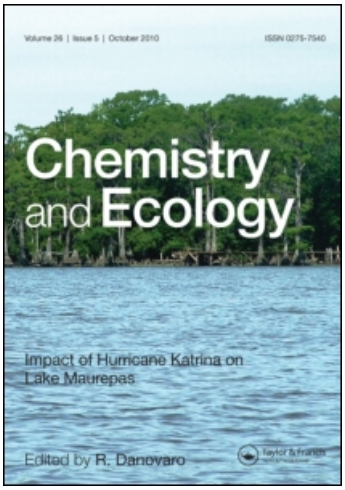

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The Effects of Acidity on Carbon Fluxes from Ombrotrophic Peat

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THE EFFECTS OF ACIDITY ON CARBON FLUXES FROM OMBROTROPHIC PEAT

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Replicate intact peat/vegetation monoliths were collected along a pollution gradient in the UK and subjected over one year to 1200 mm of simulated rainfall of the same chemical composition as they received in the field. Drainage water was analysed periodically for DOC and pH, and the decomposition rates of *Calluna vulgaris* and *Eriophorum angustifolium* leaves were measured, as well as soil atmosphere CO_2 contents and peat matric potentials. The chemical characteristics of the peats as initially sampled from the field also were determined. The results suggest that acidic precipitation has induced chemical changes in ombrotrophic peats, lowering their pH and base status, when due account is taken of calcium deposition or any mineral content. Greater DOC fluxes were observed from the more acid peats, and litter decomposition rates from these peats were reduced.

KEY WORDS: peat, acid precipitation, CO_2, matric potential, soil analysis, C sink, carbon, ombrotrophic peat, acidic deposition

INTRODUCTION

Peatlands contribute ca. 150×10^{15} g to the global reservoir of carbon and are accumulating carbon at a rate of about 0.2×10^{15} g each year (Bramryd, 1981). They are an important sink for carbon and sensitive to environmental change (Billings *et al.*, 1982). The blanket mires of the UK cover ca. 10% (2.4×10^6 ha) of the total land area and are recognised both nationally and internationally as important conservation areas (Clymo, 1984; Gorham *et al.*, 1984; Clymo, 1987; Kaakinen *et al.*, 1990).

Sensitivity of ombrotrophic peat to damage by pollution

Ombrotrophic peat bogs receive their inorganic element supplies predominantly from the atmosphere. This makes them particularly susceptible to, and potentially important indicators of, the effects of air-borne pollutants (Skiba and Cresser, 1989). Evidence for damage to peat can be obtained by observing detrimental changes to ecosystems because pollution effects manifest themselves in the flora of these areas (Sheridan and Rosenstreter, 1973; Andrus, 1986; Jassens and Glaser, 1986). However, it is also important to consider possible changes in the carbon budgets of peatlands. Changes along pollution gradients in the microbial decomposition processes or in mobilisation of carbon in peat may be a useful indicator for assessing their susceptibility to polluted atmospheric deposition effects.

A link between acid deposition and soil acidification has been established in both Europe and America (van Breemen, 1982; Skiba and Cresser, 1989; Cresser *et al.*,

1989; Clayton *et al.*, 1991), and there is now considerable evidence for acidification of hill peats (Skiba *et al.*, 1989; Smith *et al.*, 1993). However, the effects of acidification on the microbial biomass, decomposition and accumulation rates in peat soils are not well understood.

Decomposition measurements

It has been suggested that increases in nutrient status, e.g. from N and S inputs, may accelerate the decay of peat (Damman, 1978; 1986) assuming no other nutrient becomes limiting. Field studies and simulation experiments have shown, however, that rates of litter decomposition decrease at high levels of pollution (Killham and Wainwright, 1981; Moloney *et al.*, 1983; Brown, 1985; Skiba and Cresser, 1986). There are various ways in which organic matter decomposition rates in soils can be examined. The rate of CO_2 production is an indicator of microbial respiration rate (Waksman and Stevens, 1928; Silvola and Hanski, 1979; Svesson, 1980), whereas litter decomposition rate gives a relative measure of carbon turnover (Killham and Wainwright, 1981; Moloney *et al.*, 1982; Brown, 1985; Skiba and Cresser, 1986).

The meaningful study of the effects of deposition of acidifying pollutants from the atmosphere upon decomposition in peats is difficult because effects occur over diverse time scales. Short- to mid-term effects (hours to months) are much easier to assess than longer term effects (years to decades). The latter may involve, for example, interactive changes in peat accumulation rate, vegetation cover, litter deposition rate and peat structure. Peat from a single site may be used to study short- to mid-term effects in simulation experiments; however, peats from diverse sites and pollution environments must be studied to elucidate long-term effects. Unfortunately unequivocal interpretation of field-based data is then complicated because of the climatic and other differences which may occur between the sites simultaneously with pollution deposition differences.

The present paper outlines a study of key factors affecting peat accumulation rates, including soil respiration, litter decomposition, organic carbon and hydrogen ion fluxes, moisture content and temperature. Each parameter was monitored during a one year simulation experiment using intact soil-plus vegetation monoliths collected from nine Department of the Environment, UK (DOE) monitoring sites located along a pollution gradient. Turfs were assembled at a single location to minimise effects of variability in climatic parameters such as temperature, precipitation amount and distribution. Thus, over the duration of the experiment, differences observed should be attributable primarily to the combined effects of peat and precipitation chemistries.

METHODOLOGY

Peat Sampling

Areas of ombrotrophic peat (blanket/raised bog) were sampled close to DOE precipitation composition monitoring sites (UKRGAR, 1990). Nine sampling sites ranging in precipitation pH from 4.8 (Strathvaich) to 4.0 (Hatfield Moor) were chosen along a pollution gradient, as shown in Figure 1 and Table I. Samples from areas dominated by *Calluna vulgaris* were collected in June and July 1991. Intact

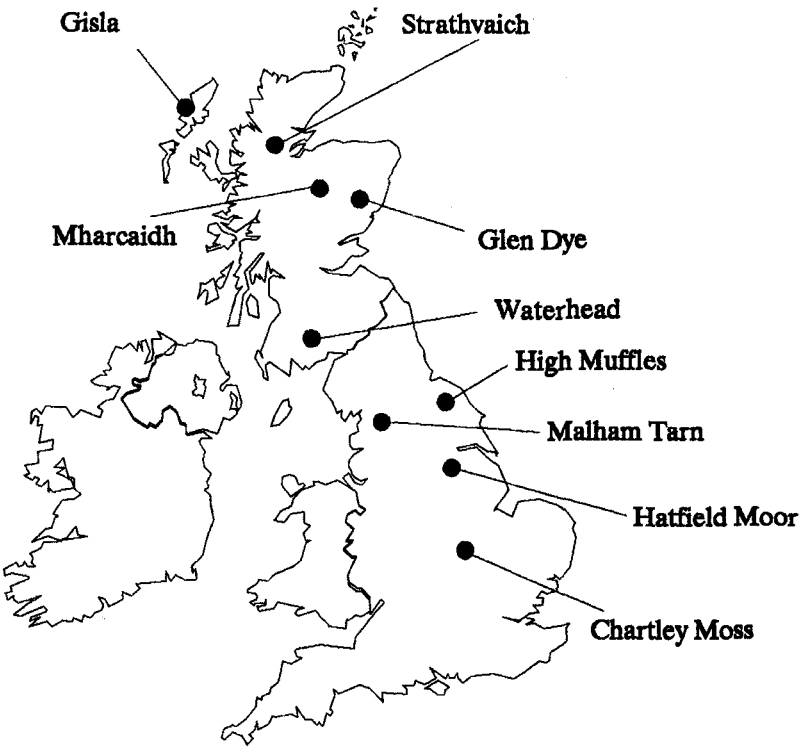


Figure 1 The sites chosen for peat sampling in the UK

Table I Mean bulk precipitation data 1986–1987 at the chosen peat sampling sites (after UKRGAR, 1990). Data are listed in order of increasing NH_4^+ concentration in rain, because this appears to be a better indicator than rain pH of peat acidification (Sanger and Cresser, unpublished results).

Site	pH	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	Mg^{2+}	Ca^{2+}	Cl^-
Gisla	4.8	0.77	0.56	0.09	5.82	0.71	0.26	10.90
Strathviach	4.8	0.72	0.28	0.04	2.23	0.28	0.14	4.15
Mharcaidh	4.7	1.10	0.68	0.11	1.33	0.17	0.18	2.34
Waterhead	4.5	1.73	1.12	0.29	1.82	0.23	0.18	3.41
Glen Dye	4.3	2.35	1.98	0.50	1.45	0.19	0.18	2.80
Malham Tarn	4.5	1.34	2.11	0.50	2.25	0.28	0.54	4.40
Chartley Moss	4.4	3.50	1.86	0.67	1.45	0.11	0.38	3.23
High Muffles	4.2	3.55	2.67	0.85	1.47	0.41	0.40	3.48
Hatfield Moor	4.0	5.33	2.85	1.01	1.66	0.31	1.12	4.79

All concentrations, except pH, are expressed in mgl^{-1}

peat turfs (460 × 320 mm) were cut from well-drained areas to a depth of 150 mm and placed in thermally insulated, expanded polystyrene containers of the same internal dimensions. Six turfs were collected from each site along with a ca. 1 kg representative peat sample which was used for routine soil chemical analyses.

Experimental Design

The turfs were placed in an unheated, shaded greenhouse in Aberdeen in a randomised plot design. Turfs were rearranged twice during the year to ensure that micro-climate effects within the greenhouse were kept to a minimum. In the field there would undoubtedly be climatic gradients associated with the pollution gradient which was used as a site selection criterion. Some turfs would be experiencing milder conditions in the glasshouse, while others would be being subjected to marginally cooler conditions than in the field. It was felt that this was acceptable, since the primary aim of the experiment was to factor out peat chemistry effects. It has been shown that pollution is a key factor regulating peat pH in the long term (Skiba and Cresser, 1989; Skiba *et al.*, 1989; Smith *et al.*, 1993). Most of the key differences in peat chemistry should reflect trends in deposition chemistry.

In the glasshouse, each of the peat turfs was subjected to simulated rainfall of the same chemical composition as that received in the field. In the natural environment, the sites receive between 800–1400 mm of rainfall a year. To minimise the number of variables, the simulated rainfall added to all sites was standardised to 1200 mm annually. This was acceptable since annual precipitation often varies at each site from year to year (UKRGAR, 1987; 1990). The formulation of this simulated rain for each site was made up using data from UKRGAR (1990) (Table I). The artificial rain was adjusted to incident pH with 0.1 M HCl as necessary. A schematic diagram of the experimental set up is shown in Figure 2. Each turf was irrigated twice a week with 1.7 l of simulated rainfall. Drainage water was collected from duplicate turfs from each site on a weekly basis, after allowing a 24 hr draining period to elapse following the second simulated rainfall event. The total volume of water from each turf was measured and a 100 ml sub-sample of the total weekly drainage water was retained for analysis. All turfs were irrigated with their respective rain composition over a 2 month period before the start of the experiment, thus minimising the risk that drainage water collected from the turfs during the experiment might show artefacts from disturbance after collection. The temperature of the greenhouse was recorded on each sampling day at 10.00 am. The lowest weekly mean 10 a.m.

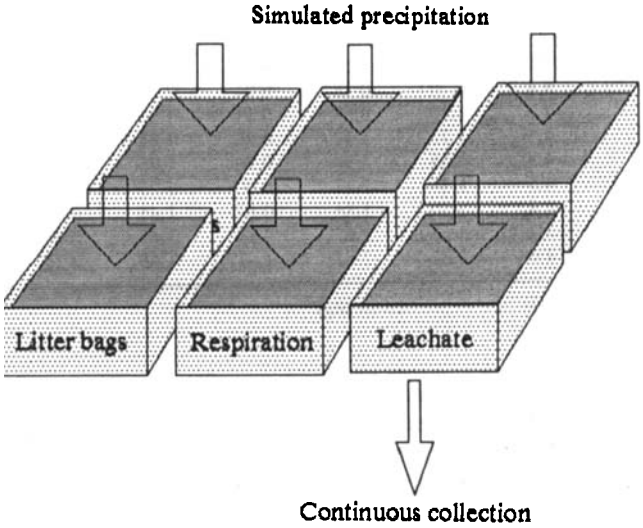


Figure 2 Experimental design for the examination of peat turfs from a single site

temperatures (ca. 2°C) were observed in weeks 19–24 (Jan/Feb) and highest (ca. 25°C) in weeks 37–43 (June/July). The temperature would undoubtedly have gone above 25°C on occasions.

Peat Drainage Water Analysis

The pH of peat turf leachates was determined immediately after collection using a combined low ionic strength glass/calomel electrode. Dissolved organic carbon (DOC) was determined using a Phase Separation TOCsin II system.

Soil Analysis

Peat samples were analysed for pH, cation exchange capacity (CEC), % base saturation (BS), moisture content and % loss on ignition (LOI). Soil pH was measured after equilibration for 1 hr with a 0.01 M $CaCl_2$ using a solution: soil ratio of 5:1. For the measurement of base saturation, 5 g of field-moist soil was extracted with 250 ml of 1 M $NH_4(C_2H_3O_2)$ and this extract was analysed for calcium, magnesium, sodium and potassium. The residual soil was washed with 80 % ethanol and then leached with 250 ml of 1 M NaCl. The amount of ammonium in this final wash was determined and results used to calculate the CEC. Dry weight was determined for each soil by drying 5 g of soil at 105 °C for 8 hr and LOI by placing the weighed, oven-dried, soil in a furnace at 850°C for 30 min.

Litter Decomposition

Four 150 × 150 mm nylon litter bags were buried to a depth of 10 mm below the surface of duplicate turfs from each site. A mesh size of 1 mm was used to ensure access by soil animals (Clymo, 1965). Two bags contained 1 g air-dried leaves of *Calluna vulgaris*, the other two 1 g of *Eriophorum angustifolium*, collected from the Glen Dye site at the end of the growth season. Decomposition was measured by the loss of air-dry weight after 12 months.

Soil Atmosphere and Matric Potential

Soil atmosphere CO_2 was collected using plastic soil atmosphere diffusion samplers permanently installed in the peat turfs (Skiba and Cresser, 1991). These were embedded at depths of 50 and 100 mm in duplicate turfs. 5 ml samples were taken twice each month and analysed for CO_2 concentration by gas chromatography.

Soil matric potential was measured at a depth of 100 mm in the same turfs monthly using permanently installed tensiometers manufactured within the department. Matric potential, which is a measure of the tenacity with which water is held by the soil matrix, was the most appropriate soil water parameter to measure because it indicates the potential flow of water to biological components of the soil-plant system (Mullins, 1991). Moreover, the measurements are non-destructive, which is important in long-term experiments.

RESULTS

Statistical analysis of the data was carried out using Statgraphics (for Spearman Rank Correlations) and Minitab (for ANOVA and LSD).

Table II Soil chemistry of different peats, listed in order of increasing NH_4^+ in precipitation, showing: % OM (organic matter), % DW (dry weight), LOI (loss on ignition as a percentage of oven-dry weight), pH in a calcium chloride paste, CEC (cation exchange capacity in moles of charge per kg of oven dry soil), % BS (base saturation).

	% OM	% DW	LOI	pH	CEC	% BS
Strathvaich	43.5	17.7	95.7	2.99	2.15	9.77
Gisla	44.1	13.4	96.6	3.02	2.44	10.0
Mharcaidh	44.4	14.4	97.3	3.01	1.92	8.07
Waterhead	44.2	19.5	96.8	2.70	2.18	7.75
Glen Dye	43.9	19.0	96.3	2.82	2.09	7.03
Malham Tarn	42.9	18.9	94.1	2.70	2.82	4.92
Chartley Moss	43.9	28.4	96.2	2.61	2.83	2.22
High Muffles	34.3	40.4	75.9	2.81	0.94	6.27
Hatfield Moor	40.8	28.9	89.7	2.86	1.98	10.6

Peat Chemistry

The characteristics of the peat samples are listed in Table II. The % dry weight (DW) is expressed relative to field-moist soil, and LOI as a % of the DW. The % organic carbon content was estimated from the LOI, using the empirical relationship derived for upland soils by Ball (1964). Moisture contents from Chartley Moss and Hatfield Moor (the more southerly raised bogs) were significantly lower than those from the more northerly blanket peats (LSD $p < 0.001$). Although there were significant differences between the soil pH from several sites, there was no correlation between peat pH and rainfall pH. This observation is to be expected, because of the variability in base cation inputs to the sites (Table I); high calcium inputs, especially, have a buffering effect (Smith *et al.*, 1993). Peat pH at unmanaged sites is primarily the net result of an ion exchange equilibrium governed by both wet and dry acidifying pollutant deposition and evapotranspiration effects, and dry deposition of base cations (Smith *et al.*, 1993). Chartley Moss (the more southerly site) had the lowest pH (pH 2.61) and Gisla (the more northerly site) the highest (pH 3.02). Peat from the High Muffles site had a relatively high mineral content, which was reflected in a high DW, low CEC and low % organic carbon content. There was no significant difference in the CEC or % organic carbon content of the soils from other sites at the time of sampling. The % base saturation, however, decreased from Strathvaich/Gisla to Chartley Moss. The Hatfield Moor peat had the highest base saturation (10.6%) and Chartley Moss the lowest (2.22%). High Muffles had a high % base saturation (6.27 %) because of its higher mineral content.

Peat Drainage Water

DOC concentrations in drainage water during the experiment are shown in Figures 3a–i. More acidic peats generally showed higher concentrations of organic carbon in drainage water and, for some sites, an increase between November and April (weeks 7–28), e.g. Glen Dye, Chartley Moss and Hatfield Moor (Figs. 3e, 3g and 3i). Drainage water from the High Muffles peat had a low organic carbon content. Between weeks 39–40 (May/June) all turfs showed elevated carbon concentration in drainage water. The greenhouse temperature during this week was also high (ca. 25°C). This flush was most apparent from sites with a low background DOC concentration e.g. Strathvaich, Gisla and Mharcaidh (Figs. 3a–c). As might be expected, the High Muffles soil did not fit within the general trend, probably because of its higher mineral content.

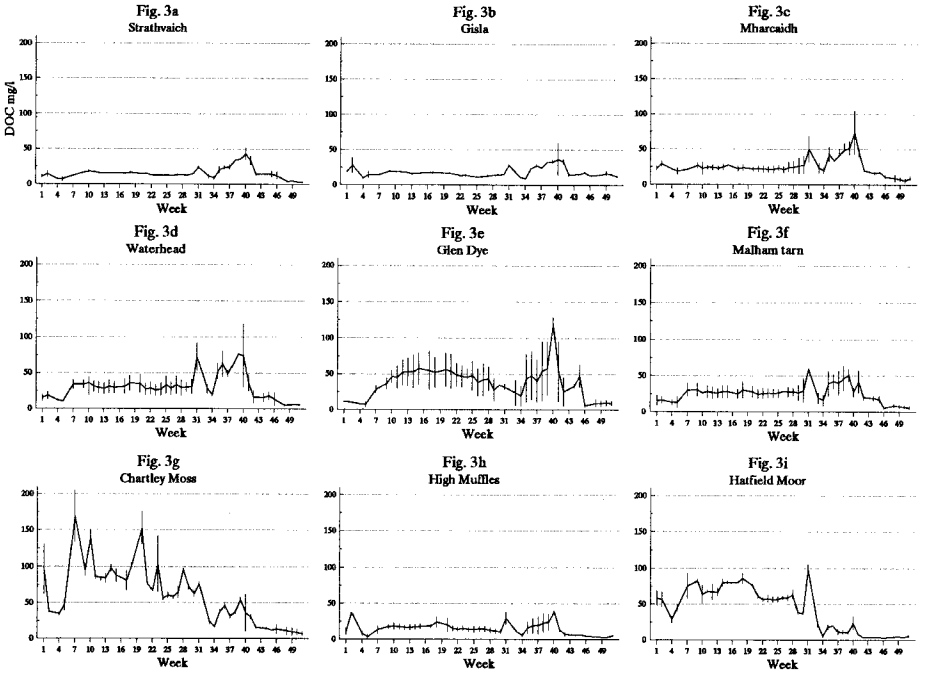


Figure 3 Dissolved organic carbon concentrations (mg l^{-1}) in drainage water from peat turfs over 51 weeks. Variability between duplicate analyses is shown by vertical bars

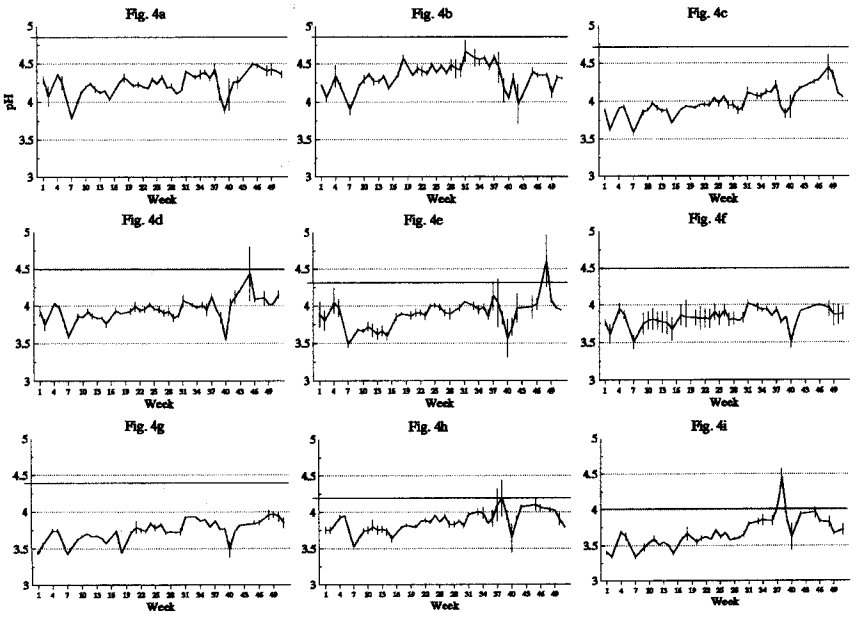


Figure 4 pH of drainage water from peat turfs over 51 weeks. Variability between duplicate analyses is shown by vertical bars. The pH of simulated rain input for each site appears as a solid horizontal line. a–i represent the same sites as in Fig. 3

Changes in the pH of drainage water from turfs over the 12 month experiment are shown in Figures 4a–i. The drainage water from all of the sites was more acid than the applied artificial rain (the solid horizontal lines on each graph). Drainage water pH was higher from areas where peat and the incident rainfall was less acidic; Strathvaich, Gisla and Mharciadh had a higher drainage water pH than Chartley Moss, High Muffles and Hatfield Motor (Fig. 4g–h cf. Fig. 4a–c). There was an increase in the pH of drainage water from all of the turfs between weeks 13 and 34. However, after week 34, several sites showed a stabilisation of pH or even a decrease in pH, e.g. Gisla (Fig. 4a).

Fluxes

Net H^+ and DOC fluxes were calculated by subtracting the total amounts of these components added to turfs in rainfall from the amounts in drainage water. These are illustrated in Figures 5a and b respectively, where the results are expressed in kg ha^{-1}.

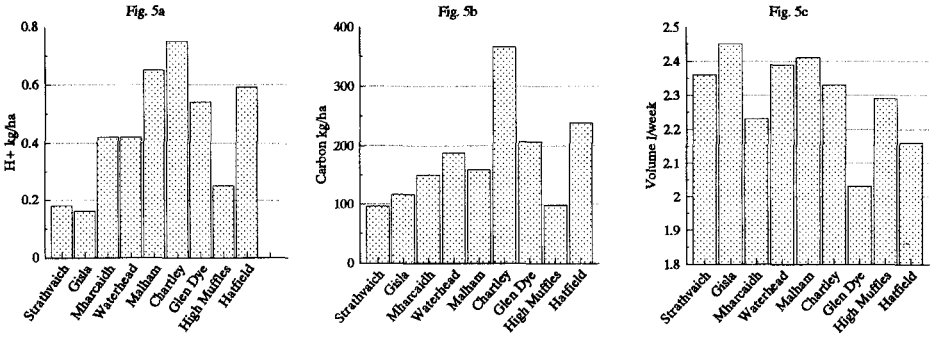


Figure 5 H^+ and carbon fluxes (kg ha^{-1}) and average weekly drainage water volume (litres) from turfs over 51 weeks

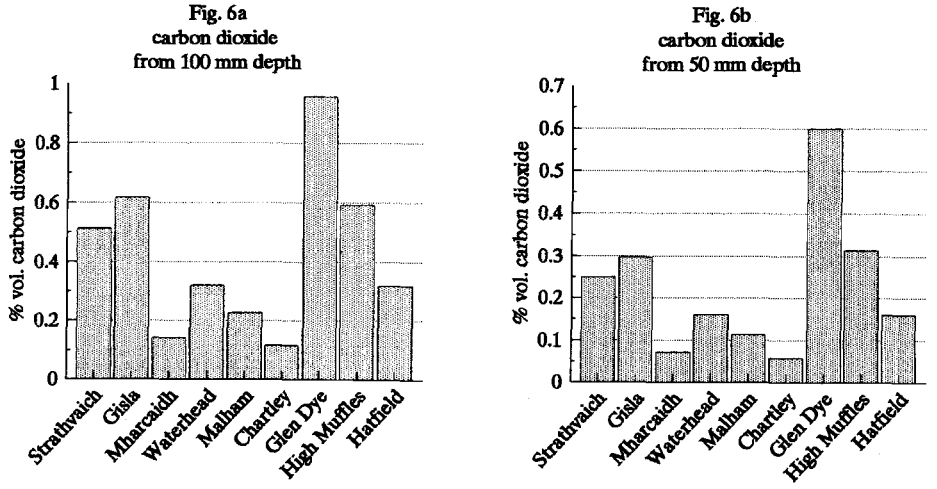


Figure 6 Average concentrations of CO_2 (% vol.) in the soil atmosphere collected at 100 and 50 mm depths

Results are plotted with sites in order of decreasing precipitation pH from Gisla to Hatfield Moor. The average volume of drainage water collected from turfs for each site is shown in Figure 5c. The largest average volume of water was collected from the Gisla turfs (ca. 2.45 l week^{-1}) and least from the Glen Dye turfs (ca. 2.00 l week ^{1}). Any trend in drainage water amount could be related to effects of the different pollution deposition rates or to climatic effects at the sites used in this experiment. Effects could be direct (e.g. peat structural change effects) or via changes in water use by vegetation.

All of the peats released H^+ during the experiment (Fig. 5a), the fluxes indicating amounts of H^+ released over and above the amounts in precipitation. The largest fluxes were observed from the Chartley Moss, Malham Tarn and Hatfield Moor turfs (0.6–0.7 kg ha^{-1}). These sites gave values ca. 5 times higher than those from Gisla and Strathvaich (0.15–0.2 kg ha^{-1}). High Muffles had a lower H^+ flux compared with the other high acid deposition sites (i.e. Chartley Moss, Malham Tarn and Hatfield Moor). If the results for High Muffles peat are excluded, the H^+ flux is positively correlated with both precipitation and peat pH (Spearman Rank Correlation $p < 0.05$). The High Muffles result probably reflects mineral weathering as a sink for H^+ at this site, because of the higher mineral content.

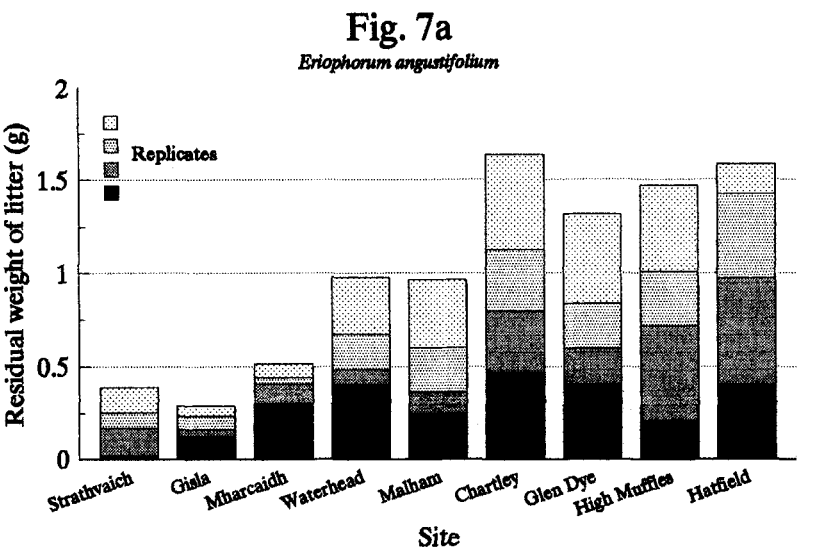
Leached organic carbon fluxes are shown in Figure 5b. All of the turfs released organic carbon, with the largest flux observed from the Chartley Moss site (ca. 370 kg ha^{-1}). High Muffles showed a relatively low carbon release (ca. 100 kg ha^{-1}). Organic carbon fluxes significantly increased with increased peat acidity ($p < 0.05$). Highest fluxes generally occurred in the more acidic sites (Chartley Moss and Hatfield Moor) and the lowest fluxes, apart from that for High Muffles, in the least acidic sites (Strathvaich and Gisla).

CO_2 Evolution

The inter-site variability is similar for CO_2 measured at both depths, with Glen Dye peats having the highest concentration of CO_2 and Mharcaidh and Chartley the lowest concentrations at both depths (Figs. 6a and b). The CO_2 concentrations at 100 mm depth were approximately twice as high as those at 50 mm depth. There was no relationship between CO_2 concentrations and either peat or precipitation chemistry. There was also no relationship between litter decomposition and these CO_2 results (Figs. 6a and b, cf. Figs. 7a and 7b). It should be noted that the CO_2 concentrations measured depended on the rate of CO_2 production and also the rate of CO_2 release from the peat. Thus, for example, wetter peats, or peats in which the pathway for CO_2 escape by diffusion to the atmosphere is more tortuous, will retain more CO_2 within the peat atmosphere.

Litter Bags

The residual weights of litter from both vegetation types and for each replicate are shown in Figures 7a and 7b. Both *Eriophorum angustifolium* (Fig. 7a) and *Calluna vulgaris* (Fig. 7b) produced similar trends along the pollution gradient. The trends were much less clear when the data were plotted in order of decreasing peat pH rather than in order of decreasing rainfall pH. Decomposition was lowest from the sites with most acid precipitation e.g. Chartley Moss, High Muffles and Hatfield Moor, and highest from sites with lowest acid deposition e.g. Strathvaich, Gisla and Mharcaidh (Figs. 7a and 7b). There was greater decomposition of the *Eriophorum* than *Calluna* in peat turfs from all sites.



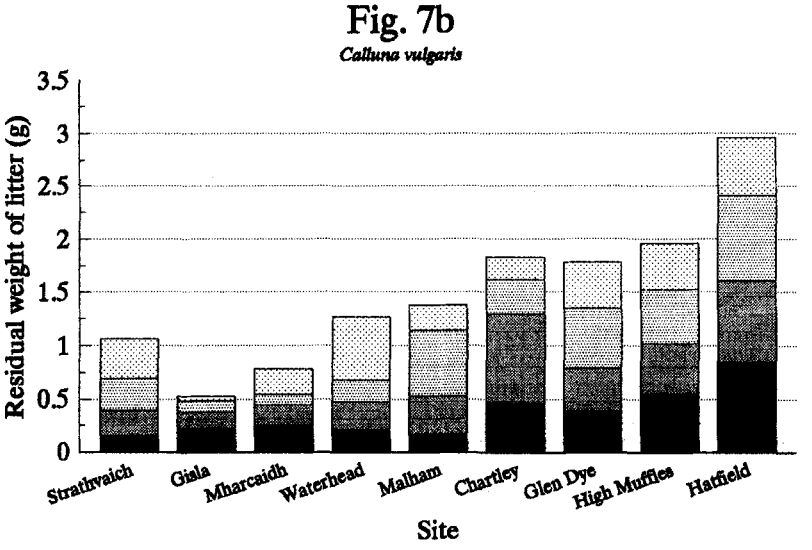


Figure 7 Residual dry weight of litter from *Calluna* and *Eriophorum* in litter bags placed in the surface of peat turfs. Replicates are shown as a stacked bar for each site

Matric Potential

Monthly tensiometer measurements at 100 mm depth (Fig. 8) showed a drop in the matric potential of turfs between March and May. However, by August the matric potential had recovered to levels similar to those before March (–1.5 to –2.5 kPa). The drying out of turfs was most apparent from sites with highest acid deposition and low peat pH (Glen Dye, Chartley Moss, High Muffles and Hatfield Moor). The lowest tensiometer reading was observed from the High Muffles peat in April

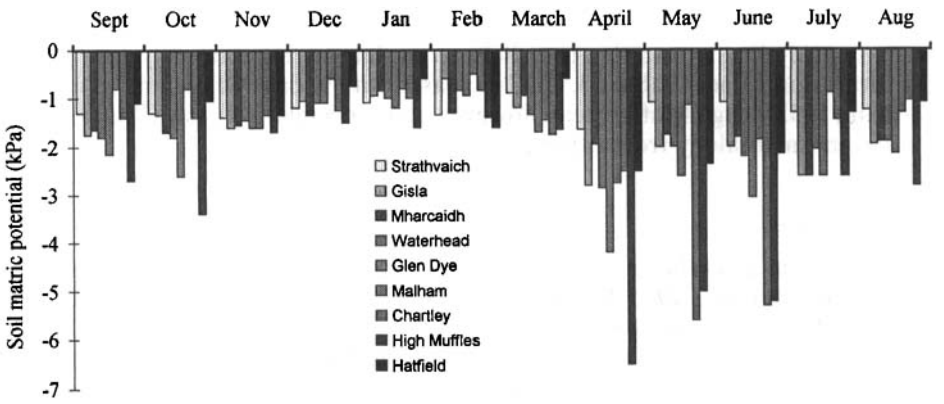


Figure 8 Matric potential from each site (kPa) during 12 months

(ca. –6.5 kPa). The matric potential of turfs from areas of low acid deposition were least affected, e.g. Strathvaich, Gisla and Mharcaidh.

DISCUSSION

Peat Chemistry

Chartley Moss, Hatfield Moor and High Muffles peats had lower moisture contents than peats from other sites in the study (LSD $p < 0.001$). There was no correlation between peat pH and moisture content. Except for the peats from Hatfield Moor and High Muffles, base saturation decreased with decreased precipitation pH, supporting the widely held view that cation exchange reactions dictate the surface chemistry of ombrotrophic peat (Damman, 1978; Clymo, 1984; Gorham *et al.*, 1986; Cresser *et al.*, 1989; Skiba and Cresser, 1989; Urban *et al.*, 1989). Peat pH showed a similar trend. The unexpectedly high base saturation at Hatfield Moor (10.6 %) is likely to be related to the large precipitation input of calcium compared with other sites (Table I). It has recently been shown that atmospheric calcium deposition should be considered when attempting to predict peat pH (Smith *et al.*, 1993). Chartley Moss, on the other hand, although receiving slightly less acidic rain, had a very low cation input and low base saturation and peat pH values. High Muffles has a much higher mineral content than the other sites (Table II), which could explain the unusually high base saturation at this site. Base cation leaching may have been induced by acid inputs at the sites in the field (Vitt and Bayley, 1984; Gorham *et al.*, 1984), although in this study there was no direct correlation for the complete data set between base saturation and precipitation pH. However, if data for High Muffles and Hatfield Moor are excluded for reasons given above, a direct relationship then emerges between precipitation pH and peat base saturation (Spearman Rank correlation $p < 0.05$), as found for Scottish peats by Skiba *et al.* (1989).

It is difficult to quantify the effect of field variation in evapotranspiration on the variation of peat chemistry between these sites. However, runoff figures (Dornkamp *et al.*, 1980); UKRGAR, 1990) were used to estimate the 'effective' pH of precipitation

for each site (H^+ load/total runoff). These suggest that Chartley Moss experiences the most acid climate and this may help to explain its exceptionally low pH and base saturation values (Table II). CEC increased with % organic carbon, as expected (Gorham, 1953). High Muffles peat, however, showed a relatively low CEC, reflecting its different mineralogy from other peats.

Drainage Water

Several short-term studies have found a positive correlation between pH and DOC in soil solution (Verry, 1975; Skiba and Cresser, 1986; Blancher and McNicol, 1987; James and Rhia, 1987; Sanger *et al.*, 1993). This is due to the acidic nature of soluble organic matter (fulvic and humic acids), which is more dissociated under alkaline conditions (Forsberg, 1988). Conversely other studies have shown that concentrations of DOC in drainage water appeared to be unaffected or even increased with increased precipitation pH (Gorham *et al.*, 1986; Krug and Isaacson, 1984; Stroo and Alexander, 1986a and b; David *et al.*, 1989). In the present work the more acid sites (with the exception of the more mineral-rich High Muffles soil) produced higher concentrations of DOC in drainage water (Figs. 3a–3i). This may be due, in part, to re-equilibration of peat turfs with reduced acid inputs during the experiment compared to those experienced in the field (Forsberg, 1988). Dry deposition, which may be particularly important, was not incorporated in this study. This trend is also reflected in the DOC flux measurements (Fig. 5b). The flow rate of water through these turfs was undoubtedly higher under experimental conditions than in the field. The mobilisation of DOC from higher water fluxes may have also resulted in increased DOC fluxes from turfs (Dalva and Moore, 1991; David *et al.*, 1992). It is also possible that the nature of the more soluble organic matter fraction differs in more acidic peats. This aspect requires further investigation. The differences observed in water retention may also influence organic matter solubilization and/or degree of decomposition.

CO_2 Evolution

A decrease in aeration (i.e. in pore size and continuity) with depth probably accounted for the higher soil atmosphere CO_2 concentrations at 100 compared with 50 mm depth (Figs. 6a and 6b). Unlike other studies however, the results show no link between soil acidity and respiration rate (e.g. Wilhelmi and Rothe, 1990). Work by Heal *et al.* (1981) suggests that most CO_2 produced from soil monoliths (ca. 50 %) could be from the respiration of plant roots. Although turfs evidently had differences in their capacity to hold water, we did not have sufficient data to relate this directly to differences in CO_2 evolution and/or retention.

Litter Bags

Over 90 % of the biomass in the surface 100 mm of ombrotrophic peat is dominated by *Enchytraeidae* (Cragg, 1961; Peachey, 1963; Standen, 1973; Heal *et al.*, 1981). Although a quantitative survey was not conducted during this study, the observation was made that under lower pollution input there was a greater abundance of worms in the proximity of the litter bags at the end of the experiment.

Litter decomposition by these animals is highly dependent on plant species and our results (Figs. 7a and 7b) agree with previous findings that decomposition of

Eriophorum is greater than that of *Calluna* (Springett, 1970; Heal and French, 1974; Coulson and Butterfield, 1978; Standen, 1978; Howard and Howard, 1980). *Enchytraeidae* are sensitive to changes in the soil environment (Standen and Latter, 1977; Bååth *et al.*, 1980; Williams and Griffiths, 1989; Heck and Roembke, 1990; Hagvar and Abrahamsen, 1990) and only the most acid tolerant species (e.g. *Cognettia sphagnetorum*) can survive in peat below pH 4.0 (Healy, 1980). Recent studies, however, have shown that atmospheric inputs of sulphur and nitrogen can reduce the population of *Cognettia sphagnetorum* in soil humus (Ohtonen *et al.*, 1992). Our results also show reduced litter decomposition with increased acidity and nitrogen and sulphur inputs (Figs. 7a and 7b). The results obtained are in accordance with the reduced enchytraeid populations observed at pH <3.8 and base saturation <10% (Bååth *et al.*, 1980; Abrahamsen, 1983). Decomposition by enchytraeids is also highly dependent upon soil moisture content (Standen and Latter, 1977; Healy, 1980). Optimum moisture for decomposition is ca. 70 % (Waksman and Purvis, 1932; Wilhelmi and Rothe, 1990). All of the peat samples examined had a moisture content between 70–90%, except for High Muffles (Table II) and there was no correlation between moisture content and litter decomposition. It is likely, therefore, that the observed differences in litter decomposition were a consequence of different peat chemistries. Further investigation is required into changes in abundance and number of enchytraeids along pollution gradients to determine the full significance of the results presented here.

Other studies from this laboratory (Skiba and Cresser, 1989; Skiba *et al.*, 1989; Smith *et al.*, 1993) suggest that peat pH and base saturation are regulated by effective precipitation pH and base cation (especially calcium) inputs. Provided the results for the mineral-rich High Muffles soil and the Hatfield Moor peat (a site with higher calcium deposition) are discounted, this experiment shows a strong direct link between precipitation pH and peat base saturation. In terms of effects upon biological activity, however, the adverse effects of site acidity will be further enhanced by the mobile anion effect in the peat soil solution at the more polluted sites. Thus, in this instance, there is a very good correlation between rainfall pH and the amount of litter decomposed, and this relationship is stronger than that between peat pH and amount of litter decomposed.

CONCLUSIONS

This study provides some support for the hypothesis that the chemistry of ombrotrophic peats and associated drainage water is dependent upon the chemistry of incident precipitation, provided base cation inputs are considered alongside precipitation pH. The peat soils sampled from areas of high acidic precipitation were characterised by a low pH and low base saturation. More acidic peats also produced higher DOC fluxes in the simulation experiment. This may have been caused by long-term chemical or physical changes. Alternatively, or in addition, the absence of dry deposition inputs, which were not included in this study, would have resulted in a lower (relative to field conditions) acid input in the simulation experiment; this could result in enhanced mobilisation of DOC.

Litter decomposition rates were apparently strongly related to precipitation chemistry, with the lowest decomposition rates from the sites receiving highest acidic inputs. The appropriate value of peat pH throughout this experiment to consider in the context of litter decomposition rates would be that of the soil solution. This

would depend on the peat pH, as measured in a calcium chloride slurry, but also upon the prevailing mobile anion content, which would be greater at a more polluted site.

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