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^{34}S tracer study of pollutant sulfate behaviour in a lowland peatland

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Abstract Field experiments were carried out in order to assess the practicality and application of $^{34}SO_4^{2-}$ as a tracer of the physical and geochemical fate of aerially derived sulfur in peat. Six enclosures were isolated in a lowland peat with high historical acid sulfate inputs at Thorne Moors, UK, and treated with regular additions of 99.9% pure $^{34}SO_4^{2-}$ for 12 months. The total ^{34}S sulfate addition resulted in negligible change to the sulfate concentration, but allowed unequivocal change to the isotopic composition of sulfate inputs relative to pre-experiment control data set. Migration and biogeochemical transformations of the ^{34}S tracer were monitored via depth-specific sampling of surface and pore-waters every 6 weeks, and sacrificial sampling of solid peat at 12, 24, and 48 week intervals. Tracer incorporation into the various sulfur forms within the surface and pore-waters, vegetation, organic and inorganic fractions of the peat was apparent through strong positive deviation of δ^{34}S from natural values (in comparison with 18 months control data set for the same site). Consistency within enclosures is good and a detailed model of sulfur cycling within each enclosure can be established but natural variability in the control data and differences between replicate enclosures prevents more quantitative assessment. The ^{34}S tracer was initially rapidly removed from surface waters. The majority of uptake was by living vegetation (5.7–33% of tracer added, mean 17.6%), or through transformation to the organic fraction of the upper peat (25 cm) after rapid bacterial reduction of sulfate to sulfide. Despite penetration of ^{34}S labelled sulfate to deeper pore-waters over time, there was no significant reduction to sulfide or subsequent incorporation into organic or inorganic fraction at these depths (>25 cm); organic and inorganic sulfur, and pore-water sulfide retained their initial unlabelled isotopic compositions. This limitation on sulfur cycling at relatively shallow depth may be attributed to diminished labile organic matter inhibiting the activity of sulfate reducing bacteria or poisoning of sulfate reducers by high dissolved sulfide, after long-term sulfur pollution of this ecosystem.

Keywords Peatland · Sulfur geochemistry · Tracers · ^{34}S isotope

Introduction

Peatlands represent a major store of carbon (currently between 250 and 450 Gt C) that have largely

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accumulated at high northern latitudes since the end of the last glaciation (Turunen et al. 2002). These ecosystems are major sources of both methane to the atmosphere (contributing 4–10% of the atmospheric methane burden; Mikaloff Fletcher et al. 2004) and dissolved organic carbon to surface waters (Urban et al. 1989). The fate of carbon in peat ecosystems is closely coupled to sulfur cycling; the amount and fate of aerially derived sulfur can produce a variety of ecological and biogeochemical effects (e.g., Ferguson et al. 1978; Lee et al. 1987; Bottrell et al. 2004). Bacterial sulfate reduction (BSR) affects the major control on sulfur cycling in anoxic peat ecosystems and creates a sink for aerially derived sulfur (e.g., Brown 1985; Bottrell and Novak 1997):

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

Sulfate is reduced to sulfide, which is free to react with iron to form inorganic iron mono-sulfide or pyrite, or with organic compounds to form organic (carbon-bonded) sulfur. BSR may be stimulated by increased sulfate loadings causing an inhibition of methane production as a result of increased competition for microbial metabolic substrates such as hydrogen, acetate and alcohols (e.g., Nedwell and Watson 1995; Shannon and White 1996; Gauci et al. 2002; Vile et al. 2003). Consumption of acidity during BSR (Reaction 1) may contribute to the attenuation of acidic atmospheric deposition (acid rain) (e.g., Giblin et al. 1990; Morgan 1995; Bottrell et al. 2004) and can control the solubility of other chemical species. Lowering of acidity may serve to render organic species more soluble, producing a link between sulfate deposition, the subsurface fate of sulfur, and DOC export from peatlands (e.g., Clark et al. 2005; Evans et al. 2006; Monteith et al. 2007). The biogeochemistry of sulfur in peatlands is thus an important influence on the export of carbon from this vast global store.

The fate of aerially derived sulfur in waterlogged peat ecosystems is complex, arising from biological cycling between five transposable components of the peat. These comprise: sulfate in surface and pore-waters; surface vegetation; organic sulfur bound up in the necromass; reduced inorganic fractions (S^0, H_2S, FeS, FeS_2); and pore-water sulfide. The biogeochemical cycling of sulfur in such systems has been studied by a variety of approaches in the past. Analysis of sulfur forms in peat enables quantification of the size of the different pools (e.g., Chapman 2001). Detailed studies of pore-water chemistry can yield further information on the nature of reactions taking place (e.g., Shotyk 1997; Steinmann and Shotyk 1997) and chemical gradients and changes in pore-water chemistry over time can be used to estimate mass fluxes and reaction rates (e.g., Bottrell et al. 2007); these methods may be enhanced by the use of stable and radioactive isotopes.

Stable sulfur isotopes (principally ^{32}S, ^{34}S) are fractionated by natural biogeochemical processes, giving characteristic ratios (expressed as $\delta^{34}S$), and can be used to track sulfur in the environment (e.g., Krouse 1977; Nriagu et al. 1987; Krouse and Mayer 2000) and specifically in peats (e.g., Novák et al. 1994; Morgan 1995; Mandernack et al. 2000). In general, the lighter ^{32}S isotope (which forms weaker bonds) will react more readily than the ^{34}S isotope; this effect is often significant during biological reactions leaving isotopic signals that allow reactions driving sulfur cycling to be defined. In ombotrophic peat, sulfur enters the system as sulfate from atmospheric deposition. Incorporation of sulfur from sulfate in bog flora is accompanied by only minor isotopic fractionation (e.g., Bottrell and Novak 1997; Coulson et al. 2005). After burial of dead flora the organic sulfur in the necromass can become enriched in ^{34}S, as the lighter ^{32}S is liberated during partial decomposition (Novák et al. 1999; Bartlett et al. 2005). Sulfate-S remaining in the surface and pore-waters is fractionated during BSR, which efficiently discriminates against the heavier sulfur isotope, ^{34}S, in favour of the lighter isotope, ^{32}S (e.g., Chambers and Trudinger 1979; Strebel et al. 1990). The sulfide produced is thus depleted in ^{34}S and the light isotopic signal can be detected in subsequent reaction products in the solid peat (sulfide species and organic sulfur) (e.g., Casagrande et al. 1980; Brown 1985; Chapman 2001; Coulson et al. 2005); whilst the remaining sulfate (in surface and pore-waters) becomes enriched in ^{34}S. This trend may become complicated by upward diffusion of sulfide and subsequent re-oxidation. In particular, a fall in the water table (e.g., as a result of drought or changing land management) can introduce oxygen into previously reduced parts of the peat profile, resulting in the oxidation of reduced sulfur forms (Bottrell et al. 2004; Clark et al. 2005), which are depleted in ^{34}S and may skew the pore-water sulfate isotopic composition.

This model of natural sulfur isotope fractionation during peat diagenesis allows the identification of the main processes within a peat ecosystem, including the relative importance of BSR (e.g., Bartlett et al. 2005), and the extent of the influence of BSR on acid attenuation (e.g., Morgan 1995). An alternative approach to understanding the fate of sulfate in peat is to apply the radioactive tracer ^{35}S as $^{35}SO_4^{2-}$ and monitor its chemical conversion and incorporation into different compartments in the peat (e.g., Brown 1985; Novák and Prechová 1995; Chapman and Davidson 2001). This approach has the advantage that the ^{35}S tracer is precisely identifiable and thus rates can readily be measured, but experiments are relatively short-term (due to the 87.4 day half life of ^{35}S) and must be performed in laboratory core experiments that are always small scale and physically and chemically disturbed through abstraction from the natural peat environment.

In this study, the complications of net natural isotopic abundance of ^{32}S and ^{34}S, and short-term limitations of ^{35}S are overcome by novel use of an isotopic tracer in the field. Experimental enclosures were treated with pure $^{34}SO_4^{2-}$ (as a supplement to natural atmospheric deposition) to provide a 'label' for aerially derived sulfate deposited to the peat surface, over a set time interval. The total ^{34}S sulfate addition resulted in negligible change to total sulfate loadings but allowed unequivocal change to the isotopic composition of sulfate inputs. The pure ^{34}S additions shifted the isotopic ratio of atmospheric deposition (from $\sim$5 to $>$ 500‰ δ^{34}S) so that sulfur transformations and geochemical pathways could be traced, in a similar way to a ^{35}S experiment. The ^{34}S tracer experiment was conducted over a 12 month period during which surface and pore-waters, vegetation and solid peat were sampled, and was successful as both a qualitative indicator of biogeochemical processes (by the appearance of un-naturally heavy isotopic compositions in the peat fractions) and a quantitative determinant of physical fate of sulfur (through geochemical mass balance).

Study site

Thorne Moors is the remains of an extensive complex of raised bog that straddles large areas of South Yorkshire and North Lincolnshire, UK. The area covers about 1,900 ha and the surviving peat only exceptionally exceeds 2.5 m. The site stands on an area of the shallow, proglacial Lake Humber, which existed about 14,000 BP. Circa 5,200 BP, the natural drainage was held back by rising sea levels and silting up of the lake, which resulted in peat formation via paludification (Van de Noort 2001). Extensive areas of peatland were subsequently lost in a bid to improve it for agricultural use, which came about through drainage and warping (the use of managed flooding to improve the land by sediment accumulation). Peat had been harvested, primarily for fuel, from the fringes of Thorne Moors since medieval times (Caufield 1991) but from the late 1880s, a resurgence in peat extraction came about through a demand for animal litter and agricultural use (Limbert 2002) resulting in a large complex of drainage ditches that extended through the peat into the underlying Lake Humber clays. The area used for the ^{34}S tracer study is in the centre of the moor and was last cut before the 1920s. A new accumulation of peat has propagated in the re-flooded, abandoned cuttings from *Sphagnum* mosses and *Eriophorum* cotton grass. Thorne Moors is now a Site of Special Scientific Interest (SSSI) and Special Area of Conservation (SAC) managed by English Nature (now Natural England).

Thorne Moors has been subjected to acidification since the industrial revolution with a legacy of heavy fossil fuel burning locally. Due to its position downwind of the large industrial cities of Nottingham, Sheffield and Leeds, SO_2 emissions are likely to have exerted a significant control on aerial deposition chemistry for over 150 years. In a similar position relative to industrializing cities, isotopic compositions of sulfur in peatlands in the southern Pennines, UK, record a progressive increase in anthropogenic sulfur loading from around 1850 (Coulson et al. 2005). This parallels the pollutant sulfur loadings recorded by sulfur isotopic compositions in archive grain samples from southern Britain (1845–1999), which show a progressive decrease in δ^{34}S (and hence increasing anthropogenic sulfur loading) to a minimum in 1972 (Zhao et al. 2003). After the early 1970s atmospheric sulfur emissions fell in Britain in response to a decline in industrial output. In the last two decades, international emission control regulations and installation of desulfurization technology have hastened the decline in acid sulfate deposition (up to 50% since 1986, Fowler et al. 2005); at Thorne Moors sulfur inputs have declined from 1.46 to 0.62 g S/m^2/year since 1994 (Bottrell et al. 2004). Under such recovery from acidification, it is important to understand the long term fate of pollutant sulfur at Thorne Moors, and the potential biogeochemical response to changing atmospheric deposition.

Methodology

Field methods

Background monitoring

For 18 months prior to tracer addition at the Thorne Moors study site aerial inputs, surface waters, pore-waters, vegetation and triplicate solid peat cores were sampled to establish control data, including the range of background isotopic compositions that arose from the effects of BSR in the peat. Samples were taken after enclosures had been installed (see below) to avoid lateral disturbance from the coring procedures.

Aerial inputs

Aerial inputs to the site were measured prior to and during the background monitoring period by sampling the bulk (wet and dry) deposition at Don Farm close to the edge of Thorne Moors. Precipitation was collected using a 200 mm diameter plastic funnel, set 1.1 m above the ground to avoid splash-back, which drained into an opaque 5 l plastic container. A small quantity of thymol was added to the container prior to sampling to act as a sulfur-free biocide.

Experiment enclosures

Experiment enclosures were established using acrylic (perspex) sheeting cut to size, secured together and carefully driven into the peat to create four walled in-situ enclosures. Enclosure walls extended 0.6 m deep in order to isolate the upper peat from lateral flow but remain open to aerial inputs. Four 1 m × 1 m enclosures ([1a], [1b], [2a], [2b]) and two 1 m × 2 m enclosures ([3a], [3b]) were created in a random pattern within the flooded bay used for the study. Surface water from each enclosure was collected every 6 weeks. Pore-waters were collected every 6 weeks from depth-specific sampling tubes that were installed in the larger, longer term enclosures ([3a], [3b]). Enclosures were sacrificially sampled for vegetation and duplicate solid peat cores at 12 weeks ([1a] and [1b]), 24 weeks ([2a] and [2b]), and 48 weeks ([3a] and [3b]).

^{34}S tracer addition

The ^{34}S tracer was added as a pH neutral $NaSO_4$ solution created from $^{34}S^0$ stock. The $^{34}S^0$ was combusted in a sealed chamber containing oxygen and hydrogen peroxide to produce $^{34}SO_2$ gas, which was converted by equilibration with the hydrogen peroxide to $H_2^{34}SO_4$. This was neutralised by titration with NaOH to create the final tracer solution. The absolute concentration of sulfur needed to produce an unequivocal change to the isotopic composition of the sulfate inputs was low ($\sim$0.5 mg/l SO_4^{2-}). The tracer solution was added via watering can at a constant dose of 100 ml/m^2 on day 0, day 22 (3 weeks), day 43 (6 weeks) and at 6 week intervals thereafter.

Surface and pore-water sampling

Surface water samples were taken using a bailing technique taking care to avoid disturbance of the peat and to reduce the movement of water from deeper in the profile. Depth-specific pore-water sampling tubes (25–35, 45–55, 65–75, and 85–95 cm) were installed into the centre of enclosures [3a] and [3b], with sealed sampling windows connected to valved extraction tubes. This set up allowed pore-water to be sampled without aeration of the sample or the anoxic peat within the enclosure. Pore-waters were recovered using a peristaltic pump to establish a vacuum and the first 5 ml of sample was discarded to flush tubing and exclude any sample that may have come into contact with air. For all water samples an aliquot was filtered (0.2 μm) for anion analyis, the remaining sample was collected in 5 l containers with an excess of copper (II) chloride to fix dissolved H_2S species as copper sulfide. Samples were refrigerated until analysis.

Vegetation and peat sampling

Vegetation samples comprising moss (*Sphagnum recurvum*) and cotton grass (*Eriophorum vaginatum*) were cropped using scissors and were stored frozen until analysis. Intact peat cores were collected using 10 cm diameter, 50 cm long PVC tubes with sharpened base. The upper peat was cut with a sharp knife to allow insertion of the core tube with minimal disturbance and compaction. Cores were capped and frozen on site to ensure the peat remained anaerobic and there could be no appreciable disturbance of the pore waters. Frozen peat cores were sliced at 2.5 cm intervals using a band saw to allow depth specific analysis.

Laboratory methods

Surface and pore-waters

Surface and pore-water samples were analysed for SO_4^{2-} and Cl^- using a Dionex-4500 Ion Chromatograph by separation on AS4 or AS14 column after C18 resin pre-treatment to remove organics.

Larger surface and pore-water samples that had been preserved with $CuCl_2$ in the field were gravity filtered. The CuS precipitate (inorganic sulfide) was recovered by filtering and purified by $CrCl_2$ reduction to H_2S and re-precipitation as CuS after reaction with known stock of $CuCl_2$ ($CrCl_2$ reduction technique, Newton et al. 1995). Inorganic sulfur or chromium reducible sulfur (CRS) was then determined by titration of the remaining $CuCl_2$; the CuS precipitate was recovered for isotopic analysis. SO_4^{2-} in the filtrate was recovered for isotopic analysis by $BaSO_4$ precipitation after the addition of a precise volume of a known sulfate stock of known isotopic composition (to dilute the tracer concentration to within analytical range).

Vegetation and peat

Sulfur fractions of the solid peat samples were separated using the $CrCl_2$ reduction technique described by Newton et al. (1995). This method recovers inorganic sulfur (CRS) as CuS precipitate (CRS was determined by titration as for surface and pore-waters, and the CuS precipitate kept for isotopic analysis as above), and produces a residue comprising the organic fraction of the peat containing C-bonded and ester sulfate sulfur (Organic-S). The organic residue was rinsed, dried and ground and combusted using a Parr oxygen bomb to oxidise all remaining sulfur species from organically bound sulfur to sulphate (Siegfriedt et al. 1951). The sulfate was washed from the bomb and further oxidised with 1% bromine solution, and purified (to remove iron) by increasing the pH and filtering off any unwanted precipitates. All sulphate was precipitated as $BaSO_4$ after acidification and addition of barium chloride solution to provide a concentration (by mass) and allow isotopic analysis. Potential contamination effects within the Parr oxygen bomb caused by ^{34}S enriched samples (particularly the moss samples) were eliminated by processing coal of known (and unaltered) isotopic composition between samples.

Vegetation samples were dried and ground and treated with the Parr bomb technique as described for the organic residue.

Isotopic analysis

Isotopic composition was determined on $BaSO_4$ precipitates (for surface and pore-water sulfate and the organic sulfur fraction of the peat and vegetation samples), and CuS precipitates (for CRS of the pore-waters and solid peat).

$BaSO_4$ precipitates were fluxed with tri-sodium trimetaphosphate ($Na_3(PO_3)_3$) at 900°C in vacuo, simultaneously reducing the resulting SO_3 to SO_2 on copper wool (Halas et al. 1982). The CuS precipitates were combusted with cuprous oxide to yield SO_2 directly (Robinson and Kusakabe 1975). The converted SO_2 samples were purified by vacuum-cryogenic techniques and analysed using a VS Sira 10 isotope ratio mass spectrometer. The raw data were corrected for instrumental and isobaric effects using standard procedures (e.g., Craig 1957). Isotope ratios are quoted as delta (δ) values per thousand (‰) relative to the international standard, Vienna-defined Cañon Diablo Troilite (V-CDT) thus:

$$\delta^{34}S(‰) = \left[\left({}^{34}S/{}^{32}S_{\text{sample}} - {}^{34}S/{}^{32}S_{\text{V-CDT}}\right)/\ {}^{34}S/{}^{32}S_{\text{V-CDT}}\right] \times 1000$$

Enrichment in ^{34}S relative to the standard produces a positive δ value and depletion a negative value. The analytical uncertainty, estimated from the analyses of standard materials is ±0.2‰.

Tracer recovery calculation and sulfur pools

Isotopic analyses were recalculated as atom % ^{34}S (taking account of the dilution by SO_4^{2-} added to enriched samples). This allowed for the calculation of the mass of ^{34}S tracer incorporated into the surface and pore-waters, vegetation and solid peat fractions. The mass of ^{34}S tracer was determined by first estimating how much ^{34}S was expected to be present in the natural system (using measured control sulfur contents and isotopic data) and subtracting this from the enriched ^{34}S content of the sample taken at the end of the experiment. This assumes that the control data (regular samples taken over an 18 month period) are representative of variability in natural isotopic compositions prior to the tracer additions. Importantly, the variability in isotopic signature in the natural environment (in the order of <20‰) is minor relative to the changes that can be affected by the addition and incorporation of the pure ^{34}S tracer (<400‰). Using this approach, the incorporation of the tracer into the CRS fraction is necessarily an under-estimate, as for some depth intervals only small yields of sulfur (as CuS precipitate) were generated and isotopic analyses were not feasible. Consequently, the calculated CRS pool only included those samples for which a complete analysis was possible.

In order to asses the migration of the ^{34}S tracer into different fractions of the peat, each enclosure was divided into nominal S pools: surface water; pore-water at 25–35, 45–55, 65–75 and 85–95 cm depth intervals; biomass (essentially vegetation above 20 cm depth); upper peat (20–25 cm of necromass); lower peat (25–40 cm of necromass). The pool sizes were calculated from: the increase in ^{34}S abundance compared to the mean of corresponding control data; mass of pool; sulfur concentration of pool.

Due to the seasonality of surface and pore water chemistry, the full range of isotopic compositions determined from control data were included in calculations of tracer mass incorporation. For the surface water pool, the volume of surface water was estimated by assuming a 10 cm surface water layer over the whole enclosure area and a porosity of 0.85 (based on mass of vegetation present in this layer). Calculated errors range from <0.1% of tracer incorporated (at highest enrichments) to 1.5% of tracer incorporated (at lowest enrichments). Pool sizes for pore-water sulfur species are sufficiently small that they account for only tiny amounts of tracer; these data are only used in a qualitative fashion.

For the solid phase, data were extrapolated from each core to the whole enclosure volume. This assumes that: the control data are representative of the range of natural isotopic compositions prior to the tracer additions; the divisions between biomass and necromass in the cores are more or less typical of these layers in the enclosures as a whole; the tracer distribution and sulfur content of the different pools are reasonably uniform within the confines of the enclosures. One of the aims of this investigation is to conclude as to the validity of such assumptions. The error estimates for the solid phase sulfur pools are based on the analytical uncertainty for the enriched samples and the variability in the ^{34}S content of triplicate control samples. Depending on the size of the pool and the degree of enrichment in each case, this error lies between 0.2 and 0.6% of tracer incorporated into the pool.

Results

Control data

Aerial inputs

Aerial inputs to the site, calculated from bulk deposition, contributed between 0.001 and 0.003 g S/m^2/day over the monitoring period (18 months) prior to the tracer experiment. Isotopic composition ($\delta^{34}S$) varied between 4.3 and 7.5‰ with lower values tending to occur in the summer months.

Control surface and pore-waters

Surface and pore-waters were collected three times over the monitoring period (18 months) prior to the tracer experiment. Sulfur chemistry varied little over this time: mean data for sulfate (as mg/l ratio to chloride) and sulfide concentration, and isotopic composition are plotted in Fig. 1a, b, respectively.

Sulfate in the surface water ranged between 0.3 and 5.1 mg/l (mean 1.8 mg/l; SD 0.8) with an isotopic composition (δ^{34}S) of between 5.6 and 8.7‰ (mean 6.7‰; SD 1.9). Lower SO_4^{2-} concentrations tended to occur in the summer months, in correspondence with higher δ^{34}S values. With depth, SO_4^{2-}/Cl^- in the pore-water shows a marked decrease to minimum value of 0.029 ($\equiv$0.4 mg/l SO_4^{2-}, SD 0.1), which is coincident with an increase in δ^{34}S values to a maximum of 46.5‰ (SD 12).

Sulfide is present in pore-waters from 25 cm and shows a steady increase with depth to maximum of 8.5 mg/l (SD 6.5) at 65 cm. Isotopic composition shows a small increase with depth from 4 (SD 2.4) to 4.95‰ (SD 5.5).

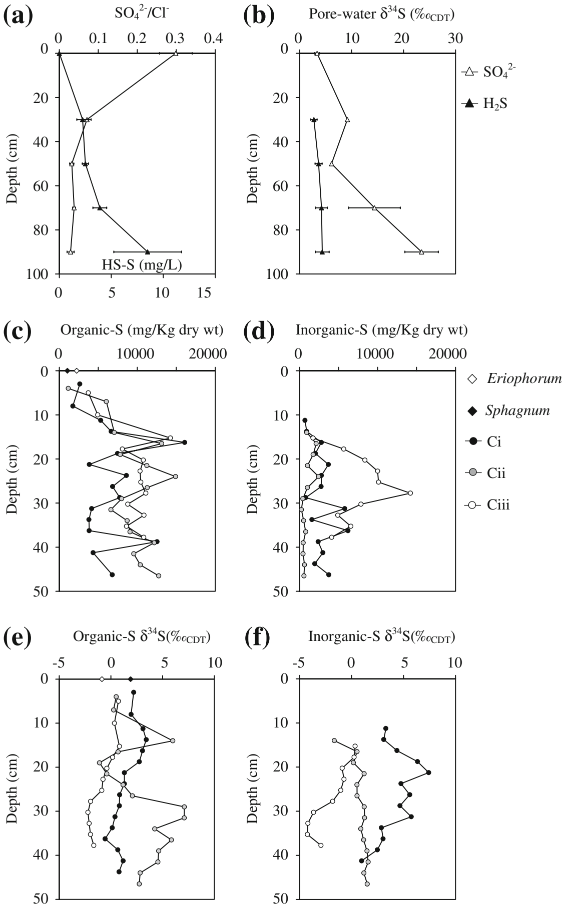


Fig. 1 Control data (from 18 month background monitoring period) for Thorne Moors: **a** surface and pore-water sulfate and sulfide concentration (mean with standard deviation); **b** surface and pore-water sulfate and sulfide isotopic composition (mean with standard deviation); **c** vegetation and peat organic sulfur concentration from triplicate cores (Ci, Cii, Ciii); **d** inorganic sulfur concentration from triplicate cores (Ci, Cii, Ciii); **e** δ^{34}S organic sulfur from triplicate cores (Ci, Cii, Ciii); **f** δ^{34}S inorganic sulfur from triplicate cores (Ci, Cii, Ciii)

Control vegetation

Sulfur content and isotopic composition for moss (*Sphagnum recurvum*) and cotton grass (*Eriophorum vaginatum*) are plotted on Fig. 1c, e, respectively. There is significant difference between the species. Sulfur content ranged from 0.06 to 0.14 wt% (600–1,400 mg/kg) for mosses and 0.14 to 0.29 wt% (1,400–2,900 mg/kg) for grasses ($T = 7.32$; $p < 0.0001$; $df = 17$). Isotopic composition (δ^{34}S) ranged from 1.22 to 2.46‰ for mosses and −0.10 to −1.78‰ for grasses ($T = 16.79$; $p < 0.0001$; $df = 21$).

Control peat cores

Organic and inorganic (CRS) sulfur content and isotopic composition for the triplicate solid peat cores (Ci, Cii, Ciii) are shown in Fig. 1c–f.

Organic sulfur (Fig. 1c) shows a general increase with depth in all cores (from ~1,150 to 14,300 mg/kg) in the first 20 cm, with relatively steady concentrations (~13,000 mg/kg) thereafter. Isotopic composition of the organic sulfur fraction ranges from −2.2 to 7.0‰ δ^{34}S (Fig. 1e). There is a gentle decline with depth in cores Ci and Ciii (from 2.20 to −0.56‰ and 0.73 to −2.10‰, respectively), whilst for Cii organic S is more variable (−1.10 to 7.00‰).

Inorganic sulfur shows more discrepancy between the triplicate cores (Fig. 1d) although broad concentration peaks are more or less discernible (Ci: 6,209 mg/kg at 36 cm; Cii: 2,439 mg/kg at 24 cm; Ciii: 14,214 mg/kg at 28 cm). Isotopic compositions for the inorganic sulfur fraction range from −4.25 to 7.42‰ δ^{34}S (Fig. 1f). Ci and Ciii show similar declining gradients below 20 cm (7.42–0.97‰ for Ci after an initial increase; 0.34 to −4.25‰ for Ciii), whereas Cii is more or less constant with depth (~1.22‰).

^{34}S tracer study

Tracer in surface water

The proportion of ^{34}S tracer incorporation in the surface water of each enclosure is shown in Fig. 2a,

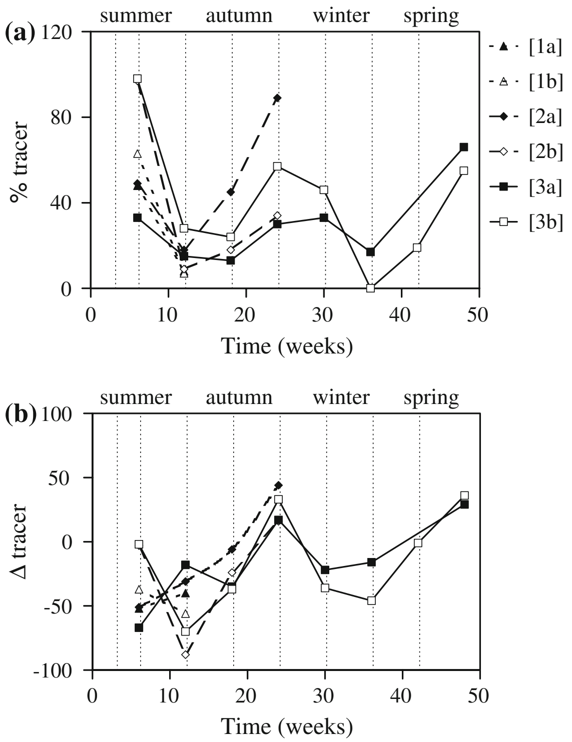


Fig. 2 ^{34}S incorporation into surface water during tracer experiment (*vertical dashed lines* indicate tracer addition event): **a** % of $^{34}SO_4$ tracer addition detected in surface water for enclosures [1a], [1b], [2a], [2b], [3a], [3b]; **b** change in tracer concentration in surface water (data has been corrected for $^{34}SO_4^{2-}$ additions)

and shows considerable change with time. Figure 2b shows the relative change in tracer abundance; data are corrected for tracer additions with negative changes indicating tracer removal and positive changes indicating tracer addition (from a source other than aerial inputs).

Following the initial tracer additions (at 0, 3 and 6 weeks) the majority of the tracer is removed from the surface water in all enclosures by 12 weeks (Fig. 2a; summer-time). Between 12 and 24 weeks (autumn-time), the tracer content of surface water increases. A comparison of Fig. 2a, b shows that this is not simply accumulation of the aerial $^{34}SO_4^{2-}$ additions, but a migration of ^{34}S tracer to the surface water from another source, most likely return of tracer from other sulfur pools that have become ^{34}S labelled. There is again, net removal of tracer from the surface water between 24 and 36 weeks (winter-time), and net transfer of tracer back to the surface water between 36 and 48 weeks (spring-time).

Tracer in pore-waters

Pore-water samples were drawn from enclosures [3a] and [3b]; the isotopic composition of pore-water sulfate and sulfide at depth are shown in Fig. 3a–d for 25–35, 45–55, 65–75, 85–95 cm depth, respectively. The appearance of the ^{34}S tracer in the pore-waters is qualitatively determined where positive shifts in the δ^{34}S values deviate significantly from natural control data.

At 25–35 cm depth there is a significant increase in SO_4^{2-} δ^{34}S values ([3a]: 21.4–55.4‰; [3b]: 3.9–99.5‰) and H_2S δ^{34}S values ([3a]: 5.3–23.9‰; [3b]: 1.2–47.6‰), with the steepest gradient after 24 weeks.

At 45–55 cm depth, SO_4^{2-} δ^{34}S values increase to a peak at 36 weeks ([3a]: 4.5–88.0‰; [3b]: 12.3–104‰) and then decline (to 9.6 and −5.18‰ at 48 weeks); H_2S δ^{34}S values increase steadily but remain within the control range ([3a]: 2.5–8.3‰; [3b]: 2.8–10.4‰).

At 65–75 cm depth SO_4^{2-} δ^{34}S values increase after 24 weeks in enclosure [3b] (−3.4 to 59.9‰) although this is within the range of control data, and remain relatively unchanged, and below control data, for enclosure [3a] (~4‰); H_2S δ^{34}S values show a small increase ([3a]: 5.4–7.3‰; [3b]: −0.4 to 7.1‰) again, close to control data. An initial high value for SO_4^{2-} δ^{34}S for [3b] is incongruous but within the control range.

At 85–95 cm SO_4^{2-} δ^{34}S values are initially high ([3a]: 133‰; [3b]: 65.1‰), decreasing in the first 12 weeks (to 1.9 and 2.1‰), before a large increase with peaks at 36 (649.7‰ for [3a]) and 42 weeks (125.0‰ for [3b]) and a subsequent decline (to 65.5 and 48.6‰ at 48 weeks). Isotopic data for H_2S in the very deep peat are limited because of the low concentration of sulfide; essentially δ^{34}S values remain close to control data throughout the experiment (<5‰).

Tracer in vegetation and peat

Duplicate cores were taken from enclosures at 12 weeks (cores [1a]i, [1a]ii, [1b]i, [1b]ii), 24 weeks (cores [2a]i, [2a]ii, [2b]i, [2b]ii), and 48 weeks (cores [3a]i, [3a]ii, [3b]i, [3b]ii). Sulfur chemistry for the

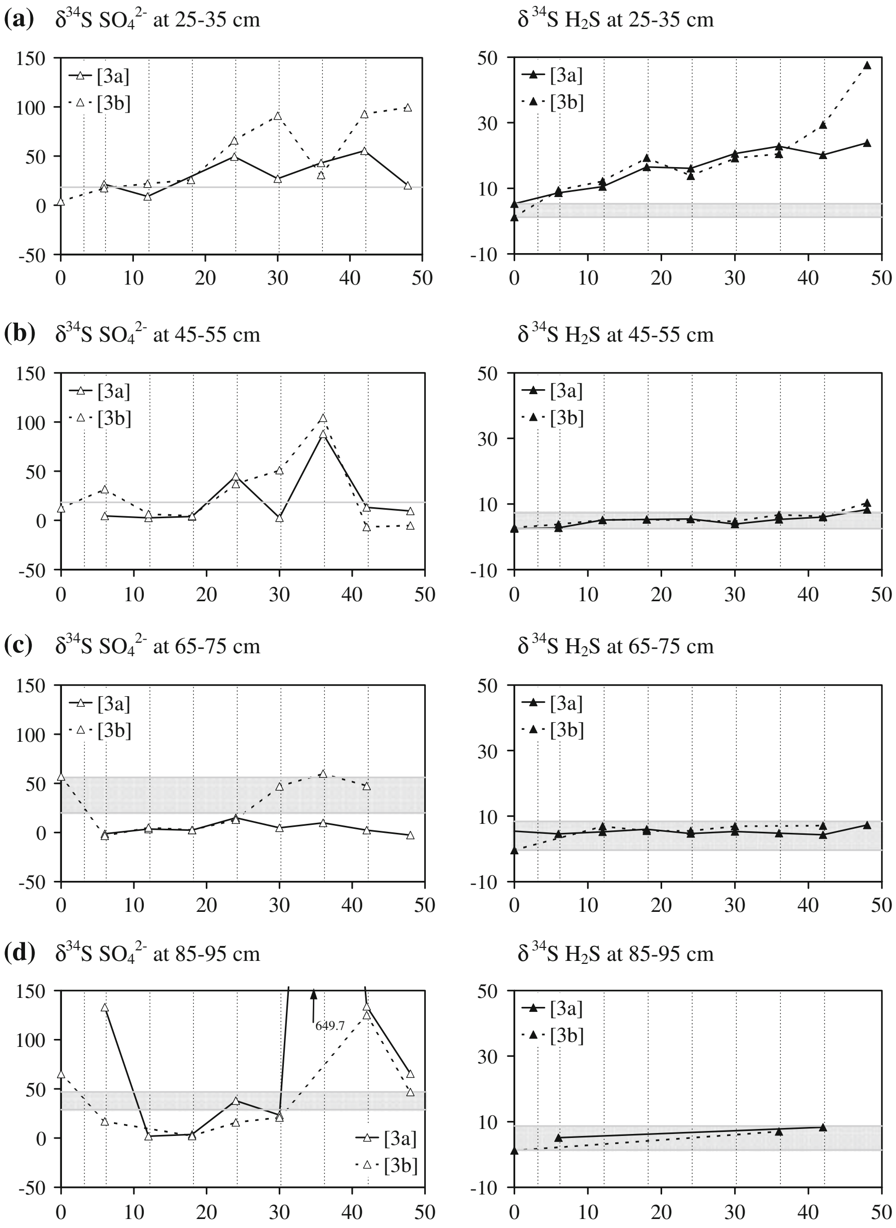
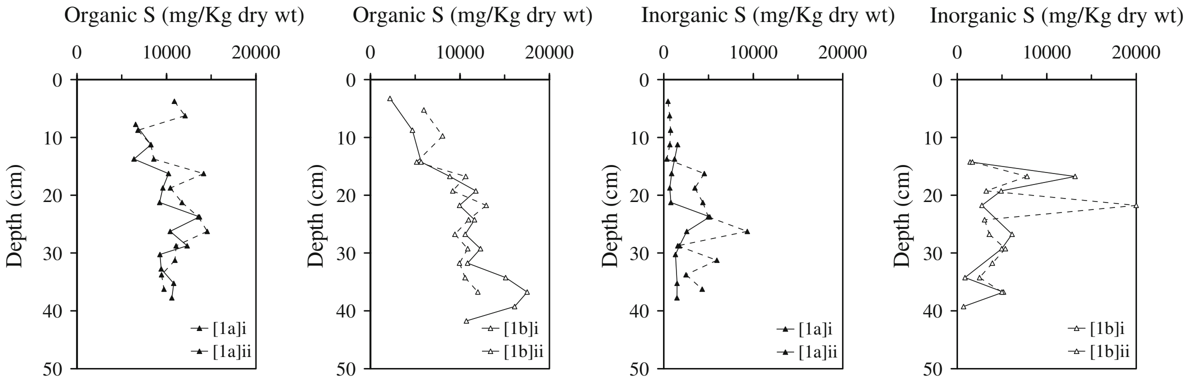


Fig. 3 Pore-water sulfate and sulfide isotopic composition during tracer experiment for enclosures [3a] and [3b] (*shaded line* indicates control data range); **a** 25–35 cm depth; **b** 45–55 cm depth; **c** 65–75 cm depth; **d** 85–95 cm depth

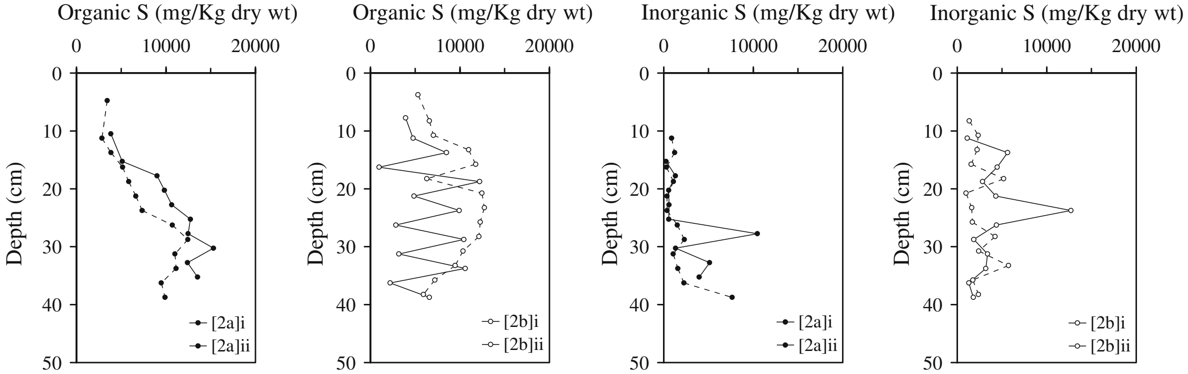
solid peat cores is shown in Fig. 4 (organic and inorganic sulfur concentrations with depth at 12, 24 and 48 weeks) and 5 (isotopic composition of the organic and inorganic sulfur fractions at 12, 24 and 48 weeks). Tracer incorporation is qualitatively determined and visually apparent by strong positive shifts in the δ^{34}S values which deviate from control data (Fig. 5), and quantitatively, as proportions of ^{34}S tracer added, in Table 1. Data show considerable variation between enclosures, demonstrating spatial variability, although general trends are similar, and within each enclosure duplicate cores show good agreement.

Tracer incorporation is restricted to the upper peat in all cores, noted by significant deviation from control data and a concave δ^{34}S depth profile for both organic and inorganic sulfur (Fig. 5). The curve is always sharp, with δ^{34}S values returning to the control range within the upper 10–20 cm. The most significant uptake of ^{34}S tracer was into vegetation (5.7–33% of tracer added, mean 17.6%), which occurs rapidly with no increase in the tracer content

(a) 12 weeks



(b) 24 weeks



(c) 48 weeks

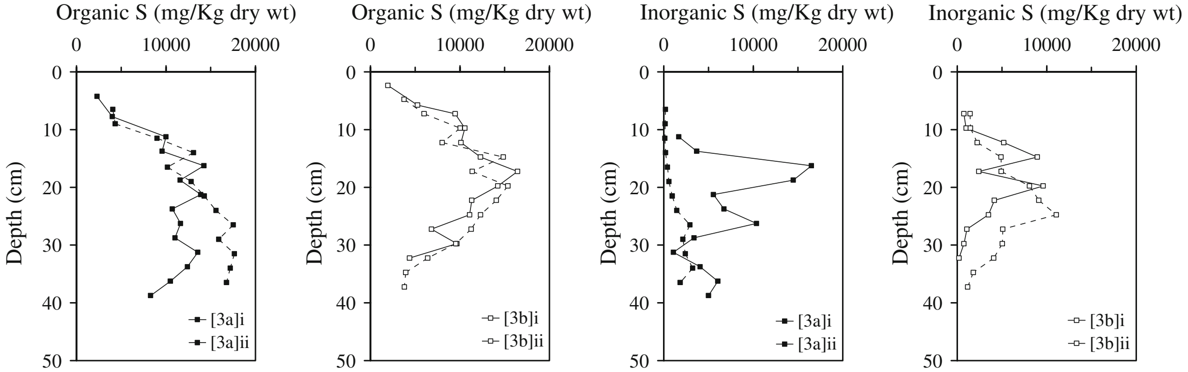
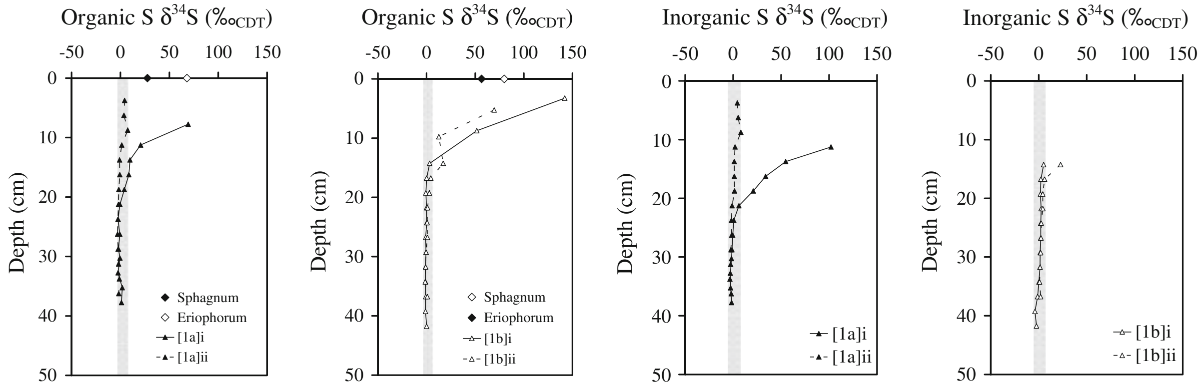


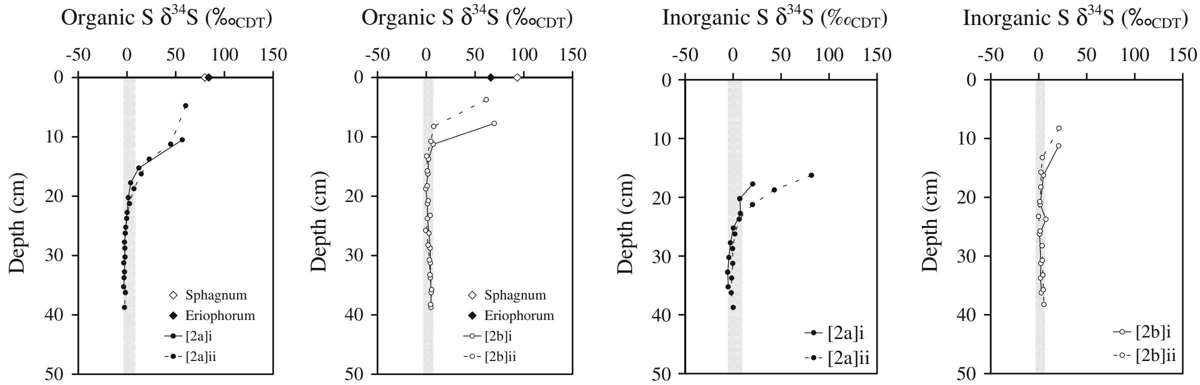
Fig. 4 Peat organic and inorganic sulfur concentration during tracer experiment: **a** 12 weeks (enclosures [1a] and [1b]); **b** 24 weeks (enclosures [2a] and [2b]); **c** 48 weeks (enclosures [3a] and [3b])

of vegetation with time during the experiment (Table 1). There was also significant tracer uptake into organic fraction of the shallowest (<25 cm) peat layers (up to 25.6% of tracer added at 48 weeks); no measurable incorporation into the peat organic fraction occurred below 25 cm depth (Fig. 5; Table 1). Incorporation of tracer into inorganic forms in the solid phase (CRS) shows a similar trend to the organic fraction; however, this was always <10% of that in the organic fraction in any sample.

(a) 12 weeks



(b) 24 weeks



(c) 48 weeks (note change in scale for Organic Sulfur)

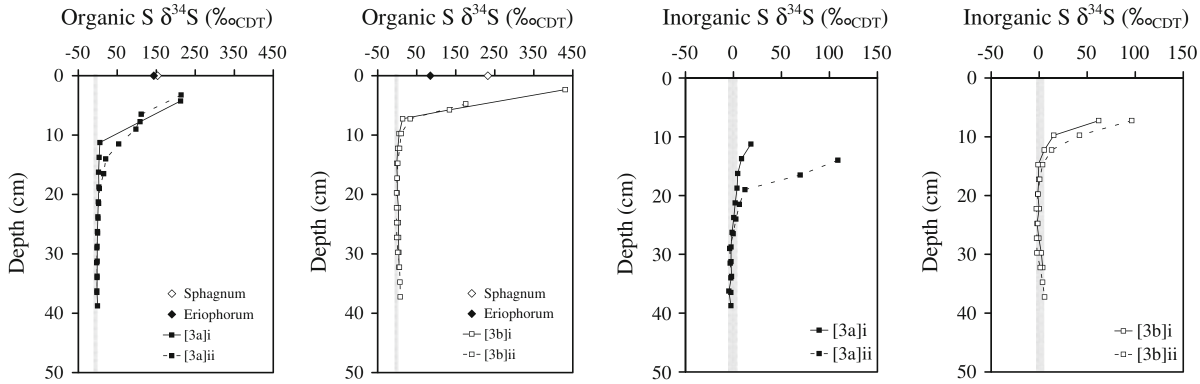


Fig. 5 Vegetation and peat organic and inorganic sulfur isotopic composition during tracer experiment (*shaded line* indicates isotopic range for control data): **a** enclosures [1a] and [1b] (sampled at 12 weeks); **b** enclosures [2a] and [2b] (sampled at 24 weeks); **c** enclosures [3a] and [3b] (sampled at 48 weeks

Absolute concentrations of sulfur in the organic and inorganic fractions of the peat are not affected by the tracer addition, and remain within the range of control data (Fig. 4; control data Fig. 1).

Discussion

Incorporation of the ^{34}S tracer into the sulfur pools of different fractions of the peat describes sulfur

Table 1 Tracer incorporation (mg/m^2 and %) in different sulfur pools of peat mesocosms

			12 Weeks enclosures [1_]		24 Weeks enclosures [2_]		48 Weeks enclosures [3_]	
			mg/m^2	%	mg/m^2	%	mg/m^2	%
Tracer added			31.50	100	47.25	100	78.75	100
S pool	Enclosure	Core						
Biomass	[_a]	i	2.60	8.3	2.61	5.5	9.00	11.4
	[_a]	ii	2.67	8.5	2.70	5.7	9.11	11.6
	[_b]	i	10.32	32.8	12.50	26.5	14.91	18.9
	[_b]	ii	10.67	33.9	12.83	27.2	15.05	19.1
Shallow peat organic-S	[_a]	i	0.00	0.0[a]	0.59	1.2	19.14	24.3
	[_a]	ii	1.55	4.9	1.16	16.0	22.36	28.4
	[_b]	i	−0.58	−1.84[a]	−0.26	−0.6[a]	0.63	0.8
	[_b]	ii	1.96	6.2	1.35	3.6	5.92	7.5
Deep peat organic-S	[_a]	i	−0.21	−0.6[a]	1.35	0.5[a]	−0.38	−0.5[a]
	[_a]	ii	0.01	0.0[a]	−0.19	0.0[a]	0.03	0.0[a]
	[_b]	i	−0.21	−0.06[a]	−0.01	−0.1[a]	−0.02	0.0[a]
	[_b]	ii	0.06	0.2[a]	−0.05	0.5[a]	0.09	0.1[a]
Total inorganic-S	[_a]	i	−0.27	−0.9[a]	−0.10	−0.2[a]	1.12	1.4
	[_a]	ii	0.10	0.3[a]	0.03	0.1[a]	2.28	2.9
	[_b]	i	−0.08	−0.3[a]	0.02	0.0[a]	−0.17	0.9
	[_b]	ii	0.26	0.8	0.37	0.91	0.30	0.4[a]
Surface water	[_a]			8		89		66
	[_b]			7		34		55
Total recovery	[_a]			18.5		103.4		105.75
	[_b]			42.85		48.5		78.85

Uncertainty due to natural abundance variation of ^{34}S varies with pool type and size but is in range 0.2–0.6% of tracer added. Pore-waters are not included as all values are less than uncertainty. Total recovery calculated as the sum of sulfur pools for each enclosure using the means for duplicate cores. Recovery approaches 100% with time, however, complete mass balance is not possible due to the heterogeneity of peat within enclosures and extrapolation of sub-sample to whole enclosure area

[a] Tracer incorporation is less than uncertainty (i.e., zero) due to natural abundance variability in controls

biogeochemistry at Thorne Moors. The sulfate tracer was rapidly removed from the surface waters with incorporation into living vegetation and removal through BSR, particularly in the summer growing season, although some recycling of the tracer to the surface waters is evident with periods of net return of ^{34}S to the surface sulfate pool in the autumn and spring. This implies short-term exchange of sulfur between surface water sulfate and one or more other sulfur reservoir, potentially through: decomposition of tracer-labelled plant biomass formed during the growing season (die-back of vegetation in autumn, e.g., Bottrell et al. 2004); reduction to sulfide followed by re-oxidation to sulfate (resulting from falling water tables in spring); formation of ester sulfate in the solid organic fraction followed by release of sulfate by hydrolysis (e.g., Mandernack et al. 2000). Removal of tracer from the surface waters in winter (36 weeks) is coincident with the highest δ values for pore-water sulphate at depth, suggesting enhanced downward advection of tracer during this time, potentially due to decreased evapotranspiration relative to natural precipitation.

Accumulation of ^{34}S in the pore-waters with conversion of ^{34}S sulfate to sulfide occurred rapidly in the shallow peat (down to 25 cm) with subsequent incorporation of ^{34}S-sulfide into the organic and inorganic fraction. Table 1 shows the % tracer incorporation into each pool and it is clear that there is a bias of tracer incorporation into the organic fraction of the peat, in accordance with previous studies (Brown 1985; Mandernack et al. 2000; Chapman 2001), most likely due to a lack of mineral substrate available for reaction and storage of sulfide as inorganic sulfur. In this study however, organic sulfur (operationally defined) comprises carbon bonded sulfur and ester sulfate so that it is not possible to determine the relative importance of ^{34}S-sulfide incorporation (from reduction of ^{34}S-sulfate) and the formation of ^{34}S-ester sulfate on the organic fraction isotopic composition.

Below 25 cm depth, penetration of ^{34}S-SO$_4$ into deeper pore-waters increases steadily with time, yet the isotopic composition of all other sulfur forms remain unchanged relative to the control data. There is no significant reduction to sulfide (and subsequent incorporation into the solid inorganic or organic fraction) or incorporation into organic fraction as ester sulfate below 25 cm depth during the 12 month experiment. Rates of BSR at this depth are negligible; (unlabelled) dissolved sulfide in the deeper peat has presumably been produced by BSR before the tracer experiment. The continued presence of historic free sulfide in the deep peat throughout the 12 month experiment is significant and suggests sulfide removal mechanisms are slow and/or limited (e.g., a lack of mineral substrate for reaction and ultimate removal of sulfide from pore-waters, Bottrell et al. 2007).

Without conversion of the ^{34}S tracer into the sulfide pool at depth, further conclusions as to the rates and mechanisms of the sulfur cycle, or the long term fate of sulfide below 25 cm depth, are limited. Rather, the inertia of the tracer demonstrates a limit to the depth of active sulfur cycling (essentially BSR) in this system. Previous work has shown that BSR will be less important relative to mineralisation of peat at depth (Bartlett et al. 2005), due to exhaustion of reactive organic matter as a metabolic substrate. Here, BSR is inhibited at a relatively shallow depth (25 cm), suggesting sulfur inputs are high relative to the peat's sulfur storage capacity. It is likely that under historically high sulfate loadings, removal of organic matter and production of sulfide by BSR has over time 'poisoned' the system relative to sulfate reducers.

The dominance of BSR in peat ecosystems is generally considered to provide a sink for sulfur (and acidity), and as such, a method for attenuation of acid rain, but this mechanism relies on storage of sulfide in the solid phase. In this heavily polluted site at Thorne Moors, acid sulfate deposition has been consistently high and it appears that this has been sufficient to exhaust the capacity of natural biogeochemical acid attenuation. Pollution of the natural system has determined a limit to the active sulfur cycle in the peat at a relatively shallow depth. Indeed, deep peat at Thorne Moors is apparently inert with respect to sulfur below 25 cm depth (over a 12 month time scale). Despite current recovery from acidification and a decrease in pollutant sulfur inputs, further changes to environmental conditions, for instance an increase in weathering due to global warming, have important implications for the fate of historic pollutant sulfur in peat ecosystems such as Thorne Moors. Oxidation of sulfide and degradation of carbon-bonded sulfur will potentially release considerable sulfate to surface waters under in-situ acidification (Clark et al. 2005; Bottrell et al. 2007). The role of peat as a sink for sulfur and carbon then, is a fragile balance; both exhaustible and reversible.

Conclusion

The ^{34}S tracer additions allowed the physical and chemical transformations of sulfur during peat diagenesis to be identified, in the field, without changes to biogeochemistry or time restraints. This is both qualitative, with obvious unnaturally high δ^{34}S values allowing the fate of sulfur to be identified, and quantitative, allowing tracer incorporation to be measured and compared between different sulfur pools (Table 1). This does require some assumptions in applying measured data to the whole enclosure, and requires robust control data to apply to mass balance calculations. Spatial variability affects a limitation to the method, as does the activity of sulfur cycling and pool size of some sulfur fractions (especially sulfide), yet it remains a relatively straightforward principle, that may be used on the small or large scale, in laboratory or field experiments.

The ^{34}S tracer study at Thorne Moors demonstrated the active sulfur cycle, and its limits within a polluted system. Sulfur cycling was active in the upper peat, largely driven by BSR; whilst deeper peat remained essentially inert with respect to sulfur cycling. Although ^{34}S sulfate was able to penetrate into deeper peat over time, this was not transformed by BSR, with any sulfide present maintaining 'natural' (pre-experiment) isotopic values. This may be explained by exhaustion of the sulfur system, where depletion in reactive organic matter limits BSR activity and a lack of mineral substrate (especially iron) for reaction and ultimate removal of sulfide from porewaters. At Thorne Moors then, the mechanism of acid sulfate attenuation (driven by BSR) is slow or exhausted, and this may be attributed to the legacy of persistent and heavy sulfur pollution in the area.

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References

Bartlett R, Bottrell S, Coulson J (2005) Behaviour of sulphur during diagenesis of a maritime ombrotrophic peat from Yell, Shetland Islands, UK. Appl Geochem 20:1597–1605

Bottrell SH, Novak M (1997) Sulphur isotopic study of two pristine *Sphagnum* bogs in the western British Isles. J Ecol 85:125–132

Bottrell SH, Coulson J, Spence M, Roworth P, Novak M, Forbes L (2004) Impacts of pollutant loading, climate variability and site management on the surface water quality of a lowland raised bog, Thorne Moors, E. England, UK. Appl Geochem 19:413–422

Bottrell SH, Mortimer RJG, Spence M, Krom MD, Clark JM, Chapman PJ (2007) Insights into redox cycling of sulfur and iron in peatlands using high-resolution diffusive equilibrium in thin film (DET) gel probe sampling. Chem Geol 244:409–420

Brown KA (1985) Sulphur distribution and metabolism in waterlogged peat. Soil Biol Biochem 17:39–45

Casagrande DJ, Gronli K, Sutton N (1980) The distribution of sulphur and organic matter in various fractions of peat: origins of sulphur in coal. Geochim Cosmochim Acta 44:25–32

Caufield C (1991) Thorne Moors. Sumach Press, UK

Chambers LA, Trudinger PA (1979) Microbiological fractionation of stable sulfur isotopes. Geomicrobiol J 1:249–292

Chapman SJ (2001) Sulphur forms in open and afforested areas of two Scottish peatlands. Water Air Soil Pollut 128:23–39

Chapman SJ, Davidson MS (2001) ^{35}S-sulphate reduction and transformation in peat. Soil Biol Biochem 33:593–602

Clark JM, Chapman PJ, Adamson JK, Lane SN (2005) Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. Glob Chang Biol 11:1–19

Coulson JP, Bottrell SH, Lee JA (2005) Recreating atmospheric sulphur deposition histories from peat stratigraphy: diagenetic conditions required for signal preservation and reconstruction of past sulphur deposition in the Derbyshire Peak District, UK. Chem Geol 218:223–248

Craig H (1957) Isotopic standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide. Geochim Cosmochim Acta 12:133–149

Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS (2006) Alternative explanations for rising dissolved organic carbon export from organic soils. Glob Chang Biol 12:2044–2053

Ferguson P, Lee JA, Bell JNB (1978) The effects of sulfur pollutants on the growth of *Sphagnum* species. Environ Pollut 16:151–162

Fowler D, Smith RI, Muller JBA, Hayman G, Vincent KJ (2005) Changes in the atmospheric deposition of acidifying compounds in the UK between 1986 and 2001. Environ Pollut 137:15–25

Gauci V, Dise N, Fowler D (2002) Controls on suppression of methane flux from a peat bog subjected to simulated acid rain sulfate deposition. Global Biogeochem Cycles 16:1004

Giblin AE, Likens GE, White D, Howarth RW (1990) Sulfur storage and alkalinity generation in New England lake sediments. Limnol Oceanogr 35:852–869

Halas S, Shakur A, Krouse HR (1982) A modified method of SO_2 extraction from sulphates for isotopic analysis using $NaPO_3$. Isotopenpraxis 18:11–13

Krouse HR (1977) Sulphur isotope abundance elucidates uptake of atmospheric sulphur emissions by vegetation. Nature 265:45–46

Krouse HR, Mayer B (2000) Sulphur and oxygen isotopes in sulphate. In: Cook PG, Herczeg AL (eds) Environmental tracers in subsurface hydrology. Kluwer, Massachusetts

Lee JA, Press MC, Woodin SJ, Ferguson P (1987) The effects of acid deposition on ombrotrophic mires. In: Hutchinson TC, Meema KM (eds) Effects of acid deposition on forests, wetlands and agricultural ecosystems. Springer, Berlin

Limbert M (2002) The mechanism of peat winning on Thorne Moors. THMCF technical report no 8. Thorne and Hatfield Moors Conservation Forum

Mandernack KW, Lynch L, Krouse HR, Morgan MD (2000) Sulfur cycling in wetland peat of the New Jersey Pinelands and its effect on streamwater chemistry. Geochim Cosmochim Acta 64:3949–3964

Mikaloff Fletcher SE, Tans PP, Bruhwiler LM, Miller JB, Heimann M (2004) CH_4 sources estimated from atmospheric observations of CH_4 and its $^{13}C/^{12}C$ isotopic ratios: 1. Inverse modelling of source processes. Global Biogeochem Cycles 18:GB4004

Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T, Wilander A, Skjelkvåle BL, Jeffries DS, Vuorenmaa J, Keller B, Kopácek J, Vesely J (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature 450:537–541

Morgan MD (1995) Modeling excess sulfur deposition on wetland soils using stable sulfur isotopes. Water Air Soil Pollut 79:299–307

Nedwell DB, Watson A (1995) CH_4 production, oxidation and emission in a UK ombrotrophic peat bog: influence of sulphate from acid rain. Soil Biol Biochem 27:893–903

Newton RJ, Bottrell SH, Dean SP, Hatfield D, Raiswell R (1995) An evaluation of the use of the chromous chloride reduction method for isotopic analyses of pyrite in rocks and sediment. Chem Geol 125:317–320

Novák M, Přechová E (1995) Movement and transformation of ^{35}S-labelled sulphate in the soil of a heavily polluted site in the northern Czech Republic. Environ Geochem Health 17:83–94

Novák M, Wieder RK, Schell WR (1994) Sulfur during early diagenesis in *Sphagnum* peat: insights from δ^{34}S profiles in peat. Limnol Oceanogr 39:1172–1185

Novák M, Buzek F, Adamová M (1999) Vertical trends in δ^{13}C, δ^{15}N and δ^{34}S ratios in bulk *Sphagnum* peat. Soil Biol Biochem 31:1343–1346

Nriagu JO, Holoway DA, Coker RD (1987) Biogenic sulphur and the acidity of rainfall in remote areas of Canada. Science 237:1189–1192

Robinson BW, Kusakabe M (1975) Quantitative preparation of sulphur dioxide, for ^{34}S/^{32}S analysis, from sulphides by combustion with cuprous oxide. Anal Chem 47:1179–1181

Siegfriedt RK, Wiberly JS, Moore RW (1951) Determination of sulfur after combustion in small oxygen bomb. Anal Chem 23:1008–1011

Shannon RD, White JR (1996) The effects of spatial and temporal variations in acetate and sulfate on methane cycling in two Michigan peatlands. Limnol Oceanogr 41:435–443

Shotyk W (1997) Atmospheric deposition and mass balance of major and trace elements in two oceanic peat bog profiles, northern Scotland and the Shetland Islands. Chem Geol 138:55–72

Steinmann P, Shotyk W (1997) Chemical composition, pH and redox state of sulfur and iron in two complete vertical porewater profiles from two *Sphagnum* peat bogs, Jura Mountains, Switzerland. Geochim Cosmochim Acta 61: 1143–1163

Strebel O, Bottcher J, Fritz P (1990) Use of isotope fractionation of sulfate-sulfur and sulfate-oxygen to assess bacterial desulfurication in a sandy aquifer. J Hydrol 121: 155–172

Turunen J, Tomppo E, Tolonen K, Reinikainen A (2002) Estimating carbon accumulation rates of undrained mires in Finland–application to boreal and subarctic regions. Holocene 12:69–80

Urban NR, Bayley SE, Eisenreich SJ (1989) Export of dissolved organic carbon and acidity from peatlands. Water Resour Res 25:1619–1628

van de Noort R (2001) Thorne Moors: a contested wetland in northeast England. In: Coles B, Oliver A, Bull D (eds) The heritage management of the wetland in Europe. Center for Wetland Resource, Louisiana State University, Baton Rouge, LA

Vile MA, Bridgham SD, Wieder RK (2003) Response of anaerobic carbon mineralization rates to sulfate amendments in a boreal peatland. Ecol Appl 13:720–734

Zhao FJ, Knights JS, Hu ZY, McGrath SP (2003) Stable sulfur isotope ratio indicates long-term changes in sulfur deposition in the Broadbank Experiment since 1845. J Environ Qual 32:33–39