

# The Carbon Chemistry of Peat: Current Knowledge and Research Needs for Climate Change Issues

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## Introduction

Peat accumulates in wet environments where the rate of accumulation of plant biomass exceeds that of decomposition. It may be many meters deep and thousands of years old at the base, and it thus affords a valuable record of past environmental conditions (Campbell et al. 2000). Below the first few centimeters, decomposition is mainly hindered by lack of oxygen. Peat is essentially compressed plant litter, often very little affected by decomposition. Understanding its chemical composition and decomposition pathways requires the techniques widely used in studies of soil organic matter (Preston 1996, 2001; Kögel-Knabner 2000), coalification (Chagué-Goff and Fyfe 1996; Dudley et al. 1990) and organic geochemistry (van der Heijden and Boon 1994; Hedges and Oades 1997; Hedges et al. 2000; Lichtfouse 2000). This basic understanding ultimately must underlie our efforts to predict the effects of climate change on peatlands and to enhance the development of mitigation or management strategies.

## Methods for Characterization of Peat

### General Methods

Peatlands have long been used for extraction of fuel, planting media, and raw materials for environmental remediation and chemical products, and drained for agriculture and managed forestry. Therefore, much research has been driven by practical considerations (Mathur et al. 1984; Preston et al. 1986; Spedding 1988; Humphrey and Pluth 1996), and assessment of peat quality has been of longstanding interest (Lévesque and Dinel 1978, 1982; Brown et al. 1990; Malterer et al. 1992). Two key components are botanical composition and degree of decomposition, the latter comprising a wide array of physical

and chemical properties. In terms of botanical composition, peats or peat layers may be derived primarily from *Sphagnum* moss, sedges and other higher plants, or woody inputs.

The von Post and rubbed fiber techniques have been commonly used to assess physical properties related to the degree of decomposition of peat. These methods are based on the breakdown of plant fibers to smaller particles through decomposition. The von Post index is particularly simple and suitable for field use, as it is based on how the substrate runs through the fingers when squeezed, whereas determination of rubbed fiber content requires simple laboratory equipment. The water-holding properties of peat have also been of great interest, especially as a single peatland may have several pools of water with different degrees of binding (Holmgren et al. 1990; Preston n.d.). These properties affect the drying characteristics of peat for commercial use, but also such characteristics as gas diffusion, which can influence drainage efficiency and methane release (Aravena et al. 1993; Buttler et al. 1994).

Because wetlands are generally nutrient-limited systems, peats tend to have high total carbon (C) and high C/N (C to nitrogen) ratios. As decomposition proceeds, the general tendency is for C to decrease and N to increase, which results in a decreasing C to N ratio, while bulk density, ash content, and cation-exchange capacity all increase. As a substitute for accurate C analysis through combustion, the Walkley-Black method or approximations based on loss on ignition are, unfortunately, still being used; the resulting data cannot be considered reliable, especially as the basis for large-scale assessment of C stocks or as input for modeling. The C and N isotope composition of plants and organic matter ( $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$ ) are also sensitive to plant inputs, environmental conditions including agricultural

practices, and decomposition processes (DeLaune 1986; Price et al. 1997; Ficken et al. 1998; Kalbitz et al. 2000; Kracht and Gleixner 2000; Rice 2000; Ménot and Burns 2001; Preston, Bhatti et al. n.d.).

### Organic Components

Beyond bulk physical and chemical properties, the C composition of peat can be characterized by a variety of organic chemical and spectroscopic techniques. Proximate analysis (PA) has long been used in studies of litter decomposition and organic matter. Samples are sequentially extracted to remove nonpolar extractable components and then polar extractable components, and are then hydrolyzed in sulfuric acid to yield an acid-insoluble residue (AIR). This approach was developed for wood products and forage analysis, and is based on a structural model of extractables (including phenolics and soluble carbohydrates), celluloses, and lignin. It has recently been adapted to quantify nine organic fractions of *Sphagnum*-derived peats (Wieder and Starr 1998). However, these operationally defined fractions are inadequate to define more complex plant substrates incorporating cutin, suberin, and tannin structures, especially if modified by decomposition (Preston et al. 1997).

This limitation has led to overuse of the term "lignin" (from "Klason lignin", the AIR from PA of wood) for the AIR fraction. However, it reflects contributions from three biopolymer components: cutin (or suberin), condensed tannins, and lignin (Ha et al. 1997; Preston et al. 1997). The latter is properly defined as a polymer of phenylpropane units, with zero, one, or two methoxyl substituents (hydroxyphenyl, guaiacyl, and syringyl units, respectively), and may be present at lower concentration than the other components. Lower plants, including *Sphagnum* and all mosses, do not even contain lignin (Williams et al. 1998), although other phenolics are present (Wilson et al. 1989), especially sphagnum acid (Rasmussen et al. 1995; Williams et al. 1998).

Recent geochemical research focuses much more on specific chemical degradations, pyrolysis, gas chromatography, and mass spectrometry to generate molecular-level analysis of biochemical components, such as individual lipids, amino acids, lignin fragments, condensed tannins, and monosaccharides. There has also been rapid development of compound-specific isotope analysis

(Macko et al. 1991; Lichtfouse 2000). There is little information on individual amino acids in peats (Preston et al. 1981; Macko et al. 1991), but total amounts, molar distribution, and stereochemistry (levorotary versus dextrorotary) are all sensitive to inputs and decomposition. Lipids generally accumulate with decomposition, and there is some information on lipids in peat, although mainly those amenable to extraction (Karunen and Kälviäinen 1988; Lehtonen and Ketola 1993; Baas et al. 2000; Nott et al. 2000).

Tannins (especially condensed tannins) are common in higher plants and, like lignin, absent from mosses (Preston et al. 1997; Preston 1999; Preston et al. 2000). While levels of chemically identifiable tannins usually decrease rapidly with decomposition, C structures derived from tannins may still be detected in peat and humus by nuclear magnetic resonance (NMR) (see next section). Occasional high levels of tannins (up to 4%) have been found in black spruce humus (Lorenz et al. 2000; Preston 2001) and may be related to high water tables. Molecular-level analysis of tannin monomer components in soil or sediment is still under development (Hernes and Hedges 2000), but a specific colorimetric analysis for extractable and nonextractable tannins (Preston 1999; Lorenz et al. 2000) can provide valuable insight into peat plant sources and decomposition processes. Using the Folin-Dennis or Folin-Ciocalteu method to analyze total phenolics of the polar extract of PA does not distinguish condensed tannins from other classes of phenolics; in addition, the extraction procedures are not optimized for condensed tannins.

Hydrolysis followed by analysis of individual monosaccharides is particularly useful for following the effects of decomposition, as the monosaccharide profile changes from plant to microbial (Morita et al. 1983; Moers et al. 1989; Moers et al. 1990; Macko et al. 1991). Analysis of lignin fragments has also proved extremely useful for understanding plant inputs and transformations due to decomposition. Although mosses do not contain lignin, they do yield some phenolics (Williams et al. 1998), and litter inputs from higher plants leave their characteristic lignin signatures.

The search for rapid methods to capture the chemical, botanical, and microbiological properties of peat has stimulated application of Fourier transform infrared spectroscopy with principal

component analysis (Holmgren and Nordén 1988; Holmgren et al. 1990; Chapman et al. 2001). However, the predictive ability of this method is generally limited to samples very similar to those in the classification set. Electron paramagnetic resonance spectroscopy has less diagnostic value, as it mainly shows a general tendency for free radicals to increase with decomposition (Holmgren et al. 1990; Karlström et al. 1994).

### Carbon-13 NMR of Peat

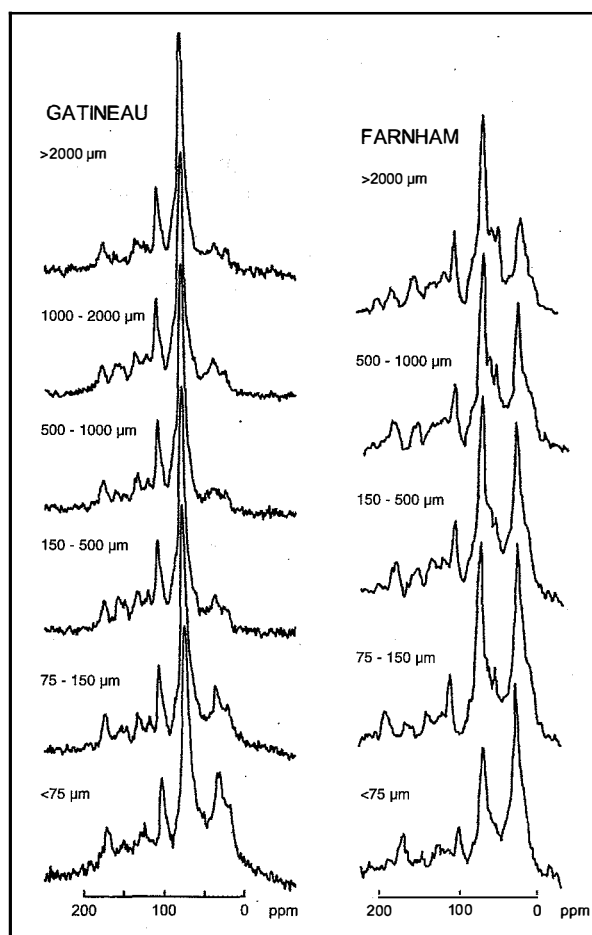
A general problem with geochemical analysis techniques is that the yields of identifiable compounds cannot account for all of the C structures, even in fresh plant materials, and may decrease severely with increasing decomposition (Hedges et al. 2000). Carbon-13 ( $^{13}\text{C}$ ) NMR spectroscopy is a powerful technique that yields an overall characterization or fingerprint of the organic composition of complex substrates such as fresh plant material, litter inputs, organic matter (Preston 1996, 2001; Kögel-Knabner 2000), and peats and mucks (Preston and Ripmeester 1982; Hammond et al. 1985; Preston et al. 1987; Nordén and Albano 1989; Preston et al. 1989; Holmgren et al. 1990; Nordén et al. 1992; Bergman et al. 2000). It is carried out on dry, powdered solids and thus can be used to examine intact samples or physical or chemical fractions. It uses high-speed spinning (magic-angle spinning or MAS), usually combined with cross-polarization (CP) from hydrogen nuclei to enhance sensitivity, the combined experiment being known as CPMAS NMR. There are definite limitations to its quantitative reliability, that is, its ability to detect all types of C with equal sensitivity. However, 20 years on, these phenomena are well understood, and quantitative or semiquantitative spectra can be obtained under suitable experimental conditions, especially for samples high in total C (Hu et al. 2000; Preston 2001).

Figure 1 shows spectra of size fractions of two peats differing in degree of decomposition (from Preston et al. 1989). Spectra of *Sphagnum* and poorly decomposed peat typically have a large signal at 73 ppm from polysaccharides (C-2, C-3, and C-5), the major biochemical component. This is accompanied by the peak for anomeric C (C-1 of polysaccharides) at 105 ppm. The peak at 30 ppm comes from alkyl C, especially in long chains ( $-\text{CH}_2-$ ), and the carboxyl signal (173 ppm) includes contributions from free acids, amides,

and esters. There is little intensity in the aromatic and phenolic regions (112–140 and 140–160 ppm, respectively).

### Changes in C Composition with Decomposition

The changes due to decomposition (here reflected in decreasing particle size) are clearly shown by NMR. The accumulation of organic



**Figure 1.** Carbon-13 cross-polarization magic-angle spinning nuclear magnetic resonance spectra of particle-size fractions of poorly decomposed Gatineau *Sphagnum* peat and well-decomposed Farnham peat with composition of 50% wood, 40% sedge, and 10% mosses. Reprinted from *Organic Geochemistry*, Volume 14, C.M. Preston, D.E. Axelson, M. Lévesque, S.P. Mathur, H. Diné, and R.L. Dudley. Carbon-13 NMR and chemical characterization of particle-size separates of peats differing in degree of decomposition, pages 393–403, copyright 1989, with permission from Elsevier Science.

matter in upland or wetland ecosystems (development of Folisols or Histosols) is due to conditions that restrict decomposition. These may include low temperatures, low oxygen and nutrient supply, excessive moisture, lack of earthworm activity, and the chemical composition of litter inputs (known as "litter quality"). The latter is a complex concept comprising nutrient content, organic composition, and physical toughness. The consequences of organic composition are poorly understood, but hard-to-decompose litter tends to be associated with high content of tannins, suberin (from bark), cutin (from leaves and fruits), and lignin from wood. Even cellulose may be in this category, if highly crystalline and well protected by association with other components (Huang et al. 1998; Preston et al. 2000), whereas sphagnum acid may have a specific inhibitory effect (Verhoeven and Toth 1995).

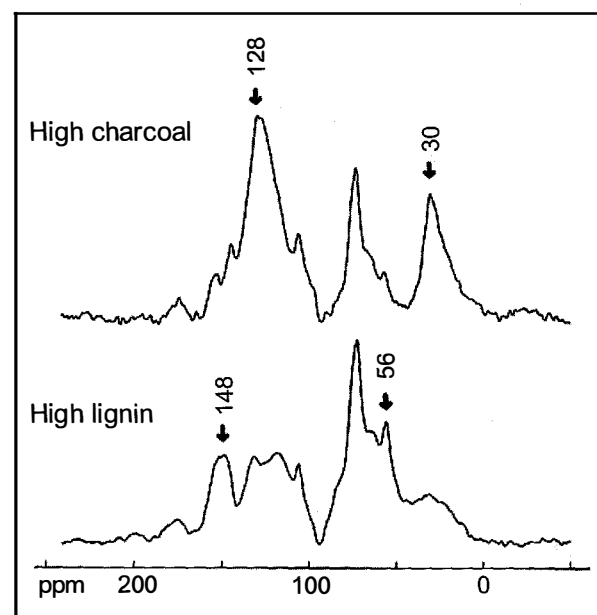
NMR studies have consistently shown that decomposition in peat is associated with a relative increase in alkyl C (lipids, 0–50 ppm) and a decrease in O- and di-O-alkyl C (60–110 ppm) mainly associated with polysaccharides. There may be a small accumulation of carboxyl C (including amides and esters), but there is often little or no change in aromatic C (Hammond et al. 1985; Preston et al. 1987; Preston et al. 1989; Holmgren et al. 1990; Nordén et al. 1992; Baldock and Preston 1995). Thus, increases in "lignin" content indicated by PA may have much less to do with accumulation of aromatics than with accumulation of alkyl C-based components. Accumulation of lignin with high aromaticity in forest floor and Lignic Folisols is generally associated with large inputs of coarse woody debris (de Montigny et al. 1993; Fox et al. 1994; Preston et al. 1998; Preston 1999; Preston, Trofymow et al. n.d.). It was found by  $^{13}\text{C}$  CPMAS NMR analysis of a woody peat from Brazil (Freitas et al. 1999) and a peatified log from Indonesia (Bates et al. 1991). Charcoal is also a source of high aromaticity in organic matter (Preston, Trofymow et al. n.d.; Schmidt and Noack 2000), and thus may also influence some peat sites (Campbell et al. 2000).

NMR spectra of organic matter fractions high in charcoal or lignin from highly decayed wood are shown in Figure 2. For the charcoal-rich sample, the prominent peak at 128 ppm comes from highly condensed aromatic structures and that at 30 ppm from the accumulation of alkyl C.

The spectrum for lignin-rich samples includes characteristic lignin peaks at 148 ppm for phenolic C, 112–140 ppm for aromatic C, and 56 ppm for methoxyl C. Both spectra also have the main peak for cellulose–hemicellulose at 73 ppm and for the aromatic C-1 at 105 ppm.

## Research Needs for Climate Change Issues

For climate change issues, filling the knowledge gaps in peat chemistry and decomposition will increase interdisciplinary cooperation. Peatlands hold vast amounts of C and factors controlling decomposition, DOC and methane release, and long-term C storage cannot be understood without reference to organic C chemistry. As noted earlier, much previous research on the C chemistry of peat and its decomposition pathways has been driven by issues surrounding the commercial use of peat or to provide insight into coal formation. Many of the detailed molecular-level studies only account for a very small fraction of the total C, and much chemical and isotope work has been from temperate or tropical peats. There are few studies providing the specific chemistry and process



**Figure 2.** Carbon-13 cross-polarization magic-angle spinning nuclear magnetic resonance spectra of charcoal-rich and lignin-rich samples of the 2- to 8-mm water-floatable fraction from 10–30 cm depth of British Columbia coastal forests (project described in Preston, Trofymow et al. n.d.).

information to complement large-scale studies of C fluxes and stocks, and the associated modeling exercises. The NMR studies analyzed peats with various degrees of decomposition as assessed by other techniques, and there do not appear to be any NMR or molecular-level analyses of time-course decomposition studies, not even to characterize the starting materials.

Climate change issues have recently stimulated much research on C stocks and fluxes in peatlands, including C isotope studies. However, this has not been accompanied by corresponding advances in C chemistry. Recent studies of decomposition have focused on environmental controls of mass loss, with assessment of substrate quality largely restricted to C and N contents (Farrish and Grigal 1988; Braeke and Finér 1990; Johnson and Damman 1991; Szumigalski and Bayley 1996; Thormann and Bayley 1997; Latter et al. 1998; Hartmann 1999; Scheffer and Aerts 2000; Thormann et al. 2001). Two studies of peat soils (rather than fresh litter) showed the importance of distinguishing different pools of C and also the limitations of PA to explain C, N, and P mineralization (Updegraff et al. 1995; Bridgham et al. 1998); by contrast the simple von Post measure of decomposition was more successful. Lähdesmäki and Piispanen (1988) examined sequences of fresh leaves, litter, and humus through PA and enzyme activity. Very narrowly focused studies of enzyme activities (Pind et al. 1994; Freeman et al. 1996) culminated in the claim that limited activity of one enzyme — phenol oxidase — could be the controlling factor for C storage in peat (Freeman et al. 2001).

Compared with the efforts expended for forests, grasslands, and agriculture, there has been little detailed process work on C flows and transformations in wetlands. Some recent studies used carbon-14 labeling to track the fate of C from litter (Domish et al. 2000) and recently assimilated C (Richart et al. 2000). The metabolic pathways of  $^{13}\text{C}$ -labeled glucose were followed with varying pH, temperature, and redox conditions (Bergman et al. 1999; Bergman et al. 2000). Van den Pol-van Dasselaar and Oenema (1999) determined methane and carbon dioxide ( $\text{CO}_2$ ) production from size and density fractions of peat.

Factors controlling production of  $\text{CO}_2$ , methane, and DOC have been examined by Moore and Dalva (1997, 2001) and by Scanlon and Moore

(2000); the latter found that  $\text{CO}_2$  production was best correlated with the von Post index of decomposition. Other recent research indicates that the radiocarbon age of peatland DOC may differ from that of the bulk peat, and that the complexities of DOC formation and movement require further investigation (Aravena et al. 1993; Bellisario et al. 1999; Chasar et al. 2000; Kracht and Gleixner 2000; Palmer et al. 2001). Compared with our understanding of DOC in forest soils (Guggenberger and Zech 1993, 1994; Kaiser et al. 2000), there has been very little chemical investigation of DOC from peatlands (Kracht and Gleixner 2000).

While environmental factors exert the primary control, substrate quality secondarily influences decomposition (Preston et al. 2000) and associated releases of dissolved and gaseous products. Its influence may be more important where decomposition is hindered by unfavorable environmental conditions. Addressing the significant current questions on C stocks and fluxes in peatlands, especially in Canada's boreal regions, requires an interdisciplinary approach to examine the relevant C chemistry with the appropriate analytical tools.

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