Recreating Atmospheric Sulphur Deposition Histories: Evidence from Stable Isotope Investigations in Ombrotrophic Peat.

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The candidate confirms that the work submitted is his own and that appropriate credit has been given where reference has been made to the work of others.

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Abstract

Ombrotrophic peat deposits are important archives of palaeoenvironmental information. Potentially, their geochemistry may also reflect environmental change by recording alterations in natural and pollutant sulphur deposition. Over much of northwest Europe, the dominant sulphur source to natural, pre-anthropogenic atmospheric inputs will have been of maritime origin, which is characteristically enriched in the heavier ^{34}S isotope of sulphur with δ^{34}S ~ +20 ‰ CDT (Canyon Diablo Troilite). By contrast, fossil fuel burning produces SO_2, which is significantly ^{34}S-depleted (0-5 ‰ CDT). Changes in the source of atmospheric sulphur inputs to peatlands may be accompanied by a change in sulphur isotope composition of sulphur taken up by growing plants. The organic sulphur isotopic composition in ombrotrophic peat sequences could thus potentially provide a record of anthropogenic impacts through the assimilation of the sulphuric acid component of acid rain into surface vegetation and its subsequent preservation in the peat profile. This was investigated by measuring sulphur isotopic compositions through peat profiles from pristine situations and from a once heavily polluted site on the southern Pennines (UK) and also through a ^{34}S tracer experiment at a waterlogged peat in northern England.

Peat type was shown to be critical in determining whether a record of isotopic compositions of aerially deposited sulphur can be preserved in ombrotrophic peat deposits. Peats need to be anaerobic enough to prevent decomposition but not so waterlogged that the production of sulphides from bacterial sulphate reduction may obscure the organic sulphur signal. Even under these conditions a primary sulphur signal is unlikely to be preserved indefinitely as diagenetic sulphide incorporation in the long term (following burial below the water-table) may eventually obscure the organic sulphur signal. Isotopic analyses of pristine and polluted peats suggest that, in the drier upland peats sampled, recent changes (~600 y) in atmospheric sulphur chemistry are preserved within the organic sulphur fraction without significant masking by diagenetic processes.

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CHAPTER 1- Rationale and Context

1.1. Introduction

Current estimates suggest that peatlands occupy an area of around 398 million hectares worldwide (Lappalainen, 1996), which is roughly 2.7 % of the land surface of the earth. While the majority are found in the more temperate boreal regions they have a truly global distribution spanning from the tropics to the arctic tundra. Their characteristic landscape harbours a specialised fauna and flora, some of which is endemic to mires in general, or to specific regions of mires. Below ground, peatlands are just as important. As well as their role in the hydrological cycle, they also function as both a source and sink for carbon and, taken as a whole, contain more carbon than is produced by the world's vegetation in a single year.

The manner of peat formation makes it an exceptional archive of the past for many forms of environmental information. The accumulation of dead organic material, with little decomposition, in an ordered stratigraphy, allows not only evidence to be gathered about the general development of the peat but also information pertaining to plant and animal biogeography (pollen and macrofossils) can be preserved and used to create a picture of past environmental conditions (see Charman, 2002). This thesis investigates further how peatlands can be used as archives of past environmental conditions by investigating the potential for peatlands to record changes in atmospheric deposition of pollutant sulphur.

Though the examination of chemical compounds in air, soil and water are useful in elucidating the role of pollutants such as sulphur, the use of stable isotopes can provide much more reliable and accurate determinations of element origin. Sulphur can exist in four stable isotopic forms (^{32}S, ^{33}S, ^{34}S and ^{36}S), though ^{32}S and ^{34}S predominate making up 95 and 4.2 % of total sulphur respectively (Macnamara and Thode, 1950). Natural processes can fractionate these isotopes, giving different sulphur sources characteristic isotopic ratios. These ratios can thus be used to track sulphur in the environment (Nriagu *et al.*, 1987). In Britain, natural sources of deposited sulphur are dominated by sea spray, which is characteristically enriched in the ^{34}S isotope (e.g. Thode *et al.*, 1961) while pollutant sulphur derived from fossil fuel combustion is typically ^{34}S depleted (e.g. McArdle and Liss, 1995).

Changes in plant distribution have often been used as 'spatial' indicators of pollution (e.g. Gilbert, 1968) yet there remains much untapped potential in the use of plants as 'temporal' indicators of pollution. The sulphur isotopic signal incorporated into vegetation at the time of growth may be preserved in the organic fraction of ombrotrophic peat profiles and as such, an isotopic record of pollutant vs. natural sulphur deposition may exist in such systems. This project aimed to characterise the sulphur signals contained in the organic fractions of peat profiles taken from a site on the southern Pennines (northern England), which has suffered from a gross level of sulphur pollution during the last 200 years (Fig. 1.1).

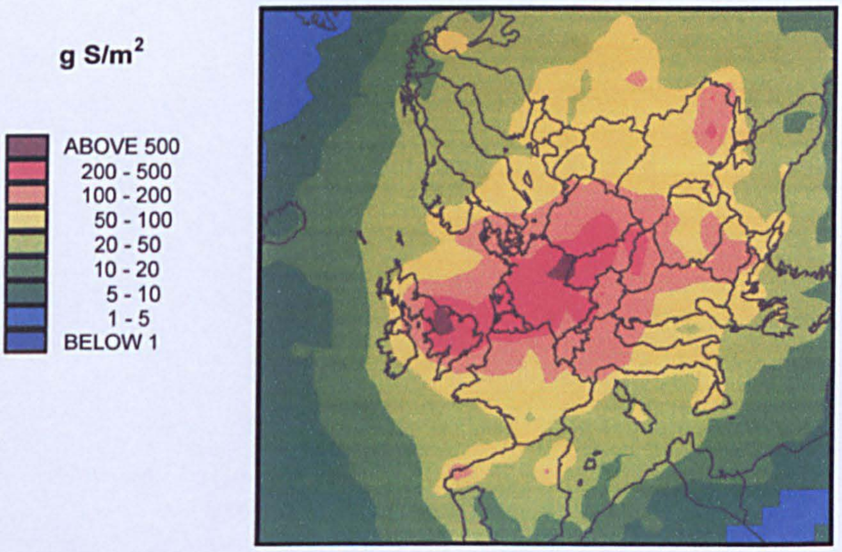

Fig.1.1. Total deposition of oxidised sulphur accumulated over the period 1880-1991 (reproduced from Mylona, 1993).

In order to clarify and validate these data peats from areas which have not suffered from significant levels of anthropogenic sulphur deposition (northern Scotland and northern Sweden) were also sampled. A ^{34}S tracer investigation was also conducted to investigate how the organically bound sulphur may be affected by below ground sulphur cycling. As such, this thesis ultimately centres upon the fate of sulphur in ombrotrophic peat. A more detailed outline of the scope of this work is presented later but it is first necessary to provide a context for this work and as such a synthesis and critique of previous studies are presented in the following section.

1.2. Sulphur cycling and the fate of excess sulphur in ombrotrophic peat

The main sulphur pools of the earth's crust are presented in Table 1.1. Sulphur is released through the weathering or rocks and is cycled principally through the atmospheric sulphur cycle. The atmospheric cycling of sulphur is markedly different between oceanic and continental zones (Fig. 1.2). In marine atmospheres the dominants inputs are derived from sea salt and biogenic emissions, whereas in continental atmospheres the most significant inputs are now dominated by SO_2 emissions from the burning of fossil fuels. Increased anthropogenic activities have thus resulted in significant local imbalances of the cyclic conversions of the sulphur, leading to a number of well-known types of pollution such as acid rain.

Table 1.1. Sulphur content of various reservoirs of the earth's crust (redrawn from Holser and Kaplan, 1966).

Rock type or reservoir	Sulphur content (10^6 Tg)
Deep oceanic rocks	2375
Continental igneous and metamorphic	6800
Sedimentary rocks	7820
Oceans	1280
Freshwater	0.003
Atmosphere	(3.6×10^{-6})

The classification of mire systems as either minerotrophic or ombrotrophic has important implications in studying elemental excess derived from acid deposition. Ombrotrophic mires are particularly susceptible to atmospheric deposition due to their dependence on atmospheric inputs as their sole supply of elements. Because this flux of elements into the mire is usually low, and annual rainfall is often high, even a small increase in supply can have serious implications for the surface vegetation especially the bryophyte flora (Lee *et al*, 1987). While sulphur in excess can be extremely toxic to plants, it is an important nutrient vital for growth and development making up around 0.1-0.2 % of total dry weight. Sulphur is usually taken up by plants as sulphate, reduced by a series of reactions to protein-bound sulphide, and then incorporated into amino acids, such as cysteine and methionine. Nearly all sulphate reduction occurs in photosynthetic tissues where it accounts for a significant amount of the ATP that is consumed. Sulphur is also emitted by plants (e.g as H_2S) yet more significant releases of sulphur take place after plant death in which organic material is decomposed. Sulphur deposited upon peatland surfaces which is not taken up by the surface vegetation diffuses into the surface layers of the peat and is then cycled below ground in the microbial sulphur cycle (Fig. 1.3), which is strongly dependent upon the anoxic/oxic conditions of the peat, itself a function of the height of the water table. The importance of the hydrological status of peat in relation to the below ground cycling of sulphur will be discussed in more depth later.

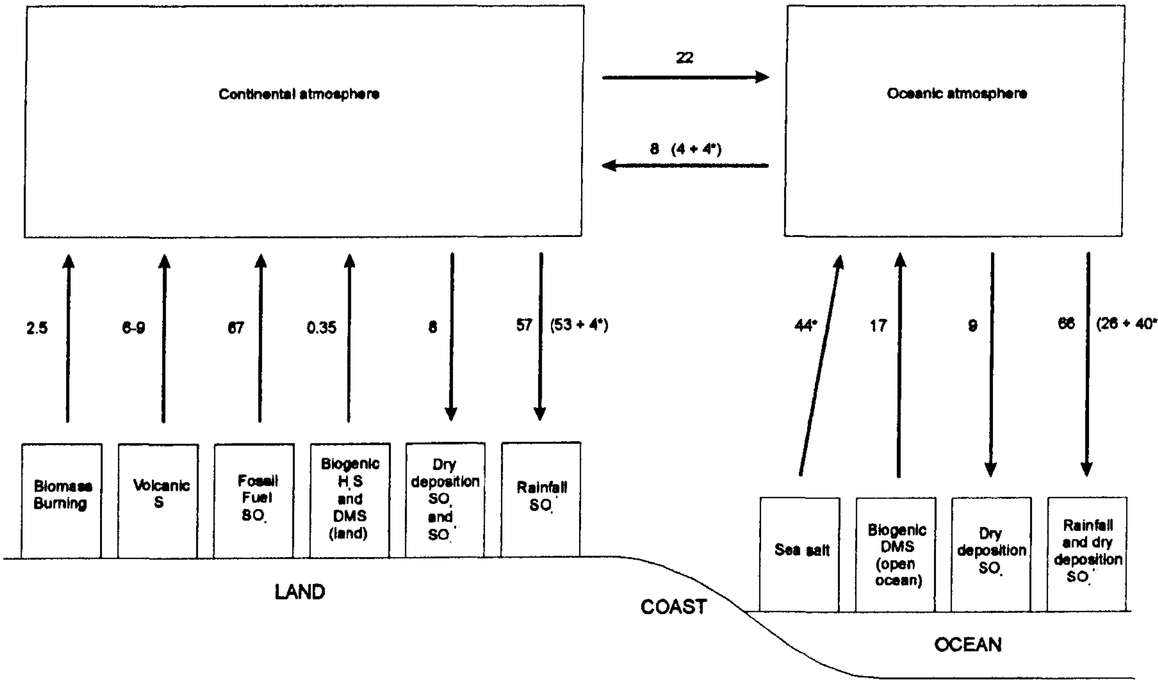

Fig 1.2. The atmospheric sulphur cycle. Values are fluxes in Tg S/yr. Values denoted by an asterisk refer to sea salt (reproduced from Berner and Berner, 1996).

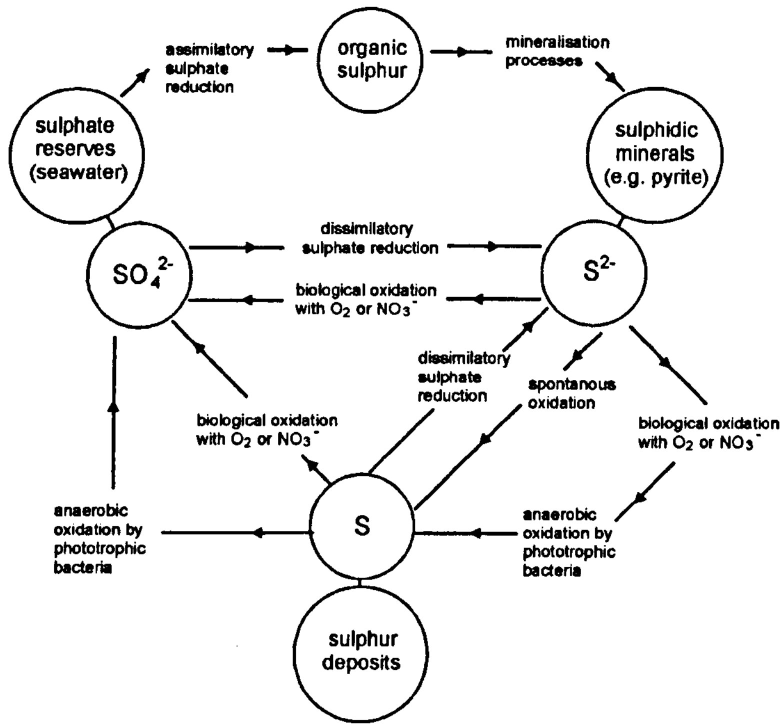

Fig.1.3.The microbiological sulphur cycle (redrawn from Robertson and Kuenen, 1992)

The use of stable isotopes can be particularly useful in understanding the biogeochemical cycling of sulphur in ombrotrophic peatlands and interactions with accompanying surface vegetation. Plants typically fractionate against ^{34}S by around 1-2 ‰, yet extreme fractionation effects, ranging up to 9 ‰, are not uncommon for some types of wetland vegetation (Trust and Fry, 1992). Uptake and incorporation of sulphur into growing mosses has been recorded as occurring with only a minimal fractionation effect (Krouse, 1977; Nriagu and Glooschenko, 1992; Trust and Fry, 1992; Novak *et al*, 1994). However, large variability has been observed for *Sphagnum sp.* (Novak *et al*, 2001).

Bottrell and Novak (1997) conducted an isotopic study of pristine *Sphagnum* bogs in two areas of the western British Isles. Principally they demonstrated that the sulphur isotopic ratio in *Sphagnum* differed only slightly from that of the sulphate deposited onto the vegetation surface emphasising the possible close association between atmospheric inputs and the bryophyte cover (see Krouse 1977; 1989). However, they showed that the isotopic composition of the bog surface waters and that of the sulphate deposited onto the vegetation surface differs markedly by 4-12‰. While 5-10% of the total sulphur input to the bogs is taken up by the growing *Sphagnum* community, the bog surface waters are far more depleted in sulphate and more strongly enriched in ^{34}S than could be attributed to *Sphagnum* sulphur uptake alone even if fractionation by *Sphagnum* was occurring. Bacterial sulphate reduction (BSR), which, owing to its obligate anaerobic character occurs at depths in wet soils (Bloomfield and Coulter, 1973), favours the lighter ^{32}S isotope (Kemp and Thode 1968; Chambers and Trudinger, 1979). This produces a much steeper concentration gradient for ^{32}S than for ^{34}S, causing the surface waters to become depleted in sulphate and become more enriched in ^{34}S.

Three possible processes have been hypothesised to explain the difference in sulphur isotopic ratio between the sulphur in *Sphagnum* and the sulphate in environmental water; genuine fractionation by *Sphagnum* (which is known to occur in plants, mosses, lichens and algae [Ishii 1953, Trust and Fry 1992, Mekhtiyeva 1971, Krouse 1977, Winner *et al* 1978, Case and Krouse 1980), a seasonal effect in atmospheric sulphur isotopic ratio, or that sulphur is assimilated into *Sphagnum* not only from sulphate deposited on its surface and from surface water, but from other sulphur species of intermediate oxidation state (Bottrell and Novak, 1997). Sulphide, which is the product of BSR and typically ^{34}S depleted, is an important component of the bog sulphur cycle. Low concentrations of sulphides, such as H_2S, can be toxic to plants (Howarth and Teel, 1979). It has been shown that H_2S inhibits the uptake of sulphate and that sulphides are fixed into plant tissues in preference to sulphate with the direct formation of cysteine (Brunold and Erismann, 1975). In estuary systems, plants with roots that extend into sulphide-rich sediments incorporate ^{34}S-depleted sulphides into their tissues (Carlson and Forrest, 1982; Fry *et al*, 1982; Fry, 1986). The survival of these plants may be attributed to the diffusion of O_2 to their roots via their stems, thereby converting the physiologically harmful sulphides to sulphate. However, for bryophytes, which are small, compact green plants with no vascular tissues and therefore no roots per se to extend down to anaerobic portions of the peat, contact with such sulphides directly would be limited to diffusive supply of sulphide to the uppermost peat layers. As such, it is unlikely that sulphide could be directly important in terms of availability to *Sphagnum* as once the sulphide diffuses out of the anaerobic layer of the peat and into the aerobic layer it would become oxidised. If the sulphide reached its highest oxidative state of sulphate, it may ultimately end up in the surface waters and therefore be accounted for in the overall sulphur isotopic ratio of sulphate in the surface waters. Yet ^{34}S depleted sulphide may be important as a source (via oxidation) of sulphur species of an intermediate oxidation state (e.g. bisulphite [HSO^-_3]). These could therefore be sources of ^{34}S-depleted sulphur to the surface vegetation, which would not be accounted for in the isotopic ratio of the surface water sulphate.

Thompson and Bottrell (1998) expanded upon the work of Bottrell and Novak (1997) by examining a polluted site and comparing this with the pristine sites. The principal finding was that the isotopic difference between the sulphur in *Sphagnum* and the sulphate in surface waters was not the same for both pristine and polluted sites (pristine 5-15‰, polluted 0-10‰). This was attributed to pristine and polluted sites having different sources of sulphur not reflected in the surface water sulphate. In both pristine and polluted sites the sulphate from wet and dry deposition is the principle source of sulphur for *Sphagnum* with bisulphite derived from BSR also playing albeit a minor role. In pristine sites the ratio of sulphur isotopes in *Sphagnum* typically reflects direct deposition, surface water sulphate and bisulphite derived from BSR. However, in polluted sites there is a fourth source, namely pollutant bisulphite derived from atmospheric deposition, which is ^{34}S enriched compared to natural bisulphite derived from sulphide oxidation.

Typically in ombrotrophic, as well as mineratrophic, peatlands there are five sulphur-containing transposable compartments; sulphur in living plant material, surface water sulphate (typically in pools or very waterlogged peatlands), pore water sulphate, reduced sulphur (dissolved and solid phase) and organic C-bonded sulphur. Though inorganic sulphur exhibits significant cycling, the organic sulphur fraction is the chief constituent of peat deposits (e.g. Brown, 1985; Weider and Lang, 1988; Novak *et al*, 1999). Novak and Weider (1992) demonstrated that in peat bogs in the USA, organic sulphur, with only one exception, was the principle form of sulphur at all depths, in all profiles, constituting 76-98 % of total sulphur in the peat and that this carbon-bonded sulphur was a much more stable end product of sulphate reduction compared to inorganic sulphur compounds. The majority of this carbon bonded sulphur is made up of the partially decomposed remains of *Sphagnum* species which, though now absent from more polluted systems, are the chief component of the ombrotrophic flora of pristine peatlands. *Sphagnum* species in such systems receive their sulphur from the direct deposition of sulphur compounds upon the surfaces of their stems and leaves, and depending on the environmental conditions, from the surrounding surface water.

Sulphate has been shown to represent only a minor component of total sulphur in peat profiles (Novak and Weider, 1992), decreasing with depth (Bayely *et al*, 1987; Shannon and White, 1996; Thompson and Bottrell, 1998). Sulphate not taken up by *Sphagnum* or other bog species is reduced to H_2S in the anaerobic portions of the peat (Brown, 1986) through dissimilatory sulphate reduction using organic material and hydrogen as electron donors. Isotopic studies show sulphate reduction to be the dominant sink for sulphate under relatively pristine conditions (Bottrell and Novak, 1997). Bacterial reduction of sulphate to sulphide is a ubiquitous process at depth in peats:

$$SO_4^{2-} + 2CH_2O \Rightarrow H_2S + 2HCO_3^- \qquad \text{(Equation 1.1)}$$

$$2H^+ + SO_4^{2-} + 2CH_2O \Rightarrow H_2S + 2CO_2 + 2H_2O \qquad \text{(Equation 1.2)}$$

This process requires anaerobic conditions and carries a large isotopic fractionation, the sulphide product being depleted in the heavier ^{34}S isotope relative to the reactant sulphate (Chambers and Trudinger, 1979; Bottrell and Novak, 1997). This leaves the residual sulphate in porewaters enriched in the ^{34}S isotope. Quantitative reduction of sulphate, will of course, produce a sulphide product with the same isotopic composition as the starting sulphate. The sulfide produced may undergo one of three types of reaction:

a) sulphide may diffuse upward in the peat into the oxic zone and be re-oxidized to sulphate;
b) sulphide may react with dissolved or particulate iron to form insoluble FeS or FeS_2;
c) sulphide may react with buried organic matter and become incorporated into the peat as carbon-bonded sulphur.

Reactions b) and c) above fix diagenetic sulphide in the peat and thus may mask any primary isotopic signal related to changing atmospheric inputs which might be recorded in plant assimilated S.

Importantly the incorporation of the sulphur signal into the surface vegetation would appear to result in very little alteration in isotopic composition during the early transformation of surface biomass into peat necromass. The top few cm of seven U.S. peatland sites were shown to reflect $\delta^{34}S$ of sulphur inputs (Novak *et al*, 1994). However, this was not shown to be the case for forest soils where forest floor moss and the A horizon were statistically different in $\delta^{34}S$ (4.0 to 2.5 ‰). Hydrological conditions and resulting aerobic/anaerobic conditions will therefore be of importance and will be discussed later in further detail.

Alterations in sulphur inputs may also be reflected, not only in alteration in the isotopic composition of organic sulphur, but in sulphur content. Data from two Swiss peat bogs, 50 km apart, appear to show that S content in surface layers of Pb-dated peat mirror SO_2 emissions during the last 50 years (Jeker and Krahenbuhl, 2001). However the peat sampled, between 40 and 60 cm, is dated to represent the last 80 or so years. Such a level of peat accumulation is considerable and as such the lead dates may not be wholly accurate, perhaps due to lead mobility within the profile (see Damman, 1978; Malmer and Holm, 1984; Pakarinen and Tolonen, 1977). Further doubts may be expressed as sub-surface maxima in sulphur content have also been recorded in other peats from around the world (Novak *et al*, 1994; Novak *et al* 1999), including more pristine peats (Chapman, 2001) where inputs have not altered significantly in recent history and as such the organic sulphur content and isotopic composition may not necessarily reflect changes in S inputs but be the product of diagenesis and the cycling of sulphur between different sulphur fractions within the peat.

The reduction of SO_4 via BSR to sulphides and their incorporation into organic fractions may therefore explain the characteristic sub-surface maxima in organic S contents, with an accompanying isotopic effect of depletion in ^{34}S (Gebauer *et al*, 1994; Novak *et al*, 1994). Such effects have been demonstrated experimentally in peat incubation experiments using ^{35}S labelled SO_4. Short-term experiments (~1 hour) showed significant incorporation of added $^{35}SO_4$ into inorganic fractions (Chapman and Davidson, 2001) whereas in longer-term experiments much of the added ^{35}S became incorporated into the organic fractions (Brown, 1985; Brown and McQueen, 1985). SO_4 is too unreactive to be directly incorporated into the organic matrix (Wilson and

Reuvey, 1976) as such; the principle route of sulphur incorporation into peat organic fractions is via the process of dissimilatory sulphate reduction (Giblin and Weider, 1992).

However, while an increase in sulphur content and a decline in $\delta^{34}S$ is a significant result of sulphide incorporation in waterlogged soils/peats, under more aerobic conditions a contrary process can occur, resulting in a decline in sulphur content and an increase in $\delta^{34}S$. Decomposition and mineralisation processes which occur at faster rates under aerobic conditions (Bridgham *et al*, 1998) can cause the preferential breaking of ^{32}S-C bonds over ^{34}S-C bonds resulting in ^{34}S enrichment in residual C-bonded S. Loss of sulphur from ester sulphates and carbon bonded S would appear to be a significant process which can replenish pore water sulphate concentrations (Groscheova *et al*, 2000).

The loss of sulphur through mineralisation/decomposition is evidenced from analyses of soil water and stream water analyses in central European watersheds in which $\delta^{34}S$ of SO_4 was isotopically lighter to that of atmospheric deposition (Novak *et al*, 2000). While such processes are more common in forested, aerobic soils (e.g. Gebauer *et al*, 1994), such conditions may exist for peat bogs, especially due to seasonal drops in water table height. Fluctuations in the level of the water table will result in either previously aerobic portion of the peat becoming anaerobic or vice versa. As such, hydrology is critical to below ground element cycling. Studies on a forested swamp site from Canada that became ombrotrophic during the summer months due to reductions in ground water underwent a lowering of water table resulting in aeration of the surface peat and the oxidation of sulphides (Devito *et al*, 1995). Upon the advent of autumn and high precipitation events, flushing of the system occurred resulting in export of sulphate from the system. This example typifies the importance of hydrology upon sulphur retention and transformation within peatlands.

Importantly for peatlands, as with most dynamic systems, fluctuations in one component can have serious knock on effects for other parts of the system. Fluctuations in water table height results in the oxidation of FeS/H_2S to SO_4. Studies by Freeman *et al* (1994) demonstrated this by experimentally lowering the water table height and then raising it again, which allowed for the re-oxidised sulphate to then become available for sulphate reduction. The microbial activity that initiates this process requires the use of organic substrates or hydrogen as electron donors. As a consequence, increased activity of the sulphate reducers results in the competitive inhibition of methanogens, the bacteria responsible for the production of methane. Methanogens reduce carbon dioxide or acetate to methane with the energy required derived from electron donors, typically H_2. However, organic compounds such as acetate can supply electrons for this process. Lovely and Klug (1986) demonstrated in freshwater sediments that as sulphate concentration increases, the concentration of acetate decreases, implying that the sulphate reducers are using acetate, an important source of electrons for methanogenesis, as an electron source. These workers proposed that at low sulphate concentrations, a methanogenic zone develops where low sulphate concentration and acetate consumption by methanogens inhibits the metabolism of sulphate reducers. Conversely, at high sulphate concentrations (>30 μM) a sulphate-reducing zone develops in which sulphate reducing bacteria maintain low concentrations of acetate, inhibiting the growth of methanogens. Other workers have however, suggested that sulphate reducing bacteria and methanogens compete principally for hydrogen (Abram and Nedwell, 1978). Studies using mixed cell suspensions containing a sulphate reducing bacterial species and a methanogen species demonstrated that the two species had different affinities for hydrogen when concentrations were <5 μM (Kristjansson *et al*, 1982). When hydrogen supply was limiting the sulphate reducing species had a five fold higher H_2 consumption rate than the methanogen species. Additions of sulphate have shown to result in the reduction of methane emissions (Freeman *et al*, 1994; Nedwell and Watson, 1995) and rates of sulphate reduction imply that carbon flow is greater via sulphate reduction than methane production (Watson and Nedwell, 1996).

Clearly the additions of sulphate to mire systems have important consequences for elemental cycling within the peat. Novak and Weider (1992) found evidence to suggest that sulphate represented only a minor contribution to total sulphur (~4 %) and that there was no indication of increasing sulphate concentration with increasing atmospheric deposition. This is the likely result of a rapid turnover time of the dissolved sulphate pool with its reduction in anaerobic peat to H_2S (Weider and Lang 1988), effectively acting as a buffer to acid deposition (Hemond, 1980).

While the microbial activity responsible for sulphate reduction increases with the additions of sulphur compounds, the activity of other microbial processes within peatland soils have been shown to decrease. The soil enzyme arysulphatase is involved in the first stages of the reduction of oxidised forms of sulphur yet under conditions of high sulphur loadings it has shown reduced activity (Press *et al*, 1985). While it has been suggested that bisulphite, a component of acid deposition, can be taken up directly by *Sphagnum*, making the role of arylsulphatse redundant (Thompson and Bottrell, 1998), sulphate remains the most significant form of sulphur that is deposited in acid deposition and therefore the cause of its reduction in activity remains unknown.

The addition of sulphur compounds to peatland systems derived from acid deposition would appear, for the most part, to be the most significant for the floral composition of the surface. Although alteration of flora composition may result in significantly more or less sulphur reaching the peat surface. Excess sulphur below the peat surface is transformed to H_2S, which may be retained in the peat by subsequent reactions with free iron species producing FeS and FeS_2 (Morgan, 1995). However, fluctuations of the water table will determine whether the peatland remains a sink or a source of sulphur (Devito and Hill, 1997) and will affect the production of methane, a potent 'greenhouse gas', of which peatlands are an important source (Cicerone and Oremland, 1988).

In light of the issues raised it would appear that below ground cycling of sulphur may indeed alter or mask any climatic record of aerially deposited sulphur preserved within the peat organic fraction. Works upon forested soils demonstrate processes that may be significant in peat bogs and differences in hydrological conditions need to be appreciated. Studies on forested soils in Czechoslovakia suggest that that a climatic record of deposition is not present due to alterations through incorporation of isotopically light sulphide derived from BSR (Novak and Bottrell, 1996). However, the range of isotopic values examined at all sites was very small (1-4 ‰), which is a likely function of natural and anthropogenic signals in the region being only moderately isotopically distinct. In areas where sulphur inputs have been drastically different through time (i.e. for more maritime regions with a period of sulphur pollution), such isotopic changes in the organic sulphur signal may be preserved in part without significant masking. Elevated $\delta^{34}S$ of organic sulphur at around 30 cm depth in a peat from Thailand is suggested to be the result of a past period of sea ingression (Jedrysek *et al*, 1996). This peat was sampled from a waterlogged mangrove swamp and therefore enrichment in ^{34}S at only this depth is unlikely to be due to high decomposition and as such may be the result of a change in past sulphur input. Alterations in inputs, when very isotopically distinct, may thus be recorded in peatlands.

The investigations upon sulphur deposition records in peat are however, not the only types of proxy measurements that have been attempted. Ice core data has shown that records of increased anthropogenic sulphur emissions during the twentieth century can be preserved in terms of sulphur content (Neftel *et al*, 1985; Preunkert *et al*, 2001; Oliver *et al*, 2003) Yet, perhaps the most interesting example of recreating sulphur proxies comes from the Broadbank experiment at Rothamstad (Zhao *et al*, 2003). This work used the $\delta^{34}S$ of wheat and straw samples dating back to 1845 to investigate whether the isotopic composition would reflect any alterations in sulphur inputs during the last ~ 150 years. While there was no correlation with sulphur content over this period there was a strong correlation between $\delta^{34}S$ and U.K SO_2 emissions ($R^2 = 0.89$). Isotope ratios declined from ~ + 6 ‰ in 1845 to –5 ‰ in the early 1970's before increasing to 2 ‰ in the late 1990's. Such data is extremely reliable as vegetation samples were collected and preserved and as such, no decomposition or diagenetic processes, as is the case of examining plant remains in peat, could have acted to alter their isotopic composition. However, a shift from the true $\delta^{34}S$ of the aerial input may have occurred due to plant fractionation so while the relative changes in isotopic composition are likely to be accurate the absolute values may not. If such shifts are known (i.e. the level of fractionation) this data and perhaps other preserved herbarium samples could be used to model alterations in sulphur inputs on countrywide or even continent scales. At present no such attempts have been made and the only sulphur deposition map through time that exists was created using SO_2 emissions data for countries in Europe (Fig. 1.1, Mylona, 1993).

The use of ombrotrophic peat profiles from various locations could essentially be used as preserved herbariums in which sulphur isotopic inputs could be preserved. However, previous isotopic investigations have raised some intriguing questions about the fate of aerially derived sulphur in ombrotrophic peat. For example, when sulphur species are deposited upon the surface of a vegetated peat bog, is the majority taken up directly by the surface vegetation or is excess sulphur cycled and partitioned between the other main transposable sulphur compartments? Also, how stable is the organic fraction and to what extent is sulphur incorporated from the other sulphur pools or degraded over time from the organic matrix? A greater understanding of the transport, metabolism and incorporation of sulphur may allow peatlands to be used as archives of recent changes in sulphur deposition. The sulphur deposited upon a given area signifies source, either natural or anthropogenic. Subsequently, if the isotopic composition of sulphur deposited upon peatland surfaces can remain relatively unchanged during its incorporation into the bog flora, and also during the transformation of the living vegetation into the non-living organic fractions, then it may be possible to use ombrotrophic peats to construct chronological records for pollutant vs. natural sulphur deposition. However, below ground sulphur cycling has been show to exhibit significant alteration effects upon the organic matrix. More work, especially upon pristine peat sites, where inputs have not changed through time, will allow a more comprehensive picture to be constructed. Comparisons with sites which have experienced significant alteration in isotopic compositions of inputs will allow further clarification of the effects of below ground sulphur cycling upon peat organic fractions.

1.3. Thesis goals

This thesis will attempt to examine the fate of sulphur in ombrotrophic peatland systems using upland peats from the southern Pennines (northern England), Abisko (northern Sweden), lowland raised peats from Thorne Moor (northern England), Forsinard (northern Scotland) and the Shetland Islands (northern Scotland). This will be largely achieved through isotopic investigations involving sulphur but also secondary evidence will also be obtained through radio and stable carbon isotope analyses as well as through standard analytical chemistry.

1.3.1. Aims

1) To assess the robustness of the sulphur signal contained in the organic fraction of pristine peatlands to determine whether an isotopic record of aerially deposited sulphur can be preserved within peat profiles.

2) To investigate whether this can be applied to polluted peatlands in order to construct the history of sulphur pollution on the southern Pennines.

3) To examine sulphur cycling in a waterlogged peat to investigate the relative importance of various processes, such as diagenesis, upon the organic sulphur fraction.

1.3.2. Objectives

a) To conduct studies to investigate the relationship between the isotopic composition of *Sphagnum* sp, *Eriophorum* sp, surface water and precipitation. This will allow an assessment of whether the isotopic signature of sulphur incorporated into surface vegetation is an accurate reflection of that of aerially deposited sulphur or whether this is masked by fractionation by surface vegetation or alterations in surface water sulphur chemistry.

b) To analyse organic sulphur signals in peats where there has been a history of sulphur pollution and compare with peats from relatively pristine sites. Such comparisons will show whether diagenetic effects significantly alter the isotopic signature of sulphur preserved in the organic fraction of peatlands and as such whether changes in sulphur signals in previously polluted peatlands can be attributed to changes in inputs rather than below ground sulphur cycling.

c) To conduct a field based manipulation study involving the addition of an isotopically rare form of stable sulphur to peat enclosures and to track the tracer sulphur signal over a 12-month period. This approach will enable accurate determinations of sulphur fate in ombrotrophic peat, which will be used to assess the extent of sulphur transformations and cycling between the 5 transposable sulphur-containing compartments, and used ultimately to examine whether these processes can alter the isotopic signature of sulphur in the organic fraction.

1.4. Experimental considerations

The U.K provides a perfect opportunity for investigations of this nature for three reasons. Firstly, its geography means that natural sulphur inputs are dominantly marine in origin with an elevated isotopic composition markedly different to that of anthropogenic emissions. Secondly, during the Industrial Revolution, huge amounts of sulphur, derived principally from the burning of coal, was released and consequently deposited upon the surrounding landscape. Thirdly, these large centres of industrial activity ring the peatlands of the southern Pennines and consequently the changes in sulphur inputs may be preserved in these peats. Therefore southern Pennine peat was sampled as well as pristine peats from northern Scotland and northern Sweden.

However, there are important considerations to be made when trying to investigate and obtain meaningful data from peat bogs. Peat accumulation, especially in upland peats, varies resulting in a very heterogeneous topography. The different types of topography recognised are; hummocks, high ridges, low ridges, *Sphagnum* hollows, mud-bottom hollows, drought-sensitive pools, permanent pools, erosion channels, erosion hags and peat mounds (see Nature Conservancy Council, 1988). Consequently a sampled stratigraphy is likely to be skewed during its development between these different microforms. Peat accumulation rates can vary from 20cm to a metre per thousand years but sometimes peat accumulation can stop altogether. If we were to sample at an area of peat that had not been actively accumulating, say over the past 250 years, trying to observe any recent records of atmospheric deposition change in the peat would obviously be impossible. Also, due to different rates of peat accumulation, replication may be made problematic. However, while signals may be skewed, it is likely that similar patterns in isotope geochemistry may be observed, albeit at different depths.

Heterogeneous peat accumulation, however, is not the only consideration when trying to interpret peatland stratigraphy. Hydrological alteration, either spatially or temporally will have important consequences for peatland chemistry. The height of the water table is critical in determining the extent of elemental cycling as well as anaerobic conditions, which has obvious implications for the cycling of sulphur. A lowering of the water table will result in the oxidation of isotopically light sulphur, produced from bacterial sulphate reduction, which may diffuse to the surface layers upon rewetting and thus becoming available for uptake by the surface vegetation. Also, the process of BSR itself may make a study such as this difficult, especially in the most waterlogged peats. The process favours the lighter ^{32}S isotope. If there is a high rate of sulphur reduction, surface waters will not only become depleted in sulphate but any remaining sulphate will also become enriched in ^{34}S thereby significantly altering the isotopic composition of the sulphate that was deposited on the surface of the bog. Therefore there is the potential for the isotopic composition of surface water sulphate to reflect not only that which is deposited aerially but also the extent of below ground sulphur cycling. This obviously has important implications when trying to use peat profiles as proxies for changes in atmospheric sulphur deposition.

In drier, upland peats, where the peat surface is typically above the water table then the above problems associated with alterations in surface water sulphur will obviously be negated. However, in both situations, dry and waterlogged peats, isotopic alteration from the respective sulphur source may still occur during sulphur uptake and assimilation by the bog flora. There is some degree of fractionation between different isotopes of sulphur by all vegetation. While the level of fractionation is typically family or genus specific most plants fractionate by the order of 1-2 ‰ (Trust and Fry, 1992). Consequently if plant biogeography remained the same throughout a peatlands recent history the fractionation rate would be the same and we should simply be able to observe a slight, but constant, shift from the original sulphur signal in the environmental water. However, in terms of the Pennines, we have a situation where there have been significant changes in the bog flora during the life of the deposit and hence, the potential exists for alterations in rates of fractionation.

Another important point to address is to what extent the sulphur signal incorporated into the surface vegetation is preserved during its transformation into peat and how stable this signal is through time. Other than the organically bound sulphur in the peat there are two other pools of sulphur, pore water/surface water sulphate and sulphide. These two pools may act in some way to alter or distort the preserved signal. The direct incorporation of sulphate into the organic fraction is unlikely as sulphate is typically unreactive and would require conversion to a more activated form before it could be incorporated into organic compounds (Wilson and Reuveny, 1976). However, sulphate, as discussed can be reduced by bacterial sulphate reduction and therefore may indirectly influence the organic sulphur fraction. H_2S can be incorporated into humic acids (part of the organic fraction) (Casagrande *et al*, 1979) and a direct labelling experiment of ^{35}S-SO_4 into an anaerobic peat core suggests that there is direct incorporation of H_2S into the organic matrix (Brown, 1985). To what extent these processes affect the isotopic composition of the original incorporated sulphur signal is as yet unknown and will be critical when trying to use peatlands as archives of sulphur deposition.

1.5. Summary

The importance of appropriate site selection when investigating the fate of sulphur cannot be overstated. Sites in Britain are perfectly suited to such investigations with upland peats in the north of England that have had a long and gross history of sulphur pollution during the Industrial Revolution as well as blanket peats from northern Scotland that can be considered relatively pristine.

In studying peatland processes, it is important to recognise and consider the different types of peats and their varied topographies, hydrological uniformity, or lack of it, belowground sulphur cycling, as well as the vegetation history of the peat. Specifically we need to examine whether sulphur deposited aerially upon peat surfaces can become incorporated into vegetation and then upon plant death preserved in the peat, with little or no alteration in its isotopic signature.

Investigations on the sulphur chemistry of peat bogs will be the principle focus of this thesis but in light of the problems and concerns outlined in this chapter other analyses will also be conducted to try and reinforce and provide other evidence for changes observed in sulphur chemistry. Such work will include the examination of carbon isotope signatures in the peat. Changes in the carbon signature can reflect environmental perturbations, either through changes in plant cover or perhaps through sulphur stresses during the Industrial Revolution. Radiocarbon and pollen data will also be correlated with any changes in sulphur isotope chemistry. The methods employed for all of these analyses will be described in the following chapter.

CHAPTER 2- Methodology

2.1. Introduction

The sampling and analytical methods described in this chapter were used principally to investigate the elemental compositions of peat and the isotopic ratios of sulphur and carbon therein. Cations and anions in surface and pore waters were also analysed and pollen grains separated and identified.

2.2. Precipitation collection

Bulk deposition was collected at sites in Sweden and in northern England to investigate the isotopic signature of aerially deposited sulphur. Precipitation was sampled as illustrated by the sampling diaries for Abisko (see chap 3) and Thorne (see chap 6). Because sulphur in rainfall is typically low (i.e. 1-2mg l^{-1}) and that isotopic analyses require a minimum quantity of SO_4, collections were made only when there was enough sample to obtain an isotopic composition. As such, sampling periods are determined by periods of rainfall/drought.

Collectors were positioned in open areas (no forest canopy) so that sulphur collected was derived solely from bulk deposition to prevent contamination from stemflow and throughflow.

Rainfall was collected in 200 mm diameter polyethylene funnels placed level and at least 1m above the ground surface to prevent contamination by splash back. Rainfall drained into 5 litre plastic jerry cans wrapped in black plastic and each containing 1 g of thymol to inhibit the growth of microorganisms. Snowfall was collected and allowed to melt and subsequently treated as rainwater samples. Rainwater samples were then processed for isotopic analysis.

2.3. Peat/vegetation collection and processing

Peat cores/monoliths collected from sites in northern England (southern Pennines), northern Sweden (Abisko) and northern Scotland (Forsinard and Shetland) were frozen immediately in dry ice, transported to the lab and stored in freezers. This prevents oxidation of the peat, which would result in reduced forms of sulphur, especially H_2S, becoming oxidised to SO_4 and H_2SO_4.

The frozen peat was sliced in regular intervals and each slice was processed via the chromous chloride reduction method (Newton *et al.*, 1995) to remove pore water sulphate, which was not recovered, and reduced sulphur species (S, H_2S, FeS, FeS_2). This method allows the direct use of the frozen peat sample and involves boiling the ground sample with 40 ml of acidified (10% HCl) 1 *M* $CrCl_2$ solution and 20 ml of concentrated HCl by the following reaction:

$$4H^+ + 2Cr^{2+} + FeS_2 \rightarrow 2H_2S + 2Cr^{3+} + Fe^{2+} \qquad \text{(Equation 2.1)}$$

This takes place in a sealed reaction vessel under a flow of purified N_2. The reduced inorganic S species in the sample (FeS, FeS_2, H_2S) are released as H_2S and carried by the flow of nitrogen through a bubble trap containing a solution of 0.1 *M* CuCl resulting in the formation of CuS, which was used for stable isotope analysis of the sulphide fraction.

$$H_2S + Cu^{2+} \rightarrow CuS + 2H^+ \qquad \text{(Equation 2.2)}$$

The amount of H_2S evolved from the sample was determined by titrating the Cu remaining in solution with 0.1 *M* EDTA. Three to four drops of glycine cresol red (0.5% aqueous) was used as an indicator and the titration was buffered with 60 ml of 1 *M* sodium acetate solution (adjusted to pH 5.5 with acetic acid).

This method results in an isotopic shift of +0.55 ± 0.14‰ with CuS precipitate being enriched in ^{34}S relative to sample and is an artefact of the valency change from S^- to S^{2-}

when pyrite becomes reduced to H_2S (Newton *et al*, 1995). These shifts are included when calculating the $\delta^{34}S$ of sulphide samples extracted by this method.

After extraction of reduced sulphur species, the remaining material (organic fraction) was washed, filtered, dried and then ground to a fine powder. Samples were then combusted in a Parr oxygen bomb allowing the liberation of C-bonded sulphur as free SO_4. Resulting solutions were treated with bromide to act as a final oxidant and any iron species were precipitated through the addition of 10% NH_3 solution. Samples were gravity filtered to remove iron precipitates and SO_4 was recovered by precipitation as $BaSO_4$ at pH 2.5-3.5 by addition of an excess of $BaCl_2$ solution and subsequent filtration onto pre-weighed filter membranes to determine sulphur yield gravimetrically.

$$BaCl_2 + SO_4 \rightarrow BaSO_4 + Cl^- \qquad \text{(Equation 2.3)}$$

Vegetation was collected at various sites to investigate sulphur content and isotopic composition. Samples, when possible to do so, were collected at least 1 m away from each other. Samples were dried and ground into a fine powder which was then combusted using a Parr oxygen bomb and sulphur recovered as outlined above.

2.4. Isotopic analyses

2.4.1. Sulphur

Due to new instrumentation in the laboratory two methods were employed to investigate the isotopic signature of sulphur. Most samples were processed by the first method. Importantly, both methods have the same degree of error)

2.4.1.1. Method 1

$BaSO_4$ precipitates were quantitatively converted to SO_2 by fluxing with $Na_3(PO_3)_3$ at 900°C in vacuo and immediate reduction of the resulting SO_3 on copper wool (Halas *et al.*, 1982). Sulphide samples were combusted with cuprous oxide to yield SO_2 directly

(Robinson and Kusakabe, 1975). The SO_2 gases were purified by standard vacuum-cryogenic techniques and analysed on a VG SIRA 10 isotope ratio mass spectrometer.

2.4.1.2. Method 2

Firstly, $BaSO_4$ and CuS precipitates are converted to SO_2 using a EuroEA3028-HT elemental analyser. Samples were weighed into light containers of oxidisable metal and dropped at preset times into a vertical quartz tube heated at 1030°C, through which a constant stream of helium is maintained. When the samples are introduced, the helium stream is temporarily enriched with pure oxygen and flash combustion takes place. Quantitative combustion is then achieved by passing the gases over WO_3 and then over reduced copper to remove excess oxygen. The resultant gas mixture is then passed through a gas chromatographic column before being admitted to and analysed by a Micromass IsoPrime mass spectrometer.

2.4.1.3. Sulphur- calculation of $\delta^{34}S$

The raw data (m/e 66/64 ratios) were corrected for instrumental and isobaric effects by standard procedures (e.g. Colman, 1980). Isotope ratios are quoted as delta values in per thousand (‰ or per mille) relative to an international standard, Canon Diablo Troilite (CDT) according to:

$$\delta^{34}S = \left[\frac{(^{34}S/^{32}S)_{spl}}{(^{34}S/^{32}S)_{std}} -1 \right] \times 10^3$$

Equation 2.4

Thus enrichment in ^{34}S relative to the standard is expressed as a positive value and depletion as a negative value. Analytical uncertainty, estimated from analyses of standardised materials is ± 0.2‰.

2.4.2. Carbon isotopic analysis

Peat samples for organic carbon isotope analysis are dried at 60°C for 24 hours. The preparation method is that described in Boutton (1991) with minor modifications. 6mm OD quartz tubes, sealed at one end and CuO are pre-combusted at 550°C for 8 hours to remove any organic contaminants. 2mg of peat is mixed with an excess of CuO and loaded into a numbered tube with a 15cm length of both copper and silver metal wire. The tubes are then evacuated to below 1mbar pressure and sealed. The tubes are then combusted at 870°C for 12 hours, whereupon they are slowly cooled to room temperature. They are then cracked under vacuum, and the CO_2 gas cryogenically purified.

Purified gas samples were analysed using a VG Sira-10 gas source mass spectrometer and the data corrected using standard procedures (Craig, 1957). The carbon isotopic composition is reported in standard δ notation in per mille units (‰) relative to the PDB (Pee dee belemnite) standard.

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{spl}}{(^{13}C/^{12}C)_{std}} - 1 \right] \times 10^3$$

Equation 2.5

2.5. Elemental analysis (C, H and N)

A Carlo-Erba Elemental Analyser model 1106 was used to determine total carbon, hydrogen and nitrogen. The organic samples are weighed into light containers of oxidisable metal and dropped at preset times into a vertical quartz tube heated at 1050°C, through which a constant flow of helium is maintained. When the samples are introduced, the helium stream is temporarily enriched with pure oxygen. Flash combustion takes place, primed by the oxidation of the containers. Quantitative combustion is then achieved by passing the gases over Cr_2O_3. The mixture of the combustion gases is transferred over a reduction reactor filled with copper at 650°C to eliminate excess of oxygen then, without stopping, it is introduced into the chromatographic column, heated at about 80°C and packed with porapak QS. The individual components are then separated, and eluted in the order N_2-CO_2-H_2O and are measured by a thermal conductivity detector.

2.6. $\delta^{34}S$ Tracer preparation and addition for isotopic enrichment study at Thorne Moor.

2.6.1. Tracer preparation

475mg of elemental sulphur (for details of enrichment see Tables 2.1, 2.2) provided by Euriso-Top™ was combusted in heavy-duty glass vessels producing isotopically rich SO_2, which was trapped with H_2O_2, forming H_2SO_4. The solution was neutralised with sodium carbonate and made up to a volume of 3 L to which 19.32 g of NaBr was added as a conservative tracer so that any dilution effect upon the sulphate added could be observed. Overall the solution contained 0.474 mg mL^{-1} of isotopically enriched SO_4 and 6.44 mg mL^{-1} of NaBr (a SO_4/Br ratio of 0.0736).

Table 2.1. Isotopic composition of prepared tracer solution

Isotope	32	33	34	36
Content %	0.04	0.42	99.50	0.04

Table 2.2. Chemical impurities of tracer solution

Element	Ag	Al	Ca	Cu	Fe	Mg	Mn	Si
ppm	10	300	500	10	50	50	70	100

2.6.2. Site plots and sampling

Four small enclosures (1x1 m), identified as 1A and 2A (harvested after 3 months) and 1B and 2B (harvested after 6 months) and 2 larger, long-term enclosures (1x2 m) identified as 1C and 2C were constructed from acrylic sheet inside an untreated wooden frame and installed into areas of raised peat at Thorne Moors. This served to isolate the higher portions of the peat (depth of 0.7 m) and the surface water so that the tracer added would be confined to a set area of bog for detailed study.

For each tracer addition 100 mL of tracer solution was administered per m^2 so that each plot received the same volume of tracer per unit area (47.44 mg SO_4 m^2). Tracer was administered as recorded in the sampling diary (Table 2.5).

Table. 2.3. Sampling and Tracer addition diary for Thorne Moors investigation

Time scale	Actual Date	Tracer addition	Type of sampling	
			Surface water/ Pore water	Coring and cropping
Day 0	7.6.01		✓	✓ Controls
Day 1	29.6.01	✓		
3 Weeks	19.7.01	✓		
6 Weeks	8.8.01		✓	
12 Weeks	21.9.01		✓	✓ Enclosures A
12 Weeks + 1 day	24.09.01	✓		
18 Weeks	1.11.01		✓	
24 Weeks	13.12.01		✓	✓ Enclosures B
24 Weeks + 1 day	14.12.01	✓		
30 Weeks	24.12.01		✓	
36 Weeks	7.3.02		✓	
36 Weeks + 1 day	8.3.02	✓		
42 Weeks	18.4.02		✓	
48 Weeks	7.6.02		✓	✓ Enclosures C

Pore water was recovered via depth sampling tubes inserted to different depths in the peat (enclosures 1C and 2C) using a peristaltic pump. Surface water was sampled by carefully bailing water from the pool in order to minimise the movement of water from deeper in the peat profile. The water recovered was sampled directly into 5 litre canisters containing a weighed quantity of copper chloride in order to recover H_2S as copper sulphide. All water samples were filtered to collect copper sulphide and any sulphate in the remaining sample was recovered as $BaSO_4$, and ashed at 500°c to remove organic contaminants.

For each pore water and surface water sample a small sub-sample was taken for cation and anion analysis. Samples for cation analysis were filtered to 0.45μm, acidified in the field, and measured by Fisons Maxim 110 ICP-AES against a seven-point calibration for iron and manganese. During analysis a standard was run every 5 samples to ensure accuracy. Samples for anion analysis were filtered to 0.2μm and organics removed using a C18 (endcapped) resin cartridge and analysed by Dionex-4500 IC with AS4 or AS14 column. A standard was ran for every 10 samples and compared against a 6-point calibration.

Three peat cores were sampled at day 0 (TC-A, TC-B and TC-C) prior to tracer addition along with surface vegetation. At 3 months, enclosures 1A and 2A were harvested by firstly taking 2 peat cores from each followed by vegetation cropping. This was repeated at 6 months (enclosures 1B and 2B) and at 12 months (enclosures 1C and 2C). Peat cores are labelled according to the enclosure sampled from, for example, peat cores sampled from enclosure 1A are identified as 1A-1 and 1A-2.

2.6.3. Sample processing and considerations

When dealing with isotopically enriched samples in the laboratory it is important to ensure that contamination of unenriched samples does not occur. A potential problem was identified in the combustion of peat and plant samples using the Parr Oxygen combustion bomb. Unlike the other materials in the lab, acid washing was not possible, so it was important to investigate whether conventional washing techniques would remove enough residual sulphur to limit any obvious contamination effects. As such a number of tests were conducted to investigate using heavily enriched *Sphagnum* samples and a homogenous coal sample. Control coal samples were combusted to yield less sulphur than enriched samples to give a worst case scenario of contamination i.e. most enriched samples with large S yield (flooding the bomb) followed by unenriched samples with only a small yield. Results from Experiment 1 (Table 2.4) show that under such worse case scenario conditions there is a 1-1.5 ‰ deviation away from the true values and importantly, this effect was shown to persist in following samples. From the yields precipitated it would appear that there must only be a very small residual quantity of sulphur left in the bomb after running an enriched sample. However, this residual sulphur has a greatly elevated $\delta^{34}S$ and is exerting the small shift in isotopic composition.

Table 2.4. Parr bomb ^{34}S contamination test results – Experiment 1

Run order	Sample id	mg combusted	S mg yield	$\delta^{34}S$
Coal-small	PBT2-1	100	1.2	1.4
Coal-small	PBT2-2	100	1.0	1.9
Coal-small	PBT2-3	100	1.4	1.5
Enriched *Sphagnum*	PBT2-4	2220	4.6	66.4
Enriched *Sphagnum*	PBT2-5	2240	5.3	91.6
Enriched *Sphagnum*	PBT2-6	2260	6.0	107.6
Coal-small	PBT2-7	100	1.3	2.8
Coal-small	PBT2-8	100	1.0	2.9
Coal-small	PBT2-9	100	1.1	2.9

If we can thus contaminate this residual enriched sulphur persisting in the Parr oxygen bomb with a more natural signal then alteration in isotopic composition of more 'natural' samples will not occur. As such it is necessary to flood the bomb directly after an enriched sample with a more natural sample. This is confirmed by the results of experiment 2 (Table 2.5). Therefore, after running all enriched samples a large coal sample was combusted followed by a smaller coal sample of which the isotopic composition was determined to check that any residual isotopic effect had been removed before running further samples.

Table 2.5 Parr bomb ^{34}S contamination test results – Experiment 2.

Run order	Sample id	mg combusted	S mg yield	$\delta^{34}S$
Coal-big	PBT3-1	500	4.1	3.7
Coal-small	PBT3-2	100	1.4	1.9
Coal-small	PBT3-3	100	1.4	1.9
Enriched *Sphagnum*	PBT4-1	2580	6.7	60.1
Coal-big	PBT4-2	500	4.3	1.0
Coal-small	PBT4-3	100	1.4	1.9
Coal-small	PBT4-4	100	1.2	1.8

Water, vegetation and peat samples were processed as previously described however it was necessary to adjust their isotopic composition prior to isotopic analysis to bring their values within the accepted analysis range of mass spectrometry. A stock standard solution (1mg/ml SO_4; $\delta^{34}S$ – 0.5‰, s.d. 0.3) was prepared and a measured volume added to each enriched sample immediately prior to precipitation as $BaSO_4$. Precipitates were then analysed as in methods 1 and 2 and true $\delta^{34}S$ values were calculated as below.

$$\text{True } \delta^{34}S = \left[\text{total } \delta^{34}S - \left[\left[\frac{\text{mass } SO_{4\,\text{std}}}{\text{mass } SO_{4\,\text{total}}} \right] \times \delta^{34}S_{\text{std}} \right] \right] \times \left[\frac{\text{mass } SO_{4\,\text{total}}}{\text{mass } SO_{4\,\text{spl}}} \right]$$

Equation 2.6

Another important consideration was in the determination of sulphur enriched surface vegetation. The cropped *Sphagnum* from the enclosures will have three forms of sulphur associated with its biomass; organically bound sulphur, i.e. what has been assimilated into the plant tissues, intracellular SO_4, and surface water SO_4 persisting on the surfaces of the vegetation. One of the main purposes of the tracer investigation was to examine how much of the tracer sulphur becomes incorporated into the surface biomass. However, the potential exists for this information to be obscured by contamination from the very enriched surface water SO_4 on its stems and leaves, as well as from the intracellular SO_4. Intracellular SO_4 in *Sphagnum* moss is likely to be similar in isotopic composition to the very enriched surface water because *Sphagnum* acts like a sponge (water content ~90 %), soaking up the surface water it is bathed. As such, *Sphagnum* moss was washed in distilled water and the water was squeezed out. This process was then repeated. While repeated washings in distilled water will remove surface water SO_4 and to some extent intracellular SO_4 due to osmotic effects, there is a potential for some intracellular SO_4 to remain. Though this may be small in concentration, its isotopic composition may be so high as to affect the organically bound sulphur signature. Therefore data from control *Sphagnum* sampled prior to tracer addition and surface water chemistry during the 12-month investigation were used to investigate a 'worst case scenario' of how intracellular SO_4 may affect the isotopic analysis of organically bound sulphur in *Sphagnum*. To do this two principle assumptions were made. Firstly that the sulphur content of surface waters was equal to intracellular SO_4 contained within the cells of *Sphagnum* and secondly that it is has the same isotopic composition. These assumptions were deemed valid, as *Sphagnum* is known to have extremely porous hyaline cells, exerting little control over what enters and leaves. Therefore using the sulphur concentrations and isotopic compositions of waters during the tracer investigation and from control *Sphagnum* an isotopic mass balance was used to determine how intracellular SO_4 might affect the isotopic composition of *Sphagnum* if no incorporation of tracer into biomass occurred.

Control *Sphagnum* has a mean sulphur content of 0.1 %, a mean water content of 90.0 % and a mean $\delta^{34}S$ of 1.9. Some of the most extreme surface waters $\delta^{34}S$ were observed during the investigation at 48 weeks in enclosure 2C (0.8634 S mg L, $\delta^{34}S$ 248.5 ‰). This data was therefore used in the isotopic mass balance to examine the potential effects of intracellular sulphur under worst-case scenario conditions. In 10 g of *Sphagnum*, 9 g (9 ml's) will be intracellular water and 1 g solid. Consequently we have a biomass solid fraction with 1 mg S ($\delta^{34}S$ 1.9 ‰) and an intracellular water fraction containing 0.00776 mg S ($\delta^{34}S$ 248.5). An isotopic mass balance indicates only a 1.9 ‰ enrichment factor under worst-case scenario conditions if no intracellular water was removed.

$$(0.99228 \times 1.9) + (0.007716 \times 248.5) = 3.8 ‰ \qquad \text{Equation 2.7}$$

However, because the *Sphagnum* was frozen prior to analysis, which would result in the breakage of cell membranes, and also through repeated washings and 'wringing' out of the *Sphagnum* such an effect, even though small, should be minimised.

2.6.4. Calculation of tracer fate

The % of tracer residing in surface waters was determined by calculating how much SO_4 was expected to be in the top 5 cm's of the waters contained by the enclosures by using sulphur content and isotopic data. Control data from day 0 was used as a baseline for isotopic composition, which does not take into account seasonal variability in isotopic compositions. However, such differences are slight (range of <10 ‰ – See Chap 5). The large enrichments in ^{34}S will significantly dwarf any natural variations, which have more recently been minimised due to damming of the bays at Thorne moors over recent years.

The fate of the tracer (% incorporated) into the various fractions within the peat was calculated by examining the isotopic compositions of the organic and inorganic sulphur in the peat cores sampled from all 6 of the enclosures and comparing them to the three control peat cores collected prior to tracer addition.

The difference in the percentage of ^{34}S between the control and enriched cores was used to calculate how much ^{34}S (mg) had been potentially added to bring about the change in $\delta^{34}S$ in the enriched core fractions. ^{34}S content in the peat cores fractions were summed for each treatment (i.e. biomass in controls cores and for both cores from each enclosure) and % ^{34}S calculated. Control ^{34}S % was subtracted from enriched ^{34}S % and this difference was used to calculate how much ^{34}S (mg) had been potentially added to each sulphur fraction in the enriched cores (see appendix D for detailed calculations). This value was scaled up for each enclosure to calculate how much of the tracer administered had been taken up into each of the sulphur containing fractions. Enriched sulphur fractions were also compared against minimum and maximum ^{34}S % in the control core fractions in order to express the level of natural variation in ^{34}S content within unenriched peats.

Using this approach incorporation of the tracer into the total inorganic sulphur pool (H_2S, S^0, FeS and FeS_2) can only be an underestimate as in some cases only small yields of sulphur were obtained and as such isotopic analyses was impossible. Therefore the calculation can only include the samples of which isotopic composition was known.

Due to differences in humification, the organic fraction of each peat core was divided into 3 principle regions and analysed as different fractions. These were; the surface biomass (essentially the living vegetation), an upper necromass layer (to a depth of 20-25 cm) and a lower necromass layer (depth below ~25 cm).

In order to calculate the % of tracer incorporated into the various fractions a number of assumptions were made.

1) that the contribution of the stable isotopes ^{33}S and ^{36}S to the total sulphur content of the different fractions will be minimal and therefore not considered in the calculations.

2) that control data is representative of variability in isotopic compositions of the peat fractions prior to tracer addition.

3) that the division between biomass and necromass layers in the two cores sampled are roughly representative of the depths of these layers in the enclosure as a whole.

4) that tracer distribution and sulphur content in the surface and porewaters will be reasonably uniform within the area confined by the enclosure.

2.7. Pollen analyses

Peat samples were sub sampled from peat slices prior to isotopic analysis so to relate to isotopic compositions. The peat was physically broken down by boiling ~1g in a 10% solution of sodium hydroxide for 30 minutes. The remaining material was sieved to remove larger plant debris and cellulose was removed by washing, boiling and centrifuging in firstly, glacial acetic acid and then in a solution of acetic anhydride and sulphuric acid. The pollen debris was again washed in sodium hydroxide and distilled water before being mounted for analysis by light microscopy. Due to the nature of the deposit (low arboreal pollen levels) a total pollen count of 500 was deemed more suitable than a standard 150-tree grain count.

2.8. Radiometric analyses

Peat samples were dried and sent to the Radiocarbon Dating Laboratory at the University of Waikato in New Zealand where all chemical pre-treatment was also carried out. This consisted of acid washing in 10% conc. HCl and rinsing, washing in hot 0.5% NaOH, acid washing in 10% conc. HCl, rinsing and drying. The base insoluble fraction was selected for dating. Radiometric result as per Stuiver and Polach,

1977. This is based on the Libby half-life of 5568 yr with correction for isotopic fractionation applied.

CHAPTER 3. Preservation of Environmental Sulphur Isotope Records in Pristine Peats

3.1. Introduction

Peat deposits are widespread over temperate and higher latitudes and have accumulated during the Holocene and previous interglacials. They are important archives of palaeoenvironmental information through pollen (e.g. Tallis, 1964a), as well as faunal records (e.g. Lavoie *et al.*, 1997). Potentially too, their geochemistry may also reflect environmental change (e.g. Jedrysek *et al.*, 1996, Shotyk *et al.*, 1996) and maritime versus continental location (c.f. Shotyk, 1997 vs. Shotyk *et al*, 1996) and in this respect their sulphur chemistry may be particularly important as a record of the timing and extent of anthropogenic atmospheric sulphur inputs. Over much of northwest Europe, the dominant sulphur source to natural, pre-anthropogenic atmospheric inputs will have been of maritime origin, which is characteristically enriched in the heavier ^{34}S isotope of sulphur with $\delta^{34}S \sim +20$ ‰ (e.g. Thode *et al.*, 1961). By contrast, fossil fuel burning produces SO_2, which is significantly ^{34}S-depleted (e.g. McArdle and Liss, 1995). Many lowland raised bogs and upland blanket bogs are ombrotrophic, receiving all their nutrient and other chemical inputs from atmospheric deposition. Changes in the source of atmospheric sulphur inputs to peatlands may be accompanied by a change in sulphur isotope composition of sulphur taken up by growing plants. The organic sulphur isotopic composition in ombrotrophic peat sequences could thus potentially provide a record of anthropogenic impacts through the assimilation of the sulphuric acid component of acid rain into surface vegetation and its subsequent preservation in the peat profile.

Incorporation of sulphur into peats is not a simple process. Uptake and assimilation of sulphate into plants is known to involve a small degree of isotopic fractionation although, importantly, this has been shown to be similar in a wide range of vegetation types. Typically $\delta^{34}S$ values average ~1.5 ‰ less than that of environmental sulphate (see Trust and Fry, 1992 for review), however, larger fractionations have been reported for *Sphagnum* species which dominate pristine peat bogs (Bottrell and Novak, 1997). Also, sulphur is present in more than one form in peats and may be incorporated at more than one stage, with later diagenetic sulphide, produced by bacterial reduction of sulphate, being added to that initially assimilated by living plants.

The purpose of this chapter is to examine the extent to which diagenesis may have obscured the primary S isotopic record in pristine peats. Data are presented on sulphur fractions and their isotopic compositions from a peat deposit of mid-Pleistocene age in a maritime setting and also three modern pristine peats, which have accumulated under different conditions. The mid-Pleistocene deposit unarguably predates any anthropogenic sulphur emissions. It also has a long post-depositional history through at least one glacial-interglacial cycle when different diagenetic processes could have operated to mask or alter the primary isotopic signal. The modern pristine peats were sampled from Lumbister (Shetland Islands), Forsinard (N.E. Scotland) and Abisko (N. Sweden) (Fig. 3.1). Lumbister and Forsinard are areas distant from sulphur emissions during the Industrial Revolution yet exposed to high levels of sulphur inputs from ocean derived sulphate. As such sulphur inputs will be isotopically heavy. Abisko, is located in a mountainous region of northern Sweden close to the border with Norway, and as such, receives more 'continental' natural sulphur inputs, which are isotopically light.

3.2. Study Sites

3.2.1. Fugla Ness

Fugla Ness lies on the northwest coast of North Roe in the Shetland Isles, between Scotland and Norway (Fig. 3.1) (GR HU356301). The geology and pollen analyses of the peat deposit are reviewed by Lowe (1984), Sutherland (1991) and Hall *et al.* (1983).

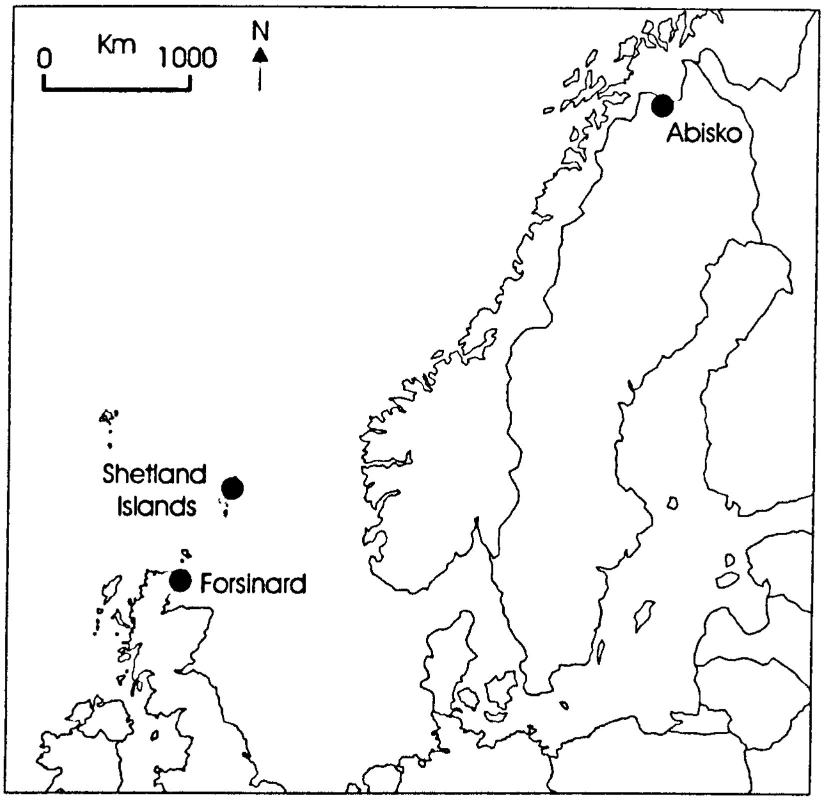

Fig. 3.1. Location of field sites.

The deposit lies stratigraphically between two glacial tills and must have formed during a previous interglacial. The presence of pollen from thermophilous trees suggests an interglacial period warmer than the present, since woodland has not colonized the Shetland Isles during the present Holocene interglacial. The deposit is generally thought to date from Isotope Substage 5e (c. 128ka), one of the two warmest periods in the North Atlantic over the last 600ka (Ruddiman and McIntyre, 1976). The peat deposit was sampled by S. Bottrell and R. Newton in June 1996. The lowest few mm of the peat contained silty bands, above this lay 320 mm of homogenous well-humified peat with rare siltier horizons. The upper part of the peat contained more lithic clasts and a large proportion of woody material. The peat surface was cut back and the peat sampled as a series of horizontal spits. Lithic clasts and woody material were removed prior to analysis. Surface waters were sampled from five areas of blanket bog near the west coasts of Mainland, North Roe and Yell in the Shetland Isles (see Fig. 1). Care was taken not to include deeper porewaters when sampling. Dissolved sulphate was quantitatively recovered as $BaSO_4$ for isotopic analysis. Sample processing of Fugla peat was conducted by D. Hatfield and S. Bottrell at the University of Leeds.

3.2.2. Lumbister

Lumbister is located on the island of Yell in the Shetland Islands (GR HU500900). The geology is varied metamorphic rocks overlaid by Quaternary till sand, blanket peats and peaty podsols between 30-150 m.a.s.l. Rainfall is typically 1000-1500 mm y^{-1}, with an average mean daily temperature of 7.5 °C. From April to September the excess of precipitation over evapotranspiration is approximately 200 mm. Two large monoliths were sampled along with surface vegetation.

3.2.3. Forsinard

Forsinard is situated in the Scottish county of Sutherland (GR NC900450), which along with Caithness makes up the region commonly referred to as 'The Flow Country'. The area of peat in the Flow Country is vast with approximately 401,375 ha of the region covered by ombrotrophic blanket peat (52 % of total region) (Nature Conservancy Council, 1988). This has been made possible due to a suitable climate and topography. Rainfall at the study site at Forsinard is around 1000-1500mm per annum which is much lower than western Sutherland but the high number of wet days results in a consistently moist peat, which along with a average daily mean temperature of 8°C, is particularly suitable for peat accumulation. The Forsinard pool complex is approximately 155 m.a.s.l. and comprises 641 permanent pools, within an area less than 0.25 km^2 (Belyea and Lancaster, 2002). Solid geology is that of intrusive rocks (mainly granite) and siliceous and semipeltic granulites with igneous and meta-sedimentary portions approx equal in amount resulting in a relatively impervious bedrock layer. Fen peat began to accumulate around 9000 years ago and then blanket peat started to cover the landscape around 6800 years ago (Charman, 1992). Vegetation cover consists of *Sphagnum* Spp. (Fig. 2.8.), *Racomitrium* l. (Hedw.) Brid, sedges (e.g. *Trichophorum caespitosum* (L.) Hartman, *Eriophorum* Spp., *Carex* Spp and small shrubs (e.g. *Calluna vulgaris* (L.) Hull, *Myrcia gale* (L.) and emergent stands of *Menyanthes trifoliata* (L.) (Belyea and

Lancaster, 2002). Three peat cores were sampled from a waterlogged pool complex along with a number of *Sphagnum* samples from the surface of the pool.

3.2.4. Abisko

Abisko is located on the southern shore of Lake Torneträsk at an elevation of 385 m above sea level. The mean annual temperature is - 0.5 °C. July is the warmest month with a mean temperature of +11 while January is the coldest with a mean temperature of -12 °C. Mean annual precipitation is extremely low at around 320 mm (data from the metrological database at Abisko Naturvetenskapliga Station). All of these factors result in a growing season that lasts only slightly longer than three months (Rosswall *et al*, 1975). A small area of blanket bog close to the scientific station (68°21'N, 18°50'E) was chosen for study. The mire covers an area of around 200 m^2, which is surrounded by birch scrub on the southern side with the northern limits bordering the banks of Lake Torneträsk. The typical mixed mosaic of fen and bog common to northern Fennoscandia (Mårtensson, 1956) can be observed at this site with the drought tolerant *Sphagnum fuscum* dominant (Vascular flora present included; *Empetrum hermaphroditum* Hagerup, *Rubus chamaemorus* L., *Vaccinium microcarpum* (Turcz.) Schmalh., *Drosera rotundifolia* and *Betula nana* L.). Though a number of *Sphagnum* species have been recorded in this region (Persson, 1965) only *S. fuscum* and *S. girgensohnii* were observed at the site. Two peat cores were taken from the peatland (one analysed), which had dried significantly during the summer months. *Sphagnum* samples were taken of both species present.

3.3. Results

3.3.1. Fugla Ness

Concentration and isotopic ratios for organic S and sulphide S of the peat are presented as a vertical profile in Fig. 3.2. The sulphidic-S is present at generally much lower concentration than organic-S and exhibits a very wide range of isotopic compositions (from -10.4 to +58.6 ‰), while in most samples the organic-S isotopic composition lies in a narrower range between +7 and +12 ‰. There is a tendency to low sulphide concentrations in the peat where sulphide $\delta^{34}S > +20$ ‰ (Fig. 3.3) whereas there is no correlation between $\delta^{34}S$ and organic sulphur content (Fig. 3.4).

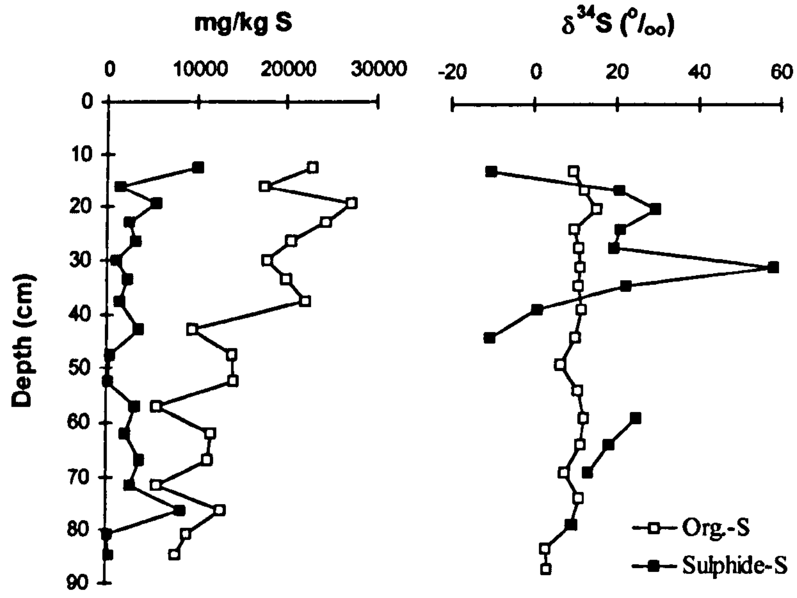

Fig.3.2. Depth versus S content and $\delta^{34}S$ in Fugla Ness peat.

The difference in isotopic composition between peat organic S and surface water sulphate are plotted as a histogram in Fig. 3.5. Also plotted are data for differences in sulphur isotopic composition between growing *Sphagnum* and surface water sulphate for relatively pristine bogs in Connemara and Mull (Bottrell and Novak, 1997). When these differences are compared and when only data from pure peat is considered (i.e. clay-peat interbeds excluded), there is no significant difference (t= 0.72, d.f. = 12, p= 0.48) between the isotopic composition of the Fugla Ness peat organic sulphur and that which would be expected for *Sphagnum* growing under maritime influenced conditions.

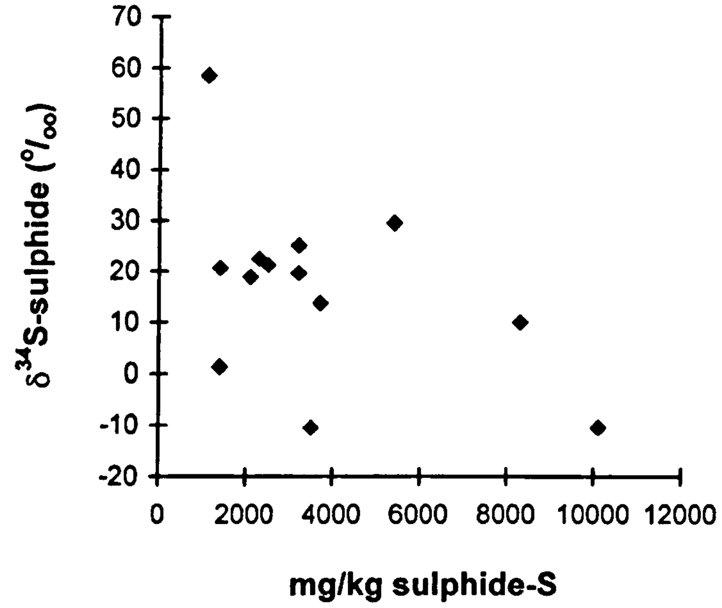

Fig.3.3. Wt% sulphide-S versus δ^{34}S-sulphide in Fugla Ness peat.

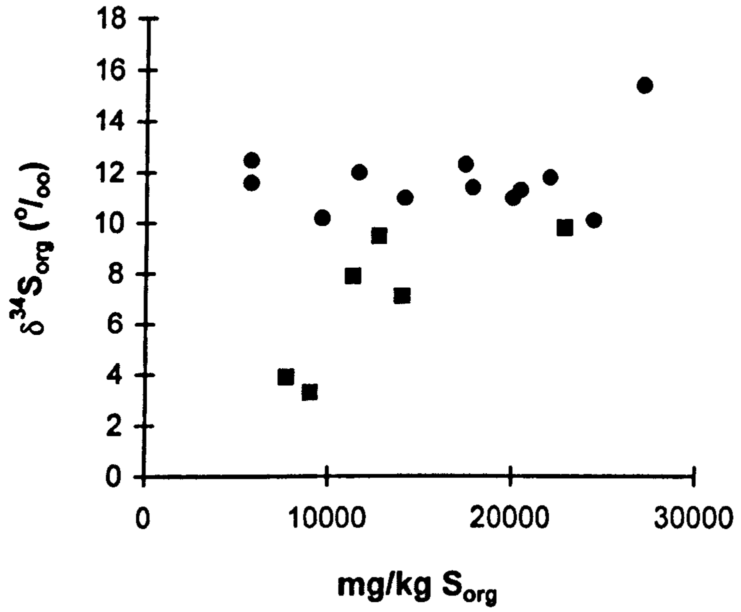

Fig.3.4. Wt% S organic fraction versus δ^{34}S-organic fraction in Fugla Ness peat (solid square = clay peat interbed, solid circle = pure peat).

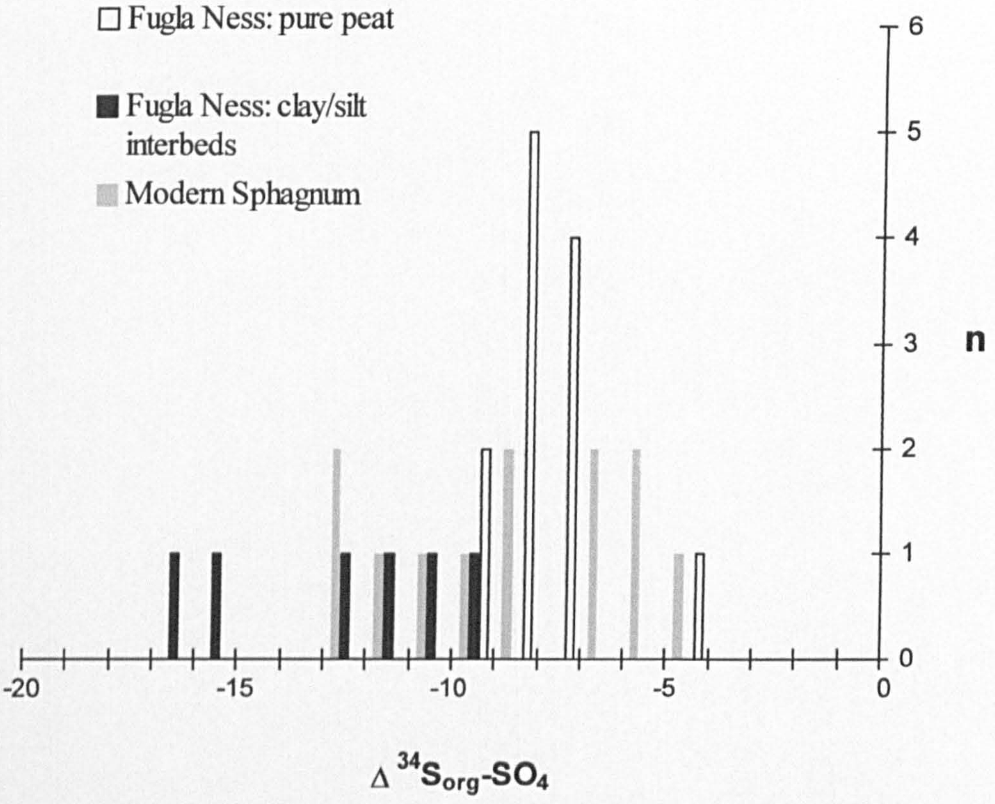

Fig.3.5. $\delta^{34}S$ frequency differences between organic sulphur component and surface water sulphate (a surface water sulphate value of +19.6 ‰ applied in the case for Fugla Ness peat).

3.3.2 Lumbister

Radiometric analyses allowed for peat accumulation rates to be calculated for three parts of one of the monoliths (SH1). Samples were dated as 1178 ± 45 BP at 41 cm (WK-12431) and 406 ± 45 BP (WK-12432) at 27 cm. Peat accumulation rates were 0.067 cm y-1 (0-27 cm), 0.018 cm y-1 (27-41 cm) and 0.035 cm y-1 (0-41 cm).

Organic sulphur concentrations showed little variation in the upper 30 cm until between 30 and 40 cm where there is a pronounced peaking in both profiles (~800 to ~950 mg/kg dry weight) (Fig.3.6). Inorganic sulphur concentrations also show a tendency to increase with depth, although this is less marked in monolith SH-2.

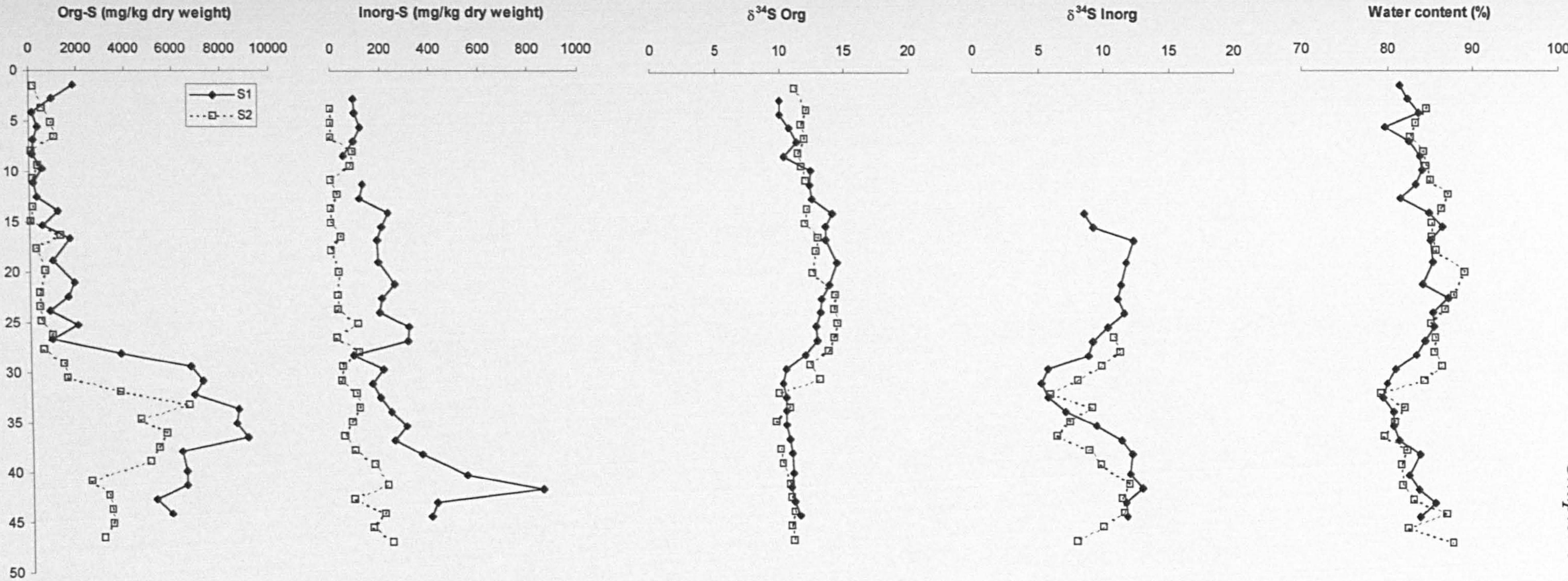

Fig. 3.6. Sulphur content, isotopic compositions and water content in Lumbister peat.

Isotopic compositions are remarkably similar between both profiles. $\delta^{34}S$ of the organic fraction is relatively consistent in the surface layers (top 5 cm) (SH1- 10.0 to 11.0 ‰; SH2- 11.2 to 12.2 ‰). $\delta^{34}S$ shows a gradual increase with depth, peaking at 14.4 and 14.5 ‰ in SH1 and SH2, respectively. Isotopic compositions then decline in the deepest peats sampled. Total range for the variability in the organic fractions is 4.4 ‰ in SH1 and 4.8 ‰ in SH2.

Calculated mean peat accumulation rates (derived from radiometric analyses) for the upper and lower zones of the profile were used to calculate mean ages for peat slices in the upper and lower zones respectively. Mean age is plotted against organic sulphur isotopic composition in Fig. 3.7. The small alteration in $\delta^{34}S$ is shown to occur in around the last 500 years.

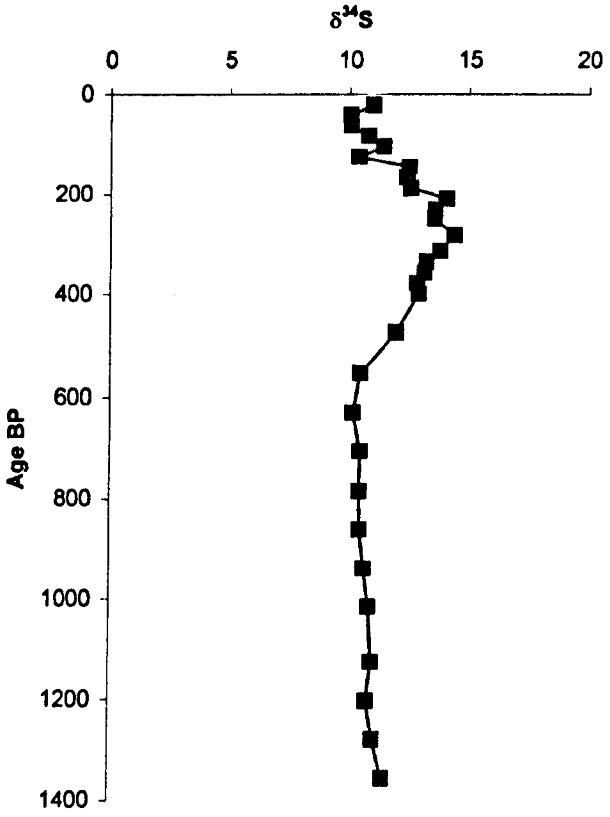

Fig. 3.7. $\delta^{34}S$ versus calculated mean age in Lumbister peat (SH-1).

Both monoliths exhibit similar patterns in inorganic $\delta^{34}S$ with depth with a pronounced negative excursion between 30 and 40 cm, which correlates well with the shift to more negative isotopic compositions in the organic fractions.

OrgS/C shows a similar relationship to that of OrgS vs. depth with a progressive increase to around 27 cm, below which there is a significant peak (Fig.3.8). This alteration is also paralleled by a change in water content. Water content was reasonably consistent throughout the profile, ranging between 80 and 90 % (Fig. 3.6) yet between 25 and 30 cm there is a pronounced drop towards the base of the peat sampled.

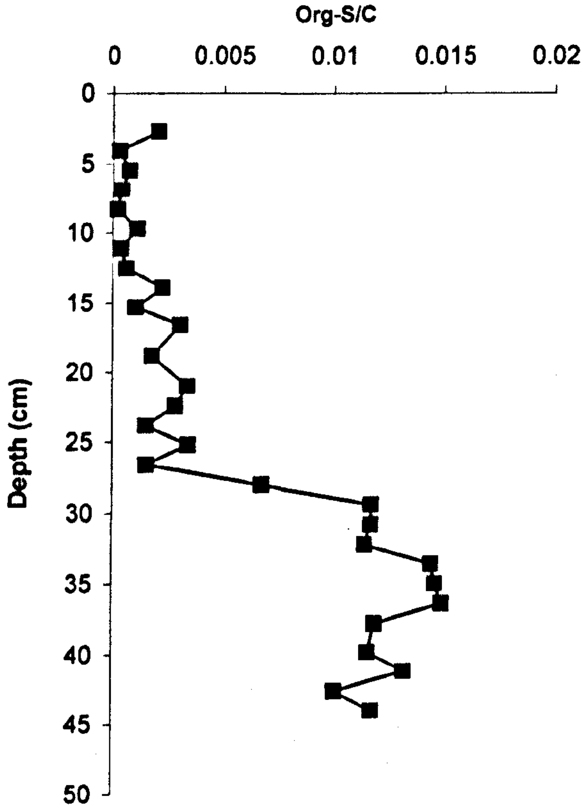

Fig. 3.8. Organic sulphur/carbon versus depth in Lumbister peat (SH-1).

Surface waters from Shetland have a mean isotopic composition of 18.8 ‰ (s.d.=2.12, n=4). *Sphagnum* was much lighter, relative to the surface waters, with a mean $\delta^{34}S$ of 8.9 ‰ (s.d.= 0.25, n = 4).

3.3.3. Forsinard

Peat from Forsinard was dated at 456 ± 70 BP at 36 cm giving an accumulation rate of 0.079 cm y-1 (1 cm = 12.7 y).

The organic sulphur content was lowest in all of the cores at the surface (Fig. 3.9). The total range was between ~2000 and ~8000 mg/kg dry weight between the three cores sampled. Core 1 shows a weak trend to increasing sulphur content with depth. Core 2 exhibits the least degree of variability, with a slight decrease from the surface until the deeper sections in which there is slight deviation to increased sulphur contents. Core 3 exhibits the largest degree of variability and over the largest ranges with no obvious patterns discernable.

Inorganic sulphur contents are equally variable among the three cores. Core 1 broadly has a trend to increasing sulphur content with depth, while cores 2 and 3 show a number of peaks at various depths in the profiles.

Organic $\delta^{34}S$ is consistent between all three cores in the surface layers (largely made up of living surface vegetation)(12.5, 12.4 and 13.1 ‰ respectively). However, $\delta^{34}S$ increases with depth. In cores 1 and 2 there is a gradual increase with the highest value recorded in the deepest peat sampled, yet in core 3, the highest $\delta^{34}S$ is seen around 13 cm (18.0 ‰) followed by a gradual decline with depth (15.5 ‰ at ~43 cm).

Inorganic $\delta^{34}S$ profiles exhibit similar alterations in isotopic pattern and absolute values to that of organic $\delta^{34}S$ (range ~10 to ~20 ‰). Inorganic sulphur compositions are relatively light in the surface layers before becoming more enriched with depth.

Water content was high throughout the profiles, being the wettest of the peat types sampled, ranging between 90 and 98 %.

Sphagnum sampled from pools had a mean $\delta^{34}S$ of 13.504 ‰ (n=12, s.d = 1.0) and a mean sulphur content of 0.19 % (n=12, s.d.=0.05).

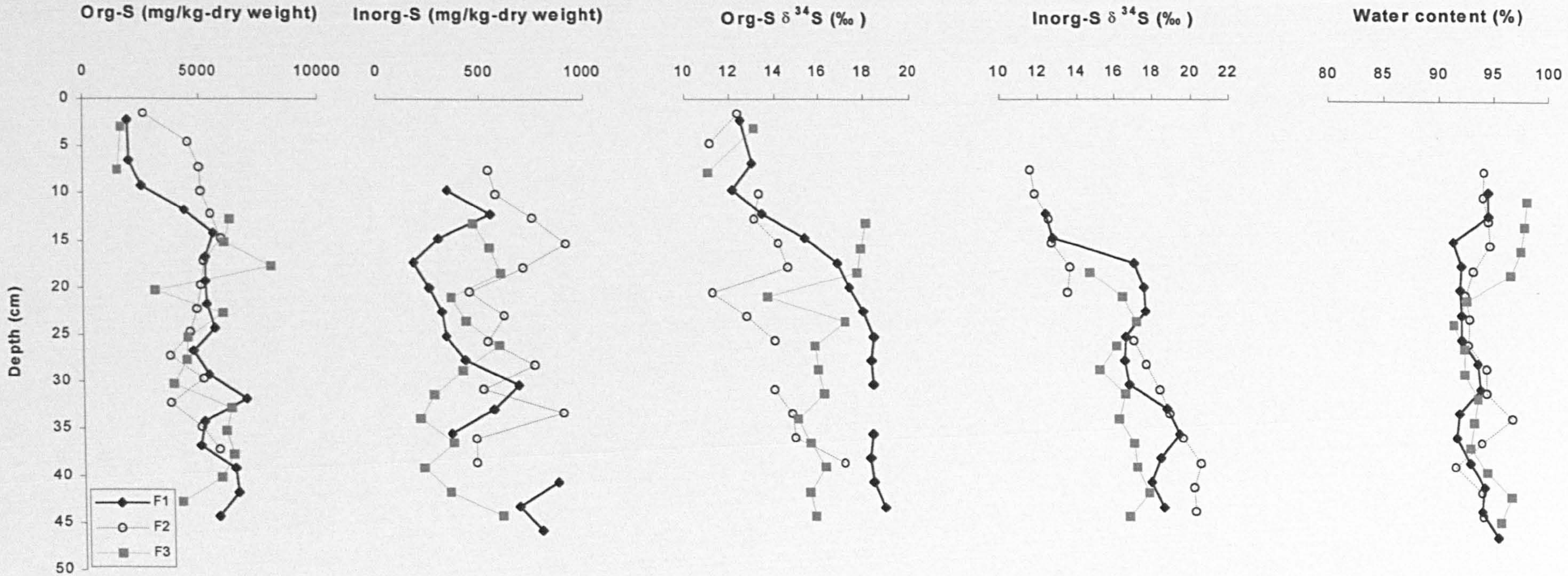

Fig. 3.9. Sulphur content, isotopic compositions and water content in three waterlogged peat cores sampled from Forsinard (NE Scotland).

3.3.4 Abisko

Aerial sulphur inputs were ^{34}S-depleted relative to that expected for peats under maritime situations. Isotopic compositions ranged between 3.3 and 4.9 ‰ (Table 3.1).

Table 3.1. Isotopic composition of bulk sulphur inputs at Abisko (2000/01).

Sampling period	$\delta^{34}S$
7/00 to 10/00	4.9
10/00 to 6/01	3.3
6/01 to 7/01	4.7

The chief form of sulphur in Abisko peat was organically bound (Fig.3.10). Organic sulphur content shows a large degree of variability in the profile although concentrations only range between ~10 and ~600 mg/kg dry weight. Inorganic sulphur concentrations were very low throughout the profile ranging between 7 and 47 mg/kg dry weight. Such small yields prevented isotopic analyses of the inorganic fraction.

Organic $\delta^{34}S$ shows a somewhat variable trend of enrichment with depth, from 6.7 ‰ in the uppermost layer to 14.8 ‰ at 22 cm. At the bottom of the profile values become significantly lighter (-0.9 to 3.5 ‰).

Water content was reasonably constant through the profile (57– 68 %) and had the lowest values obtained for all of the pristine peats studied.

$\delta^{34}S$ was significantly different between the two species of *Sphagnum* sampled ($t = 5.76$, d.f.= 7, $p = 0.0007$). *Sphagnum fuscum* had a mean $\delta^{34}S$ of 6.4 ‰ (sd = 0.402) and *Sphagnum girgensohnii* had a mean of 7.7 ‰ (sd = 0.298). However, there was no significant difference between the sulphur content of the two species ($t = 1.11$, df.= 4, $p = 0.33$). *Sphagnum fuscum* had a mean sulphur content of 0.10 % (sd = 0.067), while *Sphagnum girgensohnii* had a mean sulphur content of 0.06 % (sd = 0.004).

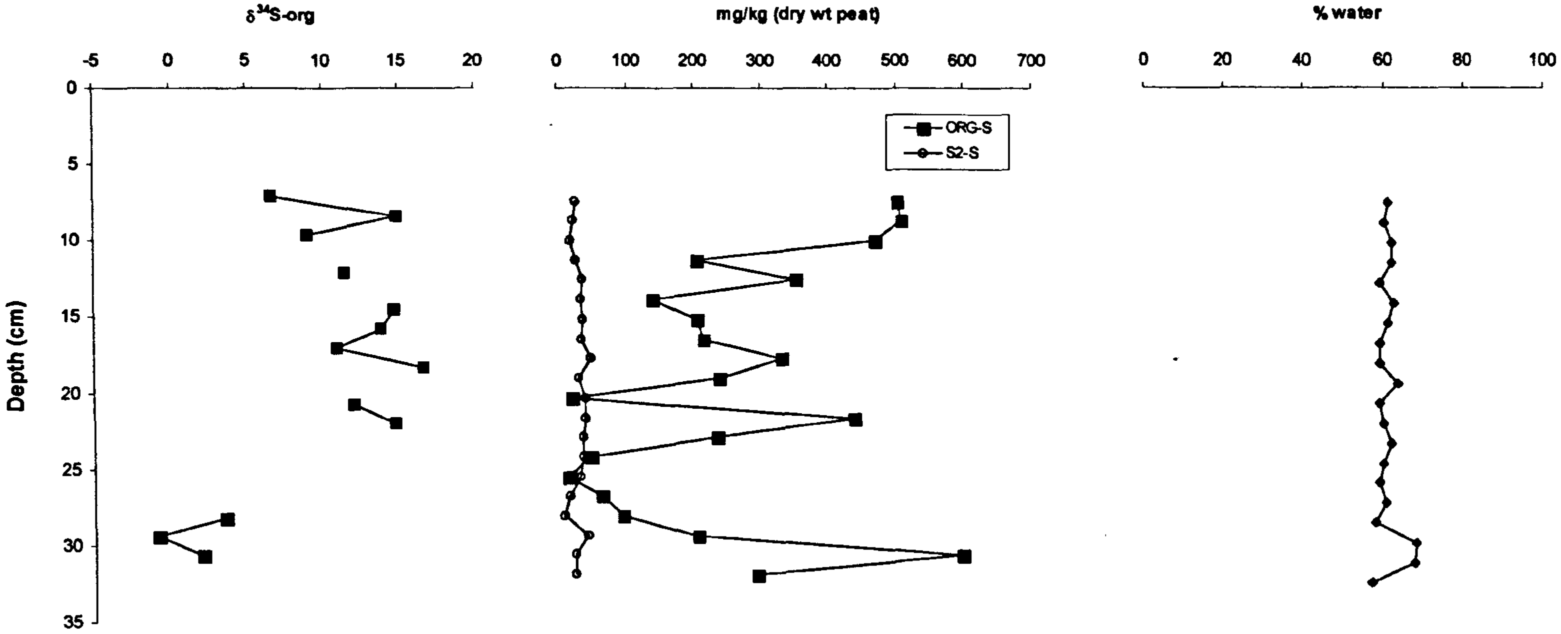

Fig. 3.10. Sulphur content, isotopic compositions and water content in Abisko peat.

3.4. Discussion

3.4.1. Fugla Ness

Sulphidic-S in peats is produced by bacterial sulphate reduction under reducing conditions at depth in the peat. The sulphate inputs to the Fugla Ness peat will have been marine dominated with $\delta^{34}S$ ~+20 ‰ (Thode *et al.*, 1961). The large isotopic fractionation involved in bacterial dissimilatory sulphate reduction means that a single step reduction process could produce sulphide with isotopic compositions in the range ~-20 to +20 ‰ (Bottrell and Raiswell, 2000), depending on the proportion of sulphate reduced and the isotopic enrichment factor. Most of the sulphide isotopic compositions from the Fugla Ness peat lie within this range (Fig. 3.2) and these could be explained by this simple process. However, six samples have higher ^{34}S values than +20 ‰, ranging up to +58.6 ‰. These ^{34}S-enriched sulphides have to have formed from a sulphate reservoir with a $\delta^{34}S$ value higher than +20 ‰ and most probably resulted from a second-stage, quantitative reduction of sulphate in porewaters, which had previously undergone a phase of partial sulphate reduction during which ^{34}S-depleted sulphide had been removed from solution. This would leave a porewater with a lower concentration of sulphate with $\delta^{34}S$ > +20 ‰. Clearly such porewaters would only be capable of producing small amounts of sulphide relative to the primary porewaters and there is indeed a tendency to low sulphide concentration in the peat where sulphide $\delta^{34}S$ > +20 ‰ (Fig. 3.3).

The isotopic composition of the organically bound sulphur shows little variation in $\delta^{34}S$ with depth. Most values fall within a narrow range from +9.9 to +12.3‰ and in this group, other than two exceptions, there is no correlation between $\delta^{34}S$ and organic sulphur content (Fig. 3.4). These exceptions are; (1) a high value of +15.2‰ and (2) samples of peat from zones where peat-clay interbeds occur. Peat from such zones have lower $\delta^{34}S$ values suggesting the incorporation of an increased proportion of diagenetic H_2S into the organic fraction. Diagenetic H_2S production is an obligate anaerobic process and as such, the hydrology of the peat is critical in controlling the fluxes between oxidised and reduced forms of sulphur (Bayley *et al.*, 1986; Freeman *et al.*, 1994; Mandernack *et al.*, 2000). Clays belong to the smallest class of mineral particles

(<0.002 mm) with a high capacity for water retention and ion exchange and commonly reduce soil permeability. Clays may thus exert significant effects upon elemental mobility and cycling and redox conditions within a peat. These characteristics may have played a role in altering the dynamics of bacterial dissimilatory sulphate reduction within the peat, leading to an increased concentration and/or residence time of H_2S within a peat horizon. Thus in clay-rich horizons incorporation of sulphur into peat as organic sulphur may have been promoted.

The exposed coastal setting of Fugla Ness (Fig. 3.1) has important implications for the isotopic nature of the aerially derived sulphur inputs it receives. Sulphate in the surface water of the bog in which the peat formed will have been dominated by large inputs of sea water-derived sulphate, with a $\delta^{34}S$ close to the marine sulphate value of +20‰. This has been confirmed by analysis of sulphate from surface waters in blanket peat at the present day close to western coasts of the Shetland Isles. Despite the fact that there may be an isotopically light anthropogenic sulphur component, the surface waters have a mean sulphate $\delta^{34}S$ of 19.6 ‰ (± 2.6 ‰/sd/n=5), indistinguishable from the marine sulphate composition.

The isotopic shift between pure peat organic $\delta^{34}S$ and the mean surface water sulphate value of +19.6 ‰ is 7.9‰ (range from 4.2 to 9.5 ‰/ ±1.3 ‰/sd) for the Fugla Ness peat, and is indistinguishable from the shifts observed in Connemara and Mull (Fig. 3.5). Therefore, the shift at Fugla Ness can be largely attributed to isotopic fractionation by the surface vegetation (see Bottrell and Novak, 1997), chiefly *Sphagnum*, and that diagenetic processes have had only a minimal net effect on organic sulphur isotopic compositions in the clay-free peats. Therefore, in pure peats, the organic sulphur isotopic signal may reflect (with an ~8.5 ‰ fractionation) the surface water sulphate, which was incorporated during growth of the bog flora and as such, an environmental record of sulphur deposition may be preserved within ombrotrophic peat profiles.

3.4.2. Lumbister

Organic $\delta^{34}S$ is remarkably consistent, not only with depth, but between the two monoliths sampled (Fig.3.6). Both monoliths show a steady isotopic profile with little variation. Total variability including both cores is only 4.4 ‰. This is therefore suggestive of a peat type in which very little alteration, either through decomposition, or through the incorporation of sulphide, derived from BSR, has taken place. However, there is a significant enrichment in organically bound sulphur content below 25 cm in the monoliths, which can only relate to the addition of sulphur from inorganic sulphur pools. This has occurred, without alteration in the isotopic composition of the organic fraction, because reduced sulphur derived from BSR in this peat type has a similar isotopic composition to that of the originally preserved sulphur. The surface vegetation (a combination of *Sphagnum* and *Eriophorum*) would appear to have exerted a fractionation effect of around 10 ‰ during uptake and assimilation of the primary sulphur signal. A similar fractionation effect, as evidenced from the isotopic profiles, is also obvious in the inorganic sulphur fraction. This is likely due to low to medium rates of BSR. When rates are low, less sulphur is taken up from the total input and the fractionation effects associated with BSR become more prominent.

If aerial inputs had changed with a markedly different isotopic composition during the last 200 years or so, we would expect this change to be preserved in the upper layers where there is little incorporation of inorganic sulphides. However, this markedly different isotopic composition would have manifested itself in the inorganic sulphur pool, which would alter, in varying degrees, the organic S signature in the deeper peat.

3.4.3. Forsinard

When compared, the three isotopic organic sulphur profiles are widely variable (Fig. 3.9). Importantly, this is the wettest peat sampled, taken from a waterlogged pool complex near the northern Scottish coast. This has resulted in a much larger effect of BSR than observed in the low ridge peat from Shetland. There are high concentrations of inorganic sulphur (574 mg/kg at 10 cm in core F2) all the way to the surface layers (as opposed to Shetland where the upper 10 cm has inorganic sulphur content maxim of

120 mg/kg) as well as in terms of organic sulphur (c.f. Shetland), even though inputs at both of these sites should have been similar throughout the lives of the deposits. Consequently, there has been significant incorporation of sulphur, derived from BSR, throughout the profile. This incorporation of inorganic sulphur has, however, had a different effect to that observed in the peat from Shetland with the organic sulphur signal becoming enriched with ^{34}S with depth.

This is because in waterlogged peats, the isotopic signature of sulphur in sulphides derived from BSR can closely resemble the aerial component due to high rates of BSR resulting in the uptake of the majority of sulphur deposited (therefore very little net fractionation between input and sulphide sulphur). Waterlogged peats may also allow for an unobtrusive diffusion pathway for the aerially deposited sulphate down to the BSR zone.

Therefore, at Forsinard, in contrast to modern peat from Shetland, the isotopically heavy inputs are reflected in the inorganic sulphur isotopic compositions because the majority of aerially deposited sulphur is cycled via BSR. Incorporation of isotopically heavy BSR-produced sulphide shifts the organic sulphur signal away from the values resulting from vegetation fractionation.

3.4.4. Abisko

At Abisko sulphur inputs are isotopically lighter, reflecting a continental input (derived mainly from weathering processes)(Table 3.1). This lighter sulphur signal is present in the surface vegetation yet the isotopic signature of organically bound sulphur in the peat shows a very variable but obvious enrichment in ^{34}S with depth (Fig. 3.10). This is the result of the unusual conditions in which this peat has accumulated. The peatlands in this area are exposed to very hot summers and very cold prolonged winters, which cause these peats to dry out and rewet each year. Drying of the peat provides conditions, which favour decomposition, resulting in preferential release of lighter ^{32}S (Bridgham *et al*, 1998) and thus a residual enrichment of ^{34}S in the organic sulphur fraction.

Inorganic sulphur concentrations are very low in the sampled peat and are the likely result of both low input and low water content. Sulphate reducing bacteria are obligate anaerobes, so BSR is favoured by a high water content (which promotes anaerobic conditions) and also by high sulphur inputs. However, sulphur inputs at Abisko, as is the case in continental settings, are typically low so that the surface vegetation is taking up the majority of aerially deposited sulphur for growth. This was shown to be the case in another pristine continental peats (Steinmann and Shotyk, 1997) in which sulphur inputs were providing less sulphur than that required for optimum plant growth. Sulphur content of the *Sphagnum* growing at Abisko was much lower than that observed in the *Sphagnum* from Forsinard.

3.5. Summary and Conclusions

3.5.1. Mid-Pleistocene peat

Organic sulphur in Fugla Ness peat is significantly ^{34}S depleted compared to surface water sulphates dominated by maritime inputs. However, for pure peat samples, this shift is consistent with fractionations observed for *Sphagnum* growth in modern peatlands and there is thus no evidence for significant diagenetic effects.

Organic sulphur in clayey peats was systematically more depleted in ^{34}S compared to purer organic peats, indicating a greater contribution of diagenetic H_2S in to the organic fraction after its initial formation.

Diagenetic alteration of organic sulphur isotopic compositions in pure peats appears to be minimal and thus organic sulphur in peat sequences may record changes in isotopic compositions of atmospheric sulphur inputs through time.

3.5.2. Modern Pristine peats

The conditions under which the three modern pristine peat types sampled had accumulated were very different and have led to significant differences in sulphur content and isotopic compositions.

Sulphur inputs, derived from sea spray, were high at the Shetland site. The peat was sampled from a low ridge and therefore not waterlogged so that there were only moderate rates of BSR. In this situation the isotopic composition of recent inputs may be preserved in the top portions of the peat.

Inputs to Forsinard were also high, however, these peats were sampled from a waterlogged pool complex in which there was significant rates of BSR, even in the surface layers, leading to the masking of the originally preserved organic sulphur signal by diagenetic processes.

At Abisko, sulphur inputs are very low so that the majority of aerially deposited sulphur is taken up directly by the surface vegetation, and therefore not available for cycling into BSR. Hence, there is little potential for modification in the organic sulphur signal through sulphide incorporation. However, seasonal changes in climate have produced a situation in which decomposition is significant within the peat, leading to alteration in the isotopic signature of the organically bound sulphur.

Peat type is critical in determining whether alteration in isotopic compositions of aerial sulphur can be preserved in ombrotrophic peat. Peats need to be anaerobic enough to prevent decomposition but not so waterlogged that the production of sulphides from BSR may obscure the organic sulphur signal. Even under these conditions a primary sulphur signal is unlikely to be preserved indefinitely as diagenetic sulphide incorporation in the long term (> 600 y) may eventually obscure the organic sulphur signal. This may have occurred in the ancient peat from Fugla but because sulphide may have had a similar isotopic composition to the resultant organic fraction after plant fractionation (as evidenced in the modern Shetland peat), there may have been little alteration in the isotopic profile.

CHAPTER 4 – Atmospheric Records of Sulphur Deposition in Ombrotrophic Peat: Evidence from the Southern Pennines.

4.1. Introduction

In Britain, natural sources of atmospherically deposited sulphur are dominated by sea spray, which is characteristically enriched in the ^{34}S isotope (Thode *et al.*, 1961), while pollutant sulphur, derived from fossil fuel combustion, is typically ^{34}S depleted (McArdle and Liss, 1995). Any changes in the sulphur isotopic composition of aerial inputs may potentially be preserved during sulphur uptake and assimilation by surface vegetation of peatlands and subsequent preservation in the organic fraction of the peat profiles after plant death.

Evidence presented in the preceding chapters suggests that the isotopic sulphur signal contained within the organic fraction of pristine peatlands may remain relatively unmasked by diagenetic/decomposition processes. As such, the potential exists for previously polluted peats, such as those of the southern Pennines, to contain an environmental archive of sulphur deposition.

The expansion of the industrial cities of Manchester, Sheffield and Leeds during the Industrial Revolution (~1750-1950) led to the gross deposition of atmospheric pollutants, namely sulphur, onto the surface of the Pennines (see Ferguson and Lee, 1983). However, since the 1950's there have been substantial reductions in SO_2 deposited on the southern Pennines. Figures show that annual emissions of SO_2 from the U.K have decreased from over 3000 $Kt.S.yr^{-1}$ at the beginning of the 1970's to under 1500 $Kt.S.yr^{-1}$ by 1994 (U.K.R.G.A.R., 1997). Forecasts for future levels of deposition estimate a similar pattern of continuing reductions in SO_2 emission. The reductions in emissions that have taken place have been brought about largely through change of fuel usage, the decline of heavy industries in Britain, use of sulphur depleted ores and fuel stocks, improved pollutant removal processes, the building of tall chimney stacks to increase dispersal, and through the closure of less efficient coal-fired power stations (Mellanby, 1979; U.K.R.G.A.R., 1997).

While sulphur pollution reached its highest levels at the end of the First world war (Ferguson and Lee, 1983), the release of sulphur from anthropogenic activities occurred well before the Industrial Revolution. Mining and smelting of the lead ore galena (PbS) is known to have begun on the Pennine mining fields after the arrival of the Romans in 74 AD. The use of lead for plumbing and lining roofs for waterproofing increased the demand for lead during the 12th century due to the widespread castle building programme of Henry II as well as through the building activities of the many monastic communities (Raistrick and Jennings, 1989).

Lead analyses of a peat profile taken from a site on the High Peak in Derbyshire show a small peak in lead values in the profile around 500 AD, which may represent early lead mining activities in Derbyshire, as well as a sustained increase in lead concentration which begins around 1460 AD (Lee and Tallis, 1973). A purchase order for lead at the end of the 14th century states specifically the use of the High Peak for lead extraction:

> 1394. Feb. 24 *'Appointment of Thomas de Neville and Thurston del Boure esq. To take, provide and buy in person or by deputies for repair of the King's great hall at Westminster, 100 fothers of lead in the High Peak and elsewhere in County Derby, and in the counties of York and Nottingham, paying therefore £4 a fother and to take carriage for the same with power to arrest and imprison contrairiants'* (cited in Raistrick and Jennings, 1989).

Though natural inputs of sulphate deposited upon the southern Pennines will be isotopically heavy, reflecting maritime inputs (20.1 ‰), only a small amount will be deposited due to the distance of the Pennines from the coast (~85 km) as most of the sulphate derived from sea spray will be deposited over the first 20 km inland. This is confirmed from analyses of rainfall from Castleton (10 km from southern Pennine site) conducted from June 1995 to May 1996, which give an average SO_4 concentration in rainfall of 11.08 mg L and an average annual rainfall isotopic composition of 4.1 ‰ (Bottrell *et al*, 2000). As anthropogenic sulphur inputs will typically range between 0 and 1 ‰, a simple isotopic mass balance indicates that only around 2.2 mg L of SO_4 in rainfall is derived from a natural maritime source, hence, any small-scale activities, prior to the Industrial Revolution, such as smelting, in and around the southern Pennines may significantly alter the isotopic composition of deposited sulphur away from the natural signal. Thus, if the organic sulphur fraction accurately preserves isotopic alterations in sulphur inputs, we would expect to see significant changes; not only in the peat accumulated over the past 250 years, relating to the Industrial Revolution, but perhaps in peat dating back 600 years, when smelting activities began to proliferate. Thusly, peats from the southern Pennines (High Peak) were sampled and analysed to investigate whether any such changes in sulphur inputs are preserved within the peat profile.

4.2. Study Site and approach

The southern Pennines is situated in the north of England (Fig.4.1.) part of which falls within the area known as the Peak District. The peat is classified as an upland peat, which in some places has been artificially drained (see Conway, 1947; 1949). The vegetation is principally Cotton Grass (*Eriophorum vaginatum*) but localised patches of *Sphagnum sp.* (typically *S. recurvum*) are observed. The climate of the southern Pennines, as with much of the Peak District, differs from that of the flanking lowlands. The effect of elevation results in reduced mean temperatures and increased precipitation. The diversified relief means that there is marked local variation not only between the valleys and adjacent uplands but also between one valley and another (Edwards *et al*, 1974). As such, generalisations for the southern Pennines are unhelpful and consequently no useful climate data relating to the specific site investigated can be presented here. However, as explained, mean temperatures will be lower and precipitation will be higher at the field site (488 m.a.s.l.) than that of the surrounding lowlands. Such conditions have encouraged the onset and accumulation of peat over much of the region, with as much as 5 metres of peat overlying a bedrock of millstone grit.

The upland blanket peats of the southern Pennines can be highly variable in terms of surface topography, in part due to differences in peat accumulation rates but also due to significant erosion of the peat commencing around 900 AD (see Tallis, 1965; 1985;

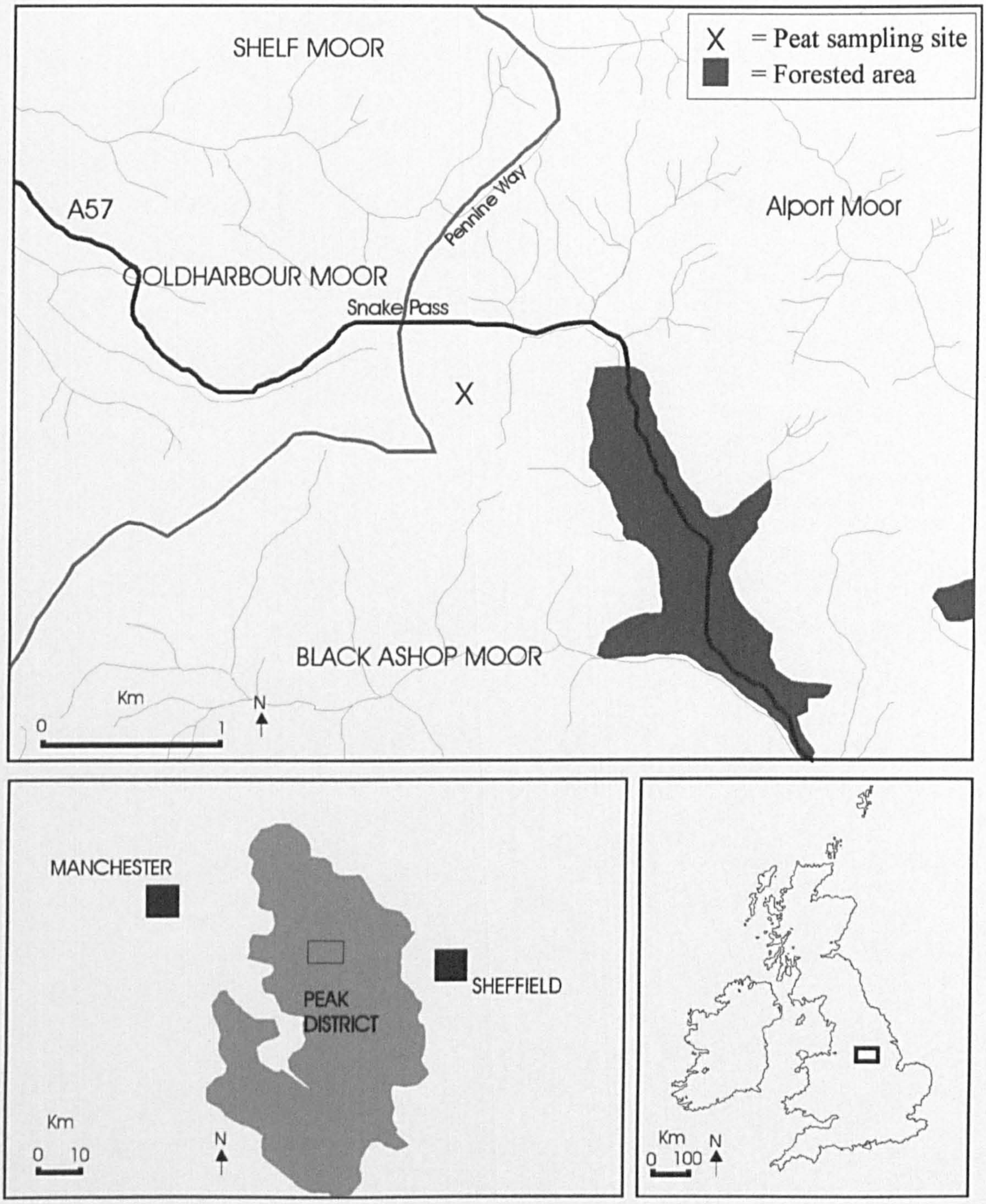

Figure 4.1. Location of field site on the southern Pennines, U.K.

1994; 1995). The latter has produced pronounced gullies between hummocks at parts of the site.

Such variation in topography implies variation in peat stratigraphy and as such may result in differing isotopic profiles. Hence the three main types of peat landforms were identified and sampled from a site on Featherbed Moss (High Peak-GR SK 092 925): high ridge hummock peat surrounded by extensive and deep networks of gullies, low ridge hummock peat with little signs of surrounding erosion, and drought sensitive pools. Each type of peat form was sampled in duplicate for determination of depth profiles of sulphur isotopic composition and sulphur content, with two samples from each peat type sent for radiometric analysis. Further to this one monolith taken from a hummock from the heavily eroded area was further analysed for elemental composition, carbon isotopes and for pollen composition.

Surface vegetation (*Sphagnum* and *Eriophorum*) was also sampled for modern organic sulphur content (biomass) for comparison with the peat organic fractions (necromass). Due to the present day paucity of *Sphagnum*, only one area with *Sphagnum* cover could be located at the peat-sampling site. This was the waterlogged pool where two peat cores were sampled.

4.3. Results

4.3.1. Radiometric analyses

Radiocarbon dates allowed for peat accumulation rates to be calculated for three parts of the high ridge and low ridge hummock peat profiles (Table 4.1). High ridge peat (HR-1) proved to the oldest type of peat sampled with an age of 1866 ± 49 BP at 45cm (WK- 12438) and 1497 ± 44 BP at 30cm (WK- 12439) giving a total accumulation rate of 0.024 cm y^{-1}. From the surface to a depth of 30 cm the accumulation rate is 0.020 cm y^{-1} and from 30-45 cm the rate is much higher at 0.044 cm y^{-1}.

Low ridge peat (LR-2) was dated as 894 ± 47 BP at 45cm (WK- 12436) and 604 ± 45 BP at 25 cm (WK- 12437) with a calculated total accumulation rate of 0.040 cm y^{-1}.

The accumulation rates of the separate parts of the profile were very similar to the total accumulation rate with 0.040 cm y^{-1} from the surface to 25 cm and 0.042 cm y^{-1} between 25 and 36 cm depth.

Table 4.1. Mean accumulation rates in southern Pennine peat (derived from radiometric analyses).

Peat type	Depth (cm)	Accumulation rate (cm y-1)
High ridge	0-30	0.020
	30-45	0.044
	0-45	0.024
Low ridge	0-25	0.040
	25-36	0.042
	0-36	0.040

Radiocarbon dates for pool peat were inconsistent relative to depth. Peat at a depth of 38 cm was dated at 641 ± 52 BP (WK- 12435), yet peat higher up the profile at 27-30 cm (i.e. more recently accumulated), yielded a date of 819 ± 47 BP (WK-12434). This may be due to a disturbance during peat formation or more likely a consequence of the movement of organic material from the upper to lower portions of the waterlogged peat (A. Hogg, Pers. com.).

4.3.2. Organic sulphur content

Organic sulphur concentrations are highly variable between the different types of peat sampled (Table 4.2; Fig. 4.2). Concentrations were highest for peat sampled from waterlogged pools, peaking at ~6500 mg/kg (0.65% peat dry weight) at a depth of 25 cm. Sulphur concentrations in the drier high and low ridge peats were similar to each other with concentrations ranging from ~700 to 2800 mg/kg. High ridge hummock peat shows much variability, but elevated sulphur concentrations are present in both profiles at around 25cm. Low ridge peat shows a greater degree of variability with no clear trends obvious.

Table 4.2. Peat type and sulphur concentration at southern Pennine site

Peat form	Organic S (mg/kg peat dry Wt.)	Inorganic S (mg/kg peat dry Wt.)
High Ridge	700-2800	0-300
Low Ridge	160-2800	0-290
Pools	380-6579	250-1400

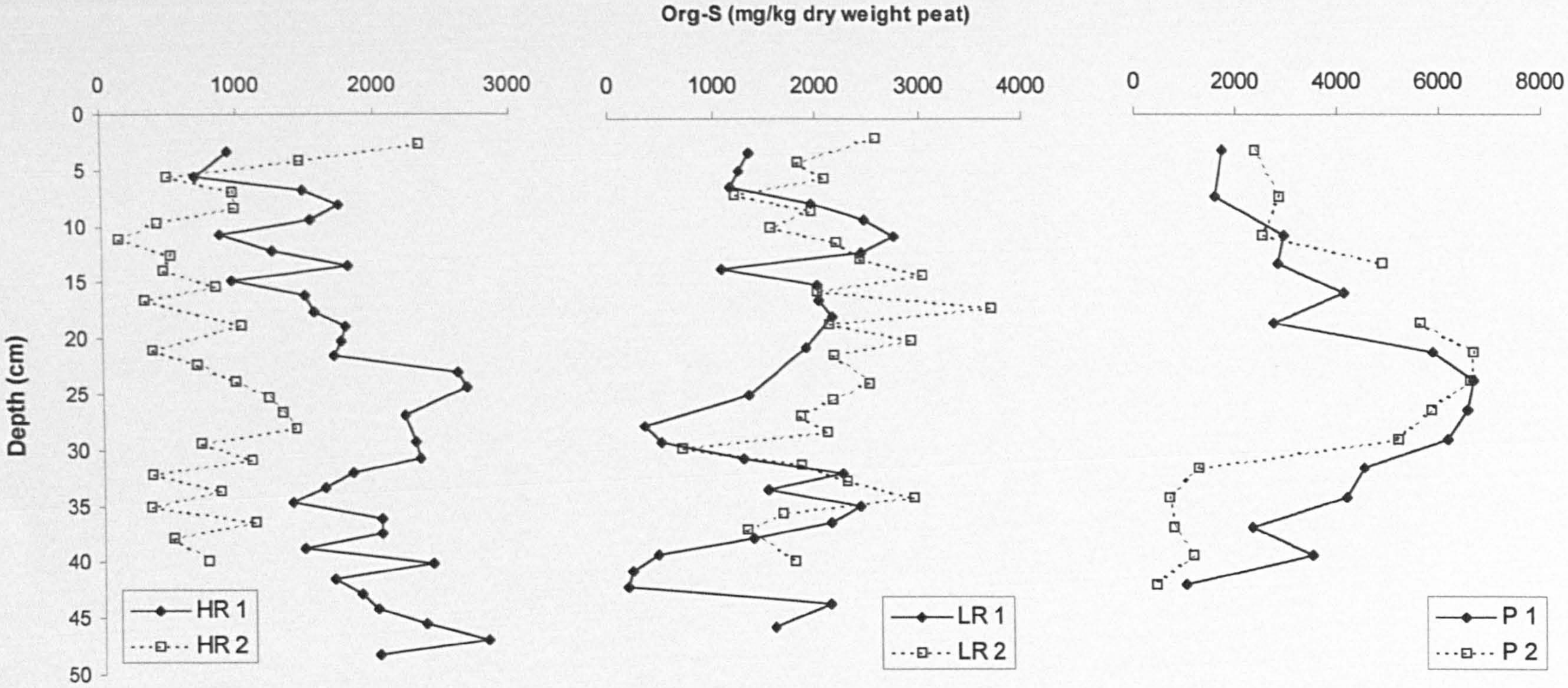

Fig. 4.2. Organic sulphur content vs. depth in high ridge, low ridge and waterlogged peat from the southern Pennines.

4.3.3. Inorganic sulphur content

Peat monoliths sampled from high and low ridges showed similar ranges in sulphide content with maximum values of around 300 mg/kg (peat dry weight) (Table 4.2; Fig. 4.3). Low ridge peats show a trend to increased sulphide content at the base of the sampled sections, whereas high ridge peats show a very weak trend to increased S concentration with depth. Waterlogged peats had a much greater inorganic sulphur content with maximum values of around ~1400 mg/kg. Pronounced peaks in sulphide were present in the waterlogged peats between the depths of 15 and 25cm.

4.3.4. Organic sulphur isotopic compositions

The $\delta^{34}S$ of the organic fractions show marked variation with depth ranging from 2.7 to 13.3 ‰ in high ridge peat, -1.1 to 11.4 ‰ in low ridge peat, and –2.3 to 6.2 ‰ in waterlogged peat (Fig. 4.4.). The two high ridge monoliths exhibit extremely similar patterns in $\delta^{34}S$ versus depth, although somewhat skewed from each other so that the patterns are present at slightly different depths. Peat close to the surface has lightest values (3-4 ‰) and a large increase in $\delta^{34}S$ takes place over a short interval below this, with the heaviest compositions (11-13 ‰) occurring at 11-12 cm. Below this depth $\delta^{34}S$ generally declines with depth.

The two low ridge peats also show an extremely similar pattern in isotopic composition in organic sulphur with depth. The heaviest values occur at around 25 cm (~11 ‰). Above this depth (towards the surface) there is a decline in $\delta^{34}S$ until ~5 cm (0 to 2 ‰) at which, there is then a return to heavier values in the surface layers (4.5-6 ‰).

The waterlogged peat profiles show a large degree of similarity in $\delta^{34}S$ with depth, exhibiting minima in the midsections of each core (20-30 cm depth). Organic sulphur in the deepest peat sampled has an isotopic range between 3 and 8 ‰. Above this, there is a steady decline in $\delta^{34}S$ until ~ 20 cm (-2 to -2.5 ‰) at which the organic fraction becomes isotopically heavier towards the surface (4 to 6 ‰).

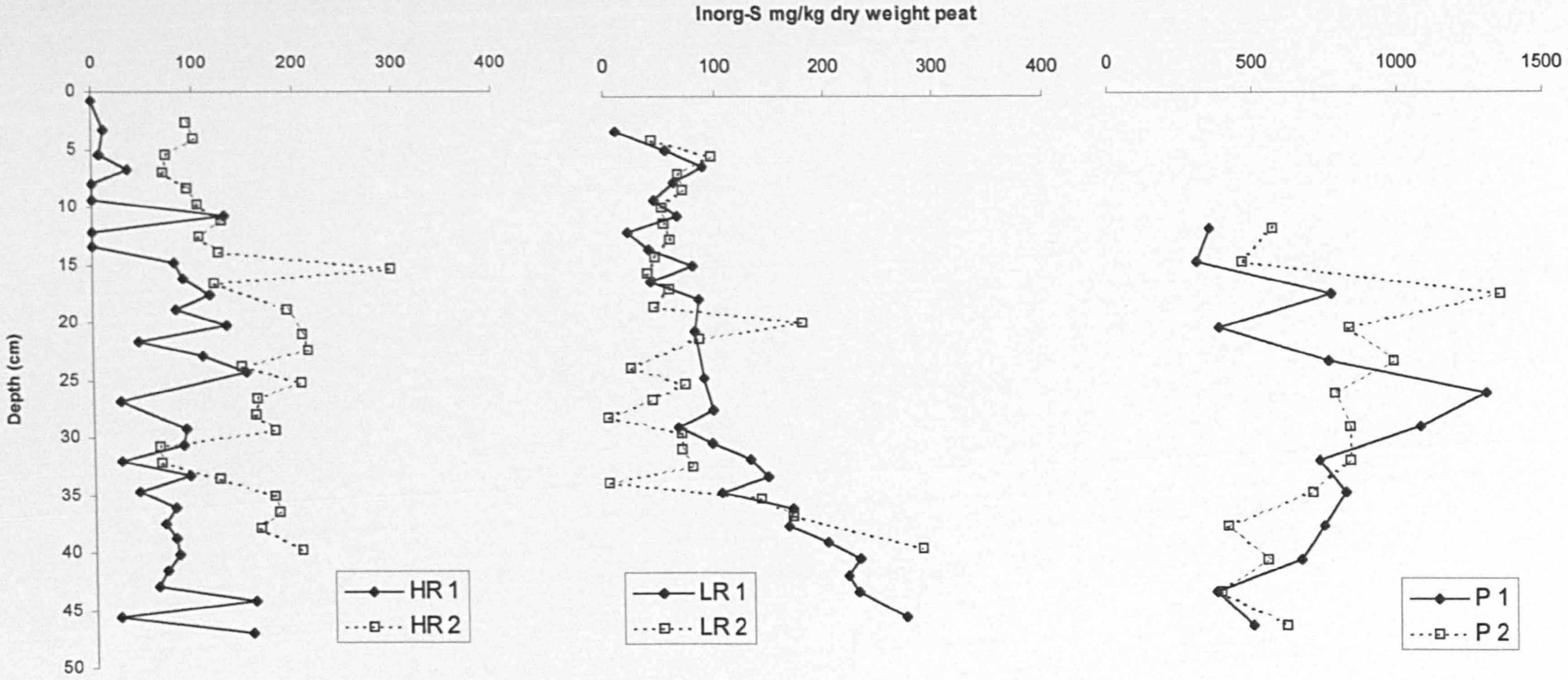

Fig. 4.3. Inorganic sulphur content vs. depth in high ridge, low ridge and waterlogged peat from the southern Pennines.

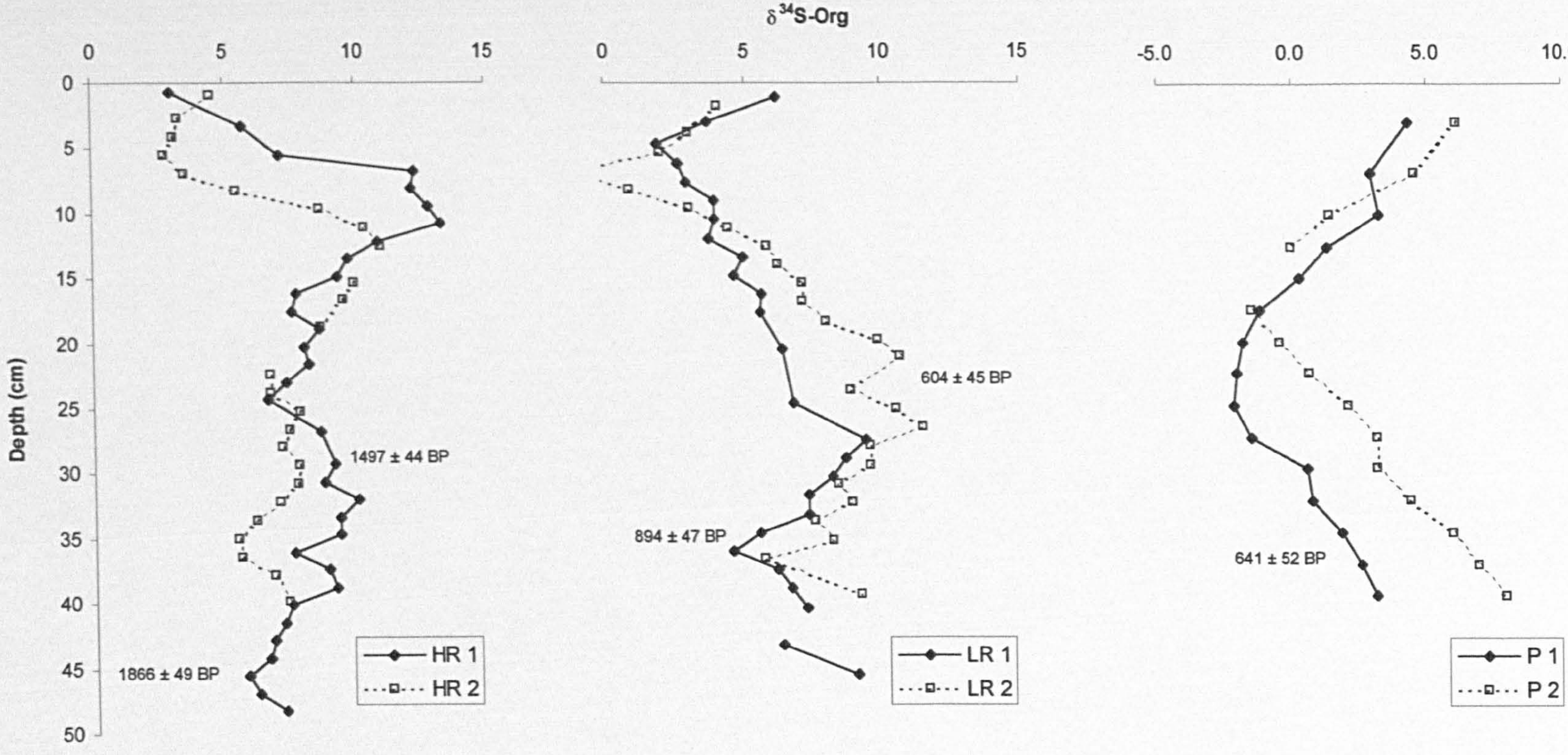

Fig. 4.4. δ^{34}S-Org vs. depth in high ridge, low ridge and waterlogged peat from the southern Pennines.

Using radiometric data the sulphur isotopic composition of the organic fraction was plotted against mean age for the high and low ridge hummock peats (Fig. 4.5) (n.b waterlogged peat not plotted due to uncertainty over dated material). There is a close correlation between the two drier peats (high ridge and low ridge hummocks). From 600 years to the present day both high ridge and low peats show a decline in $\delta^{34}S$. Low ridge peat also shows a slight enrichment in ^{34}S in the surface layers.

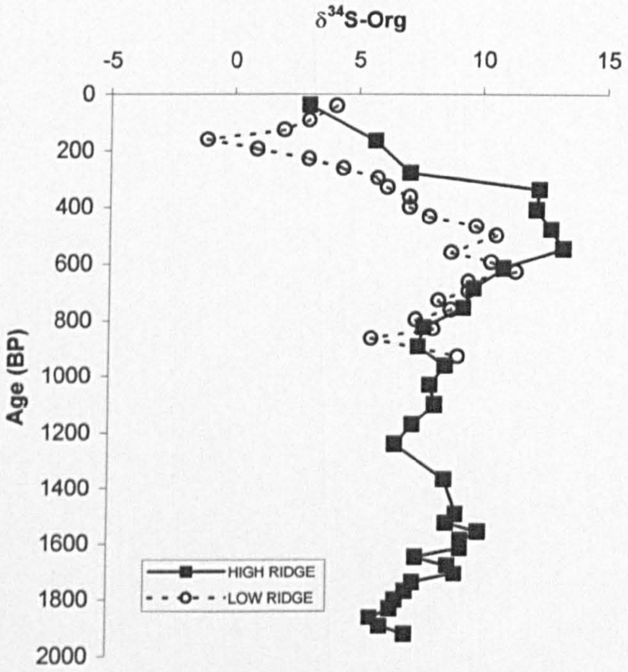

Fig. 4.5. $\delta^{34}S$ versus age in high and low ridge southern Pennine peat.

4.3.5. Inorganic sulphur isotopic compositions

There was less variability in isotopic range in inorganic sulphur than that of the organic fraction. $\delta^{34}S$ ranges were –9.1 to 6.8 ‰ in high ridge peat, -4.6 to 2.1 ‰ in low ridge peat and –2.7 to 6.0 ‰ for peat cores sampled from waterlogged pools (Fig. 4.6). High ridge peat shows a general trend of lightening in sulphide-$\delta^{34}S$ with increasing depth while low ridge peat is much less variable. The waterlogged peat cores exhibit similar isotopic patterns in inorganic sulphur as they do for organic sulphur with lighter values midway through the profile.

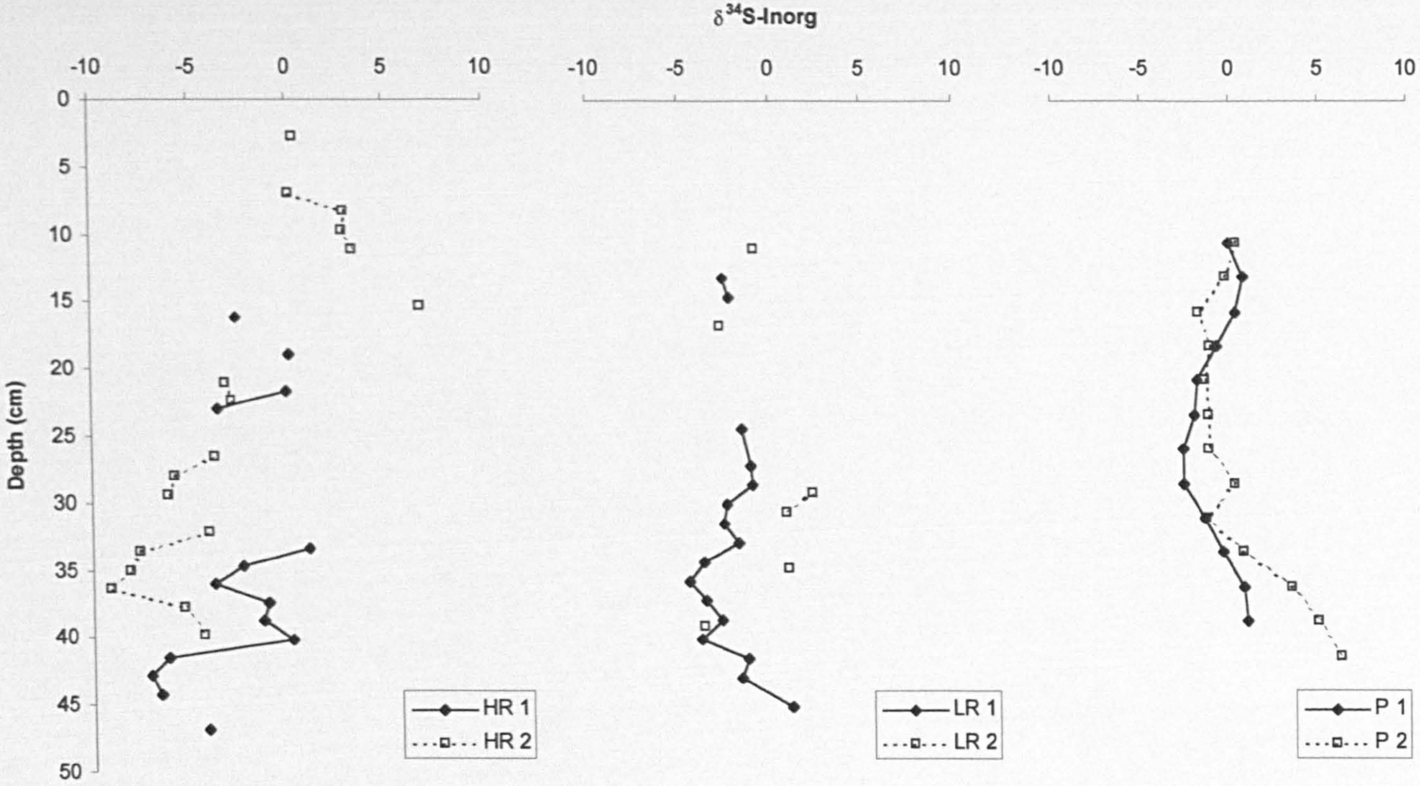

Fig. 4.6. δ^{34}S-Inorg. Vs. depth in high ridge, low ridge and waterlogged peat from the southern Pennines.

4.3.6. High ridge hummock peat (Monolith HR1)

4.3.6.1. Elemental analysis

Carbon content ranges between 46.3 and 52.2 % and nitrogen between 2.1 and 4.0 % in the profile (Fig. 4.7). Organic sulphur/carbon parallels the relationship shown by that of the organic sulphur content (Fig. 4.2) with a significant peaking in sulphur versus carbon between 20 and 30cm (Fig 4.8).

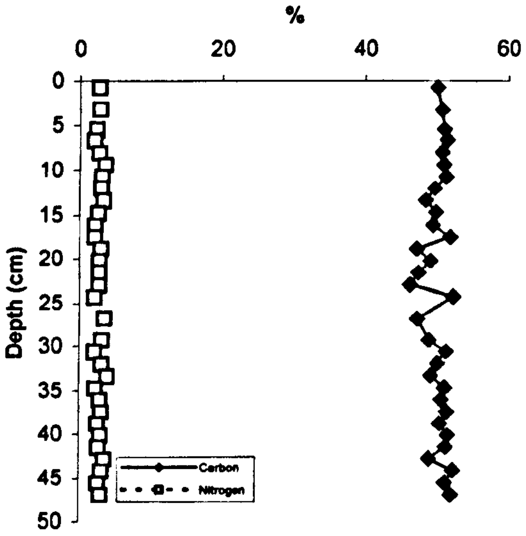

Fig. 4.7. Elemental composition of high ridge southern Pennine peat

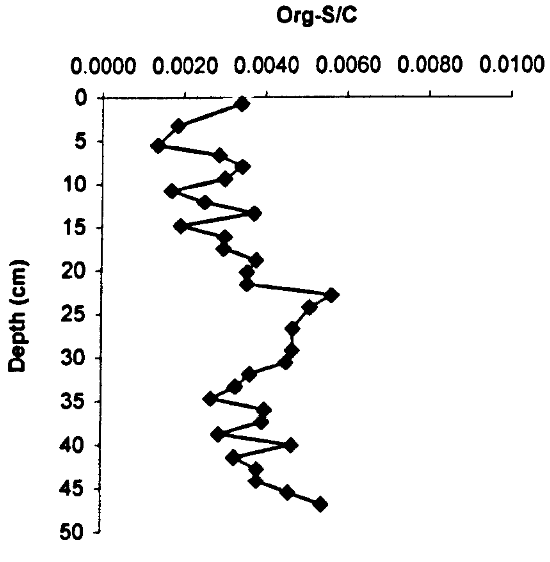

Fig. 4.8. Org-S/total C of high ridge southern Pennine peat

4.3.6.2. Carbon isotopic compositions

$\delta^{13}C$ varies little throughout the profile ranging from –28.2 to –26.7 ‰ (Fig. 4.9). Three distinct trends in the profile can be identified; the lower part of the peat where isotopic compositions are light, the middle portion of the peat where values are heavier, and the surface layers where values become again lighter.

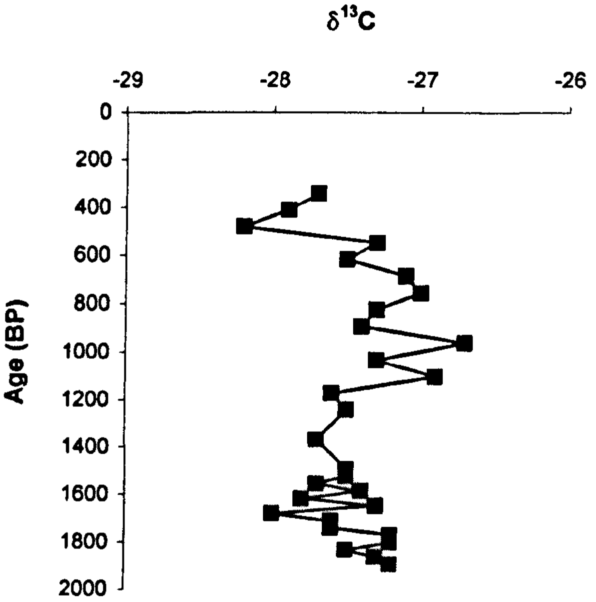

Fig. 4.9. $\delta^{13}C$ versus depth in high ridge southern Pennine peat

4.3.6.3 Pollen profiles

Arboreal pollen composition changes little throughout the peat profile. *Corylus, Quercus, Alnus* and *Betula* make up the majority of pollen composition with minor contributions from *Ulmus, Fraxinus, Salix* and *Pinus*. *Pinus, ulmus* and *Fraxinus* become more prominent at the very top of the profile (Fig. 4.10). There are significant changes in non-arboreal pollen (Fig. 4.11). *Sphagnum* spores are most prominent between 10 and 30 cm but decline towards the top of the profiles. This decline is accompanied by an increase in the *Cyperaceae*, relating principally to the cotton grass, *Eriophorum vaginatum*. *Sphagnum* and *Cyperaceae* components are also plotted against mean age (derived from radiometric analyses) and show that this transition in plant biogeography begins around 600 years BP (Fig. 4.12).

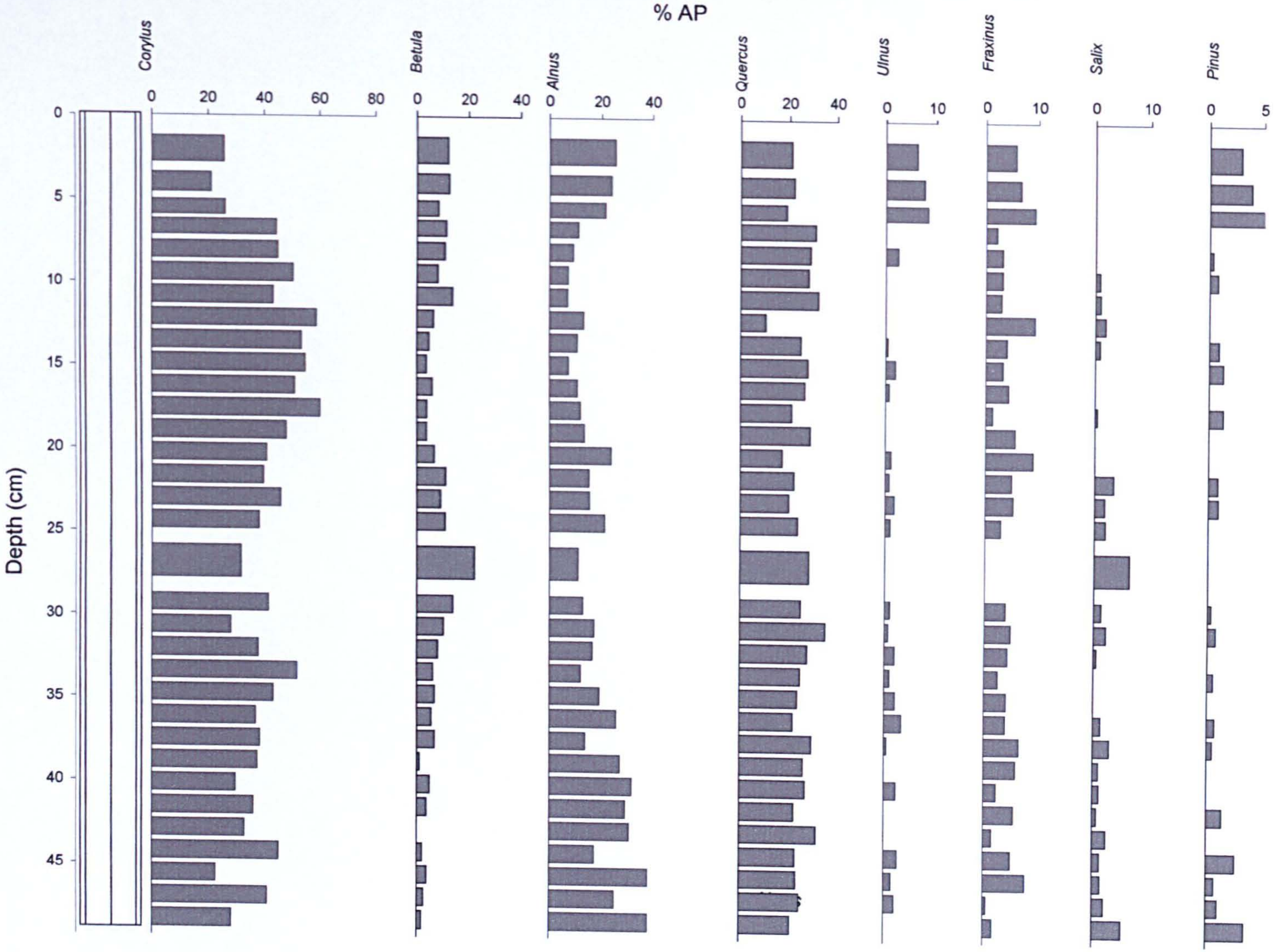

Fig. 4.10. Arboreal pollen diagram for southern Pennine site (HR-1) (note x axis scales differ)

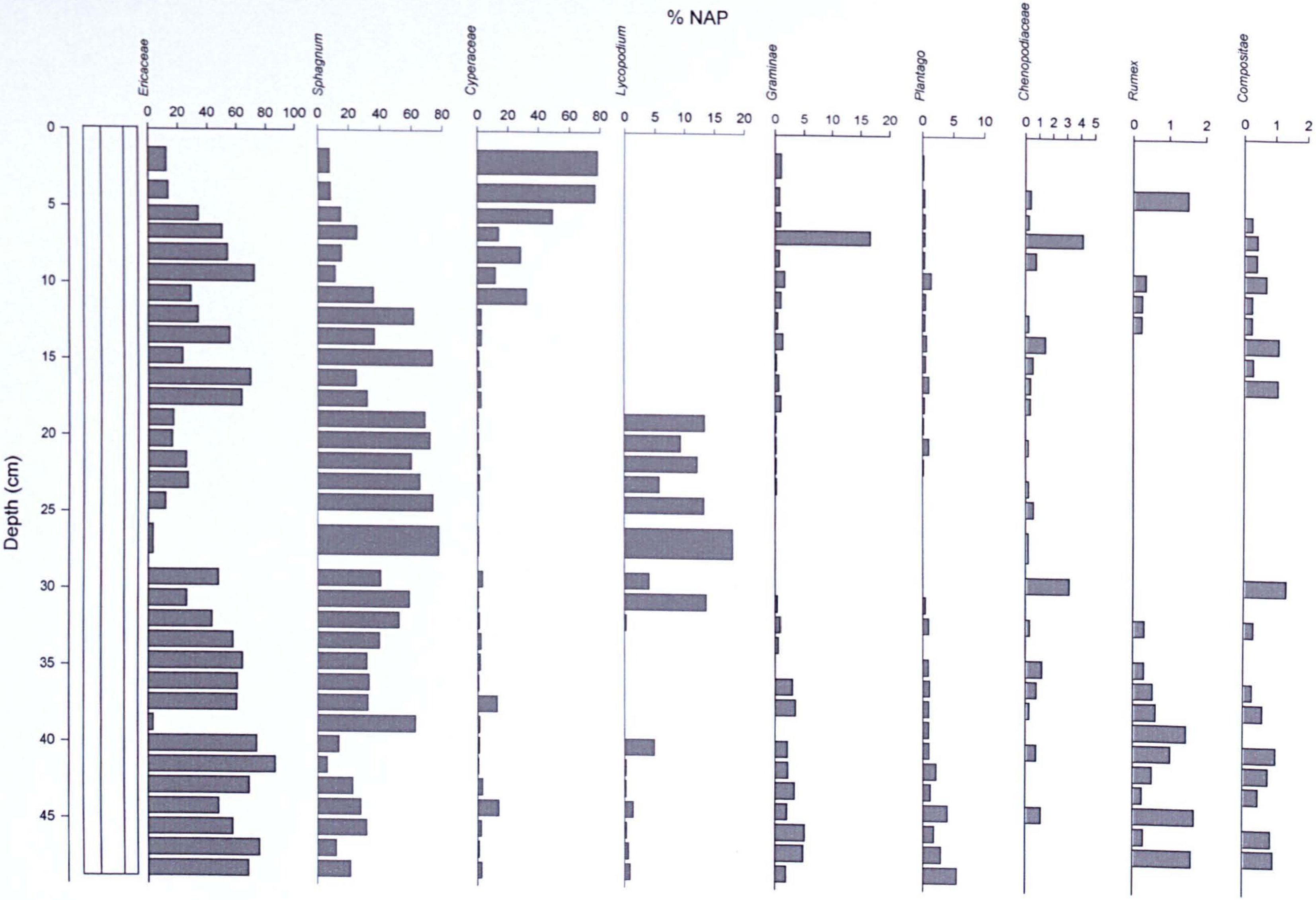

Fig. 4.11. Non-arboreal pollen diagram for southern Pennine site (HR-1) (note x axis scales differ)

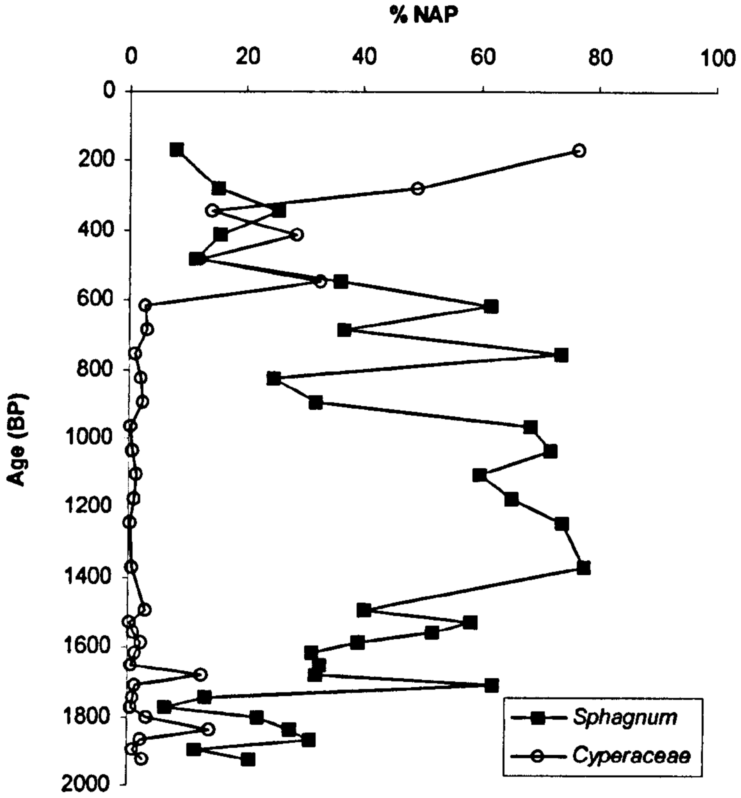

Fig. 4.12. *Sphagnum* and *Cyperaceae* pollen components vs. age in high ridge southern Pennine peat.

4.3.7. Surface vegetation

Organic sulphur isotopic composition was found to be significantly different between *Sphagnum* and *Eriophorum* growing in the waterlogged pools (T= 2.23, d.f.= 25, $p<0.05$) (Fig. 4.13). Mean $\delta^{34}S$ was 2.2 (s.d. 0.4) and 1.7 ‰ (s.d. 0.9) for *Sphagnum* and *Eriophorum* respectively. However, sulphur content of surface vegetation was not found to be significantly different (T= -0.59, d.f. = 31, p = 0.56) (Fig. 4.14). No correlations were found between sulphur content and $\delta^{34}S$ in *Sphagnum* or *Eriophorum* (Figs. 4.15, 4.16).

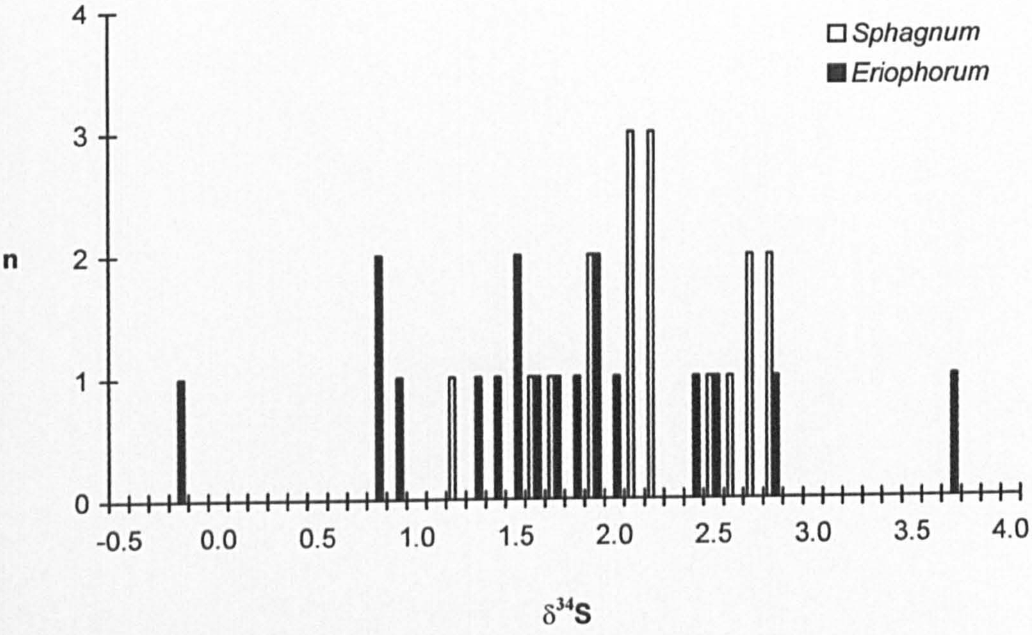

Fig. 4.13. Distribution range of δ^{34}S in vegetation sampled from a pool on the southern Pennines

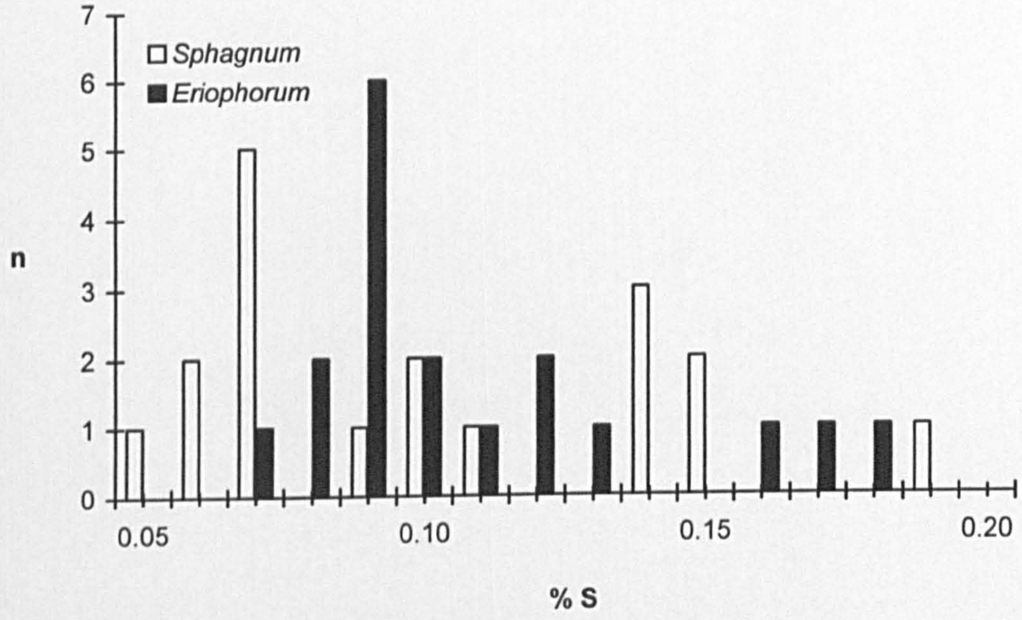

Fig. 4.14. Sulphur content range in vegetation sampled from a pool on the southern Pennines

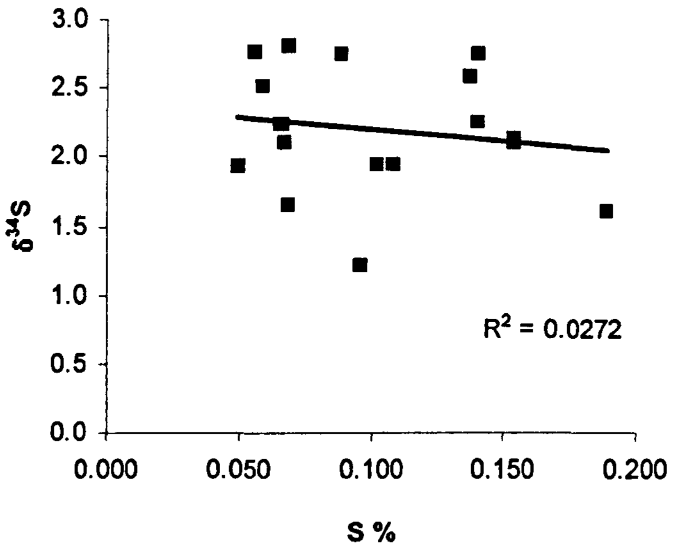

Fig. 4.15. δ^{34}S versus sulphur content in *Sphagnum* sampled from a pool on the southern Pennines.

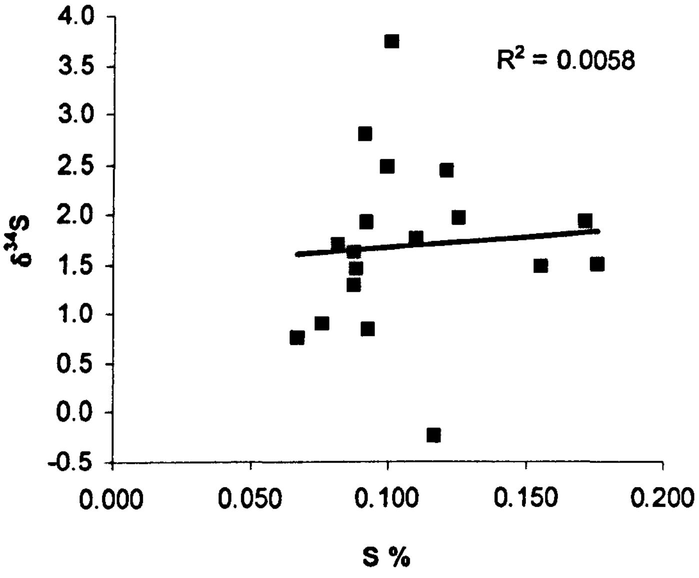

Fig. 4.16. δ^{34}S versus sulphur content in *Eriophorum* sampled from a pool on the southern Pennines

4.4. Discussion

Organic sulphur is known to be the chief form of sulphur in ombrotrophic peat (Brown, 1985; Weider and Lang, 1988; Novak *et al*, 1999) and this was found to be the case for all of the peat profiles studied from the southern Pennines (Table 4.2). Sub-surface maxima in organic sulphur content were also apparent in all of the peats (Fig. 4.2) again concurring with previous work in ombrotrophic peats (Novak *et al*, 1994; Novak *et al*, 1999; Chapman, 2001).

The surface vegetation sampled from one of the waterlogged pools at the site was found to be isotopically distinct with *Eriophorum* ^{34}S-depleted relative to *Sphagnum*. This may be due to a difference in the rate of isotopic fractionation during uptake and assimilation of sulphur but could also be the result of different sources of sulphur being available to the bog flora. The roots of *Eriophorum* extend down into the underlying peat where isotopically light sulphides may be available for uptake. Sulphides are generally toxic to plants but vascular plants growing in flooded wetland soils, such as *Eriophorum* produce arenchyma (Sculthorpe, 1985), a tissue with extensive gas spaces, which would allow for oxidation of reduced isotopically light sulphur making it available for uptake.

Previous workers have demonstrated that surface vegetation is similar in sulphur isotopic composition to peat surface layers (Novak *et al*, 1994). However, *Sphagnum* sampled from the waterlogged pools at this site was ^{34}S depleted relative to surface biomass peat layers (made up of *Sphagnum* remains) of the waterlogged peat cores (1.3 - 4.0 ‰). The surface biomass layers were poorly humified, with little evidence of decomposition and hence, at this stage, the only likely cause may be a recent change in a local pollutant source.

The plotting of δ^{34}S of the peat organic fraction versus mean age shows a remarkably close correlation between high and low ridge hummock peat (Fig. 4.5). Between 900 and 600 years, values are in some cases within instrumental error (± 0.2 ‰), even though these are two very different peats, which accumulated at different rates and were sampled over 200 m apart. From 600 years to the present day there is a diverging of the high and low ridge isotopic profiles yet the pattern remains the same with a significant lightening in $\delta^{34}S$. In the low ridge hummock peat we also see a slight return to heavier values in the uppermost layers of the peat.

This close correlation between the high and low ridge peat age profiles is suggestive of there being a preserved aerial sulphur signal, because, although anthropogenic sulphur emissions began nearly 2000 years ago, data from lead analyses of peat from this site (Lee and Tallis, 1973) show that significant smelting activities commenced only around 600 years BP. Thus, this is when we would expect to begin to see higher levels of SO_2 being released into the atmosphere to impact upon the isotopic composition of aerially deposited sulphur.

Uncertainty over peat dates acquired for the waterlogged peats meant that no comparison could be made between these peats and the drier hummock peats. As such the dating of the most isotopically light organic sulphur, between 20 and 25 cm, in the waterlogged peat was not possible and hence, no correlation between the period pertaining to the Industrial Revolution can be made. However, the sulphur isotope profiles of the organic fraction in the waterlogged peats are a more likely consequence of below ground sulphur cycling, namely through the incorporation of isotopically light sulphide, derived from bacterial sulphate reduction (BSR), rather than any change in sulphur input. BSR rates will be higher in wetter and unperturbed peats. The waterlogged peats, of all those sampled, have the largest yields of inorganic sulphur (Table 4.2) as well as a peak in organic sulphur at the same depth in which we see the peak in light sulphur (Figs. 4.2, 4.4).

The high ridge and low ridge peats are much drier, especially in the top portions of the profile and are therefore more likely to reflect a preserved aerial signal due to minimal rates of BSR and subsequent masking by sulphide incorporation. OrgS/C in the top of the high ridge profile do not suggest any significant incorporation of sulphide from BSR into the organic fraction (Fig. 4.8). Inorganic sulphur concentrations in the surface layers of the high and low ridge peats are much lower relative to the deeper portions of the peat and lower also than the concentrations seen in the surface layers of the waterlogged peats (Fig. 4.3).

Vegetation at this site was demonstrated in this study to closely resemble local inputs and diagenesis was demonstrated to not be significant within the past 600 years in the high ridge peat profiles. Therefore the amount of anthropogenic derived SO_4 in rainfall to the site during the last 600 years was calculated using the $\delta^{34}S$ of the organic fraction in one of the high ridge profiles as an accurate proxy for that aerially deposited. Analyses of modern local rainfall suggest that only 2.2 mg/L of SO_4 in rainfall is derived from a natural maritime source ($\delta^{34}S$ of 20.1 ‰). This data was used along with isotopic values for that of coals (mean $\delta^{34}S$ of 0.0 ‰) and galena (mean $\delta^{34}S$ of -8.5 ‰)(Robinson and Ineson, 1979) in an isotopic mass balance (Equation 4.1) to plot how much each would contribute to rainfall SO_4 deposition, through burning and smelting, respectively, in order to produce isotopic compositions of that observed in the organic sulphur peat fractions (Fig. 4.17). Between 250 and 150 years ago, smelting of lead ore and the burning of coal occurred concurrently and as such suggested contributions of total anthropogenic SO_4 lie within the area shaded (Fig. 4.18).

$$\text{Total } \delta^{34}S = \underbrace{(\delta^{34}S \times (\%SO_4/100))}_{\textbf{Natural } SO_4} + \underbrace{(\delta^{34}S \times (\%SO_4/100))}_{\textbf{Anthropogenic } SO_4} \qquad \text{Equation 4.1}$$

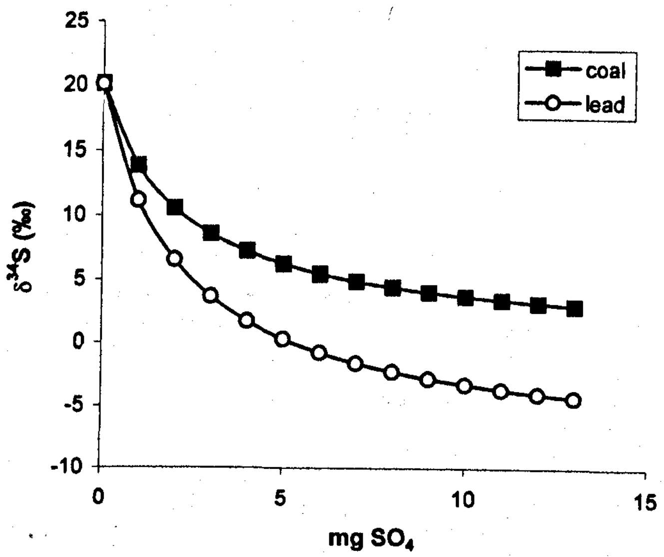

Fig 4.17. Calculated contributions of anthropogenic derived SO_4 from coal burning and lead smelting in order to produce isotopic shifts in aerial inputs to the southern Pennines.

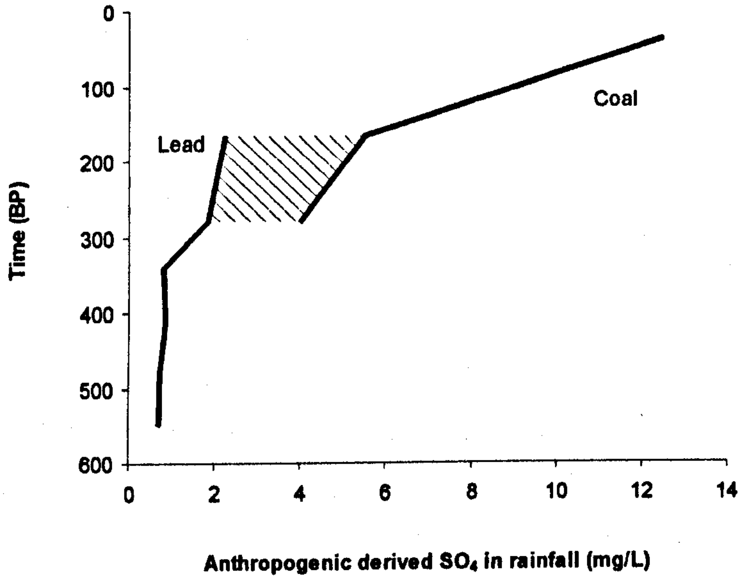

Fig. 4.18. Anthropogenic derived SO_4 contributions to rainfall during the last 600 years at the High Peak (data calculated using isotopic compositions of organic sulphur fractions, coal and galena minerals, modern rainfall and radiometric analyses).

The small alteration in carbon signature, observed in the high ridge hummock profile (Fig. 4.9) is unlikely to be due to a change in atmospheric source. Although the burning of fossil fuels can cause isotopic values of around -30 ‰ (natural values ~ -7 ‰ – see O'Leary, 1981), the peat samples analysed for carbon isotopic signature were found, after dating, to represent the period prior to the Industrial Revolution.

The role of hydrology can be critical in determining the isotopic composition of carbon in *Sphagnum* tissues (Williams and Flanagan, 1996). Hence, a record of alteration in hydrological conditions may have been preserved after plant death in the organic fraction of the peat. *Sphagnum* is a C_3 plant yet under waterlogged conditions the isotopic composition of *Sphagnum* will be affected by a restriction in the diffusion pathway of atmospheric CO_2 into the photosynthetic cells. Typically, *Sphagnum* moss will be covered by at least a film of water, which restricts the movement of CO_2 to the photosynthetic cells so that most of the available CO_2 will get taken up by the *Sphagnum* mats (Rice, 2000) resulting in less marked isotopic discrimination. However, a lowering of the water table below that of the surface vegetation will result in the removal of the diffusive barrier to CO_2 resulting in carbon isotope discrimination more typical of C_3 plants (Rice and Giles, 1996; Rice, 2000).

Changes in plant biogeography during the life of the deposit may also have contributed to an alteration in $\delta^{13}C$ of the organic fraction. However, variation in carbon isotopic signature in modern *Sphagnum* has shown to be much greater than that reported here in the organic fraction of the high ridge hummock profile (Proctor *et al*, 1992; Rice, 2000). As such, the relative uniformity in the absolute $\delta^{13}C$ values observed within the high ridge peat, which has undergone significant changes in surface flora composition, may be a product of diagenetic processes, which through partial degradation of specific fractions of the organic material may result in an organic fraction with a much less varied carbon isotopic composition relative to surface biomass. For example in marine plants, $\delta^{13}C$ of lipids and lignin have been shown to be 4-6 and 2-4 ‰ lighter, respectively, relative to total plant biomass (see Tyson, 1995). Hence if one fraction is degraded faster than another there may be significant isotopic alteration.

The sulphur isotopic data is supported by the pollen profiles derived from the dated high ridge peat profile. The isotopic enrichment in organically bound sulphur beginning at 600 years BP correlates well with the decline of *Sphagnum* and an increase in Cyperaceae pollen (typically *Eriophorum vaginatum*) (Figs. 4.5, 4.12). Today the incidence of *Sphagnum* moss in northern Britain is exceptionally low when compared to the levels of abundance recorded in the past (see Lewis, 1904; Moss, 1913) and this has been attributed to the deposition of sulphur during the Industrial Revolution. Tallis (1964a) described *Sphagnum* as being largely absent from the peat surface in the southern Pennines, except for some small, localised occurrences, with the majority of the surface being dominated by the cotton grass *Eriophorum vaginatum*.

The data from this investigation suggests that the decline of *Sphagnum* and the increase in *Eriophorum* may have begun prior to the Industrial Revolution, when smelting activities on the high peak and surrounding areas proliferated. Whether this is a direct result of localised atmospheric deposition of pollutant sulphur is unclear. Significant alteration in surface vegetation composition on the southern Pennines has been shown to have occurred on a number of occasions prior to the Industrial Revolution and any other anthropogenic activities (Tallis, 1964a; 1964b) and have therefore probably related to natural variations in climatic and environmental conditions (e.g. drought). Although drying of the bog surface can indeed lead to the replacement of *Sphagnum* species by *Eriophorum* (Pearsall, 1941; Conway, 1947; 1949), it is widely accepted that atmospheric deposition of sulphur during the Industrial Revolution, which has been implicated in the loss of other bryophytes (Nowell, 1866; Gilbert, 1968) and in the disappearance of lichens (Grindon, 1859; Hill, 1971), was a major contributing factor to this most recent change in plant biogeography (see Ferguson and Lee, 1983).

In high ridge hummock peat older than 600 years there is a somewhat varied isotopic profile. This may be the product of small-scale alteration in aerial inputs due to smelting activities, which are known to have occurred during the life of the deposit. However, it is more likely that this very deep peat has been subject to at least one of two processes:

i) partial decomposition, which liberates ^{32}S resulting in a ^{34}S enriched organic fraction (see Bridgham *et al*, 1998)

ii) the addition of isotopically light sulphide, derived from BSR (e.g. Brown, 1985)

The latter is likely to have been predominant, as Org-S/C increases below the depth relating to 600 years in the high ridge peat (Fig. 4.8).

4.5. Summary

The history of sulphur pollution in Britain and its geography have contrived to produce a unique system in which to examine changing inputs in sulphur through time. Natural and pollutant sulphur are extremely isotopically distinct in maritime Britain (natural = 20.1 ‰; anthro. = 0-1 ‰), yet the distance of the southern Pennines from the coast means that only a small amount of natural sulphate is present in that aerially deposited upon the peat surface. As such, even very small-scale activities, such as the smelting of lead ore prior to the Industrial Revolution, can sufficiently alter the aerial sulphur signal. Therefore, under these circumstances, the peatlands of the southern Pennines are an extremely sensitive archive for changes in atmospheric sulphur deposition.

CHAPTER 5- Impacts of Pollutant Loading, Climate Variability and Site Management on the Surface Water Quality of a Lowland Raised Bog, Thorne Moors, E. England.

5.1. Introduction

Ombrotrophic bogs are supplied with all their nutrients and water from the atmosphere through precipitation, making them extremely vulnerable to the effects of atmospheric pollutants. Over much of northwest and central Europe and the eastern United States, the burning of fossil fuels has increased the atmospheric loadings of sulphur to peat bogs and other ecosystems with consequences for their biochemistry and ecology (e.g. Ferguson *et al.* 1978; Gorham *et al.* 1985; Lee *et al.* 1987). However, the biogeochemistry of sulphur in peatlands and peatland waters is complex and factors other than atmospheric loading of sulphate can influence the chemistry of surface and pore-waters. Uptake of sulphur by growing plants provides a sink for sulphur inputs. In unpolluted continental settings, where sulphur inputs are low because of the lack of marine influence, this may form the dominant sink, with sulphur behaving almost as a limiting nutrient (Steinmann and Shotyk 1997). Bacterial sulphate reduction (BSR) also removes sulphate, by dissimilatory conversion to sulphide in deeper anoxic porewaters,

$$2H^+ + SO_4^{2-} + 2CH_2O \Rightarrow H_2S + 2CO_2 + 2H_2O \qquad (1),$$

Downward diffusion of sulphate into the zone of low sulphate concentration thus produced can be a major sink for sulphate from surface water in peat bogs of high natural or pollutant sulphur input (Brown 1985; Bottrell and Novak 1997). Note that BSR consumes acidity (H^+) and thus tends to neutralize acidity associated with acid sulphate pollution inputs, provided the sulphur remains stored in the reduced form, sulphide (e.g. Gorham et al. 1985, Morgan 1995).

The location of the zone of BSR and its effectiveness as a sink for sulphate are dependent upon water table height, which can exhibit inter-annual as well as seasonal variation. A drop in water table can lead to the introduction of oxic waters into previously anoxic parts of the peat, leading to oxidation of reduced forms of sulphur in the peat. This process can act as a source of both sulphate and acidity to the surface waters (e.g. Braekke 1981; Mandernack *et al.* 2000). Sulphate may also be liberated through the partial decomposition of surface vegetation following burial and by hydrolysis of ester sulphate (e.g. Groscheova *et al.* 2000). Thus the sulphate concentration in surface water reflects a balance between atmospheric inputs and generation of sulphate, on the one hand, and losses to sulphate reduction and assimilation during biomass production on the other.

BSR is characterized by a large selectivity between the two most abundant stable isotopes of sulphur. Bacteria preferentially reduce the lighter ^{32}S isotope, so sulphide produced is depleted in the heavier ^{34}S isotope, while residual sulphate becomes progressively enriched in ^{34}S. These isotopic changes can be measured and used to identify the effects and products of BSR. In this chapter we examine the sulphur geochemistry of a raised bog complex in eastern England, which receives significant pollutant sulphur inputs and has been subjected to large changes in water levels due to a period of drought conditions. We examine the effects of these influences on surface water sulphate chemistry and the cycling of sulphur within the bog.

Sphagnum species dominate the flora of ombrotrophic bogs and, via differential preservation in the peat catotelm, may constitute an even larger proportion of material preserved as peat than they do in the living biomass. *Sphagnum* has leaves one cell thick and no cuticle and is thus directly exposed to atmospheric deposition and has previously been used to study levels of anthropogenic loading and its early effects on vegetation (e.g. Lee and Woodin, 1988). As part of this work we have examined the reaction of *Sphagnum* sulphur content to changing surface water sulphate concentration and its potential to record past changes in surface water sulphur geochemistry.

5.2. Study Site

Thorne Moors (grid reference SE7113 to SE7517, Fig. 5.1) is the remnant of an extensive complex of raised bog, which covered large areas of South Yorkshire and North Lincolnshire. This area of peatland currently amounts to 1918 ha and the depth of the surviving peat only exceptionally exceeds 2.5 m. The site occupies an area of the pro-glacial Lake Humber that existed around 13,000 BP. At around 5200 BP, natural drainage was impeded by rising sea levels and silting up of the lake, which resulted in the development of peat formation through paludification (Van de Noort 2001). Large areas of peatland have been lost through drainage and warping (use of floodwater to raise the level of land through sediment accretion) in order to improve it for agricultural use. Peat cutting has been carried out, primarily for fuel, since at least medieval times (Caufield, 1991). However from the 17th century, the ancient trade in peat as a fuel from Thorne Moors declined due to the increased availability of coal. It was not until the late 1880's that there was a revival in peat extraction through the demands for animal litter and horticulture (Limbert, 2002). This removal of peat, initially by hand graving and later through mechanisation, resulted in a major network of drainage ditches which cut through the peat into the underlying Lake Humber Clays. Most of the samples used in this study are from a small area in the centre of the peatland, which were last cut before the 1920's and managed as a National Nature Reserve by English Nature since 1985 (Roworth, 1991). At this site the maximum depth of in-situ peat is *c.* 3.5 m. A newer peat accumulation has formed in the abandoned cuttings from *Sphagnum* and *Eriophorum.* Since 1992, when the area under English Nature management increased dramatically, damming of drainage ditches has been used to restrict water losses towards the north, where peat extraction has until recently taken place, and towards the other margins, where land is drained for agriculture (Roworth, 2000).

All samples were collected during spring months from various locations around Thorne Moors, mainly from isolated pools with growing *Sphagnum* (samples sites A through J) but also from drainage ditches immediately adjacent to the pools (sample sites N through Q). In 2000, a series of samples were collected from the same two sites throughout the year. Although different numbers of samples were collected in each year, the same collection and analytical protocol was followed throughout. Samples were collected and processed by a number of workers from 1994 to 2000 (the data was collated from unpublished work, some of which taken from M.Sc. theses [Spence, 1999; Berry, 2001] undertaken under the supervision of S.H. Bottrell at the University of Leeds) and as such, this chapter represents a synthesis of previous work conducted at Thorne Moors in order to investigate changes in surface water chemistry over a number of years to determine its effects upon bog vegetation and also to discuss the results in relation to sulphur cycling within the peat.

Data analyses and statistical comparisons were conducted using Mann-Whitney and Kruskal-Wallis non-parametric tests (see Zar, 1984), these being appropriate for the variably sized samples compared in this study.

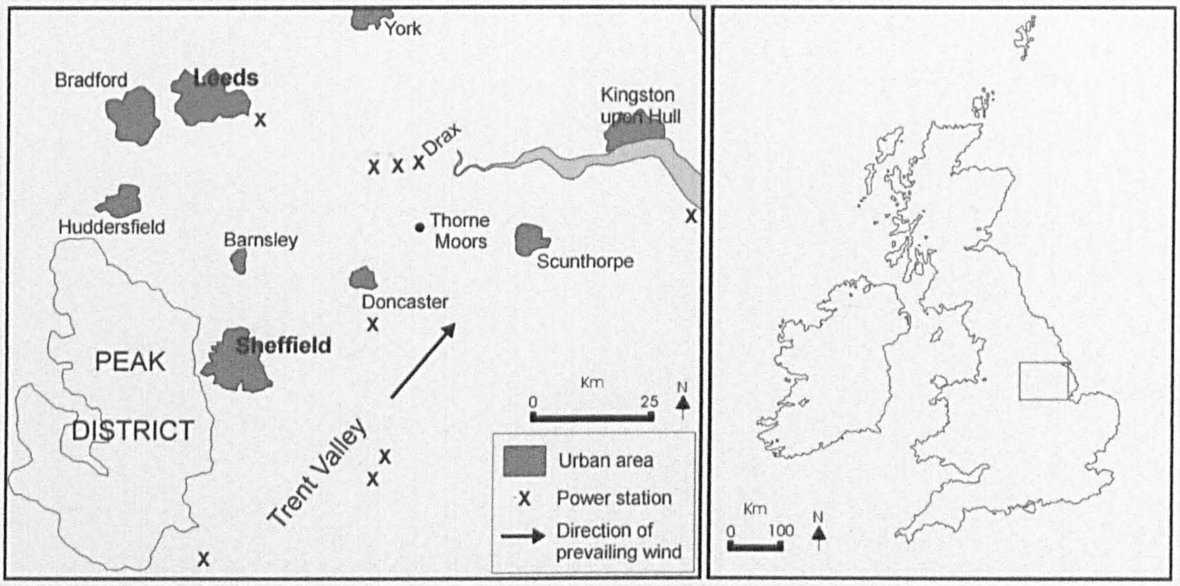

Fig. 5.1. Location of Thorne Moors, urban areas and power stations, eastern England, U.K.

5.3. Results

5.3.1. Peat Density Profiles

Depth profiles of peat strength, a proxy for peat density, were investigated in 1999 and are presented in Fig. 5.2. Each curve is the mean of three separate profiles at each site. The upper 15 to 20 cm of all profiles have zero strength, corresponding to the low density, porous peat acrotelm. Below, this peat density increases. There is a gradual increase down to 66 cm at Site B, but sites A and C show sudden large increases (at 35 cm and 55 cm, respectively). These correspond to the base of the former cutting and the interface between new peat growth (around 100 years old) and the much older peat accumulation.

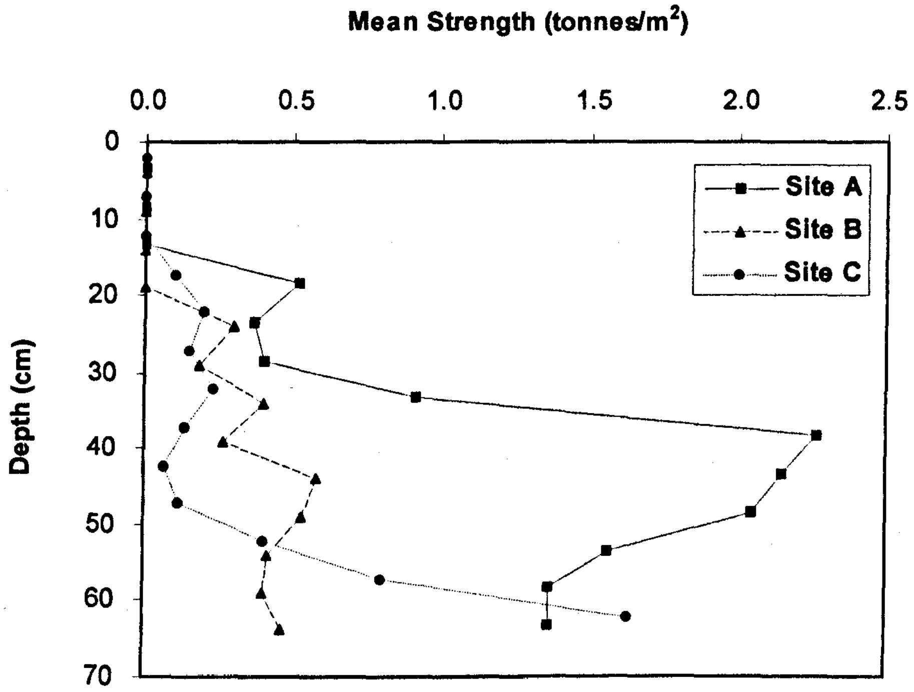

Fig. 5.2. Depth profiles of the mean strength of peat at sites on Thorne Moors.

5.3.2. Sulphur inputs

Bulk sulphur inputs to the site (calculated from analyses of bulk open area deposition i.e. $\sum$\{vol x concentration\} for each year divided by area of collector) are presented in Table 5.1 and are plotted in Figure 5.3 along with data on total UK power station sulphur emissions.

Table 5.1. Bulk sulphur inputs to the raised bog surface at Thorne Moors (1994-2000).

Date	Sulphur input ($g/m^{-2}/a^{-1}$)
Mar94-Mar95	1.46
Mar95-Mar96	1.28
Mar96-Mar97	0.80
Mar97-Mar98	0.96
Mar98-Mar99	0.84
Mar99-Mar00	0.62

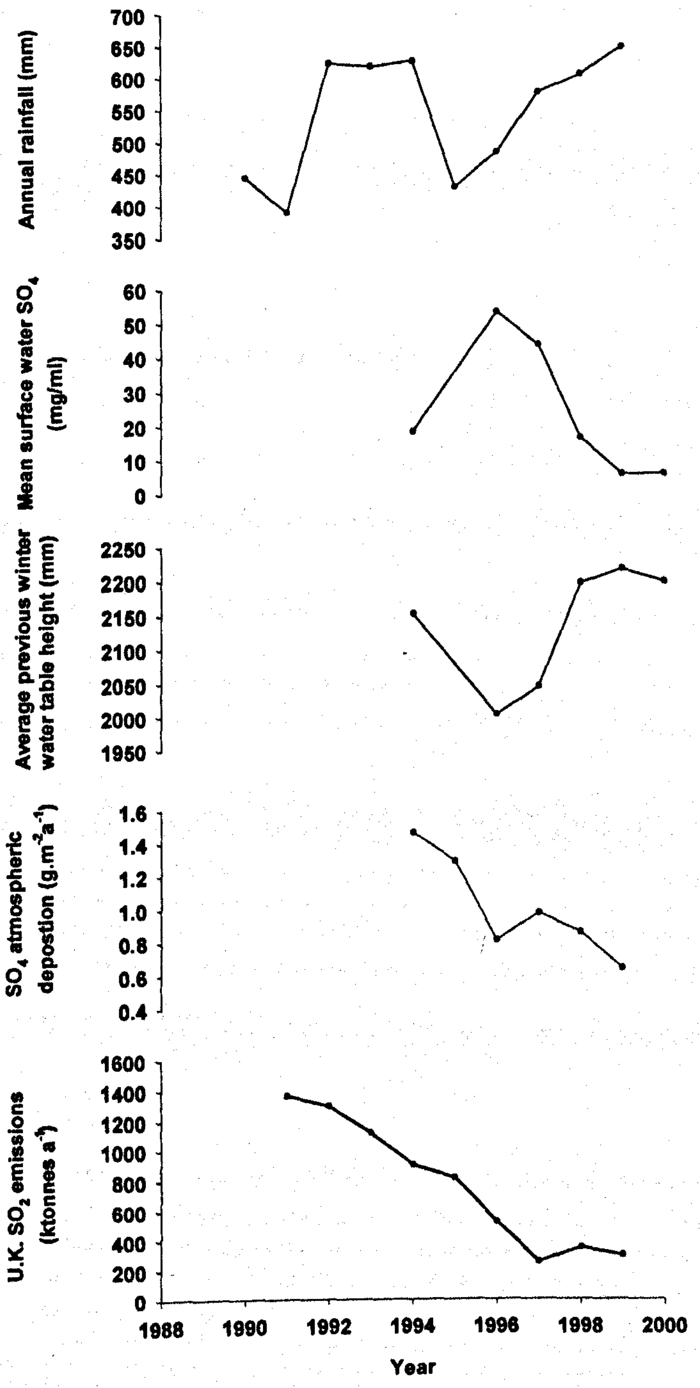

Fig. 5.3. Total U.K. power station SO_2 emissions (National Power, 1999) compared with bulk rainfall, mean surface water sulphate concentrations, previous winter water table and local bulk sulphur inputs at Thorne Moors.

The site is located close to several heavily industrialized and urbanized areas of NE England (Fig. 5.1) and consequently sulphur inputs are high as a result of atmospheric pollution. The Drax power station, a major point source of atmospheric sulphur emission 14 km northwest of the site, was retrofitted with a flue-gas desulphurization system in 1997. However, there is no marked decrease in sulphur inputs at Thorne at this time, inputs actually fall more in line with emissions from power generation in the UK generally (but decrease slightly less so, Fig. 5.3). The prevailing wind is from the south-west and west and the plume from the stack at Drax will normally be thermally buoyant for tens of kilometres, significantly further than its distance from Thorne Moors. Pollutant sulphur inputs to Thorne Moors are more likely derived from industrial and power generation sources in the Sheffield and Trent valley areas upwind of the site, so desulphurization at Drax did not have any particularly large impact on sulphur deposition here.

5.5.3. Surface Waters

Sulphate concentrations and sulphate S isotopic compositions of surface and ditch water over the period 1994-2000 are presented in Table 5.2.

Table 5.2. Sulphate concentrations and isotopic compositions of surface and ditch water at Thorne Moors (*denotes single sample).

	Surface water				Ditch water				
Year	Mean ppm	S.E.	Mean $\delta^{34}S$	S.E.	Mean ppm	S.E.	Mean $\delta^{34}S$	S.E.	Surface water SO_4 vs. ditch water SO_4 (Mann-Whitney U-test)
1994	18.0	1.0	10.6	1.2	5.6	0.9	23.7	3.0	$U=0, n_1=8, n_2=4$, $p<0.05$
1995	-	-	-	-	-	-	-	-	
1996	52.4	12.8	6.1	1.2	-	-	-	-	
1997	42.4	6.6	10.7	0.9	35.6	6.1	9.9	0.1	$U=12, n_1=7, n_2=4, p>0.05$
1998	15.3*	-	-	-	-	-	-	-	
1999	4.3*	-	-	-	-	-	-	-	
2000	4.3	1.9	-	-	1.7	0.1	-	-	$U=18, n_1=4, n_2=4, p<0.05$

Samples were collected every year in the spring (May-June) to correspond with the end of a relatively stable over-winter water table (Fig. 5.4). The surface waters show considerable variation in concentration with time (Fig. 5.3). Site B has the most continuous record and, in years where multiple sites were sampled, the site B value is close to the mean of sites sampled and always within one standard deviation of the mean (Fig. 5.5a). Variation at Site B may thus be generally representative of the site as a whole in years where other data are unavailable. This also holds true for variation in SO_4/Cl in surface waters through time (Fig. 5.5b). In 2000, samples were also collected throughout the year at sites B and C (Table 5.3).

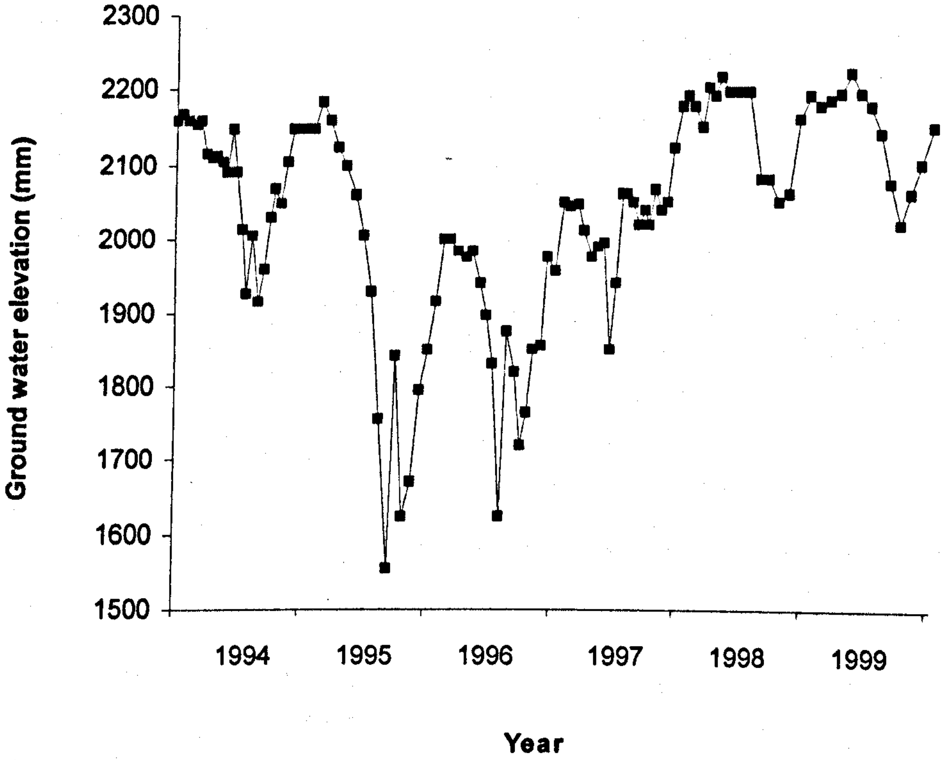

Fig. 5.4. Temporal changes in water table elevation at study site near the centre of Thorne Moors. This peizometer is in the centre of peatland block and 200 m from nearest drainage ditches.

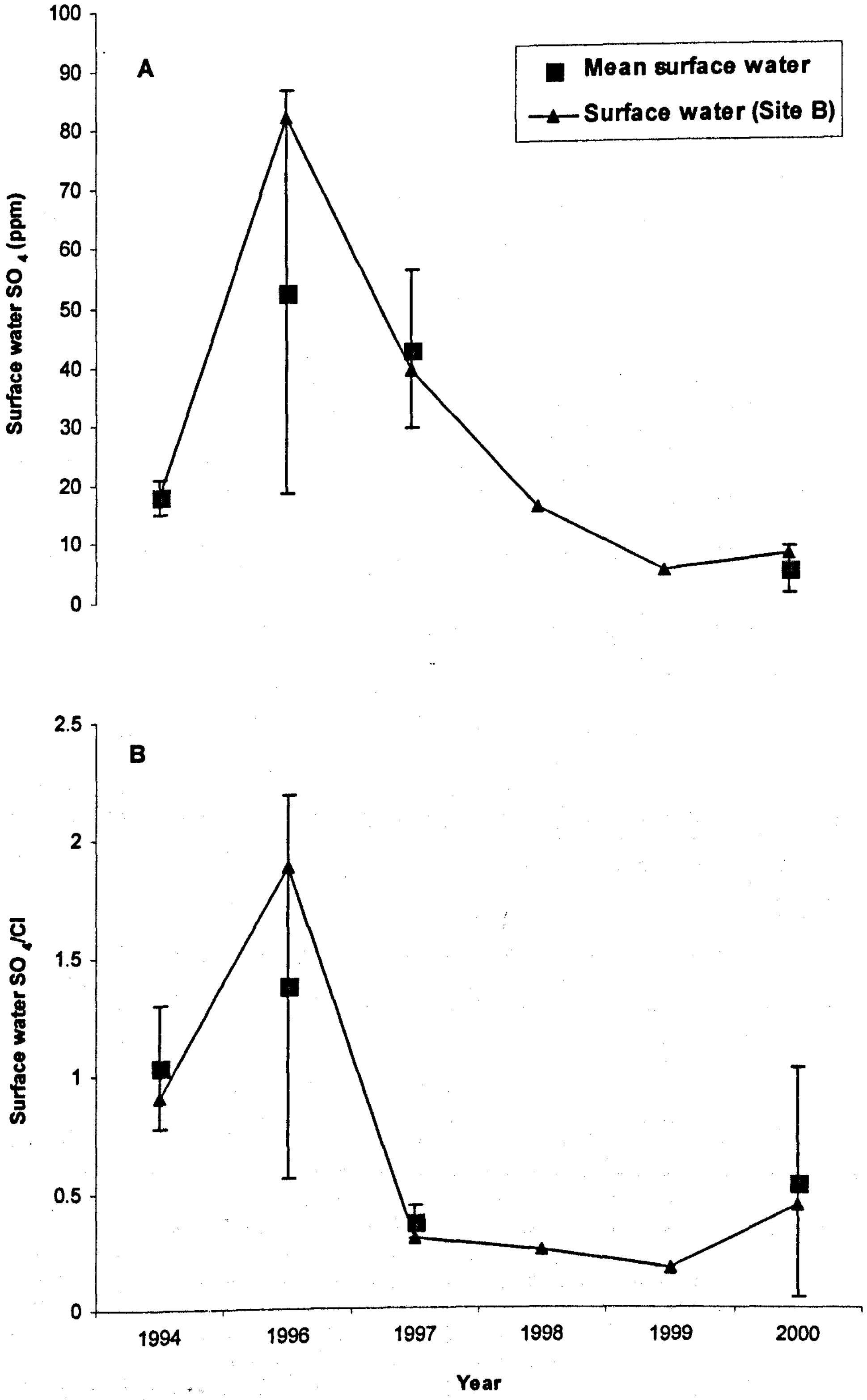

Fig. 5.5. a: Mean surface water SO_4 and surface water SO_4 at site B versus time (error bars represent one standard deviation); b: Mean SO_4/Cl in surface waters and SO_4/Cl in site B surface water versus time (error bars represent one standard deviation).

Table 5.3. Variability of surface water sulphate concentration at sites B and C during the year 2000.

Date (year 2000)	Surface water sulphate concentration (mg L^{-1})	
	Site B	Site C
March	7.0	7.9
May	5.9	4.3
June	1.3	2.9
July	1.0	1.0
August	5.1	5.0
October	6.7	7.5
November	1.8	2.9

The overall trend with time in sulphate concentration is from moderately high values (18.0 ± 2.9 mg L^{-1} SO_4) in 1994 to a wider range with many much higher values (52 ± 34 mg L^{-1} SO_4) in 1996, followed by a decline to lower values (~ 4 mg L^{-1} SO_4) by 1999 and 2000 (Fig. 5.5a). There is a wide range of surface water values in any one year, particularly 1996, because each pool sampled will respond to local variables as well as factors affecting the whole site. However, surface water sulphate concentrations differ significantly between different sampling years (Kruskal-Wallis: H=11.44, df = 2, p = 0.003). Surface water sulphate concentrations were significantly greater in 1996 than in 1994 and 2000 (non-parametric multiple comparison test, $p<0.05$) (Fig. 5.6). Also plotted on Fig. 5.3 are records of rainfall (Roworth, 2002), water table elevation and bulk sulphur inputs for the site.

5.3.4. Ditch waters

In both 1994 and 2000 the ditches immediately surrounding the surface water sites had markedly lower sulphate concentrations than the surface water pools, and in 1994 the ditch water sulphate was markedly enriched in ^{34}S (Table 5.2). In 1997 there is no significant difference between ditch and surface waters in terms of either sulphate concentration or isotopic composition (Table 5.2).

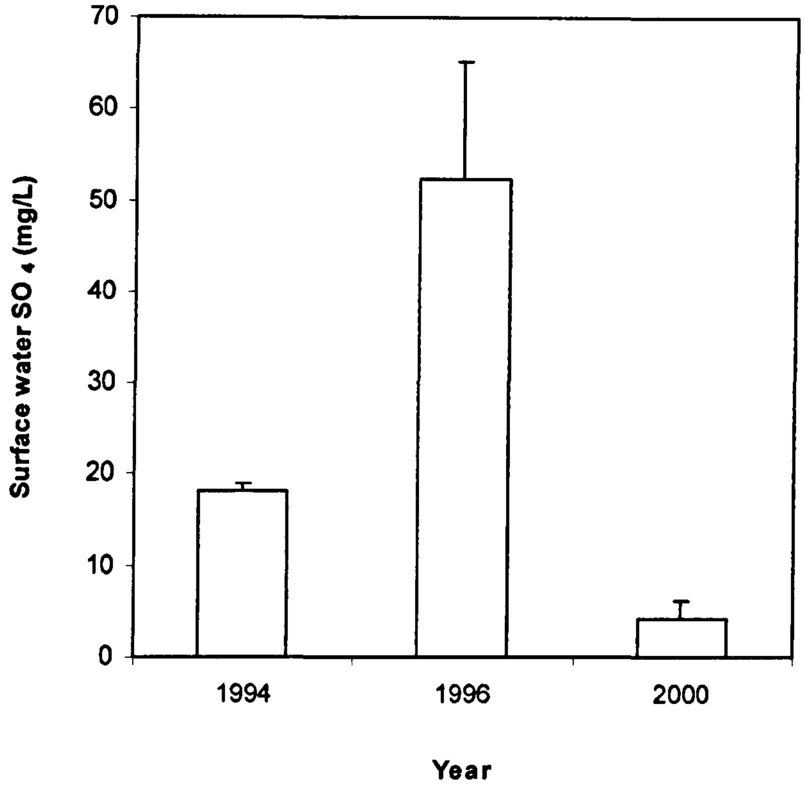

Fig. 5.6. Mean surface water SO_4 versus year sampled. All means differed significantly from each other (non-parametric multiple comparison test, $p<0.05$).

5.3.5. *Sphagnum* sulphur content

Sphagnum sulphur contents were measured over three years and the results presented in Fig. 5.7. There was a highly significant difference in the sulphur content of *Sphagnum* sampled in different years (Kruskal-Wallis: H = 16.51, df = 2, $p< 0.001$). *Sphagnum* sulphur content was significantly greater in 1996 than in 1994 and 2000 (Non-parametric multiple comparison test, $p<0.001$). There was no significant difference in the sulphur content of *Sphagnum* sampled in 1994 and that of 2000. The chlorophyllose cells of *Sphagnum* leaves are continually exposed to changes in the chemical composition of the pool water, which might result from episodes of atmospheric pollution or due to alterations in belowground hydrology. Variation in surface water sulphur chemistry at sites on Thorne Moors can be observed in the sulphur content of *Sphagnum*. The increase in sulphur content of *Sphagnum* in 1996 accompanies the rise in surface water sulphate at this time.

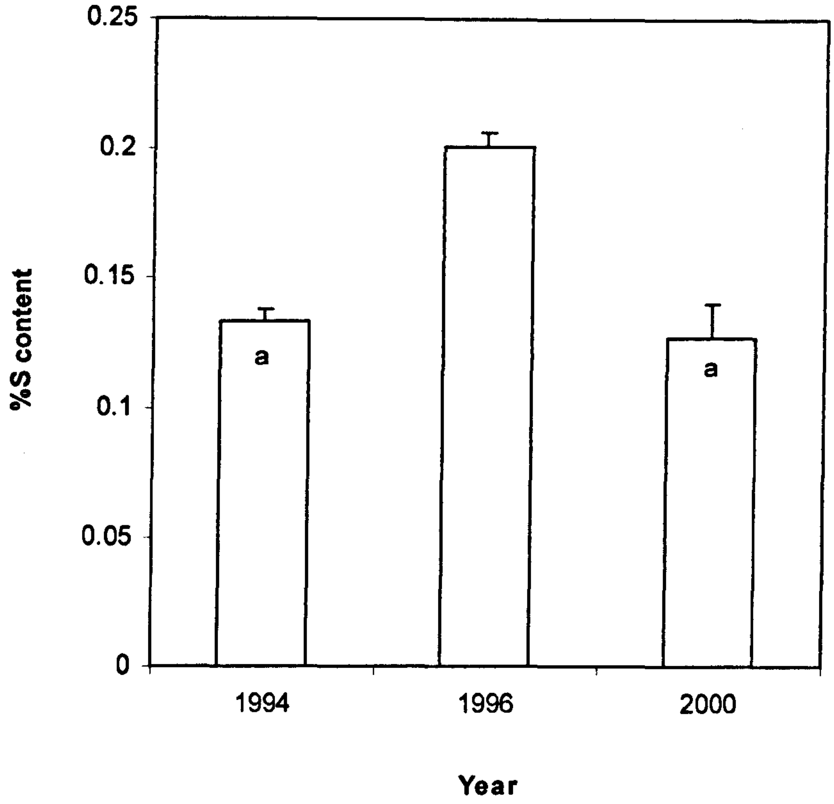

Fig. 5.7. Mean sulphur content of *Sphagnum* versus year sampled. Means with the same letter do not differ significantly from each other (non-parametric multiple comparison test, $p<0.05$).

5.4. Discussion

5.4.1. Influences on surface water sulphate concentrations

Surface water sulphate concentrations at Thorne Moors have varied significantly over the monitoring period (Fig. 5.3) whereas variation at a site within a year is far smaller (Table 5.3). Sulphur inputs have fallen over the period (Fig. 5.3, Table 5.1); hence changes in input cannot directly account for the marked peak in surface water concentrations in the 1996 data. Of note is the low rainfall and subsequent low groundwater elevation (water table) over the 1995-1996 period (Figs. 5.3 and 5.4). The elevated surface water sulphate concentrations correlate well with this period of drought (Fig. 5.3) and there is a remarkably good inverse correlation between springtime surface water sulphate concentration and previous winter water table (Fig. 5.8, correlation significant at the 99% confidence level). It is therefore likely that lowering of the water table led to one or more of:

i) the oxidation of solid phase sulphide within the peat profile resulting in increased sulphate supply to the surface waters;

ii) suppression of sulphate reducing activity as oxygen becomes more available in the system, effectively expanding the depth range over which oxic respiration dominates and forcing sulphate reducing activity deeper into the profile.

iii) residual concentration of sulphate by increased evapotranspiration losses of water during the drought. Some increase in sulphate concentration by evapotranspiration will have occurred, but this will also have affected the concentration of the more chemically conservative chloride ion. The temporal trend in SO_4/CL in Fig. 5b shows that sulphate increased in concentration more than chloride at most sites from 1994 to 1996, so factors other than evaporative concentration were influential in the increase in sulphate concentration at this time.

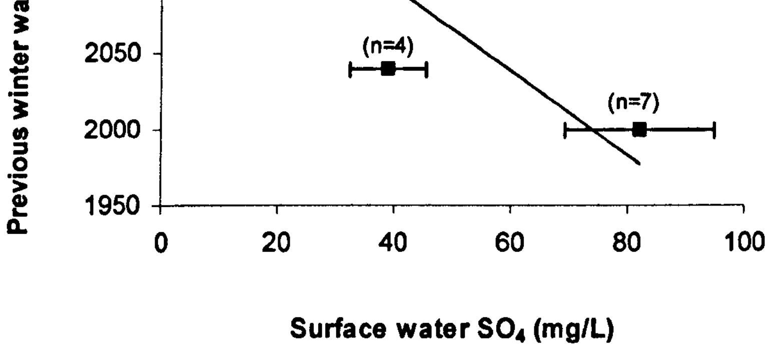

Fig. 5.8. Previous winter water table height versus surface water SO_4 concentration. The point with n = 8 data has error bars within the block plotted.

Thus the primary cause of increased surface water sulphate concentration in 1996 was due to factors i) and ii) above as a consequence of the fall in water table as a result of low rainfall (Fig. 5.3, 5.8). Subsequently, water tables have been restored to higher levels, a result of both increased rainfall and management work to dam ditches and outlets. This has resulted in a progressive decrease in surface water sulphate concentration (Table 5.2, Fig. 5.5a) as the site has recovered and BSR has been re-established as an effective sink for sulphate. Higher water tables will restrict the generation of sulphate by oxidation of sulphur species in the peat profile. By 2000 surface water sulphate concentrations had fallen to well below the pre-drought 1994 values (4.3 ± 1.96 mg L^{-1} vs. 18.0 ± 1.0 mg L^{-1}; Table 5.2 and Fig. 5.5a). These lower concentrations reflect the declining pollutant sulphur input to the site over this period (Fig. 5.33, Table 5.1) and/or more stable water tables resulting from the management of the site.

5.4.2. Relationships between surface and ditch waters

In 1994 and 2000 ditch waters had significantly lower sulphate concentrations than the surface water pools (Table 5.2). This could be due to either or a combination of:

i) increased evaporation affecting the surface waters compared to the ditches, leading to more extreme evaporative concentration in the surface waters;

ii) greater influence of BSR on the ditch waters compared to the surface pools, whereby more sulphate has been removed from the ditch waters resulting in lower concentrations.

In 1994 the ditch water SO_4 was markedly enriched in ^{34}S compared to the pool surface waters (Table 5.2). Simple evaporative concentration in the surface waters would produce no isotopic effect. Thus ditch waters are not simply overflowing surface waters but have been influenced by BSR. Note that in 1997, when the water table was lowered following drought, there is no significant difference between ditch and surface waters in terms of either sulphate concentration or isotopic composition (Table 5.2) and the ditch waters were thus unaffected by BSR. This suggests that the BSR affecting the ditch waters takes place dominantly during sub-surface flow from surface water pools to ditches (if sulphate reduction were a significant process in the ditches themselves then ditch waters would always be affected by BSR). Peatlands are characterised by high permeability in shallow layers, around 10 to 30 cm thick, and markedly decreased permeability at depth (Chanson and Siegel, 1986 and see Fig. 5.2). When the water table is high the flow path through the shallow, high permeability layers is (at least in part) in the anoxic zone of the peat and hence BSR affected waters drain to the ditches (A in Fig. 5.9).

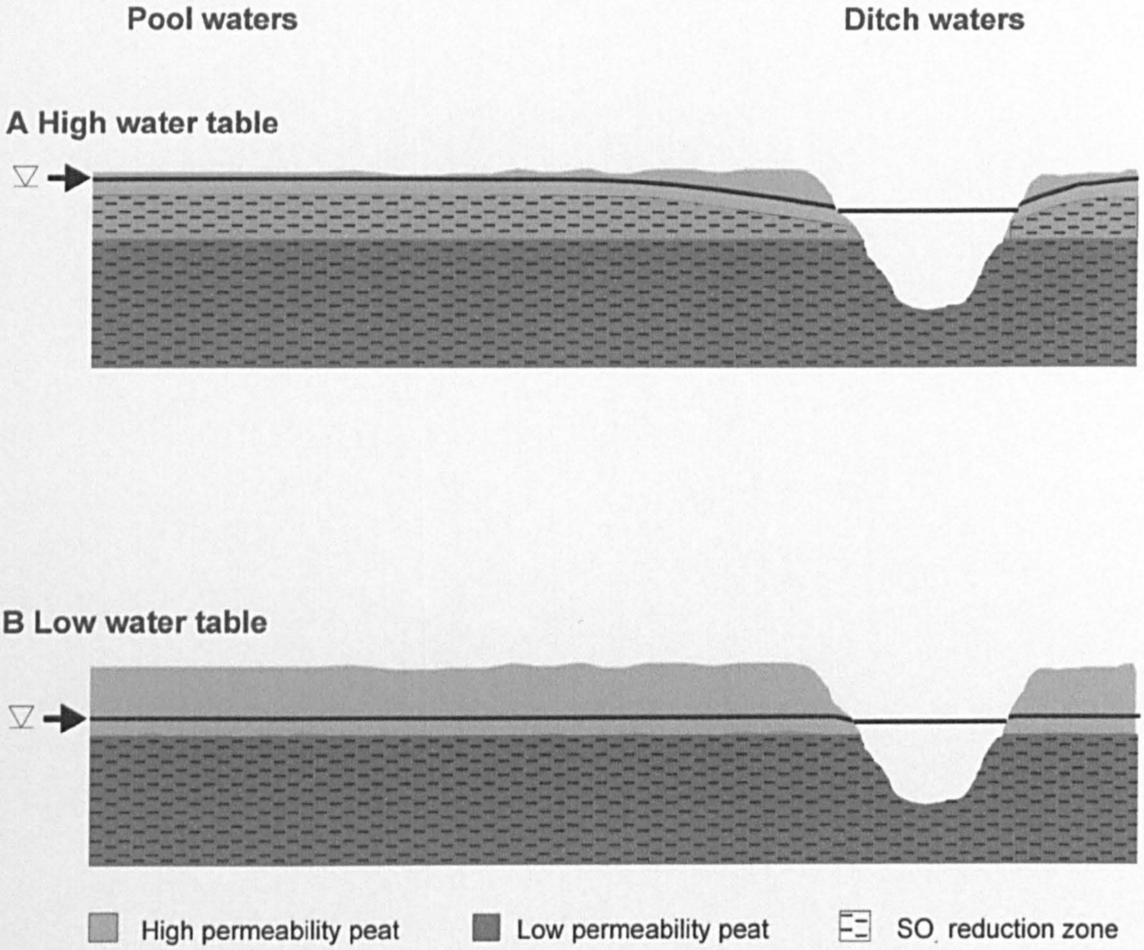

Fig. 5. 9. Proposed effect of changes in water table elevation upon ditch water sulphur chemistry. A. High water table means that a significant component of the flow into ditches is through saturated peat in the upper, more permeable zone and therefore in the sulphate reducing zone. Hence SO_4 in water draining to ditches is enriched in ^{34}S. B. Under low water table conditions the permeable flow pathway is dominantly or totally above the sulphate reduction zone and waters draining to ditches are minimally affected by bacterial sulphate reduction.

When water tables are lowered, the sulphate reduction zone lies deeper in the profile, below the hydraulically permeable zone and the flow path is thus dominantly or completely in the oxic zone (B in Fig. 5.9); hence waters entering the ditches are unaffected by BSR. At Thorne Moors this effect may be very significantly enhanced by the cut-over nature of the peat. The profiles in Fig. 5.2 show that the new growth in some of the bays is of limited thickness (40-60 cm) above the cut level. Thus the fall in water level in 1995/6 and 1996/7 lowered the water table to the level of the cut surface (Fig. 5.4). At this point, active sulphate reducing bacteria (which are obligate anaerobes) will be confined to the saturated old growth peat, and this will provide a less labile organic substrate, further impeding sulphate reduction. Under these conditions, water draining through the lowest permeable part of the new growth peat will be largely unaffected by sulphate reduction.

5.4.3. Management of sulphate in bog waters

Surface water sulphate concentrations in ombrotrophic peatlands are the product of a dynamic equilibrium between sulphate sources (atmospheric inputs and sulphate produced by oxidation/degradation reactions in the peat) and sulphate sinks (BSR and uptake by plant growth). In near-natural "pristine" systems with low sulphur inputs, surface water sulphate concentrations are low as removal by plant growth is able to keep pace with natural inputs (Steinman and Shotyk 1997). When systems suffer disturbance (i.e. pollutant sulphur loading or falling water tables and sulphur oxidation reactions) that increases sulphate inputs above the ability of plant growth to remove it, surface water sulphate concentrations will increase in response. Under these conditions, downward diffusion to uptake by BSR becomes an increasingly important sulphur sink (e.g. Bottrell and Novak 1997). Very high sulphur inputs exceed the ability of the BSR sink to remove sulphate, resulting in highly elevated surface water sulphur concentrations. Thus surface water sulphate concentrations can be used as an indicator of the wetland's ability to respond to environmental change. This signal is recorded in the sulphur content of growing *Sphagnum* and potentially other plants. Novak *et al.* (2001) demonstrated a relationship between acid sulphate inputs to wetlands and *Sphagnum* sulphur content using data from sites with differing atmospheric inputs.

Their study showed that in relatively pristine coastal sites with high natural sulphate inputs *Sphagnum* sulphur contents were relatively depressed, indicating an effect of the nature of sulphur deposition on uptake by *Sphagnum*. This effect was investigated by Thompson and Bottrell (1998), who concluded that uptake of partially reduced sulphur species associated with pollutant deposition was the most likely explanation. Thus in the present study the relationship between *Sphagnum* sulphur content and surface water concentrations is simplified by the dominance of a single (pollutant) sulphur input.

At Thorne Moors sulphate in surface water shows a clear trend:

i) moderate concentrations under high pollutant loadings before drought;
ii) elevated concentrations under declining pollutant loadings during drought and lowered water tables;
iii) recovery to low concentrations as water tables recovered (due to increased rainfall and site management) whilst pollutant loadings continued to fall.

The declining surface water sulphate concentrations under conditions of high pollutant sulphur inputs imply the attenuation of acid sulphate pollution by BSR (Reaction 1). This may be important in allowing the establishment of more natural, low surface water sulphate conditions but can only be effective if water tables are maintained, as falling water tables will promote oxidation reactions and generation of acidity. This is particularly marked at Thorne as the peatland is now dominated by growth in reflooded cut bays. If the water table falls to the level of the base of the cut bays, the zone of active sulphate reducing bacteria will be confined to the less labile substrate of the old growth peat. This will further inhibit BSR, making it extremely unlikely that BSR will be able to keep pace with sulphate inputs. Thus management to maintain a stable water table in cut over peatlands will promote regrowth under conditions as near as possible to natural conditions.

5.5. Summary and Conclusions

Surface-water sulphate concentrations can be used as an indicator of the hydrological and environmental status of a raised bog system with respect to the system's ability to cope with acid sulphate loading. *Sphagnum* sulphur concentrations parallel changes in surface-water sulphate concentrations, thus sulphur concentrations of neo-fossil *Sphagnum* and *Sphagnum* peat may contain historical records of the changing status of peatlands as a result of drainage and/or industrial sulphur pollution.

Thickness of the unsaturated zone is more important, on annual timescales at least, than pollutant loading in determining surface water sulphate concentration. Under lowered water tables, sulphate can be generated by oxidation reactions in the unsaturated zone and consumption of sulphate by bacterial reduction is suppressed, leading to elevated surface water sulphate concentrations. This is particularly true of cut-over peatlands where there is a marked contrast between new growth and old growth substrates. Management of the site to maintain stable, and ideally high, water levels is thus crucial to establishment of a near-natural equilibrium in which sulphate consumption can keep pace with sulphate inputs and better cope with acid sulphate pollution.

CHAPTER 6 – The Fate of Sulphur in a Waterlogged Raised Peatland: A ^{34}S tracer investigation

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6.1. Introduction

Alterations in sulphur deposition through time may be preserved, in part, in the organic fraction of peatlands. However, the elucidation of the fate of aerially deposited sulphur is complicated by the inter-cycling of sulphur between five transposable compartments within the peat stratigraphy; surface water sulphate, surface vegetation (biomass), organically bound sulphur (necromass), reduced inorganic fractions (S^0, H_2S, FeS, FeS_2), and pore water sulphate. Importantly, the movement of sulphur between these different compartments can, in differing degrees, be accompanied by isotopic fractionation effects. The isotopic composition of surface water sulphate may not necessarily reflect that which was deposited aerially as bacterial sulphate reduction (BSR) may result in enrichment in ^{34}S in the surface waters. The same process, as described in chapter 5, may also lead to intermittent ^{34}S depletion in surface water sulphate when there is a fall in water table height leading to oxidation of light dissolved sulphide that may diffuse to the surface waters.

Assimilation of sulphur into bog flora is also accompanied by a fractionation effect, and, after plant death, the organically bound sulphur can become ^{34}S enriched, as lighter ^{32}S is released during partial decomposition (Bridgham *et al*, 1998). However, a contrary effect may also occur whereby isotopically light sulphides, produced from BSR, become incorporated into the organic matrix resulting in a lightening of the preserved sulphur signal. H_2S has been shown to be incorporated into humic acids (part of the organic fraction) (Casagrande *et al*, 1979) and a direct labelling experiment of $^{35}S\text{-}SO_4$ into an anaerobic peat core suggests that there is direct incorporation of H_2S into the organic matrix (Brown, 1985). Clearly, a better understanding of the importance of all these processes is vital in determining whether a record of atmospheric sulphur inputs can be preserved in peatlands.

The data presented in previous chapters suggests that in dry, upland blanket peats an archive of atmospheric deposited sulphur inputs may be preserved within the peat profile, with only minimal masking by diagenetic and decomposition processes. However, in more waterlogged peats the effect of these processes upon the originally incorporated sulphur signal appeared more marked. Therefore, the potential exists for the incorporation of sulphides, which make up a significant sink of sulphur in waterlogged peats to completely obscure the primary sulphur signal that was incorporated by the surface vegetation.

A ^{34}S experiment was conducted to examine the interrelationships that exist between the 5 transposable sulphur compartments through the application of pure ^{34}sulphate onto the surface of a waterlogged peatland in northern England and tracking its movements in different compartments of the peat over a 12-month period. A waterlogged peat, due to hydrological uniformity, provides an excellent opportunity to examine the inter-cycling of sulphur at a highly magnified scale. Such a peat enables not only for data to be collected from harvested peat cores at different times during the investigation period but also surface waters and porewaters can be collected at regular intervals during the study. This allows for a comprehensive analysis of sulphur movement within the peat.

The addition of pure ^{34}S generates extremely elevated δ^{34}S and therefore 'unnatural' isotopic signals within the sulphur containing compartments. However, it is first necessary to establish the range of natural variability that exists within the peatland system. As such the final area of research in this thesis will be divided into two parts, the first part of this chapter will look at natural sulphur isotope signals at the site prior to tracer addition, while the second section will go on to examine the fate of the ^{34}S tracer.

Though the pure ^{34}S will dwarf any seasonal variation in sulphur chemistry, it is important to gain an understanding of how changes in inputs and alteration in water table during the year may affect the isotopic geochemistry of sulphur in the surface waters and porewaters. Therefore part of the data presented in this chapter will be a synthesis of surface water and porewater data taken during the year 2000 (replotted from Berry, 2001).

6.2. Study site

General information relating to Thorne Moor has been discussed in the preceding chapter. This work concentrated on one specific site on Thorne Moor, a previously cut over bay which, due to artificial damming, has maintained a high and stable water table over a number of seasons (Fig. 6.1) (known as site B in previous chapter). This has resulted in the proliferation of *Sphagnum* sp. over much of the bay.

Fig. 6.1. Location of Thorne Moors, UK. (X= sample site)

Four small enclosures (1x1 m) and 2 larger, long-term enclosures (1x2 m) were constructed from acrylic sheet inside a untreated wooden frame and installed into areas of peat at Thorne Moor. This served to isolate the higher portions of the peat and the surface water so that the tracer added would be confined to a set area of bog for detailed study. Control data (day 0); surface waters were sampled from each of the plots. Depth sampling tubes were installed into the two larger enclosures (1C and 2C) for pore water sampling. Control peat cores and vegetation samples (*Sphagnum recurvum* and *Eriophorum vaginatum*) were collected from the bay prior to tracer addition. Comprehensive discussion on the methods and experimental approach employed in this chapter is presented in Chapter 2.

6.3. Results

6.3.1. Control data (prior to tracer addition)

6.3.1.1. Aerial inputs

Bulk sulphur inputs to the site (calculated from analyses of bulk open area deposition) are presented in Table 6.1. Total sulphur deposited from June 2001 to June 2002 was 0.7625 g-S m^{-2}, a slight increase from that recorded from 1999 to 2000 (see Table. 5.1). The isotopic composition was variable throughout the year with a decrease in $\delta^{34}S$ during the summer and autumn months.

Table 6.1. Bulk sulphur inputs and isotopic composition at Thorne Moors (2001/02).

Sampling period	g. S. m^{2}.d^{-1}	$\delta^{34}S$
30/6/01 - 10/8/01	0.00336	4.3
10/8/01 – 20/11/01	0.0026	5.4
20/11/01 – 1/2/02	0.0022	7.1
1/2/02 – 30/6/02	0.0014	7.5

6.3.1.2. Surface and pore waters

Surface waters were sampled from the enclosures prior to tracer addition. Sulphur data is presented in Table 6.2. Whereas sulphate concentration is quite variable, ranging between 1.8 and 6.4 ppm, $\delta^{34}S$ of the surface water sulphate is reasonably constant with all samples within one per mil of each other (mean = 4.3 ‰, s.d. = 0.40). On a molar basis S^{2-} is more important than sulphate in many of the samples (mean = 1.6 ppm, s.d. = 0.07).

Table 6.2. Surface water sulphur chemistry at Thorne Moors (prior to tracer addition).

Enclosure	S-SO_4 (ppm)	S-SO_4 µM	δ^{34}S-SO_4	S-H_2S (ppm)	S-H_2S (µM)
1A	2.1	66.2	3.9	1.4	43.7
1B	1.8	56.3	4.8	1.8	56.1
1C	0.6	20.2	4.8	1.4	43.7
2A	0.6	18.4	4.3	1.8	56.1
2B	0.9	27.8	3.9	1.5	46.8
2C	1.0	31.9	4.4	1.6	49.9

Sulphate was normalised against Cl concentration and pore water profiles are presented in Figure 6.2 (This data is presented with absolute Cl concentrations in appendix C). Both enclosures show a significant decline in SO_4/Cl from surface waters to pore waters. H_2S concentrations are relatively low until ~70 cm after which there is a large peak with concentrations reaching over 800 µM (Fig. 6.3).

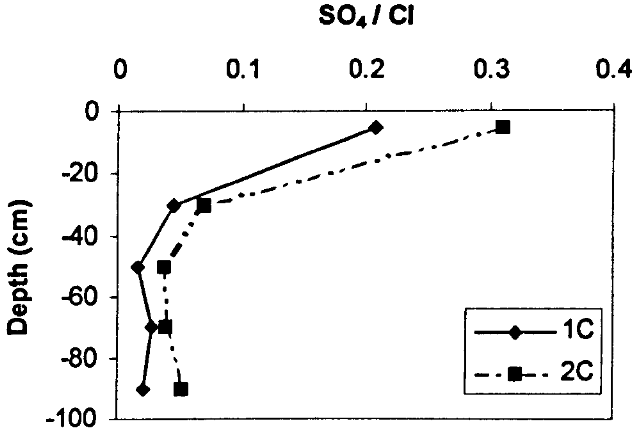

Fig. 6.2 SO_4/Cl versus depth in control surface and pore waters at Thorne Moors sampled prior to tracer addition.

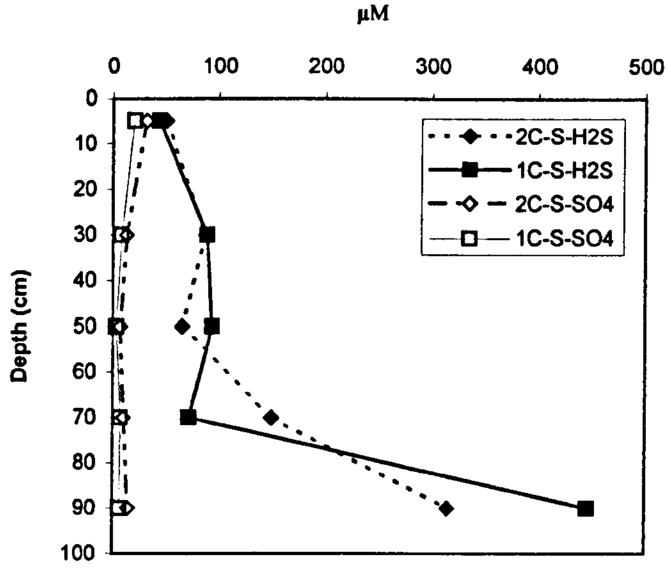

Fig. 6.3 S-SO_4 and S-H_2S concentration with depth in control surface and pore waters at Thorne Moors sampled prior to tracer addition

Isotopic analyses were complicated by the small quantities of sulphate and sulphide present in the samples. As such, only a limited number of analyses could be successfully completed (Fig. 6.4). However, an almost complete profile is present for one of the enclosures (2C). Sulfidic-S $\delta^{34}S$ ranges from –5 to +10 ‰ when looking at both enclosures together. While there is only pore water sulphate data for enclosure 2C there is an obvious marked enrichment in ^{34}S with depth with a maximum $\delta^{34}S$ of 65.1 ‰ at the bottom of the profile.

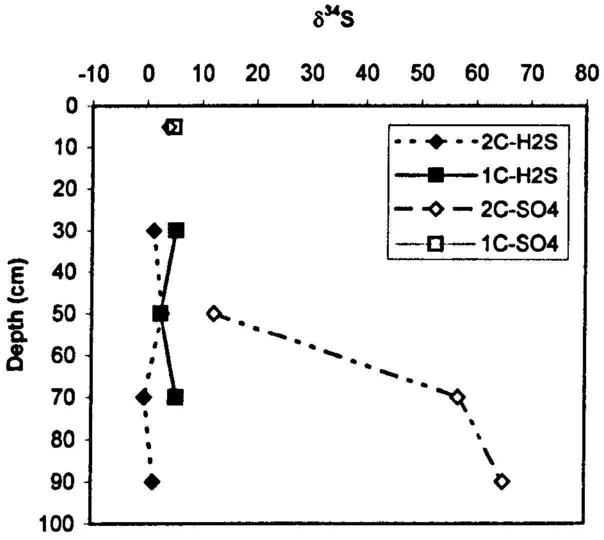

Fig. 6.4 Sulphur isotopic compositions versus depth in control surface and porewaters at Thorne Moors sampled prior to tracer addition

Surface water and porewater samples were also collected at different times during 2000 to investigate seasonal variation in sulphur chemistry (data from Berry, 2001). SO_4/Cl profiles show a consistent trend during the year declining with depth (Fig. 6.5). Surface water sulphate was 7.0 ppm in March and 5.9 in May, before declining to 1.3 and 1.1 ppm for June and July respectively. Concentrations then increased to 5.1 in August and 6.7 in October, before again declining in November to 1.8 ppm (Fig. 6.6). H_2S concentrations increased in the porewaters with depth, although this was more pronounced in July, October and November (Fig. 6.6).

Sulphate concentrations were always low, and as such, only a very limited number of isotopic analyses were possible. Only two surface water isotopic compositions were obtained (8.7 ‰ in January and 3.8 ‰ in October). H_2S was also low in the surface waters. The isotopic variation of H_2S in the porewaters had a relatively narrow range, from ~2 to 9 ‰ (Fig. 6.7).

6.3.1.3. Vegetation

The sulphur content of *Sphagnum* ranged from 0.05 and 0.15 weight % sulphur (mean 0.1029 %) while *Eriophorum* ranged from 0.1 to 0.3 % (mean 0.223 %) (Fig. 6.8). There was a highly significant difference between the sulphur content of *Eriophorum* and *Sphagnum* ($T= 7.32$, $p< 0.0001$, d.f. = 17).

$\delta^{34}S$ of sulphur in *Sphagnum* ranged from 1.4 to 2.5 ‰ (mean 1.903 ‰) and -1.8 to 0.1 ‰ (mean -0.868 ‰) (Fig. 6.9) for *Eriophorum*. A highly significant difference was found between the isotopic composition of *Eriophorum* and *Sphagnum* ($T = 16.79$, $p< 0.0001$, d.f.= 21).

There was no correlation between sulphur content and isotopic sulphur signature in either *Sphagnum* or *Eriophorum* (Figs. 6.10; 6.11).

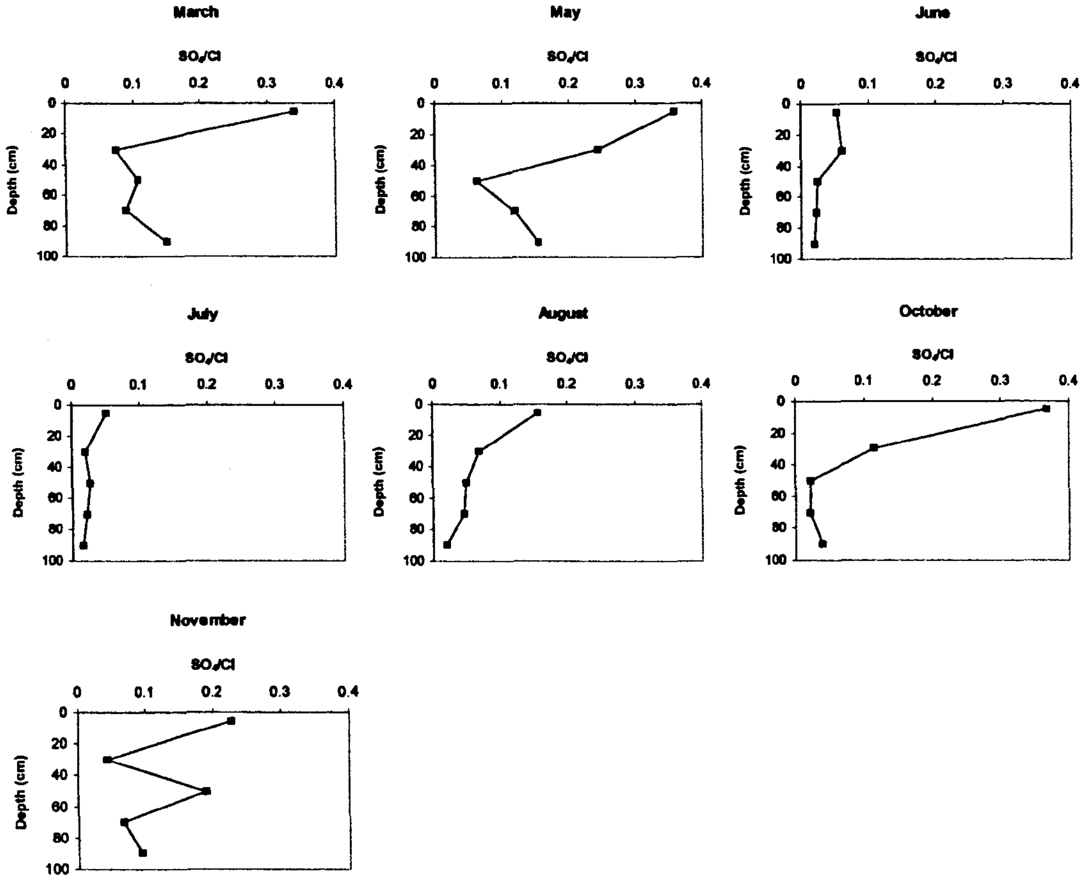

Fig 6.5. SO_4/Cl versus depth in surface and porewaters at Thorne Moors during 2000 (data replotted from Berry, 2001)

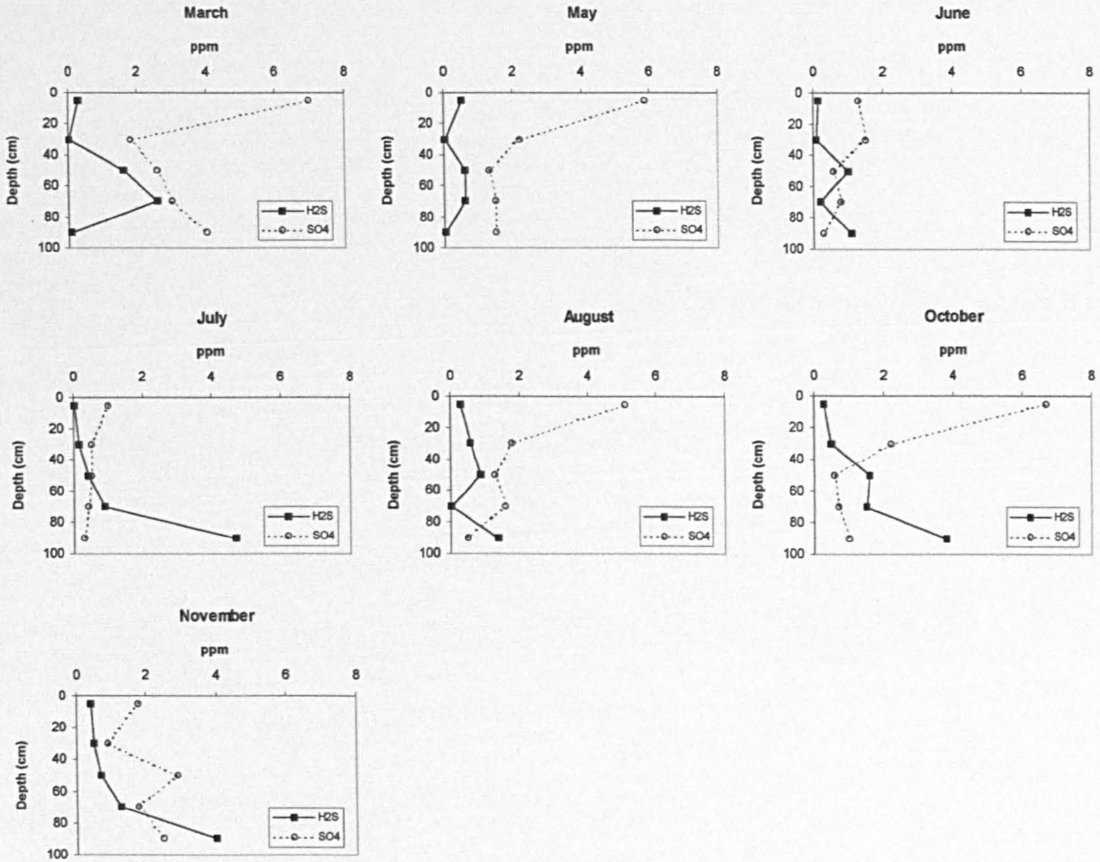

Fig. 6.6. SO_4 and H_2S versus depth in surface and porewaters at Thorne Moors during 2000 (data replotted from Berry, 2001).

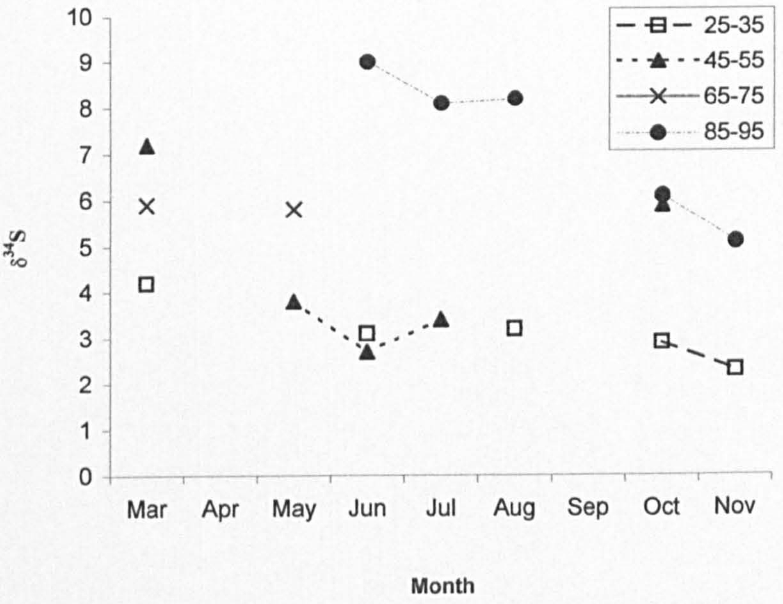

Fig 6.7. Porewater $\delta^{34}S$-H_2S at Thorne Moors during 2000 (replotted from Berry, 2001)

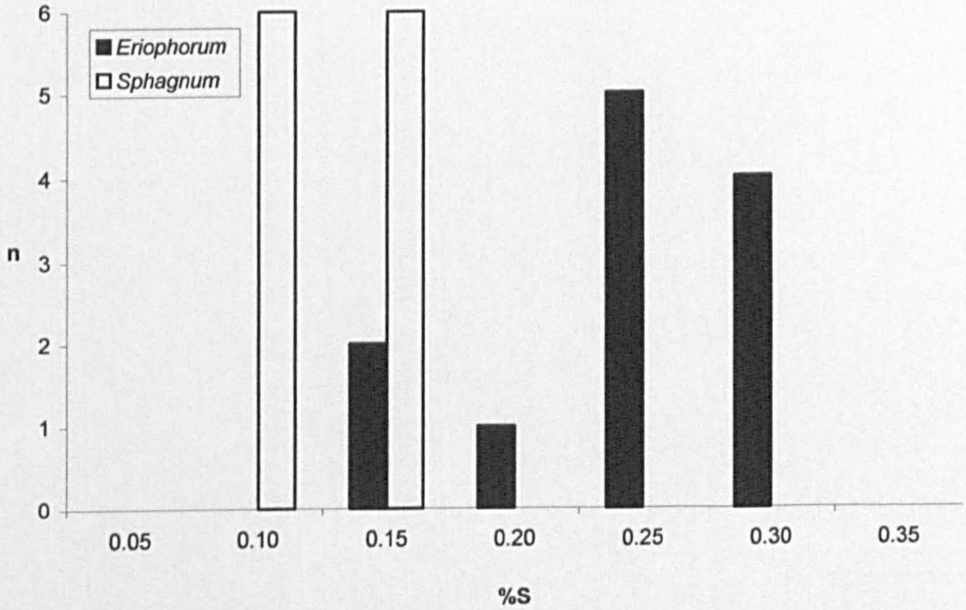

Fig 6.8 Sulphur content of control *Eriophorum* and *Sphagnum* at Thorne Moors sampled prior to tracer addition

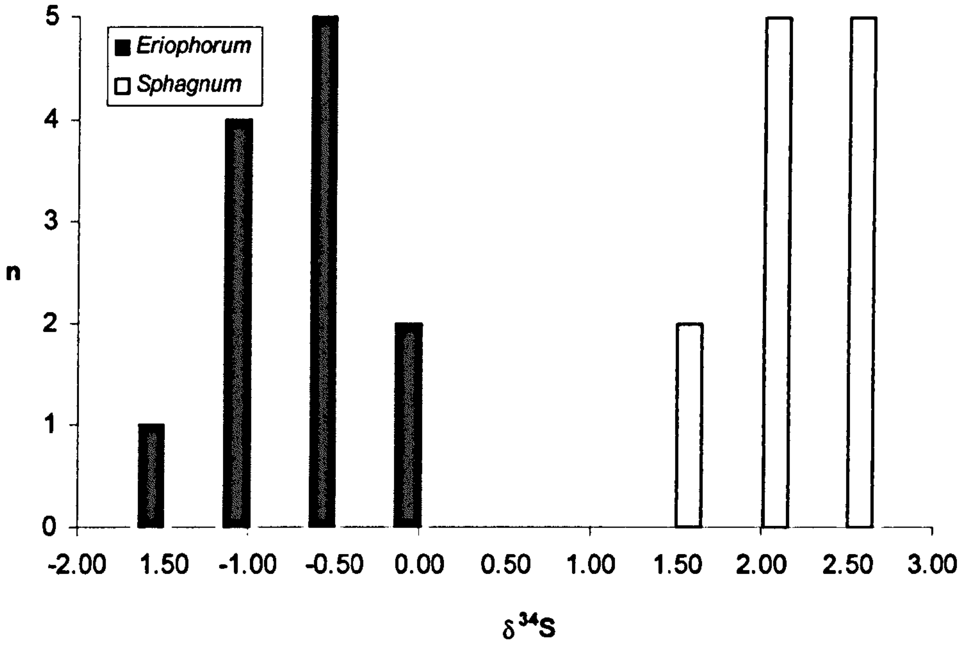

Fig 6.9. $\delta^{34}S$ **of control** ***Eriophorum*** **and** ***Sphagnum*** **at Thorne Moors sampled prior to tracer addition**

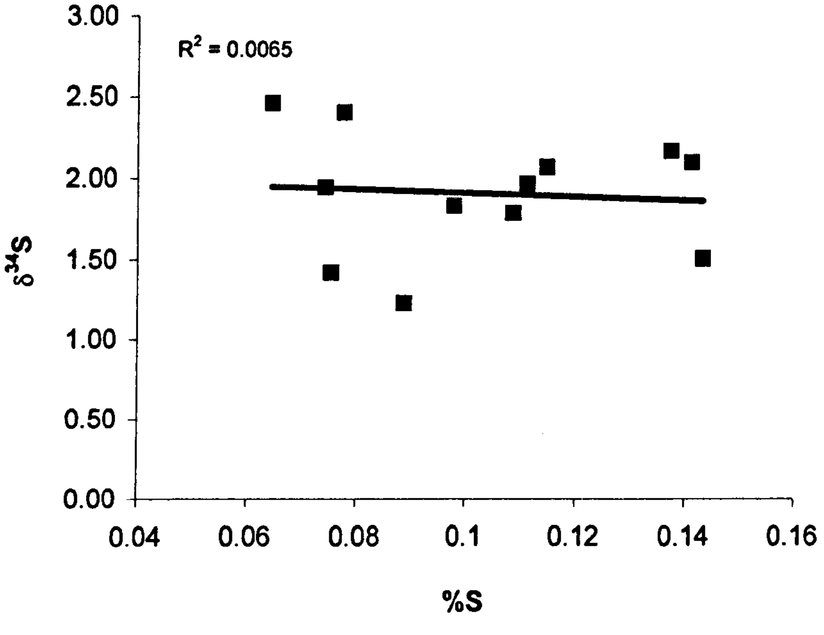

Fig. 6.10. $\delta^{34}S$ **versus sulphur content in control** ***Sphagnum*** **at Thorne Moors sampled prior to tracer addition**

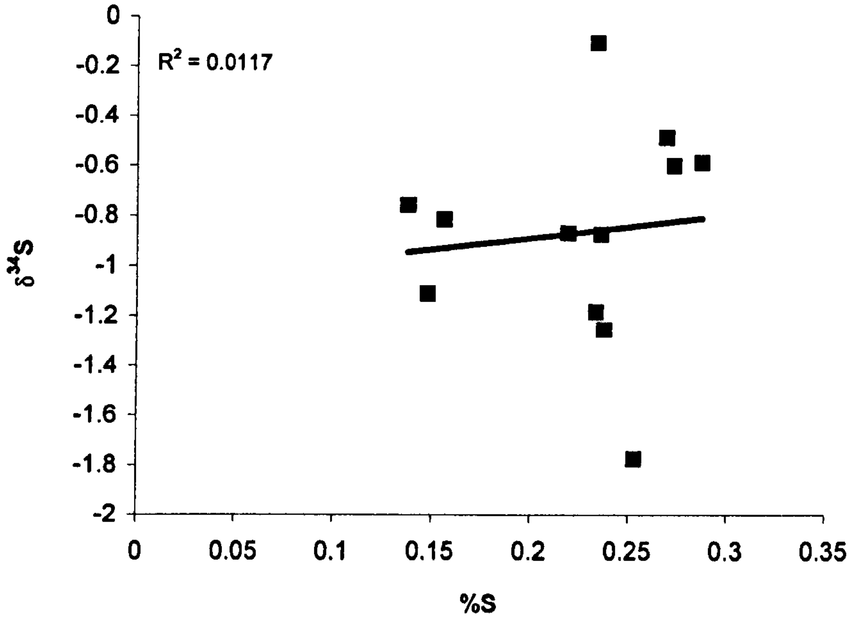

Fig. 6.11. $\delta^{34}S$ versus sulphur content in control *Eriophorum* at Thorne Moors sampled prior to tracer addition

6.3.1.4. Peat

All three of the control cores showed significant variation in inorganic sulphur content with depth (Fig. 6.12), ranging between 700 and 6000 mg/kg in core TCA, 200 and 2500 mg/kg in core TCB, and 1700 and 14000 mg/kg in core TCC. In each core there is a broad peak in concentration in the subsurface, though this occurs at different depths in each core.

Though scattered and variable, similar patterns of organic sulphur content with depth are present in all of the control cores, with sulphur contents lying between 4000 and 15000 mg/kg dry weight peat (Fig. 6.13).

Inorganic $\delta^{34}S$ is highly variable between the three cores (Fig. 6.14). All of the cores exhibit markedly different ranges in $\delta^{34}S$ yet in the TCA and TCC cores, a similar trend, whereby $\delta^{34}S$ decreases with depth is apparent. Core TCB, however, shows a weaker trend in the opposite sense. $\delta^{34}S$ of the organic fractions is also similar in TCA and TCC cores although the absolute values differ by around 1 and 2 ‰ (Fig. 6.15). Core TCB is more variable, with zones of isotopically light organically bound sulphur from 3 to 8 cm and 15 to 25 cm, while the other parts of this core have elevated $\delta^{34}S$ relative to the other cores. Sulphur content was not found to be correlated with $\delta^{34}S$ for either the organic or inorganic fractions in any of the control cores (Fig. 6.16).

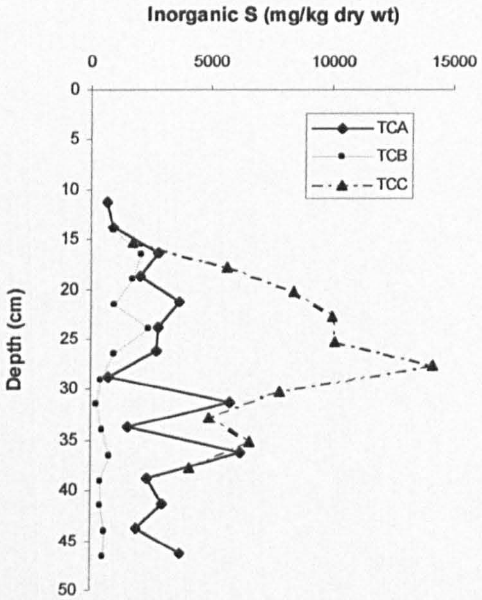

Fig. 6.12. Inorganic S content versus depth in control peat from Thorne Moors

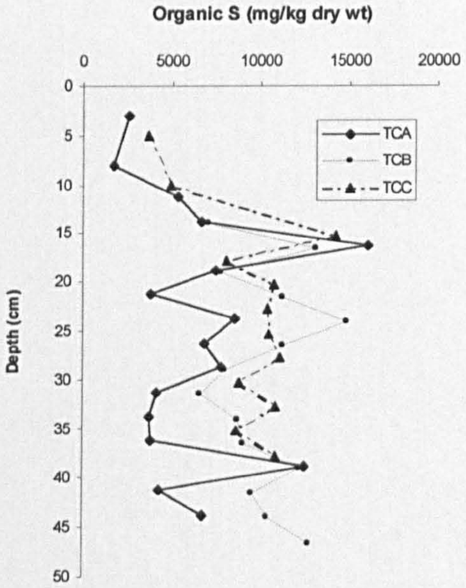

Fig. 6.13. Organic S content versus depth in control peat from Thorne Moors

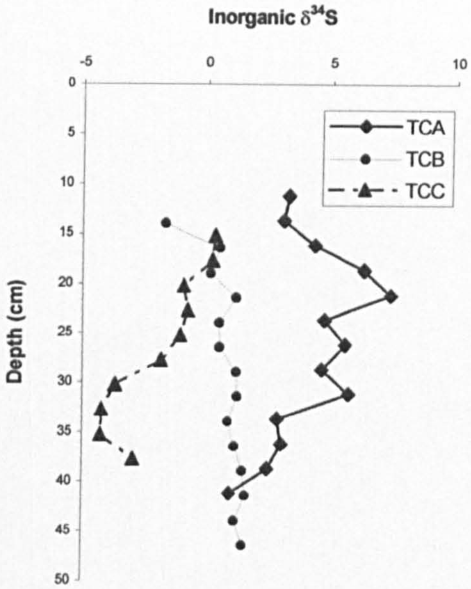

Fig. 6.14. Inorganic δ^{34}S versus depth in control peat from Thorne Moors

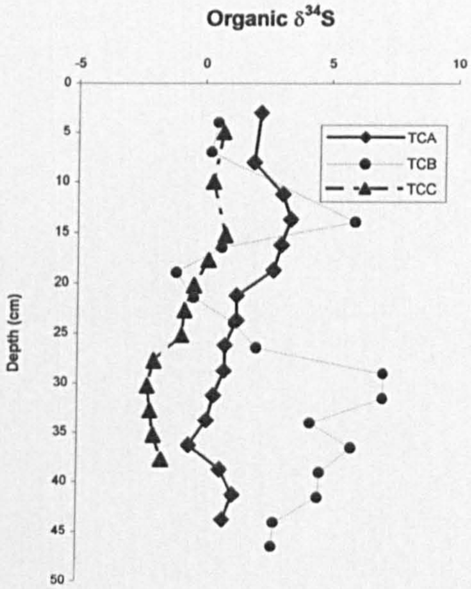

Fig. 6.15. Organic δ^{34}S versus depth in control peat from Thorne Moors

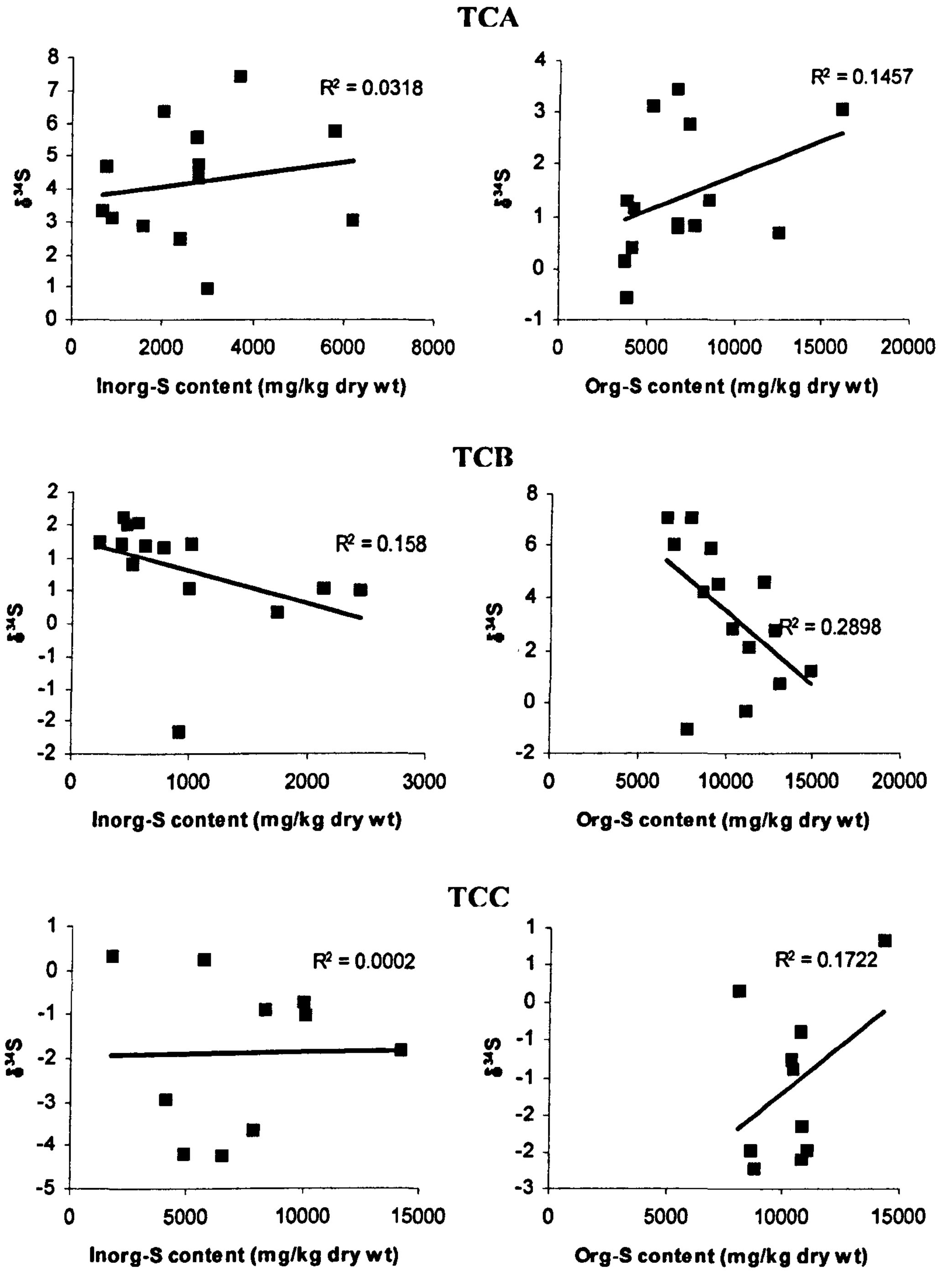

Fig. 6.16. Sulphur content versus isotopic composition in control peats from Thorne Moors

6.3.2. Tracer investigation

6.3.2.1. Surface and porewaters

S-SO_4/S-H_2S and SO4/Cl show a consistent decline from the surface waters to the deeper portions of the peat throughout the investigation except at 30 weeks where an increase is observed at the 25-35 cm depth interval (Fig. 6.17).

Br concentrations were below detection limits (<0.1 ppm) before 24 weeks, apart from in surface water samples at 6 and 18 weeks (Fig. 6.17). After 24 weeks Br had increased yet the high ratio of SO_4 to Br in waters in each of the sampling visits demonstrates the low Br concentrations throughout the study. When data was available there was a decline in SO_4/Br from the surface waters to the middle portions of the peat. However, unlike SO_4/Cl, we see in some cases (30, 36 and 42 weeks), an increase in SO_4/Br in the deepest waters sampled.

The ratios of Fe/Cl show a reasonably consistent pattern with depth in both of the enclosures throughout the study with a trend of increasing Fe/Cl from the surface waters to the porewaters of the middle portions of the peat and then a decline to the 85-95 cm depth interval (Fig. 6.17). However, this pattern is much less marked in enclosure 2C.

Elevated compositions after tracer addition were pronounced yet no consistent trends in δ^{34}S-SO_4 versus depth during the 48-week study can be identified (Fig. 6.17). At 6 weeks there is a general decline in δ^{34}S from the surface waters to the porewaters. Yet in enclosure 1C there is a significant increase with a δ^{34}S of 133 ‰ at the 85-95 cm depth interval. At 12 and 18 weeks there is a decrease in δ^{34}S-SO_4 from the surface waters with increasing depth. While at 24 weeks, δ^{34}S increases from the surface waters to 25-35 cm before declining at 65-75 cm and then increasing again in the lower peat.

At 30 weeks surface water sulphate in enclosure 1C has an extremely elevated δ^{34}S (552 ‰). The isotopic pattern observed at 12 and 18 weeks is repeated with a decline in δ^{34}S-SO_4 from the surface waters to the deeper porewaters. While samples collected at 36 weeks showed a typically inverse pattern with δ^{34}S-SO_4 increasing from the surface

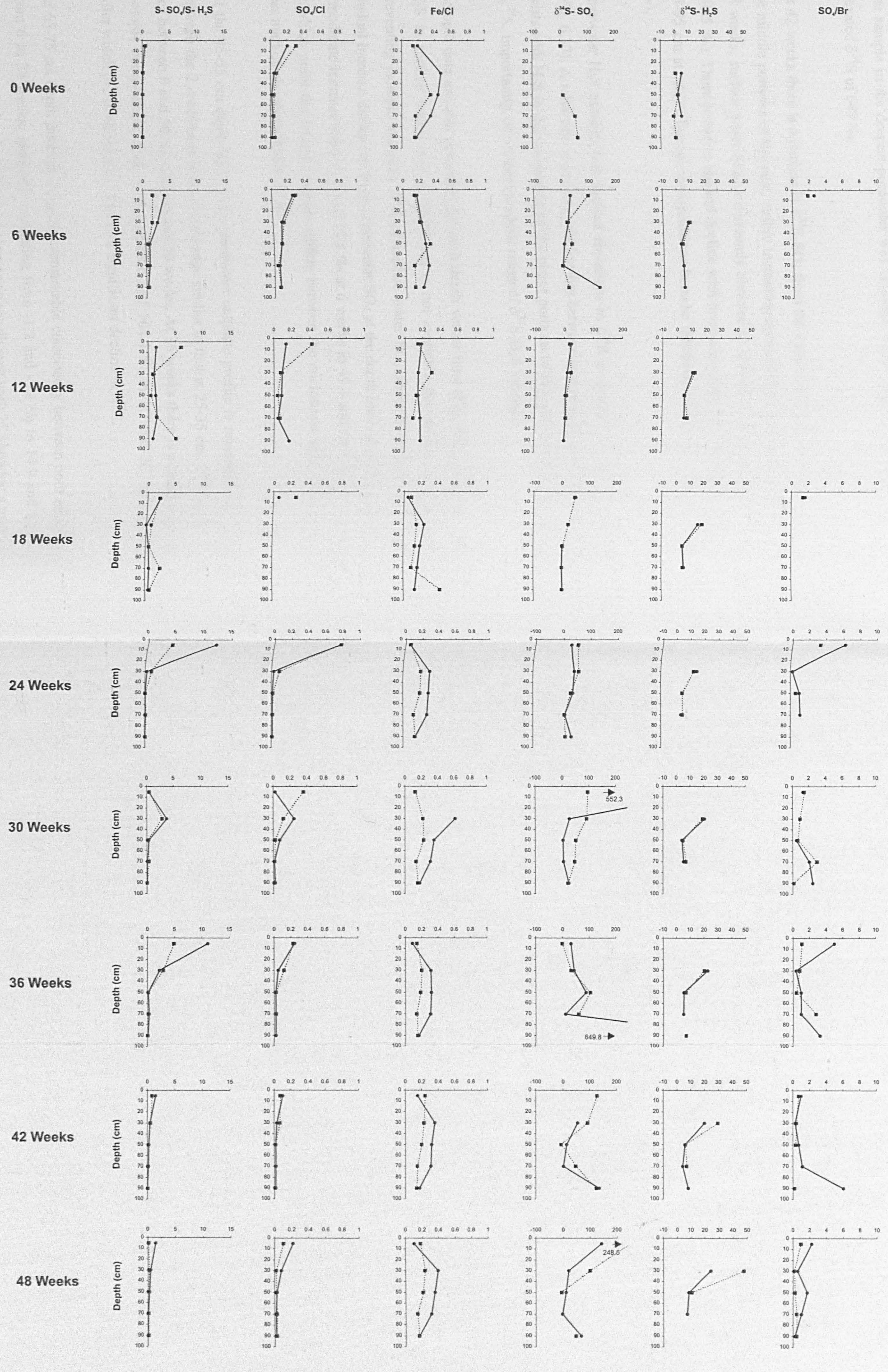

Fig 6.17.. Surface and pore water chemistry during 48 week tracer investigation at Thorne Moors (close circles = enclosure 1C, closed squares = enclosure 2C).

waters to 45-55 cm. There is then a small decrease to the 65-75 cm depth interval. Only one sample in the deepest porewater was obtained. This sample showed an extremely elevated $\delta^{34}S$ of 649 ‰.

At 42 weeks there is a decline in $\delta^{34}S$-SO_4 from the surface waters to the porewaters of the middle portions of the peat, before increasing again at the bottom of the profile. At 48 weeks, surface water SO_4 is extremely elevated in isotopic composition (143.3 and 248.5 ‰). There is then a marked decline with increasing depth until the depth interval 85-95 cm at which isotopic compositions become markedly elevated (125.2 and 134.3 ‰).

Porewater H_2S exhibits less marked elevations in $\delta^{34}S$ as compared to porewater SO_4 (Fig. 6.17). A relatively consistent relationship between isotopic composition and depth exists with H_2S in the porewaters of the upper portions of the peat being more enriched in ^{34}S. Importantly, over time the upper range of $\delta^{34}S$-H_2S increases.

Isotopic data are also presented for each depth versus time (Fig. 6.18). Data for $\delta^{34}S$-H_2S in surface waters and at 85-95 cm is not available due to low concentrations preventing isotopic analysis. $\delta^{34}S$ of surface water SO_4 showed, for the most part a gradual increase during the study. Porewater SO_4 at the depth interval 25-35 cm showed a moderate increase from 21.4 and 17.4 ‰ at 6 weeks to 49.4 and 65.9 ‰ at 24 weeks, at which point the isotopic pattern differs between the enclosures with 1C showing a less marked elevation to that of 2C.

At the 45-55 cm depth interval the porewater sulphate profile is reasonably consistent between the 2 enclosures with a total range similar to that at 25-35 cm. $\delta^{34}S$ of the SO_4 lies between 0 and 50 ‰ until around 30 weeks. At 36 weeks there is a marked peak in isotopic composition, with values of 88.0 and 104.4 ‰ in 1C and 2C, respectively. After which (42 to 48 weeks), there is a significant decline in $\delta^{34}S$.

At 65-75 cm depth interval, there is a remarkable consistency between both enclosures from 6 to 24 weeks, gradually increasing from -1.2 and -3.4 ‰ to 14.9 and 13.0 ‰. However, after 24 weeks the isotopic compositions diverge with 2C showing a marked

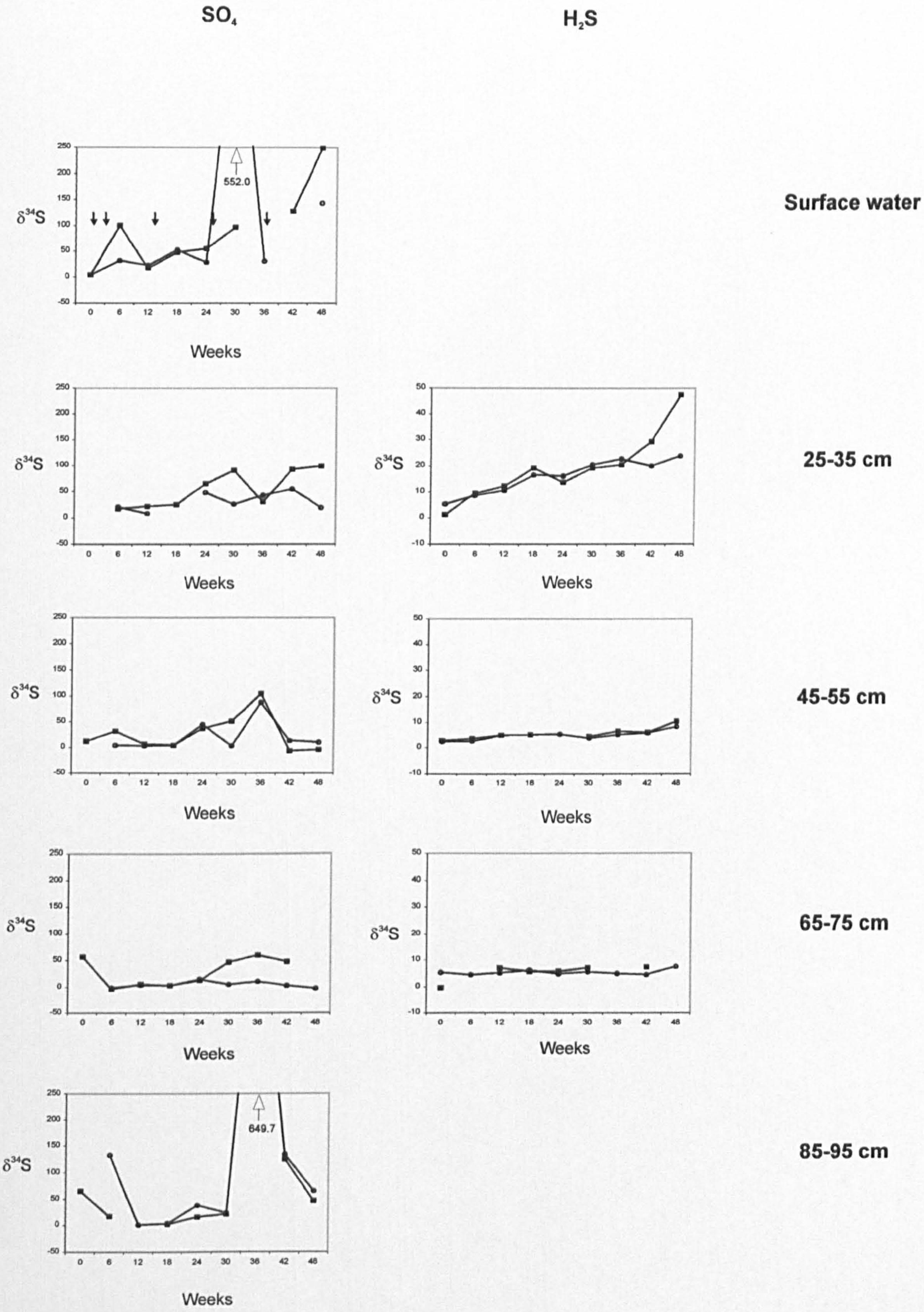

Fig. 6.18. Isotopic composition of SO_4 and H_2S in surface waters and porewaters during 48 week tracer investigation at Thorne Moors (open circles = enclosure 1C, closed squares = enclosure 2C, solid arrows indicate tracer addition events).

increase until 36 weeks (59.9 ‰) followed by a small decline. In enclosure 1C, $\delta^{34}S$-SO_4 decreases to –2.6 ‰ at 48 weeks. At 85-95 cm 1C and 2C both show a reasonable degree of consistency with time with values lying within a range typical of the other porewater depths. There is a tendency for isotopic compositions to increase over time.

Porewater H_2S, as outlined previously, exhibits a narrower, and what can be considered, a more 'natural' range, than that of porewater SO_4 (Fig. 6.18). H_2S ranged between 0-50 ‰ at 25-35 cm, 2-12 ‰ at 45-55 cm and 4-8 ‰ at 65-75 cm. At both 25-35 and 45-55 cm $\delta^{34}S$-H_2S increased significantly over time. Whereas at 65-75 cm, there was little alteration in the isotopic composition of the porewater H_2S during the course of the study.

There is a strong correlation between tracer addition events and elevation in surface water $\delta^{34}S$ (Fig. 6.19).

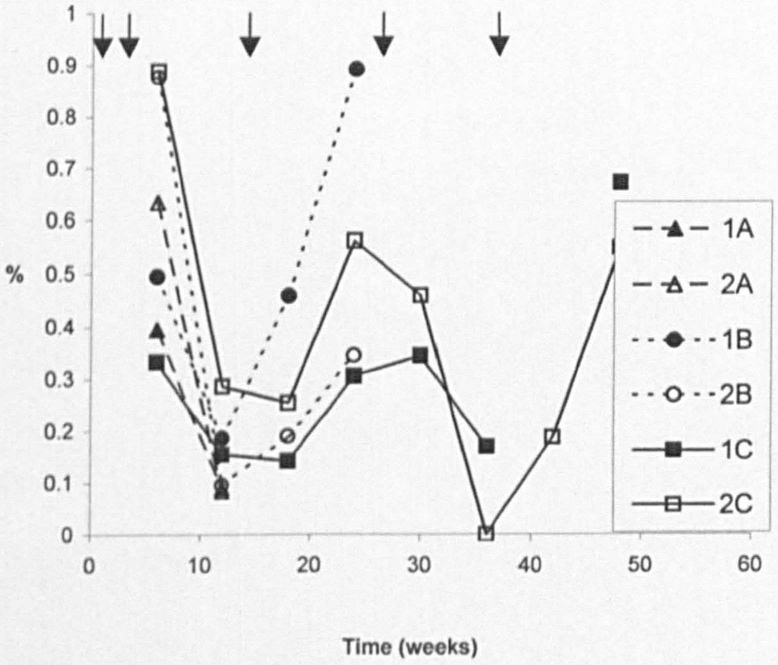

Fig. 6.19. % of tracer residing in surface waters during 48 week investigation at Thorne Moors (arrows represent tracer addition event).

The % of tracer residing in the surface waters ranged from 0.33 to 0.88 between the enclosures recorded at the first sampling trip (6 weeks), declining to 0.83 to 0.28 % at 12 weeks. After the 3rd tracer addition (12 weeks + 1 day) there is marked enrichment (0.14 to 0.45 %) in surface water $\delta^{34}S\text{-}SO_4$. At 18 weeks there is a progressive increase in $\delta^{34}S$ from 18 weeks to 24 weeks even though there is no tracer addition event between these sampling times. After tracer addition at 24 weeks + 1 day there is only a slight increase in $\delta^{34}S\text{-}SO_4$ in enclosure 1C at 30 weeks (0.30 to 0.34 %), while there is a decrease in enclosure 2C (0.55 to 0.45 %). After the last tracer event (36 weeks + 1 day) there is another sustained increase observed at 42 weeks (0.18 % n.b. only one data point available), increasing further at 48 weeks (0.54 to 0.67 %).

6.3.2.2. *Vegetation*

Mean $\delta^{34}S$ of vegetation in the enriched enclosures exhibited marked differences with time, progressively increasing from 3 to 12 months (Table 6.3). Enrichment in *Sphagnum* relative to *Eriophorum* was the most pronounced in the 3 and 12-month enclosures. Importantly, the standard deviations are, in every case, greater for *Sphagnum* samples than that recorded for *Eriophorum*.

Table 6.3 $\delta^{34}S$ of vegetation harvested from ^{34}S-enriched enclosures at Thorne Moors.

Enclosure	*Sphagnum*			*Eriophorum*		
	n	$\delta^{34}S$ mean	St dev	n	$\delta^{34}S$ mean	St dev
1A	8	68.00	28.6	12	27.61	11.24
2A	12	79.83	18.99	12	56.57	16.11
1B	12	79.87	29.46	12	83.91	20.5
2B	9	93.28	27.61	12	66.05	9.65
1C	12	151.3	55.9	12	143.45	22.15
2C	12	232.2	59.5	11	84.87	16.11

6.3.2.3. Peat

6.3.2.3.1 Organic and inorganic sulphur content

Cores sampled from the 3-month enclosures show a gradual trend of increasing organic sulphur content with depth although this is less marked in enclosure 1A than in 2A (Fig. 6.20). Inorganic sulphur content was considerably more variable, with pronounced peaks at a number of depths (Fig. 6.20).

Organic sulphur content in the cores from enclosure 1b (6-months) shows a high level of consistency between the 2 cores with an increase with depth (Fig. 6.21). At the very deepest peat sampled there is a slight decrease in sulphur content. However, in enclosure 2b organic sulphur content is extremely variable in 2b1 with extreme alterations with almost each depth interval. While core 2b2 shows a very broad peak in sulphur content with high sulphur contents in the surface necromass layers.

Inorganic sulphur content was consistent between the cores in both 6-month enclosures. Inorganic sulphur content was greater in enclosure 2b (Fig. 6.21). Whereas there was a weak trend towards increasing inorganic sulphur with depth in 1b, there was much greater variability in enclosure 2b.

Organic sulphur content in enclosure 1C (12 months) shows a strong increase from the surface layers until ~ 25cm at which organic sulphur content declines towards the deepest peat sampled (Fig. 6.22). A similar pattern can be observed in enclosure 2C, although the decrease in sulphur content occurs higher up the profile between 15 and 20 cm.

Inorganic sulphur content sampled from enclosure 1C is markedly different between the two cores sampled (Fig. 6.22). Inorganic sulphur content in core 1C-2 exhibits a small, yet steady increase with depth, while in core 1C-1 there is pronounced peaks at around 15 and 27 cm before declining towards the deepest peat sampled. Inorganic sulphur in enclosure 2C is much more constant. In the upper necromass layers sulphur increases steadily until between 20 and 25 cm before declining again in the deep peat to values similar to that seen in the surface layers.

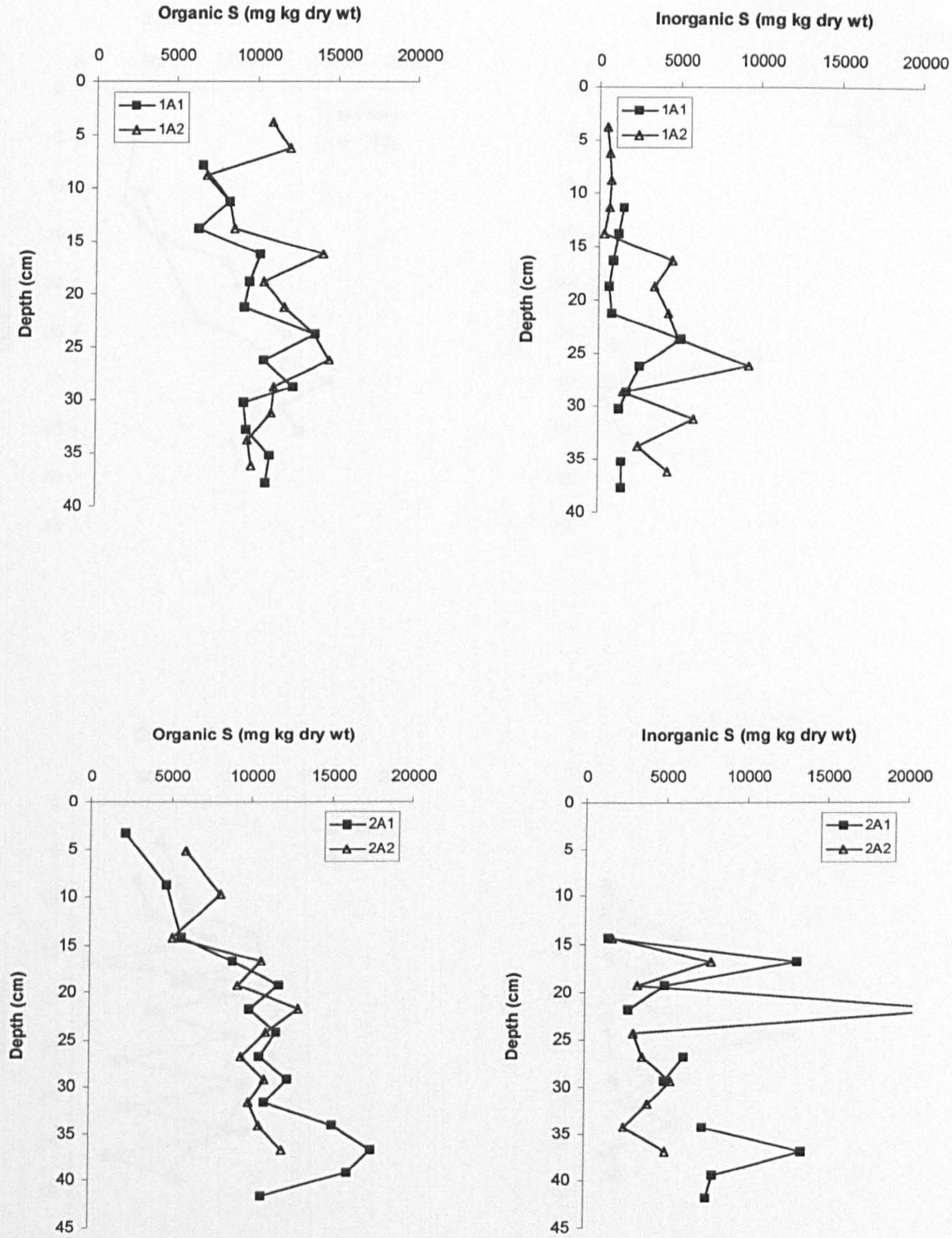

Fig. 6.20. Inorganic and organic sulphur content in peat cores sampled 3 months after tracer addition at Thorne Moors.

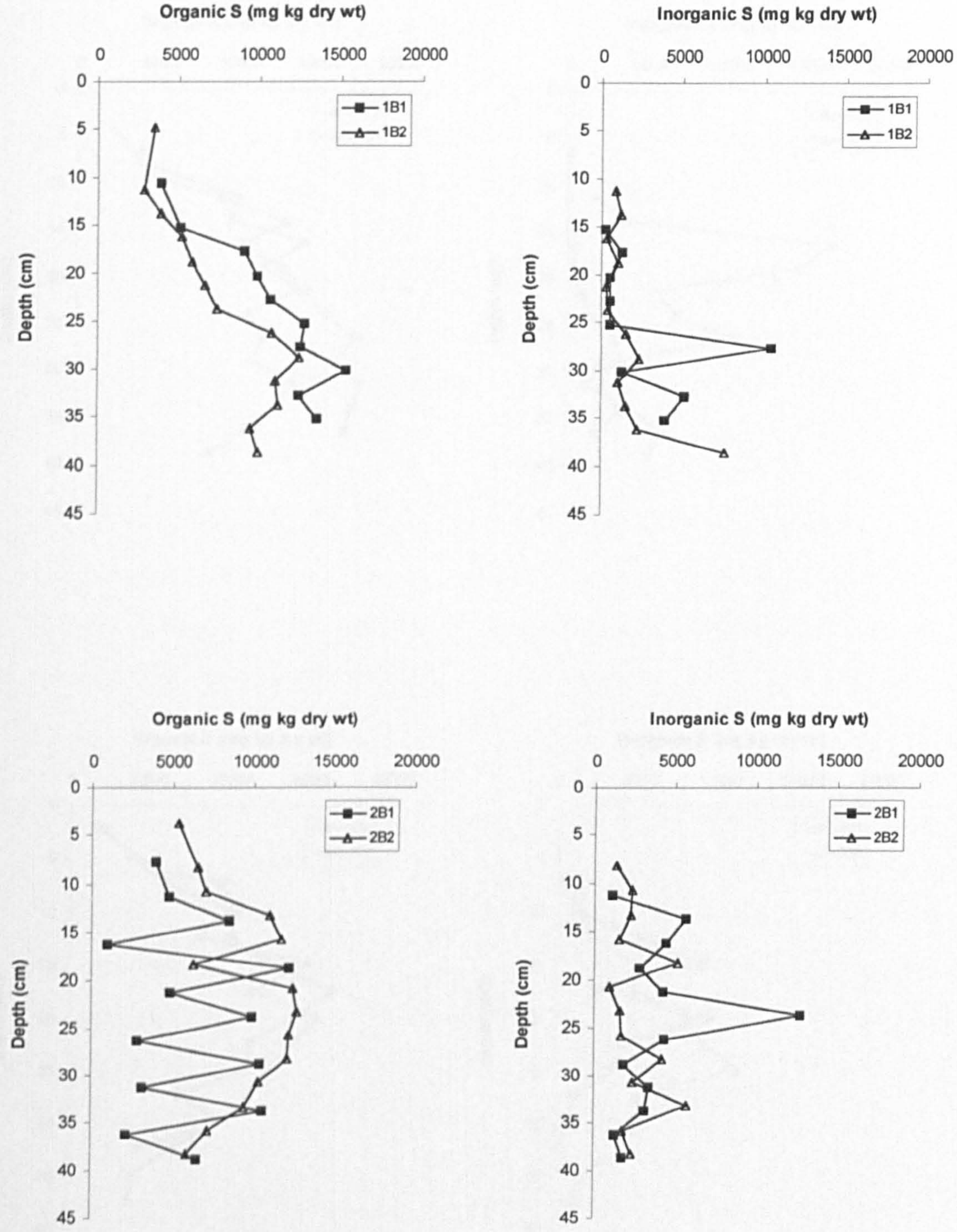

Fig. 6.21. Inorganic and organic sulphur content in peat cores sampled 12 months after tracer addition at Thorne Moors.

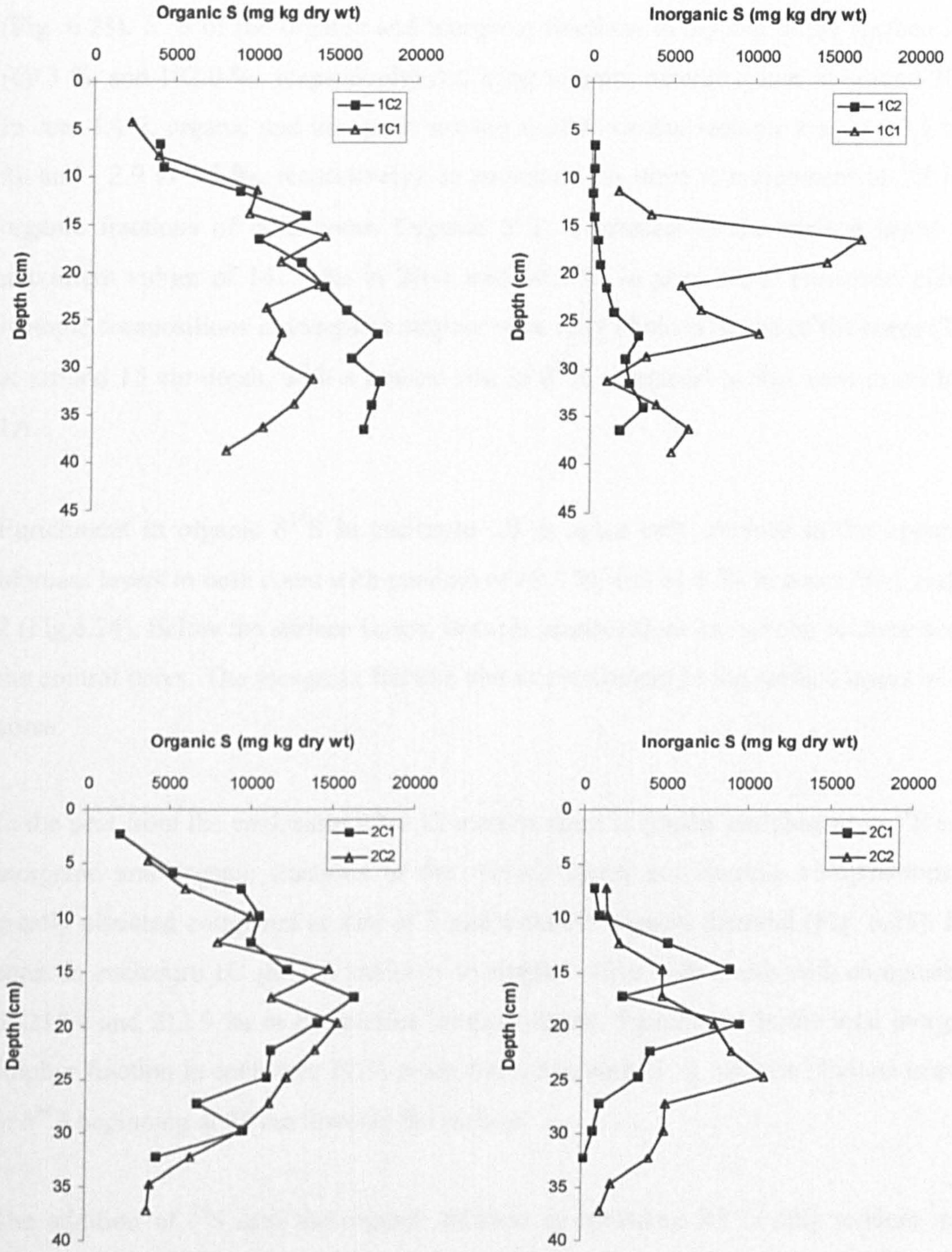

Fig. 6.22. Inorganic and organic sulphur content in peat cores sampled 12 months after tracer addition at Thorne Moors.

6.3.2.3.2. Isotopic compositions

In enclosure 1A incorporation of tracer ^{34}S is obvious in only one of the cores (1A-1) (Fig. 6.23). $\delta^{34}S$ of the organic and inorganic fractions is highest in the surface layers (69.3 ‰ and 102.0 ‰, respectively) declining to more natural values at around 20 cm. In core 1A-2, organic and inorganic sulphur exhibit similar isotopic ranges (-3.4 to 8.0 ‰ and - 2.9 to 7.5 ‰, respectively). In enclosure 2A there is enrichment in ^{34}S in the organic fractions of both cores. Organic $\delta^{34}S$ is greatest in the surface layers with maximum values of 142.0 ‰ in 2A-1 and 69.5 ‰ in core 2A-2. However, elevated isotopic compositions in inorganic sulphur were only obvious in one of the cores (2A-2) at around 15 cm depth, with a modest rise in $\delta^{34}S$ compared to that seen in enclosure 1A.

Enrichment in organic $\delta^{34}S$ in enclosure 2B is again only obvious in the uppermost biomass layers in both cores with maxima of 69.7 ‰ and 61.6 ‰ in cores 2B-1 and 2B-2 (Fig.6.24). Below the surface layers, isotopic compositions are similar to those seen in the control cores. The inorganic fraction shows enrichment in the surface layers of both cores.

In the peat from the enclosures after 12 months there is similar enrichment in ^{34}S in the inorganic and organic fractions in the surface layers but isotopic compositions are greatly elevated compared to that of 3 and 6-month organic material (Fig. 6.25). Both cores in enclosure 1C show a tendency to similar values with depth with compositions of 212.4 and 213.9 ‰ in the surface biomass layers. Enrichment in the total inorganic sulphur fraction in enclosure 1C is more marked in core 1C-2, with an obvious increase in $\delta^{34}S$ beginning at 20 cm towards the surface.

The addition of ^{34}S into the organic fraction in enclosure 2C is only evident much higher up the profile than that seen in all of the other cores. However, the $\delta^{34}S$ in the uppermost biomass layer of core 2C-1 is the highest recorded (430.5 ‰). Enrichment in the inorganic sulphur fraction is pronounced in both cores, beginning at around 15 cm increasing towards the surface layers.

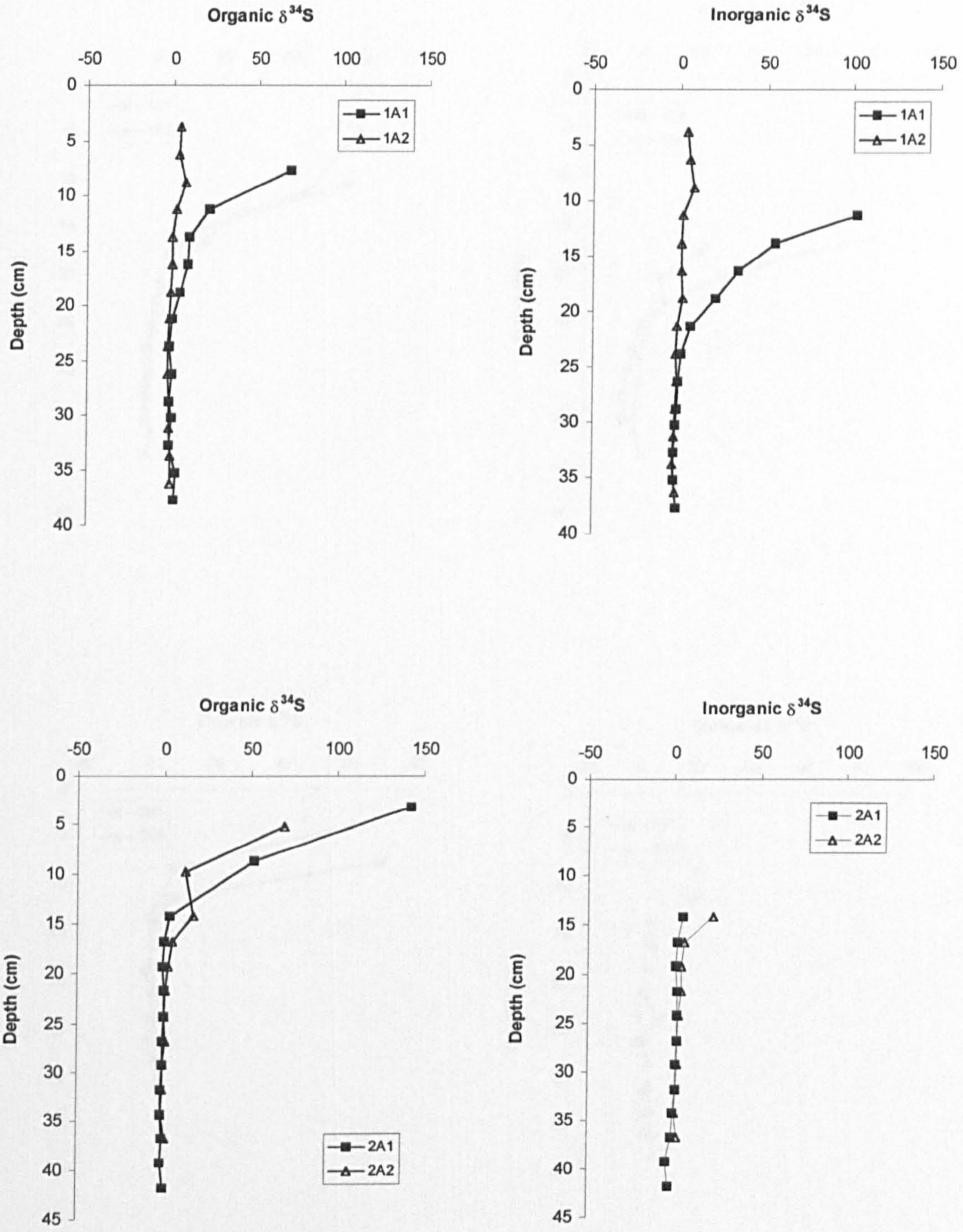

Fig. 6.23. δ^{34}S of inorganic and organic fractions in peat cores sampled 3 months after tracer addition at Thorne Moors.

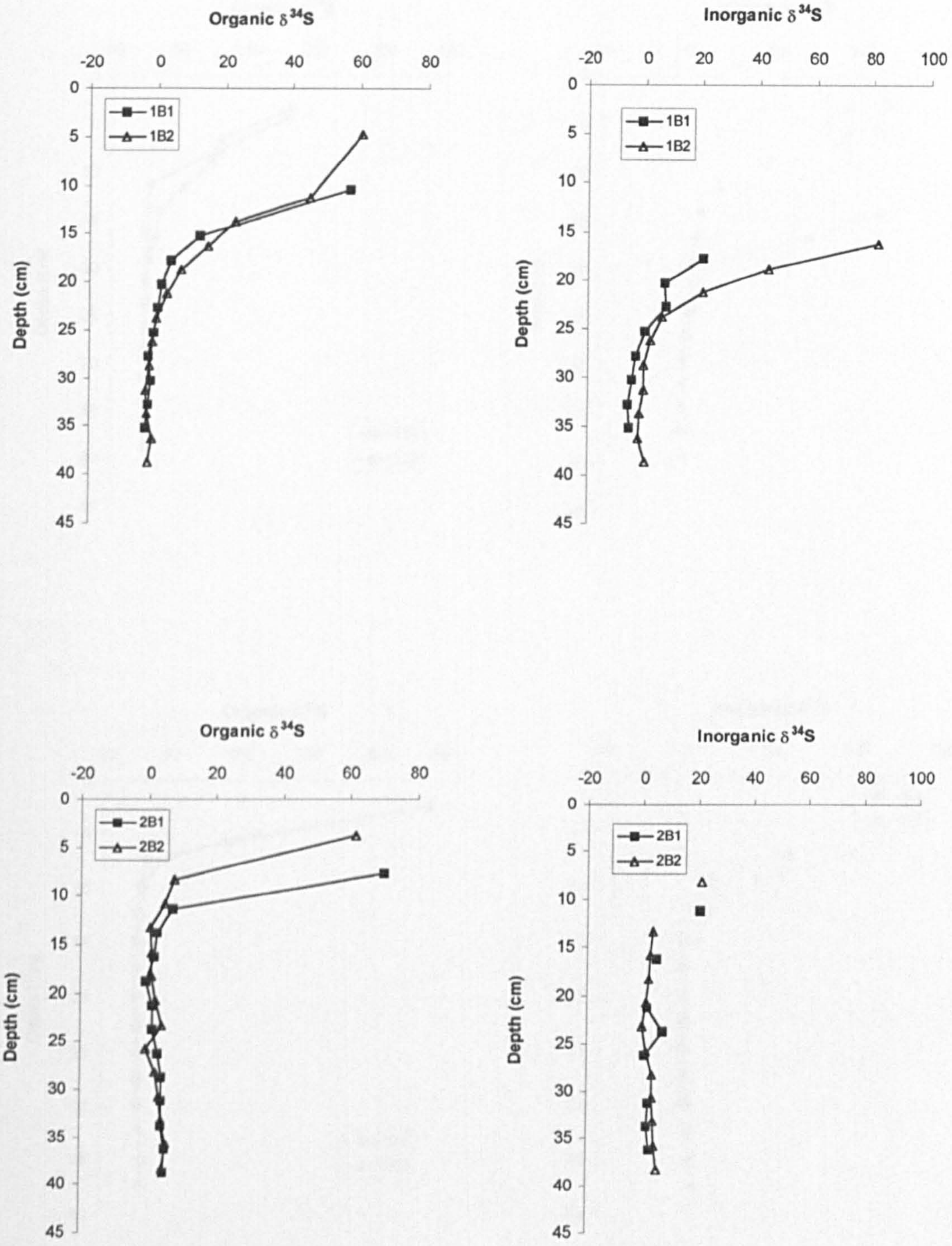

Fig. 6.24. $\delta^{34}S$ of inorganic and organic fractions in peat cores sampled 6 months after tracer addition at Thorne Moors.

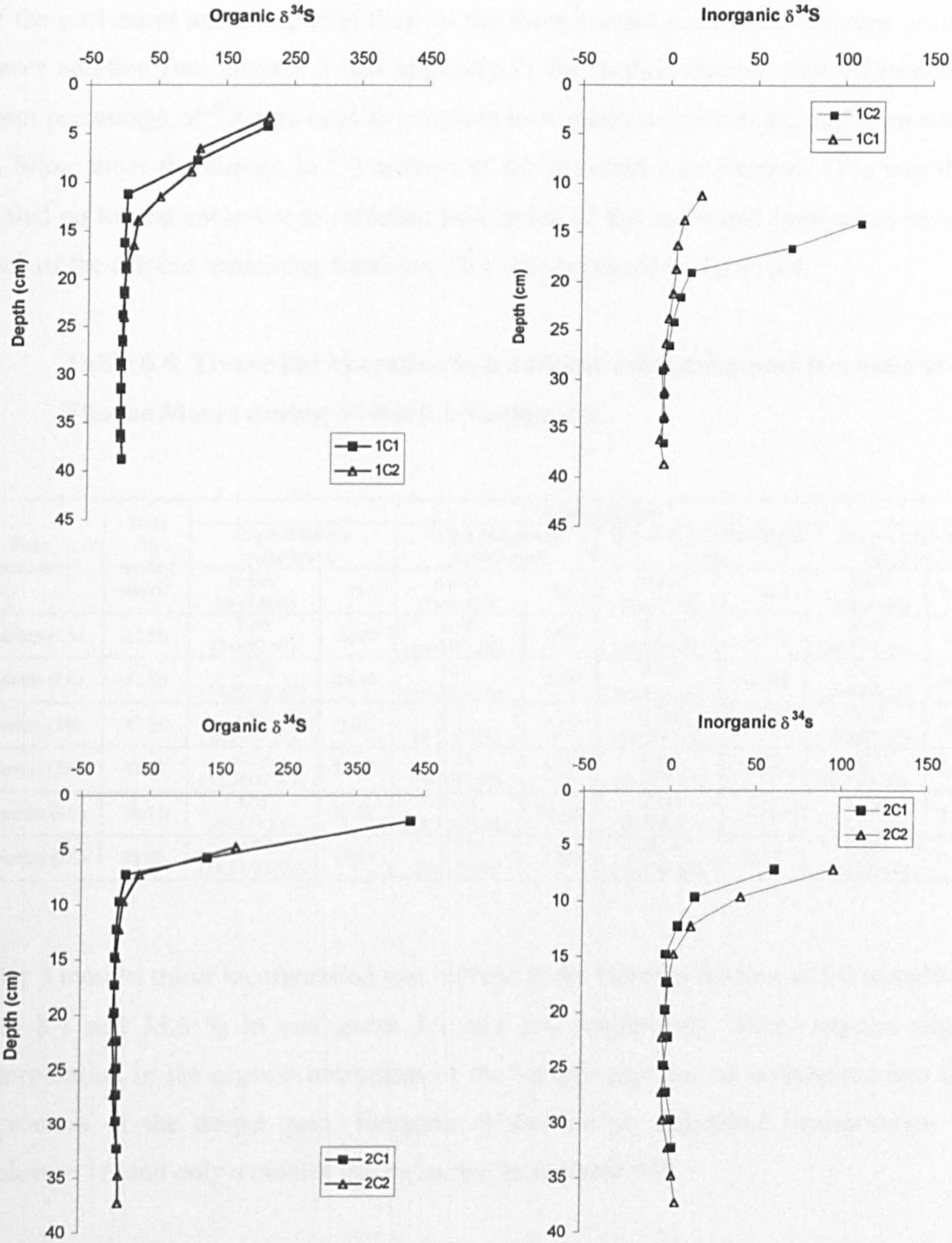

Fig. 6.25. $\delta^{34}S$ of inorganic and organic fractions in peat cores sampled 12 months after tracer addition at Thorne Moors.

The fate of the tracer (% incorporated) was calculated by examining the isotopic compositions of the organic and inorganic sulphur in the peat cores sampled from all 6 of the enclosures and comparing them to the three control peat cores collected prior to tracer addition (see chapter 2 and appendix D for further details). The difference in atom percentage of ^{34}S was used to calculate how much sulphur in mg had been added to bring about the change in ^{34}S content in the enriched core fraction. This was then scaled up for the enclosure to calculate how much of the tracer had been taken up into each of the sulphur containing fractions. This data is plotted in Table 6.4.

Table 6.4. Tracer incorporation into sulphur containing peat fractions at Thorne Moors during 48-week investigation.

Time (enclosure)	Total ^{34}S applied mg/m^2	^{34}S incorporation							
		Org-S-Biomass (vegetation)		Org-S-Necromass (surface peat)		Org-S-Necromass (deep peat)		Inorg-S (H_2S, S_0, FeS, FeS_2)	
		mg/m^2 (min/max)	%	mg/m^2 (min/max)	%	mg/m^2 (min/max)	%	mg/m^2 (min/max)	%
3 months (1A)	31.50	2.65 (2.60/2.67)	8.43	0.48 (-0.00/1.55)	1.52	-0.110 (-0.21/0.01)	-0.349	-0.06 (-0.27/0.10)	-0.19
3 months (2A)	31.50	10.58 (10.32/10.67)	33.58	0.21 (-0.58/1.96)	0.66	-0.089 (-0.21/0.06)	-0.283	0.12 (-0.08/0.26)	0.37
6 months (1B)	47.25	2.67 (2.61/2.70)	5.66	0.77 (0.59/1.16)	1.62	-0.108 (-0.19/-0.01)	-0.228	-0.02 (-0.10/0.03)	-0.05
6 months (2B)	47.25	12.74 (12.50/12.83)	26.95	0.24 (-0.26/1.35)	0.51	0.069 (-0.05/0.21)	0.146	0.22 (0.02/0.37)	0.47
12 months (1C)	78.75	9.07 (9.00/9.11)	11.52	20.14 (19.14/22.36)	25.58	-0.097 (-0.38/0.03)	-0.123	1.79 (1.12/2.28)	2.27
12 months (2C)	78.75	15.01 (14.91/15.05)	19.05	2.27 (0.63/5.92)	2.89	0.014 (-0.02/0.09)	0.017	0.10 (-0.17/0.30)	0.13

After 3 months tracer incorporation was highest in the biomass fraction of the sampled s with 8.4 and 33.6 % in enclosures 1A and 2A, respectively. There appears slight incorporation in the organic necromass of the surface peat but no enrichment into the necromass of the deeper peat. Inorganic S showed no calculated incorporation in enclosure 1A and only a modest incorporation in enclosure 2A.

In the peat sampled at 6 months, there is slightly less enrichment in the biomass fractions of the sampled cores (5.7 and 27.0 %) than that observed in the 3-month enclosures. Little incorporation was again observed in the other fractions.

After 12 months the % of incorporated tracer in the biomass was 11.5 and 19.1 % in 1C and 2C, respectively. However, the most significant incorporation of tracer was observed in the upper necromass layer in enclosure 1C (25.6 %). Again there was little incorporation into the deeper peat, but the largest enrichment in all of the inorganic fractions examined was observed in 12-month enclosure 1C (2.3 %).

6.4. Discussion

6.4.1. Control variability

Surface water sulphate concentrations were low and relatively uniform across all of the enclosures sampled, ranging between 1.8 and 6.4 ppm. These values are similar to those observed in 2000 (~4 ppm), which had showed a large decline since 1996 (~52 ppm). This was the result, as outlined in chapter 5, of artificial damming of the wetland resulting in the water table being maintained over a number of seasons and establishing BSR as an effective sink for aerially deposited sulphate (see Hemond, 1980; Weider and Lang, 1988).

Similarly, $\delta^{34}S$ of surface water sulphate was reasonably consistent, ranging between 3.9 and 4.8 ‰, implying a reasonably close association with aerial inputs. This has however, not been shown to be the case for more pristine situations. Bottrell and Novak (1997) demonstrated that in two areas of the western British Isles, the sulphur isotopic ratio in bog waters differed between 4 and 12 ‰ from that aerially deposited. As hydrology is critical to the cycling of sulphur in peat, and thusly its isotopic composition, it would appear that the artificial damming of the peat at Thorne might have retarded fluctuations in water table height and as such, seasonal variability. Previous work at Thorne Moor showed that $\delta^{34}S$ of bulk deposited sulphur was between 4.0 and 7.3 ‰ between 1999 and 2000 (Berry, 2001), which is a small range especially when seasonal variation is considered. Sulphidic-S in the surface waters is very low (1.4 to 1.8 ppm) as most is oxidised after diffusion to the surface from the deeper peat. This process could explain the small lightening effect observed in surface water sulphate relative to aerial inputs.

Further down the pore water profiles, SO_4/Cl begins to decrease due to conversion of sulphate to sulphide by bacterial sulphate reduction. Because this favours the lighter isotope (Kemp and Thode, 1968; Chambers and Trudinger, 1979) any remaining residual sulphate will become enriched in ^{34}S. This is evidenced in enclosure 1C (Fig. 6.3) with pore water SO_4 reaching a $\delta^{34}S$ of 65.1 ‰ at ~90cm depth.

Surface waters and porewaters sampled during the year 2000 show a reasonably consistent picture. Sulphate declined in respect to the conservative chloride ion with depth due to conversion to reduced H_2S by BSR (Figs. 6.5, 6.6) (see Bayley, *et al*, 1987; Shannon and White, 1996; Thompson and Bottrell, 1998). Sulphate concentrations in surface water did differ depending upon the time of year, with a decline in June and July (Fig.6.6). This is likely due to a decrease in rainfall input.

The isotopic composition of SO_4 in summer rainfall (4.3 ‰ -Table 6.1), surface water SO_4 prior to tracer addition (3.9 to 4.8 ‰ -Table 6.2) and H_2S from the top of the peat profile (1.2 to 5.3 ‰ -Fig. 6.3) are remarkably similar, even though we would expect significant fractionation effects during the cycling of sulphur between the surface and porewaters due to BSR. This was also shown to be the case in the previous investigation at this site during 2000 (Berry, 2001) with H_2S ranges in porewaters down to 90 cm differing from aerially deposited SO_4 by ~ 1 to 4 ‰.

For the isotopic composition of H_2S to be similar to that of aerial inputs there would need to be the almost wholesale take up of sulphate from the surface waters so that no fractionation effect by BSR could manifest itself. This would demand significant rates of BSR within the peat as inputs to Thorne are relatively high (Table 6.2) compared to more pristine continental sites (see Steinmann and Shotyk, 1997). Such heightened BSR activity is evidenced in the pore water profiles, which show a significant decline in SO_4/Cl with depth (Fig. 6.2) and a massive increase in H_2S concentrations in the deepest depth sampled (315 to 446 μM) (Fig. 6.3). H_2S is very reactive and will preferentially react with organic acids and also with a number of metals within the porewaters, especially free iron, forming FeS and FeS_2 (Brown, 1985; Brown and MaQueen, 1985; Giblin and Weider, 1992; Chapman and Davidson, 2001) Significant levels of these are present in the peat profiles sampled (Fig. 6.9). As such, in the peats sampled from Thorne, the reduced inorganic sulphur pools at depth may act as a significant sink for aerial inputs, effectively acting as a buffer against acid deposition (see also Hemond, 1980).

If BSR is taking up nearly all of the available sulphate deposited aerially, then we would naturally expect to find only minimal levels of sulphate in the surface waters and that any present would have a markedly elevated isotopic composition. Yet, this is not the case. Surface water SO_4 ranges from 1.8 to 6.4 ppm and, as outlined previously, have a similar isotopic composition to aerial inputs and to the H_2S in the upper layers of the pore waters. Surface water SO_4 may be similar in isotopic composition because of continuous H_2S oxidation from the sub surface layers. However, acid deposition effects are typically sporadic and it is therefore conceivable that in between such events, the majority of surface water SO_4 is taken up by BSR, explaining the similar isotopic composition in sulfidic-S and that surface water SO_4 concentrations and isotopic compositions are the result of the most recent deposition event. Future work could examine this further by sampling on a weekly basis between rain events.

The paucity of isotopic data for surface water SO_4 throughout 2000, due to low yields of sulphate, leaves a gap in the control data required to establish the seasonal variation. Although the addition of pure ^{34}S to the peat surface would dwarf any such variation it is important to gain an understanding of the true range throughout the year. However, because the effects of seasonal variation can only manifest itself in two ways; either a drop in water table leading to the oxidation of light sulphides to sulphate (Freeman *et al*, 1994; Devito *et al*, 1995) and upward diffusion to the surface, or through the alteration in sulphur inputs during the year; then we can safely assume that the isotopic composition of surface water SO_4 during the year will lie within the ranges that exist for these two components. The range for sulphidic $\delta^{34}S$ was between 2 and 9 ‰ during the months sampled in 2000 (Fig. 6.7), while aerial inputs during 2000 ranged between 4.0 and 7.3 ‰. These isotopic ranges are used to characterise the maximum possible natural range for surface water sulphate isotopic compositions during the tracer investigation.

Importantly, there are significant differences in terms of sulphur content and isotopic composition between the principle bog flora. *Sphagnum* has a higher sulphur content (1%) than *Eriophorum* (0.2 %) and shows $\delta^{34}S$ values ~2 ‰ heavier. Such differences are the likely result of variation in sulphur availability. *Sphagnum* takes up sulphur aerially deposited upon its surfaces and from the surrounding surface waters in which it is typically bathed. *Eriophorum*, however, takes up sulphur through its roots, which extend into the surface layers of the peat, where sulphate concentrations are much lower than at the surface. However, previous work on bog flora sampled from Thorne Moors has demonstrated much greater variation in sulphur content of *Sphagnum* than that observed between *Sphagnum* and *Eriophorum* sampled during this experiment (Novak *et al*, 2001) and as such caution should be exercised in the interpretation of the control data.

Differences in sulphur isotopic composition of the bog flora are difficult to interpret. Importantly, the isotopic composition of the bog flora is the result of variations in isotopic sources during a number of growing seasons. Evidence exists in previous chapters that *Sphagnum* may exert an extreme fractionation effect upon the sulphur that becomes assimilated into its tissues (~8.5 ‰). However, in this case, the differences between the available sources of sulphur and sulphur in *Sphagnum* fall within a much narrower range (see Thompson and Bottrell, 1998). Interestingly, the isotopic signature of organically bound sulphur in *Eriophorum* is lighter still (-0.8 ‰). This perhaps can be attributed to, as in the case of the southern Pennines, the roots of *Eriophorum* plants extending down into the surface layers of the peat, where there is a source of isotopically light sulphide. As such, there is potential for sulphides to become oxidised to sulphate, by the movement of oxygen through the air spaces in the plant tissue to the roots (see Roura-Carol and Freeman, 1999).

The sub-surface peaks in inorganic sulphur content are typical of a waterlogged peat with defined zone of sulphate reduction in the anaerobic sub-surface layers (e.g Weider and Lang 1988). However, the magnitude of the peaks would appear quite variable between the three control cores. Differences in peat density, hydrology and *Sphagnum* cover may have contributed to such differences. $\delta^{34}S$ of the inorganic fraction is equally variable, appearing relatively constant with depth in core TCC, yet in TCA and TCB there is obvious variation throughout the profile. Also in core TCC the inorganic fraction was relatively light compared to core TCA.

Organic sulphur content is also quite variable with depth in all of the cores sampled. However, similar patterns are obvious with a pronounced peaking at around 15cm. Similar subsurface maxima in organic sulphur have been reported in a number of peats, polluted and pristine, and probably relate to the incorporation of reduced sulphur derived from BSR (Novak *et al*, 1994; Novak *et al* 1999; Chapman, 2001; Jeker and Krahenbuhl, 2001). The isotopic composition of the organic fraction shows remarkable similarity and consistency with depth between cores TCA and TCC. However core TCB has a much wider range (~8 ‰).

6.4.2. Tracer addition

The decline in surface water SO_4-$\delta^{34}S$ during certain periods of the study can be related to dilution by rain events as well as movement of SO_4 down the peat profile and subsequent take up by BSR (Brown, 1985; Morgan, 1995). However, in two instances (18 to 24 weeks and 42 to 48 weeks) surface waters become more enriched even though tracer addition has not taken place during these periods (Fig. 6.19). One possibility is elemental flux between *Sphagnum* cells and surrounding waters so that isotopically enriched sulphur originally taken up by the very porous hyaline cells of *Sphagnum* (see Clymo and Hayward, 1982) is fluxing between the cells and the surface waters. The enrichment effect may also be associated with rain events. The tracer was administered by spraying evenly over the surface of the enclosure, parts of which were covered by *Sphagnum* moss above the water level. Precipitation may have washed enriched sulphur sprayed on to the surfaces of the moss into the surrounding waters.

Examination of the biomass as a whole (Table 6. 4) does not show a strong correlation with time of tracer exposure and the % of tracer incorporated even though the isotopic composition of individual samples of surface vegetation increased with time (Table 6.3). However the standard deviations of the vegetation $\delta^{34}S$ were extremely high implying a high degree of patchiness in tracer uptake in the enclosures. This places a fundamental limitation on certainty of the calculation of % of tracer in the various sulphur-containing compartments. Patchiness in surface water SO_4 as well as in incorporation into the surface vegetation implies that incorporation into the peat profiles will also have lacked uniformity and this has important consequences when trying to scale up % incorporation of tracer in the cores to that incorporated into the enclosures as a whole.

This is most important in the case of the very small reported incorporations into the inorganic sulphur pool and into the deep necromass layers. The range of natural variability dwarfs such small changes (Table 6.4), but the potential for enclosure patchiness also results in further doubt on how useful such data is in interpreting the fate of the tracer.

In spite of these problems, the isotopic compositions do show a marked incorporation into the organic and inorganic fractions in the upper portions of the sampled cores (Figs. 6.23, 6.24, 6.25). As such it appears that diagenetic processes can significantly alter the primary organic signal in waterlogged peats when the aerial source is markedly different. This confirms the findings of numerous workers who have demonstrated the potential for isotopic alteration of the organic fraction through the incorporation of sulphide derived from BSR (e.g. Gebauer *et al*, 1994; Novak *et al*, 1994). Lab incubation experiments with $^{35}SO_4$ have shown that after only 1 hour there can be significant incorporation into the inorganic sulphur fractions (Chapman and Davidson, 2001), while in longer term incubations much of the ^{35}S became incorporated into the organic fraction (Brown, 1985).

There is a significant and consistent decline in S-SO_4/S-H_2S and in SO_4/Cl with depth (Fig. 6.17), due to take up of SO_4 by BSR in the anaerobic sub-surface layers (Hemond, 1980; Weider and Lang, 1988). Significant concentrations of H_2S, the product of BSR, are present in the porewaters (Fig. 6.17). The H_2S is ^{34}S enriched after 6 weeks of tracer addition and becomes more so with time at 25-35 and 45-55 cm depth intervals (Fig. 6.18).

However, there is only a modest enrichment in porewater H_2S (Figs. 6.17, 6.18) compared to the $\delta^{34}S$ of the total inorganic fraction (H_2S, S_0, FeS and FeS_2) observed in the peat profiles (Figs. 6.23, 6.24, 6.25). H_2S was collected in the surface waters (top 5 cm) and between 25 and 35 cm. The isotopic profiles of the peat cores imply that a large proportion of SO_4 is reduced between these depths and is readily converted to FeS and

FeS_2. There is enough reactive iron in the porewaters to facilitate this with Fe/Cl ratios showing a broad peak with depth (Fig 6.17).

The peat profiles suggest that the tracer was mainly incorporated into the surface layers but there is evidence for substantial movement of the tracer into the deeper peat. Br added along with the enriched sulphur has proved not to be a particularly sensitive indicator in assessing ion movement through the peat profile, due to dilution resulting in concentrations below detection limits until around 24 weeks in the study. In spite of this there does appear to be marked isotope enrichment in porewater SO_4 earlier in the investigation. However, it is possible that these could simply be the result of natural variations in sulphur isotopic composition. It is often extremely difficult to obtain control data for porewater SO_4- $\delta^{34}S$ due to low SO_4 concentrations but at day 0 (prior to enrichment study) extremely elevated compositions of 51.0 and 65.1 ‰ were recorded at depths 65-75 and 85-95 cm, respectively (Fig. 6.17, 6.18). Such elevated isotopic compositions are possible due to the selectivity of BSR for the lighter ^{32}S isotope (Thode *et al*, 1961; Kemp and Thode, 1968). As influx of SO_4 down the profile is slow, BSR will continually remove ^{32}S from a SO_4 pool that is replenished at only a very limited rate, especially in the deeper peat, resulting in extreme ^{34}S enrichment in the residual porewater.

However, the enrichment in porewater $\delta^{34}S$ observed at 85-95 cm during the study is far too great to be a product of simply BSR and is instead a consequence of tracer movement into the porewaters, especially at 36 weeks in enclosure 1C (649.8 ‰). Such an extreme enrichment is the likely result of very low natural SO_4 concentrations at this depth so that even only a small influx of the enriched ^{34}S derived from the tracer would dominate.

The elevated $\delta^{34}S$ of porewater H_2S and porewater SO_4 is therefore suggestive of the movement of the administered tracer into the deeper peat but we generally do not observe any obvious incorporation into the solid sulphur fractions (organic and total inorganic) in the peat cores below 25 cm. This is the likely consequence of low tracer concentrations and of increased sulphur contents of the inorganic and organic fractions. Inorganic sulphur content shows a general increase with depth in the peat cores sampled

(Figs.6.20, 6.21, 6.22). As such, incorporation of the moderately enriched H_2S will be dwarfed by the high sulphur content of the total inorganic sulphur fraction.

Organic sulphur content is also shown to increase with depth (Figs. 6.20, 6.21, 6.22) which is typical of waterlogged peaks (e.g. Weider and Lang, 1988; Novak and Weider, 1992; Chapman, 2001) This is the result of gradual, but sustained, incorporation of H_2S into the organic fraction during the life of the deposit. As such, as in the case for the total inorganic sulphur pool, the incorporation of the ^{34}S enriched H_2S, is not sufficient to significantly alter the $\delta^{34}S$ of the organic sulphur. This can be demonstrated by a simple mass balance using data from one of the cores (1C-1) and from the depth sampling tubes in enclosure 1C. Sulphur content and isotopic composition for H_2S in the region 25-35 cm was compared to that of organic sulphur in this region. H_2S had a markedly elevated isotopic composition (23.9 ‰) but only a low sulphur mass (0.71 mg). Whereas, the peat in this fraction had a isotopic composition of 1.4 ‰ with a much higher sulphur mass (37.9 mg). Even if all of the H_2S were incorporated into the peat at this depth the isotopic composition of the organically bound sulphur would only increase to 1.8 ‰, a shift of only 0.4 ‰.

6.5. Summary and conclusions

Natural variability in sulphur content and isotopic composition in the various sulphur containing transposable compartments was established in a raised ombrotrophic peatland prior to an enriched sulphur tracer study.

Low sulphate concentrations (1.8 - 6.4 ppm) in surface waters persisting after continued management. Consistent $\delta^{34}S$ compositions (3.9 - 4.8 ‰) are suggestive of a close association with aerial inputs and provide an excellent baseline signal prior to enriched sulphur addition.

High inputs of sulphur, as well as a persistent high water table, result in significantly elevated BSR activity, and therefore inorganic sulphur pools (namely H_2S, FeS and FeS_2) act as significant sinks for aerial inputs.

Sulphur in bog flora is isotopically light compared to aerial sulphur inputs and surface water sulphate. *Sphagnum* and *Eriophorum* show significant differences in sulphur content and isotopic composition.

Organic $\delta^{34}S$ shows remarkable consistency between two of the cores studied. Total range was around 9 ‰ between –2.2 and 7.0 ‰. Inorganic $\delta^{34}S$ range was around 12 ‰ between –4.3 and 7.4 ‰.

The addition of pure ^{34}S at regular intervals during the 48-week investigation resulted in significant alteration in the isotopic signature of various sulphur containing compartments within the peat profile. Tracer concentration in the surface waters was always low yet there was a strong correlation between $\delta^{34}S$ and tracer addition events.

Enrichment of porewater SO_4 and H_2S led to significant alteration in organic and inorganic (s) isotopic compositions in the surface layers. Incorporation of H_2S into these fractions at increased depths was not generally evident due likely to a combination of less enriched sulphur reaching the deeper porewaters and also due to higher sulphur content of the solid sulphur pools resulting in a dwarfing of the contribution of the enriched H_2S.

CHAPTER 7- Conclusions and Further Work

7.1. Introduction

The conclusions of this work will be considered in the order of the aims listed in chapter 1. In summary, these were:

1) To assess the robustness of the sulphur signal contained in the organic fraction of pristine peatlands, to determine whether an isotopic record of aerially deposited sulphur can be preserved within peat profiles.

2) To investigate whether this can be applied to polluted peatlands in order to reconstruct the history of sulphur pollution on the southern Pennines.

3) To examine sulphur cycling in a waterlogged peat to investigate the relative importance of various processes, such as diagenesis, upon the organic sulphur fraction.

7.2. Preservation of environmental sulphur in pristine peats

Three modern pristine peats and one ancient peat were sampled and analysed to investigate whether the isotopic composition of sulphur inputs could be preserved in the organic fraction of ombrotrophic peat (Table 7.1). Previous work suggested that the organic sulphur fraction of peat was susceptible to two processes, which were strongly dependent upon hydrological conditions.

i) partial decomposition, which liberates ^{32}S resulting in a ^{34}S enriched organic fraction (see Bridgham *et al*, 1998)
ii) the addition of isotopically light sulphide, derived from BSR (e.g. Brown, 1985)

Table 7.1. Summary of pristine peat sulphur contents and isotopic compositions.

Peat type	Organic S (mg/kg peat dry Wt.)	Organic S δ^{34}S (‰)	Inorganic S (mg/kg peat dry Wt.)	Inorganic S δ^{34}S (‰)
Ancient deposit	5700-27100	3.3-15.4	100-10100	-10.4-58.6
Low Ridge Shetland	100-9000	9.9-14.5	0-900	5.1-12.9
Pools Forsinard	1500-8000	11.0-18.6	200-900	11.5-20.2
Dry peatland Abisko	0-600	-0.9-16.7	0-50	*

Peat type was shown to be critical in determining whether an environmental archive of sulphur deposition could exist within the profile. Low ridge hummock peat from Shetland proved to be the most suitable. However, only short to medium term changes in input are likely to be preserved due to the incorporation of sulphides, derived from bacterial sulphate reduction (BSR), into the organic fraction at depth (e.g. Novak and Weider, 1992). The organic fraction of peat sampled from waterlogged pools at Forsinard (NE Scotland) was masked by sulphide incorporation throughout the profile while peat from Abisko (N. Sweden) was exposed to a annual cycle of drying and wetting resulting in significant decomposition of the organically bound sulphur.

Although organic sulphur in the modern peat from Shetland was significantly ^{34}S depleted compared to surface water sulphates dominated by maritime inputs, this shift was consistent with fractionations observed for *Sphagnum* growth in modern pristine peatlands (Bottrell and Novak, 1997) and there was thus no evidence for significant diagenetic effects. As such, in drier peats there is significant potential for archives of atmospheric deposited sulphate to be preserved.

The ancient peat sampled from Fugla Ness had similar sulphur isotopic compositions to the modern peat sampled on Shetland but sulphur contents were significantly greater implying the incorporation of sulphide derived from BSR. However, because this sulphide may have had a similar isotopic composition to that incorporated by the surface vegetation it would appear that there has been little isotopic alteration.

7.3. Creating deposition histories: Evidence from southern Pennine peat

The sulphur isotopic profiles in ombrotrophic upland peat from the southern Pennines, an area with a gross history of sulphur pollution during the Industrial Revolution were analysed to investigate whether the significant changes in isotopic composition of sulphur inputs during the life of the deposit may be preserved within the peat stratigraphy.

There were significant differences between the isotopic compositions and sulphur contents of the three peat types sampled (Table 7.2). The data derived from pristine peats suggested that waterlogged peats would be unsuitable for recording an archive of sulphur inputs due to significant incorporation of sulphides derived from BSR. This was shown to be the case in peat sampled from a pool complex on the southern Pennines. Inorganic and organic sulphur contents were highest in this peat type indicating high increased rates of BSR within the profile.

Table 7.2. Summary of southern Pennine peat sulphur contents and isotopic compositions.

Peat type	Organic S (mg/kg peat dry Wt.)	Organic S $\delta^{34}S$ (‰)	Inorganic S (mg/kg peat dry Wt.)	Inorganic S $\delta^{34}S$ (‰)
High Ridge	700-2800	2.7-13.3	0-300	-9.1-6.8
Low Ridge	160-2800	-1.1-11.4	0-290	-4.6-2.1
Pools	380-6579	-2.3-6.2	250-1400	-2.7-6.0

Isotopic analyses, along with radiometric data and pollen analyses, suggest that in the drier upland peats sampled, recent changes (~600 y) in atmospheric sulphur chemistry are preserved within the organic sulphur fraction without significant masking by diagenetic processes. The pronounced negative excursion in organic $\delta^{34}S$ is in stark contrast to the relatively consistent isotopic compositions observed in an equivalent peat type sampled from a pristine situation at Lumbister (Fig. 7.1).

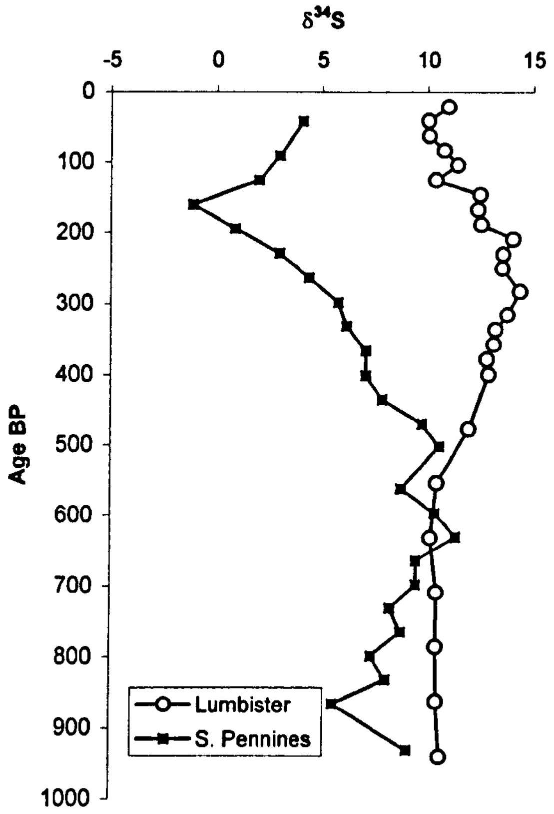

Fig.7.1. $\delta^{34}S$ of organic sulphur versus age in low ridge hummock peat sampled from Lumbister and the southern Pennines

7.4. Sulphur cycling in waterlogged peats

Variations in surface water sulphur chemistry were reviewed for a waterlogged raised peatland in the northeast of England from 1994 to 2000. While, the magnitude of sulphur inputs were important, belowground cycling of sulphur, dependent upon water table height, played a dominant role in affecting sulphate concentration of the surface waters.

The increase in surface water sulphate in 1996 was accompanied by a significant rise in the sulphur content of *Sphagnum* moss growing on the surface of the pools. As such the sulphur content of *Sphagnum* may act as a proxy for variations in surface water sulphur chemistry. This increase, a result of oxidation of isotopically light sulphides, will have been accompanied by an isotopic alteration, which will have meant that the isotopic composition of vegetation in waterlogged peats may not accurately reflect that of which is aerially deposited but that of the hydrological status of the wetland.

However, the data from the tracer investigation at Thorne Moors suggested that environmental changes, either in terms of aerial inputs or through alterations in water table, are unlikely to be preserved after plant death within the peat profile of waterlogged wetlands due to significant alteration by diagenetic processes. Although not strongly time dependent due to tracer patchiness, the addition of pure ^{34}S at regular intervals during a 48-week investigation resulted in the significant alteration of various sulphur containing compartments, namely into the bog flora and in the inorganic and organic fractions of the surface peat

7.5. Summary and further work

This thesis has further emphasised the potential for peatlands to act as archives of environmental change. However, not all peatlands are useful for this purpose and selectivity is necessary due to significant belowground elemental cycling in the more waterlogged peats. For a peat to record changes in sulphur chemistry it needs to be wet enough to prevent decomposition but not so waterlogged that diagenetic sulphide incorporation obscures the primary organic sulphur signal. Location is also important. If a peatland is distant from its source of natural sulphur then only a small amount of sulphur will be aerially deposited on its surface yet its isotopic composition will still be very isotopically distinct and as such, if anthropogenic activities, even at a very local scale proliferate, then this would significantly alter the isotopic composition of the aerial input. This appeared to be the case for the southern Pennines where early lead smelting activities prior to the Industrial Revolution may be represented within the peat profile, demonstrating that in certain situations, peatlands can be extremely sensitive archives of changes in aerially deposited sulphur. As such, further applications in this respect may be possible. Peatlands close to sites of volcanic activity, such as in New Zealand, Iceland or the Falklands, may contain an archive of volcanic events by recording changes in the isotopic composition of sulphur. However, diagenetic effects, even in 'ideal' peat, would eventually compromise this potential in the long term.

Further work is necessary in clarifying the nature of sulphur isotopic fractionation by peatland vegetation, especially *Sphagnum* species. Some quite large fractionations were suggested in *Sphagnum* samples taken from pristine settings. However, from the southern Pennines, *Sphagnum* and *Eriophorum* appeared less isotopically distinct from the aerial sulphur component. Although no aerial sulphur isotopic compositions were sampled for this site, rainfall collected between 1995 and 1996 10 km away suggests that there would appear to be a reasonably close association between isotopic composition of aerial inputs and vegetation. Therefore, laboratory experiments are suggested to further clarify the results presented in this thesis, especially as they are the most extreme levels of fractionation seen in land, marine or freshwater plants (see Trust and Fry, 1992). It is likely that isotopically light sulphur derived from bacterial sulphate reduction with depth may be exerting some influence upon the isotope chemistry of the surface vegetation, which would be more so in the case of vegetation habiting in and around waterlogged areas.

The ^{34}S tracer investigation at the waterlogged wetland demonstrated that diagenetic incorporation of sulphides into the organic fraction acts to obscure any primary sulphur signal. This should be further investigated in the upland drier peats, such as those typical of the southern Pennines, in which the level of the water table is much deeper. This would allow further clarification on the robustness of the originally preserved sulphur signal in these peats.

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Appendix A Peat profiles

Table A-1. Geochemical data and sulphur isotopic compositions for Fugla Ness peat

	Sample ID	Mean Depth (mm)	%H_2O	%Ash	%Sulphide-S	$\delta^{34}S$-Py	%Org. S	$\delta^{34}S$	%C	%H	%N	%O	U (ppb)	Pb (ppb)	U/Pb	$\Delta^{34}S_{Org}$-$SWSO_4$
Pure peat	FN-B	159	54.2	30.8	0.14	20.7	1.74	12.3	41.7	4.75	0.55	20.3	21029	36101	0.583	-7.3
	FN-D	194.5	52.5	30	0.54	29.6	2.71	15.4	45.5	4.54	0.72	16	8099	18522	0.437	-4.2
	FN-E	229.5	53.3	31.3	0.25	21.3	2.44	10.1	47.8	4.54	0.7	13	5200	16453	0.316	-9.5
	FN-F	265	51.7	27.7	0.32	19.7	2.04	11.3	46.1	4.54	0.7	18.6	12818	38687	0.331	-8.3
	FN-G	300	54	30.2	0.11	58.6	1.78	11.4	48.6	5.26	0.49	13.8	6972	19788	0.352	-8.2
	FN-H	336	54.2	30.3	0.23	22.5	2	11	45.8	4.77	0.55	16.4	8848	24248	0.365	-8.6
	FN-I	378	47.2	39.7	0.14	1.3	2.2	11.8	51.4	4.22	0.61	1.7	11961	18980	0.630	-7.8
	FN-J	426.5	35.9	71.5	0.35	-10.4	0.96	10.2	19.2	1.37	0.39	6.2	4242	8591	0.494	-9.4
	FN-M	523	33.7	69.9	0.01		1.41	11	16.5	2.02	0.19	10	2260	9557	0.236	-8.6
	FN-N	571	37.6	61.9	0.32	25.2	0.57	12.5	25.8	2.16	0.56	8.7	3888	15431	0.252	-7.1
	FN-O	619.5	41.7	53.9	0.21	18.9	1.16	12	31	3.61	0.34	9.8	5074	21986	0.231	-7.6
	FN-Q	716	50.7	34.5	0.27		0.57	11.6	42	4.27	0.48	17.9	5990	25014	0.239	-8
Peat/Clay interbed	FN-A	123.5	53.8	36.1	1.01	-10.4	2.28	9.8	41.3	3.86	0.62	14.8	7996	15714	0.509	-9.8
	FN-L	475	39.3	66.4	0.03		1.4	7.1	29.2	3.39	0.41	0	2798	7014	0.399	-12.5
	FN-P	668	43.5	54.9	0.37	13.8	1.13	7.9	35.5	3.88	0.51	4	4527	18807	0.241	-11.7
	FN-R	764.5	51.6	32.9	0.83	10	1.27	9.5	45.3	4.44	0.85	85.6	7016	27447	0.256	-10.1
	FN-S	808	56.5	30.2	0.01		0.9	3.3	44.4	5.57	0.32	18.6	8778	31881	0.275	-16.3
	FN-T	846.5	52.1	50.7	0.03		0.77	3.9	34.8	3.55	0.45	9.7	11883	32066	0.371	-15.7

Table A-2. Sulphur content, isotopic compositions and calculated mean age of Lumbister peat (monolith SH-1)

	Sample	Depth	% water	%S-InorgS	INORGmg/kg/dry weight	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS	mean age	%C	OrgS/C
SH1	SH1/1	1.4	81.51	0.0000	0.00		0.1866	1865.78	10.97	21.04		
	SH1/2	2.7	82.41	0.0091	91.42		0.0977	977.09	10.04	40.58	48.19	1.19
	SH1/3	4.1	83.71	0.0096	95.79		0.0141	140.69	10.07	61.62	48.55	0.79
	SH1/4	5.5	79.71	0.0120	119.55		0.0361	361.12	10.79	82.67	49.54	0.60
	SH1/5	6.9	82.54	0.0094	94.32		0.0203	203.17	11.43	103.71	51.2	0.49
	SH1/6	8.3	83.73	0.0055	55.38		0.0123	122.89	10.40	124.75	51.27	0.41
	SH1/7	9.7	83.99	0.4691			0.0565	565.06	12.49	145.79	50.82	0.35
	SH1/8	11.1	83.24	0.0127	126.69		0.0187	186.86	12.41	166.83	50.06	0.30
	SH1/9	12.5	81.49	0.0114	113.61		0.0318	318.04	12.56	187.88	50.57	0.27
	SH1/10	13.9	84.83	0.0231	231.07	8.52	0.1170	1170.02	14.07	208.92	52.45	0.25
	SH1/11	15.3	86.40	0.0207	206.64	9.14	0.0548	548.07	13.60	229.96	52.92	0.23
	SH1/12	16.6	84.95	0.0185	184.84	12.24	0.1668	1668.03	13.57	249.50	54.75	0.22
	SH1/13	18.8	85.22	0.0192	192.00	11.67	0.0948	948.06	14.40	282.56	53.51	0.19
	SH1/14	21	84.02	0.0259	259.06	11.30	0.1858	1857.57	13.81	315.63	55.24	0.18
	SH1/15	22.4	87.00	0.0204	204.10	10.99	0.1602	1601.90	13.24	336.67	56.64	0.17
	SH1/16	23.8	85.14	0.0195	194.80	11.53	0.0815	814.57	13.17	357.71	54.07	0.15
	SH1/17	25.2	85.26	0.0315	314.63	10.24	0.2007	2007.49	12.85	378.76	59.03	0.16
	SH1/18	26.6	84.23	0.0309	309.10	9.10	0.0913	912.71	12.93	399.80	60.4	0.15
	SH1/19	28	83.21	0.0088	87.81	8.70	0.3811	3810.98	12.01	477.00	56.6	0.12
	SH1/20	29.4	80.86	0.0208	207.95	5.63	0.6703	6703.50	10.49	554.20	57.22	0.10
	SH1/21	30.8	79.82	0.0166	166.09	5.14	0.7195	7195.33	10.20	631.40	61.3	0.10
	SH1/22	32.2	79.27	0.0194	193.98	5.67	0.6855	6854.67	10.49	708.60	59.82	0.08
	SH1/23	33.6	80.57	0.0239	238.95	6.94	0.8667	8667.05	10.48	785.80	59.89	0.08
	SH1/24	35	80.57	0.0304	304.09	9.30	0.8606	8605.80	10.50	863.00	58.71	0.07
	SH1/25	36.4	81.16	0.0254	254.47	11.26	0.9035	9034.69	10.68	940.20	60.35	0.06
	SH1/26	37.8	83.68	0.0365	364.62	12.07	0.6300	6300.24	10.88	1017.40	52.88	0.05
	SH1/27	39.8	82.35	0.0545	544.68	11.97	0.6466	6466.38	11.01	1127.68	55.71	0.05
	SH1/28	41.2	83.50	0.0853	853.13	12.87	0.6481	6480.74	10.80	1204.88	48.93	0.04
	SH1/29	42.6	85.41	0.0424	423.87	11.56	0.5220	5220.49	11.07	1282.08	51.75	0.04
	SH1/30	44	83.69	0.0398	398.06	11.66	0.5862	5861.54	11.50	1359.28	49.74	0.04

Table A-3. Sulphur content and isotopic compositions of Lumbister peat (monolith SH-2)

	Sample	Depth	% water	%S-InorgS	INORGmg/kg/dry weight	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS
SH2	SH2/1	1.5					0.0191	191.15	11.21
	SH2/2	3.7	84.54	0.0000	0.00		0.0534	533.82	12.15
	SH2/3	5.1	83.31	0.0000	0.00		0.0904	904.11	11.71
	SH2/4	6.5	82.64	0.0000	0.00		0.1033	1033.42	11.98
	SH2/5	7.9	84.14	0.0088	88.24		0.0110	110.23	11.45
	SH2/6	9.3	84.47	0.0080	79.60		0.0362	362.25	11.76
	SH2/7	10.7	84.98	0.0000	0.00		0.0138	137.89	12.04
	SH2/8	12.1	86.97	0.0025	25.20				
	SH2/9	13.5	86.17	0.0000	0.00		0.0142	142.35	12.13
	SH2/10	14.9	85.05	0.0000	0.00		0.0068	67.69	11.98
	SH2/11	16.3	85.01	0.0042	42.07		0.1283	1282.96	12.99
	SH2/12	17.6	85.60	0.0000	0.00		0.0286	286.01	12.80
	SH2/13	19.8	88.96	0.0030	29.74		0.0626	626.45	12.55
	SH2/14	22	87.66	0.0028	28.04		0.0405	405.28	14.27
	SH2/15	23.4	86.62	0.0025	25.04		0.0390	390.34	14.20
	SH2/16	24.8	84.96	0.0105	104.78		0.0467	466.59	14.45
	SH2/17	26.2	85.49	0.0021	21.10	10.64	0.0910	909.85	14.21
	SH2/18	27.6	85.34	0.0110	109.67	11.16	0.0566	565.72	13.76
	SH2/19	29	86.20	0.0046	45.69	9.76	0.1379	1379.40	12.33
	SH2/20	30.4	84.14	0.0041	40.55	7.94	0.1517	1517.07	13.09
	SH2/21	31.8	78.95	0.0099	98.97	5.83	0.3725	3724.58	9.89
	SH2/22	33.2	81.89	0.0110	109.87	8.95	0.6620	6620.34	10.68
	SH2/23	34.6	80.73	0.0082	81.79	7.30	0.4610	4610.24	9.64
	SH2/24	36	79.46	0.0047	46.97	6.33	0.5646	5646.30	
	SH2/25	37.4	82.13	0.0087	87.36	8.78	0.5352	5352.48	9.93
	SH2/26	38.8	81.40	0.0168	167.78	9.68	0.4978	4978.06	10.17
	SH2/27	40.8	81.59	0.0224	224.17	11.89	0.2451	2451.26	10.73
	SH2/28	42.2	82.88	0.0085	85.31	11.27	0.3184	3183.62	10.81
	SH2/29	43.6	86.73	0.0210	209.60	11.47	0.3334	3333.98	11.07
	SH2/30	45	82.19	0.0159	159.29	9.79	0.3376	3375.71	10.77
	SH2/31	46.4	87.52	0.0239	239.17	7.77	0.2971	2970.58	10.95

Table A-4. Sulphur content and isotopic compositions of Abisko peat.

Sample	Depth	% water	%S-InorgS	InorgS mg/kg(dry wt)	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS
C1A	2.35						10.86
C1B	5						9.12
C2	7.12	61	0.0025	25.46	0.0502	502.24	6.7
C3	8.36	60	0.0021	21.23	0.0507	507.42	14.9
C4	9.6	62	0.0018	18.02	0.0468	467.73	9
C5	10.83	62	0.0027	26.56	0.0204	203.82	
C6	12.07	59	0.0036	35.98	0.0353	352.66	11.5
C7	13.31	63	0.0034	34.26	0.0138	138.48	
C8	14.55	61	0.0036	36.00	0.0203	203.14	14.7
C9	15.79	59	0.0034	33.73	0.0213	213.10	13.9
C10	17.02	59	0.0047	46.52	0.0330	329.75	11
C11	18.26	64	0.0031	30.62	0.0236	236.41	16.7
C12	19.5	59	0.0039	39.11	0.0019	18.91	
C13	20.74	60	0.0039	39.02	0.0437	436.69	12.1
C14	21.98	62	0.0036	35.66	0.0234	233.62	14.8
C15	23.21	60	0.0036	35.86	0.0046	46.14	
C16	24.45	59	0.0031	30.84	0.0014	13.92	
C17	25.69	61	0.0015	15.15	0.0060	60.43	
C18	26.93	58	0.0007	7.33	0.0093	92.89	
C19	28.17	68	0.0041	40.73	0.0203	203.16	3.5
C20	29.4	68	0.0024	23.74	0.0596	596.28	-0.9
C21	30.64	57.1	0.0023	23.23	0.0293	292.68	2

Table A-5. Geochemical data for southern Pennine high ridge hummock peat (HR-1)

HR 1

Sample	Depth	% water	%S-InorgS	InorgS-mg/kg	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS	mean age	δ^{13}C	% Sulphur	% Carbon	% Nitrogen	orgS/C
SPC1	0.75	78.3	0.0000	0.00		0.1703	1702.84	3	38.3		0.17	50.1	2.8	0.0034
SPC2	3.25	70.6	0.0011	11.17		0.0937	936.80	5.7	166.1		0.09	50.78	2.9	0.0018
SPC3	5.50	61.6	0.0008	7.74		0.0695	695.37	7.1	281.1		0.07	51.07	2.41	0.0014
A2	6.68	81.9	0.0036	35.54		0.1475	1474.75	12.3	341.3	-27.7	0.15	51.48	2.13	0.0029
A3	8.04	86.4	0.0000	0.00		0.1738	1737.92	12.2	410.6	-27.9	0.17	50.77	2.81	0.0034
A4	9.39	87.7	0.0000	0.00		0.1537	1537.29	12.8	480.0	-28.2	0.15	51.06	3.63	0.0030
A5	10.75	85.8	0.0131	130.80		0.0873	873.08	13.3	549.3	-27.3	0.10	51.35	3.21	0.0017
A6	12.11	87.6	0.0000	0.00		0.1248	1247.87	10.9	618.7	-27.5	0.12	49.79	3.12	0.0025
A7	13.46	87.4	0.0000	0.00		0.1802	1802.01	9.7	688.0	-27.1	0.18	48.53	3.41	0.0037
A8	14.82	87.0	0.0081	80.74		0.0961	960.54	9.3	757.4	-27	0.10	49.98	2.7	0.0019
A9	16.18	87.6	0.0090	89.57	-2.58	0.1491	1491.40	7.7	826.7	-27.3	0.16	49.54	2.24	0.0030
A10	17.54	84.6	0.0116	116.15		0.1551	1551.32	7.5	896.1	-27.4	0.17	51.97	2.21	0.0030
A11	18.89	88.2	0.0083	82.60	0.13	0.1788	1787.56	8.6	965.4	-26.7	0.19	47.3	3.04	0.0038
A12	20.25	88.7	0.0133	132.60		0.1749	1748.89	8	1034.8	-27.3	0.19	49.19	2.83	0.0036
A13	21.61	85.8	0.0046	45.76	-0.02	0.1692	1692.15	8.2	1104.1	-26.9	0.17	47.53	2.84	0.0036
A14	22.96	86.3	0.0108	108.10	-3.59	0.2611	2611.47	7.3	1173.5	-27.6	0.27	46.36	2.78	0.0056
A15	24.32	87.9	0.0152	151.81		0.2673	2672.65	6.6	1242.8	-27.5	0.28	52.4	2.14	0.0051
B1	26.80	89.9	0.0027	26.94		0.2218	2217.67	8.6	1369.5	-27.7	0.22	47.33	3.51	0.0047
B2	29.28	86.7	0.0091	91.20		0.2289	2289.48	9.1	1496.1	-27.5	0.24	49.03	3.19	0.0047
B3	30.64	88.4	0.0089	88.54		0.2324	2324.08	8.7	1526.9	-27.5	0.24	51.46	2.2	0.0045
B4	31.99	89.9	0.0027	27.18		0.1822	1822.17	10	1557.6	-27.7	0.18	50.23	3.21	0.0036
B5	33.35	88.2	0.0095	94.68	1.01	0.1619	1619.32	9.3	1588.4	-27.4	0.17	49.33	3.99	0.0033
B6	34.71	87.5	0.0044	43.54	-2.34	0.1379	1379.29	9.3	1619.1	-27.8	0.14	51.28	2.35	0.0027
B7	36.06	90.2	0.0080	79.89	-3.85	0.2032	2031.60	7.5	1649.9	-27.3	0.21	50.83	2.98	0.0040
B8	37.42	87.4	0.0069	68.92	-1.10	0.2033	2033.20	8.8	1680.6	-28	0.21	51.6	3.16	0.0039
B9	38.78	85.7	0.0079	78.82	-1.35	0.1466	1465.63	9.1	1711.4	-27.6	0.15	50.65	2.6	0.0029
B10	40.13	86.5	0.0082	82.04	0.10	0.2414	2413.72	7.4	1742.1	-27.6	0.25	51.73	3.02	0.0047
B11	41.49	87.8	0.0071	71.18	-6.24	0.1683	1682.54	7.1	1772.9	-27.2	0.18	51.45	2.73	0.0033
B12	42.85	86.9	0.0061	61.27	-7.15	0.1881	1881.04	6.7	1803.6	-27.2	0.19	49.12	3.55	0.0038
B13	44.21	88.6	0.0158	157.67	-6.62	0.2000	2000.02	6.5	1834.4	-27.5	0.22	52.42	3.17	0.0038
B14	45.56	88.2	0.0023	23.26		0.2360	2359.81	5.7	1865.1	-27.3	0.24	51.36	2.67	0.0046
B15	46.92	89.3	0.0154	153.92	-4.23	0.2820	2819.82	6.1	1895.9	-27.2	0.30	52.19	3.01	0.0054

Table A-6. Sulphur content and isotopic compositions of southern Pennine high ridge hummock peat (HR-2)

	Sample	Depth	% water	%S-InorgS	InorgS-mg/kg	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS
	SPD1	1.00					0.2178	2177.66	4.51
HR 2	SPD2	2.70	76.7	0.0094	93.76	0.41	0.2338	2338.00	3.285435
	SPD3	4.10	80.5	0.0101	101.04		0.1456	1456.01	3.091989
	SPD4	5.50	79.3	0.0074	74.06		0.0488	487.79	2.748085
	SPD5	6.90	78.6	0.0071	70.91	0.22	0.0972	971.85	3.511122
	SPD6	8.30	78.1	0.0095	94.71	3.01	0.0976	975.99	5.48857
	SPD7	9.70	75.8	0.0104	104.02	2.96	0.0414	414.43	8.626694
	SPD8	11.10	78.0	0.0128	127.61	3.41	0.0125	125.47	10.335467
	SPD9	12.50	80.2	0.0105	105.27		0.0513	513.44	11.023275
	SPD10	13.90	83.1	0.0126	125.58		0.0457	457.01	
	SPD11	15.30	83.9	0.0297	296.63	6.77	0.0837	837.10	9.927081
	SPD12	16.60	82.1	0.0121	120.56		0.0310	309.87	9.518695
	SPD13	18.80	88.4	0.0192	191.96		0.1024	1024.04	8.626694
	SPD14	21.00	87.4	0.0207	206.77	-3.14	0.0375	374.98	
	SPD15	22.40	87.5	0.0213	212.85	-2.81	0.0698	698.12	6.681487
	SPD16	23.80	86.1	0.0147	147.02		0.0974	973.96	6.702981
	SPD17	25.20	87.0	0.0206	206.20		0.1219	1218.59	7.809922
	SPD18	26.60	84.5	0.0161	161.26	-3.73	0.1317	1316.88	7.390789
	SPD19	28.00	85.7	0.0160	160.47	-5.80	0.1410	1410.15	7.111367
	SPD20	29.40	85.7	0.0180	179.80	-6.15	0.0716	716.15	7.756187
	SPD21	30.80	86.4	0.0064	64.00		0.1083	1082.81	7.723946
	SPD22	32.20	86.4	0.0066	66.33	-4.06	0.0353	353.43	7.003897
	SPD23	33.60	85.4	0.0124	123.61	-7.63	0.0861	861.21	6.090402
	SPD24	35.00	85.7	0.0178	178.30	-8.10	0.0352	351.56	5.391847
	SPD25	36.40	86.6	0.0183	183.07	-9.10	0.1114	1114.11	5.510064
	SPD26	37.80	86.7	0.0164	163.83	-5.40	0.0508	508.03	6.745969
	SPD27	39.80	89.0	0.0204	204.09	-4.42	0.0756	756.08	7.304813

Table A-7. Sulphur content and isotopic compositions of southern Pennine low ridge hummock peat (LR-1)

	Sample	Depth	% water	%S-InorgS	InorgS-mg/kg	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS
	SPA1	1.00					0.2566	2566.25	6.17
LR 1	SPA2	2.90	76.1	0.0011	10.91		0.1350	1350.24	3.7
	SPA3	4.50	75.2	0.0055	55.33		0.1249	1249.31	1.9
	SPA4	5.90	87.5	0.0089	88.92		0.1169	1169.16	2.6
	SPA5	7.30	83.3	0.0062	61.88		0.1954	1954.31	2.9
	SPA6	8.70	81.6	0.0044	43.88		0.2482	2481.51	3.9
	SPA7	10.10	83.3	0.0064	64.02		0.2765	2764.74	3.9
	SPA8	11.50	85.5	0.0019	19.42		0.2447	2447.03	3.7
	SPA9	12.90	85.9	0.0039	39.16	-2.59	0.1082	1081.98	4.9
	SPA10	14.30	88.1	0.0078	77.82	-2.29	0.2015	2015.10	4.6
	SPA11	15.70	86.0	0.0040	40.37		0.2022	2022.09	5.6
	SPA12	17.10	89.8	0.0083	83.36		0.2155	2155.46	5.5
	SPA13	19.80	89.0	0.0079	79.01		0.1894	1893.74	6.3
	SPA14	23.80	87.3	0.0088	87.53	-1.59	0.1339	1338.64	6.7
	SPA15	26.50	88.1	0.0095	95.30	-1.19	0.0333	333.33	9.3
	SPA16	27.90	87.1	0.0063	63.10	-1.13	0.0495	495.28	8.6
	SPA17	29.30	87.4	0.0093	93.01	-2.50	0.1284	1284.44	8.1
	SPA18	30.70	88.7	0.0129	128.55	-2.66	0.2244	2244.24	7.2
	SPA19	32.10	88.2	0.0145	144.64	-1.87	0.1510	1509.73	7.2
	SPA20	33.50	89.2	0.0102	101.86	-3.83	0.2417	2417.32	5.4
	SPA21	34.90	89.4	0.0167	166.65	-4.60	0.2125	2124.66	4.4
	SPA22	36.30	91.6	0.0164	163.67	-3.75	0.1369	1369.05	6
	SPA23	37.70	91.4	0.0199	199.10	-2.89	0.0446	445.70	6.5
	SPA24	39.10	91.5	0.0229	228.78	-4.00	0.0205	204.58	7.1
	SPA25	40.50	91.0	0.0218	218.37	-1.46	0.0161	160.52	
	SPA26	41.90	91.3	0.0227	227.18	-1.83	0.2110	2110.27	6.2
	SPA27	44.00	90.3	0.0270	270.12	0.96	0.1572	1572.02	8.9

Table A-8. Sulphur content, isotopic compositions and calculated mean age of southern Pennine low ridge hummock peat (LR-2)

	Sample	Depth	% water	%S-InorgS	InorgS-mg/kg	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS	mean age
LR 2	SPB1	1.70	78.8	0.0000	0.00		0.2586	2586.48	4.09	41.8
	SPB2	3.70	77.6	0.0043	43.15		0.1827	1827.40	3	91.0
	SPB3	5.10	80.7	0.0096	96.19		0.2091	2091.25	2	125.5
	SPB4	6.50	82.0	0.0066	66.10		0.1202	1202.16	-1.1	159.9
	SPB5	7.90	86.5	0.0069	69.42		0.1951	1951.48	0.9	194.3
	SPB6	9.30	84.7	0.0051	50.88		0.1561	1560.65	3	228.8
	SPB7	10.70	84.2	0.0053	52.62	-0.87	0.2201	2200.53	4.4	263.2
	SPB8	12.10	85.9	0.0058	57.52		0.2430	2430.00	5.8	297.7
	SPB9	13.50	87.3	0.0044	43.73		0.3033	3032.73	6.2	332.1
	SPB10	14.90	86.7	0.0038	37.82		0.2008	2007.65	7.1	366.5
	SPB11	16.30	84.7	0.0056	56.35	-2.76	0.3696	3696.10	7.1	401.0
	SPB12	17.70	87.1	0.0043	42.58		0.2135	2135.33	7.9	435.4
	SPB13	19.10	88.6	0.0178	177.73		0.2919	2918.92	9.8	469.9
	SPB14	20.40	90.0	0.0083	83.17		0.2166	2166.19	10.6	501.8
	SPB15	22.85	88.2	0.0021	21.50		0.2515	2515.24	8.8	562.1
	SPB16	24.25	88.2	0.0070	70.06		0.2158	2157.76	10.4	596.6
	SPB17	25.65	87.1	0.0040	40.41		0.1839	1838.70	11.4	630.2
	SPB18	27.05	86.4	0.0000	0.00		0.2103	2102.62	9.5	663.9
	SPB19	28.45	87.5	0.0066	66.13	2.13	0.0697	697.26	9.5	697.6
	SPB20	29.85	88.6	0.0065	65.20	0.72	0.1849	1848.90	8.3	731.3
	SPB21	31.25	89.4	0.0074	74.33		0.2287	2286.70	8.8	765.0
	SPB22	32.65	89.8	0.0000	0.00		0.2941	2941.15	7.4	798.7
	SPB23	34.05	90.2	0.0137	137.20	0.87	0.1659	1659.18	8.1	832.3
	SPB24	35.45	90.8	0.0167	166.83		0.1307	1307.00	5.6	866.0
	SPB25	38.15	93.6	0.0286	286.22	-3.84	0.1771	1770.70	9.1	931.0

Table A-9. Sulphur content and isotopic compositions of southern Pennine pool peat (P-1)

	Sample	Depth	% water	%S-InorgS	InorgS-mg/kg	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS	mean age
P 1	SPE1A	3.00					0.1723	1723.11	4.29	50.7
	SPE1B	7.00					0.1597	1597.39	2.95	118.3
	SPE2	10.25	97.7	0.0351	350.60	-0.12	0.2944	2943.96	3.220754	173.2
	SPE3	12.75	94.1	0.0304	304.27	0.74	0.2811	2811.34	1.280106	215.5
	SPE4	15.25	94.9	0.0766	765.54	0.28	0.4131	4130.80	0.235953	257.7
	SPE5	17.75	91.1	0.0378	378.45	-0.83	0.2737	2736.72	-1.261721	300.0
	SPE6	20.25	93.0	0.0756	755.80	-1.87	0.5860	5860.37	-1.894541	342.2
	SPE7	22.75	93.5	0.1300	1300.28	-2.08	0.6636	6636.45	-2.147669	384.5
	SPE8	25.25	91.3	0.1072	1072.19	-2.73	0.6516	6516.04	-2.263686	426.7
	SPE9	27.75	91.0	0.0723	722.91	-2.69	0.6145	6144.57	-1.588678	469.0
	SPE10	30.25	89.8	0.0814	814.27	-1.50	0.4505	4504.67	0.446893	511.2
	SPE11	32.75	85.3	0.0737	737.31	-0.52	0.4157	4156.50	0.636739	553.5
	SPE12	35.25	85.7	0.0657	656.55	0.67	0.2295	2294.90	1.712533	595.7
	SPE13	37.75	86.4	0.0365	365.17	0.81	0.3462	3462.04	2.482464	638.0
	SPE14	40.25	86.5	0.0489	489.28		0.0979	979.17	3.062549	680.2

Table A-10. Sulphur content, isotopic compositions and calculated mean age of southern Pennine pool peat (P-2)

	Sample	Depth	% water	%S-InorgS	InorgS-mg/kg	δ^{34}S-InorgS	%S-OrgS	Org-S mg/kg	δ^{34}S-OrgS
P 2	SPF1A	3.00					0.2389	2389.13	6.17
	SPF1B	7.00					0.2866	2866.27	4.52
	SPF2	10.25	93.8	0.0567	567.34	0.35	0.2516	2515.65	1.353935
	SPF3	12.75	91.8	0.0457	457.29	-0.25	0.4869	4868.81	-0.059363
	SPF4	15.25	94.4	0.1348	1347.85	-1.81			
	SPF5	17.75	91.0	0.0830	830.16	-1.17	0.5612	5612.32	-1.54649
	SPF6	20.25	85.5	0.0978	978.36	-1.47	0.6641	6641.19	-0.533978
	SPF7	22.75	81.5	0.0777	776.57	-1.30	0.6579	6579.19	0.584004
	SPF8	25.25	84.4	0.0827	826.61	-1.28	0.5829	5829.45	2.007849
	SPF9	27.75	86.6	0.0826	826.14	0.17	0.5168	5167.76	3.09419
	SPF10	30.25	91.7	0.0698	698.16	-1.48	0.1246	1245.66	3.104737
	SPF11	32.75	89.1	0.0403	402.63	0.67	0.0644	643.75	4.328189
	SPF12	35.25	86.7	0.0542	541.92	3.36	0.0734	733.93	5.910239
	SPF13	37.75	83.8	0.0376	376.35	4.85	0.1106	1105.56	6.827828
	SPF14	40.25	90.3	0.0608	608.20	6.05	0.0380	380.34	7.882528

Table A-11. Non-arboreal pollen compositions (%) in southern Pennine high ridge hummock peat (HR-1)

Sample	Depth (cm)	*Sphagnum*	*Ericaceae*	*Cyperaceae*	*Graminae*	*Plantago*	*Chenopodiaceae*	*Rumex*	*Compositae*	*Lycopodium*	*lactucae*	*Total NAP*
SPC2	3.8	7.9	13.5	76.6	0.8	0.5	0.5	0.3	0.0	0.0	0.0	393
SPC3	5.5	15.0	34.0	49.0	1.0	0.5	0.3	0.0	0.3	0.0	0.0	394
A2	6.7	25.4	50.2	14.1	16.6	0.4	4.1	0.0	0.4	0.0	0.0	241
A3	8.0	15.6	53.9	28.5	0.8	0.4	0.8	0.0	0.4	0.0	0.0	256
A4	9.4	11.4	72.2	12.1	1.8	1.4	0.0	0.4	0.7	0.0	0.0	281
A5	10.7	36.0	29.1	32.7	1.1	0.6	0.0	0.3	0.3	0.0	0.0	361
A6	12.1	61.9	33.7	2.7	0.5	0.5	0.2	0.2	0.2	0.0	0.0	409
A7	13.5	36.6	55.7	2.9	1.5	0.7	1.5	0.0	1.1	0.0	0.0	273
A8	14.8	73.8	23.4	1.1	0.3	0.6	0.6	0.0	0.3	0.0	0.0	363
A9	16.2	24.8	69.8	2.2	0.7	1.1	0.4	0.0	1.1	0.0	0.0	278
A10	17.5	31.8	64.0	2.5	1.1	0.4	0.4	0.0	0.0	0.0	0.0	283
A11	18.9	68.7	17.0	0.4	0.2	0.2	0.0	0.0	0.0	13.5	0.0	483
A12	20.2	72.3	16.2	0.6	0.2	1.0	0.2	0.0	0.0	9.5	0.0	487
A13	21.6	60.1	25.8	1.4	0.2	0.2	0.0	0.0	0.0	12.3	0.0	489
A14	23.0	65.5	27.0	1.2	0.2	0.0	0.2	0.0	0.0	5.9	0.0	426
A15	24.3	74.1	11.5	0.4	0.0	0.0	0.6	0.0	0.0	13.3	0.0	510
A16	26.8	77.9	3.2	0.6	0.0	0.0	0.2	0.0	0.0	18.2	0.0	539
B1	29.3	40.5	47.7	3.2	0.0	0.0	3.2	0.0	1.4	4.1	0.0	220
B2	30.6	58.7	25.8	0.4	0.4	0.4	0.0	0.0	0.0	13.7	0.4	453
B3	32.0	52.2	43.3	1.0	1.0	1.0	0.3	0.3	0.3	0.3	0.3	314
B4	33.3	39.6	57.5	2.2	0.6	0.0	0.0	0.0	0.0	0.0	0.0	313
B5	34.7	31.5	64.2	1.5	0.0	0.9	1.2	0.3	0.0	0.0	0.3	327
B6	36.1	33.1	60.6	0.6	3.0	1.1	0.8	0.6	0.3	0.0	0.0	363
B7	37.4	32.2	60.5	12.9	3.5	1.0	0.3	0.6	0.6	0.0	0.0	311
B8	38.8	62.6	3.2	1.2	0.0	1.0	0.0	1.5	0.0	0.0	0.0	406
B9	40.1	13.6	73.9	1.1	2.1	1.1	0.8	1.1	1.1	5.1	0.3	376
B10	41.5	6.5	86.7	0.5	2.2	2.2	0.0	0.5	0.8	0.3	0.3	367
B11	42.8	22.2	68.9	3.3	3.3	1.3	0.0	0.3	0.5	0.3	0.0	392
B12	44.2	27.8	47.9	14.0	2.0	4.0	1.2	1.7	0.0	1.4	0.0	349
B13	45.6	31.4	57.6	2.4	5.2	1.8	0.0	0.3	0.9	0.3	0.0	328
B14	46.9	11.8	76.0	1.0	4.9	3.0	0.0	1.6	1.0	0.7	0.0	304
B15	48.3	20.9	68.2	2.7	1.8	5.5	0.0	0.0	0.0	0.9	0.0	110

Table A-12. Arboreal pollen compositions (%) in southern Pennine high ridge hummock peat (HR-1)

Sample	Depth (cm)	*Corylus*	*Betula*	*Alnus*	*Quercus*	*Ulmus*	*Fraxinus*	*Salix*	*Tilia*	*Pinus*	*Carpinus*	*Juniper*	Total AP
SPC2	3.8	21.0	12.4	21.9	23.8	7.6	6.7	0.0	0.0	3.8	0.0	2.9	105
SPC3	5.5	26.2	8.4	18.7	21.5	8.4	9.4	0.0	1.9	5.6	0.0	0.0	93
A2	6.7	44.3	11.3	30.9	11.0	0.0	2.1	0.0	0.3	0.0	0.0	0.0	291
A3	8.0	44.8	10.8	28.8	9.0	2.4	3.1	0.0	0.7	0.4	0.0	0.0	288
A4	9.4	50.6	8.2	28.0	7.0	0.0	3.1	0.8	0.8	0.8	0.0	0.0	257
A5	10.7	43.2	13.6	32.0	6.8	0.0	2.9	1.0	0.5	0.0	0.0	0.0	206
A6	12.1	58.9	6.5	10.3	13.1	0.0	9.4	1.9	0.0	0.0	0.0	0.0	107
A7	13.5	53.5	4.9	24.8	10.6	0.4	4.0	0.9	0.0	0.9	0.0	0.0	226
A8	14.8	54.9	3.9	27.7	7.1	1.9	3.2	0.0	0.0	1.3	0.0	0.0	155
A9	16.2	51.2	6.0	26.6	10.7	0.8	4.4	0.0	0.4	0.0	0.0	0.0	252
A10	17.5	60.1	4.0	21.1	11.8	0.0	1.3	0.4	0.0	1.3	0.0	0.0	228
A11	18.9	48.1	3.9	28.9	13.5	0.0	5.8	0.0	0.0	0.0	0.0	0.0	104
A12	20.2	40.9	6.8	17.1	23.9	1.1	9.1	0.0	1.1	0.0	0.0	0.0	88
A13	21.6	39.8	11.0	22.0	15.3	0.9	5.1	3.4	0.9	0.9	0.0	0.0	118
A14	23.0	46.0	9.0	19.8	15.3	1.8	5.4	1.8	0.0	0.9	0.0	0.0	111
A15	24.3	38.2	10.8	23.5	21.6	1.0	2.9	2.0	0.0	0.0	0.0	0.0	102
A16	26.8	31.8	22.2	28.6	11.1	0.0	0.0	6.4	0.0	0.0	0.0	0.0	63
B1	29.3	41.7	13.7	25.0	13.0	1.0	4.0	1.3	0.0	0.3	0.0	0.0	300
B2	30.6	28.3	10.1	35.5	17.4	0.7	5.1	2.2	0.0	0.7	0.0	0.0	138
B3	32.0	38.0	8.0	28.0	16.8	2.0	4.5	0.5	0.0	0.0	1.0	0.0	200
B4	33.3	52.0	61.2	25.0	12.2	1.0	2.6	0.0	0.5	0.5	0.0	0.0	196
B5	34.7	43.4	6.8	23.8	19.6	2.1	4.3	0.0	0.0	0.0	0.0	0.0	235
B6	36.1	37.0	5.5	21.9	26.0	3.4	4.1	1.4	0.0	0.7	0.0	0.0	146
B7	37.4	38.7	6.8	30.0	14.0	0.5	6.8	2.9	0.0	0.5	0.0	0.0	207
B8	38.8	37.8	1.0	26.5	27.6	0.0	6.1	1.0	0.0	0.0	0.0	0.0	98
B9	40.1	29.8	4.8	27.4	32.1	2.4	2.4	1.2	0.0	0.0	0.0	0.0	84
B10	41.5	36.2	3.6	22.5	29.7	0.0	5.8	0.7	0.0	1.5	0.0	0.0	138
B11	42.8	32.8	0.0	32.0	31.2	0.0	1.6	2.4	0.0	0.0	0.0	0.0	125
B12	44.2	45.4	2.0	23.0	17.8	2.6	5.3	1.3	0.0	2.6	0.0	0.0	152
B13	45.6	22.6	3.7	23.4	38.7	1.5	8.0	1.5	0.0	0.7	0.0	0.0	137
B14	46.9	41.2	2.6	25.0	25.5	2.1	0.5	2.1	0.0	1.0	0.0	0.0	192
B15	48.3	28.1	1.8	21.1	38.6	0.0	1.8	5.3	0.0	3.5	0.0	0.0	57

Table A-13. Compiled data for arboreal and non-arboreal pollen compositions in southern Pennine high ridge hummock peat (HR-1)

Sample	Depth (cm)	Total AP	Total NAP	Total	%AP	%NAP	no of NAP taxon	no of AP taxon	Taxon number
SPC2	3.8	105	393	498	21.1	78.9	8	7	15
SPC3	5.5	93	394	487	19.1	80.9	7	9	16
A2	6.7	291	241	532	54.7	45.3	7	6	13
A3	8.0	288	256	544	52.9	47.1	7	8	15
A4	9.4	257	281	538	47.8	52.2	7	9	16
A5	10.7	206	361	567	36.3	63.7	7	7	14
A6	12.1	107	409	516	20.7	79.3	8	6	14
A7	13.5	226	273	499	45.9	54.1	7	8	15
A8	14.8	155	363	518	29.9	70.1	7	7	14
A9	16.2	252	278	530	47.6	52.5	7	6	13
A10	17.5	228	283	511	44.6	55.4	7	7	14
A11	18.9	104	483	587	17.7	82.3	6	5	11
A12	20.2	88	487	575	15.3	84.7	7	7	14
A13	21.6	118	489	607	19.4	80.6	6	9	15
A14	23.0	111	426	537	20.7	79.3	6	8	14
A15	24.3	102	510	612	16.7	83.3	5	7	12
A16	26.8	63	539	602	10.5	89.5	5	5	10
B1	29.3	300	220	520	57.7	42.3	6	8	14
B2	30.6	138	453	590	23.4	76.6	7	8	15
B3	32.0	200	314	514	38.9	61.1	10	9	19
B4	33.3	196	313	509	38.5	61.5	4	8	12
B5	34.7	235	327	562	41.8	58.2	7	6	13
B6	36.1	146	363	509	28.7	71.3	8	8	16
B7	37.4	207	311	518	40.0	60.0	8	8	16
B8	38.8	98	406	504	19.4	80.6	5	6	11
B9	40.1	84	376	460	18.3	81.7	10	7	17
B10	41.5	138	367	505	27.3	72.7	8	7	15
B11	42.8	125	392	517	24.2	75.8	8	5	13
B12	44.2	152	349	501	30.3	69.7	8	8	16
B13	45.6	137	328	465	29.5	70.5	8	8	16
B14	46.9	192	304	496	38.7	61.3	8	8	16
B15	48.3	57	110	167	34.1	65.9	6	8	14

Table A-14. Sulphur content and isotopic compositions in Thorne moors control peat

	Sample	mean depth	% water	%S-InorgS	InorgS mg/kg	δ^{34}S-InorgS	%S-OrgS	OrgS mg/kg	δ^{34}S-OrgS
TCA	TCA1A	3					0.2634	2634.4	2.20
	TCA1B	8					0.1737	1736.8	1.95
	TCA 2	11.25	97.07	0.0691	691.0	3.30	0.5316	5315.8	3.10
	TCA 3	13.75	95.38	0.0907	907.2	3.10	0.6658	6657.9	3.42
	TCA 4	16.25	98.11	0.2789	2789.3	4.37	1.6094	16093.7	3.06
	TCA 5	18.75	98.20	0.2029	2028.8	6.35	0.7472	7471.9	2.75
	TCA 6	21.25	98.04	0.3697	3696.5	7.42	0.3855	3854.7	1.30
	TCA 7	23.75	97.50	0.2798	2798.3	4.76	0.8617	8617.5	1.30
	TCA 8	26.25	97.46	0.2761	2761.0	5.60	0.6837	6836.9	0.84
	TCA 9	28.75	93.86	0.0777	777.5	4.66	0.7758	7758.3	0.82
	TCA 10	31.25	95.39	0.5787	5787.3	5.75	0.4149	4149.4	0.39
	TCA 11	33.75	94.42	0.1576	1576.2	2.87	0.3806	3805.5	0.13
	TCA 12	36.25	94.75	0.6209	6209.0	3.03	0.3835	3835.1	-0.56
	TCA 13	38.75	93.16	0.2383	2383.5	2.48	1.2541	12540.7	0.67
	TCA 14	41.25	92.72	0.2988	2987.9	0.97	0.4335	4335.4	1.18
	TCA 15	43.75	91.41	0.1946	1946.1		0.6802	6802.4	0.79
	TCA 16	46.25	93.81	0.3752	3752.1				
TCB	TCB1A	4					0.1152	1151.6	0.51
	TCB1B	7					0.6035	6034.7	0.26
	TCB 2	14	93.00	0.0918	918.2	-1.66	0.7060	7060.0	5.98
	TCB 3	16.5	95.00	0.2126	2126.0	0.53	1.3133	13133.4	0.69
	TCB 4	19	93.00	0.1741	1741.3	0.17	0.7818	7818.3	-1.10
	TCB 5	21.5	97.00	0.1007	1006.5	1.21	1.1236	11235.9	-0.40
	TCB 6	24	96.00	0.2439	2438.7	0.52	1.4920	14919.7	1.18
	TCB 7	26.5	93.00	0.1000	1000.2	0.53	1.1290	11289.8	2.08
	TCB 8	29	94.00	0.0419	418.7	1.22	0.8001	8000.8	7.10
	TCB 9	31.5	93.00	0.0230	230.1	1.25	0.6620	6620.2	7.09
	TCB 10	34	95.00	0.0515	514.5	0.89	0.8706	8705.8	4.24
	TCB 11	36.5	93.00	0.0780	780.5	1.16	0.9071	9070.6	5.85
	TCB 12	39	92.00	0.0465	465.0	1.48	1.2188	12187.6	4.62
	TCB 13	41.5	91.00	0.0440	439.8	1.60	0.9556	9555.5	4.54
	TCB 14	44	96.00	0.0625	624.7	1.18	1.0392	10392.3	2.82
	TCB 15	46.5	92.00	0.0555	555.1	1.51	1.2763	12763.2	2.74
TCC	TCC1A	5					0.3729	3729.1	0.73
	TCC1B	10					0.4930	4929.6	0.34
	TCC 2	15.25	97.47	0.1719	1719.0	0.34	1.4266	14265.8	0.82
	TCC 3	17.75	98.71	0.5660	5659.6	0.25	0.8095	8094.5	0.16
	TCC 4	20.25	97.95	0.8382	8381.7	-0.90	1.0787	10787.4	-0.39
	TCC 5	22.75	97.95	1.0010	10010.0	-0.73	1.0365	10365.1	-0.76
	TCC 6	25.25	97.03	1.0124	10123.6	-1.04	1.0454	10454.4	-0.88
	TCC 7	27.75	96.07	1.4214	14213.9	-1.82	1.1104	11104.4	-1.97
	TCC 8	30.25	93.29	0.7869	7868.6	-3.66	0.8781	8781.2	-2.22
	TCC 9	32.75	89.36	0.4901	4900.7	-4.21	1.0864	10864.1	-2.11
	TCC 10	35.25	90.50	0.6568	6568.3	-4.25	0.8630	8629.9	-1.98
	TCC 11	37.75	92.86	0.4108	4108.0	-2.95	1.0835	10834.6	-1.66

Table A-15. Sulphur content and isotopic compositions in enriched peat (3 months)

		Sample	Depth	% water	%S-InorgS	InorgS mg/kg	δ^{34}S-InorgS	%S-OrgS	OrgS mg/kg	δ^{34}S-OrgS
3 months	**1A1**	1A1/1	7.75					0.6550	6550.50	69.30
		1A1/2	11.25	98.9	0.1540	1539.65	102.04	0.8256	8255.85	20.66
		1A1/3	13.75	98.1	0.1197	1196.99	54.79	0.6370	6369.74	9.78
		1A1/4	16.25	96.6	0.0869	868.89	33.86	1.0228	10228.32	8.56
		1A1/5	18.75	95.8	0.0666	666.46	20.95	0.9596	9595.59	3.98
		1A1/6	21.25	93.9	0.0781	780.51	5.99	0.9234	9234.17	-0.45
		1A1/7	23.75	95.7	0.5132	5131.94	0.67	1.3689	13689.07	-2.44
		1A1/8	26.25	96.4	0.2557	2557.43	-0.44	1.0409	10408.90	-0.64
		1A1/9	28.75	93.8	0.1744	1744.13	-1.25	1.2313	12313.15	-1.96
		1A1/10	30.25	94.2	0.1302	1301.67	-1.73	0.9266	9266.07	-0.43
		1A1/11	32.75	96.4			-2.94	0.9412	9412.48	-2.45
		1A1/12	35.25	92.9	0.1479	1479.43	-2.69	1.0807	10806.67	1.86
		1A1/13	37.75	93.4	0.1468	1468.25	-1.62	1.0603	10602.69	1.06
	1A2	1A2/2	3.75	99.1	0.0463	463.13	4.37	1.0884	10883.67	4.31
		1A2/3	6.25	97.7	0.0647	647.30	5.30	1.2076	12075.86	3.59
		1A2/4	8.75	97.9	0.0752	751.56	8.04	0.6806	6805.53	7.47
		1A2/5	11.25	98.2	0.0675	675.21	2.03	0.8256	8255.85	1.40
		1A2/6	13.75	92.7	0.0337	336.77	1.13	0.8578	8578.13	-0.86
		1A2/7	16.25	98.8	0.4526	4525.91	1.22	1.4153	14152.96	-0.65
		1A2/8	18.75	98.1	0.3473	3473.45	1.41	1.0435	10435.25	-1.65
		1A2/9	21.25	95.2	0.4359	4359.13	-1.10	1.1729	11729.23	-2.06
		1A2/10	23.75	91.6	0.4969	4968.62	-1.83	1.3564	13564.14	-2.56
		1A2/11	26.25	92.4	0.9330	9329.85	-1.56	1.4559	14558.65	-2.91
		1A2/12	28.75	90.0	0.1557	1557.39	-2.35	1.1069	11069.27	-2.33
		1A2/13	31.25	92.6	0.5924	5924.28	-2.67	1.0951	10951.04	-1.92
		1A2/14	33.75	91.4	0.2478	2477.61	-3.35	0.9443	9443.24	-1.12
		1A2/15	36.25	90.9	0.4285	4284.85	-1.98	0.9718	9718.48	-1.72
	2A1	2A1/1A	3.25					0.2174	2174.31	142.02
		2A1/1B	8.75					0.4687	4687.34	51.63
		2A1/2	14.25	94.5	0.1426	1426.19	5.02	0.5657	5656.92	3.15
		2A1/3	16.75	96.9	1.3166	13165.64	2.19	0.8869	8869.09	0.13
		2A1/4	19.25	95.4	0.4902	4902.35	1.65	1.1776	11775.76	-0.69
		2A1/5	21.75	91.7	0.2749	2748.55	2.45	0.9959	9958.81	-0.04
		2A1/6	24.25	88.6			2.08	1.1630	11630.36	0.27
		2A1/7	26.75	91.5	0.6125	6125.30	2.07	1.0588	10587.85	-0.90
		2A1/8	29.25	90.8	0.4963	4962.90	1.42	1.2296	12296.28	-0.48
		2A1/9	31.75	89.2			1.25	1.0849	10849.33	-1.09
		2A1/10	34.25	87.9	0.7295	7295.35	0.12	1.5105	15104.80	-0.99
		2A1/11	36.75	90.7	1.3446	13445.81	-1.25	1.7519	17519.11	-0.90
		2A1/12	39.25	88.9	0.7987	7987.10	-4.00	1.6116	16116.24	-1.09
		2A1/13	41.75	91.9	0.7557	7556.84	-2.44	1.0721	10720.65	0.06
	2A2	2A2/1A	5.25					0.5958	5958.46	69.50
		2A2/1B	9.75					0.8060	8060.08	12.65
		2A2/2	14.25	97.5	0.1688	1687.96	22.70	0.5155	5154.84	17.11
		2A2/3	16.75	98.7	0.7796	7796.42	5.98	1.0649	10649.03	4.48
		2A2/4	19.25	96.5	0.3232	3232.37	4.11	0.9192	9191.52	2.84
		2A2/5	21.75	96.8	2.3069	23069.14	4.22	1.2946	12946.38	1.11
		2A2/6	24.25	95.8	0.3050	3050.34	2.50	1.0972	10972.12	0.56
		2A2/7	26.75	95.3	0.3574	3574.23	2.28	0.9433	9433.18	0.96
		2A2/8	29.25	94.8	0.5370	5370.35	1.96	1.0873	10872.63	-0.43
		2A2/9	31.75	95.3	0.3922	3921.87	1.34	0.9950	9949.71	-0.91
		2A2/10	34.25	92.2	0.2485	2485.04	0.82	1.0575	10575.17	-1.40
		2A2/11	36.75	95.9	0.4989	4988.95	1.90	1.2003	12002.71	0.85

Table A-16. Sulphur content and isotopic compositions in enriched peat (6 months)

		Sample	Depth	% water	%S-InorgS	InorgS mg/kg	δ^{34}S-InorgS	%S-OrgS	OrgS mg/kg	δ^{34}S-OrgS
6 months	**1B1**	1B1/1	10.5					0.3839	3838.83	56.79
		1B1/2	15.25	97.2	0.0245	245.23		0.5113	5113.41	12.27
		1B1/3	17.75	98.1	0.1303	1302.73	20.45	0.9000	8999.86	3.82
		1B1/4	20.25	96.5	0.0547	546.54	6.95	0.9825	9825.39	1.40
		1B1/5	22.75	95.7	0.0576	575.57	7.60	1.0644	10643.64	0.18
		1B1/6	25.25	93.3	0.0548	548.36	0.25	1.2732	12732.29	-1.20
		1B1/7	27.75	96.1	1.0462	10461.71	-2.87	1.2473	12473.10	-2.45
		1B1/8	30.25	94.0	0.1310	1310.34	-4.36	1.5312	15312.10	-2.02
		1B1/9	32.75	94.3	0.5115	5114.53	-5.66	1.2408	12407.89	-2.54
		1B1/10	35.25	91.5	0.3954	3953.77	-5.19	1.3533	13532.89	-3.35
	1B2	1B2/1	4.75					0.3430	3430.43	60.27
		1B2/2	11.25	98.6	0.0873	872.65		0.2846	2846.36	44.86
		1B2/3	13.75	98.4	0.1213	1213.25		0.3850	3850.02	22.86
		1B2/4	16.25	98.1	0.0290	289.77	81.75	0.5150	5150.00	14.73
		1B2/5	18.75	98.7	0.1073	1072.74	43.01	0.5840	5840.23	7.18
		1B2/6	21.25	97.5	0.0357	356.73	20.29	0.6627	6626.79	2.65
		1B2/7	23.75	95.8	0.0363	362.94	6.30	0.7340	7340.31	-0.15
		1B2/8	26.25	97.3	0.1505	1504.76	1.95	1.0702	10702.02	-1.65
		1B2/9	28.75	95.5	0.2294	2293.85	-0.52	1.2449	12448.76	-2.16
		1B2/10	31.25	94.5	0.1050	1049.59	-0.31	1.1004	11004.06	-3.29
		1B2/11	33.75	94.4	0.1564	1564.07	-1.57	1.1131	11130.57	-2.86
		1B2/12	36.25	91.2	0.2243	2243.24	-1.96	0.9474	9473.63	-1.52
		1B2/13	38.75	94.3	0.7633	7633.06	0.16	0.9895	9895.28	-2.48
	2B1	2B1/1	7.75	86.8				0.3928	3928.18	69.74
		2B1/2	11.25	92.9	0.1112	1111.77	20.80	0.4763	4762.84	7.10
		2B1/3	13.75	97.6	0.5623	5622.65		0.8496	8495.57	2.34
		2B1/4	16.25	96.4	0.4458	4457.60	4.90	0.0961	960.84	1.80
		2B1/5	18.75	95.7	0.2822	2821.85		1.2204	12203.76	-0.45
		2B1/6	21.25	96.3	0.4305	4304.98	1.50	0.4865	4865.10	1.20
		2B1/7	23.75	94.5	1.2707	12706.76	7.52	0.9921	9920.98	1.25
		2B1/8	26.25	94.5	0.4375	4374.79	0.90	0.2829	2829.37	2.70
		2B1/9	28.75	91.6	0.1846	1845.78		1.0436	10436.41	3.96
		2B1/10	31.25	94.7	0.3382	3382.06	2.20	0.3168	3168.11	4.20
		2B1/11	33.75	92.4	0.3183	3183.30	1.82	1.0592	10591.76	4.20
		2B1/12	36.25	90.2	0.1291	1290.62	2.70	0.2195	2194.87	5.10
		2B1/13	38.75	92.9	0.1786	1786.37		0.6578	6577.89	4.80
	2B2	2B2/1	3.75					0.5309	5309.41	61.56
		2B2/2	8.25	95.9	0.1341	1341.39	21.11	0.6579	6579.31	7.68
		2B2/3	10.75	97.9	0.2335	2334.93		0.7040	7039.58	4.68
		2B2/4	13.25	95.4	0.2222	2221.59	3.81	1.0972	10972.28	0.49
		2B2/5	15.75	96.3	0.1550	1549.72	2.46	1.1762	11762.31	1.12
		2B2/6	18.25	95.1	0.5187	5187.40	2.19	0.6302	6301.71	0.95
		2B2/7	20.75	95.0	0.0981	980.99	1.09	1.2463	12463.29	2.11
		2B2/8	23.25	91.9	0.1616	1616.07	-0.29	1.2735	12735.49	4.07
		2B2/9	25.75	91.2	0.1690	1689.89	1.45	1.2267	12266.63	-0.55
		2B2/10	28.25	91.7	0.4223	4222.96	3.47	1.2123	12123.00	2.05
		2B2/11	30.75	90.1	0.2393	2392.92	3.77	1.0341	10340.63	3.26
		2B2/12	33.25	91.4	0.5722	5722.45	4.32	0.9468	9467.97	3.87
		2B2/13	35.75	92.5	0.1738	1738.46	4.73	0.7190	7190.28	5.58
		2B2/14	38.25	92.1	0.2370	2370.07	5.39	0.5922	5922.04	4.47

Table A-17. Sulphur content and isotopic compositions in enriched peat (12 months)

		Sample	Depth	% water	%S-InorgS	InorgS mg/kg	δ^{34}S-InorgS	%S-OrgS	OrgS mg/kg	δ^{34}S-OrgS
12 months	**1C1**	1C1/1A	4.25					0.2293	2293.21	212.42
		1C1/1B	7.75					0.3999	3999.44	108.42
		1C1/2	11.25	93.3	0.1677	1677.00	18.20	1.0004	10003.89	5.49
		1C1/3	13.75	98.2	0.3671	3671.35	8.45	0.9570	9570.35	3.62
		1C1/4	16.25	98.7	1.6502	16502.34	4.47	1.4240	14240.49	2.16
		1C1/5	18.75	98.6	1.4476	14475.71	3.71	1.1582	11582.27	2.96
		1C1/6	21.25	97.2	0.5546	5546.32	1.87	1.3889	13888.55	1.46
		1C1/7	23.75	97.0	0.6725	6724.61	0.36	1.0709	10708.93	0.41
		1C1/8	26.25	97.0	1.0357	10356.65	-1.39	1.1630	11630.16	-0.74
		1C1/9	28.75	96.4	0.3376	3376.44	-2.46	1.1013	11013.32	-1.49
		1C1/10	31.25	92.1	0.1066	1066.47	-2.50	1.3554	13554.20	-1.36
		1C1/11	33.75	91.3	0.4053	4052.59	-1.94	1.2400	12399.65	-1.63
		1C1/12	36.25	88.3	0.6036	6036.33	-4.77	1.0497	10496.72	-2.12
		1C1/13	38.75	94.4	0.4992	4991.69	-2.56	0.8278	8278.45	-0.50
	1C2	1C2/1	3.25	93.0						213.88
		1C2/2	6.5	92.0	0.0183	183.17		0.4053	4053.04	111.64
		1C2/3	9	93.0	0.0148	147.82		0.4325	4324.78	97.91
		1C2/4	11.5	89.0	0.0118	117.64		0.9005	9005.45	53.97
		1C2/5	14	91.0	0.0191	190.75	108.83	1.3078	13077.53	20.56
		1C2/6	16.5	93.0	0.0407	406.76	69.65	1.0169	10169.39	15.18
		1C2/7	19	94.0	0.0572	572.09	12.03	1.2822	12821.69	4.18
		1C2/8	21.5	93.0	0.0939	938.85	6.29	1.4284	14284.30	2.50
		1C2/9	24	95.0	0.1449	1449.33	2.58	1.5591	15590.72	0.99
		1C2/10	26.5	93.0	0.2920	2920.01	-0.27	1.7524	17523.91	-0.12
		1C2/11	29	92.0	0.2128	2127.62	-3.90	1.5897	15897.21	-2.16
		1C2/12	31.5	91.0	0.2402	2402.30	-3.27	1.7655	17655.44	-2.41
		1C2/13	34	92.0	0.3226	3226.04	-2.72	1.7190	17190.11	-1.66
		1C2/14	36.5	91.0	0.1830	1829.81	-2.71	1.6768	16767.75	-2.31
	2C1	2C1/1A	2.35					0.1948	1947.58	430.54
		2C1/1B	5.75					0.5259	5258.58	134.08
		2C1/2	7.25	95.4	0.0734	733.90	62.00	0.9468	9468.40	13.94
		2C1/3	9.75	90.8	0.0988	987.69	15.14	1.0553	10552.87	4.98
		2C1/4	12.25	93.1	0.5193	5193.17	5.26	1.0119	10118.64	1.51
		2C1/5	14.75	91.7	0.8941	8941.46	-1.16	1.2296	12296.32	-0.97
		2C1/6	17.25	90.9	0.2404	2403.64	-0.42	1.6444	16443.68	0.20
		2C1/7	19.75	92.0	0.9601	9600.98	-1.53	1.4239	14239.15	0.13
		2C1/8	22.25	92.8	0.4142	4142.08	-0.05	1.1322	11321.66	3.21
		2C1/9	24.75	94.9	0.3485	3484.53	-2.23	1.1082	11081.66	3.04
		2C1/10	27.25	85.3	0.1073	1073.41	-0.44	0.6821	6820.71	3.47
		2C1/11	29.75	90.0	0.0743	742.93	2.11	0.9661	9661.27	4.19
		2C1/12	32.25		0.0188	187.69	3.59	0.4369	4369.22	4.74
	2C2	2C2/1	4.75					0.3760	3759.70	175.64
		2C2/2	7.25	96.7	0.1430	1429.94	96.36	0.5997	5997.41	33.49
		2C2/3	9.75	95.6	0.1471	1471.13	41.99	1.0026	10026.21	10.33
		2C2/4	12.25	93.5	0.2224	2223.68	12.92	0.8015	8015.27	6.10
		2C2/5	14.75	90.5	0.4895	4894.64	3.54	1.4841	14841.38	1.52
		2C2/6	17.25	90.6	0.4911	4910.59	0.50	1.1369	11369.35	-0.35
		2C2/7	19.75	93.4	0.8069	8069.21	-1.22	1.5365	15365.47	-1.40
		2C2/8	22.25	94.0	0.9112	9112.28	-3.03	1.4064	14064.29	-1.65
		2C2/9	24.75	93.6	1.1073	11072.72	-1.46	1.2301	12300.93	-1.31
		2C2/10	27.25	92.1	0.5088	5088.22	-2.70	1.1257	11256.69	-1.07
		2C2/11	29.75	94.3	0.5037	5036.60	-2.30	0.9542	9541.88	1.78
		2C2/12	32.25	95.5	0.4078	4078.25	1.03	0.6395	6394.83	5.93
		2C2/13	34.75	94.2	0.1791	1790.56	3.46	0.3943	3942.56	7.24
		2C2/14	37.25	93.4	0.1157	1157.13	5.61	0.3788	3788.00	7.83

Appendix B Peatland Vegetation

Table B-1. Water content, sulphur content and isotopic composition of peatland vegetation

Site	Species	Sample	Water content (%)	Sulphur content (%)	$\delta^{34}S$
S. Pennines	*Sphagnum recurvum*	ST1	92.3	0.11	1.94
		ST2	93.5	0.15	2.14
		ST3	94.4	0.14	2.75
		ST4	94.1	0.14	2.60
		ST5	93.3	0.14	2.25
		ST6	93.2	0.15	2.11
		ST7	94.6	0.09	2.75
		ST8	95.0	0.06	2.52
		ST9	94.7	0.06	2.76
		ST10	95.7	0.07	2.81
		ST11	94.1	0.05	1.93
		ST12	95.0	0.07	1.66
		ST13	95.0	0.10	1.94
		ST14	95.7	0.07	2.24
		ST15	94.6	0.07	2.24
		ST16	93.5	0.19	1.61
		ST17	95.3	0.10	1.22
		ST18	94.7	0.07	2.10
	Eriophorum vaginatum	ET1	53.8	0.09	2.79
		ET2	58.3	0.09	1.62
		ET3	54.5	0.18	1.49
		ET4	58.3	0.13	1.96
		ET5	60.0	0.17	1.93
		ET6	50.0	0.10	3.74
		ET7	40.0	0.10	2.48
		ET8	61.5	0.11	1.76
		ET9	60.0	0.09	1.45
		ET10	77.8	0.09	1.30
		ET11	66.7	0.12	2.42
		ET12	68.4	0.12	-0.23
		ET13	72.7	0.09	0.84
		ET14	66.7	0.16	1.47
		ET15	73.3	0.08	0.90
		ET16	69.6	0.07	0.76
		ET17	66.7	0.08	1.69
		ET18	54.5	0.09	1.92
Forsinard	*Sphagnum*	FS1		0.17	11.29
		FS2		0.22	12.71
		FS3		0.15	12.38
		FS4		0.18	13.55
		FS5		0.13	13.29
		FS6		0.28	13.53
		FS7		0.13	14.67
		FS8		0.23	14.60
		FS9		0.17	14.26
		FS10		0.16	13.48
		FS11		0.22	13.07
		FS12		0.23	14.49
Shetland	*Sphagnum*	L1S			9.02
		L2S			8.55
		L3S			9.22
		L4S			8.92
	Eriophorum vaginatum	L1G			12.47
		L2G			9.95

Abisko	***Sphagnum fuscum***	ASF1		0.21	5.72
		ASF2		0.11	6.62
		ASF3		0.07	6.70
		ASF4		0.04	6.50
		ASF5		0.05	6.61
	Sphagnum girgenshoii	ASG1		0.07	7.84
		ASG2		0.06	7.24
		ASG3		0.06	7.70
		ASG4		0.06	8.05
		ASG5		0.06	7.77
Thorne (controls)	***Sphagnum recurvum***	S3-1	94.8	0.06	2.4552
		S3-2	93.3	0.07	1.9404
		S3-3	80.4	0.08	1.4143
		S3-4	92.8	0.11	2.0635
		S3-5	87.0	0.11	1.7837
		S3-6	89.1	0.10	1.8285
		S3-7	92.0	0.08	2.3992
		S3-8	91.0	0.14	2.1642
		S3-9	89.0	0.14	1.5039
		S3-10	91.0	0.14	2.0971
		S3-11	90.0	0.09	1.2241
		S3-12	89.0	0.11	1.9628
	Eriophorum vaginatum	E3-1	73.0	0.27	-0.598
		E3-2	57.0	0.14	-0.757
		E3-3	66.0	0.24	-1.253
		E3-4	49.0	0.16	-0.815
		E3-5	55.0	0.23	-0.104
		E3-6	70.0	0.23	-1.182
		E3-7	69.0	0.29	-0.587
		E3-8	53.0	0.22	-0.87
		E3-9	56.0	0.15	-1.111
		E3-10	71.0	0.27	-0.485
		E3-11	55.0	0.25	-1.776
		E3-12	64.0	0.24	-0.874
Thorne (enriched)	***Sphagnum recurvum* 3 months**	S1A1		0.36	66.76
		S1A2		0.34	36.83
		S1A3		0.45	98.07
		S1A4		0.43	121.14
		S1A5		0.43	38.98
		S1A6		0.22	56.16
		S1A7		0.49	63.41
		S1A8		0.55	63.03
		S2A1		0.27	48.08
		S2A2		0.28	87.32
		S2A3		0.20	80.14
		S2A4		0.30	57.51
		S2A5		0.30	93.16
		S2A6		0.23	84.06
		S2A7		0.32	72.81
		S2A8		0.17	112.12
		S2A9		0.22	81.44
		S2A10		0.18	107.14
		S2A11		0.17	71.71
		S2A12		0.24	62.50

6 months	2BS1	0.26	99.86
	2BS2	0.23	75.89
	2BS3	0.26	133.93
	2BS4	0.24	118.76
	2BS5	0.31	54.35
	2BS6	0.29	66.48
	2BS7	0.21	93.26
	2BS8	0.32	74.38
	2BS9	0.27	122.58
	1BS1	0.15	48.71
	1BS2	0.14	85.89
	1BS3	0.17	85.15
	1BS4	0.15	61.54
	1BS5	0.24	46.19
	1BS6	0.16	77.08
	1BS7	0.18	154.15
	1BS8	0.17	90.46
	1BS9	0.17	71.04
	1BS10	0.14	90.09
	1BS11	0.19	50.01
	1BS12	0.24	98.14
12 months	2CS1	0.11	208.25
	2CS2	0.16	192.04
	2CS3	0.14	228.97
	2CS4	0.10	205.03
	2CS5	0.09	227.79
	2CS6	0.14	304.19
	2CS7	0.07	202.60
	2CS8	0.04	338.57
	2CS9	0.07	335.22
	2CS10	0.07	186.66
	2CS11	0.11	185.35
	2CS12	0.15	171.19
	1CS1	0.14	170.01
	1CS2	0.08	150.69
	1CS3	0.14	85.10
	1CS4	0.09	159.41
	1CS5	0.14	127.57
	1CS6	0.11	153.57
	1CS7	0.18	94.86
	1CS8	0.12	196.88
	1CS9	0.12	112.93
	1CS10	0.11	287.00
	1CS11	0.09	181.19
	1CS12	0.19	96.51
Eriophorum vaginatum	E1A1	0.18	23.97
3 months	E1A2	0.15	25.44
	E1A3	0.11	24.70
	E1A4	0.28	28.01
	E1A5	0.21	24.24
	E1A6	0.17	25.67
	E1A7	0.23	24.50
	E1A8	0.21	36.57
	E1A9	0.21	17.82
	E1A10	0.86	24.29
	E1A11	0.74	16.47
	E1A12	0.69	59.66

	E2A1	0.12	43.91
	E2A2	0.13	55.93
	E2A3	0.13	44.96
	E2A4	0.13	71.68
	E2A5	0.11	73.40
	E2A6	0.14	73.27
	E2A7	0.15	72.12
	E2A8	0.20	55.29
	E2A9	0.17	76.63
	E2A10	0.21	35.85
	E2A11	0.23	38.41
	E2A12	0.14	37.44
6 months	2BE1	0.10	51.28
	2BE2	0.11	68.15
	2BE3	0.18	56.34
	2BE4	0.14	76.93
	2BE5	0.09	55.45
	2BE6	0.08	72.27
	2BE7	0.08	68.82
	2BE8	0.09	76.31
	2BE9	0.10	71.03
	2BE10	0.13	63.65
	2BE11	0.14	54.08
	2BE12	0.10	78.32
	1BE1	0.19	86.42
	1BE2	0.13	102.98
	1BE3	0.10	64.83
	1BE4	0.22	61.51
	1BE5	0.14	63.56
	1BE6	0.11	75.92
	1BE7	0.14	89.13
	1BE8	0.14	83.54
	1BE9	0.08	83.67
	1BE10	0.21	78.25
	1BE11	0.14	79.92
	1BE12	0.21	137.16
12 months	1CE1	0.10	97.83
	1CE2	0.10	151.64
	1CE3	0.12	173.39
	1CE4	0.11	157.05
	1CE5	0.10	136.47
	1CE6	0.11	163.06
	1CE7	0.10	132.57
	1CE8	0.10	120.21
	1CE9	0.14	164.88
	1CE10	0.09	150.99
	1CE11	0.16	121.33
	1CE12	0.14	151.93
	2CE1	-0.01	
	2CE2	0.09	56.78
	2CE3	0.09	99.07
	2CE4	0.10	118.32
	2CE5	0.09	72.84
	2CE6	0.07	73.53
	2CE7	0.09	81.06
	2CE8	0.11	88.91
	2CE9	0.09	79.61
	2CE10	0.08	87.11
	2CE11	0.09	96.11
	2CE12	0.09	80.26

Appendix C Surface and porewaters analysis

Table C-1.Surface and porewater chemistry at Thorne Moors during 48 week investigation

	Sample	Depth	mg/l (ppm)				SO_4/Cl	SO_4/Br	Fe/Cl	$\delta^{34}S\text{-}SO_4$	$\delta^{34}S\text{-}H_2S$
			Cl	Br	SO_4	Fe					
0 weeks	1C SW	-5	9.3604	0	1.9442	1.798	0.21		0.19	4.80	
	1C 25-35	-30	16.9302	0	0.7674	8.0543	0.05		0.48		5.30
	1C 45-55	-50	19.0254	0	0.2976	8.3658	0.02		0.44		2.50
	1C 65-75	-70	23.4288	0	0.6624	8.1742	0.03		0.35		5.40
	1C 85-95	-90	28.6614	0	0.6246	5.0102	0.02		0.17		
	2C SW	-5	9.8716	0	3.0641	1.3411	0.31		0.14	3.90	
	2C 25-35	-30	17.6034	0	1.2402	4.2919	0.07		0.24		1.20
	2C 45-55	-50	17.4966	0	0.6444	6.0837	0.04		0.35	12.30	2.80
	2C 65-75	-70	23.892	0	0.9504	3.979	0.04		0.17	56.90	-0.40
	2C 85-95	-90	27.0072	0	1.3872	4.1415	0.05		0.15	65.10	1.20
	1A SW	-5	14.0347	0	6.3607	1.7637	0.45		0.13	3.90	
	1B SW	-5	9.0301	0	5.4109	1.0799	0.60		0.12	4.80	
	2A SW	-5	9.9695	0	1.7669	1.2806	0.18		0.13	4.30	
	2B SW	-5	11.7913	0	2.6722	2.2919	0.23		0.19	3.90	
6 weeks	1C SW	-5	21.1	2.04	5.36	3.476	0.25	2.63	0.16	32.82	
	1C25-35	-30	41.68	<0.1	4.71	8.697	0.11		0.21	21.42	8.61
	1C45-55	-50	28.41	<0.1	2.7	6.966	0.10		0.25	4.54	2.75
	1C65-75	-70	25.31	<0.1	1.76	7.093	0.07		0.28	-1.23	4.61
	1C85-95	-90	20.4	<0.1	1.54	4.316	0.08		0.21	133.03	5.12
	2C SW	-5	15.03	2.31	4.31	1.999	0.29	1.87	0.13	99.26	
	2C25-35	-30	24.75	<0.1	3.36	4.7	0.14		0.19	17.40	9.38
	2C45-55	-50	29.23	<0.1	2.92	8.929	0.10		0.31	31.81	3.83
	2C65-75	-70	30.94	<0.1	1.34	3.336	0.04		0.11	-3.38	
	2C85-95	-90	33.25	<0.1	2.48	3.653	0.07		0.11	17.09	
	1A SW	-5	10.15	0.971	4.726		0.47	4.87		42.71	
	1B SW	-5	11.29	<0.1	5.53		0.49			45.42	
	2A SW	-5	24.45	<0.1	8.52		0.35			38.52	
	2B SW	-5	13.89	<0.1	8.78		0.63			50.24	
12 weeks	1C SW	-5	25.91	<0.1	3.62	4.8127	0.14		0.19	23.92	
	1C25-35	-30	33.06	<0.1	3.09	4.8536	0.09		0.15	8.93	10.46
	1C45-55	-50	50.61	<0.1	4.37	7.3698	0.09		0.15	2.47	5.14
	1C65-75	-70	43.27	<0.1	1.99	7.3993	0.05		0.17	3.49	5.24
	1C85-95	-90	27.23	<0.1	4.62	4.8839	0.17		0.18	1.92	
	2C SW	-5	22.88	<0.1	9.73	3.4015	0.43		0.15	17.84	
	2C25-35	-30	26.72	<0.1	2.08	8.0954	0.08		0.30	22.00	12.16
	2C45-55	-50	40.59	<0.1	1.62	5.1443	0.04		0.13	6.43	5.14
	2C65-75	-70	36.94	<0.1	2.43	3.3614	0.07		0.09	4.97	6.94
	2C85-95	-90				4.0953					
	1A SW	-5	32.14	2.56	3.16		0.10	1.23		17.63	
	1B SW	-5	35.63	0.67	3.16		0.09	4.72		31.35	
	2A SW	-5	26.8	<0.1	3.42		0.13			15.51	
	2B SW	-5	39.16	<0.1	3.53		0.09			16.75	
18 weeks	1C SW	-5	30.24	1.23	2.03	1.45	0.07	1.65	0.05	52.08	
	1C25-35	-30	32.24	<0.1	<0.1	7.98			0.25		16.47
	1C45-55	-50	36.17	<0.1	<0.1	7.22			0.20	3.88	5.29
	1C65-75	-70	42.5	<0.1	<0.1	7.28			0.17	2.44	5.99
	1C85-95	-90	32.54	1.78	<0.1	4.49			0.14	3.75	
	2C SW	-5	14.9	2.95	3.99	1.32	0.27	1.35	0.09	48.16	
	2C25-35	-30	32.47	<0.1	<0.1	5.13			0.16	25.83	19.31
	2C45-55	-50	36.78	<0.1	<0.1	5.06			0.14	4.46	5.28
	2C65-75	-70	36.6	<0.1	<0.1	3.56			0.10	2.50	5.47
	2C85-95	-90	8.74	<0.1	<0.1	3.83			0.44	2.11	
	1B SW	-5	14.8	<0.1	3.41		0.23				96.91
	2B SW	-5	10.52	<0.1	2.61		0.25				54.19

	Sample	Depth	mg/l (ppm)				SO_4/Cl	SO_4/Br	Fe/Cl	$\delta^{34}S$-SO_4	$\delta^{34}S$-H_2S
			Cl	Br	SO_4	Fe					
24 weeks	1C SW	-5	10.932	1.348	8.455	0.62	0.77	6.27	0.06	29.12	
	1C25-35	-30	23.043	2.805	0.694	7.5	0.03	0.25	0.33	49.43	16.10
	1C45-55	-50	24.535	0.333	0.354	7.67	0.01	1.06	0.31	44.86	
	1C65-75	-70	25.881	0.268	0.311	7.57	0.01	1.16	0.29	14.88	4.69
	1C85-95	-90	31.014	<0.01	0.49	4.63	0.02		0.15	38.04	
	2C SW	-5	9.798	2.296	7.635	0.63	0.78	3.33	0.06	54.81	
	2C25-35	-30	22.855	<0.01	2.215	4.97	0.10		0.22	65.87	13.77
	2C45-55	-50	23.903	0.674	0.412	4.94	0.02	0.61	0.21	37.01	5.38
	2C65-75	-70	27.331	<0.01	0.4	3.51	0.01		0.13	12.98	5.47
	2C85-95	-90	27.581	<0.01	0.254	3.92	0.01		0.14	15.93	
	1B SW	-5	12.786	2.828	10.569		0.83	3.74		62.46	
	2B SW	-5	9.883	1.634	8.429		0.85	5.16		32.35	
30 weeks	1C SW	-5	23.383	0.443	0.587	<0.01	0.03	1.33		552.27	
	1C25-35	-30	13.319	0.01	3.284	8.17	0.25		0.61	27.00	20.61
	1C45-55	-50	21.436	3.24	1.629	7.66	0.08	0.50	0.36	2.70	3.94
	1C65-75	-70	23.935	0.178	0.358	7.51	0.01	2.01	0.31	4.78	5.30
	1C85-95	-90	25.375	0.195	0.471	4.62	0.02	2.42	0.18	23.40	
	2C SW	-5	12.632	3.162	4.584	1.63	0.36	1.45	0.13	96.03	
	2C25-35	-30	22.826	2.974	2.749	4.99	0.12	0.92	0.22	91.07	19.22
	2C45-55	-50	22.496	0.825	0.516	5.11	0.02	0.63	0.23	51.00	4.72
	2C65-75	-70	26.445	0.145	0.43	3.61	0.02	2.97	0.14	46.91	6.95
	2C85-95	-90	24.81	1.321	0.209	3.83	0.01	0.16	0.15	20.92	
36 weeks	1C SW	-5	23.599	1.146	5.753	2.073	0.24	5.02	0.09	31.20	
	1C25-35	-30	23.469	2.812	1.129	7.3	0.05	0.40	0.31	43.00	22.84
	1C45-55	-50	23.985	0.401	0.412	7.653	0.02	1.03	0.32	87.96	5.30
	1C65-75	-70	24.314	0.474	0.478	7.43	0.02	1.01	0.31	9.90	4.84
	1C85-95	-90	28.43	0.184	0.606	4.775	0.02	3.29	0.17	649.76	
	2C SW	-5	12.34	2.571	2.83	1.764	0.23	1.10	0.14	-1.11	
	2C25-35	-30	22.321	3.227	2.574	4.483	0.12	0.80	0.20	30.76	20.52
	2C45-55	-50	26.178	1.245	0.548	4.873	0.02	0.44	0.19	104.48	6.75
	2C65-75	-70	26.015	0.168	0.472	3.573	0.02	2.81	0.14	59.93	
	2C85-95	-90	25.407			3.786			0.15		6.96
42 weeks	1C SW	-5	26.659	2.735	2.699	3.974	0.10	0.99	0.15		
	1C25-35	-30	22.093	2.695	0.763	7.92	0.03	0.28	0.36	55.36	20.16
	1C45-55	-50	23.931	0.65	0.47	7.604	0.02	0.72	0.32	13.21	5.97
	1C65-75	-70	25.058	0.38	0.438	7.689	0.02	1.15	0.31	2.41	4.34
	1C85-95	-90	29.721	0.071	0.427	5.113	0.01	6.01	0.17	134.31	8.29
	2C SW	-5	23.963	2.364	1.75	5.821	0.07	0.74	0.24	127.39	
	2C25-35	-30	22.243	3.486	1.522	5.045	0.07	0.44	0.23	92.83	29.38
	2C45-55	-50	24.731	1.285	0.417	4.847	0.02	0.32	0.20	-6.73	6.17
	2C65-75	-70	26.146			3.814			0.15	47.31	7.09
	2C85-95	-90	29.268	1.752	0.323	3.996	0.01	0.18	0.14	125.25	
48 weeks	1C SW	-5	25.451	2.462	5.561	2.7	0.22	2.26	0.11	143.30	
	1C25-35	-30	22.641	3.054	1.808	8.921	0.08	0.59	0.39	20.30	23.92
	1C45-55	-50	23.293	0.377	0.623	8.3	0.03	1.65	0.36	9.60	8.32
	1C65-75	-70	25.328	0.508	0.5	7.919	0.02	0.98	0.31	-2.60	7.34
	1C85-95	-90	29.534	2.212	0.503	4.9	0.02	0.23	0.17	65.50	
	2C SW	-5	24.626	2.657	2.587	4.5	0.11	0.97	0.18	248.50	
	2C25-35	-30	22.511	3.338	0.483	5.3	0.02	0.14	0.24	99.50	47.64
	2C45-55	-50	23.165	1.857	0.427	4.9	0.02	0.23	0.21	-5.18	10.43
	2C65-75	-70	26.084	1.729	0.705	3.7	0.03	0.41	0.14		
	2C85-95	-90	24.362	1.273	0.563	3.9	0.02	0.44	0.16	46.80	

Appendix D Thorne Moor data (1994-2000)

Table D-1 Depth profiles of the mean strength of peat at sites on Thorne Moors

	Depth (cm)	Mean strength (tonnes/m2)
Site A	3	0.0
	8	0.0
	13	0.0
	18	0.5
	23	0.4
	28	0.4
	33	0.9
	38	2.3
	43	2.2
	48	2.1
	53	1.6
	58	1.4
	63	1.4
Site B	4	0.0
	9	0.0
	14	0.0
	19	0.0
	24	0.3
	29	0.2
	34	0.4
	39	0.3
	44	0.6
	49	0.5
	54	0.4
	59	0.4
	64	0.5
Site C	2	0.0
	7	0.0
	12	0.0
	17	0.1
	22	0.2
	27	0.2
	32	0.2
	37	0.1
	42	0.1
	47	0.1
	52	0.4
	57	0.8
	62	1.6

Table D-2. Total U.K. power station SO_2 emissions (National Power, 1999), bulk rainfall, mean surface water sulphate concentrations, previous winter water table and local bulk sulphur inputs at Thorne Moors.

year	annual rainfall (mm)	mean surface water SO_4	Previous winter water table height (mm)	SO_4 atmospheric deposition (g.m2.a-1)	U.K. SO_2 emissions (ktonnes a^{-1})
1990	444				
1991	389				1363
1992	622				1294
1993	616				1117
1994	624	18	2150	1.46	898
1995	425			1.28	811
1996	479	52.4	2000	0.8	518
1997	572	42.5	2040	0.96	250
1998	599	15.27	2190	0.84	343
1999	641	4.3	2210	0.62	292
2000		4.3	2190		

Table D-3. Mean surface water SO_4 and surface water SO_4 at site B. Mean SO_4/Cl in surface waters and SO_4/Cl in site B surface water.

Year	Mean surface water SO_4 (ppm)	Mean SO_4/Cl	Site B Surface water SO_4/Cl	Site B Surface water SO4 (ppm)
1994	18.02 (sd/2.9)	1.04 (sd/0.3)	0.91	18.1
1996	52.4 (sd/34.0)	1.37 (sd/0.8)	1.88	81.9
1997	42.48 (sd/13.4)	0.37 (sd/0.1)	0.30	38.9
1998			0.25	15.3
1999			0.17	4.3
2000	4.3 (sd/3.9)	0.53 (sd/0.5)	0.44	7.0

Table D-4. Mean sulphur content of *Sphagnum*.

Year	mean s content	sd
1994	0.13286	0.00496
1996	0.20123	0.00513
2000	0.1267	0.0133

Table D-5. Temporal changes in water table elevation at study site.

Date	Ground water elevation (mm)
30-Dec-93	2160
19-Jan-94	2168
8-Feb-94	2160
28-Feb-94	2155
15-Mar-94	2160
30-Mar-94	2115
15-Apr-94	2110
30-Apr-94	2113
15-May-94	2105
30-May-94	2090
15-Jun-94	2150
30-Jun-94	2090
15-Jul-94	2015
28-Jul-94	1925
15-Aug-94	2005
31-Aug-94	1915
17-Sep-94	1960
3-Oct-94	2030
20-Oct-94	2070
6-Nov-94	2050
24-Nov-94	2105
10-Dec-94	2150
25-Dec-94	2148
11-Jan-95	2148
4-Feb-95	2150
1-Mar-95	2185
25-Mar-95	2160
19-Apr-95	2125
14-May-95	2100
9-Jun-95	2060
4-Jul-95	2005
29-Jul-95	1930
23-Aug-95	1755
18-Sep-95	1555
10-Oct-95	1840
2-Nov-95	1625
25-Nov-95	1670
16-Dec-95	1795
8-Jan-96	1850
31-Jan-96	1915
23-Feb-96	2000
17-Mar-96	1999
9-Apr-96	1985
1-May-96	1975
20-May-96	1985
9-Jun-96	1940
29-Jun-96	1895
18-Jul-96	1830
8-Aug-96	1625
28-Aug-96	1875
17-Sep-96	1820
7-Oct-96	1720
26-Oct-96	1765
14-Nov-96	1850
5-Dec-96	1855
26-Dec-96	1975
16-Jan-97	1955
6-Feb-97	2050
27-Feb-97	2045
20-Mar-97	2047
10-Apr-97	2010
1-May-97	1975
22-May-97	1990
9-Jun-97	1995
25-Jun-97	1850
11-Jul-97	1940
27-Jul-97	2060
12-Aug-97	2060
29-Aug-97	2050
15-Sep-97	2020
1-Oct-97	2040
17-Oct-97	2020
2-Nov-97	2065
18-Nov-97	2038
7-Dec-97	2050
27-Dec-97	2120
15-Jan-98	2175
4-Feb-98	2190
23-Feb-98	2175
15-Mar-98	2150
3-Apr-98	2200
23-Apr-98	2190
12-May-98	2215
4-Jun-98	2195
2-Jul-98	2195
3-Aug-98	2195
2-Sep-98	2080
1-Oct-98	2080
30-Oct-98	2050
28-Nov-98	2060
27-Dec-98	2160
25-Jan-99	2190
24-Feb-99	2175
26-Mar-99	2185
25-Apr-99	2193
23-May-99	2220
22-Jun-99	2192
20-Jul-99	2175
19-Aug-99	2140
18-Sep-99	2075
16-Oct-99	2020
15-Nov-99	2060
14-Dec-99	2100
18-Jan-00	2150

Appendix E Tracer Calculations

Calculation of % ^{34}S

$$\delta 34S = \left[\frac{(34S/32S)_{spl}}{(34S/32S)_{std}} -1 \right] \times 10^3$$

$$\delta 34S = \left[\frac{(34S/32S)_{spl}}{(1/22.22)_{std}} -1 \right] \times 10^3$$

$$(34S/32S)_{spl} = (\delta 34S/10^3)+1) \times (1/22.22)$$

$$^{34}S_{mg} = \left[\frac{S_{mg}}{(1/(34S/32S)_{spl}) +1)} \right]$$

$$^{34}S_{\%} = (^{34}S_{mg}/ S_{mg}) \times 100$$

Calculation of mg ^{34}S added into fraction

$$^{34}S_{mg} = \left[\frac{(\%\,^{34}S_{enriched} - \%\,^{34}S_{control})}{100} \right] \times S_{mg}$$

Calculation of tracer-derived ^{34}S incorporation

$^{34}S_{mg}$ added per g x (sulphur fraction area$_{cm^3}$ x dry wt of fraction$_g$ in 1 cm^3)