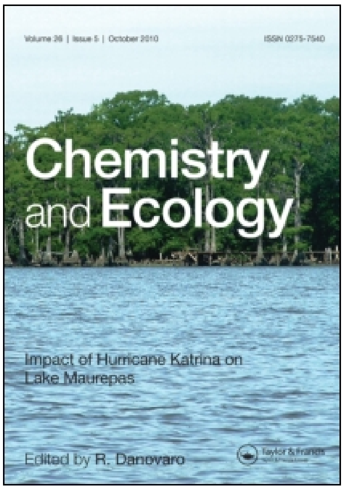


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# TOLERANCE OF *CALLUNA VULGARIS* AND PEATLAND PLANT COMMUNITIES TO SULPHURIC ACID DEPOSITION

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*(In final form 30 March 2004)*



Critical loads offer a unique way of evaluating impacts of acid deposition by quantifying environmental sensitivity. The critical loads of acidity for UK peat soils have been based upon an arbitrary reduction in pH of 0.2 units. This chemical shift needs to be better related to adverse effects on sensitive biological receptors. It is known that effective precipitation pH equates closely to soil solution pH, and the latter is directly linkable to biotic effects of pH change. On continuation of a long-term experiment assessing impacts of simulated acid rain on peat microcosms in a realistic outdoor environment, *Calluna vulgaris* continued to flourish at acid deposition loads well above the existing critical load. *Calluna* plants were harvested and analysed, and acid deposition treatments to the microcosms continued to allow natural vegetation to regenerate. A diverse mixture of moorland plants and bryophytes established at acidity treatments well above the existing critical load, and only a very high acid load resulted in no natural regeneration. A critical effective rain pH value of 3.6 is suggested as a basis for setting critical loads. At this pH, *Calluna* grows well, and a healthy diverse vegetation community re-establishes when harvested. It is suggested that the peat critical load should be set at the acid load that, at any specific site, would result in a mean effective precipitation pH of 3.6.

*Keywords*: Critical load; Peat; *Calluna vulgaris*; Effective rain pH; Bryophytes

## 1 INTRODUCTION

Peat soils susceptible to acidification by atmospheric pollutant deposition are widespread in the UK. Their negligible reserves of weatherable soil minerals have resulted in critical loads of acidity for peats being derived differently from those for mineral soils (Smith *et al.*, 1992; Gammack *et al.*, 1995; Hornung *et al.*, 1995). The response of organic soils to acidic deposition is determined by their hydrology, the chemistry of any lateral drainage water which flushes the peat, and the chemistry of atmospheric inputs (Hornung *et al.*, 1995).

Based on laboratory simulation experiments and the assumption of a pre-industrial peat in equilibrium with 'pristine' rain and current calcium deposition, Skiba and Cresser (1989) introduced the concept of effective rain pH (total acid load divided by runoff) for critical load calculations (Bull *et al.*, 1991, 1992; Smith *et al.*, 1992). Smith *et al.* (1992) set the critical load of peats to the level of deposited acid that would reduce the peat $pH_{CaCl_2}$ by 0.2 pH units compared with "pristine" conditions, and field data showed that predictions of peat pH

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were accurate (Cresser, 2000). The approach assumes that peat functions as a cation exchanger with characteristics independent of the physical conditions under which the peat formed. Wilson *et al.* (1995) criticised this as an oversimplification, as decomposition, nitrate uptake and organic acid production needed to be taken into account, too.

Defining critical loads with respect to a pH shift of 0.2 pH units was rather arbitrary, the value being primarily chemistry-based and only loosely related to known biological impacts. Sanyi (1989) had shown, in a glasshouse experiment, that liming of peat from Glen Dye, NE Scotland back to "pristine" pH values resulted in a 40% increase in the root and shoot growth rate of *Calluna vulgaris* over 6 months. The change corresponded to a pH increase of c. 0.5 pH units (Sanyi, 1989), and it was thus inferred that critical load had been substantially exceeded at such a pH shift. Therefore, a smaller reduction in peat pH of 0.2 pH units was chosen as a maximum acceptable level of acidification (Hornung *et al.*, 1995). The experiment was not, however, conducted under field conditions or for a long period, and insufficient data were available for a reliable dose–response relationship to be identified.

Data from subsequent studies linking biological change to chemical change suggest that the chosen value of 0.2 pH units may have been over-precautionary. Yesmin *et al.* (1995) showed statistically significant declines in enchytraeid worm populations in *Calluna* moorland peats from along a pollution gradient. However, a substantial exceedance of critical load would have been necessary to induce a significant decline in the total enchytraeid population (Yesmin *et al.*, 1995). A significant reduction in the degree of mycorrhizal infection of *Calluna* roots with declining pH was found by Yesmin *et al.* (1996), but their study did not establish that 0.2 pH units of acidification was appropriate for setting critical load. The best correlation they found ($r = 0.970$, $n = 6$, $P < 0.05$) between the degree of mycorrhizal infection and any of the pollutant deposition parameters studied was with effective rain pH (Yesmin *et al.*, 1996).

Intuitively, it is likely to be the "effective" concentrations of acidifying pollutants that invoke a biological response because both soil solution and precipitation equilibrate with the peat solid phase. The approach of using predicted pH in $CaCl_2$ pastes is hardly relevant to the effects of peat pH on its associated flora and fauna (Cresser, 2000). In particular, it ignores the crucial importance of the mobile anion effect on soil solution (White and Cresser, 1998; White *et al.*, 1995). Cresser (2000) concluded that for peat soils, critical load quantification could only sensibly be based upon the prediction of the pH of peat soil solutions. This could then be meaningfully related to biological and physicochemical effects (Sanger *et al.*, 1996; Cresser *et al.*, 1997).

Peat $pH_{water}$ is higher than the pH of peat soil solution, because the mobile anion effect is reduced by dilution. Dawod (1996) developed a novel procedure to estimate peat $pH_{water}$ at zero dilution based upon successive dilution and graphical interpolation to find the zero dilution value. He showed that the pH values of peat soil solution equalled almost exactly the effective rain pH values at the sites from which the peat had been collected. Further evidence to support this observation is provided by Proctor and Maltby (1998) from their work on pools in peat bogs, and from a 3-year experiment in which simulated acid rain was applied to *Calluna*/peat microcosms (Parveen *et al.*, 2001).

In the latter experiment, *Calluna* thrived at acid deposition loads well above the critical load. The plants were harvested after 3 years, and natural vegetation was allowed to regenerate for a further 2 years. A biodiverse mixture of moorland plants and bryophytes re-established at acid treatment values well above the critical load, and only an acid deposition load corresponding to a very high exceedance visibly damaged the *Calluna* over the first 3 years and stopped subsequent natural regeneration. The results after 6 years of continued twice-weekly supplement of artificial rain indicate that critical loads of acidity set for peat soils were substantially over-precautionary. Based on a current critical load assessment of soils, large areas of the country must have critical loads that are exceeded, but in these upland regions, it has not been possible to show ecological damage occurring. Mapped changes in the distribution of *Calluna vulgaris* (Preston *et al.*, 2002) confirmed this hypothesis. The above discussion suggests that a lower effective rain pH could be used to set critical loads of acidity for UK peat soils. This paper reports the composition of the harvested *Calluna vulgaris* from the peat microcosms experiment after 3 years of simulated sulphuric acid deposition, and the nature of the vegetation that subsequently re-established. The objective of the paper is to select an effective rain pH value for setting critical loads of acidity, by establishing biological links and critical thresholds, below which no statistically significant damage occurred.

## 2 MATERIALS AND METHODS

### 2.1 Microcosm Experiment

The peat used was sampled in April 1997 at Sheildaig in N.W. Scotland (OS grid reference NG852485), where the effective rain pH based on deposition data from 1989 to 1992 was c. 4.1. Hand-sorted and partially dried peat was used to fill sets of four replicate 10 l pots, each used to grow a 3-year plant of *Calluna vulgaris* cultivar in an outdoor-simulated acid-rain experiment in Aberdeen. Pots were watered twice a week with synthetic rainwater, supplementing ambient Aberdeen rain, giving a total of c. 2000 mm of precipitation per year with effective rain pH values ranging from 4.80 down to 2.52. At 6 months, 10 new shoots from each plant were sampled (in September) and analysed for N, P, base cations and pigments. This was repeated annually. The plants were harvested and analysed in 2000, after 3 years of treatment. Drainage water was also analysed periodically. Parveen *et al.* (2001) provide full details of the experimental design and methodology used and the initial treatment effects on the growth of *Calluna* and on the chemistry of the pre-harvest soil solutions.



Treatment application continued following transfer of microcosms to the walled garden at York University where natural vegetation was allowed to regenerate. The experimental design in York mimicked that in Aberdeen, but acid loads and effective rain pH were recalculated based on hydrological and deposition data in York. The mean average rainfall and runoff data (1991–1995) from the two gauging stations in closest proximity, the Nidd at Hunsingore Weir and the Ouse at Skelton (Natural Environment Research Council, 1998), were used to estimate a mean annual evapotranspiration value of 445 mm. Given an annual average rainfall of 437 mm in York (calculated using rainfall data from March 2001 to March 2002), the artificial rain treatments resulted in the microcosms receiving an annual total precipitation of 1782 mm. Based on the calculation of annual evapotranspiration for York, the effective rainfall (precipitation excess) becomes 1337 mm. The new effective rain pH values for the experiment, based on ambient plus treatment acid deposition at York, were then estimated as total $H^+$ load divided by precipitation excess.

The simulated rain supplements contained sulphuric acid concentrations to give a range of total $H^+$ loads (including $H^+$ in York rainfall) of approximately 8 (H0), 153 (H1), 472 (H2), 789 (H3), 3017 (H4) and 9376 (H5) mmol $m^{-2}$ $year^{-1}$, which equates to effective rain pH values ranging from pH 5.22 to pH 2.15. The loads more than encompass the acid deposition range encountered in the UK, so a lack of damage under the more extreme treatments would suggest that critical loads previously set are grossly over cautious.

### 2.2 Historical Data

To complement the analysis of current results, raw data from the Aberdeen phase of the experiment (plant yield, drainage water and soil data) were also considered. Soil solution and pigment data, collected both prior and subsequent to the results reported in the 2001 paper by Parveen *et al.*, are also considered.

### 2.3 Current Data

Soil solution sampling and analysis for pH, base cations, ammonium and nitrate were carried out as described by Parveen *et al.* (2001). All analysis was completed within 6 d of sampling

### 2.4 Plant Species Identification

All plant species present in each pot following natural regeneration were identified. As a quantitative indication of plant growth, the abundance of mosses was also estimated as the percentage cover of the peat surface.

### 2.5 Statistical Analysis

Data were analysed using the Excel package. Treatment effects were tested by ANOVA, and where significant effects were found, LSD values were calculated between individual treatment means at $P \leq 0.05$ using the statistical package SPSS11.



## 3 RESULTS

### 3.1 Effects of Enhanced Sulphuric Acid Deposition on Soil Solution

Parveen *et al.* (2001) showed that for the first two years of the experiment, soil solution receiving more acidic rainfall exhibited significantly higher ($P < 0.05$) $H^+$ concentrations and that soil solution closely approached effective rain pH, as predicted. Soil solution pH and effective rain pH were again strongly correlated in November 2002 after more than 5 years of treatment ($r^2 = 0.998$). For the H3 treatment, the soil solution pH was c. 3.6 in November 2002 and had not dropped to 3.2, the effective rain pH for the acid treatment load. This apparent difference was to be expected because the sampling was performed under wet conditions, minimizing the mobile anion effect.

After 6 years of acid deposition treatments, highly significant ($P < 0.05$) treatment effects on mean $Ca^{2+}$ concentration in soil solution were found. Consistent with Parveen *et al.* (2001), treatment effects up to H4 resulted in significant enhancement of $Ca^{2+}$ concentration in soil solution, but the effect was not sustained to H5. At this gross acidity, the majority of $Ca^{2+}$ was leached out. $Mg^{2+}$ showed few and only weak significant differences with treatment ($P < 0.01$) with similar initial effects to those observed for $Ca^{2+}$ (Fig. 1).

Significant treatment effects on mean total dissolved N (TDN) concentration in soil solution were found ($P < 0.05$), together with apparently highly ($P < 0.001$) significant effects on mean $NH_4^+$-N and organic-N concentrations. Significant differences in mean $NO_3^-$-N concentration in soil solution were found between treatments. There was such a highly significant enhancement of $NH_4^+$-N and thus TDN concentration in peat soil solution receiving the highest annual $H^+$ load that the data distribution is non-normal, and the linear regression analysis results are inappropriate for making inferences about what happens over the H0–H4 range (Fig. 2). The H5 effect probably reflects the absence of uptake of $NH_4^+$ by vegetation. $NO_3^-$-N concentration in soil solution with this treatment load was also significantly higher than for other treatments, suggesting the absence of $NO_3^-$ uptake by vegetation and possibly reduced denitrification rate (Fig. 3).

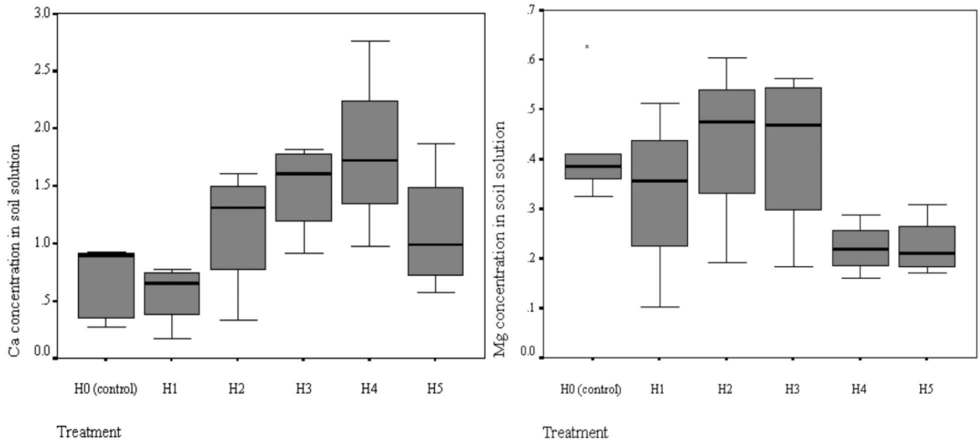


FIGURE 1 Box plots providing visual summaries for comparison of treatment effects on $Ca^{2+}$ and $Mg^{2+}$ concentrations (ppm) in soil solution (* indicates outlier value).



## 3.2 Effects of Enhanced Sulphuric Acid Deposition on the Composition of *Calluna vulgaris*

No significant treatment effects on chlorophyll a and b were found over 3 years in *Calluna* new shoot concentrations. Visual foliar yellowing was evident just prior to final harvesting (September 2000) only on plants receiving the highest acid deposition (H5), but even at this gross acidity, the effect on pigment concentrations was not statistically significant ($P > 0.5$).

Analysis of harvested *Calluna* plants to determine mean uptakes (above ground growth only) of plant nutrients after 3 years of treatment showed significant effects on the yields

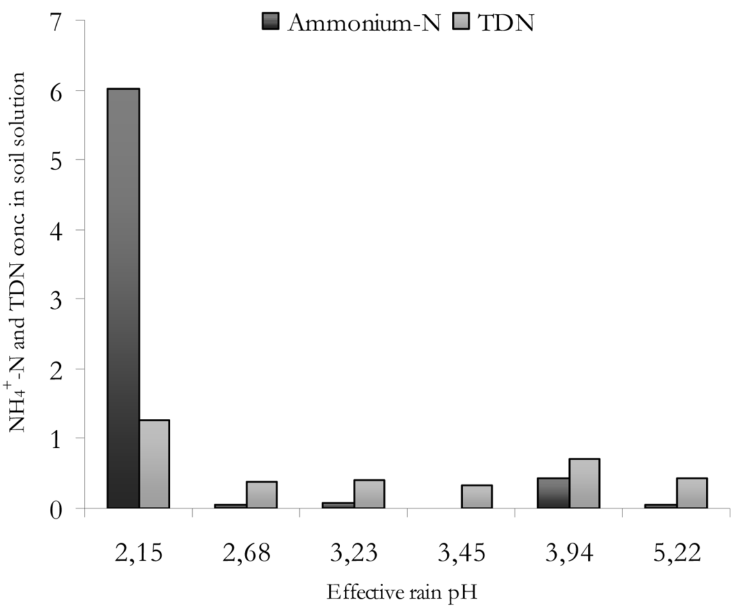


FIGURE 2 Treatment effects on mean TDN and $NH_4^+$-N concentrations (ppm) in soil solution after 5 years of acid treatment.

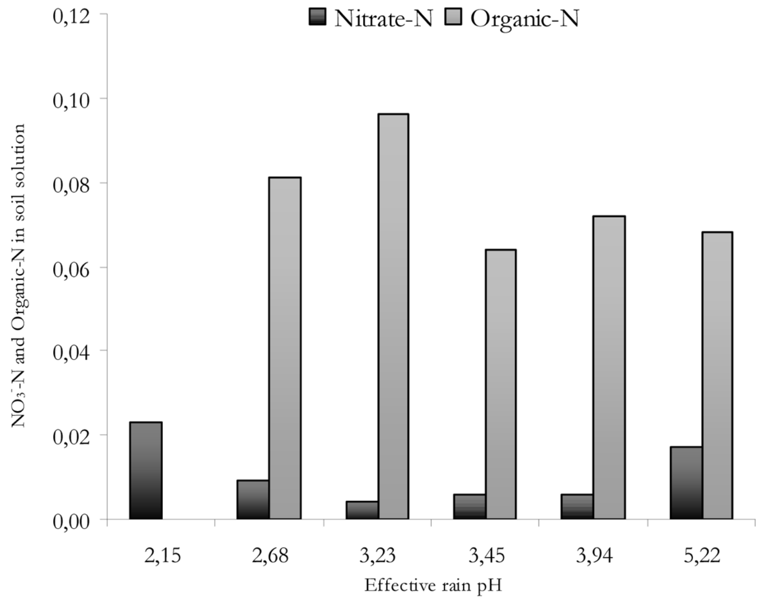


FIGURE 3 Treatment effects on mean $NO_3^-$-N and Organic-N concentrations (ppm) in soil solution after 5 years of acid treatment.



of $Na^+$ ($P < 0.1$), $K^+$ ($P < 0.01$) and P ($P < 0.05$). However, no significant differences were found between peat microcosms receiving H3 treatment and the control treatments for any of the nutrients determined ($Ca^{2+}$, $Mg^{2+}$, N, $K^+$, P and $Na^+$). The mean element uptakes of $Na^+$ and P by *Calluna* plants receiving the effective rain pH $\geq$ 3.94 (H2, H1 and H0) were statistically lower than the uptakes by plants receiving the higher acid treatments (effective rain pH $\leq$ 2.65, H4 and H5). $K^+$ uptake increased significantly with increasing acid load (Fig. 4).

## 3.3 Effects of Enhanced Sulphuric Acid Deposition on Vegetation Regeneration

Few immediately obvious systematic treatment effects on re-establishment were observed, apart from the complete absence of plants in the microcosms receiving the highest acid load (effective rain pH 2.15). For other treatments, *Calluna*, together with a biodiverse vegetation community, re-established at all treatment levels. The lack of regeneration at the greatest acid load was coupled with visual evidence of the remains of *Calluna* flower litter that had failed to decompose even after 2 years.

Correlation analysis between bryophyte abundance and effective precipitation pH provided evidence of highly significant treatment effects where acid deposition adversely affected the growth of some moss species, notably *Hypnum* ($r = 0.96$, $P < 0.001$), *Ceratodon purpureus* ($r = 0.81$, $P < 0.05$), Sphagnum ($r = 0.57$, $P < 0.05$) and *Campylopus* ($r = 0.52$, $P < 0.05$). Liverwort was favoured by an intermediate level of acidity, being most dominant in microcosms receiving the H3 (effective rain pH 3.23) treatment, with *Mnium hornum* being dominant in only one of the four H3 replicates. *Erica tetralix* and *Juncus* were also present in the H3 and control treatment microcosms. All species appeared to be able to thrive in less acidic conditions, while below a soil solution ~pH 3.6, declines in abundance were apparent. However, based on current critical load assignments to peat soils, a diverse and appropriate flora has been sustained on soil subject to gross exceedance.

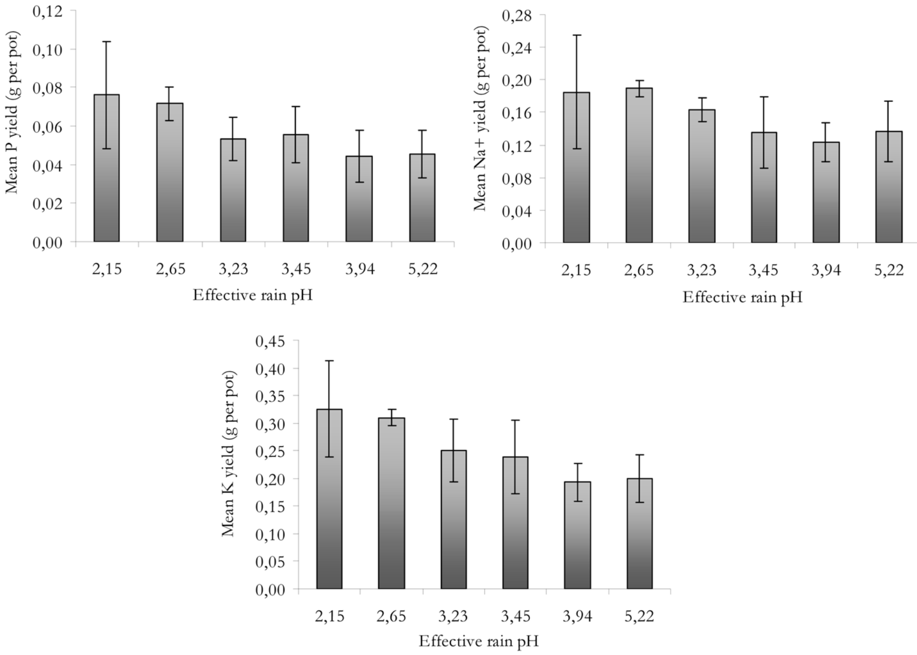


FIGURE 4 Treatment effects on mean yield (g/pot) of $Na^{+}$, $K^{+}$ and P in harvested *Calluna* plants after 3 years of sulphuric acid treatment.



# 4 DISCUSSION

## 4.1 Effects of Enhanced Sulphuric Acid Deposition on Peat Chemistry

### *4.1.1 Treatment Effects on Soil Solution pH*

According to Skiba and Cresser (1989), effective ion concentrations in rain should be directly linked to peat and peat soil solution chemistry, since concentrations, and not fluxes, regulate ion-exchange processes. As discussed in the Introduction, agreement between peat soil solution pH and effective precipitation pH is good. Therefore, we may assume that an effective precipitation pH corresponding to a peat soil solution pH at which vegetation communities are not significantly adversely effected could be used to set critical loads. The results of this study suggest that the appropriate value is pH 3.6

The long-term effect of acid deposition on peat soil solution pH over the 6-year time span of the experiment indicated trends towards equilibria (Parveen *et al.*, 2001). The most recent samples showed very small differences to values recorded previously. The small difference was explained by the wet climate at the time of sampling (see Section 3.1).

### *4.1.2 Treatment Effects on Calcium and Magnesium Concentrations in Soil Solution*

The mobile anion effect and the small but significant mineral content of the peat may explain why significantly higher concentrations of $Ca^{2+}$ were detected in soil solutions from pots receiving the higher acid deposition treatments H3 and H4 ($r = 0.76$, $P < 0.001$) and why, initially, higher $Mg^{2+}$ concentrations were also detected. At gross acidity (H5), the $Ca^{2+}$ concentration declined, while significantly lower $Mg^{2+}$ concentrations in soil solution were detected at H4 and H5. This suggests that leaching rates were so fast for these more acid treatments that lower concentrations of $Ca^{2+}$ and $Mg^{2+}$ were seen at an earlier stage.

The significance of the correlation coefficients between the base cation concentrations in soil solution and effective rain pH ($Ca^{2+}$ $r = 0.53$, $P < 0.05$; $Mg^{2+}$ $r = -0.72$, $P < 0.001$) suggests a sharp shift in the $Ca^{2+}$:$Mg^{2+}$ ratio in response to treatment effects. This is shown in Table I. The soil solution $Ca^{2+}$:$Mg^{2+}$ ratio increased with treatment effects (for soil solution sampled in November 2002), and only at a gross acidity of the H5 treatment was a decline in the $Ca^{2+}$:$Mg^{2+}$ ratio seen. This may be explained by the greater ongoing replenishment of $Mg^{2+}$ from sea spray, compared with $Ca^{2+}$ inputs.

The $Ca^{2+}$ concentration in soil solution, unlike that in plant tissue, for the H3 treatment (pH 3.23) was significantly different ($P < 0.05$) to that of the lower treatments (H0 and H1). However, since a significantly higher $Ca^{2+}$ concentration was found in soil solution, this is probably not deleterious. The H3 treatment effects on $Mg^{2+}$ in soil solution were not significantly different from those of lower acid treatments (H0–H2), suggesting a lack of chemical effect at the H3 treatment level. Clearly, then, this analysis provides no obvious evidence against the selection for setting peat critical loads of an effective rain pH of 3.6 as a proxy for soil solution pH at H3.



### *4.1.3 Treatment Effects on Soil Solution Nitrogen Content*

A loss of soil N in response to treatment effect was anticipated by Parveen *et al.* (2001). In that study, there was no effect on peat total N concentration. Here, however, treatment effects are significant for soil solution, with differences in $NH_4^+$-N being relatively most important in assessing disruption to N cycling, as its abundance is an order of magnitude greater than that of other N species in soil solution. The greatly elevated $NH_4^+$ and TDN concentrations at H5 occur because little ammonium is nitrified in microcosms receiving a gross acid deposition load, plant uptake of N is absent, and the mobile anion effect is very important to both $H^+$ and $NH_4^+$. The high acidity of the H5 treatment, coupled with a lack of plant cover, causes serious disruption to normal N cycling resulting from a failure of litter decomposition, too (Cresser *et al.*, 1997). Over the range H0–H4, such disruption did not appear to be important.

The treatment effects on nitrate-N concentration in soil solution suggest that in "good" soil conditions, as depicted by the control pots especially, nitrification occurs (Fig. 3). However, interpretation of treatment effects of nitrification on $NO_3^-$ in soil solution is complicated because of competing influences of $NO_3^-$ uptake. Nitrate ions are available for uptake by plant roots but are mobile and easily leached out of soil solution. This suggests that the decline in $NO_3^-$-N as acidity increases may be related to a decline in the effectiveness of

TABLE I Effects of enhanced sulphuric acid deposition on $Ca^{2+}$:$Mg^{2+}$ ratio of peat soil solution after 5 years of treatment application.

| | *Concentration ($\mu mol_c\ l^{-1}$)* | | |
|---|---|---|---|
| *Treatment* | *Ca* | *Mg* | *Ca:Mg ratio* |
| 5.22 (H0) | 33.6 | 34.8 | 1.0 |
| 3.94 (H1) | 28.1 | 27.2 | 1.0 |
| 3.45 (H2) | 56.9 | 35.9 | 1.6 |
| 3.23 (H3) | 74.1 | 34.6 | 2.1 |
| 2.65 (H4) | 82.4 | 18.1 | 4.9 |
| 2.15 (H5) | 55.2 | 18.4 | 3.0 |

nitrification. Any precipitation input of nitrate ion will be taken up immediately by foliage or by the roots of the vegetation community re-established on the peat soil and incorporated into organic compounds. Clearly, then, $NO_3^-$-N concentration in soil solution declines with treatment. However, the uptake effect is less for H4 and H5 treatments, so nitrate-N concentrations in soil solution are higher. This is in accordance with the earlier statement of Sanger *et al.* (1996) that at heavily polluted sites, litter decomposition is so strongly slowed down that little nitrogen is mineralized, and under such conditions, nitrate-N inputs tend to be retained by vegetation. A virtually constant production of organic N was evident in microcosms with substantial plant cover (H0–H4 treatments). The lack of plant cover in all H5 microcosms is the key to the lack of production of soluble organic N, since it originates, at least partly, from plant leachates.

The above points together explain the statistically significant treatment effect on total dissolved nitrogen (TDN) concentration in soil solution. The significantly higher abundance of TDN for microcosms receiving the H5 treatment can be directly related to the dominance of ammonium-N.

It is important to note, however, that in all cases, the H3 treatment effects were not significantly different to the lower treatment effects (H0–H2). Clearly, then, no obvious evidence of a chemical effect with the H3 treatment is provided by the analysis of N species in soil solution. Thus, there is no evidence in N cycling against the selection of an effective rain pH of 3.6 as reasonable for setting peat critical loads.



## 4.2 Effects of Enhanced Sulphuric Acid Deposition on Plant Chemistry

### *4.2.1 Treatment Effects on Calluna vulgaris*

Although declines in concentrations of chlorophyll *a* and *b* in new shoots seemed visible in both 1999 and 2000, neither trend was significant. Thus, chlorophyll data do not provide any indication of critical load exceedance.

As in the earlier study by Parveen *et al.* (2001), increasing treatment acidity significantly increased the mean uptake of $K^+$ ($r = -0.89$, $P < 0.001$) in harvested *Calluna*. The cause of this remains unknown, but clearly, more $K^+$ is being taken up by plant biomass in the acidified microcosms. Peat acidification will lower the peat CEC, so it is possible that this will result in a temporary increase in $K^+$ saturation of exchange sites, thus enhancing plant $K^+$ uptake. There was no significant $K^+$ effect on harvested *Calluna* plants for H3 compared with H0–H2, providing no evidence against the selection of an effective rain pH based on the H3 treatment.

*Calluna* plants took up significantly more P and $Na^+$ in conditions of gross acidity (P: $r = -0.87$, $P < 0.001$; $Na^+$: $r = -0.78$, $P < 0.001$). Sulphate may be displacing phosphate from anion exchange sites into soil solution, from which the phosphate would be more readily taken up by plants in response to increasing treatment acidity. The uptake of $Na^+$ with increasing treatment acidity could be related to the postulated increased leaching of $Ca^{2+}$ and $Mg^{2+}$ at gross acidity. In such conditions, more of the cation exchange sites on the peat would be occupied by $Na^+$, making this nutrient more readily plant available. The replenishment rate of $Na^+$ by atmospheric inputs tends to be higher than that for $Ca^{2+}$, providing a further explanation for its availability and increased assimilation by *Calluna* plants. However, given these chemical effects, it is important to note that the mean yields of both these major nutrients present in harvested *Calluna* plants receiving the H3 treatment, as with $K^+$, showed no significant differences from either the lower or higher acid deposition treatment loads.

### 4.2.2 Treatment Effects on the Abundance of Bryophytes

The most striking feature of the bryophyte data was the abundance of *Campylopus* in comparison with other moss species. *Campylopus* is nationally scarce and usually confined to upland habitats in the north of Britain. Significant correlations were detected between the abundance of *Campylopus* and soil solution pH, which is a proxy for effective rain pH. At the gross acidity of the H5 treatment, *Campylopus* failed to establish, but this was also consistent with both $NH_4^+$-N concentration ($r = -0.82$, $P < 0.001$) and resultant TDN concentration in soil solution ($r = -0.89$, $P < 0.001$). The failure to establish may thus be indicative of disruption to N cycling caused by gross acidity.

Treatment effects on the abundance of *Hypnum* were highly significant ($r = 0.96$, $P < 0.001$), and its abundance also correlated with soil solution pH ($r = 0.89$, $P < 0.001$), suggesting the desirability of further investigation into the distribution of this species along pollution gradients. Its tolerance for pollution and a range of exposure conditions results in *Hypnum* being a very common moss species throughout the British Isles (Hale, 2002). In less strongly acidic conditions *Hypnum* can thrive, and only in acid conditions of gross exceedance of the current critical load values does this species fail to establish. Supporting this suggestion is the significant association detected between *Hypnum* abundance and $Ca^{2+}$ concentration in soil solution ($r = 0.57$, $P < 0.01$). The ameliorative effect of $Ca^{2+}$ in artificial rain was beneficial for its establishment. The adverse conditions created through high $NH_4^+$-N and consequently high TDN in soil solution were significantly associated with the abundance of *Hypnum* ($r = -0.54$ and $r = -0.47$, respectively, both at $P < 0.05$).

For *Ceratodon purpureus*, there was no correlation between abundance and $NH_4^+$-N in soil solution, but there was a highly significant correlation between abundance and effective rain pH ($r = 0.81$, $P < 0.001$) and soil solution pH ($r = 0.49$, $P < 0.005$). The greater tolerance of this species than other moss species to higher ammonium levels led to the postulation that its abundance may dominate over other species. In practice, it did not dominate, suggesting that its relative abundance must be affected by other coincidental factors, *e.g.* acidity. Its significant negative association with liverwort ($r = -0.55$, $P < 0.01$) suggests that this species may be a dominant competitor, and this suggestion is consistent with the abundance of liverwort and the absence of *Ceratodon purpureus* in pots receiving H1, H3 and H4 treatments. A strong positive association was detected between *Hypnum* and *Ceratodon purpureus* ($r = 0.76$, $P < 0.001$), and in comparison with *Hypnum*, treatment effects on the abundance of *Ceratodon purpureus* were also highly significant ($r = 0.81$, $P < 0.001$). Further investigation into the distribution of this species along pollution gradients would be of interest.

Sphagnum failed to establish in more acidic conditions. Its abundance correlated positively with soil solution pH ($r = 0.57$, $P < 0.01$) and negatively ($P < 0.001$) with ammonium-N ($r = -0.78$) and nitrate ($r = -0.80$), and consequently TDN ($r = -0.76$) in soil solution. Its strong correlation with organic N ($r = 0.92$, $P < 0.001$) is consistent with its failure to establish at gross acidity reflecting the importance of plant biomass to organic-N in soil solution.

Though common in a variety of acidic habitats, the abundance of *Polytrichum formosum* was not significant in this study. According to Hale (2002), *Mnium hornum* and *Dicranium scoparium* are prominent mosses in many habitats, being tolerant of conditions ranging from neutral to more acidic environments. Their scarcity here, found respectively only in individual pots in the H3 and H4 treatments, hindered analysis but highlights the possibility of acid tolerance.

The abundance of Sphagnum and the presence of *Hypnum*, *Ceratodon purpureus*, *Campylopus*, *Mnium hornum* and liverwort in all treatment pots receiving the H3 acid deposition load supports the suggestion that at this level of a pollutant deposition, there is no evidence for damage from enhanced sulphuric acid treatment. Thus, it should be questioned whether there is any logical reason for not using the soil solution H3 treatment pH for selecting critical loads of acidity. Effective rain pH at this level has clearly not caused any visible biological damage to bryophyte species that have managed to establish, which suggests that at this effective concentration, a diverse moorland community is likely to be sustainable.

## 5 CONCLUSIONS

This study supports the suggestion that effective rain pH could be used as a criterion for setting peat critical loads once linked to response of potentially sensitive biological receptors (Cresser, 2000). It confirms that the selection of a single effective rain pH value is appropriate and could be used as a basis for setting critical loads of acidity for peat soils.

Although advances have been made into understanding the biological and physical consequences of acidification of peat soils, more detailed investigations of the effects of peat acidification are required not only to improve understanding of the stability implications of changing peat physical properties in response to acid deposition loads but also for the quantification of critical thresholds for ecologically important biotic populations.



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