ENVIRONMENTAL CHANGE RESEARCH CENTRE

UNIVERSITY COLLEGE LONDON

Research Report

No. 31

The historical record of trace metal, fly-ash and persistent organic pollutant deposition to Loch Coire nan Arr, a remote lake in North-West Scotland.

N.L. Rose[1] and B. Rippey[2]

1996

[1]Environmental Chagne Research Centre, University College London,
26 Bedford Way, London. WC1H 0AP
[2] University of Ulster Freshwater Laboratory, Traad Point, Ballyronan,
Co. Londonderry, BT45 6LR

Contents Page

List of Tables

List of Figures

Executive Summary

Loch Coire nan Arr is a site remote from industrial emissions such that long-range transport followed by atmospheric deposition is the only pollutant source. In March 1996, ten lake sediment cores (CNA11-20) were taken from the deepest area of the loch. The cores were cross-correlated and dated using lithostratigraphy and spheroidal carbonaceous particle (SCP) profiles. CNA11 was analysed for Pb, Zn, Cu, Ni, Cr, Cd and As. The remaining cores were amalgamated into 15 year time slices and analysed for a number of organic pollutants: hexachlorobenzene (HCB), toxaphene, chlordane, aldrin, dieldrin, endrin, DDT, Mirex, pentachlorophenol, lindane, PAHs, PCBs, C10 - C13 chlorinated paraffins and hexabromobiphenyls. Dioxins (PCDDs) and furans (PCDFs) had already been studied at this site (Rose, 1996a). The main conclusions were as follows:

- There is evidence for low level contamination by Pb, Zn, Cu and As. Concentrations show a decrease since 1985, but are still clearly above pre-industrial levels. There is no evidence for Hg contamination.

- SCP, from the high temperature combustion of fossil-fuels, are unambiguous indicators of deposition from these sources, and show low levels of contamination. Concentrations are amongst the lowest in the UK and have been showing a decline since the late 1970s.

- Both ΣPCB and individual PCB congener concentrations were low in contemporary sediments. PCB concentrations were lower than in many European mountain lakes and lakes on Svalbard in the Arctic. The PCB concentration peak showed good agreement with other chlorinated pollutants e.g. PCDD/Fs.

- PAH concentrations were low with peak values approximating to the background concentrations at other UK sites. The peak concentration of ΣPAH and most of the individual PAH compounds occurred in 1920 - 1934, earlier than any of the other industrial pollutants (PCB, PCDD/F, metals, SCP). A low level non-industrial source such as local coal and wood burning may be the cause of this pattern.

- All other organic pollutants measured as part of this study were below their analytical detection limit. Although these detection limits were quite high, these were the best available at the time given the rapid turn round of samples required by the project deadline. These results only allow the conclusion that levels of these pollutants are "low" at Loch Coire nan Arr.

- The metals, SCP, PAH and PCB data suggest that Loch Coire nan Arr is one of the least polluted sites in the UK and amongst the lowest in Europe. It is therefore suggested that the detection limits for the organics would need to be significantly improved before they were suitable to quantify the levels anticipated.

- One problem was the lack of UK data with which to compare the results. Very few PAH and PCB data exist for the UK and almost none for the other organic pollutants. It is very important that this work is undertaken at other UK sites and the UK Acid Waters Monitoring Network lakes would provide coverage of the major pollutant gradients.

- This study has shown that Loch Coire nan Arr is located in one of the most pristine areas of the UK. Once analytical techniques allow a reduction of detection limits (especially in the pesticide compounds) it is recommended that a site in this area is studied further in order that UK background concentrations are more precisely determined.

1. Introduction

The use of lake sediments to determine the extent of contemporary and past environmental contamination is well known and the development of dating techniques means that sediments can now be used to identify the onset, rate and variation in contamination through time. Present day impact of airborne contaminants on the environment can only be placed in an historical context if background levels can be assessed in this way.

Although sediments do not provide the detailed information obtainable from continuous monitoring, they do not suffer from short-term variability problems and do not require many years of sampling in order to determine depositional trends. In addition, palaeoecological techniques have the advantage that they are being analysed with state-of-the-art instrumentation and therefore the problems of harmonising poor quality datasets from a number of different sources, analysed in various ways often over periods of decades, do not exist.

1.1. Selection of substances

As a signatory to the Convention on Longe-Range Transboundary Air Pollution (LRTAP), under the auspices of the UNECE, the United Kingdom is involved in deliberations on the agreement of a protocol to reduce emissions of the heavy metals, Hg, Cd and Pb. These metals are emitted to the atmosphere principally from industrial sources and are able to undergo long range transport prior to deposition. In addition to these priority metals, a number of others, for example, Cu, Zn, Cr, Ni and As are under consideration for inclusion in the protocol along with a number of persistent organic compounds. Many of these metals and organics have long been identified as harmful due to their toxicity, persistence and bioaccumulation and consequently were included on the first EEC priority black list. A sub-set of these became the UK Department of the Environment's 'Red List' in July 1988.

The organic compounds under consideration in this report are as follows: hexachlorobenzene (HCB), toxaphene, chlordane, aldrin, dieldrin, endrin, DDT, Mirex, pentachlorophenol, lindane, PAHs, PCBs, dioxins (PCDDs), furans (PCDFs), C10 - C13 chlorinated paraffins and hexabromobiphenyls. In addition to these pollutants, the sediment record of spheroidal carbonaceous particles (SCP) is determined and discussed. These pollutants are used in this study mainly for sediment core correlation purposes, but their sediment record also provides an unambiguous record of deposition from the high temperature combustion of fossil-fuels, from which they are solely derived.

2. Site selection

Loch Coire nan Arr was selected for its remoteness from pollutant sources and for the well monitored nature of the lake, its biota and catchment.

2.1. Loch Coire nan Arr: lake and catchment

Loch Coire nan Arr (Grid reference NG 808 422) lies on the Torridonian sandstones of the Applecross area north of Loch Carron and Kyle of Lochalsh (Figure 1a). The catchment is extensive (897 ha) and dominated on three sides by steep corrie cliffs which rise to a maximum altitude of 896 m at Beinn Bhan (Figure 1a). The loch and its catchment receive an annual rainfall of ca.2800 mm (1988) with a wet deposited acidity of 0.37 kg H^+ ha^{-1} yr^{-1} and wet deposited non-marine sulphate of 5.18 kg S ha^{-1} yr^{-1} (Patrick *et al.*, 1991). The catchment is unafforested, except for a small block of failed conifers to the east of the loch, and is characterised by acid moorland species, notably *Calluna*, *Molinia* and *Eriophorum*.

The loch itself lies at 125 m altitude and covers an area of 11.6 ha. It receives drainage at its northern end from the Allt Coire nan Arr and elsewhere along the loch from a series of small precipitous inflows. The loch drains via the Russell Burn to the sea 2 km away. The bathymetry of Loch Coire nan Arr is a simple single basin reaching 12 m at its maximum depth (Figure 1b).

Pollutant sources to Loch Coire nan Arr are solely atmospheric and long-range. The site is remote from industrial sources, located 85 km west of Inverness, and almost equidistant from Glasgow (190 km), Dundee (190 km), Edinburgh (210 km) and Aberdeen (215 km). Belfast is 310 km to the south and Newcastle 370 km to the south-east. Prevailing wind directions at the site are from the west and south-west taking airborne pollutants emitted from these cities away from the site.

As part of the UK Acid Waters Monitoring Network, since its inception in 1988, it is one of the most regularly monitored freshwaters in the UK. In addition, a number of previous palaeoecological studies have been undertaken at the site (Section 2.2) and a great deal of information is therefore available on the lake water chemistry, biology and sediment record. Loch Coire nan Arr is also one of the six UK sites represented in the UNECE International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters).

2.2. Previous studies and monitoring at Loch Coire nan Arr

2.2.1. Palaeoecological evidence for acidification

As part of a Department of the Environment funded project on regional acidification, Loch Coire nan Arr was first cored in 1986 (Flower *et al.*, 1993). The results of this study showed that although low levels of atmospheric pollutant deposition were recorded in the sediments (from SCP analysis) diatom analysis showed no evidence for acidification and therefore it was concluded that the critical load for sulphur of the site had not been exceeded.

2.2.2. Acid Waters Monitoring Network

Loch Coire nan Arr is one of the least acid sites in the AWMN. As well as quarterly water chemistry, epilithic diatoms, aquatic macrophytes, macroinvertebrates and fish are all regularly studied. Contemporary (1988-1993) water chemistry shows that although the site is sensitive there are no significant trends relating to acidification (Patrick *et al.*, 1995). Similarly, there are no changes relating to water chemistry apparent from the contemporary biology. However, contrary to the previous palaeolimnological study (Flower *et al.*, 1993), a slight acidification was observed in an AWMN re-coring exercise (1991) with a diatom reconstructed pH change of 0.3 units since the 1930s. Metals (Zn & Pb) and SCP analyses confirmed low levels of atmospheric contamination with the SCP profiles showing a decrease in post-1975 sediments.

2.2.3. Historical record of PCDD/Fs

In February 1994 ten sediment cores were taken from Loch Coire nan Arr in order to study the historical record of PCDD/Fs stored in the sediments (Rose, 1996a). This work was the subject of a report to the Department of the Environment and the main conclusions are summarised in Section 4.3.14.

3. Sampling and Analytical Methodologies

3.1. Coring

In March 1996, 10 short sediment cores (CNA 11-20) were taken from a flat area just north of the deep 12 m point using a Glew gravity corer (Glew, 1991) fitted with wide diameter (73 mm i.d.) perspex tubes. The cores (except CNA11) were extruded vertically in the field at 0.5 cm intervals down to 5cm depth and then at 1cm intervals from 5cm to the bottom of the core. CNA 11 was extruded in 0.5cm intervals for its full length (22.5cm). Each sample was placed into a separate, numbered, hexane-washed, glass petri-dish and sealed using cellulose tape to prevent contamination. The samples were then returned to London and stored at 4°C prior to analysis.

3.2. Lithostratigraphy

The percentage dry weight for each sample was obtained by accurately weighing approximately 1 g of wet sediment in a pre-weighed crucible, drying the sediment at 105 °C for 16 hours and re-weighing the crucible. Organic matter content was determined as a percentage loss-on-ignition by placing the crucible containing the dried sediment in a muffle furnace at 550 °C for two hours.

3.3. Spheroidal carbonaceous particles (SCPs)

Analysis for SCPs followed the procedure described in Rose (1994) and involved the removal of unwanted fractions of the sediment by selective chemical attack. SCPs, despite being physically fragile, are resistant to strong acids and so HNO_3, HF and HCl can be used to remove organic matter, silicate (biogenic and mineral) and carbonate minerals respectively. A sub-sample of the resulting suspension is evaporated onto a coverslip, mounted onto a microscope slide and counted at x400 using a light microscope.

3.4. Core correlation and amalgamation

In order that the ten sediment cores could be amalgamated into the appropriate time slices for subsequent persistent organics analysis the cores had to be correlated both to each other and to a previously ^{210}Pb dated core (CNA9) taken in 1994 from approximately the same location in Loch Coire nan Arr as CNA11-20. These correlations were undertaken using the dry weight, loss-on-ignition and SCP profiles determined for each core (Figures 2 & 3).

The dry weight profiles showed a number of useable peaks and troughs within the CNA11-20 dataset but although useful for inter-core correlation these were of limited use when correlating to CNA9 as the dry weight profile of this core showed few features. However, CNA9 showed a dry weight maximum dating to 1860 ± 18 (by ^{210}Pb) and this feature was also present in the current set of cores. This allows independent confirmation for the start of the SCP profile which also dates to about this time.

Core dating using SCP profiles is a technique that has been employed for over ten years (Renberg & Wik, 1984; 1985) and relies on the fact that SCP profiles occur consistently in the sediments of lakes within a region. It also assumes that there is no transport or movement of particles (other than normal sediment processes) within the sediment column. Given the potential for disturbance in many lakes, it is a technique which works remarkably well.

Once one or two SCP profiles within a region have been dated reliably (using ^{210}Pb or varve counting) then dates can be ascribed to other cores within that region using features of the SCP profile. The SCP profile for Loch Coire nan Arr is discussed further in Section 4.2, but generally there are three features of the SCP profile which are useful for core dating (Rose *et al.*, 1995).

i) the start of the SCP record (1860)
ii) the rapid increase in SCP concentration (1960)
iii) the SCP peak (1978 ± 2 in Scotland)

This last feature is generally the most reliable as it is usually unambiguous and is the most precisely defined of the three. Together with reinforcement from the independent ca.1860 dry weight peak and the known surface date, this approach provides four reliable dating horizons distributed over 130 years. Dates for sections of the cores between these fixed points are extrapolated using calculated sediment accumulation rates. Figure 4 shows the SCP cumulative concentration profiles for the ten cores showing that SCP accumulation through time exhibits a reasonable level of consistency in all ten cores over the 130 year time period especially and over the most recent 3-4 cm (ca.25 years).

The dates attributed to the ten cores are given in Table 1 and depth/date profiles are shown in Figure 5. This Figure emphasises the consistency of the profiles and shows that the majority of the cores show close agreement with the mean, which itself is a smooth curve. Confidence in the attributed dates is therefore reasonably high, and again, this is especially so in the post-1960 period.

Core amalgamation

The quantities of sediment required for organics analysis were such that after sub-samples had been removed from CNA11 for metal analyses and from all cores for lithostratigraphic and SCP analyses, the ten cores were bulked into appropriate time intervals. The sediment accumulation rate at Loch Coire nan Arr, combined with the mass requirements for the required analyses meant that the finest resolution possible for the organics study was 15 years. The metals analyses were undertaken on every 0.5cm of CNA11 and this corresponds to approximately five year resolution in the upper parts of the core and 8-10 years towards the base.

3.5. Trace Metals

The analytical methods used for the determination of trace metals in sediments have been validated through precision and spiking recovery tests and been shown to be accurate with precision fit for this work (Rippey *et al.*, 1982). Two methods were used, one for Na, Pb, Zn, Cu, Ni, Cr, Cd and As and one for Hg.

In the first method, around 0.3 g of dry (105 °C) sediment was digested in Teflon beakers with HF, HNO_3 and $HClO_4$ (Bock, 1979: Rippey *et al.*, 1982). The residue was taken up in HCl and the metals determined by flame (Na, Pb, Zn, Cu, Ni and Cr: Perkin Elmer 2380) and graphite furnace (Cd and As: Perkin Elmer 4100ZL) atomic absorption spectrometry. The precision of the results are 0.08 mg Na g^{-1}, 3.0 μg Pb g^{-1}, 2.4 μg Zn g^{-1}, 1.7 μg Cu g^{-1}, 5.6 μg Ni g^{-1} 0.54 μg Cr g^{-1}, 0.33 μg Cd g^{-1} and 0.44 μg As g^{-1}. The absolute accuracy of results is better than ± 20 %.

In the method for Hg, around 0.3 g of dry (65 °C) sediment was digested in conical flasks with HNO_3 and $HClO_4$ (Skare 1972). Hg was determined by flameless atomic absorption spectrometer (Perkin Elmer MHS10 hydride accessory and 2380) with sodium borohydride reductant. The precision of results is 0.05 μg Hg g^{-1} and the absolute accuracy better than ± 20 %.

3.6. Organics

The following methodologies were provided by Bernard Bushby and Alwen Fernandez of Analytical Services at AEA Technology plc.

3.6.1. Polychlorinated biphenyls (PCBs)

Approximately 30 g of air dried sample was Soxhlet-extracted with hexane/acetone after the addition of a cocktail of internal standards (^{13}C labelled PCBs 28, 52, 101, 118, 138, 153 & 180). After extraction, the solvent was reduced to a few mls by nitrogen blow down and the hexane remaining was dried over sodium sulphate and subjected to a bulk acid clean-up with acid impregnated silica. It was then reduced again to a volume of approximately 1 ml by blowing down under a stream of nitrogen. The extract was then further subjected to column chromatography clean-up on florisil. The PCB fraction was collected and blown down to a few hundred microlitres in a small vial. A syringe standard cocktail of ^{13}C labelled PCBs (77, 126 & 169) was then added before measurement. This was to allow for the calculation of internal standard recoveries, by comparison of the ratios of response achieved for internal standards against syringe standards in the samples to those obtained from a control solution.

Measurement was achieved using a Hewlett Packard 5970 GC-MS equipped with a 50m DBS 0.2 μm film capillary column. The mass spectrometer was operated in selective ion monitoring (SIM) mode. The ions recorded are listed below.

Isomer		Mass 1	Mass 2
244-T3CB	PCB 28	256	258
2525-T4CB	PCB 52	292	290
3434-T4CB	PCB 77		
54525-P5CB	PCB 101	326	328
24534-P5CB	PCB 118		
34534-P5CB	PCB 126		
234245-H6CB	PCB 138	360	362
245245-H6CB	PCB 153		
345344-H6CB	PCB 169		
2345245-H7CB	PCB 180	394	396

^{13}C Standards	Isomer	Mass 1	Mass 2
Internal	28	270	272
	52	304	302
	101	338	340
	118	338	340
	138	372	374
	153	372	374
	180	408	406
Syringe	77	304	306
	126	338	340
	169	372	374

Quantification was carried out using peak areas. A standard run at the time of analysis was used to calculate a relative response factor (RRF) for each compound compared to its isotopically labelled internal standard. The results were corrected for the laboratory reagent blank. Total PCBs were estimated using an extrapolated value derived from the total PCB levels (T3 to H7 total congeners) and the sum of the seven isomers.

3.6.2. Polycyclic aromatic hydrocarbons (PAHs)

Approximately 30 g of air dried sediment was accurately weighed into a Soxhlet-extraction thimble and a cocktail of deuterated internal standards was added (D8 naphthalene, D8 acenaphthylene, D10 acenaphthene, D10 fluorene, D10 anthracene, D10 pyrene, D10 chrysene, D12 benzo(b)fluoranthene, D14 dibenzo(ah)anthracene, D12 benzo(ghi)perylene). The sample was then Soxhlet-extracted with 200 mls of hexane/acetone. After extraction the solvent was dried over sodium sulphate and the solvent reduced to a volume of about 2 mls by blowing down under a stream of nitrogen or compressed air. A syringe standard cocktail of D-PAHs (D10 fluoranthene and D12 benzo(a)pyrene) was then added before measurement using GC/MS. The purpose of the syringe standard was to allow for the calculation of internal standard recoveries. This was achieved by comparison of the ratios of response achieved for internal standards against the syringe standards in the samples to those obtained from a control solution.

As with the PCBs, measurement was achieved using a Hewlett Packard 5970 GC-MS equipped with a 50m DBS 0.2 μm film capillary column. The mass spectrometer was operated in selective ion monitoring (SIM) mode. The ions recorded are listed below.

Compound	Native ion (amu)	D-Ion (amu)
Naphthalene	128	136
Acenaphthylene	152	160
Acenaphthene	154	164
Fluorene	166	176
Phenanthrene	178	
Anthracene	178	188
Fluoranthene	202	212
Pyrene	202	212
Benzo(a)anthracene	228	
Chrysene	228	240
Benzo(b)fluoranthene	252	264
Benzo(k)fluoranthene	252	
Benzo(a)pyrene	252	264
Indenopyrene	276	
Dibenzo(ah.ac)anthracene	278	292
Benzo(ghi)perylene	276	288

(amu = atomic mass units)

Quantification was carried out using peak areas. A standard run at the time of analysis was used to calculate a relative response factor (RRF) for each compound compared to its isotopically labelled internal standard.

3.6.3. Organochlorine pesticides

The method employed was based upon the principles employed by the US EPA, procedure 8270B, the determination of semi-volatile organic compounds by GC/MS.

10 g of air dried sample was Soxhlet-extracted for 16 hours with an azeotropic mix of hexane and acetone. The extract was then concentrated to a small volume of hexane and the level of possible interferences in the extract was estimated. If this was low the target compounds were measured by GC/MS. However, if necessary, a clean-up procedure using column chromatography on florisil was used to isolate the pesticides (EPA 5620A). A Table listing the specific ions used to monitor the pesticides is given below:

Pesticide	Ion mass	Internal Std.
Hexachlorobenzene	284/286	^{13}C HCB
γ-BHC Lindane	181/183	^{13}C HCB
Aldrin	261/263	^{13}C HCB
Dieldrin	261/263	^{13}C HCB
Endrin	261/263	^{13}C HCB
p,p'-DDT	235/237	^{13}C HCB
Mirex	272/274	^{13}C HCB
Pentachlorophenol	266/268	^{13}C HCB

Quantification was carried out using peak areas. A standard run at the time of analysis was used to calculate a relative response factor (RRF) for each compound compared to its isotopically labelled internal standard. Deuterated anthracene was added as a syringe standard to enable the recovery of the ^{13}C labelled HCB standard to be estimated.

It should be noted that pentachlorophenol is extremely adsorbent and tends to stick to glass or silica on the inserts of GC injectors and other apparatus. A procedure involving derivitisation such as methylation to form a less active compound which lends itself to easier measurement is recommended. However, this requires a separate analysis which cannot be performed simultaneously with the other pesticides.

3.6.4. Chlordane, Toxaphene, C10 - C13 Chlorinated paraffins and Hexabromobiphenyls.

The following extraction method was used to generate a single extract which was subsequently used for the measurement of all four analyte groups.

Approximately 5 g of air dried and finely ground sample was spiked with 500 ng of ^{13}C labelled hexachlorobenzene (as an internal standard) and extracted ultrasonically for 20 minutes using 15 ml of n-Hexane (Glass distilled grade). The process was repeated and the extracts combined and concentrated using a gentle stream of dry air. The concentrated extracts were then centrifuged to remove any suspended particles and the clear extracts removed and made up to volume. The clarity and colourlessness of the extracts suggested that further clean-up was not required. A syringe standard (deuterated anthracene) was added to the sample extracts prior to GC-MS analysis. A method blank was run with each batch of samples.

All measurements were carried out on a Hewlett-Packard 5890 GC-MS (5970) system using a 60 x 0.22 mm DB-5 GC column. Toxaphene, chlordane and hexabromobiphenyl were measured in the selected ion monitoring (SIM) mode and quantification for these analytes was carried out relative to the ^{13}C internal standard used. Measurements for chlorinated paraffins were carried out in the GC-MS scan mode over the range 50 - 700 amu. The recorded spectra were then compared against library spectra available for mono and di-chlorinated species.

4. Results and Discussion

4.1. Trace Metals

The metal concentration data are given in Table 2.

The remote nature of Loch Coire nan Arr and the lack of sources of contamination in the catchment ensures that any trace metal contamination must be by deposition from the atmosphere. Occasionally, changes in the sedimentation processes in a lake, for example, from variations in sediment yield from the catchment or sediment movement within the lake, alter the trace metal concentrations. Analysis of the results must ensure that the influence of this factor on trace metal concentrations is assessed. The changes in loss-on-ignition (Figure 2) are small, so the metal concentrations can be expressed in terms of per gram dry weight, rather than being corrected for variations in organic content.

The main feature of the dry weight - depth profile of sediment core CNA11 is the drop in dry weight between 15 cm and 10 cm. The values are stable above this depth. The Na concentration - depth profile (Figure 6) is similar to that of dry weight and very similar to an earlier core (ARR2, 1986) (Flower *et al.*, 1993). Indeed, the small peak in Na concentration at 15.25 cm is at similar depth to that in ARR2 (16.5 cm).

Although small, it must be confirmed that the changes in sedimentary Na concentration are associated with changes in trace metal concentration. This is achieved by examining the variation of trace metal concentration with that of a major cation. Figure 6 shows that the relationship between Pb and Na can be used to establish that low level Pb contamination starts above 19 cm (early 19th century), with the main increase above 13.5 cm (late 19th century). Above 10 cm (1920s), contamination is at its greatest and there is an improvement above 2 cm (1985).

The Zn concentration is unaffected by changes in Na (Figure 7). Contamination starts above 19 cm (early 19th century), is greatest above 10 cm (1920s), and there is an improvement above 2 cm (1985), similar to Pb. The single high value at the top of the sediment core is a "surface effect".

There is a small but detectable amount of Cu contamination. The concentration only rises above background above 13.5 cm (late 19th century), with the greatest rise above 10 cm (1920s). The overall increase in Cu concentration is small and this, along with earlier rise is Pb and Zn contamination (early 19th century) establishes that the degree of Cu contamination is small.

There is no evidence for Ni and Cr contamination. The peak in Cr concentration at 15 cm depth (mid-19th century) coincides with peaks in Na and dry weight and this indicates that changes in the sedimentation process were responsible for this feature.

There is little evidence for contamination by Cd. The Cd concentration is slightly higher below 17 cm depth. The Na concentration is also higher in this part of the core and this indicates that the higher Cd concentration is due to a change in the constitution of the sediment. Above this layer, the concentration is constant, only increasing above 2 cm (1985). We can not tell from the evidence if this is due to recent contamination, but this is unlikely as Pb, Zn and Cu all show a drop in contamination at this time.

The As concentration increases above 10 cm (1920s), which is the depth at which Pb, Zn and Cu concentrations rise most strongly, and so we have evidence for As contamination. The lower concentrations around 6 and 2 cm depth are unlikely to be due to variations in the rate of supply of As from the atmosphere, but to diagenetic effects. As is sensitive to changes in oxidation-reduction and so these low concentrations may be due to release from the sediment when reducing conditions prevail. There is no evidence for Hg contamination.

We have developed a method to compare the degree of contamination of the atmosphere by trace metals using a single sediment core from each lake. This uses the contamination and dry sediment burden since 1900 to account for the influence of sedimentation rate on the accumulation rate of chemicals in sediments. Figure 8 shows that the 19 lakes in Wales and central and southern Scotland have a similar level of Pb contamination from the atmosphere and so fall on a single trend line of contamination against dry sediment burden. This trend line defines the time-average contamination Pb concentration in the sediments of these lakes. It is 263 μg Pb g^{-1} and isoconcentration lines are shown on the Figure. The four lakes in Ireland fall below the trend line for Wales and central and southern Scotland because the degree of contamination is less and contamination of the atmosphere is even lower at the ten lakes from North and West Scotland. The sediment core CNA11 and two earlier ones (ARR2 - 1986 and ARR5 - 1991) are also shown and they are part of the North and West Scotland group. This analysis shows that, while there is Pb contamination of the atmosphere above Loch Coire nan Arr, it is amongst the lowest in the UK. The same is likely to be true for Zn, Cu and As.

4.2. Spheroidal Carbonaceous Particles

The SCP profiles for the ten cores are given in Figure 3 and in this study were primarily used for core correlation and dating purposes (Section 3.4). However, the SCP lake sediment record also provides unambiguous information on the deposition of pollutants from fossil-fuel combustion sources. In the UK SCP are only produced from the high temperature combustion of coal and oil, for example, from the power generation industry. SCP are not produced naturally and therefore show good agreement with the sediment record of PAH (Broman *et al.*, 1990). Similarly, the spatial distribution of SCP in lake surface sediments is known to show good agreement with other fossil-fuel derived pollutants, for example sulphur (Rose & Juggins, 1994).

Although some variability is seen within the ten profiles, both in terms of concentrations and shape, generally all the Loch Coire nan Arr profiles show the trends seen in sediments throughout the UK. The three features used for dating (see Section 3.4.) are thought to correspond to periods in the history of industrial development (Rose *et al.*, 1995) and are present in all the cores. This suggests that the sediment record is likely to be complete and relatively undisturbed. The start of the particle record generally occurs in the mid-19th century, typically ca.1860 for Scotland, at about the time of the start of large scale electricity production as a result of the Industrial Revolution. The rapid increase in SCP concentration in the 1950s/1960s is attributed to the rapid development in post-1945 electricity production, and the final feature, the concentration peak (ca.1978 in Scotland), is attributed to the introduction of particle arresting technology and to a lesser extent the decline in heavy industry.

Loch Coire nan Arr is remote from any SCP sources with the nearest being on the Firth of Forth (Longannet, Methil) approximately 200 km away. The SCP record therefore suggests that long distance transport of atmospheric pollutants has had a low level but measurable impact on the site for almost 150 years. This is confirmed by the Hull Acid Rain Model (HARM) (Metcalfe & Whyatt, 1995) for sulphur which suggests that the main power station sources for Loch Coire nan Arr are located in the English Midlands (Fiddler's Ferry, Ferrybridge, Ironbridge) with lesser impacts from sources in Scotland and Northern Ireland (S.Metcalfe pers. comm.).

The remoteness of the site from any single source and the variety of possible sources at greater distances suggests that deposited pollutants stored in the sediment record are likely to be derived from a number of sources which are then integrated in the atmosphere or in the water column prior to deposition. There is no reason to suspect that this situation has changed greatly over the last century.

4.3. Organics

4.3.1. PCBs

PCBs were first synthesised in the USA in 1929 and in the UK in 1954. They are widely used in dielectric fluids in transformers and capacitors, plasticisers in paints, sealants and adhesives and components of hydraulic fluids in gas turbines and vacuum pumps. Evidence now suggests that some PCB species form during combustion processes and are emitted from coal-fired power stations and car exhausts (Granier & Chevreuil, 1991) and municipal and chemical waste incineration (e.g. Boers *et al.*, 1993). PCBs are released into the environment via industrial emissions, landfill leaching and failure of electrical equipment (Sanders *et al.*, 1992) and enter the atmosphere by direct emissions or by volatilisation from soil and water. PCBs are very persistent and their hydrophobic and lipophilic properties mean that in the lake environment they tend to bind to organic rich particulates and become incorporated into the sediment by deposition. They can also enter the aquatic food chain where they bioaccumulate.

Seven individual PCB congeners (28, 52, 101, 118, 138, 153 & 180) were analysed and these were selected due to their inclusion in draft EC legislation. In addition, total PCB (ΣPCB) were estimated using an extrapolated value derived from the total PCB levels (T3 to H7 total congeners) and the sum of the seven isomers.

The sediment concentrations of ΣPCB and the seven PCB isomers for Loch Coire nan Arr are given in Table 3 and Figure 9. The profile for ΣPCB appears to be fairly consistent before the turn of the century after which concentration increases to a peak in 1965-1979 followed by a decrease in the upper, 1980-1996, sample. Of the individual isomers, PCB 28, 118, 138 and 180 are below the analytical detection limit (0.1 ng g^{-1}) until the early part of this century and are detected for the first time in 1920-1934. PCB 52 is first detected in 1860-1874, PCB 101 in 1830-1844, whilst PCB 153 was detected in the pre-1830 sample. Once above the detection limit, PCB 28 and 52 show little trend in concentration, whilst the others follow a similar pattern to ΣPCB, increasing to a maximum in 1965-1979 and decreasing in the most recent sample. The timing of these concentration maxima is in good agreement with peak UK production of PCB (1965-1975). Only PCB 118 differs from this pattern showing a maximum sediment concentration in 1950-1964.

The only other study of PCB in lake sediments in the UK is for Esthwaite Water in the English Lake District (Sanders *et al.*, 1992) where the peak concentration was seen to be at a similar date to that of PCB 118, in 1955-1965, earlier than the UK production peak. It is interesting to note that the temporal trends for PCB at Loch Coire nan Arr are similar to those recorded for PCDD/Fs, also atmospherically deposited organochlorine pollutants. PCDD/F results (from Rose, 1996a) are discussed more fully in Section 4.3.14.

ΣPCB and all PCB isomers are detected in the sediment record prior to the date of the first synthesis in the UK and ΣPCB, PCB 52, 101 and 153 are detected prior to the first ever synthesis in 1929. This observation has been reported in other sediment studies including sites in the Arctic (Rose, 1996b) and the UK (Sanders *et al.*, 1992). Sanders *et al.* suggest several possible explanations:

For PCBs detected prior to synthesis in the UK (1929 - 1954) the possibility exists for long-range transport from mainland Europe (against prevailing winds) or from the USA. For pre-1929 PCBs there are a number of possibilities. First, that PCBs may have been transferred from recent sediments to deeper sediments by sampling and extruding methods or by within-lake processes such as bioturbation or sediment mixing by physical means. Second, contamination could have occurred during analysis. Third, the peaks on the chromatogram may be from non-PCB species with the same retention time, and fourth, there is a real pre-industrial PCB signal.

Although considerable care is taken during sampling and extrusion, the first possibility cannot be totally discounted. The second is unlikely given the blank analyses undertaken in parallel with the samples and the third is also unlikely given the analytical cross-checking procedures.

PCB formation under natural combustion conditions (e.g. forest fires) still requires conclusive proof although the presence of low molecular weight PCBs have been reported as a result of combustion (e.g. coal-fired power station and vehicle emissions). Biogenic production of PCB is also thought to be a possibility (Sanders *et al.*, 1992). With a small but increasing number of studies, undertaken by different laboratories, demonstrating pre-industrial levels of PCBs the evidence for a natural combustion or biogenic source of these compounds also increases. Currently however, the historical record of PCB in the UK remains ambiguous and further work is needed to confirm the true picture.

What is certain from the Loch Coire nan Arr study is that there has been a clear decline in ΣPCB and individual congener concentration at this remote site in the north-west of Scotland. This supports the findings of Sanders *et al.* (1992) at Esthwaite Water.

Figure 10 compares the concentrations of ΣPCB and individual PCB congeners in the Loch Coire nan Arr surface sediment with data from recent studies in European mountain lakes (AL:PE) (Camarero *et al.*, 1995), Svalbard in the Arctic (Rose, 1996b) and Esthwaite Water (Sanders *et al.*, 1992). The Figure shows that for plots of ΣPCB against individual PCB congeners (180 & 153) lake types appear to fall on straight lines, although the slopes of these lines are different for the lake groups. Thus PCB data from the European mountain lakes fall on one straight line whilst those from Svalbard fall on a different one. This seems to suggest that for each set of lakes the PCB source is similar within a group but possibly different between groups. For ΣPCB v PCB 180 the data points for Loch Coire nan Arr and Esthwaite Water, the only UK sites on the Figure, fall between the lines suggesting either a third source, or a combination of the other two. For ΣPCB v PCB 153 Loch Coire nan Arr appears to fall on the Svalbard line whilst for PCB 101 v PCB 52 all data points appear to fall along the same line.

The reasons for these results are at present unclear but may be due to source effects or possibly transport and depositional processes such as differential volatilisation / condensation with latitude. Many of the European mountain lakes are at low latitudes (e.g. 37°N - 45°N) and so if this were the cause there would be a maximum difference between these sites and the Svalbard sites for the heavier compounds (PCB 180, 153), and a minimum for the lighter ones (PCB 28, 52). This may explain why the plot of ΣPCB v PCB 180 and ΣPCB v PCB 153 show significant differences between the slopes of the lines, whilst for PCB 101 v PCB 52 (also PCB 28 v PCB 52 - not shown) the sites all fall along the same line. The UK sites, at intermediate latitudes, appear to fall between the two. Further data are needed to confirm this.

Whether this is the reason behind these results or not, the fact remains that Loch Coire nan Arr plots at the lowest end of all these diagrams showing that, with respect to contemporary PCB concentrations, it is one of the least polluted sites in Europe including lakes on Svalbard above the Arctic Circle. Further afield, Loch Coire nan Arr has similar contemporary ΣPCB sediment concentrations to Lake Superior (Baker *et al.*, 1991) and falls approximately between the contemporary ΣPCB concentrations of two Alaskan Arctic sites (Gubala *et al.*, 1995).

4.3.2. PAHs

PAHs are formed largely by the incomplete combustion of organic materials, including fossil-fuels, petroleum, crude oil and their products. They can also be produced naturally, for example by forest fires, although the contribution of natural sources is currently small in comparison with anthropogenic emissions. Like PCBs, PAHs are widely distributed in the environment and may enter the aquatic environment by direct discharge of effluent or surface run-off. They are also transported in the atmosphere and deposited by atmospheric deposition. Broman *et al.* (1988) noted that major carriers of PAH to accumulating sediments were black carbon particles from sources such as vehicle exhaust, central heating boilers and incinerators. In a later study, Broman *et al.* (1990) showed a significant correlation between 14 PAH and SCP from fossil-fuel combustion. PAHs have a low solubility in water and are likely to become attached to particulate matter on entering the aquatic environment, after which they are subject to the same physical processes (bioturbation, resuspension etc.) as PCBs. PAHs have been used as a record of the deposition history of the products of fossil-fuel combustion as they are little altered during transport through the atmosphere or during burial in sediments (Rippey, 1990).

Sixteen PAH compounds, listed by the World Health Organisation, were analysed. These were naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indenopyrene, dibenzo(ah.ac)anthracene and benzo(ghi)perylene. The limit of detection was 1 ng g^{-1}. ΣPAH was estimated from the sum of the 16 compounds.

ΣPAH

The ΣPAH concentration profile is given in Figure 11. The ΣPAH concentration profile shows a broad curve and it is difficult to distinguish where an increase begins over and above background. The peak for ΣPAH (1719 ng g^{-1}) occurs in 1920-1934 after which there is generally a decline to the present.

PAH data for UK sediments are limited. Studies have been undertaken on river sediments (River Thames - Taylor & Lester, 1995; River Derwent - Evans *et al.*, 1990) but for lake sediments there are few. Sanders *et al.* (1993) analysed the sediment record for Esthwaite Water and found the maximum concentration of ΣPAH (42,000 ng g^{-1}) to occur in 1950-1955. Surface concentrations (1985-1990) decreased to 17,600 ng g^{-1} with a pre-1850 'background' concentration of between 1,600 and 2,600 ng g^{-1}. The maximum ΣPAH concentration for Loch Coire nan Arr is therefore of the same order as that of the background concentration for Esthwaite Water and it is perhaps not a surprise that the ΣPAH peak at Loch Coire nan Arr is less well defined. This lack of definition may also explain why the maximum at Loch Coire nan Arr occurs almost 30 years earlier than that of Esthwaite Water. Alternatively this mis-match may be caused by ΣPAH at Loch Coire nan Arr only comprising the total of the 16 compounds. As concentrations are low, unmeasured PAH in even moderate concentrations could change the ΣPAH peak to a later date. However, this seems unlikely as most of the individual PAH have coincident peaks at this time and the PAH species considered by Sanders *et al.* (1993) to be important to the ΣPAH (benzo(b)fluoranthene, benzo(a)pyrene and indenopyrene) are also the ones in highest concentration at Loch Coire nan Arr suggesting the important compounds have been included. Additionally, the peak in benzo(a)pyrene is also found at this date and this is earlier than the peak in other north-west Scotland sites (Rippey, 1990) (see below).

Table 4 compares ΣPAH in the surface sediments of Loch Coire nan Arr with other recent studies. From this Table it can be seen that Loch Coire nan Arr concentrations are higher than European mountain lake sites in Spain, Austria and Portugal and lakes on Svalbard and in the Canadian Arctic. This is in contrast to the PCB data where Loch Coire nan Arr concentrations were seen to be of a similar order to these sites. However, ΣPAH concentrations for Loch Coire nan Arr are similar to surface concentrations at Lac Noir in the French Alps and to acid sensitive sites in the USA, and lower than concentrations in Esthwaite Water in the UK, mountain lake sites in Slovakia and Poland, Lake Michigan and Adirondack mountain lakes in the USA.

Individual PAH compounds

The concentration profiles of the 16 PAH compounds are shown in Table 5 and in Figure 12. Naphthalene, acenaphthylene, acenaphthene, anthracene and fluorene appear to show no particular temporal patterns although naphthalene is high (>70 ng g^{-1}) throughout and may show a decrease through time. The other four have low concentrations (<15 ng g^{-1}) at all times. The other eleven compounds show similar temporal patterns to the ΣPAH profile, i.e. a broad curve with generally poorly defined peaks.

Of the other eleven compounds, nine have maximum concentrations at the same time as ΣPAH (1920-1934), the exceptions being benzo(b)fluoranthene (1890 - 1904) and benzo(ghi)perylene (1905-1919). These individual PAH peaks are also approximately 30 years earlier than the Esthwaite Water maxima. The benzo(ghi)perylene peak is also later in Esthwaite (1945-1950) by about the same period although in Esthwaite Water, the benzo(b)fluoranthene peak is at a similar time to other PAH compounds (1965-1970).

Little data appear to exist for naphthalene and so it is difficult to determine why this lightest of PAH compounds appears to be at a high concentration throughout the core. This may be due to a natural source which has changed little through time. Similar naphthalene results were determined for lake sites on Svalbard in the Arctic where a natural source may be the only realistic explanation for early levels of this compound.

The agreement between the maxima for nine PAH compounds suggests that this was the period of maximum PAH deposition from whatever source. The absolute concentrations of these compounds are very low suggesting that the PAH source is either small or remote. The timing of this peak (1920-1934) is not consistent with other peaks in pollutant deposition, suggesting that the main influence is not high temperature coal or oil combustion (SCP; metals) or other industrial emissions (PCB; PCDD/F; metals). It is also highly unlikely that emissions from road vehicles or ships was greater during the 1920s in this area than at present. The source of the PAHs is therefore unclear, but the synchronicity of the peaks and steady increase and decrease on either side does suggest that the cause has a source rather than being due to random variability.

There are two possibilities. First, Flower *et al.* (1993) show that the SCP increase appears to take place earlier at Loch Coire nan Arr (1930s) than elsewhere in Scotland (1960s) although the reason for this is unclear. Although this SCP increase has not been seen at this time in the present study, early fossil-fuel related deposition may have had an impact at the site. Second, it is possible that the source may be low level domestic wood and coal use in the area.

There appears to be little change in relative concentrations of PAH compounds through time, although over the period covered by this study sources of PAH must have changed. For example, the sediment records of SCP, metals, PCB and PCDD/F at Loch Coire nan Arr show that atmospheric deposition from industrial sources has become detectable at the site. PAH are in much higher concentrations than any of these other organics and yet there appears to be no change in PAH correlating to the increases in these other pollutants and by inference their related atmospheric sources. Sanders *et al.* (1993) suggested that this lack of change in PAH through time may be due to a 'weathering' process of the PAH in the atmosphere or the sediments leading to a more homogenous mixture. If this is the case, concentrations of the individual compounds and ΣPAH may change but relative concentrations may not.

Zhang *et al.*(1993) suggest that the phenanthrene:anthracene ratio is higher (around 14 times) in sediments from remote sites than from urban or near urban sites where the ratio decreases to around 10. Emissions of coal, oil and wood combustion have a ratio of approximately 3.0. They also suggest that the fluoranthene:pyrene ratio may indicate urban influence and decrease with increasing urbanisation.

At Loch Coire nan Arr the phenanthrene:anthracene ratio has varied between 9.8 and 15 over the period covered by the study although there has been no trend to these changes. The fluoranthene:pyrene ratio has increased gradually over the period from 1.4 in the pre-1830 sample to 1.8 in the most recent sample. This would suggest a decrease in urban influence at Loch Coire nan Arr over the period and, although the site remains remote from urban locations, with the increase in vehicular activity in this area it is difficult to credit that urban influence is now less than it was 150 years ago.

Table 6 shows a comparison between contemporary levels of individual PAH at Loch Coire nan Arr and recent studies at other lake sites. The comparison with the data from Svalbard lakes (Rose, 1996b) shows an interesting pattern. For the lighter PAH (i.e. naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) the concentrations in the Svalbard surface sediments are generally higher than those in Loch Coire nan Arr. For the remainder of the PAH, i.e. those heavier than anthracene, the pattern is reversed and the PAH concentrations in the surface sediment at Loch Coire nan Arr are greater than the Svalbard sites. The reason for this may be the volatilisation / distillation effect discussed previously for PCBs. The lighter PAH will be more easily volatilised and will move to higher latitudes whilst the heavier PAH are less likely to do so. Consequently, the Svalbard sites become enriched with the lighter PAH with respect to heavier ones.

The comparison with Esthwaite Water data (Sanders *et al.*, 1993) shows that all individual PAH are far lower in the Loch Coire nan Arr sediments. Benzo(a)pyrene data for other UK sites are reported in Rippey (1990) including two sites in the north-west of Scotland (Lochan Uaine and Lochan Dubh) and one site in the Trossachs region north of Glasgow, Loch Tinker.

Zhang *et al.*, (1993) suggest that benzo(a)pyrene may be indicative of petroleum combustion and this would certainly explain the reason why Loch Tinker and Esthwaite Water show much greater benzo(a)pyrene concentrations (approximately 30 and 140 times respectively). Lochan Uaine and

Lochan Dubh concentrations are also 3-5 times higher whilst the other site reported by Rippey (1990), Lilla Öresjön in southern Sweden, also shows higher benzo(a)pyrene concentrations (15 times) in surface sediments than Loch Coire nan Arr.

Like ΣPAH, concentrations of individual PAH compounds in the surface sediment of Loch Coire nan Arr are much lower than acid sensitive sites in the Adirondack Mountains, USA (Heit *et al.*, 1981) and also small forest lakes in Finland (Wickstrom & Tolonen, 1987). In comparison with European mountain lake sites, the concentrations of individual PAH in Loch Coire nan Arr surface sediments are far lower than sites in the polluted Slovakian and Polish Tatra Mountains and lower than sites in the Spanish Pyrenees. Concentrations are approximately of the same order as sites in the Austrian and French Alps but greater than other Spanish sites in the Gredos and Sierra Nevada Mountains. However, benzo(a)pyrene concentrations at Loch Coire nan Arr are amongst the lowest of all these sites and only higher than the three cleanest sites in the European mountain lake dataset.

4.3.3. Hexachlorobenzene

The hexachlorobenzene results are given in Table 7 and show that at all sediment depths / time intervals the sediment concentration is below the detection limit of 10 ng g^{-1}. These concentrations are at least an order of magnitude lower than published results for Lake Ontario (113 ng g^{-1}; reported in Coakley *et al.*, 1993), and may be of the same order as HCB concentrations in European mountain lakes (0.4 - 6.3 ng g^{-1}). Remote Alaskan lakes show similar or lower concentrations of HCB (0.1 - ca.1.0 ng g^{-1}). These are summarised in Table 8.

4.3.4. Lindane (γ-HCH)

Lindane was not found at levels above the analytical detection limit (20 ng g^{-1}: 1996 - 1950; 25 ng g^{-1}: pre-1950) in any of the samples. There are very few references in the literature for sediment lindane concentrations, and none for comparable sites or for any sites in the UK. The only recent reported instance is for an Egyptian lake, Lake Manzala, surrounded by agricultural land (Abou-Arab *et al.*, 1995). Consequently, input of pesticides to this lake have been high and this is reflected in the reported lindane concentration for surface (1991) sediments of 6900 - 20,300 ng g^{-1}.

4.3.5. Aldrin, Dieldrin, Endrin

The detection limit for the analytical techniques of all three of these pesticides is 10 ng g^{-1} and this was not exceeded in any of the samples. There are no UK data with which to compare these results, and elsewhere, apart from a study on Lake Manzala in Egypt (Abou-Arab *et al.*, 1995) and Lake Kariba in Zimbabwe (Zaranyika *et al.*, 1994) which both show high concentrations of the three pesticides (Table 9), recent studies appear to focus exclusively on dieldrin.

Dieldrin concentrations in Loch Coire nan Arr are below the analytical detection limit at all sediment depths (< 10 ng g^{-1}) and it is therefore difficult to compare them to other studies. However, they are likely to be of a similar order to recent sediment concentrations in studied lakes in north-east Minnesota (Kosian *et al.*, 1995) and also some sites in the Canadian Arctic (Muir *et al.*, 1995) (Table 9). These latter sites also show some very low concentrations (0.10 ng g^{-1} for 1986/7) and it is likely that the dieldrin concentrations in Loch Coire nan Arr are higher than this.

4.3.6. p,p'-DDT

The p,p'-DDT data for the Loch Coire nan Arr samples are given in Table 7 and show that for all sediment levels concentrations are below the analytical detection limit. For the upper three levels (1996 - 1950) re-analysis of the samples reduced the detection limit from an initial 50 ng g^{-1} to 25 ng g^{-1}. However, this lower limit still exceeded sediment concentrations and it is unclear how far below this value they actually fall.

Table 10 shows recently reported literature values for DDT concentrations in lake sediments. These are reported in a number of ways, as "DDT", "ΣDDT" and as "p,p'-DDT" but it is to the latter which the Loch Coire nan Arr data should be compared. It can be seen from the Table that even the lower detection limit of 25 ng g^{-1} is well above any other reported p,p'-DDT concentrations, even at sites where concentrations would be expected to be higher than those in Loch Coire nan Arr, for example. Lake Biwa in Japan and more especially Esthwaite Water in the English Lake District. It has been seen that sediment concentrations of other chlorinated organics (e.g. PCBs - Section 4.3.1.) for Loch Coire nan Arr are 3 - 10 times lower than those for Esthwaite Water and it might be expected that p,p'-DDT would follow a similar pattern. If this is the case then the lowered detection limit of 25 ng g^{-1} is still more than 20 times too high for expected concentrations.

4.3.7. Mirex

Mirex (1,1a,2,2,3,3a,4,5,5,5a,5b,6-dodecachlorooctahydro-1,3,4-metheno-1H-cyclobuta[c,d]-pentalene: $C_{10}Cl_{12}$; Dechlorane) is used as a pesticide, a fire retardant and for use in pyrotechnics. It is an unreactive compound and persists in the environment, and this, taken with its high lipophilicity which promotes biomagnification, has generated the concern for mirex levels in aquatic biota, and particular fish and fish-eating birds (Sergeant *et al.*, 1993).

The Loch Coire nan Arr data for mirex are given in Table 7 and show that the analytical detection limit (50 ng g^{-1}) is not exceeded in any of the sediment samples.

All recent literature on mirex sediment concentrations comes from the USA and Canada and the majority of this is on the Great Lake systems, including both lake sediments and fluvial lake sediments (Table 11 & 12). Fluvial lake sediments appear to have much lower concentrations presumably due to unusually high flow rates. Lake Ontario is the most studied system with two reported dated sediment cores analysed for mirex (Halfon & Allan, 1995; and data reported in Comba *et al.*, 1993) and a surface sample (in Coakley *et al.*, 1993). The results from these studies seem consistent and show contemporary levels of 20 - 25 ng g^{-1} with a peak of 62 - 64 ng g^{-1} in the late 1960s and 1970. This maximum concentration for Lake Ontario is therefore greater than the mirex concentrations found in Loch Coire nan Arr at any time although contemporary levels could be similar.

4.3.8. Pentachlorophenol

The pentachlorophenol (PCP) results are given in Table 7 and show that at all sediment depths / time intervals the sediment concentration is below the detection limit of 50 ng g^{-1}.

PCP is a chemical used in the treatment and preservation of wood and there are very few references to contemporary sediment concentrations in the literature. Diamond *et al.* (1996) report a range of PCP concentrations for Lake Ontario although these have been taken from other studies and give concentrations of 8 - 31 ng g^{-1} for recent sediments (pre-1984). These Lake Ontario values are therefore of equal or greater magnitude than the Loch Coire nan Arr data.

PCP is rapidly transformed by photolysis in the water column and this may be one reason why little has been published on sediment concentrations. Diamond *et al.* (1996) suggest that 80% of the PCP entering Lake Ontario is transformed in this way with advective flow removing much of the remainder such that only 1% of the PCP entering the system is retained in the sediments. It is also suggested that for the Lake Ontario system only a very small fraction is from atmospheric sources. It should therefore be expected that sediment concentrations of PCP at Loch Coire nan Arr, where all input is atmospheric, would be very small, well below a 50 ng g^{-1} detection limit.

4.3.9. Chlordane

Loch Coire nan Arr sediment chlordane concentrations are given in Table 7 and show that at all sediment depths / time intervals chlordane is below the analytical detection limit. At most levels this is 10 ng g^{-1} but rises to 12 and 15 ng g^{-1} in the levels corresponding to the late 19th century. However, this is a total chlordane figure and so for the two individual isomers the detection limit is approximately half this. Neither isomer is detectable at these levels.

Literature sediment concentrations for chlordane are limited and no recent data exist for the UK. Reported data are divided between total chlordanes and the specific α- and γ-isomers. Remote sites in Alaska (Gubala *et al.*, 1995) and the Canadian Arctic (Muir *et al.*, 1995) show concentrations of <0.5 ng g^{-1} for total chlordanes and the specific isomers respectively, whilst marine sediments in Casco Bay, Maine, give concentrations for total chlordane of between 0.01 and 4.91 ng g^{-1} and Rhone river sediments gave values below detection limits of 7.0 and 6.6 ng g^{-1} for the α- and γ-isomers respectively. Without more data it is not possible to place the Loch Coire nan Arr results in any further context.

4.3.10. Toxaphene

Toxaphene is a complex mixture hundreds (and possibly thousands) of polychlorinated compounds and isomers. It is variously reported as having been used as an insecticide (Howdeswell & Hites, 1996; Stern *et al.*, 1996) pesticide and piscicide (Miskimmin & Schindler, 1994) and is semivolatile, hydrophobic and extremely persistent. Although heavily used between the mid-1960s and mid-1970s it is completely banned in certain areas of the world. Because of the complex nature of the compound, toxaphene data are usually reported as total values although some workers have attempted to study major components of the whole (e.g. Stern *et al.*, 1996).

The Loch Coire nan Arr data are given in Table 7 as total toxaphene and all sediment concentrations fall below the analytical detection limit of 200 ng g^{-1}. Once again, this is a high limit of detection and is therefore of limited use. However, due to the nature of toxaphene this detection limit can be qualified to state that no specific toxaphene isomer is present above 10 ng g^{-1}.

Literature data are rare for sediment concentrations of toxaphene and non-existent for the UK.

Howdeswell & Hites (1996) provide the only sediment profiles for toxaphene in the recent literature, for eight sites in Lake Ontario, reporting concentrations of between 6 - 16 ng g^{-1} in recent (1985) sediments and a peak of up to 55 ng g^{-1} in 1970. Like many compounds however, the profile suggests low concentrations of toxaphene in the sediment prior to its first manufacture (ca.1945). Lower concentrations of toxaphene (0.01 - 7.4 ng g^{-1}) are reported for recent sediments from lakes in the Canadian Arctic (Muir *et al.*, 1995). With the current dataset it is impossible to make any comparisons with these literature values except to suggest that it is possible that Loch Coire nan Arr concentrations fall somewhere between the Lake Ontario and the remote Arctic lake concentrations.

4.3.11. Hexabromobiphenyls

The data for hexabromobiphenyl concentrations in the Loch Coire nan Arr sediments are given in Table 7. All concentrations are below the analytical detection limit of 20 ng g^{-1} (25 and 30 ng g^{-1} for two samples in the late 19th century). As for toxaphene and chlordane, these limits of detection result from multiple isomers and detection limits for individual isomers are below the limits presented.

No recent data for hexabromobiphenyls in lake sediments have been reported in the literature for the UK. or elsewhere, although some data exist for biological samples and show biomagnification up the food chain (Jansson *et al.*, 1993). It is therefore not possible to compare the Loch Coire nan Arr data with other lake sediment results.

4.3.12. C10 - C13 chlorinated paraffins

The scan spectra obtained (50 - 700 amu) were compared with library spectra for mono- and di-chlorinated species. No spectra matching the library reference spectra were observed for any of the samples. However, the lack of any positive signal for the lower molecular weight compounds may be indicative of the absence of higher chlorinated congeners.

4.3.13. Long chain aliphatics

The spectra for C10 - C13 chlorinated paraffins did indicate the presence of a number of long chain aliphatics in all samples although they did appear to be more common in the most recent samples. These long chains are in the C20 - C40 range and possible identifications for these are: hexacosane, tetracontane, eicosane, 3-methylpentadecane and triacontane. Typical sources of these aliphatics are heavy oils, for example heating and lubrication oils.

4.3.14. Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

The present day and historical trends in PCDD/Fs were analysed for Loch Coire nan Arr in a previous study undertaken by the National Environment Technology Centre, AEA Technology and reported to the Air Quality Division of the Department of the Environment in March 1996 (Rose, 1996a).

These analyses were performed on a series of sediment cores (CNA1-10) taken in February 1994 and consequently this was not repeated in the present study. The results of this earlier work are dealt with in detail in the report but a summary of the main points, taken from Rose (1996a), are as follows:

i) The most recent sample, covering the period 1970 - 1993, indicates that PCDD/F contamination is being received from atmospheric sources. The total PCDD/F concentration (488 ng kg^{-1}) and I-TEQ (3.4 ng kg^{-1}) indicate that Loch Coire nan Arr sediments are among the least contaminated freshwaters of those reported in the UK.

ii) The historical record of PCDD/F concentrations over the 1800 - 1993 time period indicated the presence of PCDD/Fs in the environment prior to large scale industrial activity in the UK. Concentrations start to increase above background levels during the 1860s and 1870s reaching a peak in the 1950s and 1960s and decreasing to the present day (Figure 13). Increases in PCDD/Fs since large-scale industrialisation in the late 1800s has been attributed to increased fossil-fuel combustion and to growth in the chemical industry in the 1930s and 1940s. The more recent decrease in concentrations may be due to increasing controls on production and use of chlorinated chemicals and a decrease in the consumption of fossil-fuels and of leaded petrol.

iii) The contribution of the different homologue groups to total PCDD/Fs has remained broadly similar since the 1800s, with OCDD being dominant throughout. This is consistent with other studies and may be due to atmospheric processes during transport enhancing the higher chlorinated species regardless of source. Minor changes in the homologue profile suggest changing sources have had some impact but these are of a lesser magnitude than reported in other studies.

iv) A comparison of the distribution of 2,3,7,8-substituted isomers in recent sediments with atmospheric deposition samples in a rural northern English site show clear similarities. This may suggest a common UK deposition profile at areas remote from industrial and urban centres.

4.4. Analytical detection limits

Excepting the PAH and PCB results, the detection limits for the organics analyses presented in this report have been found to be disappointingly high.

Analytical Services at AEA Technology plc were the only UK laboratory offering analyses of all the required analytes in a 'turn round' time suitable for the Department of the Environment's reporting deadline, and the detection limits presented here are the best that this laboratory are able to offer.

It has recently been brought to our attention, however that at least some of these compounds can be analysed within the UK at better detection limits. The laboratory at the University of Lancaster is developing techniques for some of these analytes under contract to the Department of the Environment, (Air Quality). However, this information only became available after analysis had been undertaken.

The PAH, PCB and metals data suggest that Loch Coire nan Arr is a clean site with respect to atmospherically deposited pollutants and even with greatly improved detection limits some of these compounds may still be undetectable. However, very low concentrations of organic pollutants have been detected at sites in the Canadian and Alaskan Arctic (Muir *et al.*, 1995; Gubala *et al.*, 1995) and techniques therefore do exist that ought to be able to detect the required analytes at the levels likely to be found in the sediments of Loch Coire nan Arr. The exception to this may be pentachlorophenol which may degrade before deposition in the sediment record. These Arctic studies have not included quite the same breadth of analytes that has been attempted here and it may be that either a larger project or a more focused one would be more beneficial.

Even though Loch Coire nan Arr values are known to be low, "less than detection limit" values do not allow for good comparisons with other studies even if they existed within the UK. An attempt at measuring some of these pollutants in UK sediments was entirely new and so the study suffered from ignorance of expected concentrations. This study has obtained a better idea of these and any future study will benefit from it.

5. Conclusions

Despite the advantages of using lake sediments to determine historical trends and contemporary concentrations of atmospherically deposited pollutants almost no comparable information exists for many organic pollutants for the UK. It is therefore impossible to place the Loch Coire nan Arr data in any spatial context although the site is now thought to be amongst the least polluted in the UK.

The unpolluted nature of the site, with respect to atmospheric deposition at least, was emphasised by the concentrations of those pollutants which were detectable. For example, the PAH peak concentrations at Loch Coire nan Arr are of the same order as the background at other sites and similarly, the PCB concentrations were amongst the lowest in Europe. Metals data also show the site to be amongst the cleanest in the UK.

Unfortunately the detection limits for most of the organic pollutants were not sufficient to say anything about their atmospheric deposition at such a remote site other than that they are 'low' and this is obviously not satisfactory. This is especially the case as there is so little UK, and indeed, world-wide, sediment data with which to compare many of the organochlorine results. This makes the need for further work in the UK even more imperative.

What is clear from this study is that remote lakes are good sites for studying the record of changes in air quality and atmospheric deposition. Both the PAH and PCB data are in agreement that atmospheric concentrations of these pollutants are decreasing and this is supported by the limited data available from elsewhere. However, despite this current decrease contemporary levels of ΣPCB, all individual PCB congeners, Pb, Zn and Cu are clearly above pre-industrial levels.

There is a good agreement between most of the measurable pollutants (PCB, PCDD/F, metals) as to the time of maximum pollutant concentration in surface sediments and the current trend in decreasing deposition. This suggests that the main source of these pollutants is long-range transport from remote industrial sources. The exception to this is PAH, where the peak concentrations are low with respect to background (at Loch Coire nan Arr and especially other UK sites) and the timing of the peak disagrees with the timing of the maxima for all the other measurable pollutants. This suggests that the source of PAH is perhaps not industrial and that maybe this is a local, low level source, for example from the domestic combustion of wood and coal.

6. Recommendations for further research

There are two ways forward from this study.

1. The main problem with interpreting data of this nature is that there are no other UK data with which to compare. It is therefore impossible to place Loch Coire nan Arr in any spatial context within the UK. This work therefore needs to be undertaken at sites in other areas of the UK where deposition is known to differ. This will enable the current study to be placed in a better context. The UKAWMN sites would be a good starting place for such a study as the Network covers the major gradients of pollutants in the UK (Rose, 1993) and are uncontaminated from non-atmospheric sources. However, an extra one or two sites would be useful in the Midlands and the south of England where the Network has no lake sites.

2. The sediment concentrations of many of the pollutants at Loch Coire nan Arr have been shown to be below the detection limit of the UK's main analytical laboratory. It is now our understanding that these may not be the lowest detection limits available in the UK and that techniques are being developed which may offer further improvements. It is crucial that background levels of these pollutants are determined at a pristine site and it has been shown that Loch Coire nan Arr is located in such an area. Therefore, this work should be undertaken at a similar site in order that UK background levels can be more accurately determined. It is also recommended that a longer time period be allowed for this work than was available for the current study, in order that the best laboratories can be identified and used, even if this means using facilities outside the UK.

Acknowledgements

Thanks are due to Simon Patrick, Don Monteith, Chris Curtis and Simon Harlock for help in the field and to Ewan Shilland and Simon Dobinson for their work in the laboratory.

We would also like to thank Bernard Bushby and Alwen Fernandez at AEA Technology plc for undertaking the organics analyses and for discussion of the results.

We are grateful to Cath Rose (AEA Technology plc) for the use of her report on the PCDD/F data from Loch Coire nan Arr, and also to Kevin Jones and Bondi Gevao of the University of Lancaster for their help in searching for UK sediment data.

References

Abou-Arab, A.A.K, Gomaa, M.N.E., Badawy, A. & Naguib, K. (1995). Distribution of organochlorine pesticides in the Egyptian aquatic ecosystem. *Food Chem.* **54**: 141-146.

Baker, J.E., Eisenreich, S.J. & Eadie, B.J. (1991). Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenyl congeners in Lake Superior. *Environ Sci. Technol.* **25**: 500 - 509.

Bishop, C.A., Koster, M.D., Chek, A.A., Hussell, D.J.T. & Jock, K. (1995). Chlorinated hydrocarbons and Hg in sediments, red-winged blackbirds (*Agelaius phoeniceus*) and tree swallows (*Tachycineta bicolor*) from wetlands in the Great Lakes-St. Lawrence basin. *Envir. Toxicol. Chem.* **14**: 491-501.

Bock, R. (1979). *A handbook of decomposition methods in analytical chemistry.* International textbook company.

Boers, J.P., De Leer, E.W.B., Gramberg, L. & De Koning, J. (1993). Levels of coplanar PCBs in flue gases of high temperature processes and their occurrence in environmental samples. *Short papers of the 13th International Symposium on Chlorinated Dioxins and Related Compounds.* (Vienna, Austria - September 1993). Volume 11, 233-236.

Broman, D., Colmsjö, A., Ganning B., Näf, C. & Zebühr, Y. (1988). A multi-sediment trap study on the temporal and spatial variability of polycyclic aromatic hydrocarbons and lead in an anthropogenic influenced archipelago. *Environ. Sci. Technol.* **22**: 1219-1288.

Broman, D., Näf, C., Renberg, I. & Wik, M. (1990). The importance of spheroidal carbonaceous particles for the distribution of polycyclic aromatic hydrocarbons in an estuarine-like urban coastal water area. *Chemosphere.* **21**: 69-77.

Camarero, L., Catalan, J., Pla, S., Rieradevall, M., Jimenez, M., Prat, N., Rodriguez, A. Encina, L., Cruz-Pizarro, L. Sanchez-Castillo, P., Carrillo, P., Toro, M., Grimalt, J., Berdie, L., Fernandez, P. & Vilanova, R. (1995). Remote mountain lakes as indicators of diffuse acidic and organic pollution in the Iberian Peninsula (AL:PE 2 studies). *Wat. Air Soil Poll.* **85**: 487-492.

Carignan, R., Lorrain, S., Lum, K. (1994). A 50-year record of pollution by nutrients, trace metals and organic chemicals in the St. Lawrence River. *Can. J. Fish Aq. Sci.* **51**: 1088-1100.

Christensen, E.R. & Zhang, X. (1993). Sources of polycyclic aromatic hydrocarbons to Lake Michigan determined from sedimentary records. *Envir. Sci. Technol.* **27**: 139-145.

Coakley, J.P., Nagy, E. & Serodes, J-B. (1993). Spatial and vertical trends in sediment-phase contaminants in the Upper Estuary of the St. Lawrence River. *Estuaries* **16**: 653-669.

Comba, M.E., Norstrom, R.J., Macdonald, C.R. & Kaiser, K.L.E. (1993). A Lake Ontario-Gulf of St.Lawrence dynamic mass budget for Mirex. *Environ. Sci. Technol.* **27**: 2198-2206.

Diamond, M.L., Mackay, D., Poulton, D.J. & Stride, F.A. (1996). Assessing chemical behaviour and developing remedial actions using a mass balance model of chemical fate in the Bay of Quinte. *Wat. Res.* **30**: 405-421.

Evans, K.M., Gill, R.A. & Robotham, P.W.J. (1990). The source, composition and flux of polycyclic aromatic hydrocarbons in sediments of the River Derwent, Derbyshire, UK. *Wat. Air Soil Poll.* **51**: 1-12.

Flower, R.J., Jones, V.J., Battarbee, R.W., Appleby, P.G., Rippey, B., Rose, N.L. & Stevenson, A.C. (1993). *The extent of regional acidification in north-west Scotland: Palaeoecological evidence.* A report to the Department of the Environment. Environmental Change Research Centre, Research Paper No. 8.

Furlong, E.T., Cessar, L.R. & Hites, R.A. (1987). Accumulation of polycyclic aromatic hydrocarbons in acid sensitive lakes. *Geochim. Cosmochim. Acta.* **51**: 2965-2975.

Glew, J.R. (1991). Miniature gravity corer for recovering short sediment cores. *J. Paleolim.* **5**: 285-287.

Granier, L. & Chevreuil, M. (1991). Automobile traffic: a source of PCBs to the atmosphere. *Chemosphere* **23**: 785-788.

Gubala, C.P., Landers, D.H., Monetti, M., Heit, M., Wade, T., Lasorsa, B. & Allen-Gil, S. (1995). The rates of accumulation and chronologies of atmospherically derived pollutants in Arctic Alaska, USA. *Sci. Tot. Environ* **160/161**: 347-361.

Halfon, E. & Allan, R.J. (1995). Modelling the fate of PCBs and Mirex in aquatic ecosystems using the TOXFATE model. *Envir. Int.* **21**: 557-569.

Heit, M., Tan, Y., Klusek, C. & Burke, J.C. (1981). Anthropogenic trace elements and polycyclic aromatic hydrocarbon levels in sediment cores from two lakes in the Adirondack acid lake region. *Wat. Air Soil Poll.* **15**: 441-464.

Howdeshell, M.A. & Hites, R.A. (1996). Historical input and degradation of toxaphene in Lake Ontario sediment. *Environ. Sci. Technol.* **30**: 220-224.

Jansson, B., Andersson, R., Asplund, L., Litzen, K., Nylund, K., Sellstrom, U., Uvemo, U-B., Wahlberg, C., Wideqvist, U., Odsjo, T. & Olsson, M. (1993). Chlorinated and brominated persistent organic compounds in biological samples from the environment. *Envir. Toxicol. Chem.* **12**: 1163-1174.

Kosian, P.A., Hoke, R.A., Ankley, G.T. & Vandermeiden, F.M. (1995). Determination of dieldrin binding to dissolved organic material in sediment pore water using a reverse-phase separation technique. *Envir. Toxicol. Chem.* **14**: 445-450.

Lockhart, W.L., Wilkinson, P., Billeck, B.N., Brunskill, G.J., Hunt, R.V. & Wagemann, R. (1993). Polycyclic aromatic hydrocarbons and Hg in sediments from two isolated lakes in central and northern Canada. *Wat. Sci. Tech.* **28**: 43-52.

Metcalfe, S.E. & Whyatt, J.D. (1995). Modelling future acid deposition with HARM. In: *Battarbee, R.W. (ed.) Acid Rain and its Impact: The critical loads debate.* p27-36. ENSIS Publishing. London.

Miskimmin, B.M. & Schindler, D.W. (1994). Long-term invertebrate community response to toxaphene treatment in two lakes. 50 year records reconstructed from lake sediments. *Can. J. Fish Aq. Sci.* **51**: 923-932.

Muir, D.C.G., Grift, N.P., Lockhart, W.L., Wilkinson, P., Billeck, B.N. & Brunskill, G.J. (1995). Spatial trends and historical profiles of organochlorine pesticides in Arctic lake sediments. *Sci. Tot. Environ.* **160/161**: 447-457.

Patrick, S., Juggins, S., Waters, D. & Jenkins, A. (1991). *The United Kingdom Acid Waters Monitoring Network: Site descriptions and methodology report.* ENSIS publishing. London 63pp.

Patrick, S., Monteith, D.T. & Jenkins, A. (1995). *UK Acid Waters Monitoring Network: The first five years. Analysis and interpretation of results.* April 1988 - March 1993.

Renberg, I. & Wik, M. (1984). Dating recent lake sediments by soot particle counting. *Verh. Internat. Verein. Limnol.* **22**: 712-718.

Renberg, I. & Wik, M. (1985). Soot particle counting in recent lake sediments. An indirect dating method. *Ecological Bulletin.* **37**: 53-57.

Rippey, B. (1990). Sediment chemistry and atmospheric contamination. *Phil Trans. Roy. Soc. Lond.* **B327**: 311-317.

Rippey, B., Murphy, R. J., & Kyle, S. W. (1982). Anthropogenically derived changes in the sedimentary flux of Mg, Cr, Ni, Cu, Zn, Hg, Pb and P in Lough Neagh, Northern Ireland. *Env. Sci. Tech.* **16**: 23-30.

Rose N.L. (1993). *An assessment of the potential of the United Kingdom Acid Waters Monitoring Network to monitor the impact of atmospheric trace metals and persistent organic compounds on freshwaters.* Environmental Change Research Centre, University College London, Research Paper No. 9.

Rose, N.L. (1994). A note on further refinements to a procedure for the extraction of carbonaceous fly-ash particles from sediments. *J. Paleolim.* **11**: 201 - 204.

Rose, C.L. (1996a). *An historical record of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) deposition to a remote lake site in North-West Scotland.* A report to the Department of the Environment, Air Quality Division.

Rose, C.L. (1996b). *PCBs and PAHs in Svalbard lake sediment cores.* A report to University College London.

Rose, N.L. & Juggins, S. (1994). A spatial relationship between carbonaceous particles in lake sediments and sulphur deposition. *Atmos. Env.* **28**: 177-183.

Rose, N.L., Harlock, S., Appleby, P.G. & Battarbee, R.W. (1995). Dating of recent lake sediments in the United Kingdom and Ireland using spheroidal carbonaceous particle (SCP) concentration profiles. *Holocene.* **5**: 328-335.

Sanders, G., Jones, K.C., Hamilton-Taylor, J. (1992). Historical inputs of polychlorinated biphenyls and other organochlorines to a dated lacustrine sediment core in rural England. *Environ. Sci. Technol.* **26**: 1815-1821.

Sanders, G., Jones, K.C., Hamilton-Taylor, J. & Dorr, H. (1993). Concentrations and deposition fluxes of polynuclear aromatic hydrocarbons and heavy metals in the dated sediments of a rural English lake. *Envir. Toxicol. Chem.* **12**: 1567-1581.

Sergeant, D.B., Munawar, M., Hodson, P.V., Bennie, D.T. & Huestis, S.Y. (1993). Mirex in the North American Great lakes. New detections and their confirmation. *J. Great Lakes Res.* **19**: 145-157.

Skare, I. (1972). Microdetermination of Hg in biological samples. Part III, Automated determination of Hg in urine, fish and blood samples. *Analyst* **97**: 148-155.

Stern, G.A., Loewen, M.D., Miskimmin, B.M., Muir, D.C.G. & Westmore, J.B. (1996). Characterisation of two major toxaphene components in treated lake sediment. *Env. Sci. Tech.* **30**: 2251-2258.

Taylor, P.N. & Lester, J.N. (1995). Polynuclear aromatic hydrocarbons in a River Thames sediment core. *Envir. Tech.* **16**: 1155-1163.

Wickstrom, K. & Tolonen, K. (1987). The history of airborne polycyclic aromatic hydrocarbons (PAH) and perylene as recorded in dated lake sediments. *Wat. Air Soil Poll.* **32**: 155-175.

Zaranyika, M.F., Mambo, E. & Makhubalo, J.M. (1994). Organochlorine pesticide residues in the sediments of selected river bays in Lake Kariba, Zimbabwe. *Sci. Tot. Env.* **142**: 221-226.

Zhang, X., Christensen, E.R & Yan, L-Y. (1993). Fluxes of polycyclic aromatic hydrocarbons to Green Bay and Lake Michigan sediments. *J. Great Lakes Res.* **19**: 429-444.

Table 1. Dates attributed to the ten cores from dry weight, loss-on-ignition and SCP profiles.

Depth (cm)	CNA 11	CNA 12	CNA 13	CNA 14	CNA 15	CNA 16	CNA 17	CNA 18	CNA 19	CNA 20
0.0	1996	1996	1996	1996	1996	1996	1996	1996	1996	1996
0.5	1993	1993	1992	1992	1993	1992	1992	1993	1994	1993
1.0	1990	1989	1987	1989	1991	1989	1989	1989	1992	1991
1.5	1987	1986	1983	1985	1989	1985	1985	1986	1990	1988
2.0	1984	1982	1978	1982	1986	1982	1982	1982	1988	1986
2.5	1981	1979	1974	1978	1984	1978	1978	1978	1986	1983
3.0	1978	1976	1971	1975	1981	1972	1972	1975	1984	1981
3.5	1974	1972	1967	1971	1979	1965	1965	1973	1982	1978
4.0	1969	1968	1964	1968	1977	1959	1960	1970	1980	1975
4.5	1964	1964	1960	1964	1973	1954	1949	1968	1978	1972
5.0	1960	1960	1957	1960	1969	1948	1938	1965	1976	1969
6.0	1954	1952	1946	1951	1960	1940	1927	1960	1971	1966
7.0	1950	1943	1933	1942	1951	1933	1916	1949	1967	1963
8.0	1945	1935	1919	1933	1941	1925	1905	1937	1962	1959
9.0	1940	1926	1905	1924	1932	1918	1894	1926	1950	1955
10.0	1927	1918	1890	1915	1922	1910	1883	1914	1937	1945
11.0	1914	1909	1877	1906	1913	1903	1872	1903	1925	1935
12.0	1901	1901	1864	1897	1903	1895	1862	1891	1912	1925
13.0	1888	1892	1851	1888	1894	1888	1850	1880	1900	1914
14.0	1875	1884	*1838*	1879	1884	1880	*1839*	1868	1888	1903
15.0	1862	1875	*1825*	1870	1875	1873	*1828*	1857	1876	1891
16.0	1850	1867	*1811*	1861	1865	1866	*1817*	*1845*	1864	1878
17.0	*1838*	1859	*1798*	1852	1856	1857	*1806*	*1834*	1850	1865
18.0	*1826*	1850	*1785*	*1843*	*1846*	1850	*1795*	*1822*	*1837*	1853
19.0	*1814*	*1842*	*1772*	*1834*	*1835*	*1842*	*1784*	*1811*	*1825*	*1841*
20.0	*1802*	*1833*	*1760*	*1825*	*1826*		*1773*	*1800*	*1812*	*1829*
21.0	*1790*		*1747*							*1817*
22.0	*1776*		*1734*							*1805*
23.0			*1722*							*1793*
24.0										*1781*
25.0										*1770*

NB. Dates in italics are extrapolated beyond oldest attributed date.

Table 2. Sediment metal concentration data for CNA11.

Depth cm	Sodium mg/g	Lead µg/g	Zinc µg/g	Copper µg/g	Nickel µg/g
0-0.5	7.41	30.8	86.8	16.6	8.8
0.5-1.0	9.36	28.7	37.2	10.9	3.9
1.0-1.5	9.31	41.4	33.1	10.5	6.4
1.5-2.0	8.23	48.2	45.5	11.4	7.7
2.0-2.5	9.09	49.5	52.1	12.4	8.3
2.5-3.0	7.41	47.9	53.4	12.7	9.6
3.0-3.5	7.92	55.5	50.3	11.9	10.7
3.5-4.0	8.25	50.1	49.8	11.5	6.5
4.0-4.5	7.40	85.2	54.0	11.8	8.0
4.5-5.0	7.12	60.8	57.6	12.8	12.6
5.0-5.5	9.27	57.0	52.5	10.8	7.7
5.5-6.0	9.67	43.9	41.6	9.3	7.6
6.0-6.5	9.78	56.0	47.3	9.0	9.8
6.5-7.0	8.89	58.4	52.4	9.6	10.5
7.0-7.5	8.39	46.9	61.6	10.8	8.6
7.5-8.0	8.58	55.8	59.8	11.4	8.5
8.0-8.5	8.33	58.7	54.5	11.8	9.5
8.5-9.0	7.91	56.9	55.0	10.5	9.1
9.0-9.5	8.42	56.6	55.2	10.9	7.7
9.5-10.0	9.43	56.0	59.9	11.3	8.1
10.0-10.5	9.18	32.8	32.0	8.7	8.1
10.5-11.0	9.33	40.1	36.5	8.8	11.2
11.0-11.5	9.19	38.4	44.0	10.9	9.6
11.5-12.0	8.96	33.3	37.7	10.1	9.1
12.0-12.5	10.73	26.9	34.6	8.7	13.0
12.5-13.0	10.82	23.7	37.8	10.3	6.5
13.0-13.5	9.87	4.8	39.1	10.7	10.0
13.5-14.0	9.65	14.7	40.7	10.1	10.1
14.0-14.5	11.57	22.1	31.9	9.3	10.8
14.5-15.0	11.13	7.3	30.8	8.9	6.7
15.0-15.5	14.53	16.5	28.7	8.9	11.5
15.5-16.0	14.47	11.4	25.3	9.8	13.8
16.0-16.5	13.10	18.7	32.6	10.8	11.4
16.5-17.0	11.28	14.2	27.1	9.9	10.7
17.0-17.5	10.79	23.9	26.1	9.0	15.0
17.5-18.0	11.50	20.7	31.9	8.8	8.1
18.0-18.5	12.98	21.7	33.7	9.1	9.7
18.5-19.0	11.65	20.4	28.3	9.9	8.0
19.0-19.5	11.71	1.7	22.3	8.8	9.7
19.5-20.0	10.47	2.6	23.2	9.2	5.1
20.0-20.5	11.83	4.1	25.3	9.6	6.2
20.5-21.0	12.86	9.9	23.3	9.2	7.1
21.0-21.5	14.35	7.5	23.2	8.7	8.9
21.5-22.0	13.71	8.9	23.6	8.9	9.7
22.0-22.5	16.54	12.5	22.2	8.8	8.5

Table 2. (cont.)

Depth	Chromium	Cadmium	Arsenic	Mercury
cm	μg/g	μg/g	μg/g	μg/g
0-0.5	6.8	4.71	14.0	0.088
0.5-1.0	6.4	3.96	12.8	0.063
1.0-1.5	8.1	3.68	6.7	0.054
1.5-2.0	8.1	0.88	5.5	0.070
2.0-2.5	10.8	0.32	6.4	0.086
2.5-3.0	9.6	0.61	7.3	0.096
3.0-3.5	9.3	0.49	9.5	0.099
3.5-4.0	9.0	1.41	10.7	0.075
4.0-4.5	9.6	1.93	8.7	0.081
4.5-5.0	11.0	1.33	11.5	0.111
5.0-5.5	9.6	1.55	9.6	0.078
5.5-6.0	9.2	0.88	5.8	0.066
6.0-6.5	10.1	0.73	5.7	0.097
6.5-7.0	10.9	0.50	6.0	0.110
7.0-7.5	11.1	0.82	9.0	0.085
7.5-8.0	10.6	1.38	11.6	0.081
8.0-8.5	10.3	0.68	14.6	0.095
8.5-9.0	10.5	0.59	11.4	0.089
9.0-9.5	9.8	0.76	11.6	0.075
9.5-10.0	11.3	1.11	10.1	0.078
10.0-10.5	5.9	0.56	4.9	0.082
10.5-11.0	8.0	0.21	6.8	0.100
11.0-11.5	7.9	1.04	5.6	0.095
11.5-12.0	8.8	0.72	4.5	0.110
12.0-12.5	7.2	0.45	3.7	0.120
12.5-13.0	8.7	0.54	6.2	0.065
13.0-13.5	8.8	0.80	5.8	0.099
13.5-14.0	8.0	0.37	6.7	0.113
14.0-14.5	10.6	0.96	4.4	0.091
14.5-15.0	10.3	1.19	5.6	0.057
15.0-15.5	15.6	0.18	6.5	0.110
15.5-16.0	17.6	0.12	3.8	0.135
16.0-16.5	12.9	0.37	6.1	0.105
16.5-17.0	11.0	0.34	7.0	0.099
17.0-17.5	11.4	1.37	4.8	0.140
17.5-18.0	10.5	2.54	6.7	0.085
18.0-18.5	12.2	1.08	6.0	0.100
18.5-19.0	10.1	1.79	6.1	0.075
19.0-19.5	10.2	2.31	4.8	0.095
19.5-20.0	9.6	1.36	5.2	0.050
20.0-20.5	11.5	1.00	5.2	0.059
20.5-21.0	10.8	3.44	4.8	0.070
21.0-21.5	11.8	1.32	5.0	0.088
21.5-22.0	12.3	0.87	5.9	0.090
22.0-22.5	12.0	1.80	5.5	0.080

Table 3. PCB results. All values in ng g^{-1}.
The term 'nd' denotes that the isomer has not been detected at the limit of detection shown in the brackets.

Sample	CNA-A	CNA-B	CNA-C	CNA-D	CNA-E	CNA-F	CNA-G	CNA-H	CNA-I	CNA-J	CNA-K	CNA-L
Date	1996 - 1980	1979 - 1965	1964 - 1950	1949 - 1935	1934 - 1920	1919 - 1905	1904 - 1890	1889 - 1875	1874 - 1860	1859 - 1845	1844 - 1830	Pre - 1830
244-T3CB (28)	0.11	nd(0.1)	nd(0.1)	0.11	0.12	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)
2525-T4CB (52)	0.18	0.20	0.16	0.18	0.13	0.15	0.13	0.10	0.16	nd(0.1)	nd(0.1)	nd(0.1)
24525-P5CB (101)	0.33	0.41	0.34	0.33	0.19	0.14	0.18	nd(0.1)	0.11	0.10	0.10	nd(0.1)
24534-P5CB (118)	0.19	0.17	0.46	0.22	0.18	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)
234245-H6CB (138)	0.50	0.65	0.40	0.29	0.15	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)
245245-H6CB (153)	0.58	0.71	0.39	0.20	0.16	0.31	0.11	nd(0.1)	0.12	0.14	nd(0.1)	0.25
2345245-H7CB (180)	0.49	0.96	0.35	0.55	0.12	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)	nd(0.1)
ΣPCB	8.8	11.8	8.7	7.0	3.9	2.5	2.1	1.2	1.9	1.5	nd(1.0)	1.9
Standard Recovery	70	82	79	70	77	43	56	74	85	65	58	62

Table 6. Concentrations of individual PAH compounds in surface sediments from Loch Coire nan Arr compared with recent literature results. All values in ng g^{-1}.

Site	**Loch Coire nan Arr**	Svalbard Lakes	Esthwaite Water, UK	Adirondack Lakes, USA	Finnish Lakes	Lilla Öresjön, Sweden	Loch Tinker, UK	Lochan Dubh, UK	Lochan Uaine, UK.
	This study	Rose, 1996b	Sanders *et al.*, 1993	Heit *et al.*, 1981	Wickstrom & Tolonen, 1987	Rippey, 1990			
Napthalene	**82**	40-212							
Acenaphthylene	**6**	0-15							
Acenaphthene	**4**	0-77							
Fluorene	**7**	4-29							
Phenanthrene	**36**	4-354	540	154-324	100-110				
Anthracene	**3**	4-25	110	21-32					
Fluoranthene	**53**	7-54	3230	463-1236	250-290				
Pyrene	**29**	3-39	3040	320-934	120-160				
Benzo(a)anthracene	**14**	0	1850	78-362	60-1000				
Chrysene	**62**	0-29							
Benzo(b)fluoranthene	**119**	0-26	1770	358-1784	800-3700				
Benzo(k)fluoranthene	**44**	0-18	710	115-558					
Benzo(a)pyrene	**14**	0	1960	128-690	60-2000	200	450	70	50
Indenopyrene	**88**	0	2620	315-1294	100-1900				
Dibenzo(ah.ac)anthracene	**11**	0		30-92	50-1200				
Benzo(ghi)perylene	**54**	0	2370	303-1356					

Table 6 (cont.). Concentrations of individual PAH compounds in surface sediments from Loch Coire nan Arr compared with recent European mountain lake cores. All values in ng g^{-1}.

Site	**Loch Coire nan Arr**	L.Aguilo Spain	L.Caldera Spain	Arresjøn Svalbard	L.Cimera Spain	L.Escura Portugal	L.Redo, Spain	L.Noir, France	Schwarzsee Austria	Starolesnienske Slovakia	Dlugi Staw, Poland
Napthalene	**82**										
Acenaphthylene	**6**										
Acenaphthene	**4**										
Fluorene	**7**	24	4	6	1	9	2	3	6	23	25
Phenanthrene	**36**	179	42	47	10	52	41	33	47	617	442
Anthracene	**3**	16	0.8	3	0.5	2	2	2	3	49	32
Fluoranthene	**53**	469	18	20	22	78	76	71	77	1757	1439
Pyrene	**29**	326	13	17	17	3	38	46	38	1161	855
Benzo(a)anthracene	**14**	149	4	4	5	13	14	20	18	376	372
Chrysene	**62**										
Benzo(b)fluoranthene	**119**	848	13	31	27	91	124	96	112	2389	1724
Benzo(k)fluoranthene	**44**	519	9	13	16	64	21	48	63	1522	1021
Benzo(a)pyrene	**14**	269	5	5	5	21	15	23	37	751	503
Indenopyrene	**88**	883	14	34	23	82	50	59	93	1809	1509
Dibenzo(ah.ac)anthracene	**11**	166	0.4	5	3	12	9	10	18	263	232
Benzo(ghi)perylene	**54**										

Table 7. Organics results. All values in ng g^{-1}.
The term 'nd' denotes that the compound has not been detected at the limit of detection shown in the brackets.

Sample	CNA-A	CNA-B	CNA-C	CNA-D	CNA-E	CNA-F	CNA-G	CNA-H	CNA-I	CNA-J	CNA-K	CNA-L
Date	1996 - 1980	1979 - 1965	1964 - 1950	1949 - 1935	1934 - 1920	1919 - 1905	1904 - 1890	1889 - 1875	1874 - 1860	1859 - 1845	1844 - 1830	Pre - 1830
Hexachlorobenzene	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)
Lindane	nd(20)	nd(20)	nd(20)	nd(25)	nd(25)	nd(25)	nd(25)	nd(25)	nd(25)	nd(25)	nd(25)	nd(25)
Aldrin	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)
Dieldrin	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)
Endrin	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)
p,p'-DDT	nd(25)	nd(25)	nd(25)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)
Mirex	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)
Pentachlorophenol	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)	nd(50)
ΣToxaphene	nd(200)	nd(270)	nd(200)	nd(200)	nd(200)	nd(200)	nd(200)	nd(200)	nd(330)	nd(200)	nd(200)	nd(200)
Hexabromobiphenyl	nd(20)	nd(20)	nd(20)	nd(20)	nd(20)	nd(20)	nd(20)	nd(25)	nd(30)	nd(20)	nd(20)	nd(20)
ΣChlordane	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(10)	nd(12)	nd(15)	nd(10)	nd(10)	nd(10)

Table 8. Hexachlorobenzene concentrations reported in the literature compared to this study. All values in ng g^{-1}

Site	Concentration	Date	Reference
Loch Coire nan Arr, U.K.	**< 10**	**1996 to pre 1830**	**This study**
Lake Ontario, Canada	113	pre 1989	in Coakley *et al.*, 1993
Lac Saint-Pierre, Canada	0.5	pre 1989	in Coakley *et al.*, 1993
Laguna Aguiló, Spain	1.1	1993	Camarero, *et al.*, 1995
Laguna Redó, Spain	0.90	1993	Camarero, *et al.*, 1995
Laguna Cimera, Spain	0.44	1993	Camarero, *et al.*, 1995
Lagoa Escura, Portugal	0.95	1993	Camarero, *et al.*, 1995
Laguna Caldera, Spain	6.30	1993	Camarero, *et al.*, 1995
Wonder Lake, Alaska	0.7	1991	Gubala *et al.*, 1995
Schrader Lake, Alaska	0.1	1992	Gubala *et al.*, 1995
L382, Canadian Arctic	0.36	1987	Muir *et al.*, 1995
L375, Canadian Arctic	0.43 0.47 0.25 0.31 0.19 0.25 0.06 0.0	1988 1984 1979 1973 1967 1961 1955 1948	Muir *et al.*, 1995
Far Lake, Canadian Arctic	0.29 0.13 0.03	1986 1939 1918	Muir *et al.*, 1995
Hawk Lake, Canadian Arctic	1.28 1.5 0.53 0.31 0.34	1973 1961 1944 1927 1906	Muir *et al.*, 1995
Amituk Lake, Canadian Arctic	0.97 0.42 0.15 0.13 0.11 0.16	1980 1968 1955 1942 1925 1906	Muir *et al.*, 1995
Sophia Lake, Canadian Arctic	0.11 0.13 0.05	1979 1946 1895	Muir *et al.*, 1995
Buchanan Lake, Canadian Arctic	1.03	1985	Muir *et al.*, 1995
Hazen Lake, Canadian Arctic	1.01 0.97 0.69	1986 1976 1964	Muir *et al.*, 1995

Table 9. Aldrin, Dieldrin and Endrin concentrations reported in the literature compared to this study. All values in ng g^{-1}.

Compound	Site	Concentration	Date	Reference
Aldrin **Dieldrin** **Endrin**	**Loch Coire nan Arr, UK.**	**<10** **<10** **<10**	**1996-pre 1830** **1996-pre 1830** **1996-pre 1830**	**This study**
Dieldrin	Airport Pond Pequaywan Lake West Bearskin Lake (NE Minnesota)	16.20 - 19.10 6.68 - 10.93 2.52 - 3.36	pre 1993	Kosian *et al.*, 1995
Aldrin	Lake Manzala, Egypt	10,300 - 30,200	1991	Abou-Arab *et al.*, 1995
Aldrin Dieldrin Endrin	Lake Kariba, Zimbabwe	17 - 410 2,270 - 22,800 5,120 - 28,300	pre 1994	Zaranyika *et al.*, 1994
Dieldrin	L382, Canadian Arctic	0.10	1987	Muir *et al.*, 1995
Dieldrin	L375, Canadian Arctic	0.31	1988	Muir *et al.*, 1995
Dieldrin	Far Lake, Canadian Arctic	0.05	1986	Muir *et al.*, 1995
Dieldrin	Hawk Lake, Canadian Arctic	3.17	1985	Muir *et al.*, 1995
Dieldrin	Amituk Lake, Canadian Arctic	1.18	1980	Muir *et al.*, 1995
Dieldrin	Sophia Lake, Canadian Arctic	0.25	1979	Muir *et al.*, 1995
Dieldrin	Buchanan Lake, Canadian Arctic	0.24	1985	Muir *et al.*, 1995
Dieldrin	Hazen Lake, Canadian Arctic	0.10	1986	Muir *et al.*, 1995

Table 10. DDT concentrations reported in the literature compared to this study. All values ng g^{-1}.

Compound	Site	Concentration	Date	Reference
p,p'-DDT	**Loch Coire nan Arr, UK**	**<25**	**1996-1950**	**This study**
		<50	**pre 1949**	
p,p'-DDT	Esthwaite Water, UK	1.5	1990	Sanders *et al.*, 1992
		5.6	1958	
		0.5	1929	
		<0.5	1899	
DDT	Lake Erie	5.8 - 70.3	'Recent'	Various, reported in Rowan & Rasmussen, 1992
	Lake Huron	13.1 - 25.7		
	Lake Michigan	24.4		
	Lake Ontario	62.2		
	Lake St. Clair	6.6		
	Lake Superior	2.4		
p,p'-DDT	Wonder Lake, Alaska	0.145	1991	Gubala *et al.*, 1995
p,p'-DDT	Schrader Lake, Alaska	0.027	1992	Gubala *et al.*, 1995
p,p'-DDT	Lake Biwa, Japan - north	2.0 - 1.1	Upper (1987-88)	Kawabe *et al.*, 1992
		2.1 - 1.3	Lower	
	Lake Biwa - south	2.0 - 9.0	Upper (1987-88)	
		2.4 - 5.8	Lower	
ΣDDT	Lake Superior	3	1985	Golden *et al.*, 1993
		3	1980	
		5	1970	
		4	1960	
		2.5	1940	
		1.5	1920	
ΣDDT	Lake Michigan	50	1985	Golden *et al.*, 1993
		60 - 120	1980	
		75 - 90	1970	
		10 - 70	1960	
		0 - 40	1940	
		<10	1920	
ΣDDT	Lake Ontario	40	1985	Golden *et al.*, 1993
		60 - 90	1980	
		100 - 300	1970	
		180	1960	
		0 - 120	1940	
		0 - 50	1920	
p,p'-DDT	L382	0.46	1987	Muir *et al.*, 1995
	L375	0.09	1988	
	Far Lake	<0.01	1986	
	Hawk Lake	1.97	1985	
	Amituk Lake	0.20	1980	
	Sophia Lake	0.01	1979	
	Buchanan Lake	0.07	1985	
	Hazen Lake	0.04	1986	
	(All Canadian Arctic)			

Table 11. Mirex lake sediment concentrations reported in the literature compared to this study. All values in ng g^{-1} dry sediment except * ng g^{-1} wet sediment.

Site	Concentration	Date	Reference
Loch Coire nan Arr	**<50**	**1996 - pre 1830**	**This study**
Lake Ontario	24.7	'Recent'	In: Coakley *et al.*, 1993
12 wetlands around Lakes Huron, Erie and Ontario	0.05 - 0.40 *	1991	Bishop *et al.*, 1995
Lake Ontario	21 21 52 64 41 14 2 2	1986 1976 1969 1967 1963 1961 1958 1953	Halfon & Allan, 1995
Lake Ontario	20 62 1 0	1982 1970 1960 1950	In: Comba *et al.*, 1993

Table 12. Mirex fluvial lake sediment concentrations reported in the literature. All values in ng g^{-1}.

Site	Concentration	Date	Reference
Lac Saint-Pierre, Canada	<0.01	'Recent'	In: Coakley *et al.*, 1993
Lake St. Francis, St. Lawrence River basin	0.75 0.25 1.2 0 0	1992 1980 1970 1960 1950	Carignan *et al.*, 1994
Lake St. Louis, St. Lawrence River basin	0.08 0.35 0.2 1.6 0.2 0	1992 1980 1970 1962 1960 1950	Carignan *et al.*, 1994
Laurentian Trough	0.19 - 0.58 0.08 - 0.38 0.05 - 0.65 <DL - 0.22 <DL - 0.25 <DL - 0.01	1990 1980 1970 1960 1950 1940	Comba *et al.*, 1993

Figure 1a. Location map and catchment of Loch Coire nan Arr

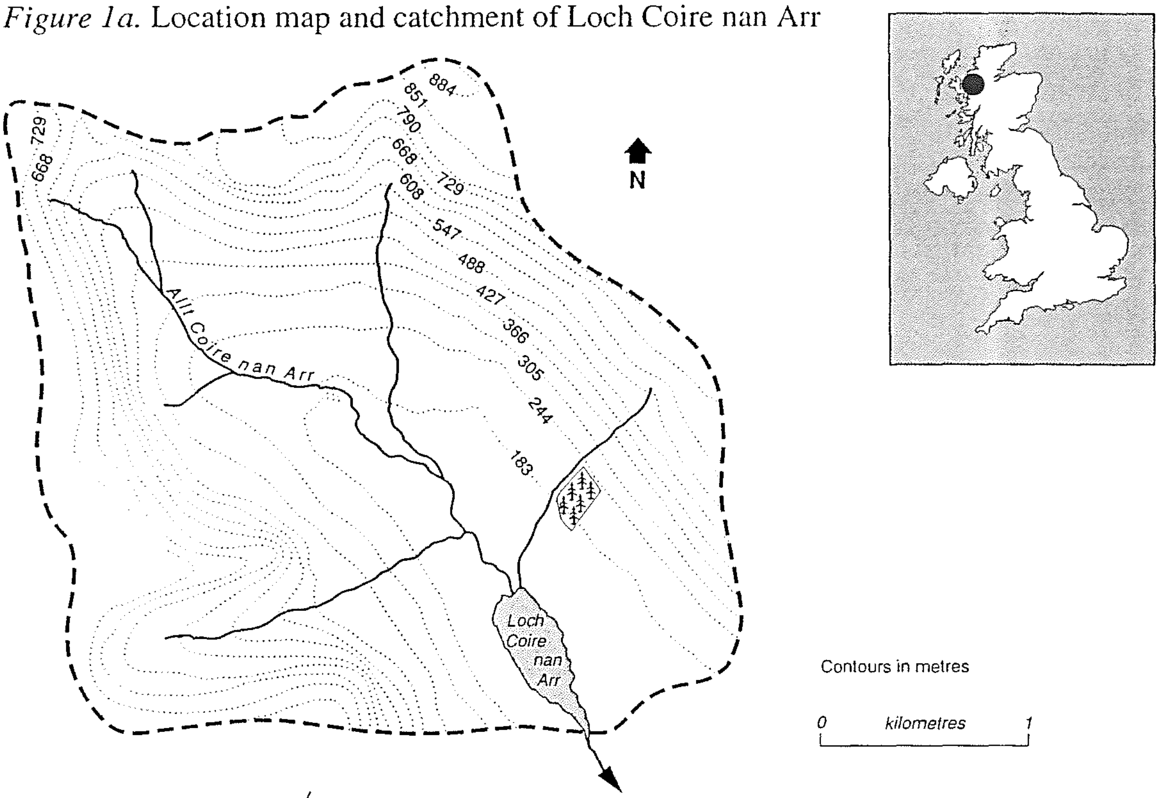


Figure 1b. Bathymetry of Loch Coire nan Arr

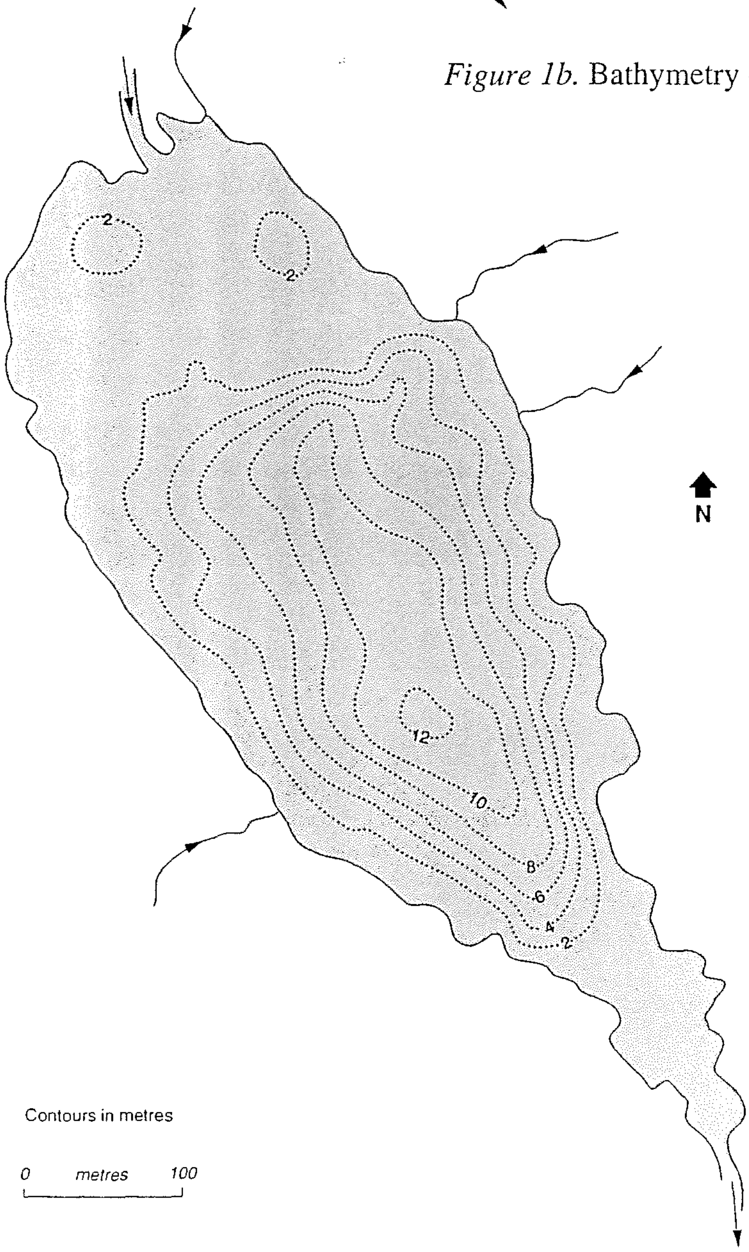
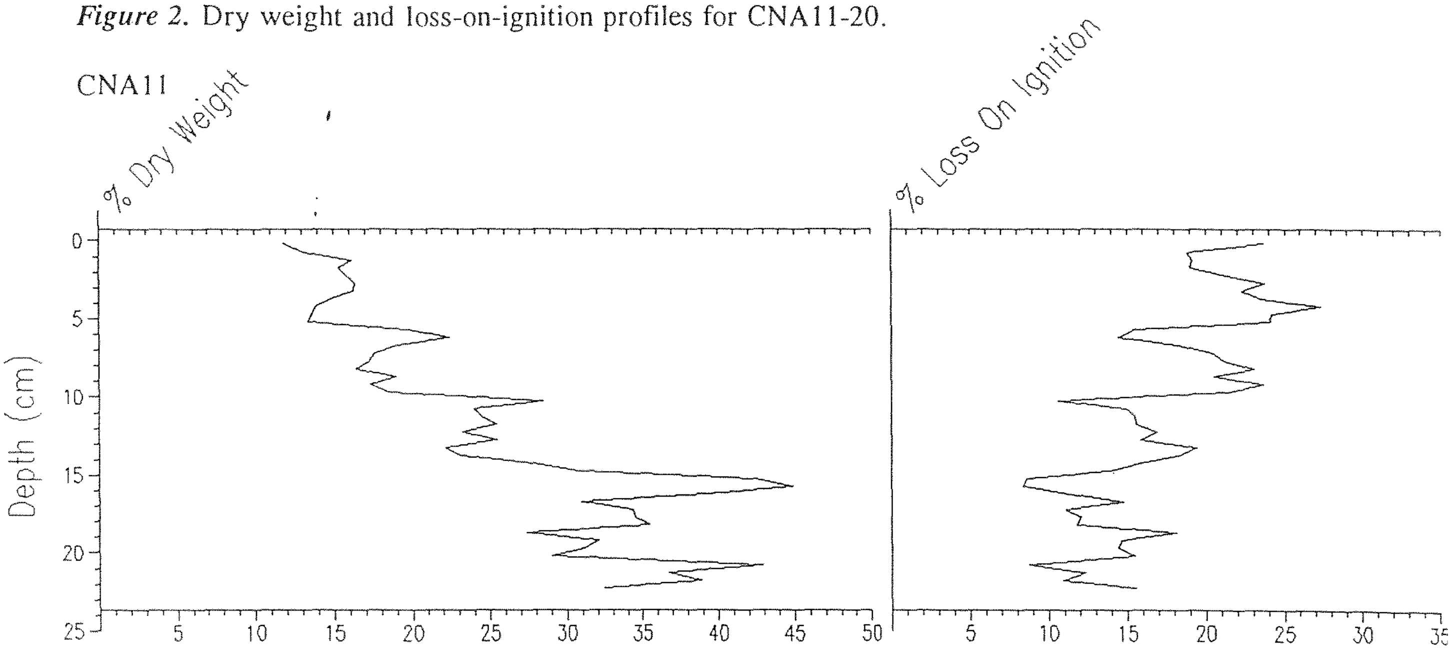
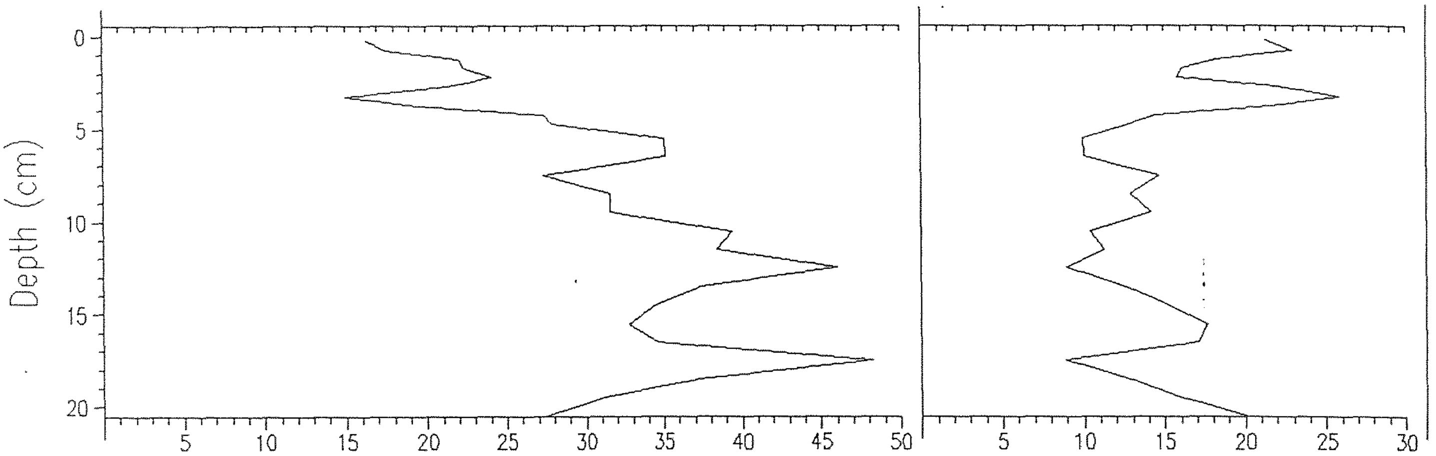


Figure 2. Dry weight and loss-on-ignition profiles for CNA11-20.

CNA11



CNA12



CNA13

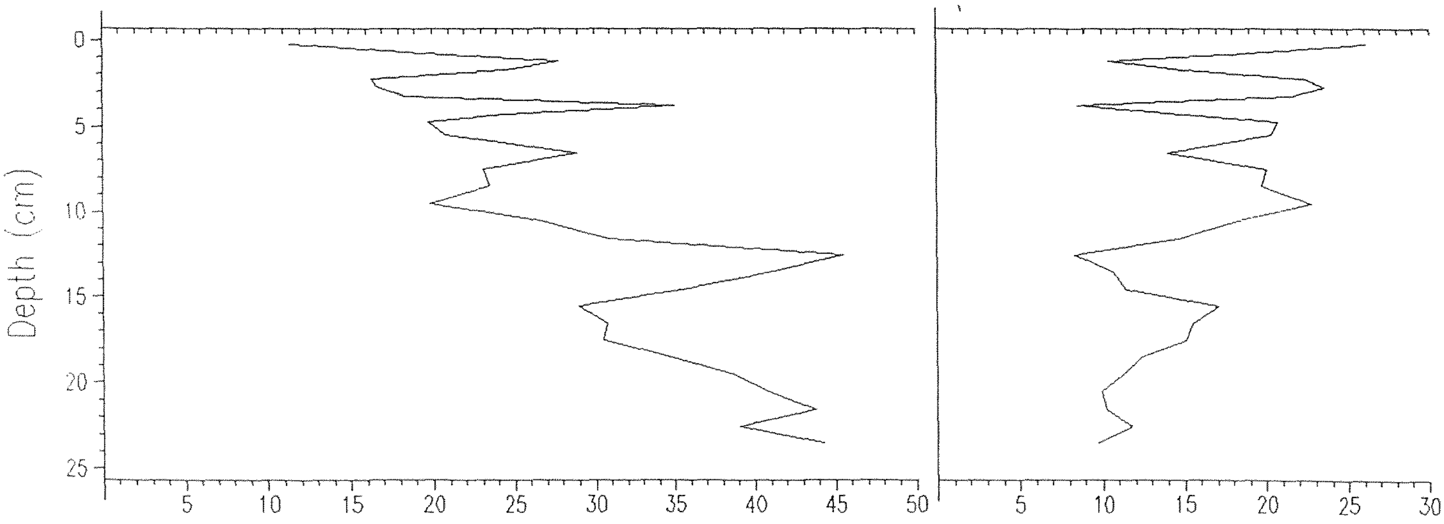
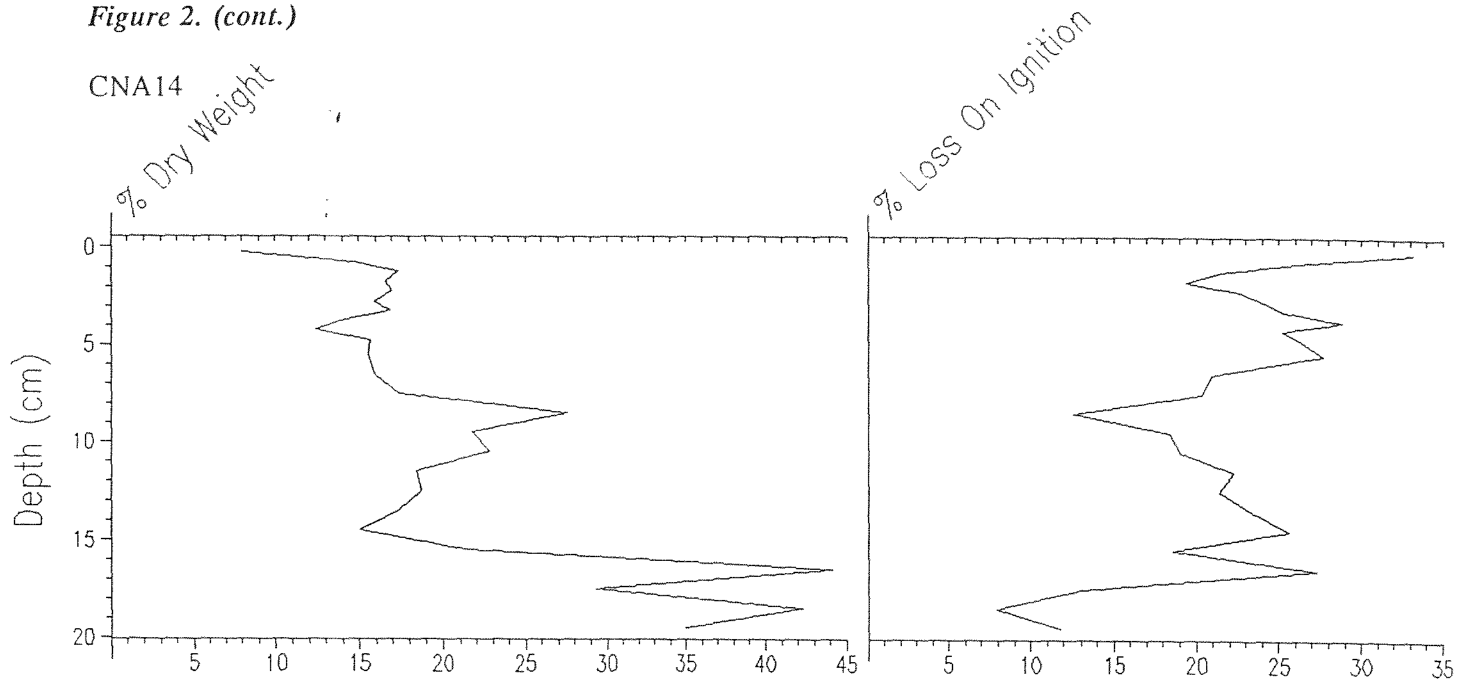
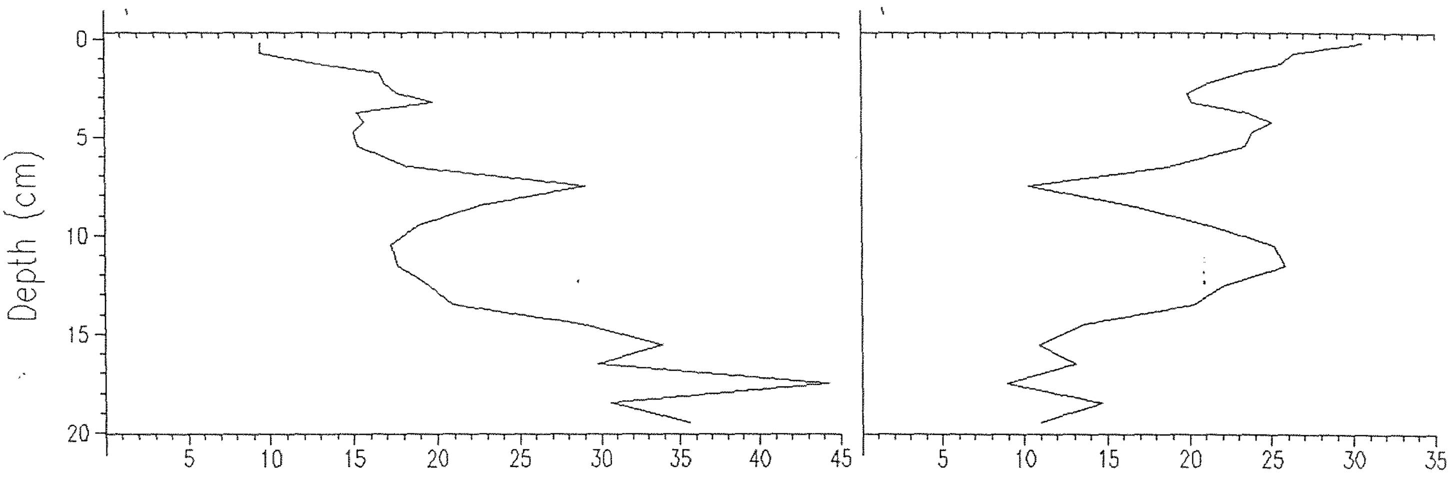


Figure 2. (cont.)

CNA14



CNA15



CNA16

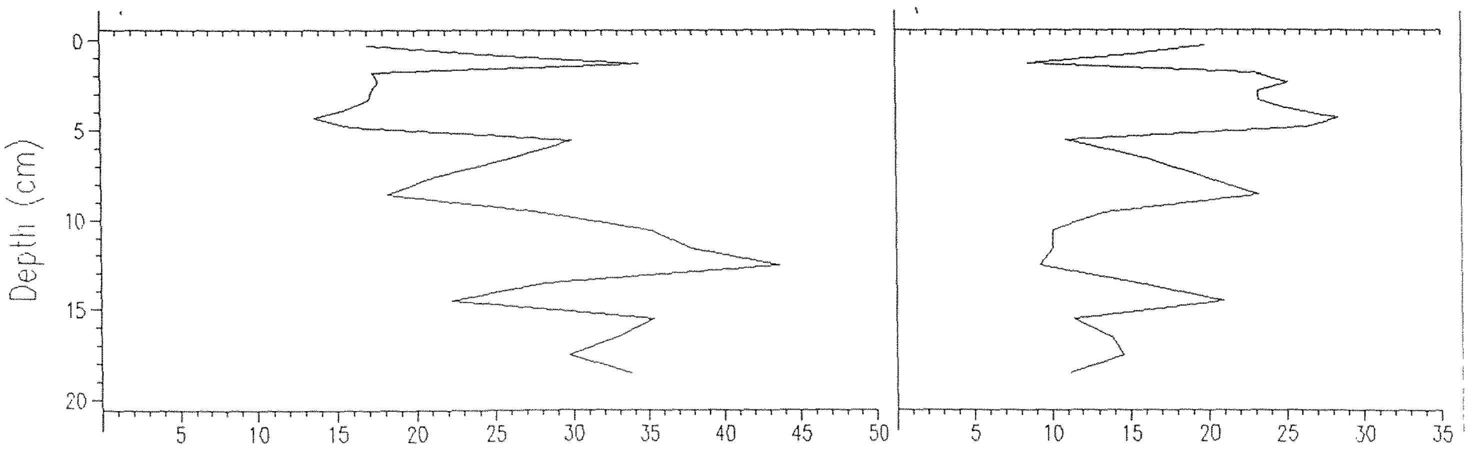
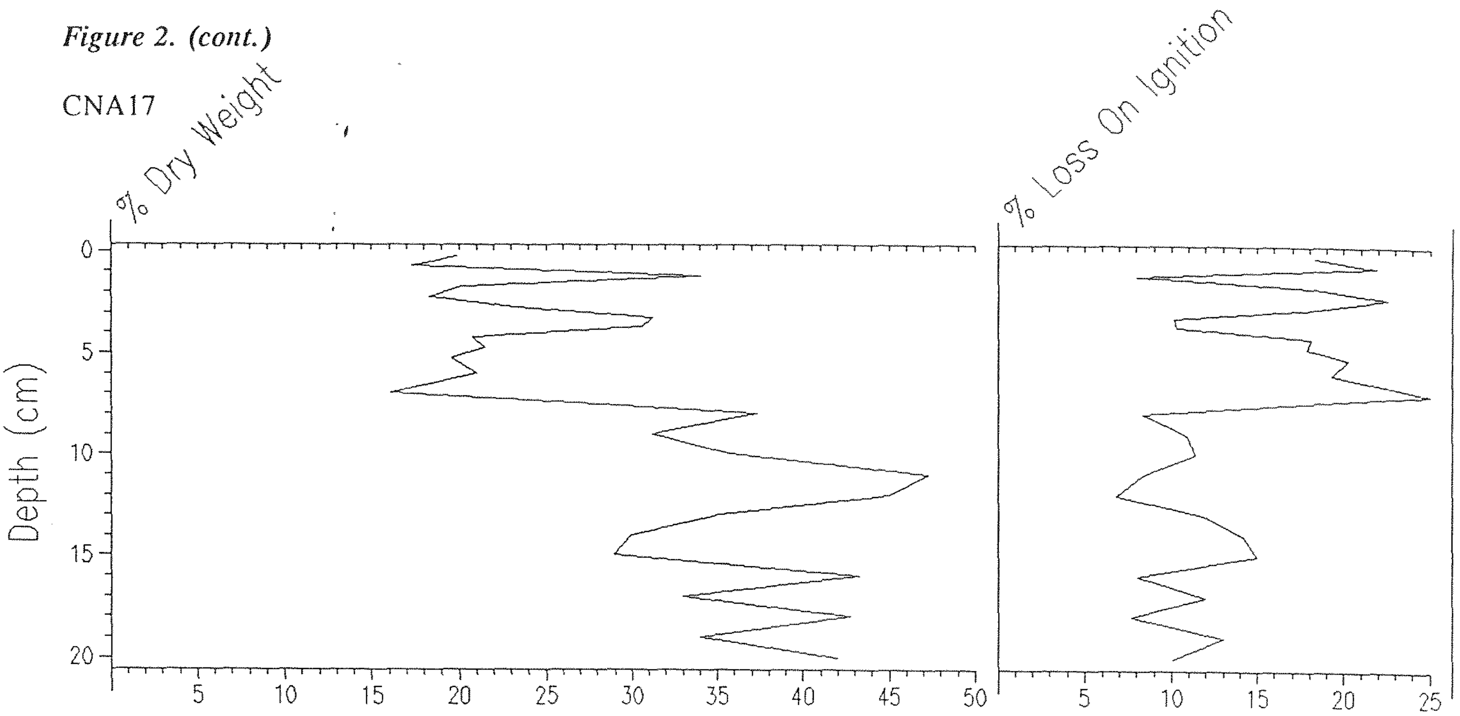
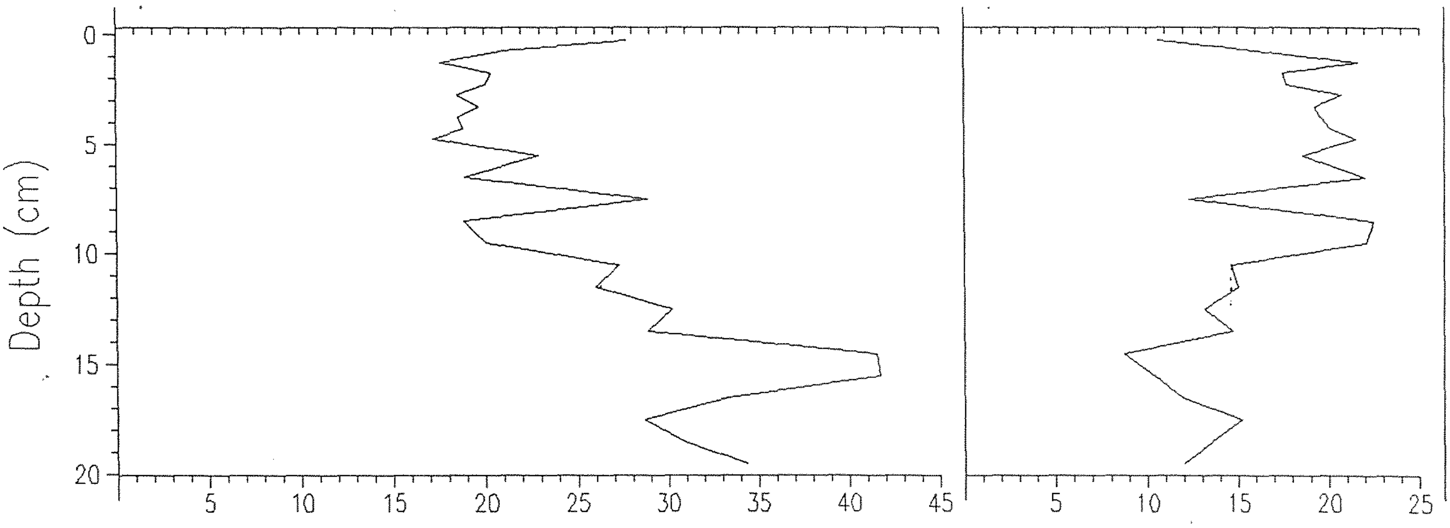


Figure 2. (cont.)

CNA17



CNA18



CNA19

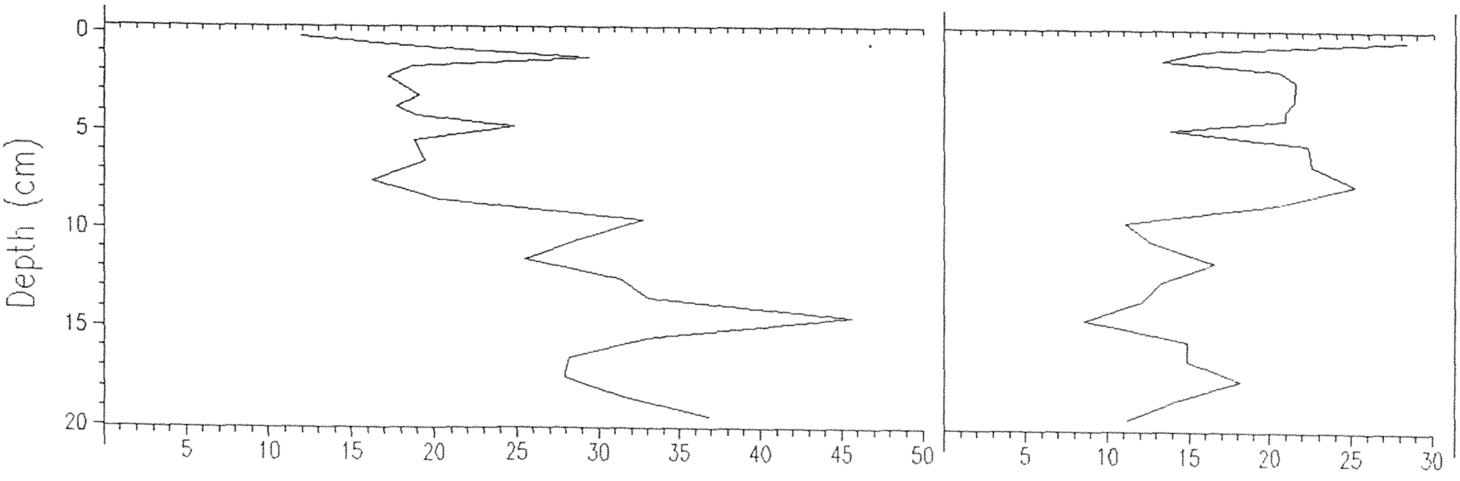


Figure 2. (cont.)

CNA20

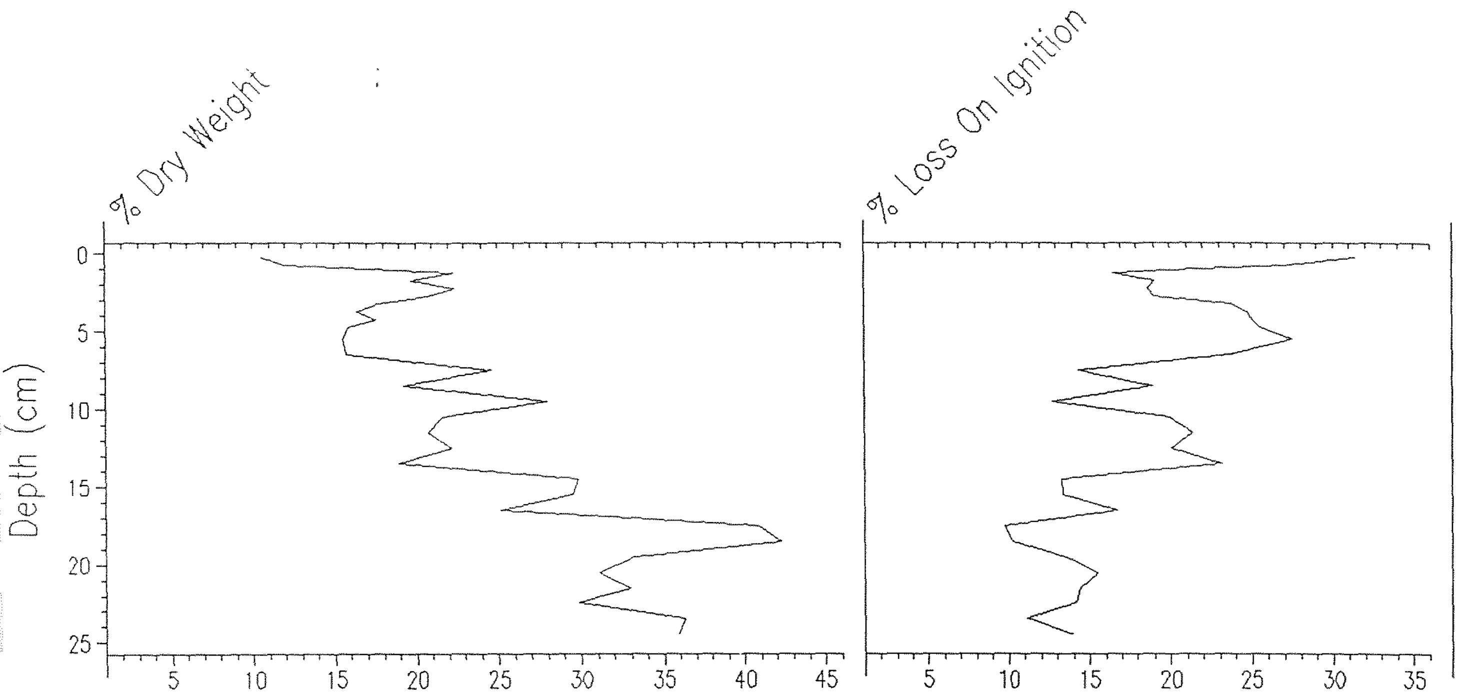


Figure 3. Spheroidal carbonaceous particle profiles for CNA11-20.

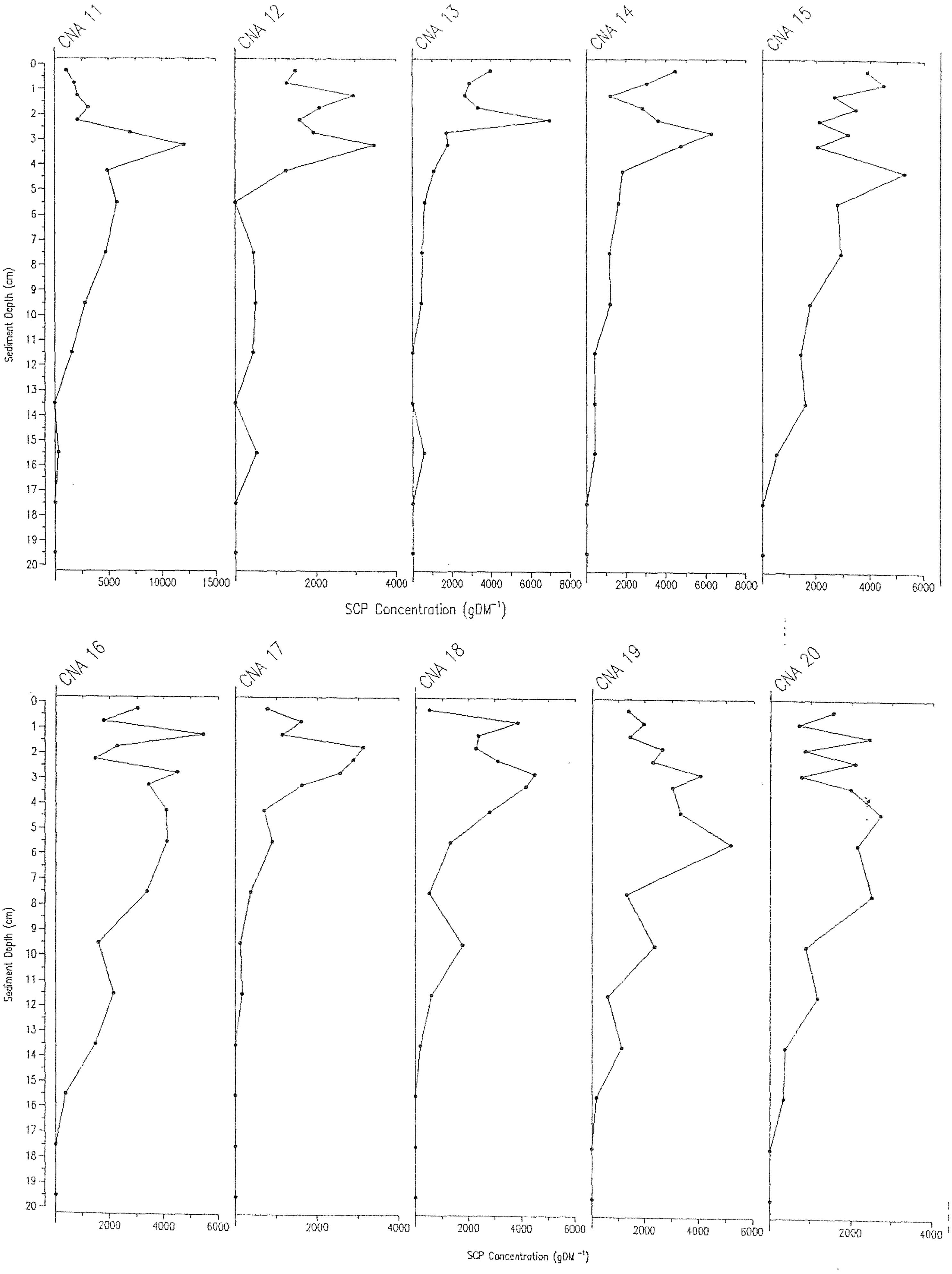


Figure 4. Cumulative percentage spheroidal carbonaceous particle profiles for CNA11-20.

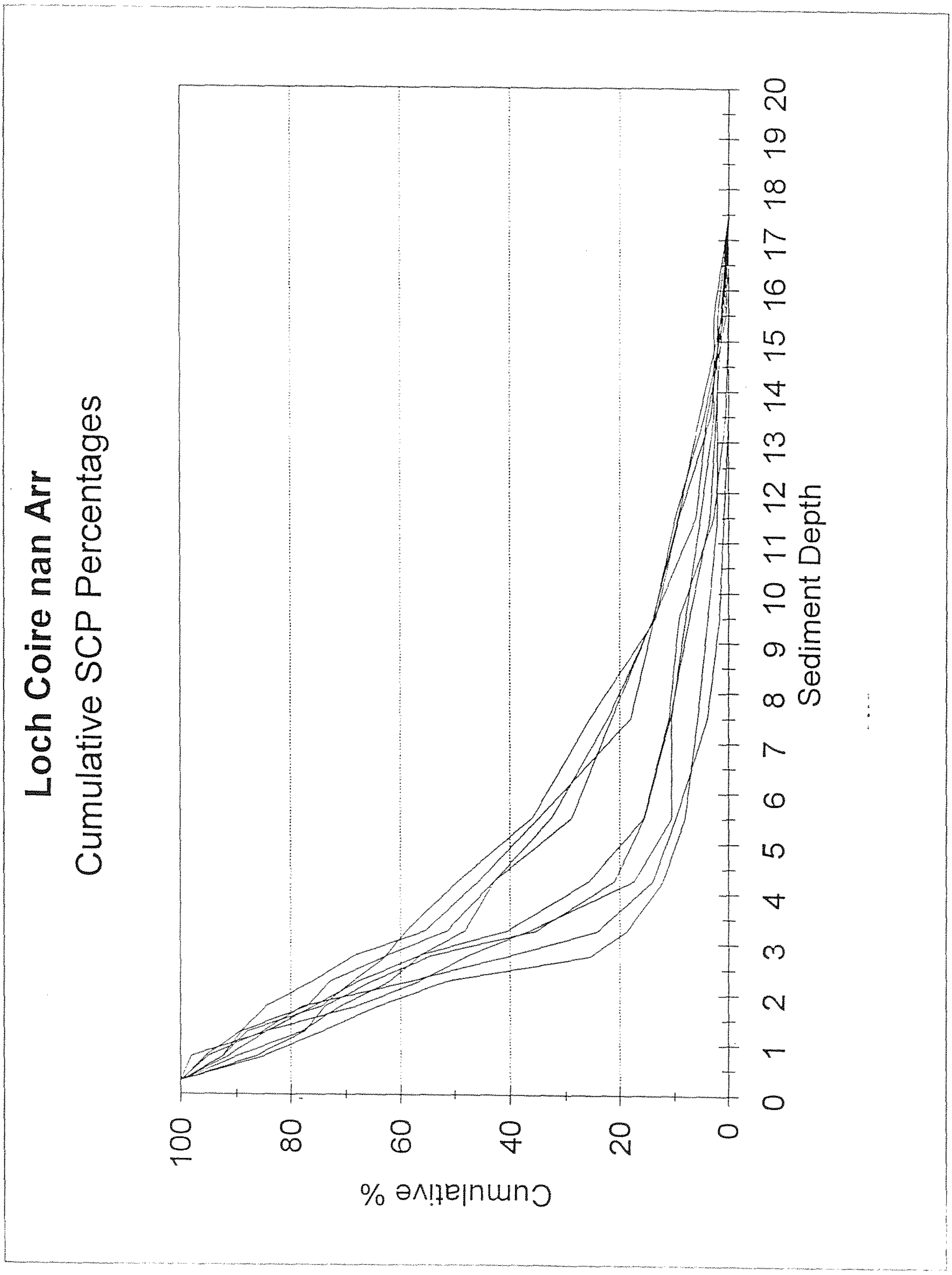
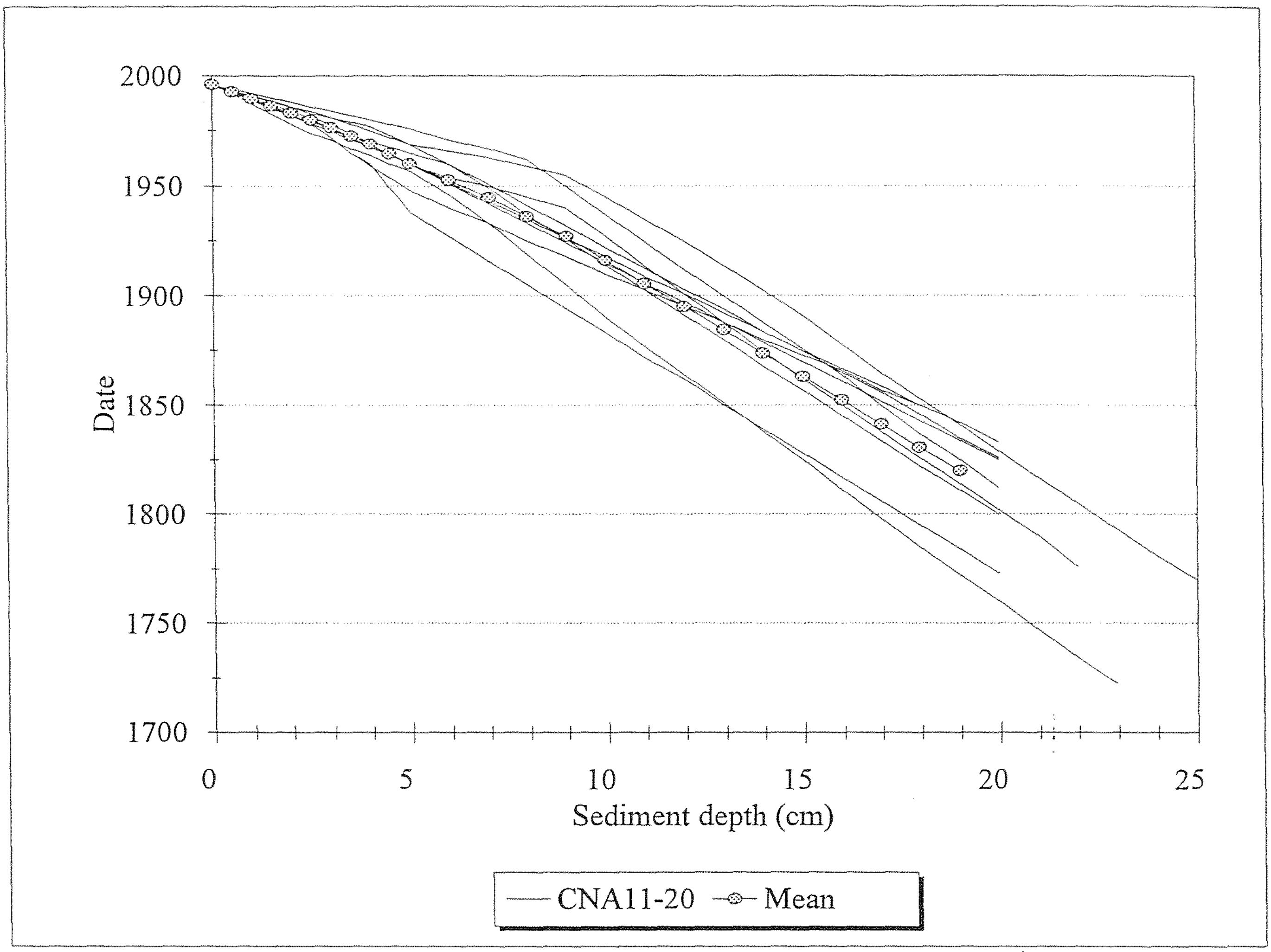


Figure 5. Date / depth profiles for CNA11-20.



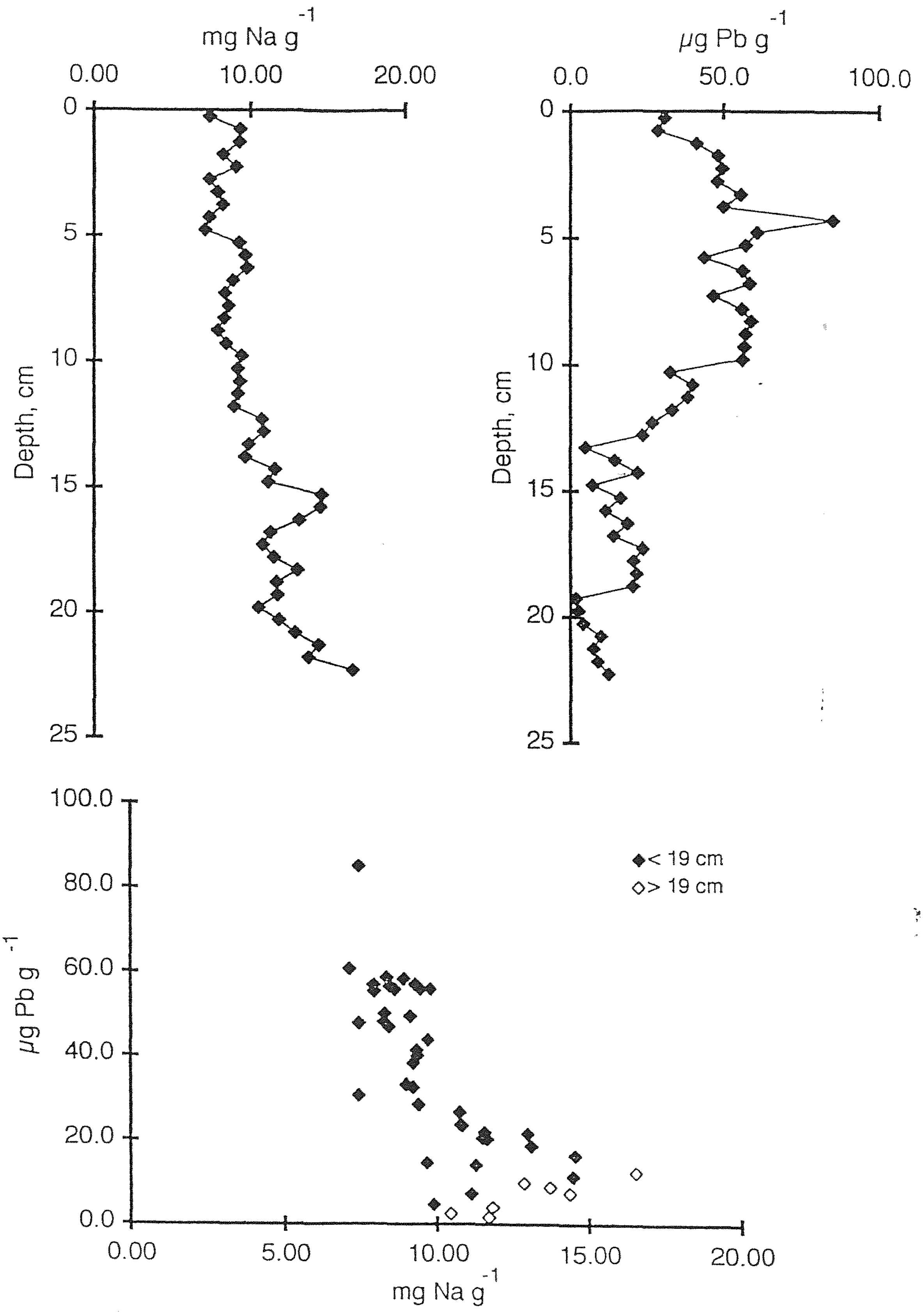


Figure 6. Variation of the sodium and lead concentration with depth and the relationship between lead and sodium concentrations in the sediments of CNA11.

Figure 7. Zinc, copper, nickel, chromium, cadmium, arsenic and mercury concentration profiles for the CNA11 sediment core.

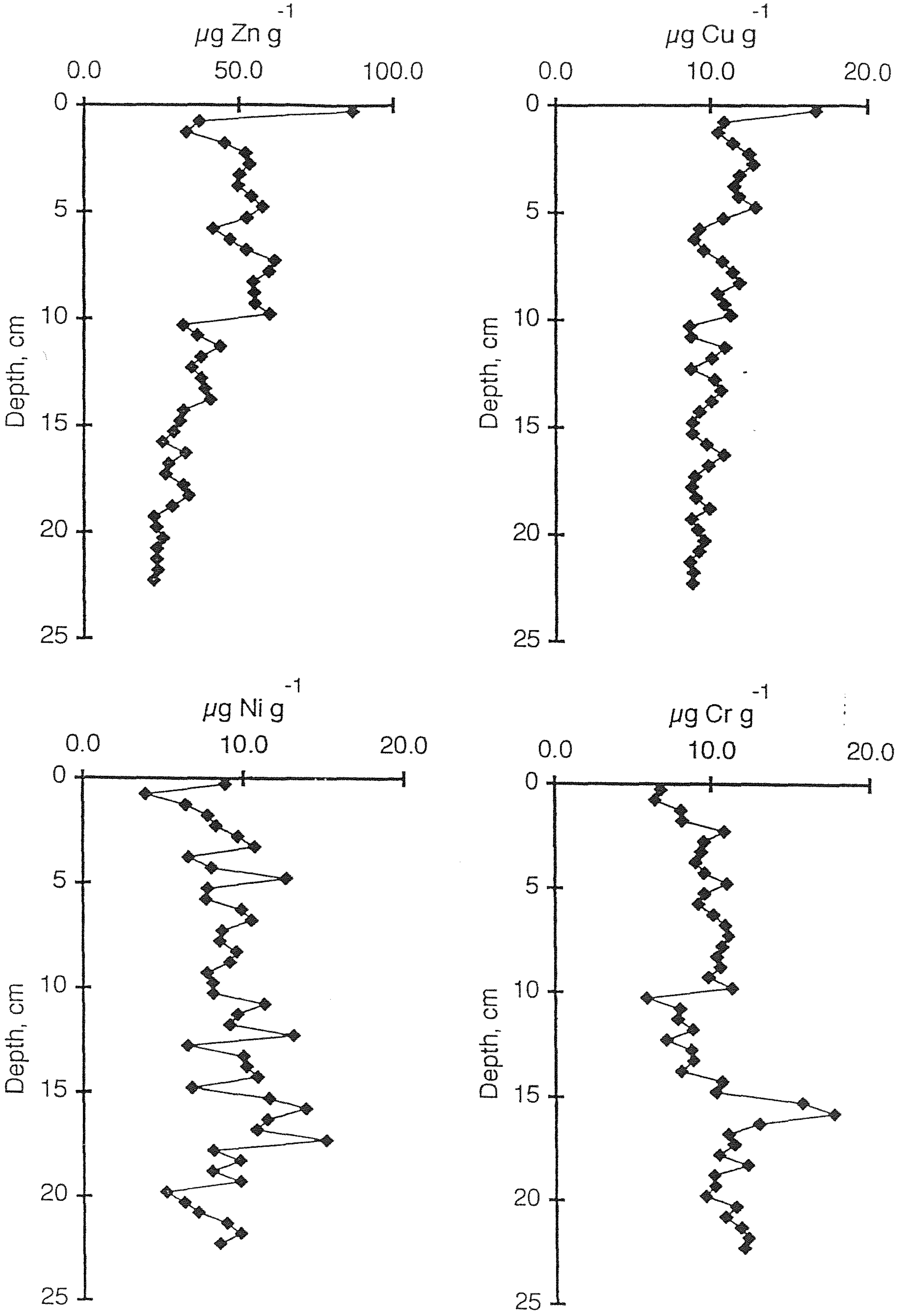


Figure 7. (cont.)

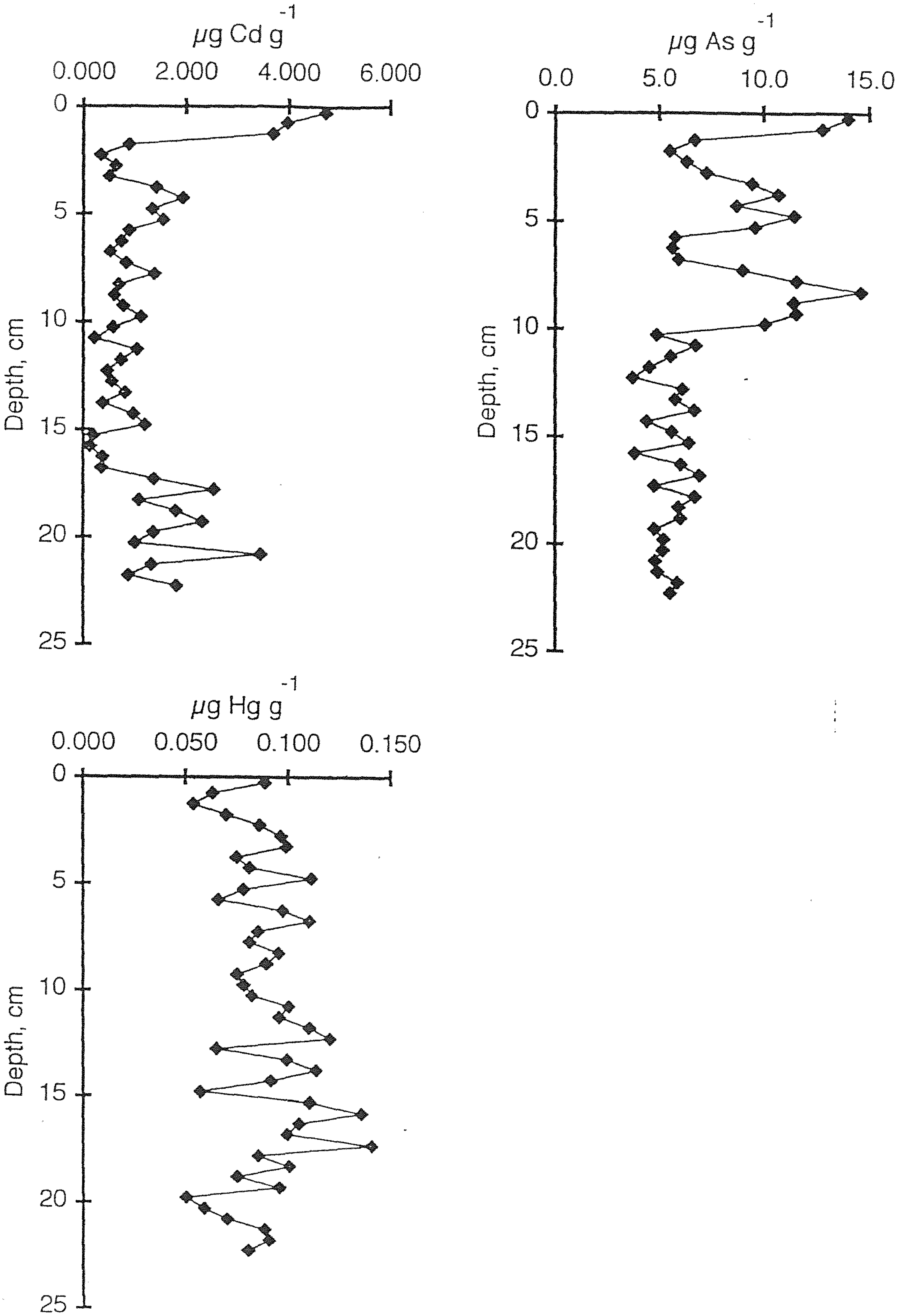
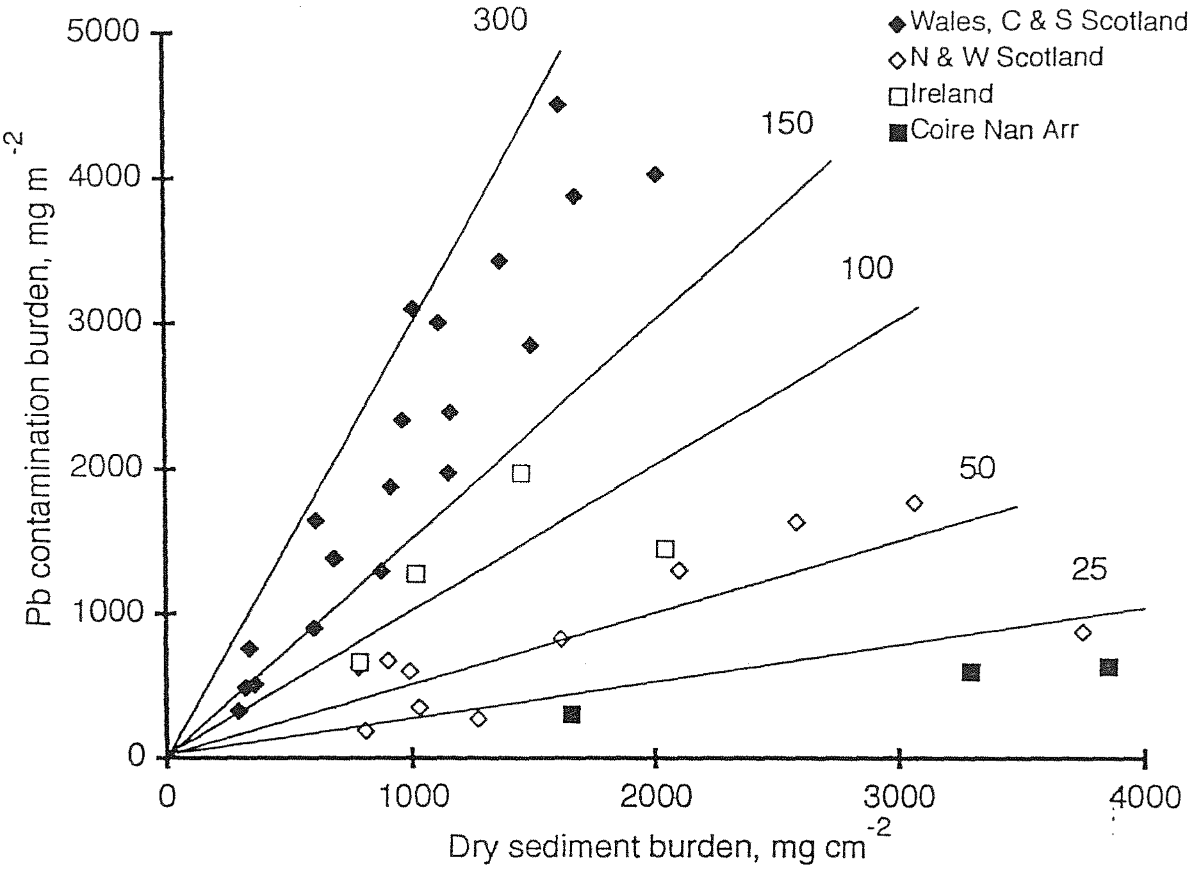


Figure 8. The variation of lead contamination burden since 1900 with dry sediment burden. Isoconcentration lines for equal sedimentary contamination in $\mu g\ g^{-1}$ are shown.



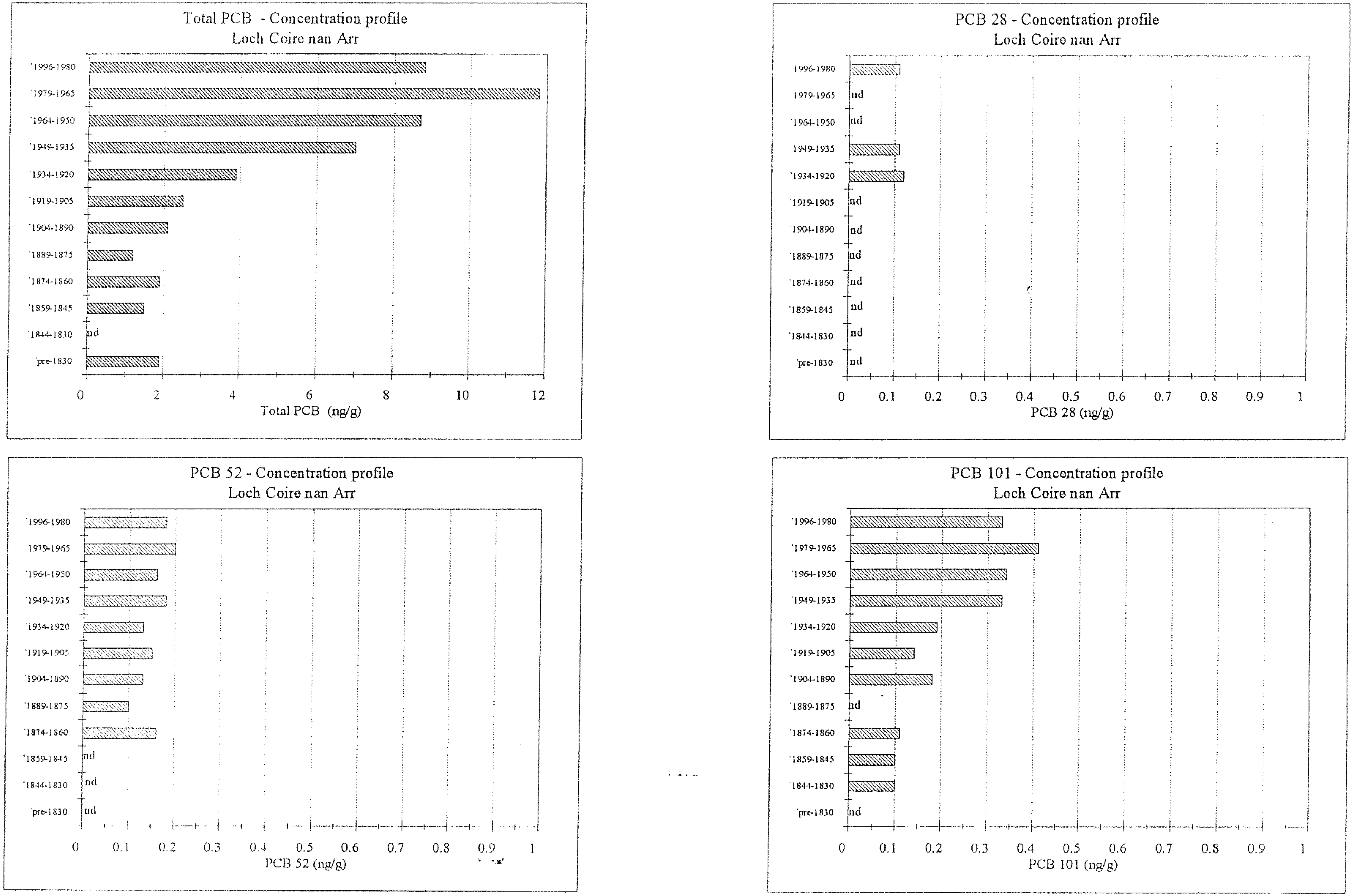


Figure 9. Total PCB and individual PCB congener profiles for Loch Coire nan Arr.

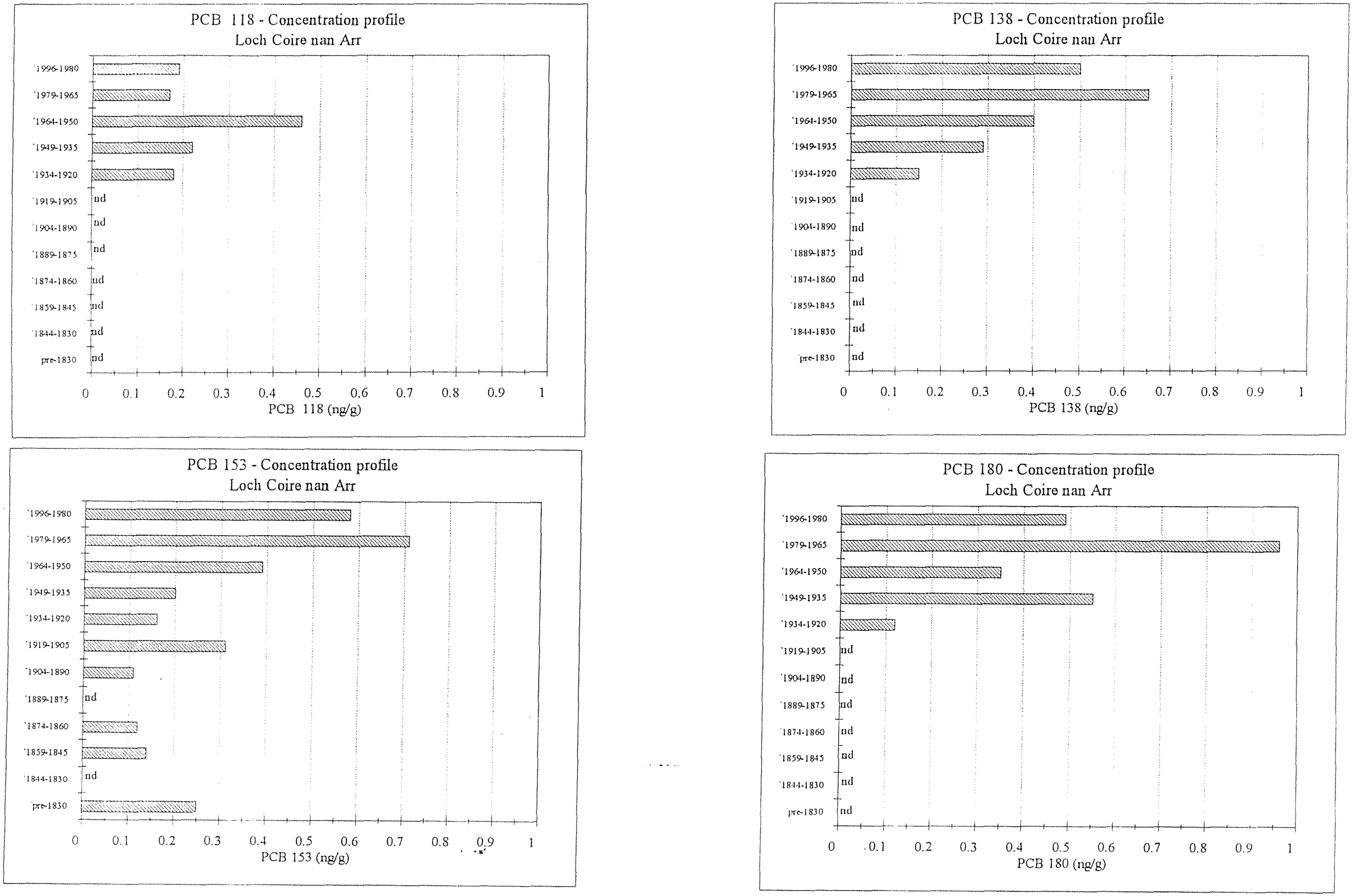
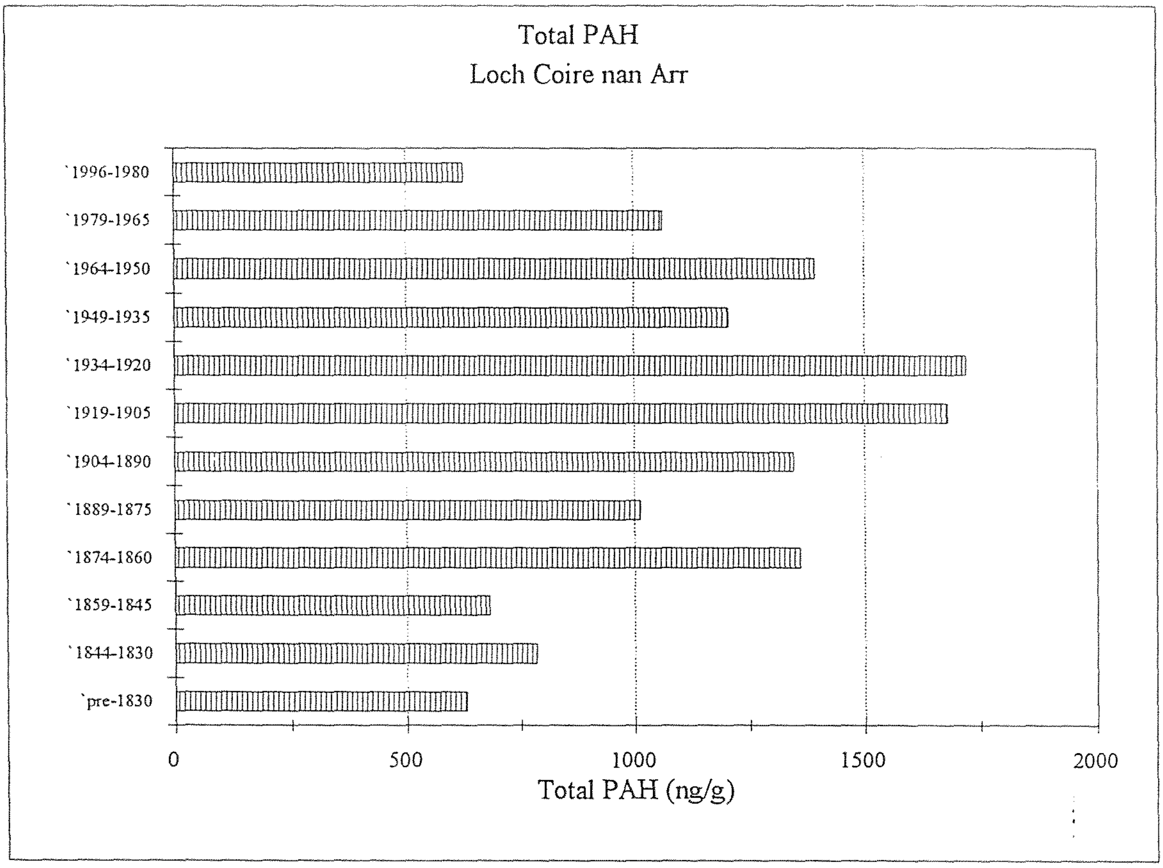


Figure 9. (cont.)

Figure 11. Total PAH profile for Loch Coire nan Arr calculated as the sum of the 16 individual compounds.



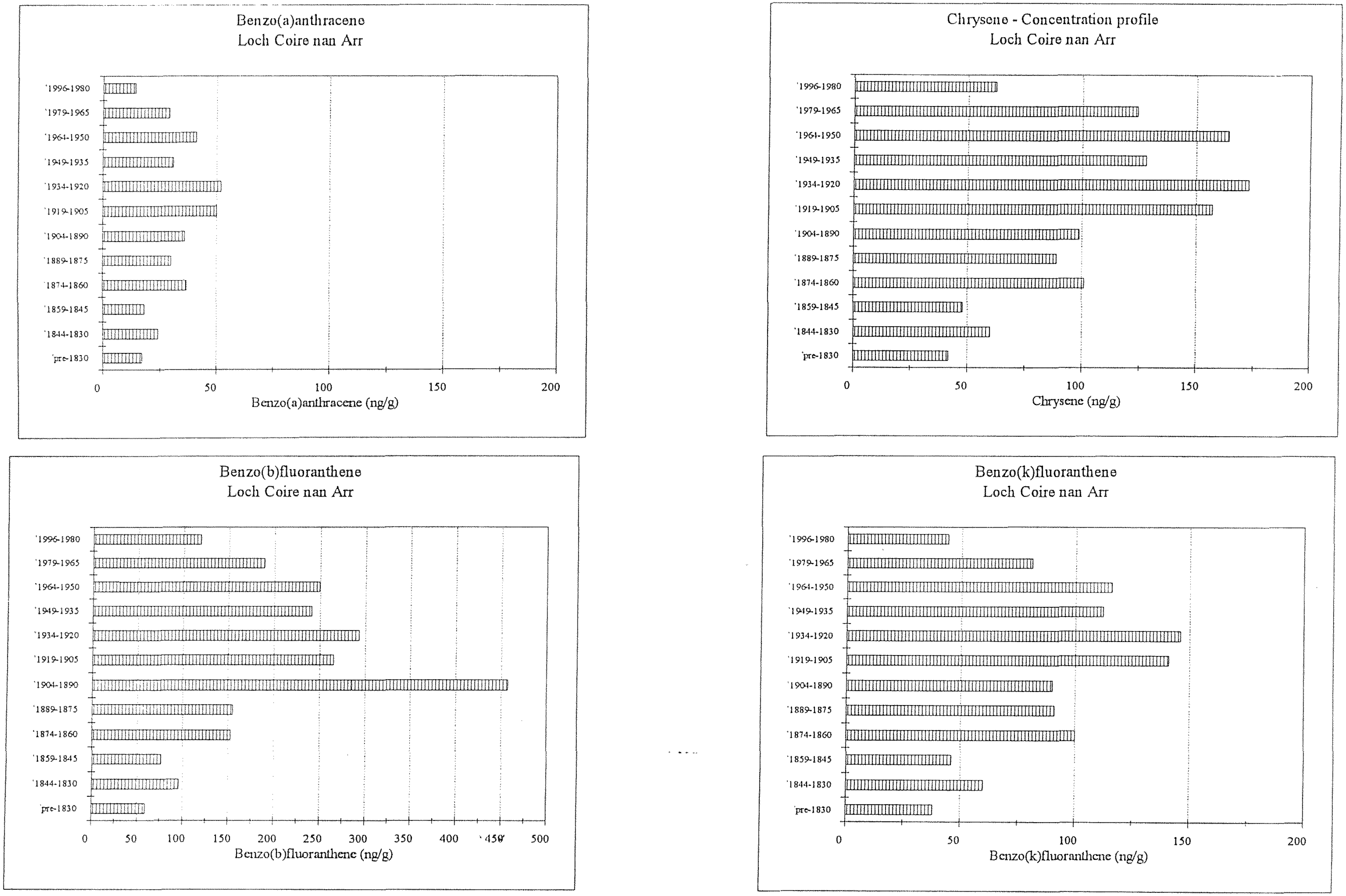
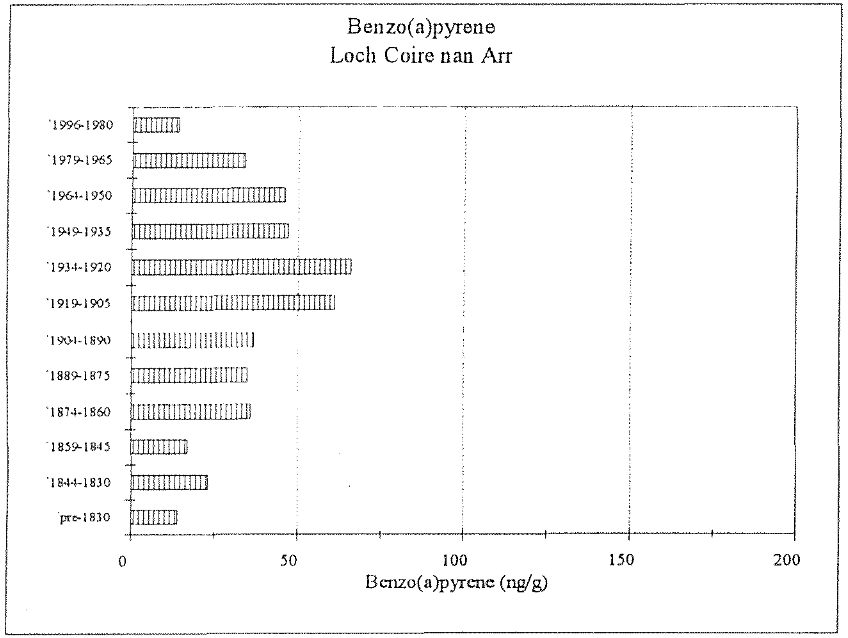
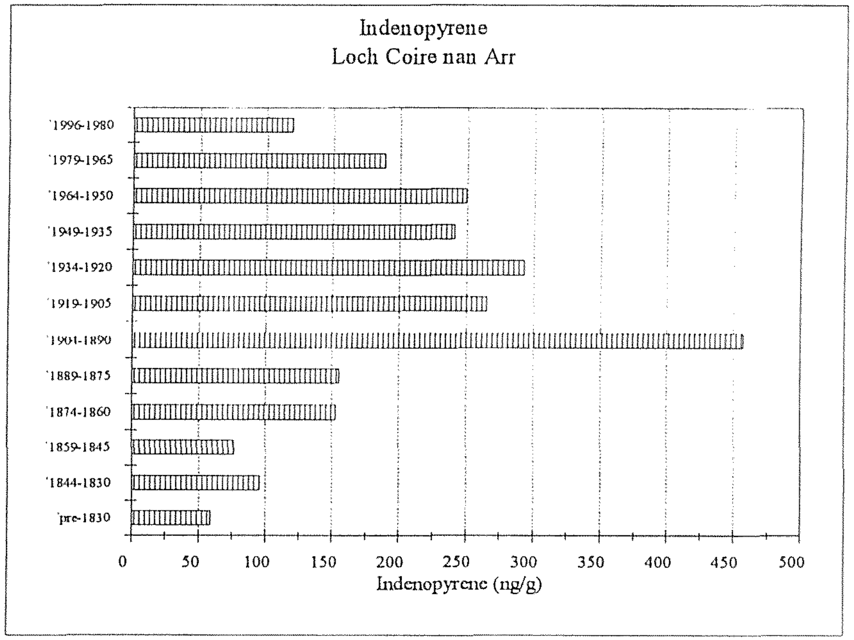
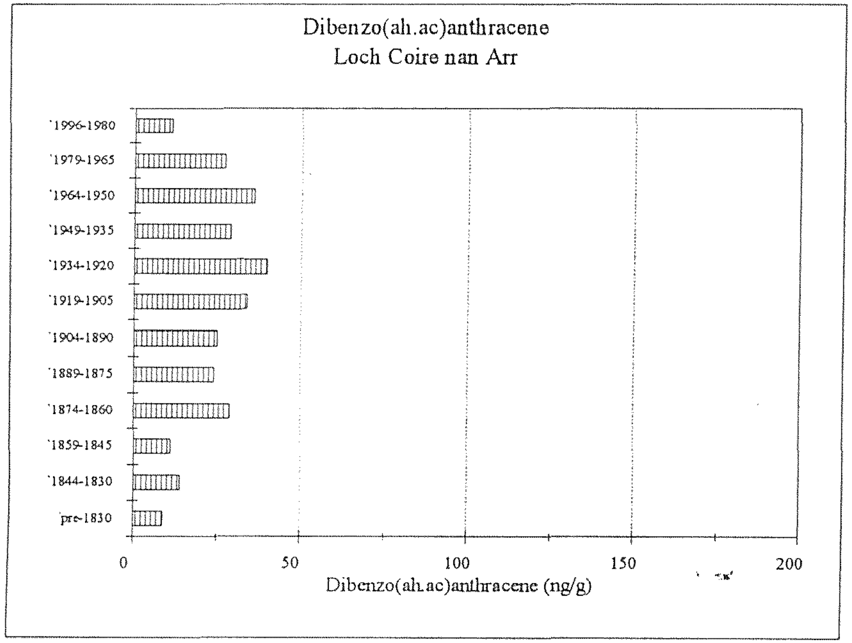


Figure 12. Concentration profiles for individual PAH compounds for Loch Coire nan Arr.







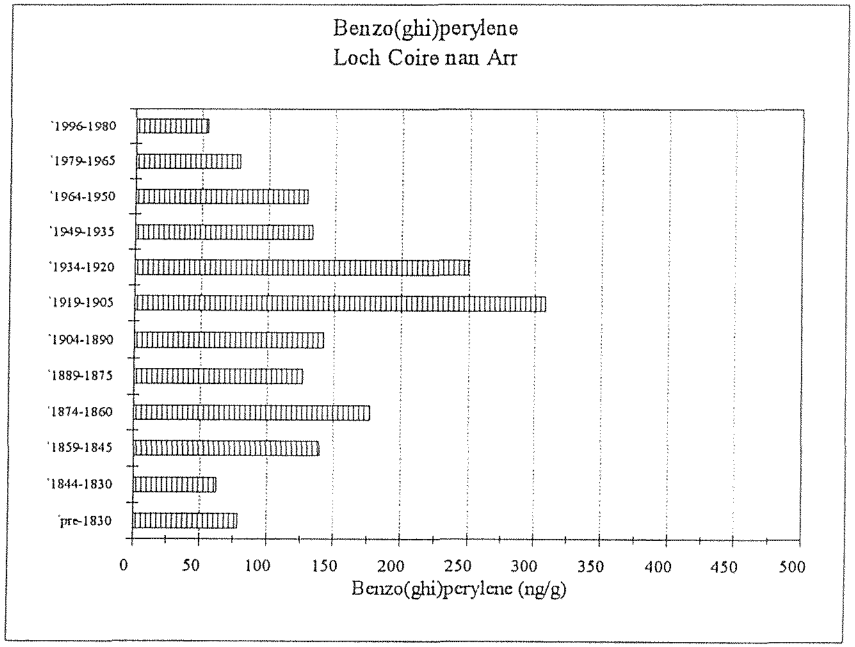


Figure 12. (cont.)

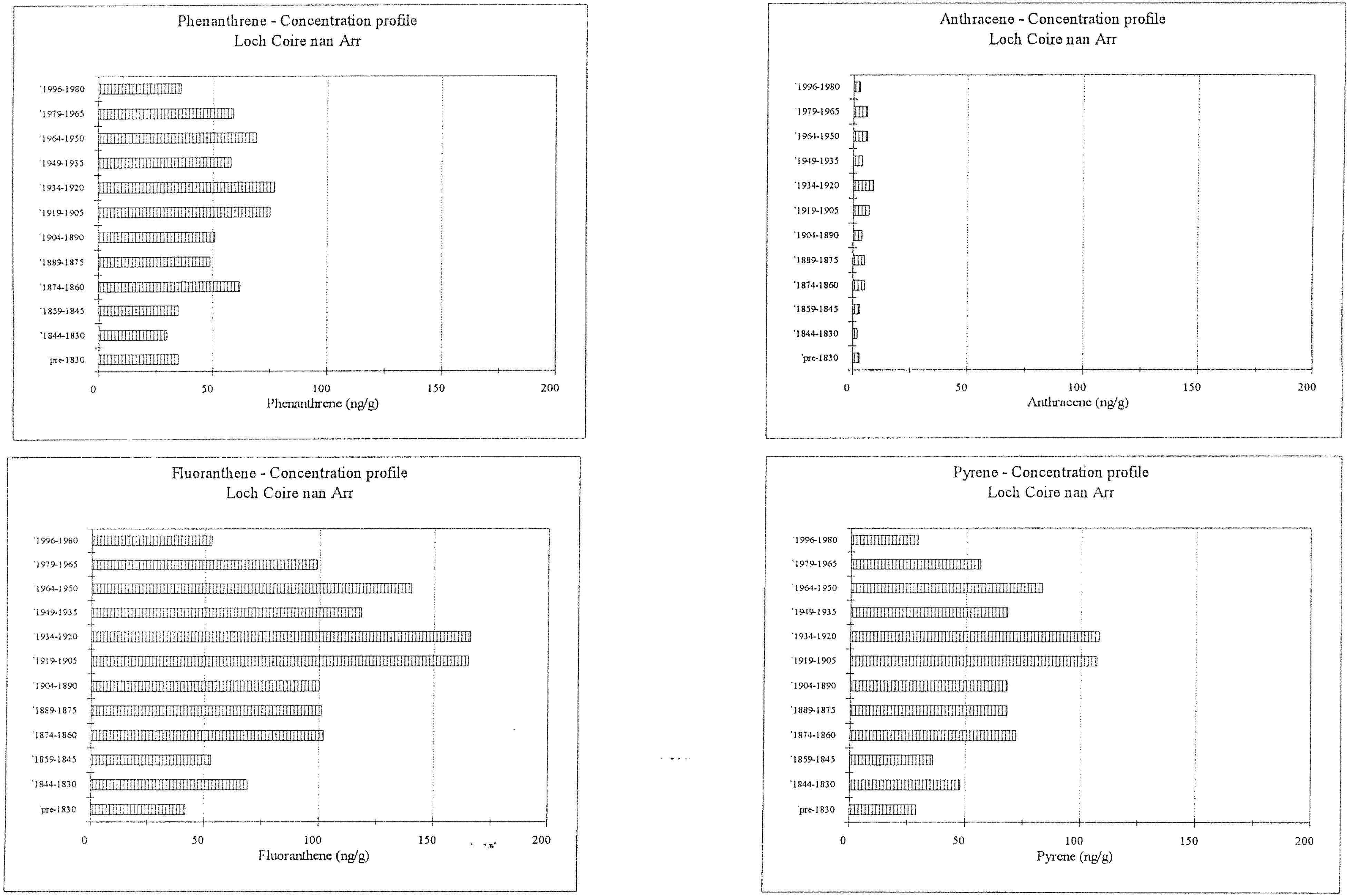


Figure 12. (cont.)

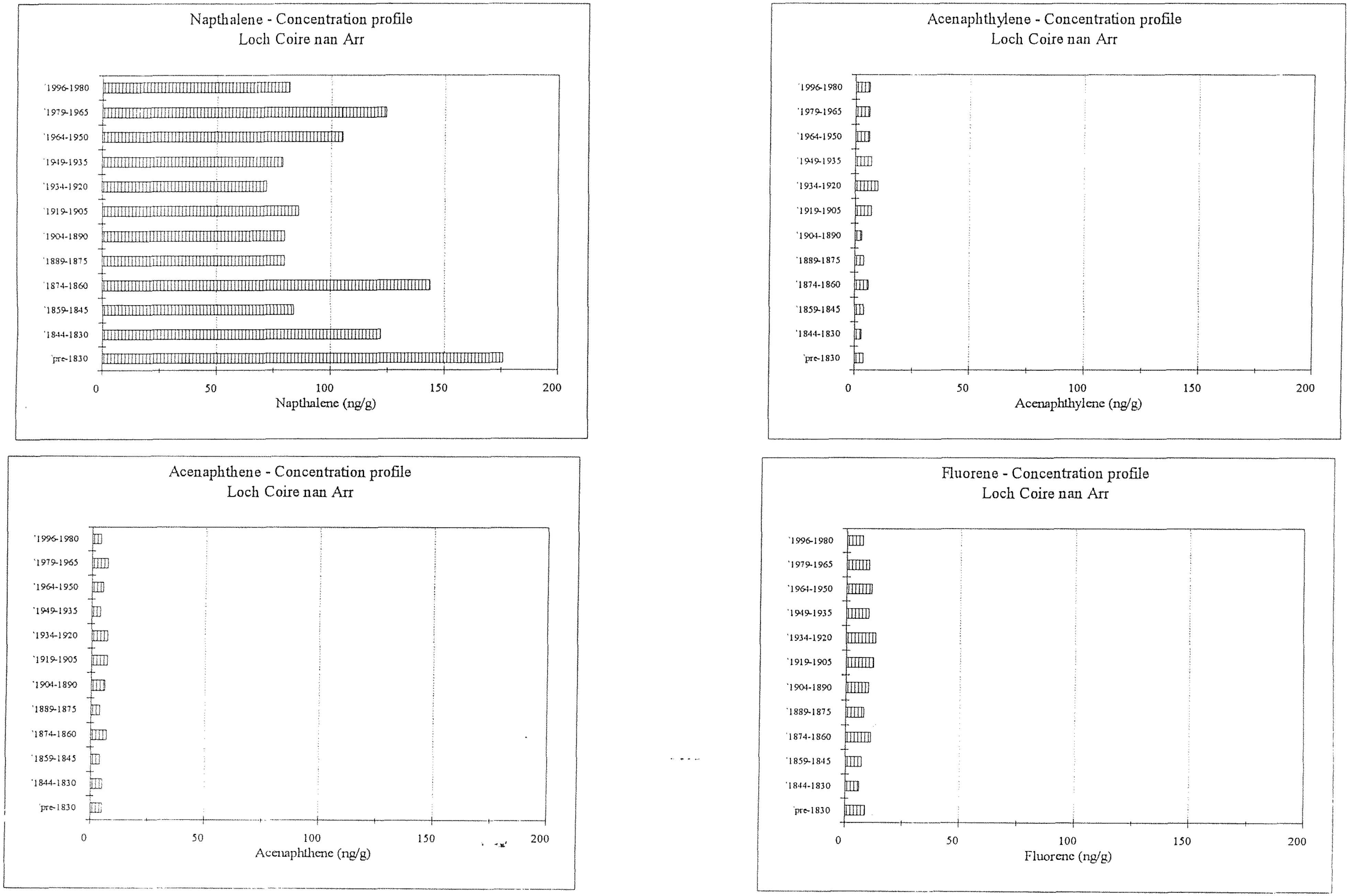


Figure 12. (cont.)

Figure 13. PCDD/F concentration profile for Loch Coire nan Arr (taken from Rose, 1996a)