The recent palaeolimnology of Woolmer Pond, Hampshire, with special reference to the documentary history and distribution of the Natterjack toad, *Bufo calamita* L.

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1.0 Introduction.

Recent acidification of freshwaters in the UK is an important environmental problem,the regional extent of which is only now becoming clear. In both Scotland and Wales many upland lakes situated on resistant bedrock are acidified (Fritz et al. 1986, Harriman et al. 1987, Flower et al. 1987). In England however, such sites are uncommon outside the Lake District and the Pennines and recent acidification of surface waters in lowland England has yet to be demonstrated. A few suitable sites are known but their occurrence is mainly restricted to base-poor areas in the south-east of the country, typically on the Upper and Lower Greensands of Cretaceous age.

Acid ponds and pools in south-east England are important habitats for acidophilous plants and a few sites still support viable though impoverished breeding populations of the Natterjack toad (Bufo calamita) (see Beebee & Griffin 1977, Beebee 1987). The Natterjack toad is recognised as a rare species in the UK and was given special protection under the Wild Creatures and Wild Plants Act 1975 (later updated by the Wildlife and Countryside Act 1981). Physical disturbance and loss of habitat are usually cited as causing the demise of the Natterjack in south-east England (Beebee & Griffin 1977, Bridson 1978). However, recent water acidification may be an important factor at some sites, causing habitat loss through the impairment of breeding ability. This study examines the evidence for habitat acidification at a very acid (pH <4.5) site, Woolmer Pond, in East Hampshire (Figure 1).

In this report evidence for increased acidity of Woolmer Pond is sought for by diatom analysis of a ^{210}Pb dated sediment core. In addition the sediment core is analysed for spherical carbonaceous particle ('soot') and trace metal contamination. Other aspects of the environmental history of Woolmer Pond are obtained from pollen analysis of the core and from documentary records which commence for the site with an account of its natural history by Gilbert White (1788-89).

2.0 Site description.

Woolmer Pond (Figure 1) (O.S. Grid. Ref. SU788319) lies on the Lower Greensands of east Hampshire. In 1986 the area of open water measured about some 1.4 ha (Figure 1). The pond formerly occupied a much larger area but now an extensive marginal zone is dominated by Juncus and Molinia tussocks. Water depth varies seasonally but is always less than 60 cm and at the time of sampling (September 1985) maximum depth was only about 30 cm. Much of the surface sediment in the pond is covered with a carpet of Sphagnum moss. The outflow is now redundant and inflow streams are no longer discrete. The modern water level is maintained by direct precipitation. The pond water is strongly acidic, fairly low in dissolved ion concentrations and is moderately coloured (Table 1). There are several minor sources of alkalinity in the general area of the pond (Beebee 1987). These comprise a small sewage effluent discharge south-east of the pond and leachates from limestone road-fill in the south-west. None appear to have any significant effect on the quality of the open water. However, these local sources of alkalinity are very important for the few Natterjack toads which remain in the vicinity of the pond, although breeding pairs are now confined to several small wet areas in the general vicinity of the main pond (Beebee 1987).

Table 1 Water chemistry of Woolmer Pond, 1982. Ionic concentrations are in mg l^{-1}. * indicates measurements made in August 1985.

pH	4.0-4.5	4.4*	Total Fe	0.2
Conductivity ($uS\ cm^{-1}$)	109		Total Alk.	0.0
Na	9.9		Cl	6.0
K	3.3		SO_4	10.0
Ca	3.0		PO_4	0.13
NH_3	0.5		NO_3	ND

The pond lies in an area of low relief and the catchment (Figure 1) is ill-defined. Beyond the *Juncus* swamp an acid heathland vegetation is developed on well-drained podsols formed over sands. The heathland is dominated by *Calluna vulgaris*. The catchment also supports a woodland of *Pinus sylvestis* with *Betula* and *Salix* also common. Military activity around the pond is and has been intense. Currently the eastern section of the *Juncus* swamp is being cleared of vegetation and organic detritus as part of a Ministry of Defence restoration plan.

According to climatic records (Barrett *et al.* 1983, Barrett *et al.* 1987), Woolmer Pond is in an area of high sulphate deposition and the site lies at the boundary between 1.0 - 2.0 and 2.0 - 4.0 g of dry deposited S m^{-2} (1983 data). The pH of rainfall varies between 4.3 and 4.6. No data on total deposited acidity exists for the area but it is probably between 0.02 - 0.04 g H^+ m^{-2} y^{-1}.

2.1 Documentary history.

Around 1787 Gilbert White (1788-89, Letter VIII) described Woolmer Pond as a clear-water pool and estimated the area to be 66 acres (26.7 ha). He also noted that the pond had a clean sandy bottom and was stocked with several species of fish, although they did not thrive well. At this time the Woolmer Pond catchment seems to have been a treeless acid heathland dominated by *Calluna vulgaris* and *Pteridium*.

Natterjack toads were first reported in the Woolmer area by Bell (1839). Examination of 19th century maps shows that land around the pond had been partially afforested by 1872, although the size of the pond itself remained unchanged (cf. White 1788-89). In

1858 the area was occupied by the military (MoD records, unpublished). In the 1920s Lady Anne Brewis (in litt.), a local naturalist, wrote specifically about the fauna of Woolmer. She recorded that 1926 was a particularly good year for breeding Natterjacks and that the population of toads exceeded several hundred. She also noted that fish were apparently absent from the pond at that time and described the pond as being open water with a sandy bottom. However, by 1938 when the pond was visited by Balfour-Brown (1940) a carpet of Sphagnum had grown over the bottom of the pond.

Major physical disturbance of the pond and its environs began in the late 1930s, mainly as a result of Ministry of Defence wartime contingency plans. A network of railway lines was established around the north, east and south sides of the pond and perhaps more importantly for the pond biota, the site was drained. Examination of aerial photographs from September 1945 confirm that the site was by then dry. However, in 1951 when the site was visited by Ovenden (in litt.) open water was again present.

Despite these disturbances some Natterjacks were observed breeding at Woolmer Pond throughout the 1950s and early 1960s (Le Brocq in litt.). However, by 1963 observations of Natterjacks successfully breeding at Woolmer Pond were restricted to the south-east and south-west corners of the pond. Since this date there have been no observations of Natterjacks breeding in the main pond.

Routine measurements of water chemistry, particularly pH, began for Woolmer Pond in 1974 but no significant changes or trends are apparent in the data (Beebee unpublished).

3.0 Sediment history.

The gross stratigraphy of sediments underlying Woolmer Pond is approximately known (Figure 2) from a previous survey in 1978 (S. Everett, unpubl.). The pond occupies a depression in the Lower Greensands that has been partly infilled with organic matter. The lower section of infill lies on iron rich sand and is about 30 cm thick and consists of highly humified peat mixed with sand. This sandy layer is overlaid by c. 5 cm of fibrous peat with woody plant remains. A sand lens occurs above the fibrous peat and is covered with a surface layer of organic detritus. Interestingly, Gilbert White notes that peat cutting was formerly extensive in the Woolmer area and the occurrence of wood peat in the stratigraphy could indicate that the pond owes its origin to this activity in the Middle Ages or earlier. Roberts (1986) notes that many ponds were constructed for fish farming in southern England in the medieval period but identifies Woolmer Pond as a Royal fishpond.

The recent palaeolimnology of Woolmer Pond was investigated by analysis of a short sediment core obtained from the central area of open water. The core was collected in August 1985 by pushing a 5.5 cm diameter plexiglas tube into the surficial sediment. On return to the laboratory the core was extruded and sectioned at 1 cm intervals. After subsampling, the sediment was analysed as follows:

3.1 Stratigraphy and basic gravimetric analyses.

The sediment core measured 28 cm in length of which the top 0 - 6 cm section was composed of coarse black organic detritus (Figure 3) and appeared to be composed mainly of Sphagnum remains. The 6 - 8 cm section consisted of mixed detritus and sand below which pure sand occurred. Below about 19 cm organic fragments became common within the sand layer and at 25 cm to the core base the sediment was composed entirely of wood peat. The gross sediment stratigraphy (Figure 2) indicates that the core had sampled the three upper layers of sediment present at the site.

Gravimetric measurements for wet density, percentage dry weight (from weight loss at 95° C), and percentage loss on ignition (from weight loss at 550° C) were made on each 1 cm slice of sediment (Table 2, Figure 3). Wet density and percentage dry weight measurements are clearly related and show similar changes with highest values occurring in the sandy section of the core between 6 cm and 24 cm depth. Loss on ignition values varied in a reciprocal manner with those of wet density and percentage dry weight. Above 6 cm and below 24 cm over 80% of the sediment dry weight is organic matter.

Table 2 Results of gravimetric analysis for wet density, percentage dry weight and percentage loss on ignition of the Woolmer Pond core.

Sediment depth (cm)	Wet density (g cm^{-3})	Dry weight (%)	Loss on ignition (%)
0.0 - 1.0	1.0315	8.4	70.3
1.0 - 2.0	1.0310	8.3	69.7
2.0 - 3.0	1.0455	9.1	69.7
3.0 - 4.0	1.0610	7.7	72.0
4.0 - 5.0	1.0590	8.5	76.2
5.0 - 6.0	1.0930	15.0	55.0
6.0 - 7.0	1.3865	54.2	7.6
7.0 - 8.0	1.4295	54.2	8.5
8.0 - 9.0	1.6910	71.8	2.6
9.0 - 10.0	1.6960	73.7	1.4
10.0 - 11.0	1.6985	76.1	1.7
11.0 - 12.0	------	----	---
12.0 - 13.0	1.7035	76.6	1.7
13.0 - 14.0	------	----	---
14.0 - 15.0	1.6666	74.5	2.2
15.0 - 16.0	------	----	---
16.0 - 17.0	1.3300	68.6	7.7
17.0 - 18.0	1.2310	67.3	8.3
18.0 - 19.0	1.3595	69.4	8.3
19.0 - 20.0	1.0400	38.4	19.2
20.0 - 21.0	1.0395	35.3	32.5
21.0 - 22.0	<1	32.3	26.9
22.0 - 23.0	<1	40.8	28.8
23.0 - 24.0	<1	33.2	27.0
24.0 - 25.0	<1	25.9	44.2
25.0 - 26.0	<1	15.8	81.0
26.0 - 27.0	<1	21.9	61.4
27.0 - 28.0	<1	28.4	33.6

Note: wet density values <1 are caused by air spaces associated with woody fragments in certain sediment samples.

3.2 Radiometric analysis and sediment chronology.

Dating of the Woolmer Pond sediment core was carried out by calculating concentrations of unsupported ^{210}Pb at selected levels throughout the core and assuming a constant rate of supply (CRS) of the isotope to the sediment surface (Appleby and Oldfield 1978). Unsupported ^{210}Pb was determined from measurements of total ^{210}Pb and ^{226}Ra; ^{137}Cs concentrations were also measured. All radiometric measurements were by direct gamma counting of untreated sub-samples of dry sediment and analytical methods follow Appleby et al. (1986). Results and estimated sediment dates according to the CRS model (Appleby and Oldfield 1978) are shown in Table 3.

The unsupported ^{210}Pb inventory of the core is 9.14 pCi cm^{-2} and represents a mean supply rate of 0.28 pCi cm^{-2} y^{-1}. This value is close to the flux for other lowland UK sites and suggests that isotope supply reflects the atmospheric flux. There is no detectable unsupported ^{210}Pb below 8 cm depth and this is probably linked with the transition from organic sediment to sand at the 6 - 8 cm depth level. The sand layer is likely to introduce some unknown error into the dating estimate because of at least two factors: large sand grains will tend to diminish gamma radiation emission by self-absorption and secondly, ^{210}Pb active organic particulate matter is unlikely to be retained by sand. These effects will tend to make the deeper sediment in the core section containing unsupported ^{210}Pb too old. There is however, some agreement between the 1936 ^{210}Pb date within the organic/sand transition layer at 6.5 cm and the documentary evidence for a change from sand to organic detritus by 1938 (see Section 2.1). Above the transition layer the CRS model indicates a doubling of the sediment accumulation rate since 1960, possibly caused by increased deposition of organic debris from encroachment of macrophytes at the site. Similarity of ^{210}Pb concentrations over the top 5 cm of the core could indicate sediment mixing rather than increasing sediment accumulation, though clear differences in heavy metal geochemistry over this section (see below) would tend to suggest the latter explanation. Another interpretation of the ^{210}Pb profile is that the strongly acid overlying water (pH 4.0 - 4.5) has desorbed lead from the uppermost sediment (cf. Simola _et al._ 1985) which would then cause all the calculated dates to be too old.

Table 3 Results of radiometric analysis of the Woolmer Pond Core and sediment chronology calculated using the CRS model (see text) of unsupported ^{210}Pb.

Depth	Total ^{210}Pb	Unsupported ^{210}Pb	^{226}Ra	Date	Sediment accumulation	Error
cm	pCi g^{-1}	pCi g^{-1}	pCi g^{-1}	AD	cm^{-1} y^{-1}	%
0.0	---	---	---	1985	----	---
0.5	8.51	7.8	0.7	1984	0.40	9.6
1.0	---	---	---	1982	0.37	9.3
1.5	9.20	8.8	0.5	1981	0.33	9.0
2.0	---	---	---	1979	0.30	8.7
2.5	---	---	---	1977	0.28	8.3
3.0	---	---	---	1976	0.26	7.9
3.5	9.70	9.5	0.2	1974	0.24	7.5
4.0	---	---	---	1972	0.16	6.7
4.5	10.3	9.8	0.3	1969	0.08	5.8
5.0	---	---	---	1961	0.07	6.2
5.5	---	---	---	1953	0.06	6.5
6.0	---	---	---	1944	0.05	6.8
6.5	4.1	3.5	0.5	1936	0.04	7.2
7.5	2.2	1.8	0.4	----	----	---
8.5	0.0	-0.2	0.2	----	----	---
13.5	0.1	-0.2	0.3	----	----	---
19.5	0.3	-0.2	0.4	----	----	---
27.5	0.0	-0.2	0.2	----	----	---

3.3 Trace metal geochemistry

The core was analysed at selected levels for four trace metals, lead, zinc, copper and nickel using standard spectrophotometric techniques (see Rippey et al. 1982). Results in Table 4 and Figure 4, show clearly that these metals are present in much higher concentrations above 7 cm than below this depth in the sediment. Trace metal concentrations rise by a factor of approximately four between 7.5 and 6.5 cm depth, corresponding closely with increasing organic content of the sediment. At the core top zinc and lead show declines in concentration above 3.5 and 2.5 cm depth respectively, the decline is particularly marked for zinc. Copper shows a small decline in concentration over the top few cm and nickel only shows a lower concentration in the top 0.0 - 0.5 cm section.

Although the metals show increased concentration beginning in the 1930s, the change in sediment composition during this period makes interpretation of the timing of trace metal enrichment difficult. These trace metals will be strongly adsorbed by organic material whereas sand will have little interaction with dissolved metal ions. Hence, it is possible that metal increases reflect increased loading or the change in sediment type, or both. In the absence of any known trace metal effluents entering the pond the trace metal profiles offer good evidence of atmospheric sources for the zinc, lead, copper and probably nickel contamination. The evidence of atmospheric contamination is:

i) If metal concentrations are merely a reflection of the amount of organic matter in the sediment then the basal organic layer should also have high metal concentrations.

ii) If metal concentrations were determined by scavenging by organics then copper, which has a high affinity for organic material, would be expected to be most enriched.

iii) The relative concentrations of the trace metal are indicative of atmospheric contamination (Rippey et al. 1982) and correspond with results from other sediment cores from Welsh (eg. Fritz et al. 1986) and Scottish lakes (eg. Battarbee et al. 1985) where contamination from atmospheric sources has been demonstrated.

The decline in concentration, particularly of lead and zinc, in the top 2 - 3 cm is an interesting feature of this core and could indicate metal desorption by the overlying acid water or a recent decrease in metal contamination. If however, the ^{210}Pb chronology is assumed to be accurate then the trace metal accumulation rates can be calculated (Figure 4). This Figure clearly demonstrates the effect of an increasing rate of gross sediment accumulation at the core top and shows that the accumulation rate of zinc declines in the surface 2 cm of sediment (post-1970s). Conversely accumulation rates of the other metals are at maximum values in the top 2 cm of sediment. Interpretation of these observations is difficult, trace metal declines in the most recent sediments, on both a per gramme sediment and accumulation rate basis, have been recorded in cores from several Welsh lakes (eg. Fritz et al. 1986), but the timing was different from that inferred for this site. The deposition of trace metals from the atmosphere has declined since about 1970 (Cawse 1981, Ruhling and Tyler 1984) so the fall in zinc flux may reflect this. On the other hand if declining atmospheric flux were the only factor involved then the other metal fluxes would be expected to decline also. It is well known that zinc sedimentation and retention is impaired in low pH waters (Norton <u>et</u> <u>al.</u> 1981, Salomons and Forstner 1984) and as only zinc declines in Woolmer Pond sediment it is likely that the pH effect predominates at Woolmer Pond, rather than any drop in atmospheric flux.

Table 4 **Trace metal concentrations in the Woolmer Pond sediment core**

Depth (cm)	Zn (ug g^{-1})	Pb (ug g^{-1})	Cu (ug g^{-1})	Ni (ug g-1)
0.5	218	230	84	32
1.5	316	267	85	39
2.5	410	292	99	36
3.5	478	283	99	34
4.5	484	290	98	33
5.5	490	298	111	33
6.5	206	125	59	13
7.5	42	30	10	4
9.5	34	23	8	4
12.5	25	6	3	5
18.5	29	18	4	5
24.5	31	8	7	8

3.4 Carbonaceous particle analysis

Lake sediments often contain carbonaceous spherules (5-100 µm diameter) that have originated from fossil fuel combustion (Griffen and Goldberg 1981, Renberg & Wik 1985a). Selected sub-samples of the Woolmer Pond core were analysed for these spherules using the method of Renberg & Wik (1985b). Results are shown in Figure 5 where the spherules are expressed in terms of concentration. Very few spherules are present in sediment below 7 cm or prior to the 1930s. Above 7 cm the concentration and accumulation rate increases to highest values in the top 2 cm or post 1970s sediment. The absence of these spherules in the sand layer prior to the 1930s indicates that either they were not deposited at the site then or that the sand in Woolmer pond represents an old non-accumulating substratum.

Although it is not yet possible to ascribe these spherules to any particular form of fossil fuel combustion, the probable timing of their increase in the Woolmer sediment core suggests that oil combustion is an important source. Whatever the precise source, these spherules offer strong evidence that Woolmer Pond has been and still is heavily impacted by atmospheric pollution.

3.5 Pollen analysis

Selected 1 cm sections of the core were sub-sampled and prepared for pollen analysis using standard methods (Stevenson *et al.* 1987). Major changes in pollen types are recorded in the core (Figures 6 and 7), particularly for the arboreal component where between 11.5 and 7.5 cm depth the frequency of *Quercus* declines markedly as *Pinus* increases. Herbaceous pollen also changes with *Calluna vulgaris* declining over the same depth section as the Gramineae and Cyperaceae increase. Aquatic plant pollen show variable occurrence with low abundances of *Littorella uniflora* and *Nyphaea* below 9.5 cm depth and *Typha latifola* occurring in the top 11.5 cm section. *Sphagnum* spores have an unusual distribution showing lowest frequencies (<10%) between 7.5 and 11.5 cm depth.

The major shifts in pollen frequencies occur several cm before the gross stratigraphic change from sand to organic detritus recorded in the top section of the core. This suggests that changes in pollen frequency probably reflect changes in the composition of pollen influx to the site rather than a change in sediment stratigraphy. The main inference from the pollen diagrams is that pre-1930s afforestation with pine replaced oak woodland and suppressed *Calluna* in the area surrounding the lake. The Cyperaceae profile probably reflects the development of the *Juncus* swamp and indicates that the process of basin invasion was well underway by the 1930s. Presumably this change was further promoted by water level lowering in the 1940s (see Section 2.1). Unfortunately the *Sphagnum* spore profile does not provide a record of the growth of the moss over the pond bottom. Frequencies are equally high at the top and bottom of the core and although the pond bed is currently carpeted with *Sphagnum* it is possibly reproducing in the aquatic environment by vegetative means rather than by spore production.

3.6 Diatom analysis

Sub-samples of sediment from every 1 cm section of sediment were prepared for diatom analysis using standard methods (Battarbee 1986). However, below 7 cm depth diatoms were progressively less abundant in the sediment and below 13 cm depth diatoms were virtually absent. Poor preservation of diatoms coincided with increasing sand content of the sediment, possibly indicating that ground water movement or downward seepage of the overlying water is responsible for the gradual dissolution of diatoms. In the upper organic layer diatom preservation was good with little sign of dissolution or valve breakage. However, analysis of this section of the core was compounded by taxonomic difficulties associated with the most common taxon which, for the purposes of this report, is referred to as *Eunotia carolina* v. *1*. This species dominates the diatom assemblage in the upper core section where it accounts for almost 80% of the count. The taxon shows some similarity to *Eunotia pectinalis* but is distinct in having a ventrally convex margin between the two proximal raphe nodules. It is to be described as a new species (Carter and Flower in review).

The biostratigraphic changes in percentage abundances of all the diatom taxa encountered in the core are shown in Figure 6. The most clear frequency change in this core is the increased abundance of *Eunotia carolina* v. *1* between 8 and 4 cm depth, corresponding with the period pre-1936 to 1972. Other less common taxa, *E. lunaris*, *E.* cf. *carolina* and *Nitzschia ganderheimensis*, also increase approximately concomitantly with *E. carolina* v. *1*. Several taxa show clear declines in abundance as *E. carolina* v. *1* assumes dominance, for example *Fragilaria virescens*, *E. pectinalis* v. *minor*, *Melosira perglabra* v. *florinae*, *Frustulia rhomboides* v. *saxonica* and *Pinnularia* spp. achieve highest frequencies in the 8 to 13 cm section of the core. Several taxa, *Tabellaria flocculosa*, *Anomoeoneis vitrea*, *Eunotia veneris*, *Achnanthes microcephala* and *Stauroneis kriegeri*, are unusual in having their maximum abundances in the transition section of the core between 8 - 6 cm, where *Eunotia carolina* v. *1* is beginning to increase.

3.7 pH reconstruction

Reconstruction of historical pH values for Woolmer pond is made difficult for two main reasons. pH values are normally computed from the abundances of diatom pH preference groupings (Flower 1986) and as *Eunotia carolina* v. *1* has not been previously described in the literature, its pH preference is unknown. Secondly, dating of the core is not secure and cannot be extended beyond the mid-1930s because of the change in sediment type at 6 - 7 cm depth. Despite these constraints evidence of pH change in the pond can be produced if past pH values are calculated firstly with *E. carolina* v. *1* accorded an acidobiontic preference and secondly with an acidophilous preference. Nearly all species in the *Eunotia* genus belong to one of these two categories and it seems reasonable to assume that *E. carolina* v. *1* is at least acidophilous. It is probably acidobiontic since it is currently flourishing in Woolmer Pond were the pH is normally below 4.5.

Consequently three pH curves have been calculated for Woolmer Pond (Figure 7), two result from using *E. carolina* v. *1* as acidobiontic and acidophilous in a multiple regression equation relating lake water pH to diatom pH preference (Flower 1986) and one curve results from the Index B method of pH calculation (Renberg and Hellberg 1982) with *E. carolina* v.*1* as acidiobiontic. pH values calculated from the surface sediment using both computational methods with *E. carolina* v. *1* as an acidobiontic diatom are between 4.4 and 4.5 and are in good agreement with the measured pH. The pH of 5.1 resulting from assuming *E. carolina* v. *1* is acidophilic is in poor agreement with measured pH. The pH values over the dated section of the core, down to 6.5 cm, show no trend changes, but below this depth pH increases to between 5.4 and 6.2 depending on the pH reconstruction method used.

4.0 Discussion

Both documentary and stratigraphic evidence show that Woolmer Pond has been subjected to considerable disturbance in the past. Two hundred years ago the pond was much larger than today, was relatively free of aquatic macrophytes, had a sandy bottom and was probably oligotrophic. Since that time the pond has been drained, the surface sediment has become carpeted with Sphagnum and Juncus and Molinia have encroached over 90% of its area. The available documentary evidence suggests that sandy surface sediment in the pond became covered with Sphagnum sometime between 1926 and 1938. This period agrees with the ^{210}Pb chronology which dates the base of the upper organic section of the core to around 1936. Drainage of the pond in the 1940s therefore precedes the development of the Sphagnum mat and also apparently precedes at least the initial encroachment of the Molinia/Juncus swamp, as indicated by the rise in Cyperaceae pollen which begins before 1936 (between 12 and 16 cm depth in the core). There are no data concerning changes in water level at the pond, although it is highly likely that the level after draining is considerably less than the pre-1940s level and this will have promoted further expansion of the marginal swamp.

The main feature of the Woolmer Pond sediment core is the change in gross stratigraphy at between 6 and 7 cm depth where a lower sandy layer changes to one of organic detritus. This change undoubtedly has a major effect on the metal profiles in the sediment. The absence of unsupported ^{210}Pb and very low concentrations of trace metals below 6 cm depth is related to the stratigraphic change since sand grains have little affinity for adsorbing metals. Hence a ^{210}pb chronology can only be tentatively established for the post-1936 period and the onset of trace metal contamination of the site can not be ascertained. There is only a very low concentration of 'soot' particles below the organic layer and it is not clear whether this represents the beginning of particulate contamination from the atmosphere or the change in stratigraphy. However, the concentrations of both trace metals and 'soot' in the upper 6 cm of sediment strongly indicate that pollution from atmospheric sources has impacted the site over at least the past 45 years. The main change in species composition of the sediment core diatom assemblage can not be attributed to the stratigraphic change as circumneutral taxa such as Fragilaria virescens begin to decline sharply at 9 cm depth, well before the change to organic detritus. This is good evidence that the site began to acidify strongly in the pre-1930s period, sometime before Sphagnum grew over sandy sediment.

With regard to the cause of the acidification of Woolmer Pond, it has been shown that atmospheric pollution (Flower et al. 1987,) and afforestation (Harriman and Morrison 1980) can cause recent acidification of susceptible freshwaters. Furthermore, development of a Sphagnum community is also known to cause water acidification (Clymo 1984). For Woolmer Pond there is evidence that all three factors have ocurred at the site and since the main period of acidification, as inferred from the diatoms (9.5 to 6.5 cm depth), occurs before the ^{210}Pb chronology begins, it is difficult to evaluate fully their relative importance. However, as the acidification period occurs prior to 1936 drainage and other associated land use changes can probably be excluded as the primary cause of acidification. It is known from documentary evidence that Sphagnum expanded in the pond between 1926 and 1938 and from the core analyses it is known that sometime before 1936 diatoms preferring less acid water decreased in abundance. Despite problems in the interpretation of the core data there is a plausible explanation of the observed changes in Woolmer Pond: at least since the 1920s acid deposition has caused water acidification and promoted the growth of Sphagnum and has diminished the abundance of diatoms intolerant of strongly acid water.

A comparison of the acidification history of Woolmer Pond with Natterjack toad records indicates that the toad population apparently persisted through the main pre-1936 period of acidification and other major land use changes (including habitat drainage) and that breeding success only ceased in the early 1960s. There is little evidence of increased acid or trace metal pollution in the 1960s and the diatom record indicates that the pH has been stable at around 5.0, or more probably around 4.5, depending on the pH reconstruction used, since the pre-1936 period. The important observation of Sphagnum in Woolmer Pond in 1938 confirms that the water was by then strongly acid. The Natterjack toad usually avoids sites where the pH is less than 5.5; larval development is severely restricted below this pH and is prevented entirely at pH 4.5 (Beebee and Griffin 1977). It is therefore thought unlikely that the Natterjack toad has bred successfully at Woolmer Pond since at least the 1930s. A reproductively stressed Natterjack population has persisted at the pond since this time probably by tolerating large larval mortalities and by exploiting the two very localized sources of alkalinity in the pond (Beebee 1987). Absence of recruitment from other Natterjack populations by loss of less acid habitats in the vicinity of Woolmer and/or change in the alkalinity sources within the pond could possibly account for the post-1960s disappearance of the breeding population in Woolmer pond.

5.0 Executive summary

1) Although the hydrology of Woolmer Pond has been severely disturbed, the diatom record in a dated sediment core is sufficiently good to show that the pond acidified at some time before the 1930s.

2) Evidence from the trace metal and carbonaceous ('soot') profiles in the core indicate that the site has been strongly affected by pollution from atmospheric sources.

3) Acid deposition is the most likely cause of the acidification before 1930 and the maintenance of low pH values since that time.

4) The Natterjack toad is unlikely to have bred successfully at Woolmer since at least the 1930s although a residual population persisted at Woolmer Pond until the 1960s by exploiting local point sources of alkalinity.

5) Work in progress in the nearby Cranmer Pond site should help to refine the time-scale of acidification in the Woolmer Pond area.

Fig. 1. Woolmer Pond and its catchment.

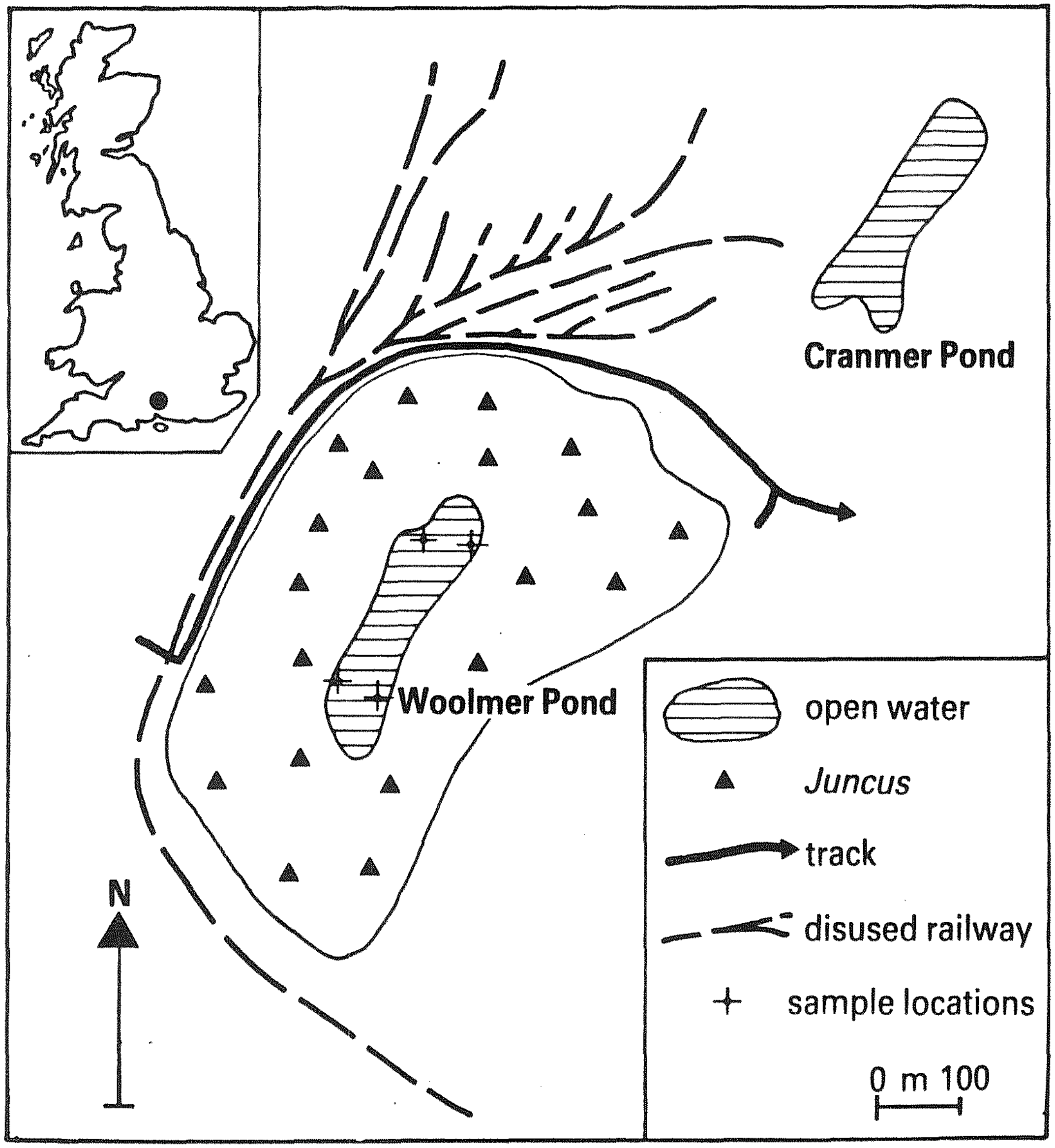


Fig. 2. Cross section of the Woolmer Pond substrata

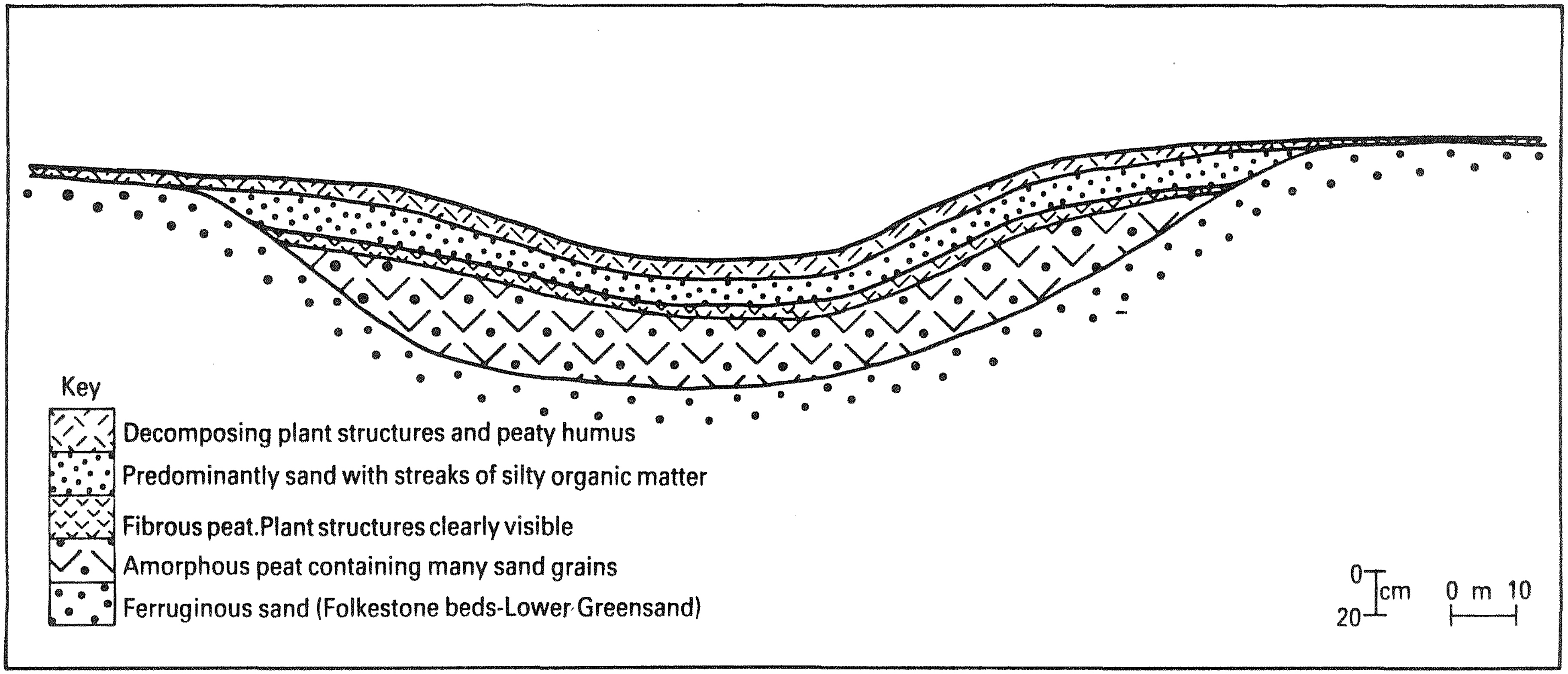


Fig. 3. Gravimetric data and stratigraphy for the Woolmer Pond Core.

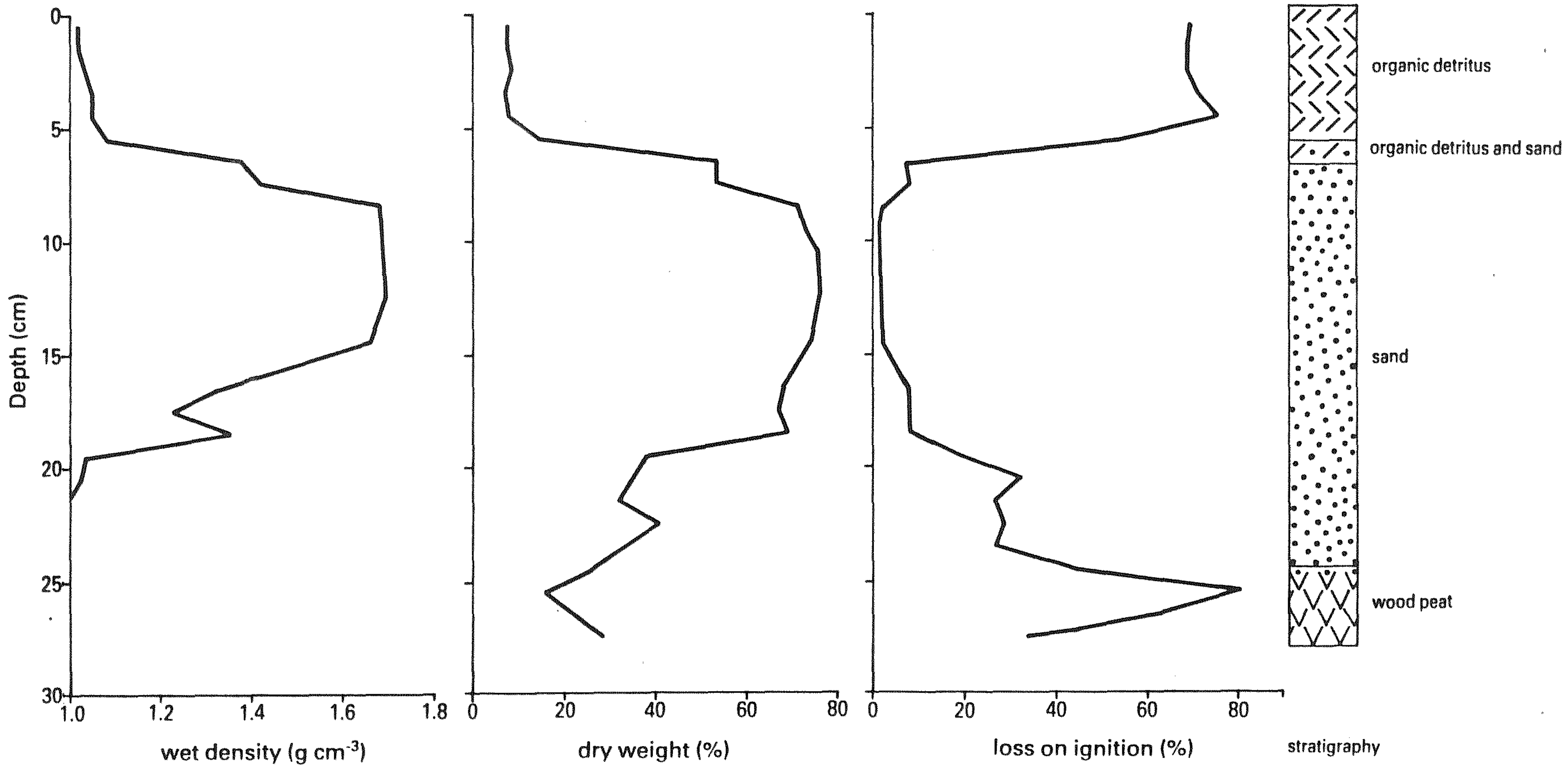


Fig. 4. Trace metal profiles for the Woolmer Pond Core.

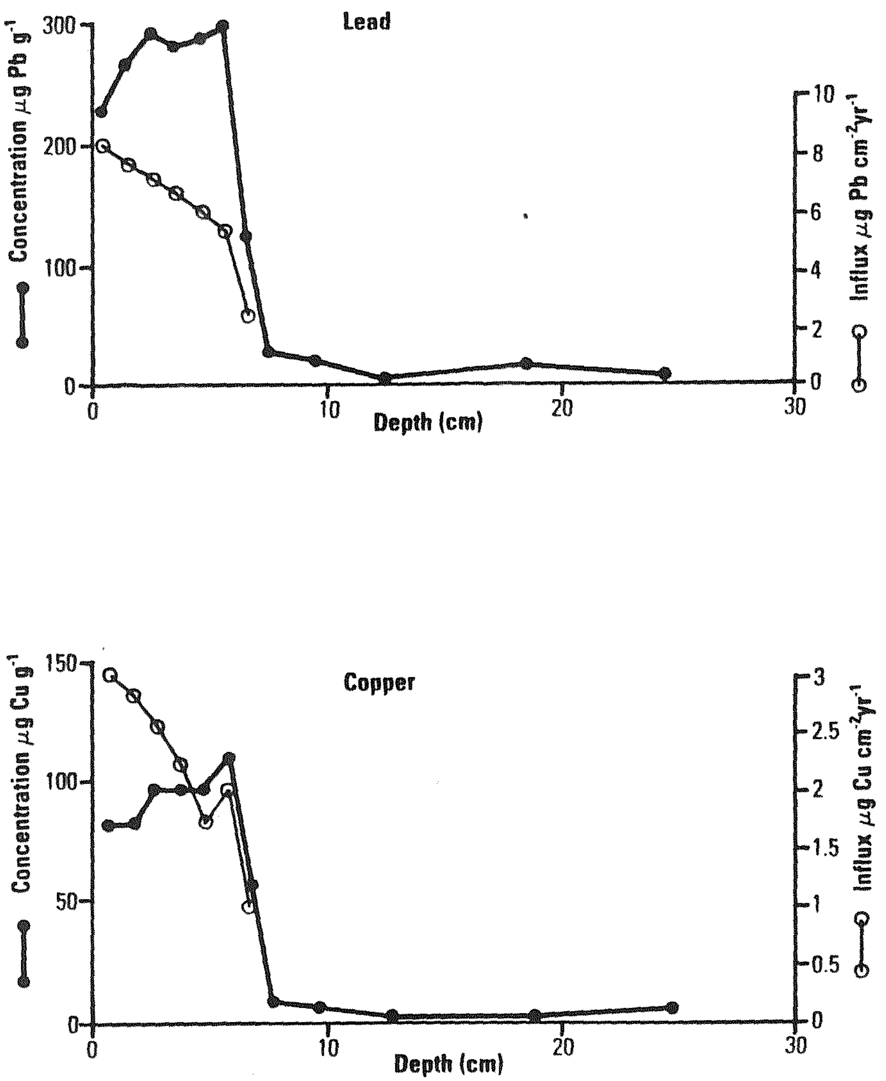


Fig. 4 Cont.

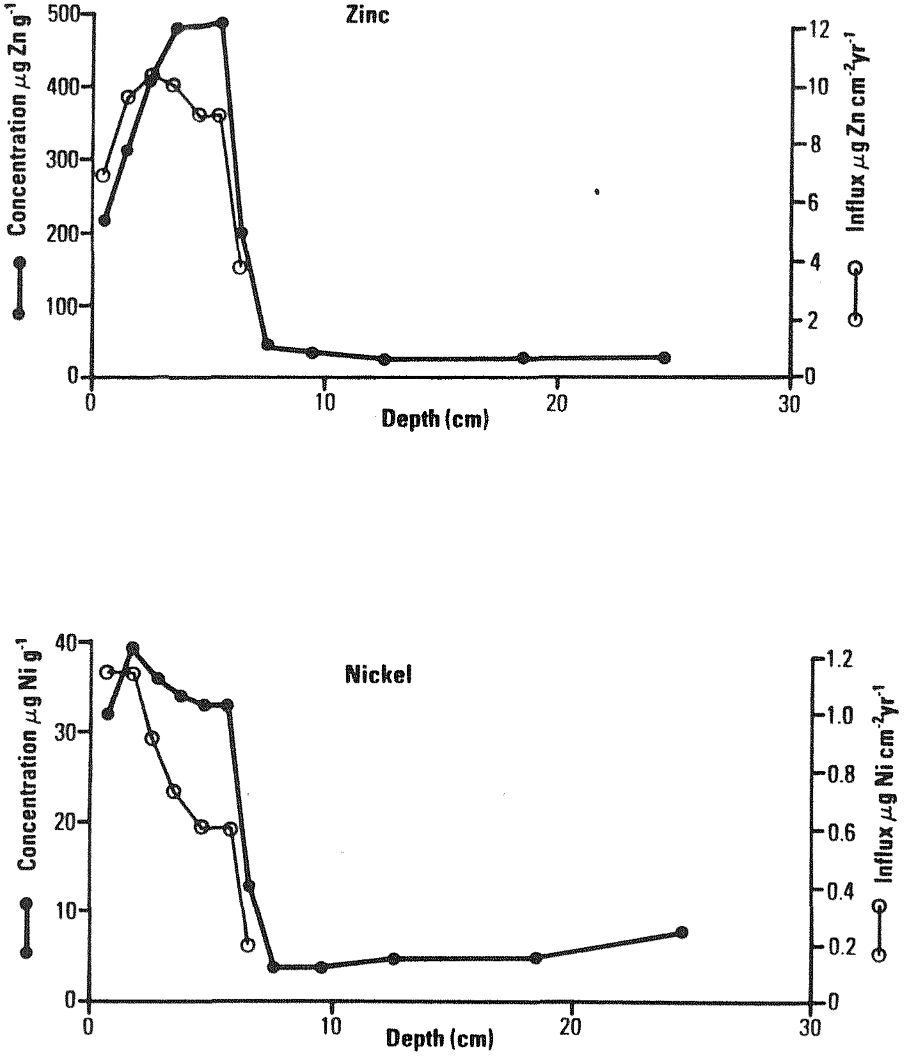

Zinc
Concentration µg Zn g⁻¹
Influx µg Zn cm⁻²yr⁻¹
500
400
300
200
100
0
12
10
8
6
4
2
0
0
10
20
30
Depth (cm)
Nickel
Concentration µg Ni g⁻¹
Influx µg Ni cm⁻²yr⁻¹
40
30
20
10
0
1.2
1.0
0.8
0.6
0.4
0.2
0
0
10
20
30
Depth (cm)

Fig. 5. Concentration of carbonaceous particles in the Woolmer Pond Core.

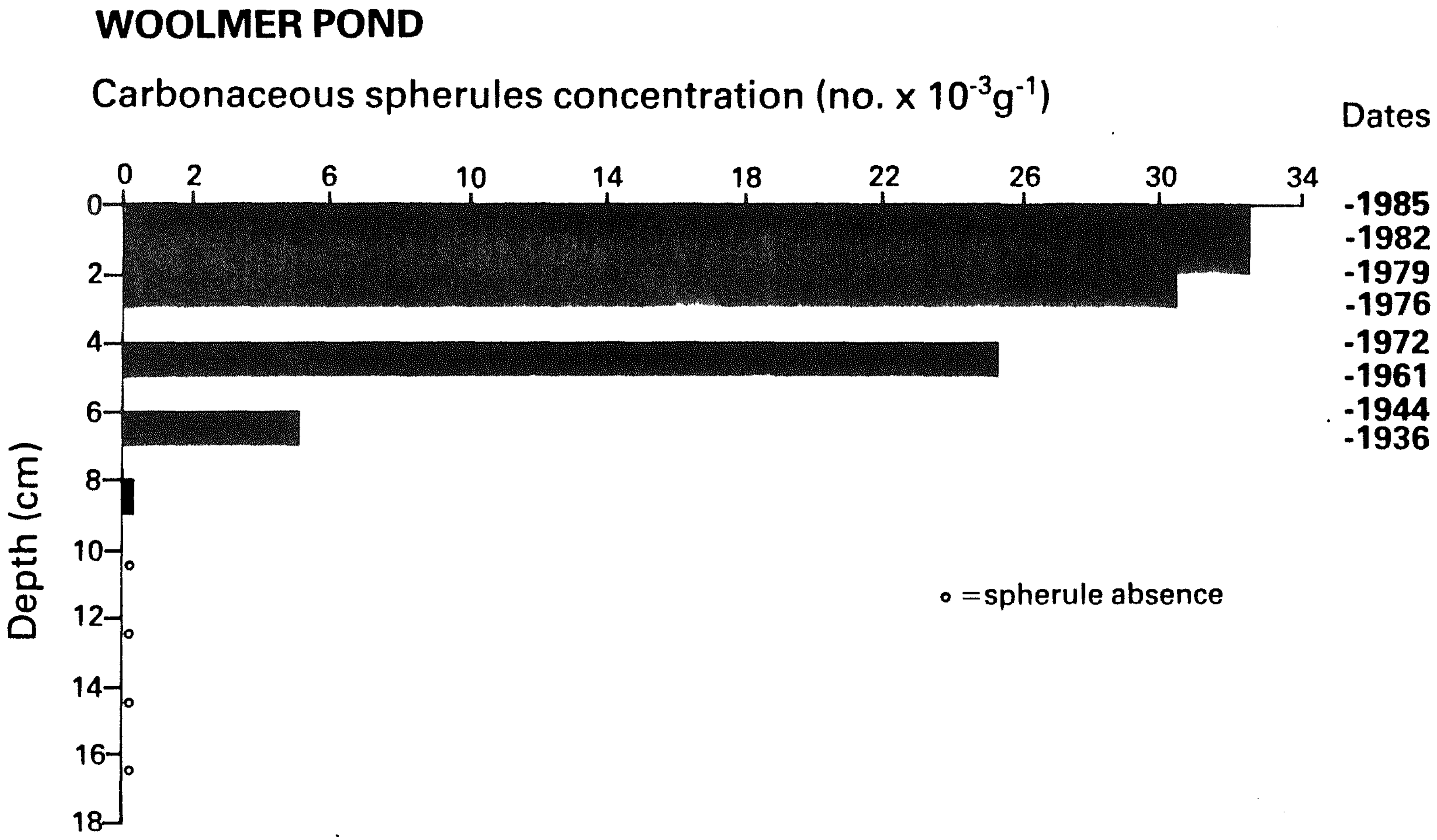
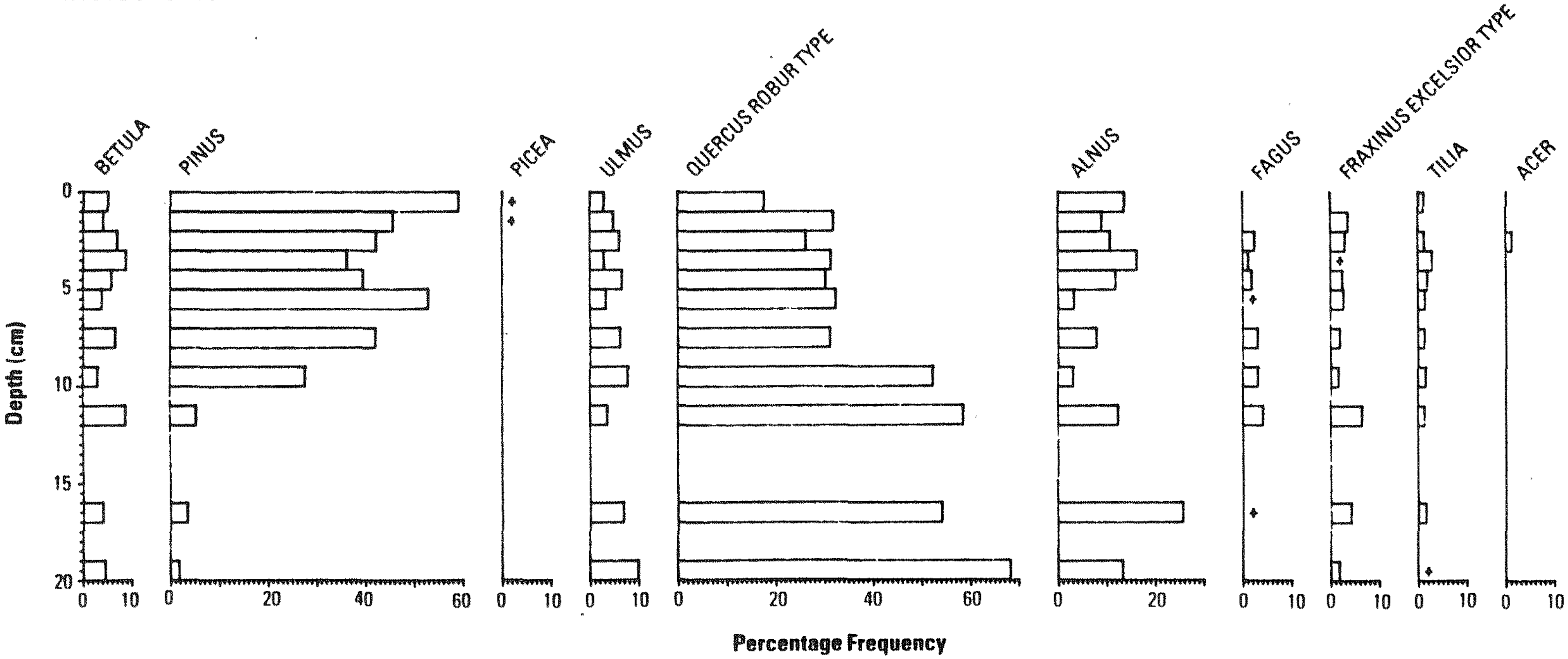


Fig. 6. Summary pollen diagram for the Woolmer Pond Core. Trees expressed as a percentage of the Arboreal pollen. All other groupings as a percentage of the Arboreal pollen plus peatland indicators.



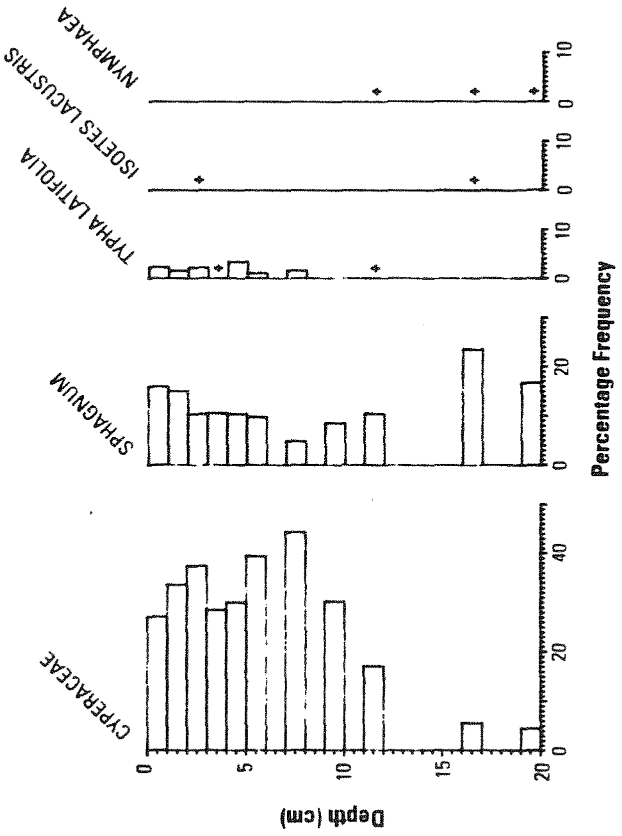

CYPERACEAE
SPHAGNUM
TYPHA LATIFOLIA
ISOETES LACUSTRIS
NYMPHAEA
Depth (cm)
0
5
10
15
20
Percentage Frequency
0
20
40
0
20
0
10
0
10
0
10
+

Fig. 6 Cont.

Fig. 7. Summary pollen diagram for the Woolmer Pond Core. All taxa expressed as a percentage of the Arboreal pollen plus peatland indicators.

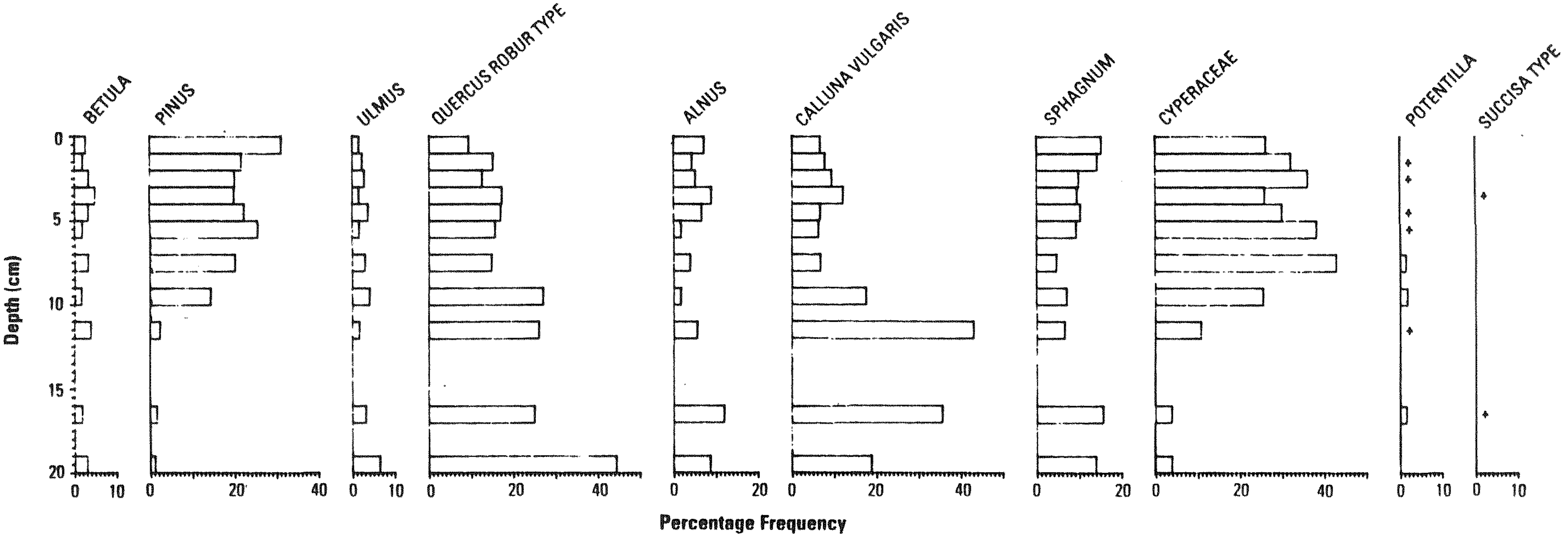


Fig. 8. Percentage frequency of diatoms in the Woolmer Pond Core. (+ indicates presence at <2% frequency).

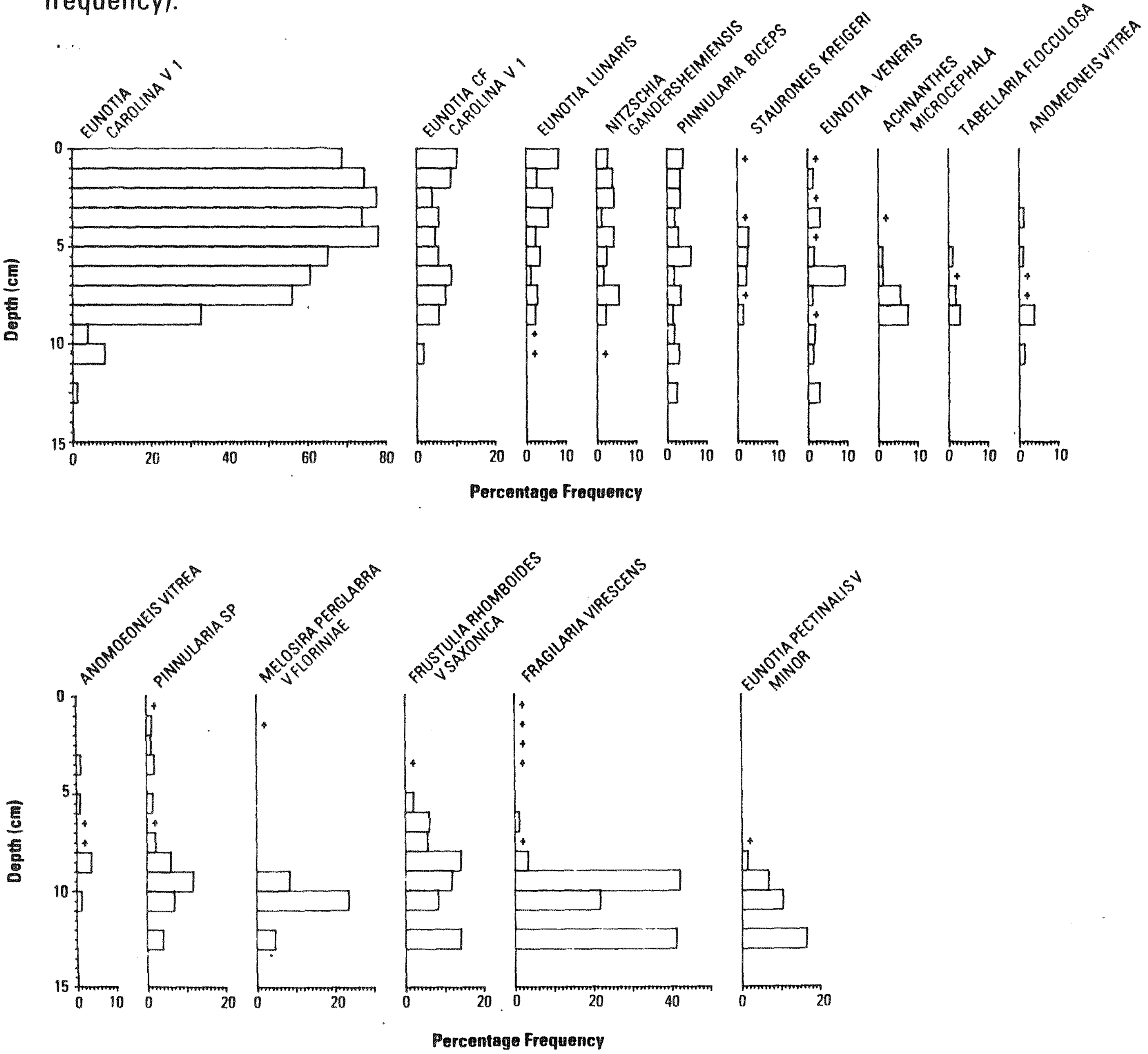


Fig. 8 Cont.

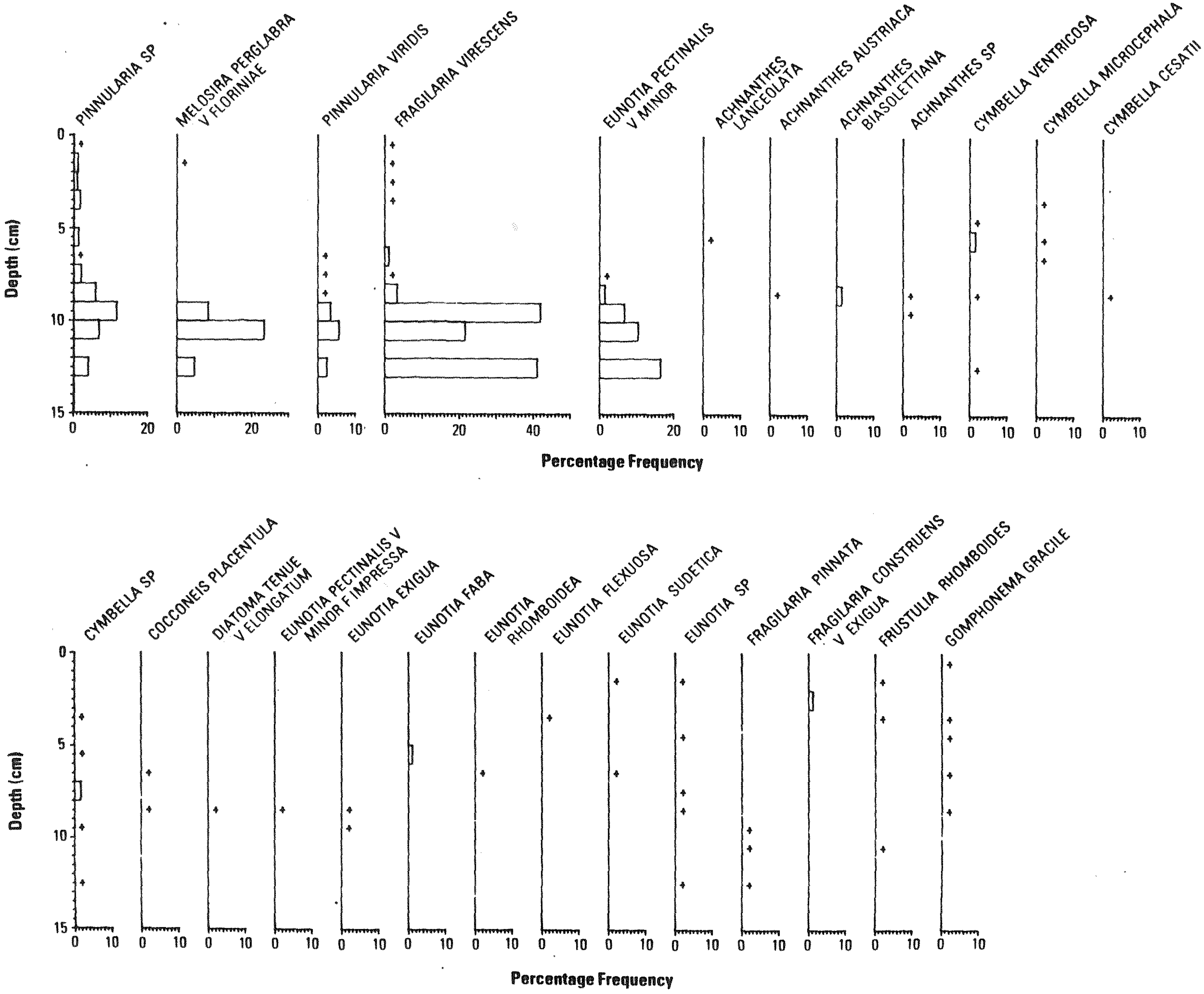

PINNULARIA SP
MELOSIRA PERGLABRA V FLORINIAE
PINNULARIA VIRIDIS
FRAGILARIA VIRESCENS
EUNOTIA PECTINALIS V MINOR
ACHNANTHES LANCEOLATA
ACHNANTHES AUSTRIACA
ACHNANTHES BIASOLETTIANA
ACHNANTHES SP
CYMBELLA VENTRICOSA
CYMBELLA MICROCEPHALA
CYMBELLA CESATII
Depth (cm)
0
5
10
15
20
40
Percentage Frequency
CYMBELLA SP
COCCONEIS PLACENTULA
DIATOMA TENUE V ELONGATUM
EUNOTIA PECTINALIS V MINOR F IMPRESSA
EUNOTIA EXIGUA
EUNOTIA FABA
EUNOTIA RHOMBOIDEA
EUNOTIA FLEXUOSA
EUNOTIA SUDETICA
EUNOTIA SP
FRAGILARIA PINNATA
FRAGILARIA CONSTRUENS V EXIGUA
FRUSTULIA RHOMBOIDES
GOMPHONEMA GRACILE
Depth (cm)
Percentage Frequency

Fig. 8 Cont.

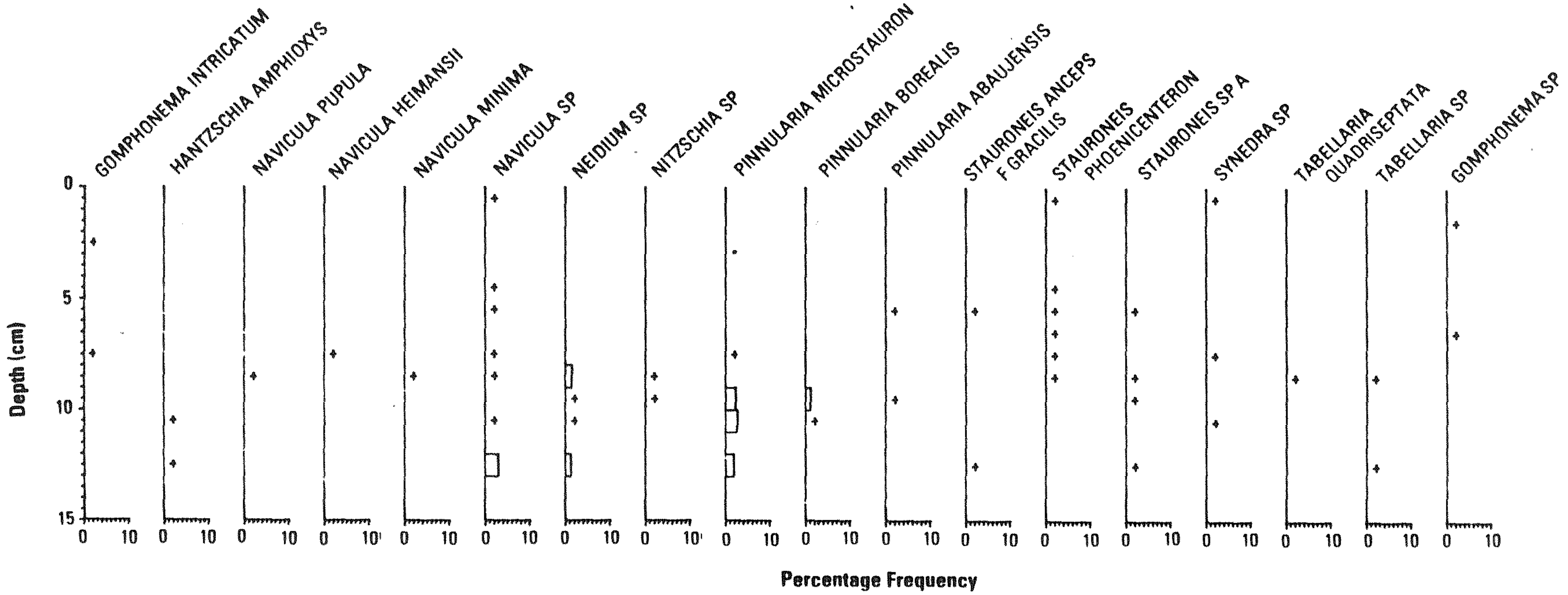
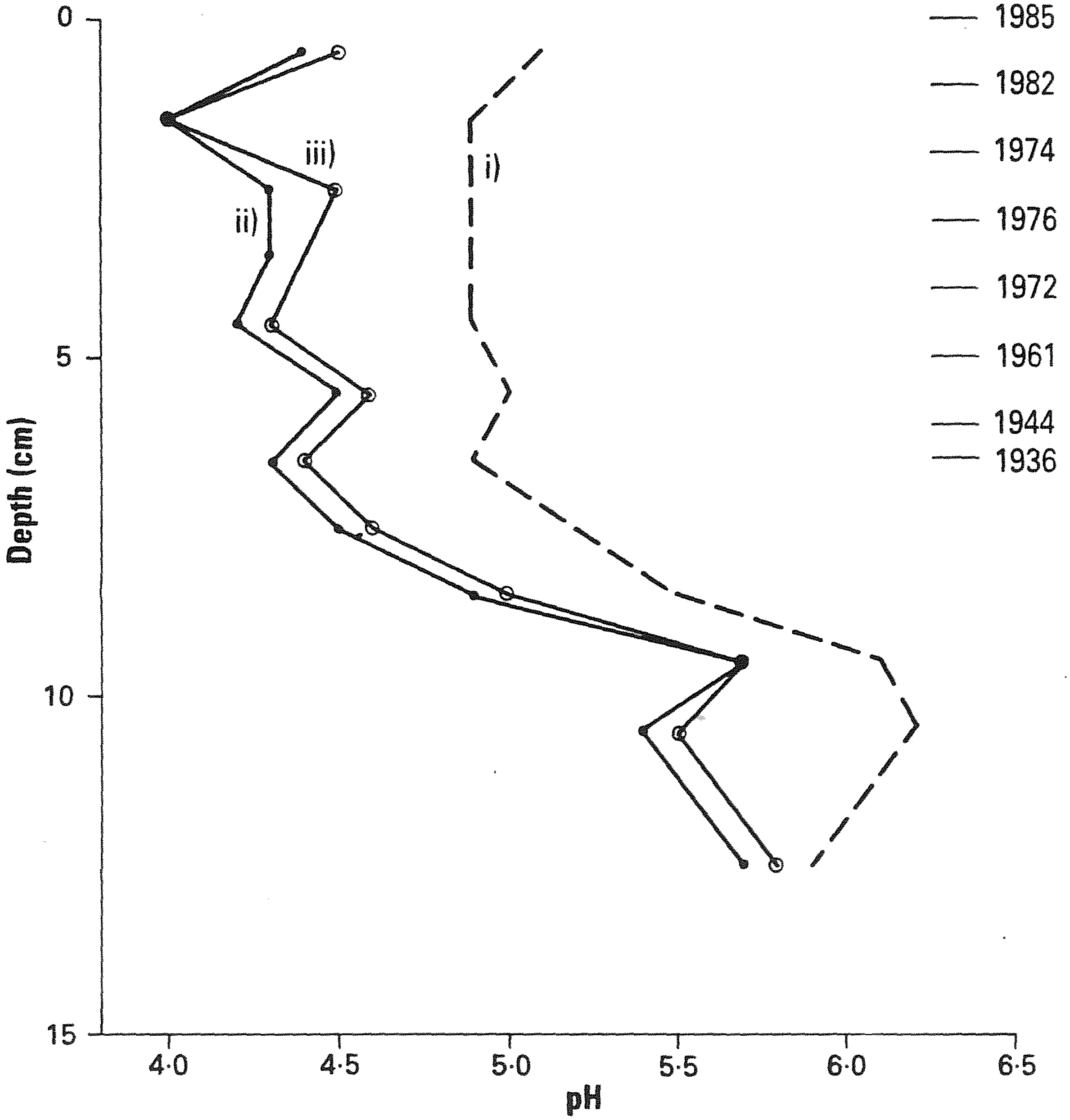

GOMPHONEMA INTRICATUM
HANTZSCHIA AMPHIOXYS
NAVICULA PUPULA
NAVICULA HEIMANSII
NAVICULA MINIMA
NAVICULA SP
NEIDIUM SP
NITZSCHIA SP
PINNULARIA MICROSTAURON
PINNULARIA BOREALIS
PINNULARIA ABAUJENSIS
STAURONEIS ANCEPS F GRACILIS
STAURONEIS PHOENICENTERON
STAURONEIS SP A
SYNEDRA SP
TABELLARIA QUADRISEPTATA
TABELLARIA SP
GOMPHONEMA SP
Depth (cm)
0
5
10
15
0
10
Percentage Frequency

Fig. 9. pH reconstructions for Woolmer Pond, calculated from diatom assemblages in the sediment core.



i) *E. Carolina* v. 1 as acidopholous.
ii) *E. Carolina* v. 1 as acidobiontic.
iii) *E. Carolina* v. 1 as acidobiontic.
Curves i) and ii) are calculated by multiple regression (Flower 1986).
Curve iii) is calculated using Index B (Renberg and Hellberg 1982).

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Geochemistry; Dr B. Rippey. University of Ulster Limnology Laboratory, Traad Point, Drumenagh, Magherafelt, Co. Derry, N.Ireland.

^{210}Pb dating; Dr P.G. Appleby. Department of Applied Mathematics, University of Liverpool, PO Box 147, Liverpool L69.

Carbonaceous particles; Ms. J. Darley. Palaeoecology Research Unit, University College London, 26, Bedford Way, London WC1.

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