The Effects of Liming On Soil Chemistry at Loch Fleet, Scotland

E. J. Wilson[a]; B. W. Bache[b]
[a] National Power, Research and Engineering, Swindon, UK [b] Department of Geography, Downing Place, Cambridge, UK

PLEASE SCROLL DOWN FOR ARTICLE

THE EFFECTS OF LIMING ON SOIL CHEMISTRY AT LOCH FLEET, SCOTLAND

E. J. WILSON* and B. W. BACHE**

National Power, Research and Engineering, Whitehill Way, Swindon, SN5 6PB, UK.
**Department of Geography, Downing Place, Cambridge CB2 3EN, UK*

An experiment to investigate how the water quality of acid lakes can be improved by liming the surrounding catchment was begun at Loch Fleet, Scotland in 1984. The effects on the soils of three sectors of the catchment where limestone was added in 1986 are reported here, following analysis of soils sampled in 1987, 1988 and 1991. The effect of the lime on soil chemistry was still evident in 1991, with about 15% of free lime remaining in the hydrochemical reaction zone of sectors IV and VI and nearly 50% in sector VII. However, this free lime appeared to be dissolving too slowly to maintain large amounts of exchangeable calcium in the soils, indicating that the treatment is starting to become less effective. The fall in the mean exchangeable calcium in the reaction zone between 1988 and 1991 was mirrored by a drop in mean soil pH over the 5 years post-liming from 6.1 to 5.6 on sector IV and from 5.9 to 5.4 on sector VI, whereas mean pH remained constant at about 6.0 in the limed areas of sector VII. Using soil data to predict longevity suggests that the exchangeable calcium remaining on the catchment at the end of 1991 will maintain target water quality in the loch until sometime during 1994. The soil pH is likely to fall to between 5.2 and 5.3 by this time. If the region of hydrochemical reaction is assumed to extend to a depth of 20 cm rather than 5 cm, target water quality is predicted to be maintained until the end of 1995. When the free lime remaining on the catchment is included as a source of acid neutralising capacity, calculations show that treatment may remain effective until around the year 2000.

KEY WORDS: Exchangeable calcium, hydrochemistry, liming, Loch Fleet, soil pH

INTRODUCTION

The main objective of the Loch Fleet project was to restore conditions in the acid lake to provide suitable water quality for brown trout (Howells and Dalziel, 1992). However, the chemical characteristics of natural water bodies are determined primarily by the soil and rock through which the water flows prior to entering the stream or lake (Bache, 1984). Direct liming of lakes has been practised extensively, especially in Sweden (Olem, 1990) and although this gives an immediate increase in lake pH, it is unlikely to be maintained for upland lakes in the UK because (i) a relatively short residence time means that the improved water is soon flushed out and (ii) excess lime that drops to the bottom of the lake may become inactivated by being covered with sediment, humic and clay material (Sverdrup *et al.*, 1984), although the evidence for this is uncertain. The rationale for liming the catchment rather than liming the lake itself is to provide a more sustained source of neutralising capacity in the soil profile which will interact with acid waters flowing through it into the lake. Whether catchment liming results in a *long-term* improvement in lake quality depends on upon how long the soil's neutralising capacity (free lime, exchangeable calcium and high pH) lasts. This is the main topic addressed here.

Three sectors of the Loch Fleet catchment were limed in 1986. Profile core samples were taken from these sectors in October 1986, December 1987 and December 1988, and the results of the analyses reported in Wilson *et al.* (1992). The results of a further sampling in December 1991 are reported here and compared with those from the earlier samplings. The previous report (Wilson *et al.*, 1992), when examining the results of the 1987, and 1988 samplings, discussed the processes affected by catchment liming in detail. It was then too early to determine a threshold soil composition which could provide water of sufficient quality to support brown trout, or to estimate how long the treatment would remain effective. A further three years of chemical reaction between the added lime, the rain input and the soil has now taken place. The results reported here provide a firmer basis for determining the soil chemistry required to maintain target water quality (the 'threshold soil composition') and to predict treatment longevity.

MATERIALS AND METHODS

Soil sampling and preparation

Details of the lime applications in 1986 are given in Bell (1992) and Dalziel (1994). Briefly, 23.9 t ha^{-1} of limestone slurry was applied to 4.6 ha of the forested sector IV, 21.3 t ha^{-1} of limestone powder was applied to 6.4 ha of moorland on sector VI and 10 t ha^{-1} of limestone powder was added to 10 ha of wetland on the 32.1 ha sector VII. Core samples of ten profiles were taken from each of the limed areas in December 1991, using plastic drain pipe of 25 cm depth and 86 cm^2 cross-sectional area. Results of the 1986 sampling showed that most of the free lime was restricted to the litter layer, so an additional 20 litter samples were taken on sectors IV and VI from 1987 onwards. The sampling sites were the same as those used for the previous samplings in 1987 and 1988 reported by Wilson *et al.* (1992).

Following collection, the soil cores were stored at $-25°C$ until analysis. After thawing, the cores were sectioned to the required depths, i.e. for sectors IV and VI: litter, depth 1 (0–2.5 cm), depth 2 (2.5–5 cm), depth 3 (5–10 cm) and depth 4 (10–15 cm), and for sector VII, depth 1 (0–5 cm), depth 2 (5–10 cm), depth 3 (10–15 cm) and depth 4 (15–20 cm). The sectioned samples were dried to constant weight at 35°C and ground or milled (< 2 mm) prior to analysis. The results were corrected to dry weight at 105°C. The dry bulk density (volume weight) of each subsample was determined so that results could be calculated on a land area basis in addition to dry weight of material.

Chemical analysis

The same chemical properties were determined as in previous years i.e. pH (in 0.01 M CaCl$_2$ solution, 1:10 ratio), exchangeable cations, exchangeable acidity, base saturation and %CaCO$_3$, but some of the methods for the 1991 sampling were slightly different from the previous ones (Wilson *et al.*, 1988). Exchangeable cations were determined on all samples after extraction with 0.5 M BaCl$_2$ solution buffered at pH 8.5 with triethanolamine, in which CaCO$_3$ is virtually insoluble; a comparison for a selection of the samples with the previous more-complicated method showed no significant

differences. Exchangeable acidity was determined by the standard method for acid soils by extraction with 1.0 M KCl solution and titration with NaOH; this gives a lower value than the hydrolytic acidity determined by NH_4OAc extraction at pH 7 on previous samplings. Cation-exchange capacity was calculated as the sum of exchangeable cations and exchangeable acidity. The change in the exchangeable acidity method gives a somewhat higher base saturation than previously, so that these two properties are not strictly comparable with the results of the previous samplings.

Statistical analysis

The sampling design produced ten experimental values for each variate at each depth, except for the litter layers on sectors IV and VI where 30 samples were taken. The results and discussion below are based on sample means, but in many cases the variability was high and the data were not normally distributed. This was particularly so for % free $CaCO_3$ (for which a majority of values were zero, but with occasional very high values, reflecting the uneven initial distribution of lime) and % base saturation (for which many values were 100%), and the data for these two variates were transformed to **arc sin $\sqrt{\text{variate}}$** values. Changes in soil chemistry from 1988 to 1991 at each depth were analysed statistically by the t-test. Two t-statistics were calculated for equal and unequal variance in the sample groups. The variance was tested for equality by an F-folded statistic (2 tailed t-test) using $p = 0.05$ as a threshold level (Steel and Torrie, 1980). Satterthwaite's (1946) approximation was used to calculate the degrees of freedom associated with the t statistic for samples with unequal variance. Statistically significant results of the t-test, compared to data of the previous sampling are shown above the bar, using conventional notation: * for $p < 0.05$, ** for $p < 0.01$ and *** for $p < 0.001$.

RESULTS

The large amount of data that was generated has been condensed to show the means for each depth and each sampling date on bar charts. Occasions where the primary data reveal effects that are obscured by the means are referred to in the discussion. Free lime, exchangeable calcium, and total calcium (i.e. exchangeable + free lime), are all expressed on a land area basis as $t\,ha^{-1}$ of $CaCO_3$ in Figures 1–3 and the soil acidity parameters are shown in Figures 4–6.

Sector IV (forest)

Most of the free lime remaining (Fig. 1a) is in the upper part of the profile, and this has not decreased significantly since 1988. The small amount of lime recorded previously in depths 3 and 4 has disappeared, presumably by dissolution. There has been a significant decrease with time in exchangeable calcium (Fig. 2a) in the upper layers, which is also reflected in the total calcium (Fig. 3a) but there has been no significant change at lower depths. This loss of calcium is the result of leaching and gradual re-acidification

Figure 1   A comparison of the mean free lime remaining at each depth in 1987 (⊠), 1988 (▨) and 1991 (■).

Figure 2 A comparison of the mean exchangeable calcium remaining at each depth in 1987 (▩), 1988 (▨), and 1991 (■).

Figure 3   A comparison of the mean total calcium remaining at each depth in 1987 (▧), 1988 (▨) and 1991 (■).

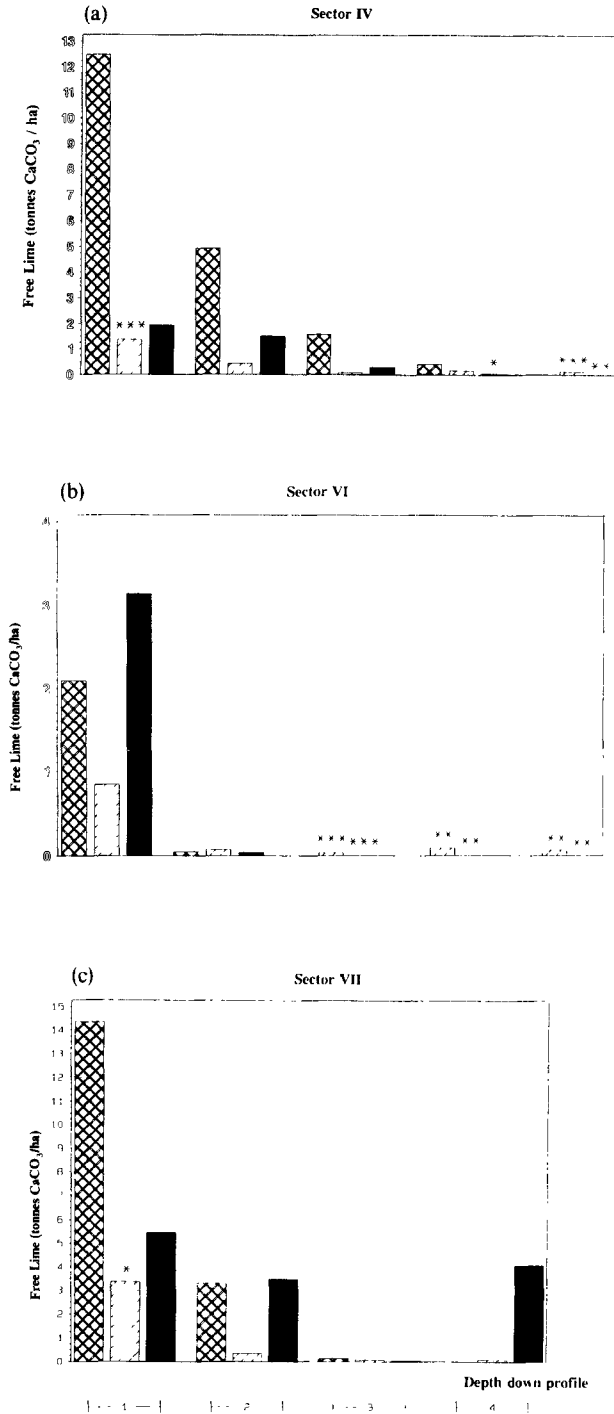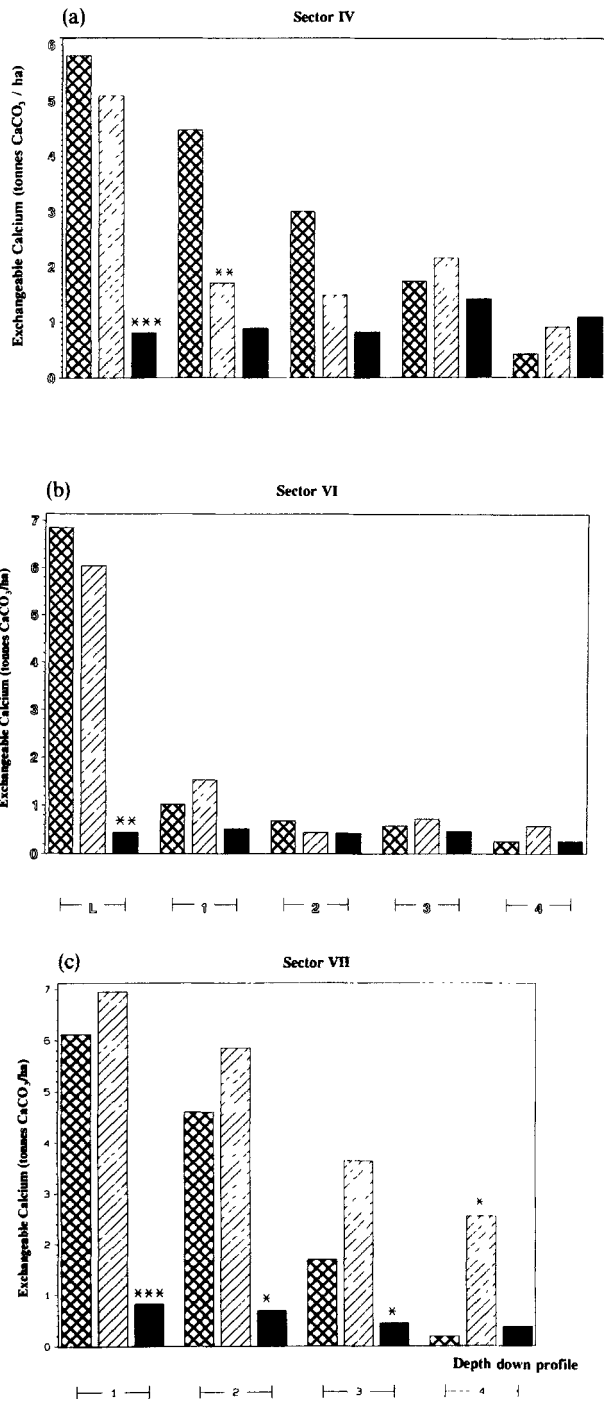**Figure 4**   A comparison of the mean pH at each depth in 1987 (▨), 1988 (▧) and 1991 (■).

Figure 5   A comparison of the mean exchangeable acidity at each depth in 1987 (▨), 1988 (▧) and 1991 (■).

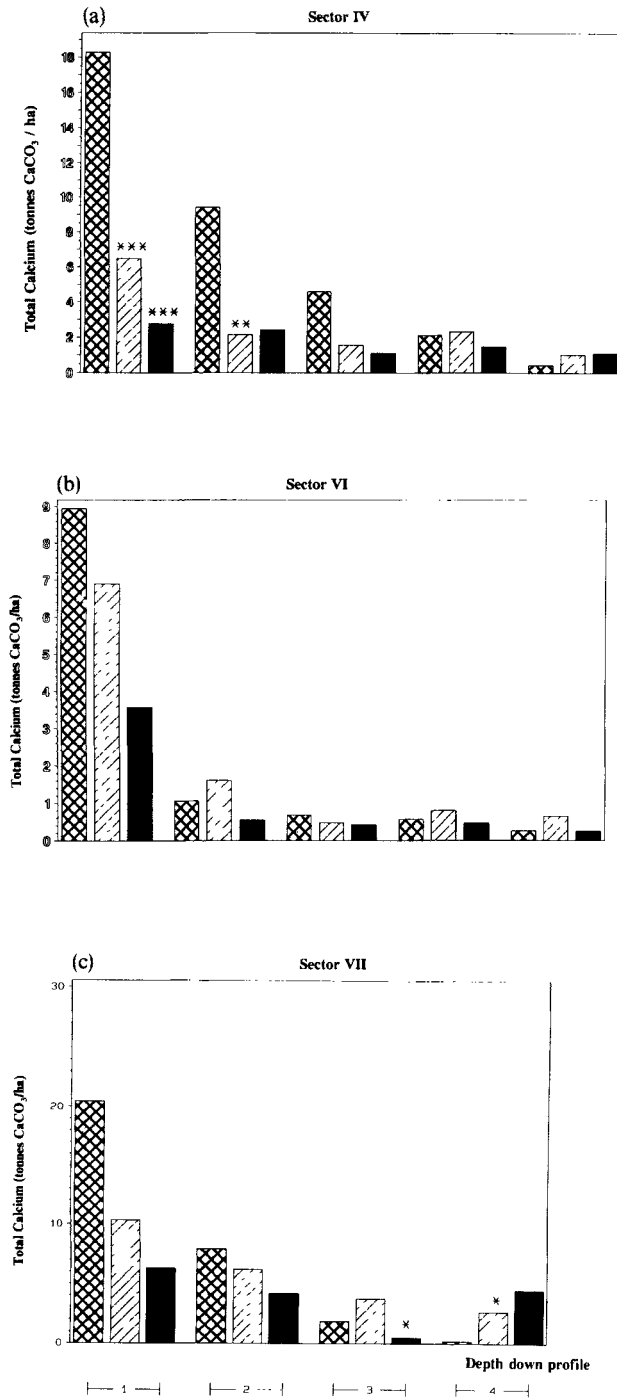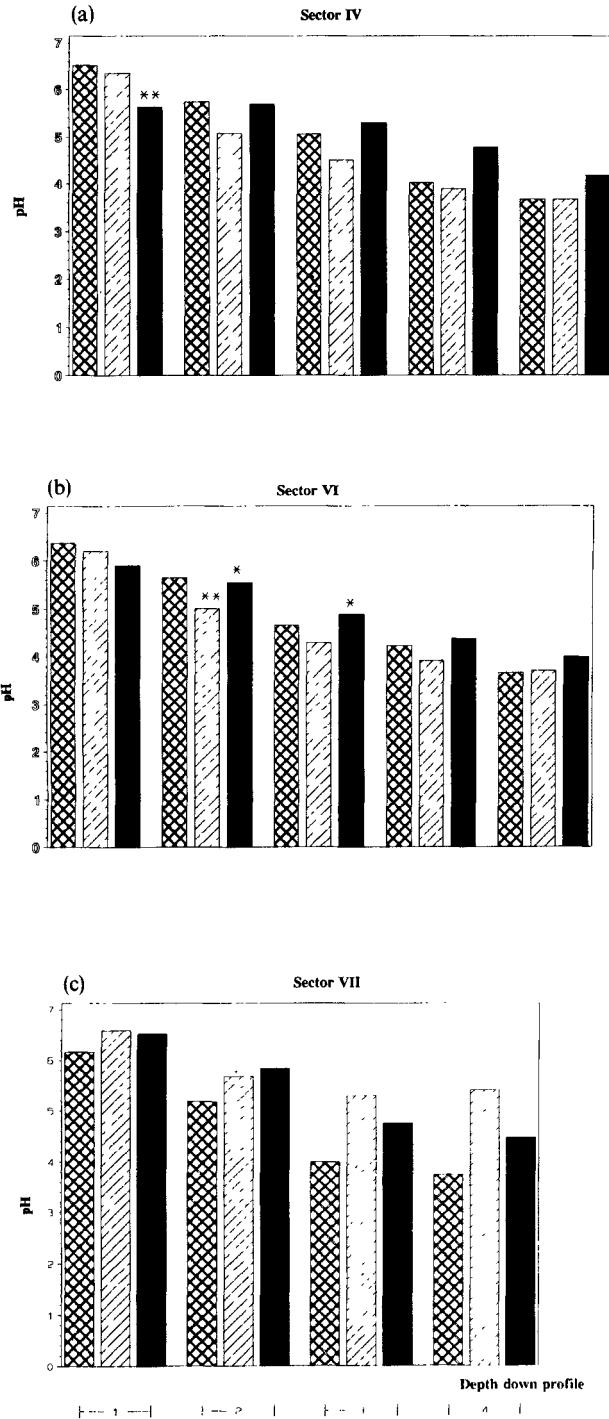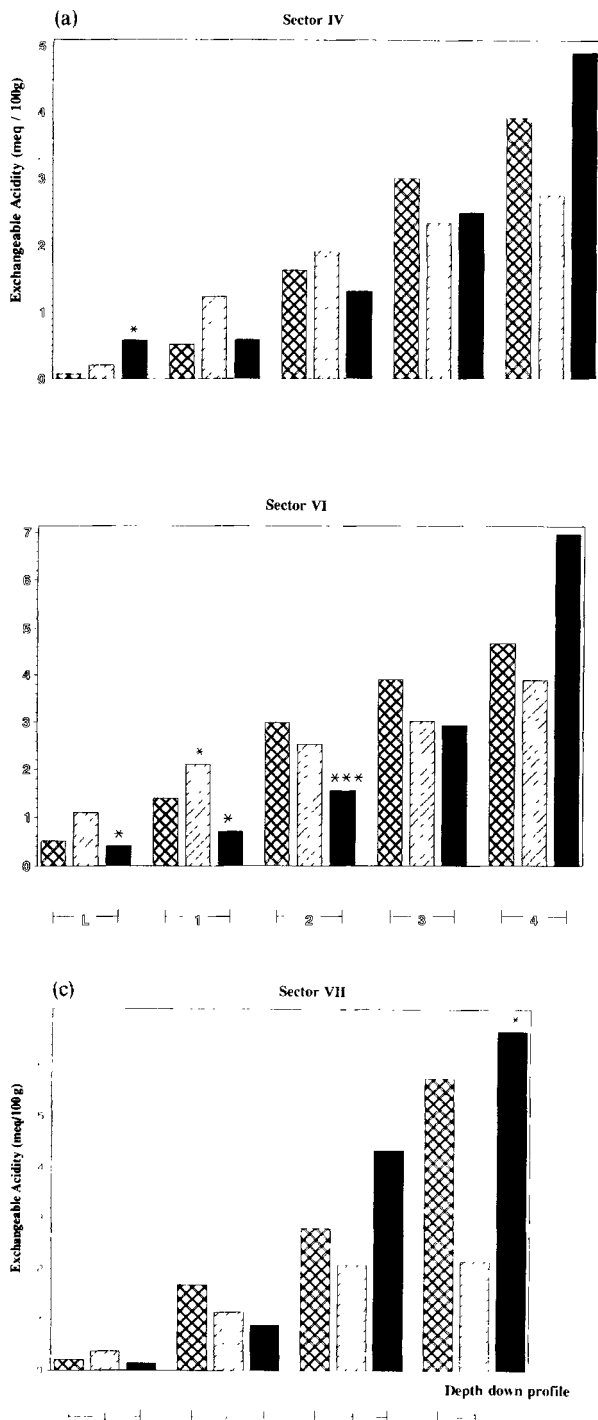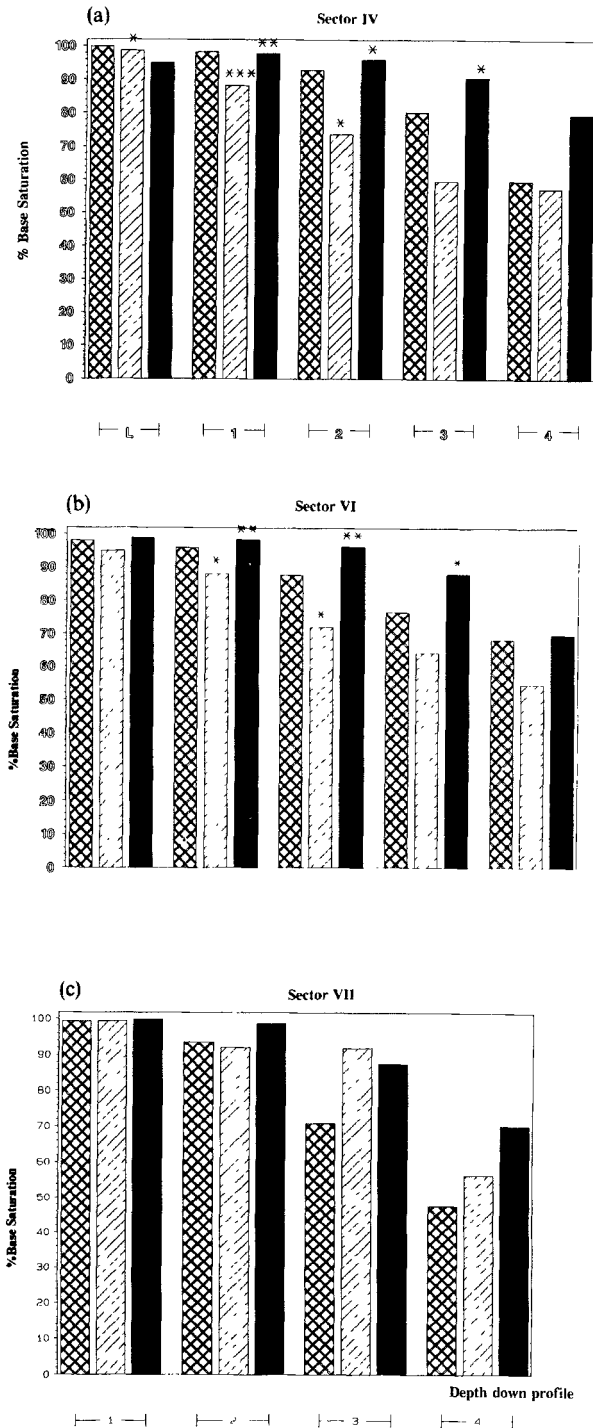**Figure 6** A comparison of the mean % base saturation at each depth in 1987 (▨), 1988 (▧) and 1991 (■).

of the soils, and is reflected in the pH and exchangeable acidity (Figures 4 and 5) for the litter layer, but not at lower depths on this sector. These properties all indicate increasing acidity with depth, but no significant changes have occurred with time in the deeper layers of the profile.

Sector VI (moorland)

As on sector IV there has been no significant decrease in free lime (Fig. 1b) since 1988 in the litter layer or depth 1. At lower depths the decrease is significant, the small amounts of lime present at depth in 1988 having dissolved by 1991. The distribution of free lime down the profile is even less uniform than on sector IV, most of it remaining in the litter layer where it is in a good position to react with incoming rain. There is a significant decrease over time in exchangeable calcium (Fig. 2b) in the litter layer (indicating leaching) but no significant difference at lower depths. The dissolution of free lime at depth 2 and below is reflected in a slight but significant increase in pH and base saturation. The effect of the added lime may be gradually working down the profile, but this is not supported by an increase in mean exchangeable calcium.
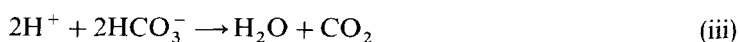
Sector VII (Wetland source area)

Here, there is a more even distribution of free lime down the profile than on sector VI (Fig. 1c), apart from one anomalous sample which was very high in free lime at depth 4. There has been no significant change in free lime at any depth between 1988 and 1991, however. Exchangeable calcium in the upper three layers decreased significantly over this period (Fig. 2c) and is reflected in a (non-significant) decline in total calcium values (Fig. 3c). Changes in the acidity variables are generally small and non-significant, apart from an increase in exchangeable acidity in depth 4. These results indicate that the lime that remains is not dissolving, and may be chemically deactivated or physically unavailable.

The 1991 results differ from those of previous years most clearly in showing a significant reduction in the exchangeable calcium on all three sectors (Fig. 2) indicating that acid inputs are now being buffered by calcium exchange. Calcium leached from the soil in this way does not appear to be replenished by calcium dissolution from free lime.

DISCUSSION

The reaction of free limestone with the acid peat has three components: the dissolution of calcium carbonate, the dissociation of organic acids combined with the exchange of hydrogen for calcium, and the neutralisation of hydrogen by bicarbonate. This results in a rise in soil pH and an increase in exchangeable calcium:

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca^{2+} + 2HCO_3^- \qquad \text{(i)}$$

$$R(COOH)_2 + Ca^{2+} \longrightarrow R(COO)_2Ca + 2H^+ \qquad \text{(ii)}$$

$$2H^+ + 2HCO_3^- \longrightarrow H_2O + CO_2 \qquad \text{(iii)}$$
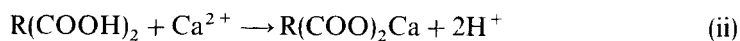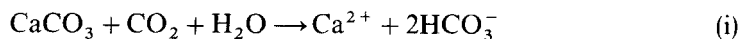
In the vicinity of dissolving lime particles, exchangeable calcium will be in equilibrum with free lime, pH will be approximately 7 and the exchange capacity of the peat (pH-dependent charge) will be saturated with calcium. Away from the immediate influence of a particle of dissolving lime, the continuing input of rain (pH4–5) will gradually remove exchangeable calcium and increase the acidity of the soil, the reverse of reaction (ii) above. Free lime will be depleted gradually by dissolution, the soil will acidify by cation exchange and the products will be removed in drainage water. While this will ensure a reasonable calcium concentration and pH in the lake water, and prevent the mobilisation of toxic monomeric Al^{3+} ions from the soil, this reserve of exchangeable calcium will be limited once the free lime is no longer available to replenish it.

It is important to define the zone of hydrochemical reaction, or acrotelm. The studies of Nisbet and Nisbet (1992) on hydrological plots in the forest and moorland sectors indicated that 87–90% of water flow on these peats was through the litter and the upper 5 cm (depths L, 1 and 2), and even across the surface. However, Bishop and Richards (1992), using isotope hydrograph separation techniques on sectors VI and VII, considered that rain displaced pre-event water from a depth down to 20 cm. The main reactions are likely to occur in the upper layers, which is clearly shown in the change in chemical properties of the soils with depth down the profile. Most of the free lime remained in the upper layers, with very little change in soil chemistry below 10 cm, although there may have been a little movement down the profile *via* cracks or pipes in the peat. This indicates that water flow is predominantly lateral, consistent with estimates of a hydrochemical reaction zone in the upper 20 cm of peat.

An idealised schematic diagram indicating the balance between free lime and exchangeable calcium at the catchment level was given by Wilson *et al.* (1992) and this is reproduced as Figure 7. This shows that as free lime decreases, the reserve of exchangeable calcium increases up to point X on the time axis. This reserve will be maintained while free lime is available to replenish the exchangeable calcium used in buffering acidity. When all the free lime dissolves, or becomes physically or chemically unavailable (point Y), exchangeable calcium will begin to decrease. Beyond point Y, the effectiveness of the treatment will depend on the size of this reserve of exchangeable calcium. As it begins to decline, water quality in the loch will deteriorate. The soil chemistry at point Y is considered to be the 'threshold soil composition', beyond which the beneficial action of the lime-treated soil on lake waters will not be maintained. Once the threshold soil composition has been reached, the decline in water quality will be gradual. Having empirically determined the soil chemistry at this point, the time for which the treatment will remain effective beyond it can be predicted.

As expected, the free lime in the upper layers of the soil profile decreased in the first few years following liming. The rate of dissolution was quite slow (and not statistically detectable) during the first year and a half on sectors IV and VII. This was followed by a significant decrease in the amount of free lime remaining in the litter layer between 1987 and 1988 (Fig. 1). On sector VI, however, there was a rapid loss of free lime from the surface layers immediately following treatment (1986 to 1987). This probably reflects an initial washoff of surface lime directly into the loch, the result of the combination of unevenly spread lime and flashy runoff on sector VI. The exchangeable calcium increased rapidly on all three sectors following liming, consistent with the observed decrease in free lime.
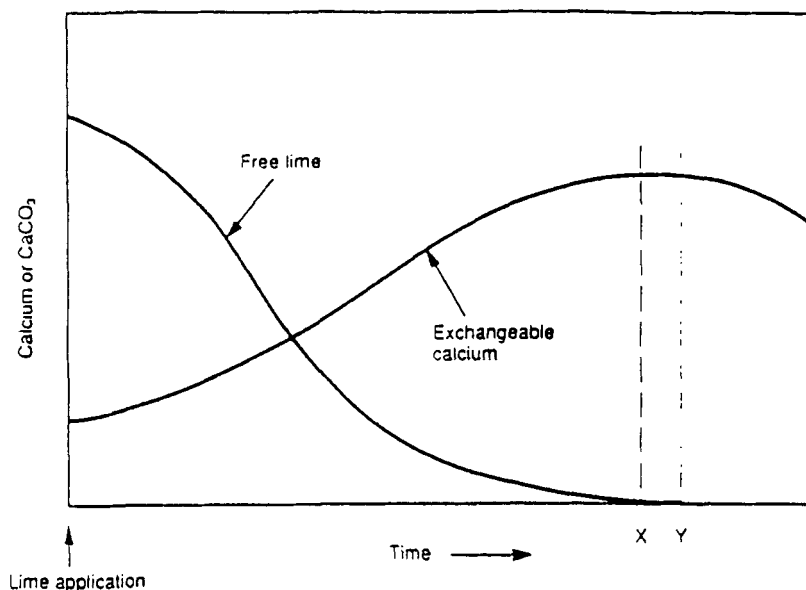
Figure 7 Schematic diagram of the partitioning of limestone over time between free lime and exchangeable calcium.

Between 1988 and 1991, the total calcium remaining in the litter layer on sector IV decreased significantly due to large decrease in exchangeable calcium without any significant decrease in free lime (Fig. 2). The same trend appears below the litter but is not significant. It appears that the turning point Y (Fig. 7) was reached between 1988 and 1991 as far as the litter layer is concerned, although free lime was still present in the acrotelm. The mean pH of the litter and the top 5 cm of the peat profile was then 5.6.

On sector VI, similar changes in soil chemistry are apparent. Free lime in the litter layer has not decreased significantly between 1988 and 1991, and was detected in only 3 of 10 samples. The amount of exchangeable calcium at this depth has decreased significantly during this period, however. As on sector IV, it appears that the point has been reached where exchangeable calcium is buffering inputs of acidity and is not being replenished by calcium from the dissolution of free lime (point Y, Fig. 7). The small amounts of free lime found at depth have dissolved completely, maintaining an approximately constant exchangeable calcium supply over time in these layers. The mean pH of the litter and the top 5 cm is 5.4, rather lower than for sector IV, and this is accompanied by lower mean exchangeable calcium values than for sector IV.

Sector VII shows rather similar patterns as sectors IV and VI between 1988 and 1991, with little change in free lime (Fig. 1) and a decline in exchangeable calcium in the surface layers of the profile (Fig. 2). However, an important difference is that much more free lime remains in the acrotelm, and was detected in 8 of 10 samples. This free lime is clearly still buffering acid deposition, as indicated by a mean pH of 6.0 in the two

upper layers. Hydrological differences between the sectors may account for the slower rate of lime depletion on sector VII. High flow rates occur for less than 0.5% of the time and ponding in the wetland area where the lime was applied is common (Dickson, 1992). The shallow gradient of the wetland area, combined with the porous structure of *Sphagnum*, reduces the wash-out of lime into the loch on sector VII compared with sectors IV and VI. It appears that the threshold soil composition (point Y, Fig. 7) has not yet been reached on sector VII.

There are two possible explanations for the continuing presence of free lime while exchangeable calcium is dropping. The first is that particles of limestone may have become deactivated by an organic coating. X-ray diffraction analysis of calcium particles from peat carried out three years after liming at Loch Fleet (Allison, 1989) provided no evidence for this and the primary data here show that wherever lime was present the pH of the samples was high. A more likely explanation is that free lime is still dissolving where it occurs, but too slowly for a decrease to be detected because of the high variability in the amounts of free lime. This helps to explain the results for all three sectors, which show that exchangeable calcium in the upper layers of the profile had declined significantly, while apparently the free lime had not.

Both the interpretation of changes in soil chemistry and predictions of treatment longevity are complicated by the high spatial variability in samples from a given sector. This reflects the uneven spreading of the lime caused by difficult weather conditions at the time. The presence of free lime particles in the soil sample obviously influences the other chemical properties. The water quality data are less variable (Dalziel, 1994) since stream discharge integrates runoff from all parts of the sector.

Predicting treatment longevity using soil data

The liming treatments applied to the catchment on sectors IV, VI and VII improved the water quality of the loch sufficiently to support a population of brown trout. These changes occurred within six months of liming (Dalzel et al., 1991). More important than the speed of response, however, is the sustainability of the improvement. The length of time the treatment remains effective is one of the most important factors in evaluating the relative suitability of catchment liming and direct lake liming for acid mitigation in the UK. Predictions of treatment effectiveness time at Loch Fleet have been made using hydrochemical flux data and are reported in this volume (Dalziel, 1994).

Soil analyses at the end of 1991 indicated that exchangeable calcium was the primary source of neutralising capacity for acid inputs on sectors IV and VI. Although free lime was still present in the upper horizons of the soil profile on these sectors, it did not appear to be making a significant contribution to calcium released into the loch, nor to be replenishing calcium removed from the exchanger. On sector VII exchangeable calcium was also declining but acidity was still being buffered by free lime to some extent in 1991. The lime remaining on the wetland area is unlikely to have a very great influence on water quality since the runoff from sector VII as a whole is very high. For predicting treatment longevity, it is assumed that the threshold soil composition has been reached on all three sectors, a reasonable approximation for sector VII in

practical terms. At this stage (point Y, Fig. 7) the length of time for which the treatment remains effective depends on the size of the pool of exchangeable calcium. When this calcium falls to preliming levels, we can expect the threshold water quality specified for fish survival (Howells and Dalziel, 1992) to be breached. Treatment longevity after December 1991 can be predicted from a knowledge of the amount of exchangeable calcium remaining and the rate at which it is lost to the loch, i.e. the calcium flux.

The pool of exchangeable calcium which can contribute to maintaining the improved water quality is that in excess of the amount present before lime was applied; this has been calculated as the amount above 53% base saturation, the mean base saturation of samples from the untreated areas. Table I shows the exchangeable calcium in excess of pre-liming values measured at the beginning of 1992, and the amounts predicted to remain in subsequent years. This pool of calcium is depleted by subtracting the annual flux of calcium into the loch from each sector, using measured values for 1992 and 1993, and predicted estimates for 1994 extrapolated from the fluxes measured between 1986 and 1993. All calcium fluxes have been adjusted for the 'background' or preliming flux from each sector (Dalziel, 1994). When all the 'excess exchangeable calcium' has been used to neutralise acidity in this way, the soil chemistry will have reverted to pre-liming values.

These calculations predict that water quality will deteriorate to pre-liming conditions towards the end of 1993 on sector VI and towards the end of 1994 on sectors IV and VII. In terms of fish survival, it is the calcium concentration in the loch that is important. This is calculated as the sum of the potential calcium fluxes from treatments on sectors IV, VI and VII divided by 2.19×10^9 (the turnover volume of the loch in litres), plus the 'background' pre-liming calcium concentration of the loch (0.9 mg 1^{-1}).

Table I   The amount of exchangeable calcium and rate of removal to the loch at the start of 1992 and in subsquent years (assuming an acrotelm of 5 cm).

Year	Exchangeable Calcium in excess of 53% base saturation (keq)	Flux of Calcium (keq yr^{-1})
a) Sector IV		
1992	106.1	38.2
1993	67.9	40.8
1994	27.1	39.3*
1995	zero	
b) Sector VI		
1992	78.30	38.8
1993	39.5	41.3
1994	zero	
c) Sector VII		
1992	147.29	53.8
1993	93.5	50.9
1994	42.6	48.1*
1995	zero	

* Predicted value

Although the exchangeable calcium is predicted to fall below the pre-liming values on sector VI during 1993, the calcium flux from sectors IV and VII will be sufficient to maintain calcium concentration in the loch above $2 \, mgl^{-1}$. By 1994, however, the calcium concentration in the loch is predicted to fall to about $1.7 \, mg \, l^{-1}$, below the threshold specified for fish survival. This prediction may be somewhat pessimistic in that free lime on sector VII is still buffering inputs of acidity.

It is also possible to estimate a "threshold soil pH", the soil pH when water quality begins to deteriorate. During the five year period of soil sampling, from 1986 to 1991, mean pH in the acrotelm fell from 6.1 to 5.6 on sector IV, and from 5.9 to 5.4 on sector VI. Assuming pH continues to fall at a rate of 0.1 units per year, soil pH in 1994 will be 5.3 and 5.2 on sectors IV and VI respectively. On sector VII, pH in the upper 5 cm has fallen from 7.25 in 1986 to 6.5 in 1991, a rate of 0.15 units per year, so that the threshold pH in 1994 is estimated as 6.1 on sector VII. pH in the upper 5 cm has remained fairly static since 1987, indicating that acidity is still being buffered by the remaining free lime.

Soil chemistry predictions and hydrochemical flux data.

Predictions made in 1991 of calcium fluxes based on hydrochemical data (Dalziel *et al.*, 1991) indicated that loch water calcium concentration would fall below the target value of $2 \, mg \, l^{-1}$ during 1993. The calcium flux from sector VII was underestimated by this model, however, and in practice loch water quality remained suitable for fish throughout 1993 (mean calcium concentration of $2.1 \, mg \, l^{-1}$). The most recent hydrochemical data up to April 1994 show that calcium concentrations on sector VII and in the loch itself are still above the target but may soon fall below it (Dalziel, 1994). If this is so, predictions based on soil data for the target water quality draining sector VII and in the loch itself will be broadly correct. The picture is rather different for predictions of water quality in the drainage streams from the other two sectors. The soil chemistry model predicts that water quality will fall to pre-liming levels towards the end of 1993 and 1994 on sectors VI and IV respectively. This appears to be rather pessimistic in the light of the recent measurements that show that calcium concentrations in streams draining these sectors in April 1994 were well above the target value and likely to remain so for many years (Dalziel, 1994).

Treatment longevity for the drainage streams on sectors IV and VI may have been underestimated by assuming the region of hydrochemical reactivity in the soil at Loch Fleet is limited to the litter layer and the upper 5 cm. If, instead, we consider this region to extend to a depth of 20 cm, as indicated by the ^{18}O isotope studies (Bishop and Richards, 1992), the pool of exchangeable calcium available for neutralising inputs of acidity will be larger and we can expect the treatments to remain effective for longer. The exchangeable calcium in December 1991 (in excess of pre-liming values) has been recalculated on this assumption. This pool has been depleted using the same annual fluxes as before, to determine the time when water chemistry will fall below the target values (Table II). The treatment is predicted to remain effective until 1996 on sector IV, until early 1995 on sector VI, and until early 1996 on sector VII. Calculating the predicted calcium concentration for the loch as a whole shows that target water quality will be breached towards the end of 1995.

Table II   The amount of exchangeable calcium and rate of removal to the loch at the start of 1992 and in subsequent years (assuming an acrotelm of 20 cm).

Year	Exchangeable Calcium in excess of 53% base saturation (keq)	Flux of Calcium (keq yr^{-1})
a) Sector IV		
1992	193.3	38.2
1993	155.1	40.8
1994	114.3	39.3*
1995	75.0	39.3*
1996	35.7	39.3*
1997	zero	39.3*
b) Sector VI		
1992	124.42	38.8
1993	85.6	41.3
1994	44.3	38.8*
1995	5.5	38.8*
1996	zero	38.8*
c) Sector VII		
1992	202.6	53.8
1993	148.8	50.9
1994	97.9	48.1*
1995	49.8	48.1*
1996	1.7	48.1*
1997	zero	48.1*

It has been assumed that the free lime remaining on the catchment is not available to neutralise acidity. This is based on the soil analyses which showed that there had been no significant decrease in free lime between 1988 and 1991 and that calcium removed from the exchanger was not being replenished by the dissolution of free lime. If, however, the remaining free lime is neutralising acidity, then we can expect the treatment to remain effective for longer than predicted above. On sector VII it is highly likely that the free lime is decreasing at too slow a rate to be detected statistically, due to the high variability of the amounts of free lime. If free lime is included, the water quality of the loch is predicted to remain suitable for fish beyond the year 2000.

References

Allison, A. J. (1989) Report on the examination of peat sample ex Loch Fleet. British Coal Report SCLN 498/89.

Bache, B. W. (1984) Soil-water interactions. *Philosophical Transactions Royal Society. (London)* **305B:** 393–407.

Bell R. M. (1992) Liming design and strategy at Loch Fleet. pp 153–171 in *Restoring Acid Waters: Loch Fleet 1984–1990.* Howells, G. and Dalziel, T. R. K. (eds), Elsevier Applied Science, London

Bishop, K. H. and Richards, K. S. (1992) Shallow flow pathways or pre-event water? pp 121–133 in *Restoring Acid Waters: Loch Fleet 1984–1990.* Howells, G. and Dalziel, T. R. K. (eds), Elsevier Applied Science, London

Dalziel, T. R. K., Dickson, A. and Proctor, M. V. (1991) Calcium flux calculations and predictions of catchment liming effectiveness at Loch Fleet, Galloway, Scotland. pp 223–242 in *International Lake and Watershed Liming Practices*. Olem, H., Schreiber, R. K., Brocksen, R. W. and Porcella, D. B. (eds), Terrene Institute, Washington, D. C.

Dalziel, T. R. K. (1994) Deposition inputs, water quality and liming effectiveness. *Chemistry and Ecology* (this volume).

Dickson, A. (1992) Hydrological considerations. pp 113–120 in *Restoring Acid Waters: Loch Fleet 1984–1990*. Howells, G. and Dalziel, T. R. K. (eds). Elsevier Applied Science, London

Howells, G. and Dalziel, T. R. K. (Eds) (1992) *Restoring Acid Waters: Loch Fleet 1984–1990*. Elsevier Applied Science, London, 421 pp.

Nisbet, A. F. and Nisbet, T. R. (1992) Interactions between rain, vegetation and soils. pp 135–139 in *Restoring Acid Waters: Loch Fleet 1984–1990*. Howells, G. and Dalziel, T. R. K. (eds). Elsevier Applied Science, London

Olem, H. (1990) *Liming Acidic Surface Waters*, Lewis Publishers Inc., Michigan. 331pp.

Satterthwaite, F. W. (1946) An approximate distribution of estimates of variance components. *Biometrics Bulletin*, **2:** 110–114.

Steel, R. G. D. and Torrie, J. J. (1980) *Principles and Procedures of Statistics*. McGraw Hill, 2nd ed.

Sverdrup, H., Rasmussen, R. and Bjerle, I. (1984) A simple model for the reacidification of limed lakes, taking the simultaneous de-activation and dissolution of calcite in the sediments into account. *Chemica Scripta*, **24:** 53–66.

Wilson, E. J., Roberts, D. J. and Skeffington, R. A. (1988) The effect of lime application to the Loch Fleet catchment on tree and soil chemical properties an initial report. Central Electricity Generating Board Research Report TPRD/L/3283/R88.

Wilson, E. J., Hudson, G and Snith B. F. L. (1992) Soils of acid catchments before and after liming, pp199–228 in *Restoring Acid Waters: Loch Fleet 1984–1990*, Howells, G. and Dalziel, T. R. K. (eds). Elsevier Applied Science, London.