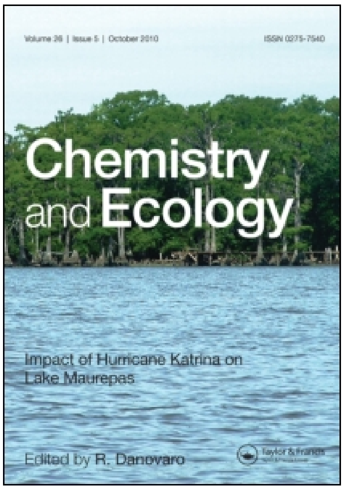

Chemistry and Ecology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455114

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To cite this Article Parveen, Zakia , Smart, Richard , White, Catherine , Gammack, Shimna , Deacon, Claire and Cresser, Malcolm(2001) 'Effects of Simulated Sulphuric Acid Deposition On *Calluna Vulgaris*/Peat Microcosms and Associated Soil Solutions', Chemistry and Ecology, 17: 4, 293 — 314

To link to this Article: DOI: 10.1080/02757540108035560

URL: http://dx.doi.org/10.1080/02757540108035560

Chemistry and Ecology, 2001, Vol. 17, pp. 293–314
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EFFECTS OF SIMULATED SULPHURIC ACID DEPOSITION ON *CALLUNA VULGARIS*/PEAT MICROCOSMS AND ASSOCIATED SOIL SOLUTIONS

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(Received 5 July 2000; In final form 28 August 2000)

Calluna vulgaris/peat microcosms have been used in an outdoor simulated acid rain experiment to test a series of hypotheses about sulphuric acid deposition effects upon the growth of *Calluna* on peat soil, namely: (1) Initially, enhanced acid input will enhance base cation and ammonium concentrations in soil solution. This may enhance uptake of these species, increasing foliar concentrations of base cations and nitrogen, and possibly foliar chlorophyll a and b concentrations. (2) If changes are induced in nutritional status, they may influence plant growth. (3) In the longer term, enhanced ammonium and base cation solubility occurring as a consequence of cation exchange reactions will lead, especially in winter months, to enhanced leaching losses. Hence any positive effects upon plant nutrition will not be sustainable. (4) The peat will acidify significantly over two years, in the shorter term primarily as a consequence of an enhanced mobile anion effect. (5) Acidification may reduce the rate of mineralisation of organic phosphorus and, in a phosphorus-deficient peat soil, this may lead to reduced foliar phosphate concentration and possibly induce phosphorus deficiency.

Most of these hypotheses were supported to some extent by the experimental results. The peat soil solution pH fell immediately in response to the acid treatments, and longer-term acidification continued progressively over the two years of the experiment. In the first year, the treatments significantly influenced the calcium, magnesium, phosphorus and nitrogen status of the leaves from *Calluna* new shoots, whereas in the second year calcium, potassium and phosphorus were influenced. However, in both years foliar phosphate concentration was enhanced, rather than reduced, in response to increased acid load. Foliar carbon and nitrogen concentrations fell with increasing acidity of

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applied rain in the first year, but the effect was much less pronounced in the second year, becoming insignificant for nitrogen. In spite of clearly visible reduction of greenness of the whole plants with treatment early in the growth season in both years, autumn shoot leaf sampling only showed a significant effect on pigments for chlorophyll b in the second year.

Keywords: Peat; Acidification; *Calluna vulgaris*; Chlorophyll; Nitrogen leaching; Phosphorus; Base cations

INTRODUCTION

There is considerable circumstantial evidence from regional surveys that Scottish upland mineral soils with low weathering rates are sensitive to acidification by atmospheric deposition (Barton *et al.*, 1994; White and Cresser, 1995; White *et al.*, 1995; White *et al.*, 1997). Additional mechanistic evidence that such soils acidify comes from leaching experiments with soil cores (White and Cresser, 1999) and plant/soil microcosms (Sanger *et al.*, 1996; Yesmin *et al.*, 1996a and b). These demonstrate both the enhanced base cation leaching which is indicative of acidification at the process level, and both short- and longer-term falls in soil drainage water pH. The short-term pH effects are associated with increased mobile anion concentrations, which increase equilibrium concentrations of H^+ in soil solution (White and Cresser, 1998).

Ombrotrophic peats, which are widespread in the uplands of Great Britain (Smith *et al.*, 1992), are particularly sensitive to acidification by atmospheric acid deposition. This is due to the absence of any base cation inputs whatsoever from mineral weathering (Bull *et al.*, 1992; Dawod and Cresser, 1997; Hornung *et al.*, 1995; Skiba and Cresser, 1989; Skiba and Cresser, 1989; Skiba *et al.*, 1989; Smith *et al.*, 1992). Moreover, for peats, processes such as sulphate physico-chemical adsorption, which may help to buffer against soil acidification in the short term (Barton *et al.*, 1997; Barton *et al.*, 1999; Chao *et al.*, 1965; Johnson and Henderson, 1979; Sanger *et al.*, 1994a), are much less significant.

The sensitivity of a soil to acidification by inputs of acidifying pollutants from the atmosphere is quantified in terms of its "critical load", the deposition flux of H^+ which is thought not to cause significant damage to the soil ecosystem function (Bull, 1993; Hornung *et al.*, 1995; Nilsson and Grennfelt, 1988). Although biological damage symptoms, such as adverse effects on plant growth or on aquatic life, are more immediately obvious than chemical damage in most ecosystems, soil chemical properties are used to quantify critical load. For critical loads to be environmentally relevant, however, it is important to be able to relate chemical "damage" criteria to some adverse biological effect. The widespread occurrence in Scotland of soils evolved from rocks such as granite and quartzite and sandstones (Barton *et al.*, 1994) leads to large areas of the country having soils with low critical loads (Bull *et al.*, 1992; Hornung *et al.*, 1995). It also leads to several areas where critical load, based on assessment of soil, is exceeded. In such areas, therefore, it should be possible to demonstrate that ecological damage is occurring.

Concern about acidification of peat and of acid mineral soils in the British uplands is not therefore caused simply by adverse effects on pH and base saturation (Sanger *et al.*, 1996) *per se*. It is more a response to possible adverse effects upon soil biological properties (Sanger *et al.*, 1994b; Yesmin *et al.*, 1995 and 1996c) and/or soil physical properties (Cresser *et al.*, 1997), and associated effects upon drainage water (and hence surface freshwaters) and upon the plant communities supported. The chemistry of soil and its associated drainage water is inextricably inter-linked (Billett and Cresser, 1992; Skiba and Cresser, 1989). As peats acidify, the associated drainage waters acidify too. Evidence for acidification of peat soil solution in response to acid deposition therefore also provides evidence for risk of acidification of upland rivers in catchments with peat soils in the riparian zone.

It has been suggested that a reduction in pH (as calcium chloride pastes) of 0.2 pH units for peat soils that are already very acid would be unacceptable, especially bearing in mind that the pH scale is logarithmic. Thus such a pH shift could serve as a useful damage criterion for peats when quantifying their critical loads (Bull *et al.*, 1992; Hornung *et al.*, 1995; Smith *et al.*, 1992). This concept has been accepted in the UK, and used for mapping critical loads of peat soils. However, this approach has recently been questioned, on the grounds that peat pH in water, or, better still, peat soil solution pH, would be more appropriate than peat pH measured as a calcium chloride paste (Cresser, 2000). Proctor and Maltby (1998) recently showed that the H^+ ion concentration of surface water collected from ombrotrophic peat bogs from all over Britain could be predicted from the effective (*i.e.*, corrected for dry deposition) pH of precipitation. However, regardless of whether a shift in pH (water) or a shift in pH ($CaCl_2$) is used for quantifying peat critical loads, it remains to be proved unequivocally that a pH reduction of only 0.2 unit really would seriously adversely effect functioning of peat and/or the growth of the vegetation species such as *Calluna vulgaris* that it usually supports.

Another potential problem with the critical loads approach is that values assessed from assumptions made about of soil equilibrium conditions provide no indication of the dynamics of change (Cresser, 2000). Estimations of natural weathering rates have been made from catchment studies (Edwards *et al.*, 1985), and some evidence for time scale of acidification has come from resampling sites and reanalysis after time intervals of a few decades (Billett *et al.*, 1998 and 1990). However, far fewer attempts have been made to estimate rates of soil acidification in response to acid deposition load. An exception is for peats, where results from simulation experiments were used to predict rates of pH change (Skiba and Cresser, 1989). The results suggested that a period from a few years to a decade or more would be required to reach a new equilibrium state in response to a change in acid deposition load. However, this has not been ratified experimentally under realistic conditions.

The purpose of the experiment described in this paper was to establish, using *Calluna vulgaris*/peat microcosms in a realistic outdoor simulated acid rain experiment, that peat pH did indeed change significantly over a period of two years, and, in an attempt to find symptoms characteristic of damage when critical load was exceeded, to test a series of hypotheses about sulphuric acid deposition effects upon the growth of the *Calluna*. It was thought that enhanced sulphuric acid input initially would increase base cation and ammonium concentrations in soil solution, which could increase uptake of these species by *Calluna* in the short term, and thus increase leaf concentrations of base cations and nitrogen. It was further thought that an increase in leaf nitrogen concentration could lead to an increase in leaf chlorophyll a and b concentrations, and changes in plant nutritional status could influence plant growth. In was also thought that, over the longer term, enhanced ammonium and base cation solubility as a consequence of cation exchange reactions would lead, especially at times of the year when plant growth rate and nutrient uptakes were low, to enhanced leaching losses. Hence any positive effects upon plant nutrition were expected to be not be sustainable for more than a few months. It was postulated in addition that peat acidification might reduce the rate of mineralisation of organic phosphate and, in a phosphorus-deficient peat soil, this might lead to reduced leaf phosphate concentration, and possible phosphorus deficiency.

MATERIALS AND METHODS

Peat was collected from a relatively unpolluted area of Great Britain (Shieldaig, in north western Scotland; Ordinance Survey Grid Reference NG852 485). The peat, which was taken from the top 50 cm of a 1 m deep peat profile at a *Calluna* heathland site, had a relatively high pH (water) of 4.82 compared to the pH values of around 3.9 for peat drainage water in north east Scotland (Skiba and Cresser, 1989). This might be expected for this relatively unpolluted area. As far as practically possible, obvious roots were removed as the sample was taken. On return to the laboratory, the peat was partially air dried by spreading to a ca. 3 cm layer on polythene sheets on tables in a vacant room. The peat was turned frequently, further obvious root fragments being removed, until the moisture content was sufficiently low to allow it to pass readily through a 5 mm sieve. Replicate sub-samples were then taken for chemical analysis by routine methods (Tab. I).

TABLE I Selected properties of Sheildaig peat

pH (water)	4.22
pH ($CaCl_2$)	3.56
Moisture (%)	190
C (%)	38.4
N (%)	2.03
C : N ratio	19
K_{Exch} ($mmol_c$ kg^{-1})	1.68
Na_{Exch} ($mmol_c$ kg^{-1})	1.94
Mg_{Exch} ($mmol_c$ kg^{-1})	9.29
Ca_{Exch} ($mmol_c$ kg^{-1})	11.8
CEC ($mmol_c$ kg^{-1})	1107
Base Saturation (%)	0.23
Al_{Exch} ($mmol_c$ kg^{-1})	27.31
Ca : Al ratio	0.43

Partial drying of the peat facilitated homogenisation and potting. Complete air-drying could have changed the peat excessively, and made it hydrophobic. To allow for possible variation in moisture content, therefore, pots were filled by volume rather than weight of peat. Thus 8.5 litres of sieved peat was added from a calibrated bucket to each of a series of 24 pots. Each pot was 21.5 cm deep, and had an upper diameter of 25.5 cm.

Healthy third year *Calluna vulgaris* plants of a single cultivar (to minimise variation) were obtained from a nursery in Northumberland. The nursery potting compost was carefully teased from the roots of the 3 year plants with gloved fingers and a fine spray of water. Some loss of fine roots occurred, but this was minimal and the plants with cleaned roots still had a very extensive root system. Each *Calluna* plant was potted immediately after washing in homogenised peat, and the pots were then randomised. The transplants were kept in a sheltered position outdoors for one month prior to acid treatment application. The plants and peat were sprayed periodically when necessary with deionized water to maintain a suitable moisture content.

The pots were then moved to randomised positions on a 10 cm layer of washed coarse granite chips covering a layer of heavy duty black polythene at the bottom of a 30 cm deep trench in the Cruickshank Botanic Garden in Aberdeen. The space between the pots was then filled with more washed coarse granite chips, to 1 cm below the pot rims. Thus all plants were subjected to the same climate and prevailing outdoor temperature, and the peat was protected from inappropriately low and high temperature extremes below the surface.

Acid Treatments and Their Application

As well as natural Aberdeen rainfall, all the potted plants received a twice-weekly supplement of artificial rain, sprinkled gently over the plants and the surface of the peat, to give a total annual rainfall supplement of 1345 mm. This contained the treatments. The average annual rainfall for Aberdeen is 655 mm. Thus the artificial rain treatments resulted in the microcosms receiving an annual total precipitation of 2000 mm, a realistic value for many parts of Scotland. If it is assumed that the annual evapotranspiration for Aberdeen for moorland vegetation is 410 mm, the effective rainfall (precipitation excess or drainage) becomes 1590 mm. This value was used to calculate effective rain pH, as described by Smith *et al.* (1992).

The simulated rain supplements contained sulphuric acid concentrations to give a range of total H^+ loads (including H^+ in Aberdeen rainfall) of approximately 25, 100, 260, 430, 1560 and 4900 mmol cm^{-2} yr^{-1}. The precise precipitation formulation is shown in Table II. The simulated rainfall contained, in addition, background concentrations of base cations and anions appropriate for north east Scotland. This is essential for simulated rain experiments with soil organic horizons, because the peat chemistry depends upon the relative amounts of all cations in the precipitation (Cresser *et al.*, 1997).

The six treatments (H0–H5) corresponded to total H^+ loads that more than encompass the acid deposition range encountered in the UK uplands, and higher levels correspond to substantial critical load exceedance. This was deliberate, in spite of the fact that atmospheric SO_2 concentrations and non-marine sulphate deposition in the UK have been declining steadily since the late 1970s (Broughton *et al.*, 1998). It should be remembered that the aim of the experiment was to see if quantifiable symptoms of biological plant damage could be found that could be related to chemical changes observed. This was most likely to be achieved at deposition levels substantially in excess of critical load. Lack of damage under such extreme conditions would suggest that critical loads set for peat soils were over cautious, which would have implications for future pollution abatement strategies.

Soil Solution Sampling and Analysis

A rhizon soil solution sampler (Jones and Edwards, 1993) was inserted through the surface of the peat in each pot to sample soil solution from

TABLE II Summary of the concentrations (μmol l^{-1}) of the solute species in treatments for the enhanced sulphuric acid deposition experiment. Also shown is the approximate effective rain pH, calculated as described by (Smith *et al.*, 1993)

Treatment	*H_2SO_4-H^+*	*NaCl*	*$MgSO_4$*	*$CaCl_2$*	*Effective pH*
H0	0	118	14.4	7.1	4.80
H1	56.4	118	14.4	7.1	4.19
H2	175	118	14.4	7.1	3.78
H3	293	118	14.4	7.1	3.57
H4	1121	118	14.4	7.1	3.01
H5	3485	118	14.4	7.1	2.52

0–10 cm depth, approximately half way between the plant and the pot rim. This allowed soil solution anion and cation composition to be monitored at regular intervals over approximately 24 months (704 days). Soil solution samples were taken at 4-week intervals in the first year and at 6-week intervals over the second year. Thus day zero in time-series graphs for treatment effects was 28 days after the first treatment applications. Upon collection, samples were immediately analysed for pH. They then were stored at 4°C prior to determination of ammonium by automated colorimetry, base cations (Ca^{2+} and Mg^{2+} by atomic absorption spectrometry, Na^+ and K^+ by flame emission spectrometry) and major mobile anions (SO_4^{2-}, Cl^-, NO_3^-, PO_4^{3-} by ion chromatography). Generally analysis was completed within 7 days of sampling.

Soil Sampling and Analysis

The initial peat was analysed in triplicate before the start of the experiment in October, 1997 (Tab. I), and, thereafter, to assess treatment effects on the soil, in October, 1998 and in April and October, 1999. Sample availability was limited for these subsequent analyses, so only pH and carbon and nitrogen were determined. The samples for periodic assessment of treatment effects were taken to a depth of 10 cm using a 10 mm stainless steel cork borer. Roots were carefully removed by hand sorting (using polythene gloves) prior to analysis of the peat.

Plant Growth Measurements and Plant Sampling and Analysis

Growth parameters monitored non-destructively included number of flowering shoots per plant, and, as a quantitative estimate of plant bushiness, the % bare peat surface visible from directly above. The latter was estimated three times by eye for each pot, and the mean value taken. Both parameters were measured in October in both 1998 and 1999. Plant height was measured in 1999 only, because there were no apparent height trends in 1998.

Plant samples were taken in October in 1998 and 1999. Ten random shoots were harvested from each plant from the current season's growth. Leaves were removed from the stems and analysed for chlorophyll a and chlorophyll b (Cresser and O'Neill, 1980), carbon, nitrogen and base cations (Cresser and Parsons, 1979). The pigments were extracted by grinding a sub-sample of fresh material under liquid nitrogen and extracting with 80% acetone. The remainder of the leaf sample was oven dried at 80°C, weighed and ground, and a 100 mg sub-sample was subjected to a Kjeldahl digestion for base cation analysis (Cresser and Parsons, 1979). A further small sub-sample was used for carbon and nitrogen determination using a CNS analyser.

Statistical Analysis

All data were analysed using the package SPSS9. Treatment effects were tested by ANOVA. Where significant effects were found, LSD values were calculated between individual treatment means at $P \leq 0.05$.

RESULTS

Effects of Enhanced H^+ on *Calluna vulgaris*

All plants put on a large amount of new growth over both years of the study. There were relatively few obvious treatment effects upon the growth of the *Calluna vulgaris* plants, however. Plants for H4 and H5 treatments were noticeably less green early in the growing season in both years, but especially in 1999, and flower abundance was conspicuously greater at the higher acid treatments H4 and H5. As shown in Table III, however, the number of flowering shoots was variable, and only the H5 treatment in the first season resulted in an obvious large and highly significant enhancement in the number of flowering shoots. As expected, the number of flowering shoots, reflecting the strong growth rate, was higher in 1999 compared with 1998 for all the treatments. No attempt was made to ascertain mean flowering shoot length.

Although the percentage of visible soil was observed to decrease with increasing level of H^+ treatment, the effect was not significant. Similarly, apparent effects on plant mean height observed in the second year also proved to be not significant.

TABLE III Effects of enhanced H_2SO_4 deposition on number of flowering shoots on the individual *Calluna vulgaris* plants and leaf pigment concentrations (g kg^{-1}, means of 3 determinations) after 12 and 24 months of treatment application. LSD values corresponding to treatment effects differing significantly at 5% are also shown at the end of each row

	Treatment						
Determinant/year	*H0*	*H1*	*H2*	*H3*	*H4*	*H5*	*LSD 5%*
Flowering shoots/98	121	103	134	104	111	172	27
Flowering shoots/99	179	181	209	175	182	226	n.s.
Chlorophyll a/98	1.66	1.89	1.94	1.74	1.69	1.57	n.s.
Chlorophyll a/99	1.72	1.43	1.26	1.12	1.25	1.07	n.s.
Chlorophyll b/98	0.86	0.90	0.94	0.84	0.80	0.73	n.s.
Chlorophyll b/99	0.92	0.70	0.60	0.54	0.59	0.49	0.23

In spite of the visible foliar yellowing for the higher acid treatments (H4 and H5) early in each growth season, there was no significant treatment effect on the concentration of chlorophyll a in either year, and the effect on chlorophyll b was only significant in the second year (Tab. III).

Effects of enhanced sulphuric acid deposition on the nutritional status of *Calluna* leaves from new shoots are presented in Table IV. In 1998, calcium concentration increased significantly ($P > 0.05$) in

TABLE IV Effects of enhanced H_2SO_4 deposition on nutrient element and carbon concentrations (g kg^{-1}, means of 3 determinations) and on C:N ratio of the *Calluna vulgaris* leaves after 12 and 24 months of treatment application. LSD values corresponding to treatment effects differing significantly at 5% are also shown at the end of each row

	Treatment						
Determinant/year	*H0*	*H1*	*H2*	*H3*	*H4*	*H5*	*LSD 5%*
Calcium/98	4.60	4.30	4.47	4.64	5.49	3.43	0.48
Calcium/99	4.11	4.16	4.93	5.71	5.61	5.78	0.65
Magnesium/98	1.33	1.33	1.32	1.25	1.23	0.94	0.13
Magnesium/99	1.21	1.27	1.30	1.26	1.11	1.14	n.s.
Potassium/98	4.32	3.69	3.82	3.41	4.29	4.24	n.s.
Potassium/99	3.43	3.26	3.97	4.80	4.90	6.27	0.92
Phosphorus/98	1.46	1.60	1.49	1.52	2.07	2.13	0.35
Phosphorus/99	1.10	0.91	1.09	1.22	1.57	2.18	0.32
Nitrogen/98	11.3	8.9	9.3	8.9	8.1	7.5	1.5
Nitrogen/99	12.4	10.2	9.7	10.2	9.9	9.9	n.s.
Carbon/98	514.	517.	512.	511.	498.	492.	7.4
Carbon/99	521.	502.	502.	500.	490.	496.	15.5
C:N ratio/98	45.5	59.1	56.4	57.8	63.7	66.1	10.3
C:N ratio/99	44.2	49.8	52.2	50.3	49.9	50.4	n.s.

response to the H4 treatment compared to values for the H0–H3 treatments, but at H5 was significantly lower than for all other treatments. In 1999, however, calcium concentration increased more regularly with increasing H^+ application.

In 1998, new shoot foliar magnesium concentration systematically and significantly ($P > 0.05$) decreased with increasing H^+ application, but there was no significant effect by the following year. For sodium, no significant effects were observed. In 1998, there was no significant treatment effect on leaf potassium concentration, but in 1999 potassium concentration increased consistantly and significantly with sulphuric acid application rate (Tab. IV). Contrary to the initial hypothesis, foliar phosphate concentration increased significantly ($P > 0.05$) with sulphuric acid application in both years (Tab. IV).

Carbon concentration significantly ($P > 0.05$) decreased with increasing sulphuric acid application rate in both 1998 and 1999. New shoot leaf nitrogen concentration decreased markedly with increasing H^+ application, but the effect was only statistically significant in the first year (Tab. IV). Treatment effects on foliar carbon and nitrogen concentrations led to a substantial and highly significant decrease in C:N ratio in the first year, but by the end of the second growth season the trend was no longer significant.

Effect of Enhanced H^+ on Soil Chemical Properties

Soil pH, whether measured with water and calcium chloride, decreased significantly ($P > 0.05$) with increasing sulphuric acid application on all four sampling dates (Tab. V). There was a sharp and substantial pH fall for pH (water) in October, 1997 for the H2 to H5 treatments. This trend was slightly less pronounced in October, 1998, but very clear again in April and October, 1999. The peat pH($CaCl_2$) time series data in Table V show clear systematic trends for H3 to H5. The longer-term trends in pH are clearer for the calcium chloride data than for the water data.

Early on in the experiment in 1997, carbon concentration showed apparently significant ($P > 0.05$) differences between some treatments (Tab. VI), but these did not suggest any obvious systematic treatment effect. There was no apparent trend in the carbon % over time. In October, 1997 and April, 1999 there were some significant differences

TABLE V Effects of enhanced H_2SO_4 deposition on peat pH with water and with calcium chloride (means of 3 determinations) at times shown. LSD values corresponding to treatment effects differing significantly at 5% are also shown at the end of each row

	Treatment						
pH medium/time	*H0*	*H1*	*H2*	*H3*	*H4*	*H5*	*LSD* 5%
Water/10/97	4.19	4.21	4.04	4.03	3.65	3.32	0.13
Water/10/98	4.29	4.69	4.42	4.29	3.85	3.40	0.10
Water/04/99	4.90	4.73	4.38	4.17	3.64	3.13	0.13
Water/10/99	4.54	4.38	4.09	4.00	3.67	3.13	0.10
Calcium chloride/10/97	3.73	3.69	3.66	3.66	3.52	3.34	0.18
Calcium chloride/10/98	3.81	3.75	3.63	3.65	3.35	2.99	0.05
Calcium chloride/04/99	3.84	3.75	3.67	3.62	3.35	2.90	0.15
Calcium chloride/10/99	3.82	3.61	3.50	3.52	3.30	2.73	0.10

TABLE VI Effects of enhanced H_2SO_4 deposition on peat carbon and nitrogen concentrations (%) and C:N ratio (means of 3 determinations) at the times shown. LSD values corresponding to treatment effects differing significantly at 5% are also shown at the end of each row

	Treatment						
Determinant/time	*H0*	*H1*	*H2*	*H3*	*H4*	*H5*	*LSD* 5%
Carbon %/10/97	36.5	41.7	38.9	34.3	38.0	37.8	3.0
Carbon %/10/98	34.8	35.9	35.5	33.5	34.7	35.8	n.s.
Carbon %/04/99	34.4	34.9	34.9	35.6	35.5	35.2	n.s.
Carbon %/10/99	37.8	36.6	37.8	37.1	37.1	34.8	n.s.
Nitrogen %/10/97	2.22	2.53	2.39	2.06	2.23	2.25	0.19
Nitrogen %/10/98	1.80	2.01	2.04	1.91	1.99	1.94	n.s.
Nitrogen %/04/99	2.02	1.62	1.46	2.04	2.07	1.95	0.23
Nitrogen %/10/99	2.15	2.04	1.98	2.07	2.02	1.92	n.s.
C:N ratio/10/97	16.5	16.5	16.3	16.6	17.1	16.8	n.s.
C:N ratio/10/98	20.0	17.9	17.4	17.5	17.5	18.5	n.s.
C:N ratio/04/99	17.1	21.6	24.4	17.5	17.1	18.1	2.1
C:N ratio/10/99	17.6	18.0	19.2	17.9	18.4	18.2	n.s.

in peat nitrogen concentration between treatments, but again there were no systematic effects either with treatment or with time. Nor were there any obvious systematic trends in peat C:N ratio either with treatment or over time (Tab. VI), in spite of some apparently significant treatment effects in April, 1999. The differences between the values for %C and %N between Table I and Table VI are indicative of natural variation in the peat composition (heterogeneity). Of necessity, only small samples could be taken to analyse for the peat time series plots. Bearing in mind that the peat had only been passed through a 5 mm sieve prior to use, the sample size was probably too small to detect relatively small effects.

Effect of Enhanced H^+ Deposition on Soil Solution

As expected, soil solution from soils receiving the more acid rainfall exhibited significantly ($P < 0.05$) higher H^+ concentrations almost from the outset through to the end of the experiment. Treatments with higher acid rainfall also resulted in substantial longer-term increase of H^+ concentration over time. Treatments were applied twice weekly from early July, 1997, and it appears that chemical equilibration had still not been fully attained by September, 1999 (day 704 in Fig. 1). There were corresponding highly significant treatment effects on soil solution sulphate concentration (Fig. 2). Other mobile anions, such as chloride (Fig. 3), showed no clear significant differences with treatments. The short-term treatment effects of sulphate concentration were clear throughout (Fig. 2). Longer-term effects were much less pronounced than those for H^+ (Fig. 1), and the sulphate time series plots exhibited greater variability. Chloride concentrations in soil solution were lower for the acid treatments over days 252–348 (25/06/98–30/09/98) and days 620–662 (30/6/99–10/8/99) (Fig. 3). This corresponded closely to seasonal summer troughs in marine salt

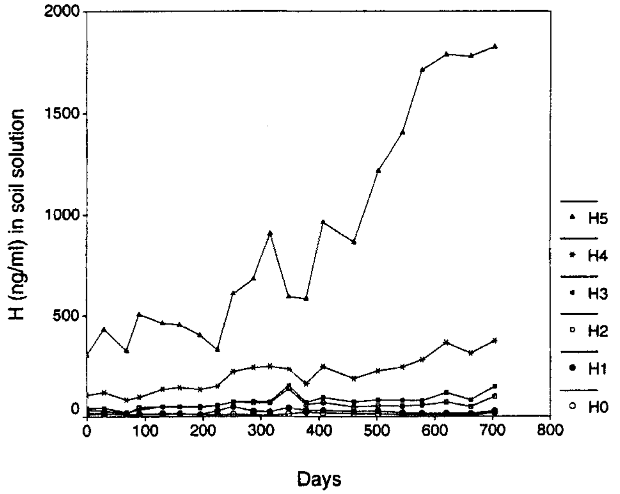

FIGURE 1 Treatment effects on time series plots for H^+ concentration in peat soil solution from day 0 (14/10/97) to day 704 (22/09/99). In Figures 1–5, day 0 is 28 days after the first treatment application, and follows 8 twice-weekly applications in total. Individual points are the means of four determinations. Treatments H0–H5 are as listed in Table II.

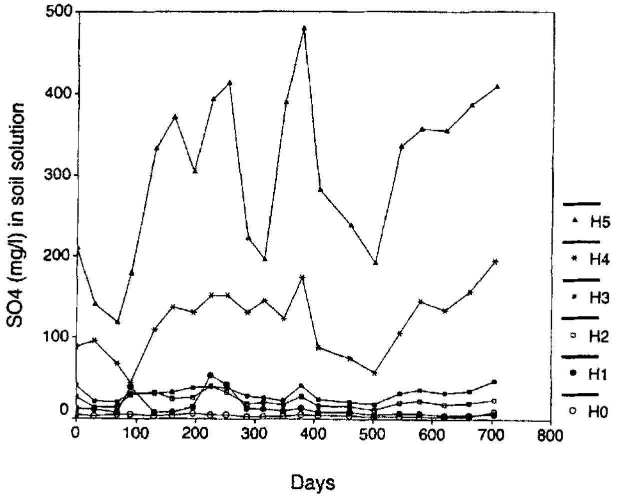

FIGURE 2 Treatment effects on time series plots for SO_4^{2-} concentration in peat soil solution from day 0 (14/10/97) to day 704 (22/09/99). Individual points are the means of four determinations. Treatments H0–H5 are as listed in Table II.

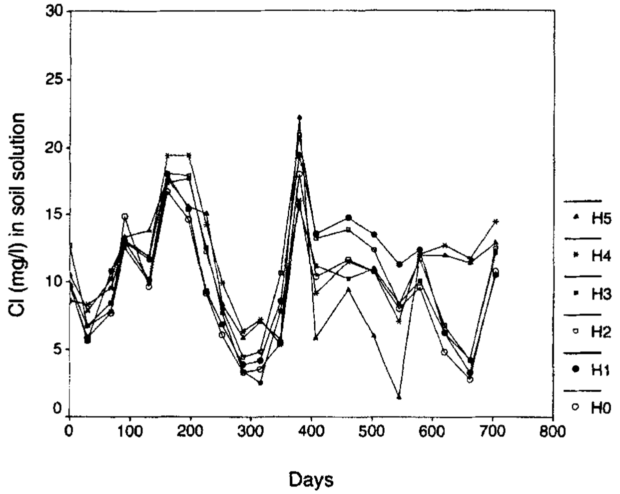

FIGURE 3 Treatment effects on time series plots for Cl^- concentration in peat soil solution from day 0 (14/10/97) to day 704 (22/09/99). Individual points are the means of four determinations. Treatments H0–H5 are as listed in Table II.

concentrations in Aberdeen precipitation (graphs not shown), and associated seasonal summer troughs are seen in the time series plots for sodium in peat soil solution (Fig. 4).

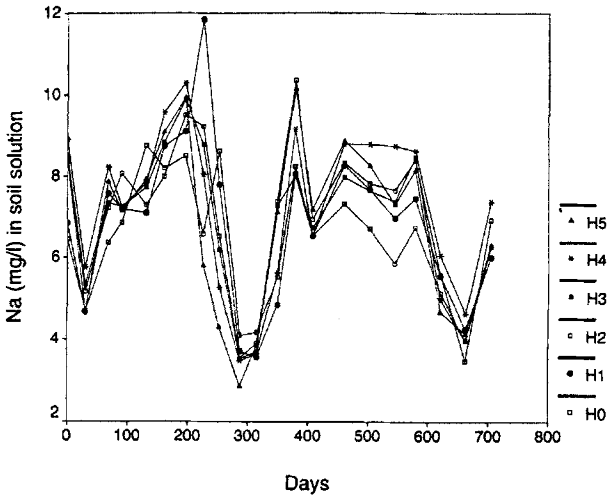

FIGURE 4 Treatment effects on time series plots for Na^+ concentration in peat soil solution from day 0 (14/10/97) to day 704 (22/09/99). Individual points are the means of four determinations. Treatments H0–H5 are as listed in Table II.

At the beginning of the experiment, highly significant enhancement of calcium concentration in the peat soil solution was observed due to treatment effects (Fig. 5). Soil solution data for the first five months of the experiment were analysed on a month by month basis to look for evidence of treatment effects. For calcium, the treatment effect was significant at $P < 0.001$ in October, November, December and February, and at $P < 0.01$ in January. This treatment effect was not sustained throughout the two years. However, even after 2 years the H0 treatment still resulted in the lowest calcium concentration. In July/September, 1998 (days 287–348) and late June/September, 1999 (days 620–704), calcium concentrations in soil solution tended to be lower.

The concentration of magnesium in soil solution showed similar initial large treatment effects to those observed for calcium, but there was no systematic long-term effect on magnesium concentration in soil solution. When the data was analysed on a month-by month basis, the treatment effect on soil solution magnesium concentration was significant at $P < 0.001$ in October, 1997, and at $P < 0.05$ in November, 1997 and January, 1998.

Potassium concentrations in soil solution were low (almost all $< 0.6\,\mathrm{mg\,l^{-1}}$) and rather variable throughout the experiment, and showed no clear systematic trend either with treatment or over time.

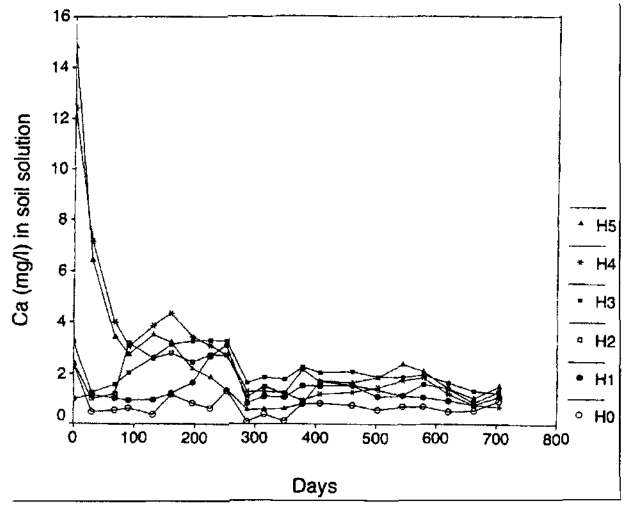

FIGURE 5 Treatment effects on time series plots for Ca^{2+} concentration in peat soil solution from day 0 (14/10/97) to day 704 (22/09/99). Individual points are the means of four determinations. Treatments H0–H5 are as listed in Table II.

DISCUSSION

Treatment Effects on Peat Chemistry

The most striking feature of the peat chemistry data is the almost immediate effect on soil solution pH caused by the increasing mobile anion (sulphate) concentration for the H2 to H5 treatments. This is obvious in Figure 1, and flags once again the importance of the mobile anion affect when quantifying acid deposition effects on soil pH and assessing likely biological impacts (White and Cresser, 1998).

The longer term effects on soil solution pH over the two-year time span of the experiment suggest the time scale of a few years for change in peat pH in response to change in acid deposition load, as advocated by Skiba and Cresser (1989), is indeed realistic. The results at H3–H5 for the peat pH($CaCl_2$) in Table V also suggest that the equilibration period is slightly longer than two years. Unlike the equilibration experiments of Skiba and Cresser (1989), in the present study the growth of the *Calluna vulgaris* will also have influenced the dynamics of pH change.

If the conclusions of Proctor and Maltby (1998) and Cresser (2000) are correct, the peat soil solution pH values at the end of the experiment should be approaching the calculated effective rain pH values listed in Table II. The soil solution H^+ concentrations in the latter stages of the experiment were converted to pH values to allow this comparison to be made. The values for the H1 to H5 treatments, and the corresponding effective rain pH values (shown in parentheses) were: H1, 4.40 (4.19); H2, 3.92 (3.78); H3, 3.71 (3.57); H4, 3.40 (3.01); and H5, 2.75 (2.52). The agreement is good, bearing in mind that equilibrium had not yet been reached, and biological N and S transformations and plant base cation uptake effects were not considered.

In previous microcosm simulation experiments with nitrogen additions, significant and substantial declines in peat C:N ratio have been observed over 12 months (Yesmin *et al.*, 1996a). In the present experiment, it was thought that the sulphuric acid inputs would displace ammonium, resulting in enhanced ammonium leaching, and a possible decline in soil nitrogen content and C:N ratio. The results in Table VI show that this was not what happened in practice. In this study treatment application commenced in July, 1997, but monitoring of soil and soil solution only started in October, 1997. It is possible that some additional ammonium leaching occurred over the intervening period, but there is no obvious difference between the initial peat nitrogen concentration of 2.03% in Table I and the nitrogen concentrations in Table VI for October, 1997. Differences would be hard to detect, because the small size of the peat samples that had to be taken resulted in a high LSD value (Tab. VI).

There are other possible reasons for lack of a treatment effect on peat total nitrogen concentration. (1) Compared with the total amount of nitrogen in 8.5 litres of peat, the amount of nitrogen lost by leaching, even over 2 years, would be small, so losses could easily be masked by natural variation. (2) Much of the ammonium nitrogen leached from the surface few centimetres of the peat could be retained lower in the peat, either by biological uptake or by cation exchange. (3) Uptake of nitrogen into the increasing plant biomass would partially mask any change in the peat nitrogen concentration or C:N ratio. Such an effect should be reduced at higher acid treatments, as leaf nitrogen concentration declined with increasing acidity. However, any reduction in the effect of plant uptake would be small, because the peat total nitrogen pool would be much larger than the plant biomass nitrogen pool. (4) The extent of ammonium leaching would depend partially on the mineralisation rate of organic nitrogen. The latter would almost certainly be slowed as the peat acidified. This could slow the rate of loss of soil total nitrogen. With hindsight, it would have been informative to monitor leached nitrogen species fluxes directly, and nitrate mineralisation rates, but this was not done.

Treatment Effects on the *Calluna vulgaris*

The optimum pH($CaCl_2$) for *Calluna vulgaris* is usually assumed to be at around 4.2 (Niers and van der Boon, 1985), so significant decline in growth might have been anticipated in response to the acid treatments. However, effects on height or bushiness (as reflected by visible soil %) were not significant in the present study. Foliar nitrogen concentration declined in response to treatment, however, and this could adversely effect *Calluna* yield in the longer term. There was a consequential decline in chlorophyll concentrations in 1999, although this was only significant for chlorophyll b.

The present experiment only covered 2 growth seasons. Residual effects of nutrients in the nursery-grown plants could have partly offset any potential adverse effects on plant nutrient concentrations. Moreover, caution is needed in interpretation of treatment effects upon plant nutrient concentrations when yield data are not available. Reductions in plant growth arising as a consequence of treatment effects may lead to relative increases in foliar concentrations of some plant nutrients which do not reflect changes in nutrient availability *per se*.

Although there was enhanced calcium in soil solution, and probably enhanced calcium leaching over the autumn of 1997, the treatment effect was to increase significantly foliar calcium concentration, especially by the end of the second growth season (Tab. IV). Probably calcium is more readily taken up by *Calluna vulgaris* from soil solution than from the cation exchange sites. Acidification of the peat would lower its cation exchange capacity, and this might temporarily enhance calcium availability. It is possible that the positive effects on calcium solubility and plant calcium uptake early on in the experiment offset adverse effects of peat acidification on *Calluna* growth for the duration of the experiment. Thus longer-term experiments may be required to demonstrate any adverse consequences of peat pH.

Surprisingly to the authors, increasing treatment acidity also substantially increased potassium concentration in the second season. In marked contrast, foliar magnesium concentration fell in response to increasing acidity. The increasing acidity would be expected to reduce the retention of magnesium inputs from the atmosphere and/or the treatments by the peat. Sulphuric acid deposition is also known to cause foliar leaching of magnesium and calcium from *Calluna* (Skiba *et al.*, 1986) and other shrubs (Willey and Hackney, 1991). These effects together could explain the observed effect for magnesium. The cause of the enhanced potassium concentration remains unknown. It is possible that less potassium is being taken up by peat microbial biomass in the acidified peat, but this must remain speculative at present.

There were marked increases in leaf phosphate concentration in response to increasing treatment acidity (Tab. IV). Clearly this is not indicative of the authors' postulated decrease in phosphate availability due to reduced rate of mineralisation of organic phosphate. The most probable explanation would seem to be increased competition between sulphate and phosphate for adsorption sites. This would not normally be expected for a peat, but the Shieldaig peat has a carbon concentration of only 38.4%, which is indicative of a small but significant mineral content, and hence of a capacity for phosphate adsorption. The exchangeable aluminium concentration (Tab. I) could also be indicative of a significant mineral content in the peat, since in the authors' experience most peat soils have extremely low extractable aluminium concentrations.

It is also possible that suppression of growth in response to treatment contributed to the increase in foliar phosphate concentration. However, the concentration change is too substantial to be fully explained in terms of growth suppression, since no such suppression was visibly apparent.

CONCLUSIONS

The results confirmed previous hypotheses that the rate of change of soil pH in response to acid load change is of the order of a few years and that effective rain pH provides a good measure of likely soil solution pH. This supports the suggestion by Cresser (2000) that effective rain pH could be used as a criterion for setting peat critical load, provided a critical pH shift can be defined. Treatment effects on *Calluna vulgaris* growth were small, suggesting that longer experiments would be needed to demonstrate these effectively. However, significant effects on the leaf concentrations of calcium, potassium, nitrogen, phosphorus and chlorophyll b were found, which would almost certainly influence growth in the longer term. The experiment highlights the need for longer term experiments on peat soils, and for more detailed studies of effects of peat acidification on nitrogen mineralisation dynamics and on phosphorus cycling within peat.

Acknowledgements

The authors are indebted to the UK Department of the Environment, Transport and the Regions and to NERC for financial support for this research, and to the Commonwealth Scholarship Commission for the award of a Commonwealth Fellowship to Zakia Parveen.

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