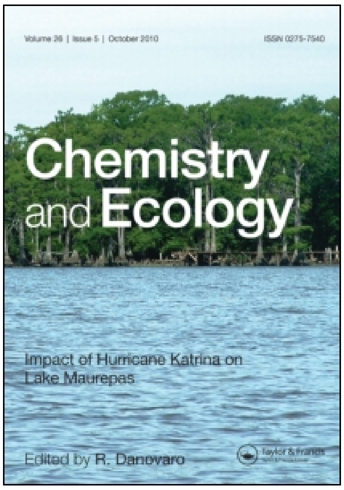

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Deposition Inputs, Water Quality and Liming Effectiveness

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DEPOSITION INPUTS, WATER QUALITY AND LIMING EFFECTIVENESS

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Rainfall quantity and quality, and stream and loch water quality have been monitored throughout the Loch Fleet Project. This has allowed the effects of liming of parts of the catchment to be monitored, and assessments made of the effectiveness and duration of these treatments. Rainfall over 1989–1993 fluctuated around the long-term average of 2100 mm. Over this time, year by year variations in acid or sulphate loading from deposition was evident and quite substantial. There was no trend, however, reflecting reductions in national sulphur emissions. Liming parts of the catchment in 1986 increased stream and loch water pH and calcium concentrations and reduced inorganic aluminium concentrations. Improved stream and loch water quality has been maintained for more than eight years since liming.

KEY WORDS: Deposition inputs, water quality, liming effectiveness, Loch Fleet

INTRODUCTION

It was recognized at the start of the Loch Fleet Project that deposition and water quality information were critical to the assessment of recent acidification and that improvement of acid conditions in the loch and its tributary streams must be achieved before trout could be reintroduced successfully. The proposed trial treatments of the catchment would be monitored effectively by a regular regime of water quality sampling. This monitoring would also provide data from which the effectiveness of lime applications and expected timing of reacidification could be assessed.

METHODS

Over the period 1984 to 1989, staff were on-site on a weekday basis, providing the opportunity for routine Monday to Friday collection of bulk deposition (rainfall), stream and loch water samples. From September 1989, when staff were no longer resident on-site, sample collection became less frequent, usually two-weekly for deposition and water quality.

Rainfall *frequency* and *quantity* were measured automatically using a Meteorological Office Solid State Event Recorder (SSER) (at a frequency of 2 mm rain received). Rainfall *quality* was analysed from samples taken using a standard 5-inch diameter bulk collector set 30 cm above ground level, located in the north west of the catchment (Figure 1). Trials were carried out by placing similar equipment in alternative locations and at different altitudes within the site, but these failed to demonstrate any significant differences. Major ions in rain were analysed, including chloride, sulphate, nitrate, ammonium, sodium, calcium, magnesium and potassium. Sample collection during 1989–1994, less frequent than earlier in the Project, provided a cumulated sample for analysis and did not allow such easy recognition of episodes of unusual rain quality. However, it was still possible to match heavy rainfall events with some aspects of stream water chemistry.

Stream and loch water samples over 1989–1994 were taken at five locations (see Figure 1) using automatic sampling equipment. Samples were taken daily at about 1200 h (noon). Collected samples were removed fortnightly for analysis of pH, calcium and total aluminium concentrations. In addition, a combined sample for each fortnight was analysed for other major ions. Until 1991, flow measurements, using automatic measuring and recording equipment, were also made at these sites (with the exception

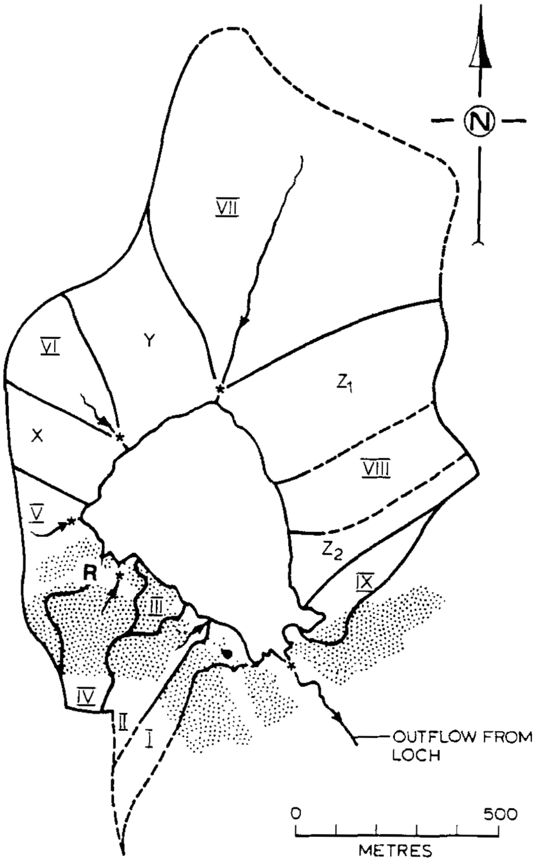

Figure 1 The Loch catchment, showing the position of the rainfall collector (and SSER gauge): *R*, and the main stream and loch water sampling points:*.

of sector V). This allowed the calculation of hydro-chemical fluxes for individual sectors and for the whole catchment.

Runoff samples were also collected on a two-weekly schedule from other sectors of the catchment (I, II, Z_1, VIII, IX–see Figure 1) and from downstream of the loch, and analysed for major ions.

Handling and chemical analysis of rain, stream and loch water samples continued as previously reported, the responsibility for this being with ScottishPower's East Kibride laboratory (see Howells and Dalziel, 1992).

RESULTS

Deposition

Rainfall in 1989 and 1993 was below the long-term average (2100 mm), while it was higher in 1990 and 1992; in 1991 it was close to the long-term average. Over 1989–1993, mean annual rainfall was 2192 mm and the mean weighted pH, 4.68 ($[\mathrm{H}]^+ = 21\ \mu\mathrm{g\,l^{-1}}$). The mean minimum (i.e. bulk deposition only) deposited load of hydrogen ion was $0.05\ \mathrm{g\,m^{-2}}$, and non-marine sulphur $1.81\ \mathrm{g\,m^{-2}}$. Data on the concentrations of all major ions recorded in rain samples are given in Table 1. Chloride provided the major anion component (on an equivalent basis), while nitrate and ammonium together were approximately equivalent to sulphate. Potassium was largely insignificant in rain (and TOC virtually absent).

Deposition input data for Loch Fleet can be set in the context of other regional estimates (e.g. Loch Dee, Loch Ard) and for some Scandinavian sites (Table II).

Stream and loch water quality

The runoff water quality from the sectors IV, VI and VII, limed in 1986 (see Table III), has maintained the loch water above the target quality set to ensure brown trout survival (pH > 6.0, $[\mathrm{Ca}^{2+}] > 2\ \mathrm{mgl^{-1}}$, $[\mathrm{Al}]_{\mathrm{total}} < 100\ \mu\mathrm{g\,l^{-1}}$ (Howells and Dalziel, 1992)). The initial improvement after liming these sectors, and the progressive changes since, are shown in Figure 2(a–d). For comparison, data from sector V over the same

Table I Deposition (rainfall) mean weighted concentrations, 1989–1993. Units: $\mu\mathrm{eq\,l^{-1}}$

Year	mm	pH	H^+	Cl^-	SO_4^{2-} (a)	SO_4^{2-} (b)	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
1989	1963	4.82	15	149	50	38	16	21	133	3	11	23
1990	2440	4.85	14	168	59	46	12	15	148	3	19	25
1991	2167	4.64	23	219	82	63	16	17	184	0	23	39
1992	2497	4.72	19	117	61	49	24	9	101	0	32	22
1993	1891	4.45	35	105	71	63	45	10	97	2	20	16
Means	2192	4.68	21	152	64	52	22	14	133	5	31	25

SO_4^{2-} (a) is total sulphate deposition. SO_4^{2-} (b) is non-marine sulphate deposition

Table II Mean rainfall and deposition input concentrations for other sites in the UK, and elsewhere, in recent years., Units: $\mu eq\,l^{-1}$ (Ref. Hornung *et al.*, 1990).

Location	mm	pH	H^+	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}
Birkenes, southern Norway	1352	4.35	45	58	74	38	38	56	4	9	13
Gardsjon, southern Sweden	1130	4.30	52	47	42	43	64	30	3	4	4
Loch Dee, south west Scotland	2728	4.80	16	130	51	4	24	111	4	7	24
Loch Ard, central Scotland	2238	4.50	32	156	60	11	25	136	6	17	27
Bedgellert, north west Wales	2181	4.44	36	144	25	3	13	131	4	15	30
Plynlimon, west Wales	2513	4.67	21	106	21	12	17	85	2	4	10
Llyn Brianne, central Wales	1868	5.20	6	110	47	5	5	93	5	16	21

Table III Liming treatments applied in April 1986

Sector	*Treatment*	*Application*	*Sector totals*
IV	Limestone slurry	23.9 t ha^{-1} beneath tree canopy	110 t limestone
VI	Limestone dust	21.3 t ha^{-1} over moorland	136 t limestone
VII	Limestone dust	10 t ha^{-1} selectively to wetland area	106 t limestone

period shows water quality for unlimed "control" conditions (Figure 2e). The calcium concentrations and pH in runoff from sectors IV and VI still exceed those before liming (see Figure 2a and b). However, in the main spawning stream, the Altiwhat, on sector VII, and in the loch itself, water quality is approaching target water quality (Figure 2c and d). On all sectors, although total aluminium concentrations have risen since initial reductions after liming, the toxic inorganic fraction has remained low. This is shown in Figure 3 for stream water on sector VII. The effectiveness of liming sectors IV, VI and VII, in terms of the water quality of the loch, are discussed in more detail below. In addition to the 1986 programme of liming, treatments to several other sectors of the Fleet catchment were made in spring 1987 (see Table IV) to test lower lime doses and alternative treatments. Overall, these minor treatments have had little effect on loch water chemistry, mainly because the flows from these sectors are comparatively small.

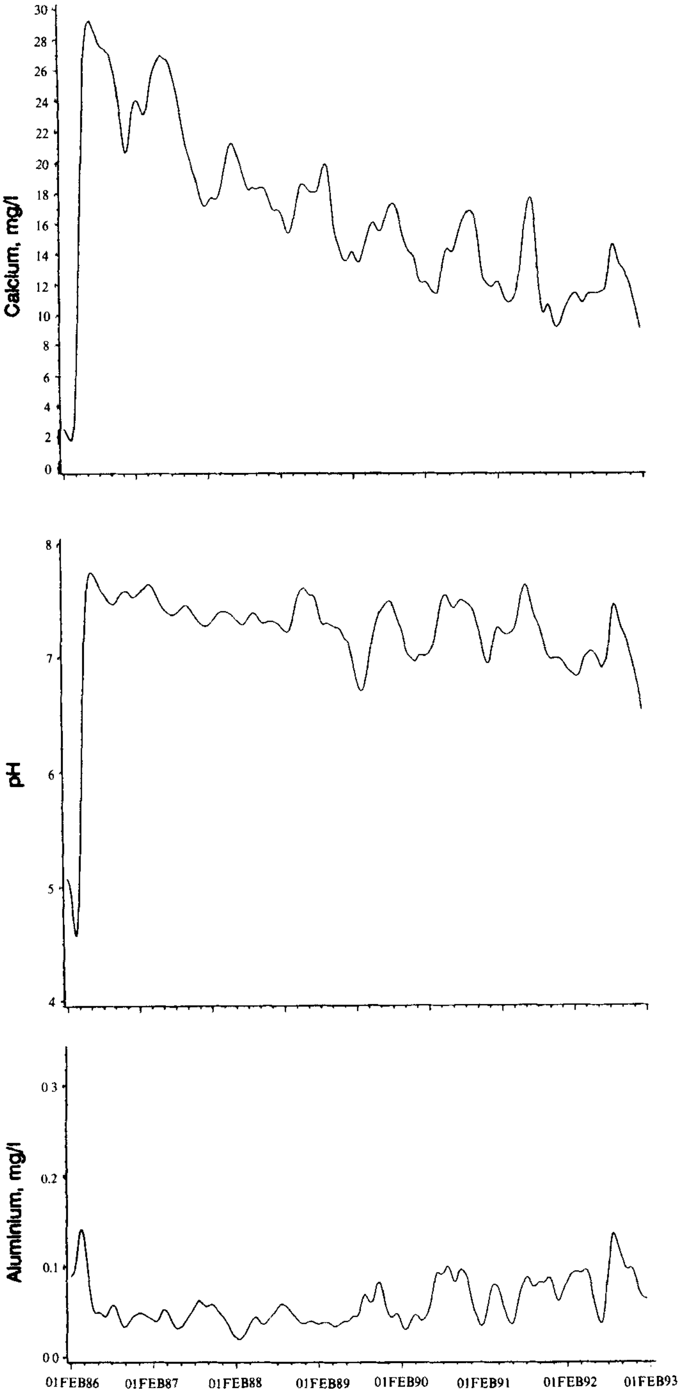

Figure 2a Drainage water quality on sector IV from February 1986 to February 1994. Liming was carried out in April 1986.

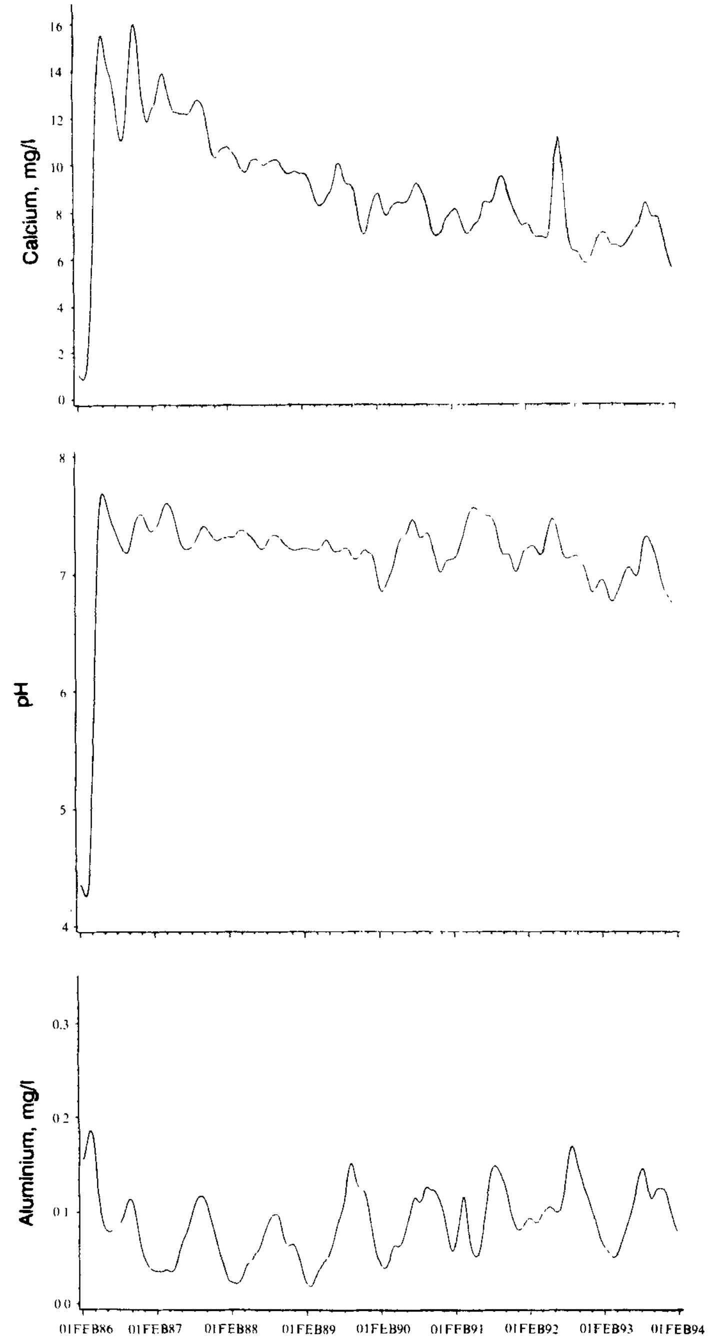

Figure 2b Drainage water quality on sector VI from February 1986 to February 1994. Liming was carried out in April 1986.

Also, in some instances (sectors I and II) the changes in runoff water chemistry were only short-lived. These treatments are, however, of interest in the context of possible more widespread low-level liming on similar terrain. On sector II, acidity was moderated slightly following liming in 1987 (pH 4.50 rising from 3.98), and more effectively on

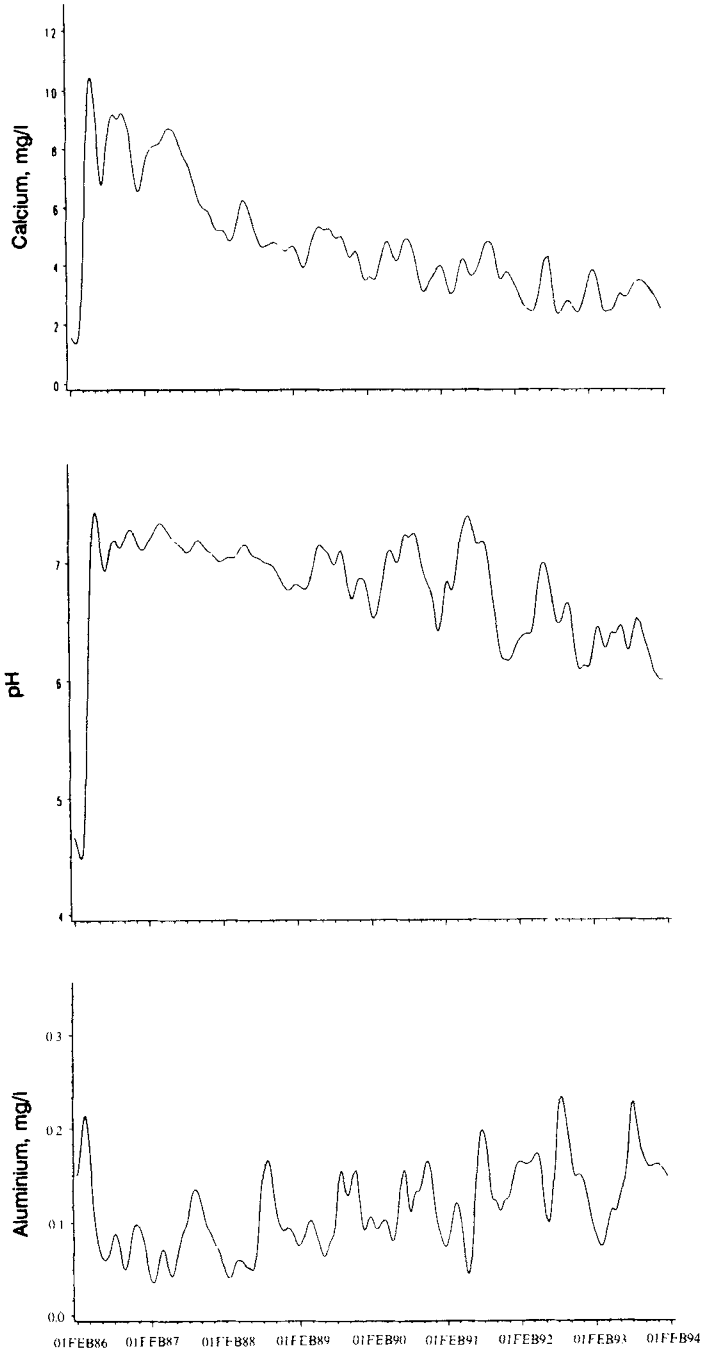

Figure 2c Drainage water quality on sector VII from February 1986 to February 1994. Liming was carried out in April 1986.

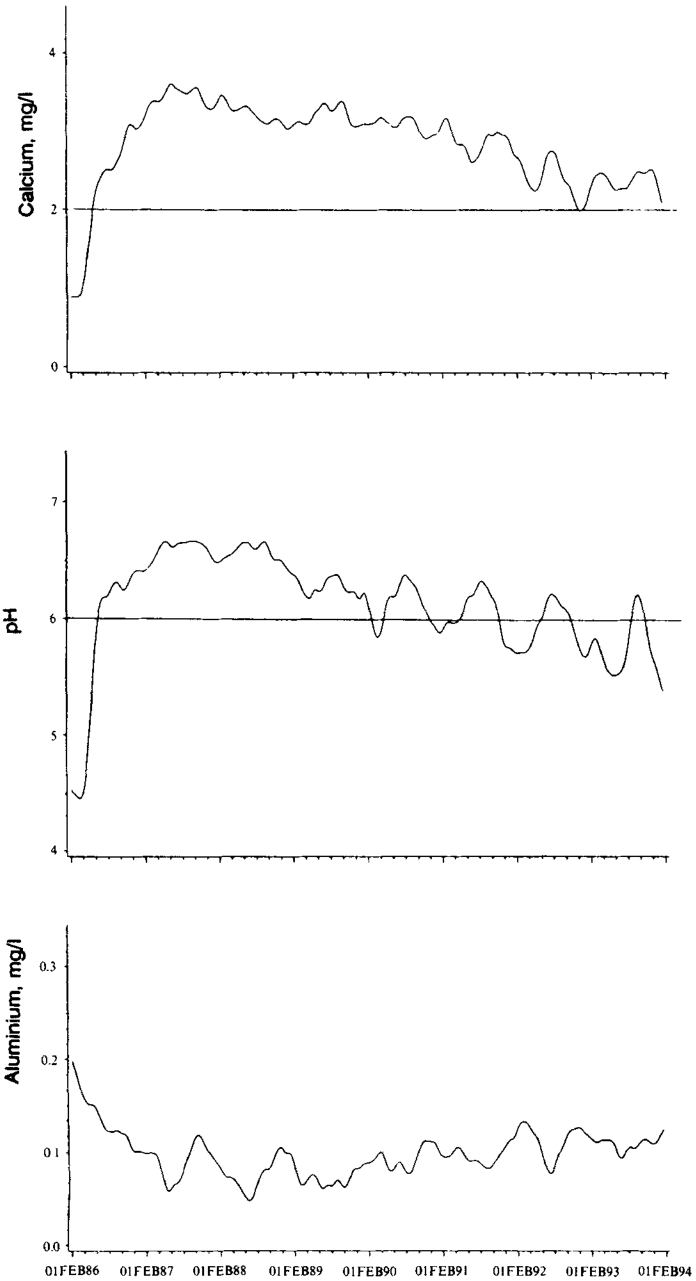

Figure 2d Water quality at the loch outlet from February 1986 to February 1994. Liming of parts of the catchment was carried out in April 1986.

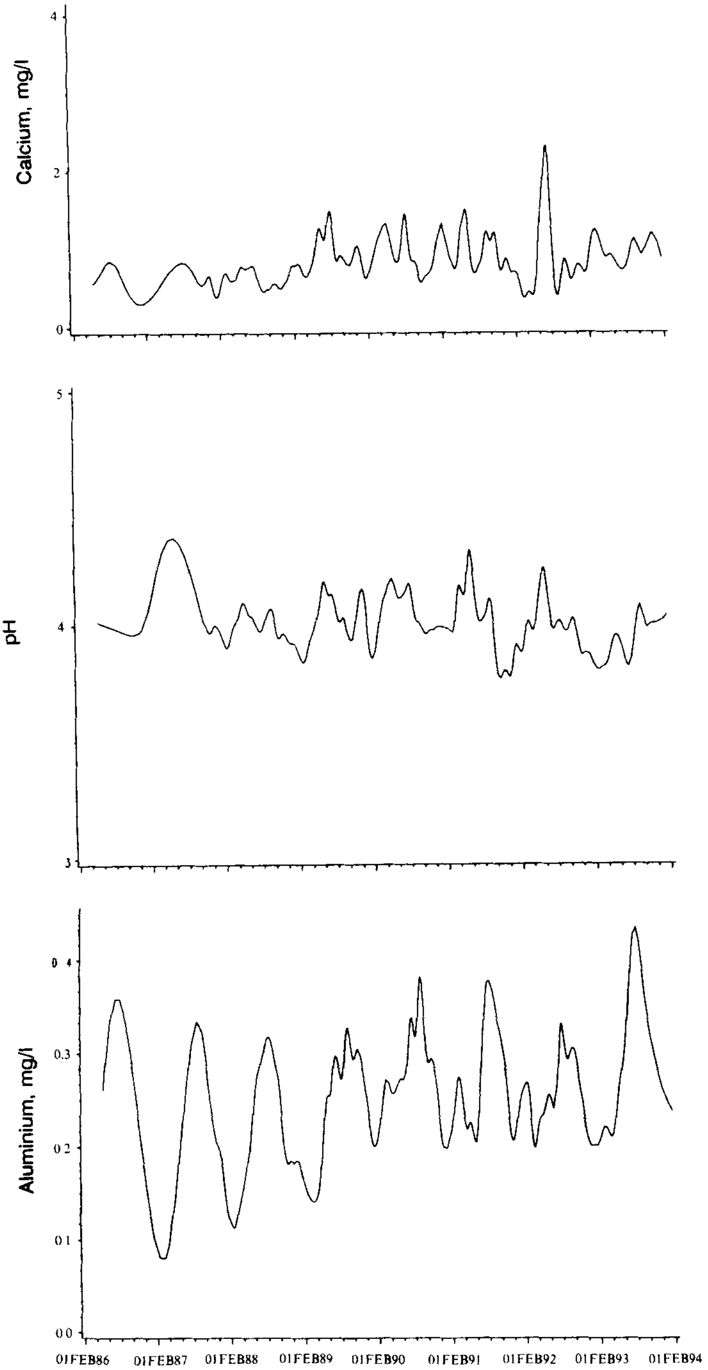

Figure 2e Drainage water quality on sector V from February 1986 to February 1994. Sector V was not limed.

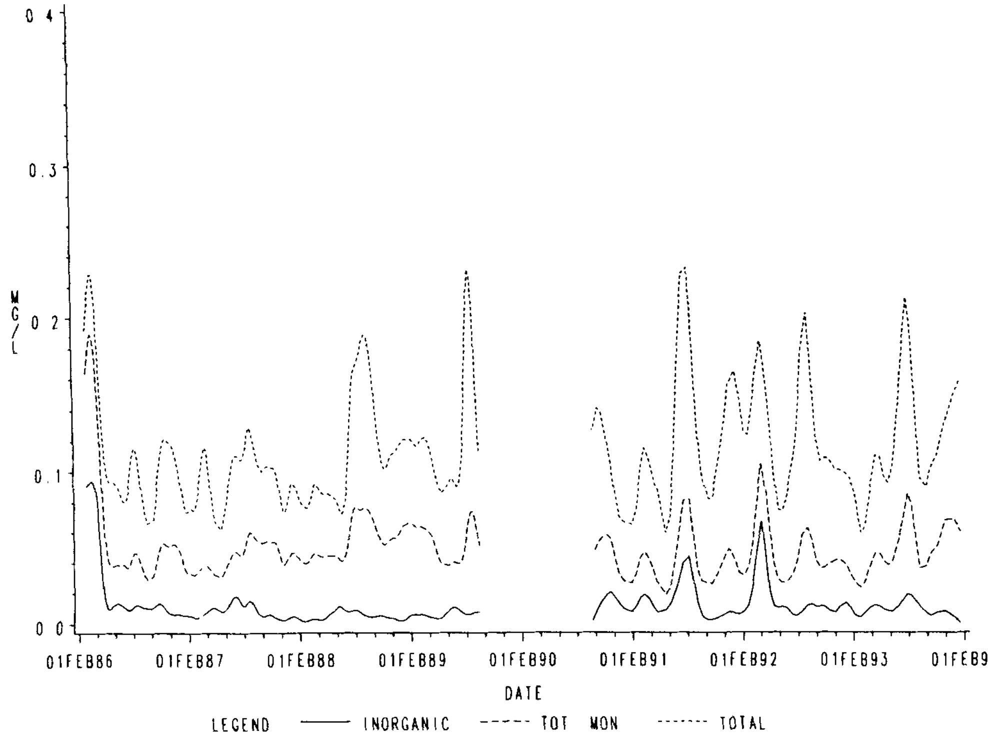

Figure 3 Aluminium fractionation data for stream water on sector VII (Altiwhat) from February 1986 to February 1994.

Table IV Liming (and other) treatments applied in 1987

Sector	*Treatment*	*Application*	*Sector total*
I	Fertiliser	1 t ha^{-1} below tree canopy	4 t fertiliser
II	Limestone dust and fertiliser (separately)	5 t limestone ha^{-1} 1 t fertiliser ha^{-1} below tree canopy	18 t limestone 4t fertiliser
VIII	Muirburn	–	–
IX	Limestone pellets	7.5 t ha^{-1} over moorland	15 t limestone
Z_1	Limestone	5 t ha^{-1} over moorland	60 t limestone

sector Z_1 (pH 6.03 rising from 4.39), and also on sector IX (pH 6.03 rising from 4.52). Little change was recorded in the runoff from sector VIII, which was burned (pH 4.19 rising from 4.15).

Alkalinity in runoff from sectors Z_1 and IX rose to 500 and 300 μeql^{-1}, respectively, following liming, and positive alkalinity was still present (>60 and >100 μeql^{-1}, respectively) in 1993.

Hydro-chemical fluxes

Hydro-chemical flux calculations for major ions have been calculated for the three main limed sectors (IV, VI and VII, 1986 treatments) and for the loch outlet for the period 1985 to 1992. These allow comparisons to be made of liming forest, moorland and wetland source areas, and the response of the catchment as a whole, along with in-lake processes. Flux data for 1985–1990 are given in Howells and Dalziel (1992). Unfortunately, because of difficulties with stream flow measurement, the last year for which hydro-chemical flux data have been calculated is 1990–1991. These data are given in Table V, and can be compared with those of earlier years (see Dalziel *et al.*, 1992).

Although year-to-year variations exist, except for calcium (and acidity), no significant changes in the effluxes of other major ions can be attributed to liming. Consistently, the major anion fluxes are those of chloride. The efflux of nitrate is always relatively small, due to its effective uptake within the catchment (particularly on the afforested sector IV) and the loch. In addition to the year-to-year differences, quarterly stream water data, shown for sector IV in Table VI, demonstrate considerable seasonal variation in ion concentrations, especially with regard to the nutrients nitrate and ammonium. Although the deposition input of ammonium is significant (see Table I), in this nitrogen-limited ecosystem only very low concentrations of ammonium and nitrate (see Table VI) reach the loch in runoff, especially in the April to September period. Higher deposition of sea salts (sodium, chloride), typically in the first quarter of the year, is reflected in their higher concentrations in runoff. In turn this may explain the winter peaks of aluminium mobilised from the catchment (e.g.control sector V, Figure 2e).

Liming effectiveness

Considerable attention, not surprisingly, has focused on the effectiveness of the main liming treatments applied to sectors IV, VI, and VII in April 1986. The rapid improvements in stream and loch water quality following these treatments can be seen in Figure 2; the liming can be described as having been effective in providing and maintaining an adequate water quality for brown trout survival in the loch through to 1993/94. However, any assessment of effectiveness must also consider the length of time

Table V Hydro-chemical flux data for deposition (rain) and runoff from sectors IV, VI, VII and the whole catchment, 1990–91 (mid-April to mid-April). Units: water–l ha^{-1}, ions–keq ha^{-1}

	In	*Out*			
	Rain	*IV*	*VI*	*VII*	*Whole*
Water	2.15×10^7	1.36×10^7	2.09×10^7	1.60×10^7	1.30×10^7
Cl^-	3.87	4.64	4.82	3.87	3.66
SO_4^{2+}	1.36	1.42	2.02	1.47	1.27
NO_{3-}	0.33	0.15	0.30	0.25	0.21
Na^+	3.25	3.58	4.29	3.40	2.92
Mg^{2+}	0.62	1.03	1.66	0.77	0.64
Ca^{2+}	0.58	9.49	8.94	2.92	1.99
H^+	0.41	0.001	0.001	0.003	0.01

Table VI Quarterly means for stream water chemical concentrations (sector IV), 1989–1993. Units: μeql^{-1}.

	Cl^-	SO_4^{2-}	NO_3^-	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
(a) 1989								
Jan.-Mar.	422	99	19	279	0	5	814	70
Apr.-jun.	367	107	11	281	2	1	849	88
Jul.-Sept.	324	147	6	248	0	1	941	106
Oct.-Dec.	307	102	9	250	0	3	812	81
Mean	355	114	11	265	0	3	854	86
(b) 1990								
Jan.-Mar.	477	117	18	324	0	1	694	72
Apr.-Jun.	400	107	8	309	0	0	768	92
Jul.-Sept.	326	100	5	242	0	1	827	96
Oct.-Dec.	336	101	11	256	0	0	713	76
Mean	385	106	11	283	0	0	751	84
(c) 1991								
Jan.-Mar.	363	134	20	300	0	0	644	82
Apr.-Jun.	302	126	8	253	0	0	657	94
Jul.-Sept.	279	101	5	244	0	0	807	102
Oct.-Dec.	443	135	10	308	4	0	676	85
Mean	347	124	11	276	1	0	696	91
(d) 1992								
Jan.-Mar.	280	111	18	240	0	0	571	71
Apr.-Jun.	281	100	7	246	0	0	643	87
Jul.-Sept.	231	170	5	219	0	1	668	89
Oct.-Dec.	243	95	8	196	0	3	488	66
Mean	259	119	10	225	0	1	593	78
(e) 1993								
Jan.-Mar.	494	144	18	346	2	7	565	82
Apr.-Jun.	360	95	12	291	3	5	607	89
Jul.-Sept.	274	134	4	224	3	6	644	97
Oct.-Dec.	282	162	13	262	0	8	554	95
Mean	353	134	12	281	2	7	593	91

(a) that the treatments continue to produce good quality *stream water*, and (b) that the treatments will maintain the *loch water* quality at or above the target.

Calcium flux calculations made since liming show that considerable quantities of applied calcium (as limestone) still remain on the limed sectors (sector IV: 7,541 kg ha^{-1} or 80% of that applied; sector VI: 6,697 kg ha^{-1} or 84%; sector VII: 805 kg ha^{-1} or 62%). Figure 4 shows this for the three sectors; the amounts of applied calcium remaining each April, after the initial application made in 1986, are shown as histograms, with the trend in mean annual stream water calcium concentrations superimposed. These show that on each sector, stream water calcium concentration declined fairly rapidly following the initial increase after liming, but has now started to level off: on sector IV to between 10 and 15 mg l^{-1}, on sector VI to between 5 and 10 mg l^{-1}, and on sector VII to between 2 and 4 mg l^{-1}.

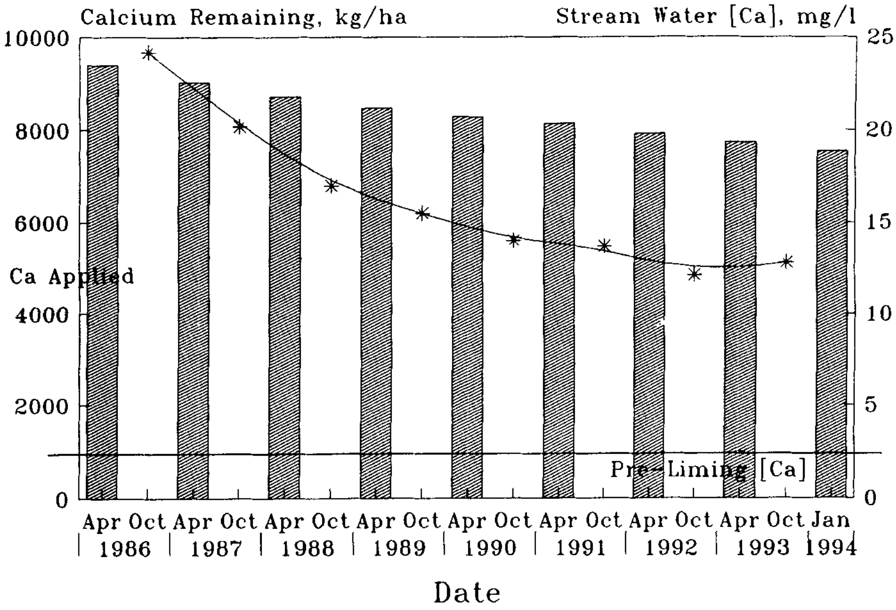

Figure 4a Calcium remaining each year (April) on sector IV (bars). The bar for April 1986 shows amount applied through liming. Superimposed are the mean annual stream water calcium concentrations (stars) between each April following liming, with the trend line through the points drawn.

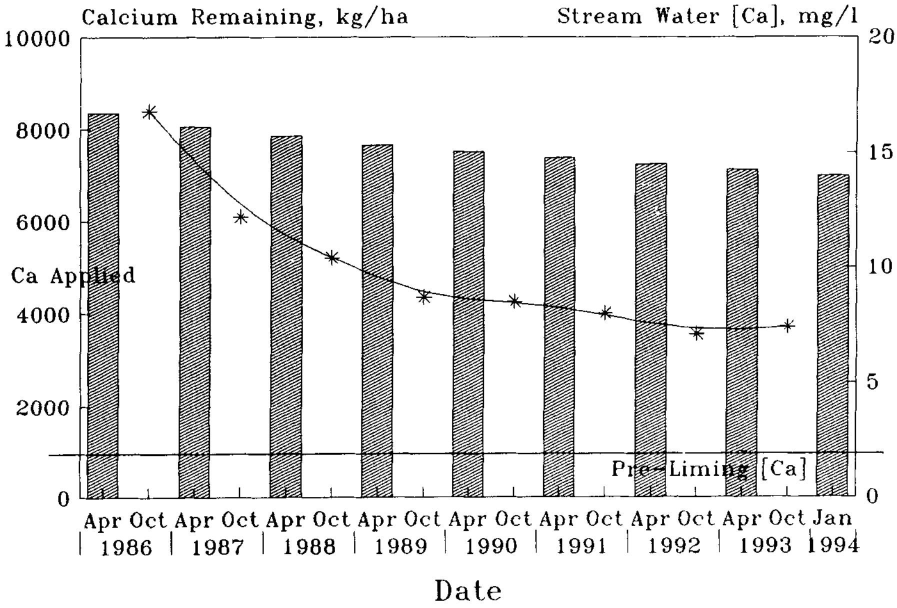

Figure 4b Calcium remaining each year (April) on sector VI (bars). The bar for April 1986 shows amount applied through liming. Superimposed are the mean annual stream water calcium concentrations (stars) between each April following liming, with the trend line through the points drawn.

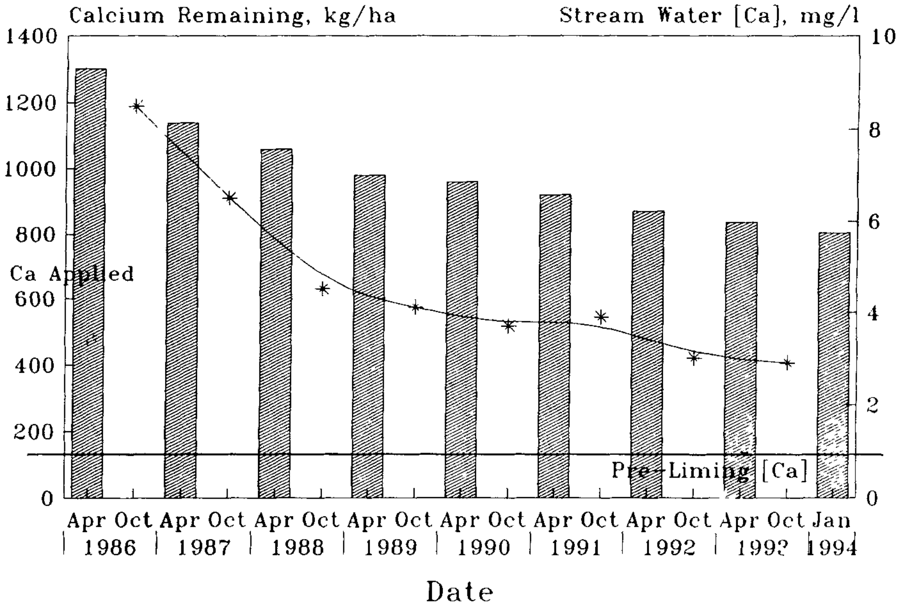

Figure 4c Calcium remaining each year (April) on sector VII (bars). The bar for April 1986 shows amount applied through liming. Superimposed are the mean annual stream water calcium concentrations (stars) between each April following liming, with the trend line through the points drawn.

Using hydro-chemical flux data, predictions of future stream water calcium concentrations on the limed sectors were made in 1989, $3\frac{1}{2}$ years after liming (Dalziel *et al.*, 1991). These suggested that runoff from sectors IV and VI, and conditions in the loch would be maintained to the end of the century, but for sectors VII a pH < 6 could be expected in 1993. So far, the predictions have been proved to be broadly correct, with the exception of sector VII, for which they were slightly pessimistic. Notwithstanding this, as previously mentioned, water quality on sector VII will soon fall below target (see Figure 2c).

Calcium concentration and pH in stream water from sectors IV and VI, however, remains as predicted, considerably higher than that pre-liming. What, then, is the prognosis for the length of time over which *loch water quality* will remain satisfactory for trout survival? The following calculations serve to show that water quality above the target set (pH > 6, [Ca] > 2 mg l^{-1}) may not be maintained for much longer.

In the year before liming (mid-April 1985 to mid-April 1986) the fluxes of calcium from sectors IV, VI and VII were;

IV:	130.9 kg
VI:	96.2 kg
VII:	636.9 kg
Total:	864 kg (from 43.1 ha)

This can be described as "background" calcium flux.

Assuming uniform calcium export, it can be calculated that the whole catchment (111 ha) contributed 2225 kg. Flow measurements made at the loch outlet over that year showed that 2.42 × 10^9 litres of water flowed from the loch. It can thus be calculated that the calcium concentration of this water was 0.9 mg l^{-1}, consistent with measured values.

The target calcium concentration to be attained after liming was set at > 2 mg l^{-1}. Over the period 1985–1991, during which time hydro-chemical flux calculations were possible, mean annual water loss from the loch at the outlet was measured as 2.19 × 10^9 litres. To maintain a calcium concentration in the loch of 1.1 mg l^{-1} greater than 0.9 mg l^{-1} requires an additional 2409 kg of calcium. This must come from the limed sectors. Sectors IV, VI and VII must, therefore, contribute 2409 kg of calcium in addition to their "background" contribution of 864 kg (i.e. a total of 3273 kg).

Mean annual volumes of stream water from each sector measured over 1985–1991 were;

IV:	7.39 × 10^7 litres
IV:	1.25 × 10^8 litres
VII:	5.72 × 10^8 litres
Total:	7.71 × 10^8 litres

Using predictions of stream water calcium concentrations (Dalziel *et al.*, 1991), along with mean annual volumes of stream water from each sector, predicted fluxes of calcium from the sectors can be calculated. Predictions of mean calcium concentrations and the total calcium flux from the three sectors each year from 1991–1992 are shown in Table VII. *Actual* mean concentrations and total amounts of calcium contributed are also given for 1991–1994.

Table VII shows that, although the stream water calcium concentrations of sectors IV and VI are predicted to remain well above pre-liming values until the end of the century (14 years after liming), the calcium concentration of the loch would fall below the target of 2 mg l^{-1} sometime in 1993 (when the total calcium contributed from the sectors was predicted to have fallen below 3273 kg). This has not happened, largely due to the contribution to the loch water chemistry made by the Altiwhat, the stream draining sector VII. The high volume of water it contributes, compared with that from sectors IV and VI, is crucial. Since the predictions of calcium concentration for sector VII were somewhat pessimistic (cf. values in parentheses in Table VII), the loch calcium concentration has not yet breached the target value.

Table VII Predictions of stream water calcium concentrations and total fluxes of calcium from the 1986-limed sectors. (Actual values for 1991–1994 are shown in parentheses).

Year	*Ca Concentration, mg l^{-1}*			*Total Ca, Kg*
	IV	*VI*	*VII*	
1991-92	15.2 (13.7)	8.4 (8.0)	2.6 (3.9)	3661 (5107)
1992-93	14.7 (12.1)	8.1 (7.0)	2.2 (3.0)	3357 (4349)
1993-94	14.2 (1.28)	7.8 (7.4)	1.9 (2.9)	3111 (4394)
1994-95	13.8	7.5	1.7	2929
1995-96	13.5	7.3	1.6	2825
1996-97	13.2	7.2	1.6*	2790
1997-98	12.9	7.0	1.6*	2743
1998-99	12.7	6.9	1.6*	2716

* Predictions for sector VII made only until 1995-96

These calculations, which involve the mass transport (or fluxes) of calcium rather than only concentrations, refute earlier suggestions (e.g. Dalziel *et al.*, 1991) that the contributions made by sectors IV and VI will be sufficient to maintain the loch calcium concentration above the target value until next century. As a corollary, they also serve to emphasise the need for any catchment liming to be targetted where there will be sufficient flux (mass transport) of applied calcium in stream flow to the lake.

The loch water quality will also be influenced by the treatments made to some sectors of the catchment in 1987 (Table IV), although, as indicated earlier, it is likely that such influences are minimal.

The target water quality for Loch Fleet and its tributary streams was set at pH > 6, $[Ca^{2+}] > 2 mg l^{-1}$ and $[Al]_{total} < 100 \mu g l^{-1}$, to assure satisfactory conditions for the complete brown trout life-cycle. It is likely that once this target quality is breached, adult survival in the Loch will be unaffected initially, although it is likely that recruitment to the population will be affected. Continued monitoring of the Loch and Altiwhat water quality, and of the fish population structure, should serve to demonstrate the suitability or otherwise of the target water quality originally set.

SUMMARY AND CONCLUSIONS

Rainfall over 1989–1993 at Loch Fleet fluctuated around the long-term average of 2100 mm. Although year by year variations in acid or sulphate loading from deposition were evident and quite substantial, there was no trend to reduced acid deposition matching reported changes in national sulphur emissions over the same time (Irwin *et al.*, 1993).

The increases in stream and loch water pH and calcium concentrations and the reduction in inorganic monomeric aluminium concentrations following liming parts of the catchment in 1986 have been maintained. Predictions made earlier of stream and loch water quality have been proved to be broadly correct for sectors IV and VI, although Altiwhat (sector VII) and loch water quality now show signs of falling to below target levels within the next few years. Stream and loch water quality monitoring is continuing.

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