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Benzene polycarboxylic acid — A useful marker for condensed organic matter, but not for only pyrogenic black carbon

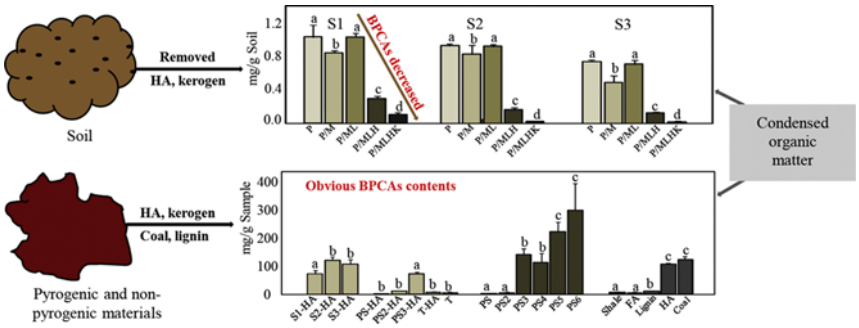
Zhaofeng Chang [a], Luping Tian [a], Fangfang Li [a], Yuwei Zhou [a], Min Wu [a,*], Christian E.W. Steinberg [b], Xudong Dong [a,c], Bo Pan [a], Baoshan Xing [d]

[a] Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China
[b] Humboldt-Universität zu Berlin, Laboratory of Freshwater and Stress Ecology, Arboretum, Späthstr. 80/81, 12437 Berlin, Germany
[c] Medical School, Kunming University of Science and Technology, Kunming 650500, China
[d] Stockbridge School of Agriculture, University of Massachusetts, Amherst, MA 01003, USA

HIGHLIGHTS

- Sequential removal of soil fractions leaves 2.4–10.1% BPCAs in black carbon.
- Soils of different depth show similar distribution patterns of BPCAs.
- BC-like structure of organic matter may be referred to BPCA-probed OM content.
- BPCA biomarkers are useful fingerprints to probe OM properties and sources.

GRAPHICAL ABSTRACT



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ABSTRACT

Benzene polycarboxylic acid (BPCA) molecules are a widely used marker method for the qualitative and quantitative analysis of pyrogenic black carbons (BC). Based on an overview of the development and chemical reaction mechanism of the BPCA method, we propose that the commonly used BPCA markers may not be solely indicative of BC but more generally of condensed organic matter in soils and aquatic systems. First, we sequentially removed the soil fractions and observed that the BPCA contents were abundant in humic acids (HAs). After sequential treatment, the residual particles were supposed to contain BC and minerals; however, the BPCAs in the residue accounted for only 2.4–10.1% of that detected in the entire soil. In addition, substantial quantities of BPCAs were detected in both thermally treated samples and composted biomass. Furthermore, humic acids extracted from all the samples showed that obvious BPCA contents in the samples accounted for 0.1–121.7 mg/g. Therefore, soil fractionation may also partly extract BCs as suggested by BPCAs in the HAs of the biochars. However, organic matter without any thermal treatment may contain BPCAs. A series of standard substances without any BC showed high BPCA content in the samples from 5.9–124.5 mg/g. These observations create a serious concern for the proper application of BPCAs as a marker for BCs. Combining a systematic literature review of BPCA that deviates from BC content, we suggest that the BC-like structure of organic matter may be referred to as BPCA-probed organic matter content, which could be a more useful term for studies on the multimedia environmental behaviors of contaminants.

* Corresponding author.
E-mail address: kustless@gmail.com (M. Wu).

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1. Introduction

Because of their highly hydrophobic surface, porous structure and light absorbance properties, carbon contents with aromatic structures play an important role in the environment. These layered and porous carbon contents with enriched aromatic structure are generally referred to as condensed carbon structures or black carbon (BC). For example, BC in the environment is receiving a great deal of attention because of its significant role in global warming, contaminant adsorption, and its health risk as a primary pollutant in fine particulate matter (PM2.5). BC is generally thought to originate from pyrogenic sources, e.g., from the incomplete combustion of biomass and fuels (Cornelissen et al., 2005). It is quantified using various techniques, including thermal oxidation (Yang and Guo, 2015), chemical oxidation (Wang et al., 2014) and as isotope techniques (Bird and Ascough, 2012). All these methods provide an estimated amount of BC. Adopting the specific marker concept, investigators developed a marker-based BC analysis method, namely, the benzene polycarboxylic acids (BPCAs) method (Glaser et al., 1998). The basic idea of this method is that during the BC oxidation by strong acids under high temperature and pressure, the benzene ring will be cleaved and oxidized. Consequently, carboxylic acids will be introduced on the cleaved benzene rings. Based on the contents of condensed ring structures in the detected BPCA, investigators thus are able to describe the properties and trace back the origin of BCs. Previous investigators have proven that a series of BPCA molecules were produced when the condensed carbon clusters were oxidized. These detected BPCA molecules did not naturally occur and thus could specifically refer to BC. Therefore, researchers were able to describe the origin and aromaticity of BC from BPCA contents (Lehndorff et al., 2014; Schneider et al., 2010). This method has been applied to the estimation of BC in soils (Borchard et al., 2014), sediments (Sánchez-García et al., 2013), charcoals (Wiedner et al., 2013), aerosols (Gaviño et al., 2004), and even water (Khan et al., 2016). The BPCA marker technique is even more powerful when the stable isotope technology is incorporated. For example, the ^{13}C isotope signature of BPCA could be analyzed to more accurately trace BC sources (Rodionov et al., 2010).

One of the most attractive applications of the BPCA marker approach is to probe BC properties. In previous studies, BPCA-indicated that the C content and the proportions of B6CA in charcoals were positively related to pyrolysis temperatures (Schneider et al., 2010). The estimation of pyrolysis temperatures is even possible through the B6CA-C content (Schneider et al., 2013). Previous investigators also suggested that B6CA/BPCA values could be used as an indicator of aromatic condensation or aromaticity of BC. The higher B6CA/BPCA values generally correlated with higher aromaticity or condensation (Wiedemeier et al., 2015). Alternatively, B5CA/B6CA is suggested to be negatively correlated with the combustion temperature (Wolf et al., 2013).

The distribution patterns of individual BPCA molecules are used to identify BC sources (Roth et al., 2012). The ratio of B5CA/B6CA < 0.8 is always referred to in domestic fires: 0.8–1.4 for grass burning and 1.3–1.9 for forest fires (Boot et al., 2015; Wolf et al., 2013). The ratios of B6CA/B4CA < 2, >2, and >7 were related to BCs from grass, urban soils, and fossil fuels, respectively (Lehndorff et al., 2014). Thus, these parameters greatly broaden our understanding regarding BC properties and their fate.

Although investigators have emphasized the promising application potential of the BPCA method for the BC description, great discrepancies have been noted in the literature results. For example, the conversion factor between BPCA and BC contents varies greatly depending on various reference materials (Brodowski et al., 2005; Glaser et al., 1998). The BPCA components, especially B3CA and B4CA, could be overestimated because of the contribution of non-pyrogenic organic matter (Kappenberg et al., 2016). Clearly, B4CA input may alter B6CA/B4CA values and thus interfere with the BC source assignment. Recently, Acksel et al. (2016) even pointed at the uncertainties of using B5CA/B6CA ratios to trace BC sources because of the selective preservation or cleavage of condensed BC into less condensed structures in the environment.

Based on the above discrepancies, we conducted a comparative analysis of the literature results and measured BPCA molecular markers in representative samples. The applicability of BPCA in organic matter characterization and thus the proper use of BPCA markers will be extensively discussed for condensed organic matter. How specific is the BPCA marker approach in characterization of BC and the identification of its sources?

2. Materials and methods

2.1. Sequential removal of soil carbon-rich components

Soil samples from different depths (0–20 cm, 20–40 cm, and 40–60 cm were denoted as S1, S2, and S3, respectively) were collected from Xishuangbanna, Yunnan, which was far from local industrial sources. All of the soil particles were air-dried, ground, and passed through a 20 mesh (840 μm) sieve. The process of sequential removal of the soil fractions was adopted from Song et al. (2002). Previous studies confirmed that this method will not change the properties of organic matter as confirmed using ^{13}C NMR spectrometry (Masiello and Druffel, 1998). We combined acid demineralization, base extraction and dichromate oxidation to remove the soil fractions, namely mineral, HA and kerogen, respectively. Briefly, 70 g of soil was treated in 300 mL of 6 M HCl for 20 h at 60 °C. The mixture was then centrifuged and the residue was rinsed with three times in 2 M HCl. The soil residue was then demineralized in HCl (6 M) + HF (22 M) for 20 h at 60 °C and washed repeatedly with ultrapure water until the pH approached 7.0. The obtained particles were dried at 60 °C and were referred to as P/M (soil after mineral removal). A part of P/M was Soxhlet-extracted for 72 h to remove the extractable organic matter. After extraction, the solid particles were dried at 60 °C and referred to as P/ML (soils after mineral and lipid removal). The P/ML samples were placed in 0.1 M NaOH solution and extracted for 12 h. The mixture was then centrifuged at 1000 ×*g* for 15 min and the supernatant was transferred to 5 L beakers. The extraction procedure was repeated several times until the supernatant was light yellow. The solid particles were dried at 60 °C and referred to as P/MLH (soils after mineral, lipid, and HA removal). The supernatants were acidified with 6 M HCl to pH 1.0. The precipitated HA was washed using ultrapure water to remove the chloride and freeze dried. The P/MLH samples were then subject to kerogen removal. Briefly, P/MLH samples were placed in bottles containing a mixture of 0.1 M $K_2CrO_7 + H_2SO_4$ to oxidize kerogen with minimal damage to BC (Wolbach and Anders, 1989). The corresponding chemical reaction was maintained in a water bath at 55 ± 1 °C for 60 h. An additional $K_2CrO_7 + H_2SO_4$ mixture was added to ensure an overdose of the oxidant. The bottles were then placed in a cold-water bath for 5 min and centrifuged. The residues were washed 5 times with ultrapure water, dried at 60 °C, and then referred to as P/MLHK (i.e., soils after mineral, lipid, HA, and kerogen removal).

2.2. Preparation of carbon-rich samples of different degrees of maturity

Analyzing BPCAs in carbon-rich samples at different degrees of maturity will provide an important basis for comparison. In addition to the HAs obtained in the last section above, both thermally treated (biochars) and composted biomasses were used. For biochar preparation, peanut shells were obtained from a local market. Air-dried peanut shells were oven-dried at 45 °C and then smashed with a grinder. The smashed particles were wrapped in aluminum foil and placed in a muffle furnace for pyrolysis at 200, 300, 400, 500, or 600 °C for 4 h. The muffle furnace was provided with a continuous flow of N_2 to maintain an O_2-poor atmosphere. The charred peanut shells were passed through a 60 mesh (250 μm) sieve and stored for further use. Furthermore, the HAs were extracted from 200 and 300 °C biochars according to the above extraction procedure. Commercial Pu′er tea was selected as