The disappearance of *Sphagnum imbricatum* from Butterburn Flow, U.K.

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Abstract

The disappearance of the previously abundant moss species *Sphagnum imbricatum* has been investigated at Butterburn Flow, northern England, using organic geochemical, elemental, macrofossil, pollen and testate amoebae analyses. Variations in the assemblage of peat-forming plants were tracked using the macrofossil distributions as well as the relative chain lengths of *n*-alkanes and concentrations of 5-*n*-alkylresorcinols and triterpenols. No significant changes to the vegetation assemblage could be detected prior to the loss of *S. imbricatum*. Variations in water depth were reconstructed using a testate amoebae transfer function and inferred qualitatively using bulk elemental composition and biomarkers for changing redox conditions in the bog sub-surface: the degree of isomerisation in the C_{31} hopanes, and the concentrations of bishomohopanol and archaeol. Pollen analysis reconstructed the landscape surrounding the mire and identified indicators for human disturbance. The results suggest that bog surface wetness increased with the transition from *Sphagnum imbricatum* to *Sphagnum magellanicum*, but the increase was not large and *S. imbricatum* had previously survived similar periods of wetness. However, the loss of *S. imbricatum* coincides with increasing human disturbance surrounding the bog, which may have altered nutrient inputs to the bog surface from agriculturally derived dust, to the detriment of *S. imbricatum* but to the benefit of *S. magellanicum* and *Eriophorum vaginatum*. It is proposed here that the stresses imposed by the combination of changing nutrient inputs and a rapidly rising water table drove the disappearance of *S. imbricatum* from Butterburn Flow at ca. cal. AD 1300.

1. Introduction

One of the most dramatic features of north-west European late Holocene peat archives is the disappearance of the previously abundant moss species *Sphagnum imbricatum (S. austinii)* from British, Irish and German peatlands (e.g. Barber, 1981; Barber et al., 2003; Dickson, 1973; Godwin and Conway, 1939; Green, 1968; Langdon and Barber, 2005; Mauquoy and Barber, 1999a; Mauquoy et al., 2002; Overbeck, 1975; Smith, 1985; Stoneman et al., 1993; van Geel and Middeldorp, 1988; Wimble, 1986). At some sites the disappearance is abrupt, occurring over a period that may span only decades, and generally results in a shift of the *Sphagnum* assemblage towards *Sphagnum magellanicum*, *Sphagnum* section *Cuspidata*, *Sphagnum papillosum* or *Sphagnum* section *Acutifolia* (Mauquoy and Barber, 1999a; van Geel and Middeldorp, 1988). The timing of the disappearance varies between sites, but typically occurs between cal. AD 1030 to cal. AD 1730 (e.g. Barber et al., 2003; Mauquoy and Barber, 1999a; van Geel and Middeldorp, 1988). The resulting scarcity of *S. imbricatum* at the present day has proved problematic for developing quantitative macrofossil transfer functions for palaeo-environmental reconstructions, because the species is now restricted to only part of its former niche (Stoneman et al., 1993). It is now found in the high levels of hummocks and well above the water table (e.g. Flatberg, 1986), in contrast to its much broader past distribution which includes associations with known hydrophilous *Sphagnum* species (Stoneman et al., 1993). These discrepancies between the modern and past distributions of *S. imbricatum* complicate the understanding of the possible environmental changes that may have driven its disappearance.

At many sites, the decline of *S. imbricatum* is associated with increased mire surface wetness (Barber, 1981; Mauquoy and Barber, 1999a; Mauquoy et al., 2002; Stoneman, 1993). Human interference related to drainage, burning or grazing, has also been linked to the loss of *S. imbricatum* (e.g. Pearsall, 1956; Piggot and Piggot,

1963); however, there is evidence that *S. imbricatum* can withstand such disturbance (Chapman and Rose, 1991; Lindsay et al., 1988; Slater and Slater, 1978). On ombrotrophic mires, where the primary nutrient source is airborne through precipitation and/or aeolian deposition (e.g. Aerts et al., 1992), the disappearance of *S. imbricatum* has been linked to variations in nutrient supplies to the bog surface. Different nutrient tolerances have been observed between peat-forming plant species, particularly for the growth-limiting nutrient, nitrogen (e.g. Aerts et al., 1992; Moore et al., 2005; Rudolph and Voigt, 1986). Van Geel and Middeldorp (1988) proposed that nitrate inputs at Carbury Bog, Ireland, increased after intensified human disturbance of the surrounding land, to the detriment of *S. imbricatum.* In addition to these environmental influences, competition between species may also have influenced the *Sphagnum* assemblage during the late Holocene, with the highly competitive *S. magellanicum* (e.g. Green, 1968) perhaps forcing *S. imbricatum* from the mires (Mauquoy and Barber, 1999a; Stoneman et al., 1993).

Previous investigations of the disappearance of *S. imbricatum* have applied bulk elemental composition, plant macrofossils, testate amoebae and pollen analyses to evaluate potential driving mechanisms. Here, we expand on this multi-proxy approach to investigate the disappearance of *S. imbricatum* from a British site, by coupling these techniques with organic geochemical analyses to gain a detailed understanding of the factors driving the loss of *S. imbricatum.*

Organic geochemical (biomarker) analyses have recently shown great potential to reconstruct changes in vegetation assemblages, temperature and mire surface wetness in ombrotrophic peat profiles. Biomarker analyses of peat-forming plants have identified a number of compounds, with variable specificity, which may be used to identify families, genera or even species of vegetation inputs. These include straight chain hydrocarbons (*n*-alkanes), whose chain-lengths differ between

Sphagnum and non-*Sphagnum* species (Baas et al., 2000; Nott et al., 2000); 5-*n*-alkylresorcinols, that in peat-forming plants have been found only in sedges (Avsejs et al., 2002); and a group of triterpenoids, the taraxeroids, which have been identified in Ericaceae rootlets (Pancost et al., 2002). A positive relationship between the deuterium/hydrogen isotopic composition of individual *n*-alkanes and growing season temperatures from historical data sets spanning the last ca. 220 years has also been identified (Xie et al., 2004; Xie et al., 2000). As water table depth influences oxygen and hydrogen availability near the peat surface and thus affects the microbially mediated oxidation, reduction and dehydration transformations of organic matter within the bog, biomarkers may also aid the reconstruction of past water table variations (Pancost et al., 2003). For example, acid-catalysed stereochemical transformations in hopanes have been linked to changing bog surface wetness (Pancost et al., 2003), and biomarkers specific to the Archaea have been found in their highest concentrations within the catotelm, the perennially saturated and anoxic peat deposit that lies beneath the water table (Weijers et al., 2004). In contrast, biomarkers of aerobic microbial populations are expected to relate to the aerated and periodically saturated upper layer covered by the living peat-forming vegetation that forms the acrotelm.

Described herein are the results of a multi-proxy investigation into the disappearance of *S. imbricatum* at the Butterburn Flow mire in northern England. This site forms the British member of the suite of European bog profiles collected by the ACCROTELM programme. A previous investigation of macrofossil and testate amoebae records at Butterburn Flow detected a rapid demise of *S. imbricatum*, but did not explore the causes nor constrain the timing of this transition (Hendon and Charman, 2004). We combine bulk elemental composition, macrofossil and pollen analyses with a refined testate amoebae water table depth transfer function (Charman et al., 2007) and with established and new biomarker proxies focussing on lipid distributions. The primary

aim of the study is to explore the underlying factors responsible for the disappearance of *S. imbricatum*, in particular addressing whether these can be attributed to (a) changing mire wetness, or (b) the impact of human management of the wider landscape surrounding the mire.

2. Methods

2.1 Study site and sampling

The ombrotrophic mire of Butterburn Flow (Figure 1) lies within the Border Mires Special Area of Conservation (SAC) in northern England, at an altitude of c. 280 m (latitude: 55° 5' N, longitude: 2° 30' W). It lies near to, but beyond the influence of, the forestry plantations of Kielder and Spadeadam Forests, with hydrological boundaries defined by the River Irthing and Lawrence Burn (Hendon and Charman, 2004). It is one of only four peat bogs in the UK which is transitional between an ombrotrophic raised bog and a patterned mire (narrow ridges divided by open water pools). The vegetation is dominated by *Sphagnum* mosses (*S. magellanicum* and *S. papillosum*), with constant *Erica tetralix*, *Narthecium ossifragum* and *Vaccinium oxycoccus*. *Andromeda polifolia* is also abundant, with some *Calluna vulgaris* occurring on hummock microforms. Hollow microforms possess *Rhynchospora alba*.

A core from the top 1 m of the mire was recovered using a Wardenaar corer (Wardenaar, 1987). A further 3 m was recovered using a Russian corer (7 cm x 50 cm). The coring site (maximum peat depth, 797 cm) was chosen after establishing the depth and nature of the peat stratigraphy by sinking a series of 6 test boreholes on two intersecting transects (see the sampling protocols detailed in Barber et al., 1998). One-centimetre slices were taken and sub-sampled for macrofossil, testate amoebae, pollen and biomarker analysis. Prior to analysis, the sub-samples for biomarker and elemental analyses were stored in a freezer at -20ºC. The remaining sub-samples were stored in a refrigerator at 4ºC until analysis.

2.2 Plant macrofossil analysis

Identification and quantification of plant macrofossils followed the protocol developed for the ACCROTELM programme, combining the Quadrat and Leaf Count macrofossil analysis (QLCMA) technique (Barber et al., 1994; Barber et al., 1998; Mauquoy and Barber, 1999b), and the technique described by Speranza et al. (2000) and Mauquoy et al. (2002). A 5 cm^3 peat sub-sample was gently boiled with 5% KOH (to dissolve humic and fulvic acids) and disaggregated on a 125 µm sieve using distilled water. Macrofossils retained on the sieve were transferred to a glass beaker with enough distilled water to float the remains. These were scanned using a low power (x10 to x50) stereo-zoom microscope. Well-preserved epidermal tissues of monocotyledon species were identified using x400 magnification. A random selection of at least 100 *Sphagnum* leaves were identified at x400 magnification to the lowest taxonomic level, and are expressed as percentages of the total identifiable *Sphagnum.*

2.3 Pollen and testate amoebae analyses

A cylindrical sampler of 1.1 cm diameter was used for pollen sample selection. Pollen samples were treated with KOH and acetolysed (Fægri and Iversen, 1989). To estimate concentrations, tablets with *Lycopodium clavatum* L. spores were added to the samples (Stockmarr, 1971). Testate amoebae identification and quantification followed the ACCROTELM programme protocol, based upon Charman et al. (2000). A 2 cm^3 sub-sample from each level was soaked in distilled water for 3-4 h or overnight, boiling for 10 min if necessary to aid disaggregation. To give quantitative concentration data, two tablets of the exotic marker innoculum *Lycopodium clavatum* L. were added, having been dissolved in dilute HCl then diluted with distilled water before addition to the sample. Each sample was then washed through a 300 um mesh, then back-sieved through 15 um to remove the fine fraction detritus. Material

from the fraction 15-300 um were centrifuged at 3000 rpm for 5 min, decanted, and mounted in water and analysed immediately. Past water table depths were reconstructed using the transfer function described by Charman *et al.* (2007), which is based on analyses of modern testate amoebae from 8 sites along two transects from Ireland to Estonia and from the Faeroe Islands to Spain. Water table depths on raised mires vary throughout the year, reaching minimum levels during the driest periods of the summer months, with rapid recovery during rainfall events. Measured water tables in the modern training set were taken during the growing season, but excessively dry periods were avoided so that the reconstructed water table depths represent approximate average conditions. Although we refer to absolute values (cm depth) in the text, these should be interpreted as a measure of relative wetness changes.

2.4 Elemental analyses

Freeze-dried sub-samples of c. 3-4 cm^3 volume were homogenised and ground to pass through a 0.5 mm sieve. Aliquots were analysed in duplicate using a Carlo-Erba EA1108 elemental analyser to determine percentage carbon, nitrogen, and hydrogen. Percentage inorganic carbon was determined using a Strohlein Instruments Coulomat 702 carbon analyser adapted to analyse CO_2 liberated from H_3PO_4 digestion. Elemental compositions were determined as percent of the dry weight of peat analysed. Total organic carbon was calculated as the difference between total percentage carbon and total inorganic carbon.

2.5 Biomarker analyses

Lipids were extracted on sub-samples of the freeze-dried and homogenised sediment using repeated ultrasonication with dichloromethane/methanol (1:1, v/v). The total lipid extracts were hydrolysed with a 0.5 M methanolic sodium hydroxide solution for 1 h at 70ºC, and the neutral fraction was recovered using hexane. The neutral

fractions were further fractionated into apolar and polar fractions using alumina columns, eluting with hexane/dichloromethane (9:1, v/v) and then methanol/dichloromethane (2:1, v/v). All polar fractions were derivatised prior to analysis using *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylsilyl chloride (Sigma Aldrich) to yield the corresponding trimethylsilyl ethers. All fractions were analysed by gas chromatography (GC) and GC/mass spectrometry (GC/MS) following exactly the procedures described by Avsejs et al. (Avsejs et al., 2002).

2.6 Chronology

Radiocarbon dates around the interval 90 – 50 cm are listed in Table I. The age-depth model has been calculated using Bpeat software, as described fully in Yeloff *et al.* (2006). All samples were analysed at 2 cm intervals, corresponding to an average temporal resolution of ca. 22 years between sampling points given that peat accumulation rates may have varied slightly through the interval of study (Yeloff et al., 2006). Biomarker and elemental analyses were performed at 1 cm intervals for a selection of samples spanning the disappearance of *S. imbricatum*.

3. Results

3.1 Macrofossils, pollen and testate amoebae

The Butterburn Flow macrofossil record (Figure 2) records a rapid replacement of *S. imbricatum* by *S. magellanicum* between 70-72 cm depth. The *Sphagnum imbricatum* mosses identified in the peat profile are all likely to be *Sphagnum austinii*, since the site is a nutrient poor, acid peat bog. *Sphagnum affine* species occur in minerotrophic fens and/or in transitions from fen to bog ecosystems, therefore the sub-fossil branch leaves of *Sphagnum imbricatum* are unlikely to belong to this species. The switch in dominant *Sphagnum* species occurred within c. 22 calendar years or less, centred on cal. AD 1295. The transition is marked by a discrete interval at 72 cm dominated by

the monocotyledons, particularly *Eriophorum vaginatum* (Figure 2). Below 72 cm, *S. imbricatum* dominated the total macrofossil assemblage, with percentage abundances generally exceeding 70%. With the disappearance of *S. imbricatum*, total *Sphagnum* inputs fall to around 50%, and monocotyledons and ericaceous species become significant contributors to the macrofossil assemblage (Figure 2).

The proportion of arboreal pollen decreases from 90 to 85 cm then remains relatively constant until 76 cm when it decreases further (Figure 2). *Corylus* starts to decrease at 76 cm, while *Alnus* begins to decrease at 75 cm. *Betula* remains relatively constant until 73 cm, where it rises abruptly. *Quercus* rises slightly at 76 cm. Poaceae, *Plantago lanceolata* and *Rumex acetosella* abundances increase significantly at 76 cm, and remain at relatively high levels until 69 cm, where arboreal pollen types start to increase in abundance again. Between 75 and 72 cm all pollen taxa also show an increase in their absolute concentrations, maximising at 74 cm (ca. cal. AD 1295). As all pollen types show this trend it cannot have been driven by changes to the vegetation assemblage. Rather, the increased pollen concentrations suggest that peat accumulation rates fell during this interval.

The water table depth reconstruction from the testate amoebae reveals a gradual increase in water table depth between 90 and 74 cm depth in the Butterburn Flow profile (Figure 2). At 74-70 cm there is a shift towards a higher water table, with mean values above 74 cm of ca. 7 cm water depth (Figure 2).

3.2. Elemental composition

Total organic carbon (TOC) percentages at Butterburn Flow are high, ranging from 45-50 % of the dry weight of the peat (Figure 3). Total percentage nitrogen is low, generally below 1.6 % (Figure 3). As a result, organic carbon/nitrogen (C/N) is high, between 30 and 50, and is strongly and inversely correlated with percentage nitrogen.

The highest C/N values are found below 79 cm, above which both the mean value and variability in C/N falls to a mean of c. 35, and a subtle but progressive decrease in C/N occurs above 66 cm. There is a pronounced decrease in C/N between 74-71 cm, where both TOC and total percentage nitrogen are high (Figure 3).

3.3. Lipid biomarkers

The solvent extractable lipid content of the Butterburn Flow peat is high, at around 5 % dry weight. We focus here on a suite of lipids that have previously been linked to either specific peat-forming vegetation types or to chemical transformations/microbial activity driven by changing redox conditions (Table II). The dominant lipids in the peat are higher plant derived sterols and *n*-alkanols, however, previous work has shown that these lack the specificity of other components that are the main focus of this investigation, namely: n-alkanes, hopanes, triterpenes, triterpenols, hopanols, 5-*n*-alkylresorcinols and archaeol. The mean concentrations of the latter components are given in together with elemental concentrations (Table II).

3.3.1 n-Alkanes

The dominant *n*-alkanes at Butterburn Flow have chain lengths between C_{21} to C_{33}, with a mean total concentration of 140 µg g^{-1} (Table II). There is a strong odd-over-even preference in *n*-alkane chain lengths, consistent with a higher plant origin. The C_{31} homologue dominates for the entire interval of study, with concentrations generally falling in the range 50-100 µg g^{-1}. A significant contribution is also made by the C_{33} *n*-alkane (generally 15-60 µg g^{-1}). The shorter chain homologues are dominated by *n*-C_{23} and *n*-C_{25}, but these occur at much lower concentrations (<40 µg g^{-1}).

Below 72 cm the concentration of the C_{23} n-alkane ranges from 30-40 μg g^{-1}, but falls dramatically to mean concentrations of ca. 15 μg g^{-1} and becomes less variable above 72 cm (ca. cal. AD 1317, Figure 4). Similar trends occur in when comparing the relative inputs of C_{23}, C_{25} and C_{31} n-alkanes, as shown by the fall in n-C_{23}/n-C_{25}, although with an apparently anomalously high value at 72 cm (Figure 4), and in n-C_{23}/n-C_{31}, although the decrease in the latter takes place at a slightly lower depth of 76 cm (Figure 4).

High concentrations of the C_{31} n-alkane occur between 75-71 cm (Figure 5) and increase progressively above 62 cm. The concentration of the C_{31} n-alkane relative to other long-chain homologues is expressed as n-C_{33}/n-C_{31} and as the average chain length of the long chain n-alkanes, ACL_{27-33} (Figure 5). Both highlight the dominance of n-C_{31} at Butterburn Flow, with highest values occurring below 74 cm and between 66-65 cm.

3.3.2 Triterpenoids

The triterpenoids are significant components of the Butterburn Flow lipid extracts, with a mean total concentration of 750 μg g^{-1} (Table II). The triterpenols dominate, particularly taraxerol (taraxer-14-en-3β-ol; up to 500 μg g^{-1}). Two degradation products of the triterpenols are also found at Butterburn Flow, albeit at low concentrations (<60 μg g^{-1}): taraxer-14-ene (from taraxerol) and taraxast-20-ene. The highest concentrations of the triterpenols (>700 μg g^{-1}) are found between 88-84 cm and 72-52 cm (Figure 5).

3.3.3 5-n-Alkylresorcinols

The 5-n-alkylresorcinols at Butterburn Flow all contain alkyl side chains with lengths of C_{19}, C_{21}, C_{23} and C_{25}, with the C_{23} alkylated homologue always the most abundant.

For the majority of the sections, 5-*n*-alkylresorcinols are not detectable. However, their concentrations are high at 72 and 71 cm (>1000 $\mu g\ g^{-1}$) and also increase above 60 cm, although values are relatively low at <400 $\mu g\ g^{-1}$ (Figure 5).

3.3.4 Hopanoids

Hopanoids are significant components of the total lipid extracts, with mean total concentrations of 570 $\mu g\ g^{-1}$ (Table II). The dominant hopanol recovered was bishomohopanol (17β(H),21β(H)-dihomo-hopan-32-ol), with maximum concentrations of 1330 $\mu g\ g^{-1}$ at 56 cm (Figure 6). Hopanes form only minor components, and are dominated by the C_{31}-hopanes. Both the 17α(H),21β(H) and 17β(H),21β(H) C_{31}-hopane epimers are present. The $\delta^{13}C$ values of the two C_{31}-hopanes at Butterburn Flow range from -25.9 ‰ to -26.8 ‰ and are enriched relative to the C_{23} and C_{31} *n*-alkanes (mean values of -31.9 ‰ and -31.5 ‰, respectively).

The bishomohopanol depth profile can be broadly divided into three horizons (Figure 6): between 84-78 cm concentrations are below the mean (<490 $\mu g\ g^{-1}$), between 76-60 cm concentrations are close to the mean, and, finally, above 60 cm concentrations reach their maxima for the interval of study. Above 78 cm relatively low concentrations of bishomohopanol occur on two occasions of a short duration: at 72 cm and at 60-58 cm (Figure 6).

The relative concentrations of the two C_{31}-hopane isomers are expressed as $\beta\beta/(\alpha\beta+\beta\beta)$ (Pancost et al., 2003). At Butterburn Flow, $\beta\beta/(\alpha\beta+\beta\beta)$ is relatively stable and low below 74 cm. Above 74 cm, there is a progressive increase from 0.09 at 74 cm to 0.12 at the top of the section (Figure 6).

3.3.5 Archaeol

Archaeol is present in low concentrations at Butterburn Flow (5-40 μg g^{-1}). The depth profile of archaeol concentrations can be broadly divided into three intervals (Figure 6): below 78 cm concentrations are low; between 78-64 cm concentrations are moderate; and above 58 cm concentrations reach their maxima. Exceptions to the overall increase in archaeol concentration through time occur at 72 cm and at 60-58 cm, where concentrations are very low.

4. Discussion

We have examined the past environmental history of Butterburn Flow associated with the loss of *S. imbricatum* and the emergence of *S. magellanicum* in the late 13th century using a combination of macrofossil, pollen, testate amoebae, bulk chemical and molecular proxies. We focus here on evidence for changes to: (i) the peat-forming plant assemblage, (ii) bog surface wetness, and (iii) nutrient inputs as a result of human disturbance in the landscape surrounding Butterburn Flow.

4.1. Evidence for a changing vegetation assemblage

The disappearance of *S. imbricatum* at Butterburn Flow is a rapid event in the macrofossil record, occurring between 74-72 cm, cal. AD 1295. This is followed by an increased contribution of monocotyledons and Ericaceae to the macrofossil assemblage, and the establishment of *S. magellanicum* as the dominant *Sphagnum* species. These trends are also clearly reflected in the absolute concentrations and chain-length distributions of the *n*-alkanes, which show little variation below 74 cm but large transitions focussed in the 76-72 cm horizon (Figure 4).

At Butterburn Flow there is a strong correlation between the low molecular weight *n*-alkanes (C_{23} and C_{25}) and *Sphagnum* macrofossil abundance. The shift from *S. imbricatum* to *S. magellanicum* is tracked by decreases at 76-72 cm in the absolute concentration of the C_{23} *n*-alkane, and in *n*-C_{23}/*n*-C_{25} and *n*-C_{23}/*n*-C_{31}. The reduction

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in C_{23} associated with lower *Sphagnum* macrofossil records are consistent with previous studies that identified the C_{23} *n*-alkane as a biomarker for *Sphagnum* in general (Baas et al., 2000; Nott et al., 2000). Interestingly, at Butterburn Flow, both *n*-C_{23}/*n*-C_{31} and *n*-C_{23}/*n*-C_{25} appear to record specific *Sphagnum* species. The dramatic but short-lived decline in total *Sphagnum* to only 5% at 72 cm is not recorded in *n*-C_{23}/*n*-C_{31}, and reduced *n*-C_{23}/*n*-C_{31} variability above 72 cm contrasts with increased variability in *Sphagnum* macrofossil abundance (Figure 4). These relationships probably reflect a sensitivity of *n*-C_{23}/*n*-C_{31} to the unusual *n*-alkane distributions in *S. magellanicum*, which contains high concentrations of both the C_{25} and C_{31} *n*-alkanes (Baas et al., 2000; Corrigan et al., 1973; Nott et al., 2000). Due to these specific characteristics of *S. magellanicum*, both *n*-C_{23}/*n*-C_{31} and *n*-C_{23}/*n*-C_{25} are particularly effective at recording changes in the dominant *Sphagnum* species at Butterburn Flow.

Despite the potential contribution of the C_{31} *n*-alkane from *S. magellanicum* above 72 cm, the relative chain length distributions of the high molecular weight *n*-alkanes (*n*-C_{33}/*n*-C_{31}, and ACL_{27-33}) show trends that broadly reflect the *n*-alkane distributions found in monocotyledons (high C_{31} concentrations) and Ericaceae (high C_{33} concentrations). Low values in both *n*-C_{33}/*n*-C_{31}, and ACL_{27-33} between 74-72 cm highlight the increased concentration of the C_{31} *n*-alkane in the macrofossil horizon dominated by *E. vaginatum* (Figure 5). This trend is also clear in the high concentrations of the 5-*n*-alkylresorcinols, which are present in Cyperceae such as *E. vaginatum* but absent from *Sphagnum*, lichens and Ericaceae (Avsejs et al., 2002). All records of monocotyledon inputs to Butterburn Flow show a rapid and large increase centred on the transition between *S. imbricatum* and *S. magellanicum*, and generally higher inputs in the *S. magellanicum* horizon.

The remaining macrofossil input to Butterburn Flow is from the Ericaceae, which can be tracked using the relative distributions of the high molecular weight *n*-alkanes (*n*-

$C_{33}/n\text{-}C_{31}$, and $ACL_{27\text{-}33}$) and the triterpenols. These trends are consistent with the high concentrations of the C_{33} n-alkane and the triterpenols reported in Ericaceae, particularly *Erica tetralix* and *Calluna vulgaris* (Nott et al., 2000; Pancost et al., 2002). At <20%, ericaceous remains form a minor component of the Butterburn Flow macrofossil assemblage, yet the triterpenoids are found in higher concentrations than the n-alkanes (Table II). The only significant difference between triterpenol concentrations and Ericaceae macrofossil inputs occurs between 76 to 72 cm. Here, the triterpenols are present in high concentrations but ericaceous macrofossils are either absent or in very low abundance (Figure 5). This suggests that during deposition of the 76-72 cm horizon, Ericaceae could have continued to be an important part of the peat-forming plant assemblage, but their macrofossil remains have been degraded.

Neither the macrofossil nor biomarker records identify any significant change to the vegetation assemblage on Butterburn Flow prior to the disappearance of *S. imbricatum*. The transition from a *S. imbricatum*-dominated assemblage to one comprised of *S. magellanicum*, monocotyledons and Ericaceae is rapid, occurring within an interval of ca. 44 years, or probably somewhat longer given the pollen concentration evidence for temporarily slower peat accumulation during this period. The hypothesis that *S. imbricatum* declined in response to competition from *S. magellanicum* is not supported by the complete absence of the latter from the macrofossil assemblage until after *S. imbricatum* has disappeared. In contrast to other locations in the region (e.g. Hendon and Charman, 2004; Mauquoy and Barber, 1999a), at Butterburn Flow an 'intermediate' vegetation assemblage dominated by monocotyledons, marks the transition. This may simply reflect *E. vaginatum* responding to an ailing *Sphagnum* species prior to the establishment of *S. magellanicum*, and appears a very localised signal given that previous investigations

at Butterburn Flow did not detect an *Eriophorum*-dominated horizon associated with the demise of *S. imbricatum* (Hendon and Charman, 2004).

4.2 Evidence for changing bog wetness

One line of evidence that we draw on to assess changes in bog wetness are biomarkers for microbial activity and microbially mediated chemical transformations (Figure 5), that reflect the oxygen and hydrogen availability in the bog subsurface and thus by the relative depth of the acrotelm. Synchrony between the macrofossil record and the biomarkers related to microbial activity and chemical transformations is not expected at the fine (centimetre) scale, as while environmental change might alter vegetation at the bog surface, the associated microbial response occurs in the subsurface. However, the process of peat compaction acts to minimise these offsets; for example, fungus associated with *Calluna vulgaris* rootlets has been found only 1-2 cm below the corresponding above-ground remains of *Calluna* in peat profiles (van Geel, 1978). We focus here upon the trends in microbial indicators rather than the fine-scale variability in order to determine past changes in bog surface wetness and its relationship to the macrofossil records.

Several proxy records from Butterburn Flow record changing bog surface wetness in the upper part of the *S. imbricatum* horizon. A steady increase in water table depth between 90-74 cm is recorded by the testate amoebae and increasing C/N up to ca. 80 cm. The C/N values of peat reflect the protein content, and to a lesser extent the amino sugar content, of the organic matter. These differ between plant types but also due to the diagenetic processes affecting the organic matter post-deposition, including microbial decay and cycles between aerobic and anaerobic conditions (Kuhry and Vitt, 1996; Muller and Mathesius, 1999). High C/N values are found in mosses including *Sphagnum,* but also in the acrotelm where preferential loss of nitrogen occurs by aerobic decay (Kuhry and Vitt, 1996). In contrast, low C/N values

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are found in vascular plants and also in the catotelm, due to preferential loss of carbon under anaerobic conditions (Belyea and Warner, 1996; Borgmark and Schoning, 2005; Kuhry and Vitt, 1996). The increasing C/N at Butterburn Flow between 90-80 cm is unlikely to reflect the relative inputs from vascular plants and *Sphagnum*, as there is little change to the macrofossil record at this time. Rather, it likely indicates a preferential loss of nitrogen due to increasingly dry, aerobic conditions at the surface of Butterburn Flow between ca. cal. AD 1100 and ca. cal. AD 1250. This corresponds well to a previous testate amoebae derived water table reconstruction at Butterburn Flow and other Border Mire sites, that identified low water tables until around cal. AD 1300 (Hendon et al., 2001).

The concentrations of the microbial biomarkers, archaeol and bishomohopanol, decrease between 90 and 76 cm (Figure 6). Archaeol is a biomarker for the Archaea, which in peat deposits are probably largely methanogenic and thus active in the catotelm (Pancost and Sinninghe Damsté, 2003), where archaeal lipids are found in high concentrations (Weijers et al., 2004). The falling archaeol concentrations between 90 and 76 cm are consistent with increasingly aerobic sub-surface conditions at a time when other proxies indicate an increase in water table depth. However, the archaeol concentrations at Butterburn Flow are positively correlated (r^2 = 0.57) to bishomohopanol concentrations (Figure 6). This relationship was unexpected, given that bishomohopanol is a sedimentary diagenetic product of the bishomohopanoids synthesised largely by aerobic bacteria (e.g. Innes et al., 1997; Ourisson and Albrecht, 1992), although they have recently been recognised in anaerobic bacteria (Blumenberg et al., 2006; Fischer et al., 2005; Hartner et al., 2005; Sinninghe Damsté et al., 2004). The $\delta^{13}C$ values for the C_{31} hopanes, being enriched relative to those of the *n*-alkanes, argue against a methanotrophic origin (e.g. Raghoebarsing et al., 2005), and instead suggest a heterotrophic origin, consistent with observations from other peat deposits (Pancost et al., 2003; Pancost and

Sinninghe Damsté, 2003). The controls over microbial activity and biomarker production at Butterburn Flow thus appear more complex than simply redox conditions alone, and may reflect substrate availability linking two different microbial communities. Further work is thus required to elucidate the controls over microbial processes operating in peat deposits and to utilise this information for palaeo-environmental reconstruction.

The falling water table recorded by the testate amoebae and C/N between 90-75 cm culminates in a maximum water table depth, c.15 cm, occurring at 74 cm (ca. cal. AD 1295), the final horizon in which *S. imbricatum* is detected. Above 74 cm the testate amoebae record a rapid rise in the water table by c. 10 cm, centred on the transition from *S. imbricatum* to *S. magellanicum*. Testate amoebae taxa show rapid changes at this time, in particular a sudden drop in abundance of *Trigonopyxis arcula* and an increase in *Amphitrema wrightianum*. There is a possibility of an association between *Sphagnum* taxa and testate amoebae taxa due to morphological differences in the bryophytes. This possibility is discounted here because the relationship between the taxa concerned and hydrological conditions is found consistently across a very wide range of peatlands and host vegetation throughout Europe and North America (Booth, 2008; Charman and Hendon, 2000).

The hopane $\beta\beta/(\alpha\beta+\beta\beta)$ signal also increases above 74 cm, although more gradually than the rapid increase identified in the testate amoebae water table reconstruction. The relative contribution from the $17\alpha(H),21\beta(H)$- and $17\alpha(H),21\beta(H)$-homohopanes, as recorded by $\beta\beta/(\alpha\beta+\beta\beta)$, has been proposed to be linked to bog surface wetness *via* the rapid acid-catalysed isomerisation of the $\beta\beta$-isomer to give the $\alpha\beta$-isomer (Pancost et al., 2003; van Dorselaer et al., 1975). This relationship is based on the unusual presence and even dominance of the $17\alpha(H),21\beta(H)$ isomer in peats

(Dehmer, 1993; Dehmer, 1995; Pancost et al., 2003; Pancost et al., 2000; Quirk et al., 1984; Volders, 2003; Xie et al., 2004), given that this compound is usually associated with thermal transformation of biologically-synthesised hopanoids with the 17β(H),21β(H) stereochemistry. Although $\beta\beta/(\alpha\beta+\beta\beta)$ at Butterburn Flow shows very little variation compared to previously published work (Pancost et al., 2003), the increase in $\beta\beta/(\alpha\beta+\beta\beta)$ above 74 cm is unlikely to reflect a diagenetic trend, because lower $\beta\beta/(\alpha\beta+\beta\beta)$ values (<0.1) occur between 42-26 cm. Thus, we attribute the increase in $\beta\beta/(\alpha\beta+\beta\beta)$ above 74 cm to reduced acidity and isomerisation as a result of increased in bog surface wetness, although minor, associated with the disappearance of *S. imbricatum*.

Lower C/N values in the *S. magellanicum* horizon and the first appearance of *S. cuspidatum* in the macrofossil record are consistent with a shift towards wetter bog surface conditions. The transition is also marked by very low C/N and a reduction in peat accumulation rates between 75-72 cm, the latter suggested by the high concentrations of all pollen taxa. Where low C/N and low peat accumulation rates were observed at Walton Moss, they were related to periods of increased decomposition and bog wetness or to reduced primary productivity due to lower spring-summer temperatures (Mauquoy et al., 2002).

At Butterburn Flow, a shift to lower $n\text{-}C_{23}/n\text{-}C_{31}$ occurs at 76 cm and low $n\text{-}C_{33}/n\text{-}C_{31}$ and ACL_{27-33} in the *n*-alkanes occurs between 74-66 cm. Nott et al. (2000) found that cool summer (growing season) temperatures over the last 150 years at Bolton Fell Moss corresponded to low $n\text{-}C_{23}/n\text{-}C_{31}$. Low $n\text{-}C_{33}/n\text{-}C_{31}$ and ACL_{27-33} in the *n*-alkanes have been linked to cooler and/or more humid conditions, although not in peatlands (Gagosian and Peltzer, 1986; Hinrichs et al., 1997; Pancost et al., 2003; Rinna et al., 1999). A decrease in $n\text{-}C_{33}/n\text{-}C_{31}$ similar to that found at Butterburn Flow was

observed in an older peat deposit from the Netherlands, where the horizon was believed to reflect a transition to a cool, wet oceanic climate ca. 2.6 ka (Pancost et al., 2003). Thus, the *n*-alkane distributions could indicate cooler and wetter conditions at Butterburn Flow after ca. cal. AD 1300. However, as discussed above, the *n*-alkanes at Butterburn Flow are dominated by the C_{31} *n*-alkane, whose absolute concentration shows a strong and positive correlation to monocotyledon inputs. The increase in monocotyledon inputs and thus C_{31} *n*-alkane concentrations above 72 cm may therefore account for much of the observed shifts in the *n*-alkane distributions.

The pronounced minima in C/N between 75-72 cm are restricted to the horizon dominated by monocotyledon macrofossils, particularly *E. vaginatum*. Given that lower C/N are found in vascular plants compared to mosses (Kuhry and Vitt, 1996), and the dominance of the monocotyledon macrofossil inputs compared with the *Sphagnum*-dominated horizon below, the C/N minima between 75-72 cm probably largely reflect the changing vegetation assemblage, but may also contain a record of the particularly wet conditions in this horizon.

Taking into consideration the complexity of the controls over many of the records presented here, it is still possible to identify a sequence of changing bog surface wetness at Butterburn Flow associated with the transition from *S. imbricatum* to *S. magellanicum*. The bog surface became increasingly dry prior to ca. cal. AD 1295 (90-75 cm), when a rapid rise of the water table by 10 cm took place in ca. 44 years or perhaps slightly longer. Hendon *et al.* (2001) also described an interval of high water tables on Butterburn Flow from ca. AD 1400-1900 based on testate amoebae analyses, our results appear to capture the onset of this shift in association with the loss of *S. imbricatum*. However, our results also show that *S. imbricatum* had not only survived but also dominated the macrofossil assemblage during earlier intervals of similar levels of bog surface wetness prior to ca. cal. AD 1230, below 80 cm depth.

Here, the reconstructed water table depth of c. 7 cm suggests wetter conditions than those found at the transition to *S. magellanicum* at 72 cm (water table depth c. 9 cm), yet *S. imbricatum* is the dominant macrofossil. Moreover, the trends towards increasing wetness at 72 cm suggested by the biomarker and elemental results are relatively minor and gradual compared to previously reported changes in biomarker distributions; in some cases, the changes identified with the loss of *S. imbricatum* are significantly smaller than those observed elsewhere in the depth profile. Furthermore, *S. imbricatum* also returned after temporary absences during wet phases in earlier millennia (Mauquoy et al., under review). The results presented here thus suggest that although water table depth did change with the demise of *S. imbricatum*, it was unlikely to be the sole driving mechanism.

2.3 Evidence for disturbance around Butterburn Flow

The transition from *S. imbricatum* to *S. magellanicum* occurs in synchrony with pollen evidence for intensified human disturbance in the areas surrounding Butterburn Flow, marked by high concentrations of Poaceae, *Plantago lanceolata* and *Rumex acetosella* between 76-69 cm. This relationship was also identified at Carbury Bog, Ireland (van Geel and Middeldorp, 1988) and in part of Walton Moss, UK (Mauquoy et al., 2002), and linked to increasing inputs of dust derived from anthropogenically disturbed soils (through cultivation, deforestation and overgrazing). Van Geel and Middeldorp (1988) suggested that this dust could be responsible for airborne eutrophication, to the detriment of *S. imbricatum*. This mechanism focuses on the differing sensitivities of *Sphagnum* species and vascular plants to nitrogen, which is an important but growth-limiting nutrient in many peatlands and is principally supplied by atmospheric deposition (Aerts et al., 1992). *E. vaginatum* is highly sensitive to variable nitrogen inputs (Silvan et al., 2004), and although nitrogen hinders or increases production in different *Sphagnum* species (Aerts et al., 1992; Bayley et al., 1987; Malmer et al., 2003; Rudolph and Voigt, 1986; Tamm, 1955), *S. magellanicum*

responds positively to increasing nitrogen inputs (Aerts et al., 1992; Bayley et al., 1987; Malmer et al., 2003; Rudolph and Voigt, 1986; Silvan et al., 2004; Tamm, 1955). The shift to dominance by *E. vaginatum* and then *S. magellanicum* at Butterburn Flow, in synchrony with anthropogenic disturbance surrounding the bog, is thus consistent with a response in the vegetation assemblage to increasing nitrogen inputs. Increased burning of the local peat forming vegetation does not appear to have occurred since the number of macrofossil charcoal fragments spanning the depth interval 76-69 cm are relatively constant (Mauquoy et al., under review).

It is unclear how *S. imbricatum* responds to changes in nitrogen supply, but it may simply have been unable to compete with the increasing production by *E. vaginatum* and *S. magellanicum* at Butterburn Flow in response to changing nutrient inputs. The disappearance of *S. imbricatum* at Butterburn Flow ca. cal. AD 1295 is accompanied by a combination of both rapidly increasing bog surface wetness and human disturbance of the surrounding area. It is perhaps this critical combination that was responsible for driving the disappearance of *S. imbricatum.* Although *S. imbricatum* had survived earlier wet intervals, both the testate amoebae and C/N indicate that the rate of change in the water table depth at ca. cal. AD 1295 was the highest of the period between ca. cal. AD 1100 – 1600. The stress placed on *S. imbricatum* may thus have been higher than during previous intervals of rising water tables, or alternatively the nutrient stresses imposed by increasing nitrogen inputs may have made *S. imbricatum* particularly sensitive to environmental change. We propose that the disappearance of *S. imbricatum* resulted from rapidly rising water tables, coupled with an increased dust-derived nutrient input that was conducive to production by *E. vaginatum* and *S. magellanicum* but detrimental to the dominance and survival of *S. imbricatum*.

6. Conclusions

The disappearance of the previously abundant moss species *S. imbricatum* was investigated at Butterburn Flow, in northern England. The combination of refined testate amoebae, macrofossil and elemental and analyses and new organic geochemical proxies enabled vegetation inputs to be tracked and the production and preservation of organic matter to be investigated. A complex picture of microbial activity in peats was identified from the concentrations of biomarkers linked to heterotrophic (bishomohopanol) and anaerobic (archaeol) microbial activity.

The results presented here have provided new insights into the significant loss of *S. imbricatum* from macrofossil records in mires across the British Isles, and reveal that a combination of environmental factors may have driven the demise of *S. imbricatum*:

1. Macrofossil distributions and a suite of biomarkers (C_{23}, C_{25}, C_{31} and C_{33} *n*-alkanes, 5-*n*-alkylresorcinols, triterpenols) track vegetation change, and indicate that the loss of *S. imbricatum* was a rapid event. *S. imbricatum* was replaced within ca. 22 years by increasing *E. vaginatum* and monocotyledons, followed quickly by *S. magellenicum* and a more diverse assemblage including other *Sphagnum* taxa and Ericaceae.

2. Testate amoebae, C/N and the isomerisation ratio of the C_{31}-hopanes $[\beta\beta/(\alpha\beta+\beta\beta)]$ record a rapid increase in bog surface wetness with the disappearance of *S. imbricatum*. However, this shift seems unlikely to have been the only control over the loss of *S. imbricatum*, as *S. imbricatum* had survived earlier periods of comparable wetness at this site.

3. The loss of *S. imbricatum* and the shift to wetter conditions occurred when increased human disturbance to the surrounding landscape beginning ca. cal. AD 1295 is detected in the pollen record.

Thus, it is concluded that the alteration of nutrient inputs to Butterburn Flow as a result of human disturbance resulted in increased competition from other peat-

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forming plants, which in combination with a rapid increase in bog surface wetness, appear to have been detrimental to the survival of *S. imbricatum* at Butterburn Flow from ca. cal. AD 1295.

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Tables

Table I. ^{14}C AMS measurements around the interval of study, 90 – 50 cm depth, including 95% confidence intervals of the Bpeat age model.

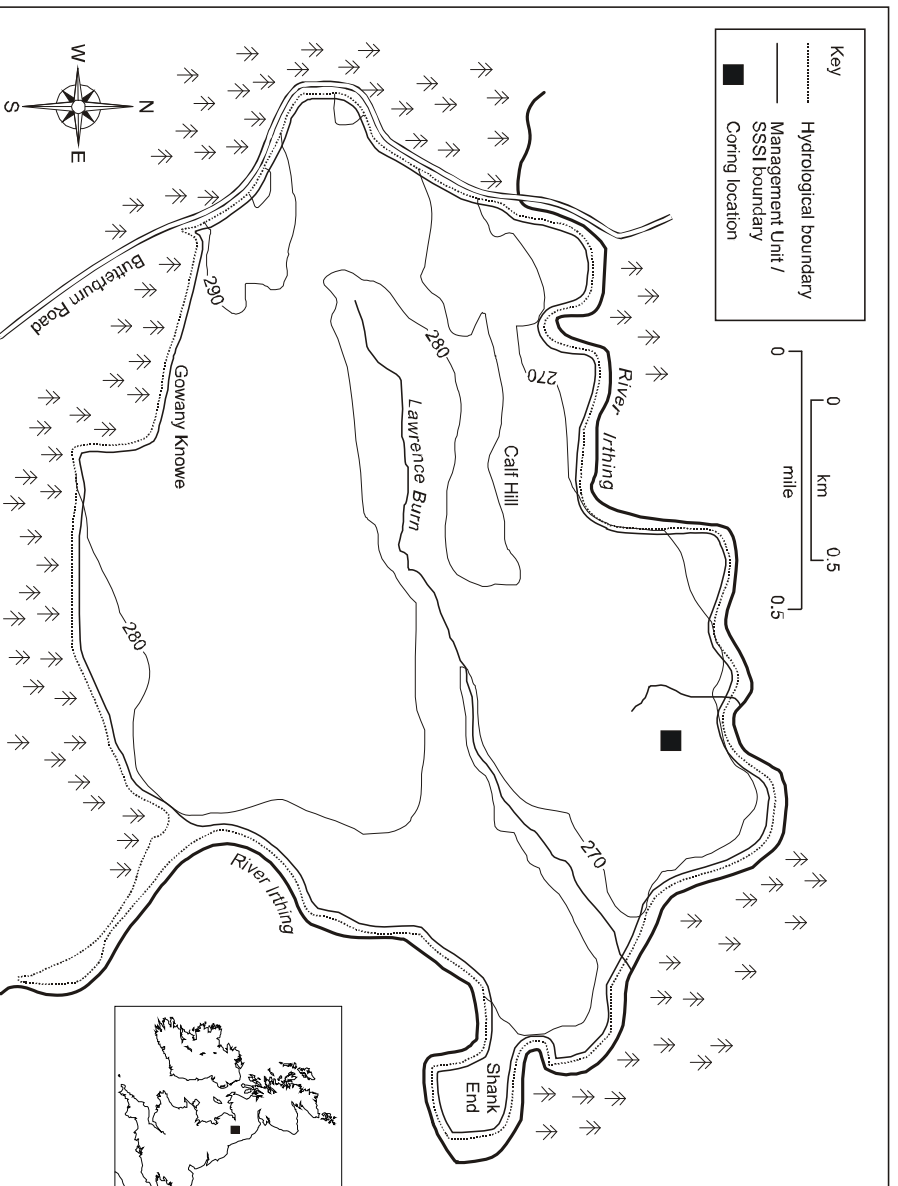| GrA	Sample composition	Midpoint sample depth (cm)	^{14}C age (yr BP)	Bpeat 95% age range (max – min yr BP)
GrA-28681	*Sphagnum magellanicum* leaves	49.5	305 ± 35	377 - 364
GrA-28682	*Sphagnum magellanicum* leaves	53.5	260 ± 35	418 – 417
GrA-26857	*Sphagnum* stems	59.5	485 ± 35	497 – 484
GrA-26858	*Sphagnum* stems & charred *Calluna vulgaris* leaves	61.5	710 ± 40	524 – 511
GrA-26814	*S. magellanicum* & *S.* section Acutifolia leaves	63.5	455 ± 30	538 – 524
GrA-26859	*Sphagnum* stems	67.5	735 ± 40	591 – 578
GrA-24777	*S. magellanicum* leaves and stems	69.5	505 ± 40	604 – 591
GrA-26860	*S. imbricatum* stems, leaves & branches	75.5	920 ± 35	671 – 658
GrA-26815	*S. imbricatum* stems, leaves & branches	77.5	860 ± 35	712 – 685
GrA-26862	*S. imbricatum* stems, leaves & branches	79.5	1080 ± 60	725 – 698
GrA-26883	*Sphagnum imbricatum* stems & leaves	91.5	830 ± 35	859 – 832

Table II. Mean elemental and lipid compositions at Butterburn Flow for the interval of study, 50-90 cm depth.

Elemental composition	Percentage
Total organic carbon	46.7
Total nitrogen	1.3
Total sulphur	0.9

Lipids	Concentration (μg g^{-1})
Triterpenoids	
Triterpenols	*730*
Triterpenes	*17*
Sum	747
Hopanoids	
Bishomohopanol	*486*
Hopanes	*88*
Sum	574
n-alkanes (sum)	140
5-*n*-alkylresorcinols (sum)	177
Archaeol	15

Figures

Figure 1. Location map of Butterburn Flow. The coring location is marked by a solid square. Adapted from Hendon and Charman (2004) by permission from Hodder Arnold Journals (© Edward Arnold (Publishers) Ltd, www.hodderarnoldjournals.com)

Figure 2. Selected macrofossils, pollen (% and influx) and reconstructed water table depth based on testate amoebae.

Figure 3. Depth profiles of the elemental composition of the bulk peat. All are expressed as percentages of the dry weight of peat analysed. The transition between *S. imbricatum* and *S. magellanicum* is shown by the horizontal grey line and corresponds to the horizon dominated by *Eriophorum vaginatum* macrofossils a.) total organic carbon; b.) total nitrogen; c.) total organic carbon / total nitrogen (C/N).

Figure 4. Depth profiles of *Sphagnum* composition and short-chain *n*-alkane distributions. Shading as in Figure 3. a.) macrofossil distributions of the three *Sphagnum* species found in Butterburn Flow expressed as percentages of the total assemblage; b.) C_{23} / C_{31} *n*-alkanes c.) C_{23} / C_{25} *n*-alkanes d.) the absolute concentration of the C_{23} *n*-alkane.

Figure 5. Depth profiles of non-*Sphagnum* components and the distributions of the long-chain *n*-alkanes and total *n*-alkanols. Shading as in Figure 3. a.) the relative abundance of monocotyledon macrofossils; b.) the relative abundance of Ericaceae macrofossils. Note that the x-axis has been expanded relative to a.); c.) the concentration of the C_{31} *n*-alkane; d.) C_{33} / C_{31} *n*-alkanes e.) the average chain length (ACL) of the long-chain *n*-alkanes. ACL_{27-33} calculated as $ACL = \Sigma(i*X_i)/\Sigma X_i$ where X is the *n*-alkane concentration and i ranges from 27 to 33 (Schefuβ et al., 2003); f.) the total concentration of the triterpenols. The concentration of the dominant triterpenol, taraxerol, is shown by the open symbols; g.) the relative abundance of the sedge macrofossils; h.) the total concentration of the 5-*n*-alkylresorcinols.

Figure 6. Depth profiles of biomarker distributions related to organic matter degradation and to microbial activity. Shading as in Figure 3. a.) the testate amoebae water table reconstruction; b.) archaeol concentrations; c.) bishomohopanol concentrations; d.) the ratio between the $C_{31}17\alpha(H)21\beta(H)29$-methylhopane ("$\alpha\beta$") and $C_{31}17\beta(H)21\beta(H)29$-methylhopane ("$\beta\beta$").
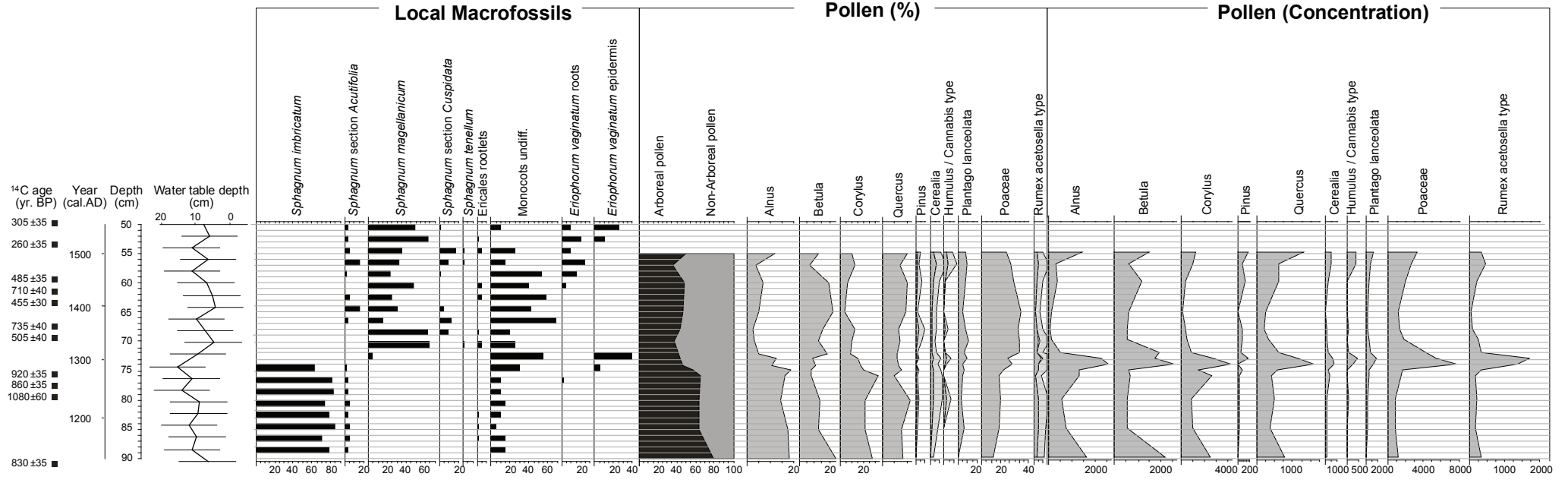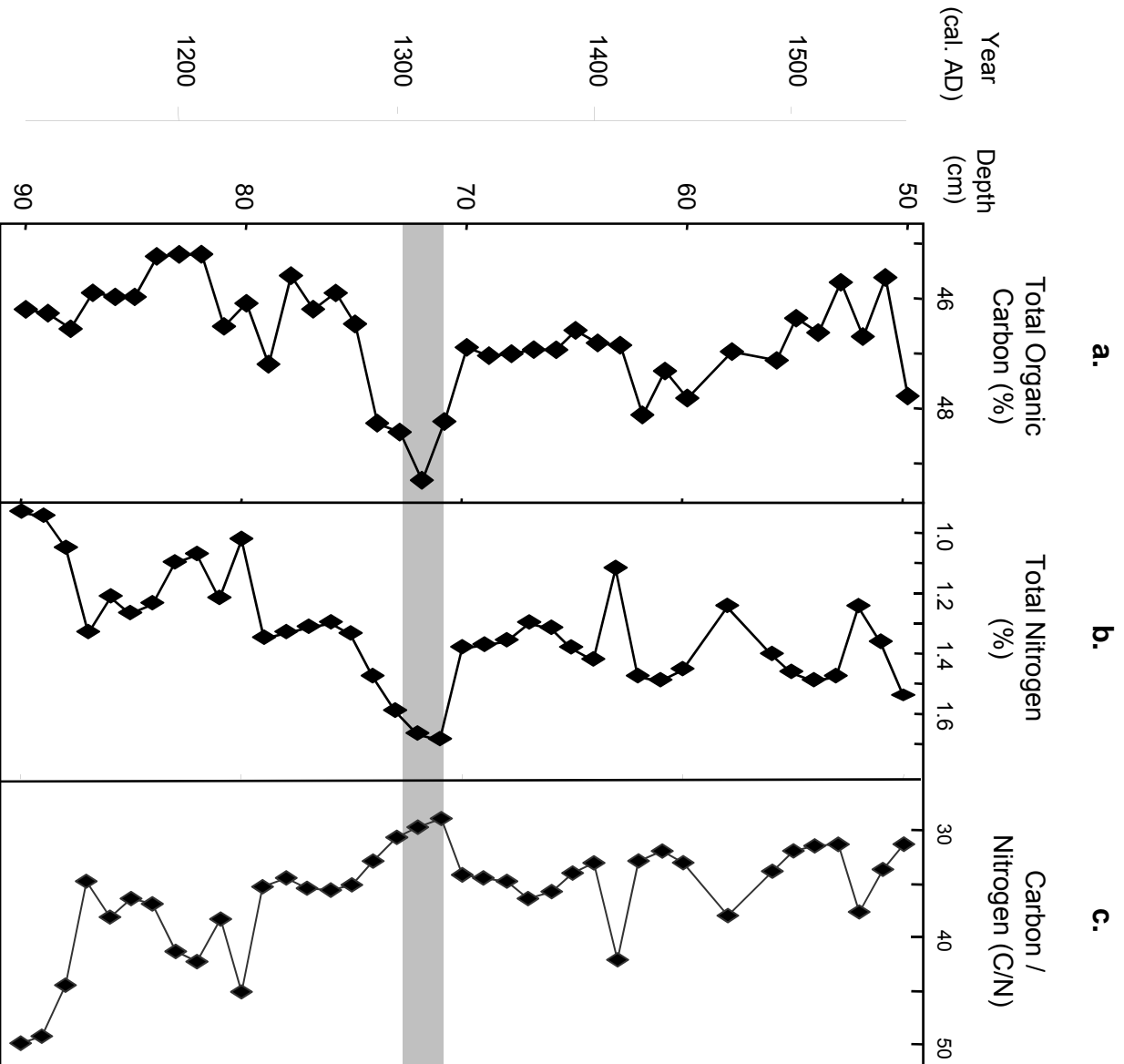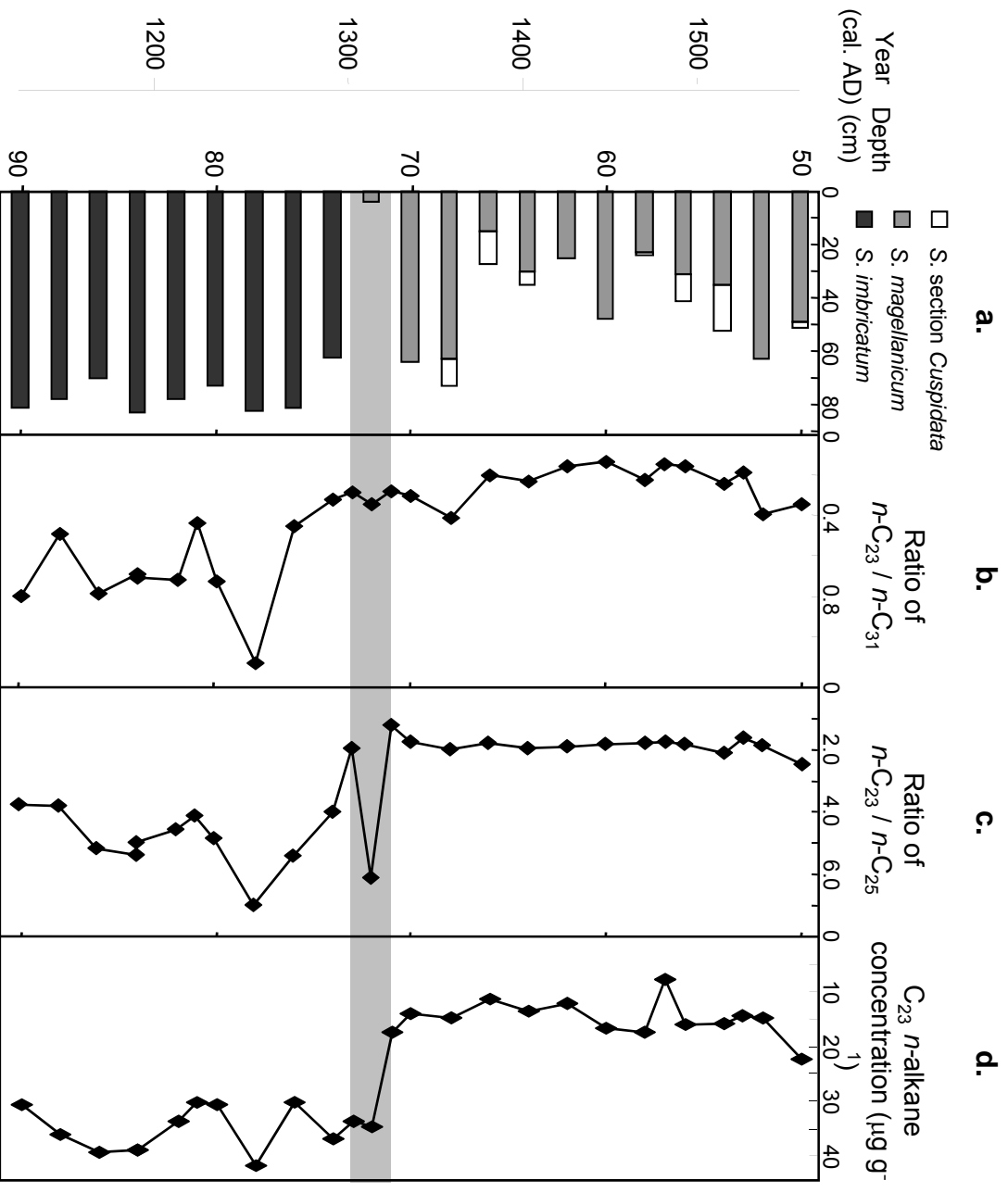
Figure 1:

Key

- .... Hydrological boundary
- ———— Management Unit / SSSI boundary
- ■ Coring location

Local Macrofossils — **Pollen (%)** — **Pollen (Concentration)**

¹⁴C age (yr. BP)	Year (cal.AD)	Depth (cm)
305 ±35		50
260 ±35	1500	55
485 ±35		
710 ±40	1400	60
455 ±30		65
735 ±40		
505 ±40	1300	70
920 ±35		75
860 ±35		
1080 ±60	1200	80
		85
830 ±35		90

Water table depth (cm): 20 10 0

Local Macrofossils taxa: *Sphagnum imbricatum*, *Sphagnum* section *Acutifolia*, *Sphagnum magellanicum*, *Sphagnum* section *Cuspidata*, *Sphagnum tenellum*, Ericales rootlets, Monocots undiff., *Eriophorum vaginatum* roots, *Eriophorum vaginatum* epidermis

Pollen (%) taxa: Arboreal pollen, Non-Arboreal pollen, Alnus, Betula, Corylus, Quercus, Pinus, Cerealia, Humulus / Cannabis type, Plantago lanceolata, Poaceae, Rumex acetosella type

Pollen (Concentration) taxa: Alnus, Betula, Corylus, Pinus, Quercus, Cerealia, Humulus / Cannabis type, Plantago lanceolata, Poaceae, Rumex acetosella type

Figure 3

Figure 4

Figure 5

Figure 6