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ILLINOIS SUSTAINABLE TECHNOLOGY CENTER
PRAIRIE RESEARCH INSTITUTE

RR-124
December 2014
www.istc.illinois.edu

RR-124

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December 2014

Submitted to the
Illinois Sustainable Technology Center
Prairie Research Institute
University of Illinois at Urbana-Champaign
www.istc.illinois.edu

The report is available on-line at:
http://www.istc.illinois.edu/info/library_docs/RR/RR124.pdf

Printed by the Authority of the State of Illinois
Patrick J. Quinn, Governor

ACKNOWLEDGEMENTS

The authors thank:

- Will Gillespie (ISWS) for supplying the corn stover.
- Wei Zheng and B.K. Sharma (ISTC) for biochar preparation.
- Steve Peterson (USDA/ARS) for surface area measurements.
- Jillian O'Connell for assistance with the sorption and bioavailability experiments.
- Wacker Chemical Corporation, Adrian, MI for a sample of Cavasol® HPCD.
- Wei Zheng, Steve Peterson, Elizabeth Luber, and Nancy Holm for helpful review comments.

This project was supported by the Illinois Sustainable Technology Center, a division of the Prairie Research Institute at the University of Illinois at Urbana-Champaign (Grant No. HWR12221).

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SYMBOLS AND ABBREVIATIONS

Symbols in italics are from equations in the Methodology chapter.

ARS	Agricultural Research Service
ASE	Accelerated solvent extraction
BET	Brunauer-Emmett-Teller
C_{Dissol}	Dissolved concentration
C_{MeOH}	Concentration in methanol extract
G	Earth's gravity. In centrifugation, 1320 x G means 1320 times earth's gravity.
g	Gram(s)
GCMS	Gas chromatography-mass spectrometry
HPCD	2-hydroxypropyl-β-cyclodextrin
K_d	Distribution coefficient
K_p	Partition coefficient
K_{POM}	Partition coefficient for POM
MDL	Method detection limit
L	Liter
LPM	Liters per minute
M	Moles per liter
mg	Milligram(s), 10^{-3} g
$m^2\ g^{-1}$	Square meters per gram
mg kg^{-1}	Milligrams per kilogram
mg L^{-1}	Milligrams per liter
μg	Microgram(s), 10^{-6} g
μg kg^{-1}	Micrograms per kilogram
μg L^{-1}	Micrograms per liter
μg m^{-2}	Micrograms per square meter
mL	Milliliters
mm	Millimeters
μm	Micrometers
M_{Diss}	Dissolved mass
M_{Part}	Mass partitioned to POM or silicone
M_{Sorb}	Mass sorbed to char
M_{Tot}	Total mass
m/z	Mass to charge ratio, mass spectrometry
ng	Nanogram(s), 10^{-9} g
ng/mL	Nanograms per milliliter
nm	Nanometers
PAH	Polycyclic aromatic hydrocarbon
POM	Polyoxymethylene
psi	Pounds per square inch
PTFE	Polytetrafluoroethylene
Q_{Char}	Concentration sorbed to char
Q_{POM}	Concentration partitioned to POM
RPD	Relative percent difference

RPM	Revolutions per minute
SIS	Selected ion storage
SPME	Solid phase microextraction
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
V_{MeOH}	Volume of methanol extract

ABSTRACT

Biochars were produced by slow pyrolysis of corn stover under a nitrogen atmosphere at 450°, 550°, and 750°C. The chars were subjected to artificial aging, i.e., repeatedly freezing and thawing or incubating moist char at 60° and 110°C. A total of 12 materials was produced and characterized. The total polycyclic aromatic hydrocarbon (PAH) contents of 450° and 550° chars were 1.4 and 0.2 mg kg^{-1}, respectively. Extraction and analysis of PAHs in the 750^{o} char was performed, however the quality control associated with this assay indicated that PAHs could not be quantitatively extracted from this material by standard methods. Sorption and mild extraction experiments were performed. Mild extraction with 2-hydroxypropyl-β-cyclodextrin (HPCD), mimics bioaccessibility. Pyrene was used as a probe compound. The sorption data were well described by Freundlich isotherms. Pyrene sorption was strong for all chars, with the amount sorbed at 1 μg L^{-1} dissolved pyrene ranging from 10^{6} to over 10^{7} μg kg^{-1}. The pyrene content of the chars was too low to be detected in the HPCD extracts, so the chars were spiked with pyrene and allowed to equilibrate before extraction. Only 10 to 15% of added pyrene was HPCD-extractable from the 450° char and 1 to 5% from the 550° and 750° chars. Aging had small but measureable effects on both sorption and HPCD extraction of pyrene.

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INTRODUCTION

Pyrolysis is an emerging technology that creates bio-products by heating biomass in an oxygen-free or low-oxygen atmosphere. The four potential products generated from this process include a liquid product (bio-oil), syngas, energy, and biochar, a form of black carbon. Black carbon is also produced by the incomplete combustion of biomass or fossil fuel. As a byproduct of bio-oil and bio-gas production, biochar may be generated in large quantities if biofuels prove to be economically viable. Biochar has useful properties that may make it a good soil amendment. It can improve the cation exchange capacity of soil; retain nutrients and herbicides/pesticides; reduce emissions of nitrous oxide, a greenhouse gas; and improve moisture retention (Liang et al., 2006; Spokas et al., 2009; Ding et al., 2010; Laird et al., 2010a; Laird et al., 2010b; Si et al., 2011; Case et al., 2012). Chars are suspected to be stable for long periods (Lehmann et al., 2006; Kuzyakov et al., 2009), so biochar may therefore be suitable for carbon sequestration. However, biochar contains carcinogenic polycyclic aromatic hydrocarbons (PAHs). PAH concentrations and profiles are a function of the feed material and the pyrolysis conditions (Brown et al., 2006; Hale et al., 2012; Fabbri et al., 2013). Solid waste regulations may severely limit land application of biochar because of its PAH contents. Standards in the U.S. and several other countries limit the total PAH contents of soil amendments to 6 to 20 mg kg^{-1} (International Biochar Initiative, 2012). Consequently, biochar may be regarded as a hazardous waste or a valuable commodity based in part on its PAH content and the bioavailability of the PAHs.

PAHs are a class of compounds that contain multiple fused benzene ring subunits. Naphthalene, which has two rings, is the simplest of these compounds. Although over 100 PAHs and alkyl-PAHs are known, the United States Environmental Protection Agency (USEPA) has identified 16 of them as priority pollutants (USEPA, 1981). Seven of the 16 PAHs are classified as B2, probable human carcinogens. These compounds are benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene. The remaining nine PAHs are classified as D, not classifiable as to human carcinogenicity. Appendix A gives the structures and pertinent physical and chemical properties of the 16 priority PAHs.

Overall, PAHs are poorly soluble in water. The water solubilities of the priority PAHs range from 30 mg L^{-1} to 0.0005 mg L^{-1} and generally decrease as the number of rings increases. The octanol-water partition coefficients of the priority PAHs range from 1.9×10^3 to 6.9×10^6. These data indicate that PAHs are hydrophobic and would have an affinity for black carbon and organic material associated with soils and sediments. For example, a commercial wood char was found to readily sorb three PAHs (Wang et al., 2006). Clearly, this material has a much higher PAH sorption capacity than its original PAH content.

Background levels of individual PAHs in agricultural soils range from 5 to 900 μg kg^{-1} (ATSDR, 1995). Under the Resource Conservation and Recovery Act (RCRA), wastes such as discarded commercial chemical products, off-specification products, container residues, and spill residues are classified as hazardous wastes when the concentrations of any of the 16 PAHs exceed standards (USEPA, 2012). Therefore, solid waste regulations may severely limit biochar land application if it has a high enough PAH content. The state of Illinois regulates soil PAH concentrations in accordance with the Tiered Approach to Corrective Action Objectives (TACO)

(IEPA, 1997). Site considerations for this procedure depend on chemical properties, carcinogenic class, potential to contaminate groundwater, intended land use, and background chemical concentrations.

The potential uptake of PAHs from biochar by plants, earthworms, or other soil-dwelling organisms is also of concern (Sohi et al., 2010). However, even though biochar contains PAHs, these contaminants may be largely immobile and unavailable to soil organisms. Black carbon is known to strongly sorb PAHs and to limit their solubility in sediment and soil (Accardi-Dey and Gschwend, 2003; Lohmann et al., 2005). As a form of black carbon, biochar sorbs PAHs strongly (Hale et al., 2011; Shen et al., 2012). Therefore, when biochar is applied to soil, any PAHs that are present are likely to be strongly sorbed by the biochar and their dissolved concentrations, the fraction that is immediately bioavailable, are orders of magnitude less than either their total concentrations or their aqueous solubilities (Weissenfels et al., 1992).

Black carbon has been shown to control PAH bioavailability in sediment and soil (Accardi-Dey and Gschwend, 2002; Accardi-Dey and Gschwend, 2003; Lohmann et al., 2004; Lohmann et al., 2005). The addition of activated carbon (another form of black carbon) to sediment reduced the bioaccumulation of native PAHs (already present, not spiked) in a sediment-dwelling worm (Cornelissen et al., 2006). There was less PAH accumulation by earthworms from soil-biochar mixtures spiked with PAHs than from soils without biochar spiked with the same PAHs at the same levels (Beesley et al., 2010; Gomez-Eyles et al., 2011). The likely explanation is that PAHs sorb strongly to all forms of black carbon, including biochar. Therefore, adding biochar to soil would probably make contaminants of concern, such as PAHs, less bioavailable.

Activated carbon addition has been found to be effective for the immobilization of hydrophobic contaminants in sediments and soils (Beckingham and Ghosh, 2011; Oen et al., 2012; Oleszczuk et al., 2012). Biochar is being studied as a lower-cost alternative sorbent for this purpose (Beesley et al., 2011; Ghosh et al., 2011; Denyes et al., 2012; Nguyen and Pignatello, 2013; Ogbonnaya and Semple, 2013). If successful, this application of biochar has the potential to add value to the pyrolysis platform and may increase its economic viability.

Microbial metabolism of PAHs is considered to be the most prevalent of degradation pathways for these compounds in soils (Sims and Overcash, 1983). The rate of degradation is related to soil conditions such as organic content, structure and particle size, presence of other chemical contaminants, and the characteristics of the microbial populations present (Wilson and Jones, 1993). The addition of biochar to soils may sharply reduce the solubility and therefore the bioavailability of PAHs, thereby reducing the rate of PAH degradation.

The strong sorption of PAHs to black carbon is likely due to pi-pi interactions between planar PAH molecules and planar, graphite-like black carbon particles (Gustafsson and Gschwend, 1997; Keiluweit and Kleber, 2009). Pyrolysis conditions (temperature, oxygen content of the pyrolysis atmosphere, reactor design, and cooling conditions) and starting material affect the aromatic content of biochar (Sun and Zhou, 2008; Brewer et al., 2009; Keiluweit et al., 2010). Therefore, different biochars are likely to have different inherent PAH concentrations and sorption properties. Because sorption limits PAH bioavailability, different biochars are likely to limit PAH bioavailabilities to different extents. To make matters more complex, the chemical and physical properties of biochar may change over time (aging) when it is exposed to various environmental conditions (Hale et al., 2011).

The total concentrations of PAHs are poor indicators of their uptake or biodegradation in soil or sediment (Kreitinger et al., 2007). However, the terms "bioavailable" and "bioavailability" seem to have been used rather loosely. To define the terms more precisely, Semple et al. (2004) suggested that the bioavailable fraction of a compound is "… that which is freely available to cross an organism's cellular membrane from the medium the organism inhabits at a given time," while the bioaccessible fraction is "…what is actually bioavailable now plus what is potentially bioavailable." The bioavailable fraction is operationally defined as the freely dissolved concentration (Reichenberg and Mayer, 2006), which can be measured by passive sampling (Muijs and Jonker, 2012). The bioaccessible fraction is operationally defined by so-called mild extraction (Gouliarmou and Mayer, 2012). This fraction seems to be a reliable indicator of the ecological effects of PAHs (Dean and Scott, 2004; Lei et al., 2006).

The compound 2-hydroxypropyl-beta-cyclodextrin (HPCD) is a promising mild extractant for PAHs. The amounts of HPCD-extractable PAHs have been found to be good predictors of PAH biodegradation for both spiked and native PAHs (Kelsey et al., 1996; Reid et al., 2000; Cuypers et al., 2002; Allan et al., 2007; Papadopoulos et al., 2007). Similarly, the amount of PAH uptake by earthworms was found to be correlated to the HPCD-extractable PAH fractions (Kelsey et al., 1996; Khan et al., 2011).

Biochar can be produced from essentially any kind of biomass, but corn stover, the crop residue (leaves and stalks) that remains after harvest, is particularly relevant to Illinois. Because ethanol production accounts for 40% of the national corn harvest (Roberts and Tran, 2013), as the demand for ethanol increases, so shall the demand for corn. Illinois is one of the major producers of corn, and a great deal of acreage of this state is dedicated to this crop. Therefore, biochar created from corn stover could potentially add value to an Illinois crop residue and could provide Illinois farmers with a locally produced biochar soil amendment.

The objectives of the project were to: (1) subject corn stover biochars to artificial aging, (2) determine the PAH contents of the un-aged and aged biochars, (3) characterize the sorption of a probe PAH compound to the un-aged and aged biochars, and (4) determine the bioaccessibility of the probe compound in the un-aged and aged biochars. This characterization can be used to indicate the suitability of the biochar as a soil amendment or as a material that may be useful for soil or sediment remediation.

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METHODOLOGY

Biochar Production

Corn stover was ground to approximately 2 mm with the aid of a Wiley (Swedesboro, NJ) grinder. Slow pyrolysis of the corn stover was achieved with a Thermolyne (Dubuque, IA) 79400 tube furnace. Corn stover was weighed in a metal pyrolysis boat which was covered with aluminum foil. The boat was placed in the tube furnace, the system was sealed, and system was then purged with nitrogen gas at 10 psi and 10 LPM for 30 minutes. Next, an ice-cooled condensation system was attached to the outlet of the tube furnace, the system was allowed to heat up to the target temperature, and the temperature was held at the target value for two hours. The system was then allowed to cool to the ambient temperature overnight under nitrogen. The biochar was then removed from the metal boat and the masses of the solid and liquid products were measured. The biochar was stored at -15^{o}C until needed. Biochar was produced at pyrolysis temperatures of 450°, 550°, and 750°C. These materials are referred to as CS450, CS550, and CS750 for the remainder of the report. Because of the small amounts of material used in the sorption and bioaccessibility experiments (5 – 10 mg), all biochars were ground with a mortar and pestle and sieved (<125 μm).

Artificial Biochar Aging

Artificial aging of biochars was conducted using a subset of the methods of Hale et al. (2011). Char samples were weighed into glass bottles with Teflon®-lined lids and deionized water equivalent to 40% of field capacity was added. The aging treatments were: (1) freezing and thawing on a daily schedule, (2) incubation at 60°C, and (3) incubation at 110°C. All samples were weighed daily, and deionized water was added as needed to bring the samples up to their 40% field capacity weights. The 110° samples dried out completely every day, while the other samples rarely had to have water added. Because a smaller quantity of CS550 than CS450 or CS750 was produced, CS550 was aged at 60° and 110° only, with no freezing and thawing treatment.

Biochar Surface Area and Field Capacity

The surface areas of un-aged and aged biochars (ground and sieved) were determined by nitrogen adsorption using the Brunauer-Emmett-Teller (BET) method. Selected samples were analyzed by the U.S. Department of Agriculture, Agricultural Research Service, National Center for Agricultural Research Utilization, Peoria, IL.

The field capacities of the chars were estimated by saturating overnight with deionized water, pouring into a tared filter in a conical funnel, and weighing the filter plus wet char after it stopped draining.

Determination of Total PAH Contents of Biochar

Char samples were homogenized with the aid of a Millipore (Billerica MA) end-over-end tumbler at a rate of 30 RPM for 1 hour. Total PAH concentrations were determined by pressurized solvent extraction (USEPA, 1998) and gas chromatography-mass spectrometry

(USEPA, 1996). Extractions were performed with a Dionex (Westmont IL) 300 Accelerated Solvent Extractor (ASE) with acetone-hexane (1:1). Briefly, 4 g of corn stover or 2.0-2.5 g of biochar were loaded into 33 mL ASE cells. The extraction system was operated at 100°C and 1500 psi with a static time of 5 minutes, flush volume of 60%, purge time of 100 seconds, and four cycles of extraction per cell. Samples to be extracted were not pre-dried due to the concern of target PAH losses by volatilization.

Fresh biochar samples were extracted within seven days of production. Analytical recoveries were characterized using p-terphenyl-d14 as a surrogate. This substance was spiked into the cells before extraction. All corn stover and fresh biochar samples were extracted in triplicate. Single samples of aged biochar were extracted due to limitations of sample size and processing capacity of the ASE system. Each extraction batch included a reagent blank, a reagent blank spike, and a matrix spike containing the 16 target PAHs.

Extracts were concentrated and solvent exchanged with hexane in Zymark (Charlotte, NC) Turbovap 500 closed-cell concentrators. The units were operated at 40^{o}C and samples were never allowed to concentrate below 1 mL due to concern of target PAH loss. Corn stover extracts were concentrated to 5 mL, filtered through a 0.45 μm PTFE syringe filter, and then diluted to a final volume of 10.0 mL. All biochar extracts were concentrated to a final volume of 1.0 mL with no filtering because there were no visible particulates.

Analysis of the target PAHs was performed with a Varian (Walnut Creek CA) 3800 gas chromatography system coupled to a Saturn 2000 mass spectrometer (GCMS). Separation of the target PAHs was achieved with a Restek (Bellefonte PA) Rtx5-MS capillary column (30 m x 0.25 mm x 0.25 μm film thickness) with a 5 m guard column.

The mass spectrometer was operated in selected ion storage mode (SIS). In SIS mode, only the ions of interest for target compounds are targeted and measured. This mass spectrometry technique enhances sensitivity, reduces sample matrix interferences, and reduces ion space charging. The GCMS operating parameters and retention times and quantification ions for the target PAHs are given in Appendix C.

Calibration standards were prepared from certified reference materials procured from AccuStandard (New Haven, CT). The instrument was calibrated at the beginning of each assay over a range of 5 to 1000 ng mL^{-1}. Any sample containing a target compound above the calibration range was diluted such that the concentration observed was within the calibration range. All calibration curves had r^2 values of 0.99 or greater. Independent calibration verification standards were prepared from certified reference materials procured from AccuStandard (New Haven CT) with different lot numbers than those utilized for calibration standards. Analysis of independent standards was preformed post-calibration, after every 15 sample injections, and post sample analysis. Naphthalene d-8, Acenaphthene d-10, Phenanthrene d-10, Chrysene d-12, and Perylene d-12 were spiked in all standards and post-extract samples as an internal standard. For each analysis batch, one sample was run in duplicate and one sample was spiked.

Selection of Probe PAH and Analytical Method for Sorption and Bioaccessibility Experiments

Because of time and resource limitations, we selected one PAH for the sorption and bioaccessibility experiments. Pyrene was selected because the freely dissolved concentration of pyrene was found to be well correlated with dissolved concentrations of other PAHs in sediments (Arp et al., 2011). Synchronous fluorescence spectrometry, the analytical method used in all sorption and bioaccessibility experiments in this project, offers some advantages over chromatographic methods. The detection limits are very low (sub-$\mu g\ L^{-1}$) (Andrade-Eiroa et al., 1998). Aqueous supernatants and HPCD and methanol extracts can be analyzed directly, i.e., without sample clean-up or chromatographic separation (Andrade-Eiroa et al., 1998; Hua et al., 2007).

Sorption Experiments

Preliminary sorption experiments with fresh (un-aged) CS450 were modeled on those of Accardi-Dey and Gschwend (2002). Biochar was suspended in 1 mM $CaCl_2$ in centrifuge tubes with Teflon®-lined caps and mixed to suspend the char. Pyrene was added and the tubes were placed in an end-over-end mixer where they were allowed to equilibrate for seven days. The samples were centrifuged and pyrene was determined in the supernatant. The sorbed pyrene concentration was calculated from the mass balance (the amount added minus the amount remaining in solution). These experiments were designed so that the pyrene concentration at equilibrium was less than 100 $\mu g\ L^{-1}$, which is below the aqueous solubility of pyrene (Mackay et al., 1992), and that the sorbed fraction was 20 to 80% of added pyrene. The sorption parameters of sedimentary black carbon (Accardi-Dey and Gschwend, 2002) were used in calculations to design the initial sorption experiments. Sorption kinetics experiments (Appendix D) showed that equilibrium was reached within two days. However, seven days were allowed for equilibration in the preliminary sorption equilibrium experiments to insure that the systems reached equilibrium.

There were three types of control samples. Blanks, which had 1 mM $CaCl_2$ but no char or pyrene, were used to check for contamination. Samples with char but no added pyrene were used to check for any pyrene desorption from the char. Pyrene was never detected in any blanks or char-only controls. Samples with no char but added pyrene were used to check for any losses during equilibration. The pyrene recovered from these samples satisfied the same criterion as analytical spike recovery (80 to 120%), so it was assumed that any pyrene losses (e.g., volatilization or sorption to container walls) were minimal. All treatments, including sorption samples and controls, were run in triplicate.

In the preliminary experiments, the dissolved pyrene concentration could clearly be no lower than the detection limit of ~1 $\mu g\ L^{-1}$. However, dissolved PAH concentrations in soils and sediments are typically in the ng L^{-1} range (Hawthorne et al., 2005). To reach this "environmentally relevant" concentration range, the sorption experiments (after the preliminary ones) used a second solid phase to compete with biochar for added pyrene. For the experiments with CS450, the competing substance was polyoxomethylene (POM). Silicone was used in the experiments with CS550 and CS750.

Jonker and Koelmans (2001) found that PAHs, including pyrene, partition to POM. That is, the sorbed amount is proportional to the aqueous concentration (Equation 1),

$$Q_{POM} = K_p C_{Dissol} \quad (1)$$

where Q_{POM} is the concentration of pyrene partitioned to POM (μg kg^{-1}), C_{Dissol} is the freely dissolved pyrene concentration (μg L^{-1}), and K_p (L kg^{-1}) is the partition coefficient. POM coupons were cut from sheets 0.005 in. (127 μm) thick from C. S. Hyde (Chicago, IL). The coupons were of a convenient size (4.0 x 1.5 cm) and mass (~0.1g) for use with the centrifuge tubes and vials used in the experiments. The coupons were cleaned by soaking twice overnight in methanol, soaking twice overnight in deionized water, and air drying.

The results of a preliminary pyrene/POM sorption kinetics experiment (Appendix D) were in qualitative agreement with those of Jonker and Koelmans (2001), who found that equilibrium was attained after 10 days. Jonker and Koelmans (2001) allowed 28 days for equilibration in their experiments with environmental samples, including soot, a form of black carbon. It was decided to allow at least 30 days equilibration in the present work. The pyrene-POM sorption isotherm was linear and the partition coefficient (K, the slope of the line) was 22,450 L kg^{-1} (Log K_{POM} 4.35). Jonker and Koelmans (2001) and Cornellissen et al. (2008) determined pyrene Log K_{POM} values of 3.76 and 4.04, respectively. The reason for the differences may have been the different sources of POM.

Because of the long equilibration time with POM, it would have been impossible to finish all of the planned experiments before the end of the project. Cornelissen et al. (2008) found that passive samplers constructed from silicone tubing attained equilibrium with dissolved PAHs within 28 days. Haftka et al. (2008) found that pyrene partitioning to silicone-coated solid-phase microextraction (SPME) fibers approached equilibrium within three days. We conducted sorption kinetics experiments with pyrene and silicone tubing and found that these systems also reached equilibrium within three days (Appendix D), despite the fact that the tubing was thicker (~1 mm) than the SPME coating used by Haftka et al. (2008) (0.0125 mm). As for pyrene-POM partitioning, the isotherm was linear. The distribution coefficient (the slope of the isotherm) was 14,100 L kg^{-1} (Log K_p 4.15). This result agrees fairly well with the silicone-pyrene Log K_p value determined by Yates et al. (2007) of 4.49. The difference may have been due to different materials. The sorption experiments with CS550 and CS750 used silicone rubber as the competing phase. One experiment with CS550 and POM was performed for comparison.

In a sorption experiment with a competing solid phase, the biochar and a coupon of POM or silicone (0.1 g) were added to bottles with Teflon®-lined caps, mixed to suspend the char, and pyrene was added. The bottles were placed in an end-over-end mixer and mixed for at least 30 days for POM or 5 days for silicone. After equilibration, the coupons were removed from the bottles, wiped with a moist tissue to remove adhering char, and placed in methanol in glass vials with Teflon®-lined caps to extract the pyrene. PAHs may undergo photodegradation (Gauthier et al., 1986).Therefore, the vials were covered with aluminum foil to protect the contents from light. At least three days without mixing were allowed for extraction from POM or 24 hours for silicone. The concentration of pyrene in the methanol extracts (C_{MeOH}) was determined by synchronous fluorescence, and the mass of pyrene partitioned to the POM (M_{Part}) was calculated by multiplying by the volume of methanol (V_{MeOH}) (Equation 2).

$$M_{Part} = C_{MeOH} V_{MeOH} \quad (2)$$

The mass balance on pyrene is given by Equation 3,

$$M_{Tot} = M_{Dissol} + M_{Part} + M_{Sorb} \quad (3)$$

where the subscript *Tot* indicates total pyrene and *Dissol*, *Part*, and *Sorb* indicate masses of pyrene that are freely dissolved, partitioned to POM, and sorbed to char, respectively. The mass of dissolved pyrene was much less than that of partitioned and sorbed pyrene. As a result, Equation 3 simplifies to Equation 4.

$$M_{Tot} \approx M_{Part} + M_{Sorb} \quad (4)$$

The concentration of pyrene sorbed to the char (Q_{Char}) is calculated by rearranging Equation 4, substituting Equation 2, and dividing by the mass of char (M_{Char}) (Equation 5).

$$Q_{Char} = \frac{M_{Tot} - C_{MeOH} V_{MeOH}}{M_{Char}} \quad (5)$$

The concentration of pyrene partitioned to POM (Q_{POM}) is calculated by dividing M_{Part} (Equation 2) by the mass of POM (M_{POM}) (Equation 6).

$$Q_{Part} = \frac{C_{MeOH} V_{MeOH}}{M_{POM}} \quad (6)$$

The dissolved pyrene concentration is calculated by combining Equations 1 and 6 and rearranging (Equation 7).

$$C_{Dissol} = \frac{C_{MeOH} V_{MeOH}}{M_{POM} K_{POM}} \quad (7)$$

Sorption experiments were designed so that the equilibrium dissolved pyrene concentration was less than 100 μg L^{-1} and that 20 to 80% of the added pyrene was partitioned to the POM or silicone. (The aqueous solubility of pyrene at room temperature is ~130 μg L^{-1} (Mackay et al., 1992)). For the highest total concentrations, pyrene was added in stages and allowed to equilibrate for 24 hours between additions so that the aqueous concentration would always be below 100 μg L^{-1}.

The controls for the competing-solid-phase experiments were similar to those with biochar only. Blanks, which had 0.1 M $CaCl_2$ and a coupon but no char or pyrene, were used to check for contamination. Control samples with char and coupon but no added pyrene were used to check for any pyrene desorption from the char. Pyrene was never detected in any blanks or char-only controls. Samples with no char but with a coupon and added pyrene were used to check for any losses. The pyrene recovered from these samples satisfied the same criterion as analytical spike recovery (80 to 120%), which indicated that pyrene losses to bottle walls or Teflon® cap liners were minimal. All sorption samples and controls were run in triplicate.

Pyrene was added as a concentrated (100 mg L^{-1}) methanol solution. The resulting methanol volume fraction was less than or equal to 0.3% (v/v). The aqueous solubility of pyrene is increased by just 4% by 0.3% methanol compared to pure water (Munz and Roberts, 1986; Kwon and Kwon, 2012). Therefore, its effect on pyrene sorption to biochar was assumed to be negligible.

For all sorption experiments, a Freundlich isotherm (Equation 8) was fit to the data,

$$Q_{Char} = K_f C_{Dissol}^{\ t} \tag{8}$$

where C_{Dissol} was either measured directly in the preliminary experiments or calculated from Equation 7, Q_{Char} is the concentration of pyrene sorbed to biochar (μg kg^{-1}) (Equation 5), and K_f and t are adjustable parameters. Fitting was done with Origin (OriginLab, Northampton, MA), using the Levenberg-Marquardt algorithm (Bevington, 1969).

Designing the sorption experiments involved setting the char and competing sorbent (POM or silicone) weights and pyrene addition so that 20 – 80% of the added pyrene would be sorbed to the competing sorbent. That is, so that there would be a measureable but not overwhelming change in the pyrene concentration. The calculations were based on the mass balance on pyrene (Equation 9),

$$C_{Tot} = C_{Dissol} + C_{Part} + C_{Sorb} \tag{9}$$

where C_{Tot}, C_{Dissol}, C_{Part}, and C_{Sorb} are the total, dissolved, partitioned, and sorbed concentrations (μg L^{-1}), respectively. Substituting Equations 1 and 8 into Equation 9 gives an equation in which the only variable is C_{Dissol}.

$$C_{Tot} = C_{Dissol} + K_{Part} M_{POM} C_{Dissol} + K_f M_{Char} C_{Dissol}^{\ t} \tag{10}$$

In Equation 10, the symbols have the same meaning as in earlier equations. Equation 10 was solved numerically using the Solver utility in Microsoft Excel®.

To design the first sorption experiment with un-aged CS450, the sorption parameters for sedimentary black carbon (Accardi-Dey and Gschwend, 2002) were used. The sorption experiments with aged CS450 and un-aged CS550 were designed using the parameters from un-aged CS450. The experiments with aged CS550 were designed using the sorption parameters for un-aged CS550. Similarly, the experiment with un-aged CS750 was designed using the sorption parameters for un-aged CS550 and the experiments with aged CS750 were designed using the sorption parameters for un-aged CS750.

Bioaccessibility Experiments

A sample of HPCD, Cavasol® W7 HP, was obtained from Wacker Chemical Corporation (Adrian, MI). The sample was eventually used up and another batch of HPCD had to be purchased to finish the project. Wacker was contacted to purchase more HPCD, but a representative indicated there would be a delay of several weeks in delivering the HPCD. Therefore, the next batch of HPCD was obtained from Sigma-Aldrich. The nominal molecular

weight of HPCD from both suppliers was the same, so it was assumed they had the same chemical properties.

The HPCD extraction experiments were modeled on the work of Reid et al. (2000). Although the soil to solution ratio in that study was 1 g to 10 mL, the black carbon content of the soil was most likely 5-10% of the organic carbon concentration or ~1% (Meredith et al., 2012). Therefore, it was decided to use 10 mg of biochar in all extraction experiments. Preliminary experiments with CS450 showed that there was not enough extractable pyrene to detect by fluorescence. Therefore, pyrene was added. First, biochar was suspended in 30 mL deionized water in centrifuge tubes with Teflon®-lined caps. Pyrene was added and the tubes were placed in an end-over-end mixer and allowed to equilibrate for at least three days. The samples with the highest added pyrene concentrations were centrifuged and the supernatants analyzed for pyrene. There never was any detectable pyrene in the supernatants, i.e., it was essentially completely sorbed. The supernatants were returned to their tubes. (Less than 0.3 mL liquid remaining in the cuvet, so the liquid volume in the centrifuge tube changed by less than 1%.) Solid HPCD sufficient to give a concentration of 0.06 M was added and the tubes mixed with a vortex mixer. The tubes were returned to the end-over-end mixer and the extraction proceeded overnight. After 20 hours of extraction, the tubes were centrifuged (1320 x G) and the pyrene concentrations in the supernatants were determined by synchronous fluorescence.

The controls in the HPCD extractions were similar to those of the sorption experiments. Blanks had HPCD only. There were also control samples with HPCD and biochar but no added pyrene. Pyrene was never detected in any of these samples. All treatments, including controls and extraction samples, were run in triplicate.

Determination of Dissolved Pyrene Concentration

For all sorption and bioaccessibility experiments, dissolved pyrene was determined by synchronous fluorescence spectrometry (Andrade-Eiroa et al., 2010a; Andrade-Eiroa et al., 2010b) using a Gilford (Nova Biotech, El Cajon, CA) Fluoro IV spectrofluorometer. The excitation and emission slit widths were 5 nm. The difference between excitation and emission wavelengths was 38 nm. Pyrene gave a peak-shaped signal with a maximum at excitation and emission wavelengths of 336 and 374 nm, respectively.

Calibration standards were prepared in the same matrix as the samples (electrolyte solution, HPCD solution, or methanol). The instrument sensitivity was adjusted to either that of the highest calibration standard or a quinine solution (Velapoldi and Mielenz, 1980). The method detection limit (MDL) as estimated by the method of Glaser et al. (1981) for a calibration range of 0 – 100 $\mu g\ L^{-1}$ was 0.5 – 1.0 $\mu g\ L^{-1}$. The MDL for lower calibration ranges was probably lower than 0.5 $\mu g\ L^{-1}$ but was not determined. For every batch of samples (up to 24), at least two samples were run in duplicate to check measurement precision. At least one sample per batch was spiked with pyrene to check for any matrix effects. There was one method blank per batch. Acceptance criteria were relative average deviation of 20% or less for the duplicates and 80 to 120% for the spike recoveries. These criteria were satisfied for all batches.

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RESULTS

Biochar Production

The solid yields decreased and the gas yields increased as the pyrolysis temperature increased (Figure 1). Pyrolysis at 450°C yielded 32% solid (biochar), 42% liquid (bio-oil), and 26% non-condensable gas. Pyrolysis at 550°C yielded 29% solid (biochar), 39% liquid (bio-oil), and 33% non-condensable gas. Pyrolysis at 750°C yielded 26% solid (biochar), 40% liquid (bio-oil), and 37% non-condensable gas.

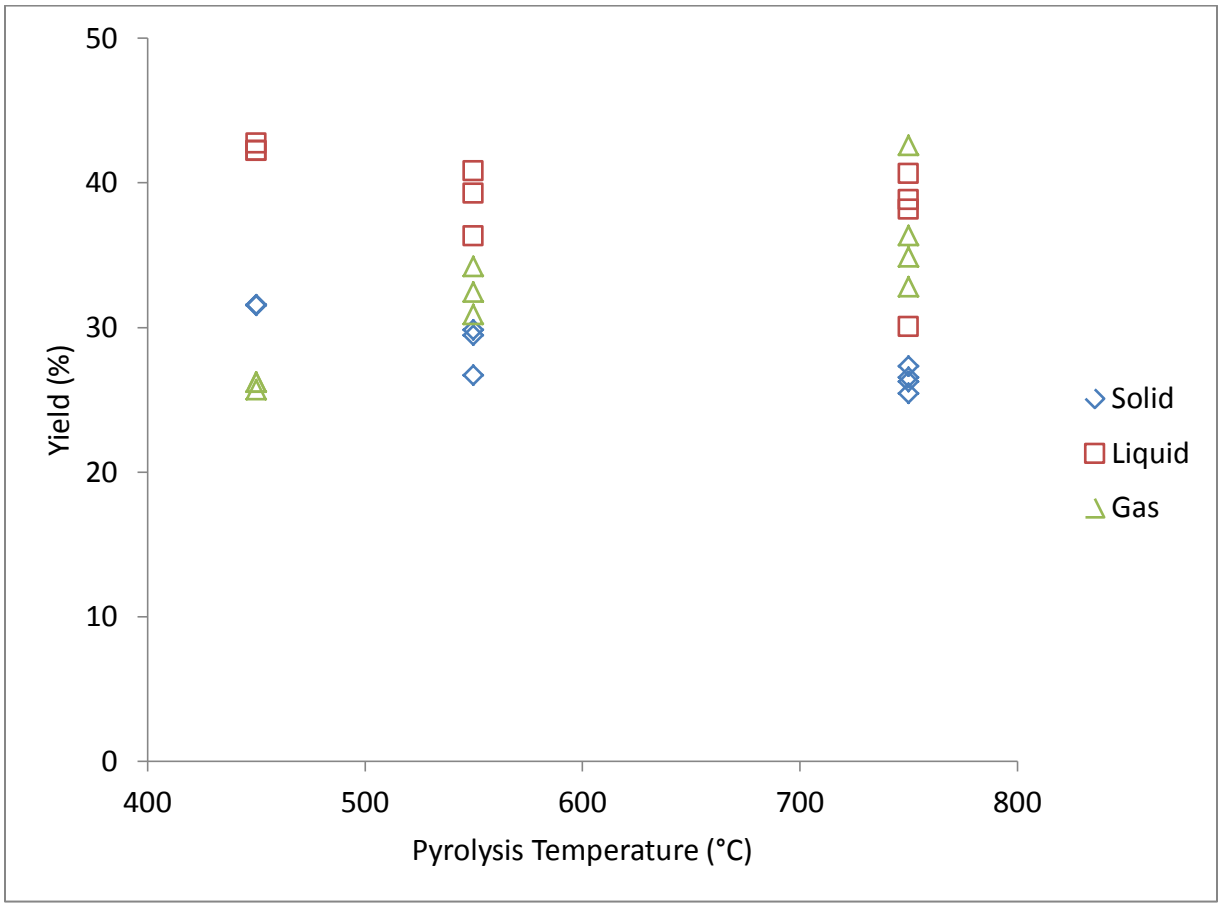

Figure 1. Yields of solid (biochar), liquid, and non-condensable gas from corn stover pyrolysis.

Biochar Surface Area and Field Capacity

The N_2-BET surface areas of the un-aged CS450 and CS550 chars were 11 m^2 g^{-1}. The field capacities of all three materials were approximately 8 g H_2O per g biochar. This result is fairly close to the results of Kinney et al. (2012), who measured field capacities of 10 ± 2 g g^{-1} for corn stover char produced at 400 to 600°C.

Total PAH Contents of Biochars

The total contents of the target PAHs in the corn stover feedstock were all very low, with a median value of 0.028 mg kg^{-1} (Table 1). Anthracene was the only compound detected in all three replicates. However, the anthracene results were near the contamination levels observed in the reagent blank (Table 2), and caution should be used when interpreting the data for this sample type. Four other PAHs were detected in only one prep batch. Eleven of the PAHs were undetectable in all preparation batches. It is unclear if the presence of trace PAHs are due to the actual contamination of plant materials in the field or if contamination occurred during sample transport, handling, and preparation.

Table 1. Total contents of USEPA-16 PAHs in corn stover.

Compound	Prep 1	Prep 2	Prep 3	Median
	Surrogate Recovery			
Terphenyl-d14 (Surrogate)	86%	96%	92%	92%
	Content (mg kg^{-1})			
Naphthalene	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthylene	< 0.01	< 0.01	< 0.01	< 0.01
Acenaphthene	< 0.01	< 0.01	< 0.01	< 0.01
Fluorene	< 0.01	< 0.01	< 0.01	< 0.01
Phenanthrene	< 0.01	< 0.01	0.013	< 0.01
Anthracene	0.013	0.013	0.014	0.013
Fluoranthene	0.027	< 0.01	< 0.01	< 0.01
Pyrene	0.013	< 0.01	< 0.01	< 0.01
Benz[a]anthracene	0.012	< 0.01	< 0.01	< 0.01
Chrysene	< 0.05	< 0.05	< 0.05	< 0.05
Benzo[b]fluroanthene	< 0.01	< 0.01	< 0.01	< 0.01
Benzo[k]fluoranthene	< 0.01	< 0.01	< 0.01	< 0.01
Benzo[a]pyrene	< 0.01	< 0.01	< 0.01	< 0.01
Indeno[1,2,3,c,d]perylene	< 0.05	< 0.05	< 0.05	< 0.05
Dibenzo[a,h]anthracene	< 0.05	< 0.05	< 0.05	< 0.05
Benzo[g,h,i]perylene	< 0.05	< 0.05	< 0.05	< 0.05
Total Target PAH	0.064	0.013	0.028	0.028

The reagent blank associated with the corn stover feedstock extraction indicated low-level contamination of anthracene and fluoranthene (Table 2). All surrogate recoveries associated with the corn stover feedstock samples were within the acceptance criteria (80% to 120%). Benzo[b]fluroanthene recovered high for the reagent blank spike, the matrix spike, and the analytical sample spike (128%, 144%, and 133% respectively). However, this issue is of little concern because no benzo[b]fluroanthene was found in any of the corn stover feedstock samples. All other recoveries were within the acceptance criteria. Anthracene was the only target PAH detected in all three corn stover extracts, and the percent relative standard deviation (%RSD) of the measurements was 6%.

Table 2. QA Results for total contents of USEPA-16 PAHs in corn stover.

Compound	Reagent Blank	Reagent Blank Spike Recovery	Matrix Spike Recovery	Analytical Spike Recoveries
Terphenyl-d14 (Surrogate)		83%	81%	79%
Naphthalene	< 0.01	53%	87%	104%
Acenaphthylene	< 0.01	73%	60%	118%
Acenaphthene	< 0.01	77%	79%	105%
Fluorene	< 0.01	93%	95%	113%
Phenanthrene	< 0.01	86%	76%	89%
Anthracene	0.017	81%	84%	98%
Fluoranthene	0.014	96%	91%	115%
Pyrene	< 0.01	79%	81%	90%
Benz[a]anthracene	< 0.01	120%	111%	128%
Chrysene	< 0.05	117%	105%	115%
Benzo[b]fluroanthene	< 0.01	128%	144%	133%
Benzo[k]fluoranthene	< 0.01	120%	100%	91%
Benzo[a]pyrene	< 0.01	120%	116%	111%
Indeno[1,2,3,c,d]perylene	< 0.05	92%	115%	114%
Dibenzo[a,h]anthracene	< 0.05	98%	97%	117%
Benzo[g,h,i]perylene	< 0.05	98%	113%	117%
Average Recovery		95%	96%	108%

The median total PAH value for un-aged CS450 biochar was 1.4 mg kg^{-1} (Table 3). The contents of 13 of the 16 USEPA PAHs were above the MDL in this char. Clearly, the PAHs were produced by pyrolysis and not carried over from the feed material. Naphthalene, acenaphthene, benzo[b]fluroanthene, and benzo[g,h,i]perylene in CS450 were at concentrations near those observed in reagent blanks (Table 4). All other PAHs observed in the samples were at concentrations well above those in the blank. Dibenzo[a,h]anthracene was undetectable in all three prep batches and acenaphthylene and benzo[k]fluoranthene were undetectable in two of the three batches. The most abundant PAHs were the three- and four-ring compounds phenanthrene, pyrene, benz[a]anthracene, anthracene, and fluorene. Agreement among the replicates was generally good for all PAHs. The median total PAH content was 1.42 mg kg^{-1}.

Table 3. Total contents of USEPA-16 PAHs in corn stover biochar produced by pyrolysis at 450°C.

Compound	Prep 1	Prep 2	Prep 3	Median
	Surrogate Recovery			
Terphenyl-d14 (Surrogate)	98%	91%	90%	91%
	Content (mg kg^{-1})			
Naphthalene	0.041	0.051	0.043	0.043
Acenaphthylene	< 0.002	0.013	< 0.002	< 0.002
Acenaphthene	0.009	0.014	0.012	0.012
Fluorene	0.122	0.128	0.148	0.128
Phenanthrene	0.256	0.259	0.288	0.259
Anthracene	0.138	0.127	0.163	0.138
Fluoranthene	0.106	0.111	0.129	0.111
Pyrene	0.212	0.188	0.195	0.195
Benz[a]anthracene	0.165	0.159	0.138	0.159
Chrysene	0.149	0.142	0.157	0.149
Benzo[b]fluroanthene	0.023	0.025	0.021	0.023
Benzo[k]fluoranthene	< 0.002	< 0.002	0.002	< 0.002
Benzo[a]pyrene	0.080	0.079	0.084	0.080
Indeno[1,2,3,c,d]perylene	0.091	0.084	0.038	0.084
Dibenzo[a,h]anthracene	< 0.008	< 0.008	< 0.008	< 0.008
Benzo[g,h,i]perylene	0.033	0.041	0.028	0.033
Total Target PAH	1.424	1.421	1.446	1.424

About 50% of the target PAHs were present at low levels in the reagent blank associated with the CS450 extraction (Table 4). All surrogate recoveries associated with the CS450 extracts were within the acceptance criteria. All reagent blank spike, matrix spike, and analytical sample spike recoveries were within the acceptance criteria. All %RSD for triplicate extractions for concentrations greater than ten times the method detection limits (MDL) were within the acceptance criteria. In addition, the relative percent difference (%RPD) of the analytical sample duplicate was within the acceptance criteria for all concentrations greater than ten times the MDL.

Table 4. QA data for total contents of USEPA-16 PAHs in corn stover biochar produced by pyrolysis at 450°C.

	Reagent Blank	Reagent Blank Spike Recovery	Matrix Spike Recovery	Analytical Spike Recoveries	Analytical Sample Duplicate	
					Difference	Relative Difference[a]
	mg kg^{-1}				mg kg^{-1}	
Terphenyl-d14 (Surrogate)	110%	98%	102%	91%	12%	12%
Naphthalene	0.016	98%	102%	91%	0.043	5%
Acenaphthylene	< 0.002	53%	55%	108%	0.006	
Acenaphthene	0.008	65%	78%	101%	0.011	22%
Fluorene	< 0.002	78%	84%	101%	0.135	10%
Phenanthrene	< 0.002	99%	91%	86%	0.273	7%
Anthracene	< 0.002	82%	97%	86%	0.181	27%
Fluoranthene	< 0.002	90%	85%	95%	0.117	10%
Pyrene	< 0.002	85%	103%	88%	0.216	2%
Benz[a]anthracene	0.004	110%	94%	86%	0.175	6%
Chrysene	0.003	103%	100%	91%	0.177	18%
Benzo[b]fluroanthene	0.010	93%	113%	91%	0.026	13%
Benzo[k]fluoranthene	< 0.002	104%	84%	93%	< 0.002	
Benzo[a]pyrene	0.012	77%	93%	94%	0.054	37%
Indeno[1,2,3,c,d]perylene	< 0.008	103%	94%	77%	0.091	1%
Dibenzo[a,h]anthracene	0.013	114%	72%	92%	< 0.008	
Benzo[g,h,i]perylene	0.012	82%	83%	103%		12%
Average		90%	88%	93%		13%

Note: [a]Relative difference not calculated if one of replicates was a nondetect.

The total target PAH content of CS550 was only 0.18 mg kg^{-1}, which is significantly lower than that of CS450 (Table 5). Because low-level contamination was observed with the CS450 extraction, new ASE cell cleaning and storage procedures were developed and implemented. The reagent blank associated with the CS550 extraction indicated only low-level contamination of phenanthrene (Table 6). Phenanthrene results for this compound in CS550 are near the level observed in the reagent blank. Clearly, caution should be used when interpreting the data for this compound in this sample type.

Table 5. Total contents of USEPA-16 PAHs in corn stover biochar produced by pyrolysis at 550°C.

Compound	Prep 1	Prep 2	Prep 3	Median
	Surrogate Recovery			
Terphenyl-d14 (Surrogate)	102%	81%	84%	84%
	Content (mg kg^{-1})			
Naphthalene	0.024	0.022	0.020	0.022
Acenaphthylene	< 0.002	< 0.002	< 0.002	< 0.002
Acenaphthene	0.012	0.008	0.008	0.008
Fluorene	0.004	0.003	0.005	0.004
Phenanthrene	0.013	0.009	0.010	0.010
Anthracene	0.007	0.007	0.007	0.007
Fluoranthene	0.007	0.006	0.006	0.006
Pyrene	0.009	0.005	0.006	0.006
Benz[a]anthracene	0.014	0.010	0.009	0.010
Chrysene	0.023	0.021	0.021	0.021
Benzo[b]fluroanthene	0.026	0.011	0.006	0.011
Benzo[k]fluoranthene	0.030	0.013	0.009	0.013
Benzo[a]pyrene	0.024	0.013	0.012	0.013
Indeno[1,2,3,c,d]perylene	0.028	0.024	0.030	0.028
Dibenzo[a,h]anthracene	< 0.005	< 0.005	< 0.005	< 0.005
Benzo[g,h,i]perylene	0.037	0.030	0.010	0.030
Total Target PAH	0.258	0.182	0.158	0.182

Table 6. QA data for total contents of USEPA-16 PAHs in corn stover biochar produced by pyrolysis at 550°C.

			Prep 5	Prep 3	Prep 1	
	Reagent Blank	Reagent Blank Spike Recovery	Matrix Spike Recovery	Analytical Spike Recoveries	Analytical Sample Duplicate	
	mg kg^{-1}				mg kg^{-1}	Relative Difference [a]
Terphenyl-d14 (Surrogate)		89%	107%	98%	0.966	5%
Naphthalene	< 0.002	53%	54%	91%	0.020	21%
Acenaphthylene	< 0.002	52%	95%	114%	< 0.002	
Acenaphthene	< 0.002	99%	94%	103%	0.009	20%
Fluorene	< 0.002	96%	94%	115%	0.004	9%
Phenanthrene	0.0046	93%	107%	96%	0.011	14%
Anthracene	< 0.002	73%	83%	94%	0.008	9%
Fluoranthene	< 0.002	84%	101%	101%	0.006	19%
Pyrene	< 0.002	83%	74%	98%	0.009	9%
Benz[a]anthracene	< 0.005	103%	90%	100%	0.012	19%
Chrysene	< 0.01	79%	76%	117%	0.022	5%
Benzo[b]fluroanthene	< 0.005	97%	96%	105%	0.025	6%
Benzo[k]fluoranthene	< 0.005	86%	82%	97%	0.022	31%
Benzo[a]pyrene	< 0.005	82%	72%	104%	0.026	7%
Indeno[1,2,3,c,d]perylene	< 0.005	84%	72%	111%	0.025	10%
Dibenzo[a,h]anthracene	< 0.005	87%	89%	112%	< 0.005	
Benzo[g,h,i]perylene	< 0.005	86%	72%	89%	0.038	4%
Average		84%	86%	103%		12%

Note: [a]Relative difference not calculated if one of the replicates was a nondetect.

All surrogate recoveries associated with the CS550 extracts were within the acceptance range. Acenaphthylene in the reagent blank spike recovered below the target recovery (52%); however, it recovered well in the sample matrix spike (95%). The low recovery should not be a great concern since it appears to be an isolated event in the reagent blank spike, and acenaphthylene was not observed in any samples above the MDL. With the exception of acenaphthylene in the reagent blank spike, all reagent blank spike, matrix spike, and analytical sample spike recoveries were within the acceptance criteria. The %RSDs for triplicate extracts of CS550 were much more variable than those observed for CS450; however, concentrations for all target PAHs were near the MDL and were less than 10 MDL. The RPDs for the analytical duplicate sample were within the acceptance criteria with the exception of benzo(k)fluoranthene. However, this

compound concentration was also less than ten times the MDL, so the actual concentration is uncertain.

The CS750 char had the lowest measured total PAH content of all the un-aged chars (Table 7). However, the low surrogate recoveries indicate that the PAH contents were unreliable. The reagent blank associated with the CS750 extraction indicated low-level contamination of fluoranthene, phenanthrene, fluorene, and pyrene (Table 8) and the contents of these analytes in CS750 were near the contamination levels observed in the reagent blank. Therefore, caution should be used when interpreting the data for these compounds in this sample type. The surrogate recoveries observed for the reagent blank and the reagent blank spike were within the acceptable range, which indicates the low surrogate recoveries were not due to volatility or errors in spiking. In addition, recoveries for the post-extract analytical sample spike indicate that the low recoveries are not due to ion suppression or other matrix interferences. The matrix spike sample for CS750 also produced poor PAH recoveries for target compounds; however, it was observed that the three most volatile PAHs recovered much better than the other PAHs. Naphthalene, acenaphthylene, and acenaphthene in the matrix spike recovered 23%, 17%, and 36%, respectively. All analytical spike recoveries for CS750 were within the acceptable range. The %RSDs for triplicate extracts and %RPDs for the analytical sample duplicate were all within the acceptable criteria for target PAHs above the MDL.

Table 7. Total contents of USEPA-16 PAHs in corn stover biochar produced by pyrolysis at 750°C.

Compound	Prep 1	Prep 2	Prep 3	Median
	Surrogate Recovery			
Terphenyl-d14 (Surrogate)	3%	2%	3%	3%
	Content (mg kg^{-1})			
Naphthalene	0.0037	0.0039	0.0036	0.0037
Acenaphthylene	< 0.002	0.0048	0.0050	0.0049
Acenaphthene	< 0.002	0.0047	0.0047	0.0047
Fluorene	< 0.002	0.0034	0.0039	0.0037
Phenanthrene	0.0055	0.0050	0.0053	0.0053
Anthracene	0.0067	< 0.002	0.0071	0.0069
Fluoranthene	0.0045	0.0045	0.0048	0.0045
Pyrene	0.0034	0.0034	0.0035	0.0034
Benz[a]anthracene	< 0.004	< 0.004	< 0.004	< 0.004
Chrysene	< 0.009	< 0.009	< 0.009	< 0.009
Benzo[b]fluroanthene	< 0.004	0.0044	0.0045	0.0044
Benzo[k]fluoranthene	< 0.004	< 0.004	< 0.004	< 0.004
Benzo[a]pyrene	< 0.004	< 0.004	< 0.004	< 0.004
Indeno[1,2,3,c,d]perylene	< 0.009	< 0.009	< 0.009	< 0.009
Dibenzo[a,h]anthracene	< 0.009	< 0.009	< 0.005	< 0.005

Benzo[g,h,i]perylene	< 0.009	< 0.009	< 0.009	< 0.009
Total Target PAH	0.0239	0.0342	0.0422	0.0342

Table 8. QA data for total contents of USEPA-16 PAHs in corn stover biochar produced by pyrolysis at 750°C.

Compound	Reagent Blank	Reagent Blank Spike	Matrix Spike	Analytical Spikes	Analytical Sample Duplicate	
	mg/kg				Difference mg/kg	Relative Difference[a]
			Prep 4	Prep 3	Prep 1	
	Surrogate Recoveries					
Terphenyl-d14 (Surrogate)	86%	108%	3%	101%		3%
	Samples					
Naphthalene	< 0.002	89%	23%	87%	0.0041	11%
Acenaphthylene	< 0.002	102%	17%	91%	< 0.002	
Acenaphthene	< 0.002	102%	36%	95%	< 0.002	
Fluorene	0%	109%	8%	95%	0.0036	
Phenanthrene	1%	108%	0%	84%	0.0056	2%
Anthracene	< 0.002	108%	1%	97%	< 0.002	
Fluoranthene	0%	116%	0%	105%	0.0046	2%
Pyrene	0%	107%	0%	101%	0.0035	2%
Benz[a]anthracene	< 0.004	105%	4%	114%	< 0.004	
Chrysene	< 0.009	114%	2%	115%	< 0.009	
Benzo[b]fluroanthene	< 0.004	99%	1%	104%	< 0.004	
Benzo[k]fluoranthene	< 0.004	104%	1%	111%	< 0.004	
Benzo[a]pyrene	< 0.004	118%	3%	111%	< 0.004	
Indeno[1,2,3,c,d]perylene	< 0.009	110%	0%	93%	< 0.009	
Dibenzo[a,h]anthracene	< 0.009	101%	0%	118%	< 0.009	
Benzo[g,h,i]perylene	< 0.009	93%	5%	96%	< 0.009	
Average Recovery		105%	6%	101%		4%

Note: [a]Relative difference not calculated if one of the replicates was a nondetect.

Figure 2 shows the spike and surrogate recoveries for the un-aged chars. The only low recoveries were for CS750. Figure 3 shows the target PAH profiles for all three un-aged chars. For all but the high molecular weight PAHs, the contents in CS450 were generally much higher than in the other two higher-temperature biochars.

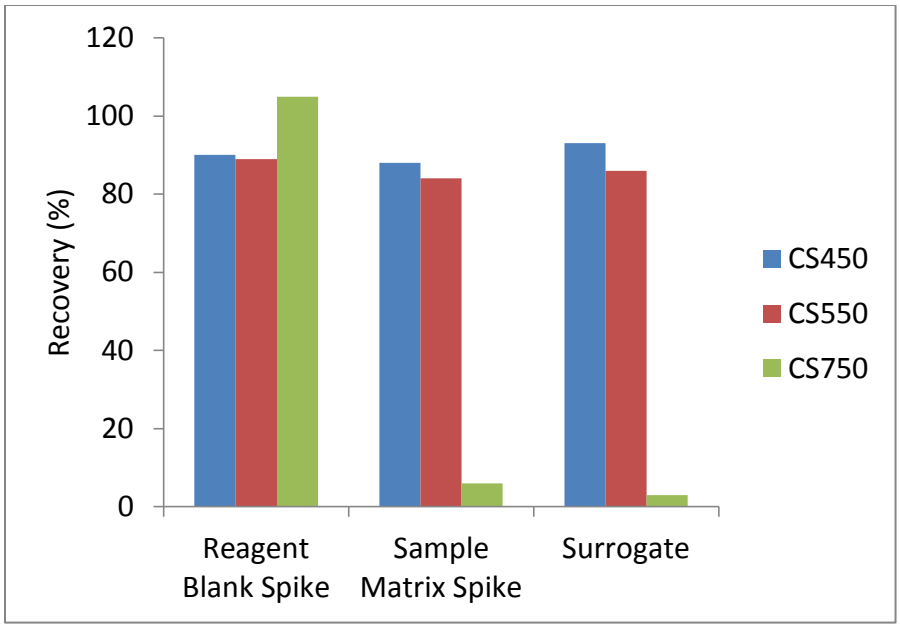

Figure 2. Spike and surrogate recoveries for PAH extraction from un-aged chars.

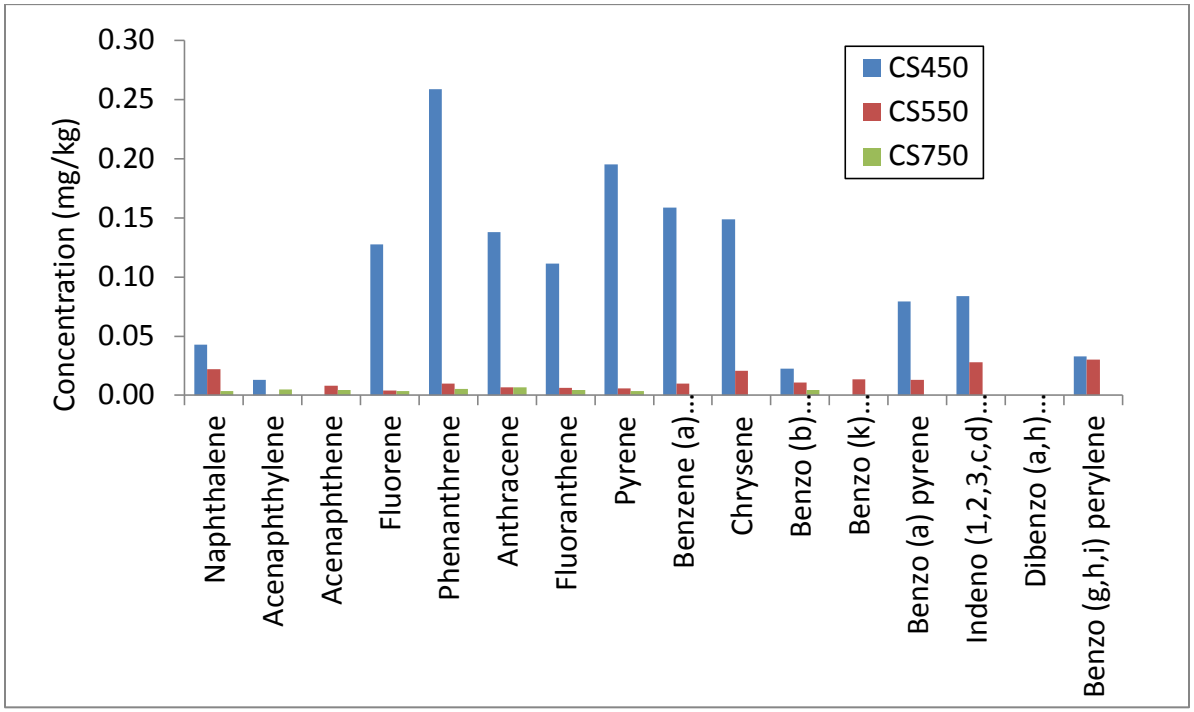

Figure 3. PAH profiles for un-aged biochars.

Table 9 shows the total target PAH contents of the artificially aged chars and Figure 4 compares total PAH contents in un-aged and aged chars. Total target PAHs for CS450 aged at different temperatures decreased as the aging temperature increased. Aging of CS550 had no apparent effect on total target PAH concentrations. Total target PAHs in CS750 aged at different temperatures remained about the same at -15^{o}C, drastically increased at 60^{o}C, and then decreased to levels comparable to the fresh sample at 110^{o}C.

The reagent blank associated with the aged corn stover biochar extraction samples indicated only low-level contamination of benz(a)anthracene (Table 10). Benz(a)anthracene levels for this compound in the aged biochar samples were near the contamination level observed in the reagent blank, and caution should be used when interpreting the data for this compound in this sample type.

Table 9. Total contents of USEPA-16 PAHs in artificially aged corn stover biochar.

Pyrolysis Temperature	450°C	750°C	450°C	550°C	750°C	450°C	550°C	750°C
Aging Treatment	Freeze-Thaw	Freeze-Thaw	60°C	60°C	60°C	110°C	110°C	110°C
	Surrogate Recovery							
Terphenyl-d14 (Surrogate)	74%	28%	78%	84%	70%	110%	85%	94%
	Content (mg kg^{-1})							
Naphthalene	0.022	0.011	0.021	0.054	0.013	0.019	0.053	< 0.005
Acenaphthylene	< 0.005	< 0.005	< 0.005	0.006	0.007	0.009	< 0.005	< 0.005
Acenaphthene	<0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005
Fluorene	0.019	< 0.005	0.019	0.007	0.006	< 0.005	< 0.005	< 0.005
Phenanthrene	0.083	0.009	0.067	0.052	0.025	0.046	0.055	0.006
Anthracene	0.028	< 0.005	0.019	0.013	0.006	0.006	0.013	< 0.005
Fluoranthene	0.046	< 0.005	0.030	0.027	0.017	0.017	0.024	< 0.005
Pyrene	0.101	0.006	0.079	0.029	0.033	0.036	0.034	0.009
Benz[a]anthracene	0.033	0.010	0.018	0.016	0.014	0.007	0.008	0.006
Chrysene	0.064	0.011	< 0.005	0.057	0.036	0.050	0.030	0.014
Benzo[b]fluroanthene	0.006	< 0.005	0.005	0.008	0.008	< 0.005	< 0.005	< 0.005
Benzo[k]fluoranthene	0.006	< 0.005	< 0.005	< 0.02	0.014	< 0.005	< 0.005	< 0.005
Benzo[a]pyrene	0.012	< 0.005	0.008	< 0.02	0.011	< 0.005	< 0.005	< 0.005
Indeno[1,2,3,c,d]perylene	0.048	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Dibenzo[a,h]anthracene	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Benzo[g,h,i]perylene	0.030	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Total Target PAH	0.500	0.047	0.267	0.269	0.189	0.191	0.216	0.035

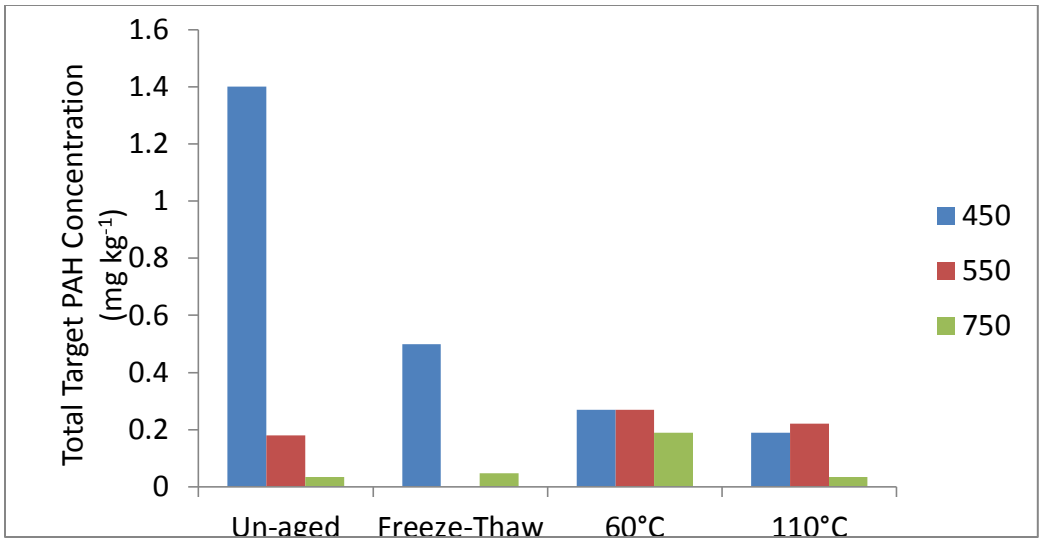

Figure 4. Total target PAH contents of un-aged and aged biochars.

Table 10. Quality control parameters for total PAH determinations of artificially aged biochars.

	Reagent Blank	Reagent Blank Spike	Analytical Spikes	Analytical Sample Duplicate	
	mg kg^{-1}			mg kg^{-1}	Relative Difference[a]
Terphenyl-d14 (Surrogate)		104%	118%		2%
Naphthalene	< 0.005	76%	96%	0.025	10%
Acenaphthylene	< 0.005	91%	84%	< 0.005	
Acenaphthene	< 0.005	85%	77%	< 0.005	
Fluorene	< 0.005	92%	82%	0.015	24%
Phenanthrene	< 0.005	95%	91%	0.089	7%
Anthracene	< 0.005	75%	78%	0.030	5%
Fluoranthene	< 0.005	98%	88%	0.049	7%
Pyrene	< 0.005	100%	107%	0.105	4%
Benz[a]anthracene	0.010	116%	83%	0.026	2%
Chrysene	< 0.005	105%	105%	0.052	26%
Benzo[b]fluroanthene	< 0.005	116%	76%	< 0.005	20%
Benzo[k]fluoranthene	< 0.005	112%	94%	< 0.005	
Benzo[a]pyrene	< 0.005	105%	80%	0.009	
Indeno[1,2,3,c,d]perylene	< 0.02	74%	89%	0.059	32%
Dibenzo[a,h]anthracene	< 0.02	102%	113%	< 0.02	20%
Benzo[g,h,i]perylene	< 0.02	98%	100%	0.033	
Average		97%	90%		13%

Note: [a]Relative difference not calculated if one of replicates was a nondetect.

Surrogate recoveries for aged CS750 chars were higher than for un-aged CS750 char (Figure 5). Surrogate recoveries for CS450 and CS750, aged at 60°C, were 78% and 70%, respectively. All other surrogate recoveries associated with this extraction batch were within the acceptance criteria. No sample matrix spike was prepared with this extraction batch due to lack of sample mass needed for preparation. Anthracene recovery in the reagent spike was slightly low (75%); however, all other target PAHs in this sample were recovered within acceptable ranges.

Acenaphthene, anthracene, and benzo[b]flouranthene recovered slightly low in the analytical spike sample, with recoveries of 77%, 78%, and 76%, respectively. For samples with PAH concentrations greater than ten times the MDL, the RPDs for duplicate samples were within the acceptable range.

The surrogate recovery for CS750 aged by freezing and thawing was low (28%) but much greater than those obtained for un-aged biochar produced at the same temperature. Surrogate recoveries for the CS750 aged at 60°C and 110°C increased as the aging temperature increased. Surrogate recoveries for CS450 aged by freezing and thawing and at 60°C were slightly lower than those observed for un-aged material prepared at the same temperature; however, it is uncertain if this effect is real or if it is an artifact of inconsistent spiking and uncertainty in GCMS measurements. Surrogate recoveries for CS550 did not change due to aging at different temperatures, but no sample was available for aging by freezing and thawing. Although surrogate recoveries increased with the aging temperature of CS750, the PAH results may still be questionable due to potential losses from volatilization of target compounds during storage at elevated temperatures.

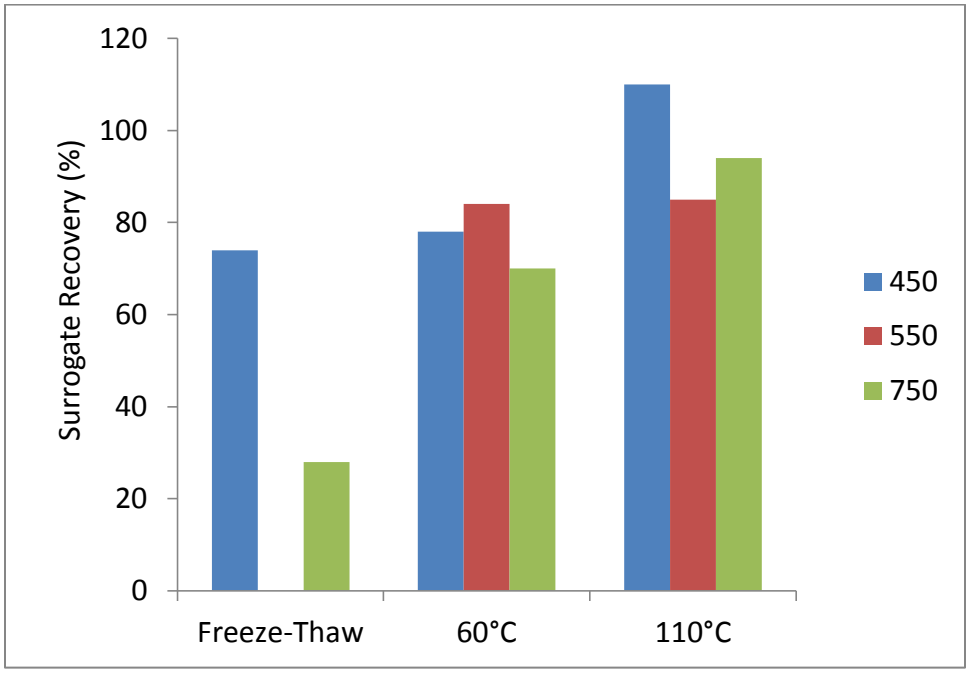

Figure 5. Surrogate recoveries for artificially aged biochars.

The individual PAH compounds generally followed the pattern of total PAH contents in CS450 chars. The concentrations decreased from un-aged to freeze-thaw to 60°C to 110°C (Figure 6). In contrast, the aged CS550 char had higher concentrations of two- to four-ring PAHs than un-aged CS550 (Figure 7). However, the five-ring PAHs were only detected in un-aged CS550. For CS750 (Figure 8), many of the three- and four-ring PAHs were highest in the 60°C-aged char. Some five-ring compounds were undetectable for all treatments.

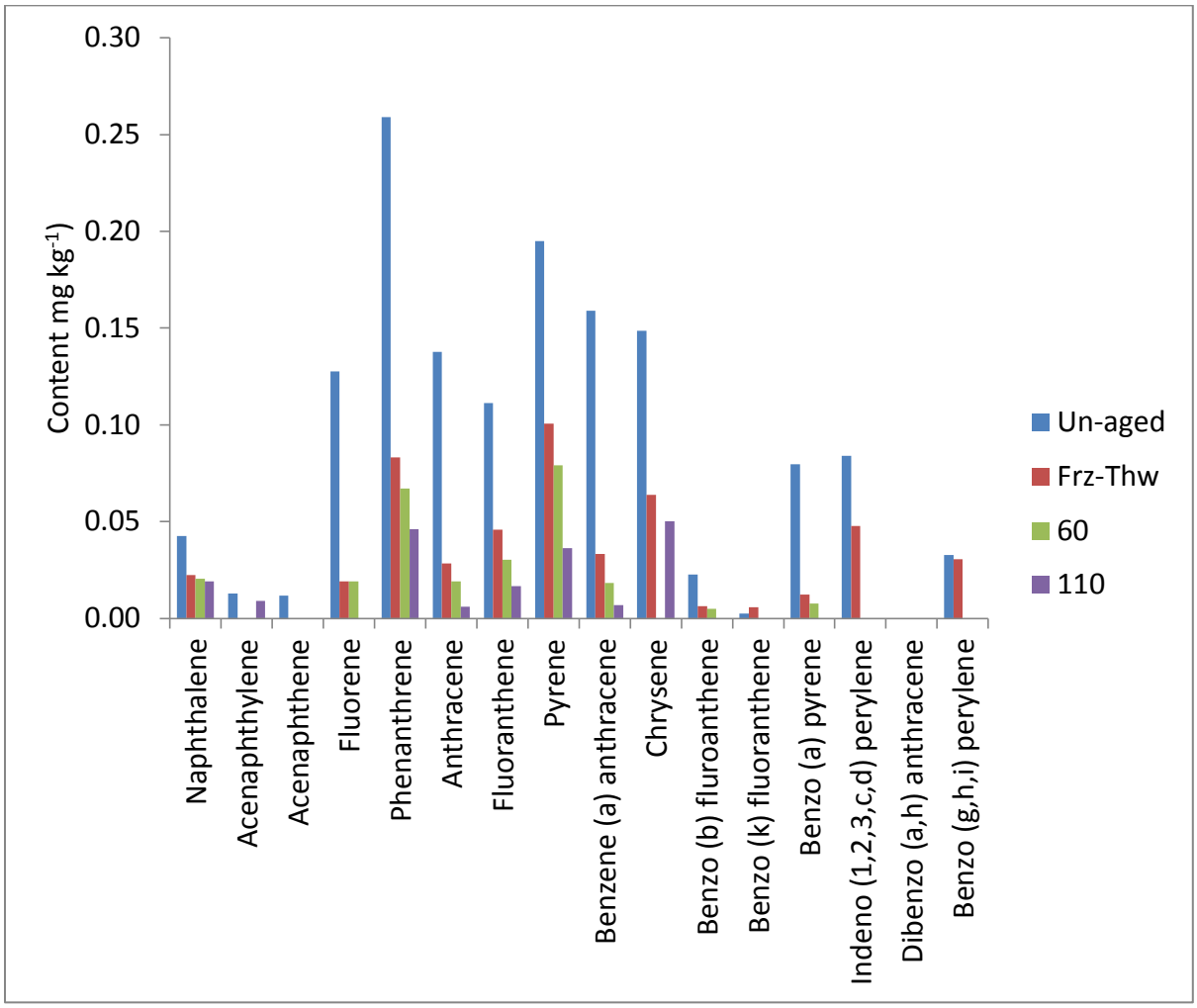

Figure 6. PAH profiles for un-aged and artificially aged CS450 biochar. Nondetects are shown as zero.

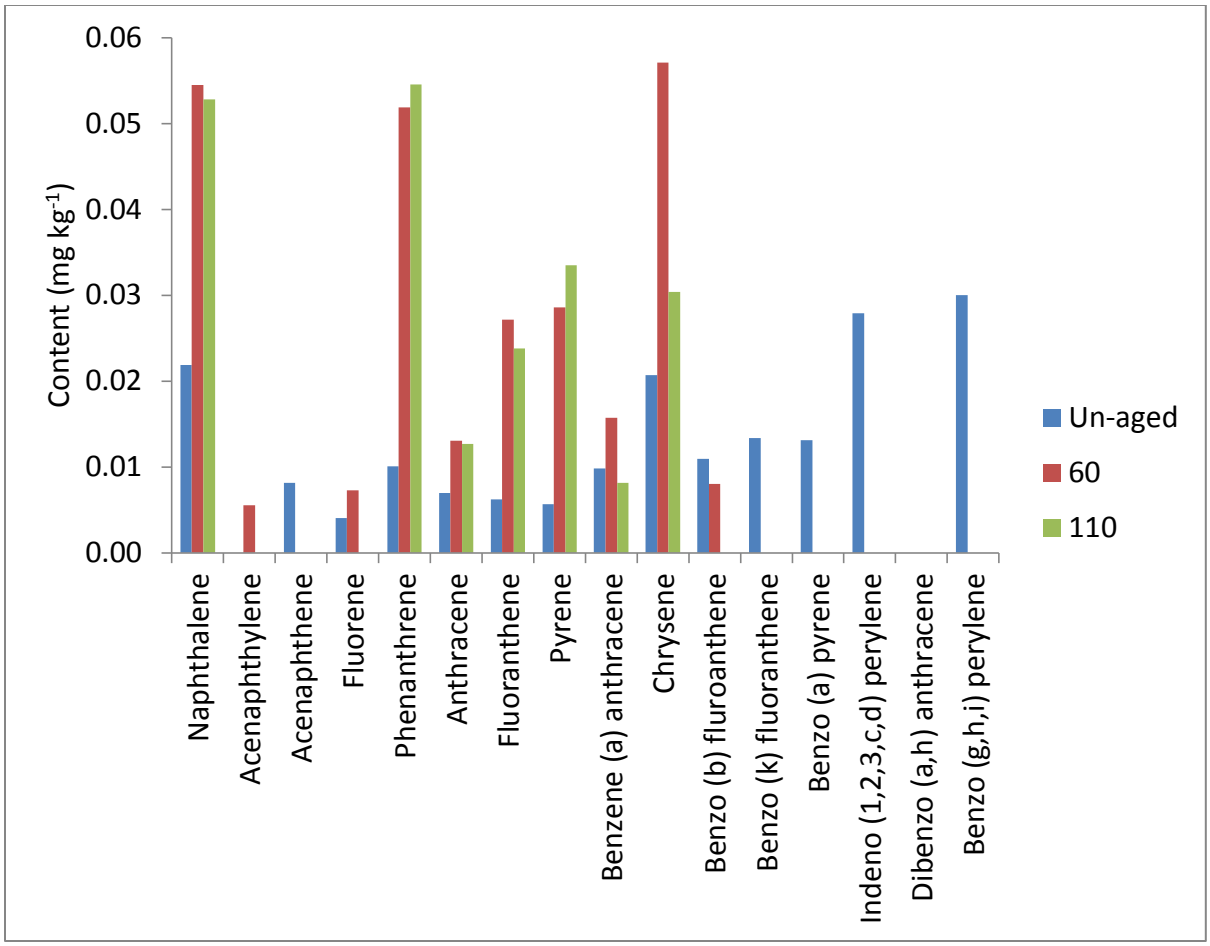

Figure 7. PAH profiles for un-aged and artificially aged CS550 biochar. Nondetects are shown as zero.

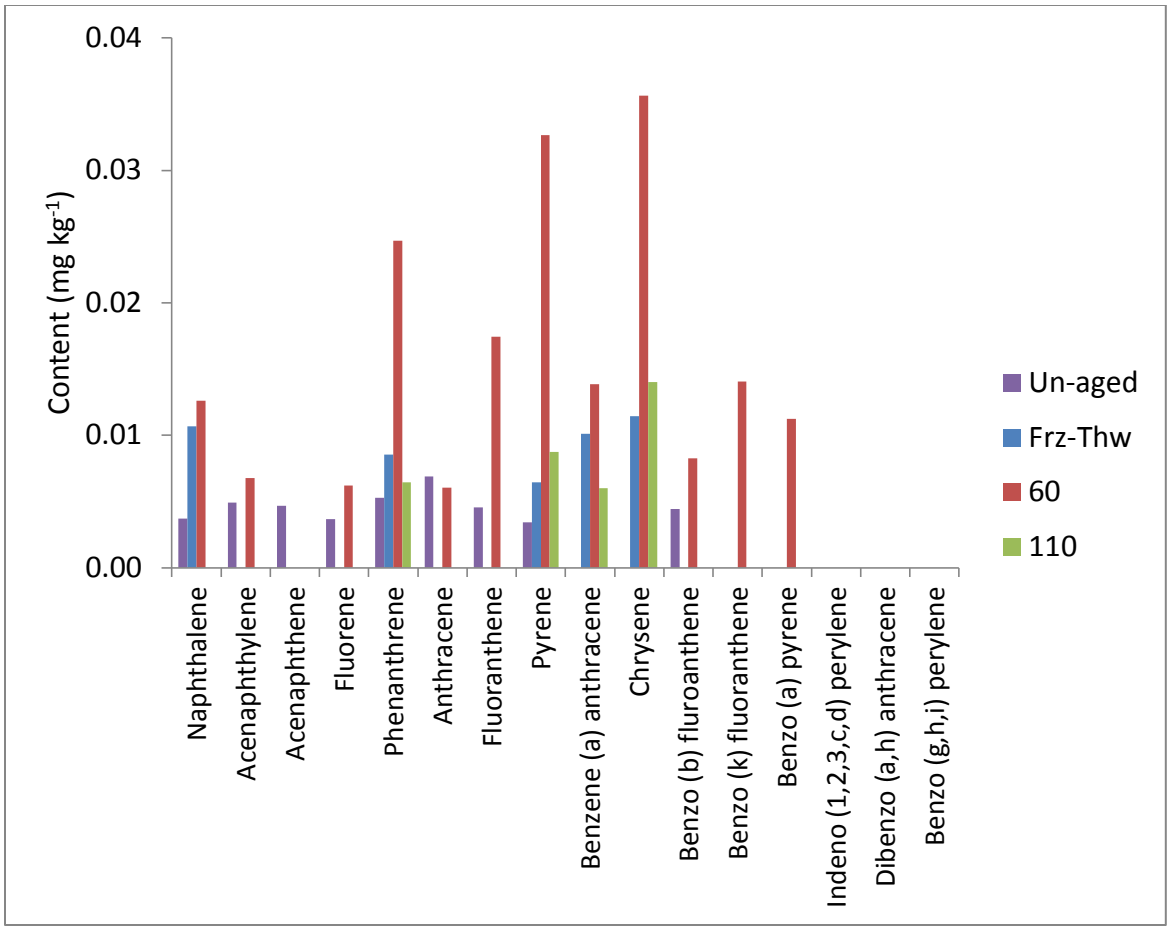

Figure 8. PAH profiles for un-aged and artificially aged CS750 biochar. Nondetects are shown as zero.

Sorption of Pyrene to Biochar

Pyrene sorption to biochar was nonlinearly related to the dissolved pyrene concentration (Figure 9). The curve is a Freundlich isotherm fit to the data (Equation 8). Because of the wide range of dissolved pyrene concentrations, it is convenient to plot sorption data on a log-log plot (Figure 10). The residuals (differences between the Freundlich model fit and the data) for the lowest dissolved pyrene concentrations may appear large because of the logarithmic scale. However, examination of Figure 9 shows that the residuals are actually comparable for all data points.

Figure 11 compares the sorption data for the three un-aged chars. The degree of sorption is similar for CS450 and CS550 for dissolved pyrene concentrations above 0.1 μg L^{-1} and diverges for lower concentrations. Pyrene sorption is greater for CS750 than for the other two chars at all dissolved pyrene concentrations.

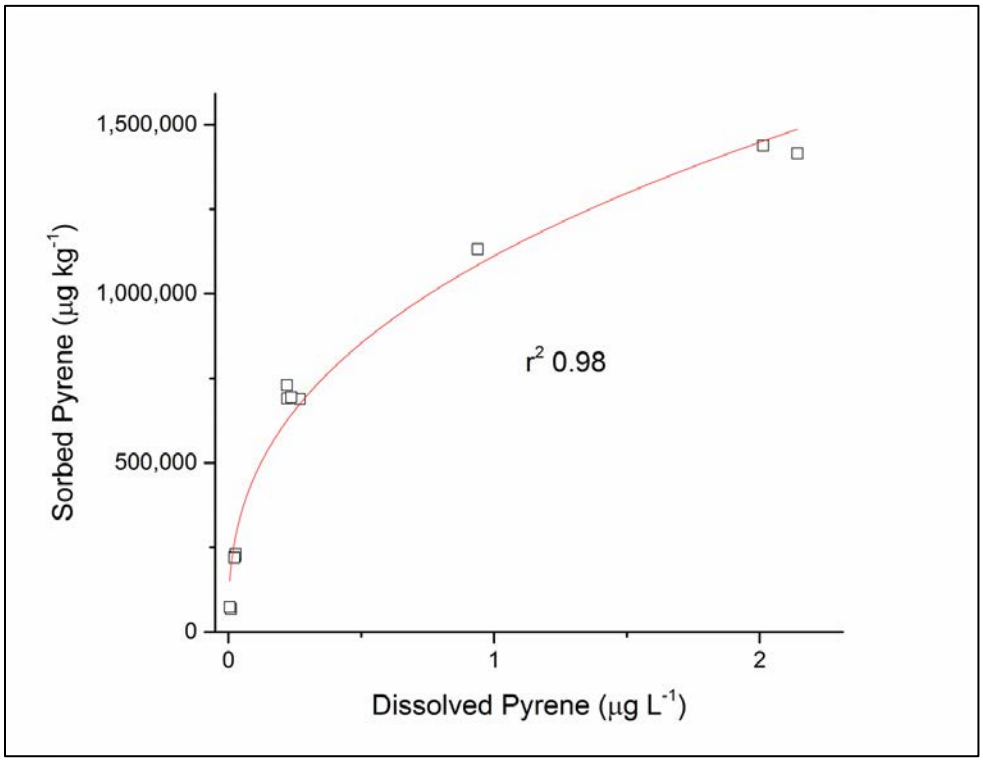

Figure 9. Pyrene sorption isotherm, un-aged 550° char, plotted on linear x- and y-axes.

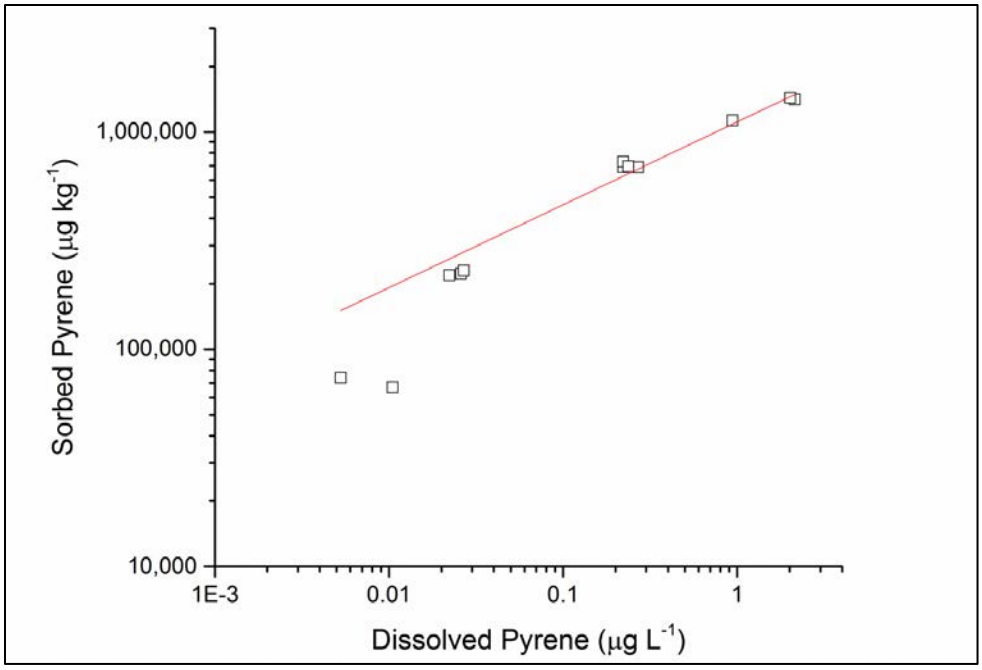

Figure 10. Pyrene sorption isotherm, un-aged 550° char, plotted on logarithmic x- and y-axes.

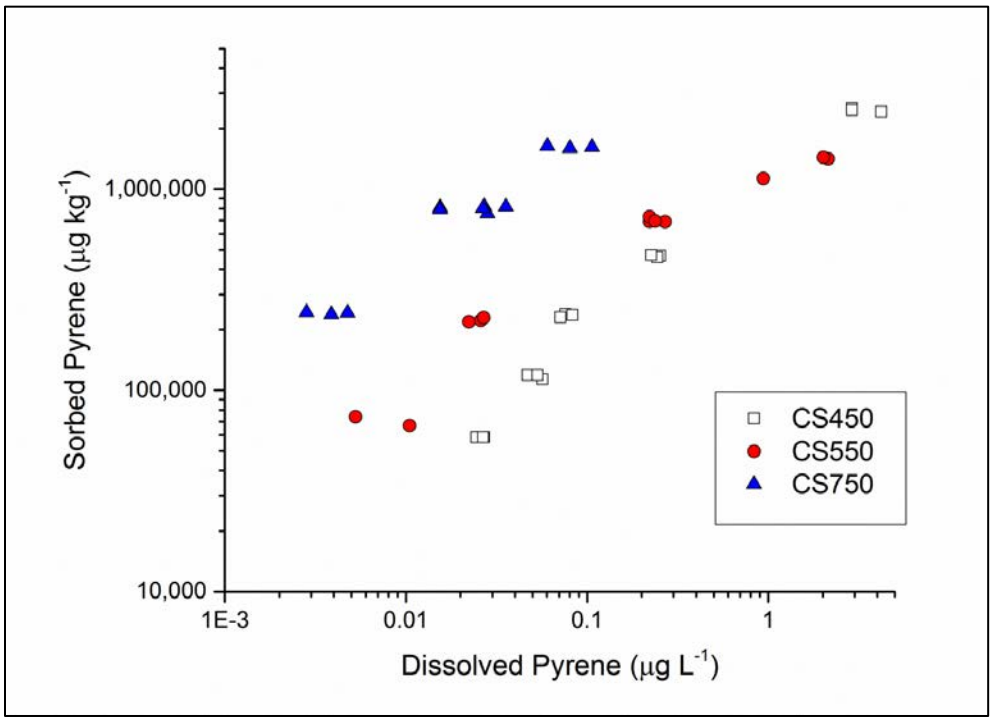

Figure 11. Pyrene sorption isotherms for un-aged biochars.

The effects of artificial aging on pyrene sorption were different for each biochar. For CS450 (Figure 12), there was little difference between the un-aged, freeze-thaw, and 60°C chars. Sorption to CS450 char aged at 110°C was weaker than to the other three chars by roughly a factor of two for 0.1 – 10 μg L^{-1} dissolved pyrene. For CS550 (Figure 13), sorption to the aged chars was stronger than to the fresh char by up to a factor of three. For un-aged CS550, the points for the isotherm measured with the silicone and POM sorbents agreed well at low and high dissolved pyrene concentrations but differed by up to a factor of two at intermediate concentrations. For CS750 (Figure 14), sorption to fresh and aged chars was most similar at low dissolved pyrene concentrations and diverged at higher concentrations. Sorption to freeze-thaw char was somewhat stronger than to un-aged char, while sorption to the 60°C- and 110°C-treated chars was somewhat weaker. The Freundlich equation parameters for all sorption experiments are given in Table 11. The Freundlich constants (K) are generally greatest for the CS750 chars, while the exponents (t) are largest (the isotherms are the least nonlinear) for the CS450 chars.

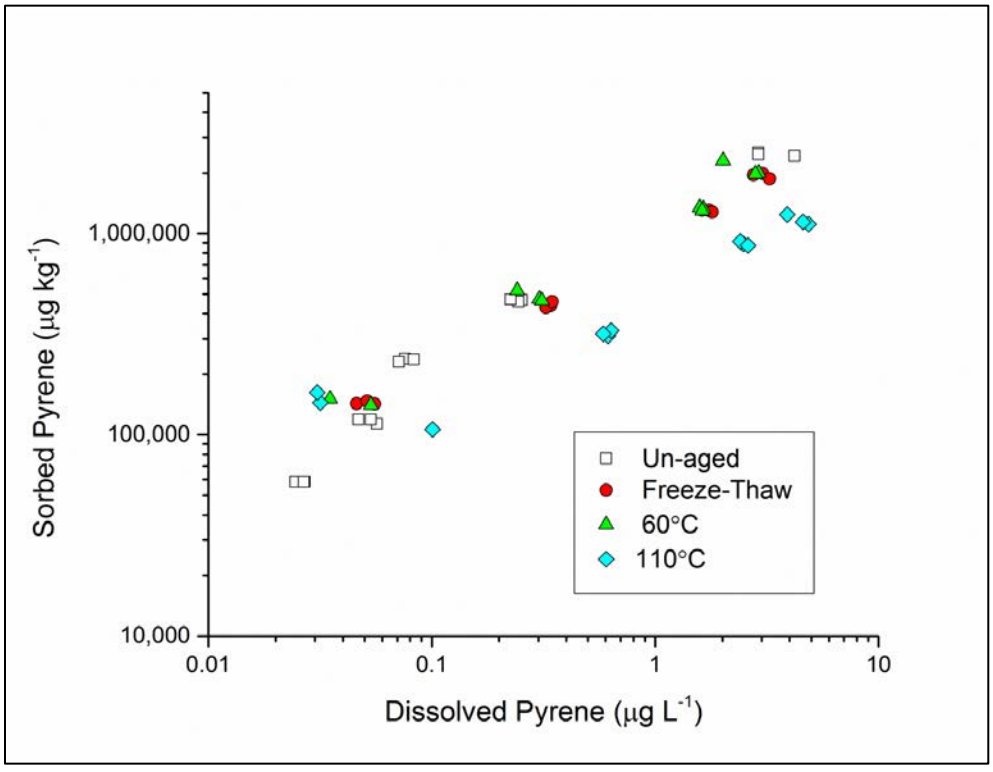

Figure 12. Pyrene sorption to un-aged and artificially aged CS450 biochar.

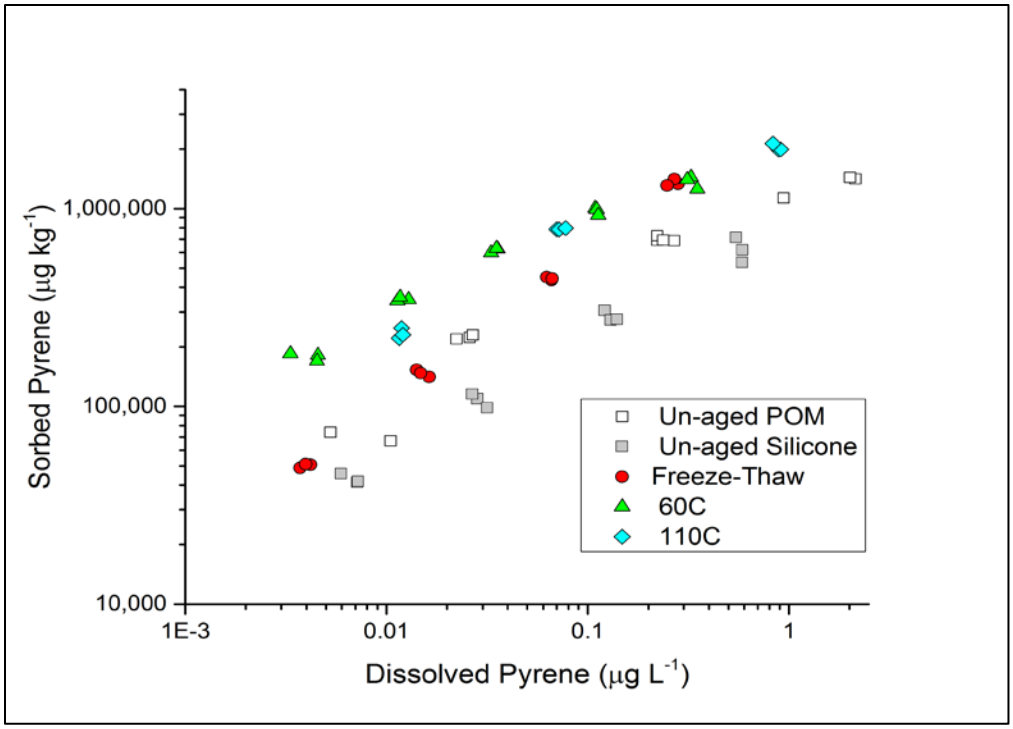

Figure 13. Pyrene sorption to un-aged and artificially aged CS550 biochar.

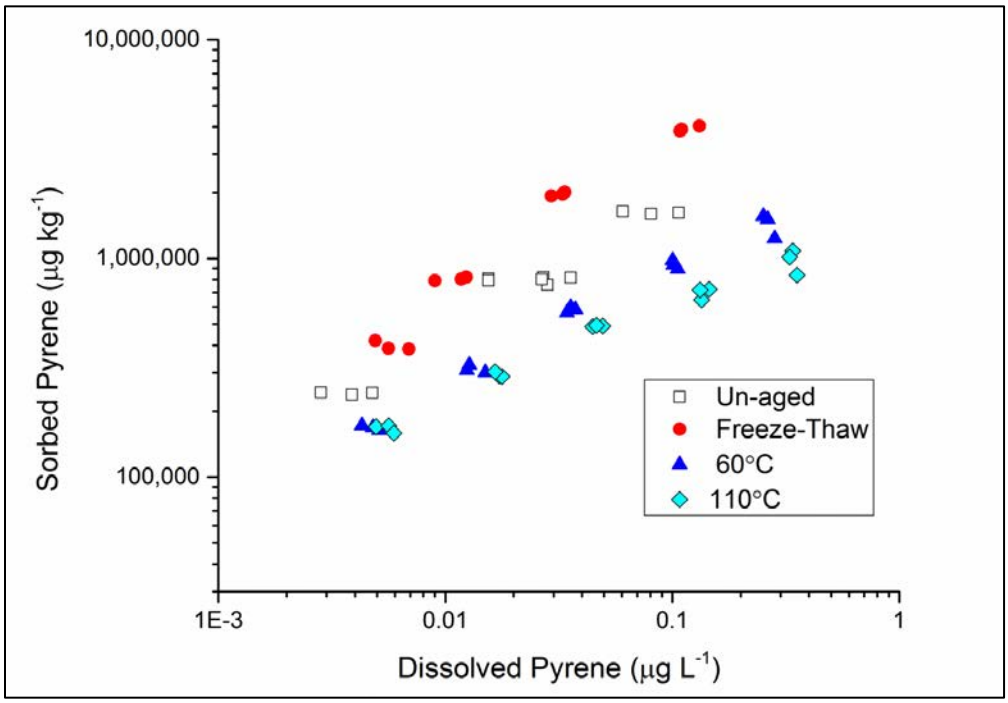

Figure 14. Pyrene sorption to un-aged and artificially aged CS750 biochar.

Table 11. Freundlich isotherm parameters for sorption of pyrene to biochar.

Pyrolysis Temperature	Aging Treatment	K (L kg^{-1})^t		t		r^2
		Value*	Standard Error*	Value	Standard Error	
450	Un-aged	1.17	0.072	0.61	0.05	0.975
450	Freeze-Thaw	0.92	0.033	0.66	0.04	0.990
450	60C	1.08	0.099	0.63	0.11	0.921
450	110C	0.51	0.038	0.56	0.06	0.963
550	Un-aged	1.11	0.030	0.38	0.02	0.979
550	Freeze-Thaw	3.79	0.150	0.78	0.02	0.997
550	60C	2.17	0.10	0.39	0.02	0.973
550	110C	2.17	0.066	0.42	0.03	0.985
750	Un-aged	5.79	1.11	0.53	0.06	0.913
750	Freeze-Thaw	15.3	1.38	0.63	0.03	0.983
750	60C	2.73	0.189	0.48	0.03	0.965
750	110C	1.50	0.081	0.39	0.03	0.962

Note: *Multiply numbers in these columns by 10^6. For example, the K value for un-aged CS450 is $1.17x10^6$ with a standard error of $7.2x10^4$.

Bioaccessibility Experiments

Figure 15 shows the HPCD-extractable pyrene contents of pyrene-spiked CS450 char (un-aged and artificially aged). The data are scattered for the un-aged char, but 10 to 17% of the added pyrene was extractable. Data for the aged CS450 chars are less scattered and are similar for all three aging treatments with 7 to 10% extractable. The results for un-aged and freeze-thaw-aged CS550 are similar to those for un-aged CS450 (Figure 16). For un-aged CS550 and added pyrene concentrations of 20 to 60 mg kg^{-1}, the median extractable pyrene content was 14%. For freeze-thaw-aged CS550 and added pyrene concentrations of 50-100 mg kg^{-1}, the median extractable pyrene was 3.5%. For the 60° and 110° aged CS550 chars, the HPCD-extractable pyrene was undetectable for the same spiking levels. For 200 to 600 mg kg^{-1} pyrene spikes, only 1 to 3% was extractable. For CS750, the median extractable pyrene was less than 2% in un-aged and aged chars (Figure 17). The HPCD extraction results are summarized in Table 12. Clearly, the HPCD-extractable pyrene results indicate that sorbed pyrene is mostly inaccessible.

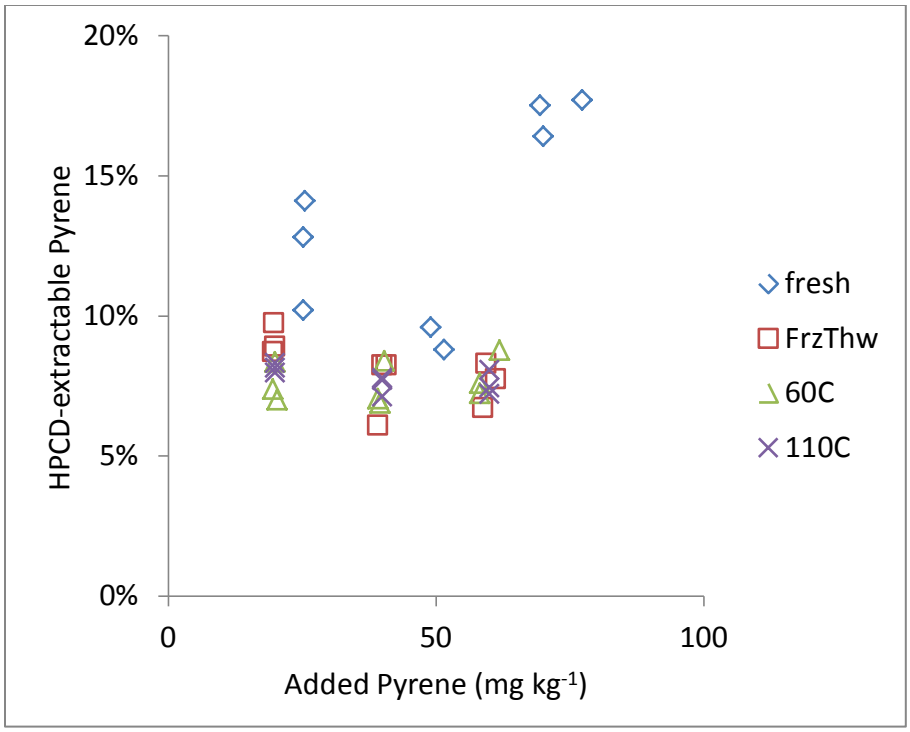

Figure 15. HPCD-extractable pyrene in spiked CS450 biochar.

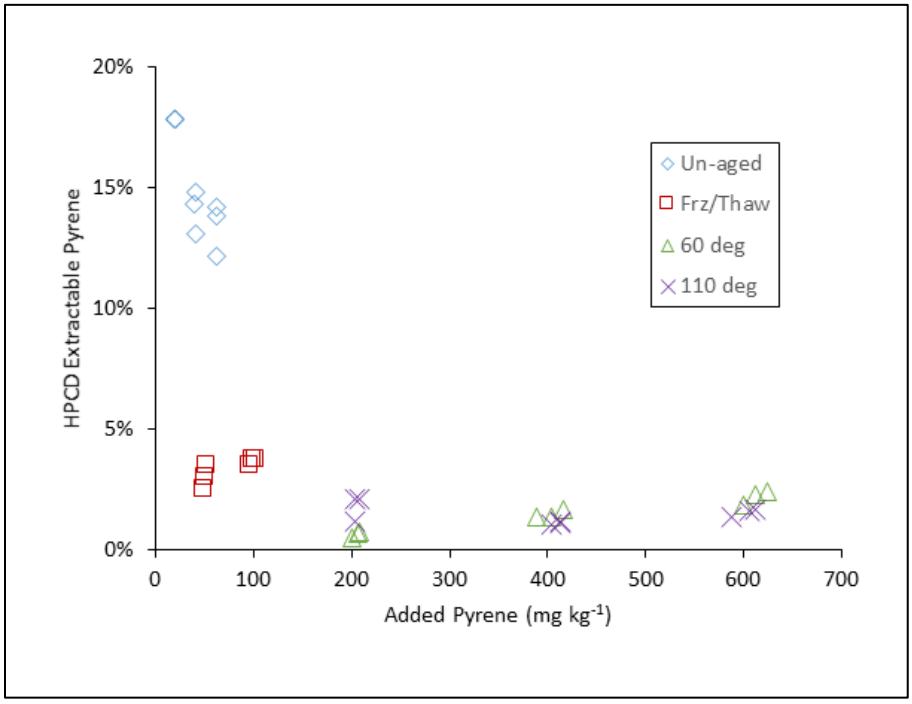

Figure 16. HPCD-extractable pyrene in spiked CS550 biochar.

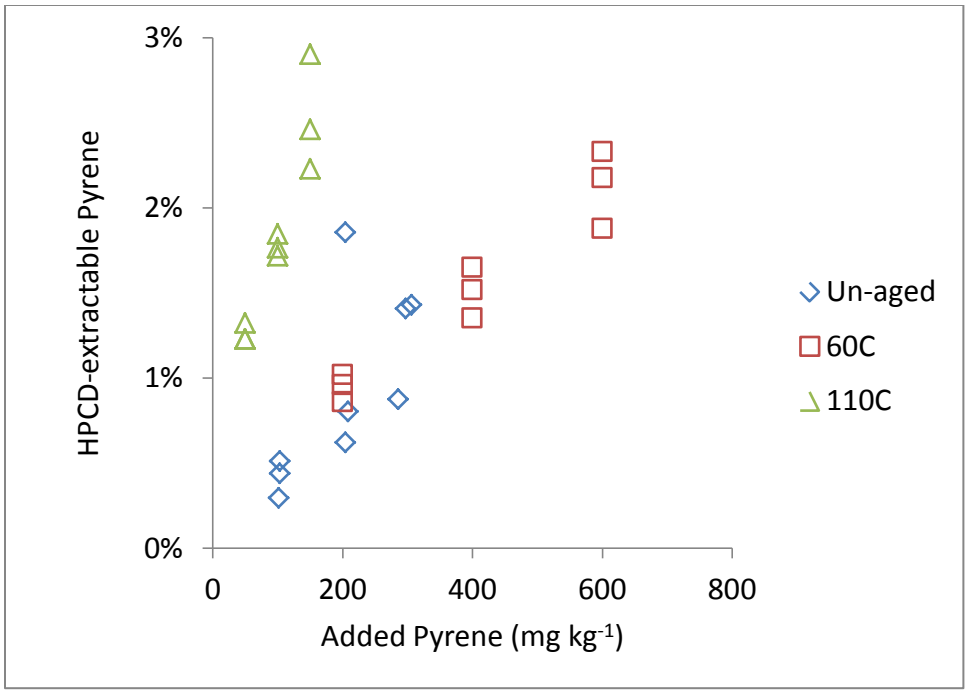

Figure 17. HPCD-extractable pyrene in spiked CS750 biochar.

Table 12. HPCD-extractable pyrene in spiked corn stover biochar.

		Median extractable pyrene			
			Aging Treatment		
Pyrolysis Temperature	Added Pyrene (mg kg^{-1})	Un-aged Char	Freeze/Thaw	60°C	110°C
450	20 - 70	13.5%	8.2%	7.4%	7.8%
550	20 - 100	14.3%	3.5%	<0.5%	<0.5%
550	200 - 600	--	--	1.3%	1.3%
750	200 - 600	0.8%	< 0.5%	1.5%	1.8%

Note: -- indicates no experiment for these conditions.

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DISCUSSION

Biochar Yields as a Function of Pyrolysis Temperatures and End Use

Pyrolysis of corn stover at 450°C produced greater quantities of biochar than those generated at higher temperatures. However, the total PAH contents and adsorption properties also changed as the pyrolysis temperature was increased. From a large-scale biochar production perspective, the desired end use will dictate the pyrolysis temperature utilized. If carbon sequestration is the goal of biochar production, then the corn stover biochar created at 450°C will produce the greatest solid product yield. However, this material will contain more PAHs and will sorb PAHs less strongly than materials created at higher temperatures. Total PAHs may be reduced in this material by aging, but this will increase the cost of an already low-value product. Furthermore, this does not address the environmental fate and transport of fugitive PAHs. However, if use as a soil amendment is the desired application, then a lower PAH content and improved PAH adsorption and retention properties may outweigh the lower solid product yield observed for corn stover biochar created at greater temperatures.

Surface Area

Figure 18 compares the N_2-BET specific surface areas of CS450 and CS550 with published values for corn stover chars. For pyrolysis temperatures up to 550°C, specific surface areas range from 4 to 25 $m^2\ g^{-1}$. For 600°C char, the maximum value is 74 $m^2\ g^{-1}$. The range in values for each temperature may have been due to different heating rates, particle sizes, and pyrolysis method/equipment (tube furnace, kiln, fluidized bed, etc.). The one 450°C fast pyrolysis char had a surface area more than twice as large as those of all of the slow pyrolysis chars. For all other temperatures, slow pyrolysis chars had higher surface areas than fast pyrolysis chars. Appendix D gives the surface areas and literature citations for the data plotted in Figure 18.

CS450 had a specific surface area at the upper end of the range for slow pyrolysis chars. CS550 had a surface area in the middle of the range for fast pyrolysis chars and was about half that of the other 550°C slow pyrolysis char. For both CS450 and CS550, the published surface areas were within a factor of two of the present work.

Total PAH Content

The total EPA-16 PAH concentration of CS450, 1.4 mg kg^{-1}, is similar to the result of Hale et al. (2012), who found 1.9 mg kg^{-1} total PAH in 450°C corn stover char. However, CS550 had 0.2 mg kg^{-1}, whereas Hale et al. (2012) found 1.7 mg kg^{-1} in 550° char. Hale et al. (2011) measured 1.0 mg kg^{-1} total PAHs in 600° char. Hale et al. (2011 and 2012) used soxhlet extraction, the "gold standard" for extraction of organic compounds from solid matrices, whereas pressurized solvent extraction was used in the present work. However, the surrogate recovery was acceptable for both CS450 and CS550 in the present work. Therefore, the difference in extraction methods is probably not the reason for the discrepancy.

The total PAH content of the biochar produced was found to be dependent on the pyrolysis temperature. As the pyrolysis temperature was increased from 450°C to 550°C, the PAH content

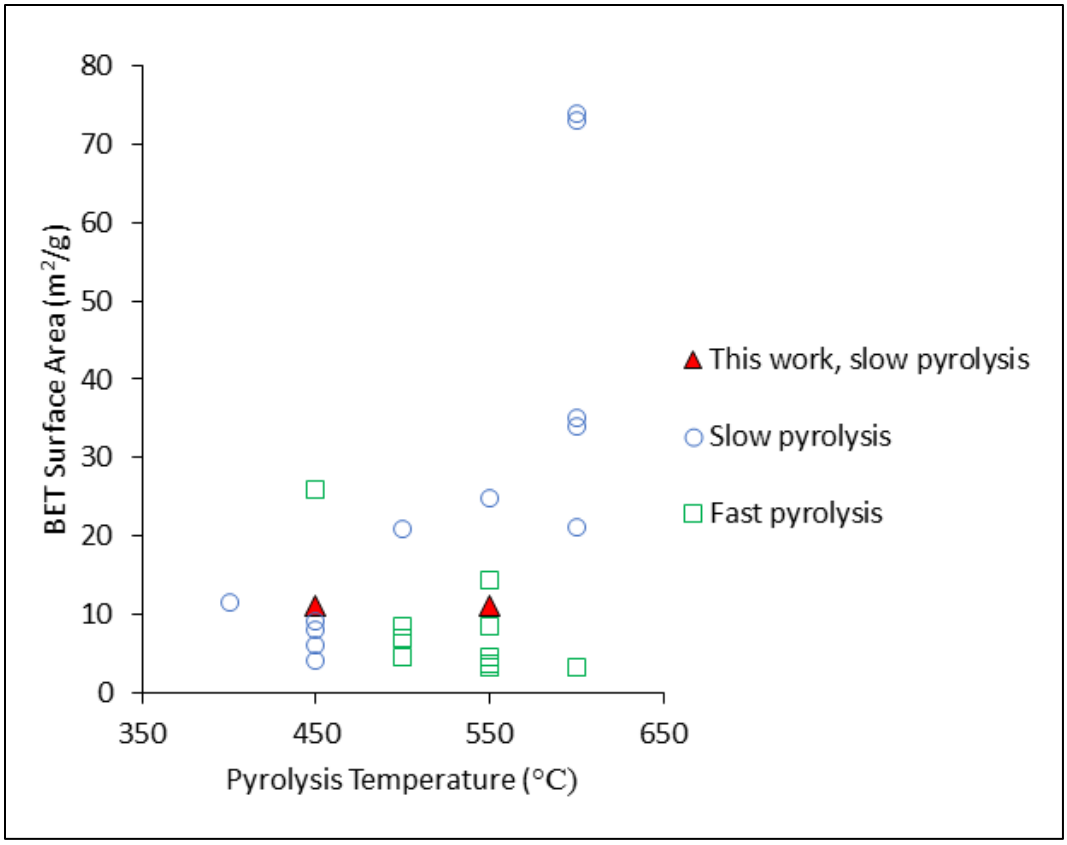

Figure 18. Comparison of BET surface areas in the present work with published values.

was reduced by a factor of 8. In addition, CS450 contained higher concentrations of the carcinogenic PAHs benzo[a]anthracene, benzo[a]pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene.

Surrogate recovery was acceptable for CS450 and CS550 but very low for CS750. Hale et al. (2012) analyzed a wide range of biochars for PAHs and used deuterated PAHs to monitor their extractions. In some cases, recovery was lowest for the materials produced at the highest temperatures. However, their lowest recovery was 56%, in contrast to 2 to 3% for CS750.

Sorption of Pyrene

Figure 19 compares pyrene sorption results for un-aged and aged CS550 from the present work and 600°C corn stover char from Hale et al. (2011). Freundlich isotherms fit all data sets very well (i.e., linear plots on a log-log graph). For a given dissolved pyrene concentration, the Hale et al. (2011) data plot approximately one log unit lower than the CS550 data. The slopes of the log-log plots in the present work are lower than those of Hale et al. (2011) (i.e., the isotherms are more convex on a linear plot). In the present work, artificial aging caused increased sorption by a factor of two (0.3 log units), whereas for Hale et al. (2011), aging decreased pyrene sorption. The reason for these differences in sorption behavior is unknown, but one factor may be differences in pyrene-accessible surface areas.

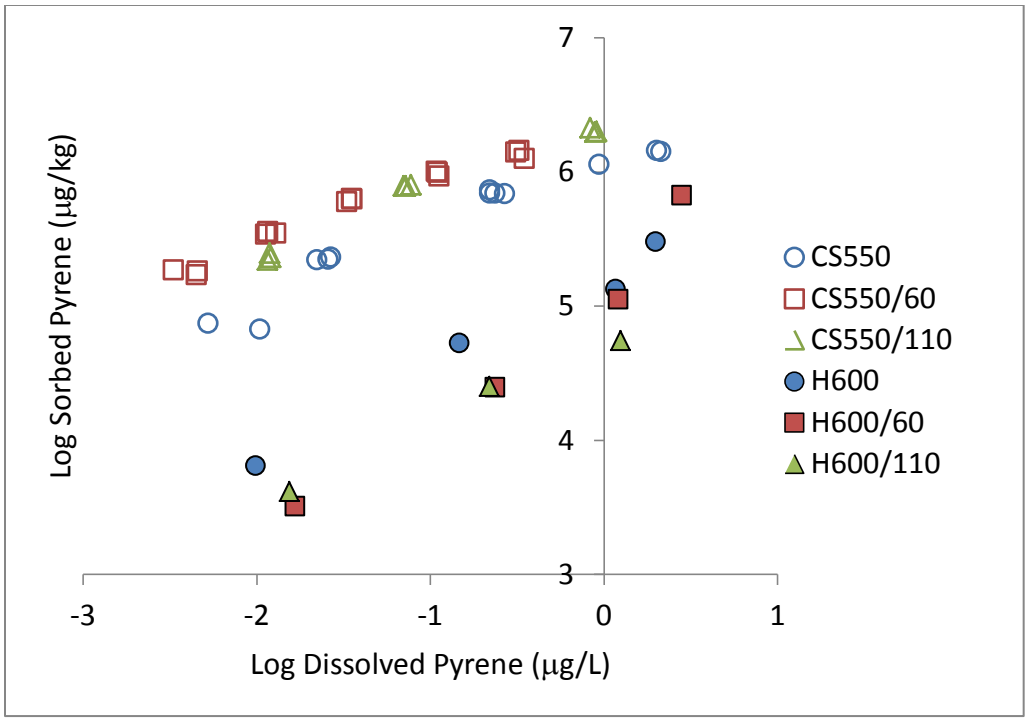

Figure 19. Comparison of pyrene sorption isotherms of slow pyrolized corn stover biochar. Open symbols - present work. Filled symbols - Hale et al. (2011).

The degree of pyrene sorption was strongest for the char pyrolized at 750°C. This result was observed for the surrogate used in the total PAH analysis, terphenyl-d14, and the PAH matrix spike performed in this extraction batch (Table 7 and Table 8).

When these compounds were spiked on the CS750 before extraction, their recoveries were extremely low. Even under rigorous extraction conditions that are the standard method for removing PAHs from solid samples (100°C, 1500 psi, and hexane-acetone (1:1) at a solvent to sample ratio of 40 mL g^{-1}), these compounds were so strongly adsorbed to the material that they could not be removed. This effect was not observed for the CS450 or CS550 materials under the identical conditions. However, this was also observed in the isotherm experiments with pyrene spiked at lower concentrations.

Interestingly, the strong adsorption phenomenon observed with the un-aged CS750 changed as the material aged and was exposed to elevated temperatures (Table 9). Artificial aging increased the surrogate recoveries for this material. Although the cause has not yet been determined, its implications can be important. If biochar is to be used as a soil amendment or for a sorption medium, then over time the sorption strength of the material may diminish.

Bioavailability and Bioaccessibility of PAHs in Biochar

For aged CS550 and un-aged and aged CS750, only 1 to 5% of the added pyrene was HPCD-extractable. Hale et al. (2012) measured soluble PAH concentrations in equilibrium with corn

stover biochar by POM partitioning. The dissolved PAHs are assumed to be bioavailable (Reichenberg and Mayer, 2006). The amount of POM-extractable pyrene calculated from Equation 7 and their dissolved pyrene concentrations, mass of POM, pyrene-POM partition coefficient, and mass of char were 0.8 and 1.2% for their 450° and 550° chars, respectively. These results are, perhaps coincidentally, comparable to HPCD-extractable fractions of pyrene for CS550 and CS750.

PAHs Associated with Biochar: Potential to Contaminate Groundwater and Land Use Considerations

Contamination of groundwater by PAHs as a result of land application of any of the corn stover biochars characterized in the present work is unlikely. The total concentrations of priority PAHs in the biochars were very low. The priority PAHs have low water solubilities and high hydrophobicities. The PAHs sorb very strongly to the biochar as indicated by pyrene sorption. The addition of biochar to soils may provide a sink for PAHs rather than a source; however, the frequency of application and how the material ages could be important factors to consider.

For a typical biochar soil application rate (5% by weight) (Sohi et al., 2010; Xu et al., 2012) and soil containing negligible amounts of PAHs, then application of the highest total PAH-containing corn stover biochar, CS450, would have a final total PAH concentration of 0.07 mg kg^{-1}. This concentration is in the range of PAH concentrations of agricultural soils in the U.S., 0.005 mg/kg to 0.900 mg kg^{-1} (ATSDR, 1995). The total PAH concentrations in urban and non-urban soils average 10 to 25 mg kg^{-1} (Kay et al., 2003; EPRI, 2004). Therefore, typical application rates of the corn stover biochars created in this study would not elevate total PAH concentrations above the national average for agricultural soils. In addition, total PAH concentrations would be at least two orders of magnitude less than those observed near the Chicago area (IEPA, 1997).

The total PAH content of corn stover biochar is therefore most likely not a concern for use in agricultural soils. Application of this material should not increase total PAH soil contents above those already observed. The soil, biochar, and plant tissue interaction could potentially play a role in uptake of these compounds. However given the low bioaccessibility of PAHs adsorbed to biochar, plant uptake is unlikely. Consequently, the addition of biochar to agricultural soils may reduce plant PAH uptake. Native PAHs in soil amended with corn stover biochar may be more strongly attracted to biochar and become less available for plant uptake. Furthermore, PAHs from air deposition or other sources may also become less bioavailable to plants in soils amended with biochar. These would be fruitful areas of research.

CONCLUSIONS

The N_2-BET surface area of un-aged corn stover biochar depends strongly on the pyrolysis temperature. The surface areas of CS550 and CS750 were both roughly ten times that of CS450. Artificial aging increased the surface area of CS450 by up to a factor of five and those of CS550 and CS750 by roughly 50%.

The total concentrations of USEPA priority PAHs were highest in CS450, lower in CS550 by a factor of seven, and apparently even lower in CS750. However, the CS750 results were questionable because of very low surrogate compound recoveries. The concentrations of many individual compounds were also higher in CS450 than in CS550. Artificial aging lowered total PAHs in CS450 char according to the following pattern: un-aged > freeze-thaw > 60°C > 110°C. The concentrations of individual compounds in un-aged and aged CS450 char followed the same order with the aging treatment. Volatilization may have caused some of the decreases. Aging had no clear effects on total PAH concentrations in the CS550 and CS750 chars. Surrogate recoveries from artificially aged CS750 chars were better than for un-aged CS750.

Pyrene sorbed strongly to all chars, un-aged and artificially aged. Sorbed concentrations ranged from $10^5 – 10^7$ mg kg^{-1} for dissolved concentrations of $10^{-3} – 10^{-1}$ μg L^{-1}. For un-aged chars, the sorbed pyrene concentrations increased in the order CS450 < CS550 < CS750 for dissolved pyrene concentrations less than or equal to 0.1 μg L^{-1}. Artificial aging had minor effects on pyrene sorption to CS450 and CS550 chars. Sorbed concentrations were the same within a factor of two for un-aged and aged chars. Sorbed pyrene concentrations differed by up to an order of magnitude for different aging treatments of CS750. All pyrene sorption data were fit very well ($r^2 > 0.9$) by Freundlich isotherms.

The bioaccessibility of pyrene in native biochars, which was operationally defined by extraction with HPCD, was impossible to determine because of both low concentrations and low extractabilities. For un-aged and artificially aged CS450 and un-aged CS550 chars, pyrene had to be added at concentrations of 20 to 60 mg kg^{-1} to have detectable pyrene in the extracts. For the un-aged chars, 10 to 15% of the added pyrene was HPCD-extractable. For the aged CS550 chars and un-aged and aged CS750 chars, 50 to 600 mg kg^{-1} pyrene had to be added and only 1 to 3% of that was HPCD-extractable. These results suggest that corn stover biochar may be useful for immobilizing PAHs and other hydrophobic compounds in contaminated soils and sediments.

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RECOMMENDATIONS

Polyoxomethylene is an accepted material for characterizing sorption of hydrophobic compounds to biochar and other forms of black carbon (Jonker and Koelmans, 2001; Hale et al., 2011; Hale et al., 2012). However, the equilibration time for PAHs and POM is almost one month (Jonker and Koelmans, 2001). We switched from POM to silicone as the competing phase in our sorption experiments because silicone has a similar pyrene partition coefficient but a much shorter equilibration time. We recommend sorption experiments using both materials to determine whether silicone is a good material for sorption experiments.

Although the standards regulating land application of biochar are based on total extractable PAHs, only small fractions of PAHs are bioavailable (Weissenfels et al., 1992; Ruus et al., 2010; Ruus et al., 2013). Passive sampling (sorption to POM or silicone) has been used to estimate the bioavailability of PAHs in biochar (Hale et al., 2012), sediment (Vinturella et al., 2004; Muijs and Jonker, 2012), and soil (Gomez-Eyles et al., 2012). We recommend experiments using both POM and silicone as passive sorbents to see if the results are comparable. It would be useful to determine the bioavailabilities of PAHs from biochar, soil, and biochar-soil mixtures. Experiments such as these would be a useful complement to studies of PAH uptake by plants or animals from biochar-soil or biochar-sediment mixtures.

In the present work, artificial aging simulated the extreme environmental conditions (heating, freezing, wetting, and drying) to which biochar may be subjected (Hale et al., 2011). Cross and Sohi (2013) suggested oxidation is a likely effect of biochar aging and used heat and concentrated hydrogen peroxide to simulate that aging process. Another potential biochar aging effect is the coating of the biochar surface with soil organic matter and a concomitant reduction in micropore accessibility (Teixido et al., 2013). Researchers have used humic and fulvic acid (Pignatello et al., 2006; Zhou et al., 2010), tannic acid (Qiu et al., 2009), and lipids (Kwon and Pignatello, 2005) to simulate this pore blockage. We recommend experiments to characterize the effects of the different aging methods on PAH sorption and bioavailability.

Activated carbon has been used as an amendment to remediate soil and sediment contaminated with PAHs and other hydrophobic organic compounds (Beesley et al., 2010; Chai et al., 2011; Oleszczuk et al., 2012; Ogbonnaya and Semple, 2013; Wang et al., 2013). Because of its strong sorption of pyrene, we recommend experiments with corn stover biochar to assess its effectiveness in immobilizing (reducing the bioavailability and bioaccessibility of) PAHs in soil and sediment.

The standard method for extraction of PAHs from biochars was ineffective for corn stover biochar created at 750°C. A preparation method for more efficient extraction of PAHs from these materials is necessary from an evaluation and regulatory perspective. In addition, the standard method for extraction and analysis of PAHs in biochars is very costly and time consuming. Therefore, other more efficient and cost-effective methods are desirable.

PAHs are but one class of contaminants that may be associated with biochar. Other possible classes of compounds of concern include phenols, furans, and heterocyclic nitrogen compounds. We recommend testing POM and silicone for partitioning of selected compounds from these

other contaminant classes. If one or both materials are suitable, then methods for freely dissolved and extractable fractions could be developed.

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Xia, X., X. Chen, X. Zhao, H. Chen and M. Shen. 2012. Effects of Carbon Nanotubes, Chars, and Ash on Bioaccumulation of Perfluorochemicals by Chironomus Plumosus Larvae in Sediment. *Environmental Science & Technology* 46(22): 12467-12475.

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Yates, K., I. Davies, L. Webster, P. Pollard, L. Lawton and C. Moffat. 2007. Passive Sampling: Partition Coefficients for a Silicone Rubber Reference Phase. *Journal of Environmental Monitoring* 9(10): 1116-1121.

Zhou, Z. L., H. W. Sun and W. Zhang. 2010. Desorption of Polycyclic Aromatic Hydrocarbons from Aged and Unaged Charcoals with and without Modification of Humic Acids. *Environmental Pollution* 158(5): 1916-1921.

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APPENDIX A. STRUCTURE AND PROPERTIES OF PRIORITY-POLLUTANT POLYCYCLIC AROMATIC HYDROCARBONS

Table A-1. Structure and properties of the 16 USEPA priority PAHs.

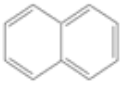
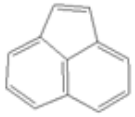
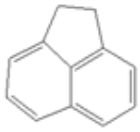
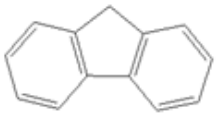
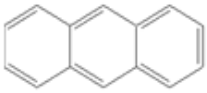
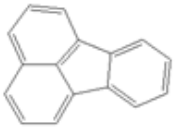
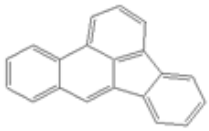
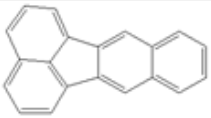
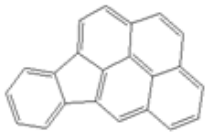
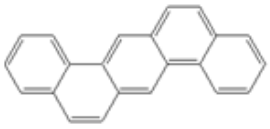
Compound	CAS#	Formula	Structure	Water Solubility (mg/L)	Octanol-Water Partition Coefficient (Log K_{ow})
Naphthalene	91-20-3	$C_{10}H_8$		30.0	3.29
Acenaphthylene	208-96-8	$C_{12}H_8$		3.93	4.07
Acenaphthene	83-29-9	$C_{12}H_{10}$		1.93	3.98
Fluorene	86-73-7	$C_{13}H_{10}$		1.69 -1.98	4.18
Phenanthrene	85-01-8	$C_{14}H_{10}$		1.20	4.45
Anthracene	120-12-7	$C_{14}H_{10}$		0.076	4.45
Fluoranthene	206-44-0	$C_{18}H_{10}$		0.20 – 0.26	4.90
Pyrene	129-00-0	$C_{16}H_{10}$		0.132	4.88

Table A-1. (continued)

Compound	CAS#	Formula	Structure	Water Solubility (mg/L)	Octanol-Water Partition Coefficient (Log K_{ow})
Benzo[a] anthracene	56-55-3	$C_{18}H_{12}$		0.010	5.61
Chrysene	218-1-9	$C_{18}H_{12}$		0.0028	5.16
Benzo[b] fluoranthene	205-95-2	$C_{20}H_{12}$		0.0012	6.04
Benzo[k] fluoranthene	207-8-9	$C_{20}H_{12}$		0.00076	6.06
Benzo[a] pyrene	50-32-8	$C_{20}H_{12}$		0.0023	6.06
Indeno[1,2,3,c,d] pyrene	193-35-9	$C_{22}H_{12}$		0.00062	6.58
Dibenzo[a,h] anthracene	53-70-3	$C_{22}H_{14}$		0.00050	6.84
Benzo[g,h,i] perylene	181-25-2	$C_{22}H_{12}$		0.00026	6.50

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APPENDIX B. TOTAL PAH DETERMINATION

Table B-1. Varian 3800 gas chromatograph operating parameters.

Injection Volume	4 μL	
Injection Temperature	300°C	
Injection Mode	Splitless	
Pulse Pressure	40 psi	
Pulse Duration	0.80 min	
Helium Carrier Flow Rate	2.0 ml/min	
Oven Program		
Temperature, °C	Rate, °C/min	Hold, min
45	0.0	1.00
130	43.0	0.00
180	12.0	0.00
240	7.0	0.00
320	12.0	10.00
Transfer line Temperature	300°C	
Trap Temperature	200°C	
Manifold Temperature	45°C	
Ionization Mode	Electron Impact	
Emission Current	20 μA	
Ion Prep Technique	Selected Ion Storage (SIS)	

Table B-2. Internal standard assignments, retention times, and storage/quant masses for PAH mass spectrometer measurements.

Analyte Name	Internal Standard Assignment	Retention Time, min	Quant Ion, m/z
Naphthalene d8 ISTD	-	4.510	136.0
Naphthalene	Naphthalene d8 ISTD	4.555	128.1
Acenaphthylene	Acenapthene d10 ISTD	6.607	152.1
Acenaphthene d10 ISTD	-	6.829	162.0 + 164.0
Acenaphthene	Acenapthene d10 ISTD	6.898	153.0 + 154.0
Fluorene	Acenapthene d10 ISTD	7.766	165.0 + 166.0
Phenanthrene d10 ISTD	-	9.733	188.0
Phenanthrene	Phenanthrene d10 ISTD	9.777	178.1
Anthracene	Phenanthrene d10 ISTD	9.886	178.1
Pyrene	Chrysene d12 ISTD	13.579	202.1
Terphenyl d14 Surrogate	Chrysene d12 ISTD	14.281	244.0
Benzene (a) anthracene	Chrysene d12 ISTD	17.210	228.1
Chrysene d12 ISTD	-	17.270	240.0
Chrysene	Chrysene d12 ISTD	17.321	228.1
Benzo (b) fluoranthene	Perylene d12 ISTD	19.754	252.1
Benzo (k) fluoranthene	Perylene d12 ISTD	19.799	252.1
Benzo (a) pyrene	Perylene d12 ISTD	20.375	252.1
Perylene d12 ISTD	-	20.512	264.0
Indeno (1,2,3,c,d) pyrene	Perylene d12 ISTD	22.354	276.1
Dibenzo (a,h) anthracene	Perylene d12 ISTD	22.534	278.1
Benzo (g,h,i) perylene	Perylene d12 ISTD	22.702	276.1

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APPENDIX C. SORPTION AND EXTRACTION PRELIMINARY EXPERIMENTS

The kinetics of pyrene sorption to biochar were characterized by weighing 5.0 ± 0.5 mg CS450 into 20 glass centrifuge tubes with Teflon®-lined caps, adding 1 mM $CaCl_2$, adding identical amounts of pyrene, and continuously mixing end over end in the dark to avoid any photochemical transformation of pyrene. Control samples with char but no pyrene were used to check for any desorption of pyrene from the char, with pyrene but no char to check for any losses to the tube surfaces or cap linings, and with no pyrene or char (blanks) to check for any contamination from the tubes. Duplicate samples were collected periodically, centrifuged, and analyzed for pyrene by synchronous fluorescence. The control samples were analyzed at the end of the experiment. Pyrene was undetectable in the blanks and samples with no pyrene added. Pyrene recoveries from the samples with no char were in the acceptable range of 80 – 120% of the expected values. The results are shown in Figure C-1. Most of the pyrene was sorbed in the first 24 hours, although there were small but significant changes until about 4 days. There was good agreement between duplicates on all days.

The kinetics of pyrene partitioning to POM were characterized by adding POM coupons (1 cm^2, 0.09 g) cut from 5 mil (0.005 in.,127 μm) thick POM (C. S. Hyde Co., Chicago, IL) to six glass bottles with Teflon®-lined caps containing 100 μg L^{-1} pyrene in deionized water. The control samples were bottles with coupons but no pyrene (blanks) and pyrene but no coupons. The bottles were mixed end over end in the dark. All treatments were run in triplicate. At various times up to 21 days, a sample was poured from each bottle, analyzed by synchronous fluorescence, and poured back into the bottle. The relative fluorescence was set with a quinine standard (1 mg L^{-1}, 3 μM) before each set of measurements. The results are shown in Figure C-2.

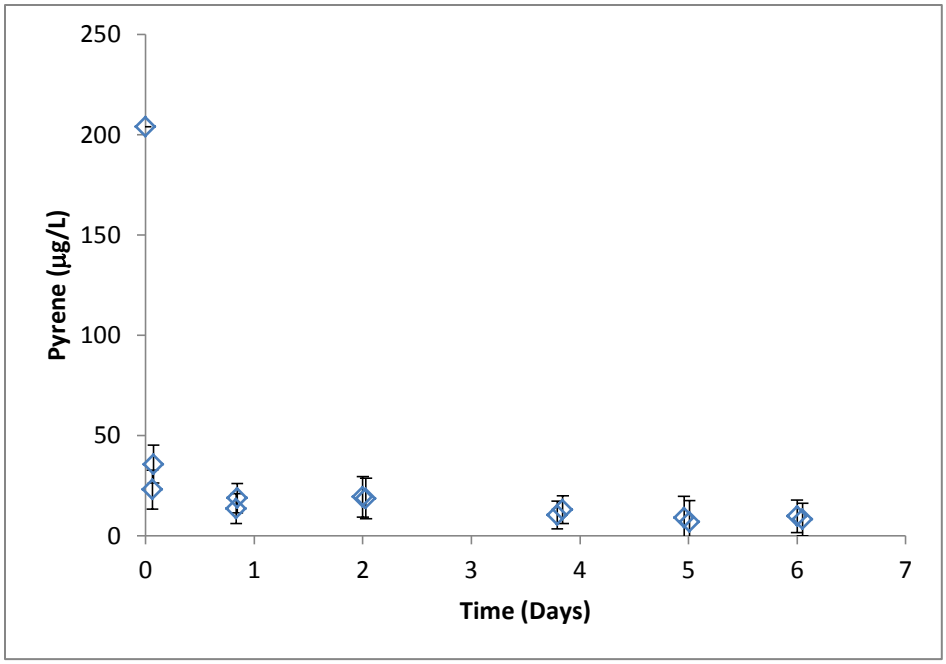

Figure C-1. Kinetics of pyrene sorption to corn stover char CS450. Overlapping symbols offset in the x direction for clarity. Error bars show 95% confidence intervals.

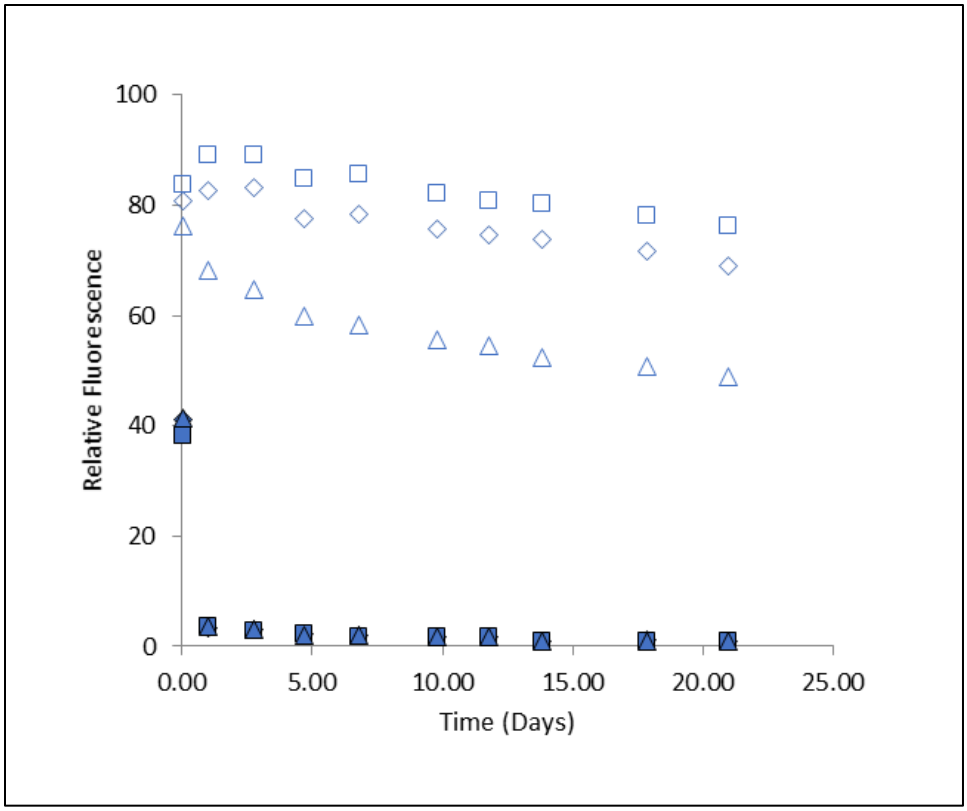

Figure C-2. Kinetics of partitioning of pyrene to POM. Different symbols are used to show replicates. Open symbols are for bottles with POM, filled symbols are for bottles with no POM.

Over half of the pyrene was partitioned within the first hour and over 95% in the first day. However, there were measureable decreases up to day 14 and the measurements fluctuated slightly after that. There was good agreement among the replicates for all sampling times. The pyrene concentrations in two of the control samples without POM decreased slowly with time, possibly due to sorption to the Teflon® cap linings. The pyrene concentration in the third bottle decreased much more rapidly. The reason for the different behavior is unknown.

After the last measurement of pyrene-POM partitioning, the coupons were placed in methanol and the samples were mixed end over end in the dark. After 24 and 48 hours the methanol extracts were analyzed by synchronous fluorescence. Approximately 78% and 82% of the pyrene was recovered after 24 and 48 hours, respectively (Figure C-3). There was good agreement between the replicates. Subsequent experiments showed that mixing was unnecessary for quantitative extraction of pyrene from POM.

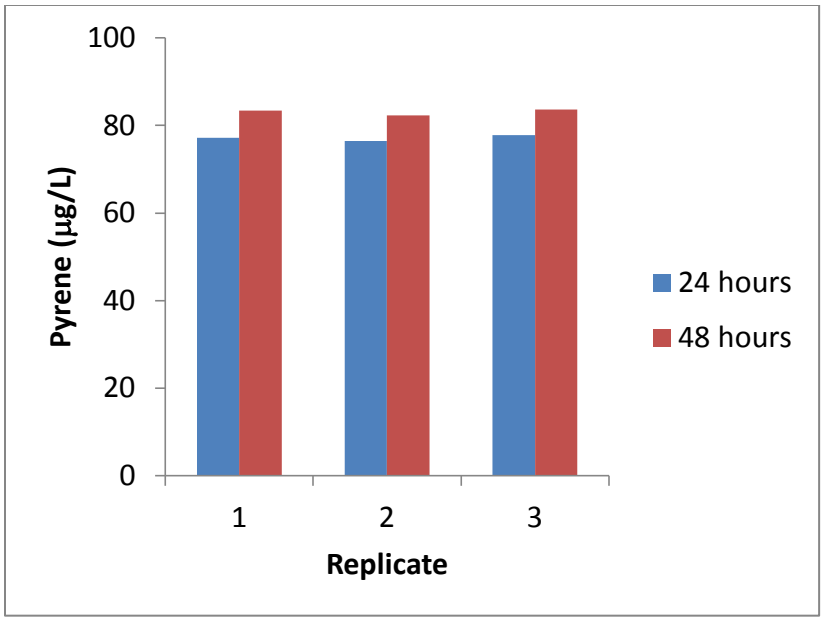

Figure C-3. Extraction of pyrene from POM.

To determine the pyrene-POM partition coefficient, POM coupons were cut, cleaned with detergent and methanol, soaked in deionized water twice overnight to remove methanol partitioned into the POM, and air dried. They were weighed to 0.1 mg and added to centrifuge tubes containing deionized water. Varying amounts of pyrene were added to the tubes and they were mixed end over end in the dark. After 30 days of mixing, pyrene in the supernatants was determined by synchronous fluorescence. The results are shown in Figure C-4.

The isotherm was linear and the partition coefficient (slope of the isotherm) was 22,450 L kg^{-1} (Log K_p 4.35).

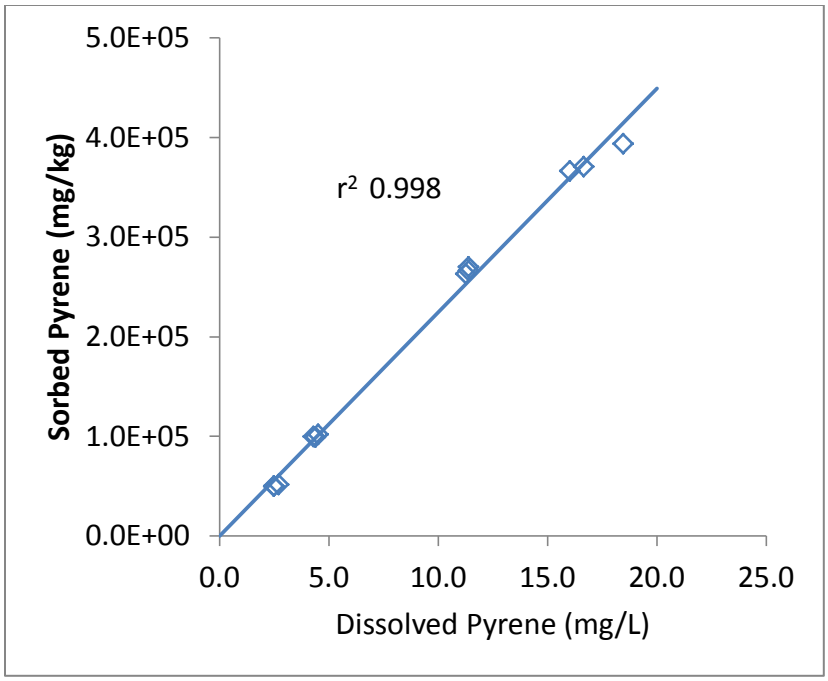

Figure C-4. Isotherm for pyrene partitioning to POM.

For pyrene-silicone partitioning kinetics experiments, silicone rings (2 mm, 0.14 g) were cut from pump tubing (Masterflex® size 18; O. D. 0.31 in., 9.9 mm; wall thickness 0.0625 in., 1.6 mm). A solution of 50 μg L^{-1} pyrene in deionized water was added to six bottles with Teflon®-lined caps. Silicone rings were added to three bottles and three bottles served as the control. The bottles were mixed end over end as in the biochar sorption experiments. At various times the relative fluorescence was set using 1 mg L^{-1} quinine as a fluorescence standard and the fluorescence of the samples was measured. The solutions were poured back into the tubes after each measurement. The results are shown in Figure C-5. While the measurements were only semi-quantitative, the system clearly reached equilibrium between two and three days.

After the last pyrene-silicone partitioning kinetics measurement, the rings were rinsed with deionized water, dried with a tissue, and placed in methanol in brown glass vials with Teflon®-lined caps. At various times the fluorescence of the extracts and a methanol blank was measured. The relative fluorescence was set with a quinine standard for each set of measurements. The vials were mixed immediately before the measurements but otherwise were unmixed. The results are shown in Figure C-6. The curve is for a pseudo-first-order model. As for the partitioning, the measurements were semi-quantitative because only relative fluorescence values were measured. However, the extraction was clearly complete within a few hours.

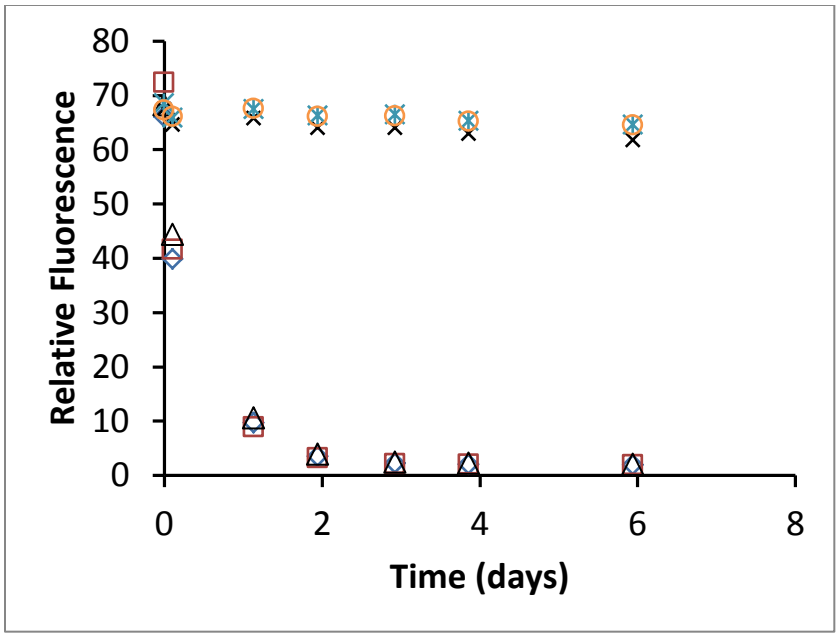

Figure C-5. Pyrene-silicone partitioning kinetics. Different symbols are used to show replicates.

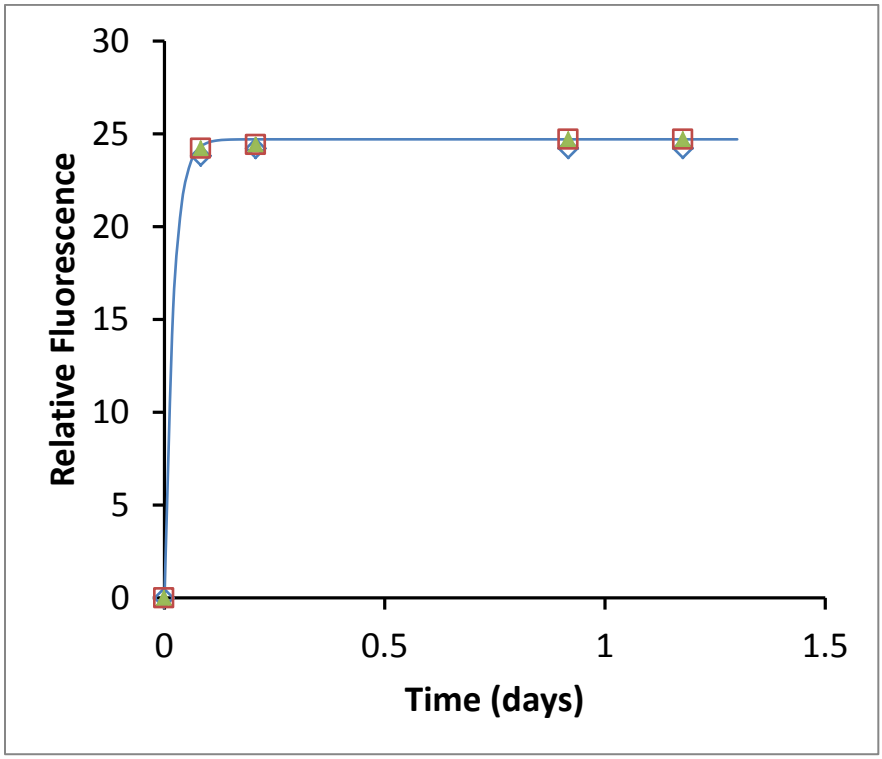

Figure C-6. Kinetics of extraction of pyrene from silicone.

To determine the partition coefficient for pyrene and silicone, several coupons (~0.2 g) were soaked 24 hours in methanol, soaked 24 hours in deionized water, and air dried. They were weighed into amber bottles with Teflon®-lined caps and deionized water was added. Varying amounts of pyrene were added to the bottles. For bottles scheduled to get more than 100 μg L^{-1}, pyrene was added 100 μg L^{-1} at a time with 24 hours allowed between spikes. This was done to avoid exceeding the aqueous solubility of pyrene. After the last spike was added the systems were given five days to equilibrate. Pyrene was determined in the supernatants by synchronous fluorescence. Sorption was characterized by a linear isotherm (Figure C-7).

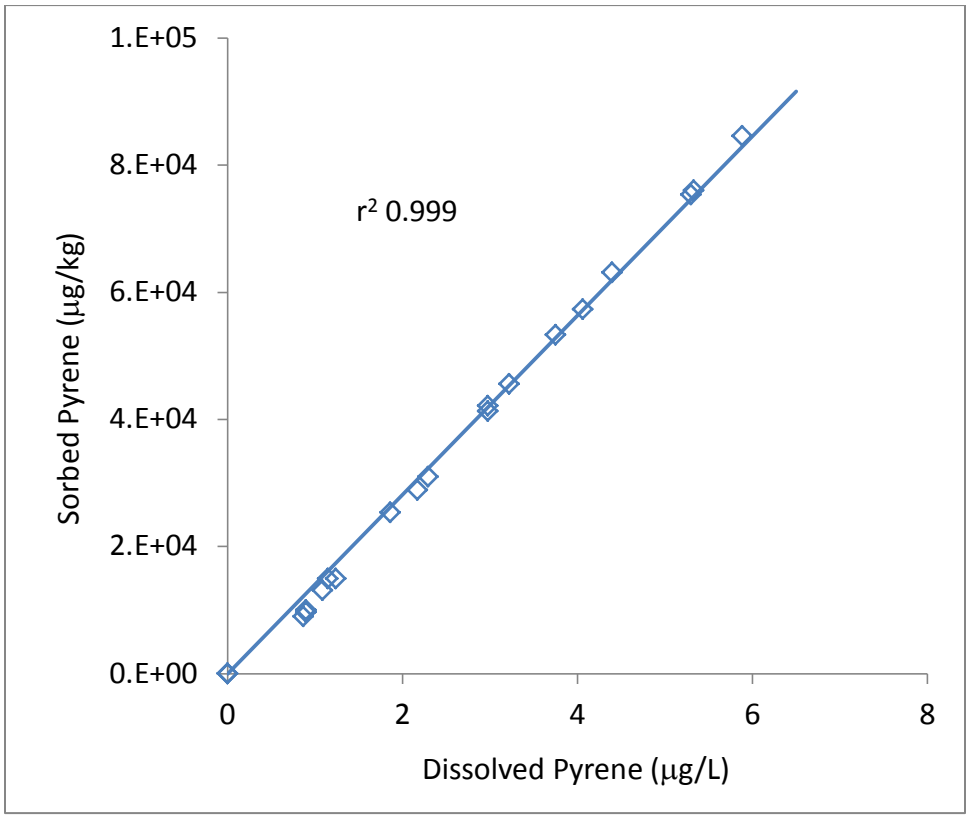

Figure C-7. Silicone-pyrene partitioning isotherm.

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APPENDIX D. PUBLISHED N_2-BET SURFACE AREAS OF CORN STOVER BIOCHAR

Table D-1. Comparison of specific surface areas of corn stover biochar from the present work with published results.

Pyrolysis Temperature (°C)	Specific Surface Area‡ (m^2 g^{-1})	Notes	Reference
450	11.0	<125 μm	Present work
550	11.0		
550	24.8	Slow pyrolysis	(Brewer et al., 2011)
550	3.3 – 14.3	Fast pyrolysis	
500	4.5	Fast pyrolysis	(Brewer et al., 2012)
600	3.3	Fast pyrolysis	
500	8.5	Fast pyrolysis	
500	20.9	Slow pyrolysis	(Brewer et al., 2009)
500	7.0	Fast pyrolysis	
*	67.2	*	(Chai et al., 2011)
450	26.0	Fast pyrolysis, <160 μm	(Lee et al., 2010)
600	74.0	Slow pyrolysis	(Peterson et al., 2013)
450	4.0 – 9.0	Slow pyrolysis	(Sun et al., 2012)
600	21.0 – 73.0	Slow pyrolysis, different heating rates	
410	4.2	*	(Fabbri et al., 2012)
505	17.0		
515	10.0		
400	11.6	Slow pyrolysis	(Xia et al., 2012)

Note: *Pyrolysis temperature or rate of change not given.