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Solvent-Extractable Polycyclic Aromatic Hydrocarbons in Biochar: Influence of Pyrolysis Temperature and Feedstock

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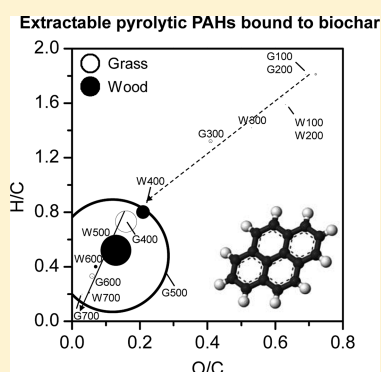
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S Supporting Information

ABSTRACT: Despite the increasing agricultural use of biochar as a way of combining the utilization of biomass for energy production with the removal of CO₂ from the atmosphere, it is not known how variations in pyrolysis temperature and feedstock type affect concentration and composition of polycyclic aromatic hydrocarbons (PAHs) that inevitably form and associate with biochar. To close this knowledge gap, we quantified 11 unsubstituted three- to five-ring PAHs as well as alkylated forms of phenanthrene and anthracene in grass and wood chars produced in 100 °C increments across a temperature range (100 to 700 °C). Our results show that solvent-extractable PAH concentrations in biochars produced at heat treatment temperatures (HTTs) of 400 and 500 °C greatly exceed those observed at higher and lower temperature, supporting a low HTT solid-phase formation mechanism operable at temperatures commonly used for industrial biochar production. The maximum extractable yield of 'pyrolytic' unsubstituted PAHs for grass (22 μg g⁻¹ at HTT = 500 °C) greatly exceeds the value for wood (5.9 μg g⁻¹). Moreover, PAH signatures (e.g., total monomethylphenanthrene to phenanthrene ratios, MP/P ~2–3) at intermediate temperatures (400 °C) resemble those of fossil oils rather than that commonly attributed to pyrolytic products. Further research is needed to characterize the PAH evolution in modern pyrolysis reactors and assess the fate of biochar-bound PAHs in soils and sediments. Various commonly applied PAH ratios and indicator compounds show promise as markers for specific feedstock materials and pyrolysis conditions of biochars in environmental systems.



INTRODUCTION

Charred residues produced by incomplete combustion (or pyrolysis) of plant biomass are important natural constituents of soils and sediments.^{1,2} In recent years, the biochar strategy has been proposed as a way of combining utilization of biomass for energy production with the removal of CO₂ from the atmosphere by using the residual chars as a fertility enhancing soil amendment.^{3,4} The application of biochar to soil and sedimentary systems ideally serves three purposes: (i) long-term sequestration of carbon (C), (ii) fertilization and/or remediation of soils and sediments, and (iii) biomass waste management. To avoid unintended consequences of biochar applications and to allow for the implementation of sustainable practices, it is necessary to determine concentrations and signatures of polycyclic aromatic hydrocarbons (PAHs) associated with biochars (termed sorbed PAHs here) produced under a range of pyrolysis conditions and from structurally different starting materials.

Pyrolysis of biomass is known to produce a wide variety of low and high molecular weight (LMW and HMW, respectively) PAHs depending on the biomass type, pyrolysis conditions, and kinetic factors (e.g., gas circulation).^{5–7} Many of these PAHs

are classified as Priority Pollutants and are heavily regulated by the US EPA due to their carcinogenic, mutagenic or teratogenic properties.⁸ PAHs resulting from natural combustion events, such as forest fires, and from anthropogenic activities, such as wood processing and general industrial activities, are some of the most widespread pollutants in soils and sediments.^{9–11} Substantial concentrations of sorbed PAHs in biochar are of concern because of their longevity and the potential impact on human and environmental health.

One of the main EPA risk assessment tests is based on the assumption that toxicity to soil and sediment organisms is directly proportional to the amount of available PAHs in porewater.⁸ PAHs tend to partition readily into natural organic carbon phases in soil and sediments^{12–14} and are therefore perceived as partially inert on short time scales. However, recent evidence indicates that PAHs do bioaccumulate in plants over time.^{15,16} To develop sustainable management schemes for

Received: May 30, 2012

Revised: July 26, 2012

Accepted: July 30, 2012

Published: July 30, 2012



large-scale biochar operations in soil and sedimentary systems, we need to know the extent that biochar serves as a carrier for sorbed PAHs formed during the pyrolysis process.

The mechanisms by which pyrolytic production of PAHs occur are complex and have been widely studied since the 1950s (see refs 5 and 6 for references). Unsubstituted (or parent) PAH compounds are produced via two principal pathways during biomass pyrolysis:

- (1) At temperatures $<500\text{ }^{\circ}\text{C}$, PAH formation proceeds via unimolecular cyclization, dehydrogenation, dealkylation, and aromatization of ligneous and cellulosic plant biopolymers as well as lipids such as resins and steroids.⁶ This process eliminates functionalities in the native compounds (as H_2O , CO_2 , CH_4 , H_2S , etc.), leaving behind aromatized (i.e., oxidized) structures. For example, resinous substances, such as abietic and pimaric acids, common in softwood, undergo dehydrogenation to retene (1-methyl-7-isopropylphenanthrene) and pimaranthrene (1,7-dimethylphenanthrene).^{17–19} These alkyl-substituted PAHs then undergo direct nuclear condensation preferentially across the alkyl group with further cyclization.⁶
- (2) At temperatures $>500\text{ }^{\circ}\text{C}$, PAHs form through a free radical pathway followed by pyrosynthesis into larger aromatic structures.^{6,20} In pyrolysis (the primary reaction), organic compounds are partially cracked to small unstable radicals (e.g., ethynyl, $\text{HC}\equiv\text{C}^{\bullet}$ and 1,3-butadiene radicals, $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{C}^{\bullet}\text{H}$). This step is followed by pyrosynthesis (or secondary reaction) in which these radicals fuse into unsubstituted and thermodynamically more stable low-molecular weight (LMW) parent PAH such as naphthalene.²¹ With increasing temperature and residence time, these LMW PAHs have been proposed to grow via the “zig-zag addition process” into tertiary HMW PAHs such as the more toxic benzo[a]pyrene and benzo[g,h,i]perylene.²² In this scheme, ring addition occurs through a sequence of four and two C atom additions to ring positions with the highest π -electron density. These tertiary pyrolysis products are thought to become significant at temperatures $>650\text{ }^{\circ}\text{C}$.^{23,24}

In the past, research on biomass-derived pyrolytic PAH yields and compositions has been concerned mostly with toxic airborne PAHs such as those found in wood stove smoke,^{18,25} traffic soot,^{26,27} and volatile tars^{23,28} associated with tobacco combustion (e.g. refs 28 and 29). Despite the current interest in biochar as a soil and sediment amendment, surprisingly little is known about the concentration and composition of PAHs that sorb to the solid matrix during pyrolysis. Ledesma et al.³⁰ and Masek et al.³¹ reported that large amounts of PAHs are created at temperatures greater than $700\text{ }^{\circ}\text{C}$. Most biochar pyrolysis facilities operate at heat treatment temperatures (HTT) of 400 to $600\text{ }^{\circ}\text{C}$, and thus the risk associated with PAHs has been considered negligible. However, Brown et al.³² found the highest concentration of solvent-extractable PAHs in biochars produced between 400 and $500\text{ }^{\circ}\text{C}$, Kloss et al.³³ detected higher concentration of PAHs such as phenanthrene between 400 and $450\text{ }^{\circ}\text{C}$ than at HTT of $525\text{ }^{\circ}\text{C}$, and Hauteville et al.³⁴ found high yields of various (alkylated) PAHs at lower temperatures ($<300\text{ }^{\circ}\text{C}$). The latter were primarily LMW PAHs, but some HMW PAHs, e.g. benzo[a]pyrene, were also formed.^{28,29} Our own X-ray spectroscopy and diffraction

results³⁵ led us to suspect substantial PAH levels in biochars produced by low to mid temperature ($300\text{--}500\text{ }^{\circ}\text{C}$) pyrolysis. In addition to pyrolysis temperature, the type of feedstock biomass appears to be a factor influencing the concentration and composition of PAHs present in the biochar matrix. A recent survey of PAH levels in 50 different biochars showed that concentrations in biochar produced from corn stover were up to four times greater than for coconut shells or sawdust.³⁶

Thus, it appears that two concerns related to PAH bioaccumulation in soils and sediments as a result of biochar application need to be addressed: (1) The total yields and composition of PAHs in biochars produced at low and mid temperature (HTT = $300\text{--}500\text{ }^{\circ}\text{C}$) must be determined, and (2) the feedstocks most likely to produce biochar with higher PAH levels need to be identified. The resulting principal objective of this work is to provide a qualitative and quantitative assessment of PAHs associated with biochars produced from wood and grass biomass across a range of HTT. For this purpose, we quantified eleven 3- to 5-ring EPA priority pollutant PAH homologues (anthracene, phenanthrene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[fluoranthene], benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and benzo[g,h,i]perylene) by gas chromatography – mass spectrometry (GC-MS) in biochars produced across a well-characterized char temperature series³⁵ from Ponderosa Pine wood and Tall Fescue grass. The related retene, alkylated (mono-, di-, and trimethylated) phenanthrenes and anthracenes were also determined to gain additional insight into the formation mechanisms and pathways of PAHs and to provide data for improvement of retrospective PAH source allocations in environments affected by anthropogenic or natural (e.g., wildfire-derived black carbon) inputs of charred biomass.

MATERIALS AND METHODS

Char Preparation. Grass (Tall Fescue straw, lignin-poor) and wood (Ponderosa Pine wood, lignin-rich) biochars were produced via pyrolysis under oxygen-limited conditions in $100\text{ }^{\circ}\text{C}$ increments across a temperature range from 100 to $700\text{ }^{\circ}\text{C}$ as described previously³⁵ and prepared for solvent-extractions as detailed in the Supporting Information.

Hydrocarbon Extraction. Grass and wood chars (100 mg) were spiked with a solution containing three perdeuterated standards (d_{10} -phenanthrene, d_{10} -fluoranthene, d_{12} -benzo[a]pyrene). A contact time of 20 min was allowed before the chars were extracted with a 1:1 toluene/methanol mixture ($3 \times 10\text{ mL}$ each) using a Dionex accelerated solvent extraction (ASE) system ($100\text{ }^{\circ}\text{C}$ and 1000 psi). Toluene-methanol was shown to be the most efficient solvent mixture for extraction of PAH from soot³⁷ – a carbonaceous sorbent with properties similar to biochar – and was thus chosen as the extraction solvent for this study. The combined extraction solution was then partitioned into hexane ($3 \times 10\text{ mL}$) after addition of deionized water (10 mL). Combined hexane fractions were washed against a 50% saturated, aqueous NaCl solution and subsequently dried overnight over anhydrous Na_2SO_4 granules. The hexane was then evaporated to $\sim 1\text{ mL}$ using a Zymark Turbopap and subsequently just to dryness under a gentle stream of prepurified nitrogen gas. The resultant total extractable lipid (TEL) residue from each sample was separated by column chromatography on silica gel into an aliphatic hydrocarbon, a PAH, and a polar fraction (e.g., ref 38).

PAH Identification and Quantification. PAH extracts were analyzed by selective ion monitoring using a HP5890A gas

Table 1. Polycyclic Aromatic Hydrocarbon Concentration (ng/g^a) in Char Temperature Series as Identified by Gas Chromatography-Mass Spectrometry

| biochar | compounds | abbrev | heat treatment temperature (°C) | | | | | | |
|---------|-----------------------------|---------|---------------------------------|-----|-------|-------|-------|------|-----|
| | | | 100 | 200 | 300 | 400 | 500 | 600 | 700 |
| grass | phenanthrene | PHEN | 17 | 23 | 48 | 986 | 5320 | 203 | 74 |
| | anthracene | ANT | 4 | 2 | 5 | 384 | 1300 | 17 | |
| | 3-methylphenanthrene | 3MP | 2 | 2 | 4 | 335 | 445 | 6 | 5 |
| | 2-methylphenanthrene | 2MP | 3 | 2 | 10 | 720 | 757 | 8 | 5 |
| | 2-methylanthracene | 2MA | | | | 441 | 160 | | |
| | 4- and 9-methylphenanthrene | 4MP/9MP | 1 | 1 | 6 | 560 | 197 | 5 | |
| | 1-methylphenanthrene | 1MP | 1 | 1 | 6 | 613 | 333 | 4 | |
| | 1,7-dimethylphenanthrene | 1,7DMP | | | 4.1 | 837 | 281 | 2 | 10 |
| | fluoranthene | FLUO | 3 | 5 | 72 | 512 | 2081 | 103 | 21 |
| | pyrene | PYR | 3 | 6 | 242 | 689 | 2150 | 236 | 24 |
| | retene | RET | 2 | 3 | 48 | 99 | 11 | 6 | 10 |
| | benz[a]anthracene | BaA | 1 | 2 | 28 | 246 | 1150 | 16 | 7 |
| | chrysene | CHRY | 10 | 401 | 216 | 608 | 1210 | 124 | 6 |
| | benzofluoranthenes | BFs | 2 | | 5 | 229 | 4030 | 148 | 19 |
| | benzo[e]pyrene | BeP | 2 | 1 | 6 | 294 | 2150 | 85 | 18 |
| | benzo[a]pyrene | BaP | | 2 | | 165 | 976 | 21 | |
| | indeno[1,2,3-cd]pyrene | INPYR | | | | 179 | 1540 | 25 | |
| | benzo[ghi]perylene | BPERY | | | 3 | 155 | 1210 | 32 | |
| | ΣPAH ^b | | 50 | 452 | 916 | 15520 | 30200 | 1040 | 190 |
| | ΣCOMB ^c | | 21 | 416 | 572 | 3080 | 16500 | 789 | 95 |
| | ΣPHEN ^d | | 25 | 33 | 339 | 11600 | 12200 | 232 | 95 |
| | ΣDMP | | | | 109 | 5860 | 4630 | | |
| | ΣTMP | | | | 107 | 2450 | 505 | | |
| | TOC (wt%) | | 49 | 47 | 60 | 77 | 82 | 89 | 94 |
| wood | phenanthrene | PHEN | 29 | 41 | 63 | 840 | 2080 | 191 | 46 |
| | anthracene | ANT | | 4 | | 94 | 294 | 14 | 6 |
| | 3-methylphenanthrene | 3MP | 2 | 4 | 3 | 204 | 161 | 5 | |
| | 2-methylphenanthrene | 2MP | 3 | 6 | 3 | 619 | 319 | 5 | |
| | 2-methylanthracene | 2MA | | | | 81 | 47 | | |
| | 4- and 9-methylphenanthrene | 4MP/9MP | | 3 | 4 | 303 | 94 | 6 | |
| | 1-methylphenanthrene | 1MP | | 4 | 11 | 1107 | 212 | 5 | |
| | 1,7-dimethylphenanthrene | 1,7DMP | | 4 | 723 | 6120 | 165 | 3 | |
| | fluoranthene | FLUO | 7 | 12 | 7 | 175 | 315 | 55 | 12 |
| | pyrene | PYR | 29 | 25 | 11 | 296 | 639 | 95 | 18 |
| | retene | RET | 31 | 134 | 7280 | 4960 | 8 | 9 | 8 |
| | benz[a]anthracene | BaA | 2 | 2 | 21 | 203 | 389 | 19 | 43 |
| | chrysene | CHRY | 24 | 92 | 99 | 462 | 509 | 131 | 239 |
| | benzofluoranthracenes | BFs | 1 | 3 | 2 | 162 | 590 | 121 | |
| | benzo[e]pyrene | BeP | 2 | 2 | 2 | 211 | 595 | 80 | |
| | benzo[a]pyrene | BaP | | | 1 | 82 | 203 | 15 | |
| | indeno[1,2,3-cd]pyrene | INPYR | | | | 60 | 260 | 24 | |
| | benzo[ghi]perylene | BPERY | | | | 76 | 297 | 26 | |
| | ΣPAH ^b | | 130 | 332 | 12000 | 26600 | 8030 | 801 | 373 |
| | ΣCOMB ^c | | 66 | 137 | 143 | 1730 | 3800 | 566 | 313 |
| | ΣPHEN ^d | | 65 | 191 | 11900 | 24700 | 3900 | 221 | 54 |
| | ΣDMP ^e | | | | 1150 | 9950 | 851 | | |
| | ΣTMP ^e | | | | 3340 | 6760 | 169 | | |
| | TOC (wt%) | | 51 | 51 | 55 | 74 | 82 | 89 | 92 |

^aConcentrations are expressed in ng PAH per g biochar. ^bSum of total PAHs and their methylated derivatives. ^cSum of 'pyrolytic' PAHs without methylated derivatives. ^dSum of phenanthrene and its methylated derivatives. ^eSum of dimethylated (DMP) and trimethylated (TMP) phenanthrenes.

chromatograph interfaced to a HP5971 benchtop mass spectrometer. PAH separations were accomplished using a 100% methylsilicone capillary column (J&W DB1 - 30 m × 0.32 mm i.d.; 0.25 μm film thickness) with helium as the carrier gas and temperature programming (100–270 at 5 °C/min, 270–310 at 3 °C/min, and isothermal hold at 310 °C for 25

min). Just prior to analysis, each PAH fraction was dissolved in a specific volume of iso-octane (50 μL) containing a known concentration of d₁₂-chrysene. Individual PAH were detected using the response of the mass-to-charge (*m/z*) ratio corresponding to their molecular weight. Quantification was accomplished by an internal standard method using the

response factor (RF, ng/area) for d_{12} -chrysene determined on each run of the GC-MS and the response factor of each PAH to d_{12} -chrysene (RRF) determined for all unsubstituted PAH using a composite external standard. In the case of all alkylated phenanthrenes, the RRF determined for unsubstituted parent PAH (phenanthrene) was assumed to apply. The formula used to calculate PAH concentration (ng/g biochar) was

$$[\text{PAH, ng/g}] = \text{RRF} \times \text{RF} \times \text{areaPAH} \times \text{dilution volume} / \text{wt}/\% \text{reco}$$

where dilution volume is the volume of iso-octane used to dissolve the PAH fraction relative to the volume of this solution injected on the GC-MS, wt is the mass (g) of biochar analyzed, and %reco is the percentage of perdeuterated standard added to each sample that is quantified analytically. The latter term is assumed to provide a measure of extraction efficiency for specific PAHs.

Extraction efficiency was based on recoveries for the set of perdeuterated PAH standards (d_{10} -phenanthrene, d_{10} -fluoranthene, d_{12} -benzo[a]pyrene) spiked into the biochars prior to sample extraction by ASE and subsequent chemical workup. Details on the standards used to correct the recovery of the specific compounds and on extraction recoveries of all standards can be found in the Supporting Information.

RESULTS AND DISCUSSION

Total PAH Yields Across the Temperature Range.

Table 1 lists concentrations of unsubstituted 3- to 6-ring PAHs and alkylated phenanthrene and anthracene homologues extracted from both the grass and wood biochar temperature series. All biochar samples analyzed here contained measurable PAH quantities albeit spanning a wide range of concentrations. Total yields of the identified PAHs including the methylated derivatives (ΣPAH) are small between 100 and 200 °C, increase at 300 °C, show a maximum at 500 °C (grass) and 400 °C (wood), and decrease from 500 to 700 °C (grass) and 400 to 700 °C (wood). The observed concentration range across the temperature series is remarkably similar for grass (0.05–30.2 $\mu\text{g g}^{-1}$) and wood biochar (0.13–26.6 $\mu\text{g g}^{-1}$). However, ΣPAH maxima occur at different temperatures for the grass and wood biochar. The maximum for wood biochar occurs at 400 °C where ΣPAH exceeds that of grass biochars by a factor of 2, whereas maximum ΣPAH in grass biochar occurs at higher HTT (500 °C) and exceeds ΣPAH of wood biochars by a factor of ~ 3.7 .

While the yield of total extractable PAHs (ΣPAH) is similar for grass and wood biochars across the range of HTTs, there are significant differences in the PAH composition. The most abundant PAHs extracted from grass biochar are CHRY and PYR at 300 °C, PHEN, various MPs and PYR at 400 °C, and PHEN and benzo[fluoranthrenes (BFs) at 500 °C (Table 1). In wood biochar, 1,7DMP and RET dominate the PAHs at 300–400 °C with a significant contribution from other MPs, while PHEN dominates at 500 °C. Alkylated derivatives (specifically, methylated PHEN and ANT as well as RET) contribute more to the total yield (ΣPAH) in wood than in grass biochar (Table 1).

Maximum concentrations of individual extractable PAHs with known carcinogenic, mutagenic, and teratogenic properties (BaA, CHRY, BFs, BaP, and BPERY) range from 0.5 to 8.6 $\mu\text{g g}^{-1}$. The highest yields are extracted from grass and wood biochars produced at 500 °C (8.6 and 1.8 $\mu\text{g g}^{-1}$, respectively).

These concentrations are higher than previously reported for wood and straw biochar (0.07 and 0.12 $\mu\text{g g}^{-1}$), in the same range as that for chimney soot (8 $\mu\text{g g}^{-1}$), and significantly lower than that for diesel soot and urban dust (29 $\mu\text{g g}^{-1}$).³⁹

It appears that the largest amounts of PAHs of particular environmental and human health concern are extracted at temperatures falling within the preferred range used for large-scale biochar production. Considering the strong capacity of biochars to act as a sorbent for PAHs,⁴⁰ this situation might not be a major problem. However, it has been shown that individual biochar components become oxidized, both biotically and abiotically, once the biochars enter soils and sediments.^{41,42} Hockaday et al.⁴³ demonstrated transport of char-derived substituted PAHs through soil into freshwater systems, and Rey-Salgueiro⁴⁴ conclude that a related material - wood ash - can be considered "stable PAHs reservoirs for long [times], which continuously release low levels of PAHs to runoff waters". It remains to be shown how physical and chemical weathering processes or microbial degradation alter the sorptive capacity of biochar over time and thus the retention of sorbed PAHs.

Characterization of 'Pyrolytic' (Unsubstituted) PAHs Across the Temperature Range. The evolution of extractable 'pyrolytic' PAHs (ΣCOMB) is shown in Figure 1.

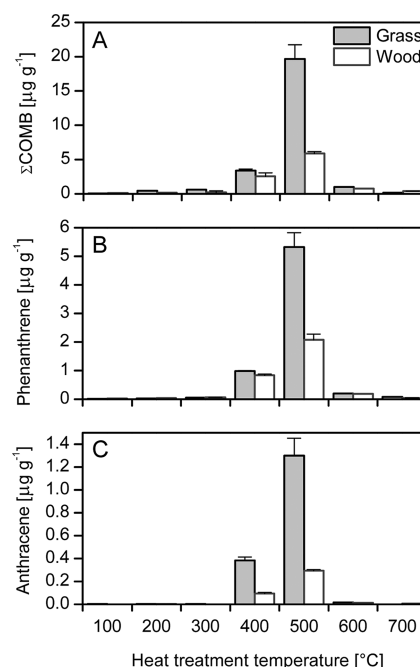


Figure 1. (A) Total concentrations of characteristic pyrolytic PAHs (ΣCOMB = sum of FLUO, PYR, BaA, CHRY, BFs, BeP, BaP, INPYR, and BPERY) across the 100–700 °C heat treatment temperature (HTT) range; (B) total phenanthrene; and (C) anthracene concentrations for comparison. Error bars represent the standard deviation of two replicate extractions.

Typical 'pyrolytic' or combustion origin PAHs are represented by the sum of nine major combustion specific compounds (ΣCOMB) which include FLUO, PYR, BaA, CHRY, BFs, BeP, BaP, INPYR, and BPERY³⁸ (see Table 1 for definition of abbreviations). Figure 1A shows the evolution of ΣCOMB extracted from wood and grass chars across the entire temperature range. For both plant materials, ΣCOMB is low at HTT < 300 °C, increases substantially at 400 °C, and is

greatest in biochars produced at 500 °C. The relative contribution of 5- to 6-ring PAHs gradually increases relative to 2- to 4-ring PAHs as HTT increases from 300 to 500 °C (Figure 1-SI) consistent with a loss of LMW PAH according to volatility in this pyrolysis experiment.

The extractable yield of Σ COMB is much different on a per g concentration basis for grass relative to wood. The maximum for grass biochar ($21.8 \mu\text{g g}^{-1}$ at 500 °C) exceeds that of wood biochar ($5.87 \mu\text{g g}^{-1}$) by a factor of ~ 3.7 . Notably, concentrations of Σ COMB are comparable or even higher than those for similar sets of parent PAHs in rural and urban soils. Nam et al.⁹ found levels for a similar range of PAHs from 0.042 to $11.2 \mu\text{g g}^{-1}$ (mean of $0.640 \mu\text{g g}^{-1}$) and 0.009 to $1.05 \mu\text{g g}^{-1}$ (mean of $0.15 \mu\text{g g}^{-1}$) in soils across the UK and Norway, respectively, resulting largely from natural forest fires. Urban soils near industrial areas⁴⁵ show concentrations for a similar suite of PAHs to range from 0.09 to $4.5 \mu\text{g g}^{-1}$.

Figures 1B and 1C show how the evolution of extractable PHEN and ANT across the biochar temperature series mimics that of pyrolytic PAHs, i.e., highest yields at 500 °C and distinctly higher yields for grass than for wood biochars. This pattern indicates that 3-ring PHEN and ANT serve as precursors for 4- and 5-ring segments of 'pyrolytic' PAHs. Linear regression analysis of the Σ COMB data reveals a linear relationship between Σ COMB yield and PHEN concentration ($R^2_{\text{grass}} = 0.997$ and $R^2_{\text{wood}} = 0.999$). The slope of the regression line for wood biochars ($[\text{PHEN}] = 0.367 \pm 0.007 \times [\Sigma\text{COMB}] - 43.1 \pm 18.1$) is significantly ($p < 0.005$) greater than that of grass biochar ($[\text{PHEN}] = 0.246 \pm 0.003 \times [\Sigma\text{COMB}] - 33.8 \pm 22.9$). On this basis, the quantitative relationship between PHEN and Σ COMB is different for grass and wood. Further investigation is required to determine if this relationship provides a robust predictor for pyrolytic PAH evolution during the process of production from different feedstocks.

Despite these quantitative differences, signatures of 'pyrolytic' PAH of grass and wood biochar show very similar compositional patterns at HTTs of 400 and 500 °C (Figure 2-SI). Only minor variations are seen for FLUO, PYR, and BFs. However, there are both quantitative and qualitative differences in the methylated fraction (see below).

The observation that Σ COMB yields in grass and wood biochars are greatest at pyrolysis temperatures of 500 °C, with substantially lower yields at higher or lower temperatures, indicates that pyrolytic PAH production occurs in a relatively narrow temperature window. To relate Σ COMB yields to structural information of the biochars, the evolution of these combined, unsubstituted PAH yields was plotted as a function of H/C and O/C elemental ratios of both grass and wood biochars across the 100–700 °C heat treatment temperature (HTT) range (Figure 2). H/C and O/C atomic ratios of both biochars follow the trajectory associated with dehydration reactions.³⁵ The most dramatic loss of H and O occurs between 300 and 500 °C. At 300 °C, the biochars are subjected to initial dehydration and depolymerization reactions (loss of H and O containing functional groups) that form small, volatile dissociation products.^{35,46} At 400 and 500 °C, however, an 'amorphous' biochar phase comprised of volatile, low-molecular weight aliphatics and aromatic compounds (such as PAHs) that arise from the thermal transformation of lignin and cellulose is formed.³⁵ This amorphous phase is thought to consist of intermediates such as pyranones, anhydro sugars, phenols, quinones, pyrroles, and furans as well as small (poly)aromatic units and thermally more stable aromatic lignin residues.^{35,47}

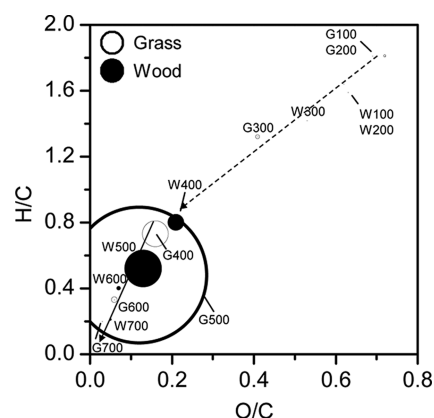


Figure 2. Van Krevelen diagram showing the evolution of H/C and O/C elemental ratios for both grass and wood biochars across the 100–700 °C heat treatment temperature (HTT) range. The total area of the circles represents the relative concentration of characteristic pyrolytic PAHs (Σ COMB = sum of FLUO, PYR, BaA, CHRY, BFs, BeP, BaP, INPYR, and BPERY) recovered from grass (GXOO) and wood (WXOO) biochars produced at the indicated HTT. H/C and O/C values are taken from ref 35. O/C and H/C values for materials produced between HTTs of 100 and 400 °C follow the dehydration line (dashed arrow). At higher HTTs, more H is lost relative to O, indicating that H-stripping (aromatization) becomes a more significant process.

Our results show that the formation of this amorphous biochar phase at 400 and 500 °C coincides with the highest Σ COMB yields. At higher HTT, this amorphous phase (or volatile matter) is increasingly removed from the biochar matrix,³⁵ and the extractable yield of pyrolytic PAHs declines accordingly.

Characterization of Methylphenanthrenes Across the Temperature Range. The ratio of methylphenanthrenes to phenanthrene (MP/P) is commonly used to distinguish pyrogenic from petrogenic sources of PAHs.^{11,48} MP/P ratios present in combustion residues are generally less than 1 and typically range from 2 to 6 in unburned fossil fuel mixtures.⁴⁹ Figure 3A shows that the MP/P ratios determined for grass and wood biochar produced at HTT of 400 °C range from 2 to 3, values that are noted characteristically in crude oils.⁵⁰

The PAH composition and, particularly, MP/P ratios within soils and sediments is thought to reflect the source(s) from which the PAHs were derived. Our results indicate that PAHs in the amorphous biochar phase observed at 400 °C have molecular signatures similar to that of unburned fossil materials (i.e., crude oil) and do not resemble typical 'pyrolytic' products.^{17,49} This finding suggests that both natural and deliberate inputs of grass and wood biochars produced at this HTT have the potential to shift the 'source' signatures of natural PAHs in soils and sediments toward a more fossil-like signature.

Changing Molecular Signatures of Methylated Phenanthrenes. The molecular signatures of extractable mono-, di-, and trimethylated phenanthrenes (MP, DMP, and TMP) and their parent PAH (PHEN) at 400 and 500 °C provide additional insights into the PAH formation pathways in grass and wood biochars. Figure 4 shows large variation in the amounts of MP, DMP, and TMP extracted from grass and wood biochar generated at 400 °C. The chromatograms of grass biochar feature a more diverse set of DMP and TMP peaks than observed in wood biochars. However, the chemical

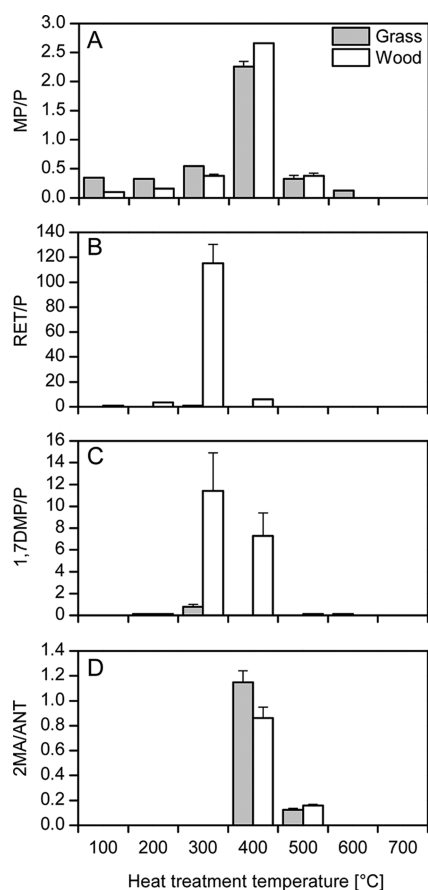


Figure 3. Concentrations of extractable (A) total MPs, (B) RET, (C) 1,7DMP, and (D) 2-MA shown relative to their parent PAHs (PHEN and ANT, respectively) extracted from grass and wood biochars across the 100–700 °C heat treatment temperature (HTT) range. Error bars represent the standard deviation of two replicate extractions.

fingerprints change significantly at a HTT of 500 °C, with chromatograms becoming quite similar.

Figure 5 compares the abundance of extractable MP, DMP, and TMP relative to their parent PHEN in biochars produced at 400 and 500 °C. Wood biochars produced at 400 °C show a continuous increase in the order of MP < DMP < TMP. At 500 °C, however, this trend is reversed, and relative yields decline in the order of MP ~ DMP > TMP. Such a pattern could be explained by continuous stripping (i.e., elimination) of methyl groups from methylated phenanthrenes to form PHEN as temperatures increase from 400 to 500 °C. An alternative explanation is that cracking reactions may generate free radicals (i.e., free radical pathway) that subsequently fuse into the thermodynamically more stable PHEN (i.e., pyrosynthesis).

A similar trend can be observed for grass biochars, with the exception that DMP yields are far greater at both temperatures. If DMP were excluded, a general shift from TMP to MP could be observed as temperature increases from 400 to 500 °C, indicating increasing demethylation as for the case of wood biochars.

Evolution of Retene, 1,7-Dimethylphenanthrene, and 2-Methylantracene Across the Temperature Range. Comparison of yields for alkylated phenanthrenes to their respective parent PHEN provides insights into PAH formation pathways during pyrolysis. Coniferous wood, such as Ponderosa pine used for this study, contains diterpenoid resins – most

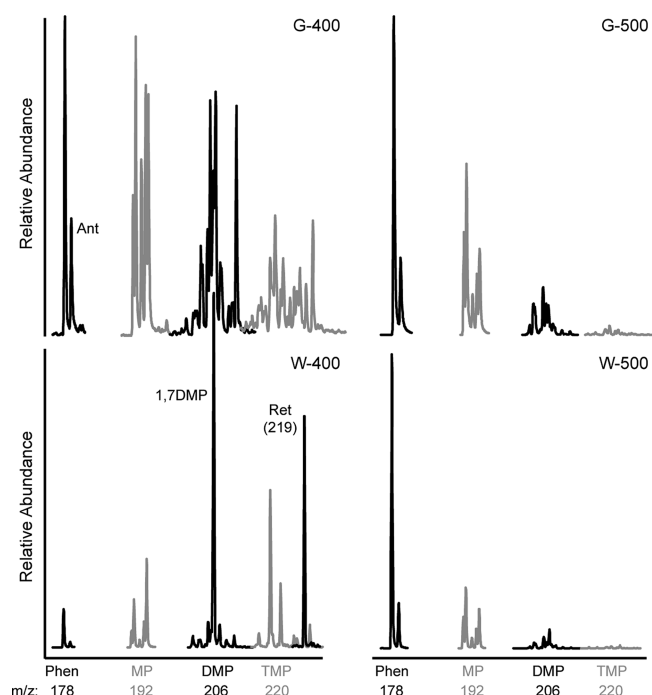


Figure 4. Chromatograms of monomethylated phenanthrenes (MP), dimethylated phenanthrenes (DMP), and trimethylated phenanthrenes (TMP) and their parent PAH phenanthrene (PHEN) extracted from grass and wood chars produced at HTTs of 400 and 500 °C. Peak inserts for ANT and RET are given for comparison.

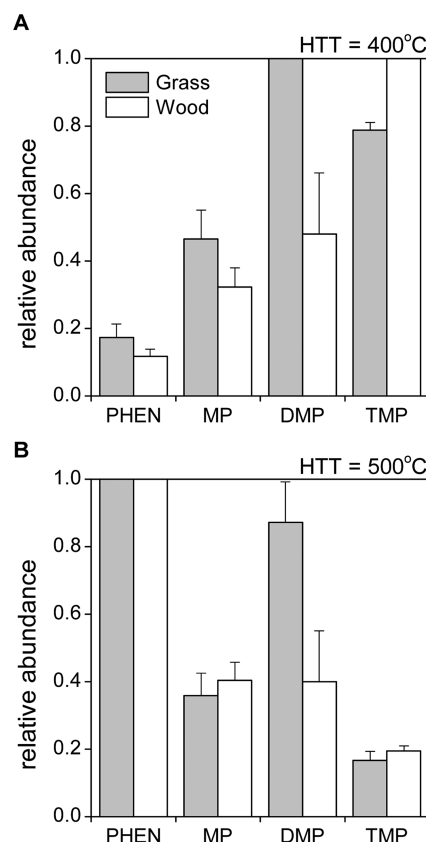


Figure 5. Relative abundance of mono-, di-, and trimethylated phenanthrenes in wood and grass biochars produced at heat treatment temperatures (HTTs) of (A) 400 °C and (B) 500 °C. Ratios in each plot were normalized to the highest value.

notably abietic and dehydroabietic acids.⁶ Pyrolysis of these resins within the wood is known to promote demethylation, decarboxylation, and aromatization reactions to form aromatic alteration products, namely pimarane (1,7DMP) and retene (RET).¹⁸ Accordingly, we observed the highest contents of 1,7DMP ($6.12 \mu\text{g g}^{-1}$) and RET ($7.28 \mu\text{g g}^{-1}$) in wood biochars (Table 1). Figure 3 shows the abundance of 1,7DMP and RET relative to their parent PHEN for wood biochars formed at HTT of 300 °C. Negligible amounts of extractable 1,7DMP and RET are created during the pyrolysis of grass biomass and in wood biochars produced below 300 °C. Values for 1,7DMP/PHEN and RET/PHEN ratios dramatically decline at 500 °C, suggesting complete demethylation and formation of the parent PAHs at this temperature.

Analysis of methylated PAH homologues shows that the formation of 1,7DMP and RET from resinous precursors in wood is greatest at HTT of 300 and 400 °C and that transformation of these intermediates into the respective parent PAHs appears to be completed at HTT > 400 °C. Extracted yields of 1,7DMP are comparable to values reported for soot generated during pine wood combustion.²⁵ Although the presence of 1,7DMP in air particulates has long been known (e.g., ref 25), our results suggest that 1,7DMP detected in soil, sediment, and aqueous systems may also originate from the biochar residue of vegetation fires in forests ecosystems. Our yields of extractable RET are also in line with reports from other authors. Brown et al.³² found RET concentrations of $3.6 \mu\text{g g}^{-1}$ in wood biochars produced at 450 °C and negligible amounts at higher temperatures. Hauteville et al.³⁴ report the highest abundance of RET at 280 °C. The combined evidence confirms that RET represents a molecular marker for low-temperature pyrolysis of coniferous wood.¹⁸ Many vegetation fires have maximum ground temperatures ranging from 250 to 400 °C.^{51,52} Together this evidence suggests that the RET abundance can help to distinguish engineered biochars pyrolyzed at higher temperatures from biochars (or black carbon) produced during natural wildfires in coniferous forests.

2MA, another abundant methylated PAH, shows the greatest relative abundance at 400 °C in both wood and grass biochars (Figure 3D). 2MA appears to form at slightly higher HTTs than 1,7DMP and RET. Conversion of 2-MA to its parent compound ANT is most obvious at HTT of 500 °C as indicated by the drop in the 2-MA/ANT ratio and appears to be completed at 600 °C. In contrast to 1,7DMP and RET, 2MA is formed during the pyrolysis process of both wood and grass feedstocks (Figure 3D). In addition, the linear 3-ring arrangement of 2MA does not have a structurally similar natural precursor among resinous compounds. The origin and formation pathways of 2MA in pyrolysis products are not very well understood, but our results indicate that (i) 2MA formation is independent of feedstock and (ii) the aromatic backbone of 2-MA is created by nuclear condensation reactions of smaller free radicals, rather than by stripping reactions of a natural 3-ring precursor molecule. 2-MA may thus serve as a molecular marker for the onset of nuclear condensation reactions at low-to-mid temperature pyrolysis conditions that is equally applicable to grass and wood biochars.

Environmental Implications. In summary, our results demonstrate that total yield and composition of PAHs associated with the biochars analyzed here are strongly dependent upon feedstock material and pyrolysis temperature. While grass biochar contained significantly higher levels of PAHs than wood biochar, the highest concentration of

extractable PAHs occurred in both feedstocks when they were subjected to HTTs between 400 and 500 °C. This finding is consistent with the presence of an amorphous phase of highly aromatic, low-MW pyrolysis products detected with spectroscopic methods at this charring stage (6). More importantly, it will represent a regulatory hurdle for the potential use of these biochars as a soil amendment. Maximum allowable concentrations for biosolids considered for the application to agricultural land are $6 \mu\text{g g}^{-1}$ according to the U.S. EPA⁵³ and 3–6 $\mu\text{g g}^{-1}$ in E.U. countries.⁵⁴ In the case of wood ash, which is commonly used as a forest soil fertilizer, recommended PAH concentration in the ash should not exceed $2 \mu\text{g g}^{-1}$.^{55,56} Both wood and grass biochars produced at HTTs between 400 and 500 °C in our study greatly exceed these values, a result that is in good agreement with the findings by Kloss et al.³³ It is noteworthy that these biochars were stored for a 6-month period before PAHs extraction and analysis. Chemical reactions induced by chemically modified or ‘aged’ biochar surfaces^{57,58} likely reduced the amount of solvent-extractable PAH due to the oxidation of surface-adsorbed PAHs during storage. For this reason, PAH concentrations measured in our chars represent minimum values. Conversely, we expect that freshly pyrolyzed biochars are carriers of even higher loads of sorbed PAHs and suggest that robust quality control measures should be taken before biochars are applied to soil.

HTT \geq 600 °C minimize concentrations of extractable PAHs, possibly due to volatilization of the amorphous phases, nuclear condensation into larger, nonextractable sheets,³⁵ and/or the strong sorptive retention by the more condensed biochar phases.⁴⁰ High-temperature biochars thus appear to be more suitable for soil application as they (i) minimize the risk of adding biochar-derived PAHs and (ii) have great capacity to immobilize PAHs present in the soil.

Our results also show that MP/P values measured in grass biochars at HTTs of 400 °C are very similar to those measured in fossil oils. This similarity indicates that the amorphous organic phase, often operationally termed ‘volatile matter’, has molecular PAH signatures more similar to unburned, diagenetic fossil materials than that commonly considered typical of high temperature ‘pyrolytic’ products.

Wood biochar produced at HTTs between 300 and 400 °C showed the highest yields of 1,7DMP and RET. While RET has long been known as a molecular marker for wood smoke,¹⁸ our results establish that it can also serve as an indicator for coniferous biochars generated by low-temperature pyrolysis. For example, analysis of the RET concentrations (both absolute and relative to ΣCOMB PAH concentrations) in charred materials left behind after wildfires in coniferous forests may yield information about fire intensity (less RET with higher temperature burns).^{59,60} Finally, RET concentration could be a useful criterion to assess the quality of engineered biochar produced from coniferous wood.

■ ASSOCIATED CONTENT

📄 Supporting Information

Details on pyrolysis procedures, storage conditions, and PAH quantification. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank OSU undergraduates, Sara Anthony and Emery Collins, for valuable assistance in the laboratory. This work was supported by the Department of Crop and Soil Science and Subsurface Biosphere Initiative (both Oregon State University) start-up funds to M. Kleber and the Coastal Margin Observation and Prediction (CMOP) Science and Technology Center funds for education and research to F. G. Prahl.

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