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TREATMENT OPTIONS FOR THE REMOVAL OF EMERGING POLLUTANTS OF CONCERN

By
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ABSTRACT

Biochemically active compounds (BACs), such as endocrine disrupting chemicals (EDCs), antimicrobial compounds, and other pharmaceutically active compounds, are ubiquitous in wastewater treatment plant effluents and in drinking water sources impacted by wastewater discharges. The presence of BACs in the aquatic environment is an issue of concern because EDCs can cause gender bending in fish. Also, antimicrobial compounds may lead to the evolution of antibiotic-resistant bacteria. While it is unclear whether human health effects can be expected at BAC concentrations that have been measured in drinking water, the public is concerned about the presence of such compounds in their drinking water.

The principal objective of this research was to assess, at the bench scale, the BAC removal effectiveness of drinking water treatment processes that are currently employed by member utilities of the North Carolina Urban Water Consortium (UWC). Studied treatment processes included: (1) ferric sulfate coagulation, (2) PAC adsorption plus alum coagulation, (3) potassium permanganate ($KMnO_4$) preoxidation, and (4) preozonation. For the evaluation of PAC adsorption and preozonation processes, experiments were conducted in two drinking water sources (Piedmont Reservoir water, Cape Fear River water) and one wastewater treatment plant effluent (WWTPE).

Results obtained with a 12-compound micropollutant mixture that was spiked into Piedmont Reservoir water at environmentally relevant concentrations (~250-600 ng/L) showed that ferric sulfate coagulation (70 mg/L ferric sulfate pentahydrate, pH 5.6) removed only one BAC (tetracycline). $KMnO_4$ preoxidation (3 mg/L dose, 48-hour contact time) effectively oxidized four BACs (acetaminophen, atenolol, carbamazepine, and tetracycline) and partially oxidized two (trimethoprim, erythromycin); the remaining six micropollutants (atrazine, bezafibrate, caffeine, DEET, sulfamethoxazole, and TCEP) were not measurably oxidized by $KMnO_4$. Addition of 20 mg/L PAC and 55 mg/L alum led to the removal of all 12 micropollutants, and removal percentages ranged from 66% for sulfamethoxazole to >95% for trimethoprim. Addition of 3.5 mg/L O_3 (O_3:TOC ratio ~0.7 mg O_3/mg TOC), effectively oxidized 11 of the 12 compounds in the micropollutant mixture, and oxidation percentages for the 11 compounds ranged from ~79% for atrazine to >90% for the remaining 10 compounds. Ozonation was not effective for controlling the flame retardant TCEP, however.

PAC particle size was one factor that was investigated to assess effects on BAC removal and treated water quality. Compared to as-received PAC (d_{50} = 17 µm), superfine PAC (S-PAC, d_{50} = 0.3 µm) yielded dramatically higher BAC removals, especially at short contact times. For example, to achieve 90% removal of the weakly adsorbing BACs sulfamethoxazole and ibuprofen, as-received PAC doses of 75 mg/L or greater were required in jar tests. In contrast, S-PAC doses of 15-25 mg/L were required to achieve the same treatment objective. Furthermore, TOC and UV_{254} removals by S-PAC were about 2-3 times those achieved with as-received PAC.

With respect to ozonation, an O_3 dose corresponding to 1 mg O_3/mg TOC is expected to yield ~99% transformation or greater for a wide range of BACs in all three of the tested waters. Results of model predictions and validation experiments suggest that reasonable ozone doses lead to meaningful levels of BAC oxidation in both drinking water sources and in highly treated wastewater.

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1. INTRODUCTION

The presence of biochemically active compounds (BACs) such as endocrine disrupting chemicals (EDCs), antimicrobial compounds, and other pharmaceutically active compounds (PhACs) in the aquatic environment is an issue of concern to the public and to water quality and treatment professionals. Many drugs that are administered to humans and animals are not fully metabolized. As a result, a substantial percentage of human and veterinary drugs are excreted, primarily via urine. Also, unused pharmaceuticals are often flushed down the toilet or poured down the drain. Many BACs are poorly removed during conventional wastewater treatment (Ternes, 1998, Nasu et al., 2001, Paxeus, 2004, Göbel et al., 2007), and WWTP discharges are therefore an important source through which BACs are introduced into the environment and into drinking water sources. Numerous BACs have been detected in surface and ground water (Lindsey et al., 2001, Kolpin et al., 2002, Heberer, 2002, Yang et al., 2004, Jones et al., 2005).

Although BACs are typically present at trace levels (ng/L range) in finished drinking water, the public is concerned about potential human health effects associated with chronic BAC exposure (Loos et al., 2007, Vieno et al., 2007, Benotti et al., 2009). While BAC concentrations in drinking water are well below the levels that would expose consumers to therapeutic doses, the effects of chronic exposure to trace concentrations of BACs are not well understood (Snyder et al., 2003, Jones et al., 2005). One study has shown that a mixture of EDCs and PhACs at nanogram per liter levels has the potential to induce adverse effects in human cell lines (Pomati, et al., 2006). To date, no drinking water standards or guidelines have been issued in the United States, but four estrogen compounds were recently added to the third Contaminant Candidate List (CCL3) of the USEPA. If risk assessors and epidemiologists are to link any adverse health outcomes with BAC exposure, a better understanding of their occurrence and removal in drinking water is critical.

Ecotoxicological effects of BACs have been demonstrated in a wide range of studies (Fry and Toone, 1981, Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001, Hayes et al., 2002). The presence of EDCs may cause intersexuality in fish (Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001) and demasculinize frogs (Hayes et al., 2002). Also, antimicrobial compounds may lead to the evolution of antibiotic-resistant bacteria (Baquero et al. 2008). A USGS study found that at least 80% of male smallmouth bass caught in Virginia and Maryland tributaries of the Potomac River grew eggs (Farenthold, 2006). In addition, 54% of male largemouth bass caught in the Potomac River near the Blue Plains wastewater treatment plant (WWTP) of Washington D.C. showed signs of feminization and 23% were intersex. While the specific cause of the feminization of male fish in the Potomac watershed has not yet been identified, other studies have linked incidents of intersexuality to the presence of EDCs that enter streams through WWTP discharges (Guillette et al., 1994, Folmar et al., 1996, Harries et al., 1996, Jobling et al., 1998, Jenkins et al., 2001, Hayes et al., 2002).

2. OBJECTIVES

The principal objective of this research was to assess, at the bench scale, the BAC removal effectiveness of drinking water treatment processes that are currently employed by member utilities of the North Carolina Urban Water Consortium (UWC). The following treatment processes were investigated: (1) powdered activated carbon (PAC) adsorption, (2) preozonation, (3) potassium permanganate preoxidation, and (4) coagulation with ferric sulfate.

The focus of the experimental work was on the two most effective treatment processes for BAC control, PAC adsorption and ozonation. For PAC adsorption and preozonation, experiments were conducted in two drinking water sources (Piedmont Reservoir water, Cape Fear River water) and one wastewater treatment plant effluent.

Specific objectives related to PAC adsorption were to evaluate the effects of the following factors on BAC removal:

1. PAC type (coal-based, wood-based, lignite-based);
2. PAC particle size (as-received and submicrometer-sized PAC, or S-PAC);
3. background water matrix;
4. solution/coagulation pH;
5. presence of metal hydroxide floc; and
6. timing of PAC addition relative to the addition of the coagulant (simultaneous addition of PAC and coagulant, PAC addition 5 minutes prior to coagulant, PAC addition 9 minutes into the flocculation process).

Specific objectives related to BAC oxidation by ozone included:

1. determine the ozone decay rate in each water
2. determine the ratio of hydroxyl radical to ozone concentration (R_c) in each water
3. from the ozone decay rate and R_c, predict the extent of BAC oxidation in each water at two ozone doses
4. validate BAC oxidation predictions for five BACs

3. BACKGROUND

The presence of pharmaceutically active compounds (PhACs) in surface and ground water has been a growing concern over the last decade. Several studies have illustrated that prescription and non-prescription drugs are present at detectable levels in surface and ground waters, in drinking water sources, and in treated drinking water (Halling-Sorensen et al., 1998, Lindsey et al., 2001, Heberer et al., 2002, Kolpin et al., 2002, Boyd et al., 2003, Yang et al., 2004). Due to advances in analytical techniques, it is feasible to measure trace compounds in the environment even at the low ng/L level. Pharmaceuticals that have been detected include antibiotics, analgesics, anti-inflammatory drugs, lipid regulators, beta-blockers, antiepileptic drugs, steroids, and hormones. In the United States, a study conducted by the US Geological survey detected antibiotics in about 22% of samples collected from 139 streams in 30 states (Kolpin et al. 2002). The most frequently detected antibiotics were triclosan (~ 60% of samples), trimethoprim (~ 27% of samples), lincomycin (~ 19% of samples), and sulfamethoxazole (~ 19% of samples). Concentrations of antibiotics in US surface waters are typically below 1 μg/L (Kolpin et al. 2002). Similar surveys have been done in the European Union (EU). Hirsch et al. (1999) detected erythromycin (max. 1.7 μg/L), roxithromicyn (max. 0.56 μg/L), and sulfamethoxazole (max. 0.48 μg/L) in many German surface water samples. Zuccato et al. (2006) detected at least 14 pharmaceuticals in the Po river in Italy, Lincomycin was the major pharmaceutical detected with a maximum concentration of 0.25 μg/L and a median concentration of 0.033 μg/L.

The presence of antimicrobial compounds in the environment is of concern because their presence can lead to the evolution of antimicrobial-resistant bacteria. Organisms can attain resistance by mutation or by acquisition of the genetic information that encodes the resistance (Kümmerer, 2004, Baquero et al., 2008). It is thought that diverse ecological niches are formed throughout the environment, in which the gene transfer mechanisms (conjugation, transduction and transformation) can occur. As a result, water sources could be considered as a potential pool of resistant genes and a medium for their propagation (Davison 1999, Jones et al. 2003, Schwartz et al. 2003). In addition, some studies have evaluated the effect of antibiotics on aquatic organisms; results of these studies suggest that higher concentrations than those present in the environment are required to produce any damaging effects (Snyder et al., 2005). It is important to note, however, that aquatic organisms are exposed to a diverse mixture of trace contaminants, and potential synergistic effects involving pharmaceuticals at sub-inhibitory concentrations are unknown (Flaherty and Dodson, 2005).

3.1. Sources and Pathways for BAC Entry into the Aquatic Environment

Depending on utilization and disposal patterns, BACs will enter the environment by different pathways. Pharmaceuticals are administrated in three ways: therapeutic (human and veterinary applications), prophylactic (as a preventive treatment – primarily in veterinary applications), and as growth promoters in livestock production (Willis, 2000). In 2001, the Union of Concerned Scientists estimated that 70 percent of the antibiotics produced in the US were utilized for non-therapeutic veterinary purposes (Mellon et al., 2001). The Federal Food, Drug, and Cosmetic Act establishes that if an antibiotic is used or becomes important in human medicine, the drug will be prohibited for non-therapeutic use in animals unless the FDA establishes there is no risk for human health. In contrast to the U.S., the EU banned the use of all antibiotics for livestock growth promotion in 2006 (Cogliani et al. 2011).

Figure 1 summarizes possible pathways for pharmaceutical occurrence in the environment (Heberer 2002). Medical substances used in human and veterinary applications are subject to different metabolic reactions and are released from the organism either unchanged or as metabolites via urine and feces. Most of the drugs used for veterinary purposes will be (1) directly discharged into water in aquaculture applications, (2) excreted directly on pastures or (3) spread onto agricultural land during land application of manure or sludge from lagoons containing animal waste. Antibiotics, that are disposed of on soils and in landfills can eventually contaminate groundwater (Jorgensen et al. 2000). BACs are also released into the environment through the effluents from municipal wastewater treatment plants. Several studies have shown that the biodegradability of certain BACs is low during wastewater treatment; e.g., antibiotics have been detected in wastewater treatment plant (WWTP) effluents at concentrations as high as 6 μg/L (Hirsch et al., 1999). Although there are no established regulatory limits on pharmaceuticals in WWTP effluents, the FDA requires environmental risk assessment for new pharmaceuticals with predicted environmental concentrations greater than 1 μg/L (Snyder et al., 2005).

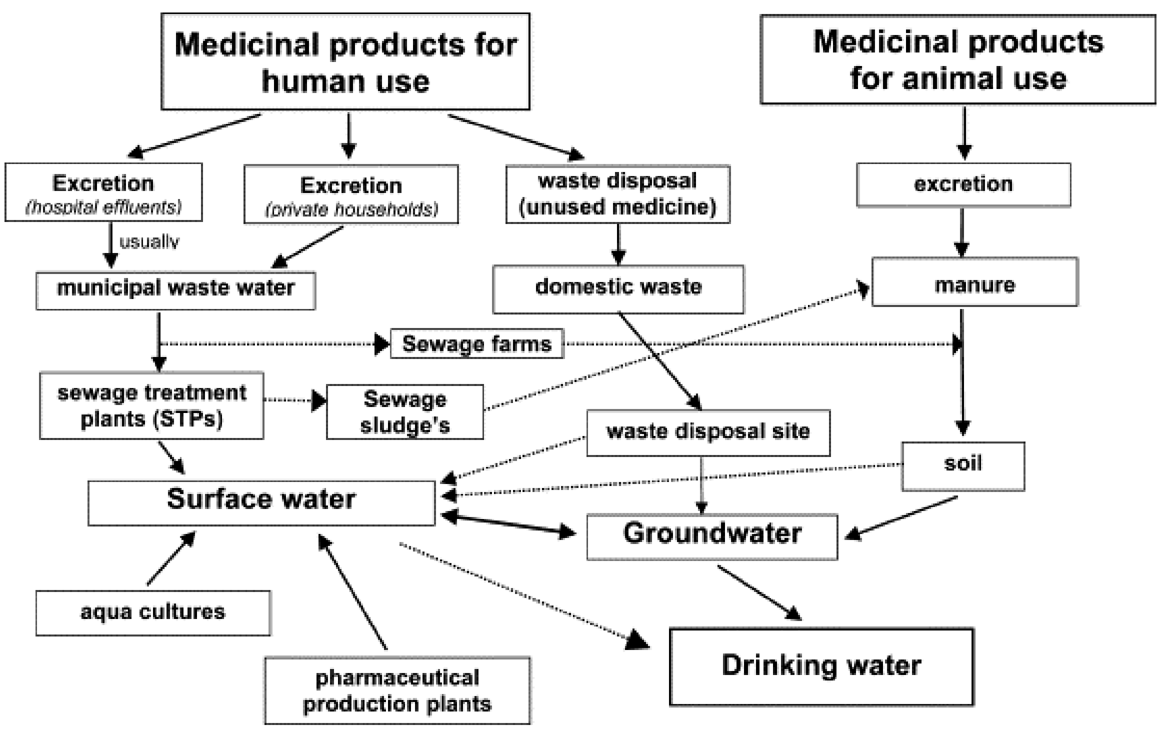


Figure 1. Possible sources and pathways for the entry of BACs into the aquatic environment (Heberer, 2002).

3.2. Physical-Chemical Treatment Processes for BAC Control

Conventional Surface Water Treatment. Conventional water treatment processes such as coagulation, sedimentation and filtration achieve minimal removal of BACs. Aluminum sulfate and ferric chloride coagulants or chemical lime softening removed less than 20% of most of the 60 micropollutants that were studied by Westerhoff et al. (2005). Removal of pharmaceuticals by coagulation and flocculation is dependent on the compound's propensity to sorb to particles. Consequently hydrophobic compounds with high octanol-water partition (log K_{ow}) coefficients can potentially be removed by coagulation/flocculation. However, many pharmaceuticals are polar and have a negligible tendency to sorb to particles. Westerhoff et al. (2005) found that the removal of sulfamethoxazole (antimicrobial, log K_{ow} = 0.89) by alum coagulation was statistically insignificant (less than 20 percent), but for pharmaceuticals with higher log K_{ow} values significant removal was observed, e.g. 33% removal was obtained for erythromycin-H_2O (antimicrobial metabolite, log K_{ow} = 3.06) during alum coagulation. Similar results were found for lime softening processes (Adams et al., 2002, Westerhoff et al., 2005).

Potassium Permanganate. The oxidation of BACs by potassium permanganate ($KMnO_4$) has been studied only to a limited extent. Hu et al. (2009, 2010) determined rate constants describing the removal of carbamazepine, ciprofloxacin, lincomycin, and trimethoprim. Among the studied BACs, $KMnO_4$ reacted most rapidly with carbamazepine and most slowly with ciprofloxacin. Hu et al. (2010) also reported that $KMnO_4$ did not react with sulfonamides, such as sulfamethoxazole and sulfamethizole. Under representative drinking water treatment conditions, a $KMnO_4$ dose of 2 mg/L oxidized 80-90% carbamazepine after 10 minutes, 10-55% lincomycin after 30 minutes, and <10% trimethoprim after 120 minutes. With a $KMnO_4$ dose of 6 mg/L, the extent of trimethoprim oxidation was <20% after 120 minutes. The results of Hu et al. (2010) suggest that $KMnO_4$ is not a suitable broad-spectrum treatment alternative for BACs. With respect to removal of biochemical activity, Hu et al. (2011) showed that $KMnO_4$ oxidation products of ciprofloxacin, lincomycin, and trimethoprim exhibited negligible antimicrobial activity.

Ozone. Prior studies have shown that ozone effectively oxidizes many BACs in both drinking water and wastewater treatment (e.g. Westerhoff et al. 2005, Huber et al. 2005). In many instances, ozone targets functional groups that are responsible for the biochemical activity of a compound. As a result, ozonation products of antibiotics tend to lose their antimicrobial activity (e.g. Dodd et al. 2009). Similarly, ozone effectively destroys the estrogenic activity of both natural and synthetic estrogens (e.g. Huber et al. 2004, Kamiya et al. 2005). An ozone dose of 0.5 mg/L was shown to oxidize more than 90% of some BACs (e.g., diclofenac and carbamazepine) while other BACs (e.g., clofibric acid and dieldrin) were poorly oxidized (<20%) even at an ozone dose of 3 mg/L (Westerhoff *et al*., 2005, Adams *et al*., 2002, Ternes *et al*., 2002).

During ozonation, BAC oxidation partly results from the direct oxidation by molecular ozone and partly from the oxidation by hydroxyl radicals that form as ozone reacts with constituents such as dissolved organic matter in the surface water matrix. Therefore, the contaminant oxidation rate can be described by the following expression:

$$\frac{d[C]}{dt} = k_{O_3}\left[C\right]\left[O_3\right] + k_{OH}\left[C\right]\left[{}^{\cdot}OH\right] \qquad \text{(eq. 1)}$$

where the terms in square brackets are the molar concentrations of the contaminant [C], ozone [O_3], and the hydroxyl radical [$^{\bullet}OH$], and k_{O3} and k_{OH} are the second order rate constants describing the oxidation of the contaminant by ozone and by the hydroxyl radical, respectively. Furthermore, Elovitz and von Gunten (1999) showed that in a given water matrix, the ratio of the hydroxyl radical and ozone concentrations ($R_c = [^{\bullet}OH]/[O_3]$) stays approximately constant. Therefore,

$$\frac{dC}{dt} = k_{O_3}[C][O_3] + k_{OH}[C][^{\cdot}OH] = k_{O_3}[C][O_3] + k_{OH}R_c[C][O_3] = \left(k_{O_3} + k_{OH}R_c\right)[C][O_3] \qquad \text{(eq. 2)}$$

or in integrated form:

$$\ln\left(\frac{C}{C_0}\right) = -\left(k_{O_3} + k_{OH}R_c\right)\left(\int [O_3]\,dt\right) \qquad \text{(eq. 3)}$$

where $\int [O_3]\,dt$ is the ozone exposure. Second order rate constants describing the oxidation of BACs by ozone and by hydroxyl radicals have been determined in several studies (e.g., Huber et al. 2003, 2005; Dodd et al. 2006; Ikehata et al. 2006; Suarez et al. 2007).

Powdered Activated Carbon. Among the wide range of BACs, some compounds showed higher adsorbability by PAC than others. Over a 4-hour contact time, addition of 5 mg/L of PAC removed >90% of testosterone and trimethoprim but removed only about 10% of sulfamethoxazole and ibuprofen (Westerhoff *et al*., 2005). The observed diversity in removal efficiencies is attributed to the diverse physicochemical properties of the BACs (Yu *et al*., 2009).

Although the adsorbability of many BACs has been measured, little is known about the factors that control the effectiveness of activated carbon adsorption processes. To date, few studies have evaluated BAC adsorption by PAC. Adams *et al.* (2002) found that background NOM in natural water adversely affected antibiotic adsorption by PAC, especially at lower PAC doses. Westerhoff *et al.* (2005) observed that log K_{ow} values of pharmaceuticals are reasonable indicators of the removal effectiveness that can be achieved by powdered activated carbon (PAC) adsorption processes. Furthermore, removal percentages of pharmaceuticals were independent of the initial contaminant concentration (Rossner et al., 2009). Additional information about BAC adsorption is needed. For example, since many BACs are ionizable, the solution pH affects their degree of ionization and hydrophobicity, and thus their adsorbability, but the effects of solution (or coagulation) pH on BAC adsorption has not been extensively studied.

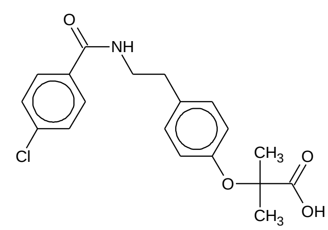
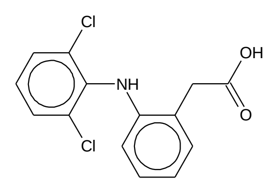
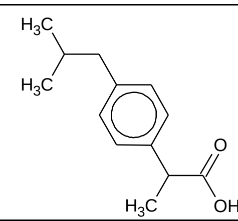
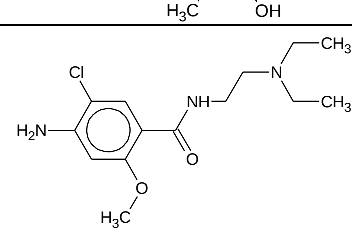
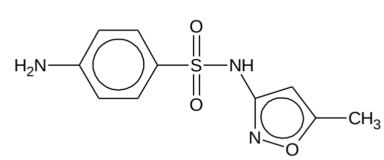
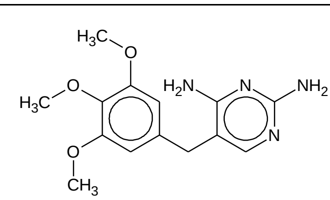
Recent studies found that sub-micrometer powdered activated carbon (S-PAC) greatly enhances the removal of NOM and micropollutants such as taste and odor compounds (Matsui et al., 2009). To date, no information about the effectiveness of S-PAC for BAC removal is available in the published literature. The work of Matsui et al. (2009) shows that the greater effectiveness of S-PAC for NOM removal is attributed to both a higher equilibrium adsorption capacity for NOM and faster adsorption kinetics. For micropollutants such as taste and odor compounds, S-PAC exhibits faster adsorption kinetics than a corresponding as-received PAC, but the equilibrium adsorption capacity is similar for both S-PAC and as-received PAC.

4. MATERIALS AND METHODS

4.1. Target Compounds

The six BACs that were selected for bench-scale treatability tests are shown in Table 1. The selected compounds are commonly found in effluent-impacted water bodies and are expected to span a range of adsorbabilities and ractivities towards ozone and potassium permanganate.

Table 1. BACs for bench-scale treatability studies at μg/L levels

Compound Name	Abbreviation	Compound Class	Molecular Structure
bezafibrate	BZF	lipid regulator	
diclofenac	DCF	non-steroidal anti-inflammatory	
ibuprofen	IBP	analgesic	
metoclopramide	MCP	antiemetic	
sulfamethoxazole	SMX	antibiotic	
trimethoprim	TMP	antibiotic	

Physical-chemical characteristics of the selected BACs, including the octanol-water partition coefficient of the neutral form (log K_{ow}) and the octanol-water partition coefficient at pH 7 (log D) are summarized for each BAC in Table 2. The pK_a values illustrate that BZF, DCF, IBP, and SMX are predominantly present in their anionic form at neutral pH. In contrast, the cationic form of MCP dominates at pH 7. For TMP, cationic and neutral forms coexist in almost equal proportions at neutral pH.

Table 2. Properties of selected pharmaceuticals

Compound	Molecular Weight (g/mol)	pK_a		log K_{ow}	log D (pH 7)*
		Acid [0/-]$^{\&}$	Base [+/0]$^{\&}$		
BZF	361.82	3.3*, 3.7**		2.5*	-0.93
DCF	296.15	4.2$^{+,*}$, 4.1**		4.5$^{+,*}$	1.77
IBP	206.28	4.9^{+}, 4.4*, 4.5**		4.0^{+}, 3.5*	0.94
MCP	299.8		9.3^{+}, 9.1*, 9.2**	2.6^{+}, 2.2*	-0.06
SMX	253.28	5.8*		0.9^{+}, 0.7*	-0.22
TMP	290.32		7.1^{+}, 7.0*	0.9^{+}, 0.6*	0.27

& [0/-] indicates compound transitions from neutral to anionic form, [+/0] indicates compound transitions from cationic to neutral form

* Predicted with Advanced Chemistry Development (ACD/Labs) Software v. 11.02 (as listed in SciFinder Scholar)

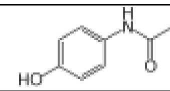
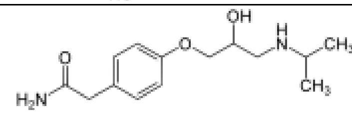
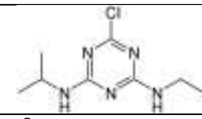
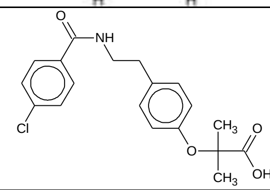
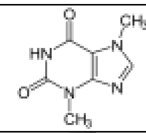
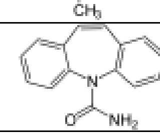
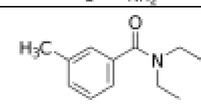
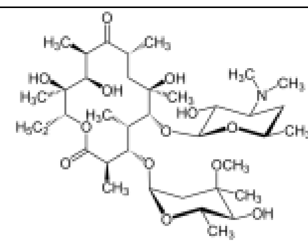
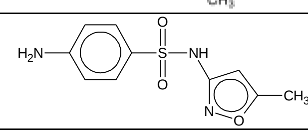
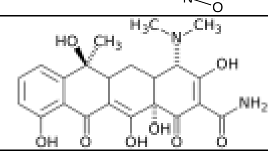
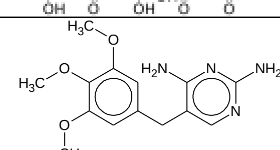
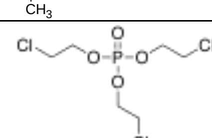
** Predicted by SPARC v. 4.6 (http://archemcalc.com/sparc)

+ Experimentally determined values as listed in EPI Suite v. 4.0 database

SMX, BZF, IBP, and DCF stock solutions were prepared daily in phosphate buffered ultrapure (DI) water (pH 7); TMP stock solutions were prepared in acidified DI water (pH 4) to enhance solubility; and MCP stock solutions were prepared in DI water. Stock solutions were prepared at concentrations of 2.0 mg/L, and stock solutions were filtered through a 0.22-µm PTFE membrane before use. The targeted initial pharmaceutical concentration was ~100 µg/L (<0.5 µM) for coagulation, adsorption, and ozone oxidation tests and ~50-70 µg/L for $KMnO_4$ oxidation tests. The selected concentrations are sufficiently low that the determined removal percentages are expected to match those obtained at concentrations more commonly encountered in the environment.

Additional experiments were conducted with a mixture of twelve micropollutants (Table 3) that were spiked into OWASA water at environmentally relevant concentrations (250-600 ng/L). Three of the twelve compounds in Table 3 match those tested at higher concentrations: bezafibrate, sulfamethoxazole, and trimethoprim. A stock solution of the twelve BACs was prepared in methanol (~20 mg/L of each micropollutant). Aqueous BAC solutions were prepared by (1) adding the required volume of BAC stock to a glass bottle, (2) evaporating the methanol, and (3) adding the desired volume of water to dissolve the BAC residue in the bottle. Methanol was evaporated to eliminate interferences with oxidation reactions. For example, methanol acts as a promoter of radical chain reactions during the decomposition of ozone in water (Staehelin and Hoigne 1985).

Table 3. BACs for bench-scale treatability studies at ng/L levels

Compound Name	Compound Class	Chemical Structure
acetaminophen = paracetamol	analgesic	
atenolol	beta blocker	
atrazine	herbicide	
bezafibrate	lipid regulator	
caffeine	stimulant	
carbamazepine	anticonvulsant	
DEET	insect repellent	
erythromycin-hydrate	antibiotic	
sulfamethoxazole	antibiotic	
tetracycline	antibiotic	
trimethoprim	antibiotic	
tris(2-chloroethyl)phosphate (TCEP)	flame retardant	

4.2. Water

Experiments were conducted in two North Carolina drinking water sources and one wastewater treatment plant effluent (WWTPE). The drinking water sources were raw OWASA water (either 100% Cane Creek Reservoir water or 50/50 University Lake/Cane Creek Reservoir blend, Carrboro, NC) and raw Cape Fear River water (Wilmington, NC). The WWTPE was collected at the North Cary Water Reclamation Facility (Cary, NC) after UV disinfection. Upon collection, water was stored in 55-gal stainless steel drums at 4°C. Water was filtered through 0.45-µm membranes prior to use unless specified otherwise. Dissolved organic carbon (DOC) concentrations, UV_{254} absorbance, specific ultraviolet absorption ($SUVA_{254}$), pH, alkalinity, and total hardness of the three waters used for PAC adsorption experiments are shown in Table 4. Water quality characteristics were similar for other phases of the research were similar.

Table 4. Water quality characteristics of tested waters

	DOC (mg/L)	**UV_{254} (cm^{-1})**	**$SUVA_{254}$ (L/mg-m)**	**pH**	**Alkalinity (mg/L as $CaCO_3$)**	**Hardness (mg/L as $CaCO_3$)**
OWASA	5.2	0.141	2.7	7.2	28.8	30.0
Cape Fear	6.6	0.269	4.1	7.4	18.8	24.5
Cary WWTPE	7.3	0.169	2.3	8.0	70.3	60.0

Additional PAC adsorption experiments were conducted with an activated sludge sample collected from the North Cary Water Reclamation Facility. The activated sludge sample had a pH of 7.5 and a mixed liquor suspended solids concentration of 2800 mg/L.

4.3. Powdered Activated Carbons (PACs)

Three as-received PACs prepared from different base materials and with different activation methods were studied (Table 5). Three PACs (NuChar, Hydrodarco B, and WPH) were used in their as-received form. In addition, a superfine version of the WPH PAC was prepared, which was termed S-WPH. The mean diameter of S-WPH was ~0.3 µm while those of the as-received PACs were in the range of 17-25 µm.

Table 5. PAC types

PAC Name	Manufacturer	Material	Activation Method
NuChar	MeadWestvaco	Wood	Chemical
Hydrodarco B	American Norit	Lignite Coal	Thermal
WPH	Calgon Carbon Corporation	Bituminous Coal	Thermal
S-WPH	Custom-made	Bituminous Coal	Thermal

4.4. Batch Tests to Determine BAC Adsorption Kinetics on PAC

Batch kinetic tests were performed with the four PACs shown in Table 5. BACs were spiked at an initial concentration of ~100 µg/L into the water of interest. Experiments were conducted in 32-oz. amber glass bottles, and solutions were mixed with a PTFE-coated magnetic stir bar.

Experiments were conducted without pH adjustment unless otherwise specified. After taking samples to determine the initial BAC concentrations, the desired amount of PAC was added and continuously mixed. Samples for BAC analysis were taken after PAC contact times of 2, 5, 10, 15, 30, 60 and 120 minutes. Additional samples were taken after a contact time of 2 weeks for experiments conducted with the waters in Table 4, and after 1, 2, and 8 days for experiments conducted with activated sludge. Solution pH was measured at the beginning and end of each kinetic test (Orion pH meter 420 A, Fisher Scientific, Pittsburgh, PA).

4.5. Batch Tests to Determine BAC Oxidation by Potassium Permanganate

A $KMnO_4$ stock solution (10 mM) was prepared by dissolving 16 mg $KMnO_4$ (reagent grade, Sigma Aldrich) in 10 mL DI water. The $KMnO_4$ stock was stored at 4°C. A quenching solution was prepared by diluting 10 mL of a 0.0375 N sodium thiosulfate solution to 500 mL with DI water. The thiosulfate solution was kept in brown bottles for up to one week.

Experiments were conducted in a 250-mL beaker that was placed on a magnetic stir plate, and reactor contents were mixed with a PTFE-coated magnetic stir bar. Initially, BAC dosing solution was spiked into 104.5 mL OWASA water such that the initial BAC concentration was between ~50-70 µg/L. Before adding $KMnO_4$, a 4.5-mL sample was drawn into a glass syringe to determine the initial pharmaceutical concentration. As was the case for all subsequent samples (see below), the syringe contained 0.5 mL of the thiosulfate quenching agent. The reaction was initiated by spiking 200 µL of $KMnO_4$ stock solution into the reactor, yielding an initial $KMnO_4$ concentration of 20 µM or 3.2 mg/L. Once the $KMnO_4$ was added, 4.5-mL samples were drawn into 5-mL glass syringes containing 0.5 mL of the thiosulfate quenching solution after the following reaction times: 30 seconds, 1, 5, 10, 15, and 30 minutes. The thiosulfate solution was used to stop the reaction between $KMnO_4$ and the pharmaceuticals by quenching the $KMnO_4$ residual. After 30 minutes, an additional 5-mL sample was taken with a syringe containing no thiosulfate. This sample was analyzed spectrophotometrically at 526 nm to determine the remaining $KMnO_4$ concentration. All samples were filtered through 0.22-µm PTFE filters prior to analysis.

An additional experiment was conducted to determine the $KMnO_4$ decay rate in OWASA water and to assess the time required to completely dissipate a KMnO4 dose of 3 mg/L. Based on the results of that experiment, an additional $KMnO_4$ oxidation experiment was conducted with the 12-compound BAC mixture (Table 3). In this experiment, raw OWASA water was spiked with the BAC mixture (methanol was evaporated as described above), and samples were taken prior to the addition of 3 mg/L $KMnO_4$ and 48 hours after $KMnO_4$ addition, a time when no measurable $KMnO_4$ residual remained.

4.6. Batch Tests to Determine Ozone Decay Rates and BAC Oxidation by Ozone

Ozone Stock Solution. Ozone was generated by passing oxygen through an ozone generator (Pacific Ozone). The product gas from the ozone generator was bubbled through DI water in a glass flask that was placed in an ice bath. Typical ozone stock solution concentrations were 25-32 mg/L. The ozone stock solution concentration was measured prior to dosing each reactor, and the volume of stock solution dosed into the reactor to obtain the desired initial concentration was adjusted accordingly. Ozone concentrations of the stock solution were measured with a spectrophotometer at a wavelength of 258 nm.

Ozone decay rate and oxidation rate of para-chlorobenzoic acid (p-CBA). Ozone decay rates were determined experimentally for each of the three waters at two ozone doses as shown in Table 6. The targeted ozone doses corresponded to ozone:TOC ratios of ~0.4 and 0.7 mg O_3/mg-C. In addition, oxidation rates of para-chlorobenzoic acid (p-CBA) were measured to determine R_c, the ratio of the hydroxyl radical to ozone concentration, in each water and at each ozone dose.

Table 6. Ozone doses for the determination of ozone and p-CBA decay rates

Water	Targeted Ozone Concentration (mg/L)
Cane Creek Reservoir	1.75
	3.5
Cape Fear River	2.5
	4.5
Cary WWTP Effluent	2.25
	4.4

Experiments were conducted in 20-mL amber glass EPA vials that were filled with the water of interest. Water in the reactors was spiked with p-CBA to obtain an initial p-CBA concentration of 1 µM, and reactors were continuously mixed with PTFE-coated magnetic stir bars. At predetermined times after the addition of ozone (5 sec, 10 sec, 20 sec, 30 sec, 1 min, 2 min, 4 min, 6 min, 8 min, 10 min, 20 min, and 30 min, or until the ozone concentration was non-detectable for two consecutive data points), ozone residuals in the reactors were quenched with 125 µL of 10 mM cinnamic acid. Cinnamic acid reacts quickly with the residual ozone to stoichiometrically form benzaldehyde (Dodd et al. 2006). For the t=0 samples, cinnamic acid was added to the vial prior to ozone dosing. Ozone residuals were determined from benzaldehyde concentrations (Dodd et al. 2006).

BAC Oxidation by Ozone. For each water and ozone concentration, the removal of five BACs was tested (all compounds in Table 1 except MCP). BACs were dosed without methanol carrier at a concentration of <0.5 µM. In parallel, a reactor containing no BACs but 125 µL of cinnamic acid was dosed with ozone to determine the initial ozone concentration. The reactors were mixed for a time that was sufficient for the ozone to completely dissipate, as determined from ozone decay rate experiments.

4.7. Jar tests

Jar tests were conducted to evaluate the following treatments:

1. Alum only at pH 5.8 and 6.2
2. Ferric sulfate only at pH 5.6
3. PAC only at pH 5.8 and 6.2
4. PAC addition prior to, simultaneously with, or after alum addition

Jar tests were conducted with a programmable jar testing apparatus (Phipps & Bird, Richmond, VA). Alum stock solutions were prepared daily by dissolving aluminum sulfate (technical grade, Fisher Scientific) into DI water. Pharmaceutical stock solutions were spiked into well mixed water to obtain initial pharmaceutical concentrations of ~100 µg/L. Initial concentration samples were taken after 20 minutes of mixing at 100 rpm. Acid or base was then added as needed for pH adjustment and mixing was paused. The OWASA jar testing protocol was used as follows: (1) rapid mix at 100 rpm for 30 seconds, (2) flocculate at 25 rpm for 36 minutes, and (3) settle for 3.5 minutes without mixing. Additional samples for turbidity analysis were also taken after 10 minutes of settling. The following water quality parameters were measured in the settled water: DOC, UV_{254}, turbidity, pH, and pharmaceutical concentrations.

4.8. Analytical methods

BAC Analysis. Concentrations of the six BACs, with which experiments were conducted at higher initial concentrations (Table 1), were determined by a high-performance liquid chromatography (HPLC, Breeze, Waters Corporation, Milford, MA) system equipped with a dual-wavelength UV detector. Pharmaceuticals were separated on a C18 column (2.6 µm, 4.6 × 100 mm, Kinetex C18 100A, Phenomenex, Torrance, CA). Prior to analysis by direct injection, samples were filtered through a 0.22-µm PTFE membrane. Concentrations in bench-scale tests were sufficiently high that samples could be analyzed by direct injection, i.e. without sample preconcentration. A gradient method was used for the analysis of SMX, TMP and MCP. Eluent A consisted of 50% v/v acetonitrile and 50% v/v 25 mM ammonium acetate buffer (pH 5) and eluent B of 10% v/v acetonitrile and 90% v/v 25 mM ammonium acetate buffer (pH 5). Each analysis started with 100% eluent B. From 1 to 9 minutes, the eluent was ramped linearly from 100% eluent B to 75% eluent B and 25% eluent A. Isocratic methods were used for BZF, DCF, and IBP. For BZF, the mobile phase was 25% v/v acetonitrile and 75% v/v 25 mM ammonium acetate buffer (pH 5). For DCF and IBP, the mobile phase was 37% v/v acetonitrile and 63% v/v 25 mM ammonium acetate buffer (pH 5). The mobile phase flow rate was 1 mL/min for all analyses. The detector wavelength was set at 266 nm for SMX, 238 nm for TMP, 274 nm for MCP, 240 nm for BZF, 282 nm for DCF, and 222 nm for IBP.

For ozone oxidation tests conducted at higher initial concentrations, the HPLC column and mobile phase composition were changed because benzaldehyde was an additional analyte. Pharmaceuticals were separated on a RP-Amide C16 column (5 µm, 3.0 × 250 mm, Supelco, Sigma-Aldrich, St. Louis, MO). Isocratic methods were used for five pharmaceuticals (TMP, SMX, IBP, BZF, and DCF), benzaldehyde, and pCBA. For benzaldehyde and pCBA, the mobile phase was 35% v/v acetonitrile and 65% v/v 5 mM phosphate buffer (pH 2.2). For BZF, IBP, and DCF the mobile phase was 50% v/v acetonitrile and 50% v/v 5 mM phosphate buffer (pH 2.2). For TMP, the mobile phase was 10% v/v acetonitrile and 90% v/v 5 mM phosphate buffer (pH 2.2). For SMX, the mobile phase was 25% v/v acetonitrile and 75% v/v 5 mM phosphate buffer (pH 2.2). The mobile phase flow rate was 0.43 mL/min for all analyses.

For experiments conducted at environmentally relevant concentrations, samples were analyzed by liquid chromatography/tandem mass spectrometry (LC-MS/MS) following a solid-phase extraction step.

Solid Phase Extraction (SPE). Extraction of the BAC analytes from pH-adjusted (pH 6) and 0.45 µm-filtered aqueous samples was achieved through the use of solid phase extraction (SPE) using a Supelco visiprep (Bellefonte, PA) extraction manifold. The Waters (Milford, MA) Oasis hydrophilic-lipophilic balance (HLB) 3 cc (60 mg) SPE cartridges were pre-conditioned with 6 mL methanol followed by 1 mL 0.1%formic acid in methanol and then 8 mL laboratory-grade water (LGW) (Ye, 2005). In order to quantify the concentration of the target analytes using the method of standard addition, raw water samples were split into eight 250-mL sample aliquots so as to present two unspiked samples (US) and six calibration samples (Cal) (Table 7).

Table 7. Concentration of Standard Addition Levels used for Quantification

BAC	Cal 1	Cal 2	Cal 3	Cal 4	Cal 5	Cal 6
	(ng/L)					
	Raw Water Calibration					
Acetaminophen	5.6	56.3	112.6	281.5	506.7	675.6
Atenolol	5.2	51.7	103.4	258.5	465.3	620.4
Atrazine	5.2	52.2	104.3	260.8	469.4	625.8
Bezafibrate	5.5	55.3	110.6	276.5	497.7	663.6
Caffeine	5.3	52.8	105.5	263.8	474.8	633.0
Carbamazepine	5.0	50.4	100.8	252.0	453.6	604.8
DEET	4.9	48.6	97.1	242.8	437.0	582.6
Erythromycin-H_2O	5.2	52.3	104.6	261.5	470.7	627.6
d3-Caffeine	4.8	48.5	96.9	242.3	436.1	581.4
Sulfamethoxazole	5.2	52.2	104.3	260.8	469.4	625.8
Tetracycline	5.2	52.0	104.0	260.0	468.0	624.0
Trimethoprim	5.0	50.0	100.0	250.0	450.0	600.0
TCEP	5.0	50.0	100.0	250.0	450.0	600.0

In order to chelate the metal ions in the samples and prevent them from binding to active sites on the solid phase cartridge, which would lower analyte retention and recovery, 1 mL of a Na_2EDTA stock solution was added to each sample aliqout. After connecting the sample aliquots contained in 250-mL amber glass bottles to the SPE cartridges through Teflon tubing, the samples were extracted at a flow rate of approximately 5 mL/min. After rinsing the sample aliquot bottles, lines, and cartridges with LGW just before the last part of the sample was pulled through the Teflon tubing, the cartridges were dried under vacuum (18 mm Hg) for five minutes to remove excess water. Sample elution was performed using 8mL of 0.1% formic acid in methanol by gravity in approximately 20 minutes, and sample extracts were collected in 10mL silanized clear glass conical vials. Samples were then concentrated under ultra high purity (UHP) nitrogen (National Welders, Morrisville, NC) using a Pierce (Rockford, IL) Reacti-Vap Model 18770 to a volume of approximately 50 µL on a VWR Scientifics Products (West Chester, PA) Standards Heatblock, at ~45°C for approximately two hours. Samples were then reconstituted to a target concentration of 250µL using 9/1 LGW/methanol and a glass syringe was used to add 10 µL of the 1.25 mg/L simeton internal standard solution. The internal standard, which was chosen because it is not found in the environment, accounts for variability between sample volume injection during instrumental analysis, and the area of each analyte is normalized to this standard. Sample extracts were then vortexed using a Thermolyne type 16700 mixer (Dubuque, IA), and then filtered through 0.45-µm Laboratory Supply Distributors (Millville, NJ) syringe tip filters into 250-µL glass inserts in liquid chromatography (LC) autosampler vials. Sample extracts were stored in the freezer up to a week until LC-MS/MS analysis.

LC-MS/MS Method. Analysis of sample extracts was completed using a Varian (Walnut Creek, CA) ProStar solvent delivery module (Model 210) which used a gradient binary mobile phase system comprised of 100% acetonitrile (B), and 0.1% formic acid in LGW (A). Table 8 shows the gradient program used for both positive electrospray ionization (+ESI) (Ye, 2005). Both mobile phases were filtered through 0.45-µm Whatman filters from Fisher Scientific (Pittsburgh, PA) before use. The mobile phases were pumped through a Metachem Technologies, Inc. Degassit Unit (Torrance, CA), in order to remove any dissolved gases. The flow rate of the mobile phase was 0.2 mL/min. A Varian ProStar autosampler (Model 430) (Walnut Creek, CA) injected 20µL onto a Varian C18 guard column (3cm x 2mm, 3µm) (Walnut Creek, CA) and a Varian (Torrance, CA) Pursuit C-18 analytical column (15 cm x 2 mm, 3 µm) was used interfaced to a Varian (Walnut Creek, CA) 1200L triple quandrupole mass spectrometer. Varian MSWS Software Version 6.8 was used for data analysis. Liquid nitrogen (99.99%) was used as the drying gas, UHP argon the collision gas (CID) in positive ionization mode (+ESI). Table 9 shows the mass spectrometer parameters used in the analytical methods (Ye, 2005).

Table 8. Mobile Phase Gradient used for LC-(+/-)-ESI-MS/MS (flow rate=0.2mL/min)

Time (min)	%A (0.1% Formic Acid in LGW)	%B (100% Acetonitrile)
0	90	10
2	90	10
25	10	90
27	10	90
28	0	100
38	0	100
47	90	10
55	90	10

Table 9. Source Dependent Mass Spectrometer Parameters

Parameter	+ESI
CID gas Pressure (mTorr)	1.5
Detector (V)	1320
Drying gas Temperature (°C)	300
Spray Chamber Housing (°C)	50
Spray Shield (V)	600
Nebulizing gas Pressure (psi)	55
Drying gas Pressure (psi)	18
Needle (V)	5000

Mass spectrometry acquisition data for target analytes used in the analysis are shown in Tables 10 and 11. The ion transitions and collision energies shown in Tables 10 and 11 were determined by infusing individual 1 mg/L standards of each target BAC in 9/1 LGW/MeOH in the Varian 1200L MS (Palo Alto, CA) using a Harvard Apparatus syringe pump (Holliston, MA). The molecular ion of the BAC was targeted in Q2 and as the collision gas increased from 0-50V the characteristic breakdown ions were determined. The target analytes were broken up into several groups of compounds that were analyzed in separate sample injections in order to maximize sensitivity and increase analyte resolution. Although the same chromatography is used the MS is programmed using instrument software to target different ion transitions in each method. To this end, target analytes will not co-elute or lose sensitivity due to increasing the target analyte transitions. As a result, in order to analyze all BACs a total of three injections for each sample extract were made. It can be seen in these tables that the presence of both a major and minor ion were used in the quantification and confirmation of an analyte, respectively. These major and minor ions are characteristic fragments (or daughter ions) of the parent compound under the utilized analytical conditions and confirmation is achieved by calculating the ratio of the daughter ions in a sample. Table 12 summarizes the acquisition data for the internal standard. Optimized parameters for each compound were obtained through analysis of individual standards by directly infusing the standards into the mass spectrometer using a Harvard Apparatus syringe pump (Holliston, MA) and optimizing instrumental conditions.

Before the analysis of extracted drinking water samples several quality control measures were taken. Several injections of the solvent, 9/1 LGW/methanol, were analyzed to ensure that the solvent and instrument were free of contamination. In addition, the sensitivity of the instrument was verified using a BAC mixture standard and caffeine. Finally, the method for each group was run with the BAC mixture at 50 µg/L before sample analysis in order to evaluate retention times and analytical sensitivity.

Percent recovery of the target BAC analytes in the samples was evaluated throughout the extraction procedure by determining the instrument response of a surrogate standard. That is, the area of the surrogate standard was determined in each sample to determine the variability between sample extracts.

Table 10. Optimized Acquisition Data for Group 1 (+ESI) Compounds

BAC	Retention Time major (minor)	Parent Ion	Major Ion (Collision Energy)	Minor Ion (Collision Energy)
	minutes	*m/z*	*m/z* (volts)	*m/z* (volts)
Acetaminophen	5.3 (N/A)	151.9	110.0 (11.5)	N/A
Caffeine-d^3 (Surrogate)	7.9 (8.0)	198.1	140.8 (12)	112.8 (16.5)
Tetracycline	10.5 (10.95)	445.3	427.0.3 (8)	410.0 (16)
TCEP	18.2 (18.27)	285.0	160.8 (7.5)	222.8 (6.0)
Erythromycin-H_2O	17.3 (17.42)	734.6	158.0 (19)	82.9 (27)

Table 11. Optimized Acquisition Data for Group 2 (+ESI) Compounds

BAC	Retention Time major (minor)	Parent Ion	Major Ion (Collision Energy)	Minor Ion (Collision Energy)
	minutes	*m/z*	*m/z* (volts)	*m/z* (volts)
Atenolol	4.3 (4.2)	267.2	144.9 (17)	189.9 (10.5)
Trimethoprim	9.2 (9.2)	291	229.9 (20.5)	122.9 (20.5)
Sulfamethoxazole	13.6 (13.6)	253.9	155.9 (14)	107.9 (18.5)
Atrazine	18.3(18.7)	216	173.9 (10.5)	95.8 (21)
Carbamazepine	16.6 (16.6)	237	193.9 (12)	192.0 (18.5)
DEET	16.6 (18.6)	192.2	118.9 (14)	90.8 (26)
Bezafibrate	20.8 (20.8)	362.2	138.9 (17)	120.9 (19.5)

Table 12. Optimized Acquisition Data for Internal Standard

Standard	Retention Time major (minor)	Parent Ion	Major Ion (Collision Energy)	Minor Ion (Collision Energy)
	minutes	*m/z*	*m/z* (volts)	*m/z* (volts)
Simeton (Internal)	9.8 (N/A)	198.0	123.9 (16)	Not observed

Turbidity. Turbidity was measured using a turbidity meter (2100P Turbidimeter, HACH) that was calibrated and checked with primary and secondary turbidity standards (HACH, Loveland, CO).

Total and Dissolved Organic Carbon. TOC and DOC were measured with a total organic carbon analyzer (Model TOC-5000A, Shimadzu Scientific, Columbia, MD). UV_{254} absorbance was measured with a UV/vis spectrophotometer.

Solution pH. Solution pH was measured with a calibrated pH meter (Orion pH meter 420 A, Fisher Scientific, Pittsburgh, PA).

Ozone Stock Solution Concentration. Ozone concentrations in ozone stock solutions were measured directly by spectrophotometry. A 1-mL sample of stock solution was brought to below pH 2 with 2.9 mL of phosphoric acid and the absorbance was measured at 258 nm. The molar absorptivity of ozone is 2900 M^{-1} cm^{-1} (Bader and Hoigne 1981).

5. RESULTS AND DISCUSSION

5.1. Coagulation / Flocculation / Sedimentation

Table 13 summarizes results of jar tests, in which the removal of SMX and TMP by alum coagulation was evaluated. SMX and TMP removal by alum coagulation was minimal (<5%) at both pH 5.8 and 6.2, as expected (e.g., Westerhoff et al. 2005). Coagulation pH did not have a measurable effect on SMX and TMP removal, but it did affect natural organic matter removal. As shown in Table 13, NOM removal, as measured by DOC and UV_{254} absorbance, was higher at pH 5.8 than at pH 6.2.

Table 13. Pharmaceutical, DOC, and UV_{254} removal by coagulation/flocculation/ sedimentation. Water: OWASA. Coagulant: Alum. Coagulant dose: 55 mg/L.

Parameter	Removal (%)	
	pH 5.8	pH 6.2
SMX	3.1	2.8
TMP	3.0	3.6
DOC	50.6	47.7
UV_{254} absorbance	64.2	59.1

Additional jar tests were conducted to determine the effectiveness of ferric sulfate coagulation for (1) removing SMX and TMP (dosed at ~100 µg/L each) and (2) removing constituents in the 12-compound micropollutant mix (dosed at concentrations of 250-600 ng/L each). Jar tests conducted to assess SMX and TMP removal at pH 5.4 and 5.8 illustrate that ferric sulfate coagulation was not effective for SMX and TMP removal at either coagulation pH (Table 14). The tested coagulant dose was 70 mg/L ferric sulfate pentahydrate. However, higher NOM removal percentages were obtained with ferric sulfate than with alum, especially at pH 5.4. On a molar basis, 0.18 mM Al and 0.29 mM Fe were added in the jar tests. Thus, the higher NOM removals obtained with ferric sulfate were at least partly a result of the higher metal ion dose.

Table 14. Pharmaceutical, DOC, and UV_{254} removal by coagulation/flocculation/ sedimentation. Water: OWASA. Coagulant: Ferric sulfate pentahydrate. Coagulant dose: 70 mg/L.

Parameter	Removal (%)	
	pH 5.4	pH 5.8
SMX	3.6	3.5
TMP	3.4	2.7
DOC	62.9	56.2
UV_{254} absorbance	71.9	66.2

An additional jar test was conducted to evaluate ferric sulfate coagulation for the removal of micropollutants at ng/L levels. In this test, OWASA water was spiked with 12 micropollutants (Table 3) at concentrations of 250-600 ng/L. The resulting solution was coagulated with 70 mg/L ferric sulfate pentahydrate at pH 5.6. Of the 12 compounds that were spiked, measurable removal was only obtained for tetracycline (74% removal). Observing tetracycline removal by coagulation is consistent with the results of Choi et al. (2008), who showed that tetracycline is amenable to removal by polyaluminum chloride (PACl) coagulation. At pH 5.6, tetracycline is present in zwitterionic form, and Choi et al. (2008) suggested that coagulant species can neutralize zwitterion charges such that products can be removed by subsequent solid-liquid separation processes.

5.2. PAC Adsorption Kinetics

Batch kinetic tests were conducted to determine the rate of BAC adsorption by PAC. Goals of the batch kinetic tests were to (1) compare the adsorbability of the six pharmaceuticals selected for this project (Table 1), (2) determine the effect of pH on the adsorbability of pharmaceuticals, (3) compare the effectiveness of three commonly used PACs (Table 5) and one superfine PAC, and (4) determine the effect of the background water matrix on pharmaceutical removal.

Adsorbability of pharmaceuticals. To compare the adsorbability of the six BACs in Table 1, batch kinetic data were obtained with NuChar PAC that was added to OWASA water (after filtration through a 0.45-µm membrane). Results for the six BACs are compared in Figures 2 and 3 for PAC doses of 10 and 20 mg/L, respectively. The data in Figures 2 and 3 illustrate that MCP and TMP were the most adsorbable among the tested BACs; BZF and DCF were in the moderately adsorbable range; and IBP and SMX were the least adsorbable among the tested BACs. Based on the results shown in Figures 2 and 3, subsequent adsorption experiments focused primarily on TMP and SMX, which bracket the adsorbabilities of the selected pharmaceuticals.

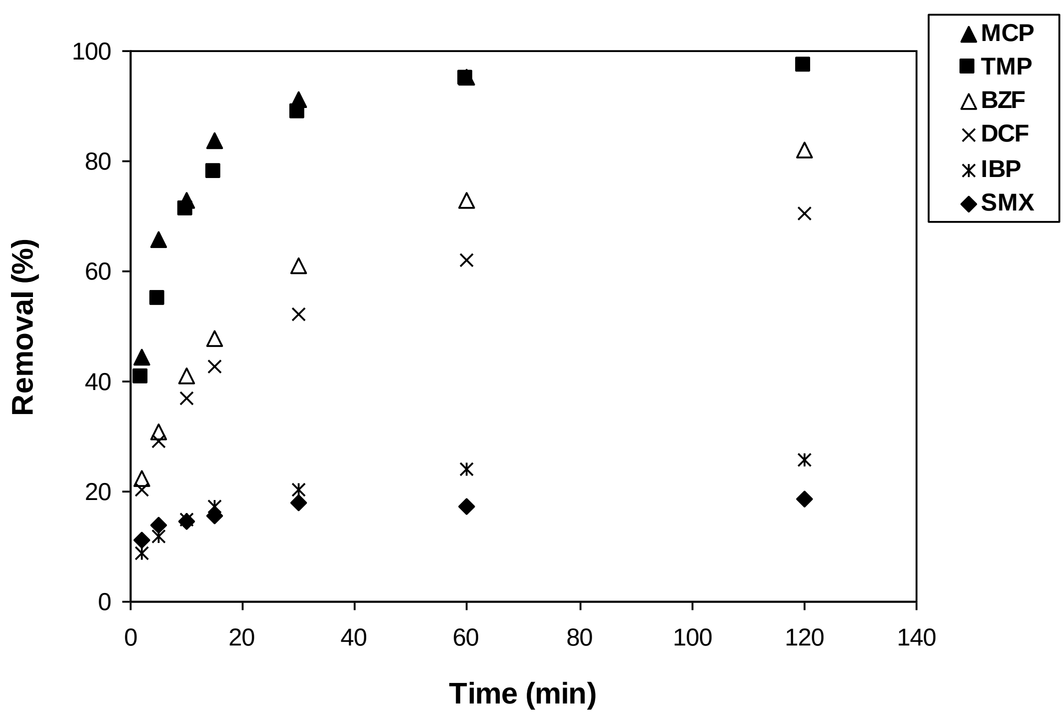


Figure 2. Adsorption uptake kinetics for six pharmaceuticals. Water: OWASA, PAC type: NuChar, PAC dose: 10 mg/L, pH: 7.

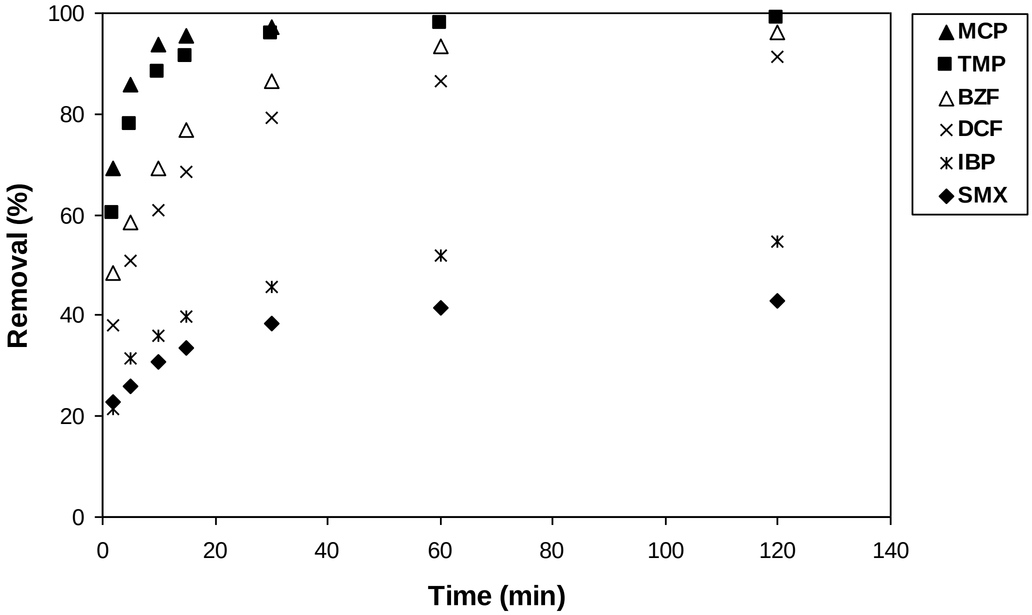


Figure 3. Adsorption uptake kinetics for six pharmaceuticals. Water: OWASA, PAC type: NuChar, PAC dose: 20 mg/L, pH: 7.

Effect of pH on SMX and TMP adsorbability. In Figures 4 and 5, SMX and TMP adsorption kinetics are compared, respectively, at pH 4, 5.5 and 7. NuChar PAC doses were 20 mg/L for SMX and 5 mg/L for TMP. The lower PAC dose for TMP was chosen to more clearly illustrate pH effects on TMP removal. For SMX, removal increased with decreasing pH, especially between pH 7 and pH 5.5 (Figure 4). For TMP, the opposite trend was found; removal decreased with decreasing pH (Figure 5). The results in Figures 4 and 5 can be explained by the acid/base characteristics of SMX and TMP. The pK_a of SMX is 5.8, which means that at pH 5.8, 50% of SMX exists in the neutral form and 50% in the anionic form. When the pH increases above pH 5.8, the anionic form begins to dominate, and when the pH decreases below pH 5.8, the neutral form begins to dominate (Figure 6a). The neutral form of SMX is less soluble than the anionic form, and as a result, SMX adsorbability increases as the fraction of the neutral form increases; i.e., with decreasing pH.

For TMP, the cationic form dominates at pH values below its pK_a of 7.1, and the neutral form dominates at pH values above pH 7.1 (Figure 6b). Again, the neutral form is less soluble than the ionic form. Therefore, TMP adsorbability increases as the fraction of the neutral form increases; i.e., with increasing pH.

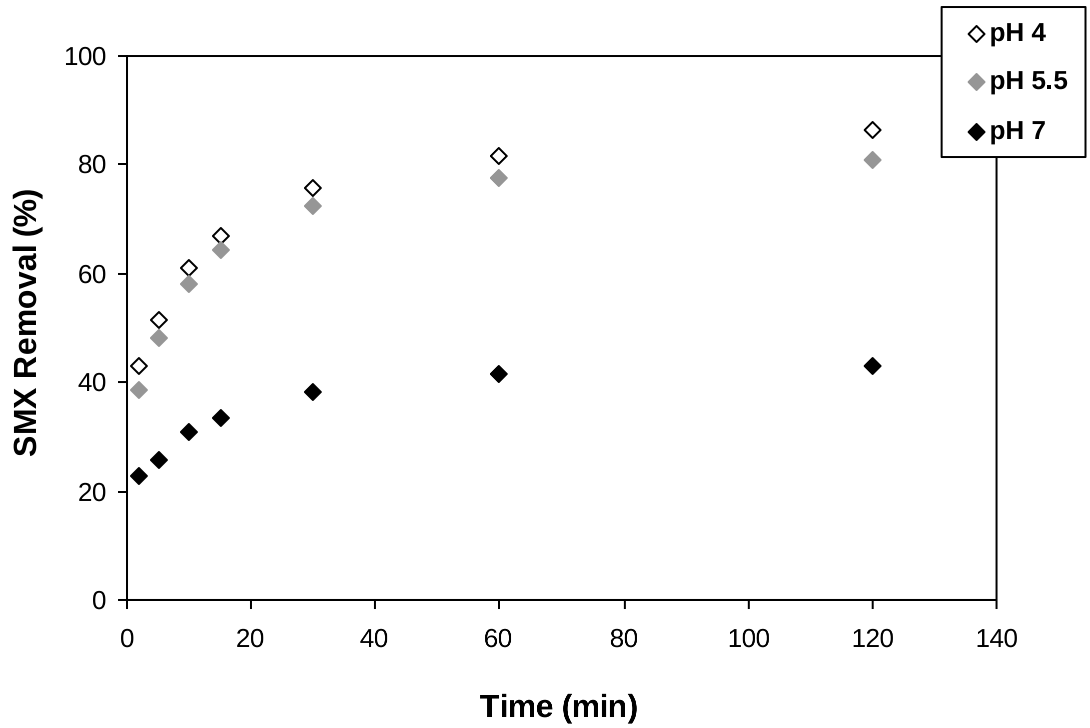


Figure 4. Effect of pH on SMX adsorption uptake. Water: OWASA, PAC: NuChar, PAC dose: 20 mg/L.

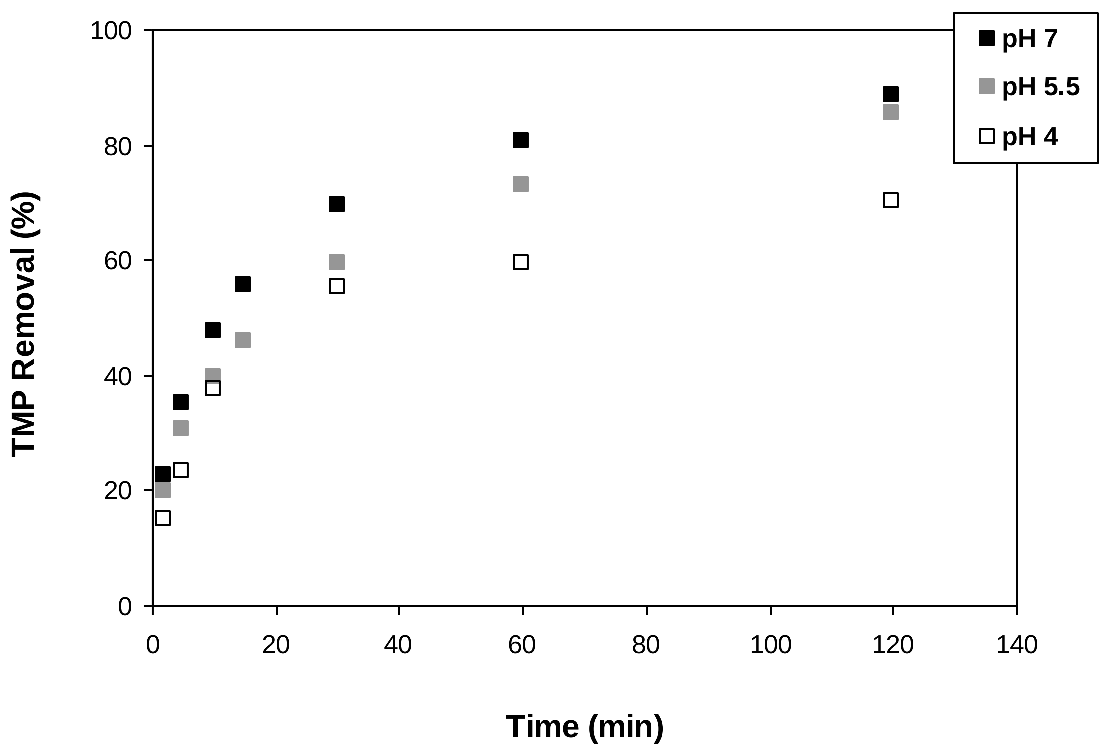


Figure 5. Effect of pH on TMP adsorption uptake. Water: OWASA, PAC: NuChar, PAC dose: 5 mg/L

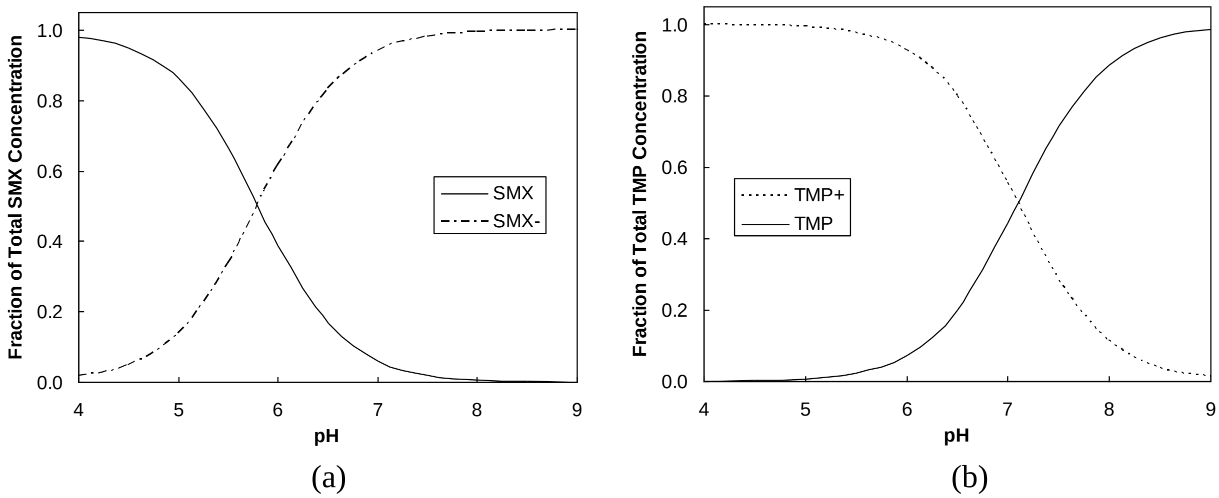


Figure 6. Speciation of (a) SMX and (b) TMP as a function of pH

Background water matrix effects. SMX and TMP removals obtained in two NC drinking water sources and one WWTPE are summarized in Figure 7. The waters differed primarily in their DOC concentrations (5.2 mg/L for OWASA, 6.6 mg/L for Cape Fear river, 7.3 mg/L for Cary WWTPE). The results in Figure 7 show that differences in TMP and SMX removal were small between the two drinking water sources (Cape Fear river and OWASA water). This observation illustrates that the concentration of competing background organic matter in Cape Fear river water did not differ substantially from that in OWASA water. In contrast, the background organic matter in the WWTPE exerted a stronger competitive effect. The effect of the WWTPE matrix was especially pronounced for SMX because the WWTPE exhibited both a higher DOC concentration and a higher pH. As discussed in the previous section, SMX is a weak organic acid that transitions from the neutral to the anionic form as pH increases. As a result, the adsorbability of SMX decreases with increasing solution pH. The effects of the WWTPE matrix on TMP removal were less pronounced. TMP is a weak organic base that transitions from the cationic to the neutral form as pH increases. As a result, its adsorbability increases with increasing pH. Even though the pH of the WWTPE was higher than that of the two drinking water sources, TMP removal was lower in the WWTPE. Thus, the WWTPE contained organic matter that competed more strongly with the trace organic contaminants than the organic matter in the two drinking water sources.

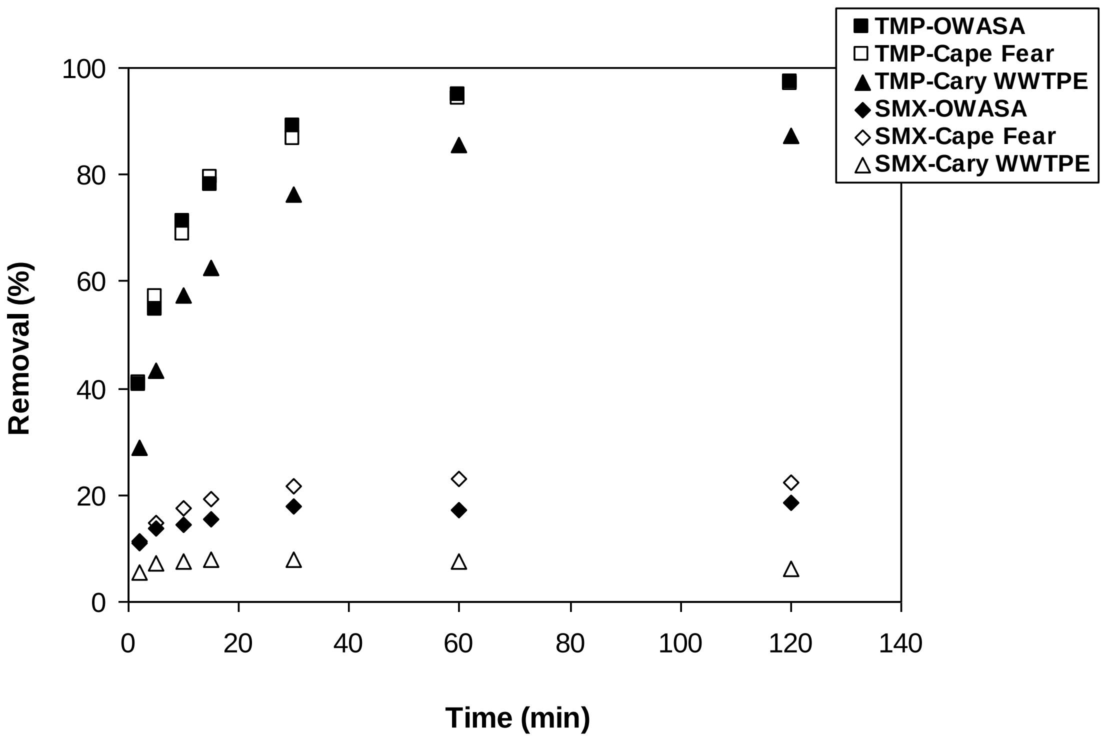


Figure 7. SMX and TMP adsorption uptake kinetics from OWASA, Cape Fear river, and Cary WWTPE waters. PAC: NuChar, PAC dose: 10 mg/L.

Additional batch kinetic tests were conducted to assess the effectiveness of PAC for BAC removal from an activated sludge sample. The activated sludge sample, collected at the North Cary Water Reclamation Facility, had a mixed-liquor suspended solids concentration of 2800 mg/L and a pH of 7.5. These tests were conducted to (1) compare differences in PAC performance in low and high suspended solids environments; i.e. in WWTP effluent relative to activated sludge and (2) to assess whether the combination of PAC addition and biological activity enhances to overall removal/transformation of BACs.

As shown in Figure 8, SMX and TMP removals were similar in the activated sludge and WWTP effluent samples. SMX removals were somewhat higher in the activated sludge samples relative to the WWTP effluent samples while the reverse was the case for TMP. These results are most likely attributable to pH differences between the two samples – the lower pH of the activated sludge sample led to a higher percentage of SMX in the neutral form and a higher percentage of TMP in the cationic form, enhancing SMX removal while adversely affecting TMP removal. Overall, the presence of the mixed liquor suspended solids did not appear to affect the PAC effectiveness for SMX and TMP removal.

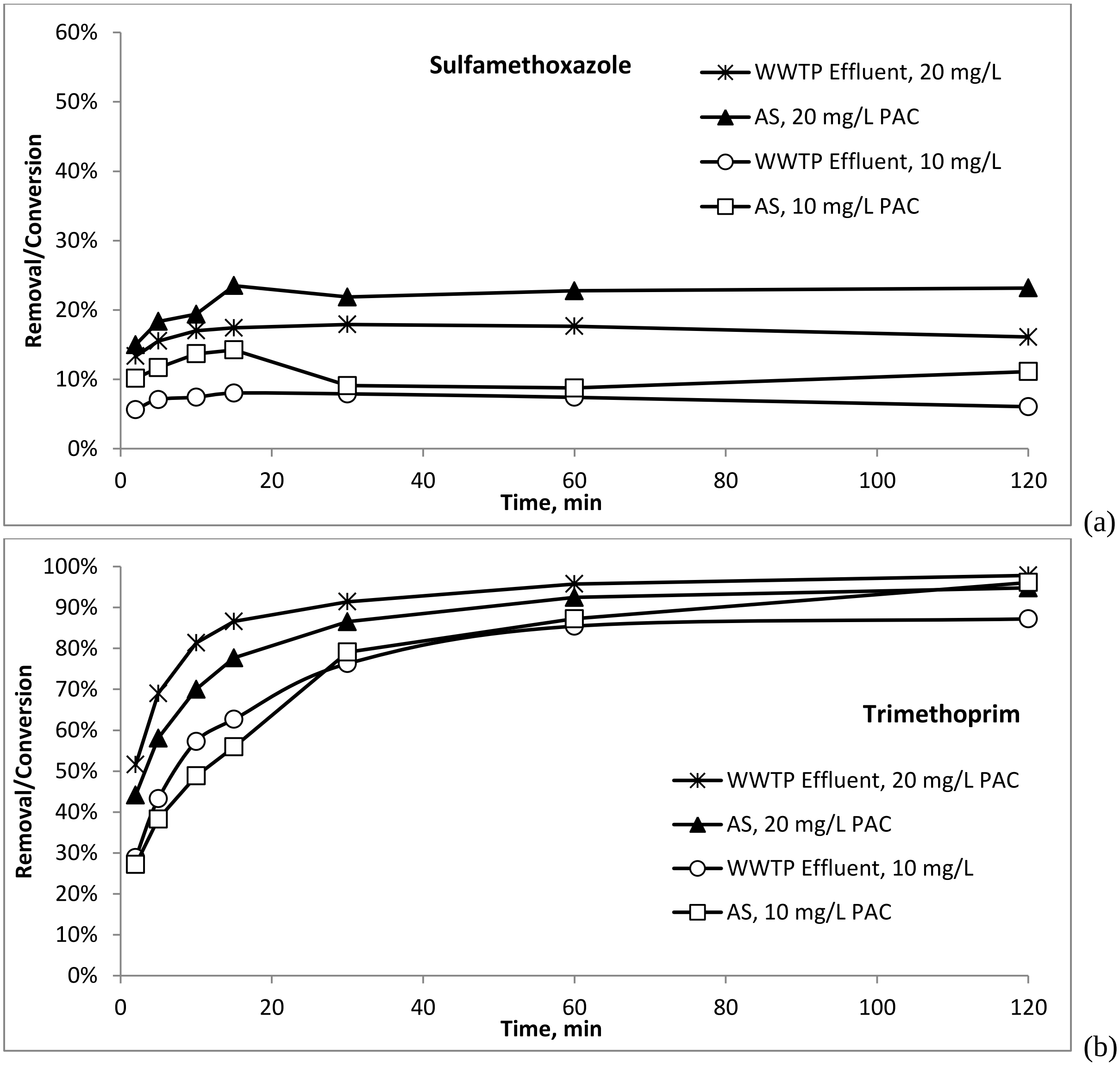


Figure 8. Comparison of PAC effectiveness for (a) sulfamethoxazole and (b) trimethoprim removal from wastewater treatment plant effluent and activated sludge. PAC: NuChar.

Effect of PAC type. The effect of PAC type on SMX removal from OWASA water is shown in Figures 9 and 10. In Figure 9, SMX uptake data are shown for PAC contact times of up to 2 hours. In Figure 10, SMX uptake data are compared at contact times of 15 minutes, 2 hours, and 2 weeks, the latter indicating the maximum uptake capacity that is achieved at adsorption equilibrium. All PACs were tested at a dose of 10 mg/L. As shown in Figure 9, SMX removals among the three as-received PACs (NuChar, Hydrodarco-B, WPH) were similar (~20% removal after a contact time of 60 minutes). There were small differences in the SMX uptake rates among the as-received PACs; e.g., SMX removal during the first 20 minutes was somewhat higher with NuChar PAC than with WPH and Hydrodarco B PACs. At longer contact times, SMX uptake was slightly higher with WPH PAC.

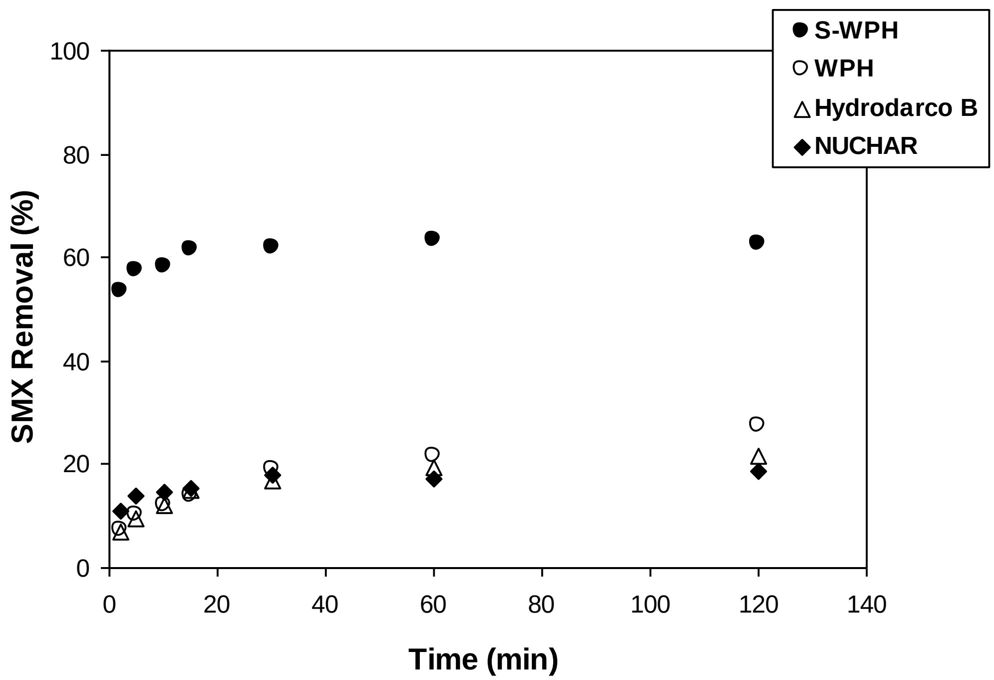


Figure 9. Effect of PAC type on SMX removal kinetics. Water: OWASA, PAC dose: 10 mg/L.

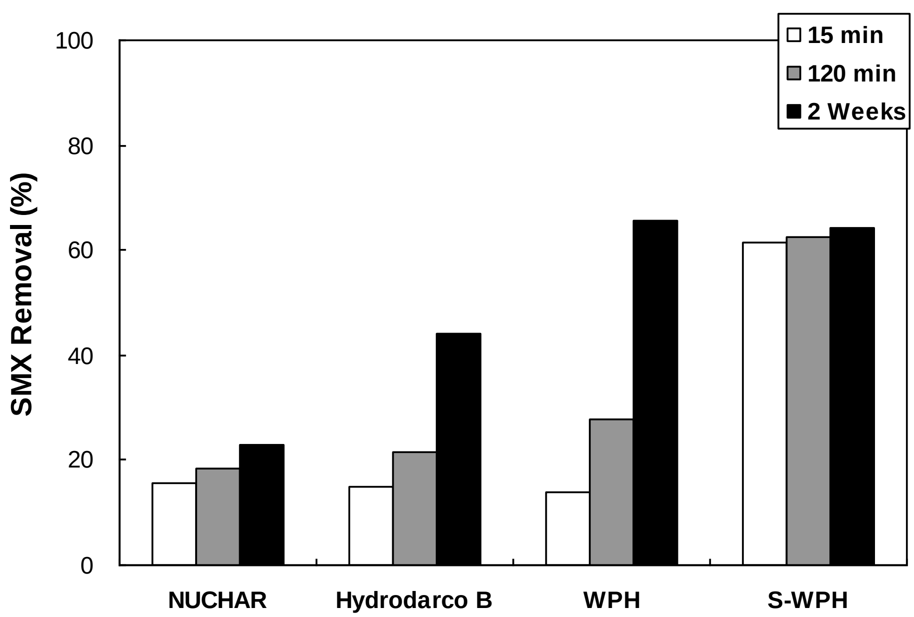


Figure 10. SMX removal at non-equilibrium (15 min, 120 min) and at equilibrium (2 weeks). Water: OWASA, PAC dose: 10 mg/L.

In contrast to the results obtained with the as-received PACs, SMX removal with the superfine version of WPH (S-WPH) was approximately three times higher, ~60% after a contact time of 60 minutes. The greater effectiveness of S-WPH may have been the result of faster kinetics and/or a larger equilibrium uptake capacity. To distinguish between the two, SMX uptake results from longer-term experiments were compared for WPH and S-WPH after a contact time of 2 weeks (Figure 10). A comparison of the 2-week data for WPH and S-WPH in Figure 10 shows that the SMX adsorption capacities of the as-received and superfine versions of WPH were similar. Therefore, the grinding process did not change the maximum uptake capacity for SMX, only the SMX uptake kinetics.

More generally, the results shown in Figure 10 permit a comparison between SMX uptake at short contact times, when adsorption kinetics are important, and at long contact times, when adsorption equilibrium is important. At adsorption equilibrium, the following order in SMX uptake was observed: WPH ~ S-WPH > Hydrodarco B > NuChar. In contrast, at very short contact times, the order was S-WPH >> NuChar > WPH ~ Hydrodarco B. Relative to SMX uptake at equilibrium, SMX uptake after a contact time of 15 minutes was ~96% for S-WPH, ~67% for NuChar, ~34% for Hydrodarco B, and ~21% for WPH. These results illustrate that almost the entire adsorption capacity of S-WPH was utilized after 15 minutes of contact. In contrast, less than one quarter of the WPH adsorption capacity was utilized at the same contact time. Thus, the use of S-PAC may allow utilities to almost fully utilize the equilibrium uptake capacity of PAC, even when PAC contact times are short, as is often the case.

The effect of PAC type on TMP removal from OWASA water is compared in Figures 11 and 12. In Figure 11, TMP uptake data are shown for contact times of up to 2 hours. For TMP, distinct differences between the three as-received PAC types (NuChar, WPH, Hydrodarco B) were observed. TMP uptake was in the order of NuChar > WPH >> Hydrodarco B. As was the case with SMX, the superfine version of WPH (S-WPH) produced greater TMP removals than any of the as-received PACs (Figure 11). The better performance of S-WPH was primarily a result of improved adsorption kinetics, because the maximum TMP adsorption capacity that was measured after a contact time of 2 weeks was identical for WPH and S-WPH (Figure 12). Because of the rapid adsorption kinetics that can be achieved with S-WPH, almost the entire TMP adsorption capacity was utilized after a contact time of 15 minutes. In contrast, only ~30-50% of the TMP adsorption capacity was utilized after a contact time of 15 minutes for the as-received PACs (Figure 12).

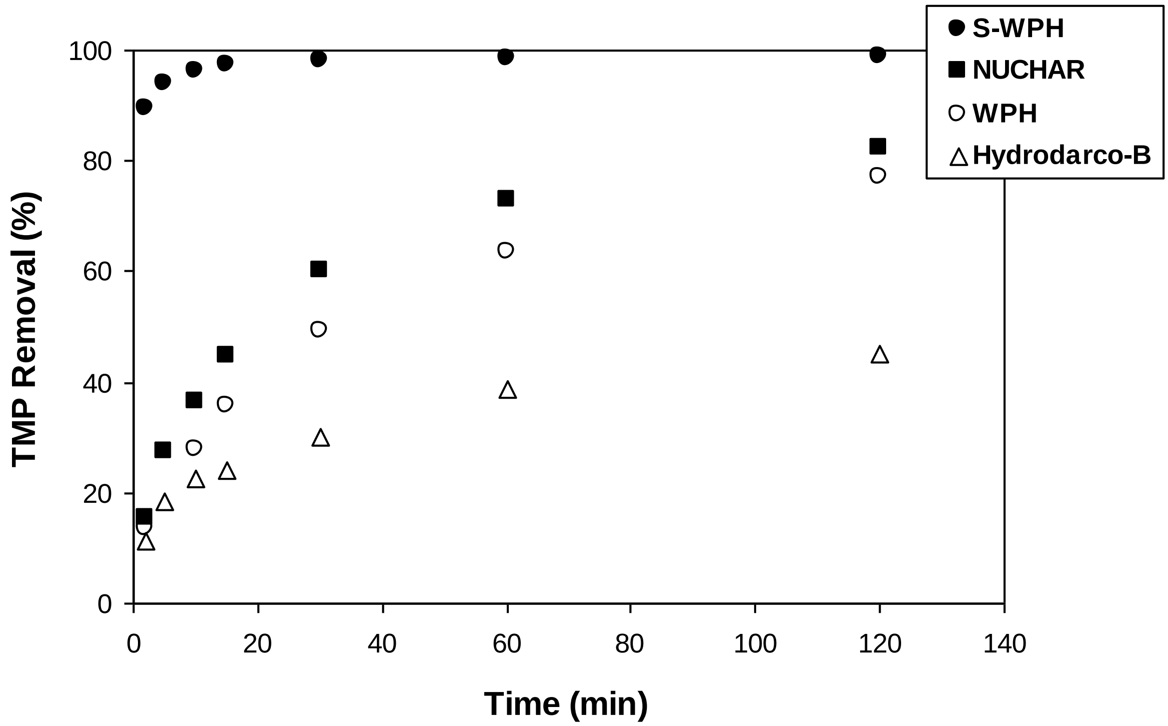


Figure 11. Effect of PAC type on TMP removal kinetics. Water: OWASA, PAC dose: 5 mg/L.

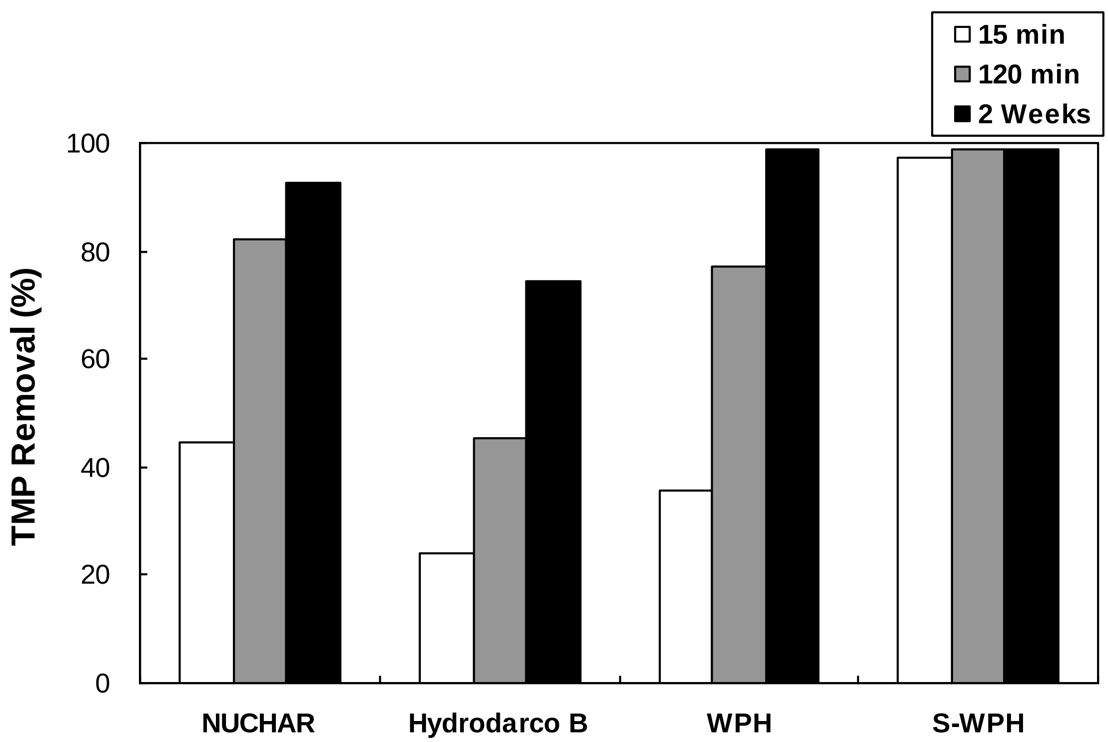


Figure 12. TMP removal at non-equilibrium (15 min, 120 min) and at equilibrium (2 weeks). Water: OWASA, PAC dose: 5 mg/L.

NOM Removal. In addition to BAC uptake rates, NOM uptake rates were measured by conducting DOC and UV_{254} absorbance analyses (Figures 13 and 14). NOM removal was measured after contact times of 2 hours (non-equilibrium condition) and 2 weeks (equilibrium condition), and results are shown for a PAC dose of 10 mg/L. After a contact time of 2 hours, DOC removal was ~10% or less for the as-received PACs and ~20% for S-WPH. UV_{254} removal ranged from ~8-13% for the as-received PACs and was almost 35% for S-WPH. The results for S-WPH suggest that meaningful NOM removal can be achieved with a reasonable S-PAC dose of 10 mg/L.

At equilibrium, NOM uptake was in the order S-WPH > NuChar > WPH > Hydrodarco B (Figures 13 and 14). Thus, grinding WPH PAC to a finer particle size not only enhanced adsorption kinetics but also increased its maximum adsorption capacity for NOM. One possible explanation for the greater NOM adsorption capacity of S-WPH is that NOM may be able to penetrate only a certain distance into PAC particles (Ando et al., 2011). In that case, a larger percentage of the S-WPH particles is accessible to NOM than is the case for as the as-received WPH.

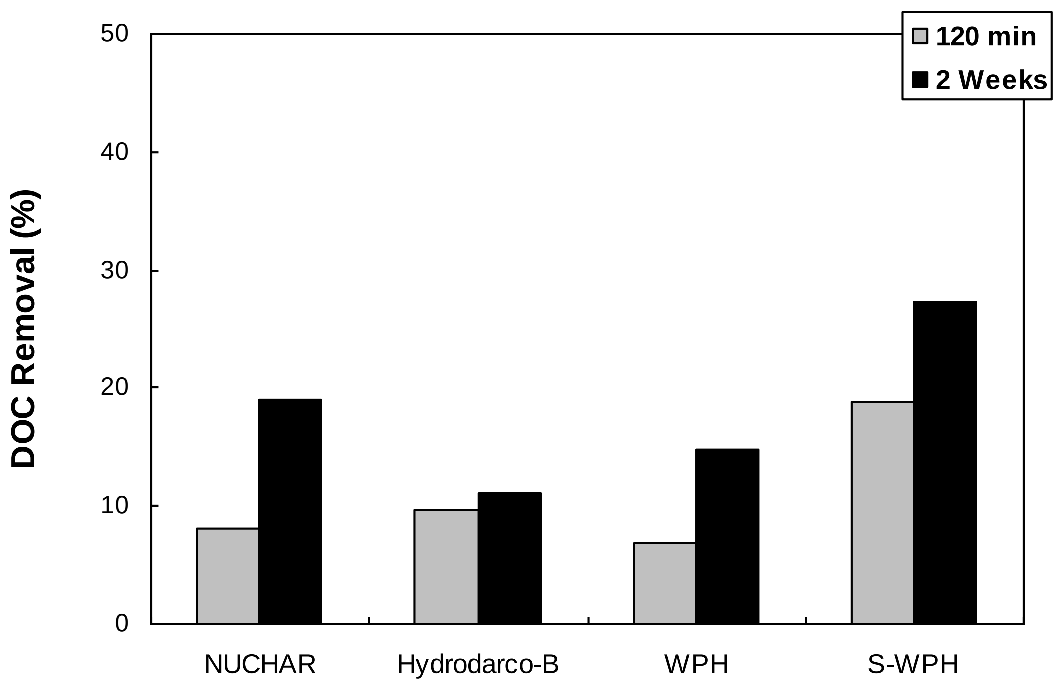


Figure 13. Effect of PAC type on DOC removal. Water: OWASA, PAC dose: 10 mg/L.

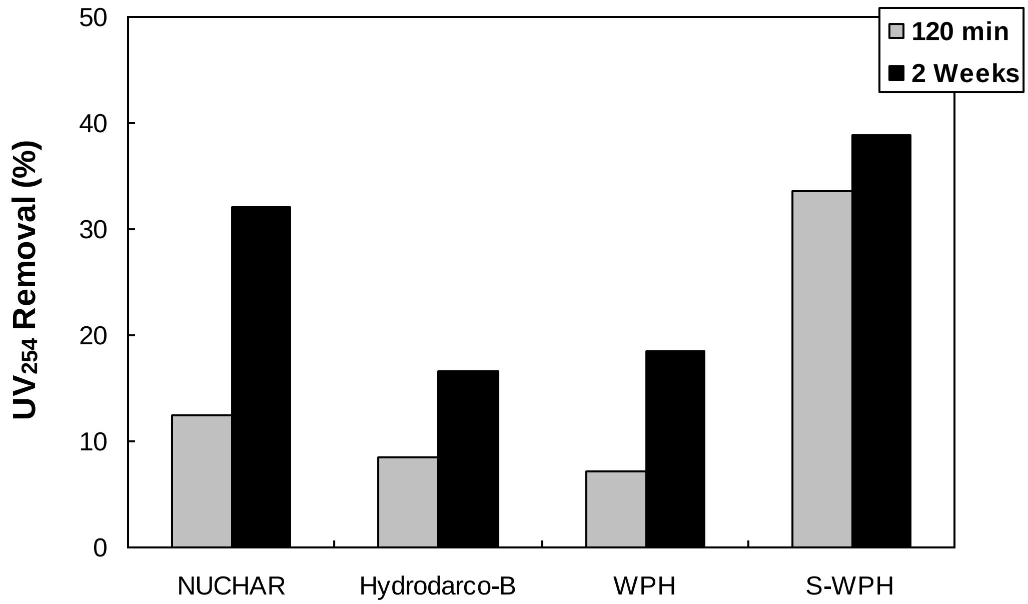
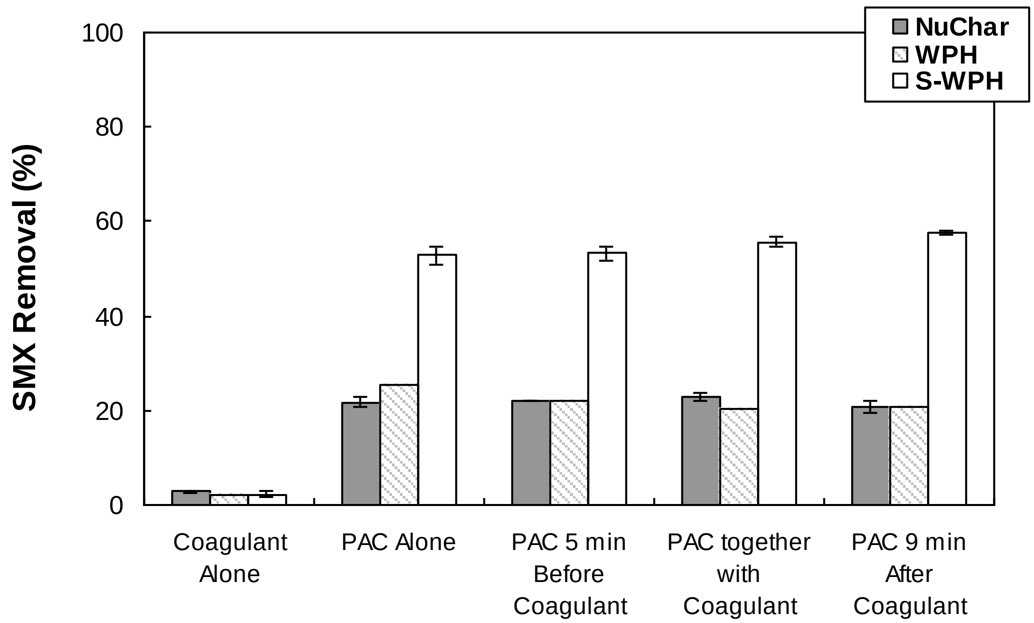


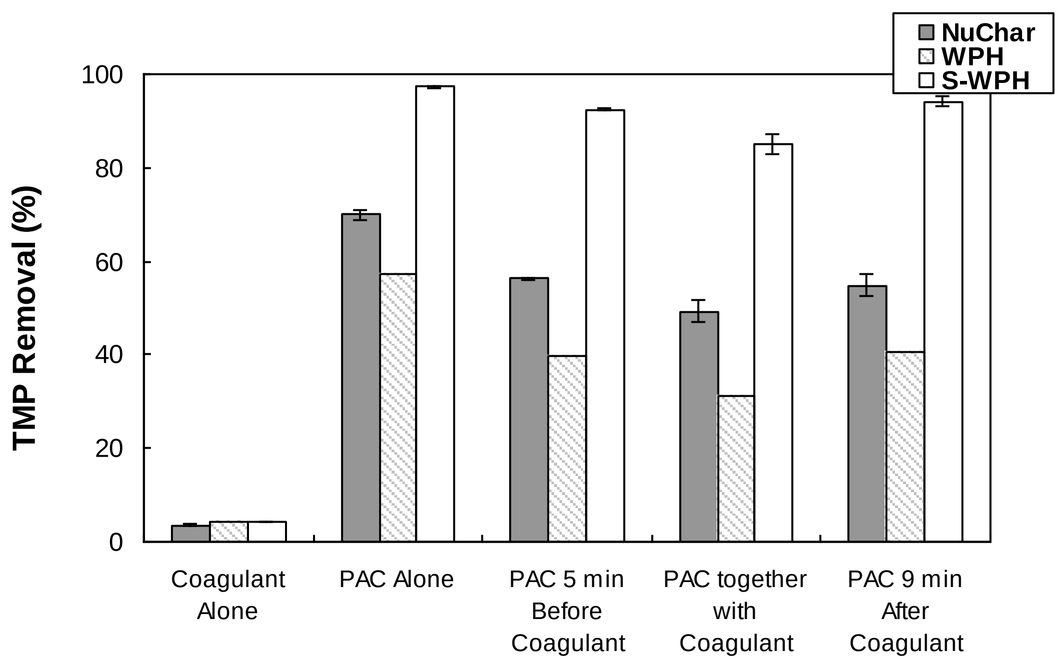
Figure 14. Effect of PAC type on UV_{254} removal. Water: OWASA, PAC dose: 10 mg/L.

BAC Removal by PAC in the Presence of Aluminum Hydroxide Floc. One goal of this study was to determine the effect of PAC type and dose on BAC removal in jar tests in which PAC was present together with aluminum hydroxide floc. An additional objective was to evaluate the timing of PAC addition relative to the coagulant addition (simultaneous addition of PAC and coagulant, PAC addition 5 minutes prior to coagulant, PAC addition 9 minutes into the flocculation process). The tested alum dose of 55 mg/L and coagulation pH of 6.2 are typical for the OWASA water treatment plant.

Figure 15a compares SMX removal data obtained in jar tests conducted with NuChar, WPH and S-WPH. The tested PAC dose was in each case 5 mg/L, and the coagulation pH was 6.2. Aluminum hydroxide floc and timing of PAC addition relative to alum addition did not affect SMX removal. However, SMX removals obtained with S-WPH were 2.1-2.8 times those obtained with NuChar and WPH. For TMP, removals with S-WPH were 1.7-2.7 times those obtained with NuChar and WPH (Figure 15b). The presence of aluminum hydroxide floc had an adverse effect on TMP removal by all three PACs, and TMP removal was lowest when PAC was added together with alum. The interference of the aluminum hydroxide floc may be related to electrostatic repulsion between TMP, which is predominantly present in cationic form at pH 6.2, and positively charged aluminum hydroxide floc. The interference of the aluminum hydroxide floc was largest when PAC was added together with alum.



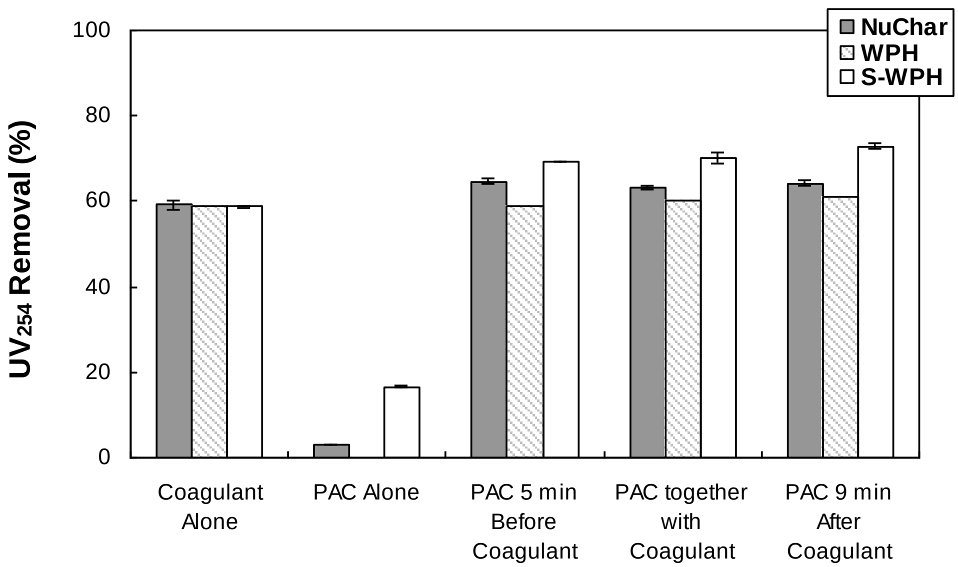
(a)



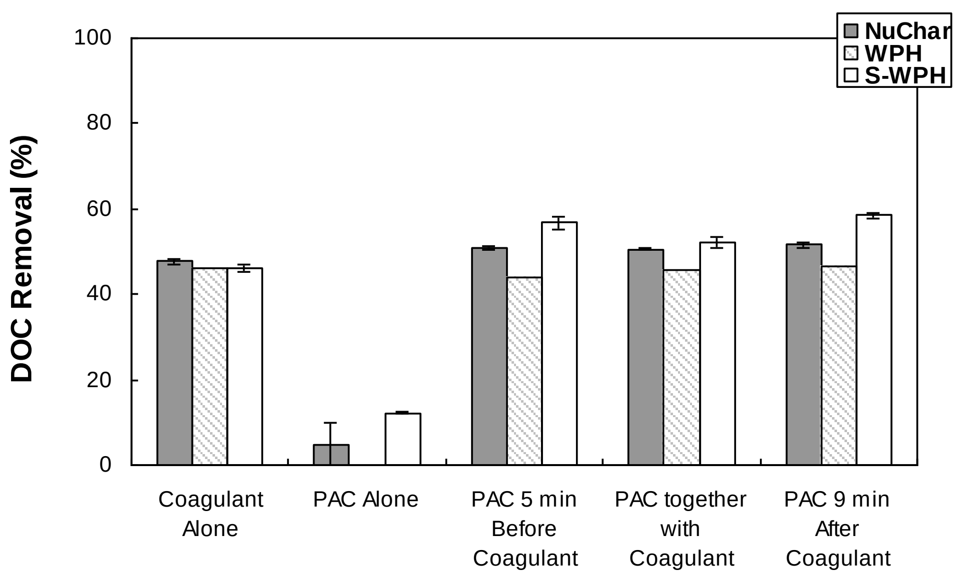
(b)

Figure 15. Effect of PAC type on (a) SMX and (b) TMP removal in jar tests evaluating timing of PAC addition. Removals with coagulant alone and PAC alone are shown for reference. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC dose: 5 mg/L, pH: 6.2.

Figure 16 compares NOM removal obtained with alum only, PAC only, and the combination of alum and PAC treatment. UV_{254} removal was ~60% with alum only and was enhanced by less than 5% with 5 mg/L NuChar and WPH, and by 10% with 5 mg/L S-WPH. Treatment with S-WPH alone lowered the UV_{254} absorbance by 17%, which was larger than the 10% increment obtained beyond what was obtained with alum only. Therefore, the presence of aluminum hydroxide floc may have had a negative effect on the adsorptive removal of NOM by S-WPH. It is also possible, however, that alum coagulation removed a NOM fraction that was adsorbed when S-WPH was added alone.



(a)



(b)

Figure 16. Effect of PAC type on NOM removal as measured by (a) UV_{254} and (b) DOC in jar tests evaluating timing of PAC addition. Removals with alum alone and PAC alone are shown for reference. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC dose: 5 mg/L, pH: 6.2.

The turbidity removal data in Figure 17 suggest that the addition of S-WPH adversely affected turbidity removal. Poorer turbidity removal in the presence of S-WPH was more pronounced after the shorter settling time (3.5 minutes, Figure 17a) than after the longer settling time (10 minutes, Figure 17b). The results in Figure 17 further suggest that poorer turbidity removal was a greater issue when (S-)PAC was added after alum, i.e., 9 minutes into the flocculation process.

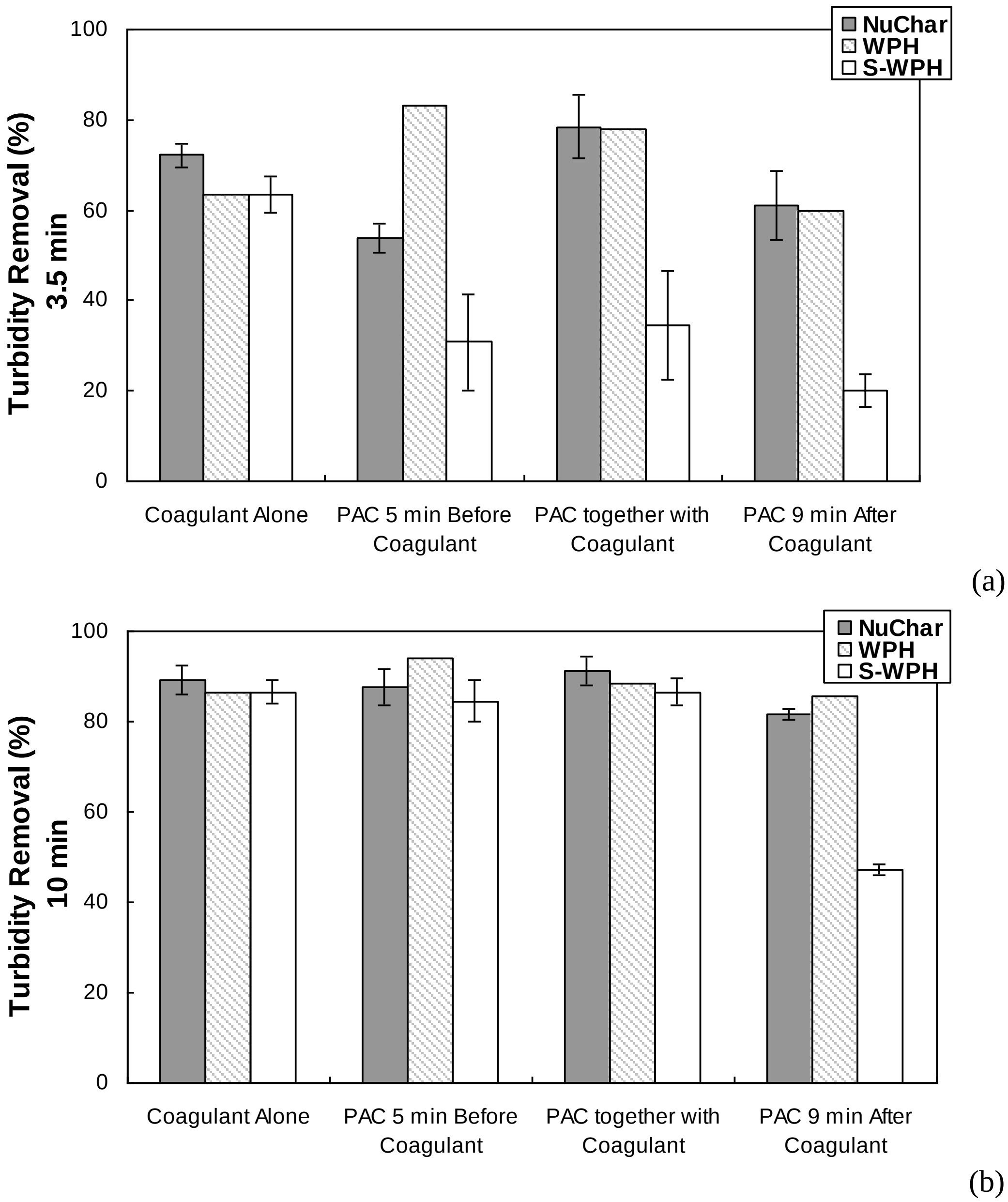


Figure 17. Effect of PAC type on turbidity removal after (a) 3.5 and (b) 10 minutes of settling. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, PAC dose: 5 mg/L, pH: 6.2.

To assess the effect of PAC dose on BAC removal, jar tests were conducted with SMX and IBP, the two least adsorbable BACs tested in this study. Wood-based NuChar, lignite-based Hydrodarco B, and coal-based WPH PACs were evaluated, and the coal-based PAC was tested in both the as-received and the S-PAC forms. As shown in Figure 18a, SMX removal was most effectively accomplished with S-WPH, and a dose of 20 mg/L produced 90% SMX removal. Among the as-received PACs, SMX removal was in the order NuChar>WPH>Hydrodarco B. To obtain 90% SMX removal, the required dosage for NuChar was about 90 mg/L while that for WPH and Hydrodarco B was >100 mg/L. Results for IBP were similar to those obtained with SMX (Figure 18b). IBP removal was most effectively accomplished with S-WPH, and a dose of about 25 mg/L produced 90% IBP removal. To obtain 90% IBP removal, the required dosage for NuChar was about 100 mg/L while that for WPH and Hydrodarco B was >100 mg/L. Thus, 90% SMX and IBP removal is not achievable with as-received PACs at doses typically employed in drinking water treatment.

Another drinking water source, Cape Fear river water, and Cary WWTPE were also tested with NuChar, WPH and S-WPH. Both waters had higher background NOM concentrations than the OWASA water as measured by UV_{254} absorbance and DOC concentration. Again, S-WPH greatly enhanced SMX and IBP removal relative to the removals that could be achieved with the as-received PACs. In Cape Fear water, to obtain 90% SMX removal, the required dose for S-WPH was about 15 mg/L while that for NuChar and WPH was 75 and 100 mg/L, respectively (Figure 18c). For 90% IBP removal, the required dosage of S-WPH was 30 mg/L, while that for NuChar and WPH was ≥100 mg/L (Figure 18d). The higher background NOM concentration in Cary WWTPE adversely affected BAC adsorption by PACs, and thus the required (S-)PAC doses for 90% BAC removal were higher. To obtain 90% SMX and IBP removal in the WWTPE, a dosage of 30 mg/L was required for S-WPH, while those for NuChar and WPH were much larger than 100 mg/L (Figure 18, panels e and f).

The results in Figure 19 show that alum coagulation alone yielded about 60% NOM removal, as measured by UV_{254} absorbance. The addition of 30 mg/L S-WPH PAC produced approximately 25% NOM removal beyond that achieved with alum coagulation. In contrast, the addition of 100 mg/L as-received PAC produced only ~15-20% NOM removal beyond that achieved with alum coagulation. NOM removal was negligible with PAC doses of 5 and 20 mg/L, and increased slowly as the PAC dose was increased to 100 mg/L (Figure 19). Among the three tested as-received PACs, DOC removal did not differ substantially, but removal of UV_{254}-absorbing compounds was somewhat greater with WPH PAC at higher doses.

The settled water turbidity data in Figure 20 suggests that as the PAC dose increased, floc settleability improved. As the particle concentration in the water increased with increasing PAC dose, the collision frequency may have increased. As a result, the rate of particle aggregation could have been faster, which may have yielded larger floc particles. In addition, incorporation of more PAC particles into floc likely increased floc density and thus floc settleability. The higher settled water turbidity results for S-WPH suggest that S-WPH was less effectively incorporated into settleable floc than as-received WPH.

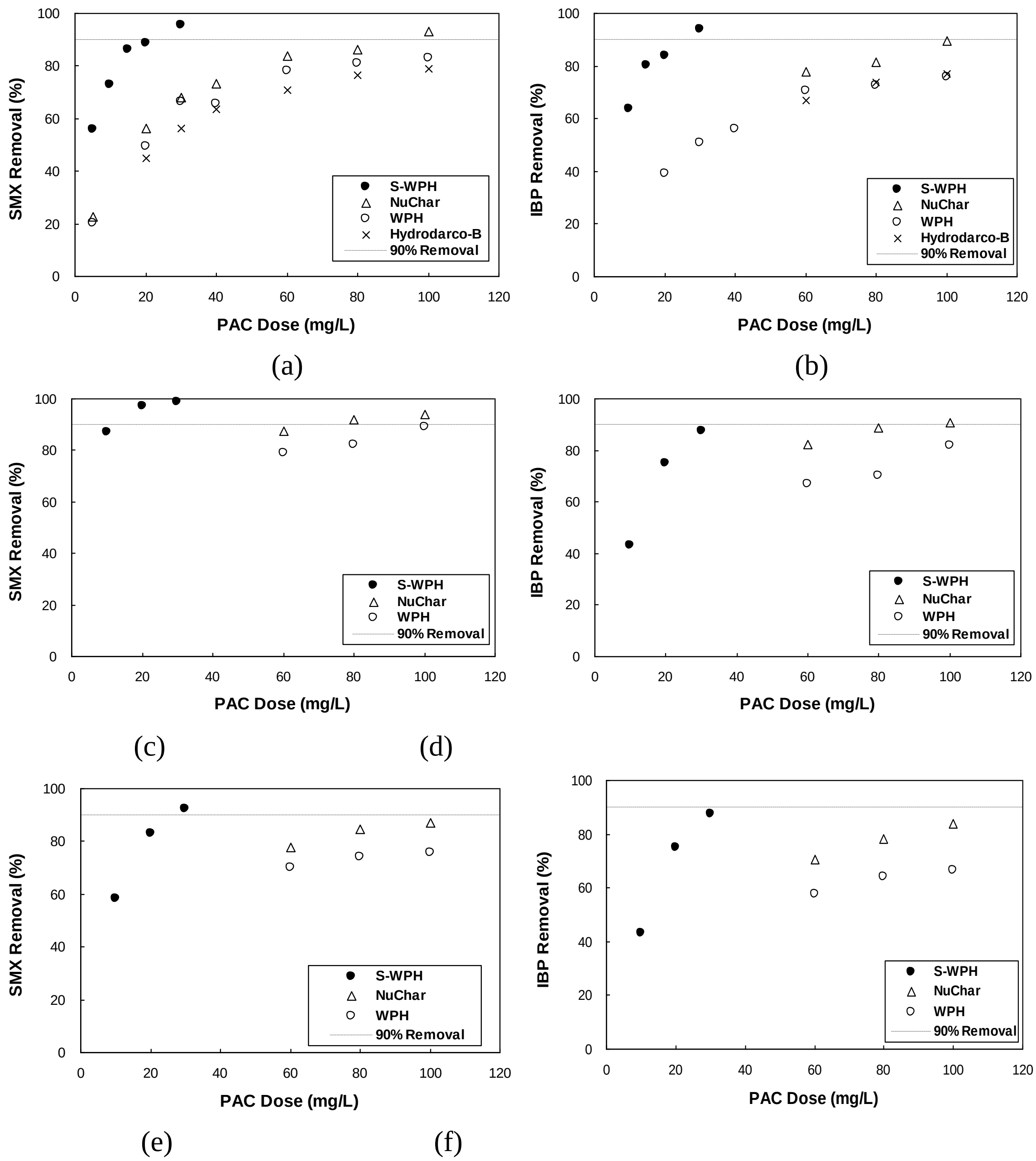
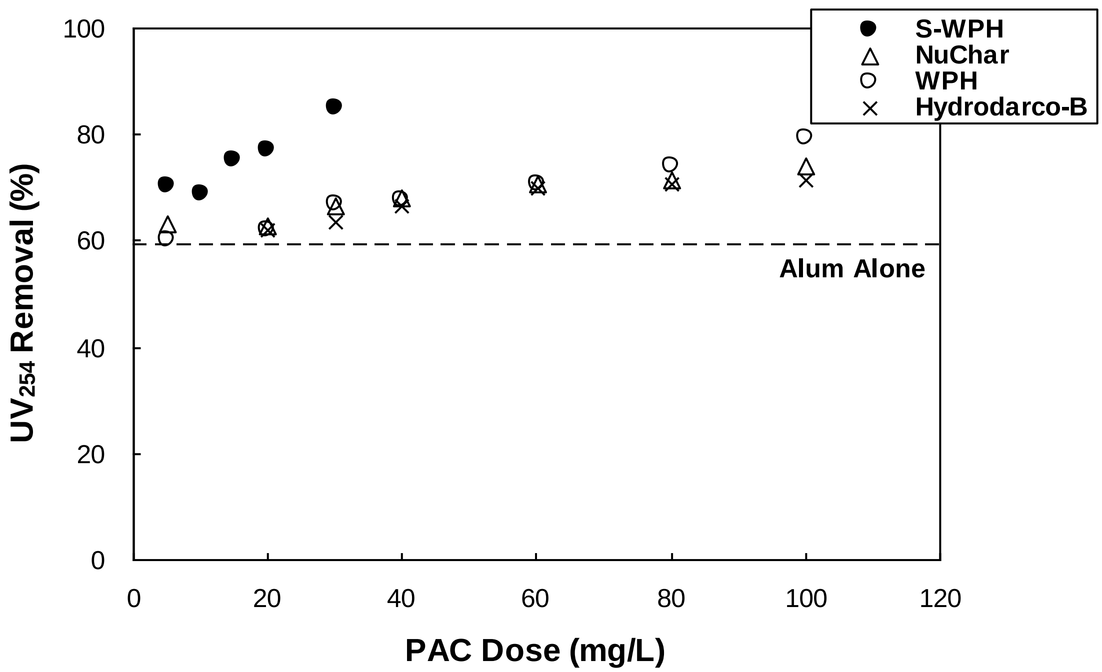
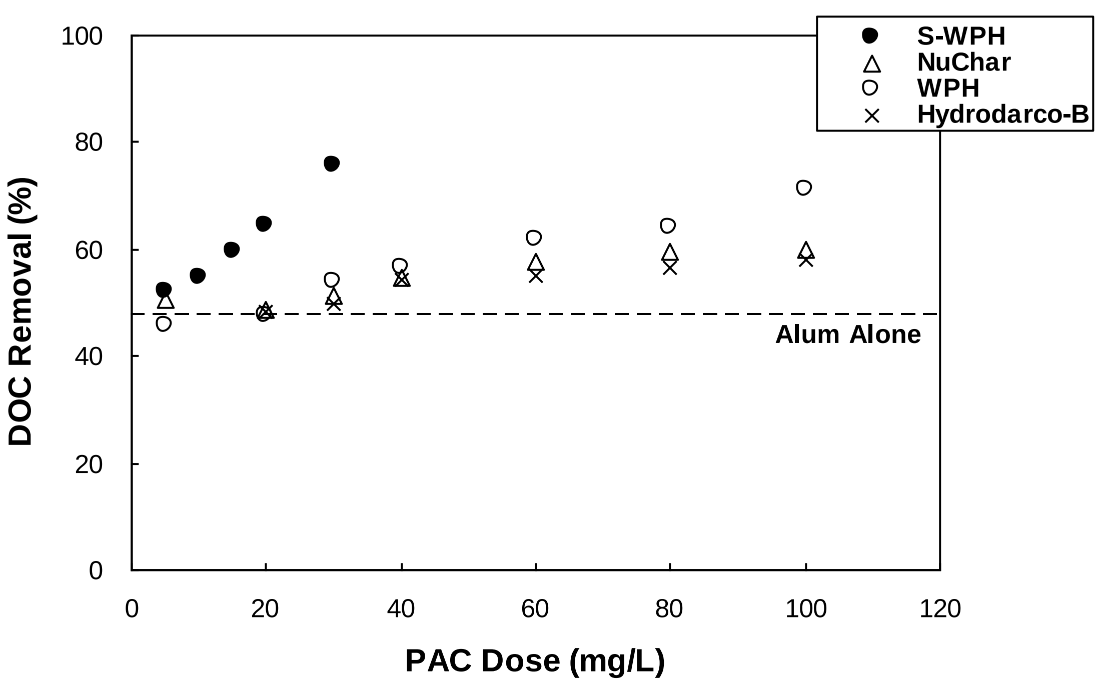


Figure 18. Effect of PAC dose on SMX (a, c, e) and IBP (b, d, f) removal with PAC added together with coagulant. Water: OWASA (a, b), Cape Fear (c, d), Cary WWTPE (e, f), coagulant: alum, coagulant dose: 55 mg/L, pH: 6.2.



(a)



(b)

Figure 19. Effect of PAC dose on NOM removal as measured by (a) UV_{254} and (b) DOC with PAC added together with coagulant. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, pH: 6.2.

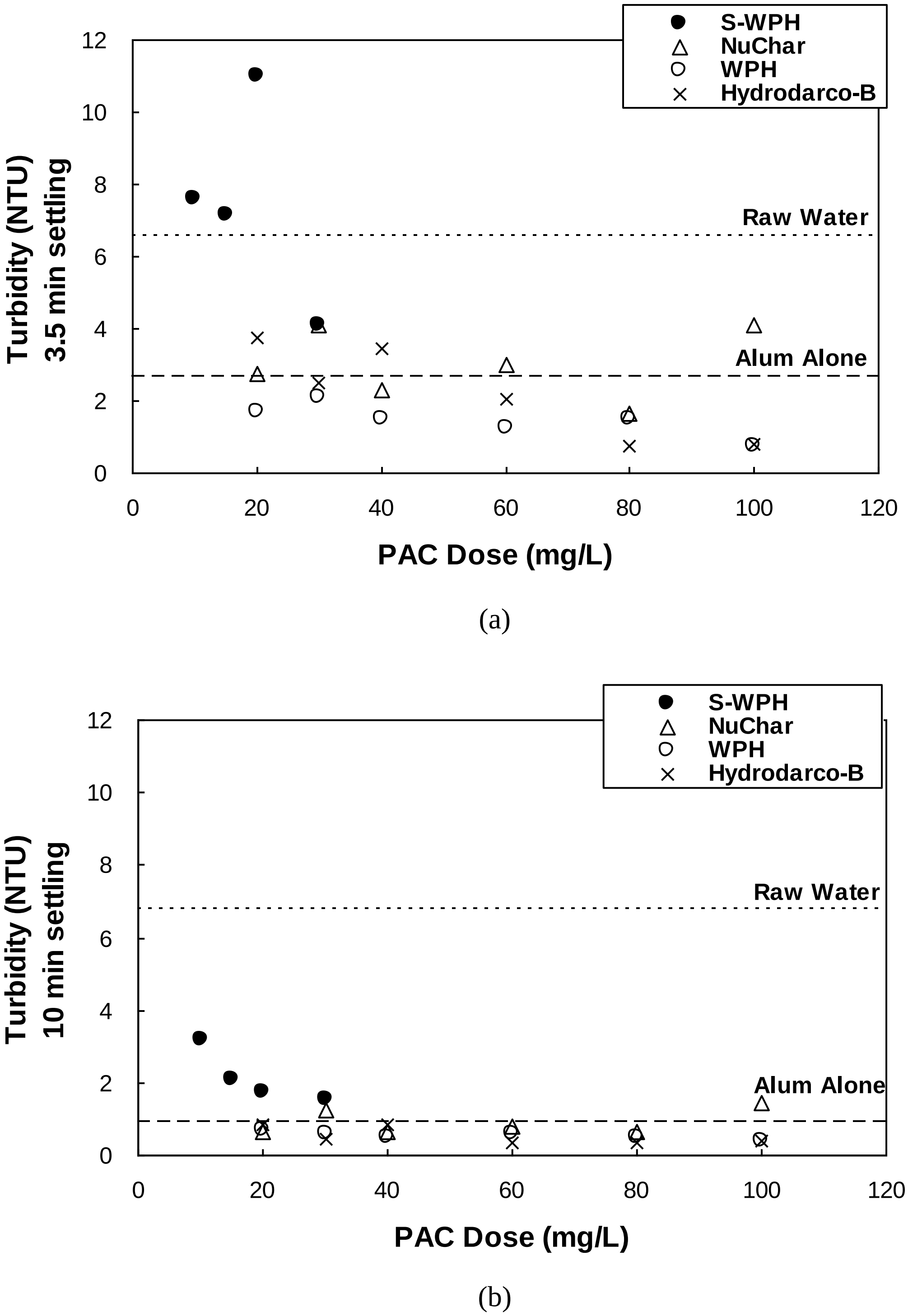


Figure 20. Effect of PAC dose on turbidity after (a) 3.5 and (b) 10 minutes of settling. Water: OWASA, coagulant: alum, coagulant dose: 55 mg/L, pH: 6.2.

Micropollutant Mixture at Environmentally Relevant Concentrations. An additional jar test was conducted to assess the effectiveness of PAC adsorption for the removal of twelve micropollutants (Table 3) that were spiked into OWASA water at environmentally relevant concentrations (~250-600 ng/L). Wood-based NuChar PAC was added at a dose 20 mg/L together with 55 mg/L alum to raw OWASA water, and the coagulation pH was 6.3. As shown in Figure 21, all 12 micropollutants were removed in the presence of PAC and alum, and removal percentages ranged from ~66% for sulfamethoxazole to >95% for trimethoprim. For the three compounds that were tested at higher concentrations (~100 µg/L, Figure 3), the removal order remained the same at lower initial BAC concentrations (Figure 21); i.e. SMX<BZF<TMP. SMX removal shown in Figure 3 was lower than in the jar test conducted at environmentally relevant concentrations because of differences in solution pH (pH 7 for batch kinetic test, Figure 3; pH 6.3 for jar test, Figure 21). In a jar test conducted with an initial SMX concentration of ~100 µg/L and a coagulation pH of 6.2, a SMX removal percentage of about 57% was obtained with a NuChar PAC dose of 20 mg/L (Figure 18a), a result that matches fairly well with the results shown in Figure 21.

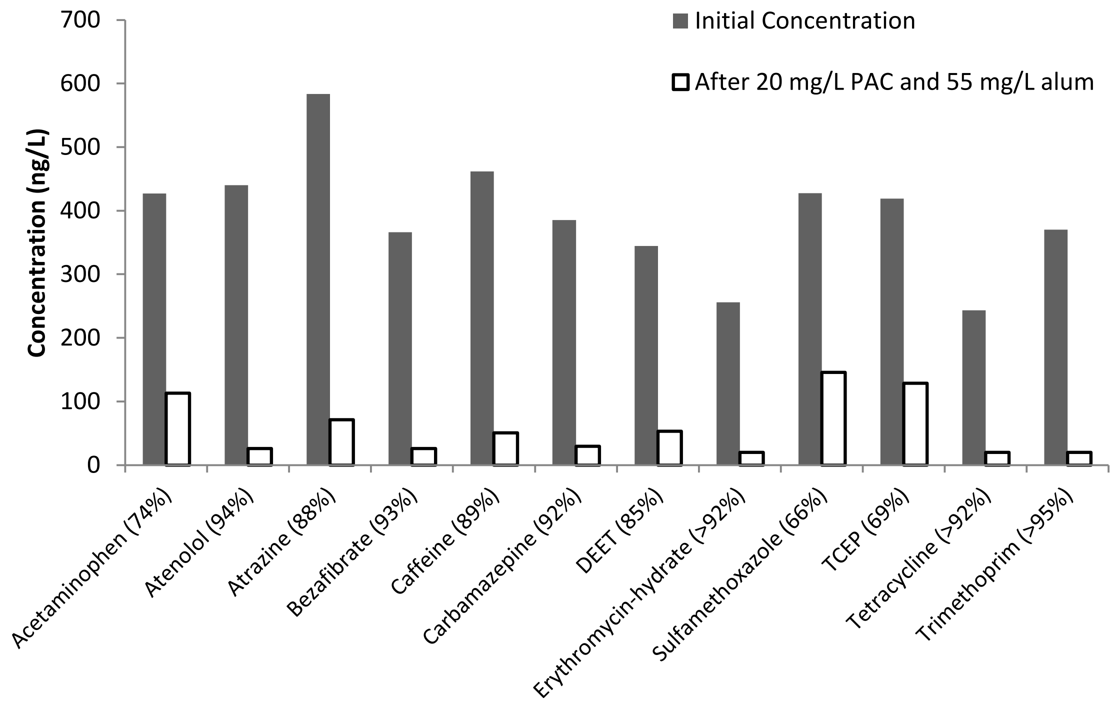


Figure 21. Initial micropollutant concentrations and micropollutant concentrations following treatment with 20 mg/L PAC and 55 mg/L alum. Water: OWASA. Coagulation pH: 6.3.

Combined Adsorptive Removal and Biological Transformation in Activated Sludge. The final assessment of PAC performance consisted of batch kinetic tests that were conducted with activated sludge to which (1) no PAC was added, (2) 10 mg/L NuChar PAC was added, and (3) 20 mg/L NuChar PAC was added. Batch kinetic tests were conducted with the following BACs, each spiked at a concentration of ~100 µg/L:

- bezafibrate (BZF)

- diclofenac (DCF)
- ibuprofen (IBP)
- sulfamethoxazole (SMX)
- trimethoprim (TMP)

Results for the tests conducted in the absence of PAC suggest that BZF, IBP, SMX, and TMP were biodegradable over the 8-day time span while DCF was essentially recalcitrant (Figure 22). The addition of PAC aided the removal of (1) moderately to strongly adsorbing compounds (e.g. BZF, TMP) at short contact times and (2) recalcitrant DCF. In contrast, the addition of PAC had only a small effect on a readily biodegradable but weakly adsorbable compound, such as IBF. In the case of SMX, which is weakly adsorbable and relatively difficult to biodegrade, the addition of PAC may have accelerated the onset of SMX biodegradation, a result that can be explained by biofilm formation on the PAC particles.

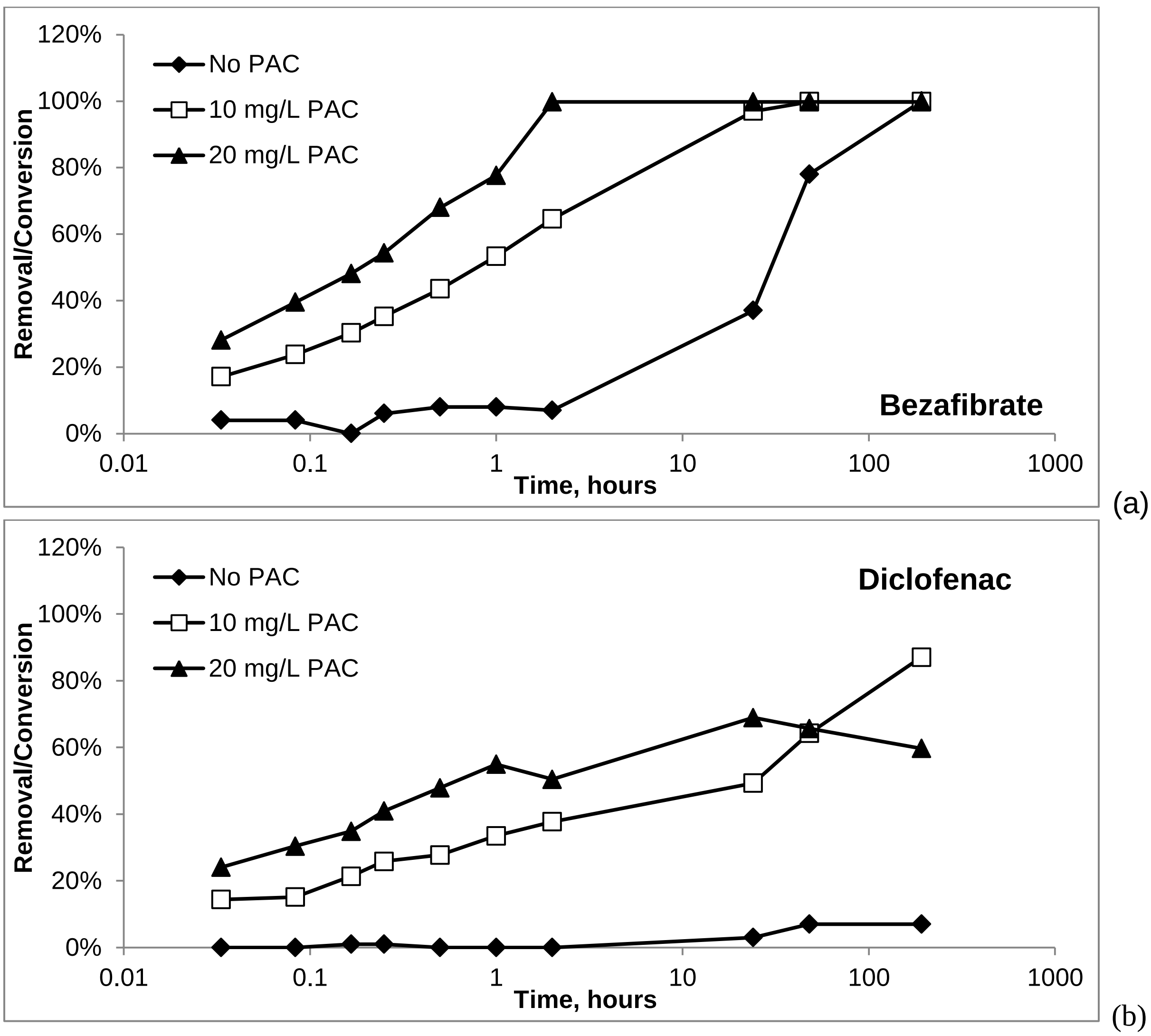
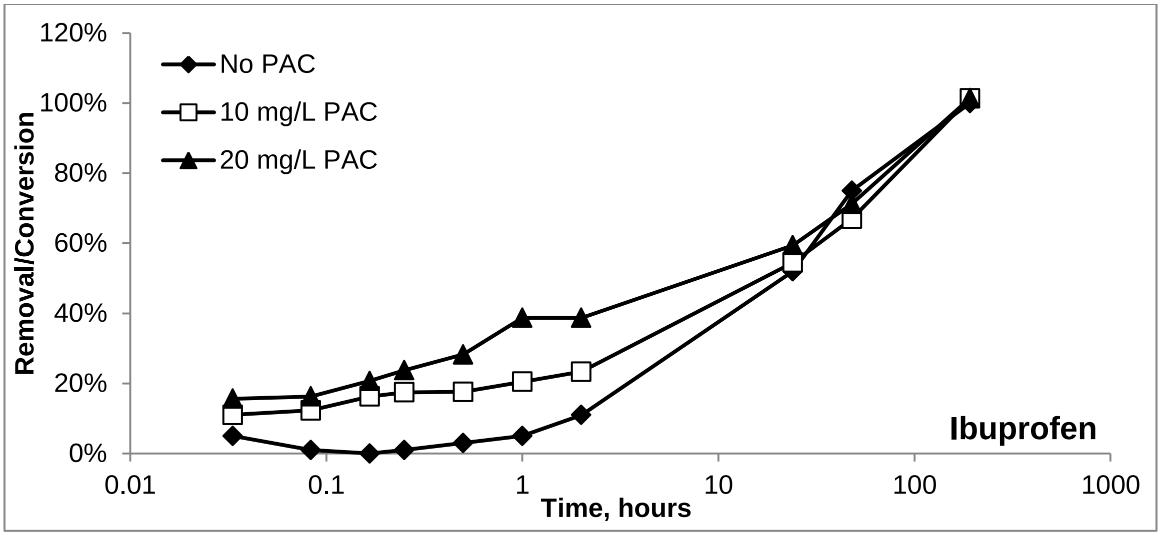
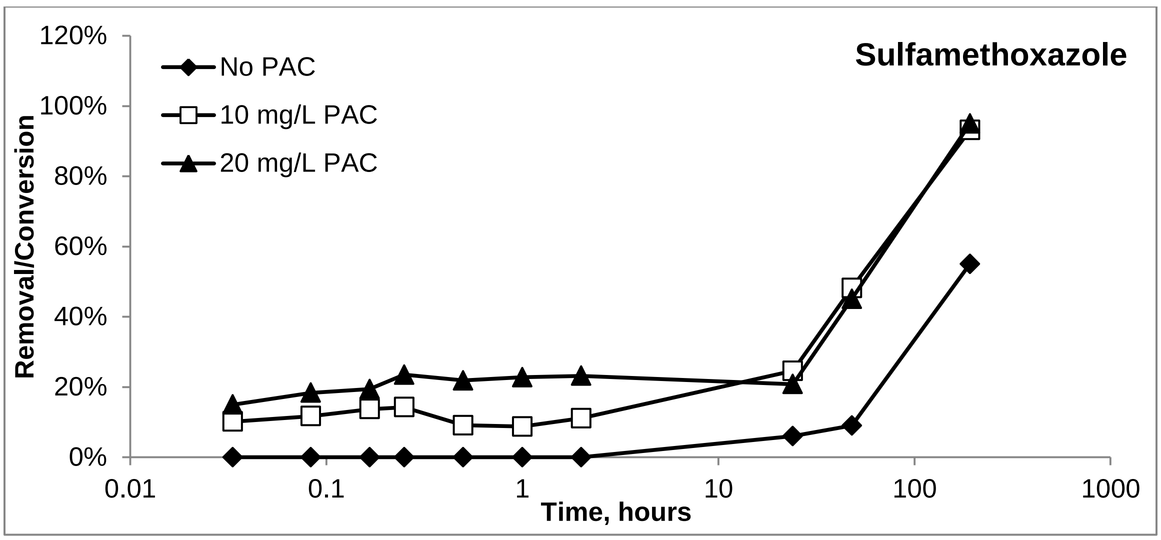


Figure 22. Effect of PAC addition on BAC removal from/transformation in activated sludge: (a) bezafibrate, (b) diclofenac.



(c)



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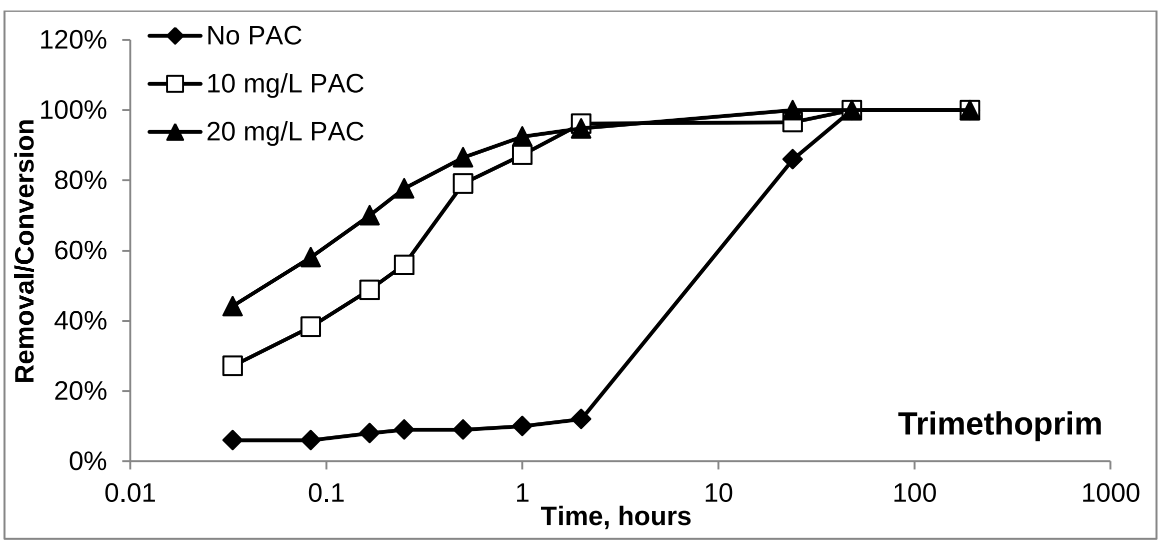


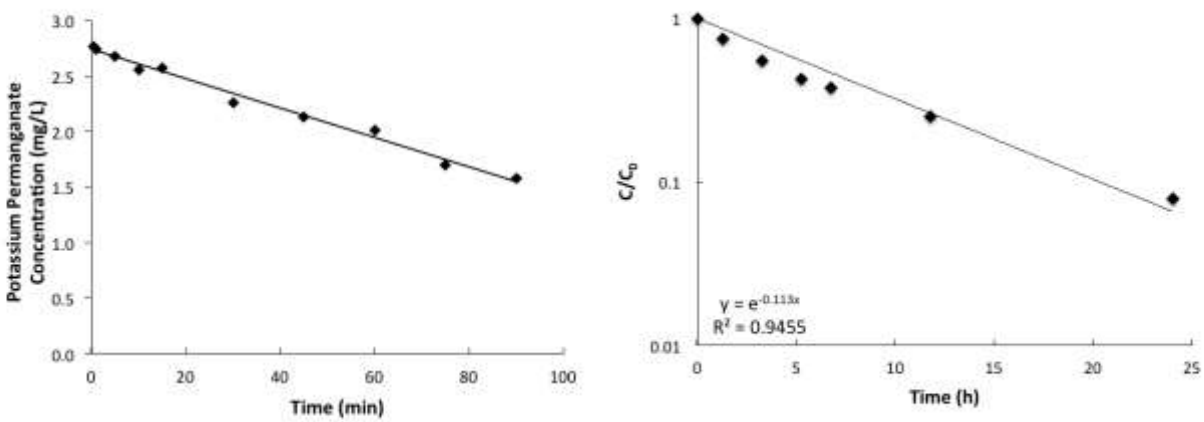
(e)

Figure 22 (cont.). Effect of PAC addition on BAC removal from activated sludge: (c) ibuprofen, (d) sulfamethoxazole, and (e) trimethoprim.

5.3. Potassium Permanganate Preoxidation

Batch tests were conducted in raw OWASA water to determine whether potassium permanganate ($KMnO_4$) is effective for the oxidative transformation of BACs. Tests were conducted with an initial $KMnO_4$ concentration of 3.2 mg/L and initial pharmaceutical concentrations of ~50-70 µg/L.

Initially, tests were conducted in raw OWASA water to determine the decay rate of $KMnO_4$ (Figure 23). Upon addition of 3.2 mg/L $KMnO_4$ to OWASA water, approximately 0.4 mg/L reacted within the first thirty seconds, after which point, the $KMnO_4$ residual decayed linearly over the first 90 minutes (Figure 23a). Over a longer time period, $KMnO_4$ decay was more appropriately described by a first-order exponential decay. Approximately 90% of the initially added $KMnO_4$ had decayed after a contact time of 20 hours (Figure 23b).



(a) (b)

Figure 23. $KMnO_4$ decay rate in OWASA water: (a) first 90 minutes, (b) over 24 hours.

Figure 24 summarizes concentration profiles for six BACs after the addition of 3.2 mg/L $KMnO_4$ to OWASA water (note that the y-axis does not start at zero!). Starting concentrations of each BAC were 55-70 µg/L. Parent compound removal after a contact time of 30 minutes ranged from <5% for TMP to ~5% for SMX, BZF, and MCP, ~10% for IBP and ~20% for DCF. These results suggest that $KMnO_4$ is not effective for the control of pharmaceuticals in drinking water when $KMnO_4$ contact times are short.

An additional experiment was conducted to assess the ability of $KMnO_4$ to oxidize twelve micropollutants (Table 3) that were spiked into OWASA water at environmentally relevant concentrations (~250-600 ng/L). The $KMnO_4$ dose was 3 mg/L, and parent compound removal was assessed after a contact time of 48 hours, which was sufficiently long to allow essentially complete decay of the added $KMnO_4$ (Figure 23b). As shown in Figure 25, $KMnO_4$ was able to oxidize acetaminophen, atenolol, carbamazepine, and tetracycline such that the four BACs were non-detectable after 48 hours. In addition, ~40% of TMP and ~20% of erythromycin were oxidized by $KMnO_4$ over the same time period. In contrast, no measurable removal was observed for the remaining six micropollutants (atrazine, bezafibrate, caffeine, DEET, sulfamethoxazole, and TCEP). Hu et al. (2009, 2010) reported rate constants for the oxidation of BACs by $KMnO_4$ that were in the order carbamazepine > lincomycin > trimethoprim. In the current study, carbamazepine also exhibited a high reactivity towards $KMnO_4$ while TMP and erythromycin, a compound that is structurally similar to lincomycin, exhibited moderate to low reactivities towards $KMnO_4$. Similar to Hu et al. (2010), the results obtained here illustrate that SMX is not oxidized by $KMnO_4$. Overall, the $KMnO_4$ preoxidation results show that $KMnO_4$ is not an effective broad-spectrum oxidant for the control of BACs and other micropollutants.

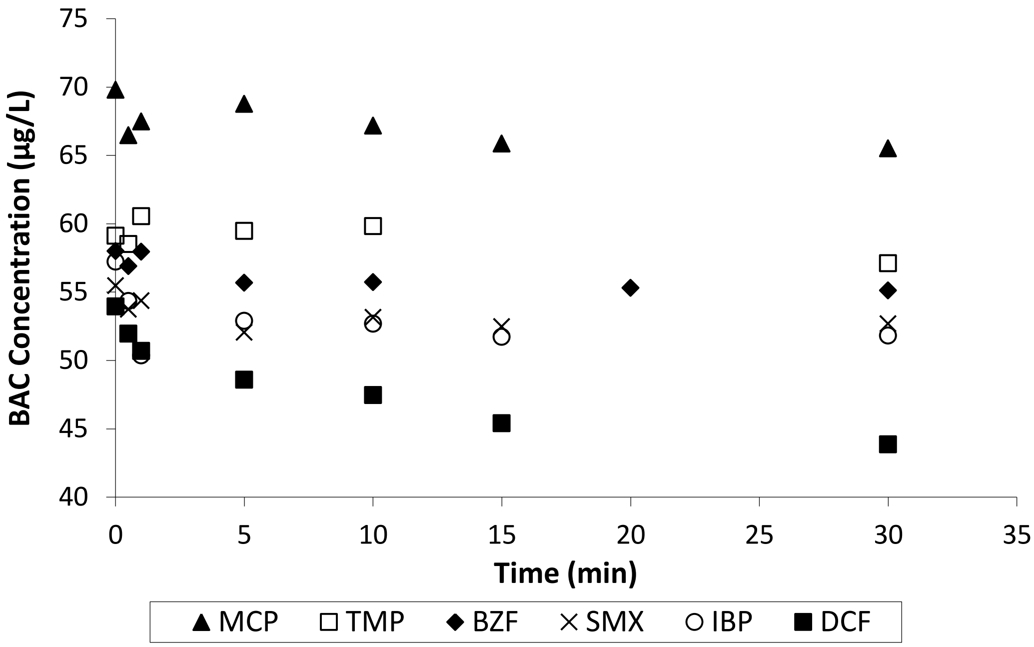


Figure 24. Concentration profiles of six BACs following the addition of 3.2 mg/L $KMnO_4$ into OWASA water.

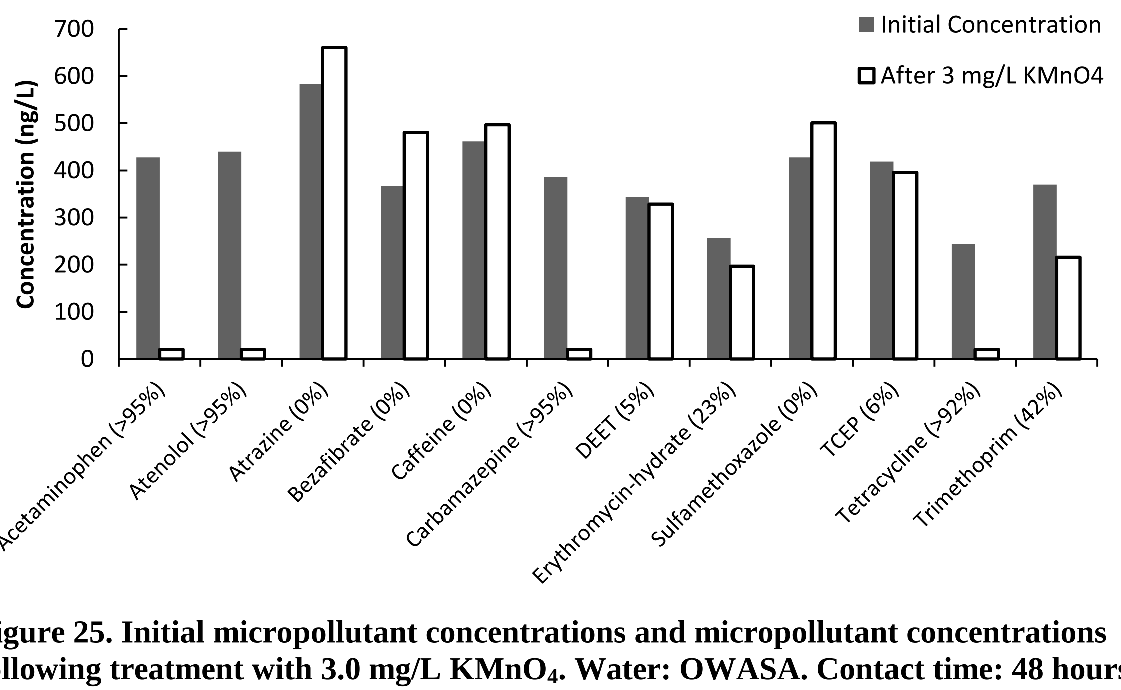


Figure 25. Initial micropollutant concentrations and micropollutant concentrations following treatment with 3.0 mg/L $KMnO_4$. Water: OWASA. Contact time: 48 hours.

5.4. Ozone Oxidation

Batch tests were conducted to determine if ozone is an effective for the oxidation of selected BACs and if BAC removal can be predicted in each water from the ozone decay rate and R_c values.

Ozone Decay and p-CBA Oxidation Rates. Batch tests were conducted to determine (1) the first-order rate constant (k) describing ozone decay in each water, (2) the instantaneous ozone demand of each water ($[O_3]_{0,fit}/[O_3]_{0,actual}$), and (3) the ratio of the hydroxyl radical concentration to the concentration of ozone (R_c) in each water.

To obtain k and $[O_3]_{0,fit}/[O_3]_{0,actual}$, ozone decay was measured as a function of time in each water, and data were described by a first order decay model as follows:

$$ln\frac{[O_3]}{[O_3]_{0,fit}} = -kt \qquad \text{(eq. 4)}$$

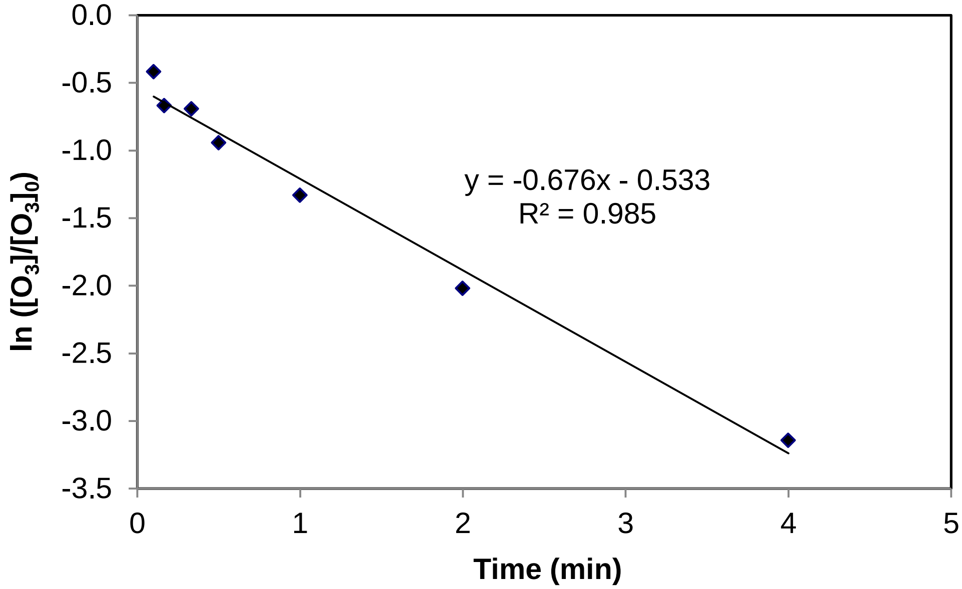
Values of k and $[O_3]_{0,fit}$ were obtained by linear regression, and $[O_3]_{0,actual}$ was determined experimentally.

R_c values were determined from p-CBA oxidation rate data that were plotted as a function of ozone exposure (Elovitz and von Gunten 1999) and evaluated as follows:

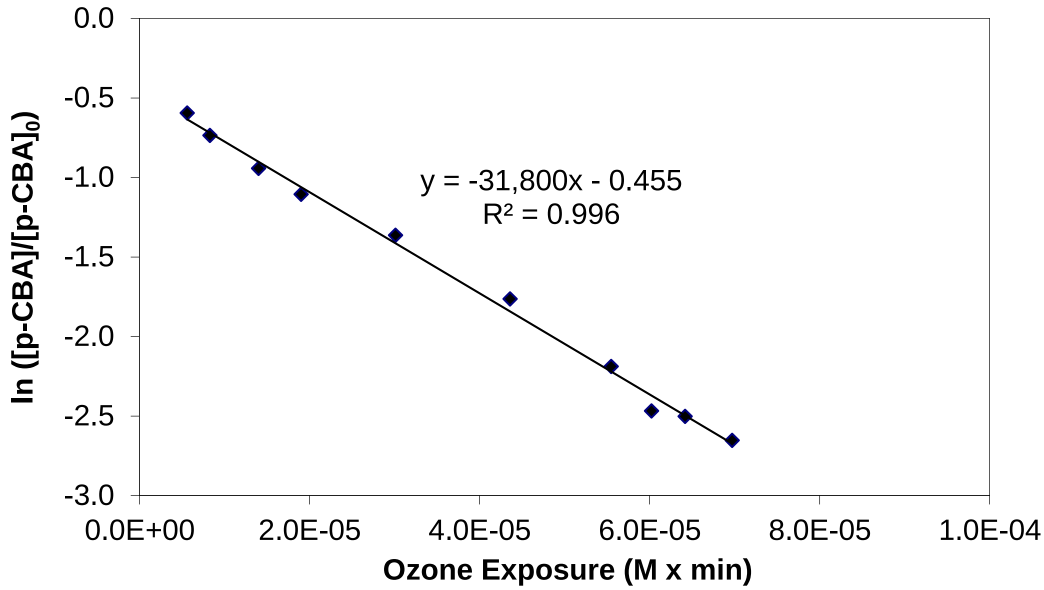
$$ln\frac{[p\text{-}CBA]}{[p\text{-}CBA]_0} = -k_{OH,p\text{-}CBA} * R_c * \int[O_3]\,dt \qquad \text{(eq. 5)}$$

The ozone exposure ($\int[O_3]\,dt$) was calculated from the area under the ozone decay curve, and $k_{OH,p\text{-}CBA}$ is the second order rate constant describing the reaction between the hydroxyl radical and p-CBA ($k_{OH,p\text{-}CBA} = 5x10^9$ M^{-1} s^{-1}, Buxton et al., 1988).

Ozone decay and p-CBA oxidation data were used to determine k, instantaneous ozone demand, and R_c values for each water and ozone dose. Figure 26 summarizes representative data obtained with Cane Creek Reservoir water and an ozone dose of 3.25 mg/L. Ozone decay rate and p-CBA oxidation rate data for additional ozone doses and waters are summarized in Appendix 1.



a)



b)

Figure 26. Ozone decay rate (a) and p-CBA oxidation rate (b) in Cane Creek Reservoir water. Ozone dose: 3.25 mg/L.

The rate constants describing ozone decay (k), ratios of fitted to measured initial ozone concentrations ($[O_3]_{0,fit}/[O_3]_{0,actual}$), and R_c values for each water and ozone dose are summarized in Table 15.

Table 15. Ozone decay rate constants, ratios of fitted to measured initial ozone concentrations, and R_c values for three waters at two ozone doses.

Water	Ozone Dose (mg/L)	O_3:TOC	k (min^{-1})	$[O_3]_{0,fit}/[O_3]_{0,actual}$	R_c
Cane Creek Reservoir	1.48	0.32	3.060	0.489	3.37×10^{-7}
	3.25	0.71	0.676	0.587	1.05×10^{-7}
Cape Fear River	2.48	0.42	7.820	0.522	9.34×10^{-7}
	4.74	0.79	0.804	0.540	1.19×10^{-7}
Cary WWTP Effluent	2.18	0.33	4.990	0.321	4.55×10^{-7}
	4.17	0.63	0.913	0.634	1.02×10^{-7}

As shown in Table 15, both k and R_c values were higher at the lower ozone doses. Higher k values indicate that ozone decayed more rapidly at lower ozone concentrations. As a result, the hydroxyl radical concentration relative to the ozone concentration (R_c) was higher than that at higher ozone doses. For the three waters tested here, a strong linear trend between k and R_c was obtained ($r^2 = 0.97$, n = 6). It is also interesting to note that k and R_c values for the treated wastewater were similar to those for the Cane Creek Reservoir water. Although effluent organic matter in wastewater likely enhanced hydroxyl radical formation relative to the natural organic matter in surface water, the enhanced hydroxyl radical formation was likely counterbalanced by the higher alkalinity of the wastewater (~75 mg/L as $CaCO_3$ compared to ~25 mg/L as $CaCO_3$ in the surface water) because carbonate species act as hydroxyl radical scavengers.

BAC Oxidation by Ozone. The oxidation of BZF, IBP, SMX, TMP, and DCF was determined experimentally at two ozone doses in each water. Table 16 summarizes the parent compound removal percentages that were measured for each BAC. The results in Table 16 illustrate that essentially complete removal was obtained for SMX, TMP, and DCF at the lower O_3 doses (~0.3-0.4 mg O_3/mg TOC) and for all 5 compounds at the higher O_3 doses (0.6-0.9 mg O_3/mg TOC). BZF and IBP proved to be the most challenging to remove from WWTPE; at the lower O_3 dose, 70% parent compound removal was obtained for each compound (Table 16).

Table 16. Experimentally determined percent parent compound removal for five model BACs. Ozone doses are $[O_3]_{0,actual}$

Water	Parent Compound Removal (%)									
	BZF		IBP		SMX		TMP		DCF	
	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%	$[O_3]_o$ mg/L	%
Cane Creek Reservoir	1.72	94.5	1.77	87	1.86	> 99	1.73	> 99	1.83	> 99
	3.68	> 95	4.06	> 99	3.86	> 99	3.68	> 99	4.06	> 99
Cape Fear River	2.03	94.5	2.14	92	2.39	> 99	2.28	> 99	2.50	> 99
	4.47	> 95	4.48	> 99	4.43	> 99	4.47	> 99	4.48	> 99
Cary WWTP Effluent	2.00	70	2.09	70	2.21	> 99	1.76	> 99	1.94	> 99
	3.80	> 95	4.08	> 99	4.28	> 99	3.80	> 99	4.08	> 99

Parent Compound Removal Predictions. The extent of BAC oxidation in a given water was predicted from:

$$\frac{[BAC]}{[BAC]_0} = e^{[\frac{([O_3]_{0,actual}}{k}\frac{[O_3]_{0,fit}}{[O_3]_{0,actual}})(k_{OH}R_c + k_{O_3})(e^{-kt}-1)]} \qquad \text{(eq. 6)}$$

where k_{OH} and k_{O3} are the second order rate constants describing the rate of BAC oxidation by the hydroxyl radical and by ozone, respectively. Values for k_{OH} and k_{O3} were compiled from the literature. The ultimate conversion, as time approaches infinity (or ozone has completely reacted away), is given by the expression:

$$\frac{[BAC]}{[BAC]_0} = e^{-[\frac{([O_3]_{0,actual}}{k}\frac{[O_3]_{0,fit}}{[O_3]_{0,actual}})(k_{OH}R_c + k_{O_3})]} \qquad \text{(eq. 7)}$$

Finally, percent parent compound removal was calculated with the expression:

$$\%\ Parent\ Compound\ Removal = \left(1 - \frac{[BAC]}{[BAC]_0}\right) \times 100 \qquad \text{(eq. 8)}$$

To distinguish between contributions of molecular ozone and hydroxyl radicals to the extent of BAC oxidation, the fraction of BAC removal due to reaction with the hydroxyl radical was determined from:

$$f_{OH\cdot} = \frac{k_{OH}R_c}{k_{OH}R_c + k_{O_3}} \qquad \text{(eq. 9)}$$

The parent compound removal percentages attributable to hydroxyl radicals and due to ozone were calculated by multiplying percent parent compound removal (eq. 9) by f_{OH} for hydroxyl radicals and $(1-f_{OH})$ for ozone.

Using equations 7 and 8, the extent of BAC oxidation by ozone at ozone doses of ~0.35 mg O_3/mg TOC and ~0.7 mg O_3/mg TOC was predicted for 26 BACs in all three waters. Second order rate constants describing the oxidation rates by molecular ozone (k_{O3}) and by the hydroxyl radical (k_{OH}) were obtained from the literature (Table 17).

Table 17. Second order rate constants describing the oxidation of BACs by ozone and by hydroxyl radicals (from Huber et al. 2003, 2005; Dodd et al. 2006; Ikehata et al. 2006; Suarez et al. 2007)

Compound Name	Compound Class	k_{O3} (M^{-1} s^{-1})	k_{OH} (M^{-1} s^{-1})
Amoxicillin	β-lactam antibiotic	6×10^6 (pH 7)	3.93×10^9 (pH 5.5)
Penicillin G	β-lactam antibiotic	4.8×10^3 (pH 7)	7.3×10^9 (pH 7)
Cephalexin	β-lactam antibiotic	8.7×10^4 (pH 7)	8.5×10^9 (pH 7)
Azithromycin	Macrolide antibiotic	1.1×10^5 (pH 7)	2.9×10^9 (pH 7)
Roxithromycin	Macrolide antibiotic	6.3×10^4 (pH 7)	8.2×10^9 (pH 7)
Tylosin	Macrolide antibiotic	5.1×10^5 (pH 7)	5.4×10^9 (pH 7)
Sulfamethoxazole	Sulfonamide antibiotic	5.5×10^5 (pH 7)	5.5×10^9 (pH 7)
N(4)-Acetyl-sulfamethoxazole	Sulfonamide antibiotic metabolite	2.5×10^2 (pH 7)	6.8×10^9 (pH 7)
Ciprofloxacin	Fluoroquinolone antibiotic	1.9×10^4 (pH 7)	4.1×10^9 (pH 7)
Enrofloxacin	Fluoroquinolone antibiotic	1.5×10^5 (pH 7)	4.5×10^9 (pH 7)
Trimethoprim	Dihydrofolate reductase inhibitor antibiotic	2.7×10^5 (pH 7)	6.9×10^9 (pH 7)
Lincomycin	Lincosamide antibiotic	6.7×10^5 (pH 7)	8.5×10^9 (pH 7)
Tetracycline	Tetracycline antibiotic	1.9×10^6 (pH 7)	7.7×10^9 (pH 7)
Vancomycin	Glycopeptide antibiotic	6.1×10^5 (pH 7)	8.1×10^9 (pH 7)
Amikacin	Aminoglycoside antibiotic	1.8×10^3 (pH 7)	7.2×10^9 (pH 7)
Triclosan	Antimicrobial agent	3.8×10^7 (pH 7)	5.4×10^9 (pH 7)
Carbamazepine	Anticonvulsant	~ 3×10^5 (pH 7)	8.8×10^9 (pH 7)
Diazepam	Anti-anxiety agent	0.75 (pH 7)	7.2×10^9 (pH 7)
Diclofenac	Non-steroidal anti-inflammatory	~1×10^6 (pH 7)	7.5×10^9 (pH 7)
Naproxen	Non-steroidal anti-inflammatory	~2×10^5 (pH 7)	9.6×10^9 (pH 7)
Ibuprofen	Analgesic	9.6 (pH 7)	7.4×10^9 (pH 7)
Estrone	Natural estrogen	9.4×10^5 (pH 7)	2.6×10^{10}
17α-Ethinylestradiol	Synthetic estrogen contraceptive	~3×10^6 (pH 7)	~1×10^{10} (pH 7)
Bezafibrate	Lipid regulator	590 (pH 5-10)	7.4×10^9 (pH 7)
Clofibric acid	Lipid regulator metabolite	2550 (pH 6.5)	2.38×10^9
Iopromide	X-ray contrast medium	<0.8 (pH 5-10)	3.3×10^9 (pH 7)

For the 26 BACs, predicted parent compound removals in Cane Creek Reservoir water are shown in Figure 27. For each compound, the fractional removals attributable to molecular ozone and the hydroxyl radical are indicated. At the lower ozone dose, essentially complete parent compound removal was predicted for 18 of the 26 compounds. At the higher ozone dose, >95% parent compound removal was predicted for all BACs except iopromide. For the majority of the BACs, oxidation by molecular ozone dominated overall parent compound removal, suggesting that their oxidative transformation is more effectively accomplished under conditions that favor long ozone half lives (high alkalinity, no H_2O_2 addition). These BACs, which exhibit higher k_{O3} values, were effectively oxidized by ozone, even at O_3:TOC ratios. For compounds with lower k_{O3} values (e.g., iopromide, diazepam, ibuprofen, N(4)-acetyl-sulfamethoxazole, bezafibrate), for which oxidation was governed by the hydroxyl radical, lower parent compound removals were predicted (Figure 27). Predicted BAC transformation percentages in Cape Fear River water and Cary WWTPE are summarized in Appendix 2.

a)
b)

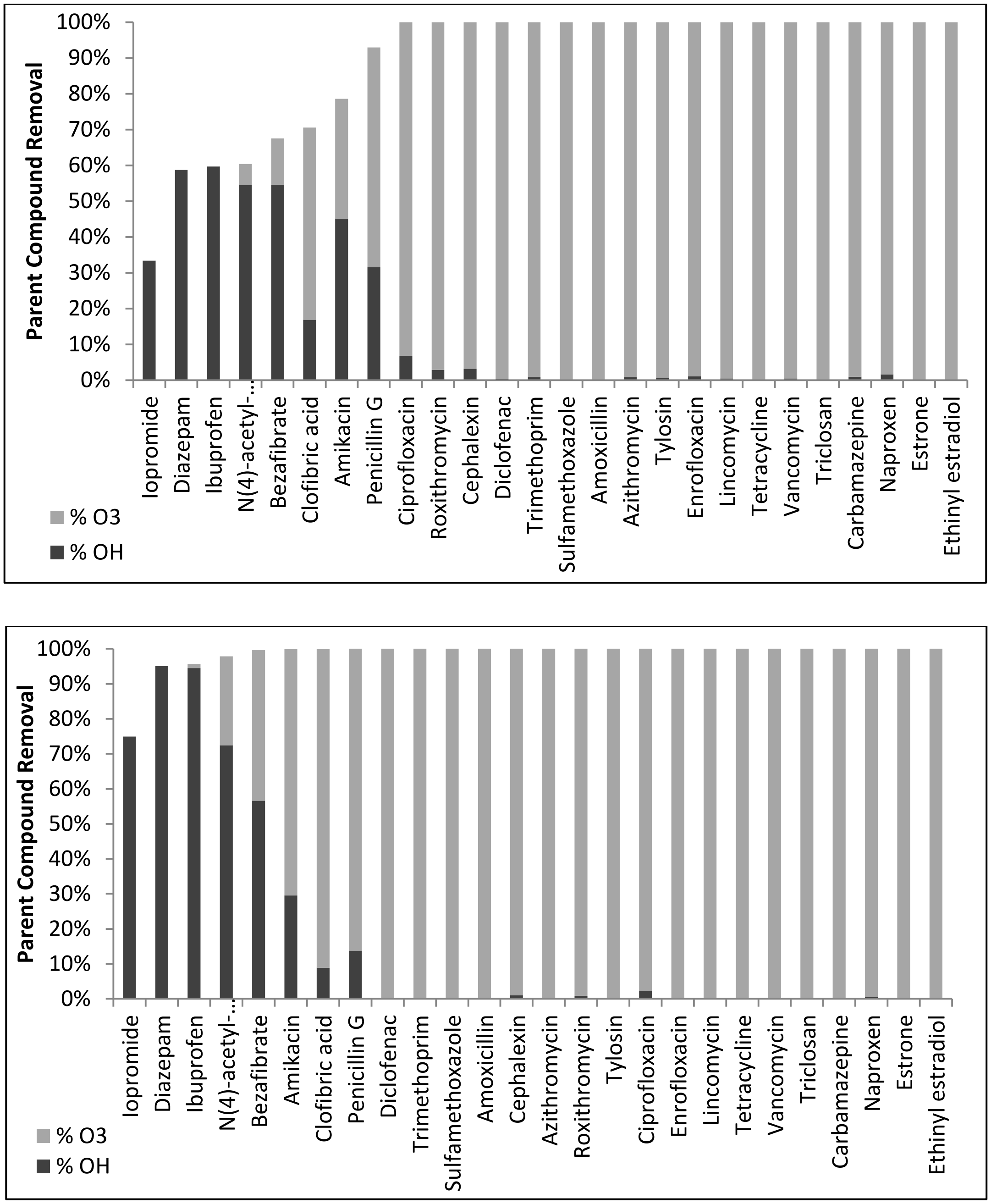


Figure 27. Predicted parent compound removal percentages in Cane Creek Reservoir water with (a) 1.75 mg/L ozone (0.38 mg O_3/mg TOC) and (b) 3.5 mg/L ozone (0.76 mg O_3/mg TOC)

Validation of Model Predictions. Model predictions were compared with experimental results obtained for BZF, IBP, DCF, TMP, and SMX (Figure 28). The dashed error bars for the predicted removals represent the predicted range based on uncertainty in (1) the second order rate constants k_{O3} and k_{OH}, (2) the R_c values, and (3) the k values for ozone decay. Upper and lower bounds of the 95% confidence intervals of k, k_{O3}, k_{OH}, and R_c were used to determine the predicted range of parent compound removals. The error bars indicate that uncertainty in the predictions is substantial when BAC oxidation was incomplete (see BZF and IBP at lower ozone doses).

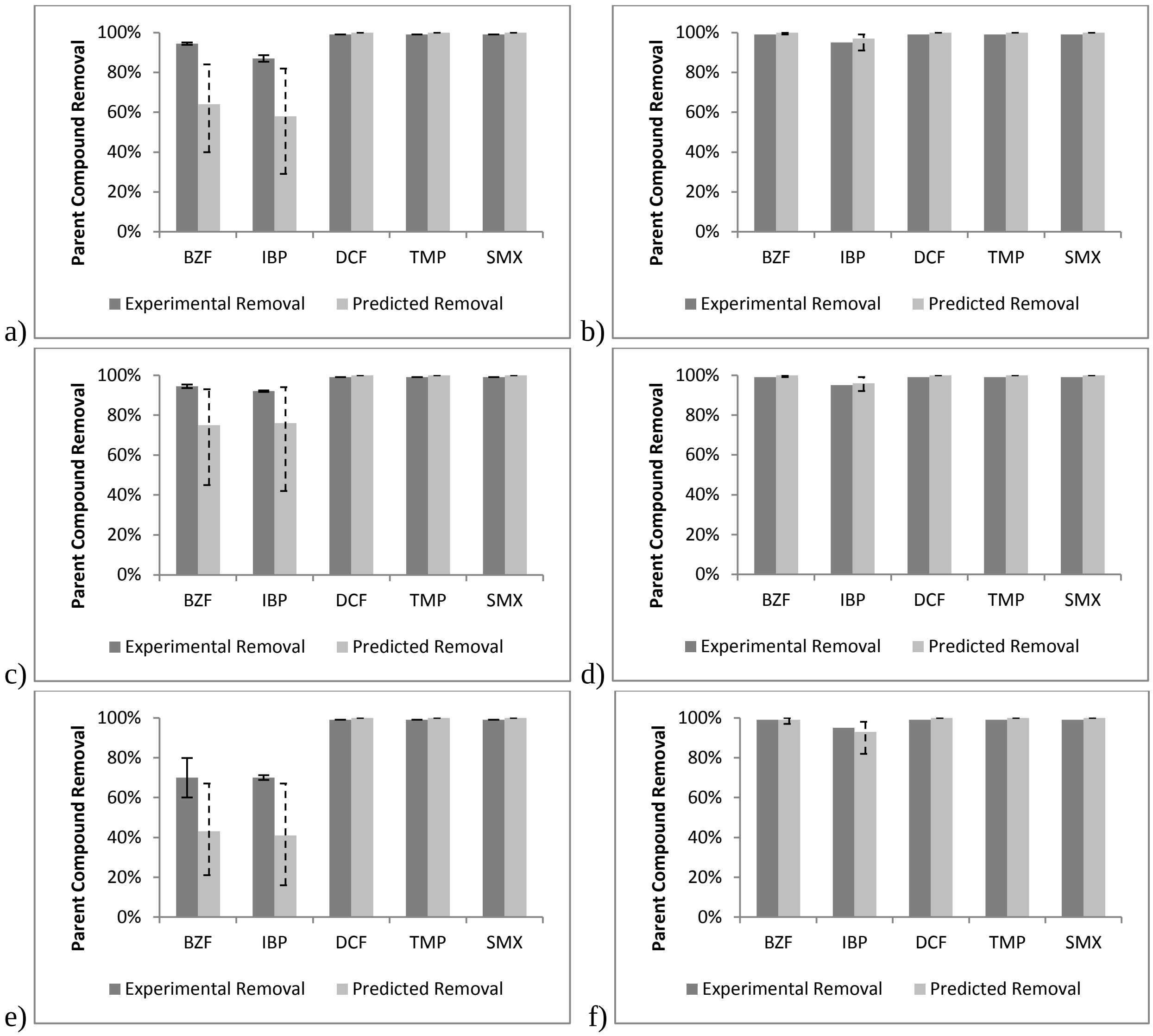


Figure 28. Comparisons of predicted and experimentally determine BAC removals from (a) Cane Creek with 1.75 mg/L O_3, (b) Cane Creek with 3.5 mg/ L O_3, (c) Cape Fear with 2.5 mg/L O_3, d) Cape Fear with 4.5 mg/L O_3, (e) WWTPE with 2.25 mg/L O_3, and (f) WWTPE 4.4 mg/ L O_3.

For higher ozone doses, both predictions and experimental data indicate essentially complete parent compound removal for all five BACs (Figure 28b, d, and f). At lower ozone doses, predicted and experimental removals compared well for DCF, TMP, and SMX (Figure 28a, c, e), the compounds for which oxidative transformation was essentially complete. For BZF and IBP, however, experimentally determined parent compound removals exceeded predicted removals at the lower O_3 doses. Model predictions were made assuming a constant R_c value throughout the entire ozone decay. It has been shown that the R_c value decreases in the period immediately following the addition of ozone (Buffle et al. 2006), and this phenomenon was not captured in the experimental and modeling approaches presented here. The negative y-axis intercept in Figure 26b illustrates that R_c values were higher during the initial period of ozone exposure, for which no data could be collected (t < 5 sec). As a result, the removal predictions for compounds for which oxidative removal is dominated by the hydroxyl radical, as is the case for IBP and BZF, were lower than experimentally determined removals.

An additional experiment was conducted to assess the ability of ozone to oxidize twelve micropollutants (Table 3) that were spiked into OWASA water at environmentally relevant concentrations (~250-600 ng/L). The ozone dose was 3.5 mg/L (O_3:TOC ~0.7 mg O_3/mg TOC), and parent compound removal was assessed after a contact time of 20 minute, which was sufficiently long for ozone to decay completely (Figure 26a). As shown in Figure 29, ozone effectively oxidized 11 of the 12 compounds in the micropollutant mixture, and oxidation percentages for the 11 compounds ranged from ~79% for atrazine to >90% for the remaining 10 compounds. Ozonation was not effective for controlling the flame retardant TCEP, however. For the three compounds that were also studied at higher initial concentrations (BZF, SMX, TMP), the results obtained at environmentally relevant concentrations confirmed that essentially complete transformation is achieved when ozone is dosed at an O_3:TOC ratio of ~0.7 mg O_3/mg TOC (Figure 28b).

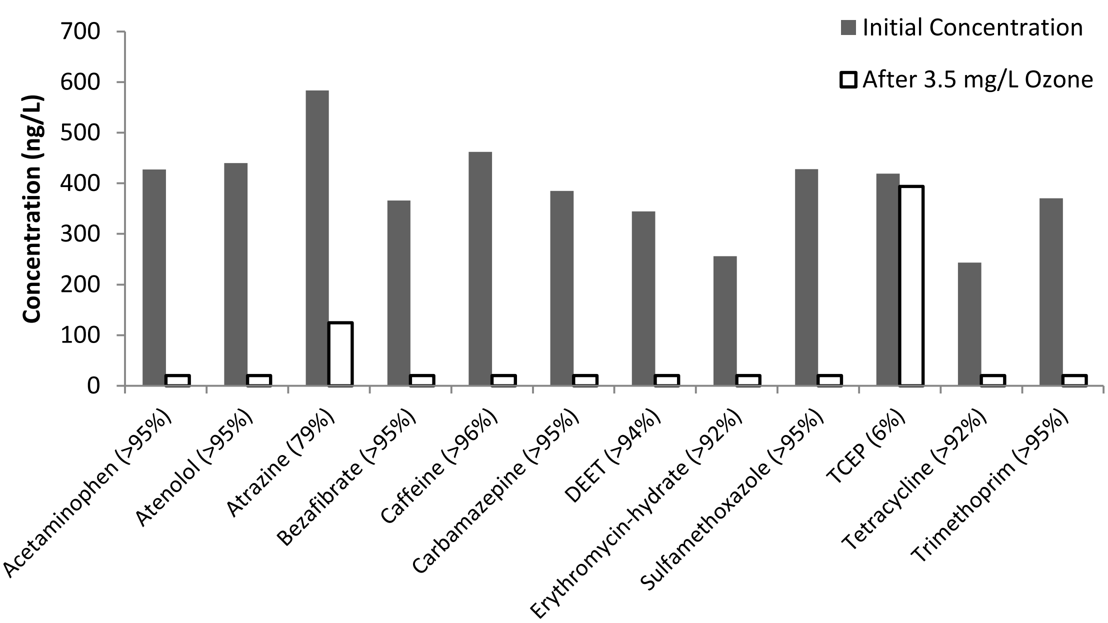


Figure 29. Initial micropollutant concentrations and micropollutant concentrations following treatment with 3.5 mg/L O_3. Water: OWASA.

Ozone Dose Prediction for 99% Parent Compound Removal. Ozone doses required to achieve 99% parent compound removal were predicted for the four compounds that were most difficult to oxidize by ozone (iopromide, diazepam, ibuprofen, and N(4) acetyl-sulfamethoxazole, see Figure 27). TCEP was not included in this analysis because of its recalcitrance towards oxidation by ozone. For the predictions, values for k, $[O_3]_{0,fit}/[O_3]_{0,actual}$, and R_c were used that corresponded to the higher O_3 doses in Table 15. Table 18 illustrates that O_3 doses of ~1 mg O_3/mg TOC will be sufficient to achieve 99% parent compound removal for all compounds except iopromide. Ozone doses in this range are not uncommon during preozonation of North Carolina surface waters. As a result, utilities employing this treatment practice can expect to effectively oxidize 25 of the 26 BACs, for which parent compound removal predictions were made in this study. To achieve 99% parent compound removal for iopromide, ozone doses >2 mg O_3/mg TOC would be required. Such doses are cost-prohibitive for the tested waters. In addition, byproduct formation (e.g. bromate) can become increasingly problematic as the O_3 dose is increased. One interesting result in Table 18 is that the effectiveness of ozone for BAC transformation is similar in the tested surface waters and in the WWTP effluent. This result suggests that the ozonation of WWTP effluents, an important source of BACs, can effectively oxidize BAC parent compounds at doses (costs) that closely match those required during the preozonation of surface waters with moderate levels of TOC.

Table 18. Predicted ozone doses for 99% parent compound removal in three waters

Water	Compound	O_3 Dose for 99% Parent Compound Removal (mg/L)
Cane Creek Reservoir	Iopromide	12.2
	Diazepam	5.6
	Ibuprofen	5.4
	N(4) acetyl-SMX	4.4
Cape Fear River	Iopromide	13.9
	Diazepam	6.4
	Ibuprofen	6.2
	N(4) acetyl-SMX	5.2
Cary WWTPE	Iopromide	15.7
	Diazepam	7.2
	Ibuprofen	6.9
	N(4) acetyl-SMX	5.6

6. Conclusions

The overall objective of this research was to evaluate the BAC removal effectiveness of treatment processes commonly employed to treat NC surface waters. The following treatment processes were investigated: (1) coagulation with ferric sulfate, (2) PAC adsorption plus alum coagulation, (3) potassium permanganate preoxidation, and (4) preozonation. A summary of key results obtained with a 12-compound micropollutant mixture that was spiked into OWASA water at environmentally relevant concentrations (~250-600 ng/L) is shown in Figure 30 and can be described as follows:

- Ferric sulfate coagulation was able to remove ~75% tetracycline, but removals of the remaining 11 micropollutants was negligible.
- The addition of 20 mg/L NuChar PAC and 55 mg/L alum led to the removal of all 12 micropollutants, and removal percentages ranged from 66% for sulfamethoxazole to >95% for trimethoprim.
- Preoxidation with 3 mg/L $KMnO_4$ effectively transformed four BACs (acetaminophen, atenolol, carbamazepine, and tetracycline). Partial oxidation was achieved for trimethoprim (~40%) and erythromycin (~20%), while no measurable oxidation was obtained for the remaining six compounds (atrazine, bezafibrate, caffeine, DEET, sulfamethoxazole, and TCEP). These results illustrate that KMnO4 is not an effective broad spectrum oxidant for the control of BACs and other micropollutants.
- Addition of 3.5 mg/L O_3 (O_3:TOC ratio = 0.7), effectively oxidized 11 of the 12 compounds in the micropollutant mixture, and oxidation percentages for the 11 compounds ranged from ~79% for atrazine to >90% for the remaining 10 compounds. Ozonation was not effective for controlling the flame retardant TCEP, however.

For the two most effective treatment options for BAC removal, PAC adsorption and ozonation, additional experiments were conducted. The following conclusions were derived from ozonation data:

- Both the ozone decay rate (k) and the ratio of hydroxyl radical to ozone concentration (R_c) were higher at the lower of the two tested ozone doses. R_c values in the two surface waters and the WWTP effluent ranged from $3x10^{-7}$ to $9x10^{-7}$ at the lower ozone dose (~0.35 mg O_3/mg TOC) and from $1.0x10^{-7}$ to $1.2x10^{-7}$ at the higher ozone dose (~0.7 mg O_3/mg TOC).

- The magnitudes of k and R_c were similar for the WWTP effluent and the OWASA raw water. Although effluent organic matter in wastewater likely promoted hydroxyl radical formation more effectively than the natural organic matter in surface water, the enhanced hydroxyl radical formation was likely counterbalanced by the higher alkalinity of the wastewater (~75 mg/L as $CaCO_3$ compared to ~25 mg/L as $CaCO_3$ in the surface water) because carbonate species act as hydroxyl radical scavengers.

- Using the k and R_c values together with the second order rate constants describing BAC oxidation by molecular ozone and hydroxyl radicals, the extent of BAC transformation was predicted for 26 BACs. Based on the predictions, an O_3 dose corresponding to 1 mg

O_3/mg TOC is expected to yield ~99% transformation or greater for 25 of the 26 BACs in all three of the tested waters. The most recalcitrant among the 26 compounds for which predictions were made, iopromide, would require an ozone dose of >2 mg O_3/mg TOC to achieve 99% oxidation. The results of the model predictions and validation experiments suggest that reasonable ozone doses lead to meaningful levels of BAC transformation in both drinking water sources and in treated wastewater.

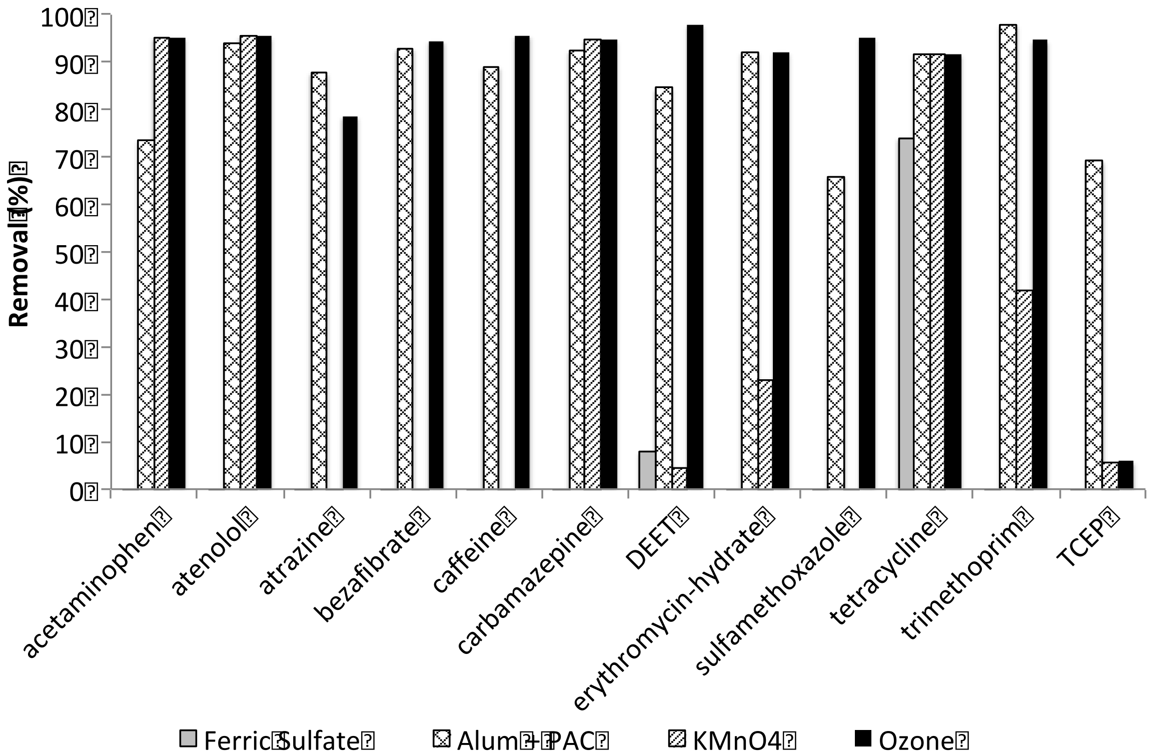


Figure 30. Summary of micropollutant removal/oxidation percentages achieved with treatment processes commonly employed to treat NC surface waters. Treatment conditions: (1) coagulation with 70 mg/L ferric sulfate pentahydrate at pH 5.6, (2) 20 mg/L NuChar PAC in combination with 55 mg/L alum at pH 6.3, (3) 3 mg/L $KMnO_4$ and a contact time of 48 hours, and (4) 3.5 mg/L ozone. Micropollutants were spiked into raw OWASA water at initial concentrations ranging from 250 to 600 ng/L.

The following conclusions were derived from PAC adsorption data:

- Over the 2-hour duration of batch kinetic tests, TMP removal was strongly affected by PAC type while SMX removal was not. For TMP, wood-based PAC was most effective, followed by coal-based PAC and finally lignite-based PAC. At adsorption equilibrium, coal based PAC exhibited the largest adsorption capacity for both SMX and TMP. The wood based PAC had the lowest adsorption capacity for SMX, and the lignite based PAC had the lowest adsorption capacity for TMP.

- PAC particle size strongly affected BAC and NOM removal. Compared to the as-received PAC, adsorption kinetics of BACs and NOM were faster with S-PAC. In addition, a higher NOM adsorption capacity was obtained with sub-micrometer PAC (S-PAC).

- Because of their acid-base characteristics, the removal of BACs is affected by solution pH. Over the tested pH range of 4 to 7, removal of the weak acid SMX increased with decreasing pH (or as the anionic form of SMX became less prevalent). Removal of the weak organic base TMP increased with increasing pH (or as the cationic form of TMP became less prevalent).

- Differences in TMP and SMX removal were small between the two drinking water sources (Cape Fear River and OWASA water). This observation illustrates that the concentration of competing background organic matter in Cape Fear River water did not differ substantially from that in OWASA water. In contrast, the background organic matter in the WWTPE exerted a stronger competitive effect and lowered the BAC removal effectiveness of PAC.

- The presence of aluminum hydroxide floc did not significantly affect SMX removal, but it adversely affected TMP removal. Most likely, electrostatic repulsion between cationic TMP and positively charged metal hydroxide floc, in which the PAC was embedded, contributed to this result.

- The timing of PAC addition relative to the addition of the coagulant was important for TMP removal, but not for SMX removal. TMP removal was lower when PAC was added together with coagulants than when PAC was added either 5 minutes before the coagulant or 9 minutes into the flocculation step. The timing of PAC addition also affected turbidity removal. When PAC was added before or together with coagulants, turbidity removal was generally greater than that obtained in tests in which PAC was added 9 minutes into the flocculation process. To obtain the best settled water quality in terms of BAC and turbidity removal, PAC should be added before the coagulant (e.g. at the intake).

- The application of sub-micrometer diameter PAC (S-WPH) achieved a given BAC removal percentage at lower doses than as-received PACs. To obtain 90% removal of weakly adsorbing SMX and IBP, S-WPH doses in the 15-25 mg/L range would be required in the tested NC drinking water sources. In the WWTP effluent, the S-WPH dose required to achieve 90% SMX and IBP removal is ~30 mg/L. For the as-received PACs, 90% removal of SMX and IBP required PAC doses of 75 mg/L or greater. The addition of S-WPH also enhanced NOM removal relative to that obtained with as-received PACs. Settled water turbidity in samples that received S-WPH were higher than those that received as-received PAC. Flocculant aids may therefore be required to effectively incorporate S-PAC into settleable floc. The application of S-PAC is promising because both meaningful BAC and NOM removal can be obtained at reasonable S-PAC doses.

- The presence of activated sludge biosolids did not measurably affect BAC removal by PAC.

- The addition of PAC to activated sludge basins can (1) enhance the removal of strongly adsorbing BACs at short contact times, (2) remove recalcitrant BACs, and (3) possibly enhance biodegradation of BACs if biofilms form on the PAC surface.

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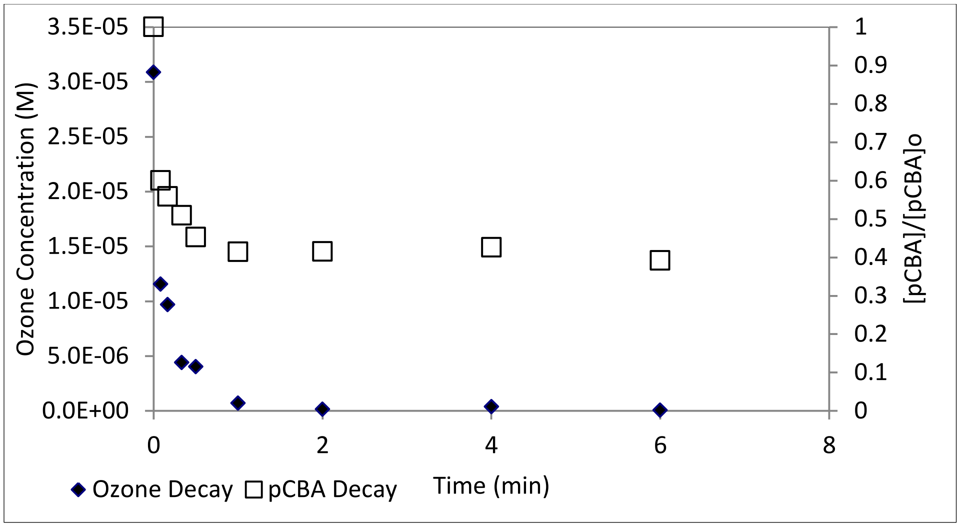
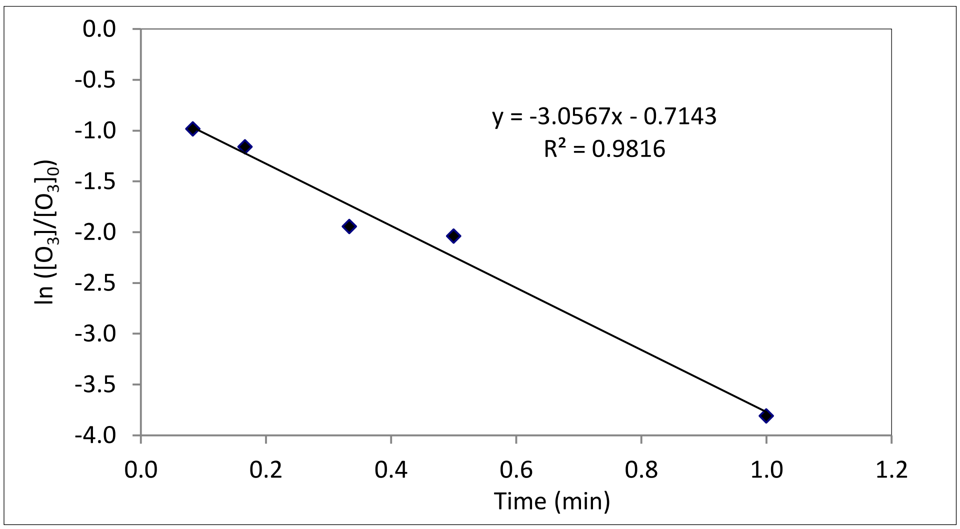
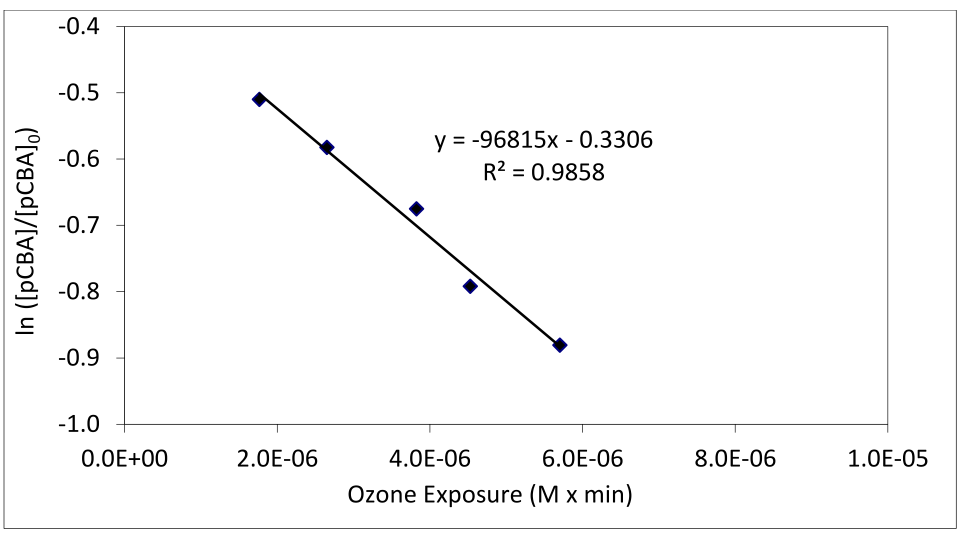
Appendix 1: Ozone Decay and p-CBA Oxidation Rates

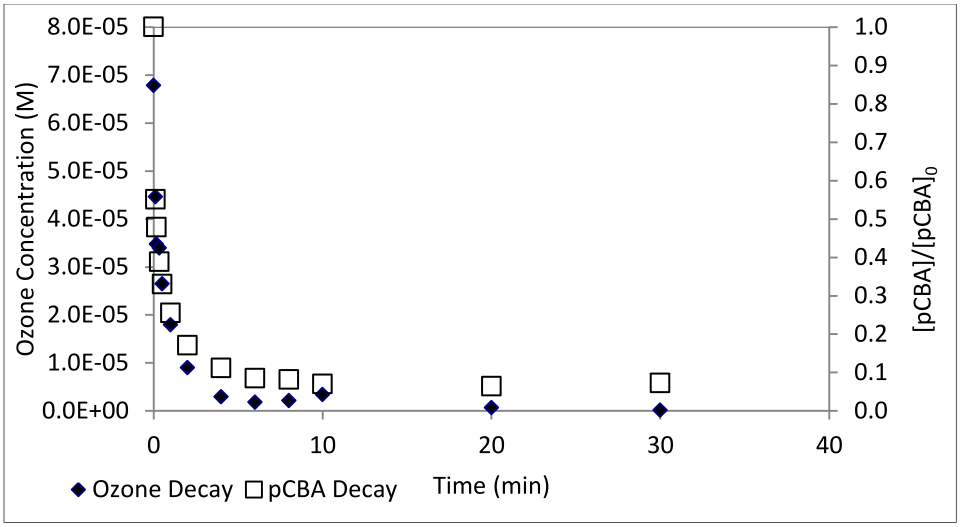
A. Cane Creek $[O_3]_0 = 1.75$ mg/l

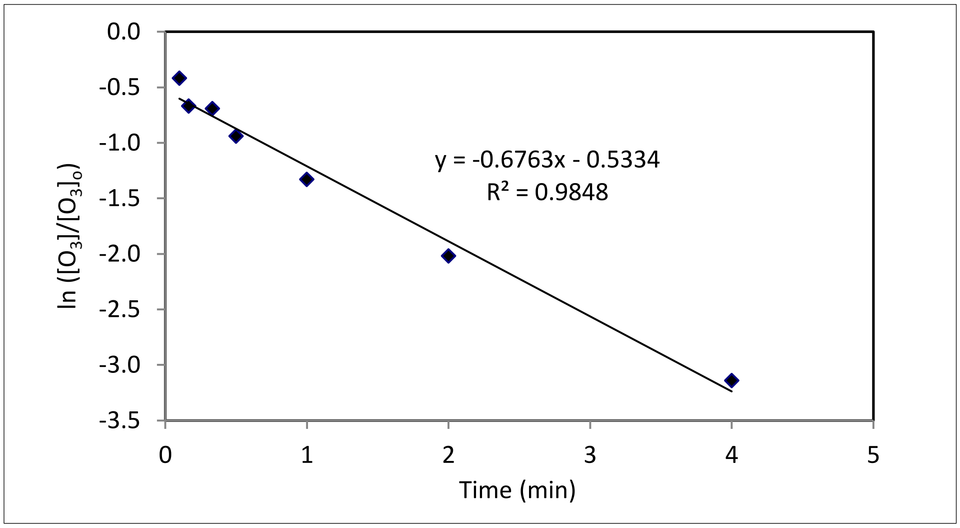


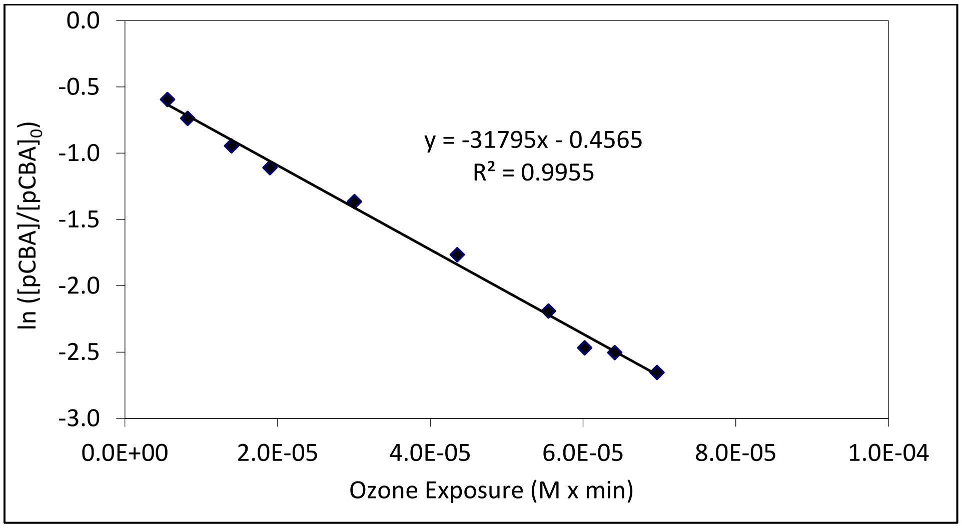




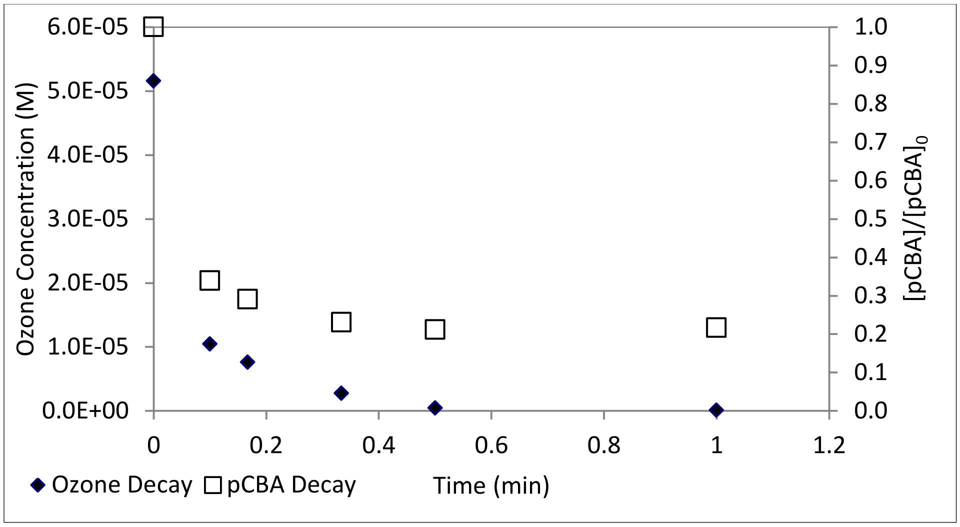
B. Cane Creek $[O_3]_0$ = 3.5 mg/l

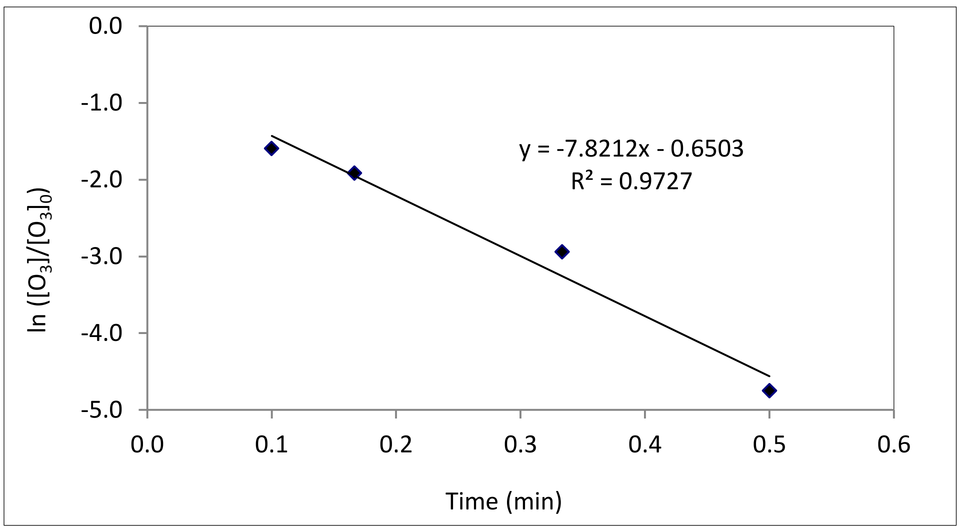


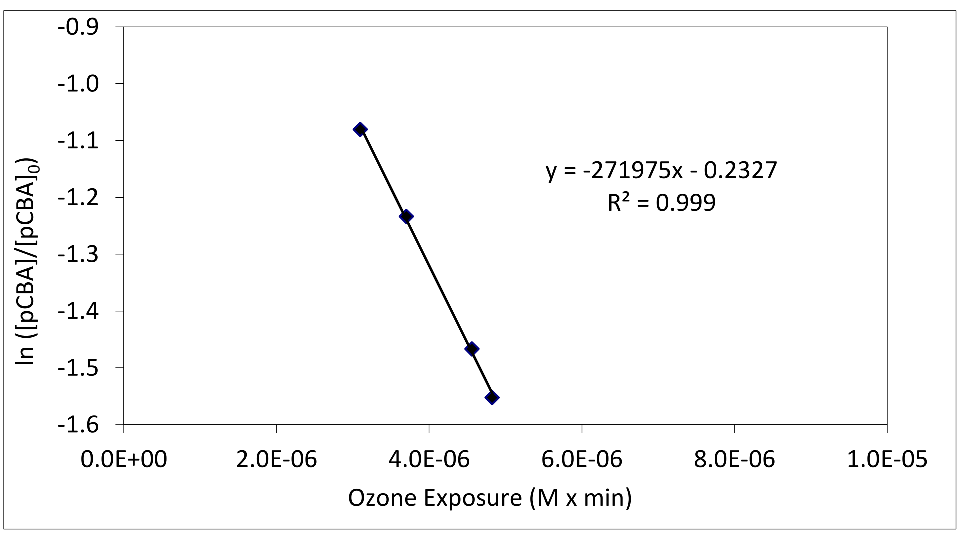




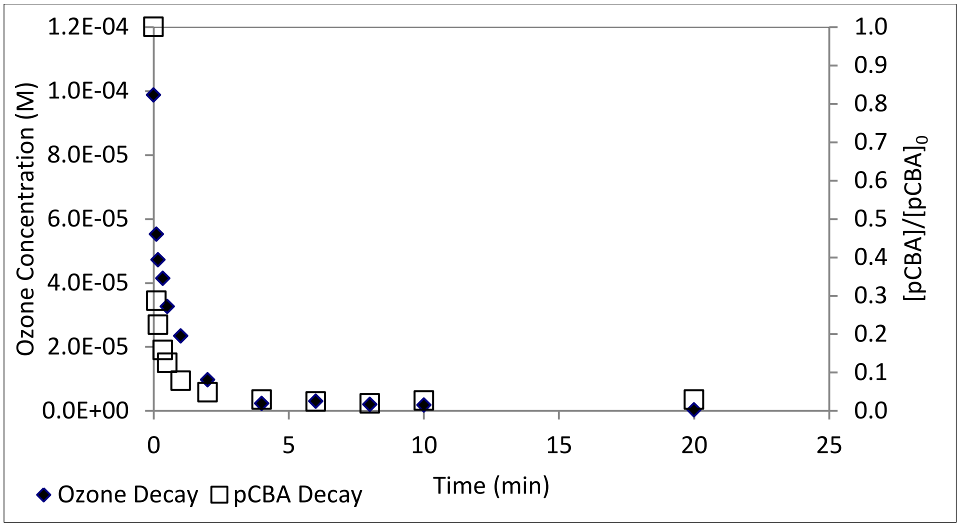
C. Cape Fear $[O_3]_0 = 2.5$ mg/l

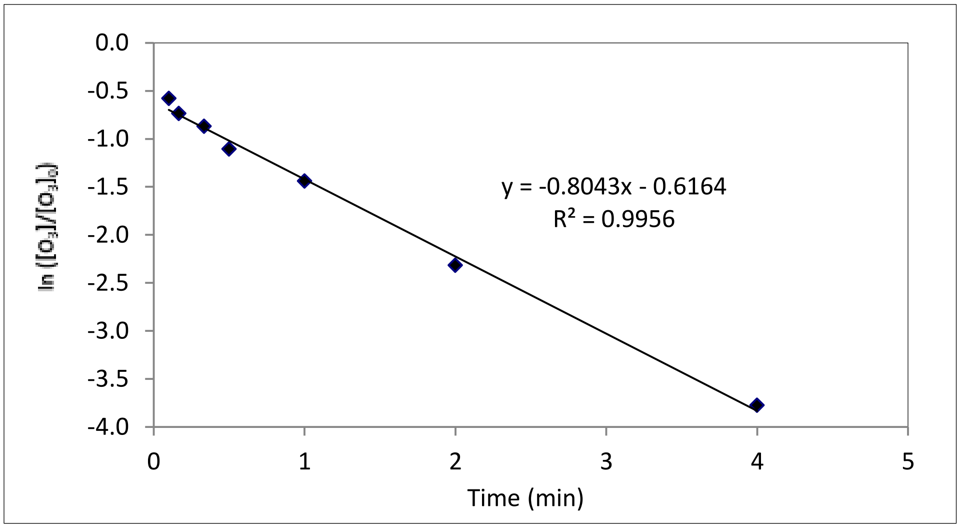


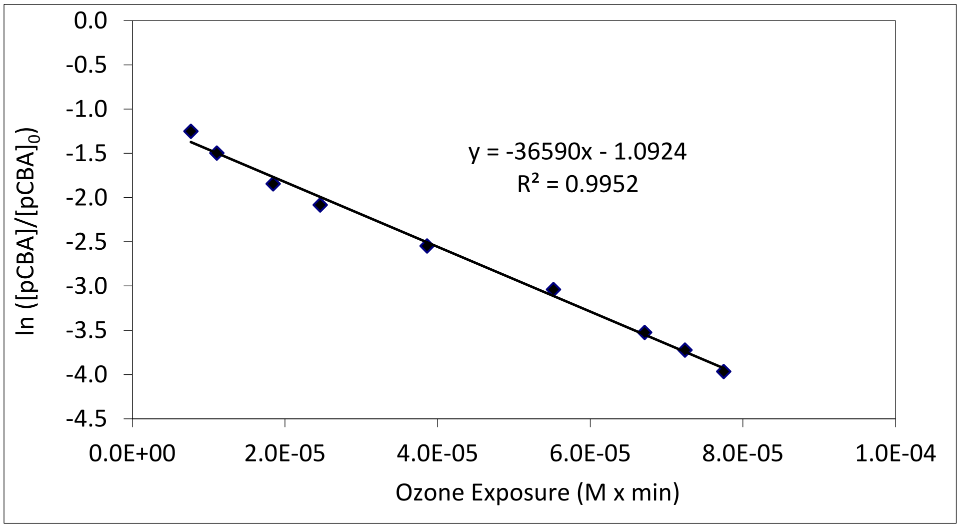




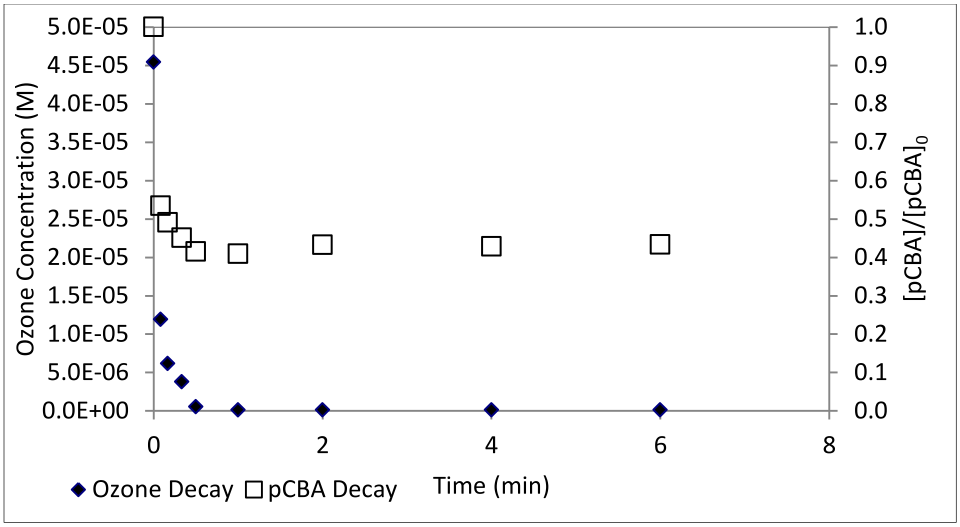
D. Cape Fear $[O_3]_0$ = 4.5 mg/l

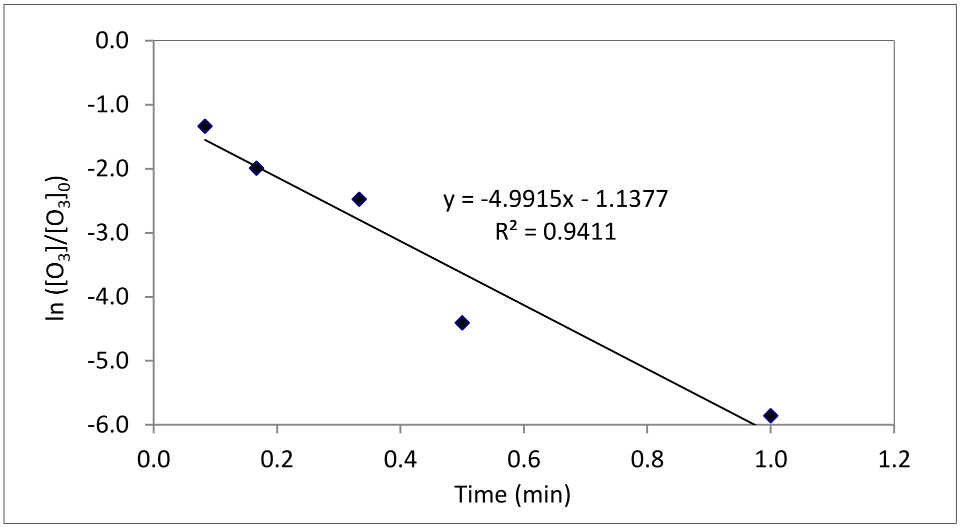


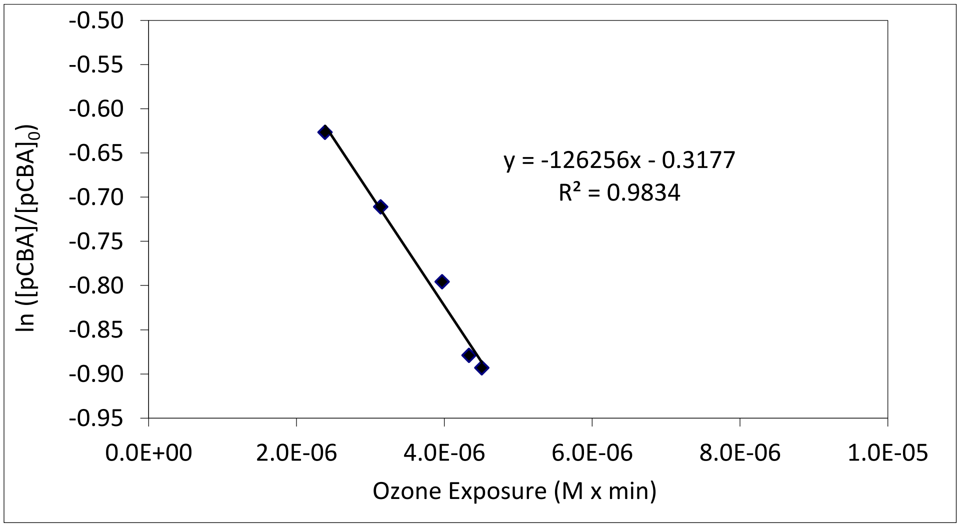




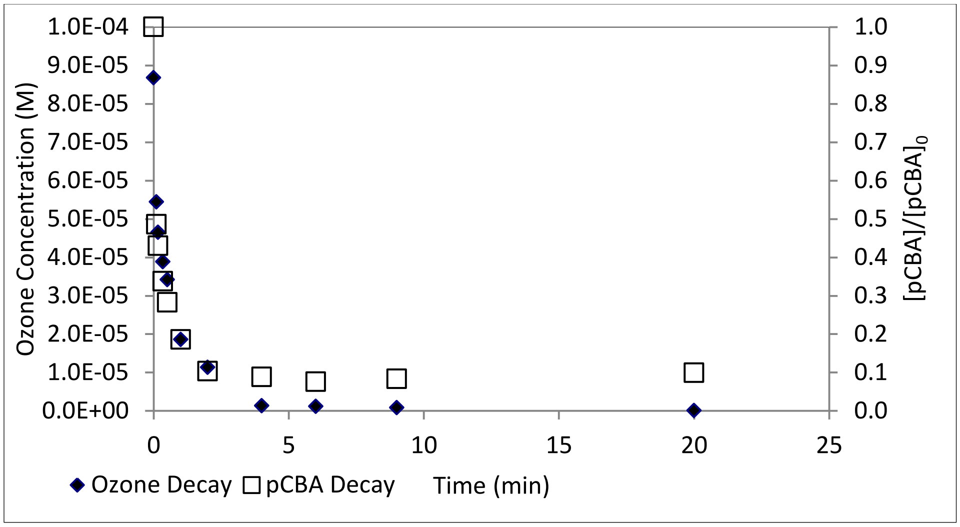
E. Cary WWTPE $[O_3]_0$ = 2.25 mg/l

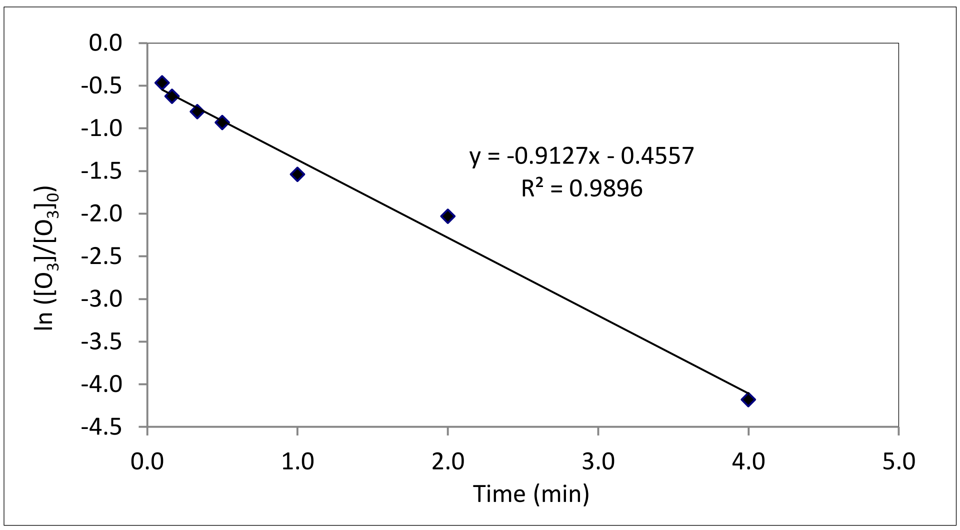


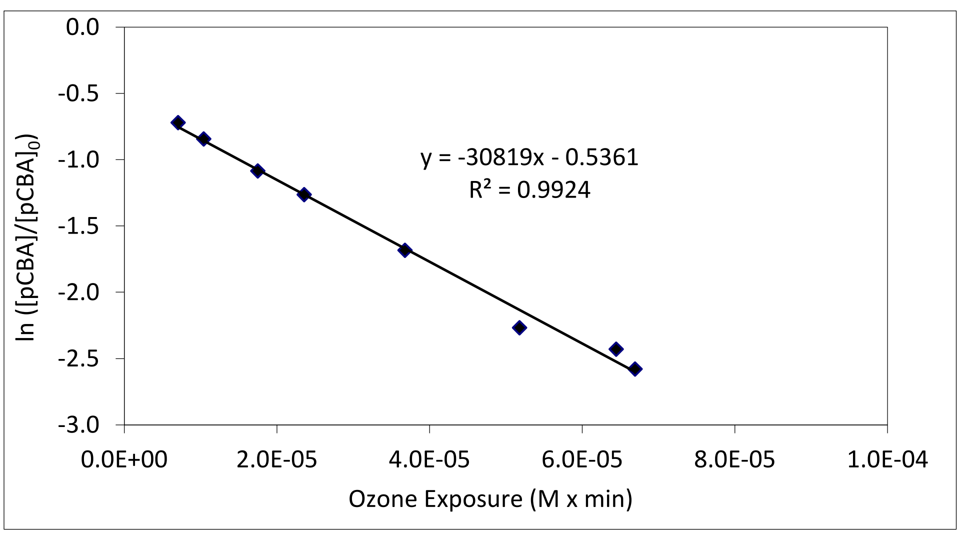




F. Cary WWTPE $[O_3]_0$ = 4.4 mg/l



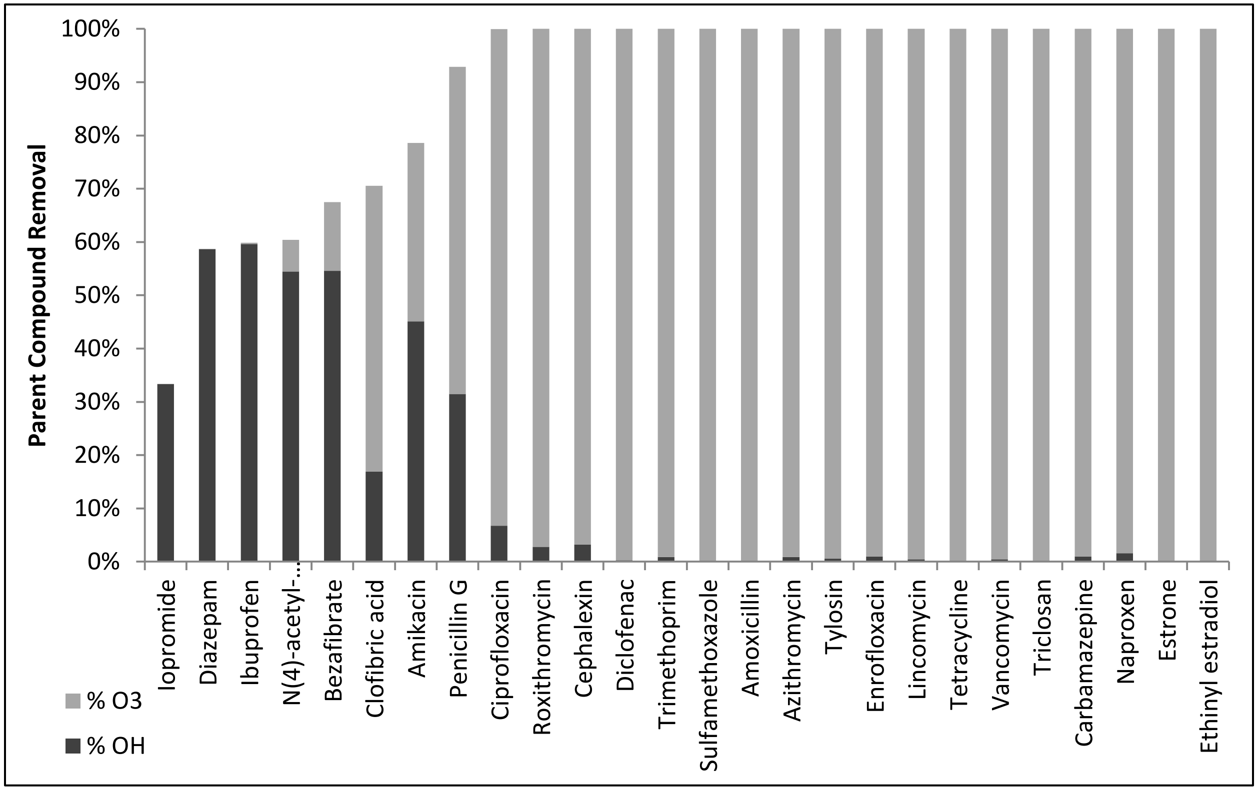




Appendix 2 – BAC Removal Predictions at Two Ozone Doses in Two Drinking Water Sources and a WWTP Effluent

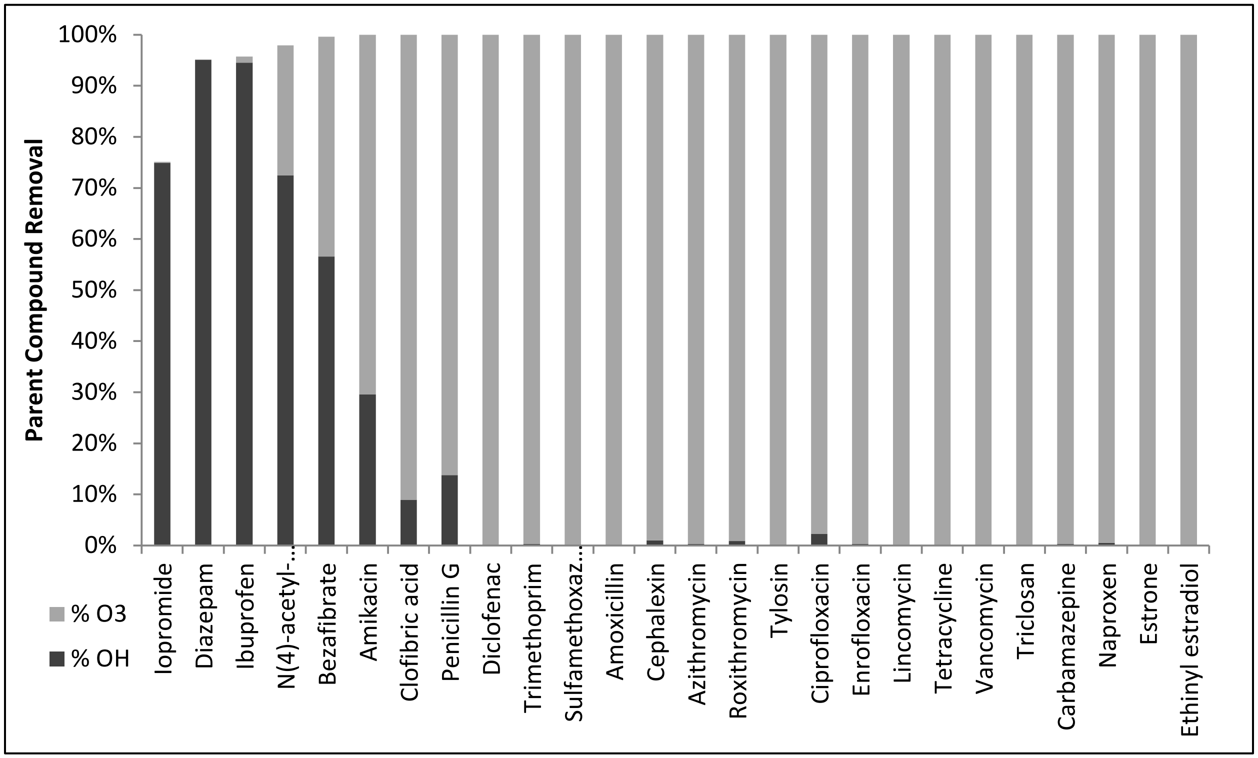
A. Cane Creek $[O_3]_0 = 1.75$ mg/l

Pharmaceutical	f_{OH}	Percent Removal
Iopromide	0.998	32%
Diazepam	1.000	57 (29-
Ibuprofen	0.996	58 (29-
N(4)-acetyl-SMX	0.902	59%
Bezafibrate	0.809	66 (41-
Clofibric acid	0.239	69 (60-
Amikacin	0.574	77%
Penicillin G	0.339	92 (87-
Ciprofloxacin	0.068	100%
Roxithromycin	0.028	100%
Cephalexin	0.032	100%
Diclofenac	0.003	100%
Trimethoprim	0.009	100%
Sulfamethoxazole	0.001	100%
Amoxicillin	0.000	100%
Azithromycin	0.009	100%
Tylosin	0.005	100%
Enrofloxacin	0.010	100%
Lincomycin	0.004	100%
Tetracycline	0.001	100%
Vancomycin	0.004	100%
Triclosan	0.000	100%
Carbamazepine	0.010	100%
Naproxen	0.016	100%
Estrone	0.001	100%
17a-ethinylestradiol	0.000	100%



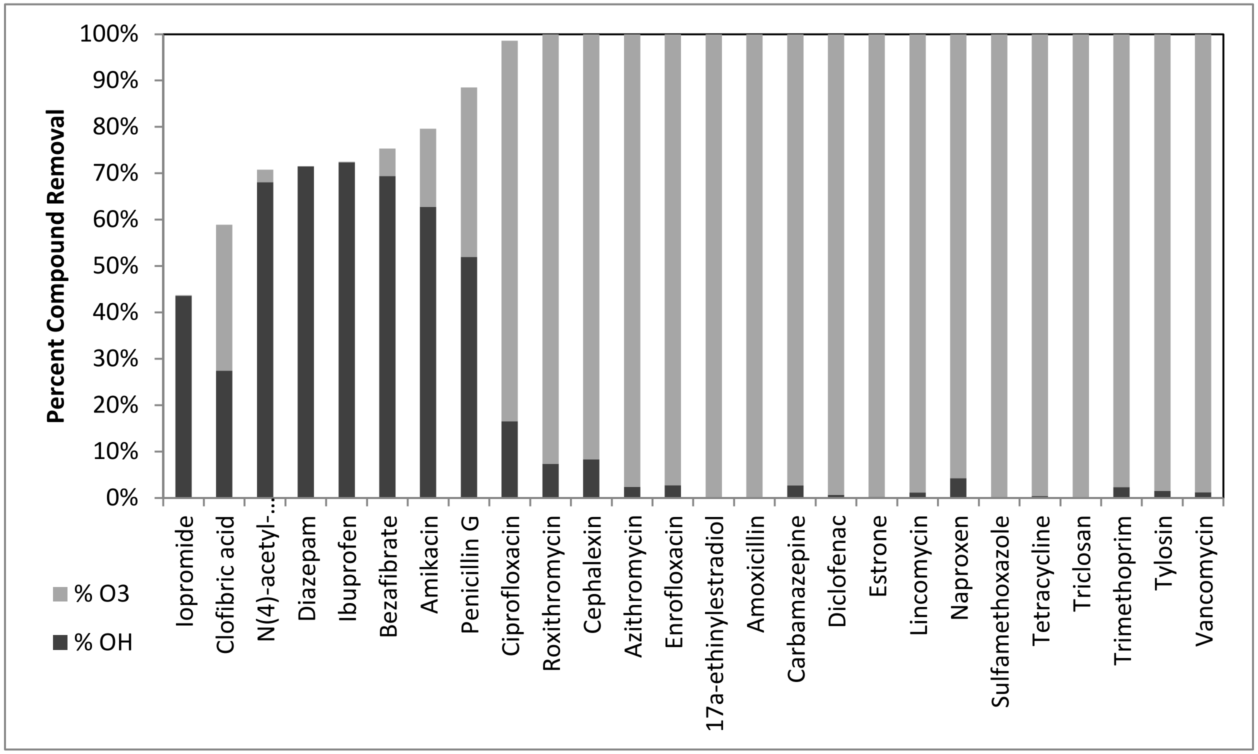
B. Cane Creek $[O_3]_0 = 3.5$ mg/l

Pharmaceutical	f_{OH}	Percent Removal
Iopromide	0.998	75%
Diazepam	0.999	95 (88-99)%
Ibuprofen	0.988	96 (88-99)%
N(4)-acetyl-SMX	0.741	98%
Bezafibrate	0.568	100%
Amikacin	0.296	100%
Clofibric acid	0.089	100%
Penicillin G	0.138	100%
Diclofenac	0.001	100%
Trimethoprim	0.003	100%
Sulfamethoxazole	0.000	100%
Amoxicillin	0.000	100%
Cephalexin	0.010	100%
Azithromycin	0.003	100%
Roxithromycin	0.009	100%
Tylosin	0.002	100%
Ciprofloxacin	0.022	100%
Enrofloxacin	0.003	100%
Lincomycin	0.001	100%
Tetracycline	0.000	100%
Vancomycin	0.001	100%
Triclosan	0.000	100%
Carbamazepine	0.003	100%
Naproxen	0.005	100%
Estrone	0.000	100%
17a-ethinylestradiol	0.000	100%



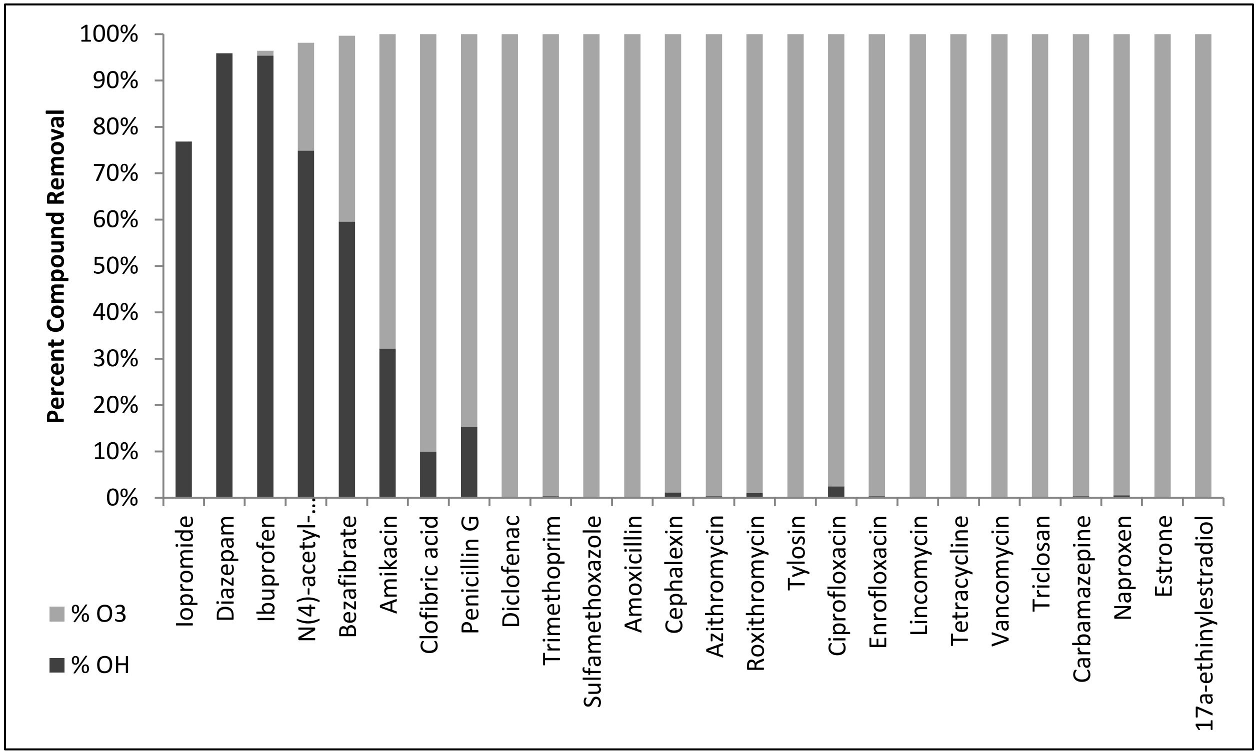
C. Cape Fear $[O_3]_0 = 2.5$ mg/l

Pharmaceutical	f_{OH}	Percent Removal
Iopromide	0.998	44%
Clofibric acid	0.466	59 (45-73)%
N(4)-acetyl-SMX	0.962	71%
Diazepam	1.000	71 (39-92)%
Ibuprofen	0.999	72 (39-93)%
Bezafibrate	0.921	75 (45-93)%
Amikacin	0.789	80%
Penicillin G	0.587	89 (76-96)%
Ciprofloxacin	0.168	99%
Roxithromycin	0.074	100%
Cephalexin	0.084	100%
Azithromycin	0.024	100%
Enrofloxacin	0.027	100%
17a-ethinylestradiol	0.000	100%
Amoxicillin	0.001	100%
Carbamazepine	0.027	100%
Diclofenac	0.007	100%
Estrone	0.003	100%
Lincomycin	0.012	100%
Naproxen	0.043	100%
Sulfamethoxazole	0.002	100%
Tetracycline	0.004	100%
Triclosan	0.000	100%
Trimethoprim	0.023	100%
Tylosin	0.015	100%
Vancomycin	0.012	100%



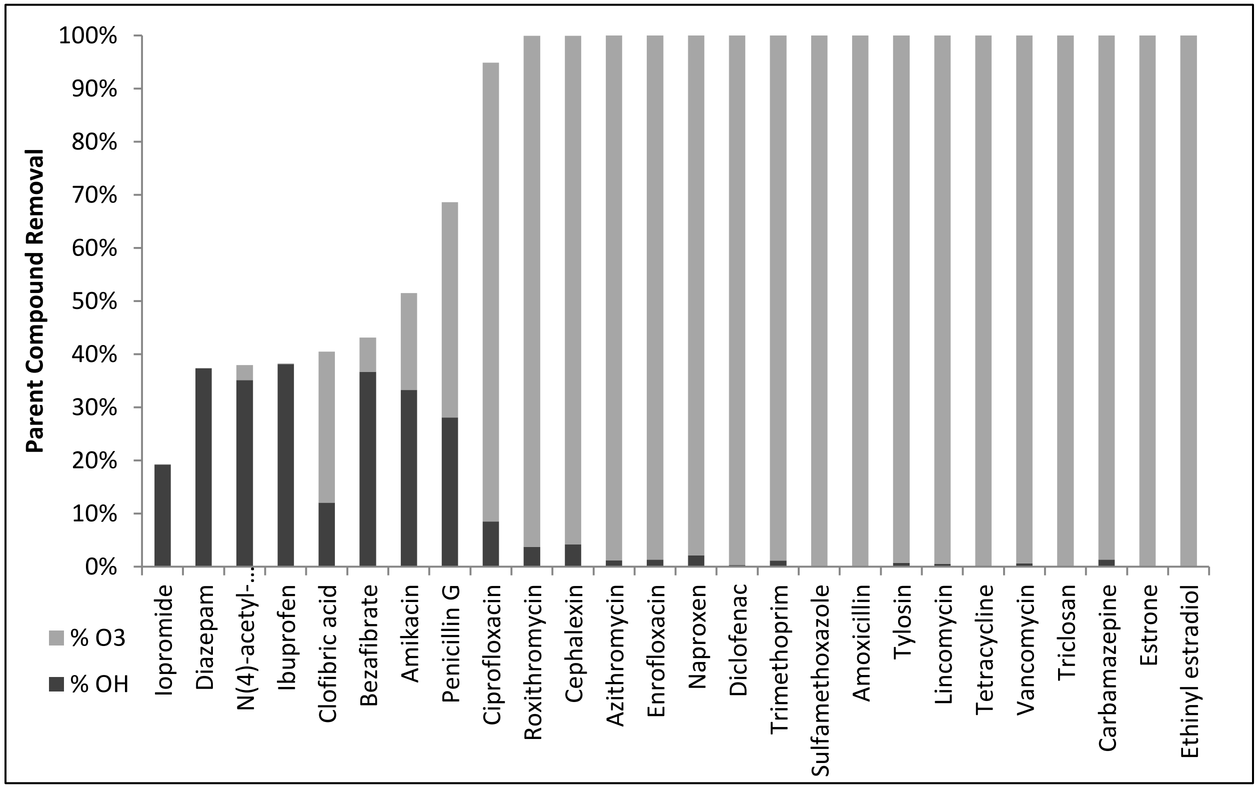
D. Cape Fear $[O_3]_0 = 4.5$ mg/l

Pharmaceutical	f_{OH}	Percent Removal
Iopromide	0.998	77%
Diazepam	0.999	96 (92-98)%
Ibuprofen	0.989	96 (92-99)%
N(4)-acetyl-SMX	0.763	98%
Bezafibrate	0.598	100 (99-100)%
Amikacin	0.322	100%
Clofibric acid	0.100	100%
Penicillin G	0.153	100%
Diclofenac	0.001	100%
Trimethoprim	0.003	100%
Sulfamethoxazole	0.000	100%
Amoxicillin	0.000	100%
Cephalexin	0.011	100%
Azithromycin	0.003	100%
Roxithromycin	0.010	100%
Tylosin	0.002	100%
Ciprofloxacin	0.025	100%
Enrofloxacin	0.004	100%
Lincomycin	0.002	100%
Tetracycline	0.000	100%
Vancomycin	0.002	100%
Triclosan	0.000	100%
Carbamazepine	0.003	100%
Naproxen	0.006	100%
Estrone	0.000	100%
17a-ethinylestradiol	0.000	100%



E. Cary WWTPE $[O_3]_0 = 2.25$ mg/l

Pharmaceutical	f_{OH}	Percent Removal
Iopromide	0.998	19%
Diazepam	1.000	37 (14-62)%
N(4)-acetyl-SMX	0.925	38%
Ibuprofen	0.997	38 (14-64)%
Clofibric acid	0.298	40 (32-50)%
Bezafibrate	0.851	43 (21-67)%
Amikacin	0.645	51%
Penicillin G	0.409	68 (57-80)%
Ciprofloxacin	0.089	95%
Roxithromycin	0.038	100%
Cephalexin	0.043	100%
Azithromycin	0.012	100%
Enrofloxacin	0.013	100%
Naproxen	0.021	100%
Diclofenac	0.003	100%
Trimethoprim	0.011	100%
Sulfamethoxazole	0.001	100%
Amoxicillin	0.000	100%
Tylosin	0.007	100%
Lincomycin	0.006	100%
Tetracycline	0.002	100%
Vancomycin	0.006	100%
Triclosan	0.000	100%
Carbamazepine	0.013	100%
Estrone	0.001	100%
17a-ethinylestradiol	0.000	100%



Appendix 2 – BAC Removal Predictions at Two Ozone Doses in Two Drinking Water Sources and a WWTP Effluent

F. Cary WWTPE $[O_3]_0 = 4.4$ mg/l

Pharmaceutical	f_{OH}	Percent Removal
Iopromide	0.998	72%
Diazepam	0.999	94 (84-99)%
Ibuprofen	0.987	95 (85-99)%
N(4)-acetyl-SMX	0.734	97%
Bezafibrate	0.560	99 (98-100)%
Amikacin	0.289	100%
Clofibric acid	0.087	100%
Penicillin G	0.134	100%
Diclofenac	0.001	100%
Trimethoprim	0.003	100%
Sulfamethoxazole	0.000	100%
Amoxicillin	0.000	100%
Cephalexin	0.010	100%
Azithromycin	0.003	100%
Roxithromycin	0.009	100%
Tylosin	0.002	100%
Ciprofloxacin	0.021	100%
Enrofloxacin	0.003	100%
Lincomycin	0.001	100%
Tetracycline	0.000	100%
Vancomycin	0.001	100%
Triclosan	0.000	100%
Carbamazepine	0.003	100%
Naproxen	0.005	100%
Estrone	0.000	100%
17a-ethinylestradiol	0.000	100%