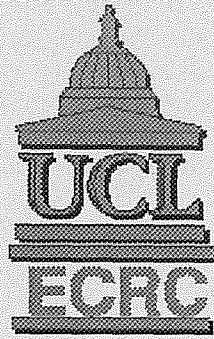# ENVIRONMENTAL CHANGE RESEARCH CENTRE

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A Palaeolimnological Study of the Water Quality of Lakes in the Vosges Mountains of France

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EXECUTIVE SUMMARY

1. A palaeolimnological study has addressed issues of nutrient enrichment and acidification in the Vosges Mountains of eastern France.

2. Many of the lakes exhibit evidence of disturbance in the sediment record probably as a result of water level fluctuations.

3. Eutrophication

a) Detailed diatom and sediment chemistry analyses of a sediment core from Lac de Gérardmer suggest that before the twentieth century the lake was oligotrophic and experienced little variation in water quality.

b) The first, slight, increase in nutrient input to the lake is recognised, from changes in the diatom flora, around 1900 and further diatom changes in the early 1960s suggest a further increase in nutrient loading.

c) Historical changes in total phosphorus concentrations have been calculated using a diatom-based transfer function.

d) This new method shows that a peak in reconstructed total phosphorus concentration in the lake water is dated to the mid-1970s and coincides with observed water quality decline at this time. Although this phosphorus peak represents a doubling of pre-1900 values, maximum concentrations were, at 8.2 μg l^{-1}, far short of eutrophic conditions.

e) Since 1980 there is some evidence for a slight reversal of the enrichment trend.

4. Acidification

a) The carbonaceous particle record in sediment cores from all the lakes studied shows that the region has been exposed to atmospheric contamination from oil and coal burning over the nineteenth and twentieth centuries.

b) This acid deposition record is correlated with the fossil-fuel combustion histories of both France and Germany.

c) One site (Lac des Corbeaux), examined in detail, shows clear evidence of acidification from the sediment diatom record, dating from the mid-nineteenth century.

d) There is no firm evidence of acidification at any of the other sites investigated and a range of reconstructed water chemistries is apparent from acid or fairly acid lakes which may be vulnerable to acidification, to lakes where the most significant change in water quality appears to result from nutrient enrichment rather than acidification.

5. Recommendations

a) A more wide-ranging, critical loads-based survey following internationally agreed protocols is recommended to extend this palaeolimnological study in this and other sensitive regions of France.

b) New methods of phosphorus reconstruction, exemplified at Lac de Gérardmer, should be used at other sites in France where eutrophication is a problem, to ascertain the history, causes and extent of water quality change.

1. INTRODUCTION

Palaeolimnological techniques have been widely used in the United Kingdom, Scandinavia and North America to identify the incidence, causes and history of lake acidification (eg. Charles and Whitehead 1986, Battarbee *et al.* 1988, Battarbee *et al.* 1990). Associated statistical methods have been developed which now permit surface water acidity (pH) to be accurately reconstructed through time from the diatom record of dated lake sediment cores (eg. Stevenson *et al.* 1989, Birks *et al.* 1990a, 1990b).

The nutrient history of lakes may also be traced utilising diatom and associated evidence from dated sediment cores (eg. Battarbee 1986, Anderson *et al.* 1990), and statistical methods similar to those used to reconstruct pH are now being developed to reconstruct other parameters such as phosphorus concentrations (eg. Anderson 1992, Anderson *et al.* 1992).

Such techniques represent an important tool for water managers and conservators by allowing historical pre-pollution (baseline) conditions to be determined and by documenting the history, extent, and potentially the cause, of water quality change.

The Vosges Mountains of Eastern France contain lakes on sensitive geologies which are susceptible to acidification and at least one major lake in the area (Lac de Gérardmer) has experienced nutrient enrichment. The purpose of this study is therefore twofold:

1:    To investigate the palaeolimnology of Lac de Gérardmer, with reference to the recent history of nutrient input to the lake.

2:    To investigate the palaeolimnology of some oligotrophic lakes in the region, in particular Lac des Corbeaux, with reference to recent acidification from anthropogenic sources.

Funds were not available for important analyses such as ^{210}Pb dating or detailed diatom analysis at all sites, in addition the region presents some problems for extensive palaeolimnological research as many of the lakes are utilised for water supply or storage and experience fluctuating water levels with the associated potential for disturbance in the littoral zone and interference with sedimentation processes. This report therefore represents a general survey and evaluates the potential for utilising palaeolimnological techniques to assess and reconstruct aspects of recent water quality history in the Vosges region.

2. SITES

The main body of sites are situated in the central Vosges mountains of France in the Cornimont - La Bresse region and to the east and south of the town of Gérardmer. The location of the study sites are shown in Figure 2.1 (the location of Lac de la Maix which lies to the north of the main study area is shown separately in Figure 5.19). With the exception of Lac de Gérardmer which is larger and has a more diverse catchment, the lakes are comparatively small and lie in forested catchments above 600 m. Although all the lakes occur in basins which are presumably of glacial origin, most are dammed by barrages or sluices and the extent to which they are natural or artificial waterbodies is not always clear.

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Figure 2.1   Location of map of study sites
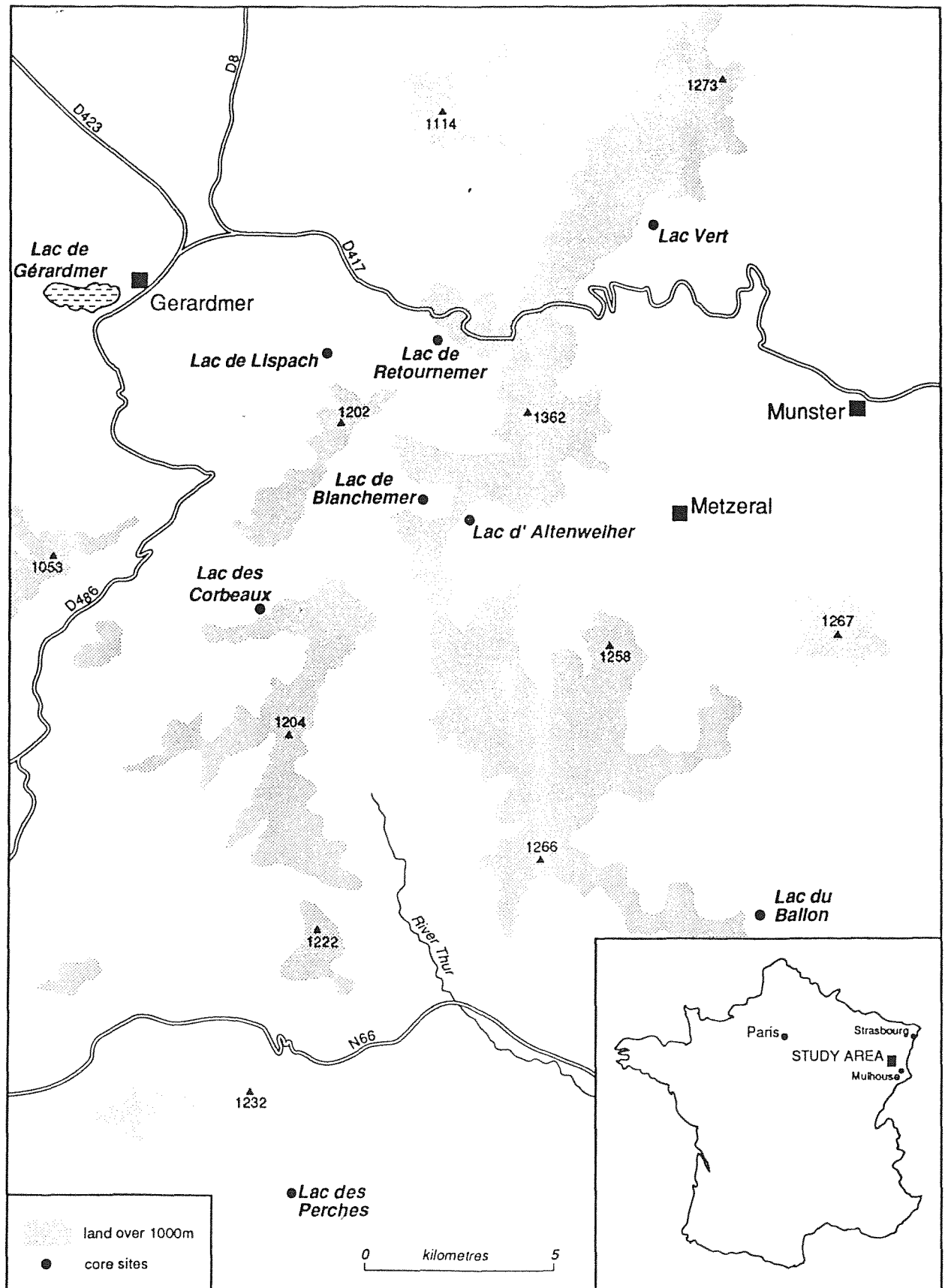
3.   METHODS

A brief introduction to the techniques used is given below. Further information may be found in Stevenson *et al.* 1987, Rose 1990 and Stevenson *et al.* 1991.

Bathymetric survey

A detailed bathymetric survey was only undertaken at Lac des Corbeaux. Water depth was measured from a boat following transect lines, using an echo sounder with a chart recorder. The locations of the measured depths were recorded by shore-based survey stations. These locations were then transferred to large scale maps and digitised using MAPICS computer mapping software to produce contour maps of the lake basin. From this the volume and mean depth of the lake was calculated.

Sediment coring

Cores are generally taken from the deepest part of the lake where the sediment record is usually the longest. In this study, cores were taken using either a Kajak gravity corer, a mini-Mackereth corer, a wide diameter piston corer, or a Livingstone corer. Where several cores were taken from the same site, the core with the least disturbed surface was used as the master core for analysis. The cores were usually sliced into 0.5 or 1.0 cm slices, dried at 30°C and stored dry until required. Alternatively, the cores were stored wet, either as whole cores or as sub-samples, at 4°C.

Routine sediment analysis

The wet density, percentage dry mass (weight loss at 105°C) and percentage loss on ignition (LOI) (at 550°C) of each sample or slice was determined following extrusion but prior to being dried. This gives an indication of the proportions of mineral and organic material in the sample.

Radiometric dating

A full explanation of the use of ^{210}Pb for dating lake sediments can be found in Appleby & Oldfield (1978) and Appleby *et al.* (1986). Briefly, a chronology extending back 150 years can be constructed by measuring the down-core decline in the activity of the naturally occurring radio-isotope ^{210}Pb, which has a half life of 22.26 years. The measurement of ^{226}Ra allows the amount of ^{210}Pb generated within the sediment itself to be removed from the calculation, leaving only the excess or 'unsupported' ^{210}Pb to be used to construct a chronology.

The occurrences of the man-made isotopes ^{137}Cs, ^{134}Cs and ^{241}Am can be used as additional dating points in recent sediments. ^{137}Cs and ^{241}Am were introduced into the atmosphere from 1954 onwards as a consequence of atmospheric nuclear testing. These inputs increased steadily until 1963 when a ban on atmospheric nuclear testing caused a sharp decline in the fallout of these isotopes. This maximum serves as a marker for 1963 in sediments. However, caesium can diffuse through the sediments in certain soft water lakes resulting in some lakes preserving a clearer record of this event than others. The Chernobyl accident in 1986 resulted

in the release of ^{137}Cs and ^{134}Cs and their presence in the uppermost sediments of a core provide useful evidence for an intact core top.

Carbonaceous particles

Spheroidal carbonaceous particles are generated as a result of high temperature fossil-fuel combustion. They vary in size from 200 microns to less than 1 micron. When emitted to the atmosphere they are dispersed over a wide area and consequently are deposited in lakes. These particles are resistant to chemical attack and can therefore be isolated in sediment and quantified by using chemical methods to remove other unwanted fractions of the sediment (Rose 1990). Carbonaceous particle analysis of lake sediments can therefore indicate the extent to which a lake has been exposed to atmospheric pollution from fossil-fuel sources. The trends in carbonaceous particle concentration down a core can also be used to approximately date a core in the absence of ^{210}Pb data (Renberg & Wik 1984).

In this study at least ten levels were analysed from each core to enable some approximate dates to be allocated to sediment levels in the absence of ^{210}Pb data.

Diatom analysis and environmental reconstruction

Diatoms are siliceous, single-celled algae which inhabit a wide range of aquatic habitats. In lakes they may be found growing either as plankton or as phytobenthos, attached to stones, sand and plants around the margins of the lake. After death they accumulate in the sediment and although the cell contents decompose through time, the basic silica structure, by which one taxon can be identified from the next, remains unaltered. In order to identify diatoms under a light microscope, the sediment is treated with hydrogen peroxide (H_2O_2) to remove the organic, non-siliceous fractions. The diatoms are then concentrated and mounted in a high refractive index medium on a glass slide. A known number of microscopic markers can be added to a known weight of sediment to determine the concentration of the diatoms, enabling 'absolute' numbers of the different taxa to be recorded, in addition to expressing each taxon as a proportion of the rest.

Diatoms are particularly sensitive to the chemical environment in which they live. Consequently their preservation in sediments allows past chemical environments to be reconstructed provided the sediment can be dated and the relationship between the environmental variable and each commonly occurring diatom taxon can be defined. This is achieved by collecting a data-set of recent water chemistry and surface sediment diatom assemblages from a wide range of lakes. The response of the diatoms to lake chemistry can then be modelled by regression and this model applied to preserved diatom assemblages in sediments to infer lake chemistry in the past. This type of reconstruction has been usually applied to water pH and associated variables (TOC, aluminium), and more recently to nutrients (eg. Anderson 1992, Anderson *et al.* 1992, Fritz *et al.* 1992, Hall & Smol in prep.). In the acidification component of this report, the modern diatom/lake water chemistry data-set collected for the Surface Water Acidification Programme (SWAP) (Battarbee *et al.* 1990) has been used to interpret the diatom data from lakes. In order to quantify the diatom response to nutrient input in Lac de Gérardmer, data from Scandinavian and Northern Irish sites were used. The Swedish component of this calibration data-set, in particular, is derived from lakes with very similar characteristics to Lac de Gérardmer (Anderson 1992). Diatom response to

lake chemistry in the data-set was defined using weighted averaging (WA) regression, which was then used to calibrate fossil assemblages (Stevenson *et al.* 1991).

Sediment chemistry

Chemical analysis of the sediment core from Lac de Gérardmer was carried out to determine the history of two sources of contamination: the contamination of the atmosphere above the lake by trace metals and changes in the phosphorus content of the water column. The approach used is as follows. Firstly, the concentration-depth profiles of the major cations in the sediment (magnesium, sodium, potassium and calcium) are examined to determine if there have been changes in the nature of the sedimentary material over the time-span covered by the core. These chemical properties, along with sediment dry mass (which is mainly determined by particle size) and organic material (as measured by LOI), define the basic sediment composition. Changes to the sediment composition caused by soil erosion, land-use changes and variations in climate, alter the composition of the material derived from the catchment which eventually form the bulk of the sediment. It must be established if there have been any changes in sediment composition because there can also be associated changes in trace metal and phosphorus concentrations. Only then can we make a correct interpretation of the trace metal and phosphorus profiles. These are then examined to establish if there have been any changes (usually increases) in concentration which might indicate contamination. Trace metal contamination, especially in rural or remote lakes, is usually due to deposition from the atmosphere, whereas increased phosphorus input is usually from waste-water.

4.   THE PALAEOLIMNOLOGY OF LAC DE GÉRARDMER, WITH REFERENCE TO THE RECENT HISTORY OF NUTRIENT INPUT TO THE LAKE.

Introduction

Lac de Gérardmer is a large lake 2 km long and 750 m wide situated beside the town of Gérardmer (see Figure 2.1). It has a single basin, as shown by the bathymetry in Figure 4.1 (Delebeque 1898). The lake is known to be thermally stratified in summer and inversely stratified in winter under ice cover. Other physical characteristics are listed in Table 4.1.

The catchment consists predominantly of granitic bedrock yielding waters with a pH below 7.0. There is little water chemistry data extant for this lake, that which is available is summarised in Table 4.2. Vegetation cover is predominantly coniferous forest. The catchment is generally sparsely populated although it does include part of the town of Gérardmer. In summer the human population is greatly increased by the occupation of second homes and camp-sites around the lake shore.

During the 1970s there was growing concern over nutrient inputs from the increasing summer population to the lake and the effect this was having on water quality and biota. A survey was undertaken to calculate a budget for these nutrients and it was found that the lake was receiving 'excess' loadings of nitrogen and phosphorus, as defined by Vollenweider (1975) and that phosphorus was the nutrient limiting biomass production (C.T.G.R.E.F. 1977). This nutrient enrichment had the effect of greatly increasing algal production during the summer with serious consequences for the use of the lake for fishing (the salmonid fish population being largely replaced by perch and roach), recreation and water supply. The detrimental effects of high algal populations were compounded by the effects of the decomposition of this increasing supply of organic matter in late summer and autumn resulting in the deoxygenation of the hypolimnion, as illustrated in the water and sediment sampling programme undertaken in 1976 (C.T.G.R.E.F. 1977). This deoxygenation was considered a threat to the remaining fish stocks. As a result, measures have been taken to reduce the input of nutrients to the lake including the installation of a drainage network around the lake to divert discharges from the campsites. In view of the relatively short residence time of the lake water it was hoped that effects of these measures should already be apparent and detectable in the sediment record.

Table 4.1.   Lac de Gérardmer: site characteristics (from C.T.G.R.E.F. 1977)

Lake altitude (m)	660.0
Catchment area (ha) (excluding lake)	1239.0
Catchment relief (m)	410.0
Maximum depth (m)	36.2
Mean depth (m)	16.9
Lake area (ha)	115.5
Lake volume (m^3 x 10^6)	19.5
Residence time (months)	16.0

Table 4.2.   Lac de Gérardmer: water chemistry data

	July 1989[1]	April 1992[2]
pH	7.25	6.73
Conductivity (μS cm^{-1})	70.3	77.0
Alkalinity (μeq l^{-1})	89.0	88.0
Na$^+$ (μeq l^{-1})	387.0	399.0
K$^+$ (μeq l^{-1})	21.0	20.0
Mg^{++} (μeq l^{-1})	62.0	58.0
Ca^{++} (μeq l^{-1})	180.0	189.0
Cl$^-$ (μeq l^{-1})	384.0	498.0
NO$_3^-$ (μeq l^{-1})	19.0	23.0
SO$_4^-$ (μeq l^{-1})	128.0	139.0
Total Phosphorus (μg l^{-1})	< detection limit	12.0

[1] analyses by CNRS Centre de Sedimentologie et de Geochimie, Strasbourg

[2] analyses by Freshwater Laboratory, Scottish Office Agriculture and Fisheries Department, Pitlochry, Scotland

Sediment stratigraphy

Two cores, each about 90 cm long, were taken in July 1989, in 20 m of water on the broad shelf to the east side of the lake basin (Figure 4.1). The core with the better preserved sediment surface/water interface, GERA1, was chosen for analysis and extruded in the laboratory. The top 20 cm were sliced at 0.5 cm intervals and the remainder of the core at 1 cm intervals. Changes in the core were noted as follows:

0-3 cm	dark brown organic sediment with traces of fine sand.
3-6 cm	dark brown organic sediment with approximately 25% diatoms and a trace of fine sand.
6-13 cm	very dark brown organic sediment with approximately 25% diatoms and traces of fine sand and silt.
13-30 cm	mid-brown organic sediment with approximately 25% diatoms and some silt.
30-40 cm	gradual transition to a lighter coloured mid-brown sediment with approximately 25% diatoms and traces of silt.
40-90 cm	mid-brown organic sediment with 50% organic detritus, (base) 50% diatoms.

The wet density, percentage dry mass and LOI values are shown in Figure 4.2. There are no major changes in these profiles although the slight increase in percentage dry mass in the top 20 cm accompanies the presence of silt and fine sand.

Radiometric dating

The chronology derived from the ^{210}Pb data is shown in Table 4.3 below. There are only small divergences between the CRS and CIC dating models and both models indicate a more or less constant sediment accumulation rate over the past 130 years of about 0.0217 g cm^{-2} yr^{-1}. The chronology given in Table 4.3 and Figure 4.3 is based on the CRS model.

The ^{137}Cs results (Table 4.4) show a maximum activity in the topmost sediments of the core. The ^{134}Cs data show that the greater part of this activity can be attributed to Chernobyl fallout. Using the ^{134}Cs data, the total ^{137}Cs activity can be partitioned into a Chernobyl component, and the component deriving from other sources such as atmospheric nuclear weapons testing. The weapons testing component has a well defined peak at about 4.75 cm. It would appear that this feature is a record of the 1963 fallout maximum and the good agreement between this date and the ^{210}Pb dates is shown on Figure 4.3.

The ^{241}Am record (Table 4.4) is less distinct, with peaks at 5.25 cm and 3.25 cm, dated 1957 and 1971 respectively. This may be a function of the difficulty of measuring ^{241}Am in this core; the relatively high ^{238}U activities giving rise to large adjacent ^{234}Th gamma peaks. The results do however give general support to the conclusion from the ^{210}Pb and ^{137}Cs data of a mid-1960s date for sediments at around 4.5 cm depth.

Table 4.3   Lac de Gérardmer: ^{210}Pb Chronology with sediment accumulation rates.

Depth (cm)	Date	+/- (yrs)	g cm^{-2} yr^{-1}	cm yr^{-1}	+/- (%)
0.0	1989				
0.5	1987	1	0.0272	0.23	7.4
1.0	1985	1	0.0257	0.208	7.1
1.5	1982	2	0.0242	0.187	6.8
2.0	1980	2	0.0236	0.174	6.8
2.5	1976	2	0.0238	0.169	7.1
3.0	1973	2	0.0241	0.164	7.4
3.5	1970	2	0.0234	0.154	7.9
4.0	1967	2	0.0219	0.0139	8.7
4.5	1963	3	0.0213	0.130	9.6
5.0	1959	3	0.0216	0.127	10.6
5.5	1955	4	0.0208	0.120	11.8
6.0	1950	4	0.0188	0.109	13.1
6.5	1945	5	0.0168	0.097	14.4
7.0	1941	5	0.0161	0.093	16.6
7.5	1937	6	0.0167	0.097	19.5
8.0	1933	6	0.0186	0.109	22.5
8.5	1929	8	0.0186	0.109	15
9.0	1925	8	0.0186	0.109	15
9.5	1921	10	0.0186	0.109	15
10.0	1917	11	0.0186	0.109	15
10.5	1913	11	0.0186	0.109	15
11.0	1909	12	0.0186	0.109	15
11.5	1905	13	0.0186	0.109	15
12.0	1901	13	0.0186	0.109	15
12.5	1897	14	0.0186	0.109	15
13.0	1893	14	0.0186	0.109	15
13.5	1889	15	0.0186	0.109	15
14.0	1885	16	0.0186	0.109	15
14.5	1882	16	0.0186	0.109	15
15.0	1878	17	0.0186	0.109	15
15.5	1874	17	0.0186	0.109	15

Table 4.4 Lac de Gérardmer: ^{137}Cs, ^{134}Cs and ^{241}Am data

Depth (cm)	^{137}Cs pCi g^{-1}	^{134}Cs pCi g^{-1}	^{241}Am pCi g^{-1}
0.25	16.01	8.15	0.0
1.75	13.04	8.16	0.0
3.25	7.27	2.44	0.16
4.25	5.24	0.0	0.06
5.25	5.42	0.0	0.11
6.75	2.66	0.0	0.0
7.75	2.05	0.0	0.0
8.75	1.38	0.0	0.0
11.75	0.89	0.0	0.0
13.25	0.80	0.0	0.0
16.25	0.29	0.0	0.0
20.5	0.22	0.0	0.0
24.5	0.0	0.0	0.0

Carbonaceous particle analysis

This core shows much higher concentrations of particles (Figure 4.4) than in any other core analysed from the region (cf. Section 5). This may be due to physical differences between the lakes, (residence time for example), rather than differences in atmospheric inputs. The Lac de Gérardmer core shows a decrease in particle concentration at the surface with the peak occurring at about 1983. This is later than any dates attributed to peaks in dated cores from the United Kingdom, although the date of this peak varies regionally (Rose 1991). Because this is the only ^{210}Pb dated sediment core from this region of France that shows a surface decline, allocated dates from carbonaceous particle evidence should be treated with caution until further dating from other sites is available. Similar to the Lac des Corbeaux core (see Section 5a), the Lac de Gérardmer core shows a sharp increase in concentration in the 1940s and an early start to the profile (c. 1800). During analysis, amorphous carbonaceous material was noted between 6 cm and 13 cm (the first half of this century). It is possible this is contamination from domestic fires.

Diatom analysis

Full diatom analysis, with counts of 400-500 valves per sample, has been carried out on all samples in the top 6.5 cm of the core and on samples at 7 cm, 8 cm, 10 cm, 12 cm, 14 cm, 16 cm, 18 cm, 20 cm, 40 cm, 60 cm and 80 cm depths. Additionally, pH and total phosphorus (TP) were reconstructed on all samples and diatom concentrations were determined for samples in the top 20 cm.

Diatom assemblages

A diagram showing the percentage proportions of all taxa greater than 1% and their distribution down the core, is shown in Figure 4.5. By far the most abundant diatom at this site is *Aulacoseira subarctica* Type 2. This taxon is clearly separate from *Aulacoseira subarctica* and has been identified in other regions, for example in Northern Sweden (Anderson & Korsman 1990) where it is commonly found in waters with a high dissolved organic carbon content (Stevenson *et al.* 1991). Its presence here is not surprising since Lac de Gérardmer was known as a 'yellow' (ie. humic) lake prior to its eutrophication. This planktonic diatom constitutes up to 80% of the assemblages below 20 cm (pre-nineteenth century) with the remainder comprising other generally planktonic taxa such as *Asterionella formosa* and *Aulacoseira distans* var. *laevissima*. Above this level benthic taxa such as *Achnanthes minutissima* and other *Achnanthes* taxa become more common, although *A. subarctica* Type 2 remains dominant.

The most significant floristic change in the core is the increase in *Cyclotella stelligera* in the mid - late nineteenth century (above 14 cm). The proportion of *C. stelligera* reaches a peak in the late 1950s (5-5.5 cm depth). After this *Asterionella formosa* increases. *Fragilaria* species such as *F. construens* var. *venter* and *F. virescens* var. *exigua* are also significant in the top 10 cm of the core.

Diatom concentrations

The changes in the dominant species in the top 20 cm of the core can also be expressed as concentrations of cells per gram dry mass of sediment (Figure 4.6). From the concentration data it can be seen that the decline in *A. subarctica* Type 2 is 'real' and not simply the proportional effect of an increasing population of *C. stelligera*. It is also interesting to note that the peak in *Asterionella* percentages and concentrations at 4.5-5 cm is accompanied by a decline in most of the common taxa and also a decline in the total flux of diatoms to the sediment.

pH reconstruction

The reconstructed pH for the core is shown in Figure 4.5. The reconstructed pH fluctuates between 6.8 and 7 with all samples below 20 cm depth reconstructing at pH 7. The reconstructed pH of the surface sediment compares well with the measured pH (Table 4.2).

Phosphorus reconstruction

The pre-enrichment 'baseline' TP concentration between 60-40 cm is 4.7 μg l^{-1} and there is a small increase in reconstructed TP to 6.2 μg l^{-1} at 21-20 cm which appears to be inversely related to the *Aulacoseira subarctica* Type 2 profile. The reconstructed TP above 20 cm is shown in Figure 4.7. In general the profile is stable at between 5.0-6.5 μg l^{-1}. There are two small peaks at 4.75 cm (6.9 μg l^{-1}) and 2.25 cm (8.2 μg l^{-1}) (1961 and 1978 respectively), caused by an increase of *Asterionella formosa* at these levels. Above 2.25 cm TP concentrations decrease and stabilise to a value of c. 7 μg l^{-1} at the sediment surface (1989). It is difficult to compare the diatom-inferred TP value from the surface sediment with

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contemporary water chemistry. Summer TP values in 1989 fell below the detection limit of the analytical laboratory (Table 4.2) and are unlikely to reflect lake chemistry at the time of maximum diatom growth in the spring. Similarly, the value of 12 μg l^{-1} recorded by more stringent analysis in April 1992, can not be considered representative of mean chemistry and relates to conditions almost three years after the sediment core was taken. Despite these limitations the ability to reconstruct TP values in the <15 μg l^{-1} range, indicates that these techniques, previously applied to more enriched sites, are able to address problems of nutrient enrichment at the critical, low end, of the TP scale in lakes.

Sediment chemistry.

i. *Major cations*

The dry mass, LOI (Figure 4.2) and major cation concentration-depth profiles (Figure 4.8) show that there have been small changes in sediment composition over the length of the Gérardmer core. These features broadly relate to changes in sediment stratigraphy. Above 30 cm, where some silt appears in the sediment, LOI drops, while above 20 cm, where some fine sand is found, the dry mass increases. This implies a slight coarsening of the sediment and is consistent with the appearance of sand and silt. In the top 3 cm of sediment the LOI increases and the dry mass drops greatly, reflecting an increase in the water content of the surface sediment.

The variation in major cation concentrations correlate with changes in percentage dry mass (Figure 4.9). The profiles are unchanged even when the concentrations are corrected for changes in organic content. Magnesium and sodium concentrations are positively correlated with dry mass, except above 4.5 cm where the dry mass drops because of lack of sediment compaction. Potassium is positively correlated with dry mass with a break point above 27 cm. This is approximately the depth where some silt appears in the sediment. It may be that the silt is partly composed of a silicate mineral which has a higher potassium content. The calcium-dry mass relationship shows a break point at 12 cm, which is a little above where the fine sand appears. Again it may be that the fine sand has a component with a slightly higher calcium concentration. Another feature of the calcium profile is the peak in concentration between 28 cm and 31 cm. This appears to be a real feature, rather than a rogue result, as there are two samples with elevated concentrations.

Overall, the major cation data indicate there are changes in the sediment composition which may relate to a general increase in erosion from the catchment. These changes are most evident above 30 cm depth where some silt appears in the sediment, but compared with many upland lakes studied in Britain and Ireland, these changes are not large.

ii. *Trace metals*

The lead, zinc, copper and nickel metal concentration-depth profiles (Figure 4.10) show that the changes in sediment composition have little effect on the trace metal concentrations. The lead and nickel concentrations rise slightly above 30 cm depth, but the main increases are above 15 cm (1880) for lead and 13.5 cm (1890) for the other metals. The trace metal concentrations have constant background values of c. 36 μg Pb g^{-1}, c. 45 μg Zn g^{-1}, c. 8 μg Cu g^{-1} and c. 13 μg Ni g^{-1} below 15 cm but they rise strongly above this depth. The increase

is ten times or more for lead, zinc and copper. As the sediment accumulation rate is fairly constant over the dated part of the core, the trace metal flux-depth profiles show similar trends to the concentration-depth profiles. The very high zinc concentration at 0.5 cm is a surface effect and does not indicate a recent large input of zinc to the lake.

The increase in lead, zinc and copper concentrations during the nineteenth century is found in many lakes in northern and western Britain and Ireland and is due to deposition of trace metals from a polluted atmosphere. In the Lac de Gérardmer additional inputs may originate from catchment sources. It is difficult to compare the degree of trace metal contamination between lakes when only one core is available from each site, but we have used the relationship between trace metal contamination and dry sediment burdens since 1900 for comparison. The trace metal burden in Lac de Gérardmer was computed from the excess of the measured concentration above the background values since 1900 (12 cm), while the dry sediment burden was calculated from the dry mass and density values over the same period.

Figure 4.11 shows the position of Lac de Gérardmer in relation to data from a range of lakes in Wales. There will always be considerable scatter in a diagram constructed in this way, but the results indicate that there is no great difference in the amount of lead and zinc contamination from the atmosphere in the two areas. The greater scatter in the zinc diagram is because the amount of zinc retained in the sediment of these Welsh lakes drops as the lake pH falls. Many of the Welsh lakes have been acidified by deposition from the atmosphere.

iii.   *Phosphorus*

Iron and Manganese were determined because these elements are frequently associated with the sediment-water interactions of phosphorus in lakes, especially in lakes which stratify and become deoxygenated. During prolonged deoxygenation of the hypolimnion, the sedimentary manganese and iron concentrations drop as these elements are released into the water column. Some of this iron and manganese would then be lost via the outflow during the autumn overturn, whilst the remainder is re-precipitated to the sediment. The iron and manganese profiles in this core show no evidence of this process (Figure 4.12) although seasonal deoxygenation may still have occurred if water loss via the outflow was reduced in summer. The small changes in iron and manganese are similar to those of magnesium and sodium and are probably related to changes in sediment composition. The strong increase in concentration of both metals above 4.5 cm is due to enrichment in the oxidised zone of the sediment.

The phosphorus concentrations do change slightly throughout the core (the decline in concentration between 25 cm and 15 cm for example) but most of this is probably a response to changes in sediment composition (Figure 12). Generally the phosphorus concentrations are higher than in many other lakes (concentrations are usually less than 1 mg g^{-1}) and this may be due to high natural concentrations in rocks in the catchment. Thus a change in phosphorus concentration above 30 cm depth accompanying changes in sediment composition is not unexpected. The layer of higher phosphorus concentration between 1.5 cm and 2.5 cm depth may correspond to the period of increased enrichment of the lake around 1976, although this increase is no greater in magnitude than fluctuations in concentration seen further down the core, for example between 23 cm and 25 cm. Diagenesis may produce high phosphorus concentrations at or just below the sediment surface but the peak in concentration at 1.5 cm to 2.5 cm below the surface is unlikely to be a diagenetic effect. The slight increase in

sediment accumulation rate and organic content above 3.5 cm is to be expected if the lake has become more eutrophic; the increased phytoplankton production leading to an increasing concentration of organic material in the sediment and thus an increased sediment accumulation rate.

In the top 1.5 cm of the core the phosphorus profile decreases while the iron and manganese profiles increase in the oxidised sediment zone. This seems to represent a decreased flux of phosphorus to the sediment. If phosphorus input to the sediment had remained unchanged over this period, it would be seen to increase with the iron and manganese.

Discussion

i.   *The pre-1850 status of the lake*

The lithostratigraphy of the core suggests there has been little fluctuation in sediment source below 30 cm. Between 30 cm and 20 cm there seems to have been a slight change in sediment type which is indicated most clearly by changes in the major cation and phosphorus sediment chemistry profiles. However, these changes are not great when compared to sediment composition changes seen in some lakes in the United Kingdom. (Battarbee *et al.* 1988).

The consistency in the diatom flora below 40 cm appears to represent the lake in its stable pre-enrichment state, with a pH of about 7.0 and a reconstructed TP value of around 4.7 µg l^{-1}. The diatom flora is dominated by planktonic taxa with few diatoms from benthic communities (ie. rocks and larger aquatic plants near the shore). The lack of epiphytic diatoms suggests that aquatic macrophyte beds were not abundant around the lake. At some point between 40 cm and 20 cm there is a slight shift in the diatom assemblages where *A. formosa* and *Aulacoseira subarctica* Type 2 declines and *Achnanthes minutissima* increases. This occurs over the same period as the change in sediment composition and may represent a change in the substrate of the littoral habitat for benthic taxa.

ii.   *Evidence for post-1850 nutrient enrichment*

The ^{210}Pb chronology indicates that there is at least 120 years of uninterrupted sedimentation recorded in the core and this is supported by the carbonaceous particle record which also suggests that Lac de Gérardmer was receiving atmospheric contamination for most of the nineteenth century. The trace metal data also indicate increased atmospheric trace metal deposition from the late nineteenth century.

The sediment characteristics suggest there has been a slight change in sediment composition over the nineteenth and twentieth centuries with a small increase in mineral material above 20 cm depth in the core. This could be as a result of increasing human activity in the catchment, such as road building, farming and forestry, although the changes are not great.

The most significant change in the diatom flora, the increase in *Cyclotella stelligera*, occurs around the turn of the century. This floristic change coincides with a darkening of the sediment colour and is likely to be the initial diatom response to increasing nutrient input. It is followed a little later by increases in taxa associated with littoral habitats, such as the

Fragilaria species, suggesting the development of aquatic macrophyte beds around the lake. From the sedimentary phosphorus data it is not possible to link these changes with increased input of phosphorus to the sediment since the increasing concentrations of phosphorus seen from 1900 onwards may be due to changes in sediment source.

The increase in *Asterionella* between 1959 and 1963 is probably a response to increased nutrient input. In core studies at other sites, *Asterionella formosa* has been associated with increased nutrient loading (eg. Haworth 1984). Enrichment leads to an increase in diatom biovolume (not necessarily indicated in the flux of cells to the sediment) which in turn increases the demand for silica. *Asterionella* is able to compete for silica early in the growing season leaving less for the later *Cyclotella* population as the lake stratifies.

The higher levels of sedimentary phosphorus between 1.5 cm and 2.5 cm, supported to some extent by sediment accumulation rate and organic content data, could indicate that the supply of phosphorus to the lake increased in the mid-1970s. There are however, problems in interpreting the sedimentary phosphorus record. The total phosphorus content of the sediment contains phosphorus in all forms including particulates and does not necessarily reflect the past availability of phosphorus as a plant nutrient (eg. Engstrom & Wright 1984).

The diatom flora suggest the supply of phosphorus as a plant nutrient was not greatly increased since diatom taxa associated with advanced eutrophication, such as *Stephanodiscus* species, are absent. However, the reconstructed TP profile does show a small but significant increase over the past 30 years and there are indications of increased nutrient input to the lake around 1961 and 1978 with peaks of reconstructed TP of 6.9 and 8.2 μg l^{-1} respectively. Allowing for a possible error of two years in the chronology at this level (Table 4.3) it is probable that the latter peak reflects the elevated nutrient content of the water postulated in 1976 (C.T.G.R.E.F. 1977).

Together, the chemical and biological sediment records suggest that the eutrophication of the lake was not as advanced as the sampling programme carried out in 1976 suggested. Indeed as all reconstructed and measured TP values for the lake fall well below 25-40 μg l^{-1} (cf. Forsberg & Ryding 1980, Jones & Lee 1982, Vollenweider 1989) it is more appropriate to talk of 'enrichment' rather than 'eutrophication' at Lac de Gérardmer. The summer of 1976 was exceptionally warm, dry and sunny and it could be that the symptoms of advanced eutrophication (such as deoxygenation and manganese release from the sediments) were not typical of summer conditions in the lake over several years. However, seasonal deoxygenation is not always evident from the sedimentary manganese record. Additionally, the response of other algae commonly associated with eutrophication, such as blue-green species, has not been assessed (through the use of pigment analysis), in this core.

iii.   *Evidence for a recent decrease in nutrient input*

Because the sediments suggest only a small degree of enrichment, evidence for reversal of this trend is also likely to be small. The increase in *Cyclotella stelligera* above 1.5 cm (c. 1982) suggests a reversal in the previous trend of gradual nutrient enrichment. The slight increase in benthic taxa in the surface sediment could suggest an increase in the extent of littoral habitats possibly as a result of increased transparency of the water in summer, or as a result of restrictions on motor boat use on the lake. The sedimentary phosphorus data also

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suggest that phosphorus input to the lake has declined since 1982 and this may be a response to the measures taken to reduce the nutrient input to the lake following the report in 1977.

Lac de Gérardmer: conclusions

1) The core from Lac de Gérardmer contains at least 120 years of uninterrupted sediment record.

2) The pre-twentieth century diatom record suggests an oligotrophic lake with little variation in water quality.

3) The first indication of an increase in nutrient input to the lake is a change in the diatom flora around 1900.

4) Diatom changes in the early 1960s suggest a further increase in nutrient loading but at no stage has the lake become eutrophic.

5) The reconstruction of TP values from the diatom data indicate a shift in total phosphorus from c. 4 μg l^{-1} before 1900 to a maximum of 8.2 μg l^{-1} in the mid-1970s.

6) There is some evidence for a slight reversal in the enrichment trend since 1980.

Figure 4.1   Lac de Gérardmer: bathymetry

- ● Core location
- Contours in metres

0   metres   250
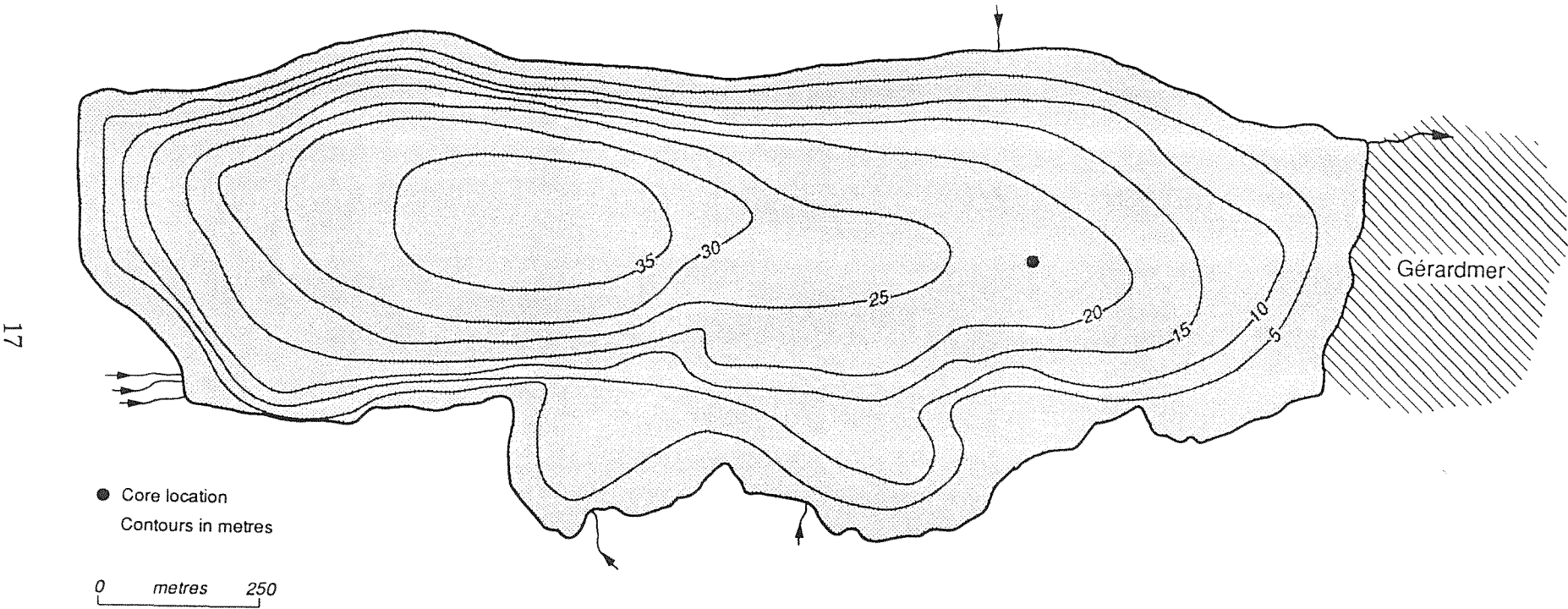
Figure 4.2   Lac de Gérardmer: sediment characteristics

Wet density · Dry weight · Loss on ignition
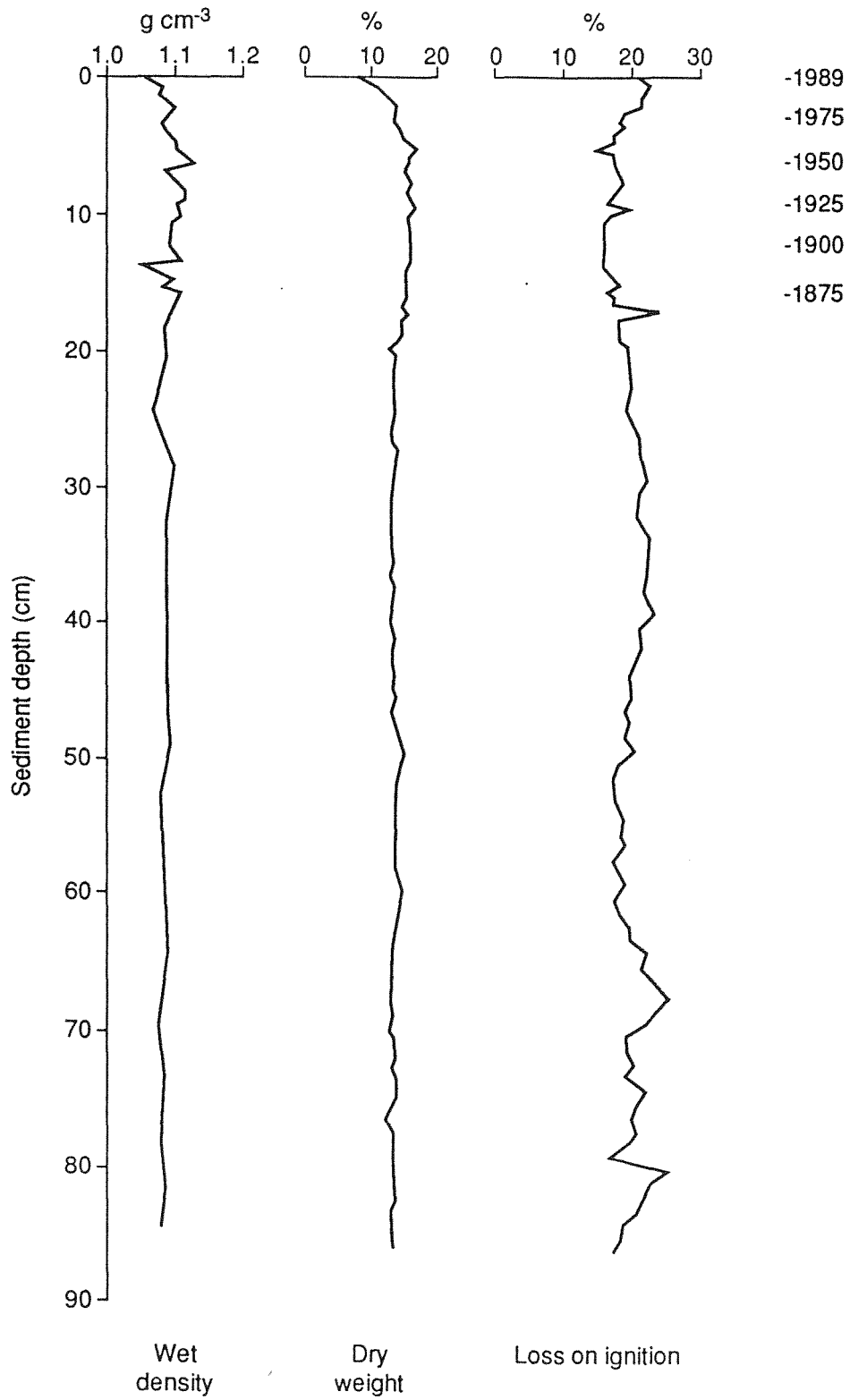
Figure 4.3   Lac de Gérardmer: ^{210}Pb chronology

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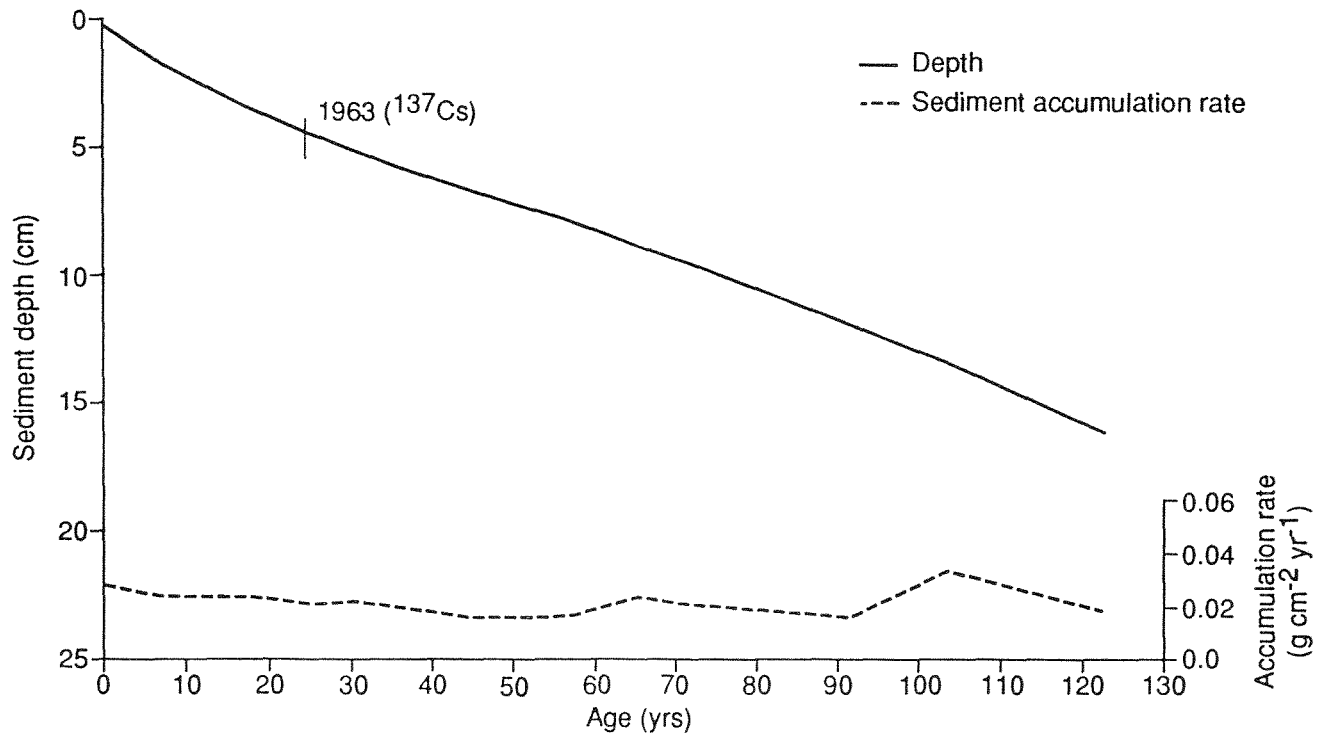
Figure 4.4   Lac de Gérardmer: carbonaceous particle concentrations plotted against
sediment depth
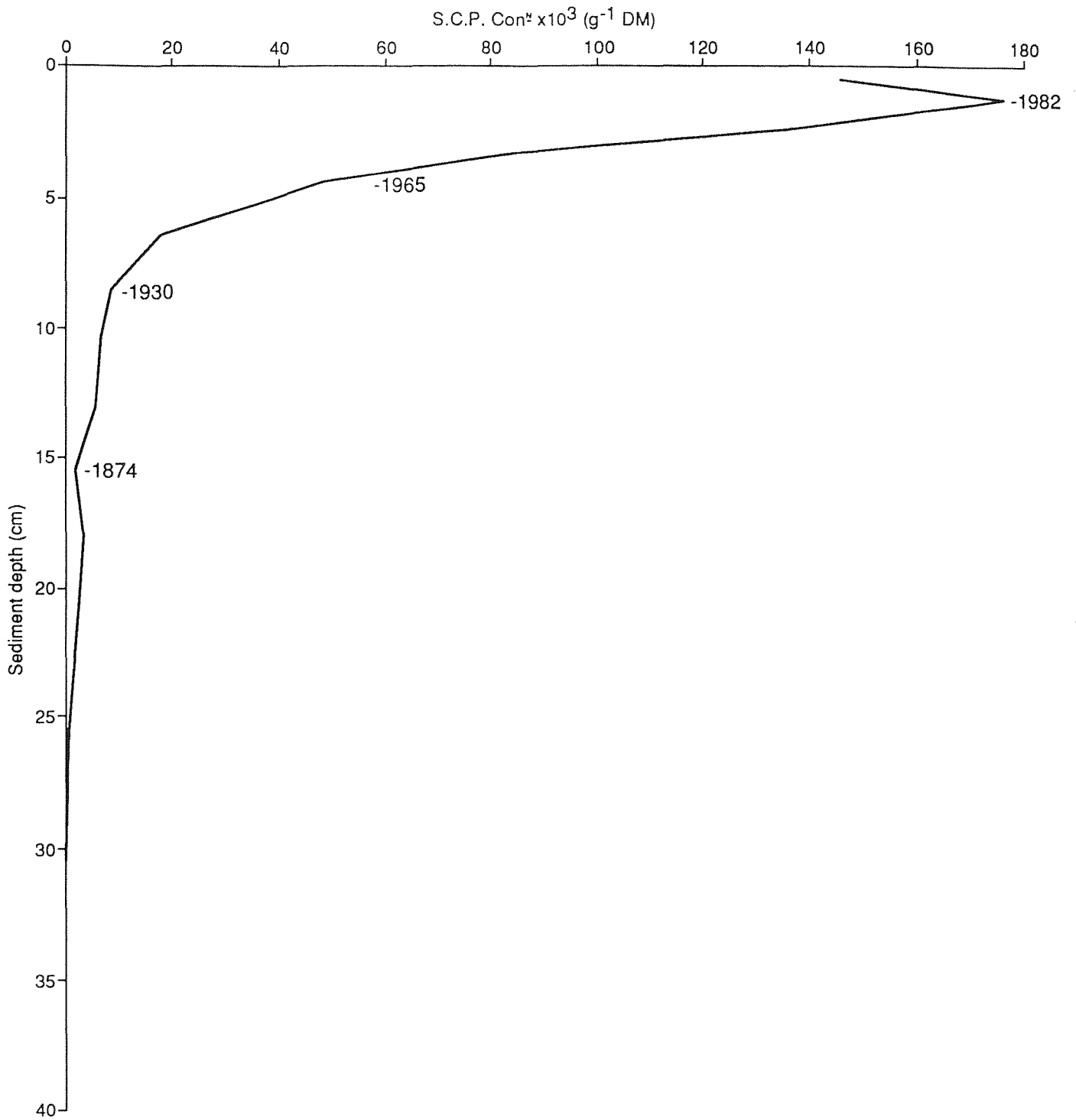
Figure 4.5 Lac de Gérardmer: summary diatom diagram and pH reconstruction plotted against sediment depth

Percentages of all taxa >1%
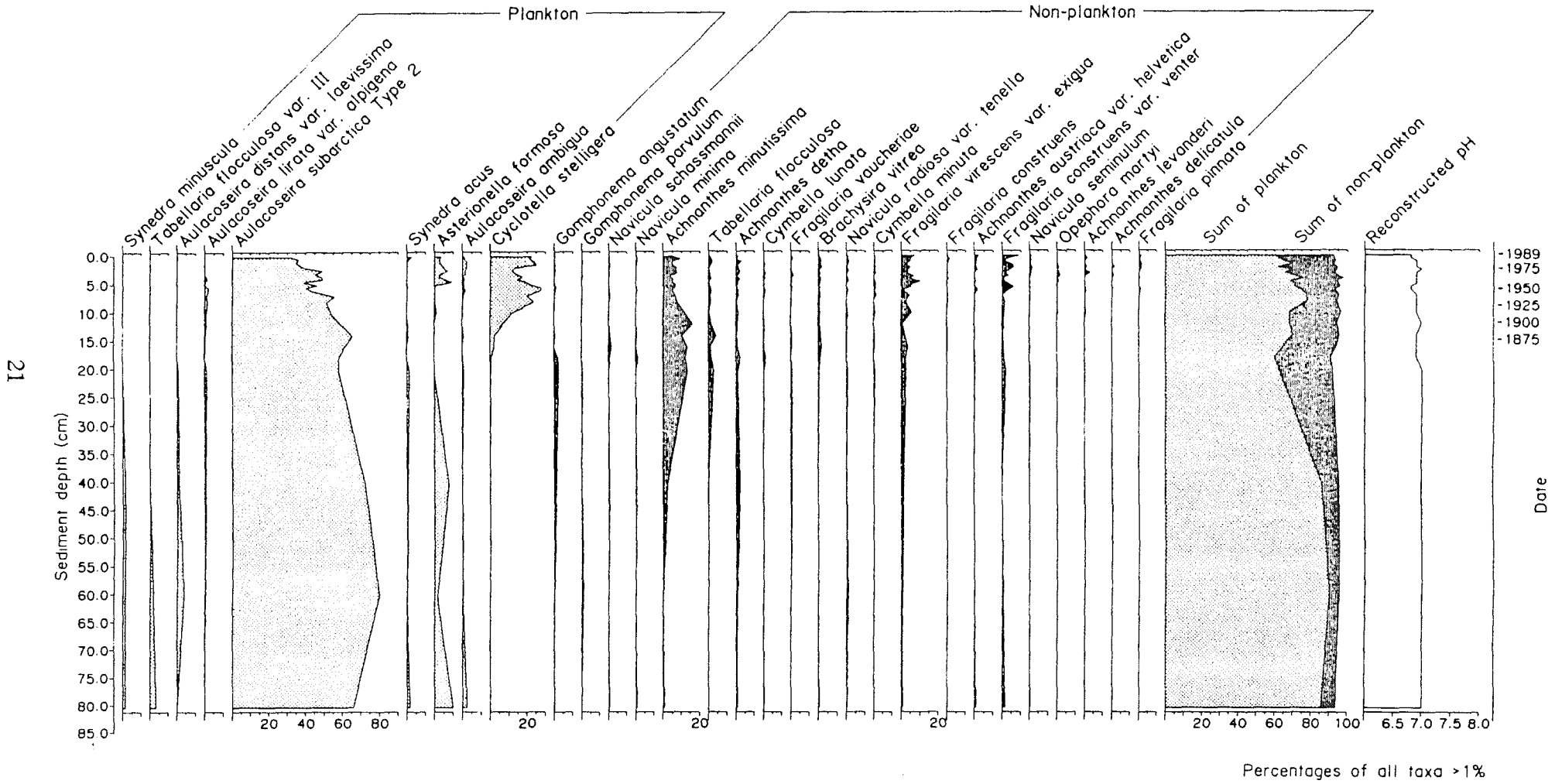
Figure 4.6   Lac de Gérardmer: percentage and concentration of major diatom taxa and diatom flux plotted against sediment depth
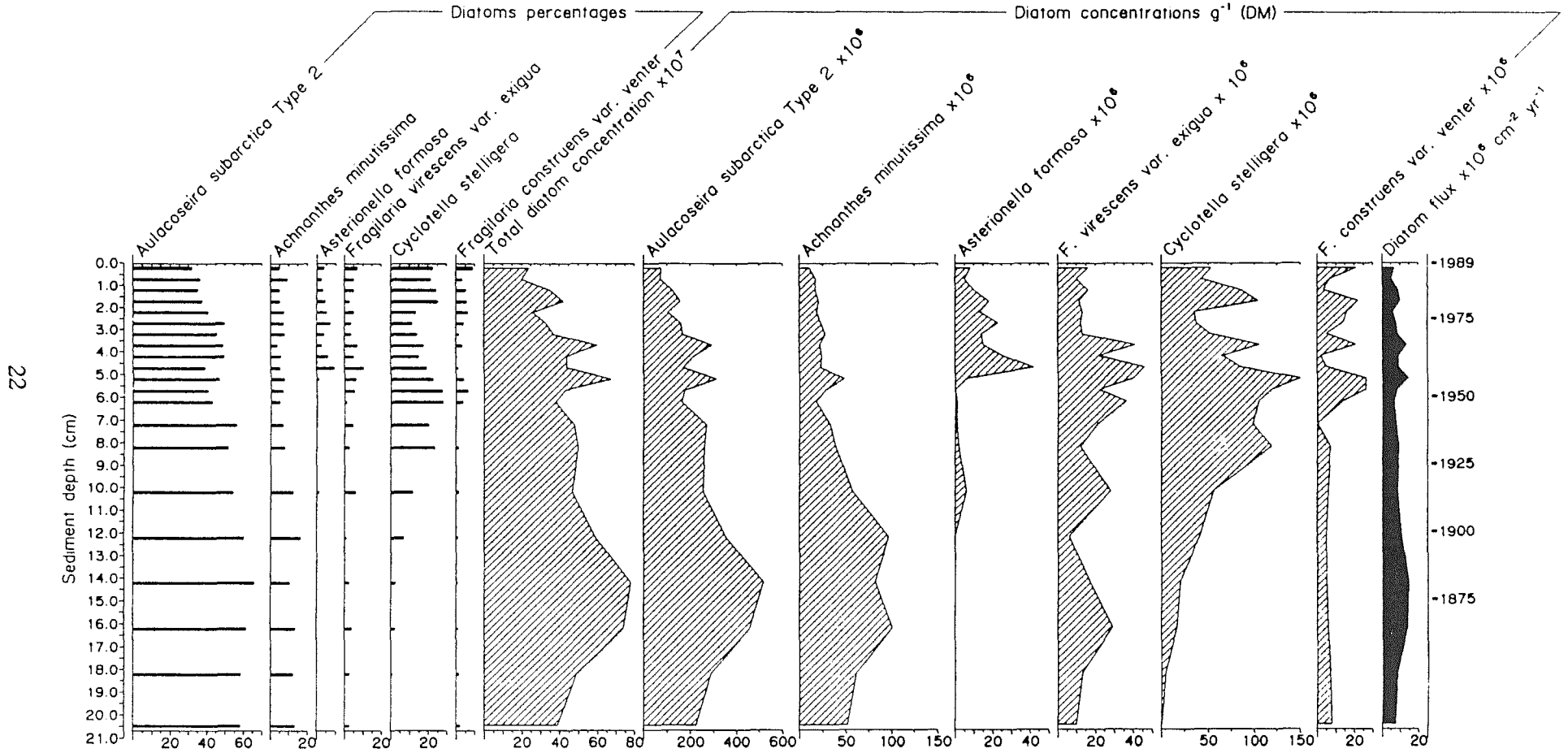
Figure 4.7   Lac de Gérardmer: phosphorus reconstruction

Diatom—inferred total phosphorus
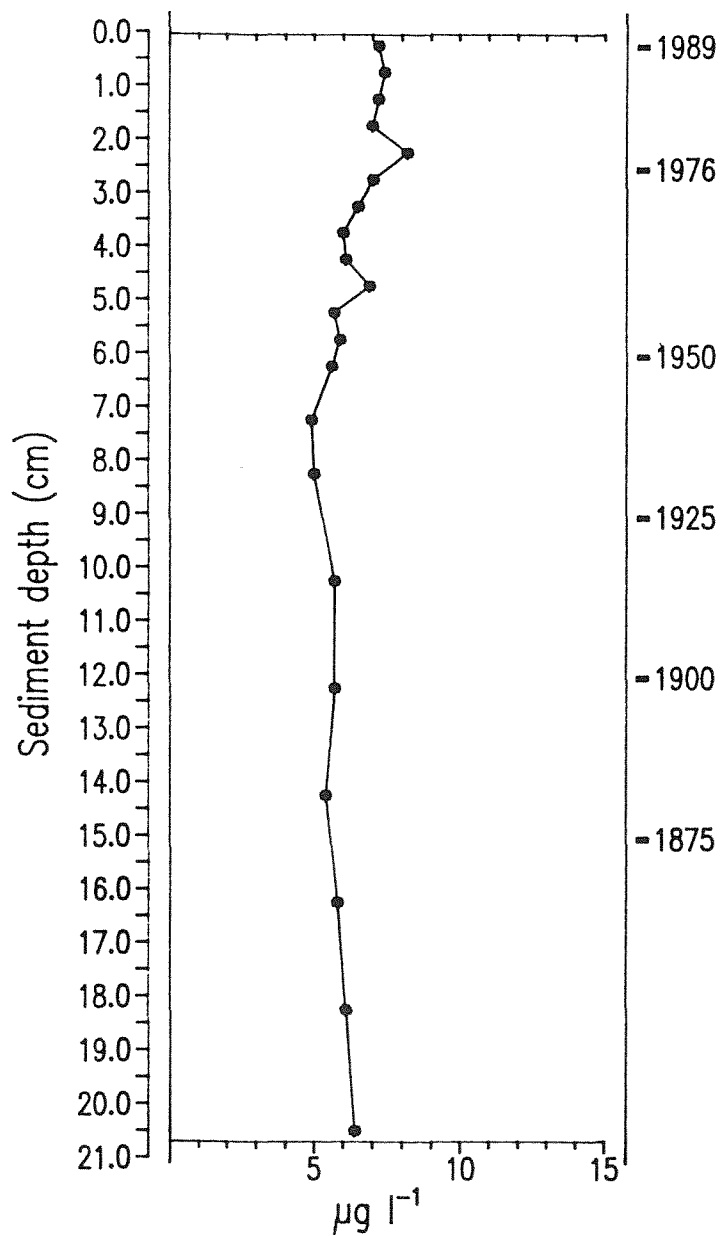
Figure 4.8   Lac de Gérardmer: major cations plotted against sediment depth
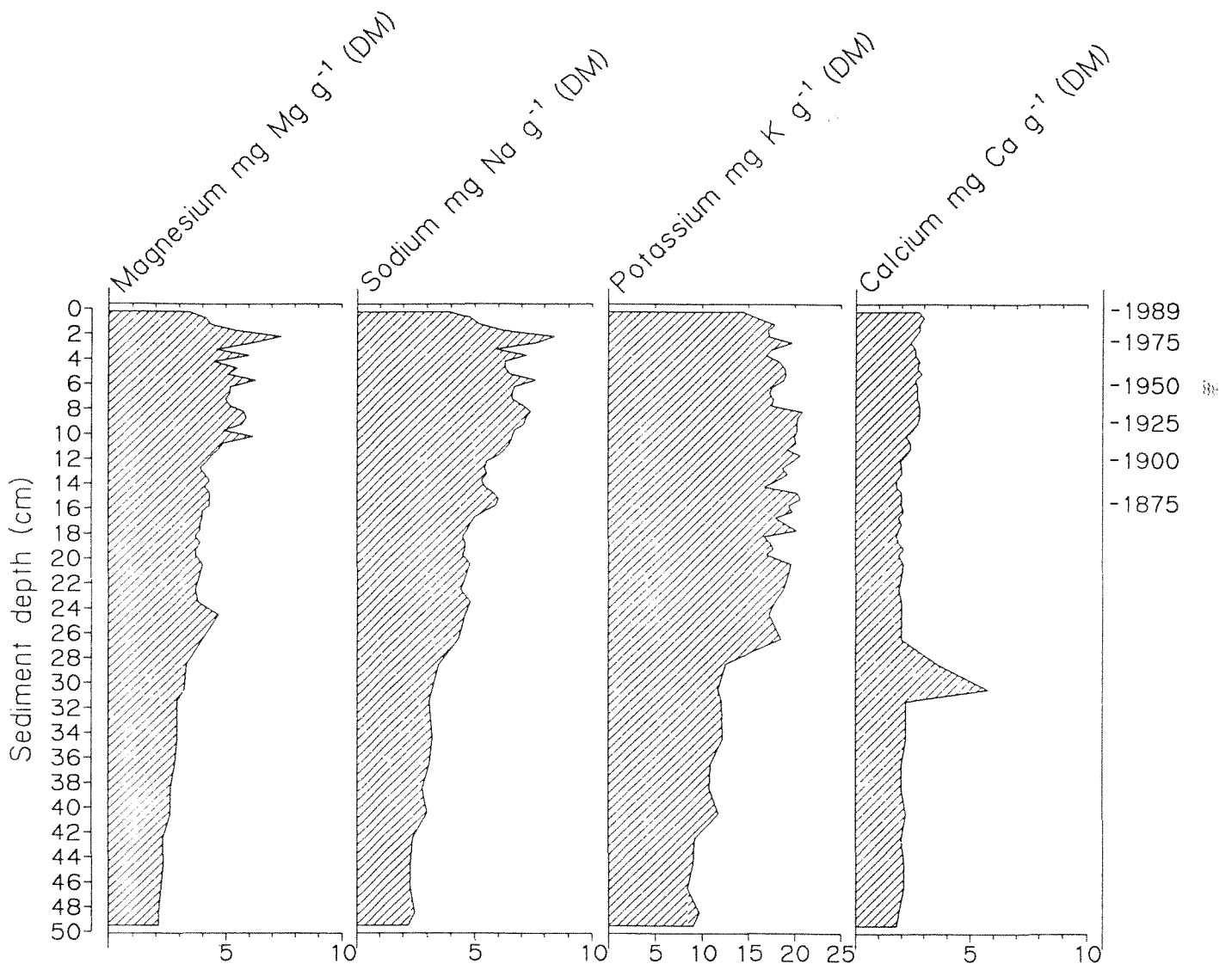
Figure 4.9 Lac de Gérardmer: major cations plotted against percentage dry mass
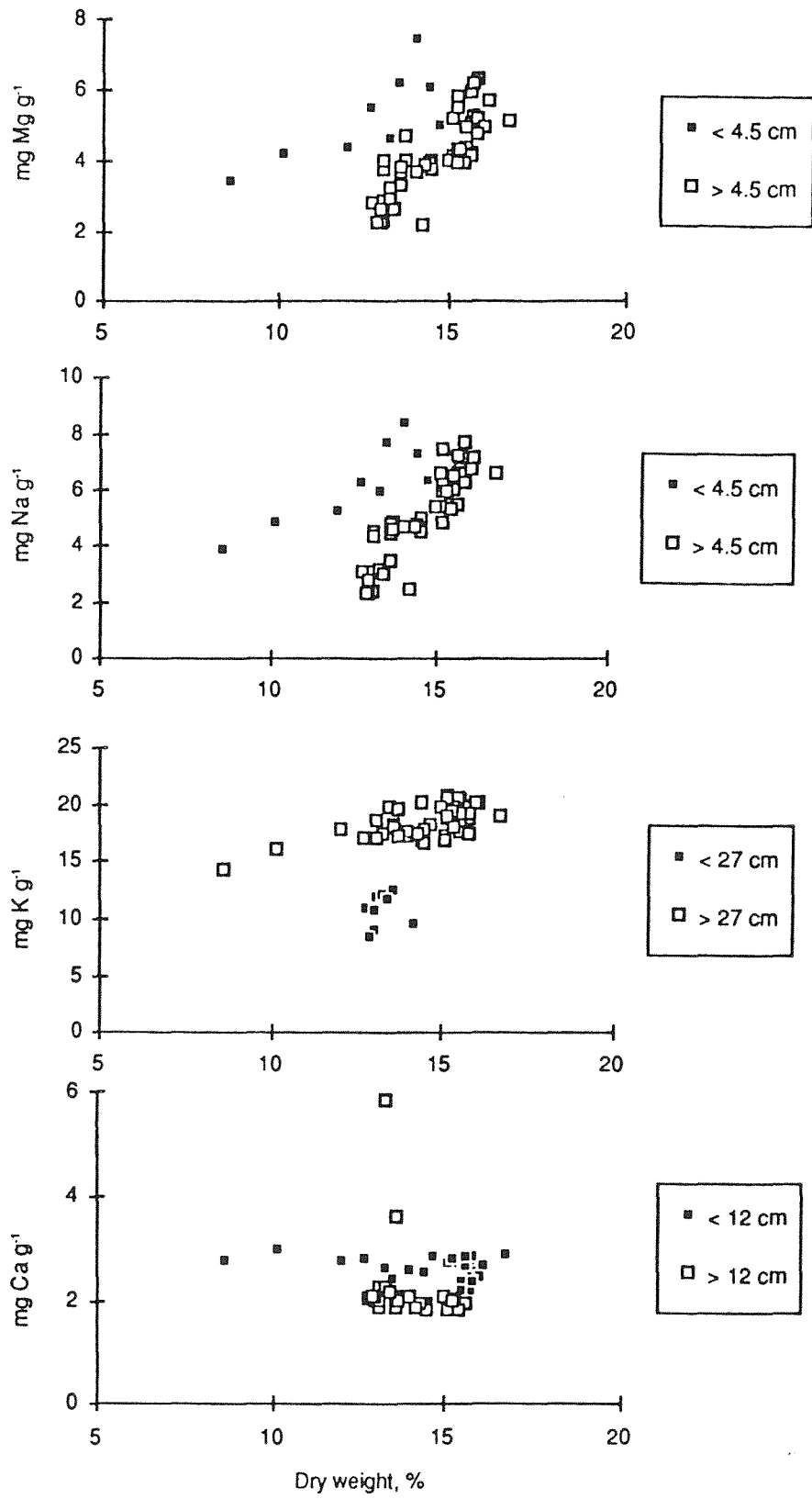
Figure 4.10   Lac de Gérardmer: trace metals plotted against sediment depth
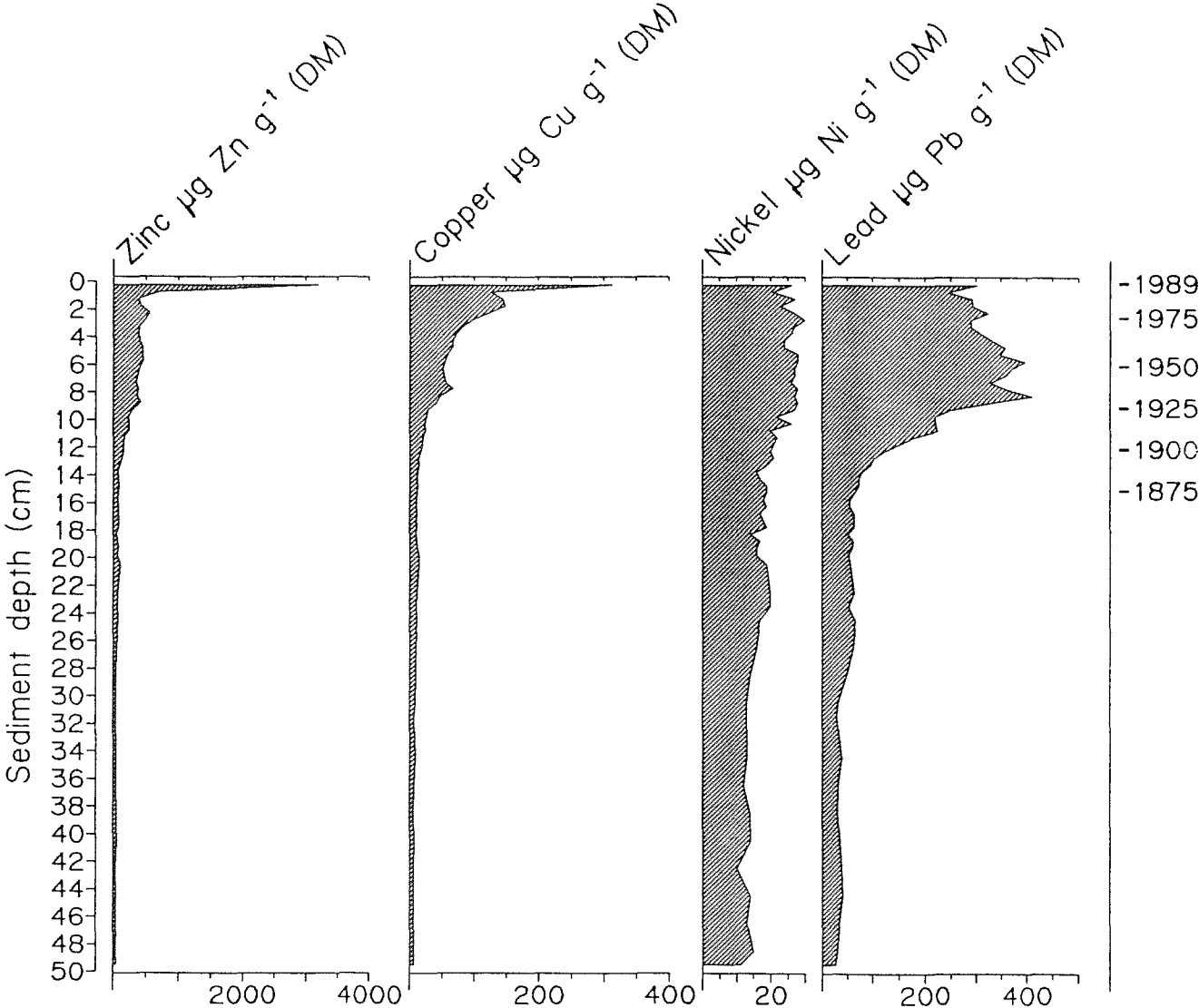
Figure 4.11 Comparison of the lead and zinc contamination in Lac de Gérardmer with a series of lakes in Wales.
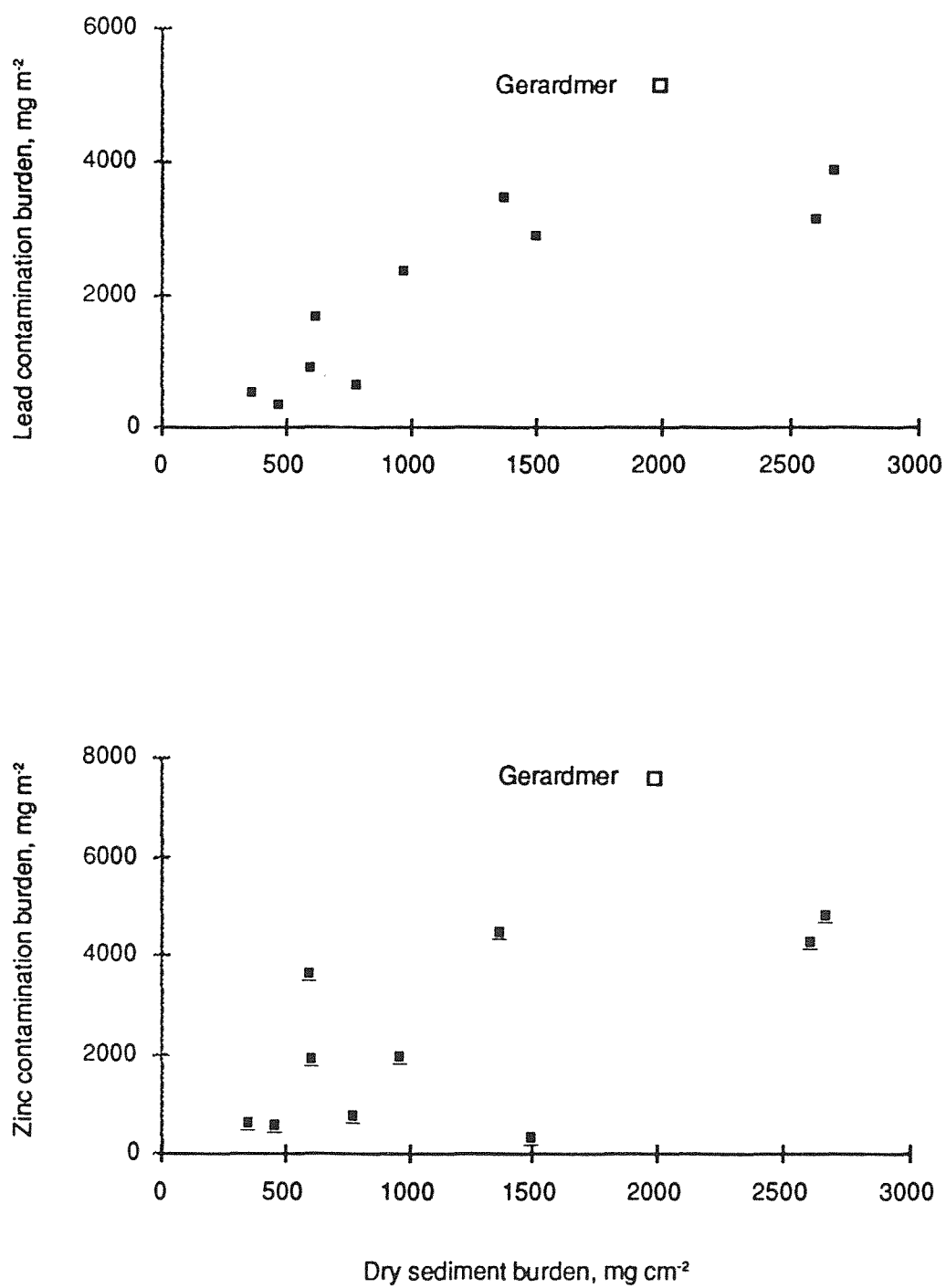
Figure 4.12 Lac de Gérardmer: phosphorus, manganese and iron concentrations plotted against sediment depth
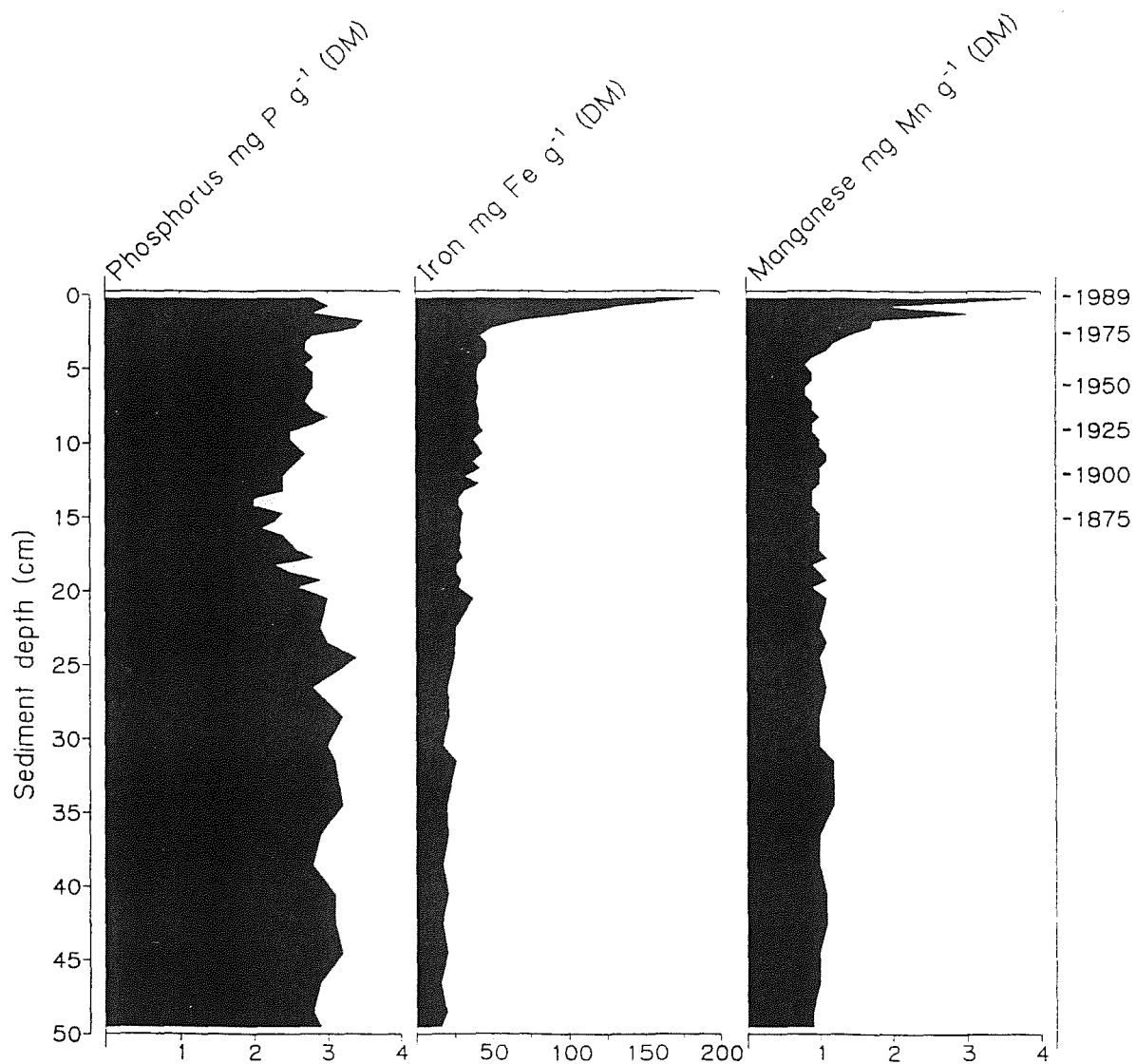
5 THE PALAEOLIMNOLOGY OF LAC DES CORBEAUX AND OTHER OLIGOTROPHIC LAKES IN THE VOSGES REGION, WITH REFERENCE TO RECENT ACIDIFICATION FROM ANTHROPOGENIC SOURCES.

5a INTRODUCTION

Studies of the chemical characteristics of precipitation and selected surface waters in the Cornimont - La Bresse area of the Vosges mountains in the mid-1980s revealed the existence of at least four 'acidified' rivers and two sensitive lakes in the region (Massabuau *et al.* 1988). pH values were observed to fluctuate significantly, being lowest at snowmelt and after heavy rain and highest in dry periods. Depressed pH values were also associated with high (sometimes very high, >200 μg l^{-1}) aluminium concentrations in streamwater. Histories of fishery decline and disappearance provided further evidence of an acidification problem. The postulated cause, of acid atmospheric deposition upon poorly buffered rocks, was supported by comparison with surface waters which were not 'acidified' in areas just 20-35 km away where precipitation characteristics were similar but where the geology provided a greater degree of buffering capacity (Fritz *et al.* 1984, Probst *et al.* 1987).

The numerous lakes in the Cornimont - La Bresse area makes possible an assessment of the extent and history of acidification utilising palaeolimnological techniques. Accordingly, a detailed palaeolimnological assessment of one lake, Lac des Corbeaux, and sample surveys at a series of other lakes, were conducted in August 1987 and July 1989.

5b LAC DES CORBEAUX

Introduction

Lac des Corbeaux is situated in the hills near the town of La Bresse (see Figure 2.1). The catchment is unpopulated although there is a cafe just outside the catchment and the lake does attract a number of visitors in the summer. The catchment bedrock is granitic. The whole catchment is forested, principally with conifers with a small amount of deciduous woodland. The lake itself is dammed and is subject to significant water level fluctuations. A forest track runs around its perimeter. Physical characteristics of the site are described in Table 5.1.

Although no long-term or detailed water chemistry is available, Lac des Corbeaux was identified by Massabuau *et al.* (1988) as sensitive to acidification. The lake possesses moderate alkalinity (cf. Appendix 1) and available data show a pH range of 5.6-6.9 (Table 5.2). Local anglers claim that the reproduction of brown trout, which started to decline from the local rivers in the late 1960s, was increasingly impaired in the Lake.

Table 5.1   Lac des Corbeaux: site characteristics.

Lake altitude (m)	887.0
Catchment relief (m)	231.0
Maximum depth (m)	22.0
Mean depth (m)	10.38
Lake area (ha)	9.93
Lake volume (m^3 x 10^6)	1.03

Table 5.2   Lac des Corbeaux: reported measured pH values

Date of sample	pH
November 1985 (Massabuau *et al.* 1987)	6.80
May 1986 (Massabuau *et al.* 1987)	5.60
March 1987 (Massabuau *et al.* 1987)	6.00
July 1989 (analysis at CNRS Strasbourg)	6.64
April 1992 (analysis at SOAFD Pitlochry)	6.90

Bathymetric survey

The bathymetry of Lac des Corbeaux is shown in Figure 5.1. The lake consists of one basin with a wide, gently sloping central valley. The maximum depth is 22 m.

Sediment stratigraphy

A short core, 18 cm long (CORB1), was taken from the lake in August 1987 at 21 m depth (Figure 5.1), with a kajak gravity corer. This was extruded at 1 cm intervals in the field and has been dated and analysed for diatoms and carbonaceous particles. A further long core was taken in July 1989 using a Livingstone piston corer and 7.4 m of sediment was retrieved, including pink clay presumably of glacial origin at the base of the sequence. This core is being stored whole at 4°C but has not been analysed for this study.

Core CORB1 consists of dark brown fine detritus. There are no marked variations in the composition of the sediment throughout the core although there is a trend of a decreasing proportion of organic matter and an increasing amount of mineral material towards the top of the core. This is indicated in the percentage dry mass and LOI data in Figure 5.2.

Radiometric dating

The unsupported ^{210}Pb profile shows the sediment accumulation rate to be generally slow, with 9.5 cm below the surface being dated to 1826. Within the last 40 years however, there has been a gradual increase in the sediment accumulation rate from around 0.0053 g cm^{-2} yr^{-1} during the period 1900-1945 to recent values over 0.010 g cm^{-2} yr^{-1}. There is also a suggestion of an episode of accelerated sedimentation around 1860-1870. A chronology based on the CRS ^{210}Pb dating model is shown in Figure 5.3 and in Table 7.

Table 5.3   Lac des Corbeaux: ^{210}Pb chronology with sediment accumulation rates

Depth cm	Date	+/- (yrs)	g cm^{-2} yr^{-1}	cm yr^{-1}	+/- (%)
0.0	1987				
0.5	1984	2	0.0145	0.147	8.2
1.0	1980	2	0.0124	0.117	6.9
1.5	1975	2	0.0102	0.087	5.5
2.0	1969	2	0.0095	0.078	6.2
2.5	1962	2	0.0088	0.068	6.9
3.0	1953	2	0.0073	0.056	7.5
3.5	1944	3	0.0057	0.045	8.1
4.0	1932	3	0.0056	0.044	10.8
4.5	1921	4	0.0055	0.043	13.5
5.0	1909	6	0.0053	0.041	19.3
5.5	1896	8	0.0050	0.040	25.2
6.0	1886	11	0.0071	0.057	36.9
6.5	1877	14	0.0093	0.074	48.6
7.0	1870	17	0.0106	0.088	59.0
7.5	1864	19	0.0119	0.102	69.4
8.0	1855	21	0.0096	0.082	77.9
8.5	1845	24	0.0072	0.062	86.5
9.0	1835	26	0.0049	0.043	95.1
9.5	1826	28	0.0026	0.023	103.7

The ^{137}Cs results (Table 5.4) show a maximum activity in the topmost sediments of the core. The ^{134}Cs data indicate that part of the activity at this level can be attributed to Chernobyl fallout. Using the ^{134}Cs data, the total ^{137}Cs activity can be partitioned into a Chernobyl component and a component derived from other sources such as atmospheric nuclear weapons testing. These calculations indicate a rapid increase in ^{137}Cs activity above the 4 cm level,

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reaching peak values around 2.5 cm. The level at which the initial increase occurs is well before 1954, the date at which ^{137}Cs was first released into the environment, and is an indication of the mobility of this isotope in many lake sediments. Further evidence of this is seen in the rapid diffusion of Chernobyl-derived ^{134}Cs. The ^{241}Am record (Table 5.4) is less distinct, but shows an initial peak at 2.5 cm, the same depth at which the non-Chernobyl ^{137}Cs reaches its maximum values. This level is dated 1962 by the CRS model. It would thus seem reasonable to associate this level with the 1963 fallout maximum, supporting the evidence for a recent acceleration in accumulation given by the ^{210}Pb. An unusual feature of the ^{241}Am profile is the presence of this isotope in the most recent sediments. Data from a number of sites indicates that this isotope is considerably less mobile than ^{137}Cs. The sustained level of non-Chernobyl ^{137}Cs above 2 cm points to a continued input of these isotopes.

Table 5.4   Lac des Corbeaux: ^{137}Cs, ^{134}Cs and ^{241}Am data

Depth cm	^{137}Cs pCi g^{-1}	^{134}Cs pCi g^{-1}	^{241}Am pCi g^{-1}
0.5	16.48	3.76	0.12
1.5	11.70	1.63	0.06
2.5	9.29	0.86	0.12
3.5	5.57	0	0
4.5	1.66	0	0
5.5	0.60	0	0
6.5	0.16	0	0
7.5	0.18	0	0
8.5	0.03	0	0
9.5	0.02	0	0
10.5	0	0	0

Carbonaceous particle analysis

The profile begins at a very early date (c.1800) indicating contamination from nineteenth century fossil fuel combustion (Figure 5.4). The accumulation of particles appears to accelerate from the late nineteenth century and increases still further after 1940 (3.5 cm). This post-1940 increase in carbonaceous particle accumulation also occurs in Lac de Gérardmer (Figure 4.4) and is comparable to that found in cores from the United Kingdom (eg. Rose 1991) and Sweden (eg. Renberg & Wik 1984).

Most cores in the United Kingdom and cores from other sites in the Vosges show a decrease in particle concentration at the surface. However, the Lac des Corbeaux core does not show such a feature. This may be due to reduced time resolution due to the slow sediment accumulation rate and coarser sampling interval of 1 cm. In the United Kingdom this recent decrease has been attributed to the move to fewer, larger power stations fitted with more

efficient particle arrestors following the introduction of national clean air and pollution control legislation (Rose 1991).

Diatom analysis

Diatom analysis was carried out on 12 samples from core CORB1. Between 400 and 500 valves were counted from each sample. A full diatom diagram showing taxa exceeding 1% in the total count is shown in Figure 5.5. A summary of the changes, including a chronology and pH reconstruction, is shown in Figure 5.6.

Diatom assemblages

As in Lac de Gérardmer, the pre-nineteenth century diatom flora is dominated by *Aulacoseira subarctica* Type 2. Other taxa present include periphytic species such as *Achnanthes minutissima, A. detha* and *Fragilaria virescens* var. *exigua*. Above 8 cm (about 1850) another *Aulacoseira* species, *A. lirata* var. *alpigena* appears and continues to increase in proportion to the sediment surface. *Achnanthes austriaca* var. *helvetica* and *Pinnularia subcapitata* var. *hilseana* also increase at this time. Later, above 5 cm (c. 1909), *Fragilaria virescens* var. *exigua* declines accompanied by an increase in *Achnanthes marginulata*.

pH reconstruction

The pH reconstruction (Figure 5.6) shows clear evidence of increasing acidification from the mid-nineteenth century. Prior to 1850 (8 cm depth) the pH was around pH 6.3 to pH 6.6, with one lower value of pH 6.2 at 16 to 17 cm depth where the sample contains a larger proportion of *Fragilaria virescens* var. *exigua*. Above 8 cm the reconstructed pH declines abruptly by 0.4 pH units in 1 cm (15 years). This decline continues until the 1930s, reaching a value of pH 5.5. There appears, however to have been no substantial change in pH since then. The absence of detailed modern water chemistry data makes comparison of this reconstructed surface value with the contemporary measured situation, difficult. pH reconstruction based on diatom analysis yields values which represent the mean conditions prevailing for the period in question. The reconstructed surface pH of 5.5 falls marginally below the recorded range of 5.6-6.9 (Table 5.2) and probably provides a more representative description of modern pH in the lake than the rather sporadic water chemistry data.

Discussion

Despite a slow sediment accumulation rate, the radioisotope data show core CORB1 contains a complete sediment record from the early-nineteenth century. The carbonaceous particle record supports this. Comparison with the carbonaceous particle data from Lac de Gérardmer shows both lakes contain a similar record in terms of the pattern and timing of changes in the profiles, although the slower accumulation rate and coarser sampling interval at Lac des Corbeaux may have obscured any decline in surface concentration, as seen in Lac de Gérardmer.

It is also interesting to compare the diatom results from both lakes because in the early-nineteenth century their diatom populations were dominated by the same taxon, *A. subarctica*

Type 2. Since then both lakes have undergone water quality changes as a result of anthropogenic inputs. In the case of Lac de Corbeaux, the diatom changes appear to be a response to increasing acidification. There is clear evidence from the carbonaceous particle data that there is a history of atmospheric contamination of the lake over the same time period, so it seems probable that the acidification is related to increasing acid deposition in the area.

In contrast to most acidified lakes studied in the United Kingdom (eg. Battarbee *et al.* 1988), the degree of acidification does not increase after the early to mid-twentieth century, despite the evidence from the carbonaceous particle data that contamination was increasing over this period. Without more information on changes in land-use within the catchment over the last seventy years, it is difficult to explain why acidification did not progress further. If the dam or the peripheral road were built from a material with a higher base cation content than the catchment bedrock, this could contribute sufficient alkalinity to prevent further acidification of the lake.

Figure 5.1   Lac des Corbeaux: bathymetry

Core location

Contours in metres

0   metres   100
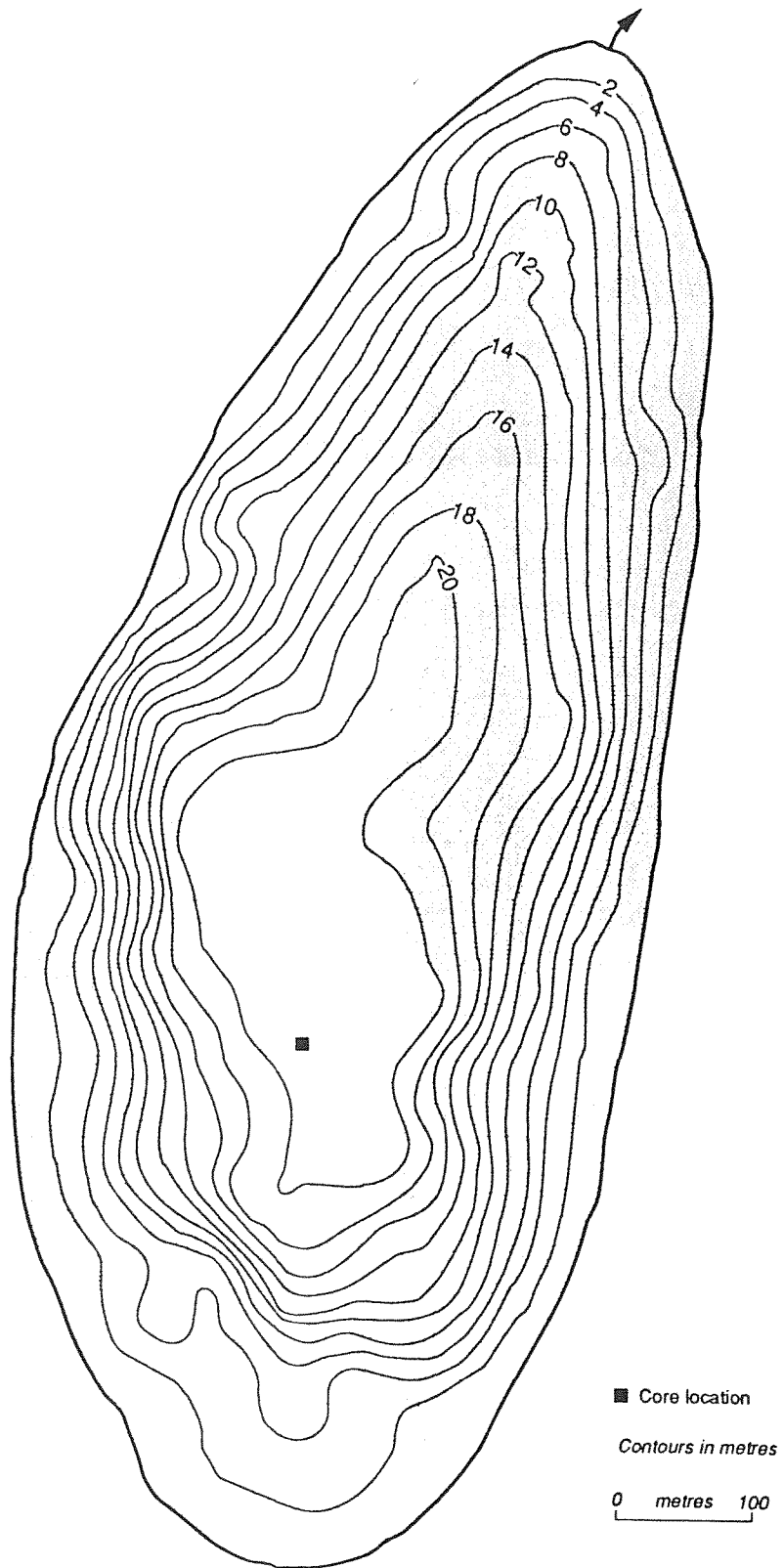
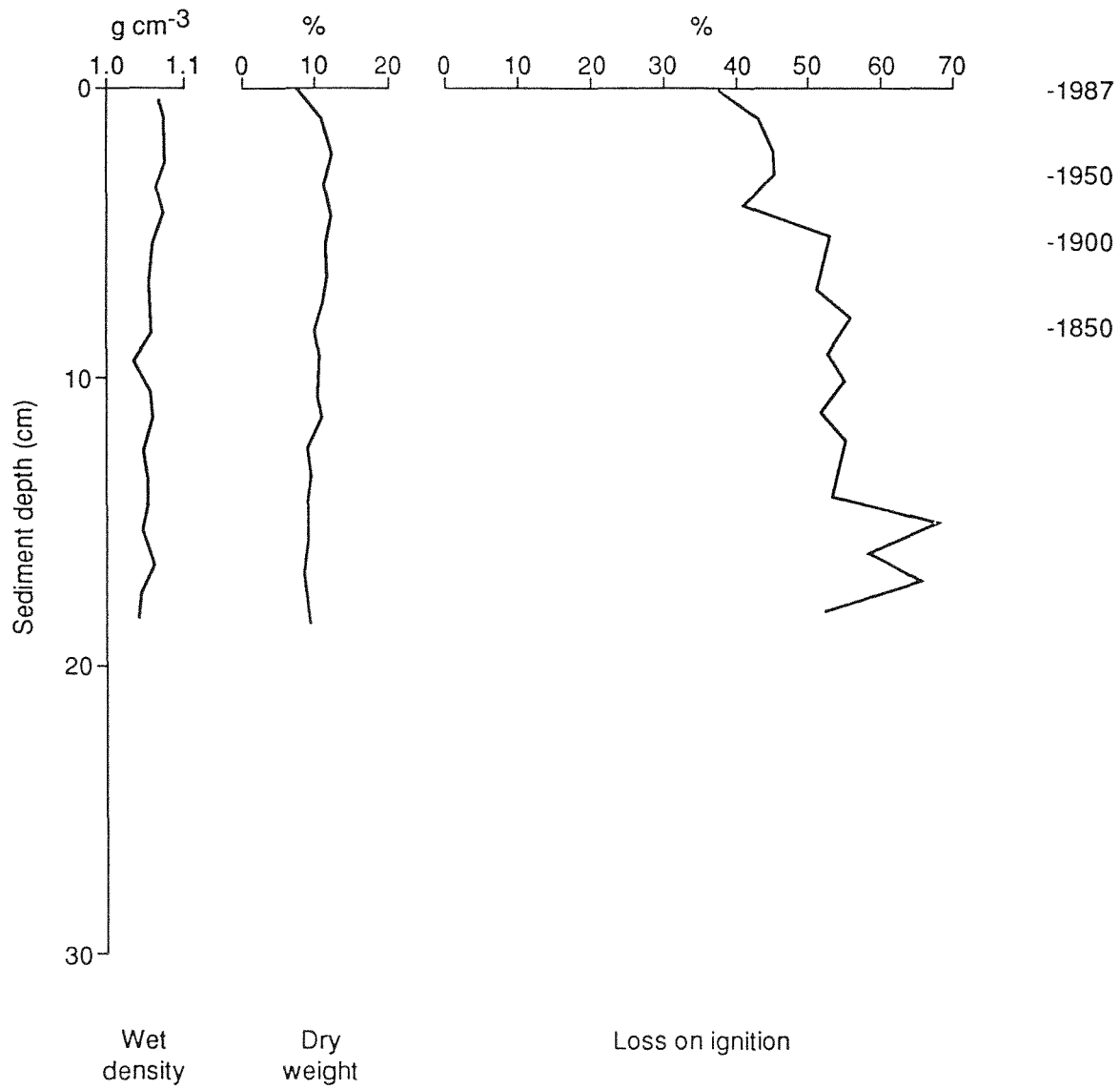**Figure 5.2   Lac des Corbeaux: sediment characteristics**

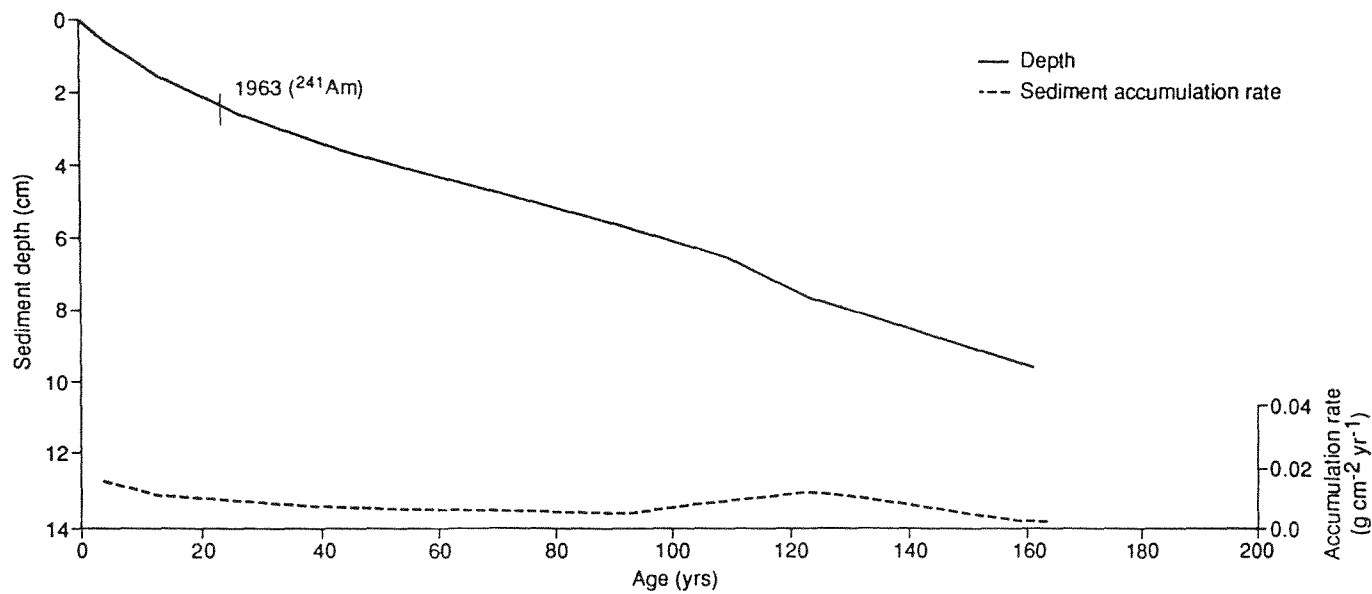**Figure 5.3   Lac des Corbeaux: ^{210}Pb chronology**

Figure 5.4   Lac des Corbeaux: carbonaceous particle concentrations plotted against
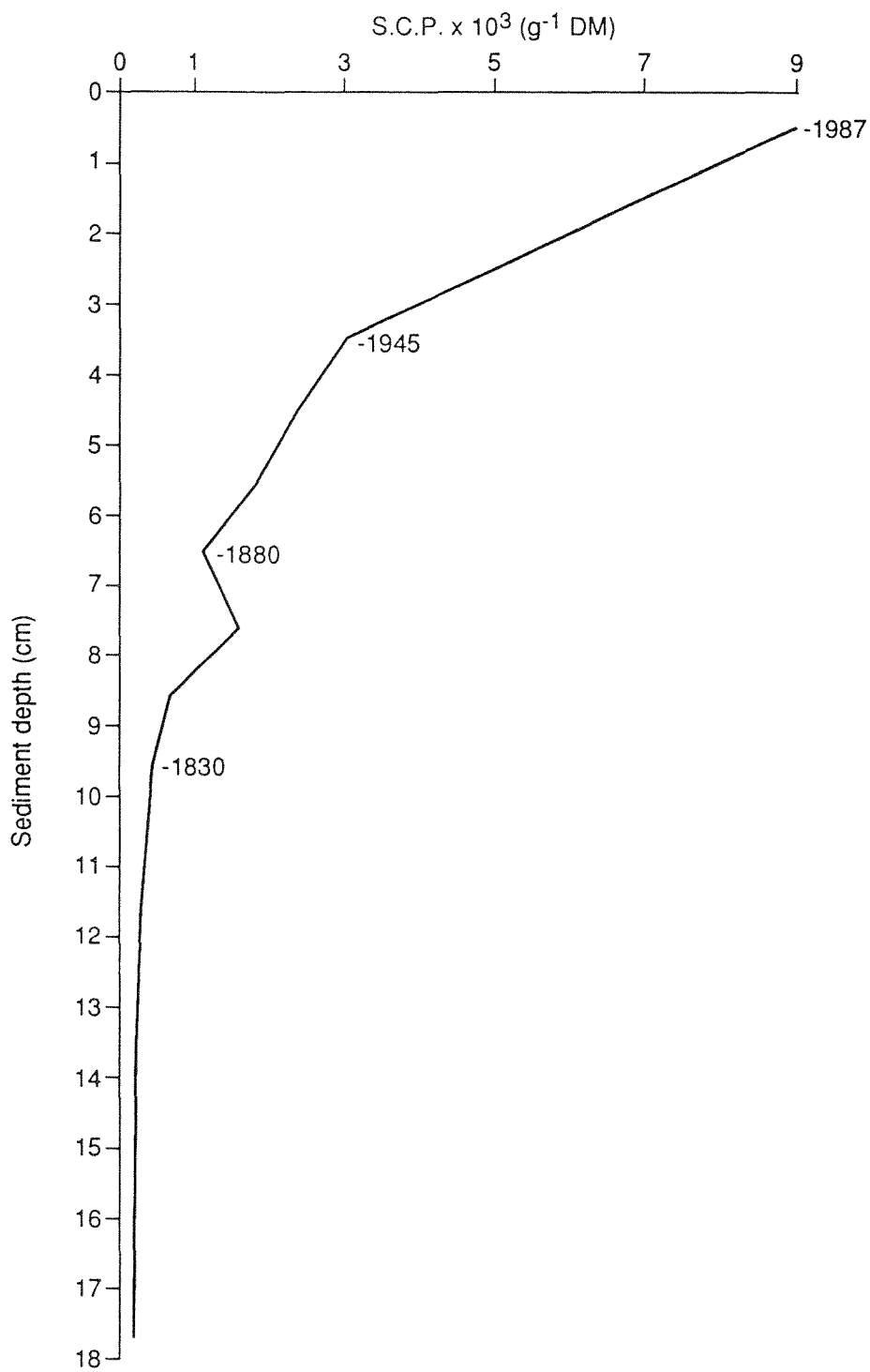sediment depth

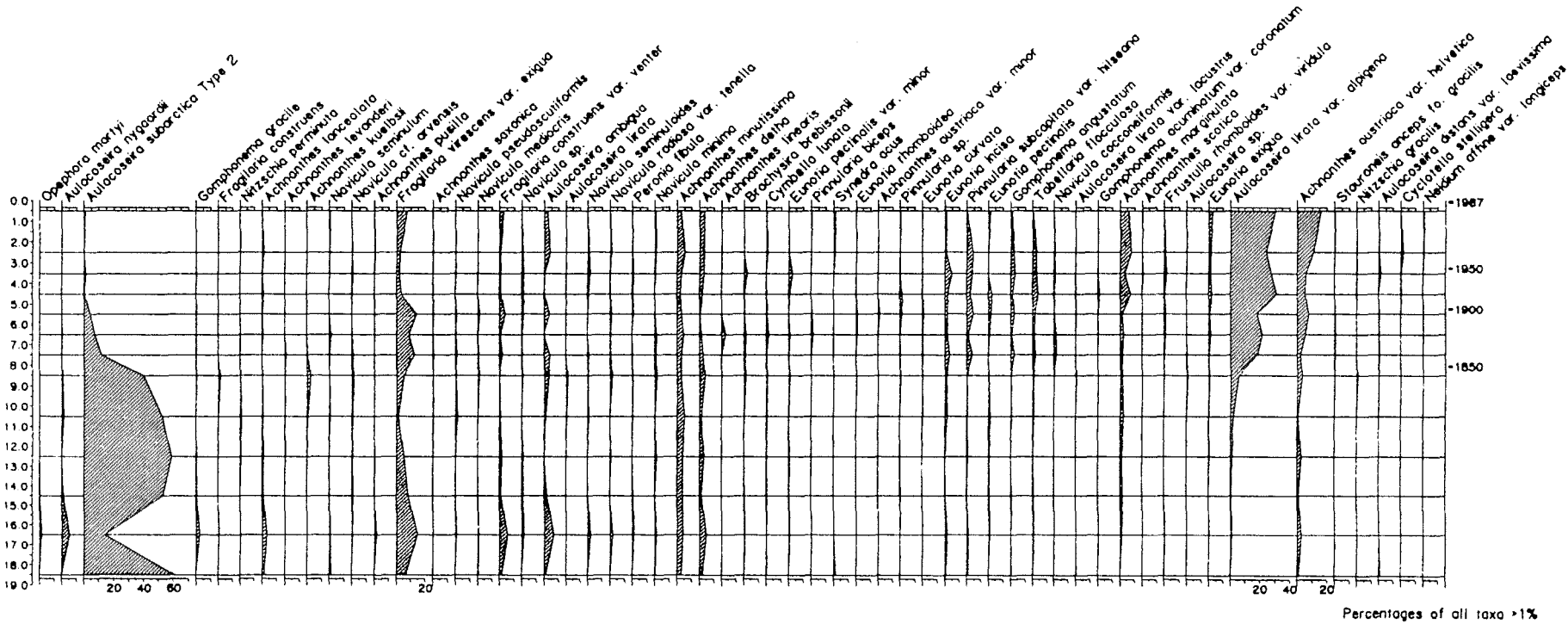Figure 5.5   Lac des Corbeaux: diatom percentages plotted against sediment depth

Figure 5.6   Lac des Corbeaux summary: diatom diagram and pH reconstruction

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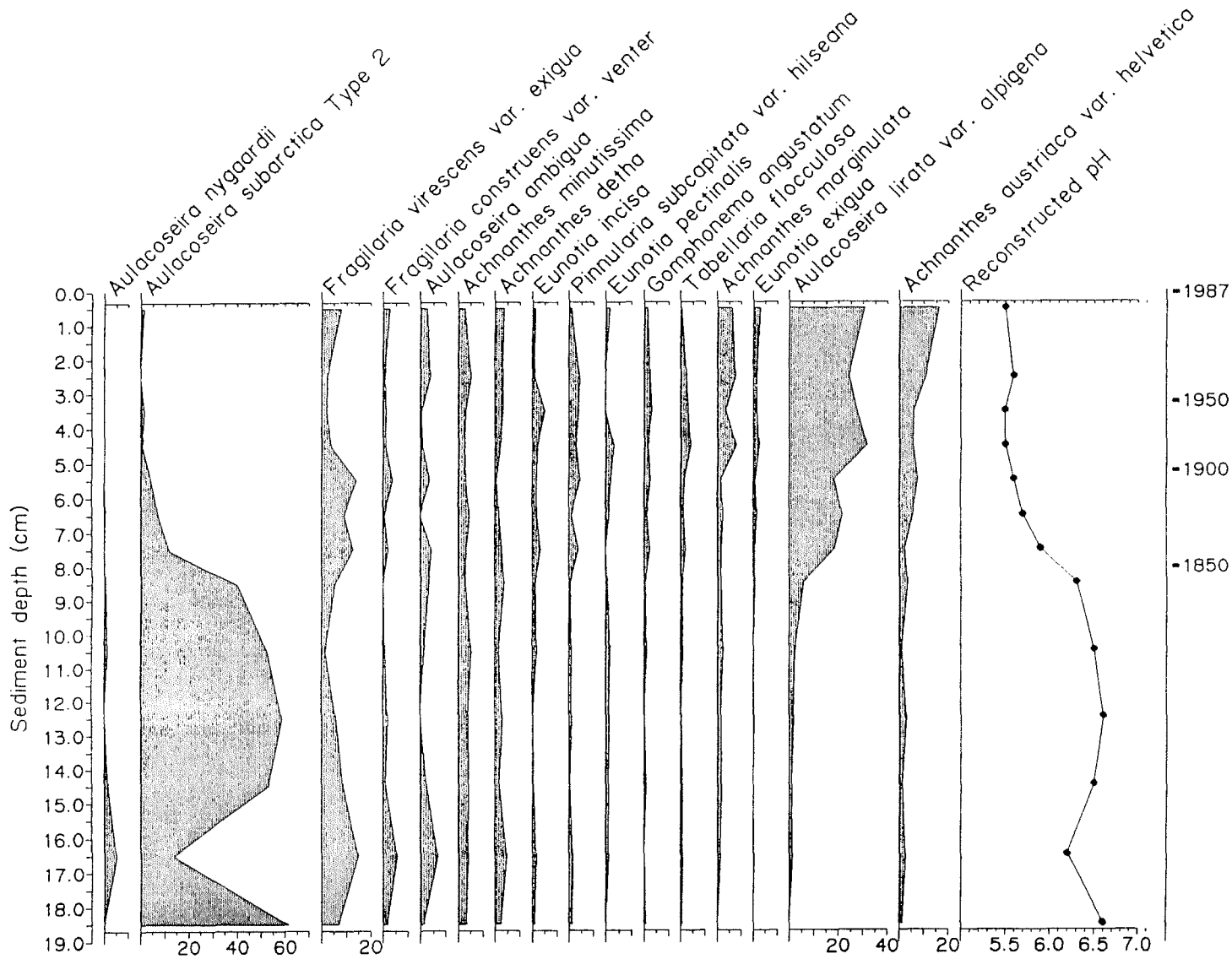
5c   LAC D'ALTENWEIHER

Site description

Lac d'Altenweiher (Figure 2.1) is a reservoir, built in 1886 for water supply. The lake lies at 926 m and has a maximum depth of 14 m. The catchment (maximum altitude 1305 m) is covered by a mixed deciduous and coniferous forest. At the time of sampling in July 1989 the lake had a pH of 6.81 and an alkalinity of 79 μeq l^{-1} (Appendix 1).

Sediment stratigraphy

Two cores were taken at the deepest point of the lake in July 1989 and ALTE2 was chosen for analysis. The core is 13 cm long but the sediment appears substantially disturbed below 5 cm with evidence of an old soil horizon. This is evident from the dry mass and LOI profiles (Figure 5.7). Above 5 cm the sediment is dark brown, fine grain detritus.

Carbonaceous particle analysis

The carbonaceous particle profile is shown in Figure 5.8. The small amount of lake sediment at this site means little information regarding useful dating is available. A concentration peak occurs between 1 cm and 1.5 cm which could be dated to the early 1980s and suggests that the surface sediment is recent.

Diatom analysis

Diatom analysis was carried out on the surface sediment and on sediment at 3.5 cm depth (above the disturbed sediment). The summary diatom diagram with reconstructed pH is shown in Figure 5.9. The diatoms present are all typical of waters with a pH range 5.8-6.5. There is a decline in the species *Synedra acus* in the surface sediment and a corresponding increase in the attached taxa, such as *Achnanthes minutissima*. This results in a slight decline in reconstructed pH from 6.4 to 6.2 but this could be the result of a change in physical factors as much as a response to changes in water chemistry. In water supply reservoirs fluctuations in water level can affect the availability of diatom habitats.

Discussion

The limited depth of sediment in this lake, and the compressed soil-type horizon below 5 cm suggests that the lake has been drained in the last 25-30 years. There appears to have been no major change in the lake chemistry since this event.

Figure 5.7   Lac d'Altenweiher: sediment characteristics

Dry weight   Loss on ignition

Figure 5.8   Lac d'Altenweiher: carbonaceous particle concentrations plotted against sediment depth
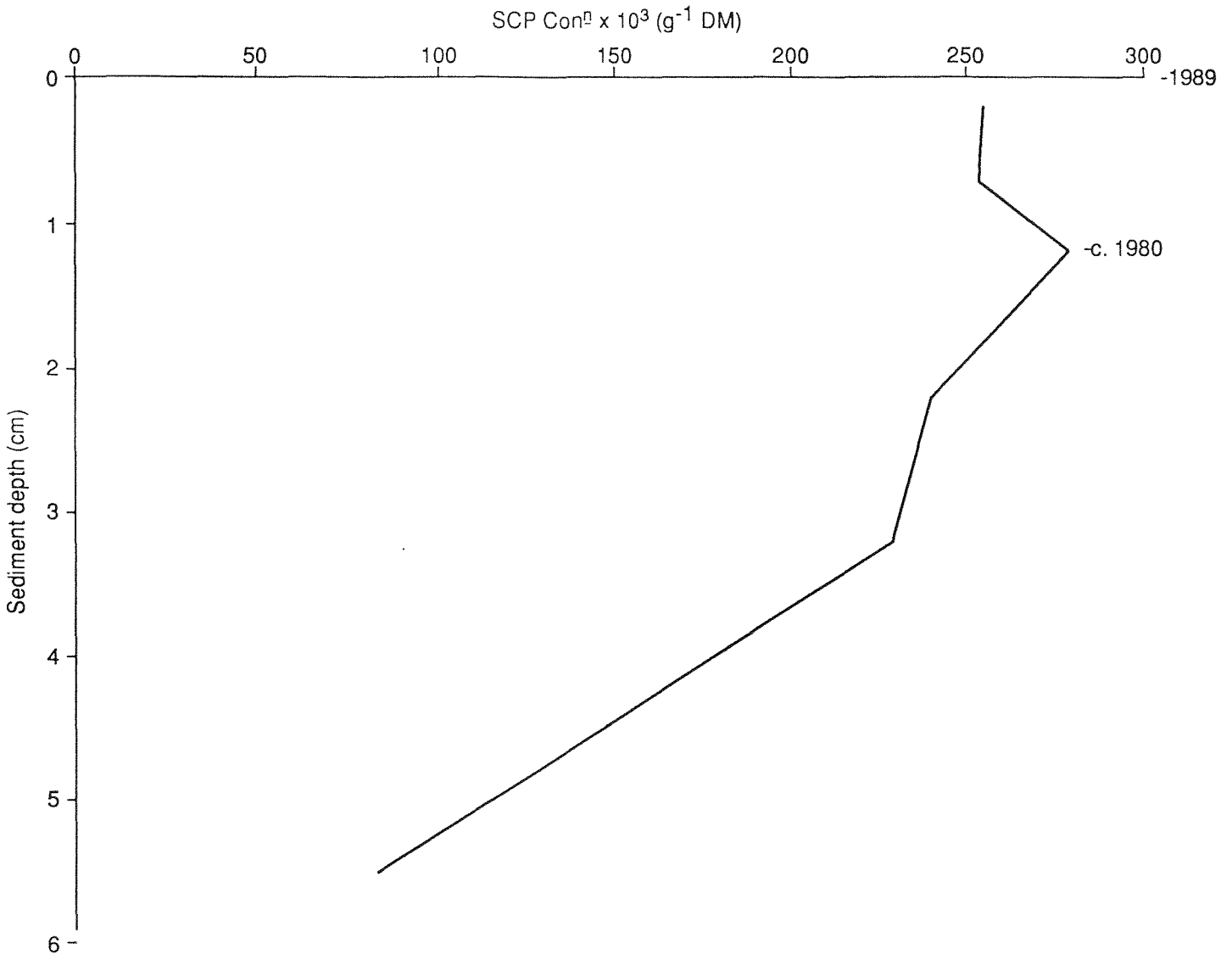
Figure 5.9   Lac d'Altenweiher diatom diagram and pH reconstruction

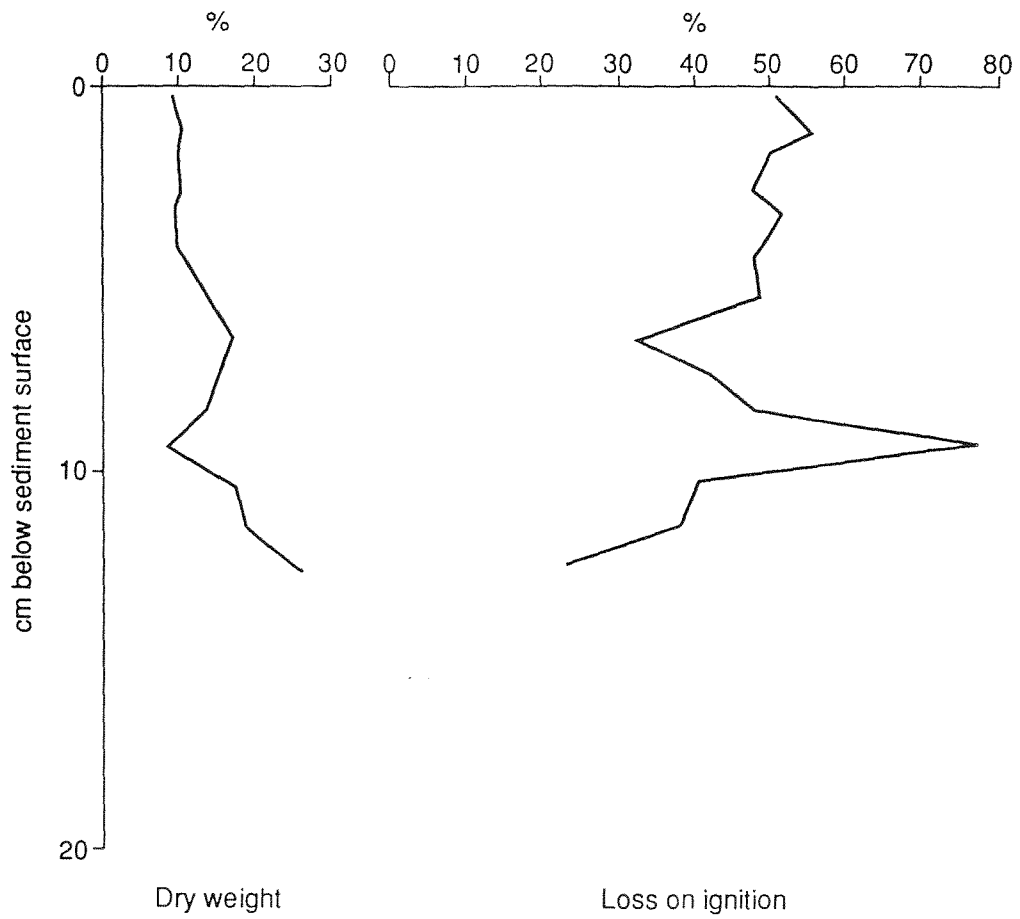Diatom taxa plotted as percentages (>1%) of total count
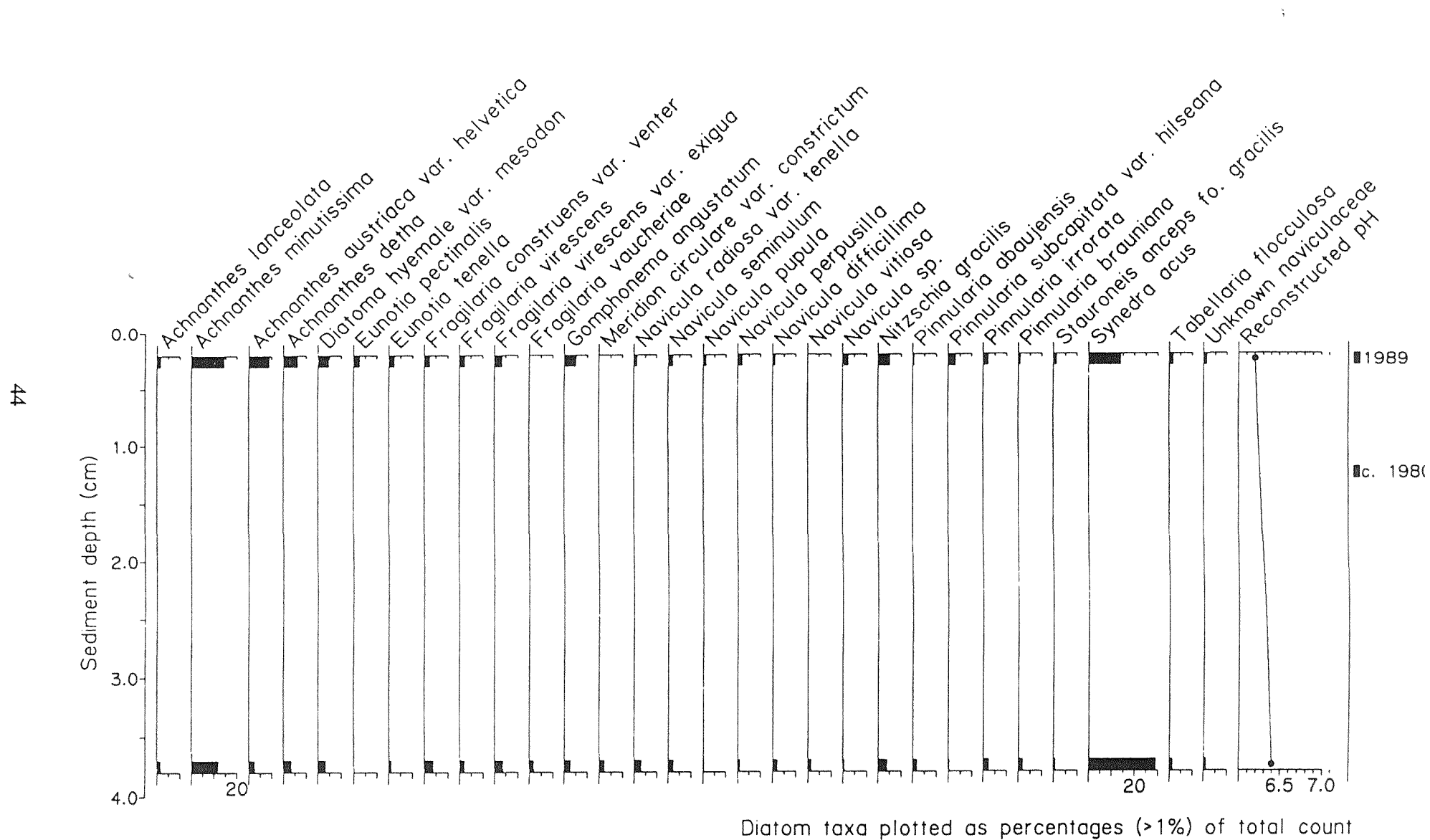
5d   LAC DE BALLON

Site description

Lac de Ballon (Figure 2.1) lies at 986 m and has a maximum depth of 24 m. It is dammed and the water supplies a small hydro-electric power station on the outflow. The lake showed signs of recent draw-down of the water at the time of sampling. The catchment rises to the peak of Le Grand Ballon (1424 m) and is predominantly spruce forest with some deciduous trees. The lake water is well buffered and had a pH of 7.1 in July 1989 (Appendix 1).

Sediment stratigraphy

Two kajak cores were taken from the deepest part of the lake in July 1989. Core BALL1 was chosen for analysis. The stratigraphy of the core shows some evidence of water level fluctuation with bands of inwashed mineral material between layers containing more organic matter (Figure 5.10).

Carbonaceous particle analysis

This core shows a peak in carbonaceous particle concentration at 1.0-1.5 cm which if allocated to the early 1980s suggests an accumulation rate of about 2 mm yr^{-1} (Figure 5.11). If this accumulation rate is assumed constant then the sharp increase in concentration at 9 cm dates to the 1940s. However, the fluctuation in dry mass and LOI samples suggest that the sediment accumulation rate may vary down the core. The bottom of the profile is not reached at the bottom of the core (12-13 cm), although there is a value of zero at 9.5-10 cm. This may be due to marked dilution of the particle concentration by the high mineral component of this sample.

Diatom Analysis

The surface sample and the samples from 2 cm, 4 cm, 8 cm and 12 cm depths were analysed for diatoms and a summary diatom diagram and pH reconstruction is presented in Figure 5.12. The sediment assemblages in this lake are dominated by three taxa; *Asterionella formosa*, *Fragilaria brevistriata* and *Synedra acus*. There is some fluctuation in the proportions of these taxa with *S. acus* increasing above 8 cm but then decreasing between 2 cm and the surface. The reasons for these fluctuations are not clear but may be related to the increases in dry mass which occur over the same period. The pH reconstruction suggests pH has been in the range of 7.0-7.3 for the last 30 years which corresponds well with the measured pH of 7.1.

Discussion

The core contains evidence of recent water level fluctuations which may have lead to the changes in the diatom flora. There is no evidence of any gross change in pH in recent years and it is unlikely that this lake is sensitive to acidification at present levels of acid deposition.

Figure 5.10   Lac de Ballon: sediment characteristics

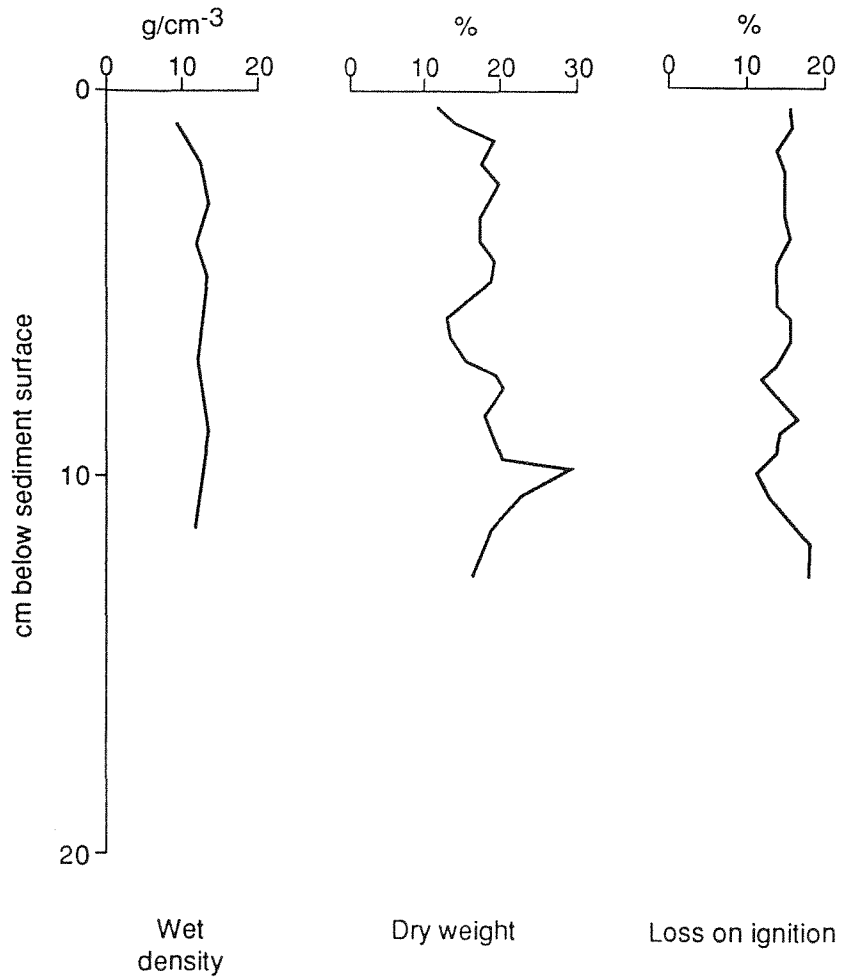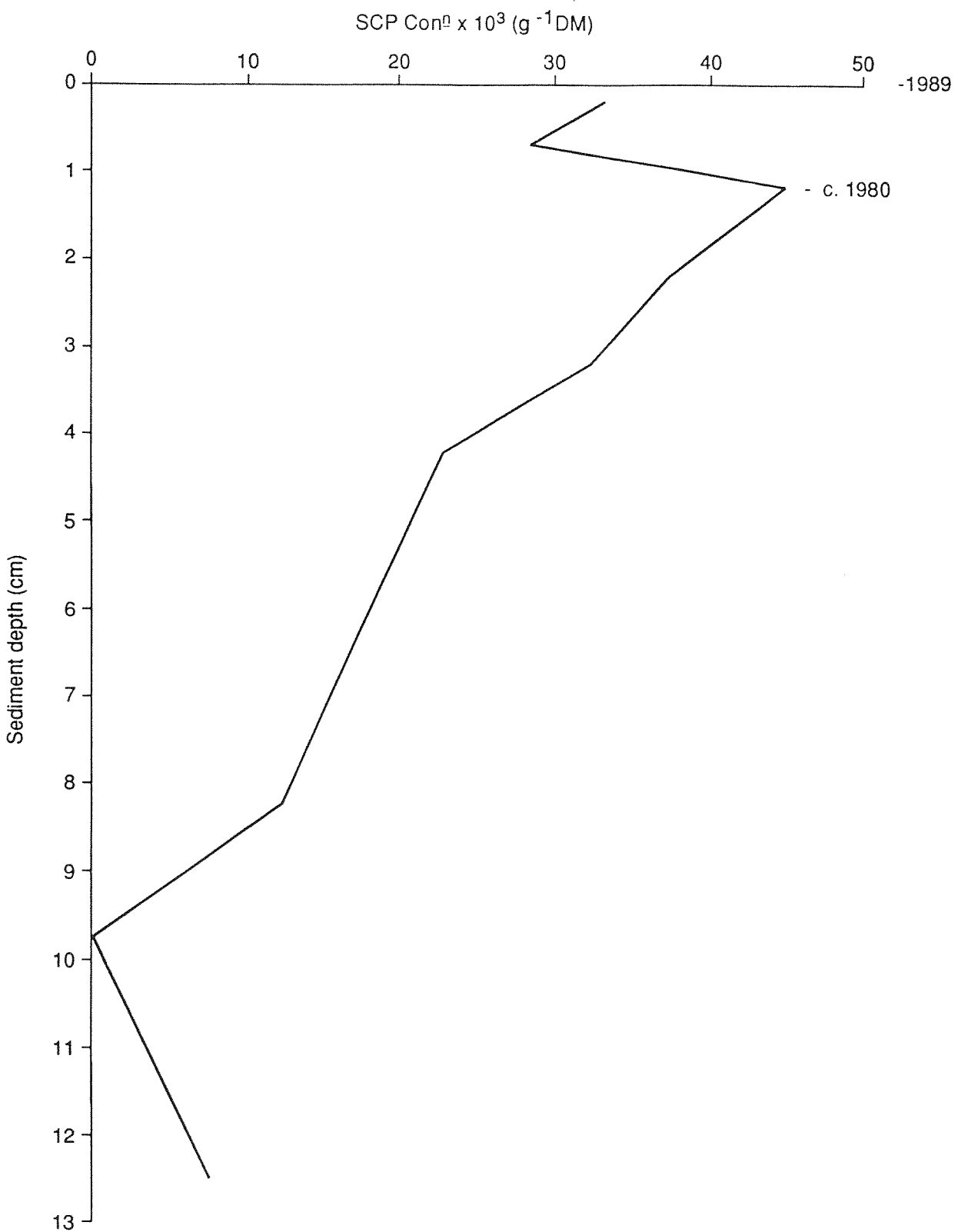**Figure 5.11** Lac de Ballon: carbonaceous particle concentrations plotted against sediment depth

Figure 5.12 Lac de Ballon: diatom diagram and pH reconstruction

Diatom taxa plotted as percentages (>1%) of total count

48

5e   LAC DE BLANCHEMER

Site description

Lac de Blanchemer (Figure 2.1) lies at an altitude of 994 m and has a maximum depth of 17 m. Water level in the lake is controlled by a dam with sluices. The south-eastern end of the lake has an extensive reed bed. The catchment (maximum altitude 1209 m) vegetation is mixed coniferous and deciduous forest. In July 1989 the lake had a pH of 6.80 and an alkalinity of 92 μeq l^{-1} (Appendix 1).

Sediment stratigraphy

Two short cores were taken with a kajak gravity corer at the deepest point of the lake in July 1989. Core BLAN2 was chosen for analysis. The sediment is dark brown fine detritus with a decreasing amount of fine mineral material up the core. At 12 cm there is a peak in the mineral content. The percentage dry mass, wet density and loss on ignition profiles are shown in Figure 5.13.

Carbonaceous particle analysis

The carbonaceous particle profile for this core is shown in Figure 5.14. A peak in concentration occurs at 4.0-4.5 cm and if this correlates to the early 1980s then the accumulation rate is about 5 mm yr^{-1}. Such an accumulation rate would date the rapid increase in particle concentration at 20 cm to the late 1940s. The bottom of the core is at 27 cm and the bottom of the profile falls below this depth. The depression in concentration between 9 and 10 cm is probably related to the peak in dry mass in the same part of the core, indicating dilution of the particle record by inwashed mineral material.

Diatom analysis

Diatoms were analysed from the surface sediment and from 2 cm, 4 cm, 8 cm and 15 cm depths. A summary diatom diagram and pH reconstruction are shown in Figure 5.15. The most obvious change between the 16 cm assemblage and 8 cm is the loss of the planktonic taxa *Asterionella formosa* and *Synedra acus*. These taxa have been replaced by periphytic diatoms such as the *Achnanthes* species and *Fragilaria construens* var. *venter*. These floristic changes result in an overall decrease in reconstructed pH from 6.6 to 6.2.

Discussion

The carbonaceous particle profile suggests the core contains sediment dating from the beginning of this century. The loss of the two planktonic species could be interpreted as a response to a slight decline in pH but is more likely to be the result of a decrease in water transparency or a change in the distribution of diatom habitats, brought about by changes in the water level for example.
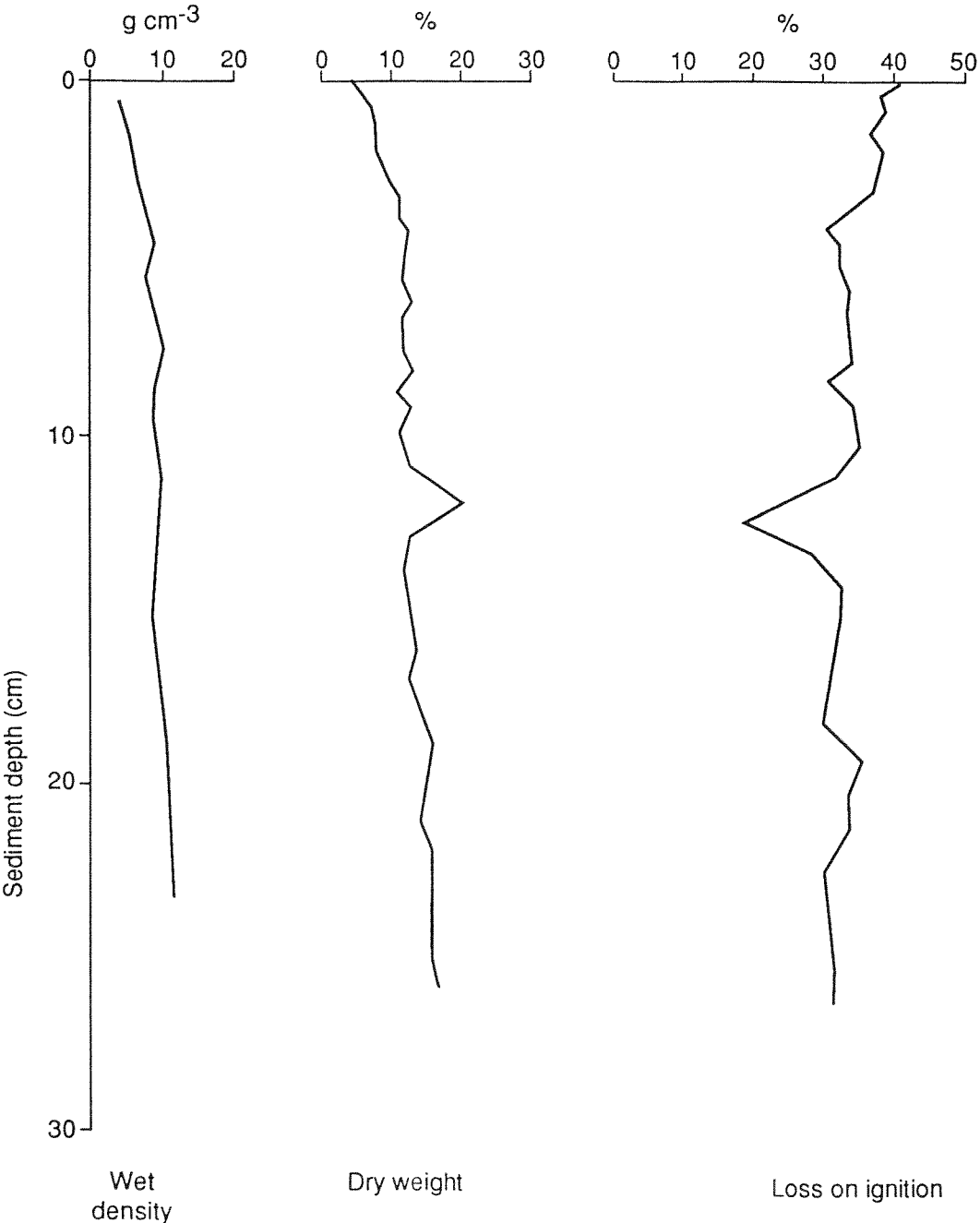
Figure 5.13   Lac de Blanchemer: sediment characteristics

Figure 5.14 Lac de Blanchemer: carbonaceous particle concentrations plotted against sediment depth
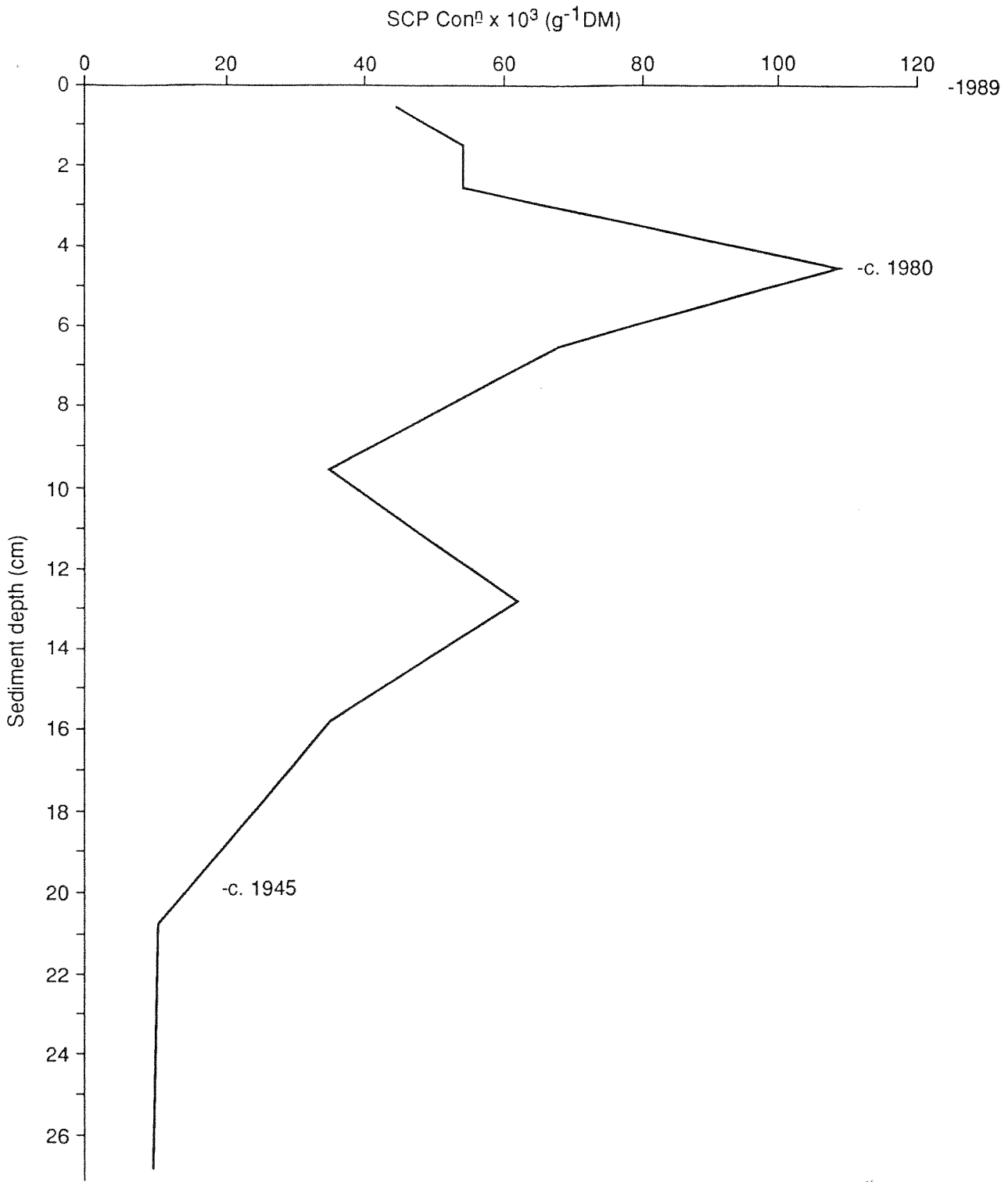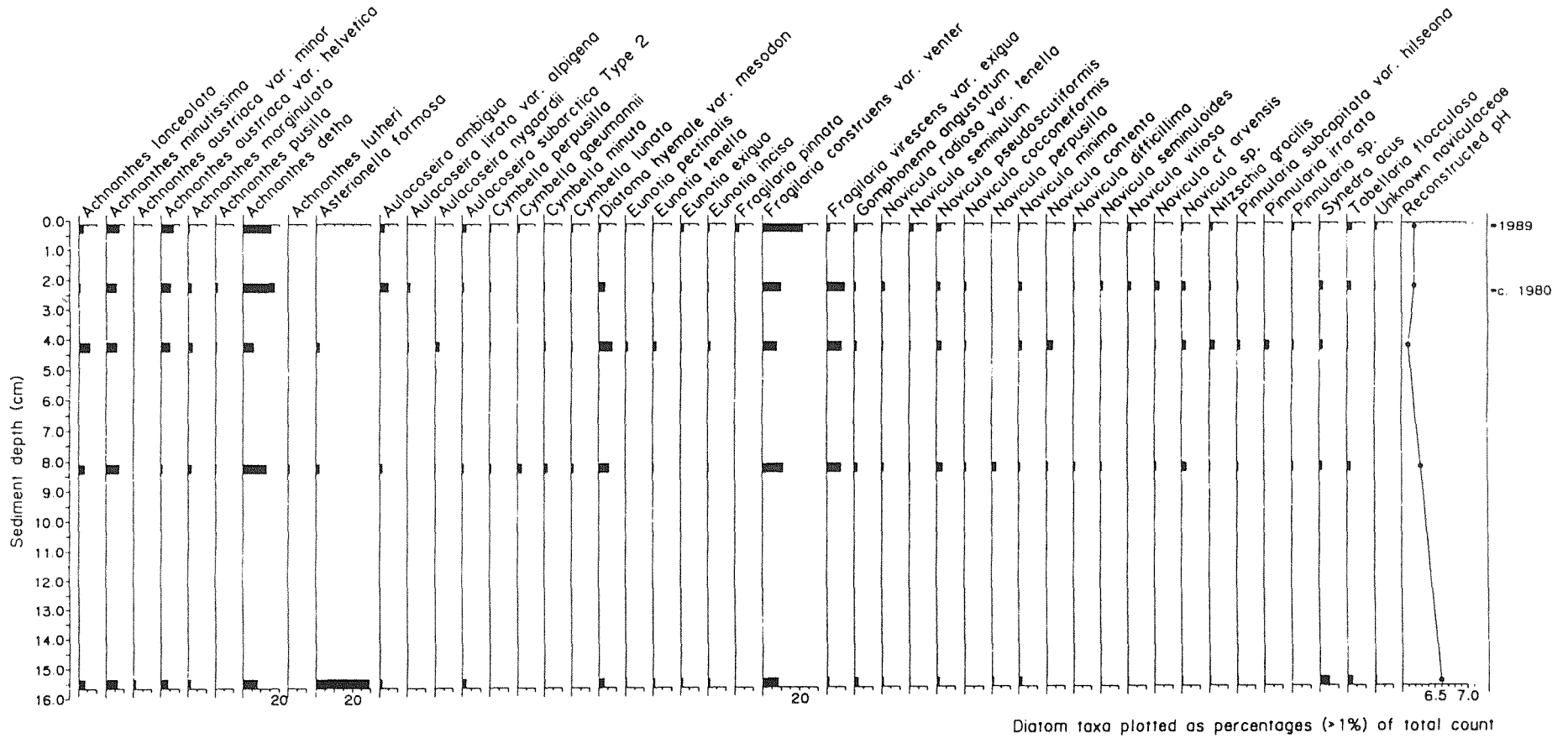
Figure 5.15   Lac de Blanchemer: diatom diagram and pH reconstruction

52

5f   LAC DE LISPACH

Site description

Lac de Lispach is a brown water lake lying at 909 m with a maximum catchment altitude of 1161 m (Figure 2.1). The lake is shallow (1.5 m at its deepest) with extensive reed-swamp at the margins. Originally the lake covered a smaller area, surrounded by forest. When the forest was felled, a dam was built across the outflow to raise the water level. The catchment is vegetated with a mixed deciduous and coniferous forest. The catchment is populated and includes a hotel. A road passes along one side of the lake. In July 1989 the lake had a pH of 6.69 and an alkalinity of 55 μeq l^{-1} (Appendix 1).

Sediment stratigraphy

Two cores were taken with a kajak gravity corer in July 1989 and core LISP1 chosen for analysis. The sediment consists of dark brown organic detritus. The dry mass and LOI data (Figure 5.16) show an increase in organic matter down the core.

Carbonaceous particle analysis

Carbonaceous particle concentrations are shown in Figure 5.17. The concentration peak of this core is at 1.0-1.5 cm and, like the core from Lac de Ballon this suggests an accumulation rate of approximately 2 mm yr^{-1}. The sharp increase in particle concentration is difficult to pinpoint because there are few points on the profile and there is a higher than expected value between 9.5-10 cm. Although there are very few points on this curve with which to allocate dates, the data suggest that the sediment accumulation rate varies down this core. The reason for suggesting this is that although the rapid increase in concentration occurs at about 8 cm (late 1940s), the bottom of the profile is reached at between 13-15 cm which seems rather high in the core (early twentieth century) if sediment accumulation rate is constant. A probable explanation is that the sediment at 12-13 cm dates from around the time that the dam was built and because the area of the lake was greatly increased as a result, sediment accumulation at the core site may only date from this time. The carbonaceous particle profile is therefore likely to be truncated below 10 cm.

Diatom analysis

The surface sediment and samples from 2 cm, 4 cm, 8 cm and 12 cm were analysed for diatoms. A summary diatom diagram and pH reconstruction are shown in Figure 5.18.

The sediments contain many *Eunotia* and *Pinnularia* species typical of shallow, peaty environments. Floristic changes occur at two levels in the core. Between 8-12 cm there is an increase in *Achnanthes austriaca* var. *helvetica* and *Fragilaria construens* var. *venter*. In the surface assemblage *Achnanthes austriaca* var. *minor* increases and to some extent replaces *A. austriaca* var. *helvetica*. With the exception of *F. construens* var. *venter*, the taxa are usually associated with pH <5.5. However, *F. construens* and its varieties are usually found at pH >6.0 so its presence here is surprising. The pH reconstruction indicates there has been little change over the period represented by the core, with the reconstructed pH around 5.3 which is significantly different from the recorded pH of 6.69 (Appendix 1).

The surface assemblage does differ slightly from a list of diatom species in two samples taken from the lake in 1980 (Pierre 1982). In the 1980 samples *Rhoicosphenia curvata* was common but there is no evidence of it in the core. The taxa *Achnanthes austriaca* and *A. austriaca* var. *helvetica* fo. *minor* are not mentioned in the 1980 species list, although this is perhaps less surprising since these are periphytic species and are less likely to be caught in a plankton sample.

Discussion

The carbonaceous particle data suggest that the core does not contain a full record of the nineteenth and twentieth centuries. The core base may date from the early twentieth century. The diatom changes seen do not suggest there has been a change in water quality over the time-span of the core. However, with the reconstructed pH around 5.3 this lake could be considered sensitive to acidification.

Figure 5.16   Lac de Lispach: sediment characteristics

Figure 5.17 Lac de Lispach: carbonaceous particle concentrations plotted against
sediment depth

SCP Conⁿ x 10³ (g⁻¹DM)

Figure 5.18   Lac de Lispach: diatom diagram and pH reconstruction

Diatom taxa plotted as percentages (>1%) of the total count

57
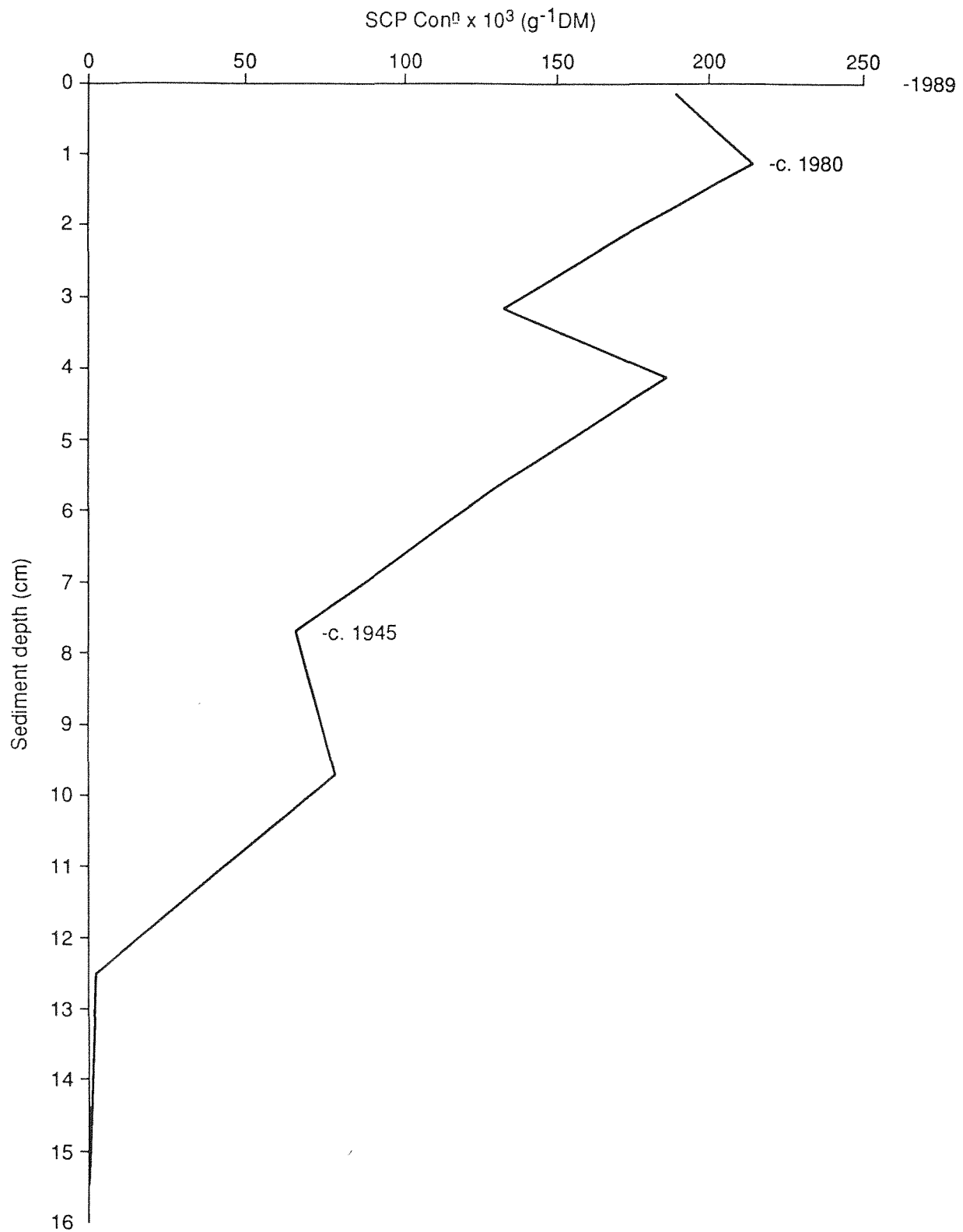
5g   LAC DE LA MAIX

Site description

Lac de la Maix is a small round lake (approximately 150 m diameter) in the northern part of the Vosges (Figure 5.19), maximum water depth is 12.4 m. The lake lies at 679 m altitude and has a forested catchment (maximum altitude 800 m) of predominantly Norway spruce with some broadleaf trees. The bedrock geology is red sandstone. There are three small inflow streams and an outflow channelled through a concrete pipe, although there appears to be no method of lake level control.

A water sample taken at the time of coring (July 1989) records a pH of 5.6 (Appendix 1) which compares with a sample in April 1992 of 4.9. Other determinands sampled on these occasions confirm the relative sensitivity of the site to acid deposition: alkalinity was recorded as 5 μeq l^{-1} (July 1989) and -7 μeq l^{-1} (April 1992). The lake also has a notably high aluminium concentration (cf. Appendix 1).

The lake has a rich macrophyte flora with extensive stands of *Menyanthes trifoliata, Carex rostrata, Nuphar lutea* and *Sphagnum* sp. There is also a diverse invertebrate population.

Sediment stratigraphy

Two long (90 cm) and two short (25 cm) cores were taken from the deepest point of the lake in July 1989. Core MAIX1 (25 cm) was used for analysis. The core is composed of fine dark brown organic detritus with an increasing proportion of mineral material towards the base of the core. The percentage dry mass and LOI profiles are shown in Figure 5.20.

Carbonaceous particle analysis

The carbonaceous particle profile for this core is shown in Figure 5.21. The concentration peak occurs between 4.0-4.5 cm which if dated to the early 1980s (cf. Lac de Blanchemer) suggests an accumulation rate of about 5 mm yr^{-1}. Unfortunately, the core is only 25 cm long and it is difficult to determine where the rapid increase in concentration occurs as particle concentration is increasing rapidly from this bottom level. If this is where the concentration starts increasing rapidly then this would date at the 1940s assuming a constant accumulation. The bottom of the profile is not reached.

Diatom analysis

Samples from the core surface and 2 cm, 4 cm, 8 cm and 24 cm depths were analysed. A summary diatom diagram with pH reconstruction are shown in Figure 5.22 The flora is indicative of an oligotrophic lake with *Brachysira brebissonii, Aulacoseira lirata* var. *alpigena, Aulacoseira distans* var. *laevissima* and *Fragilaria virescens* var. *exigua* as the abundant taxa. There are no major changes in species up the core and the pH reconstructs to between 5.4-5.5 throughout the core, which is close to the measured pH at the time of coring (Appendix 1).

Discussion

The initial nineteenth century increase in carbonaceous particles is not recorded in this core so the core does not contain the full record of atmospheric contamination. It seems likely, however, that the base of the core at 24 cm predates 1940. The diatom data suggest there has been little change in lake chemistry over the past fifty years, although with a pH around 5.5 the lake would be expected to be sensitive to increased inputs of acidity. Analysis of a longer core would show whether there was evidence of earlier acidification, as noted in the Lac des Corbeaux where *Aulacoseira lirata* var. *alpigena* increased up the core.

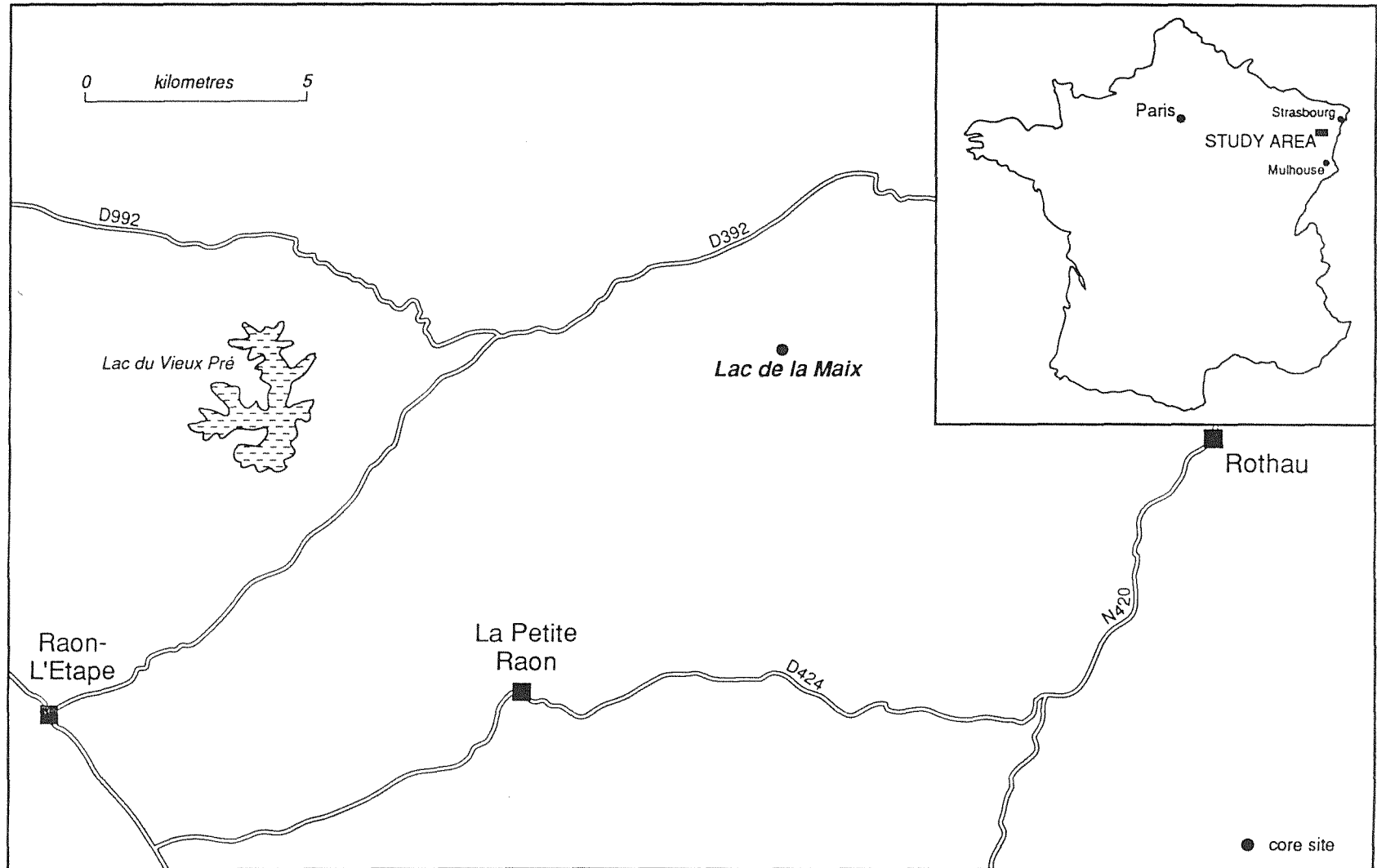**Figure 5.19   Map showing the location of Lac de la Maix**

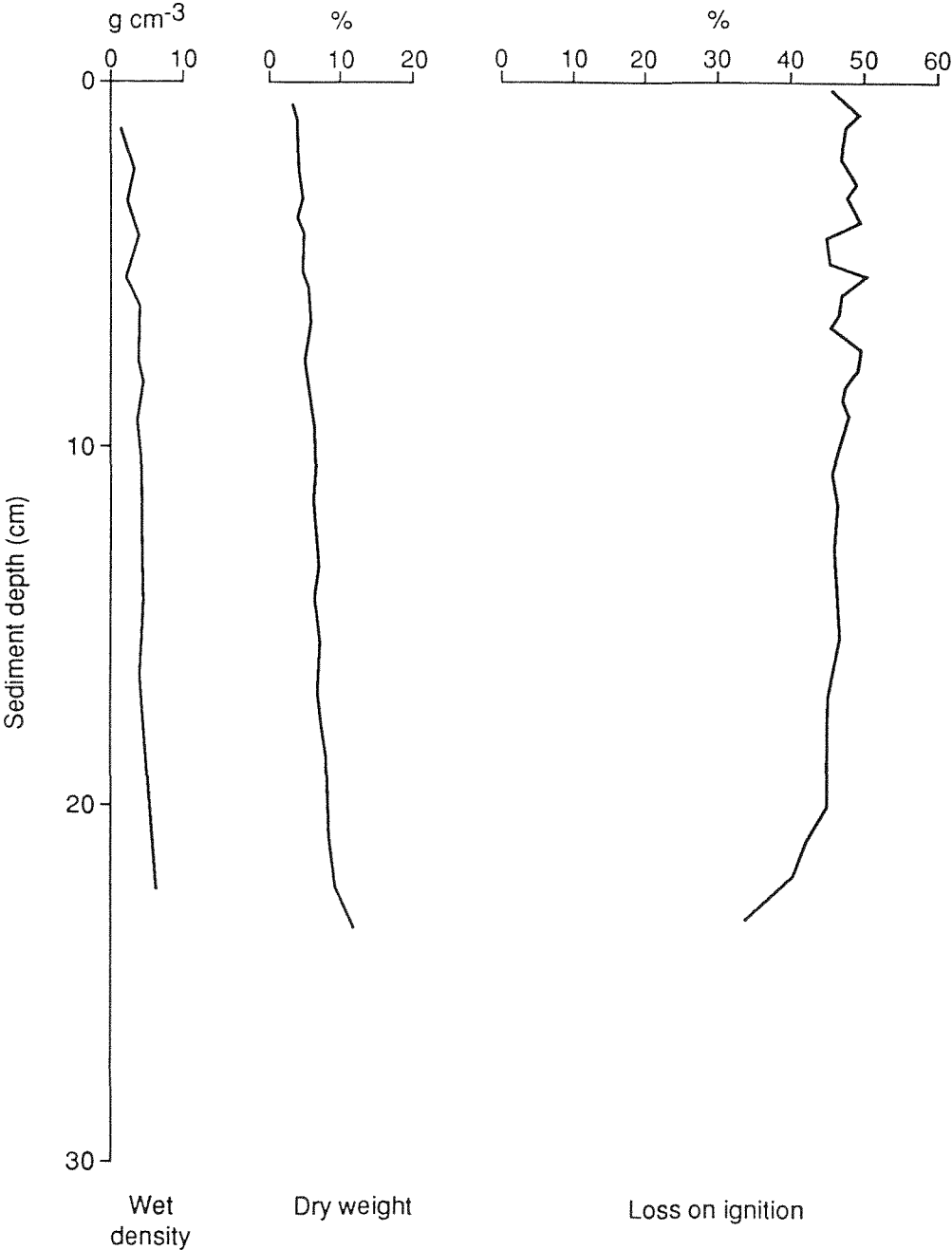Figure 5.20   Lac de la Maix: sediment characteristics

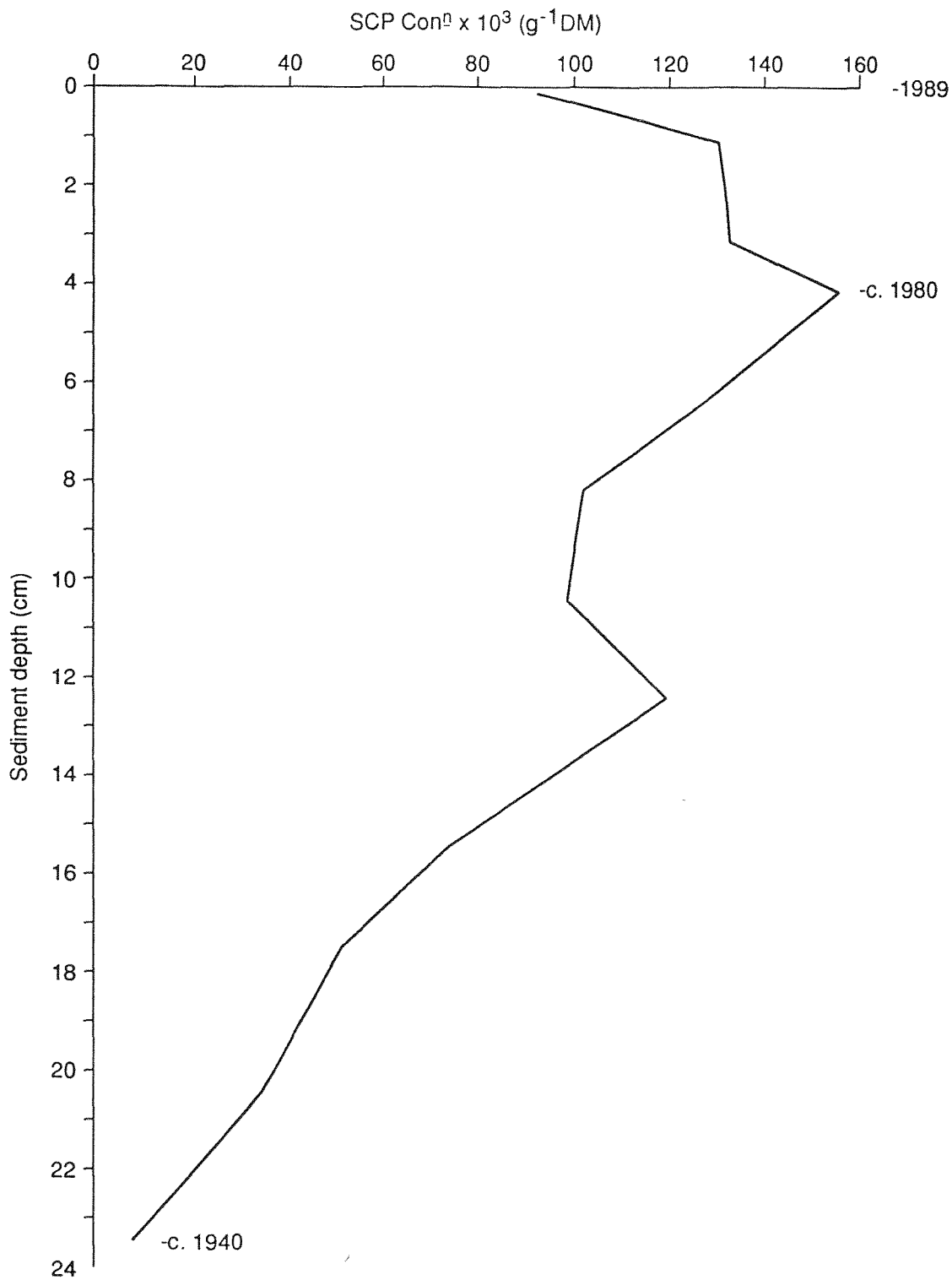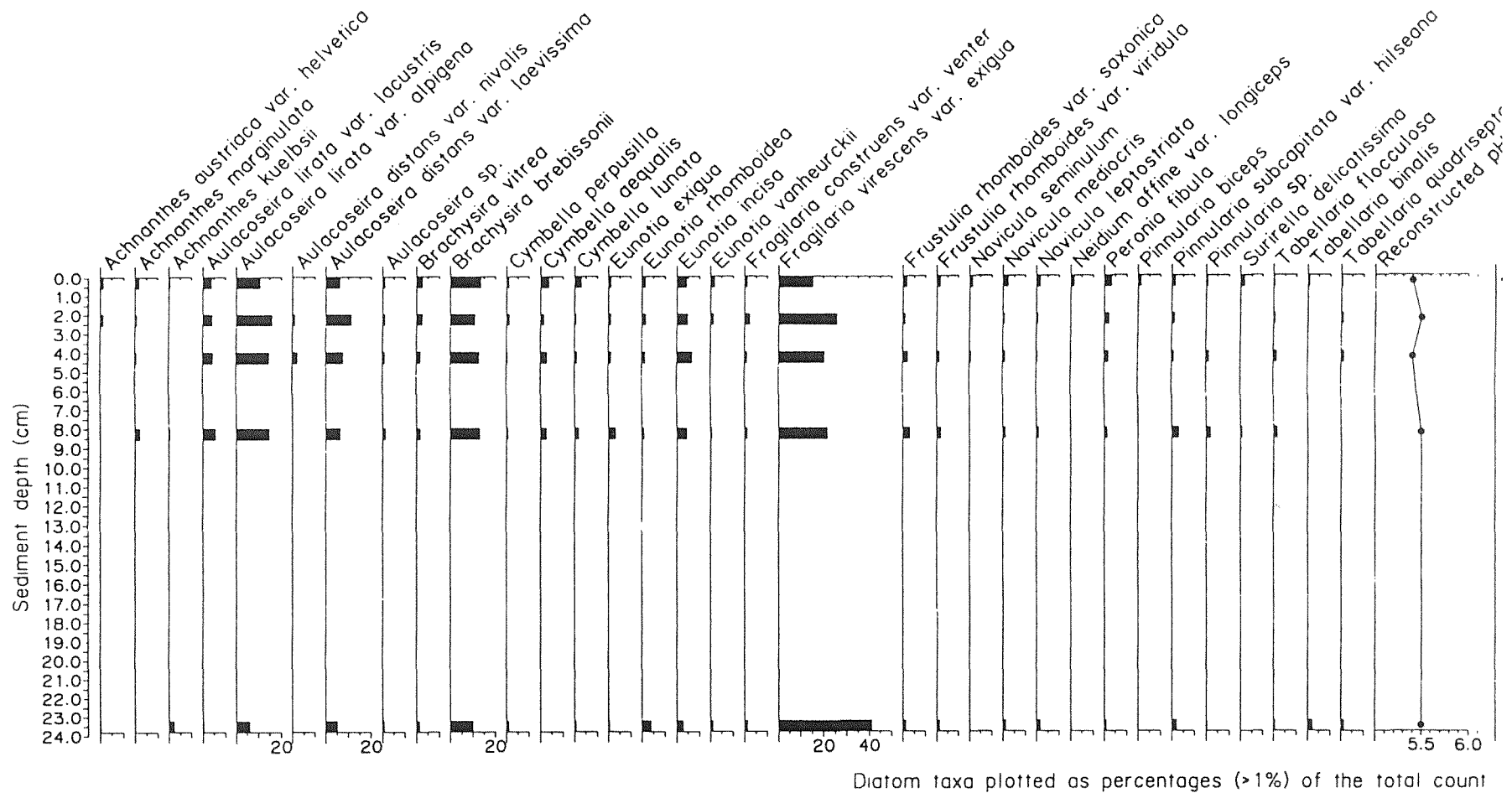Figure 5.21 Lac de la Maix: carbonaceous particle concentrations plotted against sediment depth

Figure 5.22   Lac de la Maix: diatom diagram and pH reconstruction

Diatom taxa plotted as percentages (>1%) of the total count

63

5h   LAC DES PERCHES

Site description

This lake lies at the south of the study area (Figure 2.1), at 985 m altitude. The water level is artificially raised by a dam on the outflow. Maximum water depth was 17 m. The catchment (maximum altitude 1222 m) is small and steep sided with a predominantly deciduous woodland vegetation. The lake has a relatively high pH (7.62 in July 1989) and the lake water is strongly buffered (alkalinity - 533 μeq l^{-1}, calcium - 544 μeq l^{-1}) (Appendix 1).

Sediment stratigraphy

Two cores were taken with a kajak corer, at the deepest point in July 1989. Core PERC1 was chosen for analysis. The core consists of dark brown organic detritus with paler bands of mineral-rich material. These show up as peaks in the dry mass profile (Figure 5.23).

Carbonaceous particle analysis

The carbonaceous particle profile for the core is shown in Figure 5.24. The particle concentration peak occurs at 1.0-1.5 cm in this core and so the accumulation rate is probably about 2 mm yr^{-1}. The rapid increase in particle concentration occurs at 8-9 cm which dates this section to the 1940s. The bottom of the particle profile is not reached by the bottom of the core (25-26 cm) which at constant accumulation rate would be dated to around the 1860s. This is in agreement with the two ^{210}Pb dated cores from Lac de Gérardmer and Lac des Corbeaux, which suggested that the particle profile in this region started early in the nineteenth century.

Diatom Analysis

Diatoms were analysed from the surface sediment and from 24 cm depth. A summary diatom diagram and pH reconstruction are shown in Figure 5.25. The dominant diatoms (*Asterionella formosa*, *Cyclotella radiosa* and *Synedra acus*) are all planktonic taxa indicative of fairly nutrient rich conditions. The increase in *A. formosa* and *S. acus* in the surface sediment suggests the nutrient supply to the lake has increased in recent years. The reconstructed pH is around 7.1-7.2. This reconstructed value falls slightly below that of the spot sample taken in July 1989 (7.6) (Appendix 1).

Discussion

Carbonaceous particle analysis suggests there is approximately 100 years of sedimentation recorded in the core. Over this period the diatom data suggest there has been an increase in nutrient input to the lake. This lake does not appear sensitive to acidification and there is no indication of acidification over the time-span of the core.

Figure 5.23   Lac des Perches: sediment characteristics
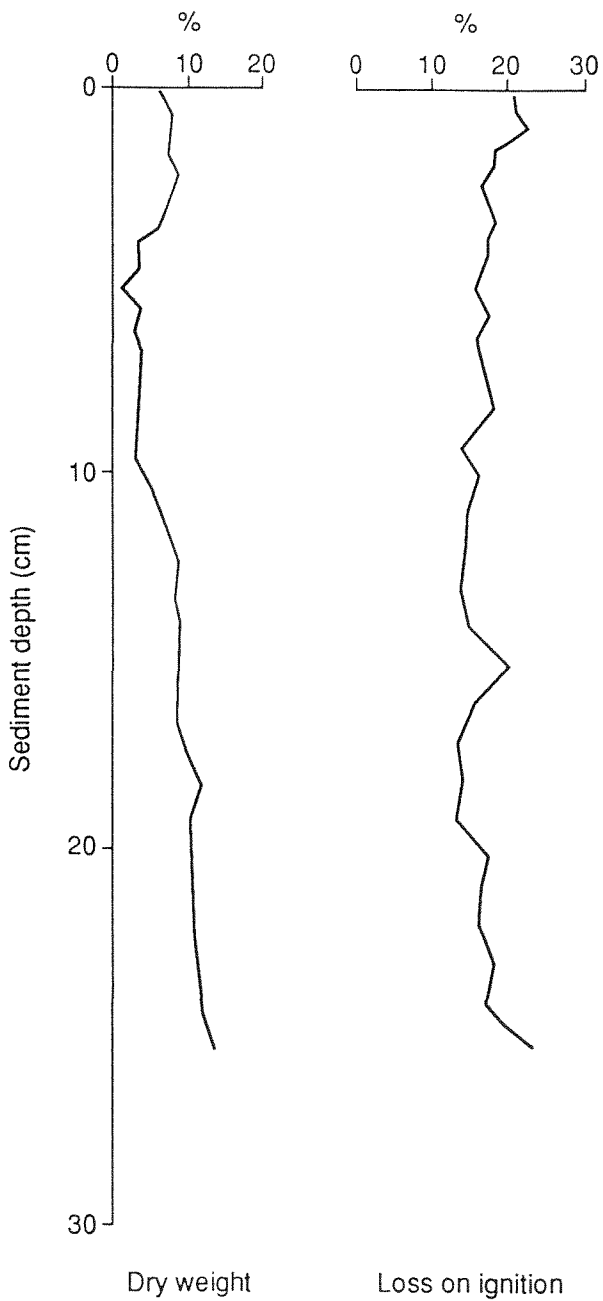
Figure 5.24 Lac des Perches: carbonaceous particle concentrations plotted against
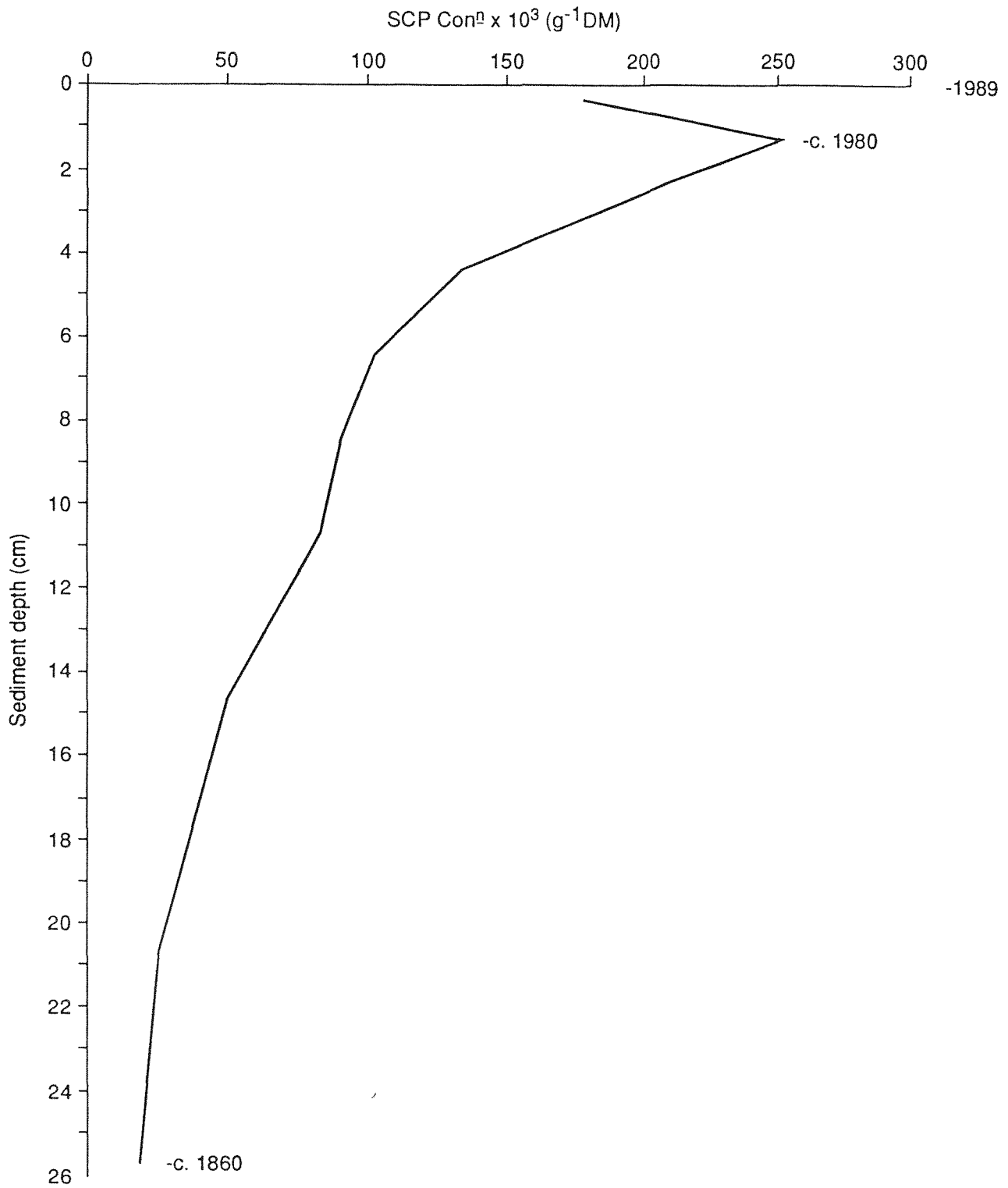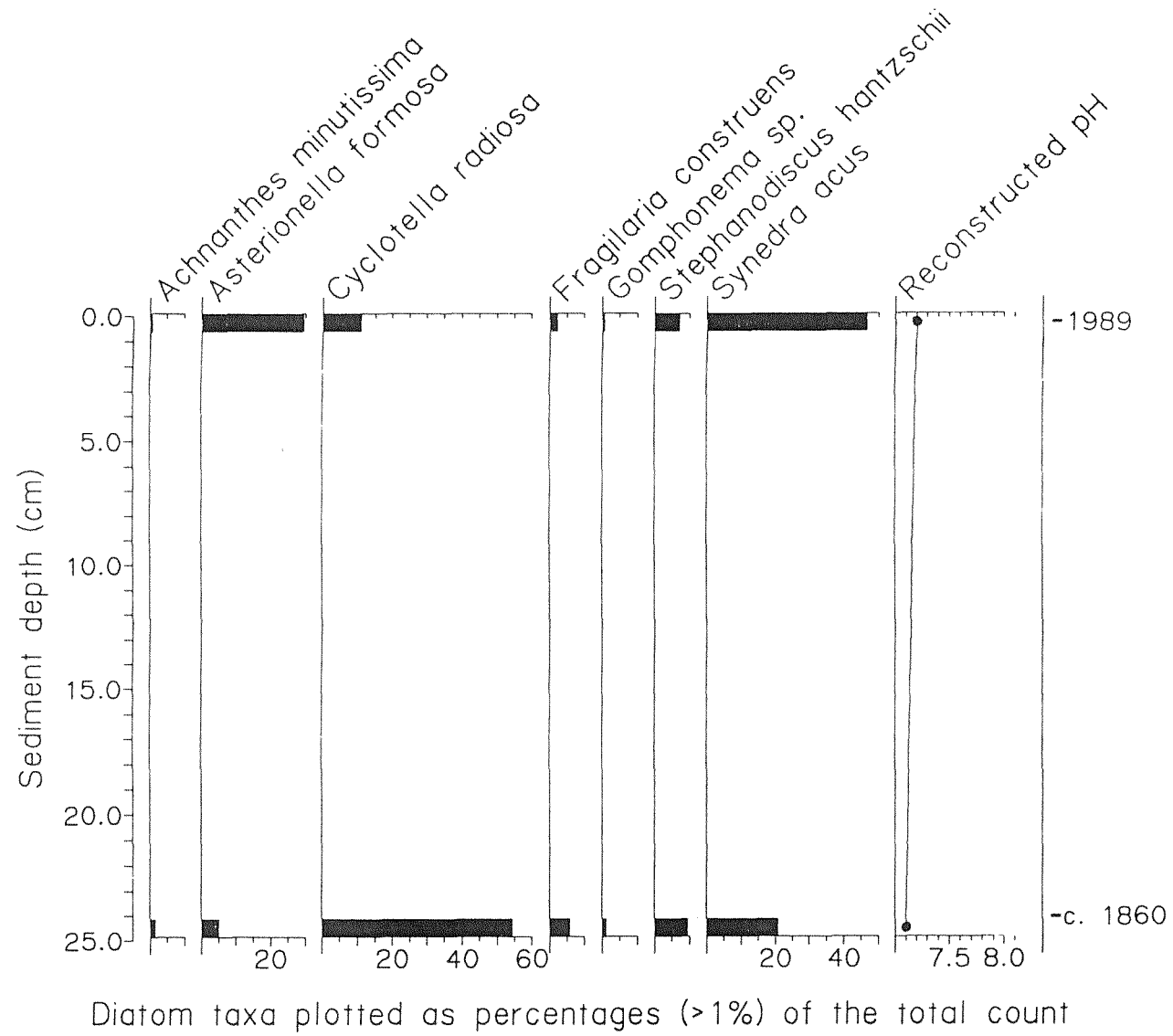sediment depth

SCP Con$^{\underline{n}}$ x 10^3 (g^{-1}DM)

Sediment depth (cm)

-1989

-c. 1980

-c. 1860

Figure 5.25　Lac des Perches: diatom diagram and pH reconstruction

Diatom taxa plotted as percentages (>1%) of the total count

5i   LAC DE RETOURNEMER

Site description

Lac de Retournemer (Figure 2.1) lies in a broad valley at 776 m altitude, surrounded by pasture. Much of the catchment (maximum altitude 1306 m) is forested. Maximum water depth is 14 m and the lake has a small sluice on the outflow. A road and several houses are present in the catchment.

Sediment stratigraphy

Two Kajak cores were taken in 12 m water depth in July 1989. Core RETO1 was chosen for analysis. The top 4 cm is a brown organic sediment. Below this the mineral component of the sediment increases suggesting episodes of erosion from the catchment or littoral zone. The changes in sediment composition are evident in the dry mass and LOI profiles in Figure 5.26.

Carbonaceous particle analysis

The carbonaceous particle profile is shown in Figure 5.27. A peak in concentration occurs between 1.5-2.0 cm suggesting an accumulation rate of about 3 mm yr^{-1}. Below this point the accumulation rate may not be constant throughout this core. There are two indications for this. Firstly, the rapid increase in concentration above 19 cm occurs earlier than would be expected if one simply extrapolates the recent sediment accumulation rate back down the core Secondly, the particle profile is not the 'typical' shape that would be expected with a core which has constant accumulation (cf. Lac Blanchemer, Lac des Perches, Lac Vert). The bottom of the particle profile is not reached at the bottom of the core.

Diatom analysis

The surface sample and samples from 2 cm, 4 cm, 8 cm and 20 cm depth in RETO1 have been analysed for diatoms. A summary diatom diagram including the pH reconstruction are shown in Figure 5.28. The poor state of preservation of the diatoms in this core may result from post-depositional re-working of the sediment since disturbances in sediment accumulation are indicated by the fluctuations in the mineral component. Most of the diatom frustules observed were incomplete. The diatom species present all suggest a mesotrophic lake moving towards eutrophic conditions. The main change in the diatom flora occurs between 20 cm and 2 cm with an increase in *Asterionella formosa*. *Achnanthes minutissima* decreases over the same period. This, along with the significant proportions of *Synedra acus*, suggests an increasing nutrient supply to the lake. There is an indication of a reversal in this trend in the surface assemblage where *A. formosa* has declined significantly and *F. construens* var. *venter* and *A. minutissima* increase. The reconstructed pH follows the trend in the *A. formosa* curve, increasing from 6.6 to 7.3 up the core before declining to pH 6.7 at the surface. The only available measured pH data (April 1992) records a value of 6.91.

Discussion

The core contains evidence of disturbances in the sediment accumulation rate, as shown in the sediment characteristics (dry mass and LOI profiles), the carbonaceous particle profile and the degree of diatom valve breakage. This may be linked to catchment disturbances or water level control. The diatom changes within the core suggest a history of nutrient enrichment rather than acidification. Since the base of the carbonaceous particle profile is truncated it is difficult to place a definite timescale on the changes but it is probable the changes have occurred over the last 50 years. The diatom data suggest a decrease in nutrient loading above the carbonaceous particle peak at 1.5 cm, placing the timing of this decline after 1980.

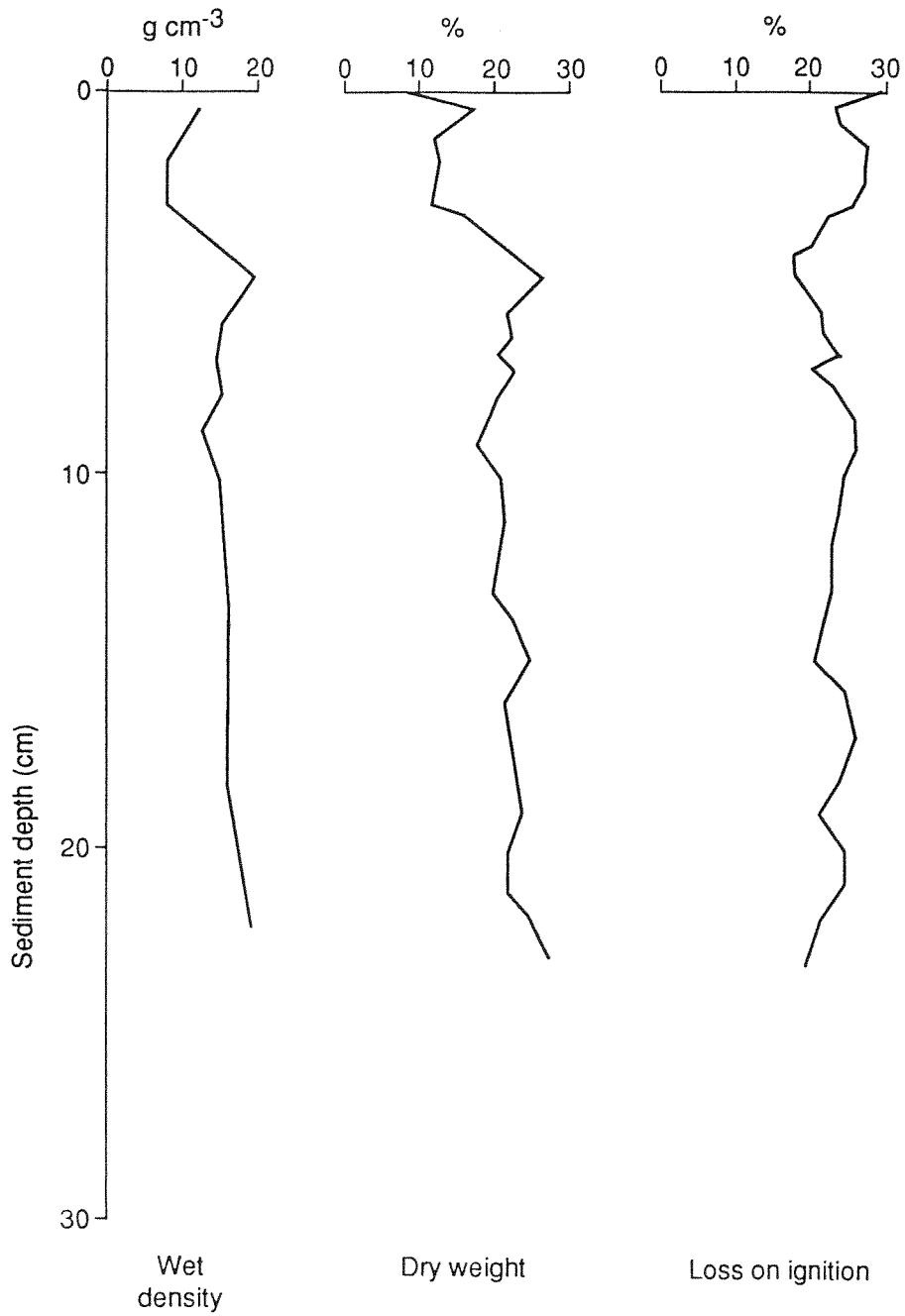**Figure 5.26   Lac de Retournemer: sediment characteristics**

Figure 5.27   Lac de Retournemer: carbonaceous particle concentrations plotted against
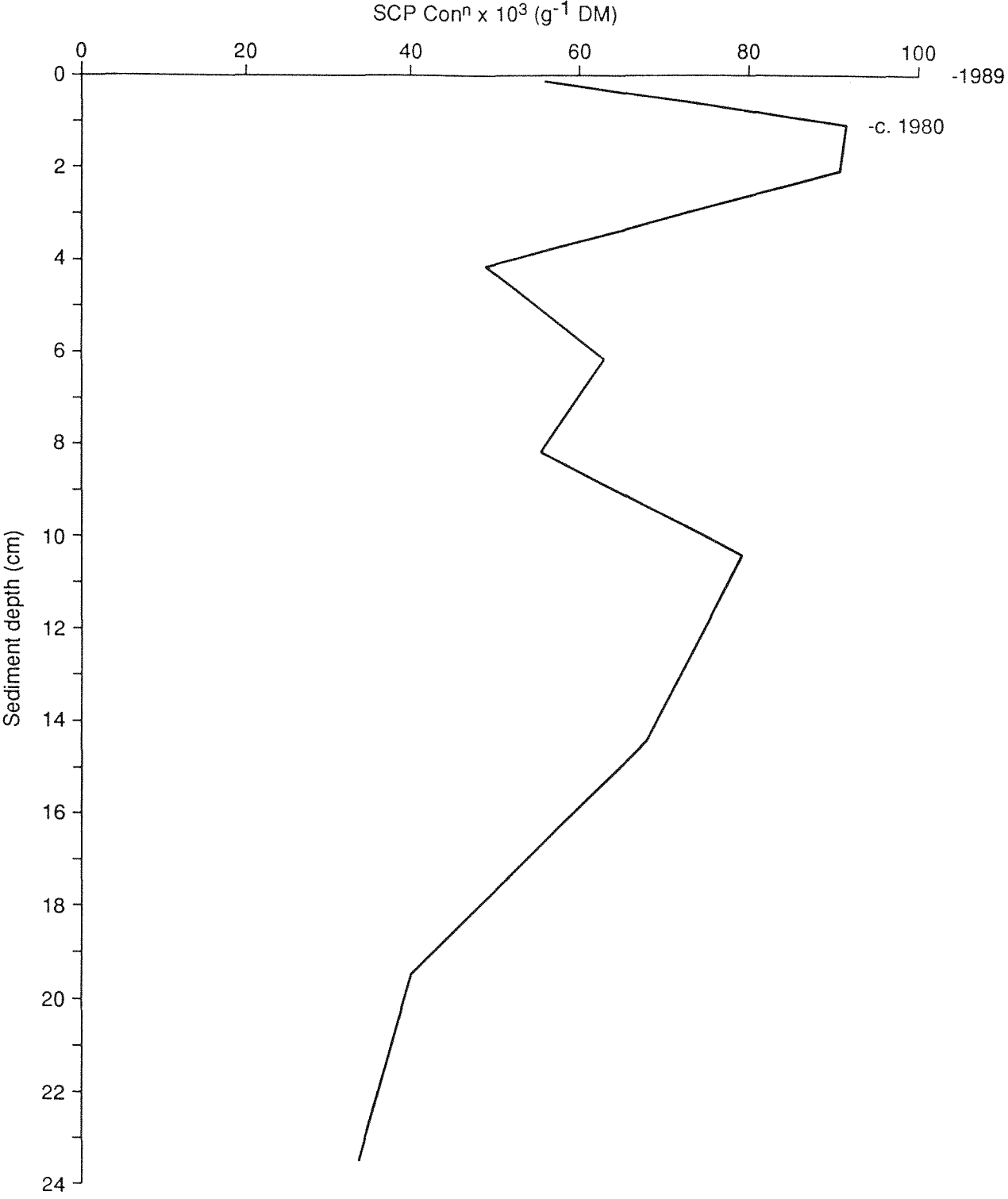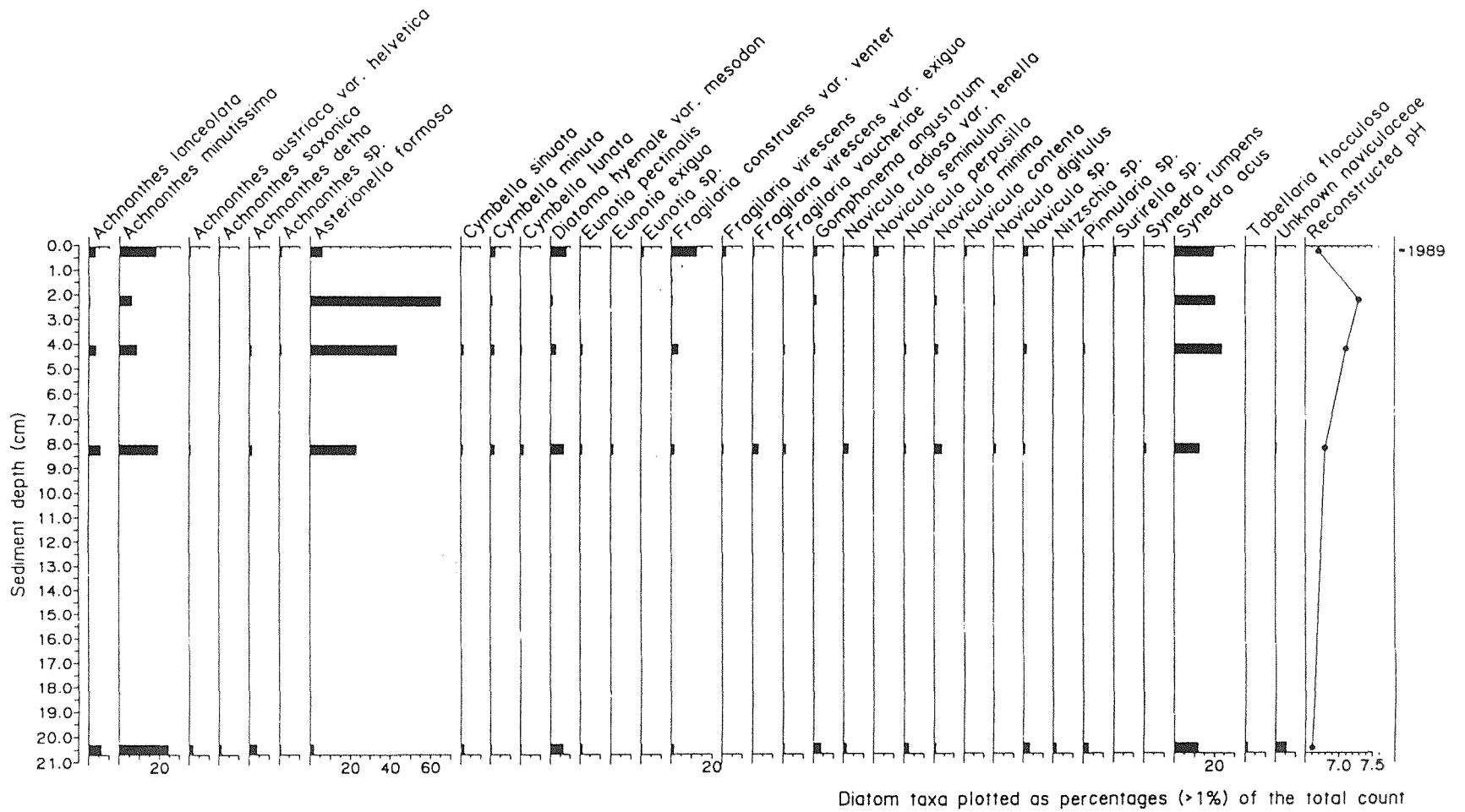sediment depth

Figure 5.28   Lac de Retournemer: diatom diagram and pH reconstruction

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Diatom taxa plotted as percentages (>1%) of the total count

5j   LAC VERT

Site description

Lac Vert (Figure 2.1) lies at 1100 m altitude with the highest point of the catchment at 1228 m. Water level (maximum depth 20 m) in the lake is artificially raised by a dam. The catchment is forested entirely by mature spruce trees right up to the waters edge. In July 1989 the lake had a pH of 7.0 and an alkalinity of 104 μeq l^{-1} (Appendix 1).

Sediment stratigraphy

Two kajak cores were taken from the deepest point of the lake in July 1989. Core VERT1 was chosen for analysis. The sediment is a mid-brown organic detritus with a high diatom content. The dry mass and LOI profiles are shown in Figure 5.29 and indicate a steady increase in the mineral component of the sediment down the core.

Carbonaceous particle analysis

The carbonaceous particle profile is shown in Figure 5.30. The concentration peak occurs at 4.0-4.5 cm which, if dated to the early 1980s suggests an accumulation rate of about 5 mm yr^{-1}. The shape of the curve suggests that the peak may be above this level, perhaps at 3.0-4.0 cm altering the accumulation rate to about 3-4 mm yr^{-1}. Such an accumulation rate would date the rapid increase in concentration at about 14 cm to the 1940s. The bottom of the profile is not reached at the bottom of the core at 30-31 cm (1880s - 1900s) although the particle concentrations are very low here and it is probable that the profile does not extend much further below this point.

Diatom Analysis

Three samples from the surface sediment, 2 cm and 20 cm depths have been analysed. A summary diatom diagram and pH reconstruction are shown in Figure 5.31. This site is unusual in its lack of diversity in the diatom flora. The assemblages are dominated by *Aulacoseira subarctica* Type 2 along with *Synedra acus* and *Asterionella formosa*. All these taxa are planktonic and benthic taxa are extremely rare. The reconstructed pH values of all three samples is pH 7.0 which corresponds exactly with that measured at the time of sampling (Appendix 1).

Discussion

Although the proportions of the main diatom taxa fluctuate, there is no evidence of any gross changes in the lake chemistry. This lake is unlikely to become acidified as a result of acid deposition. The predominance of planktonic taxa may be due to the lack of suitable diatom habitats around the lake margins as a result of shading by coniferous trees planted close to the waters edge.

Figure 5.29   Lac Vert: sediment characteristics

Dry weight   Loss on ignition
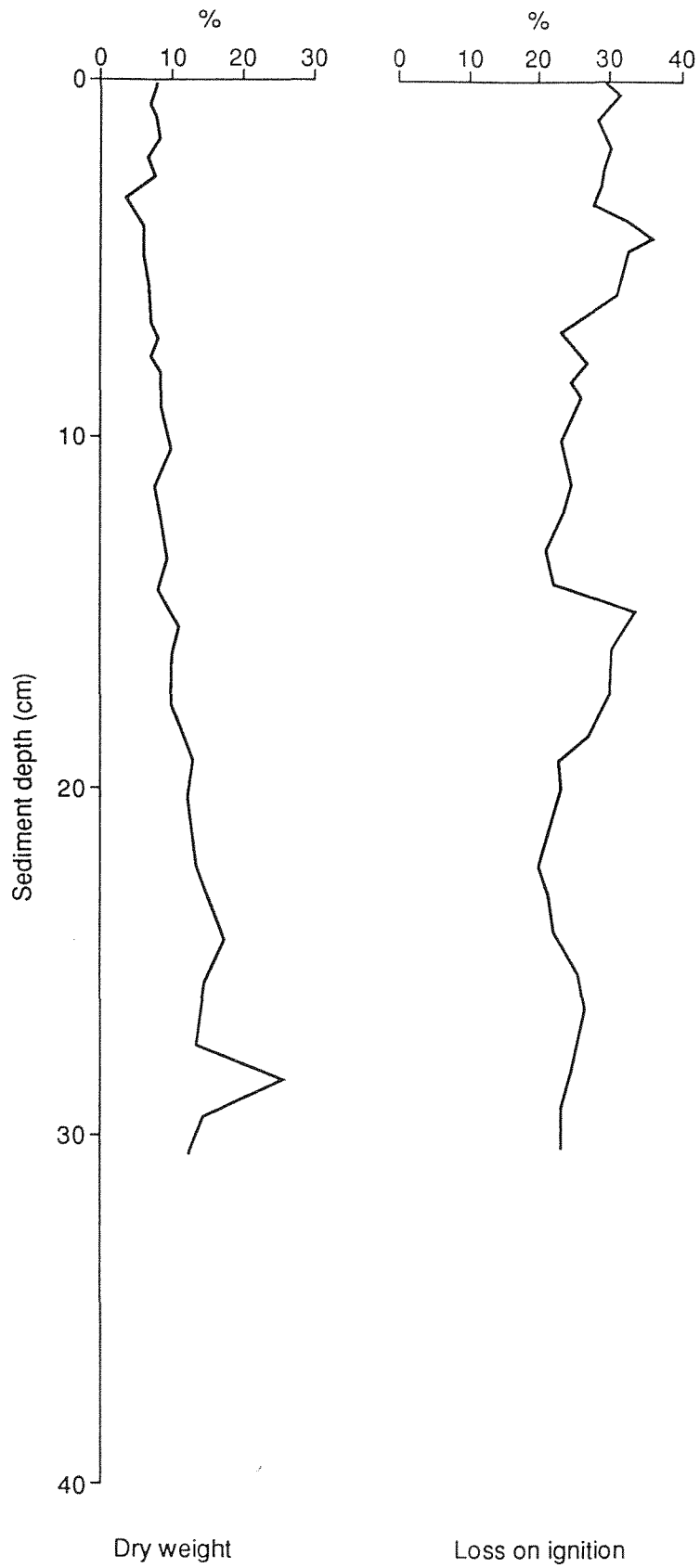
Figure 5.30   Lac Vert: carbonaceous particle concentrations plotted against sediment depth

Figure 5.31 Lac Vert: diatom diagram and pH reconstruction
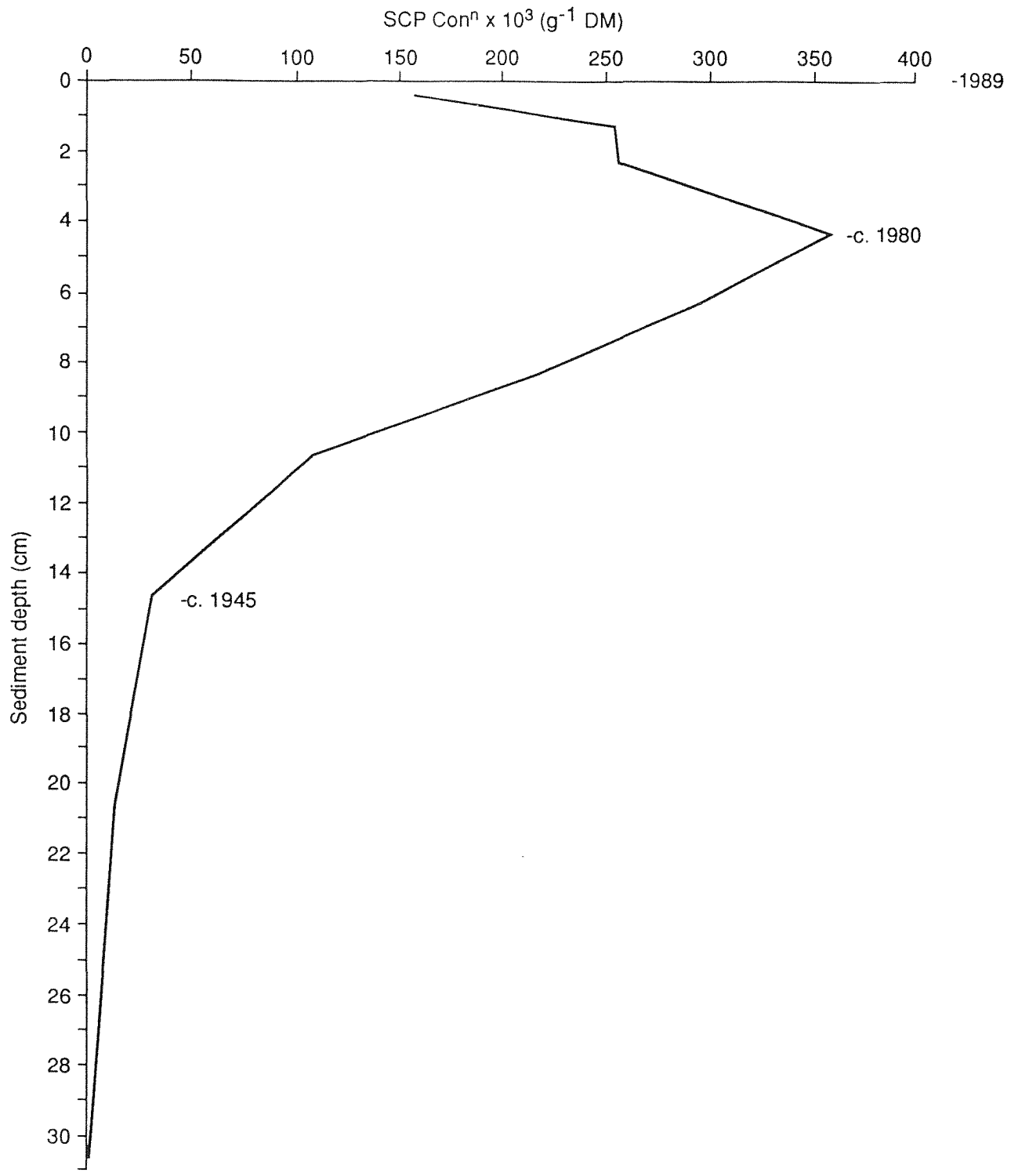
5k   GENERAL DISCUSSION

Deposition history

The carbonaceous particle profiles for the cores analysed confirm that the Vosges region has been exposed to atmospheric contamination from combustion sources over the nineteenth and twentieth centuries. In the two dated cores from Lac de Gérardmer (Section 4) and Lac des Corbeaux, the features on the carbonaceous particle profiles are dated to approximately the same time as similar features on profiles from cores in the United Kingdom (Rose 1991). However, the deposition histories of the two regions are unlikely to be the same so the carbonaceous particle profiles from these cores from the Vosges region should be compared to French (and German) statistics.

Figure 5.32 shows electricity production for France between 1929 and 1989 (United Nations 1952, 1976, 1979, 1981, 1986, 1990 & 1991). Both thermal (ie. coal, oil and gas, but not nuclear) and total (including nuclear and hydroelectric) are shown. Solid fuels (hard coal and lignite) represent the majority of the thermal production. It can be seen that in recent years that there has been an increase in nuclear energy electricity production and a decrease in the use of fossil-fuels. The peak in electricity production from fossil-fuels occurred in 1976 and since then there has been a general decrease in their use. Figure 5.33 shows the same data for both West and East Germany. The curve for East Germany shows that most of the electricity produced has been from fossil-fuel sources and that there has been no reduction in recent years. The curves for West Germany follow similar trends to those of France, although at any one point in time they are much higher. Again the introduction and increase in the use of nuclear energy has shown a decline (although this is less marked) in the use of fossil-fuels for electricity production. The peak in the use of fossil-fuels for electricity production in West Germany occurs in 1979.

In United Kingdom cores, the peak in particle depositions occurred in 1976-1977, but this has been only detectable in sediment cores taken after 1985. This delay in response by the sediment was attributed to a variety of factors such as bioturbation and the effects of water currents (Rose 1991). If such a delay also occurs in the Vosges cores then a peak in particle deposition around 1980 may not be seen in a core taken in 1987 (Lac des Corbeaux) but would be seen in cores taken in 1989. Such a peak occurred in West German electricity production. The French peak occurred in 1976 and it might be expected that this should have been seen in these cores.

In many of the cores there is a significant decrease in particle concentration at the surface (eg. Lac de Blanchemer, Lac Vert) and this is in closer agreement with the French electricity production curve for fossil-fuels than the West German case where the reductions are lower. West German electricity production has, however, always used substantially more fossil-fuels in the production of electricity than their French counterparts.

It seems therefore that the particle profiles in the Vosges sediment cores mainly reflect French combustion. However, it is likely that to some degree a combination of the two countries emissions are represented here and further work is would be required to determine the extent of each contribution.

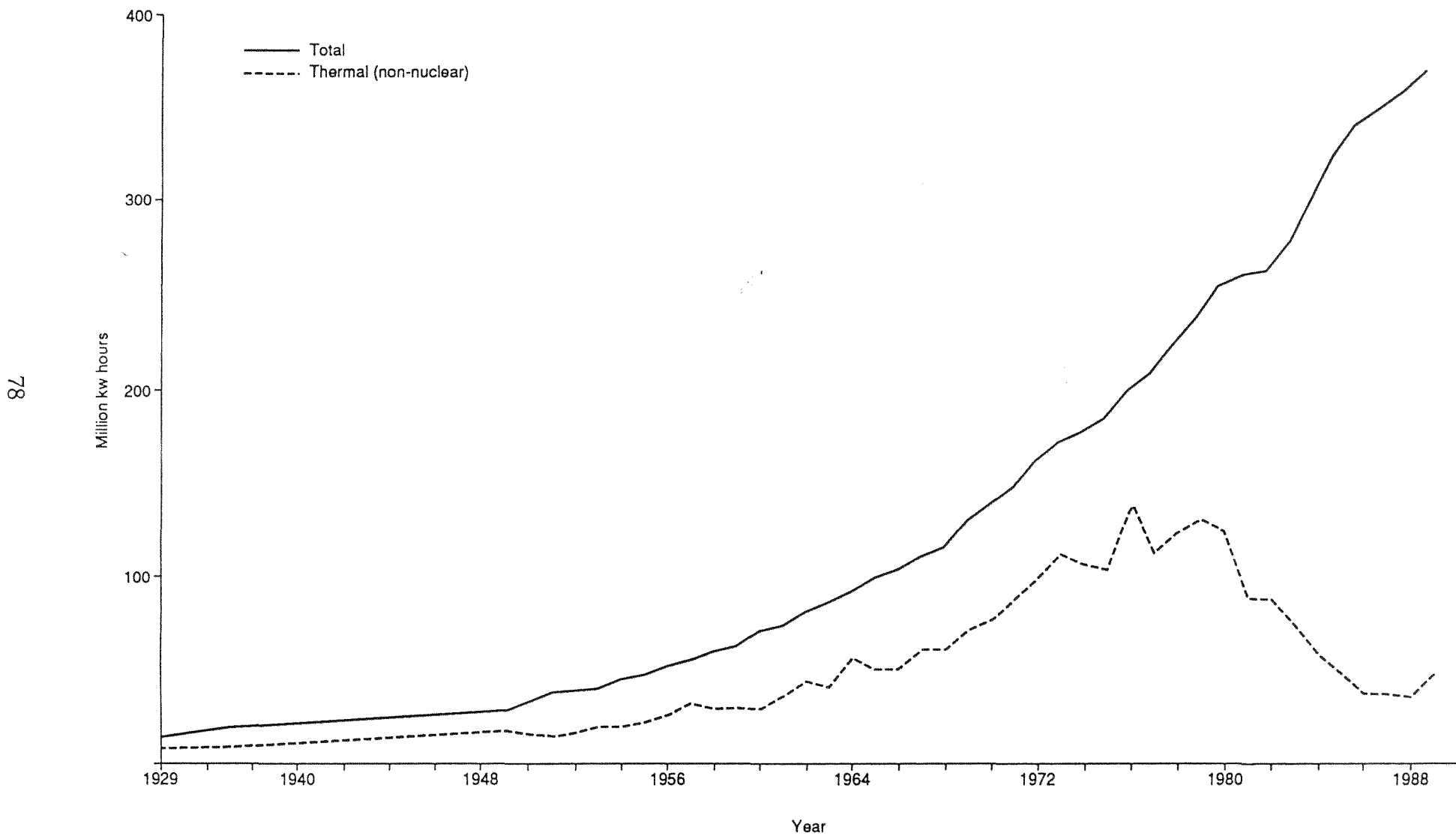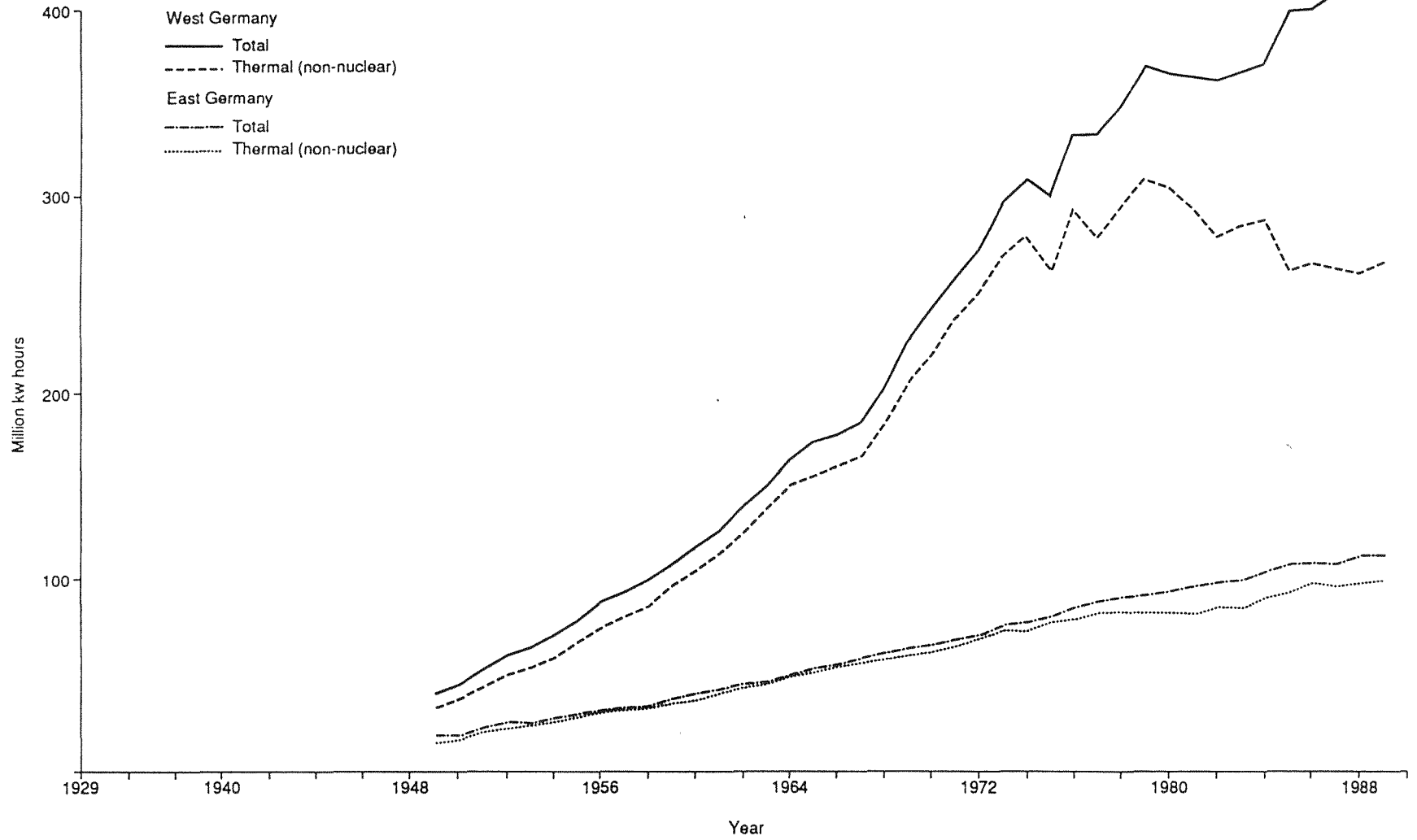**Figure 5.32   Electricity production, France, for the years 1929 - 1989**

Figure 5.33   Electricity production, Germany, for the years 1949 - 1989.

Acidification history

Of the nine sites investigated in this acidification study, only one site, Lac des Corbeaux, shows clear evidence of recent acidification. Two sites, Lac de Lispach and Lac de la Maix have fairly acidic diatom floras and could be vulnerable to acidification although there is no evidence that the lakes have acidified over the time-span of the cores. Cores from the remaining sites, with the exception of Lac de Blanchemer, show no evidence of recent acidification and from the diatom floras would appear to be insensitive to acid deposition at current rates. In the case of Lac de Retournemer the diatoms suggest the lake has received increased nutrient loading in recent years.

The diatom changes in Lac de Blanchemer could indicate mild acidification but since the floristic changes are accompanied by evidence of changes in sediment source, the diatom response may be linked to physical factors such as water level change, reduced transparency of the water or diatom habitat change. This problem of interpretation typically occurs in lakes where the water level is artificially controlled and where there may be rapid changes in water level over a short period of time. With the exception of Lac de la Maix, all the lakes in this study have an artificially maintained water level. In the cores from Lac d'Altenweiher, Lac de Ballon, Lac de Blanchemer, Lac de Lispach, Lac des Perches and Lac de Retournemer there is evidence of past fluctuations in water level in both the physical sediment characteristics and the carbonaceous particle concentrations.

Fluctuations in water level result in the erosion of coarser sediment from the littoral area which is then transported to the sediment deposition areas. The distribution of diatom habitats, and therefore the species composition of the diatom populations, will also change with water level changes. Larger decreases in water level may lead to the re-distribution of diatom deposits, resulting in the deposition of 'old' diatom valves above recently deposited diatoms. The poor preservation of diatoms suggests this may have occurred in Lac de Retournemer. For these reasons therefore, lakes with artificially maintained water levels are not ideal for core-based studies of past water quality. Despite this, this study shows that not all lakes with water level controls have a disturbed sediment record.

The lack of modern measured water chemistry data with which to compare and calibrate surface sediment pH reconstructions is a hinderance to a definitive assessment of water quality from palaeolimnological data. However, the stringency of palaeolimnological pH reconstructions have been validated many times and we may be confident that those presented here provide an accurate and representative record of mean water quality and the rate and magnitude of any recent change.

The limited data available (cf. Table 5.2, Appendix 1) suggest that there are wide short-term and spatial fluctuations in the water chemistry (notably pH) of surface waters in the Vosges, it is also apparent from this study and further indicated by Massabuau et al. (1988) that there is a significant difference in response to acid deposition by surface waters over relatively small distances elsewhere within the Vosges region. To assess fully the acidification status of surface waters throughout the region a combined water chemistry, diatom and mathematical modelling exercise (cf. CLAG 1992) should be undertaken on streams and lakes throughout the Vosges Mountains. This would allow critical loads and critical load exceedances to be calculated according to international protocols. Additionally, more detailed information is

required on forest and associated management practices in specific catchments to ascertain the extent to which land-management is responsible for short-term fluctuations and longer-term change in water quality.

Conclusions

1) Lakes in the Vosges region have been exposed to atmospheric contamination over the nineteenth and twentieth centuries. Carbonaceous particle profiles from the 10 Vosges lakes show fairly consistent patterns. With more ^{210}Pb dating higher confidence could be placed on the allocation of dates by these indirect means although these results suggest that there should be good agreement between sites.

2) It seems likely that carbonaceous particles are entering the lake from both France and West Germany. It is probable that this is mostly due to French combustion of fossil-fuels to produce electricity although further work would be necessary to determine the extent of each countries input to this region.

3) Lac des Corbeaux shows clear evidence of acidification dating from the mid-nineteenth century.

4) Lac de la Maix appears to be sensitive to acidification but there is no evidence of acidification in the short core analysed. Analysis of a longer core from this site, accompanied by ^{210}Pb dating would be worthwhile since this site appears to have a fairly fast sediment accumulation rate (compared with Lac des Corbeaux) and no artificial control on the outflow.

5) Two of the lakes, Lac de Retournemer and lac des Perches appear to have received increased nutrient loadings

6) Six lakes show evidence of disturbance in the sediment record probably as a result of water level fluctuations.

7) The spatial variation of water quality history and contemporary status within the Vosges region is confirmed by this study. From an acidification perspective, a more extensive, critical loads-based survey would be an appropriate extension to this palaeolimnological study.

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Appendix 1   Water chemistry: spot samples from study sites, July 1989[1]

	L. des Corbeaux	L. d'Alt-enweiher	L. de Ballon	L. de Blan-chemer	L. de Gerardmer	L. de Lispach	L. de la Maix	L. des Perches	Lac Vert
pH	6.64	6.81	7.10	6.80	7.25	6.69	5.60	7.62	7.00
Conductivity ($\mu S\ cm^{-2}$)	20.22	21.75	35.12	22.60	70.33	27.12	35.04	61.09	22.74
Alkalinity ($\mu eq\ l^{-1}$)	40	79	171	92	89	55	5	533	104
Na^+ ($\mu eq\ l^{-1}$)	56	44	77	51	387	124	54	49	78
K^+ ($\mu eq\ l^{-1}$)	8	12	9	9	21	5	41	7	8
Mg^{2+} ($\mu eq\ l^{-1}$)	34	56	66	62	62	40	54	56	44
Ca^{2+} ($\mu eq\ l^{-1}$)	92	86	198	96	180	86	108	544	96
Total Al ($\mu g\ l^{-1}$)	59.4	34.0	35.1	51.1	34.8	84.0	202.0	12.3	28.7
Cl^- ($\mu eq\ l^{-1}$)	39	36	68	44	384	105	58	32	34
NO_3^- ($\mu eq\ l^{-1}$)	30	13	33	7	19	<1	57	<1	<1
SO_4^{2-} ($\mu eq\ l^{-1}$)	78	64	72	58	128	56	158	78	76
PO_4^{3-} ($\mu eq\ l^{-1}$)	*	*	*	*	*	*	*	*	*

[1] Analyses by A. Probst CNRS/University of Strasbourg
* below detection limit

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