

Toward a “Molecular Thermometer” to Estimate the Charring Temperature of Wildland Charcoals Derived from Different Biomass Sources

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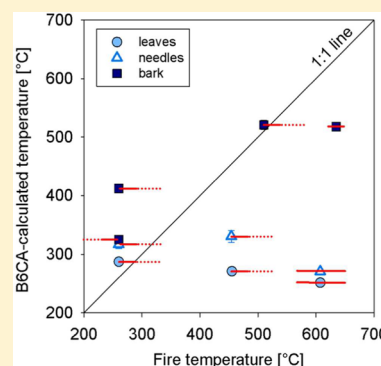
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ABSTRACT: The maximum temperature experienced by biomass during combustion has a strong effect on chemical properties of the resulting charcoal, such as sorption capacity (water and nonpolar materials) and microbial degradability. However, information about the formation temperature of natural charcoal can be difficult to obtain in ecosystems that are not instrumented prior to fires. Benzene polycarboxylic acids (BPCA) are molecular markers specific for pyrogenic carbon (PyC) which can provide information on the degree of aromatic condensation in charcoals. Here we apply the BPCA molecular marker method to a set of 10 charcoals produced during an experimental fire in a Pitch pine–scrub oak forest from litter and bark of pitch pine and inkberry plants in the Pinelands National Reserve in New Jersey, USA. We deployed temperature-sensitive crayons throughout the burn site, which recorded the maximum air temperature and made comparisons to the degree of thermal alteration recorded by BPCA molecular markers. Our results show an increase of the degree of aromatic condensation with monitored temperatures for bark biomass, while for needles no clear trend could be observed. For leaf-derived charcoals at increasing monitored fire temperatures, decreasing degree of aromatic condensation was obtained. This suggests that molecular markers can be used to roughly estimate the maximum fire temperatures experienced by bark and wood materials, but not based on leaf- and needle-derived materials. Possible applications include verifying declared pyrolysis temperatures of biochars and evaluating ecosystem fire temperature postburn.



1. INTRODUCTION

Wildfires are important sources of pyrogenic carbon (PyC) in the environment,¹ produced in the form of residues (charcoal) and solid condensates from the gas phase (soot).² The maximum temperature during the fire event, besides other factors such as source biomass and oxygen limitation, is a major control of charcoal properties such as C content, surface area, and degree of condensation.^{3–6} In experimental fires temperature-sensitive crayons can be used to keep record of the maximum air temperatures during the fire event.⁷ In contrast, for wildfires the formation temperature of charcoals is unknown in most cases. However, this temperature is valuable to know because the environmental fate of charcoals strongly depends on the extent of heating to which they were exposed.^{8,9}

As a result of different biomass sources and variable conditions during wildfires, different types of charcoals are produced.¹⁰ The result is a mixture of charcoals which are different by their degree of condensation,¹¹ covering a broad range of the “combustion continuum”,^{12,13} a term which was introduced to describe different forms of pyrogenic material from slightly charred biomass to charcoals and soot.

For charcoals produced under natural fire conditions, a conceptual model has been suggested which accounts for heat-altered biopolymers with comparatively small polyaromatic clusters.^{14,15} This idea adds to the concept of pyrogenic carbon as mainly composed of highly condensed aromatic structures.¹⁶

Benzene polycarboxylic acids (BPCA) molecular markers are specific for PyC and are used to determine fire residues in different environmental matrices.^{17–20} With this approach it is possible to detect PyC down to the finely distributed nanoscale size fraction. Furthermore, the molecular markers allow for estimating the degree of condensation of PyC, information which was directly linked to the formation temperature of a set of laboratory-produced charcoals.^{21,22} These results suggest that the yield of one of the molecular markers (B6CA) can be used to estimate the formation temperature of fire residues. A similar relationship between B6CA contribution (expressed as B5CA/B6CA ratio) and charcoals produced under different fire

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regimes was established by Wolf et al.¹⁰ In their work Wolf et al.¹⁰ demonstrated the general ability of molecular markers to differentiate among natural charcoals produced under various fire regimes.

Here we used regression parameters from Schneider et al.²² to calculate the formation temperature of the charcoals from an experimental fire based on the B6CA yield of the charcoals, and compare this estimated temperature with the monitored temperature during the fire event. The aim of this study is to see how different biomass sources influence the chemical properties of the charcoals produced under wildfire conditions.

2. EXPERIMENTAL SECTION

Site Description. We collected charcoal and biomass from an experimental fire conducted by the New Jersey Forest Fire Service near the Warren Grove Bombing Range in the Pinelands National Reserve of Southern New Jersey. The mean annual precipitation is about 1160 mm, the coldest month is February (-1 – 2 °C), and the warmest month is July (23 – 25 °C).²³ The 400 000 ha Pinelands National Reserve encompasses upland and wetland forests. Stands dominated by Pitch pine (*Pinus rigida* Mill.) are characterized by a higher frequency of wildfires than most forests in the northeast US, but the site had not been burned for at least 15 years.

Experimental Fire and Sample Collection. The burn site was located immediately south of the Warren Grove Bombing Range in the Stafford Forge Wildlife Management Area in the Pinelands. The stand was dominated by Pitch pine, and had a dense understory of inkberry (*Ilex glabra* (L.) Gray), an evergreen shrub in the holly family (Aquafoliaceae), and blueberry (*Vaccinium* spp.). The experimental burn encompassed three intensities of fire: ground fire (plot A), intermediate fire (plot B), and hot crown fire (plot C).

Preburn, fine fuels on the forest floor totaled 1190 ± 214 g m⁻² for 1-h fuels and 144 ± 78 g m⁻² for 10-h fuels (for definition of 1-h and 10-h fuels, see ref 7). No char was observed in the litter layer, or on pitch pine stems before the burn. Postburn loading was 593 ± 189 g m⁻² for 1-h fuels and 173 ± 44 g m⁻² for 10-h fuels. Total consumption of the forest floor was estimated at 566 g m⁻², an intermediate value for fuel consumption during experimental fires conducted from 2004 to 2010 in the Pinelands.²⁴ Before the fire, we set up three 1-m tall metal stakes on which we hung ceramic tiles marked with temperature-sensitive crayons (Tempilstik Industrial and Tempilstik Pro). Tiles were hung on the stakes at 5 cm and 1 m heights using soft steel bailing wire. A second set of tiles were hung from the closest pitch pine tree at 2 m height, also using bailing wire. Stakes were located within 3 m of the trees. Tiles marked with crayons were within 0.5 m of the shrubs, but were not in direct contact with leaves or the canopy. All tiles survived intact.

The experimental fire was ignited by the New Jersey Forest Fire Service on Sunday, March 22, 2009, and we collected samples and tiles the following Tuesday, March 24, 2009. We collected postfire litter samples from the forest floor within a 1 m radius of each of the stakes. Litter samples were collected from 3–5 subplots around the stakes, and then pooled to form individual samples. Samples collected at 5 cm can be mixed to some extent with material produced higher up, but most of the charred material stems from the preburn litter layer. Inkberry leaves were identified by their sclerophyllous habit and due to the fact that it was the only species with green leaves at that time of the year (only evergreen shrub species). In the case of

needles, no other species with needles than pitch pine were present in the stand. Additionally, we scraped charred bark from the pitch pine tree closest (within 3 m) to each stake. At stake C we were able to recover charred bark from both 1 and 2 m. At plots A and B the fire did not reach 2 m, but we were able to recover charcoal from 1 m. All charcoal was newly produced, because there had been no recent fires in this stand. The samples were sealed in polyethylene bags and shipped to Rice University and University of Zurich for storage and analysis. The postfire litter and charcoal samples were placed in aluminum trays and dried in an oven at 50 °C.

Charcoal Preparation. Using a lighted magnifying lamp, we picked charcoal particles from each sample. The charcoal in each bag was composed of two parts: fine dust and plant remains that were clearly identifiable by species, either pitch pine trees or inkberry shrubs. Each bag contained material spanning the entire combustion continuum, from uncharred biomass to biomass that was completely black and friable. It was not uncommon to see individual biomass samples that contained both completely charred and completely unburned portions. We picked only charcoal particles that were dark black and broke easily to the touch, shaving off uncharred material if necessary. We examined each particle picked to ensure that it was charred entirely through, rejecting particles that were not obviously completely charred.

Pyrogenic Carbon Analysis. For sample preparation we followed the protocol as outlined by Dittmar¹⁸ and Schneider et al.²² for benzene polycarboxylic acid (BPCA) separation using high performance liquid chromatography (HPLC). In brief, about 15 mg of ground charcoals was weighed into quartz tubes, 2 mL of 65% HNO₃ was added, and samples were digested at 170 °C for 8 h. Prior to analysis, the solution was filtered with a polyethersulfone (PES) 0.22- μ m syringe filter (BGB Analytik AG, Boeckten, Switzerland). The chromatography settings were slightly different from those used by Schneider et al.²² and were as follows: mobile phase A was a solution of 0.89:0.79 g Na₂HPO₄·2H₂O/NaH₂PO₄·2H₂O and 1.38 g of tetrabutylammonium hydrogen sulfate (TBAHS) in 1000 mL of H₂O. Solution pH was adjusted to pH 5.7. Mobile phase B was 1.38 g of TBAHS in 1000 mL of methanol. Dried sample were redissolved in 1.5 mL of solution solvent (mobile phase A without TBAHS), and further diluted 120:1300 μ L in solution solvent. Injection volume was 1 μ L. BPCA separation was performed on an Agilent 1290 Infinity system equipped with a reversed phase C18 column (Agilent Poroshell 120 EC C18). All analyses were done in triplicate (SE 0.6–10.5 g BPCA-C kg⁻¹ OC).

Elemental Analysis. We analyzed the C, H, and N contents (SE 2.8, 2.5, and 3.4%, respectively) at Rice University on a Costech ECS 3010.

Statistics and Calculations. All statistical analyses were performed with SPSS statistics package 18.0. For the comparison of means we used a one-way ANOVA, followed by the Tukey post hoc procedure ($p < 0.05$).

To calculate the charring temperature based on the B6CA-C yields we used data from Schneider et al.²² There a linear regression was calculated for B6CA-C yield in grass and wood charcoals and the respective pyrolysis temperature (250–700 °C). Calculated regressions for grass and wood thermosequences were very similar, so we used a regression formula based on the combined grass and wood data set:

$$T_{\text{calc}} = \frac{B6CA - C[\text{g kg}^{-1} \text{OC}] + 65.703}{0.293} \quad (1)$$

3. RESULTS AND DISCUSSION

Fire (Air) Temperature As Estimated by Temperature-Sensitive Crayons. Temperature-sensitive crayons indicate maximum temperatures during the fire event ranging from ≤ 260 °C to 650 °C (Table 1). We grouped the samples into

Table 1. Overview of Fire Residues Obtained from Three Experimental Fire Plots (A, B, and C)^a

temperature class (°C)	pine bark 100 cm	pine needles 5 cm	inkberry leaves 5 cm
≤ 260	A		
>260	B	A	A
>455		B	B
>510	C ^b		
570–650	C ^c	C	C

^aTemperature-sensitive crayons were placed at different sampling heights near three types of source biomass (pine bark, pine needles, inkberry leaves). According to data obtained by the temperature-sensitive crayons, samples were grouped into five fire temperature classes. ^bLocated at 200 cm height. ^c620–650 °C.

five fire temperature classes: ≤ 260 , >260 –455, >455 –510, >510 –570, and >570 –650 °C. Registered temperatures at the three locations increase in the order plot A < plot B < plot C, which fits with the observations made during the fire event, where three different fire types were observed: ground fire (plot A), intermediate fire (plot B), and hot crown fire (plot C).

Our temperature observations are similar to those of other experimental fires monitored using temperature-sensitive paints. In a similar experimental fire conducted in a subtropical scrub oak ecosystem, registered temperatures were 370–760 °C on the forest floor and 260–820 °C at 50 cm height.⁷ Another experimental fire conducted in a Mediterranean sclerophyllous shrub ecosystem registered peak soil surface temperatures between 218 and 240 °C for low fuel loads (2 kg m⁻²) and 418–448 °C at higher fuel loads (4 kg m⁻²).²⁵ Furthermore, Gimeno-Garcia et al.²⁵ found generally good agreement between peak fire temperatures as measured by temperature-sensitive paints and thermocouples.

Elemental Composition. Whereas the carbon contents (61–78 mass %) of all collected charcoal pieces were in a range similar to other experimental fire residues,^{1,26,27} only the bark biomass showed an increase in C content with fire temperature as recorded by temperature-sensitive crayons. In contrast, no such trend was observed for the needle and leaf biomass (Table 2). H/C ratios decreased in the order inkberry leaves > pine needles > pine bark. We found a decreasing H/C ratio with fire temperature in the case of pine bark and needles, indicating increasing degree of aromatic condensation.^{28,29} On the other

hand, H/C ratios increased with registered fire temperature in the inkberry leaves (Table 2).

Decreasing H/C ratios are associated with decreasing N/C ratios in the bark and leaf material (Figure 1), highlighting a

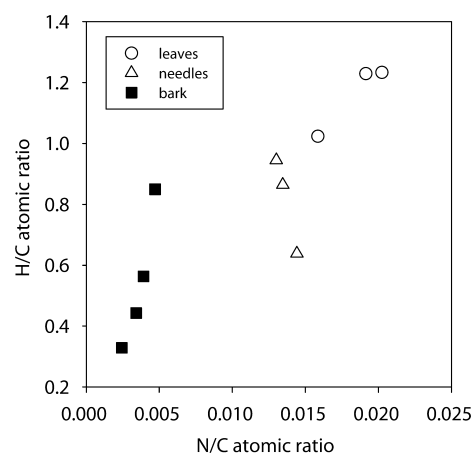


Figure 1. H/C and N/C atomic ratios in charcoals derived from bark, needle, and leaf biomass produced at different temperatures in an experimental burn.

positive relationship between H and N, and point to a synchronous depletion in these two elements relative to C. For the needle material a slightly better preservation of N compared to H could be observed. During fires, organic N can be preserved in forms of “black N” in heterocyclic aromatic structures.¹⁴ Higher N contents in leaves and needles compared to bark are reflected in the higher N/C ratios of the resulting charcoal (Figure 1). Losses of H upon heating of biomass occur mainly in the form of gases, such as CH₄ and H₂O.²⁸ Overall, the heating process of biomass is associated with a relative preservation of C compared to H and N. Other studies found increasing N/C ratios with increasing temperature for wood charcoals.^{28,30} However, different pyrolysis conditions of laboratory-produced charcoals in the mentioned studies vs charcoals from experimental burn of the present study might play a role here.

Pyrogenic Carbon Quantity. Molecular marker analysis allowed us to estimate the amount of condensed aromatic forms of pyrogenic C in the charcoal samples as the yield of seven benzene polycarboxylic acids (BPCA). The yield of BPCA-C consistently increased in bark charcoal with temperature, ranging from 86 g kg⁻¹ OC for biomass samples exposed to ≤ 260 °C to about 194 g kg⁻¹ OC at the highest temperatures (620–650 °C, Figure 2). The BPCA-C in leaf- and needle-derived charcoals decreased at increasing registered fire temperatures, from 72 (at >260 °C) to 41 g kg⁻¹ OC (at 570–650 °C) for leaf-derived charcoals and from 97 (at >260 °C) and 109 (at >455 °C) to 86 g kg⁻¹ OC at highest fire

Table 2. Elemental Composition (mg g⁻¹) and Atomic H/C and N/C Ratios of Fire Residues Collected from Different Heights after Controlled Burn Experiment

plot	pine bark 200 cm					pine bark 100 cm					pine needles 5 cm					inkberry leaves 5 cm				
	C	H	N	H/C	N/C	C	H	N	H/C	N/C	C	H	N	H/C	N/C	C	H	N	H/C	N/C
A						655	47	4	0.8	0.005	659	52	10	0.9	0.013	628	54	12	1.0	0.016
B						723	34	3	0.6	0.004	644	47	10	0.9	0.013	614	63	14	1.2	0.019
C	778	28	03	0.4	0.003	776	21	2	0.3	0.002	678	36	11	0.6	0.014	619	64	15	1.2	0.020

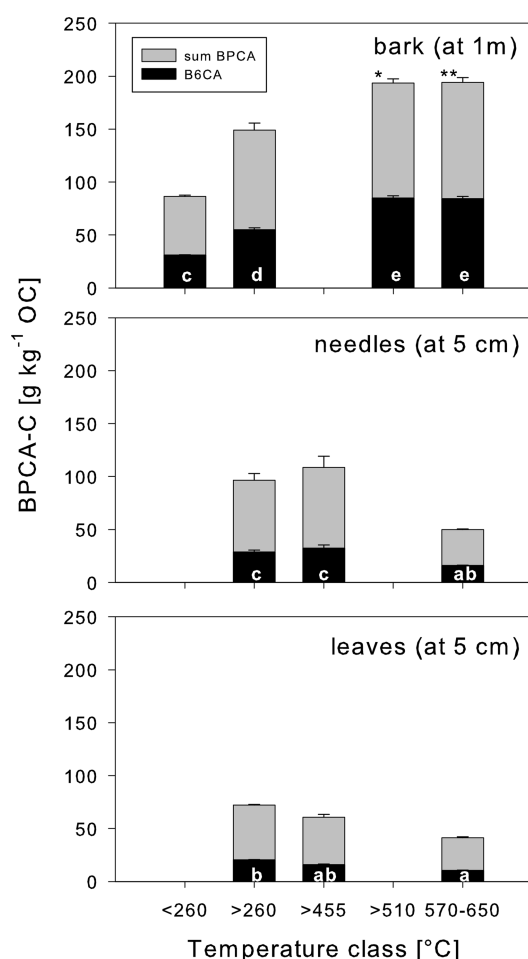


Figure 2. Pyrogenic carbon content (quantified as BPCA-C) in experimental fire charcoals with different source biomass (pine bark, pine needles, inkberry leaves) collected from three plots with five fire temperature classes. B6CA-C, a subfraction of BPCA-C, is a measure for the degree of condensation in charcoals. Pine bark was collected at 1 m height (*2 m, **620–650 °C); needles and leaves were collected from the litter layer at 5 cm above ground. B6CA-C concentrations were compared with one-way ANOVA, followed by the Tukey post hoc procedure, where letters (a–e) indicate pairwise differences. Error bars indicate standard error of laboratory replicates ($n = 3$).

temperature (570–650 °C) for needle-derived charcoals. Consequently, no clear trend in BPCA-C yield for needle and leaf charcoal could be observed, and BPCA-C yield per gram OC in needle- and leaf-derived charcoal was always significantly lower compared to bark-derived charcoal produced at the same temperature (Figure 2).

Pyrogenic Carbon Quality. The BPCA method provides additional quality information about pyrogenic matter, making use of the systematic change in the relative contributions of the individual molecular markers. The yield of mellitic acid (B6CA-C per OC) is indicative of the degree of aromatic condensation in charcoals.²¹ In the experimental fire charcoal samples we found B6CA-C yields from 11 to 85 g kg⁻¹ OC (Figure 2), which represent 26–44% of the total BPCA-C yields. Pine bark charcoals have the highest proportional yields of B6CA-C (31–85 g kg⁻¹ OC), while those of pine needles (16–33 g kg⁻¹ OC) and inkberry leaves (11–21 g kg⁻¹ OC) are significantly lower in B6CA-C. The B6CA-C relative yield follows the same trend described earlier for the total BPCA, with a clear increase with

fire temperature for the bark charcoals, but no clear trend in the soft tissue charcoals.

For samples derived from bark material, the charring process at increasing temperature was clearly reflected in the increasing C content, total BPCA-C and B6CA-C yield, and decreasing H/C ratios. Here we found a significant increase of B6CA-C yields with measured fire temperatures for charcoal produced from pine bark (Figure 2). The properties of charcoal produced from inkberry leaves, however, showed the opposite trend, with increasing H/C ratios and decreasing total BPCA-C and B6CA-C yields at increasing fire temperature. Charcoal samples produced from pine needles at different temperatures showed no consistent change in their properties. Small cluster sizes of condensed aromatic carbon in charred leaf materials can explain the low BPCA-C and B6CA-C yields detected by the molecular marker method, because these structures are not detectable with the applied method.³¹ Such types of fire-derived materials can have considerable contributions of alkyl-C and with significant N, O and S substitutions,^{14,15} and furans can make up an important fraction of aromatic C in charcoals derived from cellulose,¹⁵ which are not detected with the molecular marker method.

Comparison of Estimated and Measured Fire Temperature. In a next step we compared the properties of laboratory-produced charcoal from a thermosequence (200–1000 °C) with our results for the experimental fire charcoals. We used the linear relationship between B6CA-C yields and pyrolysis temperature described in Schneider et al.²² to calculate a formation temperature for the experimental fire charcoals based on the B6CA-C yield (eq 1). The relationship between estimated and monitored fire temperature is shown in Figure 3. The data points for the bark samples group around the 1:1 line, indicating that B6CA-C calculated temperatures approximately agree with the monitored fire temperatures.

Although exposed to temperatures of 570–650 °C, the chemical structure of leaf- and needle-derived charcoals is more similar to charcoals produced at much lower temperatures of about 250 °C (Figure 3). Consequently, the agreement of estimated and measured fire temperature of these samples is

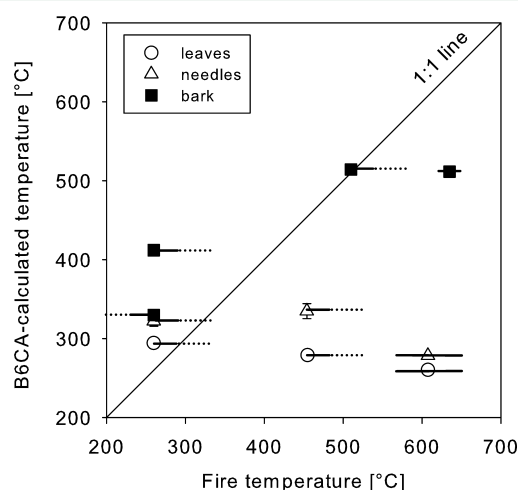


Figure 3. Range of fire temperatures for charcoals derived from bark, needle, and leaf biomass as estimated by temperature-sensitive crayons (x-axis) compared to estimated formation temperatures based on the B6CA-C yields in the charcoals (y-axis). Error bars indicate standard error of laboratory replicates ($n = 3$).

poor and data points for leaf- and needle-derived charcoals fall well off the 1:1 line.

Some discrepancy between the temperatures can probably be explained by the differences in the formation conditions such as composition of pyrolysis atmosphere and heat treatment duration when comparing the laboratory-produced thermosequences (5 h hold of maximum temperature under constant N₂ flow) with experimental fire charcoals (exposure time to maximum temperature of minutes to few hours under oxygen containing atmosphere). A bias between lab-produced charcoals and samples produced under field conditions due to different oxygen supply was also observed by Wolf et al.¹⁰

Another aspect is the heterogeneity of fire temperatures observed in experimental fires. Temperatures in fire events can be extremely variable,^{7,25,32,33} and in most cases samples cannot be collected exactly where the temperature was measured. However, in this study the error introduced by spatial heterogeneity of fire temperatures was addressed by pooled sampling in order to obtain a representative stand mean for each of the plots at the different heights.

Higher B6CA-C yields in bark-derived charcoals could be due to the higher resistance of the bark material against fire. Another explanation is oxygen limitation inside logs exposed to high temperatures during fires, which results in the pyrolysis of bark rather than combustion by fire. The results suggest that the bark biomass is more resistant to high temperature fires and survives to produce charcoal at higher temperatures, an observation that was also made by McBeath et al.¹¹ In contrast, the morphology of leaves and needles is such that they can much less withstand high temperatures. Because of their flat and thin shape, areas in these samples of O₂ low enough to create charcoal are unlikely to occur, and only charcoal produced at lower temperatures survives. Consequently, the fire residues of needle and leaf biomass had low PyC contents at highest temperatures, showing that leaves and needles get consumed by the fire under such conditions.

Further, different biomass sources (grass and wood in the laboratory study vs bark, leaf, and needle in the experimental fire event) would also lead to some deviation between estimated and measured fire temperatures, because biomass source material properties are known to influence resulting properties of charcoals.^{34–36} Low B6CA-C yields in needles and leaves could be explained by lower content in precursor biomolecules such as lignin compared to the woody bark tissue, as high lignin contents were shown to increase charcoal yields.^{10,37} Lower charcoal yields were also observed for laboratory-produced grass charcoals compared to wood charcoals produced at the same temperature.^{5,22} However, in another study comparing charcoals made from bark and wood differences in chemical and physical properties were shown to be small compared to the differences caused by different pyrolysis temperature.³⁵

Another difference between bark material and the leaf and needle material is the higher mobility of the charred leaf and needle particles compared to bark, which in many cases remains attached to the tree trunk. With the experimental setup used in the present study it is possible that some needle- and leaf-derived charcoal was not produced exactly where the air temperature during the fire event was measured. The finely distributed leaf and needle fraction would be rapidly physically homogenized on the landscape in ways that bark is not and higher mobility would lead to a faster mixing with pre-existing

charcoal.^{26,38} This implies that the charcoals we are seeing are a mix of materials formed at many temperatures.³⁹

The low content of highly condensed aromatic structures in charcoals derived from leaf biomass under natural fire conditions was described before by Alexis et al.³⁹ They also stated that in this aspect leaves would be similar to grass charcoals. Nocentini et al.²⁷ analyzed charcoals of different sizes by a combined spectroscopic and wet-analytical method approach, and found higher degree of charring in coarser particles derived from wood and bark biomass compared to finer fractions mainly derived from needle biomass. The low degree of condensation in leaf- and needle-derived charcoals is also reflected in their elemental properties (see Elemental Composition).

In terms of comparability of natural and laboratory-produced charcoals our results demonstrate that results from laboratory charcoals produced under oxygen-free atmosphere made from grass and wood biomass cannot be easily translated to leaf charcoals. In contrast, wood and bark biomass obviously behave more similarly under laboratory pyrolysis and natural fire conditions. Consequently, in the latter case, laboratory studies can give useful information about formation of wood-derived charcoals under natural conditions. To minimize the divergence between estimated and measured temperatures, a broader data basis including diverse biomass sources would be needed for calibration.

Environmental Implications. For bark- and wood-derived charcoals produced by natural wildfires the “molecular thermometer” can be used to estimate charring temperature in three categories: charcoals can be categorized in low (≤ 260 °C), intermediate (>260 – 510 °C), and high fire temperatures (>510 – 650 °C). For charcoals derived from leaf and needle biomass, the performance of the thermometer was poor, showing a negative trend between estimated and measured temperature. Our results show that wildfire charcoals produced from leaf and needle biomass exhibit lower degree of aromatic condensation than can be expected from the registered fire temperature. Future work should aim at optimizing the “molecular thermometer” by including a broader range of biomass types for calibration.

Possible applications of the “molecular thermometer” are the use as a quality indicator to verify declared pyrolysis temperatures of biochars and the estimation of past fire conditions of recent wildfires.

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Notes

The authors declare no competing financial interest.

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