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Note

Modification of the weak nitric acid digestion method for the quantification of black carbon in organic matrices

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ABSTRACT

The weak nitric acid digestion method (also known as KMD) is a method to quantify black carbon (BC) in mineral soil. Here we extended the use of this methodology from mineral samples to organic matrices. We tested this methodology on known mixtures of pyrolyzed pine wood and needles (at 300 °C and 550 °C) and non-pyrolyzed pine needles and measured: (1) the fraction of pyrolyzed material identified as BC by the methodology, (2) the fraction of non-pyrolyzed pine needles identified as BC, and (3) the precision of the method. We found that the fraction of pyrolyzed-C identified as BC ranges from 10% (needles at 300 °C) to 90% (wood at 550 °C), indicating that the weak nitric acid digestion method can be extended to measure BC in organic matrices and that the methodology can be used in studies aimed to quantify BC stocks in post-fire environments.

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1. Introduction

The ability to quantify black carbon (BC) in organic matrices is essential to quantify the stocks of BC that remain in situ after a fire for carbon (C) budget purposes (Pingree et al., 2012; Santín et al., 2016), because BC may represent an important soil C-sink due to its inherent chemical recalcitrance relative to other types of organic material (Schmidt et al., 2011). Furthermore, quantifying BC in organic matrices is an essential step to reconstruct past-fire history in peat bogs using charcoal as a proxy for wildfires (Conedera et al., 2009). To date, a wide range of methods have been used for estimating BC in environmental samples; however, many of these methods require specialized equipment and instrumentation, are time-consuming and therefore costly, like ^{13}C nuclear magnetic resonance spectroscopy (Baldock et al., 2004; Miesel et al., 2015), benzene polycarboxylic acid molecular markers (Wiedemeier et al., 2013; Kappenberg et al., 2016), and hydrogen pyrolysis (Wurster et al., 2012). There is therefore a pressing need for simple quantitative methods for estimating BC content in soils using commonly available laboratory supplies and equipment.

The weak nitric acid method (KMD; Kurth et al., 2006) enables the isolation and quantification of the fraction of BC in mineral soil samples. It has been widely applied to estimate BC stocks in mineral soil (Mackenzie et al., 2006; Bélanger and Pinno, 2008; Ball et al., 2010; Licata and Sanford, 2012; Soucémarianadin et al., 2014), and hand-picked charcoal particles (Pingree et al., 2012). KMD has two main assets: simplicity and a direct ecological interpretation of the results. However, little is known on the applicability of the method to organic matrices (e.g., forest floor material) and on the specificity, precision and bias of the method. We established an experiment to answer the following research questions: (1) Bias: How much pyrolyzed material is identified as BC by the method? (2) Specificity: How much non-pyrolyzed material is identified as BC? (3) Precision: how large is the unexplained variance? We hypothesized that the method, with few modifications, can be applied to organic matrices and that the method has a higher specificity for BC than for non-pyrolyzed organic matter.

2. Materials and methods

Pyrolyzed materials were prepared from pine needles collected in a Scots pine (*Pinus sylvestris* L.) plantation at the University's Tree Research Center (Lansing, Michigan, USA) and pine wood was collected from standing dead jack pine trees (*Pinus banksiana* Lamb.) near Mio, Michigan. Each material was ground to pass a 1 mm screen and pyrolyzed (charred) in 700 ml glass jars (Ball Corporation, Broomfield, Colorado, USA) wrapped entirely with aluminium foil to limit oxygen availability. The jars were filled to the brim with the material to minimize air space and the availabil-

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ity of oxygen during the charring process. Each material was pyrolyzed for five hours at 300 °C and 550 °C in a muffle furnace. We then created four types of mixtures by mixing each type of pyrolyzed material into non-pyrolyzed pine needle matrix (ground to < 1 mm) from 0% to 100% mass ratio with steps of 10%, before pulverizing each mixture to a fine powder and drying it at 70 °C. C and N contents of the non-pyrolyzed and pyrolyzed materials were determined by elemental analysis (Costech, Italy, combustion temperature 1000 °C; Table 1). We modified the KMD method by diluting an aliquot of each organic mixture to 10% mass ratio by mixing it with pulverized quartz sand. To facilitate the initial mixing of pulverized quartz + organic sample we used a vortex set at maximum speed for approximately 30 s, followed by inverting or rolling the vials to ensure homogenization before taking a subsample for the digestion. The reasons for the dilution were to: (1) obtain a total C concentration similar to a typical mineral soil, and (2) decrease the amount of foaming that occurs during the reaction between hydrogen peroxide and organic matter (see Licata and Sanford, 2012). We digested 0.5 g of each mixture in a block digester (Seal Analytical BD50, USA) at 100 °C for 16 h. To minimize the evaporation of the solution during digestion, the tubes were capped with tear-drop stoppers. The digestion process generates some foam that can either erupt out of the digestion tubes or adhere to the walls of the tubes once the foam dries. To prevent these two foam-related problems, we intermittently and temporarily sealed the tubes with a stopper and agitated them until the foam was again dissolved in the digestion solution. We performed the intermittent tube agitations inside a ventilated hood because pressure can build up in the tube while the tube is closed with the sealed stopper, even over very short periods of time. We replaced the sealed stopper with the tear-drop stopper at the end of the agitation. The process was repeated every time a consistent amount of foam formed in the tubes. The formation of foam usually stopped four hours after the beginning of the digestion. After the digestion we agitated the tubes to thoroughly suspend the digested residue into the solution before filtering (Whatman, grade 2) under vacuum. The solid residue collected on the filters was dried on the filter paper (70 °C for 24 h) and weighed. The solid digestion residues were then measured for C concentration as stated above.

3. Calculation

BC concentration was calculated with Eq. (1):

$$BC = (C_{post\_digestion}/C_{pre\_digestion}) \times 100 \quad (1)$$

where $C_{pre\_digestion}$ and $C_{post\_digestion}$ are the C mass before and after digestion, respectively.

We fitted the data to the two-pool mixing model described in Eq. (2) using a Bayesian approach:

$$C_{post\_digestion} \sim N_{truncated(0,+\infty)}(Fr \times C_{pre\_digestion\_non\_pyrolyzed} + Fp \times C_{pre\_digestion\_pyrolyzed}, \sigma) \quad (2)$$

where $C_{pre\_digestion\_non\_pyrolyzed}$ and $C_{pre\_digestion\_pyrolyzed}$ are the masses of C in the mixture before the digestion derived from the non-pyrolyzed pine needles, and the pyrolyzed pine needles or wood, respectively. Fr and Fp are estimated parameters, and represent the fraction of C identified as BC by the KMD method of the non-pyrolyzed (raw) and pyrolyzed material, respectively. The parameter σ is the error term and was estimated as a linear function of the predicted value (Eq. (3)):

$$\sigma = CV \times (Fr \times C_{pre\_digestion\_non\_pyrolyzed} + Fp \times C_{pre\_digestion\_pyrolyzed}) \quad (3)$$

where CV is the estimated parameter representing the coefficient of variation.

We assumed that the C in the samples post-digestion was distributed as a truncated normal distribution in the interval [0, Inf], because C mass cannot take negative values.

The advantage of using a Bayesian approach in this experimental setup is twofold: first, the three parameters represent a direct answer to the research questions. Fr represents the *specificity* of this method for BC (i.e., how much non-pyrolyzed pine needle-C is identified as BC), Fp is the *bias* (i.e., how much pyrolyzed-C is recognized as BC by the methodology), and the CV is a measure of the *precision* of the method expressed by the ratio between the unexplained variance (i.e., the measurement error) and the expected value. Second, the model can be tailored to follow the distribution of the response variable and the domain of the parameters. The priors of the parameters were uninformative. For the parameters Fr and Fp the prior was a uniform distribution in the closed interval [0, 1] because these two parameters represent the fraction of the C before the digestion that was identified as BC. The CV was a uniform distribution in the interval [0, $+\infty$] because the domain of the standard deviation (σ) are the real positive numbers. The characteristics of our Markov-Chain-Monte-Carlo model fitting procedure were: number of iterations: 4000, burn-in: 2000, thinning rate: 5. The convergence of the model was assessed using the potential scale reduction factor (R-hat < 1.01; Gelman and Rubin, 1992). The model was fit using Markov-Chain-Monte-Carlo and the software JAGS interfaced to R through rjags (Plummer, 2015). Significant differences among parameters were assessed by deriving the mean differences among parameters.

4. Results and discussion

The correlation between the amount of pyrolyzed material in the mixture and the proportion of C identified as BC was positive and significant for all four types of pyrolyzed material (Fig. 1b, $P < 0.0001$). We found that each pyrolyzed material had a distinct BC concentration (parameter Fp), with means ranging from 10%

Table 1
Descriptive statistics on element concentrations of the pyrolyzed and non-pyrolyzed materials and estimates of model parameters that represent the specificity, bias and precision of the modified KMD method. The first three columns show means (± standard deviations) ($n = 2$) of non-pyrolyzed and pyrolyzed pine needle and wood for C and N concentration and C:N ratio. The last column shows mean values of the posterior distribution for Fr and Fp parameters (shown in the fourth column) estimated from the model described in Eq. (1), for each type of material; numbers in parentheses indicate the 2.5% and 97.5% percentiles of the posterior distributions, and letters indicate significant differences among parameters.

Material	C concentration	N concentration	C:N ratio	Model parameter	BC concentration
Unit of measure	(mass%)		(mass ratio)		(% of pre-digestion C)
Pine Needle (not pyrolyzed)	47.59 (0.06)	1.39 (0.10)	34.3 (2.5)	$Fr_{needle\_not\_pyrolyzed}$	5.4 (4.8, 5.6) a
Pine Needle 300 °C	58.08 (1.83)	1.51 (0.04)	38.5 (0.1)	$Fp_{needle\_pyrolyzed\_300}$	10.4 (9.2, 11.7) b
Pine Needle 550 °C	62.74 (0.18)	1.39 (0.01)	45.0 (0.5)	$Fp_{needle\_pyrolyzed\_550}$	57.4 (52.5, 62. 9) c
Pine Wood 300 °C	76.88 (0.56)	0.30 (0.04)	26.0 (36)	$Fp_{wood\_pyrolyzed\_300}$	23.8 (21.7, 26.3) d
Pine Wood 550 °C	91.43 (0.1)	0.79 (0.01)	115.8 (0.7)	$Fp_{wood\_pyrolyzed\_550}$	89.9 (83.1, 97.5) e

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