

Effects of Chemical, Biological, and Physical Aging As Well As Soil Addition on the Sorption of Pyrene to Activated Carbon and Biochar

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S Supporting Information

ABSTRACT: In this study, the suitability of biochar and activated carbon (AC) for contaminated soil remediation is investigated by determining the sorption of pyrene to both materials in the presence and absence of soil and before as well as after aging. Biochar and AC were aged either alone or mixed with soil via exposure to (a) nutrients and microorganisms (biological), (b) 60 and 110 °C (chemical), and (c) freeze–thaw cycles (physical). Before and after aging, the pH, elemental composition, cation exchange capacity (CEC), microporous SA, and sorption isotherms of pyrene were quantified. Aging at 110 °C altered the physicochemical properties of all materials to the greatest extent (for example, pH increased by up to three units and CEC by up to 50% for biochar). Logarithmic K_{Fr} values ranged from 7.80 to 8.21 (ng kg^{-1})(ng L^{-1})^{−nF} for AC and 5.22 to 6.21 (ng kg^{-1})(ng L^{-1})^{−nF} for biochar after the various aging regimes. Grinding biochar to a smaller particle size did not significantly affect the sorption of d_{10} pyrene, implying that sorption processes operate on the subparticle scale. Chemical aging decreased the sorption of pyrene to the greatest extent (up to 1.8 log unit for the biochar+soil). The sorption to AC was affected more by the presence of soil than the sorption to biochar was. Our results suggest that AC and biochar have a high sorption capacity for pyrene that is maintained both in the presence of soil and during harsh aging. Both materials could therefore be considered in contaminated land remediation.

Biochar: fresh or aged?
activated or unactivated?

1. INTRODUCTION

Black carbon (BC) is the term used to describe carbon formed through the incomplete combustion of fossil fuels and biomass and covers a continuum of materials ranging from slightly charred biomass to soot¹ with varied physicochemical properties. This work focuses on the possible use of activated carbon (AC) and biochar as amendments to contaminated soil. AC and biochar differ primarily in their preparation method, source material, and the resulting physicochemical properties of the products, but in previous work, AC has been added to contaminated field soil² and sediment³ in order to sequester organic pollutants and reduce their mobility and bioavailability. The addition of just a few percent AC has reduced the concentration of DDT,⁴ PAHs, and PCBs⁵ available to be assimilated by biota^{6,7} and leach to the surrounding environment,⁸ in some cases by 90% or more. However, the application of AC to a large area of contaminated land could become expensive, the cost of production and use of AC being approximately \$2 kg^{−1} when applied at a 5% dose.⁵ By contrast, the use of biochar could be cheaper in a remediation sense because the waste source materials may be essentially free and the production of biochar at lower temperatures is less energy and cost intensive. However, it is unclear if the positive results reported for AC could be replicated for biochar as adding biochar to hydrophobic organic pollutant contaminated soil or sediment with the goal to remediate has not been thoroughly investigated.^{9–11}

A prerequisite for the application of AC or biochar in contaminated soil remediation is a high pollutant sorption capacity that is maintained in the presence of soil and is sustained over a long period of time, especially when exposed to changing environmental conditions. AC has a high sorption capacity for many organic pollutants, for example logarithmic AC–water partitioning coefficients have been reported to range from 5.49 to 9.72 L kg^{−1} for the 16 USEPA defined PAHs.^{12,13} However, this sorption capacity can be reduced by one to 2 orders of magnitude in the presence of soil or sediment^{2,14,15} due to the fouling of AC by other anthropogenic contaminants or dissolved natural organic matter. In addition, following the amendment of a BC material to a contaminated soil or sediment, abiotic and/or biotic processes (so-called aging) could affect the BC properties and the strength of contaminant sorption. However, studies thus far indicate AC may resist such aging as its sorption capacity for PCBs was maintained even after 5 years in the field.¹⁶ For biochar, logarithmic Freundlich sorption coefficients for phenanthrene have been reported to range from 3.8 to 5.1 L kg^{−1} (determined at a mg concentration level) for a material produced from pine needles at

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temperatures from 100 to 700 °C¹⁷ (compared to 7.8¹² and 8.76¹³ L kg⁻¹ for AC). For natural chars the sorption of phenanthrene was greater, with log partitioning coefficients of 5.0 to 6.1 L kg⁻¹.¹⁸ In the same manner as AC, this sorption capacity of biochar can be reduced by the presence of soil, illustrated by a 28% decrease for hydroquinone sorption,¹⁹ a 60% decrease in diuron sorption²⁰ and a reduction from 4.3 to 2.2 in the phenanthrene logarithmic Freundlich partitioning coefficient when biochar produced from pine needles at 400 °C was mixed at 0.1% w w⁻¹ into soil.¹⁷

Studies to investigate the change in biochar sorption capacity over time are scarce^{20,21} but several reports of changing physicochemical properties following aging can be found.^{19,21–24} A variety of laboratory methods have been used to artificially age biochars; a modified Soxhlet extraction,²⁴ leaching with distilled water for 100 days²⁵ and exposure to ambient conditions for 12 months.²⁰ However, Cheng and Lehmann²¹ measured the adsorption of hydroquinone on oak char following artificial aging at 30 and 70 °C as well as natural field aging. These authors observed a significant decrease in the amount of hydroquinone sorbed by the biochar incubated at 70 °C (2.65 mg g⁻¹) and by the field aged material (4.28 mg g⁻¹), compared to the unaged material (9.61 mg g⁻¹). Yang and Sheng²⁰ aged soil, wheat ash biochar, and ash amended soil under ambient laboratory conditions for 1, 3, 6, and 12 months and showed that the adsorption of diuron was reduced 50–60% after 1 month when compared to an unaged sample.

In the present work, the feasibility of the use of biochar in polycyclic aromatic hydrocarbon contaminated soil remediation was assessed and compared to AC. This was achieved by quantifying the sorption of d₁₀ pyrene to biochar and AC, with and without soil, before and after artificial aging. Short-term harsh aging via biological, chemical, and physical systems was used to investigate the long-term sorption behavior of pyrene as these aging regimes could provide an indication of hundreds to thousands of years of natural environmental processes. Mixing with soil allows an assessment to be made regarding the reduction in the sorption of target pollutants by AC and biochar under such conditions. Carrying out aging experiments on environmentally relevant time scales is very difficult especially as knowledge and information needed to make decisions regarding the use of biochar in environmental management is now required.

2. MATERIALS AND METHODS

2.1. Sorbent Materials. Biochar was produced from corn stover residues (*Zea mays* L.) at 600 °C using a slow pyrolysis method in a continuous flow gas unit and a residence time of 20 min. The AC was produced from anthracite coal (Jacobi Carbon, Kalmar, Sweden). The biochar was collected after passing through a 2 mm mesh size sieve, the average particle size of AC was 20 μm (with 80% of particles smaller than 45 μm) and no further processing was carried out. An agricultural soil (fine-loamy, mixed, mesic Glossoboric Hapludalf from the Cornell University Robert Musgrave Research Farm, Poplar Ridge, New York) currently undergoing field experiments with the biochar used here was air-dried prior to use and passed through a 2 mm sieve. The concentration of native PAHs was measured in the sorbents via a Soxhlet extraction (toluene, 70 mL, 6 h, 160 °C) and resulting total PAHs (USEPA defined compounds) were 1.00 ± 0.04 μg/g, 1.3 ± 0.4 μg/g and 0.040 ± 0.004 μg/g, for biochar, AC and soil. The level of BC is not conclusively known for this soil, but

previous research has indicated the states in the NE of America likely have levels of 0 to 0.5% BC-C per unit weight.²⁶ BC will be used as an umbrella term throughout to refer to both biochar and AC. Basic properties of the materials are shown in Table 1.

2.2. Sample Aging. Artificial aging was carried out in the laboratory over two months. The three aging regimes used were; biological, chemical (treatment at 60 and 110 °C), and physical which are referred to as BIO, CHEM 60, CHEM 110, and PHYS, respectively, throughout the manuscript. Aging was carried out on biochar and AC alone (20 g), soil alone (100 g) or a mixture of soil and either biochar or AC (100 g with a 5% weight BC amendment). To ensure a homogeneous soil + BC mixture, batches were rolled at 10 rpm for 24 h prior to aging. All batches were maintained at 40% water holding capacity (WHC), using either a 1:1 mixture of microbial inoculum:nutrient solution (BIO system) or Millipore water (CHEM and PHYS systems).

2.3. Biological Aging. BIO aging consisted of exposing the materials to a microbial inoculum, a nutrient solution (6.38 g L⁻¹ glucose, 40.66 g L⁻¹ NH₄Cl, 4.67 g L⁻¹ KH₂PO₄, 10.00 mg L⁻¹ peptone, 24.00 mg L⁻¹ CaCl₂, 4.00 mg L⁻¹ MnSO₄, 4.00 mg L⁻¹ ZnCl₂, 4.00 mg L⁻¹ CuSO₄ and 16.00 mg L⁻¹ MgCl₂²⁷) and a glucose supplement (40 μg mg⁻¹ BC), similar to previous studies.^{23,24} The microbial inoculum was extracted from a PAH contaminated sediment sampled at Drammen, Norway and contains the groups of bacteria; *Actinobacteria*, *Proteobacteria*, and *Bacteroidetes* (personal communication P. Menyet and D. Werner). *Sphingomonas* spp. has also been identified and is a known PAH degrader.²⁸ This soil was only used for obtaining microbes, and contained 2.5% organic carbon, 0.51% BC and 38 mg kg⁻¹ PAHs.² The soil was incubated at 30 °C for 18 days to stimulate the microbial community prior to obtaining the inoculum. Soil and Millipore water were mixed and rolled end-overend (11 rpm; 2 h) and then filtered (2.7 μm) to obtain the inoculum. The nutrient solution was added to avoid any limiting environmental conditions and glucose was used to provide an easily degradable C source for microorganisms and potentially stimulate BC degradation.^{29,30}

2.4. Chemical Aging. CHEM aging was carried out by continually exposing the materials to 60 and 110 °C in airtight stainless steel containers (Sanctus Mundo, New York, USA). Water loss was monitored throughout CHEM aging and adjusted to 40% WHC. Prior to aging, batches were sterilized with sodium azide at 1% by water volume from a stock solution of 20 g L⁻¹ in order to kill native microorganisms.

2.5. Physical Aging. For PHYS aging, samples were sterilized as described above and subjected to 42 freeze–thaw cycles between –70 °C (5 h) and +20 °C (19 h).

2.6. Physical and Chemical Analysis. The WHC was determined according to a previous method.³¹ Materials were saturated with Millipore water, allowed to drain freely then dried at 110 °C for 24 h. The measured maximum WHC was the difference in dry and fully saturated weights. The elemental C, N, and O contents were determined at the University of California, Davis, USA with a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (C and N) and a HeKotech HT oxygen analyzer (O). Prior to analysis, samples were dried at 110 °C overnight and ground to a fine powder. Duplicate samples (2–10 mg) were weighed into silver capsules, treated with 60 μL 1 M hydrochloric acid to remove inorganic carbonates and dried at 60 °C overnight before analysis. The elemental H content was determined at the University of Life Sciences, Ås, Norway, using a Leco CHN 1000 and analyzing for H₂O using an infrared method. The ash

Table 1. Elemental Composition, Elemental Ratio, pH, CEC and Measured and Predicted Micropore Surface Area of the Unaged As Well As BIO (Biologically Aged), CHEM 60 (Chemical Aging at 60 °C), CHEM 110 (Chemical Aging at 110 °C) and PHYS (Physical Aging) Aged AC, Biochar, AC + Soil and Biochar + Soil

material	aging regime	C % ^a	O % ^a	H %	N % ^{a,b}	O/C ^c	C/N ^c	pH	CEC mmol _c kg ⁻¹	micropore surface area ^d m ² g ⁻¹	
										measured	predicted ^e
AC	UNAGED	81.2 ± 1.0	8.4 ± 1.8	0.03	0.2 ± 0.03	0.15	117.7	9.6	8	838	
	BIO	75.3 ± 3.8	8.0 ± 0.1	0.14	0.5 ± 0.04	0.17	86.2	6.9	nd ^h	792	
	CHEM 60	78.2 ± 3.5	9.5 ± 1.6	0.13	0.2 ± 0.04	0.17	118.3	7.9	18	838	
	CHEM 110	77.4 ± 2.5	12.2 ± 1.8	0.30	0.2 ± 0.02	0.18	120.3	6.6	54	795	
	PHYS	79.3 ± 4.0	9.3 ± 1.3	0.14	0.2 ± 0.03	0.16	112.8	8.3	100	859	
biochar	UNAGED	41.6 ± 7.5	8.1 ± 3.5	1.5	0.4 ± 0.03	1.43	94.8	9.9	278	178	
	BIO	41.5 ± 4.5	9.1 ± 0.6	1.9	0.9 ± 0.8	0.91	51.6	7.6	272	167	
	CHEM 60	28.0 ± 16.5 ^f	7.3 ± 0.4	1.3	0.3 ± 0.2	1.83	92.6	9.2	299	190	
	CHEM 110	40.6 ± 4.5	8.3 ± 1.4	1.3	0.4 ± 0.03	1.53	96.4	7.0	518	179	
	PHYS	46.0 ± 7.7	7.7 ± 2.1	1.5	0.5 ± 0.1	1.22	96.1	9.9	311	181	
AC + soil	UNAGED	5.4 ± 1.2	8.2 ± 1.2	0.5	0.3 ± 0.02	11.99	27.6	8.5	145	403 ^g	35
	BIO	6.6 ± 0.04	7.7 ± 0.03	0.6	0.4 ± 0.001	11.02	14.5	6.7	130	550 ^g	41
	CHEM 60	7.1 ± 0.7	6.0 ± 1.9	0.5	0.3 ± 0.03	11.97	29.0	7.6	214	472 ^g	40
	CHEM 110	6.3 ± 0.2	5.5 ± 1.7	0.2	0.3 ± 0.004	12.76	27.2	6.4	178	405 ^g	36
	PHYS	6.8 ± 1.4	4.1 ± 0.1	0.5	0.3 ± 0.1	10.54	30.1	7.4	139	460 ^g	39
biochar + soil	UNAGED	3.8 ± 1.1	5.6 ± 0.01	0.6	0.3 ± 0.04	18.30	19.8	7.4	138	122 ^g	21
	BIO	3.9 ± 2.2	4.5 ± 1.9	0.6	0.4 ± 0.1	16.73	10.5	6.9	150	165 ^g	21
	CHEM 60	3.5 ± 0.1	5.6 ± 0.5	0.5	0.3 ± 0.001	22.63	17.0	7.5	124	99 ^g	23
	CHEM 110	3.3 ± 0.01	6.2 ± 0.5	0.4	0.3 ± 0.004	22.75	17.7	5.8	94	137 ^g	24
	PHYS	4.7 ± 0.8	4.9 ± 0.1	0.6	0.3 ± 0.02	17.08	19.8	7.1	140	161 ^g	21
soil	UNAGED	2.4 ± 0.04	5.5 ± 2.0	0.4	0.3 ± 0.003	28.22	12.5	7.0	146	15	
	BIO	2.6 ± 0.1	3.5 ± 0.1	0.6	0.4 ± 0.02	28.78	6.6	6.9	124	13	
	CHEM 60	2.5 ± 0.01	6.5 ± 0.3	0.3	0.3 ± 0.01	31.88	11.5	7.5	105	16	
	CHEM 110	2.0 ± 0.04	6.1 ± 2.7	0.4	0.3 ± 0.01	37.77	10.2	5.8	79	16	
	PHYS	2.7 ± 0.003	6.3 ± 1.2	0.5	0.3 ± 0.01	27.69	12.3	7.5	141	16	

^a Data are shown for the mean ± standard deviation based on duplicate measurements. ^b The high %N may have arisen from the NH₄Cl in the nutrient solution used, however this can only be speculated and the C/N ratios should be viewed with caution. ^c O/C and C/N ratios are atomic ratios.

^d Measured using CO₂ as probe gas. ^e Predicted by summing 95% of the soil surface area and 5% of the BC surface area. ^f Number may not be reliable.

^g Calculated by subtracting the soil surface area from the surface area measured for the AC + soil or biochar + soil mixtures. ^h nd, not detected.

content of the materials was not determined (except for the biochar unaged) and therefore all results represent the values measured via elemental analysis. The pH was measured in water for a 1:2.5 solid weight:water volume ratio.

The potential cation exchange capacity (CEC) was determined by saturating the exchange sites of 1 g of each sample twice with 40 mL of 1 N ammonium acetate solution at pH 7, followed by replacing the adsorbed ammonium ions twice with 2 N KCl. In between this step, the sample was rinsed with isopropyl alcohol. During the CEC measurements the solution and the biochar were contained in a syringe with a thick glass wool filter which was expelled over a period of half a day to remove the solution and leave the biochar. The biochar was not lost from the system in this manner. The biochar and solution were shaken overnight prior to analysis meaning that the hydrophobicity of the biochars did not present a problem in the analysis. Particles did not float. Exchangeable cations in the acetate solution were measured after digesting the samples by treatment with HNO₃, H₂O₂, and HCl and subsequent ICP analysis. The ammonium in the KCl solution was measured using a segmental flow analyzer (Technicon Auto Analyzer, Chauncey, CT, U.S.).

The microporous surface area (SA) was determined using a Quantachrome Autosorb I with CO₂ as the probe gas according to Zimmerman et al.³² This method determines the specific SA of pores with diameters as small as 0.2 nm and because the total surface of biochar has been found to be dominated by internal nanoporosity,³³ CO₂, rather than N₂ was used here to determine the SA. Due to the higher analysis temperature of the CO₂ method (N₂ is at −198 °C) the CO₂ is not kinetically limited in its penetration into smaller nanopores.³⁴ In addition, CO₂ measurements have been correlated to the sorption affinity of organic compounds to biochars²⁵ and so are likely related to possible organic pollutant sorption sites.

2.7. Sorption Experiments. Following aging and mixing with soil, d₁₀ pyrene sorption isotherms spanning 3 orders of magnitude were obtained using a batch passive sampler method at environmentally relevant ng L⁻¹ concentrations. Pyrene contains four rings and is a common pollutant in PAH-contaminated soil and sediment. In addition, a recent study on >300 soils and sediments revealed that pyrene is the optimal PAH for the prediction of total and freely dissolved concentration of other PAHs including PAH-34 alkylated ones.³⁵ However, due to the

difference in the physicochemical properties of the PAHs, their behavior in the environment will be different. The concentration of native pyrene in the biochar, AC and soil was 0.1, 0.02, and 0.005 $\mu\text{g/g}$, respectively. Aged soil and BC (5% BC in 200 mg soil), AC or biochar only (10 mg), or soil only (3 g) were added to 50 mL glass flasks with glass lids. The glass vials were tightly sealed and did not leak during the experiment. Additional unaged systems were prepared using the same respective masses as the aged systems. Millipore water (40 mL) and strips of 55- μm thick polyoxymethylene (POM) passive samplers³⁶ (0.3 g for all batches except soil alone where 0.1 g was used) were added to vials. Prior to use, POM samplers were cleaned by cold extraction overnight in methanol, rinsing thoroughly with Millipore water and then drying. Batches were spiked with 100, 1000, 5000, and 10 000 ng d_{10} pyrene in acetone from stock solutions with concentrations between 1 and 100 $\mu\text{g mL}^{-1}$. The amount of spiked cosolvent did not exceed 1.25% of the water volume and therefore we consider that the cosolvent effect will be minimal in this system.³⁷ The BIO aged and unaged systems were spiked with sodium azide at 1% by water volume from a 20 g L^{-1} stock solution in order to eliminate any possible effect of remaining microorganisms. Flasks were rolled end over end for 1 month at 10 rpm, after which POM samplers were removed, cleaned with Millipore water and wiped with a tissue to ensure they were dry and visibly clean. POM samplers were extracted in 20 mL of 20:80 acetone:heptane for 2 days. A surrogate standard of ^{13}C pyrene was added to the solvent before extraction to monitor process recovery. The recovery was above 70% in all but a few cases and was not corrected for in subsequent analysis. The solvent was reduced to 1 mL and then eluted through a precleaned (5 mL heptane) deactivated silica gel column topped with anhydrous sodium sulfate, using 10 mL of heptane. The solvent was collected and concentrated to less than 1 mL and spiked with PCB 77 as an internal standard for quantification via GCMS.

In order to determine the concentration of d_{10} pyrene sorbed by the materials, a three (POM, water and AC or biochar) or four (POM, water, AC or biochar and soil) phase mass balance was solved for the concentration of d_{10} pyrene on the AC or biochar (C_{AC} or C_{biochar} ng kg^{-1}), either in the absence or the presence of soil (the latter by subtracting the contribution of d_{10} pyrene sorption to the soil), or solved for the d_{10} pyrene concentration on the soil alone. Examples of similar calculation methods are given in ref 38. The soil–water partitioning coefficient (K_d mL g^{-1}) was determined using unaged soil in a similar way to previous reports.^{39,40} K_d values were verified by carrying out Soxhlet extractions (70 mL toluene, 6 h extraction) of 8 of the aged soil samples. There was no significant difference (t test $P > 0.05$) between the K_d values obtained for unaged and aged soil without BC amendment, and thus the K_d values for the unaged soil were used throughout. The pyrene POM–water partitioning coefficient ($\log K_{\text{POM-w}}$ of 4.04 L kg^{-1}) was obtained from Cornelissen et al.³⁶

3. RESULTS AND DISCUSSION

3.1. Physical, Chemical, and Elemental Analysis. Investigating changes in AC and biochar physicochemical properties following mixing with soil and artificial aging could provide information able to explain any trends observed regarding the sorption of pyrene. The results of the elemental composition, pH, cation exchange capacity (CEC), and microporous SA analysis are

shown in Table 1. The aged and unaged AC was dominated by C (around 80% of dw), while the aged and unaged biochar contained approximately half that amount (range from 28 ± 16 to $46 \pm 8\%$). The oxygen content of both BC materials was similar (around 6 to 8%), while the biochar contained around 15 times more H than the AC (1.3 to 1.9% for biochar and 0.03 to 0.30% for AC). All BC samples contained very little N (around 0.3%), although the values increased upon BIO aging (to around 0.5%) for both AC and biochar, possibly reflecting the addition of NH_4Cl contained in the nutrient solution, although this can only be speculated on. The increase in all BIO systems does suggest that this is not an artifact, however. Aging did not affect the elemental composition of AC and biochar with and without soil, with the exception of an increase in H for AC alone following aging (from 0.03 to 0.30%). Oxygen to carbon ratios for AC range from 0.15 to 0.18 and for biochar from 0.91 to 1.83 in all aging regimes. This value for biochar was at the high end of a range reported for many different chars (0.06 to 0.85), while the carbon to nitrogen ratio for this biochar (52 to 96 depending on aging) was consistent with the previously reported range (7 to 500).⁴¹ There was some variability in the O/C ratio for biochar following aging, but no consistent trends were observed. The concentrations of elements important in improving soil fertility (Ca, K, Na, and Mg) are given in Table S1 in the Supporting Information, SI. Biochar was richer in all of these elements than AC, especially K which was a factor 25 higher for biochar. Previous studies on biochars have shown a decrease in C content and increase in O content following natural and artificial abiotic and biotic aging of BC materials.^{19,21–24} Here, the 2 month aging period could have been too short for significant changes to be observed (although as described below this time period could reflect a much longer time in the natural environment) and the lack of water flow through the system means that soluble material will not be lost. Specifically for biochar, the lack of change could be due to the low C content (around 49%) and the high ash content of 69% reported on a dry weight basis which could mask changes in the O/C ratio. The ash content was determined according to ASTM D1762–84 Chemical Analysis of Wood Charcoal. This method may lead to an underestimation of ash due to the volatilization of potassium, phosphorus, and sulfur.

The pH of unaged AC and biochar was highly alkaline (9.61 and 9.91 respectively) and was reduced following aging in most cases and by up to 3 units for the CHEM 110 system. This agrees with studies that exposed wood derived biochar^{22,21} to temperatures up to 70 °C and recorded a reduction in pH compared to unaged controls. The decrease in pH for those samples was accompanied by an increase in surface acidity due to the formation of carboxylic and phenolic functional groups and likely the same phenomenon is occurring here. The soil alone has a neutral pH (6.96 for unaged soil) and it remained largely unchanged when biochar or AC was added.

The cation exchange capacity (CEC) is a measure of the negative charge on the surface of a material that can be neutralized by exchangeable cations. It serves here as a measure of the oxidation of the BCs upon aging and any changes in the value could represent new or additional interaction mechanisms for d_{10} pyrene with the BCs. The most pronounced change in absolute CEC values was observed for the biochar following CHEM 110 aging where it increased from 278 to 518 $\text{mmol}_c \text{ kg}^{-1}$, probably due to oxidation processes creating hydroxy and carboxylic acid functional groups. The other aging regimes did not cause significant alterations in CEC for biochar. The absolute CEC

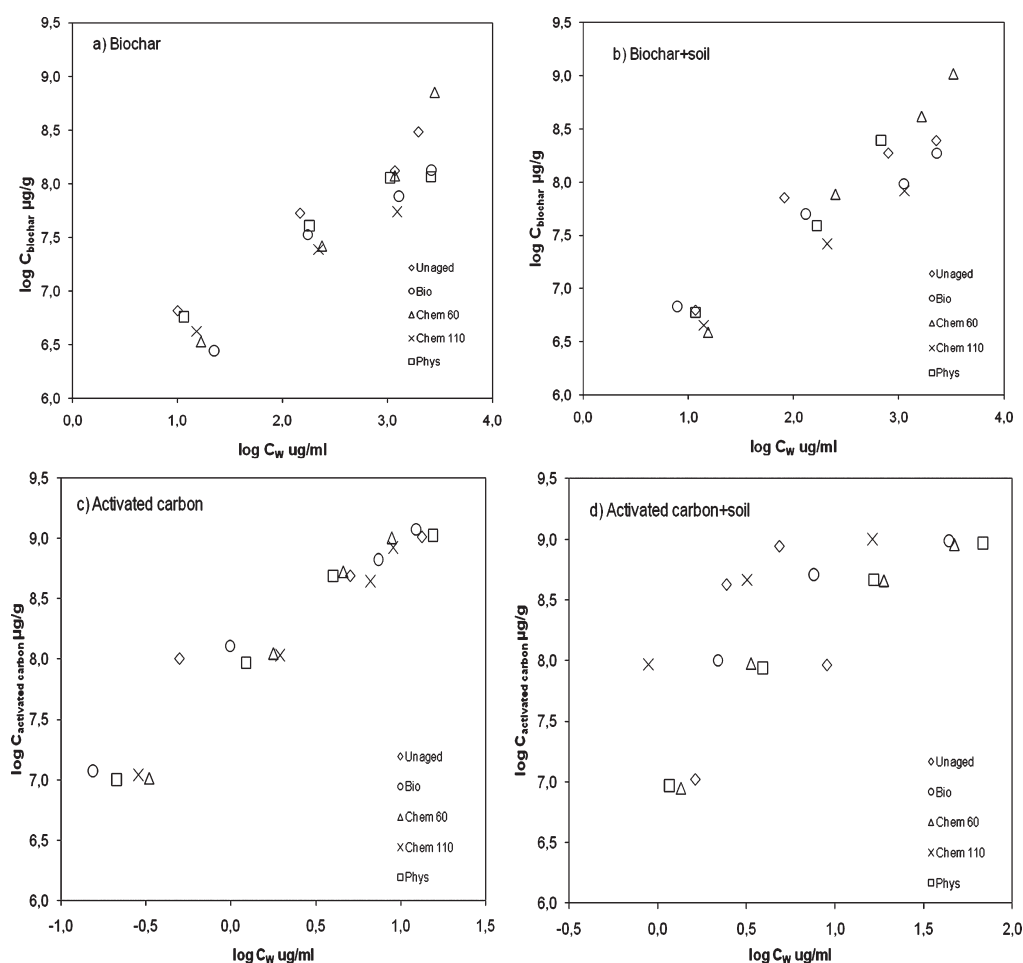


Figure 1. Sorption isotherms of d_{10} pyrene on (a) biochar, (b) biochar + soil, (c) AC and (d) AC + soil for unaged (\diamond), BIO (biological aging, \circ), CHEM 60 (chemical aging at 60°C , Δ), CHEM 110 (chemical aging at 110°C , \times) and PHYS (physical aging, \square) systems. Data are plotted as the concentration of d_{10} pyrene on the BC materials ($\log C_{\text{activated carbon}}$ or $\log C_{\text{biochar}}$), against the freely dissolved aqueous concentration measured by passive samplers ($\log C_w$).

value for AC was much lower than that for biochar, ranging from 9 to $100 \text{ mmol}_c \text{ kg}^{-1}$. The high production temperature of AC compared to biochar may cause a greater loss of volatile components which have been found to carry the acidic functional groups of these materials³³ and hence result in a low CEC. However, the CEC of AC was increased more strongly by aging than that of biochar. PHYS, CHEM 110, and CHEM 60 aging caused increases as high as 92%, 83%, and 50% for AC, compared to 11%, 46%, and 7% for biochar. These increases in CEC are much more striking than the low variability noted for the O/C ratios. CEC has a greater sensitivity for detecting oxidation because it is able to capture changes in surface properties upon aging that are not accompanied by a change in elemental composition, e.g., from ketone to phenolic functional groups.²² Elemental compositions only provide information about bulk properties, many of which are not biogeochemically relevant for how the material interacts with compounds dissolved in the soil solution.

The specific SA of AC was larger than that of biochar (up to $859 \text{ m}^2 \text{ g}^{-1}$ for AC and $190 \text{ m}^2 \text{ g}^{-1}$ for biochar) and upon aging the value generally increased. Table 1 presents the surface area of the AC or biochar in the AC+soil or biochar+soil mixture after correcting for the contribution of the soil, as well as the measured uncorrected value. For AC, these values were between 430 and

$550 \text{ m}^2 \text{ g}^{-1}$ and for biochar they were 99 to $165 \text{ m}^2 \text{ g}^{-1}$ showing that the interaction with soil reduced the SA of both BC materials. This approximately 50% reduction in SA compares well to that reported by Kwon and Pignatello,³⁴ when a char produced from maple wood at 400°C was incubated with lipids to simulate aging. Interestingly, these authors report a factor of 100 decrease in the N_2 determined SA, demonstrating that N_2 and CO_2 probe different pore sizes and thus type of SA and that the size of the probe molecules in addition to the analysis temperature can affect the SA. We note here that BIO aging in the presence of soil caused the smallest SA reduction of both the AC and biochar compared to all other aging regimes. It is hypothesized that the presence of soil facilitates microbial processes that degrade clogging moieties in the biological aging system so that the nanopore system is more accessible.

3.2. Effect of Aging Regime the Sorption of Pyrene to AC and Biochar. The sorption strength of biochar and AC, with and without soil and before and after aging was quantified by constructing four-point sorption isotherms for d_{10} pyrene. Sorption isotherms are shown in Figure 1 and Freundlich coefficients ($K_{\text{Fr}} (\text{ng kg}^{-1})(\text{ng L}^{-1})^{-n_{\text{F}}}$) and Freundlich exponents (n_{F}) are given in Table 2. Logarithmic K_{Fr} values cannot be used to compare the sorption strength due to nonlinear isotherms, and

Table 2. Carbon-Normalized Freundlich Coefficients ($\log K_{Fr} (\text{ng kg}^{-1})(\text{ng L}^{-1})^{-nF}$) and Freundlich Exponents (nF) for Unaged As Well As, BIO (Biologically Aged), CHEM 60 (Chemical Aging at 60 °C), CHEM 110 (Chemical Aging at 110 °C) and PHYS (Physical Aging) Aged AC and Biochar with and without Soil

material	aging regime	$\log K_{Fr} (\text{ng kg}^{-1})(\text{ng L}^{-1})^{-nF}$			nF
		measured (corrected for soil)	measured (BC + soil mixture)	predicted ^a	
AC	UNAGED	8.21 ± 0.01			0.70 ± 0.02
	BIO	7.98 ± 0.06			1.03 ± 0.08
	CHEM 60	7.71 ± 0.04			1.43 ± 0.06
	CHEM 110	7.70 ± 0.04			1.22 ± 0.05
	PHYS	7.83 ± 0.10			1.12 ± 0.13
biochar	UNAGED	6.17 ± 0.18			0.67 ± 0.07
	BIO	5.54 ± 0.35			0.77 ± 0.13
	CHEM 60	5.22 ± 0.38			0.99 ± 0.14
	CHEM 110	5.95 ± 0.12			0.59 ± 0.05
	PHYS	6.21 ± 0.20			0.58 ± 0.08
AC + soil	UNAGED	6.91 ± 0.44	5.53 ± 0.47	6.92	1.68 ± 0.52
	BIO	7.87 ± 0.29	6.57 ± 0.29	6.69	0.73 ± 0.26
	CHEM 60	7.03 ± 0.26	5.73 ± 0.26	6.43	1.22 ± 0.24
	CHEM 110	8.10 ± 0.17	6.80 ± 0.17	6.42	0.80 ± 0.22
	PHYS	7.09 ± 0.23	5.79 ± 0.23	6.55	1.12 ± 0.20
biochar + soil	UNAGED	7.14 ± 0.11	4.95 ± 0.35	5.32	0.38 ± 0.04
	BIO	6.78 ± 0.35	5.35 ± 0.31	5.18	0.42 ± 0.12
	CHEM 60	5.39 ± 0.09	5.36 ± 0.70	5.15	1.02 ± 0.03
	CHEM 110	5.89 ± 0.02	4.57 ± 0.04	5.25	0.66 ± 0.01
	PHYS	5.77 ± 0.33	4.49 ± 0.31	5.33	0.89 ± 0.15
soil	UNAGED	3.53 ± 0.12			0.82 ± 0.04

^a Predicted K_{Fr} values obtained by summing 95% of the soil K_{Fr} and 5% of the AC or biochar K_{Fr} .

thus K_d -values normalized to 1 ng L^{-1} were used for this comparison. These are the same as the K_{Fr} value n units $[(\text{ng kg}^{-1})(\text{ng L}^{-1})^{-nF}]$. The sorption of d_{10} pyrene to AC was 56 to 115 times greater than the sorption to biochar (at an equilibrium concentration of 1 ng L^{-1} ; Figure 1) depending on the aging regime and $\log K_{Fr}$ values were between 7.70 and 8.21 $(\text{ng kg}^{-1})(\text{ng L}^{-1})^{-nF}$ for AC and 5.22 to 6.21 $(\text{ng kg}^{-1})(\text{ng L}^{-1})^{-nF}$ for biochar (Table 2). The larger errors on the $\log K_{Fr}$ values for biochar likely reflect a greater sorption site heterogeneity arising from the inherent heterogeneity of the biochar itself. The values of the Freundlich nonlinearity coefficients nF are generally higher for the AC than for the biochar. For the AC they are around or even above one. The reason for this is probably a lack of competition between pyrene molecules, due to a combination of the low, environmentally relevant concentrations at which the sorption isotherms were measured and the high sorption capacity of the AC. For the biochar, however, nF was significantly below one. This is probably caused by a somewhat larger degree of sorbent saturation compared to AC, due to the lower sorption capacity of unactivated biochar.

It is possible that the difference in sorption capacity between the two BCs could be explained by the larger SA of AC (859 to $792 \text{ m}^2 \text{ g}^{-1}$ for AC and 167 to $190 \text{ m}^2 \text{ g}^{-1}$ for biochar) providing a greater amount of d_{10} pyrene sorption sites. It could also be that the smaller AC particle size (on average $20 \mu\text{m}$ with 80% of particles smaller than $45 \mu\text{m}$), compared to biochar (up to 2 mm) contributed to the different K_{Fr} values. To investigate this latter hypothesis more fully, the unaged biochar was ground to pass through a $75\text{-}\mu\text{m}$ sieve and the sorption isotherm experiment was repeated for this material. The resulting sorption of d_{10} pyrene

was not significantly affected (t test $P > 0.05$) by grinding. The resulting $\log K_{Fr} (\text{ng kg}^{-1})(\text{ng L}^{-1})^{-nF}$ was 5.78 ± 0.13 and n value was 0.80 ± 0.08 . This is corroborated by the results of the CO_2 SA analysis showing ground biochar had a SA of $169 \text{ m}^2 \text{ g}^{-1}$ and unground biochar a SA of $178 \text{ m}^2 \text{ g}^{-1}$, showing that the internal nanoporosity is the main factor determining sorption strength. It therefore seems that grinding does not change the SA and therefore different biochar particle sizes are expected to result in similar remediation effectiveness. Here the surface adsorption of d_{10} pyrene is not affected by particle size and in the context of the production of biochar for use in contaminated soil remediation is positive since both coarse and fine biochar particles could be used. This is the first time such an observation has been made for biochar in the context of sorption. Previously, using charcoal pieces with a diameter of 1 or 20 mm did not affect nutrient uptake or biomass production of cowpea in pot trials⁴² and when applying pieces of 10 mm and $<2 \text{ mm}$ diameter in the field, there was no difference between measured end points.⁴³ However, we note that the difference in particle size may have had an effect on aging, with a smaller particle size being more susceptible to the aging processes.

The K_{Fr} values for unaged AC and biochar are comparable to those reported previously. The \log AC-water partitioning coefficient for pyrene to anthracite-based AC was reported as 8.5 L kg^{-1} ¹² while the sorption of pyrene on soot, charcoal, and coal was less strong with $\log K_{BC}$ values between 5.71 and 6.95 L kg^{-1} .¹³ The \log Freundlich coefficients for the sorption of naphthalene and phenanthrene to pine-needle based biochar produced between 100 and 700°C were between 2.34 and 5.09 and 3.98 to 5.12 L kg^{-1} , respectively.¹⁷ James et al.¹⁸ report \log

Freundlich coefficients for the sorption of phenanthrene on natural chars in the range of 5.04 to 6.11 L kg⁻¹. It is clear that partitioning coefficients are highly dependent on BC source and production method and the concentration range at which the sorption experiment is carried out (the above experiments being carried out in the concentration range from 1 to 30 000 ng L⁻¹).

Unaged soil had the lowest sorption capacity for d₁₀ pyrene of all materials tested (log K_{Fr} 3.53 ± 0.12; Table 2). The sorption affinity of d₁₀ pyrene to AC alone was 15 000 to 48 000 times higher than the sorption to soil alone and for biochar alone was 50 to 500 times higher. This was not unexpected and is in agreement with previous studies in which wheat and rice based biochars were found to be 400 to 10 000 times more effective in sorbing diuron than soil.^{20,44,45} By adding 5% AC or biochar to the soil, the sorption capacity of the combined matrix also increased: 2400 to 37 000 and 70 to 4000 times compared to the sorption to soil alone, respectively. Previously, adding 0.1 to 5% eucalyptus biochar to soil increased the soil's sorption capacity for diuron 5 to 125 times.⁴⁶ In addition, *Pinus radiata* biochar produced at 350 and 700 °C and added to soil at a 0.5% dose increased the soil's sorption of phenanthrene 45 and 723 times compared to unamended soil.⁴⁷ Our observations suggest that both BCs hold promise as soil amendments able to enhance the soil's sorption of PAHs. The way the PAH contamination has entered the soil will largely influence how successful a remediation strategy based on biochar or AC will be. Especially in situations where PAHs are bioavailable and not strongly bound to BC, sorbent amendment is expected to be effective. This is highly likely in areas where industrial activity has resulted in pollutant concentrations that are present above those that can be sequestered by native BC.

Aging in the manners used here had variable effects on the sorption of d₁₀ pyrene by AC or biochar with and without soil. A statistical analysis of the K_{Fr} values was carried out by considering each isotherm point as an individual measurement giving four values for the statistical analysis to be carried out on. Results show that aging had no significant effect on the sorption of d₁₀ pyrene to AC alone or AC + soil (*t* test *P* > 0.05), which is not unexpected for such an inert material. In contrast, for biochar without soil both BIO and CHEM 110 aging changed the sorption (*t* test *P* < 0.05) and for biochar with soil CHEM 110 aging changed the sorption (*t* test *P* < 0.05). From the CEC analysis, it was observed that aging did cause a development of surface functional groups, especially for AC. It is thus observed that hydrophobic sorption of d₁₀ pyrene was not significantly influenced by the creation of some extra exchange sites on the surface of the BCs. Apparently, the extent of oxidation induced by our harsh aging conditions was not enough to diminish the hydrophobic interactions between d₁₀ pyrene and AC, and between d₁₀ pyrene and biochar for the PHYS and CHEM 60 systems. Changes in CEC may not play a major role in influencing the sorption of PAHs directly, although if over time changes in the biochar or AC CEC influence the conditions in the soil or sediment (as has been noted previously^{21,48}) this will indirectly affect sorption. The inclusion of additional data points in the isotherms may have improved the robustness of our results, however the overriding message that we present here; that sorption is little affected by aging or the presence of soil, would not change. Here we focus on characterizing two materials very thoroughly rather than using several more materials.

The observed limited effects of harsh aging on sorption are encouraging in the context of contaminated soil remediation as

the long-term sorption of pyrene to BCs appears to be relatively unaffected. This is supported by previous observations, where sorption of PCBs to AC was maintained after 5 years of field AC-sediment contact¹⁶ and where the sorption of simazine to biochar aged in the field for 2 years was the same as that to fresh biochar.⁴⁹ Although two months of harsh laboratory aging cannot replicate the natural environment, exposing the materials to elevated temperatures is likely to have increased the rate of any reactions that occur in the natural environment. For a reaction with an activation enthalpy of around 70 kJ mol⁻¹, increasing the reaction temperature by 10 °C from room temperature causes an increase in the reaction rate by a factor of 2. The decomposition of organic matter in sediment has been reported to be in the range of 54 to 125 kJ mol⁻¹, with most values between 50 and 90 kJ mol⁻¹.^{50–53} If similar processes were occurring during aging of AC and biochar, increasing the temperature to 60 or 110 °C for two months for CHEM aging would correspond to an approximately two and four orders of magnitude, respectively, increase in the reaction rate and could thus represent approximately 100 to 20 000 years of aging at a continuous temperature of 10 °C, respectively. However, there are ways in which this type of laboratory aging cannot simulate the natural environment, for example through possible effects of photodegradation, solubilization via water leaching (flow through), and macrofauna and flora processes. Fouling by microbially produced organic matter, which is one of the most important potential surface-altering processes, may or may not have been generated by the conditions provided by the BIO aging. As mentioned in the Introduction, previous work investigating the sorption of hydroquinone²¹ and diuron²⁰ to biochar following aging have reported a reduction in sorption.

3.3. Reduction in Sorption Capacity of AC and Biochar in the Presence of Soil. Mixing AC or biochar into soil may result in a reduction in the sorption capacity of the AC or biochar caused by the blockage of pollutant sorption sites by natural dissolved organic matter (NDOM) or other anthropogenic contaminants in the soil (so-called sorption attenuation). To assess fouling, we compare both the specific SA and K_{Fr} values in the presence and absence of soil. Table 1 shows values for the SA of the soil + BC mixtures predicted by summing 95% of the measured soil SA and 5% of the measured AC or biochar SA. For AC + soil, the predicted value is greater than the measured value suggesting when AC is mixed with soil, the soil causes an attenuation in the sorption of target pollutants. For biochar + soil, the predicted values are the same or slightly higher, implying that the sorption of target pollutants to biochar does not suffer such a great reduction in the presence of soil. In the same manner, Table 2 shows predicted K_{Fr} values obtained by summing 95% of the soil K_{Fr} and 5% of the AC or biochar K_{Fr}. These values can be compared to those measured for the BC + soil mixture. For AC + soil, the predicted value is larger than the measured value in all cases except for CHEM 110 aging and for biochar + soil predicted is larger in all cases except for BIO and CHEM 60 (however, some of these measured values have large standard deviations).

Table 2 also shows the measured values corrected for soil, i.e., just considering the sorption of d₁₀ pyrene to the BC material. Mixing AC with soil results in a lower K_{Fr} value (again with the exception of CHEM 110) by an average factor of 8. This reduction in the sorption capacity of AC upon mixing with soil agrees with previous studies.^{2,34,38,54} Results for biochar show that the presence of soil does not statistically significantly

increase the sorption capacity of biochar and suggests, in agreement with the SA results, that soil exerts a minimal effect on the sorption to biochar. Other authors have reported a decrease in the sorption capacity of biochar when it was mixed with NDOM,²⁰ humic acid,²¹ and soil.¹⁷ The difference in the pore size of the AC and biochar could be an explanation for this (although this was not measured directly).

4. ENVIRONMENTAL RELEVANCE

Biochar may be a suitable material to add to contaminated soil in order to immobilize contaminants in the same way AC is currently used. Although biochar does not have as strong a sorption capacity as AC, we demonstrated in the present study that the biochar sorption capacity was not affected to a great extent by the presence of soil and/or harsh aging, despite some observed changes in physicochemical properties. In agricultural applications, biochar may also be added in several consecutive growing cycles and in such a scenario, aging with time would become less important. In comparison to anthracite AC, the source material and production process for biochar is likely less costly. In addition, biochar amendment to soil provides the additional benefits of carbon sequestration⁴¹ and soil fertility improvement.⁵⁵ Despite the stronger sorption capacity of AC, its use could result in an overall negative environmental impact when considered in the context of a full life cycle assessment.⁵⁶ Thus, from an overall environmental perspective, biochar could be preferable to AC for the remediation of contaminated soil. It is important to be aware that biochars can display variable physicochemical properties and therefore their environmental behavior can be very different. In that respect, although a probably representative biochar was used, extending the results of this work directly to other biochars should be done with great caution, especially for lower temperature biochars that could be less stable and less sorbing than our currently used biochar. Caution should also be exercised when extending the conclusions of the sorption isotherms to different sorbent concentration ranges, especially lower temperature biochars that could be less stable and less sorbing than our currently used biochar. In the future, different biochars should be tested for their ability in environmental remediation and differences in suitability should be related to the inherent nature of the biochar. In addition an emphasis on optimization for adsorption of contaminants by changing production conditions and feedstock properties should be investigated.

■ ASSOCIATED CONTENT

S Supporting Information. Concentrations of elements important in improving soil fertility (Ca, K, Na, and Mg) are given in Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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