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A non-thermogenic source of black carbon in peat and coal

Blaine E. Hartman, Hongmei Chen, Patrick G. Hatcher *

Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529, USA

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ABSTRACT

Black carbon previously observed in peats has been attributed to various forms of pyrogenic carbon. However, a recent report has shown that a non-pyrogenic source of BC-like molecules can be obtained photochemically from dissolved organic matter. In this study, we examined well-known coal-forming peats located in the USA by solid-state ^{13}C NMR and ultrahigh resolution mass spectrometry to evaluate the contribution of photochemically produced organic matter. The presence of photochemically produced organic matter was observed in all the peat samples and suggests that photochemically induced precipitation is pervasive. To determine if these "photo" materials survive maturation, we examined a low-rank coal from the Gippsland Basin, Australia, and the presence of "photo" materials was observed, indicating that these materials are geologically preserved. Results from this study indicate that photochemically produced materials are important sources of black carbon and aliphatic like compounds to coals and possibly Type III kerogens. It is possible that these materials are precursors to ubiquitously occurring fusinite, macrinite, micrinite, and related inertinite macerals in coal.

1. Introduction

Several recent reports suggest that black carbon (BC), which broadly encompasses charcoal, soot, and other forms of pyrogenic carbon, may constitute more than half of the refractory carbon in soil and sediments (Masiello and Druffel, 1998). BC itself represents a sink for biospheric and atmospheric carbon dioxide, and is intimately tied to the biogeochemical cycling of both carbon and oxygen through its role in organic matter cycling. While the origin of BC is considered to be from thermal oxidation of organic matter at elevated temperatures, a recent report suggests that photochemical oxidation of dissolved organic matter (DOM) in peat swamps generates a similar material (Chen et al., 2014). Drawing from this observation we provide molecular evidence for BC in several peats and suggest that some, if not most, of the BC observed can be derived from photochemical alteration of DOM.

The apparent ubiquity of BC in peats and coal is well recognized, especially in coals where it is often categorized petrographically as fusinite, macrinite, micrinite, and related inertinite coal macerals (Hower et al., 2009; Mukhopadhyay and Hatcher, 1993; Stach et al., 1982). BC is a generic term used to describe several forms of pyrogenic carbon that encompasses soot, charcoal, graphite, and products of incomplete combustion (Goldberg, 1985) and in some instances, can arguably be operationally defined depending on the method used to estimate or quantify the amount of BC (Gustafsson et al., 1996, 2001; Schmidt et al., 2001). The global production of BC from all sources, including biomass burning and fossil fuel burning, has been estimated to be between 50–270 × 10^{12} of C yr^{-1} (Chen et al., 2014) with 80–90% remaining as residues in terrestrial environments (Kuhlbusch and Crutzen, 1995; Suman et al., 1997). Several investigations claim that a significant portion of the total amount of terrestrial organic carbon is in the form of BC. For instance, BC has been reported to represent as much as 30–45% of the total soil organic carbon (Glaser et al., 2000; Schmidt et al., 1999; Skjemstad et al., 1996), and 21–69% of peat carbon (Leifeld et al., 2007). On a global scale, the organic C to a depth of 1 m in peatlands contributes about 225 × 10^{15} g C compared to 2000 × 10^{15} g C for all soils (Bolin et al., 2000). If 25% of this is BC, then 56 × 10^{15} g C is the current standing stock of BC in peats.

As the peat undergoes burial and maturation in the subsurface to brown coal and then on to higher rank coals, this BC, especially charcoal, becomes recognized as fusinite macerals if it remains preserved petrographically. If the BC becomes disaggregated or finely comminuted, then it probably contributes to detrinite, micrinite, or macrinite coal macerals. As a whole, inertinite macerals often constitute lower proportions compared with the vitrinite macerals but in some cases can dominate the coal's composition, as in the case of Gondwana coals (Stach et al., 1982; Teichmüller, 1989).

Recent observations and experimentation (Chen et al., 2014) show that a non-pyrogenic source of BC-like molecules can be obtained photochemically from DOM that is predominantly derived from dissolution of a woody peat in the Dismal Swamp, Virginia, an ombrotrophic black-water swamp. The molecular characterization by electrospray ionization-Fourier transform ion cyclotron resonance-mass spectrometry (ESI-FTICR-MS) shows the material which readily flocculates when subjected to photoirradiation by simulated sunlight to contain a significant proportion of BC-like molecules. Simultaneously, molecules that

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* Corresponding author.
E-mail address: phatcher@odu.edu (P.G. Hatcher).

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are mainly aliphatic in nature are produced by the photochemical transformation of the DOM. These molecules appear to have a polycyclic aliphatic nature and are substituted by carboxyl groups. Accordingly they have been likened to molecules found ubiquitously in aquatic and marine DOM, e.g., CRAM (carboxyl-rich alicyclic molecules). The BC-like, called photoBC, and CRAM-like molecules flocculate in the water but readily redissolve in alkaline aqueous solutions much like humic acid-like substances in soils and peats. The produced molecules were not initially present in the DOM prior to photoirradiation suggesting that the photoBC molecules were generated by photodegradation.

Accordingly, we hypothesize that in peat swamps like the Dismal Swamp, this source could be quantitatively significant compared with pyrogenic sources for BC and that this process may be central to the humification of organic matter in peat. Moreover, it is likely that this flocculating organic matter contributes in the peat as a precursor to petrographically distinct submacerals of the inertinite maceral groups in coal. In the current study, we extend the studies described by Chen et al. (2014) for the Dismal Swamp, Virginia, to examine peats from other well-known coal-forming localities in the USA. We also compare the peat samples with a low-rank coal of the Gippsland Basin, Australia, which represents a more mature form of peat along the natural maturation pathway. Because peat organic matter is known to undergo significant chemical modifications at increased coal ranks and becomes less easily extracted from the coal, a requirement for ESI-FTICR-MS, we limited our study to a low-rank brown coal so as to more readily make comparisons with the organic materials in peat.

Peat samples from the Dismal Swamp, Virginia; the Okefenokee Swamp, Georgia; and the Everglades, Florida (Pahokee peat), as well as the Gippsland coal were subjected to solid-state ^{13}C NMR and ultrahigh resolution mass spectrometry for characterization of their molecular composition achieved by alkali extraction to recover a fraction of the peat and coal that can be analyzed by ESI-FTICR-MS. The extract prepared is essentially defined operationally as humic acids (HA) and usually contributes 25% of the total peat (Hatcher et al., 1983).

2. Materials and methods

2.1. Sample descriptions

A variety of samples were evaluated in this study to examine the occurrence of photochemically produced molecules in various coal-forming peats, a low-rank coal, and a naturally degraded wood sample. The three peat samples utilized for this study were collected from the Dismal Swamp, Virginia; the Okefenokee Swamp, Georgia; and the Everglades, Florida. These selected peats are representative of coal-forming environments from across the United States. The low-rank coal was collected from the upper bench of the Yallourn Open Cut (YOC) in Victoria, Australia (Bates and Hatcher, 1989). The coal sample was chosen to represent an intermediate stage of coalification. A naturally degraded Douglas fir sample was obtained from Mount Rainier, WA (Hatcher, 1987). The sample has been exposed to brown-rot fungi and as a result the cellulosic materials have been degraded and the wood is primarily lignin in character.

All samples were dried and subjected to an alkali extraction to render the materials suitable for analysis by ESI-FTICR-MS.

2.2. Humic acid isolation

The humic acids were extracted from the Dismal Swamp peat, the Okefenokee Swamp peat, the Mt. Rainier wood and the coal sample in house. These samples were prepared following a conventional humic acids procedure (Sparks et al., 1996) involving extraction with 0.5 M NaOH, removal of sodium with cation exchange resin, and precipitation by adjusting the solution to pH 2. The residue was isolated by centrifugation, rinsed with several times with dilute HCl, and freeze-dried. The Everglades peat humic acid (Pahokee peat) sample was purchased from the International Humic Substance Society.

2.3. (−) ESI-FTICR-MS analysis

Humic acid samples were prepared immediately prior to analysis. All humic acid samples had to be in solution, which was achieved by suspending between 0.5–1.0 mg of solid material in 1–3 mL of ultraquality water. For complete solubility small additions of NH_4OH adjusted the pH from pH 9 to 12. The solution was then diluted 50% with methanol for ESI-FTICR-MS analysis. Prior to analysis, the instrument was externally calibration with a polyethylene glycol standard. Each sample was introduced to a Bruker Daltonics 12 T Apex Qe FTICR-MS at a flow rate of 120 $\mu L\ h^{-1}$ using an Apollo II ESI ion source in the negative ionization mode housed at the College of Sciences Major Instrumentation Cluster (COSMIC), Old Dominion University, VA. The spray current of the ESI was optimized for each sample. Ion accumulation time in the hexapole varied for each sample, ranging between 2.0–3.0 s, before being transferred into the ICR cell, where 300–500 scans were co-added in broadband mode using a m/z range of 200–1200. The raw spectra of all the samples are displayed in Fig. S1.

2.4. (−) ESI-FTICR-MS data processing

All mass spectra were internally calibrated using naturally present fatty acids and other homologous series present within the samples (Sleighter et al., 2008). Prior to molecular formula assignment salt, and ^{13}C peaks were removed from the mass list and only peaks with a $S/N > 3$ were considered for formula assignment. Empirical molecular formulas were assigned using an in-house MatLab (The MathWorks, Inc., Natick, MA) code according to the following criteria: $^{12}C_{2-50}$, $^{1}H_{5-120}$, $^{14}N_{0-6}$, $^{16}O_{0-30}$, $^{32}S_{0-2}$, and $^{31}P_{0-2}$ within an error of 1 ppm. Treatment of the data is consistent with other published procedures (Chen et al., 2014; Stubbins et al., 2010).

2.5. Solid-state multiple cross polarization magic angle spinning ^{13}C NMR analysis

The peat and coal humic acids were examined by solid-state ^{13}C NMR. Solid-state multiple cross polarization magic angle spinning (multiCPMAS) ^{13}C spectra were acquired on a 400 MHz Bruker Avance II NMR spectrometer, equipped with a 4 mm H-X MAS probe. MultiCPMAS provides quantitative spectra that are comparable to direct polarization NMR techniques with enhanced S/N without the long experiment times (Johnson and Schmidt-Rohr, 2014). MultiCP was performed using the ramp-CP pulse program outlined in Johnson and Schmidt-Rohr (2014) consisting of 11 steps of 100 μs duration and a 1% amplitude increment from 90 to 100%. The sample (ca. 40 mg) was packed into a 4 mm zirconium rotor and sealed with a Kel-F cap for multiCPMAS analysis. The multiCPMAS acquisition parameters were as follows: spectral frequency of 100 MHz for ^{13}C and 400 MHz for ^{1}H, spinning rate of 14 kHz, 8192 scans, and line broadening of 100 Hz. The recycle delays were 0.25 s for all samples and variable repolarization period (t_z) experiments were conducted to determine the optimal time of 0.25 s.

The spectra were integrated into the following chemical shift regions: aliphatic carbon (−10–45 ppm); alkyl-O carbon (45–60, 60–95, and 95–110 ppm); aromatic carbon (110–145 ppm); aryl-O carbon (145–165 ppm); and carboxyl and carbonyl carbon (165–210 ppm). Integration regions were chosen according to Nelson and Baldock (2005). All solid spectra were externally calibrated to the glycine standard (176.03 ppm).