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Elucidating the chemical structure of pyrogenic organic matter by combining magnetic resonance, mid-infrared spectroscopy and mass spectrometry

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ABSTRACT

Fire-derived organic matter (pyrogenic organic matter, or PyOM), despite its apparent long term stability in the environment, has recently been reported to degrade faster than previously thought. Current studies have suggested that the composition and structure of PyOM can provide new insights on the mechanisms by which C and N from pyrolyzed biomaterials are stabilized in soils. To better understand the chemical structure of PyOM produced under typical fire conditions in temperate forests, samples of dual-enriched ($^{13}C/^{15}N$) *Pinus ponderosa* wood and the charred material produced at 450 °C were analyzed by solid state nuclear magnetic resonance (ssNMR), electron paramagnetic resonance (EPR), diffuse reflectance Fourier transform infrared (DRIFT) spectroscopy, and both isotopic and elemental composition (C, H, O, and N). Notably, the use of high magnetic field strengths in combination with isotopic enrichment augmented the NMR detection sensitivity, and thus improved the quality of molecular information as compared with previously reported studies of pyrogenic materials. The key molecular groups of pine wood and the corresponding PyOM materials were determined using magic-angle spinning (MAS) ^{13}C, ^{15}N, and ^{1}H NMR. Together with DRIFT and EPR measurements, ssNMR revealed the formation of a free radical-containing disordered blend of nitrogenous aromatics and heat resistant aliphatics in the PyOM due to incomplete combustion of the precursor wood. ^{13}C ssNMR and DRIFT analyses showed the removal of oxygenated aliphatics due to pyrolysis of the precursor wood and the dominant contribution of multiply-bonded and oxygenated aromatic structures in the resulting PyOM. However, the ^{18}O isotopic analyses indicated selective retention of ligneous moieties during charring at 450 °C. ^{15}N ssNMR studies implied that the nitrogenous species in PyOM corresponded to thermally altered rather than heat resistant domains of the pine wood precursor. Our molecular characterization suggests that biomaterials pyrolyzed near 450 °C may degrade in soils faster than those pyrolyzed at higher temperatures and may not represent a stable C sink in terrigenous ecosystems.

1. Introduction

Pyrogenic organic matter (PyOM) consists of a heterogeneous class of thermally altered plant materials and fossil fuel residues, ranging from mildly heated plant biomass to residues produced at progressively higher temperatures of up to 1000 °C (Goldberg, 1985). PyOM comprises a significant fraction (5–45%) of the soil organic carbon (C) pool, and represents an important sink for atmospheric CO_2 (Preston and Schmidt, 2006; Lehmann, 2007). However, recent studies have reported that PyOM may degrade at a centennial, not millennial time scale in soils (Hammes et al., 2008; Santos et al., 2012). Recent interest in better understanding the chemical structure, stocks and turnover rate of PyOM has come from the potential of PyOM to improve soil fertility in highly weathered soils (Glaser et al., 2002; Lehmann et al., 2006) and reduce the mobility of pollutants (e.g., heavy metals) in the environment (Koelmans et al., 2006; Nguyen et al., 2007). Furthermore, the amounts of PyOM produced are expected to increase from more frequent wildfires in a future warmer climate (Fried et al., 2004;

Abbreviations: CPMAS, cross polarization magic-angle spinning; DPMAS, direct polarization magic-angle spinning; DRIFT, diffuse reflectance Fourier transform infrared spectroscopy; EPR, electron paramagnetic resonance; IRMS, isotope ratio mass spectrometer; ssNMR, solid state nuclear magnetic resonance; PyOM, pyrogenic organic matter.

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Running, 2006; Bowman et al., 2009) and the production of biochar from the energy industry as a byproduct of low temperature biomass pyrolysis (Lehmann, 2007; Brewer et al., 2009).

The dynamics of PyOM in soils are influenced by its physical and chemical structure. In an incubation study, Baldock and Smernik (2002) observed decreasing PyOM degradation rates with an increase in aromatic C and oxygenated aromatic ring structures. Additionally, the role of PyOM as a sorbent for organic contaminants (Oen et al., 2006) has been attributed to its porosity and aromatic structure (Wang and Xing, 2007; Keiluweit and Kleber, 2009). These findings suggest that a better understanding of PyOM molecular structure is essential to predict its turnover rate and sorption capacity in the environment.

The composition and structure of PyOM in the environment can vary widely depending on pyrolysis conditions and initial biomass. For instance, an increase in pyrolysis temperature has been reported to result first in a rapid decline in carbohydrates, then a decrease in lignin and fatty acids accompanied by an increase in aromatic C structures, followed by a condensation of these aromatic moieties (Nishimiya et al., 1998; Baldock and Smernik, 2002; McBeath and Smernik, 2009; Keiluweit et al., 2010). Supported by evidence from elemental analysis and ^{13}C nuclear magnetic resonance (NMR), Knicker et al. (2008) proposed a model in which PyOM consists of a highly heterogeneous structure with N, O and S substituents. In addition, PyOM produced under oxic conditions at 350 °C or 450 °C was claimed to consist of small polyaromatic clusters (Knicker, 2010), a finding compatible with the accepted hypothesis that aromatic C in PyOM contains a wide range of structures, including small cross-linked aromatic clusters that are susceptible to further decomposition (Schmidt and Noack, 2000; Preston and Schmidt, 2006). Recently, Keiluweit et al. (2010) proposed four categories for PyOM, each having a unique mixture of physical properties and chemical structures, and possibly, mean residence time (MRT) in soils. Moreover, there has been an increased interest in understanding how PyOM structure and stability in soils are influenced by the presence of thermally altered nitrogen (N), an important fraction of this material (Knicker, 2010; Hilscher and Knicker, 2011b).

The use of an isotope (^{13}C and ^{15}N) enrichment approach, when integrated with high-field solid state NMR (ssNMR) data acquisition, can augment the detection of ^{13}C and ^{15}N signals from PyOM functional groups, improving the certainty of associated insights into their molecular structures. In particular, the use of isotopic enrichment provides an NMR spectrum in less time, helps to improve the spectral signal/noise ratio and to detect minor chemical species, and avoids excessive line broadening during data processing that could compromise spectral resolution of the various chemical moieties. The use of higher magnetic field strengths for NMR may also allow better discrimination among chemically similar moieties via enhanced chemical shift dispersion. In addition, spectral editing and multinuclear data collection allow more confident peak assignments to particular structural groupings. Fast magic-angle spinning (MAS) techniques facilitate to directly observe ^{1}H NMR in solid state. By augmenting cross-polarization magic-angle spinning (CPMAS) experiments with direct-polarization (DPMAS) measurements, it is possible to estimate the proportions of the molecular constituents quantitatively (Cusack et al., 2012). Finally, electron paramagnetic resonance (EPR) can detect the presence of unpaired electrons that may account in turn for technical challenges in the detection of ^{15}N NMR spectral signals of the pyrogenic products.

The objective of the current study was to investigate the chemical structure of dual-enriched (^{13}C/^{15}N) PyOM produced under typical fire conditions (450 °C) using a combination of data from solid state NMR, EPR, diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), and stable isotopic and elemental composition. A companion paper describes findings on the biological degradation of the ^{13}C and ^{15}N enriched PyOM in soils during a 180 day laboratory experiment (Santos et al., 2012).

2. Materials and methods

2.1. Wood and PyOM samples

Pine saplings were enriched using $^{13}CO_2$ and ^{15}N fertilizer under controlled conditions during their third growth year (Bird and Torn, 2006). PyOM was produced using air dried enriched pine stem wood cut into 1–2 cm long pieces and heated at 450 °C for 5 h under N_2 (Hammes et al., 2006). For comparisons of the mid-infrared properties of the 450 °C *Pinus ponderosa* PyOM with related samples, chestnut (*Castanea sativa*) wood was treated following the same procedure described above (Hammes et al., 2006), but heated at 400 °C and 500 °C, respectively. Further details about these latter samples are described by Schneider et al. (2010). Cellulose was extracted from three pine wood subsamples using a Jayme–Wise oxidation method described by Leavitt and Danzer (1993) and Panyushkina et al. (2008).

Total organic C and N were measured using a CHN gas analyzer (Costech Model 4010, Valencia, CA, USA). Stable isotope contents (^{13}C, ^{15}N) were determined using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (IRMS) (Sercon Ltd., Cheshire, UK). Oxygen elemental concentration and isotopic enrichment were determined using a PYROcube (ELEMENTAR Analysensysteme, Hanau, DE) interfaced to a Sercon 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK), and H elemental concentration was determined using a high temperature elemental analyzer (Hekatech, Wegberg, DE). Provisional delta values, expressed with respect to Vienna Standard Mean Ocean Water, were corrected based on laboratory standards and international references analyzed with the samples. Elemental and isotopic compositions for pine wood and PyOM, showing high levels of ^{13}C and ^{15}N enrichment, are summarized in Table 1. The ^{13}C enrichment of benzene carboxylic acids extracted from the enriched PyOM averaged 844 δ (Yarnes et al., 2011), similar to the bulk PyOM and its precursor wood and suggestive of a uniformly distributed isotopic label in both samples.

2.2. Solid state ^{13}C NMR spectroscopic analyses

The compositional comparisons of pine wood with subsequently produced PyOM and quantitative estimates of the observable ^{13}C nuclear spins were made using ssNMR. Reproducibility of the spectroscopic measurements and spinning sideband identification were verified by obtaining ^{13}C spectra on each sample at different rotor spinning frequencies (10.000 ± 0.015, 15.000 ± 0.015 kHz, and 30.000 ± 0.010 kHz). ^{13}C CPMAS experiments were performed to identify the carbon chemical moieties, using cross-polarization times of 1.5–2 ms and a 3 s recycle time. ^{13}C DPMAS measurements were carried out for two replicate samples to estimate the relative numbers of each carbon type, using delays between spectral acquisitions of 160 s and 50 s for pine wood and PyOM, respectively (Table 2). The ramped amplitude ^{13}C CPMAS measurements were conducted with a ^{13}C field strength corresponding to 79.6 kHz and a ^{1}H field strength that was varied linearly by 10–20% to maintain the Hartmann–Hahn matching condition at a specific spinning frequency such as 30 kHz. High power heteronuclear ^{1}H decoupling of 170–185 kHz was achieved by the SPINAL pulse sequence (Fung et al., 2000). A 4 channel Varian DirectDrive spectrometer operating at a ^{1}H frequency of 600 MHz (^{13}C at 150 MHz) and equipped with a 1.6 mm fastMAS probe optimized for high sensitivity data