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n-Alkane distributions as palaeoclimatic proxies in ombrotrophic peat: The role of decomposition and dominant vegetation

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ABSTRACT

n-Alkane distributions are frequently used as palaeoclimate proxies in ombrotrophic peat deposits. Although *n*-alkane distributions differ strongly between plant species, *n*-alkanes are not species-specific molecules. For a proper interpretation, it is important to understand the different abundances of *n*-alkanes in various plant species as well as the changes that occur when plant litter is transformed to peat. In particular because molecular markers are especially valuable in highly decomposed peat where plant remains are no longer recognizable, it is important to understand the effects of decomposition on *n*-alkane distributions.

The organic matter (OM) of a high-resolution sampled, 9 m thick, ombrotrophic peat deposit from Tierra del Fuego was analysed with pyrolysis-gas chromatography/mass spectrometry (pyrolysis-GC/MS). The same samples were analysed for carbon (C) and nitrogen (N) content. Depth profiles of C:N ratio, the summed lignin and summed polysaccharide pyrolysis products, and markers specific for *Sphagnum* spp., *Empetrum rubrum* and *Nothofagus antarctica*, enabled a reconstruction of changes in vegetation composition to be made. This reconstruction was used to examine the validity of the *n*-C_{23} alkane to indicate *Sphagnum* and the summed long chain *n*-alkanes (C_{29} and C_{31}) to reflect leaf input of the woody species *E. rubrum* and *N. antarctica*.

Our results show that even in *Sphagnum*-dominated peat, the *n*-alkane distribution is not determined by *Sphagnum* but by leaf input of *E. rubrum* and *N. antarctica*. However, good correlations between the *n*-C_{23} alkane and the *Sphagnum* marker 4-isopropenylphenol, and between the summed *n*-C_{29} and *n*-C_{31} alkanes and the marker of *N. antarctica* support that their relative change with depth can be used to indicate the abundance of these species in *Sphagnum*-dominated peat. In peat with relatively low contributions of *Sphagnum*, both *n*-alkane proxies (C_{23} and $C_{29}+C_{31}$) reflect the degree of decomposition. We evaluated the influence of *Sphagnum* dominance, decomposition, and pyrolysis on the *n*-alkane distributions in peat OM.

1. Introduction

The well-preserved stratigraphy of peat deposits can be used to reconstruct past environmental conditions (Blackford, 2000). In ombrotrophic bogs all moisture input comes from precipitation, making them particularly sensitive to variations in climate (e.g. Barber, 1993). The OM of ombrotrophic bogs stores information of local hydrology by both the composition and the degree of decay of its plant remains. Vegetation composition on peat bogs is largely determined by hydrological conditions (e.g. McMullen et al., 2004), while the degree of decay primarily depends on the supply of oxygen. Thus, both vegetation composition and the degree of decomposition of its remains are determined by depth and fluctuation of the water table.

Several studies of plant macrofossils in ombrotrophic peat have shown good correlations between past vegetation composition and local hydrology (e.g. Barber et al., 2003). Because macrofossils are often insufficiently preserved in peat deposits, recent studies have used molecular markers for a reconstruction of past vegetation. The use of biomarkers to trace the occurrence of a given plant species demands a marker to be both species-specific and recalcitrant to decomposition. Triterpenoids, wax esters (Pancost et al., 2002) and 5-*n*-alkyl-resorcinols (Xie et al., 2004) were found to meet these requirements. In addition to these specific compounds, characteristic *n*-alkane distributions are used as molecular proxies to trace plant species. *n*-Alkane distributions in peat are commonly obtained by gas chromatography/mass spectrometry (GC/MS) of the extracted lipid fraction, and compared with *n*-alkane distributions of the plant species that contribute to the peat OM (e.g. Nichols et al., 2006). However, the contribution of different plants and plant tissues to the

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peat OM (Pancost et al., 2002) and the effects of decomposition (Lehtonen and Ketola, 1993) influence the *n*-alkane distribution, and thereby complicate its interpretation.

n-Alkane distributions can also be obtained with pyrolysis-GC/MS. Pyrolysis-GC/MS gives a fingerprint of the molecular composition of the total OM, but its interpretation may be complex due to chemical rearrangements during the pyrolysis process. In addition to potential lipid biomarkers, it provides other markers, for example methoxyphenols from lignin (vascular plants) or the *Sphagnum* marker 4-isopropenylphenol (Stankiewicz et al., 1997; van der Heijden et al., 1997). Furthermore, pyrolysis-GC/MS gives information on the degree of decomposition (e.g. Kuder et al., 1998), which is important because the distribution of plant species and decomposition of their remains in peat are closely associated (Yeloff and Mauquoy, 2006).

The Harberton peat deposit (Tierra del Fuego, Argentina) represents more than 13,000 years of peat accumulation and includes a large vegetation shift from peat dominated by *Juncus* and woody species to *Sphagnum*-dominated peat (Schellekens et al., 2009 and references therein). Because studies on *n*-alkane distributions are generally related to *Sphagnum* peat, this peat record provides a good stratigraphic context for testing the validity of *n*-alkane proxies to reflect vegetation changes. Furthermore, molecular markers for *N. antarctica*, *E. rubrum* (Schellekens et al., 2009) and *Sphagnum* spp. (Stankiewicz et al., 1997; van der Heijden et al., 1997), which have been dominant plant species at Harberton according to macrofossil analysis, have been applied to the peat record. Because these plant species show large differences in their *n*-alkane distribution (Schellekens et al., 2009), changes with depth of their markers enables interpretation of *n*-alkane proxies between and within both vegetation zones (*Sphagnum* and *Juncus*-dominated peat). The objective of this study is to evaluate the influence of dominant vegetation and decomposition on the abundance and distribution of *n*-alkanes in peat OM. In addition, it offers an opportunity to validate some of the previously selected vegetation parameters by Schellekens et al. (2009).

2. Methods

2.1. Samples

Samples were obtained from a peat core (895 cm) from a raised bog located at Puerto Harberton (Tierra del Fuego, Argentina). The core was taken at a distance of 1 m from Heusser's (1989) and 20 m from that of Pendall et al. (2001). For details of the location see Markgraf (1993). The peat is primarily composed of *Sphagnum magellanicum* in the upper 600 cm, of brown mosses below 850 cm, and of *Juncus* sp. in between. In addition to pollen analysis (Heusser, 1989; Markgraf, 1993; Markgraf and Huber, 2010; Pendall et al., 2001) the core was analysed for charcoal abundance and macrofossils (Markgraf, 1993; Markgraf and Huber, 2010; White et al., 1994). Cores were taken with a 5×50 cm Russian (Macaulay) peat sampler. The upper 174 cm were sampled according to the morphology/stratigraphy. The deeper part of the core was sampled in sections of 3 cm, except at the bottom of each sub-core where the samples were 5 cm thick. The core contained three volcanic ash layers, which were sampled individually. The resulting 264 samples were air-dried, ground, homogenized and divided into sub-samples for the various analyses. Selection of samples for pyrolysis-GC/MS was based on depth, ash content, and the abundance of (wood) macro-remains, resulting in a total of 67 samples. In addition, *n*-alkane distributions of NaOH-extractable and non-extractable OM fractions of 13 of these samples previously analysed by Schellekens et al. (2009) were compared. The NaOH-extractable OM is supposed to reflect more decomposed material, and the non-extractable residue to more closely reflect relatively intact plant material (Buurman et al., 2006). Furthermore, *n*-alkane distributions of the pyrolysates of the dominant plant species at Harberton (see Sections 3 and 4.1) were compared. Bulk samples of these species were previously analysed with pyrolysis-GC/MS by Schellekens et al. (2009).

2.2. Extraction

An aliquot (0.5 g) of 13 peat samples was extracted with NaOH (0.1 M, 20 ml), shaken for 24 h under N_2 and centrifuged (1 h) at 4000 *g*. The extract was decanted and the extraction repeated a second time. The extracts were combined, acidified to pH 1 with HCl, shaken for 24 h, dialysed against distilled water (cut off 1000 D) and freeze-dried. The residues were acidified, dialysed against distilled water and freeze-dried.

2.3. Elementary analysis

All 264 samples were finely powdered (<50 μm) in an automatic agate mortar pre-cleaned with diluted HCl and MilliQ water, dried, and stored in the dark before further analysis. They were analysed for C and N by complete combustion in an auto-analyzer, Fisons CHNS-O EA-1108 for C, and LECO CHNS-932 for N.

2.4. Pyrolysis-GC/MS

The samples were pyrolysed using a Curie-Point pyrolyser (Curie temperature 600 °C) connected to a Carlo Erba GC8000 gas chromatograph. The pyrolysis products were separated on a fused silica column (Chrompack 25 m, 0.25 mm i.d.) coated with CP-Sil 51 b (film thickness 0.40 μm), with He as carrier gas. The initial oven temperature was 40 °C and the heating rate 7 °C min^{-1}. The final temperature, 320 °C, was maintained for 20 min. The GC column was connected to a Fisons MD800 mass spectrometer (*m/z* 45–650, cycle time 1 s).

Based on factor analysis of 177 pyrolysis products quantified for 13 samples of different fractions of the same peat core by Schellekens et al. (2009), 86 pyrolysis products were selected which contain information on vegetation composition and decomposition. A number of *n*-alkanes and *n*-alkenes were added, so that all chain lengths between C_{17} and C_{33} were included, which raised the number of pyrolysis products to 98. These 98 pyrolysis products were quantified for all 67 pyrograms using the peak area of the two main fragment ions for each pyrolysis product (for a list of quantified pyrolysis products and their mean abundance in the peat OM we refer to Schellekens et al. (2009)). All quantifications were checked manually. For each sample, the sum of the peak areas (total ion current, TIC) was set at 100% and relative amounts were calculated with respect to this sum. The resulting quantification gives the relative abundance of each pyrolysis product. The pyrolysis products were grouped, according to probable origin and chemical similarity, into a number of source groups: polysaccharides, aliphatic biopolymers, methyl ketones, lignins, phenols, aromatics, polyaromatics, N-compounds, steroids and triterpenoids.

3. Review of vegetation parameters

The term 'molecular marker' is used here for specific pyrolysis products of *Sphagnum* spp., *N. antarctica* and *E. rubrum*. It must be mentioned that the markers for *N. antarctica* and *E. rubrum* may only be valid within the current study; notwithstanding the good correlations with other vegetation characteristics, these markers have not been validated as species-specific pyrolysis products such as the marker for *Sphagnum*, and thus the use of the term '(molecular) marker' is provisional.

In a previous paper (Schellekens et al., 2009) parameters based on (ratios of) abundances of pyrolysis products were selected to reflect vegetation, decomposition and fire history for the Harberton peat. This selection was based on factor analysis of extractable and non-extractable fractions of 13 peat samples and on analysis of modern plant species growing on this bog. A number of the selected vegetation parameters and their interpretations are given in Table 1. Specific markers for *Sphagnum* spp., *E. rubrum* and *N. antarctica* were