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1 Preferential degradation of polyphenols from *Sphagnum* – 4-isopropenylphenol as
2 a proxy for past hydrological conditions in *Sphagnum*-dominated peat

3
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23

24 **Highlights**

- 25 • Depth records of C/N, markers for lignin, cellulose and sphagnum acid are compared for
26 peat cores
- 27 • Their relation to bog hydrology is established in five peatlands from different climatic
28 zones
- 29 • Under aerobic conditions polyphenols degrade faster than polysaccharides in *Sphagnum*
30 peat
- 31 • 4-Isopropenylphenol reflects past hydrological conditions in *Sphagnum* peat
- 32 • Interpretation of vegetation and decomposition proxies in *Sphagnum* peat is site-
33 dependent

34
35

36 **Keywords**

37 *Sphagnum* degradation; Rödmosamyran peatland; Pyrolysis-GC/MS; C/N ratio; Biomarker.

38

39 **ABSTRACT**

40 The net accumulation of remains of *Sphagnum* spp. is fundamental to the development of many
41 peatlands. The effect of polyphenols from *Sphagnum* on decomposition processes is frequently
42 cited but has barely been studied. The central area of the Rödmosamyran peatland (Sweden) is
43 an open lawn that consists mostly of *Sphagnum* spp. with a very low contribution from vascular
44 plants. In order to determine the effects of decay on sphagnum phenols, 53 samples of a 2.7 m
45 deep core from this lawn were analysed with pyrolysis gas chromatography-mass spectrometry
46 (pyrolysis-GC/MS) and compared with more traditional decomposition proxies such as C/N
47 ratio, UV light transmission of alkaline peat extracts, and bulk density. Factor Analysis of 72

48 quantified pyrolysis products suggested that the variation in 4-isopropenylphenol was largely
49 determined by aerobic decomposition instead of *Sphagnum* abundance. In order to evaluate the
50 effects of aerobic decay in *Sphagnum* peat, down-core records from different climatic regions
51 were compared using molecular markers for plant biopolymers and C/N ratio. These included
52 markers for lignin from vascular plants ((di)methoxyphenols), polyphenols from *Sphagnum* spp.
53 (4-isopropenylphenol), and cellulose (levoglucosan). Our results indicate that polyphenols from
54 *Sphagnum* are preferentially degraded over polysaccharides; consequently the variability of the
55 marker for sphagnum acid, 4-isopropenylphenol, was found indicative of decomposition instead
56 of reflecting the abundance of *Sphagnum* remains. The fact that 4-isopropenylphenol is
57 aerobically degraded in combination with its specificity for *Sphagnum* spp. makes it a consistent
58 indicator of past hydrological conditions in *Sphagnum*-dominated peat. In contrast, the
59 variability of C/N records in *Sphagnum*-dominated peat was influenced by both vegetation shifts
60 and decomposition, and the dominant effect differed between the studied peatlands. Our results
61 provide direction for modelling studies that try to predict possible feedback mechanisms between
62 peatlands and future climate change, and indicate that the focus in *Sphagnum* decay studies
63 should be on carbohydrates rather than on phenolic compounds.

64

65 **1. Introduction**

66 To understand the consequences of a changing climate, knowledge of past environmental change
67 as well as the feedback mechanisms between natural ecosystems and climate is essential.
68 Peatlands are important sources of information for such studies because they respond strongly to
69 changes in environmental conditions, in particular to hydrology (Philben et al., 2013). First,
70 peatlands are a major terrestrial carbon store (Yu, 2012), due to incomplete decomposition of

71 plant materials after death. Under a changing climate, the carbon that is stored by plant
72 photosynthesis can be released back into the atmosphere as the greenhouse gasses carbon dioxide
73 and methane (Freeman et al., 2001). Second, the relationship between hydrology, botanical
74 composition and degree of peat decomposition in peatlands provides an important contribution in
75 their functioning as a climate archive. A number of biological, physical and chemical proxies
76 have been used to study past environmental and climate changes in peatlands (Chambers et al.,
77 2012). However, many of the available proxies are influenced by multiple processes, which may
78 limit or complicate the interpretation of their environmental implications. For example, recent
79 geochemical studies indicate that the effects of decomposition should be considered when using
80 source proxies, including for stable isotopes of plant biopolymers (DeBond et al., 2013), trace
81 elements (Biester et al., 2012), biomarkers (Sinninghe-Damsté et al., 2002; Jex et al., 2014) and
82 the distribution (Andersson et al., 2012) and isotopic composition (Huang et al., 2014) of *n*-
83 alkanes.

84 The controls on peat decomposition are a key factor in our understanding of the relationship
85 between peatlands and climate. Plant inputs and their subsequent decomposition leave a
86 chemical fingerprint on the composition of the peat. Decomposition includes mineralisation to
87 carbon dioxide and water, as well as transformations of (macro)molecules that include
88 fragmentation and oxidation. Mass loss is a measure for mineralisation and can be studied by the
89 quantification of gas fluxes *in situ*; however, this only provides information of on-going
90 decomposition. The ratio of total organic carbon to total nitrogen (C/N) has been proposed as a
91 proxy for estimating mass loss, with relatively low C/N values indicating drier conditions
92 because carbon is lost during decomposition while nitrogen is preferentially preserved (Biester et
93 al., 2014). Transformations of plant remains can be studied by the chemical composition of the

94 remaining material, i.e., the peat. For example, the degree of peat humification can be inferred
95 from the colour intensity of humic substances measured using UV light transmission (%T)
96 following an alkaline extraction (8% NaOH; [Blackford and Chambers, 1993](#)). As proxies for
97 decomposition, C/N and %T will decline with increasing decomposition: C/N due to the
98 preferential loss of carbon, and %T due to the increased content of soluble organic matter.
99 However, C/N and %T do not always infer the same decomposition profile and an important role
100 for the original vegetation inputs in controlling these proxies has been proposed ([Yeloff and](#)
101 [Mauquoy, 2006](#); [Hansson et al., 2013](#)). Based on preferential decomposition, the content and
102 composition of biomacromolecules such as polysaccharides and lignin have also been used as
103 proxies ([Comont et al., 2006](#); [Jia et al., 2008](#); [Jex et al., 2014](#)).

104 Our current knowledge on the three-way relationship between the botanical composition,
105 decomposition and environmental factors in peatlands is limited ([Abbott et al., 2013](#)) making the
106 interpretation of their proxy records intricate. To obtain a fundamental understanding of peatland
107 organic matter dynamics, pyrolysis techniques are a powerful tool because they provide
108 molecular information for complex unknown mixtures of organic matter ([Nierop et al., 2005](#)).
109 This enables the study of both the plant sources of the organic matter and the superimposed
110 decomposition processes. Pyrolysis results in cleavage of chemical bonds within macromolecular
111 structures by adding heat to a sample, which in combination with gas chromatography/ mass
112 spectrometry (GC/MS), makes it possible to directly analyse non-volatile complex mixtures of
113 organic material. Pyrolysis-GC-MS provides detailed structural information, including the
114 contribution of chemical groups as well as the composition within these groups ([Huang et al.,](#)
115 [1998](#)). Pyrolysis-GC-MS has been successfully applied to study past peatland dynamics,
116 providing the composition of lignin phenols and the abundance of plant vs. microbial sugars that

117 can be related to plant source and degradation state (Kuder et al., 1998; Huang et al., 1998), as
118 well as plant-specific pyrolysis products (Schellekens et al., 2011). In addition, knowledge of the
119 molecular structure of sphagnum phenols largely depends on pyrolysis techniques (van der
120 Heijden et al., 1997).

121 Although *Sphagnum*-dominated peatlands are frequently used for palaeoclimate
122 reconstructions (Chambers et al., 2012), the decay of *Sphagnum* itself is poorly understood.
123 *Sphagnum* litter is known to have a very slow decomposition rate (Clymo, 1965), which is
124 attributed to an abundance of phenolic macromolecules (van Breemen, 1995; van der Heijden et
125 al., 1997; Freeman, 2001) that contain sphagnum acid (*p*-hydroxy- β -[carboxymethyl]-cinnamic
126 acid) or to pectin-like polysaccharides (sphagnan; Painter, 1991; Hájek et al., 2011). Sphagnum
127 acid (Hesse and Rudolph, 1992) and sphagnan (Mitchel, 1996) are mainly found in the hyaline
128 cell walls of *Sphagnum* mosses in which it is covalently linked to other cell wall biopolymers
129 (Painter, 1991; van der Heijden, 1994). Sphagnum acid is specific for *Sphagnum* spp. (van der
130 Heijden et al., 1997), and has been used to trace the abundance of *Sphagnum* in peat records
131 using pyrolysis techniques (McClymont et al., 2011; Schellekens and Buurman, 2011). There is
132 recent evidence that the decay of sphagnum phenols is related to water table depth (Abbott et al.,
133 2013; Swain and Abbott, 2013) but how this compares to other plant biopolymers remains
134 unclear. In addition, plant-specific monosaccharide compositions agreed with the macrofossil
135 record in a *Sphagnum*-dominated peat core (Jia et al., 2008) suggesting a minor effect of
136 decomposition on sphagnum polysaccharides. Indeed, these structural polysaccharides from
137 *Sphagnum* were related to its resistance against degradation (Hájek et al., 2011).

138 Here we hypothesise that sphagnum acid is preferentially lost during aerobic surface decay
139 and that its variation with depth thereby provides a sensitive proxy for past mire surface wetness

140 in (homogenous) *Sphagnum* peat. In order to test this hypothesis, a *Sphagnum*-dominated peat
141 core was studied in detail with analytical pyrolysis, C/N and %T. Pyrolysates will provide the
142 molecular structure of bulk peat samples, while C/N and %T support pyrolysis data and are used
143 to estimate mass loss and decomposition state, respectively. The Rödmosamyran mire (RMM;
144 northern Sweden) was chosen for this purpose because its central lawn is covered almost
145 exclusively by *Sphagnum* and has very wet conditions throughout the year (Rydberg et al.,
146 2010).

147 To further examine the mechanisms of *Sphagnum* decay, depth records of C/N and pyrolysis
148 parameters were applied to cores from RMM and four previously studied peatlands from other
149 climatic regions. Large areas of high-latitude peatlands are dominated by *Sphagnum*, although
150 with local differences in climate and ecology. Here we test whether local differences in botanical
151 composition, both the contribution of different *Sphagnum* species and the type and contribution
152 of vascular plants, bias the interpretation of peat chemistry. Pyrolytic parameters included
153 products specific for sphagnum acid (4-isopropenylphenol; van der Heijden et al., 1997), lignin
154 ((di)methoxyphenols) and cellulose (levoglucosan; Pouwels et al., 1989), thereby providing
155 markers for the relevant plant biopolymers in *Sphagnum* peat. From these parameters, lignin
156 provides evidence for vascular plants in peat dominated by *Sphagnum*, because *Sphagnum*
157 contains no lignin and anaerobic degradation of lignin proceeds at a relatively slow rate (Benner
158 et al., 1984). The relative abundance of cellulose and sphagnum acid can be related to
159 preferential decay of those plant compounds. By assessing the signals recorded in peatlands from
160 different regions (with different vegetation and hydrology), we test the impact of botanical
161 differences on sphagnum phenol degradation and extend its application. Along with changes in
162 the assemblages of testate amoebae (e.g. van Bellen et al., 2014), the C/N ratio is one of the few

163 proxies that can be used to infer surface wetness in homogeneous *Sphagnum* peat (Yeloff and
164 Mauquoy, 2006). The C/N ratio was determined for all peatlands, providing a measure for mass
165 loss during decomposition upon aerobic conditions. In addition, comparison of C/N records with
166 molecular parameters in peatlands which have different contribution from *Sphagnum* allows an
167 examination of the influence of source vegetation on its use as decomposition proxy.

168

169 **2. Methods**

170 *2.1. Location and sampling*

171 The RMM peatland is a nutrient-poor (oligotrophic) fen in northern Sweden that is
172 approximately 7 ha in extent (Table 1). Based on the basal age of a nearby mire (Stor Åmyran,
173 2400 BP; Oldfield et al., 1997) and the rates of isostatic rebound in this region, RMM
174 transformed into a mire between 2500 and 2800 years ago. Macrofossils characteristic of marsh
175 vegetation (e.g., *Equisetum palustre*) were visible in the basal peat layers. For details on the
176 location of the core see Rydberg et al. (2010). Much of the mire surface is covered by small,
177 thinly spaced pines (*Pinus sylvestris* L.) with a field layer consisting of mosses and dwarf shrubs.
178 In the central area of the southern half of the mire there is an open *Sphagnum* lawn of 0.25 ha
179 that consists mostly of *Sphagnum*. There is no open water on the mire surface nor are there any
180 surface inlets or outlets or signs of historical ditching in its close proximity. The vegetation of
181 the *Sphagnum* lawn is dominated by *S. centrale* and *S. subsecundum* (with minor contributions
182 from *S. palustre* and *S. magellanicum*) and some contributions from *Eriophorum vaginatum*. The
183 dominant fen peat characterising most of RMM surrounding the *Sphagnum* lawn includes *S.*
184 *centrale*, field-layer vegetation including *Calluna vulgaris* (L.) Hull and *Ledum palustre* L., and
185 sparsely spaced small pine (*P. sylvestris*).

186 Four plant species from RMM were selected for chemical analysis, these included *S. centrale*,
187 *S. magellanicum*, *E. vaginatum* and *C. vulgaris*. The 270-cm thick profile from RMM consists of
188 a Wardenaar (1987) surface core (0–66 cm) and an overlapping series of four Russian peat cores
189 (length 1 m; diameter 7.5 cm; [Rydberg et al., 2010](#)). The Wardenaar core was taken back to the
190 laboratory intact and stored frozen, whereas the Russian peat cores were cut in the field into 10-
191 cm sections. In the laboratory all field-sectioned samples were weighed and then stored frozen at
192 -18 °C until processing. In a freezer room (-18 °C) the Wardenaar core was cut in half length-
193 wise, the outermost 1 cm removed on a band saw with a stainless steel blade, hand planed into
194 even dimensions, and then cut into 2-cm-thick slices. The samples were freeze-dried, weighed
195 for calculating dry bulk density and ground in an agate ball mill before further analysis.

196 Peat cores from *Sphagnum*-dominated peatlands from other climatic zones included
197 Königsmoor (KM; Harz Mountains, Germany; [Biester et al., 2012, 2014](#)), and Butterburn Flow
198 (BBF; UK; [McClymont et al., 2008, 2011](#)), while the Harberton core (HRB; Tierra del Fuego,
199 Argentina; [Schellekens et al., 2009, Schellekens and Buurman, 2011](#)) is composed of three
200 vegetation zones, the upper two being dominated by *Sphagnum* (HRB1, HRB2) and the deepest
201 one dominated by graminoids and woody species (HRB3). A graminoid-dominated peatland that
202 has contributions from *Sphagnum* was also studied, Penido Vello (PVO; northern Spain;
203 [Schellekens et al., 2011, 2012, 2015](#)). The main characteristics of these peatlands are given in
204 [Table 1](#).

205 The *Sphagnum*-dominated peatlands (RMM, KM, BBF and HRB) differed slightly in
206 *Sphagnum* and vascular plant species ([Table 1](#)), though all peatlands shared the same ecology
207 showing an increase of vascular plant species upon drier conditions ([McClymont et al., 2008](#);
208 [Rydberg et al., 2010; Schellekens et al., 2009; Biester et al., 2014](#)). PVO is dominated by

209 graminoids including Poaceae, Juncaceae and Cyperaceae and has a low contribution from
210 several *Sphagnum* species (for details on the vegetation composition of this peatland see
211 Schellekens et al., 2011). KM and PVO were sampled at a resolution of 2 cm; for HRB the
212 upper 174 cm were sampled according to the morphology/stratigraphy, the deeper part of the
213 core was sampled in sections of 3 cm, except at the bottom of each sub-core (5 cm); BFF was
214 sampled at 1 cm intervals, of which a selection of 56 samples were analysed, because carbon and
215 nitrogen content and analytical pyrolysis were not always determined on samples from the same
216 depths, only the overlapping samples (32) were used to determine correlation coefficients.
217 Depth, age and number of samples for each core are given in [Table 1](#).

218

219 *2.2. Bulk density, ash content and %T (RMM)*

220 All samples were weighed for calculating dry bulk density. The ash content of the peat samples
221 was determined following re-drying of the sample at 105 °C and then heating the samples at 450
222 °C for 4 h. %T was measured following an alkaline extraction based on the methods of
223 Blackford and Chambers (1993). In brief, 0.020 g of peat were digested in 10 mL 8% NaOH (95
224 °C, 1 h), diluted with an equal volume of deionised water, filtered (Whatman no.1), diluted again
225 with an equal volume of deionised water and light transmission (%T) measured in triplicate
226 using a 1 cm quartz cuvette in a Hitachi U-1100 spectrophotometer at a wavelength of 540 nm.
227 Replicate analyses, both within run and between days, were within $\pm 3\%$.

228

229 *2.3. Carbon and nitrogen*

230 Elemental compositions were determined as proportion (%) of the dry weight of peat analysed.
231 The carbon and nitrogen contents of the RMM peat and plant samples were determined using a

232 PerkinElmer 2400 series analyser operating in CHN mode only. Replicate samples, included
233 approximately every 10th sample, showed a precision within $\pm 3\%$ for carbon and nitrogen. C/N
234 ratios are reported here based on a mass basis.

235 Concentrations of carbon and nitrogen for KM peat and plant samples were determined by gas
236 chromatography and thermal conductivity detection after thermal combustion in an elemental
237 analyser (Euro EA3000, Eurovector). Reproducibility of duplicates was always better than $\sim 8\%$
238 RSD (Biester et al., 2014). For BBF, freeze-dried subsamples of *c.* 3–4 cm³ volume were
239 homogenised and ground to pass through a 0.5 mm sieve. Aliquots were analysed in duplicate
240 using a Carlo-Erba EA1108 elemental analyser (McClymont et al., 2011). For HRB, peat
241 samples were analysed by complete combustion in an auto-analyser, Fisons CHNS-O EA-1108
242 for carbon, and LECO CHNS-932 for nitrogen (Schellekens and Buurman, 2011). For PVO, peat
243 samples were analysed by complete combustion in a Leco CHN-1000 auto-analyser (Pontevedra-
244 Pombal et al., 2004).

245

246 *2.4. Pyrolysis-GC/MS (RMM)*

247 Platinum filament coil probe pyrolysis (temperature 650 °C) was performed with a Pyroprobe
248 5000 pyrolyser (CDS, Oxford, USA) coupled to a 6890N gas chromatograph and 5975B mass
249 selective detector (MSD) system from Agilent Technologies (PaloAlto, USA). Samples were
250 embedded in quartz tubes using glass wool. The pyrolysis interface and GC inlet (split ratio 1:20)
251 were set at 325 °C. The GC instrument was equipped with a (non-polar) HP-5MS 5% phenyl,
252 95% dimethyl-polysiloxane column (30 m x; 0.25 mm i.d.; film thickness 0.25 μm). Helium was
253 the carrier gas at constant flow of 1 mL/min. The oven temperature program was 50 to 325 °C
254 (held 10 min) at 15 °C/min. The GC/MS transfer line was held at 270 °C, the ion source (electron

255 impact mode, 70eV) at 230 °C the quadrupole ion filter and the detector at 150 °C scanning a
256 range between m/z 50 and 500. Compounds were identified using the NIST '05 library.

257 Seventy-two pyrolysis products were quantified for 53 peat samples, including all prominent
258 peaks. In addition, the presence of some compounds was established by partial chromatograms
259 of their specific fragment ions, these included *n*-alkanes and *n*-methyl ketones, a series of lignin
260 phenols, and biomarkers that have been previously identified from pyrolysates of peatland plants
261 (Schellekens et al., 2009, 2011). The searched biomarkers included ferulic acid methyl ester
262 (graminoids) and 3-methoxy-5-methylphenol (lichens); in addition fragment ions of diterpenes
263 (*Pinus* spp.) and sesquiterpenes were also searched for. From those plant-specific pyrolysis
264 products, only ferulic acid methyl ester was detected in the RMM peat samples, but it was very
265 low in some samples (<0.02% TIC) and absent in others. Quantification was based on the peak
266 area of characteristic fragment ions (m/z) for each pyrolysis product (SI_Table 1). For each
267 sample, the sum of the quantified peak areas was set at 100% and amounts were calculated
268 relative to this. According to probable origin and similarity, the pyrolysis products were grouped
269 as follows: polysaccharides, aliphatic compounds (*n*-alkanes, *n*-alkenes, *n*-methyl ketones, *n*-
270 fatty acids, other aliphatic compounds), lignin moieties (syringyl, guaiacyl and *p*-
271 hydroxyphenyl), phenols (including polyphenols), aromatics, polyaromatic hydrocarbons, and
272 nitrogen containing compounds. To compare the abundance of phenols and polysaccharide
273 pyrolysis products between living *Sphagnum* and *Sphagnum* peat, the same 72 products
274 quantified for the peat also were quantified for pyrolysates of living *Sphagnum*.

275 For details on analytical conditions and quantification for pyrolysis of previous studies we
276 refer to Biester et al. (2014) for KM, Schellekens and Buurman (2011) for HRB, McClymont et

277 al. (2011) for BBF and Schellekens et al. (2011) for PVO; whether the 72 quantified RMM
278 pyrolysis products were included in the quantification of those cores is indicated in SI_Table 1.

279

280 2.5. Data analysis and statistics

281 The abundance of pyrolysis products depends on several factors that, apart from the composition
282 of the peat, differ between laboratories. These are, for example: the selection of pyrolysis
283 products for quantification, because they are expressed as the proportion (%) of the total
284 quantified products; the choice of m/z values for quantification; MS response factors; and
285 pyrolysis as well as GC conditions. Therefore, comparison of numerical values between different
286 peat pyrolysis studies is difficult, but the general trends will allow us to assess the variations
287 along a core (Jacob et al., 2007). Although a product with a low abundance (e.g. <1% of the total
288 quantified pyrolysis products) can be considered as statistically independent, a large number of
289 pyrolysis products have to be quantified to reach this independence. An alternative to the
290 quantification of large data sets is the use of ratios; frequently applied examples from lignin
291 geochemistry include syringyl to guaiacyl and acid to aldehyde ratios (Jex et al., 2014). In
292 relation to analytical pyrolysis, the advantage of using ratios is that quantification is simple and
293 data sets can be compared. A disadvantage is that its variation is determined by changes in both
294 numerator and denominator; because this can be influenced by several factors, information may
295 be lost. Therefore, we chose to use depth records of (groups of) pyrolysis products expressed as
296 proportion of the total quantified pyrolysis products (% TIC), as well as ratios. Ratios included
297 that of 4-isopropenylphenol to lignin pyrolysis products (I%; McClymont et al., 2011) and
298 (di)methoxyphenols to levoglucosan. The parameters are given in Table 2.

299

300 2.5.1. Factor analysis (RMM)

301 The main processes that influence the molecular composition of peat organic matter interact with
302 environmental factors and comprise changes in input material (shifts in the composition of the
303 plant cover) and decay processes. In order to identify and separate the effects of these factors on
304 peat chemistry, factor analysis was applied. Factor analysis was carried out using Statistica
305 software, version 6 (StatSoft, Tulsa).

306 Factor analysis extracts trends from complex data sets by searching for linear correlations
307 between variables, reducing this variation to a number of factors. Factor analysis was performed
308 on the 53 RMM peat samples using all 72 quantified pyrolysis products as variables ([SI_Table](#)
309 [1](#)). The identification of the underlying processes was based on the loadings of pyrolysis
310 products on each statistical factor; scores reflect the weight of each statistical factor to a given
311 sample and allows comparing the molecular chemistry with other characteristics (C/N, %T, ash
312 content and bulk density). Thus, while the variation in individual pyrolysis products can be
313 influenced by several aspects (decomposition, input, wildfire, etc.), the scores of an extracted
314 factor take into account the shared variation in all quantified pyrolysis products thereby
315 reflecting the effect of a single process on the peat chemistry.

316 The total variance explained by a factor is not indicative of its value as proxy, because it
317 depends on the number and combination of variables that show a similar distribution; a variance
318 with a higher level of explanation thus reflects major changes in peat chemistry (provided that
319 the pyrolysates are reflecting this). Although the largest set of correlated variables, i.e. the major
320 process affecting peat chemistry, is allocated into the first factor this does not mean that variables
321 with low loadings on this factor cannot have value as a proxy indicator. For example, if the first
322 factor reflects preferential degradation of polysaccharides over lignin, polysaccharide and lignin

323 pyrolysis products will have high and opposite loadings on this factor; but minor differences
324 within the lignin phenol group can be enlarged when the ratio has been included as a variable.
325 Thus, minor differences in loading or low loadings of pyrolysis products still can be noteworthy,
326 but interpretation must be carefully reasoned.

327

328 2.5.2. Comparison of proxy records

329 In order to discuss the influence of botanical source on decay parameters, an ANOVA test was
330 applied to check for significant differences of the parameters between vegetation types. For each
331 peatland, the selected proxies (Table 2) were compared using their depth records and correlation
332 coefficients. Because of local differences in environmental conditions, botany and ecology and
333 their complex relationships with peat chemistry, we rely on the major trend. For a detailed
334 interpretation of the chemistry of KM (Biester et al., 2014), HRB (Schellekens and Buurman,
335 2011), BBF (McClymont et al., 2011) and PVO (Schellekens et al., 2011) we refer to previous
336 studies.

337

338 3. Results

339 3.1. Plant analysis

340 C/N values for the dominant plant species from RMM and KM are given in Table 3. RMM
341 plants showed higher C/N ratios compared to the same species from KM, while within both
342 peatlands C/N values decreased from *Sphagnum* to *C. vulgaris* with lowest values for *E.*
343 *vaginatum*. For analytical pyrolysis of *E. vaginatum*, *S. centrale*, *S. magellanicum* and *C.*
344 *vulgaris*, 4-isopropenylphenol was specific for *Sphagnum* spp. (Ph5; van der Heijden et al.,
345 1997) and additionally two biphenyl compounds were detected solely in *Sphagnum* (Ph6, Ph7,

346 see [SI_Table 1](#); [Biester et al., 2014](#)). Furthermore, all peat pyrograms showed a double peak for
347 m/z 137+152 (G3 and Ph4, [SI_Table 1](#)). This mass spectrum is generally identified as 4-
348 ethylguaiacol (G3), the structure of which does not allow isomers. The second peak (longer
349 retention time) was detected in pyrolysates of fresh *Sphagnum* but was absent in pyrolysates of
350 the other plant species, which indicates that it is related to *Sphagnum*. The marker for graminoids
351 (ferulic acid methyl ester; [Schellekens et al., 2012](#)) was found in the *Eriophorum* plant sample,
352 but its abundance in the RMM peat samples was near the limit of detection ([Section 2.4](#)). A
353 minor amount of guaiacyl lignin was present in pyrolysates of living *Sphagnum*; this was also
354 found in pyrolysates of living *Sphagnum* from other sites ([McClymont et al., 2011](#); [Schellekens](#)
355 [et al., 2009](#)). The fact that the abundance of guaiacyl moieties was clearly higher in the
356 *Sphagnum* samples collected from the dominant pine-covered area of RMM compared with the
357 open area of the *Sphagnum* lawn supports the explanation of this phenomenon by [Abbott et al.](#)
358 ([2013](#)), who suggested that the lignin phenols dissolved in peat water have been mobilised into
359 the hyaline cells of the *Sphagnum* capitula where they are physically entrapped or bound.

360

361 3.2. Peat analysis

362 The ash content at RMM varied between 0 and 1.9% indicating the ombrotrophic nature of the
363 lawn peat, except for the two deepest samples with 9.5 and 26.6% ash (not shown) that were
364 deposited during the isostatic isolation and early formation of the mire. The chemical
365 composition of these two samples differed extremely from the other samples; they were therefore
366 excluded from the depth records. A detailed list of all quantified pyrolysis products from the
367 RMM peat samples and their mean abundance is given in [SI_Table 1](#).

368 The first three factors from factor analysis applied to the pyrolysates from RMM explained
369 67.5% of the total variance. The loadings of the first two factors are plotted against each other in
370 [Fig. 1](#). Factor 1 (F1) explained 43.9% of the variance. Factor 2 (F2) explained 12.8% of the
371 variance. The scores of F1 and F2 are plotted against depth and compared with depth records of
372 C/N, %T, bulk density and ash content ([Fig. 2](#)).

373 Mean values of the parameters provide a broad indication of peat chemistry and allow
374 comparison between peatlands ([Table 2](#)). The results of the ANOVA test indicate highly
375 significant ($P<0.01$) differences between bogs for all parameters ([Table 2](#)). In general terms,
376 RMM chemical nature is closer to that of HRB1 (both *Sphagnum*-dominated peat), characterised
377 by the highest C/N ratios, I% values, 4-isopropenylphenol, total polysaccharides and
378 levoglucosan content, and the lowest lignin content and lignin/levoglucosan ratios; while HRB3
379 and PVO (graminoid-dominated peat) represent the opposite nature (lowest C/N ratios, I%, 4-
380 isopropenylphenol, total polysaccharides and levoglucosan, and highest lignin and
381 lignin/levoglucosan ratio). KM and HRB2 showed similar, somewhat intermediate values for the
382 parameters, although much closer to those of RMM-HRB1 than to PVO-HRB3 (as indicated by a
383 cluster analysis on standardised average values of the parameters in [Table 2](#); data not shown).

384 The relationship of each pyrolysis parameter with C/N is indicated by a correlation, and
385 provides a measure for the influence of source material and decomposition ([SI_Table 2](#)). Depth
386 records of C/N and pyrolysis parameters are shown in [Fig. 3](#) for each peatland. The extent to
387 which molecular parameters varied together down-core in each bog is in addition indicated by a
388 correlation ([SI_Table 2](#)) and showed considerable differences between the vegetation types. In
389 the *Sphagnum*-dominated peatlands 4-isopropenylphenol and the summed (di)methoxyphenols
390 showed no correlation (RMM) or a rather weak negative correlation for KM ($r^2=0.32$; $n=42$;

391 $P < 0.0001$) HRB2 ($r^2 = 0.50$; $n = 18$; $P < 0.001$) and HRB1 ($r^2 = 0.34$; $n = 15$; $P < 0.02$), though when
392 the upper three samples of HRB1 were excluded the correlation increased to highly significant
393 values ($r^2 = 0.74$; $n = 12$; $P < 0.0005$). The correlation between (di)methoxyphenols and
394 polysaccharides was only evident in the graminoid-dominated PVO peat core ($r^2 = 0.59$; $n = 80$;
395 $P = 0.000000$), while the correlation between 4-isopropenylphenol and polysaccharides was
396 absent in RMM, HRB1 and HRB3, and only weak in HRB2, KM and PVO ($r^2 < 0.36$; [SI_Table](#)
397 [2](#)).

398 To provide an indication for the relative decomposition rates of polyphenols and
399 polysaccharides, the change of their pyrolysis products from living *Sphagnum* to peat and from
400 surface peat to deeper peat is indicated in [Figure 4](#) for the *Sphagnum*-dominated peatlands.
401 Because of differences in the quantification between the peatlands only phenol, 4-vinylphenol,
402 and levoglucosan (being dominant products + present in the quantification from all peatlands)
403 and 4-isopropenylphenol (specific for *Sphagnum* + present in all quantifications) were indicated
404 individually; the change in abundance of other phenolic/(poly)aromatic and polysaccharide
405 products are indicated by their sum. The polyphenol-derived pyrolysis products together
406 accounted for a decrease from surface to deeper peat from 26.2 to 9.3% and from 24.9 to 15.2%
407 of TIC in HRB and KM, respectively; while in RMM a decrease from 53.4 to 18.1% of TIC was
408 found from living *Sphagnum* to peat. Polysaccharides on the other hand clearly increased from
409 living *Sphagnum* to peat (from 41.4 to 76.8% TIC, from 63.9 to 74.2% TIC and from 48.3 to
410 59.6% of TIC for RMM, HRB and KM, respectively).

411

412 **4. Discussion**

413 *4.1. C/N in living plants*

414 Between plant species there is a similar pattern at RMM and KM where C/N decreased from
415 *Sphagnum* to *C. vulgaris* to *E. vaginatum*, which is in agreement with the generally higher C/N
416 values in *Sphagnum* compared with vascular plants (Hornibrook et al., 2000; Kleinebecker et al.,
417 2007). The C/N values of the same plant species clearly differ between the sites (Table 3). The
418 difference between sites is most prominent for *Sphagnum* and can be explained by differences in
419 nitrogen deposition, because living *Sphagnum* assimilates nitrogen from the atmosphere
420 (Heijmans et al. 2002) and central Germany receives much higher nitrogen deposition than
421 northern Sweden (Akselsson et al., 2010).

422

423 4.2. The Rödmosamyran peat record

424 The absence of markers for lichens (3-methoxy-5-methylphenol) and pine and the very low
425 abundance of the marker for graminoids (ferulic acid methyl ester) in the peat samples (Section
426 2.4) indicate a complete dominance by *Sphagnum* and prevailing wet conditions, which is in
427 agreement with the present-day situation at the centre of the mire (Rydberg et al., 2010). This
428 notwithstanding, the peat has a substantial contribution from (di)methoxyphenols (Table 2),
429 indicating a contribution from vascular plants. The high syringyl/guaiacyl ratio (mean value
430 0.39; S.D.=0.09; $n=53$; SI_Fig. 1) excludes pine as the dominant source of this lignin (Hedges
431 and Mann, 1979). In addition to ferulic acid methyl ester, parameters indicative of graminoids
432 (including *Eriophorum*) are high ratios of 4-vinylguaiacol to the total guaiacyl compounds and 4-
433 hydroxy-5,6-dihydro-(2H)-pyran-2-one to the summed polysaccharide pyrolysis products
434 (Schellekens et al., 2015). They are positively correlated ($r^2=0.41$; $P=0.000$; $n=53$; SI_Fig. 2a)
435 suggesting that a substantial part of these compounds has an *Eriophorum* source in the RMM
436 peat, which is also consistent with the present-day composition. However, no correlation

437 between either compound (4-vinylguaiacol and 4-hydroxy-5,6-dihydro-(2H)-pyran-2-one) and
438 (di)methoxyphenols was found (SI_Fig. 2bc). Catechol, on the other hand, showed high positive
439 correlation with the (di)methoxyphenol content ($r^2=0.62$; $n=52$; $P=0.000$, uppermost sample
440 excluded; SI_Fig. 2d). Catechol is a pyrolysis product of tannin (Nierop et al., 2005), which has
441 a relatively high abundance in bark or berries (Kögel-Knabner, 2002), pointing towards *C.*
442 *vulgaris* and/or *L. palustre* in the RMM peat. Although catechol was also significantly present in
443 pyrolysates of *Sphagnum*, the similarity of depth records of catechol and (di)methoxyphenols in
444 the peat (except for the uppermost sample) suggests that the variation in lignin is related to
445 changes in the abundance of *C. vulgaris*, and indicates that the precursor of catechol from
446 *Sphagnum* (polyphenols) is rapidly degraded compared with its precursor from *C. vulgaris*
447 (lignin and/or tannin).

448

449 4.2.1. Identification of environmental processes from peat pyrolysates using factor analysis

450 Most (di)methoxyphenols showed high negative loadings on F1. The fact that *Sphagnum*
451 contains no lignin indicates that F1 reflects mainly the contribution from vascular plants to the
452 peat organic matter (high negative loadings). This is confirmed by the positive loading of the
453 markers of *Sphagnum* (Ph5–Ph7); their lower loading on F1 (up to 0.4) is explained by the
454 dominance of *Sphagnum*, because a minor increase of vascular plants will not significantly
455 change the abundance of *Sphagnum* markers if the peat matrix is predominantly composed of
456 *Sphagnum* litter.

457 For peat with a relatively high contribution from vascular plant material (negative loadings on
458 F1) F2 seems to reflect aerobic degradation, compounds with positive loadings indicating a
459 higher degree of decomposition. This interpretation is based on: (i) the separation of aliphatic

460 (positive) and lignin (negative) pyrolysis products (Fig. 1), because lignin is preferentially
461 degraded over aliphatic macromolecules (Klotzbücher et al., 2011); (ii) a high negative loading
462 of 4-vinylphenol (H1), 4-vinylguaiacol (G4) and 4-vinylsyringol (S4), pyrolysis products that
463 largely originate from non-lignin phenolics (Boon et al., 1982), which are abundant in non-
464 woody tissue (Hedges and Mann, 1979) and easier to decompose than macromolecular lignin;
465 and (iii) (di)methoxyphenols with a C₃ alkyl side chain (G6, S6), which are indicative of intact
466 lignin (van der Hage et al., 1993) and showed more negative loadings compared with the other G
467 and S moieties.

468 From the compounds with positive loadings on F1 (peat with a very low contribution from
469 vascular plants), 4-isopropenylphenol (Ph5) showed the highest negative loadings on F2, while
470 most polysaccharide pyrolysis products showed moderate to high positive loadings on F2.
471 Because F2 is identified as reflecting aerobic decomposition, this means that the phenolic
472 macromolecule is preferentially degraded over polysaccharides in *Sphagnum* litter, which is not
473 in agreement with the general assumption that *Sphagnum* decay is hindered by its polyphenolic
474 network (van Breemen, 1995). Abbott et al. (2013) indeed found that the abundance of markers
475 of sphagnum acid correlated with water table fluctuations, indicating aerobic degradation of
476 sphagnum acid. Thus, it is concluded that negative values on F1 reflect the contribution from
477 vascular plant species (especially the woody species, Section 4.2), while F2 reflects aerobic
478 degradation with positive values indicating a higher degree of decomposition.

479

480 4.2.2. Chemical interpretation for RMM

481 C/N and %T are positively correlated ($r^2=0.57$; $P<0.01$; $n=53$; SI_Fig. 2e), and both showed a
482 similar trend as F1 (Fig. 3; $r^2=0.44$; $n=53$; $P=0.001$ and 0.52 ; $n=53$; $P<0.01$, respectively;

483 [SI_Fig. 2fg](#)). Bulk density, on the other hand, showed similarities with F2 ($r^2=0.36$; $n=50$;
484 $P<0.01$ without the deepest three samples; [SI_Fig. 2h](#)). This supports identification of F2
485 because bulk density has been linked to decomposition in peatlands ([Charman et al., 2013](#)). This
486 suggests that in RMM the variation in C/N and %T is related mainly to the contribution from
487 vascular plants and not solely to aerobic degradation. However, although the chemical
488 transformations caused by vascular plant input and aerobic decay can be separated using factor
489 analysis, both are related to the height of the water table. An increase in the relative importance
490 of vascular plants is thus accompanied by increasing degradation of *Sphagnum* litter in the
491 acrotelm. The opposite is not necessarily true; that is, in nearly homogeneous *Sphagnum* peat
492 such as the RMM peatland, degradation of the polyphenolic network, from which sphagnum acid
493 originates, continues under aerobic conditions independently of a small simultaneous increase of
494 vascular plants. C/N values and transmission data on the other hand are undoubtedly affected by
495 aerobic decomposition, but a small increase of vascular plants may strongly influence the
496 variance of both the C/N ratio ([Table 3](#)) and %T ([Yeloff and Mauquoy, 2006](#)), thereby enlarging
497 the decomposition effect during low water table conditions. 4-Isopropenylphenol, being
498 indisputably of *Sphagnum* origin, may therefore be a good indicator of aerobic decomposition
499 (water table height) in *Sphagnum*-dominated peat. In order to test whether these results can be
500 extrapolated, depth records of a number of molecular parameters as well as C/N were compared
501 among a number of well-documented *Sphagnum*-dominated peatlands.

502

503 4.3. Comparison of vegetation and decomposition proxies with other peat records

504 4.3.1. Polyphenols

505 Several observations confirm rapid degradation of sphagnum polyphenols under aerobic
506 conditions as proposed in [Sections 4.2.1 and 4.2.2](#). First, considering the extreme dominance of
507 *Sphagnum* in the RMM peat core, it is very unlikely that the variation in 4-isopropenylphenol
508 (from 0.21 to 2.85% TIC; [Fig. 3a](#)) reflects changes in the contribution from *Sphagnum* moss to
509 the peat. This is also evident from the much higher variation in 4-isopropenylphenol in
510 *Sphagnum*-dominated peat from Harberton (HRB1 and HRB2) compared with that of
511 polysaccharides and lignin ([Fig. 3d](#)).

512 Second, the abundance of 4-isopropenylphenol rapidly declined from fresh *Sphagnum* to peat
513 organic matter from 2.7 to 0.9% TIC for RMM ([Fig. 3a](#)), or from the surface sample to the
514 deeper peat samples from 0.7 to 0.1% TIC for KM ([Fig. 3b](#)), from 0.6 to 0.2 for I% in BBF ([Fig.](#)
515 [3c](#)) and from 2 to 0.1% TIC for HRB ([Fig. 3d](#)). Other phenolic and (poly)aromatic pyrolysis
516 products also showed a decline from living *Sphagnum* material to peat in RMM (except for Ph6;
517 [SI_Table 1](#)). A large decrease of most phenolic and some aromatic pyrolysis products was found
518 in the upper part of the *Sphagnum* peatlands ([Fig. 4](#)). Although most of these pyrolysis products
519 are not specific for *Sphagnum*, their identity, abundance and behaviour suggests sphagnum
520 polyphenols as their main source. However, in peat, a contribution from other sources is
521 apparent, demonstrated by the difference in intensity of the decrease in phenolic compounds,
522 being largest in RMM (living *Sphagnum* to peat), and decreasing from HRB1 to KM (surface to
523 deeper peat; [Fig. 4](#)). This is assigned to the contribution from vascular plants that was higher in
524 KM ([Table 2](#)). When the contribution from vascular plants increases, the proportion of phenolic
525 and aromatic pyrolysis products that originates from other sources than *Sphagnum* is increasing
526 and therefore obscuring the decay of sphagnum phenols. Thus, although the decrease of phenolic

527 and aromatic products supports decay of sphagnum polyphenols, only 4-isopropenylphenol,
528 being specific for *Sphagnum*, can be assigned to *Sphagnum* decay in peat.

529

530 4.3.2. Lignin and polysaccharides

531 Contrary to phenolic pyrolysis products, polysaccharides showed an increase from living
532 *Sphagnum* to peat (RMM) and from surface peat to deeper peat (HRB1, KM) in *Sphagnum*-
533 dominated peat (Figs. 3 and 4). For the peat records discussed here, the abundance of
534 (di)methoxyphenols reflects changes in the water table, with a higher abundance indicating
535 relatively drier conditions. However, the underlying mechanism differs between graminoid and
536 *Sphagnum* peat. We suggest that in *Sphagnum*-dominated peat (RMM, HRB1, HRB2, KM, BBF)
537 higher (di)methoxyphenols contents indicate a higher contribution from vascular plants, which
538 increase under drier conditions. Conversely, in the peatlands that were dominated by graminoids
539 (PVO and HRB3), a high abundance of (di)methoxyphenols reflected the preferential decay of
540 polysaccharides over lignin ($r^2=0.59$ for PVO; SI_Table 2; Schellekens et al., 2011, 2012, 2015).
541 The absence of a correlation between lignin and polysaccharide pyrolysis products in the deeper
542 part of HRB3 is due to the increasing mineral content and several volcanic ash layers
543 (Schellekens et al., 2009), and accordingly a considerably higher degradation state in this
544 section. In highly decomposed peat, the abundance of lignin reflects relatively fresh material,
545 because after decomposition of plant-derived polysaccharides lignin is preferentially lost over
546 highly resistant aliphatic polymers (Schellekens et al., 2014).

547 The record of the summed polysaccharide pyrolysis products showed a decreasing depth trend
548 in PVO and HRB (Fig. 3de), which indicates that polysaccharides are also degraded during long-
549 term anaerobic decay, while lignin is not mineralised anaerobically (Jex et al., 2014). The

550 decrease of polysaccharides with depth seems to be related to the contribution from vascular
551 plants (Table 1), and, apart from the generally lower abundance of polysaccharides in the
552 different vegetation zones of HRB, the depth trend within these zones is absent in HRB1
553 (*Sphagnum*-dominated), minor in HRB2 (*Sphagnum*+graminoids) and clear in HRB3
554 (graminoids+woody plants) and the PVO peatland (graminoids). The peat dominated by
555 *Sphagnum* did not show this decrease of polysaccharides with depth (RMM, HRB1, KM, Fig.
556 4a-d), thus supporting the resistance to decay of *Sphagnum*-derived polysaccharides (Hájek et
557 al., 2011).

558 From factor analysis of the RMM peat pyrolysates (Section 4.2.2) it appeared that 4-
559 isopropenylphenol reflects aerobic surface decomposition while (di)methoxyphenols indicate
560 vascular plant input. The correlation between both varied between the peatlands and was rather
561 weak (Section 3.2; SI_Table 2). This indicates that water-table drop downs do not always occur
562 together with an increase of vascular plants in *Sphagnum* peat. The variable and weak correlation
563 of 4-isopropenylphenol with (di)methoxyphenols may have various causes, such as differences
564 between the peatlands in nitrogen deposition, fluctuations of the water table, plant ecology,
565 nutrient status, and human disturbance. Though from Fig. 3 it is evident that a major increase in
566 vascular plants, indicated by the (di)methoxyphenol record, occurred together with a decrease of
567 4-isopropenylphenol while the reverse is not always true. Major shifts occurred between 35–45
568 cm (RMM) and 40–50 cm (KM), and at 182, 245 (HRB1) and 410 cm (HRB2), and also the
569 variation of both proxies at these depths was much larger for 4-isopropenylphenol than for
570 (di)methoxyphenols. Thus suggesting that decomposition of sphagnum phenols is a more
571 sensitive proxy for past water table.

572

573 4.3.3. C/N ratio

574 The C/N ratio clearly differed between the peat records and generally showed increasing values
575 with increasing contribution from *Sphagnum* (Table 2). Some exceptions are found. First, the
576 low C/N ratio in the upper 40 cm of KM and the upper 1 m of BBF is probably not related to the
577 contribution from vascular plants but instead to the high nitrogen deposition in those areas,
578 indicating an overruling influence of nitrogen deposition (Section 4.1). Second, in graminoid-
579 dominated peat, the contribution from *Sphagnum* does not play a role because its abundance is
580 low. The differences between peatlands (Table 2) clearly demonstrate the prevailing influence of
581 vegetation type (i.e. source) on the C/N ratio, caused by the lower nitrogen content in *Sphagnum*
582 than in vascular plants. Therefore, the question arises to what extent botanical shifts within a
583 single vegetation type contribute to the variation in C/N, or whether most of this variation is
584 related to mass loss during decomposition.

585 Within each of the peat records, the variation in C/N is differently correlated to pyrolysis
586 parameters. In all *Sphagnum*-dominated peatlands the correlation between C/N and
587 (di)methoxyphenols (vascular plants) was weaker than that with 4-isopropenylphenol or
588 polysaccharides (SI_Table 2), which suggests that polyphenols from *Sphagnum* are more easily
589 degraded than both lignin (dimethoxyphenols) and cellulose (polysaccharide products) in
590 *Sphagnum*-dominated peat. In *Sphagnum*-dominated cores with a low contribution from vascular
591 plants (RMM and HRB1, indicated by the (di)methoxyphenol content; Table 2), 4-
592 isopropenylphenol showed a positive correlation with C/N ($r^2=0.60$ and 0.75 for RMM and
593 HRB1 respectively; SI_Table 2). In *Sphagnum*-dominated cores with a higher contribution from
594 vascular plants such a correlation was absent (HRB2) or weaker (KM; $r^2=0.49$). The better
595 correlation of 4-isopropenylphenol with C/N in HRB1 and RMM supports that a large part of the

596 variation in C/N in these peatlands is caused by decomposition rather than small increases of
597 vascular plants upon drier conditions, which is in agreement with the interpretation of 4-
598 isopropenylphenol in the factor analysis of RMM pyrolysates; [Section 4.2.1](#)).

599

600 The decrease in polyphenol and increase in polysaccharide pyrolysis products from living
601 *Sphagnum* to peat ([Sections 4.3.1 and 4.3.2](#)) provide clear evidence for the preferential decay of
602 sphagnum phenols over sphagnum polysaccharides, which should largely explain the mass loss
603 as suggested by the decrease in C/N from 80 to 45 in HRB1 ([Fig. 3d](#)), from 60 to 40 in BBF ([Fig.](#)
604 [3c](#)), and from 35 to 20 in KM ([Fig. 3b](#)) in these samples. This is in agreement with the mass loss
605 of up to 30% during the first stage of decay found for *Sphagnum* litter ([Asada et al., 2005](#)).

606 The variation in C/N within graminoid-dominated peat (PVO and HRB3) differed from that in
607 *Sphagnum*-dominated peat. The C/N ratio in both graminoid-dominated peatlands showed a
608 much lower variation and no correlation with 4-isopropenylphenol ([SI_Table 2](#)), which is
609 explained by the low contribution from *Sphagnum* to these peats. Because cellulose is
610 preferentially lost over lignin in such peat, a negative correlation of polysaccharides with C/N
611 should be expected. However, such a correlation was only weak in HRB3 ($r^2=0.43$), and even
612 slightly negative in PVO ($r^2=0.37$; [SI_Table 2](#)). Furthermore, the C/N ratio is determined mainly
613 by nitrogen in all peatlands, while in the upper 80 cm of PVO carbon also contributed to its
614 variance ([Schellekens, 2013](#)). It is not exactly clear which factors cause these differences and
615 several processes may influence these discrepancies, including nitrogen mining ([Lindahl et al.,](#)
616 [2007; Craine et al., 2007](#)), nitrogen deposition ([Heijmans et al., 2002](#)) and the preferential
617 decomposition of carbon-poor compounds such as polysaccharides (e.g. glucose: $C_6H_{12}O_6$) over
618 compounds richer in carbon such as lignin (e.g. C_3 -guaiacol: $C_{10}H_{12}O_2$). The higher contribution

619 from carbon in phenolics (e.g. sphagnum acid: C₁₁H₁₀O₅) compared with polysaccharides and the
620 preferential degradation of phenolics over polysaccharides may also contribute to the strong
621 correlation between 4-isopropenylphenol and C/N in *Sphagnum*-dominated peat.

622

623 **5. Conclusions**

624 Phenolic compounds (sphagnum acid) as well as pectin-like polysaccharides (sphagnum) have
625 been identified as causal agents for the inhibition of *Sphagnum* decay. Our results indicate
626 preferential degradation of phenolics over polysaccharides. This suggests that inhibition of
627 degradation is not caused by sphagnum acid (van Breemen, 1995; van der Heijden et al., 1997;
628 Freeman et al., 2001), which supports the claim that polysaccharides such as sphagnum provide a
629 degree of recalcitrance to the *Sphagnum* cell walls (Hájek et al., 2011). The preferential
630 degradation of phenolics over polysaccharides in *Sphagnum* litter explains the higher
631 polysaccharide content found in *Sphagnum* peat compared with *Sphagnum* plants (Moers et al.,
632 1989; Comont et al., 2006; Schellekens et al., 2009).

633 The changes in C/N values with depth are highly influenced by plant species (*Sphagnum* vs.
634 vascular plants), decomposition and atmospheric deposition. Therefore, molecular proxies are
635 essential. The fact that 4-isopropenylphenol is relatively rapidly degraded aerobically in
636 combination with its specificity for *Sphagnum* makes it a reliable proxy-indicator of past
637 hydrologic conditions in *Sphagnum* peat, because effects of vegetation changes that may occur
638 simultaneously cannot influence its abundance.

639 The different understanding of chemical parameters in the studied *Sphagnum*-dominated
640 peatlands highlights the complexity of natural systems and the difficulty to extrapolate chemical

641 parameters, it further emphasises the importance of ecological knowledge and botanical changes
642 in the environmental interpretation of peat decomposition proxies.

643

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649

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790

791 **Figure Captions**

792 **Fig. 1.** Factor loadings of F1–F2 projection obtained with factor analysis of pyrolysates from the
793 Rödmosamyran peat samples.*

794 *Al Aliphatic hydrocarbon (including *n*-alkanes, *n*-alkenes, *n*-methyl ketones, *n*-fatty acids); G
795 methoxyphenol; S dimethoxyphenol; Ph phenolic compound; Ps polysaccharide; PA
796 polyaromatic hydrocarbon; Ar aromatic; N nitrogen containing compound.

797 **Fig. 2.** Depth records of C/N, %T, bulk density, ash content and factor scores of F1 and F2 for
798 RMM.*

799 *Note that y-axis is not on scale, each sample reflects a mixture of 2 cm in the 0–65 cm interval
800 and of 10 cm in the 65–255 cm interval.

801 **Fig. 3.** Depth records of C/N and proxy-indicators for selective degradation of polyphenols,
802 cellulose and lignin for several ombrotrophic peatlands.*

803 *Note that depth is not on scale, see [Section 2.1](#) for sample heights; pyrolysis and C/N were not
804 determined on the same sub-samples for BBF; the upper sample of the pyrolysis parameters for
805 RMM reflects values of living *Sphagnum* (open point).

806 **Fig. 4.** Proportion (% TIC) of polyphenol-derived and polysaccharide pyrolysis products in
807 living *Sphagnum* and *Sphagnum*-dominated peat.*

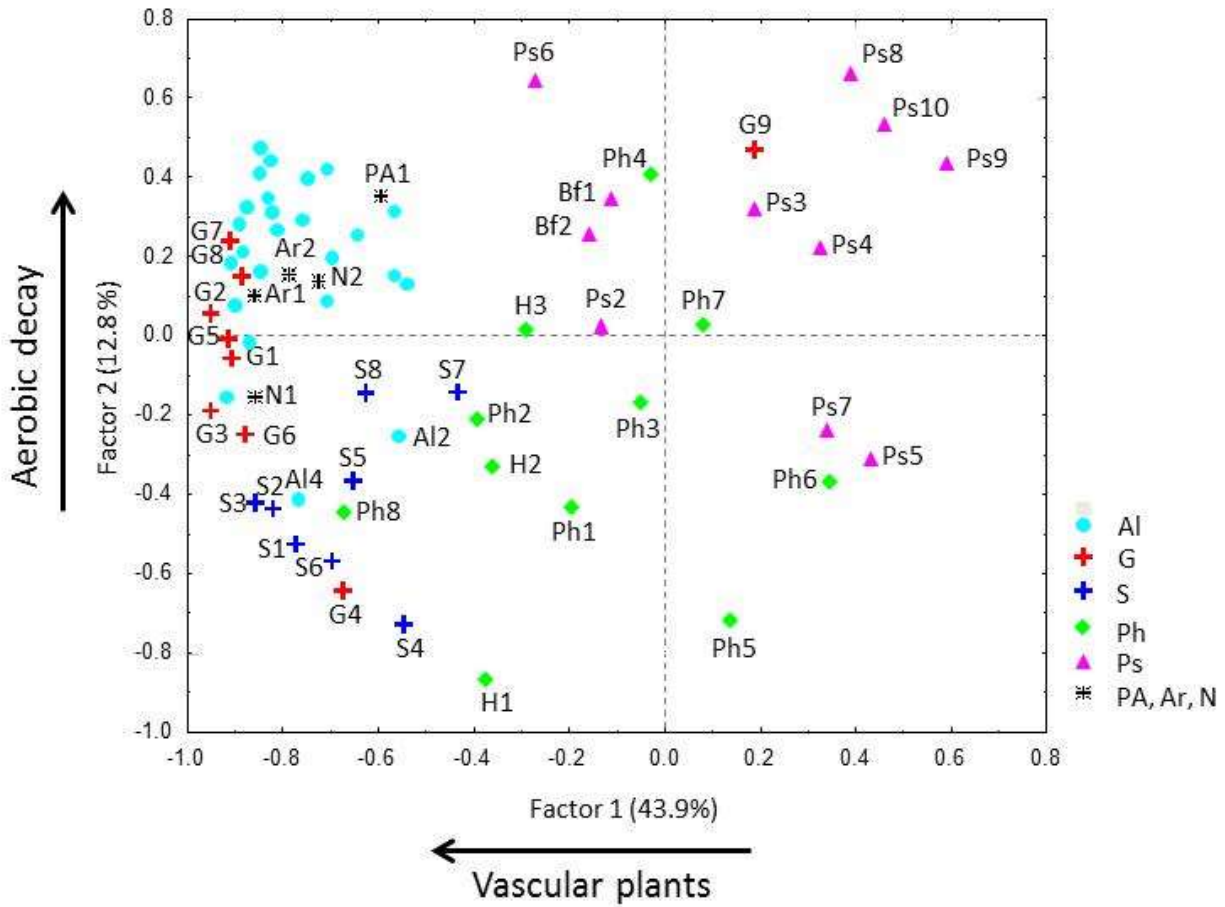
808 *Ph1 phenol; H1 4-vinylphenol; Ph5 4-isopropenylphenol; \sum Ph sum of polyphenol-derived
809 pyrolysis products; \sum Ps sum polysaccharide pyrolysis products. \sum Ph included 4-
810 isopropenylphenol, phenol, 4-ethylphenol, 4-vinylphenol in all peatlands, and additionally: C₁-
811 hydroxybiphenyl, phenolic compound (Ph4), and toluene in RMM and KM; styrene in KM; 4-
812 methylphenol, 4-acetylphenol and 4-(prop-1-enyl)phenol in RMM and HRB; 4-formylphenol in
813 HRB; and C₁-naphthalene and styrene in RMM. \sum Ps included all polysaccharide pyrolysis

814 products from [SI_Table 1](#) for RMM; for KM: compounds Ps5, Ps6, Ps9 and Ps10 ([SI_Table 1](#)), a
815 sugar compound with m/z 72+128 and 1,4:3,6-dianhydro- α -D-glucose; for HRB: Ps5, Ps7, Ps8,
816 Ps9, Ps10 ([SI_Table 1](#)), acetic acid, 2-furaldehyde, 2-hydroxy-3-methyl-2-cyclopenten-1-one,
817 1,4-anhydroxylofuranose, levogalactosan and levomannosan.

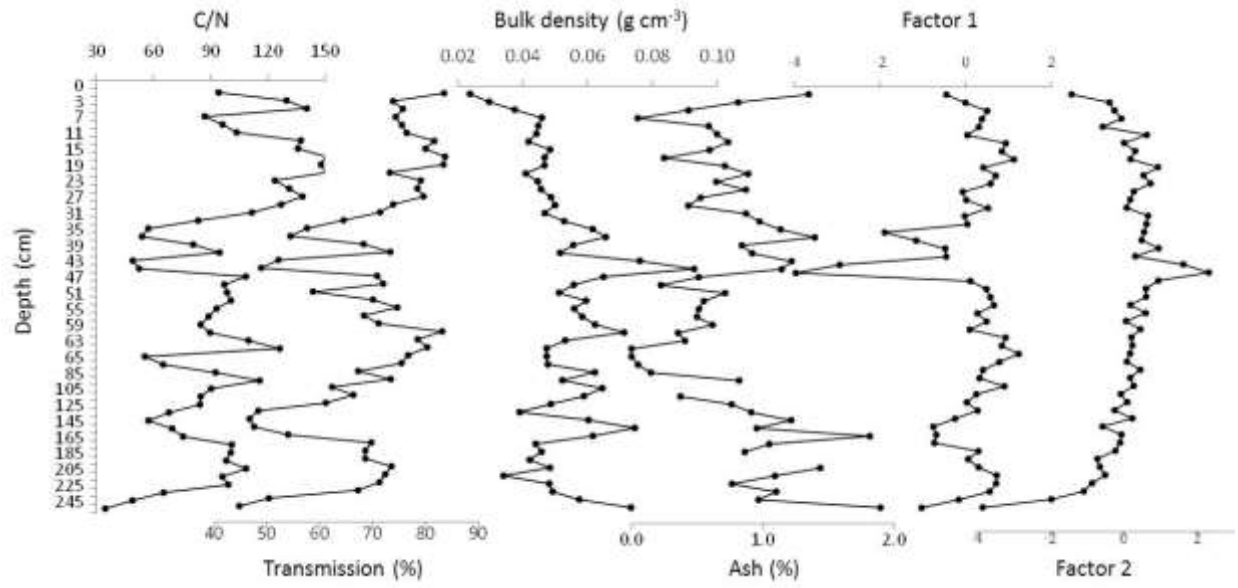
818 **SI_Fig. 1.** Depth record of the syringyl/guaiacyl ratio in RMM.

819 **SI_Fig. 2.** Correlation between chemical parameters in the RMM core.*

820 *Open symbols reflect samples that were excluded.



821
 822 **Figure 1**
 823

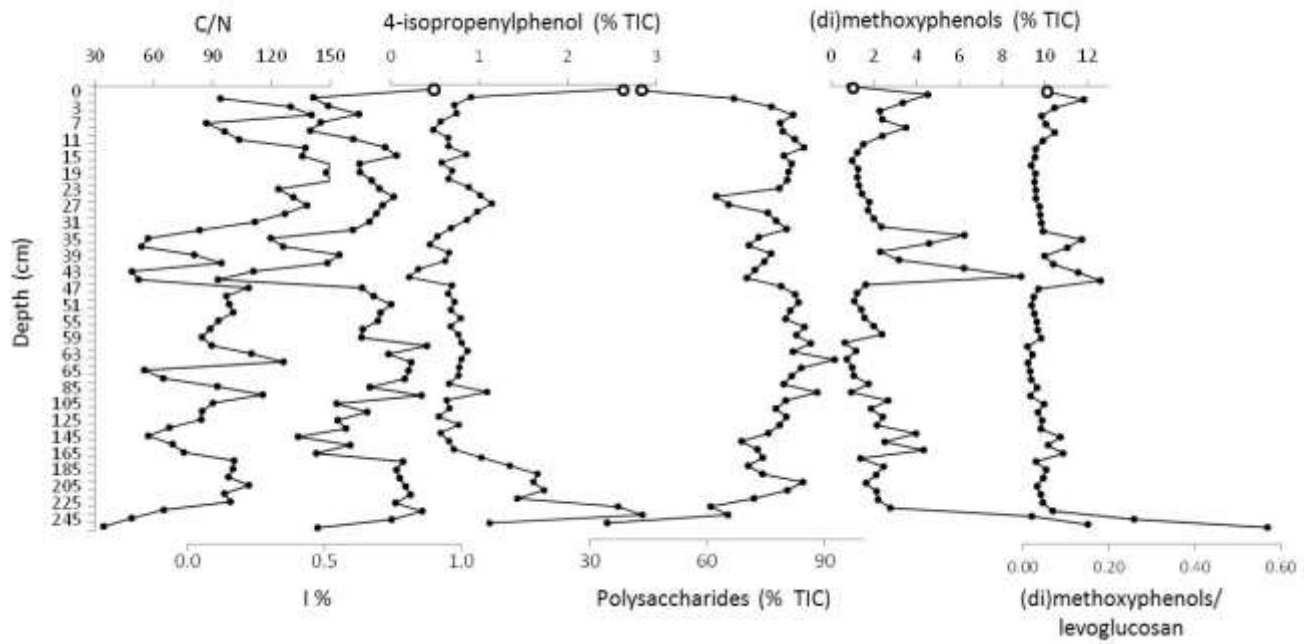


824

825 **Figure 2**

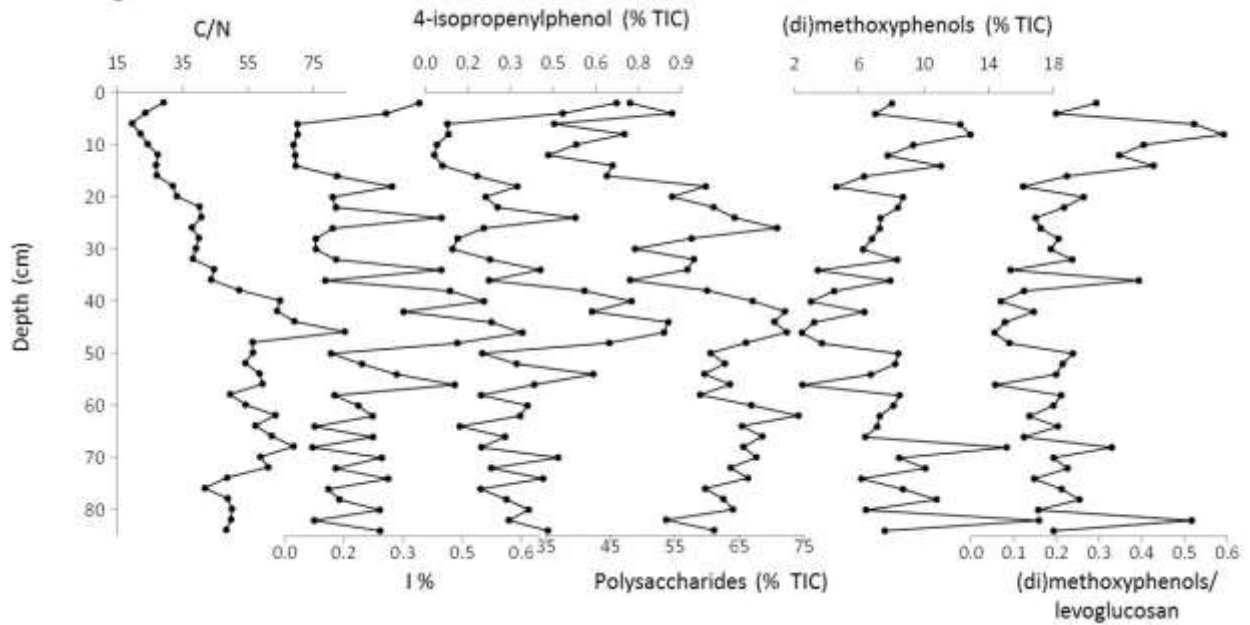
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A. Rödmosamyran



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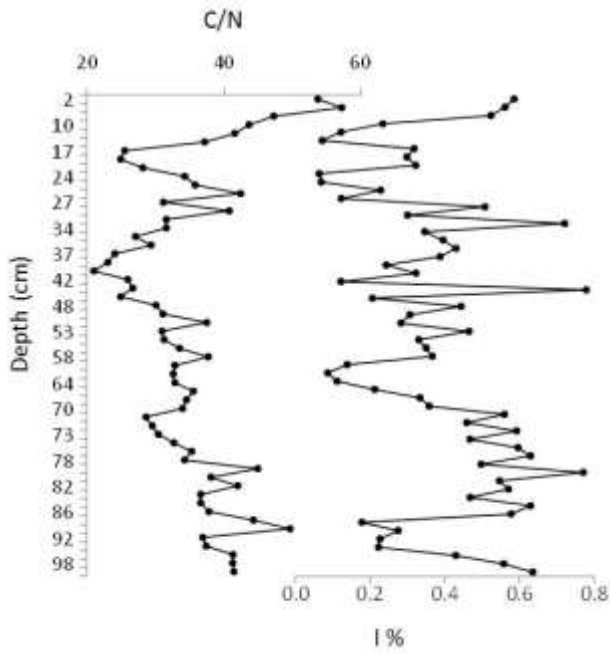
B. Königsmoor



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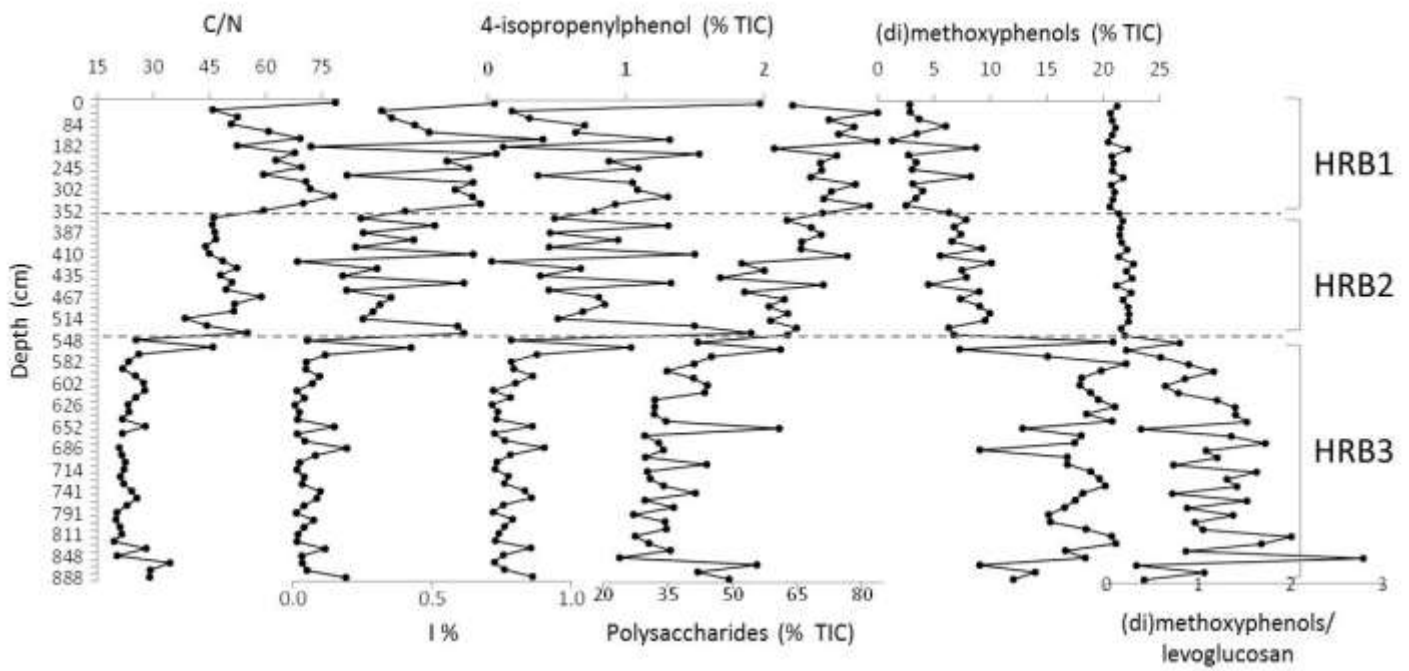
Figure 3

C. Butterburn Flow



833

D. Harberton



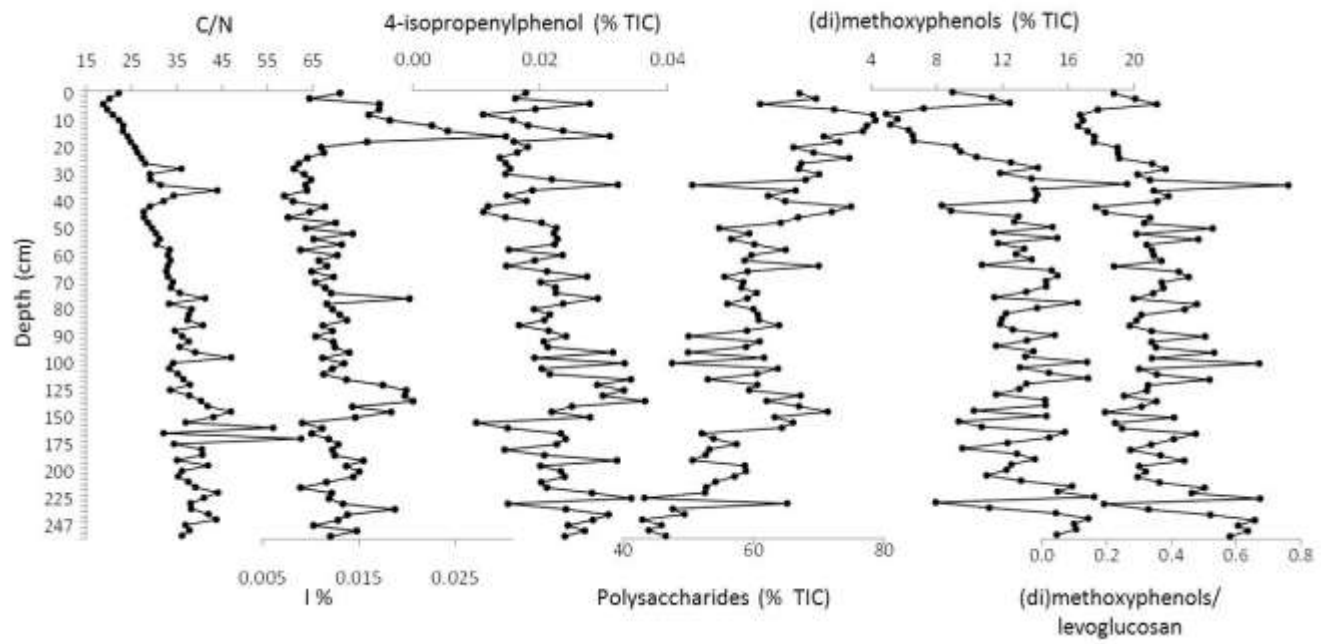
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Figure 3 Continued

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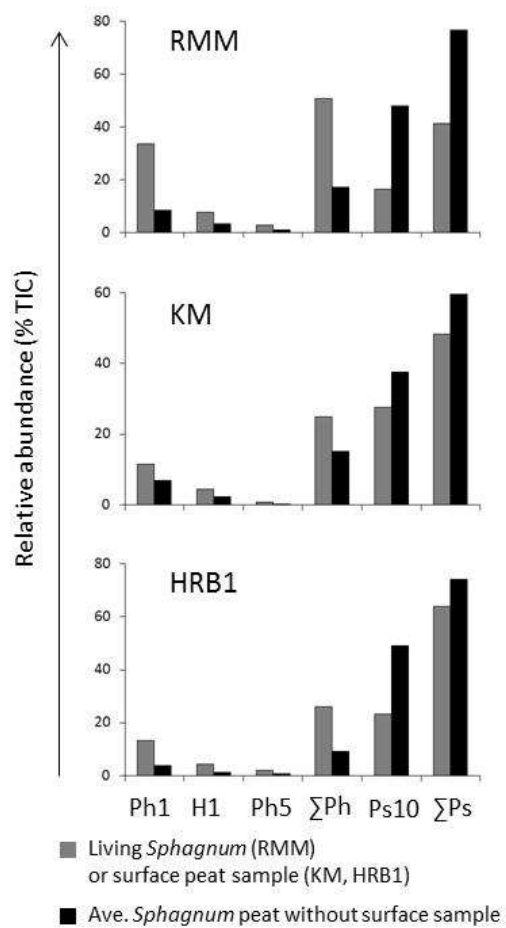
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E. Penido Vello



837
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Figure 3 Continued



840
841

842 **Figure 4**

843

844 **Table 1**

845 Characteristics of the studied peatlands

	Rödmosamyren (RMM)	Königsmoor (KM)	Butterburn Flow (BBF)	Harberton (HRB1)	(HRB2)
Location	Northern Sweden	Harz Mountains Germany	England, UK	Tierra del Fuego Argentina	
Coordinates	63°47'N 20°20'E	51°45'N 10°34'E	55°05'N 02°30'W	54°53'S 67°20'E	
Height (m a.s.l.)	40	730	280	20	
Precipitation (mm) ^a	650	790	1280	600	
Temperature (°C) ^a	2–3	8	9.2	5	
Age (cal ka BP)	0–2.8 ^b	-	850	0–3.9	3.9–5.7
Depth (cm)	0–255	0–80	0–105	0–340	340–540
Number of samples	53	42	56 ^c	15	18
Vegetation type	<i>Sphagnum</i>	<i>Sphagnum</i>	<i>Sphagnum</i>	<i>Sphagnum</i>	<i>Sphagnum</i> / Graminoids
<i>Sphagnum</i> species	<i>S. centrale</i> <i>S. subsecundum</i>	<i>S. magellanicum</i>	<i>S. magellanicum</i> <i>S. papillosum</i> <i>S. imbricatum</i>	<i>S. magellanicum</i>	<i>S. magellanicum</i>
Vascular plants	<i>Eriophorum vaginatum</i>	<i>E. vaginatum</i> Ericoids	<i>E. vaginatum</i> Ericoids <i>Narthecium ossifragum</i> <i>Rynchospora alta</i>	<i>Empetrum rubrum</i> <i>Nothofagus Antarctica</i>	<i>E. rubrum</i> <i>N. antarctica</i> <i>Juncus</i> sp.

846 ^a mean annual847 ^b estimated (see [Section 2.1](#))848 ^c carbon and nitrogen were not always determined on the same samples as those used for

849 pyrolysis

850 ^d sample at 552 cm excluded.

851

852 **Table 2**

853 Mean values of parameters that reflect degradation of lignin, sphagnum acid and cellulose in the
 854 peatlands, and values for F, probability (*P*) and homogenous groups (letters to the right of the
 855 numbers) of the ANOVA test.^a

	unit	F	<i>P</i>	RMM	KM	BBF ^b	HRB1	HRB2	HRB3	PV
C/N	-	116.9	<0.01	96 e	47 c	35 b	64 d	49 c	24 a	
I % ^c	-	148.6	<0.01	0.63 e	0.21 b	0.38 c	0.53 d	0.36 c	0.06 a	0.
4-Isopropenylphenol	% TIC	69.2	<0.01	0.92 c	0.34 b		0.90 c	0.83 c	0.16 ab	0.
Polysaccharides	% TIC	97.9	<0.01	68.9 c	59.1 b		73.5 c	62.8 b	36.8 a	61
(di)Methoxyphenols ^c	% TIC	154.2	<0.01	2.7 a	7.6 b		3.9 a	7.6 b	17.4 d	19
Levoglucosan	% TIC	86.8	<0.01	47.6 c	37.3 b		47.5 c	38.8 b	17.7 a	38
(di)Methoxyphenols/Levoglucosan ^d	-	120.1	<0.01	0.07 a	0.22 bc		0.09 ab	0.20 abc	1.10 d	0.

856 ^a Bogs with the same letter showed no significant differences; for abbreviations of the peatlands
 857 see [Table 1](#).

858 ^b Due to the limited quantification in BBF, mean values were only determined for I%.

859 ^c 4-Isopropenylphenol / (4-isopropenylphenol + guaiacol + syringol).

860 ^d In order to homogenise the quantification, (di)methoxyphenols are limited to compounds G1–
 861 G8 and S1–S8 ([SI_Table 1](#)) for all peat records.

862

863

864 **Table 3**

865 C/N values of living plant species collected at the peatlands.

Peatland	Species	<i>n</i>	C/N	C	S.D.	N	S.D.
RMM	<i>Sphagnum magellanicum</i>	3	96	44.2	0.04	0.5	0.03
	<i>S. centrale</i>	3	80	44.4	0.06	0.6	0.08
	<i>Eriophorum vaginatum</i>	2	45	47.3	0.12	1.1	0.29
	<i>Calluna vulgaris</i>	3	53	52.2	0.39	1.0	0.06
KM	<i>S. magellanicum</i>	3	48	44.0	0.08	0.92	0.03
	<i>E. vaginatum</i>	3	29	46.0	0.20	1.56	0.06
	<i>C. vulgaris</i>	3	35	49.0	0.20	1.40	0.04

866

867

868