

Cupric oxide oxidation products of northern peat and peat-forming plants

Christopher J. Williams, Joseph B. Yavitt, R. Kelman Wieder, and Natalie L. Cleavitt

Abstract: Alkaline cupric oxide oxidation and proximate analysis were used to investigate the sources and diagenetic state of organic matter in six *Sphagnum*-dominated peatlands located between Alberta, Canada, and Ohio, U.S.A. Cupric oxide oxidation was also used to characterize vascular and nonvascular wetland plant species to provide a specific biological fingerprint of these plant tissues. Oxidation of 15 species of *Sphagnum* moss released large quantities of unsubstituted *p*-hydroxyl phenolic compounds as well as the species specific sphagnum acid (*p*-hydroxy- β -[carboxymethyl]-cinnamic acid). By contrast, vascular plant tissues released large amounts of lignin oxidation products. Cupric oxide oxidation of *Sphagnum* peat from more northerly sites produced mainly *p*-hydroxyl phenolic monomers with lesser amounts of vascular lignin derived phenols. In contrast, southern sites and those dominated by woody vegetation produced oxidation products characteristic of vascular plant lignin. A distinct relationship exists between the amount of acid-insoluble Klason lignin and both the diagenetically sensitive phenolic acid to aldehyde ratios as well as the total yield of vanillyl phenolic oxidation products. We found evidence of selective decay of phenolic lignin precursors. These relationships indicate the lignin component in surficial layers of *Sphagnum*-dominated peat is influenced by both *Sphagnum* and vascular plant lignin, and the structure of lignin appears to undergo diagenetic changes in these layers. Application of an end-member mixing model revealed that lignin oxidation products poorly predicted vegetational composition of the lignin in more decomposed peat, probably as a result of selective decay of lignin structural phenols.

Key words: lignin, organic soil, proximate analysis, *Sphagnum* moss, wetland.

Résumé : Les auteurs ont utilisé l'oxydation alcaline de l'oxyde de cuivre et l'analyse de proximité pour examiner les sources et l'état diagénétique de la matière organique, dans six tourbières dominées par des *Sphagnum* spp., localisées entre l'Alberta, au Canada, et l'Ohio, aux États-Unis. L'oxydation de l'oxyde de cuivre a également été utilisée pour caractériser les espèces de plantes vasculaires et non-vasculaires des tourbières, afin d'obtenir une empreinte biologique spécifique de ces tissus végétaux. L'oxydation de 15 espèces de sphaignes conduit au relâchement de grandes quantités de composés *p*-hydroxyl phénoliques non-substitués ainsi qu'à un acide spécifique aux espèces de sphaignes (*p*-hydroxy- β -[carboxy-méthyl]-cinnamic). Au contraire, les tissus de plantes vasculaires relâchent de grandes quantités de produits d'oxydation de la lignine. L'oxydation de l'oxyde de cuivre des tourbes de sphaignes provenant des sites plus nordiques produit surtout des monomères *p*-hydroxyl phénoliques avec de moindres quantités de phénols dérivés de lignine de plantes vasculaires. Au contraire, les sites méridionaux, ainsi que ceux qui sont dominés par une végétation ligneuse, forment des produits d'oxydation caractéristiques de la lignine des plantes vasculaires. On observe une relation caractéristique entre la quantité de lignine de Klason, insoluble dans l'acide, avec l'acide phénolique diagénétiquement sensible aux ratios aldéhyde aussi bien qu'avec le rendement total des produits d'oxydation du vanillyl phénolique. Les auteurs ont obtenu les preuves d'une dégradation sélective des précurseurs des phénols de la lignine. Ces relations indiquent que la composition en lignine, dans les couches de surface de la tourbe dominée par des sphaignes, est influencée à la fois par la sphaigne et par la lignine des plantes vasculaires, et que la structure de la lignine semble subir des modifications diagénétiques dans ces couches. L'application d'un modèle de mixage terminal révèle que les produits d'oxydation de la lignine ne permettent pas de bien prédire la composition en lignine de la végétation dans les tourbes les plus décomposées, conséquence probable d'une dégradation sélective des phénols structuraux de la lignine.

Mots clés : lignine, sol organique, analyse de proximité, mousses *Sphagnum*, terre humide.
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Table 1. Location and characteristics of the sampling sites.

Site	Area (ha)	MAT ^a (°C)	MAP ^b (mm)	<i>Sphagnum</i> moss species	Vascular plant species
Bleak Lake Bog, Alberta, Canada (54°45'N, 113°10'W)	>1000	1.4	493	<i>Sphagnum fuscum</i> <i>Sphagnum angustifolium</i> <i>Sphagnum magellanicum</i>	<i>Ledum groenlandicum</i> <i>Vaccinium oxycoccos</i> <i>Picea mariana</i>
Peatland 632, Ontario, Canada (49°40'N, 93°44'W)	3	2.1	623	<i>Sphagnum angustifolium</i> <i>Sphagnum fuscum</i>	<i>Ledum groenlandicum</i> <i>Chamaedaphne calyculata</i> <i>Picea mariana</i>
S-4 Wetland, Minnesota, U.S.A. (47°30'N, 93°30'W)	5	4.2	670	<i>Sphagnum fuscum</i>	<i>Chamaedaphne calyculata</i> <i>Andromeda glaucophylla</i> <i>Kalmia polifolia</i>
Pancake Swamp, New York, U.S.A. (45°52'N, 71°58'W)	10	4.6	1177	<i>Sphagnum girgensohnii</i>	<i>Picea rubens</i> <i>Acer rubrum</i>
Labrador Hollow, New York, U.S.A. (42°45'N, 76°00'W)	40	8.1	989	<i>Sphagnum girgensohnii</i> <i>Sphagnum russowii</i> <i>Sphagnum henryense</i>	<i>Acer rubrum</i> <i>Pinus strobus</i>
Fern Lake Bog, Ohio, U.S.A. (41°15'N 81°20'W)	19	9.8	935	<i>Sphagnum recurvum</i> <i>Sphagnum fimbriatum</i>	<i>Vaccinium carymbosum</i>

^aMean annual temperature.^bMean annual precipitation.

Introduction

Plant residues decompose slowly in northern peatlands, and thus, large quantities (455 Pg; Gorham 1991) of partially decomposed organic matter (i.e., peat) have accumulated. Peat is a complex mixture of both vascular and nonvascular plant remains as well as microbes and microbial synthesized compounds (Waksman 1930). Most of our knowledge of decomposition in northern peatlands comes from studies of mass loss from litter bags and peat profiles, as well as measurements of microbial respiration in the field and laboratory (see Johnson and Damman 1993). Unfortunately, these methods offer little information about the intrinsic chemical characteristics of the peat or the nature of chemical changes that occur in peat during decomposition. However, the chemical composition of plant litter does, in part, control decay rate in upland ecosystems (Ågren and Bosatta 1996; Melillo et al. 1982) and may also in northern peatlands (Verhoeven and Toth 1995).

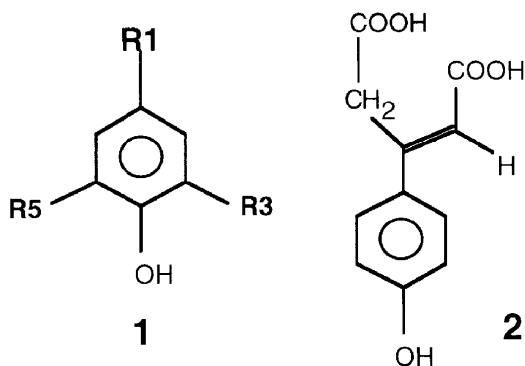
An important factor regulating the decay rate of plant litter is lignin content (Hobbie 1996). Lignin is a decay-resistant heteropolymer formed of phenylpropane units. Found in association with the plant cell wall, lignin is difficult to isolate and is usually quantified in proximate analysis as an acid-insoluble residue called Klason lignin. Standard chemical fractionation techniques that categorize organic matter into relatively labile and recalcitrant fractions usually provide a useful assessment of the degradability of organic matter but are less robust in samples with high Klason lignin content, such as peat (Ågren and Bosatta 1996). Furthermore, this technique offers little insight into the subtle changes that occur in lignin between plant types and during decomposition, even though noticeable differences have been demonstrated (Johansson et al. 1986; Benner et al. 1989). Additionally, *Sphagnum* peat can contain significant amounts of acid-insoluble matter derived from non-vascular and vascular sources, which is isolated along with plant lignin in the Klason lignin fraction of proximate analysis (Hobbie 1996). It is thought that tannins and cutins comprise most of this material (Preston et al. 1997), although it is un-

certain what role *Sphagnum* may play in chemically contributing to the acid-insoluble fraction. For example, little is known about the decay of acid-resistant compounds found in the leaves of several *Sphagnum* mosses commonly found in peat (Kroken et al. 1996). Since these poorly defined compounds may be significant in peat, and may in part control decomposition rates, their characterization is essential to the understanding of peatland carbon dynamics.

The technique of alkaline cupric oxide (CuO) oxidation (Hedges and Ertel 1982) is an effective means of characterizing the lignin component of complex natural mixtures at the molecular level. As a relatively mild oxidative technique, alkaline CuO oxidation cleaves a wide variety of ether and carbon bonds. When natural mixtures containing lignin are reacted with alkaline CuO, a suite of phenolic compounds, which characterize the amount and source of the organic matter (i.e., woody or nonwoody angiosperm or gymnosperm; Hedges and Mann 1979), are released from the lignin polymer. Furthermore, the ratio of acid to aldehyde oxidation products provide a measure of the degree of diagenetic alteration (Hedges et al. 1988a). Cupric oxide oxidation is applied in marine and coastal sediments (Hedges et al. 1982; Opsahl and Benner 1995), forest and tundra soils (Kögel-Knabner 1993; Ugolini et al. 1981), and to a lesser extent, peat (Tsutsuki and Kondo 1995). Since peat is relatively undecomposed, there is the added advantage of possibly knowing the botanical composition of the peat, which in some cases, may be more important than environmental factors in dictating the overall decomposability of the peat (Johnson and Damman 1991).

Although peat is primarily organic matter, few studies have investigated the organochemical constituents of *Sphagnum* peat (e.g., Lehto et al. 1985; Jörgensen and Richter 1992). In the research presented here we use CuO oxidation and proximate analysis to characterize samples obtained from six northern peatlands with varying degrees of organic matter decomposition and botanical origin to gain insight into the poorly defined lignin fraction. Since *Sphagnum* mosses are the

Fig. 1. Structures of (1) the major cupric oxide oxidation products and (2) sphagnum acid (*p*-hydroxy- β -[carboxymethyl]-cinnamic acid). Adapted from Hedges and Ertel 1982.



Compounds	Structure		
	R1	R3	R5
vanillin	CHO	H	OCH ₃
vanillic acid	COOH	H	OCH ₃
acetovanillone	COCH ₃	H	OCH ₃
syringaldehyde	CHO	OCH ₃	OCH ₃
syringic acid	COOH	OCH ₃	OCH ₃
acetosyringone	COCH ₃	OCH ₃	OCH ₃
ferulic acid	CH=CHCOOH	H	OCH ₃
<i>p</i> -coumaric acid	CH=CHCOOH	H	H
<i>p</i> -hydroxybenzaldehyde	CHO	H	H
<i>p</i> -hydroxybenzoic acid	COOH	H	H
<i>p</i> -hydroxyacetophenone	COCH ₃	H	H

dominant plant species in northern peatlands we included 15 species in addition to the common wetland plants, to determine specific oxidation signatures and resolve their contribution to the lignin fraction of peat. The fundamental questions we address in this study are (i) what are the major oxidation products of *Sphagnum* mosses and do they indicate a phenylpropane based lignin structure; (ii) can CuO oxidation products be used to determine the degree of decomposition of peat and, if so, which products are best related to proximate analysis estimates of decomposition; and (iii) are CuO-oxidation products useful predictors of the botanical composition of peat?

Methods

Study sites

Our six study sites (Table 1) spanned over 13° of latitude, 8.4°C of mean annual temperature, over 684 mm of total annual precipitation, and 145 days of frost-free period. One site in Canada (Bleak Lake Bog) was in the boreal region of North America, and a second Canadian site (Peatland 632) was within 100 km of the present-day boreal-temperate forest boundary (Ecoregions Working Group 1989); the remaining four sites were well within the temperate forest region. Pancake Swamp and Labrador Hollow had closed canopies of mostly conifer trees and, therefore, are categorized as conifer swamps

(Jeglum 1991). All sites have a substantial cover of *Sphagnum* mosses with an underlying peat soil. Surface water in each site is acidic (pH ranging from 3.6 to 5.7) and nutrient deficient (dissolved Ca^{2+} 12–112 $\mu\text{mol}\cdot\text{L}^{-1}$).

Specific details for the study sites are available in the following references: Bleak Lake Bog (Vitt et al. 1995); Peatland 632 (Roulet et al. 1992); S-4 Wetland (Conway 1949); Pancake Swamp (Yavitt and Fahey 1996); Labrador Hollow (Paratley and Fahey 1986); and Fern Lake Bog (Andreas and Bryan 1990).

Tissue samples

Bryophyte and vascular plant species were collected at several sites in the northeastern United States and Canada. *Sphagnum magellanicum*, *S. angustifolium*, *S. papillosum*, *S. fibriatum*, *S. cuspidatum*, *S. rubellum*, and *S. fallax* were collected at McLean Bog, a small kettle hole bog in McLean, N.Y., U.S.A. *Sphagnum girgensohnii*, *S. henryense*, *S. russowii*, and *S. squarrosum* were collected at Labrador Hollow (above). *Sphagnum fuscum* was collected at Bleak Lake Bog (above). *Sphagnum warnstorffii* and the vascular plant species were collected at Spring Pond Bog, a 225-ha poor fen in the Town of Altamont, in the Adirondack Mountain region of New York, U.S.A. The samples were sorted by hand and any foreign matter removed. All vascular material was removed from the bryophyte samples. Any damaged or abnormal-looking plant tissue also was removed. After rinsing under a light stream of water, samples were allowed to dry to a constant weight at 35°C and then were finely ground.

Peat samples

Most northern peatlands have distinct microtopography consisting of hummocks (30–50 cm above the water table) and hollows (often water-filled depressions) across their surface. To reduce spatial variability we collected peat only from hollows; although surface water was not always present at the time of sampling. Peat samples were collected with an open PVC cylinder (10 cm diameter \times 24 cm length). After a cylindrical incision through the surface of the peat was made with a sharp knife, the cylinder was tapped through the surface vegetation into the underlying peat. After partial excavation of the peat outside the cylinder, an intact peat core could be lifted from the site. A rubber cap was placed over the bottom of the cylinder and held in place with a hose clamp. Upon return to the laboratory, the cores were extruded from the cylinders and divided into three depth intervals (0–8, 8–16, 16–24 cm). Each interval was then freeze-dried and finely ground.

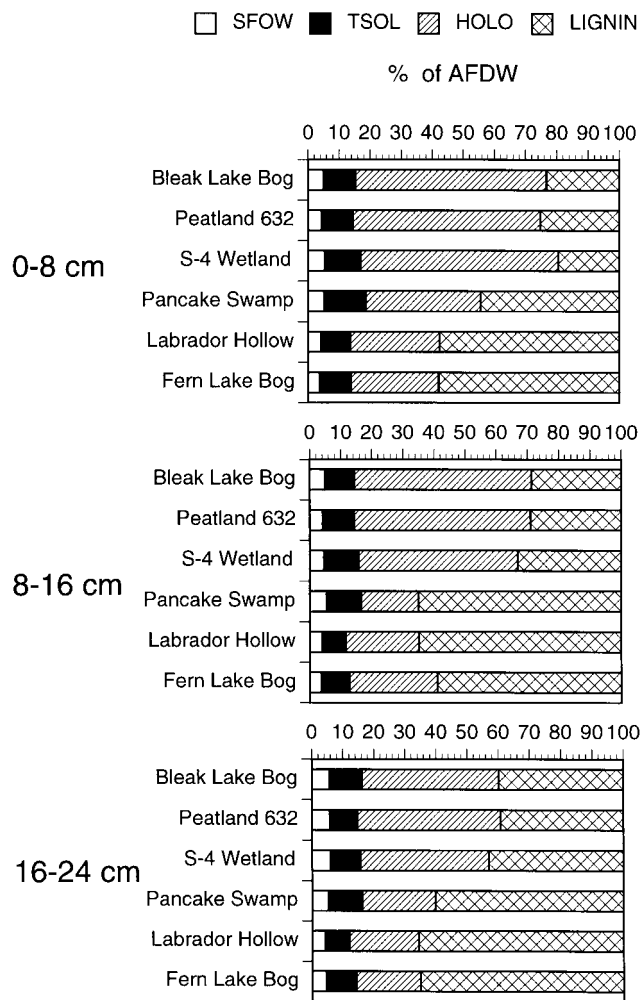
Organic matter fractionation

Separate subsamples of peat per depth interval per site were taken for analysis of organic matter fractions by proximate analysis of freeze-dried, ground material (Ryan et al. 1990, with some modifications). Soluble fats, oils, and waxes were extracted in CH_2Cl_2 in a sonicating water bath and quantified gravimetrically. The residue was extracted with hot (100°C) water followed by 72% H_2SO_4 , and polyphenols, carbohydrates, and proteins were measured colorimetrically in the water and acid extracts. On separate subsamples of the remaining material, holocellulose was determined as the mass remaining after extraction with NaClO_2 (75°C for 4 h) and lignin as mass remaining after the extraction with 13.6 M H_2SO_4 (autoclaved at 250°C, 17 psi for 1 h; 1 psi = 6.895 kPa). After each extraction step, a subsample of the solid residue was combusted (550°C, 4 h) to correct organic matter fraction values for ash content.

Cupric oxide oxidation

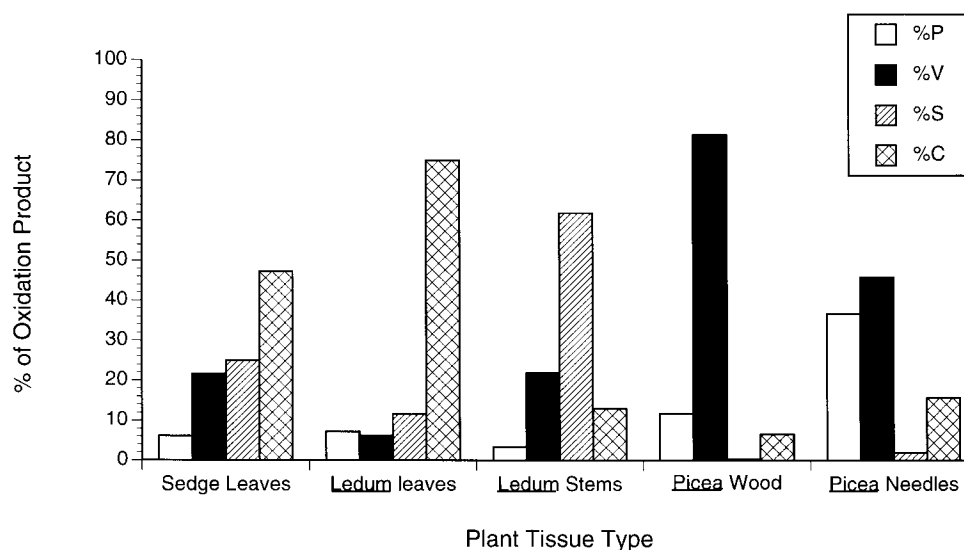
Samples were oxidized using CuO to liberate phenolic compounds from the lignin fraction (Hedges and Ertel 1982). We used the technique of Kögel and Bochter (1985) with slight modifications: a 50-mg sample was reacted with 1 g CuO and 100 mg $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ in 7 mL 0.2 M NaOH at 150°C for 3 h under a N_2 atmosphere. Following

Fig. 2. Percentage of each chemical fraction from proximate analysis of peat from three depth intervals from six northern peatlands. SFW, soluble fats, oils, and waxes; TSOL, total soluble carbohydrates; HOLO, holocellulose; LIGNIN, acid insoluble fraction; AFDW, ash free dry weight.



oxidation, samples were acidified to pH 2 and centrifuged to separate humic and fulvic acid fractions. The supernatant was spiked with an internal standard (*p*-hydroxybenzoic acid methyl ester) then subjected to solid phase extraction using disposable columns (LC-18, Supelco, Bellefonte, Pa., U.S.A.). Phenolic oxidation products were selectively eluted from the column with ethyl acetate and quantified using high performance liquid chromatography using a reversed phase Microsorb C-18 column (4 \times 250 mm; Rainin Corp., Woburn, Mass.) and UV (280 nm) absorbance spectrometry.

Twelve predominant phenolic monomers (Fig. 1) are produced from the lignin structure that may be categorized into distinct families on the basis of chemical substitution: monomethoxyl substituted vanillyl phenols (V; vanillin, vanillic acid, acetovanillone); dimethoxyl substituted syringyl phenols (S; syringaldehyde, syringic acid, acetosyringone); propenoic acid substituted cinnamyl phenols (C; ferulic acid, *p*-coumaric acid); and non-methoxyl substituted *p*-hydroxyl phenols (P; *p*-hydroxybenzaldehyde, *p*-hydroxybenzoic acid, *p*-hydroxyacetophenone). Weight ratios of sums of phenols in individual families (e.g., C/V, S/V, P/V) and ratios of acid to aldehyde phenolics are used to characterize the lignin-derived phenols. Both angiosperm and gymnosperm plant lignin produce V phenols. Syringyl phenols are produced primarily from angiosperm lignin.

Fig. 3. Relative proportion of four phenolic families in the CuO-oxidation digest of tissues from three common wetland plants.**Table 2.** Phenolic oxidation products of various *Sphagnum* mosses.

Section and species	Phenolic product ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight) ^a				
	PAD	PAL	PON	SPH-AD	CAD
Sphagnum					
<i>S. centrale</i> C. Jens.	1042	1238	4164	62	151
<i>S. henryense</i> Warnst.	1058	979	3209	47	88
<i>S. magellanicum</i> Brid.	904	1297	3792	67	162
<i>S. papillosum</i> Lindb.	1045	1539	3945	64	82
Squarrosa					
<i>S. squarrosum</i> Crome	1003	774	3352	34	106
Cuspidata					
<i>S. angustifolium</i> (Russ.) C. Jens.	715	1312	2590	34	54
<i>S. cuspidatum</i> Hoffm.	1128	1364	2962	20	160
<i>S. fallax</i> Klinggr.	1236	967	2974	44	5
<i>S. torreyanum</i> Sull.	1229	802	3263	49	6
Acutifolia					
<i>S. fimbriatum</i> Wils. & J.D. Hook	532	57	2310	23	99
<i>S. fuscum</i> (Schimp.) Klinggr.	1625	1685	4824	15	64
<i>S. girgensohnii</i> Russ.	1103	688	3022	21	6
<i>S. rubellum</i> Wils.	1138	1388	3767	26	106
<i>S. russoii</i> Warnst.	1317	1161	3929	50	147
<i>S. warnstorffii</i> Russ.	974	2167	3669	32	135

^aPAD, *p*-hydroxybenzoic acid; PAL, *p*-hydroxybenzaldehyde; PON, *p*-hydroxyacetophenone; SPH-AD, sphagnum acid; CAD, *p*-coumaric acid.

Nonwoody tissue of both gymnosperms and angiosperms produce C phenols. While V, S, and C phenols are exclusively lignin derived, *p*-hydroxyl phenols have both lignin and nonlignin sources. For this reason *p*-hydroxyl phenols are often not considered. However, we have found that oxidation of fresh *Sphagnum* releases copious amounts of *p*-hydroxyl phenols (this study), and they make up an important component of dissolved organic matter in peat (Ertel et al. 1993); hence, we have chosen to include them in our analysis of the oxidation products.

Results

The two principal fractions of peat were holocellulose and lignin (Fig. 2). Most of the holocellulose was acid-extractable

carbohydrates. Both lignin and holocellulose fractions exhibited a strong depth-dependent pattern at each site: lignin content increased with depth in the peat, whereas the amount of holocellulose decreased with depth in the peat. Overall, lignin predominated in peat from forested mire peat and Fern Lake Bog peat, whereas peat from the other three sites had mostly holocellulose. The remaining organic fractions were relatively minor and showed no clear pattern among sites or depth interval per site.

Cupric oxide oxidation of the various *Sphagnum* species yielded primarily *p*-hydroxyl phenolics (Table 2). The ketone, *p*-hydroxyacetophenone was the dominant oxidation product (mean 60%; range 53–76%), whereas *p*-hydroxybenzoic acid

Table 3. Phenolic monomer yield ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight) from the CuO oxidation of vascular wetland plants.

Phenolic ^a	Yield from species and tissue type ($\mu\text{g}\cdot\text{g}^{-1}$ dry weight)				
	Sedge leaves	<i>Ledum</i> leaves	<i>Ledum</i> stems	<i>Picea</i> wood	<i>Picea</i> needles
PAD	694	391	278	1 149	7397
PAL	1 512	212	541	2 251	1557
PON	552	107	534	572	2792
VAD	1 408	104	1 026	4 067	2839
VAL	6 721	415	6 693	20 647	9295
VON	1 581	97	1 089	2 817	2552
SAD	1 823	44	2 361	Trace	Trace
SAL	9 384	376	22 423	Trace	Trace
SON	Trace	721	133	Trace	Trace
CAD	11 049	7087	3 478	329	3577
FAD	10 202	324	1 720	1 878	1430

^aPAD, *p*-hydroxybenzoic acid; PAL, *p*-hydroxybenzaldehyde; PON, *p*-hydroxyacetophenone; VAD, vanillic acid; VAL, vanillin; VON, acetovanillone; SAD, syringic acid; SAL, syringaldehyde; SON, acetosyringone; CAD, *p*-coumaric acid; FAD, ferulic acid.

Table 4. Cupric oxide oxidation products of peat from three depth intervals from six North American peatlands.

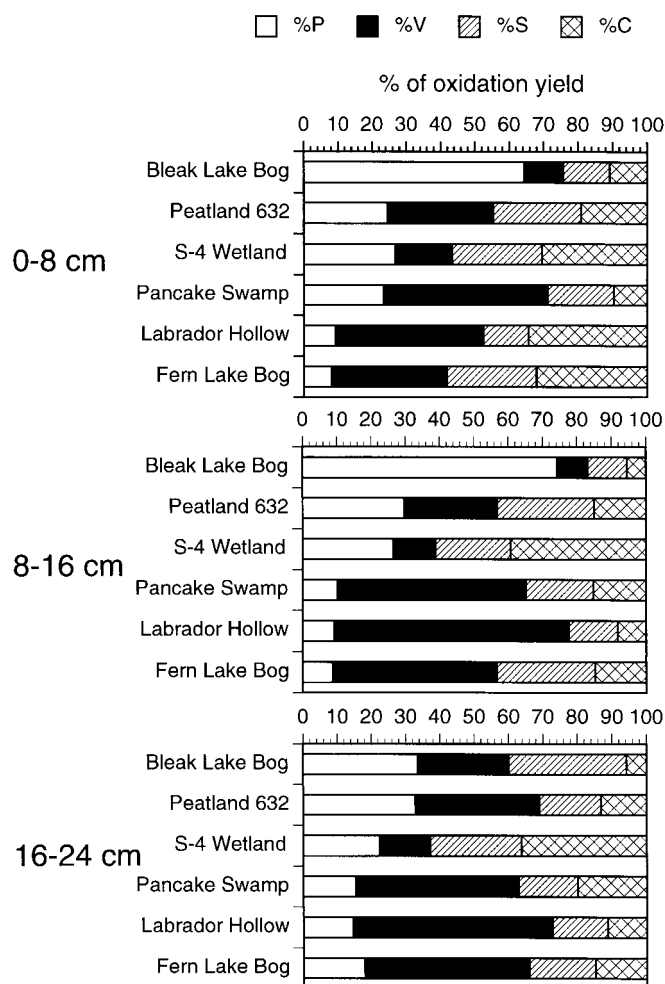
Site	Phenolic product ($\text{mg}\cdot\text{g}^{-1}$ OC) ^a										
	PAD	PAL	PON	VAD	VAL	VON	SAD	SAL	SON	CAD	FAD
0–8 cm depth											
Bleak Lake	2.4	1.7	6.0	0.2	1.3	0.3	0.1	1.9	0.1	0.7	1.0
Peatland 632	2.0	1.9	3.4	2.4	6.1	0.7	1.1	4.6	1.9	3.1	2.6
S-4 Wetland	3.0	3.3	2.7	1.2	3.6	0.8	1.3	4.9	2.6	5.4	4.8
Pancake Swamp	1.0	1.2	3.9	3.8	6.2	2.4	1.2	3.0	0.8	1.2	1.3
Labrador Hollow	1.7	1.6	1.9	4.8	15.6	4.0	1.5	4.7	1.2	2.1	17.2
Fern Lake Bog	1.4	1.1	1.0	2.6	10.7	1.2	1.7	7.5	2.1	3.8	10.0
8–16 cm depth											
Bleak Lake	2.9	2.0	6.1	0.0	1.0	0.3	0.0	1.6	0.1	0.4	0.4
Peatland 632	4.2	3.7	9.5	3.7	9.5	2.7	2.3	11.5	2.7	4.7	4.1
S-4 Wetland	6.8	8.6	8.5	1.4	8.0	1.8	2.6	12.0	5.1	20.0	15.5
Pancake Swamp	1.6	1.9	1.3	9.7	11.3	4.9	2.4	5.3	1.5	4.1	3.1
Labrador Hollow	1.0	1.1	0.7	5.3	11.9	3.6	1.1	2.5	0.7	1.0	1.5
Fern Lake Bog	0.9	1.3	1.0	4.4	9.8	3.4	2.2	6.4	1.9	2.4	3.0
16–24 cm depth											
Bleak Lake	1.7	1.3	2.8	1.0	2.9	0.7	0.7	4.3	0.9	0.4	0.6
Peatland 632	3.4	2.3	6.0	2.7	9.3	0.9	1.3	3.8	1.3	1.1	3.6
S-4 Wetland	2.6	4.3	5.2	1.4	5.4	1.2	2.0	8.9	3.6	10.4	9.3
Pancake Swamp	0.9	1.0	2.1	0.9	7.6	3.9	1.1	2.4	1.0	2.7	2.5
Labrador Hollow	1.9	1.2	1.0	4.2	9.2	3.0	1.0	2.6	0.9	1.5	1.7
Fern Lake Bog	2.6	1.6	1.4	1.9	11.1	1.9	1.9	3.4	0.7	2.0	2.6

^aPhenolic product names are given in Table 3. OC, organic carbon.

Table 5. Coefficients (ρ) for the Spearman correlations of organochemical properties with cupric oxide oxidation parameters for peat from six peatlands.

Lignin parameter	SFOW	SCARB	ACCARB	ALPH	HEMI	HOLO	LIGNIN
<i>p</i> -hydroxyl yield (P)	0.19	0.63	0.73	0.75	0.73	0.74	-0.76
Vanillyl yield (V)	-0.56	-0.85	-0.81	-0.63	-0.60	-0.61	0.72
Syringyl yield (S)	0.01	0.22	-0.02	0.11	0.01	0.07	-0.06
Cinnamyl yield (C)	-0.08	-0.01	0.03	0.18	0.07	0.10	-0.12
P/V ratio	0.14	0.62	0.71	0.69	0.68	0.73	-0.73
S/V ratio	0.45	0.82	0.78	0.70	0.66	0.68	-0.73
C/V ratio	0.20	0.55	0.58	0.61	0.43	0.54	-0.62
(Ad/Al) _v	-0.03	-0.22	-0.27	-0.37	-0.22	-0.25	0.19
(Ad/Al) _s	-0.09	-0.68	-0.73	-0.70	-0.72	-0.73	0.67

Note: Abbreviations are as follows: SFOW, soluble fats, oils, and waxes; SCARB, water-soluble carbohydrates; ACCARB, acid-soluble carbohydrates; ALPH, alpha cellulose; HEMI, hemicellulose; HOLO, holocellulose; LIGNIN, acid-insoluble residue; (Ad/Al)_v or (Ad/Al)_s, acid to aldehyde ratio for vanillyl or syringyl phenolics, respectively.

Fig. 4. Percentage of four phenolic families in the CuO-oxidation digest of peat from three depth intervals from six northern peatlands.

and *p*-hydroxybenzaldehyde occurred in about equal amounts (ca. 19% each). In addition, digested *Sphagnum* yielded minor amounts of *p*-coumaric acid and sphagnum acid, which accounted for less than 2% of the total oxidation product. On the other hand, oxidation of vascular plant matter yielded *p*-hydroxyl, V, S, and C products (Table 3). The aldehyde form of each phenolic predominated over the acid form of the phenolic in all tissue types. For example, *Picea* wood yielded copious amounts of vanillin (61% of total), whereas *Ledum* wood yielded primarily syringaldehyde. The predominance of aldehyde phenolics was less apparent in *Ledum* and *Picea* leaves. On the other hand, oxidation of *Eriophorum* tissue yielded primarily cinnamic acids. The phenolic groups varied among plants (Fig. 3); sedge and *Ledum* leaves had mostly C phenolics; *Ledum* stems had mostly S phenolics, and *Picea* plant tissue had mostly V phenolics. The total yield of phenolics was >30 mg·g⁻¹ dry weight, except for a low yield of 10 mg·g⁻¹ for *Ledum* leaves.

No single phenolic compound dominated peat chemistry across all sites or depths (Table 4). There were, however, a few apparent patterns. Vanillin yield was relatively high in most sites but, notably, not in the northernmost Bleak Lake Bog. The yield of *p*-coumaric and ferulic acid was high in some

sites, but not all depths per site. Otherwise, aldehydes were much more abundant than acidic phenolics and the ketone form, with the exception of *p*-hydroxyacetophenone in the *p*-hydroxyl fraction.

Overall, V phenolics predominated in the oxidation products of peat from Pancake Creek, Labrador Hollow, and Fern Lake peat (46–57% of the oxidation product); *p*-hydroxyl phenolics predominated in Bleak Lake Bog peat and made up a greater percentage of the oxidation product in Peatland 632 and S-4 Wetland peat than the three southern sites (Fig. 4). On average the S phenolics constitute about 20% of the oxidation product across all sites although Pancake Creek and Labrador Hollow peat had slightly lower yields of S phenolics. Cinnamyl phenolic yield was more variable than the rest of the oxidation products with S-4 Wetland producing the greatest amounts (35% of the product).

Correlation (Table 5) among CuO oxidation products and proximate fractions in peat showed a positive relationship among carbohydrate and cellulose fractions and total yield of *p*-hydroxyl phenolics as well as the compositional parameters P/V, S/V, and C/V. Furthermore, there was a positive association among the lignin fraction and total yield of V phenolics and the syringyl acid to aldehyde ratio. Total lignin-derived

phenolics ranged from 15 to 90 mg·g⁻¹ of OC among the sites and were correlated with the lignin content of the peat ($r = 0.79$).

Discussion

Proximate analysis

Klason lignin could dominate peat for two reasons. First, lignin-rich fresh plant material forms peat with greater lignin concentrations. Secondly, lignin becomes more concentrated as more labile carbon fractions like soluble carbohydrates are decomposed (Jørgensen and Richter 1992). The former may explain dominance by Klason lignin in the forested mire sites that have lignin-rich wood inputs in comparison with the un-forested peatlands. The latter explains the relative increase in Klason lignin concentration with increasing depth in the peat. Cellulose decomposition is slow in peatlands (Santelmann 1992). Nevertheless, cellulose decomposes at a faster rate than structurally more complex lignin under anaerobic conditions (Hedges et al. 1985), which may result in greater lignin concentrations in more humified peat although exceptions have been shown to exist (Baldock and Preston 1995). Therefore, the preponderance of acid-soluble carbohydrates and holocellulose in peat from Bleak Lake Bog, Peatland 632, and S-4 Wetland suggest relatively labile organic matter in these sites. Taken alone, results of proximate analysis suggest that the preponderance of Klason lignin in peat from Pancake Swamp and Labrador Hollow might best be explained by greater lignin rich inputs to the peat in the forested mires. However, CuO products (see below) indicate that the greater lignin values can just as easily be explained by increased decomposition of the peat, as in the case of Fern Lake Bog.

Sphagnum oxidation products

The oxidation of *Sphagnum* mosses with alkaline CuO released predominantly *p*-hydroxyphenyl compounds with no evidence of methyl-substituted phenolics characteristic of lignin derived phenols. Our results support recent studies that demonstrate the existence of a polyphenolic network composed of *p*-hydroxyphenyl groups in the cell wall of *Sphagnum* plants (Rasmussen et al. 1995; Wilson et al. 1989). Transmethylation pyrolysis mass spectrometry studies by van der Heijden (1994) indicate this polymer is a complex network of phenolic and benzoic monomers and dimers linked by C–C, ether, and ester bonds; it is the ether and ester bonds that cleave under alkaline CuO. Earlier studies that applied oxidative techniques to *Sphagnum* showed high yields of *p*-hydroxyl phenols, as well as small amounts of methyl-substituted phenols (e.g., vanillin, vanillic acid, syringaldehyde, etc.; Bland et al. 1968; Farmer and Morrison 1964). This suggested the presence of a lignin similar to that in vascular plants in *Sphagnum*, but it has since been shown that these compounds probably originate from contamination by vascular plant remains (Wilson et al. 1989).

Several other phenolic compounds have been isolated from the cell walls of *Sphagnum*. These include *p*-coumaric acid and the taxonomically specific sphagnum acid (Rasmussen et al. 1995). Sphagnum acid is thought to be ether bonded to cell wall polymers (van der Heijden 1994), although it also has been isolated using aqueous buffers, implying weak association with the cell wall (Rasmussen et al. 1995). We detected

both of these compounds in the oxidation digest, although in much smaller quantities than the three *p*-hydroxyphenyl compounds. Our oxidation yields of sphagnum acid were variable and lower in magnitude than those presented by Rudolph and Samland (1985). Our yields of *p*-coumaric acid averaged slightly higher than those organically extracted by Rasmussen et al. (1995). The qualitative dominance of the *p*-hydroxy monomers over cinnamic acid oxidation products may be indicative of the parent polymer, a lignin like polymer composed of simple monomers linked with simple ether and ester bonds and interspersed with cinnamic acids.

Vascular plant oxidation products

Total yield of phenolics was higher for vascular plants (except *Ledum* leaves) than for *Sphagnum* as expected, given the preponderance of lignin in vascular plants. Accordingly, there are more studies of CuO oxidation of vascular plants (Goñi and Hedges 1992; Hedges and Mann 1979). Distinction of lignin structure is usually drawn along the lines of broad groupings in plant taxonomy based on the relative amounts of three lignin precursors that give rise to the CuO oxidation monomers (Sarkanen and Ludwig 1971). For example, woody tissue from *Picea rubens* contained predominantly V monomers (dominated by vanillin), a characteristic of gymnosperm lignin (Hedges and Mann 1979). In contrast, oxidation of woody tissue from *Ledum* stems resulted in a high yield of S monomers, a characteristic of angiosperm lignin (Hedges and Mann 1979). With the exception of *Ledum* leaves, the S/V and C/V ratios of the angiosperm plant tissue analyzed here were within the range of variability for published mean values of various plant species. Notably, both *Ledum* and sedge leaves produced large amounts of C phenols. Several temperate monocot species have CuO oxidation products rich in C phenols (Goñi and Hedges 1992; Tsutsuki and Kondo 1995). Ericaceous shrubs like *Ledum* have large quantities of cinnamic acids incorporated in their tissues as secondary metabolites (Jonassen et al. 1986; Inderjit and Mallik 1996), although not necessarily incorporated into their lignin. It is possible that high yields of these compounds result from their extraction in the alkaline oxidation digest coincident to the extraction of lignin-derived monomers.

Oxidation products of peat

Analysis of weight ratios of lignin oxidation products is a common technique for determining potential source inputs to organic mixtures. The total weight ratios of S and C phenols to V phenols have been used to indicate tissue (woody or herbaceous) and plant type (gymnosperm and angiosperm; Hedges and Mann 1979) in sedimentary mixtures. This technique has not been used in the younger *Sphagnum*-derived peat of North America, although it has been applied to peat as old as 22 000 years in Japan (Tsutuski et al. 1993). These studies showed that the plant source indicators correspond reasonably well with independent measures of peat botanical origin such as palynological analysis. This is despite the fact that selective loss of phenols may compromise the ability of this technique to accurately resolve organic matter sources (Hedges and Weliky 1989).

Despite having both vascular and nonvascular sources, Tsutsuki et al. (1994) suggest the *p*-hydroxyl monomers to be a good indicator of the prevalence of *Sphagnum* remains in

Table 6. Results of ternary mixing model estimating the percent contribution of various plant lignin types in peat from six northern peatlands.

Site	Tissue type		
	% Angiosperm wood	% Nonwoody angiosperm	% Gymnosperm
Bleak Lake			
0–8 cm	29	16	55
8–16 cm	35	10	55
16–24 cm	38	0	62
Peatland 632			
0–8 cm	20	9	71
8–16 cm	27	8	65
16–24 cm	12	4	83
S-4 Wetland			
0–8 cm	32	34	34
8–16 cm	25	62	13
16–24 cm	33	47	20
Pancake Swamp			
0–8 cm	11	1	88
8–16 cm	9	3	89
16–24 cm	8	6	87
Labrador Hollow			
0–8 cm	2	13	84
8–16 cm	6	0	94
16–24 cm	7	1	92
Fern Lake Bog			
0–8 cm	15	16	69
8–16 cm	16	3	81
16–24 cm	10	3	87

Note: Initial model parameters are as follows: woody angiosperm ($S/V = 3.3$, $C/V = 0.3$), nonwoody angiosperm ($S/V = 1.5$, $C/V = 4.9$), gymnosperm ($S/V = 0.03$, $C/V = 0.1$).

peat when compared with S phenolic oxidation products. However, changes in this ratio may be brought about by diagenetic changes in peat as well as by shifts in botanical origin of the peat. As shown in this study, relatively undecomposed *Sphagnum* peat has much higher *p*-hydroxyl phenolic yields than more humified peat. A decrease in the P/V ratio with increasing degree of decomposition is consistent with reports that *p*-hydroxyl phenols are relatively labile compared with the V phenols (Hedges and Weliky 1989). Nevertheless, it is notable that, while the P/V ratio of most vascular plant material is in the range of 0.05–0.80 (cited in Hedges et al. 1988b), the P/V of fresh *Sphagnum* peat from Bleak Lake Bog was as high as 8.5. Similarly, the P/V ratio of a *Sphagnum* peat analyzed by Lehto et al. (1985) was calculated to equal 3.4. This contrasts sharply with the forested sites, which had lower P/V ratios (0.11–0.50) resulting from reduced P yields and increased V yields, probably as a consequence of increased gymnosperm litter input. Thus, in relatively undecomposed peat, the P/V ratio may serve as an adequate biomarker for *Sphagnum*-dominated peat.

Weight ratios of lignin biomarker phenols varied widely between sites and to a lesser extent between depth intervals at each site. The S/V and C/V ratios of the peat in this study are in the same range of those reported for a *Sphagnum*- and *Carex*-derived peat in Japan (Tsutuski et al. 1994) and a Finnish *Sphagnum* peat (Lehto et al. 1985) but generally

higher than those reported for marine organic sediments (Hedges et al. 1984, 1988b). Bleak Lake Bog, S-4 Wetland, and Peatland 632 peat had S/V and C/V closest to fresh plant tissue. On the other hand, we found the S/V and C/V ratios of forested mire peat to be depressed relative to the other sites. Ugolini et al. (1981) found a similar trend when comparing the lignin oxidation products of alpine tundra and boreal forest soils, the latter having lower S/V and C/V ratios. This pattern is understandable given that gymnosperm lignin is relatively enriched in V phenols compared with angiosperm lignin (Hedges and Mann 1979). However, selective loss of S and C phenolic precursors from the lignin structure could also result in similar compositional trends.

Evidence of diagenetic sensitivity in the S/V and C/V parameters is obtained from correlation analysis (Table 5) with the amounts of labile and refractory carbon fractions in a peat sample. For example, the S/V ratio is strongly correlated with peat carbohydrate and cellulose content and strongly negatively correlated with peat Klason lignin abundance. Additionally, the overall yield of V phenols exhibited a strong negative correlation with the acid-soluble carbohydrate content and strong positive correlation with the Klason lignin content. Such relationships suggest that conditions that are favorable for enhanced cellulose and carbohydrate loss are also favorable for selective loss of the syringyl precursors from the lignin structure. Since S/V does not stay constant but decreases with

increasing decomposition of peat, its use as a source type indicator should be used with caution in humified peats.

Acid to aldehyde ratios

Additional insight into the diagenetic state of peat can be gained by analyzing the ratio of phenolic acid to aldehydes in the oxidation digest. In general the elevated acid to aldehyde ratios of phenylpropanoid moieties are taken to indicate decomposition of lignin (Hedges et al. 1988a). Fresh vascular plant tissue usually gives an S acid to aldehyde ratio (Ad/Al)_s in the range of 0.1–0.2 (Hedges et al. 1988a). With the exception of Bleak Lake Bog peat, bulk peat samples analyzed in this study all had (Ad/Al)_s equal or greater than 0.2. We also found that elevated (Ad/Al)_s were accompanied by smaller amounts of labile carbon and higher lignin contents ($r = 0.67$) in a peat sample. The (Ad/Al)_s also was negatively associated with the S/V ratio ($r = -0.73$). On average, the (Ad/Al)_s was only slightly higher in the deeper peat (0.36) than the middle (0.28) and surface peat (0.25). Peat from the forested mires generally had the highest (Ad/Al)_s, although this ratio reached a maximum in the deep peat from Fern Lake Bog (0.58). Given the disparity in vegetation types between the forested mires and Fern Lake Bog, and the fact that acid to aldehyde ratios in fresh plant tissue from various plants are fairly uniform, the elevated ratios in peat from different sites indicates that similar lignin decomposition pathways may be involved at different sites. This suggests that the (Ad/Al)_s appears to be a useful indicator of the diagenetic state of the peat. The acid to aldehyde ratios for all of our peat samples are of the same magnitude as those calculated for a Finnish *Sphagnum* peat (Lehto et al. 1985) but an order of magnitude lower than those of a Japanese *Sphagnum*- or *Carex*-derived peat (Tsutsuki and Kondo 1995).

In contrast to the (Ad/Al)_s the (Ad/Al)_v exhibited no strong relationship with the different carbon fractions and no strong trend across sites or depth interval per site. This was unexpected in light of the common observation that, in many environments, (Ad/Al)_v ratios are generally more elevated than in the S family (see Hedges et al. 1988a). Degradation of wood lignin by white rot fungi has been shown to elevate both (Ad/Al)_v and (Ad/Al)_s although the magnitude of change was greater in the (Ad/Al)_v ratio (Hedges et al. 1988a). Differences in decomposer communities may result in differential change in the acid to aldehyde ratios as well. For example, fungal decomposers can have a pronounced effect on the acid to aldehyde ratios (Hedges et al. 1988a), whereas bacteria appear to have no effect (Opsahl and Benner 1993). Two complications exist in using this ratio as a diagenetic indicator: (i) vanillic acid that is ester bound to polysaccharides in some nonwoody plant tissues can cause high (Ad/Al)_v in undegraded samples (Goñi and Hedges 1992), and (ii) humic substances included in the bulk peat have elevated (Ad/Al)_v (Hanninen 1992). Both factors may explain the variability in the (Ad/Al)_v ratio between sites, although the latter may be particularly relevant in peatlands, which have large quantities of humic substances.

Mixing model

Since peat is primarily composed of plant remains it would be informative to be able to determine the relative contribution of different plant types to the organic matter pool. A simple end-member mixing model can be used for partitioning mixtures of

vascular plant debris into broad categories based on distinct differences in chemistry. For example, Ertel and Hedges (1985) developed a three component mixing model to estimate the amount and type of sedimentary vascular plant debris in marine sediments based on CuO oxidation products. The same approach can be taken with peat to explain the contribution of different peat forming plants to the lignin fraction.

In this model the weight percentages of different fresh tissue types that best fit the measured C/V and S/V values for a peat sample are calculated. Since each tissue type (i.e., woody or nonwoody gymnosperm or angiosperm) has a specific C/V and S/V value associated with it, the relative amounts of each tissue type can be solved for a given peat sample as a series of simultaneous equations. The major assumptions of such models are (i) the sedimentary plant tissues are well preserved, and (ii) individual lignin-derived phenols do not exhibit differential reactivities. In some cases these assumptions are false, leading to overestimates of woody vascular plant fractions in sedimentary mixtures (Hedges and Weliky 1989). For example, in marine sediments, angiosperm contribution is typically underestimated because of selective loss of C lignin phenolics during decomposition of the organic matter. However, in contrast to marine sediments, *Sphagnum* peat consists of a mixture of vascular and nonvascular plant detritus that often exhibit excellent preservation of plant tissues and may be a suitable environment in which to apply lignin biomarkers in a mixing model. We recognize that at least some of our samples exhibit signs of selective degradation of the S and C lignin precursors, which may lead to underestimation of angiosperm plant tissues to the lignin fraction.

We applied the mixing model of Ertel and Hedges (1985) to the results from the lignin analysis of peat studied here. Hedges and Weliky (1989) and Opsahl and Benner (1995) point out the importance of determining the lignin signatures of plant end members. We developed oxidation signatures for a small subset of common wetland plants to complement the lignin phenolic parameters given by Goñi and Hedges (1992) and Hedges and Mann (1979) for a wide range of vegetation types. In light of the wide variety of vascular plant inputs, we averaged our values with published values to achieve lignin signatures more representative of the actual peat mixtures. We present the results of the model run with woody and nonwoody angiosperm parameters as well as an average gymnosperm signature, which is an average of nonwoody and woody gymnosperm lignin parameters.

The calculated contributions of different plant lignin to peat mixtures are presented in Table 6. The most notable results of these calculations are the relatively low percentage of nonwoody angiosperm lignin estimated by the model, with the exception of the S-4 Wetland peat. Estimates of gymnosperm-derived lignin amounted to an average 68% across all sites and depths, whereas woody and nonwoody angiosperm tissue averaged to 19 and 13%, respectively. It is difficult to assess how these values compare with actual amounts of vascular tissue in these peat samples without some sort of macrofossil analysis. Even so, because of the variability that exists in differential preservation of plant tissues in peat, percentages obtained from such work would not account for amorphous materials, which in some cases can be expected to retain chemical characteristics of the original plant type (Norden et al. 1992). Given the fairly regular presence of nonwoody angiosperms such as

grasses, sedges, and leaves of ericoid shrubs in peat, the model does seem to underestimate the amount of angiosperm lignin and overestimate the amount of gymnosperm lignin in the mixture. The calculation appears relatively sensitive to the amount of vanillyl phenolics in the peat. Given the presence of vanillyl phenolics in the oxidation products of all the peat samples and the potential contribution of vanillyl phenolics by humic substances, as well as lignin, the model gives what appears to be poor estimates of angiosperm contribution, even in the relatively undecomposed peat of Bleak Lake Bog. It is notable that the relatively high C/V and S/V ratios of S-4 Wetland peat, which is rich in herbaceous vegetation, does give a corresponding higher percent contribution.

Conclusions

Cupric oxide oxidation can provide additional information to supplement the traditional proximate analysis. Two broad categories of acid-insoluble matter or lignin in peat are defined on the basis of CuO oxidation products. Samples rich in the acid-insoluble Klason lignin fraction were characterized by the relatively recalcitrant vanillyl phenolic monomers and elevated syringyl acid to aldehyde ratios, suggesting that the peat was overall more decomposed and may have poorer carbon quality. The more northern peatlands, characterized by less Klason lignin and more holocellulose, were characterized by generally greater *p*-hydroxyl monomer yields, a characteristic of fresh *Sphagnum* peat. Notably, we found no evidence of a phenylpropane-based lignin structure in *Sphagnum* mosses that were analyzed. Contrary to other studies we found that changes in the acid to aldehyde ratio of the syringyl family to be more sensitive to decomposition than the vanillyl acid to aldehyde ratio, possibly reflecting differences in the decomposer community of peatlands or an overall greater lability of the syringyl moiety in peat. The compositional trends in phenolic oxidation products did follow botanical sources of organic matter, although selective loss of biomarker phenols appears to compromise the accuracy of this technique in more humified peat. Given the heterogeneity in oxidation products of these peat samples, it is apparent that the chemical composition of lignin in northern peatlands varies considerably. Thus, further study of organochemical constituents such as peat lignin at the molecular level may provide a more mechanistic understanding of carbon cycling in northern peatlands.

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