Biochar sorbents for sulfamethoxazole removal from surface water, stormwater, and wastewater effluent

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Abstract

This study examined sorption of the human and veterinary antibiotic sulfamethoxazole (SMX) at environmentally relevant concentrations from laboratory clean water, surface water, stormwater, and wastewater effluent to wood and wastewater-sludge derived biochars produced under a wide range of conditions. SMX sorption by commercial powdered activated carbon (PAC) sorption was also quantified as a benchmark. Wood-based biochar produced around 850 °C performed similarly to PAC. Biochar sorption capacity increased with surface area up to ~400 m²/g. However, a further increase in surface area did not correspond to an increase in sorption capacity. Sorbent H:C ratios correlated with SMX uptake by PAC and wood-based biochars, but not for the sludge-based biochars. This is possibly due to an indirect influence of the high ash content in sludge-based biochars, as the isolated ash fraction exhibited negligible SMX sorption capacity. The presence of dissolved organic matter (DOM) in the natural and anthropogenic waters fouled most of the sorbents (i.e., decreased SMX uptake). The sludge-based biochars experienced less DOM fouling relative to wood-based biochar, particularly in the wastewater effluent. Biochar and PAC sorption kinetics were similar when examined over a contact time of four-hours, suggesting their performance ranking would be consistent at contact times typically utilized in water treatment systems. In the presence of DOM, SMX relative removal (C/C_0) was independent of SMX initial concentration when the initial concentration was below 10 µg/L, thus

permitting the relative removal results to be applied for different SMX initial concentrations typical of environmental and anthropogenically impacted waters.

Keywords: powdered activated carbon; trace organic contaminants; sorption kinetics; dissolved organic matter; fouling; fluorescence

1. Introduction

Synthetic organic contaminants (SOCs) can have harmful ecological and human health impacts and are often found in wastewater effluent (WWef) and stormwater (StmW) runoff. These polluted waters are the major contributors of SOCs found in aquatic ecosystems and drinking water sources (Schwarzenbach, 2006). Although existing technologies can remove or transform SOCs (e.g., activated carbon adsorption, advanced oxidation processes), economical and logistical barriers can prevent their adoption. Thus, wastewater and StmW treatment systems typically are not designed to control for SOCs. Likewise, low-income, rural, and/or remote communities often lack access to technologies that can remove SOCs present in their drinking water (Kearns et al., 2014a). A low-cost sorbent that can be produced at or near the point-of-use could enable SOCs to be treated in WWef and StmW on a larger scale as well as in drinking water where alternative options do not exist.

Biochar is a carbonaceous material produced from the pyrolysis of biomass that is often used to improve soil fertility and sequester carbon (Lehmann, 2007). There is growing interest in using biochar in various water treatment applications as it has shown the ability to control SOCs (Chen et al., 2008; Kearns et al., 2014b; Xiao and Pignatello, 2015), heavy metals (Tan et al., 2015), and microbial contaminants from water (Inyang and Dickenson, 2015; Mohanty et al., 2014). In some cases, its sorption capacity for SOCs can rival that of activated carbon (Chen et al., 2008; Kearns et al., 2014b; 2015). Moreover, it can be produced near the point of application

and/or near biomass sources, e.g., WWef can be treated by biochar generated onsite from biosolids (Smith et al., 2009). Another benefit is that biochar can be produced using technologically simple pyrolysis units such as small-scale cookstoves (Kearns et al., 2015), or large-scale integrated facilities that are designed for simultaneous biochar and energy production (Meyer et al., 2011). For these reasons, biochar can be inexpensive to produce relative to widely used sorbents, such as activated carbon, which is often generated from nonrenewable feedstocks (e.g., bituminous coal) and consumes energy to produce.

The ability of biochar to sorb SOC_s depends on its properties, which are determined by the precursor material and production conditions used (Chen et al., 2008; Kearns et al., 2014b; Xiao and Pignatello, 2015). Since biochar is typically produced from abundant biomass materials (e.g., beetle-killed pine), as well as waste biomass (e.g., sewage sludge, animal manure), a wide range of feedstocks that vary drastically in composition are often used to produce biochars that consequently have significantly different properties (Kearns et al., 2014b; Sun et al., 2015; 2013; 2011). Research has shown that the increase of the highest treatment temperature (HTT) increases the aromaticity, hydrophobicity, and surface area of biochars making them more similar to activated carbons and better sorbents (Chen et al., 2008; Kearns et al., 2014b; Sun et al., 2015). However, other studies have found poor correlations between HTTs or properties such as aromaticity and sorption capacity (Lattao et al., 2014; Xiao and Pignatello, 2015; Sun et al., 2011). Therefore, robust relationships between biochar properties and sorption performance still need to be developed.

Experimental conditions can greatly influence the relative sorption capacity of different biochars. For instance, under single-solute conditions in laboratory clean water, the isotherms of biochars produced at higher HTTs tend to be more nonlinear (i.e., Freundlich $1/n \ll 1$) and can

intersect the isotherms of biochars produced at lower HTTs (Chen et al., 2008; Lattao et al., 2014; Sun et al., 2011). Such isotherm crossover means that at high SOC concentrations (i.e., in the mg/L range and above), high-temperature biochars perform worse relative to low-temperature biochars and the opposite is true at low SOC concentrations. Although SOC_s are typically found in surface waters (SurWs), StmW runoff, and WWef at low to sub µg/L concentrations (Grebel et al., 2013; Kolpin et al., 2002; Pitt et al., 2004; Ternes, 1998), few studies have compared biochar performance with SOC_s at these levels.

When background DOM is present at much greater concentrations than SOC_s, which is typically the case in SurW, WWef and StmW, activated carbon isotherms are linear (i.e., Freundlich $1/n \approx 1$) when the SOC target sorbate concentration is varied and sorbent dose held constant (Knappe et al., 1998). Such phenomena simplify modeling SOC sorption as the relative SOC removal (i.e., C/C_0) for a given activated carbon dose remains constant over the environmentally relevant SOC concentration range. In addition, under such conditions the performance of different activated carbons is straightforward to compare because their proportional removal is independent of SOC initial concentration (SOC₀) and their isotherms do not intersect, as they are all linear. Whether biochars also exhibit linear SOC sorption in the presence of background DOM analogous to activated carbon has not been investigated.

With a few exceptions, most biochar sorption studies have been conducted under single-solute conditions and have not evaluated the influence of DOM, which is ubiquitous in natural and anthropogenic waters, on biochar sorbent performance. In addition, distinct DOM signatures can be observed in SurWs and WWef, which has been shown to significantly effect DOM competition with target sorbates for PAC sorption sites (Mostafa et al., 2014; Shimabuku et al., 2014). It is important to evaluate the performance of different biochars in representative water

matrices they may treat since the extent of DOM fouling depends on the physicochemical properties of both the sorbent and DOM (Newcombe et al., 2002). Also, SOC sorption to powdered biochar in batch systems, or granular biochar in flow-through columns, would not be expected to reach equilibrium in most full-scale applications. However, the influence of different contact times typically utilized in water treatment systems on SOC sorption by biochar has seldom been explored.

The overall objective of this study was to evaluate and compare the performance of biochar sorbents produced under a range of conditions from wood and wastewater sludge and a commercial PAC to sorb a representative of SOC_s, sulfamethoxazole (SMX), at environmentally relevant concentrations in SurW, StmW, and WWef. SMX, a human and veterinary antibiotic, was chosen because it is often found in environmental and anthropogenic waters (Kolpin et al., 2002). Additionally, SMX is challenging to remove with carbonaceous sorbents relative to many other SOC_s (Corwin and Summers, 2012; Westerhoff et al., 2005) and under conditions when a biochar or PAC can efficiently remove SMX, many other SOC_s would likely be removed as well. The presence of SMX in the environment can also be harmful to aquatic organisms and could accelerate the spread of SMX resistant bacteria (García-Galán et al., 2011). SMX has also been identified as a persistent pollutant (Loos et al., 2010) and it has been shown to be recalcitrant to biodegradation and hydrolysis (Lam et al., 2004; Zearley and Summers, 2012). Thus, technologies that can efficiently remove SMX need to be developed. To achieve the main objective of this study, the influence of different background matrices, contact times, and SMX initial concentrations on sorbent performance were examined. Additional objectives were to assess the capability of relatively simple characterization techniques to screen for effective

biochar sorbents, and to validate a modeling approach that assumes relative SOC removal by biochar is independent of SOC_0 .

2. Materials and Methods

2.1 Target sorbate.

SMX is anionic (pK_a of ~ 5.7) in the pH range of most natural aquatic systems, its $\log K_{ow}$ value is 0.89, and its MW is 253 g/mol. ^{14}C SMX was obtained from American Radiolabeled Chemicals, Inc. (St. Louis, MO) and detected by liquid scintillation counting. Its identity was verified using an Enzyme Linked Immunosorbent Assay kit (Abraxis, Warminster, PA). ^{14}C SMX was combined with nonlabeled SMX (Sigma Alrich, (St. Louis, MO)) to target different specific activities between 60 to 0.003 mCi/mmol to achieve detection limits ranging between 5 and 100,000 ng/L at a 95% confidence level. The initial SMX concentration was targeted at 100 ng/L, except in experiments where the SMX initial concentration was varied from 50 ng/L to 1,000,000 ng/L to determine the effect of SMX initial concentration on removal.

2.2 Biochar and PAC.

Using pelletized pine forestry waste, a 1-gal top-lit up-draft (TLUD) cookstove gasifier was operated in forced draft (FD) mode by placing a fan under the cookstove, which reached 850 °C for 20 min, and in natural draft (ND) mode where the drafting conditions were not supplemented with the fan, which reached 625 °C for 45 min. They are referred to as W-FD-850 °C and W-ND-625 °C, respectively. Temperatures in a TLUD are a function of the drafting conditions and cannot be adjusted independently. Two biochars were produced in a laboratory retort from wood cut into slats (15 cm x 10 cm x 1 cm), placed in a metal bin and covered with sand to exclude oxygen, and heated to 350 °C over 96 hours or to 850 °C over 8 hours. They are referred to as W-R-350 °C and W-R-850 °C, respectively. Temperatures of 350 °C and 850 °C

were chosen because ~350 °C is the lowest temperature in which pyrolysis can be guaranteed to occur (Lehman and Joseph, 2015) and 850 °C was chosen because this matches the temperature that occurred in the TLUD in FD mode. W-R-350 °C was produced from eucalyptus and W-R-850 °C was produced from pine. Biochars were also produced in a retort at 850 °C for two hours using biosolids (B-R-850 °C), dissolved air floatation thickened solids (D-R-850 °C), primary digester sludge (P-R-850 °C), secondary digester sludge (S-R-850 °C), and human fecal material (FM-R-850 °C) by placing these feedstocks in metal canisters that were covered with a lid that had a hole in the top to allow pyrolysis gasses to escape. Human fecal material was collected through voluntary donation by University of Colorado students, and all other waste materials were collected from Boulder Wastewater Treatment Facility (Boulder, CO). A pine-based biochar that is produced for use as a soil amendment was generated in a large-scale integrated facility designed for both biochar and heat-energy production, and was provided by Biochar Solutions (Carbondale, CO). Its exact production conditions are difficult to quantify as the biochar was exposed to a temperature gradient ranging between 1,200 and 400 °C. It is hereafter referred to as W-A-Biochar. A summary of biochar production conditions is provided in Table S1.

Biochars were ground by hand with a mortar and pestle to pass a US standard 325-mesh sieve (0.045 mm) and dried at least overnight at 105 °C prior to characterization and batch experiments. A widely used, high performing bituminous-based PAC (Calgon WPH) (>90% passes US standard 325-mesh sieve) was selected as a benchmark sorbent.

2.3 Sorbent characterization.

Elemental (C, N, H) analysis was conducted with a CHN Elemental Analyzer (Perkin-Elmer model 2400) as described by Kearns et al. (2014b). Oxygen content of each sample was

estimated as the remainder of mass after subtraction of C, N, H and ash components. Potentiometric titrations were conducted using a method modified from Ni et al. (2011) by adding 200 mg of each sorbent into pre-boiled water that was pH adjusted between pH 4 to 12 with HCl and NaOH in a 20 mL vial. The pH-adjusted water was also added to a blank vial without a sorbent. The pH was measured after mixing for 48 hours in an end-over-end tumbler. Surface areas were determined by fitting the BET equation to the adsorption of nitrogen (N₂) at 77 K (Brunauer et al., 1938). Micropore volumes were calculated by the t-method, and mesopore volumes were estimated by subtracting micropore volumes from total pore volumes estimated from N₂ adsorption at $P/P_o \sim 0.95$ (Barrett et al., 1951; Lippens et al., 1964). To measure ash content, a method developed by Kearns et al. (2014) was used. Two grams of each sorbent were weighed in a ceramic crucible and combusted at 550 °C for six hours, cooled to room temperature in a desiccator, and re-weighed. Ash that was used in sorption experiments and characterized by the BET method was isolated using this same approach. Ash free material (AFM) surface areas (SA) were estimated by:

$$SA_{AFM} = \frac{(SA_{comp} \times 100\%) - (SA_{Ash} \times \%Ash)}{\%AFM} \quad (1)$$

where SA_{comp} is the surface area of the composite material and SA_{Ash} is the ash surface area. Since the wood based-biochars had a small (<3.1%) ash contribution, their SA_{Ash} values were not measured. Because the average of the SA_{Ash} values measured for the sludge-based biochars and PAC is 10 m²/g, this value was used in calculations to determine the wood-based biochar's SA_{AFM} shown in Table 1. The highest SA_{Ash} measured for the sludge-based sorbents was ~20 m²/g. Using this value to determine the wood-based biochar SA_{AFM} values changed them by <0.5% relative to when SA_{Ash} values of 10 m²/g were used. Sorbent properties are provided in Table 1.

2.4 Waters.

Single-solute experiments were completed in laboratory clean water, DI, buffered at pH 7.2 (phosphate buffer 10^{-3} M). Experiments were also conducted in a SurW, WWef, and StmW that were collected from a mountain reservoir (Big Elk Meadows, CO), the Boulder Wastewater Treatment Facility (Boulder, CO), and from a StmW outfall that receives runoff from several parking lots on the University of Colorado campus (Boulder, CO), respectively. Water quality parameters for these waters are provided in Table 2.

2.5 Analytical Methods.

DOC was measured with a Shimadzu DOC-V_{SCH} (Kyoto, Japan) that used the non-purgeable organic carbon method. The pH was measured with a Corning Model 430 meter and probe (Acton, MA) according to Standard Methods 4500-H⁺.

UV absorbance at 254 nm was measured with a Cary 100 Bio UV-vis spectrophotometer (Palo Alto, CA). A Hobriba FluoroMax-4 (Irvine, CA) fluorometer was used to determine fluorescence parameters including Peak C/UV₂₅₄ and the fluorescence index (FI), which is the ratio of emission intensities at 520 nm and 470 nm at an excitation of 370 nm; detailed information describing how fluorescence data was collected is described elsewhere (Korak et al., 2014).

2.6 Batch experiments.

Non-equilibrium batch sorption experiments using contact times of four hours or less were conducted with a Phipps & Bird jar test apparatus (Richmond, VA) using 2 L square jars under the same conditions described previously (Shimabuku et al., 2014). After 5, 15, 30, 60, 120, and 240 min contact times, ~60 ml of sample was filtered using Whatman 1.2 μ m nominal pore size GF/C glass microfiber filters (Clifton, NJ). The majority of experiments were

conducted using a 60 min contact time, which should be assumed to be the case unless stated otherwise. A 60 min contact time was selected because it is representative of that used in powdered sorbent contactors in water treatment plants. A subset of apparent-equilibrium batch tests were performed in an end-over-end tumbler in the surface water in 250 mL amber bottles for 7 days. Kinetic tests up to 14 days with the W-FD-850 °C and W-R-350 °C biochars in the surface water showed that equilibrium was likely obtained within 7 days (Figure S1).

Control tests without the addition of a sorbent showed that SMX losses were negligible. To quantify experimental error, experiments that evaluated the influence of five different SMX initial concentrations (SMX_0 s) on removal, ranging between 50 ng/L and 1 mg/L, were conducted in triplicate. For each sorbent the coefficients of variation (CV) determined at the five different SMX_0 s were averaged, which resulted in CVs of 15%, 10%, 13%, 9%, and 14% for the PAC, W-FD-850 °C, W-ND-625 °C, W-R-350 °C, and B-R-850 °C respectively, with the overall CV for all sorbents equal to 12%.

3. Results and Discussion

3.1 Biochar sorbent performance.

Representative dose response behavior for four different biochars and the PAC at 60 min and 7 day contact times in the SurW are shown in Figure 1. At both contact times, the SMX sorption affinities of the different sorbents vary widely as the dose required for a given removal level spans ~2 orders of magnitude. A useful approach to quantify a sorbent's performance with a single number is to determine the dose required to remove a set percentage of a sorbate. This allows different sorbents to be compared to each other and under different conditions in a manner where the practical implications of their performance are apparent. The sorbent doses needed for 75% SMX removal using a 60 min contact time ($Dose_{75\%}$) in DI water, SurW, WWef,

and StmW are provided in Table 3. It is remarkable that the W-FD-850 °C biochar and PAC require the same Dose_{75%} in DI water considering that PAC adsorption is one of the most widely used processes for SOC control and its performance can be matched by wood-based biochar generated using a TLUD, which is a simple and inexpensive production system. In a previous study the W-FD-850 °C pine biochar also showed similar sorption capacities as the bituminous-based PAC and a granular activated carbon for MIB, Warfarin, and trihalomethanes under equilibrium conditions in DI water and the same SurW (Kearns et al., 2015). In addition, using biochar for water treatment applications may also be advantageous from a sustainability perspective. In a companion study, environmental impacts associated with using the W-FD-850 °C biochar and PAC to treat WWef and achieve the same SMX treatment objective were compared in a life-cycle assessment (Thompson et al., in prep). The W-FD-850 °C biochar had a lower environmental impact in the majority of emissions categories evaluated and beneficial impacts in several categories such as global warming potential. Table 3 also reveals that biochar Dose_{75%} values range up to ~400 times more than PAC Dose_{75%} values, indicating that not all biochar sorbents may be useful for SOC control in water treatment/environmental remediation applications. Although the relative performance of the sorbents can vary depending on the background matrix as discussed in detail in Section 3.4, the ranking of each sorbent in Table 3 is similar in all four waters (e.g., in most waters the PAC followed by the W-FD-850 °C biochar have the lowest Dose_{75%} values).

3.2 Ash sorption capacity.

Because biochar ash contents vary drastically from 1.3 to 82.4 % (Table 1), the sorption capacity of the ash was examined at a 60 min contact time. Ash was isolated from the PAC, as well as a wood-based biochar (W-FD-850 °C) and a sludge-based biochar (B-R-850 °C) by

heating these materials for six hours at 550 °C while open to the atmosphere. When dosing the isolated ash in DI water at 1.5 times the $Dose_{75\%}$ multiplied by the ash content of the sorbent from which it was derived (e.g., the B-R-850 °C ash dose was $1.5 \times 73\% \times 45 \text{ mg/L}$), SMX removal was negligible (data not shown). SA_{ash} values were also found to be much smaller than SA_{AFM} values (Table 1). Ji et al. (2011) also found that SMX sorption to biochar was dominated by the AFM by comparing sorption to deashed and untreated biochar. Although they estimated a small amount of SMX sorbed to the ash, such findings could be an artifact of the deashing procedure as washing with strong acids (1 M HCl and HF) could have altered the sorption characteristics of the AFM.

3.3 Relationships between biochar properties and performance.

Since the ash derived from B-R-850 °C, W-FD-850 °C, and PAC exhibited negligible SMX sorption capacity as discussed in Section 3.2 (which was assumed also to be the case for the ash in the other biochars) $^{AFM}Dose_{75\%}$ values, where $^{AFM}Dose_{75\%} = \%AFM \times Dose_{75\%}$ values, are used for comparing sorbent efficacy. $^{AFM}Dose_{75\%}$ values at 60 min contact times in DI water and SurW are plotted against the SA_{AFM} values in Figure 2. As SA_{AFM} increased, the $^{AFM}Dose_{75\%}$ values decreased until a plateau is reached at an SA_{AFM} of $\sim 400 \text{ m}^2/\text{g}$, regardless of whether DOM was present. Kearns et al. (2014b) found somewhat similar results studying 2,4-D uptake to biochar and activated carbon in DI water under equilibrium conditions. They found sorption capacity was low for sorbents with SA_{comp} values below $400 \text{ m}^2/\text{g}$ and increased between 400 to $600 \text{ m}^2/\text{g}$, but an improvement was not observed beyond $600 \text{ m}^2/\text{g}$. They hypothesized that a plateau arises because an increase in surface area does not necessarily correspond to an increase in high-energy sorption sites. For the low-ash sorbents (ash $\leq 6.3\%$) the $^{AFM}Dose_{75\%}$ values were positively correlated with the H:C ratios in DI water (Pearson correlation coefficient $r=0.97$,

p<0.001) (Figure 3). The AFM Doses for 90% 2,4-D removal determined from Kearns et al. (2014b), where biochar ash contents were below 11%, also showed a positive correlation with H:C ratios ($r=0.85$, $p<0.001$), which is illustrated in Supplementary Data (SD) Figure S2 as this was not depicted in the former study. Thus, surface area and H:C ratios could serve as screening metrics for biochar sorbent performance, which was also proposed by Hale et al. (2016) based on sorption data compiled for neutral organic compounds from twenty-nine different studies. Conversely, several studies have found that SOC_s, including SMX, have greater affinity for biochars that are produced at lower temperatures, have more polar functional groups, exhibit lower surface areas, and have high H:C ratios (i.e., are more aliphatic) (Lian et al., 2014; Yao et al., 2012). A potential explanation for the discrepancy could be a combination of (i) these studies were conducted with SMX at much greater levels, and (ii) at higher SOC concentrations biochars produced at greater HTTs, which tend to exhibit smaller H:C ratios, can perform worse relative to biochars produced at lower HTTs due to sorption capacity crossover because of their different slopes (Chen et al., 2008). In accord with this explanation, Zheng et al. (2013) showed that SMX sorption capacity correlated with H:C ratios for wood biochars produced between 300-600 °C when the equilibrium concentration was 500 µg/L, but not when the equilibrium concentration was 50 mg/L.

These relationships seem to imply that sorbents with lower H:C ratios, which is an indicator for aromaticity, have a stronger interaction with SMX when it is present at SOC concentrations typically found in SurW, StmW, and WWef. However, since the development of aromaticity, surface area, and microporosity as well as the loss of oxygen functional groups co-vary, these correlations do not distinguish if one or several of these properties influence SMX removal. To decouple the influence of surface area from other characteristics on biochar

performance, $^{AFM}Dose_{75\%}$ values were multiplied by their corresponding SA_{AFMS} as shown on the secondary y-axis of Figure 3. Presenting results in this way shows the surface area dose (m^2/L) needed to achieve 75% SMX removal, which is termed here $^{AFM-SA}Dose_{75\%}$. Figure 3 and SD Figure S3 show that $^{AFM-SA}Dose_{75\%}$ values increase with H:C and O:C ratios, respectively. SMX is thought to be an electron-acceptor in π - π electron donor/acceptor (EDA) complexes because it has a sulfonamide group that withdraws electrons from adjacent rings (Ji et al., 2009). In addition, heterocyclic nitrogen (Xiao and Pignatello, 2015) and oxygen (Ji et al., 2009) atoms present in SMX have been postulated to decrease electron density. Thus, the trends observed in Figure 3 and S2 might arise because aromatic systems in biochars become more electron rich, and therefore better π - π bond donors when the number of aromatic rings increases, and/or when oxygenated functional groups are removed (Lattao et al., 2014). Also, it has been proposed that oxygenated functional groups attract water clusters and hinder sorption, which could explain why performance is negatively correlated with O:C ratios (Zhu et al., 2005). Hydrogen bonding, in particular negative charge assisted hydrogen bonding, can enhance sulfonamide sorption (Teixidó et al., 2011). However, it appears that any enhancement in sorption due to an increase in the number of hydrogen-bonding sorption sites associated with oxygen functional groups is outweighed by the importance of the other factors discussed above as $^{AFM-SA}Dose_{75\%}$ values increase with an increase in O:C ratios (SD Figure S3).

For the high-ash sorbents, which were all generated at 850 °C, no correlation was found between $^{AFM-SA}Dose_{75\%}$ or $^{AFM}Dose_{75\%}$ values and elemental ratios, as $Dose_{75\%}$ values remained similar even though their corresponding elemental ratios varied substantially (Figure 3 and S2). These results concur with Hale et al. (2016) who found that neutral organic compound sorption, compiled from twenty-nine different studies, correlated well with H:C and O:C ratios for wood-

based, low-ash biochars but less so for high-ash biochars derived from heterogeneous precursors including animal manure and sewage sludge. Thus, hypothesized relationships between elemental ratios and biochar sorption performance are probably robust only *within* compositionally homologous feedstock classes where differences in elemental ratios arise from different production conditions and not from different precursor material properties.

Also, most high-ash biochar data points fall well outside of the low-ash sorbent trends shown in Figure 3 and S3, further suggesting that high-ash biochars exhibit distinct properties affecting sorption behavior. Previous studies have postulated that the presence of ash may influence SOC sorption to AFM. For instance, Sun et al. (2013) and (2015) provide convincing evidence that high ash concentrations in animal manure-derived biochars alters the spatial distribution of AFM and concentrates polar functional groups on the outer surface of biochars. For instance, they found that more oxygen was concentrated on the outer surfaces of biochars with high-ash contents relative to biochars with low-ash contents. They also showed that when they removed ash from high-ash biochars, oxygen concentrations on the outer surfaces of these biochars decreased drastically whereas bulk oxygen contents remained constant. These results are also consistent with the findings in studies that examined the influence of ash on the spatial distribution of AFM in soil organic matter (Yang et al., 2011; Kleber et al., 2007). Sun et al. (2013) and (2015) hypothesized high-ash biochars exhibited different sorption behavior compared to low-ash biochars with phenanthrene and propiconazole, respectively, because ash alters the spatial distribution of AFM.

Also, Cannon et al. (1993) found that inorganic compounds such as calcium present in granular activated carbon particles during reactivation accelerated mass loss and conversion of micropores into mesopores, which can have a significant impact on SOC sorption. In this study,

the high-ash biochars also have much higher mesopore to micropore ratios compared to low-ash biochars (Table 1), which could be a result of ash facilitating the conversion of micropores into mesopores. Alternatively, if ash preferentially resides in micropores this could also explain why high-ash biochars are more mesoporous. Additionally, the ash percentage is positively correlated with the SA_{AFM} and negatively correlated with $^{AFM}Dose_{75\%}$ values for the high-ash biochars (SD Figure S4). Thus, it is possible that the high concentrations of inorganic compounds present during high-ash biochar production modified the development of AFM physical properties and thereby influenced SMX sorption capacity.

3.4 Background matrix effect.

Batch sorption experiments conducted in the SurW yielded $^{AFM}Dose_{75\%}$ values that were at least four times greater than in DI water for all the sorbents, except the W-R-350 °C biochar (Figure 2). Thus, DOM appears to drastically decrease the sorption capacity of most biochars, most likely through direct competition for adsorption sites. While other DOM fouling mechanisms such as pore blockage can be important, when trace SOC and DOM are simultaneously exposed to fresh adsorbents as in the batch tests conducted here, direct competition is the dominant fouling mechanism (Li et al., 2003). Interestingly, minimal competition was observed with the W-R-350 °C biochar possibly because SOC partition into “rubbery” low-HTT biochars resulting in linear sorption isotherms (Chen et al., 2008). Xing et al. (1996) proposed that “rubbery” sorbents that undergo linear sorption are deficient in specific sorption sites where competition could occur. Ulrich et al. (2015) and Kearns et al. (2015) examined DOM fouling of biochar under similar conditions with trace quantities of SOC in the presence of SurW DOM. Consistent with our results, it can be seen in both studies that the DOM competitive effect can also range from being significant to minimal for different biochars.

SMX sorption was also examined in WWef with all sorbents (except the W-R-350 °C biochar since it performed poorly in DI water and SurW) and in StmW using the W-FD-850 °C biochar, B-R-850 °C biochar, and PAC (Table 3). For all the sorbents examined, the WWef and StmW induced a greater competitive effect than the SurW even though their DOC concentrations were lower (Figure 4). Previous work found that waters with larger Peak C/UVA and FI values were composed of lower molecular weight DOM and caused a greater competitive effect, as smaller DOM molecules can compete for sorption sites in micropores more effectively than larger DOM molecules that experience size exclusion (Shimabuku et al., 2014). Here, the WWef and StmW have larger Peak C/UVA values suggesting that they are comprised of a greater fraction of lower molecular weight DOM (Mostafa et al., 2014; Shimabuku et al., 2014). While the WWef also has a higher FI value than the SurW, the StmW exhibits a similar FI value as the SurW's even though its competitive effect is greater than that of the SurW. Poulin et al. (2014) found that inorganic constituents that can be present in these waters (e.g., metals) can influence fluorescence measurements, which may explain why the StmW deviates from trends we have observed previously with FI.

Overall, high-ash biochars experienced less competition than low-ash biochars in the SurW, StmW, and WWef. This might be related to the greater mesoporosity of the high-ash biochars relative to low-ash biochars (Table 1), as discussed in Section 3.3. Studies with activated carbons have demonstrated that sorbents with greater mesoporosity are less susceptible to DOM competition than more microporous sorbents (Li et al., 2003; Pelekani and Snoeyink, 1999). Unique competition interactions also occurred between different waters and biochars. For example, the low-ash sorbents experienced more competition from the WWef compared to the SurW, but the difference in competition between the two waters was less pronounced for the

high-ash biochars. One possible explanation could be that the high-ash biochar pore structure compared to the low-ash biochar pore structure is better suited to limit competition from the WWef DOM relative to SurW DOM. Alternately, or perhaps in addition to pore structure effects, one possibility could relate to the high-ash biochars possessing more oxygenated surface functional groups than low-ash biochars (Table 1). The presence of ash has been shown to concentrate oxygenated functional groups on the outer surface of biochar (Sun et al., 2013) as discussed in Section 3.3. Also, WWef typically contains more acidic moieties than SurW DOM (Imai et al., 2002). Thus, it is possible that more constituents in the WWef than in the SurW were electrostatically repelled by the greater number of outer-surface, negatively charged-oxygenated functional groups (e.g., carboxylic acids) in the AFM of the high-ash biochars compared to the AFM in the low-ash biochars. Further research is needed to test these hypotheses. It should also be noted that the surface charge of these sorbents, indicated by their point of zero charge (PZC) (Table 1, Figure S5), cannot explain differences in competition behavior. Both high-ash and low-ash biochars exhibit PZCs that range between 5 to 11, which suggests both high-ash and low-ash biochars could electrostatically repel or attract DOM. One potential reason why this analysis does not explain differences in competition behavior is because potentiometric titrations evaluate the charge state of the composite material (i.e., both the ash and AFM), but SMX predominately sorbs to AFM (see Section 3.2).

It is fortuitous that the high-ash, sludge-based sorbents experienced less competition particularly when treating WWef because utilizing these sorbents to treat wastewater could have ancillary benefits through decreasing sludge disposal and sorbent transportation costs. In addition, biochars produced from sludge collected at several different locations in the wastewater treatment facility, as well as the sludge precursor human fecal material, performed similarly

except the DAFT sludge (Table 3). Thus, wastewater treatment plants might have flexibility to collect sludge from different treatment steps to produce sludge-based biochars with consistent sorption properties. The companion study discussed in Section 3.1 also examined the environmental emissions associated with employing biosolids-based biochar to treat WWef, and found that in some scenarios the overall environmental impact of using biosolids-based sorbents can be similar to or better than using PAC (Thompson et al., in prep).

3.5 Contact time.

Since equilibrium is not achieved in many powdered adsorbent applications in water treatment it is critical to evaluate sorption kinetics to predict and compare sorbent performance. Kinetic models, such as the homogenous surface diffusion model can be used to extract diffusion coefficients. However, comparing sorption kinetics based on diffusion coefficients can be inappropriate for sorbents with very different equilibrium sorption capacities (Newcombe et al., 2002). Thus, an alternative approach was developed here after Newcombe et al. (2002) to normalize for sorption capacity and compare kinetics in WWef by plotting removals relative to the corresponding four-hour removal (RR_{4hr}) for the same sorbent dose using the following equation:

$$RR_{4hr} = \frac{C_t - C_{4hr}}{C_0 - C_{4hr}} \quad (2)$$

where C_t is the SMX concentration remaining at time t , C_{4hr} is the SMX concentration remaining at four hours, and C_0 is the SMX initial concentration. Contact times up to four hours were used because residence times are typically less than a few hours in full-scale powdered adsorbent systems, and the goal of this kinetic evaluation was to determine if the relative performance of different biochars varies within this practical timeframe.

RR_{4hr} values on a percentage basis for each sorbent (excluding the W-R-850 °C biochar and W-A-Biochar which were not examined) in the WWef are shown in SD Figure S6. Sorption kinetics for biochars and PAC appear to be similar within a four-hour contact time as RR_{4hr} values for all sorbents vary within approximately $\pm 10\%$ (SD Figure S6). This result is surprising considering that these sorbents vary widely in physicochemical properties. Box plots were constructed to summarize the range in RR_{4hr} values (Figure 5).

Chen et al. (2012) and Xiao and Pignatello (2015) are the only other studies, to our knowledge, that systematically compared batch-sorption kinetics of biochars produced at different temperatures. Both found that uptake rates varied for biochars produced at different HTTs, though different trends were observed. The discrepancy between our studies and theirs is most likely due to differences in the experimental conditions used. Although DOM was present in this study and not in the others, the effect of DOM on kinetics is often minimal when SOC_s and DOM are simultaneously exposed to fresh sorbents (Li et al., 2003). Also, Chen et al. (2012) and Xiao and Pignatello (2015) used contact times that achieved equilibrium (up to ~62 days). As discussed in Chen et al. (2012) biochar sorption kinetics can appear biphasic and behave as if there is a fast sorbing step, which reaches equilibrium in ~20 hours, and a slow sorbing step that becomes important beyond ~20 hours. Thus, only comparing sorption kinetics within a four-hour contact time, as was conducted here, would likely only evaluate the kinetics of the fast sorbing step, which limits the ability to compare this study with these other studies. However, for experiments conducted with several of the sorbents in the SurW the dose needed to remove 35% of the SMX at 60 min was the same as the dose needed to remove 75% SMX at a 7 day contact time (Figure 1). Therefore, these results suggest that sorption rates were similar for these different sorbents when contact times were extended into the slow, secondary phase of sorption.

3.6 Influence of SMX initial concentration and modeling implications.

Batch sorption studies at 60 min in the SurW were conducted by two established experimental methods: (i) varying the SMX_0 , in this case from 50 ng/L to 1,000,000 ng/L, while holding the sorbent dose constant, or (ii) holding SMX_0 constant, in this case at 100 ng/L, while varying the sorbent dose to obtain 10 to 90 percent SMX removal (SD Figure S7). Different trends emerge depending on the experimental method used, which is a phenomenon that has been observed for activated carbon (Knappe et al., 1998), but to our knowledge has not been previously demonstrated for biochars. This phenomenon probably occurs because when the sorbent dose is held constant and SMX_0 is varied (method (i)), the increased SMX concentration enables SMX to more effectively compete with DOM for sorption sites. Thus, more linear plots are produced (i.e., Freundlich $1/n \approx 1$). Conversely, when SMX_0 is held constant and the sorbent dose is varied (method (ii)), a decreasing sorbent dose causes a larger proportion of strongly competing DOM to be present relative to the number of available sorption sites. In this case, DOM competition increases, resulting in more nonlinear plots (i.e., Freundlich $1/n \ll 1$). Therefore, if background DOM is present, models such as the Freundlich equation will only fit batch sorption data collected within, but not between, experimental methods (Najm et al., 1991). However, biochars that do not experience significant DOM competition could be an exception. Note that in SD Figure S7, two distinct method-dependent plots are apparent for all sorbents except for the W-R-350 °C biochar, which experienced negligible DOM competition in the SurW for reasons discussed in Section 3.4.

Previous work with activated carbon has theoretically derived, and experimentally confirmed, that when the competitive-DOM fraction solid phase concentration is much greater than that of the target compound, the relative removal of a target compound is independent of its

initial concentration (Knappe et al., 1998). Consistent with these findings, when sorbent doses were held constant for the W-FD-850 °C, W-ND-625 °C, B-R-850 °C, and W-R-350 °C biochars, as well as the PAC, relative removal of SMX remained approximately constant when SMX_0 was varied from 50 ng/L to 10,000 ng/L (Figure 6). An ANOVA revealed that SMX_0 effected SMX relative removal when SMX_0 was $\geq 100,000$ ng/L at a 95% confidence level for each sorbent (see SD). Thus, the concentration threshold ($C_{0,Th}$), which is defined here as the concentration limit that an SOC_0 cannot exceed for removal to be independent of the SOC_0 , for SMX occurs between 10,000 and 100,000 ng/L under the experimental conditions used in the present study. To further evaluate if the SMX $C_{0,Th}$ is similar for each sorbent and if the performance of sorbents relative to each other changed for different SMX_0 s, Tukey's Test was performed by comparing % SMX_{norm} values (Equation 3) between the sorbents at different SMX_0 s:

$$\%SMX_{norm} = \frac{SMX}{SMX_{0=n}} - \frac{SMX}{SMX_{0=50 \text{ ng/L}}} \quad (3)$$

where $\frac{SMX}{SMX_{0=n}}$ is the relative SMX remaining at a given SMX_0 represented by n , and $\frac{SMX}{SMX_{0=50 \text{ ng/L}}}$ is the relative SMX remaining at SMX_0 equal to 50 ng/L. Only for the PAC and W-ND-625 °C biochar were % SMX_{norm} statistically different from each other at a 95% confidence level when the SMX_0 was $\geq 100,000$ ng/L. Thus, the SMX $C_{0,Th}$ values for each biochar and PAC appear to not be statistically different, as significant deviations between sorbents only arise at concentrations above their SMX $C_{0,Th}$ values. This is noteworthy considering that these sorbents exhibited distinct physicochemical properties. Also, it is probable that other SOC₀s exhibit relative removal by biochar that is independent of SOC_0 in different water matrices that contain DOM, which has been shown for SOC sorption by activated carbon (Knappe et al., 1998). However, further research is needed to determine $C_{0,Th}$ values for different compounds and in

different water matrices, as $C_{0,Th}$ values could vary depending on both the water matrix and target sorbate properties (e.g., sorbability).

One important implication of this study is that the $Dose_{75\%}$ values shown in Table 3 determined in the SurW, StmW, and WWef when the SMX_0 was equal to 100 ng/L would be expected to be same at any SMX_0 up to the $SMX C_{0,Th}$ specific to each water. In addition, these findings also have implications when using biochar sorbents under flow-through conditions when DOM is present, as similar relative removal breakthrough curves should be observed for a given SOC when different SOC_0 s are used that are below the SOC's $C_{0,Th}$.

4. Conclusions

This study showed that SMX sorption capacity of biochars produced by pyrolysis at ~850 °C from wood and wastewater sludge can be comparable to a commercial PAC at several practical contact times in SurW, StmW, and WWef when SMX_0 was at an environmentally relevant concentration. The presence of DOM negatively impacted SMX sorption by PAC and all biochars except the biochar produced at the lowest HTT examined, W-R-350 °C. DOM in StmW and WWef was more competitive with SMX for sorption sites than SurW DOM. H:C and O:C ratios negatively correlated with sorption by low-ash sorbents, but not with high-ash biochars. Also, high-ash biochars were subject to less DOM competition than low-ash biochars. Although SMX sorption to ash was negligible, high levels of ash might alter AFM properties (e.g., pore size distribution) that influence sorption behavior and DOM competition, though further research is needed to test this hypothesis. Over a 4 hr timeframe, PAC and biochars produced from wood and wastewater sludges pyrolyzed at temperatures ranging from 350-850 °C exhibited similar sorption kinetics. This suggests that the relative performance of different biochars might remain the same for contact times typically encountered in powdered-adsorbent

water treatment systems. For SMX, the $C_{0,Th}$ occurs between 10 and 100 $\mu\text{g/L}$ for PAC and the four biochars tested, and does not appear to vary significantly between the different sorbents. Thus, the simple modeling approach developed for activated carbon, which assumes that relative removal of SOC is independent of their initial concentration, appears to also be valid for SOC sorption by biochars. The environmental implication of this study is that biochar produced from wood and wastewater sludge has the potential to efficiently remove organic contaminants in water, stormwater, and wastewater treatment applications. In addition, producing sorbents from wastewater-sludge could decrease the accumulation of such waste.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at:

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Table 1

Table 1. Biochar and PAC physical and chemical characteristics.

	Composite Surface area ^a (m ² /g)	Ash Surface area ^b (m ² /g)	AFM Surface area ^c (m ² /g)	Micropore volume (cm ³ /g)	Mesopore volume (cm ³ /g)	Ash (%)	C (%)	H (%)	N (%)	O (%)	H:C (mol %)	O:C (mol %)	Point of Zero Charge pH
PAC	697	7.9	743	0.33	0.160	6.3	88.0	0.12	0.56	5.39	0.02	0.05	10.1
W-R-850 °C	362	- ^d	368±0.2	0.18	0.031	1.8	93.1	0.90	0.10	4.10	0.12	0.03	8.8
W-FD-850 °C	405	- ^d	417±0.3	0.16	0.116	3.1	93.7	0.54	0.12	2.54	0.07	0.02	10.5
W-ND-625 °C	172	- ^d	174±0.2	0.08	0.016	1.3	92.0	2.16	0.12	4.42	0.28	0.04	10.3
W-R-350 °C	39	- ^d	39±0.2	0.02	0.009	1.7	72.0	3.00	0.32	22.98	0.50	0.24	5.0
W-A-Biochar	315	- ^d	321±0.2	- ^d	- ^d	1.8	88.5	2.00	0.22	7.48	0.27	0.06	- ^d
B-R-850 °C	130	19.3	429	0.03	0.102	73.0	20.7	0.31	0.78	5.22	0.18	0.19	8.5
D-R-850 °C	97	10.8	500	0.03	0.063	82.4	12.2	0.43	1.21	3.80	0.42	0.23	7.7
P-R-850 °C	67	7.3	337	0.02	0.048	82.0	6.5	0.19	0.26	11.04	0.35	1.27	9.2
FM-R-850 °C	126	7.2	267	0.04	0.080	54.2	34.8	0.60	1.09	9.33	0.21	0.20	10.8
S-R-850 °C	107	10.2	277	0.03	0.074	63.7	27.6	0.58	1.64	6.45	0.25	0.18	5.0

^aBET Surface area of the ash and AFM composite

^bBET surface area of the ash isolated by heating sorbents exposed to the atmosphere for 6 hrs at 550 °C

^cBET surface areas of the AFM were determined according to equation (1). To calculate AFM surface areas for the wood-based biochars the ash surface areas were assumed to be equal to 10 m²/g, the error shown was calculated assuming ash surface areas were 0 and 20 m²/g.

^d- " Not analyzed

Table 2

Table 2. Water quality parameters.

Water	pH	DOC (mg-C/L)	SUVA (L/m/mg-C)	FI	Peak C/ UVA ₂₅₄ (RU-cm)
DI Water	7.2	1-5×10 ⁻³	-	-	-
Surface water	7.0	15.0	2.2	1.43	4.0
Wastewater effluent	7.4	7.5	2.4	1.82	7.0
Stormwater	7.5	5.0	3.0	1.41	7.1
“-” Not analyzed					

Table 3

Table 3. Biochar and PAC doses required for 75% sulfamethoxazole removal ($\text{Dose}_{75\%S}$ (mg/L)) at a 60 min contact time in 10 mM phosphate buffered pH 7.2 deionized (DI) water, surface water (SurW), wastewater effluent (WWef), and stormwater (StmW).

	DI water	SurW	WWef	StmW
PAC	10	40	70	60
W-R-850 °C	20	160	300	- ^a
W-FD-850 °C	10	80	150	150
W-ND-625 °C	125	1,150	1,700	- ^a
W-R-350 °C	4,000	4,100	- ^a	- ^a
W-A-Biochar	50	400	600	- ^a
B-R-850 °C	45	225	300	450
D-R-850 °C	75	525	600	- ^a
P-R-850 °C	60	275	300	- ^a
FM-R-850 °C	45	275	300	- ^a
S-R-850 °C	45	225	300	- ^a

^a“-” Not analyzed

Figure 1

Figure 1. Sorbent dose response curves at 1 hour (hr) and 7 day (d) contact times in the surface water. The dashed and solid lines show where the dose response curves intersect 35% and 75% sulfamethoxazole (SMX) removal, respectively.

Figure 2

Figure 2. Ash free material (AFM) sorbent doses for 75% sulfamethoxazole removal ($^{AFM}Dose_{75\%S}$) in 10 mM phosphate-buffered pH 7.2 deionized (DI) water and surface water (SurW) at 60 min contact times plotted against the AFM BET surface areas (SA_{AFM}).

Figure 3

Figure 3. Ash free material (AFM) sorbent doses for 75% sulfamethoxazole removal ($^{AFM}Dose_{75\%}$ s) (solid symbols) and $^{AFM}Dose_{75\%}$ s multiplied by the surface area (SA) of the AFM ($^{AFM-SA}Dose_{75\%}$) (hollow symbols) determined at a 60 min contact time in 10 mM phosphate-buffered pH 7.2 deionized water plotted against H:C ratios.

Figure 4

Figure 4. Sorbent doses for 75% sulfamethoxazole removal ($Dose_{75\%}$) determined at 60 min in different waters containing dissolved organic matter (DOM) normalized by the $Dose_{75\%}$ s determined in 10 mM phosphate buffered pH 7.2 deionized (DI) water. The black dashed line indicates where the $\frac{DOM-Dose_{75\%}}{DI-Dose_{75\%}}$ ratio is equal to one, which is where the $Dose_{75\%}$ in the surface water (SurW), wastewater effluent (WWef), or stormwater (StmW) is equal to that in DI water.

Figure 5

Figure 5. Box and whisker plots for removals relative to the corresponding removal at four hours (RR_{4hr} s) for all the biochars, excluding the W-R-850 °C and W-A-Biochar (which were not examined), in wastewater effluent versus time. RR_{4hr} values were determined according to equation (2).

Figure 6

Figure 6. The sulfamethoxazole (SMX) percent remaining for a given SMX₀ normalized to the SMX percent remaining at SMX₀ = 50 ng/L (%SMX_{norm}) plotted against the SMX₀ at a 60 min contact time in the surface water. %SMX_{norm} values were determined according to equation (3). Sorbent doses were held constant at 800, 170, 2,000, 80, and 40 mg/L for the W-ND-625 °C biochar, B-R-850 °C biochar, W-R-350 °C biochar, W-FD-850 °C biochar, and PAC, respectively. The error bars represent propagated error for experimental triplicates.