



## Pyrogenic molecular markers: Linking PAH with BPCA analysis



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### HIGHLIGHTS

- PAH and BPCA marker methods for pyrogenic compounds were compared using chars.
- Both methods show increasing aromatic condensation of high temperature chars.
- Relationships between the two methods were found in the lipid fraction of the chars.
- The findings confirm the validity and theoretical assumptions of both methods.
- The methods complement each other in pyrogenic carbon research.

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### ABSTRACT

Molecular characterization of pyrogenic organic matter (PyOM) is of great interest to understand the formation and behavior of these increasingly abundant materials in the environment. Two molecular marker methods have often been used to characterize and trace PyOM: polycyclic aromatic hydrocarbon (PAH) and benzenepolycarboxylic acid (BPCA) analysis. Since both methods target pyrogenic polycyclic compounds, we investigated the linkages between the two approaches using chars that were produced under controlled conditions. Rye and maize straws and their analogues charred at 300, 400 and 500 °C, respectively, were thus analyzed with both methods. Moreover, we also measured BPCAs directly on the lipid extracts, on which PAHs were analyzed, and on the respective extraction residues, too. Both methods revealed important features of the chars, in particular the increasing degree of aromatic condensation with increasing highest heating temperature (HTT). The overlap between the two methods was identified in the lipid fraction, where the proportion of benzenetricarboxylic acids (B3CAs) correlated with PAH abundance. The results confirmed the validity and complementarity of the two molecular marker methods, which will likely continue to play a crucial role in PyOM research due to the recent developments of compound-specific PAH and BPCA stable carbon ( $\delta^{13}\text{C}$ ) and radiocarbon ( $^{14}\text{C}$ ) isotope methods.

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### 1. Introduction

Pyrogenic organic matter (PyOM) is ubiquitous in the environment (Schmidt and Noack, 2000; Schmidt et al., 2001; Masiello, 2004) and relatively stable against degradation, making it part of the slow-cycling C pool (Marschner et al., 2008; Kuzyakov et al., 2014). PyOM abundance is thought to increase globally with increasing wildfire occurrence in the 21st century (Flannigan et al., 2013; Kelly et al., 2013) and as a result of industrial combustion processes and traffic (Bond et al., 2013). Moreover, it is increasingly and intentionally produced in anthropogenic biochar-systems, which have been proposed as a strategy for green

energy production, C sequestration, and soil improvement (Lehmann and Joseph, 2009; Meyer et al., 2011). With increasing PyOM production and the awareness of its importance for the C cycle, attention has been drawn to characterize these materials accurately across different disciplines (Simoneit, 2002; Hammes et al., 2007; McBeath et al., 2011). Molecular marker methods are one technique providing the opportunity to characterize PyOM. They target specifically the molecules that are produced during the combustion processes. Two different approaches are often used that both focus on the polycyclic structures typical for pyrogenic materials: (i) polycyclic aromatic hydrocarbon (PAH) analysis and (ii) the benzenepolycarboxylic acid (BPCA) method.

PAHs are small polycyclic aromatic compounds that have a long history as tracers for combustion products (Simoneit et al., 1999; Simoneit, 2002; Denis et al., 2012). They proved to be particularly useful for the source apportionment of combustion residues in soils

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and sediments, for example distinguishing between contributions of biomass burning and fossil fuel (Oros and Simoneit, 2001a, b; Yunker et al., 2002; Bucheli et al., 2004). High concentrations of PAHs are of environmental concern due to their mutagenic and carcinogenic properties (Boffetta et al., 1997; Wilcke, 2000). Thus, PAHs have recently also been heavily investigated in the context of biochar applications (Hale et al., 2012; Hilber et al., 2012; Keiluweit et al., 2012; Oleszczuk et al., 2013; Quilliam et al., 2013). After extraction with the lipid fraction from bulk PyOM (Colmsjö, 1998; Fabbri et al., 2013), they are routinely quantified with gas or liquid chromatography.

BPCAs, on the other hand, present a workaround to quantify the abundant polycyclic PyOM structures that are larger and more complex than PAHs. These more condensed aromatic C phases cannot be quantified directly as polymers using chromatographic methods. In order to analyze such pyrogenic structures, PyOM is digested with nitric acid under high temperature and pressure, which breaks the polycyclic compounds down into individual BPCAs, amenable to gas or liquid chromatography (Glaser et al., 1998; Brodowski et al., 2005; Wiedemeier et al., 2013). Pyrogenic C is thus assessed on a molecular level and can be used to estimate PyOM abundance in environmental compartments such as soils and sediments. The technique has yielded valuable insights into the slow cycling of PyOM in the pedosphere (Hammes et al., 2008; Rodionov et al., 2010) and has been helpful to illuminate the pathways of PyOM into sedimentary systems, where PyOM accounts for a quantitatively important fraction of the carbon sink (Guggenberger et al., 2008; Sánchez-García et al., 2013). The BPCA method additionally reveals information about the aromaticity, aromatic condensation and charring temperature of the analyzed PyOM when relative yields of benzenetri-, benzenetetra-, benzene-penta- and benzenehexacarboxylic acids (B3-, B4-, B5- and B6CA) are compared (Dittmar, 2008; Schneider et al., 2011; Wiedemeier et al., 2014). These qualitative parameters are indicative for the stability of PyOM in the environment and can also help to produce suitably engineered biochars (Harvey et al., 2012a).

In this study, we investigated the link between the two molecular marker approaches. Despite having different analysis windows, both methods target a part of the characteristic PyOM polycyclic aromatic features that become increasingly condensed with higher charring temperatures (McBeath et al., 2011). The aim was to test if the conceptually feasible overlap between the small aromatic PAH moieties and the larger, condensed polycyclic structures, as indicated by BPCAs, can be assessed with the two methods when applied to real pyrogenic sample materials. We thus measured PAHs and BPCAs on two different straws (rye and maize) and their corresponding chars with highest heating temperatures (HTT) of 300, 400 and 500 °C, respectively. Moreover, we also analyzed BPCAs on the same lipid extracts, on which PAHs were measured, and determined BPCAs on the resulting extraction residues, too.

## 2. Materials and methods

Chars were produced by heating rye (*Secale cereal* L.) and maize (*Zea mays* L.) straw samples for 2 h in a pre-heated muffle furnace at 300, 400 and 500 °C, respectively (Rennert et al., 2008). Al foil was used to limit oxidation during the charring process. Straw and char samples were subsequently milled to fine powder before chemical analysis.

Organic carbon contents were measured using elemental analysis (Leco CS 225, Mönchengladbach Germany). Lipids from all samples were extracted using the accelerated solvent extraction method (Dionex ASE 200, Sunnyvale, CA) with  $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$  (93/7; v/v) as described by Wiesenberget al. (2004, 2008, 2009).

Samples were sequentially extracted for 20 min in two steps at  $5 \times 10^6$  Pa and 75 °C and 140 °C, respectively. Both extracts were combined thereafter and cleaned using solid phase extraction columns fitted with KOH coated silica gel (Wiesenberget al., 2008). Aromatic hydrocarbons were then measured after sequential chromatographic separation (Radke et al., 1980) on GC/MS (HP 5890 Series II GC and HP 5989A mass spectrometer, Palo Alto, CA). Detailed data from the PAH analysis of the samples were reported by Wiesenberget al. (2009), while we here used specific statistics of these results with the focus to assess the linkages between the PAH and BPCA method.

BPCAs were measured on bulk materials (the two straws and all their charred analogues) as well as on the respective products from the lipid analysis (the lipid extracts and the lipid extraction residues). The lipid extracts of the 500 °C chars did not yield enough material to be amenable for BPCA analysis. BPCAs were analyzed following the procedure reported by Brodowski et al. (2005), i.e. bulk samples, lipid extracts and lipid extraction residues all underwent the same digestion and analysis steps. Method-inherent underestimation of PyOM was not corrected by any conversion factor (Schneider et al., 2010). For consistency purposes, we used gas chromatography protocols for both PAH and BPCA quantification. However, both methods have recently been adapted to liquid chromatography, which offers an interesting alternative for the assessment of these markers (Schneider et al., 2011), particularly in environmental samples (Denis et al., 2012; Wiedemeier et al., 2013).

Data analysis was conducted with the statistical software R (R, 2011). Changes in the distribution of individual BPCAs between the bulk samples, the lipid extracts and the lipid extraction residues were analyzed with the chi-square goodness of fit test. Relationships between BPCAs and PAHs were analyzed with linear regression.

## 3. Results and discussion

PAHs were undetectable in the straw materials, present in chars with HTT of 300 °C and highly abundant in chars that were pyrolyzed between 400 and 500 °C (Fig. 1; top). This is in line with previous studies (Brown et al., 2006; Kloss et al., 2012) and indicates the potentially problematic use of low-temperature biochars as a soil amendment due to their usually high content of harmful PAHs (Keiluweit et al., 2012). Moreover, a distinct pattern between the proportion of PAHs with different ring sizes and the pyrolysis temperature was observed: The proportion of small PAHs (3-ring) decreased while the contribution of higher molecular weight PAHs (4–6 ring) increased with increasing temperature (Fig. 1; bottom). Similar trends have been observed in other studies (McGrath et al., 2003; Brown et al., 2006; Keiluweit et al., 2012) and point to the increasingly condensed nature of the solid PyOM residue (the char) while losses of the smaller, more volatile PAHs occur with increasing charring temperature (McGrath et al., 2003).

The BPCA method detects these large, condensed polycyclic structures of non-volatile PyOM and consequently showed increasing amounts of BPCA quantity with increasing temperature in the bulk char samples (Fig. 2; black bars). Besides the total BPCA yields normalized to bulk weight, also the proportion of BPCA normalized to organic carbon increased with temperature. The latter is a measure for the aromaticity of charred materials (McBeath et al., 2011) and is consistently higher for rye-derived chars than for the maize-based char samples (Fig. 2; upper number). This difference in aromaticity was partially reflected by the data obtained from the PAH analysis, as the rye chars showed higher proportions of the larger PAHs than the maize chars (Fig. 1). However, the relationship between PAH ring sizes and aromaticity of PyOM are complex

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