NWRI GRADUATE FELLOW SEMI-ANNUAL PROGRESS REPORT

DATE: June 2017

Project Title: Biochar sorbents for the control of organic contaminants: understanding biochar structure and water quality on sorption behavior

Graduate Fellow: Kyle Shimabuku

Advisor: R. Scott Summers

Institution: University of Colorado at Boulder

Background and Introduction

Overview
Biochar is a sorbent generated from the pyrolysis of biomass that can exhibit comparable organic contaminants (OC) sorption capacities to activated carbon (Kearns, et al., 2015; Kearns, et al., 2014; Shimabuku et al., 2016; Xiao & Pignatello, 2015), and can be produced for less than one-sixth of the cost of activated carbon (Meyer et al., 2011). In addition, biochar can be a by-product of biomass energy production. Based on a life-cycle assessment, we showed that biochar is more environmentally friendly than activated carbon to control OCs for tertiary wastewater treatment (Thompson et al., 2016). Although biochar has the potential to be widely used to remove OCs in water reuse applications, a better understanding of the relationship between its production conditions and sorption behavior is needed.

Hypotheses
Hypothesis 1: Biochar sorption capacity depends on the physicochemical properties of the OC sorbate and biochar, which is determined by the production conditions. The contribution of different sorption mechanisms to the overall sorption capacity is determined by the physicochemical properties of the OC and correlates with biochar physicochemical properties.

Hypothesis 2: The decrease in OC sorption capacity of different biochars in the presence of stormwater and wastewater effluent dissolved organic matter (DOM) depends on the DOM characteristics and sorption mechanisms.

Study Goals
The goals of this study are: (i) determine how production conditions can be optimized to enhance the OC sorption capacity of biochar sorbents, (ii) gain a fundamental understanding of OC sorption mechanisms by biochar, (iii) evaluate how stormwater character, sorbate properties, and biochar production conditions influences DOM's competitive effect.

Objectives of Research Project
The overall objective of this research project is to elucidate how production conditions and precursor materials determine the physicochemical properties and concomitant OC removal efficiency of biochar sorbents. This can then inform biochar manufacturers of how to best select production conditions and biochar feedstocks to make efficient sorbents. Another objective of this research is to provide information that can inform models to predict the performance of biochar and other carbonaceous sorbents with OCs that vary in physical and chemical properties.

Needs Served by This Research

Controlling organic contaminants (OCs) will be a key challenge for wastewater and stormwater reuse because of public concern over the presence of OCs in water and increasingly stringent OC regulations. As inexpensive-fossil-fuel energy resources are depleted, standard technologies used to control OCs such as reverse osmosis and advanced oxidation processes may become more expensive as they require significant energy inputs to operate. Thus, developing biochar to remove OCs from wastewater and stormwater may fulfill the need for a low-cost, sustainable technology to control OCs in wastewater and stormwater for their reuse.

Progress to-date
Discussion of results

Influence of temperature, feedstock, surface area, and elemental ratios on biochar performance

The dose necessary to achieve 75% sulfamethoxazole removal at a 60-min contact time was determined for each sorbent, minus the ash content ($^{AFM}Dose_{75\%}$), and is plotted against surface area of the sorbent, minus any contribution of surface area from the ash (Figure 2). The ash free matter doses and surface areas are plotted since ash was found to not exhibit any sorption capacity. As $^{AFM}Dose_{75\%}$ values decrease sorption capacity increases. Thus, sorption capacity appears to increase with surface area, but eventually plateaus, suggesting that surface area alone cannot predict biochar sorption capacity (Figure 1).

Figure 1: Surface areas for the ash free material (SA_{AFM}) plotted against the ash free matter doses need for 75% sulfamethoxazole removal ($^{AFM}Dose_{75\%}$).

$^{AFM}Dose_{75\%}$ values are also plotted against H:C and O:C ratios (Figure 2). For the low ash materials, which were biochars made from wood, as H:C ratios (i.e., aromaticity) increase and O:C ratios (i.e., polarity) decrease biochar sorption capacities increase. It should be noted that as peak temperature increases, surface area increases, H:C ratios increase, and O:C ratios decrease (data not shown). Thus, these results show that as peak temperature increases, sorption capacity might also increase because of changes in surface area, aromaticity, and polarity.

For the high-ash sorbents, which were all generated at 850 °C from different wastewater sludges, no correlation was found between $^{AFM}Dose_{75\%}$ values and elemental ratios, as $Dose_{75\%}$ values remained
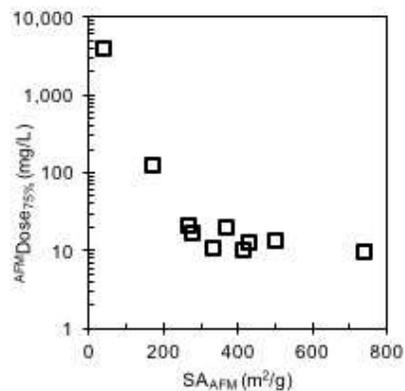
similar even though their corresponding elemental ratios varied substantially (Figure 2). Thus, relationships between elemental ratios and biochar sorption performance are probably robust only *within* compositionally homologous feedstock classes where differences in elemental ratios arise from different production conditions and not from different precursor material properties.
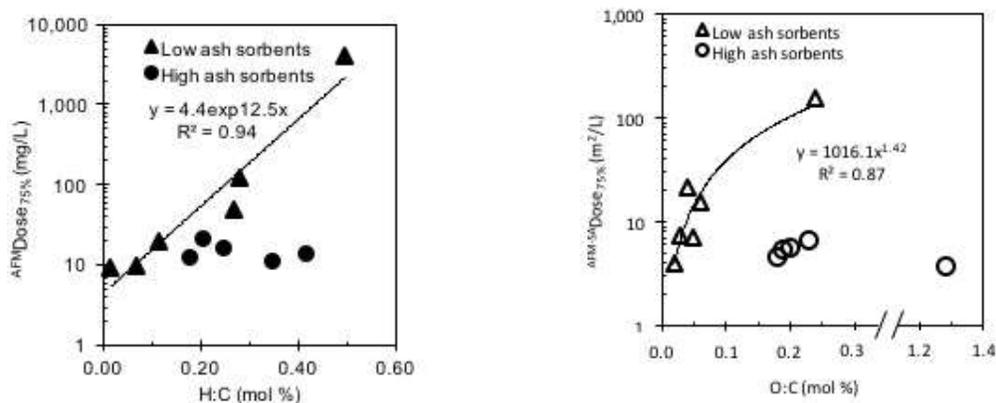

Figure 2: Ash free matter doses need for 75% sulfamethoxazole removal ($^{AFM}Dose_{75\%}$) plotted against H:C ratios (i.e., aromaticity) (a) and O:C ratios (i.e., polarity) (b). Low ash sorbents include biochar produced at different temperatures and a PAC. High ash sorbents are biochar produced from wastewater sludge.

The influence of DOM source on sorption capacity

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 are shown in Figure 3. The black dashed line indicates where the $^{DOM}Dose_{75\%}$ / $^{DI}Dose_{75\%}$ ratio is equal to one, which is where the $Dose_{75\%}$ in the surface water, wastewater effluent, or stormwater is equal to that in DI water. Greater $^{DOM}Dose_{75\%}$ / $^{DI}Dose_{75\%}$ ratios correspond to greater DOM fouling. Batch sorption experiments conducted in a surface water yielded $^{AFM}Dose_{75\%}$ values that were at least four times greater than in DI water for each sorbent except for the W-R-350 °C biochar (Figure 3). Thus, DOM appears to drastically decrease the sorption capacity of most biochars by competing for sorption sites. Interestingly, minimal competition was observed with the wood biochar produced at 350 °C (W-R-350 °C) possibly because biochars produced at the low temperature of 350 °C mainly sorb OCs by *ab*sorption. Xing et al. (1996) proposed that sorbents that *ab*sorb compounds are deficient in specific sorption sites where competition could occur, which could explain why it does not experience DOM competition.

Sulfamethoxazole sorption was examined in wastewater effluent and in stormwater with several sorbents (Figure 3). It should be noted that the dissolved organic carbon concentration was 5, 5, and 15 mg/L for the wastewater effluent, stormwater, and surface water, respectively. For all the sorbents examined, the wastewater effluent and stormwater induced a greater competitive effect than the surface water even though their DOC concentrations were lower (Figure 3). Previous work has found that waters with larger Peak C/UVA values are composed of lower molecular weight DOM and can cause 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 wastewater effluent and stormwater have Peak C/UVA values of ~7 RU-cm whereas the surface water's Peak C/UVA value is 4 RU-cm. Thus, the wastewater effluent and stormwater may be comprised of a greater faction of lower molecular weight DOM (Mostafa et al., 2014; Shimabuku et al., 2014).
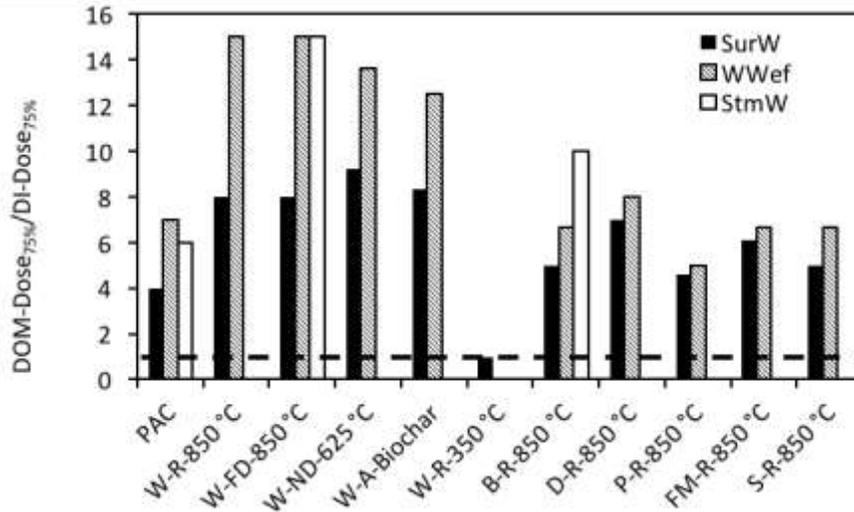

Figure 3. Sorbent doses for 75% sulfamethoxazole removal (Dose$_{75\%}$) determined at 60 min in different waters containing dissolved organic matter (DOM) normalized by the Dose$_{75\%}$s determined in 10 mM phosphate buffered pH 7.2 deionized (DI) water. The black dashed line indicates where the ^{DOM}Dose$_{75\%}$ / ^{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. These experiments where conducted with powdered activated carbon (PAC) and wood biochar (W) as well as biochar made from biosolids (B), dissolved air flotation thickened solids (D), primary wastewater sludge (P), fecal material (FM), and secondary wastewater sludge (S).

Overall, the biochars produced from wastewater sludge experienced less competition than biochars produced from wood in the surface water, stormwater, and wastewater effluent (Figure 3). This might be related to the greater mesoporosity of the wastewater sludge biochars relative to the wood biochars, as mesopore-to-micropore ratios range between 2-3.4 for the wastewater sludge biochars and 0.17-.73 for the wood biochars. 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 & Snoeyink, 1999).

Conclusions

These results show that biochar production conditions can be optimized to increase its sorption capacity. Increasing temperature likely corresponds to improved sorption capacity due to an increase in surface area, a decrease in polarity, and an increase in aromaticity, however which parameter(s) is the most important cannot be determined based on the current data set. Since physicochemical

properties vary with production conditions, our results suggest that relationships between biochar properties, its production, and sorption capacity can be developed. Hydrogen to carbon ratios may be the most useful as they are rapid and inexpensive to measure and could be used to screen for efficient biochar sorbents. However, such relationships may only be valid for biochars where the same or a similar feedstock (e.g., wood) is used. It was also shown that DOM from different sources fouled biochar sorption to varying degrees, as the wastewater and stormwater DOM was much more competitive than surface water DOM. The fluorescence indicator, Peak C/UVA, appeared to relate to the DOM competitive effect, indicating that it could be used to evaluate how effective biochar will be in different waters. In addition, the susceptibility of different biochars to DOM competition varied significantly, possibly because of differences in their physical properties. Thus, it may also be possible to produced biochars that may be less susceptible to DOM competition by selecting production conditions that increase their pore size distribution.

The implication of these findings is that biochar production conditions and the selection of biochar feedstock can be tailored to enhance their ability to control OCs in surface water, wastewater effluent, and stormwater. Since organic pollutants found in environmental waters mostly come from wastewater effluent and stormwater runoff, these low-cost sorbents could limit OC occurrence in the environment and in our water resources. Moreover, the feedstock materials used here can sometimes be viewed as waste materials. Thus, producing biochar sorbents from these materials can valorize such wastes. For instance, biochar produced from pine-beetle kill, which can be sourced from fire control efforts, and wastewater sludge, which is often landfilled or incinerated when not used as a soil amendment, could yield environmental benefits beyond making OC control more affordable.

Next steps

Currently, I am assessing the sorption of seven different OCs that vary in molecular size and functionality with biochars produced at different temperatures, durations, and gaseous conditions to evaluate how OC and biochar properties influence different sorption mechanisms. These biochars are also being characterized by N_2 and CO_2 adsorption to determine their pore size distributions. Since our previous findings showed that the DOM source had a profound impact on the competitive nature of DOM, I have collected eight different stormwaters for experimentation to evaluate how stormwater DOM source and characteristics influence its competitive effect. I also plan to use different sorption models used for activated carbon, such as the Ideal Adsorbed Solution Theory, to try and quantify the competitive effect of DOM and relate the competitive effect of DOM with the properties of biochar.

References

Kearns, J. P., Shimabuku, K. K., Mahoney, R. B., Knappe, D., & Summers, R. S. (2015). Meeting multiple water quality objectives through treatment using locally generated char: improving organoleptic properties and removing synthetic organic contaminants and disinfection by-products. *Journal of Water, Sanitation and Hygiene for Development*, *5*(3), 359–372. http://doi.org/10.2166/washdev.2015.172

Kearns, J. P., Wellborn, L. S., & Summers, R. S. (2014). 2,4-D adsorption to biochars: Effect of preparation conditions on equilibrium adsorption capacity and comparison with commercial

activated carbon literature data. *Water Research*, *62*, 20–28. http://doi.org/10.1016/j.watres.2014.05.023

Li, Q., Snoeyink, V. L., Mariãas, B. J., & Campos, C. (2003). Elucidating competitive adsorption mechanisms of atrazine and NOM using model compounds. *Water Research*, *37*(4), 773–784. http://doi.org/10.1016/s0043-1354(02)00390-1

Meyer, S., Glaser, B., & Quicker, P. (2011). Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review. *Environmental Science & Technology*, *45*(22), 9473–9483. http://doi.org/10.1021/es201792c

Mostafa, S., Korak, J.A., Shimabuku, K., Glover, C.M., Rosario-Ortiz, F., 2014. Relation between optical properties and formation of reactive intermediates from different size fractions of organic matter. In: Rosario-Ortiz, F. (Ed.), Advances in the Physicochemical Characterization of Dissolved Or-ganic Matter: Impact on Natural and Engineered Systems. ACS, Washington, DC, pp. 159e179.

Pelekani, C., & Snoeyink, V. L. (1999). Competitive adsorption in natural water: role of activated carbon pore size. *Water Research*, *33*(5), 1209–1219. http://doi.org/10.1016/S0043-1354(98)00329-7

Shimabuku, K. K., Cho, H., Townsend, E. B., Rosario-Ortiz, F. L., & Summers, R. S. (2014). Modeling Nonequilibrium Adsorption of MIB and Sulfamethoxazole by Powdered Activated Carbon and the Role of Dissolved Organic Matter Competition. *Environmental Science & Technology*, *48*(23), 13735–13742. http://doi.org/10.1021/es503512v

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. http://doi.org/10.1016/j.watres.2016.03.049

Thompson, K. A., Shimabuku, K. K., Kearns, J. P., Knappe, D., Summers, R. S., & Cook, S. M. (2016). Environmental Comparison of Biochar and Activated Carbon for Tertiary Wastewater Treatment. *Environmental Science & Technology*. http://doi.org/10.1021/acs.est.6b03239

Xiao, F., & Pignatello, J. J. (2015). Interactions of triazine herbicides with biochar: Steric and electronic effects. *Water Research*, *80*, 179–188. http://doi.org/10.1016/j.watres.2015.04.040

Xing, B. S., Pignatello, J. J., & Gigliotti, B. (1996). Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environmental Science & Technology*, *30*(8), 2432–2440. http://doi.org/10.1021/es972004i