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Carbon dynamics in peat bogs: Insights from substrate macromolecular chemistry

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Abstract. The macromolecular compositions of subfossil plants from boreal *Sphagnum* bogs and restiad bogs (New Zealand) have been studied by pyrolysis-gas chromatography/mass spectrometry to evaluate the extent of degradation in the anoxic zone (catotelm) of a peat bog. Degradation of vascular plant polysaccharides was apparent only into the upper catotelm. *Sphagnum* was degraded more slowly than vascular plants, but no cessation of degradation was observed. The inferred rate of degradation varied depending on type of plant, extent of aerobic, precatotelmic degradation, and mode of litter deposition (rooting versus at the surface). Environmental forcing on anaerobic carbon dynamics would potentially be largest if the hydrology was disturbed at a wet and vascular plant-rich site. Peat deposited under a dry regime would be relatively inert in anaerobic conditions. Although catotelmic degradation is usually not extensive, in some cases, if labile organic matter is retained in the aerobic phase (e.g., restiad bogs) a major fraction of peat is degraded in catotelm, potentially resulting in a delayed major export of ¹⁴C-old methane.

1. Introduction

About one third of global soil organic matter (OM) is stored in peatlands [Gorham, 1991]. A low turnover rate, resulting in net OM accumulation, is attributed primarily to waterlogging-induced anoxia in the catotelm layer (in the sense of Ingram [1978]). The primary pool of OM is severely depleted by aerobic degradation in the acrotelm layer (in the sense of Ingram [1978]) in the first years after deposition, before the permanent onset of anoxia. The rate and extent of catotelmic degradation are uncertain, but apparently slow [Clymo, 1983]. Characteristically, peatlands are major sources of CH₄ [e.g., Dise *et al.*, 1993] and dissolved organic carbon (DOC) emissions [e.g., Schiff *et al.*, 1998]. The information on OM dynamics comes primarily from CO₂, CH₄, or DOC flux experiments [e.g., Laine *et al.*, 1996; Moore and Dalva, 1997; Yavitt *et al.*, 2000]. On the other hand, the substrate of the degradation products is rarely defined chemically and botanically, even if substrate quality is a major factor affecting diagenesis rates [cf. Updegraff *et al.*, 1995]. If chemical data are available, they typically concern bulk peat, which imposes certain limitations on interpretations [Yavitt *et al.*, 1997; Williams *et al.*, 1998; Yavitt *et al.*, 2000]. The most informative results on the sources of methane, CO₂, and DOC were provided by radiocarbon dating. CH₄ emitted from the bog surface is consistently shown to be of recent ¹⁴C age, indicating production at the expense of recently fixed carbon [Chanton *et al.*, 1995; Charman *et al.*, 1999; Schiff *et al.*, 1998]. When old substrate is degraded, the products may be retained within the deposit or discharged into groundwater, thus remaining undetected [Charman *et al.*, 1993].

An alternative approach to peatland carbon dynamics is monitoring of temporal trends of substrate degradation. This approach is widely used in litterbag experiments [e.g., Clymo, 1983];

however, these studies are necessarily limited to several years of observations and to the relatively rapid acrotelmic processes. Peat stratigraphic profiles, conversely, provide a record of cumulative degradation since the initiation of deposition. The major benefit of such an approach is the ability to detect slow processes occurring in the catotelm, perhaps the least understood aspect of peatland OM dynamics.

In the present study, we use data on macromolecular composition of peat OM from several bog sites with variable vegetation history to answer the question of whether and where does catotelmic degradation take place. Interpretation of the result within the framework of peatland hydrology and carbon export will be attempted. The challenge of a study of peat chemical composition is the botanical heterogeneity of the material. Analytical data on bulk peat, especially from boreal bogs, must be approached cautiously because of the dominance of botanical, rather than diagenetic, signatures for bulk *Sphagnum* peat [Kuder, 2000]. Moreover, rooting results in the introduction of fresh OM into older and already degraded matrix, resulting in the “dilution” of the actual diagenetic signal. To overcome this problem, fractions of individual taxa are collected from the peat matrix and analyzed separately. Sequences of peat samples from the four sites were collected, allowing temporal coverage up to 8000 years B.P. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) was applied as a technique allowing a multifaceted characterization of macromolecular components in submilligram samples of pure botanical sub-fractions of peat matrix [van Smerdijk and Boon, 1987].

2. Methods

2.1. Locations: Environmental Setting and Sampling

Raw data for this paper come from previously published studies of a *Sphagnum* bog from Canada, a *Sphagnum* bog from Poland, and two restiad bogs from New Zealand.

The Canadian site (“Carling Lake” bog) is a part of a system of peatlands developed in the humid and cold climate of the Hudson Bay Lowland (HBL) region (northern Ontario, 51°32′N, 81°36′W). The thickness of peat was 265 cm, and ¹⁴C age was 4110 ± 70

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years B.P. at the base [Klinger *et al.*, 1994]. Several lakes occur next to or within the bog. The topography of the HBL is flat, with a series of parallel beach ridges and swales. They represent ancient coastlines of a sea retreating because of postglacial isostatic rebound. Peat accumulated between ridges, because of impediment of drainage on marine silts and clays and favorable climate during the growing season (May–September). The mean annual temperature is $\sim 0^{\circ}\text{C}$, growing season temperature averages 11.3°C , and mean growing season precipitation is 80.3 mm. Peat depositional environments on the HBL range from saltwater marshes to fens to bogs, a gradient observed moving inland from the modern shore of Hudson Bay. Accordingly, it is observed that in bog sites the basal peat was deposited under the fen regime. Present-day vegetation is characteristic of ombrotrophic conditions, consisting of stunted bog forests (*Picea mariana*, *Larix laricina*) and *Sphagnum* lawns with a number of Ericaceae (including species of *Andromeda* and *Vaccinium*). In the stratigraphic record few intervals with abundant sedges, probably *Carex*, occur. High amounts of occluded gas (CO_2 and methane?) occurred below a depth of 200 cm. At the moment of sampling the water table was between 18 and 35 cm below the surface, apparently representing an exceptionally dry season [Klinger *et al.*, 1994] and probably indicating the maximum depth of aerobic processes.

The Polish site ("Rownia pod Sniezka" bog) is a small alpine bog (~ 300 m diameter) situated within a flat water divide of the main range of the Karkonosze Mountains at an elevation of 1400 m. Annual precipitation is in excess of 1500 mm and is supplemented by dew deposition. The freeze-free season lasts only ~ 3 months. Initiation of peat deposition ~ 3500 years B.P. was attributed to a cold and humid climate and a spring contributing to waterlogging [Tolpa, 1985]. The peat layer is ~ 100 – 150 cm thick, overlaying granitic bedrock with pockets of regolite. Vegetation consists of wet *Sphagnum* lawns with sedges (*Trichophorum caespitosum*, *Carex pauciflora*, less abundant *Eriophorum*) and relatively dry hummocks with mosses, Ericaceae, and *Eriophorum vaginatum*. A number of the driest hummocks support dense stands of *Pinus mugo*.

The two New Zealand bogs, Kopouatai and Moanatuatua, are located on lowlands of North Island. They are isolated bog complexes, of $\sim 10,000$ ha each and significant peat thickness (over 8 m). Peat formation was attributed to drainage impediment on clayey soil, beginning $\sim 11,000$ – $13,000$ B.P. [Campbell, 1983]. Moanatuatua bog has been recently drained for farming. Present vegetation in both Kopouatai and Moanatuatua is dominated by restiads, especially *Empodisma minus*. Other plants include restiad *Sporadanthus traversii*, sedges (*Baumea*, *Schoenus*), *Leptospermum scoparium* (woody angiosperm), and pteridophytes and mosses [Newham *et al.*, 1995]. *Sphagnum* is present as a minor component. The climate of the New Zealand sites is warmer and drier than in the case of the boreal bogs, the mean annual temperature is 13.5°C , there are only 46 days per year with frost, and the precipitation is 1100–1300 mm. Physiological and chemical properties of the monocot *E. minus* are considered crucial to deposition of thick peat deposits in otherwise unfavorable conditions [Agnew *et al.*, 1993; Kuder *et al.*, 1998].

Details of sample collection and botanical characterization of peat are given elsewhere [Kuder and Kruge, 1998; Kuder *et al.*, 1998; Kuder, 2000]. In brief, the Canadian peat samples were collected from a fresh pit as blocks 10–20 cm thick (upper 225 cm), and an additional 100 cm of peat and 10 cm of underlying mineral soil were extracted with a piston corer from 160 to 270 cm. Before chemical and botanical analyses, blocks/core sections were sawn into slices 2–4 cm thick. At the New Zealand sites, cores of ~ 8 m length were extracted with a 6 cm diameter D-barrel (Russian) corer. Visual characterization of macroscopic humification was made after collecting the cores, and subsamples from layers of distinct characteristics were taken for more detailed study.

The samples from the Polish site were also extracted with a D-barrel corer. Subsamples of ~ 4 cm³ were taken from a continuous series of intervals with distinct visual humification or composition (2–5 cm per intervals with distinct color and fibrosity). The maximum depth of sampling was ~ 110 cm (a few centimeters short of the bedrock). Plant macrofossils were handpicked under a binocular microscope from the selected subsamples, frozen, and vacuum dried to prevent further decomposition. Also, fresh tissues of the analyzed taxa were collected and preserved. The botanical composition of peat in Canadian and Polish locations was described to identify the details of stratigraphy. In the case of the New Zealand site the physical properties were used to differentiate peat layers, because of more uniform botanical characteristics than observed in the boreal bogs.

2.2. Analytical Procedures

All chemical data were obtained by pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) of peat macrofossils (Canada and Poland sites) and peat matrix (New Zealand). Selection of plant types and organs was made to account for the volumetrically dominant ones, including *Sphagnum*, Ericaceae roots, and sedge fibers (the former two virtually dominating the studied boreal bog profiles). Additionally, a surface-deposited fraction that does not contribute significantly to bulk peat was analyzed, to allow detection of diagenetic features not apparent otherwise. Conditions of pyrolysis, gas chromatographic programs, and mass spectrometer settings are given elsewhere [Kuder and Kruge, 1998; Kuder *et al.*, 1998; Kuder, 2000]. Py-GC/MS is a degradative technique for characterization of (primarily) macromolecular/polymeric organic matter. A pulse of high temperature in the inert atmosphere (Helium carrier gas) destroys chemical bonds of a polymer, producing GC-amenable components, which are identified, quantified with a MS, and classified according to the parent biopolymer. The pyrolytic temperature (here 600°C) is optimized for maximum yield of volatile products but is low enough to prevent too much damage to the released monomers, rendering them less diagnostic of the parent material (e.g., loss of side chains or functional groups from aromatic ring of lignin monomers). It should be clearly stated that interpretation of Py-GC/MS data is based on relative abundances of given classes of compounds, not on absolute abundances. Summed abundances of all compounds characteristic of a given polymer give the estimate of the abundance of the polymer in the analyzed sample (e.g., methoxyphenols are indicative of lignin). The pyrolytic yields may differ between polymer types, so that a pyrolyzate-based estimate of a ratio of polymer *x* to polymer *y* is not necessarily the stoichiometric ratio. However, for a series of samples a trend in pyrolytic ratio parallels that of the sample composition. An example of a chromatogram with identified compounds is given in Figure 1. Details of identification of composition of pyrolyzates, including lists of identified compounds used in quantification, are given in the original references.

2.3. Criteria for Determination of the Degradation Parameters

While the research design applied here does not account for the total of peat OM, it allows more confident visualizing of diagenetic trends than results from bulk peat. Qualitative extrapolation to total peat is justified by the overall similarity of macromolecular tissue components (lignin, cellulose, etc.). Even with the taxonomic, anatomical, and physiologic variability of plant tissue and the degrading microorganisms, the plant remains are nevertheless accessible to any degrader possessing an appropriate enzymatic apparatus. While the most accessible tissues are degraded preferentially, no tissue remains unaffected, since different groups of soil microorganisms are adapted to utilize various types of tissues

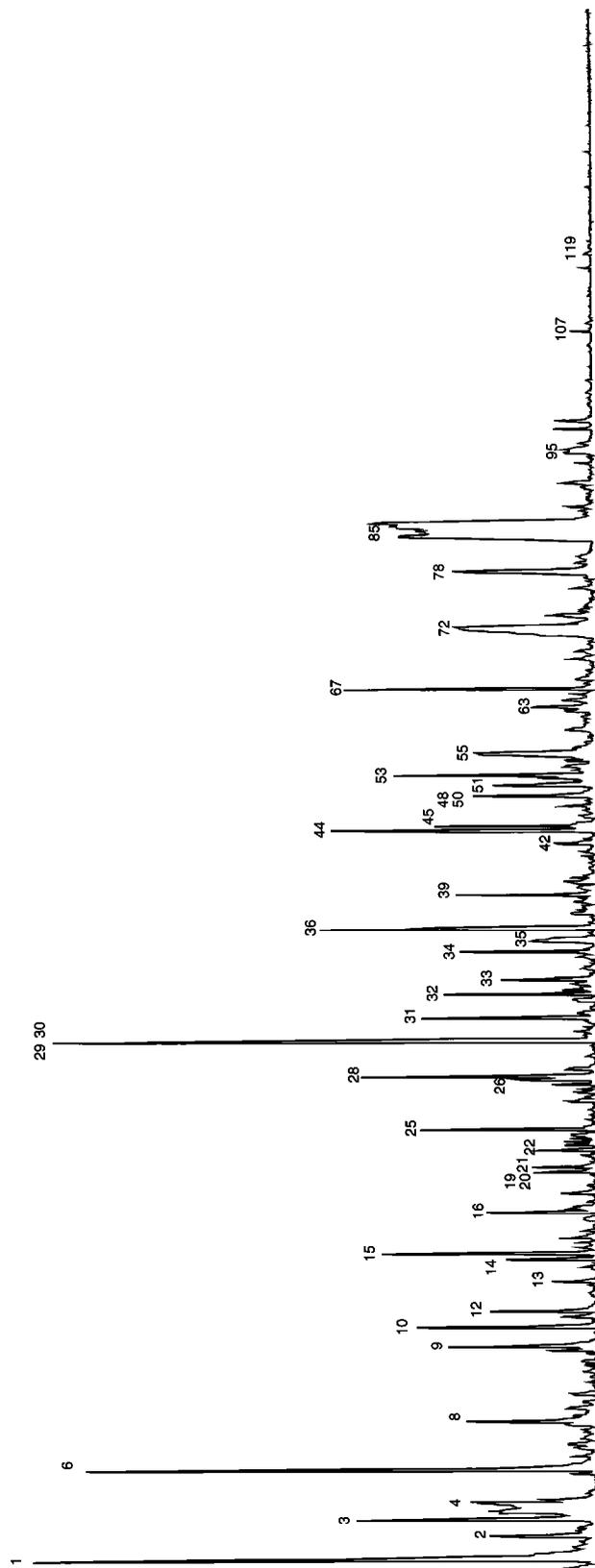


Figure 1. Pyrolyzate of subfossil *Sphagnum* stem, total ion chromatogram. Compounds are as follows: 1, pyruvaldehyde; 2, propanol; 3, butane-2,3-dione; 4, acetic acid; 6, hydroxypropanone; 8, 2-methyl-1,4-pentadiene; 9, 3-hydroxypropanal; 10, 2-hydroxybutanal-3-one; 12, 2H-furan-3-one; 13, furfuraldehyde isomer (?); 14, cyclopentenedione (?); 15, 2-furaldehyde; 16, acetolacetate; 19, 1,3-dimethylbenzene and 1,4-dimethylbenzene; 20, 5H-furan-2-one; 21, 2,3-dihydro-5-methylfuran-2-one; 22, 2-methyl-2-cyclopenten-1-one; 25, 2-hydroxy-2-cyclopenten-1-one; 26, 3-methyl-2-cyclopenten-1-one; 28, 5-methyl-2-furaldehyde; 29, phenol; 30, 4-hydroxy-5,6-dihydro-2H-pyran; 31, 3-hydroxy-2-methyl-2-cyclopentene-1-one; 32, 2-hydroxy-3-methyl-2-cyclopentene-1-one; 33, unknown; 34, 2-methylphenol; 35, unknown PS marker; 36, 3-methylphenol and 4-methylphenol; 39, 3-hydroxy-2-methyl-4H-pyran-4-one; 42, 2,4-dimethylphenol (?); 44, ethylpentanol or dimethylpentanol; 45, 4-ethylphenol; 48, anhydro- α -glucopyranose; 50, 1,2-dihydroxybenzene (catechol); 51, 2-hydroxymethyl-2-furaldehyde; 53, 4-vinylphenol; 55, anhydroxylose; 63, 1,4-dideoxy-D-glycero-hex-1-enopyranos-3-ulose; 67, isopropenylphenol; 72, levogalactosan; 78, levomannosan; 85, levoglucosan; 95, 1,6-anhydro- β -D-glucofuranose; 107, biphenylol; and 119, methyl-biphenylol (adopted from Kuder [2000]).

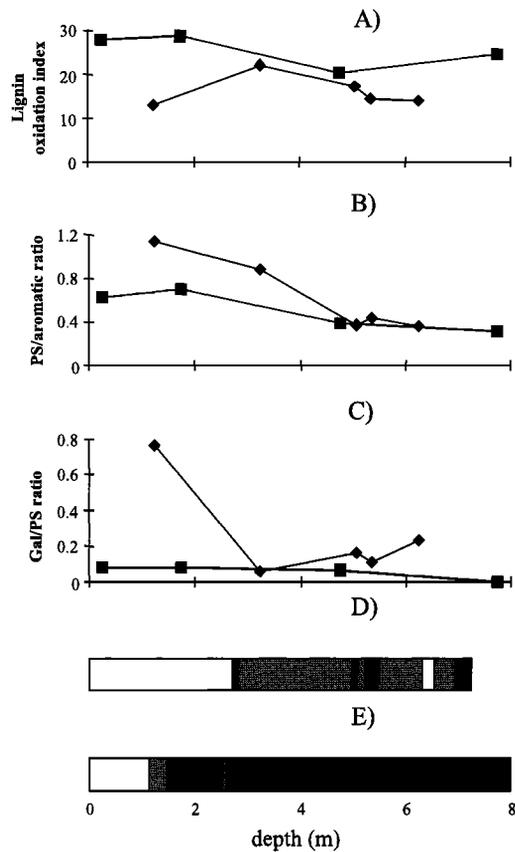


Figure 2. Degradation trends of bulk restiad peat, New Zealand. Squares indicate the Moanatuatua bog, and diamonds indicate the Kopouatai bog. (a) Lignin oxidation index: % C α acetylated to total methoxyphenols ratio (see text for explanations). Vinyl moieties are not included because of a possible affiliation with cinnamic acid fraction, not lignin. (b) Polysaccharide to aromatics ratio. (c) Anhydrogalactosan to total polysaccharide ratio. (d and e) Stratigraphic profiles of Kopouatai and Moanatuatua bogs (dark tone, sapric peat; medium tone, hemic peat; light tone, fibric peat).

[Sylvia, 1998]. In the case of peaty soil the nominal availability of substrate is overshadowed by the electron acceptor limitations, as evidenced by actual preservation of vast amounts of organic matter. In anoxic conditions the degradation efficiency decreases, and substrate bioavailability becomes a dominant limitation to microbial metabolism. Experiments with glucose amendment (providing a readily available source of carbon) show that in anoxic conditions degradation proceeds with maximum possible efficiency [Bridgman and Richardson, 1992; Bergman et al., 1998, 2000]. Another study shows that glucose amendment has no effect in lignin-poor peat, presumably still preserving enough labile polysaccharides [Yavitt et al., 1997]. Glucose did not accelerate the decay rate of peat OM, essentially precluding a chance of synergistic diagenetic effects between various tissue types [Aerts and Toet, 1997]. Therefore, if a temporal acceleration of degradation is detected in the stratigraphic record of one taxon, it is reasonable to expect that the other plant remains were similarly exposed to more vigorous degrading activity, even if the actual extent of the degradation of a given tissue does depend on its specific chemistry and structure. This expectation is supported by similar direction of degradation trends of various botanic units from the same site [Kuder, 2000].

The changes of vascular plant pyrolyzate composition that are indicative of OM loss are (1) relative decrease in abundance of polysaccharide-derived versus lignin-derived compounds, (2) relative depletion of hemicellulose-derived versus total polysaccharide compounds, (3) increase of abundance of side-chain-oxidized methoxyphenols (referred to in the following paragraphs as "lignin oxidation index"), accompanied by a decrease of propenyl-side-chain methoxyphenols, and (4) relative decrease in the dimethoxy/monomethoxyphenol ratio (S/G). The two former indices represent polysaccharide degradation, and the two latter represent lignin degradation. The term "lignin" as applied here pertains to the methoxyphenyl-propanoid polymer (in the sense of Lewis and Yamamoto [1990]). Anaerobic losses of lignin recorded by some authors can be explained by their imprecise definition of "lignin," encompassing a wider range of phenolic substances. As true lignin is degraded exclusively in the oxic zone and remains inert in anoxic conditions [Young and Frazer, 1987], the extent of lignin alterations can be used as a proxy for the cumulative exposure to aerobic degradation. Polysaccharides (PS) are also degraded in anaerobic conditions, and PS versus lignin-derived aromatics depletion has been observed in the catotelm [Kuder, 2000]. Composition of *Sphagnum* pyrolyzates is not affected by the extent of tissue degradation; instead, a visual estimation of cell wall damage via scanning electron microscopy (SEM) can be employed. By studying a sequence of samples, representing age/depth increments, it is possible to reconstruct a trend of PS depletion. The degradation trend indicates an anaerobic process if two conditions are satisfied: (1) the trend is apparent below a reasonable estimate of the acrotelm lower limit and (2) the trend is not correlated with any aerobic lignin degradation index, which would suggest instead a residual effect of a change in peat surface conditions, not of anaerobic decay. Lignin, which is not affected in anoxic environments, is used as a "standard," against which a depletion of PS is measured.

3. Results

3.1. Restiad Bogs

Mosses and vascular plants have significantly different diagenetic properties so that the chemical signature of bulk peat is predominantly affected by botanical content, not the extent of degradation [Kuder, 2000]. At the two studied restiad bogs the dominant peat component is subaerial roots of monocotyledon *Empodisma minus*. Whereas boreal bogs contain significant amounts of both *Sphagnum* and vascular plants, at the studied New Zealand sites *Sphagnum* is present but subordinate. For this reason, it is justified to use bulk peat chemical composition without introducing a bias. The two sites differ in the extent of aerobic degradation (Figure 2a), estimated using the lignin oxidation index [cf. Kuder and Kruge, 1998]. A relative decrease in PS content in pyrolyzates with depth has been observed at both sites (Figure 2b). Kopouatai bog peat retained more PS after the acrotelmic degradation, but the ratios of PS to lignin at the two sites converged at depths between 3 and 5 m, remaining stable in deeper peats. Only the basal peat (seen at Moanatuatua) was more extensively degraded, showing abnormal dehydroxylation of aromatics, depletion of hemicellulose, and generation of furan structures at the expense of PS. A major part of PS depletion at Kopouatai was achieved by removal of galactosan-bearing hemicellulose, which is only a minor component of Moanatuatua peats (Figure 2c). Pyrolysis of fresh peat-forming plants has shown that the fine rootlets of *Empodisma minus* are the source of galactosan in undegraded peat [Kuder et al., 1998]. The more extensive exposure of Moanatuatua peat to aerobic degradation was probably the cause of the absence of major amounts of pristine hemicellulose-rich rootlets in peat matrix.

3.2. *Sphagnum* Bogs

Variable content of *Sphagnum* and vascular plants in boreal bogs makes it impossible to use bulk peat data. Individual macrofossils were analyzed, *Sphagnum*, Ericaceae roots, conifer needles and sedge shoot fibers. In the case of the Canadian samples, depletion of PS was apparent, but only in the upper 100 cm of the profile (Figure 3). In older samples the PS content was stable. In fact, the depth at which PS depletion was no longer visible differed between individual species and organs: greater in the case of roots (Ericaceae) and lesser for surface-deposited conifer needles. No preferential degradation of hemicellulose in the catotelm was observed. Of the macrofossils from the site in Poland, only sedge vascular fibers were analyzed and were found to be chemically inert in the catotelm. Similarly, as in the restiad bog, basal samples both from Canada [Kuder, 2000] and Poland [Kuder and Kruge, 1998] have shown evidence of more extensive degradation: dehydroxylation of aromatics, depletion of hemicellulose, and a slight increase of abundance of furan structures in pyrolyzates. Conifer needles, which are deposited at the bog surface, and sedge fibers deposited at or close to the peat surface (and thus most affected by water table fluctuations and associated changes of biodegradation) were analyzed to determine the lignin oxidation index. Fluctuations of lignin oxidation index at both sites suggested that the water tables and extent of aerobic exposure varied. PS content in macrofossils from Canada responded to bog water table fluctuations (Figure 3). In the upper half of the profile, in the zone where excess PS has not yet been removed by anaerobes, low lignin oxidation could be correlated with high PS content and vice versa. *Sphagnum* did not show any chemical features indicative of the extent of degradation, but SEM of stem cell walls showed that damage increased with depth and also fluctuated as a function of the degree of aerobic exposure, similar to the PS content of vascular plants [Kuder, 2000].

4. Discussion

4.1. Sources of Pore Water Gases and Dissolved Organic Matter

The environmental setting of peat bogs (anoxia and oligotrophy) constrains microbial activities by limiting aerobic respiration to the acrotelm. In anoxic conditions, fermentative bacteria are able to mineralize macromolecular materials, such as cellulose [Deming and Baross, 1993]. For the sake of thermodynamic efficiency, free hydrogen (a side product of fermentation) needs to be removed from the system. In the semistagnant pore waters of a peat deposit, in the absence of alternative hydrogen consumers, methanogens are a necessary component of an anaerobic microbial consortium [Deming and Baross, 1993]. Sulfate reducers outcompete methanogens if hydrogen is a limiting factor, but the phenomenon is observed only in the topmost layer of bog peat where sulfate is supplied via precipitation [Watson and Nedwell, 1998]. Therefore an inference can be made that the extent of anaerobic degradation is proportional to methane production.

Potential carbon substrates for microbial metabolism in the catotelm are peat OM and DOC flushed from the acrotelm [Chanton et al., 1995]. The immediate products of OM degradation/depolymerization contribute to the pool of DOC. Chemical composition of DOC is a function of the substrate composition. More PS-rich substrates yield PS-enriched DOC and vice versa [Nierop and Buurman, 1998]. The results presented in this paper point to the PS-rich fraction of vascular plants (in the boreal site only in the initial phase of degradation) and *Sphagnum* as substrates available for anaerobes. Formation of carbohydrate-rich DOC in the catotelm could be expected. On the other hand, more

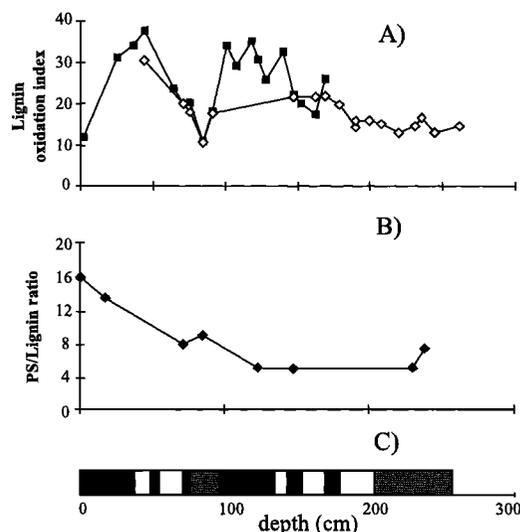


Figure 3. Degradation trends of vascular plant peats at Carling Lake bog, Ontario, Canada. (a) Conifer needles (diamonds and squares indicate tamarack and black spruce, respectively). Lignin oxidation index (percentage of C_{α} acetylated to total methoxyphenols ratio; see text for explanation). (b) Ericaceae roots and ratio of polysaccharide to methoxyphenols (lignin) ratio. Methoxyphenols, not total aromatics, are used to avoid bias due to degradation of labile tannins. (c) Stratigraphic profile. (Dark shading indicates *Sphagnum*/Ericaceae peat, medium shading indicates moss/sedge peat, and light shading indicates *Sphagnum* peat; in the lower part of the profile, sedge is accompanied by *Drepanocladus* rather than *Sphagnum*.)

efficient enzymatic degradation in the acrotelm would generate DOC relatively enriched in aromatic/aliphatic moieties, which is less energetically attractive (the statement is speculative, as no relevant molecular data on bog dissolved organic matter are available). The main implication of different compositions for DOC generated in the catotelm and acrotelm would be that mass balance calculations, e.g., based on radiocarbon age, would not necessarily reflect bioavailability. The DOC fraction flushed down from the acrotelm, relatively enriched in recalcitrant compounds, would be metabolized less efficiently than DOC generated in situ. Additionally, DOC would be radiometrically younger than dissolved gas. Such age discrepancy has been noticed [Charman et al., 1999] but hypothetically explained by more efficient downward transport of DOC than CH_4 or CO_2 .

Degradation products collected near to the peat surface yield recent radiocarbon ages [Chanton et al., 1995; Charman et al., 1999; Schiff et al., 1998]. Exported CO_2 , CH_4 , and DOC form apparently at the expense of recently fixed carbon. CH_4 formed at the very top of the catotelm dominates over the flux from deep peat. Pore water gases and DOC collected from deep layers of peat bogs show radiocarbon ages younger than the adjacent peat by several hundreds of years to over 2000 years [Chanton et al., 1995; Charman et al., 1993, 1999; Schiff et al., 1998]. Ages of pore water carbon, which are intermediate between recently fixed OM and old peat, suggest mixing of modern and generated in situ materials. The increase of pore water carbon age terminates or at least slows down in deeper peat layers [Chanton et al., 1995; Schiff et al., 1998]. These results seem to agree with substrate chemistry data: An initial distinct age increase is a result of in situ methane generation, diluted by carbon transported with descending groundwater. A cessation of anaerobic degradation of vascular plant tissues, as described in section 4.2, would limit the in situ methane generation to the slower process of *Sphagnum* degradation (or

other mosses, perhaps *Drepanocladus*, similar in their resistance to degradation; cf. Kuder [2000]). In such case the age of methane in the lower parts of the profile would be only slightly greater than the age at the depth where PS was actively depleted.

4.2. Controls of Degradation and Effects of Environmental Change on C Emission from Peatlands

The extent and rate of catotelmic degradation depend on the quality of plant litter after it is buried beneath the acrotelm. Bog hydrology regulates oxygen supply and acrotelm thickness. High peat surface wetness (PSW) results in a thin acrotelm, limited aerobic degradation, and a significant portion of labile OM left for anaerobes in the catotelm. Low PSW results in a thick acrotelm and mineralization of labile OM before it becomes available to anaerobes. Peaks of high polysaccharide content apparent in the upper part of the Canadian profile disturb the polysaccharide depletion trend and coincide with high PSW. The effects of peatland water table movements on CH₄ and CO₂ production and emission were described by a number of authors [Dise et al., 1993; Laine et al., 1996; Silvola et al., 1996; Moore and Dalva, 1997; Daulat and Clymo, 1998]. Given other parameters are kept constant, production of CH₄ increases at high water table, but CO₂ decreases. Apart from the CH₄ production increase, thinning of the acrotelm shrinks the habitat for methylotrophic bacteria [e.g., Daulat and Clymo, 1998], and anoxia fluctuations impose stress on methanogenic and (to a lesser extent) methanotrophic bacteria [Whalen and Reeburgh, 2000]. The effect of water table drawdown depends on the extent of peat decomposition, having more impact on relatively well-preserved peats [Hogg et al., 1992]. DOC export apparently is not directly affected by the water table fluctuations but depends on the amount of lateral discharge along the acrotelm and resulting flux out of the system [Moore et al., 1998; Schiff et al., 1998]. On the other hand, water table fluctuations, which produce significant changes of hydraulic head, may alter the flow system in a bog and indirectly affect DOC export. An excess of labile OM preserved upon high PSW will ultimately be degraded in the catotelm, so that old peats with variable extent of aerobic degradation (variable PSW) have uniform chemical composition (Figure 3). It has been proposed that CH₄ generated in catotelm may be migrating directly to groundwater and so remain unaccounted for in flux studies [Charman et al., 1993]. Accumulation of CH₄ in pore waters in the deeper part of peat bogs has been reported in several papers [Romanowicz et al., 1995; Brown, 1998]. A confining layer of occluded bubbles was proposed to explain such a phenomenon [Romanowicz et al., 1995], and indeed it has often been observed in peat sections, including the Canadian bog (between 180 and 200 cm). Only sporadically, when hydrostatic pressure is for some reason lowered (e.g., by a prolonged drought and water table drawdown), accumulated CH₄ is removed by ebullition [Romanowicz et al., 1995]. Samples from New Zealand suggest that a major part of the fixed OM was mineralized in the catotelm over a prolonged period of time, very likely resulting in generation of large amounts of deep, ¹⁴C-old methane (although the age of pore water CH₄ was never studied there).

Within a given set of hydrologic/climatic conditions, substrate quality is a limiting factor for anaerobes. Highly variable diagenetic responses of plant parts (e.g., apparently inert sedge fibers versus ericaceous roots versus *Sphagnum*) highlight the potential impact of the botanical composition of peat on bioavailability of deposited OM. Sensitivity to environmental forcing would be higher for peat rich in vascular plant remains. Unlike degradation of moss, degradation of vascular plant OM may produce an inert residue (thick acrotelm and intense degradation) or relatively pristine, polysaccharide-rich OM (thin acrotelm). Subsequent methane generation potential would vary accordingly. The impact of low PSW may be in part compensated with deeper rooting, protecting PS against

aerobes. *Sphagnum* withstands acrotelmic degradation relatively well [cf. Johnson and Damman, 1991; van der Heijden, 1994]. In the catotelm, slow degradation proceeds even in peats in which vascular plant OM is inert. Degradation of vascular plants leads to selective removal of PS-rich and syringyl lignin-rich cell walls [van der Heijden, 1994]. In anoxic conditions, the energetic expense of residue degradation exceed its nutritional value [Post et al., 1995]. *Sphagnum* tissues degrade without introducing changes in chemical composition [van der Heijden, 1994; Kuder, 2000], and the inhibition does not occur. Shielding of the nominally labile components (e.g., cellulose) by resistant biopolymers (e.g., lignin or polyaliphatic cuticular polymers) makes them even less attractive as a substrate, especially in anoxic conditions, unsuitable for oxidative enzymes. PS of sedge fibers with their compact texture and high lignin content are likely to be protected this way. Another good illustration of such a mechanism is degradation of spruce needles, resulting in a relative loss of lignin rather than cellulose, since a portion of the latter is apparently protected within the framework of polyaliphatic and resistant polymer on the cuticle, whereas lignocellulose of the vessels is freely accessible to the microbial attack in oxic conditions [Kuder, 2000]. Therefore the presence of labile, or "nominally labile," compounds in peat cannot be equated with bioavailability.

The effect of substrate on the rate of decomposition was best observed for restiad bogs. At the Kopouatai bog the depletion of polysaccharide in the catotelm alone resulted in a net loss of over 50% of the original lignocellulose, as estimated from pyrolyzate composition. At Moanatuatua, where there was more acrotelmic degradation, the loss was smaller (and its rate was slower), so that peat composition at both sites ultimately converged.

5. Summary

The following points summarize our conclusions.

1. Macromolecular composition of peat macrofossils and matrix from boreal *Sphagnum* bogs and New Zealand restiad bogs has been studied by pyrolysis-gas chromatography/mass spectrometry to determine degradation trends.
2. Degradation of vascular plant remains was most noticeable in the upper part of the catotelm. In the lower catotelm the vascular plant organic matter was apparently inert. *Sphagnum* was degraded more slowly than vascular plants, but no cessation of degradation was observed.
3. The fraction of mass loss and duration of catotelmic degradation varied depending on the following factors: (1) type of plant, (2) extent of aerobic, precatotelmic degradation, and (3) method of litter deposition.
4. The extent of the aerobic degradation determines whether labile OM reaches the catotelm. It depends on peat surface wetness, i.e., on the water table height. Wet peat retains a high fraction of polysaccharides, which is later used by anaerobes, potentially resulting in generation of greenhouse gases.
5. Published radiocarbon ages of DOC, CH₄, and CO₂ from peat pore waters are generally in agreement with the data presented here. The differences in age between peat, DOC, and dissolved gases may be explained by mixing of modern signatures (DOC transported from the acrotelm) with DOC generated in situ, but also by differential bioavailability of the two DOC pools.
6. Effects of an environmental change on carbon dynamics may be potentially greatest if the hydrology were disturbed at a wet and vascular plant-rich site. Peat deposited under a dry regime would be relatively inert under anaerobic conditions, having already lost much of its polysaccharides.
7. In certain cases (e.g., restiad bog from New Zealand) it is possible that a major fraction of peat is degraded in the

catotelm, potentially resulting in a large export of radiometrically old CH₄.

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