Amelioration of Streamwater Acidity by Catchment Liming-Response of Podzolic Soils to Pasture Improvement

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AMELIORATION OF STREAMWATER ACIDITY BY CATCHMENT LIMING—RESPONSE OF PODZOLIC SOILS TO PASTURE IMPROVEMENT

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The effects of agricultural improvement by cultivation, re-seeding, lime and fertiliser additions on the soil solution chemistry of acid podzolic soils have been investigated in a field experiment in a mid-Wales catchment. The treatment resulted in an increase in the pH, alkalinity and calcium content of soil waters from the surface, organic-rich horizon. In the year following treatment, soil waters in the mineral horizons became more acid and had higher aluminium concentrations than observed at the control site. This response is ascribed to soil water acidification resulting from increased nitrification rates following liming and cultivation. In subsequent years, soil water acidity in these lower horizons was neutralised by lime-rich water percolating from the surface. No changes in stream water acidity and calcium content were observed in the catchment containing the area of agriculturally improved soils. This suggests that the selective treatment of moorland catchments to improve agricultural productivity may not always be accompanied by amelioration of acid stream water.

KEY WORDS: Liming, cultivation, soil solution, acidification, catchment.

INTRODUCTION

The uplands of Wales have been dominated by acid soils for thousands of years (Smith and Taylor, 1969) giving rise to naturally acidic, poorly buffered stream waters. However, palaeolimnological evidence suggests that since the industrial revolution, acid deposition in the UK has markedly increased surface water acidity (UKAWRG, 1988). Control of the emissions of oxides of nitrogen and sulphur, the precursors to acid rain, is ultimately required if the acidity of surface waters is to be reduced. However, recent modelling studies suggest that acidified streams may take many decades to recover as soils slowly release stored sulphate (Jenkins *et al.*, 1990). In the short term more certain methods of restoring acidified waters are required.

The main options for rapid amelioration of acid surface waters are direct liming of the water body or liming of the catchment soils. Direct liming of lakes has been extensively practised in Scandinavia (e.g. Brocksen and Emler, 1988) and to a limited extent in the UK (Underwood *et al.*, 1987). An important limitation to lake liming is that the feeder streams, which are often important fish spawning and nursery

habitats, are not treated and the effective duration of the treatment is short compared with catchment liming (Turnpenny, 1992). Addition of lime directly to streams has generally not provided an adequate solution (Turnpenny, 1992). Lime dissolves relatively slowly, providing a constant supply of base cations but it may be unable to improve stream water quality during acid storm events (Milner and Varallo, 1990).

Application of lime to the land surface overcomes some of the problems encountered with direct liming of streams and lakes by providing a pool of base cations within the soil either retained on the cation exchange complex or as "free lime". Base cations are released at a rate determined by the flow rate and volume of water passing through the soil. Catchment hydrological pathways are, therefore, a major factor in determining the effectiveness of terrestrial liming techniques (Howells and Dalziel, 1992; Waters *et al.*, 1991). Several catchment liming experiments have now been undertaken in the UK, meeting with varying degrees of success (Jenkins *et al.*, 1991; Howells *et al.*, 1992). However, there is concern about the ecological effects of lime on some sensitive habitats (Clymo *et al.*, 1992; Woodin and Skiba, 1990).

Ground limestone has been used as an integral part of pasture improvement in the uplands of Wales over the last 50 years (Munro *et al.*, 1973). Treatments have ranged from the application of ground or powdered limestone to more intensive ground preparation, addition of fertilisers and re-seeding with more productive grasses (Newbould, 1985). In addition to the effects on agricultural productivity, there is evidence that streams draining improved pasture are less acid and contain lower amounts of aluminium than those flowing from unimproved moorland (Hornung *et al.*, 1986; Adams and Evans, 1989). A reduction in agricultural liming since 1959 may also have contributed to an increase in the acidity of Welsh streams (Ormerod and Edwards, 1985).

In the light of these observations, an experimental treatment was designed as part of the Llyn Brianne Acid Waters Project (Gee and Stoner, 1989; Gee, 1990) to evaluate the effectiveness of upland pasture improvement for ameliorating streamwater acidity. In this paper we examine the soil solution response to this treatment and comment on its effectiveness in ameliorating streamwater acidity.

SITE DESCRIPTION

The study site was located within a small headwater catchment of the River Camddwr known as CI3 (Figure 1). The Camddwr is one of the main inflows to the Llyn Brianne reservoir which is about 33 km from the west coast of Wales. The catchment lies at approximately 400 m above sea level and receives about 1800 mm of rainfall annually.

Soils and Vegetation

Catchment CI3 is underlain by base-poor Lower Palaeozoic mudstone bedrock. The soils at the treated site are intermediate between a ferric stagnopodzol and a brown podzolic soil (Rudeforth *et al.*, 1984) and have been mapped for the purposes of the Brianne project as an Intergrade. Thus they have a thin surface organic (O) horizon (c. 10 cm) but lack the continuous, leached, grey silty Eag horizon and iron pan found in stagnopodzols. Instead there is a thin, 2–3 cm thick, grey brown A horizon, between the O horizon and the B horizon. The latter is brownish yellow in colour with a sandy silt loam texture. At a depth of about 70–80 cm, the B horizon merges into a dark grey brown, stony silt loam C horizon containing angular mudstone fragments.
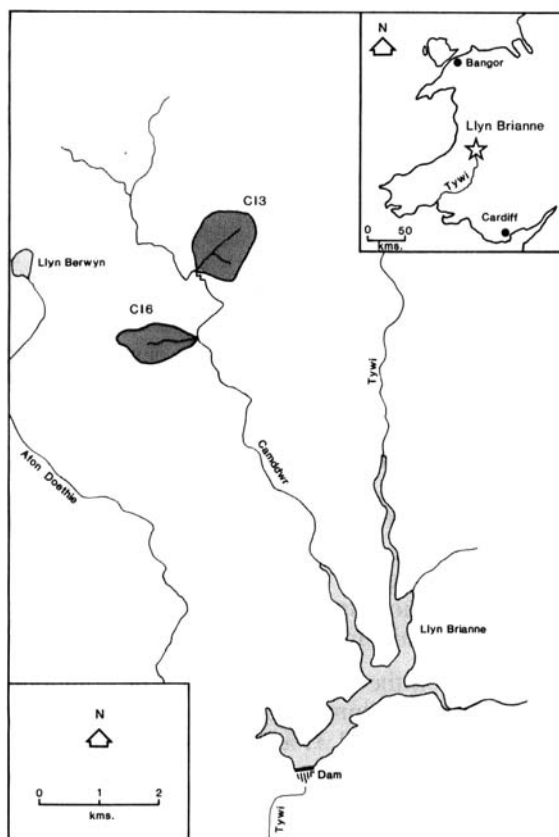
Figure 1 Location map of the Llyn Brianne area showing catchment CI3.

The soil pH is low throughout.the profile (Table 1) although the base saturation in the O horizon is high (78%). This may indicate that the soils had been treated with lime or fertiliser at some earlier date, although no documentary evidence was available. Soil pH and exchangeable aluminium content increase with depth to the B horizon.

Table 1 Chemistry of control and treated intergrade soils within catchment CI3 at Llyn Brianne.

Control	pH (CaCl₂)	Base saturation %	Exch. Al meq/100 g	Loss-on-ignition %
O	3.32	78	2.0	43
A	3.29	14	5.9	16
B	3.94	4	6.4	5
Treated				
O	5.45	99	0.1	10
A	5.10	99	0.1	15
B	3.90	28	3.6	4

The vegetation on the untreated intergrade soils is a *Nardus stricta-Galium saxatile* grassland community (NVC U5b; Rodwell, 1989). The vegetation contains a moderate cover of *Molinia* with *Festuca ovina, Nardus stricta, Agrostis capillaris* and *Polytrichum commune* also present in the sward. Re-seeding and fertilisation successfully converted the treated site to a *Lolium perenne* ley (NVC MG7) with a low floristic diversity (Ecological Surveys, 1991).

TREATMENT

A segment of about 20 ha (c. 25%) of catchment CI3 was agriculturally improved following ADAS recommendations (Le Grice, 1986, pers comm.). An area of land adjacent to the treated site was left as a control. The following treatment commenced on the 15th May 1986:

1. Ploughing of the area followed by harrowing.
2. Application of powdered (95% < 1.8 mm grain size) agricultural magnesian lime-stone (containing at least 35% $MgCO_3$) at a rate of approximately 10 tonnes ha^{-1}, followed by harrowing.
3. Applications of 5–20–15 "Sheppy" compound fertiliser at a rate of 0.75 tonnes ha^{-1} and "Sheppy-Cymru" phosphate at 0.375 tonnes ha^{-1}.
4. Seeding with Lambhill seed mixture at a rate of 42 kg ha^{-1}.

The treatment was completed on the 26th June 1986. The compound fertiliser comprised ammonium phosphate, calcium phosphate and potassium chloride. The "Sheppy-Cymru" phosphate contained 31% P_2O_5 as calcium phosphate and a small quantity of nitrogen (2%) in the ammonium form.

SAMPLE COLLECTION AND ANALYSIS

A combination of methods was used for soil water sampling at each site. In the surface organic-rich horizons, plastic zero-tension tray lysimeters were inserted beneath the soil horizon. Soil water was collected in a six litre polypropylene bottle connected to the lysimeter. In each of the mineral horizons, porous ceramic cup suction samplers (Stevens, 1981) were installed. Although problems with ceramic cups have been reported (Grover and Lamborn, 1970; Nagpal, 1982; Raulund-Rasmussen, 1989), laboratory and field studies (Hughes and Reynolds, 1988; 1990) show that these difficulties are largely overcome by laboratory leaching prior to installation followed by a prolonged period of equilibration in the field.

Three replicate sets of samplers were deployed at each site. The samplers at the control site were installed in November 1985 and data from September 1986 onwards are presented here. At the treated site, the samplers were installed immediately after the cultivation and liming. Samples collected during the ten weeks immediately following installation were discarded to allow the samplers to equilibrate to field conditions.

Soil water samples were collected fortnightly by National Rivers Authority (NRA) Welsh region staff. Individual samples were bulked by horizon and filtered through 0.45 μm membrane filters before analysis. Chemical analyses were performed at the

NRA Regional Laboratories in Llanelli using standard methods (West, 1987). In brief, alkalinity (to pH 4.5) and pH were determined on unfiltered sub-samples using a Mettler auto-titrator. Plasma emission spectroscopy was used to measure sodium, potassium, calcium, magnesium, aluminium (total filtrable) and sulphur (assumed to be SO_4). Nitrate, nitrite (negligible in all samples), ammonium, chloride and DOC were determined using standard methods on a Technicon continuous flow auto-analyser.

In 1990, soil samples for chemical analysis were collected from three pits in each of the control and treated areas. Soil pH was determined on field moist soils in a 1:2.5 soil:liquid suspension in 0.01M $CaCl_2$. Exchangeable base cations were determined on the <2 mm fraction of air dried soils using unbuffered 0.1M $BaCl_2$ as the extractant followed by analysis using atomic absorption spectrophotometry (AAS). Exchangeable aluminium was determined by AAS following extraction with 1M KCl. Loss-on-ignition was determined at 375°C for 16 hours to minimise weight losses due to thermal decomposition of the lime.

It is possible that calcium contained in the lime of the treated soils was dissolved by the barium chloride solution. To check this, cation exchange capacity values determined by the summation of individual cations and values measured directly by a compulsive exchange technique for soils containing 'free carbonates' were compared (Gupta et al., 1985; Luo, 1990). The results of the comparison suggested that dissolution of lime by the $BaCl_2$ was minimal (Luo, 1990).

RESULTS

Soil solution chemistry of the unimproved (control) soil

The solution chemistry of the unimproved soil was dominated by sodium and chloride, reflecting the high marine inputs from wet deposition in the area (Table 2). Sulphate was also a major component of the anion sum, though a proportion of this was of non-sea salt origin. The soil waters were acid (pH 4.0–5.1) with a low or negligible alkalinity (Table 3). Soil water acidity was generally greatest in the surface, organic-rich horizons, decreasing with depth to the B horizon. Aluminium concentrations increased and amounts of DOC decreased with depth down the profile (Table 4) as observed in podzolic profiles elsewhere in Wales (Neal et al., 1989; Hughes et al., 1990).

Annual mean soil water concentrations of sodium and sulphate changed little during the three years of observation, although chloride concentrations were quite variable (Table 2). There was also a large change in the amount of soil water nitrate during the second year of the study, particularly in the C horizon (Table 4). This was related to samples collected during warm, wet weather in July and August 1988 which was preceded by a relatively dry period in June. The dry weather was terminated by 10.2 mm of rain which fell on 26–28 June. Samples were collected from the site on June 29 and large concentrations of ammonium (5.9 mgN l^{-1}), nitrate (1.7 mgN l^{-1}) and sulphate (25.1 mgl^{-1}) were measured in water from the O horizon lysimeters. Nitrate concentrations increased further during the following fortnight to 2.4 mgN l^{-1} and then subsequently declined. Nitrate concentrations also increased down the profile (Table 4); nitrate becoming the dominant anion in the C horizon, accounting for approximately 50% of the anion charge in years two and three.

Table 2 Annual arithmetic mean Na, K, Cl and SO$_4$–S concentrations (mgl^{-1}) in soil waters from control (C) and treated (T) intergrade soils at Llyn Brianne. a = significantly different from control at p < 0.05 (1-Way ANOVA and F test).

Na		O	A	B	C
Year 1	C	2.8	3.0	4.3	4.3
	T	3.5	3.0	4.6	3.4
Year 2	C	3.6	3.3	6.8	4.1
	T	3.4	3.8	3.1^a	3.4
Year 3	C	3.8	4.3	4.4	5.1
	T	3.7	4.9	4.3	4.2

K		O	A	B	C
Year 1	C	3.0	0.31	1.6	1.1
	T	3.4	3.2^a	3.3^a	3.0^a
Year 2	C	3.5	0.38	2.2	1.6
	T	2.9	0.9^a	1.5^a	1.7
Year 3	C	2.6	0.49	1.0	1.4
	T	2.8	1.1	1.6	1.4

Cl		O	A	B	C
Year 1	C	7.1	4.1	9.1	9.0
	T	8.2	6.4	14.0	10.9
Year 2	C	8.7	6.5	6.7	9.8
	T	9.1	7.9	7.8	8.6
Year 3	C	10.1	7.0	7.7	8.1
	T	16.3	14.1^a	7.9	7.9

SO$_4$–S		O	A	B	C
Year 1	C	2.2	1.7	1.6	1.4
	T	4.5^a	4.6^a	3.1^a	4.8^a
Year 2	C	2.0	1.4	2.0	1.3
	T	3.2	2.9^a	3.9^a	4.0^a
Year 3	C	2.3	1.5	1.3	1.6
	T	3.9	3.8^a	4.0^a	3.5^a

Sampling period: September 1986 to September 1989.

Table 3 Annual mean pH, Ca, Mg (mgl^{-1}) and alkalinity (as mg CaCO$_3$ l^{-1}) concentrations in soil waters from control (C) and treated (T) intergrade soils at Llyn Brianne. a = significantly different from control at p < 0.05 (1-Way ANOVA and F test).

pH		O	A	B	C
Year 1	C	4.63	5.08	4.86	4.88
	T	5.32[a]	6.52[a]	4.64	4.45[a]
Year 2	C	4.62	4.91	4.68	4.53
	T	5.54[a]	6.52[a]	5.15[a]	4.90[a]
Year 3	C	4.63	4.85	4.93	4.56
	T	6.05[a]	5.96[a]	5.40[a]	5.17[a]

Ca		O	A	B	C
Year 1	C	0.8	0.4	0.6	0.7
	T	7.8[a]	11.5[a]	5.8[a]	6.1[a]
Year 2	C	0.7	0.5	1.0	1.0
	T	4.9[a]	7.0[a]	3.5[a]	3.8[a]
Year 3	C	1.0	0.6	0.6	1.0
	T	8.5[a]	11.8[a]	4.3[a]	4.1[a]

Mg		O	A	B	C
Year 1	C	0.8	0.6	0.7	1.0
	T	4.9[a]	7.2[a]	5.0[a]	5.2[a]
Year 2	C	0.8	0.7	1.2	1.5
	T	3.6[a]	5.0[a]	2.7[a]	3.0[a]
Year 3	C	1.0	0.8	0.8	1.4
	T	4.0[a]	5.0[a]	3.0[a]	3.3[a]

Alk.		O	A	B	C
Year 1	C	1.3	1.6	1.2	1.3
	T	8.0[a]	26.3[a]	5.6[a]	3.0[a]
Year 2	C	1.4	1.3	1.2	0.6
	T	10.6[a]	18.3[a]	3.1[a]	2.5[a]
Year 3	C	1.0	1.8	1.5	1.5
	T	16.7[a]	14.4[a]	4.1[a]	3.9[a]

Sampling period: September 1986 to September 1989.

Table 4 Annual arithmetic mean NO_3-N, NH_4-N, Al(tot) and DOC concentrations (mgl^{-1}) in soil waters from control (C) and treated (T) intergrade soils at Llyn Brianne. a = significantly different from control ($p < 0.05$).

NO_3-N		O	A	B	C
Year 1	C	0.1	0.3	0.8	1.0
	T	6.2[a]	6.3[a]	11.7[a]	11.6[a]
Year 2	C	0.3	<0.1	1.5	4.9
	T	3.6	2.2[a]	1.6	3.2
Year 3	C	0.2	2.3	0.7	5.0
	T	2.2[a]	4.2	2.0[a]	3.5[a]

NH_4-N		O	A	B	C
Year 1	C	0.23	<0.02	0.25	0.03
	T	1.00[a]	0.20	1.80[a]	0.61[a]
Year 2	C	0.63	<0.02	0.37	0.09
	T	3.00[a]	<0.02	0.03[a]	0.05
Year 3	C	0.13	<0.02	0.05	<0.20
	T	0.30	<0.02	0.02	0.03

Al (tot)		O	A	B	C
Year 1	C	0.26	0.26	0.45	0.61
	T	0.28	0.13[a]	2.40[a]	3.00[a]
Year 2	C	0.23	0.35	0.75	2.41
	T	0.22	0.17[a]	0.38[a]	0.86[a]
Year 3	C	0.25	0.47	0.53	2.52
	T	0.15[a]	0.14[a]	0.27[a]	0.61[a]

DOC		O	A	B	C
Year 1	C	13.5	3.1	4.4	3.0
	T	18.9	18.9[a]	3.7	3.4
Year 2	C	12.3	2.8	3.4	2.5
	T	15.9	15.6[a]	3.5	5.4[a]
Year 3	C	16.6	2.7	2.1	3.8
	T	24.4	11.9[a]	4.0[a]	4.7

Sampling period: September 1986 to September 1989.

The increase in nitrate concentrations in the untreated soil was accompanied by changes in soil water cation concentrations. In the O horizon there was no change in the acidity or aluminium content of the solution with ammonium maintaining the charge balance. In the C horizon, where the largest nitrate concentrations were recorded, soil waters became more acid and there was a fourfold increase in annual mean aluminium concentrations from 0.6 mgl^{-1} to 2.5 mgl^{-1} (Tables 3 and 4).

Effects of land improvement

In the three years following treatment, mean soil water calcium concentrations increased significantly in the surface organic-rich (O) horizon from approximately 1 mgl^{-1} in the control to between 5 and 8 mgl^{-1} (Table 3). The mean alkalinity also increased from about 1 mgl^{-1} as $CaCO_3$ in the control, to 16.7 mgl^{-1} as $CaCO_3$ by year three in the treated soil (Table 3). Soil water acidity decreased in the surface horizons by approximately 96%. Total filtrable aluminium remained similar to control concentrations (c. 0.25 mgl^{-1}) until three years after treatment (Table 4).

Soon after treatment, calcium concentrations of 15 mgl^{-1} were observed in the upper mineral horizon (A) compared with 0.5 mgl^{-1} at the control site (Figure 2a). Soil water pH increased by a unit to 6.5 and alkalinity from approximately 2 to 40 mgl^{-1} as $CaCO_3$ (Figures 2b and 3a). Calcium concentrations, alkalinity and pH remained substantially above those at the control site in subsequent years (Table 3). Annual mean aluminium concentrations were less than control values in all three years following treatment (Table 4).

Inorganic nitrogen concentrations increased significantly in the O and A horizons in the year following treatment, although concentrations declined subsequently (Table 4). In the O horizon, annual mean ammonium concentrations increased from less than 0.5 mgN l^{-1} to a maximum of 3 mgN l^{-1} in the second year following treatment. This was accompanied by a large increase in nitrate to over 6 mgN l^{-1} in year one, declining to about 2 mgN l^{-1} in year three (Table 4).

In the lower mineral (B and C) horizons, there were large increases in the amounts of calcium relative to those observed in the untreated soil. However, the mean acidity, aluminium and nitrate contents of soil waters were greater than control values during the first year following treatment (Tables 3 and 4; Figures 3b and 4). Mean nitrate concentrations in year one (c. 12 mgN l^{-1}) were over 10 times higher than in the control soil. Mean concentrations of aluminium (2.4–3.0 mgl^{-1}) were between 5 and 6 times higher than control values. Despite this, by year three there was a significant increase in the mean alkalinity of the treated B and C horizon soil waters to approximately 4 mgl^{-1} as $CaCO_3$ compared with c. 1.5 mgl^{-1} as $CaCO_3$ in the control. By the second year, acidity and aluminium concentrations in the B and C horizons had declined, although amounts of nitrate remained relatively high at between 1.6 and 3.5 mgN l^{-1}.

Concentrations of sodium were largely unaffected by the treatment although magnesium concentrations increased throughout the profile, presumably originating from the magnesian limestone. Potassium, added in the fertiliser, increased significantly in the mineral horizons in the first year but two years after treatment, mean potassium concentrations were very similar in both treated and control soils. Rapid assimilation and efficient cycling in the plant-root-soil system probably made potassium unavailable for leaching once the grass sward had developed.

Annual mean sulphate concentrations were between two and three times greater than the control values for the three years following treatment (Table 2). Increases in annual mean chloride concentrations relative to the control were also observed in the O and A horizons with a less consistent response in the B & C horizons. The additional chloride probably orginated from the potassium chloride in the fertiliser.

Annual mean DOC concentrations were enhanced in the O and A horizons following treatment, but the effect was only significant in the A horizon (Table 4). The large increase in the A horizon presumably reflects the effects of mixing the surface horizons during ploughing as well as enhanced decomposition rates in the less acid conditions.
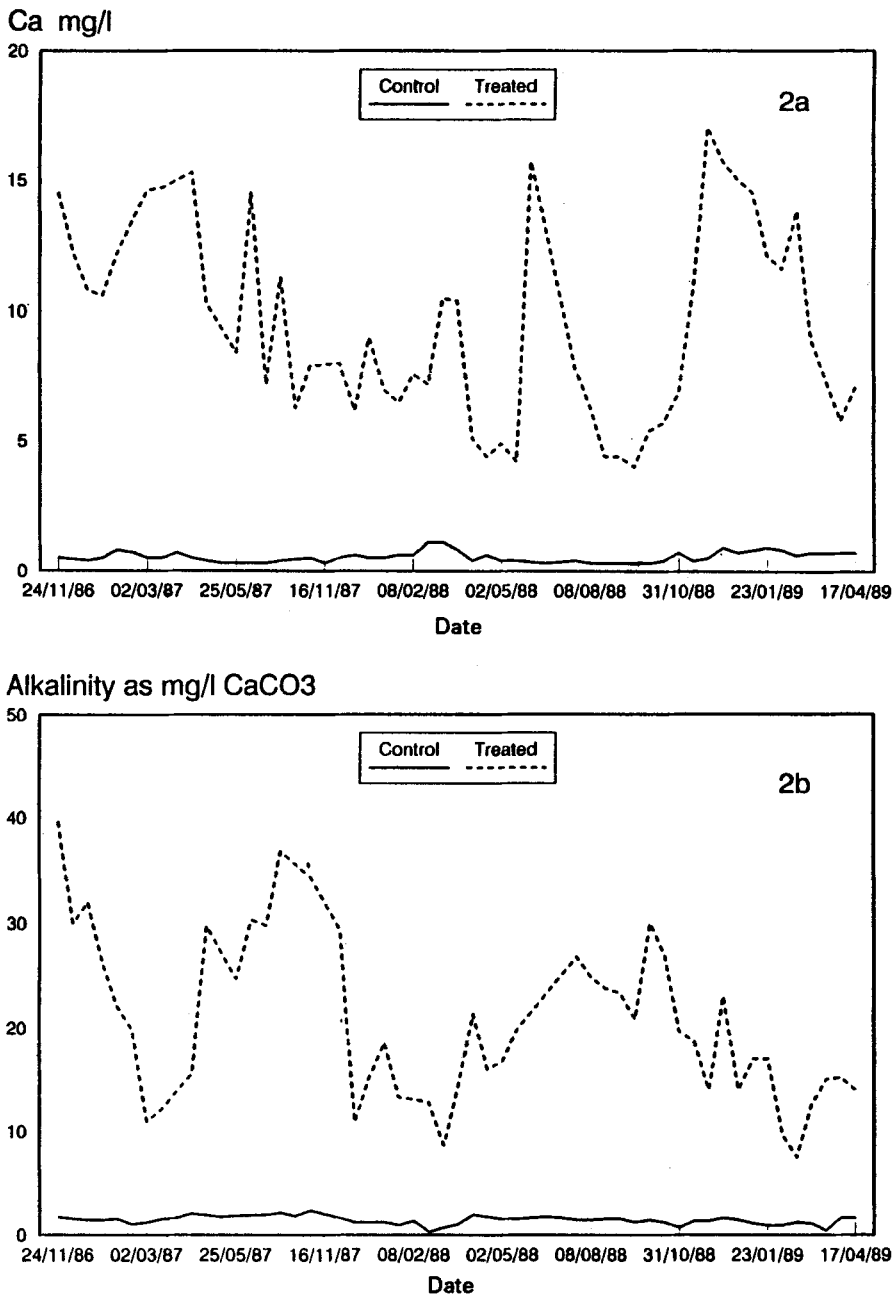
Ca mg/l

Alkalinity as mg/l CaCO3

Figure 2 Concentrations of a) calcium and b) alkalinity in A horizon soil waters from control and treated areas in catchment CI3.
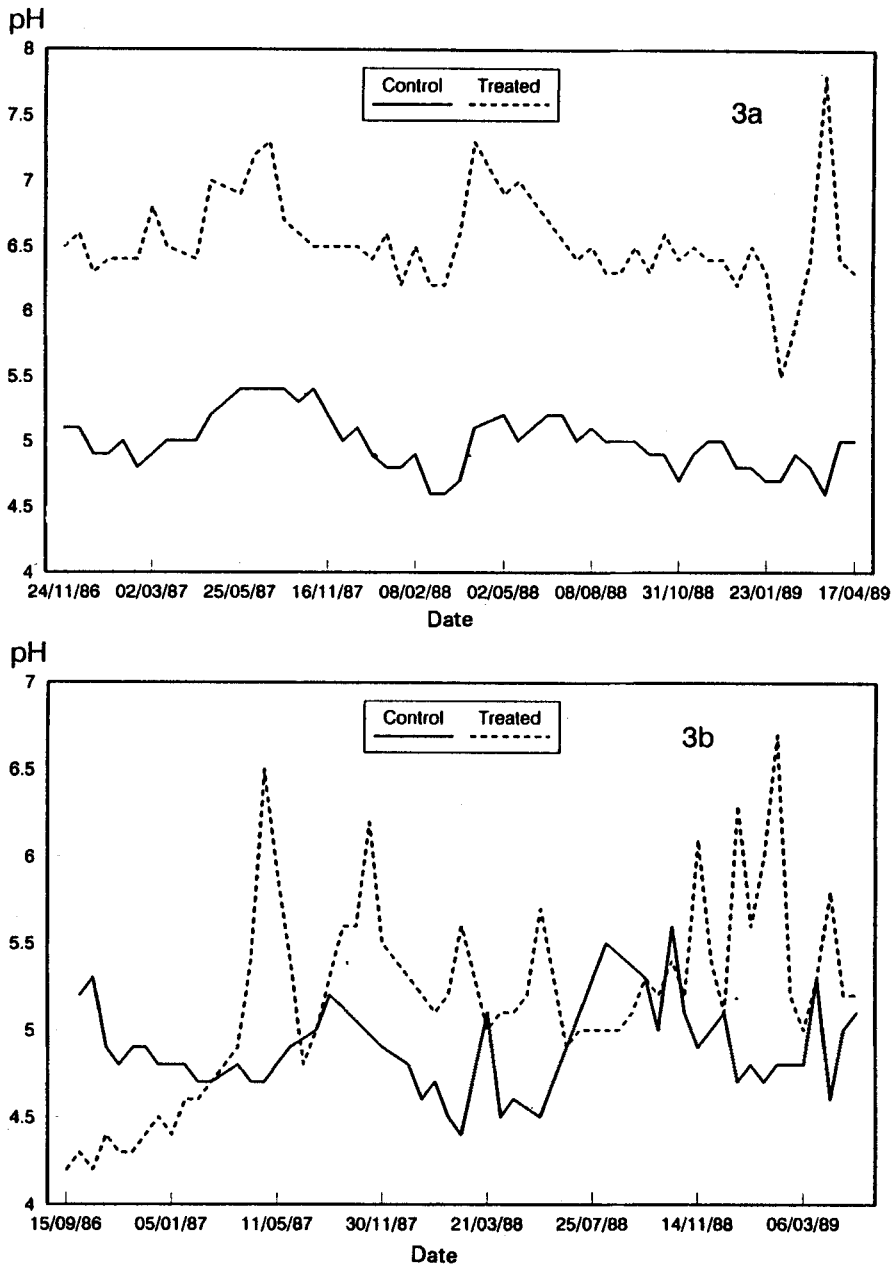
Figure 3 pH of a) A horizon and b) B horizon soil waters from control and treated areas in catchment CI3.
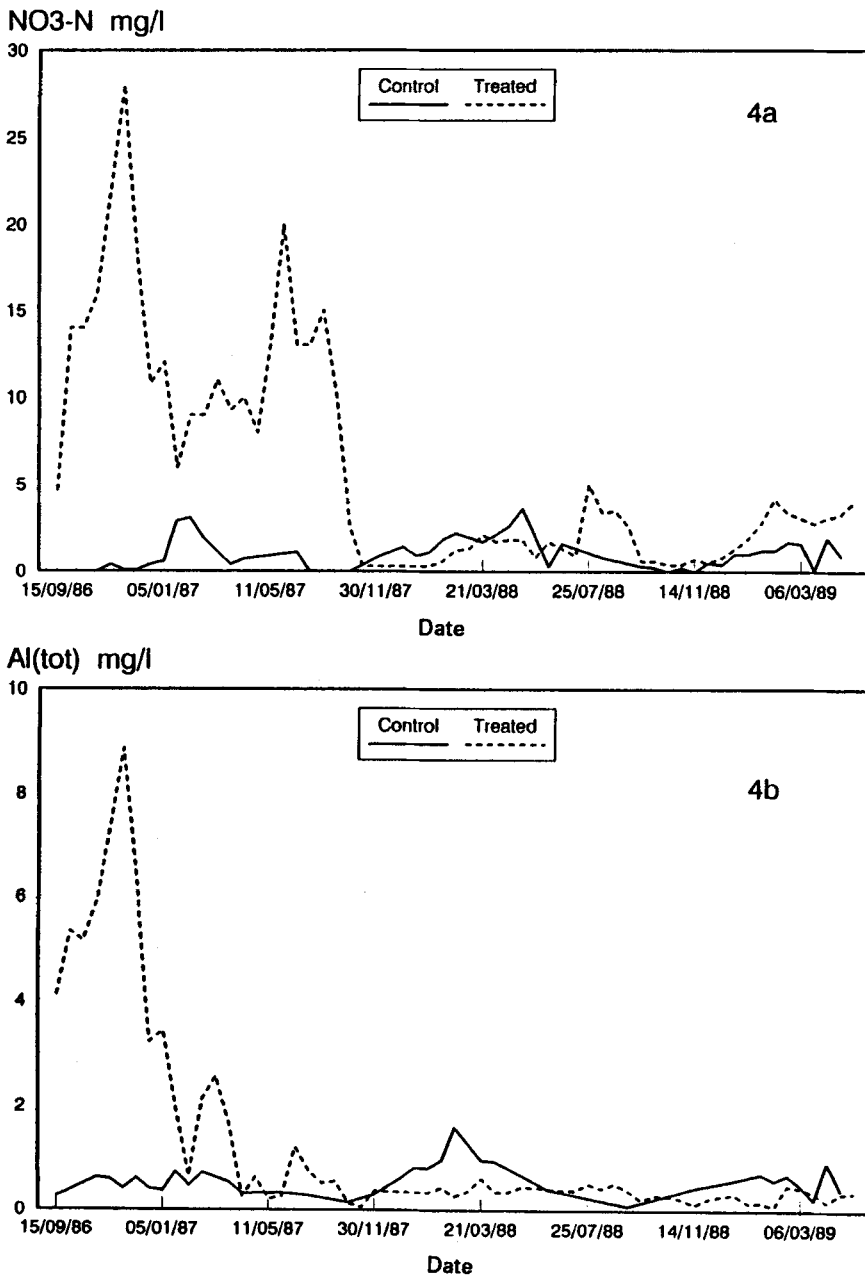
NO3-N mg/l

Al(tot) mg/l

Figure 4 Concentrations of a) nitrate-N and b) aluminium in B horizon soil waters from control and treated areas in catchment CI3.

DISCUSSION

The large increase in alkalinity in the surface O and A horizons is perhaps the most important change in soil water chemistry. It is a direct indication of the capacity of the soil solution to buffer changes in acidity in the most hydrologically active part of the soil profile. Surface ploughing was beneficial in this respect, by allowing lime to penetrate into the mineral soil. Four years after treatment, exchangeable calcium and magnesium were still much enhanced within the O and A horizons compared with the control (Table 1). Calcium (and magnesium) lost from these exchange sites by ion exchange with internally and externally generated protons will be replenished by lime dissolution. Once this lime has become exhausted or deactivated, the effectiveness of the treatment will then be mainly determined by the amounts of calcium and magnesium remaining on the exchange sites.

Liming and cultivation can increase the net mineralisation of soil organic nitrogen (Nyborg and Hoyt, 1978; Nyborg et al., 1988), resulting in elevated concentrations of inorganic nitrogen. In the treated soil, physical disturbance coupled with an increase in the amount of available ammonium and a decrease in acidity probably stimulated nitrification in the surface organic-rich horizons. The fertiliser also supplied additional ammonium and nutrients, such as phosphorus, providing a further stimulus to microbial activity (Haynes and Swift, 1988). Whilst nitrogen mineralisation and nitrification was probably most active in the surface organic-rich soil layers, nitrification may also have occurred lower in the profile (Federer, 1983). Presumably nitrate production in the first year after treatment was in excess of plant requirements, so that excess nitrate was leached to the lower soil horizons below the rooting zone. In the improved area, mineralisation and nitrification were probably active in advance of a demand from the newly sown grass, resulting in nitrate leaching to the lower soils. During subsequent years nitrate concentrations decreased in the soils, probably reflecting a decline in nitrogen mineralisation and nitrification rates. Nyborg and Hoyt (1978) have indicated that the effects of liming as a stimulus to nitrogen mineralisation are relatively short-lived and the developing sward will have provided an increasing sink for nitrogen.

Net mineralisation of soil organic nitrogen may also be stimulated following climatic perturbations such as drought followed by warm, wet weather (Birch, 1960; Sparling and Ross, 1988). This response was observed in the control plot, when the rainfall event at the end of June 1988, coupled with wet, warm conditions during the following two months, stimulated mineralisation and nitrification in the O horizon. The combination of nitrate leaching and microbial activity in these soils probably led to the accumulation of nitrate in the lowest horizons where plant uptake was negligible or absent. This climatic effect on nitrogen turnover will have been additive to and inseparable from the response to fertilisation in the treated soils.

Nitrogen transformations affect the acid-base relationships of the soil solution (Helyar, 1976; Reuss and Johnson, 1986). Nitrification of ammonium followed by nitrate leaching results in net acidification, releasing protons which can then react with the solid phases in the soil. In these soils, which contain a large pool of aluminium residing on exchange sites (Table 1) or as poorly ordered oxides and hydroxides, this will result in aluminium mobilisation by a combination of ion exchange and weathering (Reynolds et al., 1988; Adams et al., 1990).

In the surface O and A horizons of the limed soil, dissolution of calcium carbonate prevented soil water acidification associated with increased nitrification and nitrate leaching. Lower in the profile, in the absence of free calcium carbonate, soil waters

were acidified and aluminium was released, presumably by cation exchange. Samples collected four years after treatment showed that the B horizon of the treated soils contained significant quantities of exchangeable aluminium (Table 1). Soil water calcium concentrations also increased in the lower mineral horizons due to leaching from the upper soil. This was reflected in the sevenfold increase in exchangeable calcium (to 0.7 meq 100 g^{-1}) in the B horizon.

Sulphate may have been added as an impurity in the phosphate fertiliser and oxidation of organic sulphur compounds following cultivation may have been a further source of sulphate (Bache, 1984). Liming and phosphate fertilization may have provided a further stimulus to sulphur mineralisation (Jackson, 1967; Haynes and Swift, 1988). The lime itself probably did not contain significant amounts of sulphur since neither slaked nor burnt lime were used. Following the increase in pH with liming, sulphate may have been desorbed from variable charge surfaces associated with some clay minerals and soil organic matter (Korentajer *et al.*, 1983). Phosphate can also desorb sulphate from exchange surfaces (Sollins *et al.*, 1988).

Effects on stream water chemistry

Despite large chemical changes in the soil solution following liming and cultivation, Jenkins *et al.* (1991) reported that this treatment had little effect on stream water chemistry. The weighted average pH before and after treatment was very similar (Table 5), although small increases in calcium and aluminium concentrations were observed. The increase in calcium, in particular, cannot be ascribed to liming as similar increases were observed in an unlimed control catchment (CI6, Figure 1). It seems likely that the dry summers of 1988 and 1989 caused changes in the hydrological regime of the catchments which affected streamwater chemistry (Jenkins *et al.*, 1991).

Table 5 Flow weighted mean streamwater pH, calcium and aluminium concentrations for the treated catchment (CI3) and an untreated control catchment (CI6) at Llyn Brianne (after Jenkins *et al.*, 1991).

		pH	*Ca mgl^{-1}*	*Al mgl^{-1}*
Treated (CI3)	Pre-liming	5.2	0.91	0.14
	Post-liming	5.2	1.15	0.16
Control (CI6)	Pre-liming	5.2	0.97	0.13
	Post-liming	5.2	1.08	0.17

Sampling period: June 1985 to December 1989.

Given the location of the treated area within the catchment, the lack of a stream chemical response is not unsurprising. The treated area was mainly selected on agricultural criteria as being the part of the catchment most likely to provide an acceptable increase in productivity for the farmer following land improvement. The treatment was applied to uniform slopes, with well drained podzolic soils, which probably contribute relatively little storm runoff to the stream compared with the

peaty hydrological source areas at the head of the catchment. The treated slopes may contribute throughflow water in the later stages of storms, and probably contribute to baseflow. The results show that it may not always be possible to combine the objectives of increased agricultural productivity with those for improved water quality by selective improvement of acidic moorland catchments.

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