Sorption of Perfluorinated Carboxylic Acids (PFCAs) to Sewage Sludge Biochars

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Objectives

- Compare the relative abilities of sewage sludge biochars and clean wood chips to sorb perfluorinated carboxylic acids (PFCAs)
- Identify possible sorption mechanisms of PFCAs for the different biochar feedstocks
- Study the effects of increasing perfluorinated carbon chain-length, competing sorbates, and the presence of soil on sorption

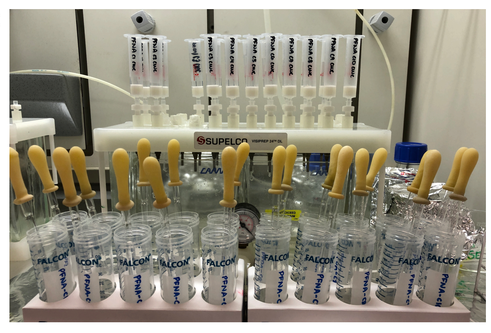
Figure 1: Biochar collection from the ETIA pyrolysis unit at Lindum AS, Norway.

Figure 2: Sewage sludge pellets (left) and sewage sludge biochar (right).

Methods

Biochar samples (pyrolysis T = 700°C):
- **ULS**: raw sewage sludge from Ullensaker WWTP (29% C)
- **DSL**: digested sewage sludge (13% C)
- **CWC**: clean wood chips (91% C)

Batch shaking tests with C5-C10 PFCAs:
- 100 mg biochar
- 50 mL water
- Spiked with individual PFCAs at 10 concentrations over four orders of magnitude
- Shaken end-over-end for >14 days
- Filtered through 0.45 µm regenerated cellulose filter



- Solid Phase Extraction (SPE) of filtrate
- Analyte quantification with LC-MS/MS at the Norwegian University of Science and Technology (NTNU), Trondheim, Norway

Results

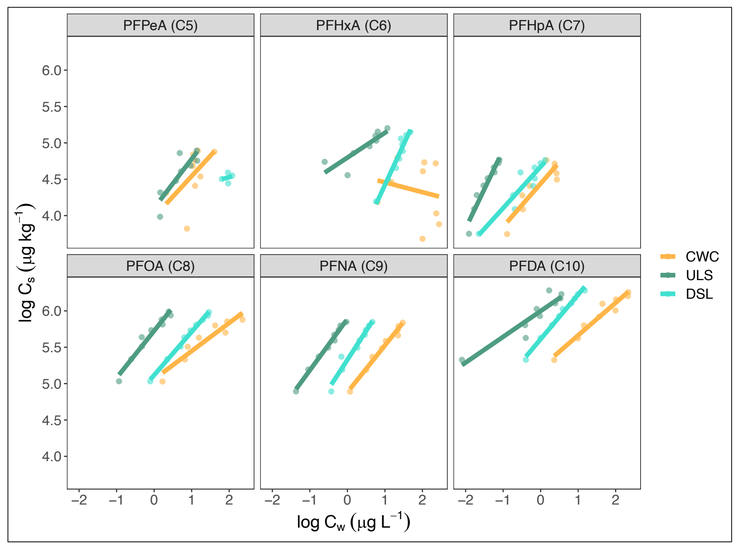


Figure 3: Freundlich sorption isotherms for each biochar sample. Log C_w is the equilibrium aqueous concentration and log C_s is the equilibrium sorbed concentration

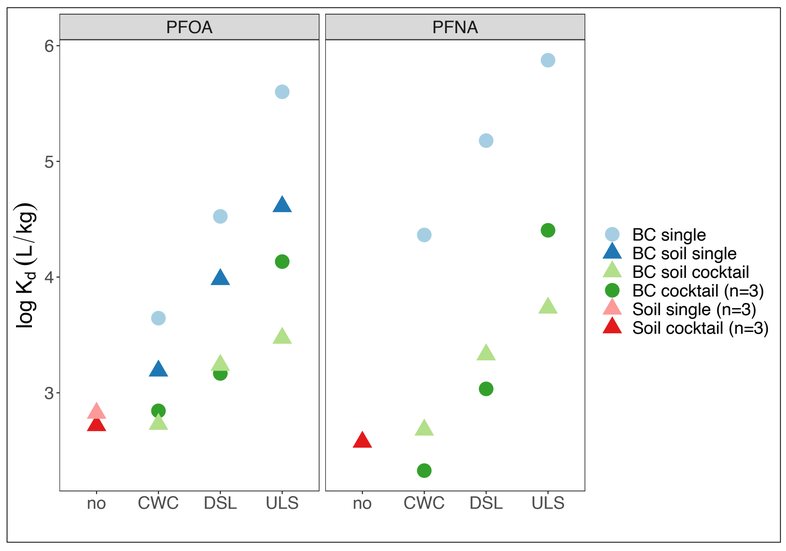


Figure 4: Sorption attenuation of PFOA spiked at 1 900 µg/L and PFNA at 1 400 µg/L for each batch test category that indicates non-linear sorption at high concentrations and pore blocking by soil

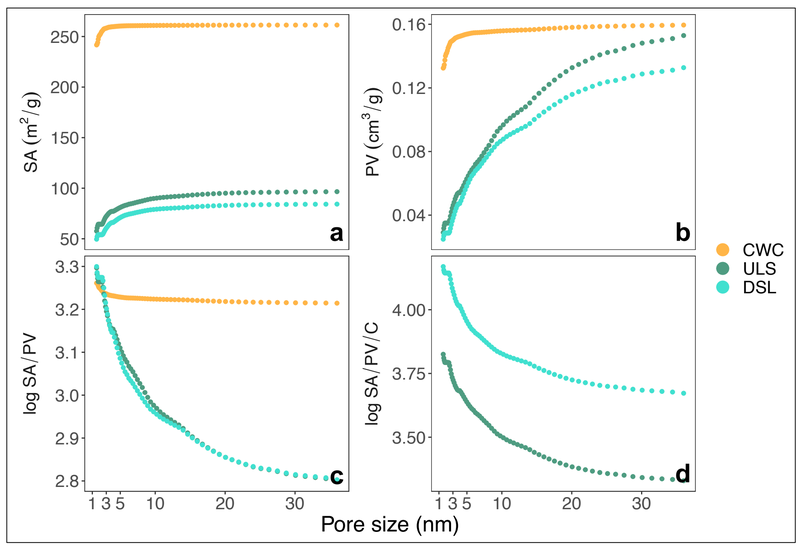


Figure 5: Distribution of pores >1.5 nm by **(a)** surface area (SA), **(b)** pore volume (PV), **(c)** log SA/PV, and **(d)** log (SA/PV)/C (C = carbon). The results were conducted by research partners at University of Florida

- Sorption increases from CWC < DSL < ULS, and with increasing perfluorinated chain-length (**Fig. 4**). The Freundlich sorption coefficients (log K_F) found in this study are equivalent to, or higher than, log K_F values for activated carbon reported in previous literature[1,2,3]
- Stronger sorption of PFCAs to sewage sludge biochars is likely due to a higher fraction of mesopores (2-50 nm, **Fig. 5c**)
- A higher carbon-fraction in the pore wall matrix (lower log SA/PV/C ratio) of ULS is hypothesized to explain why PFCAs sorb stronger to ULS than to DSL (**Fig. 5d** and **Fig. 6**)

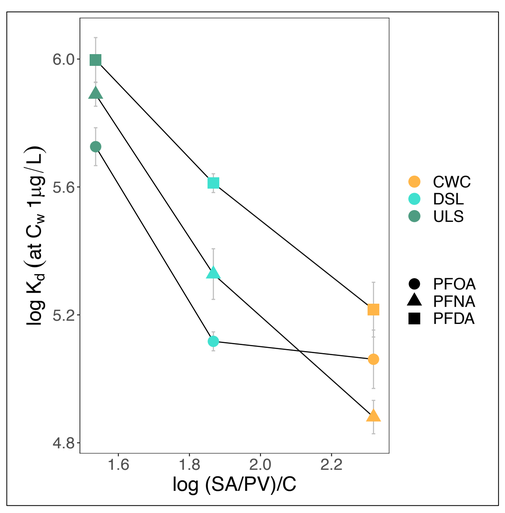


Figure 6: Relationship between log (SA/PV)/C (C = carbon) ratio and log K_d for PFOA, PFNA and PFDA across biochar samples.

Conclusion

- The strong sorption of PFCAs found to sewage sludge biochars is promising for their incorporation in a circular economy, for example their use as fertilizers, sorbents in wastewater treatment plants, or as amendments to PFAS-contaminated soil
- Future work should aim at further investigating the ratios between surface area, pore volume, carbon, and minerals (mainly Ca and Fe) in determining the sorption affinity of PFAS and other organic contaminants to sewage sludge biochars

References:
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