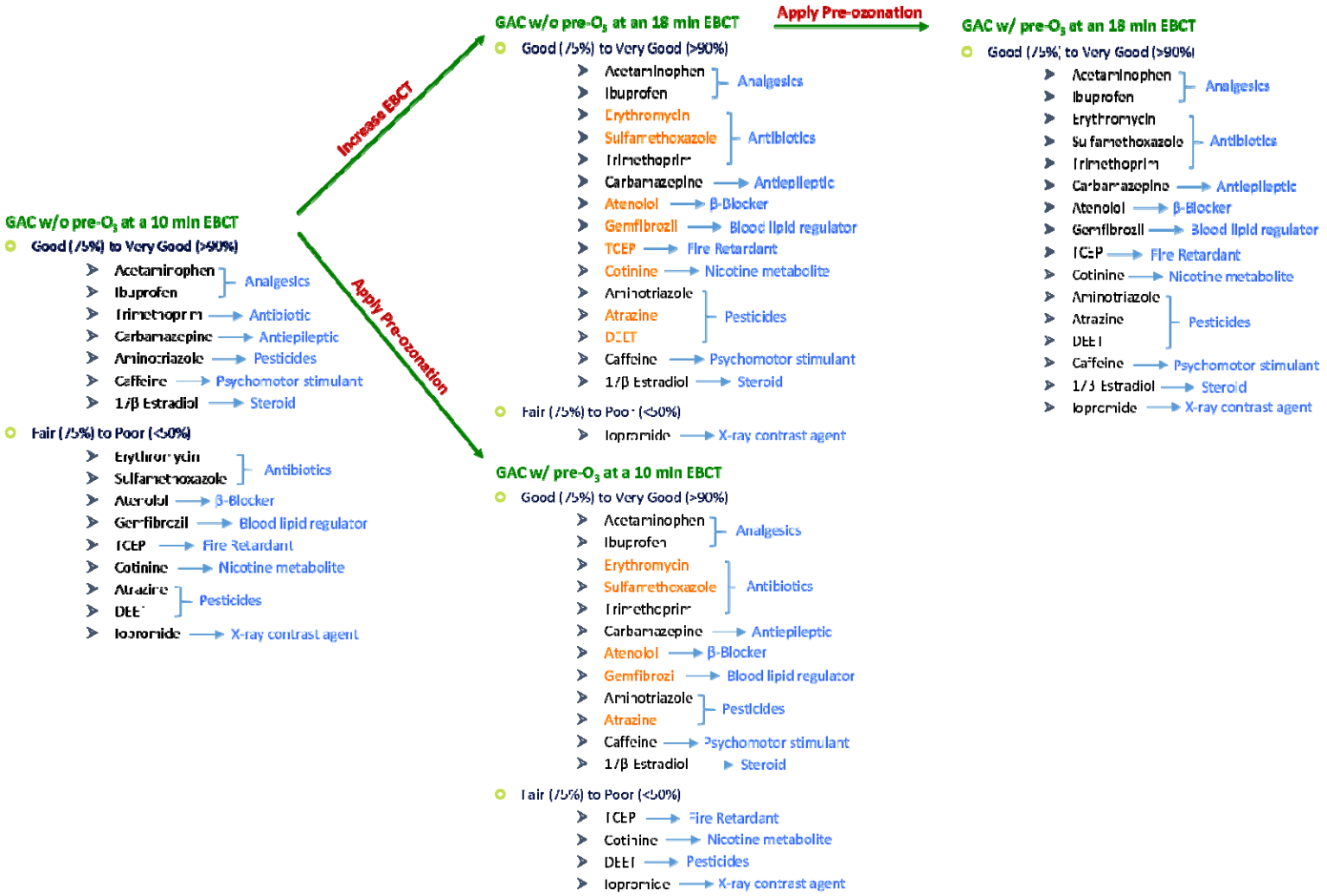


Figure 6.19 Treatablity of the indicator compounds in GAC BAFs. The improvements achieved by increasing EBCT and pre-ozonation application were summarized. Compounds with improved removals were highlighted with orange color.

ozonation was needed and removals through the process increased to 79% for iopromide at a dosage of 3 mg/L (i.e., the ozone demand). GAC BAFs with an 18 min EBCT showed significant removals with or without pre-ozonation. While at an EBCT of 10 min, the application of pre-ozonation is necessary.

DOC removal normalized to ATP is an important indicator for BAF performance. With DOC removals ranging from 200 to 600 mg/g ATP in BAFs, GAC showed significant removal efficiency (>80%) for PPCPs. With DOC removals of 100 to 200 mg/g ATP in dual media BAFs, limited removals were observed. The purpose of this study was to examine if existing filters in water treatment plants can be converted into advanced treatment processes for the removal of PPCPs. In our study, the GAC BAF has been demonstrated to be a viable and sustainable treatment process for PPCPs. Dual media BAFs, on the other hand, require pre-ozonation. Further increases in the EBCT (i.e., greater than 18 min) for the dual media BAF may be required to achieve improved PPCP removals; however, for existing filters in water treatment plants, increasing the EBCT may not be feasible. Complementary analyses of DO consumption and pH drop demonstrated consistent trends in that the GAC microbial community is unique compared to that of the dual media BAF.

Studying the microbial community structure in BAF media, influent, and effluent samples revealed greater biodiversity and evenness in BAF media compared to influents and effluents. Distinct microbial communities were observed between media and water samples (BAF influents and effluents). At the phyla level, dominant bacteria in media samples were *Proteobacteria* (31.7% to 45.3%), *Planctomycetes* (29.9% to 44.0%), and *Acidobacteria* (5.0% to 12.4%), while in influents and effluents, *Proteobacteria* (42.3%

to 63.4%), *Actinobacteria* (6.4% to 31.8%), and *Chlamydiae* (1.2% to 19.1%) were dominant. Differences were observed as well between media collected from GAC and dual media BAFs: A greater abundance of *Chloroflexi* was observed in GAC BAFs, while an increased abundance of *Acidobacteria* was found in dual media BAFs. Similar trends were observed at bacterial class and order levels.

This study is the first to demonstrate the relationship between the microbial community structure and the operational conditions in BAFs used in water treatment. The impact of media type, EBCT, and pre-ozonation on the microbial community structure was observed and assessed based on the factorial analysis. Statistically, there was a greater abundance of bacterial phyla *Chloroflexi*, *Gemmatimonadetes*, *Actinobacteria*, and *Armatimonadetes* in GAC BAFs than in dual media BAFs which may result in the greater PPCP removals. At class level, 10 bacteria were affected by the media type. Consistent with bacterial phyla, the abundance of bacterial classes *Anaerolineae* and *Chloroflexi* (belonging to *Chloroflexi* phylum), *Actinobacteria* and *Thermoleophilia* (belonging to *Actinobacteria* phylum), and *Gemmatimonadetes* (belonging to *Gemmatimonadetes* phylum) was significantly greater in GAC BAFs. EBCT was found to affect the abundance of the most dominant bacteria phylum, *Proteobacteria*. Ozone impacts the abundance of the two dominant bacteria (*α-Proteobacteria* and *Planctomycetia*) at the class level. As *Proteobacteria* were reported to degrade a number of PPCPs, the application of ozonation may not only break down the organic carbon in source water, but also increase the abundance of the PPCP degrading bacteria. Consistent with the factorial analysis, PCA supported the hypothesis that the operational conditions may affect the abundance of the PPCP degrading bacteria as well. For example, the

abundance of *Proteobacteria*, *Actinobacteria*, *Firmicutes*, and *Bacteroidetes*, were significantly associated with the change of pre-ozonation and EBCT. A number of studies have reported that bacteria associated with phyla *Proteobacteria*, *Actinobacteria*, *Firmicutes*, and *Bacteroidetes* were capable of degrading emerging contaminants.

Legionella pneumophila and *Mycobacterium gordonae* were detected in BAF effluents. However, the abundance was as low as 8.13×10^{-5} for *L. pneumophila* and 1.43×10^{-5} for *M. gordonae*. In addition, disinfection is expected to control the occurrence of *Legionella pneumophila* and *Mycobacterium gordonae*.

CHAPTER 8

FUTURE WORK

Future work recommended includes developing models to simulate transport and reaction through the BAFs. Specifically, research is needed to address tracer studies for dispersion and transport mechanisms in the BAF columns, reaction kinetics to understand the growth of the biomass on the media, and reaction kinetics for biodegradation of the emerging contaminants based on studies with the indicator compounds. Tracer studies involve modeling dispersion in the BAFs at both 10 min and 18 min EBCT. The kinetics study on the growth of the biomass will be based on the ATP and DOC concentrations in the BAFs. Zearley and Summers (2012) investigated the rate constants of 32 PPCPs in sand BAFs. In our future work, reaction rate constants for individual indicator compounds will be determined using batch reactors for both GAC and dual media BAFs. Models to predict the treatability of the indicator compounds can be developed. Optimization of the treatment processes and evaluation of the effectiveness of indicator compounds to represent emerging contaminants will be further investigated in the pilot plant study. The models will be applied as well in the pilot plant study and further validated in the full scale study.

APPENDIX A

NUTRIENTS AND TOTAL ORGANIC CARBON IN SOURCE WATER

The concentrations of nutrients and total organic carbon in the source water are shown below.

Table A.1 Concentrations of Nutrients and Total Organic Carbon in the Source Water

Date	TOC (mg/L)	NH_3_N (mg/L)	NO_3_N (mg/L)	NO_2_N (mg/L)	PO_4_P (mg/L)
9/25/2014	1.96	0.13	4.6	0.019	0.046
9/28/2014	1.93	0.12	4.4	0.018	0.059
9/30/2014	1.99	0.12	6.0	0.018	0.075
10/2/2014	2.02	0.12	5.9	0.020	0.036
10/3/2014	2.42	0.12	5.1	0.015	0.078
10/5/2014	2.61	0.14	5.0	0.016	0.052
10/7/2014	2.61	0.11	3.3	0.015	0.072
10/9/2014	2.66	0.13	4.9	0.020	0.088
10/10/2014	2.91	0.12	4.3	0.016	0.095
10/12/2014	3.09	0.12	3.1	0.015	0.078
10/14/2014	3.10	0.11	3.0	0.016	0.082
10/16/2014	3.11	0.12	3.2	0.015	0.082
10/17/2014	2.89	0.12	3.0	0.018	0.065
10/19/2014	2.98	0.12	4.5	0.015	0.069
10/21/2014	2.87	0.13	3.1	0.016	0.095
10/23/2014	2.94	0.12	3.2	0.021	0.124
10/24/2014	2.59	0.14	3.3	0.012	0.069
10/26/2014	2.77	0.12	2.1	0.012	0.062
10/28/2014	2.59	0.12	3.2	0.012	0.039
10/30/2014	2.56	0.12	3.3	0.014	0.056
10/31/2014	3.15	0.15	2.8	0.023	0.046
11/2/2014	2.98	0.15	2.8	0.024	0.059
11/4/2014	2.93	0.15	2.6	0.024	0.065
11/6/2014	2.74	0.15	4.0	0.025	0.069
11/7/2014	2.62	0.15	5.2	0.017	0.052
11/9/2014	2.60	0.13	3.5	0.018	0.046
11/11/2014	2.40	0.13	3.2	0.019	0.082
11/13/2014	2.58	0.14	5.5	0.018	0.065
11/14/2014	2.77	0.17	4.0	0.021	0.108
11/16/2014	2.73	0.16	4.7	0.024	0.065
11/18/2014	2.73	0.16	3.9	0.023	0.039
11/20/2014	2.59	0.16	3.5	0.023	0.124
11/21/2014	2.91	0.09	2.5	0.008	0.049
11/23/2014	2.87	0.09	2.7	0.008	0.065
11/25/2014	2.81	0.10	3.7	0.010	0.121
11/27/2014	2.73	0.09	3.1	0.008	0.046
11/28/2014	2.04	0.15	2.1	0.020	0.033
11/30/2014	1.98	0.14	3.0	0.021	0.046
12/2/2014	1.89	0.14	2.7	0.021	0.029
12/4/2014	2.12	0.15	3.1	0.021	0.039
12/5/2014	2.20	0.17	2.3	0.033	0.065
12/7/2014	2.18	0.17	2.2	0.033	0.036
12/9/2014	2.12	0.16	3.0	0.033	0.033
12/11/2014	2.12	0.17	2.9	0.032	0.046
12/12/2014	2.31	0.12	1.7	0.023	0.049
12/14/2014	2.21	0.11	1.8	0.025	0.036

Table A.1 Concentrations of Nutrients and Total Organic Carbon in the Source Water (Continued)

Date	TOC (mg/L)	NH_3_N (mg/L)	NO_3_N (mg/L)	NO_2_N (mg/L)	PO_4_P (mg/L)
12/16/2014	2.04	0.12	1.2	0.024	0.026
12/18/2014	2.08	0.11	1.5	0.024	0.033
12/19/2014	2.16	0.14	1.6	0.063	0.023
12/21/2014	2.16	0.13	1.7	0.065	0.062
12/23/2014	2.12	0.13	1.8	0.066	0.026
12/25/2014	2.05	0.13	2.1	0.062	0.026
12/26/2014	1.65	0.15	2.0	0.059	0.029
12/28/2014	1.61	0.15	1.7	0.060	0.023
12/30/2014	1.59	0.16	2.1	0.061	0.020
1/1/2015	1.57	0.16	2.0	0.061	0.020
1/2/2015	2.13	0.17	2.8	0.031	0.049
1/4/2015	2.01	0.16	2.6	0.031	0.033
1/6/2015	2.05	0.17	1.9	0.036	0.029
1/8/2015	2.04	0.16	2.7	0.033	0.026
1/9/2015	2.07	0.18	1.7	0.017	0.026
1/11/2015	1.92	0.18	2.4	0.016	0.059
1/13/2015	1.91	0.18	2.1	0.017	0.026
1/15/2015	1.84	0.18	2.0	0.017	0.029
1/16/2015	2.19	0.25	3.4	0.023	0.042
1/18/2015	2.13	0.24	3.2	0.022	0.046
1/20/2015	2.15	0.26	3.6	0.023	0.046
1/22/2015	2.24	0.26	3.1	0.023	0.039
1/23/2015	1.92	0.21	1.7	0.014	0.088
1/25/2015	1.81	0.21	1.4	0.012	0.026
1/27/2015	1.80	0.18	1.4	0.012	0.029
1/29/2015	1.80	0.23	1.5	0.012	0.026
1/30/2015	2.29	0.28	2.4	0.020	0.036
2/1/2015	2.16	0.27	2.3	0.021	0.039
2/3/2015	2.22	0.26	1.9	0.020	0.056
2/5/2015	2.24	0.26	2.2	0.018	0.036
2/6/2015	2.24	0.37	2.2	0.035	0.033
2/8/2015	2.23	0.37	3.2	0.040	0.039
2/10/2015	2.27	0.38	3.1	0.048	0.036
2/12/2015	2.29	0.35	2.2	0.034	0.046
2/13/2015	2.22	0.30	3.0	0.034	0.046
2/15/2015	2.23	0.31	3.2	0.033	0.036
2/17/2015	2.21	0.29	2.9	0.035	0.026
2/19/2015	2.23	0.31	2.2	0.034	0.049
2/20/2015	2.68	0.37	3.6	0.037	0.069
2/22/2015	2.50	0.41	2.8	0.039	0.036
2/24/2015	2.43	0.41	3.9	0.035	0.046
2/26/2015	2.53	0.41	2.4	0.037	0.049
2/27/2015	2.71	0.28	4.6	0.037	0.069
3/1/2015	2.68	0.30	4.5	0.038	0.039
3/3/2015	2.62	0.29	4.3	0.038	0.042
3/5/2015	2.76	0.31	4.5	0.038	0.082
3/6/2015	2.19	0.56	2.4	0.031	0.029
3/8/2015	2.18	0.51	3.0	0.034	0.023
3/10/2015	2.16	0.46	3.1	0.030	0.033
4/7/2015	1.94	0.14	1.6	0.007	0.020
4/9/2015	1.86	0.13	1.8	0.008	0.016
4/10/2015	1.68	0.06	1.6	0.007	0.020
4/12/2015	1.66	0.12	1.7	0.007	0.016
4/14/2015	1.62	0.12	1.6	0.004	0.013
4/16/2015	1.62	0.13	1.5	0.008	0.016
4/17/2015	2.13	0.10	2.2	0.010	0.069
4/19/2015	2.10	0.12	1.1	0.010	0.020

Table A.1 Concentrations of Nutrients and Total Organic Carbon in the Source Water (Continued)

Date	TOC (mg/L)	NH_3_N (mg/L)	NO_3_N (mg/L)	NO_2_N (mg/L)	PO_4_P (mg/L)
4/21/2015	2.09	0.12	1.1	0.009	0.016
4/23/2015	2.08	0.13	1.1	0.010	0.020
4/24/2015	2.25	0.12	0.8	0.008	0.020
4/26/2015	2.21	0.12	0.7	0.010	0.033
4/28/2015	1.95	0.12	0.8	0.009	0.023
4/29/2015	2.07	0.12	0.8	0.008	0.026
5/1/2015	2.10	0.09	0.9	0.008	0.020
5/3/2015	2.14	0.08	1.1	0.008	0.016
5/5/2015	2.06	0.07	0.9	0.007	0.020
5/7/2015	2.03	0.09	1.0	0.008	0.016
5/8/2015	2.31	0.13	1.3	0.019	0.029
5/10/2015	2.32	0.15	1.5	0.016	0.029
5/12/2015	2.07	0.14	1.2	0.015	0.023
5/14/2015	2.27	0.15	1.3	0.017	0.023
5/15/2015	2.74	0.11	1.5	0.033	0.029
5/17/2015	2.76	0.12	1.9	0.034	0.039
5/19/2015	2.58	0.11	1.5	0.034	0.016
5/21/2015	2.63	0.12	1.5	0.029	0.029
5/22/2015	3.48	0.30	1.8	0.051	0.059
5/24/2015	3.39	0.31	1.6	0.048	0.042
5/26/2015	3.48	0.30	2.1	0.037	0.042
5/27/2015	3.44	0.30	1.5	0.041	0.033
5/28/2015	3.33	0.31	1.8	0.048	0.044
5/29/2015	3.34	0.09	2.2	0.043	0.039
5/31/2015	3.38	0.10	2.4	0.040	0.026
6/2/2015	3.40	0.10	2.1	0.039	0.049
6/4/2015	3.39	0.10	2.1	0.040	0.033
6/5/2015	2.09	0.29	0.9	0.021	0.023
6/7/2015	2.09	0.28	0.9	0.021	0.023
6/9/2015	2.05	0.28	1.1	0.021	0.013
6/11/2015	2.90	0.20	1.5	0.028	0.059
6/12/2015	2.85	0.20	1.2	0.029	0.036
6/14/2015	2.87	0.20	1.3	0.029	0.039
6/16/2015	2.86	0.20	1.2	0.029	0.029
6/18/2015	2.80	0.19	1.1	0.029	0.056
6/19/2015	2.76	0.21	0.9	0.023	0.029
6/21/2015	2.71	0.21	0.9	0.025	0.039
6/23/2015	2.71	0.21	0.9	0.024	0.036
6/25/2015	2.56	0.23	1.0	0.024	0.029
6/26/2015	2.56	0.13	1.2	0.025	0.042
6/28/2015	2.53	0.13	1.3	0.030	0.056
6/29/2015	2.64	0.14	1.1	0.023	0.036
7/2/2015	2.61	0.13	1.3	0.030	0.023
7/3/2015	2.58	0.13	1.0	0.011	0.029
7/5/2015	2.50	0.12	1.0	0.011	0.026
7/7/2015	2.54	0.13	1.1	0.011	0.029
7/9/2015	2.48	0.12	1.0	0.014	0.020
7/10/2015	2.73	0.16	1.4	0.015	0.023
7/12/2015	2.67	0.16	1.6	0.015	0.049
7/14/2015	2.72	0.15	1.4	0.016	0.065
7/16/2015	2.74	0.15	1.3	0.015	0.069
7/17/2015	2.65	0.15	1.4	0.015	0.036
7/19/2015	2.56	0.09	1.6	0.009	0.042
7/21/2015	2.59	0.09	1.4	0.010	0.088
7/23/2015	2.53	0.10	1.3	0.012	0.065
7/24/2015	2.82	0.04	1.7	0.012	0.052
7/26/2015	2.78	0.11	2.1	0.013	0.029

Table A.1 Concentrations of Nutrients and Total Organic Carbon in the Source Water (Continued)

Date	TOC (mg/L)	NH_3_N (mg/L)	NO_3_N (mg/L)	NO_2_N (mg/L)	PO_4_P (mg/L)
7/28/2015	2.80	0.10	1.5	0.012	0.036
7/30/2015	2.75	0.10	1.7	0.012	0.020
7/31/2015	2.44	0.12	1.5	0.010	0.046
8/2/2015	2.49	0.14	1.8	0.020	0.046
8/4/2015	2.46	0.12	1.5	0.009	0.026
8/6/2015	2.25	0.12	1.6	0.011	0.039
8/7/2015	2.88	0.12	1.7	0.022	0.062
8/9/2015	2.81	0.12	1.6	0.022	0.046
8/11/2015	2.93	0.12	1.8	0.010	0.036
8/13/2015	2.96	0.12	1.7	0.009	0.075
8/14/2015	2.80	0.12	1.8	0.010	0.039
8/16/2015	2.60	0.13	2.3	0.015	0.049
8/18/2015	2.69	0.13	2.2	0.015	0.052
8/20/2015	2.55	0.12	1.7	0.017	0.036
8/21/2015	3.09	0.13	2.2	0.032	0.104
8/23/2015	2.59	0.12	2.2	0.015	0.033
8/25/2015	3.13	0.13	2.2	0.015	0.052
8/27/2015	2.90	0.12	2.2	0.015	0.046
8/28/2015	2.90	0.11	1.9	0.011	0.072
8/30/2015	2.81	0.11	1.9	0.012	0.075
9/1/2015	2.83	0.10	1.8	0.010	0.056
9/3/2015	2.70	0.11	1.9	0.011	0.036
9/4/2015	2.80	0.11	1.9	0.011	0.085
9/6/2015	2.68	0.11	2.2	0.012	0.065
9/8/2015	2.78	0.11	2.2	0.012	0.046
9/10/2015	2.72	0.11	2.1	0.012	0.062
9/11/2015	2.60	0.12	2.2	0.011	0.042
9/13/2015	2.33	0.16	1.2	0.008	0.020
9/15/2015	2.38	0.16	1.1	0.010	0.033
9/17/2015	2.16	0.16	1.2	0.008	0.036
9/18/2015	2.30	0.16	1.1	0.008	0.026
9/20/2015	3.05	0.14	2.0	0.014	0.042
9/22/2015	3.08	0.14	2.0	0.014	0.082
9/24/2015	2.77	0.14	2.1	0.015	0.042
9/25/2015	2.97	0.14	2.0	0.014	0.052
9/27/2015	2.08	0.08	2.2	0.008	0.036
9/29/2015	2.24	0.08	2.1	0.008	0.052
10/1/2015	2.03	0.08	2.2	0.008	0.033
10/2/2015	2.30	0.08	2.2	0.008	0.056
10/4/2015	1.85	0.13	1.2	0.006	0.026
10/6/2015	1.87	0.13	1.0	0.007	0.033
10/8/2015	1.71	0.13	1.1	0.007	0.059
10/9/2015	2.60	0.14	1.6	0.019	0.049
10/11/2015	2.48	0.14	1.6	0.019	0.029
10/13/2015	2.56	0.14	1.5	0.016	0.075
10/15/2015	2.37	0.14	1.5	0.017	0.091
10/16/2015	2.57	0.14	1.6	0.017	0.049
10/18/2015	2.80	0.14	1.7	0.012	0.082
10/20/2015	2.76	0.14	1.6	0.012	0.069
10/22/2015	2.58	0.13	1.7	0.012	0.046
10/23/2015	2.69	0.14	1.7	0.012	0.056
10/25/2015	2.91	0.14	2.6	0.016	0.042
10/27/2015	2.99	0.13	2.6	0.015	0.072
10/29/2015	2.96	0.13	2.6	0.016	0.075
10/30/2015	2.95	0.13	2.6	0.015	0.056
11/1/2015	2.52	0.10	1.5	0.023	0.026
11/3/2015	2.39	0.10	1.5	0.022	0.023

Table A.1 Concentrations of Nutrients and Total Organic Carbon in the Source Water (Continued)

Date	TOC (mg/L)	NH_3_N (mg/L)	NO_3_N (mg/L)	NO_2_N (mg/L)	PO_4_P (mg/L)
11/5/2015	2.24	0.10	1.4	0.023	0.029
11/6/2015	2.31	0.11	1.5	0.023	0.036
11/8/2015	2.87	0.20	1.3	0.013	0.078
11/10/2015	3.24	0.20	1.6	0.013	0.049

TOC – total organic carbon.

APPENDIX B

PARAMETERS MONITORED IN BAFS

The parameters monitored in BAFs during the bench-scale study are presented below.

Table B.1 Average pH in BAF Influents and Effluents

Date	Without Ozonation			With Ozonation		
	Influent	Effluent		Influent	Effluent	
		GAC	Dual Media		GAC	Dual Media
9/29/2014	7.04	6.88	-	7.04	6.89	-
10/1/2014	7.16	7.04	-	7.16	7.11	-
10/3/2014	7.17	6.90	7.07	7.17	6.89	7.04
10/6/2014	7.35	6.89	7.14	7.35	6.82	7.16
10/8/2014	7.23	6.91	7.14	7.23	6.90	7.15
10/10/2014	7.15	6.87	6.98	7.15	6.92	7.08
10/13/2014	7.37	6.89	7.18	7.37	6.93	7.13
10/15/2014	7.36	6.84	7.12	7.36	6.80	7.09
10/17/2014	7.37	6.83	7.03	7.37	6.75	6.95
10/20/2014	7.25	6.86	6.98	7.25	6.77	6.94
10/22/2014	7.29	6.82	6.89	7.29	6.75	6.83
10/24/2014	7.27	6.75	6.85	7.27	6.73	6.87
10/27/2014	7.05	6.85	6.74	7.05	6.78	6.75
10/29/2014	7.09	6.87	6.84	7.09	6.85	6.79
10/31/2014	7.09	6.84	6.88	7.09	6.76	6.85
11/3/2014	7.18	6.80	6.83	7.18	6.78	6.81
11/5/2014	7.21	6.78	6.87	7.21	6.73	6.82
11/7/2014	7.20	6.74	6.84	7.20	6.74	6.74
11/10/2014	7.14	6.82	6.99	7.14	6.81	6.96
11/12/2014	7.09	6.81	6.99	7.09	6.79	6.92
11/14/2014	7.14	6.87	7.01	7.14	6.85	6.98
11/17/2014	7.31	6.98	7.20	7.31	6.91	7.08
11/19/2014	7.27	6.92	7.11	7.27	6.93	7.06
11/21/2014	7.22	6.90	7.05	7.22	6.94	7.03
11/24/2014	7.12	6.86	6.99	7.12	6.85	6.94
11/26/2014	7.24	6.95	7.07	7.24	6.93	7.04
11/28/2014	7.22	6.96	7.01	7.22	6.93	7.02
12/1/2014	7.16	6.89	7.02	7.16	6.90	6.99
12/3/2014	7.12	6.86	6.98	7.12	6.92	7.00
12/5/2014	7.16	6.86	7.01	7.16	6.90	7.04
12/8/2014	7.13	6.93	7.07	7.13	6.91	7.05
12/10/2014	7.11	6.88	7.04	7.11	6.90	7.07
12/12/2014	7.11	6.90	7.04	7.11	6.94	7.03
12/15/2014	7.11	6.92	7.04	7.11	6.93	6.99
12/17/2014	7.12	6.92	7.01	7.12	6.94	6.99
12/19/2014	7.19	6.95	7.00	7.19	6.95	6.99
12/22/2014	7.08	6.90	7.03	7.08	6.91	7.02
12/24/2014	7.21	6.86	7.03	7.21	6.90	7.02
12/26/2014	7.17	6.79	7.05	7.17	6.90	7.05
12/29/2014	7.18	6.94	7.02	7.18	6.87	7.04
12/31/2014	7.07	6.89	6.99	7.07	6.86	7.01
1/2/2015	7.08	6.93	7.05	7.08	6.90	7.03
1/5/2015	7.12	6.88	7.02	7.12	6.94	7.04
1/7/2015	7.04	6.88	7.07	7.04	6.97	7.02

Table B.1 Average pH in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent	Effluent		Influent	Effluent	
		GAC	Dual Media		GAC	Dual Media
1/9/2015	7.20	6.97	7.14	7.20	7.00	7.15
1/12/2015	7.14	6.90	7.01	7.14	6.92	6.99
1/14/2015	7.02	6.89	6.99	7.02	6.90	6.94
1/16/2015	7.08	6.92	7.05	7.08	6.93	7.02
1/19/2015	7.12	6.99	7.11	7.12	6.94	7.02
1/21/2015	7.18	6.93	7.13	7.18	6.91	7.02
1/23/2015	7.08	6.96	7.03	7.08	6.97	6.98
1/26/2015	7.16	7.04	7.08	7.16	6.95	6.98
1/28/2015	7.19	7.13	7.03	7.19	7.00	7.11
1/30/2015	7.19	6.98	7.09	7.19	7.08	7.04
2/2/2015	7.29	6.97	7.20	7.29	7.02	7.12
2/4/2015	7.26	7.09	7.13	7.26	7.05	7.18
2/6/2015	7.36	7.12	7.29	7.36	7.16	7.29
2/9/2015	7.39	7.21	7.15	7.39	7.03	7.23
2/11/2015	7.27	7.10	7.20	7.27	7.06	7.27
2/13/2015	7.29	7.02	7.25	7.29	7.12	7.25
2/16/2015	7.30	7.20	7.29	7.30	7.09	7.28
2/18/2015	7.30	6.99	7.20	7.30	7.20	7.17
2/20/2015	7.18	7.18	7.16	7.18	7.05	7.15
2/23/2015	7.28	7.10	7.31	7.28	7.06	7.28
2/25/2015	7.34	7.22	7.34	7.34	7.17	7.32
2/27/2015	7.35	7.06	7.33	7.35	7.10	7.34
3/2/2015	7.36	7.15	7.37	7.26	7.11	7.09
3/4/2015	7.35	7.10	7.20	7.23	7.14	7.10
3/6/2015	7.51	7.22	7.47	7.27	7.09	7.26
3/9/2015	7.36	7.09	7.27	7.24	7.09	7.18
4/6/2015	7.24	6.97	7.20	7.17	6.99	7.08
4/8/2015	7.39	7.00	7.36	7.19	7.11	7.18
4/10/2015	7.29	7.08	7.25	7.25	7.05	7.19
4/13/2015	7.37	7.06	7.26	7.06	7.03	7.05
4/15/2015	7.28	7.02	7.19	7.30	7.08	7.21
4/17/2015	7.32	7.07	7.27	7.13	7.08	7.13
4/20/2015	7.31	7.05	7.23	7.17	7.01	7.14
4/22/2015	7.32	7.19	7.31	7.22	7.06	7.20
4/24/2015	7.36	7.09	7.29	7.17	7.11	7.13
4/27/2015	7.38	7.16	7.33	7.20	7.07	7.18
4/29/2015	7.39	7.11	7.32	7.22	7.08	7.21
5/1/2015	7.35	7.08	7.24	7.17	6.94	7.16
5/4/2015	7.17	7.05	7.14	7.17	6.96	7.16
5/6/2015	7.24	6.98	7.15	7.14	6.93	7.12
5/8/2015	7.23	7.02	7.12	7.14	6.97	7.12
5/11/2015	7.20	6.98	7.15	7.15	6.94	7.12
5/13/2015	7.20	7.06	7.16	7.16	6.91	7.14
5/15/2015	7.27	7.12	7.25	7.15	7.02	7.13
5/18/2015	7.26	7.07	7.26	7.28	6.98	7.27
5/20/2015	7.21	7.10	7.21	7.28	7.09	7.26
5/22/2015	7.28	7.17	7.25	7.28	7.18	7.23
5/25/2015	7.41	7.11	7.33	7.16	7.09	7.27
5/27/2015	7.43	7.08	7.44	7.16	7.05	7.15
5/29/2015	7.40	7.09	7.39	7.16	7.10	7.13
6/1/2015	7.39	7.12	7.36	7.16	7.11	7.12
6/3/2015	7.34	7.18	7.27	7.17	7.14	7.13
6/5/2015	7.35	7.17	7.33	7.26	7.13	7.12
6/8/2015	7.41	7.21	7.24	7.11	7.04	7.06
6/10/2015	7.37	7.13	7.32	6.99	6.99	7.06

Table B.1 Average pH in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent	Effluent		Influent	Effluent	
		GAC	Dual Media		GAC	Dual Media
6/12/2015	7.34	7.12	7.22	7.04	6.97	7.03
6/15/2015	7.28	7.11	7.26	7.03	6.91	7.02
6/17/2015	7.33	7.07	7.31	7.03	6.96	7.02
6/19/2015	7.31	7.10	7.33	7.09	6.93	7.08
6/22/2015	7.23	7.06	7.16	7.15	6.97	7.12
6/24/2015	7.30	7.01	7.29	7.04	6.96	7.03
6/26/2015	7.24	7.02	7.22	7.06	6.91	7.02
6/29/2015	7.17	7.02	7.15	7.07	6.98	7.01
7/1/2015	7.22	7.04	7.20	7.04	6.94	7.01
7/3/2015	7.14	7.03	7.16	6.98	6.83	6.98
7/6/2015	7.19	7.07	7.15	7.09	6.99	7.07
7/8/2015	7.13	6.97	7.13	7.11	6.84	7.06
7/10/2015	7.17	7.04	7.11	7.04	6.87	7.02
7/13/2015	7.13	6.88	7.15	7.09	6.88	7.06
7/15/2015	7.21	6.88	7.14	7.17	6.93	7.14
7/17/2015	7.23	7.00	7.18	7.10	6.86	7.03
7/20/2015	7.19	7.04	7.16	7.12	6.86	7.08
7/22/2015	7.20	7.08	7.16	7.05	6.90	7.02
7/24/2015	7.23	7.11	7.21	7.09	7.00	7.07
7/27/2015	7.31	7.06	7.30	7.07	6.87	7.04
7/29/2015	7.28	7.09	7.23	7.03	6.87	7.01
7/31/2015	7.30	7.15	7.23	7.19	7.00	7.15
8/3/2015	7.34	7.14	7.29	7.20	7.00	7.17
8/5/2015	7.40	7.22	7.36	7.19	7.00	7.19
8/7/2015	7.42	7.17	7.38	7.19	6.98	7.18
8/10/2015	7.44	7.22	7.44	7.08	7.04	7.05
8/12/2015	7.41	7.20	7.39	7.09	7.02	7.08
8/14/2015	7.37	7.21	7.33	7.13	7.04	7.11
8/17/2015	7.44	7.20	7.43	7.36	7.07	7.27
8/21/2015	7.32	7.16	7.29	7.12	7.00	7.10
8/24/2015	7.26	7.18	7.32	7.19	7.10	7.15
8/26/2015	7.29	7.19	7.27	7.20	7.11	7.18
8/28/2015	7.30	7.19	7.27	7.22	7.08	7.19
8/31/2015	7.24	7.14	7.22	7.19	7.13	7.19
9/2/2015	7.27	7.14	7.23	7.20	7.10	7.19
9/4/2015	7.38	7.04	7.26	7.15	6.99	7.07
9/7/2015	7.22	7.10	7.18	7.06	7.00	7.04
9/9/2015	7.23	7.12	7.20	7.14	7.04	7.10
9/14/2015	7.25	7.17	7.22	7.28	7.18	7.25
9/16/2015	7.27	7.19	7.24	7.25	7.17	7.23
9/18/2015	7.30	7.19	7.29	7.23	7.17	7.20
9/21/2015	7.38	7.24	7.36	7.31	7.21	7.29
9/23/2015	7.27	7.17	7.24	7.29	7.20	7.27
9/25/2015	7.20	7.15	7.20	7.22	7.14	7.20
9/28/2015	7.23	7.17	7.20	7.19	7.14	7.19
9/30/2015	7.23	7.16	7.21	7.23	7.15	7.22
10/2/2015	7.33	7.19	7.30	7.28	7.18	7.27
10/7/2015	7.20	7.16	7.19	7.24	7.19	7.22
10/9/2015	7.17	7.16	7.16	7.27	7.21	7.26
10/12/2015	7.30	7.19	7.30	7.28	7.21	7.23
10/14/2015	7.33	7.22	7.31	7.26	7.20	7.24
10/16/2015	7.36	7.29	7.35	7.36	7.30	7.35
10/19/2015	7.26	7.18	7.25	7.28	7.20	7.25
10/21/2015	7.24	7.19	7.24	7.27	7.20	7.26
10/23/2015	7.34	7.21	7.33	7.32	7.22	7.31

Table B.1 Average pH in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent	Effluent		Influent	Effluent	
		GAC	Dual Media		GAC	Dual Media
10/26/2015	7.40	7.30	7.39	7.29	7.24	7.42
10/28/2015	7.40	7.36	7.39	7.36	7.23	7.32
10/30/2015	7.40	7.37	7.40	7.34	7.24	7.34
11/2/2015	7.40	7.38	7.40	7.33	7.29	7.33
11/4/2015	7.42	7.39	7.39	7.33	7.32	7.37
11/6/2015	7.29	7.28	7.32	7.44	7.31	7.40
11/9/2015	7.39	7.34	7.38	7.32	7.25	7.33

Table B.2 Average Dissolved Oxygen in BAF Influents and Effluents

Date	Without Ozonation			With Ozonation		
	Influent (mg/L)	Effluent (mg/L)		Influent (mg/L)	Effluent (mg/L)	
		GAC	Dual Media		GAC	Dual Media
9/29/2014	8.18	6.13	-	8.18	6.62	-
10/1/2014	5.17	3.35	-	5.17	3.65	-
10/3/2014	6.02	4.56	5.21	6.02	3.48	5.01
10/6/2014	5.72	2.77	5.06	5.72	3.15	4.91
10/8/2014	6.24	1.66	4.98	6.24	1.67	4.18
10/10/2014	5.66	4.02	4.48	5.66	3.49	4.91
10/13/2014	5.65	3.59	4.51	5.65	1.82	4.15
10/15/2014	5.38	2.62	4.91	5.38	2.70	4.51
10/17/2014	4.83	2.22	3.61	4.83	2.04	3.73
10/20/2014	4.90	3.03	3.08	4.90	2.41	2.99
10/22/2014	5.45	1.81	2.17	5.45	1.82	1.85
10/24/2014	5.27	1.94	1.58	5.27	1.44	1.72
10/27/2014	4.96	1.92	1.85	4.96	2.13	1.90
10/29/2014	4.80	1.96	2.57	4.80	2.07	2.44
10/31/2014	5.00	2.16	2.14	5.00	1.75	2.35
11/3/2014	5.15	2.57	2.87	5.15	2.05	3.43
11/5/2014	5.01	2.03	2.04	5.01	2.25	2.16
11/7/2014	5.04	1.74	1.80	5.04	1.92	1.59
11/10/2014	5.71	3.99	4.64	5.71	4.35	4.52
11/12/2014	5.57	3.83	4.82	5.57	3.66	4.42
11/14/2014	5.64	3.95	4.66	5.64	4.68	4.35
11/17/2014	5.87	4.38	4.66	5.87	4.49	4.87
11/19/2014	4.97	3.10	4.08	4.97	3.56	4.27
11/21/2014	5.45	3.64	4.48	5.45	3.99	4.26
11/24/2014	5.26	2.55	3.44	5.26	3.67	3.64
11/26/2014	5.38	3.30	4.30	5.38	3.56	4.48
11/28/2014	5.45	2.78	4.46	5.45	4.07	4.04
12/1/2014	5.33	3.85	4.82	5.33	4.34	4.80
12/3/2014	5.49	2.96	4.50	5.49	4.25	4.43
12/5/2014	5.59	4.46	4.69	5.59	4.45	5.00
12/8/2014	5.47	3.89	4.91	5.47	3.98	4.77
12/10/2014	5.28	3.89	4.63	5.28	4.36	4.64
12/12/2014	5.22	3.79	4.77	5.22	4.03	4.67
12/15/2014	5.31	3.50	4.21	5.31	3.57	4.28
12/17/2014	4.65	3.27	3.93	4.65	3.91	4.11
12/19/2014	5.08	3.98	4.26	5.08	4.00	4.31
12/22/2014	5.03	3.66	4.23	5.03	3.61	4.27
12/24/2014	4.93	3.15	4.15	4.93	3.83	4.32
12/26/2014	4.77	3.13	4.06	4.77	3.92	4.80
12/29/2014	4.90	3.55	4.20	4.90	4.02	4.69
12/31/2014	5.50	4.42	5.06	5.50	3.72	4.71
1/2/2015	5.95	4.31	4.93	5.95	4.42	4.95
1/5/2015	5.67	4.30	4.68	5.67	4.61	4.71
1/7/2015	5.79	4.50	4.74	5.79	4.60	5.17
1/9/2015	5.44	4.31	4.86	5.44	4.10	4.98
1/12/2015	5.23	3.58	4.24	5.23	4.16	4.60
1/14/2015	5.23	3.69	4.39	5.23	3.92	4.59
1/16/2015	5.19	4.12	4.68	5.19	4.08	4.42
1/19/2015	5.60	4.53	5.19	5.60	4.59	4.89
1/21/2015	5.07	4.05	4.54	5.07	4.21	4.35
1/23/2015	5.42	3.86	4.41	5.42	4.45	4.91
1/26/2015	5.77	4.44	5.05	5.77	4.59	5.04
1/28/2015	5.52	4.76	4.86	5.52	4.49	5.30
1/30/2015	5.65	4.56	5.08	5.65	4.71	5.09
2/2/2015	5.57	4.19	4.68	5.57	4.50	4.69

Table B.2 Average Dissolved Oxygen in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent (mg/L)	Effluent (mg/L)		Influent (mg/L)	Effluent (mg/L)	
		GAC	Dual Media		GAC	Dual Media
2/4/2015	5.58	4.86	5.42	5.58	4.89	5.29
2/6/2015	5.43	4.64	5.18	5.43	4.70	5.06
2/9/2015	5.38	4.71	4.91	5.38	4.44	4.89
2/11/2015	5.26	4.30	4.84	5.26	4.44	5.24
2/13/2015	5.15	4.31	5.10	5.15	4.24	4.03
2/16/2015	5.36	4.53	5.23	5.36	4.76	5.23
2/18/2015	5.05	3.77	4.70	5.05	4.23	4.53
2/20/2015	5.31	4.73	5.23	5.31	4.74	4.90
2/23/2015	5.08	4.46	4.96	5.08	4.19	4.84
2/25/2015	6.34	5.65	6.06	6.34	5.68	6.12
2/27/2015	6.41	5.83	6.09	6.41	5.85	6.14
3/2/2015	6.44	5.57	5.97	6.07	5.69	5.65
3/4/2015	6.52	5.33	5.93	6.04	5.35	5.80
3/6/2015	6.86	5.76	6.08	6.14	5.08	5.93
3/9/2015	6.73	5.74	5.98	6.81	5.70	6.59
4/6/2015	6.55	5.43	5.17	6.38	5.06	4.38
4/8/2015	7.17	5.89	6.77	7.35	6.01	6.24
4/10/2015	7.29	7.08	7.25	7.25	7.05	7.19
4/13/2015	6.53	6.00	5.96	6.60	5.82	6.27
4/15/2015	6.75	5.54	6.45	7.06	6.32	6.48
4/17/2015	6.23	5.73	5.78	6.47	5.78	5.89
4/20/2015	6.17	5.22	6.04	6.40	5.77	5.73
4/22/2015	6.23	5.71	5.76	5.79	4.86	5.34
4/24/2015	6.60	5.87	6.07	6.27	5.09	5.90
4/27/2015	6.74	6.19	6.24	6.55	5.62	6.39
4/29/2015	6.87	5.90	6.41	6.50	5.44	6.24
5/1/2015	6.17	5.42	5.94	6.39	5.07	6.23
5/4/2015	6.48	5.27	6.14	6.68	6.22	6.62
5/6/2015	6.49	5.14	6.20	6.46	5.54	6.22
5/8/2015	4.65	4.24	4.36	5.31	4.23	4.27
5/11/2015	5.41	4.84	4.79	5.07	4.49	4.63
5/13/2015	5.67	4.30	5.01	5.34	4.61	4.58
5/15/2015	5.90	4.89	5.44	5.18	4.62	4.85
5/18/2015	5.85	5.74	5.93	5.99	4.77	5.61
5/20/2015	5.60	4.67	5.14	5.54	4.97	5.37
5/22/2015	5.90	5.13	5.41	5.88	5.31	5.74
5/25/2015	5.84	4.38	5.54	5.18	4.34	4.98
5/27/2015	5.55	4.86	5.21	5.30	4.84	5.14
5/29/2015	4.47	3.98	4.18	4.38	3.91	3.71
6/1/2015	4.77	4.17	4.55	4.84	4.14	4.38
6/3/2015	5.24	4.73	4.91	5.63	4.64	4.57
6/5/2015	4.84	4.33	4.66	4.38	3.96	4.31
6/8/2015	5.51	4.49	4.80	4.99	4.26	4.70
6/10/2015	4.82	4.27	4.22	4.18	3.58	4.10
6/12/2015	4.73	3.66	4.13	4.37	3.41	4.15
6/15/2015	4.57	3.94	4.25	4.37	3.93	4.18
6/17/2015	5.09	4.17	4.60	4.45	3.77	4.31
6/19/2015	5.05	4.34	4.55	4.43	3.60	4.22
6/22/2015	5.33	4.90	4.93	4.36	4.02	4.25
6/24/2015	5.20	4.08	4.62	4.62	3.62	4.39
6/26/2015	4.97	4.07	4.37	4.53	3.78	4.24
6/29/2015	5.24	4.31	4.57	5.14	3.89	4.65
7/1/2015	5.08	4.34	4.60	4.99	4.08	4.59
7/3/2015	5.24	4.32	4.38	4.47	3.54	4.37
7/6/2015	5.19	4.29	4.67	4.78	3.85	4.36

Table B.2 Average Dissolved Oxygen in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent (mg/L)	Effluent (mg/L)		Influent (mg/L)	Effluent (mg/L)	
		GAC	Dual Media		GAC	Dual Media
7/8/2015	5.28	4.20	4.56	4.62	3.72	4.37
7/10/2015	5.28	4.21	4.57	4.65	3.68	4.46
7/13/2015	5.16	3.73	4.33	5.07	4.49	4.48
7/15/2015	5.22	4.04	4.63	5.09	4.52	4.64
7/17/2015	5.07	4.19	4.52	4.88	4.01	4.42
7/20/2015	5.23	4.40	4.48	4.65	3.70	4.53
7/22/2015	5.27	4.28	4.83	4.84	3.61	4.33
7/24/2015	5.56	4.42	5.16	5.09	3.93	4.55
7/27/2015	5.98	4.64	4.95	5.14	3.73	4.37
7/29/2015	5.73	4.88	5.20	5.54	4.59	4.97
7/31/2015	5.48	4.30	4.88	5.50	4.26	5.00
8/3/2015	5.67	4.38	4.92	5.54	4.27	5.10
8/5/2015	5.88	4.62	4.88	5.81	4.24	4.69
8/7/2015	5.62	5.01	5.32	5.66	4.83	5.12
8/10/2015	5.95	5.71	5.69	5.02	4.26	4.56
8/12/2015	5.86	5.38	5.52	5.29	4.26	4.73
8/14/2015	5.92	5.20	5.57	5.60	4.71	5.06
8/17/2015	5.69	4.55	5.15	5.69	4.50	5.06
8/21/2015	5.24	4.49	4.76	4.93	3.89	4.49
8/24/2015	5.83	5.07	5.40	5.51	4.73	5.48
8/26/2015	5.90	5.11	5.31	5.56	4.68	5.26
8/28/2015	5.92	5.18	5.47	5.81	4.91	5.32
8/31/2015	5.65	5.30	5.48	5.83	5.17	5.40
9/2/2015	5.83	5.05	5.36	5.64	4.77	5.23
9/4/2015	5.82	4.98	5.47	5.48	4.53	5.00
9/7/2015	5.83	5.15	5.52	5.50	4.70	5.50
9/9/2015	6.42	5.85	6.11	6.32	5.59	6.15
9/14/2015	6.34	5.86	6.15	6.39	6.01	6.09
9/16/2015	6.69	6.17	6.40	6.80	6.18	6.37
9/18/2015	6.59	6.21	6.44	6.66	6.31	6.32
9/21/2015	6.43	5.77	6.31	6.84	6.24	6.49
9/23/2015	6.79	6.22	6.56	6.19	5.77	6.04
9/25/2015	6.79	6.22	6.55	6.62	6.19	6.52
9/28/2015	6.41	6.09	5.81	6.66	5.76	6.33
9/30/2015	6.77	6.11	6.75	6.19	5.79	6.08
10/2/2015	6.74	6.20	6.71	6.46	6.40	6.29
10/7/2015	6.67	6.19	6.54	6.70	6.27	6.57
10/9/2015	6.84	6.38	6.50	6.37	6.08	6.20
10/12/2015	7.34	6.61	6.67	7.05	6.64	6.74
10/14/2015	6.77	6.18	6.55	6.89	6.24	6.39
10/16/2015	7.03	6.52	7.03	6.99	6.24	6.58
10/19/2015	6.40	5.86	6.09	6.30	5.63	5.70
10/21/2015	5.76	5.30	5.42	6.01	5.07	5.70
10/23/2015	5.84	5.54	5.12	5.37	5.04	5.26
10/26/2015	5.84	5.28	5.54	6.06	4.96	5.69
10/28/2015	5.89	5.29	5.65	5.71	5.19	5.30
10/30/2015	5.87	5.33	5.64	5.65	5.23	5.28
11/2/2015	5.89	5.51	5.75	5.87	5.28	5.55
11/4/2015	5.65	5.45	5.60	5.69	5.07	5.46
11/6/2015	5.85	5.75	5.58	5.96	5.60	5.90
11/9/2015	5.72	5.47	5.43	5.68	5.30	5.57

Table B.3 Average Turbidity in BAF Influents and Effluents

Date	Without Ozonation			With Ozonation		
	Influent (NTU)	Effluent (NTU)		Influent (NTU)	Effluent (NTU)	
		GAC	Dual Media		GAC	Dual Media
10/8/2014	0.15	0.10	0.06	0.15	0.08	0.05
10/10/2014	0.14	0.08	0.06	0.14	0.07	0.05
10/13/2014	0.21	0.10	0.08	0.21	0.11	0.09
10/15/2014	0.20	0.06	0.05	0.20	0.06	0.05
10/17/2014	0.16	0.07	0.06	0.16	0.07	0.06
10/20/2014	0.26	0.11	0.11	0.26	0.11	0.10
10/22/2014	0.14	0.08	0.08	0.14	0.06	0.07
10/24/2014	0.14	0.11	0.09	0.14	0.10	0.12
10/27/2014	0.22	0.14	0.10	0.22	0.13	0.09
10/29/2014	0.17	0.08	0.09	0.17	0.13	0.07
10/31/2014	0.13	0.06	0.08	0.13	0.09	0.07
11/3/2014	0.22	0.10	0.11	0.22	0.11	0.10
11/5/2014	0.11	0.06	0.07	0.11	0.06	0.07
11/7/2014	0.13	0.06	0.09	0.13	0.08	0.10
11/10/2014	0.13	0.06	0.05	0.13	0.06	0.06
11/12/2014	0.09	0.05	0.05	0.09	0.05	0.05
11/14/2014	0.09	0.05	0.04	0.09	0.05	0.05
11/17/2014	0.10	0.08	0.06	0.10	0.07	0.05
11/19/2014	0.12	0.07	0.05	0.12	0.06	0.05
11/21/2014	0.09	0.06	0.05	0.09	0.05	0.05
11/24/2014	0.19	0.09	0.09	0.19	0.10	0.08
11/26/2014	0.16	0.07	0.06	0.16	0.07	0.06
11/28/2014	0.13	0.06	0.05	0.13	0.05	0.05
12/1/2014	0.09	0.05	0.05	0.09	0.06	0.06
12/3/2014	0.09	0.06	0.05	0.09	0.05	0.05
12/5/2014	0.08	0.04	0.05	0.08	0.06	0.05
12/8/2014	0.11	0.05	0.05	0.11	0.05	0.05
12/10/2014	0.13	0.05	0.05	0.13	0.05	0.05
12/12/2014	0.10	0.06	0.05	0.10	0.05	0.05
12/15/2014	0.13	0.07	0.07	0.13	0.07	0.05
12/17/2014	0.13	0.07	0.06	0.13	0.07	0.06
12/19/2014	0.10	0.07	0.05	0.10	0.06	0.06
12/22/2014	0.13	0.06	0.05	0.13	0.07	0.07
12/24/2014	0.16	0.07	0.06	0.16	0.07	0.06
12/26/2014	0.09	0.08	0.06	0.09	0.06	0.06
12/29/2014	0.11	0.05	0.05	0.11	0.06	0.06
12/31/2014	0.10	0.05	0.06	0.10	0.05	0.05
1/2/2015	0.09	0.05	0.05	0.09	0.05	0.05
1/5/2015	0.12	0.05	0.06	0.12	0.06	0.06
1/7/2015	0.12	0.05	0.06	0.12	0.05	0.06
1/9/2015	0.12	0.06	0.06	0.12	0.05	0.05
1/12/2015	0.08	0.05	0.05	0.08	0.06	0.05
1/14/2015	0.09	0.06	0.06	0.09	0.06	0.06
1/16/2015	0.09	0.07	0.05	0.09	0.06	0.06
1/19/2015	0.10	0.05	0.06	0.10	0.05	0.06
1/21/2015	0.07	0.05	0.04	0.07	0.05	0.05
1/23/2015	0.09	0.05	0.04	0.09	0.05	0.04
1/26/2015	0.09	0.04	0.05	0.09	0.05	0.04
1/28/2015	0.09	0.04	0.04	0.09	0.04	0.05
1/30/2015	0.07	0.04	0.05	0.07	0.05	0.05
2/2/2015	0.12	0.06	0.06	0.12	0.07	0.07
2/4/2015	0.16	0.06	0.06	0.16	0.06	0.05
2/5/2015	0.10	0.05	0.05	0.10	0.06	0.06
2/9/2015	0.10	0.05	0.08	0.10	0.05	0.06
2/11/2015	0.09	0.06	0.07	0.09	0.05	0.05

Table B.3 Average Turbidity in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent (NTU)	Effluent (NTU)		Influent (NTU)	Effluent (NTU)	
		GAC	Dual Media		GAC	Dual Media
2/13/2015	0.09	0.06	0.06	0.09	0.06	0.06
2/16/2015	0.11	0.06	0.06	0.11	0.06	0.06
2/18/2015	0.12	0.08	0.07	0.12	0.06	0.06
2/20/2015	0.11	0.07	0.06	0.11	0.05	0.06
2/23/2015	0.09	0.06	0.06	0.09	0.05	0.05
2/25/2015	0.12	0.07	0.07	0.12	0.06	0.05
2/27/2015	0.10	0.05	0.06	0.10	0.05	0.05
3/2/2015	0.14	0.07	0.05	0.14	0.09	0.07
3/4/2015	0.16	0.07	0.06	0.10	0.06	0.05
3/6/2015	0.12	0.07	0.06	0.11	0.05	0.05
3/9/2015	0.17	0.10	0.07	0.15	0.04	0.05
4/6/2015	0.21	0.08	0.07	0.12	0.05	0.05
4/8/2015	0.14	0.09	0.07	0.13	0.06	0.05
4/10/2015	0.11	0.07	0.07	0.11	0.06	0.05
4/13/2015	0.13	0.08	0.07	0.16	0.05	0.05
4/15/2015	0.12	0.06	0.06	0.15	0.07	0.06
4/17/2015	0.16	0.09	0.07	0.13	0.06	0.06
4/20/2015	0.27	0.14	0.15	0.14	0.08	0.07
4/22/2015	0.16	0.09	0.09	0.10	0.08	0.07
4/24/2015	0.14	0.09	0.09	0.12	0.08	0.06
4/27/2015	0.19	0.08	0.08	0.14	0.08	0.06
4/29/2015	0.12	0.08	0.07	0.22	0.07	0.06
5/1/2015	0.14	0.08	0.07	0.10	0.06	0.06
5/4/2015	0.15	0.09	0.07	0.18	0.07	0.06
5/6/2015	0.16	0.09	0.08	0.17	0.05	0.05
5/8/2015	0.12	0.09	0.08	0.14	0.06	0.07
5/11/2015	0.17	0.08	0.08	0.13	0.06	0.05
5/13/2015	0.17	0.08	0.06	0.15	0.09	0.06
5/15/2015	0.12	0.08	0.07	0.17	0.07	0.05
5/18/2015	0.13	0.07	0.07	0.11	0.07	0.05
5/20/2015	0.13	0.07	0.06	0.10	0.06	0.05
5/22/2015	0.12	0.07	0.07	0.11	0.07	0.06
5/25/2015	0.18	0.10	0.10	0.10	0.09	0.07
5/27/2015	0.18	0.10	0.09	0.13	0.06	0.05
5/29/2015	0.16	0.10	0.10	0.12	0.06	0.05
6/1/2015	0.17	0.10	0.08	0.10	0.05	0.05
6/3/2015	0.13	0.09	0.06	0.09	0.06	0.05
6/5/2015	0.12	0.08	0.08	0.12	0.06	0.05
6/8/2015	0.15	0.10	0.07	0.10	0.05	0.05
6/10/2015	0.15	0.08	0.08	0.11	0.05	0.05
6/12/2015	0.13	0.10	0.07	0.11	0.05	0.05
6/15/2015	0.12	0.07	0.08	0.13	0.05	0.04
6/17/2015	0.18	0.09	0.07	0.12	0.06	0.05
6/19/2015	0.11	0.09	0.07	0.12	0.05	0.04
6/22/2015	0.16	0.09	0.09	0.09	0.05	0.05
6/24/2015	0.14	0.09	0.08	0.08	0.04	0.04
6/26/2015	0.18	0.10	0.08	0.12	0.05	0.04
6/29/2015	0.14	0.09	0.07	0.11	0.06	0.05
7/1/2015	0.14	0.09	0.08	0.11	0.06	0.05
7/3/2015	0.17	0.09	0.06	0.08	0.05	0.05
7/6/2015	0.14	0.09	0.08	0.11	0.07	0.06
7/8/2015	0.13	0.09	0.07	0.11	0.07	0.05
7/10/2015	0.14	0.09	0.08	0.11	0.06	0.05
7/13/2015	0.15	0.07	0.08	0.09	0.06	0.06
7/15/2015	0.14	0.08	0.09	0.10	0.06	0.05

Table B.3 Average Turbidity in BAF Influents and Effluents (Continued)

Date	Without Ozonation			With Ozonation		
	Influent (NTU)	Effluent (NTU)		Influent (NTU)	Effluent (NTU)	
		GAC	Dual Media		GAC	Dual Media
7/17/2015	0.14	0.10	0.08	0.11	0.06	0.05
7/20/2015	0.13	0.08	0.07	0.09	0.05	0.05
7/22/2015	0.14	0.09	0.08	0.10	0.06	0.05
7/24/2015	0.14	0.08	0.08	0.11	0.06	0.05
7/27/2015	0.15	0.07	0.08	0.11	0.05	0.06
7/29/2015	0.14	0.09	0.07	0.09	0.04	0.04
7/31/2015	0.14	0.08	0.07	0.09	0.06	0.05
8/3/2015	0.13	0.09	0.07	0.09	0.06	0.05
8/5/2015	0.13	0.08	0.07	0.08	0.06	0.04
8/7/2015	0.14	0.09	0.07	0.10	0.06	0.05
8/10/2015	0.13	0.09	0.07	0.09	0.06	0.05
8/12/2015	0.12	0.08	0.07	0.09	0.06	0.06
8/14/2015	0.14	0.09	0.08	0.09	0.06	0.06
8/17/2015	0.16	0.09	0.07	0.10	0.05	0.05
8/21/2015	0.15	0.09	0.08	0.08	0.05	0.04
8/24/2015	0.13	0.09	0.08	0.09	0.05	0.05
8/26/2015	0.15	0.09	0.07	0.09	0.05	0.04
8/28/2015	0.13	0.09	0.09	0.09	0.06	0.05
8/31/2015	0.11	0.09	0.07	0.10	0.07	0.05
9/2/2015	0.14	0.09	0.09	0.09	0.05	0.06
9/4/2015	0.11	0.09	0.09	0.09	0.06	0.04
9/7/2015	0.14	0.09	0.09	0.10	0.06	0.05
9/9/2015	0.13	0.09	0.08	0.11	0.07	0.06
9/14/2015	0.12	0.09	0.09	0.12	0.08	0.06
9/16/2015	0.12	0.08	0.08	0.10	0.09	0.06
9/18/2015	0.16	0.09	0.08	0.11	0.09	0.06
9/21/2015	0.08	0.08	0.06	0.07	0.06	0.05
9/23/2015	0.11	0.09	0.06	0.09	0.06	0.05
9/25/2015	0.10	0.09	0.06	0.10	0.06	0.05
9/28/2015	0.10	0.09	0.07	0.07	0.05	0.05
9/30/2015	0.10	0.10	0.07	0.11	0.08	0.05
10/2/2015	0.10	0.07	0.07	0.08	0.06	0.05
10/7/2015	0.08	0.06	0.05	0.07	0.05	0.04
10/9/2015	0.07	0.06	0.06	0.06	0.06	0.05
10/12/2015	0.07	0.05	0.04	0.05	0.05	0.04
10/14/2015	0.09	0.06	0.05	0.09	0.05	0.04
10/16/2015	0.08	0.08	0.06	0.08	0.05	0.04
10/19/2015	0.09	0.07	0.06	0.09	0.06	0.05
10/21/2015	0.08	0.06	0.06	0.08	0.06	0.06
10/23/2015	0.09	0.08	0.06	0.08	0.06	0.05
10/26/2015	0.12	0.08	0.08	0.13	0.08	0.06
10/28/2015	0.11	0.08	0.07	0.12	0.06	0.05
10/30/2015	0.12	0.09	0.08	0.12	0.06	0.07
11/2/2015	0.13	0.10	0.06	0.11	0.07	0.06
11/4/2015	0.15	0.10	0.07	0.11	0.07	0.05
11/6/2015	0.13	0.08	0.07	0.10	0.07	0.06
11/9/2015	0.09	0.10	0.06	0.11	0.06	0.05

Table B.4 Average Dissolved Organic Carbon in BAF Influents and Effluents

Date	Without Ozonation					With Ozonation				
	Influent (mg/L)	Effluent (mg/L)				Influent (mg/L)	Effluent (mg/L)			
		GAC 1	GAC 2	DM 1	DM 2		GAC 1	GAC 2	DM 1	DM 2
11/5/2014	2.31	1.98	1.79	2.37	2.04	2.47	2.17	2.09	2.25	2.40
11/19/2014	1.49	1.33	1.32	1.30	1.31	1.42	1.33	1.32	1.27	1.25
11/26/2014	1.82	1.55	1.52	1.46	1.50	1.64	1.59	1.57	1.48	1.46
12/3/2014	1.49	1.37	1.38	1.36	1.31	1.54	1.37	1.36	1.44	1.43
12/10/2014	1.83	1.41	1.43	1.35	1.37	1.60	1.39	1.41	1.35	1.35
12/17/2014	1.69	1.53	1.49	1.38	1.43	1.60	1.48	1.52	1.42	1.44
12/24/2014	1.59	1.54	1.54	1.42	1.48	1.58	1.49	1.52	1.42	1.43
12/31/2014	1.36	1.22	1.28	1.25	1.27	1.57	1.31	1.33	1.26	1.26
1/7/2015	1.44	1.31	1.34	1.30	1.30	1.42	1.31	1.36	1.25	1.41
1/14/2015	1.41	1.35	1.34	1.33	1.37	1.45	1.36	1.34	1.33	1.39
1/21/2015	1.41	1.27	1.27	1.35	1.33	1.43	1.27	1.29	1.35	1.31
1/28/2015	1.16	1.05	1.04	1.06	1.10	1.11	1.08	1.03	1.02	1.06
2/4/2015	1.48	1.33	1.33	1.37	1.32	1.46	1.33	1.36	1.30	1.33
2/11/2015	1.49	1.46	1.46	1.39	1.38	1.47	1.37	1.35	1.32	1.32
2/18/2015	1.60	1.56	1.61	1.50	1.35	1.51	1.36	1.36	1.36	1.33
2/25/2015	1.51	1.44	1.48	1.49	1.46	1.52	1.43	1.50	1.43	1.42
3/4/2015	1.57	1.52	1.53	1.57	1.51	1.63	1.50	1.51	1.43	1.46
4/1/2015	1.52	1.40	1.46	1.44	1.38	1.50	1.35	1.43	1.36	1.32
4/8/2015	1.52	1.48	1.45	1.44	1.42	1.29	1.19	1.22	1.21	1.20
4/15/2015	1.37	1.24	1.24	1.24	1.20	1.29	1.17	1.22	1.13	1.10
4/22/2015	1.48	1.41	1.43	1.40	1.29	1.25	1.20	1.21	1.19	1.21
4/29/2015	1.51	1.42	1.47	1.42	1.39	1.35	1.27	1.28	1.19	1.20
5/6/2015	1.55	1.40	1.43	1.42	1.35	1.38	1.28	1.27	1.22	1.21
5/13/2015	1.55	1.37	1.38	1.38	1.32	1.36	1.29	1.30	1.24	1.21
5/20/2015	1.47	1.45	1.40	1.43	1.29	1.52	1.37	1.36	1.33	1.30
5/27/2015	2.04	1.77	1.74	1.76	1.73	1.74	1.57	1.53	1.55	1.47
6/3/2015	1.78	1.55	1.62	1.59	1.67	1.55	1.44	1.43	1.45	1.37
6/10/2015	1.57	1.46	1.53	1.37	1.37	1.39	1.26	1.32	1.17	1.25
6/17/2015	1.91	1.76	1.80	1.79	1.71	1.50	1.50	1.46	1.43	1.43
6/24/2015	1.88	1.78	1.81	1.80	1.71	1.53	1.49	1.46	1.39	1.37
7/1/2015	1.70	1.65	1.63	1.58	1.56	1.53	1.42	1.42	1.39	1.37
7/8/2015	1.78	1.74	1.74	1.65	1.64	1.63	1.53	1.48	1.44	1.40
7/15/2015	1.85	1.80	1.76	1.69	1.66	1.57	1.56	1.53	1.50	1.50
7/22/2015	1.80	1.74	1.68	1.65	1.65	1.49	1.49	1.48	1.44	1.36
7/29/2015	2.06	1.86	1.90	1.77	1.83	1.63	1.53	1.59	1.50	1.45
8/5/2015	1.72	1.65	1.64	1.62	1.56	1.58	1.36	1.35	1.34	1.32
8/12/2015	1.79	1.75	1.76	1.71	1.71	1.54	1.48	1.49	1.43	1.41
8/26/2015	1.84	1.80	1.80	1.76	1.74	1.66	1.55	1.56	1.50	1.46
9/2/2015	1.89	1.77	1.76	1.82	1.70	1.64	1.51	1.50	1.44	1.47
9/9/2015	1.86	1.81	1.75	1.79	1.72	1.59	1.49	1.50	1.46	1.46
9/18/2015	1.66	1.61	1.64	1.58	1.53	1.55	1.41	1.43	1.35	1.32
9/30/2015	2.00	1.86	1.88	1.81	1.97	1.76	1.61	1.65	1.58	1.61
10/7/2015	1.72	1.60	1.58	1.55	1.58	1.44	1.41	1.38	1.39	1.39
10/14/2015	1.88	1.85	1.85	1.87	1.82	1.65	1.62	1.60	1.59	1.58
10/21/2015	1.94	1.91	1.87	1.86	1.84	1.65	1.61	1.62	1.59	1.58
10/28/2015	2.05	1.98	1.99	1.98	1.97	1.79	1.71	1.72	1.71	1.71
11/4/2015	2.03	1.98	1.95	1.87	1.98	1.70	1.62	1.63	1.57	1.68

DM – dual media.

Table B.5 Average UV_{254} Absorbance in BAF Influents and Effluents

Date	Without Ozonation					With Ozonation				
	Influent	Effluent				Influent	Effluent			
		GAC 1	GAC 2	DM 1	DM 2		GAC 1	GAC 2	DM 1	DM 2
9/29/2014	0.0413	0.0366	0.0368	-	-	0.0416	0.0365	0.0353	-	-
10/1/2014	0.0328	0.0286	0.0291	-	-	0.0310	0.0280	0.0278	-	-
10/3/2014	0.0154	0.0110	0.0111	0.0153	0.0144	0.0141	0.0110	0.0101	0.0144	0.0141
10/6/2014	0.0358	0.0284	0.0273	0.0349	0.0344	0.0378	0.0281	0.0279	0.0335	0.0362
10/8/2014	0.0327	0.0273	0.0238	0.0306	0.0292	0.0316	0.0239	0.0228	0.0277	0.0277
10/10/2014	0.0274	0.0231	0.0245	0.0263	0.0273	0.0288	0.0239	0.0240	0.0255	0.0251
10/13/2014	0.0377	0.0286	0.0290	0.0368	0.0363	0.0396	0.0267	0.0265	0.0347	0.0350
10/15/2014	0.0331	0.0266	0.0261	0.0326	0.0323	0.0340	0.0260	0.0234	0.0314	0.0302
10/17/2014	0.0312	0.0236	0.0256	0.0257	0.0266	0.0283	0.0194	0.0199	0.0256	0.0244
10/20/2014	0.0413	0.0324	0.0324	0.0378	0.0382	0.0414	0.0295	0.0310	0.0361	0.0352
10/22/2014	0.0330	0.0258	0.0269	0.0291	0.0327	0.0300	0.0225	0.0264	0.0282	0.0259
10/24/2014	0.0365	0.0292	0.0297	0.0339	0.0345	0.0377	0.0279	0.0277	0.0333	0.0411
10/27/2014	0.0360	0.0284	0.0279	0.0308	0.0303	0.0395	0.0286	0.0268	0.0311	0.0286
10/28/2014	0.0383	0.0196	0.0224	0.0289	0.0310	0.0374	0.0225	0.0271	0.0302	0.0299
10/31/2014	0.0164	0.0023	0.0019	0.0105	0.0113	0.0166	0.0038	0.0052	0.0104	0.0097
11/3/2014	0.0356	0.0306	0.0302	0.0338	0.0354	0.0399	0.0322	0.0313	0.0343	0.0379
11/5/2014	0.0337	0.0235	0.0249	0.0332	0.0330	0.0345	0.0242	0.0242	0.0308	0.0274
11/7/2014	0.0404	0.0265	0.0256	0.0383	0.0414	0.0411	0.0267	0.0242	0.0380	0.0346
11/10/2014	0.0265	0.0241	0.0246	0.0256	0.0252	0.0267	0.0242	0.0244	0.0249	0.0247
11/12/2014	0.0248	0.0238	0.0234	0.0241	0.0238	0.0264	0.0225	0.0224	0.0229	0.0229
11/14/2014	0.0304	0.0260	0.0267	0.0283	0.0277	0.0289	0.0253	0.0249	0.0271	0.0261
11/17/2014	0.0226	0.0204	0.0207	0.0219	0.0220	0.0226	0.0200	0.0193	0.0199	0.0194
11/19/2014	0.0276	0.0264	0.0265	0.0273	0.0271	0.0281	0.0244	0.0239	0.0247	0.0259
11/21/2014	0.0343	0.0305	0.0307	0.0322	0.0317	0.0326	0.0288	0.0289	0.0305	0.0301
11/24/2014	0.0324	0.0283	0.0269	0.0291	0.0285	0.0317	0.0276	0.0273	0.0282	0.0288
11/26/2014	0.0317	0.0280	0.0288	0.0294	0.0289	0.0315	0.0279	0.0269	0.0280	0.0276
11/28/2014	0.0302	0.0268	0.0272	0.0279	0.0275	0.0293	0.0263	0.0255	0.0267	0.0268
12/1/2014	0.0249	0.0223	0.0226	0.0229	0.0224	0.0238	0.0208	0.0208	0.0209	0.0213
12/3/2014	0.0258	0.0245	0.0246	0.0254	0.0250	0.0258	0.0234	0.0236	0.0239	0.0238
12/5/2014	0.0260	0.0238	0.0237	0.0245	0.0243	0.0261	0.0234	0.0217	0.0232	0.0230
12/8/2014	0.0264	0.0244	0.0238	0.0250	0.0252	0.0274	0.0229	0.0228	0.0233	0.0235
12/10/2014	0.0264	0.0254	0.0257	0.0257	0.0254	0.0264	0.0239	0.0234	0.0239	0.0238
12/12/2014	0.0246	0.0234	0.0227	0.0228	0.0222	0.0237	0.0215	0.0210	0.0214	0.0215
12/15/2014	0.0266	0.0243	0.0246	0.0236	0.0246	0.0261	0.0234	0.0231	0.0226	0.0232
12/17/2014	0.0262	0.0253	0.0251	0.0255	0.0249	0.0266	0.0245	0.0240	0.0230	0.0233
12/19/2014	0.0252	0.0238	0.0237	0.0235	0.0233	0.0250	0.0226	0.0221	0.0221	0.0220
12/22/2014	0.0288	0.0238	0.0240	0.0241	0.0237	0.0276	0.0226	0.0231	0.0229	0.0234
12/24/2014	0.0252	0.0232	0.0229	0.0234	0.0228	0.0250	0.0229	0.0226	0.0221	0.0218
12/26/2014	0.0238	0.0218	0.0215	0.0215	0.0220	0.0240	0.0215	0.0210	0.0223	0.0228
12/29/2014	0.0237	0.0216	0.0217	0.0215	0.0206	0.0198	0.0184	0.0176	0.0175	0.0172
12/31/2014	0.0235	0.0216	0.0205	0.0216	0.0214	0.0233	0.0206	0.0206	0.0204	0.0205
1/2/2015	0.0264	0.0242	0.0242	0.0242	0.0240	0.0258	0.0244	0.0230	0.0216	0.0226
1/5/2015	0.0237	0.0218	0.0220	0.0217	0.0216	0.0231	0.0208	0.0205	0.0206	0.0209
1/7/2015	0.0278	0.0258	0.0257	0.0255	0.0259	0.0260	0.0241	0.0231	0.0242	0.0244
1/9/2015	0.0221	0.0197	0.0197	0.0196	0.0201	0.0218	0.0183	0.0192	0.0185	0.0189
1/12/2015	0.0265	0.0257	0.0251	0.0252	0.0246	0.0263	0.0240	0.0236	0.0234	0.0243
1/14/2015	0.0250	0.0225	0.0219	0.0218	0.0230	0.0239	0.0219	0.0217	0.0213	0.0211
1/16/2015	0.0237	0.0217	0.0214	0.0203	0.0205	0.0221	0.0195	0.0212	0.0200	0.0205
1/19/2015	0.0231	0.0217	0.0214	0.0215	0.0215	0.0210	0.0198	0.0191	0.0201	0.0206
1/21/2015	0.0255	0.0244	0.0242	0.0246	0.0245	0.0259	0.0231	0.0226	0.0231	0.0237
1/23/2015	0.0260	0.0231	0.0232	0.0242	0.0232	0.0254	0.0226	0.0218	0.0229	0.0232
1/26/2015	0.0229	0.0216	0.0216	0.0209	0.0212	0.0219	0.0207	0.0202	0.0202	0.0199
1/28/2015	0.0175	0.0157	0.0157	0.0154	0.0160	0.0164	0.0155	0.0142	0.0139	0.0147
1/30/2015	0.0165	0.0147	0.0146	0.0147	0.0149	0.0168	0.0159	0.0149	0.0152	0.0154
2/2/2015	0.0216	0.0199	0.0194	0.0199	0.0197	0.0202	0.0189	0.0189	0.0188	0.0187

Table B.5 Average UV_{254} Absorbance in BAF Influents and Effluents (Continued)

Date	Without Ozonation					With Ozonation				
	Influent	Effluent				Influent	Effluent			
		GAC 1	GAC 2	DM 1	DM 2		GAC 1	GAC 2	DM 1	DM 2
2/4/2015	0.0283	0.0268	0.0262	0.0268	0.0270	0.0272	0.0246	0.0241	0.0249	0.0246
2/6/2015	0.0239	0.0223	0.0223	0.0224	0.0226	0.0230	0.0206	0.0202	0.0211	0.0212
2/9/2015	0.0219	0.0206	0.0204	0.0205	0.0204	0.0204	0.0188	0.0184	0.0188	0.0194
2/11/2015	0.0252	0.0240	0.0237	0.0242	0.0239	0.0246	0.0222	0.0222	0.0226	0.0225
2/13/2015	0.0245	0.0227	0.0224	0.0233	0.0226	0.0237	0.0212	0.0203	0.0217	0.0214
2/16/2015	0.0269	0.0244	0.0239	0.0248	0.0250	0.0252	0.0224	0.0219	0.0226	0.0229
2/18/2015	0.0274	0.0252	0.0254	0.0255	0.0249	0.0251	0.0225	0.0224	0.0233	0.0230
2/20/2015	0.0243	0.0221	0.0213	0.0219	0.0216	0.0234	0.0202	0.0205	0.0202	0.0208
2/23/2015	0.0257	0.0238	0.0240	0.0242	0.0238	0.0248	0.0227	0.0221	0.0222	0.0224
2/25/2015	0.0281	0.0258	0.0263	0.0265	0.0262	0.0319	0.0260	0.0253	0.0255	0.0258
2/27/2015	0.0252	0.0216	0.0223	0.0237	0.0234	0.0233	0.0212	0.0204	0.0212	0.0210
3/2/2015	0.0288	0.0264	0.0258	0.0272	0.0266	0.0274	0.0245	0.0243	0.0241	0.0243
3/4/2015	0.0290	0.0264	0.0267	0.0283	0.0277	0.0275	0.0249	0.0243	0.0247	0.0250
3/6/2015	0.0281	0.0254	0.0260	0.0272	0.0262	0.0258	0.0234	0.0225	0.0236	0.0234
3/9/2015	0.0273	0.0235	0.0249	0.0257	0.0243	0.0240	0.0211	0.0211	0.0214	0.0206
4/6/2015	0.0210	0.0169	0.0171	0.0170	0.0164	0.0172	0.0159	0.0157	0.0154	0.0152
4/8/2015	0.0263	0.0227	0.0228	0.0236	0.0230	0.0229	0.0192	0.0194	0.0190	0.0185
4/10/2015	0.0217	0.0207	0.0210	0.0209	0.0196	0.0197	0.0167	0.0166	0.0161	0.0164
4/13/2015	0.0245	0.0225	0.0221	0.0223	0.0211	0.0201	0.0182	0.0185	0.0179	0.0173
4/15/2015	0.0198	0.0183	0.0187	0.0185	0.0176	0.0192	0.0165	0.0167	0.0158	0.0158
4/17/2015	0.0208	0.0182	0.0185	0.0179	0.0175	0.0174	0.0153	0.0149	0.0142	0.0141
4/20/2015	0.0246	0.0208	0.0202	0.0206	0.0191	0.0185	0.0145	0.0142	0.0141	0.0138
4/22/2015	0.0256	0.0204	0.0211	0.0199	0.0196	0.0190	0.0155	0.0149	0.0146	0.0138
4/24/2015	0.0240	0.0220	0.0217	0.0215	0.0214	0.0196	0.0179	0.0183	0.0170	0.0174
4/27/2015	0.0280	0.0238	0.0233	0.0236	0.0229	0.0211	0.0189	0.0189	0.0183	0.0191
4/29/2015	0.0243	0.0228	0.0234	0.0236	0.0215	0.0202	0.0180	0.0179	0.0181	0.0169
5/1/2015	0.0270	0.0247	0.0250	0.0243	0.0239	0.0218	0.0202	0.0196	0.0190	0.0192
5/4/2015	0.0235	0.0192	0.0193	0.0194	0.0183	0.0206	0.0153	0.0157	0.0149	0.0153
5/6/2015	0.0239	0.0215	0.0216	0.0216	0.0208	0.0175	0.0151	0.0152	0.0149	0.0161
5/8/2015	0.0230	0.0206	0.0209	0.0210	0.0201	0.0196	0.0166	0.0163	0.0161	0.0157
5/11/2015	0.0239	0.0216	0.0211	0.0206	0.0206	0.0208	0.0182	0.0180	0.0186	0.0177
5/13/2015	0.0236	0.0210	0.0213	0.0217	0.0214	0.0217	0.0190	0.0190	0.0196	0.0190
5/15/2015	0.0232	0.0208	0.0211	0.0209	0.0216	0.0189	0.0172	0.0171	0.0167	0.0166
5/18/2015	0.0232	0.0199	0.0194	0.0202	0.0197	0.0199	0.0179	0.0183	0.0182	0.0181
5/20/2015	0.0235	0.0218	0.0218	0.0220	0.0208	0.0240	0.0211	0.0202	0.0212	0.0206
5/22/2015	0.0227	0.0208	0.0199	0.0200	0.0199	0.0187	0.0166	0.0163	0.0167	0.0169
5/25/2015	0.0306	0.0277	0.0272	0.0277	0.0272	0.0275	0.0246	0.0244	0.0243	0.0240
5/27/2015	0.0340	0.0290	0.0285	0.0314	0.0303	0.0273	0.0257	0.0245	0.0249	0.0246
5/29/2015	0.0317	0.0275	0.0275	0.0258	0.0264	0.0231	0.0202	0.0196	0.0196	0.0194
6/1/2015	0.0294	0.0256	0.0256	0.0262	0.0256	0.0201	0.0179	0.0172	0.0176	0.0174
6/3/2015	0.0290	0.0245	0.0285	0.0272	0.0268	0.0245	0.0225	0.0224	0.0233	0.0226
6/5/2015	0.0263	0.0232	0.0240	0.0237	0.0238	0.0234	0.0215	0.0212	0.0217	0.0216
6/8/2015	0.0234	0.0221	0.0220	0.0210	0.0205	0.0200	0.0190	0.0185	0.0178	0.0177
6/10/2015	0.0241	0.0222	0.0240	0.0217	0.0219	0.0201	0.0173	0.0179	0.0168	0.0161
6/12/2015	0.0277	0.0260	0.0260	0.0255	0.0250	0.0222	0.0199	0.0203	0.0194	0.0193
6/15/2015	0.0253	0.0231	0.0236	0.0227	0.0227	0.0204	0.0182	0.0182	0.0180	0.0177
6/17/2015	0.0319	0.0284	0.0286	0.0290	0.0280	0.0241	0.0215	0.0209	0.0205	0.0203
6/19/2015	0.0287	0.0270	0.0269	0.0265	0.0265	0.0215	0.0204	0.0199	0.0193	0.0195
6/22/2015	0.0285	0.0265	0.0277	0.0256	0.0260	0.0218	0.0205	0.0201	0.0192	0.0191
6/24/2015	0.0314	0.0285	0.0304	0.0281	0.0280	0.0214	0.0197	0.0195	0.0194	0.0190
6/26/2015	0.0343	0.0287	0.0288	0.0280	0.0278	0.0219	0.0200	0.0199	0.0196	0.0193
6/29/2015	0.0260	0.0243	0.0244	0.0242	0.0242	0.0209	0.0181	0.0176	0.0174	0.0177
7/1/2015	0.0277	0.0271	0.0263	0.0262	0.0263	0.0209	0.0195	0.0193	0.0192	0.0194
7/3/2015	0.0265	0.0246	0.0250	0.0242	0.0246	0.0191	0.0177	0.0177	0.0174	0.0171
7/6/2015	0.0256	0.0241	0.0244	0.0224	0.0231	0.0177	0.0166	0.0155	0.0150	0.0150

Table B.5 Average UV_{254} Absorbance in BAF Influents and Effluents (Continued)

Date	Without Ozonation					With Ozonation				
	Influent	Effluent				Influent	Effluent			
		GAC 1	GAC 2	DM 1	DM 2		GAC 1	GAC 2	DM 1	DM 2
7/8/2015	0.0278	0.0259	0.0276	0.0261	0.0259	0.0213	0.0204	0.0201	0.0200	0.0197
7/10/2015	0.0276	0.0260	0.0261	0.0254	0.0252	0.0215	0.0204	0.0206	0.0199	0.0193
7/13/2015	0.0254	0.0232	0.0232	0.0235	0.0237	0.0196	0.0186	0.0185	0.0186	0.0183
7/15/2015	0.0282	0.0277	0.0262	0.0257	0.0264	0.0212	0.0193	0.0192	0.0187	0.0188
7/17/2015	0.0278	0.0274	0.0270	0.0270	0.0271	0.0217	0.0210	0.0204	0.0208	0.0205
7/20/2015	0.0274	0.0256	0.0258	0.0253	0.0253	0.0207	0.0197	0.0187	0.0184	0.0183
7/22/2015	0.0262	0.0246	0.0244	0.0246	0.0248	0.0199	0.0188	0.0189	0.0183	0.0187
7/24/2015	0.0281	0.0275	0.0275	0.0273	0.0273	0.0218	0.0208	0.0207	0.0207	0.0205
7/27/2015	0.0257	0.0239	0.0238	0.0240	0.0247	0.0189	0.0178	0.0178	0.0176	0.0175
7/29/2015	0.0291	0.0281	0.0263	0.0261	0.0270	0.0209	0.0193	0.0192	0.0190	0.0180
7/31/2015	0.0261	0.0244	0.0244	0.0244	0.0240	0.0205	0.0191	0.0189	0.0185	0.0184
8/3/2015	0.0252	0.0246	0.0244	0.0247	0.0248	0.0181	0.0172	0.0168	0.0166	0.0169
8/5/2015	0.0254	0.0243	0.0232	0.0225	0.0235	0.0160	0.0148	0.0146	0.0146	0.0143
8/7/2015	0.0256	0.0240	0.0240	0.0235	0.0242	0.0193	0.0169	0.0170	0.0162	0.0165
8/10/2015	0.0263	0.0249	0.0247	0.0238	0.0252	0.0190	0.0178	0.0180	0.0171	0.0174
8/12/2015	0.0281	0.0275	0.0259	0.0265	0.0272	0.0195	0.0183	0.0180	0.0175	0.0173
8/14/2015	0.0286	0.0277	0.0278	0.0274	0.0273	0.0226	0.0211	0.0210	0.0210	0.0209
8/17/2015	0.0299	0.0285	0.0285	0.0284	0.0288	0.0229	0.0211	0.0211	0.0206	0.0209
8/21/2015	0.0296	0.0265	0.0266	0.0272	0.0258	0.0227	0.0207	0.0207	0.0204	0.0201
8/24/2015	0.0272	0.0248	0.0248	0.0237	0.0242	0.0200	0.0193	0.0184	0.0179	0.0179
8/26/2015	0.0295	0.0281	0.0289	0.0284	0.0288	0.0232	0.0223	0.0219	0.0219	0.0220
8/28/2015	0.0288	0.0278	0.0277	0.0281	0.0278	0.0220	0.0205	0.0207	0.0196	0.0197
8/31/2015	0.0283	0.0278	0.0274	0.0269	0.0278	0.0219	0.0209	0.0205	0.0201	0.0203
9/2/2015	0.0295	0.0274	0.0275	0.0275	0.0285	0.0238	0.0213	0.0209	0.0202	0.0205
9/4/2015	0.0286	0.0276	0.0274	0.0272	0.0270	0.0219	0.0208	0.0209	0.0205	0.0204
9/7/2015	0.0271	0.0259	0.0262	0.0261	0.0270	0.0221	0.0188	0.0186	0.0186	0.0188
9/9/2015	0.0278	0.0266	0.0266	0.0260	0.0261	0.0211	0.0196	0.0192	0.0194	0.0191
9/14/2015	0.0227	0.0217	0.0218	0.0212	0.0215	0.0168	0.0155	0.0155	0.0149	0.0150
9/16/2015	0.0246	0.0228	0.0233	0.0224	0.0226	0.0189	0.0176	0.0178	0.0169	0.0165
9/18/2015	0.0268	0.0264	0.0260	0.0249	0.0266	0.0234	0.0208	0.0205	0.0198	0.0195
9/21/2015	0.0291	0.0279	0.0279	0.0272	0.0276	0.0230	0.0215	0.0217	0.0211	0.0215
9/23/2015	0.0286	0.0277	0.0274	0.0270	0.0281	0.0232	0.0207	0.0196	0.0204	0.0202
9/25/2015	0.0297	0.0285	0.0288	0.0277	0.0283	0.0227	0.0218	0.0218	0.0217	0.0212
9/28/2015	0.0234	0.0228	0.0229	0.0218	0.0229	0.0182	0.0175	0.0175	0.0173	0.0168
9/30/2015	0.0312	0.0302	0.0296	0.0286	0.0297	0.0261	0.0243	0.0242	0.0236	0.0235
10/2/2015	0.0225	0.0213	0.0217	0.0209	0.0215	0.0177	0.0168	0.0164	0.0166	0.0163
10/5/2015	0.0212	0.0204	0.0202	0.0177	0.0184	0.0149	0.0146	0.0141	0.0121	0.0118
10/7/2015	0.0228	0.0220	0.0222	0.0210	0.0220	0.0168	0.0160	0.0165	0.0153	0.0155
10/9/2015	0.0214	0.0206	0.0209	0.0199	0.0203	0.0158	0.0154	0.0150	0.0145	0.0145
10/12/2015	0.0244	0.0237	0.0239	0.0233	0.0237	0.0181	0.0174	0.0177	0.0172	0.0169
10/14/2015	0.0268	0.0266	0.0262	0.0264	0.0264	0.0199	0.0195	0.0190	0.0195	0.0192
10/16/2015	0.0265	0.0263	0.0257	0.0254	0.0256	0.0190	0.0185	0.0185	0.0181	0.0177
10/21/2015	0.0314	0.0294	0.0291	0.0291	0.0301	0.0233	0.0223	0.0223	0.0216	0.0212
10/23/2015	0.0346	0.0335	0.0334	0.0329	0.0332	0.0287	0.0270	0.0272	0.0244	0.0241
10/26/2015	0.0340	0.0324	0.0318	0.0317	0.0319	0.0260	0.0250	0.0255	0.0244	0.0239
10/28/2015	0.0357	0.0345	0.0346	0.0340	0.0342	0.0266	0.0253	0.0254	0.0254	0.0250
10/30/2015	0.0338	0.0330	0.0320	0.0315	0.0317	0.0253	0.0244	0.0243	0.0240	0.0236
11/2/2015	0.0286	0.0280	0.0278	0.0276	0.0277	0.0200	0.0194	0.0195	0.0186	0.0186
11/4/2015	0.0271	0.0266	0.0256	0.0238	0.0264	0.0187	0.0185	0.0184	0.0174	0.0173
11/6/2015	0.0295	0.0289	0.0280	0.0266	0.0272	0.0213	0.0210	0.0213	0.0200	0.0201
11/9/2015	0.0344	0.0342	0.0342	0.0316	0.0324	0.0254	0.0240	0.0243	0.0234	0.0235

DM – dual media.

Table B.5 Average ATP Concentration in the Upper, Middle, and Lower Portions of the BAF Media

Date	Without Ozonation						With Ozonation					
	GAC (ng ATP/cm^3)			Dual Media (ng ATP/cm^3)			GAC (ng ATP/cm^3)			Dual Media (ng ATP/cm^3)		
	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower
10/12/2014	62	19	5	348	356	166	49	10	5	352	359	158
10/26/2014	73	30	43	399	396	195	73	35	17	365	366	144
11/9/2014	41	18	10	341	370	193	95	22	22	360	294	109
11/23/2014	150	101	66	519	365	218	191	101	66	481	417	107
12/7/2014	153	76	101	720	363	186	207	109	100	624	382	184
12/21/2014	277	149	122	658	491	205	281	92	95	610	373	142
1/4/2015	274	268	173	514	414	226	285	203	140	591	326	131
1/18/2015	240	189	230	682	422	144	282	183	160	557	295	137
2/1/2015	353	228	199	610	405	172	265	197	129	688	374	113
2/15/2015	349	270	242	683	573	121	381	245	186	702	368	133
3/1/2015	377	274	231	781	450	114	315	244	221	774	394	234
4/12/2015	352	323	284	829	476	174	355	273	235	787	438	120
4/26/2015	368	326	294	808	577	228	371	316	253	761	562	157
5/10/2015	349	307	276	811	465	198	367	267	219	765	588	164
5/24/2015	357	307	267	837	522	173	334	286	219	726	549	146
6/7/2015	356	305	282	857	559	211	366	316	261	713	527	189
6/21/2015	343	301	265	836	561	221	348	295	250	685	491	167
7/5/2015	345	285	271	780	532	229	376	300	262	755	495	186
7/19/2015	324	311	264	786	568	221	367	297	252	767	551	188
8/2/2015	337	289	266	843	542	188	352	293	280	778	532	171
8/16/2015	339	311	278	853	641	227	369	318	276	819	524	192
8/30/2015	332	300	261	758	540	232	360	291	269	760	519	200
9/27/2015	331	287	246	826	538	199	333	299	269	730	555	198
10/11/2015	347	309	274	893	587	201	340	285	235	774	496	165
10/25/2015	354	317	281	876	585	227	345	301	257	759	561	187
11/8/2015	353	321	297	844	595	240	340	294	256	709	481	176

APPENDIX C

BAF INFLUENT AND EFFLUENT PPCP CONCENTRATIONS

PPCP concentrations in BAF influents and effluents with different operational conditions are presented below

Table C.1 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 18 min (Run 1)

Classes	Compounds	Without Ozonation			With Ozonation (3 mg O_3/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	1,400	ND	ND	ND	ND	ND
	Ibuprofen	1,200	ND	270	700	ND	25
Antibiotics	Erythromycin	ND	ND	ND	ND	ND	ND
	Sulfamethoxazole	1,500	84	870	240	15	230
	Trimethoprim	320	ND	ND	ND	ND	ND
Antiepileptic	Carbamazepine	1,000	34	630	190	7	100
Beta-Blockers	Atenolol	540	ND	91	170	ND	65
Blood Lipid Regulators	Gemfibrozil	400	20	190	71	ND	21
Fire Retardant	TCEP	420	25	400	390	ND	280
Nicotine Metabolite	Cotinine	830	100	720	610	16	520
Pesticides	Aminotriazole	6,800	4,900	5,400	4,800	1,700	ND
	Atrazine	370	15	170	240	45	140
	DEET	1,100	94	1000	750	59	290
Psychomotor Stimulant	Caffeine	7,500	120	3,500	3000	160	2,800
Steroids	17β-Estradiol	200	ND	ND	17	ND	ND
X-ray Contrast Agent	Iopromide	780	270	640	560	160	500

ND – not detected.

Table C.2 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 18 min (Run 2)

Classes	Compounds	Without Ozonation			With Ozonation (3 mg O_3/L + 0.6 mg H_2O_2/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	930	ND	ND	ND	ND	ND
	Ibuprofen	1,200	47	170	310	100	200
Antibiotics	Erythromycin	1,200	100	1,600	10	130	270
	Sulfamethoxazole	3,000	640	2,200	460	120	670
	Trimethoprim	750	ND	19	100	ND	ND
Antiepileptic	Carbamazepine	1,100	72	990	160	33	360
Beta-Blockers	Atenolol	570	9.6	110	140	8.7	120
Blood Lipid Regulators	Gemfibrozil	530	66	250	100	33	120
Fire Retardant	TCEP	700	200	550	610	140	410
Nicotine Metabolite	Cotinine	1,800	360	1,700	1,400	210	820
Pesticides	Aminotriazole	1,700	ND	850	1,600	ND	580
	Atrazine	370	58	310	230	34	170
	DEET	1,300	240	830	400	120	460
Psychomotor Stimulant	Caffeine	7,200	310	5,000	2,300	170	2,600
Steroids	17β-Estradiol	160	ND	ND	6.5	ND	ND
X-ray Contrast Agent	Iopromide	1,000	510	760	480	310	470

ND – not detected.

Table C.3 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 18 min (Run 3)

Classes	Compounds	Without Ozonation			With Ozonation (4 mg O_3/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	1,400	ND	ND	ND	ND	ND
	Ibuprofen	990	ND	82	490	52	94
Antibiotics	Erythromycin	2,000	340	1,400	280	72	140
	Sulfamethoxazole	2,900	440	2,200	490	100	230
	Trimethoprim	970	ND	47	100	ND	ND
Antiepileptic	Carbamazepine	1,200	56	950	140	ND	70
Beta-Blockers	Atenolol	510	8.5	130	130	ND	40
Blood Lipid Regulators	Gemfibrozil	500	24	200	57	7.9	27
Fire Retardant	TCEP	840	200	490	630	200	460
Nicotine Metabolite	Cotinine	1,100	130	780	780	130	490
Pesticides	Aminotriazole	7,500	ND	9,600	ND	ND	1,400
	Atrazine	380	38	300	230	36	170
	DEET	1,300	140	990	680	140	540
Psychomotor Stimulant	Caffeine	7,400	ND	5,000	2,700	ND	1,900
Steroids	17β-Estradiol	170	ND	ND	18	ND	ND
X-ray Contrast Agent	Iopromide	750	240	620	500	230	360

ND – not detected.

Table C.4 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 18 min (Run 4)

Classes	Compounds	Without Ozonation			With Ozonation (4 mg O_3/L + 0.8 mg H_2O_2/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	1,200	ND	ND	ND	ND	ND
	Ibuprofen	1,300	110	430	810	170	160
Antibiotics	Erythromycin	58	550	430	16	140	160
	Sulfamethoxazole	3,200	550	1,500	530	160	250
	Trimethoprim	770	ND	210	190	ND	8
Antiepileptic	Carbamazepine	550	83	590	300	38	190
Beta-Blockers	Atenolol	240	14	150	120	5.4	41
Blood Lipid Regulators	Gemfibrozil	470	98	320	210	47	95
Fire Retardant	TCEP	780	300	730	750	230	420
Nicotine Metabolite	Cotinine	810	170	810	560	110	330
Pesticides	Aminotriazole	1,300	ND	1,100	1,400	ND	2,800
	Atrazine	280	61	240	240	53	170
	DEET	920	200	830	600	210	310
Psychomotor Stimulant	Caffeine	6,700	680	5,100	4,900	ND	3,100
Steroids	17β-Estradiol	270	ND	14	30	ND	ND
X-ray Contrast Agent	Iopromide	930	450	800	730	440	430

ND – not detected.

Table C.5 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 10 min (Run 5)

Classes	Compounds	Without Ozonation			With Ozonation (3 mg O_3/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	1,200	310	780	370	ND	ND
	Ibuprofen	1,400	190	250	860	100	ND
Antibiotics	Erythromycin	930	520	700	160	120	82
	Sulfamethoxazole	2,100	910	1,800	290	240	130
	Trimethoprim	700	ND	240	73	ND	ND
Antiepileptic	Carbamazepine	840	220	810	190	23	54
Beta-Blockers	Atenolol	300	35	150	140	18	42
Blood Lipid Regulators	Gemfibrozil	640	230	390	97	27	8.2
Fire Retardant	TCEP	480	250	530	380	170	250
Nicotine Metabolite	Cotinine	810	380	810	1,600	190	280
Pesticides	Aminotriazole	13,000	ND	8,200	7,200	ND	2,000
	Atrazine	280	110	250	230	79	100
	DEET	980	380	790	620	230	210
Psychomotor Stimulant	Caffeine	6,600	1,600	5,200	4,400	ND	870
Steroids	17β-Estradiol	300	ND	ND	ND	ND	ND
X-ray Contrast Agent	Iopromide	1,000	920	930	840	710	400

ND – not detected.

Table C.6 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 10 min (Run 6)

Classes	Compounds	Without Ozonation			With Ozonation (4 mg O_3/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	1,200	120	160	360	90	88
	Ibuprofen	1,900	81	160	550	94	38
Antibiotics	Erythromycin	5,200	1,700	1,900	700	230	670
	Sulfamethoxazole	2,200	260	440	270	100	150
	Trimethoprim	620	ND	210	64	ND	ND
Antiepileptic	Carbamazepine	900	220	690	120	ND	47
Beta-Blockers	Atenolol	220	78	170	78	34	30
Blood Lipid Regulators	Gemfibrozil	590	100	280	53	15	12
Fire Retardant	TCEP	540	430	590	510	260	270
Nicotine Metabolite	Cotinine	320	360	430	310	300	170
Pesticides	Aminotriazole	12,000	ND	ND	13,000	4,900	8,700
	Atrazine	350	100	280	280	85	160
	DEET	1,100	330	720	680	290	300
Psychomotor Stimulant	Caffeine	4,400	220	1,100	1,900	ND	140
Steroids	17β-Estradiol	200	ND	13	13	ND	ND
X-ray Contrast Agent	Iopromide	660	490	570	580	430	380

ND – not detected.

Table C.7 PPCP Concentrations in BAF Influents and Effleunts with EBCT of 10 min (Run 7)

Classes	Compounds	Without Ozonation			With Ozonation (4 mg O_3/L + 0.8 mg H_2O_2/L)		
		Influent (ng/L)	Effluent (ng/L)		Influent (ng/L)	Effluent (ng/L)	
			GAC	Dual Media		GAC	Dual Media
Analgesics	Acetaminophen	1,500	70	150	500	61	83
	Ibuprofen	900	130	91	820	260	160
Antibiotics	Erythromycin	880	320	280	41	65	71
	Sulfamethoxazole	2,400	920	1,300	520	200	290
	Trimethoprim	640	ND	ND	220	ND	ND
Antiepileptic	Carbamazepine	850	180	490	390	70	150
Beta-Blockers	Atenolol	340	120	270	130	72	220
Blood Lipid Regulators	Gemfibrozil	570	150	180	220	78	100
Fire Retardant	TCEP	450	140	220	560	240	180
Nicotine Metabolite	Cotinine	970	370	590	720	260	250
Pesticides	Aminotriazole	2,200	110	6,400	14,000	270	4,200
	Atrazine	380	130	200	210	57	42
	DEET	1,000	400	490	670	270	260
Psychomotor Stimulant	Caffeine	5,300	1,000	2,900	4,500	370	1,600
Steroids	17β-Estradiol	290	ND	ND	22	ND	ND
X-ray Contrast Agent	Iopromide	960	660	700	670	530	440

ND – not detected.

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