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Environmental and botanical controls on peatification—a comparative study of two New Zealand restiad bogs using Py-GC/MS, petrography and fungal analysis

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Abstract

This study shows that chemical properties of two restiad species, *Empodisma minus* and *Sporadanthus traversii*, may contribute to their success as peat-formers in a climate of the North Island of New Zealand which is not conducive to raised mire development. Unlike *Sphagnum*, the equivalent northern hemisphere peat-former, restiads possess lignin in their tissues. In addition, the presence of non-lignin polyphenols (including tannins and phenolic acids) in restiads may be an important factor in peat formation due to the allelopathic decay retardation. Patterns of degradation of plant biopolymers have been examined and the pathway of degradation of monocotyledons (loss of non-lignin phenolic fraction, depolymerization via modification of side chains of β-O-4 lignin, depletion of hemicelluloses) was identified. Trends in chemical change for lignin were not necessarily paralleled by a similar change in the degree of plant structure preservation—an expression of a complex nature of degradation involving the contributions of several processes affecting different classes of biopolymers to different extents. A further finding of this study is that the degree of lignin breakdown, together with proportions of fungal hyphae and petrographic character, indicate that one of the two bogs studied, Moanatuatua, has undergone far more aerobic decay throughout its development than has its climatic and vegetational equivalent, Kopouatai. This is thought to be due to differing water tables in the two sedimentary environments. Moanatuatua developed in a flood plain distant from the sea with a migrating river system, while Kopouatai developed near the sea. A high degree of natural peat decomposition at Moanatuatua most probably precluded any further rapid decay after recent agricultural drainage.

Keywords: peatification; raised bog; pyrolysis-gas chromatography–mass spectrometry; petrography; fungal hyphae; lignin; tannin; restionaceae; *Empodisma*; *Sporadanthus*; paleoenvironment

1. Introduction

Ombrotrophic restiad bogs of northern New Zealand are ecological equivalents of raised bogs in the boreal zone. Their development, however, is associated with a different peat-forming plant community. The plant sustaining waterlogged conditions in New Zealand bogs is not *Sphagnum* moss but a herbaceous plant, *Empodisma minus*, which is a member of the Restionaceae (restiad) family. *E. minus* develops masses of roots covered with fine root-hairs, which grow vertically up towards the bog surface. Peat accumulation has been

attributed to the high water-holding capacity and base exchange properties of these roots. Senescent roots of *E. minus* form the main mass of peat; remains of other species are incorporated when protected against degradation in water-saturated root masses (Campbell, 1983; Agnew et al., 1993). In addition, conservative evaporation from the *E. minus* canopy may also partly explain its potential to form peat in an environment with moderate rainfall, high summer temperatures and arid microclimate ('wet desert' conditions, Campbell and Williamson, 1997). However, no complete analogy to boreal ombrotrophic *Sphagnum* bogs exists, as the bogs in New Zealand form in a climate which is moderately humid (rainfall 1100–1300 mm/yr) but warm. The mean annual temperature of 13.5°C and 46 days with frost which were recorded there (Newnham et al., 1995. contrast with the colder climate of the boreal zone where functionally similar raised bogs are forming (e.g., 5°C and 200 frost days in Maine, USA; Hofstetter, 1983).

Of several large restiad bog systems present on the North Island until last century, only one, Kopouatai (Fig. 1), is still essentially intact (Newnham et al., 1995). Other sites, such as Moanatuatua, have been subject to agricultural development and drainage. Such change in hydrologic conditions, besides having a negative effect on natural vegetation, accelerates decomposition by reintroducing aerobic processes of degradation to deeper layers of peat (Hogg et al., 1992).

The above two bogs were studied as examples of a (relatively) pristine and a drained system, respectively. Pyrolysis-GC/MS, petrography and fungal analysis were used to address the question of accumulation of restiad peat in an apparently unfavorable climate. Paleoenvironmental implications of chemical preservation of organic matter were analyzed.

2. Locations and methods

2.1. Locations

Kopouatai bog is an area of about 10,000 ha located on the Hauraki Plain, an old floodplain of the Waikato river, southeast of Auckland (Fig. 1). About 19,000 BP the river course moved northwest, to the Hamilton Lowlands where the other bog sampled, Moanatuatua (Fig. 1), is located. Clayey soil developed on abundant layers of volcaniclastics and prevented free drainage of water, enhancing conditions for deposition of peat in both areas since about 11,000 BP (Campbell, 1983). The Hauraki Plain is elevated only a few meters above the present sea level. The sea-level maximum at ca. 6000 BP resulted in the deposition of a sequence of deltaic and estuarine mud interbedded with peat. The subsequent seaward shift of the shoreline has paralleled accumulation of peat in the northern part of Kopouatai where the samples for this study were taken. During early peat development, there were several centers of peat deposition and a single peat dome was established relatively recently, at about 700 BP (Newnham et al., 1995).

Moanatuatua bog belongs to a system of peatlands situated on the floodplain of the Waikato river. It was once similar in size to Kopouatai but today is reduced to about 120 ha as the result of farmland encroachment. Moanatuatua developed from around 13,000 BP after the Waikato River started to entrench into its present channel rather than migrating over the floodplain surface.

Vegetation in both Kopouatai and Moanatuatua started as a minerotrophic system but during peat accumulation groundwater influence decreased and the systems became nutrient poor and dominated by restiads (*E. minus* and *Sporadanthus traversii*). *E. minus* has physical characteristics directly related to its peat-forming nature, as already described. *S. traversii* does not have these same characteristics nor does it act in a water-conserving fashion. It forms stems up to 2 m high and has a system of interlocking rhizomes without the fine root

hair of *Empodisma*. Aerenchymal tissue allows *S. traversii* to survive waterlogged conditions (Agnew et al., 1993). Apart from restiads, several other species occur, including *Sphagnum* mosses.

Recent anthropogenic disturbance has created a different hydrologic setting. Kopouatai is still relatively undisturbed with little active drainage at its margins. However, Moanatuatua is now only a fragment of the original bog and has deep drains on all its margins. At present, groundwater level at Kopouatai is 0–12 cm below the peat surface. At Moanatuatua, it is 20–40 cm deep in the center of the bog, and ca. 80 cm deep adjacent to the ditch (Fig. 2).

2.2. Sampling

Cores of approximately 8 m length were extracted with a 6-cm diameter D-barrel (Russian) corer from central sites in both the Kopouatai and Moanatuatua bogs. An additional core of 1 m length was taken near a drain at the edge of Moanatuatua reserve, where peat has dried due to the drop of groundwater level. Visual characterization of macroscopic humification was made after collecting the cores and subsamples from layers of distinct characteristics were taken for more detailed study.

2.3. Petrography

Petrographic preparation involved cutting blocks of peat about 3 X 5 X 3 cm from the cores. These blocks were freeze-dried, impregnated with resin and then polished for reflected light observation. This procedure is described in detail by Esterle et al. (1991). Location and depth of samples is shown in Table 1.

Petrographic characterization followed the procedure of Moore (1990). Point counts on polished surfaces perpendicular to bedding were made to quantify peat components. Observations were made in white light and air. The following classes of components (identified according to their reflectance and preservation of cell structures) were counted: (a) well-preserved plant parts—red to yellow color; (b) other well-preserved plant parts—gray color; (c) poorly preserved plant parts (gray color); (d) white plant parts; (e) gray particulate matrix; (f) amorphous matrix; (g) white particulate matrix. The red to yellow color (of birefringence) of some well-preserved plant parts indicated good preservation of polysaccharides (Stout and Spackman, 1989) while more degraded plant parts were gray. White particulate matter and plant parts are the result of fungal oxidation (Moore et al., 1996. or charring (Jones et al., 1991).

2.4. Fungal analysis

Samples for fungal analysis were taken from similar depths in the core to those for petrography. Location and depth of samples is indicated in Table 2. Samples were prepared following modified procedures of Miller et al. (1994. One gram dry weight samples were wetted and dispersed in 10 ml of a 5% Calgon solution. This mixture was centrifuged, the resultant pellet was resuspended in a known volume and replicate 1 ml aliquots of the mixed suspension placed on a microscope slide and covered with a cover slip. The preparation were observed at X10 to X400 using transmitted light microscopy. Numbers of fungal structures encountered during three transects left edge to right edge across the cover slip were tabulated. In addition, lengths of individual hyphal fragments were estimated and totalled for each transect.

2.5. Pyrolysis-gas chromatography–mass spectrometry

Samples were taken of the fine peat mass composed mainly of *E. minus* (called matrix in subsequent text) and macrofossils of *S. traversii* and *E. minus*. All samples of the peat mass were pulverized before pyrolysis. Sample depths are indicated in Fig. 2.

All analyses were performed with a CDS120 Pyroprobe attached to a HP5890 GC connected to a quadrupole HP5970B Mass Selective Detector. The sample in a quartz glass tube was inserted into a quartz glass liner directly above the entrance of chromatographic column. Analysis conditions were as follows: the injector temperature was kept at 275°C; temperature of pyrolysis was 612°C; pyrolysis products were swept onto a column by a flow of helium; an HP-1 chromatographic column (50 m, 0.2 mm i.d., 0.33 μm film thickness) was used; temperature program was from 40 to 300°C, rate 5°C/min; interface to MS temperature was 300°C; eluting compounds were ionized at 70 eV electron impact voltage; scan range was from 50 to 500 Da (30 to 480 Da for sub-fossil *E. minus*); scan frequency was 0.86 scans/s.

GC/MS data were processed with HP software. Compounds were identified with help of an HP on-line library of mass spectra and a compilation of publications on lignin and carbohydrates pyrolysis (Boon et al., 1987; Pouwels et al., 1987, 1989; van Smeerdijk and Boon, 1987; Ralph and Hatfield, 1991; van der Hage et al., 1993). To diminish coelution problems all quantitations were performed on summed areas of base ion peaks (Table 3), mathematically corrected using appropriate MS response factors.

3. Results

3.1. Petrography

Macroscopic humification differed between the two sites. At Moanatuatua, peat is more degraded than at Kopouatai, as seen in Fig. 2. The majority of Moanatuatua peat, below about 1 m depth, is sapric whereas at Kopouatai sapric peat is only common towards the lowermost part of the core. The state of physical degradation of plant tissues was quantified by petrographic point counting (Table 1). Moanatuatua samples contain higher proportions of plant parts than do those from Kopouatai, except at the drainage ditch site at Moanatuatua, which is similar to Kopouatai. Low amounts of white (oxidized) material is present in all three cores, although they are generally higher at Moanatuatua than Kopouatai.

3.2. Fungal analysis

The collected data included frequency of hyphae, average hyphal length, total hyphal length and frequency of spores (Table 2). Frequency of hyphae and total hyphal length give an indication of the amount of fungal activity, total hyphal length being the best estimate. Average hyphal length shows the amount of breakage of hyphae occurring. In all samples excepting the lowermost, the amount of fungal activity in the central Moanatuatua core (more total hyphae) appears to have been greater than that at Kopouatai (less total hyphae). Fungal activity is lower near the drain at Moanatuatua (less total hyphae) than in the center (more total hyphae). Breakage of hyphae produces progressively smaller hyphal lengths down the peat columns, apart from the bottom of Kopouatai.

3.3. Analytical pyrolysis

Analytical pyrolysis of specimens of fresh and sub-fossil *E. minus* and *S. traversii* and of peat matrix provided information on their diagenetic trends. Identified peaks represent major types of plant organics, i.e., cellulose and hemicellulose, lignin, non-lignin polyphenols and lipid-derived aliphatic hydrocarbons. The latter class will not be discussed further. The identified and quantified compounds are listed in Table 3 (their numbers correspond to those used in Figs. 3–8).

3.3.1. Fresh tissues

Pyrolyzates of the fresh *S. traversii* (Fig. 3A) and *E. minus* (Fig. 3B) were similar, with variation most probably due to differences between plant parts or organs. In particular, the composition of *E. minus* secondary, hairy rootlets (Fig. 3C) was distinct from central parts of roots (*E. minus*) and stem (*S. traversii*). In the case of the root and stem axes, two most notable compounds were 4-vinylphenol (**29**) and 2-methoxy-4- vinylphenol (**36**) produced by pyrolytic decarboxylation of coumaric and ferulic acids (van der Hage et al., 1993). 4-Hydroxybenzoic (**52a**) and vanillic (**57**) acids also occurred. Relatively abundant were phenol (**13**), 1,2-dihydroxybenzene or catechol (**25**) and 4-vinyl-1,2-dihydroxybenzene (**48**) (Figs. 3 and 4). In addition, several phenols (**17, 18, 23**), 2-methoxyphenols (**19, 44**, sporadically **50**), dihydroxybenzenes (**34, 43**) and 2,6-dimethoxyphenols (**39, 58, 63**) occurred in considerable quantities (Figs. 3 and 4). Other phenolic compounds listed in Table 3 were present in pyrolyzates in subordinate amounts. Lignin-derived sinapyl or coniferyl alcohols were not detected. In all but one sample, the 2,6-dimethoxy (syringyl) prevailed over 2-methoxy (guaiacyl) units (a, b in Table 4). The hydroxyphenyl units, indicated by 4-propenylphenol (*trans*) (**37**) accounted for a few percent of total lignin.

The composition and relative contribution of polysaccharide-derived pyrolysis products showed no regular differences between the two restiad species. Anhydroglucose (51) was always the dominant product present (Figs. 3 and 5), indicating a high cellulose content (Pouwels et al., 1989). Important pyrolysis products of other polysaccharides included 4-hydroxy-5,6-dihydro(2*H*)-pyran-2-one (**14**)—a xylose marker (Pouwels et al., 1987), anhydroxylose (**30**), an unidentified anhydropentose (**22**) and an anhydrohexose, possibly anhydrogalactose (**42**). The sample of *E. minus* root hairs showed a very high yield of polysaccharide products (Fig. 3C; j in Table 4), most notably a high content of anhydrogalactosan (**42**), equal to that of anhydroglucose (Fig. 5A). The same sample showed a relatively small contribution of phenolics, of which 2-methoxy-4-vinylphenol (**36**) was the most important, with secondary amounts of compounds **13, 17, 18, 19, 25, 29** (Fig. 3C). The scan range (above 50 Da) used in these analyses did not permit detection of a number of low molecular weight polysaccharide products. Therefore, the ratio of polysaccharide in the total pyrolyzate is significantly underestimated. The above data are in agreement with other monocotyledon pyrolyzates (e.g., Ralph and Hatfield, 1991; Kuder and Kruge, 1997; van Bergen et al., 1997a).

3.3.2. Decomposed tissues, changes associated with fresh to sub-fossil transition

The same compounds found in the pyrolyzates of the extant plants were detected in pyrolyzates of peat (Fig. 6). Pyrolyzates of peat matrix and several macrofossils became significantly enriched in aliphatic hydrocarbons derived from plant cuticles. Notable changes occurred in distribution of individual phenolic compounds. Several compounds which dominated the pyrolyzates of extant plants became depleted (Fig. 7). This applies to 2-methoxyphenol (**19**), 4-vinylphenol (**29**), 2-methoxy-4-vinylphenol (**36**), 2,6-dimethoxyphenol (**39**), 2-methoxy-4-formylphenol (**44**) and 4-vinyl-1,2-dihydroxybenzene

(**48**). Diagenesis and biodegradation of monocotyledon tissues have only been studied by few authors (van Bergen, 1994; van Bergen et al., 1994, 1995, 1997a; Kuder and Kruge, 1997). Early post-mortem changes have been described by Karunen and Kalviainen (1988. and Camarero et al. (1994). Our findings showing depletion of 4-vinylphenol and 2-methoxy-4-vinylphenol are in agreement with the previous studies.

Striking changes in oxygen functionality of the alkyl side-chain of methoxyphenols included a sharp increase of Cα ketones, 2-methoxy-4-acetylphenol (**52**) and 2,6-di-methoxy-4-acetylphenol (**64**) (c, d in Table 4), whereas methoxyphenol-Cα-aldehydes (**44, 61**) and Cβ-ketones (**55, 65**) did not show such enrichment or were preferentially lost (**44**). Reduction of length of the C_3 side-chains (e.g., **50** and **63** vs. **19** and **39**) could be seen (e, f in Table 4). An overall increase of (alkyl)dihydroxybenzenes (**25, 31, 34, 43**), (alkyl)benzenes (**2, 6–9**) and (alkyl)phenols (**13, 17, 18, 21, 23**) was observed in peat matrix (g–i in Table 4). Changes in alkyl side-chains in lignin fraction pyrolyzates (increase of Cα carbonyl and reduction of length. have also been reported for monocot seeds (van Bergen et al., 1997a) and for hardwoods and softwoods (Terron et al., 1995; van der Heijden and Boon, 1994; Saiz-Jimenez and de Leeuw, 1984; Mulder et al., 1991). Degradation of β-O-4 linked lignin by fungi is associated with formation of Cα carbonyl groups on alkyl side chains. It can be caused by enzymatic oxidation, intermediate to depolymerization (Tuor et al., 1995), followed by Cα–Cβ or Cβ–Cχ cleavage and carboxylation of the remaining fragment of the alkyl chain or can be a process competing with depolymerization (Chen and Chang, 1985). The concentration of methoxyphenols with C a carbonyl and carboxyl functionality may be expected to increase in degraded material. Carboxyl groups are lost during pyrolysis and only trace amounts of vanillic acid have been detected in most samples. However, by quantification of Cα ketones instead, an alternative measure of lignin degradation should be possible. Similarly, the cleavage of the side chains and depolymerization will result in a correlated decrease in the yield of moieties with propenyl side chains.

The guaiacyl to syringyl ratio in the peat matrix is higher than in fresh restiads (Fig. 9B), but guaiacyl units tend to be much more oxidized and to have shortened side chains (some macrofossils showed opposite trend; a, b in Table 4). This seems to contradict findings from other studies (Stout et al., 1988; van der Heijden and Boon, 1994) which showed that syringyl is degraded preferentially. The preferential loss of syringyl was also noted in samples of wood from Kopouatai peat (Kuder, unpublished). Further work is necessary to investigate this finding.

Pyrolyzates of individual restiad macrofossils had highly variable polysaccharide contents. The dominant compound was anhydroglucose (levoglucosan, **51**). Other anhydrosugars (**30, 42, 47**) and 4-hydroxy-5,6-dihydro(2*H*)-pyran-2-one (**14**) occurred in significantly smaller quantities. In some macrofossils furan derivatives were abundant (**3, 5, 10, 12, 28, 59**). A trend of decreasing polysaccharide abundance with depth in peat matrix was observed (j in Table 4). Due to the fact that the significant part of low m/z peaks of polysaccharide-derived products was missed by the scan range employed, the finding is not fully supported, although greater underestimation of polysaccharide content is expected in the younger samples, because of the dominance of anhydroglucose in degraded tissues (Stout et al., 1988; van Bergen, 1994; Stankiewicz et al., 1997; Kuder and Kruge, 1997). Xylose markers (**14, 30**) and anhydropentosan (**22**) are depleted in relation to anhydroglucose in all fossil samples (Fig. 5) (cf. Stout et al., 1988; van der Heijden and Boon, 1994). Anhydromannose (**47**) is significantly more abundant in the peat matrix and in several of the macrofossils than in fresh tissues (Fig. 5). Its presence in fungal hyphae (de Leeuw and Largeau, 1993) suggests this mode of enrichment, but in the peat matrix, it may also be derived from Sphagnum (van der Heijden, 1994). The lowermost interval of the Moanatuatua bog (Fig. 8) was characterized by an exceptional increase in the relative abundance of furans

(low weight polysaccharide derivatives, attributable to degradation, particularly **3, 5**) and by a strong decrease of the relative polysaccharide contribution in the pyrolyzate. In the same sample, extensive loss of methoxy and hydroxy groups from phenolic moieties was observed. A similar shift to a relatively high furan content was found by van der Heijden (1994) in *Sphagnum* from an Eemian interglacial deposit (70 ka BP). The location of our sample at the base of peat deposit could explain this finding, in that the input of mineralized and oxygenated groundwater may have overcome anoxia and facilitated efficient aerobic degradation.

3.3.3. Differences between the two bogs

For comparison of the two sites, peat matrix data were used. Change with depth of the chemical composition of the matrix (masses of fine *E. minus* fragments) was more regular than change with depth in the macrofossil samples (Table 4). This was expected given that matrix samples, as natural mixtures, yielded data averaged over a large number of individual plant fragments. The samples from Moanatuatua were more degraded that these from Kopouatai. In the case of phenolics, this was expressed as more C a oxidation (Fig. 9A) and more depletion of moieties with propenyl side-chains (e, f in Table 4). The ratio of guaiacol to syringol was lower at Moanatuatua (Fig. 9B). Generally, more xylose and galactose markers were seen in pyrolyzates of Kopouatai peats (k, l in Table 4).

4. Discussion

4.1. Sources of phenolic compounds in pyrolyzates

Monocotyledons differ from woody angiosperms in that they possess a high content of free and bound phenolics in addition to β-O-4 lignin (Lewis and Yamamoto, 1990.. By lignin, we mean a polymer with dominant β-O-4 cross-linking, according to the definitions based on structural studies (Boudet et al., 1995). Dual source of some phenolic compounds in pyrolyzates, from lignin and non-lignin materials may be therefore expected. Individual compounds in the pyrolyzates were attributed to non-lignin sources following precedents in the literature, when the interpretation was unequivocal (e.g., 4-vinylphenol, formed from coumaric acid. or when accounting for the abundance and diagenetic behavior of the compound. For example phenol is normally present in small amount in lignin or wood pyrolyzates, but becomes abundant in pyrolyzates of plant tissues rich in hydroxybenzoic acid. Several of the compounds discussed (**19, 36, 39, 44, 52, 61**) are common components of lignin pyrolyzates, but in the present situation, they were anomalously abundant and an additional source besides lignin was likely. Non-lignin phenolics are more readily depleted in the early stage of diagenesis (e.g., compounds **13, 29, 36, 48**, Fig. 4 vs. Fig. 7) (cf. Karunen and Kalviainen, 1988; Camarero et al., 1994; van Bergen et al., 1997a; Kuder and Kruge, 1997). The comparison of fresh and sub-fossil samples of the same taxon yields information similar to that obtained by sequential extraction experiments (cf. Galletti et al., 1996; Morrison and Mulder, 1994), from which the compound's source may be identified. Apart from lignin, the main classes present in our samples are monomeric compounds, either free, ester or ether bound to lignin-polysaccharide core and condensed tannins, which are discussed below.

Pyrolytic production of 2-methoxy-4-vinylphenol and 4-vinylphenol from ferulic and coumaric acids is well-known (van der Hage et al., 1993). A similar decarboxylation process may account for the production of 1,2-dihydroxy-4-vinylbenzene (**48**) produced from caffeic acid or its derivative. Caffeic acid has not been reported in pyrolyzates before, but has been otherwise detected in plant tissues (Harborne and Baxter, 1993). It is at best a minor

compound in most monocotyledons. 1,2-Dihydroxy-4-vinylbenzene has not been reported in pyrolyzates of extant species of Gramineae (Ralph and Hatfield, 1991; Morrison and Mulder, 1994; van Bergen et al., 1997a), Musaceae (Graven et al., 1996. and Hydrocharitaceae (van Bergen et al., 1995). It was detected in pyrolyzates of Cyperaceae, but only in trace amounts (Kuder and Kruge, 1997). Caffeic acid has also been reported in Hydrocharitaceae by Dahlgren et al. (1985) but no indication of its abundance was given. High content of this phenolic acid may be specific to Restionaceae. 4-Hydroxybenzoic and vanillic acids have been detected in pyrolyzates, associated with relatively high concentrations of phenol and 2-methoxyphenol. The two latter compounds are probably formed by decarboxylation of these two acids. Phenol in pyrolyzates has been previously interpreted as a phenolic acid product (van Bergen et al., 1994).

Proanthocyanidins (condensed tannins and/or monomeric units. are the most probable sources of catechol (**25**) and possibly also of other alkyl-dihydroxybenzenes present in the pyrolyzates of fresh tissues. Monocotyledons are generally rich in these substances (Dahlgren and Clifford, 1982). Pyrolytic production of catechol from B-ring of catechin, a model for condensed tannin, was confirmed by Galletti and Reeves (1992). A high concentration of catechol has been found in pyrolyzates of some extant monocot (Graven et al., 1996) and dicot (van Bergen et al., 1997b) seeds and in conifer cones (Stankiewicz et al., 1997). B-rings of proanthocyanidins with other side-chains (Harborne and Baxter, 1993) may potentially be a source of phenol, 2-methoxyphenol and 2,6-dimethoxyphenol. However, it is more likely that phenol and 2-methoxyphenol derive from hyroxybenzoic and vanillic acids, as discussed above. 2,6-Dimethoxyphenol has been found in tannin pyrolyzates (Galletti et al., 1995) and monocot pyrolyzates are often rich in this compound (van Bergen, 1994; Kuder and Kruge, 1997). Tricin, a flavonoid with appropriate side-chains on the B-ring, is common in Cyperaceae (Harborne, 1971), the pyrolyzates of which reveal abundant 2,6-dimethoxyphenol (Kuder and Kruge, 1997). Data on the chemistry of flavonoids in the Restionaceae species studied here are unavailable. An alternative source of 2,6-dimethoxyphenol in pyrolyzates could be the syringic acid present in some plants (Harborne and Baxter, 1993).

Other compounds apparently having a non-lignin source are 2-methoxy-4-formylphenol (vanillin) and, in the pyrolyzate of *E. minus* root hairs, 2-methoxy-4-acetylphenol (note its relatively high abundance vs. other guaiacyl lignin markers in Fig. 4C). Both compounds have been isolated from plants (Harborne and Baxter, 1993).

The postulated dual source of catechol (i.e., tannin and biodegraded lignin), did not permit clear conclusions to be drawn on the diagenetic behavior of tannin. It appears that lignin degradation products, not selective preservation of tannin, account for the catechol present in degraded material. This may be concluded from the ratio of catechol to alkylated dihydroxybenzenes (e.g., **34**), which sharply decreases in degraded material (e.g., Fig. 4 vs. Fig. 7).

Lignin pyrolyzates have been extensively discussed by many authors (e.g., Boon et al., 1987; Pouwels et al., 1987; van der Hage et al., 1993). In the present study several lignin pyrolysis products coincide with the non-lignin derived markers, a fact which should be considered when interpreting the results from these or similar samples.

4.2. Ecological implications of chemistry of restiad tissues

An interesting finding from the present study is that the local peat-forming species, *E. minus* and *S. traversii*, contain high proportions of phenolic acids and tannins. The phenolic compounds discussed in the previous section show allelopathic properties (Inderjit, 1996), which may facilitate exclusion of other species and finally lead to development of uniform

communities, waterlogging and initiation of peat deposition. A field study would be necessary to prove this assumption. Such mechanism would provide a good analogy with *Sphagnum*, which is able to decrease competition by acidification of the soil through base exchange and release of toxic organochemicals (Verhoeven and Liefveld, 1997).

Decay resistance is similarly increased by presence of these compounds, both due to inhibition of microbial activity (Given and Dickinson, 1975; Harborne and Baxter, 1993) and by the inherent inertness of lignin and tannin (de Leeuw and Largeau, 1993). This may be significant to the restiad's ability to form peat, particularly given that the climatic conditions on the North Island of New Zealand are not ideal for peat deposition. The high potential for peat formation by Sphagnum is partly attributed to its natural resistance to decay (Clymo, 1983). The allelopathic and decay-resistant chemistry, together with water-holding and ion-exchange properties (Agnew et al., 1993; Campbell and Williamson, 1997) make *E. minus* a close ecological equivalent of *Sphagnum* from the boreal peatlands.

4.3. Paleoenvironmental implication of degradation of organic matter

Chemistry, petrography and fungal analysis all point to Moanatuatua undergoing greater amounts of aerobic decay during its development than Kopouatai. The lignin chemistry showed differences in the oxygen functional groups and the extent of reduction in alkyl chain length at the two sites. The pyrolyzates of samples from Moanatuatua bog generally have higher relative abundances of (di)methoxy-acetylphenols (Fig. 9A), but lesser amounts of phenolic compounds with propenyl side-chains (e, f in Table 4). The different degrees of lignin oxidation at the two sites implies greater aerobic decay at Moanatuatua with lignin at this site more degraded by fungi (Kirk and Farrell, 1987). Supporting this hypothesis are the counts of fungal hyphae (Table 2). At Moanatuatua, more hyphae are generally observed than at Kopouatai, indicating greater fungal activity. Furthermore, field description of the Moanatuatua core shows that most of the peat is sapric, poorly preserved, with more abundant white, oxidized plant remains as compared with the Kopouatai core (Fig. 2; Table 1).

Why has Moanatuatua been subject to greater amounts of aerobic decay than Kopouatai? The answer may lie in the environmental setting of the two bogs. Moanatuatua has developed in a flood plain into which the Waikato River has entrenched during formation of the bog. In such a flood plain, water table levels probably were low and constantly dropping, during bog formation. In contrast, Kopouatai has developed in an area where the water table has probably always been high, controlled by the sea to the north and the Piako river on the eastern margin. Therefore, Moanatuatua peat may have often been subjected to lowered water tables and a deep zone of aerobic decay while at Kopouatai, water table remained higher and the zone of aerobic decay relatively shallow. The extent of lignin oxidation, however, varies even at the same geographic location. An example is the increased degradation which apparently occurred during deposition of peat from the 3–3.5 m interval at Kopouatai (Fig. 9A). This event probably corresponds to dry climatic conditions (700 to 1850 years BP) inferred by Newnham et al. (1995) on the basis of paleobotanic analysis.

The chemical technique applied in this study did not show a significant difference between samples collected from the drained and the pristine part of Moanatuatua bog. Both sub-sites are characterized by a high, relatively similar degree of lignin degradation. In both cases, this degradation is greater than that observed at Kopouatai. Fungal activity (expressed by total hyphal lengths) is actually lower nearer the drainage ditch (Table 2). The methodology applied, however, is biased against counting of fungal remains in coalesced peat—dry peat near the ditch had more clumps of material as opposed to the wetter peat in the center. Petrographically, the drained peat has higher particulate to amorphous matrix ratio

and a slightly lower proportion of plant parts to matrix than in the comparable sample from the central Moanatuatua. This suggests different mechanisms of degradation active at the edge, i.e., a greater prevalence of the physical breakdown of peat to particulate matrix.

It appears that Moanatuatua peat, which was generally subject to high levels of decomposition even before drainage, was depleted in labile organics (i.e., polysaccharides, compare polysaccharide contents in the top Kopouatai and Moanatuatua peat matrix samples; j in Table 4) early in its formation, evidently making it quite resistant to subsequent aerobic decay after drainage. A similar dependence was also noticed by Hogg et al. (1992), being that the effect of drainage on emission of CO_2 from peat (due to microbial decay) was related to the original degree of decomposition of peat. In peats which were already degraded, the lowering of the water table had less influence.

4.4. Structural vs. chemical degradation

In comparing the petrographic and chemical data from the peat samples, it is evident that some structural changes parallel the lignin degradation trends. These include the general humification state (as recorded in the field), the amount of amorphous matrix (Fig. 9C) and the amount of white particulate matter. However, other petrographic trends do not follow the chemical observations, such as the relative proportions of plant parts to matrix. In fact, Moanatuatua tends to have greater proportions of well-preserved plant parts (as compared to Kopouatai) but less well-preserved lignin. Also, plant part preservation (as indicated by cell wall reflectance colors) does not correlate with lignin preservation.

The explanation for the differences between petrographic measurements and lignin degradation results may be that chemical indicators of degradation are not exactly paralleling the physical breakdown of plant material. Evidently, lignin degradation may be associated with formation of white plant material (via fungal oxidation; Moore et al., 1996) and production of amorphous matrix as opposed to particulate matrix (Fig. 9C). The proportion of plant parts to matrix and the level of preservation of plant parts do not appear to be controlled by lignin degradation. At Kopouatai, in fact, the xylosan:glucosan ratio corresponds to plant part preservation suggesting that the process of polysaccharide breakdown may be an important factor in plant part disintegration (k in Table 4 vs. Table 1).

Another aspect that may affect the petrographic composition of peat is differential degradation of tissues, in this particular case hairy rootlets (high hemicellulose content, low polyphenol and lignin content) and thicker axes of roots and stems (cellulose dominating over hemicellulose, high polyphenol and lignin content). The latter, expected to degrade slower, would contribute to the coarse material, whereas fine or amorphous material would be derived from the former. Some support for this assumption is evident from the peat chemistry—at Kopouatai, the ratio of galactosan to glucosan and (except in the center of the core) xylosan to glucosan is higher, suggesting more preservation of rootlets.

5. Conclusions

(1) Chemical characteristics of the tissues of monocotyledons (*E. minus, S. traversii*) resulted in diagenetic pathways distinctly different from those known for angiosperm woods (cf. Stout et al., 1988; van der Heijden and Boon, 1994). Loss of non-lignin phenolic fraction, depolymerization via modification of side chains of β-O-4 lignin and depletion of hemicellulose were observed. Degradation of the basal peats was strongly enhanced by influx of oxygenated groundwater.

(2) Slow decomposition of lignified tissues of restiads and allelopathic properties of their phenolic acids and tannins, together with the xeromorphic adaptations of *E. minus*, may

explain the accumulation of peat in climatically unfavorable sites on North Island, New Zealand.

(3) Chemistry, petrography and fungal analysis indicate that Moanatuatua peat has undergone substantially more aerobic decay than Kopouatai. This is thought to result from their differing sedimentary environments.

(4) Drainage of peat does not necessarily result in a distinct increase in peat decay. At Moanatuatua, high degrees of peat degradation before the agricultural development can partly explain this finding.

(5) Petrographic and chemical indicators of decay do not necessarily parallel one another. Polysaccharide decay may be linked with physical breakdown of plants material and lignin decay with production of amorphous plant material.

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Table 1. Petrographic pointcounts of Kopouatai and Moanatuatua peats.
[a]Edge of the Moanatuatua reserve. Results recalculated to %.

Sampling site	Kopouatai				Moanatuatua				
depth (m)	1.40	2.93	5.35	6.30	0	1.25	4.00	7.00	0.20[a]
Plant parts (%)									
well-preserved — red	21.1	12.0	13.2	31.9	22.7	19.4	1.0	9.9	29.5
well-preserved — gray	7.5	0.0	1.7	3.0	22.1	3.6	0.0	19.7	4.2
poorly-preserved — gray	31.5	25.6	19.8	17.4	24.1	24.5	45.9	31.7	18.9
oxidized — white	0.8	5.3	0.0	0.0	0.7	7.9	1.0	2.8	3.2
total plant parts	60.9	42.9	34.7	52.3	69.6	55.4	47.9	64.1	55.8
Matrix (%)									
particulate — gray	12.0	20.3	20.6	34.9	7.6	10.8	11.5	7.0	15.8
particulate — white	3.0	0.8	1.7	3.0	2.8	0.7	2.1	0.0	0.0
amorphous	24.1	36.0	43.0	9.8	20.0	33.1	38.5	28.9	28.4
total matrix	39.1	57.1	65.3	47.7	30.4	44.6	52.1	35.9	44.2

Table 2. Fungal analysis results.

Sampling site	Depth (m)	Frequency of hyphae (no./g)	Average hyphal length (μm)	Total hyphal length (mm)/g dry wt.	No. spores/g dry wt.
Kopouatai	0.0–0.15	46	181	27.82	46,667
	0.15–0.5	51	150	25.45	30,000
	1.0–1.5	128	73	26.70	62,857
	4.0–4.5	150	35	21.15	12,000
	6.0–6.5	66	82	15.53	42,857
Moanatuatua edge	0.0–0.1	113	78	22.41	0
	0.1–0.5	106	62	26.46	4000
	0.75–1.0	56	74	11.79	25,714
Moanatuatua centre	0.0–0.5	97	226	62.53	148,571
	0.5–1.0	73	139	28.97	25,714
	3.5–4.0	126	91	38.43	46,667
	7.5–8.0	102	45	11.35	37,500

Table 3. Key list of compounds identified in pyrolyzates. Numbers as in Figs. 3–8.

No.	Base m/z	M^+	Compound name
1	60	60	acetic acid
2	91	92	toluene
3	84	84	2(*H*)-furan-3-one
4	82	82	2,4-pentadienal
5	96	96	2-furaldehyde
6	91	106	ethylbenzene
7	91	106	1,3 + 1,4-dimethylbenzene
8	104	104	styrene
9	91	106	1,2-dimethylbenzene
10	98	98	5-methyl-2-(3*H*)-furanone
11	55	96	methyl-cyclopentenone
12	110	110	5-methyl-2-furaldehyde
13	94	94	phenol
14	114	114	4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one
15	112	112	3-hydroxy-2-methyl-2-cyclopentene-1-one
16	112	112	2-hydroxy-3-methyl-2-cyclopentene-1-one
17	108	108	2-methylphenol
18	107	108	4-methylphenol + 3-methylphenol
19	109	124	2-methoxyphenol (guaiacol)
20	126	126	2-methyl-3-hydroxy-(4*H*)-pyran-4-one
21	107	122	dimethylphenol
22	57	–	pentosan anhydrosugar
23	107	122	4-ethylphenol
24	142	142	2,5-dihydroxy-2-methyl-4*H*-pyran-4-one
25	110	110	1,2-dihydroxybenzene (catechol)
26	69	144	anhydro-α-glucopyranose
27	123	138	2-methoxy-4-methylphenol
28	97	126	5-hydroxymethyl-2-furaldehyde
29	120	120	4-vinylphenol
30	57	132	anhydroxylose
31	124	124	1,2-dihydroxy-3-methylbenzene
32	140	140	3-methoxy-1,2-dihydroxybenzene
33	144	144	1,4-dideoxy-D-glycero-hex-1-enopyranos-3-ulose
34	124	124	1,2-dihydroxy-4-methylbenzene
35	137	152	2-methoxy-4-ethylphenol
36	150	150	2-methoxy-4-vinylphenol
37	134	134	4-propenylphenol (*trans*)
38	122	122	4-formylphenol
39	154	154	2,6-dimethoxyphenol (syringol)
40	164	164	2-methoxy-4-(prop-1-enyl)phenol
41	154	154	2-methoxy-6-hydroxy-4-methylphenol
42	60	162	hexosan (anhydrogalactose?)
43	123	138	1,2-dihydroxy-4-ethylbenzene
44	152	152	2-methoxy-4-formylphenol (vanillin)
45	164	164	2-methoxy-4-(prop-2-enyl)phenol (*cis*)
46	121	136	4-acetylphenol
47	60	162	hexosan (anhydromannose?)
48	136	136	1,2-dihydroxy-4-vinylbenzene
49	168	168	2,6-dimethoxy-4-methylphenol
50	164	164	2-methoxy-4-(prop-2-enyl)phenol (*trans*)
51	60	162	anhydroglucose (levoglucosan)
52	151	166	2-methoxy-4-acetylphenol
52a	121	138	4-carboxyphenol
53	166	166	2-methoxy-6-hydroxy-4-vinylphenol
54	164	164	unknown
55	137	180	2-methoxy-4-(propane-2-one)phenol
56	167	182	2,6-dimethoxy-4-ethylphenol
57	168	168	2-methoxy-4-carboxyphenol (vanillic acid)
58	180	180	2,6-dimethoxy-4-vinylphenol
59	73	162	1,6-anhydro-β-D-glucofuranose
60	194	194	2,6-dimethoxy-4-(prop-1-enyl)phenol
61	182	182	2,6-dimethoxy-4-formylphenol
62	194	194	2,6-dimethoxy-4-(prop-2-enyl)phenol (*cis*)
63	194	194	2,6-dimethoxy-4-(prop-2-enyl)phenol (*trans*)
64	181	196	2,6-dimethoxy-4-acetylphenol
65	167	210	2,6-dimethoxy-4-(propane-2-one)phenol

Table 4. Pyrolysis products of Recent species, sub-fossil plant remains and bulk peat. Local angiosperm wood (Myrtaceae family) given for comparison. Ratios calculated from summed integrated areas of base ion peaks arithmetically converted to total compounds.
[a] Sample from the drained edge of a bog; G—guaiacyl; S—syringyl; P—(alkyl)phenol except vinylphenol; D—(alkyl)dihydroxybenzenes; B—alkylbenzenes; (1) calculated on G- and S-propenes to avoid non-lignin signal; (2) calculated on all methoxylated compounds except G- and S-vinyl; aromatics include G,S,B,P,D.

Sample	*E. minus* root axis	*E. minus* root hair	*S. traversii* stem	Wood	Sub-fossil *E. minus*				Sub-fossil *S. traversii*			
					Kopouatai		Moanatuatua		Kopouatai		Moanatuatua	
depth (m)	modern	modern	modern	modern	3–3.5	5–5.5	0–0.5	4.5–5	3–3.5	5–5.5	0–0.5	4.5–5
(a) G/S (1)	0.66	0.79	0.27	0.35	0.27	2.63	0.25	6.64	0.56	0.62	0.12	2.62
(b) G/S (2)	n.a.	n.a.	n.a.	0.28	1.23	2.46	0.84	5.28	0.89	0.98	0.72	3.62
(c) G–CO–C/G–C=C–C(*t*)	0.17	1.70	0.29	0.29	2.69	0.38	0.79	0.30	1.07	0.81	2.73	0.62
(d) S–CO–C/S–C=C–C(*t*)	0.18	0.90	0.28	0.59	0.64	0.78	0.48	0.66	0.63	0.55	0.61	0.57
(e) G–H/G–C=C–C(*t*)	2.06	2.82	1.95	0.78	7.91	1.34	3.92	0.49	1.54	1.31	5.39	0.75
(f) S–H/S–C=C–C(*t*)	1.75	1.09	1.50	0.88	1.11	1.01	0.95	0.39	0.96	0.78	0.73	0.63
(g) B/(S+G)total	0.15	0.45	0.06	0.03	1.79	0.11	0.14	0.04	0.06	0.12	0.25	0.09
(h) P/(S+G)total	0.61	1.00	0.22	0.08	18.73	0.40	0.43	0.23	0.35	0.56	0.79	0.75
(i) D/(S+G)total	0.99	1.31	0.54	0.37	3.78	2.13	0.84	0.66	0.73	0.87	1.43	1.18
(j) polysacch./aromatic	0.67	4.26	0.55	0.82	1.87	0.46	1.35	1.26	0.26	0.23	3.97	1.19
(k) xylose/glucose	0.37	0.67	0.86	0.17	0.19	0.06	0.41	0.18	0.09	0.14	0.21	0.14
(l) galactose/glucose	0.01	1.07	0.11	0.34	0.47	0.15	0.16	0.02	0.05	0.12	0.08	0.01

Sample	Peat matrix									
	Kopouatai				Moanatuatua					
depth (m)	1–1.5	3–3.5	5–5.1	5.2–5.5	6–6.5	0–0.5	1.5–2	4.5–5	7.5–8	0–0.1[a]
(a) G/S (1)	0.94	1.17	1.01	1.23	1.19	0.76	0.53	0.47	0.53	0.76
(b) G/S (2)	1.37	1.61	1.40	1.45	1.54	1.19	1.30	0.96	1.09	0.99
(c) G–CO–C/G–C=C–C(*t*)	0.58	1.51	0.93	0.61	0.66	2.55	4.06	1.85	3.75	2.30
(d) S–CO–C/S–C=C–C(*t*)	0.63	1.43	0.95	0.85	0.85	2.67	2.25	1.21	4.37	2.67
(e) G–H/G–C=C–C(*t*)	1.11	1.34	1.34	0.97	1.05	2.57	3.35	2.10	9.59	2.14
(f) S–H/S–C=C–C(*t*)	0.66	0.76	0.65	0.63	0.61	0.95	0.89	0.69	1.99	1.12
(g) B/(S+G)total	1.11	0.55	0.70	0.52	0.53	0.69	1.07	0.65	3.95	0.66
(h) P/(S+G)total	1.99	1.16	1.41	1.25	1.20	1.41	2.01	1.59	5.43	1.34
(i) D/(S+G)total	1.91	1.56	1.63	1.89	1.42	1.49	1.87	1.75	0.17	1.47
(j) polysacch./aromatics	1.14	0.88	0.38	0.44	0.36	0.63	0.70	0.39	0.32	0.87
(k) xylose/glucose	0.32	0.08	0.18	0.15	0.45	0.15	0.15	0.10	0.24	0.16
(l) galactose/glucose	0.76	0.06	0.16	0.11	0.23	0.08	0.08	0.07	0.00	0.12

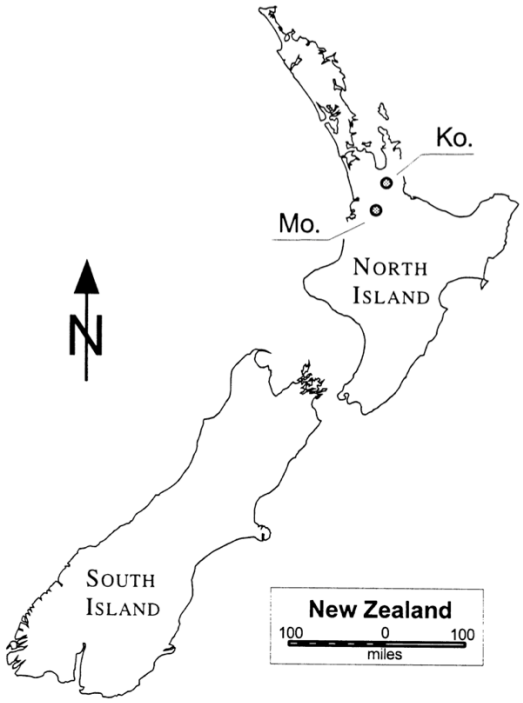

Fig. 1. Location of the sampling sites: Kopouatai (Ko) and Moanatuatua (Mo) mires.

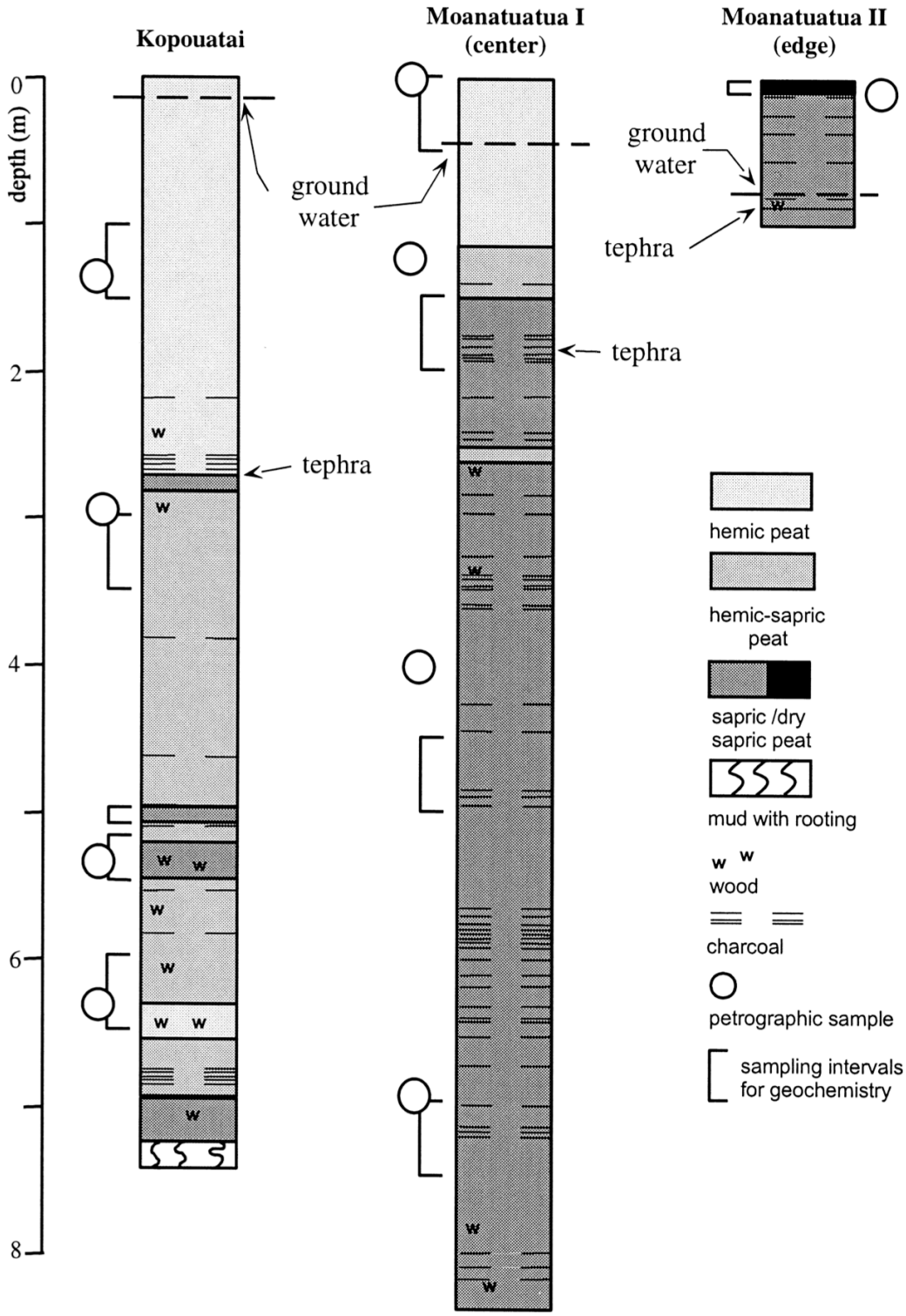

Fig. 2. Stratigraphic profiles of Kopouatai and Moanatuatua mires.

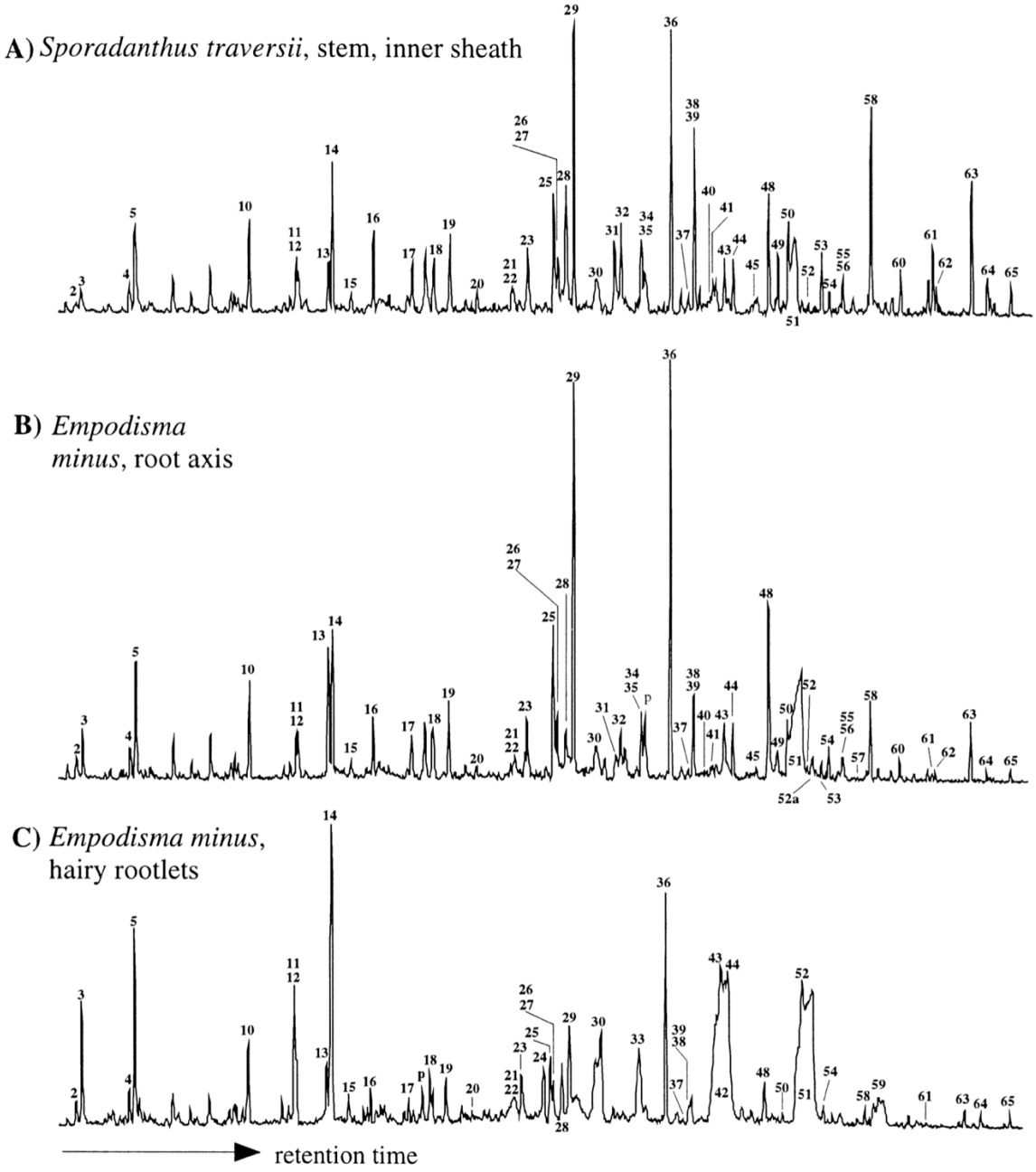

Fig. 3. Total ion current traces of pyrolysis products of extant restiads. (A) *S. traversii*, stem, inner sheath; (B) *E. minus*, root axis; (C) *E. minus*, root hairs. P—alkylphenol. Peak numbers as in Table 3.

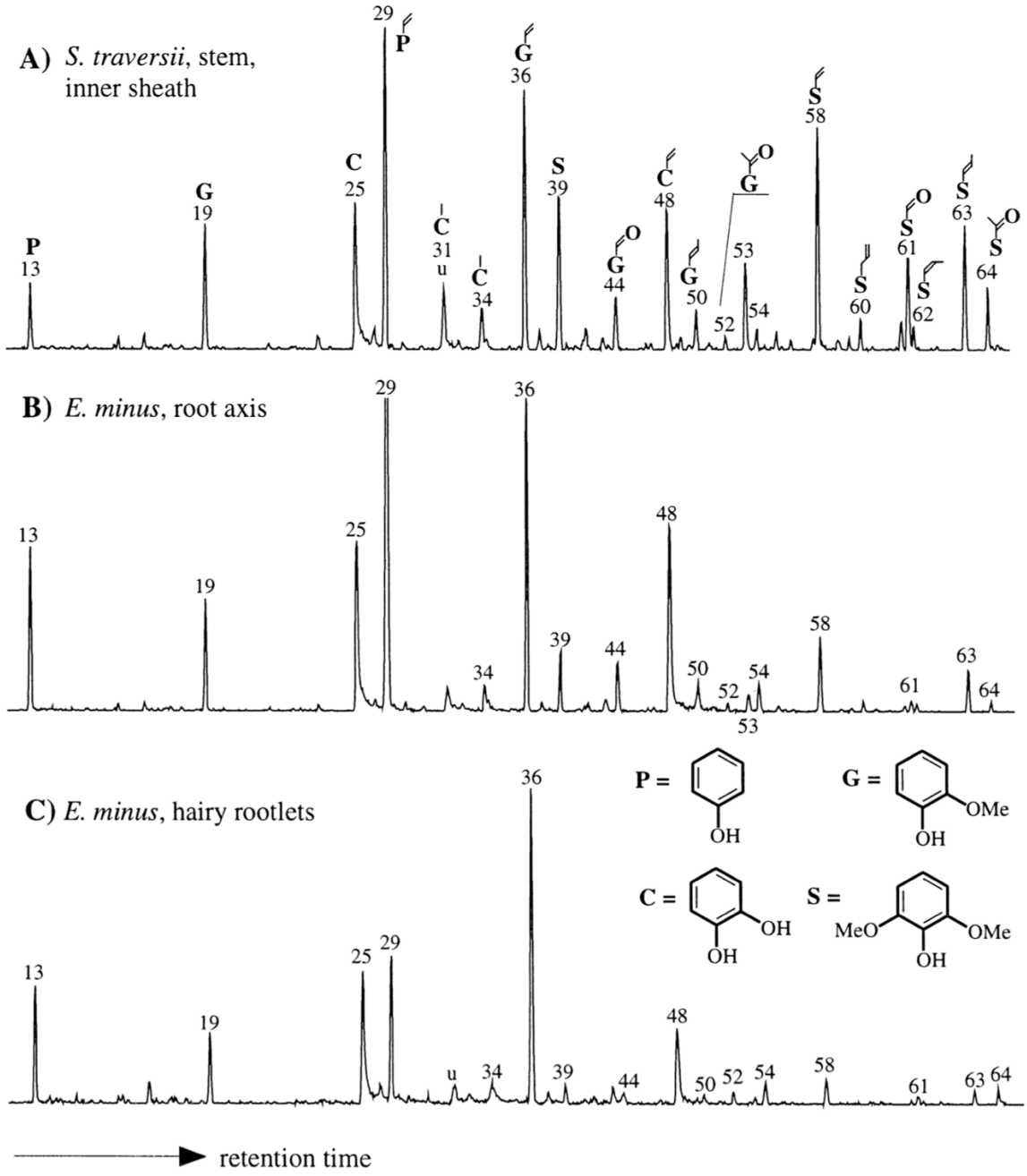

Fig. 4. Summed ion chromatograms of key phenolic compounds (m/z = 94+109+110+120+ 124+136+150+151+154+164+166+180+181+182+194) from the pyrolysis products of (A) extant *S. traversii*, stem, inner sheath; (B) extant *E. minus*, root axis; (C) extant *E. minus*, root hairs. U—unknown compound. Peak numbers as in Table 3.

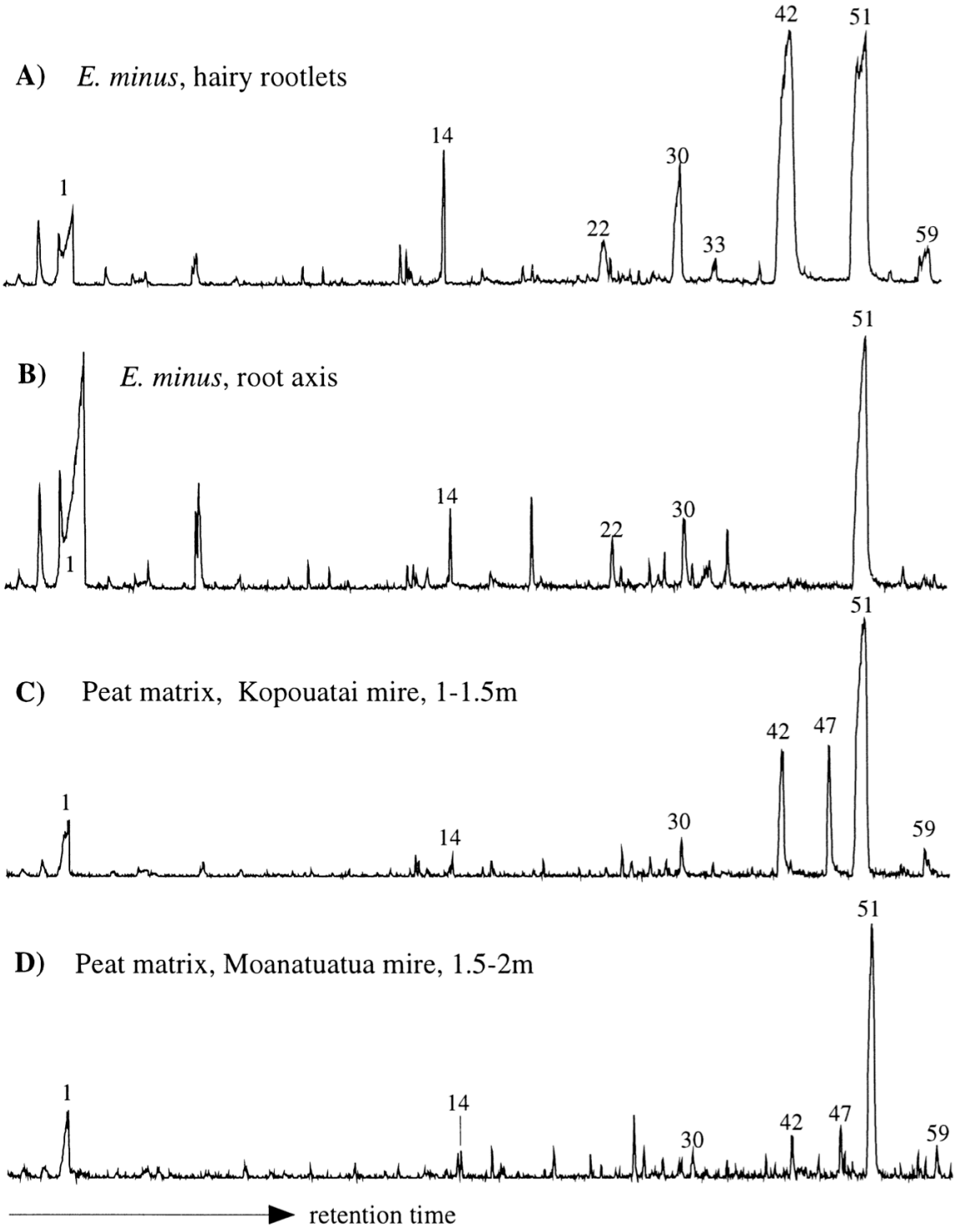

Fig. 5. Summed ion chromatograms of key polysaccharides (m/z = 57+60+73) from the pyrolysis products of (A) *E. minu*s, root hairs; (B) *E. minus*, root axis; (C) peat matrix Kopouatai mire, 1–1.5 m; (D) peat matrix Moanatuatua mire, 1.5–2 m. Peak numbers as in Table 3.

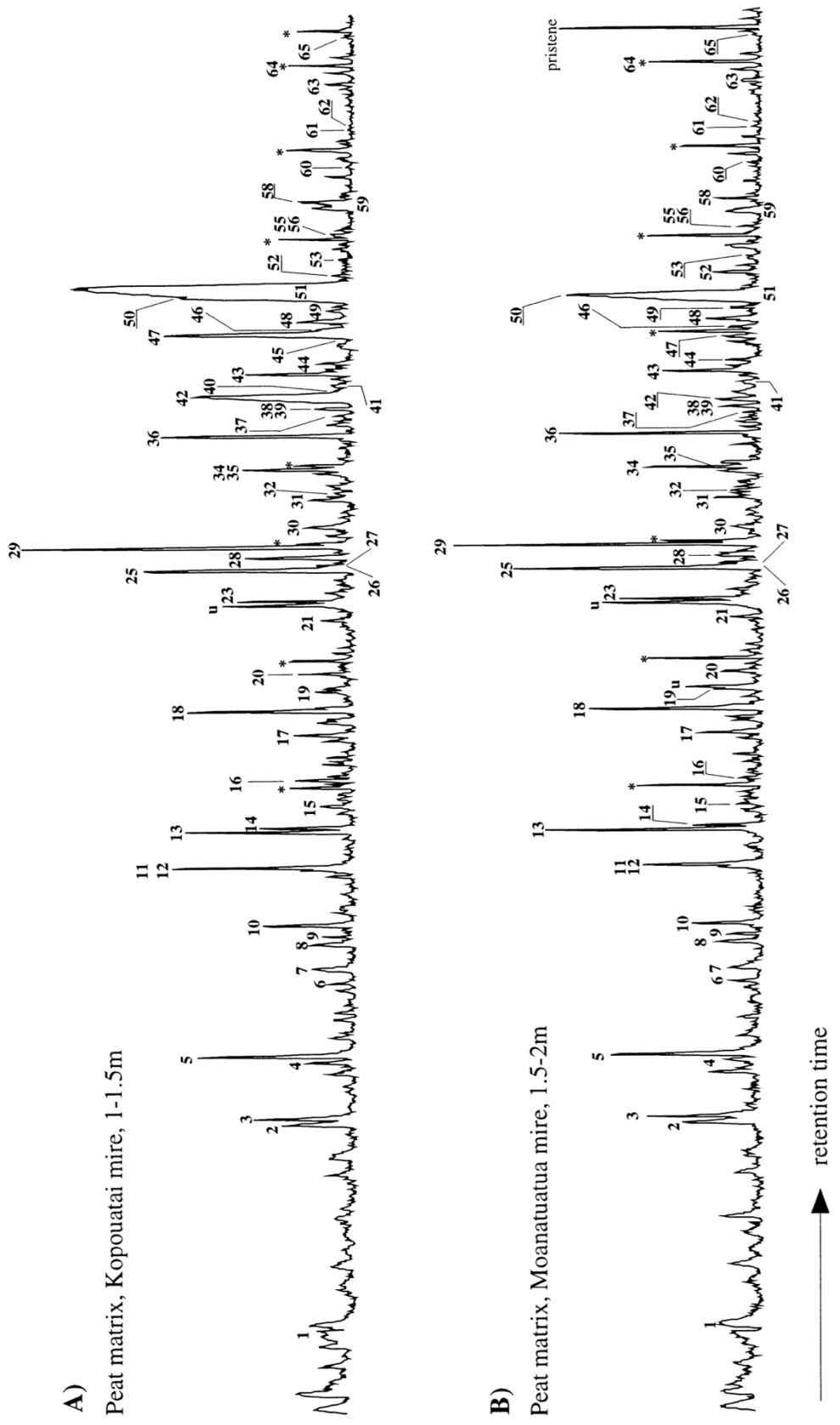

Fig. 6. Total ion current traces of pyrolysis products of bulk peat. (A) Kopouatai mire, 1–1.5 m; (B) Moanatuatua mire, 1.5–2 m. U—Unknown compound; *—aliphatic hydrocarbon. Peak numbers as in Table 3.

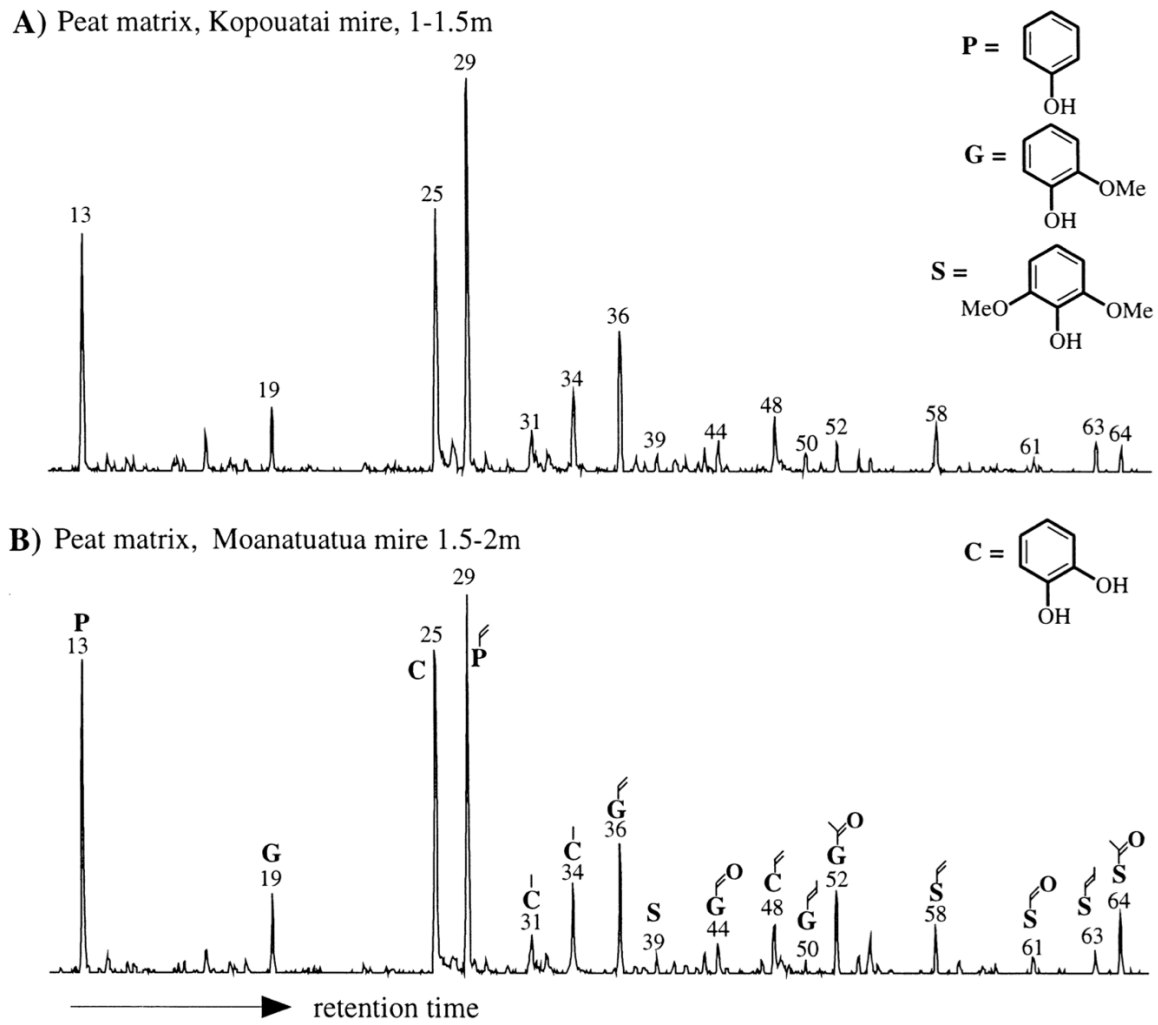

Fig. 7. Summed ion chromatograms of key phenolic compounds (m/z = 94+109+110+120+ 124+136+ 150+151+154+164+166+180+181+182+194) from the pyrolysis products of (A) bulk peat, Kopouatai mire, 1–1.5 m; (B) bulk peat, Moanatuatua mire, 1.5–2 m. Peak numbers as in Table 3.

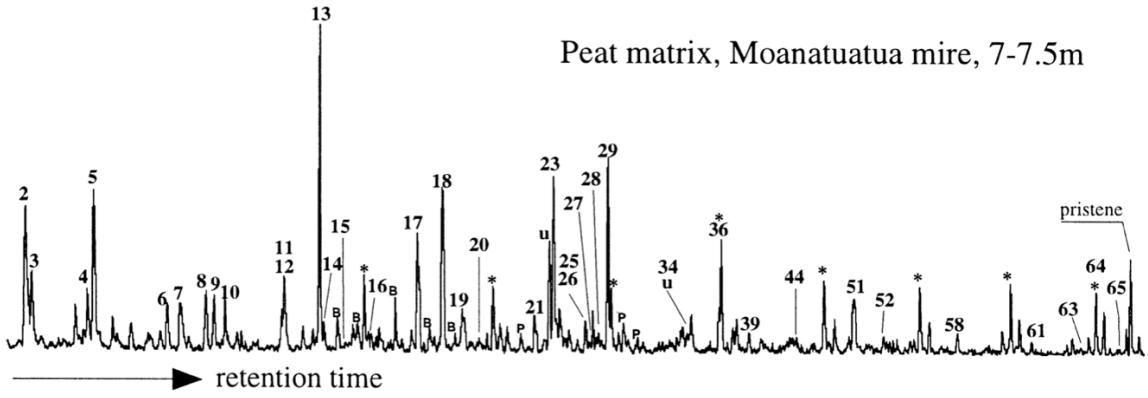

Fig. 8. Total ion current trace of pyrolysis products of bulk peat (matrix) Moanatuatua mire, 7–7.5 m. B—alkylbenzene; P—alkylphenol; *—aliphatic hydrocarbon; u—unknown. Peak numbers as in Table 3.

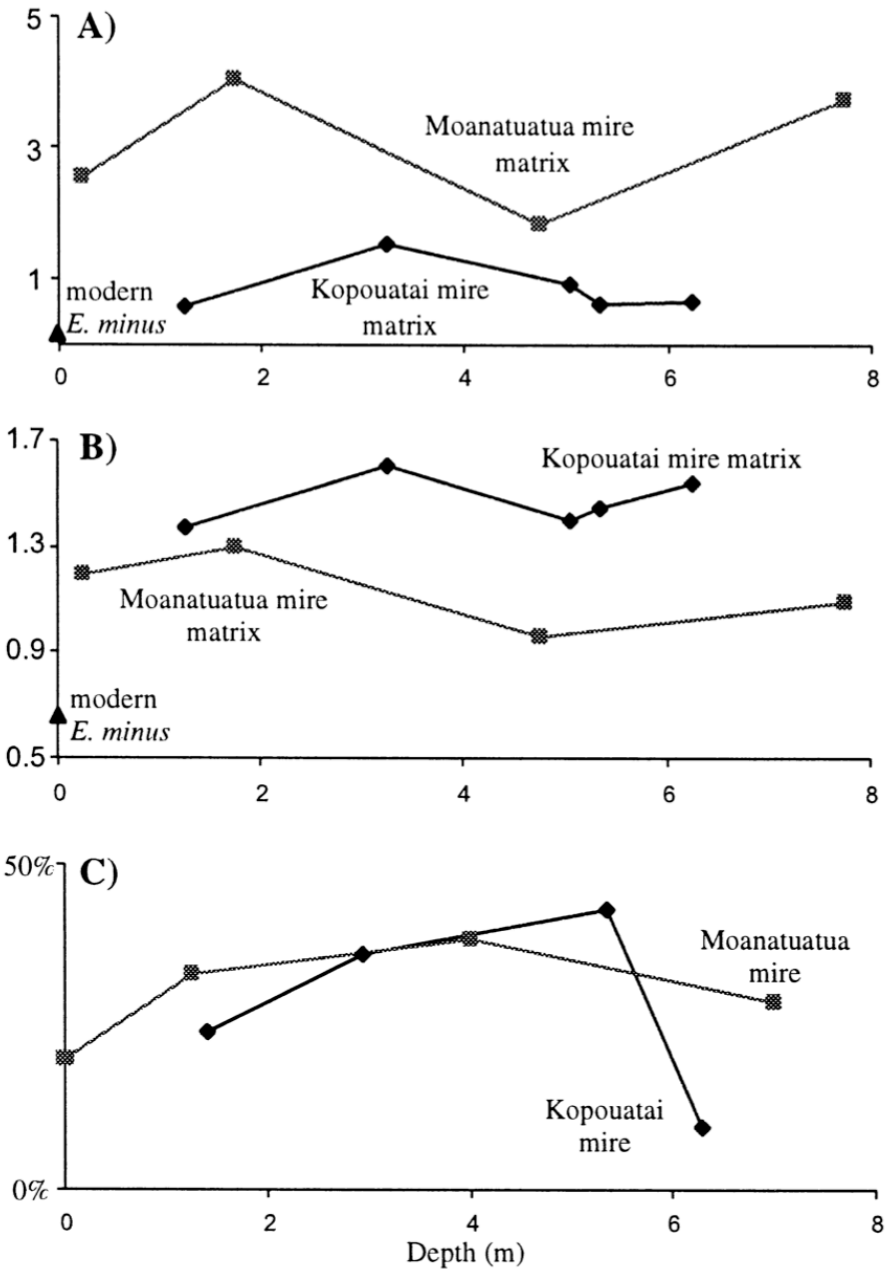

Fig. 9. Plots of change of chemical and petrographic parameters of peat matrix with depth. (A) Ratio of 2-methoxy-4-acetylphenol to all 2-methoxy-4-prop-2-enylphenol (*trans*), values as in Table 4c; (B) ratio of guaiacyl to syringyl, values as in Table 4b for matrix, Table 4a for fresh *E. minus*; (C) percentage of amorphous matrix in peat, values as in Table 1.