Lake Acidification in the United Kingdom 1800–1986

Evidence from Analysis of Lake Sediments

by

R.W. Battarbee

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Contents

Executive Summary

1. This report shows how the study of lake sediments can be used to provide a record of the timing, extent, and causes of lake acidification in the United Kingdom.

2. Additional information on land-use changes and fishery history was obtained from documentary sources and from interviews.

3. The sites studied are situated in the upland regions of Wales, Scotland and England. Most have pH values <5.5 and $Ca^{2+} < 50\,\mu eq\,l^{-1}$ and all occur in areas of moderate or high acid deposition ($>0.5\,g\,S\,m^{-2}\,yr^{-1}$). Many have poor or no fish populations. Some of the lakes are sited in National Nature Reserves, Sites of Special Scientific Interest, and National Parks.

4. Sediment cores from the sites were dated using radiometric techniques (^{210}Pb, ^{241}Am). The accumulation rate of recent sediment at most sites was found to vary from $<1\,mm\,yr^{-1}$ to $>3\,mm\,yr^{-1}$.

5. At all the very sensitive sites ($Ca^{2+} < 50\,\mu eq\,l^{-1}$) in areas of high acid deposition ($>1\,g\,S\,m^{-2}\,yr^{-1}$) major changes in diatom floras have occurred since about 1850. None of the sites now has a diatom plankton and many sensitive non-planktonic species (e.g. *Achnanthes minutissima*, *Anomoeoneis vitrea*) have been almost eliminated. These changes have been balanced by marked increases in acid-tolerant taxa such as *Tabellaria quadriseptata* and *Tabellaria binalis*. In contrast little change has taken place at non-sensitive sites (e.g. Loch Urr, Ca^{2+} $166\,\mu eq\,l^{-1}$) in areas of high acid deposition, or at very sensitive sites (e.g. Lochan Dubh, Ca^{2+} $33\,\mu eq\,l^{-1}$) in areas of low acid deposition.

6. pH reconstruction models show that all sensitive sites in high acid deposition areas are acidified and that most sites had pH values about 6.0 prior to 1850. Only two sites, Loch Tanna and Loch Enoch had pH values <5.5 at that time. In general, pH declines have varied between 0.5 and 1.5 units since 1850. Precise trends differ between sites in response to the historical pattern and intensity of acid deposition and the acid neutralising capacity of individual catchments.

7. Trace metal analysis shows that all sites have been contaminated by industrially-derived air pollutants since about 1800, and marked contamination by spherical carbonaceous particles of fossil fuel origin has occurred since 1940. At some sites the mineral magnetic record indicates fly-ash contamination.

8. There is no correlation between historical changes in moorland management (burning and grazing) and lake acidification. Indeed at many sites there has been an intensification of grazing pressure. Only at one site, Llyn y Bi, has there been both a marked decrease in burning and grazing but even here this trend post-dates the onset of acidification.

9. A variety of responses was observed at sites with recent conifer afforestation. At most sensitive sites studied the onset of acidification pre-dated planting. However at Loch Chon, a somewhat less sensitive site (Ca^{2+} $80\,\mu eq\,l^{-1}$), rapid acidification occurred some years after planting, probably as a result of the combined influence of acid deposition and pollution scavenging by the forest canopy. In some cases deep ploughing before planting caused accelerated soil erosion, and at one site, Llyn Berwyn, soil disturbance of this kind may have contributed to acidification and fish decline.

10. Agricultural lime has never been used in any of the catchments of the acidified lakes sampled for this project, so the general decline in liming in recent decades cannot be a cause of acidification.

11. The evidence at all sites considered both in this and previous studies is that the primary cause of surface water acidification is acid deposition. The overall pattern of observations cannot be accounted for by alternative hypotheses. Even where an afforestation effect is observed it is usually related to enhanced pollution interception rather than to a direct effect of the forest.

12. The full extent of acidified surface waters in the United Kingdom is not yet known. The work so far shows that all the highly acid waters in Wales, Cumbria, Galloway, Arran, Rannoch Moor, and Lochnagar and the Cairngorms are indeed likely to be acidified waters. And since the patterns are consistent both between and within regions this interpretation can be confidently extrapolated to other sensitive areas in regions of high acid deposition, especially to the Millstone Grits of the southern Pennines and the Cretaceous sandstones of south-east England. Work in progress is designed to assess the extent of acidification in north-west Scotland. Preliminary data indicate that little or no acidification of sensitive lakes has occurred in this region where acid deposition is low.

13. Acid deposition has been declining in Scotland over approximately the last fifteen years. Already the uppermost sediments of some lochs show evidence of slight improvement. These data indicate that a large reduction in acid deposition is likely to lead to a rapid response in lake chemistry and biota.

1

Introduction

1.1 Historical background

It was Angus Smith (1852) who first used the term 'acid rain', when he described the impact of coal combustion on air and precipitation chemistry in British industrial cities. However, the possibility that 'acid rain' might also have an effect on the chemistry and biology of lakes was not proposed until much later when Gorham (1958) wrote, with respect to the Cumbrian Lake District, 'such influence might best be sought in the high tarns, since they are the most dependent upon rain for nutrients'. Gorham suggested that 'examination of mud cores for microfossils would no doubt throw much light upon the problem... and it is hoped that these matters will receive some attention in the future'.

More than twenty years passed before sediment core work started. In 1980 we began to examine the recent sediments of acid lakes in Galloway, south-west Scotland, and in the last few years work of this kind has been extended to other regions of the United Kingdom. In this report we show that many upland lakes were beginning to acidify in the mid-nineteenth century, at the time Angus Smith was writing, and that by the time Eville Gorham's publications appeared many lakes were strongly acidified and some were already fishless.

Ironically, evidence for a connection between 'acid rain' and lake acidification was presented first not in Britain, but in Scandinavia. There Odén (1968) argued that acid precipitation was a large-scale problem involving long-range transport of air pollutants often across national frontiers, causing major changes in the chemistry and biology of susceptible freshwaters.

Recognition of this problem in Scandinavia led to the formulation of major research programmes in both Sweden and Norway. Surveys in Norway showed a general coincidence between fishless lakes, high non-marine sulphate concentrations of lake water and regions with high precipitation acidity (e.g. Wright *et al.* 1977). At the same time the work of Muniz and Leivestad (1980) showed that almost all fishless lakes in these regions had good fish populations in earlier times.

Although the focus of attention in the 1970s was on Scandinavia, evidence was beginning to accumulate that surface water acidification was a problem in the United Kingdom. The earliest scientific work of this nature was carried out by Harriman and Morrison from the Freshwater Fisheries Laboratory (DAFS) at Pitlochry. It was initially stimulated by concern for salmonid fisheries in recently afforested stream catchments in the Trossachs area where streams with afforested catchments were shown to have more acid conditions and poorer fisheries than adjacent moorland ones (Harriman and Morrison 1981, 1982).

To provide data on loch fisheries for comparative purposes the Pitlochry group selected a range of sites in Galloway, a region where acid surface waters had been previously identified by Howells and Rippon (1977). The Pitlochry survey was given added impetus following a collaborative sampling exercise in Galloway with Norwegian scientists (Wright and Henriksen 1980, Wright *et al.* 1980). The subsequent claim that conditions in Galloway were not significantly different from those in acidified areas of Norway and Sweden helped to draw attention to the problem in the United Kingdom. Continued monitoring of sites in this area has confirmed these conclusions (Harriman *et al.* 1987).

However, some scientists and politicians were unconvinced by the 'acid rain hypothesis' put forward to explain the occurrence of these exceptionally acid waters. Instead they were attracted by the views of Rosenqvist (1978) who argued that changes in the vegetation and soils of lake catchments were the cause of acidification (the 'land-use hypothesis'). The added possibility that some lakes might have become very acid over a period of millennia rather than over the last few decades (Pennington 1981, 1984) increased the confusion.

1.2 Lake sediment analyses of Galloway sites 1981–1984

In 1981 we designed a project, funded by the Central Electricity Generating Board (CEGB), to consider these and other possible alternative explanations for the acidification of Galloway lakes. We formulated the hypotheses as follows:

i. Lakes were naturally acid and had not changed.
ii. Acidification had occurred slowly over long periods of time (hundreds to thousands of years).
iii. Acidification had occurred recently (since 1800) but was the result of a change in the land-use or land management of the catchments involving:
   a. a decline in burning and grazing (Rosenqvist 1978)
   b. an increase in afforestation (Rosenqvist 1977, Harriman and Morrison 1982, Stoner and Gee 1985)
   c. a decrease in agricultural liming.
iv. Acidification had occurred recently (since 1800) and was the result of an increase in acid deposition from the combustion of fossil fuels.

In the study (Flower *et al.* 1987a) we compared the acidification histories of six lakes with both afforested and non-afforested catchments. All lakes were situated entirely or partially on granitic bedrock. We concluded:

i. Five of the six lakes had become significantly more acid, by between approximately 0.5 and 1.2 pH units, within the last 130 years (Flower and Battarbee 1983, Flower *et al.* 1987a).

ii. At two afforested sites, Loch Dee and Loch Grannoch, acidification began before the time of planting (Flower *et al.* 1987a).
iii. At moorland sites there had been no decrease in sheep grazing or moorland burning (Battarbee *et al.* 1985a).
iv. At one moorland site, Round Loch of Glenhead, pH levels remained approximately constant for 10 000 years before the period of recent acidification (Jones *et al.* 1986).
v. At moorland sites post-1800 sediments were contaminated by trace metals (lead, copper and zinc) and by carbonaceous particles from fossil fuel combustion (Battarbee *et al.* 1985a, and Battarbee *et al.* in press).
vi. All observations were consistent with the acid deposition hypothesis. Other potential acidifying mechanisms were either not relevant or could not explain the timing of acidification at these sites.

1.3 The present project, 1984–1987

The present project (DoE 1) funded by the Department of the Environment (DoE) (contracts PECD 7/7/139 and PECD 7/7/142) uses the Galloway results as a starting point. We argue that if lakes in Galloway with modern pH values less than about 5.5 were acidified by the effects of acid deposition, then lakes and surface waters in other parts of the United Kingdom with similar chemistry should also be acidified. These lakes would be found where areas with slow-weathering bedrock coincided with areas of high acid deposition.

Such regions can be broadly identified by comparison of Edmunds and Kinniburgh's (1986) map of groundwater susceptibility (Figure 1.1) with the precipitation chemistry maps of Barrett *et al.* (1983, 1987) for pH, H^+ and SO_4^{2-}. In simple terms this comparison suggests that all susceptible areas south and east of approximately the Great Glen Fault have been acidified to a greater or lesser extent.

Consequently, the present study concentrates on sensitive sites in Wales, Scotland and northern England within this area of high acid deposition. Although most of the sites described are those studied with funding from the DoE, reference is made where appropriate to results from other studies, especially those funded by the Royal Society Surface Water Acidification Programme (SWAP) and the CEGB. Detailed results from each site are available as individual Research Reports (Appendix 1).

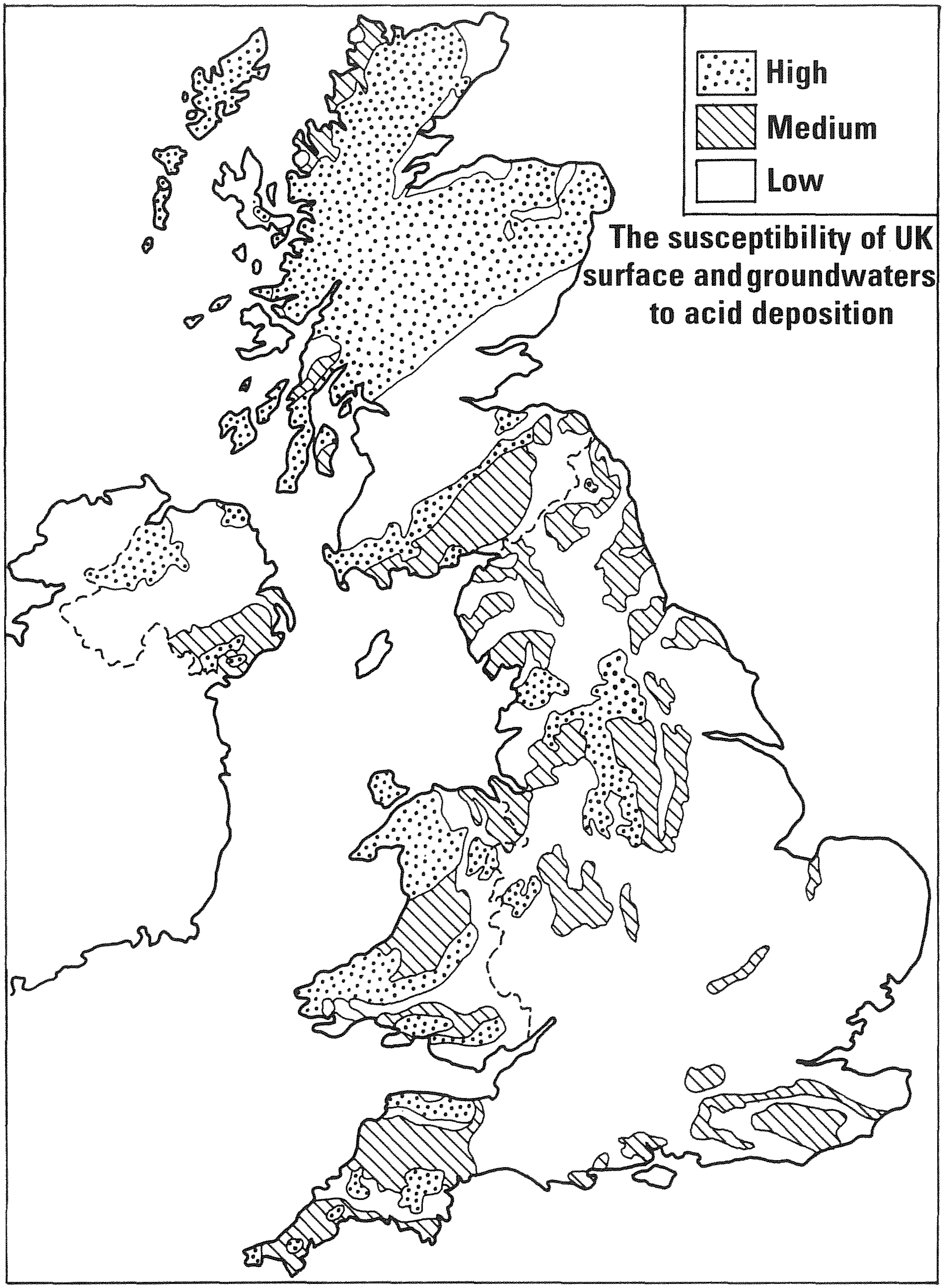


Figure 1.1 Areas of the United Kingdom showing the susceptibility of surface and ground waters to acid deposition (after Edmunds and Kinniburgh 1986).

2

Sites and Methods

2.1 Sites

Figure 2.1 shows the location of all sites from which sediment cores have been taken. These include sites studied in the context of both this and other projects as follows:

1–21—DoE funded University College London (UCL) sites included in this project; results presented here;
22–40—DoE funded UCL sites cored in association with the continuation of this project, 1987–1990 (DoE 2);
41–48—sites linked to the Royal Society SWAP project, some are briefly mentioned in this report; results available 1989;
49–52—DoE funded Freshwater Biological Association (FBA) sites in Cumbria included in this project; results presented here.
53–58—CEGB funded UCL sites in Galloway (1981–1985). Results are available in Anderson *et al.* (1986) and Flower *et al.* (1987a);
59–60—Nature Conservancy Council (NCC) funded UCL sites in south-east England. Some results are available (Flower and Beebee 1987);
61–109—Additional sites from which surface sediments have been collected for diatom/chemistry calibration purposes.

The sites described in this report (1–21, 49–52 on Figure 2.1) are grouped into regions. Except for the cases of Loch Urr and Burnmoor Tarn all the sites are acid lakes (pH < 6.0) with very low base status ($Ca^{2+} < 95\,\mu eq\,l^{-1}$). Within each region individual site choice was determined by consideration of a range of factors, including the suitability of the site for sediment coring, interests in the sites by third parties (e.g. Water Authority or River Purification Board or NCC), the status of knowledge on fish populations, and the presence or absence of catchment afforestation.

In addition, since our purpose was not only to reconstruct the pH history of each site but to evaluate hypotheses comparing catchment and atmospheric influence, great care was taken to avoid sites with multiple land-use categories, other than afforestation, and sites with past or present mining influence. In the case of natural lakes, sites with a record of hydrological disturbance were also avoided.

Possible sites were rarely rejected on grounds of inaccessibility since some of the most interesting and relevant sites occur in remote areas with difficult terrain. Where necessary helicopter transport was used to reach such sites.

2.2 Methods

2.2.1 Introduction

Any reconstruction of changing lake acidity requires accurate historical information. Since there are few useful documentary records on water chemistry or lake biota for most of our sites, lake histories are reconstructed from the lake sediment record. Although this is an indirect approach it is a powerful technique since lake sediments contain a wealth of information and accumulate rapidly enough for changes over the last 200 years to be identified clearly. If necessary, analysis can be extended backwards in time for over 10 000 years (e.g. Jones *et al.* 1986). Figure 2.2 shows a diagrammatic cross-section through a lake and its catchment and indicates the varying kinds and sources of material found in sediments that are useful in lake acidification studies.

The following sections describe how sediment cores are obtained and analysed and how the data so acquired can be used to reconstruct changes through time in lake chemistry and biology, in air quality and in the character of the catchment.

2.2.2 Fieldwork

2.2.2.1 Access

Sites with afforested catchments have forestry tracks that allow access to the edges of lakes (e.g. Llyn Berwyn), or to positions close enough to the edge to allow equipment to be carried. However, most moorland sites are relatively inaccessible for normal vehicles. Occasionally Land-Rover access was possible as at Llyn Gynon and Llyn Eiddew Bach. In other cases, such as Llyn Dulyn, small all-terrain vehicles such as Argocats were used (Figure 2.3). Many sites could not be approached by overland vehicles and helicopters were consequently used for access to Llyn y Bi, Llyn Llagi, Scoat Tarn, and Lochnagar (Figure 2.4).

2.2.2.2 Water chemistry

Water samples for chemical analysis were collected from all sites at the time of coring and at different times during the year. Samples were collected in acid-washed polypropylene one-litre bottles and stored in the dark. Chemical analyses were carried out by the Welsh Water Authority (Wales), DAFS Pitlochry (Scotland), Solway River Purification Board (Loch Urr) and the Freshwater Biological Association (Cumbria).

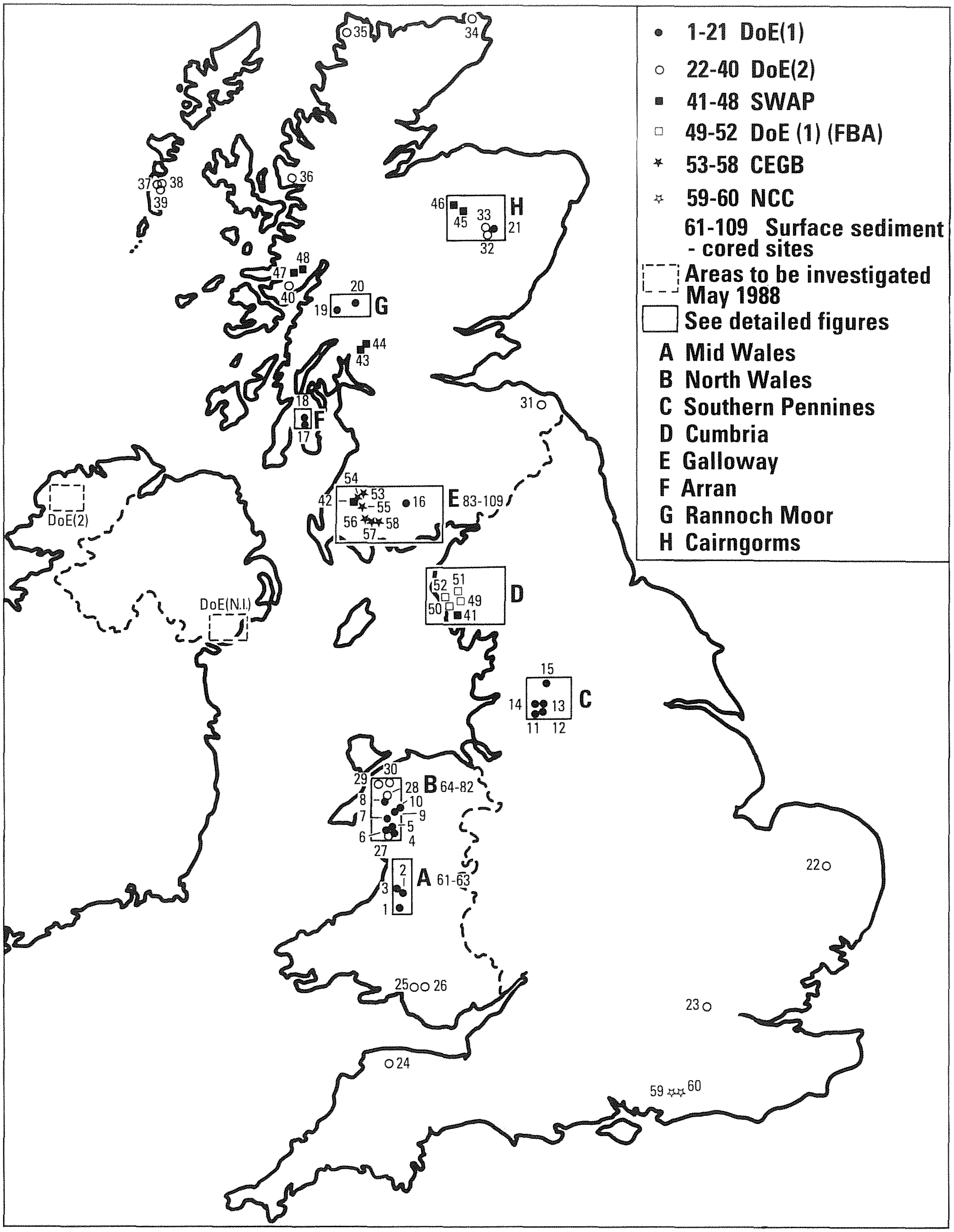


Figure 2.1 Map of the United Kingdom showing the locations of lake sites used in this and related projects.

Cores

DoE 1

1 . . . . Llyn Berwyn
2 . . . . Llyn Gynon
3 . . . . Llyn Hir
4 . . . . Llyn Cwm Mynach
5 . . . . Llyn y Bi
6 . . . . Llyn Dulyn
7 . . . . Llyn Eiddew Bach
8 . . . . Llyn Llagi
9 . . . . Llyn Gamallt
10 . . . . Llyn Conwy
11 . . . . Hurst Reservoir
12 . Swineshaw Higher Reservoir
13 . . . . Chew Reservoir
14 . . Wessenden Head Reservoir
15 . . . . Watersheddles Reservoir
16 . . . . Loch Urr
17 . . . . Loch Tanna
18 . . Loch Coire Fhionn Lochan
19 . . . . . Lochan na h'Achlaise
20 . . . . Loch Laidon
21 . . . . Lochnagar

DoE 2

22 . . . . Diss Mere
23 . . . . Hampstead Ponds
24 . . . . Pinkworthy Pond
25 . . . . Llyn y Fan Fawr
26 . . . . Llyn Cwm Llwch
27 . . . . Llyn Irddyn
28 . . . . Llyn Edno
29 . . . . Llyn Glas
30 . . . . Llyn Clyd
31 . . . . Coldingham Loch
32 . . . . Dubh Loch
33 . . . . Loch nan Eun
34 . . . . Long Loch
35 . . . . Loch na Larach
36 . . . . . . Loch Coire nan Arr
37 . . . . Loch Teanga
38 . . . Loch Airigh na h'Achlais
39 . . . . (unnamed)
40 . . . . Loch Uisge

SWAP

41 . . . . Devoke Water
42 . . . Round Loch of Glenhead
43 . . . . Loch Chon
44 . . . . Loch Tinker
45 . . . . Lochan Uaine
46 . . . . . Loch Coire an Lochan
47 . . . . Loch Doilet
48 . . . . Lochan Dubh

DoE (FBA)

49 . . . . Burnmoor Tarn
50 . . . . Greendale Tarn
51 . . . . Low Tarn
52 . . . . Scoat Tarn

CEGB

53 . . . . Loch Enoch
54 . . . . Loch Valley
55 . . . . Loch Dee
56 . . . . Loch Grannoch
57 . . . . Loch Fleet
58 . . . . Loch Skerrow

NCC

59 . . . . Woolmer Pond
60 . . . . Cranmer Pond

Surface Sediments

Wales

61 . . . . Glaslyn
62 . . . . Bugeilyn
63 . . . . Llyn Penrhaiadr
64 . . . . Llyn Bodlyn
65 . . . . Llyn Cwm Bychan
66 . . . . Llyn Tecwyn
67 . . . . Llyn Llenych
68 . . . . Llyn y Garn
69 . . . . Llyn Du
70 . . . . Llyn Barlwyd
71 . . . . Llyn yr Adar
72 . . . . Llyn Cwm Silyn Upper
73 . . . . Llyn Cwm Silyn Lower
74 . . . . Llyn Gaddair
75 . . . . Llyn Gwynant
76 . . . . Llyn Diwaunedd
77 . . . . . . Llyn Cwm Fynnion
78 . . . . Llyn Goddionduon
79 . . . . Llyn Bychan
80 . . . . Llyn Bodgynydd
81 . . . . Llyn y Parc
82 . . . . Llyn Geirionydd

Scotland

83 . . . . Loch White
84 . . . . Loch Clonyard
85 . . . . Loch Barean
86 . . . . Loch Fern
87 . . . . Loch Arthur
88 . . . . Loch Skae
89 . . . . Loch Howie
90 . . . . Lochinvar
91 . . . . Loch Stroan
92 . . . . Loch Woodhall
93 . . . . Loch Lochenbrech
94 . . . . Loch Mannoch
95 . . . . Loch Whinyeon
96 . . . . Loch Minnoch
97 . . . . Loch Harrow
98 . . . . Loch Muck
99 . . . . Loch Doon
100 . . . . Loch Finlas
101 . . . . Loch Riecawr
102 . . . . Loch Macaterick
103 . . . . Loch Kirrieroch
104 . . . . Loch Moan
105 . . . . Long Loch of Glenhead
106 . . . . Loch Trool
107 . . . . Loch Maberry
108 . . . . Loch Ochilltree
109 . . . . Loch Ronald

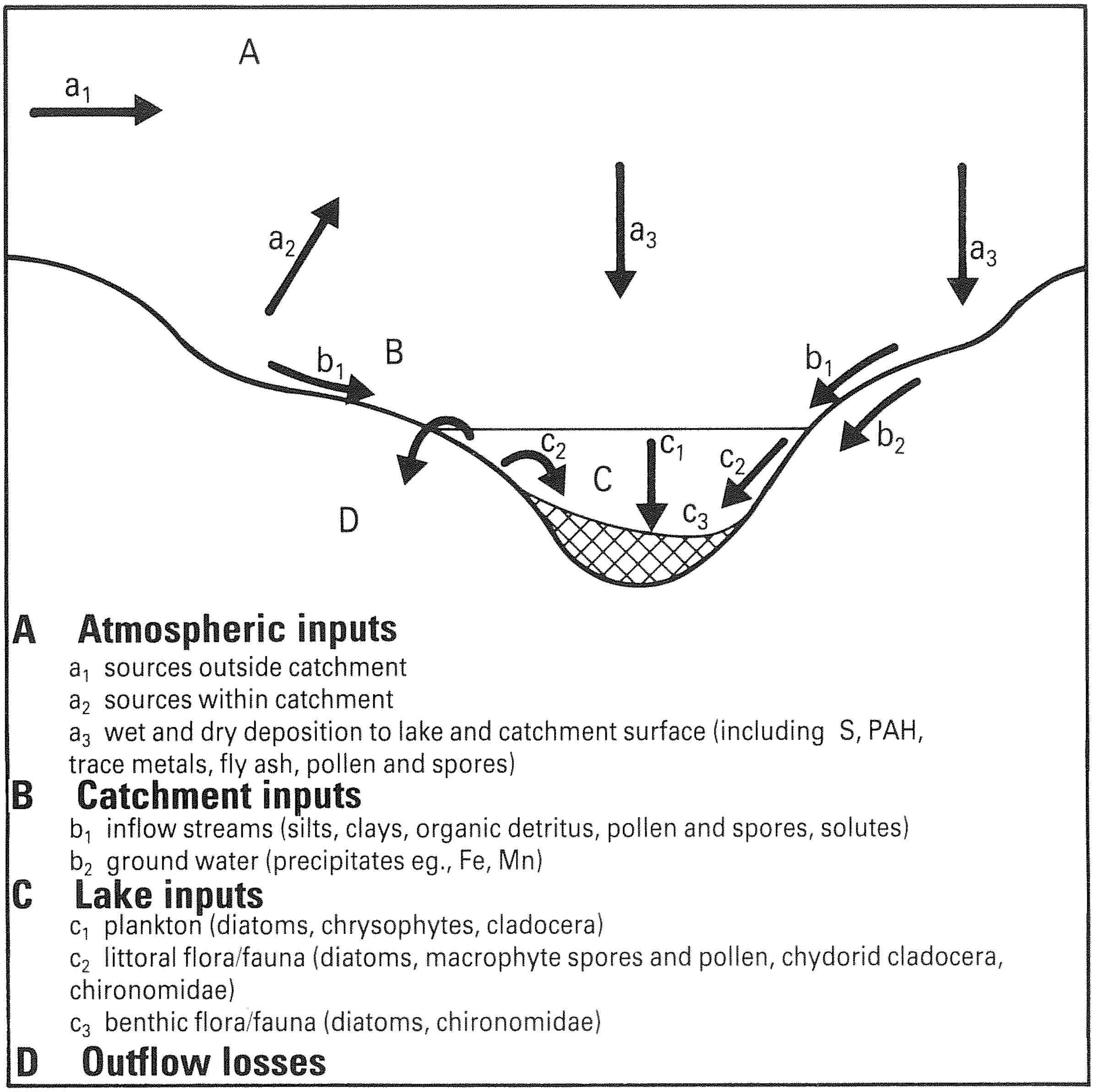


Figure 2.2 Idealised cross-section of a lake/sediment system showing the sediment sources.

To create a uniform chemical data-set all ionic concentrations were converted to micro-equivalents and all alkalinities were standardised as equivalence alkalinities, using the equation given by Henriksen (1982):

$$Alk_e(\mu eq\, l^{-1}) = Alk_l + 0.646\sqrt{Alk_l}$$

Where:

$$Alk_l = Alk_{(pH\,4.5)} - 32$$

(for titration to pH 4.5 end point)

or

$$Alk_l = Alk_{(pH\,5.0)} - 10$$

(for titration to pH 5.0 end point)

and

Alk_e = equivalence alkalinity

$Alk_{(pH\,n.n)}$ = titration alkalinity.

2.2.2.3 Lake bathymetry

Where necessary, a bathymetric survey was carried out to determine both the shape of the lake basin and to calculate lake-water volume.

Water depth was measured using an echo sounder with a chart recorder while positions were fixed using plane tables and polar alidades at precisely located stations on the shore. The shore stations continually tracked the boat along transect lines and spot depths were recorded at regular intervals, coordinated using CB radios.

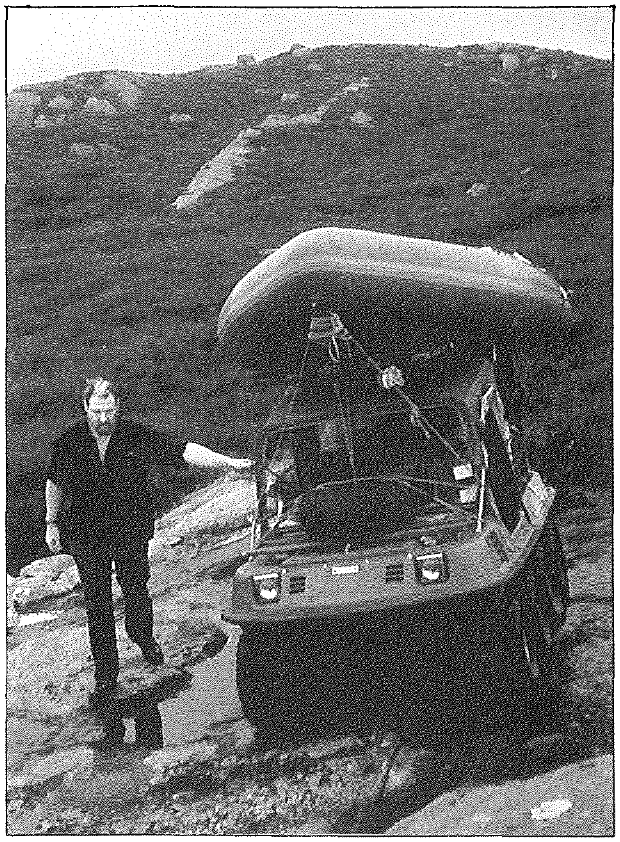


Figure 2.3 Argocat all-terrain vehicle.

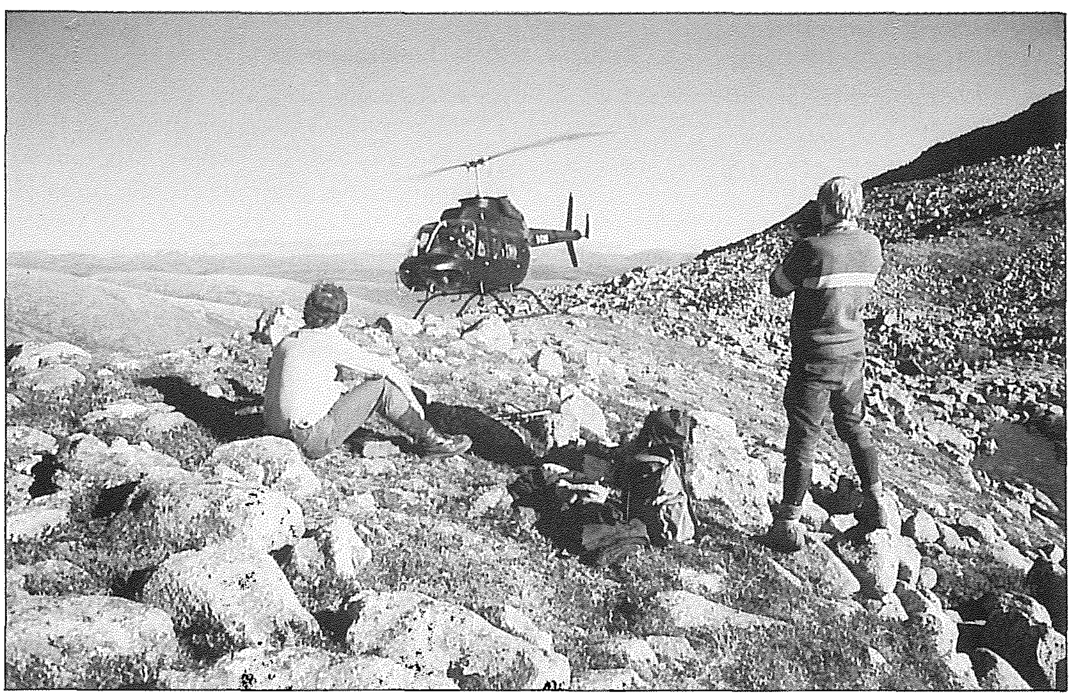


Figure 2.4 Helicopter, used to reach remote lakes.

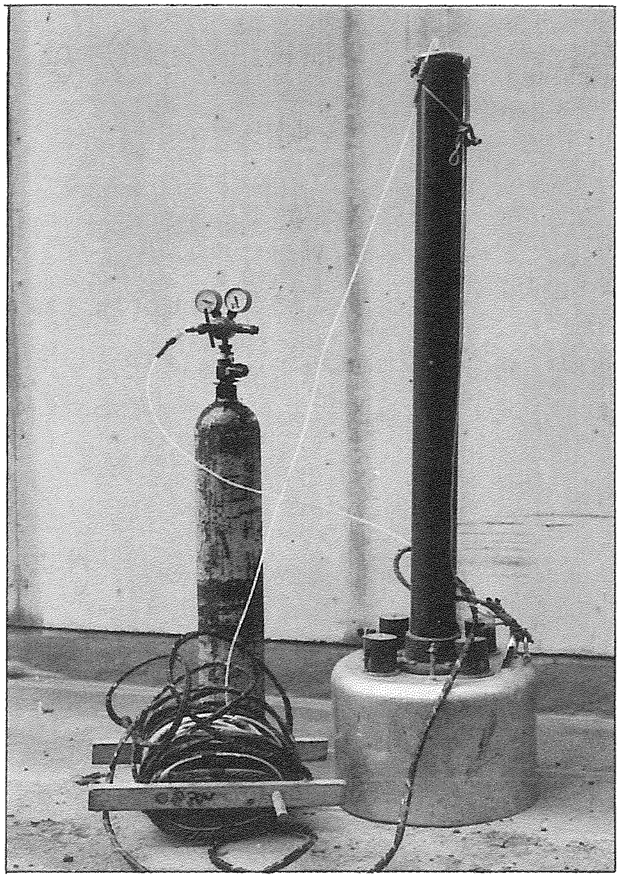


Figure 2.5 Mini-Mackereth corer.

Survey points were later plotted on large-scale maps and digitised using ISIS software (ISIS 1987). From these data contour maps and calculations of lake surface area and volume were produced (MAPICS 1987). At the same time catchment boundaries were digitised to allow the calculation of catchment areas.

2.2.2.4 Coring

All the cores analysed in this study were collected from the deepest point of the lake. Sites with a poor sediment record in the central area were abandoned for the purposes of this project.

A variety of sediment corers were used. At relatively accessible sites with water depths below about 15 m a wide diameter (8 cm) piston corer operated by rods from a small raft was used. This has the advantage of sampling a relatively large volume of sediment for every stratigraphic level chosen (usually 0.5 cm). At deep (e.g. Loch Laidon) and inaccessible sites (e.g. Lochnagar) a mini-Mackereth corer was used (Figure 2.5). Although this corer has a diameter of only 5.3 cm it can be operated from a small boat without the use of rods in both deep water and strong winds. Three replicate cores were taken at each site although all analyses were carried out as far as possible on the same core to avoid problems of correlation between cores.

Only cores that had perfectly undisturbed interfaces between the mud and water were retained. Cores were carefully transported to the laboratory for extrusion and analysis.

2.2.3 Laboratory

In the laboratory cores were extruded and sliced at 0.5 cm or 1 cm intervals. The sediment stratigraphy was described using the Troels-Smith method (Troels-Smith 1955) and sub-samples were taken for measurements of dry weight, wet density and loss-on-ignition (LOI) (organic matter) at each stratigraphic interval (cf. Figure 2.6).

Remaining sediment was dried and further sub-samples were taken and sent to The Radiometric, Mineral Magnetic and Palaeoenvironmental Research Centre at Liverpool University for ^{210}Pb dating and magnetic analysis. Since these techniques are non-destructive the same sub-samples were then passed on to the Limnology Laboratory at the University of Ulster for chemical analysis.

2.2.4 Dating

For each site a carefully evaluated chronology of sediment accumulation for approximately the last 150 years has been constructed. The main technique used was ^{210}Pb dating although other isotopes (^{137}Cs and ^{241}Am) were useful at some sites. The isotopes of interest are measured by direct gamma assay using a low background germanium detector with lead shielding. A typical gamma spectrum for a sample from Llyn Llagi is shown in Figure 2.7.

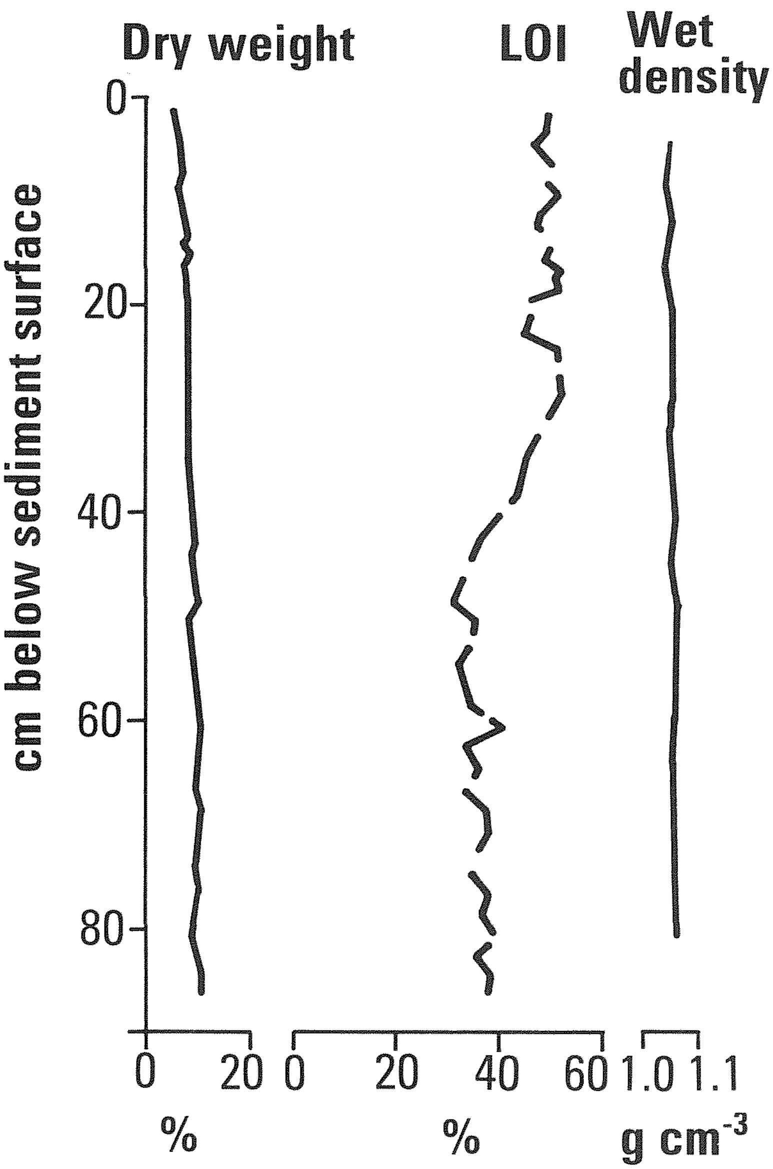


Figure 2.6 Dry weight, wet density and loss on ignition (i.e. percentage organic matter) for a core from Loch Laidon.

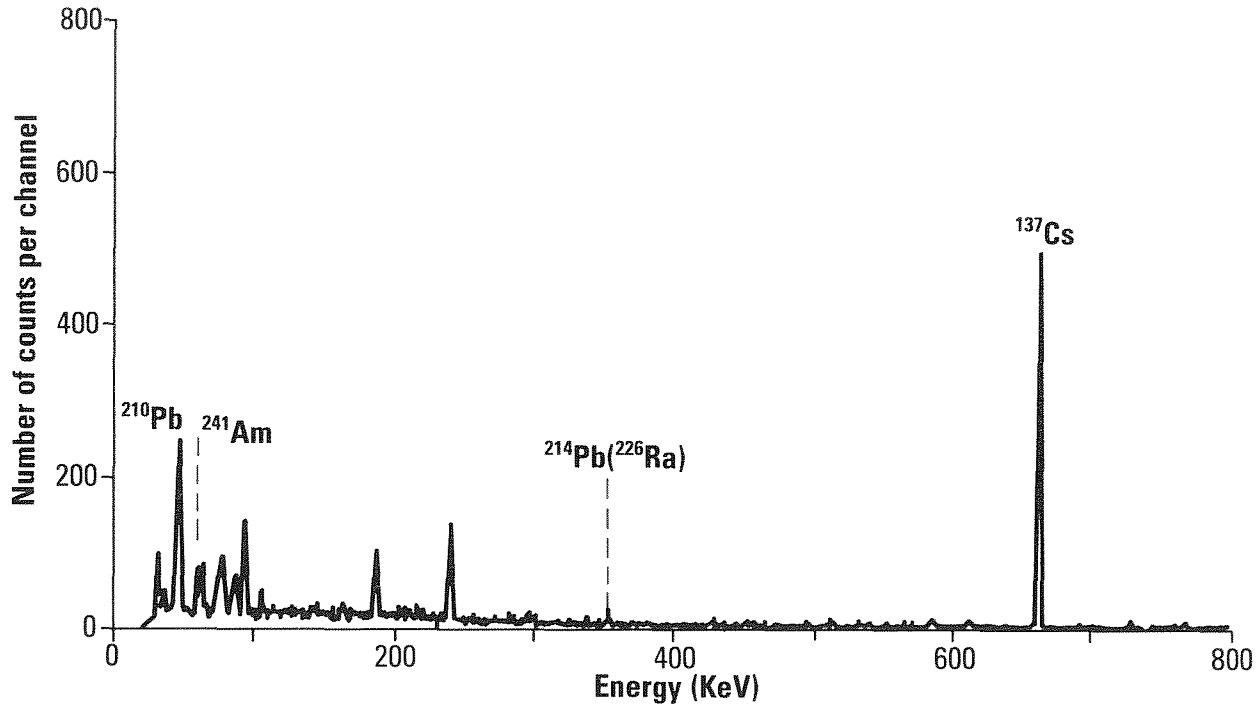


Figure 2.7 Gamma spectrum of a sediment sample from Llyn Llagi.

2.2.4.1 ^{210}Pb dating

^{210}Pb occurs naturally in lake sediments as one of the radio-isotopes in the ^{238}U decay series. It has a half-life of 22.26 years. The total ^{210}Pb activity in sediments has two components, 'supported' ^{210}Pb derived from the *in situ* decay of the parent isotope ^{226}Ra and 'unsupported' ^{210}Pb derived from the intermediate gaseous isotope ^{222}Rn via an atmospheric pathway. In most samples the supported ^{210}Pb can be assumed to be in radioactive equilibrium with ^{226}Ra so the unsupported activity at any level in a sediment core can be obtained by subtracting the ^{226}Ra activity from the total ^{210}Pb. Figure 2.8a shows the total and supported ^{210}Pb activity with depth for Llyn Llagi. The unsupported curve is shown in Figure 2.8b.

These data can be used to calculate the age of each sample given various assumptions. In this study the CRS model has usually been used (Appleby and Oldfield 1978). It is the most widely accepted model and assumes that unsupported ^{210}Pb supply to the lake is dominated by atmospheric fallout, resulting in a constant rate of supply (CRS) of ^{210}Pb from the lake waters to the sediments irrespective of changes in the sediment accumulation rate. It can therefore be used in situations where accumulation rates change rapidly in response to catchment soil erosion, a common feature of newly-afforested catchments. At sites where there is significant sediment focussing or significant inputs of ^{210}Pb from the catchment, the alternative CIC (constant initial concentration) model may sometimes be applicable. The two models give conflicting dates only when the dry mass sediment accumulation rates have varied with time. In these cases the most appropriate method has been determined by using the assessment procedures discussed in Appleby and Oldfield (1983). Figure 2.9 shows a depth versus age plot for the Llyn Llagi core. The relatively good agreement between both dating models is indicative of a reasonably constant dry mass sediment accumulation rate. Table 2.1 shows a full listing of dates and accumulation rates for this site with data interpolated for each centimetre of core depth.

2.2.4.2 ^{137}Cs and ^{241}Am dating

Lake sediments contain a record of radio-isotope fallout from the past testing of atomic weapons in the atmosphere, and most recent sediments in many parts of upland Britain contain isotopes (^{137}Cs and ^{134}Cs) from the 1986 Chernobyl nuclear accident.

^{137}Cs has a half-life of about 30 years and in many lake sediments the shape of the activity versus depth profile reflects the historically recorded fallout pattern, with a beginning in 1954 and a peak in 1963. Unfortunately in most of our study sites which have very acid waters and highly organic sediments, ^{137}Cs is quite mobile within the sediment column. The peak is usually very close to the surface sediment (later than 1963) and the beginning may be in sediment older than 100 years.

In these cases ^{241}Am measurements provide a useful alternative. This isotope also derives from nuclear fallout and a growing data-set from lakes with a wide range of pH suggest that it is considerably less mobile than ^{137}Cs. Figure 2.10 shows the ^{137}Cs and ^{241}Am profiles for Llyn Llagi. Both have a well-defined maximum at 4.25 cm but

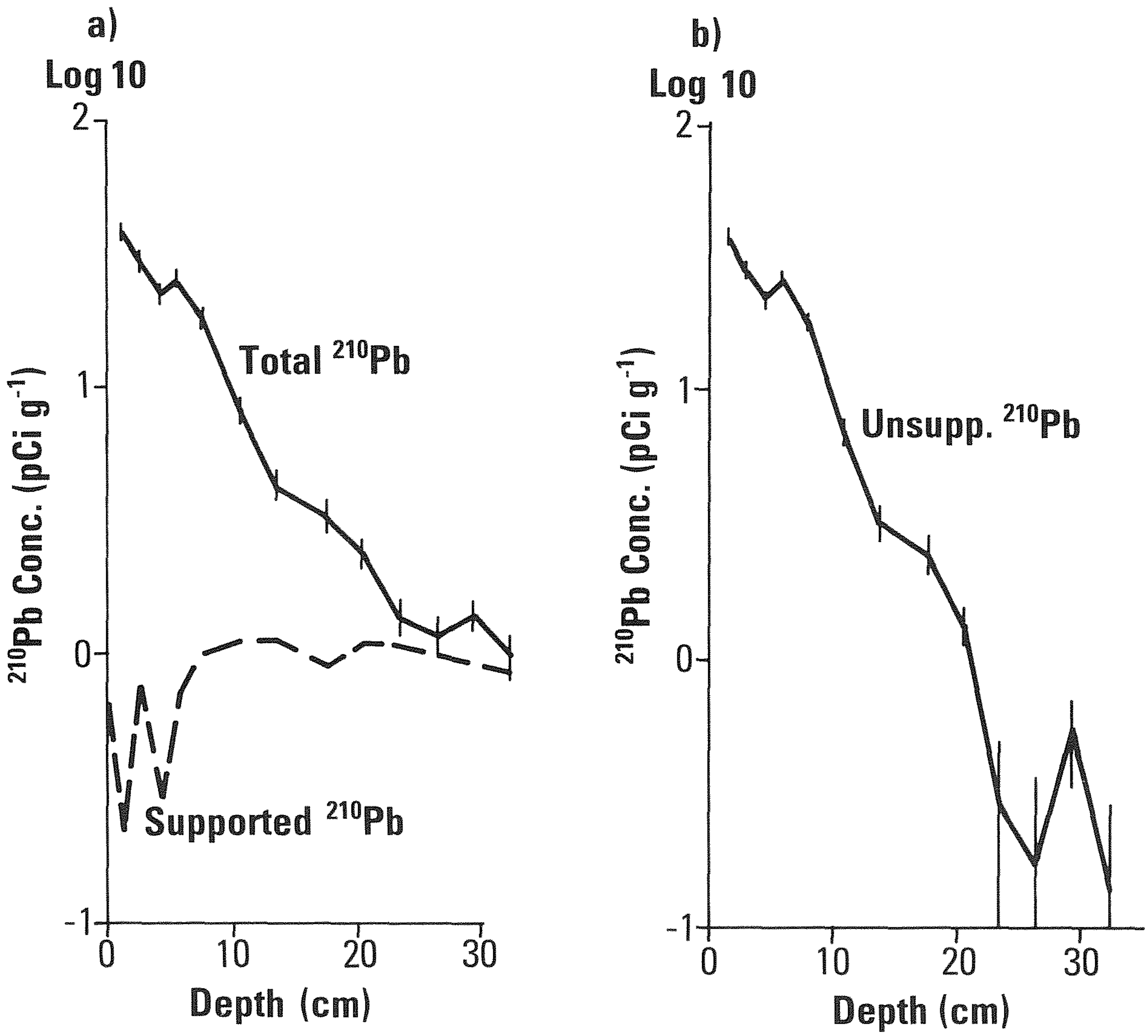


Figure 2.8 Graphs showing the concentration of ***a*** total and supported ^{210}Pb and ***b*** unsupported ^{210}Pb against sediment depth for Llyn Llagi.

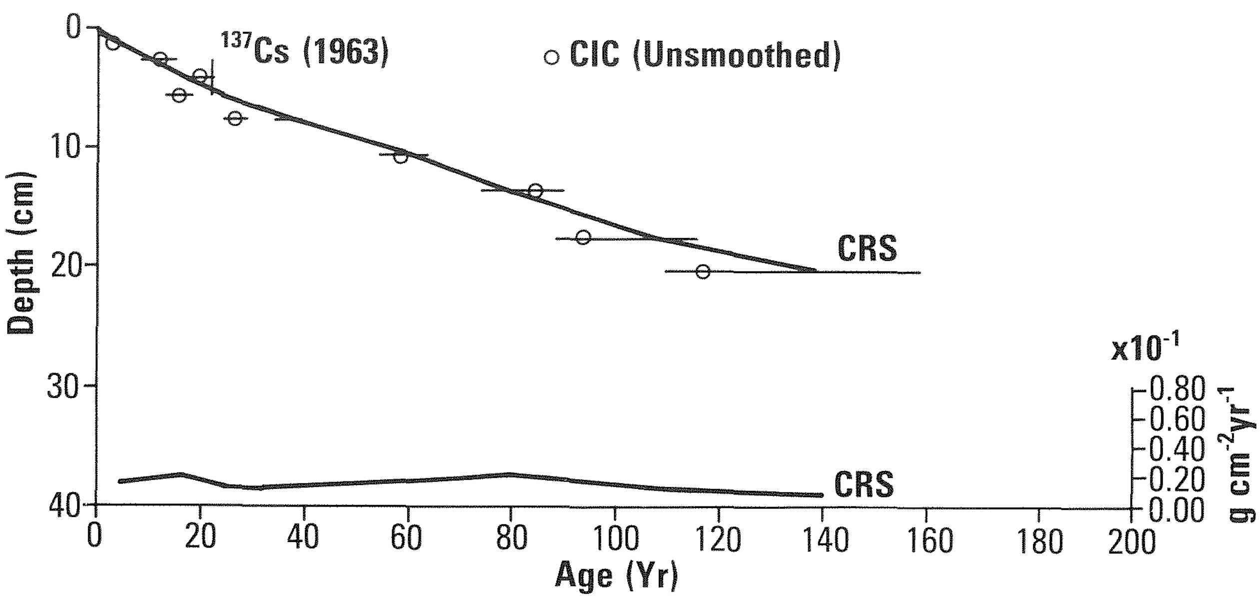


Figure 2.9 Depth and sediment accumulation rate against age profile for a core from Llyn Llagi.

Table 2.1 **CRS model ^{210}Pb chronology Llyn Llagi**

Depth cm	Dry mass g cm^{-2}	Cumul. unsupp. ^{210}Pb pCi cm^{-2}	Chronology Date AD	Age yr	error yr	Accumulation g cm^{-2} yr^{-1}	mm yr^{-1}	Standard error %
0.0	0.0000	21.17	1985	0				
1.0	0.0548	19.30	1982	3	1	0.0174	2.62	5.2
2.0	0.1261	17.07	1978	7	2	0.0182	2.48	5.7
3.0	0.2045	14.95	1974	11	2	0.0191	2.37	6.3
4.0	0.2879	13.07	1970	15	2	0.0195	2.36	7.0
5.0	0.3710	11.23	1965	20	2	0.0167	1.98	6.6
6.0	0.4555	9.48	1959	26	2	0.0136	1.56	6.1
7.0	0.5438	7.71	1953	32	2	0.0132	1.39	6.4
8.0	0.6375	6.22	1946	39	2	0.0132	1.29	7.0
9.0	0.7470	4.90	1938	47	3	0.0146	1.37	8.7
10.0	0.8565	3.86	1930	55	3	0.0160	1.46	10.3
11.0	0.9672	3.08	1923	62	3	0.0174	1.55	11.9
12.0	1.0815	2.54	1917	68	4	0.0188	1.66	13.6
13.0	1.1958	2.10	1911	74	4	0.0203	1.77	15.3
14.0	1.3105	1.72	1904	81	5	0.0207	1.80	17.1
15.0	1.4267	1.38	1897	88	6	0.0183	1.58	19.6
16.0	1.5429	1.10	1890	95	7	0.0159	1.37	22.1
17.0	1.6591	0.89	1883	102	8	0.0135	1.16	24.6
18.0	1.7760	0.68	1875	110	10	0.0115	0.97	27.0
19.0	1.8952	0.47	1863	122	17	0.0093	0.76	31.2

the ^{137}Cs curve has a substantial tail to depths earlier than the ^{210}Pb equilibrium point at 1850 (about 20 cm). The association of the 4.25 cm ^{137}Cs peak with the 1963 fallout maximum is supported by the ^{210}Pb date for this point.

2.2.5 Limnological history

2.2.5.1 Fishing history

For each of the lakes studied an attempt was made to reconstruct fishing history. For most lakes early records exist which describe the kind and quality of fishing to be had. For more recent changes interviews with land owners, anglers and farmers are the most useful techniques. The detail with which fishery history can be compiled varies greatly between lakes and depends primarily on the remoteness of the site and the intensity with which the lake was and is fished.

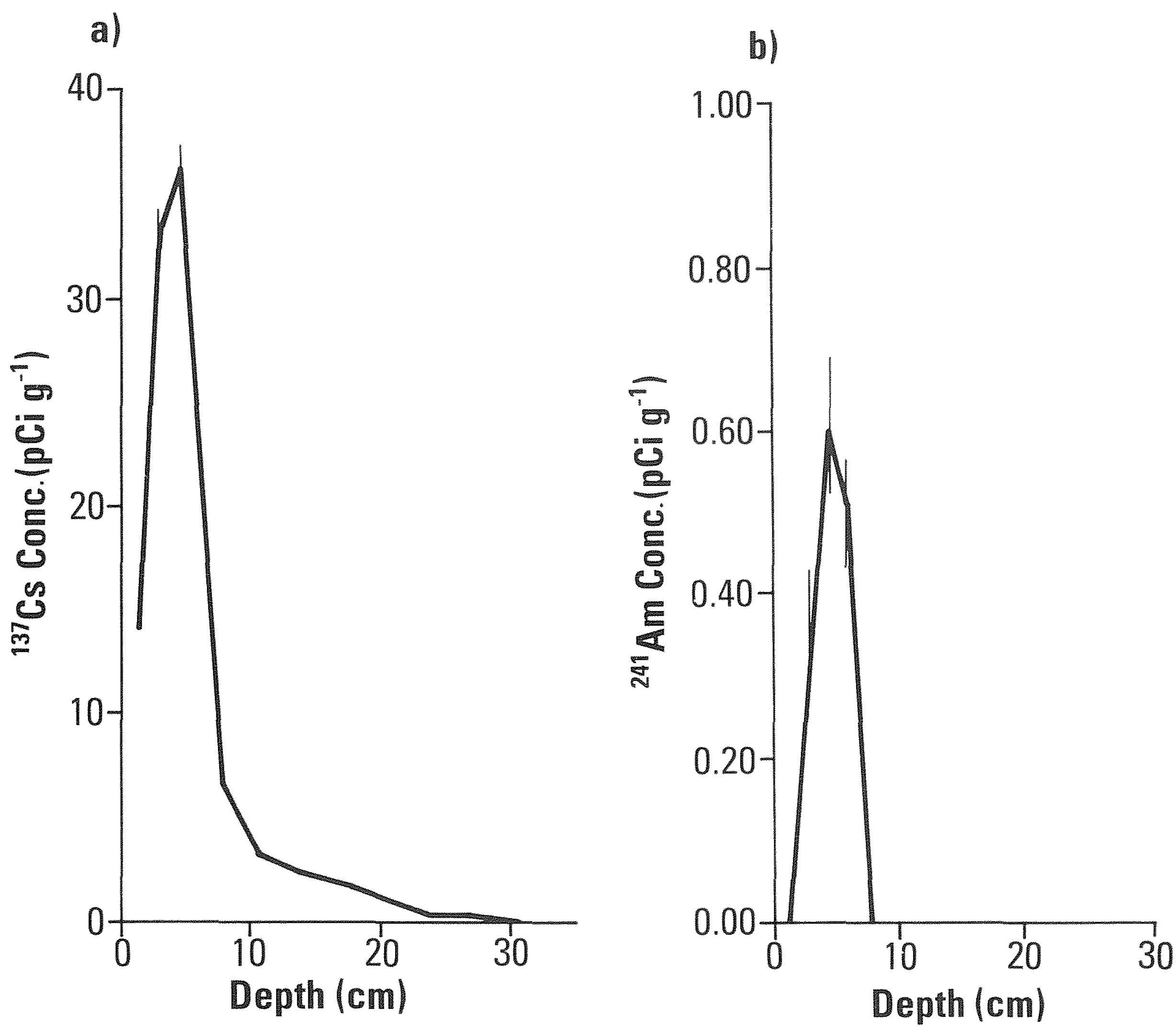


Figure 2.10 ***a*** ^{137}Cs and ***b*** ^{241}Am concentration against depth for a core from Llyn Llagi.

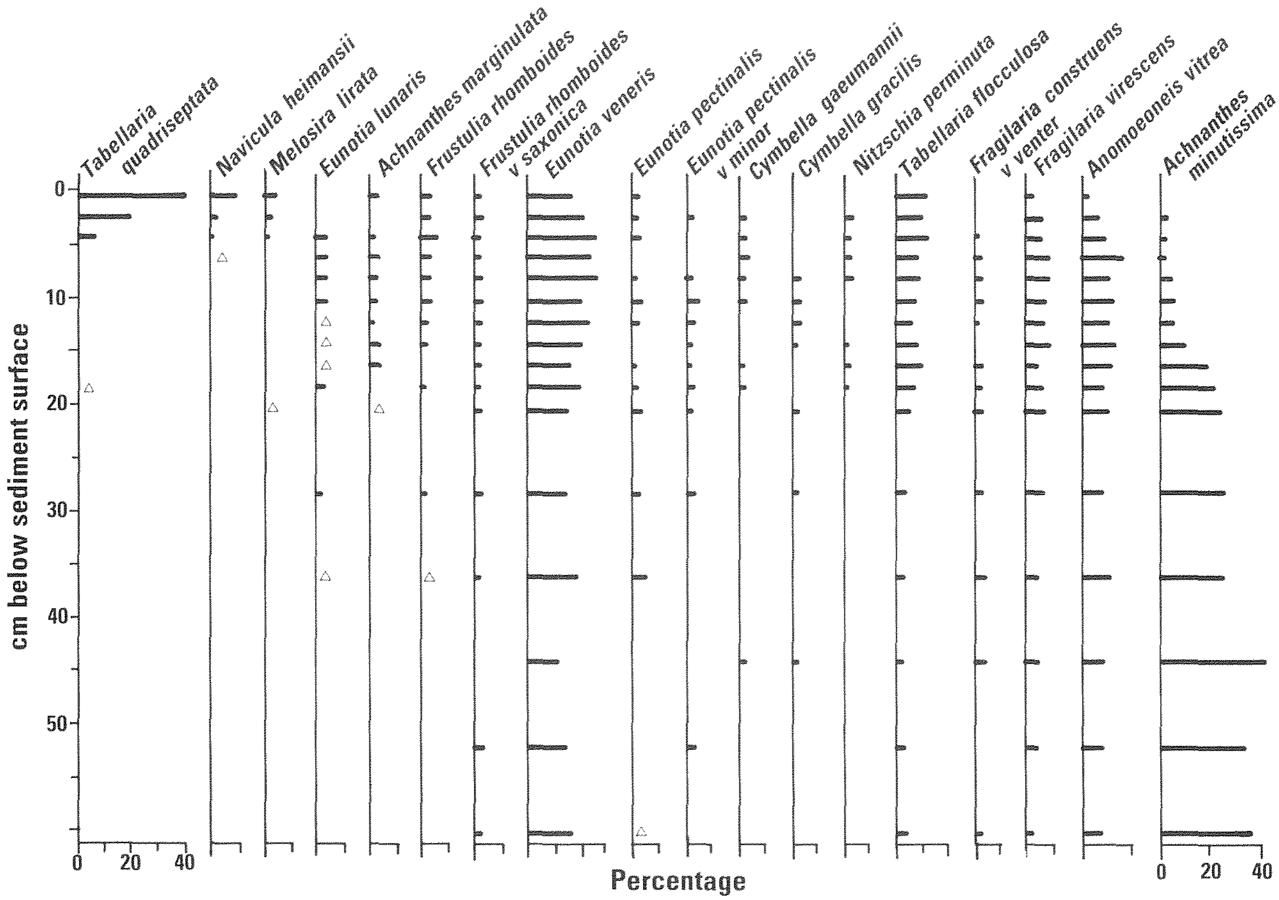


Figure 2.11 Diatom diagram for Llyn Llagi showing changes in dominant species.

2.2.5.2 Diatom analysis

Unfortunately fishery history cannot be readily reconstructed from lake sediments but lake sediments contain a wide range of other fossil material derived from various communities and habitats within the lake. Diatoms are especially important because of their usefulness in reconstructing past lake-water pH.

Diatoms occur in lakes in great abundance and diversity, inhabiting a wide range of micro-habitats. Some are adapted to life suspended in the open water (the plankton) whilst others grow attached to plants, stones and sand grains around the margins of the lake. These single-celled algae rapidly multiply in the growing season by vegetative cell division. On death they are transported by wave action to deeper water and accumulate in the sediment. Since they possess resistant siliceous cell walls they are preserved in the sediment and form a record of past lake populations. The range of species found in any one lake is strongly influenced by the chemistry of the lake water, especially pH, so diatom assemblages in sediments indirectly record changes in the past pH regime of the lake. Figure 2.11 is an example of a summary diatom diagram showing changes in the abundance of diatom species down a sediment core from Llyn Llagi.

Figure 2.12 shows some of the diatoms commonly found in acid lakes in the United Kingdom. Although detailed ecological information is available for relatively few species, most diatoms can be classified according to their pH distribution. The system used for the last 50 years was developed by Friedrich Hustedt, a German diatomist, as follows (Hustedt 1937–1939):

Acidobiontic	occurring at pH <7 with optimum $<$pH 5.5.
Acidophilous	occurring at pH about 7 with widest distribution at pH <7.
Circumneutral	equally distributed on either side of pH 7 with a circumneutral optimum.
Alkaliphilous	occurring at pH about 7 with greatest abundance at pH >7.
Alkalibiontic	occurring at values $>$pH 7

Over the last few decades (Nygaard 1956, Meriläinen 1967) and especially since 1980 (Renberg and Hellberg 1982, Charles 1985, Davis and Anderson 1985, Flower 1986) this classification system has been developed to allow pH values to be quantitatively reconstructed from diatom assemblages. The approach involves calibrating the ratio of diatom groups in modern samples with modern measured pH and then using this calibration (usually a multiple linear regression equation) to infer the pH of a fossil sample.

In this study both the Index B method of Renberg and Hellberg (1982) calibrated on a modern data-set from Galloway, and a multiple regression equation established by Flower (1986) from the same Galloway data-set have been used. Since this latter equation is a better predictor of pH in very acid conditions it is currently the most preferred method and has been used here for all sites except those in

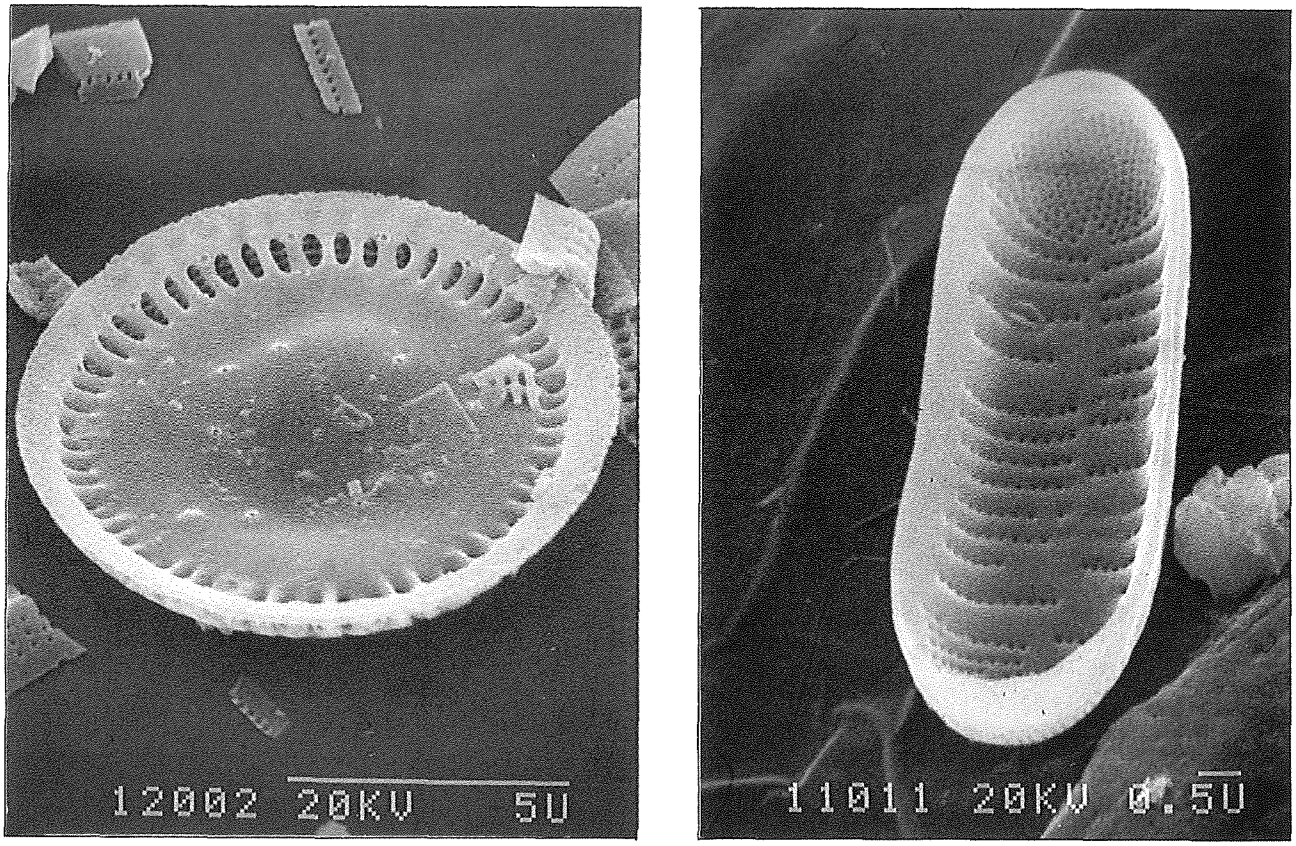


Figure 2.12 Diatoms—*Cyclotella kützingiana* and *Tabellaria binalis*.

Cumbria where the Index B method was used. The equation is as follows:

$$\mathrm{pH} = 7.82 - 0.037 acb_{\%} - 0.035 acp_{\%} - 0.013 ind_{\%} - 0.015 alk_{\%} + 0.1 alb_{\%}$$

where:

$acb_{\%}$ = percentage of acidobiontic taxa

$acp_{\%}$ = percentage of acidophilous taxa

$ind_{\%}$ = percentage of indifferent (circumneutral) taxa

$alk_{\%}$ = percentage of alkaliphilous taxa

$alb_{\%}$ = percentage of alkalibiontic taxa

and

$$r^2 = 0.82 \qquad \mathrm{SE} = \pm 0.36\,\mathrm{pH\ units.}$$

Efforts are continuing to improve diatom-based reconstruction of this nature. It is especially important to expand the calibration data-set to cover the full range of species found in cores. With this in mind a larger United Kingdom data-set is being produced from Welsh and Irish sites and these are being amalgamated with similar data-sets from Norway and Sweden within the SWAP programme. In addition, future reconstructions will be based on more ecologically appropriate non-linear models (ter Braak 1987, Stevenson *et al.* submitted).

2.2.6 Catchment characteristics

Water quality and the flora and fauna of lakes are influenced by their catchments. In studies of lake acidification it is necessary to reconstruct the history of catchments in order to separate possible catchment influences from atmospheric ones. For recent times, the study of documentary records and local interviews are the most useful techniques (Patrick 1987, Stevenson *et al.* 1987a), but changes in the character of the catchment can also be discerned from the geochemical, mineral magnetic, pollen and charcoal records of the lake sediment and from changes in the texture and accumulation rate of the sediment itself.

2.2.6.1 Documentary sources

Certain documentary sources common to investigations in Scotland, Wales and England were used. These include large-scale Ordnance Survey maps, air photographs, estate plans and records, annual parish agricultural returns, diaries and topographies and land utilisation surveys. Other sources are specific to each country, notably Tithe Survey documents (Wales and England) and the 'Statistical Account' editions (Scotland). Personal accounts, particularly by farmers and anglers, provided much important evidence of more recent change.

2.2.6.2 Pollen analysis

The most common technique for indicating vegetation and land-use change from sediment cores is pollen analysis. The method has limitations since some pollen grains are derived from areas beyond the immediate lake catchment and many important pollen groups can only be identified to genus or family level. Nevertheless much useful information can be gained from the trends in abundance of certain groups and the *Calluna*:Gramineae ratio is used here as an index of the relative importance of heathland and grassland in lake catchments. In association with other evidence, these data are used to assess the importance of land-use change in surface water acidification.

The pollen assemblages in recent sediments also record the recent afforestation of upland Britain. The emergence of spruce pollen and the expansion of pine pollen in the pollen diagrams have been useful adjuncts to the establishment of sediment chronologies. In some cases the lack of a forest expansion zone at the top of a core has been helpful in identifying cores with disturbed accumulation patterns.

Pollen analysis was carried out at all sites. Standard techniques were used for preparation and counting (Birks and Birks 1980) and identification follows Moore and Webb (1978). Pollen concentrations were established using the *Lycopodium* tablet technique (Stockmarr 1971). Detailed pollen percentage diagrams are available for all sites and are presented in individual site reports (Appendix 1).

2.2.7 Atmospheric contamination

Lake sediments record changes in atmospheric contamination in a variety of ways. In some cases the relative contributions of catchment and atmospheric sources are not clear and in others post-depositional processes modify the stratigraphic accuracy of the record. However, the range of independent techniques available is sufficiently large for most ambiguities to be resolved. In this study we have used trace metal, sulphur, polycyclicaromatic hydrocarbon (PAH), carbonaceous particle and magnetic mineral analysis.

2.2.7.1 Trace metals and major cations

The trace metal record in older lake sediments is derived from the catchment, but, since the latter part of the eighteenth century, there has been an increasing contribution from atmospheric contamination. The atmospheric flux is especially responsible for large increases in the concentration of lead, zinc, cadmium and copper in sediments.

For analysis of trace metals and major cations (calcium, magnesium, potassium, sodium, iron, manganese) accurately weighed samples of dry sediment were digested using hydrofluoric, nitric and perchloric acid. Determinations were carried out using flame atomic absorption spectrophotometry.

Detailed results are available for each site (Appendix 1). In this report only the trends of lead and zinc are given. Lead is especially stable in lake sediments and has the longest contamination record. Zinc contamination usually begins later than lead and often shows a decline in near-surface sediments in acid lakes owing to enhanced mobility of this metal at low pH levels (Norton 1986).

2.2.7.2 Sulphur

Before this study began it was hoped that the progressive increase in sulphate concentrations in surface waters in areas of high acid deposition would be reflected by increases in the concentration of total sulphur in sediments, paralleling the increases in trace metals. This view was based on observations that sulphate reduction at the sediment surface was an important process in removing sulphur from the water column and accounting for the permanent accumulation of sulphur in sediments (Cook and Schindler 1983, Rudd *et al.* 1986, Schindler 1986).

However, the extent to which the total sulphur profile from a sediment core accurately reflects the historical trend of sulphur deposition depends on the effectiveness of this process and on the extent to which sulphur in the sediment is re-mobilised by chemical and biological diagenesis and transported through the sediment pore water in response to vertical diffusion gradients (Holdren *et al.* 1984).

The sulphur record in cores examined so far is poor. Despite clear lead and zinc increases at two Welsh sites, Llyn Hir and Llyn Gynon, (Fritz *et al.* 1986, Stevenson *et al.* 1987b) the sulphur record shows no clear pattern. Since very little sediment was available sulphur analyses were discontinued. No sulphur data are presented in this report.

2.2.7.3 Polycyclicaromatic hydrocarbons (PAH)

The main sources of PAH at the earth's surface are the combustion of carbonaceous material, contamination by coal or oil, and diagenesis of certain biogenic compounds. Analysis of PAH in cores provides a record of change in the flux and type of fuel combustion products deposited from the atmosphere.

PAH analysis is carried out by solvent extraction and high performance liquid chromatography (HPLC) with fluorescence detection. A number of cores are to be analysed by this method but so far no detailed data are available. Preliminary analyses indicate the presence of PAHs in the top-most sediments of several of the lake cores.

2.2.7.4 Carbonaceous particles

Carbonaceous particles derived from fossil fuel combustion are found in considerable quantity in the upper levels of sediment cores in areas with high acid deposition (Griffin and Goldberg 1981, Renberg and Wik 1984). Detailed scanning electron microscope (SEM) and energy dispersive spectroscope (EDS) analysis shows that most of the particles have a morphology and chemical structure characteristic of oil-derived material (Figure 2.13).

Analysis of these particles has been carried out at all sites following the method of Renberg and Wik (1984). This technique involves slow oxidation of the sample with hydrogen peroxide to remove organic matter, and sedimentation of the resulting suspension on to the floor of a glass petri dish. The supernatant water is allowed to evaporate and the black spherules are then counted using a stereomicroscope at ×40 magnification.

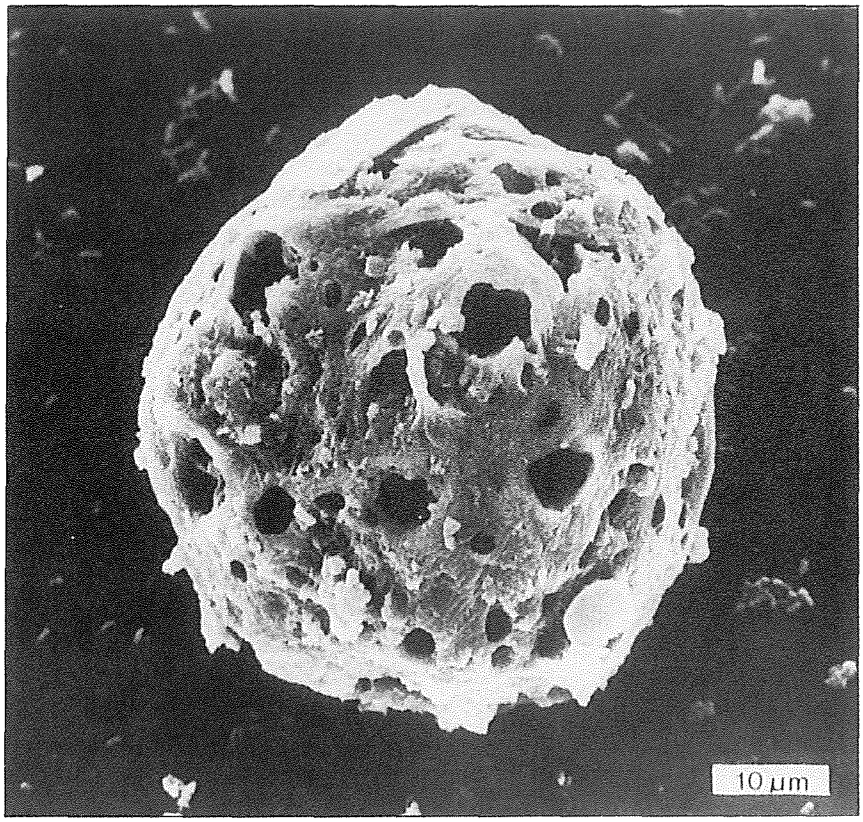


Figure 2.13 Carbonaceous particle.

2.2.7.5 Magnetic minerals

The upper levels of lake sediments contain a record of particulate atmospheric pollution that can be detected by magnetic measurements as long as the background input of magnetic minerals from the catchment is sufficiently low for the atmospheric component to be revealed. The magnetic particles that are extracted from such sediments are predominantly spherical and are identifiable as power station fly-ash.

For magnetic mineral analysis a sequence of non-destructive measurements is adopted (Thompson and Oldfield 1986, Stevenson *et al.* 1987a). Of the measurements used, the one reflecting most reliably the changing concentrations of multidomain 'soft' magnetite of the type dominating the magnetite properties of fly-ash particles, is $SIRM - IRM_{-20\,mT}$. Samples are magnetised in a Molspin Pulse Magnetiser and measurements are carried out in a Minispin portable slow speed spinner fluxgate magnetometer.

3

Regional Survey: Wales

3.1 Mid Wales

Acid lakes occur in mid and north Wales. In mid Wales three sites were selected, Llyn Hir, Llyn Berwyn, and Llyn Gynon (Figure 3.1). Llyn Hir and Llyn Berwyn were of prime interest since both were very acid (*c*.pH 4.5), fish losses were well documented, and both were to be limed in the spring of 1985 by the Welsh Water Authority (Underwood *et al.* 1987). In addition Llyn Hir has a grassy moorland catchment whilst some 90% of the Llyn Berwyn catchment has been afforested. Llyn Gynon was chosen as a somewhat less acid site (pH 4.9–5.3) with an undisturbed moorland catchment.

3.1.1 Llyn Hir

Llyn Hir lies at an altitude of 435 m in an area which receives rainfall in excess of 2000 mm yr^{-1}. It is an elongated lake which drains a small catchment of 18 ha. The lake has a maximum depth of 8.8 m (Figure 3.2).

Catchment geology is composed of Silurian mudstones and shales; soils are mainly stagnopodzols and stagnohumic gleys. *Nardus stricta* and *Festuca ovina* grassland dominate the catchment vegetation. Other site characteristics are given in Table 3.1.

Until recently Llyn Hir supported a healthy and long-established fish population (Fritz *et al.* 1986). Despite considerable stocking since the early 1960s populations deteriorated, until by 1984 it was virtually fishless. In April 1985 the Welsh Water Authority limed the lake (Underwood *et al.* 1987) but prior to liming the mean pH value was 4.8 (Table 3.2).

In July 1984 a series of short sediment cores were taken from both the south and north basins of the lake (Figure 3.2). Core HIR1 from the south basin was used for the analyses presented here.

^{210}Pb dating of core HIR1 showed a very low, but approximately constant accumulation rate of *c*.1 mm yr^{-1}, except for a period of accelerated sediment accumulation during the latter part of the nineteenth century (>3 mm yr^{-1}).

Diatom analysis of the core indicated that the planktonic species *Cyclotella kützingiana* and non-planktonic taxa characteristic of circumneutral to slightly acid water dominated the diatom flora prior to the nineteenth century. Changes began in the late-nineteenth century as these were progressively replaced by acidophilous species such as *Tabellaria flocculosa* and *Eunotia veneris* and then in the 1940s by *Tabellaria quadriseptata*, an acidobiontic species. At the same time an increase in abundance of a small *Navicula* species took place. Since we have no ecological information for this species it is not possible to reconstruct pH over the last few decades. However, it is clear that in the mid-nineteenth century pH was approximately 6.2 and that there has been a substantial decline since then to the present measured pre-liming pH of 4.8 (Table 3.3).

The trace metal, carbonaceous particle and magnetic mineral records show that there has been a marked contamination of this site by atmospheric pollutants (Figure 3.3). The slight decline in lead values in the uppermost sediment may be due to a decline in atmospheric flux over the last decade whilst the more pronounced decline in zinc values is probably more related to desorption at low pH. The main increase in the carbonaceous particle record occurs from about 1940 reflecting the developing use of oil as a fuel. The magnetic mineral increase occurs about the same time but in this case is more likely to reflect the deposition of fly-ash from coal-fired power stations.

Whilst there is abundant evidence for atmospheric contamination there is little evidence for significant land-use change. Neither pollen analysis (Figure 3.3) nor land-use records indicate a decrease in grazing pressure in the catchment over the last 200 years, and liming and burning have not been practised.

The pH of Llyn Hir has declined by over 1 pH unit since 1850. All the data are clearly consistent with the view that the acidification was caused by acid deposition.

3.1.2 Llyn Gynon

Llyn Gynon lies somewhat to the south-east of Llyn Hir at a similar altitude (420 m). It is a remote site draining to the east into the Claerwen Reservoir. The lake occupies a broad, irregular basin with a maximum depth of 11 m (Figure 3.2).

Catchment geology, as at Llyn Hir, consists of Silurian mudstones and shales. Soils and vegetation are also similar although the catchment of Llyn Gynon has more peaty soils characterised by *Molinia/Eriophorum* vegetation. *Festuca/Nardus* areas are restricted to better drained slopes where soils are stagnopodzols and stagnohumic gleys. Other characteristics are given in Table 3.1

The mean pH of Llyn Gynon of 5.2 is somewhat higher than that for Llyn Hir (Figure 3.2). The lake still supports a wild brown trout population and has not been stocked within living memory.

Cores from this site (Table 3.2) were collected during May 1985 using a mini-Mackereth corer. Core GYN3 was used for the analyses presented here. ^{210}Pb analysis of the core showed sediment accumulation rates for the nineteenth century of approximately 1 mm yr^{-1} and for the twentieth century of between 2 and 3 mm yr^{-1} The lower rate for older sediments is largely the result of sediment compaction. A small kink in the profile between 9.75 and 11.75 cm depth

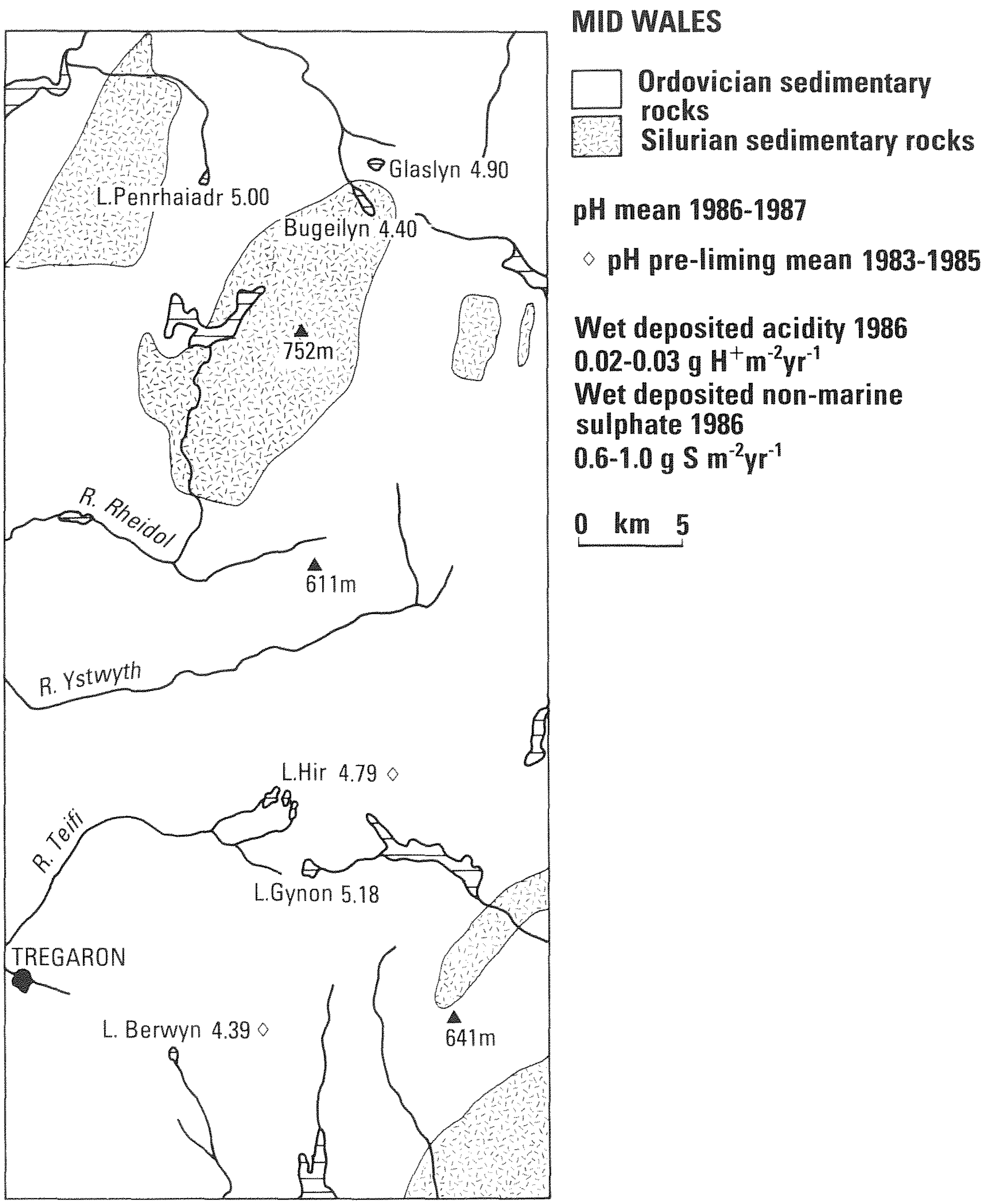


Figure 3.1 Map of mid Wales, showing core sites.

showed a slight disturbance in the accumulation pattern around 1930.

Unlike Llyn Hir the diatom record shows that planktonic diatoms were absent from Llyn Gynon over the last few centuries. However, non-planktonic taxa are very similar to those from Llyn Hir and these dominated the flora until about 1945 when an expansion of acidobiontic species including *Tabellaria quadriseptata* and *Navicula madumensis* occurred. pH reconstruction indicates a fall in pH of about 0.5 from 6.0 to 5.5 (Table 3.3). The reconstructed pH of 5.5 for the surface sediment at this site is somewhat higher than the measured mean pH of 5.2 owing to the unusually high abundance of *Fragilaria virescens* in the uppermost sediment.

The trace metal chemistry of the core shows contamination since the beginning of the nineteenth century (Figure 3.4). Carbonaceous particle contamination also occurs during the nineteenth century although the main increase in concentration occurs from about 1940 onwards in parallel with the acidification trend. This pattern is the same as for Llyn Hir, and in the absence of any notable land-use change in the catchment, acid deposition is the only

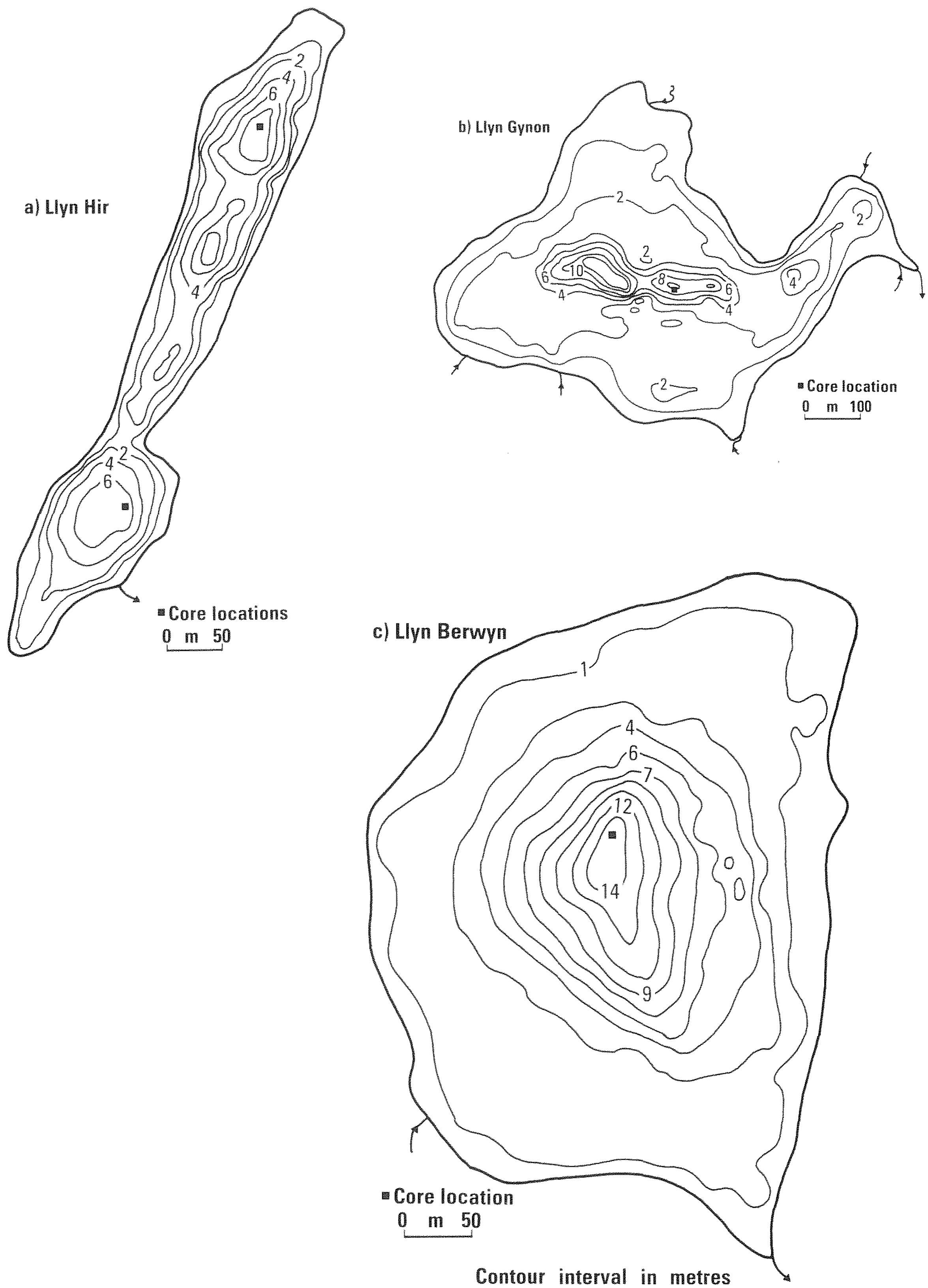


Figure 3.2 Bathymetric maps of ***a*** Llyn Hir, ***b*** Llyn Gynon and ***c*** Llyn Berwyn showing the core locations.

Table 3.1 **Mid Wales — site characteristics**

	L. Hir	L. Gynon	L. Berwyn
Grid reference	SN 789675	SN 800647	SN 743568
Core date	July 1984	May 1985	July 1984
Catchment geology	Silurian sedimentary	Silurian sedimentary	Silurian sedimentary
Catchment type	moorland	moorland	conifers/ moorland
Lake altitude (m)	435	420	438
Max. depth (m)	8.8	11.0	14.0
Mean depth (m)	2.79	2.18	3.25
Lake area (ha)	4.88	25.26	13.04
Volume ($m^3 \times 10^{-6}$)	0.14	0.53	0.42
Catchment area[1] (ha)	17.9	286.2	83.7
Catchment:lake ratio	3.67	11.33	6.42
Afforestation (%)	0	0	90
Net relief (m)	20	110	43

NOTE: [1] Excluding lake.

Table 3.2 **Mid Wales — water chemistry (mean values 1984 – 1987)**

Site	pH mean	pH n	Conductivity$_{25°C}$ $\mu S\ cm^{-1}$	Ca^{2+} $\mu eq\ l^{-1}$	Mg^{2+} $\mu eq\ l^{-1}$	K^+ $\mu eq\ l^{-1}$	Na^+ $\mu eq\ l^{-1}$	Cl^- $\mu eq\ l^{-1}$	SO_4^{2-} $\mu eq\ l^{-1}$	Alkalinity $\mu eq\ l^{-1}$	TOC $mg\ l^{-1}$	Labile Al $\mu g\ l^{-1}$
L. Hir[1]	4.79	22	44.1	46.3	–	8.3	170.1	216.7	120.5	0.00	–	–
L. Gynon	5.18	5	33.6	41.4	54.6	7.2	141.1	164.2	79.3	5.66	3.6	24
L. Berwyn[1]	4.39	26	58.3	41.2	–	6.5	261.5	234.2	165.4	0.11	–	–

NOTE: [1] Pre-liming data.

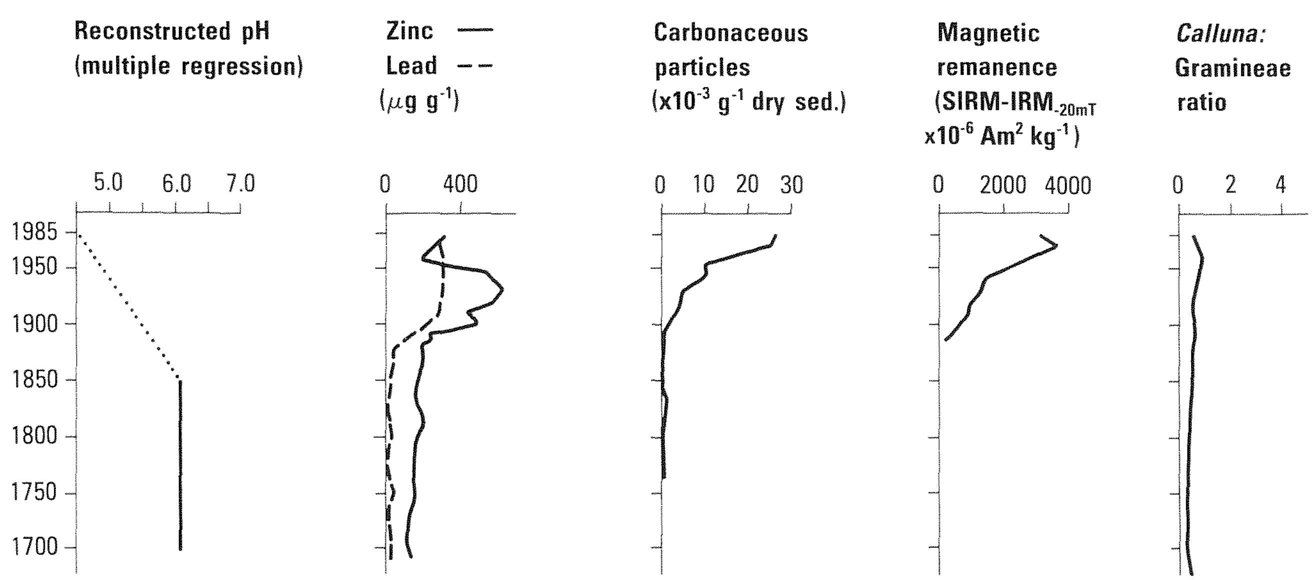


Figure 3.3 Graphs of reconstructed pH, lead, zinc, carbonaceous particles, magnetic remanence ('soft magnetite') and *Calluna*:Gramineae ratio for Llyn Hir.

plausible cause for the acidification at this site.

These data show that the acidification of Llyn Gynon has occurred relatively recently compared with Llyn Hir, despite its similar history of atmospheric contamination. Since there has been no liming and no significant burning in the catchment the lack of an early response to acid deposition at this site indicates a somewhat greater degree of neutralising capacity in the Gynon catchment.

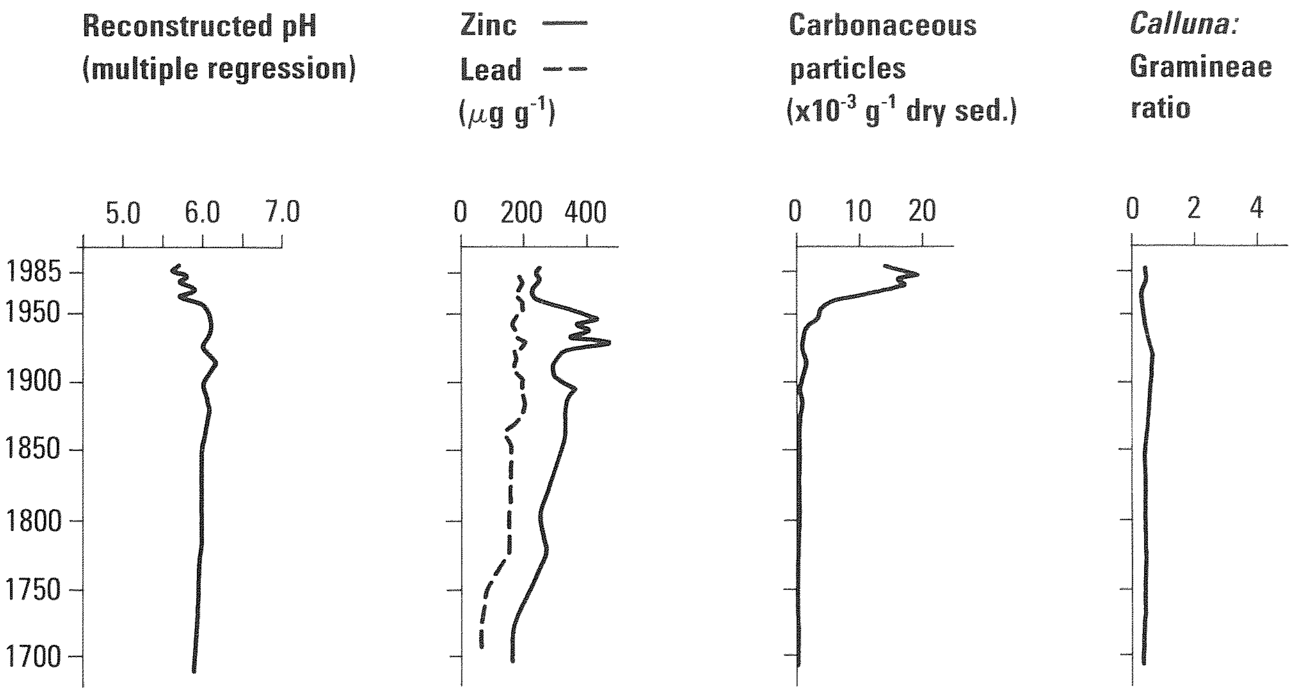


Figure 3.4 Graphs of reconstructed pH, lead, zinc, carbonaceous particles and *Calluna*:Gramineae ratio for Llyn Gynon.

Table 3.3 **Mid Wales — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
L. Hir	SN 789675	4.8[1]	1984	6.1	–	1850	1.3[2]
L. Gynon	SN 800647	5.2	1985	6.0	5.5	1945	0.5
L. Berwyn	SN 743568	4.4[1]	1987		no information yet		

NOTES: [1] Pre-liming data. [2] Calculated using modern measured pH.

3.1.3 Llyn Berwyn

Llyn Berwyn lies at an altitude of 438 m. It comprises a single basin with a maximum depth of 14 m (Figure 3.2) and drains a catchment of 84 ha (Table 3.1). The geology is Silurian siltstones and mudstones as in the case of Llyn Hir and Llyn Gynon. However, owing to the low relief of much of the catchment, soils are dominated by deep peats. Since 1962/3 most of the catchment has been drained and planted with conifer forest. Today, closed canopy forest of sitka spruce (*Picea sitchensis*) and lodgepole pine (*Pinus contorta*) covers approximately 90% of the catchment.

Local observers maintain that a rapid deterioration in the lake fishery took place after 1974, the year many additional deep drainage channels were dug. By the early 1980s the lake only supported a population of eels. The mean pH in 1984 was 4.4 (Table 3.2). In an experiment to provide conditions suitable for trout populations the lake was limed by the Welsh Water Authority in April 1985 (Underwood *et al.* 1987). The lake has since been stocked with brown trout and re-limed to maintain higher pH levels.

Sediment cores were taken in July 1984 from the deepest point in the lake (Figure 3.2). It was hoped that core analysis would help to differentiate between the effect of acid deposition and afforestation processes (including ground preparation) at this site. Unfortunately, the data indicate a hiatus in the core at about 30 cm representing a time gap of at least 150 years and including most of the period immediately prior to afforestation. A range of analyses have been carried out on this core and the results are presented in Kreiser *et al.* (1986). Because of these sedimentological problems no clear conclusions were reached.

The site was revisited in May 1987 and a new core has been taken from a different part of the lake where the sediment record appears more complete. This core has yet to be analysed.

3.2 North Wales — Snowdonia National Park

In the Snowdonia National Park of north Wales acid lakes are common. Here we present data for three groups, those on the Migneint Plateau, those on the Rhinogs, and those in the Snowdonia area itself (Figure 3.5).

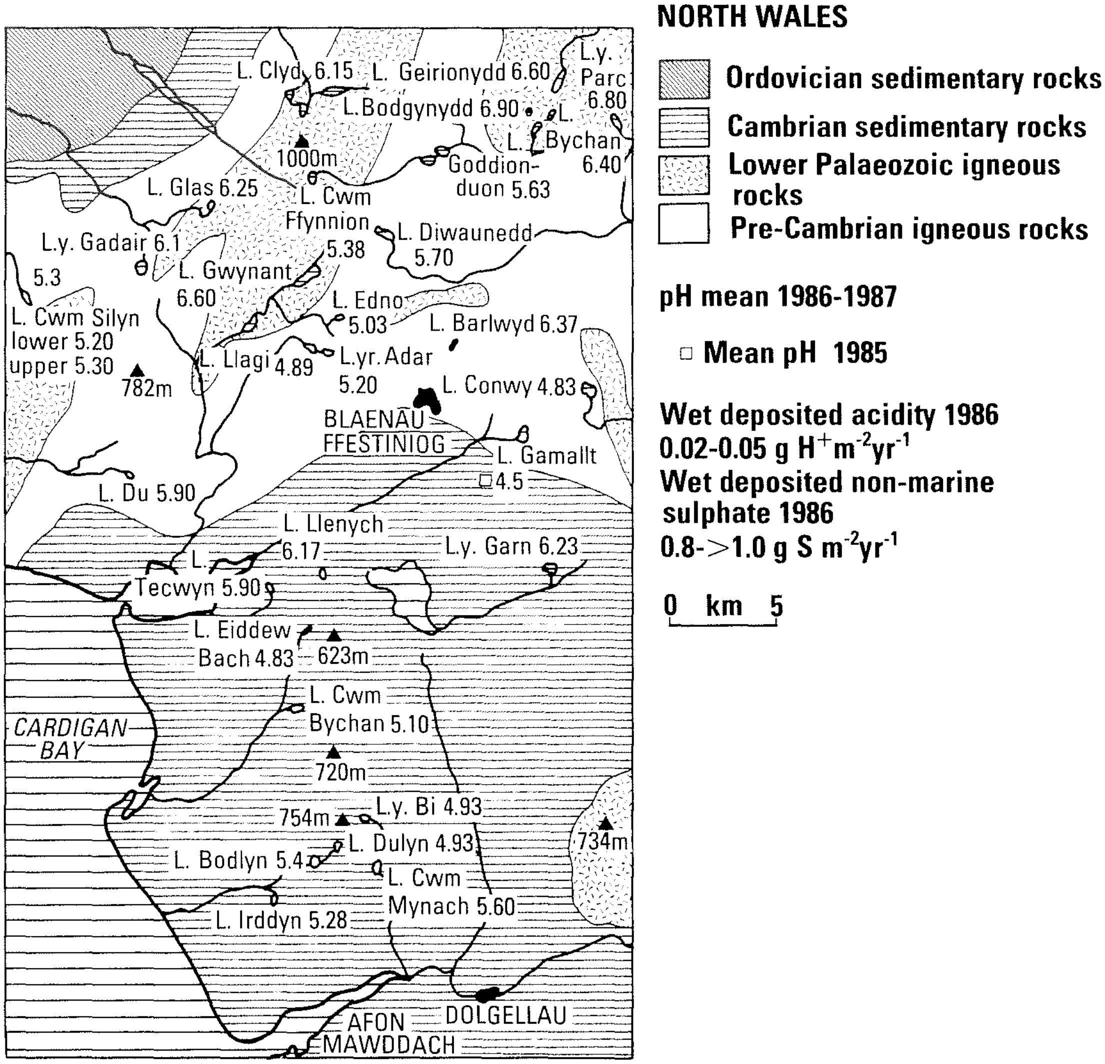


Figure 3.5 Map of north Wales showing core sites.

3.2.1 The Migneint plateau

On the Migneint there are a number of lakes with fishery problems including Llyn Gamallt and Llyn Conwy (Figure 3.5). Unfortunately, exploratory coring showed there to be a lack of suitable sediments in Llyn Gamallt, and in Llyn Conwy organic sediments were not found in the deepest area. This latter site has been revisited and good sediment cores have been obtained from a more marginal location.

Despite the lack of suitable sediment at these sites research into the history of the catchments was carried out since good records of catchment management were available following the transfer of the sites to the National Trust. Although no major land-use change has occurred in their catchments there has been a significant change in land management (Patrick and Stevenson 1986). Until 1970 both catchments were regularly burnt (for grouse at Llyn Conwy and sheep at Llyn Gamallt). Since about 1970 *Calluna vulgaris*, the dominant heathland species has developed into mature woody stands. In addition, peat drainage has occurred in both catchments and Llyn Conwy has been utilised for water supply since 1957.

Of all the lakes studied in Wales none possess such well documented and useful catchment history records as Llyn Gamallt and Llyn Conwy. The potential of these sites for evaluating catchment influences on water acidity using palaeoecological techniques is clear. Work on a core from Llyn Conwy is now taking place and we hope eventually to be able to assess whether the acidification of this site predates the post-1950 changes in its function and ownership.

3.2.2 The Rhinogs

The Rhinogs form a more or less continuous ridge running parallel to the Harlech coast from Ffestiniog to Dolgellau (Figure 3.5). There are a considerable number of lakes in the area and almost all have pH values below 5.5. Llyn y Bi (non-afforested) and Llyn Cwm Mynach (afforested)

Table 3.4 **Rhinogs — site characteristics**

	L. y Bi	L. Dulyn	L. Eiddew Bach	L. Cwm Mynach
Grid reference	SH 670265	SH 662244	SH 646345	SH 678238
Core date	May 1985	August 1985	August 1985	May 1985
Catchment geology	Cambrian sedimentary	Cambrian sedimentary	Cambrian sedimentary	Cambrian sedimentary
Catchment type	moorland	moorland	moorland	conifers / moorland
Lake altitude (m)	445	535	380	285
Max. depth (m)	3.0	6.8	8.7	11
Mean depth (m)	1.6	1.9	2.8	0.9
Lake area (ha)	2.7	1.97	1.37	5.89
Volume ($m^3 \times 10^{-6}$)	0.04	0.04	0.04	0.05
Catchment area[1] (ha)	45	51.7	10.9	152.5
Catchment:lake ratio	16.6	26.1	7.9	25.9
Afforestation (%)	0	0	0	51.3
Net relief (m)	120	80	20	395

NOTE: [1] Excluding lake.

Figure 3.6 Llyn y Bi.

were surveyed and cored in May 1985. Llyn Dulyn and Llyn Eiddew Bach were surveyed in May 1985 and cored in August 1985. A further site in this area, Llyn Irddyn, was cored in May 1987. All sites are on the Cambrian sandstones and greywackes.

3.2.2.1 Llyn y Bi

Llyn y Bi (Figure 3.6) lies at an altitude of 445 m (Table 3.4). It is a small, shallow (3 m), almost circular corrie lake on the eastern side of the Rhinogs (Figure 3.5). The mean pH of the lake is 4.9 (Table 3.5). Although pre-war records indicate that the lake contained good stocks of arctic char and brown trout (Ward 1931), and the remains of an old boat-house are present on the north-east shore, the lake is now virtually fishless.

Catchment geology consists of Cambrian greywackes and the soils are acid humic rankers. The steep backwall behind the lake is dominated by bare rock, but the more gentle slopes are covered by mature *Calluna vulgaris*. The catchment is grazed by sheep but the frequency of burning has declined considerably since the site was acquired by the National Trust in the early 1930s.

Cores were taken from the centre of the lake (Figure 3.7) in May 1985 using a modified Livingstone corer and core YBI2 was chosen for analysis.

^{210}Pb dating of the YBI2 core showed that the sediment accumulation rate at this site was exceptionally slow (0.3 mm yr^{-1}) between 1850 and 1940. An increase to 0.6–0.9 mm yr^{-1} for sediments post-dating 1940 is partly the result of an acceleration in net dry mass accumulation rates. Because of this low accumulation rate the record for the last 150 years is held entirely within the top 5 cm of sediment and the 0.5 cm slices used in this study cover between approximately 10–15 years each. The temporal resolution of the core record at this site is hence very low and consequently the dates have a considerable standard error.

The diatom record of core YBI2 gives a striking record of acidification (Fritz *et al.* 1987) as the entire diatom assemblage changes in the top 4 cm (*c.*1900–1985). Below 4 cm (before *c.*1900) the flora is dominated by circumneutral and acidophilous species including *Achnanthes minutissima*, *Anomoeoneis vitrea*, *Fragilaria virescens* and *Eunotia veneris*. The first sign of acidification occurs at the 4–5 cm level (*c.*1870–1900), above 4 cm this flora is replaced by *Navicula heimansii*, *Tabellaria binalis* and a range of other acidophilous and acidobiontic taxa. Only *Eunotia veneris* is common to the two periods. pH reconstruction from these changes (Figure 3.8) indicates that prior to 1900 pH was stable at about 5.8–6.1 but fell by over 1 pH unit between 1900 and the present day (Table 3.6).

The trace metal contamination of the lake began about 1800 with a lead increase, followed later by zinc. Carbonaceous particle and magnetic mineral contamination are clearly recorded in twentieth century sediments. Since the acidification at this site began well before the acquisition of the lake by the National Trust in the 1930s and was occurring when the catchment was regularly burnt for grouse shooting (Fritz *et al.* 1987) it is clear that the onset of acidification was not caused by land management changes. However, the extent to which the decline of burning after 1930 contributed to the continuing acidification of the lake is not known and cannot be assessed from these data.

3.2.2.2 Llyn Dulyn

Llyn Dulyn is a small upland corrie lake lying at an altitude of about 520 m on the western slopes of the Rhinogs (Figure 3.5). The lake basin has an irregular shape and the maximum water depth of 6.8 m is situated towards the northern end (Figure 3.7). There are extensive aquatic macrophyte beds in the shallow margins (Stevenson *et al.* 1987c). The lake is fed by two small inflow streams and drains to the west to Llyn Bodlyn.

The lake has a pH of 4.9 (Table 3.5). Little is known of its present fishery status since it is a remote lake only irregularly visited by anglers. Ward (1931) reported the lake to be full of fine trout and there are nineteenth century records of a char population (Fisher 1917).

The catchment geology consists of Cambrian greywackes, siltstones and sandstones. The soils vary from acid humic rankers to acid stagnohumic gleys and amorphous blanket peats depending on slope and drainage. Vegetation is dominated by moorland species with *Vaccinium*/*Festuca* communities in the drier areas and *Eriophorum vaginatum*/*Juncus squarrosus*/*Sphagnum* communities on the blanket peats. Other site details are given in Table 3.4.

Cores were taken from the deepest point (Figure 3.7) using a modified Livingstone corer in August 1985. Core DUL1 was used for the analyses presented here.

^{210}Pb dating showed that sediment accumulation rates were less than 1 mm yr^{-1} until the 1940s, but in the last 40 years rates have accelerated and the present accumulation rate is >3 mm yr^{-1}.

Prior to 1850 (below about 18 cm) diatom assemblages in the core were dominated by the circumneutral taxa *Achnanthes minutissima*, *Anomoeoneis vitrea* and *Fragilaria virescens*. Planktonic taxa are absent throughout the core. The first indication of acidification is the decline of *Achnanthes minutissima* and *Anomoeoneis vitrea*, a change seen at many other sites. However, the acidophilous species that expand and replace these taxa are somewhat unusual compared to other sites so far studied in the United Kingdom. *Tabellaria* species are poorly represented and the acid flora is dominated instead by *Melosira distans* and its varieties.

pH reconstruction (Figure 3.9) shows that these floristic changes represent a decline from 5.8–6.2 before 1850 to the present inferred pH of 4.7, a decline of over 1 pH unit (Table 3.6).

The trace metal data for Llyn Dulyn (Figure 3.9) show that the uppermost sediment is strongly contaminated by lead and zinc. But, in contrast to some sites it is not easy to detect the start of contamination, probably because of secondary influences from material eroded from the catchment between 20 and 40 cm. However, it is likely that the first point of contamination occurred between 14 cm and 18 cm, between 1800 and 1850. This interpretation is in agreement with the evidence from carbonaceous particles which occur in mid-nineteenth century sediments. The main expansion of these particles occurs in post-1940 sediments. The magnetic mineral record at Llyn Dulyn also has a clear profile increasing rapidly in the twentieth century and especially after 1940.

No appreciable land-use change has occurred in the catchment since the introduction of sheep by medieval Cistercian monks. The pollen data (Figure 3.9) show no evidence for any increase in heathland species. In view of this and the extent and timing of atmospheric contamination the acidification of this site since 1850 must be primarily related to increases in acid deposition over the last 140 years or so.

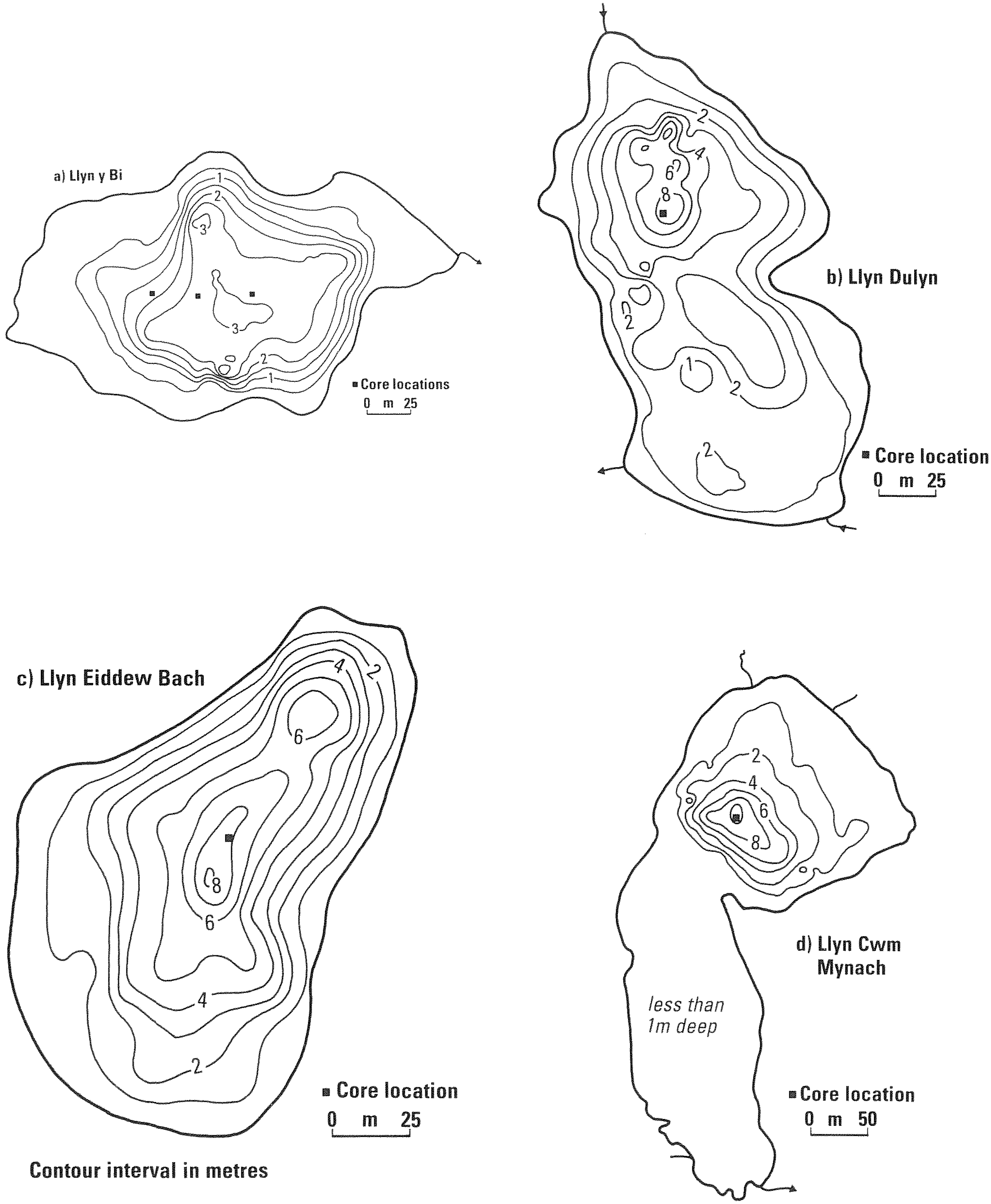


Figure 3.7 Bathymetric maps of ***a*** Llyn y Bi, ***b*** Llyn Dulyn, ***c*** Llyn Eiddew Bach and ***d*** Llyn Cwm Mynach.

3.2.2.3 Llyn Eiddew Bach

Llyn Eiddew Bach is one of the smallest lakes included in this study with a surface area of only 1.4 ha (Table 3.4). It has a maximum depth of 8.7 m (Figure 3.7) and has no distinct inflow streams. Its mean pH is 4.8 (Table 3.5). Little is known of its contemporary fishery status. It is a small lake and rarely fished, but Ward (1931) reported that the trout were of 'fine quality'.

The catchment of Llyn Eiddew Bach is small (10.9 ha) and the bedrock geology mainly comprises Cambrian greywackes. Soils are acid humic rankers and the vegetation is dominated by *Nardus/Festuca* grassland.

The lake was cored using a wide diameter piston corer in August 1985. Core EIB2 was adopted for analysis. Unfortunately, after analysis it was clear that sediment representing accumulation over the last two decades was missing from the top of the core. It is not possible to present a complete picture of changing pH through time, but it is possible to show that a substantial acidification of the lake has occurred over the last 50 years or so. The diatom assemblage in nineteenth and early-twentieth century sediments is dominated by circumneutral and alkaliphilous species and the planktonic species *Cyclotella kützingiana* was abundant. pH reconstruction for this assemblage is over 6.0. The upper 2 cm of the core show the beginning of acidification, with the decline in *Cyclotella kützingiana* and *Fragilaria construens* var. *venter*. Since this sediment is contaminated by high concentrations of carbonaceous particles the acidification began sometime after 1930. The present mean pH of the lake is 4.8 (Table 3.5) so it can be inferred that there has been an acidification of 1 to 1.5 pH units within the last 50 years at this site.

3.2.2.4 Llyn Cwm Mynach

Llyn Cwm Mynach (Figure 3.10) lies at the southern end of the Rhinogs at an altitude of 285 m. The lake has an irregular outline and comprises two distinct parts: an 11 m-deep basin in the northern half and a shallow shelf dominated by aquatic macrophytes to the south (Figure 3.7). The mean pH of the lake is 5.6 (Table 3.5). 51% of the catchment has been planted with mixed coniferous forest in the period 1967–1973 (Figure 3.11). The remaining unplanted areas consist of either bare rock or *Calluna/Vaccinium* dominated moorland. Prior to afforestation the catchment was grazed by sheep.

Sediment cores were taken from the deepest part of the lake. Core MYN5 was initially selected for analysis. However, ^{210}Pb measurements showed that the ^{210}Pb flux for this core was extremely low and that ^{241}Am, dating from the mid-1960s, was present in the top sample indicating the core was truncated. A second core, MYN1, was found to have a satisfactory ^{210}Pb inventory and this core was therefore adopted for subsequent analyses. This core has a relatively uniform accumulation rate of about 1.1 mm yr^{-1}.

Unlike many afforested sites (Battarbee *et al.* 1985b) ground preparation prior to afforestation in the Llyn Cwm Mynach catchment has not caused soil erosion and an increase in sediment accumulation rate. This is probably because of better natural drainage and the reduced need for deep ploughing at this site.

The diatom assemblages in the core are dominated by circumneutral taxa although two principal circumneutral species *Anomoeoneis vitrea* and *Achnanthes minutissima* decline from 1870 onwards. This decline is accompanied by an increase in the acidophilous taxon *Frustulia rhomboides* var. *saxonica* and acidophilous species within the *Eunotia* genus. A small proportion of acidobiontic taxa have been present since the mid-nineteenth century and these have increased somewhat since 1960.

The pH reconstruction (Figure 3.12) shows that pH was about 6.2 until the 1870s when a slight acidification began. An acceleration in the rate of acidification from the 1930s has resulted in a reconstructed pH of 5.6 for the surface sediments, in good agreement with modern measured pH (Table 3.6).

The trace metal curves (Figure 3.12) show that the beginning of contamination was in the early-nineteenth century. Lead shows a gradual rise whereas there is a more marked increase in zinc in the early-twentieth century followed by a decrease in the uppermost sediment, from about 1970. The higher zinc values at this site compared to nearby sites may be a reflection of better zinc retention at Llyn Cwm Mynach as a result of less acid conditions. The marked decrease may be partly related to increased acidification and partly to a real reduction in atmospheric contamination.

The carbonaceous particle record (Figure 3.12) shows early contamination in the late-nineteenth century and the first part of the twentieth century followed by the characteristic steep increase in concentration after 1940.

51% of the catchment was afforested with Japanese larch (*Larix leptolepis*), lodgepole pine (*Pinus contorta*) and sitka spruce (*Picea sitchensis*) between 1967 and 1973. The remainder of the catchment is moorland and used for rough grazing and has been used as such for at least the last 200 years. Grazing intensity has varied over the years and burning frequency has declined since afforestation began. There were also short-lived small manganese mines in the south-western corner of the catchment. It is unlikely that any of these activities have had a major influence on water quality of the lake although the future effect of the forest is unknown. Since acidification began well before afforestation and the related decline in moorland burning, it is probable that acid deposition is responsible for the present acidity of the lake.

3.2.3 Snowdonia

The geology of the Snowdon area itself is complex and as a consequence the region has varying susceptibility to acidification; there are many high elevation corrie lakes situated on volcanic tuff outcrops with pH values greater than 6.0. However, there are also some very sensitive areas including a small group of lakes south of Snowdon, including Llyn yr Adar, Llyn Edno and Llyn Llagi. Of these Llyn Llagi is included in the present study (Table 3.7). In addition, Llyn Edno has been cored but no data will be available until 1989. Llyn Glas (on Snowdon) and Llyn Clyd (on the Glyders) have also been cored. These have pH values

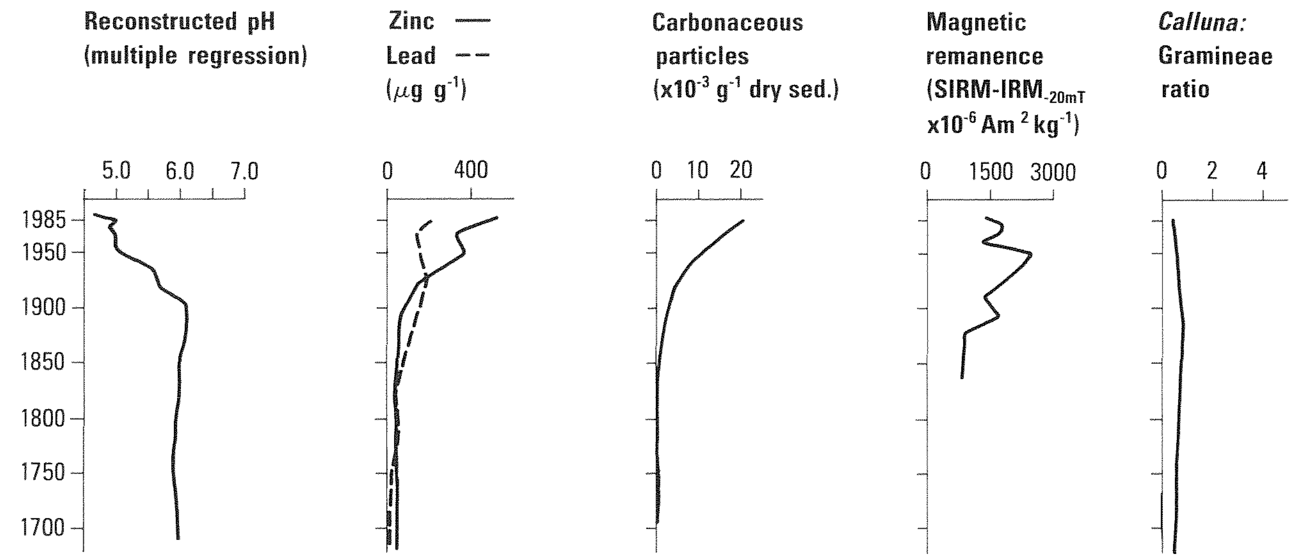


Figure 3.8 Graphs of reconstructed pH, lead, zinc, carbonaceous particles, magnetic remanence ('soft magnetite') and *Calluna*:Gramineae ratio for Llyn y Bi.

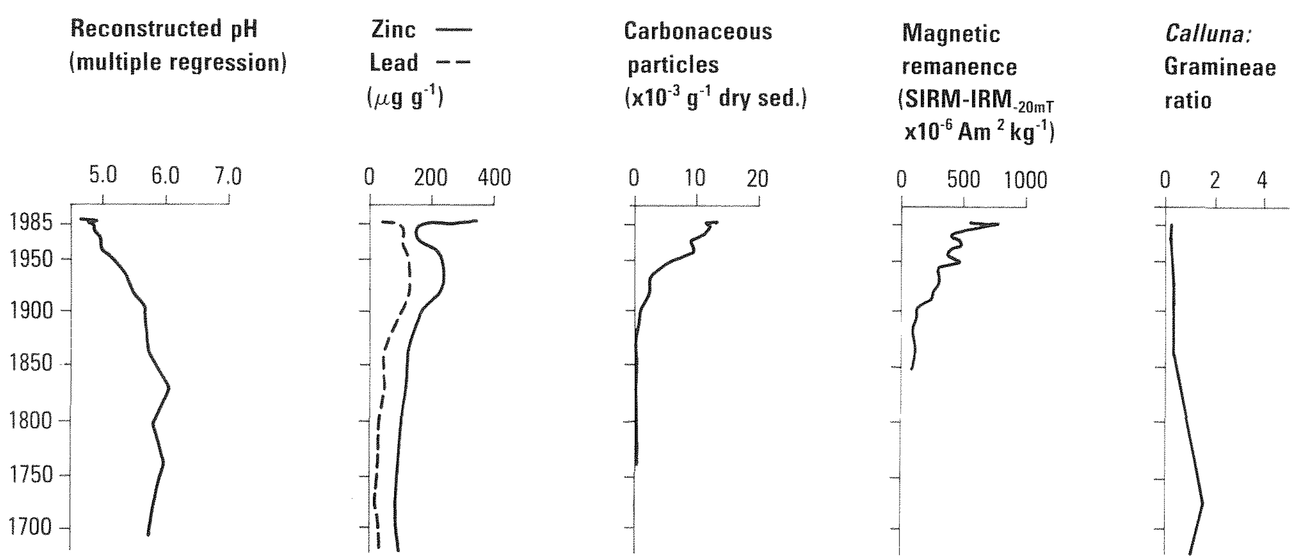


Figure 3.9 Graphs of reconstructed pH, lead, zinc, carbonaceous particles, magnetic remanence ('soft magnetite') and *Calluna*:Gramineae ratio for Llyn Dulyn.

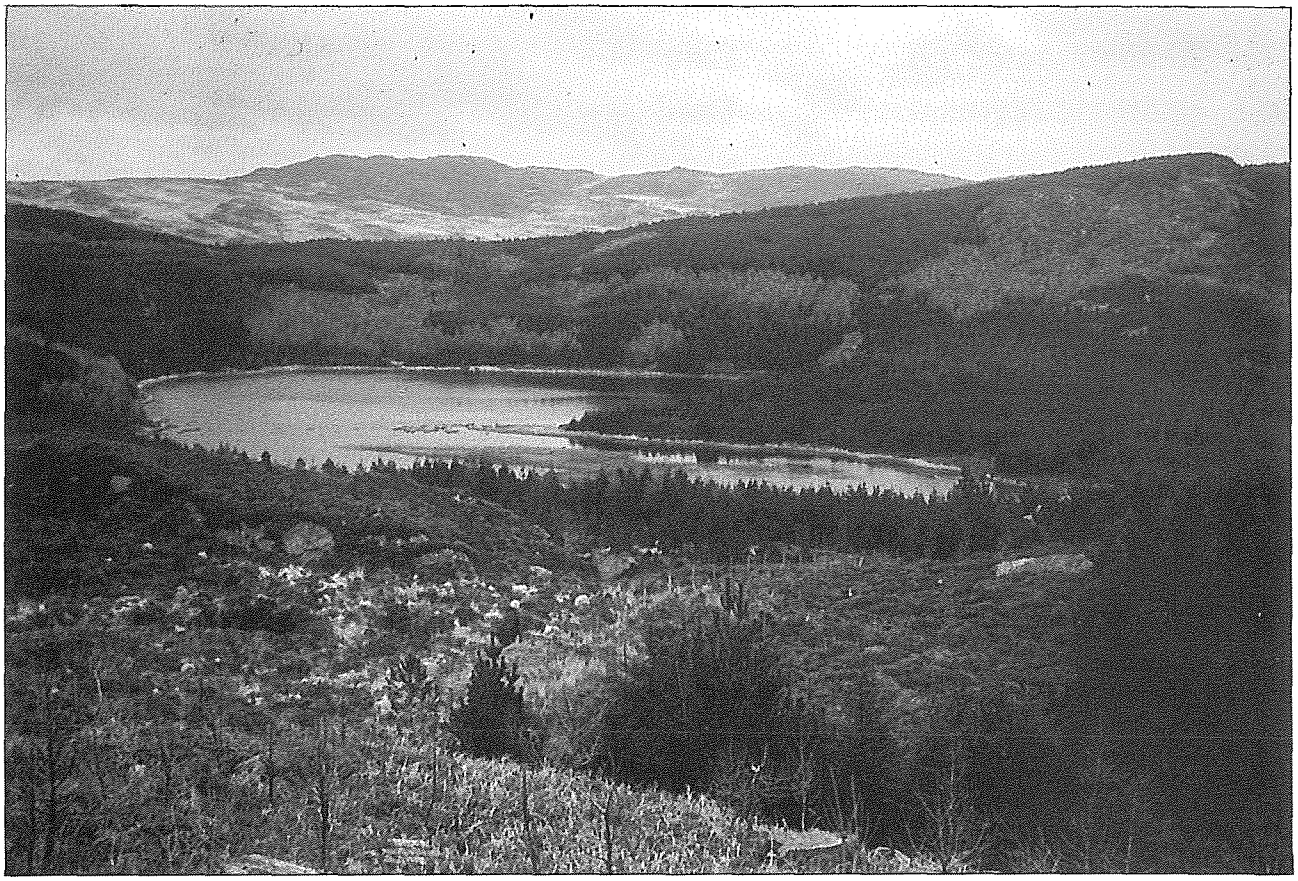


Figure 3.10 Llyn Cwm Mynach.

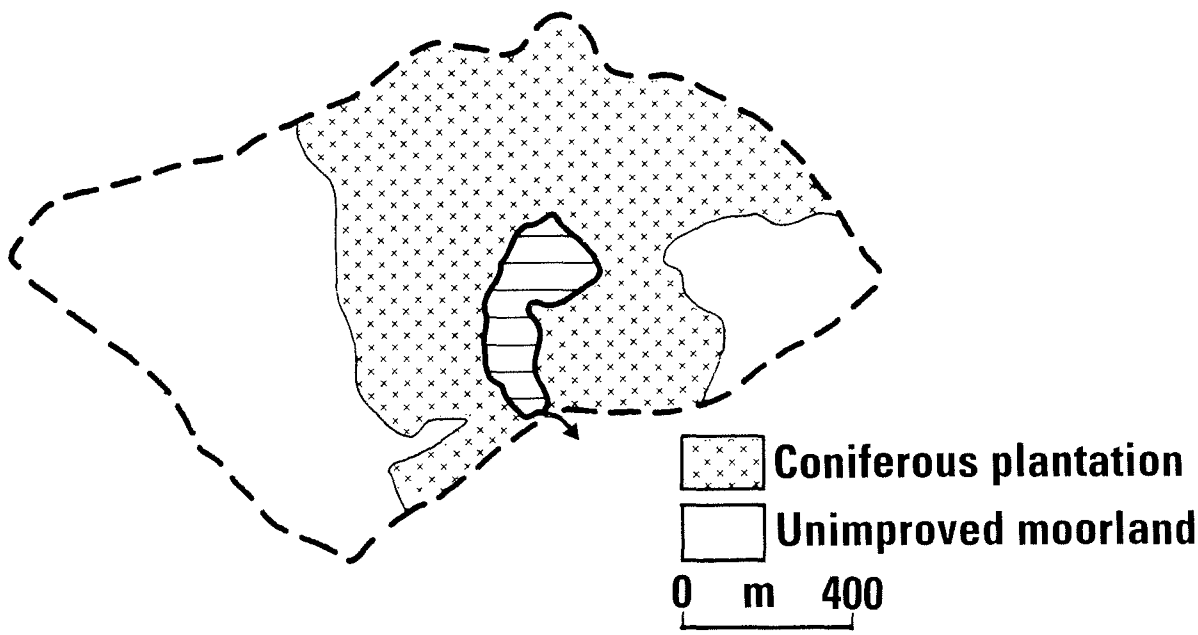


Figure 3.11 Catchment map of Llyn Cwm Mynach.

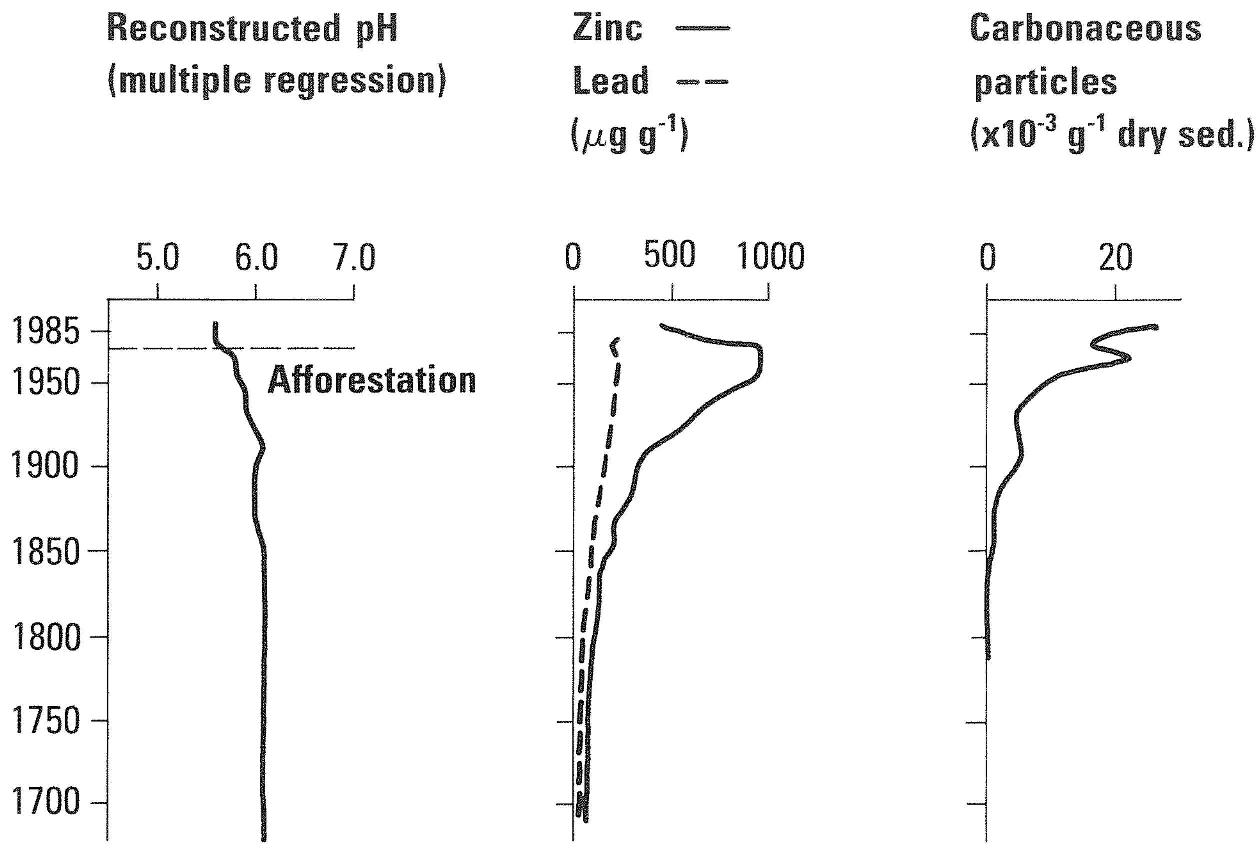


Figure 3.12 Graphs of reconstructed pH, lead, zinc and carbonaceous particles for Llyn Cwm Mynach.

Table 3.5 **Rhinogs — water chemistry (mean values 1985 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ μS cm^{-1}	Ca^{2+} μeq l^{-1}	Mg^{2+} μeq l^{-1}	K^{+} μeq l^{-1}	Na^{+} μeq l^{-1}	Cl^{-} μeq l^{-1}	SO_4^{2-} μeq l^{-1}	Alkalinity μeq l^{-1}	TOC mg l^{-1}	Labile Al μg l^{-1}
L. y Bi	4.93	9	34.0	53.1	57.1	8.1	195.7	225.4	100.4	0.29	1.2	89
L. Dulyn	4.93	9	36.2	49.4	60.5	6.3	189.4	219.4	84.7	1.16	1.5	47
L. Eiddew Bach	4.83	9	38.0	48.0	52.4	7.3	187.2	222.5	90.4	0.00	1.3	86
L. Cwm Mynach	5.60	4	38.8	68.7	48.8	5.2	183.8	211.6	87.9	35.71	1.7	62
L. Irddyn	5.28	4	40.0	60.4	57.6	6.1	194.3	197.5	95.4	2.03	0.9	39

Table 3.6 **Rhinogs — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
L. y Bi	SH 670265	4.9	1985	6.0	4.7	1900	1.3
L. Dulyn	SH 662244	4.9	1985	6.0	4.7	1850	1.3
L. Eiddew Bach	SH 646345	4.8	1985	6.6	–	?1940	1.8[1]
L. Cwm Mynach	SH 678238	5.6	1985	6.1	5.6	1850	0.5

NOTE: [1] Calculated using modern measured pH.

Table 3.8 **Snowdonia — water chemistry (mean values 1985 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ μS cm^{-1}	Ca^{2+} μeq l^{-1}	Mg^{2+} μeq l^{-1}	K^{+} μeq l^{-1}	Na^{+} μeq l^{-1}	Cl^{-} μeq l^{-1}	SO_4^{2-} μeq l^{-1}	Alkalinity μeq l^{-1}	TOC mg l^{-1}	Labile Al μg l^{-1}
L. Llagi	4.89	10	30.8	60.5	47.9	4.2	165.2	198.5	63.1	1.29	2.4	41
L. Edno	5.03	3	28.7	38.1	28.9	5.2	134.4	150.4	59.7	0.00	1.4	54
L. Glas	6.25	4	28.2	71.2	43.4	7.8	130.1	126.9	57.3	33.45	0.3	7
L. Clyd	6.15	4	29.2	55.9	48.0	7.9	123.9	134.0	65.7	33.93	0.5	6

in excess of 6.0. These sites do not appear to be acidified (Table 3.8), but the core material will be used to confirm this and to assess the trace metal and carbonaceous particle records of these sites. Data should be available by late 1989.

3.2.3.1 Llyn Llagi

Llyn Llagi lies at an altitude of approximately 360 m. It is a deep (16.5 m), almost circular lake (Figure 3.13). The main inflow is from an upstream lake, Llyn yr Adar. The mean pH of the lake is 4.9 (Table 3.8). Fish are present in the lake, but few details are known since it is not a popular site for anglers.

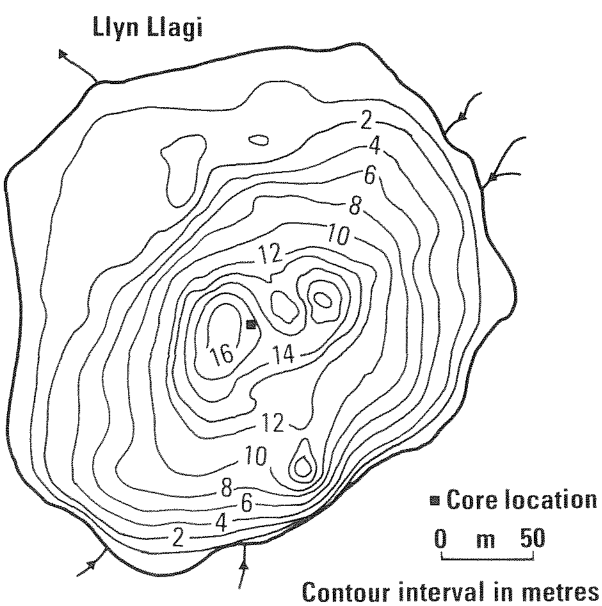


Figure 3.13 Bathymetric map of Llyn Llagi showing core location.

The catchment geology is dominated by Ordovician slates and shales, although the steep backwall is composed of a large doleritic intrusion. Soils are chiefly stagnopodzols and stagnohumic gleys; some patches of amorphous blanket peat also occur. Vegetation varies between *Festuca*, *Calluna*, *Eriophorum*, and *Molinia* dominated communities.

Table 3.7 **Llyn Llagi — site characteristics**

Grid reference	SH 649483
Core date	August 1985
Catchment geology	Ordovician sedimentary
Catchment type	moorland
Lake altitude (m)	380
Max. depth (m)	16.5
Mean depth (m)	5.8
Lake area (ha)	5.67
Volume ($m^3 \times 10^{-6}$)	0.33
Catchment area[1] (ha)	157
Catchment:lake ratio	27.7
Afforestation (%)	0
Net relief (m)	90

NOTE: [1] Excluding lake.

Cores were taken using a mini-Mackereth corer in August 1985. Core LAG1 was used for analysis. A full account of the ^{210}Pb dating of this core is given above (see Section 2.2.4.1). Sediment accumulation rates have not changed significantly (in dry mass terms) over the past 130 years. The reduced volumetric rate of < 1 mm yr^{-1} in the late-nineteenth century compared to the more recent value of 2.5 mm yr^{-1}, is largely a reflection of the greater compaction of older sediments. The last 130–140 years in the core is represented by an accumulation of about 20 cm. As a result environmental changes that have taken place over this time period can be observed in more detail at this site than at other sites in north Wales.

A summary diatom diagram for this site is shown above (Figure 3.10). The diatom-based pH reconstructions suggest that the lake had a pH between 5.9 and 6.2 before 1850 (Figure 3.14). Planktonic diatoms were absent but the flora was dominated by attached circumneutral and acidophilous species. The beginning of acidification in the lake is marked, as at many other sites by the decline of *Achnanthes minutissima* in the late-nineteenth century. An acceleration in the rate of acidification occurred after 1960, indicated by the rapid expansion of *Tabellaria quadriseptata*. A pH decline of approximately 1 pH unit has occurred between 1850 and the present day (Table 3.9).

The core chemistry data (Figure 3.14) demonstrate that trace metal contamination began in the early-nineteenth century. Nineteenth century sediments are also contaminated by carbonaceous particles, although the main increase occurs in post-1940 sediments.

As at most other sites in north Wales there is no evidence for a change in land-use and catchment vegetation that might have caused acidification. The catchment

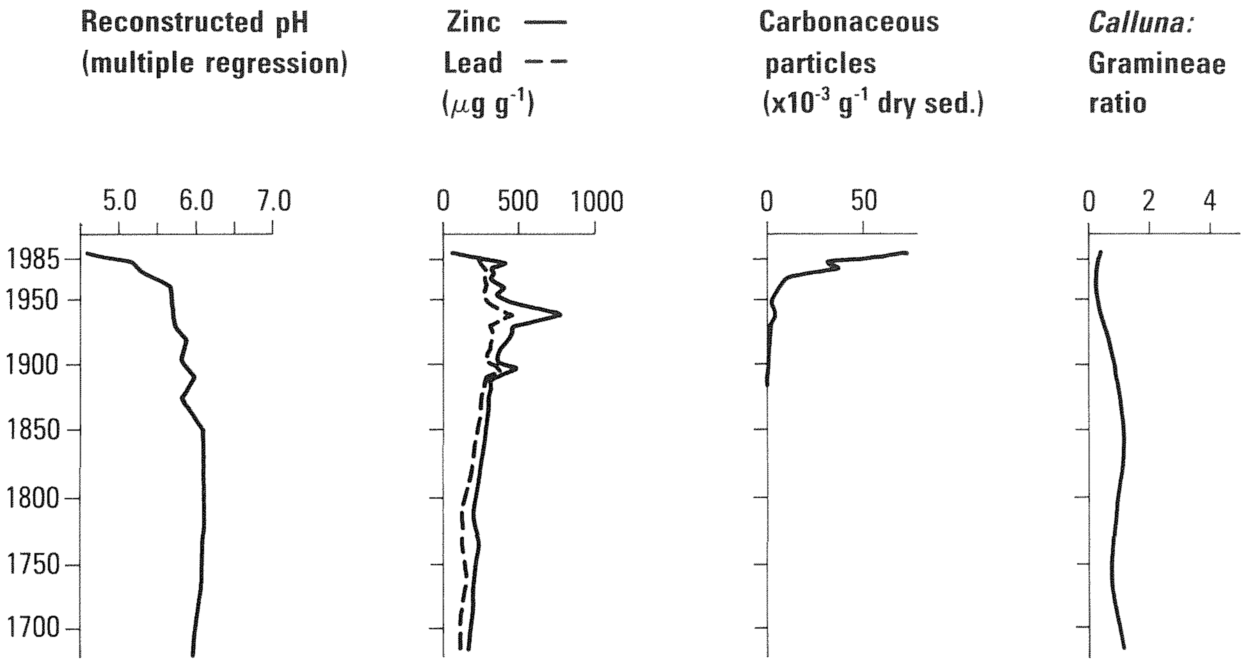


Figure 3.14 Graphs of reconstructed pH, lead, zinc, carbonaceous particles and *Calluna*:Gramineae ratio for Llyn Llagi.

Table 3.9 **Llyn Llagi — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
L. Llagi	SH 649483	4.9	1985	6.1	4.6	1850	1.5

is grazed by sheep and cattle, and pollen evidence (Figure 3.14) suggests there has been a gradual increase in grassland over recent decades.

Since the acidification cannot be accounted for by land-use changes and since the sediments present clear evidence of atmospheric contamination from 1800 onwards, an increase in acid deposition over the last 140 years or so is the only plausible explanation for the acidification at this site.

4

Regional Survey: Scotland

4.1 Introduction

Past research in Galloway (e.g. Flower *et al.* 1987a, and summarised above—Section 1.2) indicated that lakes on granitic rocks were more susceptible to acidification than those with non-granitic geology. Since granitic rocks occur commonly in Scotland four of the five Scottish sites chosen in this study were located on granitic intrusions in areas outside Galloway, keeping geology and catchment land-use constant but varying climate and altitude. In addition one site was chosen within Galloway attempting to keep climate constant but varying catchment geology. Other sites in Scotland (in the Cairngorms and in the Trossachs) have also been sampled with funding from the SWAP programme. Summary data from these sites and from Galloway sites are included here so that as full a picture as possible is presented.

The Scottish sites have been divided into six regional groups: Galloway, Arran, the Trossachs, Rannoch Moor, Lochnagar and the Cairngorms, and the north-west Highlands and Islands.

4.2 Galloway

The choice of a non-granitic site with a moorland catchment in Galloway proved difficult since there are few such sites which have undisturbed catchments. Many have afforested catchments and lowland sites tend to have considerable parts of their catchment under cultivation. Loch Urr was chosen (Figure 4.1, Table 4.1). It is a lake with some improved land and a small amount of forest in its catchment, although most of the catchment is moorland, devoted to rough grazing. Parts of the catchment have also been limed and are still limed periodically. Its present pH is 6.8. It is interesting to compare the sediment record of this site with the strongly acidified lakes nearby.

4.2.1 Loch Urr

Loch Urr lies at 190 m on Silurian sedimentary rocks in the east of the Galloway region (Figure 4.1). The loch covers 52.3 ha, is 13.2 m deep (Figure 4.2) and drains a catchment of 726 ha. It is a slightly acid loch. The concentration of base cations, particularly Ca^{2+} (166.5 μeq l^{-1}) and Mg^{2+} (129.9 μeq l^{-1}) are much higher than in other Galloway lochs which lie in granite catchments (Table 4.2), reflecting the less resistant Silurian geology of this site.

The catchment has a long history of improvement and management for pastoral and arable agriculture through liming, drainage, burning and fertilising. A central area of fields is still actively managed for sown grass. Higher and wetter areas have reverted to rough moorland and some 5% of the catchment is planted with conifers (Figure 4.3).

Table 4.1 **Loch Urr — site characteristics**

Grid reference	NX 760845
Core date	May 1984
Catchment geology	Silurian sedimentary
Catchment type	improved pasture / conifers / moorland
Lake altitude (m)	190
Max. depth (m)	13.2
Mean depth (m)	3.65
Lake area (ha)	52.3
Volume ($m^3 \times 10^{-6}$)	1.67
Catchment area[1] (ha)	725.7
Catchment:lake ratio	13.87
Afforestation (%)	*c.*5
Net relief (m)	52

NOTE: [1] Excluding lake.

The loch was cored using a mini-Mackereth corer in May 1984. Analyses were performed on core URR1.

^{210}Pb dating of the URR1 core showed that the sediment accumulation rate has been approximately constant between 1870 and 1940 at about 1.5 mm yr^{-1}. An increase (in volumetric terms) to over 2 mm yr^{-1} since 1940 is largely a reflection of the reduced compaction of near-surface sediments. The dry mass accumulation rate has changed very little over the past 100 years.

Diatom analysis of URR1 showed the predominance of planktonic species throughout the period represented by the core. The earlier part of the core, prior to the nineteenth century, contains a flora dominated by *Cyclotella kützingiana*, *Cyclotella comensis* and *Achnanthes minutissima*. These species typically occur in oligotrophic, circumneutral to slightly acid lakes. A diatom change occurs between 25 cm and 15 cm depth which corresponds with the nineteenth century period. In contrast to acidified lakes on the adjacent granitic areas where planktonic populations decline, there is an expansion of the plankton at Loch Urr. *Cyclotella pseudostelligera*, *Melosira italica* subsp. *subarctica* and a planktonic form of *Tabellaria flocculosa* increase indicating slight nutrient enrichment of the lake during this period, possibly as a result of agricultural developments in the lake catchment, especially the introduction of regular liming.

The pH reconstruction curve (Figure 4.4) shows that pH prior to 1800 was in the region of 6.5 and rose somewhat in the nineteenth and twentieth centuries to 6.7–6.8. Only three measured pH values for the lake (of 6.0, 6.4 and 7.0) are available and more measurements at different times of year are required to establish a reliable mean value.

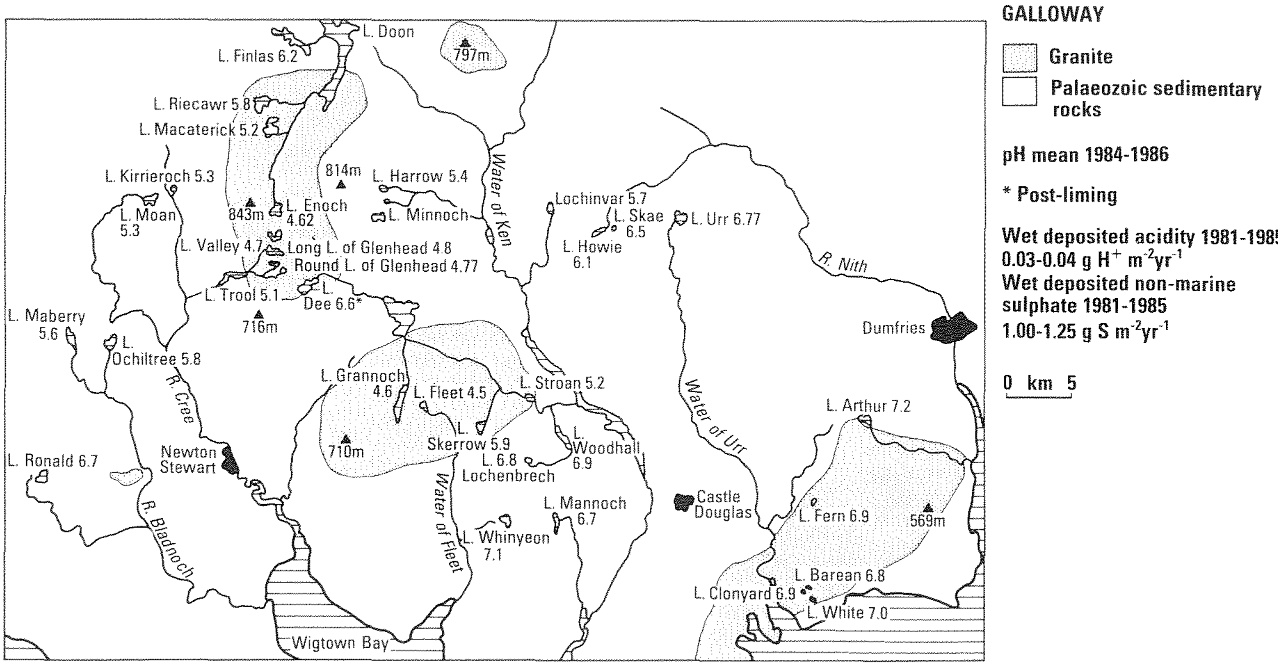


Figure 4.1 Map of Galloway showing the sites, with mean pH.

Nevertheless there is broad agreement with the diatom data and the higher values throughout and the general somewhat upward trend in recent decades is clearly in contrast with declining pH levels and trends in nearby lakes on granitic rocks (Table 4.3).

Trace metal and carbonaceous particle analysis of the Loch Urr sediments show atmospheric contamination of the same kind as at acidified sites (Figure 4.4), which indicates that the lack of acidification at this site is not related to low levels of acid deposition but to effective neutralisation of acidity by catchment soils and groundwater. The lack of an acidification has meant that the efficiency of zinc sedimentation has not been impaired and so the zinc concentration increases towards the sediment surface.

4.3 Arran

On Arran two lakes, Coire Fhionn Lochan and Loch Tanna, which occur on granite (Figure 4.5) were cored. Since sediment characteristics indicated that Loch Tanna had the best record a core from this site was chosen for analysis.

4.3.1 Loch Tanna

Loch Tanna lies at an altitude of 315 m (Table 4.4) in the centre of a granitic intrusion in the north of the island of Arran (Figure 4.5). The lake is very shallow (3 m) for its size (Figure 4.6). It has a modern pH of 5.0 (Table 4.5). In the mid-nineteenth century the loch supported a large trout population which by the 1950s had been greatly depleted.

The whole catchment of the lake lies within the boundary of the granitic area. Blanket peats dominate the catchment and vegetation is characterised by mature *Calluna*, with *Molinia* and *Eriophorum* on the wetter ground.

Table 4.4 **Loch Tanna — site characteristics**

Grid reference	NR 921428
Core date	June 1986
Catchment geology	granite
Catchment type	moorland
Lake altitude (m)	315
Max. depth (m)	3.5
Mean depth (m)	–
Lake area (ha)	32.9
Volume ($m^3 \times 10^{-6}$)	–
Catchment area[1] (ha)	300.4
Catchment:lake ratio	9.14
Afforestation (%)	0
Net relief (m)	406

NOTE: [1] Excluding lake.

The lake was cored in June 1986 using a mini-Mackereth corer. Core TAN1 was used for the analyses presented here.

Loch Tanna is in a region subject to fallout from the Chernobyl accident, and the gamma spectra for core TAN1

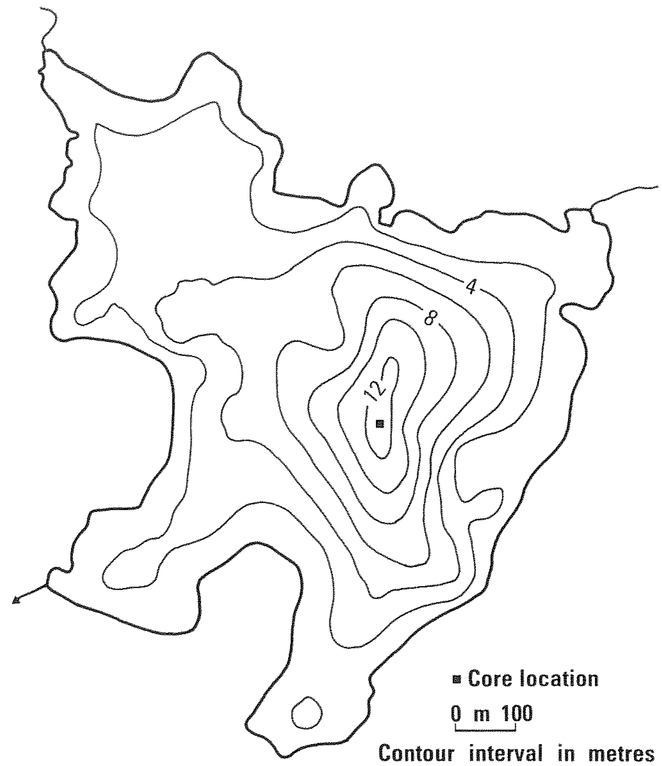


Figure 4.2 Bathymetric map of Loch Urr showing the core location.

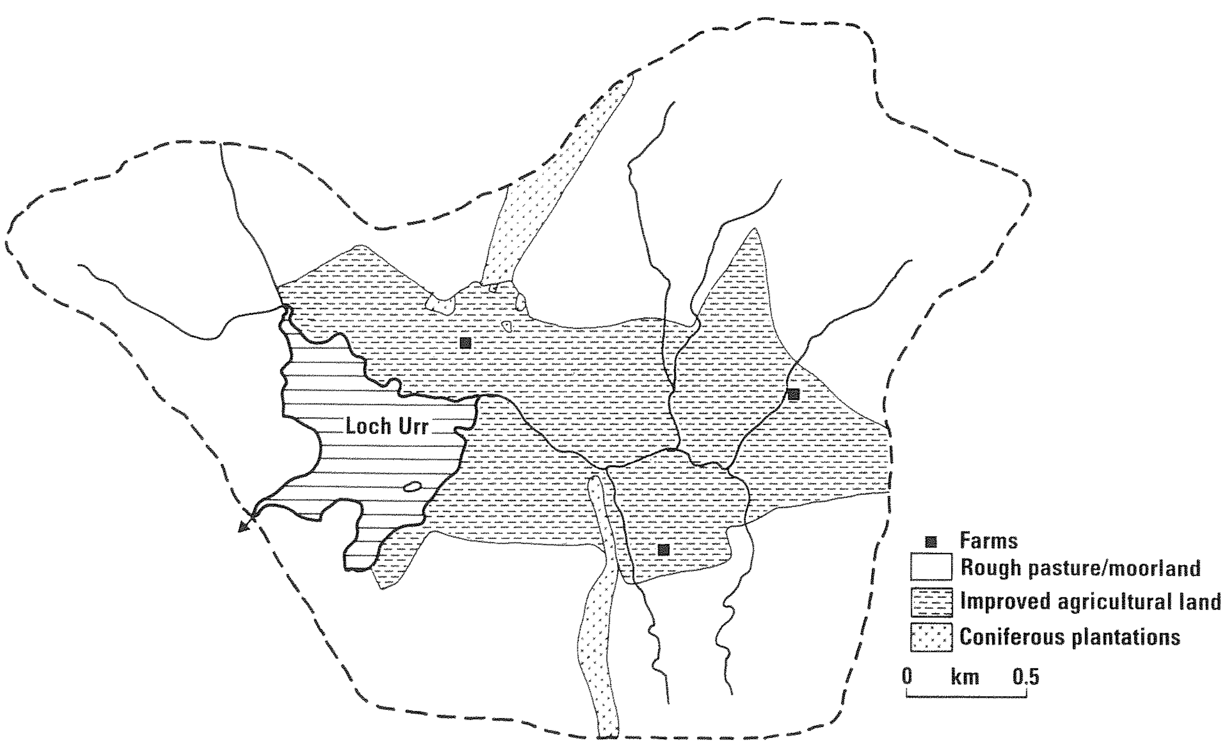


Figure 4.3 Catchment map of Loch Urr.

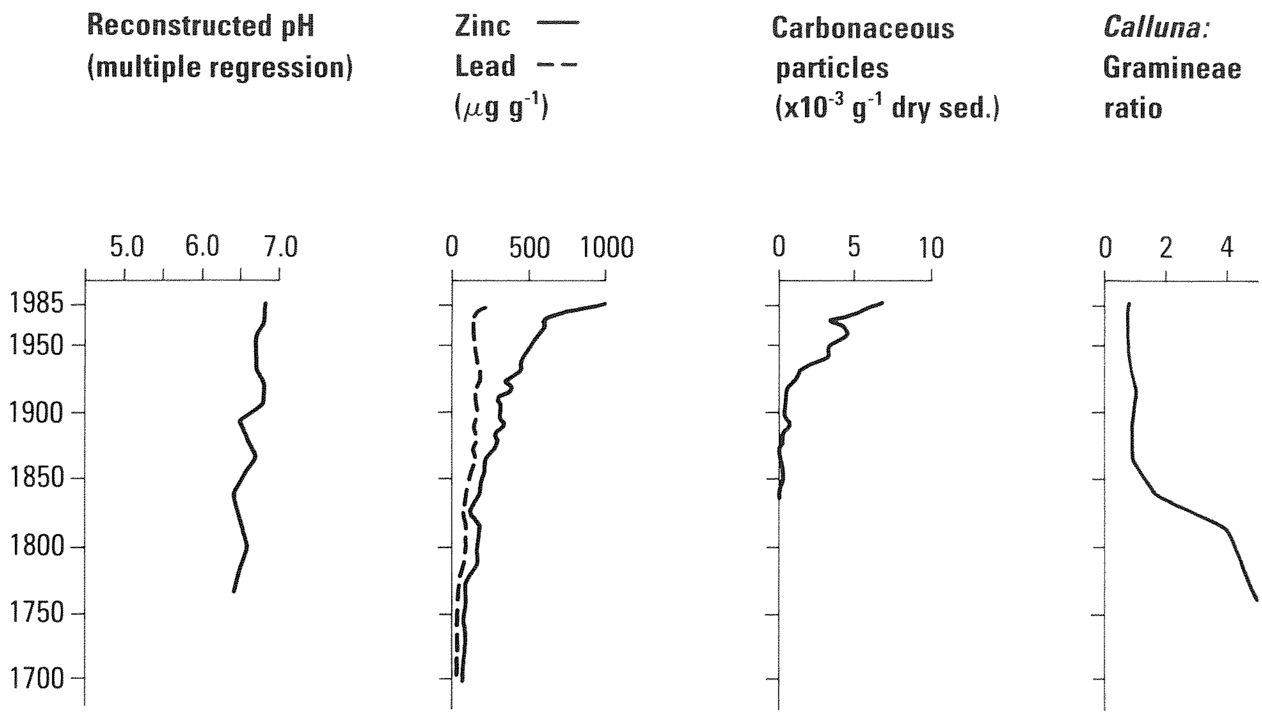


Figure 4.4 Graphs of reconstructed pH, lead, zinc, carbonaceous particles and *Calluna*:Gramineae ratio for Loch Urr.

Table 4.2 **Galloway — water chemistry (mean values 1984–1986)**

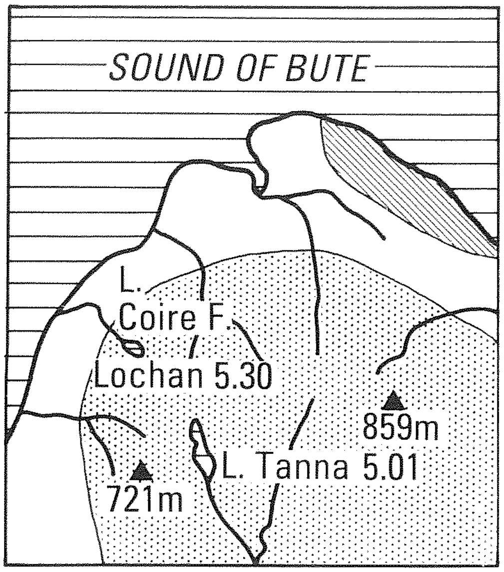
Site	pH mean	n	Conductivity$_{25°C}$ μS cm^{-1}	Ca^{2+} μeq l^{-1}	Mg^{2+} μeq l^{-1}	K^{+} μeq l^{-1}	Na^{+} μeq l^{-1}	Cl^{-} μeq l^{-1}	SO_4^{2-} μeq l^{-1}	Alkalinity μeq l^{-1}	TOC mg l^{-1}	Labile Al μg l^{-1}
On granite[1]												
L. Enoch	4.62	6	40	27	45	8	168	205	72	0	1.0	73
Round Loch of Glenhead	4.77	6	41	41	51	9	191	224	89	0	2.2	61
On Silurian sedimentary rocks[2]												
L. Urr	6.77	3	57.3	166.5	129.9	11.2	181.8	247.3	148.7	60.52	–	–

NOTES: [1] Measured by DAFS Pitlochry. [2] Measured by the Solway River Purification Board.

Table 4.3 **Galloway — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
L. Enoch	NX 446851	4.5	1982	5.3	4.4	1840	0.9
L. Valley	NX 444817	4.7	1981	5.6	4.6	1860	1.0
Round Loch of Glenhead	NX 450804	4.7	1981	5.9	4.9	1860	1.0
L. Dee	NX 466788	5.3	1980	6.2	5.5	1890	0.7
L. Grannoch	NX 542700	4.7	1980	5.7	4.7	1930	1.0
L. Fleet	NX 560698	4.5	1985	5.8	4.6	1975	1.2
L. Skerrow	NX 605682	5.3	1980	5.9	5.8	–[1]	–[2]
L. Urr	NX 760845	6.8	1984	6.5	6.8	–[1]	–[2]

NOTES: [1] Not applicable. [2] Not significant.



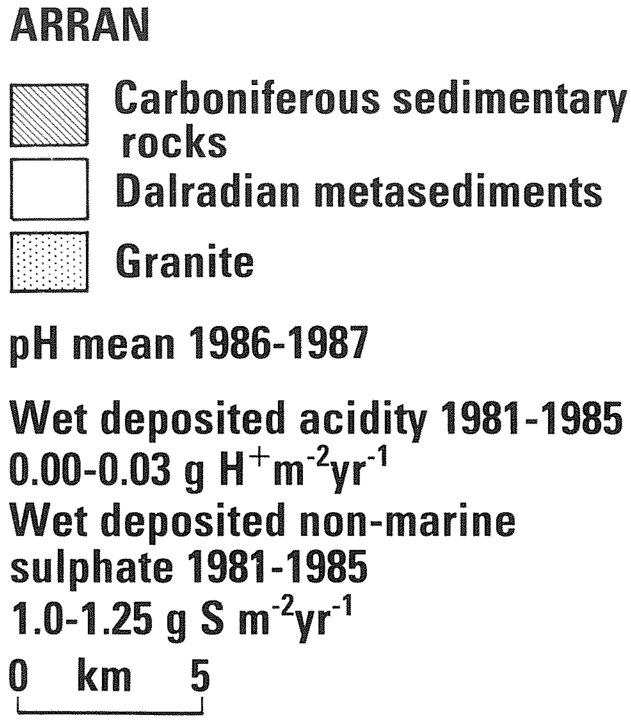


Figure 4.5 Map of Arran showing core sites.

confirmed the presence of very high ^{137}Cs activities in the topmost sediments together with significant concentrations of the short-lived isotopes ^{134}Cs and ^{103}Ru.

^{210}Pb dating of the core showed that the sediment accumulation rate in the late-nineteenth century was very low at <0.5 mm yr-1.. There appears to have been a significant acceleration (in dry mass terms) during the first half of the twentieth century and current accumulation rates exceed 1 mm yr^{-1}.

Diatom analysis of TAN1 showed that prior to 1800 the lake had a relatively unchanging flora dominated by *Anomoeoneis vitrea*, *Eunotia denticulata*, *Navicula heimansii* and *Frustulia rhomboides* var. *saxonica*. These are mainly acidophilous taxa indicating that Loch Tanna was quite an acid lake even before 1800. Despite this naturally acid condition a clear acidification began in the mid-nineteenth century. *Anomoeoneis vitrea* began to decline and several acidophilous and acidobiontic species including *Tabellaria quadriseptata*, *Tabellaria binalis* and *Semiorbis hemicyclus* increased.

pH reconstruction (Figure 4.7) shows a decline from about 5.1 at the beginning of the nineteenth century to 4.6–4.7 in the 1950s and 1960s. The reconstructed pH of 4.7 for the surface sediment compares with a mean measured pH for the lake at present of 5.0 (Table 4.6).

The trace metal trends for this core (Figure 4.7) are not very clear since the usual increase in concentrations of lead and zinc in nineteenth and twentieth century sediments is less marked than at other sites. This is particularly the case for zinc and may be the result of the natural low pH of the lake. However, the carbonaceous particle and magnetic records are typical, showing the expected marked increase in values after 1940.

The Loch Tanna catchment is utilised for low-intensity sheep grazing and the *Calluna*:Gramineae ratio in the sediment shows a reduction over the last century in the relative amounts of heathland species in the area. These data indicate that the acidification was not caused by land-use changes. The timing of the acidification and the presence of high concentrations of carbonaceous particles indicate that acid deposition is the only plausible explanation.

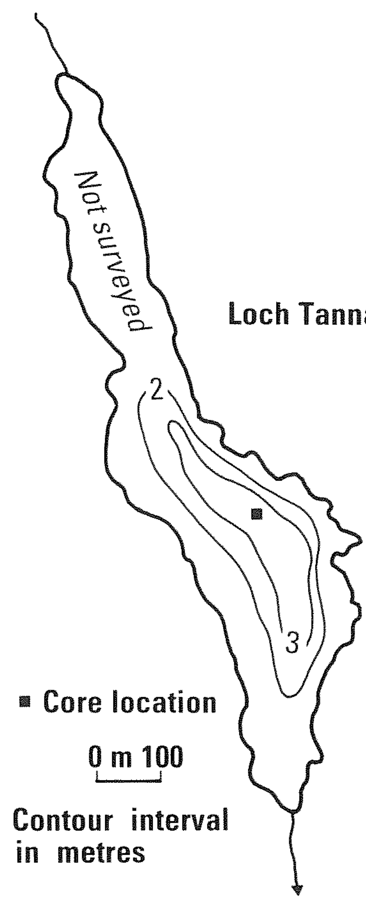


Figure 4.6 Bathymetric map of Loch Tanna showing the core location.

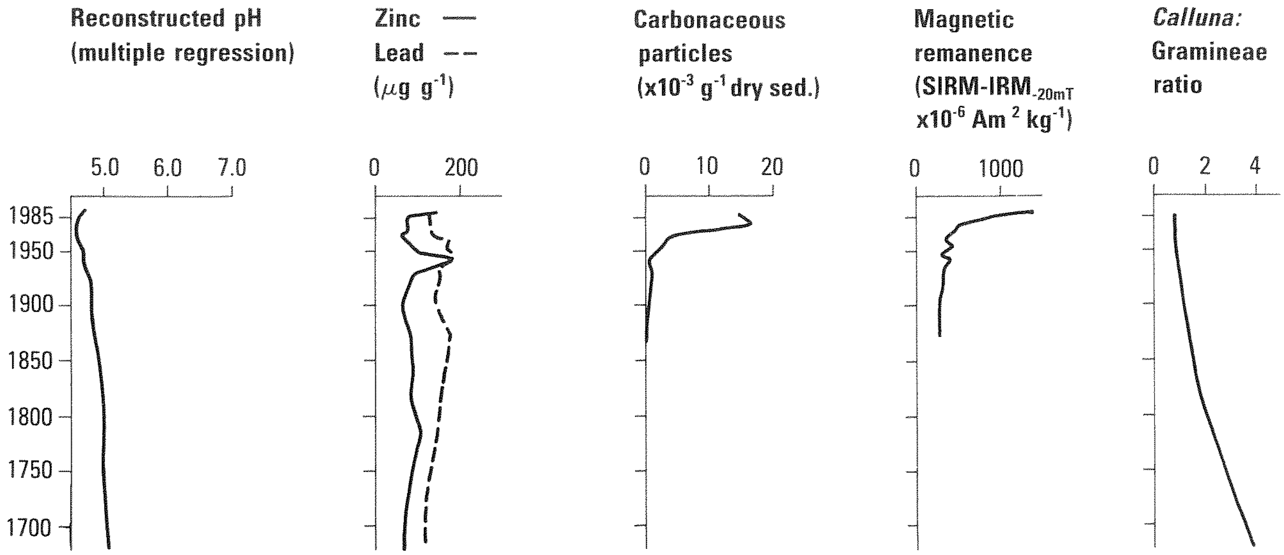


Figure 4.7 Graphs of reconstructed pH, lead, zinc, carbonaceous particles, magnetic remanence ('soft magnetite') and *Calluna*:Gramineae ratio for Loch Tanna.

Table 4.5 **Arran — water chemistry (mean values 1986 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	K^+ µeq l^{-1}	Na^+ µeq l^{-1}	Cl^- µeq l^{-1}	SO_4^{2-} µeq l^{-1}	Alkalinity µeq l^{-1}	TOC mg l^{-1}	Labile Al µg l^{-1}
L. Tanna	5.01	7	47.0	36.7	67.6	12.1	238.6	218.3	91.0	0.00	1.8	87
Coire Fhionn Lochan	5.30	5	52.4	51.2	73.0	12.8	277.8	301.7	106.7	1.41	1.0	123

Table 4.6 **Loch Tanna — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
Loch Tanna	NR 921428	5.0	1986	5.0	4.6	1850	0.4

Table 4.7 **Trossachs — water chemistry (mean values 1985 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	K^+ µeq l^{-1}	Na^+ µeq l^{-1}	Cl^- µeq l^{-1}	SO_4^{2-} µeq l^{-1}	Alkalinity µeq l^{-1}	TOC mg l^{-1}	Labile Al µg l^{-1}
L. Tinker	5.74	4	29.2	79.2	38.8	8.0	121.0	141.8	64.2	18.12	3.6	5
L. Chon	5.24	5	39.0	79.4	49.4	7.2	175.2	188.4	85.4	2.32	2.2	30

4.4 The Trossachs

Two sites in the Trossachs region, Loch Chon and Loch Tinker, have been studied as part of the Royal Society SWAP project. These sites were chosen to provide a historical perspective for SWAP work being carried out on an adjacent experimental stream catchment in the Loch Ard Forest (cf. Mason 1987) and to assess the impact of afforestation on acidity in this part of Scotland. Loch Chon and Loch Tinker are situated on similar lithologies. The catchment of Loch Chon is extensively afforested whereas Loch Tinker, the control site, has an open moorland catchment. Loch Chon has a much lower pH than Loch Tinker despite

Table 4.8 **Trossachs — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
L. Tinker	NN 445068	5.7	1985	6.4	6.0	1850	0.4
L. Chon	NN 421051	5.2	1986	6.4	5.5	1900[1]	0.9

NOTE: [1] Main change after afforestation (post-1970).

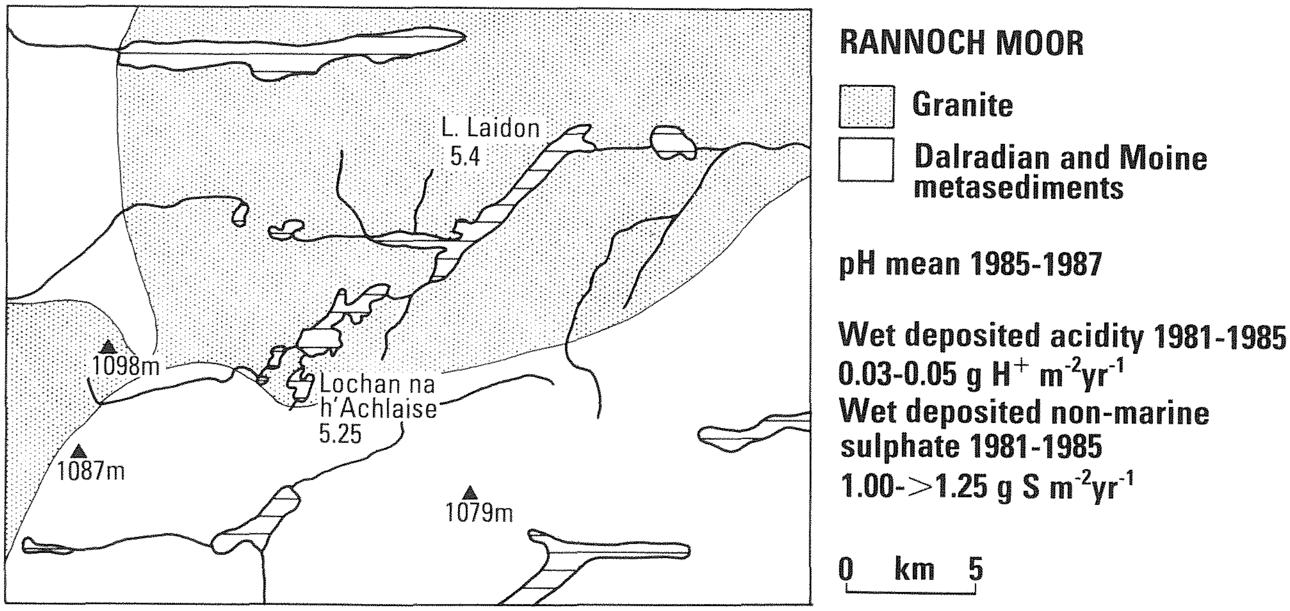


Figure 4.8 Map of Rannoch Moor showing the coring sites.

almost identical Ca^{2+} values (Table 4.7).

The analyses show that Loch Tinker has been slightly acidified since 1850 (Table 4.8) and that Loch Chon has been acidified strongly only after the planting of conifers in the catchment. In this area where the mica-schist geology offers more neutralising capacity than granite it is apparent that afforestation has helped to promote acidification, probably because of increased scavenging of dry and occult deposition by the forest canopy (Harriman and Morrison 1982). Full details will be presented elsewhere.

4.5 Rannoch Moor

On Rannoch Moor two sites were cored, Lochan na h'Achlaise and Loch Laidon (Figure 4.8). Cores from both sites were analysed but Lochan na h'Achlaise, a shallow exposed lake has a disturbed sediment record, possibly resulting from the inwash of old sediment associated with nearby road construction and lake level lowering. Fortunately the record from Loch Laidon was excellent and this site is therefore taken to represent this region of Scotland.

4.5.1 Loch Laidon

Loch Laidon is a large oligotrophic lake lying at an altitude of 282 m (Table 4.9). The site has special value since part of the lake is located in the Rannoch Moor National Nature Reserve, and the whole lake and its catchment (Figure 4.9) are designated as a Site of Special Scientific Interest (Flower *et al.* 1987b, 1988).

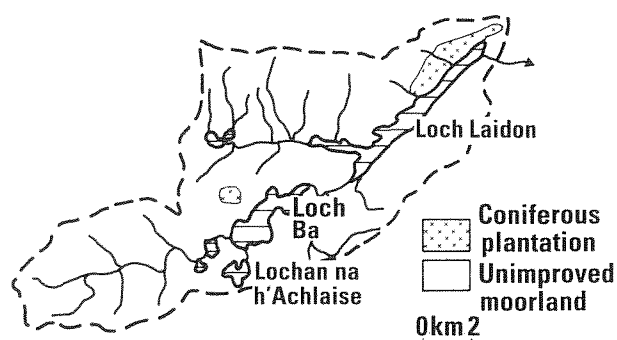


Figure 4.9 Catchment map of Loch Laidon.

The bathymetry of the lake was surveyed by Murray and Pullar (1910) (Figure 4.10). The maximum depth of the lake is 39 m and the mean pH of the water is 5.4 (Table 4.10). The lake is well known for its brown and ferox trout although there are some suggestions that the fishery has declined in recent years (Flower *et al.* 1987b, 1988).

Table 4.10 **Rannoch Moor — water chemistry (mean values 1985 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	K^+ µeq l^{-1}	Na^+ µeq l^{-1}	Cl^- µeq l^{-1}	SO_4^{2-} µeq l^{-1}	Alkalinity µeq l^{-1}	TOC mg l^{-1}	Labile Al µg l^{-1}
L. Laidon	5.40	21[1]	24.8	41.3	31.0	6.25	132.0	130.0	45.5	12.81	3.1	3
Lochan na h'Achlaise	5.25	5	36.4	41.8	32.6	7.0	210.4	248.0	45.8	3.47	2.8	3

NOTE: [1] R. Harriman, personal communication (pH only).

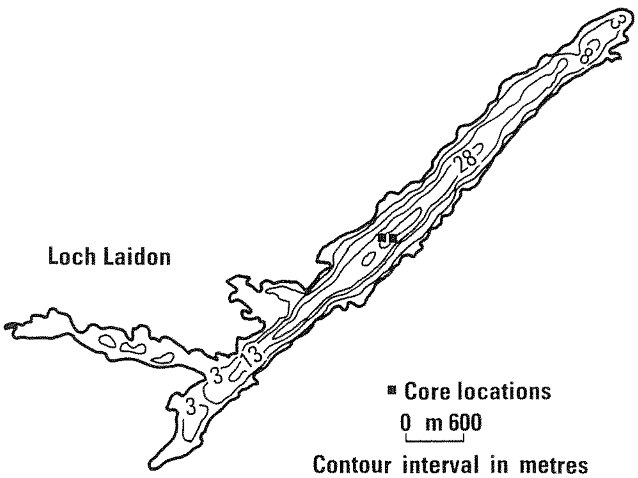


Figure 4.10 Bathymetric map of Loch Laidon showing the core location.

The catchment is extensive and includes a number of smaller lochs (Figure 4.9). It lies primarily on granite with a small area of quartz-feldspar-granulite of the Moine series in the far south-west. Blanket peats dominate catchment soils, and vegetation consists of acid wet heathland species, although two small coniferous plantations are also present.

Table 4.9 **Loch Laidon — site characteristics**

Grid reference	NN 380542
Core date	July 1985
Catchment geology	granite
Catchment type	moorland / conifers
Lake altitude (m)	282
Max. depth (m)	39
Mean depth (m)	10.7
Lake area (ha)	473
Volume ($m^3 \times 10^{-6}$)	50.0
Catchment area[1] (ha)	11637
Catchment:lake ratio	24.6
Afforestation (%)	2.8
Net relief (m)	836

NOTE: [1] Excluding lake.

Sediment cores were taken from the deepest part of the lake (Figure 4.10) in July 1985 using a mini-Mackereth corer. LAI1 was used for all analyses except carbonaceous particle analysis which was carried out on core LAI3.

^{210}Pb dating of core LAI1 showed that sediment accumulation rates were relatively constant from 1835 to about 1970 at between 1.4 and 1.9 mm yr^{-1}. A small increase since 1970 to between 2.0 and 2.8 mm yr^{-1} is partly the result of accelerated sediment accumulation, possibly resulting from soil inwash associated with the small coniferous plantings.

Before 1860 the diatom assemblage of the core is constant, dominated by the circumneutral taxa *Anomoeoneis vitrea* and *Cyclotella kützingiana*. However, after 1860 *Cyclotella kützingiana* begins to decrease rapidly and acidophilous species such as *Tabellaria flocculosa* and *Frustulia rhomboides* increase. The acidobiontic species *Tabellaria quadriseptata* also becomes important. A period of more rapid change takes place after the 1920s as *Anomoeoneis vitrea* and *Achnanthes microcephala* decline.

pH reconstruction from these changes (Figure 4.11) indicates that the mean pH of the lake has decreased in a gradual manner from about pH 5.8 in the 1850s to 5.3 by 1985 (Table 4.11).

The trace metal profiles for Loch Laidon (Figure 4.11) indicate significant atmospheric contamination of the site. The first clear signs of contamination occur at the 23 cm level (*c.*1850), about 10 years before the first evidence of acidification. Contamination from carbonaceous particles does not occur until after about 1930, but then there is a steep increase in values reaching a maximum in the 1970s. No magnetic data are shown from this site since the atmospheric signal is entirely masked by catchment-derived material.

Although the Loch Laidon catchment is very large and more diverse than other sites, there is no evidence from pollen analysis (Figure 4.11) and land-use records that catchment changes have taken place that could have promoted the acidification of the loch. The catchment is dominated by wet acid soils that only support rough moorland grazing and some post-1960 afforestation. Burning, mainly for grouse, has decreased considerably in recent years because of poor grouse returns and NCC management policy.

Loch Laidon receives substantial atmospheric contamination and has experienced a clear acidification. However, the contamination began somewhat later than at other sites and the acidification is not as pronounced as other lakes with similar Ca^{2+} levels. This is possibly because of its distance from sources of pollution and the lower total sulphur deposition at this site than at others further south.

4.6 Lochnagar and the Cairngorm Mountains

The Cairngorms comprise the largest granitic upland area in Britain and form Britain's largest National Nature Reserve. Lochnagar, separated from the main Cairngorms by the

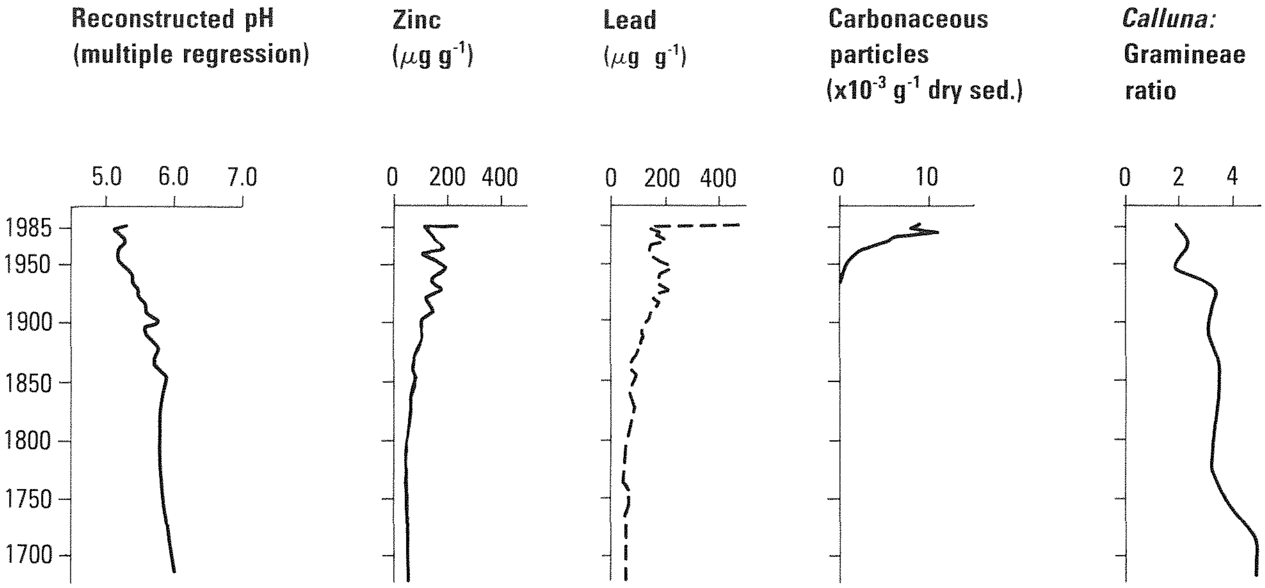


Figure 4.11 Graphs of reconstructed pH, lead, zinc, carbonaceous particles and *Calluna*:Gramineae ratio for Loch Laidon.

Table 4.11 **Loch Laidon — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
Loch Laidon	NN 380542	5.4	1985	5.8	5.3	1860	0.5

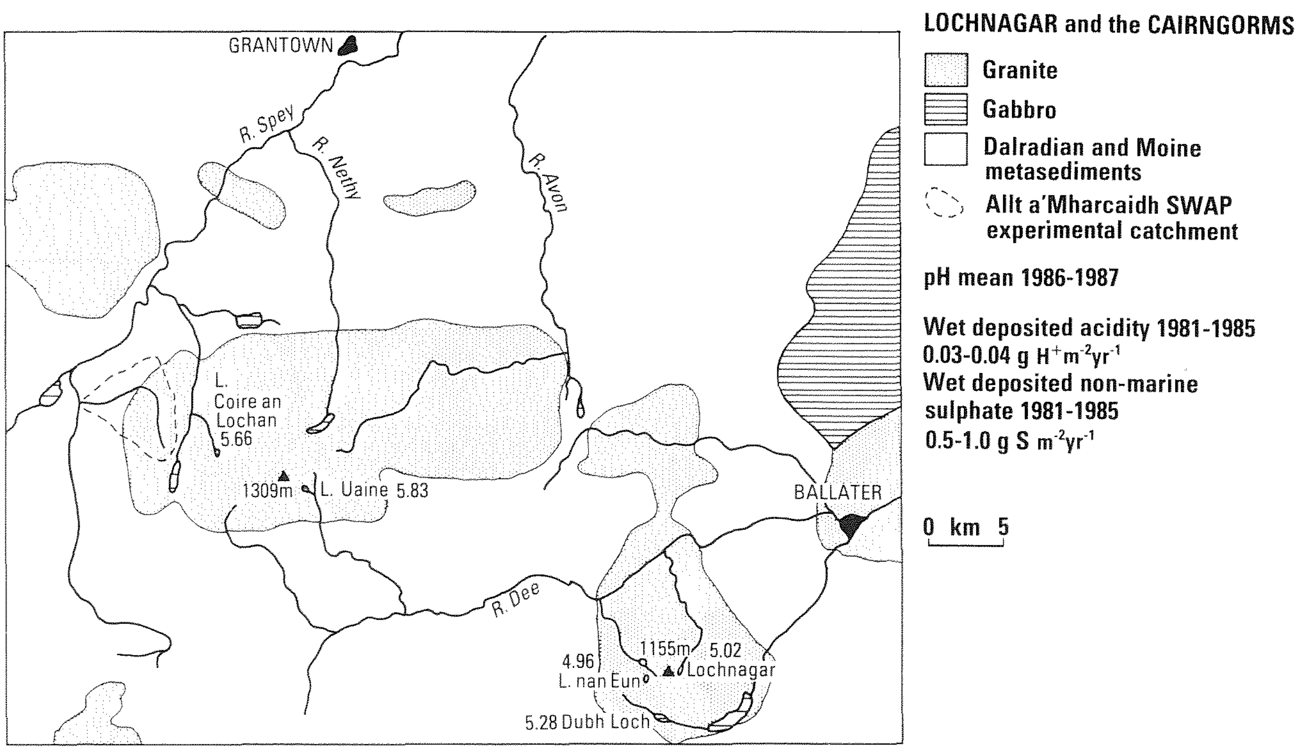


Figure 4.12 Map of Lochnagar and the Cairnorms showing the core sites.

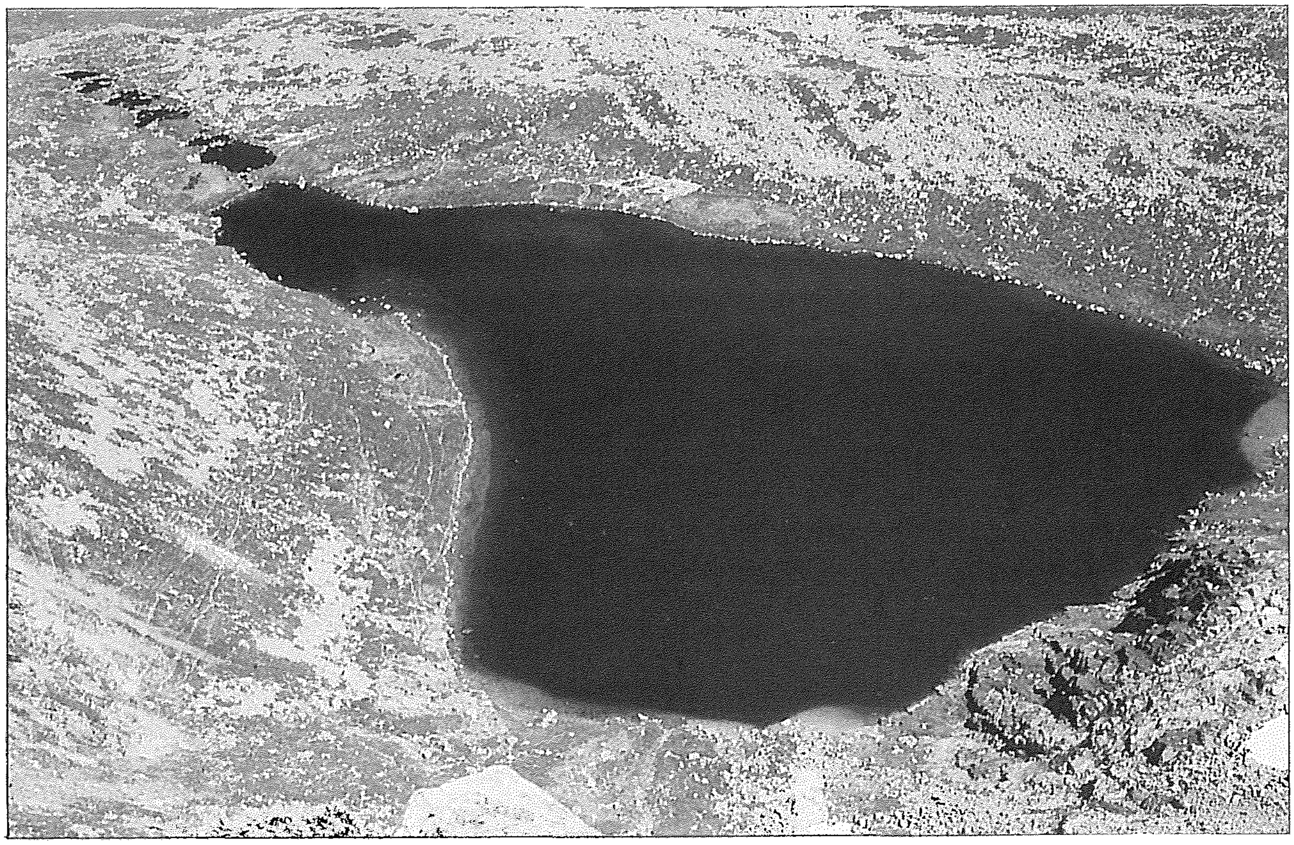


Figure 4.13 Lochnagar.

Dee valley, is also a major granitic intrusion and a Scottish Wildlife Trust Reserve.

A number of high altitude corrie lochs were cored in this area (Figure 4.12). Lochan Uaine (below Ben Macdhui) was chosen as a SWAP site to provide historical information for the experimental stream catchment study in the nearby Allt a'Mharcaidh (Harriman *et al.* 1987) whilst Lochnagar (below Lochnagar mountain), on the Balmoral Estate was chosen in this project. Other sites in this area (Figure 4.12) are included in the current (DoE 2) project.

Table 4.12 **Lochnagar — site characteristics**

Grid reference	NO 252859
Core date	June 1986
Catchment geology	granite
Catchment type	moorland
Lake altitude (m)	785
Max. depth (m)	24
Mean depth (m)	8.4
Lake area (ha)	9.8
Volume ($m^3 \times 10^{-6}$)	0.82
Catchment area[1] (ha)	91.9
Catchment:lake ratio	9.37
Afforestation (%)	0
Net relief (m)	370

NOTE: [1] Excluding lake.

4.6.1 Lochnagar

Lochnagar (Figure 4.13) is a small corrie loch at an altitude of 785 m (Table 4.12). It has a maximum depth of 24 m (Figure 4.14) and a current pH of 5.0 (Table 4.13). The loch is remote and little is known of its history as a fishery.

The catchment geology comprises granite which is exposed as a steep corrie backwall. Considerable portions of the catchment at the base of the backwall are covered by lightly vegetated screes and the flatter lower level ground is composed of blanket peats supporting ericaceous vegetation.

The lake was cored in June 1986 using a mini-Mackereth corer. Core NAG3 was used for the main analyses.

Radiometric measurements of the core showed the presence of elevated levels of ^{137}Cs in the surface sediment indicating contamination at this site from Chernobyl fallout. A peak of ^{241}Am at the 2.75 cm level indicates the fallout maximum of 1963 associated with atomic weapons testing. This date is in perfect agreement with the ^{210}Pb chronology which shows a very slow sediment accumulation rate of between 0.4 and 1 mm yr^{-1} between 1880 and 1970. During this period there was very little change in the dry mass accumulation rate though the past decade has seen a significant increase in sediment input, giving rise to a current

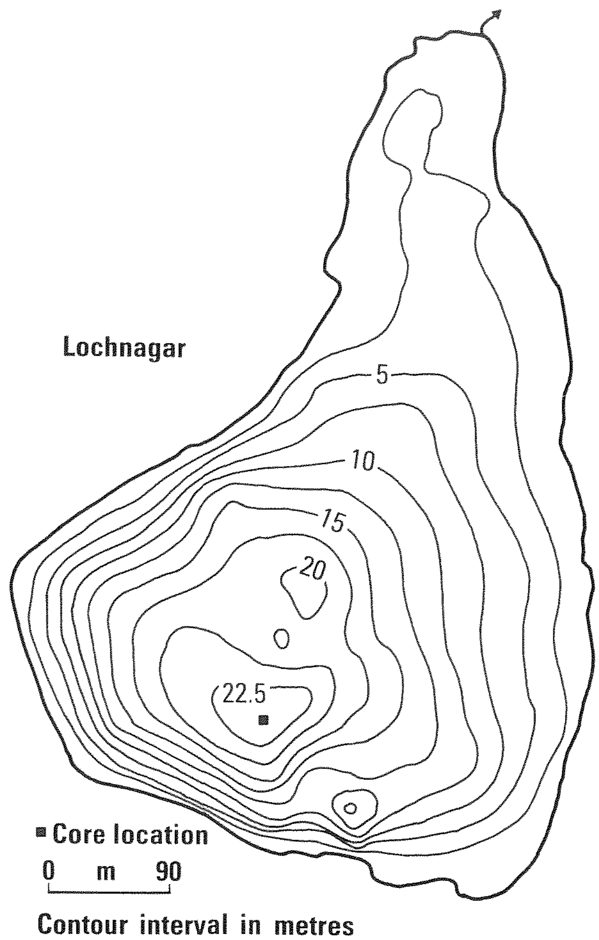


Figure 4.14 Bathymetric map of Lochnagar showing the core location.

Table 4.13 **Lochnagar and Cairngorms — water chemistry (mean values 1986 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	K^{+} µeq l^{-1}	Na^{+} µeq l^{-1}	Cl^{-} µeq l^{-1}	SO_4^{2-} µeq l^{-1}	Alkalinity µeq l^{-1}	TOC mg l^{-1}	Labile Al µg l^{-1}
Lochnagar	5.02	6	21.4	30.2	33.7	7.5	89.0	76.2	66.0	0.00	0.8	57
Dubh Loch	5.28	3	17.3	27.3	21.3	5.3	72.3	67.7	54.0	1.37	1.6	55
L. nan Eun	4.96	3	22.3	29.7	26.3	5.7	82.3	55.0	62.3	0.00	0.5	128
Lochan Uaine	5.83	3	40.5	69.0	59.5	10.0	191.0	215.0	82.0	14.79	0.4	56
L. Coire an Lochan	5.66	4	17.8	28.8	19.8	7.8	67.0	81.7	47.3	13.73	0.2	75

accumulation rate of 1.8 mm yr^{-1}. Unfortunately, it is not possible to date sediments prior to about 1880 because of the presence of an inwash horizon at 8–11 cm. This has unusually high values of ^{226}Ra and prohibits an accurate estimate of unsupported ^{210}Pb at a time when unsupported ^{210}Pb levels are close to background.

Diatom analysis of this site shows a clear acidification sequence. However, because of the problem of dating outlined above it is difficult to be precise about its timing. The best estimate is that acidification began in the mid-nineteenth century. A linear extrapolation of the rate of sediment accumulation back from 1880 (7 cm) to the first sign of acidification (10 cm) gives a date of 1800. However, since this minerogenic section of sediment is likely to have accumulated much more rapidly than sediment above 7 cm a more recent date is probable.

The first acidification is indicated by a decline in *Fragilaria virescens* and increase in *Achnanthes marginulata* above 10 cm. A more pronounced change occurs after 1880 as several circumneutral species decrease. *Achnanthes marginulata* continues to increase accompanied by *Achnanthes austriaca* var. *minor* and *Melosira distans* var. *nivalis*.

The acidophilous diatom flora at Lochnagar has some differences from floras at similar pH but lower altitude. Acidobiontic *Tabellaria* species are absent and the

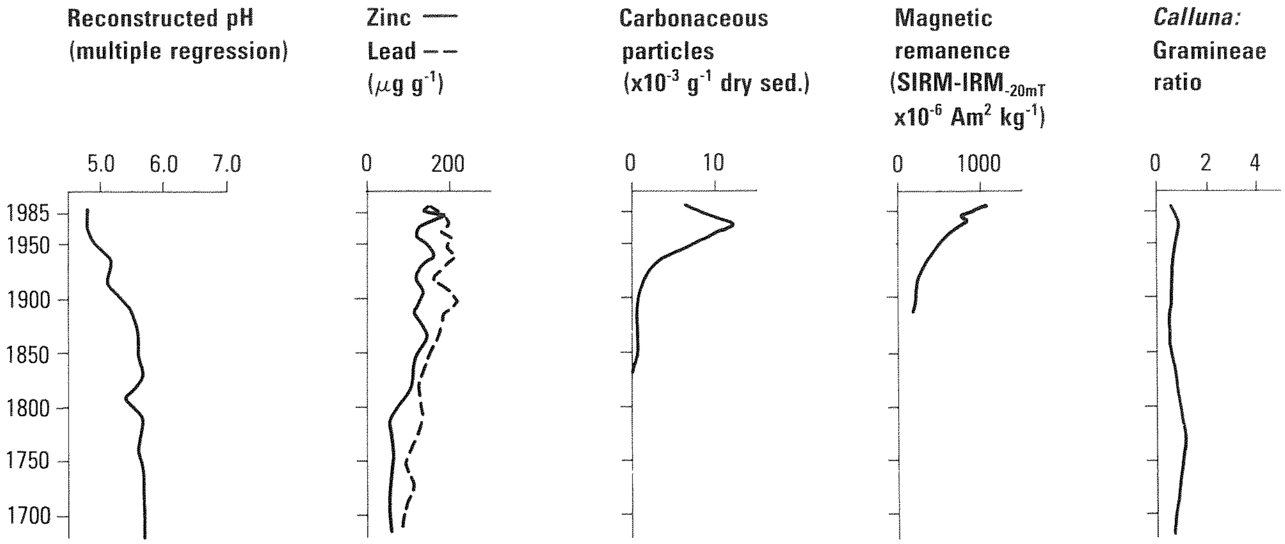


Figure 4.15 Graphs of reconstructed pH, lead, zinc, carbonaceous particles, magnetic remanence ('soft magnetite') and *Calluna*:Gramineae ratio for Lochnagar.

Table 4.14 **Lochnagar and Cairngorms — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
Lochnagar	NO 252859	5.0	1986	5.7	4.8	1850	0.9
Dubh Loch	NO 238828	5.3	1986	5.7[1]	5.2	–[2]	0.5
Loch nan Eun	NO 230854	5.0	1986	6.0[1]	4.8	–[2]	1.2
Lochan Uaine	NO 001981	5.8	1986	5.8	5.7	–[3]	–[4]

NOTES: [1] Refers to the base of the core. [2] Core not yet dated. [3] Not significant. [4] Not applicable.

dominant species are *Achnanthes*, especially *Achnanthes marginulata* and a range of *Achnanthes marginulata* varieties. Since some of these taxa are not well described in the literature and their pH preference is unknown it is difficult to derive an accurate pH reconstruction at this site. The curve shown in Figure 4.15 has been constructed excluding these species. It shows a pH shift from about 5.7 in the mid-nineteenth century to 4.8 at the core top. This compares with a mean measured pH of 5.0 (Table 4.14).

As at other sites Lochnagar has been contaminated by trace metals and carbonaceous particles. Increases in the concentration of lead and zinc in the sediment (Figure 4.15) date from the beginning of the nineteenth century. The carbonaceous particle record shows some late-nineteenth century and early-twentieth century contamination and a typical marked increase in concentration from about 1930 to a maximum in about 1970 (Figure 4.15). The magnetic mineral record also shows a clear increase in recent decades.

Since the catchments of the high Cairngorm lochs are not subject to land-use and land management practices that might affect their water quality, the only plausible cause for the acidification of this site, and others in the area, is acid deposition.

4.7 The north-west Highlands and Islands

The north-west Highlands and Islands are areas of relatively low acid deposition in the United Kingdom (Barrett *et al.* 1987). No strongly acidified lake has yet been found in this area but there are a number of shallow, brown-water lakes with pH below 5.0, such as Long Loch and Loch na Larach (Table 4.15), where the acidity is primarily due to organic acids, and there are clear-water lakes with very low Ca^{2+} values but relatively high pH (>5.5), such as Lochan Dubh, and Loch Coire nan Arr (Table 4.15).

A range of these lakes have been cored in the region (Figure 2.1). We hypothesise that the lakes have been only slightly affected by atmospheric contamination and that there will be little evidence of recent (post-1800) acidification from the diatom record. Preliminary analyses for Lochan Dubh (Table 4.15) show slight contamination by carbonaceous particles and a small decline in pH (Table 4.16). Other analyses are in progress and results will be available in 1989.

Table 4.15 **North-west Highlands and Islands — water chemistry (mean values 1986–1987)**

Site	pH mean	n	Conductivity$_{25°C}$ µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	K^+ µeq l^{-1}	Na^+ µeq l^{-1}	Cl^- µeq l^{-1}	SO_4^{2-} µeq l^{-1}	Alkalinity µeq l^{-1}	TOC mg l^{-1}	Labile Al µg l^{-1}
Long Loch	4.96	5	241.4	128.0	388.0	43.8	1723.2	2006.7	260.0	0.00	9.1	9
L. na Larach	4.88	5	135.4	63.4	188.8	24.4	1004.0	947.0	120.8	0.00	5.8	8
L. Teanga	5.70	1	163.0	110.0	255.0	23.0	981.0	1160.0	233.0	12.04	–	–
L. Coire nan Arr	6.31	6	39.2	43.3	59.2	13.3	216.2	263.0	45.8	27.90	2.2	2
Lochan Dubh	5.64	6	29.0	33.2	40.2	8.0	163.0	185.4	109.6	9.75	2.8	11
L. Doilet	5.79	6	43.8	54.0	60.5	12.5	238.7	277.0	70.6	15.43	2.4	7

Table 4.16 **Lochan Dubh — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
Lochan Dubh	NM 895710	5.6	1986	5.5	5.2	–[1]	0.3

NOTE: [1] Core not yet dated.

5

Regional Survey: England

5.1 Introduction

In England areas sensitive to acidification are more geologically diverse than in Wales and Scotland. These areas include parts of Cumbria, especially those on Eskdale granite and Borrowdale volcanic rocks, parts of the Pennines on Carboniferous millstone grits, outcrops of Cretaceous sandstones in south and south-east England and the granitic intrusions of south-west England, including Dartmoor (Kinniburgh and Edmunds 1986).

Unfortunately, only the Cumbrian region supports a large number of natural lakes that can be used for lake sediment analysis. In other regions of England, mainly beyond the limit of the last glaciation, ponds, pools and reservoirs can be used if they are older than 50–100 years and if the accumulated sediment has not been disturbed by dredging, water draw-down or some other process.

5.2 Cumbria

Five sites in Cumbria (Figure 5.1) are in the process of study (Haworth 1985, Haworth *et al.* 1987). Results from four of these (Table 5.1) are reported here. All are situated on the western side of the region in the Wasdale-Eskdale area. Three of the sites (Scoat, Low and Greendale Tarns) are very acid, and two are slightly acid (Devoke Water and Burnmoor Tarn) (Table 5.2). The study of sediments from Devoke Water forms part of a SWAP project, results of which will be published elsewhere.

Sediment cores from these sites were collected using a mini-Mackereth corer. Diatom analysis has been carried out on all cores and pH reconstruction uses the Index B technique (Renberg and Hellberg 1982) rather than the multiple regression technique used for other sites listed in this report.

5.2.1 Scoat Tarn

In the Scoat Tarn core a very marked decline of the planktonic species *Cyclotella kützingiana* occurs between 15 and 20 cm. This is followed by decreases in many circumneutral species, such as *Achnanthes minutissima* and *Anomoeoneis vitrea* var. *lanceolata* above 12 cm. These taxa are replaced mainly by the acidophilous species *Achnanthes marginulata* and *Frustulia rhomboides*, and in the uppermost sediment by acidobiontic taxa such as *Tabellaria binalis* and *Melosira distans* var. *nivalis*.

The Index B pH reconstruction (Figure 5.2) indicates a decrease of pH from 6.1 at the base of the core to 4.6 at the present (Table 5.3). The main acidification dates from about 1850 although the *Cyclotella* decline occurs somewhat before that time.

Analyses of zinc and magnetic minerals in the core show that this site has received a considerable amount of atmospheric contamination since 1800 (Figure 5.2).

5.2.2 Greendale Tarn

The Greendale Tarn core has been dated by ^{210}Pb. Acidification at this site is clearly indicated by the decrease in *Achnanthes minutissima*, *Cymbella lunata* and *Fragilaria virescens* after about 1900, and the expansion of the more acid tolerant taxa *Eunotia veneris*, *Frustulia rhomboides* (and varieties), *Tabellaria quadriseptata*, *Navicula heimansii* and *Melosira distans* var. *nivalis*. The pH change is from pH 6.0 in the nineteenth century to the present pH of 4.9 in the surface sediment (Figure 5.3).

5.2.3 Low Tarn

The Low Tarn core has not yet been dated, but a clear recent acidification is apparent with a sharp decline from pH 6.0 to 4.6 in the uppermost 15 cm (Figure 5.3). The acidification is marked by the expansion of mainly acidophilous species including *Navicula heimansii*, *Eunotia veneris* and *Peronia fibula*.

5.2.4 Burnmoor Tarn

Burnmoor Tarn has a present mean pH of 6.4 (Table 5.2). Planktonic forms dominate the diatom assemblage throughout the core and reconstructed pH remains constant at about 6.2 (Figure 5.3). Nevertheless, decreases in the proportion of the *Cyclotella* plankton and increases in *Anomoeoneis vitrea* and *Frustulia rhomboides* in post-1850 sediments suggests a shift to a more acid flora over the last 100 years indicating that some alkalinity has probably been lost at this site, but not sufficient to cause a significant pH change (Table 5.3).

5.2.5 Devoke water

A preliminary study of the core from Devoke Water, a lake with a present pH of 6.1, suggests that a decrease in planktonic *Cyclotella* taxa and an increase in acidophilous species have occurred between the base of the core and the top. pH reconstruction indicates a shift from about 6.6 to about 6.1. No dates are yet available for this core.

Although there is only a small amount of information for recent catchment change and atmospheric contamination at these sites, notably from Scoat Tarn (Haworth *et al.* 1987), it is clear that the very pronounced acidification since 1850 at Scoat, Greendale and Low Tarns is similar to the acidification found in Wales and Scotland and almost certainly results from acid deposition.

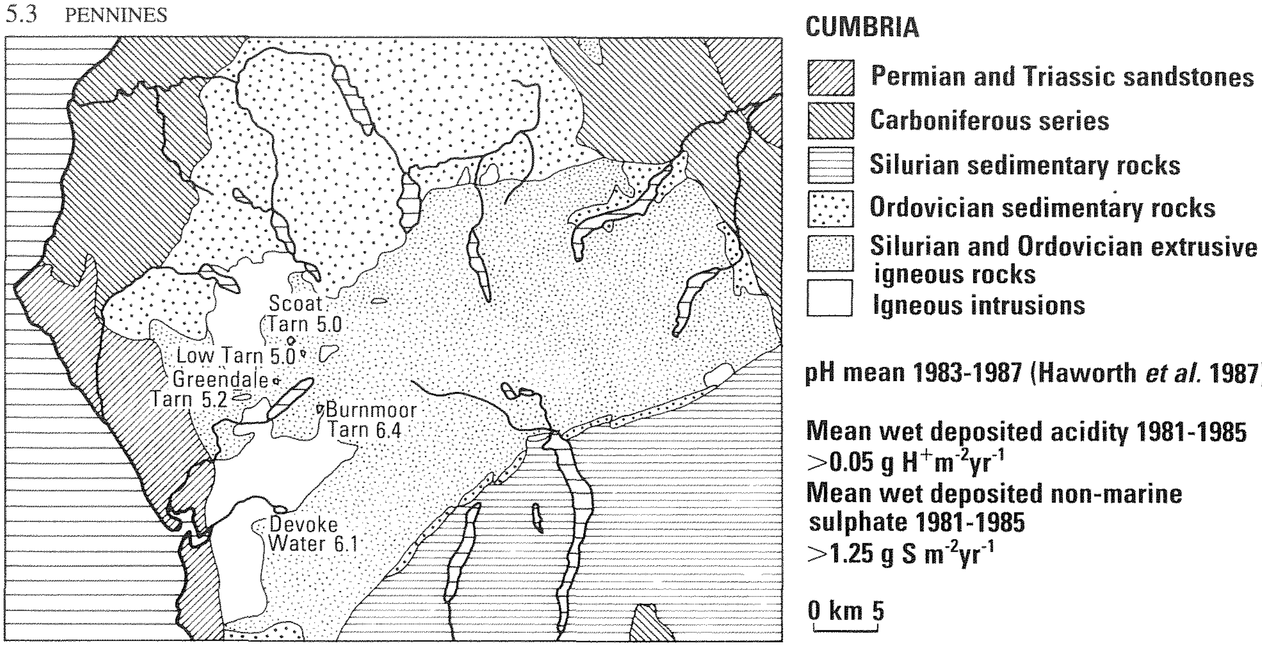


Figure 5.1 Map of Cumbria showing core sites, with mean pH.

Table 5.1 **Cumbria — site characteristics**

	Scoat Tarn	Low Tarn	Greendale Tarn	Burnmoor Tarn
Grid reference	NY 159104	NY 163091	NY 146074	NY 184044
Core date	1984	1984	1984	1979
Catchment geology	Ordovician volcanics	Ordovician volcanics	Ordovician volcanics	Ordovician volcanics / Granite
Catchment land use	moorland	moorland	moorland	moorland
Lake altitude (m)	602	480	405	252
Max. depth (m)	20	3	9	13
Mean depth (m)	10	1.6	–	–
Lake area (ha)	5.2	3.5	2.1	24.0
Volume ($m^3 \times 10^{-6}$)	0.42	0.06	–	–
Catchment area[1] (ha)	95	52	83	226
Catchment:lake ratio	18.2	15	40	9.4
Afforestation (%)	0	0	0	0
Net relief (m)	239	321	287	712

NOTE: [1] Excluding lake.

Table 5.2 **Cumbria — water chemistry[1] (mean values 1983 – 1987)**

Site	pH mean	n	Conductivity$_{25°C}$ µS cm^{-1}	Ca^{2+} µeq l^{-1}	Mg^{2+} µeq l^{-1}	K^+ µeq l^{-1}	Na^+ µeq l^{-1}	Cl^- µeq l^{-1}	SO_4^{2-} µeq l^{-1}	Alkalinity[2] µeq l^{-1}	TOC mg l^{-1}	Labile Al µg l^{-1}
Scoat Tarn	5.0	19	45.5	41	53	11	174	202	63	−7	–	–
Low Tarn	5.0	16	49.9	59	55	7	174	191	85	−5	–	–
Greendale Tarn	5.2	13	47.8	53	62	6	188	209	85	−3	–	–
Devoke Water	6.1	137	58.0	124	87	11	227	266	141	26	–	–
Burnmoor Tarn	6.4	14	47.3	98	66	9	186	207	96	48	–	–

NOTES: [1] Analysed by T.R. Carrick. [2] Alkalinity by Gran titration.

5.3 Pennines

The southern Pennines of England include the most acid surface waters in the United Kingdom. Streams and reservoirs with pH below 4.5 and total aluminium concentration exceeding 200 µg l^{-1} are very common (North West Water 1987). These data are consistent with the very high levels of acid deposition (dry and wet) in the Pennine area (Barrett *et al.* 1987).

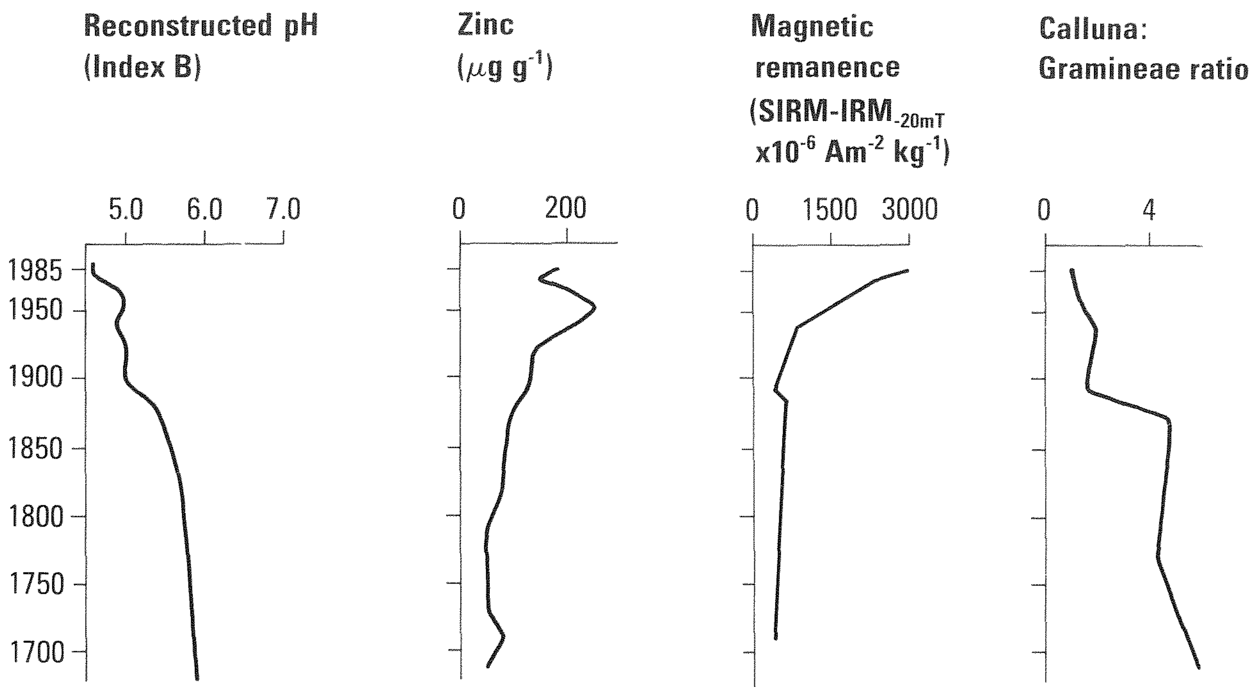


Figure 5.2 Graphs of reconstructed pH, zinc, magnetic remanence ('soft magnetite') and *Calluna*:Gramineae ratio for Scoat Tarn.

Table 5.3 **Cumbria — pH change**

	Grid reference	Modern pH (measured)	Date of core	pH 1800 (inferred)	Modern pH (inferred)	First point of change	pH change
Scoat Tarn	NY 159104	5.0	1984	6.0	4.6	1850	1.4
Low Tarn	NY 163091	5.0	1984	6.0[1]	4.6	–[2]	1.4
Greendale Tarn	NY 146074	5.2	1984	6.0	4.9	1900	1.1
Devoke Water	SD 163970	6.1	1985		no information yet		
Burnmoor Tarn	NY 184044	6.4	1979	6.3	6.2	–[3]	–[4]

NOTES: [1] Refers to the base of the core. [2] Core not yet dated. [3] Not applicable. [4] Not significant.

Given the proximity of this area to the major nineteenth and twentieth century industrial areas of Yorkshire, Lancashire and the north Midlands it might be expected that surface waters in sensitive areas of the Pennines would have acidified earlier and more rapidly than sites more geographically distant in Wales, Scotland and, to a lesser extent, Cumbria.

Unfortunately, only a few natural lakes, and none of them on sensitive bedrock, occur in the southern Pennine area. Consequently a study was made of the suitability of acid reservoirs and reservoir sediments for the purpose of environmental reconstruction (Anderson *et al.* 1988).

There are many problems with the use of reservoirs. First, few reservoirs are sufficiently old for our needs. Second, the use of reservoirs for drinking water (and canal balancing purposes) entails periodic draw-down and the erosion and re-deposition of sediments. Third, frequent draw-down prevents the establishment of stable habitats around the margins of the lake for the growth of plants and algae. And fourth, diatom concentration in reservoir sediments can be very low owing to a combination of low diatom productivity and extremely high sediment accumulation rates.

The second of these problems can sometimes be circumvented by coring in marginal areas and avoiding deeper zones near the dam face where re-worked sediments are more likely to occur. The third problem can be partially resolved by detailed survey of modern diatom floras in reservoirs. Diatoms do occur around reservoirs, especially on stone surfaces, and the species assemblage does reflect water quality. A specialised pH:diatom relationship could be established for such sites but this has not yet been carried out.

However, although many reservoirs are of little use for diatom studies because of these problems, they may still be used for tracing the more recent history of atmospheric contamination.

5.3.1 Watersheddles Reservoir

Starting with a list of over 200 reservoirs an attempt was made to locate a test site which was over 100 years old, had undisturbed sediments, a pH below 5.5 and a good diatom

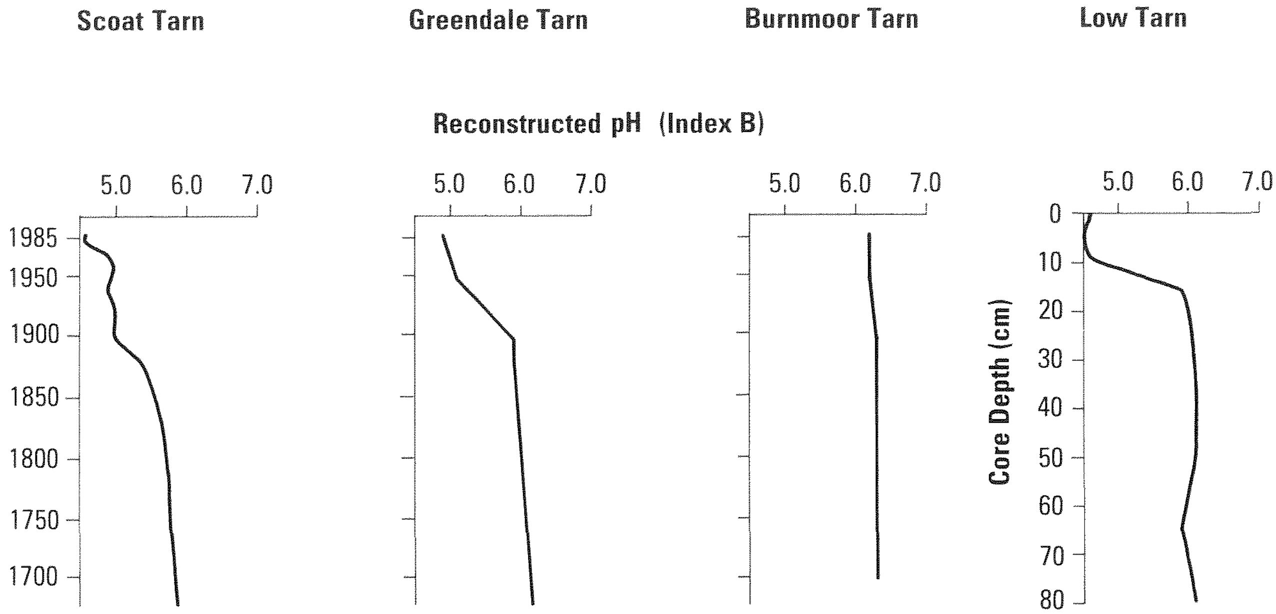


Figure 5.3 Graphs of reconstructed pH for Cumbrian lakes.

record. After coring a short-list of sites (Figure 5.4) (Anderson *et al.* 1988) Watersheddles Reservoir, near Keighley in West Yorkshire, was chosen. It lies at an altitude of 335 m on Millstone Grits. The reservoir is 15 m deep, has a mean pH of 4.1 and drains a predominantly moorland catchment covered by blanket peats.

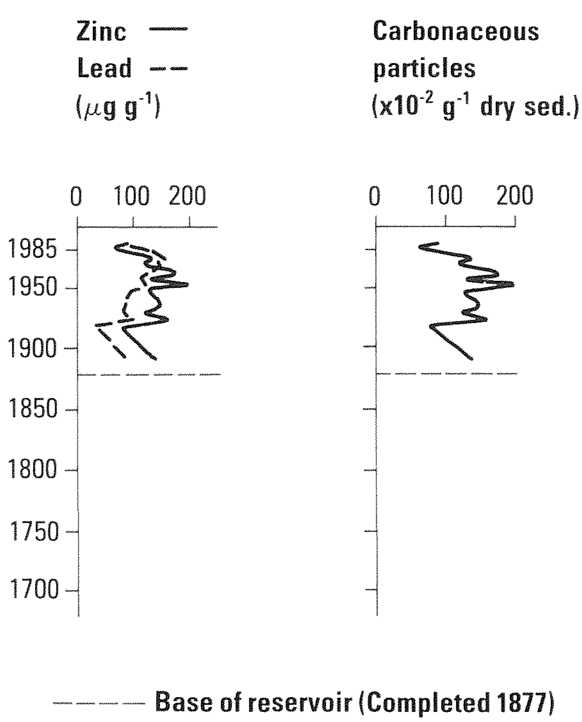


Figure 5.6 Graphs of zinc, lead and carbonaceous particles for Watersheddles Reservoir.

It was built in 1877 as a head-water reservoir. Although its water level varies by up to 2 m within the year it has only been strongly drawn-down on two occasions since 1945. In April 1986 a detailed stratigraphic survey of the reservoir was carried out and a series of cores taken (Figure 5.5).

Table 5.4 **Watersheddles Reservoir—site characteristics**

	Natural catchment	Including catchwaters
Grid reference	SD 965382	
Core date	May 1986	
Catchment geology	Carboniferous sedimentary	
Catchment land use	moorland / improved pasture	
Lake altitude (m)	335	
Max. depth (m)	15	
Mean depth (m)	5.5	
Lake area (ha)	15.9	
Volume ($m^3 \times 10^{-6}$)	0.87	
Catchment area[1] (ha)	225	500
Catchment:lake ratio	14.1	31.4
Afforestation (%)	0	0
Net relief (m)	123	
Mean pH 1979–1986[2]	4.06	

NOTES: [1] Excluding lake.
[2] From 310 Yorkshire Water Authority determinations.

Core WATL4 was chosen for analysis. The core penetrated the 1870 land surface at a depth of 70 cm. Radiometric dating of the core showed pronounced peaks in ^{137}Cs and ^{241}Am at 14.5 cm corresponding to the 1963 peak in radioactive fallout resulting from atomic weapon testing. The ^{210}Pb chronology is in reasonable agreement with this, although some uncertainties occur in earlier sediments probably as a result of the rapid initial accumulation of sediment

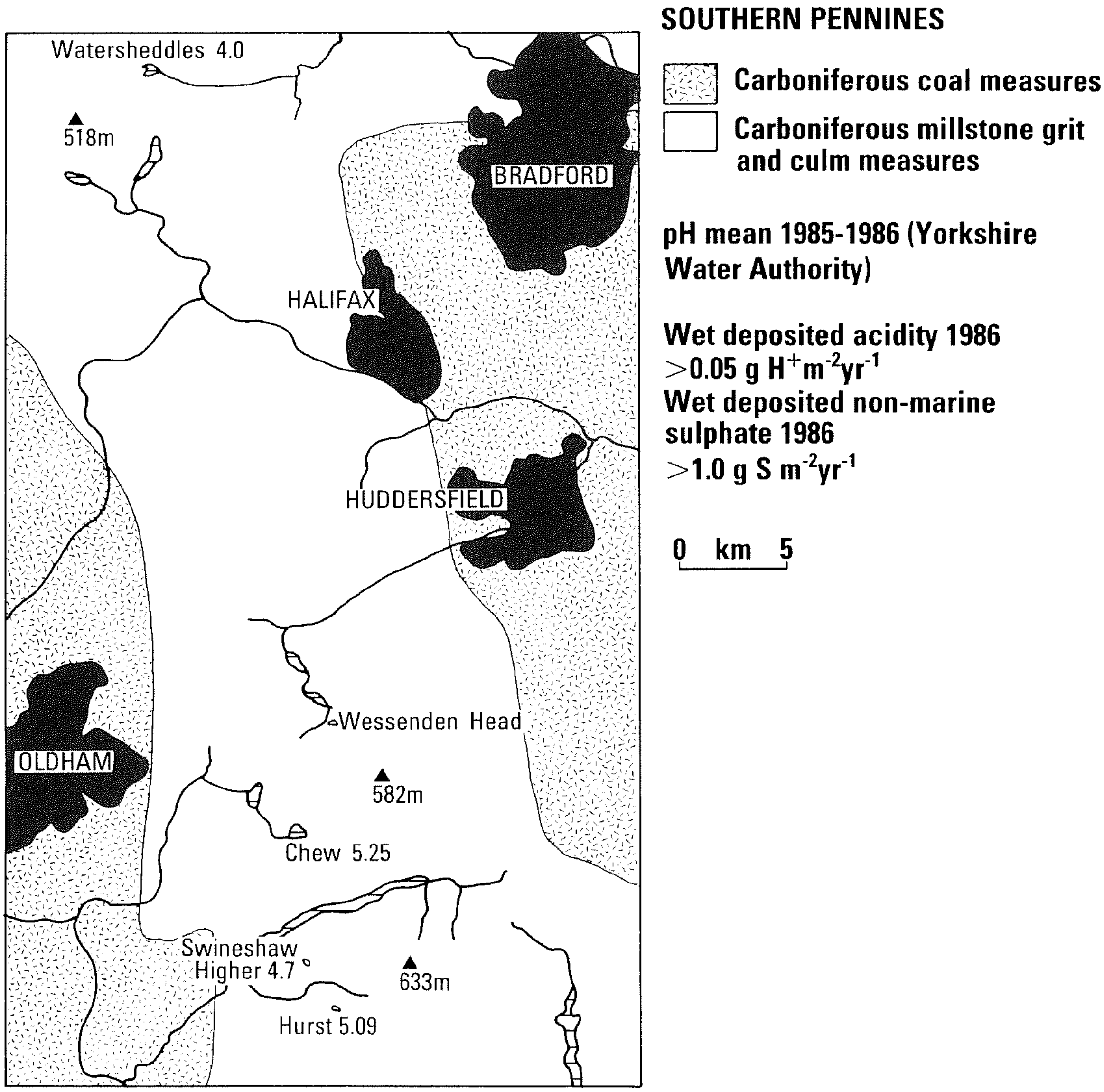


Figure 5.4 Map of the Southern Pennines showing core sites.

following the construction of the reservoir. The sediment accumulation rate since about 1900 has varied between 4 and 7 mm yr^{-1}, substantially more rapid than most natural lake sediments, but slower than many reservoirs.

Diatom concentrations in core WATL4 were low and preservation was variable but it was possible to construct a full diatom diagram (Anderson *et al.* 1988). The flora is very impoverished compared with that of a natural lake. This is either a result of the extreme acidity of the reservoir or the instability of the marginal habitats. Three taxa dominate throughout the core, *Eunotia exigua*, *Eunotia tenella* and *Pinnularia microstauron*. There are few trends and little evidence of any major change in water quality during the 100 years or so represented by the core. Although it is not possible to reconstruct pH because of the inapplicability of current models to this kind of site the flora represents exceptionally acid conditions with pH probably below 5.0 throughout. This suggests either that surface waters in this area are naturally very acid or, more likely, that acidification to pH < 5.0 occurred before the construction of the reservoir. The paucity of very old reservoirs with suitable sediments precludes a full evaluation of these alternatives.

The record of atmospheric contamination at Watersheddles is quite good (Figure 5.6). The data show that trace metal contamination was already occurring when the reservoir was being built. The basal sediments have high levels of lead and zinc. A small amount of copper and nickel contamination is also apparent. Concentrations rise to a maximum in the 1950s and decrease in the 1970s. In comparison to more remote rural areas where trace metal contamination began about 1800 it is not surprising that the basal sediments of Watersheddles are contaminated. Indeed a pre-1800 contamination might be expected in the Pennines.

Analysis of carbonaceous particles confirms that atmospheric contamination was occurring at the time of reservoir

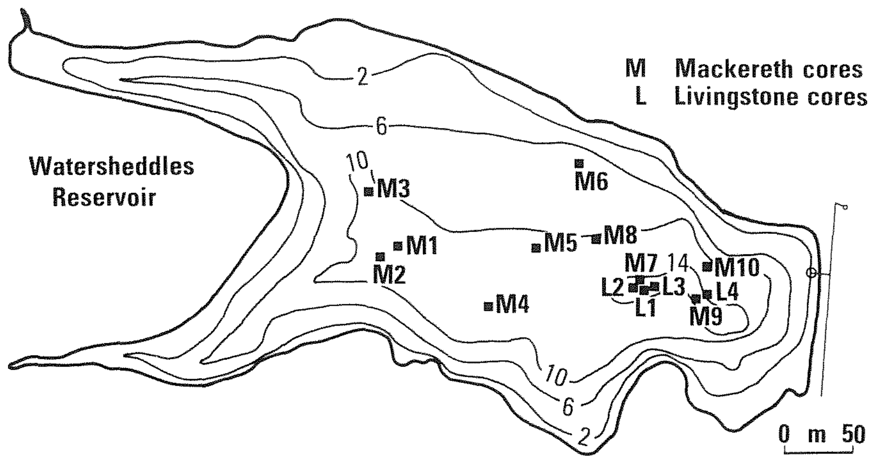


Figure 5.5 Bathymetric map of Watersheddles Reservoir, showing core locations.

construction. These particles are present in substantial concentrations in the early-twentieth century. Concentrations rise rapidly after 1940 to a maximum in the early 1970s and there is some evidence of a decrease in recent years (Figure 5.6).

Reservoirs and reservoir sediments are far from ideal systems for environmental reconstruction, and are considerably inferior to natural lakes. They are insufficiently old to allow pre-pollution baseline conditions to be established and sediments can be re-worked. However, in the absence of alternatives, with careful choice of sites and a full knowledge of potential problems they can be used to monitor recent (post-1940) change in atmospheric contamination and water quality. In this context, it is preferable in any future study to concentrate on these aspects rather than to attempt to reconstruct pre-1900 conditions.

5.4 South and south-east England

Exceptionally acid surface waters occur in south and south-east England in areas underlain by de-calcified sandstones. Studies of the sediments of a number of shallow acid pools in this region are now in progress. So far only data for Woolmer Pond (Hampshire) are available (Flower and Beebee 1987), which show that acidification has taken place in the twentieth century and that post-1940 sediments are strongly contaminated by trace metals and carbonaceous particles. The evidence suggests that the decline of natterjack toads in this area is at least partly the result of the acidification of breeding sites.

5.5 South-west England

South-west England has many areas sensitive to acid deposition. The extent of acidification in this area is unknown. Acid deposition is relatively low (Barrett *et al.* 1987) and no strongly acid waters are known. Work is in progress on sediments from Pinkworthy Pond on Exmoor and further work is planned to examine the sediments of other ponds and pools in the region.

6

Discussion

6.1 Suitability of sites

With the exception of the Migneint area of north Wales and the Pennines in England, sites with excellent sediment records were found in all regions. Since completing this project Llyn Conwy in the Migneint has been re-surveyed and good new cores are now available. In the Pennines it is unlikely that sites recording early (pre-1850) acidification exist, although good records of atmospheric contamination are likely to be found in the few natural alkaline lakes in the region. Some reservoir sediments hold a good record of twentieth century contamination and could be used to monitor improvements in air quality.

Despite the availability of good sites in most regions a number of interesting sites were rejected either after an initial survey or at a later stage of analysis. Most problems were associated with extremely asymmetric sediment distribution (Llyn Conwy, Llyn Berwyn), truncations (Llyn Gamallt, Llyn Eiddew Bach) or hiatuses within the core (Llyn Berwyn, Llyn Eiddew Bach, Lochan na h'Achlaise). In many cases truncations and hiatuses are impossible to detect in the field and only become apparent after laboratory analysis. Pollen analysis was found to be one of the most useful techniques in identifying problem cores.

Recognition of these difficulties underlines the need to carry out detailed bathymetric and sediment surveys in exposed upland lakes before a final choice of master-core location is made (cf. Anderson *et al.* 1986), and also illustrate the side-benefits of carrying out a wide range of analyses on the same core material.

6.2 Chronology and accumulation rates

A good sediment chronology was obtained for almost all sites. Few sites had perfectly log-linear ^{210}Pb decay curves but changes in slope caused by increases in sediment accumulation rate were accommodated by the use of the CRS model. When present there was usually a good agreement between the occurrence of ^{241}Am in the core and the ^{210}Pb date for 1963. ^{137}Cs concentrations, on the other hand, rarely agreed with either the ^{210}Pb dates or the ^{241}Am peak. These results were expected since ^{137}Cs is known to be mobile in the sediments of acid lakes (Davis *et al.* 1984). Measurable ^{137}Cs was often found below the ^{210}Pb equilibrium level (usually pre-1850).

The accuracy of ^{210}Pb dating for nineteenth century sediments was sometimes poor, partly owing to the larger standard error of measurements of old sediment and partly owing to inwash and rapid accumulation rate at some sites during this period causing dilution of unsupported ^{210}Pb to values indistinguishable from background levels (e.g. at Lochnagar and Watersheddles Reservoir).

The chronologies established for each site showed that there was considerable variability in sediment accumulation rate both through time at a site and also between sites. Rates vary depending on catchment:lake ratios, stability of catchment soils, water residence time and the pattern of sediment distribution within the lake.

Table 6.1 shows the range of sediment accumulation rates for different time periods for all undisturbed sites. Except for Watersheddles Reservoir which has a much higher accumulation rate than other sites ($7\ mm\ yr^{-1}$) values vary from $< 1\ mm\ yr^{-1}$ to $> 3\ mm\ yr^{-1}$. Those with higher rates (e.g. Llyn Llagi) have very good chronological resolution and all things being equal, are the most suitable for monitoring by repeat sediment coring.

An additional advantage of the radiometric dating has been the calibration of lead, zinc and carbonaceous particle curves for dating purposes. In particular the lead rise and the carbonaceous particle rise can now be used to identify approximately the 1800 and 1940 levels in United Kingdom lake sediments (cf. Renberg and Wik 1984).

6.3 Diatom trends

Diatom analysis of the recent sediments of acidified lakes in the United Kingdom shows that in almost all cases the pre-acidification (before 1850) floras of these lakes were remarkably stable. The same species occurred in approximately the same proportions at each site for hundreds of years, despite shifting land management patterns and climatic changes.

At many sites during the pre-acidification period a significant proportion of the diatom assemblage comprised planktonic forms, especially *Cyclotella kützingiana*. However, at some sites plankton was absent or rare despite apparently stable conditions and a relatively high pH. So far the reasons for this difference between sites are not known although auxiliary factors such as water depth and nutrient availability may be important.

In cores from all acidified sites studied, *Cyclotella kützingiana*, where originally present, is the first species to decline. In most cases (e.g. Llyn Hir, Loch Laidon, Scoat Tarn) the decline is abrupt and absolute.

The non-planktonic flora at most sites prior to acidification is dominated by *Achnanthes minutissima*, *Anomoeoneis vitrea* and *Fragilaria virescens*. These are species that have mainly circumneutral pH distributions but are also found in abundance mixed with more acidophilous forms between pH 5.5 and 7.0. Where acidification is rapid these taxa often decline together, but where the change is more gradual the decline is sequential and almost always in the order *Achnanthes minutissima*, *Anomoeoneis vitrea* and then *Fragilaria virescens*, (cf. Fritz *et al.* 1986), an order that indicates the relative sensitivity of these species to increasing acidity and co-factors (Flower *et al.* 1987a).

Table 6.1 **Comparisons of sediment accumulation rates**

		Mean accumulation rates (mm yr^{-1})		
Region	Site	Post 1950	1910–1950	Pre 1910
Wales	Llyn Gynon	2.02	1.96	1.01
	Llyn Hir	0.90	0.89	1.70
	Llyn Cwm Mynach	1.29	1.08	0.93
	Llyn Dulyn	1.89	1.28	0.58
	Llyn y Bi	0.64	0.50	0.29
	Llyn Llagi	2.09	1.76	1.17
Scotland	Loch Urr	2.16	1.84	1.50
	Loch Tanna	1.11	0.89	0.32
	Loch Laidon	2.11	1.84	1.49
	Lochnagar	1.02	0.74	0.47
England	Watersheddles	6.30	5.00	–
	Scoat Tarn	1.12	1.10	0.66
	Greendale Tarn	1.11	0.90	0.78

As these sensitive circumneutral species decline a proportionate increase in acidophilous species occurs. These are invariably species already present in reasonable abundance in the pre-acidification flora, such as *Tabellaria flocculosa*, *Frustulia rhomboides* and varieties, *Eunotia veneris*, *Achnanthes marginulata* and *Navicula heimansii*.

Further acidification leads to the elimination of circumneutral taxa, to the continued expansion of some acidophilous species and to the appearance and increase of acidobiontic taxa such as *Tabellaria quadriseptata*, and *Tabellaria binalis*. However, the response of any one site is variable. In Wales *Tabellaria binalis* is dominant in Llyn y Bi but is rare elsewhere. *Tabellaria quadriseptata* is important at Llyn Llagi and Llyn Gynon at the present time, whereas neither of these are common in Llyn Dulyn where the acidification is reflected by a continuing expansion of acidophilous forms, especially *Melosira* spp. Responses in Scotland can be equally variable: at Lochnagar the recent sediments are dominated by *Achnanthes marginulata* but acidified sites in Galloway usually have an abundant *Tabellaria* flora. The reasons for this variability are not known but are probably related to differences in water transparency, variations in micro-habitats, water colour and other factors.

At the two higher pH sites chosen for analysis, Loch Urr in Galloway and Burnmoor Tarn in Cumbria, only slight trends in diatom assemblages are recorded and in both cases the floras are dominated by planktonic taxa, including *Cyclotella kützingiana* and circumneutral non-planktonic taxa, especially *Achnanthes minutissima* and *Anomoeoneis vitrea*.

6.4 pH trends

At all sites except Loch Urr, Burnmoor Tarn and Lochan Dubh, a clear post-1850 acidification is indicated by the trends in diatom assemblages. Quantification of these trends using the multiple regression approach (Flower 1986) gives results in good agreement with measured pH for modern day samples. However, at some sites (e.g. Llyn Hir) a full reconstruction is not possible because of the numerical importance of unknown species. In these cases the approximate pH change can be inferred from the difference between the diatom-based pH for the pre-acidification period and the measured pH of today.

At most of the acidified sites those with present pH levels below 5.0 had pH levels about 6.0 prior to 1850. Only two sites, Loch Enoch and Loch Tanna, had pH values below 5.5 at that time. These data show that sites with zero or negative alkalinity prior to *c*.1850 were exceptionally rare.

The largest inferred pH declines occurred in the Welsh lakes in the Rhinog area. Here pH has probably decreased by 1.0 to 1.5 pH units. These are lakes with extremely clear water (TOC < 1 mg l^{-1}) and the lack of a significant organic acid input from the catchment was probably the reason for their relatively high pre-acidification pH.

In general, pH declines since 1850 have varied from about 0.5–1.5 pH units.

Although sensitive areas in Scotland, northern England and Wales have been acidified to a similar extent and over the same broad time period (since 1850) there is considerable variation between sites in the timing of these changes and in the acidification trajectory.

In Wales acidification began in the mid- to late-nineteenth century at Llyn Hir, Llyn Dulyn and Llyn Llagi, in the early twentieth century at Llyn y Bi, but not until the mid-1940s at Llyn Eiddew Bach and Llyn Gynon. In Scotland acidification began at many sites in the mid-nineteenth century but at other sites it was delayed until the turn of the century (e.g. Loch Dee) or later (Loch Grannoch and Loch Chon). In Cumbria some upland tarns started to acidify in the mid-nineteenth century (Scoat Tarn) but other sites (e.g. Greendale Tarn) did not begin to change until about 1900. And at some sites, although the first sign of acidification occurred in the mid-nineteenth century an acceleration in the rate of acidification occurred after 1940 (e.g. Llyn Llagi).

Although we have as yet insufficient catchment information to explain in detail why this kind of variation has

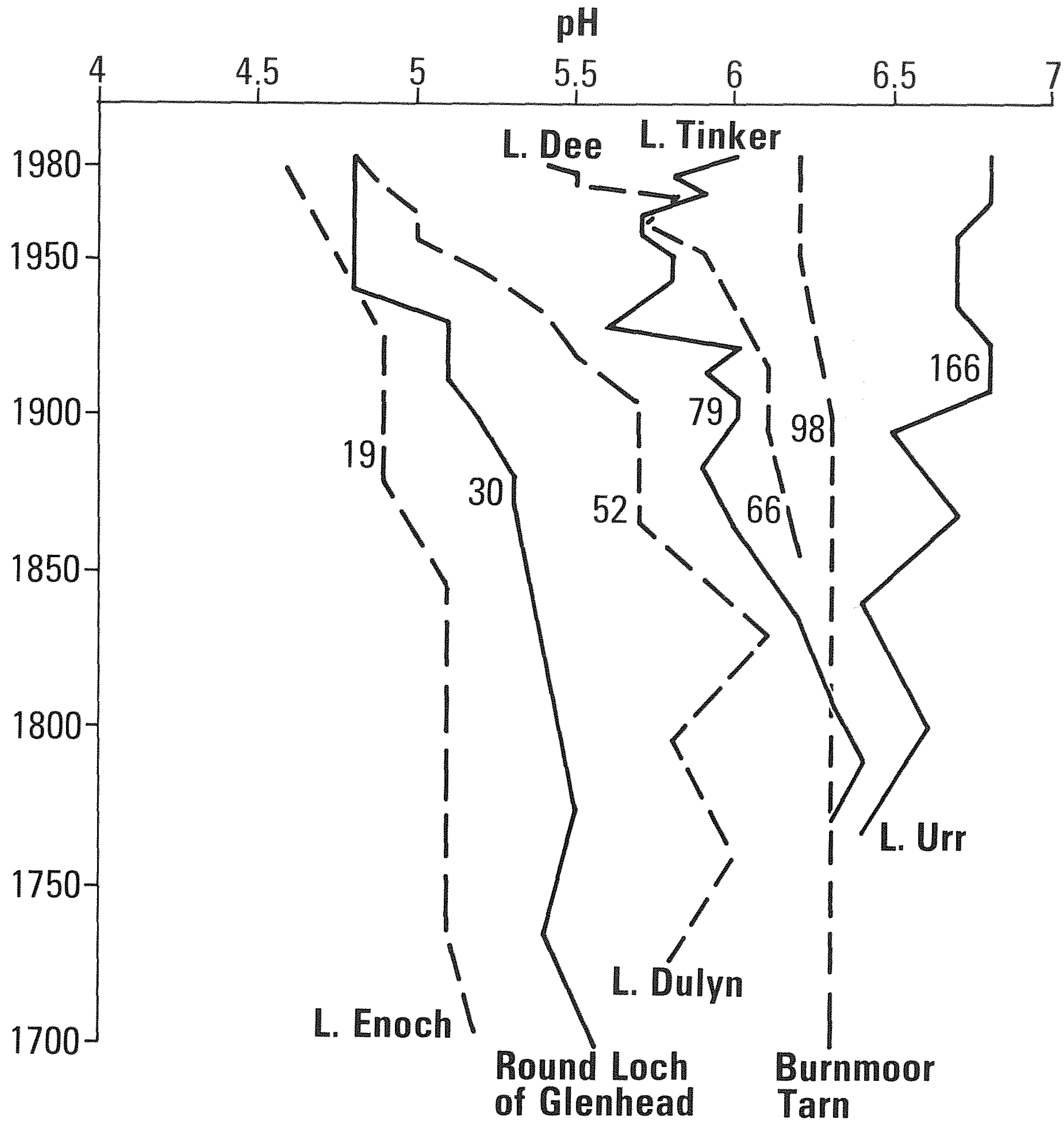


Figure 6.1 Comparison of reconstructed pH trends for a series of sites with increasing lake water calcium values. Ca^{2+} as $\mu eq\,l^{-1}$.

occurred it is clear that the response of any site depends on the historical pattern and intensity of acid deposition and the general neutralising capacity of the catchments.

The most sensitive sites (Loch Enoch, Loch Valley, Lochnagar, ($Ca^{2+} < 35\,\mu eq\,l^{-1}$) appear to have acidified continuously from *c.*1850 until the present. At less sensitive sites (Loch Dee, Loch Tinker — Ca^{2+} 50–80 $\mu eq\,l^{-1}$) or sites with lower acid deposition (Loch Laidon, Lochan Dubh — Ca^{2+} 30–40 $\mu eq\,l^{-1}$), the acidification has been slow and slight, and in the case of Burnmoor Tarn and Loch Urr, with $Ca^{2+} > 95\mu eq\,l^{-1}$, acidification has not occurred despite their location in areas of high acid deposition (Figure 6.1).

6.5 Trends in atmospheric contamination

6.5.1 Trace metals

Significant increases in the concentration of lead and zinc occur in the recent sediments of all the sediment cores so far analysed. Short-term fluctuations in concentrations are related to occasional dilutions caused by periods of soil inwash.

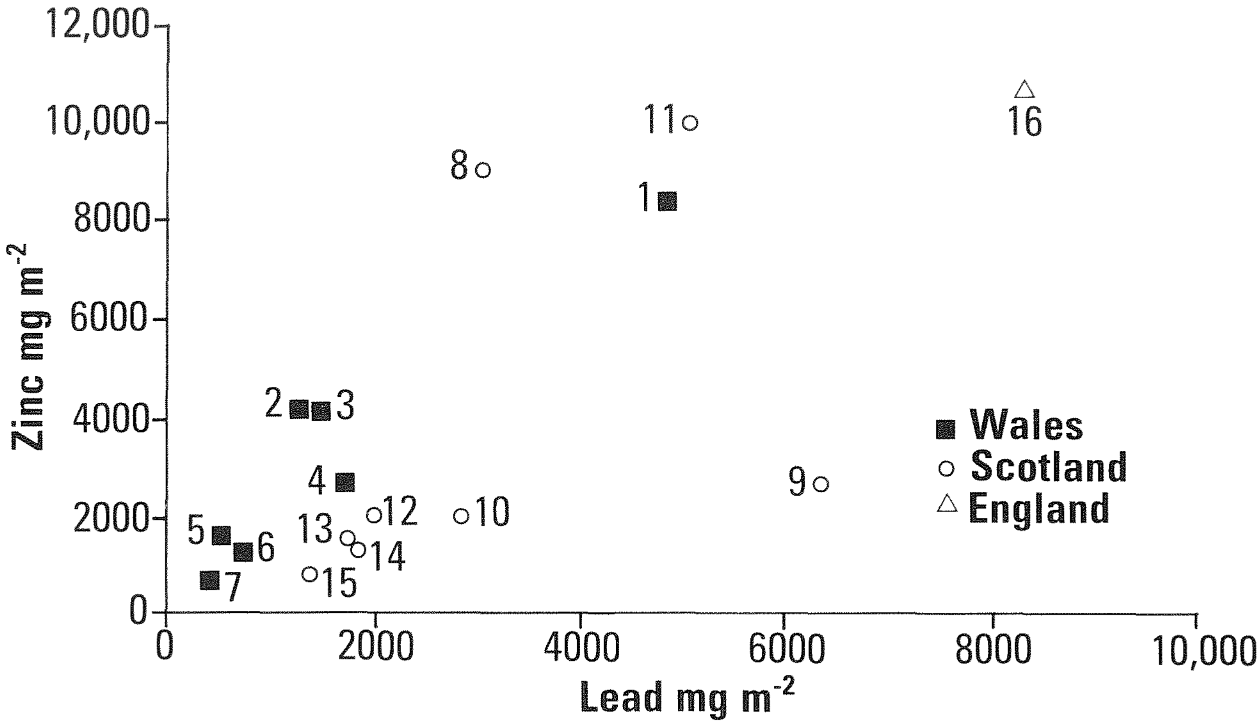


Figure 6.2 Between site comparison of lead and zinc sediment fluxes: see Table 6.2 for the key to the sites.

The initial increase in the lead curve represents the first clear impact of atmospheric contamination, and in most sites studied this point is dated to about 1800 in both Scotland and Wales, pre-dating the beginning of acidification in these regions by about 50 years. At most sites the lead curve rises to a maximum in the mid-twentieth century before falling somewhat in recent years. In the nineteenth century and early-twentieth century the lead burden was probably related to lead smelting and primary industry. However, in recent decades lead used as an anti-knock agent in petrol products has been a more important source.

The zinc curves often follow the lead curves but at some sites the initial increase occurs somewhat after that of lead and in a number of cases (e.g. Loch Enoch, Round Loch of Glenhead, Llyn Hir) marked decreases in zinc concentration occur in the uppermost sediment. This is almost certainly not the result of an equivalent reduction in atmospheric zinc contamination but of a decrease in the efficiency of zinc sedimentation in increasingly acid waters. The zinc curve for Loch Urr, a non-acidified high pH site, indicates the more likely zinc trajectory. Figure 6.2 shows that cumulative flux (since 1900) of zinc is substantially reduced relative to lead at the most acidified sites. Figure 6.2 also shows that overall the zinc to lead ratio at Welsh sites is higher than at Scottish sites suggesting that the two regions are receiving trace metals from a different mixture of pollution sources, or that there is selective transport of these aerosols.

The wide range of values for both lead and zinc burdens between sites both in Scotland and Wales (Table 6.2) is related more to the differences in sediment accumulation rate between sites than to any difference in trace metal deposition. Llyn Gynon and Llyn Hir are only 2.5 km distant and lie at a similar altitude yet the flux since 1900 at Llyn Gynon is three times that at Llyn Hir for both metals. The very high values for the Watersheddles Reservoir in the Pennines can be explained in a similar way although the historic atmospheric flux may also have been higher in this more industrialised region.

6.5.2 Carbonaceous particles

Carbonaceous particles of the kind produced by the combustion of fossil fuels were observed in quantity at all the lakes under study. SEM and EDS analysis of the particles in modern sediments indicate that the majority can be related to fuel oil (Figure 2.13), and the major increase in particle concentration in recent sediments at all sites is probably related to the rapid expansion in the use of this energy source since about 1940. A contribution from coal-fired furnaces is also likely, despite the low carbonaceous content of most modern fly-ashes.

At most sites there are also significant concentrations of particles in late-nineteenth and early-twentieth century sediments. Since coal was the most important fuel used during this period it is probable that these particles are mainly coal-derived.

Despite the large geographical range of sites, the historical trends between sites in Wales and Scotland are very similar (Figure 6.3). Only Loch Laidon, the most north-westerly site in Scotland in this study, has significantly lower concentrations than others. This observation indicates that the far north-west of Scotland is likely to be relatively free from atmospheric contamination of this kind.

Table 6.2 **Summary of zinc and lead fluxes**

Region	No.	Site	Total dry sediment since 1900 mg cm^{-2}	Total Zn since 1900 mg m^{-2}	Total Pb since 1900 mg m^{-2}	Total Zn/Pb
Wales	1	Llyn Gynon	2655	8383	4854	1.73
	4	Llyn Hir	616	2707	1738	1.56
	6	Llyn Dulyn	628	1238	728	1.70
	5	Llyn Eiddew Bach	600	1681	509	3.30
	3	Llyn Llagi	1427	4180	1427	2.93
	7	Llyn y Bi	250	677	406	1.67
	2	Llyn Cwm Mynach	605	4255	1259	3.38
South-west Scotland (Galloway)	9	Loch Enoch	2018	2695	6336	0.43
	10	Round Loch of Glenhead	904	2049	2853	0.72
	8	Loch Urr	1866	9017	3049	2.96
Central Scotland	13	Loch Laidon	1015	1542	1746	0.88
	11	Loch Tinker	1617	9982	5092	1.96
	15	Loch Tanna	903	860	1350	0.64
	14	Lochnagar	972	1349	1809	0.75
	12	Lochan Uaine	1614	2101	1991	1.06
England	16	Watersheddles	8050	10610	8360	1.27

Analyses of sites in this region are now in progress in an attempt to assess how 'clean' this region is. A recently completed analysis of the Lochan Dubh core supports this conclusion.

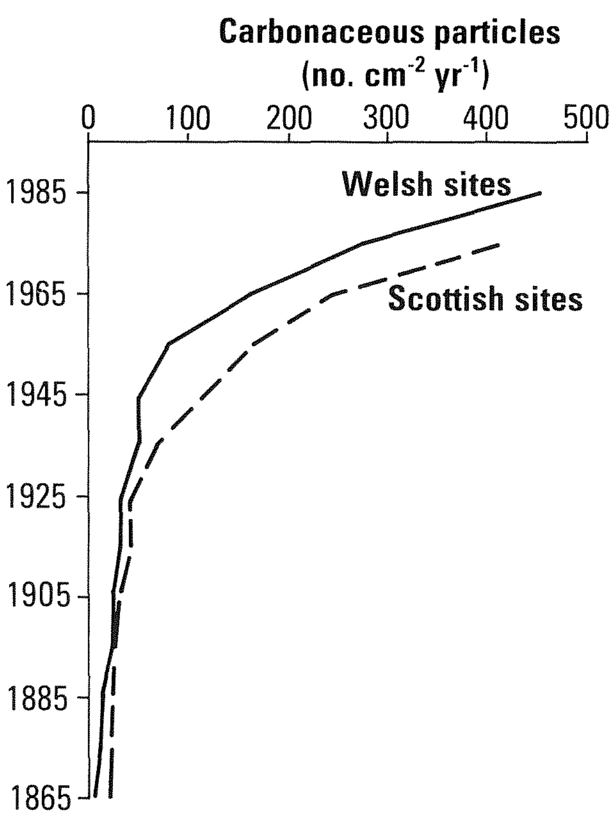


Figure 6.3 Comparison of the mean carbonaceous particle flux for Wales and Scotland.

6.5.3 Magnetic minerals

The magnetic record in lake sediments is derived from both catchment and atmospheric inputs. At some sites the catchment input is dominant and obscures the atmospheric signal. At others a clear atmospheric record linked to fly-ash deposition (Oldfield *et al.* 1987) is present. Of the Welsh sites studied Llyn Hir, Llyn Dulyn and Llyn y Bi provide the best data. Figure 6.4a compares the flux of 'magnetite' as approximated from the 'soft' part of the isothermal remanence. Although there is some evidence of earlier contamination the curves steepen after about 1940 in accordance with similarly dated evidence at ombrotrophic bog sites in northern Britain (Oldfield *et al.* 1987) and with the carbonaceous particle evidence presented here for lake sites. Figure 6.4b shows similar data for the Scottish sites Loch Tanna and Lochnagar. The trends at these two sites are even clearer than for the Welsh sites. At Loch Tanna there is a continuous increase from the nineteenth century, but the steepest increase is post-1945 and post-1960. At Lochnagar there is little evidence of pre-1940 increases but the post-1960 increase is especially marked.

There is general agreement between the carbonaceous particle and magnetic curves reflecting a major increase in the contamination of the atmosphere by particles of fuel combustion origin since 1940. However, the carbonaceous particles are predominantly derived from fuel oil whereas the 'magnetite' is thought to be derived from coal burning. The steep increase in 'magnetite' accumulation at Lochnagar after 1960 is not paralleled by the carbonaceous particle record and might, therefore, be an independent measure of the impact of large tall-chimney, coal-fired power stations built in the United Kingdom since 1960.

6.6 Trends in catchment land-use and management

Changes in land-use and management that might have influenced lake-water acidity have been assessed using pollen

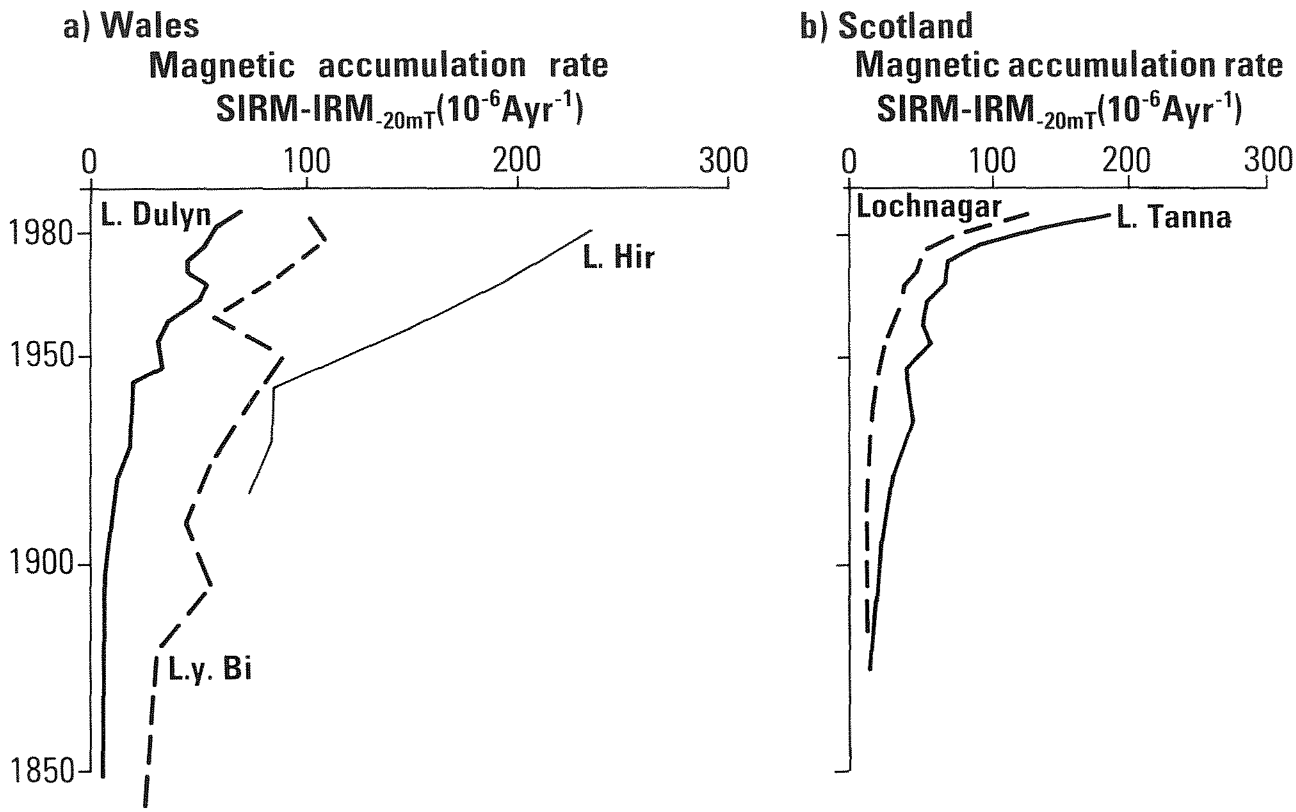


Figure 6.4 Between-site comparison of 'soft magnetite' flux.

analysis, documentary records and site-based interviews.

6.6.1 Pollen analysis

The detailed pollen records are presented in Research Papers (Appendix 1) on a site basis. For the non-afforested sites the critical question is whether a significant shift from grassland to heathland has taken place at the same time as lakes were acidified. This can be assessed from trends in the pollen frequency of *Calluna vulgaris*, the most common heathland species in British moorlands, in comparison with trends in the frequency of grass (Gramineae) pollen expressed as a ratio.

In the case of the six unafforested lakes from Wales all show that very little change has occurred within each of the catchments over the last 200 years. With the exception of Llyn y Bi, the evidence suggests any change that has taken place has been in the direction of graminoid domination rather than the reverse. This parallels trends already observed for Galloway (Battarbee *et al.* 1985a). The Llyn y Bi case (Figure 3.8) is exceptional and probably the result of a decrease in burning in the catchment (see below).

In Scotland, the trend at all sites towards Gramineae and away from *Calluna* is even more marked.

6.6.2 Documentary records and interviews

Documentary sources of information relate more to human use and management of land than to vegetation history. As such they complement as well as reinforce the pollen record. Data mainly refer to afforestation, grazing, burning, draining and liming practices.

In Wales two of the study sites, Llyn Berwyn and Llyn Cwm Mynach, have catchments afforested from 1962 and 1967 respectively. In the case of Llyn Berwyn the catchment was also drained in 1962 and 1974. Far less draining was required at Llyn Cwm Mynach before tree planting.

For moorland sites in Wales some catchments were enclosed in the late-eighteenth and early-nineteenth century. From the mid-nineteenth century onwards there was a general replacement of wether flocks by ewes and lambs with a consequent decline in winter stocking densities (Patrick 1987). However, in the post-1945 period some catchments have experienced a significant increase in stocking densities.

With the exception of the Llyn Eiddew Bach and Llyn Hir catchments, which were never regularly burnt, there has been a decline or cessation of burning in other catchments. This has either been the result of National Trust policy, in the case of Llyn y Bi, Llyn Conwy and Llyn Gamallt, or the proximity of forestry plantations as in the case of Llyn Cwm Mynach. Only at Llyn y Bi, of the sites cored, has this decline resulted in a *Calluna* dominated catchment, probably because this trend has been accompanied by a simultaneous decline in grazing intensity.

Excluding the afforested sites, partial draining has only occurred at Llyn Conwy and Llyn Gamallt in an attempt to improve the moorland for grouse shooting and sheep grazing. There is no evidence for the practice of liming in any of the catchments studied in Wales.

The catchments studied in Scotland are far less homogeneous in terms of their land-use/management characteristics than those in Wales since they are much more widely distributed and span a greater range of sizes and altitudes.

The catchment of Loch Urr, the non-acidified lake in Galloway (Figure 4.3), contains a significant area which has been improved and managed for arable and pastoral agriculture for at least the past 250 years. Regular regimes of burning, drainage and liming have been undertaken over the years to improve and maintain the quality of the land.

The catchment of Loch Laidon has a long history of low-intensity grazing by sheep and deer. Two small sectors of the catchment have been afforested and burning, a regular practice through to the late 1940s has declined in recent years as a result of NCC management policy, the expense of gamekeeping and poor grouse returns. At Loch Tanna, burning to maintain good grouse populations is the only management practice in the catchment and in this case is still a regular feature. Lochnagar is a remote high altitude lake with an undisturbed catchment. There is no evidence for, nor rational expectation of, past or present land management.

In summary, except for afforestation at two sites studied in Wales there is no evidence of land-use change in any of the catchments studied. However, there have been a variety of changes in land management. In some cases there has been an increase in grazing intensity, at some a decrease in burning. But only rarely has there been a decrease in burning accompanied by a decrease in grazing. Only in these cases is it relevant to consider land management changes as a possible contributor to surface water acidification, and it has been shown elsewhere (Jones *et al.* 1986) that such changes are unlikely to promote intense acidification.

6.7 Extent of surface water acidification in the UK

Our work in Galloway between 1981 and 1984 showed that recent (post-1850) acidification had occurred at lakes lying on the two upland granitic areas in that region (Flower and Battarbee 1983, Battarbee *et al.* 1985a, Flower *et al.* 1987a). The extension of our work to other regions of the United Kingdom shows that similar acidification has occurred at lakes in mid and north Wales on Lower Palaeozoic sedimentary and metamorphic rocks, in Cumbria on Borrowdale volcanic strata, and throughout Scotland southeast of Loch Ness on granites. Exceptionally acid waters also occur in the English Pennines. Although sufficiently old sediments are not available for analysis in this region it can be strongly argued that these waters are also acidified.

Only a small number of lakes have been analysed in each of the regions considered. However, the patterns are so consistent both within and between regions that this interpretation can be confidently extrapolated to other sites with similar modern water chemistry in these areas. The number of acidified lakes is far greater than the number of fishless lakes (cf. Maitland *et al.* 1987) since fish extinction occurs relatively late in the acidification process, often after many decades of population reduction.

Although many of the sites are quite remote almost all are of special interest since they are situated in National Parks, National Nature Reserves, Sites of Special Scientific Interest and National Trust areas.

The full geographical extent of acidification is not yet known. Work in progress (Figure 2.1) is designed to reconstruct the recent history of sensitive sites in the north-west of Scotland, in Ireland, and in parts of lowland England. Preliminary evidence suggests that very sensitive sites in the north-west of Scotland have not been acidified to any marked extent.

6.8 Causes of surface water acidification

The results of this study reinforce the conclusion of our earlier Galloway work (Battarbee *et al.* 1985a) that the primary cause of surface water acidification is acid deposition. All the evidence is consistent with the acid deposition hypothesis and the overall pattern of observations cannot be accounted for by alternative hypotheses. Afforestation, where it occurs can also be important but its effect is variable from site to site.

6.8.1 Acid deposition

The palaeolimnological evidence for acid deposition as a cause of surface water acidification is as follows:

a. At all acidified sites the beginning of rapid acidification post-dates 1800 AD. At many sites the starting point is about 1850 although some lakes do not begin to be affected until later. For Llyn Gynon and Llyn Eiddew Bach acidification begins after 1940.

b. At all sites the beginning of acidification is never before the first evidence of trace metal contamination. An increase in lead values in the cores occurs in the late-eighteenth to early-nineteenth century.

c. Cores from all acidified sites have high concentrations of carbonaceous particles that are derived from fossil-fuel combustion.

d. Although few cores from areas of very low acid deposition have yet been analysed, sensitive sites in north-west Scotland, such as Lochan Dubh (Ca^{2+} 33μeq l^{-1}), are only slightly acidified. The only lochs with pH below 5.0 in this area are shallow, brown-water sites (TOC >8 mg l^{-1}).

e. Although there have been changes in burning and grazing regimes in many of the catchments studied these have led in most cases to a decline in heathland vegetation rather to an increase. At Llyn y Bi, the only site with a well-documented increase in catchment *Calluna*, acidification began before the reduced burning policy was implemented when the lake became National Trust property.

f. There is no evidence of liming ever having taken place in the catchments of any of the acidified sites studied. Cessation of that practice may therefore be excluded as a potential acidification mechanism.

g. Acidification at Llyn Cwm Mynach, a site with an afforested catchment, began before afforestation. This was also the case at sensitive Galloway sites (Flower *et al.* 1987a).

6.8.2 Afforestation

Palaeolimnological evidence presented here and elsewhere suggests that conifer afforestation can have both a direct and indirect effect on the acidity of surface waters as follows:

a. At Llyn Berwyn, documentary evidence and limited core data (Section 3.1) suggests that soil disturbance following deep drainage not only caused soil erosion and inwash but also acidification and damage to fish stocks.
b. At Loch Fleet (Figure 4.1) (Anderson *et al.* 1986) acidification followed afforestation. At this unusual site acidification may be the result of a combination of factors including the scavenging effect of the forest and the erosion of peat following land drainage. The latter process caused a thick layer of acid organic peat-derived sediment to be deposited across the bed of the loch and this may have sealed the lake from a source of calcium-rich groundwater.
c. Furthermore, recent work funded by the Royal Society SWAP project has indicated the importance of afforestation in causing acidification indirectly through the scavenging mechanism. At Loch Chon afforestation occurred in 1951–1955. Since planting was carried out on the steep catchment slopes by hand, soil disturbance did not occur. However, acidification accelerated about 15 years after planting although no further acidification occurred at this time at Loch Tinker, a control site with a moorland catchment.

6.9 Monitoring and reversibility

Where sediment accumulation rates are sufficiently rapid contemporary trends in acidity can be monitored by repeat coring of the lakes described here. Already the uppermost sediments of some Scottish lakes show slight signs of improvement (Battarbee *et al.* 1988) probably in response to post-1970 reductions in acid deposition in Scotland (Harriman and Wells 1985). These preliminary data indicate that a large reduction in acid deposition is likely to lead to a rapid response in lake chemistry and biota. However, no signs of improvement have yet been detected at Welsh or English sites.

Figure 6.5 Map of United Kingdom core sites showing pH change (1800–1985).

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Appendix 1

Palaeoecology Research Unit Research Papers

Relating to Contract PECD 7/7/139

1986

16 FRITZ, S.C., STEVENSON, A.C., PATRICK, S.T., APPLEBY, P.G., OLDFIELD, F., RIPPEY, B., DARLEY, J. & BATTARBEE, R.W. Palaeoecological evaluation of the recent acidification of Welsh lakes. I, Llyn Hir, Dyfed.

18 KREISER, A., STEVENSON, A.C., PATRICK, S.T., APPLEBY, P.G., RIPPEY, B., DARLEY, J. & BATTARBEE, R.W. Palaeoecological evaluation of the recent acidification of Welsh lakes. II, Llyn Berwyn, Dyfed.

19 PATRICK, S.T. & STEVENSON, A.C. Palaeoecological evaluation of the recent acidification of Welsh lakes. III, Llyn Conwy and Llyn Gamallt, Gwynedd (site descriptions, fishing and land use/management histories).

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20 STEVENSON, A.C., PATRICK, S.T., FRITZ, S.C., RIPPEY, B., OLDFIELD, F., DARLEY, J., HIGGITT, S.R., & BATTARBEE, R.W. Palaeoecological evaluation of the recent acidification of Welsh lakes. IV, Llyn Gynon, Dyfed.

21 PATRICK, S.T. Palaeoecological evaluation of the recent acidification of Welsh lakes. V, The significance of land use and land management.

23 FRITZ, S.C., STEVENSON, A.C., PATRICK, S.T., APPLEBY, P.G., OLDFIELD, F., RIPPEY, B., DARLEY, J., BATTARBEE, R.W., HIGGITT, S.R. & RAVEN, P.J. Palaeoecological evaluation of the recent acidification of Welsh lakes. VII, Llyn y Bi, Gwynedd.

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26 STEVENSON, A.C., PATRICK, S.T., KREISER, A. & BATTARBEE, R.W. Palaeoecological evaluation of the recent acidification of susceptible lakes: methods utilised under DoE contract PECD 7/7/139 and the Royal Society SWAP project.

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30 ANDERSON, N.J., PATRICK, S.T., APPLEBY, P.G., OLDFIELD, F., RIPPEY, B., RICHARDSON, N., DARLEY, J. & BATTARBEE, R.W. An assessment of the use of reservoir sediments in the southern Pennines for reconstructing the history and effects of atmospheric pollution.

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