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LAKE ACIDIFICATION IN THE UNITED KINGDOM II: A PRELIMINARY REPORT TO THE DEPARTMENT OF THE ENVIRONMENT UNDER CONTRACT PECD 7/10/167

Series editor: S.T. Patrick

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Afforestation and lake acidification: a comparison of four sites in Scotland	Ms A. Kreiser
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Lake acidification studies in the Snowdonia National Park	Dr S. Fritz
Acidification at an afforested site in mid-Wales - Llyn Berwyn	Ms A. Kreiser
The palaeoecological use of reservoir sediments for reconstructing the history of atmospheric pollution; Tunnel End, West Yorkshire	Dr V.J. Jones
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Acknowledgements

The project participants wish to acknowledge the financial support of the Department of the Environment. Certain aspects of this work are linked with other major research projects funded by the Royal Society (SWAP) and the CEGB. Field assistance and technical coordination was provided by Mr D. Monteith. Many of the diagrams presented in this report were prepared by Tim Aspden, Louise Saunders and Robert Bradbrook.

1 INTRODUCTION

This report summarises progress made in Department of the Environment project PECD 7/10/167 - "causes and extent of lake acidification in the United Kingdom". It includes data and results available at the present time and indicates where work is still in progress. We expect that all work will be completed on schedule and that a final report will be issued shortly after completion of the contract (March 31st 1990).

This project, which began on April 1st 1987, is a continuation of the previous DoE-funded project which was completed in July 1987 (Battarbee *et al.* 1988). The general aim of these projects has been and is, to define the causes and extent of lake acidification in the United Kingdom. A further project, the Royal Society-funded Surface Water Acidification Project (SWAP), has been conducted alongside the DoE work and was designed to complement it by placing emphasis on the development of techniques (quality control, taxonomy, transfer functions, database development) as well as site studies. The SWAP results are published by the Royal Society (Battarbee *et al.* 1990).

The present project is divided into several sub-projects (Table 1.1, Figure 1.1). Each is concerned with a specific problem. Most also contribute to the aim of the main project while others (eg. the stream diatom survey) are independent studies. The various sub-projects correspond to the sections of this report.

1.1 SUMMARY

Remote mountain lakes: Cairngorms and Lochnagar (Section 2)

Five sensitive high altitude sites have been studied in this region of medium acid deposition. Although there is some variability between sites the data indicate that considerable acidification has taken place since 1850 and that sites are significantly contaminated by carbonaceous particles and trace metals. The results support the acid deposition hypothesis and, because all sites are above the limit of cattle and sheep grazing, they can also be used to refute the 'land-use' hypothesis.

Low deposition areas: north west Scotland (Section 3)

Our hypothesis is that if there is a dose - response relationship between sulphur deposition and lake acidification then sensitive lakes in this region of Scotland should be less acidified than sites to the south (eg. Galloway) in high deposition areas. Data for four clear water sites in north west Scotland strongly support this hypothesis. Three sensitive sites are not acidified and one very sensitive site is only slightly acidified. The lack of acidification at these sites is correlated with the very low levels of carbonaceous particles in the sediments.

Low deposition areas: north west and western Ireland (Section 4)

We have no sulphur deposition data for the north west and west of Ireland, but we can argue from extrapolation from UK and EMEP data that deposition in this area should be low. Our hypothesis here was that sensitive sites would not be acidified and we hoped that lakes in Donegal might be used for reference purposes. However, our data are beginning to indicate that the most sensitive sites in Donegal (eg. Lough Maam) are slightly acidified although less sensitive sites (eg. Lough Veagh) are not acidified. Carbonaceous particle concentrations are very low, similar to those in north west Scotland, but clearly Donegal can not be regarded as a 'pristine' area.

Afforestation: Scotland (Section 5)

In this major sub-project we compared sites with afforested (Loch Chon) and non-afforested (Loch Tinker) catchments in an area of high sulphur deposition (the Trossachs) with more sensitive, but otherwise similar afforested (Loch Doilet) and non-afforested (Lochan Dubh) in an area of lower deposition (Strontian/Loch Shiel). Our hypothesis was that afforestation can exacerbate lake acidification and that the processes involved are related more to scavenging of dry deposition than by base-cation uptake and soil acidification. The results showed a post-afforestation acceleration in acidification at Loch Chon when the non-afforested control site (Loch Tinker) showed no change, indicating a forest effect. At Loch Doilet only a slight acidification, similar to that at the control site (Lochan Dubh) was recorded, suggesting that the forest effect is more likely related to scavenging than forest growth factors.

Acid brown-water lochs in low deposition areas (Section 6)

Coastal brown water lakes in areas of low acid deposition in north west Scotland can have very low pH values (<5.0). We hypothesised that these acid conditions arose from natural acidity and not from post-1800 increase in acid deposition. The results from two sites show, in general, that this hypothesis is supported, but poor diatom preservation and the inadequacy of our database for coloured lakes, have prevented a rigorous test. It is likely that the diatoms in these environments are influenced by water colour and salinity as well as pH.

Snowdonia National Park (Section 7)

A number of sites in this area were selected to extend our coverage of lakes in this geologically complex area.

Llyn Conwy was an important lake for angling. It was cored unsuccessfully in our previous DoE project. We now have good cores which contain a clear record of recent acidification.

Llyn Glas and Llyn Clyd are two high altitude lakes with somewhat higher alkalinities than many sites in the region. They were cored in the 1970s as part of a Ph.D. investigation into the long-term (10,000 year) evolution of lakes, consequently the most recent sediments were not sampled. Our project is designed to assess whether there is evidence for recent acidification.

Llyn Irddyn is a site in the Rhinnogs with slightly higher pH and calcium than sites in that region which were included in our previous DoE project. We hypothesised therefore, that the site should be less acidified than the nearby lakes Llyn Dulyn and Llyn y Bi. Preliminary data indicate that this hypothesis is confirmed.

Afforestation in mid-Wales: Llyn Berwyn (Section 8)

This acidified site which has both an afforestation and liming history was first cored in our previous project but the cores were found to be unsuitable. A satisfactory new core is now being analysed. The core contains good evidence of extremely rapid sediment accumulation associated with catchment drainage activities and suggests that the main period of acidification occurred after afforestation. This site may have suffered more from afforestation influences than from acid deposition, although it is not yet clear whether the acidification results from soil disturbance, base-cation uptake or canopy scavenging.

Acidification and atmospheric contamination of Pennine reservoirs (Section 9)

Our previous project demonstrated that there are very few acid sites in the Pennines suitable for palaeolimnological analysis because of the effects of water drawdown on reservoir sediments. However, one possible suitable site is Tunnel End Reservoir near Huddersfield. This was constructed as a canal feeder reservoir but is now abandoned and has had a stable water level for the last few decades. Work is in progress to assess its suitability as a site for reconstructing post-1970 atmospheric contamination history.

Epilithic diatoms in Scottish streams: Scottish baseline survey (Section 10)

We have analysed over 750 diatom samples from 149 stream sites in Scotland as part of the DoE funded Scottish River Purification Boards baseline survey. Comparison of these data with measured stream chemistry show a very good overall relationship between inferred and measured pH, indicating that diatoms in streams can be used as an excellent technique for monitoring stream acidity.

Carbonaceous particles (Section 11)

A methodological sub-project was designed to improve our laboratory preparation of carbonaceous and other fly-ash particles from lake sediments. In combination with funding from the CEGB on a related project we have made significant advances and now have a more robust and sensitive technique. It is now possible to distinguish between coal and oil-derived carbonaceous particles. Application of this technique to the surface sediments of Loch Tinker indicate that about 70% of the carbonaceous particles at the site are derived from coal combustion.

1.2 REFERENCES

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Battarbee, R.W., Anderson, N.J., Appleby, P.G., Flower, R.J., Fritz, S.C., Haworth, E.Y., Higgett, S., Jones, V.J., Krieser, A., Munro, M.A.R., Natkanski, J., Oldfield, F., Patrick, S.T., Raven, P.J., Richardson, N.G., Rippey, B. and Stevenson A.C. (1988) **Lake acidification in the United Kingdom.** ENSIS, London.

Figure 1.1 Location of lake and sub-project sites

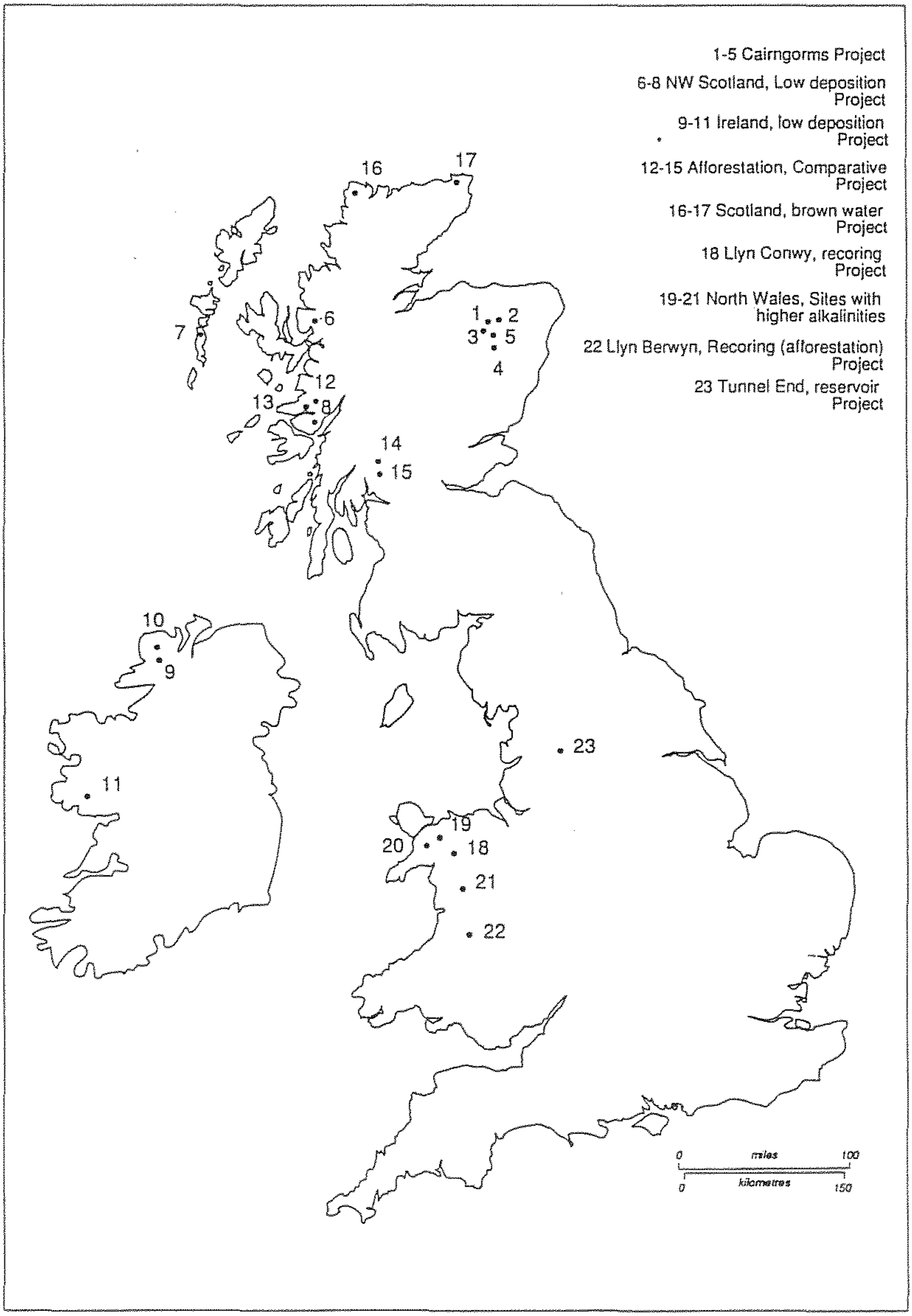


Table 1.1 Key to lake and sub-project sites (Figure 1.1)

Site no.	Lake	Sub-project
1	L. Coire an Lochan	Cairngorms
2	L. Uaine	"
3	L. nan Eun	"
4	Dubh Loch	"
5	Lochnagar	"
6	L. Coire nan Arr	Low deposition areas (NW Scotland)
7	L. Teanga	"
8	L. Uisge	"
9	L. Veagh	Low deposition areas (west Ireland)
10	L. Maam	"
11	L. Maumwee	"
12	L. Dubh	Afforestation (comparative)
13	L. Doilet	"
14	L. Tinker	"
15	L. Chon	"
16	L. na Larach	Brown water (north Scotland)
17	Long Loch	"
18	L. Conwy	Snowdonia: L. Conwy recoring
19	L. Clyd	Snowdonia: sites with higher alkalinities
20	L. Glas	"
21	L. Irddyn	"
22	L. Berwyn	Afforestation (L. Berwyn recoring)
23	Tunnel End	Pennine reservoirs

2 ACIDIFICATION IN THE CAIRNGORMS AND LOCHNAGAR

2.1 INTRODUCTION

The Cairngorm area forms the largest single area of land over 1000 m in the UK and is of considerable conservation value. The Cairngorm mountain plateau is a National Nature Reserve.

Lochnagar and the Cairngorms are situated in an area of moderate acid deposition (c. 0.95 g S yr^{-1}) on sensitive granite geology (Kinniburgh and Edmunds 1986, Wells *et al.* 1986). The sites selected are all remote, above the tree line and have undisturbed catchments.

The aim of the project is to evaluate whether lakes in the area have acidified as a result of increases in acid deposition and thereby to test the 'land-use' hypothesis (eg. Rosenqvist 1977, 1978). Five lakes have been investigated (Figure 1.1), three from the Lochnagar area (Lochnagar, Loch nan Eun and Dubh Loch - Figure 2.1) and two from the Cairngorms (Lochan Uaine and Coire an Lochan - Figure 2.1). Results from Lochnagar have been published elsewhere (Battarbee *et al.* 1988, Patrick *et al.* 1989).

2.2 THE STUDY SITES

The landscape of the Cairngorms and Lochnagar has been heavily influenced by ice action; the area was a major centre for the accumulation and dispersal of ice during the last glaciation. The highest sites; Lochan Uaine, Coire an Lochan and Loch nan Eun were formed as moraine dammed corrie lakes. Indeed Coire an Lochan and Lochan Uaine are two of the highest lakes in the British Isles (at 998 m and 950 m respectively). Snow generally occupies the catchments to a varying extent between November and May. The lochs freeze each winter and partial ice cover may last from November to June in many years, with a complete ice cover between January and April which can approach 1 m thickness by early March. Snow and ice melt therefore comprise an important input to the lochs.

The lower altitude site - Dubh Loch, lies in a deeply incised glacial trough, with a deposit of hummocky drift over 30 m thick lying around the outflow (Sissons and Grant 1972).

Geology

The Cairngorms and Lochnagar are both situated on granite bedrock (Figure 2.1). The Lochnagar granitic complex forms a circular area of about 170 km^2. It is a fine to medium grain granite consisting of oligoclase, quartz and biotite, usually grey in colour with a pink tinge due to the alkali-felspars (Barrow and Craig 1912). The ring is zoned; from an early diorite unit at the periphery, through a medium grained adamellite, to a fine grained adamellite at the centre (Oldenshaw 1974). Dubh Loch lies at the perimeter of the mass, and the catchment includes some diorite (which is richer in MgO, CaO, TiO_2, P_2O_5, Sr and Ba) (Harrison pers comm.). Lochnagar lies on the medium grained adamellite and Loch nan Eun lies on the second phase of the fine grained adamellite (Oldenshaw 1974).

The Cairngorm granite covers an area of about 360 km^2 and consists of two important units, the main granite which is a more or less even grained microcline-oligoclase-biotite granite and the porphyritic granite which has conspicuous felspar phenocrysts (Harry 1965). Lochs Uaine and Coire an Lochan are situated on the deep red coloured main granite.

In terms of both mineralogy and major element chemistry the Lochnagar and Cairngorm granites are identical. They are both biotite granites with SiO_2 contents between 70-75%, Ca <2%, Al_2O_3 <15%, Na_2O around 4%. Trace element characteristics are however quite different. The Cairngorm granite is markedly richer in Rb, U, Th, Y, Nb, Li, F, Be, and rare earth metals, and poorer in Sr and Ba than the Lochnagar granites (Harrison pers comm).

Vegetation, Land-use and soils

Vegetation description mainly follows vegetation maps produced by the upland survey of the Nature Conservancy Council (Horsfield pers. comm.). The vegetation types described are based on the work of McVean and Ratcliffe (1962), with additions from Birks and Ratcliffe (1980). The nomenclature of the higher plants follows Clapham *et al.* (1981). Soils and land-use descriptions are based on 1:50,000 soil survey maps and Billett (pers. comm.).

Loch nan Eun is characterised by alpine soils, with rankers and lithosols on the steep slopes. The catchment vegetation consists of dwarf shrub heath communities (*Calluna vulgaris* and *Vaccinium myrtillus*) on the flatter areas, with snowbed *Nardus* grassland and species poor *Deschampsia caespitosa* grassland on the steeper slopes.

The catchment of Dubh Loch is dominated by free-draining, predominately alpine soils (>75%), with rankers on the north side of Broad Cairn and Creag an Dubh Loch. Deep peat also occurs in the wetter depressions above and below Dubh Loch and Loch Buidhe. The vegetation is mainly a *Calluna - Eriophorum* blanket bog community, with dry *Calluna* heath in the better drained areas. Species poor *Deschampsia caespitosa* grassland occurs on the scree slopes on the southern side of the catchment.

Loch Coire an Lochan and Lochan Uaine are characterised by alpine heath and snow bed communities. At Coire an Lochan snowbed *Nardus* grassland and snowbed *Vaccinium myrtillus* heath occur and an *Empetrum nigrum - Rhacomitrium* heath community is also important. A *Deschampsia flexuosa* grassland also occurs on the screes.

The high altitude and remoteness of these sites means that active land-management has been restricted. Three of the sites (Lochan Uaine, Loch Coire an Lochan, and Loch nan Eun) lie well above the limit of sheep grazing in the region (Scottish Development Department 1967). Red deer range across the catchments in the Lochnagar area, but stalking in the area is now rare (Clark 1981). The catchments of Lochan Uaine and Coire an Lochan are so high, rugged and remote that it is unlikely that they have ever been used for deer stalking or grouse shooting.

Water and atmospheric quality

Table 2.1 gives water quality data for the lakes, Lochnagar is included for comparison. The Lochnagar sites have lower pHs (about pH 5) and lower alkalinities (0.0-1.37 μeq l^{-1}) than the Cairngorm lakes (pH above 5.5, alkalinity >13 μeq l^{-1}). Lochan Uaine has a rather unusual chemistry with high Ca^{2+} and Mg^{2+} values, perhaps indicating the presence of alkalinity sources in the catchment, it also has high levels of Na^+ and Cl^-. Ca^{2+} levels give a good indication of the susceptibility of waters to acidification (Battarbee *et al.* 1988) and the low levels (<30 μeq l^{-1}) at the sites (with the exception of Lochan Uaine) suggest they are sensitive to acidification. With the exception of Dubh Loch the lakes are very clear with low total organic carbon (TOC) values and secchi-disc depth values of >6 m have been recorded (Patrick pers. comm.). The higher TOC level at the Dubh Loch is probably a reflection of the greater proportion of peat in its catchment. Differences in SO_4^{2-} concentrations and pH values between the five lakes probably reflect differences in sulphur retention in the catchments and lake sediments together with differences in alkalinity production in both catchments and sediments (cf. Cook *et al.* 1987). Despite these differences SO_4^{2-} concentrations are high, reflecting the moderate level of sulphur deposition in the area.

Data concerning atmospheric quality (Table 2.2) are available from an Institute of Terrestrial Ecology (ITE) collector situated about 3.5 km to the east of Lochnagar. Modelled sulphur deposition levels (Table 2.3) have also been calculated from the Harwell trajectory model (Derwent pers. comm.). These range from 8.4-10.1 kg S ha^{-1} yr^{-1} reflecting a moderate level of atmospheric contamination. The more highly polluted Galloway area has by contrast sulphur deposition levels of >12 kg ha^{-1} yr^{-1}.

Black snowfalls, with a low pH (c. 3.0) and a large particulate component (fly ash from fossil fuel combustion), have also been reported from the area. For example in February 1984 an area of about 200 km^2 was affected. Episodes such as these could make an important contribution to the annual input of industrially derived atmospheric inputs (Davies *et al.* 1984).

Table 2.1 Water quality Lochnagar and the Cairngorms

	Lochnagar sites			Cairngorm sites	
	Lochnagar	Dubh Loch	L. nan Eun	Lochan Uaine	L. Coire an Lochan
mean pH	5.02	5.28	4.96	5.83	5.66
Conductivity $\mu S\ cm^{-1}$	21.4	17.3	22.3	40.5	17.8
Ca^{2+} $\mu eq\ l^{-1}$	30.2	27.3	29.7	69.0	28.8
Mg^{2+} $\mu eq\ l^{-1}$	33.7	21.3	26.3	59.5	19.8
K^+ $\mu eq\ l^{-1}$	7.5	5.3	5.7	10.0	7.8
Na^+ $\mu eq\ l^{-1}$	89.0	72.3	82.3	191.0	67.0
Cl^- $\mu eq\ l^{-1}$	76.2	67.7	55.0	215.0	81.7
SO_4^{2-} $\mu eq\ l^{-1}$	66.0	54.0	62.3	82.0	47.3
Alkalinity (Alk_e) $\mu eq\ l^{-1}$	0.00	1.37	0.00	14.79	13.73
TOC mg l^{-1}	0.8	1.6	0.5	0.4	0.2
Labile Al $\mu g\ l^{-1}$	57.0	55.0	128.0	56.0	75.0

Table 2.2 Annual average data from the ITE bulk monthly collector at Lochnagar (μeq l^{-1}).

	1978-1987 average	1987
Acid H^+	37	25
Ammonium NH_4^+	18	15
Na^+	37	44
K^+	3	4
Ca^{2+}	17	10
Mg^{2+}	14	8
Cl^-	49	42
NO_3^-	19	19
SO_4^{2-}	48	34

Source; N. Cape (pers. comm.)

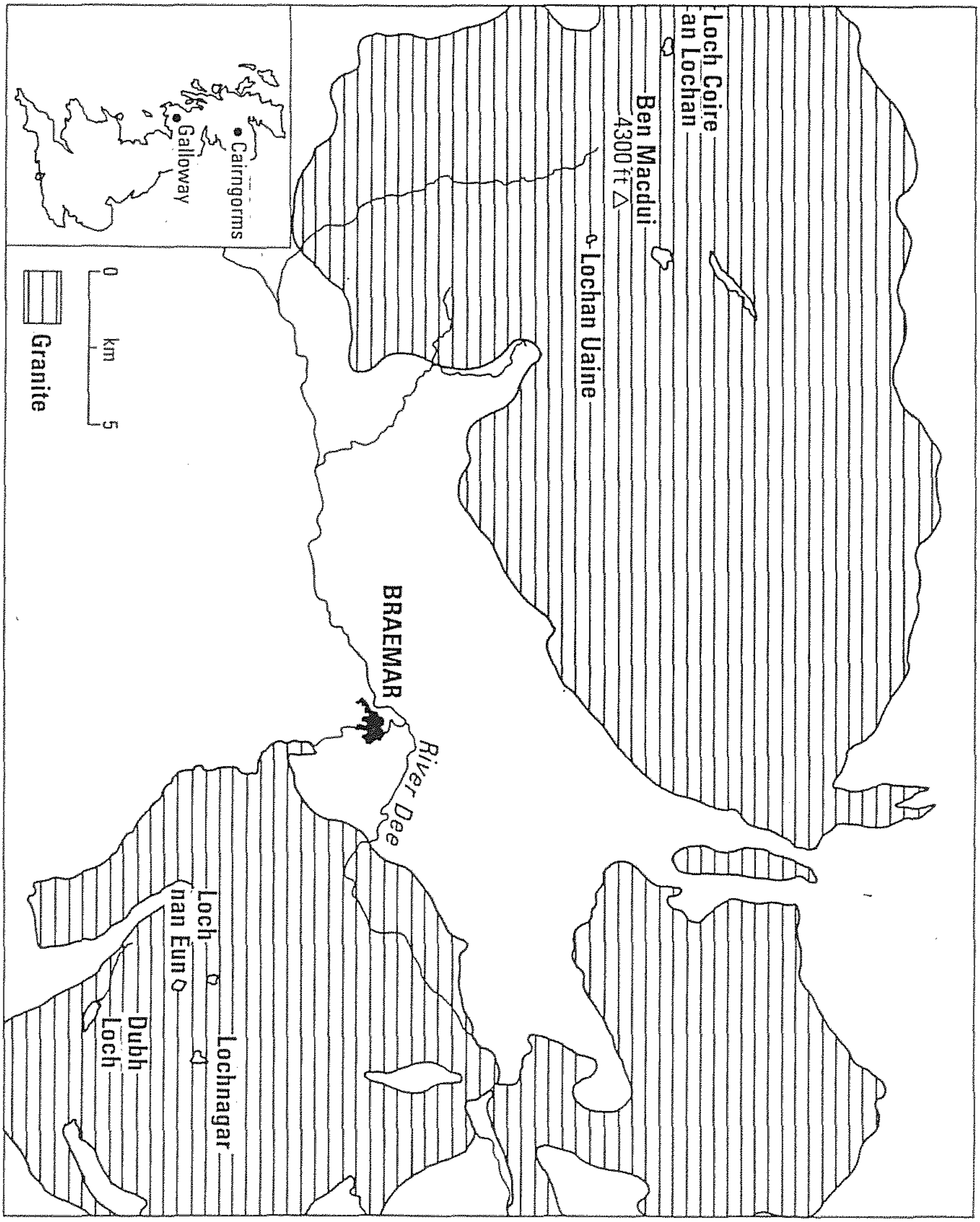
Table 2.3 Sulphur deposition Lochnagar and the Cairngorms

	Lochnagar	**Dubh Loch**	**L. nan Eun**	**Lochan Uaine**	**L. Coire an Lochan**
Dry deposited S (kg ha^{-1} yr^{-1})	5.889	5.986	5.846	4.899	*
Wet deposited S (kg ha^{-1} yr^{-1})	4.042	4.095	4.012	3.537	*
Total deposited S (kg ha^{-1} yr^{-1})	9.931	10.081	9.858	8.436	*

* no data available

Source; Harwell trajectory model

Figure 2.1 Cairngorm and Lochnagar study sites



2.3 METHODS

Sediment cores were retrieved from the sites in June 1986 using a mini-Mackereth corer (Mackereth 1969). Methods for lithostratigraphic, biostratigraphic, radiometric, magnetic and carbonaceous particle analysis follow the Royal Society Surface Water Acidification Project (SWAP) protocol (Stevenson *et al.* 1987).

2.4 RESULTS

2.4.1 Loch Coire an Lochan

Bathymetry

A full bathymetric survey of this site was precluded by partial ice cover. It was apparent that the loch comprised a concentric basin with a deepest measured water depth of 20 m. Sediment cores were taken in 18 m water depth (Figure 2.2).

Lithostratigraphy

From 6-60 cm the sediment is a light grey diatomaceous mud with a low (c. 10% LOI) organic content (Figure 2.3). Above 5 cm the sediment is a greyish brown colour and the organic content, as measured by loss on ignition (LOI) increases to c. 18% with concomitant declines in wet density and dry weight measurements.

Dating

In progress

Diatom analysis

A summary diatom diagram is presented in Figure 2.4. Floristic changes occur throughout the core, in the top 3 cm the values of *Fragilaria virescens*, *F. lata*, *F.* cf. *oldenburgiana* and *Brachysira vitrea* fall and there are increased abundances of *Achnanthes austriaca* f. *minor* and *A. marginulata*. Below 3 cm the flora is not stable; *F. lata* is only found in levels above 18 cm and *B. vitrea* starts to decline above 20 cm. Acidobiontic forms account for >10% of species at the top and bottom of the profile (*Aulacoseira distans* v. *nivalis*).

Diatom concentrations are shown in Figure 2.5. Concentrations are high throughout, but there is a trend of falling concentrations towards the top of the core.

pH was reconstructed using the multiple regression of species preference groups method (Figure 2.6); this gives a value of 5.8 at the bottom of the core (57 cm) and 5.2 at the surface, but there is not a clear trend of steadily declining pH. The current measured pH is 5.6.

Carbonaceous particle analysis

The results of carbonaceous particle analysis are shown in Figure 2.7. Carbonaceous particles were only found to be abundant in the surface sediment sample (0-0.5 cm), below this level counts were low and very few particles were observed below 4.5 cm. Results below 4.5 cm are also rather unreliable since the counts recorded approach the limit of detection (c. 100 particles g^{-1}).

Magnetics

In progress

Geochemistry

In progress

Figure 2.2 L. Coire an Lochan: coring location

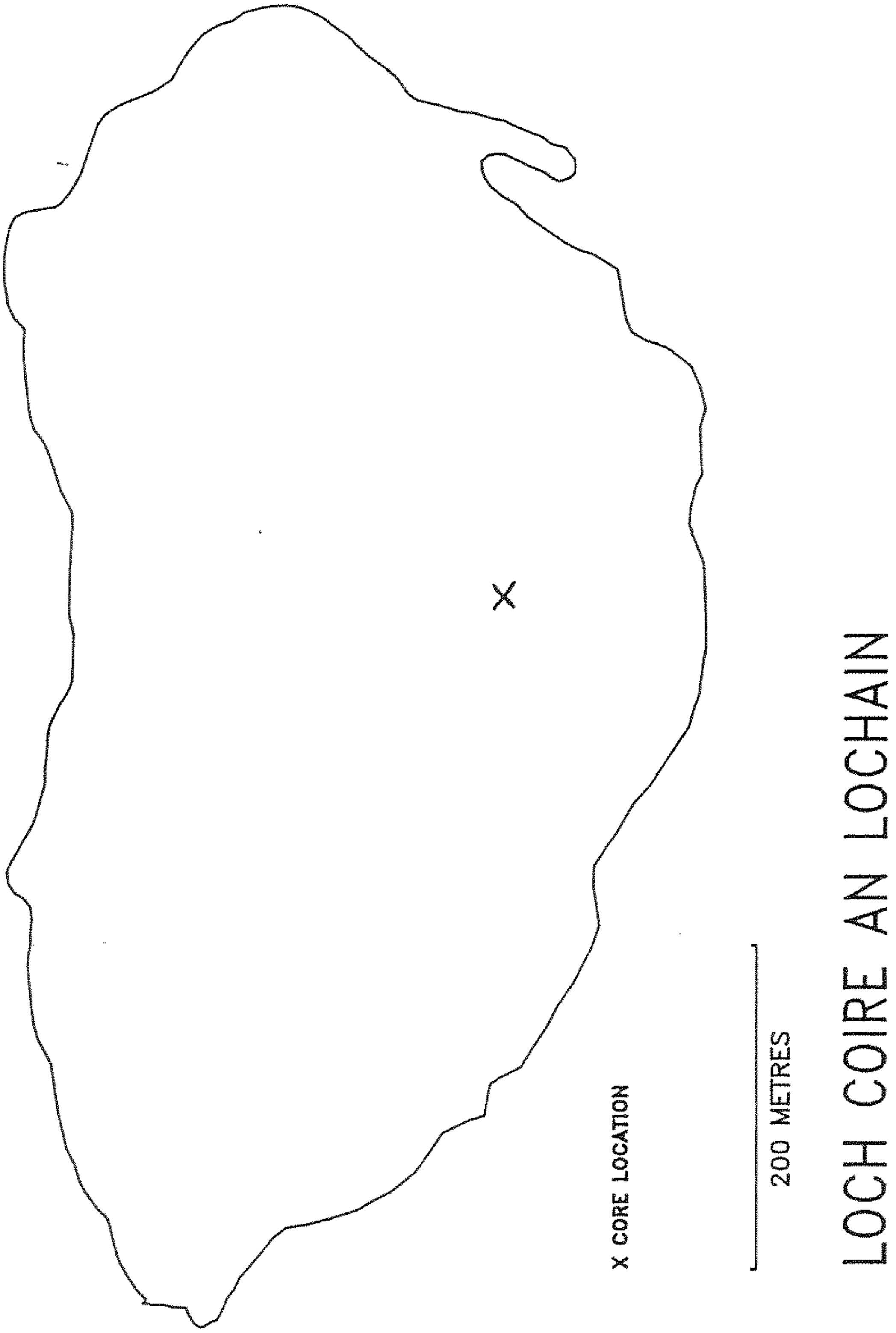


Figure 2.3 L. Coire an Lochan: lithostratigraphy

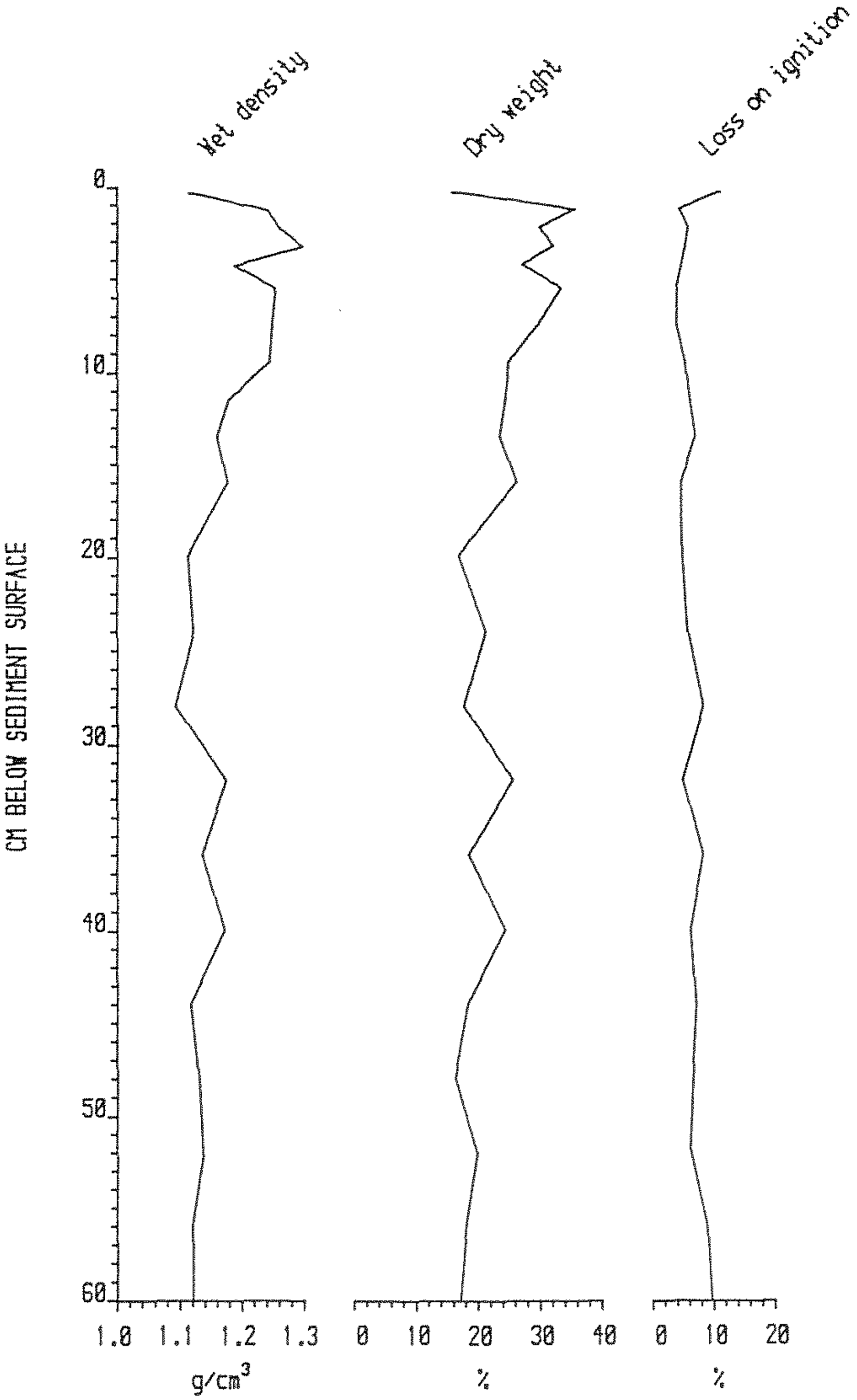


Figure 2.4 L. Coire an Lochan: diatom summary diagram

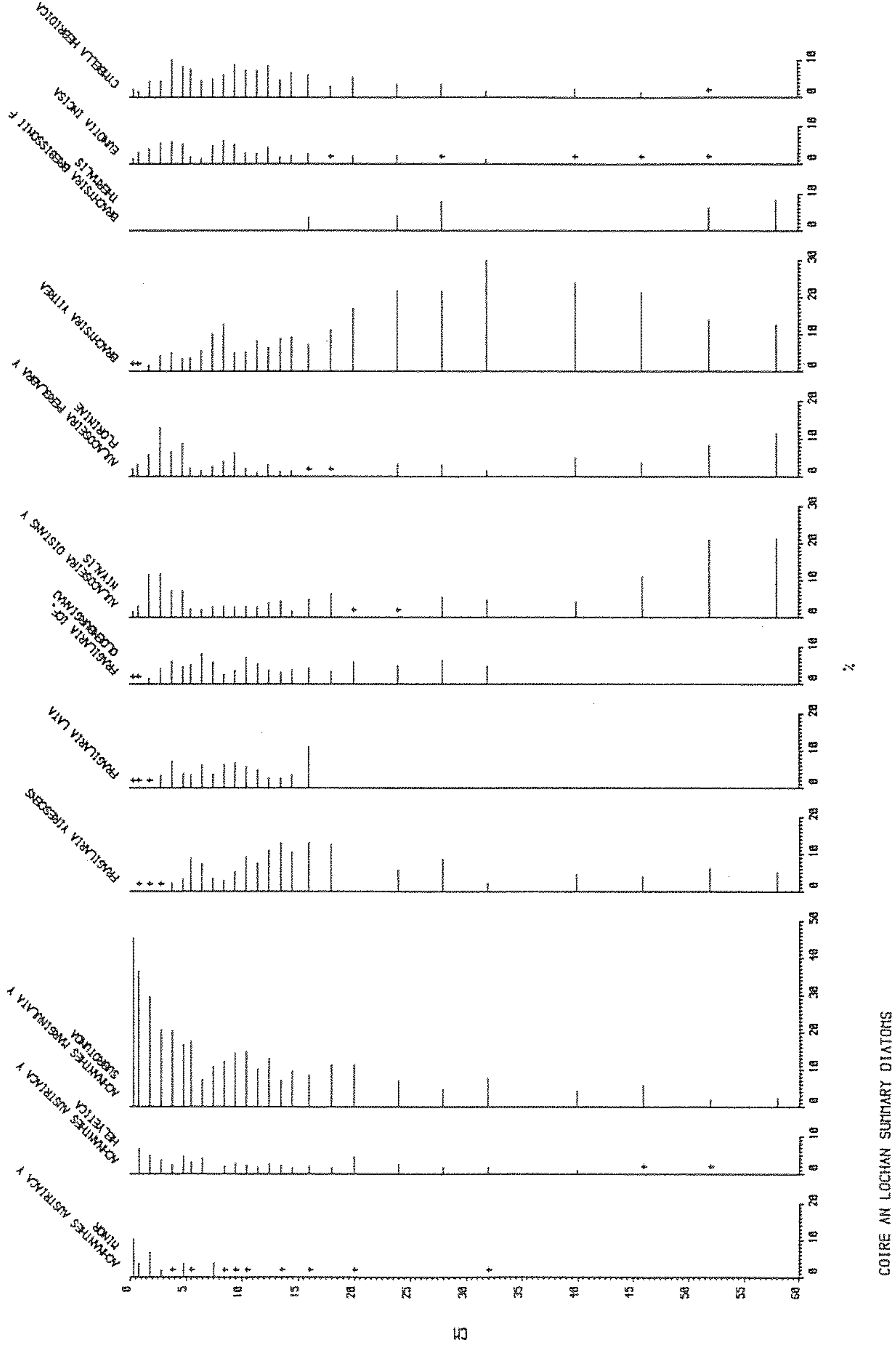


Figure 2.5 L. Coire an Lochan: diatom concentration (x 10^8 g^{-1}), showing 95% confidence limits

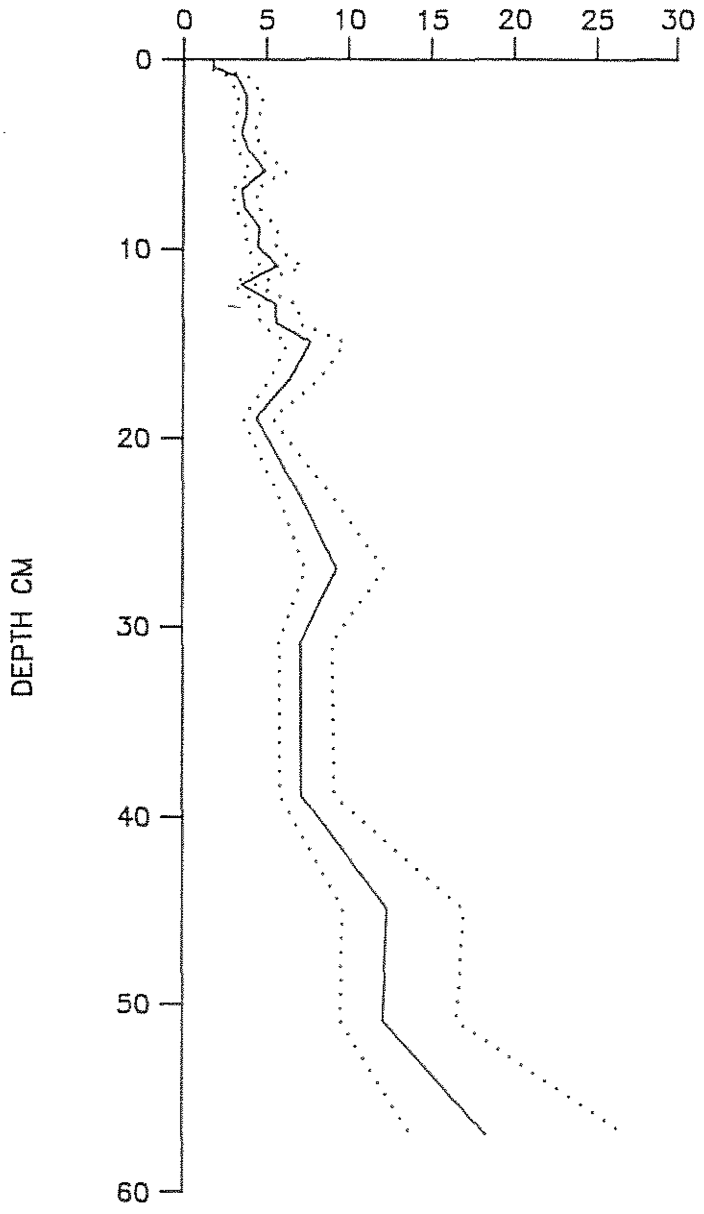


Figure 2.6 L. Coire an Lochan: pH reconstruction (multiple regression)

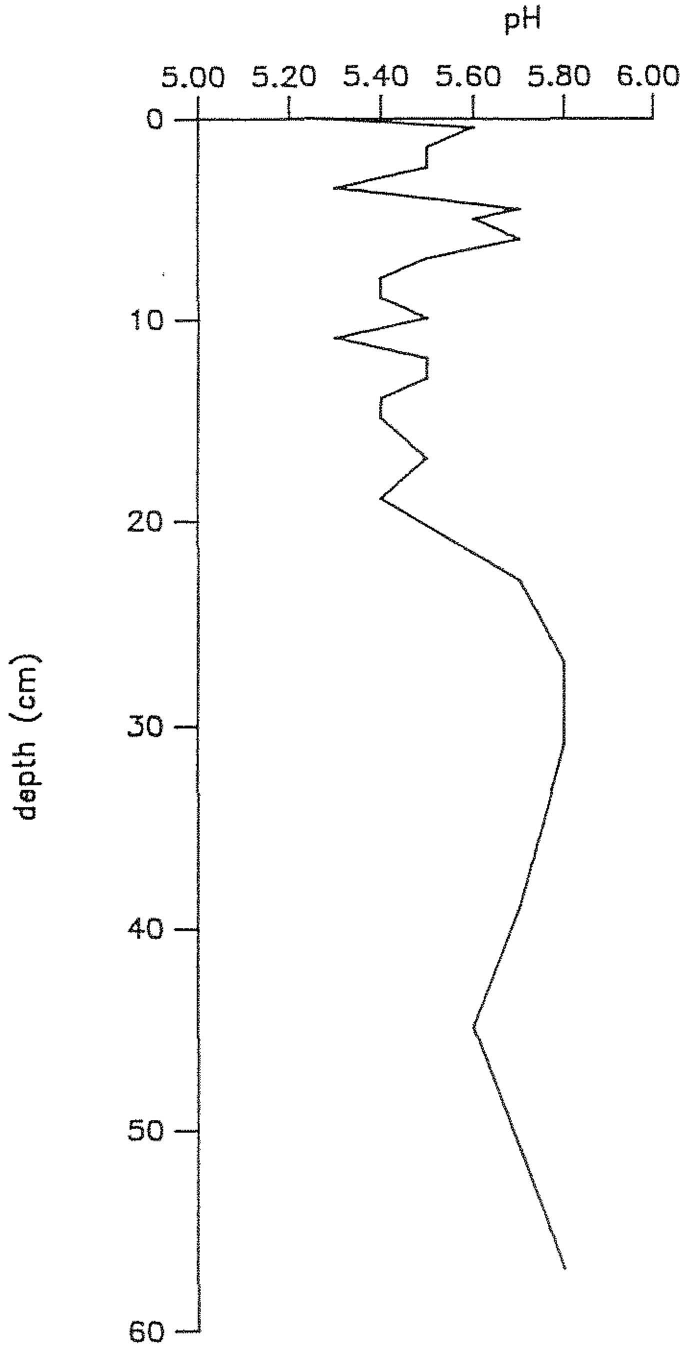
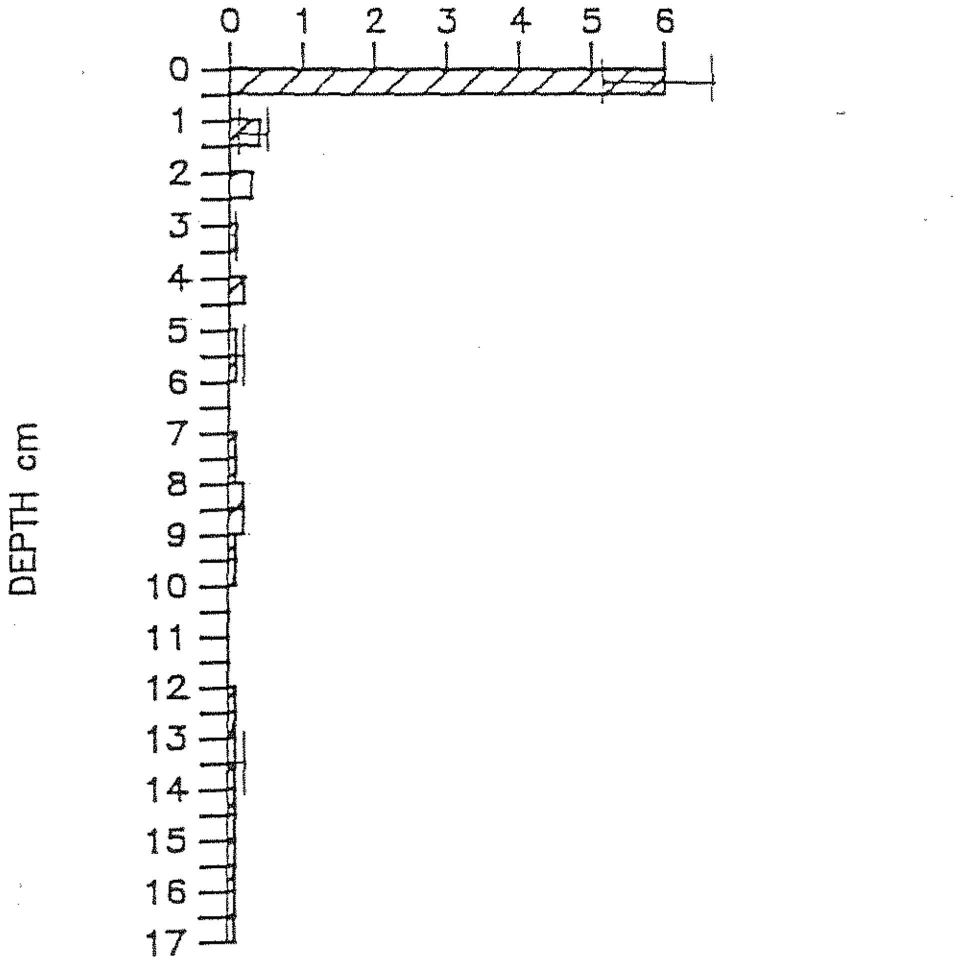


Figure 2.7 L. Coire an Lochan: carbonaceous particle profile (x 10^3 g^{-1})



2.4.2 Lochan Uaine

Lochan Uaine was included jointly in the SWAP programme (Battarbee and Renberg 1990) and DoE projects. Within SWAP it was selected as a lake site to complement the Allt a Mharcaidh experimental stream catchment. Here it is used to extend the regional coverage of sites in this area.

Bathymetry

A bathymetric survey revealed a single deep basin with a maximum water depth of 20 m (Figure 2.8). Sediment cores were extracted from 19 m.

Lithostratigraphy

The sediment is an inorganic diatomaceous mud with percentage LOI values of around 10% throughout the core (Figure 2.9). The inorganic nature of the sediment is also reflected in the high dry weight and wet density values. The peaks in dry weight and wet density tend to coincide, for example at 12-13 cm and 28-29 cm. There is evidence of an inwash of catchment material at 28 cm, since coarse sand and unhumified roots were also found at this level.

Dating

The ^{210}Pb and ^{226}Ra results are given in Table 2.4. The ^{137}Cs and ^{134}Cs results (corrected for decay) are given in Table 2.5. There was no detectable ^{241}Am activity. Table 2.6 gives values of a range of other radioisotopes determined by the gamma spectra.

Lochan Uaine is in a region which received moderate Chernobyl fallout, with the presence of significant concentrations of the short-lived fallout isotope ^{134}Cs in the topmost sediments (Table 2.5).

The site is unusual since it has very high ^{226}Ra activity in the sediments (about 10 times the value typical of other UK sites). The high unsupported ^{210}Pb activity of the near-surface sediments and high ^{210}Pb inventory of the core presumably reflects, to some extent, a higher ^{210}Pb flux from the atmosphere arising from enhanced ^{222}Rn diffusion rates from the soils of the region. Using the estimated ^{134}Cs:^{137}Cs ratio in Chernobyl fallout of 0.64 (see Flower *et al* 1988), the component of the ^{137}Cs inventory derived from Chernobyl fallout was estimated to be 2.1 pCi cm^{-2}, leaving a balance of 13.1 pCi cm^{-2} resulting from nuclear weapons testing fallout. This is comparable to the ^{137}Cs inventories of cores obtained from other Scottish lakes and is perhaps an indication that the high ^{210}Pb does not arise either from sediment focusing or from enhanced inputs of surface soils from the catchment.

^{210}Pb chronologies have been calculated using both the CRS and CIC ^{210}Pb dating models (Appleby and Oldfield 1978) and the results are given in Figure 2.10. The decline in ^{210}Pb activity above 1.75 cm (dated 1969) appears to indicate a recent acceleration in sediment accumulation rates. Since the CIC model can not date non-monotonic features the CIC chronology has made use of the CRS dates for this part of the core. Between 1.75 cm and 5.75 cm (dated c. 1900) the two models are in good agreement, both indicating a fairly constant accumulation rate of c. 0.017 g cm^{-2} yr^{-1}. The divergence at lower levels is probably due to errors in the CRS dates arising from the very high ^{226}Ra activity. The chronology given in Table 2.7 is based principally on the CRS model, but makes use of the mean accumulation rate given by the CIC model for calculating dates in the lower part of the core.

The ^{137}Cs activity in this core has a well defined peak in the sample at 2.5-3.0 cm. The definition of this peak is even more pronounced when allowance is made for Chernobyl fallout in the top 1 cm and would appear to exclude the possibility of mixing as an explanation for the depressed ^{210}Pb activity in the near surface sediments. The ^{137}Cs profile appears to confirm the association of the ^{137}Cs peak with the 1963 fallout maximum, although the presence of significant amounts of ^{137}Cs down to the ^{210}Pb equilibrium depth indicates significant downward diffusion.

Diatom analysis

A summary diatom diagram is shown in Figure 2.11. Below about 12 cm the diatom flora is fairly and stable dominated by circumneutral species such as *Fragilaria virescens*, *Brachysira vitrea*, *Achnanthes minutissima*, together with acidophilous *Achnanthes* species, which contribute about 40% of the assemblage. Above about 10 cm there are a number of floristic changes the most dramatic of which is the sudden increase of *Achnanthes austriaca* v. *alpina*. The acidophilous species *Achnanthes scotica* declines above 10 cm and small increases in species such as *Eunotia exigua*, *Cymbella aequalis*, and *Achnanthes marginulata* f. *major* also occur.

The high concentration ($>10^7$ valves g^{-1}) of diatoms throughout the core (Figure 2.12) reflects the high diatomaceous component in the sediment. Concentrations are fairly uniform although there is a drop at 12 cm coincident with lithostratigraphic evidence for an inwash event. Diatom concentrations subsequently recover towards the top of the core.

Lochan Uaine exhibits many of the taxonomic problems associated with small *Achnanthes* taxa found at upland sites in the Cairngorms and Wales (Flower and Jones 1989). These taxa have been classified as acidophilous in the SWAP diatom database, although in some cases they have rather low mean abundance weighted pH values.

The loch has always been dominated by acidophilous and circumneutral species, with very few acidobiontic species. One species, generally classified as acidobiontic, *Aulacoseira distans* v. *nivalis*, occurs at about 5% abundance throughout the core. Below 9 cm acidophilous species contribute to less than 50% of the assemblage and circumneutral species make up between 20-35%. Above 9 cm acidophilous species are found at abundances >50% and apart from one level, circumneutral taxa contribute <20% of the assemblage. Although there is no substantial increase in acidobiontic forms there is floristic evidence of a slight acidification above 9 cm. Correspondence analysis also shows a distinct change in the diatom flora above about 12 cm.

Weighted averaging (WA) and multiple regression of pH preference groups were used to reconstruct pH (Figure 2.13). Both models show a slight acidification above 9 cm (c. 1850). The multiple regression model shows a decline from pH 5.7-6.1 to pH 5.5-5.6. The WA method shows a slight acidification from pH 5.4-5.6 to pH 5.1-5.4. The WA method reconstructs 0-0.5 cm to pH 5.1 and the multiple regression method reconstructs this level to 5.5; the present pH of the loch is 5.8.

This core illustrates some of the problems associated with the WA approach to pH reconstruction. Problems of poor fit were found to occur above 24 cm, this is probably due to the fact that many of the *Achnanthes* species found at this site are uncommon in the SWAP diatom data base and therefore reconstruction is likely to be unreliable.

Pollen analysis

The pollen profile (Figure 2.14) is dominated by open habitat species; *Calluna*, Gramineae and Cyperaceae. Tree pollen is dominated by *Pinus* and values of *Picea* in the top 2 cm could reflect recent coniferous planting in the region. The unusually high values of *Lycopodium annotinum* and *Huperzia selago* spores in the profile reflect the alpine heath vegetation of the catchment. There is no evidence of an increase in *Calluna* at the expense of Gramineae in recent past, confirming the improbability of major land-use change in the area.

Carbonaceous particle analysis

20 sediment samples from 0-20 cm were analysed, the results are presented in Figure 2.15. Few carbonaceous particles ($<0.3 \times 10^3$ g^{-1}) are present below 3.5 cm; above 3.5 cm (c. 1940) the concentration of carbonaceous particles rises to the surface. Other particles of a similar size and shape where also observed. These were found to be resistant to pressure and also had a shiney surface, these are tentatively described as solid spheres.

Magnetics analysis

In progress

Geochemistry

In progress

Table 2.4 L. Uaine: ^{210}Pb data

Depth	Dry Mass	^{210}Pb Concentration				^{226}Ra Concentration	
		Total		Unsupp			
cm	gcm^{-2}	pCig^{-1}	±	pCig^{-1}	±	pCig^{-1}	±
0.25	0.0742	93.53	2.07	78.12	2.18	15.41	0.68
0.75	0.2233	99.63	1.40	83.25	1.46	16.38	0.42
1.75	0.4744	127.10	1.87	103.87	1.96	23.23	0.58
2.75	0.7243	96.57	1.24	75.58	1.30	20.99	0.40
3.75	1.0449	60.45	1.04	38.77	1.12	21.68	0.42
4.75	1.3715	45.45	0.92	19.95	1.01	25.50	0.42
5.75	1.6881	40.02	0.93	14.63	1.05	25.39	0.48
6.75	2.0543	32.51	0.71	11.40	0.80	21.11	0.36
7.25	2.2600	35.59	0.88	5.22	1.01	30.37	0.49
8.25	2.6034	25.14	0.71	−1.19	0.82	26.33	0.42
9.75	3.2303	26.09	0.74	−1.13	0.85	27.22	0.42

Table 2.5 L. Uaine: ^{137}Cs and ^{134}Cs data

Depth	^{137}Cs Conc		^{134}Cs Conc	
cm	pCig^{-1}	±	pCig^{-1}	±
0.25	10.35	0.48	4.91	0.61
0.75	13.63	0.32	3.09	0.58
1.75	17.27	0.42	0.00	0.00
2.75	11.17	0.29	0.00	0.00
3.75	5.28	0.20	0.00	0.00
4.75	2.24	0.14	0.00	0.00
5.75	1.39	0.16	0.00	0.00
6.75	0.59	0.11	0.00	0.00
7.25	0.23	0.12	0.00	0.00
8.25	0.38	0.10	0.00	0.00
9.75	0.38	0.10	0.00	0.00
Inventories:	15.22±0.38 pCicm^{-2}		1.35±0.15 pCicm^{-2}	

Table 2.6 L. Uaine: miscellaneous radioisotope data

Depth	^{226}Ra	^{238}U	^{235}U	^{228}Ac	^{228}Th	^{40}K
cm			$pCig^{-1}$			
0.25	15.41	47.61	5.89	4.82	12.31	41.40
0.75	16.38	62.06	7.14	7.34	10.85	53.50
1.75	23.23	98.59	11.04	8.23	11.60	47.29
2.75	20.99	79.08	9.69	7.04	11.43	37.86
3.75	21.68	70.80	9.03	7.96	13.19	43.46
4.75	25.50	77.96	9.74	8.15	12.17	44.06
5.75	25.39	77.28	9.93	8.27	13.75	43.84
6.75	21.11	59.54	7.08	6.69	11.20	50.10
7.25	30.37	72.07	9.04	6.74	13.00	52.15
8.25	26.33	49.40	6.32	6.11	13.04	48.65
9.75	27.22	54.83	6.97	8.27	13.68	39.85

Table 2.7 L. Uaine: ^{210}Pb chronology

Depth	Dry Mass	Date	Age		Sedimentation Rate		
cm	gcm^{-2}	AD	yr	±	$gcm^{-2}yr^{-1}$	$cmyr^{-1}$	± (%)
0.00	0.0000	1986	0				
0.25	0.0742	1984	2	2	0.0383	0.129	3.6
0.50	0.1487	1982	4	2	0.0349	0.123	3.3
0.75	0.2233	1980	6	2	0.0314	0.118	3.1
1.00	0.2861	1977	9	2	0.0281	0.107	3.1
1.25	0.3488	1975	11	2	0.0248	0.095	3.2
1.50	0.4116	1972	14	2	0.0215	0.084	3.3
1.75	0.4744	1969	17	2	0.0182	0.073	3.4
2.00	0.5369	1966	20	2	0.0176	0.068	3.5
2.25	0:5993	1962	24	2	0.0171	0.064	3.6
2.50	0.6618	1958	28	2	0.0165	0.060	3.7
2.75	0.7243	1955	31	2	0.0159	0.056	3.8
3.00	0.8044	1950	36	2	0.0161	0.055	4.1
3.25	0.8846	1945	41	2	0.0164	0.054	4.4
3.50	0.9647	1940	46	2	0.0166	0.053	4.8
3.75	1.0449	1935	51	2	0.0168	0.052	5.1
4.00	1.1265	1930	56	2	0.0173	0.053	5.8
4.25	1.2082	1925	61	2	0.0177	0.055	6.4
4.50	1.2898	1920	66	2	0.0181	0.056	7.1
4.75	1.3715	1916	70	3	0.0186	0.058	7.8
5.00	1.4506	1912	74	3	↑	↑	↑
5.25	1.5298	1907	79	4			
5.50	1.6089	1903	83	4			
5.75	1.6881	1898	88	5			
6.00	1.7796	1893	93	6	0.0178	0.050	≈20%
6.25	1.8712	1888	98	7			
6.50	1.9627	1883	103	8			
6.75	2.0543	1878	108	9			
7.00	2.1571	1872	114	10			
7.25	2.2600	1868	120	11	↓	↓	↓

Figure 2.8 L. Uaine: bathymetry (contour intervals in metres)

Figure 2.9 L. Uaine: lithostratigraphy

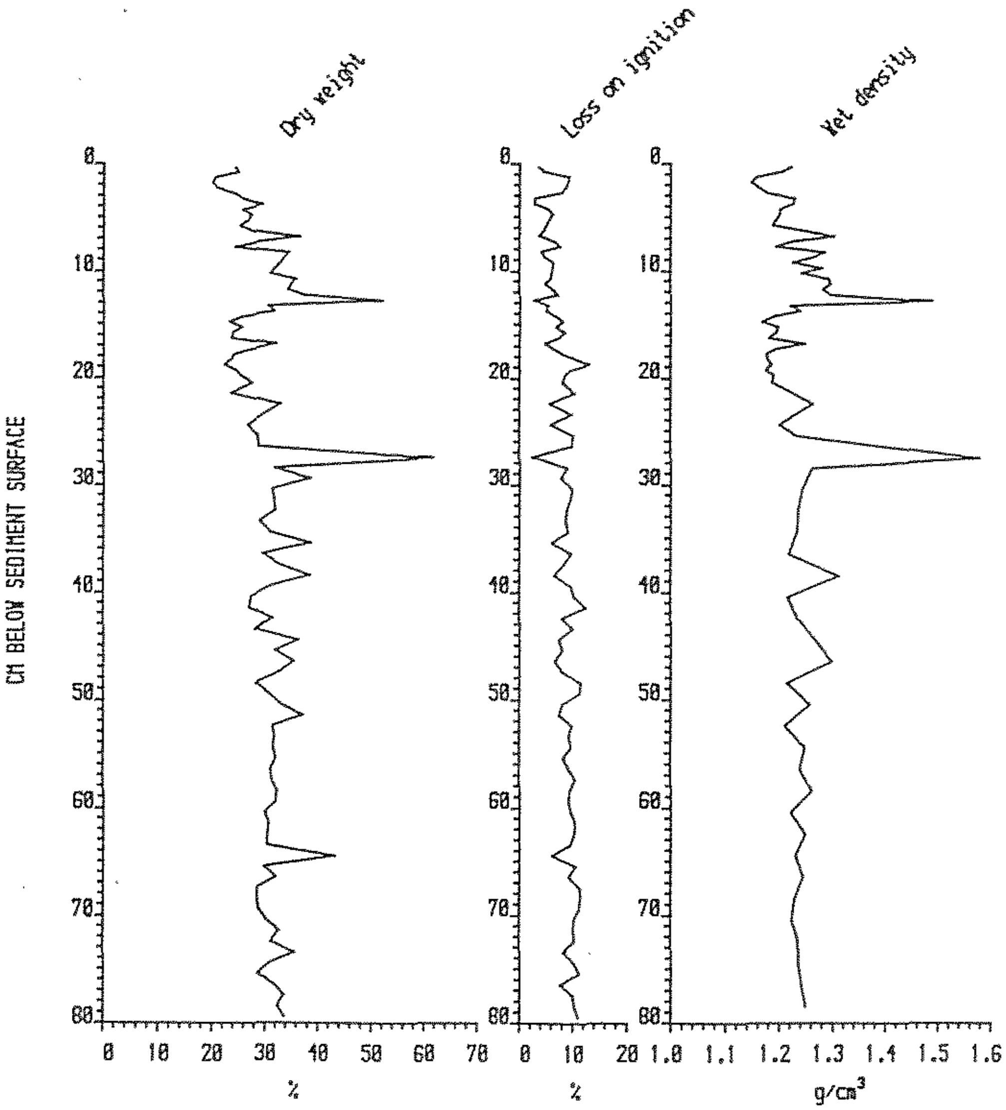


Figure 2.10 L. Uaine: ^{210}Pb chronology

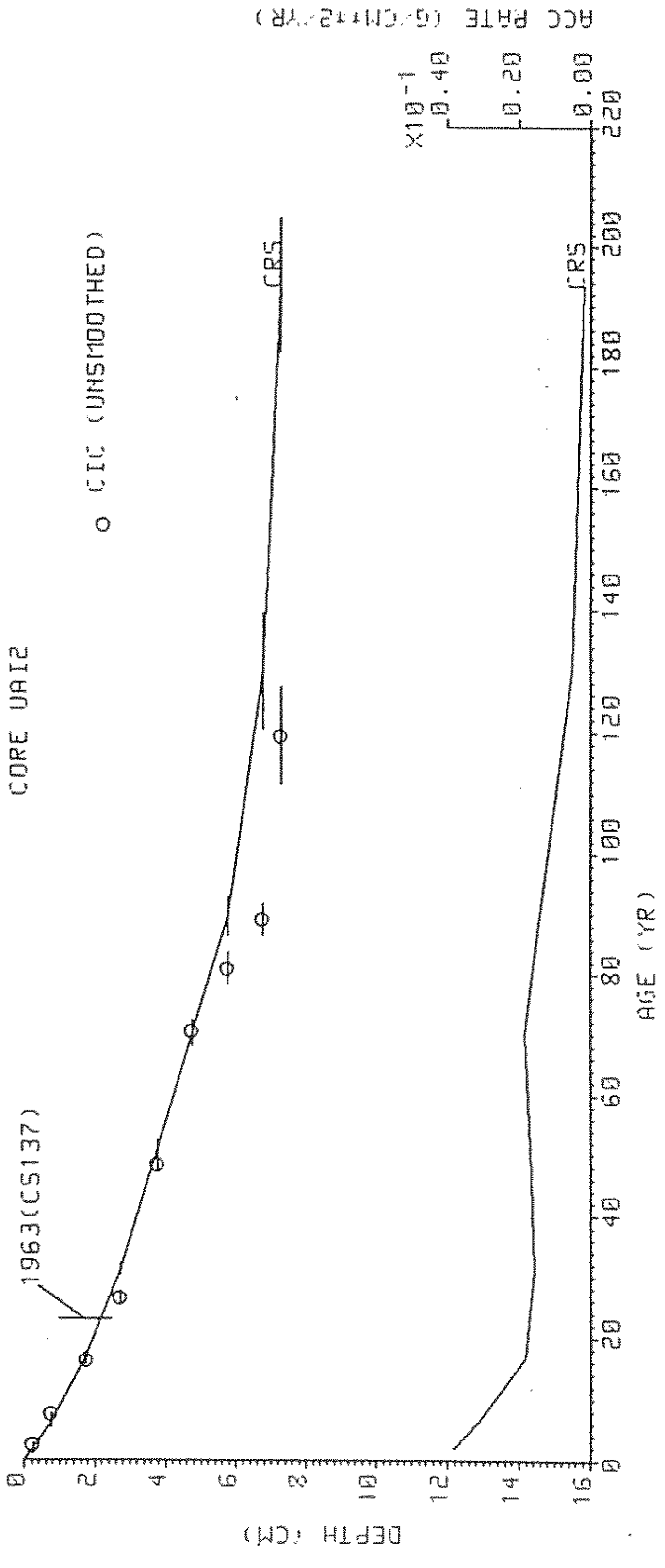


Figure 2.11 L. Uaine: diatom summary diagram

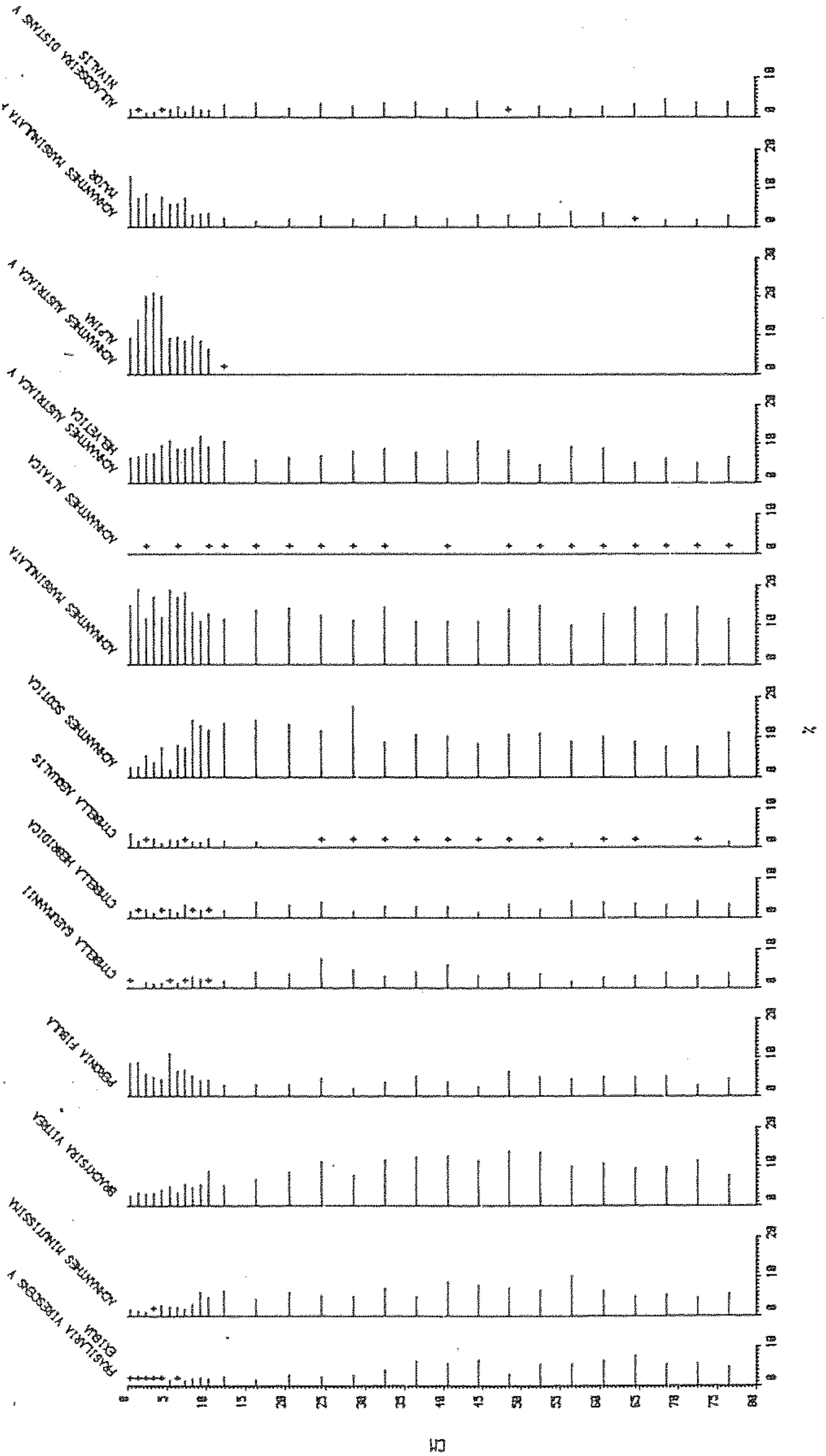


Figure 2.12 L. Uaine: diatom concentration (x 10^8 g^{-1}), showing 95% confidence limits

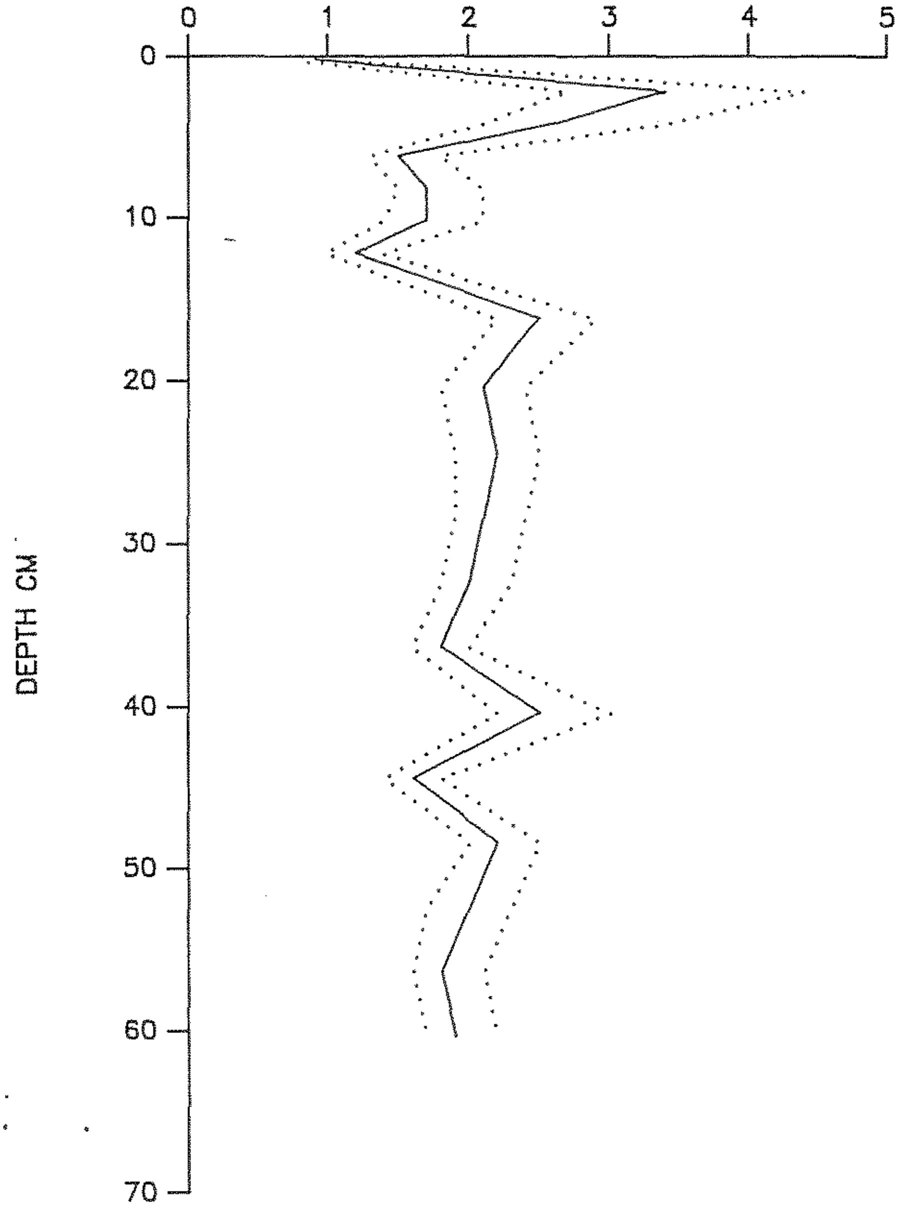


Figure 2.13 L. Uaine: pH reconstructions

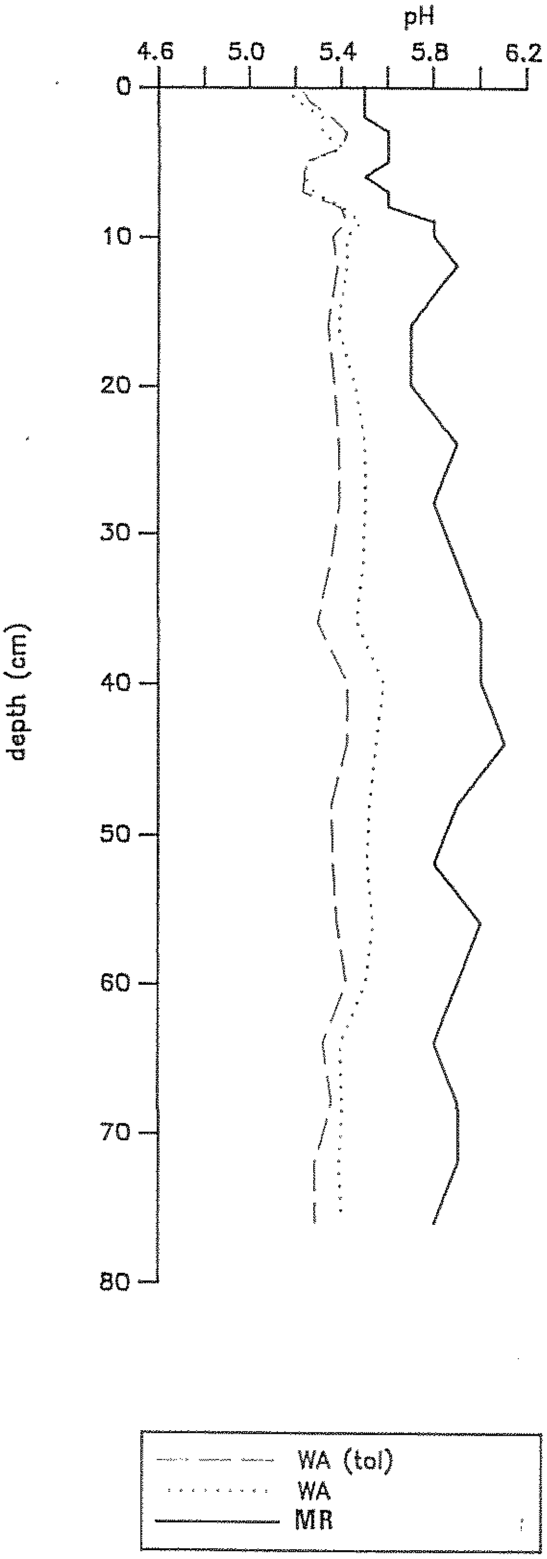


Figure 2.14 L. Uaine: summary pollen diagram

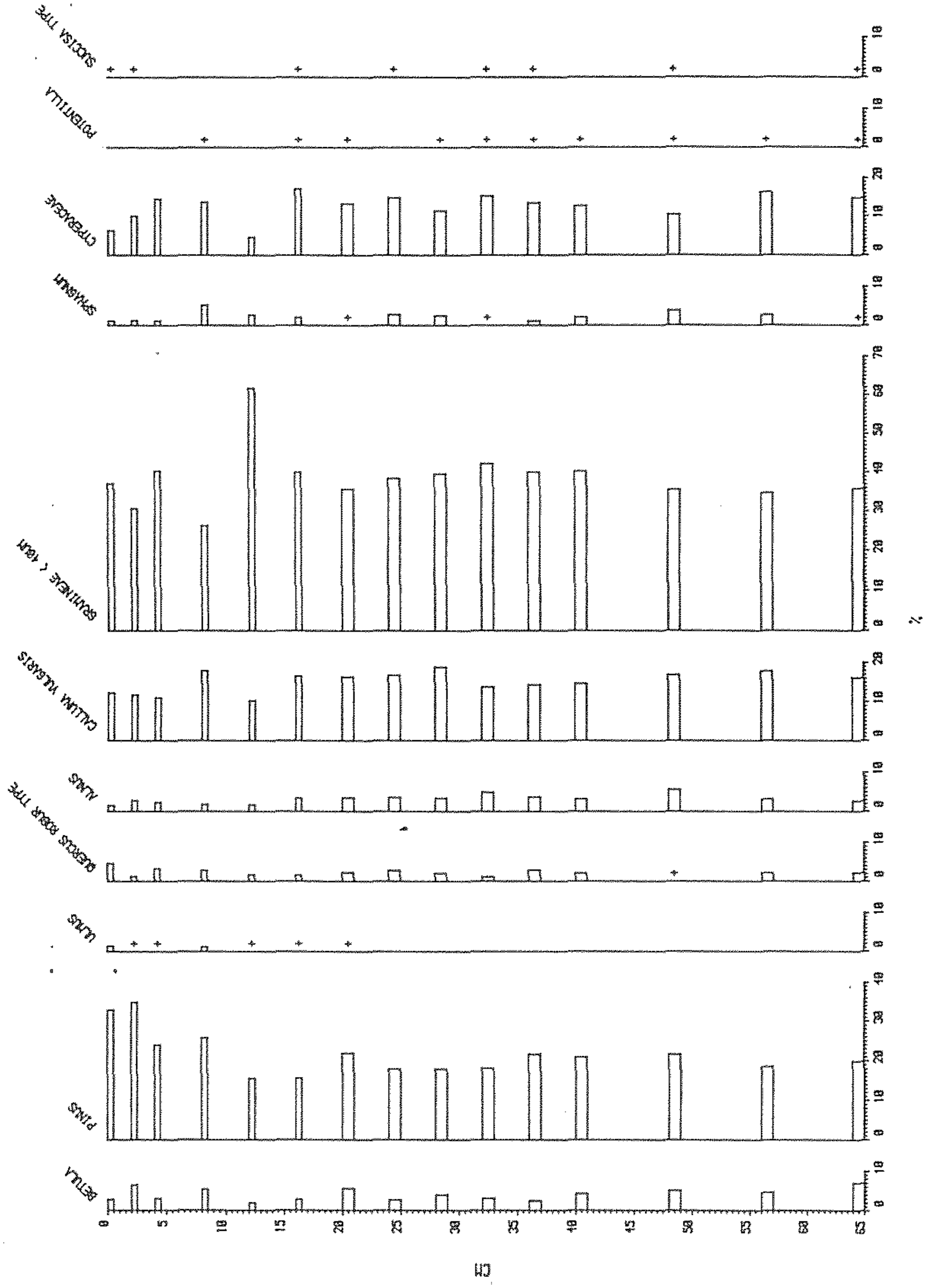
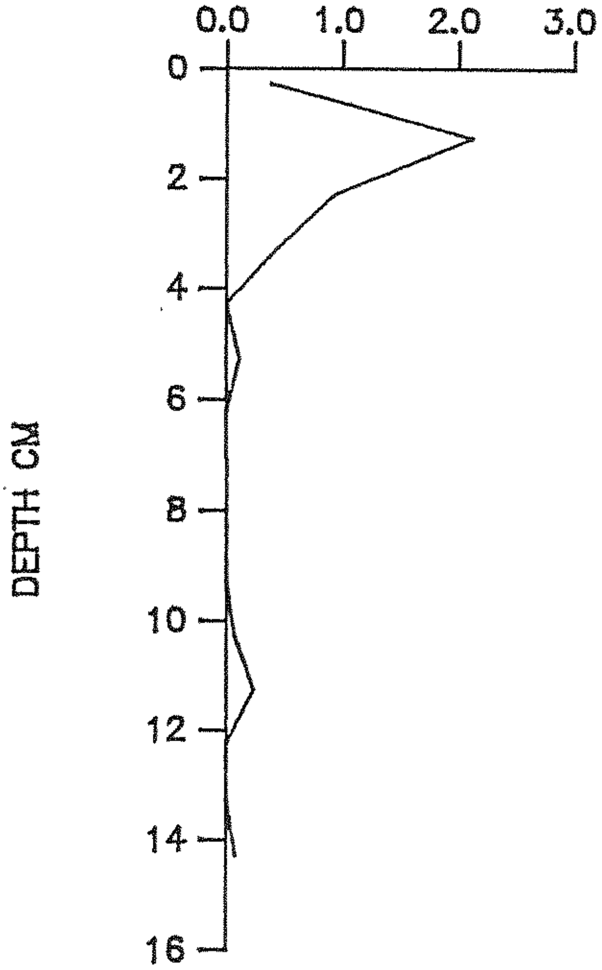


Figure 2.15 L. Uaine: carbonaceous particle profile (x 10^3 g^{-1})



2.4.3 Loch nan Eun

Bathymetry

A bathymetric survey indicates a deep (maximum depth 23 m) single basin offset to the south west towards the back wall of the corrie in which the lake lies (Figure 2.16). Sediment cores were taken in 22 m of water.

Lithostratigraphy

The sediment is inorganic diatomaceous mud, with low percentage LOI values throughout the core (Figure 2.17). Below 25 cm it is dark greyish brown in colour with LOI values of around 20%. Above 25 cm there is a colour change to a black sediment with a concomitant decrease in the LOI to about 15%, this is associated with a sandy lens; LOI values then increase slowly towards the top of the core. There is also an increase in dry weight and wet density values above 25 cm which probably represents a period of increased catchment erosion.

Dating

In progress

Diatom analysis

A summary diatom diagram is shown in Figure 2.18. A series of clear floristic changes occur beginning at about 20 cm, where values of the circumneutral species *Cymbella lunata* fall. At 10 cm the circumneutral planktonic species *Cyclotella kuetzingiana* shows a dramatic decline, from levels of 30-40% below 10 cm to levels of <5% at 5 cm. At 6 cm the circumneutral species *Achnanthes minutissima* and *Brachysira vitrea* decline together with *Achnanthes scotica.* Above 10 cm there are increases in acidophilous taxa particularly *Achnanthes marginulata* and *A. marginulata* f. *major* and there is also an increase in the acidobiontic *Aulacoseira distans* v. *nivalis.*

There is a decline in diatom concentration throughout the core (Figure 2.19) from values of around 10^9 valves g^{-1} at the bottom of the core to values of around 2-3 x 10^8 valves g^{-1} at the core top. These changes do not appear to be closely associated with any lithostratigraphic features and could possibly reflect changing sediment accumulation rates. Above about 25 cm the low diatom concentrations could be due to their dilution by inwashed catchment material (see above).

Figure 2.20 shows the diatom pH preference groups. Below 10 cm the assemblage is dominated by circumneutral (>50%) and acidophilous forms (25-35%). Above 10 cm the percentage of acidophilous forms increases to 45% at 8 cm and 70% at the sediment surface; circumneutral forms decline above 10 cm to 5% of the assemblage at 0.5 cm. Acidobiontic diatoms also increase above 10 cm, but only contribute >10% in the topmost sample.

Reconstructed pH values calculated by the multiple regression of pH preference groups method are shown in Figure 2.21. From 10-52 cm the recalculated pH ranges from 5.8-6.2; below 52 cm reconstructed pH values are >6.5, but these values may be unreliable because of the large percentage of *A. subarctica* v. *subborealis*, which has not been assigned a pH preference category. The pH drops to 5.6 at 10 cm and continues to fall to pH 4.8 at the sediment surface; the current measured pH of the lake is 5.0.

Pollen analysis

Figure 2.22 presents a pollen diagram from this site. The core can be divided into two major zones at 20 cm. Below 20 cm the pollen spectra suggest an early to mid-postglacial vegetation type dominated by high percentages of tree pollen. The base of the core can be tentatively dated to about 7000 years BP., as values of *Alnus* rise and *Pinus* values fall with the establishment of the mid-atlantic forests of central Scotland. At about 50 cm values of *Ulmus* pollen decline and levels of ruderals increase (eg. *Plantago lanceolata*, *Rumex*), which can be roughly dated to about 5000 years ago. Above this level there is an expansion of peatland indicator taxa (*Calluna*, Gramineae and *Sphagnum*) and intensification of forest clearance is recorded from 40 cm onwards, where values of *Plantago lanceolata* and *Rumex* reach 3-5%.

If this interpretation of the pollen diagram is correct and the bottom of the core can be dated to approximately 7000 years ago, then either this core represents an extremely low sediment accumulation rate, or there is at least one hiatus in the sediment record. The former possibility is unlikely since the core would represent a rate of accumulation ten times slower than that found at other upland Scottish lochs. The possibility that an inwash event with an accompanying increase in sediment accumulation rate occurred around 25 cm has already been discussed. This would also explain the decline in *Isoetes* at this point (Figure 2.22), an aquatic species known to be sensitive to changes in water transparency caused by inwash events (Birks 1972). A hiatus could also occur at this point, since the pollen assemblages above and below 20 cm are quite different.

Carbonaceous particle analysis

Twenty sediment samples from 0-20 cm were analysed for carbonaceous particles, the results are presented in Figure 2.23. Generally there are very low amounts ($<0.4 \times 10^3$ g^{-1}) of carbonaceous particles below 5 cm, although one level, 18.5-19 cm has slightly higher values (0.8×10^3 g^{-1}). Above 5 cm the concentration of carbonaceous particles increases substantially, giving a value of 9.1×10^3 g^{-1} at the sediment surface.

Many irregular dark grey and black particles were also found throughout the profile, which may represent a product of catchment burning and between 2.5-7 cm the sediment was noticeably more black in colour.

Geochemistry

In progress

Magnetic analysis

In progress

Figure 2.16 L. nan Eun: bathymetry (contour intervals in metres)

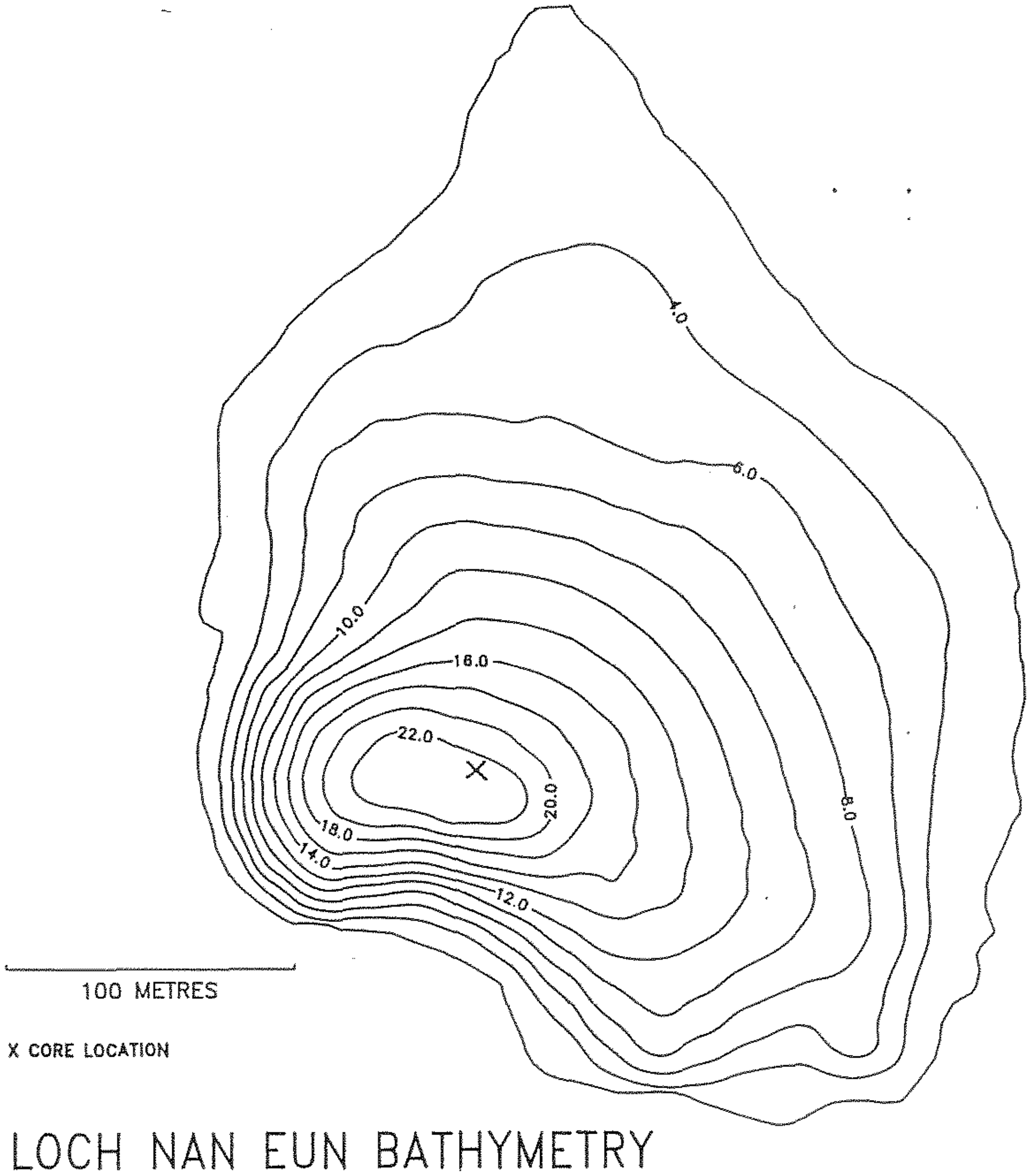


Figure 2.17 L. nan Eun: lithostratigraphy

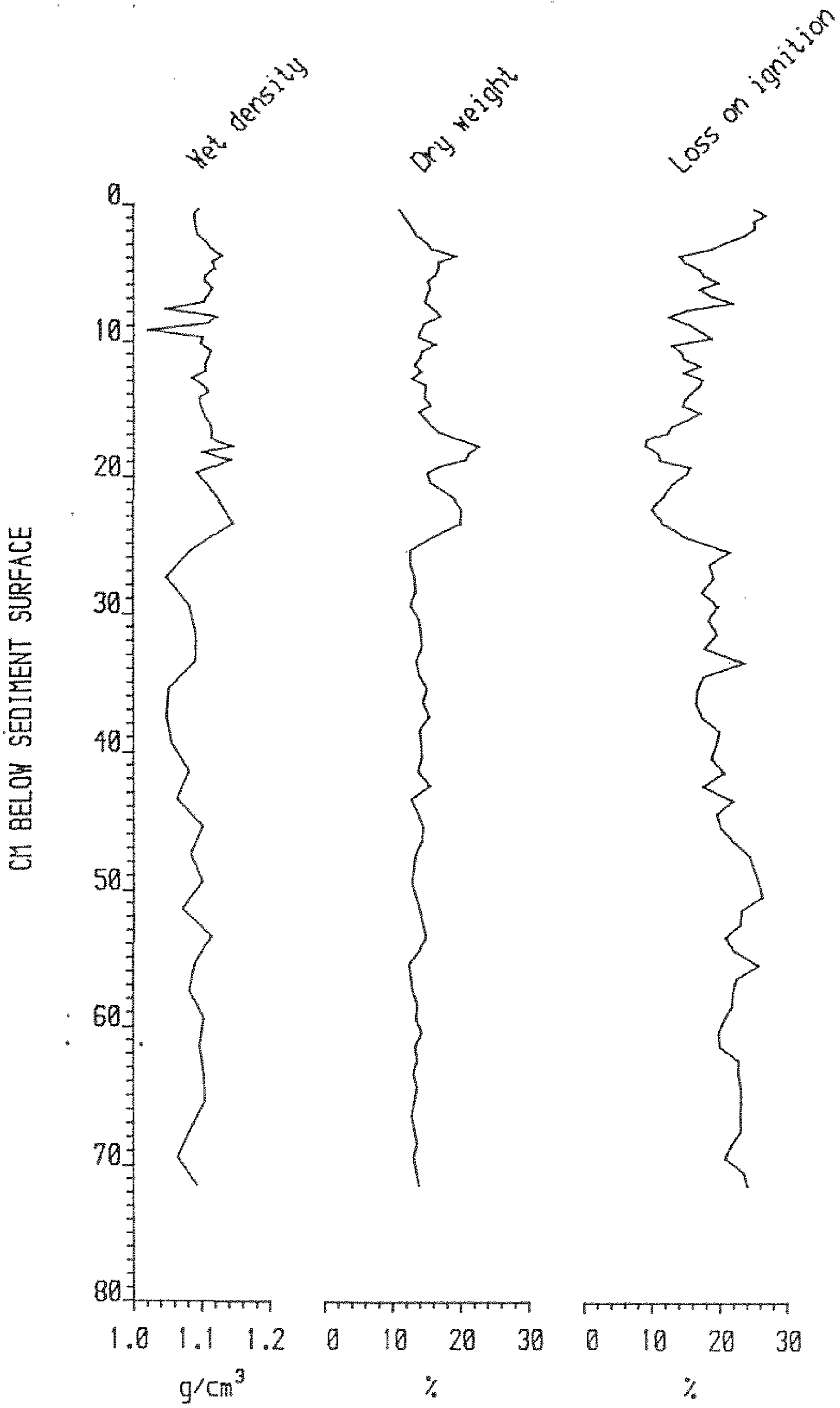


Figure 2.18 L. nan Eun: diatom summary diagram

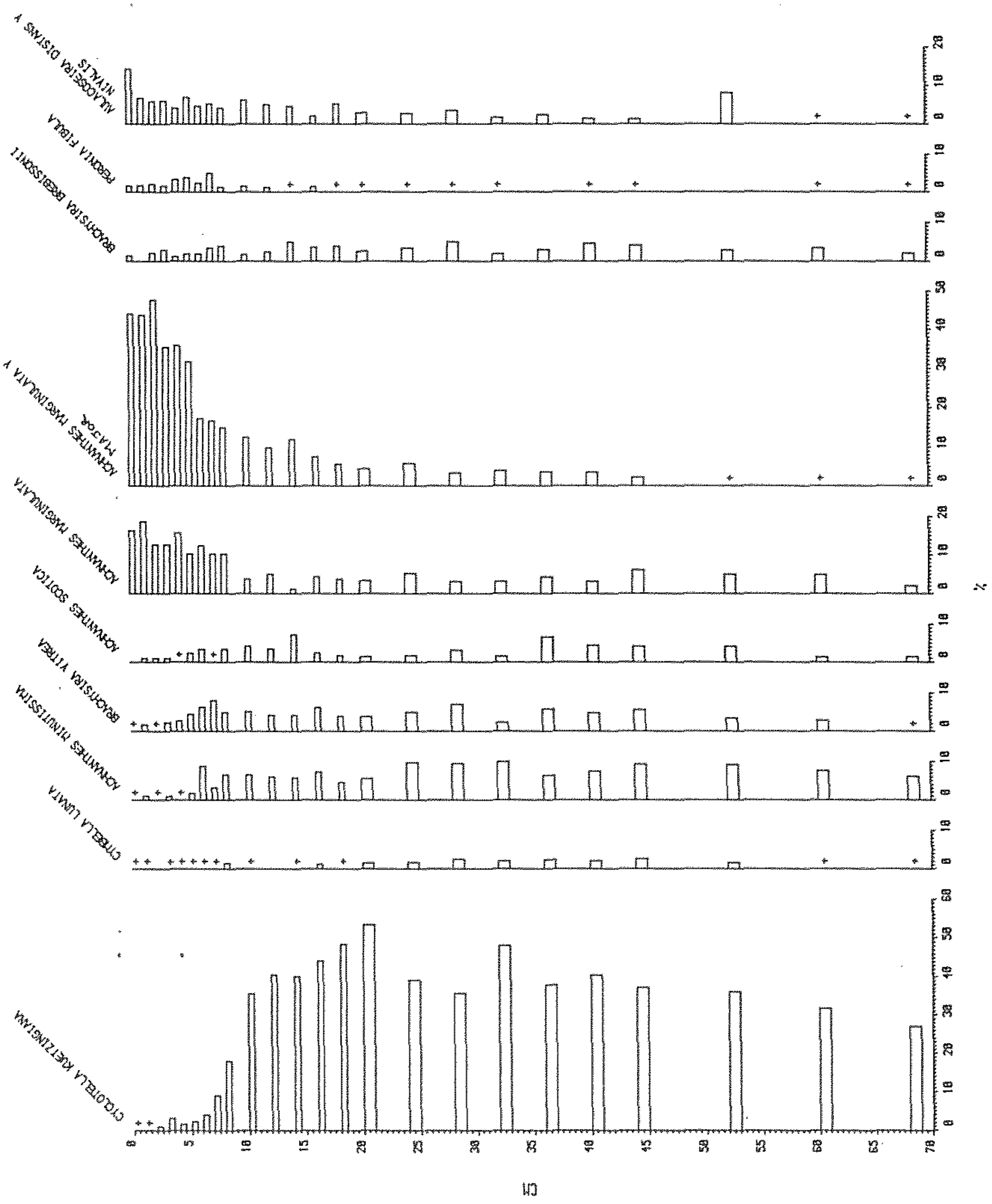


Figure 2.19 L. nan Eun: diatom concentration (x 10^8 g^{-1}), showing 95% confidence limits

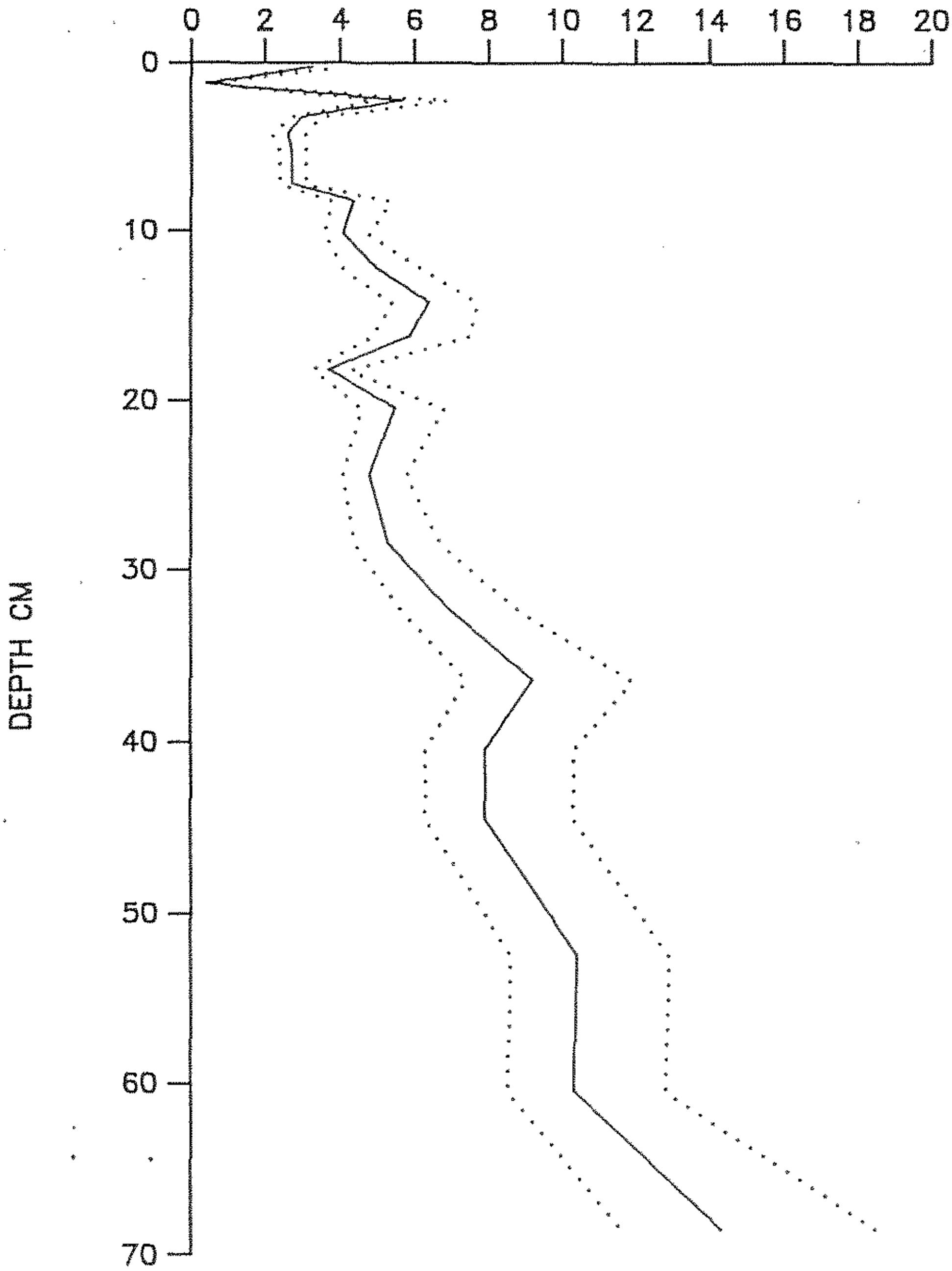


Figure 2.20 L. nan Eun: diatom pH preference groups

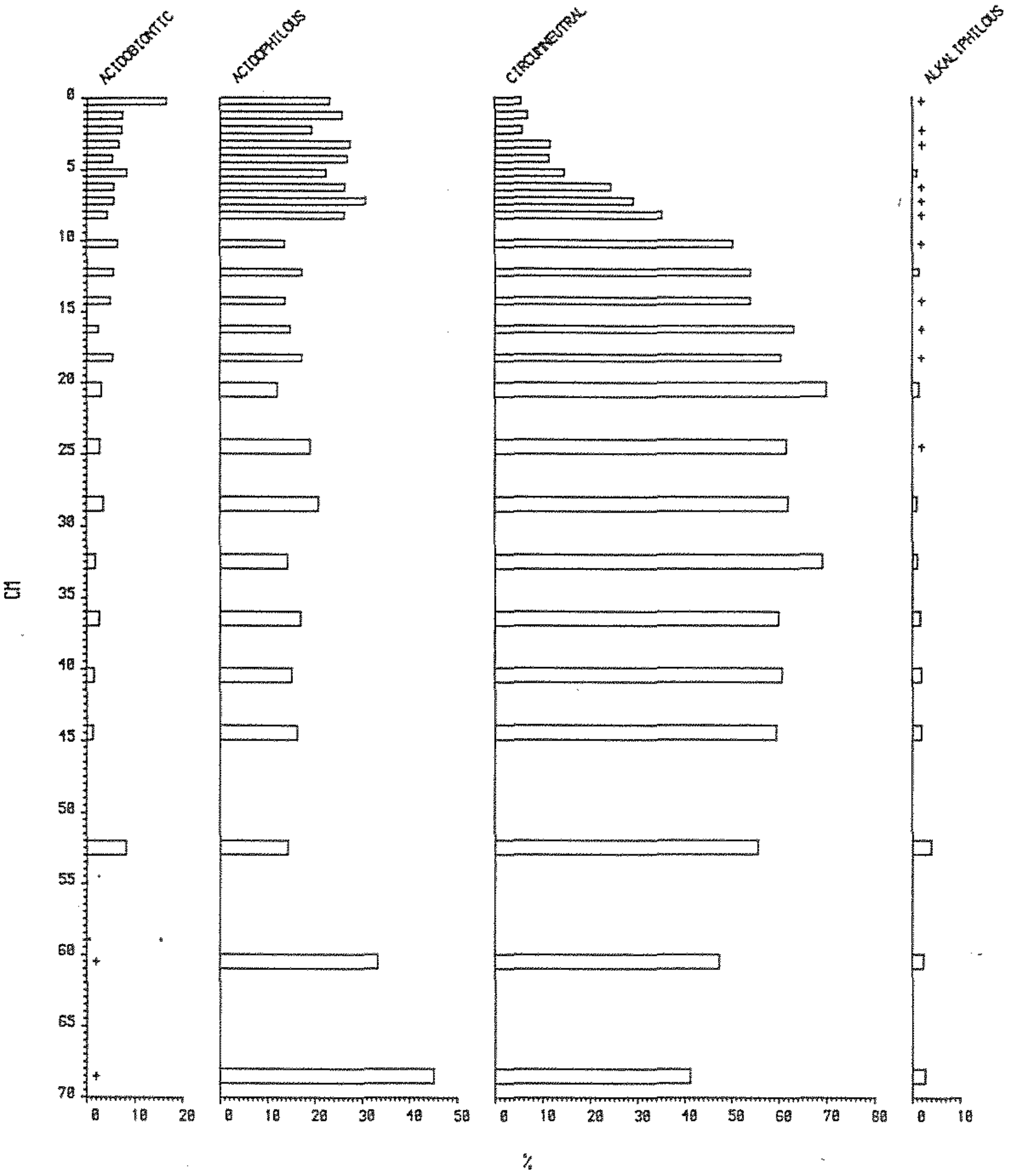


Figure 2.21 L. nan Eun: pH reconstruction (multiple regression)

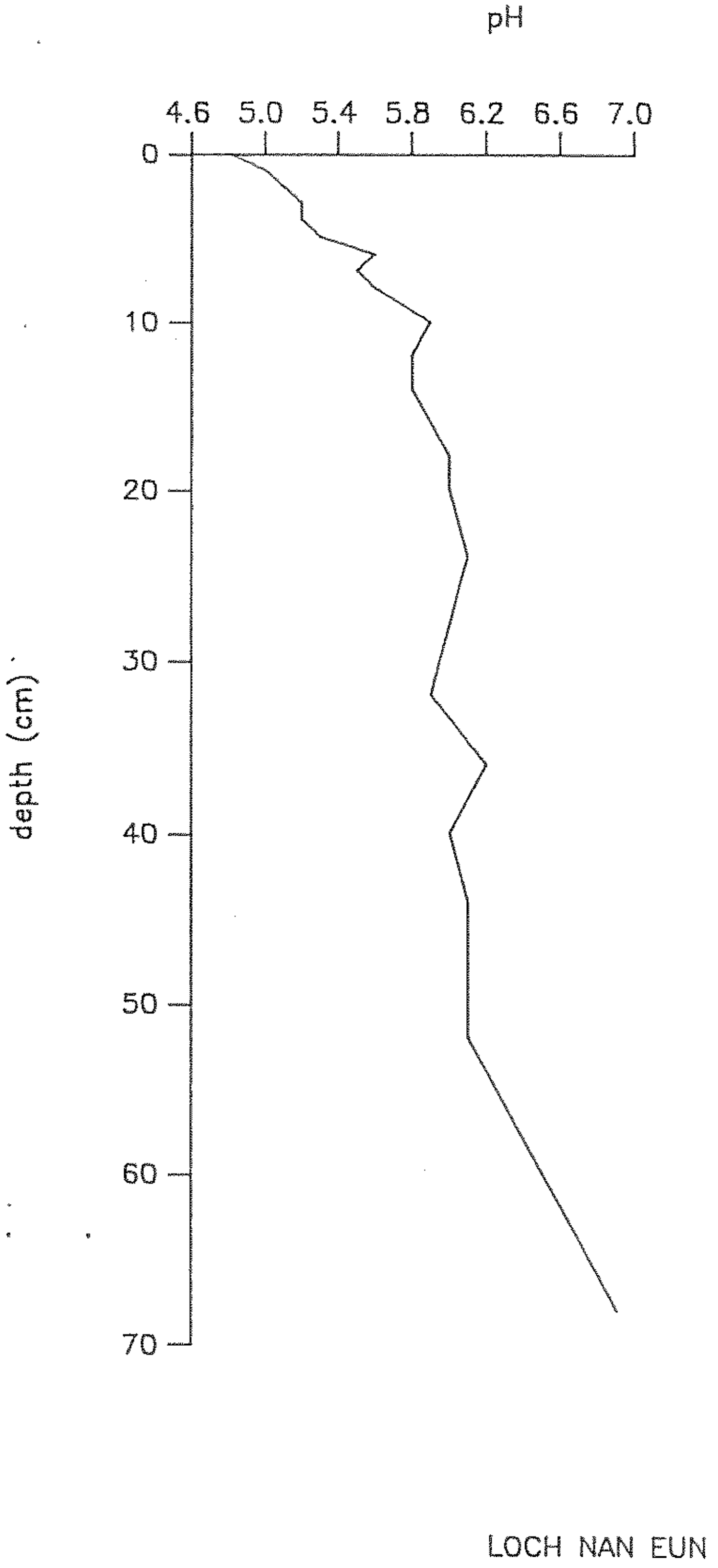


Figure 2.22 L. nan Eun: summary pollen diagram

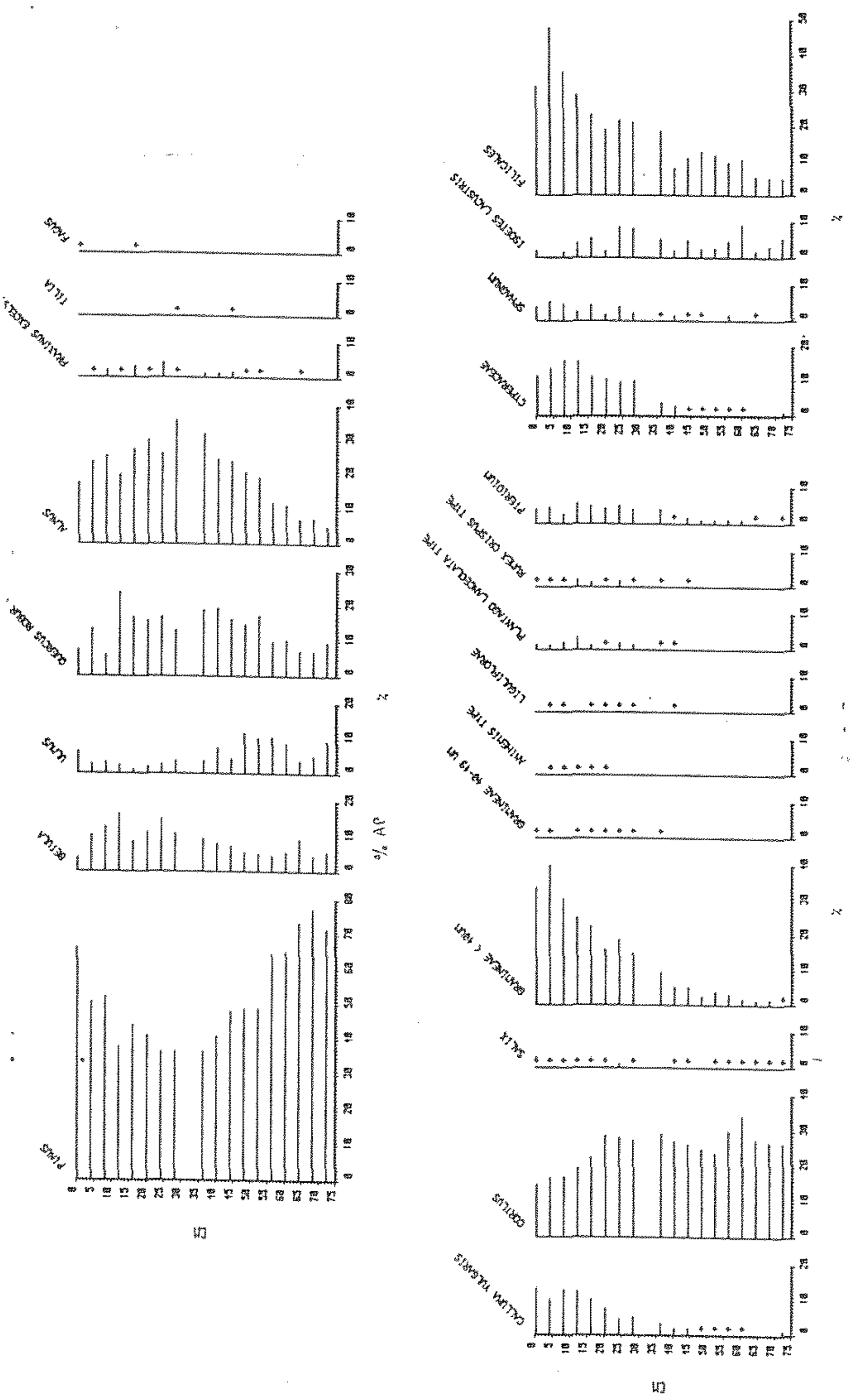
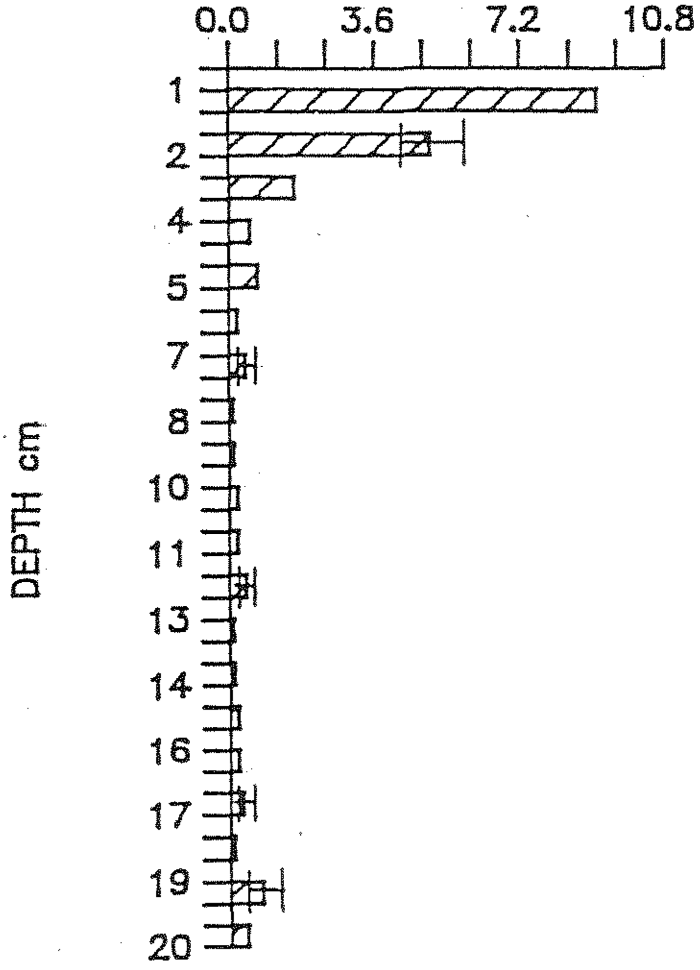


Figure 2.23 L. nan Eun: carbonaceous particle profile (x 10^3 g^{-1})



2.4.4 Dubh Loch

Bathymetry

A bathymetric survey (Figure 2.24) reveals a deep (maximum depth 21 m) basin confined in the centre of the loch within the steep valley sides. To the north and south the contours rise more gently to the broader, shallower areas adjacent to the inflow and outflow of the loch. A sediment core was retrieved from 19 m water depth.

Lithostratigraphy

The sediment is a dark brown organic detritus mud, and LOI values fluctuate between 50-70% over most of the core (Figure 2.25). There is a distinct drop in the LOI at 14-15 cm, which is associated with a peak in the percentage dry weight. Wet density values are fairly uniform throughout the core.

Dating

^{210}Pb and ^{226}Ra results are given in Table 2.8. The ^{137}Cs and ^{134}Cs results (corrected for decay since the Chernobyl incident) are given in Table 2.9. Traces of ^{241}Am were observed and these are apparent in Table 2.9. The presence of enhanced ^{137}Cs activities in the topmost sediments, in conjunction with the short-lived isotope ^{134}Cs is indicative of Chernobyl fallout.

The unsupported ^{210}Pb profile is fairly linear and there is consequently little divergence between the chronologies determined by the CRS and CIC models (Appleby and Oldfield 1978). However, near the base of the core the relatively high ^{226}Ra activity gives rise to large uncertainties in the dating parameters. The chronologies given by these models are shown in Figure 2.26. Both models date 18 cm to c. 1900 and give a mean sediment accumulation rate since then of 0.0216 ± 0.0043 g cm^{-2} yr^{-1}. The mean accumulation rate since 1850 is calculated to be 0.0232 g cm^{-2} yr^{-1} and it would thus appear that there has been no major shift in accumulation rates over the last 150 years. Because the CRS model effectively smooths out minor irregularities in the ^{210}Pb activity the chronology given in Table 2.10 is based principally on CRS information. At greater depths, where the uncertainties in the dating parameters become relatively large, dates have been calculated using the mean accumulation rate.

The ^{210}Pb dates suggest that 1963 should occur at about 5-6 cm depth in the core and that 1958 should occur at about 7-8 cm. The ^{137}Cs data give some general support to these dates, although there is some ^{137}Cs down to 25 cm, the principle rise (representing 1954-1958) occurs at about 8 cm. In addition, when Chernobyl ^{137}Cs is excluded, the residual weapons fallout component would appear to peak at between 3-6 cm. Further support is given by the ^{241}Am data, which show a small peak at 6-7 cm, dated by ^{210}Pb to 1959-1963.

Diatom analysis

A summary diatom diagram is presented in Figure 2.27. There are only very slight floristic changes at this site. Values of *Achnanthes minutissima* and *Fragilaria vaucheriae* decline at about 30 cm. Above 30 cm *Cymbella aequalis*, *Cymbella hebridica*, and *Eunotia exigua* are more abundant. The circumneutral species *Brachysira vitrea* and *Tabellaria flocculosa* decline slightly above 18 cm, this is accompanied by an increase in *Achnanthes marginulata*. Above 3 cm the acidobiontic species *Tabellaria quadriseptata* increases.

Diatom concentrations increase from the bottom of the core to 26 cm (Figure 2.28), they then decrease to 14 cm and then increase again towards the sediment surface. There does not appear to be any obvious correlation with the lithostratigraphy and sediment accumulation rates are fairly constant over this period.

Acidobiontic forms increase above 30 cm (1842 ± 34 years) to make up >10% of the flora (Figure 2.29). There is also a small increase in the percentage of acidophilous forms and the values of circumneutral taxa fall to <15% above this level. The reconstructed pH results indicate that below 30 cm the pH was between 5.6-5.8 (Figure 2.30). There was therefore a slight drop in pH in the mid-nineteenth century, from 5.6-5.8 to c. 5.3 (at 26 cm). There was a period of higher pH (5.6-5.7) between 1967-1975 (3-5 cm), from then pH decreased to the surface value of 5.3. The modern measured pH is 5.3.

Pollen analysis

The tree pollen is dominated by *Pinus* and there is a slight increase in Gramineae over *Calluna* in the top 20 cm. On the whole the profile is very stable (Figure 2.31), an open peatland community must have existed during the period represented by the entire core.

Carbonaceous particle analysis

22 sediment samples from 0-24 cm were analysed for carbonaceous particles. The results are presented in Figure 2.32. Below 16 cm (c. 1912) there are very low levels of carbonaceous particles ($<0.5 \times 10^3$ g^{-1}). From 16-8 cm the concentrations increase slightly and above 8 cm (c. 1955) they increase sharply to give a peak of 15.2×10^3 g^{-1} at 2.5-3 cm (c. 1977). The concentrations then fall slightly to the surface. The carbonaceous particle record therefore indicates the start of atmospheric contamination at the beginning of the twentieth century, with a increase after 1950 and a peak in the late 1970s.

Magnetic analysis

In progress

Geochemistry

In progress

Table 2.8 Dubh loch: ^{210}Pb data

Depth	Dry Mass	^{210}Pb Concentration				^{226}Ra Concentration	
		Total		Unsupp			
cm	gcm^{-2}	pCig^{-1}	±	pCig^{-1}	±	pCig^{-1}	±
0.25	0.0219	18.72	1.40	15.70	1.45	3.02	0.38
0.75	0.0656	19.57	1.49	16.58	1.54	2.99	0.37
2.75	0.2382	17.61	0.85	12.43	0.88	5.18	0.22
4.75	0.4358	14.05	1.02	9.97	1.05	4.08	0.25
6.75	0.6337	10.18	0.83	6.11	0.86	4.07	0.22
8.25	0.7958	10.75	1.03	6.69	1.06	4.06	0.27
9.75	0.9579	8.37	1.11	4.80	1.15	3.57	0.29
12.75	1.2626	6.41	0.84	3.68	0.87	2.73	0.22
16.75	1.7364	5.02	0.72	2.07	0.75	2.95	0.20
19.75	2.0567	4.35	0.44	0.66	0.46	3.69	0.13
24.50	2.5756	3.69	0.45	1.33	0.46	2.36	0.11
29.50	3.1232	2.50	0.25	0.27	0.27	2.23	0.10
34.50	3.6586	2.48	0.28	-0.60	0.29	3.08	0.08
38.50	4.0245	2.75	0.21	0.52	0.23	2.23	0.09
40.50	4.2250	2.95	0.31	-0.17	0.32	3.12	0.09

Table 2.9 Dubh Loch: ^{137}Cs, ^{134}Cs and ^{241}Am data

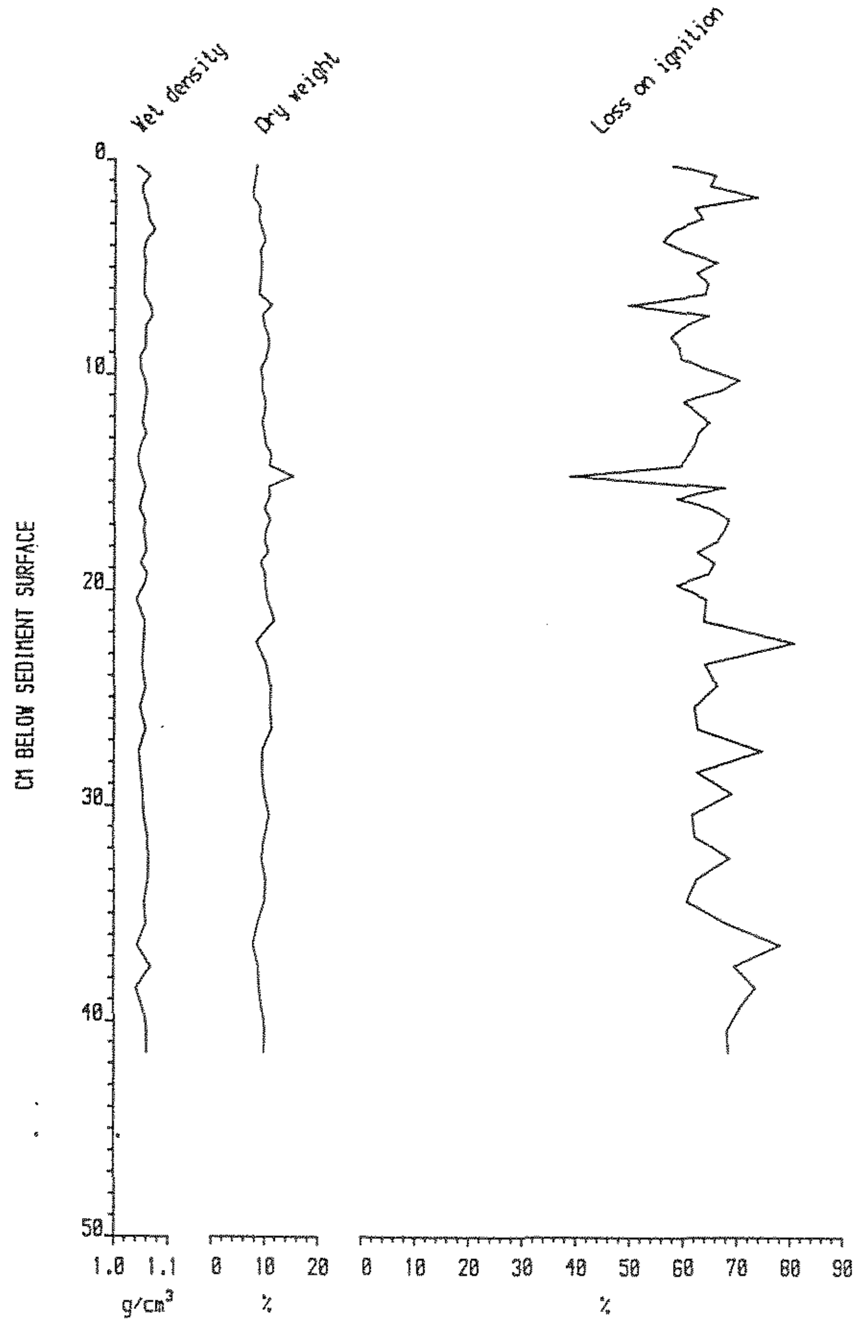
Depth	^{137}Cs Conc		^{134}Cs Conc		^{241}Am Conc	
cm	pCig^{-1}	±	pCig^{-1}	±	pCig^{-1}	±
0.25	7.95	0.36	1.49	0.34	0.00	0.00
0.75	6.94	0.36	0.00	0.00	0.00	0.00
2.75	4.68	0.19	0.00	0.00	0.00	0.00
4.75	4.30	0.23	0.00	0.00	0.00	0.00
6.75	3.87	0.20	0.00	0.00	0.05	0.00
8.25	2.18	0.22	0.00	0.00	0.00	0.00
9.75	0.72	0.21	0.00	0.00	0.00	0.00
12.75	0.46	0.17	0.00	0.00	0.00	0.00
16.75	0.32	0.14	0.00	0.00	0.00	0.00
19.75	0.15	0.08	0.00	0.00	0.00	0.00
24.50	0.14	0.07	0.00	0.00	0.00	0.00
29.50	0.00	0.05	0.00	0.00	0.00	0.00
34.50	0.00	0.00	0.00	0.00	0.00	0.00
38.50	0.00	0.00	0.00	0.00	0.00	0.00
40.50	0.02	0.05	0.00	0.00	0.00	0.00
Inventories:	4.48±0.17 pCicm^{-2}		0.07±0.02 pCicm^{-2}		0.01±0.01 pCicm^{-2}	

Table 2.10 Dubh Loch: ^{210}Pb chronology

Depth	Dry Mass	Chronology			Sedimentation Rate		
		Date	Age				
cm	gcm^{-2}	AD	yr	±	$gcm^{-2}yr^{-1}$	$cmyr^{-1}$	± (%)
0.00	0.0000	1987	0				
1.00	0.0872	1983	4	2	0.0222	0.254	11.3
2.00	0.1735	1979	8	2	0.0229	0.253	11.2
3.00	0.2629	1975	12	2	0.0232	0.249	11.7
4.00	0.3617	1971	16	2	0.0227	0.236	13.5
5.00	0.4605	1967	20	3	0.0231	0.232	15.6
6.00	0.5595	1963	24	3	0.0263	0.259	18.0
7.00	0.6607	1959	28	4	0.0275	0.266	20.3
8.00	0.7688	1955	32	4	0.0226	0.211	22.2
9.00	0.8768	1950	37	5	0.0227	0.214	25.6
10.00	0.9833	1945	42	6	0.0237	0.227	28.8
11.00	1.0849	1941	46	7	0.0225	0.211	29.7
12.00	1.1864	1936	51	8	0.0213	0.196	30.5
13.00	1.2922	1931	56	9	0.0202	0.182	32.9
14.00	1.4107	1925	62	11	0.0193	0.173	39.8
15.00	1.5291	1918	69	13	0.0184	0.164	46.6
16.00	1.6476	1912	75	15	0.0175	0.155	53.5
17.00	1.7631	1906	81	17	0.0190	0.169	62.9
18.00	1.8699	1901	86	20	0.0275	0.250	79.7
19.00	1.9766	1896	91	23	↑	↑	
20.00	2.0840	1891	96	25			
21.00	2.1933	1887	100	27			
22.00	2.3025	1882	105	29			
23.00	2.4117	1877	110	31			
24.00	2.5210	1872	115	33	0.0224	0.203	
25.00	2.6304	1867	120	33			
26.00	2.7399	1862	125	33			
27.00	2.8494	1857	130	33			
28.00	2.9589	1852	135	33			
29.00	3.0684	1847	140	33	↓	↓	
30.00	3.1767	1842	145	34			

Figure 2.24 Dubh Loch: bathymetry (contour intervals in metres) (X = core location)

Figure 2.25 Dubh Loch: lithostratigraphy



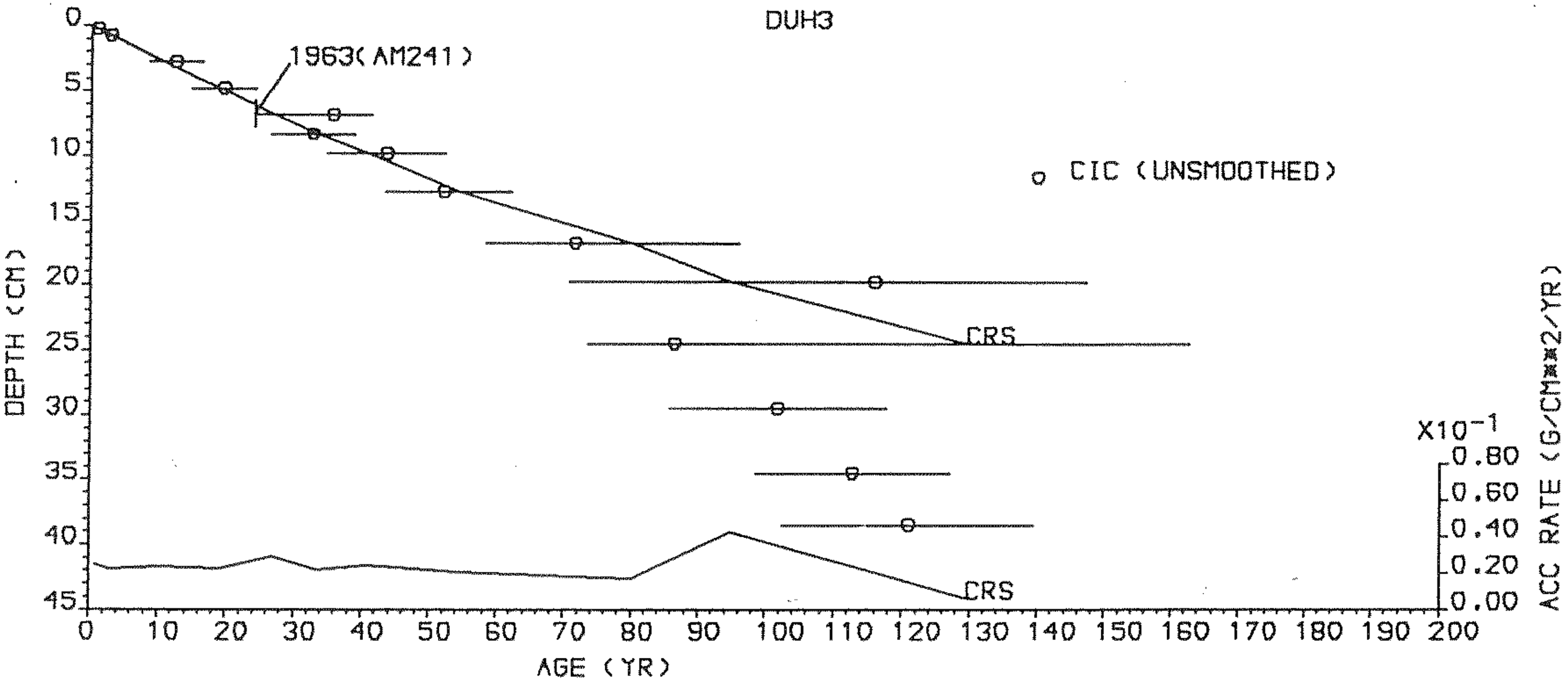


Figure 2.26 Dubh Loch: ^{210}Pb chronology

Figure 2.27 Dubh Loch: diatom summary diagram

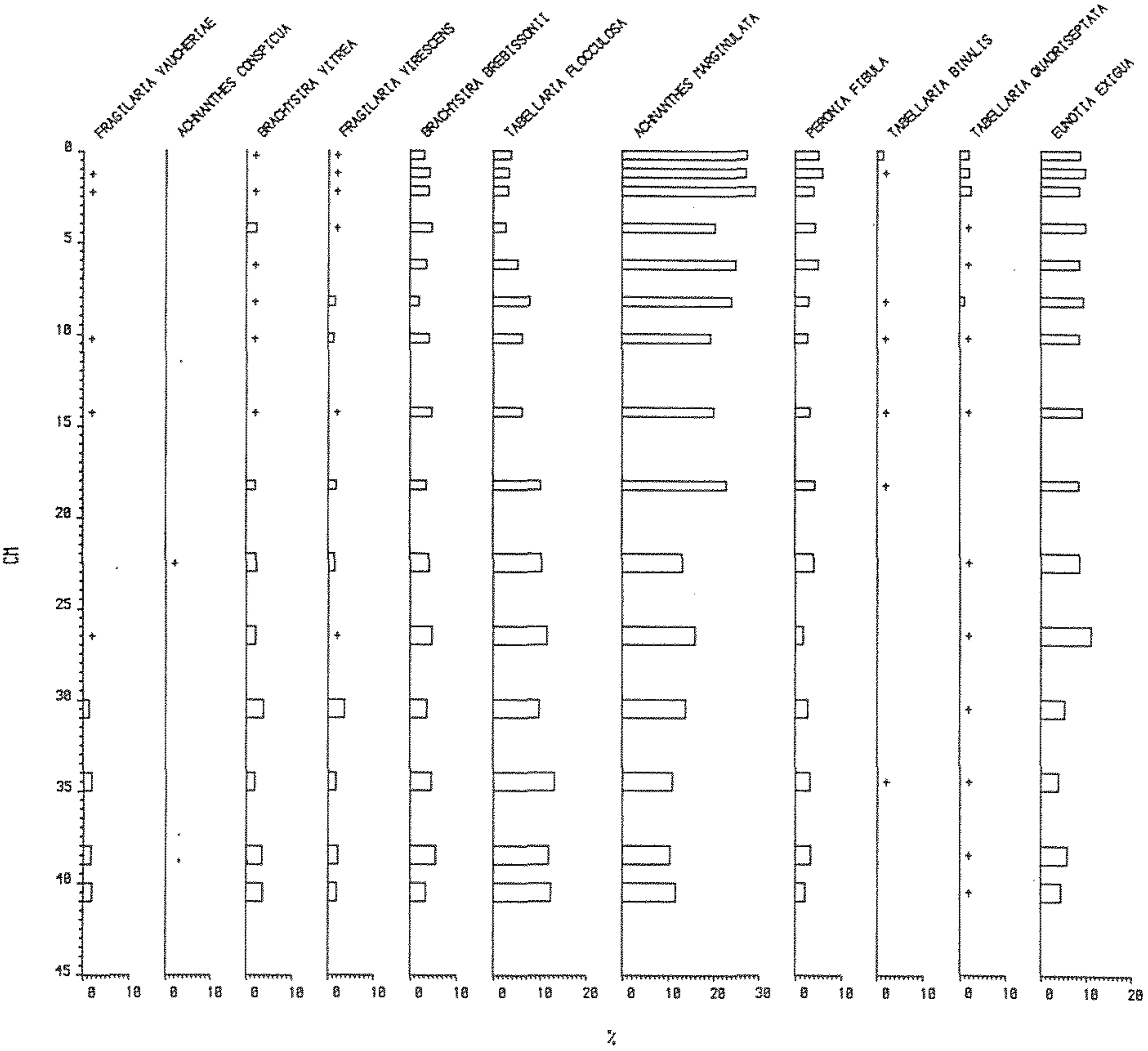


Figure 2.28 Dubh Loch: diatom concentration (x 10^8 g^{-1}), showing 95% confidence limits

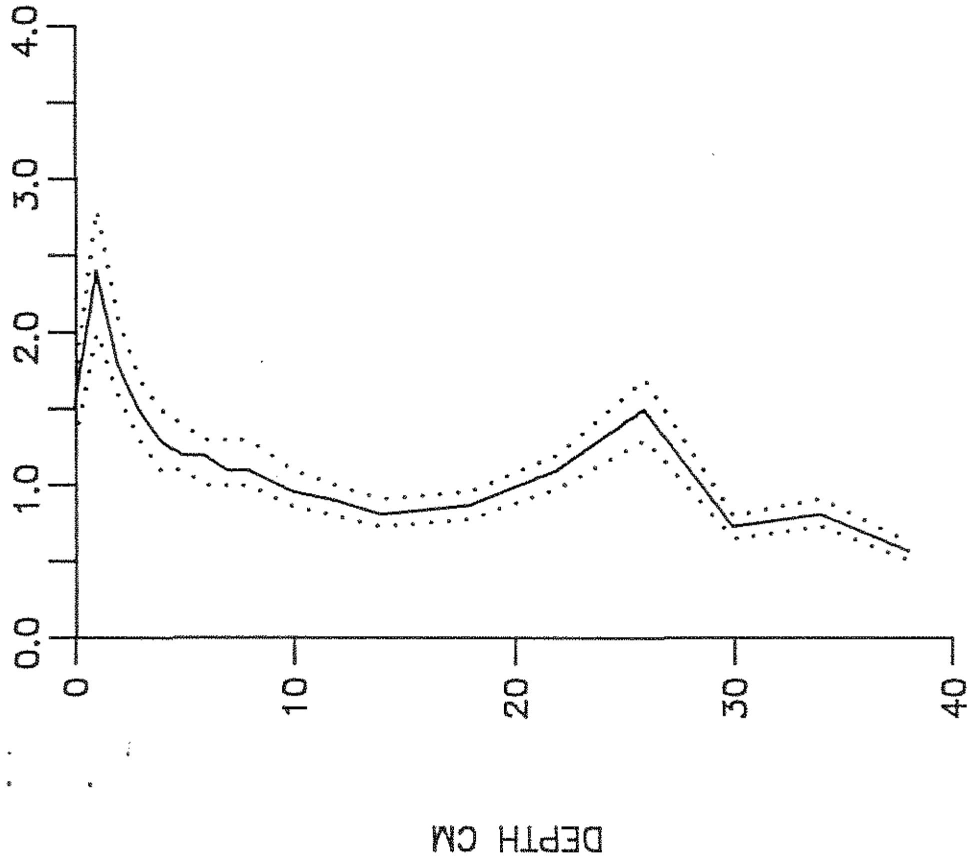


Figure 2.29 Dubh Loch: diatom preference groups

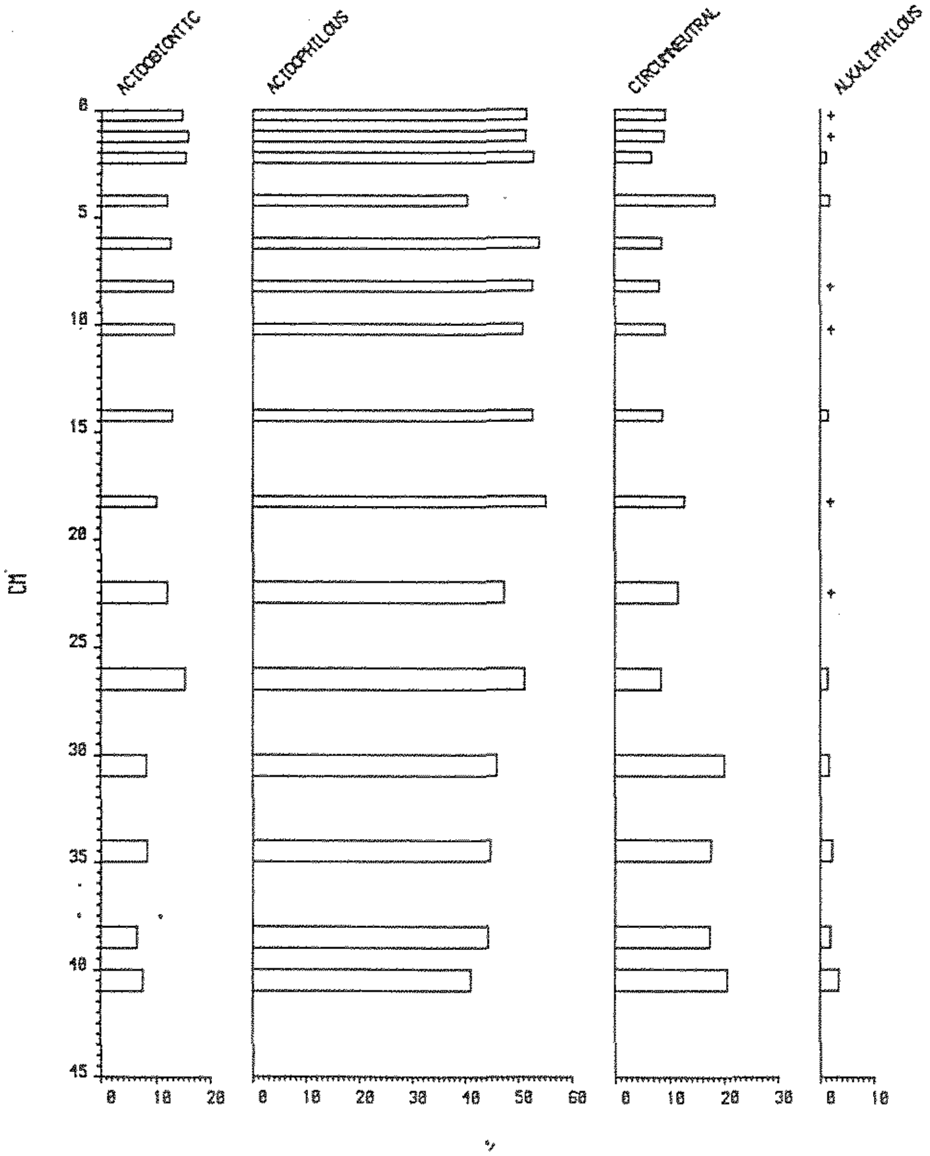


Figure 2.30 Dubh Loch: pH reconstruction (multiple regression)

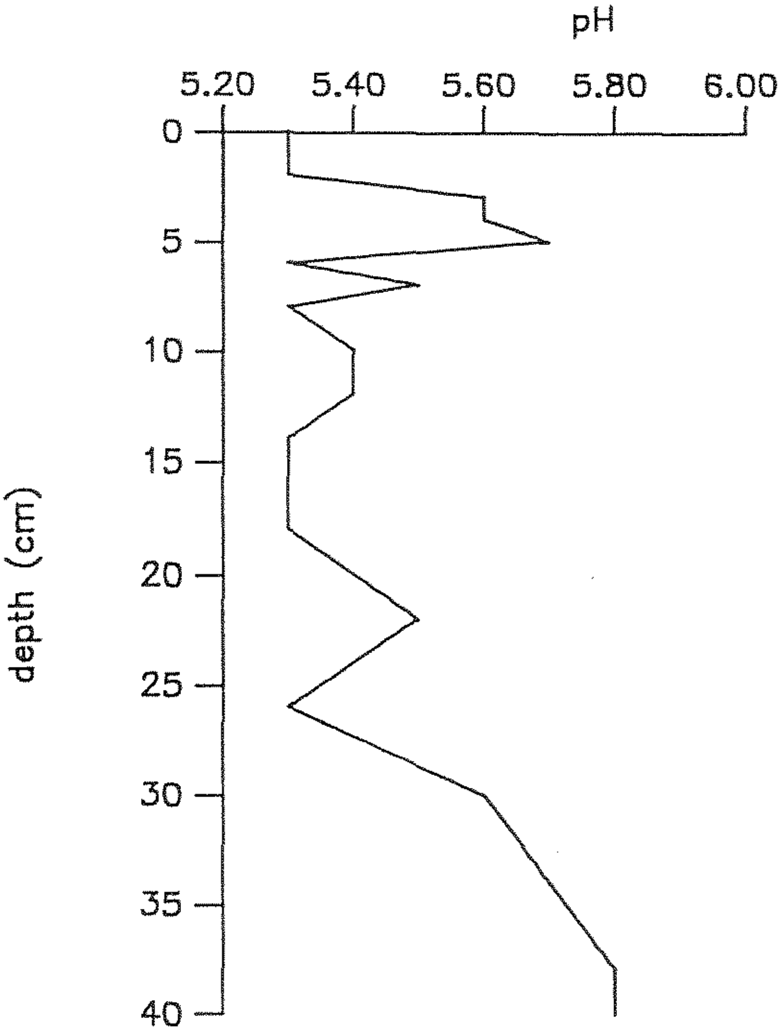


Figure 2.31 Dubh Loch: summary pollen diagram

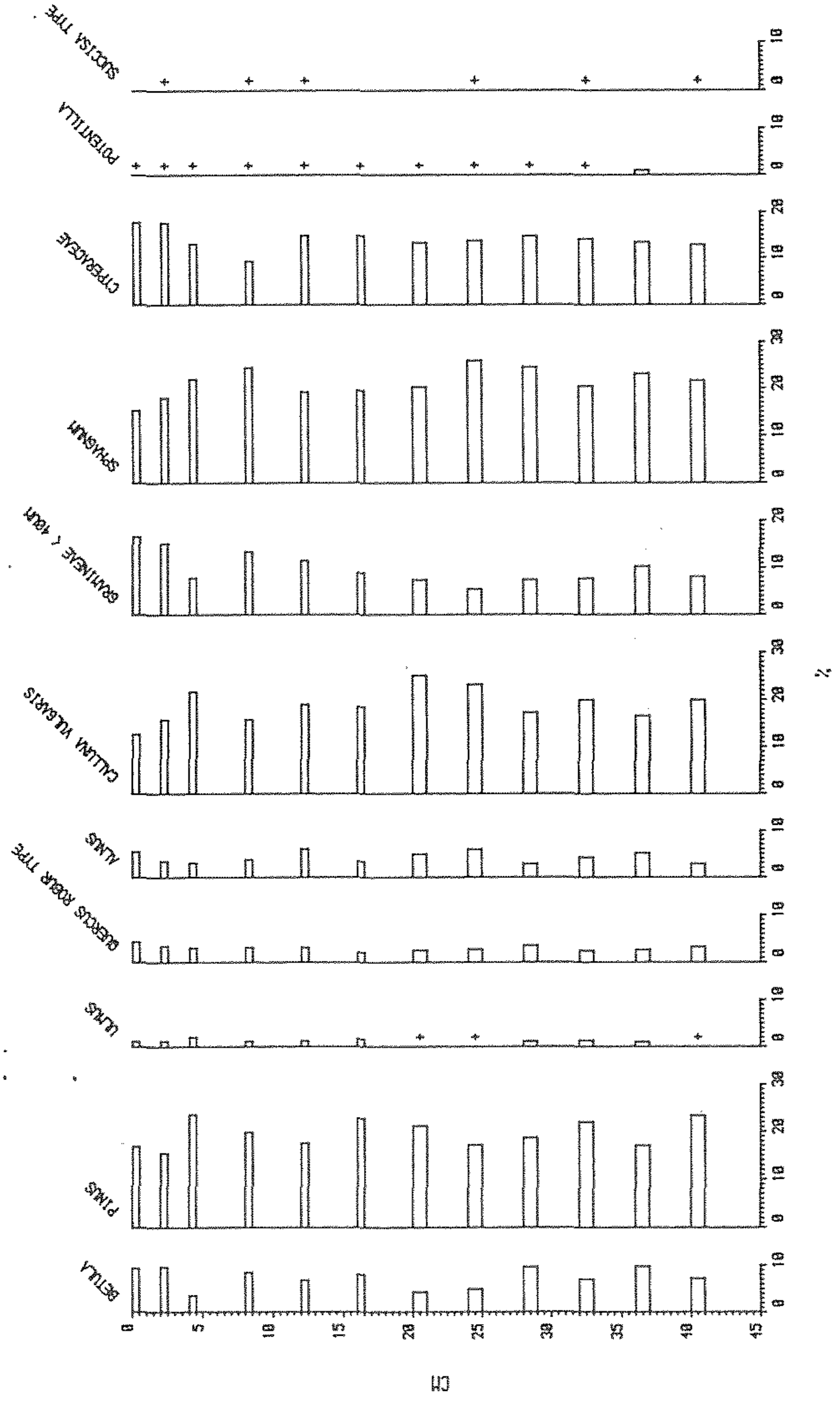
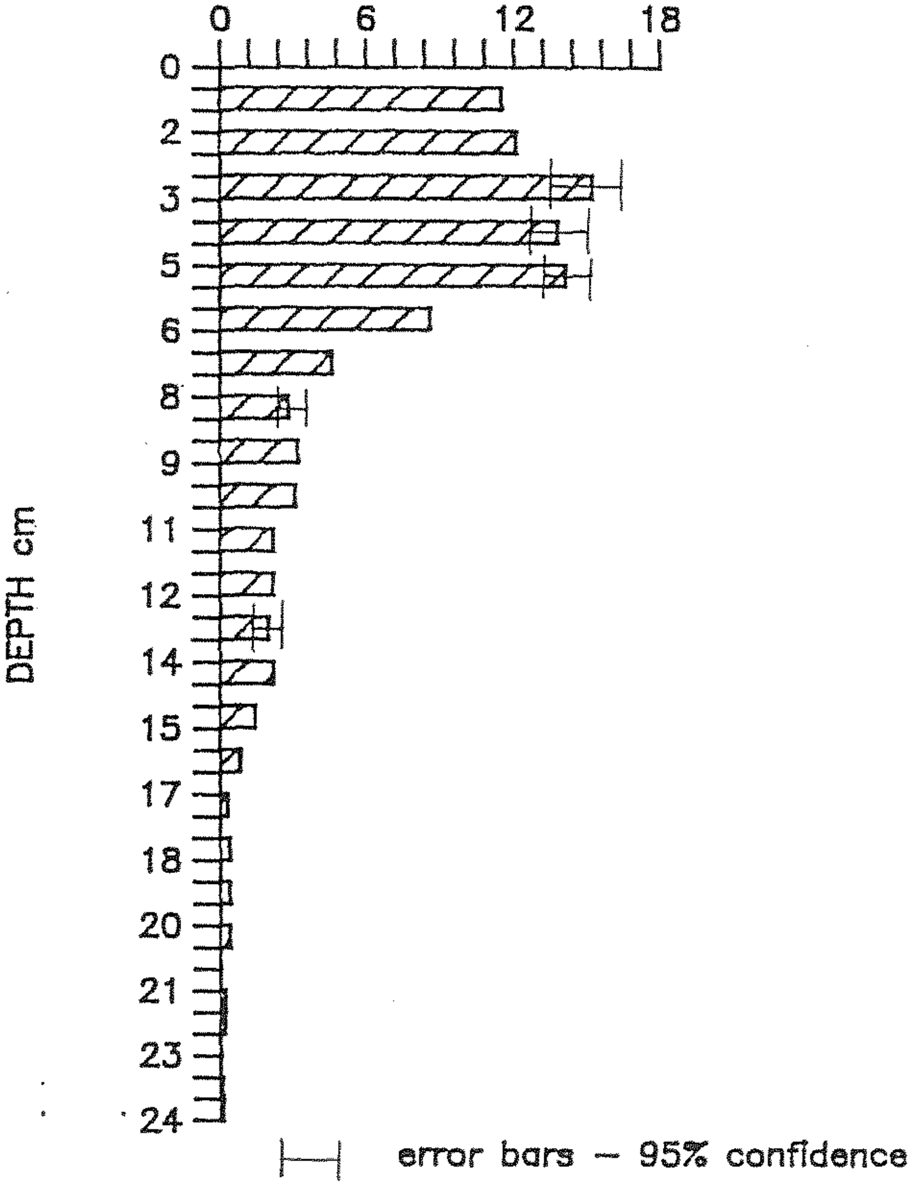


Figure 2.32 Dubh Loch: carbonaceous particle profile (x 10^3 g^{-1})



2.5 DISCUSSION

The available data from the Cairngorm and Lochnagar sites is summarised in Table 2.11. The interpretation of the results is rather difficult at present since important data are still awaited from the dating and magnetics centres at Liverpool University and the geochemists at the University of Ulster. However, certain conclusions may already be presented.

Evidence of lake acidification

The results of diatom floristic analysis and pH reconstruction are available for each of the sites. There is no evidence for strong acidification at either of the two Cairngorm sites, Loch Coire an Lochan and Lochan Uaine. At Loch Coire an Lochan, the reconstructed pH values fluctuate and there is no evidence of a steady decline in pH. At Lochan Uaine, a slight acidification of <0.5 of a pH unit is recognised, which commenced around 1850.

Within the Lochnagar sites, Loch nan Eun shows convincing evidence of strong acidification. Here pH values drop from pH >6.0 to pH <5.0, however, this core has yet to be ^{210}Pb dated. At Dubh Loch there was a slight drop in pH (<0.5 pH unit) in the mid-nineteenth century. At Lochnagar (Patrick *et al* 1989) acidification also began in the mid-nineteenth century and at this site there was a decline of almost a whole pH unit.

It would appear that lakes in this area of north east Scotland have acidified since about 1850, but to varying degrees. Differences in the degree of sensitivity to acidification between individual sites are difficult to explain, but probably relate to variations in the influence of geology, vegetation, hydrology and soil type within lake catchments.

Evidence for atmospheric contamination

All sites have increasing concentrations of carbonaceous particles towards the top of the cores. The date of the start of this atmospheric contamination appaears to range from the mid-nineteenth century (Lochnagar), to early-twentieth century (Dubh Loch) to about 1940 (Lochan Uaine). Because it is unlikely that nearby sites have significantly different histories of carbonaceous particle deposition the apparent discrepancy between these dates may be partly the result of dating problems, especially at Lochan Uaine, or to the relative insensitivity of the carbonaceous particle analysis used at these sites. More sensitive techniques now available (see Chapter 11 - this report) could be used to define the carbonaceous particle profiles more precisely.

Additional evidence for the role of atmospheric deposition will emerge from the geochemical and magnetic analyses currently in progress.

2.6 PRELIMINARY CONCLUSION

Because these sites are extremely remote and as there is no evidence from the pollen record or from documentary evidence (cf. Patrick *et al.* 1989, 1990) to suggest that land-use or land-management change has had a significant effect on lake water quality during the last 200 years, the most likely cause of their recent acidification is acid deposition. The timing and nature of the changes at these sites are consistent with the acid deposition hypothesis.

Table 2.11 Site summaries

	pH before 1st acidification	pH after 1st acidification	change
Lochnagar	5.7	4.8	0.9
Loch nan Eun	6.0	4.8	1.2
Dubh Loch	5.7	5.4	0.3
Lochan Uaine			
Mult Regression	5.9	5.6	0.3
Correspondence analysis	6.0	5.5	0.5
Loch Coire an Lochan	*	*	*

* recent acidification uncertain

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3 NORTH WEST SCOTLAND; THE EXTENT OF REGIONAL ACIDIFICATION

3.1 INTRODUCTION

By examining a series of sensitive lakes on a gradient from high to low acid deposition it is possible to show that the extent of acidification varies according to the level of sulphur deposition in a way that can be predicted from an empirical dose - response model (Battarbee 1989). In the project described below three sensitive sites from areas of low sulphur deposition were examined to determine whether acid deposition has affected these remote lakes and if so whether it has been sufficient to exceed a critical load above which ecological change occurs.

Loch Coire nan Arr lies on the Torridonian sandstones of the Applecross area (Figure 1.1) where sulphur deposition is estimated to be 0.71 g S m^{-2} yr^{-1}. This site is included in the DoE UK Acid Waters Monitoring Project. Loch Uisge is situated to the south on granodiorite geology in the Morvern Area (Figure 1.1), where estimated sulphur deposition is 0.76 g S m^{-2} yr^{-1}. Both are clear water sites with a mean pH >6 (Table 3.1), their Ca^{2+} levels are <70 µeq l^{-1} which suggests that they are sensitive to acidification (Battarbee *et al* 1988). Their relatively high Na^{+} and Cl^{-} concentrations reflect a marine influence which is a consequence of proximity to the coast. Loch Teanga lies on South Uist in the Outer Hebrides (Figure 1.1), an area which falls between the 0.8 and 0.4 g isolines for annual non-marine sulphur deposition over the British Isles. Loch Teanga is more acid than the other sites in this sub-project and has a water chemistry which clearly reflects its exposure to marine influence (Table 3.1)

The sites were cored in June 1986 (Loch Coire nan Arr and Loch Uisge) and September 1987 (Loch Teanga). Methods for lithostratigraphic, biostratigraphic, radiometric, magnetic and carbonaceous particle analysis follow the Royal Society Surface Water Acidification Project (SWAP) protocol (Stevenson *et al* 1987).

Table 3.1 Lake water quality

		Loch Coire nan Arr		Loch Uisge		Loch Teanga
pH		6.47	(5.8-7.0)	6.39	(5.9-6.8)	5.7
TOC	mg l^{-1}	2.2	(0.6-3.6)	4.8	(2.0-7.5)	*
Cond.	μS cm^{-1}	39	(26-60)	38	(26-80)	163.0
Alkalinity (Alk$_e$)	μeq l^{-1}	27.9		*		12.04
Na^+	μeq l^{-1}	216	(145-332)	213	(152-324)	981.0
Ca^+	μeq l^{-1}	43	(36-58)	67	(44-95)	110.0
Mg^{2+}	μeq l^{-1}	59	(38-108)	57	(35-95)	255.0
K^+	μeq l^{-1}	13	(6-34)	15	(8-41)	23.0
SO_4^{2-}	μeq l^{-1}	45	(35-57)	50	(43-63)	233.0
Cl^-	μeq l^{-1}	263	(143-436)	220	(128-433)	1160.0
NO_3^-	μeq l^{-1}	3.6	(1-8)	2.2	(1-3)	*
Al	μg l^{-1}					
Total		24	(14-34)	136	(22-361)	*
non labile		22		*		*
labile		2		*		*

Determinations: Loch Coire nan Arr and Loch Uisge = 1986-1987 mean based on 6 measurements, the range of values found is indicated in parentheses; Loch Teanga = 1987 spot sample; * indicates determination not made.

3.2 RESULTS

3.2.1 Loch Coire nan Arr

Bathymetry

The bathymetry of Loch Coire nan Arr is shown in Figure 3.1. The loch has a very simple profile with a single basin falling to 12 m at the deepest point. This is quite typical of glacial corrie lakes throughout the British Isles.

Lithostratigraphy

Lithostratigraphic results are presented in Figure 3.2. Percentage LOI values are relatively low throughout the core, never rising above 40%. This is in contrast with cores obtained from brown water lakes with very peaty catchments which can have LOI values of >70%. The dry weight and wet density profiles mirror the LOI profile with troughs in LOI corresponding with peaks in dry weight and wet density. These features most probably represent inwash events of mineral material from the lake catchment.

Dating

In progress

Diatom analysis

A summary diatom diagram is shown in Figure 3.3. The diatom profile is remarkably uniform with no major changes in species abundance over the time period represented by the profile. The assemblage is dominated by the circumneutral species *Achnanthes minutissima*, *Fragilaria virescens* v. *exigua* and *Brachysira vitrea*; the alkaliphilous *Fragilaria vaucheriae* is also present at abundances >5%, as are a number of acidophilous species (eg. *Eunotia incisa* and *Frustulia rhomboides* v. *saxonica*).

Diatom concentration results (Figure 3.4) show a period of relatively low concentration between 50-20 cm which is probably due to dilution by inwashed material. Concentrations subsequently rise to the top of the core.

pH was reconstructed using the multiple regression of pH preference groups method (Figure 3.5). The results suggest that pH in the loch has been >6.0 throughout the time period represented by the core. pH appears to have been fairly stable and there is no evidence of any acidification at this site. The surface sediment has a reconstructed pH of 6.5 which is in good agreement with the current mean measured pH (6.47).

Pollen analysis

A summary pollen diagram is shown in Figure 3.6. The pollen assemblage is dominated by peatland indicator taxa; in particular *Calluna vulgaris*, with Cyperaceae, *Sphagnum* and *Potentilla* also being important. Tree pollen is low, and is dominated by *Pinus*, most probably derived from long distance transport from coniferous plantations. *Isoetes* spores are only present at a low abundance from 40-30 cm, this corresponds with diatom and lithostratigraphic evidence for an inwash event and it is likely that the inwash caused a decrease in transparency leading to a decrease in *Isoetes*. Similar events have been described elsewhere in the British Isles (Stevenson *et al.* 1990).

Carbonaceous particle analysis

The carbonaceous particle concentration (Figure 3.7) is extremely low (6×10^2 g^{-1}) at Loch Coire nan Arr compared to sites situated in areas of high atmospheric deposition, (eg. at the Round Loch of Glenhead a concentration of 9×10^4 g^{-1} was found in the surface sediment). However, although concentrations are very low there is evidence of an increase in concentration above 8 cm which probably represents the first influence of atmospheric contamination which has commonly been dated to the mid-nineteenth century at other British sites (Battarbee *et al* 1988).

Geochemistry

In progress

Figure 3.1 L. Coire nan Arr: bathymetry (contour intervals in metres) (X = coring location)

Figure 3.2 L. Coire nan Arr: lithostratigraphy

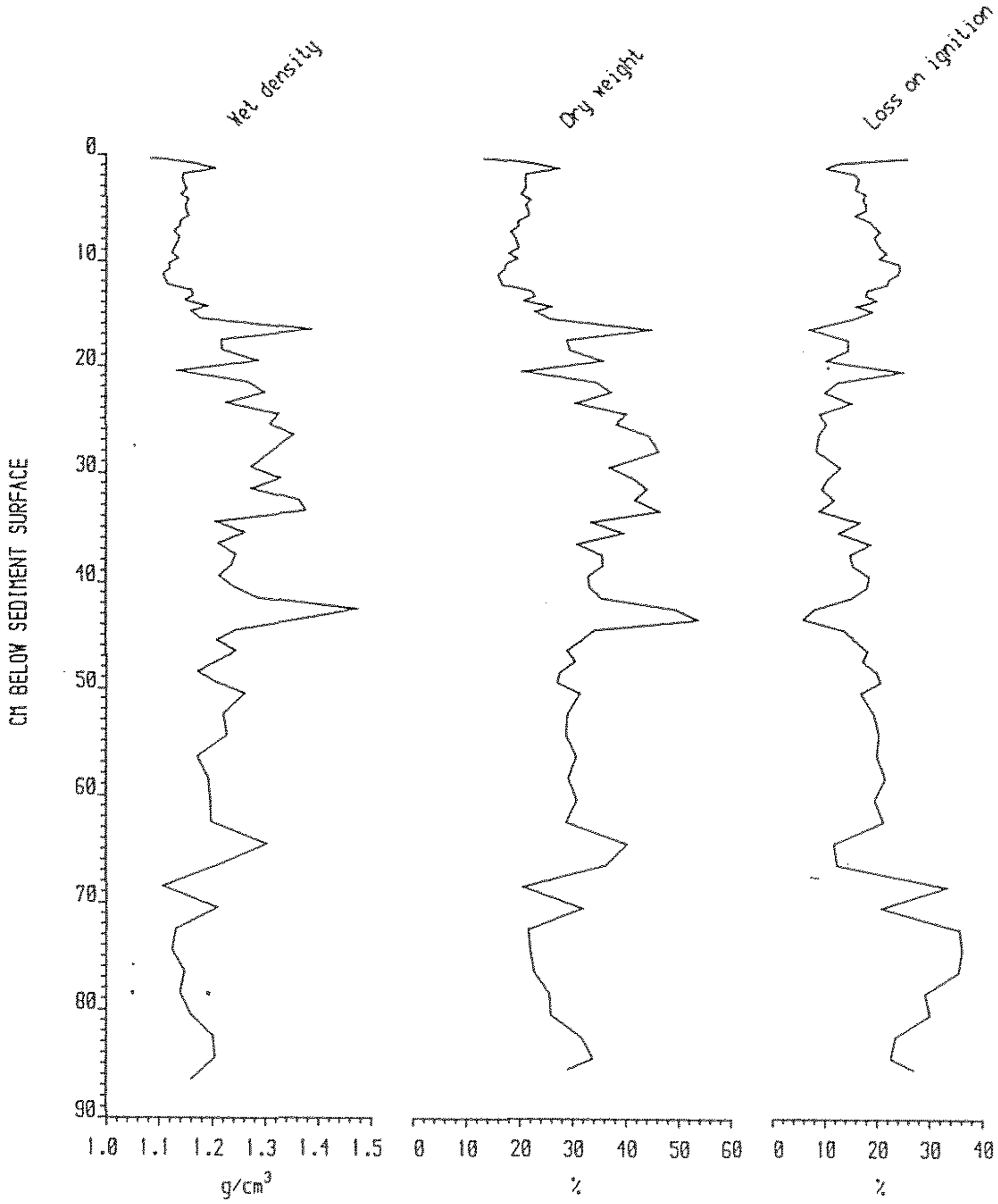


Figure 3.3 L. Coire nan Arr: diatom summary diagram

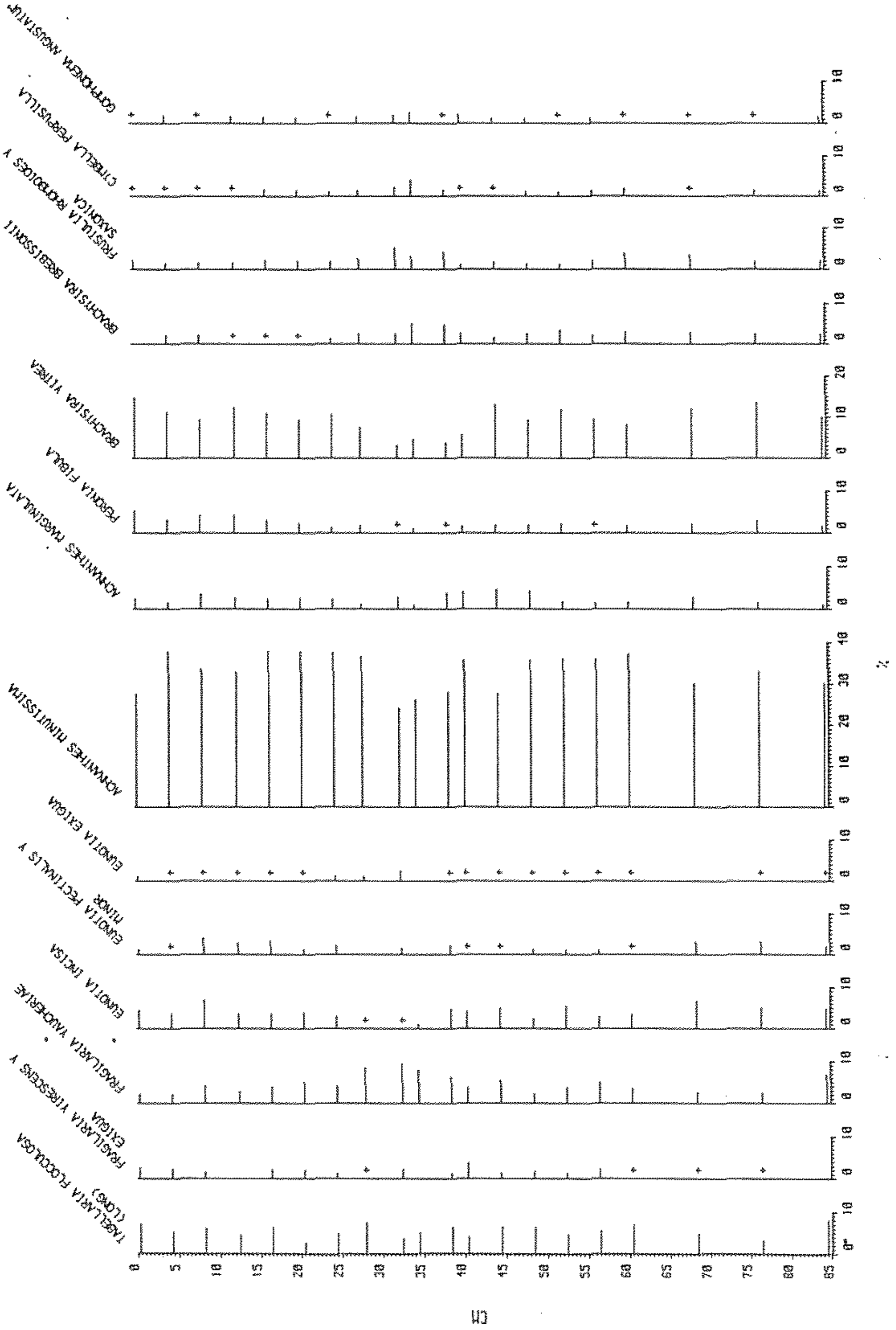


Figure 3.4 L. Coire nan Arr: diatom concentration (x 10^7 g^{-1}), showing 95% confidence limits

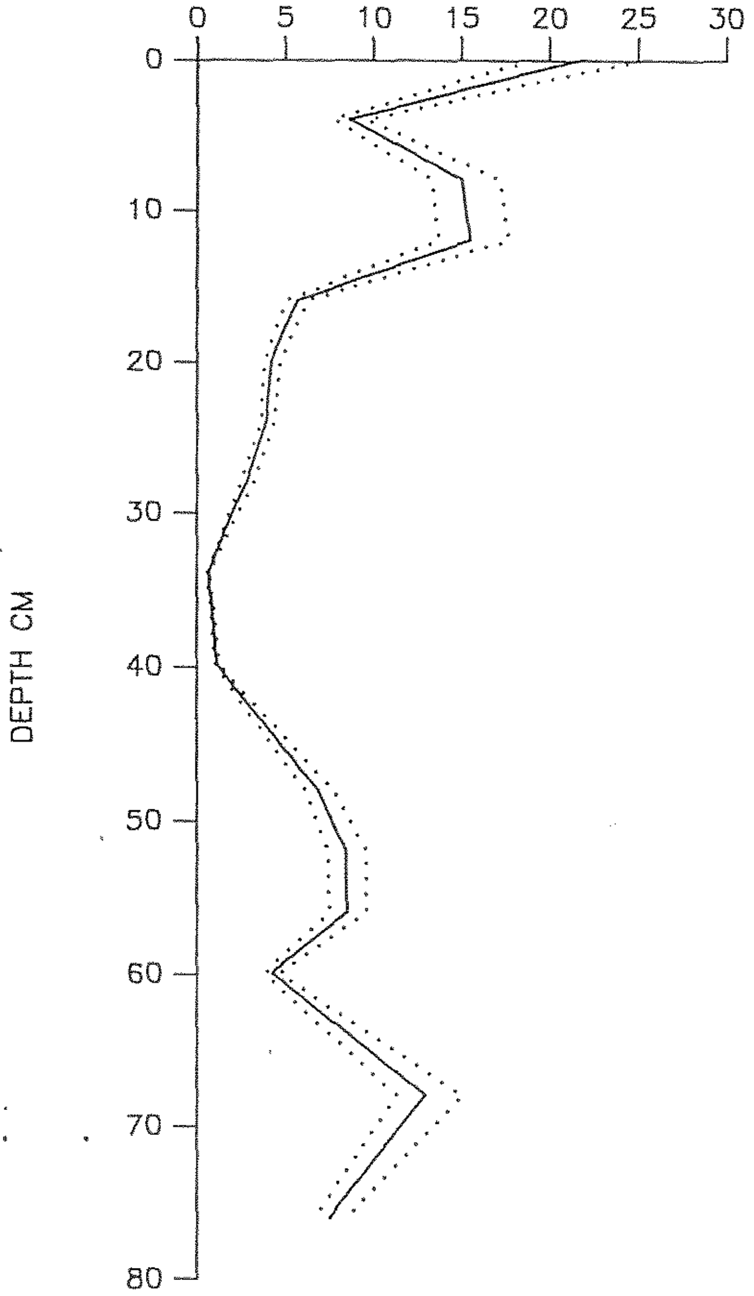


Figure 3.5 L. Coire nan Arr: pH reconstruction (multiple regression)

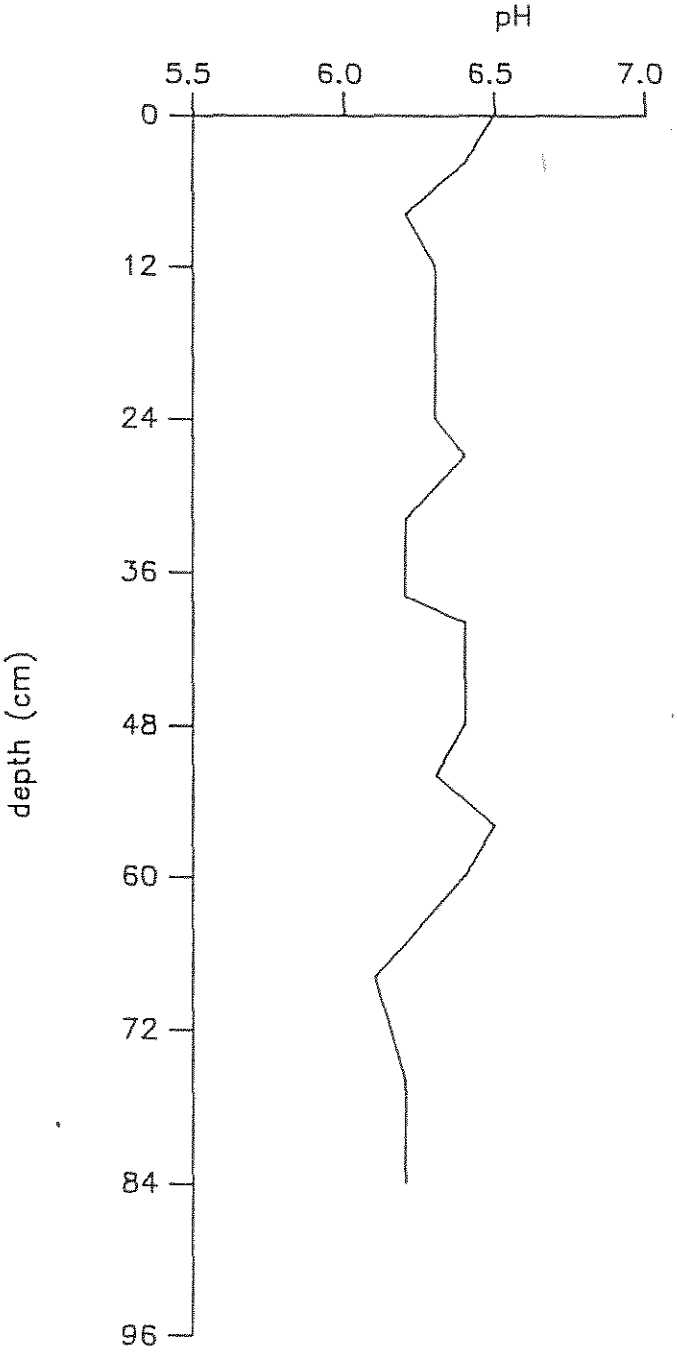


Figure 3.6 L. Coire nan Arr: summary pollen diagram

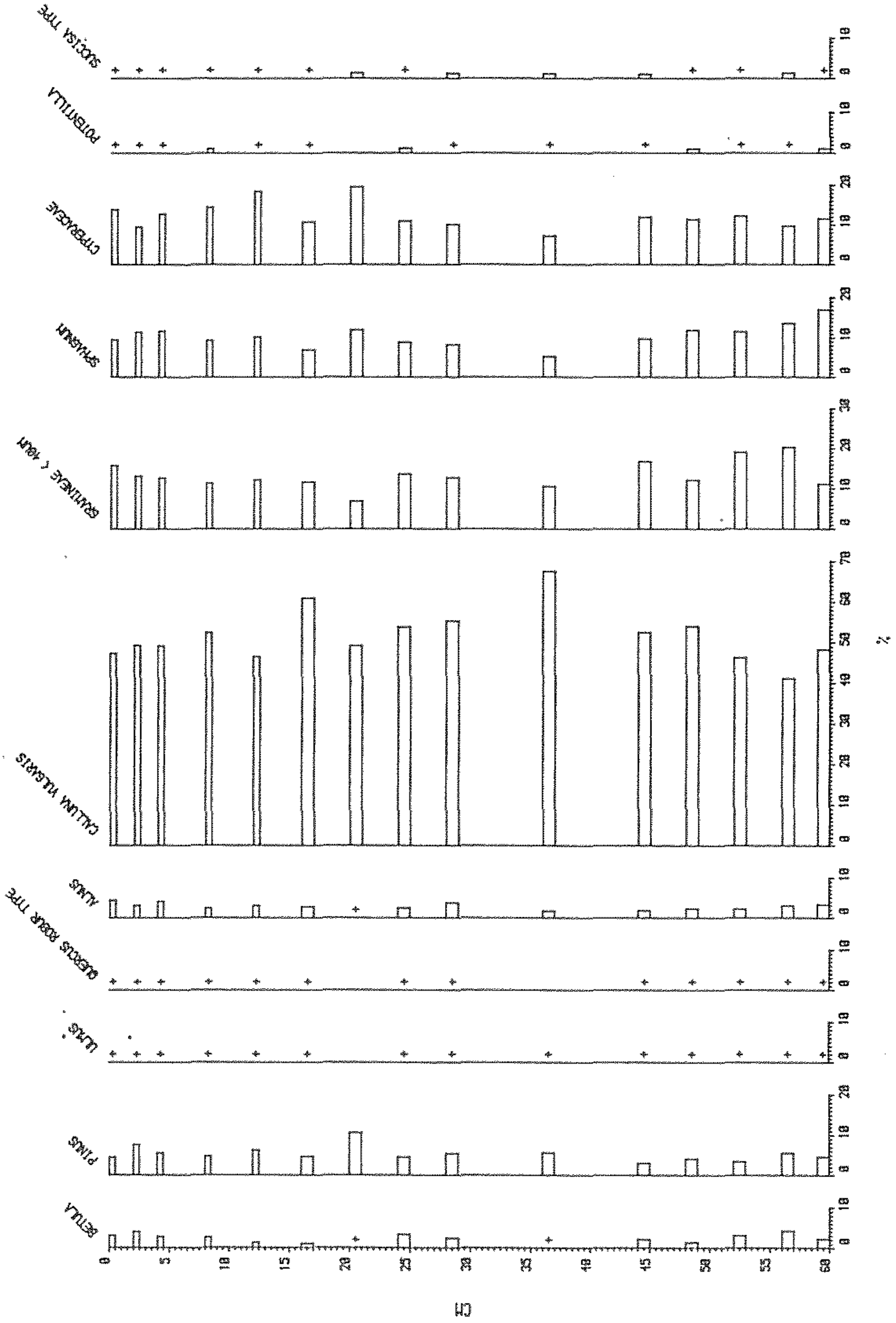
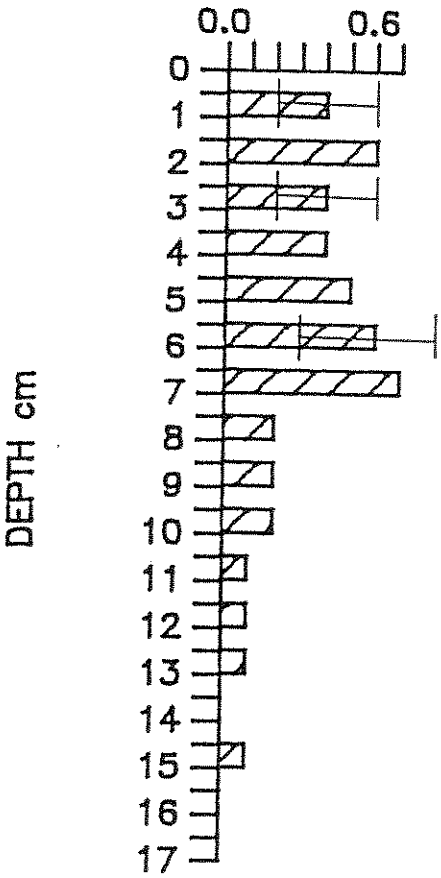


Figure 3.7 L. Coire nan Arr: carbonaceous particle profile (x 10^3 g^{-1})



error bars = 95% confidence
gds−1 = per gramme dry sediment

3.2.2 Loch Uisge

Lithostratigraphy

Loch Uisge has higher LOI values than those observed at Loch Coire nan Arr (Figure 3.8). At the bottom of the profile LOI values fluctuate at around 50%. There is a sharp drop in LOI above 37 cm which is accompanied by a peak in both the wet density and dry weight. This probably represents a period of catchment erosion leading to the inwash of mineral material. It also should be noted that the sediment between 31-36 cm was dark greyish brown, whilst that above and below this level was either black or dark brown in colour. Above 32 cm LOI values rise to over 30% and fluctuate between about 30-40% to the top of the profile.

Diatom analysis

A summary diatom diagram is shown in Figure 3.9. Like Loch Coire nan Arr the diatom profile is remarkably stable, with no major shifts in the dominance of species. Throughout the core the circumneutral species *Achnanthes minutissima* is dominant with abundances of around 30%. Other circumneutral taxa such as *Brachysira vitrea*, *Cymbella lunata*, *Cyclotella stelligera* and *Tabellaria flocculosa* are also common. *Cyclotella stelligera* is the only true planktonic form at this site and it is interesting that the abundance of this species falls above 35 cm, where there is lithostratigraphic evidence for an inwash event. It is possible that changes in water transparency associated with the inwash caused the decline of this species and similar changes with other planktonic *Cyclotella* species have been observed elsewhere (Jones *et al.* 1989).

The diatom concentrations (Figure 3.10) are relatively stable at this site but there is some evidence of dilution associated with the inwash event between 31-36 cm.

pH was reconstructed using the multiple regression of pH preference groups method (Figure 3.11). The reconstructed pH is very stable throughout the profile varying from 6.0-6.4, with no evidence of acidification. The reconstructed pH at the sediment surface is 6.1 which compares well with the mean measured current pH of the loch of 6.39.

Pollen analysis

In progress

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Figure 3.8 L. Uisge: lithostratigraphy

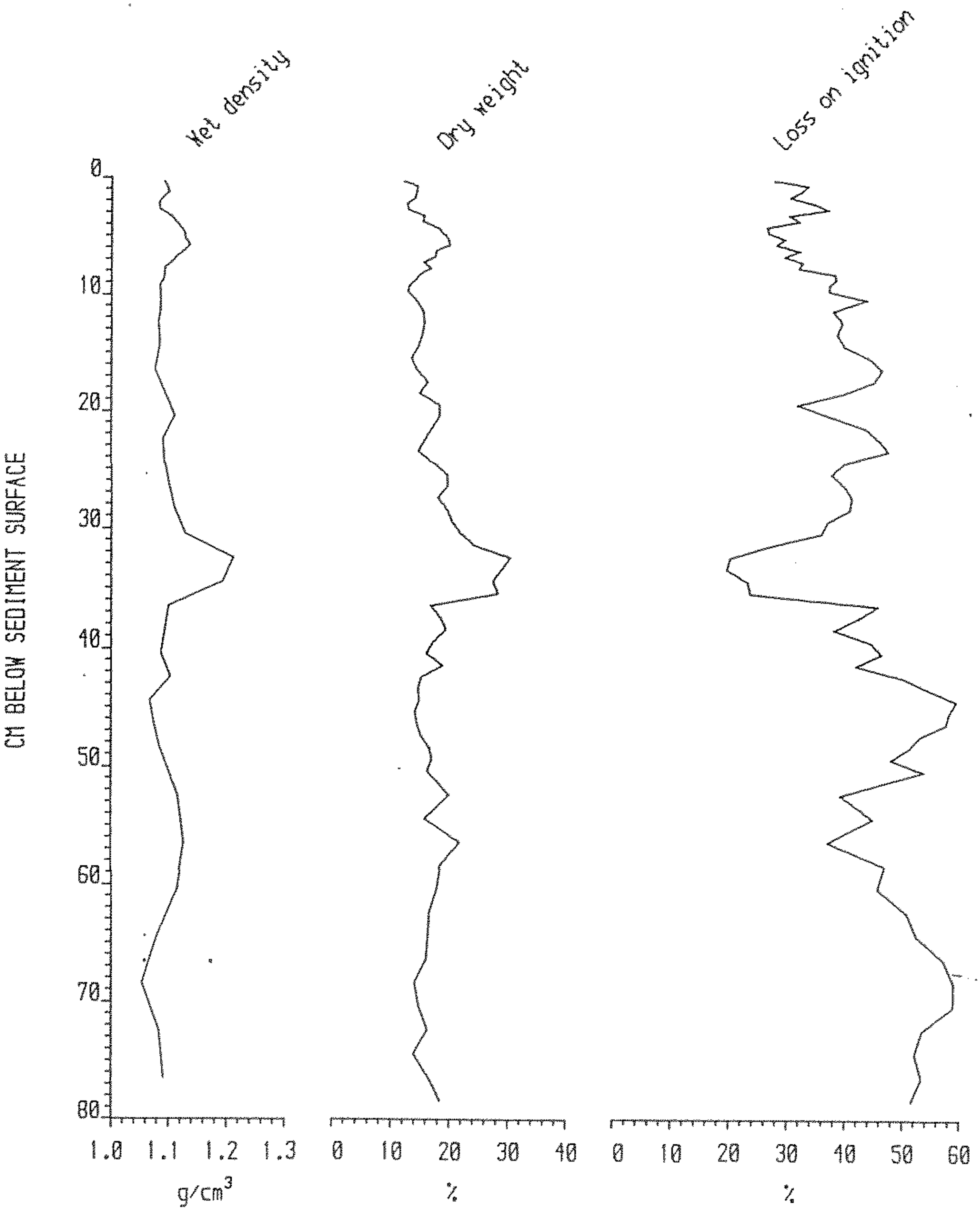


Figure 3.9 L. Uisge: diatom summary diagram

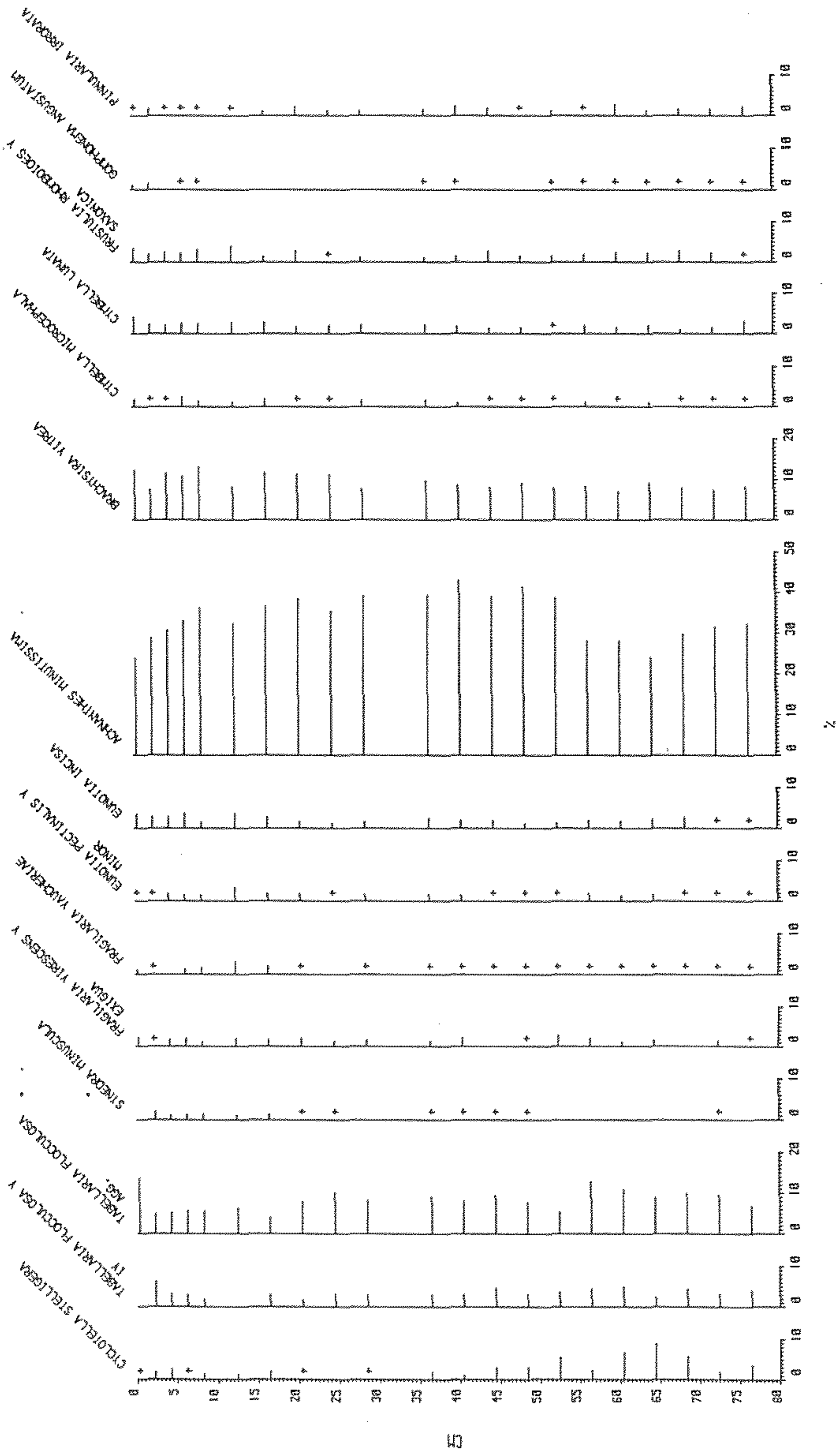


Figure 3.10 L. Uisge: diatom concentration (x 10^7 g^{-1}), showing 95% confidence limits

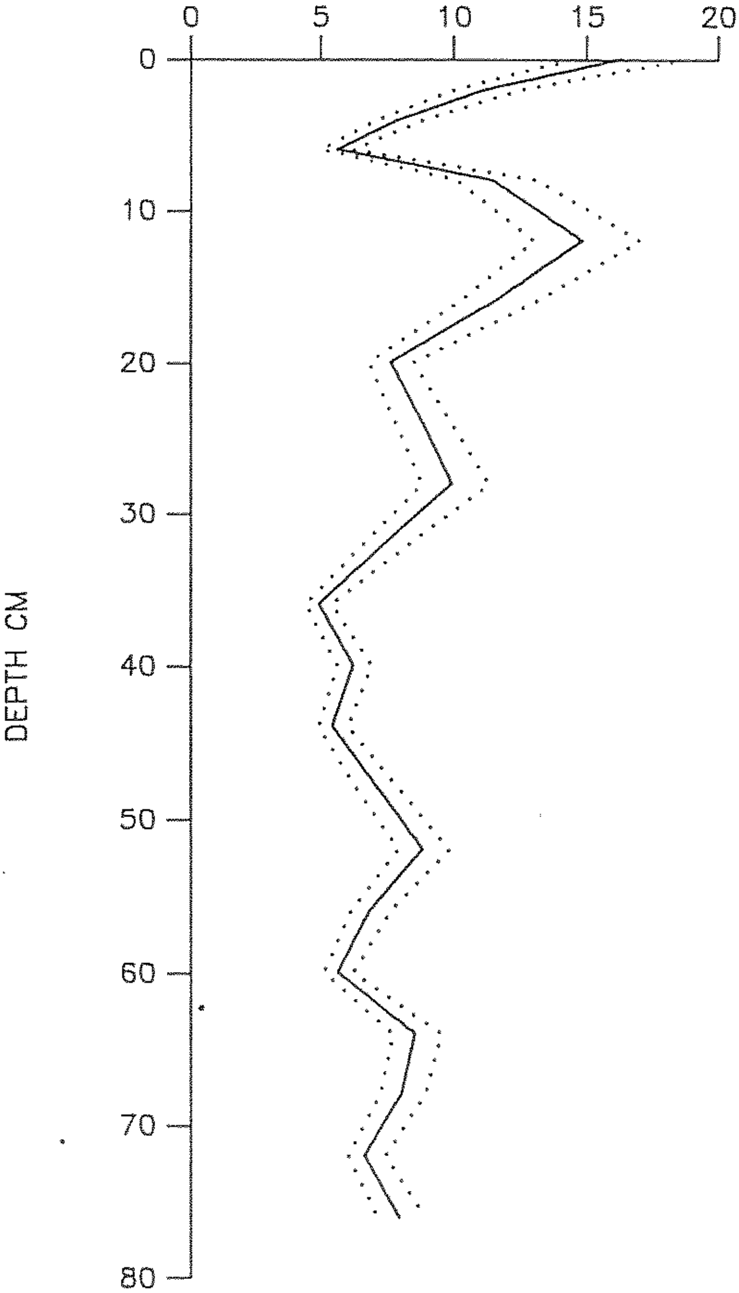
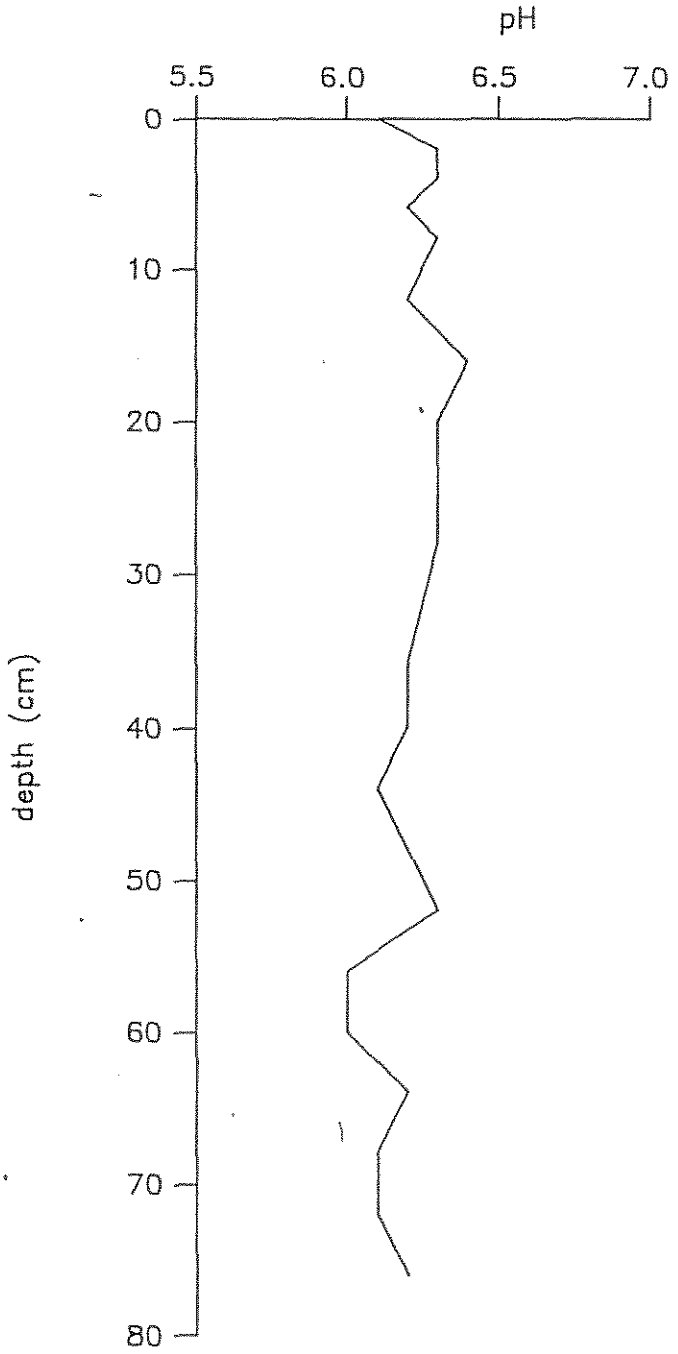


Figure 3.11 L. Uisge : pH reconstruction (multiple regression)



3.2.3 Loch Teanga

The lake is located at 25 m altitude and its catchment lies on resistant metamorphic rocks (Lewisian Gneiss) which possess little acid neutralizing capacity. The catchment is relatively very small, of low relief, and has no significant drainage streams. Blanket peat is abundant within the catchment and the dominant vegetation type is *Calluna* heath which is extensively burnt for sheep grazing. The lake is oligotrophic, mildly acid and relatively deep with a maximum depth of 20 m (Figure 3.12 - Flower and Nicholson 1986). Sediment in the deepest area consists of grey late-glacial clay and the more recent organic sediments were subsequently found deposited mainly on the shallower slopes in the southern portion of the basin. The point finally selected for coring is shown on Figure 3.12. Coring of this lake was carried out using Livingstone coring apparatus. Potentially, a full post-glacial sediment sequence of 5.3 m was obtained. Results presented here will pertain mainly the most recent sediment.

Loch Teanga possesses steeply shelving rock margins and this combined with the peat stained water suppresses extensive macrophyte growth within the lake. However in the shallower northern arms of the lake, *Juncus bulbosus* is common and elsewhere where gravels or mud extend into the photic zone *Isoetes lacustris* is fairly abundant. Nothing is known about the invertebrate or plankton communities of this lake but reports that it supports a small population of undersized trout indicates that feeding potential is poor.

Lithostratigraphy

The percentage dry weight curve (Figure 3.13) shows no major changes except for a slight but sustained trend towards declining values from the core base to c. 12 cm depth. Furthermore, between 12 and 2 cm values are marginally but consistently higher than in the immediately preceding section. There are also two small and isolated dry weight peaks at 134 and 155 cm depth. These increases are associated with low values for organic content and indicate an accelerated supply of minerogenic material to the lake. Most variation occurs in the LOI profile (Figure 3.13) which shows a trend towards increasing values from c 30% at 145 cm to about 65% at 20 cm depth but superimposed on this trend are three major peaks at 80, 46 and 20 cm. Minor peaks also occur at 138 and 110 cm depth. In the top 20 cm of sediment LOI values decline from to about 35%, approaching those at the core base. At about 13 cm depth there is a small but distinct increase in sediment dry weight.

Because low values in the LOI profile do not coincide with peaks in dry weight the dominant process determining the LOI profile is considered to be inwash pulses of organic material (corresponding to the LOI peaks) rather than minerogenic inwash pulses causing depressed LOI values. Hence, the LOI profile is probably a record of peat erosion events within the catchment, most likely caused by catchment over-burning in the past. Of these peat erosion pulses the most recent seems to be the most intense and is followed by an increase in mineral soil erosion, as evidenced by the slight dry weight increase in the upper 13 cm of the core.

Dating

The unsupported ^{210}Pb inventory for the core was calculated to be 11.6 pCi cm^{-2} which represents a constant flux of 0.36 pCi cm^{-2} yr^{-1}. The unsupported ^{210}Pb is fairly linear (Figure 3.14) and consequently there is little discrepancy between the sets of dates generated by both the CRS and CIC dating models (Appleby and Oldfield 1978). Both models indicate a mean sediment accumulation rate of 0.012 g cm^{-2} yr-1 since 1900. Figure 3.15 and Table 3.2 show the chronologies for the cores calculated using both the CRS and CIC models. For the lower depths in the core where uncertainties in the dating parameters become relatively large dates have been calculated using the mean accumulation rate calculated from both models. The lowest dated level in the core is 21.5 cm (1863) from which the accumulation rate declines from 0.19 cm yr^{-1} to 0.139 cm yr^{-1} by 4.5 cm depth (1963) and above this level the accumulation rate increases. In terms of dry matter accumulated per year there is relatively little change, the lowest rate occurs at 12 cm which increases to a minor peak at 9.5 cm and a larger peak at 1 cm depth.

Loch Teanga is a region subject to fallout from the Chernobyl accident and the gamma spectra confirmed the presence of high ^{137}Cs in the core top together with significant concentrations of the associated short-lived isotope ^{134}Cs (Figure 3.16). Since the ^{134}Cs : ^{137}Cs ratio in Chernobyl fallout is about 0.6, the component of the ^{137}Cs inventory deriving from this fallout is estimated to be 1.7 pCi cm^{-2}, with the remainder (7.6 pCi cm^{-2}) resulting from weapons testing fallout. The ^{137}Cs profile extends down to 37 cm and offers further evidence of the mobility of this isotope in lake sediment and the ^{134}Cs profile reveals the presence of Chernobyl ^{137}Cs down to at least 2 cm (dated to 1979).

Diatom analysis

The summary diatom frequency diagram (Figure 3.17) shows that below 21 cm depth or the 1860s the composition of the sedimentary diatom assemblage was very stable despite the variations in gross sediment stratigraphy. This lower section is characterised by approximately similar abundances of *Fragilaria virescens* v. *exigua*, *Brachysira vitrea* and the planktonic diatom *Cyclotella kutzingiana* v. *minor*. Above this depth at 18 cm or the 1870s the assemblage composition begins to change slightly as *C. kutzingiana* declines and *Peronia fibula* increases. *C. kutzingiana* v. *minor* declines further and drops to c. 5% abundance by 7 cm depth or the 1950s and after reaching a peak abundance of c. 15% *Achnanthes minutissima* follows a similar pattern of decline. Over this period *B. vitrea* increases irregularly to a peak abundance of almost 30%. After the 1950s *B. vitrea* frequencies decline somewhat and those of *A. minutissima* and *C. kutzingiana* v. *minor* remain low but small increases in *Peronia fibula* and *Eunotia pectinalis* v. *minor* occur. The frequencies of *F. virescens* peak at 17 cm, 9 cm and 2 cm depths showing little consistent trend towards change, however frequencies increase in the upper 5 cm as those of *B. vitrea* decline. The increase in minerogenic material around 12-10 cm depth may influence changes in abundance at this depth in the core.

The influence of pulses of inwashed material can be clearly seen in the diatom concentration curve for this core (Figure 3.18). Low diatom concentrations at c. 20, 45 and below 65 cm depths coincide with increasing LOI values of the three major inwashed pulses of peat (cf. Figure 3.13). Immediately above 14 cm depth the diatom concentration declines further as minerogenic inwash causes further dilution (cf. dry weight increase in Figure 3.13).

Assessment of acidity change in the lake as recorded by the diatom assemblage is made clearer by combining the diatoms into pH preference groups (Figure 3.19). The circumneutral group shows an initial change with a small decline at 19 cm depth (1870s) but the group then increases to about 15 cm depth (1890s) before declining irregularly to the core top. Correspondingly, the acidophilous group declines from 19 cm to 15 cm before increasing irregularly to achieve their maximum abundance at the core top. Only minor shifts occur in the alkaliphilic group. These pH groups can be used to reconstruct the pH history of the lake (Flower 1986) and this is shown in Figure 3.20. Within the ^{210}Pb chronology, inferred pH shows a slight decline to pH 6.1 at around 20 cm depth (1860s) before increasing to pH 6.3 by the late-nineteenth - early-twentieth century period. After about 1915 the pH declines and after a period of recovery in the 1950s, it falls again to 6.0 at the core top.

Although not fully apparent from the pH reconstruction, the diatom distributions indicate a slight shift to more acid conditions over the past c. 100 years, this assertion will be assessed using more stringent reconstruction techniques.

Pollen analysis

Pollen analysis has been performed on the whole 5 m sediment sequence, however only the record of vegetation change over the upper metre, particularly the upper 20 cm, is relevant to this study. The pollen summary diagram (Figure 3.21) shows that from below 1 m depth to about 30 cm the proportion of *Calluna* pollen increases from around 30% to almost 90% and totally dominates the pollen sum at this upper section. Tree pollen declines over the lower section of the core as *Calluna* increases, *Quercus* declines from c. 30% to insignificant levels by 70 cm depth and although *Pinus* pollen similarly declines it retains a significant presence an shows an increase in the surface sediment. These changes indicate that trees where formerly common around Loch Teagna, but it is unclear whether the pollen peaks around 175 cm depth are from direct supply by a then extant woodland or from reworking of then already fossil deposits. Since this peak coincides with a major decline in *Isoetes* spores (Figure 3.21) the latter may be correct. Disturbance indicators such as *Plantago lanceolata* are present throughout the upper 2 m of sediment and indicate human impacts on the catchment vegetation. Consequently, the increase in *Calluna* pollen in the upper part of the core is thought to derive both from an increased abundance in the catchment and from increased peat erosion. The latter is suspected since *Calluna* pollen achieves peak abundances as organic content of the core increases (cf. Figure 3.13).

The increase in *Pinus* pollen at the core top is probably caused by long distance transport of pollens from plantations. The grass pollen (Figure 3.21) shows a similar increase to that of *Calluna* but continues to increase in the nineteenth and early-twentieth century period as *Calluna* declines. This again is attributable to anthropogenic interference in the catchment, probably burning for sheep grazing.

Carbonaceous particle and ash sphere analysis

These analyses were performed following the methods of Rose (1989a, b). The carbonaceous particle profile (Figure 3.22) shows a characteristic trend with concentrations showing a sustained increase beginning in the 1940s and accelerating to 1960s. The concentrations increase during the 1970s period but level off in the 1980s. The ash sphere concentration profile (Figure 3.23) shows similar timing in increased concentrations, but levels-off earlier, in the mid-1970s.

The similarity of the carbonaceous particle and ash profiles suggests a predominantly coal burning origin for the former. However there is an order of magnitude difference in concentration between the two sedimentary components. Furthermore the subsequent divergence of the two profiles could be related to the presence of a small oil burning power station only 4 km north of Loch Teanga, located on the north east coast of South Uist.

Despite any local contamination effects, surface sediment concentrations of carbonaceous particless in Loch Teanga are over an order of magnitude less than in the acidified Galloway lakes. The surface concentration of carbonaceous particles in Loch Teanga is however similar to that found in surface sediments from lakes in the west of Ireland (Rose pers. comm.), but is almost half the concentration found in Lough Maam, north west Ireland (Chapter 4 - this report), and much less than the concentration found in Blue Lough, north east Ireland (Patrick *et al* 1989).

Much amorphous particulate carbon was present in the Loch Teanga core that is not formed by high temperature combustion. Its presence probably results from domestic fires or most likely from catchment peat burning.

Geochemistry

Sediment profiles of lead, zinc and magnesium are presented in Figure 3.24. In recent sediments the magnesium is normally associated with clastic particulates eroded from catchment sources whilst lead and zinc are derived, at least in part, from atmospheric pollution (Rippey pers. comm.). In Loch Teanga, all three elements show increases in concentration in the upper 20 cm or post - mid-nineteenth century sediment. However, magnesium exhibits a sharp increase between c. 12 and 10 cm depth, over which period concentrations more than double. Zinc and lead, on the other hand, increase in a fairly steady manner from c. 20 cm depth (c. 1879) to the core top.

Clearly the post-1850 profiles of zinc and lead are modified by variations in erosion of catchment clastic material containing these elements or of organic material with very low concentrations of these elements. The relatively very low concentration at c. 20 cm depth undoubtedly arises from the dilution effect of inwashed peat since the core LOI profile has its major peak at this depth (Figure 3.13). Furthermore, at 12-10 cm depth the dry weight of sediment increases indicating minerogenic inwash, exactly at the point at which magnesium concentration doubles. However, above 10 cm depth, the dry weight remains fairly constant and although organic content continues to decline above 10 cm it is insufficient to account for the zinc concentration doubling in this upper section of the core.

The geochemical evidence so far available for the Teanga core clearly shows that the site is contaminated by zinc and lead from atmospheric pollution. However, because of changes in catchment supply of these elements the magnitude of this impact can not yet be estimated. Certainly this site is significantly impacted and the uppermost sediment in the core has higher zinc and lead concentrations than sites nearer centres of pollution (eg. Loch Laidon - Flower *et al.* 1988). In addition, there is no sharp decline in trace metal contamination in post-1970 sediment as occurs in the less isolated sites.

Discussion

Changes in the distribution of the diatom pH preference groups suggests that Loch Teanga has undergone mild acidification since the turn of the century. However, reconstructed pH values do not show a clear acidification trend in the past 150 years. An initial slight acidification followed by an increase in pH in the late-nineteenth century period followed by further acidification to pH 6.0 around the 1940s and fluctuations thereafter is indicated. These changes suggest influences on diatom assemblage composition other than by acid deposition. Although the catchment is disturbed by burning it is difficult to envisage inwashed diatoms affecting the pH reconstruction (cf. Battarbee and Flower 1985) at this site. There are no significant streams to supply catchment diatoms and despite slightly increased frequencies of *Pinnularia viridis* since the mid-nineteenth century, diatoms from terrestrial habitats are too scarce to affect pH inferences. This recent period of potential acidification approximately coincides with declining organic matter in the sediment (cf. Figure 3.13) which probably results from a major change in land-management. Unusually, the rate of sediment accumulation does not decline in association with organic matter decline and the rate must therefore be maintained by increased minerogenic erosion. The minerogenic component of the core shows a distinct increase at about the turn of the twentieth century (14 cm depth), possibly as a result of road construction along the northern margin of the lake.

We have argued elsewhere (eg. Battarbee *et al.* 1989, Patrick *et al.* 1990, that land-use change should not affect lake acidity significantly and this study provides no evidence that such changes have occurred, although any process which affects water quality can potentially effect sedimentary diatom assemblages and hence pH reconstrctions. Overall, it is considered that whilst variation in the frequency record of some diatom taxa (eg. *F. virescens* v. *exigua*) could be influenced by local disturbance, the recent diatom record does indicate slight acidification since the 1900s, possibly from atmospheric deposition. Improved pH reconstruction methods will hopefully translate this small change in to pH units.

A priori, low acid deposition can promote only a small degree of water acidification. Hence, if any acidification is to be detected at sites receiving low deposition it is important that catchment acid neutralising capacity (ANC) should be low. The relatively high calcium concentration at Loch Teanga could indicate significant catchment ANC at this site. So, another way of looking at possible acidification effects other than using diatoms is to examine the relationship between non-marine common cations and alkalinity in the lake water using the equation of Henriksen (1982):

where, acidification = 0.93 (Ca + Mg) -14 -alk

at Loch Teanga = 0.93 (64 + 23) -14-20 = 47

This acidification index value suggests that the lake is significantly acidified. Compared with other lakes the index value for Loch Teanga is less than half that calculated for strongly acidified sites in south west Scotland but is more than twice that calculated for moderately acidified Loch Laidon (Harriman and Wells 1985) in the central Scottish Highlands. Although the diatoms in Loch Teanga indicate slight acidification, the changes are considerably less than those found in the diatom assemblages from Loch Laidon (Flower *et al.* 1988). Furthermore, this result is incompatible with the carbonaceous particle evidence from these two lakes which show that contamination is much greater at Loch Laidon. Similarly, Lough Maam in Donegal is more contaminated than Loch Teanga but it has an acidification index of zero (see Chapter 4 - this report). It is not clear in the case of Loch Teanga whether the index is adversely influenced by dissolved organic acids, by seasalt incursions, or by the lack of chemical data for the site, but it seems that the index is too high for a lake in this location with this diatom and carbonaceous particle record.

Figure 3.12 Loch Teanga: bathymetry (from Flower and Nicholson 1986) (contours in metres), (coring location = +)

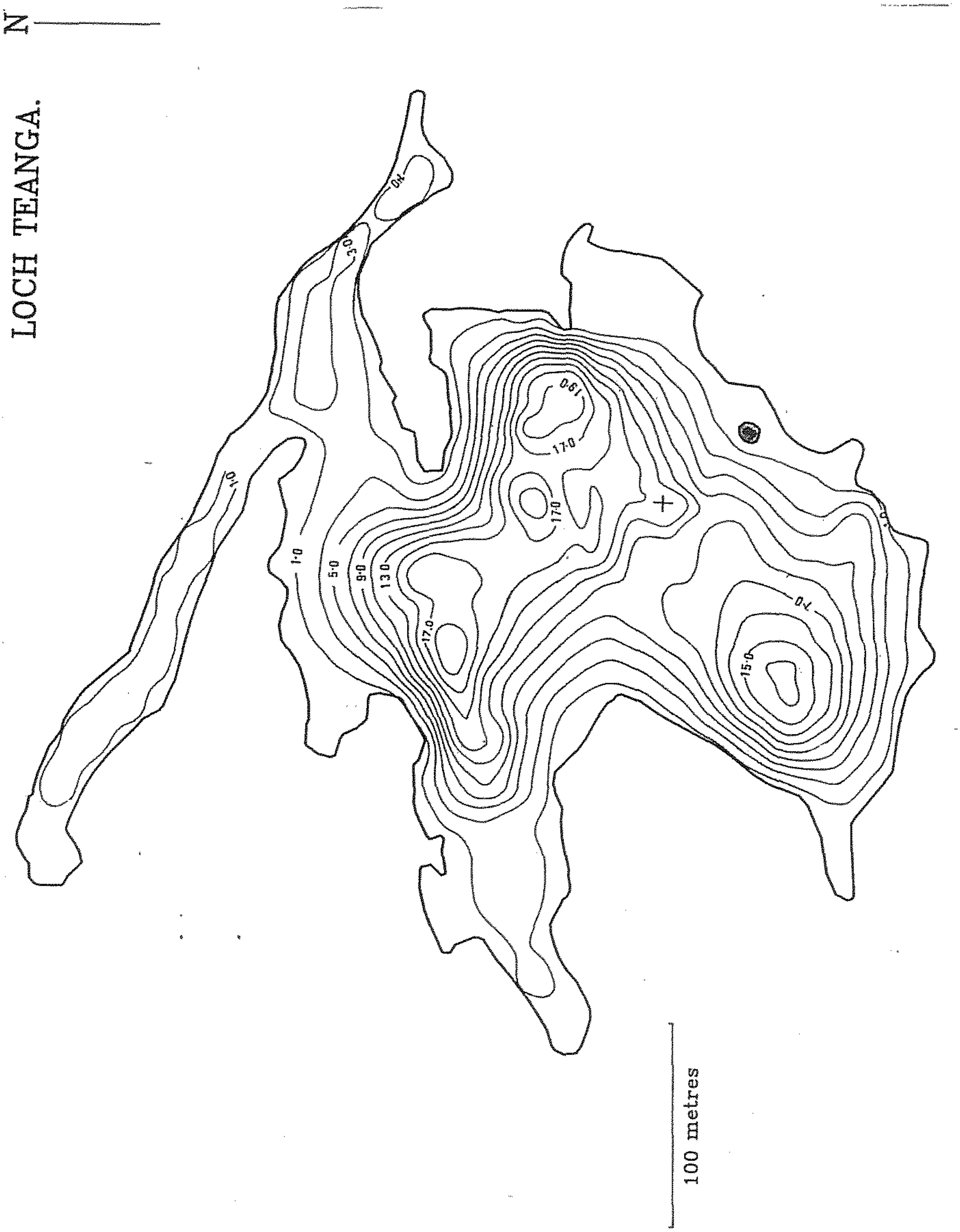
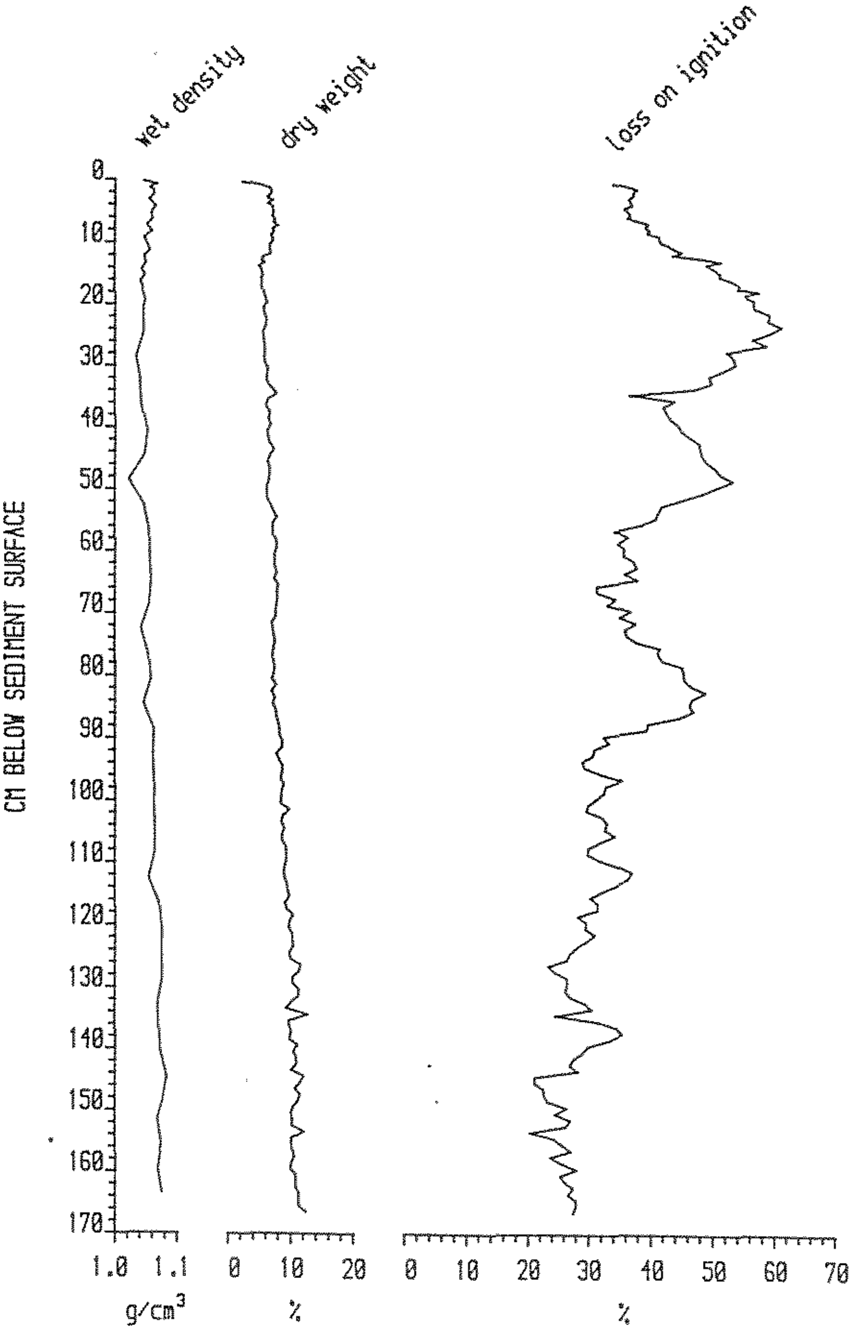


Figure 3.13 Loch Teanga: lithostratigraphy



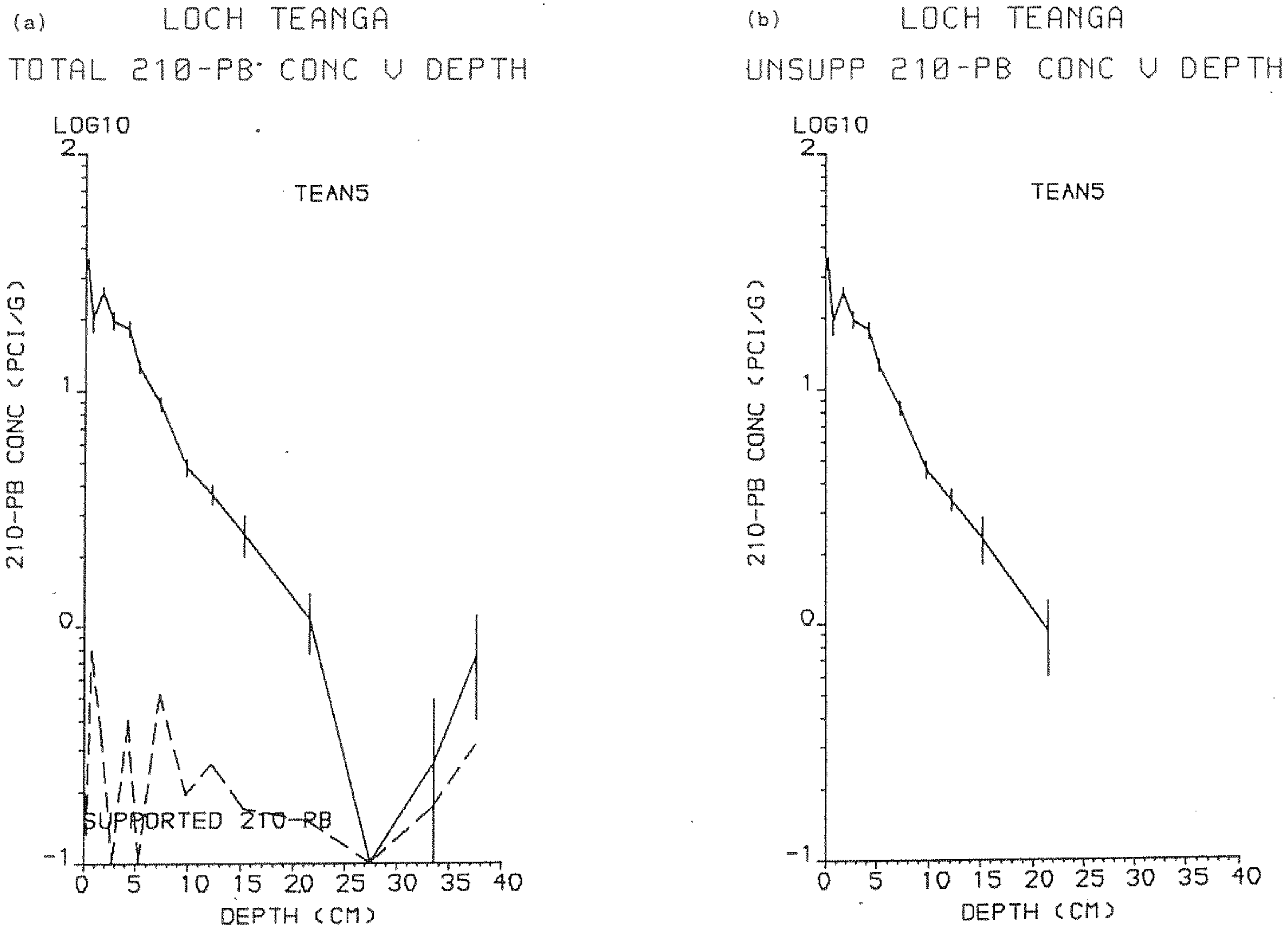


Figure 3.14 Loch Teanga: a) total and b) unsupported ^{210}Pb concentrations

Figure 3.15 Loch Teanga: sediment depth v. age curve calculated according to the CRS model (see text) with CIC dates shown as open circles.

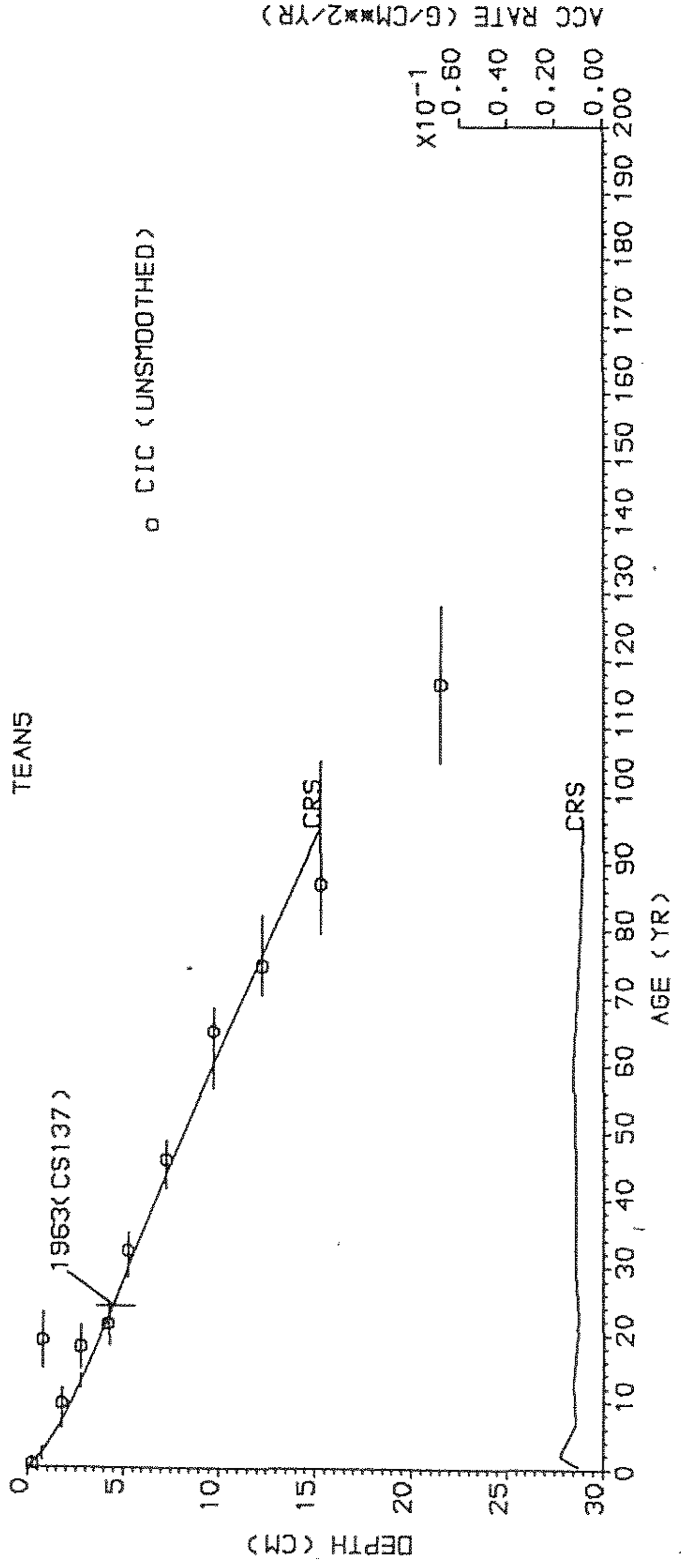


Table 3.2 Loch Teanga: ^{210}Pb chronology

Depth	Dry Mass	Chronology			Sedimentation Rate		
		Date	Age				
cm	gcm^{-2}	AD	yr	±	$gcm^{-2}yr^{-1}$	$cmyr^{-1}$	± (%)
0.00	0.0000	1987	0				
0.50	0.0161	1986	1	2	0.0141	0.302	9.2
1.00	0.0430	1984	3	2	0.0161	0.269	10.2
1.50	0.0768	1981	6	2	0.0130	0.198	7.3
2.00	0.1116	1979	8	2	0.0116	0.165	6.6
2.50	0.1475	1976	11	2	0.0120	0.169	7.8
3.00	0.1834	1973	14	2	0.0119	0.165	8.5
3.50	0.2192	1969	18	2	0.0112	0.154	8.7
4.00	0.2550	1966	21	2	0.0105	0.143	8.8
4.50	0.2921	1963	24	2	0.0104	0.139	8.6
5.00	0.3306	1959	28	2	0.0110	0.143	8.1
5.50	0.3695	1956	31	2	0.0113	0.146	8.0
6.00	0.4086	1952	35	2	0.0113	0.145	8.5
6.50	0.4477	1949	38	2	0.0112	0.145	9.0
7.00	0.4868	1945	42	3	0.0112	0.145	9.5
7.50	0.5256	1942	45	3	0.0113	0.146	10.2
8.00	0.5639	1938	49	3	0.0115	0.150	11.1
8.50	0.6022	1935	52	3	0.0117	0.154	12.1
9.00	0.6405	1932	55	4	0.0119	0.158	13.0
9.50	0.6788	1929	58	4	0.0121	0.162	13.9
10.00	0.7157	1925	62	4	0.0119	0.164	15.1
10.50	0.7514	1922	65	5	0.0115	0.162	16.4
11.00	0.7871	1919	68	5	0.0111	0.160	17.8
11.50	0.8228	1916	71	6	0.0106	0.158	19.2
12.00	0.8585	1912	75	6	0.0102	0.157	20.6
12.50	0.8908	1909	78	7	↑	↑	
13.00	0.9198	1906	81	7			
13.50	0.9488	1904	83	8			
14.00	0.9777	1902	85	9			
14.50	1.0067	1899	88	9			
15.00	1.0357	1897	90	10			
15.50	1.0653	1894	93	10			
16.00	1.0955	1891	96	10			
16.50	1.1256	1889	98	10			
17.00	1.1558	1886	101	10			
17.50	1.1860	1884	103	10	0.0115	0.194	
18.00	1.2162	1881	106	10			
18.50	1.2463	1878	109	10			
19.00	1.2765	1876	111	10			
19.50	1.3067	1873	114	11			
20.00	1.3369	1870	117	11			
20.50	1.3670	1868	119	11			
21.00	1.3972	1865	122	12			
21.50	1.4274	1863	114	12	↓	↓	

Figure 3.16 Loch Teanga: a) ^{137}Cs and b) ^{134}Cs (derived from Chernobyl fallout) concentrations

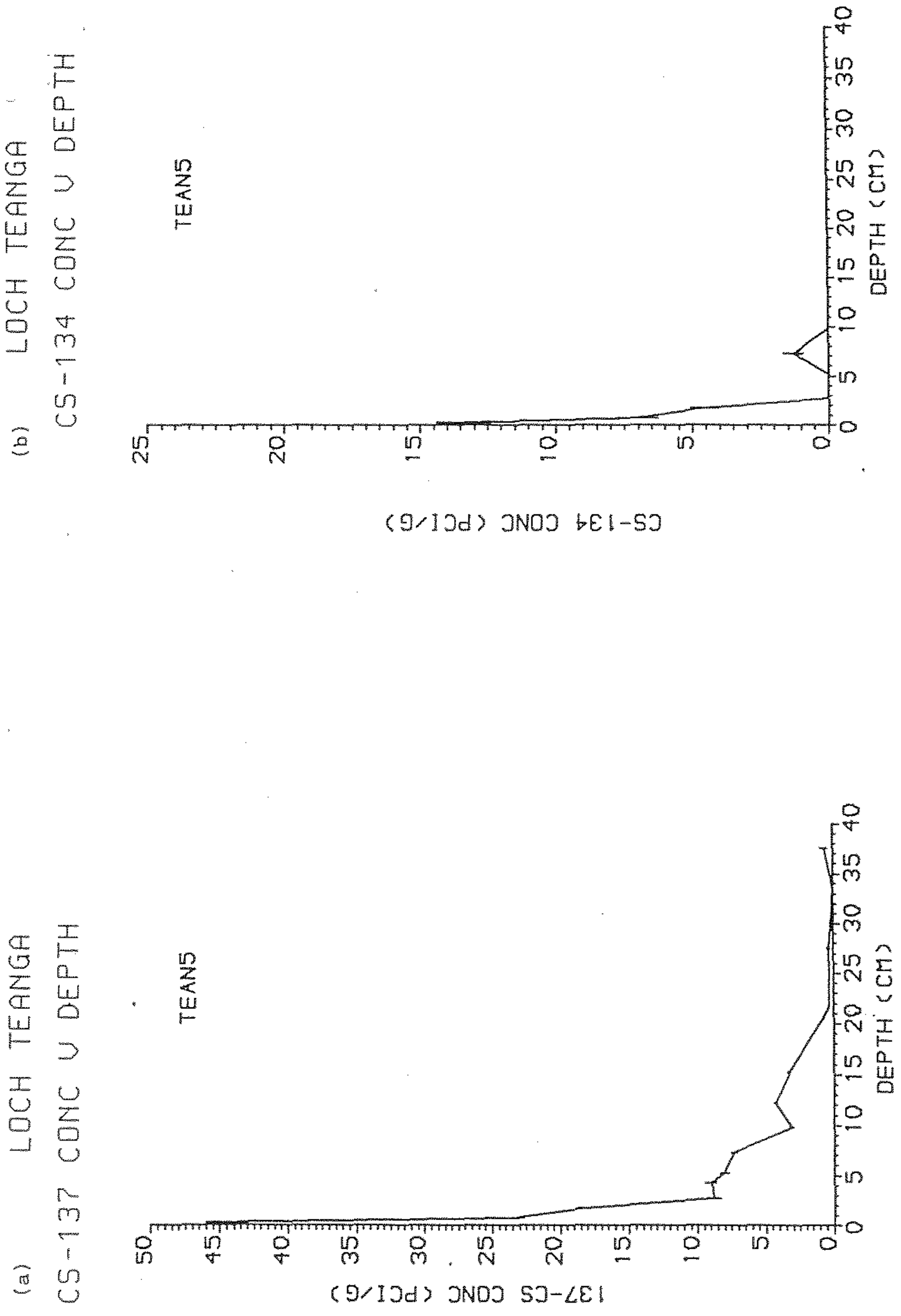


Figure 3.17 Loch Teanga: summary diatom diagram (frequencies <2% indicated by +)

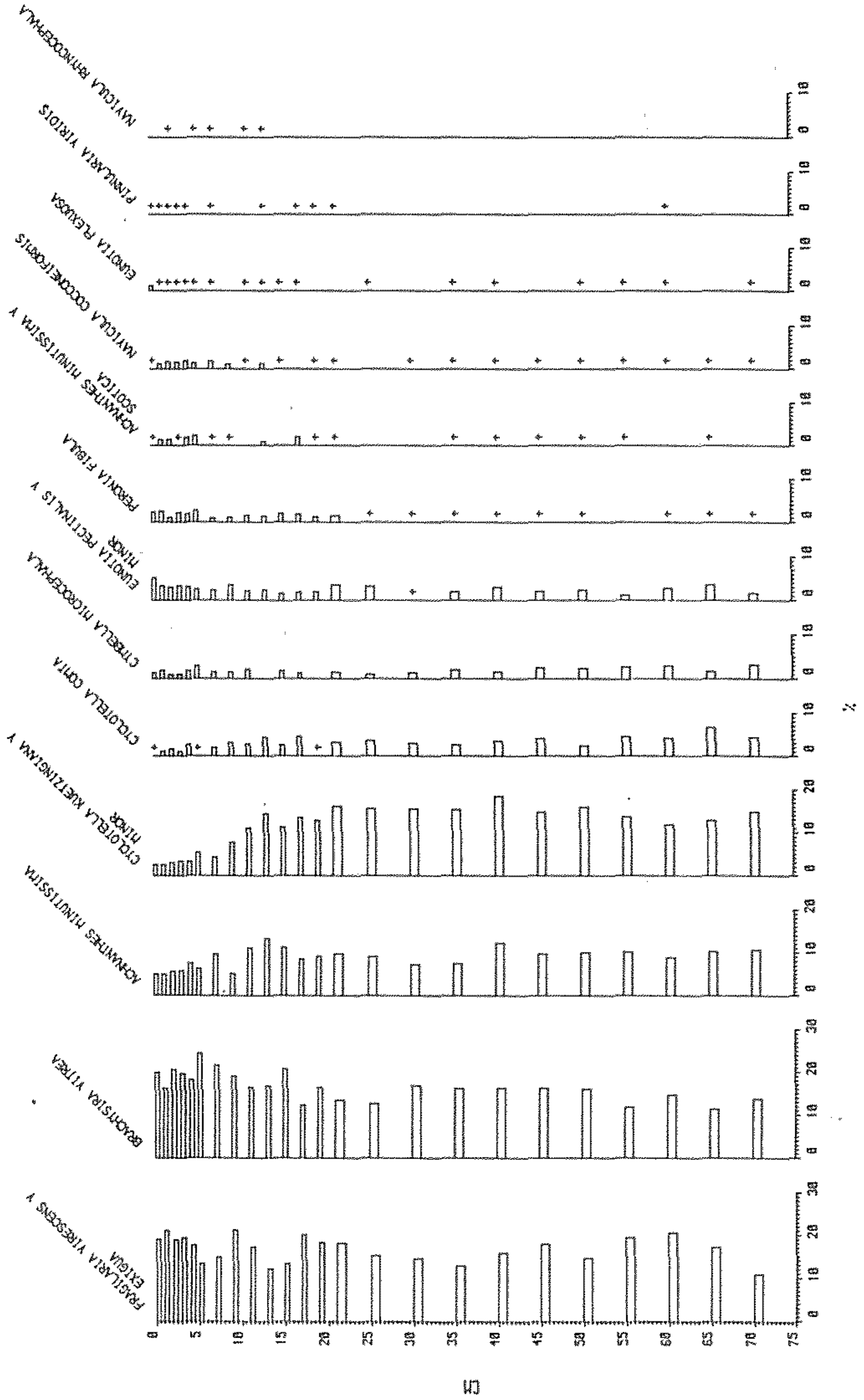


Figure 3.18 Loch Teanga: diatom concentration profile, indicating 95% confidence limits

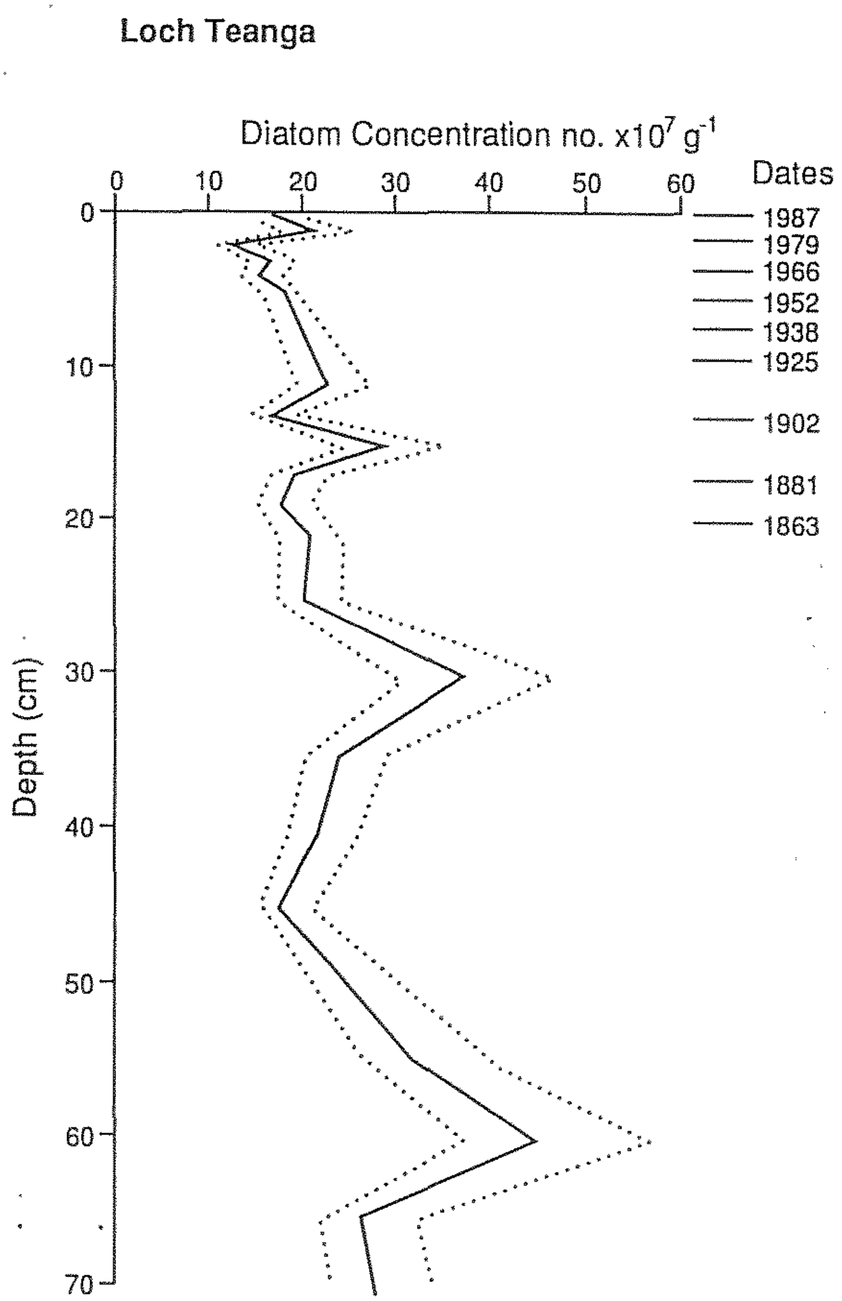


Figure 3.19 Loch Teanga: diatom pH preference groups

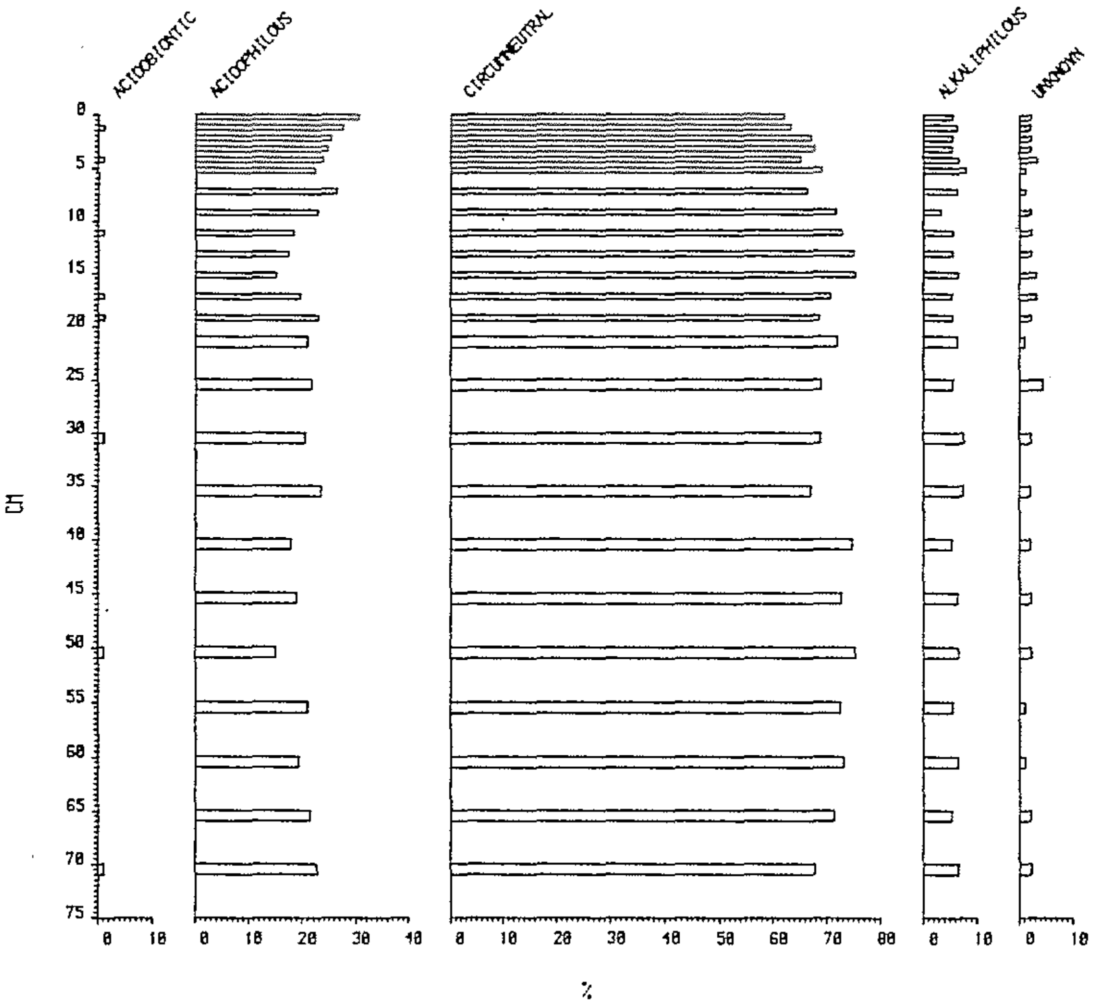


Figure 3.20 Loch Teanga: pH reconstruction (multiple regression)

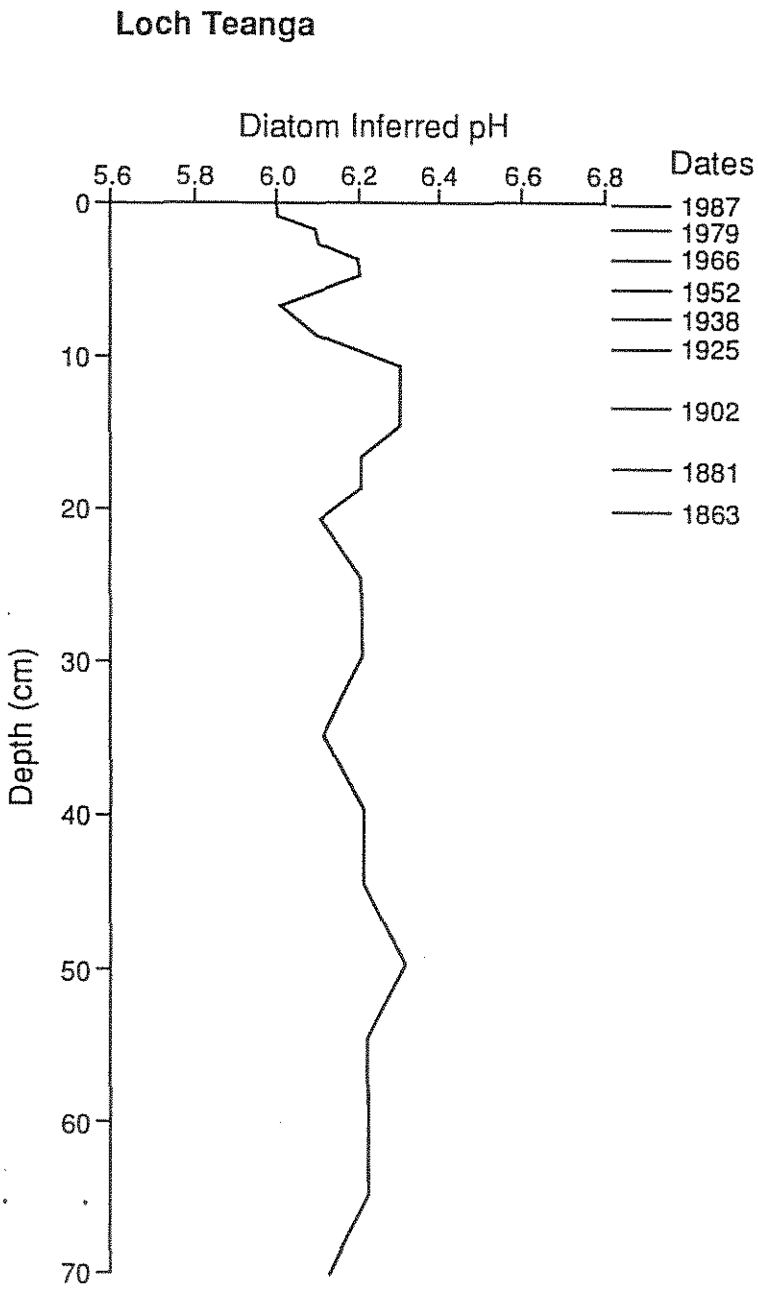


Figure 3.21 Loch Teanga: summary pollen diagram

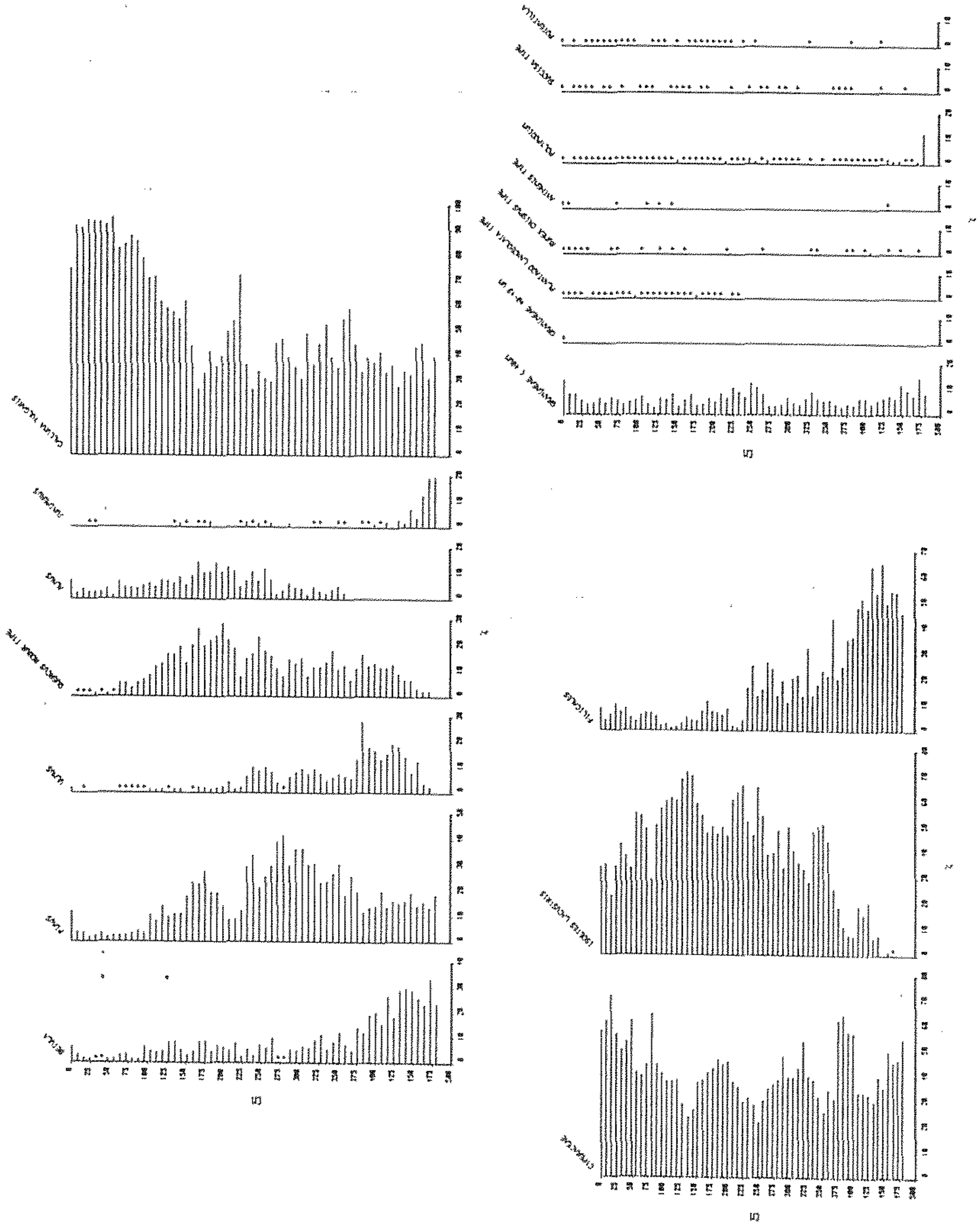


Figure 3.22 Loch Teanga: carbonaceous particle concentration profile

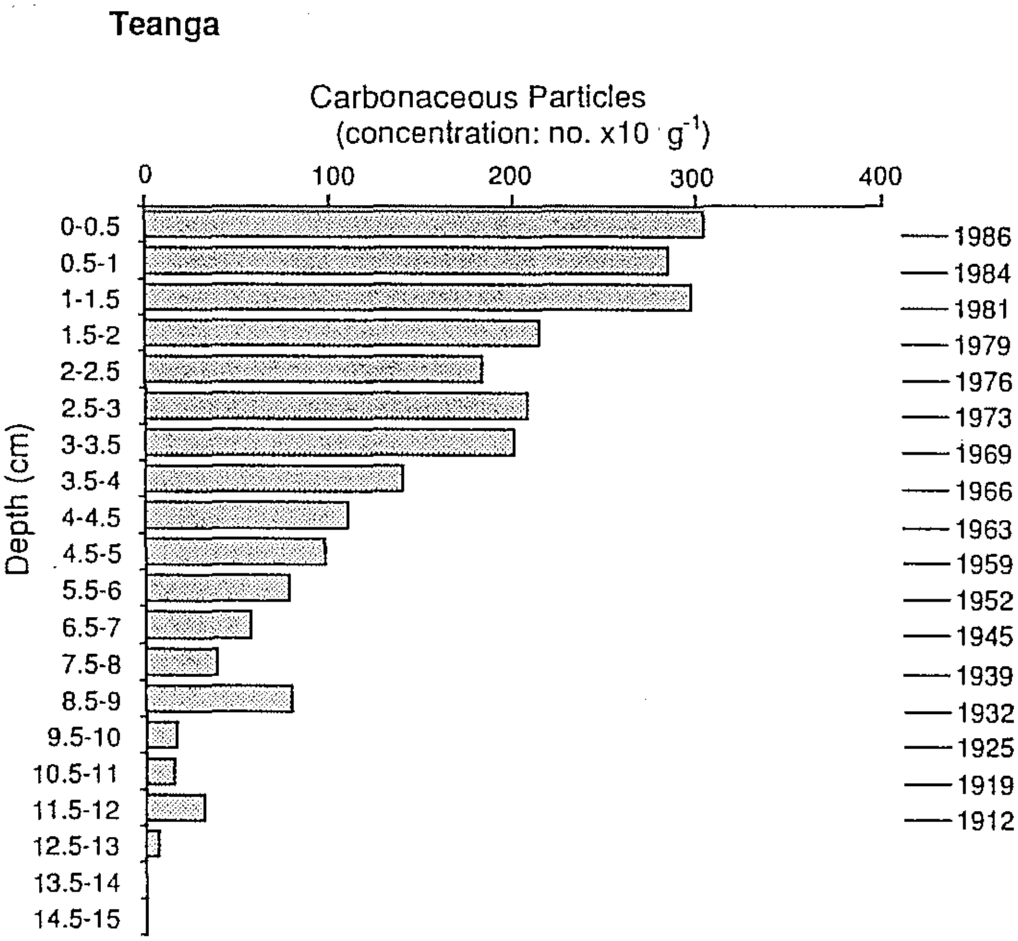


Figure 3.23 Loch Teanga: ash sphere concentration profile

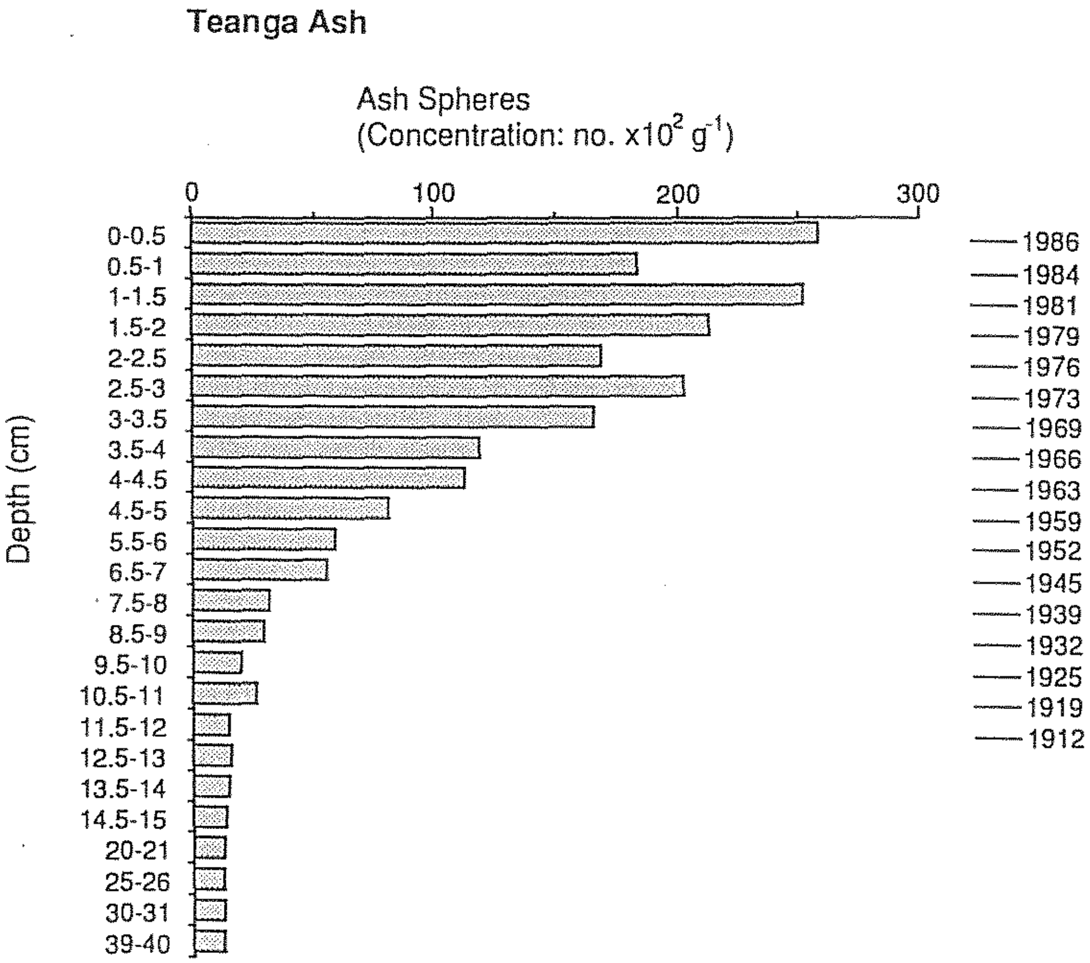
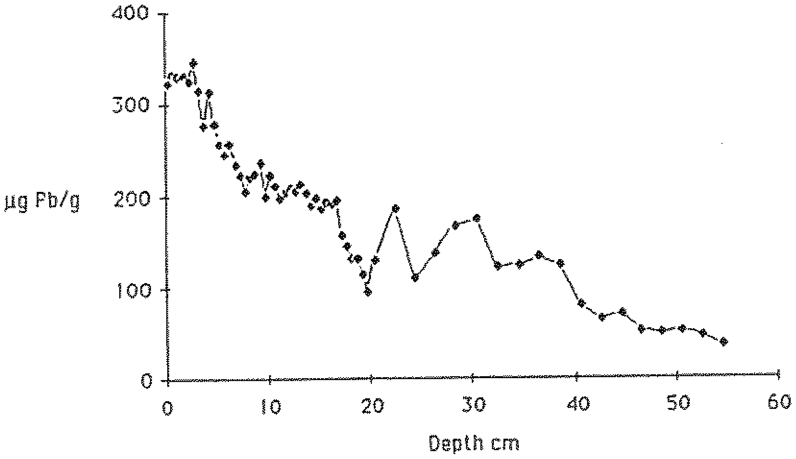
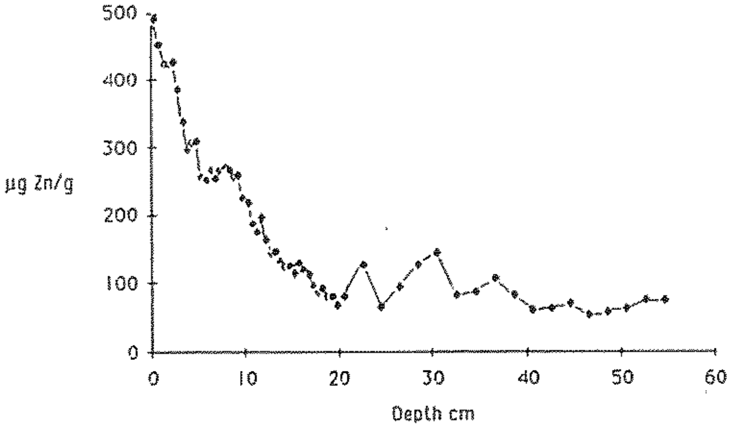
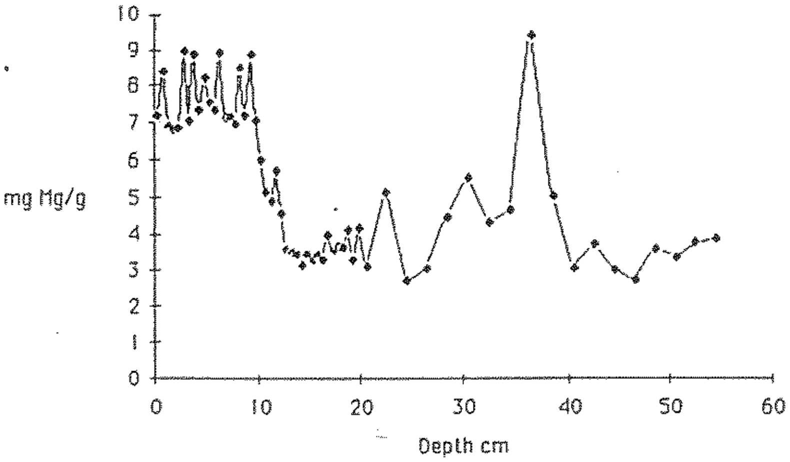


Figure 3.24 Loch Teanga: sediment concentrations of lead, zinc and magnesium







3.3 DISCUSSION AND SUMMARY OF CONCLUSIONS

Despite the absence of a chronology at Loch Coire nan Arr and Loch Uisge it is still possible to evaluate their recent palaeolimnology. Both of the sites have extremely stable diatom assemblages and neither site shows any evidence for acidification over the time period represented by the cores. There is a slight indication of atmospheric contamination in the carbonaceous particle profile form Loch Coire nan Arr, but it would appear that the low levels of contamination have not been sufficient to cause acidification. The results suggest that the sulphur deposition levels at these two sites lies below the critical load for lake acidification.

It is interesting to note that Lochan Dubh, a site very close to Loch Uisge (Figure 1.1) but with lower calcium values, is slightly acidified (Jones *et al.* 1990 and see Chapter 5 below), whereas Loch Coire nan Arr to the north, also with lower calcium values than Loch Uisge, is not acidified. These data support the dose - response model of Battarbee (1990) and indicate the importance of this region of Scotland in defining the geographical extent of acidification in the United Kingdom.

Palaeolimnological analysis of the Loch Teanga core provides considerable evidence of land-management practices in the recent past but no definitive evidence of acidification. However, the site is clearly affected by atmospheric pollution as shown by both the carbonaceous particle and trace metal records. Compared with other sites and excluding any major contamination effects by local sources it appears that Loch Teanga is much less contaminated than mainland sites to the south east, although there is little sign of any recent (post-1970s) decline in contamination. It is difficult to obtain a quasi-quantative estimate of trace metal deposition at this site because of catchment disturbance, but the carbonaceous particle record clearly shows that Loch Teanga is considerably less affected by atmospheric pollution than sites in the north of Ireland and much less than sites in south west Scotland. However, the concentration of these particles in Loch Teanga surface sediment is similar to that found at sites in the west of Ireland, possibly indicating a similar degree of air pollution in these two regions. Both areas are remote from industrial sources of air pollution but some contamination from local sources can not be ruled out since concentrations of as low as c. 1000 g^1 occur in lakes remote from any fossil fuel sources (Rose, unpubl.). This figure probably represents the 'background' degree of carbonaceous particle contamination in the United Kingdom.

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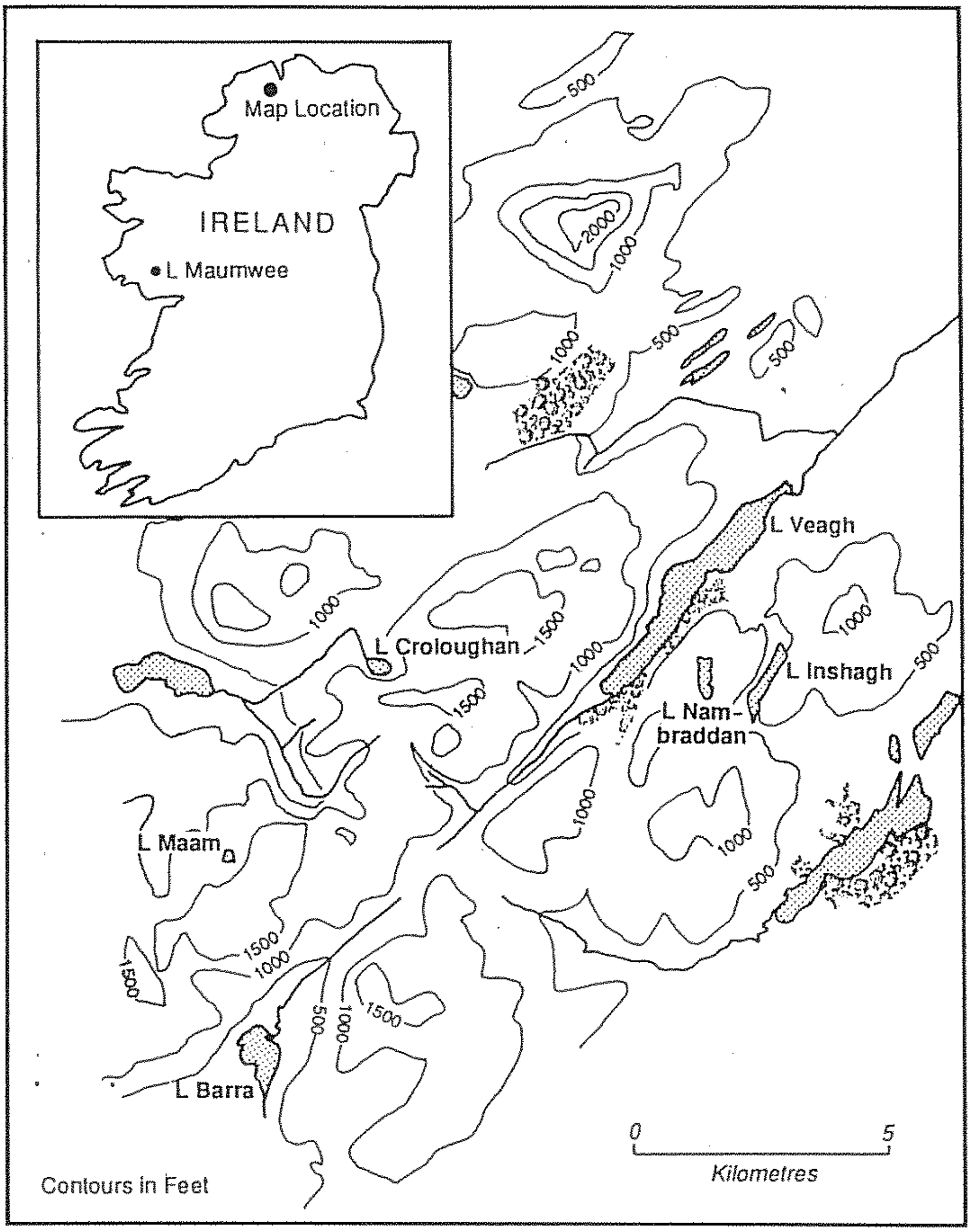
4 PALAEOECOLOGICAL EVALUATION OF THE ACIDIFICATION STATUS OF THREE LAKES IN THE WEST OF IRELAND.

4.1 INTRODUCTION

Acid deposition has caused strong acidification of lakes on susceptible geology in the Galloway region of south west Scotland (eg. Battarbee *et al.* 1989). Elsewhere in Scotland lake acidification is widespread but is less severe than in Galloway and where non-marine sulphate deposition is less than 0.8 g S m^{-2} yr^{-1} acidification is slight. Hence the acidity of lakes in the north west of Scotland appears to be virtually unaffected by acid deposition (see Chapter 3, this report). Less well known is the effect of acid deposition on susceptible systems in western regions of the British Isles and Ireland. Precipitation chemistry from sites in the south east of Ireland shows that rainfall is strongly acidic (pH 4.6-4.8) with the most acidic rain originating from northern and eastern directions (Bailey *et al.* 1986). Fewer data are available for western Ireland but acidity levels in precipitation collected at Galway sites is generally similar to those measured in unpolluted areas, except for winds from an easterly direction which tend to be more acidic. Furthermore, water chemistry data from lakes on the east and western margins of Ireland show that excess sulphate concentrations in the east are about twice those of the western sites (Bowman 1988).

Initial surveys of water chemistry (Bowman 1988) and diatoms (Flower unpubl.) indicated that lakes in the west of Ireland were largely unaffected by the low levels of acid deposition impacting this region. Susceptible lakes in the Donegal region of north west Ireland are however less than 200 km from strongly acidified lakes in Galloway, south west Scotland. This proximity suggests that either the Donegal lakes in this study will also be affected to some extent by acid deposition or if not, then the effect of acid deposition undergoes a rapid decline in a westerly direction. To test the hypothesis that susceptible lakes in western Ireland remain unaffected by acid deposition palaeolimnological analysis of several sites was undertaken. For this study, three sites were selected in granitic regions of western Ireland, two in County Donegal and one in County Galway (Figures 1.1, 4.1).

Figure 4.1 Donegal: site locations (L. Maumwee location inset)



4.2 LOUGH VEAGH, DONEGAL

Site description

Lough Veagh lies in the Glenveagh National Park in County Donegal, north west Ireland (Figure 4.1). It lies at an altitude of only 40 m but hills within the catchment rise to over 600 m. The area experiences a cool oceanic climate with mean (1973-1976) annual rainfall of 1500 mm (Telford 1977) and frosts are uncommon.

The entire Lough Veagh catchment lies on Devonian granites, which because of their great geological age are often heavily faulted and contain numerous dolerite and basalt dykes. Catchment soils are dominated by blanket peats often of considerable thickness and are often partially eroded into peat hags (Telford 1977). The blanket peat lies directly on granite rock or on minerogenic podzolized subsoils. Vegetation over much of the catchment is a typical acid moorland community where *Molinia caerulea* and *Calluna vulgaris* are common. However, there are substantial stands of native oak woodland within the catchment, particularly in the Black Burn valley and on hill slopes around the southern end of Lough Veagh. Land-use within the catchment was particularly intense during the early part of the nineteenth century (Telford 1977) being characterised by heavy grazing of sheep. Furthermore, during the 1840s a large number of drainage ditches were constructed, remains of these can still be seen on hillslopes on the west side of the lake. Land-use intensity declined after 1861 when some 46 families were ejected from the Glen Veagh estate. However, late in the nineteenth century both red deer and *Rhododendron* were introduced into the estate which have served to degrade further the remaining natural woodland.

Lough Veagh itself occupies a geological fault line but is glacially over-deepened and is blocked by morainic material at the northern end from where the outflow (Owencarron River) emerges. The lough possesses several sub-basins as shown by the bathymetric map (Figure 4.2), a maximum depth of about 48 m occurs in the southern basin. Several reports (eg. Macan and Lund 1954, Allot 1985) show that the phytoplankton of Lough Veagh is characterised by *Dinobryon* species, *Ankistrodesmus falcatus*, *Quadrigula* species and *Scenedesmus* species and by the diatoms *Cyclotella praetermissa* (*C. comta*), *Tabellaria flocculosa* and *Rhizosolema longiseta*. Planktonic and benthic invertebrates are described in Reynolds (1983), Twomey (1984) and Coyle and Murray (1989). The lake supports a good stock of trout but sea trout and salmon runs have been curtailed by installations on the outflow and lower lakes.

The biota of Lough Veagh is indicative of an infertile soft water lake and this is supported by the water chemistry (Table 4.1). The water chemistry data for May and September 1988 show some interesting differences that can be mainly attributed to relatively greater additions of wind-borne sea salts in the period immediately preceding sampling in the former period. Hence the early period is characterised by relatively high sodium and chloride concentrations but lower pH and alkalinity. There are only small differences between the concentrations of cations derived mainly from catchment sources (ie. calcium and potassium) on the two sampling dates. For all the metal ions only aluminium is present in the May 1988 sample at a concentration lower than in the September sample despite the lower pH. This is probably caused by dilution of the mainly terrestrially derived aluminium ions by greater precipitation preceding May sampling.

Table 4.1 **Water chemistry data for Lough Veagh as sampled in May and September 1988**

		May 1988	September 1988
pH		5.9	6.69
Cond.	μS cm^{-1}	83.0	*
Alkalinity (Alk$_e$)	μeq l^{-1}	30.0	39.5
Ca^{2+}	μeq l^{-1}	80.0	77.0
Mg^{2+}	μeq l^{-1}	117.0	144.0
Na^+	μeq l^{-1}	542.0	385.0
K^+	μeq l^{-1}	12.0	11.0
$S0_4^{2-}$	μeq l^{-1}	87.0	77.0
Cl^-	μeq l^{-1}	690.0	488.0
Al	μg l^{-1}		
(total acid soluble)		16.0	35.2
(labile)		4.0	*
Colour	250 nm	*	0.24

* = not determined

Methods

Several cores were collected from Lough Veagh in June 1988 using a mini-Mackereth corer (Mackereth 1969). Several coring positions were tried, in about 7 m of water towards the north end of the lake; in c 15 m depth in the mid lake sub-basin and on a fairly flat area of lake bed about 250 m off the eastern shore (Figure 4.2). The first contained a considerable amount of sand and gravel inwash throughout the sediment column; the lower portion of the second consisted of late-glacial grey clay; but the last (core VEAGIII) was composed of fairly homogeneous black organic sediment and used as the master core for dating and diatom analysis. The core was analysed using techniques described in Stevenson *et al* (1987).

Lithostratigraphy

The core was composed of fine (particles generally <0.1 mm in diameter) detrital sediment with small amounts of sand and clays and some plant fragments. In the 12-15 cm depth section the sediment was distinctly gritty in texture. Profiles of sediment wet density, percentage dry weight and LOI are shown in Figure 4.3. There is considerable down-core variation in percentage dry weight and organic matter (as indicated by the LOI curve). The greatest changes begin around 16 cm depth as percentage dry weight increases sharply from average values of around 15% to a peak of almost 40% at 14 cm depth. Organic content shows a corresponding decline from values around 20-25% and reaches a minimum value of c. 10% at 14 cm. However, above this depth organic matter rapidly increases to c. 40% by 11 cm depth, a value which is maintained to the core top.

These down core changes in percentage dry weight and organic matter reflect important changes in the quantity and composition of particulate material entering the lake from sources within the catchment. The major changes around 15 cm depth clearly relate to significant land-use changes within the catchment that have resulted in a pulse of minerogenic material entering the lake. This pulse is followed by an increased and sustained influx of organic material, almost certainly derived from accelerated erosion of catchment peat.

Dating

In progress

Diatom Analysis

Figure 4.4 presents a summary diatom diagram for the Lough Veagh core. This diagram shows that below 16 cm depth the diatom flora is fairly stable, the main variation being in the complementary changes in the relative abundances of two closely related planktonic diatoms, *Cyclotella kutzingiana* and its variety v. *minor*. *C. kutzingiana* var. *minor* is not clearly defined in the literature but is recognized here, using the light microscope, by its small size (diameter <10 µm) and an abundance of processes or of indentations/silica nodules and processes in the central area. The prevalence of the nominate variety above 40 cm depth is demonstrated in the diagram and could be of ecological significance. However, this change in the abundance of *Cyclotella* taxa probably reflects only a small change in water quality and, as far as is known, both diatoms have the same pH preference. In the basal two levels, below 60 cm depth, *Achnanthes minutissima* shows a small increase in frequency. The main diatom changes in this core begin at 16 cm depth as *C. kutzingiana* sharply declines by almost 50% as several periphytic taxa, most notably *Brachysira vitrea*, increase in abundance. The diatoms, *Aulacoseira distans* v. *tenella* and *A. lirata* v. *alpigena* also increase in abundance in the upper section of the core. The acidophilous diatom *Frustulia rhomboides* v. *saxonica* shows a small abundance peak at 16 cm depth. Other taxa such as *Fragilaria virescens* v. *exigua* show an initial decrease in abundance above 15 cm depth but increase again above c. 6 cm depth. Other taxa show variable responses over the upper 16 cm section of the core.

Compared with diatoms in plankton samples collected in the 1950s and 1970s (Macan and Lund 1954, Flanagan and Toner 1975) the sedimentary diatoms show a relatively low abundance of *Tabellaria flocculosa* and an absence of *Rhizosolema longiseta*. These differences can probably be accounted for by selectivity and representivity problems of plankton sampling and by poor preservation within the sediment of the former taxon.

The changes in diatom composition of the core seem mainly related to the soil inwash event, the record of which begins at about 16 cm depth (see above). The diatom plankton is clearly diminished by this event as would be expected by a decrease in water transparency caused by an increase in the suspended solids load in the water column. Furthermore, the increased abundances of *Aulacoseira* taxa after the initial inwash of minerogenic material could indicate a sustained increase in water colour by dissolved humic material staining the lough water (as might result from increased erosion of blanket peat into the lough).

The lake water pH over the period represented by the core was reconstructed using the multiple regression method (Flower 1986) and shows that between 20 cm depth and the core base water pH varied little from around 6.3 (Figure 4.5). At 16 cm depth the inferred pH declines by 0.4 of a pH unit to 5.9 before increasing to pre-disturbance levels at 5 cm depth. The decline of 0.2 pH units at the core top to pH 6.2 is within errors of the method but reflects a marginal increase in abundance of *T. flocculosa* in the uppermost sediment. This surface sediment inferred pH is within the range of measured lake water values and represents an integrated mean of water acidity over several years.

The significance of the decline in inferred pH around 16 cm depth associated with the inwash period is unclear. We have shown previously (Battarbee and Flower 1985) that inwashed catchment diatoms can cause errors in inferred pH values for lake water. It is also likely that this inwash event in Lough Veagh had only a very small effect on lake water pH and acidophilous diatoms such as *Frustulia rhomboides* v. *saxonica*, associated with the inwash, were derived from strongly acid environments within the lake catchment. Alternatively, it is probable that the inwash caused a general increase in lake water colour as indicated by the presence of several *Aulacoseira* taxa and the *Cyclotella* decline. A more sophisticated multivariate analysis of the floristic data should produce a significant response on a canonical correspondence analysis colour axis.

Pollen analysis

In progress

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Magnetic analysis

In progress

Discussion

In the absence of a sediment chronology interpretation of the Lough Veagh core is speculative, but if sediment conformity is assumed then certain inferences can be made. Despite no major changes in core pH values the diatom record indicates that the site has been undergoing slight but progressive water quality change over the period represented by the section below 16 cm depth. Accelerated sediment inwash, evident from c. 16 cm depth to the core top, has probably had little real effect on lake water acidity although the diatom plankton component of the assemblage is reduced following this event. The cause and onset date of accelerated inwash of sediment is unknown but it is thought that land-use changes within the catchment were responsible. Possible causes include increased grazing pressure and consequent peat erosion in the catchment particularly during the eighteenth century (cf. Telford 1977) or the establishment of peatland drainage systems in the nineteenth century.

There is no clear evidence of recent and sustained acidification of Lough Veagh but there are several factors which make this site rather unsuitable for detecting any slight acidification effects resulting from atmospheric pollution.

Catchment disturbance beginning around 16 cm depth has caused significant changes in the diatom assemblage which could mask any small effects resulting from acid deposition. The calcium concentration in this lake is higher than in any of the acidified sites in Galloway and hence the site should be better buffered against the effects of acid deposition. The calcium concentration in Lough Veagh is similar to those in Lochs Chon and Tinker in the Troassachs, sites where the diatom record indicates moderate acidification. At these sites however alkalinity is considerably lower than in Lough Veagh which enforces the diatom evidence that the Scottish sites are acidified by acid deposition.

Another approach to assessing the acidification status of Lough Veagh is to use the water chemistry data directly. The degree of water acidification can be estimated by applying the equation of Henriksen (1982):

where: acidification = 0.93 (Ca + Mg) -14 -Alkalinity

for Lough Veagh, = 0.93 $(55 + 12)^1$ -14 -40 = 8.3

[1] Mean concentrations of Ca and Mg (Table 4.1) less seasalt components.

This acidification value calculated from the relationship between base cations and the alkalinity status in Lough Veagh is small compared with that for sites known to be strongly acidified in Scotland (cf. Harriman and Wells 1985). However the Henriksen acidification index can be modified by factors other than by acid deposition. Dissolved organic matter from peat drainage can contribute 3-4 µeq of acidity per milligram of material (Harriman pers. comm.) so that acidification from atmospheric sources may be over estimated using the Henriksen formula. Furthermore, within lake generation of alkalinity is unconstrained by calcium concentration and its production would therefore serve to diminish the impact of any acid deposition. These two processes, DOC acidity and biological alkalinity generation, therefore have opposing effects on the calculated acidification index value and both must operate in Lough Veagh. The precise concentration of DOC is not known for this lake but water colour (see Table 4.1) indicates that it is not insignificant, thus increasing the index value. Alternatively, since Lough Veagh contains a significant plankton community in summer months, some alkalinity generation from this source and elsewhere must occur so reducing the index value.

Clearly, if the potential effects of DOC are taken into account then the acidification index is reduced and the actual degree of acidification from atmospheric sources is likely to be even less than that implied by the index. The only factor which could help neutralise deposited acidity as well as obscuring any change in the acidification index is significant, within-lake, alkalinity production. Lough Veagh is less oligotrophic than other smaller lakes in the same area, presumably because of enhanced supply of base cations and other ions from the basic intrusions which traverse the catchment. Hence, before discounting any ecological effects of acid deposition in this area of north west Ireland we should examine sites with lower calcium concentrations and zero alkalinity waters.

Figure 4.2 Lough Veagh: Bathymetry

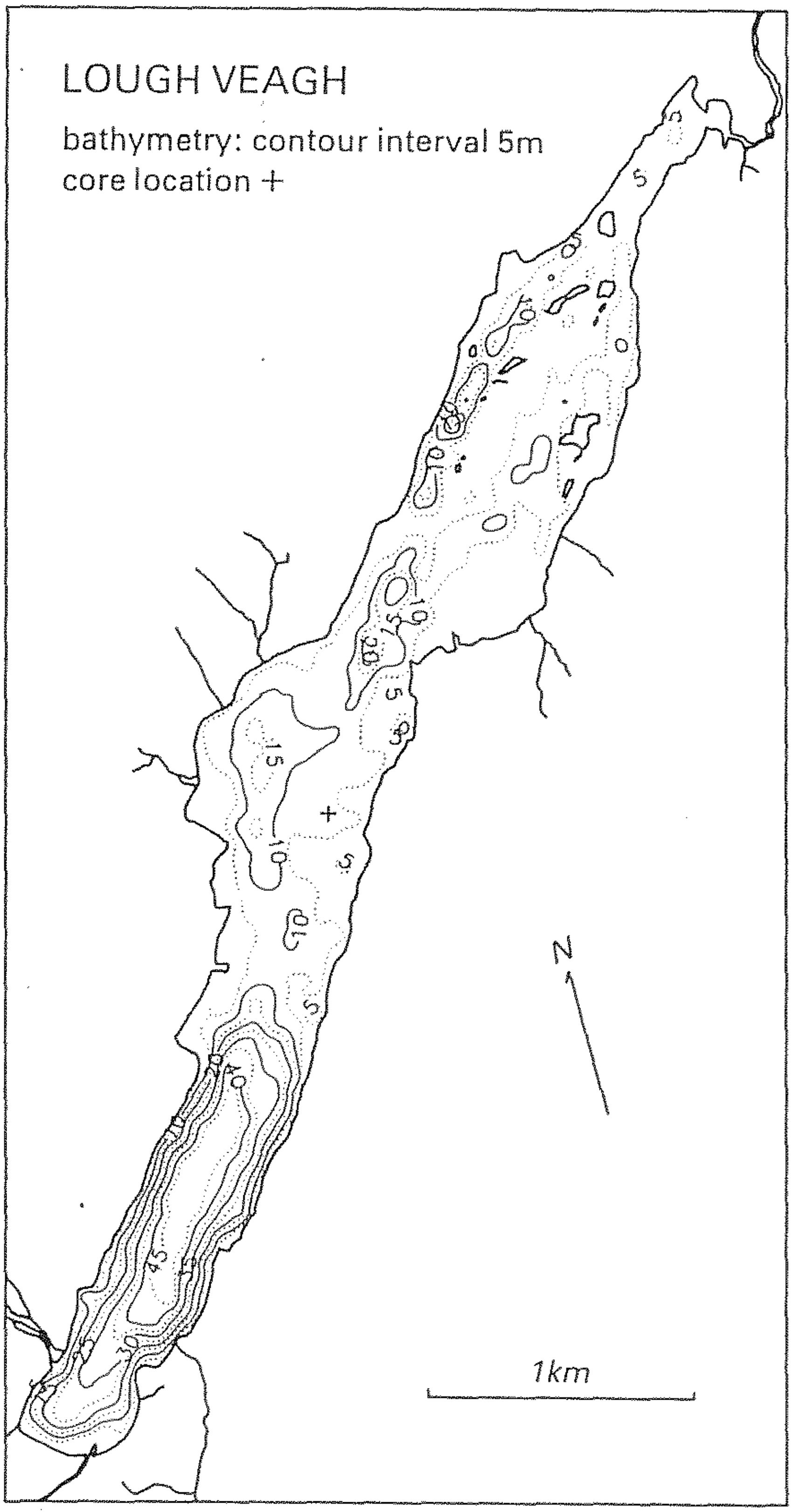


Figure 4.3 Lough Veagh: lithostratigraphy

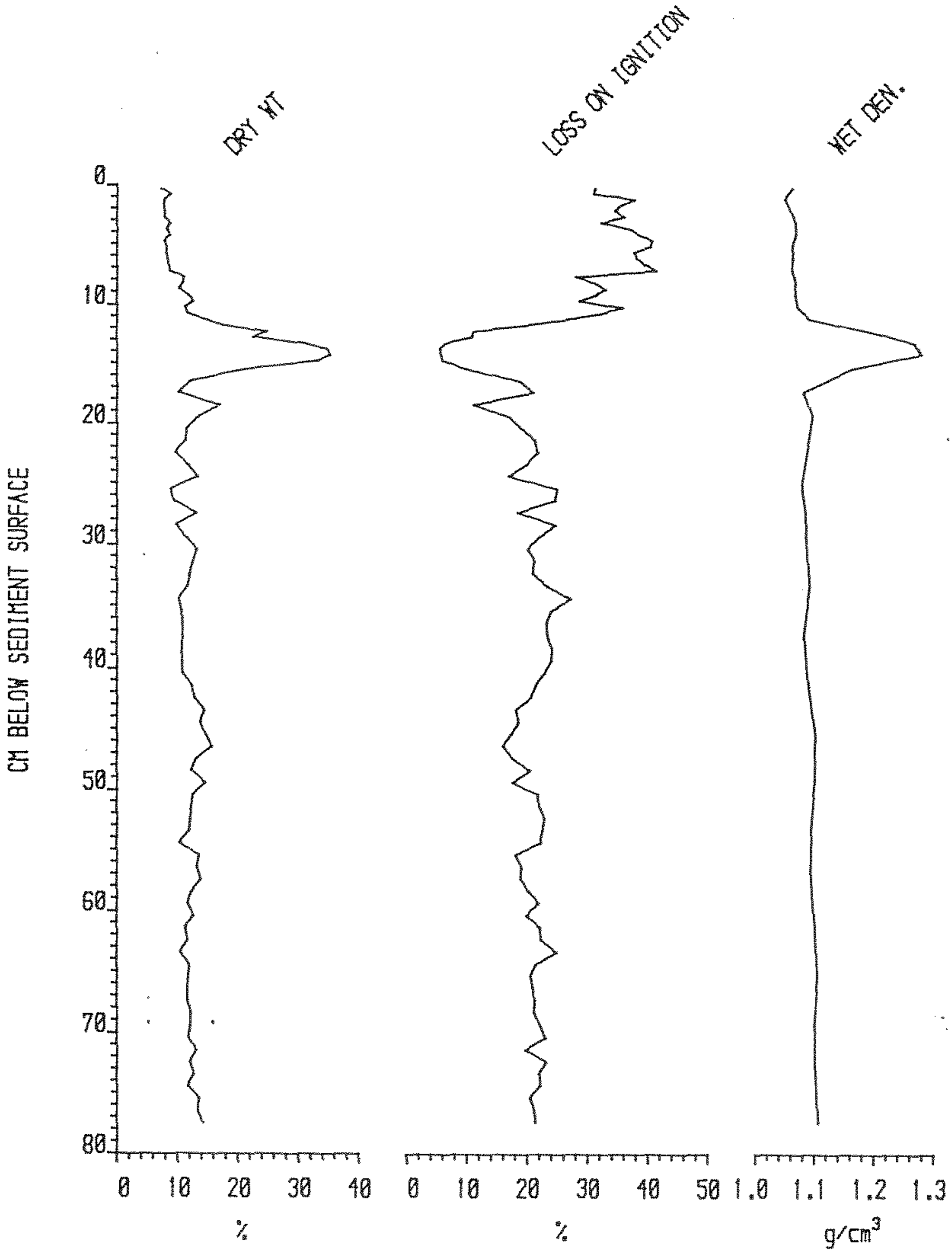


Figure 4.4 Lough Veagh: summary diatom diagram

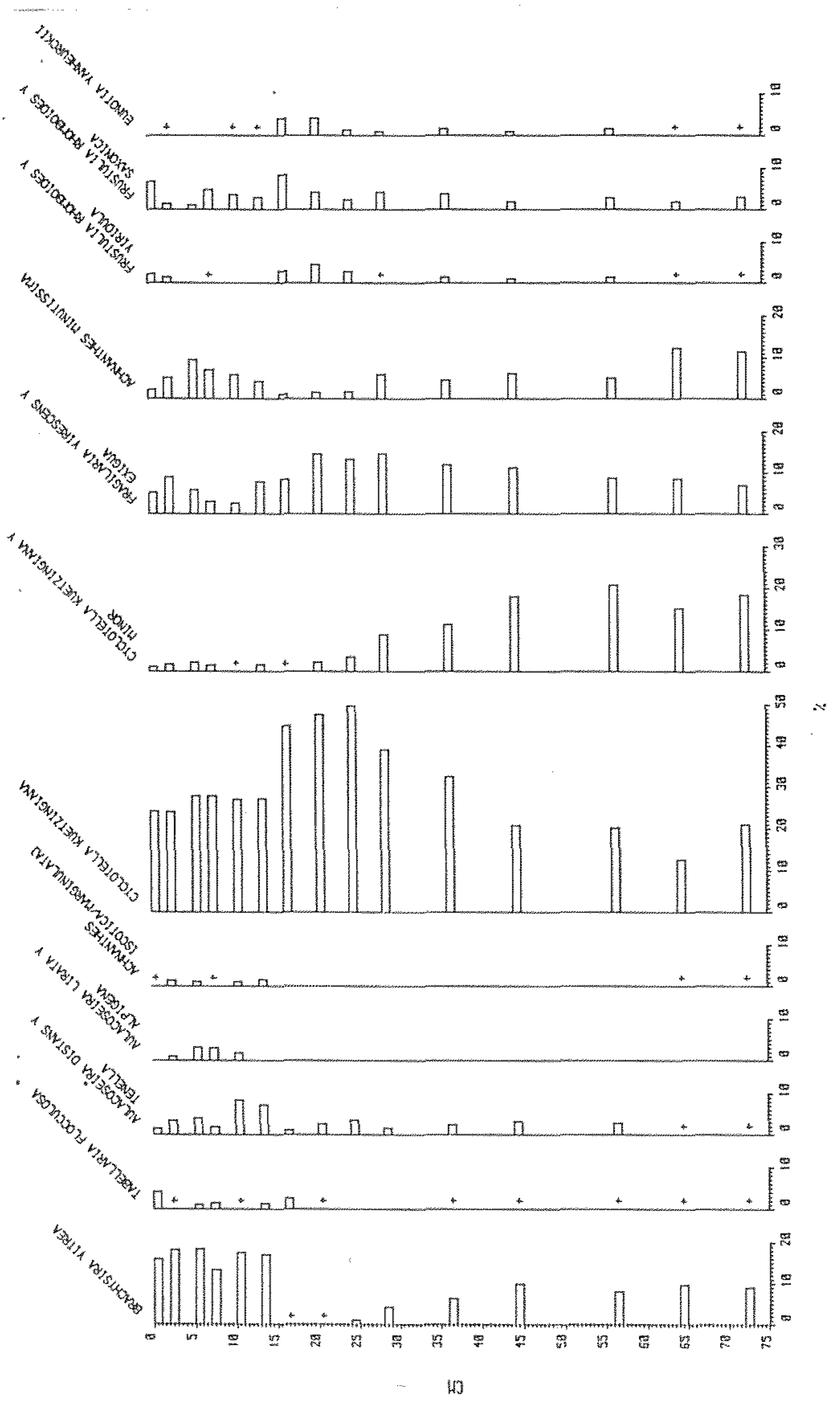
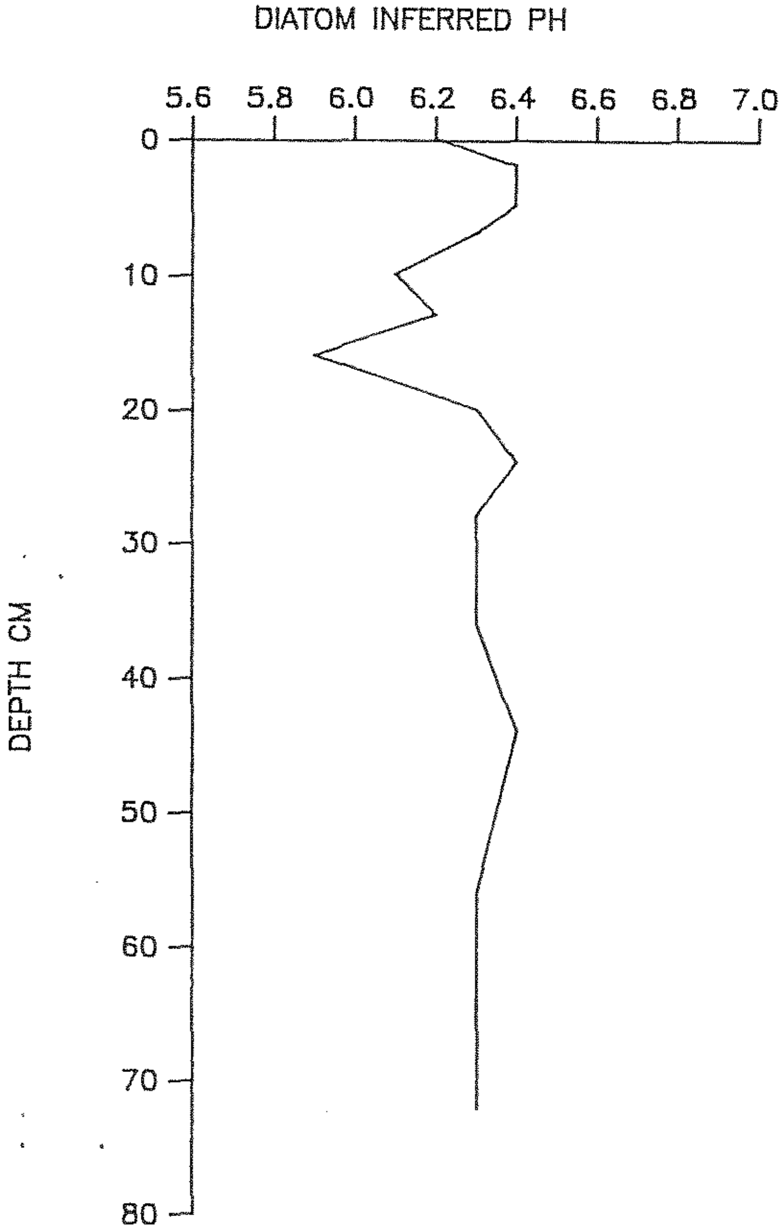


Figure 4.5 Lough Veagh: pH reconstruction (multiple regression)



4.3 LOUGH MAAM, DONEGAL

Site description

Lough Maam is a small oligotrophic lake located in the granitic uplands of the Glenveagh National Park in Donegal and lies some 10 km south west of Lough Veagh (Figure 4.1). The lake is only about 250 m in diameter and has a maximum depth of 8.5 m near its centre. It occupies a fairly sheltered position in a corrie on the north side of Slieve Snaght at 436 m altitude. Its catchment is relatively small and consists of a steep granite escarpment rising from the southern margin of the lake, less steep slopes form the east and west margins and the outflow lies at the northern margin. As far as is known there are no basic intrusions within the Lough Maam catchment. Catchment terrain varies between smooth exposures of granite, slipped granite blocks and morainic material. Blanket peat occurs on less steep areas and there is only a small amount of peat erosion in the catchment today. Catchment vegetation is dominated by *Calluna vulgaris*. The lake was well known locally for its trout but apparently these have declined in recent years, presumably as a result of either over exploitation or poor water quality.

Water chemistry for Lough Maam (Table 4.2) is typical for a site located in an acid moorland catchment influenced by inputs of wind borne seasalts. The lake water is acid and possessed zero alkalinity on both sampling occasions, however there are major differences between concentrations of common ions in the May and September samples. Sodium and chloride concentrations in the former sample are more than twice those in the latter period which points to a significant input of seasalts prior to sampling in May. Similarly over half the calcium concentration in the May sample is attributable to marine derived calcium. The lack of a marked pH depression in the May sample probably reflects the relatively small amounts of catchment peaty soils for exchange processes to operate extensively.

Table 4.2 **Water chemistry data for Lough Maam as sampled in May and September 1988**

		May 1988	September 1988
pH		5.00	5.14
Cond.	µS cm^{-1}	88.3	*
Alkalinity (Alk_e)	µeq l^{-1}	0.0	0.0
Ca^{2+}	µeq l^{-1}	63.8	25.0
Mg^{2+}	µeq l^{-1}	122.0	45.0
Na^{+}	µeq l^{-1}	507.0	206.0
K^{+}	µeq l^{-1}	13.1	8.0
SO_4^{2-}	µeq l^{-1}	81.1	52.0
Cl^{-}	µeq l^{-1}	721.9	257.0
Al	µg l^{-1}		
(total acid soluble)		50.0	44.0
(labile)		*	30.1
Colour	250 nm	0.09	0.20

* = not determined

Methods

Several sediment cores were collected from the central area of the lake in May 1988 using a mini-Mackereth corer (Mackereth 1969). MaamIII was selected as the master core. The Lough Maam core was analysed using the techniques described in Stevenson *et al* (1987) and an additional analysis, for carbonaceous particles derived from fossil fuel combustion (Rose 1989) was also applied.

Lithostratigraphy

The core was composed of fine black detrital sediment, colour being 10YR 2/2 in the upper 15 cm and 10YR 2/1 below. The sediment was very organic but appeared to contain a little more silty matter towards the base.

Core profiles of sediment percentage dry weight, LOI and wet density (Figure 4.6) show that most variation occurs in the LOI profile. This must reflect past variations in the rate of peat erosion within the catchment. There appears to be two phases of enhanced peat erosion recorded in the core. The first occurs between c. 60-50 cm depth and the more recent between c. 20-10 cm depth. A similar pattern in LOI values is shown by the other cores from this site. In the top 10 cm of the core the catchment peat appears to have restabilized, presumably by development of vegetation following a reduction or cessation of burning and/or sheep grazing.

Unlike Lough Veagh there appears to be no major inwash of mineral soil at this site.

Dating

In progress

Diatom analysis

Diatom analysis of this core is not yet complete but initial results show that there is considerable change in the down-core distribution of diatom taxa. Below about 15 cm depth *Fragilaria virescens* v. *exigua* dominates the diatom assemblage but above this depth acidophilous *Cymbella perpusilla* increases in abundance and in the top few centimetres acidobiontic *Tabellaria quadriseptata* becomes more common. The lake appears to have never supported a diatom phytoplankton community within the past one or two hundred years, although a few *Cyclotella* and *Aulacoseira* occur in the basal section of the core.

No pH reconstructions have yet been performed on the core but the diatom changes noted above indicate that the pH of this lakes has declined over the period spanned by the upper 15 cm of sediment, possibly from pH 5.5-6.0 to about pH 5.0.

Carbonaceous particle analysis

The down-core variation in carbonaceous particle concentrations (Figure 4.7) shows that these particles increase gradually in abundance from 6-2.5 cm depth. Between 2.5 cm and 1.5 cm particle concentration more than doubles to 7500 g^{-1}. There is little change in particle concentration in the top 1.5 cm of sediment.

This initial rise in carbonaceous particle concentration probably dates from the late 1930s or early 1940s and the sharp later increase corresponds to the 1960s period (cf. Flower *et al.* 1988). If such a chronology applies to this core then it indicates sediment is accumulating very slowly in Lough Maam, at about 1 mm yr^{-1}. However the increase in sediment LOI values below 10 cm depth indicates that erosion and therefore accumulation rate were higher for pre-1930s sediment.

Pollen analysis

The major feature of the summary pollen frequency diagram (Figure 4.8) is the low arboreal pollen throughout the core. Similarly, there is little change in frequencies of *Calluna vulgaris* and Gramineae throughout the core with *Calluna* contributing around 60% to the total pollen sum. Of the aquatic pollens (Figure 4.9), *Isoetes lacustris* is low throughout but shows a small decline above about 40 cm depth.

The vegetation record indicates that land-use change has been minimal at this site, otherwise the *Calluna* : Gramineae ratio would decrease towards the core top if catchment management was intensified (eg. for sheep grazing). The boulder strewn and precipitous nature of the catchment makes it highly unsuitable for exploitation by sheep although it is likely that burning of the catchment vegetation has occurred occasionally in the past. The pollen diagram gives little evidence of the inwash events suggested by the LOI profile, only the *Isoetes* decline at c. 40 cm depth could evidence the first inwash event. There is no pollen record of the second inwash beginning at 20 cm depth. There are at least two factors which could account for the absence of a pollen response to erosional events. Firstly, if the pollen record is dominated throughout by material derived from low intensity peat erosion an acceleration in erosion will not change the frequency composition of the pollen assemblage. A peat source for much of the pollen assemblage is suggested by the tree pollen frequencies, particularly *Pinus*, the constant influx of which must be derived from fossil deposits since this species disappeared from the north west of Ireland some 4000 years BP. (Telford 1977). Furthermore the catchment of Lough Maam is currently treeless and all recent arboreal pollen must be either fossil or derived from long-distance transport processes. Secondly, *Isoetes* is susceptible to erosional inwash, but since in this lake this plant can only grow in a very limited marginal location, turbidity impacts will be small.

Discussion

Lough Maam is a very oligotrophic acid upland lake that does not possess a diatom phytoplankton community. The pH is around 5.0 with zero alkalinity and fairly low calcium levels. As such this site is potentially more susceptible to any effects from acid deposition than is Lough Veagh. As with the Lough Veagh core dates are not yet available for Lough Maam, but assuming that the sedimentary sequence is conformable certain inferences can be made.

The major difference between the two sites is that the Lough Maam core contains a record of atmospheric contamination and an absence of any significant land-use changes. The diatoms show that the lake has been acidified since about 15 cm depth in the sediment and the carbonaceous particle record confirms that the site has been affected by atmospheric pollution since about 9 cm depth. The most recent diatom assemblages in the core are composed mainly of acidophilous diatoms rather than of acidobiontic taxa that characterise the most acidified Galloway lakes. Hence Lough Maam is not so strongly acidified as the heavily impacted Galloway sites. Furthermore the concentration of carbonaceous particles in the surface sediment of Lough Maam is an order of magnitude less than in surface sediments from the Galloway sites (cf. Battarbee *et al.* 1989). From a consideration of the carbonaceous particle profile and the depth at which the diatom assemblage responds to increasing acidity it is thought likely that Lough Maam began to acidify at about the same time as the Galloway sites, in the early to mid-nineteenth century.

Using means of the appropriate water chemistry data in Table 4.2 the acidification index (see above) for Lough Maam is almost zero. This does not accord with the palaeolimnological data which suggests mild but significant acidification. It is suggested that where seasalts play a major role in determining the ionic composition of lake water the index may give erroneous results. In this particular case, water chemistry data for the May 1988 sample were clearly influenced by a major seasalt incursion into the lake system. Where marine derived ions are present in many times the concentration of those derived from catchment sources errors can arise in calculating the proportional concentrations of these latter ions.

Figure 4.6 Lough Maam: lithostratigraphy

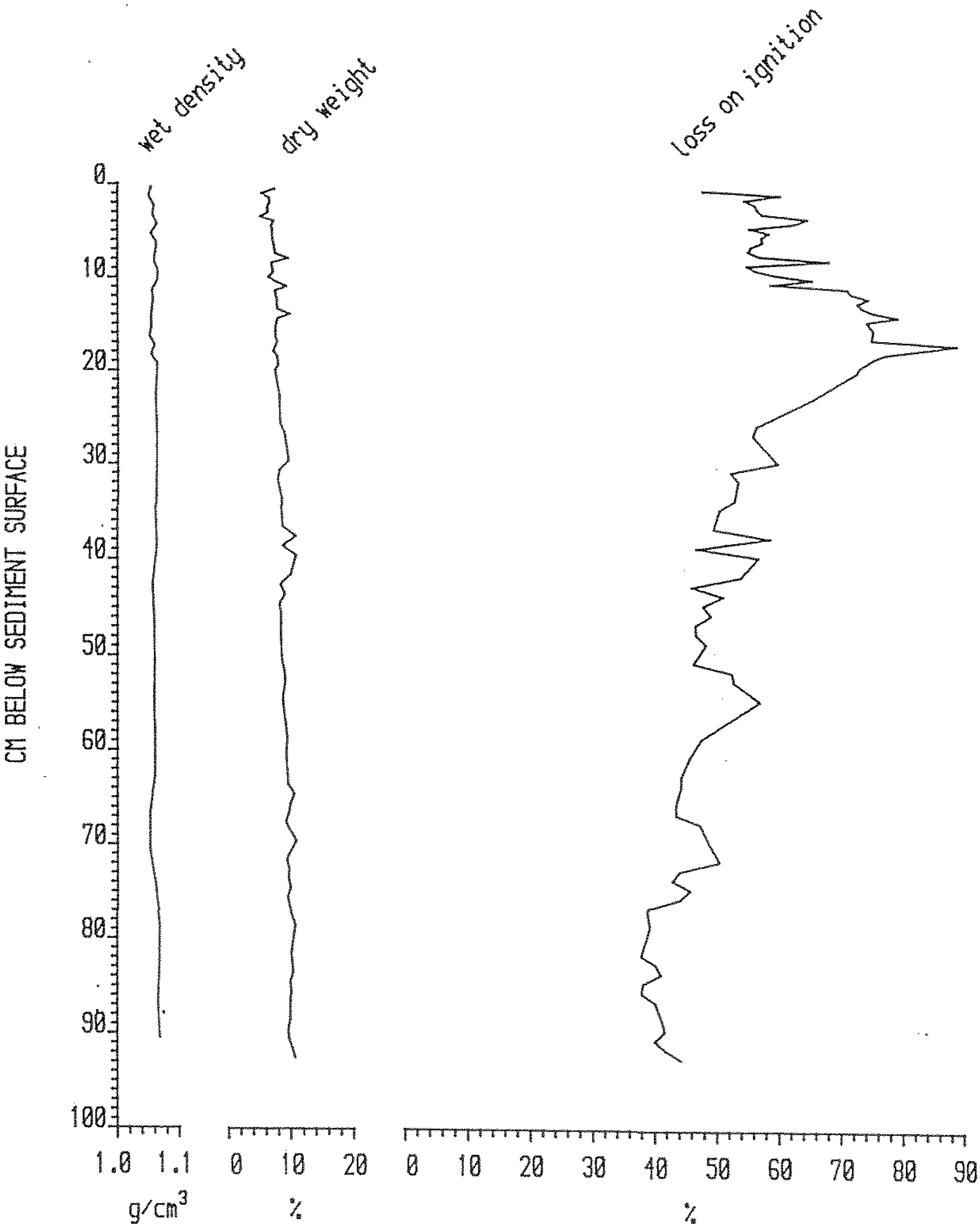


Figure 4.7 Lough Maam: carbonaceous particle profile (x 10^3 g^{-1})

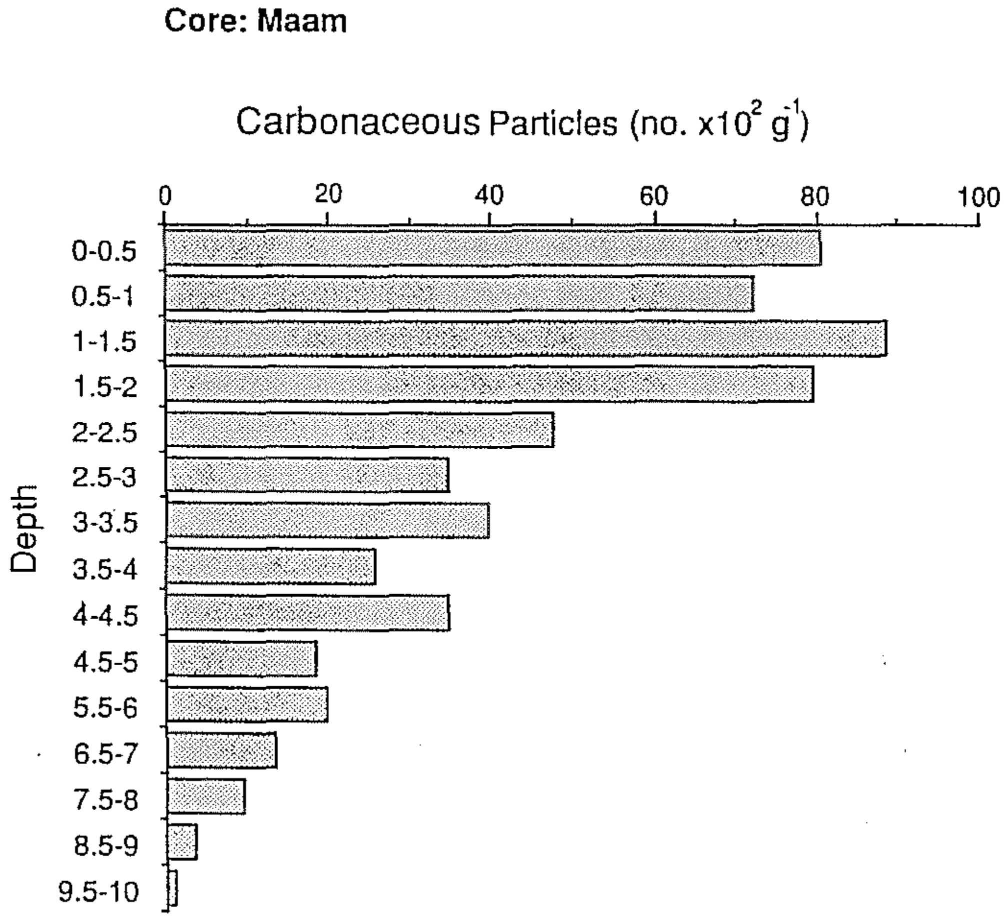


Figure 4.8 Lough Maam: summary pollen diagram (Frequencies <2% are indicated by +)

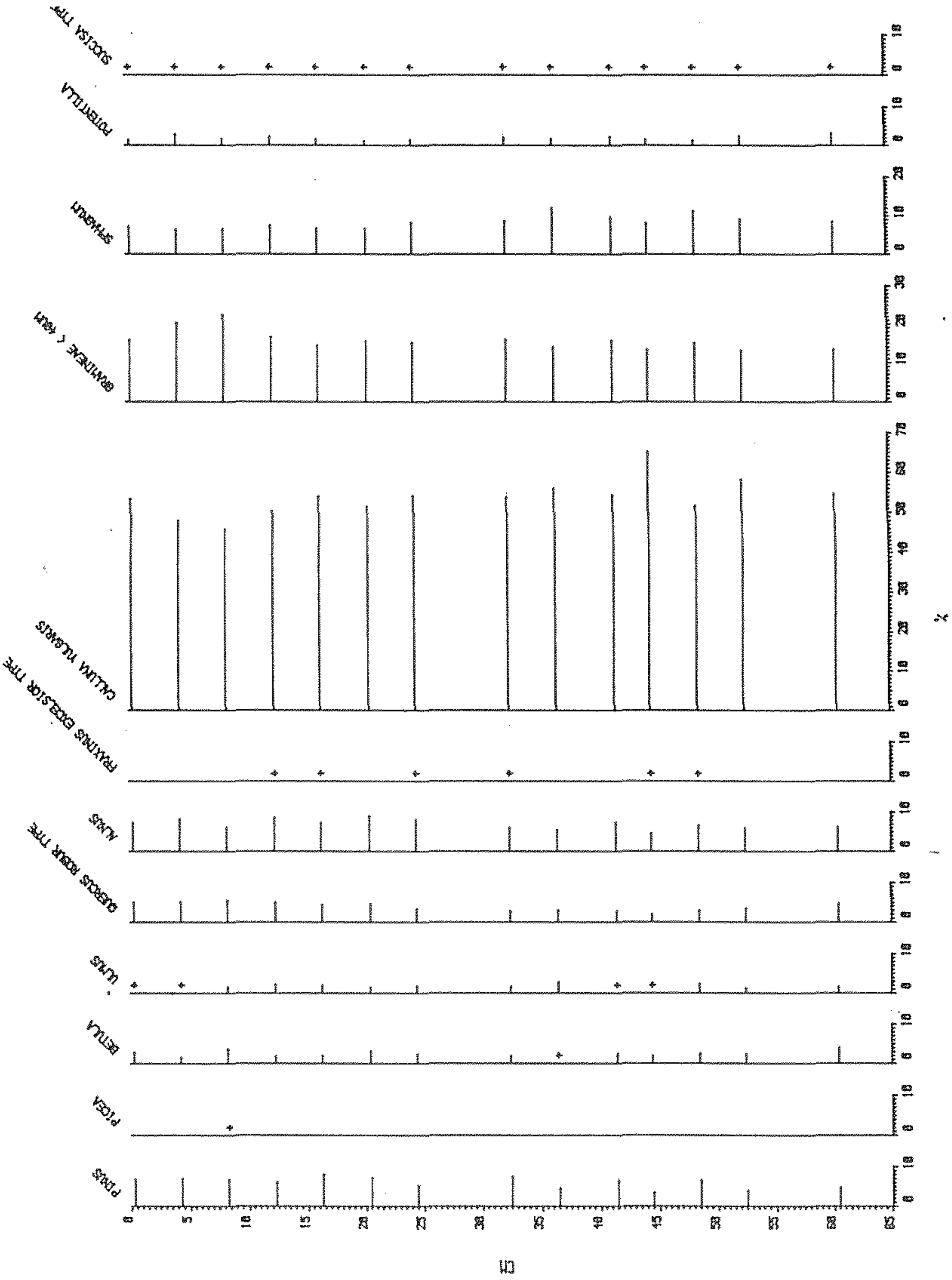
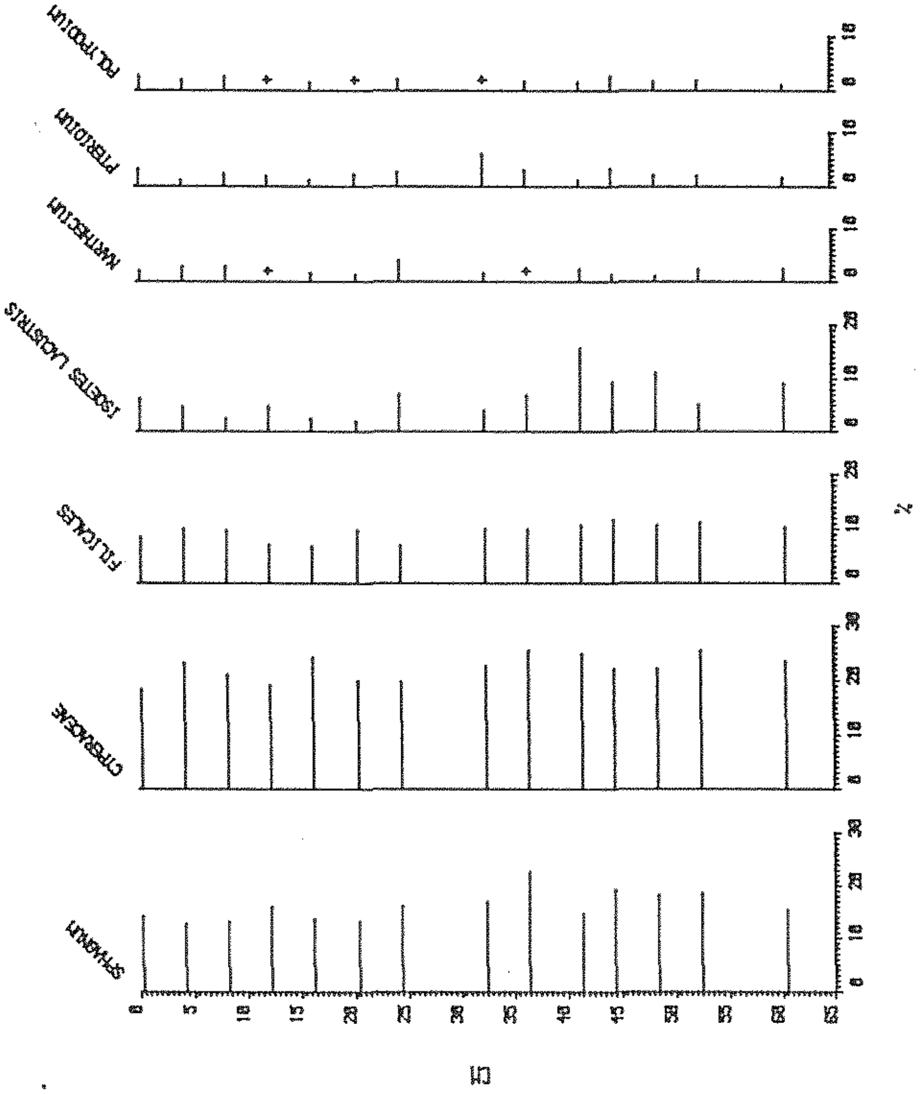


Figure 4.9 Lough Maam: aquatic and wetland plant pollen and spore frequencies. (Frequencies <2% are indicated by +)



4.4 LOUGH MAUMWEE, COUNTY GALWAY.

Site description

Lough Maumwee (Figure 1.1, 4.1) is a relatively shallow lowland (altitude 48 m) lake near Maam Cross, County Galway. It measures about 1 km by 0.6 km and has a maximum depth of almost 8 m near the north eastern shore. Catchment geology consists of quartzites and granite. Blanket peat is abundant and the acid moorland vegetation is dominated by *Molinia* grassland. Peat cutting is extensive in the catchment and some sheep grazing is practised. The catchment has probably been periodically burnt.

The lake water is moderately coloured by dissolved humic material but supports populations of trout, salmon, minnow and eels (Bowman 1988). The aquatic vegetation of Lough Maumwee is fairly sparse but is unusual in supporting a stand of *Cladium mariscus*, a plant characteristic of richer environments, on the west shore and *Eriocaulon septangulare* occurs in the littoral zone.

Water chemistry of Lough Maumwee (Table 4.3) shows that it is the least acid of the three Irish lakes under study. pH is around 6.0 and calcium and alkalinity values are relatively high. These pH and alkalinity data are somewhat surprising since pH values of 4.6-4.4 were reported for this lake in 1984 and 1985 (Bowman 1988). As with the other sites a major difference is apparent between the water chemistry on the two sampling dates in 1988 with high concentrations of sodium and chloride ions in the May sample indicating a seasalt incursion into the lake prior to sampling.

Table 4.3 Water chemistry data for Lough Maumwee as sampled in May and September 1988

		May 1988	September 1988
pH		6.01	5.94
Cond.	µS cm^{-1}	95.0	*
Alkalinity (Alk_e)	µeq l^{-1}	31.0	50.0
Ca^{2+}	µeq l^{-1}	102.0	56.0
Mg^{2+}	µeq l^{-1}	132.0	64.0
Na^+	µeq l^{-1}	648.0	226.0
K^+	µeq l^{-1}	13.0	7.0
SO_4^{2-}	µeq l^{-1}	92.0	40.0
Cl^-	µeq l^{-1}	800.0	293.0
Al	µg l^{-1}		
(total acid soluble)		6.0	7.0
(labile)		*	1.0
Colour	250 nm	0.12	0.20

* = not determined

Methods

The 83 cm long core from Lough Maumwee was analysed according to the methods of Stevenson *et al.* (1987).

Lithostratigraphy

The core consisted of fine black detrital sediment (colour 10YR 2/2) in the upper 6 cm; below 32 cm depth the sediment texture changed slightly with sand grains becoming more frequent. Gross stratigraphic changes in sediment percentage dry weight, LOI and wet density are shown in Figure 4.10. Changes are relatively minor but small peaks in the percentage dry weight curve indicate pulses of minerogenic inwash material at 80, 60, and c. 38 cm depth. These peaks correspond with low values for organic content. Above the 38 cm minerogenic peak, sediment organic matter increases irregularly from about 10% to about 30% which only slightly decreases towards the core top.

These down core changes in gross sediment stratigraphy reflect a sustained period of catchment disturbance through peat cutting and by burning to improve grazing. It is likely that the minerogenic pulses arise from erosion following the cutting of peat to the level of the minerogenic subsoils.

Dating

In progress

Diatom analysis

In progress

Carbonaceous particle analysis

In progress

Pollen analysis

In the essentially treeless landscape around Lough Maumwee it is interesting to note that tree pollen constitutes c. 30% of the down-core pollen sum and that *Pinus* pollen usually exceeds 10% above about 60 cm depth (Figure 4.11). Since natural *Pinus* woodland is long extinct in this part of Ireland the only likely source of its pollen is from reworking of fossil material by peat extraction. Ruderal pollens are also relatively high throughout the profile, again suggesting widespread disturbance of catchment soils. The *Calluna* : Gramineae ratio (Figure 4.12) initially increases up to c. 45 cm but declines a little above this depth to the core top. Interpretation of this ratio is made difficult if influx of old pollen is a significant process at this site, however a declining ratio towards the core top is compatible with the hypothesis that the vegetation has been managed for sheep grazing.

With regard to the pollen record of aquatic plants (Figure 4.13) it is interesting to note that *Isoetes* spores are in relatively high abundance throughout most of the core section indicating that erosional influxes of soil particulates has not been large enough to produced a sustained impact on the distribution of this plant. Interestingly however, the two levels of low frequency of *Isoetes* spores occurs at 55 and 31 cm closely after the upper and middle inwash pulses indicated by the percentage dry weight curve.

Discussion

Without the results of diatom and carbonaceous particle analyses from the core it is currently not possible to comment about the acidification status of Lough Maumwee. However, a brief consideration of its water chemistry indicates that the site is not particularly susceptible to acid deposition as it possesses significant alkalinity and relatively high pH despite its quartzite/granite catchment. Furthermore, aspects of the aquatic vegetation indicate that base status of the lake water is relatively high and that there are sources of base cations within the catchment from other geological formations such as basic intrusions such as occur in the Lough Veagh catchment. Application of the Henriksen equation to the water chemistry data in Table 4.3 produces an index value near zero, indicating an absence of acidification by acid deposition.

Figure 4.10 Lough Maumwee: lithostratigraphy

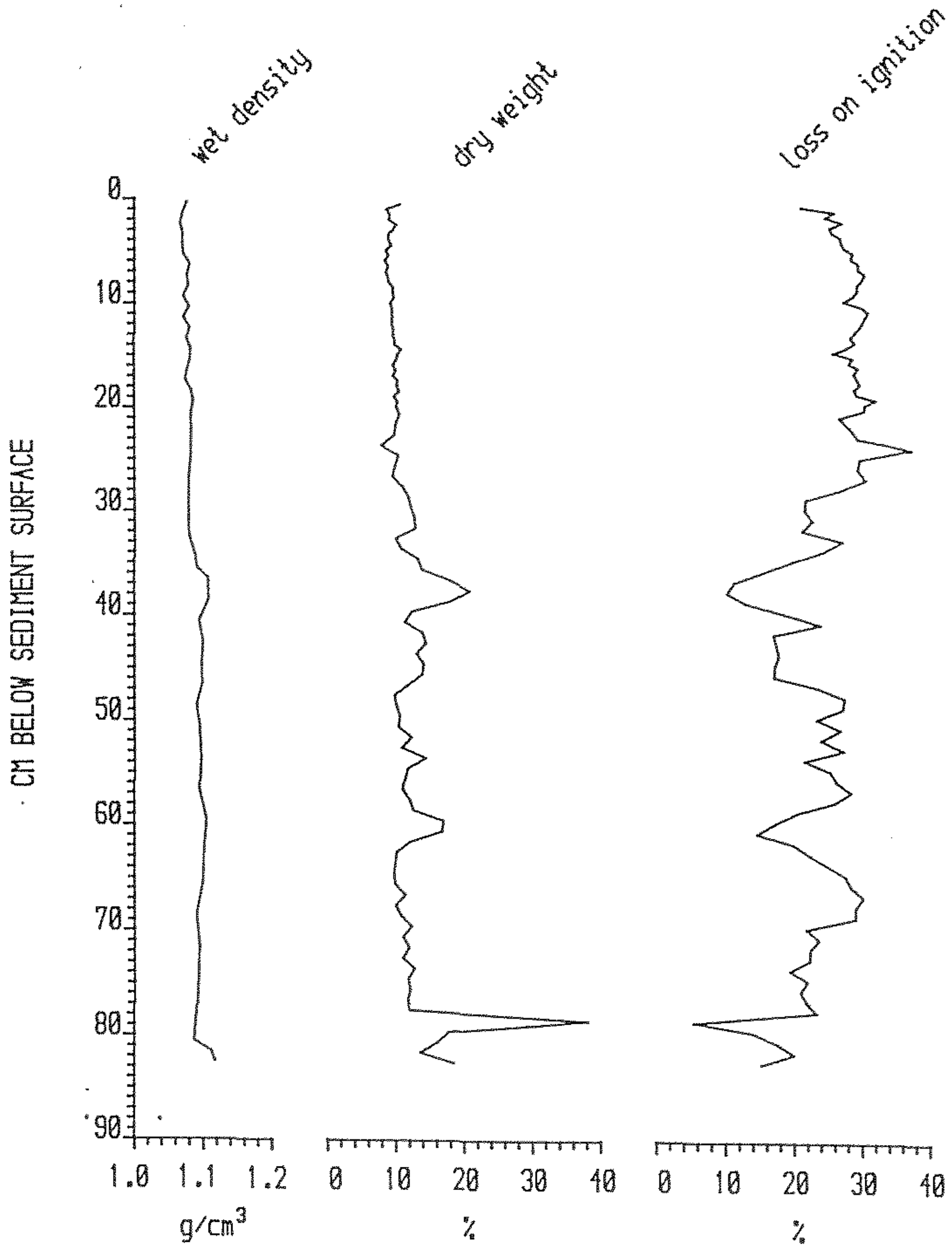


Figure 4.11 Lough Maumwee: summary pollen diagram (Frequencies <2% are indicated by +)

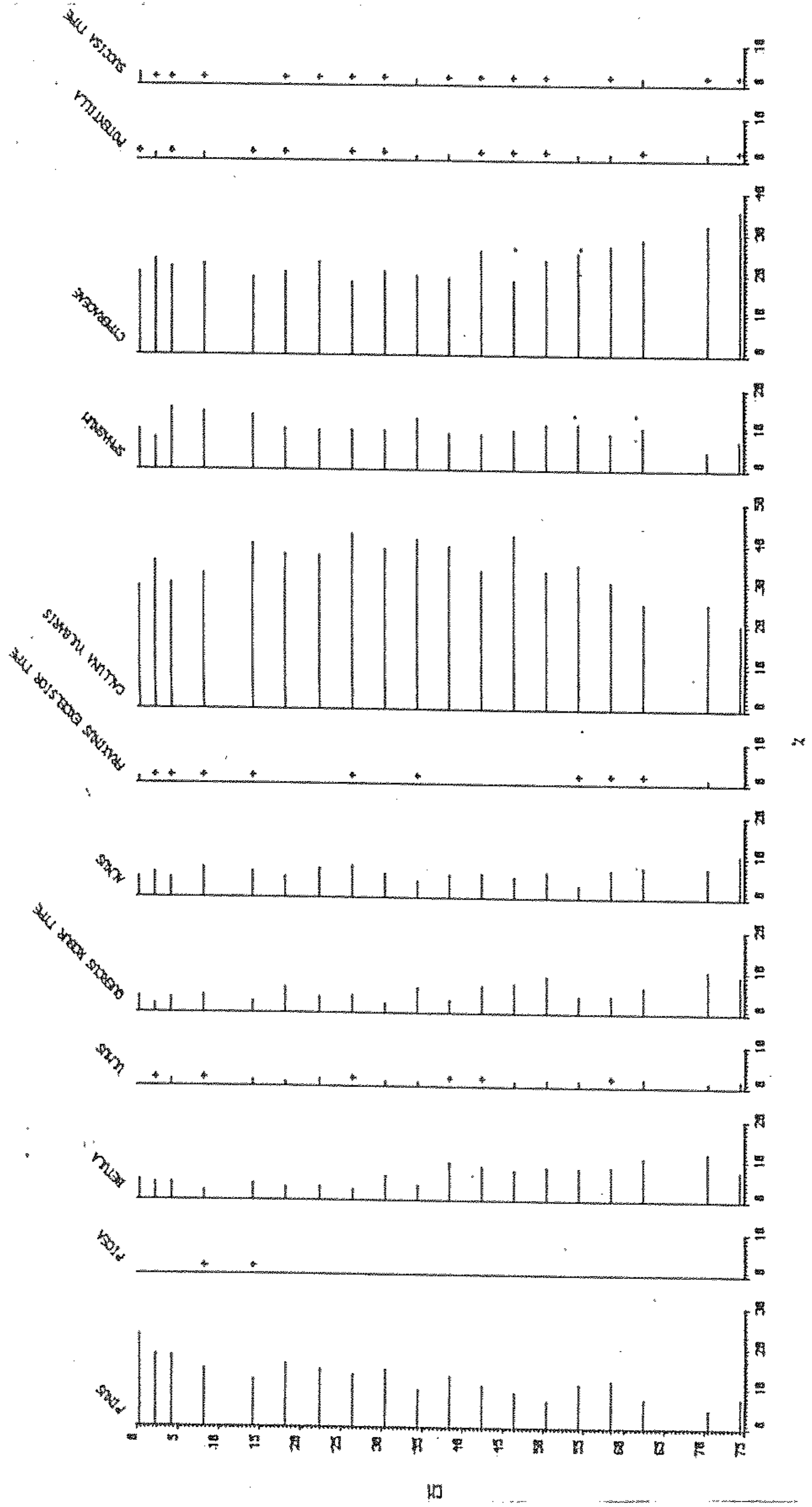


Figure 4.12 Lough Maumwee: *Calluna* : Gramineae ratio

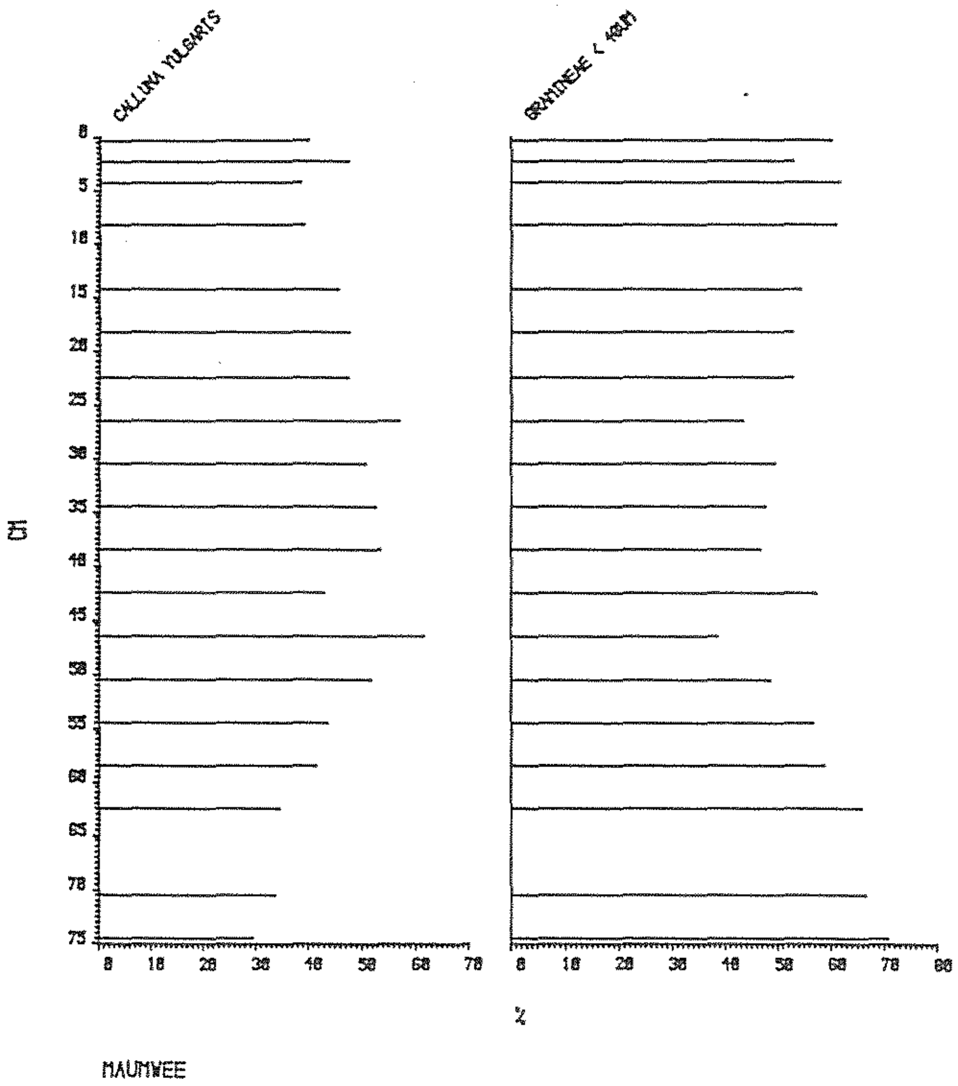
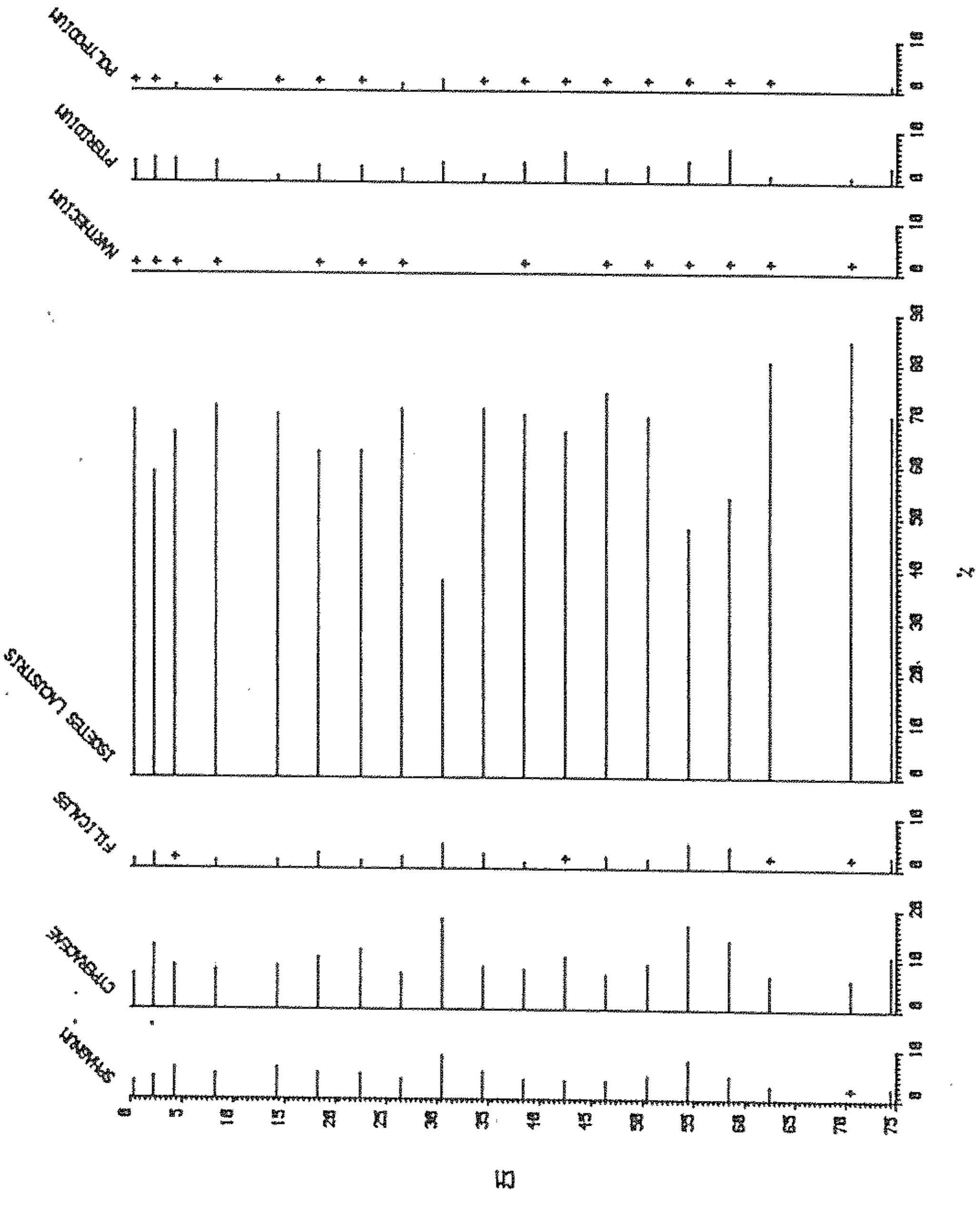


Figure 4.13 Lough Maumwee: aquatic and wetland plant pollen and spore frequencies. (Frequencies <2% are indicated by +)



4.5 CONCLUSIONS

The recent pH history of Lough Veagh indicates a mild acidification phase between 16 and c. 5 cm depth but the most recent inferred pH values are not significantly different from those below the acidification section. It is noted that the acidification event may be an artifact resulting from inwashed acidophilous diatoms (cf. Battarbee and Flower 1985).

The diatom record indicates that Lough Maam has been recently acidified and the carbonaceous particle record confirms that the site is impacted by atmospheric pollution. This site has not been so strongly affected by acid deposition as some lakes in Galloway but it is likely that the acidification process began at a similar time in the early to mid-nineteenth century.

Major seasalt incursions into the Lough Maam system and consequent effects on water chemistry causes problems in accurately proportioning the catchment contribution of anions so confounding an estimate of water acidification using the relationship between base cations and alkalinity.

Insufficient data are currently available to fully assess the historical water quality status of Lough Maumwee. A consideration of the water chemistry indicates that the site is not acidified but the pH and alkalinity are such that it is unlikely that the lake-catchment system will be sensitive to low intensity acid deposition.

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5 AFFORESTATION AND LAKE ACIDIFICATION: A COMPARISON OF FOUR SITES IN SCOTLAND (Joint SWAP and DoE programme)

5.1 INTRODUCTION

Coniferous afforestation has expanded over wide areas of upland Scotland in the mid/late-twentieth century. Many afforested upland regions are vulnerable to acidification due to their slow weathering, base-poor bedrock and high rainfall (Kinniburgh and Edmunds 1986). In Wales and Scotland comparisons of moorland streams and streams with afforested catchments show that streams draining forests tend to have a lower pH and higher aluminium and sulphate concentrations (Stoner *et al.* 1984, Harriman and Morrison 1982). This acidification effect appears to increase with the age of the plantation and there have also been reports of fish loss associated with forestry (Kreiser *et al.* 1986).

Many mechanisms have been suggested to explain how planting coniferous forests could lead to surface water acidification. These include processes linked with tree growth itself, such as the uptake of base cations from the soil which are removed from the site on harvesting, the accumulation of litter rich in humic acids on the forest floor, the loss of ground vegetation, the leaching of hydrogen ions from the canopy due to NH_4 uptake and the leaching of sulphate from the canopy. Other proposed mechanisms involve the combined effects of acid deposition and forestry such as the enhanced capture of acidic aerosols as dry deposition by the forest canopy and the direct uptake of sulphur dioxide in the leaves and subsequent leaching of sulphate (Lindberg and Garten 1988). Forests in upland locations are also efficient collectors of fine mist droplets from low cloud and the amount of deposited sulphate at these sites is consequently greater than at lower altitudes (Fowler pers. comm.). Additionally, the ground preparation techniques used prior to planting, such as ploughing and ditching, greatly increase the rate of runoff and in deep peat this increases the input of humic acids to the drainage streams. The oxidation of sulphides to sulphate as soils dry out following drainage has also been shown to lower the pH in drainage channels.

In view of the continuing afforestation of upland areas in the UK it is important to ascertain whether coniferous forestry does acidify surface waters and if so, the extent to which this acidification is related to the input of acidity from the atmosphere. Palaeolimnological techniques have already been successfully used to show that lakes in the UK have acidified as a result of acid deposition (eg. Battarbee *et al.* 1988). However, palaeolimnological studies of afforested sites have so far failed to show any conclusive evidence to link afforestation with lake acidification. The afforested sites included in previous studies are all in areas receiving moderate to high levels of acid deposition and, with the exception of Loch Fleet and Loch Skerrow in south west Scotland, they all began to acidify before the forests were planted. In the case of Loch Skerrow sources of alkalinity within the catchment have buffered the lake from acidification (Flower *et al.* 1987). Although the acidification in Loch Fleet occurs after the forest was planted in the catchment, it is not clear whether the acidification was due to the presence of the forest itself, the combined effect of forest and high levels of acid deposition or even the blocking of a groundwater source of alkalinity to the lake by the sedimentation of eroded peat following afforestation (Anderson *et al.* 1986).

It is therefore apparent that the afforested sites chosen in previous studies were not suitable for detecting the impact of forestry on surface water pH since they were either too sensitive geologically and had already acidified, or were adequately buffered against changes in pH. For this reason a project was devised to examine the impact of forestry on lake pH in two regions; one receiving high levels of acid deposition and one significantly lower levels of acid deposition. In each region a lake with an afforested catchment was chosen together with an adjacent undisturbed moorland site as a control. In this way the pH history of the afforested lake can be compared with the moorland lake in each case and the impact of the forest detected. Comparison of the pH histories between the two regions will also allow the influence of acid deposition to be assessed both independently of, and in combination with forestry.

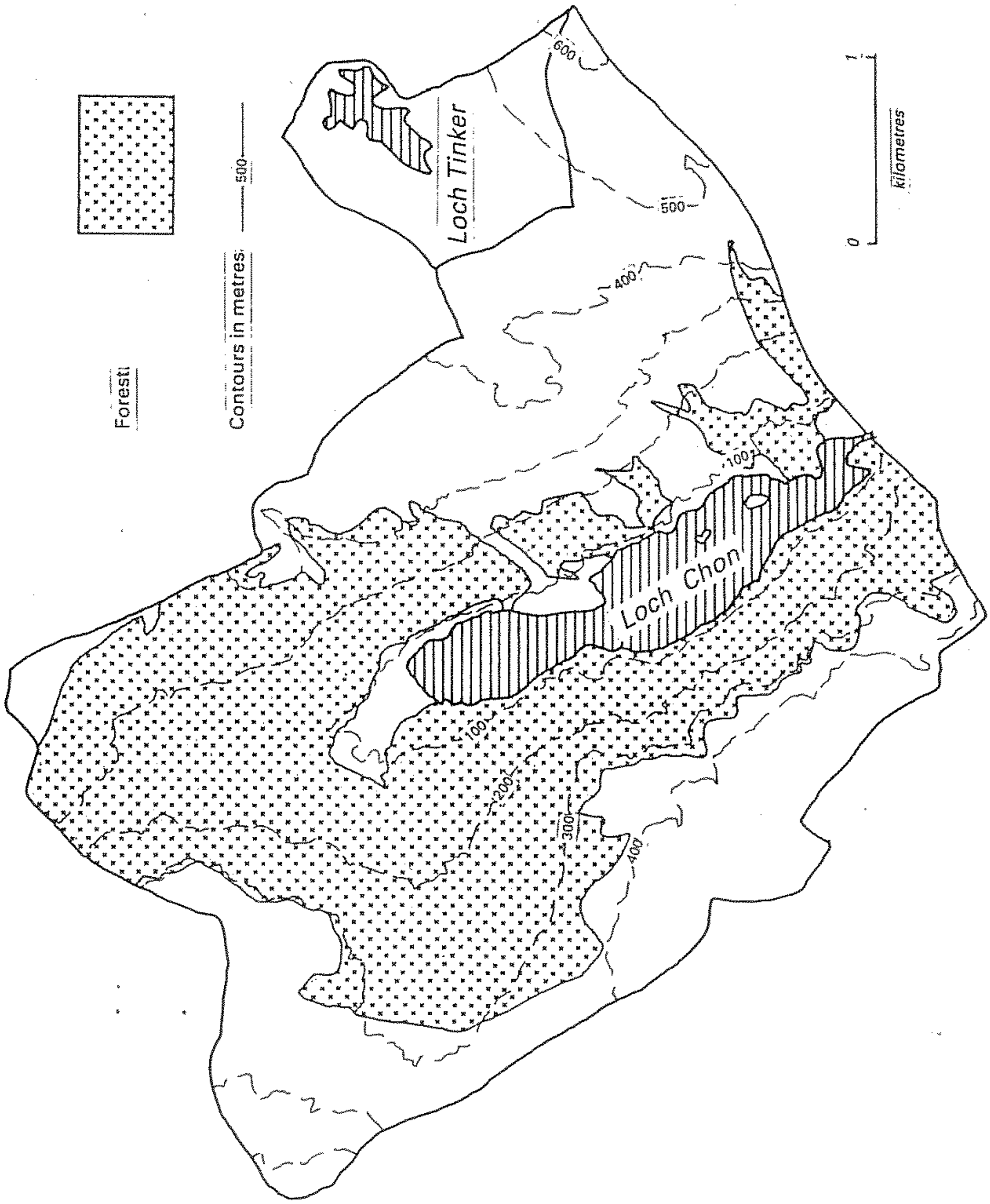
5.2 THE TROSSACHS, CENTRAL SCOTLAND

This region was chosen as the area of high deposition, receiving 1.59 g S m^{-2} yr^{-1}. The area is also in a region defined as geologically highly sensitive to acid deposition (Kinniburgh and Edmunds 1986). The two study sites (Figures 1.1, 5.1) are in the Loch Ard forest area and their characteristics are summarised in Table 5.1 below.

Table 5.1 Trossachs - characteristics of study sites

	Loch Chon	**Loch Tinker**
Grid reference	NN 421051	NN 445068
Geology	mica schists & grits	schistose grit
Catchment vegetation	conifers/moorland	moorland
% Forest	51%	0%
Lake altitude	100 m	420 m
Net relief	600 m	280 m
Maximum depth	25 m	9.8 m
Mean depth	7.6 m	3.5 m
Lake area (ha)	100	11.3
Lake volume (m^3 x 10^3)	7344	403
Catchment area (ha) excl. lake	1570	112

Figure 5.1 Loch Chon and Loch Tinker catchments



5.2.1 Catchment descriptions

Geology

The geology of the two sites is broadly similar, consisting of metamorphosed sediments of the Dalradian group (Cambrian). There are also belts of darker rocks called 'green beds' within both catchments which contain higher proportions of calcium and magnesium than the surrounding rock, but from the water chemistry (Table 5.2) they appear to supply little alkalinity to the lochs.

Vegetation

The Loch Tinker catchment contains extensive areas of blanket peat on the lower ground and is dominated by the moorland species *Calluna vulgaris* and *Molinia caerulea*. The catchment is grazed by sheep and was managed for grouse up until the 1930s by regular heather burning, but is now burnt infrequently.

Most of the lower ground in the Loch Chon catchment is planted with coniferous forest, although there is a small amount of deciduous woodland along the shores of the loch and the banks of the inflow streams. Sitka spruce predominates with some Norway spruce, Japanese larch, Scots pine and Lodgepole pine. Planting began in 1951 and continued throughout the 1950s and 1960s. The mechanical digging of drains or ploughing was not carried out in these early plantations due to the steep gradient of the slopes, although areas planted recently (since 1980) have been ploughed. Nitrogen and Phosphate fertiliser was applied by hand at the time of planting and again in the early 1960s when the first plantations did not appear to be growing well. Drains were also deepened by hand at this time and the condition of the trees improved. Later applications of phosphate fertiliser were made from the air. There has been no felling or thinning of the forest to date.

There is a small farm at the north end of Loch Chon. From the time when the Forestry Commission acquired the land in 1928 until 1960 the land around the farm was not improved or maintained in any way. In 1960 a new tenant ploughed up the meadows around the farm and planted potatoes and hay grass. Five tons of lime per acre were applied at this time and nitrogen, potassium and phosphate fertiliser were applied periodically to the hay meadows from 1960 to 1983. A few cattle (less than 40) were also kept on this land.

The high ground in the Loch Chon catchment has a moorland vegetation similar to that around Loch Tinker. A small road passes through the catchment on the east side of the loch and a subterranean aqueduct, built in the nineteenth century to carry water from Loch Katrine to Glasgow, passes along the west side of the loch. The loch has many inflow streams and some of these have been canalized where they pass over the aqueduct on the western side of the catchment. Three of these inflow streams are included in the monitoring programme being carried out by the Department of Agriculture and Fisheries for Scotland (DAFS). Soils in the catchment are also part of a survey being undertaken by the Macaulay Institute.

5.2.2 Lake descriptions

Loch Chon has two main basins (Figure 5.2). The deepest part of the loch (25 m) is a trench near the western shore. Loch Tinker also has two basins (Figure 5.3) the deepest point being 10.5 m.

The mean chemistry values for the 1985-1987 (Table 5.2) show Loch Chon to be the more acidic of the two lochs and the similarity in the calcium values suggest that some acidification has occurred. Aluminium levels in Loch Chon are higher in line with the lower pH. The higher sodium, chloride and sulphate levels in Loch Chon are in accordance with the hypothesis of increased dry and wet deposition of sea salts and acid particulates in afforested catchments. The values in parentheses for Loch Tinker in Table 5.2 are means calculated with a sample taken during a sea salt event included.

Table 5.2 Loch Chon and Loch Tinker: water chemistry (1985-1987)

		Loch Chon	**Loch Tinker**
pH		5.2	6.0 (5.4)
Cond	μS cm^{1}	39.0	25.0 (29.0)
Ca^{2+}	ueq l^{-1}	79.0	78.0 (79.0)
Mg^{2+}	μeq l^{-1}	49.0	35.0 (39.0)
K^{+}	μeq l^{-1}	7.2	6.6 (8.0)
Na^{+}	μeq l^{-1}	175.0	101.0 (121.0)
Cl^{-}	μeq l^{-1}	188.0	102.0 (142.0)
SO_4^{2-}	μeq l^{-1}	85.0	62.0 (64.0)
Alkalinity (Alk$_e$)	μeq l^{-1}	2.3	24.0 (18.0)
TOC	mg l^{-1}	2.2	3.6
Al^{3+} labile	μg l^{-1}	30.0	5.5 (5.0)

Fish

No written records exist for the fishing history of either loch although the forester in charge of issuing angling permits for Loch Chon since 1960 has been able to provide the following information (C. McNair, pers. comm.).

Loch Chon has been a popular fishing loch throughout this century due to its ease of access. Until the early 1960s the fishing was very good with up to fifty anglers at a time fishing at the weekend. In 1960 the forest was less than ten years old and the canopy had not closed. The drainage of the forest was subsequently improved and some fertiliser applied to encourage tree growth. After this there was a reduction in the number of trout caught, with catches favouring larger fish, indicating some problem with recruitment. There was also an absence of spawning in the streams draining the forested areas which had previously been good spawning grounds. It is difficult to know to what extent this was due to physical factors such as the shading of spawning streams rather than changes in water quality. No water chemistry measurements were made at this time and the reduction in fish population was generally assumed to be connected with the growth of the forest and closure of the canopy. By 1986 the fishing in Loch Chon was described as poor. Only one stream is used for spawning. This stream flows through moorland with some deciduous trees on the banks but the upper part of its catchment has recently been planted with conifers.

Loch Tinker is a more remote site and is therefore fished infrequently. However, anglers who do occasionally visit the loch report that they catch trout of a good size. There has been no reported change in the fish population in the last decade.

Figure 5.2 Loch Chon: bathymentry (contours in metres)

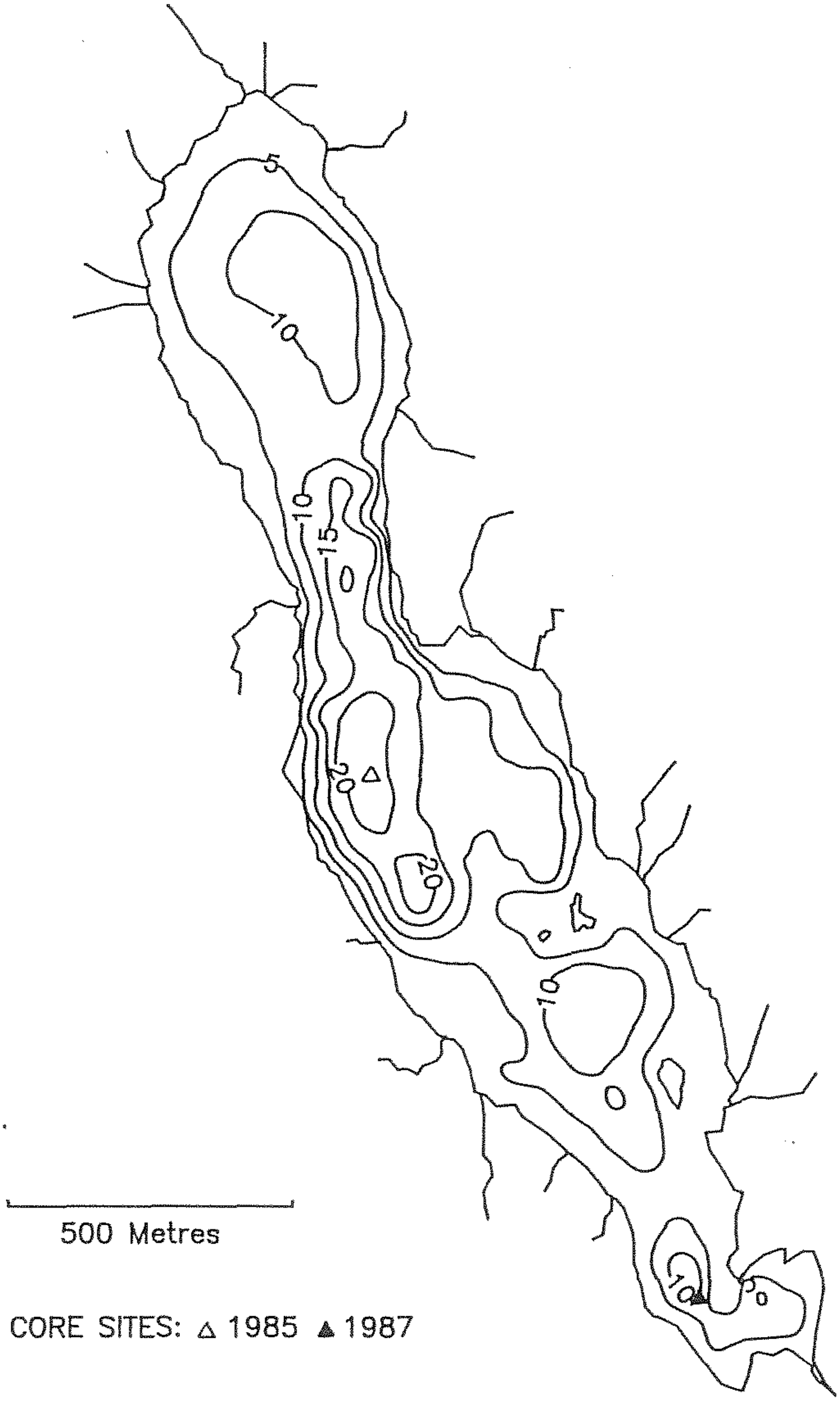
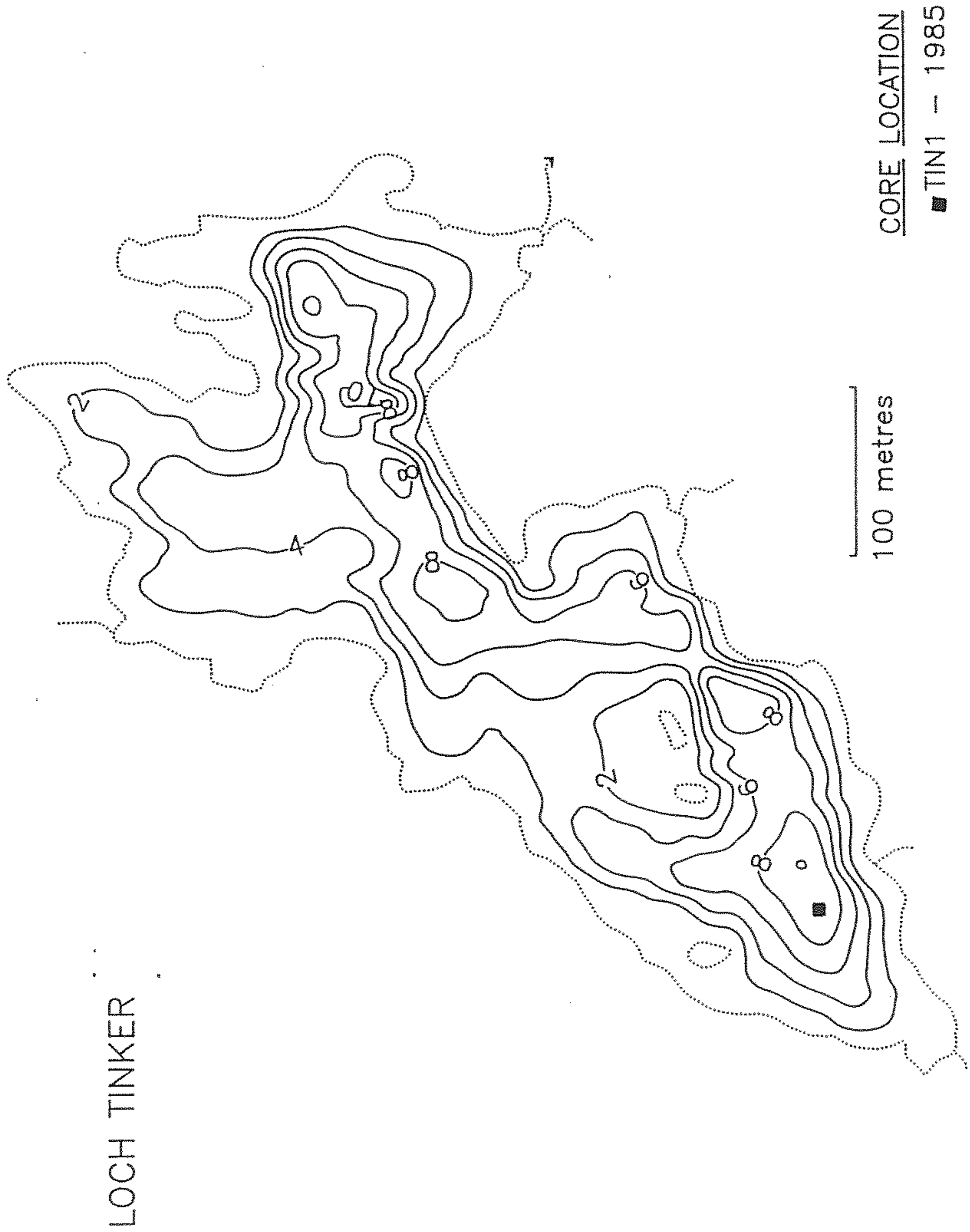


Figure 5.3 Loch Tinker: bathymetry (contours in metres)



5.2.3 Loch Chon: results

In 1985 sediment cores were taken from the deepest point in the trench on the western side of the loch, using a modified Livingstone corer. However, palynological analysis has shown that the top of these cores do not contain recent pollen and it seems probable that some slumping of older sediment from the sides of the deep trench has occurred not long before the cores were taken. Subsequent cores were taken from the southernmost basin in 1987 with a mini-Mackereth pneumatic corer (Mackereth 1969) and these proved to be satisfactory.

All laboratory methods follow those of Stevenson *et al.* (1987).

Lithostratigraphy

Core CHN875 was selected from the cores taken in April 1987 since it appeared to have an undisturbed sediment/water interface. The core can be divided into three stratigraphic zones. The sediment from 0 to 10 cm depth consists of fine, dark brown, organic detritus with some coarser detritus in the top centimetre. From 10-17 cm depth there is a gradual transition into fine grey/brown organic sediment containing a small amount of clay. The sediment appears mottled with some patches of lighter brown sediment containing more clay. Below 17 cm the sediment is an even dark grey/brown colour, consisting of fine organic detritus with a small amount of clay. There are two paler bands of sediment containing slightly more clay at 30 cm and 36 cm. These stratigraphic changes are evident in the wet density, dry weight and LOI profiles shown in Figure 5.4. The ^{210}Pb chronology for this core (see below) shows that all these changes in sediment type occurred before 1830 and are therefore not related to the recent afforestation.

Dating

Loch Chon is in a region subject to fallout from the Chernobyl accident and this is confirmed by the presence of high ^{137}Cs activities in the top sediments together with significant concentrations of the short-lived isotope ^{134}Cs and traces of ^{103}Ru. This confirms that the top of the core is recent. The unsupported ^{210}Pb inventory of the core of 9.82 pCi cm^{-2} represents a constant supply of ^{210}Pb of 0.31 pCi cm^{-2} yr^{-1} which is significantly lower than the value for nearby Loch Tinker. However, the ratio of nuclear weapons testing derived ^{137}Cs and ^{210}Pb for the two sites is very similar.

Chronologies for the core have been constructed using both the CRS and CIC ^{210}Pb dating models (Table 5.3, Figure 5.5). They indicate a constant sediment accumulation rate since 1954 of 0.013 g cm^{-2} yr^{-1}. The ^{137}Cs and ^{241}Am data also support this conclusion. Both ^{210}Pb dating models also indicate an abrupt transition in the early 1950s to this accumulation rate from an earlier accumulation rate of 0.0087 g cm^{-2} yr^{-1}. As a result the CIC model dates below this point (4 cm) are about 10 years younger than the CRS dates. The increase in accumulation rate is most probably linked to the forest planting taking place in the catchment at the time and this increase is indicated by a reduction in unsupported ^{210}Pb activity. This suggests that the CRS model is the most suitable for this site and the chronology used to interpret the results of other core analyses has been derived using the CRS model.

Diatom analysis

Diatom assemblages in core CHN875 are dominated by circumneutral and acidophilous taxa. A summary of the most abundant taxa is given in Figure 5.6. The first floristic change occurs between 10-8 cm (c. 1800-1850) when the proportions of the planktonic taxon *Cyclotella kuetzingiana* begin to decline. This loss of diatom plankton is a response seen in many lakes as they begin to acidify (eg. Battarbee *et al.* 1988). There is an increase in *Brachysira vitrea* between 8-5 cm (1850-1930) with a corresponding decline in *Achnanthes minutissima*. From 5-2 cm (1930-1973) *A. minutissima* continues to decline but there are no major changes in the other taxa, apart from a slight reduction in *Brachysira vitrea* from 5-3.5 cm (1957). Above 2 cm proportions of acidophilous taxa such as *Navicula leptostriata* and *Eunotia incisa* increase markedly up the surface.

Total diatom concentrations vary from 7.6 x10^7 cells g^{-1} to 2.1 x10^8 cells g^{-1}. In the dated portion of the core above 10 cm (1800) there is a trend of increasing concentrations reaching a peak at 4-4.5 cm (1932-1943). However, when the concentrations are expressed as cells cm^{-2} yr^{-1}, the maximum flux of diatoms to the sediment occurs at 3.5-4 cm (1951-1957) with a smaller peak at 1.5-2cm (1973-1977).

Initially, pH was reconstructed from the diatom pH preference groups using the multiple regression equation derived from 33 Galloway lochs (Flower 1986). This gave a reconstructed pH of 6.2 at 1800. The first pH change occurred at 1900 and pH declined gradually to 6.0 at about 1970. Between 1970 and 1975 pH declined rapidly to 5.6, with a reconstructed pH of 5.5 at the surface (measured pH 5.2). However, pH reconstruction using weighted averaging (Figure 5.7) produces a slightly different pattern of acidification. Weighted averaging with tolerance downweighting produces the same trend of pH change as weighted averaging but generally reconstructs 0.1 pH units lower. Weighted averaging reconstructs a pH of 6.4-6.5 at 1800 and there is a steady decline in pH over the nineteenth century, reaching 6.0-6.1 at the turn of the century. Gradual acidification continued and by 1960 the pH was 5.8-5.9. Between 1960 and 1965 there was a drop of 0.2 pH units and this acceleration of acidification continued up to the present. The reconstructed pH at the surface is 5.1-5.2, which agrees well with the measured mean pH.

The difference between the pH reconstructions using multiple regression and weighted averaging is due mainly to the dominance of three circumneutral taxa: *Cyclotella kuetzingiana*, *A. minutissima* and *B. vitrea*. When pH is reconstructed using multiple regression these taxa are amalgamated and only their overall decline influences the pH reconstruction. However, when the initial decline of *Cyclotella* (pH optima 6.5) is separated from the later decline in *A. minutissima* (pH optima 6.3) and accompanying increase in *B. vitrea* (optimum pH 5.9) the gradual change over the nineteenth century can be detected. Between 3.5-2.0 cm (c. 1960-1970) there is a rapid decline in *A. minutissima* but the proportion of *B. vitrea* remains unchanged. When pH is reconstructed for this period using multiple regression there is no appreciable change in pH until after 1970 when pH declines rapidly. However, when the differing pH optima for these two species is taken into account using weighted averaging, it would appear that the acceleration in acidification occurred from 1960 onwards.

Pollen analysis

Pollen analysis of the initial 1985 cores revealed that the top 3 cm of the cores contained a pollen assemblage typical of material found below 100 cm, indicating the slumping of old material over the most recent sediment. Pollen analysis was also used to confirm that the top sediments of the CHN875 core are recent.

Carbonaceous particle analysis

The carbonaceous particle concentrations plotted against time are shown in Figure 5.8a. There are very few particles present below 7 cm (1885). Above this point the particles increase steadily up to 3-3.5 cm (1957-1963). After 1963 there is a rapid increase in particle concentration. This is shown more clearly when the values are expressed as flux to the sediment (Figure 5.8b). The rapid increase in carbonaceous particle flux at this time is also seen in the Loch Tinker core (see below).

Geochemistry

A full report on the sediment chemistry is not yet available, but initial analysis of the zinc and lead concentrations show a steady increase from the early-nineteenth century, indicating early atmospheric contamination from industrial sources. The decline in contamination values in the 1950s is probably due to the higher input of organic material to the lake from the forest rather than a reduced supply of zinc and lead from the atmosphere.

Magnetic analysis

In progress

Figure 5.4 Loch Chon: lithostratigraphy

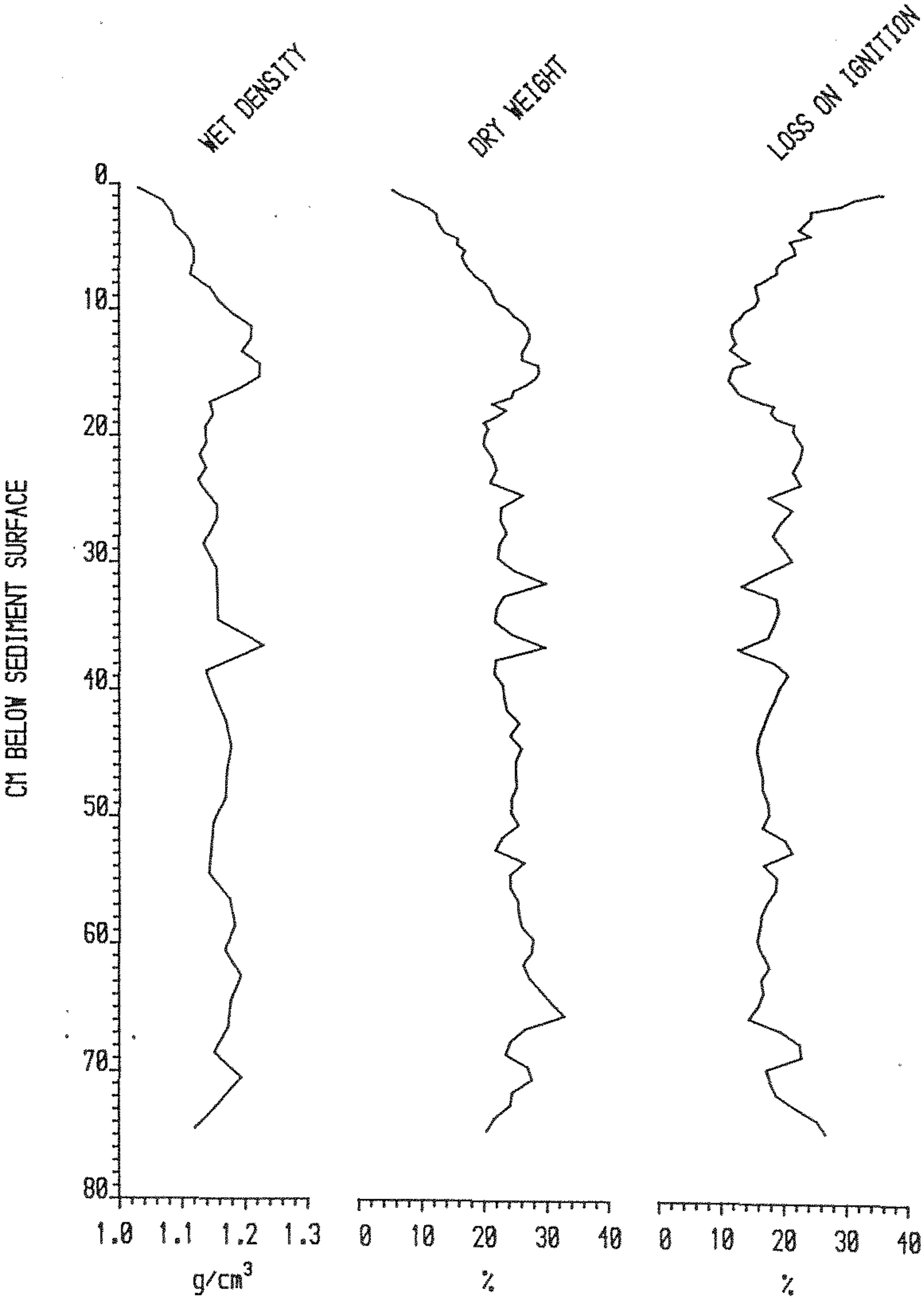


Table 5.3 Loch Chon: ^{210}Pb chronology

Depth	Dry Mass	Date	Age		Sedimentation Rate		
cm	gcm^{-2}	AD	yr	±	$gcm^{-2}yr^{-1}$	$cmyr^{-1}$	± (%)
0.00	0.0000	1986	0				
0.25	0.0141	1985	1	2	0.0143	0.229	8.3
0.50	0.0304	1984	2	2	0.0135	0.197	8.8
0.75	0.0468	1983	3	2	0.0127	0.164	9.2
1.00	0.0691	1981	5	2	0.0127	0.145	7.1
1.25	0.0914	1979	7	2	0.0127	0.125	5.1
1.50	0.1197	1977	9	2	0.0144	0.129	5.9
1.75	0.1480	1975	11	2	0.0161	0.133	6.8
2.00	0.1802	1973	13	2	0.0144	0.114	6.6
2.25	0.2125	1971	15	2	0.0127	0.095	6.4
2.50	0.2466	1968	18	2	0.0132	0.096	6.4
2.75	0.2808	1965	21	2	0.0137	0.097	6.5
3.00	0.3167	1963	23	2	0.0137	0.095	6.8
3.25	0.3526	1960	26	2	0.0137	0.094	7.1
3.50	0.3885	1957	29	2	0.0137	0.092	7.4
3.75	0.4244	1955	31	2	0.0136	0.091	7.8
4.00	0.4655	1951	35	2	0.0117	0.074	8.2
4.25	0.5066	1948	38	2	0.0097	0.057	8.6
4.50	0.5507	1943	43	2	0.0091	0.052	8.5
4.75	0.5948	1938	48	2	0.0085	0.046	8.4
5.00	0.6413	1932	54	3	0.0085	0.046	9.2
5.25	0.6878	1927	59	3	0.0084	0.045	10.0
5.50	0.7344	1921	65	4	0.0084	0.044	10.8
5.75	0.7809	1916	70	4	0.0084	0.044	11.6
6.00	0.8298	1909	77	5	0.0083	0.042	13.5
6.25	0.8787	1903	83	5	0.0081	0.041	15.3
6.50	0.9276	1897	89	6	0.0080	0.040	17.1
6.75	0.9764	1891	95	7	↑	↑	↑
7.00	1.0253	1885	101	8			
7.25	1.0742	1879	107	8			
7.50	1.1327	1871	115	9			
7.75	1.1913	1864	122	10	0.0090	0.036	≈20%
8.00	1.2498	1857	129	11			
8.25	1.3083	1849	137	12			
8.50	1.3669	1842	144	14			
8.75	1.4254	1835	151	15	↓	↓	↓

Figure 5.5 Loch Chon: ^{210}Pb chronology

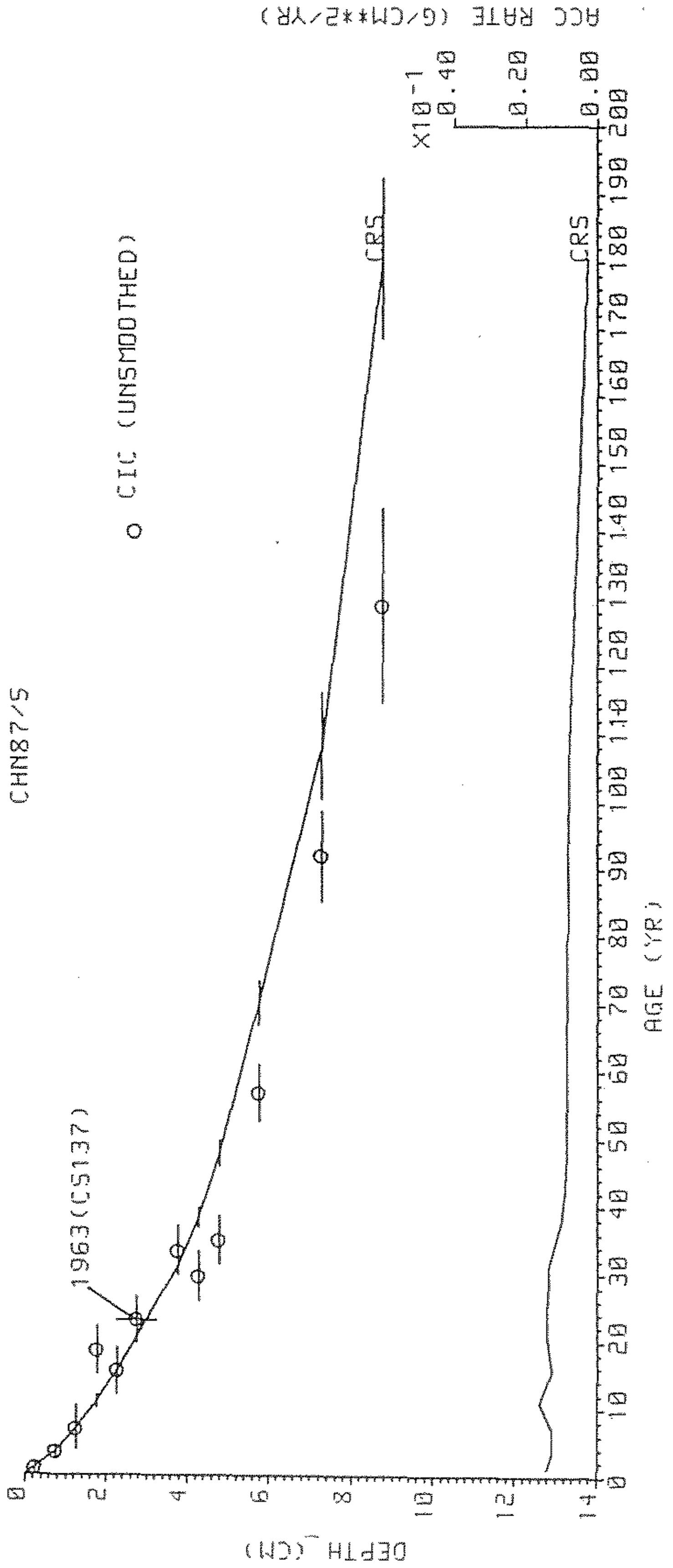


Figure 5.6 Loch Chon: diatom summary diagram

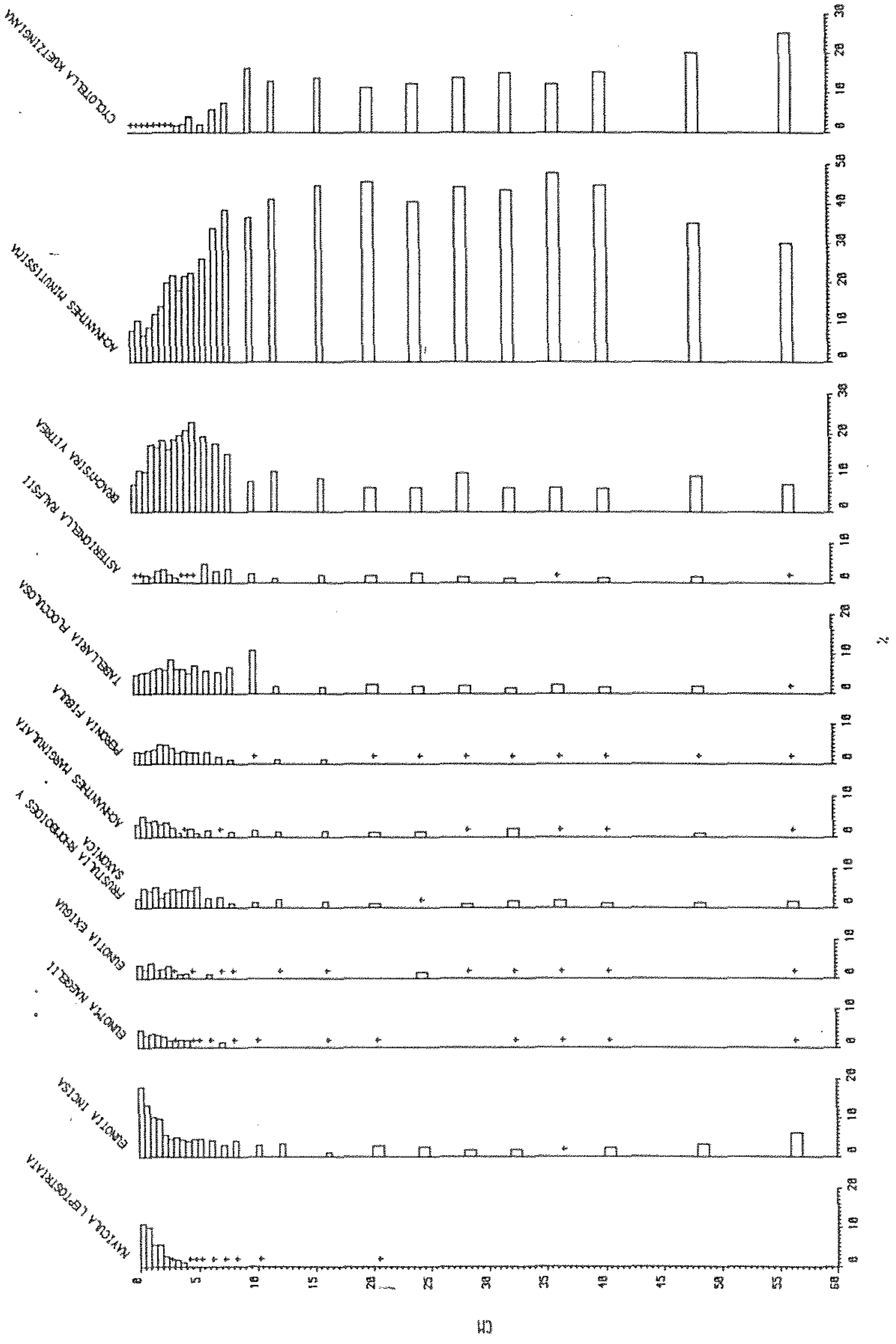
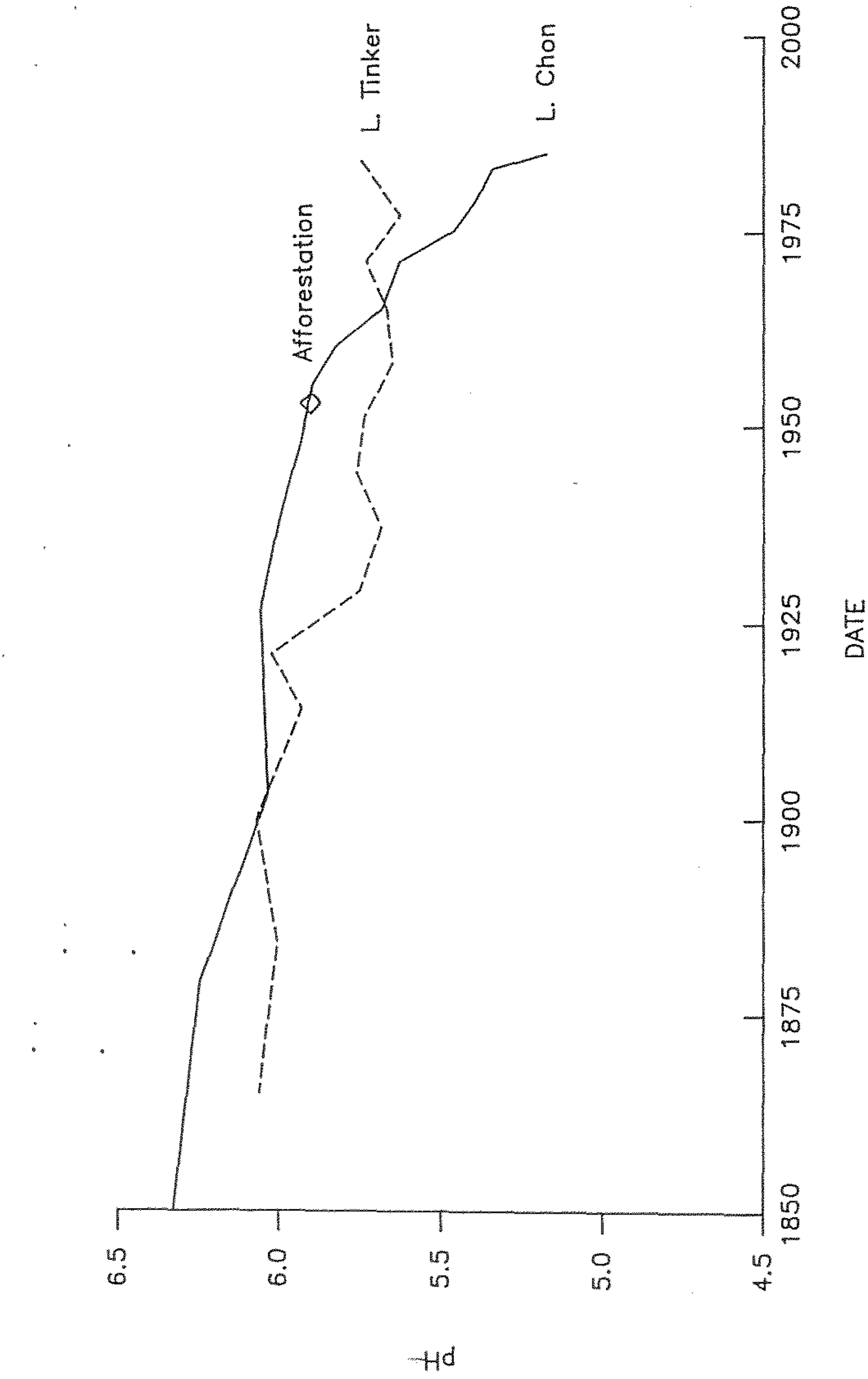


Figure 5.7 Loch Chon and Loch Tinker: pH reconstruction (WA)



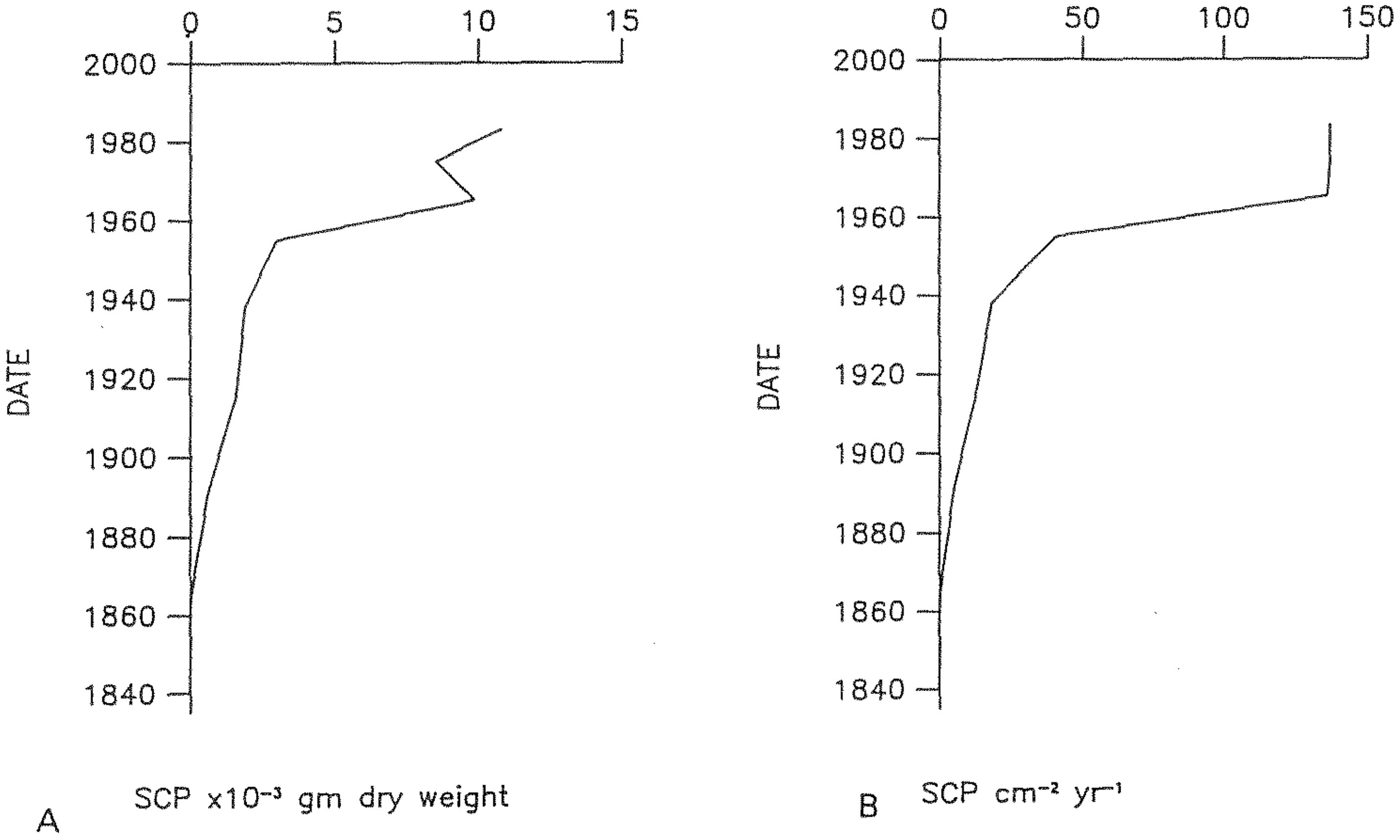


Figure 5.8 Loch Chon: carbonaceous particle record; a) concentration, b) flux

5.2.4 Loch Tinker: results

Two cores were taken from the deepest part of the loch in July 1985, using a modified Livingstone corer. Analytical methods follow those of Stevenson *et al.* (1987).

Lithostratigraphy

Comparison of the wet density, dry weight and LOI measurements for the two cores showed that both cores had similar sediment types and accumulation rates. Core TIN1 was chosen for analysis. The top 22 cm of this core consists of very dark brown organic detritus with some herbaceous plant remains. Some fine sand is also present to a variable extent and samples containing higher proportions of mineral material are evident from the increases in the percentage dry weight and at 7 cm and 16 cm. From 22-35 cm there is a gradual transition to a mid grey/brown organic sediment containing increasing amounts of clay and fine sand with some fibrous plant remains. The proportions of sand and clay vary, as can be seen from the wet density and dry weight measurements (Figure 5.9). Below 35 cm the sediment is dark grey with fine organic detritus, some clay (but less than above) and fibrous plant remains.

Dating

The core was taken prior to the Chernobyl incident so the chronology was based on the unsupported ^{210}Pb and nuclear weapons testing fallout isotopes. The unsupported ^{210}Pb inventory for the core is 18.43 pCi cm^{-2} which represents a constant supply rate of 0.57 pCi cm^{-2} yr^{-1}, higher than that found at Loch Chon (see above) but comparable with the expected atmospheric flux. Chronologies were calculated for the core using both the CIC and CRS dating models. There is little difference between the two sets of dates. In view of the reasonable ^{210}Pb flux and the inherent smoothing effect of the model, it was decided to use the CRS model to date the sediment (Table 5.4, Figure 5.10). Fortunately the disturbed sediment below 22 cm pre-dates the unsupported ^{210}Pb equilibrium level. The last c. 150 years are represented in the top 20 cm of the core, with accumulation rates varying between 0.11 and 0.17 cm yr^{-1}. There is an indication of an episode of accelerated sediment accumulation around 1870-1890 (14-16 cm). This is associated with increased ^{226}Ra and ^{40}K activities and higher sediment density, indicating a period of accelerated catchment erosion.

Diatom analysis

Diatoms were not analysed below 25 cm since this disturbed zone appears to contain very few diatoms and those that can be found are in a poor state of preservation. Changes in the principal diatom taxa down the core are summarised in Figure 5.11. The most significant change in the diatom flora of Loch Tinker has been the loss of a substantial *Cyclotella kuetzingiana* population from about 1850. The decline in *Cyclotella* appears to have begun as early as 1800. After 1850 (17.5 cm) there was an increase in the acidophilous diatom *Tabellaria flocculosa* along with the circumneutral diatom *Brachysira vitrea.* This is followed by a slight increase in *Frustulia rhomboides* v. *saxonica* at 12 cm (1900). Above 9 cm (1923) there is a decline in *Achnanthes minutissima* up to the sediment surface and an increase in *Fragilaria virescens* v. *exigua.* The surface sample has significantly more *F. virescens* v. *exigua* than any of the samples taken further down the core.

Diatom concentrations vary between 3 and 14 x 10^{6} cells g^{-1} dry weight. The diatom concentrations are depressed at three points: at 24 cm at the top of the disturbed zone, at 16 cm (1870) and at 7 cm (1939). These are the points identified by the wet density and dry weight data and also the sediment chemistry data as periods of increased catchment erosion. The flux of diatoms to the sediment follows a similar pattern, which would not be expected if the low concentrations at 7 cm and 16 cm were simply due to dilution from the catchment. One possible explanation could be that the values for sediment accumulation rate at these points has not been calculated from measurements made on sediment from these depths, but interpolated from the nearest measured levels.

Initial pH reconstructions using multiple regression of pH preference groups gave a reconstructed pH of 6.3 at 1800 declining to 6.0 by 1870 (16 cm) reflecting the loss of the *Cyclotella*. The pH was maintained at 6.0 until the mid-1920s when there was a slight shift to more acidic conditions with the reconstructed pH around pH 5.7-5.8. The surface sample, containing a higher proportion of *F. virescens* v. *exigua*, reconstructs at pH 6.1 (the measured mean pH is 6.0). pH reconstruction using weighted averaging (Figure 5.7) produces similar results although there are less fluctuations in the resulting pH against time profile. The surface sample reconstructs to pH 5.7-5.8. As in the Loch Chon reconstructions, the weighted averaging with tolerance downweighting tends to reconstruct values 0.1 pH units lower.

Pollen analysis

Figure 5.12 shows a summary diagram of the main pollen types. Pollen analysis of the dated section of the core shows an abundance of taxa indicating extensive blanket peat development in the catchment; for example, Cyperaceae, *Sphagnum* and *Calluna vulgaris*. Recent afforestation in the region is indicated by the presence of *Picea* pollen and the peak in *Pinus* in the surface sediment.

Carbonaceous particle analysis

Carbonaceous particle profiles for Loch Tinker are shown in Figure 5.13a, b. Particles are present from c. 1900 and show a significant increase from around 1950. However, the greatest increase is in the mid-1960s, as in the case of Loch Chon. The flux of particles to the sediment shows a similar trend.

Geochemistry

Within the dated section of the core high concentrations of sodium and potassium occur at 16 cm and 7 cm (1870 and 1939). This provides further evidence for short periods of catchment disturbance at these times. Zinc and lead values follow the trends seen at other polluted sites (eg. Battarbee *et al.* 1988), although some dilution of these metals has occurred at 16 and 7 cm (Figure 5.14). Sulphur concentrations also follow the same trend. There is a significant decrease in zinc, lead and sulphur after 1970 which probably reflects the decrease in input from the atmosphere.

Magnetic analysis

In progress

Figure 5.9 Loch Tinker: lithostratigraphy

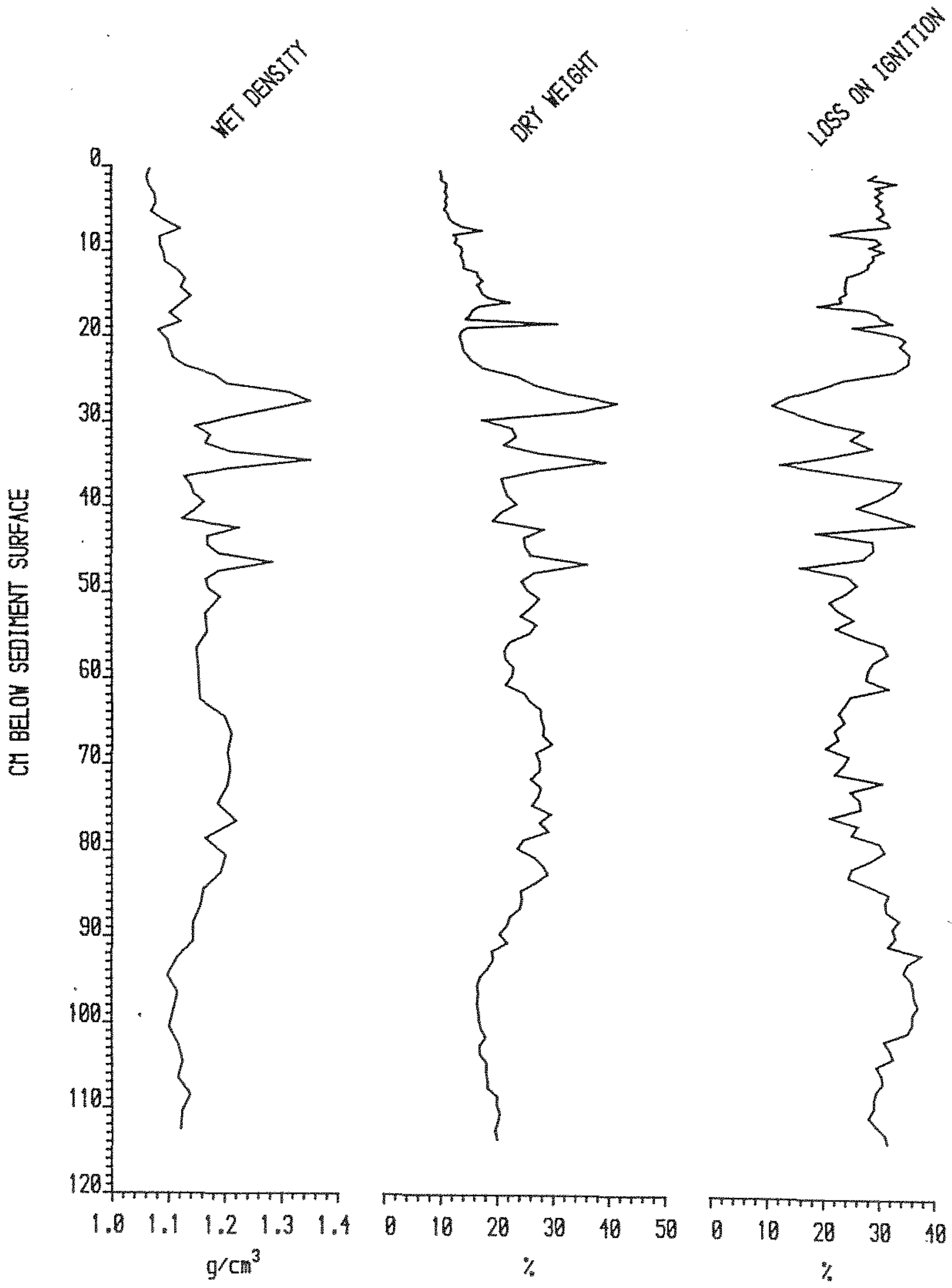


Table 5.4 Loch Tinker: ^{210}Pb chronology

DEPTH	DRYMASS	CUM UNSUPP	CHRONOLOGY			SEDIMENTATION RATE		
		PB-210	DATE	AGE	STD			% STD
CM	G/CM**2	PCI/CM**2	AD	YR	ERROR	G/CM**2YR	CM/YR	ERROR
0.00	0.0000	18.43	1985	0				
1.00	0.1127	15.31	1979	6	2	0.0193	0.166	4.8
2.00	0.2288	12.69	1973	12	2	0.0195	0.165	5.0
3.00	0.3476	10.39	1967	18	2	0.0186	0.155	5.5
4.00	0.4692	8.39	1960	25	2	0.0167	0.136	6.3
5.00	0.5940	6.77	1953	32	2	0.0177	0.136	7.5
6.00	0.7221	5.48	1946	39	2	0.0216	0.154	9.2
7.00	0.8631	4.37	1939	46	3	0.0224	0.155	11.0
8.00	1.0169	3.44	1931	54	4	0.0201	0.136	12.8
9.00	1.1707	2.71	1923	62	4	0.0179	0.118	14.7
10.00	1.3241	2.12	1916	69	5	0.0197	0.125	17.7
11.00	1.4831	1.68	1908	77	7	0.0234	0.141	22.3
12.00	1.6430	1.36	1901	84	8	0.0249	0.142	27.1
13.00	1.8276	1.10	1894	91	10	0.0233	0.153	33.0
14.00	2.0217	0.89	1888	97	12	0.0335	0.172	40.0
15.00	2.2194	0.68	1879	106	16	0.0317	0.160	46.7
16.00	2.4205	0.48	1868	117	21	0.0226	0.115	53.2
17.00	2.6217	0.35	1857	128	27	0.0136	0.071	59.6

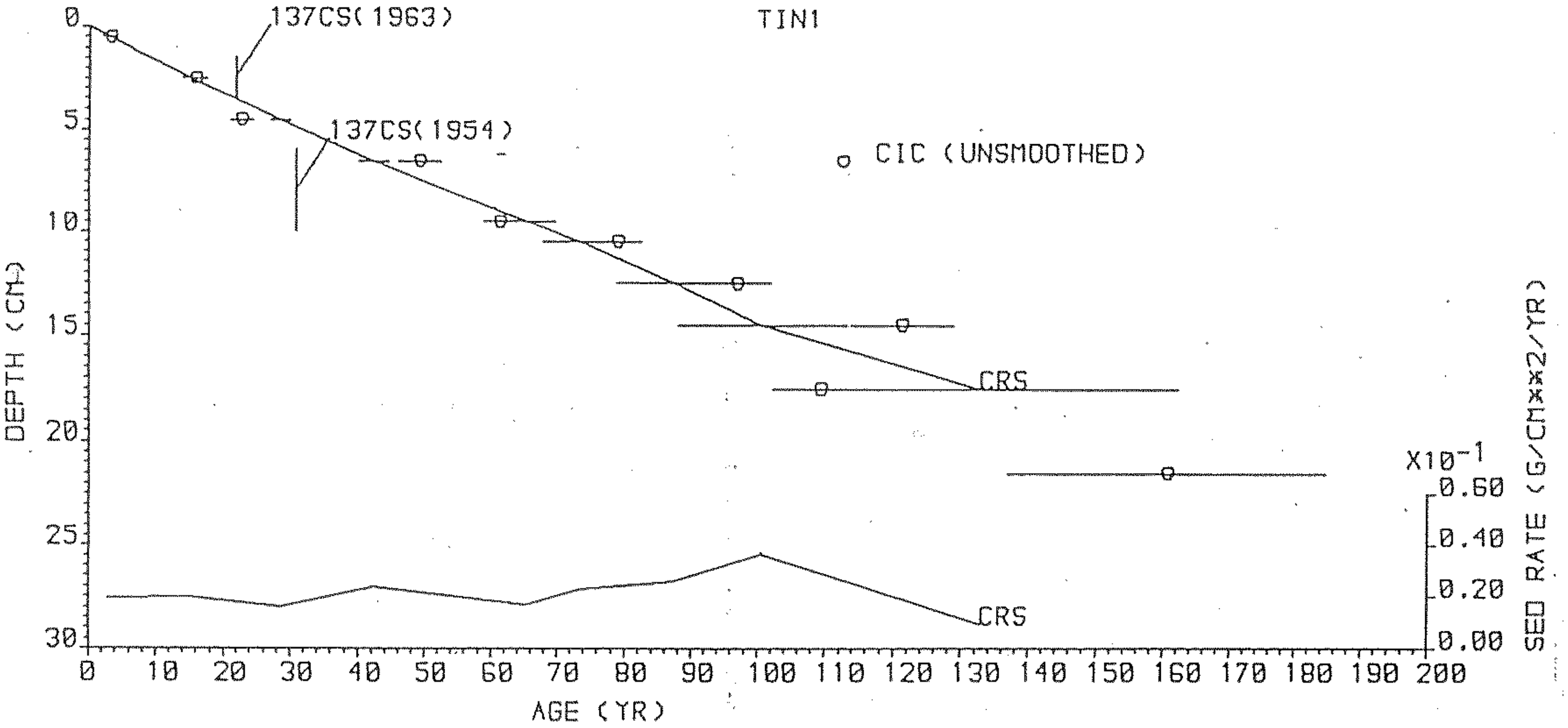


Figure 5.10 Loch Tinker: ^{210}Pb chronology

Figure 5.11 Loch Tinker: diatom summary diagram

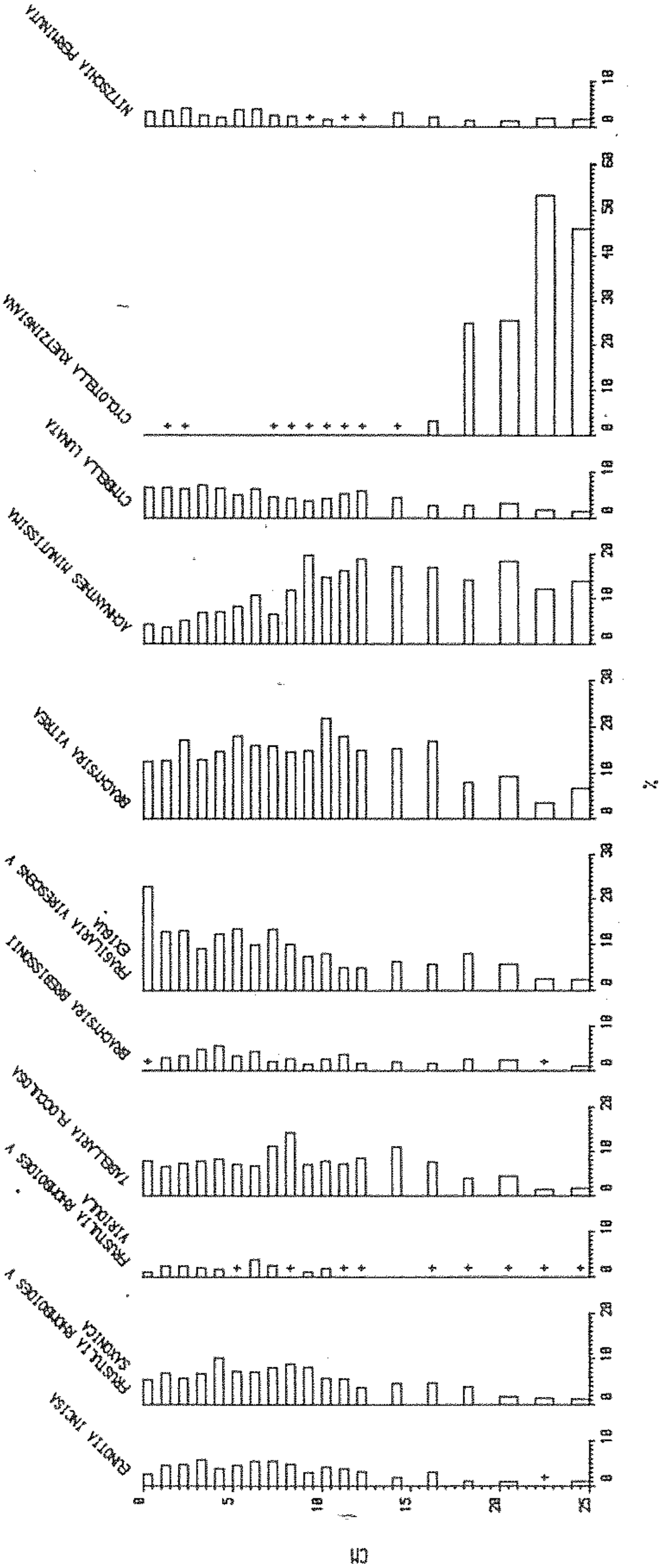
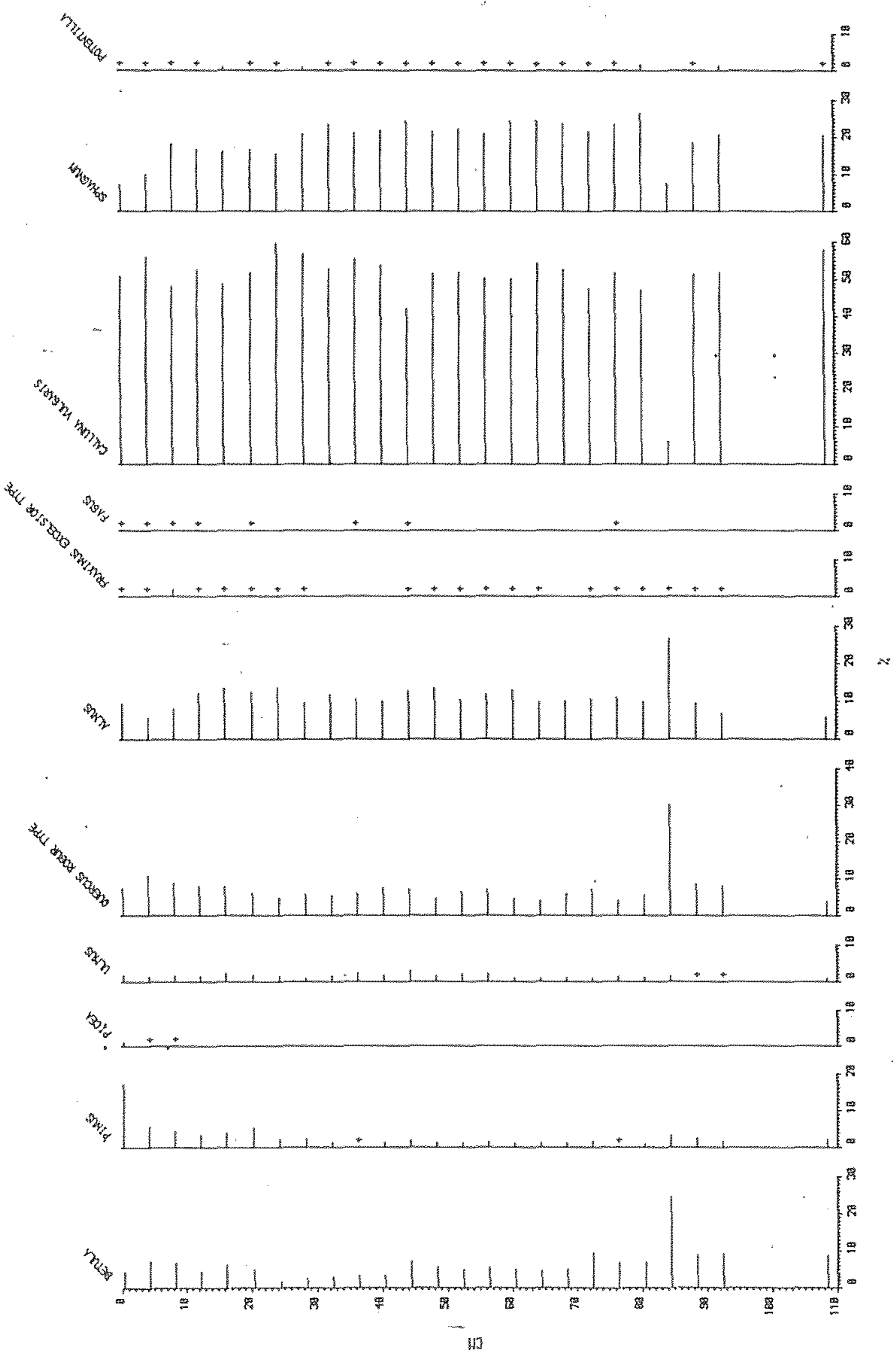


Figure 5.12 Loch Tinker: summary pollen diagram



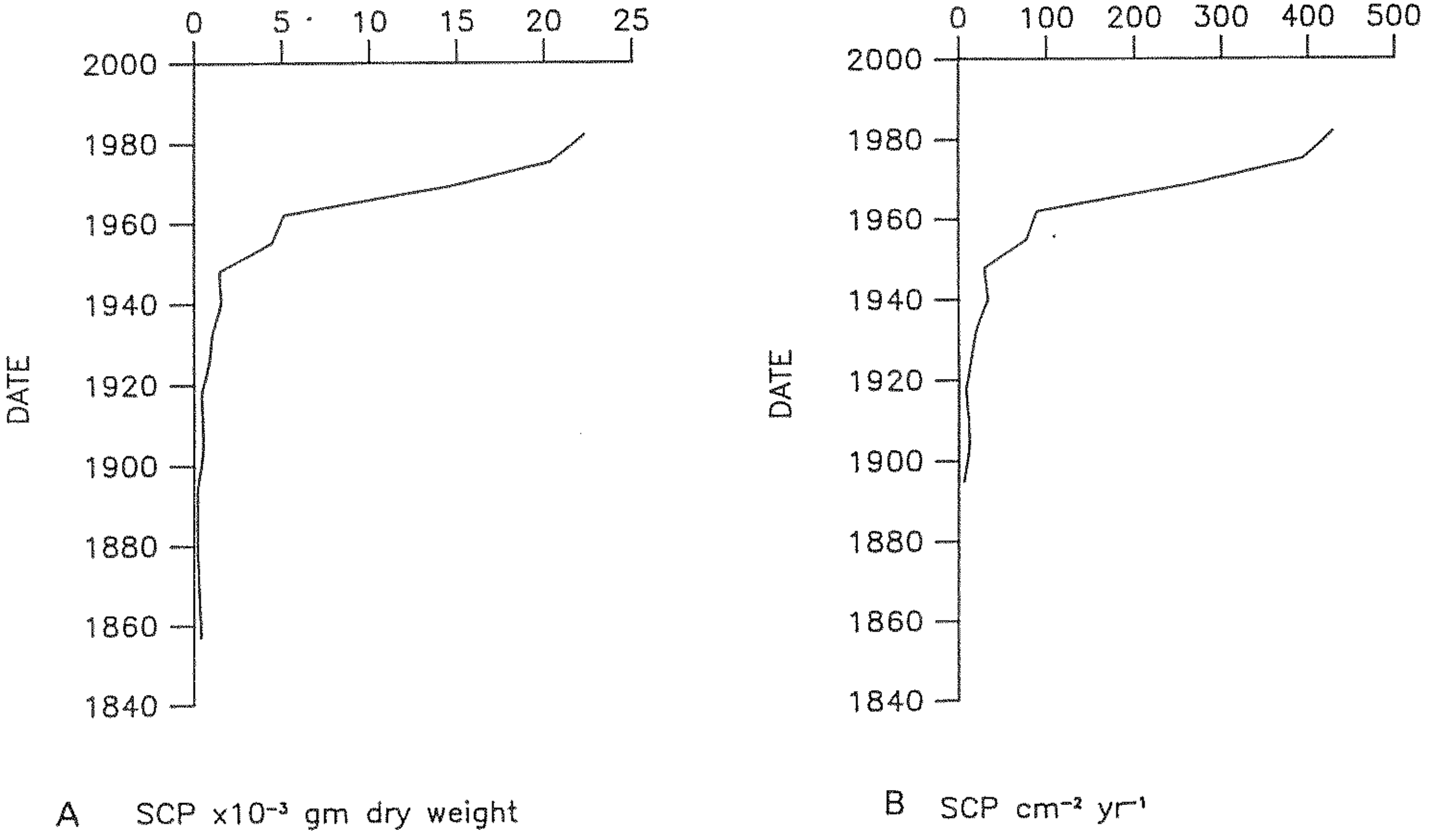
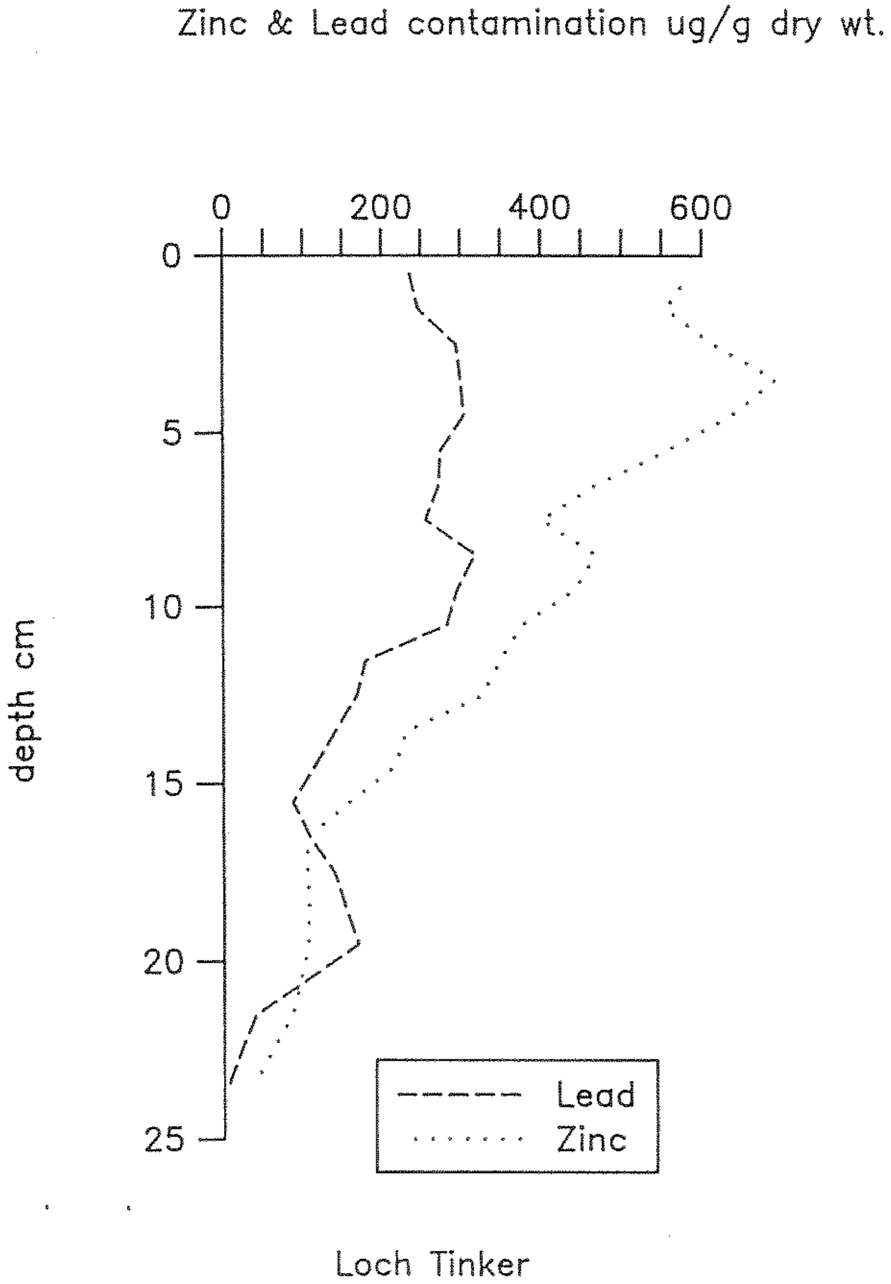


Figure 5.13 Loch Tinker: carbonaceous particle record; a) concentration, b) flux

Figure 5.14 Loch Tinker: sediment zinc and lead concentrations



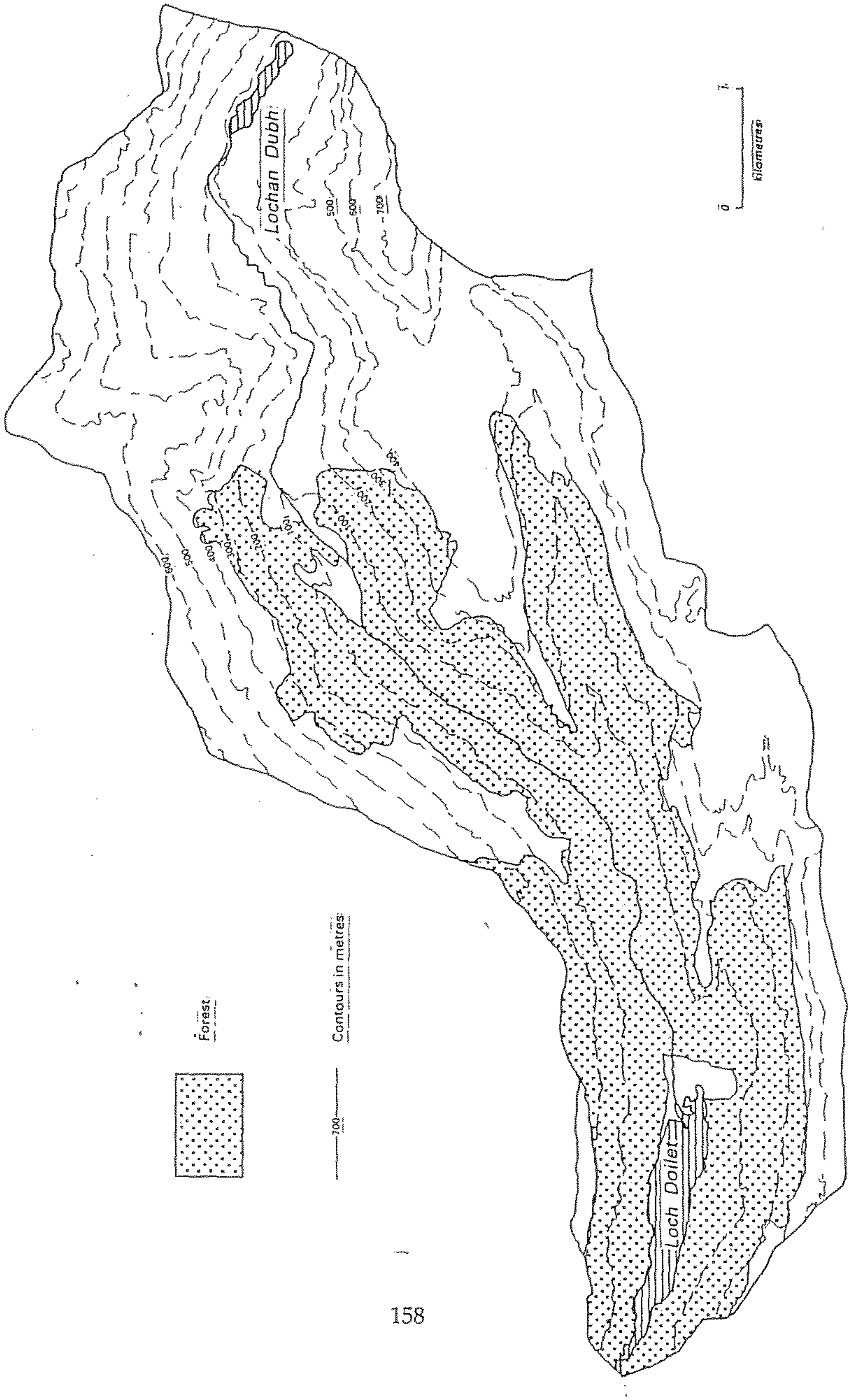
5.3 WESTERN SCOTLAND - THE STRONTIAN/LOCH SHEIL AREA

This region (Figure 1.1) was chosen as an area receiving moderate to low levels of acid deposition. Deposited sulphur amounts to 0.97 g m^{-2} yr^{-1}. The two sites chosen were Loch Doilet, the afforested site and Lochan Dubh, a small loch at the top of the Loch Doilet catchment with moorland catchment vegetation. Lochan Dubh is the source of the River Hurich which runs through the Loch Doilet catchment into Loch Doilet (Figure 5.15).

Table 5.5 Strontian area - characteristics of study sites

	Loch Doilet	**Lochan Dubh**
Grid reference	NM 808678	NM 895711
Geology	Schists & granulites	Schists & granulites
Catchment vegetation	Conifers/moorland	Moorland
% Forest	41%	0%
Lake altitude	10 m	230 m
Net relief	790 m	550 m
Maximum depth	16.8 m	9 m
Mean depth	6.3 m	1.6 m
Lake area (ha)	53	8.8
Lake volume (m^3 x 10^3)	3340	137
Catchment area (ha) excl. lake	3289	157

Figure 5.15 The Loch Doilet/Lochan Dubh catchment



5.3.1 Catchment descriptions

Geology

The entire catchment of Loch Doilet and Lochan Dubh is underlain by metamorphosed sediments of the Moine series, composed of psammitic and pelitic schists resulting from the metamorphosis of sedimentary sandstones and shales. There are a few Tertiary dolerite or basalt dykes (Phemister 1948, Richey 1961) and several areas are overlain by blanket peat.

Vegetation

In areas not under coniferous forest (Figure 5.15) the vegetation is principally dominated by *Molinia* and *Calluna*. There is a moderate amount of sheep grazing at the head of the catchment around Lochan Dubh. Some peat erosion has occurred in both catchments.

Forestry

Over 90% of the Forestry Commission plantation comprises Sitka spruce with other conifers making up the remainder, although recent plantations and second rotation crops also contain 5% hardwoods. Trees were first planted in the catchment from 1920 although only a few pockets of this original plantation remain. A substantial part of this first plantation on the north facing slopes of the river valley was destroyed by fire in 1941 and replanted in the 1960s. Extensive planting also occurred in the 1930s and 1950s. Generally no ground preparation was required in these early plantations on the steeper slopes but if any drains were made they were dug by hand. The trees were 'notched in', also by hand, at a density of c. 2900-3400 trees ha^{-1}. Planting since 1960 has involved ploughing and deep drainage in the wetter areas although trees were still planted directly into the ground on the steeper slopes. Planting has now become viable on ground further up the valley due to recent improvements in forestry techniques and the development of more tolerant varieties of Sitka spruce. The digging of cross-drains using a tracked excavator has also been introduced since 1983 leading to subsoil erosion in some places. Clear felling of the older plantations began in 1975 with replanting 3 or 4 years later. Fertiliser has been used extensively in the catchment. Prior to the 1960s basic slag (16-22% P_2O_5) was used. After 1960 superphosphates were used (18-20% P_2O_5 and 50% $CaSO_4$). From 1970 unground rock phosphate has been applied at a rate of 375 kg ha^{-1}. Prior to 1975 all fertilisers were applied by hand, generally as a spot application. Since 1975 the unground rock phosphate has been applied from a helicopter at 375-400 kg ha^{-1}.

A major programme of forest road construction began in the 1960s and the roads have been extended since then. River gravels have been extracted from the River Hurich for use in road construction since 1985, causing noticeable turbidity and deposition of silt in the littoral zone of Loch Doilet.

5.3.2 Lake descriptions

Loch Doilet is a moderately deep lake with two distinctive sub-basins both exceeding 15 m (Figure 5.16); Lochan Dubh possesses several small islands and has a more complex bathymetry with three - four shallow sub-basins and a deepest point of 9 m (Figure 5.17).

The mean chemistry values for the period 1986-1987 (6 samples from each site) are shown in Table 5.6. The value for pH of one sample from Loch Doilet is abnormally low and values for sodium and chloride are unusually high. This would indicate a 'sea salt event' and the inclusion of this sample in the mean chemistry values gives a misleading mean pH of 5.6. The mean values calculated with this sample included are given in parentheses. The calcium values show that both sites are vulnerable to acidification although neither appears strongly acidified. As in the case of Loch Chon, the higher sodium, chloride and sulphate values in Loch Doilet suggest a scavenging and concentrating mechanism in the forest.

Table 5.6 **Loch Doilet and Lochan Dubh: water chemistry (1985-1987)**

		Loch Doilet	Lochan Dubh
pH		5.9 (5.6)	5.6
Cond	μS cm^{-1}	38.0 (44.0)	29.0
Ca^{2+}	μeq l^{-1}	47.0 (54.0)	33.0
Mg^{2+}	μeq l^{-1}	49.0 (61.0)	40.0
K^+	μeq l^{-1}	12.0 (13.0)	8.0
Na^+	μeq l^{-1}	209.0 (239.0)	163.0
Cl^-	μeq l^{-1}	216.0 (277.0)	185.0
SO_4^{2-}	μeq l^{-1}	68.0 (71.0)	40.0
Alkalinity (Alk$_e$)	μeq l^{-1}	19.0 (15.0)	10.0
TOC	mg l^{-1}	2.4	2.8
Al^{3+}	μg l^{-1}		
Labile		7.0	11.0
Total		48.0	33.0

Fish

No written records are available for the two lochs. The following information was obtained from the local angling club (J. Bannaman pers. comm.)

In the past Loch Doilet was a good loch for sea trout and salmon whereas now very few are caught. The decline in fish catches dates from the beginning of clear felling in the mid-1970s and the accompanying road construction in Glen Hurich. The loss of spawning grounds resulting from changes in the stream bed sediment load is thought to be the cause of fish decline, although this can not be verified since anglers have been unable to carry out checks on the streams at spawning times. Changes in the sediment and turbidity of the water were also observed in Loch Doilet at this time.

Lochan Dubh used to have a good brown trout population, although since c. 1980 the population has been dominated by smaller fish with only a few larger individuals caught. The loch is visited infrequently by anglers owing to its inaccessibility.

Figure 5.16 Loch Doilet: bathymetry (contours in metres)

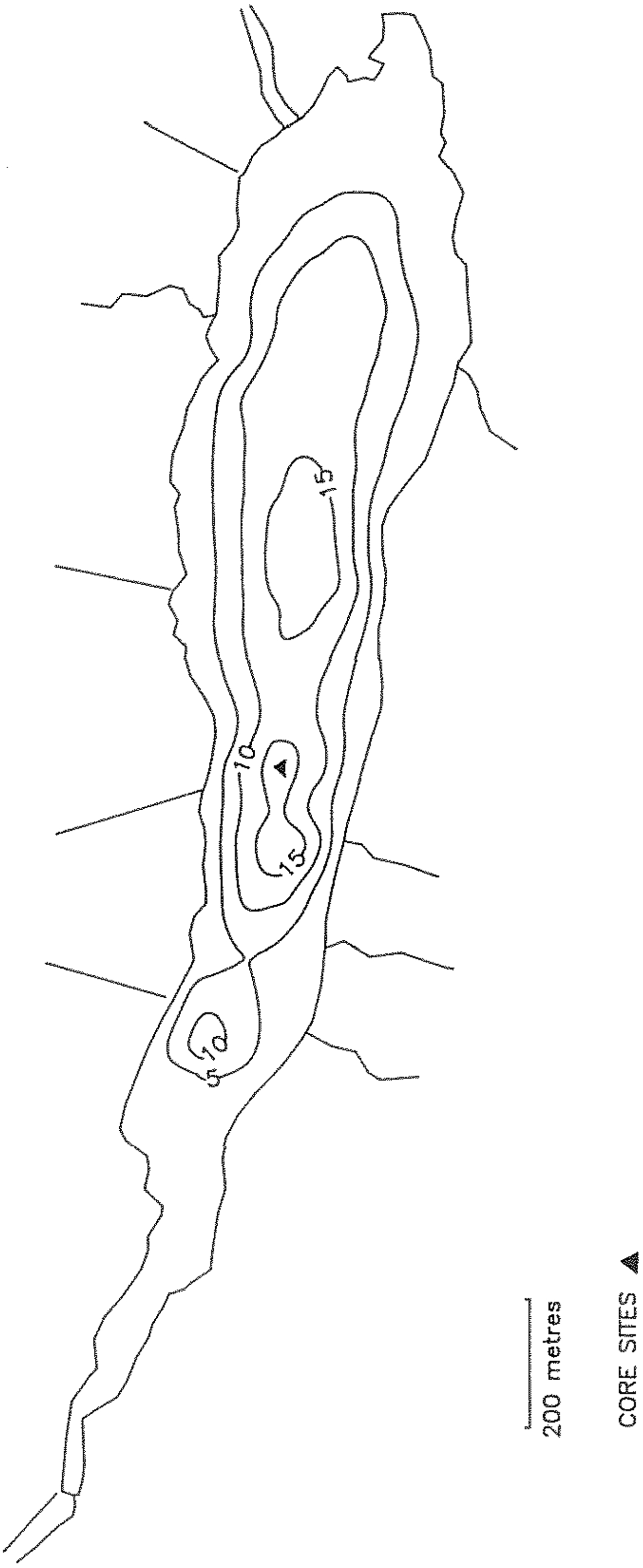
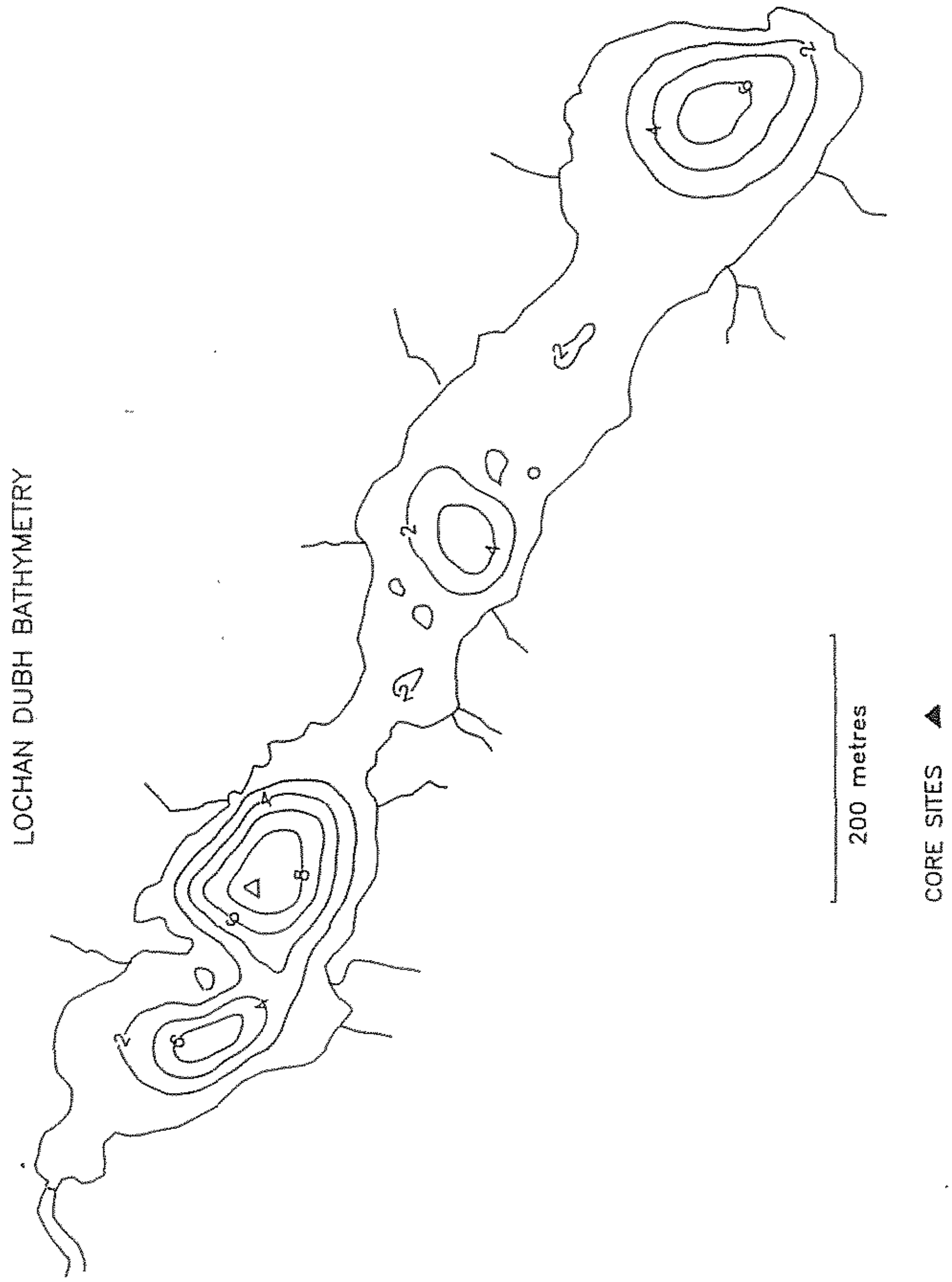


Figure 5.17 Lochan Dubh: bathymetry (contours in metres)



5.3.3 Loch Doilet: results

Two sediment cores were taken from the deepest area of the lake in June 1986, using a modified Livingstone corer. The dry weight and LOI profiles of both cores can be correlated to show similar sediment accumulation rates, but core DOI2 was chosen for analysis. Laboratory methods follow Stevenson *et al.* (1987).

Lithostratigraphy

Most of the core sediment is dark brown, fine, organic detritus with occasional coarser detritus. In both cores there is a band of slightly paler sediment (grey/brown) between 43 and 46 cm. In core DOI1 there were also some coarse herbaceous plant remains between 93 and 95 cm (Figure 5.18).

Although the dry weight and LOI values show some fluctuations (Figure 5.18), the features of rapidly increasing LOI, characteristic of cores from some afforested sites, is missing. This is no doubt due to the minimal disturbance to the soil when the bulk of the forest was planted. Later use of ploughing and mechanised drainage has taken place in relatively small areas of the catchment over 20 years or more, so the impact on the sediment accumulating in Loch Doilet might not be immediately discernable. The recent extraction of gravel from the main inflow, the River Hurich, has not resulted in a marked increase in the dry weight values at the top of the core, despite reports of large amounts of suspended sediment in the loch at the time.

Dating

The core was taken after the Chernobyl incident so the sediment was analysed for the short-lived ^{134}Cs along with ^{137}Cs and unsupported ^{210}Pb. The unsupported ^{210}Pb inventory of the core was calculated to be 19.3 pCi cm^{-2}, representing a ^{210}Pb flux of 0.60 pCi cm^{-2} yr^{-1}. This is almost twice the value in nearby Lochan Dubh and presumably reflects the longer residence time and greater sediment trapping efficiency in Loch Doilet. Calculations using the CRS ^{210}Pb model (Appleby and Oldfield 1978) indicate that the accumulation rate has increased steadily from around 0.028 g cm^{-2} yr^{-1} during the period 1880-1920 to about 0.051 g cm^{-2} yr^{-1} in the 1950s, with a peak value of 0.066 g cm^{-2} yr^{-1} around 1970. The CIC model is not suitable for dating this core due to the fluctuations in accumulation rate.

Traces of ^{134}Cs from the Chernobyl fallout were found in the surface sediment, although there was very little deposition in the area of Loch Doilet (Clarke and Smith 1988). The ^{137}Cs activity in the top 1 cm can therefore also be attributed to the Chernobyl fallout. Further down the core there is a separate ^{137}Cs peak at 9.5-10 cm which can be attributed to the 1963 peak in atmospheric nuclear weapons testing. The ^{241}Am record is less distinct but suggests that 11.5-12 cm should be dated 1963. Both these results broadly support the CRS model calculations (Table 5.7, Figure 5.19) which date these levels to the period 1961-1967. A number of sites with low pH values have been characterised by extensive ^{137}Cs diffusion within the sediment. The relative lack of ^{137}Cs mobility at this site is indicated by the well defined peak at 9.5-10 cm and is supported by the fact that approximately 90% of the ^{137}Cs inventory lies above the level dated to 1954 by ^{210}Pb.

Diatom analysis

A summary diagram of the diatom profiles from Loch Doilet is shown in Figure 5.20. The diatom assemblages generally contain the same taxa as the Lochan Dubh core (see below), although in Loch Doilet *Eunotia exigua* is present to a far greater extent and the proportion of *B. brebissonii* is greatly reduced. There are no planktonic taxa recorded in the core. The first significant floristic change is a reduction in percentages of the two circumneutral taxa *B. vitrea* and *A. minutissima* above 32 cm (about 1860) with a slight increase in the acidophilous diatom

T. flocculosa over the same period. Between 24 cm and 20 cm these trends are reversed but from 20 cm (1931) to 8 cm (1971) *B. vitrea* and *A. minutissima* continue to decline, gradually accompanied by increases in acidophilous taxa such as *Eunotia incisa* and *E. exigua* above 16 cm (1947). Above 8 cm there is no obvious change in the diatom flora.

The diatom concentration values fluctuate below 48 cm and any trends are difficult to resolve due to the wide sampling intervals. However, above 24 cm there is a steady decline in diatom concentration.

The floristic changes observed in the core result in a slight decline in the reconstructed pH (weighted averaging) (Figure 5.21) beginning at around 32 cm (1850s). Below 24 cm the reconstructed pH fluctuates between 5.8 and 6.0. The reconstructed pH declines gradually from 24 cm (1913) and more rapidly from 5.7-5.5 above 20 cm (1931) to 5.3 at the surface. This reconstructed surface sediment value is substantially different from the measured mean pH of 5.9. After the initial pH decline there are two points of slightly higher pH at c. 1931 and c. 1966.

Pollen analysis

The main pollen types are shown in Figure 5.22. Peatland indicators such as *Calluna vulgaris*, *Sphagnum* and Cyperaceae dominate throughout the core. There is an increase in *Pinus* in the top 8 cm and a trace of *Picea* in the top 4 cm as a result of the recent afforestation of the catchment. This difference in the sedimentary pollen record of the two genera is understandable, taking into account the delay between spruce planting and pollen production (10-20 years) and the relatively small amount of pollen produced by spruce compared with pine.

Carbonaceous particle analysis

The carbonaceous particle profile for Loch Doilet is shown in Figure 5.23. There is a small increase in particle concentration at 18 cm (c. 1940) but the main increase occurs above 10 cm (1966), declining slightly above 4 cm. As in the Lochan Dubh core, these concentrations are very low compared with the sites in the Trossachs.

Geochemistry

A full report on the sediment chemistry is in progress, but analysis of the trace metals zinc and lead does not show the characteristic post-1800 increase in these metals seen at other sites (eg. Battarbee *et al.* 1988). Since some contamination is evident at Lochan Dubh nearby (see below) it seems probable that in Loch Doilet low atmospheric fluxes combined with a rapid sediment accumulation rate and high mineral input from the catchment have obscured the record of atmospheric contamination.

Magnetic analysis

In progress

Figure 5.18 Loch Doilet: lithostratigraphy

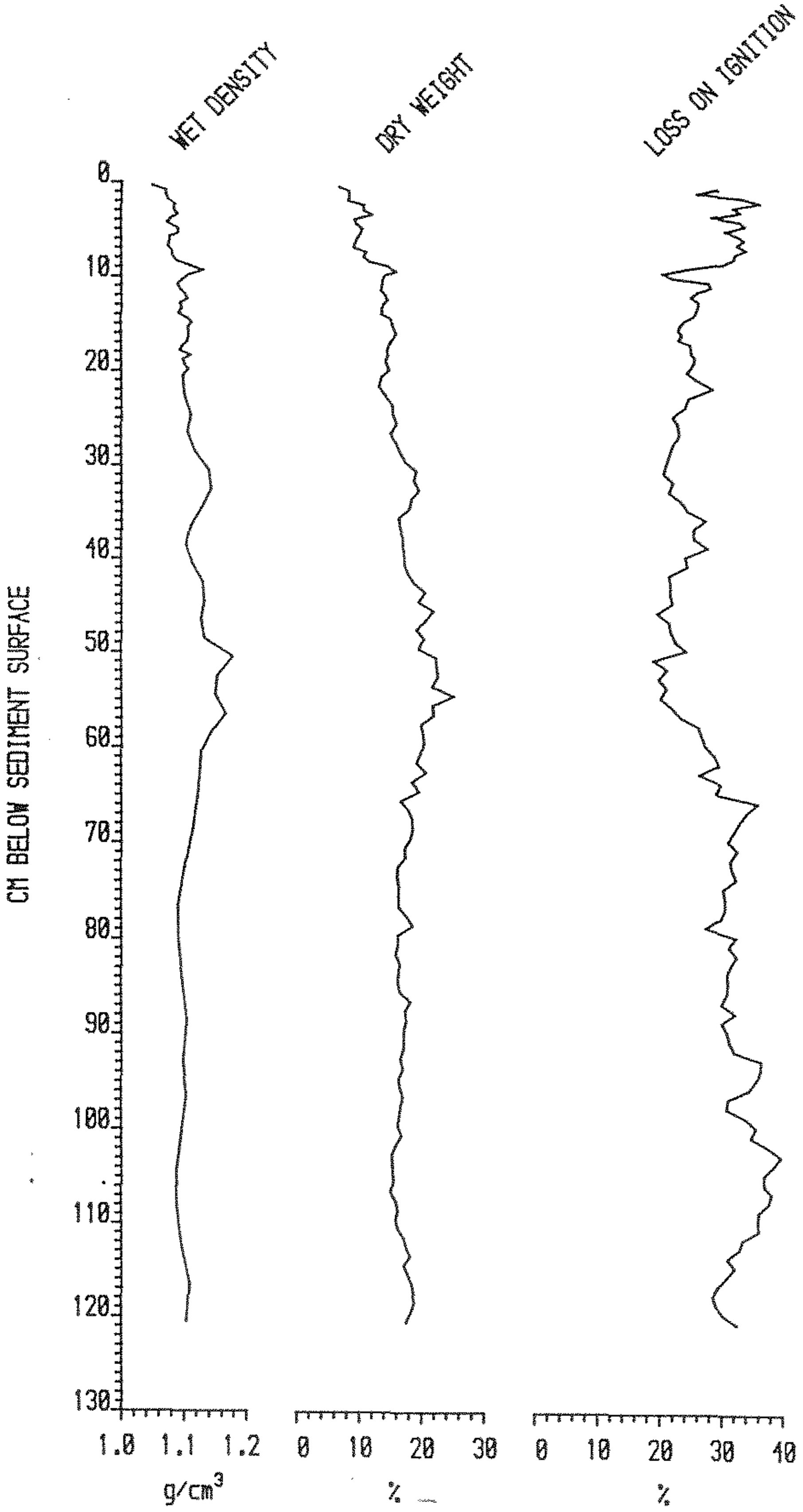


Table 5.7 Loch Doilet: ^{210}Pb chronology

Depth	Dry Mass	Chronology			Sedimentation Rate		
		Date	Age				
cm	gcm^{-2}	AD	yr	±	gcm^{-2}yr^{-1}	cmyr^{-1}	± (%)
0.00	0.0000	1987	0				
1.00	0.0825	1986	1	2	0.0863	0.925	17.5
2.00	0.1776	1985	2	2	0.0640	0.617	11.2
3.00	0.2862	1983	4	2	0.0549	0.501	9.2
4.00	0.3994	1980	7	2	0.0503	0.449	8.7
5.00	0.5125	1978	9	2	0.0457	0.398	8.2
6.00	0.6256	1976	11	2	0.0411	0.347	7.7
7.00	0.7504	1973	14	2	0.0494	0.389	9.3
8.00	0.8790	1971	16	2	0.0620	0.462	11.6
9.00	1.0075	1968	19	2	0.0747	0.535	13.9
10.00	1.1562	1966	21	2	0.0684	0.476	13.0
11.00	1.3116	1963	24	2	0.0558	0.373	11.1
12.00	1.4676	1960	27	2	0.0470	0.298	10.1
13.00	1.6257	1957	30	2	0.0494	0.308	12.1
14.00	1.7838	1954	33	2	0.0518	0.318	14.1
15.00	1.9452	1951	36	2	0.0521	0.317	15.2
16.00	2.1163	1947	40	3	0.0464	0.283	13.6
17.00	2.2874	1943	44	3	0.0407	0.250	12.0
18.00	2.4548	1939	48	3	0.0367	0.226	11.1
19.00	2.6108	1935	52	3	0.0377	0.233	12.4
20.00	2.7668	1931	56	3	0.0388	0.240	13.8
21.00	2.9228	1927	60	4	0.0399	0.247	15.1
22.00	3.0788	1923	64	4	0.0410	0.253	16.4
23.00	3.2424	1918	69	4	0.0386	0.237	17.8
24.00	3.4135	1913	74	5	0.0328	0.198	19.3
25.00	3.5847	1908	79	5	0.0269	0.159	20.8
26.00	3.7574	1901	86	6	0.0238	0.136	22.8
27.00	3.9317	1894	93	8	0.0235	0.128	25.4
28.00	4.1167	1884	103	10	0.0212	0.112	32.9
29.00	4.3122	1872	115	15	0.0168	0.087	45.4
30.00	4.5078	1860	127	19	0.0125	0.063	57.9
31.00	4.7154	1847	140	23	0.0116	0.056	67.6
32.00	4.9349	1833	154	25	0.0142	0.069	74.6

Mean ^{210}Pb Flux = 0.60±0.03 pCicm^{-2}yr^{-1}
90% Equilibrium Depth = 24.2 cm, or 3.44 gcm^{-2}
99% Equilibrium Depth = 31.9 cm, or 4.88 gcm^{-2}

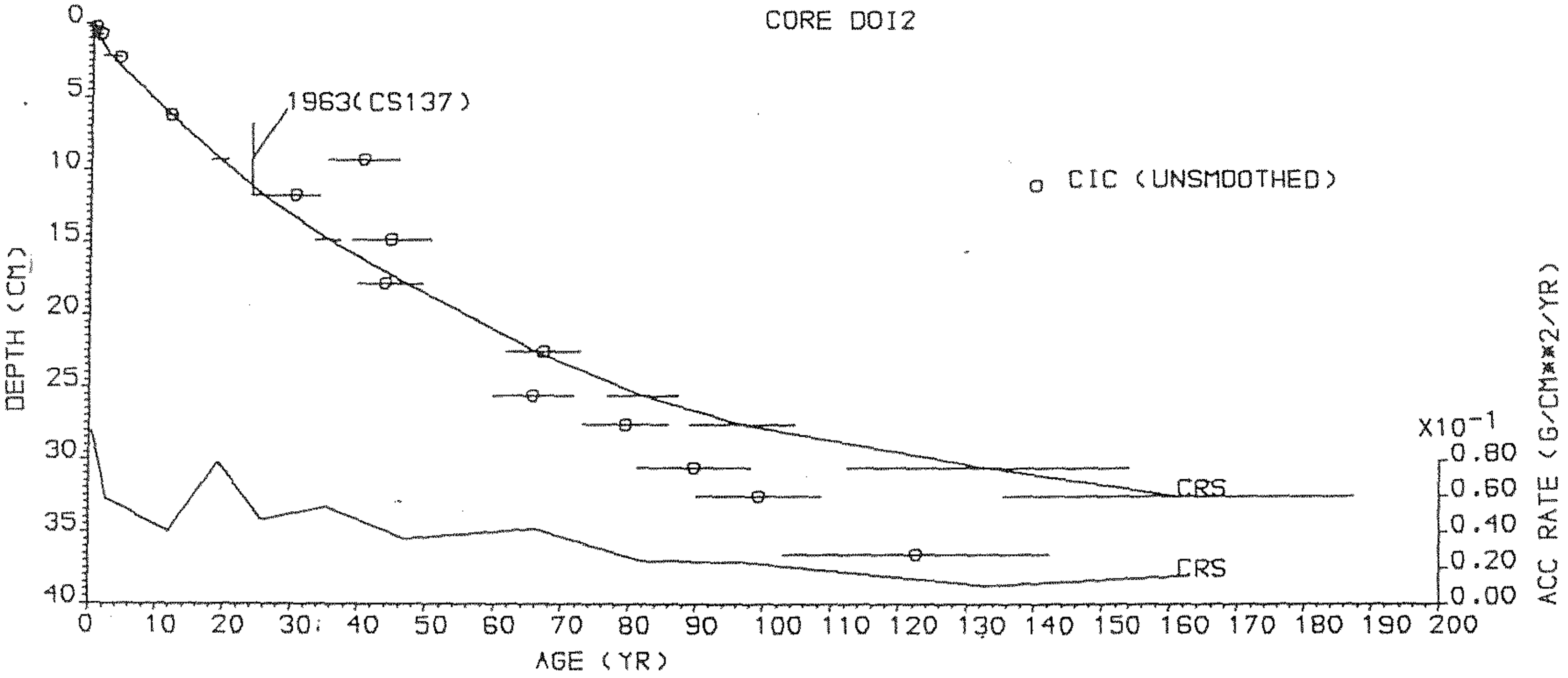


Figure 5.19 Loch Doilet: ^{210}Pb chronology

Figure 5.20 Loch Doilet: diatom summary diagram

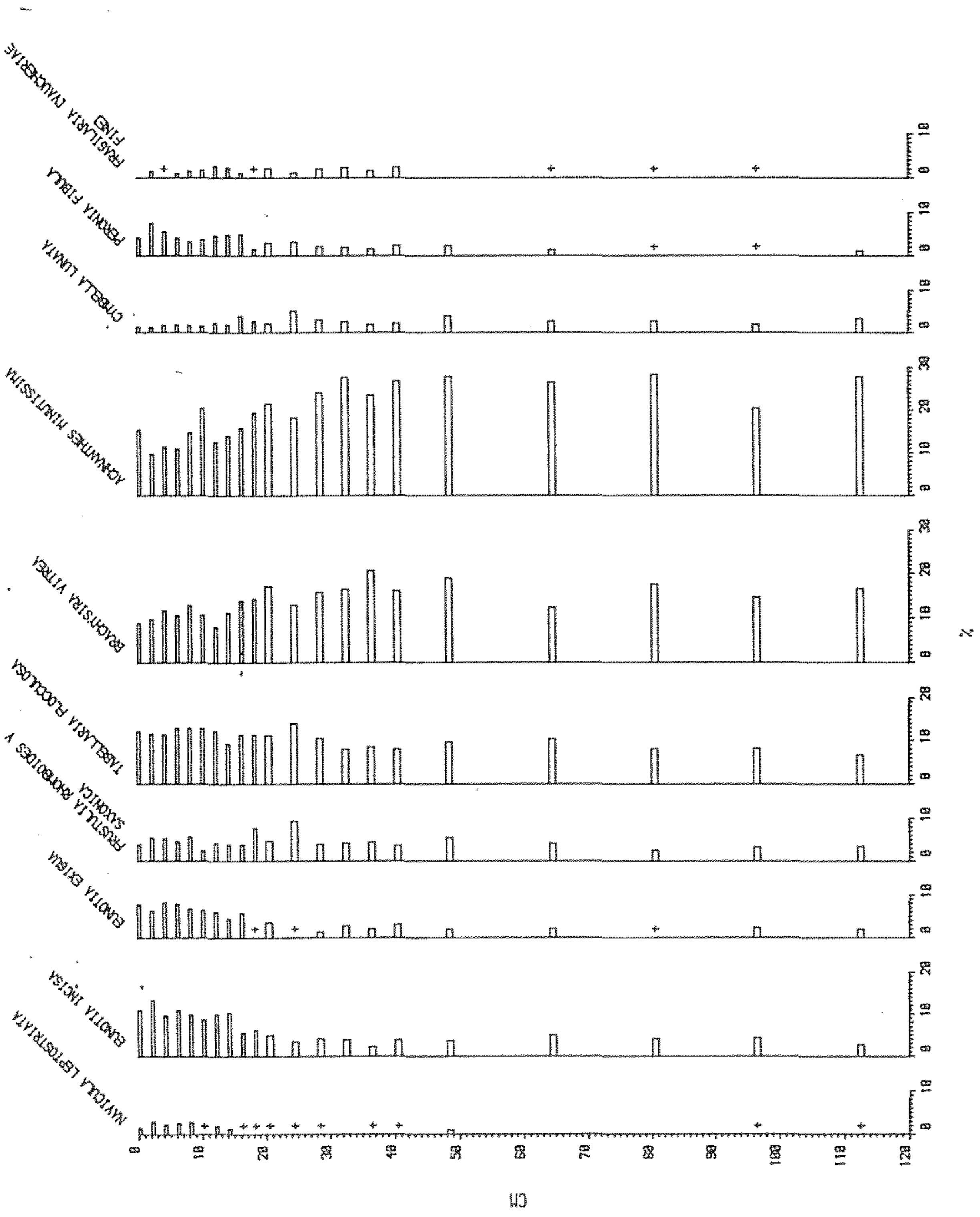


Figure 5.21 Loch Doilet and Lochan Dubh: pH reconstructions (WA)

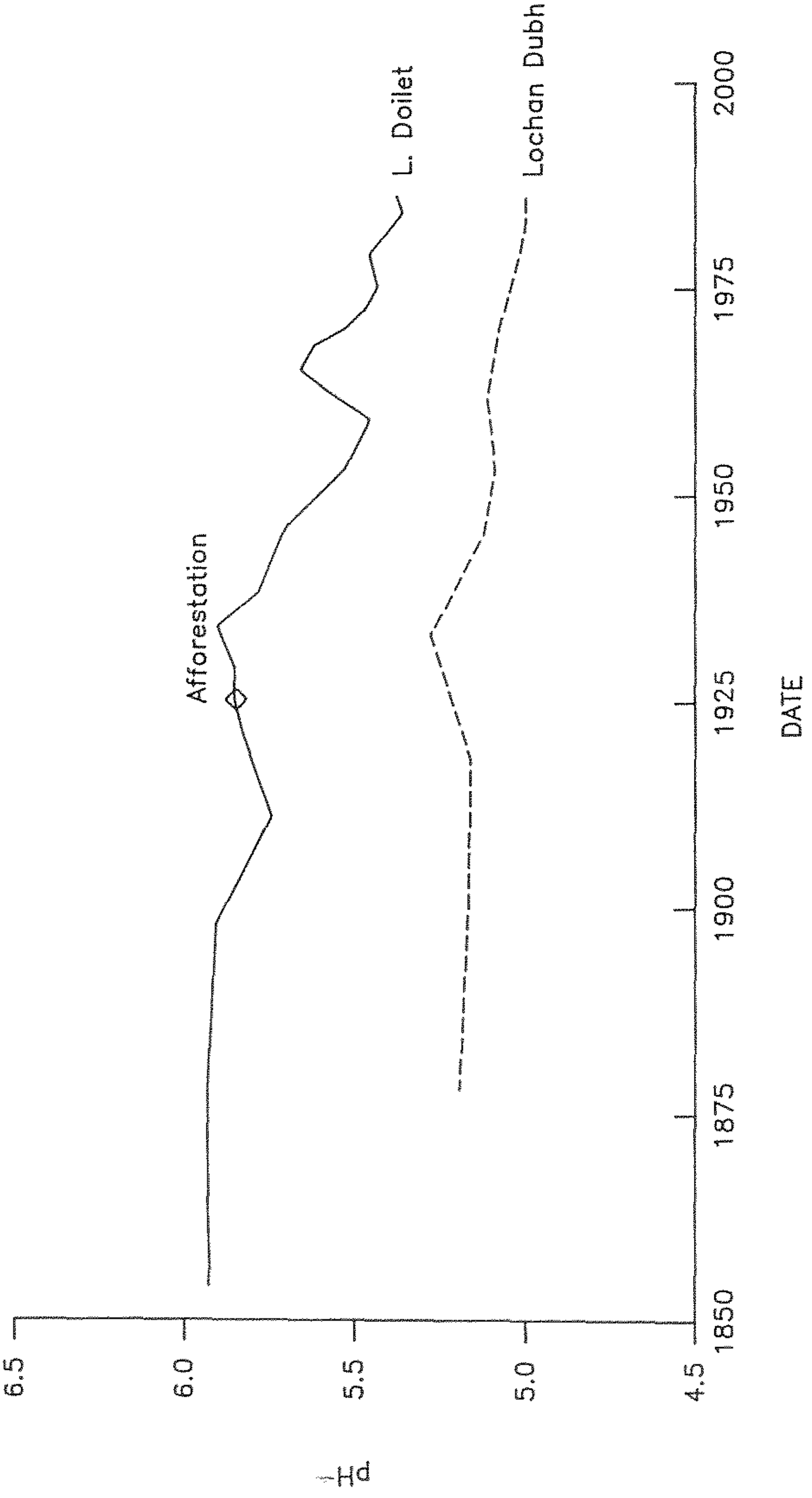


Figure 5.22 Loch Doilet: summary pollen diagram

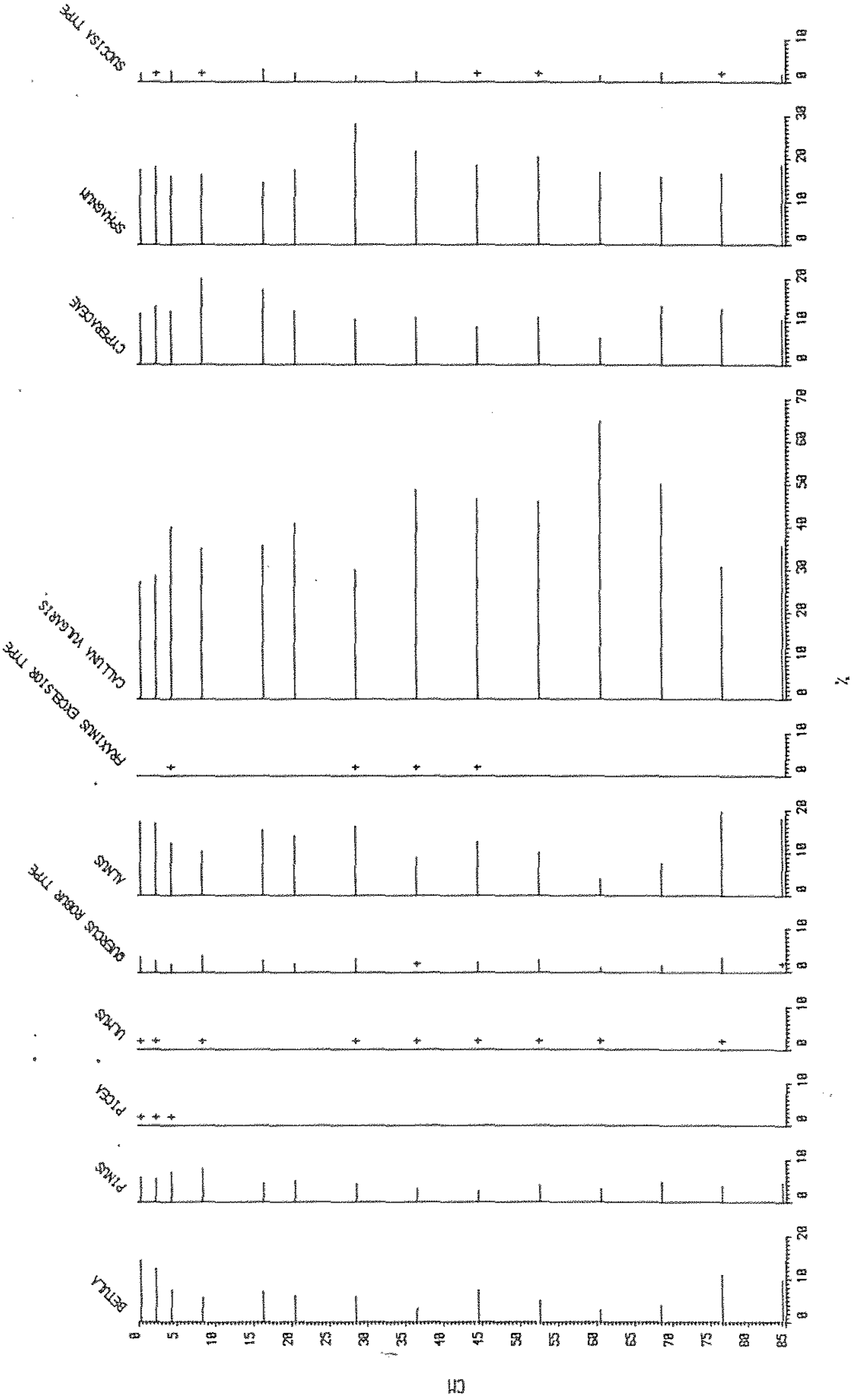
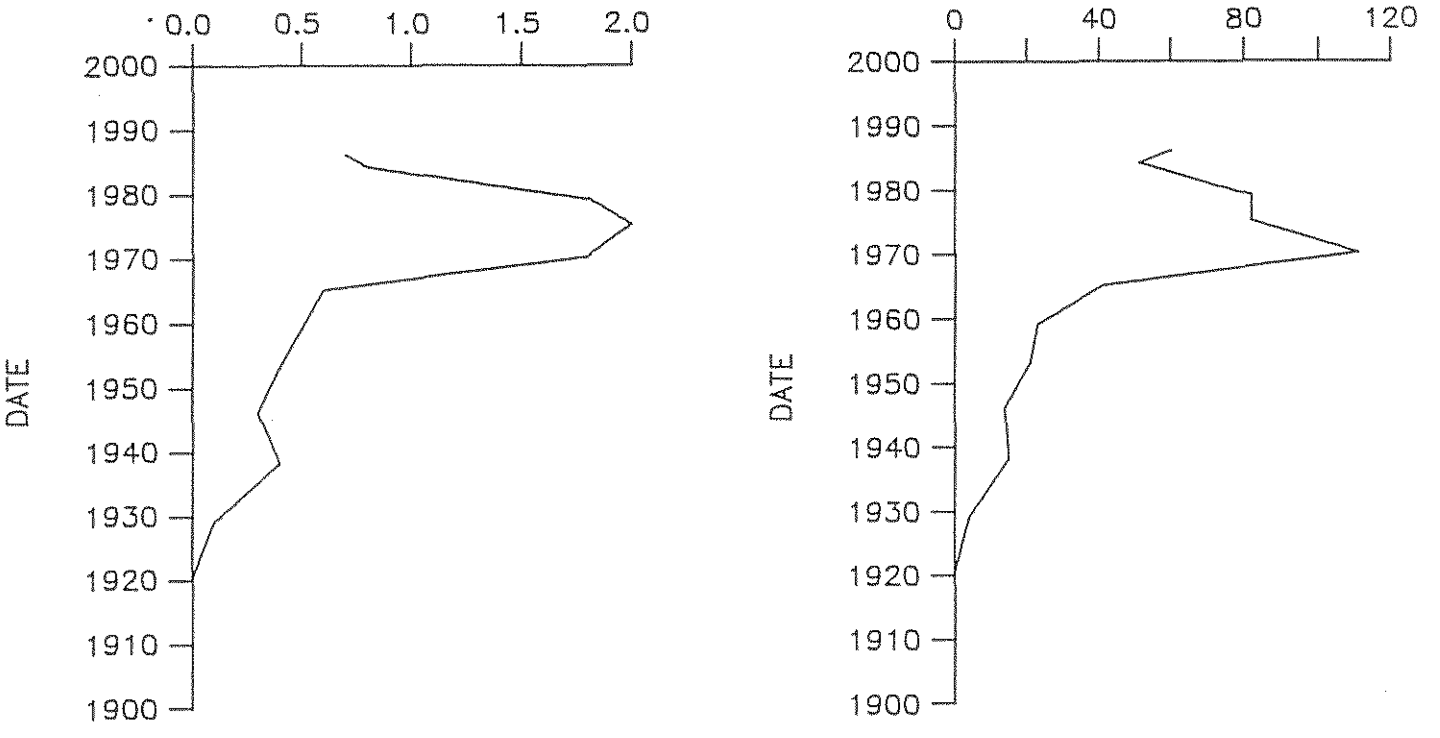


Figure 5.23 Loch Doilet: carbonaceous particle record; a) concentration, b) flux



A SCP x10^{-3} gm dry weight

B SCP cm^{-2} yr^{-1}

5.3.4 Lochan Dubh: results

Two cores were taken from the deepest part of the lake (Figure 5.17) in June 1986, using a modified Livingstone corer. Core LOD2 was chosen as the core for analysis because of its undisturbed sediment/water interface.

Lithostratigraphy

The sediment consists largely of dark brown, fine organic sediment. Flakes of mica from the schists in the catchment are evident. There is a paler grey/brown layer from 53-60 cm depth with a higher mineral content and there is also an increase in fine sand below 92 cm. These changes are reflected in the wet density, dry weight and LOI profiles (Figure 5.24) with increases in density and dry weight at 8-14 cm, 55-66 cm and 92-100 cm. The causes of these fluctuations the accumulated sediment are unclear although there is a certain amount of peat erosion in the catchment.

Dating

Although the core was taken after the Chernobyl incident there is no evidence of Chernobyl fallout isotopes in sediment. This could indicate that recent sediment is missing from the core top, but data on the Chernobyl fallout indicates that there was very little deposition in this immediate area (Clarke and Smith 1988). The unsupported ^{210}Pb inventory for the core was calculated as 11.3 pCi cm^{-2}, representing a constant supply of 0.35 pCi cm^{-2} yr^{-1}. These values are comparable to those from other sites in north west Scotland. The unsupported ^{210}Pb profile for the core is non-monotonic with the peak activities occurring 1-3 cm below the core surface. This suggests an accelerating sedimentation rate. Chronologies were calculated using both the CIC and CRS models. Calculations using the CRS model suggest the accumulation rate has increased from 0.0080 g cm^{-2} yr^{-1} at the end of the nineteenth century to 0.014 g cm^{-2} yr^{-1} during the period from 1950 to 1980, with a further increase to 0.035 g cm^{-2} yr^{-1} in the last five years. The CIC dating model places all these changes within the last 40 years. The CRS model was chosen for dating the core (Table 5.8, Figure 5.25). This places 1963 at 4 cm and 1954 at 5 cm. ^{137}Cs results show ^{137}Cs below 10 cm with a steep rise above 10 cm (1885) and again above 7 cm (1936). This is probably a result of the mobility of this isotope in the sediments of soft-water lakes. However, there is also a well defined ^{137}Cs peak at 2.75 cm along with a peak in ^{241}Am. If this reflects atmospheric nuclear weapons testing fallout then this level should be dated to 1963-1964, although the ^{210}Pb derived date is 1974. However, this ^{137}Cs peak is only 1 cm above its expected level and in view of the mobility of this isotope it was decided to use the chronology derived from the ^{210}Pb data.

Diatom analysis

The diatom flora found in the Lochan Dubh core is very similar to that found in Loch Doilet (see above), although the proportions of acidophilous taxa are greater throughout the core in Lochan Dubh. A summary diagram is given in Figure 5.26. The main floristic changes occur between 18-14 cm (pre-1800) when the proportions of the acidophilous taxa *Navicula leptostriata* and *Eunotia incisa* begin to increase accompanied by a decline in the circumneutral taxa *Brachysira vitrea* and *Achnanthes minutissima*. *Brachysira brebissonii* also declines, although it is commonly classified as acidophilous. These trends continue to the top of the core and are typical of those seen at sites which have undergone some acidification, but not to the extent where the acidobiontic taxa such as *Tabellaria binalis* and *T. quadriseptata* flourish.

The diatom concentrations fluctuate throughout the core. There is a peak in total diatom concentration at 18 cm and a dilution at 10-14 cm which accompanies the increase in wet density and dry weight at this point. The diatoms show a sustained increase in flux to the sediment from 1800 until the present, although concentrations peak at 8.25 cm (1918).

The pH reconstructions for Lochan Dubh are shown in Figure 5.21. The reconstruction of pH using weighted averaging shows an acidification trend beginning before 1800 when the reconstructed pH falls from 5.3-5.4 at 14-14.5 cm, to 5.2 at 12-12.5 cm. The gradual decline in reconstructed pH continues through the nineteenth and twentieth centuries reaching pH 5.0 at the surface. The mean measured pH is 5.55 so, like Loch Doilet, there is a consistent error in under-estimating pH down the core.

Pollen analysis

A summary pollen diagram for Lochan Dubh is given in Figure 5.27. The pollen assemblages are dominated by a typical open blanket bog flora: *Calluna, Sphagnum* and Cyperaceae. There is a small increase in *Pinus* from 4.5-6 cm (1947-1964) presumably resulting from the recent afforestation nearby. However, *Picea* is absent from the recent sediments.

Carbonaceous particle analysis

Figure 5.28 shows the carbonaceous particle concentration plotted against depth. Particle concentration is low below 10 cm (1890) but increases above this level to values around 2.9×10^3 g^{-1} at the surface which is almost two orders of magnitude less than the surface sediment of Round Loch of Glenhead in Galloway (Battarbee *et al.* 1989).

Geochemistry

A full report on the sediment chemistry is in progress. There is evidence for only a small amount of zinc contamination in Lochan Dubh beginning around 1900 (Figure 5.29). Below this the atmospheric component can not be distinguished from the background levels of zinc. There is no clear indication of lead contamination.

Magnetic analysis

In progress

Figure 5.24 Lochan Dubh: lithostratigraphy

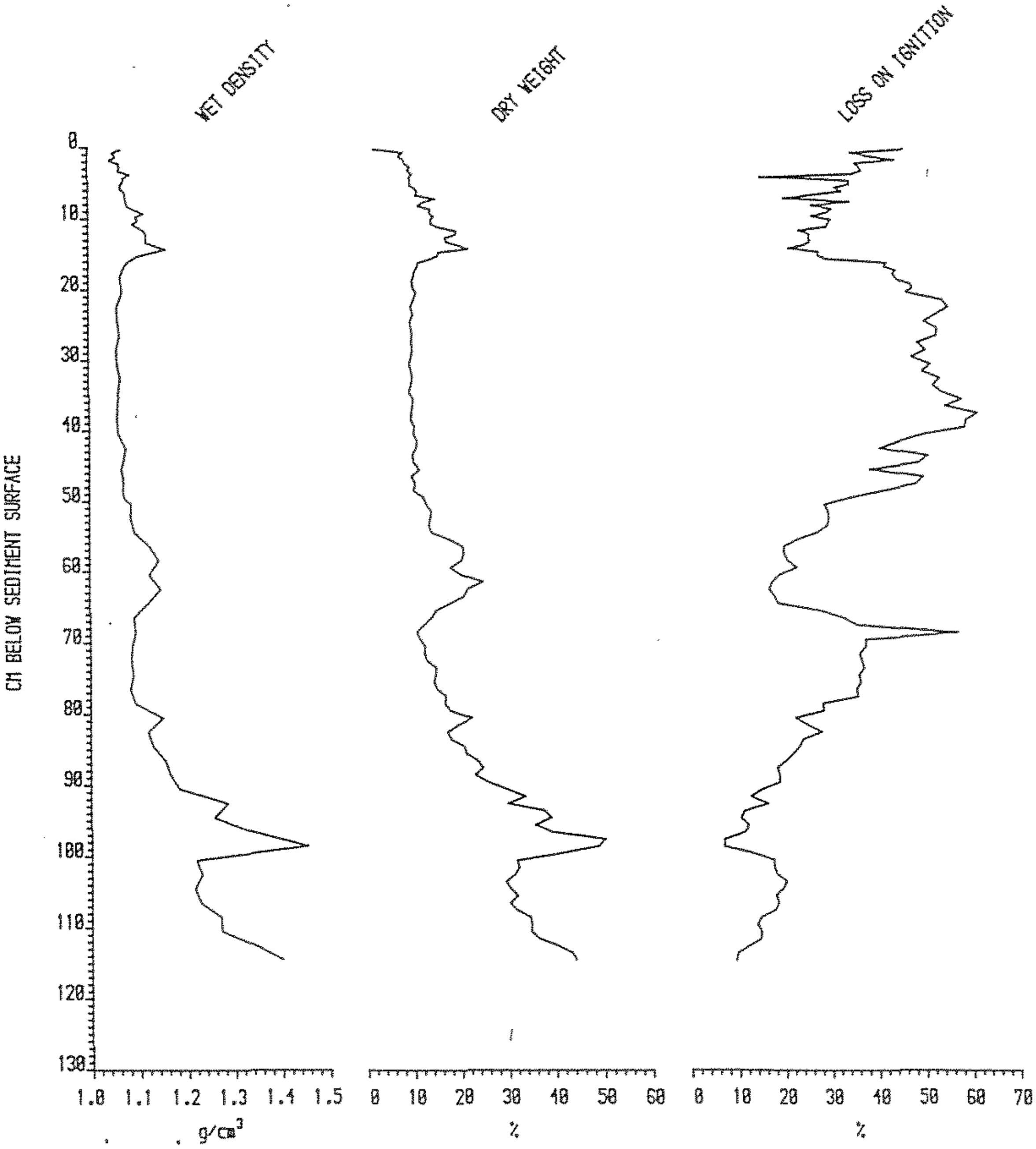


Table 5.8 Lochan Dubh: ^{210}Pb chronology

Depth	Dry Mass	Chronology			Sedimentation Rate		
		Date	Age				
cm	gcm^{-2}	AD	yr	±	$gcm^{-2}yr^{-1}$	$cmyr^{-1}$	± (%)
0.00	0.0000	1986	0				
0.50	0.0243	1985	1	2	0.0305	0.466	18.5
1.00	0.0606	1984	2	2	0.0220	0.293	10.3
1.50	0.1024	1981	5	2	0.0171	0.195	6.3
2.00	0.1497	1978	8	2	0.0159	0.173	6.4
2.50	0.1970	1975	11	2	0.0148	0.150	6.5
3.00	0.2479	1972	14	2	0.0138	0.135	6.6
3.50	0.3022	1968	18	2	0.0132	0.126	6.7
4.00	0.3565	1964	22	2	0.0125	0.117	6.7
4.50	0.4107	1959	27	2	0.0125	0.114	7.3
5.00	0.4647	1955	31	2	0.0132	0.119	8.4
5.50	0.5188	1951	35	2	0.0138	0.123	9.5
6.00	0.5761	1947	39	3	0.0136	0.116	10.4
6.50	0.6368	1942	44	3	0.0125	0.098	11.1
7.00	0.7027	1936	50	4	0.0113	0.084	12.4
7.50	0.7736	1929	57	4	0.0101	0.072	14.3
8.00	0.8446	1922	64	5	0.0088	0.061	16.2
8.50	0.9184	1914	72	6	0.0081	0.054	20.4
9.00	0.9951	1904	82	9	0.0080	0.052	26.9
9.50	1.0717	1894	92	11	0.0079	0.050	33.4
10.00	1.1506	1884	102	15	0.0077	0.047	38.5
10.50	1.2317	1872	114	20	0.0074	0.043	42.3
11.00	1.3128	1861	125	26	0.0071	0.039	46.1

Mean ^{210}Pb Flux = 0.35±0.01 $pCicm^{-2}yr^{-1}$
90% Equilibrium Depth = 8.7 cm, or 0.95 gcm^{-2}
99% Equilibrium Depth = 12.0 cm, or 1.51 gcm^{-2}

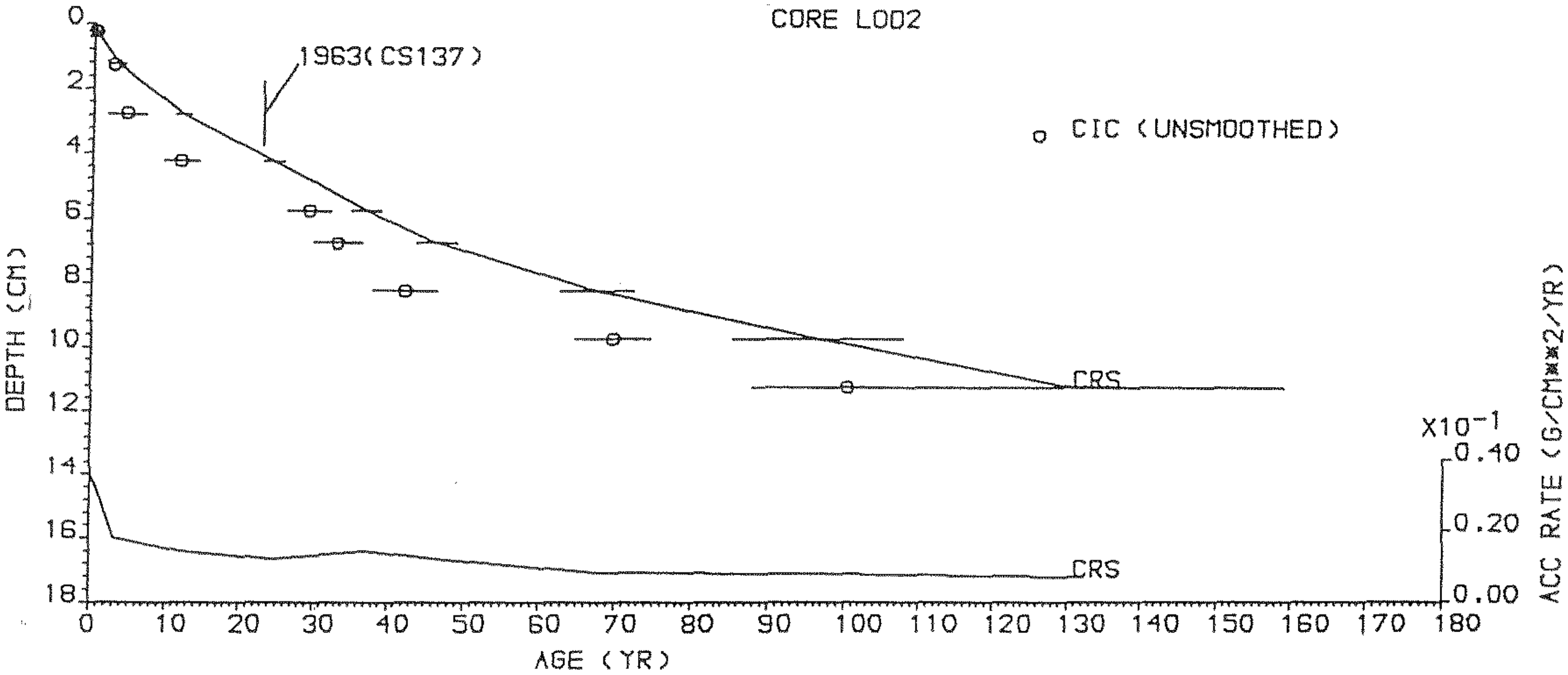


Figure 5.25 Lochan Dubh: ^{210}Pb chronology

Figure 5.26 Lochan Dubh: diatom summary diagram

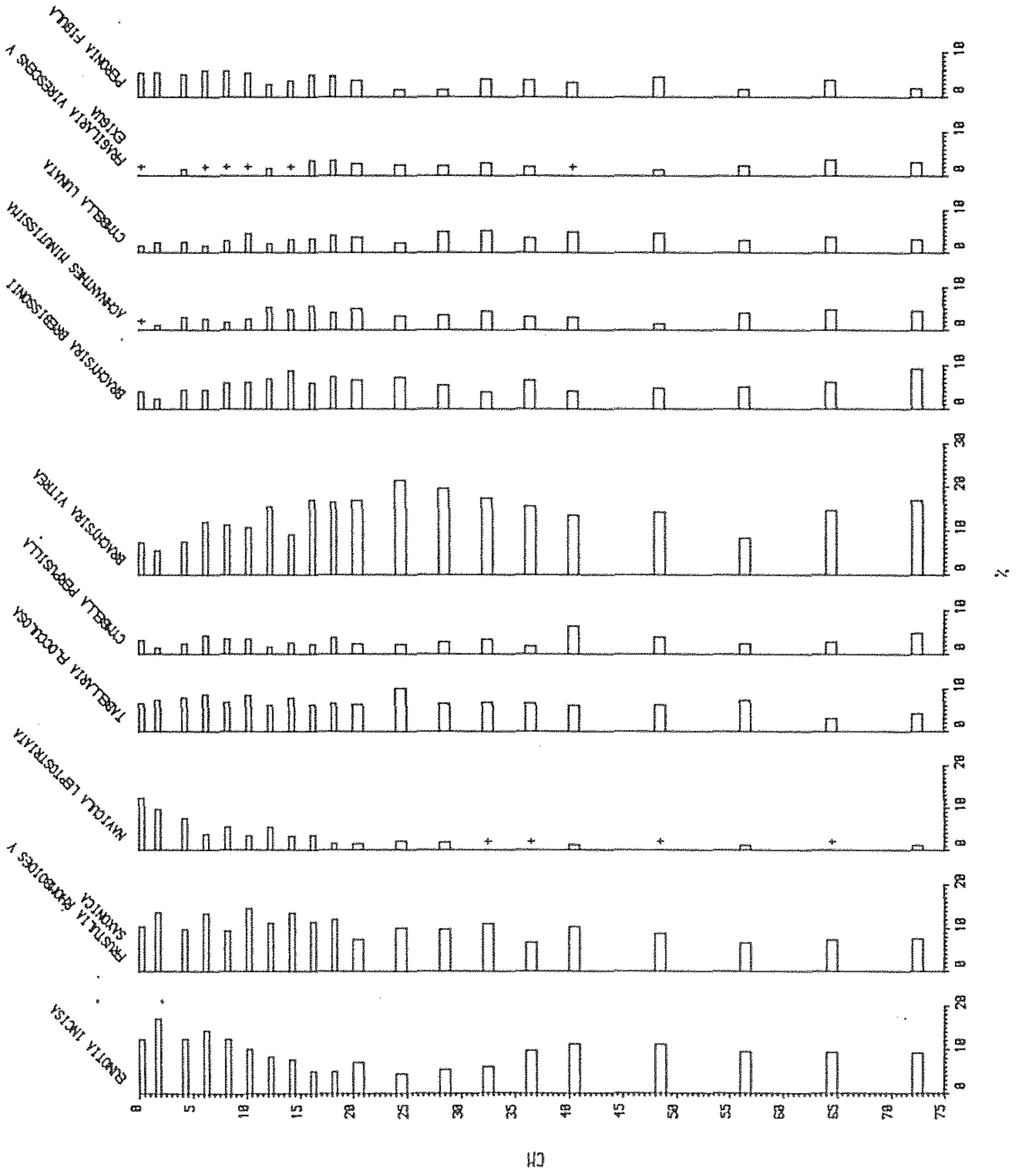
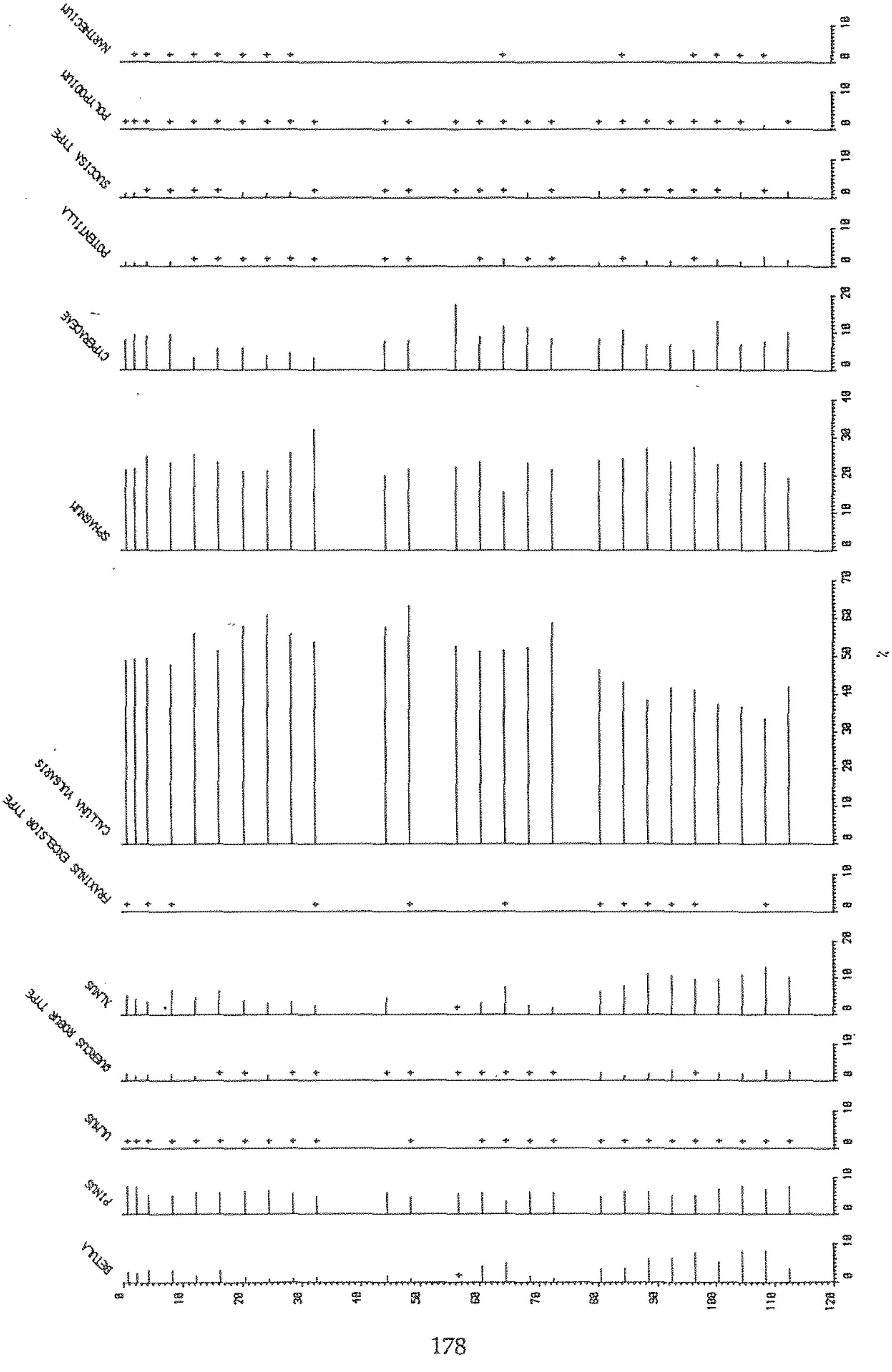


Figure 5.27 Lochan Dubh: summary pollen diagram



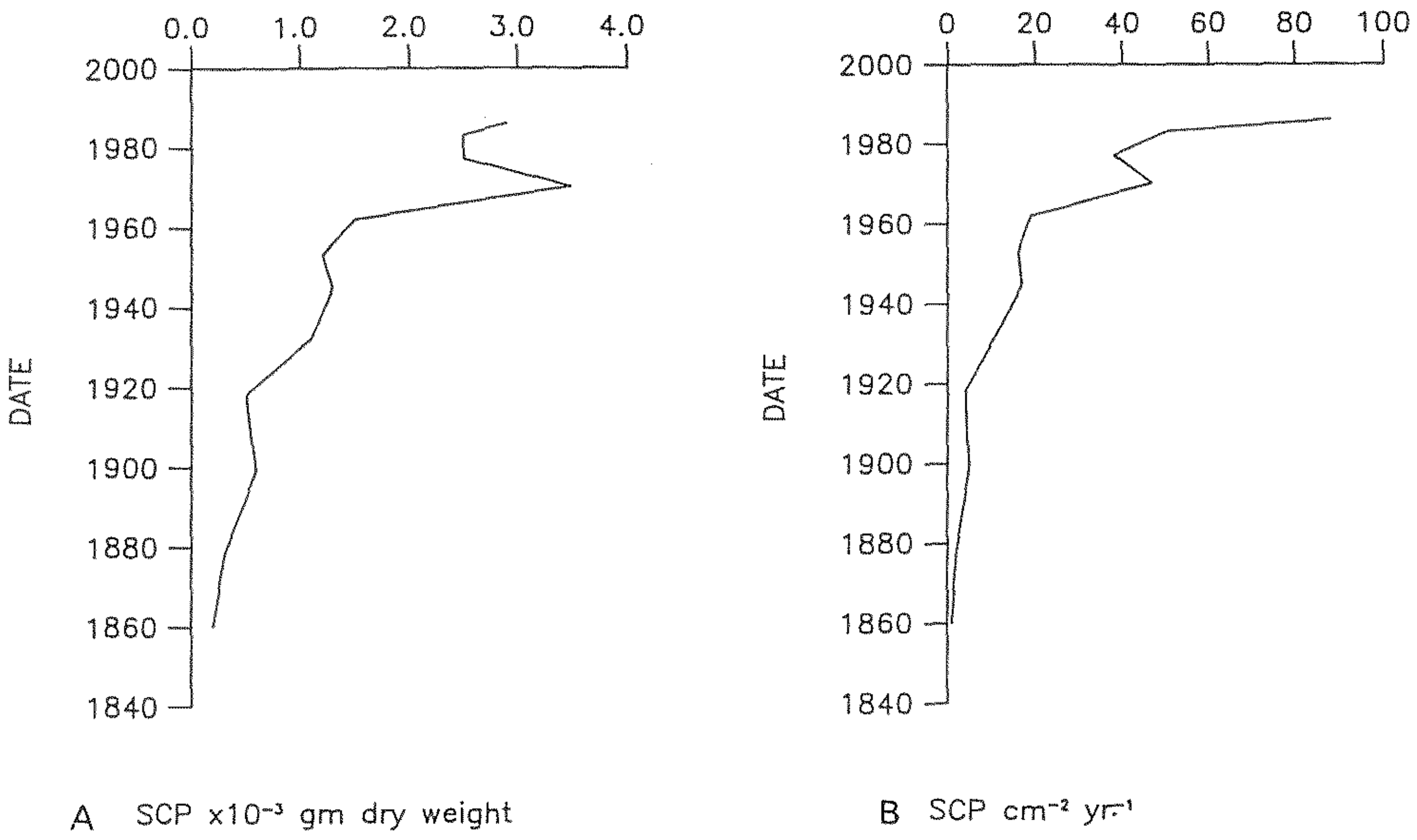
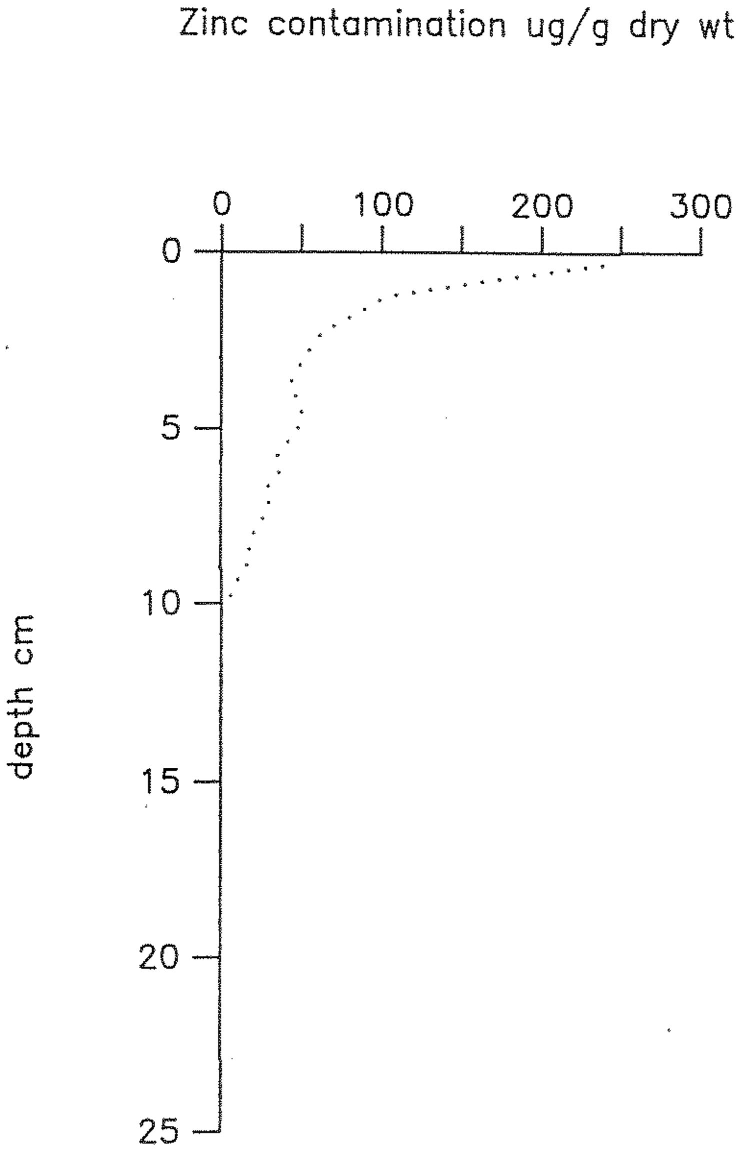


Figure 5.28 Lochan Dubh: carbonaceous particle record; a) concentration, b) flux

Figure 5.29 **Lochan Dubh: sediment zinc concentration profile**



5.4 DISCUSSION

5.4.1 Loch Chon and Loch Tinker comparison

Both lochs show acidification beginning at the same time, but the pattern of pH decline varies slightly between them. Loch Tinker appears to acidify more rapidly at first due to the larger initial planktonic diatom population. By 1960 the pH in Loch Chon had fallen from 6.4-6.5 at 1800 to pH 5.8-5.9 (Figure 5.7). A similar magnitude of change over the same time period has occurred in Loch Tinker, with a pH 6.2-6.3 at 1800 declining to pH 5.7-5.8 by 1960 (Figure 5.7). From 1960 the pH histories of the two lochs diverge. In Loch Chon there is a rapid decline in reconstructed pH to 5.2 in 1987. This point of rapid acidification corresponds with the first reports of declining fish catches in the loch.

From the carbonaceous particle data (Figure 5.8) it might be assumed that this pH decline is related to acid deposition since there is such a rapid increase in the deposition of these indicators of atmospheric contamination. However, a rapid increase in the deposition of carbonaceous particles over the same time period has also occurred in Loch Tinker (Figure 5.13). Since Loch Tinker presumably received the same levels of acid deposition at this time (if not greater) and yet it has not become significantly more acid since 1960, the difference in the acidification histories of the two lochs from this time must be related to changes in the catchments. The only land-use change at Loch Tinker over this century has been a reduction in the regularity of heather burning since the 1930s. This may have increased the amount of mature *Calluna* in the catchment and promoted soil acidification. However, this does not appear to have affected the water quality in the loch. Indeed, the rate of acidification slows down in the 1930s. Therefore in the absence of any other explanation, it would appear that the pH decline in Loch Chon from 1960 is related to the planting of the conifers in the catchment in the 1950s.

Earlier interpretations of the Loch Chon diatom data using the multiple regression pH reconstruction model have placed the rapid acceleration of acidification at c. 1970, when the forest was 15-20 years old. This suggested that the acceleration in acidification had been triggered by processes occurring in the mature, closed forest canopy. The revised date of 1960 indicates that this is not so, although acidification continued as the forest matured. By 1960 the trees planted in 1951-1952 were not growing well and had certainly not formed a closed forest canopy. Despite this, the young plantations appear to have initiated a period of rapid acidification in Loch Chon.

5.4.2 Loch Doilet and Lochan Dubh comparison

The floristic changes in the diatom assemblages suggest that both these lochs have undergone slight acidification. However, there are problems in interpreting the diatom data. There is a considerable mismatch between the surface sediment reconstructed pH and the mean measured pH of both Loch Doilet and Lochan Dubh. pH reconstruction using weighted averaging underestimates pH by 0.5-0.6 pH units. If the reconstructed pH at 1800 and the recent measured pH are compared it would appear that no acidification has occurred at either site (Figure 5.21), yet the floristic changes in the diatoms are characteristic of other sites which have undergone moderate acidification. It is possible that the mean measured pH does not reflect the true mean pH. One water chemistry sample was omitted from the calculation of the mean values at Loch Doilet because the high sea salt component of that sample had produced a much lower pH. Weekly stream water chemistry measurements in the Glen Etive area (Harriman and Wells 1986) detected sea salt effects on only two occasions during the winter months, suggesting that the inclusion of a sea salt sample in 6 samples used to calculate pH (as was the case with Loch Doilet) would produce an unrealistic mean. However, considering the proximity of Loch Doilet and Lochan Dubh to the coast it is possible ~~that~~ sea salt influences are more frequent here and the calculated means underestimate their importance.

An alternative explanation of the mismatch between the measured and reconstructed pH concerns the diatom flora. One interesting feature of the diatom flora in the Loch Doilet core is the absence of the planktonic diatom *Cyclotella* in the entire core. This is unusual for a lake of this size with a past pH of presumably at least 5.9 or more. *Cyclotella* is often the first diatom genus to respond to acidification and it ceases to grow in lakes long before other taxa show a response. It has been suggested that *Cyclotella* may respond to changes associated with acidification other than pH itself, such as dissolved metals for example. The geology of the region around Loch Doilet contains ore-bearing veins. Although there is no record of such veins occurring within the Loch Doilet catchment, a former lead mine (currently being mined for barytes) lies just outside the catchment. Unfortunately, recent water samples were not measured for heavy metals, but it is possible that Loch Doilet and Lochan Dubh have naturally higher background levels of certain dissolved metals resulting in a diatom flora typical of more contaminated sites.

Since the error in pH reconstruction appears to be consistent between the two sites and the diatom floras in both cores are similar, it seems valid to reconstruct and compare the past trends in pH for both lochs, even though exact values for pH may not be accurate.

In Lochan Dubh the onset of acidification pre-dates 1800 and the pH declines very slowly over the nineteenth and twentieth centuries up to the present. The current mean water chemistry values of pH 5.6 and calcium 33 μeq l^{-1} suggest that the overall pH change has not been great, considering its sensitivity to acidification. The carbonaceous particle data (Figure 5.29) confirm that contamination of this site by acid deposition has been low over the past 200 years and justify the choice of this region as one of low acid deposition, although the loch does appear to have been slightly acidified as a result of acid deposition over the past 200 years.

In Loch Doilet the decline in pH begins slowly around the mid-nineteenth century, increasing slightly after 1931. The greatest rate of change occurs between the early 1930s and the early 1960s (20-10.5 cm). The timing of the initial pH change in Loch Doilet suggests that the loch has responded to a slight increase in acid deposition in the nineteenth century. The difference in the time of onset of acidification between Loch Doilet and Lochan Dubh is understandable given the lower measured calcium in Lochan Dubh and its higher altitude. However, the twentieth century changes in Loch Doilet could be attributed to either acid deposition or afforestation since the rate of acidification increases slightly following the initial planting of conifers in the 1920s and early 1930s. The transient increases in pH that occurred around 1931 and 1966 could be related to forestry management since large areas were planted in the early 1930s (basic slag was used as a fertiliser on the catchment until 1960) and there was extensive forestry road construction in the 1960s.

5.5 CONCLUSIONS

The results from The Trossachs region show that Loch Chon and Loch Tinker began to acidify in the nineteenth century as a result of acid deposition. Additionally, at Loch Chon the forest caused an acceleration in the acidification of the loch from 10 years after planting. Since this is an area receiving high levels of acid deposition it is difficult to say to what extent this afforestation effect was due to the capture and concentration of atmospheric acid particulates and to what extent the forest itself had contributed to the acidity of the loch.

The results from the Strontian area of western Scotland show that past levels of acid deposition have been considerably lower than in the Trossachs. However, due to the sensitivity of the sites to acidification both Lochan Dubh and Loch Doilet show signs of slight acidification dating from the nineteenth century to the present, as a result of acid deposition from industrial sources. Therefore, it is impossible to say to what extent the forest around Loch Doilet has contributed to the slow acidification of the loch after it was planted in 1920.

However, it is clear that the forest at Loch Doilet has not resulted in the rapid acceleration in acidification seen at Loch Chon. This suggests that the post-1960 pH decline in Loch Chon was largely due to the enhanced deposition of acidic contaminants within the forest. It should be noted however, that forestry management techniques have differed between the two forested sites and the use of basic slag as a fertiliser on the Loch Doilet catchment between 1920 and 1960 could have moderated the impact of the forest on the pH of the loch.

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6 EVIDENCE FOR ACIDIFICATION IN BROWN WATER LAKES

6.1 INTRODUCTION

Lakes situated within peaty catchments often appear very brown owing to their high levels of total organic carbon (TOC). It has been suggested that these 'brown water lakes' are naturally quite acid due to the input of humic acids from the catchment. This study was designed to evaluate the recent history of two acid sites, Long Loch and Loch na Larach, which lie in areas of low acid deposition.

The location of the two sites is shown in Figure 1.1. Long Loch is situated in the far north east of Scotland on the Dunnet Head peninsular, whilst Loch na Larach is in the north west of Scotland south of Cape Wrath. Both sites have bedrock geologies which are potentially sensitive to acidification. Long Loch is on upper Old Red Sandstone and Loch na Larach is situated on the Torridonian Sandstone and Lewisian Gneiss.

The water quality of the two sites is shown in Table 6.1. Both sites are acid with a pH of less than 5.0, they also have high conductivities and elevated Na^+ and Mg^{2+} concentrations, reflecting the substantial marine influence at both sites.

Table 6.1 Lake water quality

		Long Loch	Loch na Larach
pH		4.97	4.88
TOC	mg l^{-1}	9.1	5.8
Cond.	μS cm^{-1}	241.4	135.4
Alkalinity (Alk_e)	μeq l^{-1}	0.00	0.00
Na^+	μeq l^{-1}	1723.2	1004.0
Ca^+	μeq l^{-1}	128.0	63.4
Mg^{2+}	μeq l^{-1}	388.0	188.0
K^+	μeq l^{-1}	43.8	24.4
SO_4^{2-}	μeq l^{-1}	260.0	120.8
Cl^-	μeq l^{-1}	2006.7	947.0
Al	μg l^{-1}		
Total		*	*
non labile		*	*
labile		9.0	8.0

Determinations = 1986-1987 mean based on 5 measurements. * indicates determination not made.

6.2 RESULTS

The sites were cored with a mini-Mackereth corer (Mackereth 1969) in June 1986. Methods for lithostratigraphic, biostratigraphic, radiometric, magnetic and carbonaceous particle analysis follow the Royal Society Surface Water Acidification Project (SWAP) protocol (Stevenson *et al* 1987).

6.2.1 Long Loch

Lithostratigraphy

Lithostratigraphic results are shown in Figure 6.1, the LOI profile is quite variable throughout with a clear increase in LOI at 20 cm where values rise from about 40% to about 60%. These fluctuations in LOI most probably represent the inwash of organic material from the catchment, the sustained increase at 20 cm is likely to represent a period of peat erosion. The fall in wet density and dry weight values at 20 cm reflects this inwash of less dense organic material.

Dating

In Progress

Diatom analysis

A summary diatom diagram is shown in Figure 6.2. The diatom profile can be readily split into two zones; 0-19 cm and 20-68 cm. Below 20 cm the profile is completely dominated by one species, *Fragilaria virescens* v. *exigua* which makes up 70% of the diatom assemblage. Other species which are also relatively abundant (>5%) include *Eunotia incisa*, *Brachysira vitrea* and *Eunotia pectinalis* v. *minor*. Above 20 cm there is a very marked change in the assemblage; values of *Fragilaria virescens* v. *exigua* decline dramatically to <5% and there is a marked increase in species such as *Achnanthes conspicua*, *Achnanthes saxonica*, and *Achnanthes austriaca* v. *helvetica*. There are also less marked increases of *Eunotia incisa*, *Navicula seminuloides* and *Pinnularia irrorata*. The correspondence of the floristic change with the LOI increase at 20 cm suggests that the diatom flora was influenced by the inwash of organic material into the lake.

Diatom concentrations are shown in Figure 6.3. Concentrations are quite variable below 30 cm, but above this level they are lower and more steady. There is no marked change in diatom concentration at 20 cm, this is surprising since a decrease in diatom concentration would be expected as the diatoms became diluted by inwashed material. However, it is possible that catchment diatoms could have been inwashed at this time.

pH reconstruction was attempted using the multiple regression of pH preference groups method. The reconstructed pH of the surface sediment sample was pH 6.0 which does not agree well with the current measured pH (5.0). Indeed the diatom flora, with a predominance of circumneutral and acidophilous forms is not typical of acid lakes found elsewhere in the UK. It must be emphasised that very little is known about the diatom floras of these brown water lakes and pH reconstruction will only be reliable once a surface sediment database has been compiled which takes into account TOC as well as pH gradients.

Pollen analysis

A summary pollen diagram is shown in Figure 6.4. The pollen spectrum for the time period covered by the core is dominated by peatland indicator taxa especially *Calluna vulgaris* and Gramineae. Tree pollen values are extremely low and reflect the location of the site remote from areas of woodland. There are few major changes in the pollen spectrum throughout the profile, however there is a small decline in *Calluna* pollen and an increase in Gramineae pollen towards the top of the profile which may indicate a slight increase in grazing in the area.

Carbonaceous particle analysis

In Progress

Geochemistry

In progress

Figure 6.1 Long Loch: lithostratigraphy

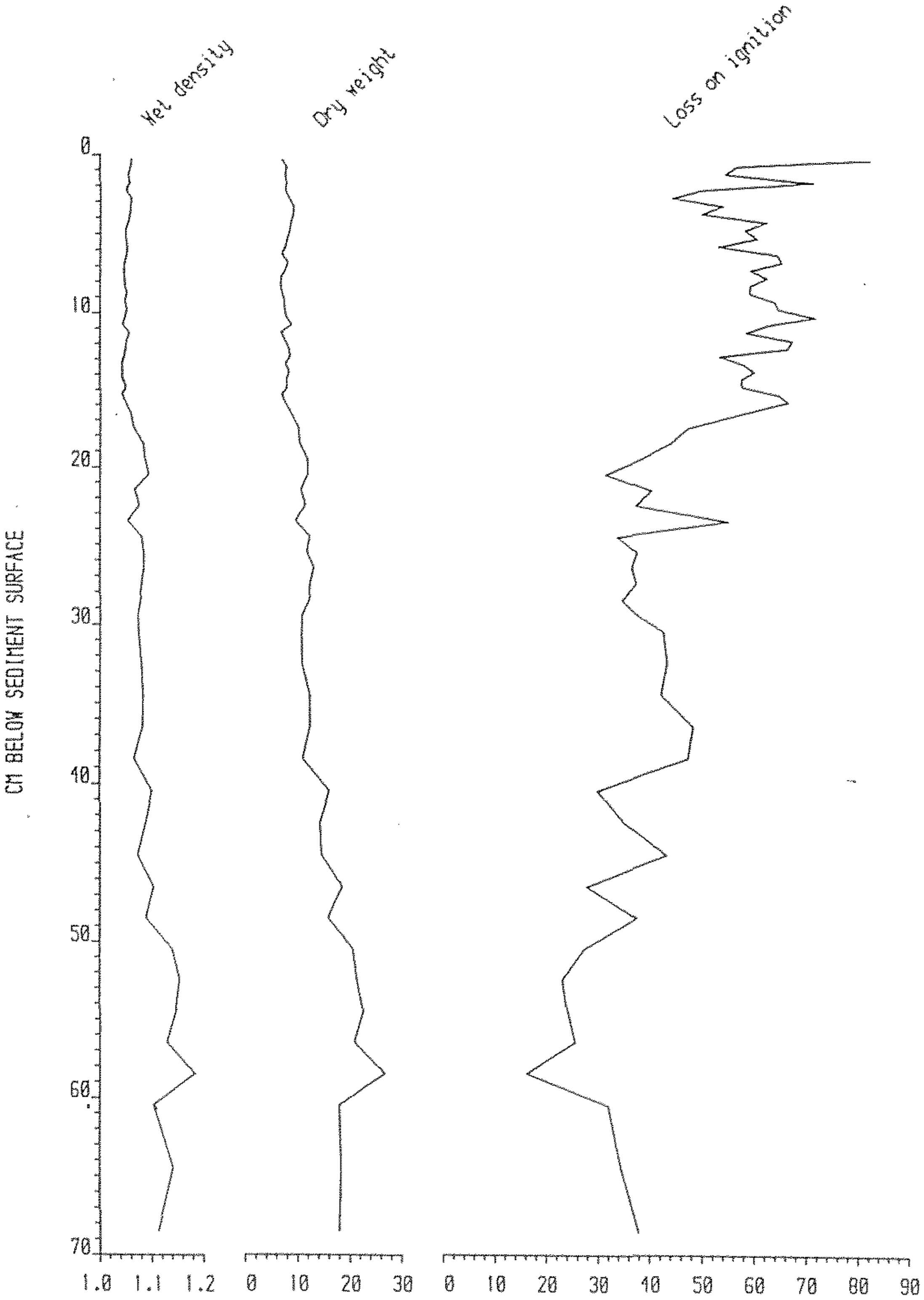


Figure 6.2 Long Loch: Summary diatom diagram

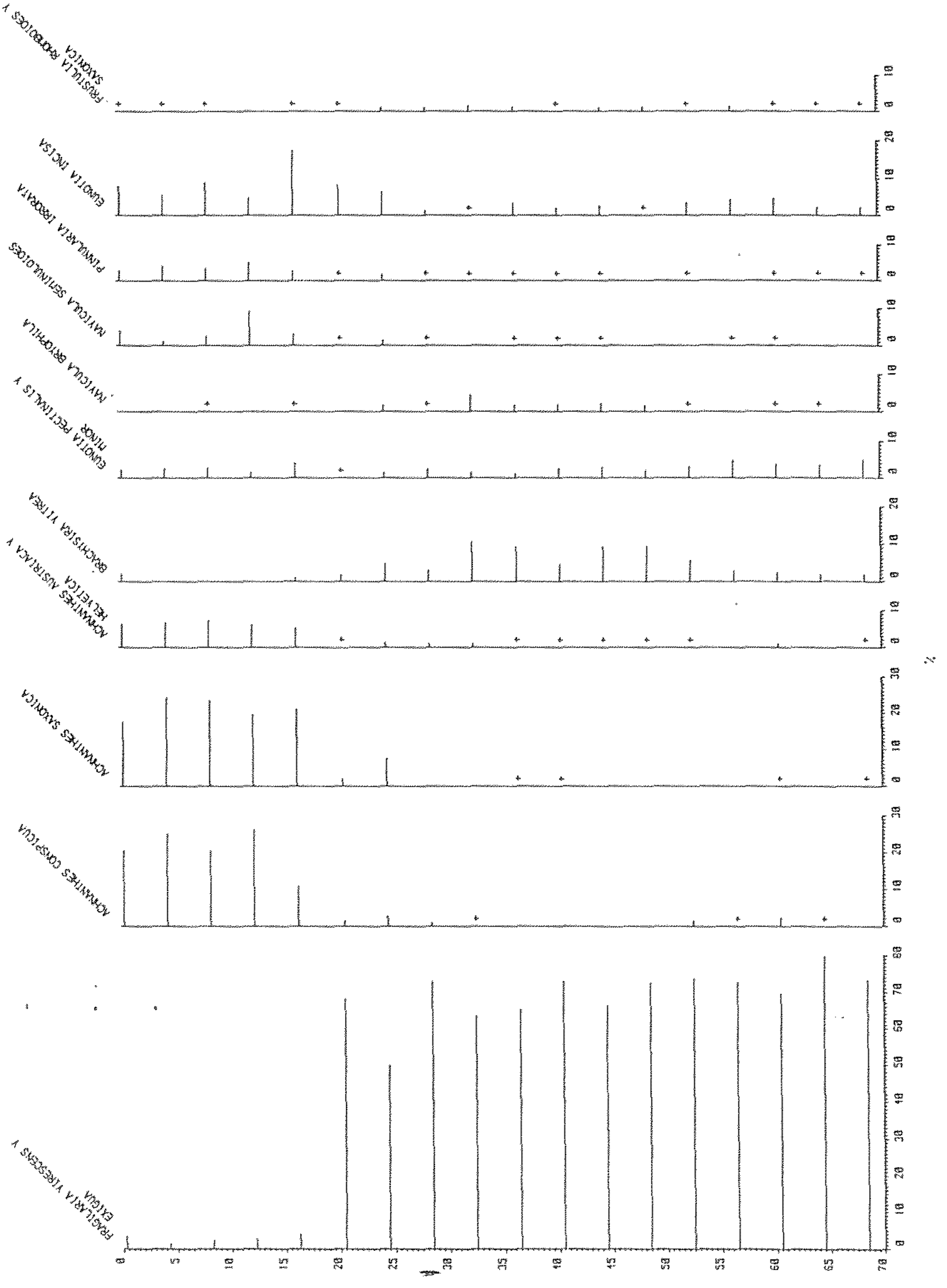


Figure 6.3 Long Loch: diatom concentration profile (x 10^8 g)

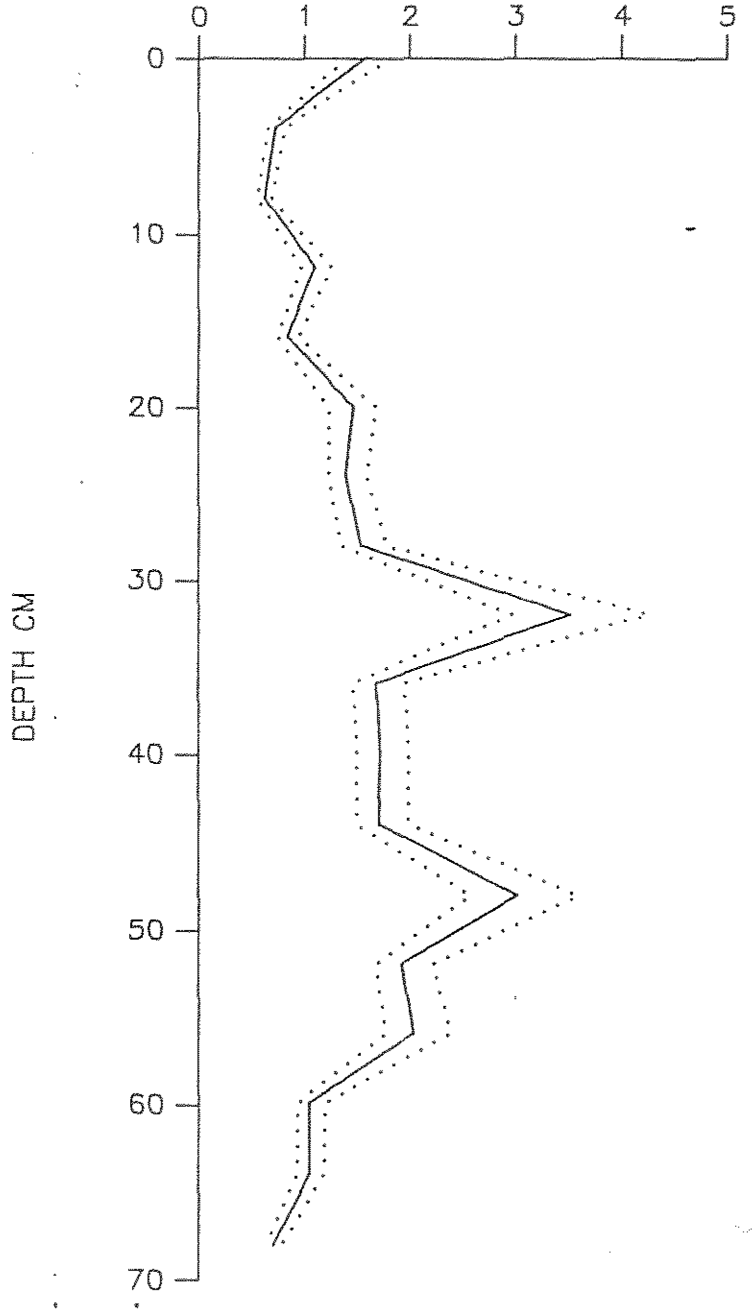
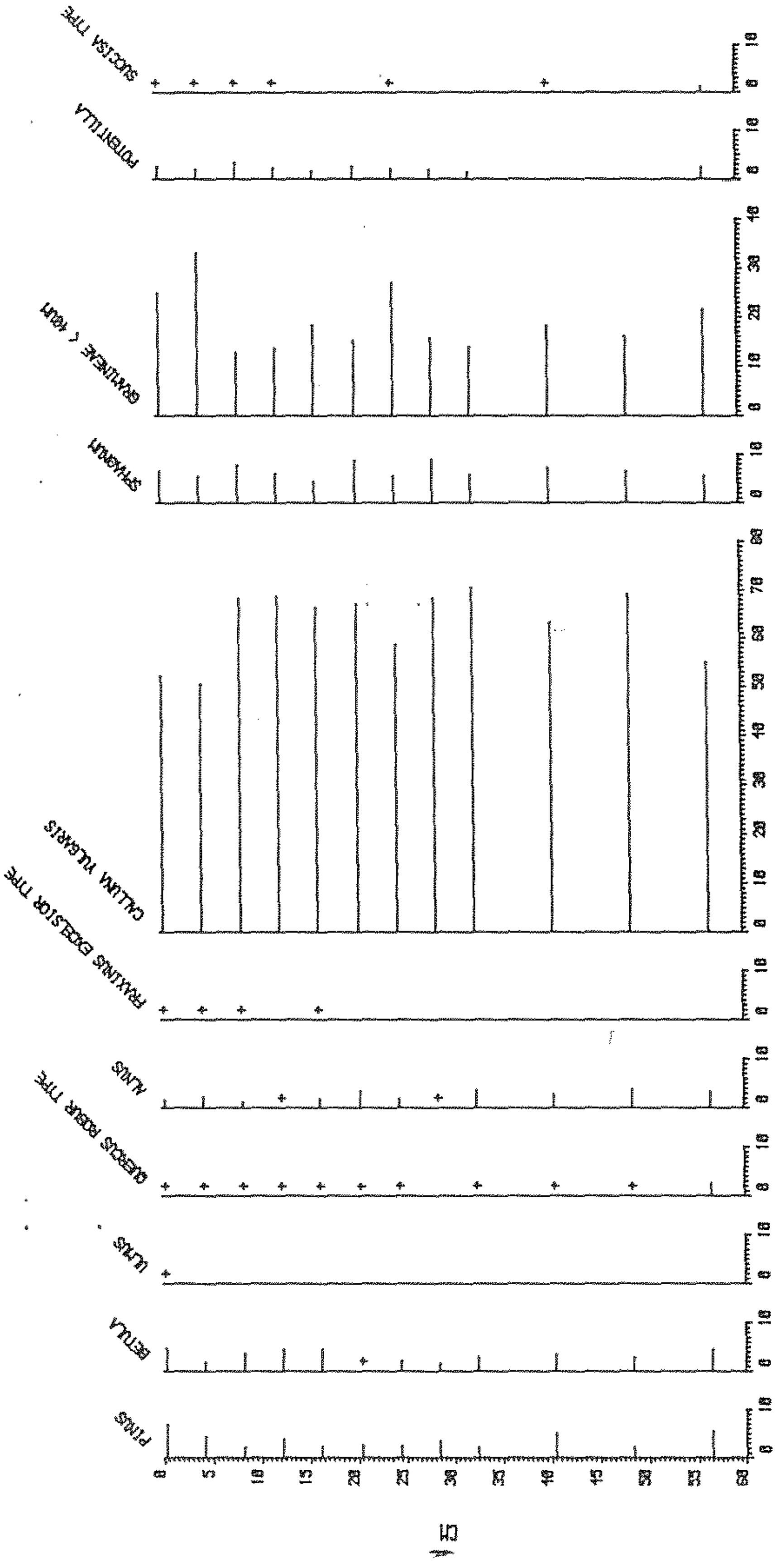


Figure 6.4 Long Loch: summary pollen diagram



6.2.2 Loch na Larach

Lithostratigraphy

Lithostratigraphic results are shown in Figure 6.5. The core shows fluctuating LOI values (between about 30-60%) below 51 cm; above this level there is a sudden increase in the LOI and values increase dramatically to about 80%. LOI values remain at this level until about 20 cm where they fall slowly to around 40%. These changes are matched by those of the dry weight and wet density curves; there are peaks in wet density and dry weight at 65, 72 and 80 cm which correlate with troughs in LOI. These probably represent inwashes of mineral material (gritty sediment was also noted at these levels). The increase in LOI above 51 cm is associated with lower dry weight and wet density values, this probably represents the onset of severe peat erosion in the catchment.

Dating

In progress

Diatom analysis

A summary diatom diagram is shown in Figure 6.6. The diatoms throughout the core were found to be broken and dissolved; for example, high percentage values of unidentified *Pinnularia* species were found throughout the profile, these represent valves which had been eroded so badly that only the central area was visible. Poorly preserved valves such as these could be derived from the lake catchment and this seems likely since their proportion increases above the onset of severe erosion at 51 cm.

Throughout the profile *Eunotia* species such as *Eunotia incisa* and *Eunotia rhomboidea* are important, together with *Fragilaria virescens* v. *exigua*, *Frustulia rhomboides* and v. *saxonica*, *Pinnularia irrorata*, *Cymbella perpusilla* and *Brachysira vitrea*. Values of these species fluctuate throughout the profile and unlike Long Loch no single species is dominant overall.

The diatom concentration results (Figure 6.7), show a sharp fall in concentration above 48 cm, which probably reflects the dilution of the diatoms by the inwashed material and there is a slight increase in diatom concentration towards the top of the core.

pH was reconstructed using the multiple regression of pH preference groups method (Figure 6.8). The results show fluctuating pH values throughout the core with a trend towards lower pH values in the top 20 cm. The surface sediment reconstructs to pH 5.6, which does not agree very well with the current measured pH of the loch (4.9). The poor reconstruction at this site and at Long Loch suggests that pH reconstruction for these coastal brown water lochs may be unreliable.

Pollen analysis

A summary pollen diagram is shown in Figure 6.9. The pollen assemblages for the time period covered by the core are dominated by peatland taxa; *Calluna*, Gramineae, Cyperaceae and *Sphagnum*. Tree pollen percentages are very low and like those found at Long Loch reflect the northern nature of the site and its remoteness from woodland.

There are few major taxa changes throughout the core, however there is a decline of *Isoetes* spores above 56 cm which is probably a response to decreased water transparency following the inwash of eroded catchment material. This response has been documented extensively elsewhere in the British Isles (Pennington 1964, Birks 1972, Bradshaw and McGee 1988, Stevenson *et al.* 1990). This erosion phase is also confirmed by the poor preservation of many of the pollen grains. The *Calluna*:Gramineae ratio (Figure 6.10) indicates a small increase in Gramineae pollen in the most recent sediments, which may reflect land-use changes in the area.

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Figure 6.5 Loch na Larach: lithostratigraphy

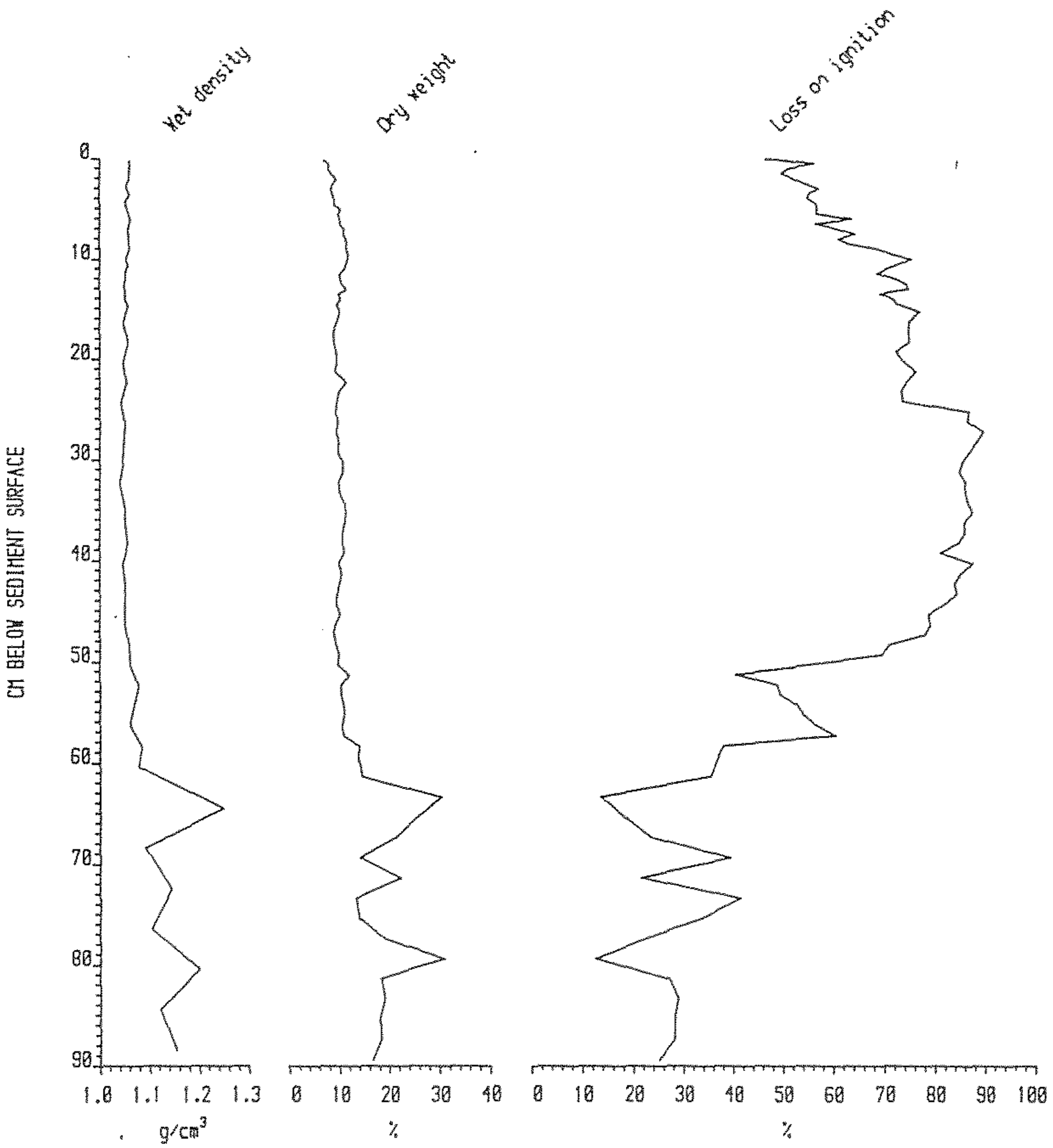


Figure 6.6 Loch na Larach: Summary diatom diagram

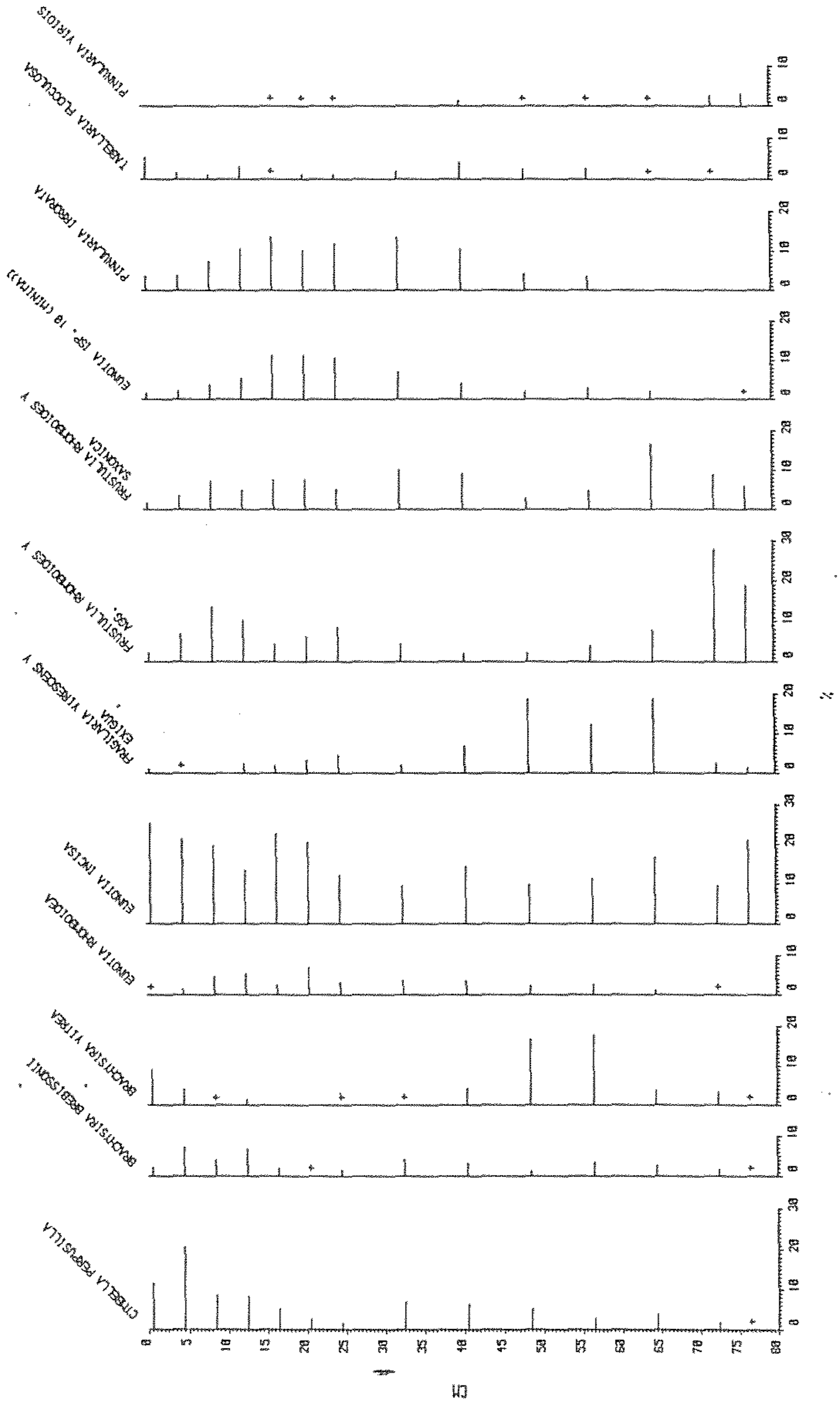


Figure 6.7 Loch na Larach: diatom concentration profile (x 10^7 g)

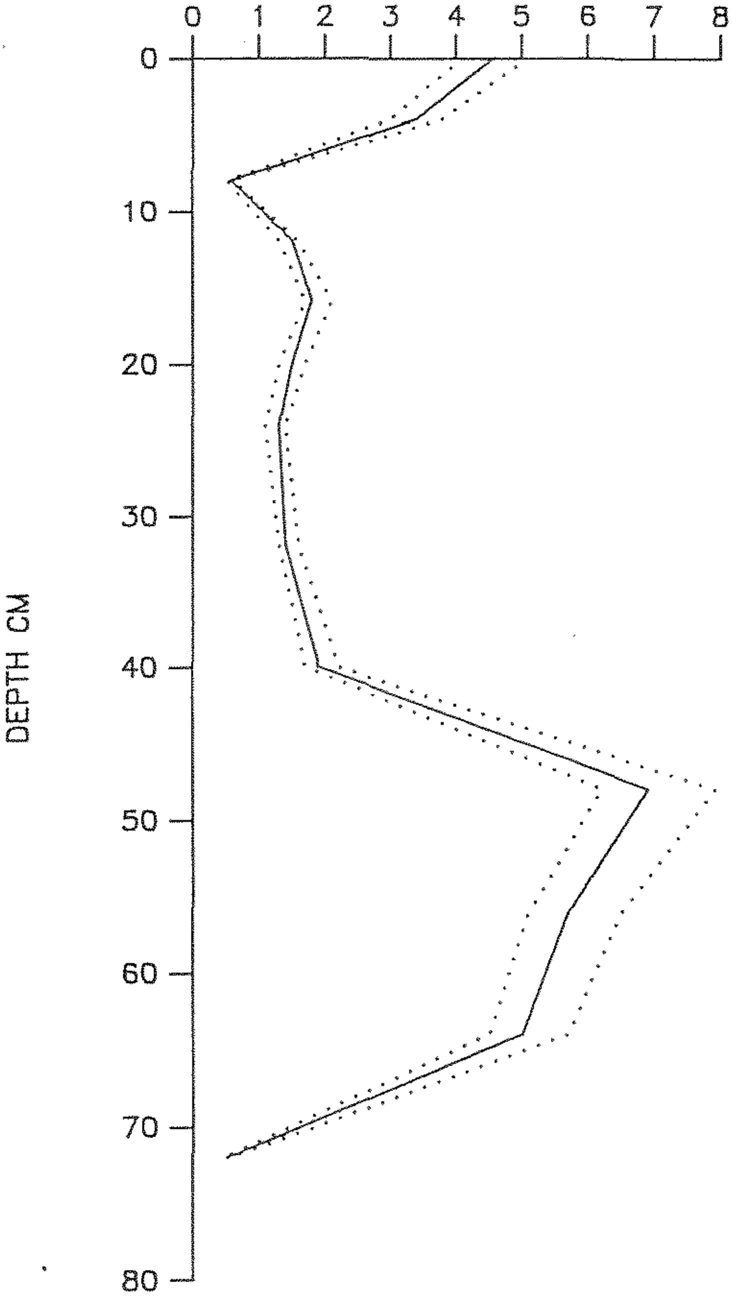


Figure 6.8 Loch na Larach: pH reconstruction (multiple regression)

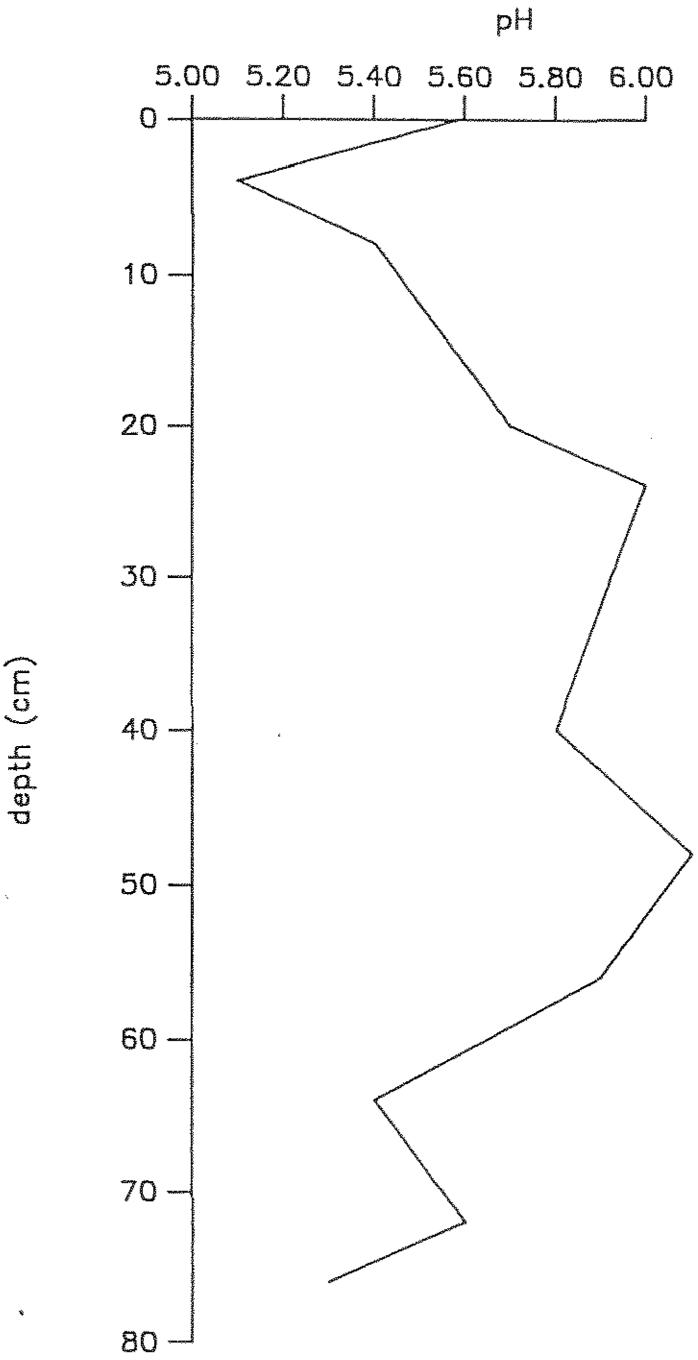


Figure 6.9 Loch na Larach: summary pollen diagram

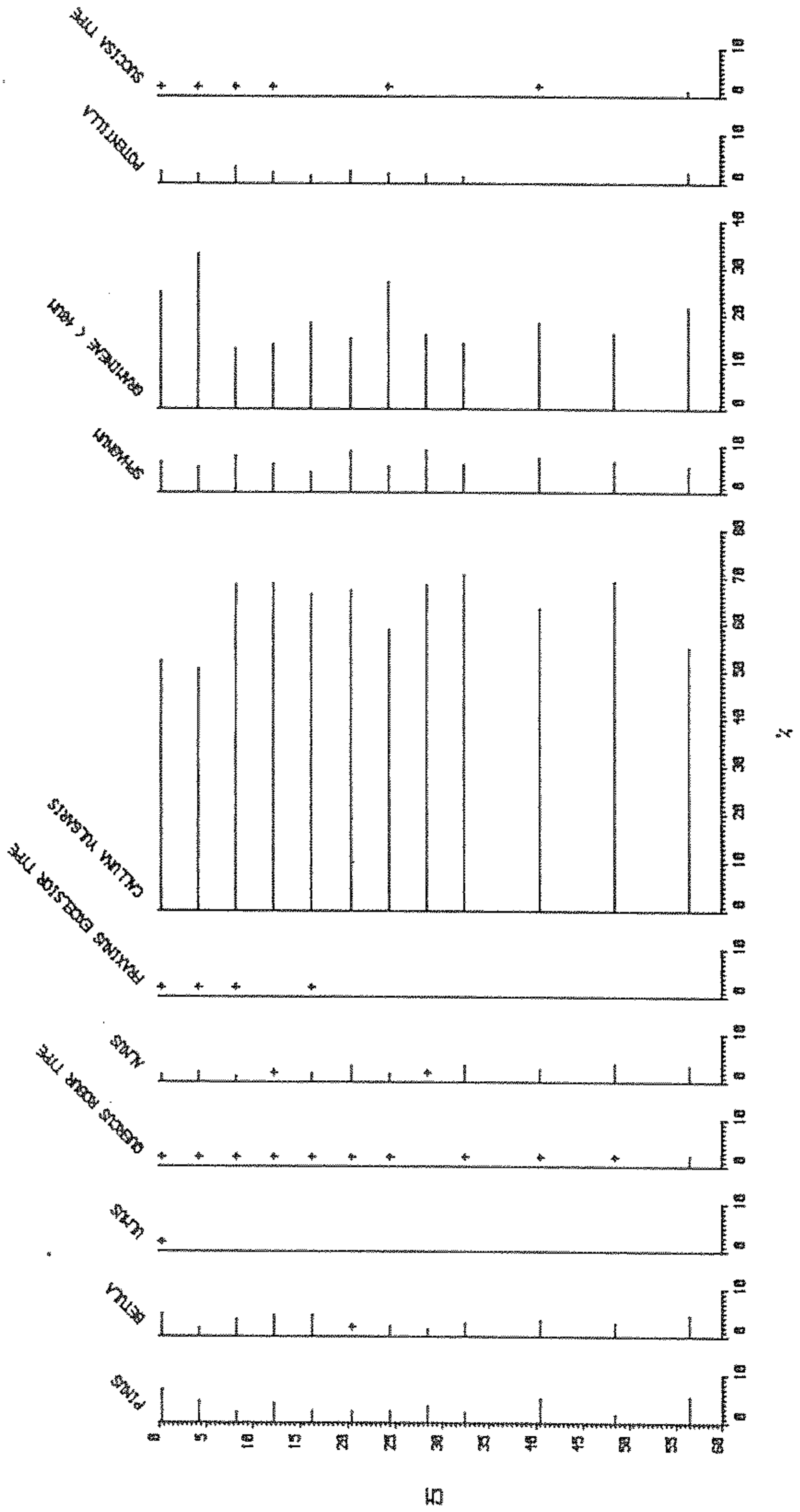
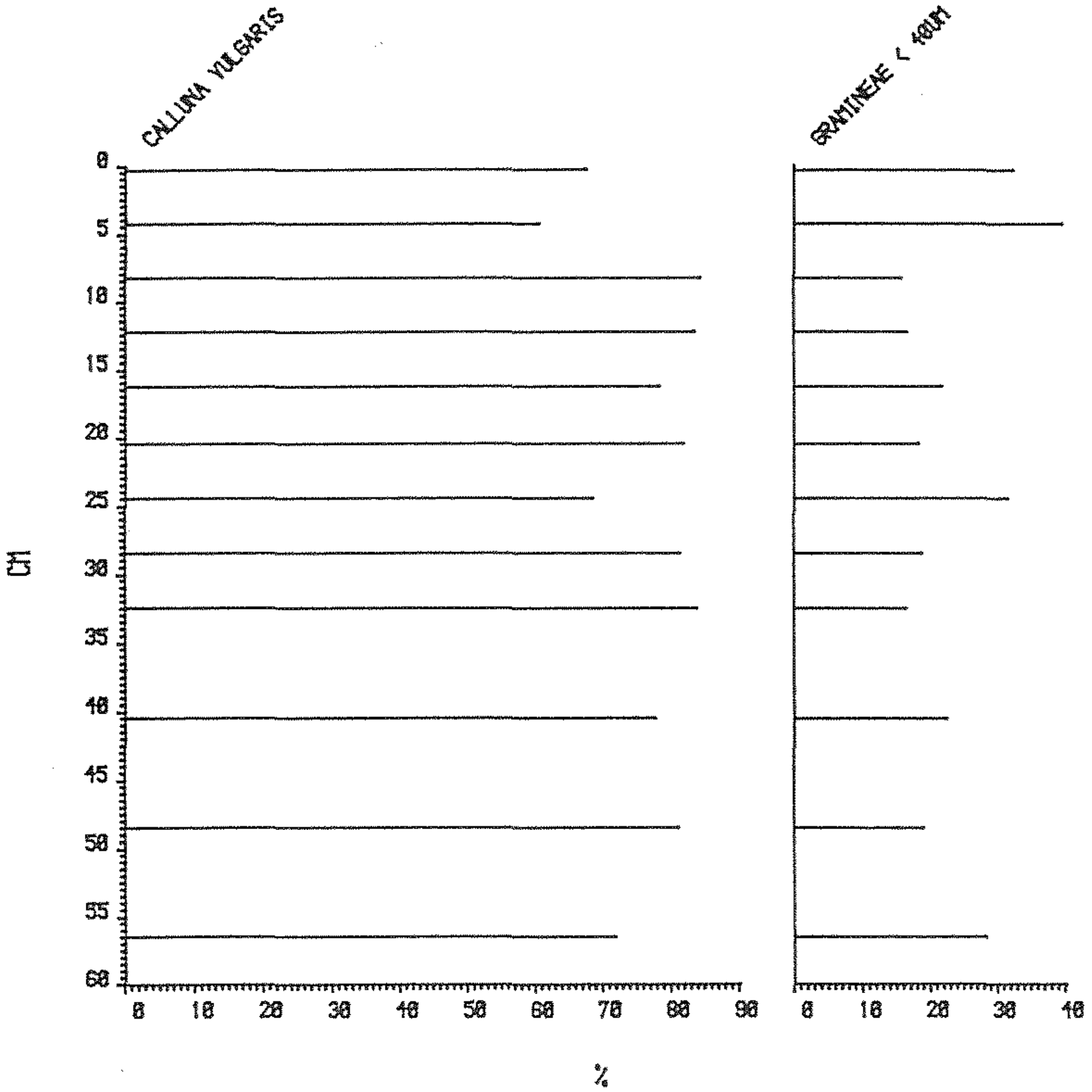


Figure 6.10 Loch na Larach: *Calluna* : Gramineae ratio



6.3 DISCUSSION

Because of the disturbed sedimentary record at Long Loch and the unavailability of dating at either site, few firm conclusions can be made about the recent history of these two lakes. However a few points may be noted at this stage. The problems of pH reconstruction at brown water sites have been highlighted in this report, the existing surface sediment data set does not cover a range of brown water sites and this needs to be extended before reliable reconstructions can be made. It is also interesting to note that both sites have clear evidence of inwash of peat from the catchment. This is a widespread phenomenon throughout the British Isles and a palaeolimnological approach is useful for determining both the timing of onset and causes of peat erosion (Stevenson *et al.* 1990).

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7 LAKE ACIDIFICATION STUDIES IN THE SNOWDONIA NATIONAL PARK

7.1 LLYN CONWY

Introduction

Llyn Conwy is located in north Wales on the Migneint Plateau (Figure 1.1). The lake was included in a previous study of Welsh lakes (Battarbee *et al.* 1988) as fishery data (Patrick and Stevenson 1986) suggested that the site had acidified since the 1960s; additional significance of water quality at Llyn Conwy arises from its use as a public water supply. It is also a good site for the palaeolimnological evaluation of the effects of upland land-management changes on water quality as unusually detailed records of the land-management history of the catchment exist (Patrick and Stevenson 1986). A sediment core (CON1) was taken from the deepest part of the lake (Figure 7.1) in 1985, but this contained only 2 cm of organic sediment overlying clay of presumably late-glacial origin. This suggested that, as in the case of Loch Fleet (Anderson *et al.* 1986) and Llyn Berwyn (Chapter 8, this report), the area of maximum organic sediment accumulation is not at the deepest point of the lake. Therefore it was decided to carry out a survey of the surface sediments of the lake, similar to that completed at Llyn Berwyn, before taking a further core.

1987 coring methods

A series of short cores were taken in transects across the lake using a Kajak gravity corer. The surface sediment from each core was analysed for the percentage dry weight and LOI (organic content) in order to determine the zone of maximum organic sediment accumulation. This was identified as an area on the south western slopes of the basin (Figure 7.1). The core CON4 was taken here using a wide diameter piston corer in 7 m of water. Laboratory analysis of this core follow Stevenson *et al.* (1987a).

Lithostratigraphy

The core consists of 172 cm of homogenous dark brown organic sediment, although there is a small amount of silt present below 136 cm. This increase in the mineral fraction is indicated in the percentage dry weight and LOI profiles (Figure 7.2) with the decrease in LOI below 136 cm.

Dating

In progress

Diatom analysis

Diatoms were analysed down to 60 cm, the summary diagram is presented in Figure 7.3. Below 30 cm the diatom flora is dominated by the planktonic taxon *Cyclotella kuetzingiana*. Other circumneutral taxa such as *Achnanthes minutissima*, *Brachysira vitrea*, *Fragilaria virescens* v. *exigua* and *Cymbella lunata* are also present together with the more acid tolerant *Tabellaria flocculosa*. Above 30 cm the proportion of the *Cyclotella* begins to decline resulting in an increase in the *Fragilaria* species. However, by 20 cm this taxon also decreases as the more acid tolerant taxa such as *Cymbella perpusilla*, *Frustulia rhomboides* v. *viridula*, *T. flocculosa* and *Eunotia incisa* increase. At 4 cm increases in the acidobiontic taxa *Tabellaria quadriseptata* and *Navicula cumbriensis* indicate a trend towards more acidic conditions.

It is interesting to note the persistence of the *Cyclotella* at around 20% of the total count in the surface sediment since this diatom is usually associated with pH values greater than pH 5.5. At many sites in the UK a decline in *Cyclotella* in the sediment record appears to mark the onset of acidification (eg. Flower and Battarbee 1983). However, in Canada diatoms of this genus have been reported in large, deep lakes with pH values as low as 4.1 (Taylor *et al.* 1987). One proposed explanation is that in deep oligotrophic lakes the littoral habitats make a proportionally smaller contribution to the total diatom production in the lake leaving more nutrients available to the plankton. This could be the case with Llyn Conwy.

A pH reconstruction for this site is in progress.

Pollen analysis

A summary diagram showing the main changes in pollen types is shown in Figure 7.4. The pollen record shows three main features. At 128 cm there is evidence of a period of erosion within the catchment. Concentrations of *Isoetes* spores are very low indicating decreasing transparency of the water and this accompanies the increase in mineral content of the sediment seen in the dry weight and LOI profiles (Figure 7.2).

The *Calluna* : Gramineae ratio provides broad indication of catchment vegetation change since land-management in upland areas often affects the ratio of the two vegetation types. The *Calluna* : Gramineae diagram (Figure 7.5) indicates a decline in *Calluna* above 20 cm, possibly indicating the start of the period when the *Calluna* was actively managed for game by controlled burning (Patrick and Stevenson 1986). A similar decline in the *Calluna* : Gramineae ratio has been seen at other sites (Battarbee *et al.* 1988). The stability in the proportion of *Calluna* in the top 6 cm could indicate the cessation of burning in the catchment in 1970 (Patrick and Stevenson, 1986).

The *Pinus* profile in Figure 7.4 indicates two main increases in values at 36 cm and at 5 cm. The 36 cm increase is probably the result of early pine plantations on estates in the area, whereas the later increase accompanied by *Picea* represents the post-1940 afforestation expansion in north Wales.

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Discussion

The diatom data show that acidification has occurred from 30 cm onwards with an increase in the rate of acidification above 6 cm. According to the hypothesis which suggests that surface water acidification may result from the development of acidic vegetation such as mature *Calluna* in lake catchments (eg. Rosenqvist 1977, 1978, Pennington 1984), the reduction of *Calluna* in the catchment from 20 cm should reduce the rate of acidification at Llyn Conwy. This does not appear to be the case. However, the increasing acidification above 6 cm does coincide with the stabilization of the *Calluna* values in the pollen analysis and may indicate the effect of a change in land-management policy on water quality. The relative importance of such change in comparison to the effects of atmospheric deposition will be assessed when ^{210}Pb dating, carbonaceous particle and geochemical analyses are completed at this site.

Figure 7.1 Llyn Conwy: bathymetry (contours in metres)

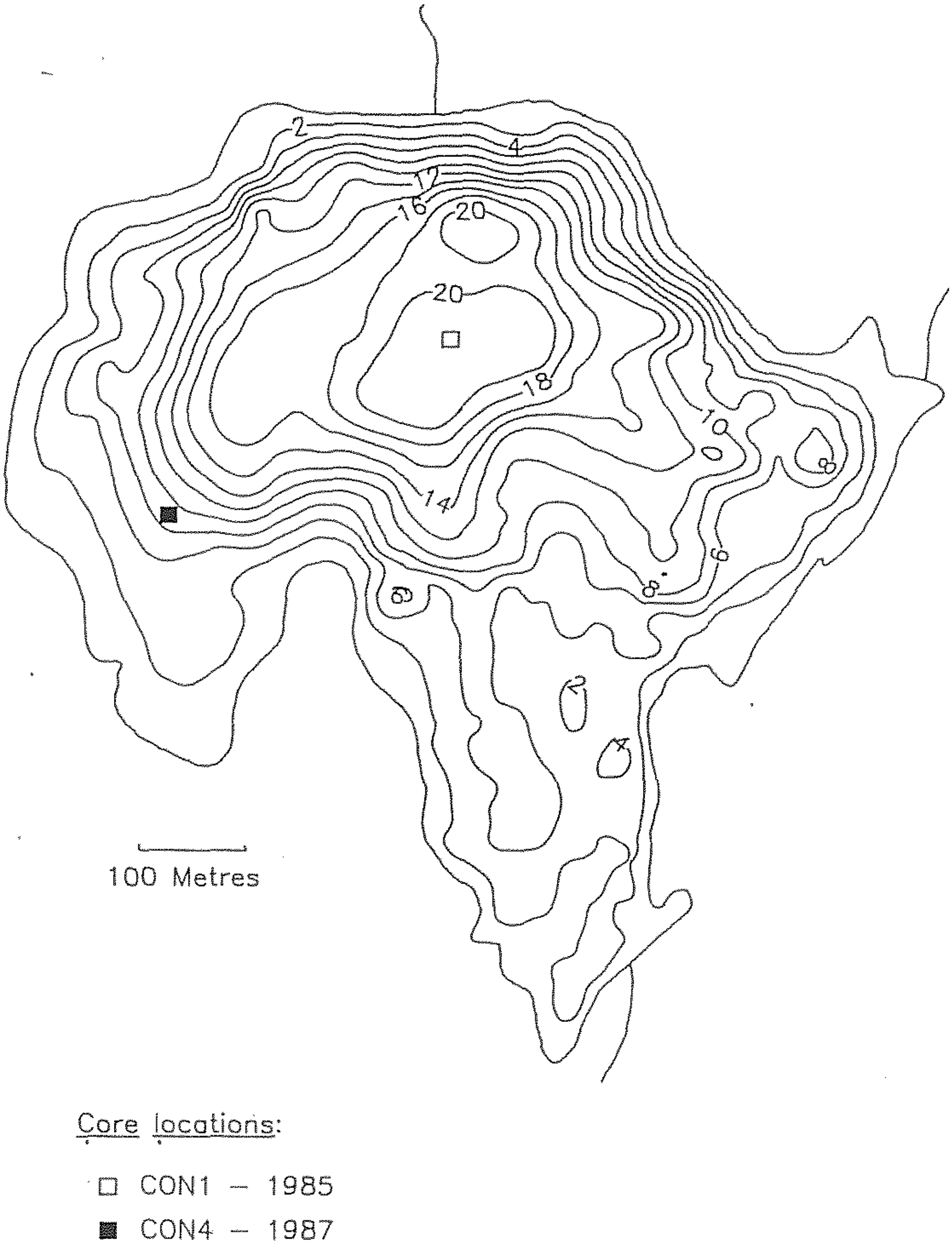


Figure 7.2 Llyn Conwy: lithostratigraphy

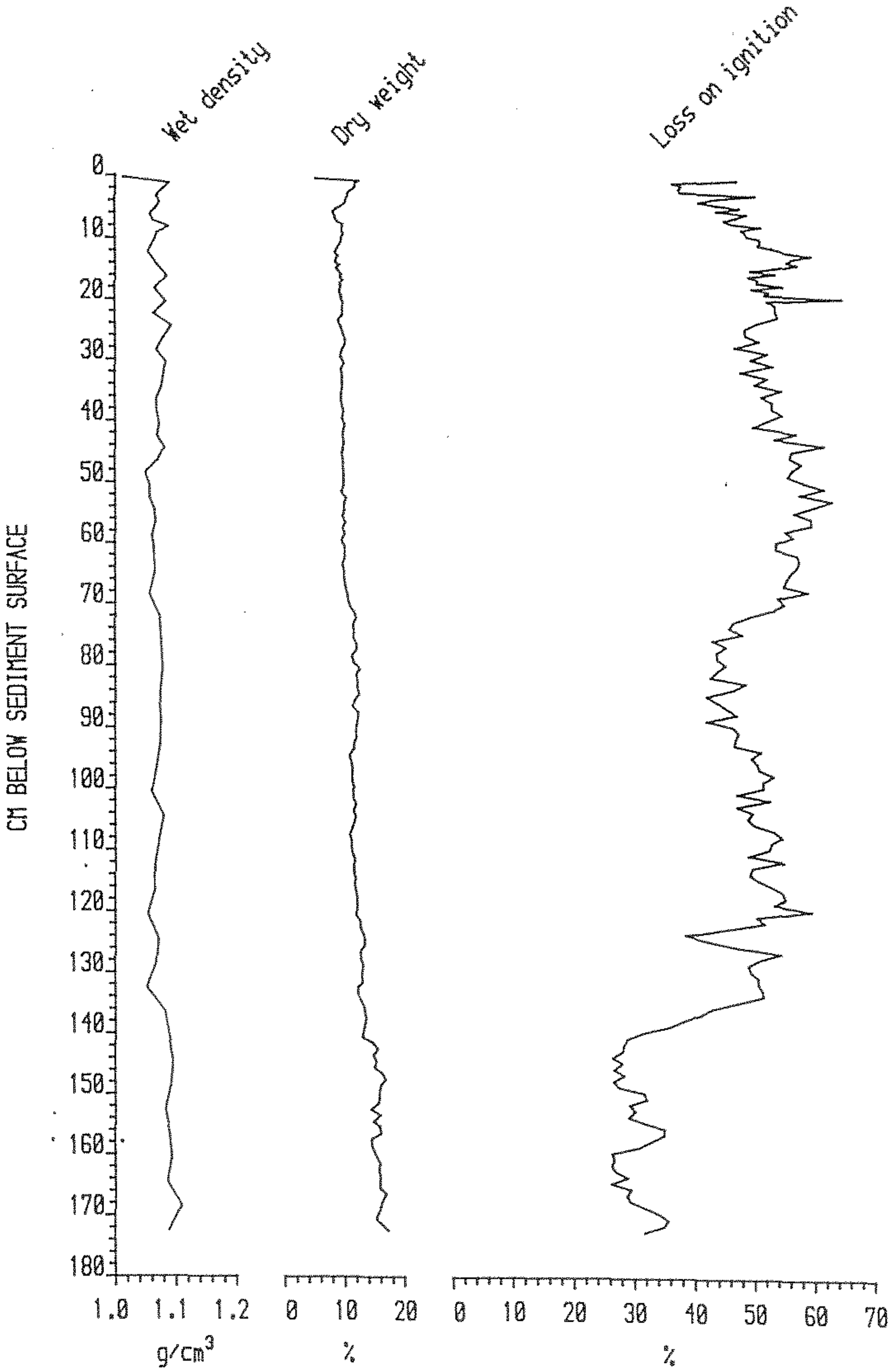


Figure 7.3 Llyn Conwy: diatom summary diagram

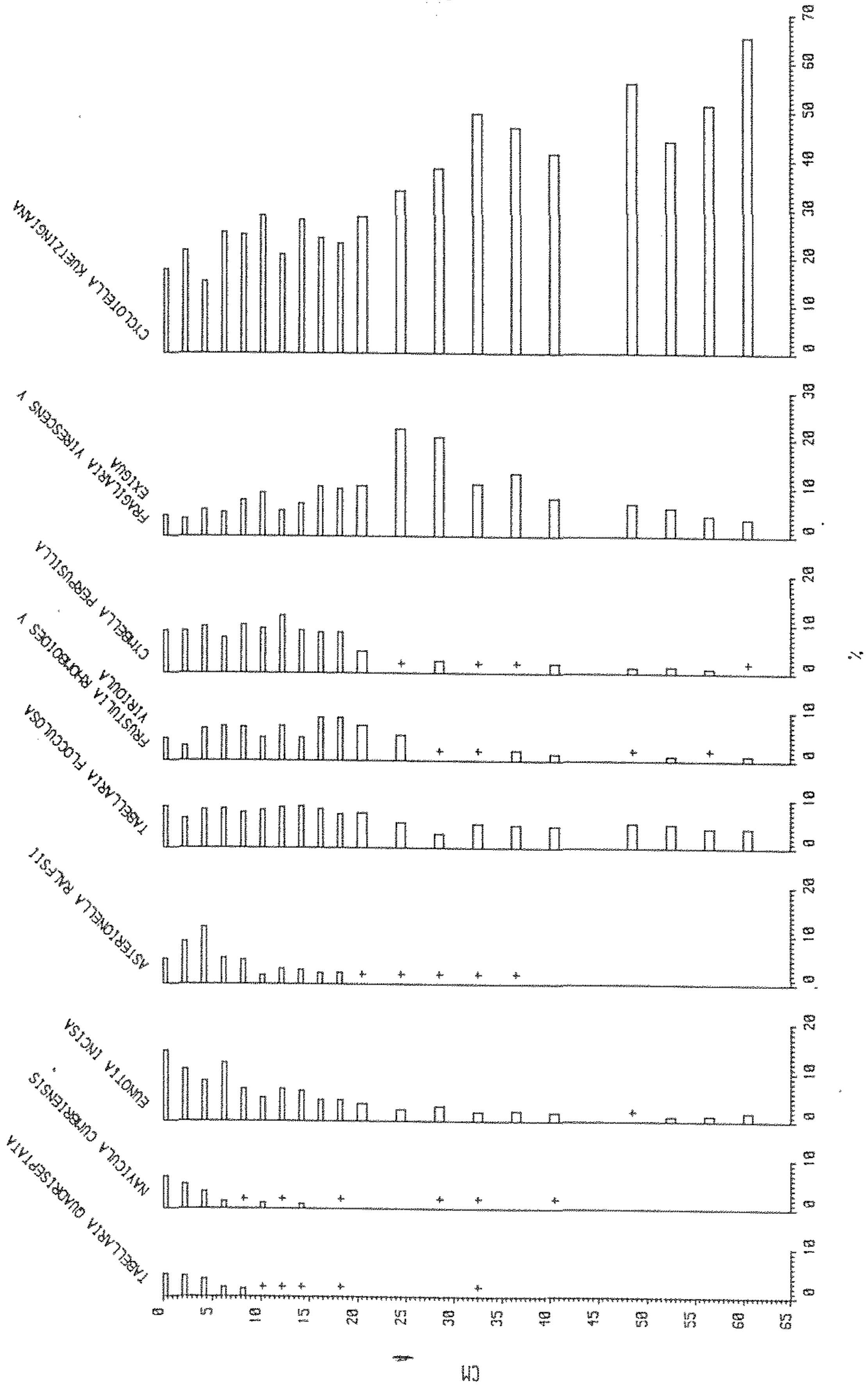


Figure 7.4 Llyn Conwy: summary pollen diagram

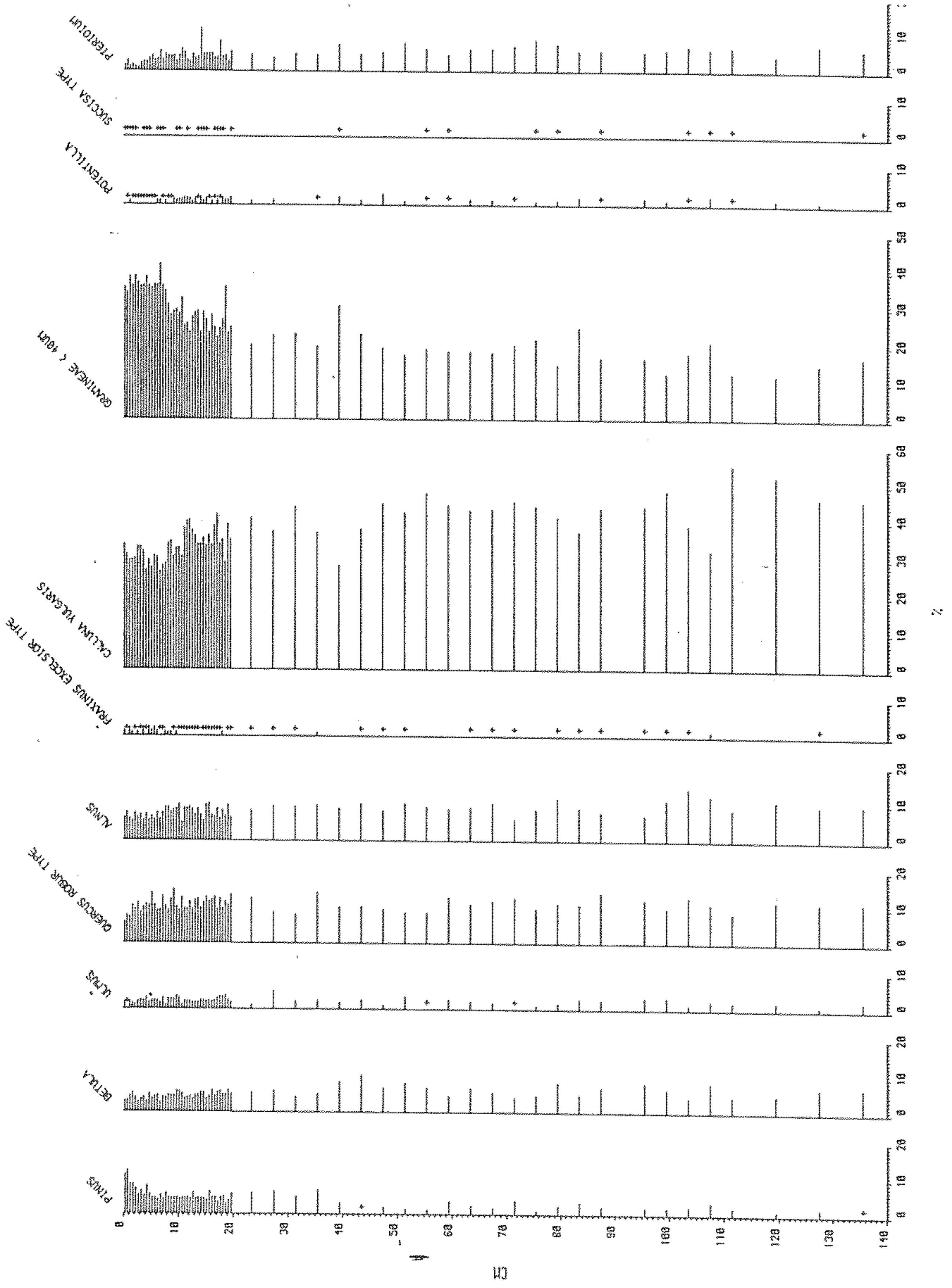
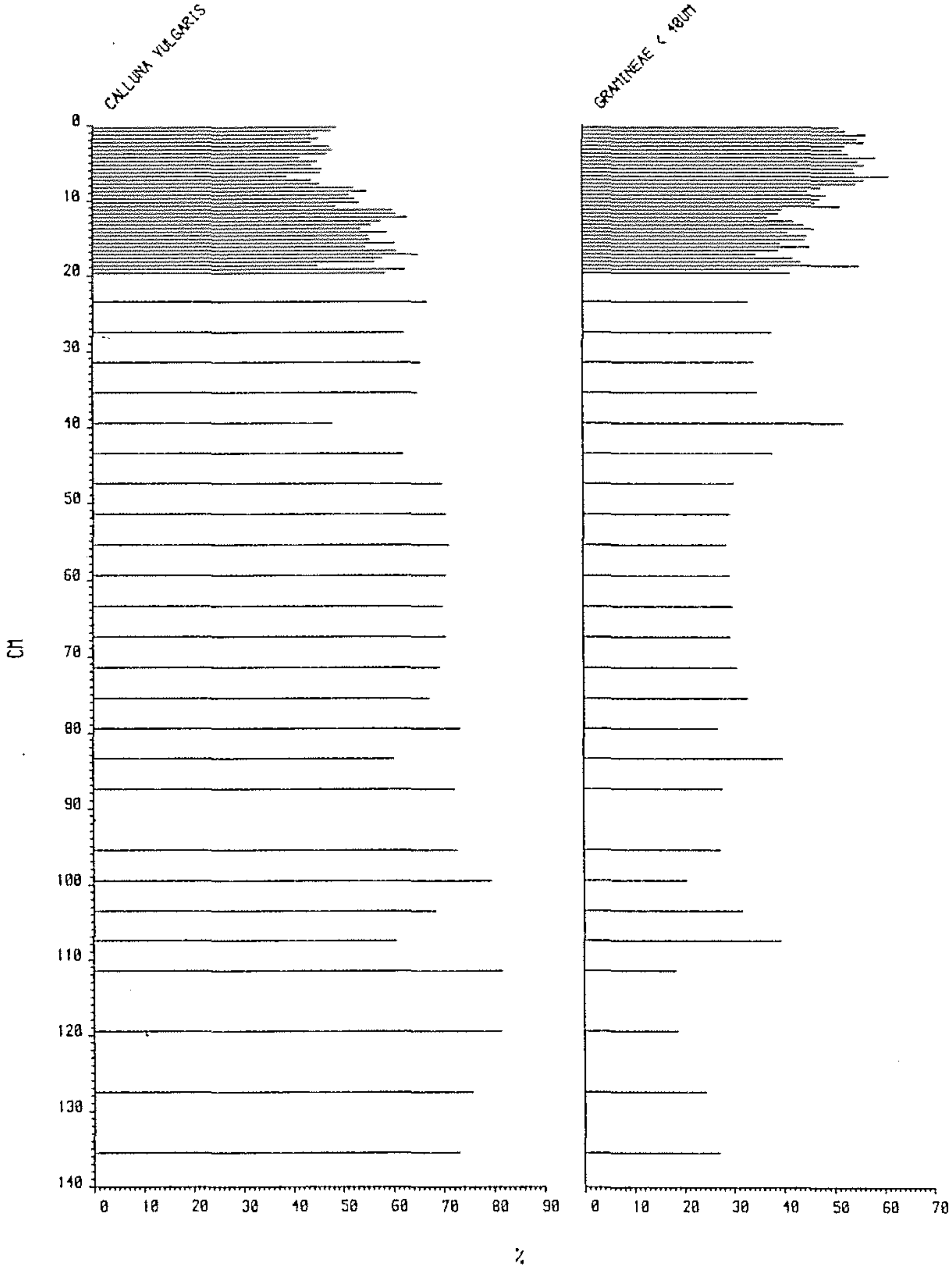


Figure 7.5 Llyn Conwy: *Calluna* : Gramineae profile



7.2 SITES WITH HIGHER ALKALINITIES

Introduction

Llyn Glas, Llyn Clyd and Llyn Irddyn (Figure 1.1) are lakes lying on potentially acid-sensitive geologies but possessing pHs, alkalinities and calcium values (Table 7.1) slightly higher than most other sites studied in Wales to date (eg. Battarbee *et al.* 1988). It is possible that these sites may have responded differently to the increased load of acid pollutants that this area of Wales has received since at least the mid-nineteenth century (Battarbee *et al.* 1988).

Llyn Glas and Llyn Clyd were studied by Walker (1977), who analysed the Holocene sediments for diatoms to reconstruct the developmental history of the lakes. However, her analyses did not include the uppermost sediments. The present study concentrates on this period and includes analyses which in combination with Walker's data will provide a complete Holocene history of limnological change for Llyn Glas and Llyn Clyd.

Table 7.1 Llyn Glas, Llyn Clyd and Llyn Irddyn: water chemistry

		L. Glas	**L. Clyd**	**L. Irddyn**
pH		6.25	6.15	5.28
Cond.	$\mu S\ cm^{-1}$	28.2	29.2	40.0
Ca^{2+}	$\mu eq\ l^{-1}$	71.2	55.9	60.4
Mg^{2+}	$\mu eq\ l^{-1}$	43.4	48.0	57.6
K^+	$\mu eq\ l^{-1}$	7.8	7.9	6.1
Na^+	$\mu eq\ l^{-1}$	130.1	123.9	194.3
Cl^-	$\mu eq\ l^{-1}$	126.9	134.0	197.5
SO_4^{2-}	$\mu eq\ l^{-1}$	57.3	65.7	95.4
Alkalinity (Alk_e)	$\mu eq\ l^{-1}$	33.45	33.93	2.03
TOC	$mg\ l^{-1}$	0.3	0.5	0.9
Al (labile)	$\mu g\ l^{-1}$	7.0	6.0	39.0

1985 - 1987 mean (n = 4)

7.2.1 Llyn Glas

Llyn Glas is a small clearwater lake at 533 m elevation, located just below the summit of Snowdon. A 101 cm core was recovered from the lake in May 1987. Laboratory analyses follow the methods of Stevenson *et al.* (1987a).

Lithostratigraphy

Sediments below 20 cm are detrital muds, with some sand and a high proportion of siliceous remains. Below 35 cm the sediments contain an increasingly higher proportion of silts. LOI values rise very gradually from c. 10% near the base of the core to around 18% at 20 cm (Figure 7.6). Above 20 cm the proportion of sand in the sediments increases and this is reflected in the declining LOI values. A small zone of elevated LOI values between 10-7.5 cm reflects *Sphagnum* and other bryophyte remains in the sediments.

Dating

In progress

Diatom analysis

The stratigraphic data (Figure 7.7) suggest that sediments below c. 20 cm overlap with the uppermost levels in the cores studied by Walker (1977). Several additional samples will be counted from the present core to match more precisely this stratigraphy with that presented by Walker.

The Llyn Glas sediments are dominated by periphytic taxa; plankton are virtually absent throughout the history of the lake (Walker 1977). The lowermost sediments are dominated by *Fragilaria brevistriata* with moderate percentages of *Achnanthes minutissima, Nitzchia* cf. *fonticola* and *Nitzchia perminuta.* These taxa are primarily alkaliphilous and circumneutral in pH preference. *Fragilaria brevistriata* and *Nitzchia* percentages decline above 48 cm and are replaced primarily by *Achnanthes minutissima* and *Synedra rumpens* together with small increases in a variety of other *Achnanthes* species.

Above 10 cm the sediments show a distinct change in the diatom assemblage, with a decline in the circumneutral *A. minutissima* and in *Synedra rumpens* and increases in several taxa, including *Achnanthes detha, Achnanthes altiaca, Achnanthes umara, Fragilaria construens* v. *pumila, Fragilaria virescens* v. *exigua* and *Aulacoseira lirata* v. *lacustris.* Some of these taxa are acidophilous and their increase in the uppermost sediments suggests some loss of alkalinity and perhaps a slight decline in pH. A pH reconstruction is in progress to ascertain the significance of this change.

Pollen analysis

In progress

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Figure 7.6 Llyn Glas: lithostratigraphy

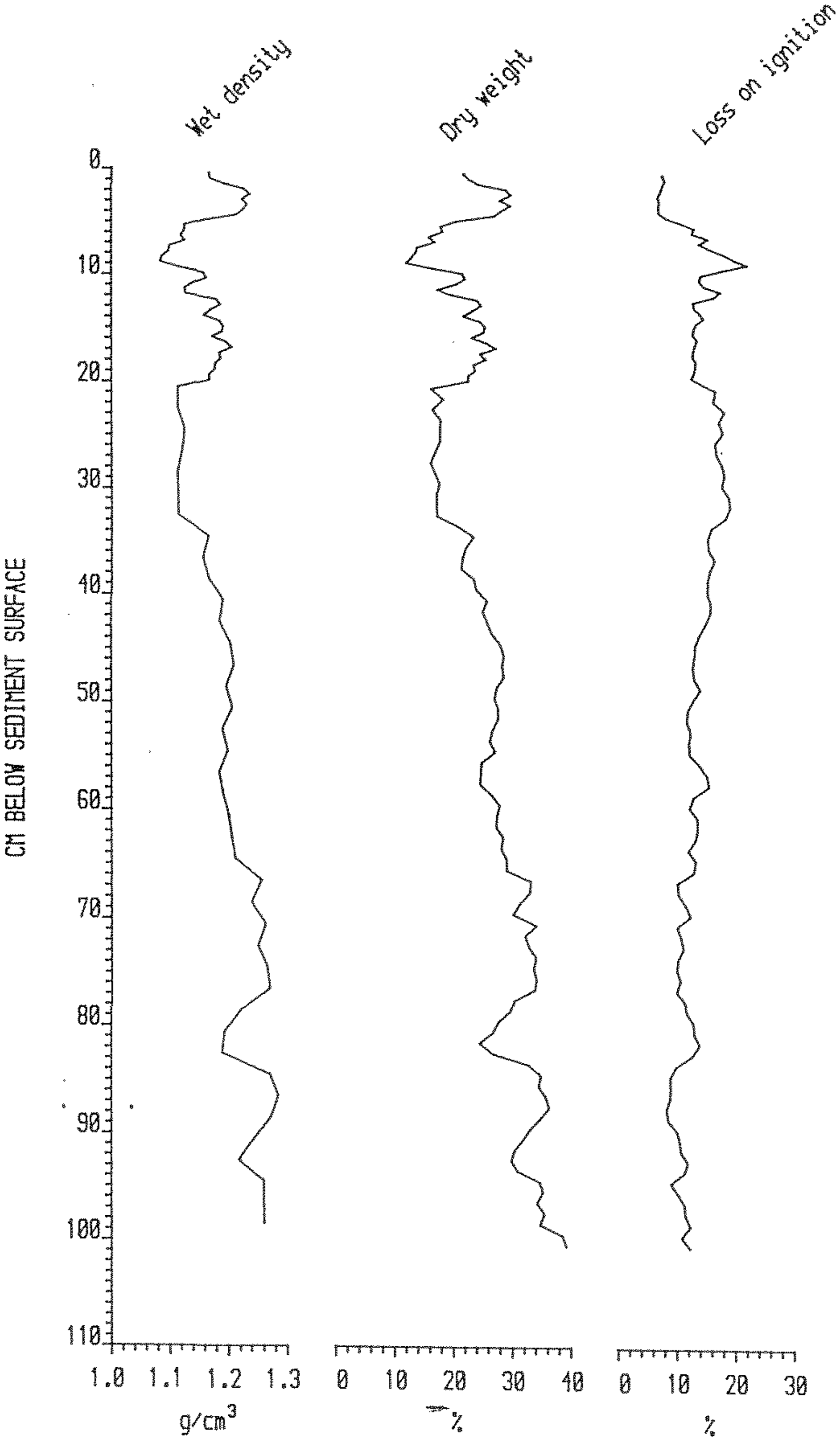
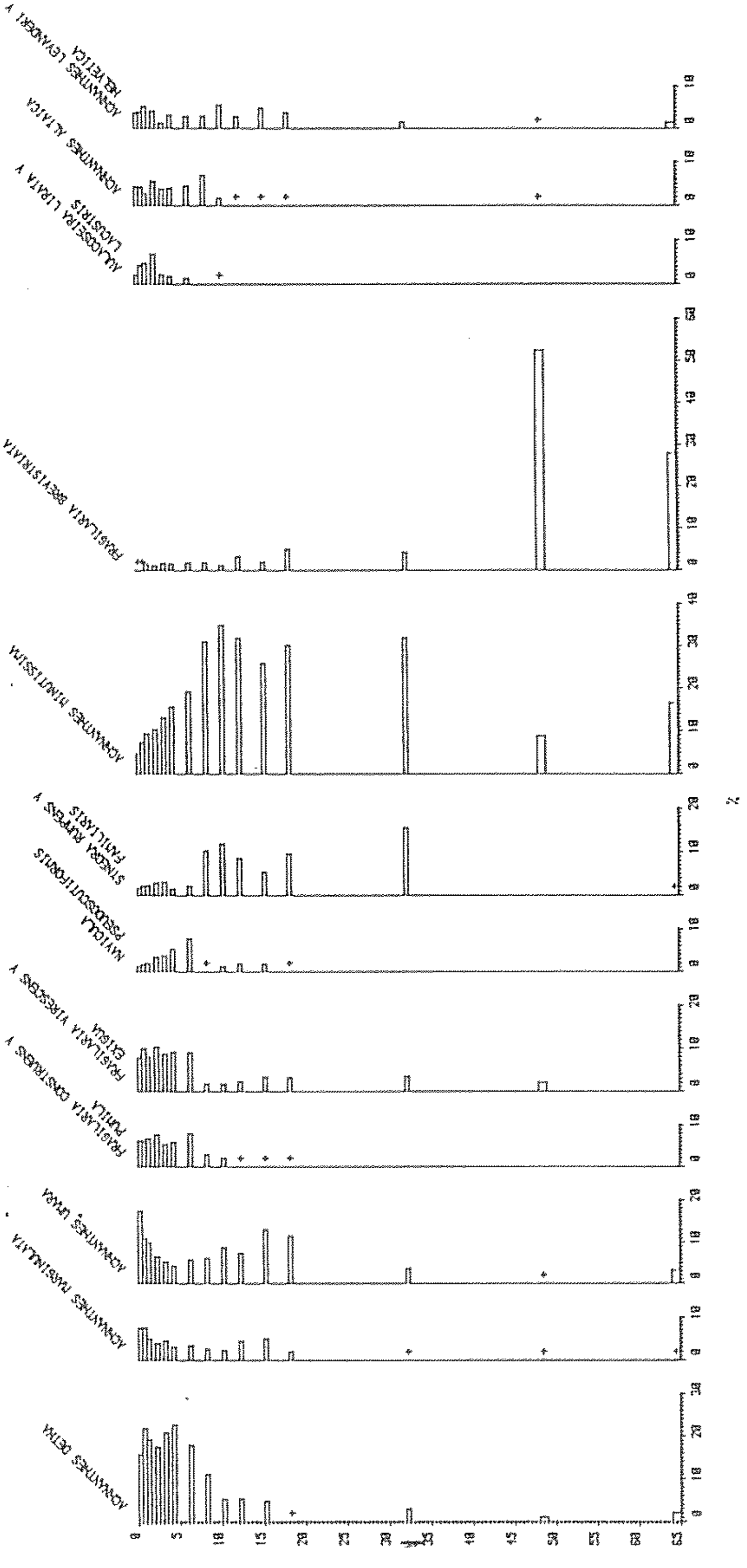


Figure 7.7 Llyn Glas: summary diatom diagram



7.2.2 Llyn Clyd

Llyn Clyd is a small lake which lies at 660 m above the Nant Ffrancon valley below the summit of Y Garn. An 86 cm core was recovered from the site in May 1987, which to date has been analysed for lithostratigraphy and pollen.

Lithostratigraphy

From the surface sediment to 5.5 cm depth the sediment is dark brown and organic. Below 5.5 cm there is a change in colour to a grey/brown sediment containing variable traces of clay, silt and fine sand. This unit of higher mineral content extends down to 44 cm and is reflected in the widely fluctuating dry weight and wet density measurements for this part of the core (Figure 7.8). Below 44 cm the sediment is again dark brown and organic with occasional fine sand grains but without the high mineral content seen in the sediment above.

Dating

In progress

Diatom analysis

In progress

Pollen analysis

Pollen analysis (Figures 7.9, 7.10) shows an increase in *Pinus* in the top 4 cm accompanied by a decrease in *Calluna vulgaris* and an increase in Gramineae and Cyperaceae. These changes could reflect recent regional vegetational changes such as coniferous afforestation in the area, but the accompanying sedimentological changes suggest discontinuity in the sediment record below 5.5 cm.

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Figure 7.8 Llyn Clyd: lithostratigraphy

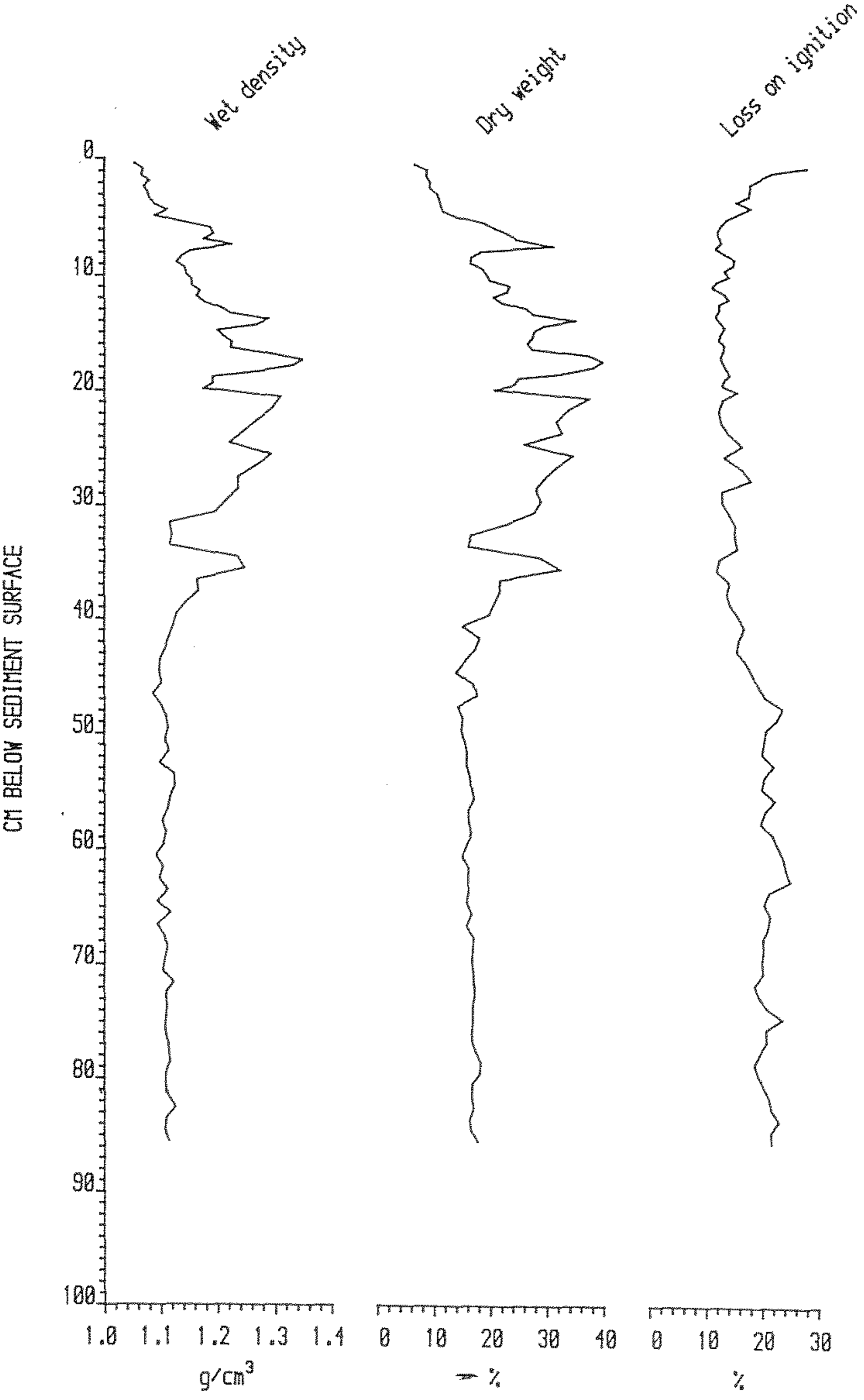


Figure 7.9 Llyn Clyd: summary pollen diagram

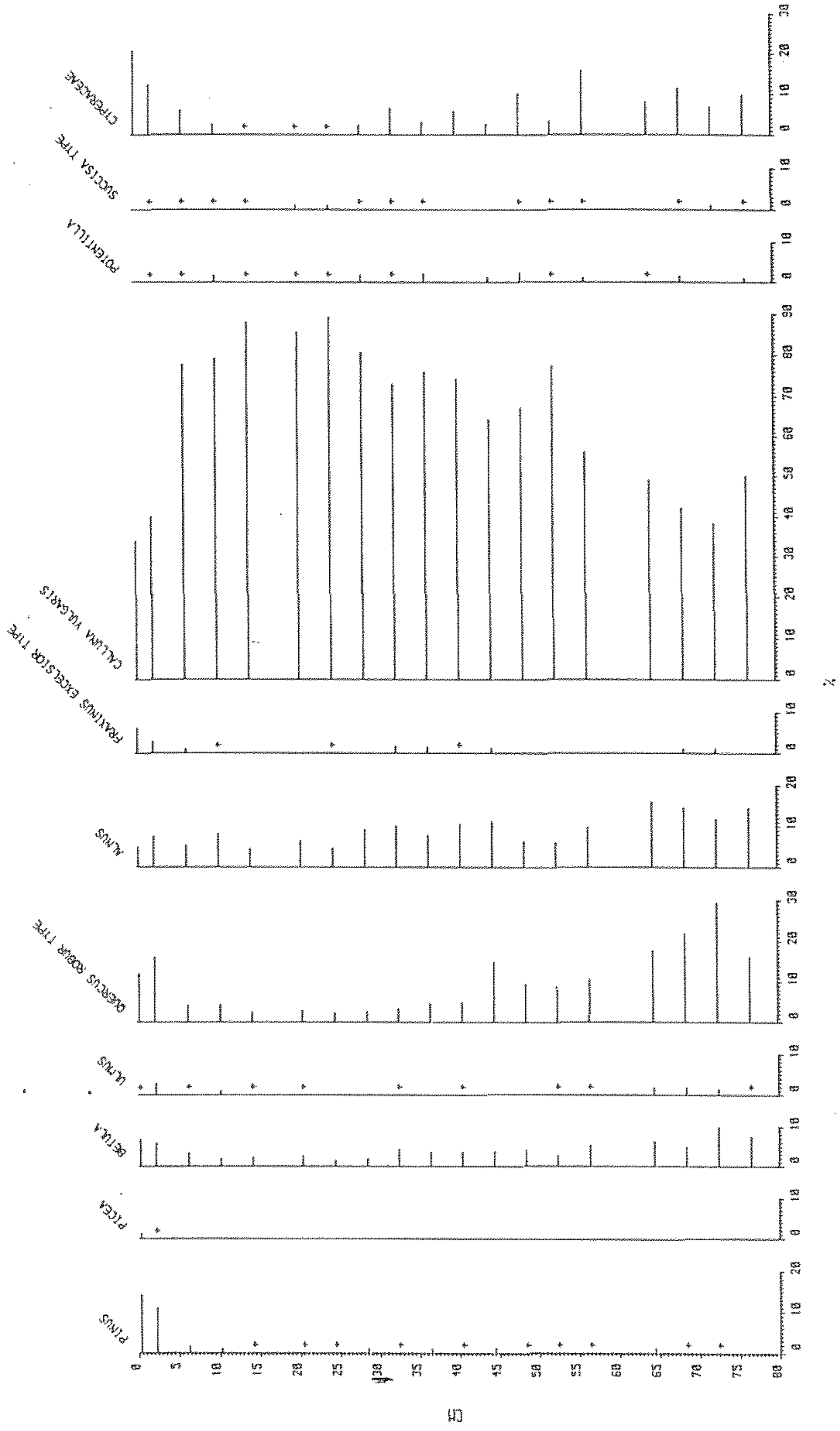
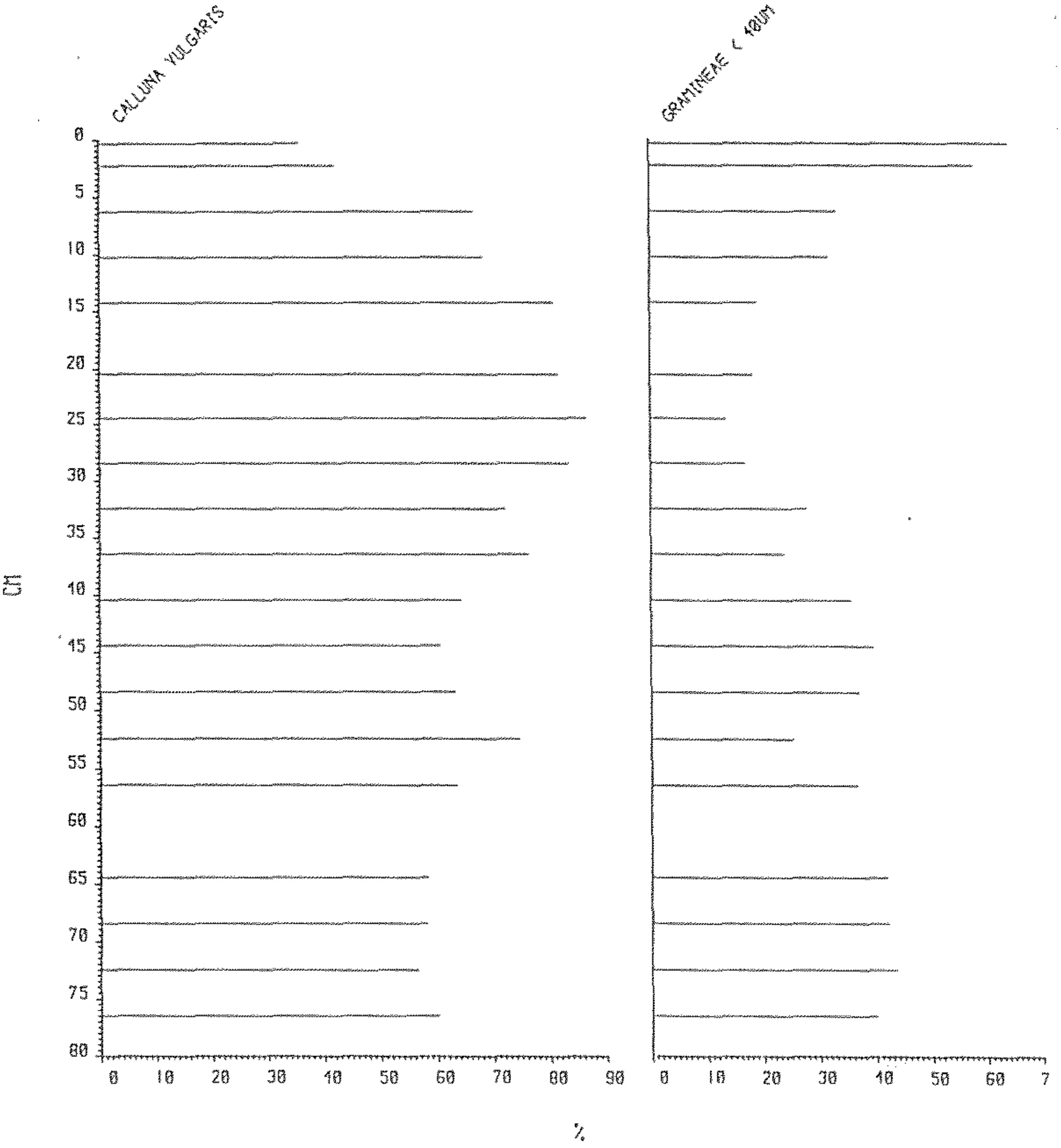


Figure 7.10 Llyn Clyd: *Calluna* : Gramineae profile



7.2.3 Llyn Irddyn

Llyn Irddyn is located at 300 m altitude on the Harlech Dome (Figure 1.1) and lies just below the small corrie lake, Llyn Dulyn, studied previously (Stevenson *et al.* 1987b). Llyn Irddyn is larger in surface area and has a higher pH, calcium and alkalinity (Table 7.1) than Llyn Dulyn, despite their proximity and similar history of atmospheric pollution. This suggests that some local source of alkalinity within the Llyn Irddyn catchment is capable of buffering acid inputs.

The lake is predominantly shallow, but with a deep basin (maximum depth 8.75 m) offset to the east (Figure 7.11). A complete sedimentary sequence of 328 cm was obtained from 6 m water depth (Figure 7.11) using a modified Livingstone corer in May 1987. The analyses discussed here follow the methods of Stevenson *et al.* (1987a) and concern the uppermost segment of the core, which extends from 142 cm to the surface.

Lithostratigraphy

The lower sediments in this sequence are very high in organic content as evidenced by LOI values of c. 40% below 90 cm (Figure 7.12). Above 90 cm the organic content declines sharply and sediments from 90-30 cm typically range from 20-30% organic, with the higher values in the uppermost part of that sequence. Above 30 cm LOI values again increase and the sediments from 30-13 cm comprise 30-45% organic matter. Above 13 cm the LOI declines to 24% at the core top.

Dating

In progress

Diatom analysis

A summary diatom diagram is presented in Figure 7.13. The presence of the planktonic *Cyclotella kutzingiana* in the lower part of the core, together with circumneutral periphyton which include *Achnanthes minutissima, Fragilaria brevistriata, Fragiaria virescens* v. *exigua, Navicula radiosa* v. *tenella* and *Navicula seminulum,* suggests a circumneutral pH for the early part of this core. A sharp decline in *Cyclotella* percentages above 48 cm is accompanied by slight increases in periphytic taxa and suggests some change in lake water chemistry, possibly a loss of alkalinity. Lower abundances of the macrophyte *Isoetes* from c. 50-20 cm (cf. Figure 7.14a) suggests a lower water clarity at this time.

Acidophilous periphyton such as *Achnanthes marginulata, Navicula leptostriata* and *Navicula mediocris* increase slightly above 8 cm, together with *Achnanthes umara* and the circumneutral *Cymbella gaeumannii.* Concurrently *Achnanthes minutissima* and other common periphytic species present in the lower part of the core, decline. The increased abundance of acidophilous species certainly suggests a loss of alkalinity and probably a decline in pH. However, small percentages of *Cyclotella kutzingiana* are present throughout these sediments, including moderately high abundances between 10-8 cm, which suggests that lake pH never declined much below c. 5.5. A detailed pH reconstruction is in progress to quantify the changes documented in the diatom record.

Pollen analysis

Pollen analysis (Figure 7.14a, b) of the full core reveals a marked depression in *Pinus* values at 216 cm accompanied by high *Betula* values. This point coincides with a clay band at 210-220 cm. Pollen analysis above this point produces a replica of the profiles seen from 260-220 cm (clearly seen from the arboreal pollen~~),~~ suggesting that at least 20 cm of post-glacial sediment has slumped over that of more recent origin at 220-200 cm depth.

The elm decline at about 5,000 years BP. is noticeable between 90 and 80 cm depth. Below this point the pollen data suggest that at least one metre of sediment has accumulated in the 1500 years prior to the elm decline. From this rate of sediment accumulation it seems likely that there is a hiatus in the sediment above 80 cm. It is possible that this coincides with the colour change in the sediment at 60 cm. The increase in *Pinus* in the top 10 cm indicates the twentieth century expansion of coniferous forest in the area.

Carbonaceous particle analysis

In progress

Geochemistry

In progress.

Figure 7.11 Llyn Irddyn: bathymetry (contours in metres)

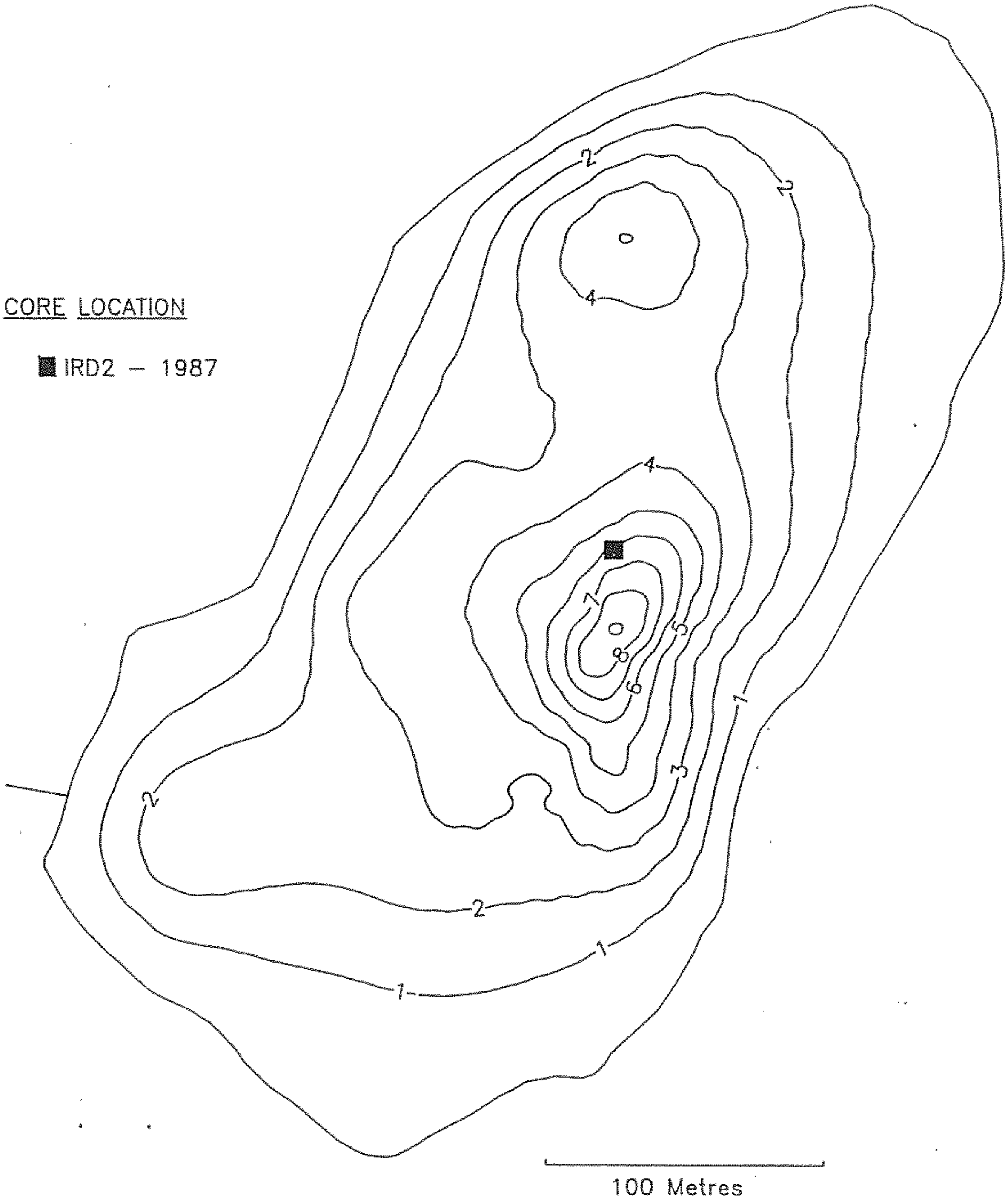


Figure 7.12 Llyn Irddyn: lithostratigraphy

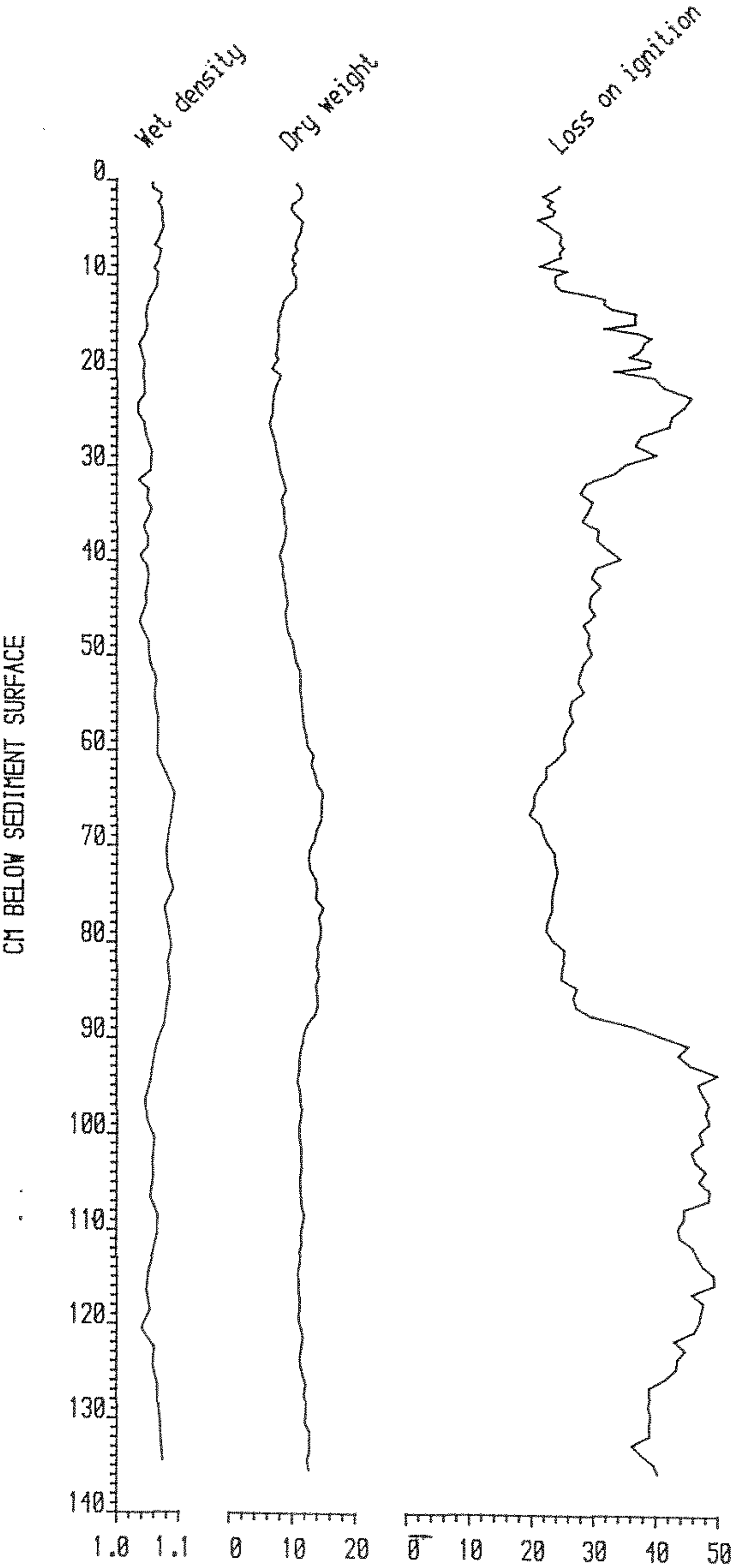


Figure 7.13 Llyn Irddyn: summary diatom diagram

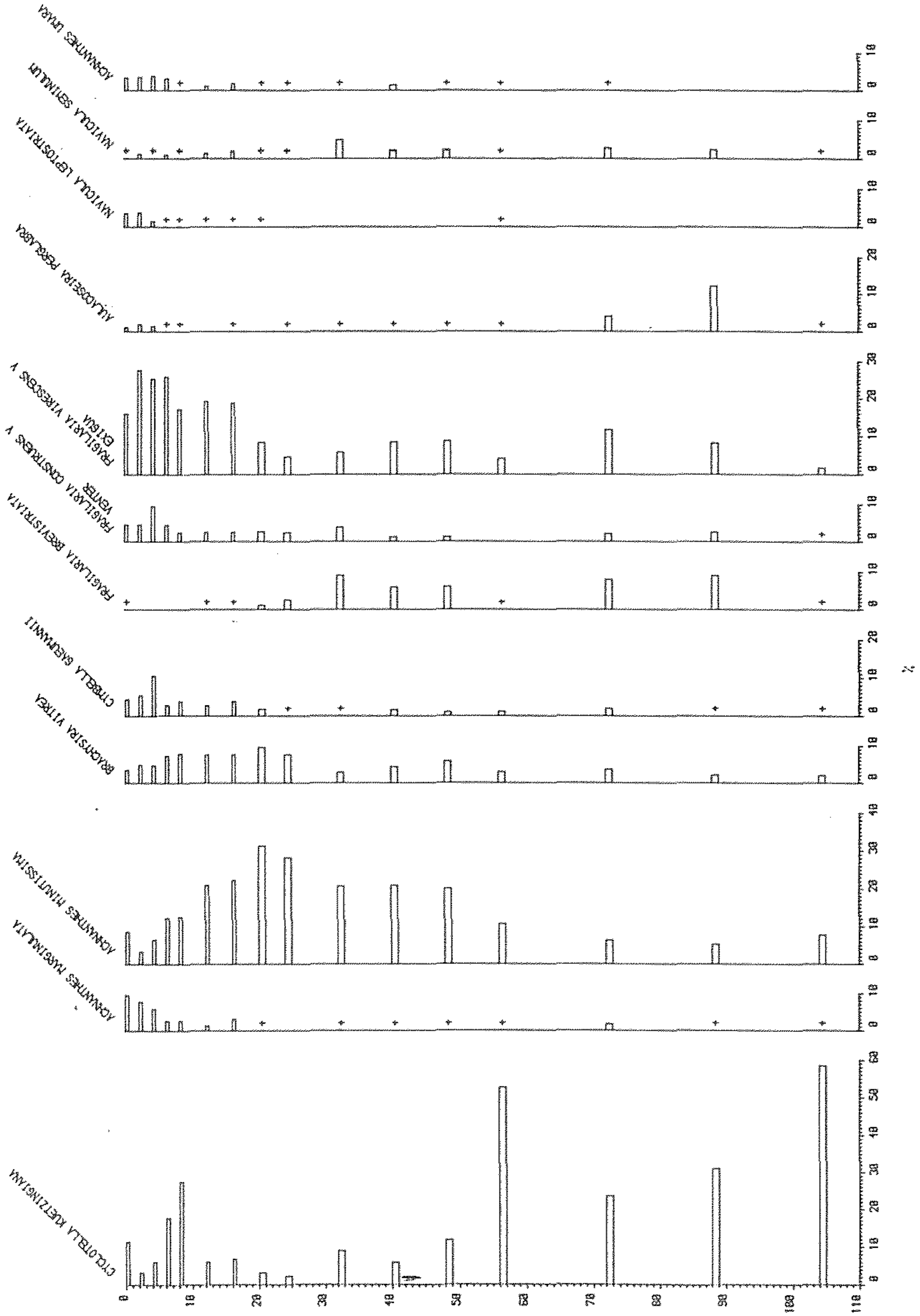


Figure 7.14a Llyn Irddyn: summary pollen diagram (0-140 cm)

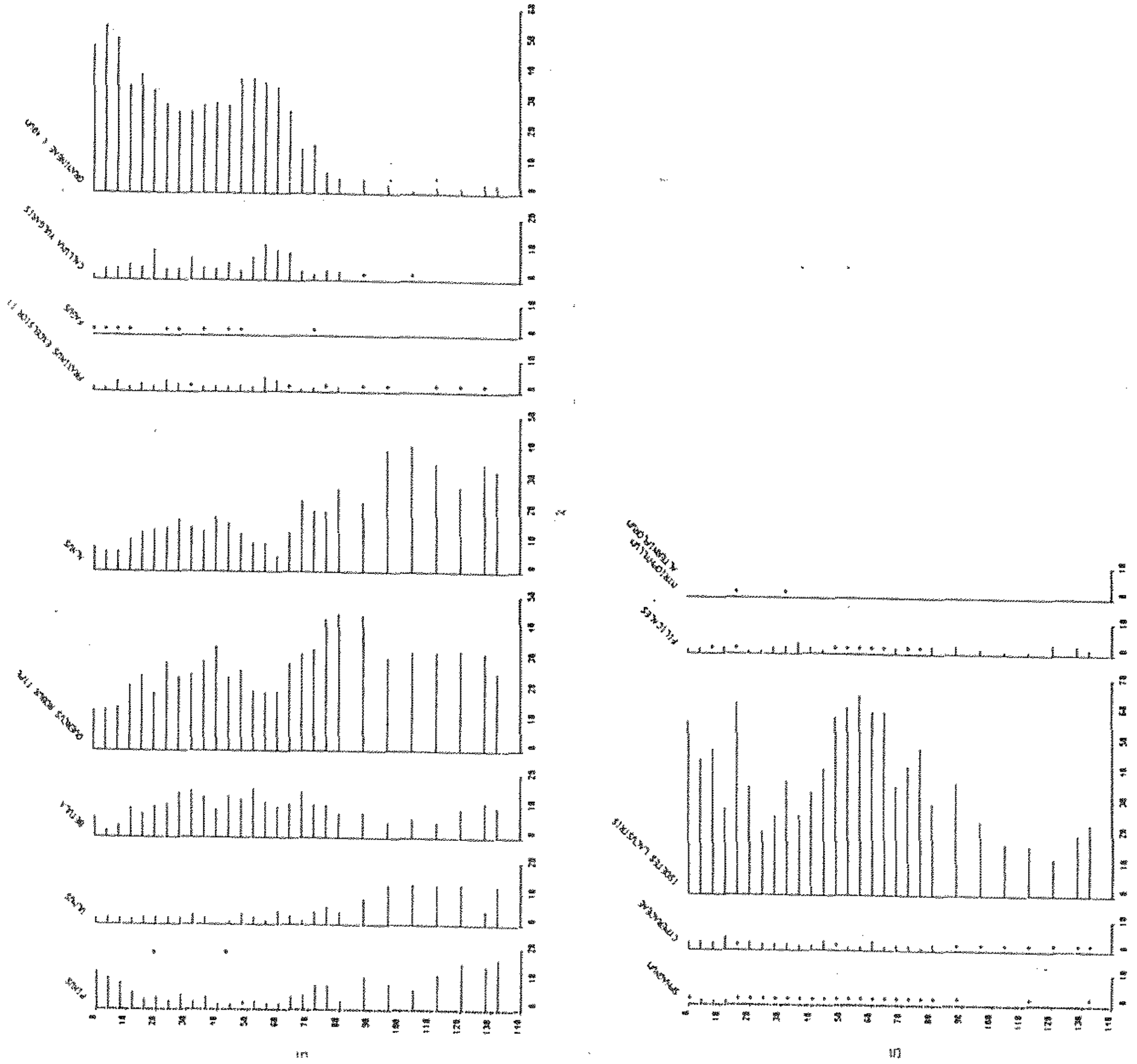
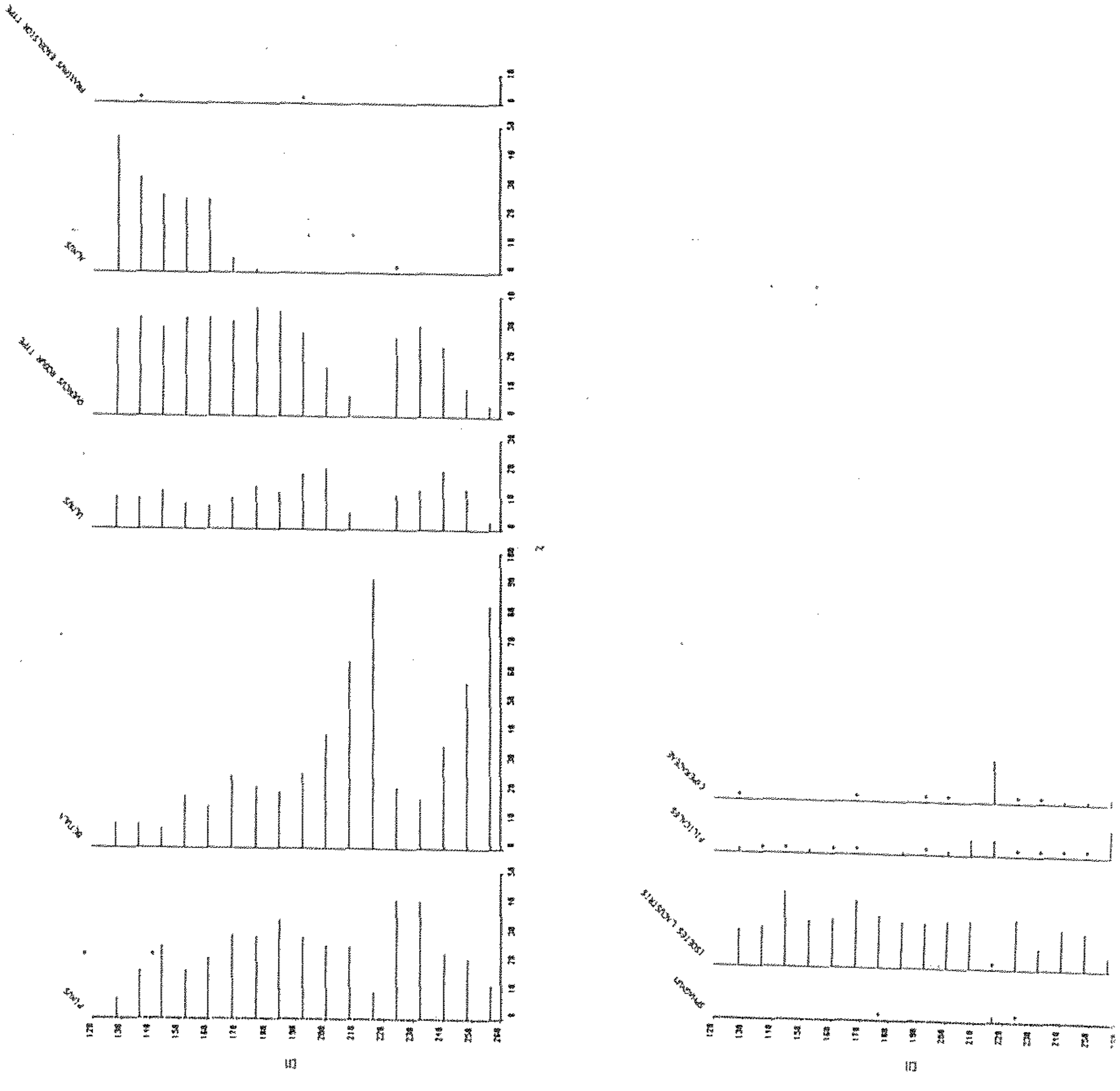


Figure 7.14b Llyn Irddyn: summary pollen diagram (120-260 cm)



7.2.4 Conclusion

In the absence of radiometric dating and particularly pH reconstructions, it is difficult to assess the recent limnological history of these three sites. However, there is evidence from the diatom record alone at Llyn Glas and Llyn Irddyn to suggest that some change in water quality, possibly a slight acidification, has occurred in the recent past at both these sites.

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8 ACIDIFICATION AT AN AFFORESTED SITE IN MID-WALES - LLYN BERWYN

8.1 INTRODUCTION

Coniferous afforestation has increased substantially in upland areas and has been linked to surface water acidification Wales (Stoner *et al.* 1984). Afforestation may promote acidification through processes associated with tree growth (Nilsson *et al.* 1982), ground preparation techniques, especially drainage (Hornung and Newson 1986) and the combined effects of acid deposition and forestry such as the enhanced capture of atmospheric acidic contaminants by the canopy and the foliar uptake of sulphur dioxide and subsequent leaching of sulphate (Lindberg and Garten 1988).

The study of lake acidification in Wales reported by Battarbee *et al.* (1988) originally included two lakes with afforested catchments; Llyn Berwyn and Llyn Cwm Mynach. Both lakes are vulnerable to acidification with mean calcium levels of 41.2 and 68.7 ueq l^{-1} respectively. The sediment record in Llyn Cwm Mynach indicates a gradual decline in lake pH of 0.5 pH unit from the late-nineteenth century. The planting of over 50% of the catchment with coniferous forest in the late 1960s did not appear to have contributed further to the acidity of the lake (Fritz *et al.* 1989).

In the case of Llyn Berwyn there have been reports of a rapid decline in fish populations over the period of afforestation and a mean pH of 4.2 in 1984 suggested the lake had been considerably acidified (Underwood *et al.* 1987). Additional interest at Llyn Berwyn is provided by its location adjacent to the Llyn Brianne system where detailed acidification studies have been undertaken in recent years (eg. Welsh Water 1987). However, the sediment cores recovered from the deepest point in the lake in 1984 did not contain a full record of lake conditions over the past 150 years so the impact of afforestation in the early 1960s could not be assessed. The lake was re-cored in 1987 with the aim of recovering a full sedimentary sequence. Results from the 1984 core and preliminary results for the 1987 core are presented here.

8.2 THE SITE

The location of Llyn Berwyn is shown on Figure 1.1. Annual rainfall is in excess of 2000 mm and annual sulphur deposition from industrial sources is in the region of 1.2 g m^{-2}. The underlying geology of base-poor Silurian shales makes the lake vulnerable to acidification. The lake was experimentally limed in 1985 and pre-liming water chemistry is summarized in Table 8.1. In 1962-1963 over 90% of the catchment was ploughed, drained and planted with conifers. The lake has a simple concentric bathymetry with a maximum depth of 15 m (Figure 8.1). A full description of the site can be found in Kreiser *et al.* (1986).

Table 8.1 Lake water quality

pH		4.39
Cond.	μS cm^{-1}	58.3
Alkalinity (Alk_e)	μeq l^{-1}	0.11
Na^+	μeq l^{-1}	261.5
Ca^{2+}	μeq l^{-1}	41.2
K^+	μeq l^{-1}	6.5
SO_4^{2-}	μeq l^{-1}	165.4
Cl^-	μeq l^{-1}	234.2

Determinations = 1984-1985 (pre-liming) mean based on 26 measurements.

8.3 RESULTS 1984 - core BER1

A one metre sediment core was taken with a mini-Mackereth corer from the deepest point of the lake (Figure 8.1) in July 1984. Analytical methods followed those of Stevenson *et al.* (1987).

Lithostratigraphy

Routine measurements of percentage dry weight, LOI and sediment density (Figure 8.2) show a pattern of sedimentation which has also been seen in cores from other afforested sites (eg. Anderson *et al.* 1986) In core BER1 the sediment below 30 cm depth represents a period of stable sedimentation. The increase in dry weight above 30 cm indicates the onset of pre-afforestation drainage and ploughing in the catchment with an inwash of mineral particles. This is followed by a rapid increase in organic content indicated by the LOI values. Examination of this sediment reveals a large proportion of poorly decomposed peat fragments, presumably resulting from the slumping of catchment peat into the freshly cut drainage channels.

Dating

An attempt was made to date the core radiometrically using ^{210}Pb analysis. Unfortunately the unsupported ^{210}Pb inventory for the core was incomplete and no unsupported ^{210}Pb could be measured below 20 cm. This suggests that sediment below this depth is pre-nineteenth century in origin. However, since it is highly probable that the mineral-rich band between 20-30 cm has resulted from pre-afforestation ploughing, it seems more likely that the pre-nineteenth century sediment lies below 30 cm. The lack of any unsupported ^{210}Pb between 20 cm and 30 cm could be caused by dilution from the catchment or dilution from older reworked sediment. The 30 cm point in the core therefore marks the point of a hiatus in sedimentation in this area of the lake covering at least 100 years. Sediment accumulation did not begin again until the increased input from the catchment in 1962.

Diatom analysis

A summary of the principal diatom taxa from core BER1 is shown in Figure 8.3. Below 25 cm the assemblages are dominated by circumneutral forms suggesting long term pH values in the range pH 5-6. There is however a clear trend towards a more acid tolerant flora above 25 cm with the greatest change occurring between 20-25 cm. This appears to suggest that the lake became rapidly more acidic with catchment drainage and ploughing. However, since there is a possibility that this section contains older, reworked sediment, this trend could simply represent a reduced supply of older sediment contamination towards the top of the inwash. The initial change in diatom flora may have occurred during the hiatus in sediment accumulation. Despite this, there is evidence for further acidification at 15 cm (after 1962) with increases in the acid tolerant taxa *Asterionella ralfsii*, *Cymbella perpusilla* and *Tabellaria flocculosa*. Although unsupported ^{210}Pb is present at 15 cm, the lack of a full ^{210}Pb inventory prevents this level from being dated.

Conclusions

Three main conclusions were drawn from the analysis of core BER1:

1. Sedimentation in the lake records large-scale catchment disturbance as a result of forestry drainage. Below this there is a hiatus in the sediment accumulation.

2. The pH of the lake has been in the range pH 5.0-6.0 over a long period in the past.

3. The lake has subsequently acidified. The initial point of change can not be dated but further acidification has occurred after 1962.

Despite the sedimentological problems encountered at Llyn Berwyn, it was decided to re-core the lake for the following reasons:

1. Similar problems were encountered in Loch Fleet, south west Scotland, but a change in coring strategy enabled a full sedimentary sequence to be recovered (Anderson *et al.* 1986).

2. The site appears to have been severely acidified with pH values declining to 4.2 from an estimated pH 5.0-6.0 and the loss of fish has been reported over the period of afforestation.

3. Over 90% of the catchment has been planted with coniferous forest between 1962 and 1963. The influence of land-use strategies other than forestry can therefore be eliminated.

4. The uniform age of the plantations in the catchment allows the effect on water quality of each of the stages of forest development (eg. drainage, initial forest growth and canopy closure) to be assessed separately.

5. Llyn Berwyn has been included in an experimental liming programme (Underwood *et al.* 1987) and is also adjacent to the Llyn Brianne acid waters project experimental catchments.

Figure 8.1 Llyn Berwyn: bathymetry (contours in metres)

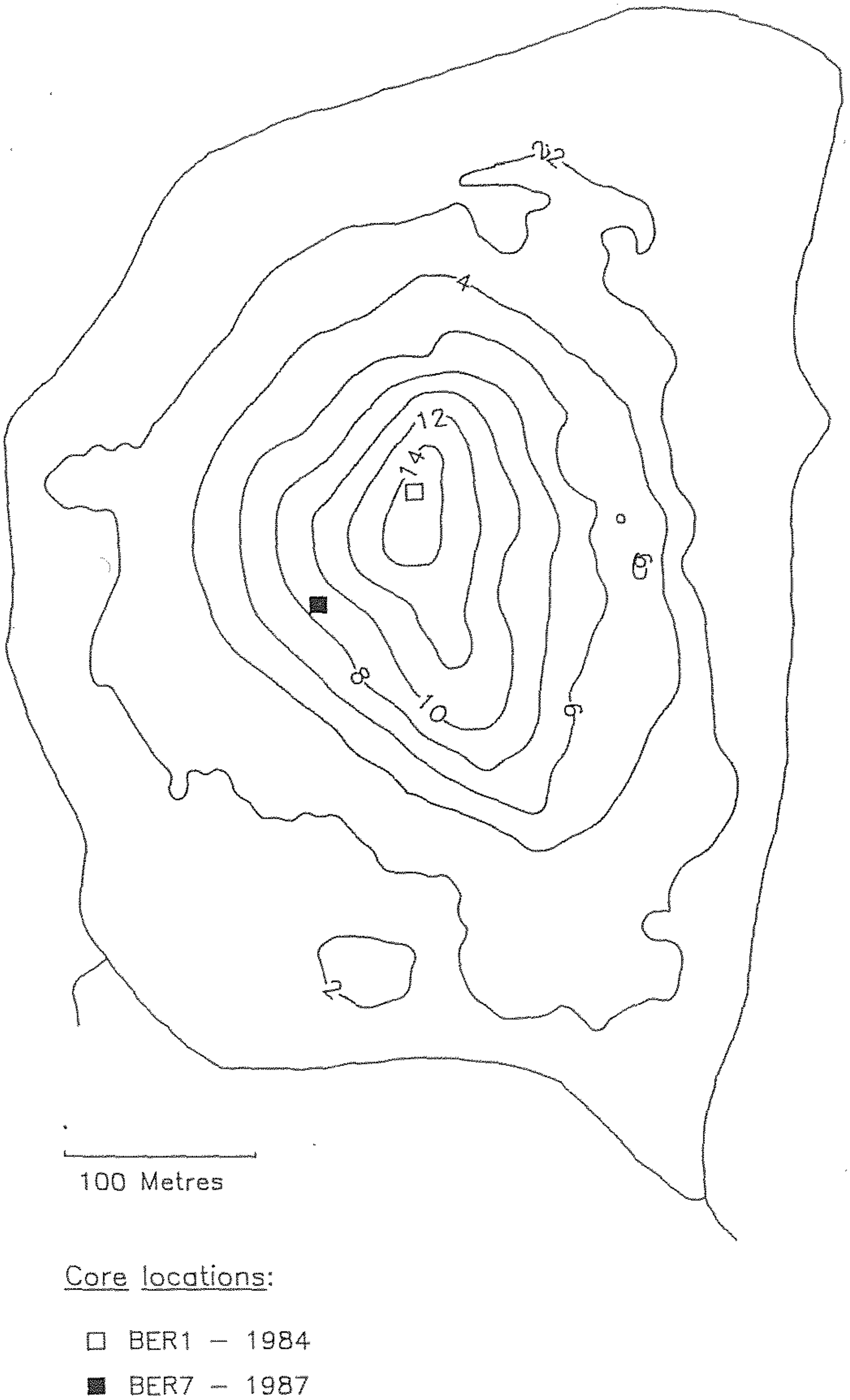


Figure 8.2 Llyn Berwyn: core BER1 (1984) lithostratigraphy

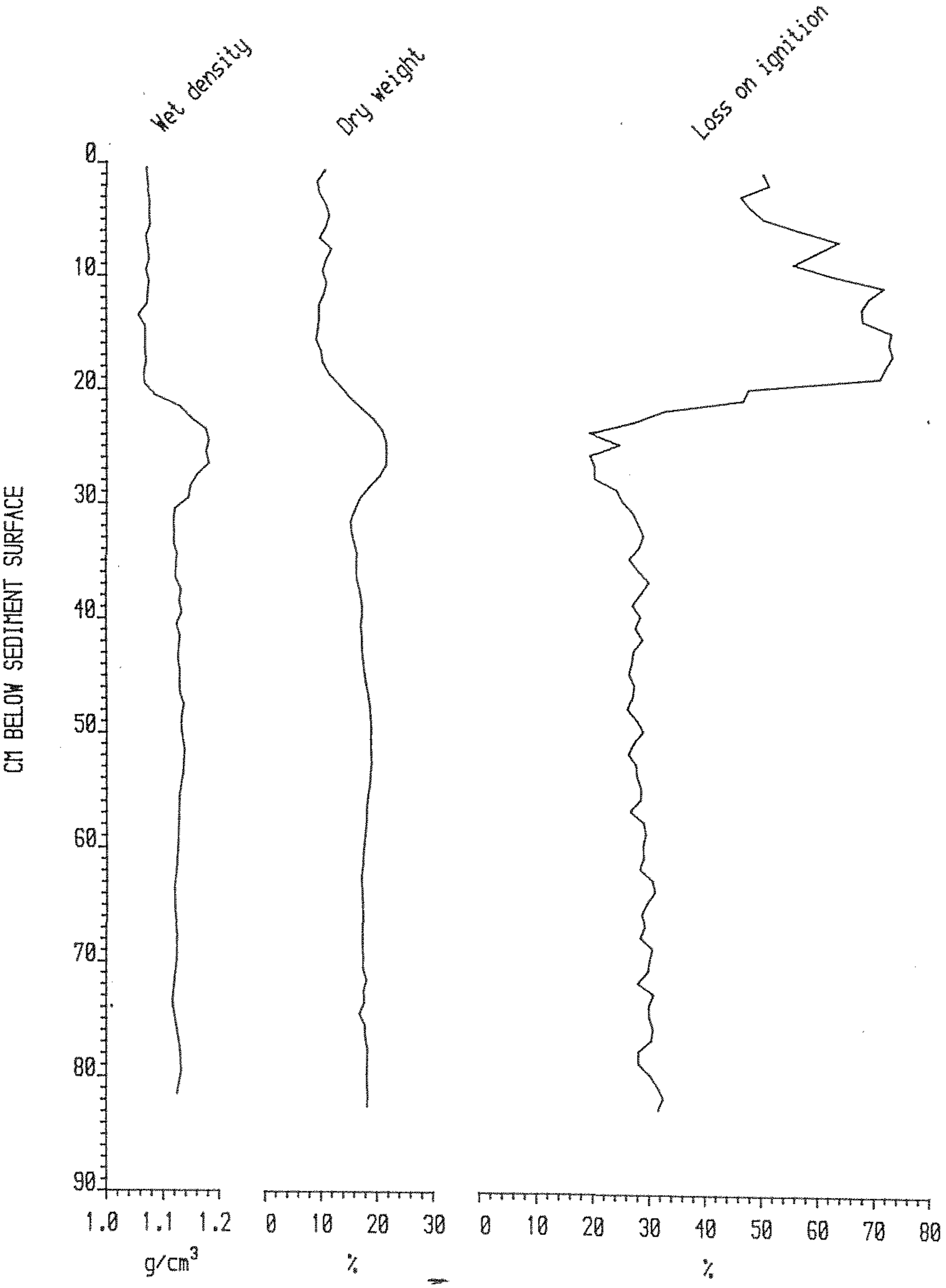
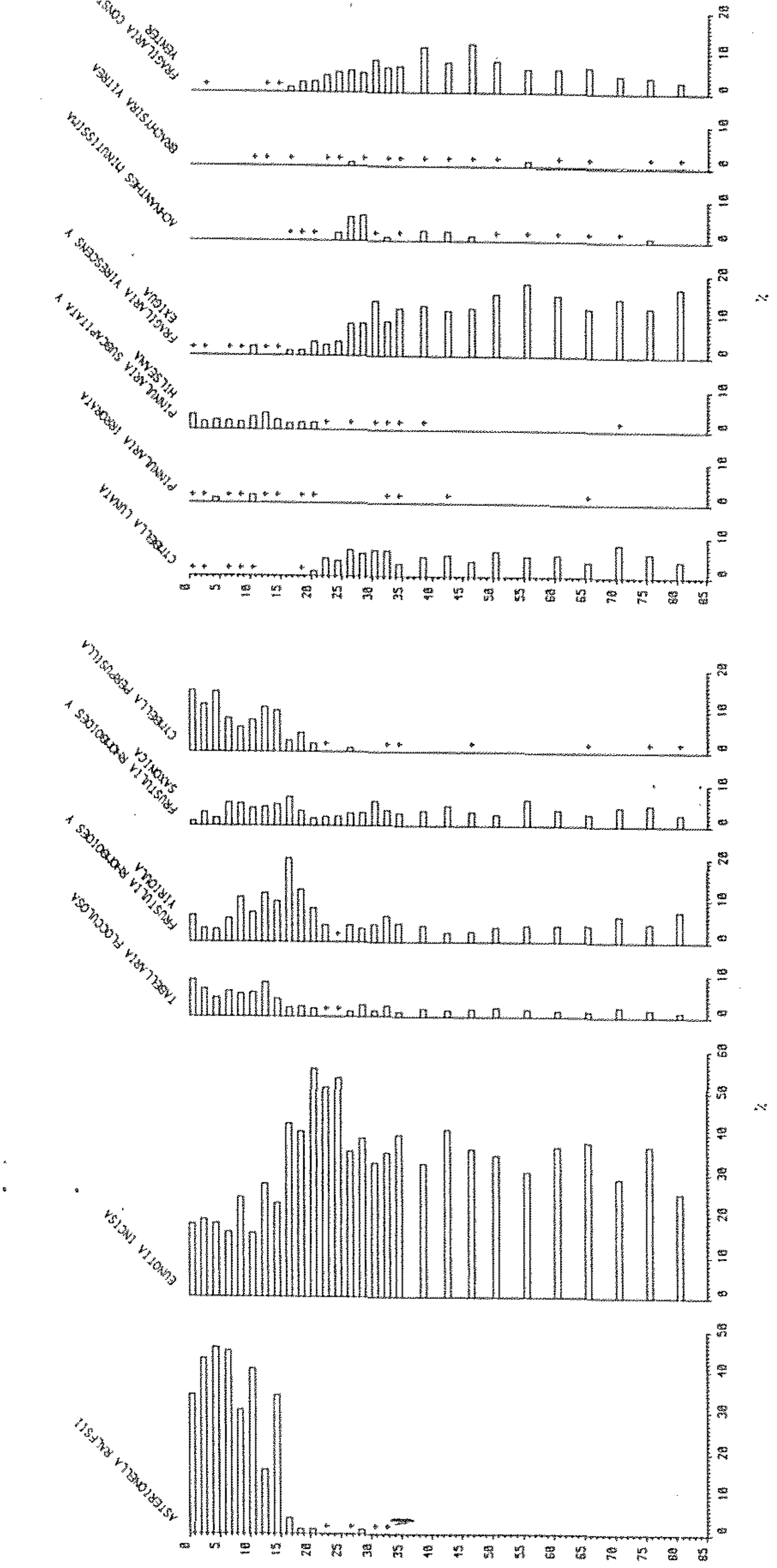


Figure 8.3 Llyn Berwyn: core BER1 (1984) summary diatom diagram



8.4 1987 CORING STRATEGY

The choice of the 1984 core location was based on the assumption that the region of maximum sediment accumulation within a lake is at the deepest point. However, recent work at Loch Fleet (Anderson *et al.* 1986) and Llyn Conwy (Chapter 7 - this report) has shown that in wind-stressed upland lakes the zone of maximum organic sediment accumulation is not always at the deepest point and intermittent deposition may occur. This appears to be the case with Llyn Berwyn. It can be assumed that in any lake the region of maximum organic sediment accumulation is where the surface sediments have the highest organic content, indicating minimal post-depositional disturbance. In order to locate this area in Llyn Berwyn a survey of the organic content of the surface sediments was carried out. Short cores were taken using a Kajak gravity corer in transects across the basin and the top 1 cm was analysed for its percentage dry weight and LOI to assess the organic content of the sediment. The sediment with the highest organic content was located to the south-west of the original coring position at 9 metres depth (Figure 8.1) and core BER7 was taken here using a piston (Livingstone) corer.

Analytical methods followed those of Stevenson *et al.* (1987).

8.5 RESULTS 1987 - core BER7

Lithostratigraphy

Core BER7 consists of 5.7 metres of organic sediments above post-glacial clays. Stratigraphic similarities with the core BER1 are apparent and the core contains the three main stratigraphic units seen in a compressed form in the much shorter core BER1; a highly organic component containing inwashed peat from the surface to 230 cm, a unit with an increasing down-core mineral component from 230 cm to 305 cm and a fine-grain organic sediment from 305 cm to 372 cm (Figure 8.4). Below 372 cm there is evidence of further episodes of mineral input to the sediment between 372 cm and 430 cm, although these are not apparent in core BER1. Below this point the organic content increases steadily down the core until the late-glacial sequence at the base. The striking difference between cores BER1 and BER7 is the rapid accumulation rate in BER7, confirming that the deepest point of this lake is not the area of maximum sediment accumulation.

Dating

In progress

Diatom analysis

Preliminary diatom analysis was carried out at widely spaced sampling intervals to a depth of 432 cm to establish the main floristic changes that have occurred over the period represented by the changes in sediment composition. A summary diatom diagram is shown in Figure 8.5. It is usual to count 500 diatom valves in each sample but to date only 200 valves have been counted for each level. Full counts will be made before the data are used to reconstruct pH. Levels where diatoms were absent or where poor preservation of some taxa may have increased the proportions of some of the dominant species are marked on the diagram.

Figure 8.5 indicates similar floristic changes up-core to those seen in BER1. The acidophilous *Eunotia incisa* is present throughout the core. In addition, circumneutral taxa such as *Cymbella lunata* and *Fragilaria virescens* v. *exigua* plus the alkaliphilous *Fragilaria construens* v. *venter* are common in the sediments below 240 cm. Between 240 cm and 220 cm a major transition occurs with the loss of the *Fragilaria* species and a rapid increase in the more acid tolerant *Tabellaria flocculosa* plus ~~an~~ increase in *Cymbella perpusilla*. This correlates with the increase seen in these species at 15 cm in the BER1 core. However, the increase in *A.*

ralfsii does not occur until somewhere between 40 cm and 60 cm.

Pollen analysis

In progress

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Discussion

The dominant change in diatom species composition at 240-220 cm coincides with a change in sediment composition from a fine-grain organic sediment below 230 cm to a poorly decomposed peaty sediment above 230 cm. This could be interpreted as either reflecting a change in water quality associated with the inwash of catchment peat or as evidence for a hiatus in the sediment record at 230 cm. However, the persistence of the circumneutral taxa throughout the period of maximum sediment inwash suggests that acidification of the lake did not begin until after 1960, assuming the mineral-rich band above 305 cm represents the beginning of pre-afforestation ploughing and does not contain older sediment as suggested for BER1. The later increase in *A. ralfsii* is interesting in the light of recent reports of the occurrence of this diatom in Loch Grannoch, south west Scotland, apparently as a response to the use of fertilisers on coniferous forest in the catchment (R. Flower, pers. comm.). Phosphate and potassium fertiliser were applied to the Llyn Berwyn catchment from the air in 1973 and it is possible that the increase in *A. ralfsii* in the sediment marks this event.

Figure 8.4 Llyn Berwyn: core BER7 (1987) lithostratigraphy

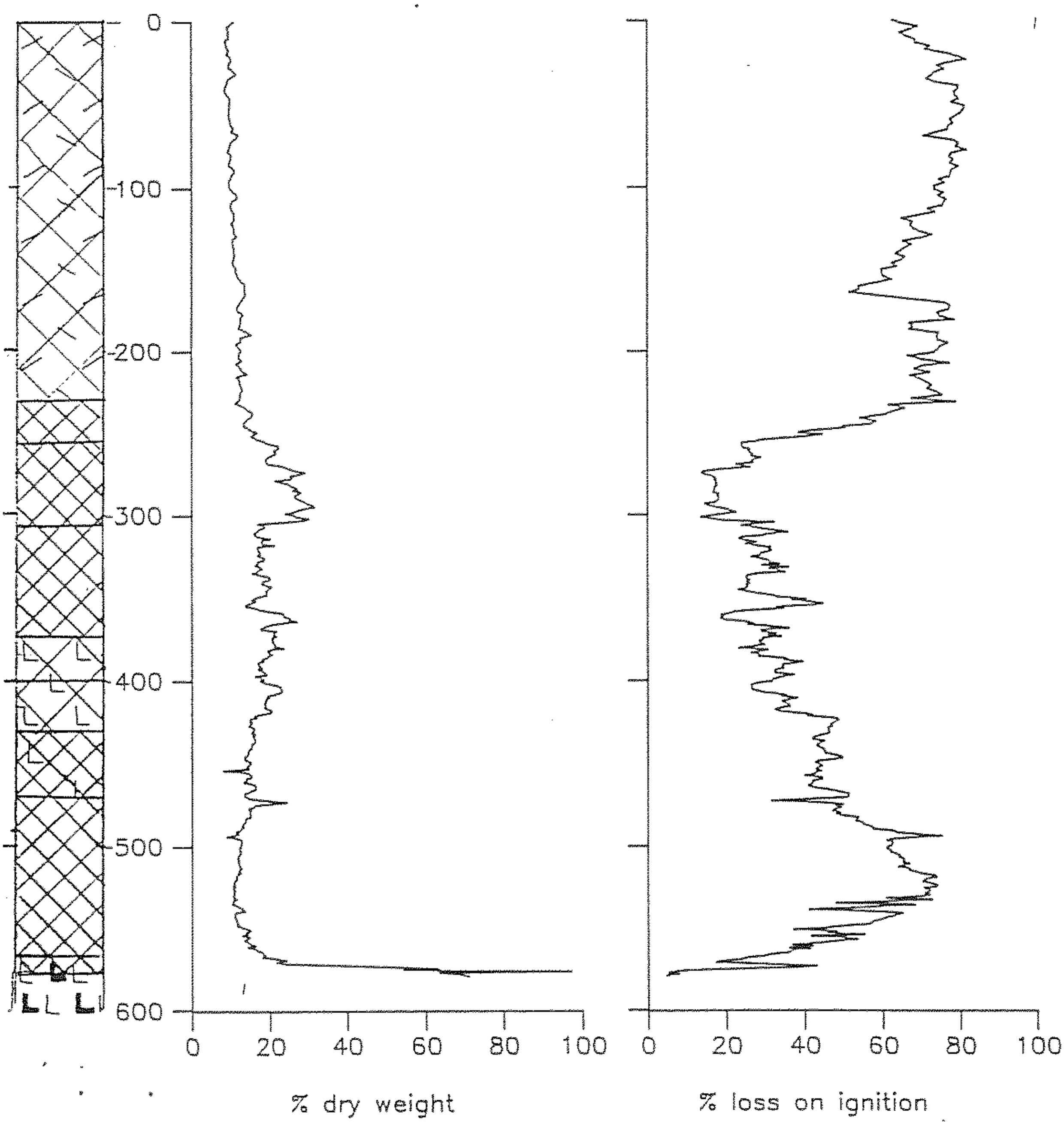
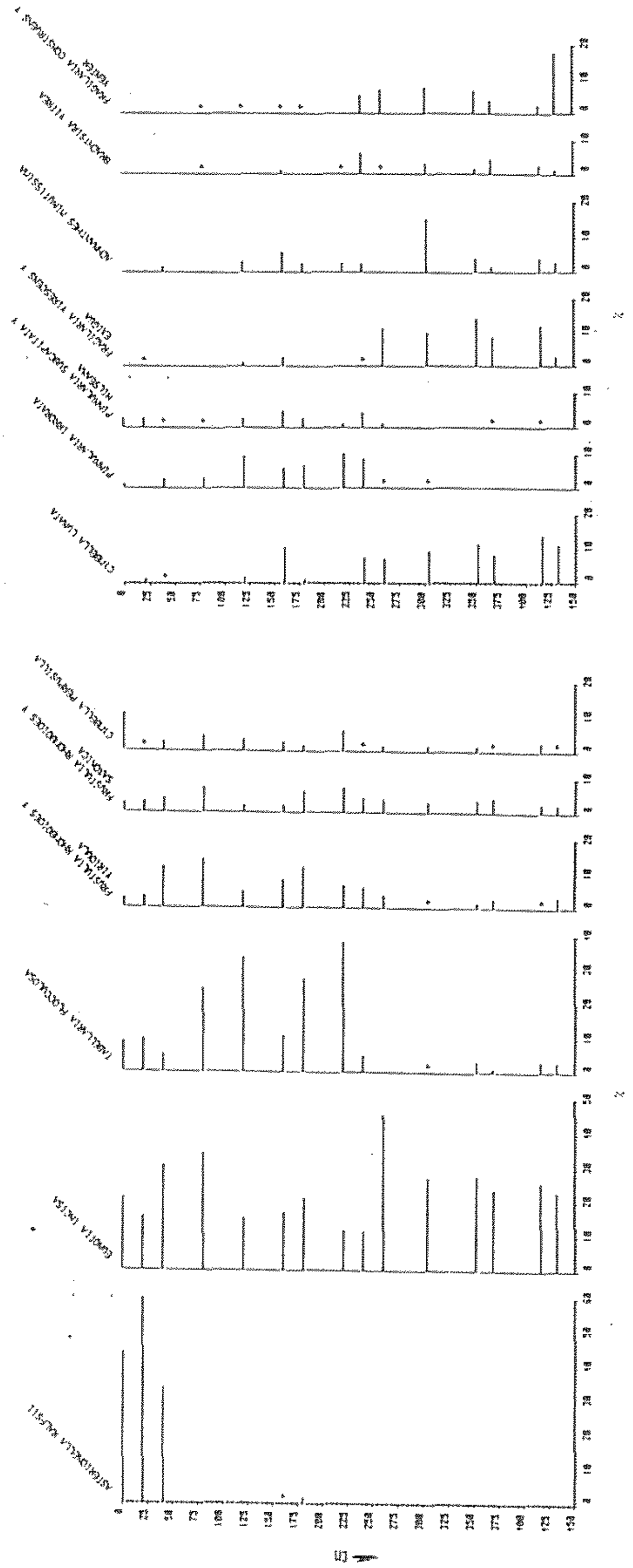


Figure 8.5 Llyn Berwyn: core BER7 (1987) summary diatom diagram



8.6 CONCLUSION

Without a chronology for core BER7 it is difficult to draw any firm conclusions from the data processed so far, although the diatom data do suggest acidification has occurred since afforestation. Provided ^{210}Pb dating reveals a contiguous sediment recovery, this long post-afforestation sequence should allow a detailed assessment of the impact of the various processes occurring with afforestation to be made. Similarly carbonaceous particle and geochemical analysis will provide evidence of atmospheric contamination at this site.

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9 THE PALAEOECOLOGICAL USE OF RESERVOIR SEDIMENTS FOR RECONSTRUCTING THE HISTORY OF ATMOSPHERIC POLLUTION; TUNNEL END, WEST YORKSHIRE

9.1 INTRODUCTION

Owing to the lack of natural, non-manipulated lakes in the southern and central Pennines, it has not been possible to demonstrate the acidification history of surface waters in potentially the most impacted area of the British Isles. In a previous report Anderson *et al.* (1988) assessed the use of reservoir sediments in the southern Pennines for reconstructing atmospheric pollution. They identified a number of problems associated with the use of such sediments for palaeolimnological studies, the most important of which was the lack of a conformable sedimentary sequence in reservoirs where erosion and reworking of sediments is common through the process of regular drawdown.

In this project a disused site was chosen where drawdown had not occurred for a number of years, to determine if it was possible to obtain a conformable sedimentary sequence. Tunnel End reservoir at Marsden, which lies about 10 km south west of Huddersfield (Figure 1.1) was built around 1820 as a feeder reservoir for the Huddersfield narrow canal, it was drained leaving only a shallow pool, around 1900, but has not been used for the last 30 or 40 years.

The site was cored using a modified Livingstone piston corer in June 1989. Although the water was shallow (c. 1-2 m), the sediments appeared to be quite homogeneous and did not have obvious sandy layers which are often associated with drawdown.

9.2 RESULTS

Lithostratigraphy

The lithostratigraphic results for core TUNN2 are shown in Figure 9.1 and the Troels-Smith descriptions are given in Table 9.1.

The sediment is quite inorganic with about 50% of its volume consisting of fine sand and silt. Its low organic content is reflected in the LOI profile, with LOI values fluctuating at around 20%. The wet density and dry weight values are high below 34 cm reflecting the mineral soil found at the bottom of the profile which is probably an inwash or sediment reworking event. Above 34 cm there are slight fluctuations in the wet density, dry weight and percentage LOI profiles which may reflect small inwash events, however there are no major changes in these profiles which would indicate substantial erosion.

Table 9.1 Troels-Smith Results

0.0-4.5 cm	Ga1 Ag1 Ld°1 Lso1 colour 5YR 2/2
4.5-5.5 cm	Ga1 Ag1 Ld°1 Lso1 Dh+
5.5-7.5 cm	Ga1 Ag1 Ld°1 Lso1 Dh++
7.5-11 cm	Ga1 Ag1 Ld°1 Lso1 Dh+ (++)
11-14 cm	Ga1 Ag1 Ld°1 Lso1 Dh+
14-18 cm	Dg1 Ag1 Ld°1 Lso1 Ga+ Dh+ (++)
19-33 cm	Ga1 Ag1 Ld°1 Lso1 Dh+ Dg+
34-38 cm	Sediment resembles a mineral soil

Dating

In progress

Diatom analysis

A summary diatom diagram is shown in Figure 9.2. The diatom assemblage is dominated throughout the profile by two species; a circumneutral species *Achnanthes minutissima* and *Eunotia exigua* which is classified as acidobiontic. Other important species in the profile include *Synedra acus*, *Fragilaria vaucheriae* and *Nitzschia palea* which are generally classified as alkaliphilous. Such a mix of species with different pH preferences is unusual and may be indicative of disturbance of the site. Alternatively it is possible that the assemblage represents a mixture of species from different sources in the catchment, for example *E. exigua* is a common diatom of peatlands and could have been washed in from the catchment. However, this is unlikely since modern diatom epiphyton samples from the site were found to be dominated by *Tabellaria flocculosa* and *E. exigua*, with low percentages of *Achnanthes minutissima*, *Gomphonema angustatum* v. *producta* and *Eunotia pectinalis* v. *minor* f. *impressa*.

The pH was reconstructed at this site using the multiple regression of pH preference groups method, this gave a reconstructed pH of 6.5 at the top of the core, with a pH range of 6.0 - 6.7 covering the time period represented by the core. The current measured pH of the site is reported to be 4.7 (Edwards pers. comm.), which does not agree with the reconstructed pH suggested by the diatom flora. The lack of correspondence between the diatom flora and measured pH at this site needs further investigation before any further attempt at pH reconstruction can be made.

Pollen analysis

In progress

Carbonaceous particle analysis

In progress

Geochemistry

In progress

Figure 9.1 Tunnel End: lithostratigraphy

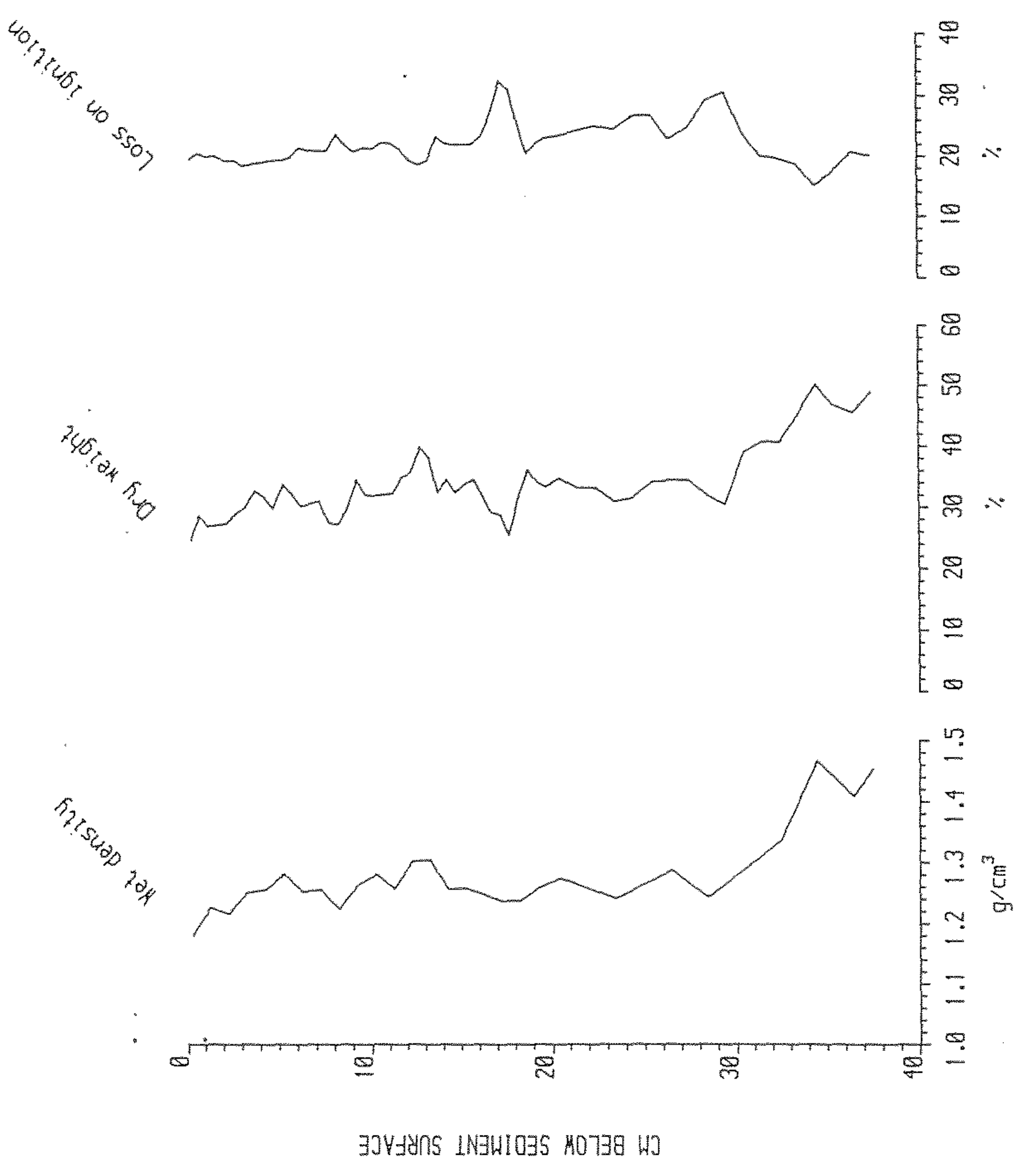
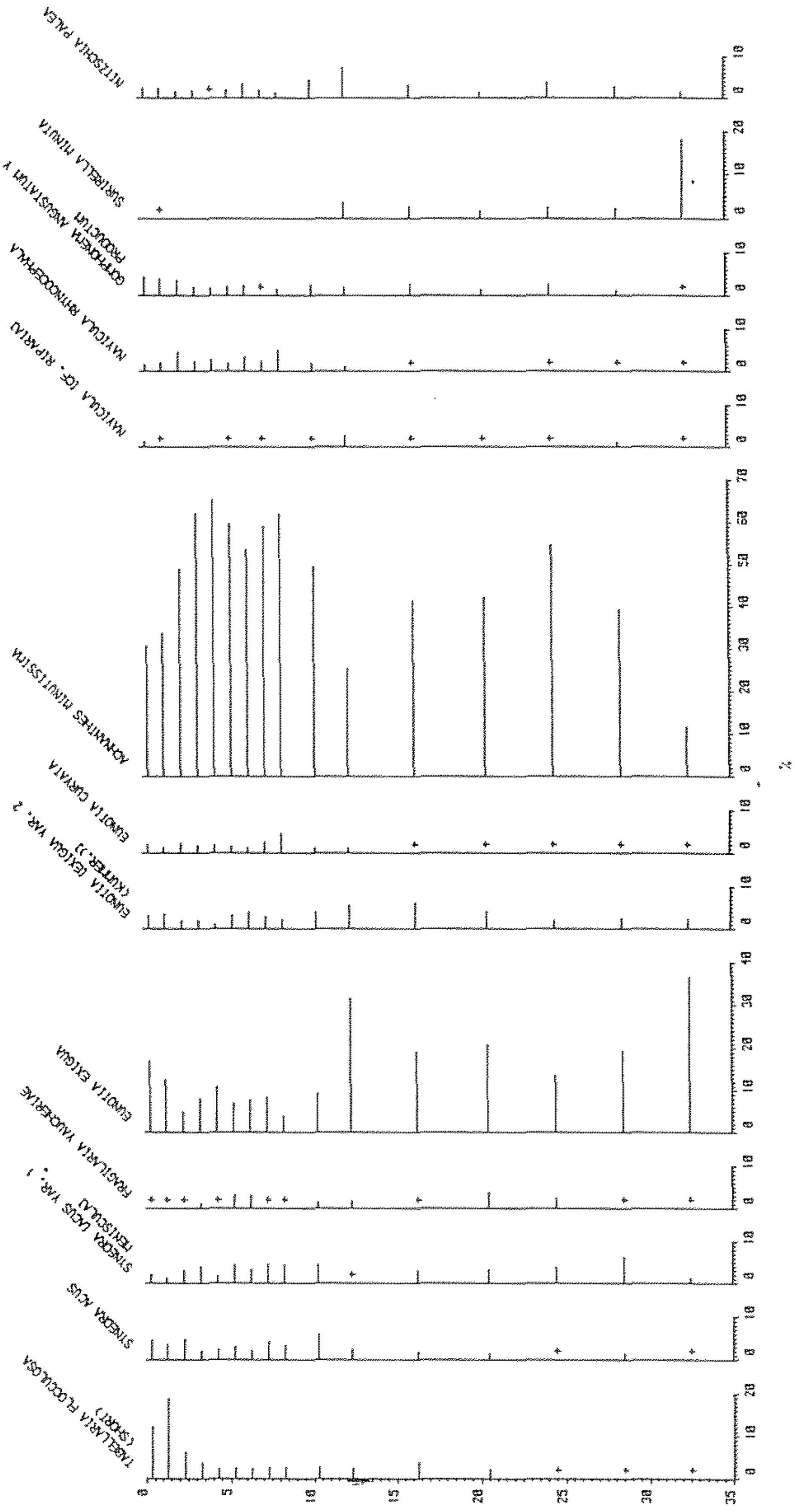


Figure 9.2 Tunnel End: summary diatom diagram



9.3 DISCUSSION

The results obtained so far indicate that there is no evidence for surface water acidification at this site, however more information on present water quality is needed, together with the completion of other palaeoecological analyses, before the results of diatom analysis can be assessed. Although this site is probably not as acid or acidified as the single pH measurement indicated, it should be valuable in assessing trends in atmospheric contamination in this region since 1970.

9.4 REFERENCES

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10 SCOTTISH ACID WATERS BASELINE STUDY: STREAM DIATOM COMPONENT.

10.1 INTRODUCTION

The diatom component of the Scottish acid waters baseline survey consists of epilithic diatom samples collected twice a year (Spring and Autumn) from 149 sites over the period 1986-1988. Many of these sites are situated in areas which have undergone recent acidification. They provide a detailed survey of the present composition of the diatom communities in these acidified, as well as non-acidified waters, against which future trends may be compared. In addition, this survey provides a large stream diatom dataset with which the relationships between diatom abundance and various parameters of water quality can be explored.

This preliminary report describes some of the main diatom communities present in a range of Scottish streams and presents an initial exploration of some of the environmental parameters influencing their composition.

10.2 METHODS

Diatoms

At each site one to five stones were selected from an area of >20 cm water depth and diatoms transferred into a wide mouthed jar using a toothbrush. Samples were fixed with formalin within 8 hours of collection. Subsequent sample preparation followed standard techniques (Battarbee 1986). Approximately 250 valves were counted in each sample and diatom counts converted to percentages for all subsequent analysis. Diatoms were identified using standard floras and taxonomic working papers produced by the Palaeoecology Research Unit. Taxonomy follows that adopted by the Surface Water Acidification Project.

Water Chemistry

All chemical determinations were made by the individual river purification boards (RPBs). Full methods and results will be available shortly (Ross *et al.* 1990). A total of seven determinands were measured by all purification boards: pH, calcium, sulphate, filtrable aluminium, alkalinity, conductivity and chloride. Results are expressed in mg l^{-1} except for filtrable aluminium ($\mu g\ l^{-1}$), pH and conductivity ($\mu S\ cm^{-1}$). All results presented here are given as site means which are simply the arithmetic mean between 4 and 10 individual determinations for each site. Additional determinands were submitted by the Clyde, Solway and Northeast RPBs but are not discussed here.

10.3 SITE CHARACTERISTICS

The location of the 149 sites is shown in Figure 10.1. Appendix 10.1 lists the site number, name and grid reference. Nearly all sites lie in areas of medium to high acid susceptibility (Kinniburgh and Edmunds 1986), and most regions north of the Highland Boundary Fault and in the Southern Uplands are represented. Figure 10.2 shows the distribution of the main catchment and water chemistry characteristics. The survey includes a wide range of catchment sizes, with 10 streams situated in very large catchments (>160 km^2). The majority of sites have either no, or less than 10% mature coniferous forest in their catchments. Figure 10.3 shows the distribution of heavily afforested catchments (>60%). These occur mainly in Galloway and the Trossachs.

Although sites were chosen to span the range from very acid to alkaline waters there is only one site, Kelty Water (site 204), with a mean pH of less than 5.0. The majority of sites (58%) have a mean pH in the range 6.0 to 7.0, with only 21 sites below 6.0. Figure 10.4 maps the areal distribution of pH and clearly shows the acid sites (pH <5.4) in Galloway, Arran and the Trossachs. The distribution of alkalinity values shows that many sites have relatively low acid neutralising capacity, with 69 sites having a mean alkalinity of less than 4 mg l^{-1} and 35 sites less than 2 mg l^{-1} (Figure 10.2).

Figure 10.5 shows the relationship between stream water calcium (in μeq l^{-1}) and total sulphur deposition (in g S m^{-2} yr^{-1}) for all 149 sites. Using calcium as an indicator of sensitivity, palaeolimnological evidence suggests that sites with a calcium : sulphur ratio of less than 1:80 have insufficient capacity to buffer the effects of acid precipitation (Battarbee 1989). Forty-five sites in this survey fall into this category and are shown by crosses in Figure 10.5.

Figure 10.1 Site Locations

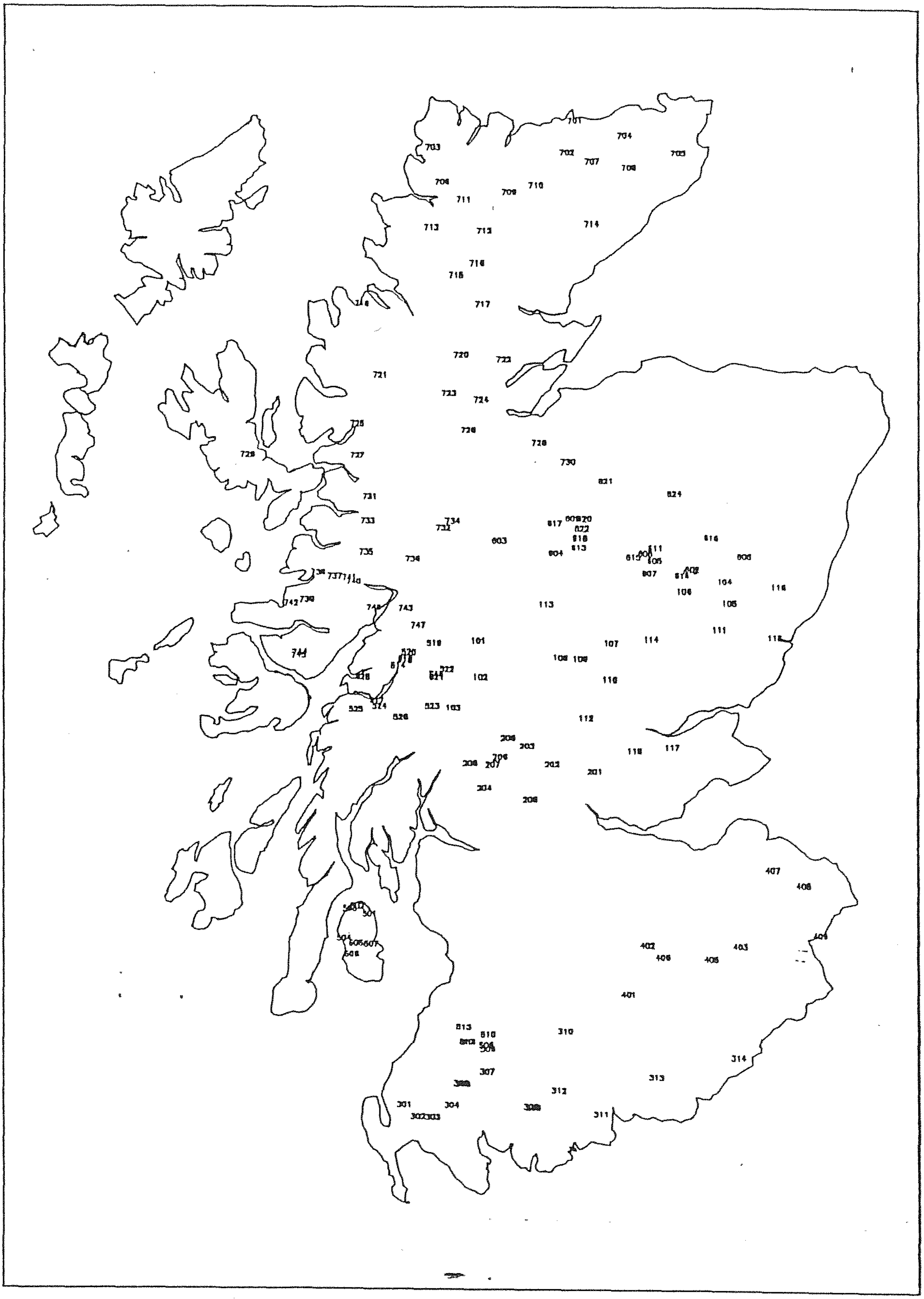


Figure 10.2 Catchment characteristics: catchment area (km²), percent catchment afforested, Distribution of alkalinity values and distribution of pH values.

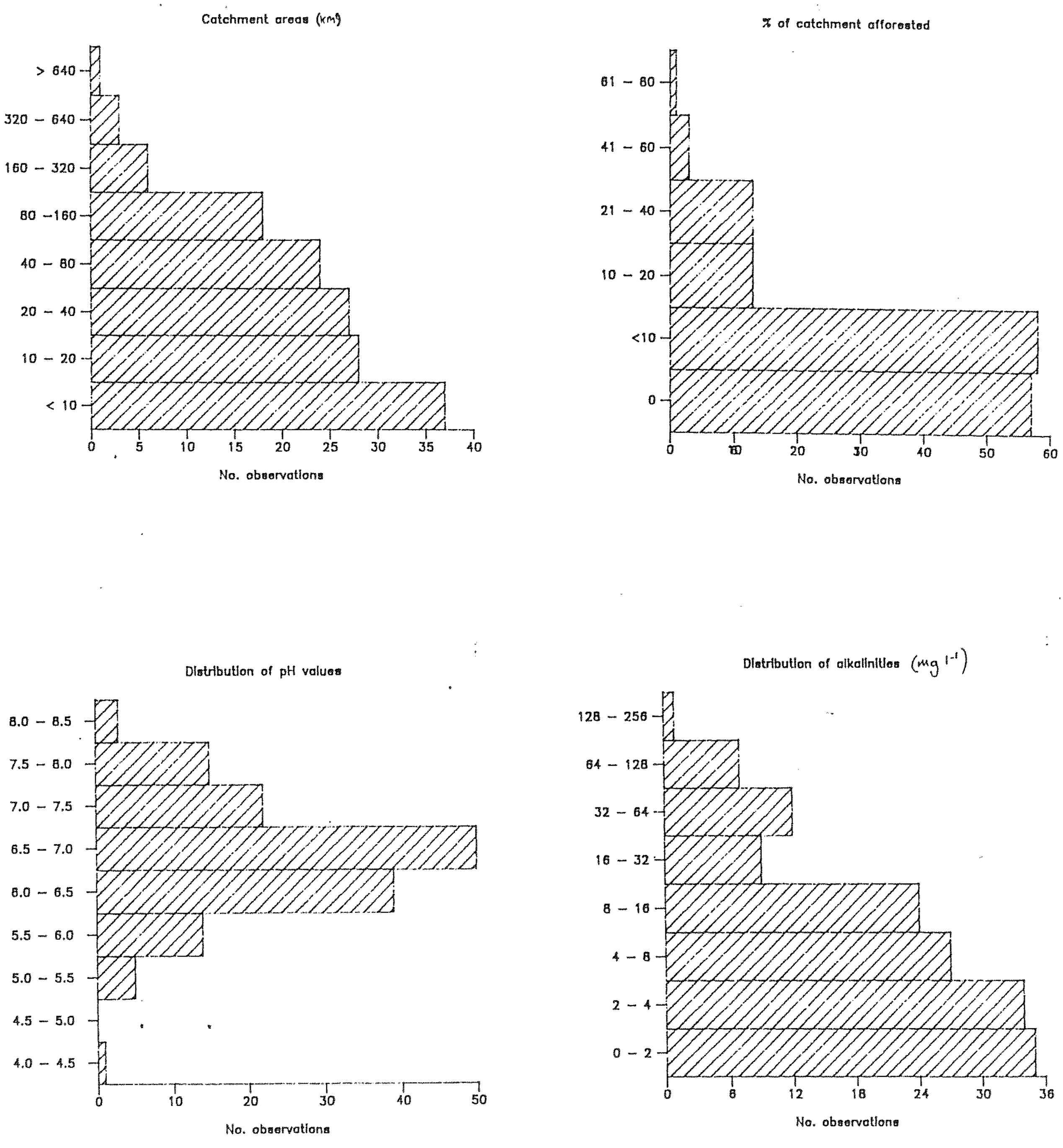


Figure 10.3 Map showing afforested catchments.

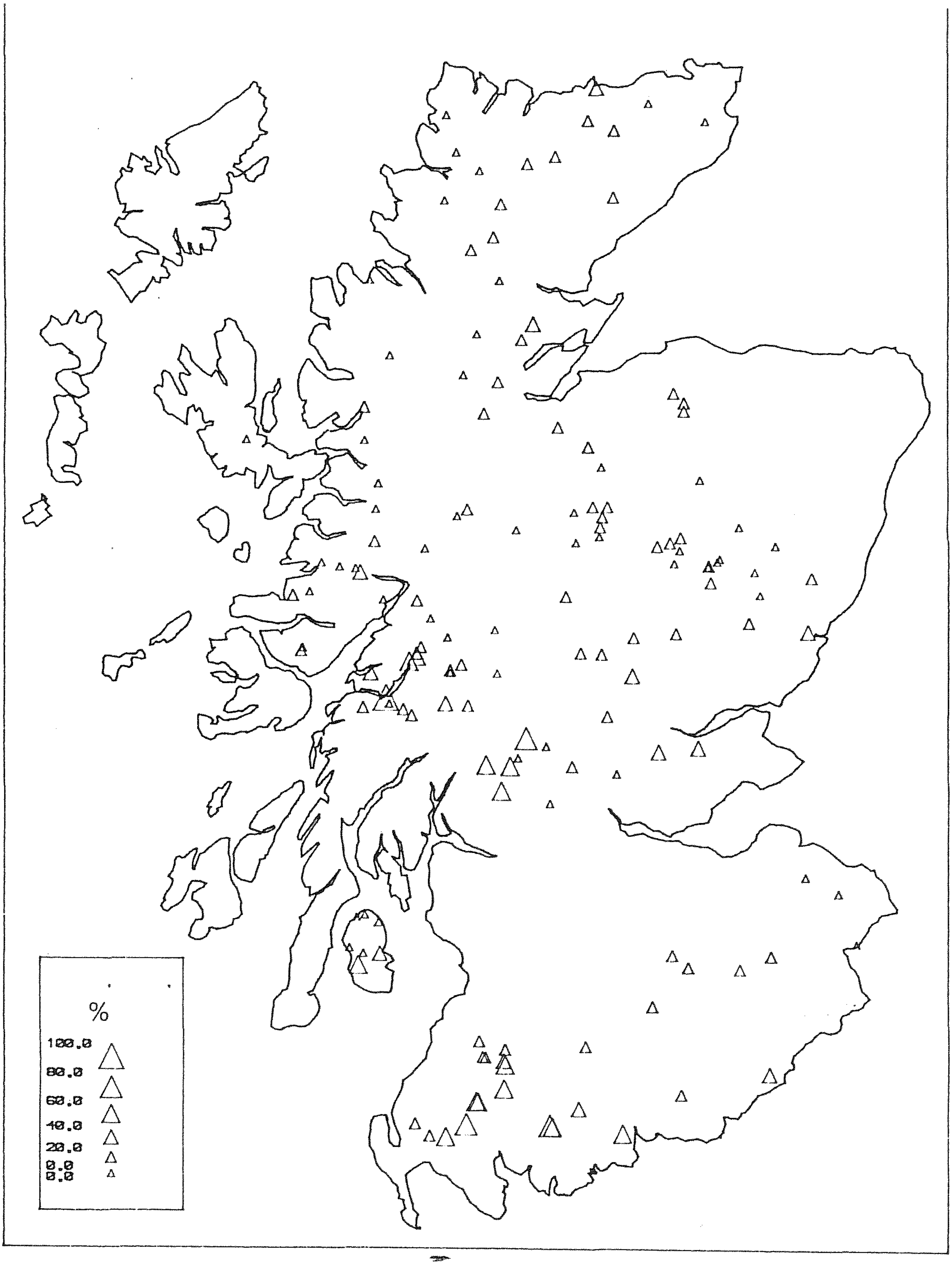


Figure 10.4 Map showing distribution of mean pH.

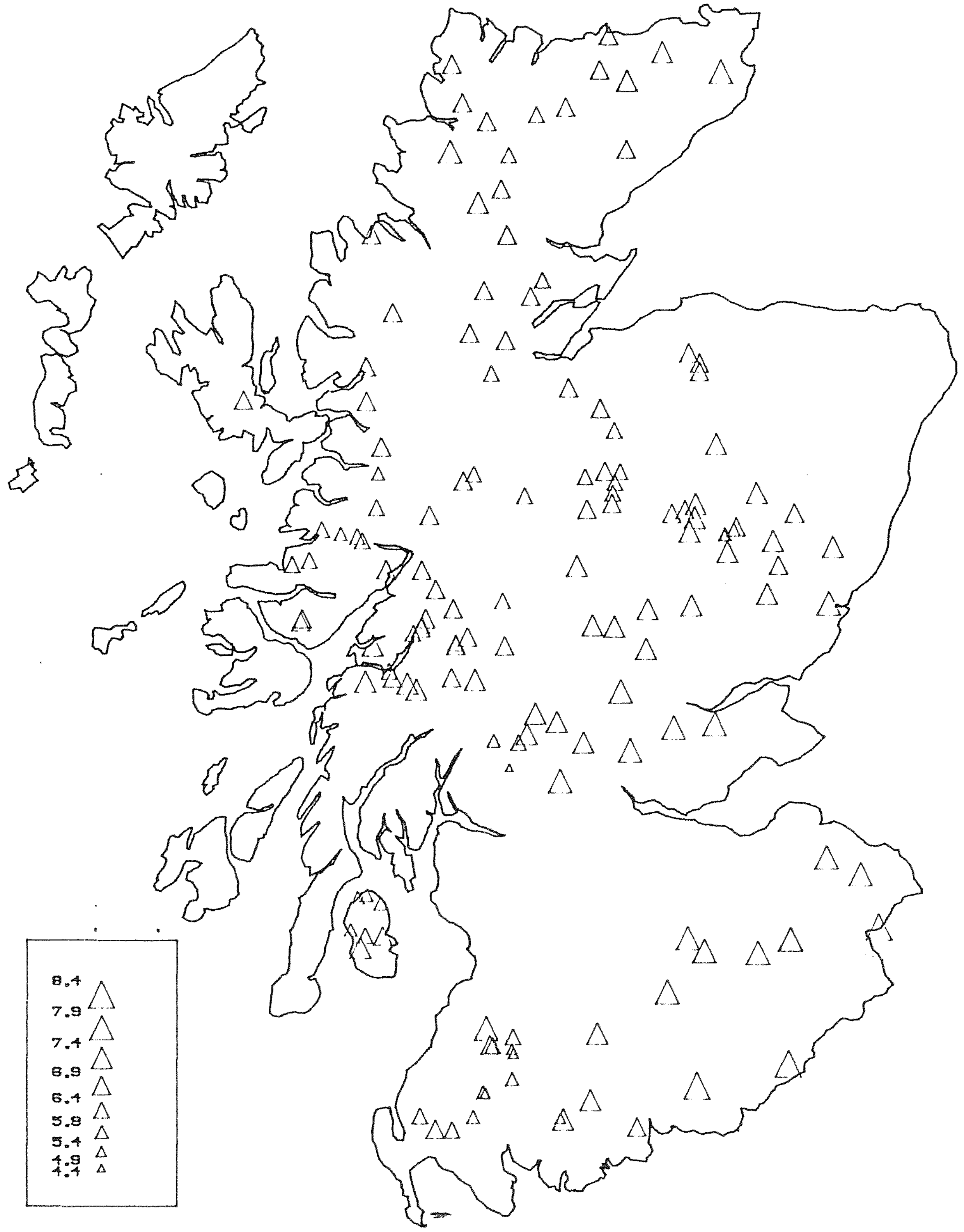
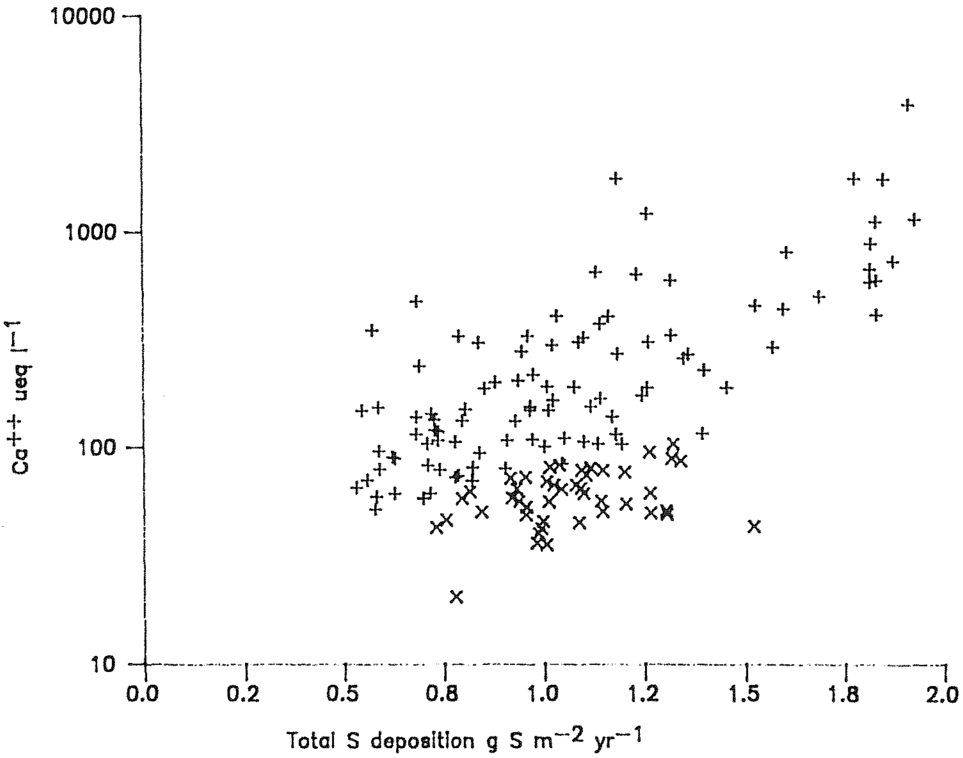


Figure 10.5 Relationship between mean stream water calcium (μeq l^{-1}) and total sulphur deposition (g S m^{-2} yr^{-1}).



10.4 DIATOM ANALYSIS

Species occurrence and abundance

A total of 773 samples were received from the RPBs. Of these, 62 samples were either barren or had too few diatoms to provide a reliable count. For this preliminary report diatom results are presented as mean assemblages for each site, derived by simply calculating the mean percentage abundance of each taxon at each of the 149 sites. Full analysis of individual samples will be presented at a later date.

Of the total of 196 diatom taxa recorded many were relatively rare, with only 160 occurring at more than one site. Similarly only 106 taxa were present at greater than 1.0% in at least one sample and only 88 were present at greater than 2.0%. Results from lake-based diatom studies indicate that there is little ecological information in the rare taxa and the reduced dataset of 88 taxa and 149 sites is used for all subsequent analysis in this report. However the use of these rare taxa as indicators of particular environmental conditions will be explored at a later date.

Figure 10.6 shows the relationship between maximum abundance and the number of sites where a taxon is present at greater than 1%. One taxon, *Achnanthes minutissima*, is found at nearly all sites and dominates the assemblage at many. Other widespread and abundant taxa are shown on the top right of Figure 10.6 (eg. *Tabellaria flocculosa* and *Gomphonema parvulum*), while widespread but less abundant forms (eg. *Synedra miniscula* and *Fragilaria vaucheriae*) are plotted centre right. Although many of the less widespread taxa are typically much less abundant (ie. <10%), there are some forms, plotted at the top left of the diagram, which have a restricted distribution, but which can be locally abundant (eg. *Achnanthes saxonica*, *Eunotia exigua* and *Eunotia naegelii*). It is apparent therefore suggests that although many sites may be dominated by a small number of very abundant taxa which occur over a wide range of environmental conditions, the majority of taxa are much more restricted in their occurrence, and many may be good environmental indicators.

Diatom sample classification

Rather than present a site by site description of the diatom results the sites have been classified into a number of groups on the basis of their diatom flora, the composition and distribution of the resulting groups providing a convenient summary of the diatom data. The initial classification was carried out using the computer program TWINSPAN with borderline cases and unstable groups re-allocated using FLEXCLUS. In both analyses *A. minutissima* was downweighted by a factor of 10. A total of six major groups and 18 subgroups were identified. The full species data are listed in Table 10.1, with sample groups and common taxa arranged to best reveal species patterns across the groups. Site numbers and groups are indicated across the top of the Table, rarer taxa are listed separately at the bottom. Summary chemistry is indicated in coded format at the bottom of the Table and listed separately as group means in Table 10.2. Figure 10.7 maps the distribution of each diatom group, the dominant and characteristic taxa of which are described below.

Group 1a:	Dominated and characterised by *E. exigua*, *E. naegelii* and *Eunotia incisa*. Occurs at acid sites (pH 4.4-5.9) with high aluminium (95-252 $\mu g\ l^{-1}$) in the Trossachs and on Arran.
Group 1b:	Dominated by *T. flocculosa*, characterised by *P. fibula*, *E. incisa*, *E. naegelii* and *Frustulia rhomboides* v. *saxonica*. Occurs at low alkalinity, acid sites with moderate aluminium levels (mean 65 $\mu g\ l^{-1}$) on Rannoch Moor and Arran.

Group 2a:	Dominated by *T. flocculosa*, characterised by *P. fibula* and *E. incisa*. Occurs at low alkalinity, acid sites on Rannoch Moor, Galloway and Arran.
Group 2b:	Dominated by *T. flocculosa*, characterised by *Brachysira vitrea*. Occurs mainly at low alkalinity, acid sites (pH 6-6.5) in Galloway and the Northern Highlands.
Group 3a:	Dominated by *G. parvulum*, *A. minutissima* and *T. flocculosa*, characterised by *A. saxonica*. Occurs in slightly acid waters (pH 6.1-6.5) with low aluminium (mean 50 μg l^{-1}) in the Trossachs and Northern Highlands.
Group 3b:	Dominated by *G. parvulum* and *A. minutissima*, characterised by *Achnanthes detha*, *A. saxonica*, *Achnanthes austriaca* v. *helvetica* and *Pinnularia subcapitata* v. *hilseana*. Occurs in moderately buffered, slightly acid waters (mean pH 6.3) with relatively high aluminium (mean 123 μg l^{-1}). Occurs mainly in Galloway and the far Northern Highlands.
Group 4:	All Group 4 sites are dominated by *A. minutissima* with subgroups characterised by the following species combinations:
Group 4a	*G. parvulum*, *Synedra miniscula* and *T. flocculosa*.
Group 4b	*Synedra acus*, *S. acus* v. *angustissima*, *B. vitrea* and *T. flocculosa*.
Group 4c	*B. vitrea* and *T. flocculosa*.
Group 4d	almost entirely dominated by *A. minutissima* with small amounts of *T. flocculosa*
Group 4e	as 4d but with small amounts of *B. vitrea*, *Cymbella microcephela* and *Cymbella* [sp. 2].
	Occurs in moderately buffered, slightly acid waters in the Northern Highlands and Grampians.
Group 5:	All Group 5 sites are similarly dominated by *A. minutissima*, with subgroups characterised by the following species' combinations:
Group 5a	*S. miniscula*, *Synedra ulna*, *Hannea arcus* and *Fragilaria vaucheriae*.
Group 5b	essentially dominated by *A. minutissima* with small amounts of *G. parvulum* and *Gomphoneis olivaceoides*.
Group 5c	*H. arcus*, *G. olivaceoides*, *Cymbella minuta* and *Cymbella ventricosa*.
	Occurs in well buffered, circumneutral waters mainly in the Grampians.
Group 6:	Group 6 samples are again dominated by *A. minutissima*, with subgroups defined by the following species combinations:
Group 6a	*F. vaucheriae*.
Group 6b	*F. vaucheriae* and *G. olivaceoides*.
Group 6c	*Cocconeis placentula* v. *euglypta* and *Cymbella sinuata*.
Group 6d	*G. olivaceoides*, *C. placentula* v. *euglypta*, *Navicula avenacea* and *C. minuta*.
	Occurs in well buffered circumneutral and alkaline waters mainly in the eastern Southern Uplands and southern Grampians.

Comparing Tables 10.1 and 10.2 it is apparent that the numerical classification has arranged the diatom groups along a pH gradient and that the transition from taxa recorded in top left to those present in the bottom right of Table 10.1 represents a transition from alkaliphilous and alkalibiontic forms to acidobiontic taxa. However, while pH appears to be the major chemical factor influencing the composition of the diatom assemblages, it is also suggested that aluminium may have an important modifying effect at high levels (ie. >100 μg l^{-1}). These relationships are further explored in the next section.

Ordination of samples, species and environmental variables

The classification described above provides a useful summary of the main floristic groups present in the data and allows these to be related to summary water chemistry. Such an approach is termed an indirect analysis, since groups are identified using the diatom data alone and chemical data are related to these after the numerical analysis. An alternative approach is to perform a direct gradient analysis where samples and sites are ordinated, but the ordination axes are constrained by the environmental data. The resulting ordination diagram will then display both patterns of sample variation which are best explained by the supplied environmental variables, as well as the species which are related to these variables. The reduced dataset listed in Table 10.1 was therefore used in a canonical correspondence analysis, with pH, conductivity, alkalinity, calcium, aluminium and chloride, together with the physical variables: catchment area, stream width and percentage afforestation supplied as constraining variables. The first two axes of the resulting ordination diagram are shown in Figure 10.8, with samples coded by their major diatom group (as defined above). Environmental variables are shown as vectors, the length giving and indication of the importance of that variable. A small number of key taxa are also plotted, using abbreviated names.

The first axis is dominated by pH, indicating the primary importance of this variable in controlling the patterns of diatom distribution. The proximity of the pH, alkalinity, calcium and conductivity vectors reflects the strong inter-correlation of these variables. High pH sites, together with their constituent taxa are plotted on the left of the diagram and the circumneutral to slightly acid sites of Groups 4 and 5 plotted in the centre.

The second axis appears to reflect the aluminium gradient, with the high aluminium sites of Group 3 plotted top centre, together with their characteristic taxon *A. saxonica.* The afforestation gradient is also related to axis 2, reflecting the occurrence of high aluminium sites in Galloway in afforested catchments. Physical variables such as stream width and catchment area do not appear to influence diatom occurrence, although there is a suggestion that the larger catchments are more heavily forested and associated with higher aluminium values.

The acid sites of Groups 1 and 2 are plotted on the right of the diagram, together with the acidobiontic taxa *E. exigua, E. incisa, P. fibula* and *E. naegelii.* The acid, high aluminium sites of Group 1 on the far right centre of the diagram are clearly distinguished from Group 2 sites plotted bottom right.

Results from the direct gradient analysis support the earlier conclusions that the changes in composition of the diatom assemblages can be directly related to pH and that aluminium has an important secondary effect.

A number of published ordinations of acid diatom assemblages often show TOC or colour to be an important secondary variable, although it is often correlated with aluminium (eg. Stevenson *et al.* 1989, Battarbee *et al.* 1989). Preliminary analysis of sites from the Northeast RPB where TOC was determined, also show TOC to be important in this subset of sites. Colour has also been obtained for the Solway sites and a full analysis will be undertaken at a later date.

Diatoms as bio-indicators

Since the first axis of the ordination diagram presented in Figure 10.8 is strongly correlated with pH, the position of a taxon on this axis can be used to give an estimate of its pH optimum. That is, the centroid of its distribution along the pH gradient. If the pH optimum of all taxa in a sample can be estimated then we have a method for inferring the stream water pH from the diatom assemblages alone: it is given by simply taking the average of the pH optima of constituent taxa, weighted by their abundance. This method of weighted averaging is implicit in canonical correspondence analysis and has been employed to derive transfer functions for pH reconstruction in the SWAP project (Birks *et al.* 1990).

Using the 149 site dataset this method has been used to estimate diatom pH optima for the 88 taxa listed in Table 10.1. These optima have then been used to infer the stream water pH for these 149 samples. Figure 10.9 shows a plot of measured mean stream water pH and diatom inferred pH. The relationship has a r-squared value of 0.84 and standard error of prediction of 0.28 pH units. A similar relationship exists for measured and inferred alkalinity (Figure 10.10) (r-squared 0.87, SE prediction 9.9 mg l^{-1}).

A much weaker relationship was found between measured and inferred aluminium, with an r-squared value of 0.41 (Figure 10.11). One reason for this weak direct relationship may be the interaction between pH and aluminium exhibited in the species response. Figure 10.12 shows a plot of pH against aluminium, with data points coded with the abundance of *E. exigua.* This taxa was identified above and in the literature (Van Dam *et al.* 1981) as tolerant of high aluminium levels. Sites where the taxa was absent are indicated by a plus, larger squares indicate increasing abundance. The Figure clearly shows the interaction of pH and aluminium, the taxon can tolerate higher pH levels at reduced aluminium concentrations and can only tolerate high aluminium levels at low pH. Weighted averaging is unsuitable for modelling the responses of taxa to more than one environmental variable, but alternative techniques such as Gaussian logistic regression are available and will be explored.

10.5 CONCLUSIONS

Although diatoms have long been used as indicators of pollution in organically enriched waters (Lange-Bertalot 1979, Wantanabe *et al.* 1986) there have been few studies of stream diatoms from acidified or acid waters (Berge 1982, Rönkkö *et al.* 1986, Battarbee *et al.* 1989). This is even more surprising given the central role diatoms have played in lake acidification studies (Battarbee 1984).

The results presented above provide a detailed description of the diatom communities from a wide range of water types throughout Scotland and provide a baseline against which future changes may be compared.

The strong relationships demonstrated above between diatom composition and water quality, especially pH, allow the development of predictive calibration functions. The wide coverage of the present study is especially important in this respect as it allows the full range of a taxon to be incorporated in the function. Such calibration functions will be useful in interpreting the trajectory of diatom assemblages at a single location, whether at sites from this survey or elsewhere (eg. the UK Acid Waters Monitoring Network). Similarly, the results above demonstrate that diatoms, coupled with accurate calibration functions, can provide a rapid and relatively inexpensive means of estimating stream mean pH. As such they may be used for a preliminary analysis to identify sites for more intensive chemical analysis, or simply used in a more extensive survey to estimate lengths of acidified streams in an area. It is also suggested that with more elaborate functions (cf. Figure 10.10) it may be used to estimate aluminium levels and TOC.

Table 10.1 **Two-way ordered sample by species matrix showing diatom groups**

Diatom abundances coded: + = <2%, 2=2-5%, 3=5-10%, 4=10-20%, 5=20-50%, 6=>50%.

Chemical determinands coded; pH: 1 = <4.5, 2=4.5-5, 3=5-5.5, 4=5.5-6, 5=6-6.5, 6=6.5-7, 7=7-7.5, 8=7.5-8, 9=8-8.5; Conductivity: 1 = <30, 2 = 30-60, 3=60-90, 4=90,120, 5=120-240, 6=>240 uS cm^{-1}; Calcuim: 1=<1, 2=1-2, 3=3-4, 4=4-16, 5=16-32, 6=>32 mg l^{-1}; SO_4: 1=<1, 2=1-2, 3=2-4, 4=4-8, 5=8-16, 6=>16 mg l^{-1}; Alkalinity: 1=<2, 2=2-4, 3=4-8, 4=8-16, 5=16-64, 6=>64 mg l^{-1}; Aluminium: 1=<30, 2=30-60, 3=60-90, 4=90-120, 5=120-150, 6>150 ug l^{-1}; Chloride: 1=<3, 2=3-5, 3=5-8, 4=8-12, 5=12-18, 6>18 mg l^{-1}; Forestry: 0 = 0; 1=<10%, 2=10-20%, 3=20-40%, 4=40-60%, 5=60-80% catchment afforested.

Table 10.1

```
                                                       Group 6               |          Group 5      |                        Group 4                        |       Group 3    |     Group 2     | Grpou 1 |
                                                                             |                       |                                                       |                  |                 |         |
                                          6d      6c          6b          6a | 5c      5b     5a    | 4e       4d           4c           4b          4a     |    3b        3a  |  2b        2a   | 1b   1a |
                                                                             |                       |                                                       |                  |                 |         |
                                      12334445|113557|1112223444445577|134567|111126666|115|166666677|1167|255556777756|777777777776|67777777777|125666677777|3333333777|5555677|15566777|55555567|557|22335|
                                      10110000|111120|0010001000002211|000203|011100012|012|000112223|0100|002221134421|011112244440|11222222334|000122212334|0000001000|1111100|01101013|00001113|013|00000|
                                      81022396|573395|7922564146784635|895592|304692884|418|646360580|2376|370231413514|306892412675|51013567694|575712379450|1234571478|2457912|10930928|34891827|263|48681|
                                              |      |                |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
Achnanthes biasolettiana                      |   ++ |++  +       ++ 2| + +  |       + |  +|       ++| + +|   +  2+ 2  |+24++++ + + | 22++++2 ++|+      +++  |2+++  ++++|++  ++4|     +  |     +  |   |     |
Achnanthes marginulata                  +    +| +    |  +++   +   +  +|++    |+ ++ ++  | ++|++ +   + |  + |   + + + + +|        +   |       + + |        +   |          |+   +  |    +   | ++    +| ++|  2+ |
Achnanthes lanceolata                  2 +2+++|++ +++|++  +  ++ ++ +  |+++   | + +++ ++| + |+       +|    | +    ++  + |            |    +  +   |+      +    |      + ++|    +  |       +|        |   |     |
Cocconeis diminuta                    +  + +  |+3++++|++     + + ++   |    ++|  +++    | + |    +    |+   |     +      |            |       +   |          + |          |       |        |        |   |     |
Cymbella lunata                               |      |    + +      ++ | +  + |      +  |  +|    +    |++ +|+ +   ++++  |++++++2+++++|++++ +++++ |++ + ++  ++ |++    2+++|+++  ++|2+++ +++| +  ++++| ++|  ++ |
Cymbella microcephala                     +   | +    |+2  + +   +  +++|+ +   |+++ +  + |   |++  +2   |+222|2  +  +  +++|++++++  + ++|2+ ++++++ +|        ++  |          |    + +|  +  +  |       +|   |+    |
Amphora pediculus                     +  + +2+|2+++ +|  + +  2++ ++  +| 2+ + |  +      | + |         |    |          + |        +   |           |            |          |      +|        |        |   |     |
Denticula tenuis                          +   |      |+++       +   + | +    |        +|   |     +   | ++2|+           |   +       +|           |     +      |          |       |        |        |   |     |
Diatoma elongatum var. tenue          +  +++  |++  +2|++++   ++ + + 3+| +3 + |+3++   + |   |   3+  + |   +|     +++ +  |++ +       +|  ++ ++4+  |        ++++| +     3++|     + |       +|        |  +|     |
Diatoma vulgare                       2   +++ |     +|       + ++++   |  +   |         | + |   +     |    |          + |            |           |            |       +  |       |        |        |   |     |
Didymosphenia geminata                ++  +   |    + |  ++   ++  ++ 2+|  + + |   ++    |   |   +++ + |  ++|     +      |           +|           |            |          |       |        |        |   |     |
Eunotia minutissima                           |      |                | +    |      +  |  +|         |    | +4     +   | +    ++  + | +   +++ + | ++         |  +  +    |++ +  +|++ +    | +  +  +| ++| ++ +|
Eunotia curvata                        +     +|    + | +              | +    |         |   |    +  + |    |  ++      + |++++  +++ + | + +++ +++ |         +  |+ +   +   |++    +|++++ +  |++  2+  | + |3+ ++|
Diatoma hyemale var. mesodon           2  ++ 2|     +|   +++ ++++++   |+ +++3|3  4++2+4|+2+|++2++23+ | ++ |  + ++++++++|    + ++    |++  + + +  |+  ++3+ +   |      ++++|  + 2  |        |        |   |  +  |
Fragilaria virescens var. exigua              |      |                | +    | +       |   |    +    |   +|+  +   + +  |++    + 3  +|     + + + |           +|   + 3+   |    +2+| ++  +  |+       |   |  +  |
Fragilaria virescens                          |      |    +           |      |  +      |   |  + ++2  | +  |        ++  |   +  +    +|+  +   +   |+  +++3  + +|         +|   ++  |   ++   |   2    |   |   + |
Gomphonema truncatum var. capitatum   +  +    |    + | +            ++| +   +| ++  2   |   | ++++    | +  |     +   +  |            |   +       |+     +    +|       +  |      +|        |        |   |     |
Gomphonema gracile                            |   +  | +  +       +   |+  +  | +    + +|   | + +   ++|++ +|++ ++  ++++ |++2+22++++  |++ + +++ +4|+++  + +++ +|       +  |++ + + |++++ +  |+    + +|  +|     |
Gomphonema intricatum                         |      | +     +      + |2     |         |   |    +   +|++  |+           |            |           |        +   |       +  |+      |        |        |   |     |
Gomphonema tergestinum                        |    + |++  +++   2 +  +|    + |+      + |   |    ++   | 2++|     +     +|+          2|       +   |        +   |       +  |     + |        |        |   |+    |
Gomphonema ventricosum                ++  +   | +  + |+22    +++    2+|++2++ |+ +      |+ +|  + +   +|    |      +  ++ |            |           |            |          |       |        |        |   |     |
Eunotia pectinalis var. minor           ++    |    + |    +    +     +| +   +| +       | + |  + + +  |+  +| + + ++++  +|+ +++ + ++  |   +++  ++ |+    2++    |++ ++    +|+   +++|++2  ++ |  +    +| ++|  +  |
Eunotia polydentula                           |      |    +           |   +  |   +  +  |+++|+ +     +|    |   +     + +|            |     +     |+   + ++   +|     ++   |+  +2  |       +|  ++  ++|   |     |
Melosira varians                      ++ ++2+ |++    |   ++  + + ++   | ++   |    +    | + |         |    |          2 |            |           |            |          |       |        |        |   |     |
Pinnularia irrorata                      + +  |   ++ |    +    +   + +| + +  |      +  |   | ++++ +++|++ +|++ + + ++  +|+ + + ++  + | + ++ ++ + |+ + +++ +  +|2++++22+++|+ +++2+|+++++ + |++22 + +|  +|+ +2 |
Navicula minima                               |      |                | +  + |         |   |         |    |            |            |           |            | +2+   +++|      +|+       |        |   |     |
Frustulia rhomboides                          |   +  |    +    +   +  | + +  |         |   | +  +    |    |          + |  +   + +  +|  +  +   + |    +       |++++ +++ +| ++++  |+    +++| +2++   |  +|   2 |
Navicula rhyncocephala                   +++  | +    |                | + +  |         |++ |    +  + | +  |       +    |     +  +   |       + + |      +   + | ++    + 2|    + +|       +|        |   |     |
Navicula schassmannii                         |    + |               2| +    |         |   |         |    |       +    |  +         |           |            |         +|      +|        |        |   |     |
Brachysira serians                            |      |            +   |      |        +|   |         |    | 4          |   +   +    |           |            |          |  ++   |        |++    + |+  |     |
Navicula tantula                       ++ +   |++++++|                | +++  |+  +  +  |   |      ++ |    |            |  +    +    |           | +    2 +   |2432+  +23|   +++3|      + |        |   |   + |
Nitzschia inconspicua                       2 |+     |         +      |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
Nitzschia palea var. tenuirostris      + ++   |++ ++ | +++   3+++4    |  ++  | ++ 2    |   |         |    |            |            |           |        2   |  +    + +|      +|        |        |   |     |
Gomphonema angustatum                         |+ +   |+++   ++3 +   + |      | ++      |+  |    +    |  + |     +      |           +|           |            |      ++  |       |        |        |   |     |
Nitzschia palea                       ++ +++3 |2+ +  |  ++   2+++4   +| +2+++|  +++    | + |         |    |     +    + |  +  +      |       +   |        +   | +++   + +|      +|      + |        |   |     |
Synedra pulchella                       ++    |+  + +|   +            |   +  |  +      |   |         |    |      +     |      +     |  +  + 2   |            | 2+    ++ |       |        |        |   |     |
Eunotia curvata var. subarcuata        +      |      |    ++         +|      |       + |   |         |   +|  2    ++ +4|  +   ++  + | +    +  + | +  ++   +  | +   ++  +|+  + + |+++  + +| +  ++ +| ++|2+  +|
Gomphoneis olivaceum                   +   ++ |+    +|      ++  ++    |  2   |    +    |   |         |    |            |            |           |            |          |       |        |        |   |     |
Achnanthes austriaca var. minor         +     |   + +|    +  +   + +++| +  + |++       | + | ++++  ++|    |     + ++   |+     +++  +|+ ++ ++++  |        ++ +|    2++   |   ++  |+ +     |  +2    |   |+ 22 |
Cymbella (sp. 2)                          +   | +    | + ++    +      |      |++   + + |+  |4   +++  |+22 |+         + |       +   2|       +   | +      +   |          |       |        |        |   |+    |
Eunotia vanheurckii var. intermedia           |      |                |   ++ |      +  |   |         | + +|++++   +   2|  +    +++  |      +  ++|     + +    |   + +    |   +   | +  ++ +|  ++  + | ++|  +++|
Eunotia (sp. 1 cf. flexella)                  |      |               +|      |         |   |       + |    |          + |+++2+ +  ++ | + + ++  ++|       +    |          |       | +  ++  |    ++  |   |     |
Eunotia (vanheurckii var. 1)                  |      |                |      |      +  |   |         |    | ++     +  4|       +    |           |     +      |          |   +   |       +| +      | ++|     |
Eunotia (sp. 13 (minutissima))                |      |             +  |      |         |   |         |    | +2        +|    +  +    |           |+           |     +    |++     |        |        | + |++  2|
Gomphonema clavatum                        +  |      |    +  +  ++   +| +++  |   +     |   |+++ +++++| + +|     + ++   |  + +       | +2 + ++  +|+ ++ + + ++ |       +++|  + +++|     + +|        |   |     |
Navicula atomus v permitis                ++  |+     |           +    |  +   |3        |  +|         |    |            |            |           |        +   |          |       |        |        |   |     |
Navicula gallica var. perpusilla              |    + | +      +    +  | 4    |  +   +  | ++|         |    |      +     |            |+      +   |        +   |          |       |        |        |   |     |
Gomphonema tackei                       +     |      |                |      |         |   |         |    |            |            |       ++  |     +      |       +2+|    + +|        |        |   |     |
Achnanthes (cf. marginulata sp2)      ++      |      |  +2         + +|+     |   +  + +| 2.|   +  +++|+  +|    +       |  +   + +   |+      +   |     +      |          |    +  |    +   |        |   |     |
                                              |      |                |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
                                              |      |                |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
                               Ph     88768897|889778|7777679888886786|768766|677786657|677|666675666|6676|666656655664|666665555657|66566556556|555555666555|5554446766|6555665|54544555|44335534|454|14334|
                             Cond     53335564|666435|3343225445562333|335322|233352113|243|222231322|2223|231222321221|322222222212|12222222222|223121222122|2332223433|2222333|12111222|22222112|211|22222|
                               Ca     44445464|656444|4444446445452443|444443|344453214|343|333231333|3443|332333322321|222222222224|22322212223|233211332122|3333224433|2222333|23222221|22121221|211|12222|
                              SO4     54445565|665434|4444446444553433|444333|345563333|454|434343343|3333|443333322333|323213222223|33323223233|444333332233|4444434334|3333333|34323333|44343333|431|44444|
                              Alk     55445565|666545|4555446556662453|545543|455454225|454|433342443|3443|332323322321|212121111214|22322212223|332221322112|3331113434|3221422|12321211|11111111|111|13111|
                               Al     1134***1|332222|1123313*3***2112|23*242|112224433|212|244434*22|1232|122123222225|222233322233|52322222222|332654*31222|5566566222|2223*22|23254122|43333263|412|54564|
                               Cl     21224314|543335|2111112233342233|132322|111311111|123|112121331|1114|131131421311|443322123211|13322223223|113121322222|3333324545|2223354|13111432|33222112|312|11232|
                           Forest     20121103|221110|1111402111000101|131110|121100110|012|100001011|0000|021121101101|011001101000|10200110000|030001000112|1134333010|1335021|01000110|00231100|010|33340|
```

Table 10.1 Cont.

```
                                                        Group 6                |         Group 5        |                        Group 4                         |      Group 3      |     Group 2      | Group 1 |
                                                                               |                        |                                                        |                   |                  |         |
                                           6d      6c           6b          6a |    5c     5b     5a    | 4e       4d            4c          4b           4a    |    3b         3a |   2b        2a   | 1b   1a |
                                                                               |                        |                                                        |                   |                  |         |
                                        12334445|113557|1112223444445577|134567|111126666|115|166666677|1167|255556777756|777777777776|67777777777|125666677777|3333333777|5555677|15566777|55555567|557|22335|
                                        10110000|111120|0010001000002211|000203|011100012|012|000112223|0100|002221134421|011112244440|11222222334|000122212334|0000001000|1111100|01101013|00001113|013|00000|
                                        81022396|573395|7922564146784635|895592|304692884|418|646360580|2376|370231413514|306892412675|51013567694|575712379450|1234571478|2457912|10930928|34891827|263|48681|
                                                |      |                |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
Navicula exilis                         ++   +3 |+++   |         ++     |    + |         |   |         |+   |            |            |           |            |      +   |       |+       |        |   |     |
Navicula gracilis                       +     3 |+++   |     +          |  +   |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
Navicula graciloides                     ++ +3  |++4   |  +   +   +     | +++  |     +   |   |+        |    |            |            |           |            |     +    |       |        |        |   |     |
Rhoicosphenia curvata                       ++2 |+3++  |     ++   +     |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
Nitzschia dissipata                     +2 +++4+|++++  | +++  +++2++ + +| ++++ | ++++    | + |        +|    |      +     |            |+      +   |      +     |         +|      +|+       |        |   |     |
Cocconeis pediculus                     +    ++ |+2++ 2|  ++  +  +++  + |  +   |  + +    |   |         |    |            |            |      +    |            |          |       |        |        |   |     |
Navicula gregaria                        ++ 224 |322+ +|+ ++  ++++4++   |  2+2 |+++++    | + |         |    |      +     |            |           |            |     +    |    +  |        |        |   |     |
Navicula avenacea                       ++ +445+|43+3 +|  +2  ++++++    |  ++  |   +4 +  | + |+       +|+   |            |            |+          |            |      +   |    +  |        |        |   |     |
Cymbella sinuata                        ++3222 +|+3322+|++++ +2+2+++++++|3 +++ |  +++   +| ++|+   +   +|+   | +          |            |+          |+           |     +    |       |  +     |        | + |     |
Cymbella ventricosa                     +++3++2+|+2++++|+23+ +++++32 +++|++2+  |+23+2+ ++|+++|+++ + +3+|++ +|+     +     | ++   ++    |+++ +  ++  |      +     | + +   +++|    +  |+       |   +    |   |     |
Gomphonema clevei                       2 22++  |++++24|2++  24+2+4+ 232|+ +2+ |+ ++++ + |+ +| +  +  +4|   +|    +  +    | +       +  |     ++ +  |   +        |+      3++|++     |        |        |   |     |
Cocconeis placentula var. euglypta      4244+3+4|456555|2+22  2+2+++++++|3 +3 3| 3++   ++| 2 |+   +    |+   |+  +        |            |         + |            |       +++|       |+       |        |   |     |
Cymbella minuta                         34+244++|22++++|+22+222333222++3|++3+++|++244 +32|+3+|+ +3++22 |++ 2|+ ++ ++++ ++| + - +    ++|2+   +   + |++    ++++  |+  +   +  | -+2+- |2+      |  +   + |   | ++  |
Synedra ulna var. ulna                  2+++++++|++ +++|++++   ++2+++  ++|2+++++|+2+++2++3|22+|2+222+22+|+++2|++ + +2+  ++|++  +      +|+ ++2++++  |+  ++ +++   | +    +2+ |    +++|       +|+       | + |     |
Gomphoneis olivaceoides                 454545+4|+23434|+3343+444444++23|2++2+ |2+2233232|223|2++++ +33|+ +2|    +  +++  |++  +  +    |4  +   ++  |+      +    |    +  +++|+++++  |+  +    |   +    |   | +   |
Achnanthes minutissima                  545454+6|543453|6555665555546666|655565|556556655|656|556565555|6666|666666666653|455555465555|55556555656|565425+55555|22++++5454|523+444|323323++|+++  ++3| +3|52+++|
Fragilaria vaucheriae                   ++223+2+|++++22|+3222++324+3+232|334433|2322+23+2|+32|343333343|2+2+|3+++2322+22 | 2++3++2+2++|++222+2+2++|+++2443224++| + + 2+4+2|++222+2|++++++++|      + |  +|+    |
Hannaea arcus                           222+++ 2|++ ++ |2322++ 322++++++|2+++++|344344355|+2+|334425423|2+3+|2+++2+++++  |+   4+     +|3+  +++ 2 +|2 +2+   +++ | +        |+   ++ |   +    |        |   |++   |
Gomphonema parvulum                     +++3++++|22+222|++++2+3++++++2++|+2+2++|3+2+23+2+|342|++222+333|2++2|2+2+++++2++ |++++33++3+++|+432++3+3+3|444442424354|5556243545|555+555|+++3 +3+|++2+2+ +|  +|++ ++|
Synedra minuscula                       ++++++ +|++ +++|++32++ ++3++++++|22+222|2++222223|322|343434434|22++|22+33323322+| +2+++33+3+2|+223232+2++|443545543334|+++ +3++33|333+34+|22+22++3|++   + +|+ +|++ + |
Cymbella [sp. 1]                         +  +   | +  + |+2 +++  + +  +  |+ + + |+2+    + |3++|3  2++++ |223+|+    + + ++ |       +   4|+   + ++   |        +   |       ++ |   +   |        |     +  |   |+    |
Synedra acus                             +  +   |    + |3++  + + + + +++|+3  2+|+2     ++|2++|++ +2++2+|2+22|2++++2+++23+|+42423++++23|432+33223+2|  +++  +++++| +       +|++ + ++|+3+ 23 +| +      | + |     |
Brachysira vitrea                        +   +  | + +++|++ +++      ++++|++ +++|++    2++|+ +|+++ ++ + |2333|32+3+2+2+23 |444423323334|43222333+33|+3++++ +3+2+|  +  + + +|3++++++|24223522|+++ 32++| 23|+2+++|
Tabellaria flocculosa                    2+++  +| + +++|+++2 2     +++++|+2 3++|++++ ++32|+++|+32++322+|++++|233322333355|554544445553|23444443433|524353544355|2++2+2++22|4543333|66566566|55556665|355|+433+|
Synedra acus var. angustissima              +   |      |++ ++   +      +| + +++|+2++  + +|+  |+   +   +|++++|+  ++ 2 +++ |22+++32 ++++|+ + 23+22+2|+   +  +22 +|        + | +   ++|++2++2 +| ++     |   |  +  |
Meridion circulare                      +++2+ ++|++++2+| ++++ +++++3 +++| +++++|2++3+++++| 2+|+++ + 22+|    | +  + + +   |   ++  ++    |+  ++ + +  |+ +54 3++  +|22 +++++43|+ + 3++|   +    |        |   |  +  |
Achnanthes austriaca var. helvetica      +  +   |++ +  | +++   +++ + + +|+ + + |+ +      |   |       + |    |  + +++ +   | +  + ++    |+    +++++ |    +  + +++|  + 35+   | + 2+++| +  ++  | ++2    |  +|+ +2 |
Achnanthes detha                                |      |               +| +    |         |   |+   +  ++| +  |     + ++   | ++   +++++ |  2+  ++ + |        ++ +|52+2+ 4++2|+++ 2+3| + ++  +|  +     |   |   ++|
Achnanthes saxonica                      +     +|    ++|   +        ++  |   ++ | +       |  4|  +     +| + +| + ++ +2++  |     + ++   | ++ +++2 + |+ 4 ++  ++++|5554633 2+|+256+4+|  + +  +|+       | + |  +  |
Frustulia rhomboides var. saxonica      +       |   ++ |   +        +   | + ++ |       + |   |    ++   | ++ |++++ +++++++|++++ +++++++|++4++++++++| ++ ++++++++|++++ +++ +|+++3+++|+2+ +2++|++22++++|3+4|+2+2+|
Pinnularia subcapitata var. hilseana      +++   | +    |  ++       +++  | + ++ |    +    |+  |+ + + +++| +  | ++  + ++   |  + +++++ + |  +   ++   |+++ + +   ++|+243+43+++| ++2+2+|+  +   +| +44+++ |++ | ++3 |
Eunotia pectinalis                              |      | +             +|     4|   +     | + |  +    + |    |       +   +|+ 2+++5++   | ++4+23++2 |      + 4 5 |  ++      |+ +++ +|   ++  +|+ +   + |  +|   2 |
Eunotia pectinalis fo. impressa            +    |     +|++ +++      ++ +| + ++2|  +    ++|+++|++   +  +|++ +|+3 3++ ++++ |2++++22+ ++ |+223++2++32|2+2+ +++ +++|++++  +++2|2++++ +|++52 +++|+3++22 +| ++| 2+  |
Brachysira brebissonii                          |      |   +            |   +  |      + +|  +|         |    |  +    +  ++|+++ ++++++++|+ ++ +++ + |+ + +    +  |          | +     |+2++3  2|+2   +++|3+2|  +++|
Eunotia rhomboidea                              |      |                | + +  |         |   |    +    |    |  + +  + +  | +        + |  + ++ +   |           +|  + ++   +| + +   | ++ ++++|+ 43++  | +2| 2+3+|
Peronia fibula                          +       |      |   +++     +    |   2 +|     +2+ |   |    2    |    |++++   +++34|4+3+++++2+2 |++++++2+ 2+|  + ++ +2+ +|        + | ++ 2 +|+2+ +2+2|54+++444|454| 33++|
Eunotia incisa                          +++     |   ++ |   +        ++ +| + + +|+     +++|   |    + +  |++  | +++++++++++|2+++ +32++++| +++++++ 3+|+++++2 + +++|+   + +   |+++2+ +|++2+++2+|33532+34|433| 4544|
Eunotia naegelii                        +       |      |   +++       + +| + + +|      ++ |   |    + +  |    |++++ + +++++|+++++++++++ | +++++++ + |  + ++ +2+ +|+      ++ |+++ + +|+++ 3++3|34+ +++3|5+3|+22++|
Eunotia exigua                          2 +     | + +++|  ++++      ++ +|++    |+     +2+|+ +|++   2+  |+++ |+22++  ++++2|+++++++3++++|+++++++++++|+33+++++++++|++ +232 ++|22+32++|+2++++++|222322+2|242|65556|
                                                |      |                |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
                                                |      |                |      |         |   |         |    |            |            |           |            |          |       |        |        |   |     |
                                      Ph        88768897|889778|7777679888886786|768766|677786657|677|666675666|6676|666656655664|666665555657|66566556556|555555666555|5554446766|6555665|54544555|44335534|454|14334|
                                    Cond        53335564|666435|3343225445562333|335322|233352113|243|222231322|2223|231222321221|322222222212|12222222222|223121222122|2332223433|2222333|12111222|22222112|211|22222|
                                      Ca        44445464|656444|4444446445452443|444443|344453214|343|333231333|3443|332333322321|222222222224|22322212223|233211332122|3333224433|2222333|23222221|22121221|211|12222|
                                     SO4        54445565|665434|4444446444553433|444333|345563333|454|434343343|3333|443333322333|323213222223|33323223233|444333332233|4444434334|3333333|34323333|44343333|431|44444|
                                     Alk        55445565|666545|4555446556662453|545543|455454225|454|433342443|3443|332323322321|212121111214|22322212223|332221322112|3331113434|3221422|12321211|11111111|111|13111|
                                      Al        1134***1|332222|1123313*3***2112|23*242|112224433|212|244434*22|1232|122123222225|222233322233|52322222222|332654*31222|5566566222|2223*22|23254122|43333263|412|54564|
                                      Cl        21224314|543335|2111112233342233|132322|111311111|123|112121331|1114|131131421311|443322123211|13322223223|113121322222|3333324545|2223354|13111432|33222112|312|11232|
                                  Forest        20121103|221110|1111402111000101|131110|121100110|012|100001011|0000|021121101101|011001101000|10200110000|030001000112|1134333010|1335021|01000110|00231100|010|33340|
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Table 10.2 Diatom groups: summary water chemistry (mean and range)

Group	pH		Ca (mg l^{-1})		Alk (mg l^{-1})		Al (ug l^{-1})	
1a	5.29	(4.44-5.87)	1.29	(.86-1.77)	1.36	(.12-5.92)	146.08	(95.00-252.45)
1b	5.93	(5.57-6.34)	.81	(.41-1.12)	.69	(.30-1.44)	65.13	(29.50-116.00)
2a	5.76	(5.27-6.39)	1.11	(.92-1.39)	.77	(.19-1.77)	79.16	(32.50-151.00)
2b	6.11	(5.89-6.49)	1.38	(.85-2.06)	2.05	(.62-4.40)	61.96	(29.18-129.89)
3a	6.41	(6.17-6.54)	1.97	(1.21-2.75)	3.93	(1.43-9.23)	49.55	(38.50-71.50)
3b	6.31	(5.65-7.12)	2.93	(1.22-5.37)	5.65	(1.30-15.60)	123.94	(45.91-176.82)
4a	6.37	(6.01-6.66)	1.58	(.72-3.07)	3.23	(1.32-7.72)	80.45	(27.13-205.04)
4b	6.54	(6.27-7.07)	1.84	(1.00-4.04)	3.89	(1.39-9.93)	53.13	(30.80-125.21)
4c	6.42	(5.59-6.63)	1.37	(.71-1.79)	2.18	(.44-3.95)	55.18	(31.90-121.32)
4d	6.66	(6.45-6.93)	2.31	(1.15-3.75)	4.92	(2.37-7.86)	43.44	(28.23-87.91)
4e	6.96	(6.80-7.25)	4.28	(2.77-5.89)	10.60	(5.54-15.95)	48.00	(23.10-86.09)
5a	6.71	(6.30-7.13)	2.59	(.79-3.97)	7.31	(2.01-13.39)	78.91	(36.70-118.14)
5b	7.12	(7.00-7.29)	6.81	(3.70-12.95)	16.72	(8.11-32.02)	31.46	(21.76-39.63)
5c	7.07	(6.30-7.88)	5.73	(.90-16.13)	15.87	(2.10-43.84)	55.07	(21.80-112.95)
6a	7.10	(6.76-7.69)	6.60	(2.95-11.86)	19.12	(5.45-46.60)	58.28	(37.50-93.90)
6b	7.39	(6.71-8.15)	10.99	(1.65-34.89)	36.35	(3.24-92.77)	43.81	(21.75-79.27)
6c	7.59	(7.15-8.17)	19.98	(5.70-35.30)	56.97	(14.16-100.71)	52.59	(38.89-63.90)
6d	7.58	(6.96-8.39)	18.51	(5.14-78.17)	56.35	(10.58-225.00)	50.85	(21.73-112.80)

Figure 10.6 Relationship between maximum abundance and number of sites where present at greater than 1% for diatom taxa with maximum abundance greater than 3%

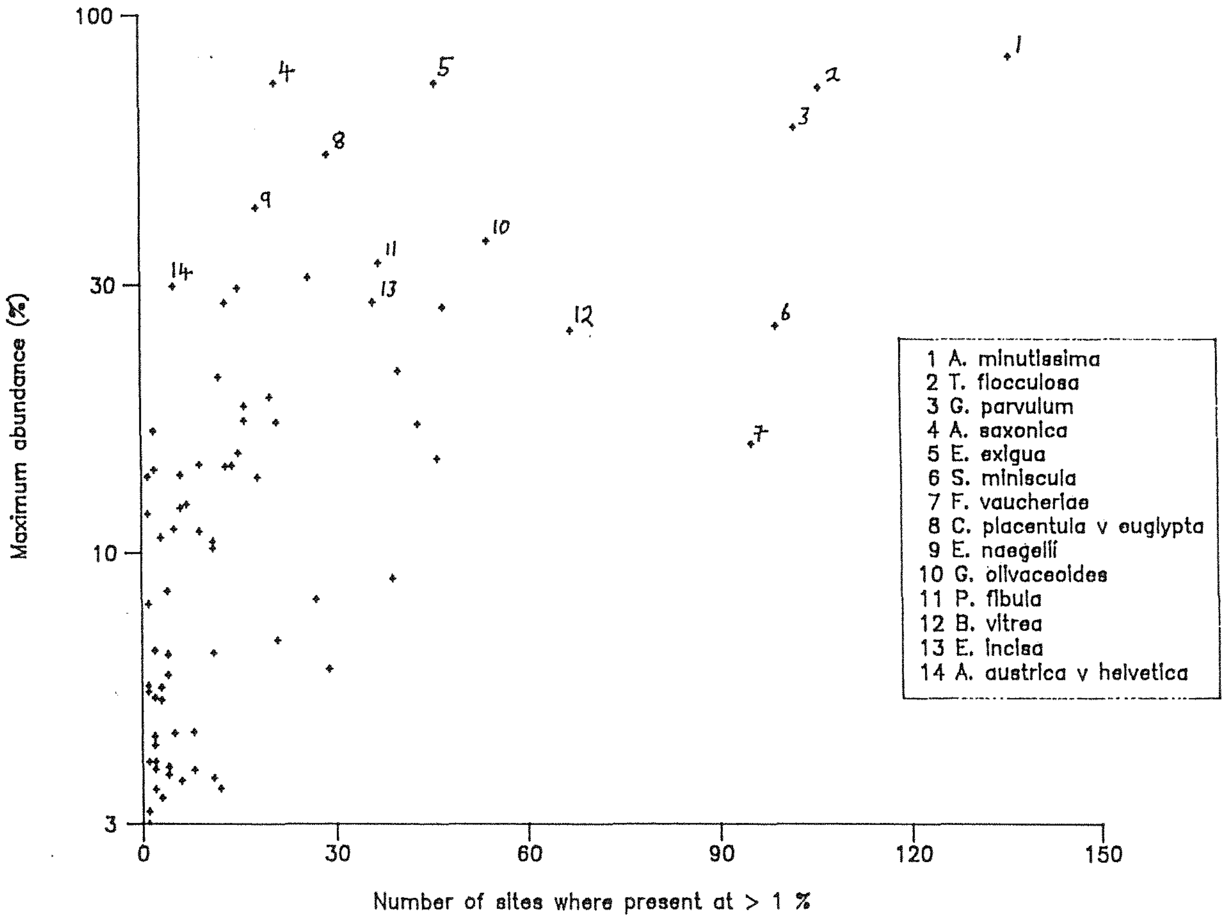


Figure 10.7 Map showing distribution of diatom groups

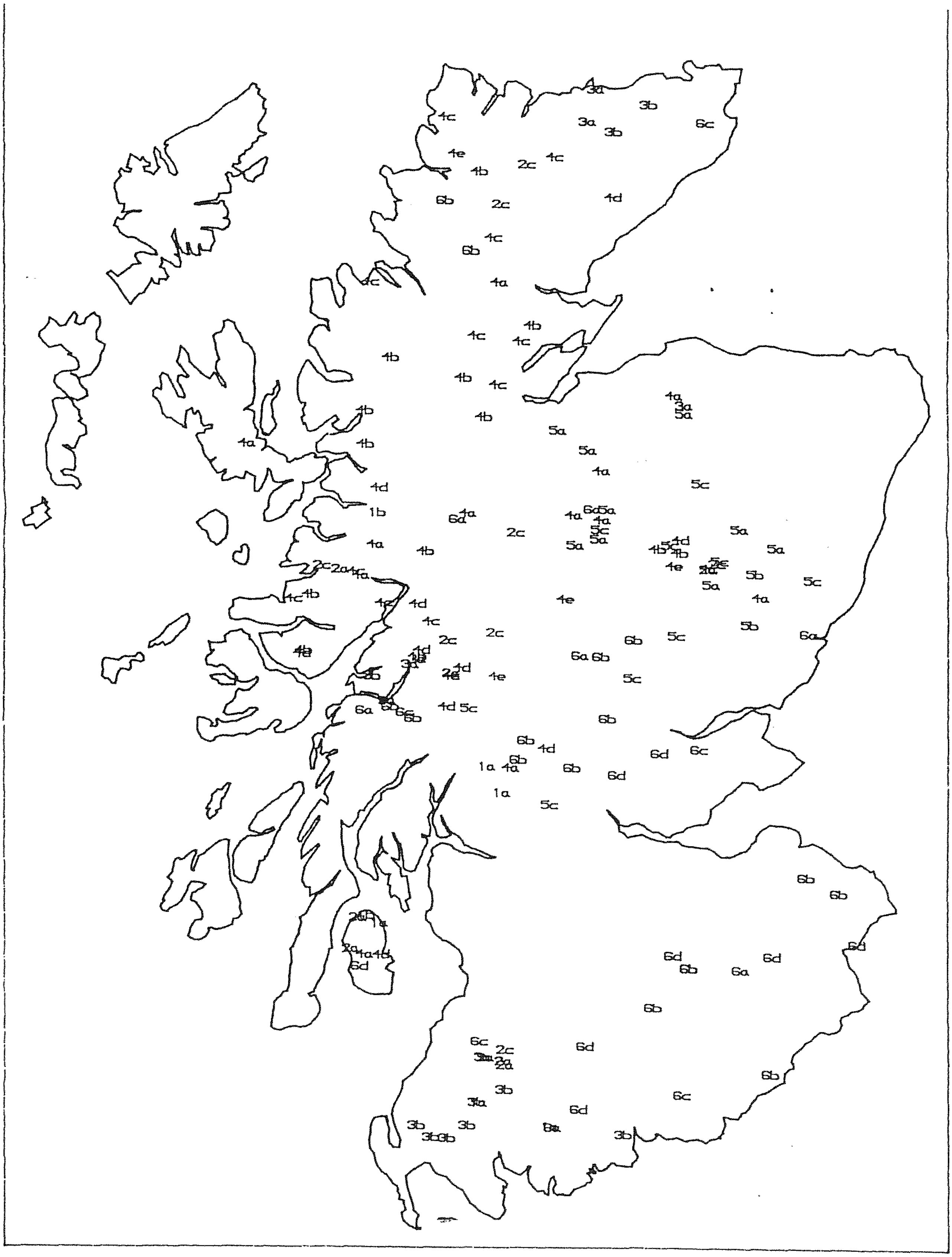


Figure 10.8 Canonical correspondence analysis ordination diagram (axes 1 and 2), showing diatom groups, environmental variables and selected taxa

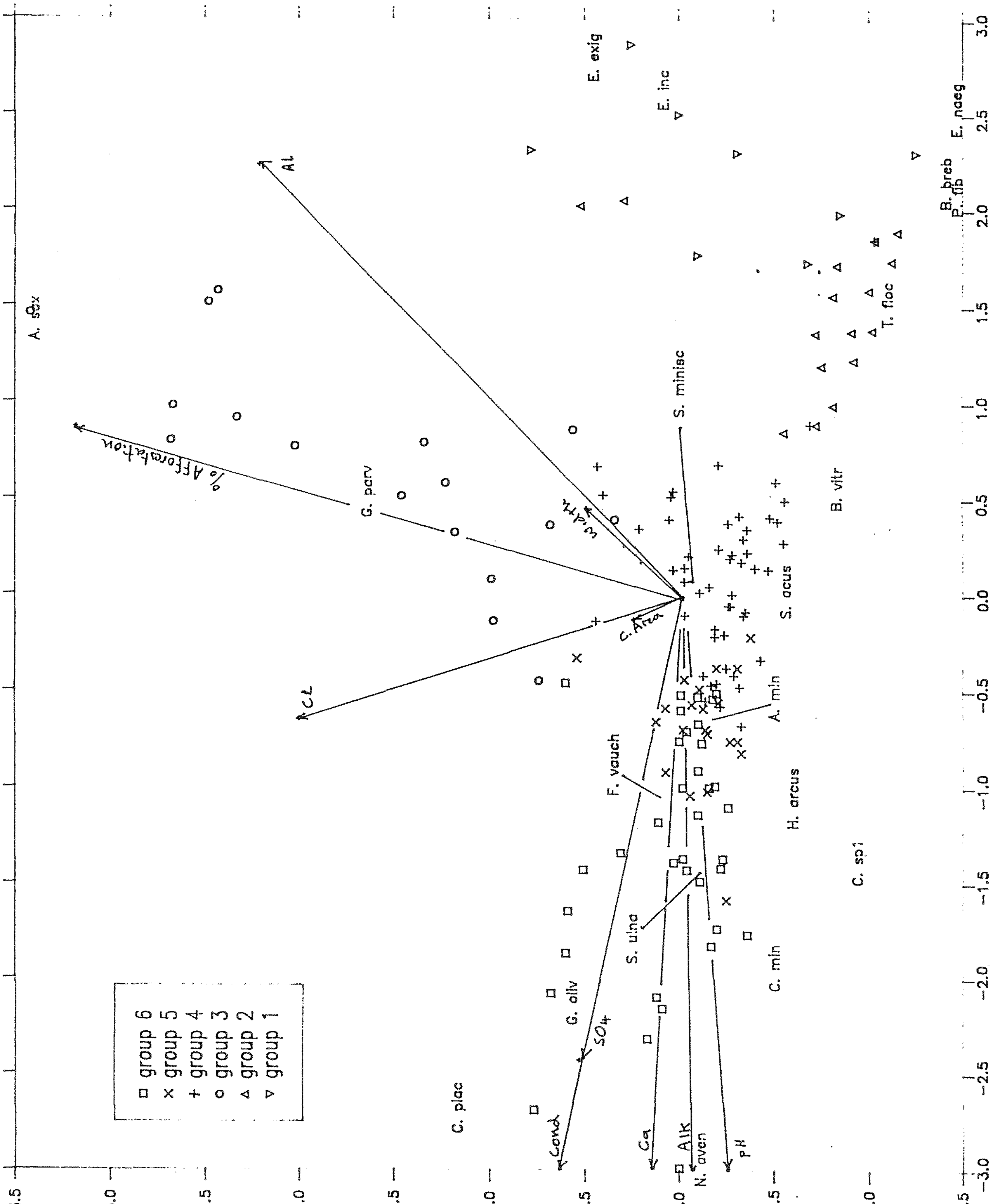


Figure 10.9 Relationship between measured and estimated mean stream water pH

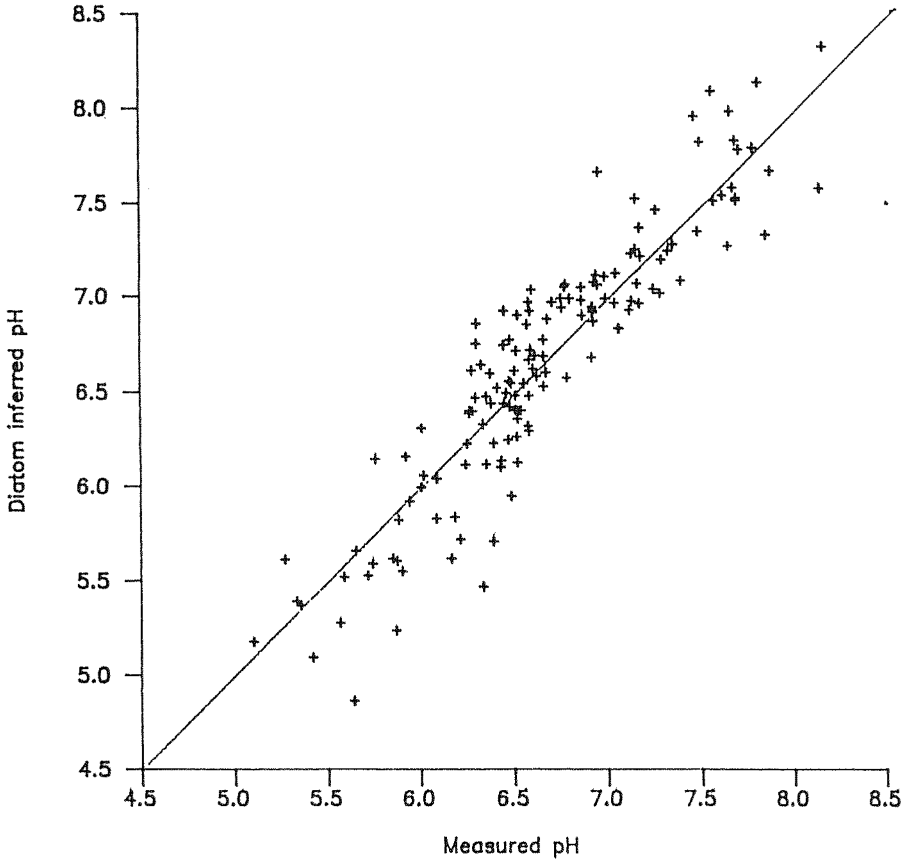


Figure 10.10 Relationship between measured and estimated mean stream water alkalinity

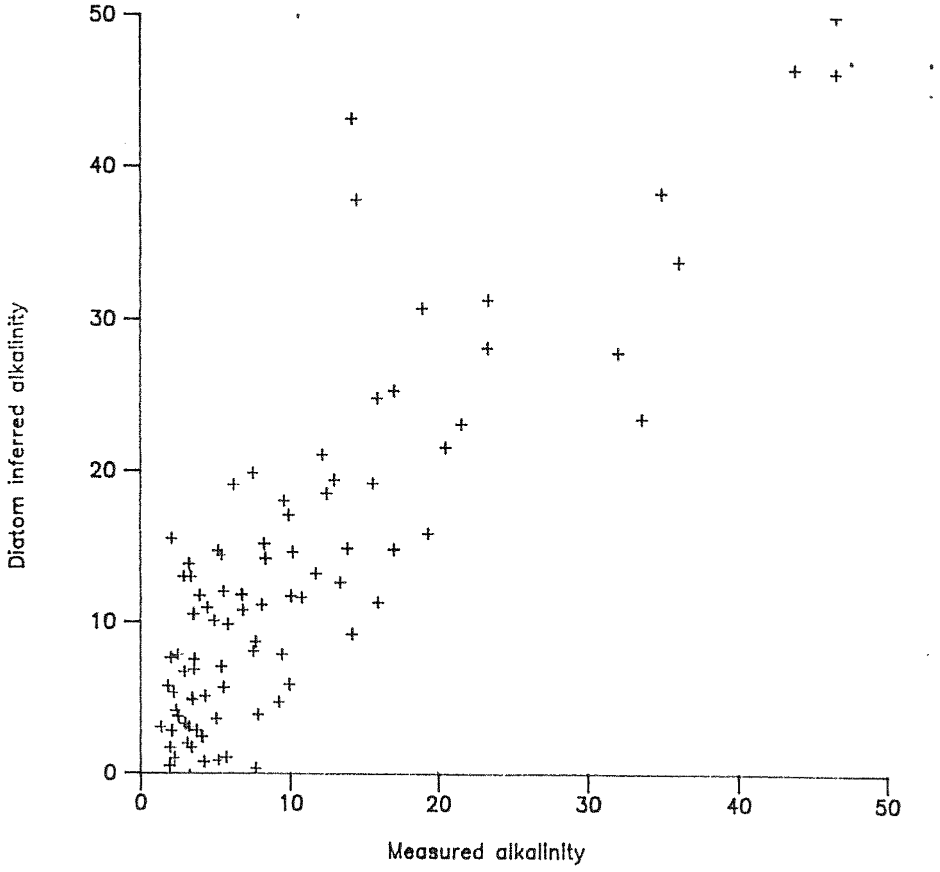


Figure 10.11 Relationship between measured and estimated mean stream water aluminium

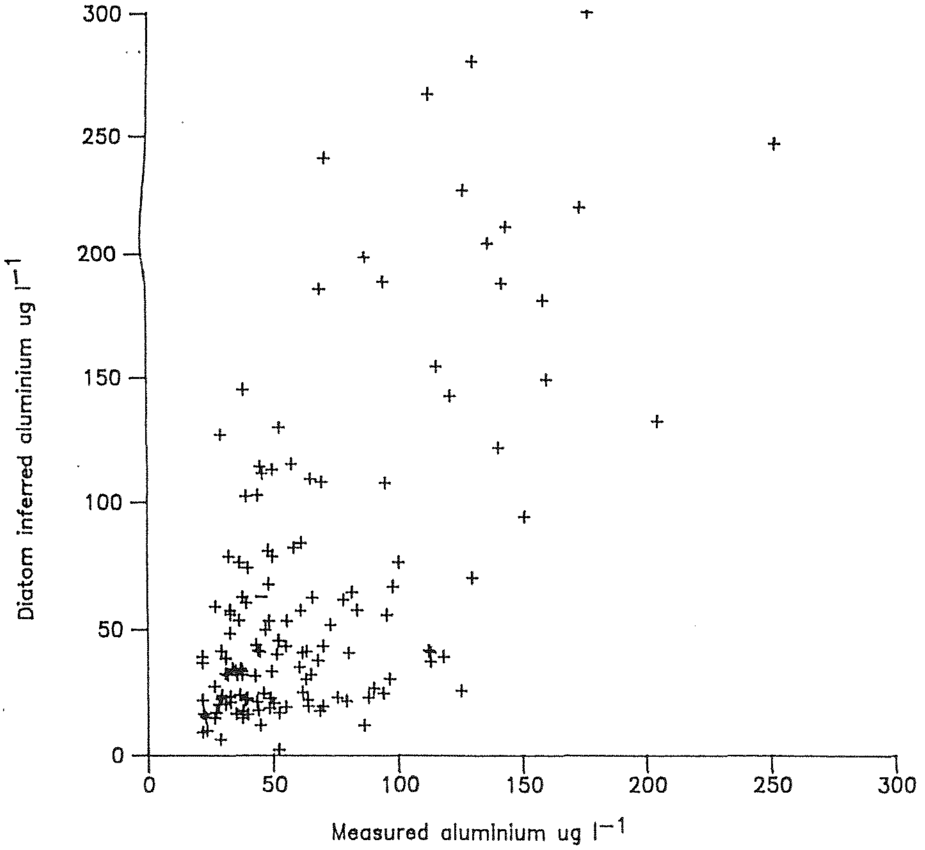
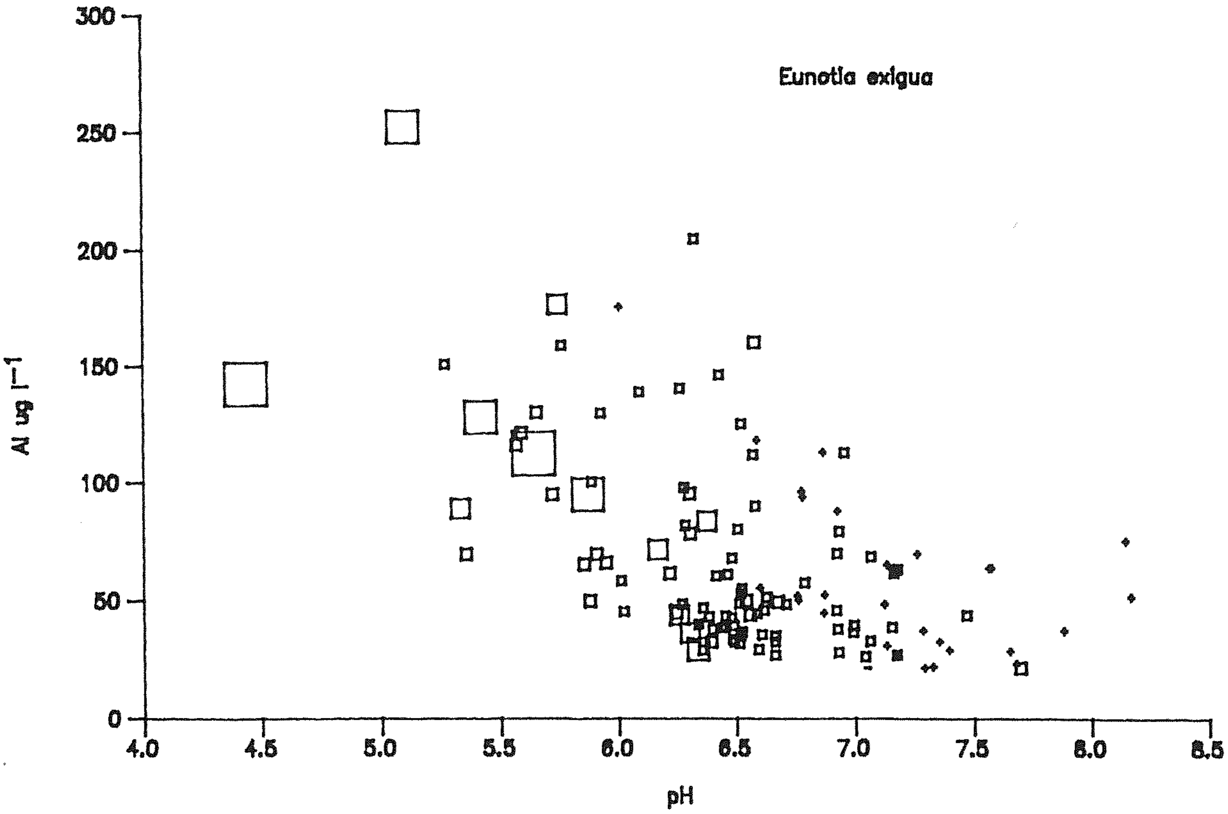


Figure 10.12 Relationship between relative abundance of *Eunotia exigua* and stream water pH and aluminium



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Appendix 10.1 List of sites and grid references.

101	Allt Eigheach	NN	442	577
102	Allt Lairig nan Lunn	NN	451	412
103	River Cononish	NN	340	289
104	Water of Mark	NO	444	804
105	West Water	NO	465	716
106	White Water	NO	275	762
107	Lochbroom Burn	NN	979	550
108	Keltney Burn	NN	774	491
109	Urlar Burn	NN	855	486
110	Ballinloan Burn	NN	974	405
111	White Burn	NO	423	609
112	Shaggie Burn	NN	878	251
113	Edendon Water	NN	716	706
114	Drumturn Burn	NO	142	566
115	Pow Burn	NO	651	577
116	Slack Burn	NO	665	783
117	Glassart Burn	NO	229	135
118	Water of May	NO	076	119
201	Brioch Burn	NN	914	036
202	Ardoch Burn	NN	741	063
203	Keltie Water	NN	640	138
204	Kelty Water	NS	467	968
205	Tighanes Burn	NN	563	168
206	Casaig Burn	NN	532	093
207	Gleann Riabhach Burn	NN	502	062
208	Unnamed Burn	NN	410	067
209	Boquhan Burn	NS	653	922
301	Main Water of Luce	NX	137	697
302	Cross Water of Luce	NX	193	651
303	Tarf Water	NX	255	648
304	River Bladnoch	NX	333	696
305	Water of Minnoch	NX	371	785
306	Water of Trool	NX	378	782
307	Cooran Lane	NX	478	833
308	Black Water of Dee	NX	654	692
309	Crae Lane	NX	664	688
310	Scar Water	NX	792	999
311	Glensome Burn	NX	938	663
312	Urr Water	NX	766	758
313	Water of Milk	NY	163	814
314	Liddel Water	NY	502	896
401	Tweed	NT	052	150
402	Biggar	NT	128	348
403	Tweed	NT	509	347
404	Southey Burn	NT	190	301
405	Lewinshope Burn	NT	389	295
406	Flosh Burn	NT	190	301
407	Whiteadder	NT	642	650
408	Cockburnlaw Burn	NT	769	590
409	Leet Water	NT	839	396
501	North Sannox Burn	NR	994	468
502	Easan Biorach	NR	943	498
503	Catacol Burn	NR	911	489

Appendix 10.1 Cont.

504	Iorsa Water	NR	884	370
505	Machrie Water	NR	937	349
506	Black Water	NR	919	304
507	Cloy Burn	NS	001	348
508	Carrick Lane	NX	476	941
509	Gala Lane	NX	482	926
510	Garpel Burn	NX	481	985
511	Water of Girvan	NX	406	954
512	River Stinchar	NX	396	956
513	Palmullan Burn	NS	382	016
514	Allt A'Bhiorain	NN	113	455
515	Allt Nan Gaoirean	NN	141	475
516	Allt Charnan	NN	144	484
517	Allt Dubh	NN	025	317
518	Linne Nam Beathach	NN	271	422
519	River Etive	NN	260	547
520	Allt Fhaolain	NN	158	509
521	Allt Tolaghan	NN	271	413
522	Water of Tulla	NN	314	444
523	River Lochy	NN	254	296
524	Allt Cruiniche	NN	037	294
525	River Lonan	NM	937	280
526	Teatle Water	NN	124	251
528	Dearg Abhainn	NM	965	411
529	River Nant	NN	019	273
602	Allt Darrarie	NO	309	852
603	Feith Talagain	NN	525	959
604	Allt Na Fearna	NN	754	911
605	Callater Burn	NO	155	883
606	Water of Feugh	NO	525	904
607	Baddoch Burn	NO	134	833
608	Quoich Water	NO	118	912
609	Allt Na Baranachd	NH	822	051
610	River Muick	NO	300	842
611	Slugain Burn	NO	159	932
612	Allt Dubh Loch	NO	265	821
613	Allt Coire Chaoil	NN	847	934
614	Glas Allt	NO	267	825
615	River Lui	NO	069	898
616	Tullich Burn	NO	387	975
617	Allt Mor	NH	749	029
618	Allt Fhearnagan	NN	851	971
619	Cowlatt Burn	NJ	173	448
620	Allt A'Mharcaidh	NH	879	050
621	Allt Ant-Slugain Dhuibh	NH	855	201
622	Allt Ruadh	NH	859	010
623	Torwinny	NJ	133	485
624	Wells of Lecht Burn	NJ	235	154
625	Allt Arder	NJ	173	417
701	River Strathy	NC	835	649
702	River Strathy	NC	803	523
703	Achriesgill Burn	NC	257	541
704	Allt Forsiescye	ND	036	590
705	Strath Burn	ND	255	521

Appendix 10.1 Cont.

706	River Laxford	NC	295	400
707	River Halladale	NC	904	485
709	River Mudale	NC	568	359
710	River Naver	NC	676	387
711	Allt Nam Albannach	NC	385	331
712	River Fiag	NC	467	205
713	Traligill Burn	NC	250	218
714	River Helmsdale	NC	901	233
715	River Oykel	NC	352	028
716	River Cassley	NC	438	078
717	River Carron	NH	461	912
718	River Gruinard	NG	962	912
719	River Vaich	NH	373	709
720	River Blackwater	NH	589	749
721	Abhainn Bruachaig	NH	038	624
722	River Glass	NH	545	689
723	River Meig	NH	321	550
724	River Orrin	NH	454	524
725	River Carron	NG	940	425
726	River Farrar	NH	401	403
727	River Elchaig	NG	942	299
728	River Nairn	NH	686	353
729	River Sligachan	NG	487	300
730	River Findhorn	NH	804	278
731	River Shiel	NG	995	134
732	Aldernaig Burn	NH	298	011
733	Allt A'Choire Beithe	NG	985	036
734	River Oich	NH	337	036
735	River Pean-Dessary	NM	979	912
736	River Arkaig	NN	173	885
737	Allt Lon A'Mhuidhe	NM	845	815
738	River Ailort	NM	775	830
739	River Moidart	NM	730	719
740	River Callop	NM	925	793
741	River Finnan	NM	907	808
742	River Shiel	NM	665	704
743	River Nevis	NN	144	686
744	River Blackwater	NM	702	506
745	River Aline	NM	697	495
746	River Scaddle	NN	013	689
747	River Leven	NN	195	618

11 FLY-ASH PARTICLE ANALYSIS FROM SEDIMENTS AS A NEW TECHNIQUE FOR MONITORING AIR POLLUTION (CEGB & DoE joint funded project)

11.1 INTRODUCTION

Identification of coal and oil-derived particles in sediments allows the extent of air pollution to be quantified through time at a site and mapped spatially between sites and countries. In some circumstances the technique can be used to trace transboundary pollution (eg. the occurrence of coal-derived particles in southern Norway and southern Sweden where coal is not burnt; the occurrence of brown coal particles in countries not burning brown coal). By examining sediments that have accumulated over the last 10-20 years the technique can be used alongside other techniques such as diatom analysis to assess the effectiveness of abatement strategies to reduce acid deposition and lake acidification. The idea of using carbonaceous particles in sediments was introduced into Europe from the USA by Dr Ingemar Renberg in Umeå, Sweden (eg. Renberg and Wik 1984). He developed a chemical digestion and stereomicroscope technique for quantifying carbonaceous particles in sediments and soils in Sweden. In the past two years we have been carrying out research in the UK aimed at improving the chemical preparation techniques for carbonaceous particles, developing a new technique for siliceous particles and finally differentiating between oil and coal particles. At the same time we have been contracted to use the technique (not differentiating between coal and oil) to map out the extent of fly-ash (and acid rain) pollution in the UK and to compare lakes in areas of high and low acid deposition in the UK, Norway and Sweden.

This Chapter describes the techniques which have been developed to allow, for the first time, the differentiation between coal and oil carbonaceous particles in the environment. The technique is entirely automated allowing rapid characterisation of large numbers of particles and enabling statistical techniques to be used to show that this differentiation can be made with over 93% of particles being correctly assigned to their fuel type. This work has been jointly funded by the CEGB and the DoE.

11.2 TECHNICAL DESCRIPTION

Sediment digestion.

Before examination by automated scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM/EDS), sediment samples are treated according to the methods defined by Rose (1989a, b) to isolate carbonaceous and siliceous fly-ash particles from the sediment matrix.

Carbonaceous particles, although physically fragile, are chemically very resistant due to being predominantly composed of elemental carbon. So an extraction method involving strong mineral acids is possible without affecting either particle morphology or surface chemistry. Based on the method developed in the USA by Griffin and Goldberg (eg. 1981), the extraction technique has been improved and shortened specifically with fuel type characterisation of the particles in mind. The method involves a basic peroxide treatment to remove organic material, and then removal of carbonate and silicate mineral matter using hydrochloric and hydrofluoric acids respectively.

Mineral ash spheres are formed by the fusing of the inorganic component of the fuel (ie. mineral veins within the coal seam), upon entering the furnace, and consequently are more a product of coal combustion than fuel oil combustion. The composition of these particles is mainly aluminosilicate with varying amounts of iron, and so they are chemically very similar to many of the sediment minerals from which they are to be extracted. This greatly restricts the range of reagents which can be used in an extraction method. The technique developed in our laboratory involves stepwise removal of organic material, biogenic silica, and some less resistant carbonates, followed by a density separation. This removes over 80% of the unwanted sediment, leaving all the mineral ash spheres.

Sample Preparation.

A few drops of particle suspension are added to the top of a column of alcohol and allowed to spread for a few seconds before the entire column is drawn through a 0.4 micron Nucleopore filter. Nucleopore filters provide an excellent substrate for this type of analysis because the particles are retained on the surface. The organic composition of the filter does not add any detectable X-ray peaks to the spectrum in the analytical system used in this work (see below).

Filter samples are mounted onto glass slides using colloidal graphite paint and coated with a thin layer of carbon by evaporation in a vacuum. This forms a conducting layer over the particles and prevents the build-up of charge on the specimen in the SEM. Carbon is used rather than a metal coating because it does not complicate the X-ray spectrum with additional peaks.

Analysis

In an electron microscope a beam of electrons is focused onto a specimen and a number of signals result. These are measured by suitable detectors and a number of possible configurations exist to optimise different types of analysis. In the JEOL 733 Superprobe both morphology (images and micrographs) and chemistry (X-ray data) may be examined. Use is made of three detected signals - secondary electrons, backscattered electrons and X-rays. This information can be gathered manually by an operator or automatically by a suitably programmed computer. Secondary and backscattered electron images may be digitised and captured on computer for further manipulation. The great advantage of these digital images is that because each pixel is represented by a single number, they can be readily stored and manipulated by computers. X-ray data are gathered using energy dispersive X-ray spectroscopy.

Automated Particle Analysis - Data Acquisition

The recent development of image analysis software has made it possible to "teach" computers to perform some parts of the analysis. This allows the acquisition of data for large numbers of particles in short periods and the rapid creation of large data sets. A variety of powerful multivariate statistical techniques are then employed to examine patterns and trends.

Data Processing

The energy dispersive X-ray spectrum is represented as a histogram of the total X-ray photons counted by each channel of the multi-channel analyser in the detection system. Each element detectable by the system has one or more characteristic energy levels at which X-rays will be detected if it is present in the sample. A background (Bremstrahlung) radiation distribution is generated by random noise and the elements present show as peaks superimposed on this. These peaks span several channels in the multichannel analyser and a convenient way to summarise the data is to delimit a "region of interest" (often termed "to paint a window") over the channels concerned and to record the total counts in the whole region. This leads to a significant reduction in required storage space since the counts for each element are now represented by a single number, and it is not necessary to have a number for each channel.

For the automated particle analysis using the DIGISCAN program, up to 25 regions of interest are defined on the spectra and the numbers of X-ray counts falling in each region (or "window") are stored. Various corrections (for background counts, peak overlap and detector efficiency) are then carried out.

The set of definitions of X-ray regions of interest and the correction factors to be applied to them, is stored in a separate computer file termed a "window file", since it will be used repeatedly to correct the results for all measured features.

The following window file was developed for the analysis of oil and coal derived carbonaceous emissions:

Table 11.1 Window file developed for analysis of oil and coal derived carbonaceous emissions

Element	Window	Background Factor	Window	Overlap Factor	Window	Eff. Factor
Na	1	0.9400	7	3.3690	22	1.0000
Mg	2	1.1000	7	0.0180	3	1.0000
Al	3	1.0000	7	0.0190	4	1.0000
Si	4	1.0000	7	0.0000	0	1.0000
P	5	1.4700	9	0.0110	0	1.0000
S	6	1.3700	9	0.0000	0	1.0000
Cl	8	0.9900	7	0.0000	0	1.0000
K	10	0.9400	9	0.0000	0	1.0000
Ca	11	0.8600	9	0.0360	10	1.0000
Ti	13	0.9200	12	0.0000	0	1.0000
V	14	0.7800	12	0.0760	13	1.0000
Cr	15	1.2800	17	0.1310	14	1.0000
Mn	16	1.0700	17	0.1110	15	1.0000
Fe	18	0.9400	17	0.0730	16	1.0000
Ni	20	0.6700	17	0.0000	0	1.0000
Cu	21	1.3300	23	0.0000	0	1.0000
Zn	22	1.1000	23	-0.0460	21	1.0000

Data Interpretation and classification.

The classification of carbonaceous particles, depends on the differences in the surface chemistry of the particles resulting from the fuel types. Typical EDS spectra of coal and oil particles are shown in Figures 11.1a and 11.1b respectively. In the past, a single chemical parameter (titanium for coal and vanadium for oil) has been used to distinguish the fuel types on a presence or absence basis. However, due to the heterogeneous nature of the fuels, these elements may or may not be present and therefore total chemistry is used in our classification of these particles.

In this case a classification scheme is a set of descriptions which define a particle type. When a feature is analysed the computer searches through the list until a description is found whose conditions are fulfilled. The feature is then ascribed to that class.

Taking reference material of known origin from oil, coal and peat fired power stations a classification scheme was built up. This resulted in 12 different categories, each with a characteristic chemistry, and to each of which could be assigned a fuel type (see Figure 11.2). Using this classification scheme over 85% of particles were placed in their correct fuel group.

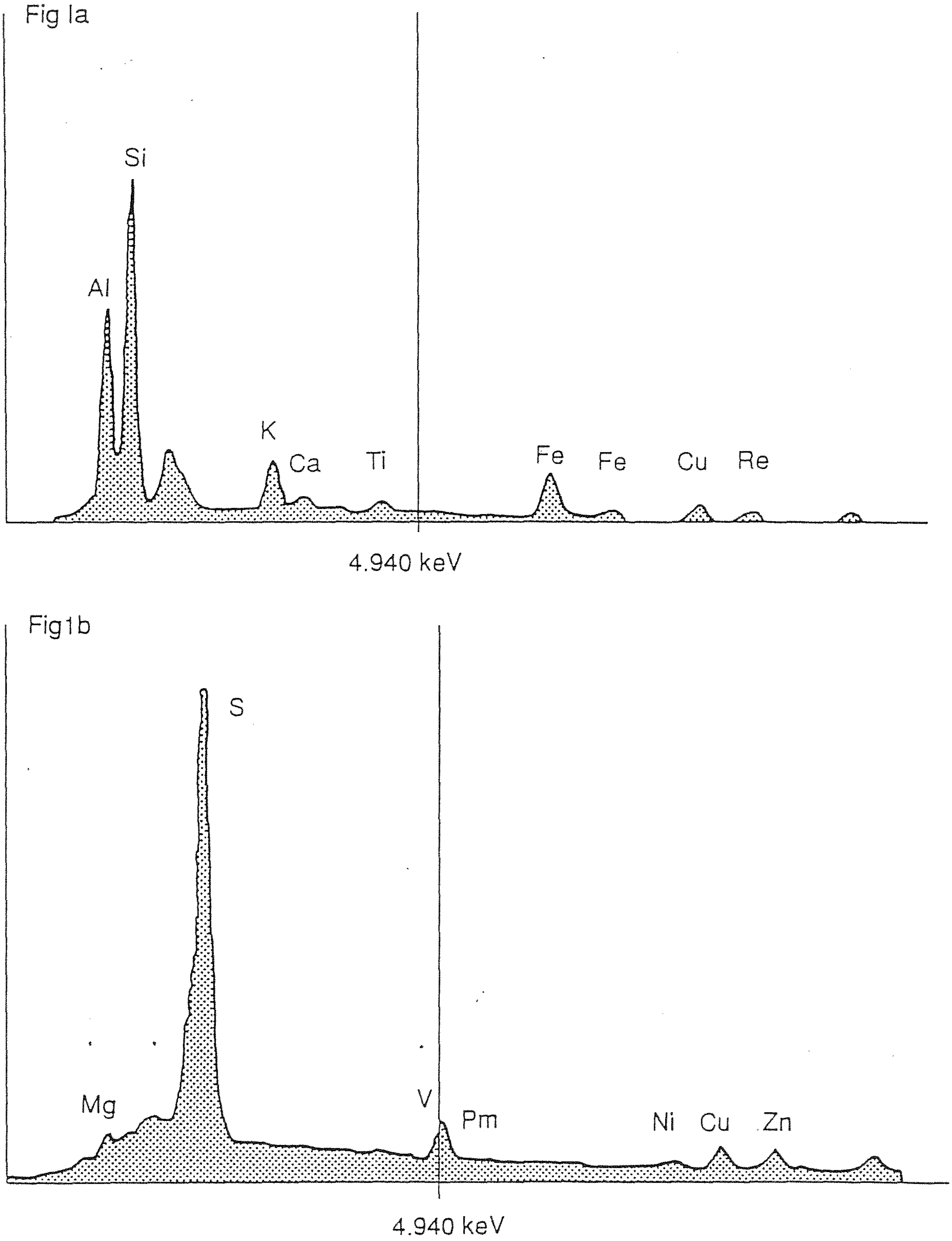
This process can be improved by using multivariate discriminant analysis. Initially, the reference material from known sources are analysed, so that particle groups of 'typical' oil and coal composition can be recognised and outliers removed. The discriminant analysis then use the total chemical data from these groups to find a multivariate axis along which the differences between the fuel types are maximised, giving a bimodal distribution, one peak representing coal and the other oil. This is shown in Figure 11.3.

This characterisation can then be tested by randomly selecting 200 particles from coal and oil sources and re-applying this discriminant analysis to see how well particles are assigned to their correct fuel type. The results show that over 93% of these particles are correctly classified. Continuing work should improve this figure even more.

11.3 APPLICATION TO SEDIMENTS

Upon application of this technique to carbonaceous particles extracted from the sediments of Loch Tinker in Scotland, a 20% oil, 80% coal figure was attained. The history of mineral ash deposition to this loch closely resembles that of the carbonaceous particles (Rose 1989a, b), confirming that the majority of particles are from coal-fired sources. After further calibration of the technique with a wider range of fuel types (brown coal, lignite) from different European power stations the method can be applied to soil and sediment samples throughout Europe.

Figure 11.1 Typical EDS spectra of carbonaceous particles from a) coal and b) oil origin



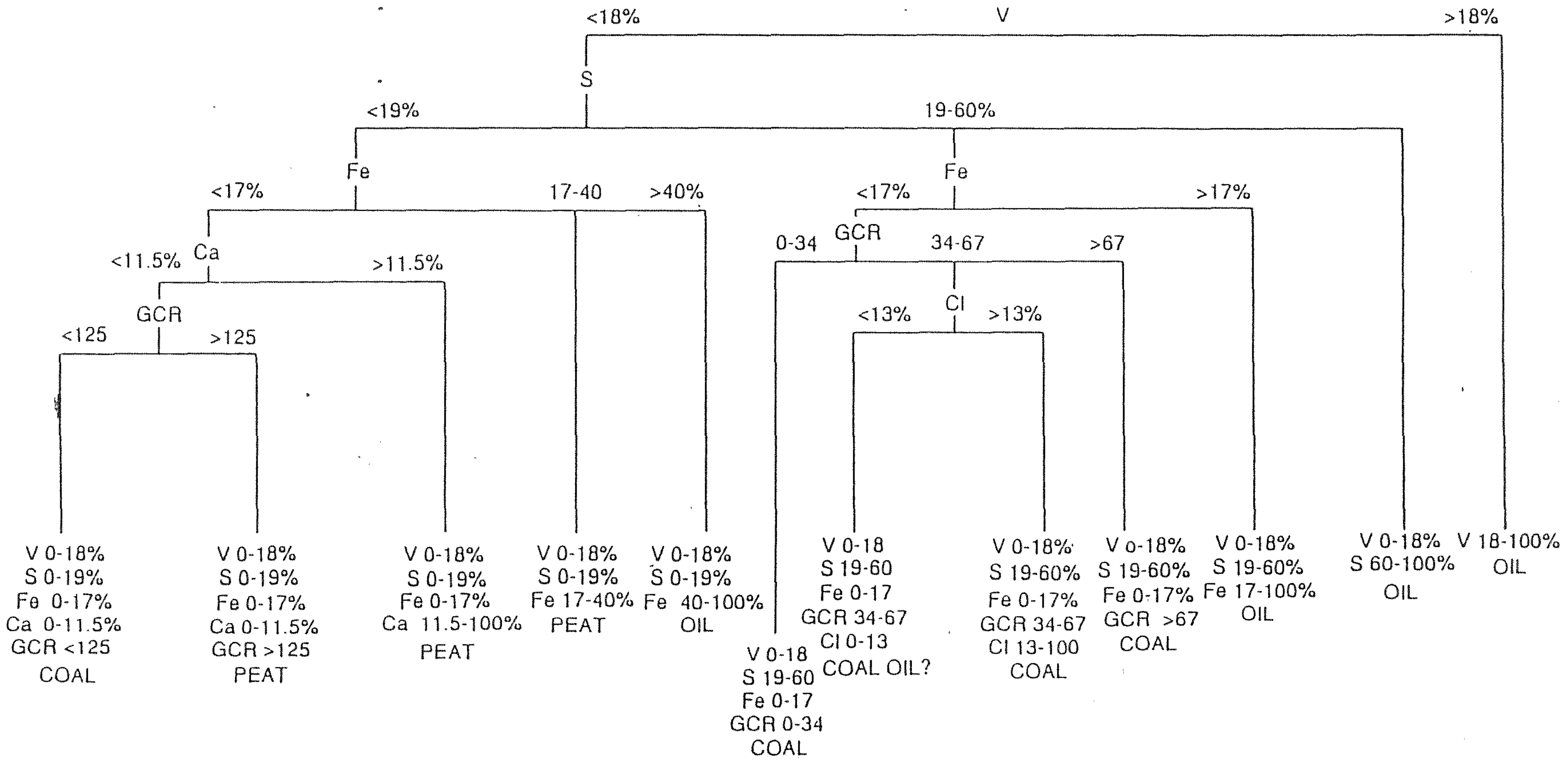
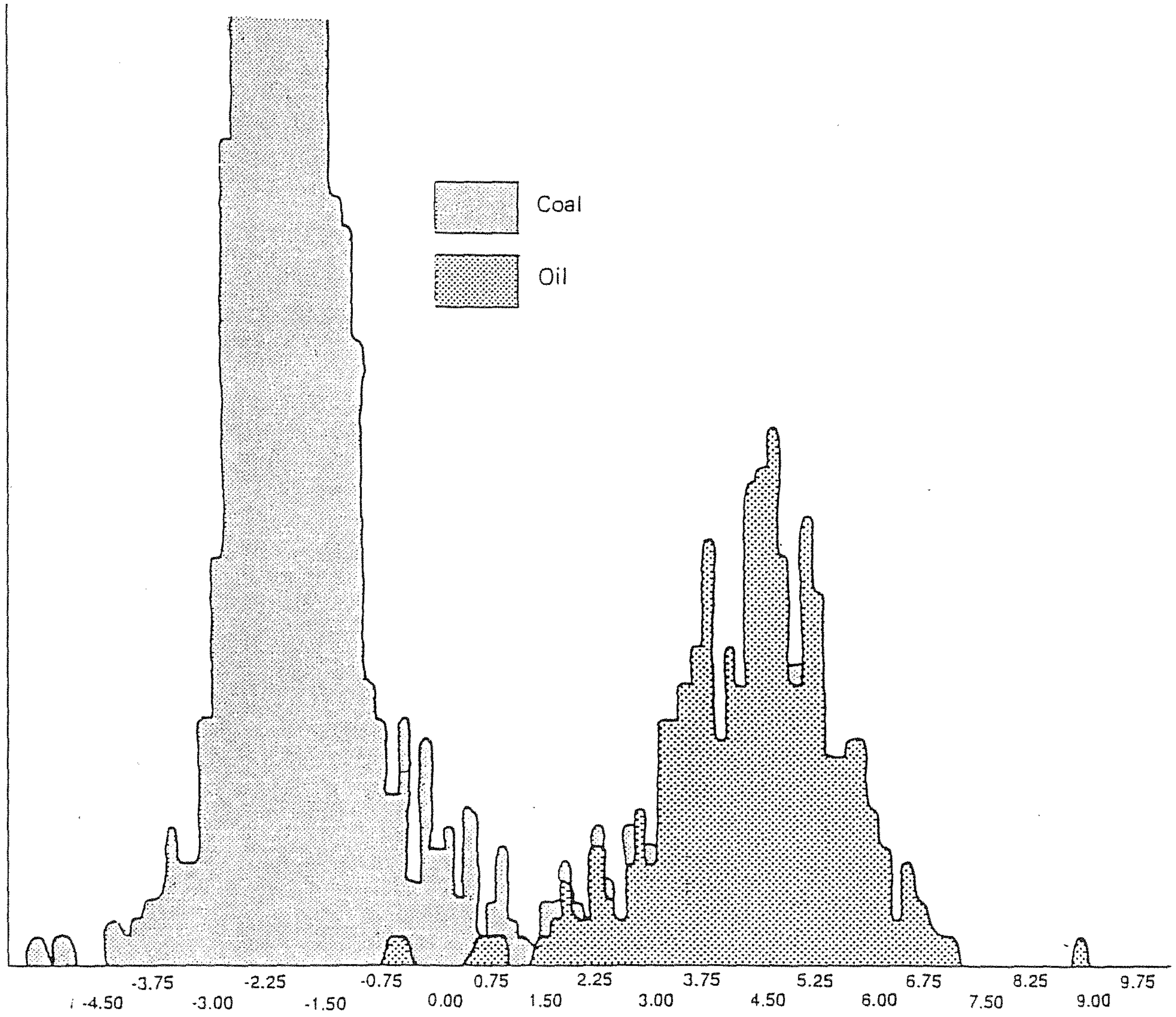


Figure 11.2 A classification scheme for carbonaceous particles using EDS derived chemistry

Figure 11.3 A graphical representation of the coal/oil characterisation using multivariate discriminant analysis



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