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# Occurrence of Organic Micropollutants in the San Juan River in Northwest New Mexico and their Removal during Drinking Water Treatment

Interim Report No. ST-2021-19192

prepared by

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# **Peer Review**

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### **Executive Summary**

A novel powdered ash-treated pine biochar (PATB) was compared to powdered activated carbon (PAC) for the removal of dissolved organic matter (DOM) and organic micropollutants (OMPs) from deionized water (DI), a raw surface water (SW), and a treated wastewater (WW). PATB performance (capacity and kinetics) was the primary focus under realistic water treatment adsorbent doses (<200 mg/L) and contact times (<120 minutes). For the removal of DOM, iohexol (IOH), sucralose (SUC), and sulfamethoxazole, PAC consistently outperformed PATB. For the more readily adsorbable OMPs carbamazepine, cotinine, DEET, and theobromine, removal by the two adsorbents was comparable. Dose response and kinetic results for each adsorbent between SW and WW for DOM, IOH, and SUC were similar as their initial dissolved organic carbon concentrations were diluted to the same range: 2.0 to 2.2 mg/L. SUC was found to have a higher affinity for PATB in DI, but ultimate removal was still limited by its lower specific surface area compared to PAC (~500 vs ~1,000 m2/g). Additional investigations included combined adsorbent treatment and projecting batch results to fixed bed breakthrough curves for hypothetical full-scale granular activated carbon and granular ash-treated biochar adsorbers using both the homogeneous surface diffusion model and pore and surface diffusion model. Journal of Environmental Engineering pre-proof manuscript is attached in the Appendix A.

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# Appendix A – Accepted Pre-Proof Manuscript for Journal of Environmental Engineering

#### Experimental and Modeling Comparisons of Ash-Treated Pine Biochar and Activated Carbon for the Adsorption of Dissolved Organic Matter and Organic Micropollutants

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#### Abstract

A novel powdered ash-treated pine biochar (PATB) was compared to powdered activated carbon (PAC) for the removal of dissolved organic matter (DOM) and organic micropollutants (OMPs) from deionized water (DI), a raw surface water (SW), and a treated wastewater (WW). PATB performance (capacity and kinetics) was the primary focus under realistic water treatment adsorbent doses (<200 mg/L) and contact times (<120 minutes). For the removal of DOM, iohexol (IOH), sucralose (SUC), and sulfamethoxazole, PAC consistently outperformed PATB. For the more readily adsorbable OMPs carbamazepine, cotinine, DEET, and theobromine, removal by the two adsorbents was comparable. Dose response and kinetic results for each adsorbent between SW and WW for DOM, IOH, and SUC were similar as their initial dissolved organic carbon concentrations were diluted to the same range: 2.0 to 2.2 mg/L. SUC was found to have a higher affinity for PATB in DI, but ultimate removal was still limited by its lower specific surface area compared to PAC (~500 vs ~1,000 m<sup>2</sup>/g). Additional investigations included combined adsorbent treatment and projecting batch results to fixed bed breakthrough curves for hypothetical full-scale granular activated carbon and granular ash-treated biochar adsorbers using both the homogeneous surface diffusion model and pore and surface diffusion model.

# Introduction

Organic micropollutants (OMPs), even at low concentrations (ng/L to  $\mu$ g/L), pose potential risks to public health and the environment, for which the commercially available granular and powdered activated carbon (GAC and PAC, respectively) are effective at removing them from drinking water and wastewater (Westerhoff et al. 2005, Summers et al. 2011, Crittenden et al. 2012, Kennedy et al. 2015, Zietzschmann et al. 2016). Alternative adsorbents to GAC/PAC have recently been developed for OMP adsorption in water, including porous  $\beta$ -cyclodextrin polymers (Ling et al. 2020) and biomass-based biochar. Biochar is produced from the primarily anoxic, although sometimes semi-oxic, pyrolysis of any number of biomass sources (e.g., pine) and has become an attractive alternative to GAC/PAC because of waste material reuse, carbon sequestration, and generally low production costs (Thompson et al. 2016, Moreira et al. 2017).

Significant advancements have been made in biochar production conditions that create high specific (internal) surface areas that increase both OMP access to, and removal within, micropores (<2 nm diameter) and mesopores (2 to 50 nm diameter) (Mohan et al. 2014, Ahmed et al. 2016, Shimabuku et al. 2016, Xiao et al. 2018, Kearns et al. 2019, Bentley and Summers 2020). For example, several high-temperature co-pyrolysis thermal air activation (CPTA) biochars have been shown to outperform conventional anoxic pyrolysis (CAP) biochars by roughly an order of magnitude for the removal of the herbicides 2,4-D and simazine (SIM) from surface water (Kearns et al. 2019). That increase was enough to significantly close the gap in equilibrium solid phase concentrations  $(q_e)$  between CPTA biochars and GAC/PAC. Others have also found post-pyrolysis thermal air oxidation (PPAO) to greatly increase biochar surface area and subsequent adsorption of the two herbicides atrazine and prometon, in addition to the hormone estriol (Xiao et al. 2018). Extended pyrolysis times from hours to days at temperatures ranging from 350 to 850°C have also been observed to close the gap between pine biochar and PAC for the removal of the antibiotic sulfamethoxazole (SUL) (Shimabuku et al. 2016). In some cases, biochars produced at much lower temperatures (250°C) have resulted in increases in SUL adsorption capacity (Lian et al. 2016). Recently, Bentley and Summers (2020) produced an effective biochar by using a relatively simple approach of presoaking the pine feedstock in a solution of ash from the same material, followed by CAP in a muffle furnace at 800°C for 2 hours. This approach yielded a pine biochar that was comparable to PAC for 2,4-D and SUL removal (approximately factor of two difference in dose), primarily by increasing total surface area from 420 m<sup>2</sup>/g to 510 m<sup>2</sup>/g and expanding OMP access to micropores by increasing mesopore surface area. To this point, biochar surface area appears to have plateaued at this upper limit range compared to  $\sim$ 700 to 1,000 m<sup>2</sup>/g for GAC/PAC (Mohan et al. 2014, Shimabuku et al. 2016, Xiao et al. 2018, Kearns et al. 2019).

A primary goal of these biochar advancements has been to achieve GAC/PAC performance for the removal OMPs, especially in terms of adsorbent cost per mass of OMP removed. Comparisons between the two adsorbents are usually performed for many different biochars instead of in-depth investigations for a single representative or best performing biochar, and are typically limited to isotherms or contact times greater those practiced in water treatment (Ahmed et al. 2016, Shimabuku et al. 2016, Inyang and Dickenson 2017, Xiao et al. 2018, Kearns et al. 2019, Bentley and Summers 2020). Most studies also tend to focus on OMP removal and effects of competitive adsorption with DOM, as opposed to examining DOM removal itself, as measured by the surrogates of dissolved organic carbon (DOC) and ultraviolet absorbance at 254 nm (UVA<sub>254</sub>). Though isotherms, typically the Freundlich isotherm ( $q=K_FC^{1/n}$ ), are useful for characterizing adsorbents including comparisons, they are not representative of PAC applications because isotherms are, by definition, based on thermodynamic equilibrium. Certainly for GAC, and likely the same for fixed bed biochar adsorbers, the Freundlich capacity  $(K_F)$  and intensity (1/n) parameters obtained from isotherm testing cannot reliably predict OMP breakthrough profiles for real waters using adsorption modeling software (Jarvie et al. 2005, Magnuson and Speth 2005, Summers et al. 2011). In response, biochar adsorption of OMPs in fixed-bed scenarios has been explicitly tested but remains limited compared to GAC studies because of their effort-intensive nature (Inyang and Dickenson 2017, Kearns et al. 2020a, Kearns et al. 2020b). Direct kinetic comparisons between biochar and GAC/PAC, either OMP removal over PAC-representative contact times or quantification of OMP surface or pore diffusion coefficients ( $D_s$  or  $D_p$ , respectively), have also been limited (Inyang and Dickenson 2017, Kearns et al. 2020a, Kearns et al. 2020b).

Given the current state of biochar research for water treatment, a maturation point has been reached where more realistic and focused treatability studies are necessary to establish practicality and inform areas for future biochar research, including whether biochar is better suited to PAC- or GAC-type applications (i.e., batch or fixed bed reactors). Therefore, the main objective of this study was to evaluate the performance of an optimized biochar relative to PAC for the removal of a range of OMPs and background DOM. Considering the ash-treated pine biochar from Bentley and Summers (2020) is (1) a relatively new biochar, (2) representative of other pine biochars (e.g., surface area, OMP removal, etc.), and (3) relatively straightforward to produce, this study sought to apply it as a barometer of biochar feasibility as an adsorbent in water treatment. Specifically, this study investigated and directly compared ash-treated pine biochar and PAC under realistic water treatment scenarios (e.g., doses, contact times) for the (1) removal of DOM, as measured by DOC and UVA254, (2) removal of seven environmentally relevant OMPs, (3) kinetics of DOM and OMP removal, and (4) extension of batch testing results to fixed bed breakthrough predictions using adsorption models. Testing was performed in deionized water (DI), a surface water (SW), and a wastewater (WW), the latter two at the same initial DOC (DOC<sub>0</sub>) concentration.

# **Materials and Methods**

#### Waters

Average raw water quality parameters and initial OMP concentrations ( $C_0$ ) are shown in Table 1 for the three different waters tested. DI with very low  $DOC_0$  concentrations (<0.1 mg/L), zero initial UVA<sub>254</sub> (UVA<sub>254,0</sub>), below detection OMPs, and high resistance (>16 M $\Omega$ ·cm) was obtained on-demand through treating Denver, Colorado, tap water using a commercial GAC and mixed ion exchange resin system (Evoqua Water Technologies LLC, Pennsylvania). Prior to testing DI alone, it was buffered to a pH of approximately 8.6 using sodium bicarbonate (NaHCO<sub>3</sub>) (S25533, Fisher Scientific, Massachusetts) to match the pH and alkalinity of the other two test waters more closely. Raw SW was collected from the San Juan River near Farmington, New Mexico, three separate times in opaque, 20 L high-density polyethylene (HDPE) carboys and shipped to Denver, Colorado. Unlike much of the San Juan River in the western US, the corridor near Farmington is anthropogenically impacted by municipal, industrial, and agricultural activities, and as such, contains some level of background OMPs. Treated WW following a fourstage Bardenpho activated sludge process for full nitrification/enhanced denitrification and ultraviolet disinfection was collected from the City of Boulder, Colorado, Water Resource Recovery Facility in opaque, 20 L HDPE carboys. Both SW and WW were stored in a refrigerator at 4°C before testing within one week of collection.

To normalize for the effect of DOC concentration on OMP adsorption and thereby isolate intrinsic DOM effects, if any, SW and WW were diluted to the same DOC<sub>0</sub> concentrations of approximately 2.0 to 2.2 mg/L, shown in Table 1, using unbuffered DI. Before dilution, average SW and WW DOC<sub>0</sub> concentrations were  $3.4\pm1.1$  and  $8.8\pm1.3$  mg/L, respectively. Sucralose (SUC) was added to target concentrations of 1,000 to 2,000 ng/L from a 100 mg/L stock solution, made using a 98% powder (AAJ6673618, Fisher Scientific) to ensure its presence. For reference, raw water SUC concentrations before spiking ranged from  $\sim 200$  to 2,000 ng/L, not known until testing was completed. All other OMPs were present at the concentrations shown in Table 1 at the time of raw water sampling and did not substantially change during water storage other than from dilutions with DI. Specific UVA254 (SUVA254) values, which are a simple measure of DOM character (e.g., aromaticity), for diluted SW (2.2 to 2.6 L/mg/m) were within typical drinking water supply ranges (2.0 to 4.0 L/mg/m) and indicate a mixture of aliphatic and aromatic DOM constituents (Edzwald and Tobiason 2011). The diluted WW SUVA254 value of 1.7 L/mg/m was lower than the common raw water supply range, indicating higher aliphatic DOM character and lower molar mass DOM (Kennedy and Summers 2015). DOM of this character is typical for a complex mixture of the original drinking water DOM, effluent organic matter (EfOM), and OMPs from wastewater treatment plants with nitrification/denitrification processes (Krasner et al. 2009). For target OMP adsorption to GAC/PAC, the presence of both low molar mass DOM and many OMPs unique to EfOM can result in increased competition and reductions in OMP adsorption capacity compared to naturally occurring DOM (Kennedy and Summers 2015, Shimabuku et al. 2016, Zietzschmann et al. 2016).

### Adsorbents

PAC was prepared by manually grinding and sieving small batches of a commercial bituminous based GAC (Norit 1240 GAC, Cabot Corporation, Massachusetts) to less than US standard mesh size 200 with a particle diameter ( $d_p$ ) cutoff of 0.075 mm. A commercial bituminous coal based GAC was chosen instead of a commercial bituminous coal or wood based PAC because (1) it was assumed to be as effective, if not slightly more effective, as bituminous coal based PAC for the removal of DOM/OMP (Kearns et al. 2019), (2) it is widely used in fixed bed adsorbers for the removal of DOM/OMPs (Summers et al. 2011), and (3) it is more relevant than PAC for extending batch results to modeling fixed bed adsorbers with the same GAC. For data analysis and modeling, PAC surface area, bulk or hypothetical bed density ( $\rho_b$ ), and particle density ( $\rho_p$ ) values were assumed to be 1,080 m<sup>2</sup>/g, 450 kg/m<sup>3</sup>, and 750 kg/m<sup>3</sup>, respectively, the latter assuming a bulk or hypothetical bed porosity ( $\varepsilon_b$ ) of 0.4 (Summers et al. 2011, Crittenden et al. 2012, Kennedy et al. 2015, Bentley and Summers 2020). Ash-treated biochar was produced from pelletized pine (Confluence Energy, Colorado) according to the methods outlined in Bentley and Summers (2020). Powdered ash-treated biochar (PATB) was prepared in the same fashion as PAC. For data analysis and modeling, PATB surface area,  $\rho_b$ , and  $\rho_p$  values were assumed to be 510 m<sup>2</sup>/g, 200 kg/m<sup>3</sup>, and 330 kg/m<sup>3</sup>, respectively, the latter assuming an  $\varepsilon_b$  of 0.4 (Bentley 2020, Bentley and Summers 2020). Adsorbent slurries using unbuffered DI with concentrations of 20 g/L were made and stored in 250 mL amber glass bottles.

### **Batch Testing**

All experiments were performed using a programmable six-jar jar tester (PB-900, Phipps & Bird, Inc., Virginia) filled with 1.0 L of DI, SW, or WW. Adsorbents were added to test waters during an initial rapid mix phase (1 minute, 300 rpm) from plastic syringes that were filled from the continuously mixed stock slurries. Doses and mixing times were purposefully targeted to match typical water treatment scenarios (Summers et al. 2011, Crittenden et al. 2012). For dose response testing, waters were mixed with doses of 10, 50, 100, and 200 mg/L for 60 minutes at 60 rpm, representative of flocculation mixing intensity. Dose response jars with doses of 10 and 50 mg/L were duplicated. For kinetic testing, waters were mixed with a dose of 50 mg/L for 120 minutes at 60 rpm, with samples taken at 10, 30, 60 (from dose response testing), and 120 minutes. For combined treatment (CT) testing, waters were mixed with (1) PAC only at 10 mg/L, (2) PAC at 10 mg/L plus PATB 50 mg/L, and (3) PAC at 10 mg/L plus PATB at 100 mg/L for 60 minutes at 60 rpm. All jars for kinetic and CT were duplicated. Raw water was sampled before adsorbent addition and mixing. Treated water was sampled immediately at the end of the targeted mixing time. All water samples were filtered through 0.45 µm Nylon membrane filters (EW-15945-27, Cole-Parmer, Illinois) using a filter holder and peristaltic pump into 500 mL amber glass bottles, subsequently split among the various analyses (Table 1).

### Water Quality Analysis

Alkalinity was measured using a digital titrator with sulfuric acid according to Method 8023 (Hach, Colorado). DOC was measured in duplicate for each jar according to Standard Method 5310C on a laboratory analyzer (M5310C, Suez, France) (APHA et al. 2017). pH and temperature were measured using a gel-filled electrode (Intellical PHC101, Hach) and portable multi-meter (HQ40d, Hach). UVA<sub>254</sub> was measured in duplicate for each jar according to Standard Method 5910 on a laboratory spectrophotometer (DR6000, Hach) (APHA et al. 2017).

To concentrate OMPs prior to analysis, 200 mL of raw or treated water sample was processed through solid phase extraction (SPE) cartridges (Oasis HLB Plus Short Cartridge, Waters Corporation, Massachusetts) using a piston metering pump at a flow rate of approximately 10 mL/min. Prior to this loading, SPE cartridges were conditioned with 5 mL of methanol (CH<sub>3</sub>OH) (BDH1135-4LP, VWR International, LLC, Pennsylvania) followed by 10 mL of high-performance liquid chromatography (HPLC) grade water (WX0008-1, MilliporeSigma, Massachusetts) using a plastic syringe. After processing raw or treated water, SPE cartridges were rinsed with an additional 10 mL of HPLC grade water. At the Arid Land Agricultural Research Center (USDA ARS, Maricopa, Arizona), OMP-loaded SPE cartridges were eluted with 3 mL of acetonitrile (CH<sub>3</sub>CN) (A996-1, Fisher Scientific) and 3 mL of methanol at 1 mL/min, evaporated under nitrogen gas (N<sub>2</sub>), and reconstituted in a 1 mL 10% acetonitrile solution. OMPs were then measured using a HPLC-tandem mass spectrometry (HPLC/MS-MS) system (Acquity UPLC System, Waters Corporation), equipped with an electrospray ionization source in positive/negative mode, and converted to concentrations using calibration curves.

Assuming 100% elution of OMPs from SPE cartridges and a concentration factor of 200, the method reporting limit (MRL) for carbamazepine (CAR), cotinine (COT), DEET (DEE), and SUL was 1 ng/L. The MRL for iohexol (IOH) and theobromine (THE) was 2 ng/L, while the MRL for SUC was 10 ng/L. These seven OMPs, shown with several relevant properties in Table 2, were chosen based on detection in a previous San Juan River treatability study (Arcadis/Malcolm Pirnie 2013) and while they covered a wide range of observed adsorbabilities on both GAC/PAC and biochars (Summers et al. 2014, Kennedy et al. 2015, Bentley and Summers 2020, Kearns et al. 2020a, Kearns et al. 2020b), it was decided before any testing that most of this study would focus specifically on the neutral OMPs IOH and SUC. The decision to focus on IOH and SUC was based on their (1) ubiquity in wastewater-impacted waters, (2) weaker adsorbability on GAC/PAC compared to other OMPs, and (3) indicator potential for the presence and removal of other OMPs (Westerhoff et al. 2005, Oppenheimer et al. 2011, Kennedy et al. 2015, Thompson and Dickenson 2020). These criteria as they relate to Westerhoff et al. (2005) and Kennedy et al. (2015) pertain to the OMP iopromide (IOP), also an X-ray contrast agent and similar to IOH in terms of its properties shown in Table 2.

### **Adsorption Modeling**

Adsorption modeling software was used to investigate OMP adsorption onto PAC and PATB. Initially, kinetic data at doses of 50 mg/L were fit using the homogeneous surface diffusion model (HSDM) (FAST 2.1) (Sperlich et al. 2008). Specific modeling assumptions were (1) OMP adsorption would follow the Freundlich isotherm, (2)  $d_p$  was 0.038 mm (half of 0.075 mm), (3) film diffusion coefficient ( $k_f$ ) was calculated using the Gnielinski correlation (Crittenden et al. 2012), and (4) 1/n was equal to 1.0, a reasonable assumption for OMP adsorption in the presence of background DOM (Corwin and Summers 2011, Summers et al. 2014). Adoption of the last assumption also implied normalized OMP concentrations, or final concentration (C) divided by  $C_0$  ( $C/C_0$ ), were independent of  $C_0$  for concentrations in the ng/L to low µg/L range (Corwin and Summers 2011, Summers et al. 2016, Zietzschmann et al. 2016). HSDMgenerated curves were iteratively fit to kinetic data by adjusting  $D_s$  and  $K_F$  to minimize residuals.

Following kinetic data curve fitting, the HSDM-determined  $D_s$  and  $K_F$  were used to project hypothetical full-scale granular activated carbon (GAC) and granular ash-treated biochar (GATB) IOH and SUC breakthrough curves using the pore and surface diffusion model (PSDM) (AdDesignS, Michigan Technological University, Michigan). The PSDM was used for projecting breakthrough curves instead of the HSDM because the model includes pore diffusion, which in fixed beds becomes increasingly important with operation time as DOM fouls adsorbent surfaces and limits surface diffusion (Jarvie et al. 2005, Corwin and Summers 2011, Summers et al. 2014, Kennedy and Summers 2015). PSDM assumptions for hypothetical GAC/GATB adsorbers were (1)  $d_p$  was 0.92 mm (12x40 US standard mesh), (2) empty bed contact time (EBCT) was 7 minutes, and (3) tortuosity ( $\tau$ ), or labyrinth factor, was equal to 1.0, a maximum pore diffusion flux value appropriate for OMPs in GAC absorbers (Summers et al. 2014).  $D_s$  values were assumed to be independent of  $d_p$ , in that they would be the same for either a  $d_p$  of 0.038 mm or 0.92 mm, a reasonable assumption at early OMP breakthrough ( $C/Co \le 10\%$ ) (Crittenden et al. 2012, Summers et al. 2014, Kearns et al. 2020b). Early OMP breakthrough is also emphasized herein because low OMP concentrations in treated water are typically the goal.

OMP breakthrough curves were generated using this approach because consistent HSDM and PSDM predictions using  $K_F$  and 1/n values, obtained either from isotherm testing or empirical fouling relationships, have remained elusive (Jarvie et al. 2005, Magnuson and Speth 2005, Corwin and Summers 2011, Summers et al. 2011). This approach follows the aforementioned studies in that instead of reducing  $K_F$  as function of deliberate DOM preloading, operation time, DOM type, and/or OMP type,  $K_F$  would inherently be reduced because of the short contact time (120 minutes) relative to isotherm or longer-term dose response testing ( $\geq 6$  days) (Summers et al. 2011, Crittenden et al. 2012, Shimabuku et al. 2016, Bentley and Summers 2020). Data would also be generated by testing with the actual water and background DOM, an advantage as their effects on OMP adsorption are system specific. Therefore, the combination of jar testing, HSDM kinetic curve fitting, and PSDM breakthrough projections represents a simplified approach for obtaining more accurate full-scale OMP breakthrough curves. This combination can specifically target early OMP breakthrough and avoid the need for resource- and time-intensive pilot-scale or rapid small-scale column test (RSSCT) studies.

# **Results and Discussion**

### **Dissolved Organic Matter Removal**

Dose response curves after a mixing time of 60 minutes for DOC and UVA254 are shown in Figs. 1a and 1c, respectively, for SW and WW. Results from all three batches of SW were averaged because removal differences between them were minor, represented by the error bars. Removal increased with dose, with better removal of UVA254 compared to DOC as expected (Summers et al. 2011), but the maximum removal using PATB was only 26% (SW) and 35% (WW) for DOC and UVA254, respectively, at a dose of 200 mg/L. At the same dose, removal using PAC was 77% (SW) and 91% (WW) for DOC and UVA254, respectively, markedly higher than 10 to 50% DOC removal using PAC at the more typical doses of 10 to 50 mg/L (Campos et al. 2000). While DOC and UVA254 removal at the lowest doses of 10 mg/L were similar (5% to 25%), the gap between PAC and PATB grew dramatically with increasing dose. Projecting removals at a PATB dose of 200 mg/L onto PAC curves indicates a factor of approximately 10 between the adsorbents, where a PAC dose of 20 mg/L would achieve the same DOC and UVA<sub>254</sub> removal. Lower DOM removal by PATB could be expected given the ~50% lower surface area compared to PAC, but this cannot solely explain the factor of 10 difference in dose. Size exclusion is expected to limit DOM adsorption to carbonaceous adsorbents with internal microporous structures (Summers et al. 2011, Kennedy and Summers 2015), so it may be that SW and WW DOM were unable access the same fraction of internal surface area in PATB as in PAC. Differences between SW and WW DOM removal (and therefore DOM solid phase concentrations  $(q_{DOM})$  because DOC<sub>0</sub> concentrations were the same) for each adsorbent were minimal, despite known differences in character between naturally occurring DOM and EfOM (e.g., molar mass distribution, aromaticity, etc.). The exception was UVA254 removal using PAC, attributable to the considerably lower WW UVA254.0 of 0.034 cm<sup>-1</sup> compared to the SW range of 0.048 to 0.058 cm<sup>-1</sup> (table 1).

Kinetic curves at doses of 50 mg/L for DOC and UVA<sub>254</sub> removal are shown in Fig. 1b and 1d, respectively, for SW and WW. At this dose, PAC increasingly outperformed PATB with increasing mixing time. A more revealing comparison between the two adsorbents by normalizing kinetics curves to removal at 120 minutes was not possible due to limited and variable DOM removal by PATB. As with any process using high surface area adsorbents, it takes time for adsorbates, in this case DOM, to diffuse into the internal pore structure and eventually attach to the surface. Beyond the 10-minute sample, DOM removal did not meaningfully increase using PATB in either water, suggesting the diffusion path length in PATB, or extent of internal pore structure accessible by DOM, was less extensive than PAC. This is consistent with the previous hypothesis concerning adsorbent surface area and dose factor differences between PAC and PATB in relation to Fig. 1a, confirming a deficient internal pore structure (i.e., less accessible by DOM) of PATB relative to PAC. Results in Fig. 1b and 1d also highlight that PATB contact times do not need to be much longer than 10 minutes for DOM adsorption capacity exhaustion at least for doses near 50 mg/L, potentially reducing reactor size

depending on the treatment scenario. Similar to dose response testing, differences between SW and WW DOM removal using both adsorbents were minimal except for UVA<sub>254</sub> using PAC due to the lower UVA<sub>254,0</sub>.

### **Organic Micropollutant Removal**

Normalized OMP concentrations after a mixing time of 60 minutes and dose of 50 mg/L for SW and WW are shown in Figs. 2a and 2b, respectively. Though OMP removal was evaluated at a range of doses, 50 mg/L data were chosen for comparison because the dose (1) is within typical PAC ranges, albeit at the higher end (Summers et al. 2011, Crittenden et al. 2012), (2) was effective for both adsorbents, (3) was duplicated during dose response testing, (4) corresponds to kinetic testing, and (5) simplifies the presentation of seven OMPs for two adsorbents and two waters. As with DOM, OMP results from the three SWs were averaged because of their similar removal represented by the error bars in Fig. 2. Some variability could be attributed to differences in SW pH, which was not held constant for each water (Table 1). Small increases in removal, averaged across the target OMPs IOH and SUC at doses of 50 mg/L, were observed with increases in pH from 8.0 to 8.8 (Table 1), specifically  $9\pm4\%$  for PAC and  $6\pm2\%$  for PATB. An increase in OMP removal with an increase in pH is consistent with an expected decrease in DOM adsorption, and by extension competition with OMPs, as DOM is rendered more hydrophilic with the deprotonation of carboxylic and phenolic functional groups (Newcombe 1994, Summers et al. 2011). The adsorption of negatively charged DOM at mg DOC/g adsorbent concentrations and the pH range in this study (7.5 to 8.8) likely also changed the initial adsorbent surface charge from net positive (PAC pHpzc: 9.7, PATB pHpzc: 9.0) (Bentley and Summers 2020) to net negative (Newcombe 1994), altering DOM and OMP adsorption behaviors with increasing contact time. While pH can affect DOM and OMP adsorption, differences in the presence of DOM were likely minimal for the one pH unit range in this study, especially in relation to the study focus: adsorbent based OMP removal differences.

As shown in Fig. 2a, DEE and THE removal by PAC and PATB were statistically the same at the 95% confidence level using one-way ANOVA, while IOH and SUC removal were significantly higher for PAC at the 95% confidence level. The other three OMPs were not present in SW at high enough concentrations to confidently quantify breakthrough behavior. Higher removals of IOH and SUC were unexpected considering the reasons for why they were chosen as target OMPs. OMP adsorbability in SW, as defined by the extent of removal, followed SUC>IOH>DEE>THE for PAC and THE>DEE>IOH>SUC for PATB, also confirmed to be similar for both adsorbents at a dose of 10 mg/L. These orders are, interestingly, complete opposites of each other and mostly inconsistent with previous findings that correlated increased adsorbability to increased OMP hydrophobicity as measured by the pH-dependent octanol-water partition coefficient (log D) (Table 2) (Magnuson and Speth 2005, Westerhoff et al. 2005, Kennedy et al. 2015, Hale et al. 2016). By contrast, the order for PAC is more consistent with

previous findings that correlated increased GAC adsorbability to increased OMP molar volume (table 2) (Crittenden et al 2012, Kennedy et al. 2015). An opposing case could be made for the PATB order, in that the smaller molar volumes of DEE and THE allowed them greater access to the more limited internal microporous structure of PATB.

Overall OMP removal trends in WW, shown in Fig. 2b, were similar to SW. On average for the four OMPs present in both waters, OMP removal was 70±16% (SW-PAC), 71±25% (WW-PAC), 38±23% (SW-PATB), and 34±31% (WW-PATB). Similar average OMP removal between SW and WW supports the earlier expectation that the impact of the small pH range in this study would be minimal. CAR and COT followed the trend of DEE and THE from Fig. 2a, exhibiting statistically insignificant differences in removal between PAC and PATB. SUL, an anionic OMP frequently observed to be weakly adsorbing (Shimabuku et al. 2016, Kearns et al. 2020a), unexpectedly followed the trend of IOH and SUC from Fig. 2a with significantly greater removal using PAC. Conversely for PATB, SUL followed the initially expected trend of IOH and SUC from Fig. 2a with minimal removal. OMP adsorbability in WW followed SUC>SUL>IOH>CAR>COT>DEE>THE for PAC and EE>CAR>THE>COT>SUL>SUC>IOH for PATB, again nearly opposite for the two adsorbents. For comparison, Westerhoff et al. (2005) observed an adsorbability order of CAR>DEE>SUL>IOP in four different waters at a PAC dose of 5 mg/L and 4-hour contact time, more aligned with the order observed for PATB in SW and WW. As with SW, adsorbability order was checked at a dose of 10 mg/L and was found to be similar for both adsorbents following the PATB trend at 50 mg/L, indicating adsorbability can also be a function of dose.

Different OMP adsorbabilities observed for both SW and WW could be expected because the two adsorbent surfaces were different in the extent of graphitic carbon development, internal surface area, internal microporous structure, surface hydrogen to carbon molar ratios (i.e., hydrophilicity and aromaticity), and surface oxygen/nitrogen to carbon molar ratios (i.e., functionality) (Hale et al. 2016, Shimabuku et al. 2016, Kearns et al. 2019, Bentley and Summers 2020). In addition to adsorbent properties, pH, and dose, OMP adsorption to carbonaceous adsorbents is simultaneously a function of other variables including OMP properties, reactor configuration, and perhaps most importantly, competition with DOM. In terms of DOM, *q<sub>DOM</sub>* values based on DOC and adsorbent mass (mg DOC/g adsorbent) were 18±1.6 (SW-PAC), 16±5.2 (WW-PAC), 5.5±1.8 (SW-PATB), and 2.9±2.4 (WW-PATB) after a mixing time of 60 minutes and dose of 50 mg/L. qDOM values based on DOC and adsorbent surface area ( $\mu g$  DOC/m<sup>2</sup> adsorbent) were 16±1.5 (SW-PAC), 15±4.8 (WW-PAC), 11±3.5 (SW-PATB), and 5.6±4.6 (WW-PATB) under the same conditions. Consistently higher *qDOM* on PAC compared to PATB (and higher  $q_{DOM}$  in SW compared to WW) could have proven detrimental to OMP adsorption depending on OMP adsorbability, increasing the relative effectiveness of PATB for the removal of DEE, for example. Nonetheless, without evaluating each OMP individually in buffered DI for each adsorbent, it is difficult to explain the opposing adsorbabilities observed between PAC and PATB in Fig. 2. These results highlight that while PATB was inferior to PAC for DOM removal as shown in Fig. 1, PATB was equivalent to PAC for the removal of certain OMPs as shown in Fig. 2.

To further evaluate the effects of background DOM and specifically SUC affinity for the adsorbent surface, average SUC solid phase concentrations ( $q_{SUC}$ ) on PAC and PATB after 60 minutes of mixing time were compared between DI, SW, and WW, shown in Fig. 3. As shown in Fig. 3a, *q<sub>SUC</sub>* values based on adsorbent mass (ng SUC/mg adsorbent) were consistently higher for PAC than PATB in all three waters. In fact, the presence of SW or WW DOM resulted in near constant *qsuc* values independent of PATB dose, as opposed to the steady decline of *qsuc* values observed with increasing PAC dose. It could be extrapolated that *qsuc*, in the presence of DOM, would be the same for both adsorbents only at very high and excessive doses (>200 mg/L), essentially allowing PATB to overcome the fouling effects of DOM. Without the presence of DOM, absolute differences in *asuc* (dose>50 mg/L) between PAC and PATB were smaller in DI than SW and WW. These results indicate DOM fouling had a greater negative effect on PATB than PAC, at least for the adsorption of SUC, likely because of the lower surface area and less extensive internal microporous structure. Accordingly, DOM removal prior to targeted OMP removal is arguably more important for PATB compared to PAC, but the presumably lower cost of PATB would have to be weighed against the increased pretreatment cost.

If  $q_{SUC}$  values were based on adsorbent surface area (ng SUC/m<sup>2</sup> adsorbent) as opposed to adsorbent mass, results were somewhat different as shown in Fig. 3b. While Fig. 3b results generally reflect Fig. 3a trends for SW and WW, *q<sub>SUC</sub>* values based on surface area were consistently higher on PATB compared to PAC in DI. Similar results were also observed by Kearns et al. (2019) for the removal of the 2,4-D from surface water based on CPTA biochar and GAC/PAC isotherms. Higher  $q_{SUC}$  values in DI based on surface area indicates a greater affinity for the surface, suggesting that if PATB surface area could be significantly increased above ~500  $m^2/g$  without negatively affecting this affinity, PATB may outperform PAC for OMP removal. For example, alkaline modifications prepared under oxygen or nitrogen gas flow have been shown to produce very high surface area biochars ( $\sim 1,100$  to 1,400 m<sup>2</sup>/g), although such alterations would certainly change surface chemistry (Ahmed et al. 2016). This conclusion of higher affinity for PATB also stems from analysis with SUC, a relatively difficult OMP for PATB to remove (Fig. 2). In this case, a higher surface area PATB may further outperform PAC for OMPs more easily removed by PATB (e.g., DEE). Ultimately, if increasing PATB surface area without impacting OMP affinity is feasible, the production costs and environmental impacts would likely increase, which would have to be weighed against the same for PAC.

### **Combined Treatment**

CT using both adsorbents was investigated to reduce the PAC dose and potentially treatment costs. Based on the opposing OMP adsorbabilities observed between PAC and PATB (Fig. 2), CT could harness synergistic effects between the two adsorbents for the removal of a wider array of OMPs. CT results are shown in Figs. 4a and 4b for SW and WW, respectively, for UVA<sub>254</sub>, IOH, and SUC. UVA<sub>254</sub> was chosen for the comparison because it has proven to be a conservative and easily measured surrogate for OMP removal, albeit with system specific relationships (Bentley 2020, Kearns et al. 2020a). In SW, the successive addition of PATB

increased removal of the three chosen parameters to a higher degree than either PAC alone at 10 mg/L or PATB alone at 50 or 100 mg/L. These increases in removal were statistically significant at the 95% confidence level using Tukey's method for UVA<sub>254</sub> and SUC, but not for IOH. The least amount of change with increasing PATB dose was observed with UVA<sub>254</sub>, for which removal significantly increased from 13% (0 mg/L PATB) to 20% (50 mg/L PATB) to 27% (100 mg/L PATB) in Fig. 4a. By comparison based on interpolating data in Fig. 1, 20 and 27% UVA<sub>254</sub> removal would require PAC doses of approximately 15 and 25 mg/L, respectively, 50 and 150% increases from 10 mg/L. Results for WW shown in Fig. 4b were analogous but progressive removal of IOH and SUC was less dramatic compared to SW, albeit significant for all constituents at the 95% confidence level. Therefore, depending on adsorbent and sludge processing costs, CT may prove useful for decreasing PAC dose and cost while targeting a wider range of OMP removal. In future studies, it is likely worth investigating the sequential addition order of the adsorbents as PAC is clearly more effective at removing DOM and mitigating DOM fouling as it pertains to OMP adsorption (Figs. 1 and 3).

### **Iohexol and Sucralose Adsorption and Modeling**

IOH and SUC adsorption was further analyzed and modeled using the HSDM and PSDM, despite their unexpected differences in adsorbability order using PAC and PATB. Normalized IOH and SUC concentrations are shown as a function of dose in Figs. 5a and 5c, respectively. As shown in Fig. 2, IOH and SUC were well removed at, and beyond, a PAC dose of 50 mg/L, while removal with PATB consistently lagged. Even at a PATB dose of 200 mg/L, IOH removal was only 38% (SW) and 17% (WW). Higher removal of SUC was observed using PATB at 200 mg/L, but still only reached 47% (SW) and 36% (WW). Removal in SW and WW using PAC were either indistinguishable (Fig. 5a for IOH) or slightly favored WW (Fig. 5c for SUC), while removal using PATB was worse in WW for all data points. EfOM could have led to increased competition for a specific and limited number of adsorption sites, more limited than PAC, and therefore relatively worse removal using PATB. Fittingly, increased competition could be mitigated with CT as opposed to solely increasing the PATB dose. For example, at a PATB dose

of 100 mg/L, SUC removal was only 11% in WW as shown in Fig. 5c. However, by adding PAC at 10 mg/L, SUC was removal was 58% as shown in Fig. 4b. It should be noted the same comparison for IOH was not performed because of the difference in removal from WW at a PAC dose of 10 mg/L between tests associated with data in Fig. 4b (37%) and Fig. 5a (10%).

Normalized IOH and SUC concentrations as a function of mixing time at a dose of 50 mg/L are shown in Figs. 5b and 5d, respectively, along with fitted HSDM curves. In both cases and like DOM removal in Fig. 1, OMP uptake kinetics were longer for PAC compared to PATB in terms of absolute increases in removals, increasing from approximately 70% at 10 minutes to >90% at 120 minutes. For PATB, removal increased from less than 10% at 10 minutes to 18% at the most for IOH in SW after 120 minutes (Fig. 5b). Bentley and Summers (2020) did observe more removal of 2,4-D using PATB in progressing from 3 hours (~40%) to 7 days (~60%), in addition to slower 2,4-D adsorption kinetics on PAC than PATB. Specifically, adsorption kinetics on

PAC were 1.4 (SW-SUC) to 2.5 (SW-IOH) times slower than on PATB based on  $D_s$  values shown in Table 3. An exception was SUC in WW, where adsorption kinetics on PAC were 1.4 times faster than on PATB. Consistently higher  $q_{DOM}$  on PAC compared to PATB may have been a cause for overall slower OMP adsorption kinetics by limiting OMP surface diffusion (Jarvie et al. 2005, Corwin and Summers 2011, Summers et al. 2014, Kennedy and Summers 2015). As expected, based on the data shown in Fig. 5, all PATB  $K_F$  values ((mg OMP/mg adsorbent)(L/mg OMP)<sup>1/n</sup>), shown in Table 3, were considerably smaller compared to PAC by factors of 35 (SW-IOH), 48 (SW-SUC), 166 (WW-IOH), and 139 (WW-SUC). Again, much larger differences in  $K_F$  values for WW indicate PATB adsorption capacity was potentially more negatively affected by the more competitive nature of EfOM (Shimabuku et al. 2016, Zietzschmann et al. 2016, Bentley 2020).

PSDM breakthrough curves for IOH and SUC are shown in Figs. 6a and 6b, respectively, and reflect the results in Fig. 5, that WW caused faster OMP breakthrough for GATB and the opposite for GAC. Considering there were no full-scale data to validate GAC breakthrough curves, they were compared to bed volumes to 10% OMP breakthrough (BV10%), calculated using the predictive model from Kennedy et al. (2015). Predicted BV10% values are shown for each OMP in Table 2 and Fig. 6. Though SW and WW were not coagulated as the model assumes, BV10% values for raw and coagulated waters at the same DOC0 concentration should be similar (Kennedy and Summers 2015). BV10% values can also be considered analogous to the anticipated absorbability on GAC/PAC, with the order of EE>CAR>COT>SUC>THE>SUL>IOH shown in Table 2, closer to the initially expected SW and WW trends observed for PATB (Fig. 2).

Predicted BV<sub>10%</sub> values in relation to the PSDM curves in Fig. 6 suggests the approach presented herein has merit, at least for early OMP breakthrough and should be investigated in future research. The lateral position of GAC breakthrough curves in Fig. 6, which represents adsorption capacity (integrated area above the curve), was partially a function of the relatively high 50 mg/L PAC dose. For high levels of OMP removal (>90%), PAC doses should theoretically be higher than GAC use rates ( $UR = \rho_b/BV$ ) (Crittenden et al. 2012), in which case choosing a more typical PAC dose of 5 to 10 mg/L may have generated breakthrough curves that underpredicted IOH and SUC adsorption capacity. For example, SUC removal was approximately 88% in SW at a PAC dose of 50 mg/L (Fig. 2a) while 12% breakthrough in Fig. 6b corresponds to a GAC UR of 19 mg/L, within weakly to moderately adsorbing OMP bins proposed in Kennedy et al. (2015). Then again, Kearns et al. (2020a) observed the opposite trend for both GAC and several biochars, in that fixed bed URs were consistently higher than batch URs for 90% removal of 2,4-D, SUL, and SIM.

Such a scenario, where generated breakthrough curves could underpredict IOH and SUC adsorption capacity, may have been the case for GATB breakthrough curves because high levels of IOH and SUC removal were not achieved at a PATB dose of 50 mg/L (Fig. 2). However, without full-scale data, it was assumed the approach could be extended to GATB as other GAC modeling methods have been extended to biochar (Kearns et al. 2020b). PSDM-generated GATB breakthrough curves in Fig. 6 demonstrate that at least for weakly adsorbing OMPs on PATB,

GATB URs would be much higher than GAC URs, by a factor of 38 to 264 (Table 3). IOH and SUC PSDM BV<sub>10%</sub> values shown in Table 3 ranged from 50 to 190 for GATB compared to 16,000 to 40,000 for GAC. As with PATB, this large difference highlights the greater importance of DOM removal for GATB compared to GAC. Kearns et al. (2020b) also observed significant pilot-scale breakthrough within hundreds of bed volumes for 11 OMPs using hardwood biochar, implying the GATB breakthrough curves in Fig. 6 and PSDM BV10% values in Table 3 are likely representative of full-scale performance. GAC and GATB URs could be reduced by operating several absorbers in parallel or series (Summers et al. 2011, Crittenden et al. 2012), but such analysis was beyond the scope of this study. A less optimistic interpretation for GATB is that given the low BV<sub>10%</sub> values shown in Fig. 6 and Table 3, which correlate to higher GATB URs, higher replacement frequencies, and do not fully consider the detrimental effects of DOM preloading/fouling deeper in the bed, is that PATB is likely a more promising approach for the removal of OMPs. As previously stated, PATB doses would theoretically be higher than GATB URs for high levels of OMP removal and would therefore represent higher adsorbent costs. However, GATB capital investment (e.g., filter boxes or pressure vessels, piping, valving) in addition to high GATB replacement frequencies would likely be more undesirable than the simplicity of dosing PATB.

Given this prospect of using GATB alone and the observed benefits of CT for PAC and PATB (Fig. 4), hypothetical CT (GAC/GATB) adsorber breakthrough curves were also projected at a 7minute EBCT and are shown in Fig. 6. Unlike the approach for PAC/PATB, which was to reduce PAC dose, the approach for GAC/GATB was to reduce the high GATB URs shown in Fig. 6 and Table 3. These CT breakthrough curves were based on the CT data shown in Fig. 4 for PAC and PATB doses of 10 and 50 mg/L, respectively, and therefore assumed a bed consisting of 83% GATB and 17% GAC by mass, with the same  $\varepsilon_b$  of 0.4 and weighted averages for  $\rho_b$  (240 kg/m<sup>3</sup>) and  $\rho_p$  (400 kg/m<sup>3</sup>).  $D_s$  values were taken as the average of SW or WW  $D_s$  values from PAC and PATB HSDM fits (Fig. 5 and Table 3). K<sub>F</sub> values were not obtained using the HSDM because CT kinetic tests were not performed. Instead, IOH and SUC K<sub>F</sub> values were obtained by equating q from the Freundlich isotherm (1/n=1.0) to q from a CT mass balance and solving for  $K_F$ , a method demonstrated previously by Corwin and Summers (2011). However, as a check on the method, K<sub>F</sub> values were also calculated for IOH and SUC in all dose response tests at doses of 50 mg/L because they were the most analogous to CT dose response testing. These  $K_F$  values were found to be lower than IOH and SUC HSDM  $K_F$  values (Table 3) by a factor of 3.7±1.2 and 2.7 $\pm$ 1.2, respectively. Therefore, IOH and SUC K<sub>F</sub> values for CT adsorber projections based on the Freundlich/mass balance method were increased by these respective factors prior to their input into the PSDM. All the same parameters that were given for GAC and GATB adsorbers are also shown for the hypothetical CT adsorber in Table 3. CT K<sub>F</sub> values were greater than GATB K<sub>F</sub> values by factors of 2.6 (SW-IOH), 16 (WW-IOH), 5.0 (SW-SUC), and 11 (WW-SUC), indicating greater benefits for treating WW, also shown by the breakthrough curves in Fig. 6. As expected based on the GAC/GATB mass ratio and CT K<sub>F</sub> values in Table 3, CT breakthrough curves fell between GAC and GATB breakthrough curves, with BV10% values (Table 3) for IOH and SUC ranging from 620 to 1,000, a significant improvement over GATB alone in terms of reducing GATB URs. Specifically, UR values dropped from a range of 1,050 to 4,000 mg/L for GATB alone, to 240 to 390 mg/L for CT, of which 83% would be attributable to GATB and

17% to GAC. Overall, these results demonstrate CT adsorbers with high GATB to GAC mass ratios could reduce URs and replacement frequencies relative to using GATB alone. Future research could also investigate a CT adsorber concept, or perhaps the addition of PAC at low doses(<10 mg/L) prior to GATB adsorbers.

# Conclusions

For the OMPs of CAR, COT, DEE, and THE, removal between PAC and PATB was the same at a dose of 50 mg/L in SW and WW. For DOM (DOC and UVA<sub>254</sub>) and the more weakly adsorbing indicator OMPs of IOH and SUC (and SUL), PAC consistently and significantly outperformed PATB over a range of realistic doses and contact times in SW and WW. IOH and SUC removal by PAC was nearly indistinguishable between SW and WW, but for PATB, EfOM had a noticeably negative impact on OMP adsorption capacity. In the absence of DOM in DI, adsorbent  $q_{SUC}$  values on a mass basis were comparable (dose $\geq$ 50 mg/L), however on a surface area basis, PATB *q<sub>SUC</sub>* values were higher, indicating the lack of surface area limits PATB from matching or exceeding PAC performance, not necessarily the surface chemistry. A synergy between PAC and PATB, or CT, was found and has potential to achieve enhanced removal of DOM and a wider range of OMPs at potentially lower treatment costs. Future research could evaluate whether PAC and PATB sequential addition order can improve OMP removal. For fixed bed treatment scenarios and related predictions, high dose PAC/PATB jar testing in combination with HSDM and PSDM modeling has potential to predict full-scale GAC/GATB adsorber breakthrough of OMPs, including CT, but needs further investigation and validation in future research. Even without full-scale breakthrough data, this method revealed the application of PATB for OMP removal is more realistic compared to GATB, not because the adsorbent UR would be lower, but because the GATB replacement frequency would be unsustainable.

#### **Data Availability Statement**

All data, models, and code generated or used during the study appear in the submitted article.

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#### Disclaimers

The views, analysis, recommendations, and conclusions in this report are those of the authors and do not represent official or unofficial policies or opinions of the United States government and the United States government takes no position with regard to any findings, conclusions, or recommendations made. As such, mention of trade names or commercial products does not constitute their endorsement by the United States government.

### References

ACS. (2021). SciFinder – Chemical Abstracts Service. Calculated using Advanced Chemistry Development (ACD/Labs) Software version 11.02. American Chemical Society. URL: scifinder.cas.org. Accessed on January 13, 2021.

Ahmed, M.B., Zhou, J.L., Ngo, H.H., Guo, W., & Chen, M. (2016). Progress in the preparation and application of modified biochar for improved contaminant removal from water and wastewater. *Bioresource Technology*, 214, 836-851.

Arcadis/Malcolm Pirnie. (2013). Navajo-Gallup Water Supply Project: 2012 Final Pilot Test Results Report.

APHA, AWWA, and WEF. (2017). Standard Methods for the Examination of Water and Wastewater, 23<sup>rd</sup> edition. A joint publication of the American Public Health Association, American water Works Association, and Water Environmental Federation.

Bentley, M.J. (2020). Enhancing biochar sorption of organic micropollutants in water treatment: Impacts of ash content and background dissolved organic matter. PhD dissertation. University of Colorado, Boulder, Colorado.

Bentley, M.J., & Summers, R.S. (2020). Ash pretreatment of pine and biosolids produces biochars with enhanced capacity for organic micropollutant removal from surface water, wastewater, and stormwater. *Environmental Science: Water Research & Technology*, 6, 635-644.

Campos, C., Schimmoller, L., Marinas, B.J., Snoeyink, V.L., Baudin, I., & Laine, J.M. (2000). Adding PAC to remove DOC. *Journal American Water Works Association*, 92(8), 69-83.

Corwin, C.J., & Summers, R.S. (2011). Adsorption and desorption of trace organic contaminants from granular activated carbon adsorbers after intermittent loading and throughout backwash cycles. *Water Research*, 45(2), 417-426.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K.J., & Tchobanoglous, G. (2012). MWH's Water Treatment: Principles and Design, 3<sup>rd</sup> edition, Chapter 15: Adsorption. John Wiley & Sons, Inc., Hoboken, New Jersey.

Edzwald, J.K., & Tobiason J.E. (2011). Water Quality & Treatment: A Handbook on Drinking Water, 6<sup>th</sup> edition, Chapter 3: Chemical Principles, Source Water Composition, and Watershed Protection. American Water Works Association, Denver, Colorado.

Hale, S.E., Arp, H.P.H., Kupryianchyk, D., & Cornelissen G. (2016). A synthesis of parameters related to bind of neutral organic compounds to charcoal. *Chemosphere*, 144, 65-74.

Inyang, M., & Dickenson, E.R.V. (2017). The use of carbon adsorbents for the removal of perfluoroalkyl acids from potable reuse systems. *Chemosphere*, 184, 168-175.

Jarvie, M.E., Hand, D.W., Bhuvendralingam, S., Crittenden, J.C., & Hokanson, D.R. (2005). Simulating the performance of fixed-bed granular activated carbon adsorbers: Removal of synthetic organic chemicals in the presence of background organic matter. *Water Research*, 39(11), 2407-2421.

Kearns, J.P., Shimabuku, K.K., Knappe, D.R.U., & Summers, R.S. (2019). High Temperature co-pyrolysis thermal air activation enhances biochar adsorption of herbicides from surface water. *Environmental Engineering Science*, 36(6), 710-723.

Kearns, J., Dickenson, E., Aung, M.T., Joseph, S.M., Summers, R.S., & Knappe, D. (2020a). Biochar water treatment for control of organic micropollutants with ultraviolet A surrogate monitoring. *Environmental Engineering Science*, ahead of print, http://doi.org/10.1089/ees.2020.0173.

Kearns, J., Dickenson, E., & Knappe, D. (2020b). Enabling organic micropollutant removal from water by full-scale biochar and activated carbon adsorbers using predictions from bench-scale column data. *Environmental Engineering Science*, 37(7), 459-471.

Kennedy, A.M., & Summers, R.S. (2015). Effect of DOM size on organic micropollutant adsorption by GAC. *Environmental Science & Technology*, 49, 6617-6624.

Kennedy, A.M., Reinert, A.M., Knappe, D.R.U., Ferrer, I., & Summers, R.S. (2015). Full- and pilot-scale GAC adsorption of organic micropollutants. *Water Research*, 68, 238-248.

Krasner, S.W., Westerhoff, P., Chen, B., Rittmann, B.E., Nam, S.N., & Amy, G. (2009). Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter. *Environmental Science & Technology*, 43(8), 2911-2918.

Lian, F., Sun, B., Song, Z., Zhu, L., Qi, X., & Xing, B. (2016). Physiochemical properties of herb-residue biochar and its sorption to ionizable antibiotic sulfamethoxazole. *Chemical Engineering Journal*, 248, 128-134.

Ling, Y., Alzate-Sanchez, D.M., Klemes, M.J., Dichtel, W.R., & Helbling, D.E. (2020). Evaluating the effects of water matrix constituents on micropollutant removal by activated carbon and  $\beta$ -cyclodextrin polymer adsorbents. *Water Research*, 173, 115551.

Magnuson, M.L., & Speth, T.F. (2005). Quantitative structure–property relationships for enhancing predictions of synthetic organic chemical removal from drinking water by granular activated carbon. *Environmental Science & Technology*, 39(19), 7706-7711.

Mohan, D., Sarswat, A., Ok, Y.S., & Pittman Jr., C.U. (2014). Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent – A critical review. *Bioresource Technology*, 160, 191-202.

Moreira, M.T., Noya, I., & Feijoo, G. (2017). The prospective use of biochar as adsorption matrix – A review from a lifecycle perspective. *Bioresource Technology*, 246, 135-141.

Newcombe, G. (1994). Activated carbon and soluble humic substances: Adsorption, desorption, and surface charge effects. *Journal of Colloid and Interface Science*, 164, 452-462.

Oppenheimer, J., Eaton, A., Badruzzaman, M., Haghani, A.W., and Jacangelo, J.G. (2011). Occurrence and suitability of sucralose as an indicator compound of wastewater loading to surface waters in urbanized regions. *Water Research*, 45(13), 4019-4027.

Shimabuku, K.K., Kearns, J.P., Martinez, J.E., Mahoney, R.B., Moreno-Vasquez, L., & Summers, R.S. (2016). Biochar sorbents for sulfamethoxazole removal from surface water, stormwater, and wastewater effluent. *Water Research*, 96, 236-245.

Sperlich, A., Schimmelpfennig, S., Baumgarten, B., Genz, A., Amy, G., Worch, E., & Jekel, M. (2008). Predicting anion breakthrough in granular ferric hydroxide (GFH) adsorption filters. *Water Research*, 42(8-9), 2073-2082.

Summers, R.S., Knappe, D.R.U., & Snoeyink, V.L. (2011). Water Quality & Treatment: A Handbook on Drinking Water, 6<sup>th</sup> edition, Chapter 14: Adsorption of Organic Compounds by Activated Carbon. American Water Works Association, Denver, Colorado.

Summers, R.S., Kennedy, A.M., Knappe, D.R.U., Reinert, A.M., Fotta, M.E., Mastropole, A.J., Corwin, C.J., & Roccaro, J. (2014). Evaluation of Available Scale-Up Approaches for the Design of GAC Contactors. Project No. 4235. Water Research Foundation, Denver, Colorado.

Thompson, K.A., Shimabuku, K.K., Kearns, J.P., Knappe, D.R.U., Summers, R.S., & Cook, S.M. (2016). Environmental comparison of biochar and activated carbon for tertiary wastewater treatment. *Environmental Science & Technology*, 50(20), 11253-11262.

Thompson, K.A., & Dickenson, E.R.V. (2020). A performance-based indicator chemical framework for potable reuse. *AWWA Water Science*, 2(5), e1191.

Ulrich, N., Endo, S., Brown, T.N., Watanabe, N., Bronner, G., Abraham, M.H., & Goss, K.U. (2017). UFZ-LSER database version 3.2.1, Leipzig, Germany, Helmholtz Centre for Environmental Research-UFZ. URL: <u>www.ufz.de/lserd</u>. Accessed on January 13, 2021.

Westerhoff, P., Yoon, Y., Snyder, S., & Wert, E. (2005). Fate of endocrine-disruptor, pharmaceutical, and personal care products during simulated drinking water treatment processes. *Environmental Science & Technology*, 39(17), 6649-6663.

Xiao, F., Bedane, A.H., Zhao, J.X., Mann, M.D., & Pignatello, J.J. (2018). Thermal air oxidation changes surface and adsorptive properties of black carbon (char/biochar). *Science of the Total Environment*, 618, 276-283.

Zietzschmann, F., Stutzer, C. & Jekel, M. (2016). Granular activated carbon adsorption of organic micro-pollutants in drinking water and treated wastewater – Aligning breakthrough curves and capacities. *Water Research*, 92, 180-187.



**Fig. 1.** Normalized DOC concentration as a function of (a) adsorbent dose and (b) mixing time and normalized UVA<sub>254</sub> as a function of (c) adsorbent dose and (d) mixing time. Mixing time was 60 minutes for dose response testing. Adsorbent dose was 50 mg/L for kinetic testing. Error bars represent the standard deviation of tests for all waters (SW) or duplicate jars (WW at doses of 10 and 50 mg/L only).



**Fig. 2.** Normalized concentrations of OMPs in (a) SW and (b) WW after a mixing time of 60 minutes and dose of 50 mg/L. Error bars represent the standard deviation of tests for all waters (SW) or duplicate jars (WW). CAR, COT, and SUL concentrations in SW were too low to confidently capture removal or exhibited erratic removal behavior. Asterisks denote significant differences at the 95% confidence level (p<0.05) between PAC and PATB for each OMP. Minimum SW  $C/C_0$  values based on MRLs would approximately be 0.03 for DEE, 0.13 for IOH, 0.01 for SUC, and 0.17 for THE. Minimum WW  $C/C_0$  values based on MRLs would approximately be 0.04 for CAR, 0.16 for COT, 0.06 for DEE, 0.03 for IOH, 0.00 for SUC, 0.02 for SUL, and 0.18 for THE.



**Fig. 3.** Average SUC solid phase concentrations,  $q_{SUC}$ , in all waters on PAC and PATB based on adsorbent (a) mass and (b) surface area after 60 minutes of mixing time. Error bars represent the standard deviation of tests for all waters (SW) or duplicate jars (DI and WW at doses of 10 and 50 mg/L only). Note: the extent of error bars that cover values less than one are not shown.



**Fig. 4.** Normalized concentrations of UVA<sub>254</sub>, IOH, and SUC as a function of a constant PAC dose of 10 mg/L in combination with increasing PATB doses (50 and 100 mg/L) in (a) SW and (b) WW after 60 minutes of mixing time. Error bars represent the standard deviation of tests for all waters (SW) or duplicate jars (WW). Letters denote significant differences at the 95% confidence level (p<0.05) between dosing combinations for each constituent.



**Fig. 5.** Normalized concentrations of IOH as a function of (a) adsorbent dose and (b) mixing time and SUC as a function of (c) adsorbent dose and (d) mixing time. Dashed lines are HSDM fits. Mixing time was 60 minutes for dose response testing. Adsorbent dose was 50 mg/L for kinetic testing. Error bars represent the standard deviation of tests for all waters (SW) or duplicate jars (WW at doses of 10 and 50 mg/L only).



**Fig. 6.** Hypothetical GAC, GATB, and CT breakthrough curves (7-minute EBCT) for (a) IOH and (b) SUC in SW and WW generated using the PSDM. GAC BV<sub>10%</sub> prediction (•) error bars represent the standard error (SE) of the model (Kennedy et al. 2015).

	General						OMP Concentrations $(C_0)$						
Water	Alkalinity	DOC	pН	UVA <sub>254</sub>	SUVA <sub>254</sub>	CAR	COT	DEE	IOH	SUC <sup>1</sup>	SUL		
	(mg/L as CaCO <sub>3</sub> )	(mg/L)	(su)	(cm <sup>-1</sup> )	(L/mg/m)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)		
DI (on-demand)	60±5	$0.05{\pm}0.01$	$8.6 \pm 0.1$	$0.000 \pm 0.000$	$0.0{\pm}0.0$	-	-	-	-	$3,400\pm520$	-		
SW (June 2020)	83±3	2.2±0.2	$8.0{\pm}0.1$	$0.058 {\pm} 0.004$	2.6±0.2	$0.9{\pm}0.5$	$1.3 \pm 1.3$	55±32	23±0.9	$1,200\pm95$	$0.4{\pm}0.1$		
SW (July 2020)	58±3	2.2±0.1	$8.1 \pm 0.1$	$0.058{\pm}0.001$	$2.6 \pm 0.0$	$2.3 \pm 2.1$	$2.6{\pm}1.6$	22±11	$4.5 \pm 0.7$	810±31	0.9±0.2		
SW (October 2020)	58±5	2.2±0.1	$8.8{\pm}0.0$	$0.048{\pm}0.003$	2.2±0.1	$8.0{\pm}2.9$	$1.9{\pm}1.4$	19±13	$18 \pm 1.4$	$1,020\pm56$	$1.1{\pm}0.1$		
WW (November 2020)	37±3	2.0±0.1	7.5±0.1	$0.034{\pm}0.001$	$1.7{\pm}0.0$	25±3.9	6.1±1.1	17±7.9	69±15	2,200±190	59±5.3		

#### **Fable 1.** Raw water quality after dilutions with unbuffered DI water.

<sup>1</sup>SUC was spiked to every water targeting 1,000 to 2,000 ng/L in addition to existing concentrations.

Table 2. Relevant OMP properties and GAC BV10% predictions using the model from Kennedy et al. (2015).

Туре	BV <sub>10%</sub> ·10 <sup>-3</sup> (SE range) <sup>1</sup>	log <i>D</i> (at pH 8.0) <sup>2</sup>	Molar Mass (g/mol)	Molar Volume (cm <sup>3</sup> /mol)	$pK_a$ (charge at pH 8.0) <sup>2</sup>	$S^3$	$V^4$
anticonvulsant	42 (21-84)	1.89	236.3	186.5	13.94 (0)	1.90	1.81
nicotine metabolite	35 (20-60)	0.07	176.2	153.6	4.72 (0)	1.49	1.39
insect repellent	52 (27-100)	2.42	191.3	194.0	-1.37 (0)	1.40	1.68
X-ray contrast agent	12 (4-30)	-2.92	821.1	373.1	11.35 (0)	5.00	4.02
artificial sweetener	32 (16-66)	0.23	397.6	234.7	12.52 (0)	2.30	2.42
antibiotic	25 (14-46)	-0.96	253.3	173.1	5.81 (-)	2.23	1.72
plant alkaloid	28 (17-46)	-1.06	180.2	112.0	9.90 (0)	1.60	1.22
	Type anticonvulsant nicotine metabolite insect repellent X-ray contrast agent artificial sweetener antibiotic plant alkaloid	$\begin{tabular}{ c c c c c } \hline Type & BV_{10\%}\cdot10^{-3}\\ (SE\ range)^1 & \\ \hline anticonvulsant & 42\ (21-84) & \\ nicotine\ metabolite & 35\ (20-60) & \\ nisect\ repellent & 52\ (27-100) & \\ X-ray\ contrast\ agent & 12\ (4-30) & \\ artificial\ sweetener & 32\ (16-66) & \\ antibiotic & 25\ (14-46) & \\ plant\ alkaloid & 28\ (17-46) & \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c c c } \hline Type & $BV_{10\%}$\cdot 10^3$ & $\log D$ \\ $(SE\ range)^1$ & $(at\ pH\ 8.0)^2$ \\ \hline $(at\ sH\ 8.0)^2$ \\ \hline $(at\ 8.0)^2$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

<sup>1</sup>SE-standard error.<sup>2</sup>ACS (2021).<sup>3</sup>Abraham polarity/polarizability (Ulrich et al. 2017).<sup>4</sup>Abraham McGowan molecular volume (Ulrich et al. 2017).

**Table 3.** IOH and SUC modeling parameters for batch (HSDM for PAC and PATB at 50 mg/L,  $d_p$ =0.038 mm) and fixed bed (PSDM for GAC, GATB, and CT at 7-minute EBCT,  $d_p$ =0.92 mm) scenarios.

Water			IOH		SUC						
Adsorbent	$D_p$	$D_s$	$K_F^1$	$k_{f}$	PSDM BV10%2	$D_p$	$D_s$	$K_F^1$	$k_f$	PSDM BV1	
Ausorbent	(m <sup>2</sup> /s)	(m <sup>2</sup> /s)	(mg/mg)(L/mg) <sup>1/n</sup>	(m/s)	(UR in mg/L)	$(m^2/s)$	(m <sup>2</sup> /s)	(mg/mg)(L/mg) <sup>1/n</sup>	(m/s)	(UR in mg/	
SW-PAC	-	3.2x10 <sup>-16</sup>	0.45	1.4x10 <sup>-2</sup>	-	-	6.5x10 <sup>-16</sup>	0.41	1.6x10 <sup>-2</sup>	-	
SW-PATB	-	7.9x10 <sup>-16</sup>	0.013	1.4x10 <sup>-2</sup>	-	-	9.1x10 <sup>-16</sup>	0.0085	1.6x10 <sup>-2</sup>	-	
SW-GAC	4.1x10 <sup>-10</sup>	3.2x10 <sup>-16</sup>	0.45	9.9x10 <sup>-6</sup>	16,000 (28)	5.3x10 <sup>-10</sup>	6.5x10 <sup>-16</sup>	0.41	1.2x10 <sup>-5</sup>	21,000 (21	
SW-GATB	4.1x10 <sup>-10</sup>	7.9x10 <sup>-16</sup>	0.013	9.9x10 <sup>-6</sup>	190 (1,050)	5.3x10 <sup>-10</sup>	9.1x10 <sup>-16</sup>	0.0085	1.2x10 <sup>-5</sup>	150 (1,300	
SW-CT	4.1x10 <sup>-10</sup>	5.6x10 <sup>-16</sup>	0.034	9.9x10 <sup>-6</sup>	620 (390)	5.3x10 <sup>-10</sup>	7.8x10 <sup>-16</sup>	0.042	1.2x10 <sup>-5</sup>	930 (260)	
WW-PAC	-	2.9x10 <sup>-16</sup>	0.58	1.4x10 <sup>-2</sup>	-	-	1.1x10 <sup>-15</sup>	0.57	1.6x10 <sup>-2</sup>	-	
WW-PATB	-	6.1x10 <sup>-16</sup>	0.0035	1.4x10 <sup>-2</sup>	-	-	8.1x10 <sup>-16</sup>	0.0041	1.6x10 <sup>-2</sup>	-	
WW-GAC	4.1x10 <sup>-10</sup>	2.9x10 <sup>-16</sup>	0.58	9.9x10 <sup>-6</sup>	22,000 (20)	5.3x10 <sup>-10</sup>	1.1x10 <sup>-15</sup>	0.57	1.2x10 <sup>-5</sup>	40,000 (11	
WW-GATB	4.1x10 <sup>-10</sup>	6.1x10 <sup>-16</sup>	0.0035	9.9x10 <sup>-6</sup>	50 (4,000)	5.3x10 <sup>-10</sup>	8.1x10 <sup>-16</sup>	0.0041	1.2x10 <sup>-5</sup>	70 (2,900	
WW-CT	4.1x10 <sup>-10</sup>	4.5x10 <sup>-16</sup>	0.056	9.9x10 <sup>-6</sup>	1,000 (240)	5.3x10 <sup>-10</sup>	9.6x10 <sup>-16</sup>	0.045	1.2x10 <sup>-5</sup>	1,000 (240	

<sup>1</sup>*l/n*=1.0 for all modeling.<sup>2</sup>Values correspond to breakthrough curves in Figure 6.