

1 Solvent-Extractable Polycyclic Aromatic Hydrocarbons in Biochar: 2 Influence of Pyrolysis Temperature and Feedstock

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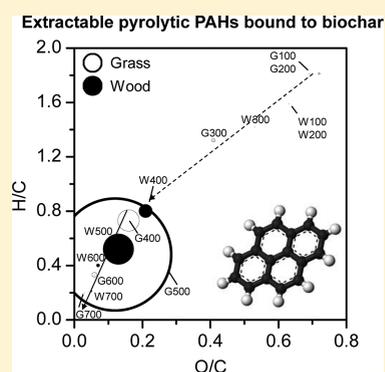
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9 **S** Supporting Information

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



28 ■ INTRODUCTION

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

46 Pyrolysis of biomass is known to produce a wide variety of
47 low and high molecular weight (LMW and HMW, respectively)
48 PAHs depending on the biomass type, pyrolysis conditions, and
49 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

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

70 The mechanisms by which pyrolytic production of PAHs
71 occur are complex and have been widely studied since the
72 1950s (see refs 5 and 6 for references). Unsubstituted (or
73 parent) PAH compounds are produced via two principal
74 pathways during biomass pyrolysis:

- 75 (1) At temperatures <500 °C, PAH formation proceeds via
76 unimolecular cyclization, dehydrogenation, dealkylation,
77 and aromatization of ligneous and cellulosic plant
78 biopolymers as well as lipids such as resins and steroids.⁶
79 This process eliminates functionalities in the native
80 compounds (as H₂O, CO₂, CH₄, H₂S, etc.), leaving
81 behind aromatized (i.e., oxidized) structures. For
82 example, resinous substances, such as abietic and pimaric
83 acids, common in softwood, undergo dehydrogenation to
84 retene (1-methyl-7-isopropylphenanthrene) and piman-
85 threne (1,7-dimethylphenanthrene).^{17–19} These alkyl-
86 substituted PAHs then undergo direct nuclear con-
87 densation preferentially across the alkyl group with
88 further cyclization.⁶
- 89 (2) At temperatures >500 °C, PAHs form through a free
90 radical pathway followed by pyrosynthesis into larger
91 aromatic structures.^{6,20} In pyrolysis (the primary
92 reaction), organic compounds are partially cracked to
93 small unstable radicals (e.g., ethynyl, HC≡C• and 1,3-
94 butadiene radicals, H₂C=CH-CH=C•H). This step is
95 followed by pyrosynthesis (or secondary reaction) in
96 which these radicals fuse into unsubstituted and
97 thermodynamically more stable low-molecular weight
98 (LMW) parent PAH such as naphthalene.²¹ With
99 increasing temperature and residence time, these LMW
100 PAHs have been proposed to grow via the “zig-zag
101 addition process” into tertiary HMW PAHs such as the
102 more toxic benzo[a]pyrene and benzo[g,h,i]perylene.²²
103 In this scheme, ring addition occurs through a sequence
104 of four and two C atom additions to ring positions with
105 the highest π -electron density. These tertiary pyrolysis
106 products are thought to become significant at temper-
107 atures >650 °C.^{23,24}

108 In the past, research on biomass-derived pyrolytic PAH
109 yields and compositions has been concerned mostly with toxic
110 airborne PAHs such as those found in wood stove smoke,^{18,25}
111 traffic soot,^{26,27} and volatile tars^{23,28} associated with tobacco
112 combustion (e.g. refs 28 and 29). Despite the current interest in
113 biochar as a soil and sediment amendment, surprisingly little is
114 known about the concentration and composition of PAHs that
115 sorb to the solid matrix during pyrolysis. Ledesma et al.³⁰ and
116 Masek et al.³¹ reported that large amounts of PAHs are created
117 at temperatures greater than 700 °C. Most biochar pyrolysis
118 facilities operate at heat treatment temperatures (HTT) of 400
119 to 600 °C, and thus the risk associated with PAHs has been
120 considered negligible. However, Brown et al.³² found the
121 highest concentration of solvent-extractable PAHs in biochars
122 produced between 400 and 500 °C, Kloss et al.³³ detected
123 higher concentration of PAHs such as phenanthrene between
124 400 and 450 °C than at HTT of 525 °C, and Hauteville et al.³⁴
125 found high yields of various (alkylated) PAHs at lower
126 temperatures (<300 °C). The latter were primarily LMW
127 PAHs, but some HMW PAHs, e.g. benzo[a]pyrene, were also
128 formed.^{28,29} Our own X-ray spectroscopy and diffraction

results³⁵ led us to suspect substantial PAH levels in biochars 129
produced by low to mid temperature (300–500 °C) pyrolysis. 130
In addition to pyrolysis temperature, the type of feedstock 131
biomass appears to be a factor influencing the concentration 132
and composition of PAHs present in the biochar matrix. A 133
recent survey of PAH levels in 50 different biochars showed 134
that concentrations in biochar produced from corn stover were 135
up to four times greater than for coconut shells or sawdust.³⁶ 136

Thus, it appears that two concerns related to PAH 137
bioaccumulation in soils and sediments as a result of biochar 138
application need to be addressed: (1) The total yields and 139
composition of PAHs in biochars produced at low and mid 140
temperature (HTT = 300–500 °C) must be determined, and 141
(2) the feedstocks most likely to produce biochar with higher 142
PAH levels need to be identified. The resulting principal 143
objective of this work is to provide a qualitative and quantitative 144
assessment of PAHs associated with biochars produced from 145
wood and grass biomass across a range of HTT. For this 146
purpose, we quantified eleven 3- to 5-ring EPA priority 147
pollutant PAH homologues (anthracene, phenanthrene, fluo- 148
ranthene, pyrene, benz[a]anthracene, chrysene, benzofluoran- 149
thenes, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, and 150
benzo[g,h,i]perylene) by gas chromatography – mass spec- 151
trometry (GC-MS) in biochars produced across a well- 152
characterized char temperature series³⁵ from Ponderosa Pine 153
wood and Tall Fescue grass. The related retene, alkylated 154
(mono-, di-, and trimethylated) phenanthrenes and anthracenes 155
were also determined to gain additional insight into the 156
formation mechanisms and pathways of PAHs and to provide 157
data for improvement of retrospective PAH source allocations 158
in environments affected by anthropogenic or natural (e.g., 159
wildfire-derived black carbon) inputs of charred biomass. 160

161 ■ MATERIALS AND METHODS

Char Preparation. Grass (Tall Fescue straw, lignin-poor) 162
and wood (Ponderosa Pine wood, lignin-rich) biochars were 163
produced via pyrolysis under oxygen-limited conditions in 100 164
°C increments across a temperature range from 100 to 700 °C 165
as described previously³⁵ and prepared for solvent-extractions 166
as detailed in the Supporting Information. 167

Hydrocarbon Extraction. Grass and wood chars (100 mg) 168
were spiked with a solution containing three perdeuterated 169
standards (d₁₀-phenanthrene, d₁₀-fluoranthene, d₁₂-benzo[a]- 170
pyrene). A contact time of 20 min was allowed before the chars 171
were extracted with a 1:1 toluene/methanol mixture (3 × 10 172
mL each) using a Dionex accelerated solvent extraction (ASE) 173
system (100 °C and 1000 psi). Toluene-methanol was shown 174
to be the most efficient solvent mixture for extraction of PAH 175
from soot³⁷ – a carbonaceous sorbent with properties similar 176
to biochar – and was thus chosen as the extraction solvent for 177
this study. The combined extraction solution was then 178
partitioned into hexane (3 × 10 mL) after addition of 179
deionized water (10 mL). Combined hexane fractions were 180
washed against a 50% saturated, aqueous NaCl solution and 181
subsequently dried overnight over anhydrous Na₂SO₄ granules. 182
The hexane was then evaporated to ~1 mL using a Zymark 183
Turbovap and subsequently just to dryness under a gentle 184
stream of prepurified nitrogen gas. The resultant total 185
extractable lipid (TEL) residue from each sample was separated 186
by column chromatography on silica gel into an aliphatic 187
hydrocarbon, a PAH, and a polar fraction (e.g., ref 38). 188

PAH Identification and Quantification. PAH extracts 189
were analyzed by selective ion monitoring using a HP5890A gas 190

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		
	∑PAH ^b		50	452	916	15520	30200	1040	190	
	∑COMB ^c		21	416	572	3080	16500	789	95	
	∑PHEN ^d		25	33	339	11600	12200	232	95	
	∑DMP				109	5860	4630			
	∑TMP				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		
∑PAH ^b			130	332	12000	26600	8030	801	373	
∑COMB ^c			66	137	143	1730	3800	566	313	
∑PHEN ^d		65	191	11900	24700	3900	221	54		
∑DMP ^e				1150	9950	851				
∑TMP ^e				3340	6760	169				
TOC (wt%)		51	51	55	74	82	89	92		

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

191 chromatograph interfaced to a HP5971 benchtop mass
192 spectrometer. PAH separations were accomplished using a
193 100% methylsilicone capillary column (J&W DB1 - 30 m ×
194 0.32 mm i.d.; 0.25 μm film thickness) with helium as the carrier
195 gas and temperature programming (100–270 at 5 °C/min,
196 270–310 at 3 °C/min, and isothermal hold at 310 °C for 25

min). Just prior to analysis, each PAH fraction was dissolved in 197
a specific volume of iso-octane (50 μL) containing a known 198
concentration of d₁₂-chrysene. Individual PAH were detected 199
using the response of the mass-to-charge (*m/z*) ratio 200
corresponding to their molecular weight. Quantification was 201
accomplished by an internal standard method using the 202

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

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

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

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

224 ■ RESULTS AND DISCUSSION

225 Total PAH Yields Across the Temperature Range.

226 Table 1 lists concentrations of unsubstituted 3- to 6-ring PAHs
 227 and alkylated phenanthrene and anthracene homologues
 228 extracted from both the grass and wood biochar temperature
 229 series. All biochar samples analyzed here contained measurable
 230 PAH quantities albeit spanning a wide range of concentrations.
 231 Total yields of the identified PAHs including the methylated
 232 derivatives (Σ PAH) are small between 100 and 200 °C,
 233 increase at 300 °C, show a maximum at 500 °C (grass) and 400
 234 °C (wood), and decrease from 500 to 700 °C (grass) and 400
 235 to 700 °C (wood). The observed concentration range across
 236 the temperature series is remarkably similar for grass (0.05–
 237 30.2 $\mu\text{g g}^{-1}$) and wood biochar (0.13–26.6 $\mu\text{g g}^{-1}$). However,
 238 Σ PAH maxima occur at different temperatures for the grass and
 239 wood biochar. The maximum for wood biochar occurs at 400
 240 °C where Σ PAH exceeds that of grass biochars by a factor of 2,
 241 whereas maximum Σ PAH in grass biochar occurs at higher
 242 HTT (500 °C) and exceeds Σ PAH of wood biochars by a
 243 factor of ~ 3.7 .

244 While the yield of total extractable PAHs (Σ PAH) is similar
 245 for grass and wood biochars across the range of HTTs, there
 246 are significant differences in the PAH composition. The most
 247 abundant PAHs extracted from grass biochar are CHRY and
 248 PYR at 300 °C, PHEN, various MPs and PYR at 400 °C, and
 249 PHEN and benzofluoranthrenes (BFs) at 500 °C (Table 1). In
 250 wood biochar, 1,7DMP and RET dominate the PAHs at 300–
 251 400 °C with a significant contribution from other MPs, while
 252 PHEN dominates at 500 °C. Alkylated derivatives (specifically,
 253 methylated PHEN and ANT as well as RET) contribute more
 254 to the total yield (Σ PAH) in wood than in grass biochar (Table
 255 1).

256 Maximum concentrations of individual extractable PAHs
 257 with known carcinogenic, mutagenic, and teratogenic proper-
 258 ties (BaA, CHRY, BFs, BaP, and BPERY) range from 0.5 to 8.6
 259 $\mu\text{g g}^{-1}$. The highest yields are extracted from grass and wood
 260 biochars produced at 500 °C (8.6 and 1.8 $\mu\text{g g}^{-1}$, respectively).

These concentrations are higher than previously reported for 261
 wood and straw biochar (0.07 and 0.12 $\mu\text{g g}^{-1}$), in the same 262
 range as that for chimney soot (8 $\mu\text{g g}^{-1}$), and significantly 263
 lower than that for diesel soot and urban dust (29 $\mu\text{g g}^{-1}$).³⁹ 264

It appears that the largest amounts of PAHs of particular 265
 environmental and human health concern are extracted at 266
 temperatures falling within the preferred range used for large- 267
 scale biochar production. Considering the strong capacity of 268
 biochars to act as a sorbent for PAHs,⁴⁰ this situation might not 269
 be a major problem. However, it has been shown that 270
 individual biochar components become oxidized, both biotically 271
 and abiotically, once the biochars enter soils and sediments.^{41,42} 272
 Hockaday et al.⁴³ demonstrated transport of char-derived 273
 substituted PAHs through soil into freshwater systems, and 274
 Rey-Salgueiro⁴⁴ conclude that a related material - wood ash - 275
 can be considered “stable PAHs reservoirs for long [times], 276
 which continuously release low levels of PAHs to runoff 277
 waters”. It remains to be shown how physical and chemical 278
 weathering processes or microbial degradation alter the sorptive 279
 capacity of biochar over time and thus the retention of sorbed 280
 PAHs. 281

Characterization of ‘Pyrolytic’ (Unsubstituted) PAHs 282
Across the Temperature Range. The evolution of 283
 extractable ‘pyrolytic’ PAHs (Σ COMB) is shown in Figure 1. 284

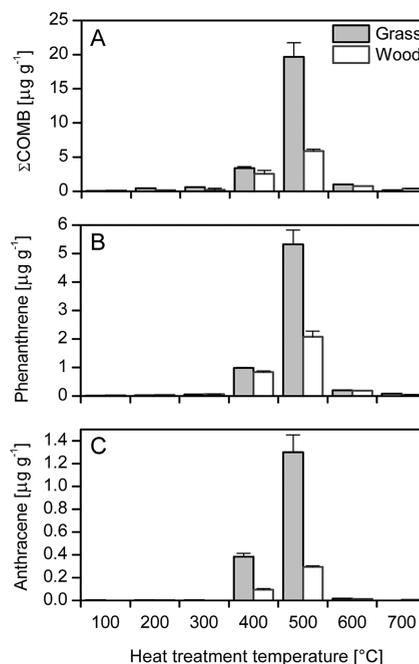


Figure 1. (A) Total concentrations of characteristic pyrolytic PAHs (Σ COMB = sum of FLUO, PYR, BaA, CHRY, BFs, BeP, BaP, INPYR, and BPERY) across the 100–700 °C heat treatment temperature (HTT) range; (B) total phenanthrene; and (C) anthracene concentrations for comparison. Error bars represent the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

Typical ‘pyrolytic’ or combustion origin PAHs are represented 285
 by the sum of nine major combustion specific compounds 286
 (Σ COMB) which include FLUO, PYR, BaA, CHRY, BFs, BeP, 287
 BaP, INPYR, and BPERY³⁸ (see Table 1 for definition of 288
 abbreviations). Figure 1A shows the evolution of Σ COMB 289
 extracted from wood and grass chars across the entire 290
 temperature range. For both plant materials, Σ COMB is low 291
 at HTT < 300 °C, increases substantially at 400 °C, and is 292

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

298 The extractable yield of Σ COMB is much different on a per
 299 g concentration basis for grass relative to wood. The maximum
 300 for grass biochar (21.8 $\mu\text{g g}^{-1}$ at 500 °C) exceeds that of wood
 301 biochar (5.87 $\mu\text{g g}^{-1}$) by a factor of ~ 3.7 . Notably,
 302 concentrations of Σ COMB are comparable or even higher
 303 than those for similar sets of parent PAHs in rural and urban
 304 soils. Nam et al.⁹ found levels for a similar range of PAHs from
 305 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
 306 $\mu\text{g g}^{-1}$ (mean of 0.15 $\mu\text{g g}^{-1}$) in soils across the UK and
 307 Norway, respectively, resulting largely from natural forest fires.
 308 Urban soils near industrial areas⁴⁵ show concentrations for a
 309 similar suite of PAHs to range from 0.09 to 4.5 $\mu\text{g g}^{-1}$.

310 Figures 1B and 1C show how the evolution of extractable
 311 PHEN and ANT across the biochar temperature series mimics
 312 that of pyrolytic PAHs, i.e., highest yields at 500 °C and
 313 distinctly higher yields for grass than for wood biochars. This
 314 pattern indicates that 3-ring PHEN and ANT serve as
 315 precursors for 4- and 5-ring segments of 'pyrolytic' PAHs.
 316 Linear regression analysis of the Σ COMB data reveals a linear
 317 relationship between Σ COMB yield and PHEN concentration
 318 ($R^2_{\text{grass}} = 0.997$ and $R^2_{\text{wood}} = 0.999$). The slope of the regression
 319 line for wood biochars ($[\text{PHEN}] = 0.367 \pm 0.007 \times [\Sigma\text{COMB}]$
 320 $- 43.1 \pm 18.1$) is significantly ($p < 0.005$) greater than that of
 321 grass biochar ($[\text{PHEN}] = 0.246 \pm 0.003 \times [\Sigma\text{COMB}] - 33.8$
 322 ± 22.9). On this basis, the quantitative relationship between
 323 PHEN and Σ COMB is different for grass and wood. Further
 324 investigation is required to determine if this relationship
 325 provides a robust predictor for pyrolytic PAH evolution during
 326 the process of production from different feedstocks.

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

333 The observation that Σ COMB yields in grass and wood
 334 biochars are greatest at pyrolysis temperatures of 500 °C, with
 335 substantially lower yields at higher or lower temperatures,
 336 indicates that pyrolytic PAH production occurs in a relatively
 337 narrow temperature window. To relate Σ COMB yields to
 338 structural information of the biochars, the evolution of these
 339 combined, unsubstituted PAH yields was plotted as a function
 340 of H/C and O/C elemental ratios of both grass and wood
 341 biochars across the 100–700 °C heat treatment temperature
 342 (HTT) range (Figure 2). H/C and O/C atomic ratios of both
 343 biochars follow the trajectory associated with dehydration
 344 reactions.³⁵ The most dramatic loss of H and O occurs between
 345 300 and 500 °C. At 300 °C, the biochars are subjected to initial
 346 dehydration and depolymerization reactions (loss of H and O
 347 containing functional groups) that form small, volatile
 348 dissociation products.^{35,46} At 400 and 500 °C, however, an
 349 'amorphous' biochar phase comprised of volatile, low-molecular
 350 weight aliphatics and aromatic compounds (such as PAHs) that
 351 arise from the thermal transformation of lignin and cellulose is
 352 formed.³⁵ This amorphous phase is thought to consist of
 353 intermediates such as pyranones, anhydro sugars, phenols,
 354 quinones, pyrroles, and furans as well as small (poly)aromatic
 355 units and thermally more stable aromatic lignin residues.^{35,47}

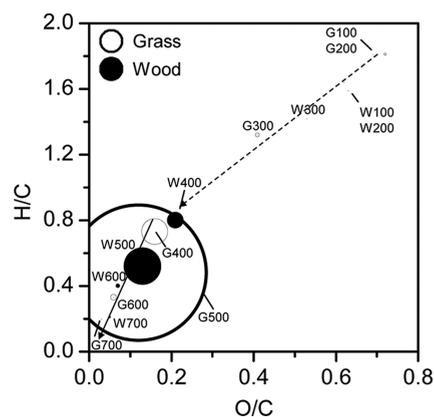


Figure 2. Van Krevelen diagram showing the evolution of H/C and O/C elemental ratios for both grass and wood biochars across the 100–700 °C heat treatment temperature (HTT) range. The total area of the circles represents the relative concentration of characteristic pyrolytic PAHs (Σ COMB = sum of FLUO, 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

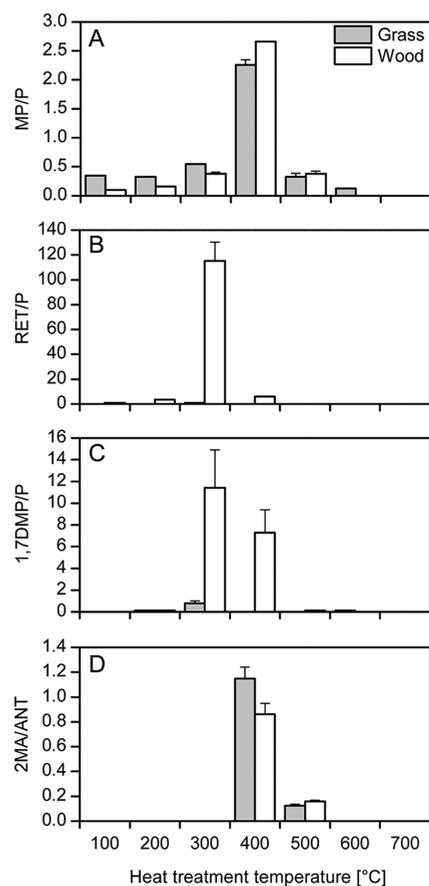


Figure 3. Concentrations of extractable (A) total MPs, (B) RET, (C) 1,7DMP, and (D) 2-MA shown relative to their parent PAHs (PHEN and ANT, respectively) extracted from grass and wood biochars across the 100–700 °C heat treatment temperature (HTT) range. Error bars represent the standard deviation of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

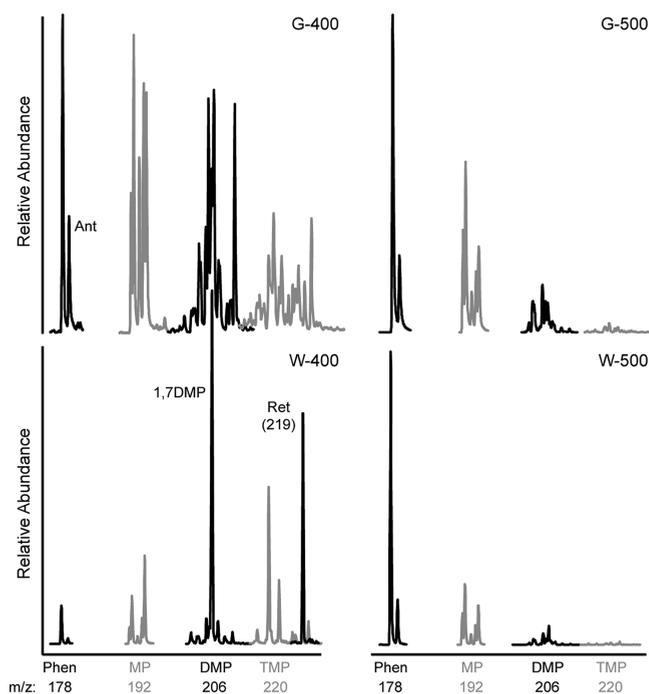


Figure 4. Chromatograms of monomethylated phenanthrenes (MP), dimethylated phenanthrenes (DMP), and trimethylated phenanthrenes (TMP) and their parent PAH phenanthrene (PHEN) extracted from grass and wood chars produced at HTTs of 400 and 500 °C. Peak inserts for ANT and RET are given for comparison.

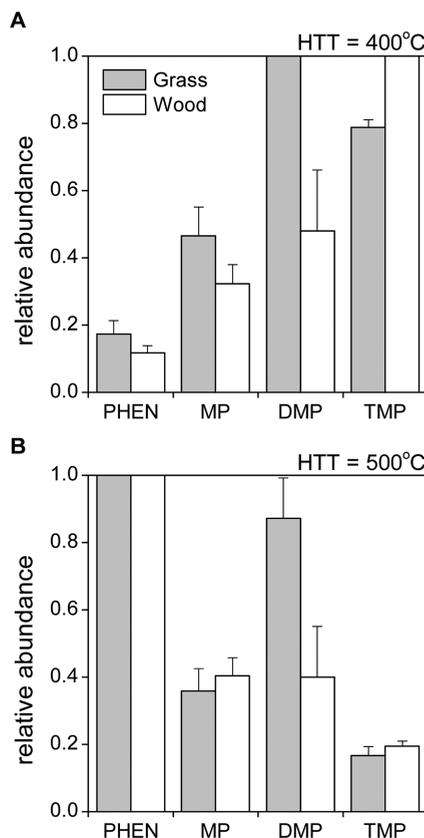


Figure 5. Relative abundance of mono-, di-, and trimethylated phenanthrenes in wood and grass biochars produced at heat treatment temperatures (HTTs) of (A) 400 °C and (B) 500 °C. Ratios in each plot were normalized to the highest value.

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

393 Figure 5 compares the abundance of extractable MP, DMP,
394 and TMP relative to their parent PHEN in biochars produced
395 at 400 and 500 °C. Wood biochars produced at 400 °C show a
396 continuous increase in the order of MP < DMP < TMP. At 500
397 °C, however, this trend is reversed, and relative yields decline in
398 the order of MP ~ DMP > TMP. Such a pattern could be
399 explained by continuous stripping (i.e., elimination) of methyl
400 groups from methylated phenanthrenes to form PHEN as
401 temperatures increase from 400 to 500 °C. An alternative
402 explanation is that cracking reactions may generate free radicals
403 (i.e., free radical pathway) that subsequently fuse into the
404 thermodynamically more stable PHEN (i.e., pyrosynthesis).

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

411 Evolution of Retene, 1,7-Dimethylphenanthrene, and 412 2-Methylantracene Across the Temperature Range.

413 Comparison of yields for alkylated phenanthrenes to their
414 respective parent PHEN provides insights into PAH formation
415 pathways during pyrolysis. Coniferous wood, such as *Ponderosa*
416 pine used for this study, contains diterpenoid resins – most

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 pimanthrene (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's 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. Hautevelle 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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540 **Notes**

541 The authors declare no competing financial interest.

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