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THE RECENT PALAEOLIMNOLOGY OF ACID LAKES IN GALLOWAY, SOUTH-WEST SCOTLAND: DIATOM ANALYSIS, pH TRENDS, AND THE RÔLE OF AFFORESTATION

R. J. FLOWER, R. W. BATTARBEE AND P. G. APPLEBY*

*Palaeoecology Research Unit, Department of Geography, University College, 26 Bedford Way, London WC1H 0AP, and *Department of Applied Mathematics and Theoretical Physics, University of Liverpool, Liverpool L69 3BX*

SUMMARY

(1) To test the hypothesis that catchment afforestation is an important cause of lake acidification in Galloway, south-west Scotland, we carried out ^{210}Pb dating and diatom analysis of sediment cores from six lakes with both unafforested and afforested catchments.

(2) Major, post-eighteenth century changes in diatom communities have occurred in all six lakes. At the unafforested sites (Round Loch of Glenhead, Loch Enoch, and Loch Valley) and the afforested site (Loch Grannoch), acidobiontic *Tabellaria quadriseptata* and *T. binalis*, have become dominant whilst those taxa indicating less acid conditions, e.g. *Anomoeoneis vitrea* and *Fragilaria virescens*, have decreased in abundance. At the afforested sites (Loch Dee and Loch Skirrow), the most significant change is loss of the diatom phytoplankton in the late nineteenth century.

(3) Recent histories of pH change reconstructed from the sediment core diatoms show that five of the six sites have been acidified by between 0·5 and 1·2 pH units within the past 140 years. The two lakes least acidified, Loch Dee and Loch Skirrow, have significant portions of their catchments in non-granitic areas.

(4) At least within the Loch Doon granite area the degree of lake acidification seems to be closely linked with altitude, which is presumably linked with rainfall, but the timing of acidification appears to be controlled by catchment factors.

(5) Acidification of the afforested sites (Loch Dee and Loch Grannoch) occurred prior to forest planting.

(6) Acid deposition is the most probable cause of acidification at these sites.

INTRODUCTION

The value of diatoms preserved in sediment cores for reconstruction of changes in lake water pH was first recognized by Nygaard (1956) and his approach, based on the classification of diatom species by pH-occurrence of Hustedt (1937–39), has since been developed by Meriläinen (1967), Renberg & Hellberg (1982), Charles (1985) and Davis & Anderson (1985). The diatom record can often provide the only reliable history of lake acidity in remote areas where regular water quality monitoring has not been carried out (Davis *et al.* 1983). Consequently, diatom analysis of lake sediment cores from acid, soft-water lakes in several countries, notably the U.S.A. (Del Prete & Schofield 1981; Davis *et al.* 1983; Charles 1984;), Canada (Dickman & Fortescue 1984), Norway (Davis & Berge 1980; Davis *et al.* 1983), Scotland (Flower & Battarbee 1983a), Sweden (Renberg & Hellberg 1982), Finland (Tolonen & Jaakkola 1983; Simola, Kenttamines, & Sandman 1985), and West Germany (Arzet, Krause-Dellin & Steinberg 1986) has already demonstrated recent acidification of over forty soft-water lakes (Battarbee & Charles

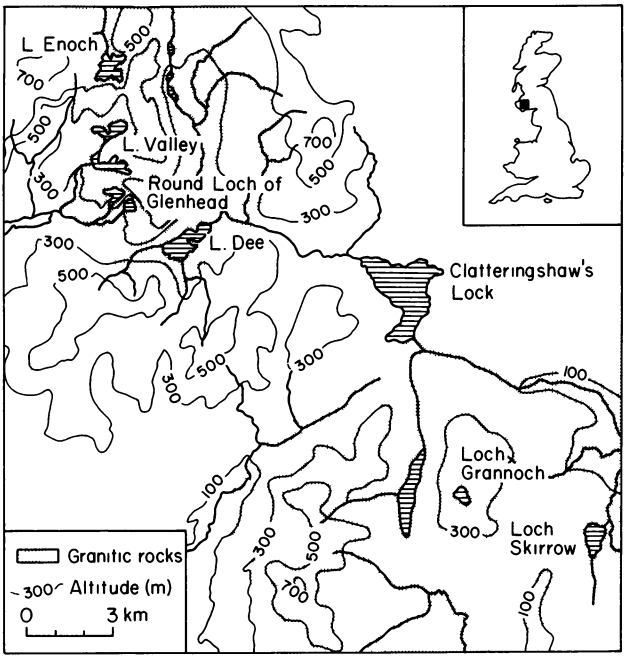

FIG. 1. The study area in Galloway, south-west Scotland, showing sample sites, the Round Loch of Glenhead, Loch Enoch, Loch Valley, Loch Dee, Loch Grannoch and Loch Skirrow, located on the Loch Doon (north) and the Cairnsmore of Fleet (south) granite plutons.

1986). The cause of this acidification is often attributed to acid precipitation, although other factors such as catchment afforestation and land-use changes have not always been specifically excluded. At several sites where recent acidification has occurred it has not been possible to separate confidently the influences of acidifying processes occurring within the catchment from those of acid precipitation (Davis *et al.* 1983).

This study is concerned with changes in lake water acidity that have occurred during the past *c.* 150 years. We attempt to evaluate the diatom evidence for lake acidification in Galloway and, to account for such acidification we particularly consider the effect of catchment afforestation. We have reconstructed the pH histories of six Galloway lakes, three with open moorland catchments and three with recently afforested catchments.

STUDY SITES

The six lake catchments selected for study are the Round Loch of Glenhead (National Grid reference NX450805), Loch Enoch (NX445851), Loch Valley (NX445817), Loch Dee (NX470790), Loch Grannoch (NX541691), and Loch Skirrow (NX605682) (Fig. 1). All the lakes lie in predominantly granitic drainage basins; the first four sites occur on the Loch Doon granite intrusion and the latter two sites occur on the Cairnsmore of Fleet intrusion. The lakes are all acid and infertile and, with the possible exception of Loch Skirrow, are thought to have lost their salmonid fishery or to have had it severely depleted during this century (Harriman *et al.* 1987).

Selected characteristics of the six drainage basins are given in Fig. 2 and Table 1. The lakes range in altitude from 130 m (Loch Skirrow) to 493 m (Loch Enoch) and with the exception of the former site have catchments with high relief and numerous steep rocky

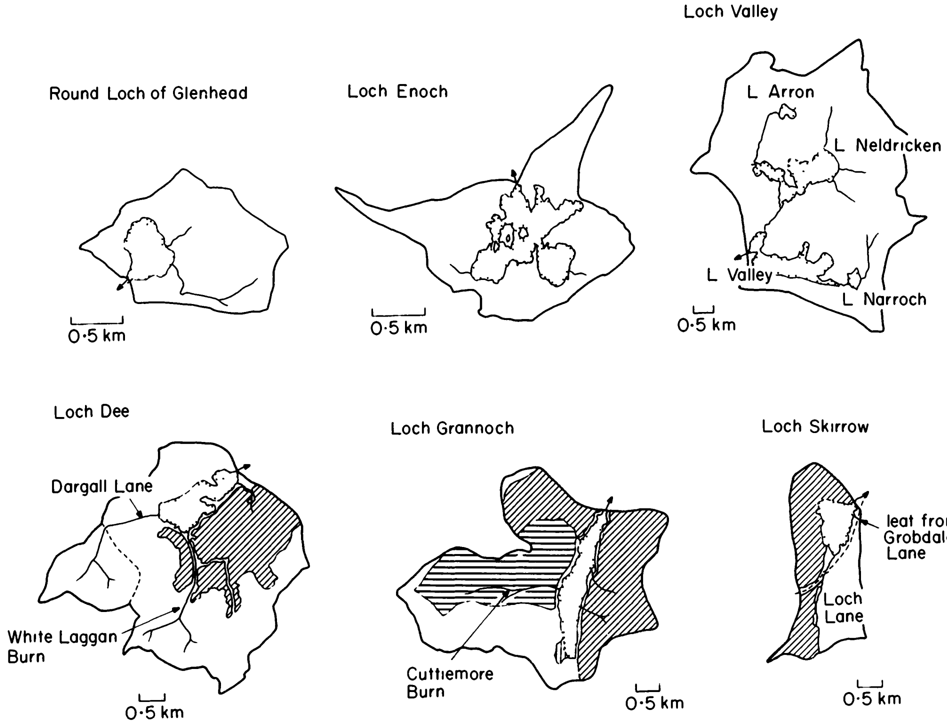

FIG. 2. Six Scottish lake catchments showing afforested areas. Diagonal hatching indicates the areas afforested in the Loch Dee catchment (1973–74), Loch Grannoch catchment (1961–62) and the Loch Skirrow catchment (1957–59). Horizontal hatching in the Loch Grannoch catchment indicates the area afforested in 1976–77. A subcatchment diverted into Loch Dee in the 1930s is indicated by a dotted line.

slopes. Two lakes, Loch Dee and Loch Grannoch, are over 100 ha in area and Loch Enoch is the deepest lake (*c.* 36 m). Loch Valley is unusual in that it is part of a linked series of lakes and receives drainage water from Loch Arron (442 m) via Loch Neldricken (349 m).

Catchment soils are essentially blanket peats developed directly on granite bedrock or on coarse drift and drainage is often poor. Catchment vegetation consists mainly of acid Molinietum heath with *Calluna vulgaris* (L.) Hull and *Myrica gale* L. locally abundant. This vegetation is partly replaced in the three afforested catchments by conifer plantations, mainly of *Picea sitchensis* (Bong.) Carriere. Afforestation of the Loch Skirrow catchment occurred in 1957–59 whilst the Loch Grannoch catchment was afforested in two phases in 1962 and 1977–78. The south-west part of the Loch Dee catchment was first planted between 1973 and 1975 and an eastern section is currently being prepared for planting. An area around the White Laggan Burn has recently been deforested and replanted with deciduous trees. The burn has been limed since 1978 to encourage fish spawning (Burns *et al.* 1984).

WATER QUALITY

The first reliable water quality measurements at the six sites were made by Harriman *et al.* (1987) between 1978 and 1982 and by Wright and Henriksen (1980) in April 1979. Further

TABLE 1. Lake and catchment characteristics for six Scottish lakes. Values in parentheses refer to measurements made by Murray & Pullar (1910); shoreline development is according to Hutchinson (1957); catchment areas exclude lake area.

	Altitude (m)	Max. depth (m)	Area (ha)	Volume ($m^3 \times 10^{-6}$)	Shoreline development	Catchment area (ha)	Ratio of catchment to lake area	Catchment afforested (%)	Date of first planting
Round Loch of Glenhead	295	13·5	12·5	0·5	1·5	95·1	7·5	—	—
Loch Enoch	493	36·0	50·1	—	2·3	185·7	3·7	—	—
Loch Valley	320	16·5	34·7	—	2·3	640·1	18·4	—	—
Loch Dee	225	14·5	100·1	3·1	1·8	1482·6	14·8	20	1973
Loch Grannoch	210	20·5	114·3	(7·4)	2·0	1287·0	11·3	70	1962
Loch Skirrow	127	10·0	50·7	(1·9)	1·3	364·1	7·2	54	1957

TABLE 2. Values of open-water pH in six Scottish lakes on various occasions since 1979. Water conductivity values ($\mu\ S\ cm^{-1}$) are shown in parentheses.

	April 1979	1978–82†	1981–82‡	May 1984	Nov. 1984	July 1985
Unafforested						
Round Loch of Glenhead	4·7 (37)	4·7	4·7 (31)	4·7 (11)	4 7 (47)	4·7 (32)
Loch Enoch	4·5 (37)	4·5	4·5 (31)	4·5 (—)	4·5 (45)	4·5 (36)
Loch Valley	4·6 (38)	4·6	4·7 (32)	4·7 (31)	4·6 (45)	4·7 (33)
Afforested						
Loch Dee§	5·2 (37)	5·0	5 3 (38)	6 7 (46)	5·5 (41)	6·6 (32)
Loch Grannoch	4·5 (49)	4·6	4·6 (40)	4·8 (—)	4·4 (62)	4·6 (46)
Loch Skirrow	5·3 (48)	5·1	—	5·5 (53)	4·7 (68)	5·9 (49)

* Wright & Henriksen (1980).
† R. Harriman (personal communication).
‡ Flower & Battarbee (1983b).
§ Limed since 1981.

pH measurements were made on eight occasions between November 1981 and November 1982 (Flower & Battarbee 1983b) and again in 1983–85 in co-operation with the Solway River Purification Board (Table 2). With the exception of Loch Dee which has been limed since 1981–82 (Burns *et al.* 1984), all the lakes had pH values below 6 at the times of sampling. The very acid (pH < 5) lakes include the three unafforested sites and Loch Grannoch; pH values for these sites are remarkably stable from year to year. In the two less acid but afforested sites, Loch Dee and Loch Skirrow, pH appears to be more variable with lower values in the winter.

Other water quality measurements made between 1979–85 are shown in Table 3. Aluminium is present in significant concentrations, particularly in the afforested sites Loch Grannoch and Loch Skirrow, indicating strongly acid runoff and possibly some effect of afforestation. Sodium and chloride are present at relatively high concentrations and are thought to be derived mainly from wind-borne sea salt (Burns *et al.* 1984). The only other common inorganic anion is sulphate and according to Wright & Henriksen (1980) it is derived principally from non-marine atmospheric sources. Bicarbonate alkalinity was very low or absent at the four most acid sites. In comparison with water quality data from the English Lake District (Carrick & Sutcliffe 1982) all six Galloway sites have low sulphate concentrations and alkalinities. Water colour is mainly attributable to dissolved humic material and shows considerable variation between the sites and between sampling dates. The least coloured water usually occurs in Loch Enoch and the most coloured in Loch Skirrow.

METHODS

Core collection

Sediment cores from the deepest point in each lake (in the south-east sub-basin for Loch Enoch) were collected using a Mackereth mini-corer (Mackereth 1969). Only cores with an undisturbed sediment–water interface were retained for analysis. Coring of Loch Dee, Loch Grannoch and Loch Skirrow was carried out in August 1980, of the Round Loch of Glenhead and Loch Valley in May 1981, and of Loch Enoch in May 1982. In the laboratory each core was extruded and sectioned at 0·5- or 1-cm intervals for

TABLE 3. Water quality measurements for six Scottish lakes made on various occasions since 1979. All concentrations are in mg l^{-1} (except $\mu g\ l^{-1}$ for Al and μequiv. l^{-1} for alkalinity); water colour is measured as light absorbance at 250 nm in 10-mm cells except cases marked ‡ in which it is measured as total dissolved organic carbon (mg l^{-1})

Unafforested												
Sites	Round Loch of Glenhead				Loch Enoch				Loch Valley			
Sampling dates	April* 1979	1981–82†	Nov. 1984	July 1985	April* 1979	1981–82†	Nov. 1984	July 1985	April* 1979	1981–82†	Nov. 1984	July 1985
Ca^{2+}	0·7	0·4	0·6	0·6	0·4	0·2	0·3	0·5	0·7	0·3	0·5	0·5
Mg^{2+}	0·6	0·3	0·6	0·5	0·5	0·2	0·5	0·5	0·6	0·2	0·6	0·5
Na^{+}	3·2	1·6	4·6	3·5	2·9	1·3	4·0	3·7	3·1	1·5	4·3	3·6
K^{+}	0·3	0·2	0·3	0·2	0·3	0·3	0·2	0·3	0·4	0·2	0·3	0·3
Al	165·0	90·0	250·0	190·0	150·0	90·0	180·0	70·0	200·0	100·0	240·0	250·0
SiO_2	—	0·5	1·6	1·5	—	0·3	1·0	0·8	—	0·3	1·4	1·3
SO_4^{2-}	5·4	2·6	3·6	4·1	4·3	2·1	2·6	3·6	5·4	1·3	4·0	4·2
Cl^{-}	5·3	4·4	10·8	8·0	5·2	3·6	10·2	3·8	5·2	4·4	11·2	7·8
Alkalinity	—	—	33·0	41·0	—	—	0·0	26·2	—	—	0·0	42·6
Water colour	2·5‡	—	0·09	1·12	1·1‡	—	0·04	0·09	2·6‡	—	0·08	0·08
Afforested												
Sites	Loch Dee				Loch Grannoch				Loch Skirrow			
Sampling dates	April* 1979	1981–82†	Nov. 1984	July 1985	April* 1979	1981–82†	Nov. 1984	July 1985	April* 1979	1981–82†	Nov. 1984	July 1985
Ca^{2+}	1·2	0·5	1·0	1·7	1·1	0·4	0·9	1·0	2·1	—	1·8	2·5
Mg^{2+}	0·8	0·3	0·7	0·7	0·7	0·3	0·7	0·6	0·9	—	1·1	0·9
Na^{+}	3·3	1·5	4·2	4·6	3·8	1·5	5·5	4·7	3·6	—	7·2	5·0
K^{+}	0·5	0·3	0·3	0·9	0·5	0·3	0·2	0·2	0·43	—	0·3	0·2
Al	95·0	70·0	200·0	200·0	310·0	130·0	350·0	501·0	220·0	—	230·0	360·0
SiO_2	—	0·3	2·6	2·3	—	0·6	3·6	2·9	—	—	2·8	0·1
SO_4^{2-}	5·6	2·7	3·7	4·2	6·7	3·0	5·3	5·8	7·3	—	7·2	5·6
Cl^{-}	5·6	5·0	10·0	6·2	6·6	3·9	11·6	8·8	8·2	—	15·2	10·0
Alkalinity	—	—	24·6	91·8	—	—	0·0	32·8	—	—	19·6	73·8
Water colour	2·5‡	—	0·11	0·24	5·5‡	—	0·17	0·18	6·5‡	—	0·22	0·27

* From Wright & Henriksen (1980).
† From Flower & Battarbee (1983b).

measurement of wet density, percentage dry weight and of organic content by loss on ignition at 550 °C (see Flower & Battarbee 1983b).

^{210}Pb dating

Selected subsamples of dry sediment from each core were analysed for ^{210}Pb according to Häsänen (1977). Reproducibility of the method was tested by triplicate analysis of the 3–4 cm sediment section from Loch Dee. A mean concentration of 25·49 pCi g^{-1} dry weight with a S.D. of $\pm$0·84 was determined. In sediment cores where the ^{210}Pb profile indicated undisturbed sediment accumulation the supported ^{210}Pb concentration was determined from the equilibrium ^{210}Pb concentration at the base of the core. In cores with irregular ^{210}Pb profiles the supported ^{210}Pb was determined from ^{226}Ra measurements (Odell 1983), and additional ^{210}Pb determinations were carried out over the disturbed sections.

Where the unsupported ^{210}Pb content indicated a ^{210}Pb flux close to estimated atmospheric flux of 0·7–1·0 pCi cm^{-2} y^{-1}, sediment chronologies were calculated using the CRS (constant rate of supply) dating model of unsupported ^{210}Pb in lake sediments (Appleby & Oldfield 1978). However, where the unsupported ^{210}Pb content indicated deviations from the atmospheric ^{210}Pb flux a best chronology was constructed based on both the CRS and CIC (constant initial concentration) dating models (Appleby & Oldfield 1978). Hence, for the Loch Dee core, chronology for the 0–7·5 cm depth section is based on the CRS model and below 7·5 cm is based on the mean of results from both CRS and CIC models. In the Loch Skirrow core the total flux of unsupported ^{210}Pb is particularly high and the entire chronology is based on the CIC model.

Diatom analysis

Sediment cores were subsampled at 0·5- or 1-cm intervals over the top 25 cm and at 2 or 5-cm intervals below this depth. Samples were cleaned in 30% hydrogen peroxide, washed by repeated centrifugation in distilled water and mounted on coverslips in Mikrops resin for examination at × 1600 magnification. Counting methods follow Battarbee (1986) and diatom concentrations were estimated by the microsphere method of Battarbee & Kneen (1982). Diatom identifications were carried out using standard floras (Hustedt 1927–66; Hustedt 1930; Cleve-Euler 1951–55; Patrick & Reimer 1966–77; Germain 1981; Foged 1954, 1972, 1977; Carter & Bailey-Watts 1981). The pH preference of individual taxa are taken from various sources including Hustedt (1937–39, 1957), Jørgensen (1948), Cleve-Euler (1951–55), Foged (1953, 1977), Cholnoky (1968), Meriläinen (1969), Renberg (1976) and van Dam *et al.* (1982).

pH reconstructions

To reconstruct pH values using diatom assemblages in the six sediment cores, two approaches have been used: Index B (Renberg & Hellberg 1982) and multiple regression of diatom pH preference groups (Charles 1985; Davis & Anderson 1985). For this study both methods have been calibrated using the relationship between surface sediment diatoms and measured mean summer pH in thirty-three Galloway lakes (Flower 1987). For Index B the linear regression equation with measured pH is:

$$\mathrm{pH} = 6{\cdot}3 - 0{\cdot}86 \log \text{Index B}$$
$$(r^2 = 0{\cdot}82,\ \text{S.E. of regression} = \pm 0{\cdot}36,\ P = <0{\cdot}001,\ n = 33)$$

where,

$$\text{Index B} = \frac{\%\ \text{circ} + 5 \times \%\ \text{acp} + 40 \times \%\ \text{acb}}{\%\ \text{circ} + 3{\cdot}5 \times \%\ \text{alk} + 108 \times \%\ \text{alkb}}$$

and acp is number of cells of acidophilous species, and appropriately acb = acidobiontic, circ = circumneutral, alk = alkaliphilous, and alkb = alkalibiontic; percentages are those of the total number of cells counted.

For multiple regression of the diatom pH preference groups with measured pH, the linear regression equation is:

$$\text{pH} = 7{\cdot}8 - 0{\cdot}035 \times \%\ \text{acp} - 0{\cdot}037 \times \%\ \text{acb} - 0{\cdot}013 \times \%\ \text{circ} - 0{\cdot}015 \times \%\ \text{alk} + 0{\cdot}100 \times \%\ \text{alkb}$$

$$(r^2 = 0{\cdot}82,\ \text{S.E. of regression} = \pm 0{\cdot}36\ P = <0{\cdot}001\ n = 33).$$

Differences between the reconstructed pH values using Index B and pH preference groups are small and both methods have the same correlation coefficients and standard errors of regression, being based on the same modern data on the occurrence of diatom species at particular pH values. The standard errors calculated for the pH reconstruction methods employed here are both $\pm 0{\cdot}36$ pH units and are similar to those calculated elsewhere (Renberg & Hellberg 1982; Charles 1985). The error associated with a particular predicted pH value will however be about twice this figure (Ryan *et al.* 1976; D. Sutcliffe, personal communication). The application of error estimates to samples not included in those used for calibration is problematic because much of the variance in the modern data is attributable to differences between sites (Davis & Anderson 1985). Changes in reconstructed pH values for a particular lake are likely to be considerably more precise than is indicated by the error estimate inferred from the modern data. This is because at any one site the physical factors such as lake morphometry and substratum composition can usually be regarded as constant over the recent past. In view of these considerations we have omitted error estimates from our inferred pH values.

RESULTS

^{210}Pb dating

Sediment chronologies in the form of age-depth curves are given in Fig. 3. In the three lakes with unafforested catchments, sediment age varies linearly with depth, indicating an absence of significant change in the rate at which sediment has been deposited during the past *c.* 180 years. The CRS and CIC models give the same chronologies for these cores. In contrast, all the afforested sites have non-linear age–depth relationships caused by recent changes in the rate of sediment accumulation. The most striking of these changes is shown in the Loch Grannoch core where the sediment accumulation rate, after catchment ploughing in 1962, has increased by a factor of ten. The Loch Dee core shows a more or less uniform sediment accumulation rate in the latter part of the nineteenth century followed by a period of declining sediment accumulation during the first part of this century. There is, however, a sharp increase in sediment accumulation rate beginning in the mid-1970s when the catchment was ploughed. In the Loch Skirrow core, linearity of the age–depth relationship below 15·0 cm suggests that the sediment accumulation rate has been fairly uniform. The CIC chronology for this core indicates that the rate of sediment accumulation has increased by a factor of about three since the mid-1950s, the period when catchment ploughing was carried out.

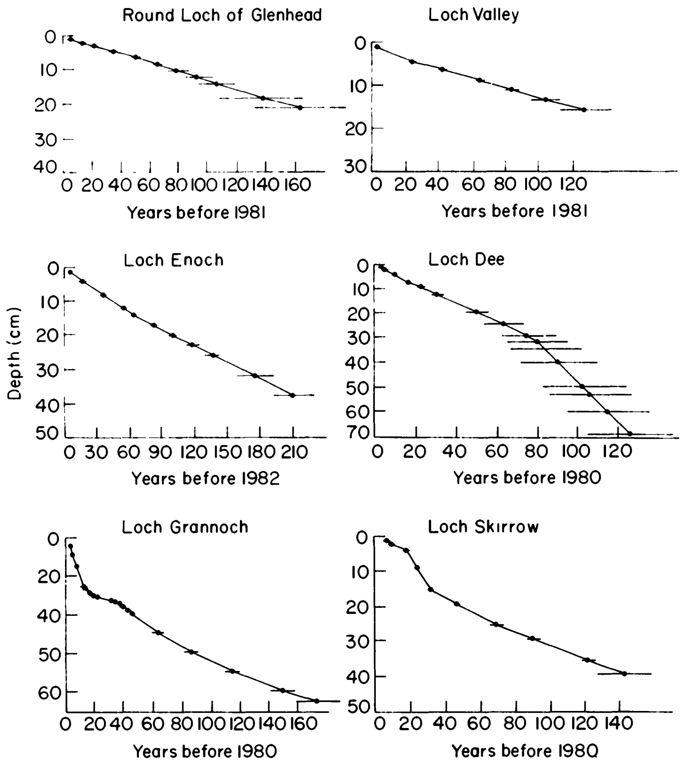

FIG 3. Sediment age versus depth curves constructed using chronologies calculated from ^{210}Pb measurements (see text) for six Scottish lakes. Error bars indicate the cumulative standard error of the sediment age based on the counting statistic alone

Percentage frequency diatom profiles

Diatom percentage frequency diagrams of selected species, together with ^{210}Pb dated levels are shown in Figs 4–9. The diatom assemblages in each core have been zoned (see dotted lines on Figs 4–9) on the eighteen most common taxa using the CONSLINK program (Gordon & Birks 1972). The diatom frequency diagrams are also summarized with regard to pH by combining the percentage counts for each taxon according to pH preference categories. Preliminary descriptions of diatoms in two cores, Round Loch of Glenhead and Loch Grannoch, have been published previously (Flower & Battarbee 1983a).

Unafforested sites

Round Loch of Glenhead (Fig. 4). The top 18 cm of this core lie within the range of ^{210}Pb dating and represent about 160 years of sediment accumulation. No chronology is available for sediment below 18 cm but extrapolation of the ^{210}Pb dates indicates that the entire core represents over 1000 years of sediment accumulation. Diatoms common in sediment below 45 cm are *Fragilaria virescens* Ralfs, *Anomoeoneis serians* v. *brachysira* (Breb) Cleve, *Eunotia veneris* (Kutz.) Muller, *Achnanthes microcephala* Kutz., *Melosira perglabara* Camburn, and a small form of planktonic *Cyclotella kützingiana* v. *planetophora* Fricke. The approximately constant percentages of these taxa indicate that

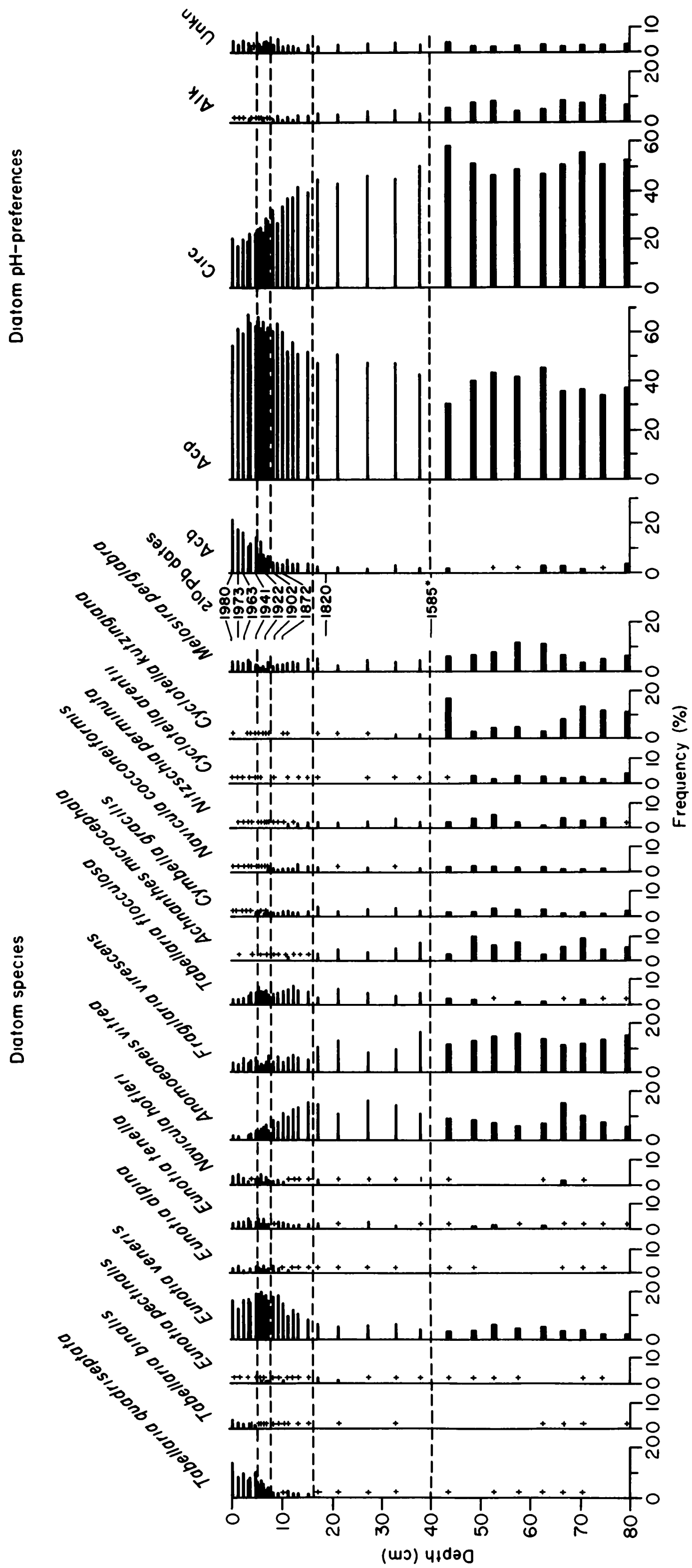

FIG. 4. Diatom percentage frequency diagram of selected species (left) and pH preference groups (right) for a sediment core from the Round Loch of Glenhead. Sediment dates are calculated from ^{210}Pb measurements; + indicates taxon present at <2%; * indicates a date estimated by extrapolation of the ^{210}Pb chronology. pH preference categories are: Acb, acidobiontic; Acp, acidophilous; Circ, circumneutral; Alk, alkaliphilous; and Unkn, unknown.

fairly stable conditions prevailed within the lake during this period. The only significant changes in diatom abundance occur with *Cyclotella arentii* Kolbe, *Melosira perglabra* and the *Cyclotella kützingiana* v. *planetophora*.

By extrapolation of the ^{210}Pb dates, the sediment of *c.* 45 cm dates to the sixteenth century and at this level several taxa began to decline, most notably *Cyclotella kutzingiana* v. *planetophora* and *Cyclotella arentii*. The percentage values of these species remain low throughout the upper section of the core. A second and more major change in the diatoms occurs at 15 cm (*c.* 1850 A.D.) as the circumneutral taxa *Anomoeoneis vitrea* (Grun.) Ross, *Fragilaria virescens* and *Achnanthes microcephala* decrease, and the acidophilous taxon *Eunotia veneris* increases in relative abundance. Also around this level the previously scarce acidobiontic species *Tabellaria quadriseptata* Knudson begins to increase in frequency, as do *Eunotia denticulata* (Breb) Rabh., *Eunotia tenella*, and *Navicula hofleri* Cholnoky *sensu* Ross & Simms 1978. Further small changes in frequency are shown in the top 5 cm (post-1940) of sediment as acidobiontic *Tabellaria binalis* (Ehr.) Grun. begins to increase but *Eunotia veneris*, *Cymbella gracilis* (Rabh.) Cleve and *Navicula cocconeiformis* Greg. decrease.

Loch Enoch (Fig. 5). The top 30 cm of this core lie within the ^{210}Pb dating range and represent the last 160 years of sediment accumulation. Diatoms common between *c.* 25 cm and the core base are *Anomoeoneis serians* v. *brachysira*, *Tabellaria flocculosa* (Roth.) Kutz., and *Frustulia rhomboides* var. *saxonica* (Rabh.) de Toni. Relative abundances of these taxa are fairly stable throughout the 25–70 cm core section but above 25 cm (*c.* 1850 A.D.) the frequencies of *Anomoeoneis serians* v. *brachysira*, together with *Tabellaria flocculosa* and *Cymbella gracilis* begin to decline sharply. This change is accompanied by increased abundance of *Eunotia veneris*, *Eunotia alpina* (Neageli) Hust. and *Peronia fibula* (Brèb. *et* Arnott) Ross. A further significant assemblage change begins at 12 cm (*c.* 1940) as *Tabellaria quadriseptata*, *Tabellaria binalis* and *Navicula hofleri* become more abundant as do, but to a lesser extent, *Eunotia bactriana* Ehr., *Eunotia trinacria* Krasske and *Asterionella ralfsii* W. Smith. Significantly, *Eunotia veneris* begins to decline in abundance at about 12 cm and returns to pre-1850 A.D. frequencies at the core top. Maximum frequency values for *Eunotia alpina*, *Peronia fibula*, *Eunotia pectinalis* v. *ventralis* (Kutz.) Rabh. and *Cymbella aequalis* W. Smith occur in the 5–20 cm section of the core.

Loch Valley (Fig. 6). The top 18 cm of this core is dated by ^{210}Pb and represents about 130 years of sediment accumulation. Below this depth or prior to *c.* 1850 A.D. there is no marked change in the diatom percentages over the remaining 52 cm of sediment. The diatom assemblage in this deeper section is consistently dominated by *Anomoeoneis serians* v. *brachysira* and *Fragilaria virescens*. A decline in the latter species, however, occurs around 35 cm depth which by extrapolation of the ^{210}Pb chronology dates approximately to the early sixteenth century. At 14 cm (*c.* 1880 A.D.) *Fragilaria virescens* again declines and is closely followed at 12 cm (*c.* 1900 A.D.) by marked decreases in *Anomoeoneis serians* v. *brachysira*, *Cymbella gracilis*, *Achnanthes recurvata* Hust., *Navicula angusta* Grun. and *Navicula cocconeiformis* at 12 cm (*c.* 1900 A.D.). These changes are coincident with increased frequencies of several acidophilous and acidobiontic taxa, *Eunotia veneris*, *Cymbella aequalis*, *Navicula heimansii* van Dam & Kooy., and *Navicula subtilissima* Cleve. Above 8 cm (post-1925) other acidobiontic taxa, *Tabellaria quadriseptata*, *Tabellaria binalis* and *Eunotia bactriana*, begin to expand, although the change is more rapid above 5 cm (*c.* 1950). In the top 5–10 cm of sediment *Cymbella aequalis*, *Navicula heimansii*, *Cymbella perpusilla* Cleve and *Tabellaria flocculosa* decrease

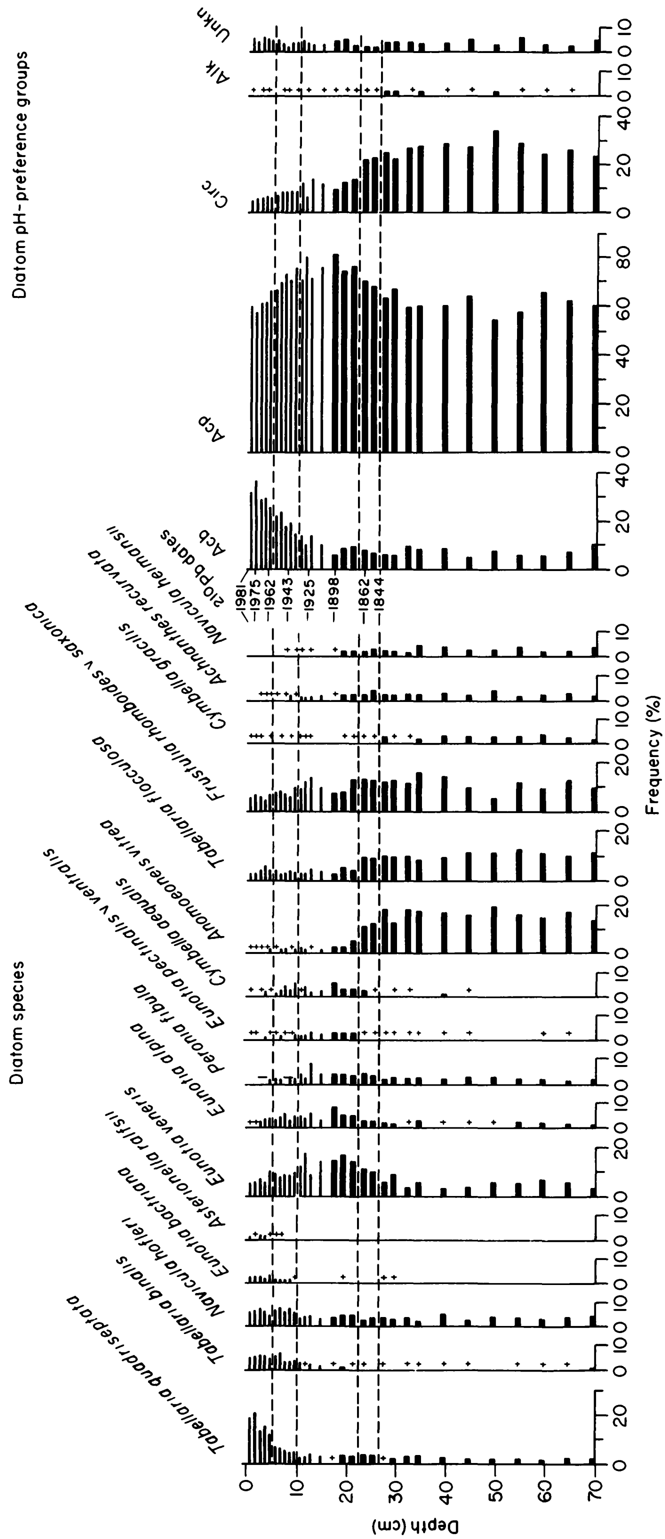

FIG. 5. Diatom percentage diagram of selected species (left) and diatom pH preference groups (right) for a sediment core from Loch Enoch sediment. For other details see the legend for Fig. 4.

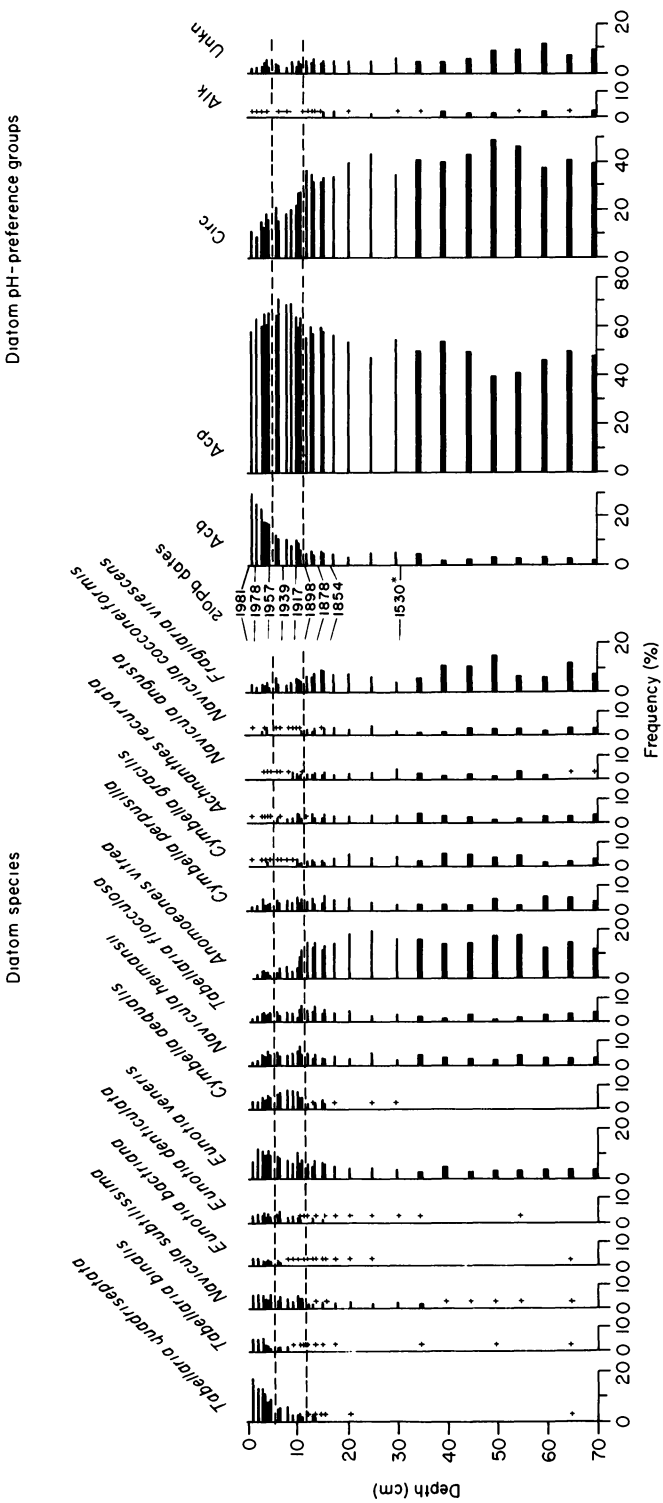

FIG. 6. Diatom percentage frequency diagram of common species (left) and pH preference groups (right) for a sediment core from Loch Valley. For other details see the legend for Fig. 4.

from maximum abundances but only in the most recent sediment section (0–0·5 cm) does *Eunotia veneris* decline.

Grouping the diatoms according to pH-preference shows that, before any major change in assemblage composition occurred, in both the Loch Enoch and Loch Valley cores the assemblages are dominated by acidophilous forms, whereas in the Round Loch of Glenhead core the circumneutral group predominates. However, in all three cores, beginning in the mid to late-nineteenth century depending on site, the acidophilous group increases in abundance whilst the circumneutral group declines. The acidophilous forms reach highest percentage abundance in the Loch Enoch core in the early twentieth century but somewhat later in the other two cores. Above this peak in all three cores the percentage of acidobiontic forms increases towards the most recent sediment whilst proportions of the acidophilous and, to a lesser extent, the circumneutral taxa decrease; the acidophilous taxa, however, remain at over 50% abundance. In the top 1 cm of the Loch Enoch and the Round Loch of Glenhead cores small increases in the acidophilous and circumneutral groups occur, respectively.

Afforested sites

Loch Dee (Fig. 7). The ^{210}Pb dating range spans the entire depth of the 70-cm core which represents about 130 years of sediment accumulation. Between 45 cm depth (*c.* 1890 A.D.) and the base of the core (*c.* 1850 A.D.) the diatom frequencies change little and three species, *Achnanthes microcephala*, *Anomoeoneis serians* v. *brachysira*, and *Cyclotella kützingiana* v. *planteophora* contribute over 60% of the total assemblage. Above 45 cm the planktonic diatoms *Cyclotella kützingiana* v. *planetophora* and the less common *Asterionella formosa* decline and by 30 cm (*c.* 1915) they occur at a frequency of < 5%. At about this level *Achnanthes microcephala* also begins to decline as the frequencies of several other species, notably *Anomoeoneis serians* v. *brachysira*, *Tabellaria flocculosa*, *Eunotia veneris*, and *Peronia fibula* begin to increase. In the top few cm (post-1970) of sediment further increases in acidophilous *Eunotia veneris* and *Tabellaria flocculosa* occur and *Eunotia alpina*, *Eunotia exigua* (Brèb.) Rabh., and *Achnanthes marginulata* Grun. reach maximum abundances in the top 0–1 cm section. Species that achieve maximum frequencies within the 2·5–5 cm section are, in order of occurrence, *Synedra rumpens* Kutz., *Navicula angusta*, *Navicula cocconeiformis*, *Achnanthes umara* Carter, and *Eunotia pectinalis* v. *minor*.

Loch Grannoch (Fig. 8). The entire 80 cm long core lies within the ^{210}Pb dating range and represents *c.* 140 years of sediment accumulation. The accumulation rate was particularly high over the top 30 cm of the core which only spans about twenty years and reflects pre-afforestation catchment ploughing beginning in 1961 (Battarbee *et al.* 1985b). The diatom assemblage in the core section below 45 cm (pre-1930) is dominated by *Tabellaria flocculosa* and *Anomoeoneis serians* v. *brachysira*. Above 45 cm a more marked floristic change occurs beginning with an increase in *Eunotia veneris* and declines in the abundance of several species, notably *Anomoeoneis serians* v. *brachysira*, *Fragilaria virescens*, *Achnanthes microcephala*, and *Cymbella gracilis*. At 35 cm depth (*c.* 1945) the acidobiontic taxa *Tabellaria quadriseptata*, *Tabellaria binalis*, and *Navicula hofleri* rapidly begin to assume importance in the flora as do several acidophilous *Eunotia* spp. At 30 cm (*c.* 1961), however, the frequencies of several of these species, particularly the *Tabellaria* taxa, rapidly diminish corresponding to the time of accelerating sediment accumulation rate. In the top 8 cm of sediment the frequencies of acidobiontic *Tabellaria* taxa again

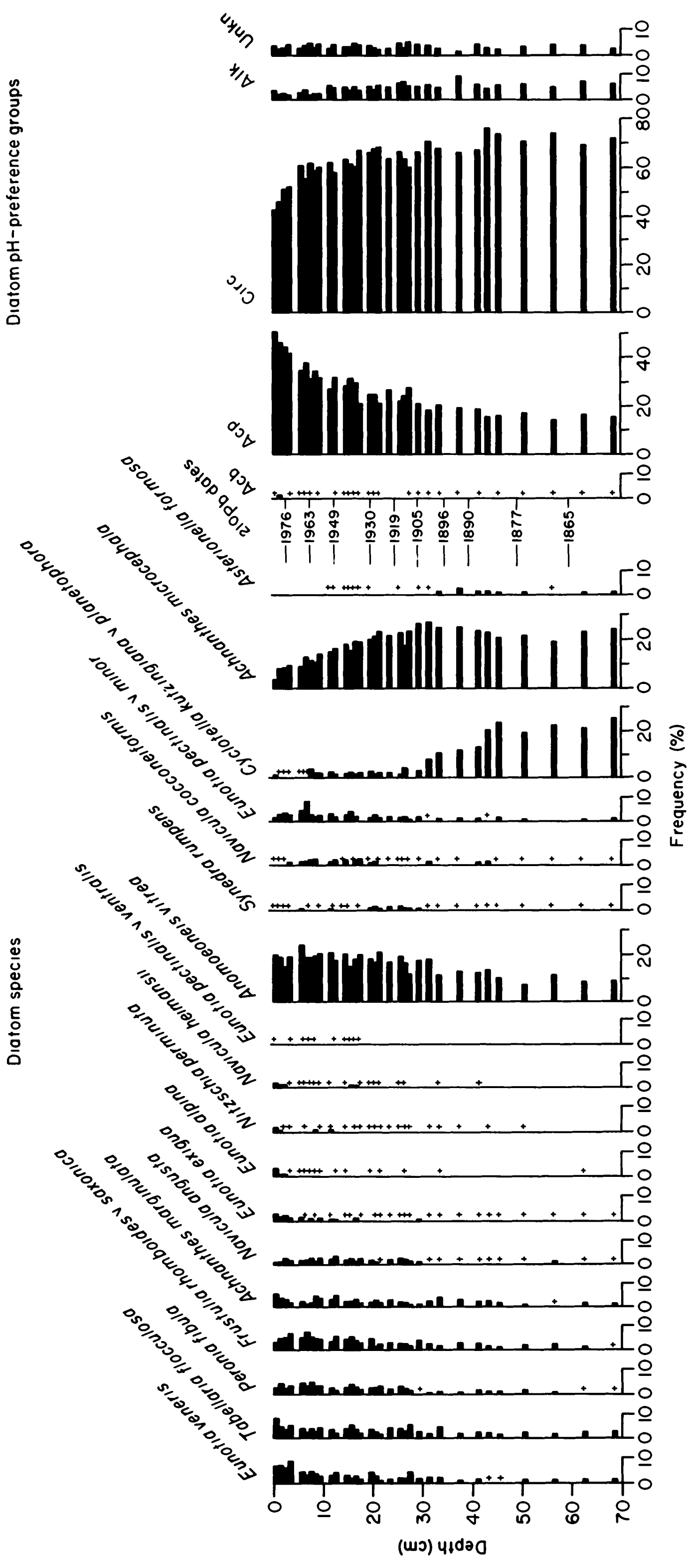

FIG. 7. Diatom percentage frequency diagram of common species (left) and pH preference groups (right) for a sediment core from Loch Dee. For other details see the legend for Fig. 4.

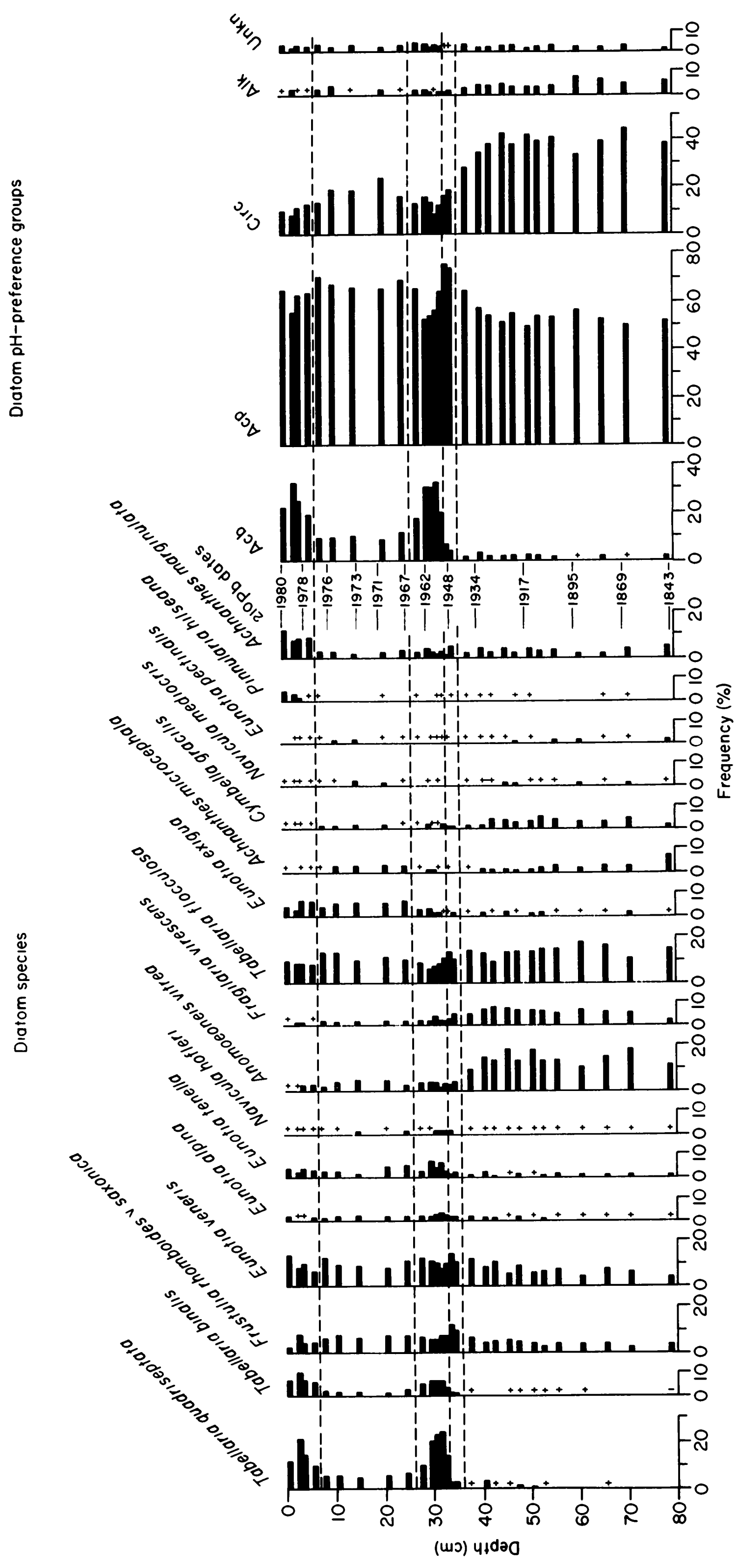

FIG. 8. Diatom percentage frequency diagram of common species (left) and pH preference groups (right) for a sediment core from Loch Grannoch. For other details see the legend for Fig. 4.

strongly increase as do *Pinnularia hilseana* Greg., *Achnanthes marginulata* and several *Eunotia* spp. These most recent floristic changes begin at the time of the second phase of catchment ploughing which occurred in 1976–77. In the fifteen years, represented by the 28–37 cm core section, between the two abundance peaks of acidobiontic *Tabellaria* taxa several less common species such as *Tabellaria flocculosa*, *Eunotia exigua*, *Eunotia pectinalis*, and *Achnanthes microcephala* increase in abundance or return to pre-35 cm frequency levels.

Loch Skirrow (Fig. 9). The top 35 cm of this 70 cm long core is dated by ^{210}Pb and represents 150 years of sediment accumulation. From 28 cm depth (*c.* 1900 A.D.) to the core base the diatom frquencies show little change, the assemblage being dominated by *Fragilaria virescens*, *Anomoeoneis serians* v. *brachysira*, *Achnanthes microcephala*, and *Frustulia rhomboides* v. *saxonica*. The two planktonic diatoms *Cyclotella kützingiana* v. *planetophora* and *Cyclotella comensis* are common in the lower part of the core and tend to be reciprocally related, with the former increasing above 55 cm. Above 28 cm floristic change begins with frequency increases of the acidophilous taxa, *Anomoeoneis brachysira* v. *thermalis*, *Frustulia rhomboides* (Ehr.) de Toni, *Tabellaria flocculosa* and decreases in the circumneutral forms *Fragilaria virescens* and particularly *Cyclotella kützingiana* v. *planteophora*. Further abundance changes occur at 21 cm (*c.* 1915) as *Frustulia* spp. begin to decline but at 15 cm (*c.* 1940) *Anomoeoneis serians* v. *brachysira* and *Achnanthes microcephala* also decline as *Fragilaria virescens* and *Cymbella perpusilla* increase. In the top few cm of sediment, corresponding to the mid 1970s, *Asterionella ralfsii* appears in the flora.

Grouping of the diatoms according to pH-preference reveals that the pre-disturbance asemblage in the Loch Grannoch core is dominated by acidophilous forms, whereas in the currently less acid sites, Loch Dee and Loch Skirrow the circumneutral group is most abundant. A gradual decline in circumneutral forms corresponding with increased abundance of the acidophilous group occurs in the Loch Dee and Loch Skirrow cores beginning about 100 and 140 years ago, respectively. In Loch Grannoch this change is later, beginning around 1930, is much more rapid and is quickly followed by an increase in frequency of acidobiontic taxa. These acidobiontic forms never exceed a low percentage abundance in the Loch Dee and Loch Skirrow cores. In the Loch Dee core the decline in abundance of circumneutral forms continues to the core top, whereas in the Loch Skirrow core these forms increase from about 1940 to 1960 before declining again. An increase in species preferring less acid conditions also occurs in recent sediments of the Loch Grannoch core as the acidobiontic group (mainly *Tabellaria quadriseptata*) sharply declines, immediately following pre-afforestation catchment ploughing in 1961. The acidobiontic forms again increase post-1977, several years after the second ploughing in the Loch Grannoch catchment. In the topmost sediment in both the Loch Grannoch and Loch Skirrow cores there is a small increase in diatoms preferring less acid conditions.

Accumulation rates and frequencies of taxa

Changes in percentage frequencies can either indicate real fluctuations in abundance of particular diatoms or merely reflect changes in abundance of other taxa. Evaluation of such changes can be carried out by calculating the accumulation rates of relevant species. Of particular interest are the percentage increase of *Tabellaria quadriseptata* in the most acid lakes, the percentage decrease of planktonic *Cyclotella kützingiana* in Loch Dee and Loch Skirrow, and the importance of these changes to other taxa. These effects can be

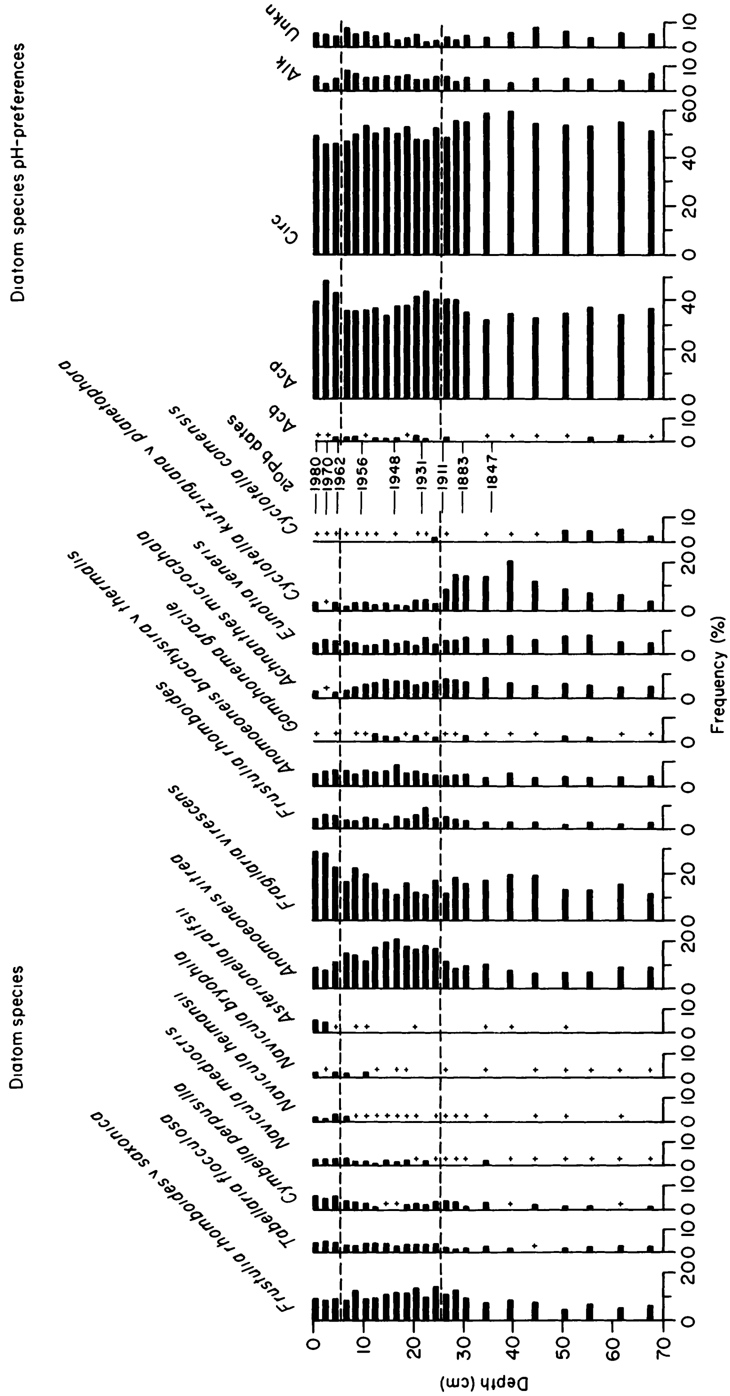

FIG. 9. Diatom percentage frequency diagram of common species (left) and pH preference groups (right) for a sediment core from Loch Skirrow. For other details see the legend for Fig. 4.

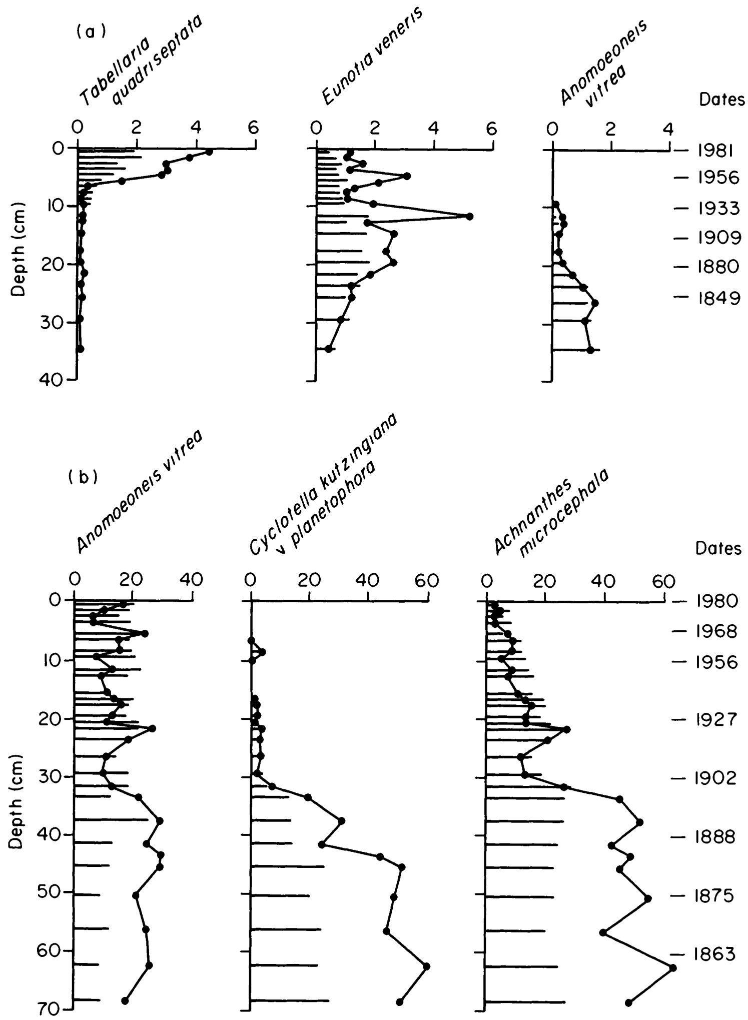

FIG. 10. Percentage frequencies (——) (% × 10^{-1}) and accumulation rates (●——●) (as cells × 10^{-5} cm^{-2} y^{-1}) of selected diatom taxa in sediment cores from (a) Loch Enoch, an unafforested site, and (b) Loch Dee, an afforested site. ^{210}Pb dates are shown in Fig. 3.

assessed using Loch Enoch and Loch Dee cores, respectively, as examples (Fig. 10). Loch Enoch shows that changes in accumulation rates of *Tabellaria quadriseptata*, *Eunotia veneris* and *Anomoeoneis vitrea* cells are in broad agreement with the percentage frequency data although the magnitude of abundance changes is diminished in the percentage data. The accumulation rates of *Cyclotella kützingiana*, *Anomoeoneis vitrea* and *Achnanthes minutissima* in Loch Dee have all declined in the upper 40 cm of the core whereas the percentage data suggest declines in *Cyclotella kützingiana* and *Achnanthes minutissima* but an increase in *Anomoeoneis vitrea*. In this case it is clear that no real increase of *Anomoeoneis vitrea* occurred and that the percentage increase indicated is an artefact of this method of expression caused by the accumulation rate of *Anomoeoneis vitrea* declining less rapidly than those of other species.

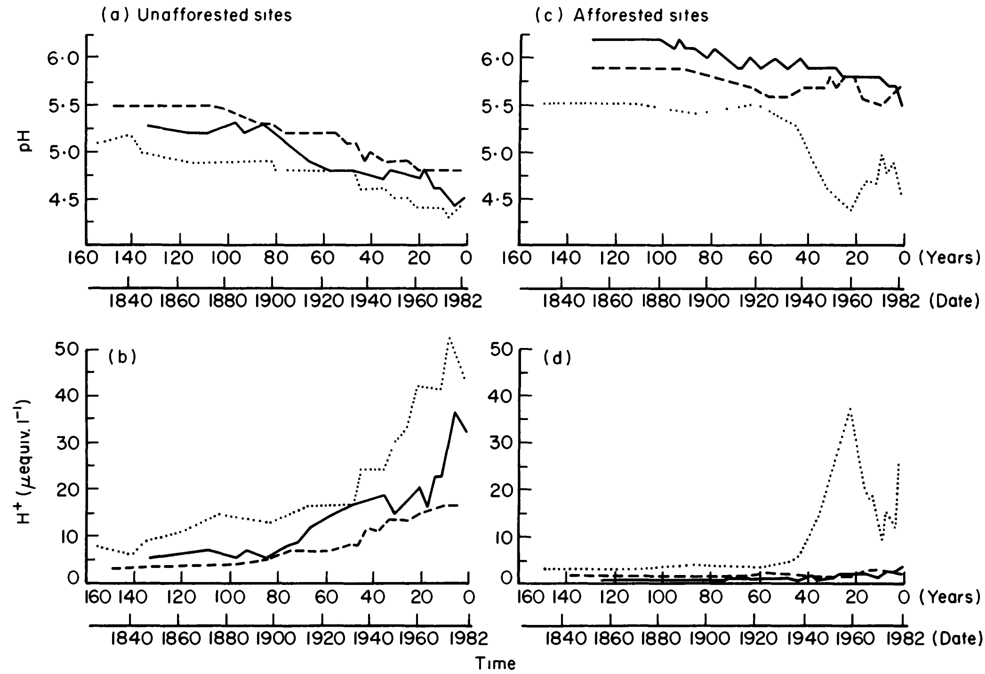

FIG. 11. The recent history of lake-water acidity changes in three unafforested Scottish sites (left), Loch Enoch (· · · ·), Loch Valley (——) and Round Loch of Glenhead (– – –) as pH (a) and H^+ concentration (b), and at three afforested sites (right), Loch Grannoch (· · · ·), Loch Dee (——) and Loch Skirrow (– – –), as pH (c) and H^+ concentration (d) reconstructed from sediment core diatom analysis.

Recent pH histories

In an attempt to produce the best estimate of past lake-water acidity we have applied both predictive pH equations to the diatom assemblages in each of the six cores and have combined the results to produce geometric mean pH values. Reconstructed pH values throughout the ^{210}Pb-dated section of each core are plotted against time in Fig. 11 as both pH and hydrogen ion concentration. Expressing inferred acidity change in terms of μequiv. $H^+ \, l^{-1}$ emphasizes the difference between reconstructed pH declines in the range 4–6. Hence, the 1935–82 0·6 pH unit decline, from 5·1 to 4·5, in Loch Enoch is equivalent to an increase of > 25 μequiv. $H^+ \, l^{-1}$ whereas in Loch Dee the 1900–1980 0·7 pH decline, from 6·2 to 5·5 is equivalent to an increase of $< 3{\cdot}0$ μequiv. $H^+ \, l^{-1}$ The curves in Fig. 11 show small differences from those previously published for the Round Loch of Glenhead, Loch Enoch and Loch Grannoch (Flower & Battarbee 1983a; Battarbee *et al.* 1985a) because the earlier work was based upon regression coefficients derived from a Scandinavian (Renberg & Hellberg 1982) rather than a Galloway modern diatom–pH data set.

Unafforested sites

Over the ^{210}Pb-dated upper section of the Round Loch of Glenhead core, the reconstructed pH shows no appreciable change until the 1870s A.D. After this date the pH begins to fall rapidly to pH 4·9 by 1945 and reaches a minimum of pH 4·8 by about

1960, a value that is maintained to the core top (1980). The *Cyclotella* decline at *c*. 45 cm depth (Fig. 2) probably also reflects a small increase in lake acidity at this time. In the Loch Enoch core pH begins to decline *c*. 1840 A.D. from pH 5·4, and proceeds steadily until *c*. 1930 to a pH of 4·8. In the mid-1930s pH then declined rapidly to a reconstructed value of 4·4 at the sediment surface (1982). The Loch Valley core prior to 1890 A.D. shows no consistent change in pH, but after this date the reconstructed pH declines rapidly from 5·6 to 4·8 by 1930. The pH appears fairly stable thereafter until the mid-1960s when it sharply declined to pH 4·5 at the sediment surface (1981). In all three cores the inferred pH declines are functions of increasing frequencies of acidophilous and acidobiontic taxa and a corresponding decrease in abundance of circumneutral forms.

Afforested sites

The pH curve for Loch Dee shows that prior to 1890 A.D. reconstructed values are constant at about pH 6·3. Above this depth however the pH declines in a gradual but occasionally irregular manner to 5·9 in the mid-1950s. Between the 1950s and 1981, pH declined further to 5·5, coinciding with the period of catchment afforestation in 1973–74 (Table 1). The Loch Dee diatom frequency diagram (Fig. 5) shows that declining reconstructed-pH reflects mainly frequency decreases of those diatoms indicative of circumneutral conditions, notably planktonic *Cyclotella kützingiana* and increases in acidophilous taxa. For Loch Grannoch the pH curve is unusual in that it has two clear minima. Before *c*. 1930 the reconstructed pH departs little from a value of 5·5, whereas above this level a rapid decline occurs to pH 4·4 by the mid-1950s. After this first pH minimum the reconstructed-pH increases to 5·0 in the early 1970s, the period when the first phase of catchment afforestation was carried out (1961–62). After *c*. 1975 the pH declined again to 4·6 at the sediment surface (1981, following the second afforestation phase (1976–77). The diatom frequency diagram (Fig. 6) clearly shows that the two pH declines reflect mainly changes in frequencies of acidobiontic *Tabellaria* spp. The reconstructed pH curve for Loch Skirrow shows a change of $<0{\cdot}4$ units over the dated upper section of the core. However, pH does show a gradual decline from 5·9 to 5·6 between the mid 1890s A.D. and the 1930s. After the 1930s the pH increases slowly to 5·8 in 1960, the period during which catchment afforestation was carried out (1957–58). After *c*. 1960 the pH declined again to 5·5 in 1970 before rising to 5·7 at the sediment surface (1981). The diatom diagram for the post-1880 A.D. section of this core (Fig. 7) shows considerable changes in frequencies of several taxa. These changes undoubtedly reflect variation in water quality but do not translate into pH deviations as the species are all classified as circumneutral.

DISCUSSION

Diatom analyses of sediment cores show that considerable floristic changes have occurred within the past 140 years at all six lakes. The diatom species, notably acidobiontic *Tabellaria quadriseptata* and *Tabellaria binalis*, indicative of strongly acid ($\text{pH}<5$) environments have recently increased in frequency at four sites: the Round Loch of Glenhead, Loch Enoch, Loch Valley and Loch Grannoch. At these sites the composition of the diatom assemblages has changed typically from circumneutral to acidophilous and to acidobiontic forms in the most recent sediments. However, at the two less acid sites, Loch Dee and Loch Skirrow, this sequence does not occur. In Loch Dee the assemblage shifts only as far as the acidophilous forms and acidobiontic taxa remain at low

TABLE 4. Occurence of important pH indicator diatoms in the sediment cores from six Scottish lochs, arranged into pH-preference groups characteristic of particular periods in the recent history of each lake. Note that species indicative of strongly acid conditions are rare in both the Loch Dee and Loch Skirrow cores.

pH indicator groups	Level of acidity indicated	Site	Period
Anomoeoneis vitrea		Round Loch of Glenhead	Pre-1860
Fragilaria virescens	Circumneutral–mildly acid (pH > 6–5·5)	Loch Enoch	Pre-1840
Achnanthes microcephala		Loch Valley	Pre-1850
Cyclotella kutzingiana		Loch Dee	Pre-1890
		Loch Grannoch	Pre-1925
		Loch Skirrow	Pre-1890
Eunotia veneris, E. alpina		Round Loch of Glenhead	1860–1940
Peronia fibula	Acid (pH 5·5–5)	Loch Enoch	1840–1920
Cymbella aequalis		Loch Valley	1850–1975
Navicula heimansii		Loch Dee	1890–1980
		Loch Grannoch	1925–1950
Tabellaria quadriseptata, T. binalis		Round Loch of Glenhead	Post 1940
Navicula hofleri, N. subtilissima	Strongly acid (pH < 5)	Loch Enoch	Post 1930
Eunotia bactriana		Loch Valley	Post 1930
		Loch Grannoch	Post 1950

abundances throughout the core. In Loch Skirrow the situation is less clear with the shift to acidophilous forms *c.* 1900 being reversed some forty years later. The main points of floristic change in all six sediment cores are summarized in Table 4, and species characteristic of the different acidity levels are picked out mainly according to CONSLINK (Gordon & Birks 1972) zoning of the diatom assemblages (Figs 2–7). This statistical analysis is a useful confirmation of assemblage change but is relatively insensitive to minor trends in the abundance of less common taxa, such as the *Cymbella gracilis* decline in the Loch Grannoch core. The acidity values, pH > 6–5·5, 5·5–5·0 and < 5, indicated in Table 1 generally accord with the diatom pH groupings, circumneutral, acidophilous and acidobiontic, respectively. One exception, however, is *Eunotia bactriana*, a species usually regarded as acidophilous (Hustedt 1931–66; Meriläinen 1969) but which here occurs with acidobiontic taxa.

The timings of increased abundances and the sequence of occurrence of diatoms characteristic of different acidity values are compatible with the hypothesis that all of the lakes have been recently acidified. However, the degree of acidification varies according to site. All six lakes currently exhibit diatom floras that are radically different from those of the pre-acidification period. Only in Loch Skirrow are some species of periphytic diatoms (e.g. *Fragilaria virescens* and *Achnanthes microcephala*), characteristic of the pre-acidification period, still common in the most recent sediment. The pre-acidification flora that occurred until between 140 and 50 years ago varies considerably between cores probably according to the level of natural acidity (Table 5). Hence, Loch Enoch the highest and probably the most naturally acid site has the most acidophilous and the least circumneutral taxa in pre-twentieth century sediment.

The spatial distribution of species occurring in the surface sediments of all six lakes, from the most acid (Loch Enoch) to least acid (Loch Skirrow), broadly parallels the sequence down the cores of acidobiontic, acidophilous and circumneutral species found in the four most acid lakes. This observation corroborates the hypothesis that in these Galloway lakes historical changes in diatom assemblages were brought about by

TABLE 5. Summary of the recent historical changes in lake water acidity in six Scottish lakes, reconstructed from the diatom assemblages in ^{210}Pb-dated sediment cores. The measured mean summer pH values, calculated geometrically for the period 1978–85 (from Flower 1986), are included for comparison with reconstructed pH data.

Site	Catchment geology	Onset of acidification	pre-acidification pH	pH *c.* 1980	pH shift	H^+ shift (μequiv. $H^+ l^{-1}$)	pH (measured)
Unafforested							
Round Loch of Glenhead	Granite	1860	5·9	4·9	−1·0	12	4·7
Loch Enoch	Granite	1840	5·3	4·4	−0·9	35	4·5
Loch Valley	Granite	1850	5·6	4·6	−1·0	22	4·7
Afforested							
Loch Dee	Granite & metamorphic	1890	6·2	5·5	−0·7	3	5·3
Loch Grannoch	Granite	1930	5·7	4·7	−1·0	18	4·7
Loch Skirrow	Granite & metamorphic	1880	5·9	5·8	−0·1	<1	5·7

competitive expansion of species better adapted to, or more tolerant of, lower pH conditions. A major exception is found in the distribution of planktonic diatoms, principally *Cyclotella* taxa. These diatoms are common in the earlier sediments of three lakes, the Round Loch of Glenhead, Loch Dee and Loch Skirrow, whereas today a significant diatom phytoplankton does not occur in any of these lakes.

The surface-sediment samples from all six lakes are overwhelmingly dominated by diatoms derived from periphytic habitats, and planktonic forms are virtually absent. The decline of planktonic *Cyclotella* spp. in the Round Loch of Glenhead, Loch Dee and Loch Skirrow, dated to pre-seventeenth century, *c.* 1890 A.D. and *c.* 1880 A.D., respectively is clearly significant. The lochs Enoch, Valley and Grannoch might always have been too acid to support a significant *Cyclotella* crop but longer cores are required to test this hypothesis. A marked decline in *Cyclotella* spp. has also been recognized in sediments of several acidified lakes in North America and Scandinavia (Almer *et al.* 1974; Renberg & Hellberg 1982; Davis *et al.* 1983; Charles 1984). Factors which might account for the decline of planktonic diatoms whilst the diatom periphyton continues to flourish are unclear but several possibilities exist. Although the hydrogen ion concentration *per se* seems to be of minor ecological importance in the 5·3–5·7 pH range, the bicarbonate buffering system ceases to be effective below this range. Below about pH 5·3 most dissolved inorganic carbon is in the form of carbon dioxide (Hutchinson 1957) and this may influence the composition of the flora (Moss 1973). Furthermore, between pH 6 and 5 the free ion concentrations of many metal species, notably aluminium, increase sharply (Stumm & Morgan 1970). In culture studies of pH effects on diatoms, Gensemer & Kilham (1984) found that removal of heavy metals in acidified media restored growth rates but noted that other factors such as nutrient concentrations could be important. Non-diatom phytoplankton such as cryptophytes and naked dinoflagellates (algae not normally preserved in sediments) occur in these six Galloway lakes today (Flower 1985 & unpublished) and have apparently replaced the *Cyclotella* plankton as pH decreased. However, in the sediments, a decline in the frequency of diatom phytoplankton is important as it is probably the first indication of increasing acidity in an oligotrophic lake.

Afforestation methods and the presence of coniferous woodland are generally thought to promote acidity in soil and in runoff water. The proposed mechanisms by which this acidification can occur are varied and include pre-afforestation ploughing causing acid production by chemical oxidation of anerobic subsoils and peats (cf. Gosling & Baker 1980; Bache 1984); depletion of soil basic cations by growing trees (Rosenqvist 1978; Nilssen, Millar & Millar 1982); and accumulation of raw acid humus in forests (Rosenqvist 1978; Krug & Frink 1983; Pennington 1984). Further, the presence of coniferous woodland is likely to enhance catchment acidification by filtering acidic substances from the atmosphere (Harriman & Morrison 1982). The opposite is also argued. In certain circumstances pre-afforestation ploughing can permit freer drainage of minerogenic subsoils, so releasing base cations and alkalinity (Ramberg 1981). An analogous biological process (Salisbury 1921) involves the cycling of base cations from weathered subsoils to the acid soil surface by deep-rooted trees.

Despite meagre field evidence and conflicting views about afforestation and acidification, a consensus of the published work suggests that afforestation of acid upland catchments with coniferous trees is likely to depress the pH of drainage water, so leading to lake acidification. Studies in Scotland (Harriman & Morrison 1982) and Wales (Stoner, Gee & Wade 1984) show that streams draining afforested catchments have lower pH and reduced salmonid populations than those draining similar but unafforested catchments. At the Galloway sites, it is possible to compare acidity trends at the unafforested and afforested sites using diatom-based reconstructions of the recent pH histories.

The unafforested sites, the Round Loch of Glenhead, Loch Enoch, and Loch Valley are located in predominantly granitic catchments and their reconstructed-pH histories show that all have been recently acidified by about one pH unit. In terms of hydrogen ion concentration however the acidity change has been greatest for Loch Enoch, the site at highest altitude. The pH values in all three lakes began to decline in the mid to late-nineteenth century but in terms of H^+ concentration the highest rate of acidification occurred in Loch Enoch between about 1940 and 1970. As far as is known there are no catchment land-use changes that can account for the increased water acidity recorded at these sites (cf. Battarbee *et al.* 1985a).

Although at an altitude of over 200 m in an afforested catchment Loch Dee is only weakly acidified compared with the three unafforested sites. The lake receives drainage water from non-granitic subcatchments on sedimentary rocks richer in base cations which possibly explains why the pre-acidification pH was relatively high and acidification proceeded slowly. Although a small pH decrease of doubtful significance occurred in the early 1970s at the time of catchment afforestation, the main acidification of Loch Dee occurred well before this (Fig. 11). Liming of the Loch Dee catchment began in 1980 (Burns *et al.* 1984) shortly before sediment coring was carried out, but effects of this activity are not recorded in the diatom fossils of the surface sediment. In Loch Grannoch, also with an afforested catchment, the pH did not begin to decline until the late 1920s but from then acidification proceeded rapidly. The pH 4·5 minimum in the late 1950s and increase after 1960 inferred from the diatoms in this core (Fig. 3) are, however, probably caused by inwashed non-acidobiontic catchment diatoms at the time of catchment ploughing (Battarbee & Flower 1985) making any effect of catchment afforestation on water pH difficult to assess. It is likely, however, that the lake water pH of Loch Grannoch has declined consistently since the 1920s, and that the lake already had a pH <5 before afforestation in the early 1960s. On the other hand, the period of maximum acidity in Loch Grannoch is close to afforestation dates and it is possible that acidification of this loch has been exacerbated by afforestation. Like Loch Dee, Loch Skirrow at the lowest altitude, receives drainage water from non-granitic subcatchments and shows only mild acidification from 1890 A.D. until *c.* 1940 when the trend is reversed. The cause of the post-1940s pH increase is not known: possible explanations are undocumented reports of liming to improve fisheries, or changes in hydrology permitting more alkaline water from the Grobdale Lane to enter the lake. Catchment afforestation appears to have had little effect on pH at this site and although a small pH decline occurs several years after planting in the late 1950s pH began to increase again by 1970.

Overall, the results indicate that once buffering capacity of a lake-catchment system to acidic inputs is exhausted then acidification proceeds rapidly, especially so for Loch Grannoch where catchment factors seem to have delayed acidification until relatively late. Although afforestation can undoubtedly cause acidification of runoff (Harriman & Morrison 1982; Stoner, Gee & Wade 1985) the hypothesis that afforestation is the major cause of increased acidity in these Galloway lakes is not supported by our evidence where the most strongly acidified site (Loch Enoch) is currently unafforested and acidification of the partially afforested sites began before trees were planted. We conclude that acid deposition is the most likely cause of acidification at these sites.

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