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Post-1970 water-chemistry changes and palaeolimnology of several acidified upland lakes in the U.K.

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Responses of four lakes to post-1970 changes in acid deposition, afforestation and liming are examined by using water quality measurements and palaeolimnological analysis. pH and non-marine sulphate concentrations at an undisturbed site approximately parallel trends in precipitation and indicate that lake water quality has improved since the late-1970s as atmospheric S emissions have declined. Carbonaceous particle contamination of the lake also declines in this period but diatom analysis shows that the ecological response to these changes are as yet small. However, at a similar but recently afforested site, major changes in sedimentary diatoms have occurred and we argue that fertilizer leaching is the cause. At the two limed sites the diatom response is proportional to liming intensity but at neither site has the pre-acidification diatom flora been re-established.

Introduction

Many upland soft-water lakes in the U.K. are now acidified by atmospheric pollution (Battarbee *et al.* 1988*a*). Recent acidification of sensitive sites typically began in the mid-19th century as industrialization and consequent sulphur oxide (SO_x) and nitrogen oxide (NO_x) emissions increased. Since the early 1970s, however, U.K. atmospheric sulphur emission has declined by about 30% (Barrett *et al.* 1987) and has led to reduced acidity in Scottish lakes (Battarbee *et al.* 1988*b*). Nevertheless, any improvement at sites remote from emission sources will be small or unsustained until emissions are further reduced (Cosby *et al.* 1986). Where rapid recovery of lakes is desired, liming has been initiated (see, for example, Underwood *et al.* (1987)) but, despite reducing acidity, further ecosystem disturbance can result (Hultberg & Andersson 1982). Other catchment management changes indirectly influence acidified lakes and afforestation methods can both exacerbate water acidification (Harriman & Morrison 1982) and increase nutrient supply (Gibson 1976).

Here, we examine responses of four acidified U.K. lakes, three in southwest Scotland and one in Mid-Wales, to contrasting post-1970 external changes. The Round Loch of Glenhead (RLGH) is located in an undisturbed peatland catchment where only sulphur deposition has changed significantly in the past two decades. At nearby Loch Grannoch an additional change has been extensive catchment afforestation in the 1960s and 1970s. Palaeolimnological techniques and water quality measurements are used to assess responses of both sites to recent changes in precipitation quality and land-use. At the former site, carbonaceous-particle analysis of sediment was used to infer changes in atmospheric contamination. Loch Fleet and Llyn Hir (Mid-Wales) were treated with 362 tonnes and less than 5 tonnes of limestone in 1986 and 1985, respectively (Brown *et al.* 1988; Underwood *et al.* 1987); the ecological response to liming is assessed by diatom analysis. A further 83 tonnes of limestone were applied to the Loch Fleet catchment in 1987.

Study procedure

Short sediment cores were collected from each of the four lakes between 1986 and 1988; sampling procedures follow Stevenson *et al.* (1987). Cores were dated by comparison with previous ^{210}Pb-dated cores from each site (Fritz *et al.* 1986; Flower *et al.* 1987; Battarbee *et al.* 1988*a*; Anderson *et al.* 1986), either by direct correlation of sediment accumulation rates or at the afforested sites where rates vary, by biostratigraphic correlation. Diatom analysis (Battarbee 1986) was done on all four cores and diatom data are summarized into pH preference groups. Historical pH values and time-tracks of floristic change were produced by numerical analysis by using mainly canonical correspondence analysis (CCA) (ter Braak 1986). Carbonaceous particle analysis of the RLGH core followed Rose (1989). Water-chemistry determinations used standard methods (Harriman *et al.* 1987). Values for pH and non-marine sulphate concentration in precipitation (at Eskdalemuir, 80 km east of the Scottish sites) were supplied by Dr J. G. Irwin.

Table 1. Annual precipitation-weighted mean pH and non-marine sulphate concentrations in precipitation for Eskdalemuir 1973–1987, annual mean of measured pH values and non-marine sulphate concentrations for the Round Loch of Glenhead (unafforested) and Loch Grannoch (afforested), where $n = 5$–12

(Water pH values calculated from sedimentary diatoms by using multiple regression (MR) (Flower 1986) and weighted averaging (WA) (Birks *et al.*, this symposium) methods. Sulphate concentrations (μeq l^{-1}) are in parentheses.)

		Round Loch of Glenhead			Loch Grannoch		
			pH reconstructed			pH reconstructed	
year	pH precipitation	pH measured	MR	WA	pH measured	MR	WA
1988	4.6 (32)	4.92 (66)	—	—	4.73 (92)	4.7	4.66
1987	4.7 (30)	4.95 (68)	—	—	4.84 (97)	—	—
1986	4.7 (33)	4.78 (80)	—	—	4.59 (122)	—	—
1985	4.7 (32)	4.87 (104)	—	—	4.67 (128)	—	—
1984	4.7 (33)	4.77 (95)	4.7	4.73	4.71 (139)	4.6	4.63
1983	4.7 (34)	—	—	—	—	—	—
1982	4.6 (35)	4.70 (—)	—	—	4.47 (143)	—	—
1981	4.4 (43)	—	—	—	4.78 (149)	—	—
1980	4.2 (53)	—	—	—	—	—	—
1979	4.4 (48)	4.69 (111)	—	—	4.64 (152)	—	—
1978	4.5 (54)	4.65 (99)	—	—	4.60 (133)	4.7	4.72
1977	4.4 (—)	—	—	—	—	—	—
1976	4.1 (—)[a]	—	4.7	4.75	—	—	—
1975	4.3 (49)	—	—	—	—	—	—
1974	4.4 (41)	—	—	—	—	5.3	5.28
1973	4.4 (52)	—	—	—	—	—	—
1972	—	—	—	—	—	—	—
1971	—	—	4.8	4.76	—	—	—

[a] Only pH measured in this year and this value is unverified.

Atmospheric deposition

Round Loch of Glenhead

Annual mean weighted pH and non-marine sulphate concentration in precipitation and in lake water at RLGH are given in table 1; pH in precipitation and lake water have both increased by between 0.2 and 0.3 units since the 1970s and sulphate has decreased by 40% and 33%, respectively. Note, the concentration of sulphate in precipitation is about half of that in lake water.

The diatom pH preference diagram (figure 1*a*) constructed from a 1988 core shows a strong shift to acidophilous and acidobiontic forms beginning between 9 and 7 cm depth as the lake acidified. Diatom changes in the post-1970's core section (top 1.5 cm) are small, acidobiontic

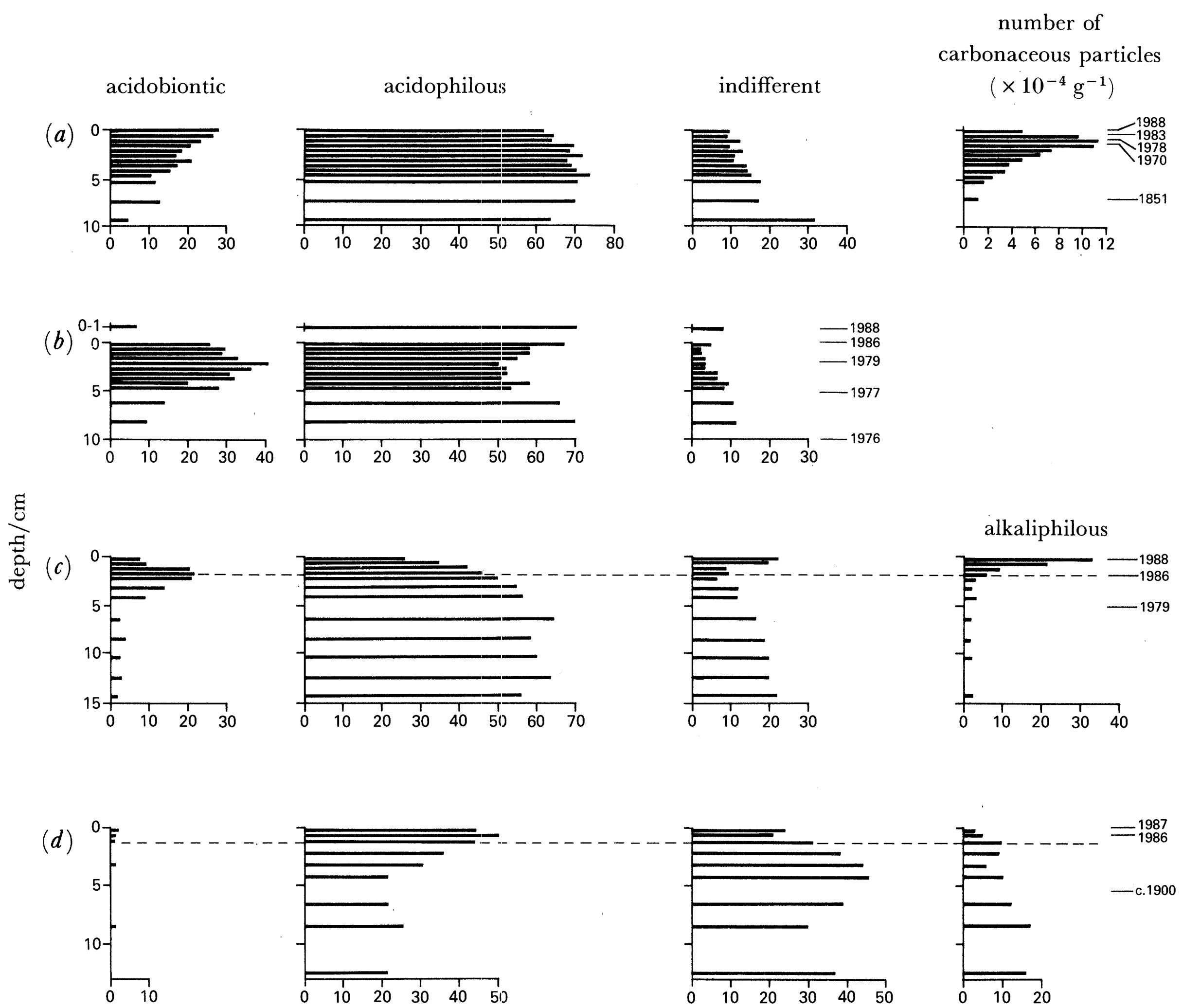

FIGURE 1. Frequency profiles of diatom pH preference groups in dated short cores from four acidified U.K. lakes. Broken lines on the latter two diagrams indicate time of liming. Note that group frequencies in a 1988 surface sediment sample (0.0–1.0 cm) are added to the top of the Loch Grannoch 1986 core diagram. The carbonaceous particle profile for the Round Loch of Glenhead core is shown upper right; (*a*) Round Loch of Glenhead 1988, (*b*) Loch Grannoch 1986 and 1988, (*c*) Loch Fleet 1988, (*d*) Llyn Hir 1987.

and indifferent (= circumneutral); diatoms slightly increase in abundance as acidophilous taxa decline. The diatom-inferred pH values of 4.7–4.8 for the period are marginally lower than corresponding measured values (table 1).

The carbonaceous particle profile for RLGH (figure 1*a*) shows low concentrations (less than $2 \times 10^4\ g^{-1}$) in sediment below 5 cm depth (pre-1910). The concentration increases strongly to peak values between 1 and 2 cm depth (1960's period) before declining in the top 1 cm (post late-1970s).

Afforestation

Loch Grannoch

Precipitation data for Loch Grannoch are as for RLGH and measured pH and non-marine sulphate concentrations are shown in table 1. Annual mean pH of lake water has increased by about 0.2 pH units and sulphate concentration has declined by about 30% since 1978.

A core collected in 1986 together with a 1988 surface sediment sample were analysed for diatoms. The combined diatom pH preference diagram (figure 1*b*) shows declining frequencies of circumneutral taxa in the mid-1970s with acidobiontic forms peaking *ca.* 1979. In the 1980s period, acidophilous taxa strongly increase as acidobiontic taxa decline. The 1988 sample contained 70% *Asterionella ralfsii*, a diatom virtually unrecorded in the lake previously. However, following a 0.5 pH unit decline in the mid-1970s, diatom-inferred pH values show no significant change in the past decade and accord with measured pH (table 1).

Limed lakes

Loch Fleet and Llyn Hir

The Loch Fleet diatom diagram (figure 1*c*) shows a rapid rise in acidobiontic forms above 5 cm depth (post late-1970s) as acidophilous taxa decline. In the top 1.5 cm, which includes post-liming sediment, both acidobiontic and acidophilous diatom frequencies rapidly decline as circumneutral and alkaliphilous taxa increase. Some downward mixing of the post-liming flora has probably occurred as alkaliphilous taxa (mainly *Synedra acus*) begin to increase in pre-liming sediment, a period when these taxa were not recorded in the lake (N. G. Cameron, unpublished results).

At the initially less acid Llyn Hir, acidophilous taxa increase from 5 cm (*ca.* 1900) to 0.5 cm depth (mid-1980s) (figure 1*d*). Only the top level contains post-liming sediment and records a minor increase in circumneutral taxa (mainly *Achnanthes minutissima*) as acidophilous taxa decline.

Numerical analysis

For diatom assemblages in each core sample, CCA axis 1 and 2 scores are plotted as time-tracks of floristic change for each lake (figure 2). Time-tracks are constrained by the British calibrational data-set of modern surface-sediment diatoms and water chemistry (Birks *et al.*, this symposium). CCA axis 1 is strongly correlated with pH (figure 2, inset) whereas the environmental gradients of axis 2 are unclear. The RLGH time-track trends across axis 1 reflecting a strong floristic response to acidification since *ca.* 1850 A.D. The analysis indicates several small pH reversals, the most recent of which concerns the top sample, representing 1980–1988. The Loch Grannoch time-track follows a similar trend but, being a core with a

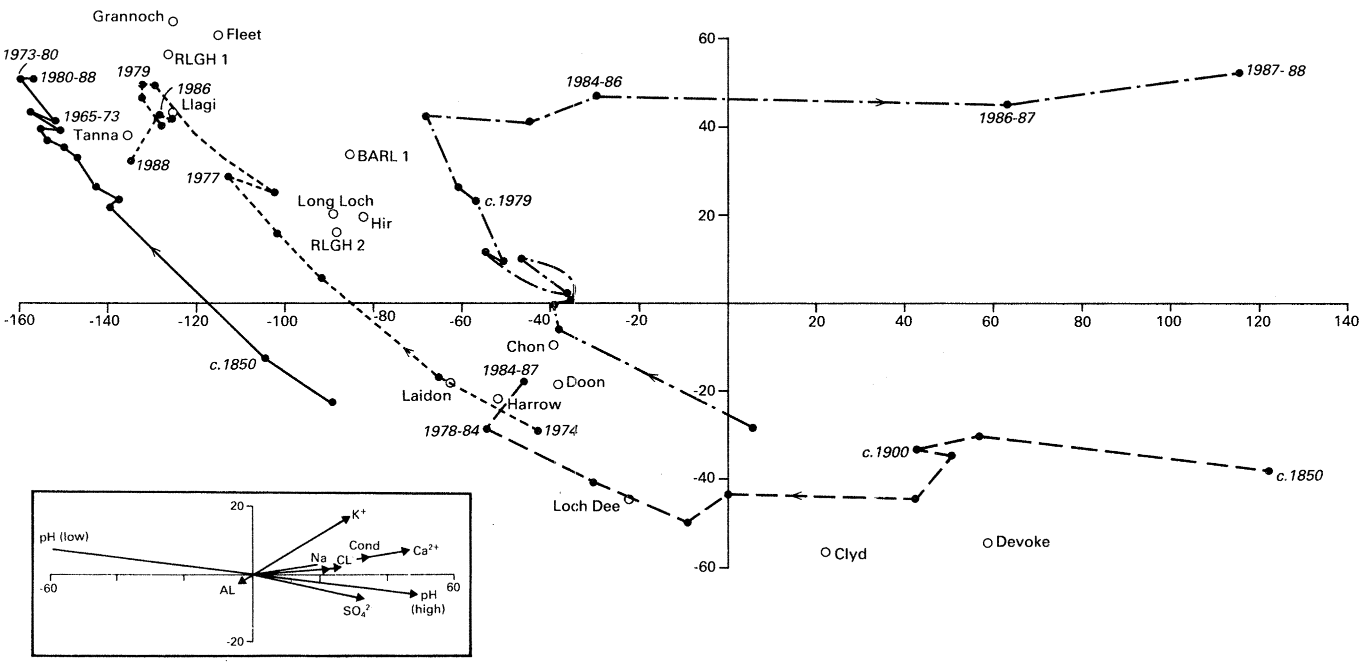

FIGURE 2. Canonical correspondence analysis (CCA) of diatom assemblages in the Round Loch of Glenhead, Loch Grannoch, Loch Fleet and Llyn Hir cores. Time-tracks of floristic change are constructed by using CCA axis 1 and 2 sample scores and are constrained by modern U.K. chemistry (see inset) and diatom samples (○), which approximately defines axis 1 as the pH axis (see text). Note, RLGH axis 1 scores are offset by −30 to improve diagram clarity. Time-tracks for the Loch Grannoch and Loch Fleet cores are constructed by using several lower levels in addition to those indicated in Figure 1; (----), Loch Grannoch; (–––), Llyn Hir; (—·—) Loch Fleet; (——), Round Loch of Glenhead.

much faster accumulation rate, it spans little more than a decade. There is a single point reversal *ca.* 1977 followed by a clear change in trend direction in 1979 as samples begin tracking down axis 2. Loch Fleet also trends across axis 1 as the lake acidified but circumneutral and alkaliphilous diatoms in the early 1980s sediment cause sample scores to reverse on axis 1, indicating a marked increase in lake pH. The reversal apparently occurs several years before liming and probably reflects down-mixing of circumneutral and alkaliphilous diatoms in the sediment. The Loch Hir time-track shows a clear acidification response from *ca.* 1850 A.D. but here the environmental variables associated with axis 2 have less influence. Although the most recent sample (1984–1987) includes the liming period, the score shows only a minor reverse on axis 1, the floristic response to liming being much less marked than in Loch Fleet.

DISCUSSION

Water-chemistry results for the RLGH clearly demonstrate that the lake has responded to post-1970 changes in precipitation chemistry. Both measured acidity and sulphate concentrations have significantly declined in lake water, and during the summer of 1988 the pH exceeded 5 for the first time since measurements began. The higher annual mean pH values recorded in 1986–1988, compared with 1978–1979, reflect higher winter pH values during the most recent period. This amelioration of pH in the winter, rather than in the diatom growing season, could partially explain the small diatom response to decreased mean acidity.

However, the diatom profiles and CCA time-tracks show that the increasing acidity trend has ceased at RLGH, confirming earlier results (Battarbee *et al.* 1988*b*). Furthermore, the carbonaceous particle record provides strong stratigraphic evidence that contamination by atmospheric particulate pollution has declined sharply in the last decade.

Although there is a similar decline in relative values, non-marine sulphate concentrations in Loch Grannoch are consistently higher, pH improvement is less marked and measurements show considerably more within-year variation. Such differences are reconcilable with known forest effects on atmospheric pollutant transfer to runoff water (Harriman & Morrison 1982; Unsworth 1984). However, unlike the RLGH, there is a major change in the diatoms at this site, beginning in the late-1970s and culminating in 1988 with a mass occurrence of *A. ralfsii*, an acidophilous diatom indicative of peatland disturbance and nutrient enrichment (Liehu *et al.* 1986). As acid deposition changes are similar to those at the RLGH it is suggested that the recent floristic changes at Loch Grannoch are an indirect result of forestry management. Phosphorus and potassium fertilizers were applied to the Loch Grannoch catchment in 1973–1985, most significantly in 1985 when 450 kg P ha^{-1}† were applied to 250 ha around the main inflow (A. Burns, personal communication). Nutrient chemistry of the lake water was not then monitored but measurements in 1988 show relatively high phosphorus concentrations, over 12 μg soluble reactive phosphate (SRP) l^{-1} in the winter months (A. Smith, personal communication). As fertilizer application to acid soils can cause significant SRP increases in surface water (Harriman 1978) it is likely that leached forest fertilizers have had a major effect on the diatom flora of this lake, despite little change in lake water pH.

Diatom changes and resulting CCA axis 1 scores clearly reflect the difference between intervention impacts at the two limed sites. The Loch Fleet catchment was limed disproportionately more heavily than was Llyn Hir and resulted in lake pH values much higher than in the past (cf. Anderson *et al.* 1986). The lake diatom flora is now dominated by taxa that were previously rare or absent. Liming of Llyn Hir was restricted to the open water and has resulted in the re-emergence of several diatoms common in the pre-acidification flora. However, a *Cyclotella* plankton has not been re-established at either limed site. Acidity mitigation measures are therefore only partially effective as pre-acidification diatom floras have not been restored. Despite claims that these lakes have now recovered and can support game fish, the structure of the ecosystem remains perturbed.

All four acidified lakes have responded to post-1970 external changes, but as yet there is no evidence of a strong positive ecological response to reduced sulphur emissions. Significant improvements in annual mean pH and non-marine sulphate concentration in RLGH and, to a lesser extent, in afforested Loch Grannoch parallel changes in precipitation chemistry and are considerably greater than average post-1970 improvements found in acid Norwegian lakes (Henriksen *et al.* 1988). Forestry practice, notably fertilizer additions, has had a greater ecological impact at Loch Grannoch than has any recent change in precipitation chemistry. Adding large quantities of lime to the terrestrial catchment of acidified Loch Fleet caused major changes in diatom communities leading to proliferation of new species rather than to re-establishment of the pre-acidification flora.

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† 1 ha = 10^4 m^2.

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