



Note

Comparison of black carbon chemical oxidation and macroscopic charcoal counts for quantification of fire by-products in sediments



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ABSTRACT

Black carbon (BC) ranges in size from submicron to millimeter scales and represents incompletely combusted or pyrolysed organic fuels (e.g., coal, petroleum, biomass etc). The content of BC in sediments or in the atmosphere has been widely used to infer fossil fuel combustion from local to regional sources. However, the assessment of natural fires (biomass burning) in the past has been conventionally performed by counting charcoal particles in different size fractions (greater than ca. 10 and 100 μm for microscopic and macroscopic charcoal, respectively) using a microscope. Because similarly sized charcoal particles can have large differences in mass, counting using microscopes may induce significant error for quantifying fire-produced BC in sediments. A popular method oxidizes BC with nitric acid to produce benzene polycarboxylic acids (BPCAs), which can be subsequently quantified using a gas chromatograph and mass spectrometer (GC-FID and GC-MS). In this paper, we provide the first parallel comparison of charcoal and BPCA analyses to assess their ability to quantitatively record BC content in experimental sediments. We find that while qualitatively comparable, the BPCA method more accurately quantifies changes in BC content than does charcoal microscopy. Additionally, we use metadata analyses of the Global Charcoal Database to contextualize our results. Further, we explore possible applications of these two methods in tandem which could provide novel insight into paleofire characteristics.

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1. Introduction

Fire is an important component of the Earth system and has important impacts on global carbon cycling and atmospheric chemistry (Crutzen and Andreae, 1990; Kasischke et al., 1995; Scott et al., 2014). Furthermore, global fire regimes are expected to be perturbed by anthropogenic climate change (Field et al., 2014). By measuring by-products of biomass burning in paleoenvironmental records, such as lake sediments, peats, bogs, and soils, we can provide historical context with which to assess the potential responses of fire regimes to climate change (Conedera et al., 2009; Mooney and Tinner, 2011). As such, accurate measurement of fire by-products in sediment matrices and subsequently relating the fire records with potential drivers and other proxy records represent an important methodology for predicting future fire changes

and understanding fire's role in the Earth System on centennial and millennial timescales.

The by-products of the incomplete combustion of biomass span a broad size continuum from submicron to millimeter scales and are collectively referred to as Black Carbon (BC; Goldberg, 1985; Hedges et al., 2000; Masiello, 2004). Importantly, BC content in sediments is not necessarily uniformly distributed (Brodowski et al., 2006; Halsall et al., 2018). By chemically treating sediment samples, sieving the residue, and enumerating charcoal particles under a microscope, paleoecologists have reconstructed local and regional fire histories from sediment records for decades (Whitlock and Larsen, 2002). However, traditional sediment-based paleoecology has relied upon the microscopy of only one segment of this spectrum: macroscopic charcoal (>100 μm ; Whitlock and Larsen, 2002; Conedera et al., 2009; Mooney and Tinner, 2011). Microscopic charcoal (>10 μm) has also been used, but involves more time-intensive methods that remain limited by microscope power in their ability to measure smaller size segments of the BC spectrum (Conedera et al., 2009). Furthermore, charcoal particles of different sizes and masses carry equal weight in the charcoal method and thus it does not quantitatively

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(weight-wise) characterize fire by-products in paleorecords. The smallest size fractions constitute the most abundant segment of the BC continuum (Brodowski et al., 2006; Halsall et al., 2018), so charcoal-based reconstructions run the risk of using variations in outlier values as the basis of their interpretations. In contrast, the digestion of BC to benzene carboxylic acids (BPCAs) has emerged as a reliable method of quantifying the full size spectrum of BC content in sediments (Glaser et al., 1998; Brodowski et al., 2005). This paper represents the first quantitative comparison of these techniques.

Here, we provide a parallel comparison of charcoal and BC analyses to assess which methodology more quantitatively measures changes in the prescribed charred mass in sediment matrices. To our knowledge, no study has compared charcoal and BC analyses using experimental samples in a laboratory setting to assess the comparability of these field-specific approaches. We present charcoal and BC analyses of experimental samples to address the following research questions: (1) Can charcoal, despite representing a small segment of the continuum, qualitatively represent total BC? (2) How do the accuracies of these methods compare? (3) What are the advantages and disadvantages of these methods?

2. Methods

2.1. Experimental samples

Experimental charcoal was produced by pyrolysis of twig and needle cuttings of live juniper (*Juniperus*) in a programmable muffle furnace at 450 °C for 4 h. Plant samples were wrapped in aluminum foil packages to ensure oxygen limitation. After charring, samples were lightly processed with a mortar and pestle to break apart any charred pieces larger than 1 mm. Experimental samples of known %BC (0.01, 0.05, 0.1, 0.25, 0.5, 0.7, 1.0) were created by mixing weighed masses of charred matter and acid washed sand (Fisher Chemical). We determined the grain size distribution of the charred matter and sand comprising our experimental samples by washing samples through a series of nested test sieves (32 μm, 63 μm, 90 μm, 125 μm, 150 μm, 250 μm, 300 μm, 355 μm) with deionized water and weighing the dried size fractions.

2.2. Charcoal analyses

Following standard procedures (Whitlock and Larsen, 2002; Chipman et al., 2015), samples were immersed in a 1:1 mixture of bleach (10%) and sodium hexametaphosphate (10%) for 24 h before washing through a 250 μm sieve with deionized water (Endecotts brass test sieve; 3 inch). Sieved samples were poured into a gridded counting tray and enumerated with a binocular dissection microscope (4–40× magnification).

2.3. Black carbon digestion analyses

The BC samples were digested to produce BPCAs by nitric acid oxidation (2 mL of 65% HNO₃) at 170 °C for 8 h (Glaser et al., 1998; Brodowski et al., 2005). This methodology has come to be used widely (Roth et al., 2012; Wolf et al., 2013; Lehndorff et al., 2015a, 2015b; Kappenberg et al., 2016). We used 25 mL polytetrafluoroethylene (PTFE)-lined hydrothermal synthesis reactors housed in steel high pressure vessels (Deschem Science Supply). Vessels were heated in an aluminum block on a hot plate (Fig. 1). Following oxidation, the extracts were dried by heating at 60 °C overnight. Subsequently, the extracts were transferred to 4 mL glass vials using 1 mL of 5% acetyl chloride in methanol, filtered through 0.2 g of sodium sulfate for retention of the solid phase, and methylated at 60 °C for 8 h. The methylated samples were

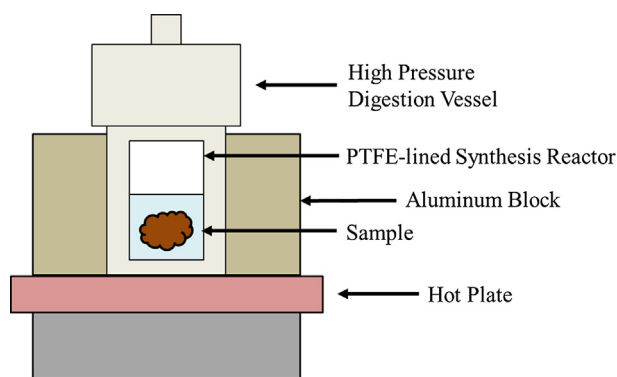


Fig. 1. Schematic representation of the laboratory apparatus used to digest Black Carbon.

dried under nitrogen flow and redissolved in 1 mL of dichloromethane (DCM) for quantification and characterization. Prior to instrumental analysis, 50 μL of an internal standard solution (100 μg mL⁻¹ nonacosane in DCM) was added to each sample. BPCAs were identified and quantified with an Agilent 6890N gas chromatograph coupled with a 5973N mass spectrometer (GC-MS) and flame ionization detector (GC-FID), respectively. Both instruments were equipped with an Agilent VF-200 ms 60 m capillary column (250 μm i.d. × 0.1 μm film thickness). External standards were used to confirm the identity of pyromellitic acid (PMA), benzene pentacarboxylic acid (PCA), trimellitic acid (TMA), hemimellitic acid (HMMA), and phthalic acid (PA). As we used experimental samples, we opted to exclude the metal elimination steps needed for natural samples.

3. Results and discussion

3.1. Charcoal and BC% as fire history proxies

Our BPCA method accurately quantifies BC%. Our results demonstrate that phthalic acid (PA), trimellitic acid (TMA), hemimellitic acid (HMMA), pyromellitic acid (PMA), and benzene pentacarboxylic acid (PCA) can each reliably quantify variable amounts of BC (0–1 g of 2% BC experimental mixture; Fig. 2). Notably, our method did not produce the six-member BPCA, mellitic acid. We hypothesize that either: (1) our charring conditions did not facilitate sufficient condensation and aromatization to produce mellitic acid during nitric acid oxidation (Schneider et al., 2010); (2) the vegetation type we charred precluded the production of mellitic acid; or (3) our methylation of the samples may have caused mellitic acid to become insoluble and thus precluded its quantification. Nonetheless, the other five BPCAs accurately quantify BC content in experimental samples.

Our analyses demonstrate that charcoal and BPCA methodologies are generally comparable, but that the BPCA method is a more accurate means of characterizing %BC (Fig. 3). In our experimental samples, we found that 0–1 %BC equated to 0–635 macroscopic (>250 μm) charcoal particles. In this way, macroscopic charcoal abundances were able to characterize low %BC concentrations. However, the accuracy of charcoal counting is lacking (R² = 0.43). In contrast, the BPCA method is much more accurate in quantifying %BC (R² = 0.82). This discrepancy is doubtless due in part to the reality that charcoal counts only consider a fraction of the total BC content of sediments. In our experimental samples, particles >250 μm compose only 15.6% of the total mass of BC (Fig. 4). In this way, charcoal counts characterize a limited segment of the total BC in sediments. Thus, while the charcoal method may be less time consuming means of inferring qualitative paleofire changes, the

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