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Influence of source vegetation and redox conditions on lignin-based decomposition proxies in graminoid-dominated ombrotrophic peat (Penido Vello, NW Spain)

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ABSTRACT

Most knowledge about the degradation of lignocellulose in natural environments is based on woody tissue and aerobic systems; however, in peatlands the contribution of graminoids to organic matter (OM) is often significant and anaerobic conditions prevail. In order to reconstruct past environmental conditions from peatlands and predict possible feedback mechanism between peatlands and climate change, a better understanding of the decomposition of graminoid tissue and the effects of anaerobic conditions on decomposition are needed. Samples (51) from the upper 1 m of the graminoid-dominated Penido Vello peatland (Xistral Mountains, Galicia, NW Spain) were analysed with pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) and ^{13}C cross polarisation magic angle spinning nuclear magnetic resonance spectroscopy (^{13}C CPMAS NMR). Carbon and nitrogen contents were also determined. Depth profiles of molecular groups identified using ^{13}C CPMAS NMR were consistent with those of depth-related distributions of quantified pyrolysis products (aliphatics, polysaccharides and aromatics). Molecular proxies were selected from peat pyrolysates to reflect the state of decay of 1) lignocellulose (the summed lignin and polysaccharide pyrolysis products, Lg and Ps, respectively), 2) lignified cellulose (levoglucosan/Ps) and hemicellulose (4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one/Ps), 3) macromolecular lignin including syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H) ratios (S/G; H/(S + G), and side chain oxidation and shortening (vanillic acid/G, syringic acid/S, 4-acetylguaiacol/G, 4-acetylsyringol/S, C_3-guaicols/G and C_3-syringols/S) and 4) non-lignin phenolic acids (4-vinylphenol/H, 4-vinylguaiacol/G). Factor analysis was applied to these proxies and 120 quantified pyrolysis products to examine the influence of possible underlying factors that could explain the observed variation. Botanical changes and several degradation stages including surface decay (both aerobic and anaerobic), aerobic sub-surface decay and depth related decay (long-term anaerobic) were identified with factor analysis and all affected the variance of lignin-based decomposition proxies. The net effect of these environmental factors on the lignin proxies was examined using their depth records. This revealed that some lignin decomposition proxies were not in agreement with the literature: 1) G and S moieties with a C_3 alkyl side chain showed no correlation with bog hydrology at the time of peat formation; 2) G and S moieties with acetyl side chains were related to both relatively dry (secondary aerobic decay) and wet (first stage of decay) conditions; 3) vanillic acid and syringic acid were related partly to ericoids (indicating dry conditions) and partly to free phenolic acids (less depleted under wet conditions); and 4) preferential decay of G over S moieties was found during the first stage of decay (both aerobic and anaerobic) and long-term anaerobic decay. These contradictions can be explained by the dominance of non-woody lignin sources (graminoids) and the prominence of anaerobic decay in peatlands. Our findings indicate that the effect of anaerobic decay and source vegetation should be considered when using lignin proxies to deduce aerobic decay in peat records.

1. Introduction

Ombrotrophic peatlands receive water and nutrients from precipitation alone. Although autogenic processes may influence the water table

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(Malmer et al., 1994), the depth of the water table within a given peatland is to a large extent dependent on precipitation. Water table depth determines oxygen availability and thereby it controls peat decomposition (Abbott et al., 2013; Philben et al., 2013). The degree of decomposition is therefore often used either as a proxy for climate (Blackford and Chambers, 1993), indicating the relative importance of drier and wetter periods, or to obtain information on the rate of organic carbon sequestration (Clymo et al., 1998).

Lignin is a major component of plant remains in peatlands, due to slow decomposition rates under anoxic conditions (Kirk and Farrel, 1987; Williams and Yavitt, 2003). Lignin is a macromolecule composed of syringyl (S), guaiacyl (G) and *p*-hydroxyphenyl (H) sub-units that are irregularly bound to each other. Its composition differs between major plant groups. In addition, non-woody tissue possesses, besides lignin, a high content of free and bound phenols that are ester- and/or ether-linked to lignin and polysaccharides in the cell wall (Hedges and Mann, 1979; Kondo et al., 1989; Lam et al., 1992; Sun et al., 2011). Apart from these source characteristics, the composition of lignin moieties can be influenced by side chain oxidation and shortening during decay (e.g. Kögel-Knabner, 2002). Thus, the composition of lignin in peat contains information about plant source and degradation state that may provide useful information about past environmental conditions (Bourdon et al., 2000; Disnar et al., 2008; Kuder and Kruge, 1998; Zaccone et al., 2008).

Knowledge of lignin transformation in soils and sediments is based mainly on aerobic decay (Thevenot et al., 2010) and woody tissue (Donaldson, 2001), while lignin research in graminoids has concentrated on forage quality (Buranov and Mazza, 2008). The effects of decomposition on graminoid tissue in peat have been studied by few authors (Kuder et al., 1998). Although anaerobic degradation of lignin proceeds at a slower rate (Opsahl and Benner, 1995) and lignocellulose can be completely degraded under anaerobic conditions (Benner et al., 1984), information about the pathways of anaerobic lignin degradation is scarce (van der Heijden and Boon, 1994; Young and Frazer, 1987). The effect of decay on the original lignin plant signal in environmental archives has been reviewed recently by Jex et al. (2014), who conclude that the interpretation of lignin proxy records demands a thorough understanding of the many processes that may be involved. In contrast, it has also been found that plant material affects the interpretation of lignin decomposition proxies in soils (Mason et al., 2009; Nierop and Filley, 2007). Because lignin composition varies between plant parts and elements of plant cells (Grabber et al., 2004), its resistance to decay may show a similar variation (Machinet et al., 2011; van der Heijden et al., 1994; Williams and Yavitt, 2003). Thus, in peatlands, with prevailing anaerobic conditions and significant contribution from graminoids, interpretation of lignin characteristics is intricate. Environmental interpretation of proxy records in peatlands is further complicated by the fact that changes in hydrology drive changes in both plant species composition and the nature and degree of decomposition (Yeloff and Mauquoy, 2006).

Pyrolysis–gas chromatography–mass spectrometry (pyrolysis–GC–MS) is applied frequently to study lignocellulosic material (Meier and Faix, 1992; Ralph and Hatfield, 1991). In addition, pyrolysis–GC–MS provides detailed information on the overall molecular composition, which benefits the interpretation of complex mixtures of organic matter in peatlands and soils. The Penido Vello peat (Galicia, NW Spain) is dominated by graminoids, with significant contributions from ericoids at some depths. A high-resolution sampled peat core in this bog has been previously studied with pyrolysis–GC–MS. Schellekens et al. (2011) combined depth records of biomarkers of peatland plants with present-day plant ecology to reconstruct bog hydrology. Assigned wet and dry periods agreed well with other European studies. Thus, the Penido Vello bog, with its dominance of graminoids and known past vegetation shifts, is particularly suited to study the effects of decomposition on the lignin composition in peat.

To separate the effects of both source material and decomposition processes, a selection of fifteen samples from the same core were previously studied in detail by Schellekens et al. (2012). Analysis of peatland plants and comparison of NaOH-extractable organic matter (reflecting decomposition) and the non-extractable residue (reflecting source vegetation; Buurman et al., 2006) allowed separation of source effects (graminoid vs. ericoid material) and different decay processes on the peat lignin composition. The results indicated that during aerobic decay at the bog surface non-lignin phenolics are rapidly lost, and alkyl side chain reduction occurred for G moieties only. Depth related lignin decay (long term anaerobic decay) caused oxidation and reduction of alkyl side chains. Sub-surface (secondary) aerobic decay during water table drawdowns caused fragmentation of lignin while lignified cellulose was less affected. The effects were sometimes contrasting, for example G moieties were preferentially degraded during aerobic decay at the surface while S moieties were preferentially degraded during sub-surface aerobic decay. The results by Schellekens et al. (2012) were based on pyrolysates from two peat fractions that were not quantified. Because analytical pyrolysis provides relative instead of absolute abundances and because relatively few samples were used, it remains unclear to which extent the results can be generalised and applied to bulk samples.

In order to evaluate the net effect of environmental factors, the present study applied a number of lignin-based parameters, extracted from Schellekens et al. (2012) to pyrolysates of 51 bulk samples from the upper metre of the Penido Vello peat core. To support the pyrolysis results, C/N and ^{13}C CPMAS NMR data were used. The purpose was to (i) identify and separate the effects of botanical shifts and several decomposition stages (aerobic and anaerobic) on the lignin composition in bulk samples, and (ii) examine the use of lignin-based decomposition proxies as a tool for (palaeo)climatic interpretation.

2. Methods

2.1. Location and sampling

Penido Vello is an ombrotrophic mire in the Xistral Mountains (Galicia, NW Spain). Location, sampling and characteristics of the bog have been described in detail by Martínez-Cortizas et al. (1997, 2002). The 3 m deep core dates back to 6000 years BC. For this study, only the samples from the upper 1 m were used (51 continuous samples of 2 cm in thickness), as this section showed better correlation between vegetation markers than the deeper part (Schellekens et al., 2011), which had been sectioned into 5 cm slices. It represents ca. 2000 years of peat accumulation. Samples were dried at 35 °C (1 week) and ground for pyrolysis without further treatment.

2.2. Vegetation shifts and characteristics in the Penido Vello peat record

The ombrotrophic section of the peat core was dominated by the graminoids *Carex durieui*, *Agrostis curtisii*, and *Molinia caerulea*, with significant contributions from ericoids (*Erica mackaiana* and *Calluna vulgaris*), *Eriophorum angustifolium*, *Festuca rubra* and mosses at some depths. Although *Sphagnum* was present in most samples its contribution to the peat biomass was low. Major vegetation shifts upon changes in hydrology have been found between *C. durieui*, *A. curtisii*, *F. rubra*, *E. mackaiana* and *C. vulgaris* (drier conditions) and *M. caerulea*, *E. angustifolium* and moss (wetter conditions; Fraga et al., 2005).

The contribution of roots to the chemistry of older peat layers may complicate a correct palaeohydrological interpretation. Plant morphology, growth characteristics, and good correlations between depth records of peatland plant biomarkers with those of decomposition proxies indicate that such root effects are negligible for Penido Vello. This aspect is discussed in detail by Schellekens et al. (2011). It is assumed that a loss of lignin phenols as dissolved organic matter is negligible because the peat is located on the summit of a mountain, without any evidence of an outlet.