

[2]

EFFECTS OF CATCHMENT LIMING AND AFFORESTATION ON THE CONCENTRATION AND FRACTIONAL COMPOSITION OF ALUMINIUM IN THE LOCH FLEET CATCHMENT, SW SCOTLAND

IAN C. GRIEVE

Department of Environmental Science, University of Stirling, Stirling FK9 4LA (U.K.)

(Received April 4, 1989; accepted after revision August 11, 1989)

ABSTRACT

Grieve, I.C., 1990. Effects of catchment liming and afforestation on the concentration and fractional composition of aluminium in the Loch Fleet catchment, SW Scotland. *J. Hydrol.*, 115: 385–396.

Concentrations of total, total monomeric and organic monomeric forms of aluminium and of iron, anions and dissolved organic carbon (DOC) in streams draining one forested and two moorland catchments in southwest Scotland were measured over a 3-year period. Catchments were limed during the study and comparisons of stream chemistry were made before and after liming under the two land-use types. Within individual events, DOC and anion concentrations increased with increasing discharge, and aluminium concentrations showed little change with discharge. In the pre-liming phase as a whole, organic monomeric Al was strongly correlated with DOC and inorganic monomeric Al was strongly correlated with anions, particularly Cl. The forested catchment had higher mean DOC and SO_4 , but lower mean Al. After liming, Al concentrations were reduced, by up to 80% for monomeric forms, and these low levels prevented observation of correlations with DOC and anions. Liming treatments were effective in both forested and moorland catchments, lasted for at least 2.5 years after treatment, and low rates of application to bog areas were as effective as entire catchment treatments.

INTRODUCTION

The effects of acid deposition on soils, vegetation and freshwaters have been studied intensively in recent years. Several experiments at the catchment scale in both western Europe and in the U.S.A. have identified the roles of weathering and ion exchange processes and of hydrological pathways in determining the acidity of freshwaters (Mason and Seip, 1985). Hydrochemical models have been calibrated and used to predict long-term changes under various deposition scenarios and under changing land use (e.g. Cosby et al., 1986; Neal et al., 1986). Such research has demonstrated the long time period which would be required for reductions in atmospheric emissions to be reflected in reduced stream acidity (Cosby et al., 1986). The most rapid method of neutralizing excess acidity thus remains the application of neutralizing materials such as limestone powder or fragments either directly to streams and lakes, or indirectly to the surface of catchment soils (Bengtsson et al., 1980).

Historically, applications of agricultural lime to increase the pH of upland soils have also resulted in increased streamwater pH (Ormerod and Edwards, 1985). Experiments using catchment liming as a management strategy have only recently been initiated in the U.K. uplands, and these have shown a very rapid increase in streamwater pH (Howells and Brown, 1987). Effects of acid deposition are not, however, confined to streamwater pH. Soil ion exchange and weathering processes together with catchment hydrology control the release of toxic metals such as aluminium into the freshwater system (Lawrence et al., 1988). Toxic forms of aluminium include mono-ionic forms of the element, but complexation with dissolved organic substances can render these non-toxic (Seip et al., 1984). Effects of liming on the fractionation of aluminium have been modelled (Davis and Goldstein, 1988), but have not been fully evaluated in relation to coniferous afforestation, to hydrological variations and to possible seasonal variations in the availability of dissolved organic matter (McAvoy, 1988).

The objectives of this investigation were to identify the separate roles of conifer afforestation, catchment liming and availability of dissolved organic matter on aluminium concentrations and their fractional composition during high flow events in the Loch Fleet catchment in southwest Scotland.

MATERIALS AND METHODS

The Loch Fleet project was initiated in 1984. Its immediate aims were to investigate various experimental acidity mitigation treatments in a small fishless loch in southwest Scotland, with the longer-term objective of restoring a self-sustaining trout fishery. Project and catchment details have been discussed fully by Howells and Brown (1987). The catchment area is 111 ha and altitude ranges from 340 to 470 m O.D. Annual rainfall is 2150 mm. Soils are peats and peaty gleys over thin drift and granite bedrock. Vegetation is 90% moorland dominated by *Calluna* and *Molinia* species; the remaining 10% was afforested in 1961 with Sitka spruce and Lodgepole pine.

Streams or ditches draining three sectors of the loch catchment area were examined. Sectors VII and VI were moorland, with respective areas of 39.7 and 4.2 ha, and mean annual flows of 23 and 2.4 l s^{-1} . Sector IV was 88% forested, with an area of 4.9 ha and mean annual flow of 2.5 l s^{-1} . All three sectors were limed in April 1986. Sector IV received 20 t ha^{-1} of limestone as slurry, sector VI received 30 t ha^{-1} of limestone dust spread by hand to the entire soil surface and sector VII received 10 t ha^{-1} of limestone dust applied only to wetland surfaces (equivalent to 2.6 t ha^{-1} to the sector). Automatic water samplers were installed at the flow-monitoring sites in each of the sectors. These were triggered either manually or by float switches to collect samples during storm events, at a sampling interval of 1 or 2 h. Some 30 events were sampled between November 1985 and November 1988. Samples were collected after each event and filtered through glass fibre filters before analysis.

Total iron and aluminium were determined by atomic absorption spectro-

photometry after drying at 80°C and dissolution in HCl. Some total Al measurements were made colorimetrically by the Catechol Violet method (Dougan and Wilson, 1974). The two procedures gave good agreement, with no significant differences in a paired sample test. Total monomeric Al was determined directly using colorimetry, and organically complexed monomeric Al was determined colorimetrically after using Na^+ ion exchange columns to remove inorganic monomeric forms (Seip et al., 1984; Lynam, 1985). Ion exchange columns were dosed with 1% H^+ resin for low-pH samples (Røgeborg and Henriksen, 1985). This procedure maintained the pH of column effluents at 4.5–5. Storage tests over 15 days indicated that variations in these fractions were undetectable in low-pH waters (cf. Røgeborg and Henriksen, 1985). Aluminium fractions thus determined were inorganic monomeric (total monomeric – organic monomeric), organic monomeric (direct) and polymeric (total – total monomeric).

Dissolved organic carbon (DOC) was determined from absorbance in 4-mm glass cells at 360 nm (Grieve, 1985a) and by aqueous carbon analyser. Absorbance measurements were calibrated against carbon measurements. The regression equation was consistent for all three sites and seasonally. Absorbance was converted to DOC using the regression equation. Chloride, nitrate and sulphate were determined routinely by ion chromatography. Some early analyses used ion-selective electrodes for analysis of chloride, turbidimetry with barium chloride for sulphate (Golterman et al., 1978) and ion exchange followed by titration to pH 4.5 for total strong acid anions

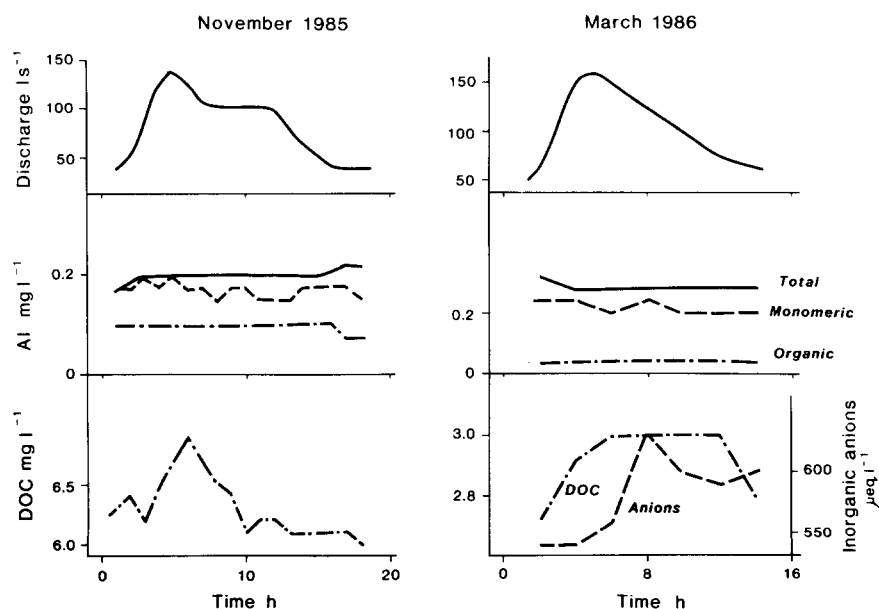


Fig. 1. Flow-related variations in chemical determinands before catchment liming in sector VII.

(Mackereth et al., 1978). Duplicate analyses indicated no significant differences between Cl determination by ion-selective electrode and by ion chromatography, and between determination of total strong acid anions by titration and by sum of separate anions from ion chromatography determinations.

RESULTS AND DISCUSSION

Flow-related variations

Some five events were sampled before the liming of the catchments. Figure 1 shows variations in aluminium, discharge, DOC, and strong acid anions for

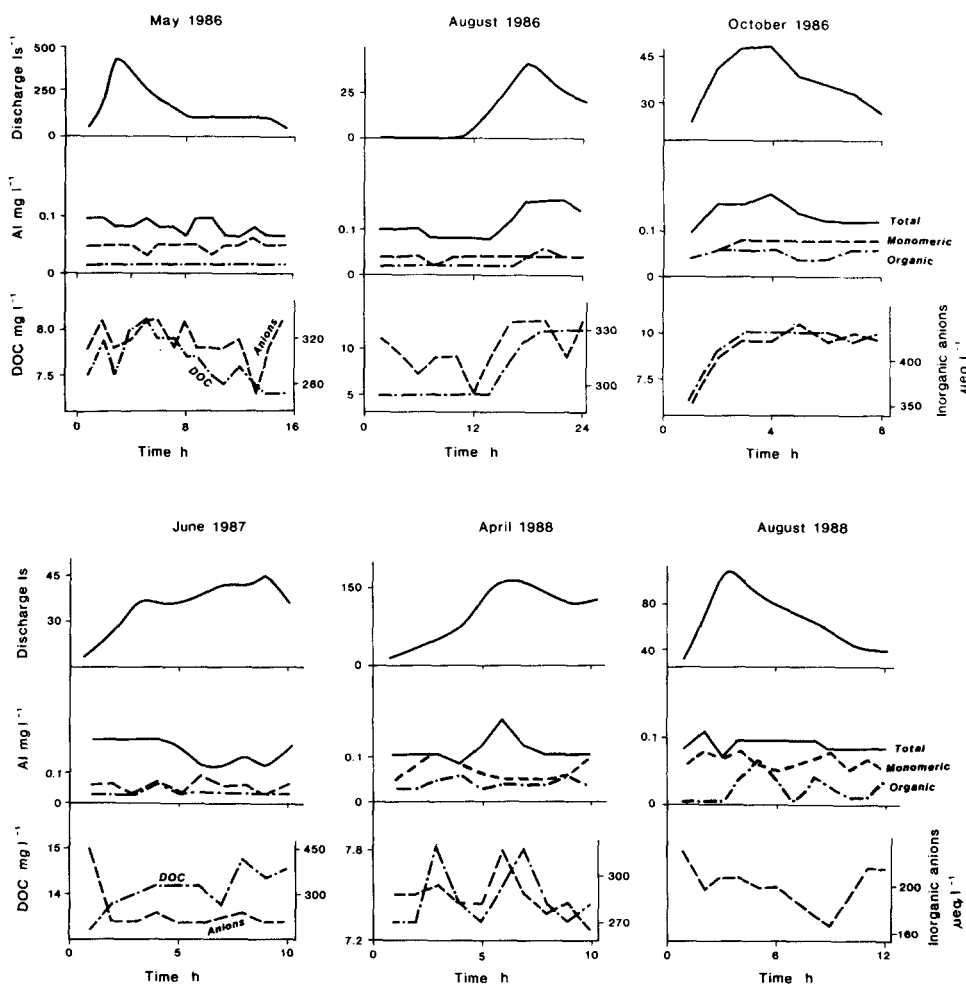


Fig. 2. Flow-related variations in chemical determinands after catchment liming in sector VII.

sector VII during events in November 1985 and March 1986. Slightly increased concentrations of DOC and anions are evident from these graphs, but flow-related variations were very small ($< 1 \text{ mg l}^{-1}$ and $< 100 \mu\text{equiv l}^{-1}$, respectively). For Al the November event displayed a complex pattern with increasing total Al but different patterns for each of the fractions. Inorganic monomeric (total monomeric – organic monomeric) Al peaked early in the event and polymeric Al peaked rather later. Organic monomeric Al showed little change with increasing flow. In the March event, inorganic monomeric Al concentrations were greater than in November and organic monomeric forms were smaller. Flow-related changes during the event in all fractions of Al were again very small.

Figure 2 shows chemical changes during selected events in the post-liming period. Changes in DOC and anions with flow were similar to those in the pre-liming period, with small rises in concentration during events. The major effect of the liming of the catchment is seen in the concentrations of aluminium. Very large reductions in both monomeric forms of aluminium were observed. Within-storm variations were small, of the order of $0.02\text{--}0.03 \text{ mg l}^{-1}$, and showed no apparent relation with flow. As a result of the reduced monomeric Al, total Al was lower by up to 50% after liming.

Flow-related within-storm variations in stream water chemistry were thus small both before and after liming, reflecting the predominantly peaty nature of the catchment soils. Mineral subsoils were thin, and were present only in less than half the 452 sampling sites in the catchment examined by the Macaulay Institute for Soil Research (1986). Peaty surface horizons retained water for most of the year. Nisbet (1986) found that 90% of flow was routed through the soil surface in both moorland and forested sites. Within-event variations in chemical constituents with sources in the upper soil or the groundwater were thus far smaller than those identified in streams draining podzolic soils in upland Scotland (Reid et al., 1981; Grieve, 1984, 1985b).

Relationships among the determinands are shown in Table 1 for both the pre- and post-liming phases. Before the liming, organic monomeric Al was very strongly correlated with variations in DOC in all three sectors. Regression equations were significantly different for the forested (IV) and moorland (VI and VII) sectors. In sector IV a low value for the slope and a high value for the y-axis intercept indicate very small, but statistically significant, variations in Al with change in DOC, whereas in sectors VI and VII DOC-related variations were slightly greater. These relationships reflected between-storm variations in DOC and associated Al, as correlations between Al_{org} and DOC within individual events were not evident from Fig. 1. After liming the correlation between organic Al and DOC was not observed, as a result of the very low Al concentrations.

Labile (inorganic monomeric) Al was strongly correlated with anions before liming. The best correlations were obtained with total strong acid anions, and in multiple regressions chloride consistently explained more of the variance in labile Al than sulphate (Table 1). The indication is thus that, before liming,

TABLE 1

Relationships among determinands

	Sector IV	Sector VI	Sector VII
Correlation coefficients			
Al(org) ^a vs. DOC			
pre-liming	0.851	0.907	0.945
post-liming	0.384	0.082	0.442
Al(lab) ^a vs. Cl			
pre-liming	0.734	0.788	0.650
post-liming	0.102	0.185	0.040
Al(lab) vs. SO ₄			
pre-liming	0.378	0.319	0.456
post-liming	-0.312	0.126	0.046
Al(lab) vs. inorg. anions			
pre-liming	0.819	0.811	0.806
post-liming	-0.223	0.167	0.040
Fe vs. DOC			
pre-liming	0.586	0.389	0.476
post-liming	0.634	0.567	0.896
Regressions			
Site IV	Al(org) = 0.02 + 0.0025 DOC ^b ± 0.00 ± 0.0002		
	Al(lab) = 0.02 + 0.08 Cl + 0.06 SO ₄ ^b ± 0.01 ± 0.02 ± 0.05		
Site VI	Al(org) = 0.00 + 0.013 DOC ± 0.00 ± 0.001		
	Al(lab) = 0.06 + 0.21 Cl + 0.01 SO ₄ ± 0.02 ± 0.05 ± 0.15		
Site VII	Al(org) = 0.01 + 0.013 DOC ± 0.00 ± 0.001		
	Al(lab) = 0.11 + 0.42 Cl - 0.51 SO ₄ ± 0.04 ± 0.10 ± 0.26		

^a Al(org) is organic and Al(lab) is inorganic monomeric Al.^b Al fractions and DOC as mg l⁻¹; Cl and SO₄ as mequiv l⁻¹.

sea-salt variations are the primary determinant of high labile Al concentrations. This reflects the proximity of the site to the west coast of Scotland, and its relative remoteness from major pollution sources which give rise to sulphate. The impact of sea-salt events on streamwater pH in the neighbouring Loch Dee catchment has been indicated by Langan (1987). As in the case of organic Al, regressions were significantly different among sectors, with sector VII showing the greatest variation in Al and sector IV showing the least. Again, the correlations reflected between-storm variations in anions, as within-storm variations were small (Fig. 1). After the catchments were limed, reductions in labile Al to very low levels obscured any relationship with anions.

Labile Al in the pre-liming period also had a strong negative correlation with DOC (Table 1). DOC has been shown to have a significant seasonal variation, with a maximum in the latter half of the year and a minimum in spring in upland streams and soil waters (Grieve, 1984). A similar trend was

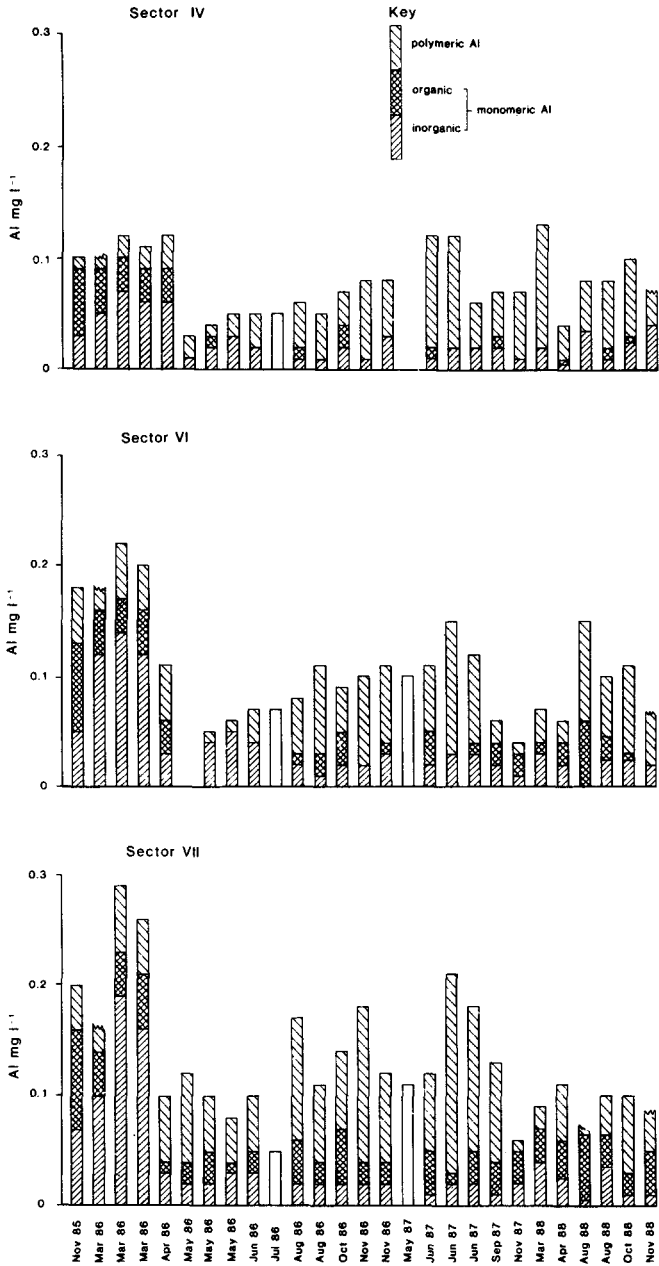


Fig. 3. Mean aluminium concentrations and fractional composition during 27 storm events.

evident in DOC at Loch Fleet, and a seasonal sine wave with a maximum in August explained between 50 and 75% of the variance in DOC in the three streams. High DOC concentrations and organic complexation reactions may thus be an important mechanism for increasing organic-bound forms of Al and reducing the concentrations of labile forms during the latter half of the year. The November event shown in Fig. 1 may reflect such a mechanism, with labile Al concentrations less than half those in the March event. McAvoy (1988) found a similar annual trend in the proportions of organic monomeric Al, with a maximum of up to 90% of the total monomeric Al in the summer-autumn months at three sites in Massachusetts.

EFFECTS OF LIMING AND OF AFFORESTATION

The immediate and obvious effect of liming was a dramatic reduction in Al concentrations of the drainage water during storm events, as seen from comparison of Figs. 1 and 2. Figure 3 summarizes mean Al concentrations and their fractional composition for all events sampled from November 1985 to November 1988. Total Al measured for the November 1988 event was very high, and did not correlate with other independent measurements. Values were thus

TABLE 2

Sector and liming differences

Liming	Sector IV		Sector VI		Sector VII	
	Before	After	Before	After	Before	After
Al(org) Mean	0.04	0.01	0.05	0.01	0.07	0.02
S.D.	0.01	0.01	0.02	0.01	0.02	0.01
Al(lab)	0.05	0.02	0.10	0.03	0.11	0.02
	0.01	0.01	0.02	0.01	0.02	0.01
Al(poly)	0.02	0.04	0.05	0.05	0.05	0.08
	0.02	0.03	0.02	0.04	0.02	0.04
DOC	8.3	11.2	4.1	10.5	4.3	8.2
	5.0	2.5	1.6	2.7	1.7	3.0
Cl	0.39	0.25	0.36	0.19	0.36	0.19
	0.08	0.07	0.07	0.06	0.07	0.06
SO ₄	0.19	0.20	0.16	0.18	0.16	0.15
	0.03	0.07	0.02	0.08	0.03	0.06
Fe	0.19	0.13	0.11	0.07	0.04	0.07
	0.04	0.04	0.03	0.05	0.02	0.03
DOC re-	0.81	-0.11	-1.07	0.33	-0.33	0.08
siduals ^a	3.8	2.0	0.76	1.91	0.64	2.52

DOC, Al and Fe are mg l⁻¹; Cl and SO₄ are mequiv l⁻¹.

^a Residuals from regression of DOC on seasonal sine wave.

omitted from Fig. 3. The rapidity of the change is evident in the events sampled in sectors VI and VII in April 1986, during the week after limestone applications. The equivalent event in sector IV, which was limed later than the other two sectors, showed no change in mean Al concentration, but a substantial reduction was seen in the next event sampled. In all three sectors, the reduction in total Al was by 50% or more of the pre-liming concentrations and was caused by substantially reduced concentrations of both organic and inorganic monomeric Al fractions. This reduction has been maintained through the 2.5 years since liming, and total monomeric Al concentrations have not exceeded 0.15 mg l^{-1} during this time, compared with a peak concentration of 0.32 mg l^{-1} before liming. The difference in the operation of the catchment systems after liming was also reflected in much-reduced correlations between Al and DOC and inorganic anions (Table 1).

Table 2 summarizes the inter-sector differences in the pre- and post-liming phases for all determinands. Reductions in both monomeric forms of Al are by 60–80% of pre-liming concentrations in all three sectors. There did not appear to be any difference in the efficacy of the different limestone application rates (greatest in sector VI, least in sector VII) in reducing monomeric Al concentrations. Table 2 also indicates a consistent and significant difference among the three sectors in Al concentrations before liming. Both of the moorland sectors showed significantly greater concentrations of all three Al fractions, and sector VII had greater organic Al than sector VI. Sector IV was earlier noted as showing less variation in Al with either inorganic anions or DOC (Table 1).

The only pattern observable in Fe was the higher mean concentration in the stream draining the forested sector both before and after liming. Mean SO_4 concentrations were similar before and after liming, DOC concentrations increased after liming, and Cl concentrations declined. DOC, SO_4 and Cl concentrations were always highest in the stream draining the forested sector.

The forested sector thus had the highest concentrations of inorganic anions and DOC, but the lowest concentrations of Al. Elevated organic contents and darker colours of streams which drain forested catchments are a source of concern to the water industry (Greene, 1987), but there have been no controlled experiments to quantify this effect. Higher concentrations of inorganic anions can be explained by the greater atmospheric filtering efficiency of a forest cover, which results in increased additions of anions in throughfall, an effect observed and modelled in other upland U.K. catchments (Neal et al., 1986; Whitehead et al., 1988). This has not, however, resulted in greater Al mobilization in the Fleet catchments. Al differences among the sectors may possibly reflect soil differences among the sectors, as sector IV is likely to have a greater proportion of till parent materials (Macaulay Institute for Soil Research, 1986).

Increased concentrations of DOC and decreased concentrations of Cl in the post-liming phase are probably not directly related to the liming. Assessment of the change in DOC is complicated by the lack of summer sampling in the pre-liming phase. As indicated above there was a strong seasonal trend in DOC concentrations, with a maximum in August. Table 2 also gives the mean values

of standardized residuals from the regression of DOC on a seasonal sine wave with an August maximum. When the seasonal component was thus eliminated the pattern was less consistent. Mean residuals in sectors VII and VI increased slightly after liming, and those in sector IV decreased, although the only statistically significant change was that in sector VI. There are no directly comparable studies of the effects of catchment liming on DOC concentrations, but Kullberg and Petersen (1987) reported no change in DOC after liming of a river in southern Sweden. Decreases in Cl concentrations in the post-liming samples can be similarly explained as an artefact of sampling. Streamwater Cl has been shown to have a winter maximum, much dampened from the winter maximum in U.K. precipitation (Neal et al., 1988).

Decreases in the monomeric Al fractions were clearly and directly related to the decreased acidity of the streams which followed the liming of the sectors. Howells and Brown (1987) reported the immediate increase in pH which followed catchment liming in April 1986. These increases were similar to pH increases of 1–2 units which were observed and modelled after liming in two catchments in southern Sweden (Warfvinge and Sverdrup, 1988). The change in the monomeric Al fractions was equally rapid, and followed the pattern modelled by Davis and Goldstein (1988) in the Adirondacks. In the latter study, reductions in spring peak monomeric Al concentrations from 0.35 to $< 0.2 \text{ mg l}^{-1}$ were predicted, very similar to the change in peak values measured here.

Timing of sampling in relation to the seasonal effect noted above resulted in higher DOC and lower Cl after liming. Higher DOC could not have contributed to the decline in organic Al, as these were positively correlated before liming. However, lower chloride concentrations could have contributed to the post-liming decreases in labile Al, given the relationships between inorganic anions and labile Al in the pre-liming phase. To test the magnitude of this possible complication, the pre-liming regressions of labile Al on inorganic anions were used to predict mean labile Al in the post-liming period which would result from the decreased chloride. Mean predicted post-liming labile Al concentrations were 0.04, 0.08 and 0.06 mg l^{-1} for sectors IV, VI and VII respectively. These figures are considerably greater than the mean measured concentrations (Table 2), and the reduction in labile Al can therefore safely be assumed to be the result of catchment liming.

CONCLUSIONS

(1) In the pre-liming phase, temporal variations in monomeric Al fractions were largely controlled by availability of mobile inorganic anions and DOC. The balance between organic-bound and labile inorganic forms varied seasonally, with larger proportions of organic-bound forms at times of high DOC.

(2) The stream draining the forested sector had highest concentrations of inorganic anions and DOC but lowest concentrations of monomeric Al. Al

variations among sectors before liming cannot therefore be explained by differences in mobilizing agents.

(3) Catchment liming had an immediate effect in reducing the concentrations of monomeric Al. The effect has continued at similar levels for 2.5 years, and cannot be related to variations in mobilizing anions. The smallest application of limestone (sector VII) was as effective in reducing Al as the largest (sector VI).

ACKNOWLEDGEMENTS

I am grateful for the financial support of the Loch Fleet Project Group for this study, and to Central Electricity Research Laboratories for supplying flow data.

REFERENCES

- Bengtsson, B., Dickson, W. and Nyberg, P., 1980. Liming acid lakes in Sweden. *Ambio*, 9: 34–36.
- Cosby, B.J., Whitehead, P.G. and Neale, R., 1986. A preliminary model of long-term changes in stream acidity in south-west Scotland. *J. Hydrol.*, 84: 381–401.
- Davis, J.E. and Goldstein, R.A., 1988. Simulated response of an acidic Adirondack lake watershed to various liming strategies. *Water Resour. Res.*, 24: 525–532.
- Dougan, W.K. and Wilson, A.L., 1974. The absorptiometric determination of aluminium in water. A comparison of some chromogenic reagents and the development of an improved method. *Analyst*, 99: 413–430.
- Golterman, H.L., Clymo, R.S. and Ohnstad, M.A.M., 1978. *Methods for Physical and Chemical Analysis of Fresh Waters*. Blackwell Scientific Publications, Oxford, 213 pp.
- Greene, L.A., 1987. The effect of catchment afforestation on public water supplies in Strathclyde Region, Scotland. *Trans. R. Soc. Edinburgh: Earth Sci.*, 78: 335–340.
- Grieve, I.C., 1984. Concentrations and annual loading of dissolved organic matter in a small moorland stream. *Freshwater Biol.*, 14: 533–537.
- Grieve, I.C., 1985a. Determination of dissolved organic matter in streamwater using visible spectrophotometry. *Earth Surf. Process. Landforms*, 10: 75–78.
- Grieve, I.C., 1985b. Annual losses of iron from moorland soils and their relation to free iron contents. *J. Soil Sci.*, 36: 307–312.
- Howells, G. and Brown, D.J.A., 1987. The Loch Fleet project, S.W. Scotland. *Trans. R. Soc. Edinburgh: Earth Sci.*, 78: 241–248.
- Kullberg, A. and Petersen, R.C., 1987. Dissolved organic carbon, seston, and macroinvertebrate drift in an acidified and limed humic stream. *Freshwater Biol.*, 17: 553–564.
- Langan, S.J., 1987. Episodic acidification of streams at Loch Dee, S.W. Scotland. *Trans. R. Soc. Edinburgh: Earth Sci.*, 78: 393–397.
- Lawrence, G.B., Driscoll, C.T. and Fuller, R.D., 1988. Hydrologic controls of aluminium chemistry in an acidic headwater stream. *Water Resour. Res.*, 24: 659–669.
- Lynam, S., 1985. Measurement of aluminium in fresh water — a method for laboratory and field use. CERL Memorandum, TPRD/L/BY/075/M85, Central Electricity Research Laboratories, Leatherhead, 14 pp.
- Macaulay Institute for Soil Research, 1986. Soils and vegetation of the Loch Fleet catchment. In: G. Howells (Editor), *The Loch Fleet Project, A Report of the Pre-intervention Phase 1984–1986*. Central Electricity Research Laboratories, Leatherhead, pp. A1.1–A1.18.
- Mackereth, F.J.H., Heron, J. and Talling, J.F., 1978. *Water Analysis: Some Methods for Limnologists*. Freshwater Biological Association Scientific Publications, Windermere, 124 pp.
- Mason, J. and Seip, H.M., 1985. The current state of knowledge on acidification of surface waters and guidelines for future research. *Ambio*, 14: 45–51.

- McAvoy, D.C., 1988. Seasonal trends of aluminium chemistry in a second order Massachusetts stream. *J. Environ. Qual.*, 17: 528-534.
- Neal, C., Whitehead, P., Neale, R. and Cosby, J., 1986. Modelling the effects of acidic deposition and conifer afforestation on streamwater acidity in the British uplands. *J. Hydrol.*, 86: 15-26.
- Neal, C., Christophersen, N., Neale, R., Smith, C.J., Whitehead, P.G. and Reynolds, B., 1988. Chloride in precipitation and streamwater for the upland catchment of River Severn, mid-Wales; some consequences for hydrochemical models. *Hydrol. Proc.*, 2: 155-165.
- Nisbet, T.R., 1986. Changes in rain and soil water chemistry on passage through a forested and unforested site at Loch Fleet, Galloway. In: G. Howells (Editor), *The Loch Fleet Project, A Report of the Pre-intervention Phase 1984-1986*. Central Electricity Research Laboratories, Leatherhead, pp. A5.1-A5.5.
- Ormerod, S.J. and Edwards, R.W., 1985. Stream acidity in some areas of Wales in relation to historical trends in afforestation and the usage of agricultural limestone. *J. Environ. Mgmt.*, 20: 189-197.
- Reid, J.M., MacLeod, D.A. and Cresser, M.S., 1981. Factors affecting the chemistry of precipitation and river water in an upland catchment. *J. Hydrol.*, 50: 129-145.
- Røgeborg, E.J.S. and Henriksen, A., 1985. An automatic method for the fractionation and determination of aluminium species in fresh waters. *Vatten*, 41: 48-53.
- Seip, H.M., Muller, L. and Naas, A., 1984. Aluminium speciation: comparison of two spectrophotometric analytical methods and observed concentrations in some acidic systems in southern Norway. *Water Air Soil Pollut.*, 23: 81-95.
- Warfvinge, P. and Sverdrup, H., 1988. Soil liming as a measure to mitigate acid runoff. *Water Resour. Res.*, 24: 701-712.
- Whitehead, P.G., Bird, S., Hornung, M., Cosby, J., Neal, C. and Paricos, P., 1988. Stream acidification trends in the Welsh uplands — a modelling study of the Llyn Brianne catchments. *J. Hydrol.*, 101: 191-212.