**The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed
between 200°C and 1000°C**

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Abstract

Environmental charcoals represent a poorly defined part of the black carbon (BC) combustion continuum, and may differ widely in their chemical and physical properties, depending on combustion conditions and source material. The benzene polycarboxylic acid (BPCA) molecular marker method is well established to quantify the BC component in charcoal, soil and sediment, although observed variations between labs could stem from subtle differences in methods. The objectives of this study were to identify and improve potential sources of analytical uncertainty. The improved method was then used to qualitatively characterize wood charred at 200–1000°C. One significant improvement of the BPCA method was to replace citric acid with phthalic acid as an internal standard, which is more stable in acidic solution and more similar to the target compounds. Also, including a soil reference material as a quality control in each analysis, proved to be a robust tool to detect for variations in reproducibility. For the thermosequence, elemental O/C and H/C ratios typically decreased with temperature to ≤ 0.03 at 1000°C, whereas BPCA concentrations peaked at 700°C. With temperature B6CA proportions increased consistently (6–98%), except for a plateau at 250–500°C. Thus, relative contributions of B6CA reflected the pyrolysis temperature, and probably also the degree of condensation of the charcoals we investigated. Future work will show if our results can be directly related to charcoal produced under oxygen limited

conditions, including charcoal formed at wildfires or so called biochar for agricultural use.

keywords: black carbon, charcoal, molecular marker, benzenepolycarboxylic acids

1 Introduction

Charcoals in the environment form a part of the black carbon (BC) combustion continuum (Masiello, 2004). Charcoals differ in their chemical and physical properties depending on several formation factors, including feedstock properties, the gas environment, the thermal ramp rate and final temperature of the carbonization process (Antal & Gronli, 2003; Brown et al., 2006). With increasing formation temperature, the pH, C content, degree of condensation, specific surface area and sorption capacity for organic pollutants of charcoals typically increase (Shafizadeh & Sekiguchi, 1983; Brown et al., 2006; Gundale & DeLuca, 2006; Chen et al., 2008), while the degradability of charcoals decreases (Bruun et al., 2008; Nguyen & Lehmann, 2009; Nguyen et al., 2010; Zimmerman, 2010). Thus, properties of charcoals produced at different temperatures may cover the whole spectrum of the BC continuum, i.e. from slightly charred biomass produced at temperatures as low as 200°C to highly aromatic charcoals at very high temperatures. Many methods used to quantify charcoal do not reflect the degree of aromatic condensation of the charcoal, e.g. when determined as oxidation residues (Wolbach & Anders, 1989; Gustafsson et al., 1997; Gustafsson et al., 2001; Simpson & Hatcher, 2004a; Simpson & Hatcher, 2004b). Additional qualitative information about the charcoal can be obtained from spectroscopic (Smernik et al., 2006; McBeath & Smernik, 2009; Keiluweit et al., 2010) and molecular marker methods (Hammes et al., 2007; Kaal & Rumpel, 2009).

Presently, there are several published molecular marker methods to measure charcoal, including analytical pyrolysis (Kaal et al., 2009), a method identifying levoglucosan (Simoneit et al., 1999) and the benzenepolycarboxylic acid (BPCA) method (Glaser et al., 1998; Brodowski et al., 2005). Analytical pyrolysis and the levoglucosan method are well suited to detect and characterize charcoals (Kuo et al., 2008; Kaal et al., 2009), but only the BPCA method yields quantitative information and additionally qualitative information about the degree of condensation of BC (Glaser et al., 1998; Brodowski et al., 2005). The BPCA method allows to assess the relative contributions of individual molecular markers, which reflect the size of the aromatic clusters. Although several authors have taken advantage of this unique feature of the BPCA method (Glaser et al., 1998; Brodowski et al., 2005; Dittmar, 2008; Hammes et al., 2008b; Ziolkowski & Druffel, 2009) a systematic testing of how the BPCA pattern reflects charring temperature is still lacking (Hammes et al., 2007). Testing the temperature dependence of the BPCA pattern, however, would require a highly reproducible analytical method covering the whole combustion continuum. The BPCA method has been used in many publications over the past decade (e.g. Rodionov et al., 2006; Brodowski et al., 2007; Hammes et al., 2008b), and Hammes et al. (2007) pointed out that the BPCA method is well suited for BC analysis in soils. In the “ring trial” study of Hammes et al. (2007), in which 17 laboratories participated, seven methods for BC analysis were tested on 12 reference materials. It became

clear from the ring trial that the BPCA method might underestimate BC in highly condensed aromatic molecules, such as soot. On the other hand, it was shown that there is a positive bias from non-BC materials like shales and coals. These potential limitations must be considered when interpreting results obtained by the BPCA method for samples that contain such forms of carbon.

Further, interlaboratory reproducibility should be improved. In the ring trial, BC concentrations varied by factors of two or more when analyzed with the BPCA method in different laboratories. The essential first step, breaking BC molecules into the BPCA, i.e. the nitric acid oxidation at 170°C, proved to be robust and reproducible (Glaser et al., 1998; Dittmar, 2008). However, the ring trial revealed that the many cleaning, transfer and derivatization steps with seemingly minor handling differences between laboratories could have resulted in disparate results.

More specifically, Hammes et al. (2007) identified several potential sources of error during BPCA analysis. First, internal standards (IS) are used to detect possible losses during sample cleaning over the resin, freeze-drying and subsequent transferring the samples into vials. In BPCA analysis, citric acid has been used as IS, despite its known instability under strongly acidic conditions (Brodowski et al., 2005) and despite the fact that its chemical structure is not very similar to the BPCA. Phthalic acid is structurally more similar to the target compounds, and so might be less susceptible to deterioration and could serve as a better internal standard. Second,

extracted soil and charcoal samples often need to be stored before further processing. BPCA themselves are known to be very stable in solution, but they might interact even with traces of polyvalent metal ions (Glaser et al., 1998), and thus affect results. But the stability of BPCA extracts from soil and charcoal samples in strongly acidic solution has not yet been tested systematically. Third, Glaser et al. (1998) observed that, once derivatized, standards and soil extracts remained stable for up to one week when stored dry, and our observation was that already traces of humidity in the vial may affect results.

The first objective of this study is to identify possible sources of error during sample handling and preparation and to propose more robust alternative steps in section 2 (Experimental). The improved method is then used for characterization of a charcoal thermosequence. In section 3 (Results and Discussion) we focus on the following question: Does charcoal pyrolyzed at temperatures ranging from 200 to 1000°C (charcoal thermosequence) produce a systematic and consistent BPCA pattern?

2 Experimental

2.1. Materials

2.1.1. Reference soil material

To test for reproducibility of the BPCA method in soils we selected a Chernozem soil (Schmidt et al., 1999), which has already been used in a multi-lab, multi-method comparison study (Hammes et al., 2007). The

Chernozem soil was sampled at 20–60 cm depth in the Hildesheim-Braunschweig region (Harsum, Germany) with 19 mass-% clay content and 20.1 g OC kg⁻¹.

2.1.2. Charcoal thermosequence

The thermosequence includes the reference wood charcoal charred at 450°C used in the ring trial study (Hammes et al., 2007), which was characterized in Hammes et al. (2006; 2008a). All other charcoals in the thermosequence were derived from the same source of biomass, cut into small wood chips (2–8mm) and produced according to the protocol described in Hammes et al. (2006). Debarked and cut chestnut wood (*Castanea sativa*) was charred in a pyrolysis furnace (Carbolite CTF 16/75, Sheffield, UK) under a N₂ atmosphere (flow 13 L h⁻¹). The temperature was raised from room temperature to 200°C at a rate of 300°C h⁻¹ and then to 250–1000°C at a rate of 50°C h⁻¹. The respective maximum temperature (200–1000°C) was held constant for 5 h to assure complete charring. In total, we produced a thermosequence of 12 charcoals (Table 1). The charcoal was collected after cooling (8 h), and stored in a cool, dry place in glass bottles with screw caps (Schott, Mainz, Germany). Samples were weighed before and after charring to determine mass loss.

2.2. Methods

2.2.1. Black carbon analysis using the BPCA method

We used the BPCA method as described by Glaser et al. (1998) with the modifications suggested by Brodowski et al. (2005). In short, the method involves a pretreatment step with 4M trifluoroacetic acid (TFA) to remove Fe and Al, followed by the conversion of BC to BPCA by nitric acid oxidation at 170°C for 8 hours. The extract is then percolated over a cation exchange resin to remove remaining polyvalent cations. Subsequently, the samples are freeze-dried and finally converted to trimethylsilyl derivatives for GC-FID (gas chromatograph equipped with flame ionization detector) analysis. All analyses were done in triplicate. For the BPCA analysis, about 500 mg of soil sample or 2–100 mg of charcoal sample (1.9–50.3 mg OC, depending on the expected BC content in order to avoid GC column overload for high BC contents) was used.

For the measurements of the charcoals with expected high BC contents (300–1000°C, Fig. 5), we doubled the amount of B5CA and B6CA standards (200 µg instead of 100 µg in 100 µl) to adjust the standard series to the higher amounts of B5CA and B6CA in the samples.

Total BPCA amounts were calculated as the sum of the seven marker molecules hemimellitic, trimellitic, pyromellitic, prehnitic, mellophanic, pentacarboxylic and mellitic acid. All BPCA data reported here was calculated without using the conversion factor 2.27 (Glaser et al., 1998). For a detailed discussion see section 3.1.

Further modifications and additional testing of the method are described in sections 2.2.2-2.2.5, addressing the following questions:

- Can phthalic acid replace citric acid as internal standard, i.e. is it less susceptible to degradation under acidic conditions?
- How long can samples be stored in the acidic extract after HNO_3 oxidation without changes in quantity or quality?
- How long can derivatized standards and soil extracts be stored without changes in quantity or quality?
- How reproducible are BPCA measurements using a soil reference material?

2.2.2. Acid stability tests of external and internal standards (citric and phthalic acid)

When adding the internal standard during sample preparation, the pH of the extract solution typically ranged from 0.8 to 1.9. We tested the stability of the BPCA in standard solution, and of the presently used internal standard citric acid compared to phthalic acid (Fig.1). External standards (hemimellitic, trimellitic, pyromellitic, pentacarboxylic and mellitic acid) were prepared by dissolving 50 mg of each compound in 100mL of deionized water in volumetric flasks. About 100 mg of internal standard citric acid were introduced in 100 mL volumetric flasks and filled up with deionized water. The same was done with the alternative internal standard phthalic acid. To test for the stability of both compounds with decreasing pH, 100 μL of each standard solution was exposed to increasing concentrations of HNO_3 , and the pH of the solutions was measured with an IQ240 glass

electrode (IQ Scientific Instruments). After that the solutions were freeze-dried and prepared for GC-FID analysis.

At $\text{pH} < 1.0$, typically encountered during sample preparation, BPCA and phthalic acid concentrations did not change, whereas citric acid concentrations decreased (Fig. 1). These results confirm that citric acid is not an ideal internal standard for BPCA analysis (Brodowski et al., 2005). Phthalic acid on the other hand, is not only stable under acidic conditions, it also does not co-elute with any of the BPCAs (Fig. 2a), and its chemical structure is more similar to the target compounds. When adding both internal standards to a set of samples for cross-checking, we recovered more than 90% of phthalic acid. In contrast, we only recovered 69% of citric acid, which proves the instability of citric acid in the acidic sample solution.

It could be possible, however, that phthalic acid is produced during charcoal oxidation, or that plasticizers in lab plastic contaminate samples with phthalic acid. To check for the presence of artifact phthalic acid, we prepared samples as described above without adding phthalic acid (Fig. 2b) and found negligible contribution of phthalic acid after oxidizing Chernozem soil samples with HNO_3 ($<0.6\%$ of total quantified area). Thus, we strongly recommend replacing citric acid by phthalic acid as an internal standard.

2.2.3. Stability of BPCA extracts from soils over time

The BPCA in the non-purified, acidic soil extracts could interact with other components (e.g. polyvalent cations, Glaser et al. 1998) when stored over

longer time (days to weeks). Even after dilution (1:5 with deionized water), the HNO_3 extract had a very low pH of 1.8, and after several days or weeks BPCA might partly deteriorate, or they might interact with the substances in the solution. To test the BPCA stability at intermediate timescales (up to one month) in the non-purified soil extracts after HNO_3 oxidation (section 2.2.1), sample extracts were stored for 3, 8 and 30 days in the diluted acid before further sample processing. Total BPCA carbon and relative contributions of individual BPCA extracted from the Chernozem reference soil did not change during 30 days of storage at room temperature under acidic conditions (Fig. 3a). Thus, after HNO_3 oxidation we can store extracts for up to a month before further sample processing without influencing the results.

2.2.4. Derivatization of BPCA standards and their long-term stability

Brodowski et al. (2005) found that complete derivatization of BPCA with BSTFA+TMCS 99:1 requires at least 24 hours before injection into GC. The long-term maximum storage time after derivatization, however, has not yet been tested (Brodowski et al., 2005). We derivatized BPCA standards, and quantified them 12 times over a period of 254 days. We could not detect any major changes in quantity or quality of the BPCA (data not shown).

In soil extracts, however, other than in pure standard solutions, derivatized BPCA probably could interfere with substances that survived the digestion and purification treatments of the samples material (e.g. traces of

polyvalent cations). To test this, we took two subsamples from a Chernozem nitric acid extract. Standards containing 80 µg of each BPCA were added to one of the two subsamples before derivatization. Samples were then derivatized and analyzed by GC-FID. For comparison, we subtracted the areas obtained for soil subsamples from the areas obtained for mixed soil/standard subsamples. The pure standard mixture was used as a control. Total BPCA-C concentrations were slightly lower for measurements with standard addition (Fig. 3b), but the BPCA pattern did not differ. We recovered 89.2, 100.8 and 96.8% of the added standards from soil extracts compared to pure standard solution after 1, 2 and 5 days, respectively (Fig. 3b). Thus, derivatized BPCA seem to interfere with soil extracts, although differences were only small and did not increase with time.

2.2.5 Quantitative and qualitative reproducibility of the BPCA method tested with a reference soil

In total, we performed 34 independent triplicate analyses of the reference soil, and selected those 16 for further statistical analysis with standard errors < 3.5 (Fig. 4).

From the repeated analysis of the reference soil we conclude that the following criteria should be considered when interpreting results obtained by the BPCA method:

1. The recovery of the internal standard reveals losses during sample processing, and should at least reach 70%.

2. The slope of the external mellitic acid standard series obtained by a linear regression is a good measure for the success of derivatization. Slopes below 0.7 indicate that a considerable part of mellitic acid standard has not been successfully transformed to trimethylsilyl derivatives.

Those runs, which failed to meet criteria 1 and/or 2, were excluded from further analysis. The repeated BPCA extractions of the soil reference material yielded a mean of 66.2 g BPCA-C kg⁻¹ OC (Fig. 4). We applied a normal distribution to the reference soil data set (standard deviation SD = 15.2, standard error SE = 2.3, n = 44). We concluded that the BPCA-C content of the reference soil probably lies between 51.1 and 81.4 g kg⁻¹ OC (as defined by the mean $\pm$ 1 SD). BPCA analyses that yield higher or lower contents could point to losses or inaccuracies while sample processing.

There was still some considerable scatter in the data even with the modifications introduced, with contents between 40.2 and 94.8 g BPCA-C kg⁻¹ OC (Fig. 4). For quality control, samples should be analyzed together with a known reference material. As always, the reference material used should have properties similar to the analyzed material (e.g. soil or marine sediment), and could include those materials already used in the ring trial (Hammes et al., 2007).

Runs which lay outside the above defined range should be considered to be repeated, either starting with a new HNO₃ extraction or with a new clean up of the stored extract (see section 2.2.3). Results obtained from the

reference material could then be used to correct for possible variations in analysis. In terms of the quality of the BC detected in the reference Chernozem soil, B6CA contribution varied between 32 and 50%, but most values were between 40 and 45% (Fig. 4). B3CA always made up the least fraction of all BPCA with contributions between 1 and 10% of total BPCA-C contents.

2.2.6 Other measurements

Elemental analysis (CHO) of the charcoals was carried out on a LECO CHN-900 and a LECO RO-478 (Mönchengladbach, Germany) in two laboratory replicates.

2.2.7 Statistics

Normal distribution of data was tested with a Kolmogorov-Smirnov test ($p < 0.05$). All statistical comparisons were conducted with SPSS version 17.0.

3 Results and discussion

3.1 Consistence and plausibility of BPCA data tested on a charcoal thermosequence

The term BC is operational defined and does not describe a substance with a defined chemical structure (Goldberg, 1985; Masiello, 2004). BC comprises all organic material that was subjected to various degrees of heating and different analytical methods capture a different part of the combustion

continuum (Hammes et al., 2007). Consequently, no “true” value for the BC content of a material exists, which we could test. Applying a thermosequence of charcoals allows us to test the BPCA method for reproducibility, consistence and plausibility, but not for accuracy per se. Not all carbon in charcoals is detected as BPCA-C. A conversion factor can be used to account for the carbon losses during sample processing, e.g. during HNO_3 oxidation in form of CO_2 and to convert BPCA-C contents into “black carbon” contents. This is done in order to obtain results that give more realistic values for BC contents in soils. The conversion factor of 2.27 is based on the mean BPCA-C contents of $441.2 \text{ g kg}^{-1} \text{ OC}$ obtained for activated and barbecue charcoal (Glaser et al., 1998). In our study we found maximum BPCA-C contents of $155.3 \text{ g kg}^{-1} \text{ OC}$ in the charcoal thermosequence. Brodowski et al. (2005) found maximum conversion factor for charcoals exceeding 4.5, which would better fit with our results but on the other hand would lead to an overestimation when applied to soils (Brodowski et al., 2005).

Also it becomes clear from our study yielding between 3.3 and $155.3 \text{ g BPCA-C kg}^{-1} \text{ OC}$ for the thermosequence charcoals that the application of a single conversion factor for different types of charcoal will always be incorrect in all but one special case, i.e. the test substance, and every charcoal which happens to be identical in chemical structure. Thus, the data presented here strongly supports the statement that any correction factor must be wrong and introduces an additional error to BC quantification. In

consequence, we recommend to not use any correction factor at all, but to report BPCA-C content in soils and charcoals as it is.

3.1.1 Elemental composition

With increasing temperature, wood showed a consistent decrease of mass, with no major changes > 600°C (Table 1). Elemental concentrations of C, H and O typically are used to represent the composition of organic matter. With increasing charring temperature, H/C and O/C ratios decreased, indicating an increasing degree of thermal alteration of the initial biomass, similar as observed and described in detail by others (Baldock & Smernik, 2002; Antal & Gronli, 2003; Hammes et al., 2006; Keiluweit et al., 2010; Zimmerman, 2010). The observed trends are in good agreement with the change in elemental composition with increasing temperature of other heat-treated biomass like cellulose (Shafizadeh & Sekiguchi, 1983; Nishimiya et al., 1998), wood (Nishimiya et al., 1998; Baldock & Smernik, 2002; Brown et al., 2006; Keiluweit et al., 2010), grass (Keiluweit et al., 2010) and peas (Braadbaart et al., 2004). At the same temperature, absolute values for H/C and O/C ratios can vary significantly, depending on the source material and pyrolysis conditions. Shorter exposure time to the final pyrolysis temperature, e.g. 5 minutes in Shafizadeh & Sekiguchi (1983) or 1 hour in Keiluweit et al. (2010), led to higher H/C ratios at the same temperature compared to H/C ratios of the thermosequence charcoals (5 hours pyrolysis), which indicates ongoing pyrolysis reactions at shorter time.

3.1.2 Black carbon quantity

We quantified total BC concentrations of the samples as BPCA-C (Fig. 5). The BPCA-C content measured for the reference charcoal (wood 450°C) in our study fits with the results obtained in the ring trial study (Hammes et al., 2007, auxiliary material Text S2) for two of three participating laboratories (161.9, 146.1 and 47.1 g BPCA-C kg⁻¹ OC, this study: 137.2 g BPCA-C kg⁻¹ OC, all data without conversion factor 2.27).

BPCA-C concentrations of the charcoals increased with charring temperature (200 to 700°C), while H/C decrease (Table 1), pointing to formation of structures containing unsaturated C such as aromatic rings. Elemental data (Shafizadeh & Sekiguchi, 1983; Antal & Gronli, 2003) and spectroscopic techniques (Knicker et al., 1996; Baldock & Smernik, 2002; Czimeczik et al., 2002) suggest increasing contents of aromatic C in woody biomass subjected to increasing levels of thermal alteration. These observations show a consistent trend despite very different heat treatment conditions, e.g. availability of oxygen and exposure time in the studies. At higher temperatures (800–1000°C), however, BPCA–C content decreased again, although small (≤ 0.02) O/C and (≤ 0.08) H/C ratios suggested a high degree of condensation. One possible explanation for the apparent discrepancy between elemental and molecular data is an incomplete HNO₃ digestion, which does not convert the very stable charcoal to BPCA. This is in accordance with the findings of the ring trial (Hammes et al., 2007),

where it was shown that highly condensed structures such as soot partly escape the analytical window of the BPCA method.

3.1.3 Black carbon quality

The contributions of individual BPCA molecular markers can be used to infer the size of the aromatic clusters (e.g. Hammes et al., 2008b). Aromatic rings at the outer margin of a black carbon molecule are more likely to produce B3CA, B4CA and B5CA, whereas B6CA can only originate from the core of the black carbon molecule. In other words, larger proportions of B6CA would reflect (on average) higher degrees of condensation of a sample. The charcoals analyzed in this study showed that with temperature relative contributions of B6CA consistently increased (Fig. 5). Low temperature charcoals (final temperature 200°C) produced very few (< 10%) B6CA. Charcoals produced at intermediate temperatures (250–500°C) produce more B6CA (10–40%), and in the high temperature charcoals (600–1000°C) B6CA contributed most to the total BPCA contents (>40%). A strong increase in the degree of condensation for wood charcoals at pyrolysis temperatures between 700 and 1000°C was also observed using X-ray photoelectron spectroscopy (Nishimiya et al., 1998).

Our data can be related to the conceptual model describing molecular changes in wood-derived charcoals produced at 100–700°C presented in Keiluweit et al. (2010). They determined the chemical structure using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. To describe

the molecular changes and increasing degree of condensation in their thermosequence they introduced the terms “transition”, “amorphous” and “turbostratic” charcoals. When comparing these conceptual charcoal types to our thermosequence charcoals, the samples produced at 200–300°C can be described as “transition charcoals”. In this part of the thermosequence, we find strongly increasing BPCA contents from 3.3 g BPCA-C kg⁻¹ OC to 83.2 g BPCA-C kg⁻¹ OC, indicating an increasing contribution of aromatic C to total OC and the loss of the properties of the original plant biomass. The dominance of B3CA, B4CA and B5CA relative contribution at temperatures up to 600°C indicates small aromatic units of “amorphous charcoal”, while at higher temperatures we find 50 to almost 98% contribution of B6CA, indicating increasing growth of graphene-like structures found in “turbostratic charcoals”. Condensation reactions of aromatic rings being the dominating process at these temperatures is also reflected in ongoing decrease of H/C ratios, while O/C ratios remain constantly low at 0.02 (Table 1).

Another approach to obtain information about the degree of condensation of charcoals is the measurement of “ring currents” (Smernik et al., 2006). This method was recently tested on a suite of thermally altered wood and grass at temperatures from 250 to 850°C under oxygen limited conditions (McBeath & Smernik, 2009), showing major increase in the degree of condensation between charcoals pyrolyzed at 450 and 850°C, which fits well

the observed increase in B6CA contribution from about 30% at 450°C to almost 80% at 800°C in the thermosequence charcoals (Fig. 5).

However, it still remains to be analytically confirmed on identical samples, how these independent methods compare and how they reflect the degree of aromatic condensation.

3.2 Relation to natural charcoal

How do our results compare to real charcoal produced in kilns or during wildfires? Probably our observations on the BPCA yields and patterns could be related to charcoal produced under similar oxygen limited conditions, including charcoal pyrolyzed in traditional kilns or so called biochar – a technical pyrolysis product used in agriculture. Analytical evidence for this statement, however, is still lacking.

It is not clear how our results, obtained on charcoal pyrolyzed under controlled conditions, compare to charcoals produced during wildfires.

Typical temperature windows for wildfires as observed in prescribed burning studies would be 275–500°C at the soil surface (Gimeno-Garcia et al., 2004; Alexis et al., 2007) and up to 800 °C (Alexis et al., 2007) or even higher (Pyne et al., 1996) in the vegetation, meaning with the thermosequence we covered common temperatures relevant for natural fires. The resulting BPCA patterns, however, could be very different depending on the conditions of the wildfire, including wind, gas composition of the atmosphere, duration of the fire event, moisture and source type of

biomass. Temperature has been shown to have a strong effect on the degree of condensation and many other physical and chemical properties of charred materials (Shafizadeh & Sekiguchi, 1983; Brown et al., 2006). If indeed temperature dominates aromaticity and degree of condensation of the charcoal formed during wildfires, then the BPCA quantities and patterns observed in our samples could reflect those found in natural charcoals. However, it would be crucial to compare BPCA quantities and patterns of charcoal formed during wildfires.

4 Conclusions

We improved the BPCA method to produce more reliable information about quality and quantity of BC in soils and charcoals and found the following results. Briefly, phthalic acid could replace citric acid as an internal standard, provided contamination with phthalic acid from lab equipment can be excluded. After HNO_3 oxidation soil extracts could be stored under acidic conditions for up to 30 days, without affecting quality and quantity of BPCA. After derivatization pure mixtures of BPCA standards mixtures could be stored for months without changes in quantity, and can serve as a rapid quality check before GC analysis. As a quality control we used the Chernozem soil reference material from the BC ring trial (Hammes et al., 2007; Hammes et al., 2008a).

When we applied the improved method to a charcoal thermosequence (200–1000°C) of charred wood, BPCA quantities consistently increased up to

700°C, which are common temperatures for wildfires (Pyne et al., 1996; Gimeno-Garcia et al., 2004; Alexis et al., 2007). Qualitative changes were small between 250 and 500°C, although elemental (C, H, O) composition suggested ongoing condensation until 1000°C. Generally, proportions of B6CA reflected the increasing pyrolysis temperature of the charcoal, and probably also the increasing degree of aromatic condensation.

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Author contribution

The study was proposed by Maximilian P. W. Schneider, Michael Hilf and Michael W. I. Schmidt. Ulrich F. Vogt provided the biomass material, his technical expertise and supervised the thermosequence experiment. Michael Hilf supervised the gas chromatography lab. Charcoal production, GC analysis and data analysis was carried out by Maximilian P. W. Schneider

and Michael Hilf. Paper writing was completed by Maximilian P. W. Schneider under the supervision of Michael W. I. Schmidt, with contributions of all co-authors.

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Figure captions

Figure 1

Detection of BPCA and two internal standards at different pH. Relative contribution of individual BPCA (left scale) and areas of citric and phthalic acid (right scale) as obtained by GC-FID measurements of standard solutions. Below pH 1 the detected area of citric acid decreases, whereas phthalic acid and BPCA are not affected by low pH.

Figure 2

Gas chromatograms of benzene polycarboxylic acids (BPCA) obtained from two independent nitric acid extractions from reference soil (Chernozem). a) Phthalic and citric acid were added. Phthalic acid does not co-elute with other BPCA. b) No phthalic acid was added to test for contamination. There is negligible contribution of phthalic acid (<0.6% of total quantified area). (1) phthalic acid (alternative internal standard); (2) citric acid (internal standard); (3) hemimellitic acid; (4) trimellitic acid; (5) pyromellitic acid; (6) mellophanic acid; (7) prehnitic acid; (8) benzene pentacarboxylic acid and (9) mellitic acid.

Figure 3

a) Stability of soil BPCA extract stored in acidic solution (pH 1.8) for 3, 8 and 30 days at room temperature. Relative contribution of individual BPCA (left scale) and total BPCA-C content (right scale) in Chernozem soil (SE for analytical replicates, n=3). No changes in quality and quantity were

observed, which shows the stability of underivatized BPCA at low pH.

b) Stability of BPCA standard added to soil extract. Measured after 1, 2 and 5 days after derivatization. Pure standard mixture of BPCA was used as a control. Relative contribution of individual BPCA (left scale) and recovery of standard mixture (right scale, control = 100%). (SE for analytical replicates, $n=3$). No changes in quality and quantity of BPCA were observed in 5 days.

Figure 4

BPCA-C content of Chernozem reference soil (white circles, right scale) as obtained by 16 independent measurements (SE for analytical replicates, $n = 3$). Relative contribution of individual BPCA (left scale) to total BPCA-C content is shown as stacked bars. The box plot on the right shows the median (black line, 67.1 g BPCA-C kg⁻¹ OC) and the interquartile range of the dataset (grey box, 53.6–80.0 g BPCA-C kg⁻¹ OC), the whiskers show minimum and maximum values.

Figure 5

BPCA-C content of chestnut wood charcoals (white circles, right scale) produced at increasing charring temperatures (SE of analytical replicates, $n=3$). Relative contribution of individual BPCA to total BPCA-C content is shown as stacked bars (left scale). BPCA-C contents of wood charcoals consistently increased for charring temperatures from 200–400°C and peak at 700°C. For charring temperatures >700°C BPCA-C contents decreased. The relative contributions of the B6CA molecular marker strongly increased with charring temperature.

Tables

Table 1

Properties of chestnut wood (*Castanea sativa*) both fresh and pyrolyzed at temperatures from 200 to 1000°C under N₂ stream.

Charring temperature [°C]	wood*	200	250	275	300	350	400	450*	500	600	700	800	900	1000
C [g kg ⁻¹]	458	503	544	642	695	734	781	682	871	938	951	960	965	963
H/C	1.6	1.32	1.16	0.79	0.69	0.52	0.46	0.7	0.36	0.24	0.14	0.08	0.04	0.03
O/C	0.8	0.66	0.55	0.37	0.28	0.24	0.18	0.3	0.08	0.03	0.03	0.02	0.02	0.02
Mass loss of initial [%]	–	12.0	29.0	47.8	55.0	59.0	69.0	60.0	69.5	74.5	72.5	73.0	75.0	73.0

*all data for wood and 450°C charcoal from Hammes et al. (2006)

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5