pH EFFECTS ON THE SORPTION OF FLUOXETINE AND SULFAMETHOXAZOLE BY THREE POWDERED ACTIVATED CARBONS

by

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ABSTRACT

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by

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Sulfamethoxazole (SMXL) and fluoxetine (FLX) are examples of ionizable pharmaceuticals and personal care products (PPCPs) that are continually introduced into the environment and are not readily removed from water and wastewater streams by currently employed water treatment technologies. The addition of powdered activated carbon (PAC) in conventional water treatment systems is one option used for the removal of ionizable (and non-ionizable) pharmaceuticals from drinking water. PACs may carry either positive or negative net surface charge depending on the pH of solution and the point of zero charge (PZC) of the PAC. This study predicted that the electrostatic interactions between three commercially available PACs (HydroDarco B, WPH, and AquaNuchar) surface charges and the charges of sulfamethoxazole's and fluoxetine's ionizable functional groups would lead to greater or lesser sorption efficiency depending on pH. The pH of samples were adjusted between experiments (pH 5, 6.3, 8.3, and 10.3) to determine if interaction between the ionizable contaminants and charged surface of PAC significantly impacted removal of the contaminant from solution. Samples were analyzed using triple quadrupole liquid chromatography. All results were recorded as

percent removal versus PAC dose. It was observed that pH of the solution did play a significant role in the removal of contaminant in a number of the experiments, but that under other conditions where greater removal was predicted based on predicted electrostatic interactions, it did not. These conditions included pH conditions where the contaminant existed predominantly in a negatively charged form, which is consistent with other findings in the literature. While not the initial focus of this study, it was observed that pore size distribution of the PACs may play a more significant role in the removal of ionizable organic compounds than electrostatic interactions. In particular fluoxetine showed greater sorption efficiency to PACs with their pore size distribution in the meso- to macro- pore size range.

(67 pages)

PUBLIC ABSTRACT

pH EFFECTS ON THE SORPTION OF FLUOXETINE AND SULFAMETHOXAZOLE BY THREE POWDERED ACTIVATED CARBONS

James D. Schneider

Pharmaceuticals and personal care products (PPCPs) are widely used throughout the world. PPCPs are emerging as pollutants of concern and may pose a risk in the future to drinking water supplies. Two such compounds are sulfamethoxazole (SMXL) and fluoxetine (FLX). These ionizable compounds are not readily removed from water by conventional water treatment technologies. Powdered activated carbon (PAC) is a useful material for removing contaminants from water and is currently used in many water treatment applications. PACs may carry either a net positive or negative surface charge depending on the pH of solution. This study examined the hypothesis that the electrostatic interactions between three PACs' surface charges and the charges of sulfamethoxazole's and fluoxetine's ionizable functional groups would lead to greater sorption efficiency than non-electrostatic interactions alone. Samples containing SMXL or FLX, were treated with varying doses of PAC, and mixed for three hours. The pH of samples were adjusted between experiments to determine if interaction between the polar contaminants and charged surface of PAC significantly impacted removal of the contaminant from solution. Analysis of the treated samples showed the effects of pH and varying PACs on the removal of SMXL and FLX from solution. It was observed that pH of the solution did play a significant role in the removal of contaminant in a number of the experiments, but that under other conditions where greater removal was anticipated based on predicted electrostatic interactions, it did not. These conditions included pH conditions where the contaminant existed predominantly in a negatively charged form. While not the initial focus of this study, it was observed that pore size distribution of the PACs may play a more significant role in the removal of ionizable compounds, especially in the case of fluoxetine, than electrostatic interactions.

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INTRODUCTION

Prevalence of PPCP's

Studies have measured the presence of pharmaceuticals and personal care products (PPCPs) in environmental samples collected throughout the world (Santos *et. al.*, 2010, Loos *et. al.*, 2013, Mohapatra *et al*., 2016, Matongo *et al*., 2015, Scott *et. al.*, 2014, Ternes *et al.*, 1998). In the United States one such study found numerous PPCPs present in the environment (Kolpin *et. al.*, 2002). Although the study was biased towards sampling sites across the United States that were expected to contain organic wastewater contaminants, other studies continue to find PPCPs in the environment. More recent reports in the United States continue to show the presence of myriad PPCPs in freshwater lakes and streams (Ferrey, 2015). Assessments have shown that multiple pharmaceutical compounds exhibit a substantial environmental risk. One assessment identified six such compounds in the Great Lakes Basin, among them fluoxetine (FLX), commonly known as Prozac, and sulfamethoxazole (SMXL), an antibiotic in the sulfonamide family of drugs (Uslu *et. al.*, 2013). In the United States no regulatory limits have been set for such compounds despite the potential for significant impacts on aquatic organisms. Attempts to assess environmental impacts to non-target organisms are ongoing (Brain *et al*., 2008, Shultz *et al*., 2011, Painter *et al*., 2009) while the effect of long term exposure to low concentrations of PPCPs is not clear.

There are multiple routes that PPCPs may find their way into the environment and eventually into drinking water facilities. Prescription drugs, like fluoxetine, may be released into the environment after passing through wastewater treatment plants. Even

after directed use, active metabolites may be present in human excretions and pass to the wastewater facilities. Most wastewater facilities are not designed to remove these micropollutants (Kolpin *et al.*, 2002; Halling-Sorensen *et al.*, 1998). Sulfamethoxazole is used both as a human and veterinary anti-biotic and may have varied routes into the environment. Animal wastes from animal feeding operations may present another route for this antibiotic to find its way into surface waters as well as ground waters (Meyer *et al.*, 2000).

Effectiveness of PPCP Removal at WWTP and WTP

Wastewater treatment plants (WWTP) and water treatment plants (WTP) employ numerous methods and technologies for the treatment of contaminated waters. These methods may include coagulation and oxidation, gravity separation, filtration, disinfection, reverse osmosis, ion exchange, adsorption, or a combination of a few. While Kolpin et al. (2002) highlighted the lack of effective treatments in wastewater treatment plants for the removal of PPCPs present during their study, later studies have investigated the addition of treatments specifically for such removal (Secondes *et al.*, 2014, Serrano *et al.*, 2011). Many of these treatments implement powdered activated carbon (PAC) use in tandem with complementary treatments to improve the effectiveness of carbon adsorption (Yoon 2007). Adsorption is the process of removing a substance from a liquid by accumulating the substance onto the solid phase of a material. This solid is referred to as the adsorbent while the target compound is called the adsorbate. In water treatment plants, PAC can be added directly to water in various locations and is usually removed by sedimentation or filtration (Crittenden *et. al.*, 2012). As improved technologies are still in

development and are not yet implemented on a large scale, the potential for PPCP's reaching WTP is still of concern. Removal of endocrine-disrupting compounds (EDC) and PPCPs has been investigated, and low removal from many forms of treatment has been observed. For example, Westerhoff *et al.* (2005) found that some compounds had low removal by all treatment processes, while others had limited removal with the addition of oxidation and carbon addition but with the caveat of needed modification for charged species. While the use of PAC has been used in U.S. water treatment as far back as 1930, the interaction of ionized functional groups within a target adsorbate and the point of zero charge (PZC) of an adsorbent has yet to be thoroughly explored in the removal of PPCPs. The acid disassociation constant, pK_a, is an equilibrium constant that expresses the extent to which an acid transfers a proton to solvent water. Ionizable compounds may exist in positively charged, negatively charged, or neutral species in aqueous solutions depending on the solution's pH and the compound's pKa. These charged species may be more apt to adsorb onto a PAC adsorbent if it is carrying an unlike surface charge. The point of zero charge of a PAC describes the condition, in this case the pH of a solution, when the charge density of its surface is zero (Clark, 2009). When the pH of a solution is above the PZC for a particular PAC, the surface will be negatively charged and is more apt to attract cations, or positively charged ions. Likewise, when the pH of a solution is below the PZC, the surface will be positively charged and is more apt to attract anions, or negatively charged ions. The interaction of pK_a and PZC may yet provide a better understanding of adsorption of PPCP's and provide further guidance to greater removal of these emerging contaminants.

Research Objective

The objective of this study was to better understand the role of pH on the sorption of fluoxetine and sulfamethoxazole to PAC, with the purpose to provide guidance in the most efficient selection of powdered activated carbon. Sulfamethoxazole and fluoxetine were chosen due to the presence of both positive and negative functional groups of the compounds at different pH values. An objective was to examine the hypothesis that that the electrostatic interactions between three PACs surface charges and the charges of sulfamethoxazole's and fluoxetine's ionizable functional groups would lead to greater sorption efficiency.

Contribution

The experiments that were conducted with three PACs showed that there were conditions where electrostatic interactions between sulfamethoxazole and fluoxetine with PAC increased removal, while in other cases the compounds were not removed more effectively due to electrostatic interactions and the hypotheses is not supported. This knowledge is important because it suggests potential for using PAC to increase removal of PPCPs under certain advantageous conditions within a water treatment system. However, caution is needed as this work examined only two compounds and three PAC's. Further work with additional compounds and PACs would be worthwhile to determine if tailored selection of PAC based on electrostatic interactions would be efficient at lowering PAC usage at treatment plants and lowering operating costs.

MATERIALS AND METHODS

To meet the objective of this study, the following tasks were undertaken:

1) Obtain pK_a values for sulfamethoxazole and fluoxetine from the literature and using SPARC, a computational approach for predicting pK_a values. From these values a set of predictions was developed.
2) Determine the relationship between pH and FLX and SMXL sorption to three PACs in experiments using contact times of no more than 3 hours to mimic typical conditions within WTPs. From these experiments, dose-response curves were constructed to compare sorption efficiency at variable pH values.
3) Compare the efficacy of the individual PACs based on PZC and other carbon characteristics, including pore size and pore size distribution, to determine if predictions were supported.

PPCP Characterization

For this study two ionizable compounds were examined, sulfamethoxazole and fluoxetine. Table 1 contains the chemical properties for both compounds. Due to the ability of both compounds to ionize, pH may play a significant role in their removal from aqueous solutions. Values for pK_a were obtained from a literature review and estimated utilizing SPARC. SPARC ("SPARC performs automated reasoning in chemistry") a physiochemical calculator based on fundamental chemical structure theory (SPARC 2014). Once these values were obtained, Marvin Sketch software (version 15.3.2, downloaded from https://chemaxon.com/ products/marvin) was used to draw the chemical species structure and create the speciation plots shown in Figures 1 and 2.

Table 1. Chemical Properties of PPCPs

Cas #	Chemical Compound	code	Molecular Weight / Surface Area	pK_a (from literature[a])	pK_a (from SPARC)	Log K_{ow}	Solubility (mg/L)
723-46-6	sulfamethoxazole	SMXL	253.3[b] / 337.6[d]	5.70-5.73	1.75, 9.28	0.89[b]	610[b]
				1.83, 5.57			
				5.6			
				1.39, 5.81			
				5.6, 5.9			
54910-89-3	fluoxetine	FLX	309.33[c] / 450.6[d]	10.1	9.53	4.05[c]	60.3[c]

[a] Taken from Qiang and Adams (2004)
[b] Taken from Howard and Meylan (1997)
[c] Taken from Adlard *et. al.* (1995)
[d] Van der Waals surface area calculated in MarvinSketch v.15.3.2

Table 1 shows that the octanol/water partition coefficients (log K_{ow}) and aqueous solubility for sulfamethoxazole and fluoxetine in their neutral forms are substantially different. These properties highlight that sulfamethoxazole in its neutral form is highly soluble in water, hydrophilic, while fluoxetine in its neutral form is not very soluble, hydrophobic. While log K_{ow} has previously been used as a rule of thumb in PAC adsorption, with lower log K_{ow} values predicting lower sorption potential, Margot *et. al.* (2013) showed that it is not always a useful predictor when dealing with ionizable compounds. In their study 70 different compounds were reviewed with respect to removal by PAC from a wastewater inlet. The authors found that positive and neutral compounds were more likely to adsorb to PAC than negative compounds, independent of their hydrophobicity. Both sulfamethoxazole and fluoxetine have ionizable functional groups. Sulfamethoxazole contains two functional groups, one acidic amine group (pKa approximately 5.7) and one basic amine group (pKa approximately 1.4). Fluoxetine contains only one base amine functional group (pKa approximately 10). The prevalence

of these acid and base functional groups and their charge across the range of pH makes these compounds prime candidates to test the hypothesis. Without this speciation, sorption of these compounds would not be reliant on pH. The SPARC model predicts pK_as at pH levels of 1.75 and 9.28 for sulfamethoxazole while observed values were determined potentiometrically at pHs of 1.85 and 5.60 (Qiang and Adams, 2004). Figure 1 illustrates the SPARC model for the speciation of sulfamethoxazole.

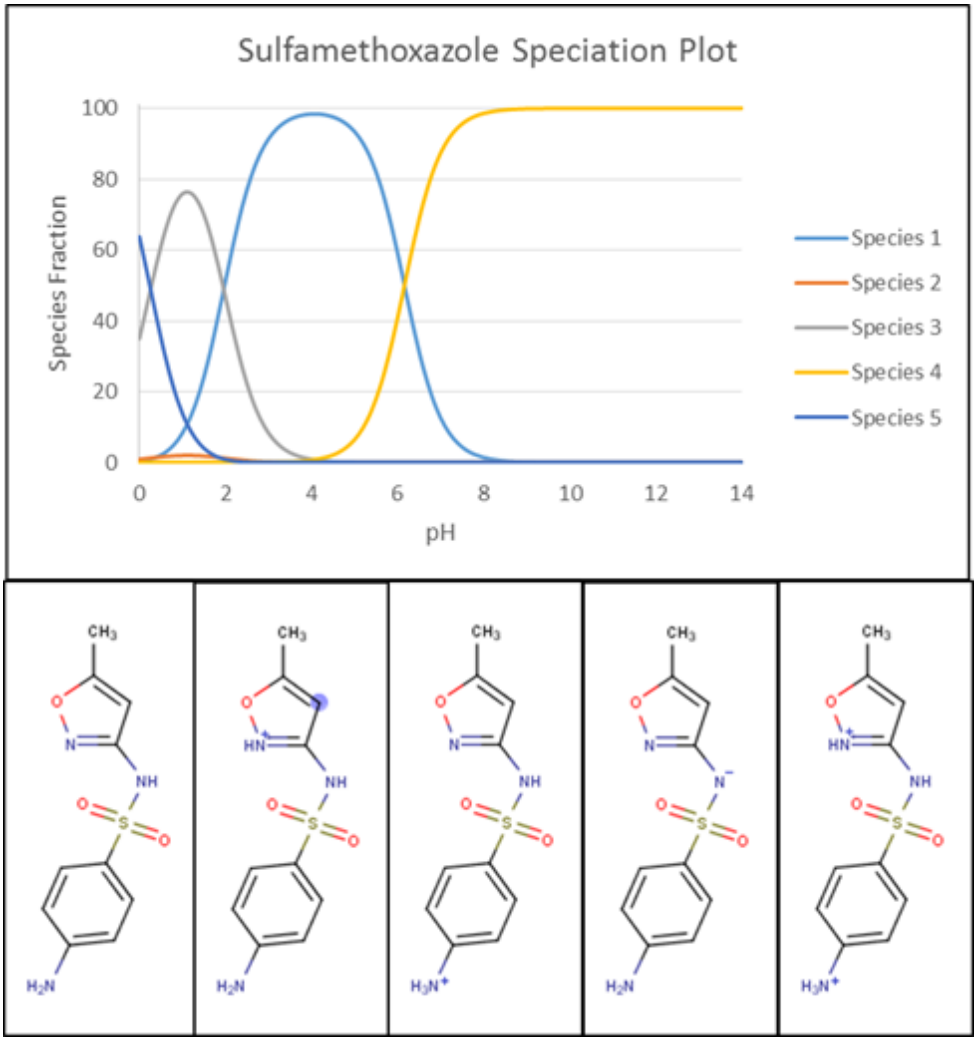

Figure 1. Speciation plot for sulfamethoxazole generated from Marvin Sketch tool.

The values from previous literature were used to formulate predictions. Sulfamethoxazole exists predominantly in a positive species below a pH of 1.85, a neutral species between pH 1.85 to 5.6, and a negative species above a pH of 5.6. From this information, a hypothesis has been determined concerning electrostatic forces that may be present between the compound and the various PACs and the subsequent adsorption onto the PAC.

Figure 2 illustrates the SPARC model for the speciation of fluoxetine. Fluoxetine dissociates at a pH of 9.53 according to the theoretical model. Literature values for the pKa of fluoxetine were found to be at a pH of 10.1 (Nakamura 2008). Below the pKa value of 9.53 fluoxetine exists in a predominantly positive species, while above the pKa

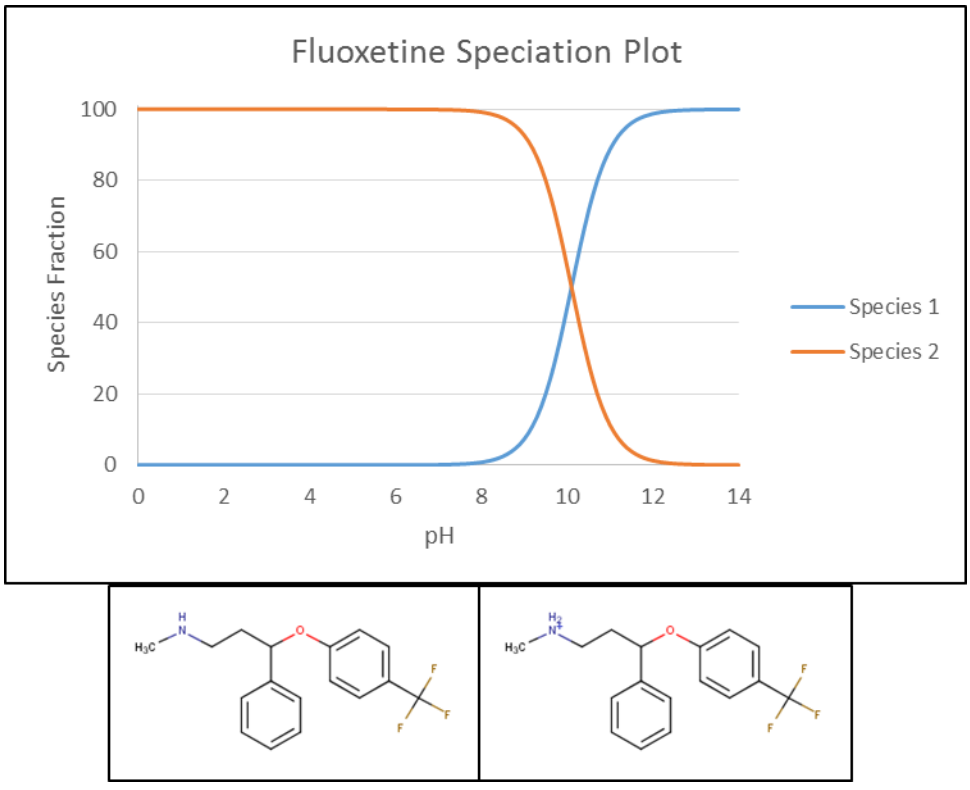

Figure 2. Speciation plot for fluoxetine generated from Marvin Sketch tool.

the species is neutral. Again, from this information a hypothesis has been generated predicting the electrostatic interaction of fluoxetine and the various PACs, and the possibility of increased sorption due to these forces.

PAC Characterization

Sorption to activated carbon has been proven effective at the removal of many dissolved organic compounds including PPCPs. Sorption to activated carbon is most effective for compounds that are nonpolar, hydrophobic, have lower molecular weights, and are uncharged (Crittenden *et al.,* 2012). Studies have implemented PAC dosages ranging from 0 to 50 mg/L and 0 to 20 mg/L to analyze the effectiveness of carbons at removing PPCPs (Adams *et al.,* 2002; Westerhoff *et al.,* 2005). For this study, a range of PAC doses has been utilized, specifically: 0, 1, 3, 10 and 30 mg/L (and 0, 0.25, 0.50, 0.75 and 1 mg/L for AquaNuchar). These ranges of PAC doses were based primarily on results of a pilot study. The pilot study utilized 0, 1, 3, 10, and 30 mg/L doses of WPH PAC and sulfamethoxazole as the target adsorbate. The results of the study showed near complete removal of sulfamethoxazole at the highest dose of 30 mg/L. When the original dose schedule was used for the AquaNuchar, nearly 100% of the target adsorbate was removed at a dose of 1 mg/L. Because of this, the dose for AquaNuchar was adjusted.

Three PAC's have been previously characterized (Shi *et al.,* 2012). The properties of these PACs are summarized in Table 2. These three carbons have varied points of zero charge. This was essential when trying to determine any effects due to the electrostatic interaction of the ionized compounds and the different carbons. The three carbons are manufactured from different material; lignite coal, bituminous coal, and wood.

Table 2. PAC Characterization.

PAC	Source	BET Surface Area[a] (m^2/g)	BET Surface Area[b] (m^2/g)	Micropore volume (cm^3/g) - %	Mesopore Volume (cm^3/g) - %	Macropore Volume (cm^3/g) - %	Zero Point of Charge
HydroDarco B (HDB)	Lignite Coal	507	510	0.140 – 22%	0.386 – 61%	0.112 – 18%	10.6
WPH	Bituminous Coal	901	1027	0.317 – 66%	0.140 – 29%	0.023 – 5%	6.1
AquaNuchar (AN)	Wood	1464	1567	0.391 – 32%	0.807 – 66%	0.029 – 2%	4.9

* Taken from Shi et al., 2012

[a] Detlef Knappe. North Carolina State University

[b] Jain et al. (2004)

The carbons also have very different physical characteristics. The BET surface area and pore size distribution, both of which may affect compound removal, are not similar for the three carbons. In addition to analyzing the removal of fluoxetine and sulfamethoxazole with each PAC individually at varying pH, the results were manipulated to look at the influence of the surface area of each carbon. Specifically, the removal efficiency was viewed as percent of adsorbate remaining per mg/L of PAC as well as meters-squared of PAC. By accounting for the difference in surface area, meters-squared per gram, a comparison of electrostatic interactions was possible.

Predicted electrostatic interactions with PAC

From the information reviewed, a set of predictions pertaining to the electrostatic interaction of the PACs and compounds has been determined to assess the effects of pH on the sorption of sulfamethoxazole and fluoxetine onto three powdered activated carbons. These predictions are based on the predicted charge of the compound species

and PZC of the PAC across the pH range. Table 3 summarizes the predictions of electrostatic forces present for sulfamethoxazole and the three carbons. Only one PAC exhibits a zone where attractive electrostatic forces predominate between sulfamethoxazole and the PAC. The majority of the pH range predicts repulsive electrostatic forces between the compound and the other two PACs. Similarly, a table of predictions for fluoxetine and the PACs has been constructed. Table 4 summarizes the predicted electrostatic forces present across the pH range. Unlike sulfamethoxazole, two of the PACs have large ranges, between pH 6 and 10, that predicts attractive forces present between fluoxetine, and WPH and AN. In this same range HDB

Table 3. Predictions for electrostatic interactions between PACs and sulfamethoxazole.

pH	SMXL	HDB	Force	WPH	Force	AN	Force
1	+	+	Repel	+	Repel	+	Repel
1.5	**+/0**	+	Neutral	+	Neutral	+	Neutral
2	0	+	Neutral	+	Neutral	+	Neutral
3	0	+	Neutral	+	Neutral	+	Neutral
4	0	+	Neutral	+	Neutral	+	Neutral
5	0	+	Neutral	+	Neutral	**0**	Neutral
6	-	+	**Attract**	**0**	Neutral	-	Repel
6.5	-	+	**Attract**	-	Repel	-	Repel
7	-	+	**Attract**	-	Repel	-	Repel
8	-	+	**Attract**	-	Repel	-	Repel
8.3	-	+	**Attract**	-	Repel	-	Repel
9	-	+	**Attract**	-	Repel	-	Repel
9.3	-	+	**Attract**	-	Repel	-	Repel
10	-	+	**Attract**	-	Repel	-	Repel
10.3	-	**+/0**	**Attract**	-	Repel	-	Repel
10.5	-	**0**	**Neutral**	-	Repel	-	Repel
11	-	-	Repel	-	Repel	-	Repel
12	-	-	Repel	-	Repel	-	Repel
13	-	-	Repel	-	Repel	-	Repel

is expected to have predominantly repulsive forces present. From these tables a prediction concerning the effectiveness of the various PACs across the range of pH has been generated.

Table 4. Predictions for electrostatic interactions between PACs and fluoxetine.

pH	FLX	HDB	Force	WPH	Force	AN	Force
1	+	+	Repel	+	Repel	+	Repel
1.5	+	+	Repel	+	Repel	+	Repel
2	+	+	Repel	+	Repel	+	Repel
3	+	+	Repel	+	Repel	+	Repel
4	+	+	Repel	+	Repel	+	Repel
5	+	+	Repel	+	Repel	0	neutral
6	+	+	Repel	0	neutral	-	Attract
6.5	+	+	Repel	-	Attract	-	Attract
7	+	+	Repel	-	Attract	-	Attract
8	+	+	Repel	-	Attract	-	Attract
8.3	+	+	Repel	-	Attract	-	Attract
9	+	+	Repel	-	Attract	-	Attract
9.5	+/0	+	Repel	-	Attract	-	Attract
10	0	+	neutral	-	neutral	-	neutral
10.3	0	+/0	neutral	-	neutral	-	neutral
10.5	0	0	neutral	-	neutral	-	neutral
11	0	-	neutral	-	neutral	-	neutral
12	0	-	neutral	-	neutral	-	neutral
13	0	-	neutral	-	neutral	-	neutral

For sulfamethoxazole the predicted sorption capacity based on electrostatic forces is as follows; HDB > AN ≈ WPH for the range of pH values to be tested. For fluoxetine, the predicted sorption capacity based on electrostatic forces is WPH ≈ AN > HDB for the 6.3 and 8.3 pH values and WPH ≈ AN ≈ HDB at 10.3.

3-Hour PAC removal Studies

Studies to simulate contact time present in water treatment facilities were conducted for fluoxetine and sulfamethoxazole. Single solute removal studies were conducted in deionized water (DI), which was produced by treating Logan, UT tap water through a Millipore filtration system. Four liters of DI water was amended with a 480 mg of monosodium phosphate to produce a 1 mM sodium phosphate buffer solution. The solution was then titrated with either sodium hydroxide (NaOH) or hydrochloric acid (HCl) to a pH of 5, 6.3, 8.3, or 10.3. For each experiment, 40 mL of buffered DI water was added to 40-mL borosilicate vials.

One mg/mL solutions of sulfamethoxazole or fluoxetine were prepared by weighing 20 mg of each chemical and adding it to 20 mL of methanol (MeOH). This "stock" solution was kept in a freezer. Prior to each experiment, an intermediate solution of 800 μg/L was created by adding 20 μL of the 1 mg/mL stock into 25 mL of MeOH. After vials had been filled with 40 mL of buffered DI water they were spiked with 100 μL of the 800 μg/L solution, leaving an initial concentration of 2 μg/L of sulfamethoxazole or fluoxetine in each vial.

Prior to each experiment, a dosing solution of PAC was created. The night prior to the experiment a crucible was filled with PAC and set in an oven held at 104 ^{o} C for approximately 12 hours. The next day, 160 mg of dry PAC was measured into a vial containing 40 mL of DI water and stirred for 20 minutes, creating a slurry. An additional dilution of the PAC slurry was necessary for the lower doses of PAC. 4 mL of the "Hi" dose slurry was pipetted into 36 mL of DI water, which was then stirred for 20 minutes,

creating a “Lo” dose slurry. Together, these two slurries were spiked into sample vials previously prepared with buffered DI water and an initial concentration of 2 µg/L of target solute. Table 5 illustrates the PAC dosing schedule for HDB and WPH.

Table 5. Dose schedule for HDB and WPH.

PAC conc (mg/L)	Spike (µL)	Stock (mg/L)
0	NA	NA
1	100	400
3	300	400
10	100	4000
30	300	4000

Due to higher sorption of the target compounds observed with the AN PAC, a separate dosing schedule was used. The AN dose schedule is shown in Table 6. AN was similarly dried overnight at 104 ^{o} C, but only 40 mg was measured into 40 mL of DI water, producing a “Hi” dose solution of 1000 mg/L of AN PAC. This was then diluted to a concentration of 100 mg/L, “Lo” dose, by pipetting 4 mL of solution into 36 mL of DI water.

Table 6. Dose schedule for AN.

PAC conc (mg/L)	Spike (µL)	Stock (mg/L)
0	NA	NA
0.25	100	100
0.5	200	100
0.75	300	100
1	400	100

Once prepared with both PAC and solute, the samples were placed on a Thermo Scientific Labquake rotator located inside a Fisher Scientific Isotemp incubator set at 20º C. The samples were left to rotate for 3 hours in the dark.

After rotation, the samples were centrifuged at 3000 rpm for 20 minutes in a Beckman Model J2-21 centrifuge.

Figure 3. Samples rotating

Figure 4. Centrifuge

After removal from the centrifuge, 1 mL of the supernatant was then pipetted into 2-mL LC/MS vials. The vials were spiked with 10 µL of 100 µg/L of atrazine d5, which was used as an internal standard for analysis. The samples were then vortexed and analyzed on the Agilent 6490 Triple Quad LC/MS.

Sample Analysis

All samples were analyzed by liquid chromatography / mass spectroscopy / mass spectroscopy (LC/MS/MS). Samples (1 mL) were injected into an Agilent Technologies® 1290/6490 LC/MS triple quadrupole system with a Jetstream electrospray ionization source. A 50mm x 2.1mm Agilent XDB C18 stationary phase column was utilized in the analysis of samples. Analysis involved two mobile phases, A and B. Mobile phase A consisted of 0.1% formic acid in de-ionized water while mobile phase B consisted of 0.1% formic acid in 90% acetonitrile and 10% de-ionized water.

Figure 5. QQQ LC/MS used for analysis.

A minimum detection limit (MDL) study for the instrument analyzing both sulfamethoxazole and fluoxetine was conducted to establish values of detection. The minimum detection limit was determined using the methodology described in 40 CFR pt. 136, app. B. For the detection studies ten replicates were used and the limits were estimated using a signal-to-noise ratio of 2.5. Calibration curves using an internal standard, atrazine d5, were generated in the range of 0.1 – 2 μg/L. From these calibration curves quantitation of samples was completed using Agilent Technologies® MassHunter Workstation software (version B.06.00).

Statistical Analysis

R statistical software was used to conduct statistical analyses. Percent relative standard deviation (%RSD) was used to construct confidence intervals and to determine significant differences.

RESULTS AND DISCUSSION

Fluoxetine Removals by PAC as a Function of pH

Studies were completed for fluoxetine using the three PACs; HDB, WPH, and AN. The dose-response curves for four pH values; 5, 6.3, 8.3, and 10.3 were included to cover the range of predicted electrostatic interactions. Figure 6 contains the data for fluoxetine removal by WPH as percent remaining versus PAC dose in mg/L.

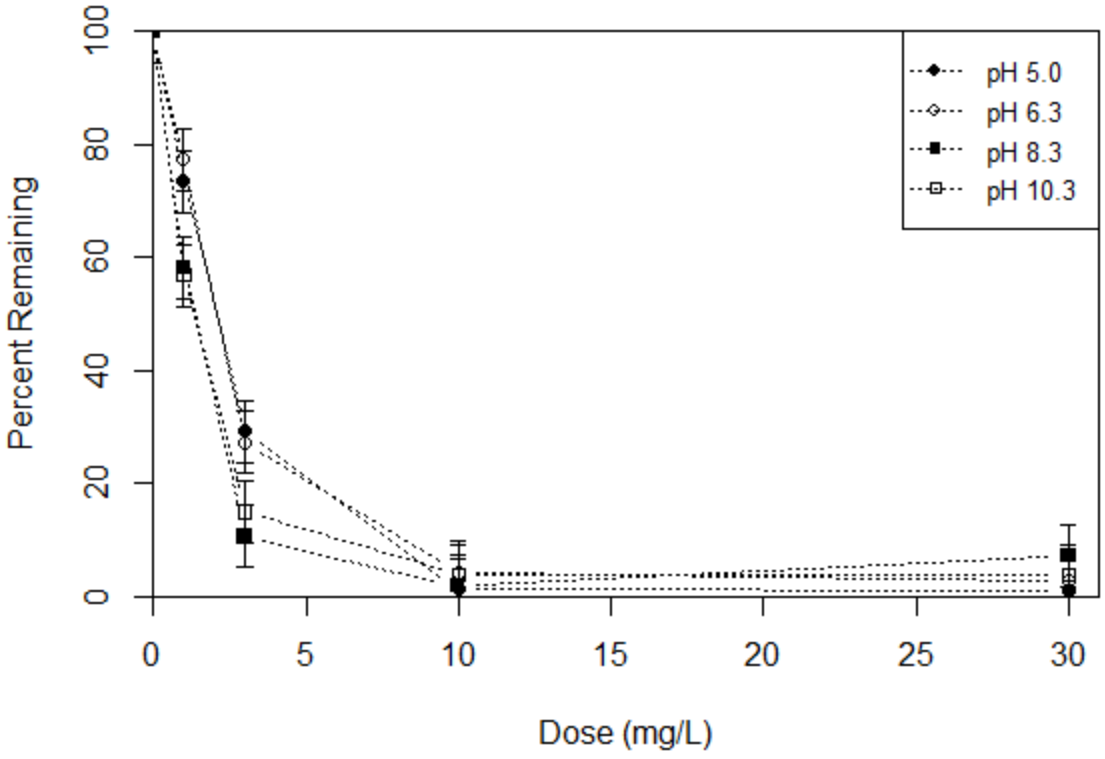

Figure 6. Effect of PAC (WPH) dose on fluoxetine removal (contact time = 3 h). Error bars represent %RSD.

A statistically significant difference in removal is present at the lower end of PAC dosage. Removals at pH 5 and 6.3 differ significantly from pH 8.3 and 10.3. The WPH

carbon achieves approximately 20% and 10% better removal at carbon doses of 1 mg/L and 3 mg/L respectively, at the higher pH values. It is also seen that as the dose of carbon approaches 10 mg/L and above there is no statistical difference in percent removal of fluoxetine. This trend is supported for the pH values except for pH 6.3. This may be explained by the fact that at pH 6.3 the WPH carbon is still near its PZC value of 6.1. When the carbon is predominantly negatively charged, at pH 8.3 and 10.3, it achieves better removal. Figure 7 presents fluoxetine percent removal with HDB carbon addition.

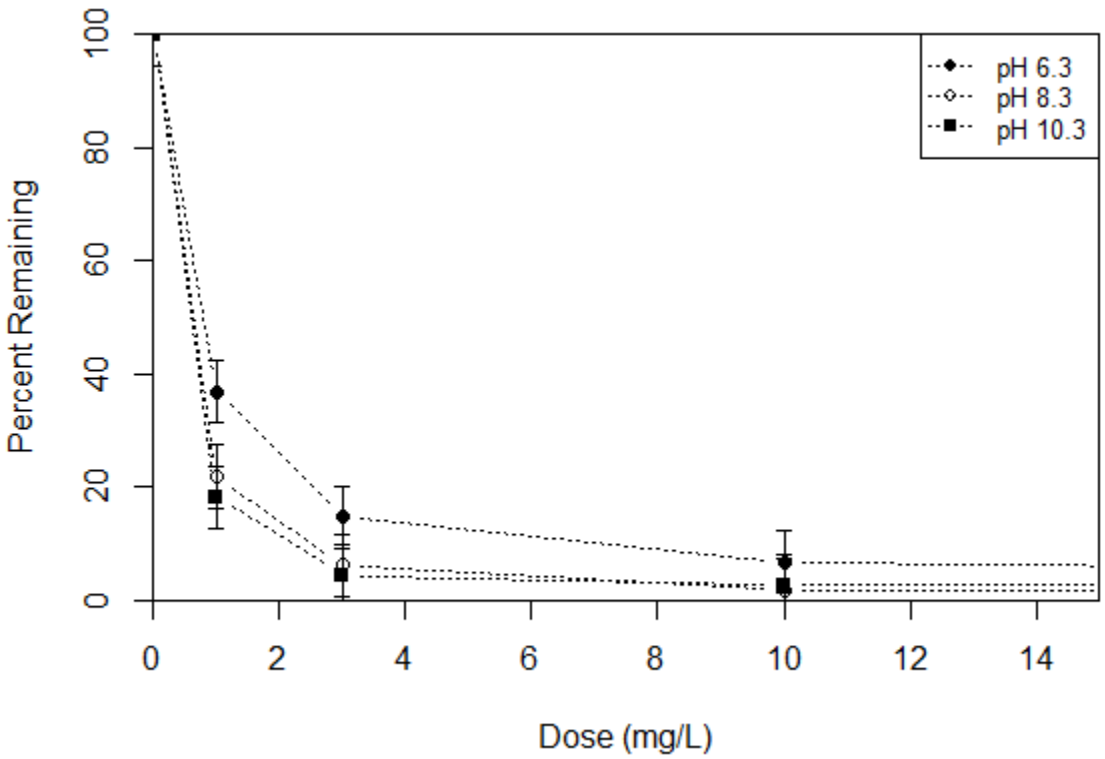

Figure 7. Effect of PAC (HDB) dose on fluoxetine removal (contact time = 3 h). Error bars represent %RSD.

Again as PAC dosage is increased no statistical difference can be found at the different pH levels. The data does reveal that at a pH value of 6.3 the HDB removes

significantly less fluoxetine at the lower dosage range than at a pH of either 8.3 or 10.3. From the predictions it was expected that a pH of 10.3 would achieve the greatest removal with 6.3 and 8.3 removing less. This is not present in the data as pH 8.3 and pH 10.3 perform statistically the same. While at a pH of 10.3 HDB does achieve the most removal, it is not statistically discernible from the removal at observed at pH 8.3. Figure 8 presents the results for fluoxetine removal with addition of the AN carbon.

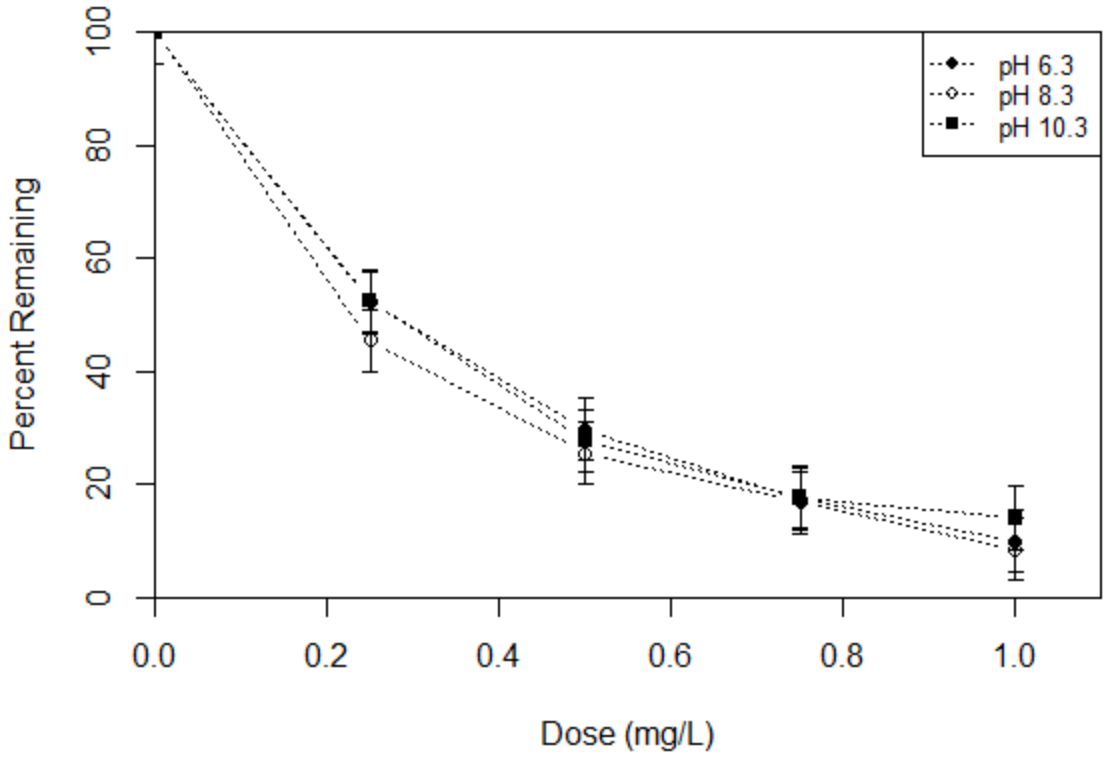

Figure 8. Effect of PAC (AN) dose on fluoxetine removal (contact time = 3 h). Error bars represent %RSD.

Due to the effectiveness of removal of AN, lower doses of the PAC were utilized to construct the dose-response curve. PAC doses of 0, 0.25, 0.5, 0.75, and 1 mg/L were utilized. This is presumed to occur due to the higher BET surface area of the AN carbon.

Across the pH levels no statistically significant difference is found in the performance of AN. It was predicted that AN would achieve greater removal at pH levels 6.3 and 8.3 due to the negative surface charge of AN and the predominantly positive species of fluoxetine at those pH levels. This prediction was not supported by the data.

Sulfamethoxazole removals by PAC as a function of pH

Studies were completed for sulfamethoxazole using the three PACs; HDB, WPH, and AN. The dose-response curves for three pH values; 6.3, 8.3, 10.3 were included to cover the range of predicted electrostatic interactions. Figure 9 illustrates percent remaining of sulfamethoxazole versus PAC dose using the WPH carbon. Across the

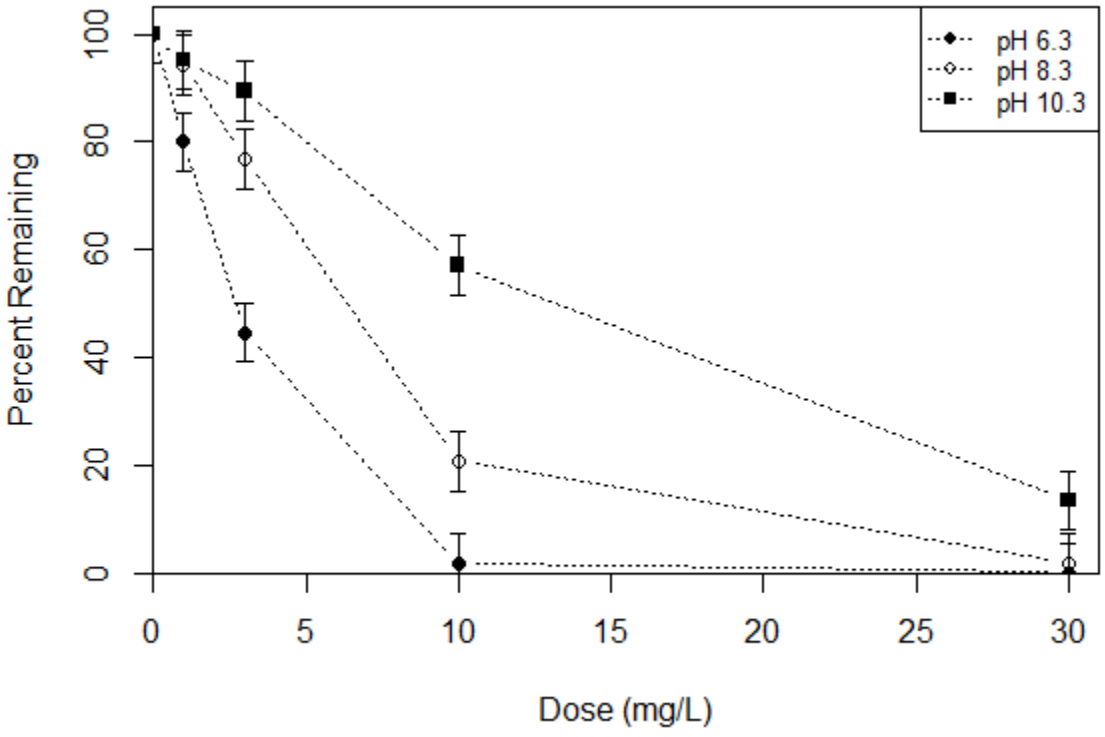

Figure 9. Effect of PAC (WPH) dose on sulfamethoxazole removal (contact time = 3 h). Error bars represent %RSD.

range of pH levels, different removal efficiencies are seen. The WPH carbon performs the greatest removal at the pH level of 6.3. This result is consistent with the predicted performance of sulfamethoxazole removal with WPH, as the compound exists approximately in a 50% neutral state and 50% negative species interacting with a negatively charged PAC at pH 6.3. It was predicted that the removal of sulfamethoxazole at the pH levels of 8.3 and 10.3 would be more closely correlated and less than that of pH 6.3. At these pH levels the predominant species of sulfamethoxazole is negatively charged with very little remaining as either neutral or positively charged species and the surface charge of the carbon being negative. The significant difference in removal between pH 8.3 and pH 10.3 is not well understood. Figure 10 presents the data for the removal of SMXL by the HDB PAC. The HDB carbon has the greatest removal of sulfamethoxazole at a pH of 6.3. This is similar to the WPH carbon but it poses a discrepancy with the hypothesis. At a pH of 6.3 the compound is split between negative and neutral species while the carbon is carrying a positive surface charge. While some effective removal should be possible due to electrostatic interactions between the carbon and compound, pH 8.3 was predicted to provide better removal. At pH 8.3 the sulfamethoxazole should exist in a predominantly negative species while the HDB is still carrying a positive charge, its PZC being 10.6. Greater removal of the sulfamethoxazole should be expected at a pH of 8.3, not 6.3. The HDB carbon has the least removal at a pH level of 10.3. This may be due to the carbon nearing its PZC and providing less favorable electrostatic interactions between the carbon and the negatively charged sulfamethoxazole species. While these behaviors do not validate this study's predictions, it does support findings by Margot *et. al.* (2013). Even with opposing electrostatic

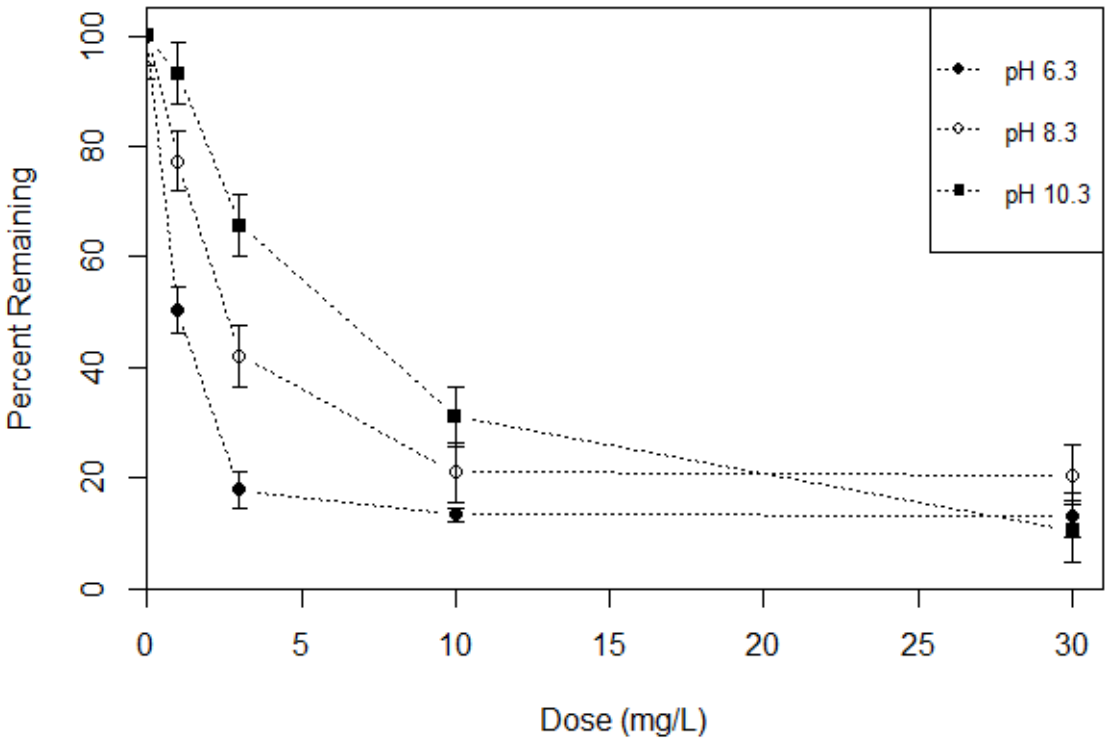

Figure 10. Effect of PAC (HDB) dose on sulfamethoxazole removal (contact time = 3 h). Error bars represent %RSD.

charges between the HDB and the negatively charged species of SMXL, the results show less sorption efficiency of the negatively charged SMXL species and may have a more substantial influence on sorption efficiency than the electrostatic interactions predicted in this study. Figure 11 presents the data for the removal of SMXL with AN. The AN carbon has the greatest removal of SMXL at the 6.3 pH level. This can be explained by the speciation of the SMXL at pH 6.3. Again, roughly half the compound is in a neutral state while half is in a negative species. The AN is carrying a negative surface charge and should exhibit greater adsorption than at the pH levels of 8.3 and 10.3. At the two higher pH levels the SMXL is predominantly negatively charged interacting with a negative

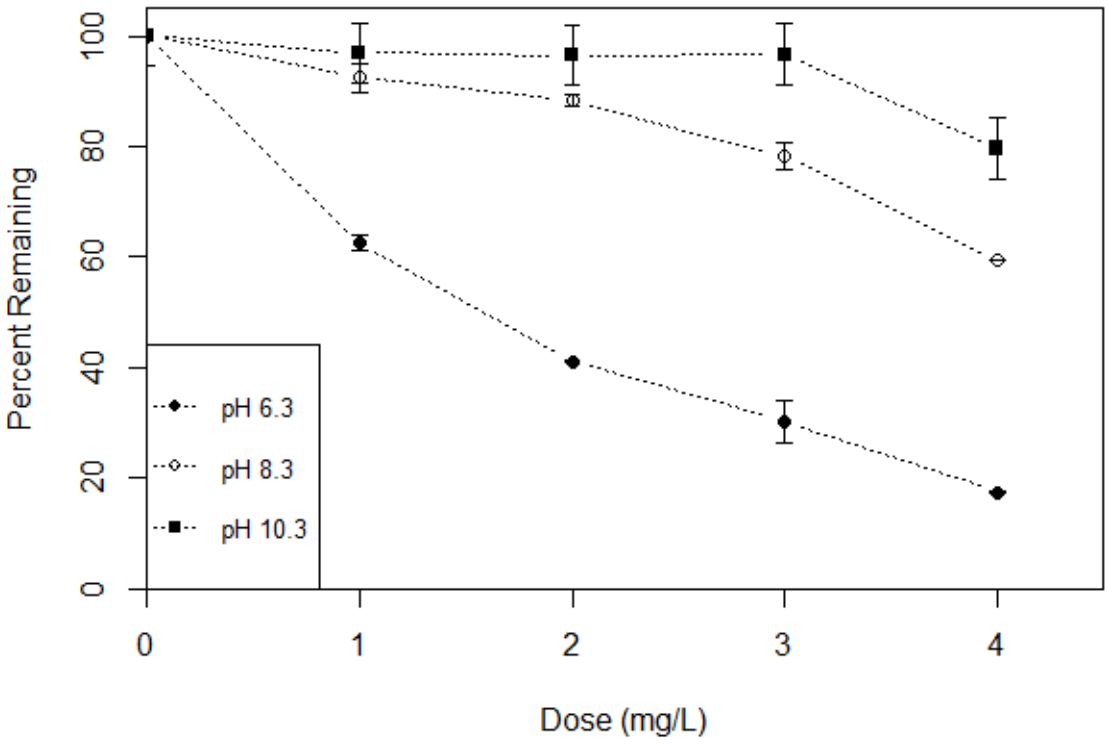

Figure 11. Effect of PAC (AN) dose on sulfamethoxazole removal (contact time = 3 h). Error bars represent %RSD.

surface charge on the AN, leading to lower sorption than at pH 6.3. The results in figure 11 support the hypothesis, but it should be noted that in all in three studies with SMXL the greatest removal was achieved at the lowest pH of 6.3 where the SMXL exists in both negative and neutral species. It may be that electrostatic interactions are not the driving force in removal of SMXL with AN, and that the neutral form of SMXL is more readily removed by PAC than its negatively charged form.

Pore Distribution and Surface Area Normalization of 3-Hour SMXL Data

Another approach was undertaken in the assessment of the PACs performance in removing fluoxetine and sulfamethoxazole. The data was normalized for surface area. As previously shown in Table 2, the PACs possess varied physical characteristics. By normalizing the data, it was possible to compare the other characteristics of the carbons, including pore size and distribution. Figures 12 illustrates the performance of the three PACs at removing SMXL at a pH of 6.3. The x-axis shows the dose as a measure of the surface area of the respective carbons.

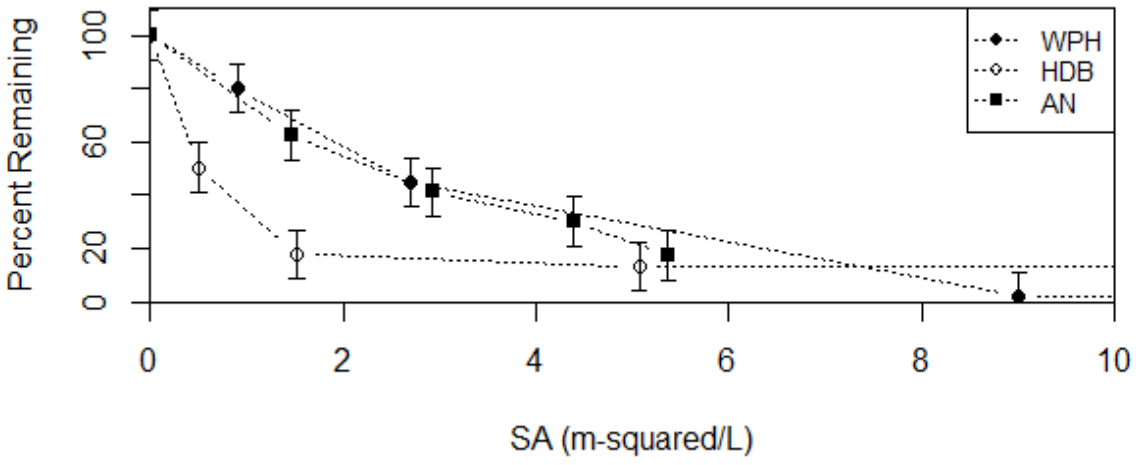

Figure 12. Effect of PAC surface area on sulfamethoxazole removal at pH 6.3 (contact time = 3 h). Error bars represent %RSD.

As hypothesized, the HDB carbon removes more SMXL than both AN and WPH. This is consistent as HDB is the only carbon that would have attractive electrostatic

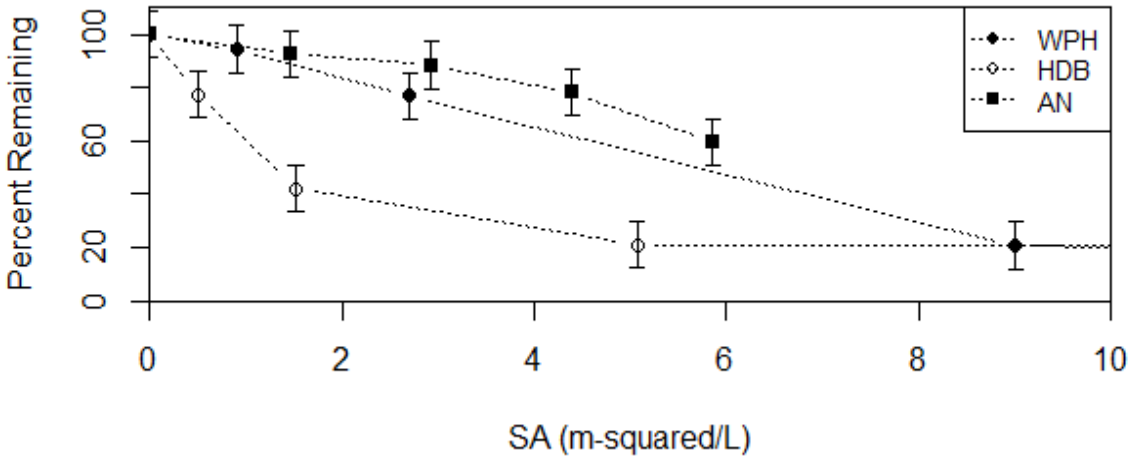

Figure 13. Effect of PAC surface area on sulfamethoxazole removal at pH 8.3 (contact time = 3 h). Error bars represent %RSD.

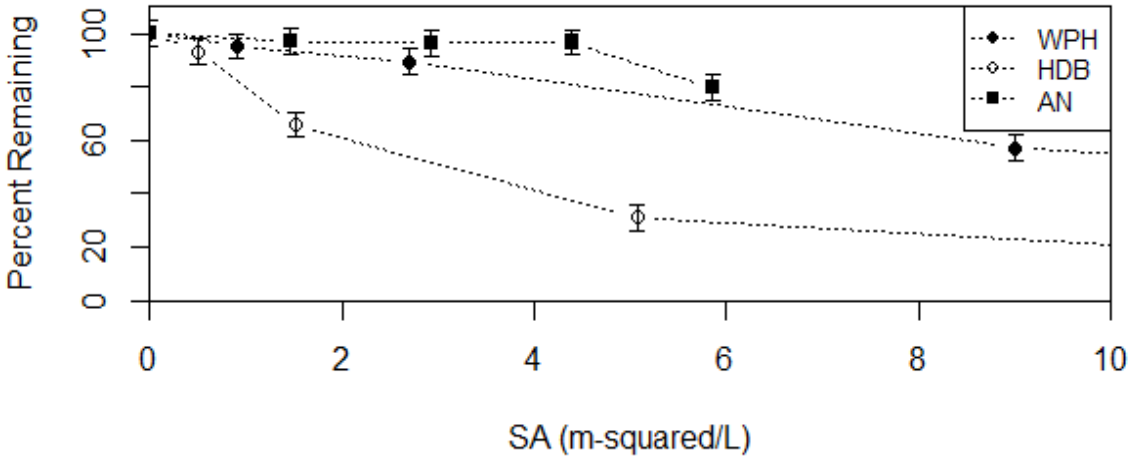

Figure 14. Effect of PAC surface area on sulfamethoxazole removal at pH 10.3 (contact time = 3 h). Error bars represent %RSD.

forces with SMXL at a pH of 6.3. Figures 13 and 14 show similar results and further support the hypothesis as AN and WPH have repulsive electrostatic forces present across

the range of pH values tested. This is not the case when the same surface area normalization is applied to the performance of the PACs at removing fluoxetine.

Pore Distribution and Surface Area Normalization of 3-Hour FLX Data

When the data for the removal of fluoxetine is normalized for surface area, it becomes apparent that electrostatic interactions are playing a less significant role. According to the predictions in Table 4, HDB was predicted to have the least suitable electrostatic interactions for FLX removal. Figure 15 shows the performance of the three PACs at a pH of 6.3 when normalized for surface area. WPH removes the least amount of FLX when compared to both AN and HDB. As shown in Table 4, AN and WPH should both be exhibiting attractive forces with fluoxetine, yet WPH has the least percent

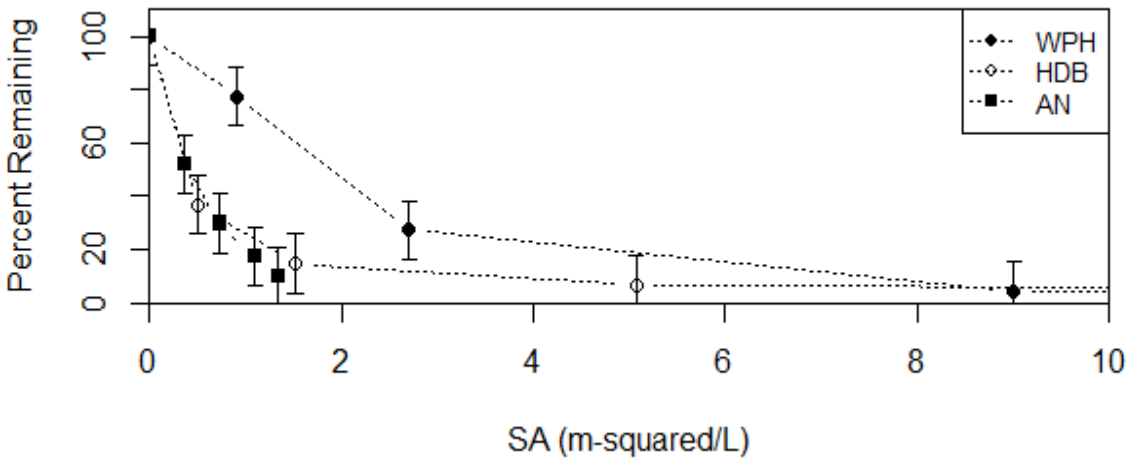

Figure 15. Effect of PAC surface area on fluoxetine removal at pH 6.3 (contact time = 3 h). Error bars represent %RSD.

removal of the carbons. This is evidence that other characteristics of the carbons are playing a more significant role in the removal of fluoxetine than electrostatic interactions. Figures 16 and 17 continue to show this trend at the other pH values tested, as HDB and AN outperform WPH in their removal efficiencies of fluoxetine.

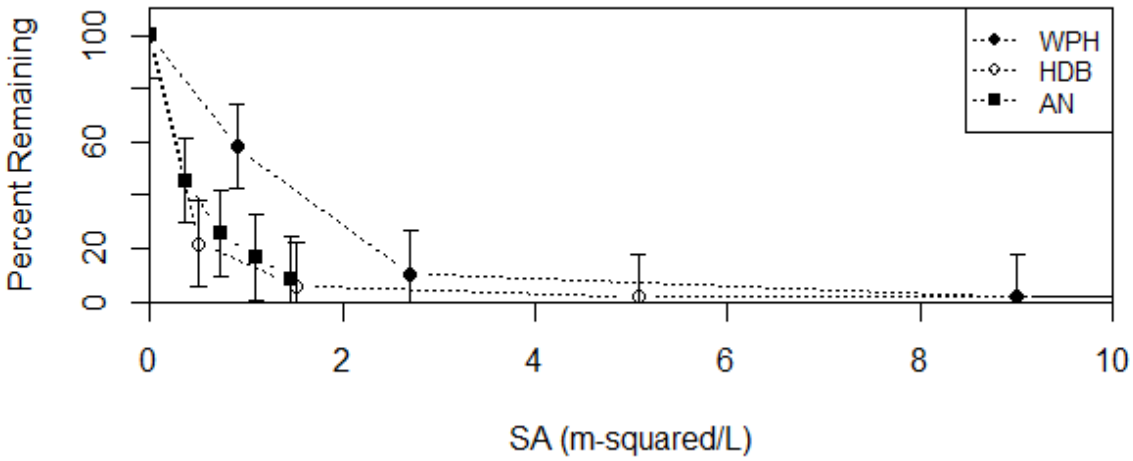

Figure 16. Effect of PAC surface area on fluoxetine removal at pH 8.3 (contact time = 3 h). Error bars represent %RSD.

Unlike the results for sulfamethoxazole removal, which followed predictions based on electrostatic interactions, the results for fluoxetine removal between the PACs when normalized for surface area do not support the hypothesis. Another mechanism seems to playing a more significant role in the adsorption efficiencies of the carbons. The previous figures illustrate that AN and HDB perform the greatest removal efficiencies of fluoxetine. Both carbons have a similar pore size distribution when compared to WPH (As seen previously in Table 2). Both AN and HDB have the majority of their pores fall

in the meso-pore and macro-pore size, 79% for HDB and 68% for AN. WPH on the other hand, has the majority of its pores falling in the micro-pore range at 66%. This difference

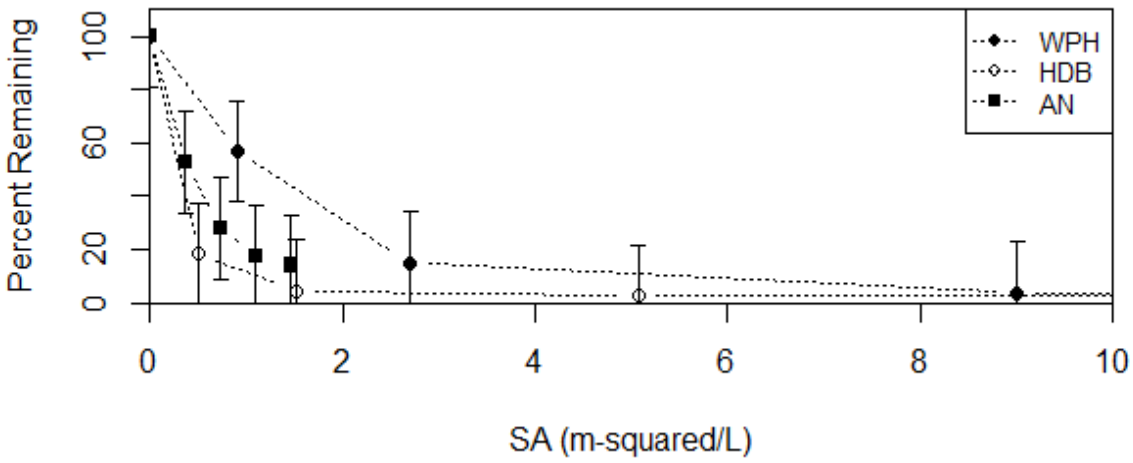

Figure 17. Effect of PAC surface area on fluoxetine removal at pH 10.3 (contact time = 3 h). Error bars represent %RSD.

in pore size distribution may have a more significant role than electrostatic interactions in the removal of fluoxetine. One reason why pore size distribution may have such a pronounced effect on the removal of fluoxetine and not sulfamethoxazole is the difference in the two compounds van der Waals molecular surface areas, 450.6 and 337.6 respectively. The larger fluoxetine molecules may not be diffusing as well into the smaller pores of the WPH compared to the AN and HDB, leading to less sorption capacity. Sulfamethoxazole's smaller molecules may have a greater ability to access these micropores.

CONCLUSIONS

The adsorption of two ionizable PPCPs, fluoxetine and sulfamethoxazole, onto three PACs was examined to evaluate the potential of leveraging electrostatic interactions to enhance removal of ionizable PPCP's at pH values relevant to water treatment. Furthermore, while electrostatic interactions were seen to play a role in removal of the target adsorbates, two scenarios in particular did not support the study's hypothesis. WPH was predicted to outperform HDB in the removal of fluoxetine due to electrostatic interactions between the compound and the respective carbons. When normalized for surface area, the results show that this is not the case. HDB consistently removed more fluoxetine than WPH. The pore distribution of the PACs seemed to play a more significant role in the sorption efficiency than pH and electrostatic interactions in this instance. Additionally, it was predicted that SMXL would be much more apt to sorb to HDB at a pH of 8.3 than FLX based on electrostatic interactions. This was not the case. While similar removal efficiencies could be achieved at the maximum PAC dosage of 30 mg/L, throughout the range of PAC doses tested, HDB removed far more FLX compared to SMXL. This may be due to the predominantly negative species of SMXL present at a pH of 8.3 and is line with other findings in the literature showing the difficulty of removing negatively charged compounds from solution using activated carbon. Further evidence of this phenomena found in this study is that for all of the experiments that utilized SMXL as the target adsorbate, greater removal efficiencies were observed at the pH value of 6.3 regardless of the PAC used. This is the only pH value evaluated in this study where at least some of the SMXL existed in a form other than the negatively

charged form. When some of the SMXL existed in its neutral form, greater removal efficiencies were observed. Finally, while it has been shown that pH and the subsequent electrostatic interaction between the PACs and target adsorbates does have an effect on sorption efficiencies, PAC surface area was more important for fluoxetine and sulfamethoxazole removal than electrostatic interactions with negatively charged compounds being most difficult to remove. Further study is needed to determine if this is true for other PACs and PPCP's or if there are still instances where selection of PAC based on pH is relevant for ionizable compounds.

ENGINEERING SIGNIFICANCE

This study attempted to discern the impact of electrostatic interactions on the removal of fluoxetine and sulfamethoxazole from the aqueous phase using commercially available powdered activated carbons. If it could be shown that a particular PAC could achieve better removal based on its PZC and the target adsorbate's charge, guidance could be provided to water utility operators so as to reduce the amount of PAC needed while effectively removing these compounds. This theoretical reduction in PAC usage could translate into lower operating costs for utilities as well as more efficient use of a material that is energy intensive to produce, the PAC itself. In this study it was shown that under certain conditions, particularly when compounds existed in a positively charged form, electrostatic interactions can play a role in increasing removal efficiencies. One major limitation of this finding is that when compounds existed in a negatively charged form no benefit was observed in selecting a PAC with predicted attractive electrostatic interactions. Other limitations of this included the examination of only two compounds and the absence of competing ions, like natural organic matter or other contaminants. In water treatment plants it would be likely that a number of PPCPs would be targeted simultaneously. Selecting one PAC that provides beneficial electrostatic conditions for one target compound may have little to no effect on another compound present that has different chemical characteristics. Furthermore, some compounds may not exist in positively charged species in the pH range normally found at water treatment and wastewater treatment plants, again limiting the usefulness of electrostatic

interactions. In these scenario, increasing the dose of PAC used may be the only option available.

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APPENDIX

Data

Table A-1. WPH Removal of FLX at pH 5 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
13-01a	5	0	FLX	2	2.25	2.19	104.95	100 ± 9.00
13-01a	5	0	FLX	2	2.14			
13-01b	5	0	FLX	2	1.91	1.99	95.05	
13-01b	5	0	FLX	2	2.06			
13-02a	5	1	FLX	2	1.47	1.52	72.47	73.46 ± 1.81
13-02a	5	1	FLX	2	1.56			
13-02b	5	1	FLX	2	1.60	1.56	74.47	
13-02b	5	1	FLX	2	1.51			
13-03a	5	3	FLX	2	0.67	0.70	33.28	29.11 ± 7.57
13-03a	5	3	FLX	2	0.72			
13-03b	5	3	FLX	2	0.47	0.52	24.96	
13-03b	5	3	FLX	2	0.58			
13-04a	5	10	FLX	2	NA	0.05	2.23	1.74 ± 0.88
13-04a	5	10	FLX	2	0.05			
13-04b	5	10	FLX	2	0.03	0.03	1.26	
13-04b	5	10	FLX	2	0.02			
13-05a	5	30	FLX	2	0.02	0.02	0.74	0.86 ± 0.23
13-05a	5	30	FLX	2	0.01			
13-05b	5	30	FLX	2	0.01	0.02	0.99	
13-05b	5	30	FLX	2	0.04			

Table A-2. WPH Removal of FLX at pH 6.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
06-01a	6.3	0	FLX	2	1.92	2.27	102.16	100 ± 3.93
06-01a	6.3	0	FLX	2	2.62			
06-01b	6.3	0	FLX	2	1.86	2.18	97.84	
06-01b	6.3	0	FLX	2	2.50			
06-02a	6.3	1	FLX	2	1.82	1.72	77.37	77.37 ± NA
06-02a	6.3	1	FLX	2	1.62			
06-03a	6.3	3	FLX	2	0.63	0.65	29.33	27.22 ± 3.83
06-03a	6.3	3	FLX	2	0.68			
06-03b	6.3	3	FLX	2	0.49	0.56	25.12	
06-03b	6.3	3	FLX	2	0.63			
06-04a	6.3	10	FLX	2	0.11	0.10	4.42	4.23 ± 0.35
06-04a	6.3	10	FLX	2	0.09			
06-04b	6.3	10	FLX	2	0.09	0.09	4.03	
06-04b	6.3	10	FLX	2	NA			
06-05a	6.3	30	FLX	2	0.05	0.05	2.40	2.77 ± 0.68
06-05a	6.3	30	FLX	2	0.05			
06-05b	6.3	30	FLX	2	0.07	0.07	3.15	
06-05b	6.3	30	FLX	2	NA			

Table A-3. WPH Removal of FLX at pH 8.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
11-01a	8.3	0	FLX	2	2.12	2.04	93.57	100 ± 11.68
11-01a	8.3	0	FLX	2	1.95			
11-01b	8.3	0	FLX	2	2.68	2.32	106.43	
11-01b	8.3	0	FLX	2	1.96			
11-02a	8.3	1	FLX	2	1.35	1.32	60.53	58.24 ± 4.16
11-02a	8.3	1	FLX	2	1.29			
11-02b	8.3	1	FLX	2	1.34	1.22	55.95	
11-02b	8.3	1	FLX	2	1.09			
11-03a	8.3	3	FLX	2	0.21	0.20	9.26	10.55 ± 2.35
11-03a	8.3	3	FLX	2	0.19			
11-03b	8.3	3	FLX	2	0.26	0.26	11.85	
11-03b	8.3	3	FLX	2	0.26			
11-04a	8.3	10	FLX	2	0.03	0.03	1.49	1.71 ± 0.40
11-04a	8.3	10	FLX	2	0.03			
11-04b	8.3	10	FLX	2	0.05	0.04	1.93	
11-04b	8.3	10	FLX	2	0.03			
11-05a	8.3	30	FLX	2	0.15	0.15	6.98	6.98 ± NA
11-05a	8.3	30	FLX	2	0.16			

Table A-4. WPH Removal of FLX at pH 10.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
08-01a	10.3	0	FLX	2	2.14	2.18	104.63	100 ± 8.42
08-01a	10.3	0	FLX	2	2.22			
08-01b	10.3	0	FLX	2	2.03	1.99	95.37	
08-01b	10.3	0	FLX	2	1.94			
08-02a	10.3	1	FLX	2	1.17	1.13	54.47	56.85 ± 4.34
08-02a	10.3	1	FLX	2	1.10			
08-02b	10.3	1	FLX	2	1.26	1.23	59.23	
08-02b	10.3	1	FLX	2	1.21			
08-03a	10.3	3	FLX	2	0.27	0.27	13.02	14.84 ± 3.31
08-03a	10.3	3	FLX	2	0.28			
08-03b	10.3	3	FLX	2	0.36	0.35	16.66	
08-03b	10.3	3	FLX	2	0.34			
08-04a	10.3	10	FLX	2	0.08	0.08	3.94	3.71 ± 0.42
08-04a	10.3	10	FLX	2	0.08			
08-04b	10.3	10	FLX	2	0.06	0.07	3.48	
08-04b	10.3	10	FLX	2	0.08			
08-05a	10.3	30	FLX	2	0.06	0.07	3.26	3.66 ± 0.73
08-05a	10.3	30	FLX	2	0.08			
08-05b	10.3	30	FLX	2	0.07	0.08	4.05	
08-05b	10.3	30	FLX	2	0.10			

Table A-5. HDB Removal of FLX at pH 6.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
16-11a	6.3	0	FLX	2	2.01	2.00	106.15	100 ± 9.07
16-11a	6.3	0	FLX	2	1.99			
16-11b	6.3	0	FLX	2	1.62	1.77	93.85	
16-11b	6.3	0	FLX	2	1.92			
16-12a	6.3	1	FLX	2	0.71	0.70	37.33	36.78 ± 0.81
16-12a	6.3	1	FLX	2	0.70			
16-12b	6.3	1	FLX	2	0.70	0.68	36.23	
16-12b	6.3	1	FLX	2	0.67			
16-13b	6.3	3	FLX	2	0.28	0.24	12.57	14.71 ± 3.15
16-13b	6.3	3	FLX	2	0.19			
16-14a	6.3	10	FLX	2	0.30	0.32	16.84	
16-14a	6.3	10	FLX	2	0.34			
16-14b	6.3	10	FLX	2	0.11	0.10	5.36	6.59 ± 1.81
16-14b	6.3	10	FLX	2	0.10			
16-15a	6.3	30	FLX	2	0.16	0.15	7.82	
16-15a	6.3	30	FLX	2	0.14			
16-15b	6.3	30	FLX	2	0.09	0.09	4.68	4.68 ± NA
16-15b	6.3	30	FLX	2	0.08			

Table A-6. HDB Removal of FLX at pH 8.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
14-11a	8.3	0	FLX	2	2.00	2.04	99.73	100 ± 0.40
14-11a	8.3	0	FLX	2	2.08			
14-11b	8.3	0	FLX	2	2.23	2.05	100.27	
14-11b	8.3	0	FLX	2	1.87			
14-12a	8.3	1	FLX	2	0.45	0.50	24.37	21.81 ± 3.78
14-12a	8.3	1	FLX	2	0.55			
14-12b	8.3	1	FLX	2	0.43	0.39	19.25	
14-12b	8.3	1	FLX	2	0.36			
14-13a	8.3	3	FLX	2	0.15	0.14	6.99	6.06 ± 1.37
14-13a	8.3	3	FLX	2	0.14			
14-13b	8.3	3	FLX	2	0.10	0.10	5.13	
14-13b	8.3	3	FLX	2	0.11			
14-14a	8.3	10	FLX	2	0.00	0.02	0.95	1.79 ± 1.24
14-14a	8.3	10	FLX	2	0.04			
14-14b	8.3	10	FLX	2	0.05	0.05	2.63	
14-14b	8.3	10	FLX	2	0.06			
14-15a	8.3	30	FLX	2	0.04	0.04	1.80	1.80 ± NA
14-15a	8.3	30	FLX	2	0.03			
14-15b	8.3	30	FLX	2	0.06			
14-15b	8.3	30	FLX	2	0.03			

Table A-7. HDB Removal of FLX at pH 10.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
15-11a	10.3	0	FLX	2	2.27	2.30	104.96	100 ± 7.42
15-11a	10.3	0	FLX	2	2.33			
15-11b	10.3	0	FLX	2	2.13	2.08	95.04	
15-11b	10.3	0	FLX	2	2.03			
15-12a	10.3	1	FLX	2	0.41	0.46	20.91	18.23 ± 3.97
15-12a	10.3	1	FLX	2	0.51			
15-12b	10.3	1	FLX	2	0.34	0.34	15.54	
15-12b	10.3	1	FLX	2	0.34			
15-13a	10.3	3	FLX	2	0.16	0.14	6.25	4.32 ± 2.86
15-13a	10.3	3	FLX	2	0.11			
15-13b	10.3	3	FLX	2	0.06	0.05	2.38	
15-13b	10.3	3	FLX	2	0.05			
15-14a	10.3	10	FLX	2	0.06	0.05	2.37	2.54 ± 0.25
15-14a	10.3	10	FLX	2	0.04			
15-14b	10.3	10	FLX	2	0.06	0.06	2.71	
15-14b	10.3	10	FLX	2	0.06			
15-15a	10.3	30	FLX	2	0.06	0.07	3.17	2.22 ± 1.39
15-15a	10.3	30	FLX	2	0.08			
15-15b	10.3	30	FLX	2	0.02	0.03	1.28	
15-15b	10.3	30	FLX	2	0.04			

Table A-8. AN Removal of FLX at pH 10.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
24-01a	10.3	0	FLX	2	1.95	1.96	100.00	100 ± 1.94
24-01b	10.3	0	FLX	2	1.92			
24-01c	10.3	0	FLX	2	2.00			
24-02a	10.3	0.25	FLX	2	1.06	1.03	52.48	52.48 ± 2.75
24-02b	10.3	0.25	FLX	2	0.97			
24-02c	10.3	0.25	FLX	2	1.06			
24-03a	10.3	0.5	FLX	2	0.63	0.54	27.69	27.69 ± 4.28
24-03b	10.3	0.5	FLX	2	0.53			
24-03c	10.3	0.5	FLX	2	0.47			
24-04a	10.3	0.75	FLX	2	0.35	0.34	17.59	17.59 ± 0.52
24-04b	10.3	0.75	FLX	2	0.33			
24-04c	10.3	0.75	FLX	2	0.34			
24-05a	10.3	1	FLX	2	0.21	0.27	14.02	14.02 ± 6.85
24-05b	10.3	1	FLX	2	0.19			
24-05c	10.3	1	FLX	2	0.42			

Table A-9. AN Removal of FLX at pH 8.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
23-01a	8.3	0	FLX	2	2.06	2.12	100.00	100 ± 4.05
23-01b	8.3	0	FLX	2	2.17			
23-02a	8.3	0.25	FLX	2	0.95	0.96	45.37	45.37 ± 2.87
23-02b	8.3	0.25	FLX	2	1.02			
23-02c	8.3	0.25	FLX	2	0.91			
23-03a	8.3	0.5	FLX	2	0.52	0.54	25.50	25.50 ± 1.53
23-03b	8.3	0.5	FLX	2	0.58			
23-03c	8.3	0.5	FLX	2	0.53			
23-04a	8.3	0.75	FLX	2	0.37	0.35	16.69	16.69 ± 0.85
23-04b	8.3	0.75	FLX	2	0.34			
23-04c	8.3	0.75	FLX	2	0.34			
23-05a	8.3	1	FLX	2	0.22	0.18	8.44	8.44 ± 2.87
23-05b	8.3	1	FLX	2	0.14			

Table A-10. AN Removal of FLX at pH 6.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
25-01a	6.3	0	FLX	2	1.91	1.98	100.00	100 ± 5.28
25-01b	6.3	0	FLX	2	2.05			
25-02a	6.3	0.25	FLX	2	0.94	1.03	52.18	52.18 ± 6.89
25-02b	6.3	0.25	FLX	2	1.13			
25-03a	6.3	0.5	FLX	2	0.63	0.59	29.72	29.72 ± 2.67
25-03b	6.3	0.5	FLX	2	0.55			
25-04a	6.3	0.75	FLX	2	0.34	0.34	17.36	17.36 ± 0.27
25-04b	6.3	0.75	FLX	2	0.35			
25-05a	6.3	1	FLX	2	0.17	0.20	9.94	9.94 ± 1.87
25-05b	6.3	1	FLX	2	0.22			

Table A-11. HDB Removal of SMXL at pH 6.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
33-01a	6.3	0	SMXL	2	1.96	2.04	105.27	100 ± 7.78
33-01a	6.3	0	SMXL	2	2.12			
33-01b	6.3	0	SMXL	2	1.82	1.84	94.73	
33-01b	6.3	0	SMXL	2	1.85			
33-02a	6.3	1	SMXL	2	0.94	0.92	47.47	50.37 ± 4.27
33-02a	6.3	1	SMXL	2	0.90			
33-02b	6.3	1	SMXL	2	1.05	1.03	53.26	
33-02b	6.3	1	SMXL	2	1.01			
33-03a	6.3	3	SMXL	2	0.30	0.30	15.65	17.81 ± 3.20
33-03a	6.3	3	SMXL	2	0.31			
33-03b	6.3	3	SMXL	2	0.39	0.39	19.98	
33-03b	6.3	3	SMXL	2	0.38			
33-04a	6.3	10	SMXL	2	0.23	0.24	12.48	13.34 ± 1.27
33-04a	6.3	10	SMXL	2	0.25			
33-04b	6.3	10	SMXL	2	0.28	0.28	14.20	
33-04b	6.3	10	SMXL	2	0.27			
33-05a	6.3	30	SMXL	2	0.23	0.20	10.50	13.20 ± 3.99
33-05a	6.3	30	SMXL	2	0.18			
33-05b	6.3	30	SMXL	2	0.32	0.31	15.90	
33-05b	6.3	30	SMXL	2	0.30			

Table A-12. HDB Removal of SMXL at pH 8.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
33-06a	8.3	0	SMXL	2	2.48	2.46	98.66	100 ± 1.98
33-06a	8.3	0	SMXL	2	2.44			
33-06b	8.3	0	SMXL	2	2.55	2.53	101.34	
33-06b	8.3	0	SMXL	2	2.50			
33-07a	8.3	1	SMXL	2	1.84	1.95	78.40	77.37 ± 1.52
33-07a	8.3	1	SMXL	2	2.07			
33-07b	8.3	1	SMXL	2	1.92	1.90	76.34	
33-07b	8.3	1	SMXL	2	1.88			
33-08a	8.3	3	SMXL	2	1.04	1.07	42.84	42.10 ± 1.09
33-08a	8.3	3	SMXL	2	1.10			
33-08b	8.3	3	SMXL	2	1.03	1.03	41.37	
33-08b	8.3	3	SMXL	2	1.03			
33-09a	8.3	10	SMXL	2	0.49	0.47	18.85	21.00 ± 3.17
33-09a	8.3	10	SMXL	2	0.45			
33-09b	8.3	10	SMXL	2	0.58	0.58	23.15	
33-09b	8.3	10	SMXL	2	0.57			
33-10a	8.3	30	SMXL	2	0.55	0.64	25.59	20.57 ± 7.42
33-10a	8.3	30	SMXL	2	0.73			
33-10b	8.3	30	SMXL	2	0.38	0.39	15.54	
33-10b	8.3	30	SMXL	2	0.39			

Table A-13. HDB Removal of SMXL at pH 10.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
33-11a	10.3	0	SMXL	2	1.93	1.95	97.82	100 ± 3.22
33-11a	10.3	0	SMXL	2	1.97			
33-11b	10.3	0	SMXL	2	1.91	2.04	102.18	
33-11b	10.3	0	SMXL	2	2.16			
33-12a	10.3	1	SMXL	2	1.86	1.84	92.44	93.15 ± 1.04
33-12a	10.3	1	SMXL	2	1.82			
33-12b	10.3	1	SMXL	2	1.84	1.87	93.85	
33-12b	10.3	1	SMXL	2	1.90			
33-13a	10.3	3	SMXL	2	1.10	1.25	62.64	65.66 ± 4.47
33-13a	10.3	3	SMXL	2	1.39			
33-13b	10.3	3	SMXL	2	1.37	1.37	68.69	
33-13b	10.3	3	SMXL	2	1.37			
33-14a	10.3	10	SMXL	2	0.65	0.68	33.99	31.01 ± 4.40
33-14a	10.3	10	SMXL	2	0.71			
33-14b	10.3	10	SMXL	2	0.50	0.56	28.03	
33-14b	10.3	10	SMXL	2	0.62			
33-15a	10.3	30	SMXL	2	0.18	0.20	10.29	10.29 ± NA
33-15a	10.3	30	SMXL	2	0.23			

Table A-14. AN Removal of SMXL at pH 6.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
35-01a	6.3	0	SMXL	2	2.18	2.19	96.39	100 ± 5.33
35-01a	6.3	0	SMXL	2	2.21			
35-01b	6.3	0	SMXL	2	2.30	2.36	103.61	
35-01b	6.3	0	SMXL	2	2.42			
35-02a	6.3	1	SMXL	2	1.49	1.44	63.41	62.50 ± 1.35
35-02a	6.3	1	SMXL	2	1.40			
35-02b	6.3	1	SMXL	2	1.37	1.40	61.59	
35-02b	6.3	1	SMXL	2	1.43			
35-03a	6.3	3	SMXL	2	0.93	0.94	41.30	41.11 ± 0.27
35-03a	6.3	3	SMXL	2	0.95			
35-03b	6.3	3	SMXL	2	0.92	0.93	40.92	
35-03b	6.3	3	SMXL	2	0.95			
35-04a	6.3	10	SMXL	2	0.63	0.63	27.66	30.19 ± 3.74
35-04a	6.3	10	SMXL	2	0.63			
35-04b	6.3	10	SMXL	2	0.72	0.74	32.72	
35-04b	6.3	10	SMXL	2	0.77			
35-05a	6.3	30	SMXL	2	0.39	0.40	17.41	17.45 ± 0.06
35-05a	6.3	30	SMXL	2	0.40			
35-05b	6.3	30	SMXL	2	0.39	0.40	17.49	
35-05b	6.3	30	SMXL	2	0.40			

Table A-15. AN Removal of SMXL at pH 8.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
35-06a	8.3	0	SMXL	2	2.50	2.48	100.00	100 ± NA
35-06a	8.3	0	SMXL	2	2.47			
35-07a	8.3	1	SMXL	2	2.35	2.34	94.18	100 ± 2.60
35-07a	8.3	1	SMXL	2	2.33			
35-07b	8.3	1	SMXL	2	2.22	2.25	90.65	
35-07b	8.3	1	SMXL	2	2.28			
35-08a	8.3	3	SMXL	2	2.16	2.18	87.64	100 ± 0.95
35-08a	8.3	3	SMXL	2	2.19			
35-08b	8.3	3	SMXL	2	2.19	2.21	88.93	
35-08b	8.3	3	SMXL	2	2.23			
35-09a	8.3	10	SMXL	2	1.95	1.98	79.86	100 ± 2.47
35-09a	8.3	10	SMXL	2	2.02			
35-09b	8.3	10	SMXL	2	1.89	1.90	76.51	
35-09b	8.3	10	SMXL	2	1.91			
35-10a	8.3	30	SMXL	2	1.46	1.47	59.35	100 ± 0.05
35-10a	8.3	30	SMXL	2	1.49			
35-10b	8.3	30	SMXL	2	1.44	1.48	59.42	
35-10b	8.3	30	SMXL	2	1.51			

Table A-16. AN Removal of SMXL at pH 10.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
35-11a	10.3	0	SMXL	2	2.51	2.55	98.16	100 ± 2.72
35-11a	10.3	0	SMXL	2	2.59			
35-11b	10.3	0	SMXL	2	2.65	2.65	101.84	
35-11b	10.3	0	SMXL	2	2.65			
35-12a	10.3	1	SMXL	2	2.45	2.45	94.27	96.96 ± 3.98
35-12a	10.3	1	SMXL	2	2.46			
35-12b	10.3	1	SMXL	2	2.57	2.59	99.66	
35-12b	10.3	1	SMXL	2	2.62			
35-13a	10.3	3	SMXL	2	2.49	2.51	96.47	96.47 ± NA
35-13a	10.3	3	SMXL	2	2.52			
35-14a	10.3	10	SMXL	2	2.35	2.42	93.20	96.65 ± 5.08
35-14a	10.3	10	SMXL	2	2.50			
35-14b	10.3	10	SMXL	2	2.57	2.60	100.09	
35-14b	10.3	10	SMXL	2	2.64			
35-15a	10.3	30	SMXL	2	1.97	1.99	76.63	79.63 ± 4.43
35-15a	10.3	30	SMXL	2	2.02			
35-15b	10.3	30	SMXL	2	2.12	2.15	82.64	
35-15b	10.3	30	SMXL	2	2.18			

Table A-17. WPH Removal of SMXL at pH 6.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
28-01a	6.3	0	SMXL	2	2.22	2.22	101.89	100 ± 1.43
28-01b	6.3	0	SMXL	2	2.15	2.15	98.68	
28-01c	6.3	0	SMXL	2	2.17	2.16	99.42	
28-01c	6.3	0	SMXL	2	2.16			
28-02a	6.3	1	SMXL	2	1.89	1.81	83.41	81.39 ± 1.76
28-02a	6.3	1	SMXL	2	1.74			
28-02b	6.3	1	SMXL	2	1.72	1.72	79.27	
28-02c	6.3	1	SMXL	2	1.77	1.77	81.49	
28-03a	6.3	3	SMXL	2	1.13	1.13	51.99	45.56 ± 9.50
28-03b	6.3	3	SMXL	2	0.87	0.85	39.12	
28-03b	6.3	3	SMXL	2	0.83			
28-04a	6.3	10	SMXL	2	0.04	0.04	2.03	1.86 ± 0.26
28-04c	6.3	10	SMXL	2	0.04	0.04	1.68	
28-05a	6.3	30	SMXL	2	0.00	0.00	0.00	ND ± NA
28-05a	6.3	30	SMXL	2	0.00			
28-05b	6.3	30	SMXL	2	0.00	0.00	0.00	
28-05b	6.3	30	SMXL	2	0.00	0.00	0.00	
28-05c	6.3	30	SMXL	2	0.00	0.00	0.00	

Table A-18. WPH Removal of SMXL at pH 8.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
28-06a	8.3	0	SMXL	2	2.14	2.14	100.40	100 ± 0.59
28-06c	8.3	0	SMXL	2	2.12	2.12	99.60	
28-07a	8.3	1	SMXL	2	2.01	2.01	94.31	93.85 ± 1.76
28-07b	8.3	1	SMXL	2	1.99	1.99	93.39	
28-07c	8.3	1	SMXL	2	2.06	2.06	96.65	
28-08a	8.3	3	SMXL	2	1.64	1.65	77.29	77.29 ± 2.52
28-08a	8.3	3	SMXL	2	1.65			
28-08b	8.3	3	SMXL	2	1.68	1.63	76.45	
28-08b	8.3	3	SMXL	2	1.57			
28-08c	8.3	3	SMXL	2	1.73	1.73	80.99	
28-09a	8.3	10	SMXL	2	0.45	0.44	20.53	20.53 ± 5.81
28-09a	8.3	10	SMXL	2	0.42			
28-09b	8.3	10	SMXL	2	0.35	0.35	16.39	
28-09c	8.3	10	SMXL	2	0.61	0.58	27.41	
28-09c	8.3	10	SMXL	2	0.56			
28-10a	8.3	30	SMXL	2	0.04	0.04	1.70	1.43 ± 0.55
28-10b	8.3	30	SMXL	2	0.02	0.02	1.16	
28-10c	8.3	30	SMXL	2	0.05	0.05	2.21	

Table A-19. WPH Removal of SMXL at pH 10.3 (contact time = 3 hours).

Sample ID	pH	Dose (mg/L)	Compound	Initial Conc. (µg/L)	Final Conc. (µg/L)	Ave. Conc. (µg/L)	Percent Remaining	Ave. Percent Remaining
29-01a	10.3	0	SMXL	2	2.13	2.15	99.36	100 ± 0.79
29-01a	10.3	0	SMXL	2	2.16			
29-01b	10.3	0	SMXL	2	2.17	2.18	101.07	
29-01b	10.3	0	SMXL	2	2.19			
29-01c	10.3	0	SMXL	2	2.15	2.15	99.57	
29-01c	10.3	0	SMXL	2	2.15			
29-02a	10.3	1	SMXL	2	2.05	2.04	94.56	94.81 ± 3.46
29-02a	10.3	1	SMXL	2	2.04			
29-02b	10.3	1	SMXL	2	1.98	1.96	90.88	
29-02b	10.3	1	SMXL	2	1.94			
29-02c	10.3	1	SMXL	2	2.18	2.14	98.99	
29-02c	10.3	1	SMXL	2	2.10			
29-03a	10.3	3	SMXL	2	1.94	1.94	89.76	88.82 ± 0.95
29-03a	10.3	3	SMXL	2	1.93			
29-03b	10.3	3	SMXL	2	1.90	1.89	87.60	
29-03b	10.3	3	SMXL	2	1.88			
29-03c	10.3	3	SMXL	2	1.91	1.92	89.11	
29-03c	10.3	3	SMXL	2	1.94			
29-04a	10.3	10	SMXL	2	1.27	1.29	59.61	56.53 ± 3.54
29-04a	10.3	10	SMXL	2	1.30			
29-04b	10.3	10	SMXL	2	1.25	1.26	58.17	
29-04b	10.3	10	SMXL	2	1.26			
29-04c	10.3	10	SMXL	2	1.26	1.12	51.81	
29-04c	10.3	10	SMXL	2	0.98			
29-05a	10.3	30	SMXL	2	0.31	0.31	14.49	13.46 ± 0.78
29-05a	10.3	30	SMXL	2	0.31			
29-05b	10.3	30	SMXL	2	0.29	0.28	13.14	
29-05b	10.3	30	SMXL	2	0.28			
29-05c	10.3	30	SMXL	2	0.27	0.28	12.75	
29-05c	10.3	30	SMXL	2	0.28			