HEAVY METAL ANALYSIS OF LAKE SEDIMENTS AS AN INDICATOR OF

ENVIRONMENTAL CONTAMINATION: AN EXAMPLE FROM ROUND LOCH OF

GLENHEAD, SOUTH WEST SCOTLAND.

Acknowledgements

Contents.

Contents cont.

Contamination : An Example from Round Loch of Glenhead, South West Scotland.

Abstract.

The technique of heavy metal analysis was used to determine the zinc, lead and copper concentrations in a single core (RLGH3) from Round Loch of Glenhead, Galloway. The sediment was digested using an HF / HNO_3 / $HClO_4$ digestion and concentrations of the heavy metals obtained from Atomic Absorptic Spectrophotometry. RLGH3 was dated by core correlation using a ^{210}Pb-dated core taken from the same site in Round Loch in 1981 (Flower and Battarbee, 1983a). The sediment accumulation rate was calculated to be 1.18 mm per annum. Quality control analysis showed the technique of heavy metal analysis to be accurate and repeatable. The sources, transport, deposition and incorporation of Zn, Cu and Pb into lake sediments were discussed in Literature Review.

Heavy metal analysis was used to determine the onset of environmental chan within the loch, to compare the timings of increases of the three metals and to study the differences in the magnitude of trace metal contamination. Variability of trace metal concentrations lower down in the core was attributed to catchment changes as these variations occurred prior to man's increasing impact on metal production. Lead showed the earliest increase of the three metals at c.1670, and increased to six times its background value. The early increase may correspond to pre-industrial mining or production of Pb in the region. Zn began to exceed the background concentration at about 22 cm (c.1844 and increased by an order of magnitude of 2.7 over the background. Cu showed a small increase at c.1860 with an increase over background values of 1.13 times.

It was established that little sediment mixing occurred within Round Loch. Due to the acidic bedrock of the catchment, Round Loch is poorly buffered against acidic precipitation, and it can be stated that Round Loch is contamin- ated both by heavy metals falling directly onto the lake from atmospheric

into the lake by acidic precipitation. Studies from Scandinavia and North
America mentioned in the discussion verify this process.

Introduction.

The analysis of heavy metals is one of a number of palaeolimnological techniques available for reconstructing past environments. Other techniques include the analysis of diatom frustules, pollen grains and soot particles. Sediment cores provide a wealth of information on man's impact on the environment and Förstner (1976) stated that "one of the most useful records contained in a lacustrine core is that of heavy metal pollution." (quoted by Farmer et al, 1980). This paper is specifically concerned with the application and effectiveness of heavy metal analysis to environmental contamination studies. It questions whether increasing zinc, lead and copper concentrations in recent sediments can be attributed to anthropogenic contamination of the atmosphere.

A 260 cm. core dating back to the post-glacial was taken from Round Loch of Glenhead in the Galloway region of South-west Scotland. The core allows the historic development of metal contamination to be studied and places recent changes (i.e. over the last 200 years) into a long-term perspective. Extensive studies on lake sediments carried out by researchers in other parts of the Northern Hemisphere are discussed in relation to Round Loch. Most studies indicate that prior to about 1800 AD fairly low metal concentrations are present in lake sediments, Between 1800 and 1900 a rapid rise in trace metals occurs in many lakes implying the deposition of heavy metals from an increasingly polluted atmosphere. This is a condition brought about by the increasing metal production during and after the Industrial Revolution. This study confirms these findings by showing that remote upland areas such as Round Loch are being contaminated by the long-range transport of atmospheric pollutants.

In order to try and interpret the heavy metal concentrations found in lake sediments it is necessary to look at the sources of the metals, the mechanisms by which they are transported through the atmosphere to the lakes and catchment areas, and the ways in which they finally reach and are preserved in the sediments.

(a) Source

Heavy metals in the atmosphere come from a variety of natural and anthropogenic sources. Nriagu (1978, 1979, 1980) reviewed the natural sources of Pb, Zn and Cu which can be seen in Table 1. Windblown dust is the most important natural source of these metals accounting for 85% of "natural" lead and 65% of "natural" copper.

The release to the atmosphere by natural sources is small compared to the annual emission from anthropogenic sources. In comparison with the totals shown in Table 1, Nriagu states that the annual output of Pb, Zn and Cu from anthropogenic sources is:

$$440 \times 10^6 \text{ kg yr}^{-1} \quad Pb$$
$$315 \times 10^6 \text{ kg yr}^{-1} \quad Zn$$
$$56 \times 10^6 \text{ kg yr}^{-1} \quad Cu$$

Thus natural sources account for only 4%, 14% and 32% of the total annual emissions of Pb, Zn and Cu respectively. The worldwide anthropogenic emissions of these metals can be seen in Table 2. 61% of anthropogenic lead comes from an automotive origin as tetraethyl lead is used as an anti-knock compound in petroleum.

Canada is the largest world producer of zinc, producing 20 - 25% of world emissions (Nriagu, 1980). Anthropogenic sources of zinc account for nearly 90% of the total annual flux and 98% of these emissions come from point sources such as smelters, utility and metal processing plants and incinerators. The extraction and industrial usage of zinc accounts for 50% of anthropogenic emissions.

Copper metal production is the most important single source of this element, accounting for 46% of anthropogenic emissions.

TABLE 1   –   Global Emissions of Cu, Pb and Zn from natural sources

$$(\text{ x } 10^6 \text{ kg yr}^{-1})$$

	Pb	Zn	Cu
Windblown dust	16.0	25.0	12.0
Forest fires	0.5	2.1	0.3
Volcanic particles	0.4	7.0	3.6
Vegetation	1.6	9.4	2.5
Sea salt spray	0.00002	0.21	0.08
Total	18.55	4.37	18.5

(Source: Nriagu, 1978, 1979, 1980)

TABLE 2   –   Global Anthropogenic Emissions of Pb, Zn and Cu

$$(\text{ x } 10^6 \text{ kg yr}^{-1})$$

	Pb	Zn	Cu
Lead production	26.70	98.6	0.29
Zinc production	15.70		
Copper production	26.60	6.60	19.80
Secondary metal production	0.77	8.10	0.33
Waste incineration	3.57	75.00	5.30
Iron & Steel production	49.70	35.10	5.90
Coal combustion	14.90	14.90	5.60
Fuel oil combustion	6.14	0.07	0.74
Wood combustion	1.15	37.20	11.50
Foundries	3.90	4.50	0.37
Anti-knock additives	267.00		

(Source: Nriagu, 1978, 1979, 1980)

(b) Transport

Point sources are responsible for emitting a large proportion of heavy metals into the atmosphere, the exception being lead emitted from car exhausts, and the contribution of each point source at any one time is strongly influence by the topography of the surrounding area, the location at height of emitters and the prevailing meterological conditions. Because of the dynamic nature of the atmosphere, metals can be transported to areas remote from their initial source. Studies have been carried out on the levels of Pb, Zn and Cu in remote locations, and Weiss et al (1975) stated that there has been a 3 - 6 times inc_ jase in the rate of Zn deposited in a Greenland ice sheet between 1900 and 1966. Analysis of polar ice cores show an increase in Cu deposition in recent times which reflects increased fallout levels in areas remote from any source of Cu emission. Murozumi et al (1969) discovered that Pb had increased in Greenland ice from less than 0.0005 ug/kg ice in c.800 BC to over 0.2 ug/kg ice in 1965, and Jaworoski (1968) reported that ice samples from the Tatra Mountains, Czechoslovakia contained sixteen times more Pb in 1960 - 6 than 1861 - 66.

A quantitive value can be given to the extent of enrichment of the airborne aerosols, known as the Enrichment Factor (E.F.). This compares atmospheric concentration of contaminant metals to concentrations found in the earth's crust, and is expressed

$$E.F. = \frac{(^{c}M \, / \, ^{c}X \text{ air})}{(^{c}M \, / \, ^{c}X \text{ crust})}$$

where

^{c}M = concentration of metal

^{c}X = concentration of reference element

(Nriagu, 1980).

If the E.F. value is greater than 1, the metal (M) is enriched in the atmosphere relative to its concentration in the crust and so a high E.F. indicates that a large fraction of the aerosol may be derived from sources other than local soil or bedrock. An E.F. equal to 1 implies that the metal is not enriched in the atmosphere, indicating a crustal source. Peirson and

Cawse (1979) stated that those elements enriched above natural levels are associated with small particles whereas natural particles, for example from wind erosion, are larger.

It has been noted by Peirson and Cawse (1979) that generally the magnitude of element enrichments are similar at many non-urban sites studied in the U.K. This suggests a uniformity of the non-urban aerosol and indicates a similarity of origin of elements or good atmospheric mixing. Cawse (1981) gave E.F. values for sampling stations in Oxon, Nottinghamshire, Suffolk and Cumbria in 1980. The value for Pb was in the range 800 - 1200, and for Zn was between 50 and 150.

Pollutants have a varied pathway from source to sink and the longer the pathways become, the more difficult it is to distinguish individual sources. Particles larger than 10 um return quickly to the earth's surface once they have entered the atmosphere (Peirson & Cawse, 1979) but smaller particles may be lifted by updraughts and turbulence to higher altitudes and disperse more widely in the troposphere. The troposphere extends from about 8km to 50km above the earth's surface and particles in the northern hemisphere may join the westerly airstreams of the middle and upper troposphere and be transported long distances.

Fischer (1983) stated that "models are often the only way of interpreting measurements to investigate long-range transport". He introduced a model to show how knowledge of the processes influencing long-range transport helps in the understanding of heavy metal concentrations in sediments. He defined the main problem when assessing long range transport to be tracking the movement of air masses. Within the boundary layer, windspeed and direction vary consider ably with height, and the difference between upper and lower level winds causes extra horizontal spread of pollutants from their source.

(c) Deposition

The removal of contaminants from the atmosphere may occur as wet or dry deposition. Wet deposition can be divided into washout, i.e. below-cloud scavenging by precipitation whereby material is transferred to falling raindrops and rainout, i.e. in-cloud scavenging where material is transferred to cloud

droplets before descent as raindrops begins. The amount of material deposited during a period of rain varies, and Struempler (1976) found that in Nebraska there was four times the amount of Zn in storm showers than in slow drizzles.

Dry deposition may represent up to 85% of the total deposition for elements such as Fe, Al and Sc which have relatively large particle size, but for elements such as Cu, Co, Pb, Zn and Se of high solubility and small particle size, dry deposition may contribute less than 30% of total element deposition. (Cawse, 1981).

Peirson and Cawse (1979) associated E.F. values with dry deposition velocity and showed that heavy metals such as Pb and Zn have low dry deposition rates (see Fig.1.). Galloway et al (1982) confirmed that the physical characteristics of a metal and its compounds largely determine the type of deposition process by saying that fine particles are transported into the troposphere and incorporated into forming raindrops. Larger particles are mainly deposited dry.

A paper by the Royal Society of London (1979) discusses contamination of the atmosphere on three scales: local, regional and global. Local pollution occurs where the source is clearly defined. Regional pollution is defined as being within a few hundred miles from the source where the contaminants are widespread and diluted. Regional pollution becomes a problem when a remote target is particularly vulnerable, e.g. acid rain falling on weakly buffered soils and lakes. Global pollution is synonymous with stratospheric pollution.

(d) Sinks

(1) Lake Sediments.

Sediments are usually regarded as the ultimate "sink" for heavy metals discharged into the environment, but relatively little is known about the mechanisms by which they are bound to the sediment or the ease with which they may be released. Part of this difficulty lies in the complex nature of the sediment which is a mixture of several components, and part lies in the number of ways in which trace metals may be bound. Current studies tend to be based on conceptual models aimed at assessing the movement of metals between sources and sinks in a system, which makes this area an interesting one

velocity and particle size

X Pb — Associated with particles with diameter less than 1um

Se X   X Zn

As X

Enrichment Factor

Mn X — Associated with particles with diameter greater than 1um

X Fe

Al X

Dry Deposition Velocity (cms/s)

(source: Peirson & Cawse, 1979)
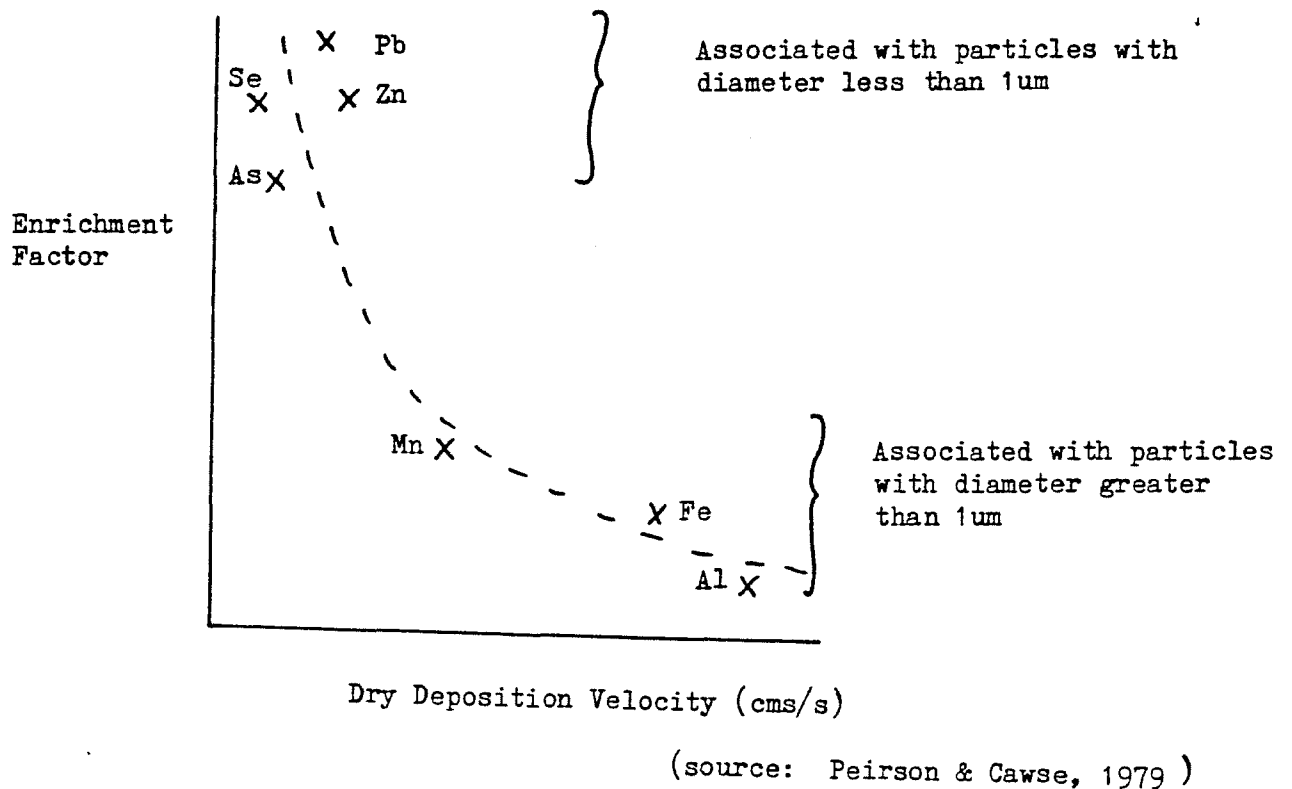
Fig. 2. Simplified biogeochemical cycle for trace metals in lakes

1. Uptake of trace metals by phytoplankton and other particulates
2. Bacterial decomposition – some may enter part 3
                             – some may be exported from the lake
3. Sedimentation
4. Adsorption
5. Metals may enter biological chain
6. Metals may interact directly with sediments
7.)
8.) Release of metals from sediment – re-enter the cycle
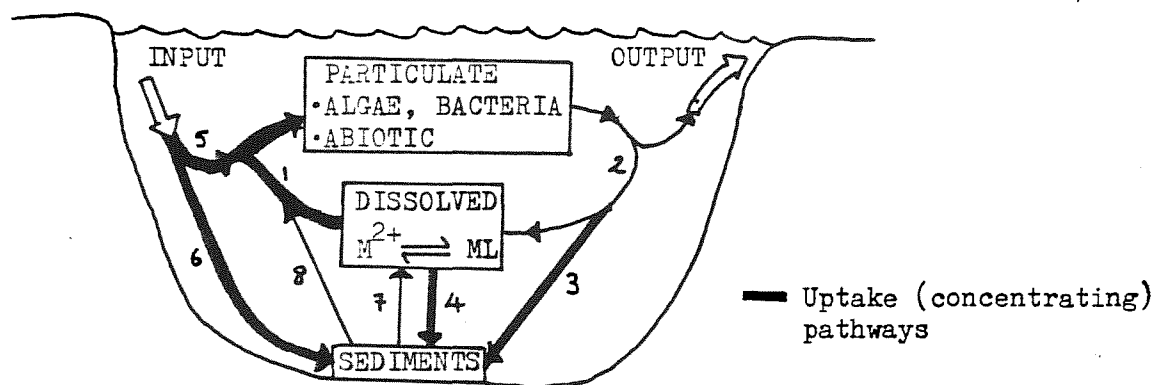
(Source – Hart, 1982)

The major mechanisms involved in the deposition of trace metals once they have reached the lake are as follows:

(a) Adsorption onto fine grained substances

(b) Sorption and coprecipitation with hydrous Fe and Mn oxides.

(c) Association with organic molecules

(d) Uptake by algae and bacteria.

Figure 2 shows a simplified cycle for trace metals in lakes. (Hart, 1982).

(a) <u>Adsorption onto fine grained substances</u>

Fine grained materials with large surface areas such as clay minerals are capable of accumulating heavy metal ions as a result of intermolecular forces. The particles have negative surface charges, thus attracting positive ions and this is known as adsorption. Figure 3 shows how the finer grained fractions of the sediment have relatively high metal concentrations. Dossis and Warren (1980) studied contamination of marine sediments and also discovered that the concentration of Zn, Pb and Cu increase with decreasing particle size.

(b) <u>Sorption and coprecipitation with oxides of hydrous Fe, Mn, carbonates</u>
    <u>and sulphates.</u>

Fe and Mn oxides represent significant sinks of heavy metals in lacustrine environments; "even a low percentage of $Fe(OH)_3$ and MnO_2 has a controlling influence on heavy metal distribution in an aquatic system." (Förstner, 1981). Fe and Mn oxides frequently occur as coatings on minerals and finely dispersed particles and Jenne (1968) proposed that these oxides are nearly ubiquitous in soils and sediments. They enter the aquatic system from ground – and surface water. Mackereth (1966) suggested that the different Zn and Cu curves in Ennerdale and Esthwaite, L. District, was due to the different transport mechanisms of iron-manganese into the sediments.

Adsorption with sulphides may be a significant process for the precipitation of heavy metals in anaerobic water although Förstner (1981) considered coprecipitation with Fe sulphide to be less effective than with Fe and Mn oxides. Förstner (1982) showed how the accumulation of Zn in a Lake Constance

Fig. 3   Grain size distribution of zinc in a sediment sample
downstream of an urbanized area, New Jersey.

Grain size fraction um
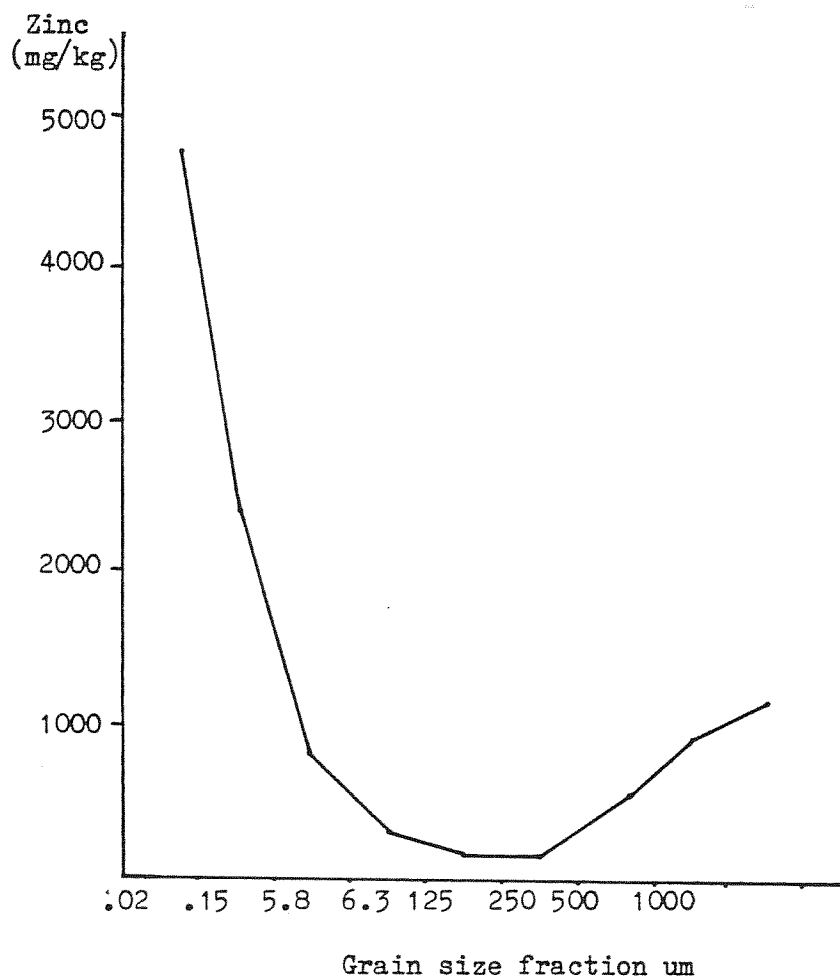
(Source: Förstner, 1982)

been noticed by Deurer et al (1978) who implied that coprecipitation with carbonates may be an important mechanism in the deposition of a number of metals.

(c) Association with organic molecules

This is probably the most important mechanism of trace metal accumulation in aquatic environments. Humic acids are very important in the accumulation process and Haworth (1971) suggested that they contain a complex core to which polysaccharides, proteins and metals are attached. The structure of humic acids varies considerably depending on its origin (allochthonous or autochthonous) and this influences results of sorption experiments (Hart, 1982).

Other organic binding agents include fulvic acid, salicylic acid and peptides. Barren (1966) suggested that Cu, Pb and Sn are strongly bonded to humic acids whereas Ca, Mn and Mg are loosely bonded. Rashid (1974) found that Cu was preferentially sorbed followed by Zn.

Förstner (1981), looking at the relative importance of different bonding mechanisms, stated that in organic systems the role of hydrous Mn and Fe oxides either becomes overshadowed by competition from the more reactive humic acids or are obscured by coatings of organic matter. Gelatinous colloidal substances formed from dissolved organic acids, spores, pollen and decayed leaves have been found to take up metal ions from the water in Perch Lake, Ontario (Jonasson, 1976).

(d) Uptake by bacteria and algae.

The biological cycle involves the uptake of trace metals by phytoplankton and their subsequent release when the phytoplankton are decomposed on the sediment surface. Another possible pathway is by the rapid uptake of heavy metals by a bacterial population followed by the incorporation of this bacterial biomass in the sediment. Hart (1982) identified this possible pathway but acknowledged that it has not been experimentally quantified.

Algae provide another pathway for sedimentary uptake of metals. Algal samples in a metal polluted stream in Missouri were reported to have contained very high concentrations of Pb, Zn and Cu (Hassett et al, 1980). Metal uptake

the metal, the algal species and the pH of the water. Briand et al (1978) found that the binding of metals is accounted for largely by certain species of green algae, diatoms and chrysomonads which constitute only a small fraction of total algal volume.

The mechanism for metal uptake by algae is not well understood although Davis (1978) provided an insight by studying the mechanism of Zn uptake in the marine alga <u>Phaeodactylum tricornitum.</u> Zn was taken onto the outside of the cell wall and diffused through into the intracellular fluid. Some Zn was then complexed with protein or enzymes. Button and Hesteller (1977) studied two algal species with different sensitivities to Cu and results showed that <u>Cyclotella meneghiniana,</u> a Cu-sensitive diatom, sorbed five times more than the Cu resistant green alga <u>Chlamydomonas reinhardtii.</u> It was suggested that the resistance of <u>Chlamydomonas</u> resulted from the Cu remaining bound to the cell wall and not entering the protoplasm. Studies on Windermere (Hamilton-Taylor, 1979; Hamilton-Taylor et al, 1984) have reported a close association between the vertical profile of <u>Asterionella formosa</u> and that of heavy metals. It has been suggested that uptake by diatoms may be an important factor in the depositional metal fluxes in lakes. Mackareth (1966) suggested that metals in algal material conveyed to the sediment may be held as insoluble sulphides in the reducing conditions of the mud. Algae are rapidly cycled and the small losses incurred per cycle may become significant when considered on a annual basis.

(2) Temporary catchment sinks.

Heavy metals from atmospheric sources will not only be deposited in the lake itself but on the surrounding catchment area. The trace metals may be held in these temporary "sinks" before they finally become incorporated in lake sediments. These temporary sinks include forests, soil and peat.

(i) <u>Forests.</u> The abundant organic exchange surfaces on forest floors provide sites for the binding of trace metals. Once bound to forest soil, subsequent reaction with the negative ions of sulphate, phosphate or carbonate may reduce the solubility of metals and impede downward migration in the soil (Smith, 1976

They estimated that the annual Pb influx to the northern hardwood forest was $266g \ ha^{-1} \ yr^{-1}$ and the output into stream water was $6g \ ha^{-1} \ yr^{-1}$. The disparity between input and output values was accounted for by the accumulation of Pb in the soil. Siccama and Smith (1980) also studied Pb, Zn and Cu concentrations in the forest floor of white pine stands in central Massachusetts in 1962 and 1978. They showed that the total Pb content had increased significantly but that Zn and Cu concentrations had decreased. They concluded that "floor humus acts to sequester Pb scavenged from precipitation." They also discovered that the total amount of Pb in the forest floor of pine stands was greater than the amount found in the hardwood forests of New Hampshire.

(ii) <u>Soils</u>. Field evidence for the increased leaching of forest soils and soil parent material due to acid precipitation is abundant. Odén (1976) estimated that podzol soils in south west Sweden have lost 55 - 70 per cent of their normal cation content due to acidic precipitation. Conductivity of lake waters in oligotrophic lakes of south west Sweden has increased by 80% since 1935 (Malmer, 1976) and it is suggested that changes in surface water chemistry are directly related to changes within the soil.

(iii) <u>Peat</u>. Livett et al (1979) analysed Pb, Cu and Zn in fifteen British peat bog sites. The noted that the deposition rate of Pb and Cu was fairly high, but the rate for Zn was lower, suggesting considerable losses by leaching from the peat surface. Heavy metals can be incorporated into peat either directly onto the peat surface or indirectly via decomposing vegetation. Studies on peat vegetation showed that <u>Calluna vulgaris</u>, <u>Eriophorum</u> spp and <u>Sphagnum</u> spp contained varying amounts of heavy metals. The studies also showed that the metals did not bind to the peat with the same affinity and that Zn is more likely to be leached than Pb or Cu.

Peat cores can be used to reflect the change in environmental pollution over time. Oldfield et al (1984) emphasised the use of ombrotrophic peat in this capacity as inputs to the peat are exclusively atmospheric. They stated that in several British sites there is a strong positive correlation between magnetic mineral concentrations and concentrations of Pb, Zn and Cu. Where

accurate dating is available it is possible to correlate magnetic stratigraphy of ombrotrophic peats with the history of regional industrialisation. Oldfield et al (1984) also mentioned the use of magnetic measurements of lake sediments in recording the history of trace metal deposition.

Diagenesis and remobilization of heavy metals.

Birks and Birks (1980) define diagenesis as the modification of environmental evidence by geological processes operating in the surrounding ecosystem, and the diagenetic process is thought to lead to the upward migration of trace metals through the sediment.

Bioturbation is the mixing action of invertebrates within the sediment and the effects of this process depend on body size, activity and depth of penetration of the animal. The two major invertebrates involved in bioturbation are chironomids and tubificid worms. The effects of bioturbating organisms include:

(1) pumping enriched interstitial water out of the sediment

(2) bringing in water richer in oxygen

(3) active transport of particulate material to the surface.

(4) discarding faecal pellets onto the surface.

(Förstner, 1981).

Bioturbation is also responsible for the downward partial mixing of sediment. Sediment-associated organisms may take up large amounts of heavy metals, and Holzinger (1977) verified the fact that high trace element concentrations can be found in tubificid worms.

Remobilization of heavy metals once they have been deposited in lake sediments is usually due to chemical changes such as:

(1) an elevated salt concentration, e.g. the addition of saline effluent to freshwater.

(2) a change in redox conditions usually in conjunction with a decrease in the oxygen potential. Fe and Mn hydroxides are dissolved allowing the release of sorbed heavy metals.

(3) the use of natural and synthetic complexing agents. The increased pollution of water by natural organic decomposition products can

affect metal remobilization from the sediment, for example Mn is reduced and solubilized by peat and humic acids.

(4) a decrease in pH can lead to dissolution of carbonates and hydroxides as well as to the increased desorption of metal cations due to competition with H^+ ions.

Site Description.

Round Loch of Glenhead is an isolated, upland oligotrophic lake with a present pH of 4.5 – 4.8 (See Fig.4 .) It is situated on a granitic intrusion surrounded by sedimentary graywakes and shales. The loch is at an altitude of 299m and has an area of 12.6 ha. The catchment (95 ha) is unafforested with blanket peats overlying the acidic granite bedrock. The catchment is regularly grazed and burnt over. This land management allows a typical upland heath vegetation to be maintained with Calluna vulgaris, Erica tetralix and E. cinerea associated with Sphagnum moss and Molinia coerulea hummocks.

The core was taken from the deepest part of the lake, and the coring site is shown in Fig. 5.

Fig. 4 Map showing the position of Round Loch of
Glenhead.
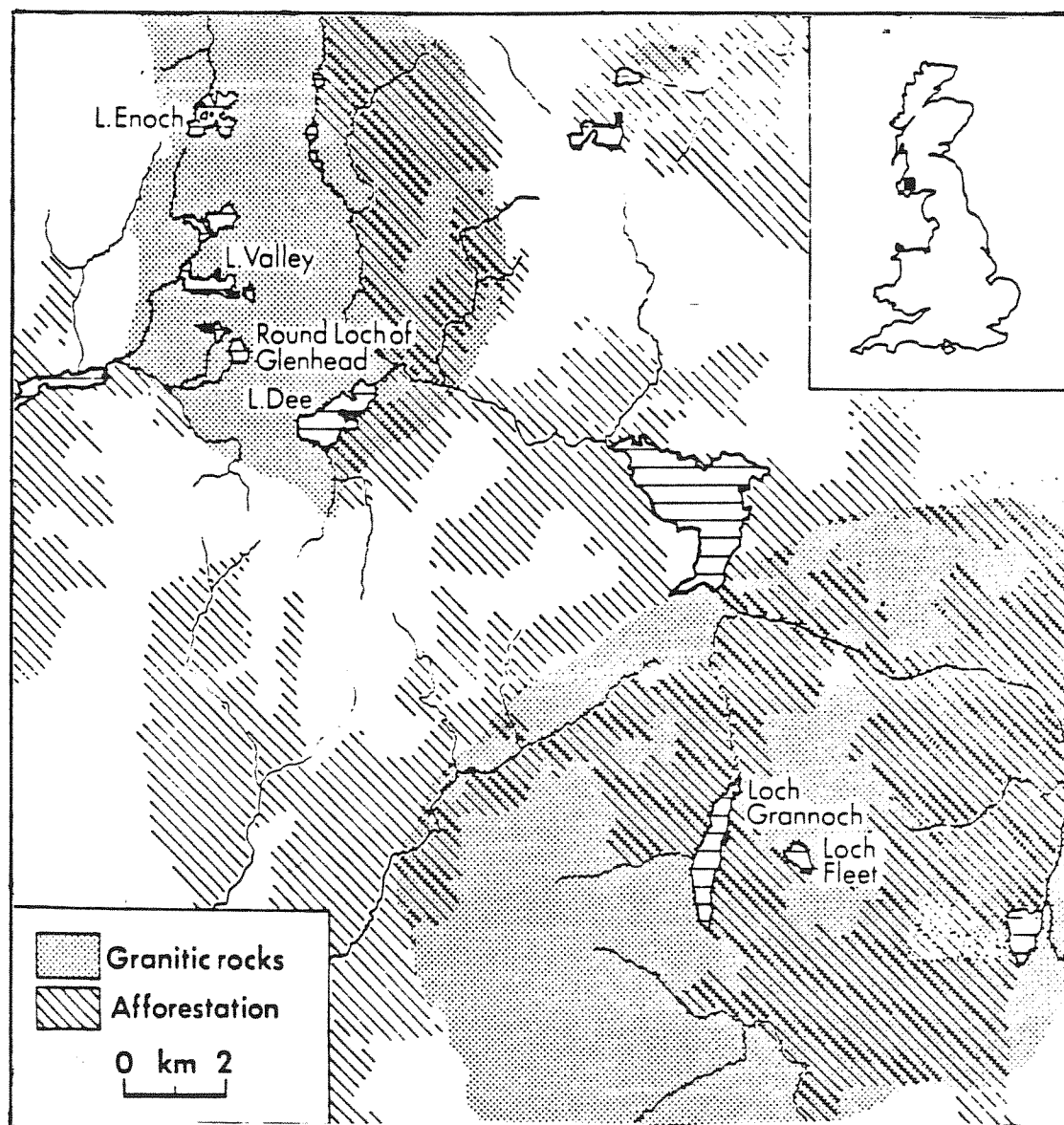
(Source: Flower and Battarbee, 1983a)

Fig. 5

Loch Glenhead Bathymetry

X coring site

Methods.

The technique used to determine heavy metal concentrations of Pb, Zn
and Cu in Round Loch of Glenhead lake sediments consisted of the following
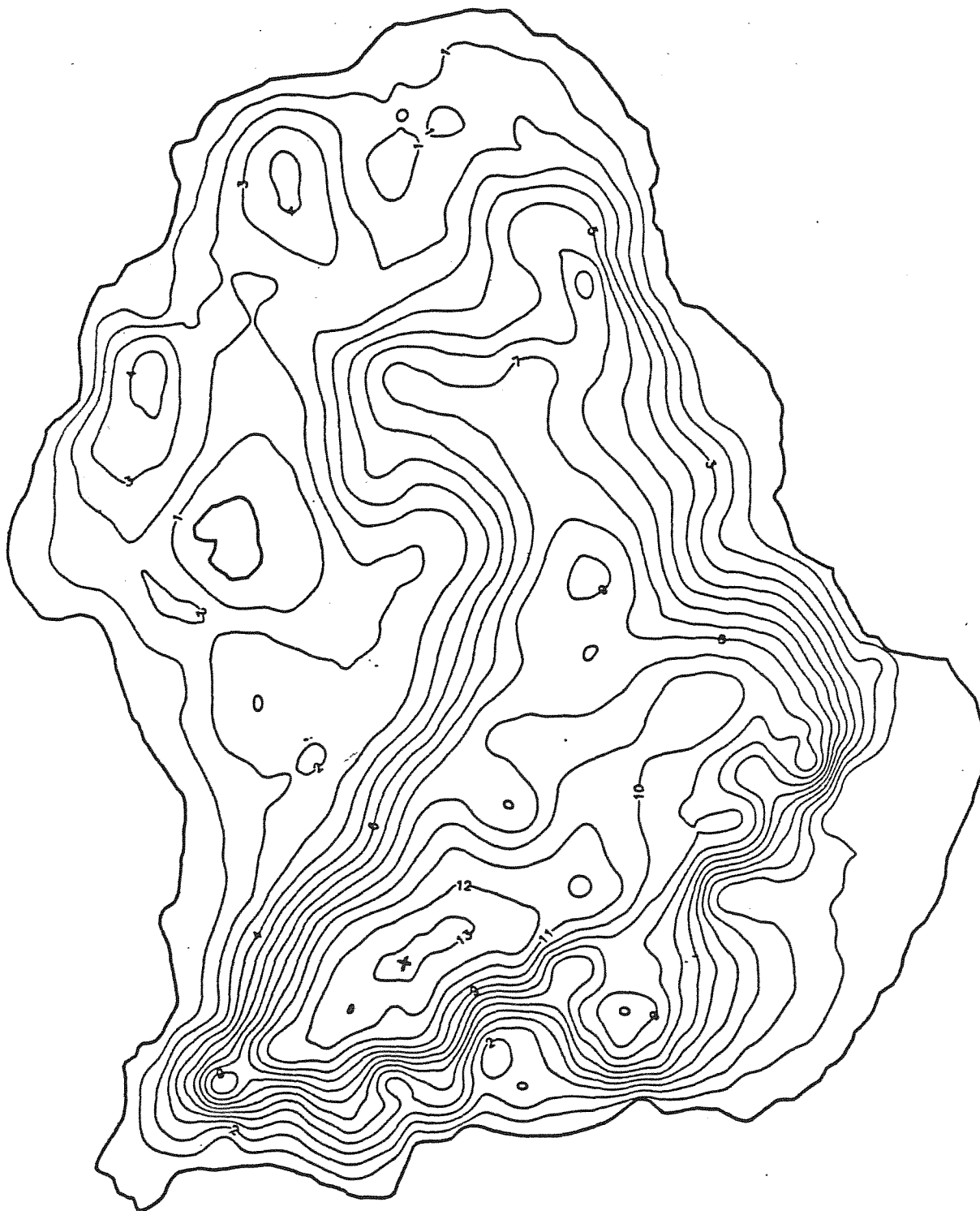four stages:

(i)   The extraction of the lake sediment core

(ii) A Sediment digestion procedure

(iii) Analysis of the digested sediment

(iv) Analytical quality control

The methodology also included an exercise in core correlation as a means
of dating the sediment.

(i) <u>Core extraction</u>

The core (labelled RLGH 3) was taken from a coring platform in the
deepest part of the lake (see Fig.5).   A modified piston corer was used to
extract the top 118 cm. of the core, and a Livingstone corer was used to
extract sediment from 119 to 262 cm. (for a method of the coring techniques
see Livingstone, 1955). The top part of the core was sealed in the extruding
tube and the bottom part carefully wrapped to prevent moisture loss.

Extrusion was carried out in the laboratory by slicing the core using
a slicer and plastic collar at the following intervals:

> 0.5 cm intervals 0 - 30 cm
>
> 1.0 cm intervals 30 - 50 cm
>
> 2.0 cm intervals 50 - 118cm

Samples were taken from the bootom part of the core using a spatula at the
following intervals:

> 2.0 cm intervals 119 - 224 cm
>
> 1.0 cm intervals 224 - 234 cm (glacial clays)
>
> 2.0 cm intervals 234 - 242 cm
>
> 1.0 cm intervals 242 - 262 cm (glacial clays)

Dry weights of the sediment samples were calculated by drying the
samples at 105°C for 24 hours, and loss on ignition (LOI) values obtained

(ii) Sediment digestion

Samples dried at 105°C in polypropelene containers were cooled in a desiccator and about 0.2g dry weight of sediment was weighed into Teflon beakers. The exact weight was noted and five blanks were added to a batch of 35 samples as a control for contamination.

Digestion was carried out on a hot plate in a fume cupboard. de Groot, Zschuppe and Salomons (1982) stated that "according to our present knowledge, the best extraction technique for estimating the contents of metals in sediment is digestion by HF in combination with strong acids." The digestion procedure used in this study was $HF/HNO_3/HClO_4$ and occurred in the following stages:

(a) 5ml HF was added to the sediment in order to decompose the silicates. Being an Ultrar reagent, the HF was pure thus minimising contamination. The HF was fumed off at a low heat.

(b) 5ml HNO_3, an oxidising agent, was added to digest organic matter.

(c) Once the HNO_3 had fumed off, 5ml $HClO_4$ was added. This is a stronger oxidising agent.

(d) If digestion was not complete, these steps were repeated reducing the amount of each reagent to 2.5ml until a clear yellowish solution remained.

(e) Once digestion had been completed the beakers were removed from the hotplate and cooled. 25ml of 0.1M HCl was then added to dissolve the metal ions, and the solution was left to stand for 15 minutes. The solution was transferred to polypropelene bottles.

(iii) Analysis of the digested sediment.

Atomic Absorption Spectrophotometry (AAS) was used to determine the concentration of Pb, Zn and Cu in the sediment digest. AAS was defined by Thompson (1980) as "the absorption of photons by an atomic vapour" and is

The instrument used in this study was a Perkin-Elmer 2380 Atomic Absoption Spectrophotometer.

The following section will consist of a brief description of instrument design, and the operational procedure to be followed to obtain the required results.

AAS has been described as a "lock and key technique" (Thompson, 1980) whereby a given element will only absorb radiation specific to that element. The basic principle is that one end of the capillary tubing from the machine is inserted into the digest. A sample of the solution is drawn up the tubing and, on reaching the nebulizer, is reduced to an aerosol of tiny droplets by the gas flow (see Fig. 6a). The aerosol passes into a spray chamber where the larger droplets run off as waste and the smaller droplets are mixed with the flame. An atomic vapour is formed and when a specific radiation wavelength is passed through it from a hollow cathode lamp, some is absorbed by the corresponding atoms in the vapour. The amount of radiation absorbed is directly proportional to the amount of the specified element in the vapour.

The required resonance line emitted by the lamp is isolated by a monochromator which also minimises the effect of background radiation. The outgoing radiation that has passed through the vapour is detected by a photomultiplier and selectively amplified. The concentration detected is digitally displayed. The instrument used allowed an average value of three readings to be displayed. A signal integration function was set at three seconds so that values were displayed every three seconds and averaged. The main components of a typical AAS can be seen in Fig. 6b.

One of the most important steps in the methodology is to set up the machine properly to obtain accurate results. The instrument should be adjusted as follows:

(i) The instrument ran off an air-acetylene system and once this had been turned on, The correct lamp for the element to be analysed was put into

Fig 6a A typical nebulizer
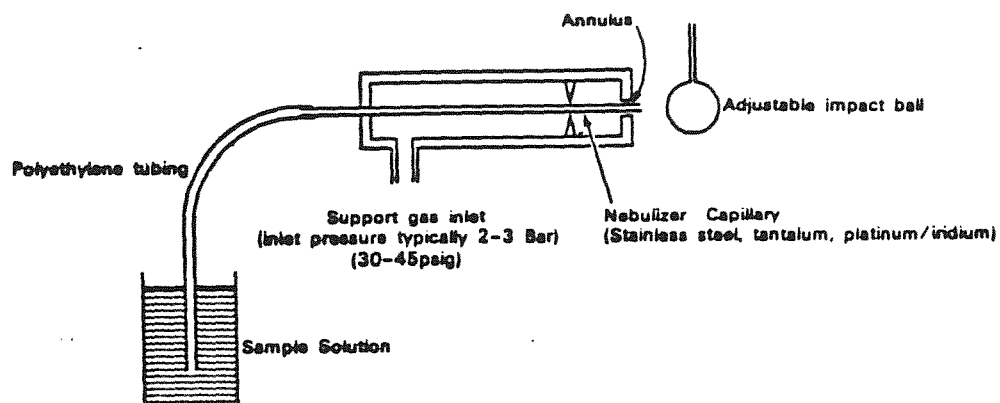

Fig. 6b Main components of an Atomic Absorption Spectrophotmeter
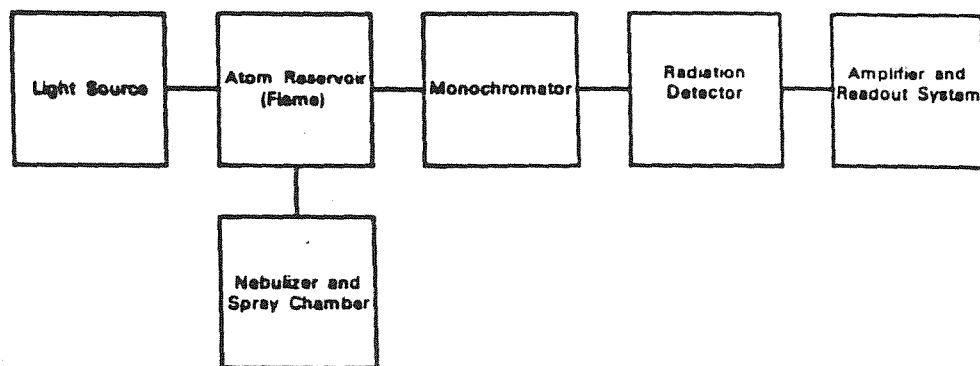
(Source: Thompson, 1980)

up, nebulizing distilled water.

(ii) The machine settings necessary for the optimum precision of results, usually specified by the manufacturer, vary according to each element. The values used in this study are shown below (Table 3).

Table 3

	Zn	Pb	Cu
(nm)	213.9	217.0	324.8
Slit (nm)	0.7	0.7	0.7
lamp current (mA)	6-7	6	8
Fuel/oxidant	18/40	24/40	20/40
Burner height	8	8	8

(iii) After the flame conditions had been set, the lamp was set at the correct wavelength (using the coarse adjustment facility) and current. The position of the lamp was adjusted to ensure maximum energy reached the detector. Any incorrect setting could lead to a significant loss of precision.

(iv) Before digests could be analysed the machine had to be calibrated. Firstly, the automatic zero function was set which nebulizes a blank solution and sets the output to zero absorbance. The automatic calibration was then set which maintains a constant response to a given standard. Two standards were used containing HCL to match the sample digests.

(v) Once the machine had been calibrated an automatic background correction system was activated to correct for non-specific background absorption. This facility is especially important for detecting Pb at trace levels as interference may enhance the readout.

Each batch run through the AAS consisted of 40 samples which were analysed for Pb, Zn and Cu. When testing for Zn and Cu the machine was recalibrated after every ten samples to ensure there was no drift, and with Pb recalibration occurred after every five samples as lead is more variable than the other elements. After the batch had been tested for one element,

the lamp had to be changed and the instrument reset for the next element.

(iv) Analytical Quality Control

The blanks tested were a control against contamination and were also used to calculate the detection limit of the instrument used. The AAs group of the Society of Analytical Chemistry define the limit of detection as "the minimum amount of an element which can be detected with a 95% certainty". (Thompson and Reynolds, 1982). It is usually expressed as two times the standard deviation.

Some of the samples were duplicated in order to test the precision of the results and repeatability of the exercise. Precision varies from element to element and can be defined as the within batch standard deviation when a sample is nebulized a given number of times. Due to a lack of excess sample material duplicates were carried out on the following three samples only:

Depth: 203 - 204 cm.
          231 - 232 cm.
          243 - 244 cm.

This also allows a standard deviation to be calculated.

Core correlation

Figure 7 shows the L.O.I curves for RLGH (Flower and Battarbee, 1981) and RLGH3. The cores were taken from the same location in Round Loch of Glenhead. The correlation point used is indicated on the profiles, and occurs at a lower depth in RLGH 3 (52 cm.) than in RLGH (44 cm.) indicating a slightly quicker accumulation rate. RLGH was dated using ^{210}Pb and Flower and Battarbee (op.cit.) calculated that RLGH had a linear accumulation rate of 1 mm. per year. The difference in accumulation rate between RLGH and RLGH 3 was calculated by dividing the correlation point depth in RLGH 3 with the depth in RLGH which gave a sediment accumulation rate of 1.18mm. per year for RLGH 3.

Fig. 7 Core correlation – the dating of RLGH 3 using LOI profiles.

RLGH LOI profile
(1981)

RLGH 3 LOI profile

cm below sediment surface

1585

correlation
point

1585

correlation
point

%

%
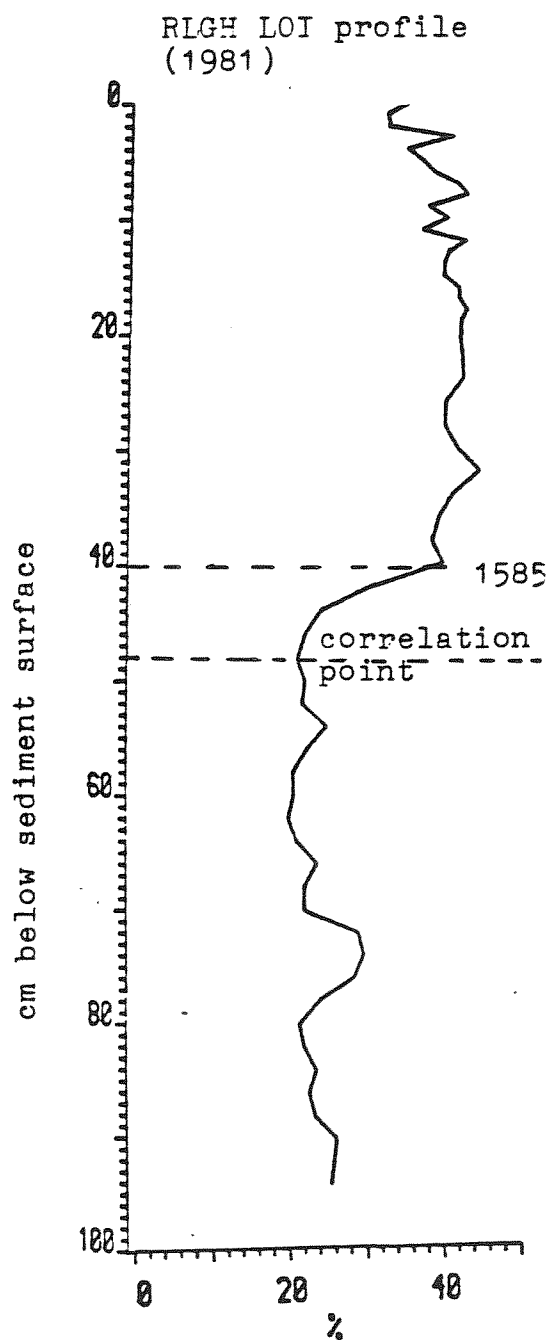
Source: Flower and
Battarbee, 1983a.
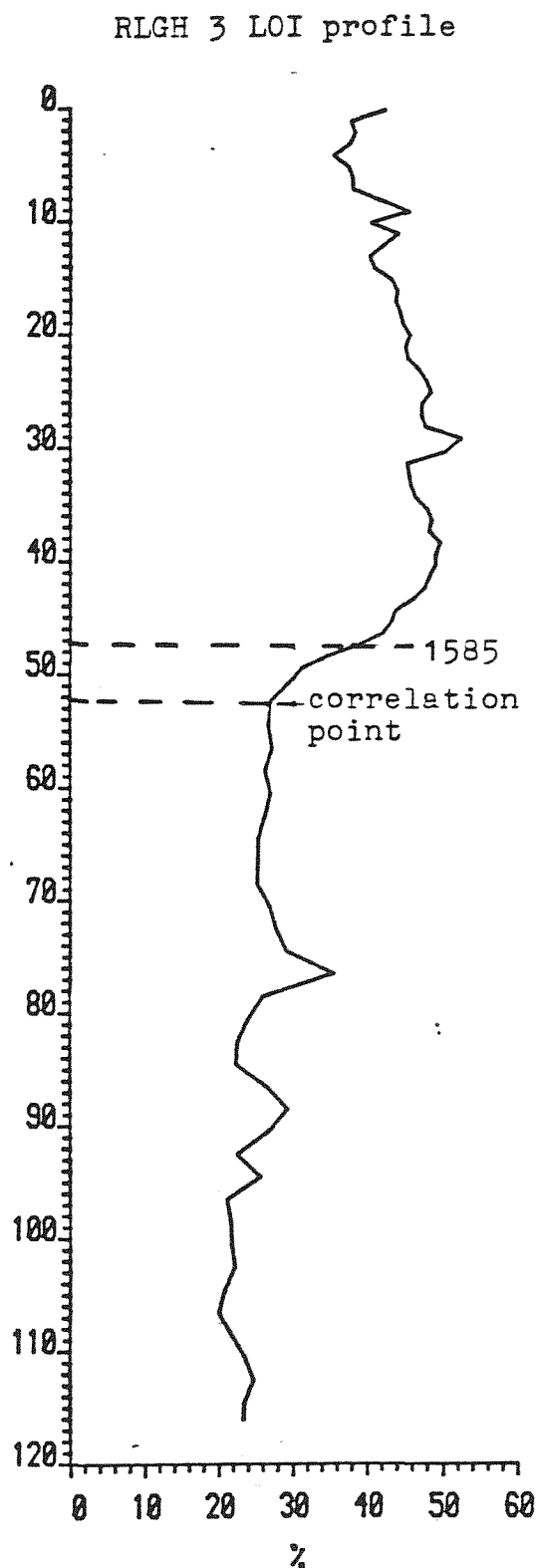
(i) Heavy Metal Analysis

The heavy metal concentrations, given in $mg.1^{-1}$ were converted to $\mu g.g^{-1}$ dry weight using the following formula:

$$\frac{C \times DIL}{W}$$

where

C = concentration of metal

DIL = dilution factor (25 ml HCL)

W = weight of sediment digested

The resulting Zn, Pb and Cu profiles are shown in Figs. 8 - 10 and the raw data given in the Appendix. The Zn profile (Fig. 8) can roughly be divided into three sections according to changes in the profile, the first being between 259 cm. and 150 cm., the second between 150 cm. and 50 cm. and the third between 50 cm. and 0 cm. Relatively low background values of about 40 $\mu g.g^{-1}$ in the first section suddenly increase at about 150 cm., and Zn concentrations in the second section fluctuate quite widely around a mean of c. 75 $\mu g.g^{-1}$. A decline in Zn concentrations can be seen at about 50 cm. between sections two and three, and then a steady increase begins reaching a concentration of 340.8 $\mu g.g^{-1}$ at 5.5 cm. (c. 1945). A fairly rapid decline ensues until 0 - 0.5 cm. where a massive increase to 757.5 $\mu g.g^{-1}$ occurs.

Figure 9 shows the Cu profile in RLGH3, illustrating the low concentrations found within the core. Relatively high amounts of Cu are found in the post-glacial clays at the bottom of the core but this decreases from about 220 cm. to 110 cm. Concentrations rise to a temporary peak at 95 cm. after which a gradual decline brings values down to as low as 7.2 $\mu g.g^{-1}$. At c. 1860 Cu concentrations begin to rise rapidly to a peak of 44.9 $\mu g.g^{-1}$ (c. 1970). A slight decline then occurs to the top of the core.

The Pb profile (Fig. 10) illustrates relatively low background levels from the post-glacial to a depth of about 40 cm. except for a sharp peak at c. 95 cm. A rapid increase in Pb concentrations begins at 40 cm. (c. 1660) to a peak of 431.4 $ug.g^{-1}$ at 9 cm. (c. 1920), and Pb values fluctuate quite
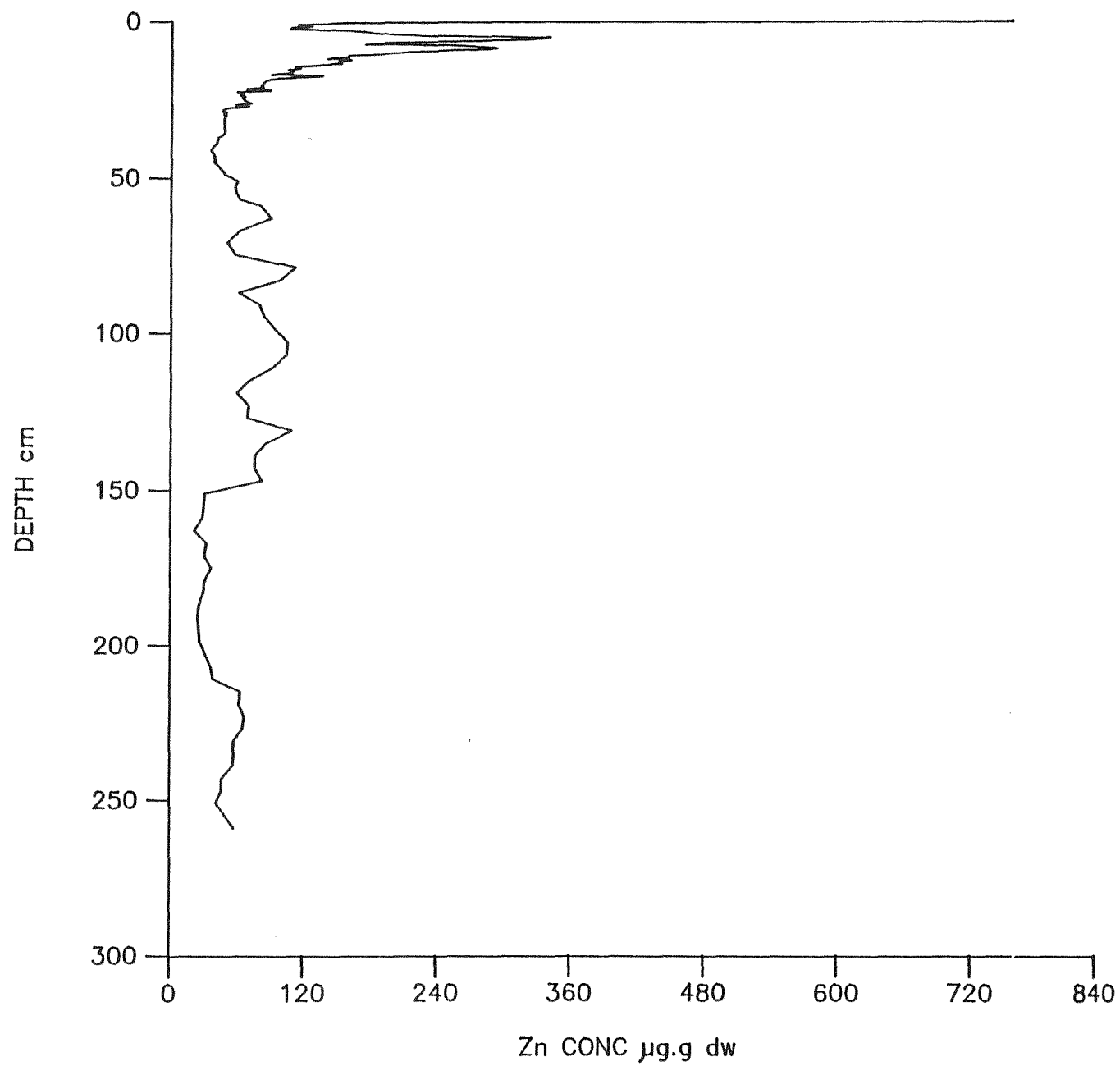
Fig. 8   RLGH 3 Zinc profile (per gram dry weight)

Fig. 10   RLGH 3 Lead profile (per gram dry weight)
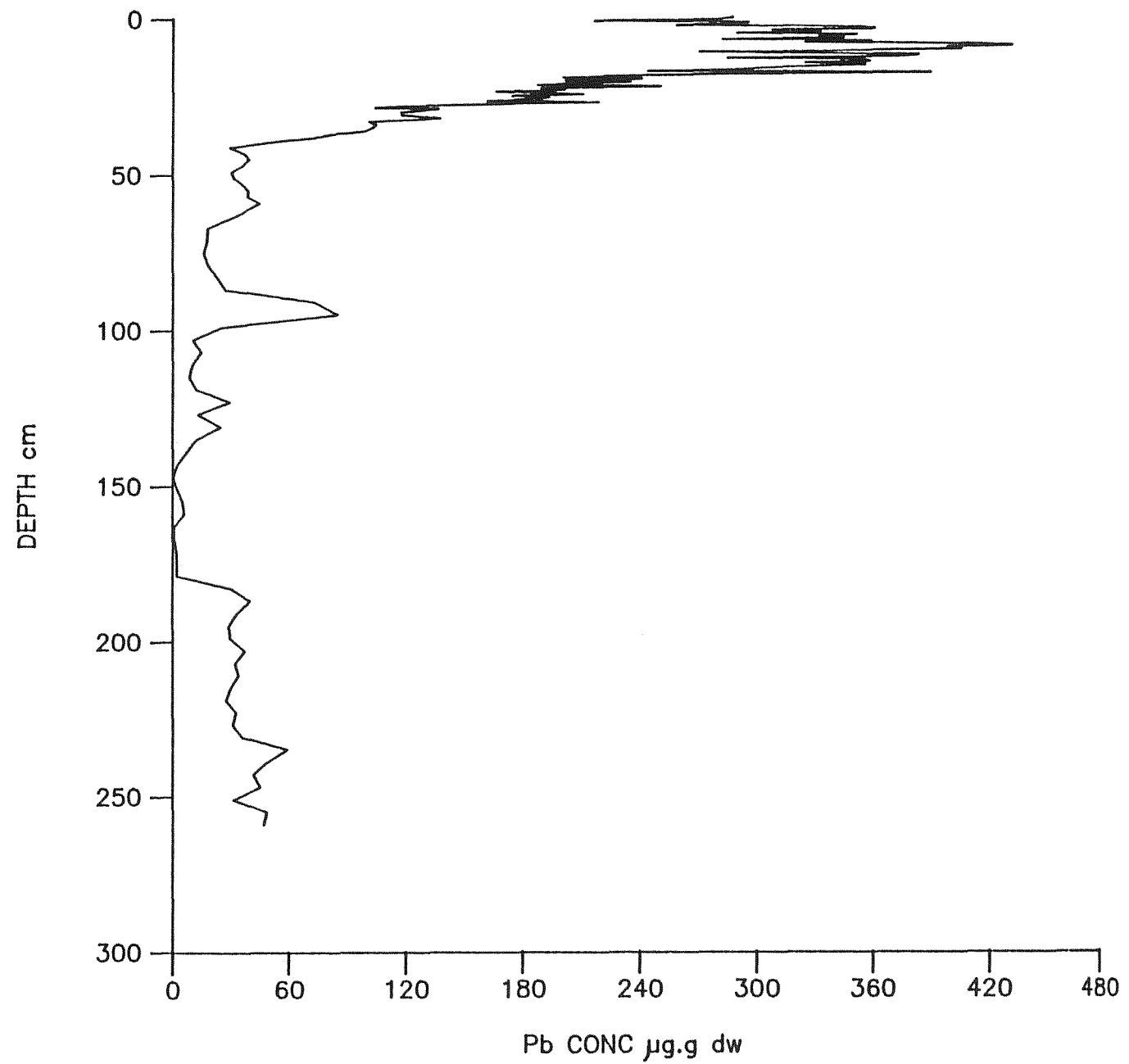
Fig. 13   RLGH 3 Lead profile corrected for organic matter
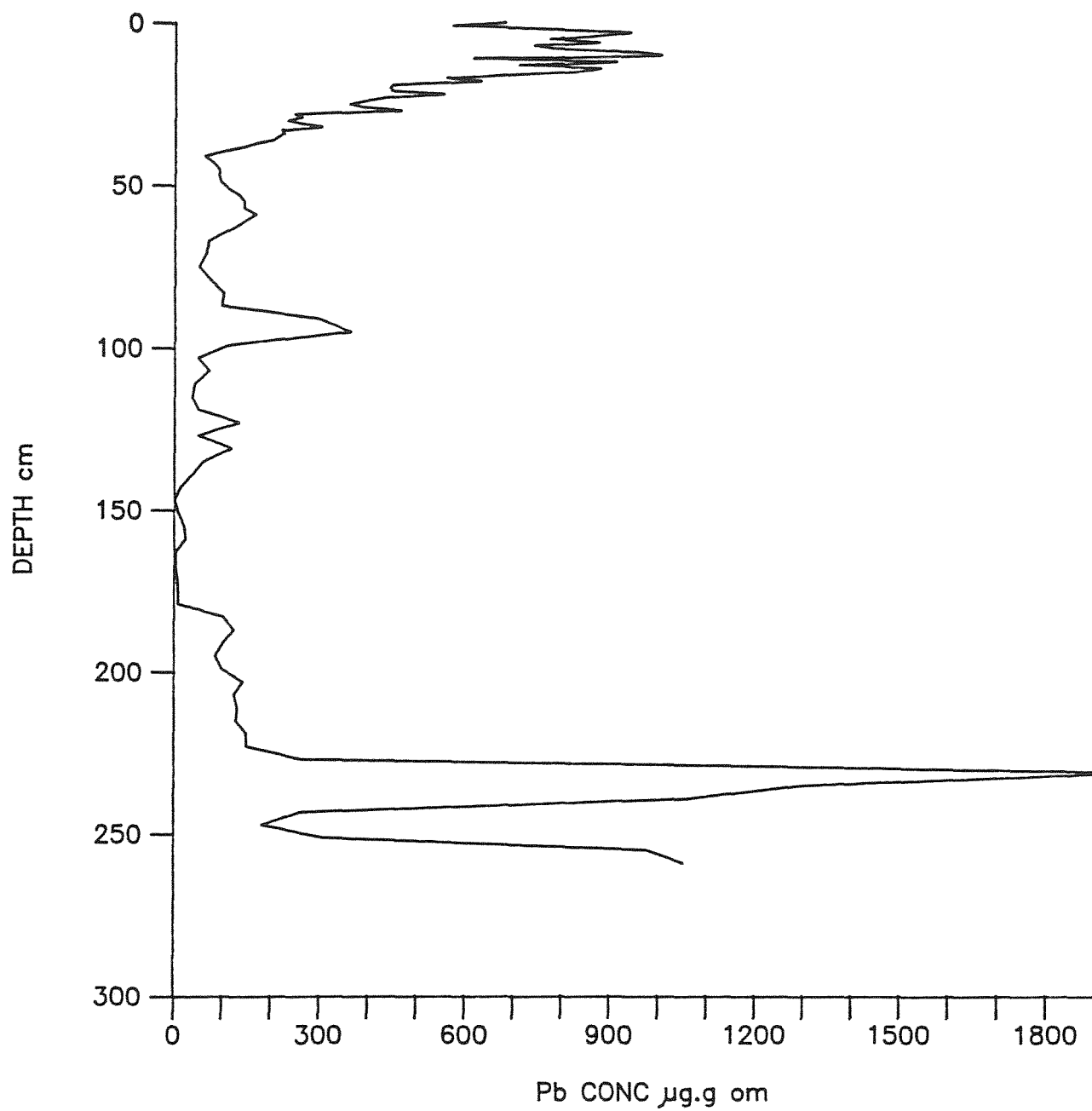
Fig. 9   RLGH 3 Copper profile (per gram dry weight)
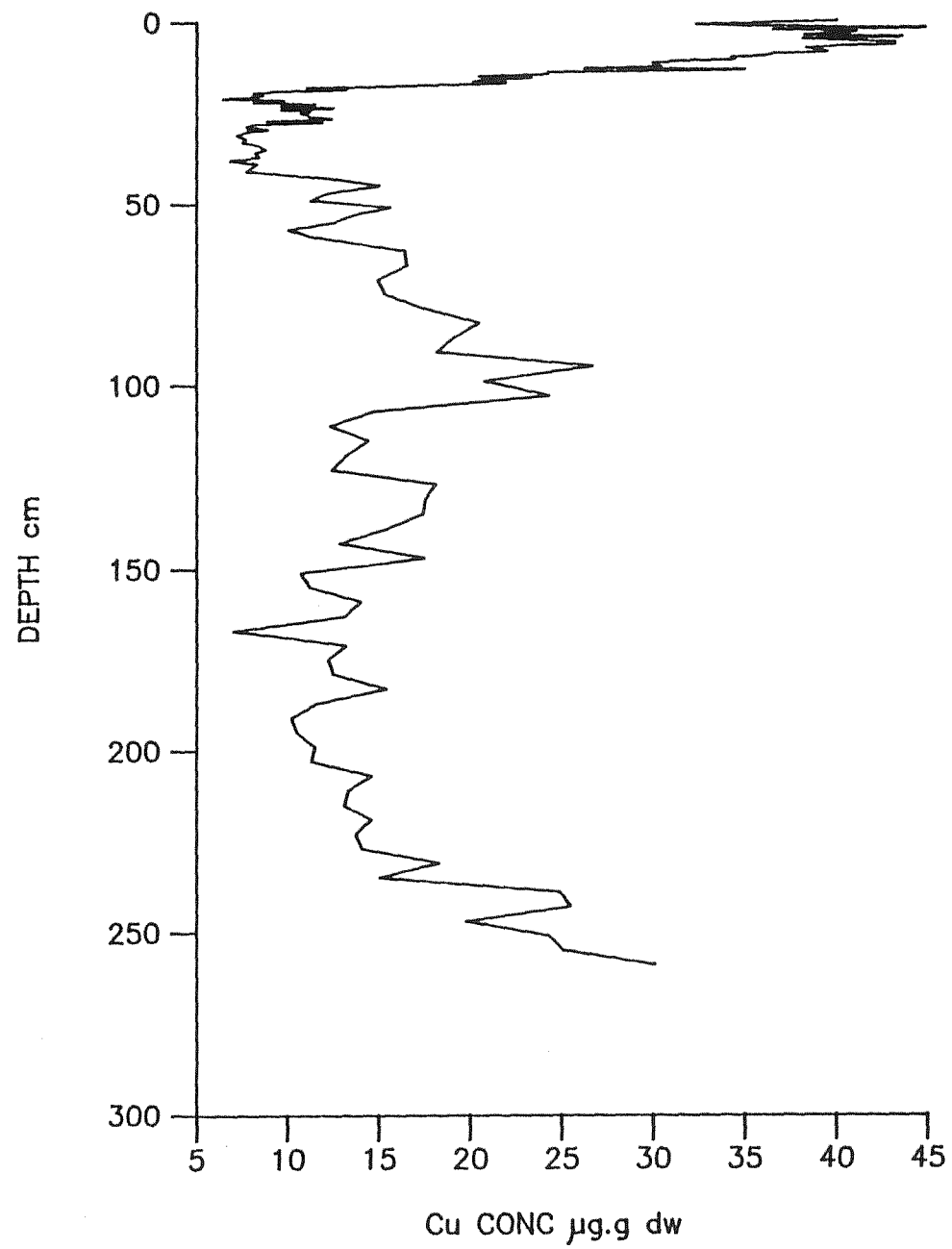
between 9 cm. and the top, but the value at 0 – 0.5 cm. (287 μg.g^{-1}) is still way above the average background value (40 μg.g^{-1}).

Figures 11 to 13 show the profiles once they have been corrected for organic matter and the concentrations are expressed in μg.g^{-1} organic matter. This exercise was undertaken to see whether the shape of the profiles would change if all the sediment consisted of organic matter. In all three corrected profiles there is a massive increase in the bottom 20 – 30 cm. which represents the glacial clays.

The Zn profile in Fig.11 shows that apart from this massive increase, the shape of the profile has remained much the same. The increase in concentration at 150 cm. is still visible as is the large increase at 0 – 0.5 cm. although the increase in Zn values in the top section has been reduced in magnitude. The general shape of the Cu profile (Fig.12) is also maintained although again, the increase at the top of the core has been reduced. This phenomenon is also illustrated in the Pb profile (Fig.13). The spike at about 95 cm. in this profile remains clear.

It is useful to try and determine the amount of "excess" metals that have been deposited in the sediment over and above the background concentrations. One method of achieving this is by taking the highest background value and the highest overall value of the metal above the take-off point. It could be argued that any increase in metal concentration up to the highest background value is due to natural processes, for example catchment factors, rather than anthropogenic factors. It is reasonable to suggest that any concentration over and above the highest background value requires an additional explanation. A second method is to use average values above and below the take-off point. This may be more representative than the first method. By subtracting the background value from concentrations above the take-off point it is possible to calculate the "excess" amount of metal that has been deposited and also the magnitude of increase of each metal over the background value.

Tables 4 and 5 show the calculation of excess values and magnitude of increase using the two methods outlined above.

Table 4

The excess concentrations of Zn, Pb and Cu in RLGH 3 using

Fig. 11   RLGH 3 Zinc profile corrected for organic matter

Zn CONC µg.g om
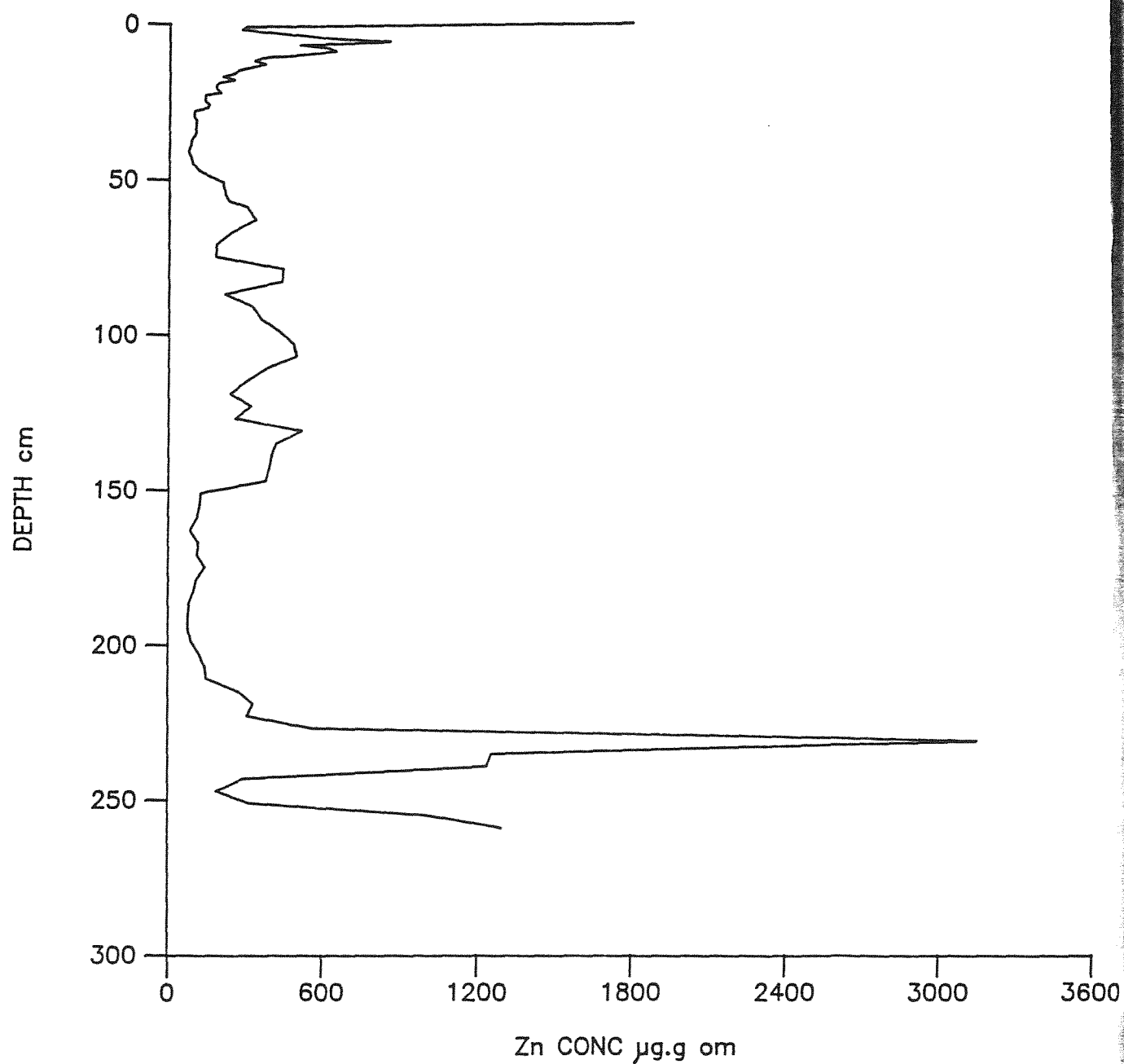
Fig. 12   RLGH 3 Copper profile corrected for organic matter

DEPTH cm

Cu CONC μg.g om
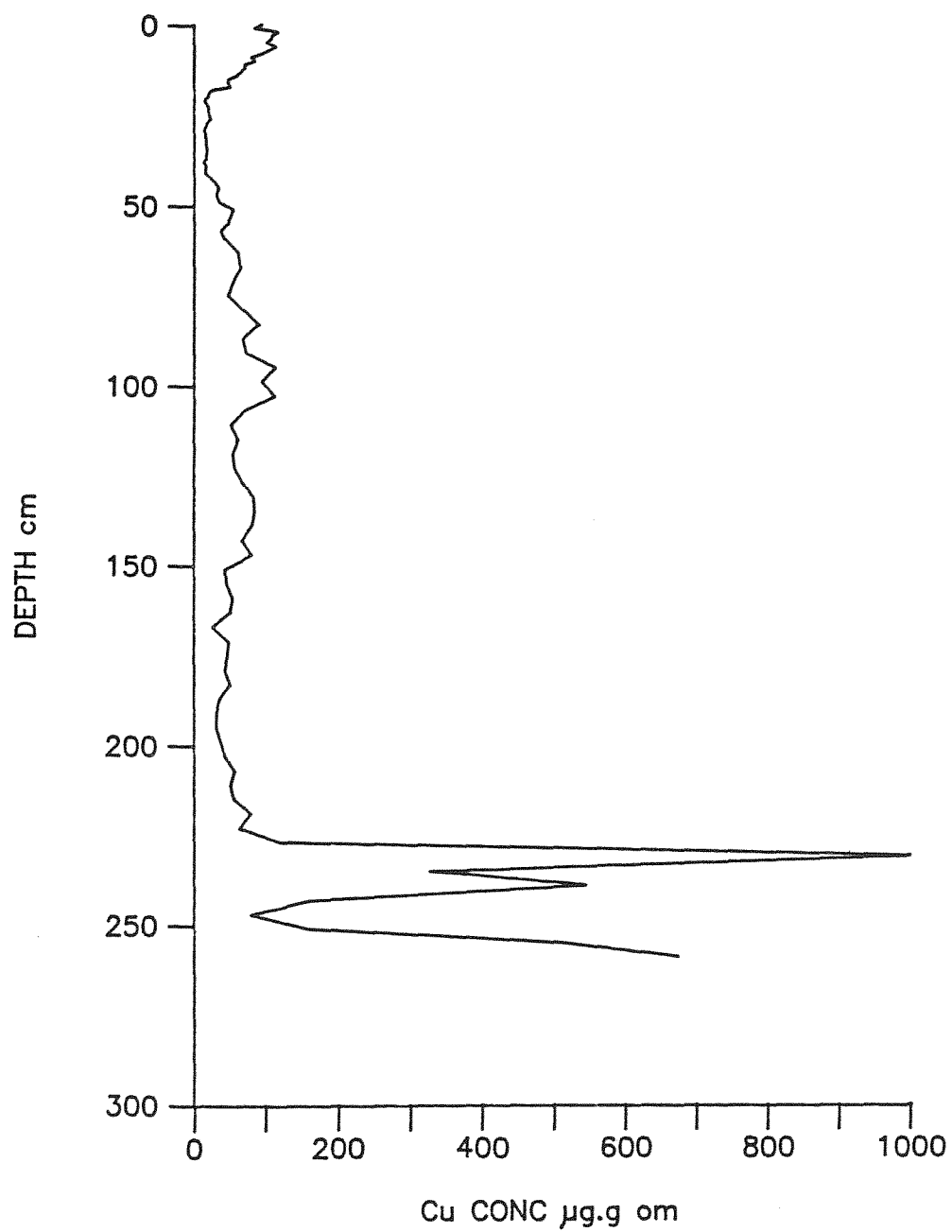
Table 4

The excess concentrations of Zn, Pb and Cu in RLGH 3 using
maximum values.

$$(\mu g.g^{-1})$$

	Maximum background	Maximum value	Excess concentration	Magnitude of increase
Zn	111.8	757·5	645·7	5·8
Pb	84·8	431·4	346·6	4·1
Cu	26·7	44·9	18·2	0·7

Table 5

The excess concentrations of Zn, Pb and Cu in RLGH 3 using
average values.

$$(\mu g.g^{-1})$$

	Average background	Average above take-off point	Excess concentration	Magnitude of increase
Zn	60	220	160	2.7
Pb	40	280	240	6.0
Cu	15	32	17	1.1

... . sediments may be calculated by
subtracting the background value from the metal concentration at each level
and multiplying by the bulk density. This value is then multiplied by the
sediment accumulation rate to obtain a flux measure in $\mu g. cm^{-2}. yr^{-1}$ (Farmer
et al, 1980). Applying this to RLGH3, the average background concentrations
for Zn, Pb and Cu were used as shown in Table 5 . The results are shown in
Figs. 14 to 16 and the data given in the Appendix.

(ii) Analytical Quality Control.

(a) Detection Limit

The blanks were used as a control for contamination and also to calculate
the detection limit of the machine. The blank concentrations are shown in
Table 6 . The detection limit can be expressed as two times the standard
deviation where,

$$S D = \sqrt{\frac{\sum x^2 - \bar{x}^2}{n}}$$

where

x = blank value

n = no. samples

Table 7 shows the standard deviation and detection limit of Zn, Pb and Cu in
RLGH3.

(b) Precision of Results

The duplicate results (Table 8) were used to determine the precision
of results using the following formula:

$$S D = \sqrt{\frac{\sum_{i=1}^{2} \triangle_i^2}{2n}}$$

Precision results (Table 9) are usually expressed as two times the standard
deviation.

(c) Core Correlation

The extrapolated dates using the ^{210}Pb dated core RLGH (Flower and
Battarbee, 1981) are shown in Table 10.

Flux Zn $\mu g.cm^{-2}.yr^{-1}$
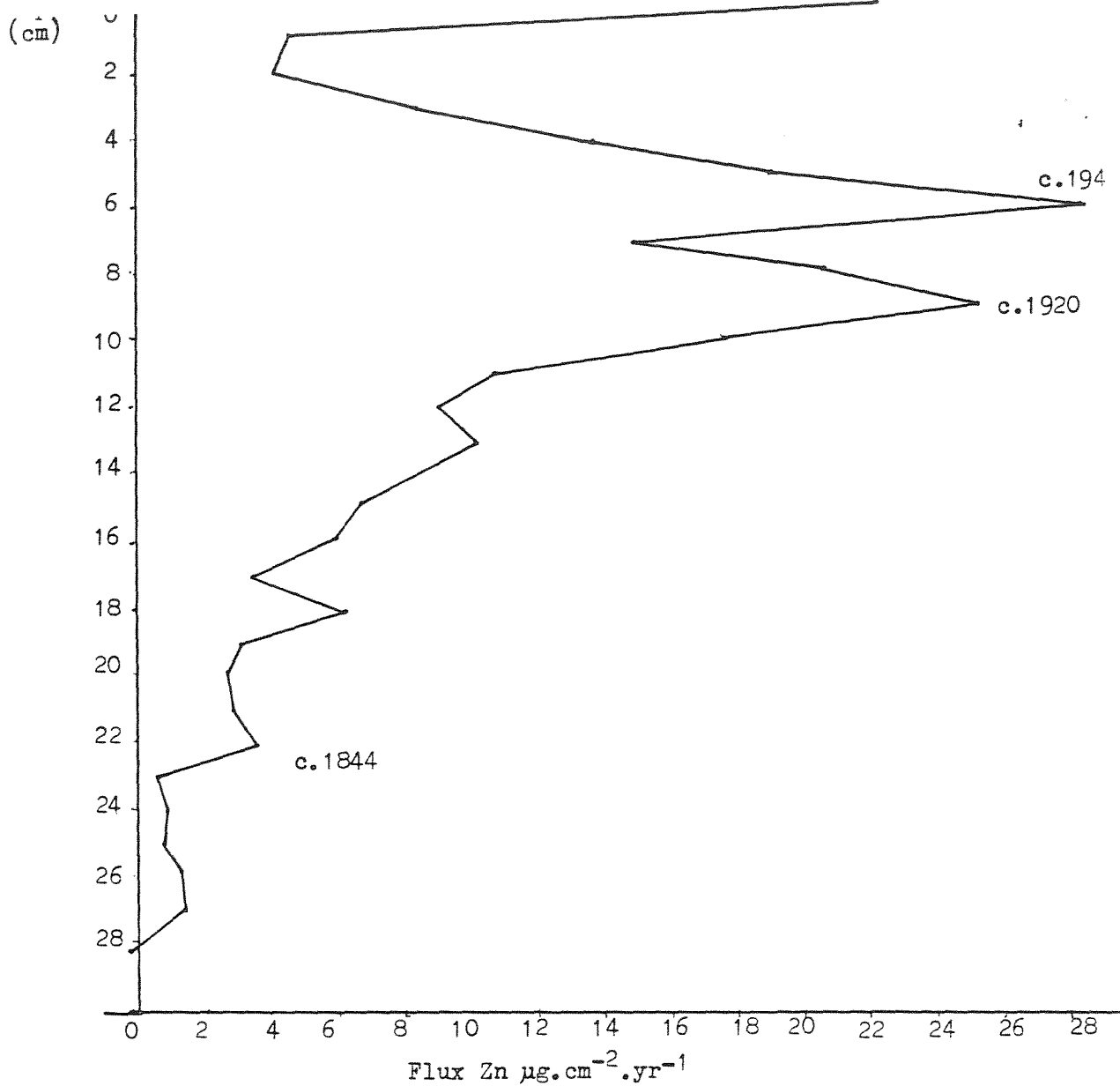
Fig. 15 Flux of Cu to RLGH 3
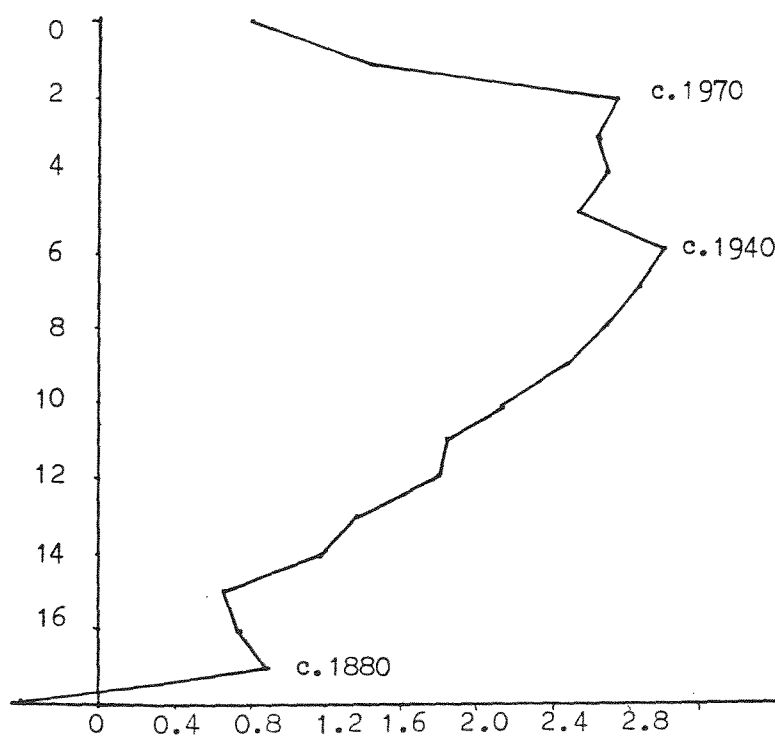
Fig 16   Flux of lead to RLGH 3

Depth (cm) on vertical axis (0 to 40), Flux μg.cm^{-2}.yr^{-1} on horizontal axis (4 to 44).

Labels on curve: c.1965, c.1920, c.1800, c.1670
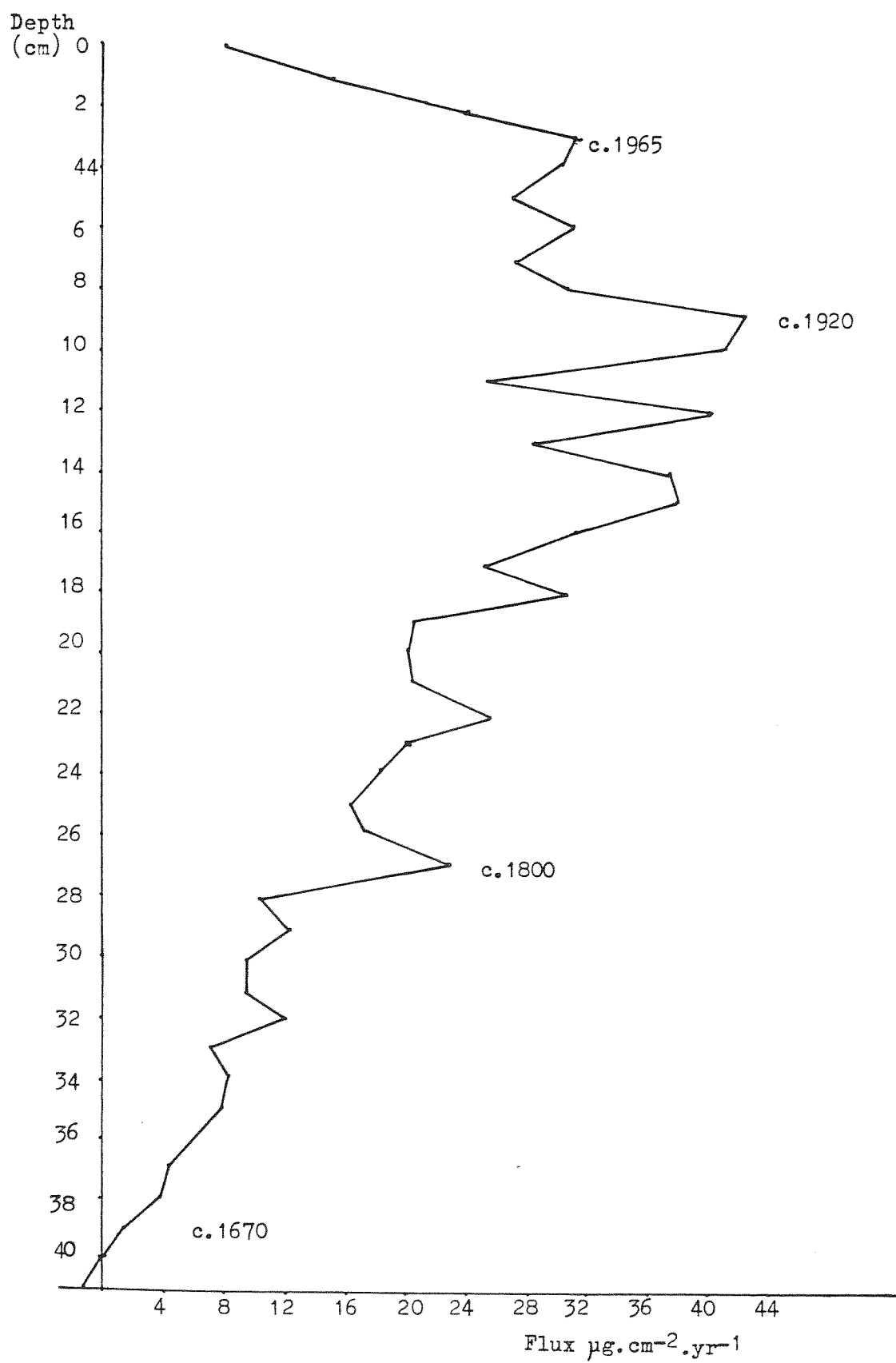
Table 6   Blank concentrations ($\mu g.g^{-1}$)

Zn	Pb	Cu
0.005	0.060	0.007
0.004	0.040	0.007
0.015	0.000	0.012
0.005	0.080	0.010
0.008	0.010	0.014
0.017	0.038	0.009
0.012	0.026	0.015
0.012	0.022	0.016

Table 7   Standard deviation from blanks and detection limit of

Zn, Pb and Cu in RLGH 3

	Zn	Pb	Cu.
S D	0.0047	0.024	0.004
Detection Limit	0.0094	0.048	0.008

Table 8   Duplicate results from RLGH 3

($\mu g.g^{-1}$)

Depth	Sample	Zn	Pb	Cu
203 – 204 cm	1	31.6	47.2	14.6
	2	34.1	54.8	14.9
231 – 232 cm	1	57.6	46.0	15.0
	2	54.7	54.7	16.3
243 – 244 cm	1	46.7	41.5	19.7
	2	47.1	54.6	21.3

Table 9   Standard deviation from duplicates and precision

of results for Zn, Pb and Cu in RLGH 3

	Zn	Pb	Cu
S D	1.57	1.71	0.85
Precision of results ($\mu g.g^{-1}$)	3.14	3.42	1.70

Table 10

Core correlation using LOI figures from RLGH3 (1984)
and RLGH (Flower and Battarbee, 1981).

Depth RLGH	Depth RLGH3	Date
0.0	0.0	$1981^{\pm 3}$
1.25	1.48	1975
2.25	2.65	1967
3.25	3.84	1958
4.75	5.61	1945
6.75	7.97	1929
8.75	10.33	1914
10.75	12.96	1901
12.75	15.05	1883
14.75	17.41	1874
18.75	22.13	1844
21.75	25.67	1817
25.0	29.50	1776
40.0	47.20	1585*

* Extrapolated date

Introduction.

The discussion is divided into two major sections. The first section deals with the methodology and results obtained from the Round Loch of Glenhead study. It considers problems encountered and improvements that could be made to the method, and discusses the accuracy and reliability of the results. The section also includes a discussion on the use of heavy metal analysis from sing cores as an indicator of environmental contamination, and an interpretation and explanation of the Zn, Pb and Cu profiles analysed from RLGH 3.

The second section aims to elaborate further on the heavy metal cycle to Round Loch by specifically applying concepts introduced in the Literature Revie Transport and deposition of heavy metals to Round Loch, diagenesis and re-mobilization within the lake sediments, and various catchment factors are discussed. Finally, the Round Loch study is compared with other studies from Great Britain, North America and Scandinavia.

Section 1.

(1) Comments on the methodology.

(a) Problems and Improvements.

Unfamiliarity with the digestion technique partly caused the first com-plication, which was that the first batch of samples took much longer than anticipated to digest. One reason for this was that the sediment had dried int a hard pellet which took some time to break down. Following samples were there-fore ground with a pestle and mortar before digestion began. A second reason for the slow digestion was the extremely peaty nature of the sediment which resisted digestion. On completion of the digestion process, an unusual black, tarry ring was left around the edge of the digestion vessels. This resistant residue was thought to be the result of weathering and mineralization processes and the slow sediment accumulation rate in Round Loch. It was interesting to note that the inorganic glacial clay sediments did not leave this tarry residue after digestion.

In some cases, the digested solution was not completely clear, but there

sediment after such a rigorous and extensive digestion process.

An improvement on the method used in this study would be to include more, blanks and replicates. The results obtained in this paper do imply that the method was accurate and contamination kept at a minimum (see part (b)) but it would be preferable, if enough sediment was available, to replicate more samples to ensure accuracy and repeatability of the experiment.

The reliability of the dates obtained in this study could be improved by using a dating technique such as ^{210}Pb. Unfortunately this technique is expensive and not readily available, so core correlation was used as a substitute. It would be useful to check on the accuracy of the core correlation by using diatoms as stratigraphic markers on the same core. Synchronous dating from both methods would increase the evidence for reliability of dates.

(b) Analytical Quality Control.

It is important to determine whether the results obtained were accurate and free from contamination in order to show that they reflect actual changes within the sediment profile. The blanks were used to find the standard deviation of the analytical technique and also to determine the limit of detection of the instrument for Zn, Pb and Cu. Table 7 shows the extremely small standard deviation values and the low detection limits indicating that the A.A.S. technique was very accurate. The only trace metal values to reach the detection limit were for Pb; at 147 - 148 cm concentrations were zero, and at 163 - 164 cm and 167 - 168 cm concentrations were $0.7 \mu g.g^{-1}$. As far as the detection limit is concerned these are the only questionable results in the analysis.

The precision of results using duplicates also allowed a standard deviation to be calculated, and Pb had the highest standard deviation at $1.71 \mu g.g^{-1}$. This is to be expected considering the inherent variability of this metal.

The accuracy of results can be tested by observing whether the concentration of the blanks is smaller than the standard deviation of the duplicates. The blank values of Zn, Pb and Cu can be seen in Table 6 and in all cases they are below the standard deviation values of the duplicates. (Table 9).

et al, 1985 unpublished). This Loch, also in the Galloway area, is situated on granitic rock in an unafforested catchment, similar to that of Round Loch. A.A.S. was carried out on the same instrument and so quality control results are comparable. Table 11 shows the precision of results from Loch Enoch which are very similar to Round Loch results (Table 9). This suggests that both sets of analyses were fairly accurate.

(2) Heavy metal analysis as an indicator of contamination.

A recent paper by Evans and Dillon (1984) looked at the legitimate uses of sediment profiles and compared site specific and whole-system studies. This study on Round Loch is site-specific as a single core was taken from the deepest part of the lake. Evans and Dillon (op. cit.) outlined the questions which can be answered using single core studies and warned against trying to obtain too much information from one core. Single-core studies are useful for determining the time of onset of environmental changes. The use of dating techniques in conjunction with heavy metal profiles allows this information to be gained. Single-core studies also allow the timing of increase of the different metals to be compared, and the relative differences in the magnitude of metal contamination can be calculated. This information has been obtained from the Round Loch core. Evans and Dillon (1984) outlined several constraints that may limit the usefulness of such a study, including sediment mixing, metal mobility and the differential bonding of metals. These problems are discussed later in the chapter.

Norton (1984) pointed out that the interpretation of trace metal profiles might be difficult if just a few elements are considered. For example, a core from Lake Blåvatn, Norway, has a very high spike at the top with Fe making up more than half of the sediment present. At about 5 cm this spike causes dips in all other elements. If all the chemical data was not available, the dips in Zn and Pb would be wrongly interpreted (Fig. 17). Davis et al (1982) experienced this phenomenon in Lake Holmvatn, Norway and stated that if the Fe enrichment at 2 cm depth in the core was absent, then the Pb, Zn and Cu surface

Table 11 Precision results of Zn, Cu and Pb from Loch Enoch

	$\mu g \cdot g^{-1}$		
	Zn	Cu	Pb
Precision of results	4.7	0.9	3.8

Table 12 Background concentrations of Zn, Cu and Pb from Loch Enoch

	$\mu g \cdot g^{-1}$		
	Zn	Cu	Pb
Background concentrations	25.4	6.2	74.6

(Source: Battarbee et al, 1985 unpublished)

a fuller knowledge of the sediment chemistry in Round Loch to help in the interpretation of the sediment profile.

An advantage in using heavy metals as indicators of contamination is that they directly reflect changes in the deposition of contaminated matter falling onto the lake and catchment. It can be argued that, because the sources of acid precipitation precursors and heavy metal contaminants are very similar, both should show an increase in sediment cores at the same time. Diatom analysis is used to reconstruct the past pH of lakes, thus indicating the effects of acid precipitation. Heavy metal analysis may have a slight advantage over this method when looking at the onset of atmospheric contamination, as acid precipitation may be buffered by the lake catchment. Davis et al (1982) noted a lag of about a century between the take-off of heavy metal concentrations and a change in diatom flora in some Norwegian lakes. However, the Round Loch of Glenhead catchment is poorly buffered against acidic precipitation and there is no lag between the indication of a decrease in pH at c 1850 and the take-off of Zn and Cu. The fact that the Pb profile took off earlier in RLGH 3 suggests that the pre-industrial mining and production methods did not release acid rain precursors into the atmosphere to any great extent.

(3) Discussion of individual profiles.

Zinc

A comparison of the crude Zn profile in RLGH 3 with the corrected profile (Figs. 8 and 11) indicate that the increase in Zn concentrations at 150 cm is real. The pollen profile for RLGH 3 (unpublished) shows that 150 cm is about the time of the elm decline (c. 5000 b.p.) which marks the Atlantic - sub Boreal transition. The profile also shows a slight increase in oak at this time. These changes occur before the time of major human impact on metal production and it is possible that vegetation changes in the catchment contributed towards the increased release of Zn to the lake. Siccama and Smith (1980) demonstrated that substantial amounts of trace metals are held in forest floors, and a change in the forest area of the catchment would be likely to lead to a change in the

be affected by changes in the catchment.

Zn concentrations begin to exceed the maximum background value (Table 4) at 18 cm (c.1870). All concentrations above the background represent an addition of Zn to the lake sediment from sources other than those accounting for the background level. The timing of this increase suggests an industrial origin of the excess Zn. The actual take-off Zn appears to occur earlier than is indicated by using the maximum background value (see Fig. 8). It seems that, after catchment disturbances in the second section of the profile, Zn concentrations above 50 cm were returning to the original, lower background value of the first section. The take-off begins at about 22 cm (c.1844) where Zn concentrations exceed the average background value of 60 μg.g^{-1} (Table 5). The peak Zn concentration of 757.5 μg.g^{-1} (0 - 0.5 cm) far exceeds the second highest concentration of 340.8 μg.g^{-1} at 5.5 cm and it is interesting to note that between 5.5 cm and 0.5 cm the Zn concentration was falling. Cawse (1981) noticed a downward trend in Zn and Pb deposition in remote British locations between 1971 and 1981, the decrease in Zn being the most noticeable. He attributed this to a decrease in industrial emissions owing to the economic recession.

Round Loch is poorly buffered against acid precipitation due to the underlying granitic bedrock and the pH of the water has dropped almost one unit since 1880 to its present level of c. 4.5. Wong et al (1984) stated that "in considering the long range transport of pollutants it is important to realize the combined effect of acid precipitation inputs and the metal cycle in acid-sensitive lakes." Increasing acidity of precipitation could explain the Zn decrease at the top of RLGH 3. Hanson et al (1982) described a phenomenon which is apparent in numerous lakes with a pH below 5.5. They found that Pb increased over time from C.1880, levelling off at the present, and that Zn also increased from about 1880 but then decreased significantly towards the present (Fig.18). Davis et al (1983) found that Zn concentrations in cores from Norway and New England decreased in the last 20 - 40 years, and Kahl et al (1984) confirmed this decrease in New England lakes. Apart from the

Fig. 17   Trace metal profiles from Lake Blåvatn.

Depth (cm)

FeO   Pb   Zn

% IGN   PPM IGN   PPM IGN
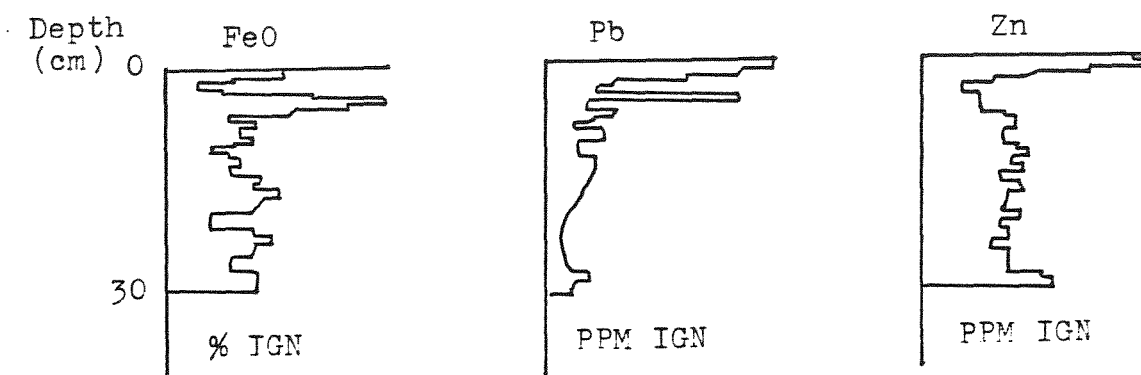
(Source: Norton, 1984)

Fig. 18   Pb and Zn profiles from selected lakes.

DREM 4.5   SPEC 4.7   UNN 4.75   MTNR 5.8   ERIC 6.3

Pb

DREM 4.5   SPEC 4.7   UNN 4.75   MTNR 5.8   ERIC 6.3

Zn
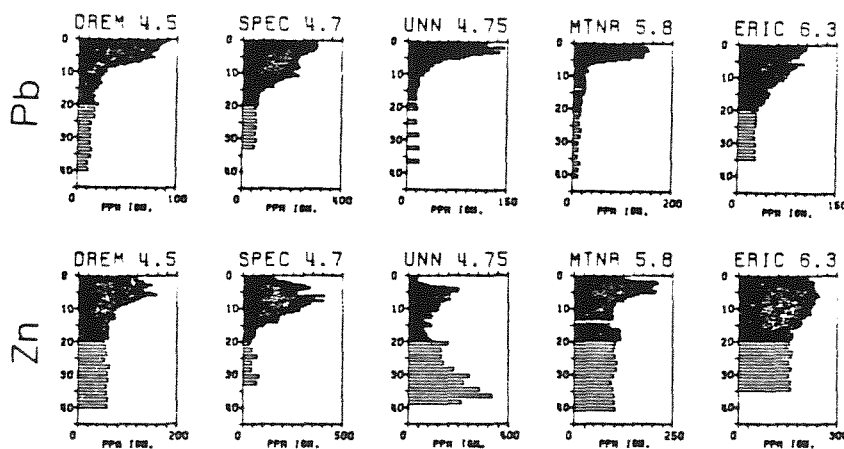
(Source: Hanson et al, 1982)

Fig 19.   Trace metal profiles from Loch Lomond.

Depth (cm)

Pb   Zn   Mn   Fe

µg.g   µg.g   %   %
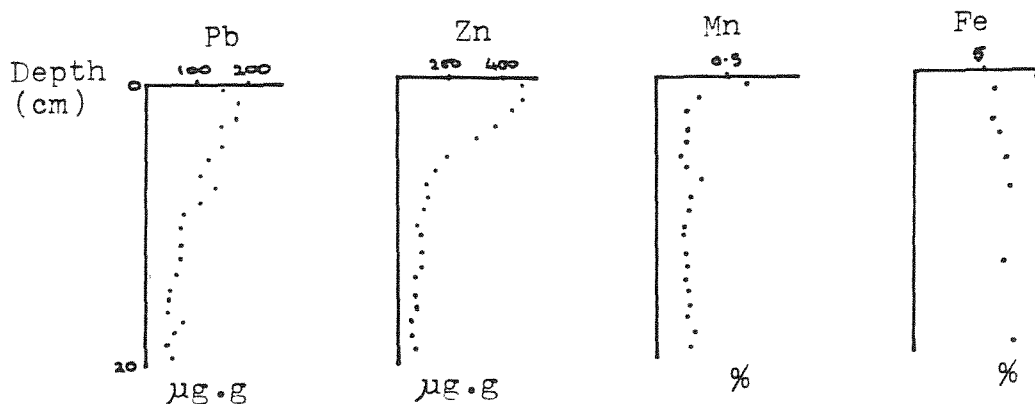
(Source: Farmer et al, 1981)

follows this general pattern and decline from 5.5 cm (c.1945).

It was suggested by Hanson et al (1982) that increasing acidity of
precipitation resulted in the leaching of Zn from the upper soil horizon and
its translocation to deeper soil horizons instead of entering surface waters.
Lake sediments derived from the top soils would therefore be impoverished in
Zn. Wong et al (1984) argued that a partial dissolution of particulate Zn
may occur at lower lake pH levels, or that Zn deposited before lake acidificati
began could be solubilized back into the water column as suggested by Förstner
(1981). Evidence indicates that Zn will remain in its soluble form in the
water column if subjected to low ambient pH levels. Kahl et al (1984) conclude
that the profile of Zn in recent sediments is a result of two processes, first,
increased atmospheric loading with time, and second, greater terrestrial and
aquatic leaching due to increasingly acidic precipitation.

The RLGH3 Zn profile follows the general pattern of a recent Zn decline
seen in the sediments of Scandinavian and North American acidic lakes, apart
from the sudden increase at 0.5 cm. This rise in Zn concentrations could be
due to analytical error, but the sample was tested a number of times on a
correctly adjusted instrument, so this seems unlikely. The top sample may have
been contaminated either on extraction from the lake, or during the extrusion
and digestion process. There was insufficient sediment to replicate this sampl
but it is unusual that the Pb and Cu profiles (Figs. 10 and 9) do not show a
similarly high concentration if the sediment was contaminated. Moreover, the
blanks do not show any sign of Zn contamination (Table 6). This suggests that
the digestion procedure did not cause contamination.

Norton et al (1978) looked at increased Zn loadings in New England lakes ar
stated that an increase in Zn concentrations was concurrent with increasing
acidity of precipitation. The authors gave several suggestions as to why Zn had
increased and some of these can be applied to Round Loch. One possibility is
the washout of Zn from the soil into the lake as a result of acidic precipitatio
Zn may have been deposited onto the catchment of Round Loch from atmospheric
sources and released from the soil by acid rain. This is supported by Livett

Pb or Cu. A second possibility may be the upward mobility of Zn within the lake sediment causing an accumulation in the top sample. However, it seems unlikely that Zn would accumulate in such large quantities in the top half centimetre of the sediment but occur at much lower concentrations in the second half centimetre.

Tables 4 and 5 show the magnitude of increase of Zn over the background level. The figure given in Table 5 probably more accurately reflects the increase in Zn, as this method of calculation reduces the effect of the unrepresentative top value. The flux rate of Zn (Fig. 14) interestingly shows that the highest flux to RLGH 3 occurred at 6 – 7 cm. depth (c.1938) and not at 0 – 0.5 cm. depth which represents the highest Zn concentration in $\mu g.g^{-1}$. This suggests that remobilization of Zn has occurred either in the sediment or within the catchment to increase Zn concentrations in the top sample.

The flux rates illustrated in Figs. 14 – 16 are core-specific amd not representative of the whole lake because of the variability of sediment accumulation rates in the lake. There is even a slight difference in sedimentation rate between RLGH and RLGH 3 (1 mm.yr^{-1} and 1.18 mm.yr^{-1} respectively). In order to obtain a flux rate for Round Loch a whole-lake study would be required. Evans and Dillon (1984) stressed this point and criticised a study by Goldberg et al (1976) in which the atmospheric flux to the Palace Moat in Tokyo was calculated using a single core.

Lead

The noticeable spike in Pb concentrations at about 95 cm. (Fig. 10) consists of two sample points indicating that it is not the result of contamination. The pollen profile for RLGH 3 (unpublished) shows that 90 – 100 cm. marks the spread of blanket peats in the catchment, with an increase in Sphagnum pollen. This change in catchment characteristics could account for the variability in the Pb profile. (Livett et al, 1979).

The Pb profile more than any other illustrates the huge increase of metal concentration at the top of the core. The take-off point occurs earlier than

concentration is 35 cm (c.1700). However, as with Zn concentrations, it is more representitive to use average values in calculating excess and magnitude of increase figures, as the spike at 95 cm. which gives the highest background value is not typical of the other background concentrations. The average background figure (Table 5) is exceeded at 39 cm. depth (c.1670). Table 5 shows an increase of Pb concentrations since c1670 of six times the background. Flux calculations (Fig. 16) show the highest Pb flux to RLGH 3 was at 9 cm. concurrent with the highest Pb concentration.

The earlier take-off of Pb could be due to the pre-industrial mining (especially in the Southern Uplands) and processing of lead. Farmer et al (1980 stated that industrialization in the Glasgow area began in the 15th. and 16th. centuries, and the foundation of the chemical industries in the mid-17th. century allowed the establishment of iron works at c.1750. Early industrial developments such as these could account for the beginnings of the Pb rise which increased rapidly during the following centuries. It is likely that emissions from the Glasgow region enter into the regional air masses and affect deposition in the Galloway area. It is interesting to note that Davis et al (1983) found that in Norway, Pb generally began to increase in the 1600s and 1700s, but mainly in the 1800s when pollution by Zn and Cu were detected. This corresponds to the metal increases in Round Loch.

The slight decrease in Pb concentrations between 9 cm. and the top of RLGH3 (Fig. 10) could be explained by a decrease in metal production in the last ten years as suggested by Cawse (1981). A second explanation may be that acid precipitation remobilizes Pb from the lake sediment and Wong et al (1984) indicated that in extremely acidic lakes of pH below 4.5, metals other than Zn may be regenerated into the water from the sediments. Davis et al (1982) studied the release of Pb from lake sediments. They experimented with sediments from Lake Sagamore and Woods Lake in the Adirondack State Park, New York State, and discovered that the initial release of Pb began at a pH of 3.2 in Sagamore and 3.8 - 4.0 in Woods Lake. These results were about 2 - 3 pH units lower than pHs predicted by other models. If Davis et al (op. cit.) are correct,

mobilization of Pb from the sediments.

The fact that the Pb profile takes off before Zn or Cu suggests that the recent increases in metal concentrations are not due to catchment changes. Pb is the least mobile trace metal of the three and if catchment changes were the cause of rising metal concentrations, it would come into solution last, showing a later increase in the trace metal profile.

Copper.

Cu shows the least variability of the three metals analysed in RLGH 3 and is present in much lower concentrations (Fig. 9). A slight increase in Cu concentrations is evident at the top of the core. A relatively large amount of Cu is evident in the glacial clays accounting for the huge peak at the bottom of the core in Fig. 12. There is a small peak at 95 cm and the spread of blanket peats may also have affected Cu concentrations. As with the Zn profile, Cu concentrations return to lower background levels above 50 cm and the Cu take-off appears to be at 18.5 cm (c.1860). The concentrations level out between 9 cm and 0 cm with values varying between 35 $\mu g.g^{-1}$ and 44 $\mu g.g^{-1}$.

Cu values begin to exceed the maximum background concentration (26 $\mu g.g^{-1}$) at 13.5 cm (c.1905). It is reasonable to argue that the excess deposition of Cu between c.1860 and c.1905 resulted from the increased production of Cu in the post-Industrial Revolution era, although anthropogenic influences seem to have had a lesser effect on Cu emissions than on Zn and Pb. (See magnitude of increase figure, Table 5). This is illustrated in Tables 1 and 2 which give global, natural and anthropogenic emissions for Cu, Pb and Zn. Jeffries and Snyder/and Nriagu et al (1982) studied lakes at Sudbury, Ontario, and found that
(1981)
Cu concentrations decreased rapidly with distance from the metal smelter. They attributed this to the fact that Cu particles are larger than Zn particles and so are deposited by dry deposition near to their source. This may also explain the lower Cu concentrations in RLGH 3.

Section 2.

(i) Transport and deposition of Zn, Pb and Cu in Round Loch of Glenhead.

The regional sources of pollution that affect deposition in the Galloway

in the Lake District, and the industrial areas of Northern Ireland. These
sources emit contaminants into the atmosphere where they are circulated in the
regional air masses. The prevailing wind is from the south-west which indicates
Northern Ireland as one of the most likely sources of contaminants. Rippey
et al (1982) reported that trace metal contaminants in Lough Neagh, Northern
Ireland, form part of a global pattern. This suggests that atmospheric con-
tamination on a global scale also leads to the deposition of trace metals onto
the lake and catchment of Round Loch. The importance of the global distribution
of trace metals has been emphasised by evidence for contamination in polar ice
sheets (Weiss et al, 1975, Murozumi et al, 1969). Because of the small particle
size of trace metals such as Zn, Pb and Cu, they are likely to reach the loch
by wet deposition rather than dry deposition (Galloway et al, 1982).

It is important to consider the contribution of the bedrock to heavy metal
concentrations in lake sediments. The weathering of rock releases heavy metals
in a form which can be incorporated into sediments. Round Loch is situated on
an igneous granitic intrusion, and Flanagan (1973) gives an indication of the
levels of Cu, Pb and Zn likely to be found in a typical granite :

$$Cu \quad = \quad 12 \ mg.kg^{-1}$$
$$Zn \quad = \quad 31 \ mg.kg^{-1}$$
$$Pb \quad = \quad 85 \ mg.kg^{-1}$$

(Flanagan, 1973 quoted by Bowen, 1979)

These values are very low compared to elements such as Al ($81 \ 500 \ mg.kg^{-1}$),
Fe ($19 \ 000 \ mg.kg^{-1}$) and Na ($30 \ 000 \ mg.kg^{-1}$), indicating that inputs of Pb, Zn
and Cu from the bedrock are likely to be of less importance than atmospheric
inputs to Round Loch.

It is impossible to state catagorically which mechanisms are the most
important in the transfer of trace metals from the lake water to the sediment
in Round Loch, as detailed information is lacking in this field. Hart (1982)
commented that, "our knowledge has not yet developed to the point where accurate
quantitative predictions can be made." Because the Round Loch catchment
consists mainly of organic blanket peats it is likely that the association of
metals with organic molecules plays an important role. The digestion procedure

metals by bacteria and algae is very much an unknown phenomenon at the present time. Some research has been carried out on the uptake of metals by individual algal species, e.g. work by Hamilton-Taylor (1979) on *Asterionella formosa* and Button and Hesteller (1977) on the Cu-sensitive *Cyclotella meneghiniana*, and more work of this nature is required before quantitative predictions can be made. The uptake of trace metals by micro organisms could be a significant factor in Round Loch, although it is probably more important in eutrophic lakes which support massive algal blooms.

(ii) Diagenesis and Remobilization in Round Loch of Glenhead.

Farmer et al (1980) studied cores from Loch Lomond and discovered that Fe and Mn, after reduction below the core surface, migrated upwards through the pore water to be reoxidised and fixed in the surface layer, giving a large peak in the profiles at the top of the core. The Pb and Zn profiles did not match those of Fe and Mn, however, the upward increase being more gradual (see Fig. 19 This suggested that the diagenetic effects, if any, leading to the upward mobility of Pb and Zn were much less important than for Fe and Mn. Farmer et al (op.cit.) then suggested that the profiles of Pb and Zn could be interpreted in terms of anthropological effects, and diagenetic effects could be excluded. They argued that this was reasonable in view of the trends of metal production and release to the environment since the onset of the Industrial Revolution, and the relative immobility of Pb and Zn formed under reducing conditions at depth in the sediment. Although Mn and Fe profiles are not available for RLGH 3, the Zn, Pb and Cu profiles do not exhibit a typically mixed form, i.e. the increase in concentrations is not confined to the top 2 - 3 cm of sediment, but is visible to depths of 40 cm in the case of Pb. Moreover, a profile in which sediment mixing had occurred would have a less spiky appearance than the RLGH 3 Zn, Pb and Cu profiles as mixing tends to smooth out irregularities in metal profiles.

Farmer et al (op.cit) also suggested that if trace metal and ^{210}Pb profiles reached background concentrations at a common depth, there would be a strong suggestion of sediment mixing. RLGH (Flower and Battarbee, 1981) was dated

accumulation rate in RLGH 3. The background level is reached at about 22 cm
and the heavy metal profiles (Figs. 8 to 10) show that the Zn, Pb and Cu
background levels are reached at 26.5 cm, 39 cm and 18.5 cm respectively.
The soot particle profile for RLGH 3 is shown in Fig. 21 and the background
value is reached at about 9 cm. All this evidence indiates that there is no
mixed zone on RLGH 3.

Round Loch sediments are not laminated, therefore some mixing does occur,
and as Moeller et al (1984) stated, mixing can "drastically alter the chrono-
logical interpretation of ^{210}Pb profiles." However, the available evidence
suggests that mixing is not a serious problem in interpreting information gained
from core analysis in Round Loch.

Förstner (1981) outlined four mechanisms by which trace metals in lake
sediments may be mobilized (see literature review chapter), and three of these
may be relevant to Round Loch. The first mechanism is by the pollution of lake
water by natural complexing agents such as peat which reduce and solubilize trac
metals, the second is remobilization by microbial activity, and the third is
a decrease in pH which can lead to desorption of metal cations by cation
exchange.

(iii) Catchment factors

It has already been stated that granitic bedrock contains very small
quantities of Zn, Pb and Cu and so it is likely that heavy metal deposits
found in the catchment come from atmospheric sources. Livett et al (1979)
have shown that Pb, Zn and Cu accumulate in blanket peat vegetation and that
these metals are differentially distributed within species such as Calluna
vulgaris and Sphagnum papillosum. They discovered that Zn was more mobile
within plants and thus more susceptible to leaching. Research such as this
applied to the Galloway area would be valuable in determining the release and
movement of heavy metals from catchment vegetation and would help explain the
trace metal concentrations held in lake waters and sediments.

Battarbee (1984) and Battarbee et al (1985, unpublished) have tried to
show that the increasing acidity of Galloway lakes since c 1850 is due to acid

Fig. 20   Cumulative unsupported ^{210}Pb profile for RLGH 3
(using ^{210}Pb data from Flower and Battarbee, 1983a)

Depth (cm) — vertical axis

Cumulative unsupported ^{210}Pb (p.Ci.cm^{-2}) — horizontal axis
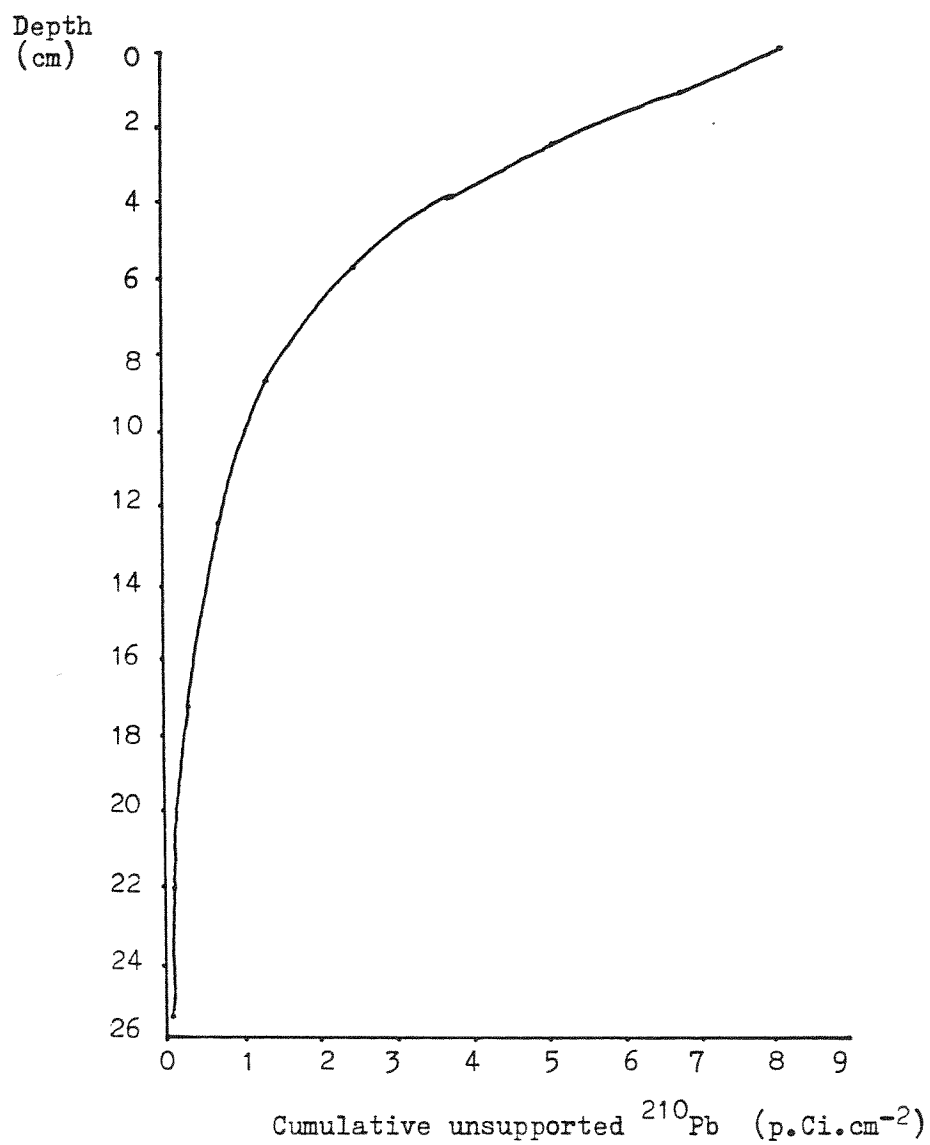
Fig. 21   RLGH 3   Soot spherules $(g^{-1}$ dw$)$
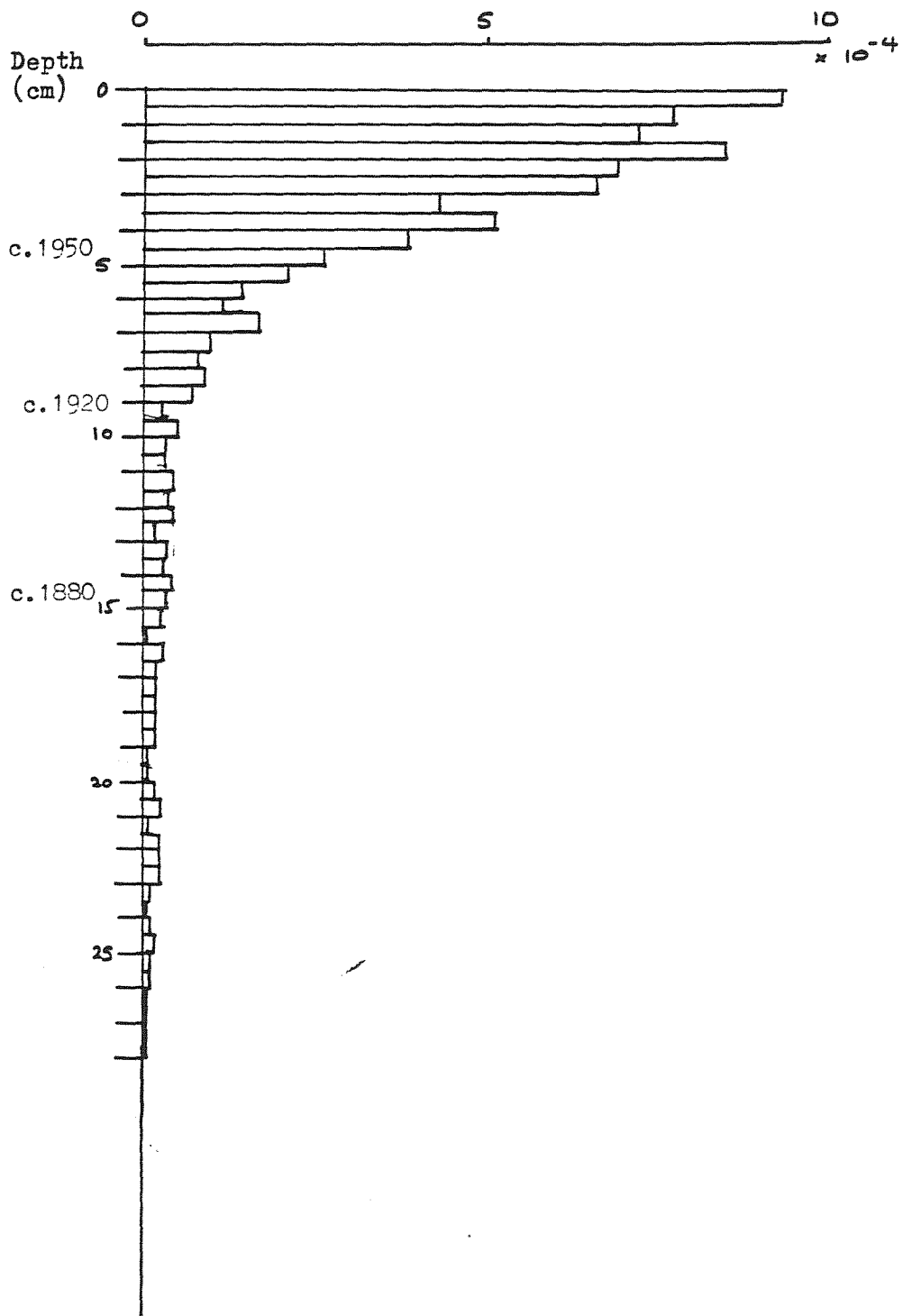
precipitation and not to a long-term change in lake pH afforestation or a land use change. The weight of evidence that they have amassed favours the acid precipitation hypothesis. This suggests therefore that not only are metals deposited onto the catchment from the atmosphere, but they are remobilized by increasing acidity of precipitation (especially Zn) and not by a natural acidification of the catchment.

(iv) A Comparison of Round Loch with other Northern Hemisphere studies.

Work has recently been completed on Loch Enoch, Galloway (Battarbee et al, 1985 unpublished) which is situated in a similar site to Round Loch of Glenhead. It also has a granitic unafforested watershed. Diatom analysis shows evidence of increased acidification in c.1840 which is comparable with the date given for Round Loch (c.1850). The Zn profile from Loch Enoh (Fig.22 shows a large increase at the top of the core but not to the same order of magnitude as the RLGH 3 Zn increase at 0 - 0.5 cm. The background levels for Loch Enoch Zn, Pb and Cu profiles are given in Table 12 and some differences can be seen when comparing these figures with the RLGH 3 background levels in Table 5. This may be due to slight differences within each catchment, e.g. different capacities to retain heavy metals and it would be interesting to study a long core from Loch Enoch to look at catchment changes lower down. Battarbee et al (op.cit.) stated that the increase in trace metal concentration can be attributed to increased deposition from the atmosphere. It is therefore reasonable to assume that the same is true of Round Loch of Glenhead.

Other studies carried out in Great Britain are mainly concerned with eutrophic, lowland lakes but they all stress the importance of atmospheric deposition in the post-Industrial Revolution as a factor in causing trace metal increases in sediments. For example, studies on Lake Windermere (Hamilton-Taylor, 1979, Hamilton-Taylor et al 1984) and Blelham Tarn (Ochsenbein et al, 1983) showed that atmospheric sources of trace metals were important in explaining heavy metal fluxes in the lakes since about 1830. Sediment from Lough Neagh, Northern Ireland shows a large increase in Cu, Cr, Zn, Pb and Hg after about 1880 (Rippey et al, 1982). The authors concluded that background atmospheric sources make a substantial contribution to recent sediment

Fig. 22

LOCH ENOCH

Lead **Zinc** **Copper** **DATES (AD)**
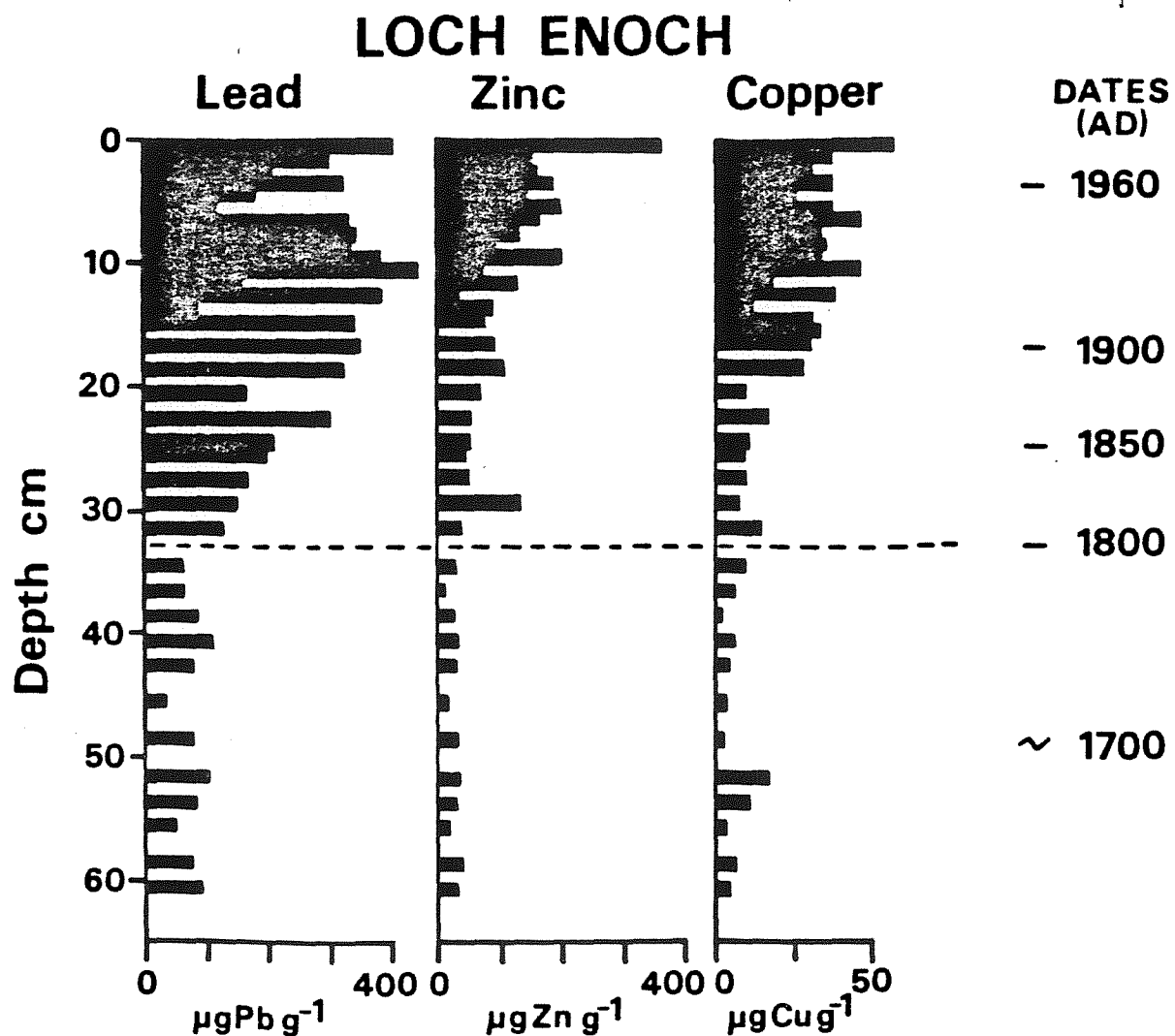
(Source: Battarbee et al, 1985, unpublished)

Fig.23 Pb, Zn and Cu profiles from Lake Holmvatn, Norway.
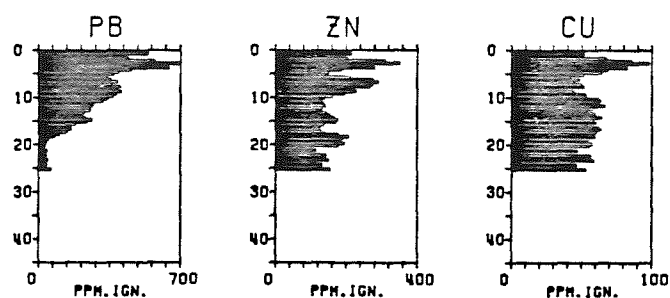
(Source: Davis et al, 1983)

contamination by trace metals. Newton Mere, Cheshire is a closed kettle lake and so the only source of heavy metals is atmospheric. Heavy metal concentrations including Cu, Pb and Zn have increased in Newton Mere sediments in recent times (Oldfield et al, 1983). Jones (1984) suggested that Pb, Cu and Zn enrichment in Langorse Lake, Brecon Beacons, was due to aerial depositi from the south-westerly winds that sweep across Wales.

These studies emphasize three important points. First, the timings of trace metal increases in the U.K. are very similar and coincide with increasin; metal production during and after the Industrial Revolution. Second, because there is such a large body of evidence supporting the arguement of an anthro-pogenic source of trace metals since the 19th. century, it is reasonable to assume that the recent Zn, Pb and Cu increases in RLGH 3 are a result of atmospheric deposition onto the lake and catchment. The fact that Pb increases earlier in Round Loch than in other British sites suggests that some local mining or early production of the metal may have been responsible for the Pb rise. Third, it is important to emphasize that although acid precipitations - heavy metal associations are important evidence of heavy metal contamination can be found without evidence for increasing acidity of lakes. This is because lowland or eutrophic lakes are buffered against acid precipitation and so do not show a pH decrease. However, they do hold a record of trace metal increases.

The coincident increases of heavy metals in lake sediments are not confined only to the U.K. Lakes in Ontario, Canada, have been extensively researched. For example, Evans and Dillon (1982) studied a meromictic lake in Muskoka-Haliburton and the sediment record showed an increase in Pb from about 1880 to the present, but as local sources of Pb are very small, the authors suggested that the primary source of Pb is from long-range transport. A strong similarity between Pb patterns in Ontario and Lake Michigan (Edgington and Robbins, 1976) led Evans and Dillon (1982) to suggest that coal and oil consumption on a continental scale is having an impact on these lakes. Profiles of Pb in lake sediments were seen as ideal for demonstrating the impact of atmospheric inputs in Algonquin Provincial Park (Wong et al, 1984). Similar

levels of Pb enrichment in Algonquin sediments, Adirondack State Park, New York (Galloway and Likens, 1979; Troutman and Peters, 1980), and sites in New England (Hanson et al, 1982) led Wong et al (1984) to conclude that this was the result of long-range transport of comparable intensity for large areas of continental North America. Schlesinger et al (1974) emphasized the importance of the westerly continental air masses on the precipitation concentrations of Pb, and it is possible that atmospheric contaminants enter into the prevailing winds and are transported on an intercontinental scale to Britain, Europe and Scandinavia.

A study comparable with that on Round Loch of Glenhead was carried out by Davis et al (1982) on Lake Holmvatn, Southern Norway. The lake, situated on a granitic watershed, is vulnerable to acid precipitation due to its low buffering capacity. The pH in the mid 1970s was about 4.7. Davis et al (op.cit) found Pb concentrations to increase upcore from about 1835 to the present. Zn concentrations increased later at c.1910 and Cu at 1945. (See Fig. 23). They concluded that the concentrations in the sediments related primarily to atmospheric loading, sediment focusing and surface water pH. The trace metals in RLGH 3 increase in the same sequence but much earlier (Figs. 8 to 10). Battarbee (1984) found that acidification of lakes in south-west Finland and Sweden also occurred much later than in Scotland, i.e. c.1960 in Scandinavian lakes compared with C.1850 in Round Loch of Glenhead. They attributed this to a post war increase in emissions from oil combustion.

Henriksen and Wright (1978) sampled lake water concentrations of Zn, Pb, Cu and Cd in Norwegian lakes situated in "pristine, undisturbed areas." They stated that the heavy metal concentrations reflect only natural inputs and anthropogenic inputs via the atmosphere. They discovered that heavy metal concentrations in southern and south-eastern Norway exceeded "background" levels of northern lakes, and concluded that this was due to atmospheric deposition associated with acidic precipitation. Precipitation over Scandinavia is highly polluted by H, SO_4 and NO_3 which are emitted from the combustion of fossil fuels in the highly industrialized areas of Europe.

The Scandinavian studies are comparable with the situation in Round Loch

as they emphasize both the importance of atmospheric deposition in remote areas and the increased mobilization of metals from the catchment due to acidification of precipitation.

Conclusion.

A number of valid conclusions can be drawn from this study.

(1) The analytical quality control results show that heavy metal analysis, using a rigorous digestion procedure, is a precise and accurate way of determining the concentrations of trace metals in lake sediments. Heavy metal analysis is a useful indicator of environmental contamination and when this method is used in conjunction with other palaeolimnological techniques, an extremely accurate and informative picture can be obtained illustrating past environmental changes. Heavy metal analysis of single cores can be used to detect the take-off, timing and magnitude of change of trace metals in lake sediments. Sediment mixing may cause problems in interpretation, but it has been established that RLGH3 does not contain an obviously mixed zone.

(2) It may be assumed that very little Zn, Pb and Cu is present in lake sediments prior to the onset of industrial activities in the eighteenth and nineteenth centuries. The analysis of a long sediment core dating back to the post-glacial illustrates clearly that this is a fallacy and that concentrations of trace metals do fluctuate quite considerably lower down in the core. Some of the variability may be due to analytical noise, but catchment changes are likely to cause most of the early variation in trace metal concentrations. Analysis of a long core is also useful to place recent changes into a long-term perspective.

(3) The granitic bedrock underlying Round Loch of Glenhead contains only small amounts of Zn, Pb and Cu. The Literature Review emphasized the importance of anthropogenic over natural sources of heavy metals in the atmosphere. Evidence for the synchronous take-off of heavy metal profiles across the Northern Hemisphere in both oligotrophic and eutrophic lake sediments must indicate the influence of man in contaminating the air masses on a local, regional and global scale.

(4) Of the three metals analysed, Pb concentrations increased first. This early rise (c.1670) was attributed to local mining and early industrial development in the Glasgow region (Farmer et al, 1980). This is likely to be a local

effect as other U.K. lake studies (e.g. Hamilton-Taylor, 1979: Rippey et al, 1982) recorded a later Pb rise (c.1830 - 1850). A causal link was suggested between the Pb spike at 95 cm. and the spread of blanket peats in the catchment at this time. It was concluded that the increase of Pb concentrations of six times the background value after c.1670 could not be attributed to catchment changes only.

The elm decline and corresponding changes in the afforested area of Round Loch may have led to the increased leaching of Zn, hence the increased concentrations at 150 cm. Zn concentrations took off at c.1844 and exceeded backgrou concentrations by 2.1 times. The timing of the Zn increase in RLGH 3 corresponded to the increase of Zn concentrations in other Northern Hemisphere studies (e.g. Davis et al, 1983; Hanson et al, 1982), suggesting that an explanation other than catchment changes is required. Suggestions were put forward trying to explain the huge increase of Zn at 0.5 - 0 cm. in RLGH 3 but no firm conclusion was reached.

The Cu profile showed little variability below 18.5 cm. (c.1860). After this time a slight increase of 1.13 times the background value began.

The pollen profile for RLGH 3 (unpublished) shows that there have been no major catchment changes over the last 200 years. It is suggested that the recent heavy metal increases in Round Loch are due to the deposition of Zn, Pb and Cu onto the lake and catchment from an increasingly polluted atmosphere.

(5) Round Loch of Glenhead was acidic prior to 1850 but since then a rapid decrease in pH has occurred resulting in the present pH of c.4.5. The most likely explanation for this seems to be the increase of acidic precipitation (see Flower and Battarbee, 1983; Battarbee, 1984) since the beginning of the nineteenth century. The timing of the increase in heavy metals and decrease in pH of Round Loch is very similar. It has been suggested that increased atmospheric loading of heavy metals and acid precipitation precursors since the Industrial Revolution is responsible for the changes seen in the lake sediment.

BIBLIOGRAPHY

1. ALLEN, S.E., GRIMSHAW, H.M., PARKINSON, J.A., QUARMBY, C. and
        ROBERTS, J.D. (1976) - "Chemical Analysis."
        in Chapman, S.B. (ed) "Methods in Plant Ecology."

2. BATTARBEE, R.W. (1984) - "Diatom analysis and the acidification of
        Lakes."
        Phil. Trans. R. Soc. Lond. B 305 p 451 - 477

3. BATTARBEE, R.W., FLOWER, R.J., STEVENSON, A.C. and RIPPEY, B.
        (1985, unpublished) - "Lake acidification in Galloway :
        A Palaeoecological test of competing hypotheses."

4. BOWEN, H.J.M. (1979) - "Environmental chemistry of the elements."
        (Academic Press)

5. CAWSE, P.A. (1981) - "Trace elements in the atmosphere of the U.K."
        Paper given at E.S.N.A. meeting, Aberdeen.
        28th. Sept. - 2nd. Oct. 1981

6. DAVIS, A.O., GALLOWAY, J.N. and NORDSTROM, K.D. (1982)
        "Lake acidification: its effects on Pb in the sediment of two
        Adirondack lakes."
        Limnol. Oceanogr. 27 (1) p 163 - 167

7. DAVIS, R.B., NORTON, S.A., HESS, C.J. and BRAKKE, D.F. (1983) -
        "Palaeolimnological reconstruction of the effects of atmospheric
        deposition of acids and heavy metals on the chemistry and
        biology of lakes in New England and Norway."
        Merilainen, J., Battarbee, R.W. and Huttunen, P. (eds)
        Proceedings III Inter - Symposium.
        Paleolimnology Development Hydrobiology (E. Junk, The Hague)

8. DILLON, P.J. and EVANS, R.D. (1982) "Whole - lake lead burdens in
        sediments of lakes in southern Ontario, Canada."
        Hydrobiologia 91 p 121 - 130

9. DOSSIS, P. and WARREN, L.J. (1980) - "Distribution of heavy metals
        between the mineral and organic debris in a contaminated
        marine sediment."
        in Baker, R.A. (ed) - "Contaminants and Sediments Vol. 1."
        (Ann Arbor Science)

10. EBDON, D. (1977) - "Statistics in Geography : a practical approach."
        (Basil Blackwell, Oxford).

11. EDGINGTON, D.N. and ROBBINS, J.A. (1976) - "Records of lead deposition
        in Lake Michigan sediments since 1800."
        Env. Sci. & Technol. 10 (3) p 266 - 274

12. EVANS, R.D. and DILLON, P.J. (1982) - "Historical changes in anthropogenic
        lead fallout in Southern Ontario, Canada."
        Hydrobiologia 91 p 131 - 137

13.   EVANS, R.D. and DILLON, P.J. (1984) - "Site - specific vs.
        whole - system measurements of trace metals in sediments."
        Proceedings of a workshop on palaeolimnological studies
        of the history and effects of acid precipitation.
        Maine, May 1984.
        Organized by S.A. Norton.

14.   EVANS, R.D., SMITH, P.J. and DILLON, P.J. (1983) - "Anthropogenic
        Zinc and Cadmium burdens in sediments of selected Southern
        Ontario lakes."
        Can. J. Fish Aquat. Sci. 40 p 570 - 579

15.   FARMER, J.G., SWAN, D.S. and BAXTER, M.S. (1980) - "Records and
        sources of metal pollutants in a dated Loch Lomond sediment
        core."
        Sci. of the Total Env. 16 p 131 - 147

16.   FISCHER, B.E.A. (1983) - "A review of the processes and models of
        long-range transport of air pollutants."
        Atmosph. Environ. 17 (10) p 1865 - 1880

17.   FLOWER, R.J. and BATTARBEE, R.W. (1983) - "Diatom evidence for
        recent acidification of two Scottish lochs."
        Nature 305 p 130 - 133.

18.   FLOWER, R.J. and BATTARBEE, R.W. (1983 a) "Acid lakes in the Galloway
        uplands, South-west Scotland : Catchments, water quality
        and sediment characteristics."
        Working paper No.6, December 1983.
        Palaeoecology Research Unit, Dept. Geography,
        University College, London.

19.   FÖRSTNER, U. (1977) - "Metal concentrations in recent lacustrine
        sediments."
        Arch. Hydrobiol. 80 (2) p 172 - 191

20.   FÖRSTNER, U. (1981) - chapters in "Metal pollution in the aquatic
        environment." (2nd. rev. ed.)
        Forstner, U. and Wittmann, G.T.W. (eds).
        (Springer - Verlag).

21.   FÖRSTNER, U. (1982) - "Accumulative phases for heavy metals in
        limnic sediments."
        Sly, P.G. (ed) - "Developments in Hydrobiology 9. Sediment/
        Freshwater Interaction." (Dr. W. Junk, The Hague).

22.   GALLOWAY, J.N. & LIKENS, G.E. (1979) - "Atmospheric enhancement of
        metal deposition in Adirondack lake sediments."
        Limnol. Oceanogr. 24 (3) p 427 - 433.

23.   GALLOWAY, J.N., THORNTON, J.D., NORTON, S.A. and VOLCHOK, H.L.
        (1982) - "Trace metals in atmospheric deposition : a review
        and assessment."
        Atmosph. Env. 16 (7) p 1677 - 1700.

24. GOLDBERG, E.D., HODGE, V., KOIDE, M. and GRIFFIN, J.J. (1976) –
    "Metal pollution in Tokyo as recorded in sediments in the
    Palace Moat".
    Geochemical Journal 10 p 165 – 174

25. GOLDMAN, C.R. and HOME, A.J. (1983) – "Limnology"
    (McGraw – Hill Book Co.)

26. GOLTERMAN, H.L., CLYMO, R.S. and OHNSTAD, M.A.M. (1978) –
    "Methods for physical and chemical analysis of fresh water."
    I.P.A. Handbook No. 8.
    (Blackwell Scientific)

27. de GROOT, A.J., ZSCHUPPE, K.H. and SALOMONS, W. (1982) –
    "Standardization of methods of analysis for heavy metals in
    sediments."
    Sly, P.G. (ed) – "Developments in Hydrobiology 9. Sediment/
    Freshwater Interaction. (Dr. W. Junk, The Hague).

28. HAMILTON-TAYLOR, J. (1979) – "Enrichment of Zinc, Lead and Copper
    in recent sediments of Windermere, England."
    Env. Sci. & Technol. 13 (6) p 693 – 697.

29. HAMILTON-TAYLOR, J., WILLIS, M., and REYNOLDS, C.S. (1984) –
    "Depositional fluxes of metals and phytoplankton in Windermere
    as measured by sediment traps."
    Limnol. Oceanogr. 29 (4) p 695 – 710.
*

30. HART, W.T. (1982) – "Uptake of trace metals by sediments and
    suspended particulates : a review."
    Sly, P.G. (ed) – "Developments in Hydrobiology 9. Sediment/
    Freshwater Interaction." (Dr. W. Junk)

31. HASSETT, J.M. and JENNETT, J.C. (1980) – "Heavy metal accumulation
    by algae."
    Baker, R.A. (ed) – "Contamination and Sediments, Vol. 2"
    (Ann Arbor Science).

32. HENRIKSEN, A., and WRIGHT, R.F. (1978) – "Concentrations of heavy
    metals in small Norwegian lakes."
    Water Research 12 p 101 – 112

33. HUTCHINSON, G.E. (1957) – "A treatise on limnology
    Geography, Physics and Chemistry."
    (Chapman & Hall, New York : Wiley, London)

34. JEFFRIES, D.S. and SNYDER, W.R. (1981) – "Atmospheric deposition
    of heavy metals in Central Ontario."
    Journal: Water, Air & Soil Pollution 15 p 127 – 152

35. JONES, R. (1984) – "Heavy metals in the sediments of Llangorse Lake,
    Wales, since Celtic – Roman times."
    Verh. Internat. Verein Limnol. 22 p 1377 – 1382

36.   KAHL, J.S., NORTON, S.A. and WILLIAMS, J.S. (1984) - "Chronology, magnitude and palaeolimnological record of changing metal fluxes related to atmospheric deposition of acids and metals in New England."
Bricker, O.P. (ed) - "Geological Aspects of Acid Deposition."
(Butterworth)

37.   LANTZY, R.J. and MACKENZIE, F.T. (1979) - "Atmospheric trace metals: global cycles and assessment of mans impact."
Geochim. et Cosmochim. Acta 43 p 511 - 525.

38.   LAZRUS, A.L., LORANGE, E. and LODGE, J.P. (1970) - "Lead and other metal ions in U.S. precipitation."
Env. Sci. Technol. 4 (1) p 55 - 58

39.   LEE, G.F. (1975) - "Transport of heavy metals in the environment."
Krenkel, P.A. (ed) - "Heavy metals in the aquatic environment."
Suppl. to Progress in Water Technology.

40.   LEE, J.A. and TALLIS, J.H. (1973) - "Regional and historical aspects of lead pollution in Britain."
Nature 245 p 216 - 218.

41.   LERMAN, A. (ed) (1978) - "Lakes : Chemistry, Geology, Physics."
(Springer - Verlag).

42.   LIVETT, E.A., LEE, J.A. and TALLIS, J.H. (1979) - "Lead, zinc and copper analysis of British Blanket Peats."
J. Ecol. 67 p 865 - 892.

43.   LIVINGSTONE, D.A. (1955) - "A light weight piston sampler for lake deposits."
Ecology 36 p 137 - 139.

44.   MACKERETH, F.J.H. (1966) - "Some chemical observations on post-glacial lake sediments."
Phil. Trans. R. Soc. Lond. 250 B p 165 - 213

45.   MOELLER, R.E., OLDFIELD, F. and APPLEBY, P.G. (1984) - "Biological sediment mixing and its stratigraphic implication in Mirror Lake (New Hampshire, U.S.A.)
Verh. Internat. Verein. Limnol. 22 (1) p 567 - 572

46.   NORTON, S.A., DUBIEL, R.F., SASSEVILLE, D.K. and DAVIS, R.B. (1978) - "Palaeolimnological evidence for increased zinc loading in lakes of New England, U.S.A.
Verh. Internat. Verein. Limnol. 20 p 538 - 545

47.   NORTON, S.A. (1984) - "The Interpretation of Metal Chemistry."
Proceedings of a workshop on palaeolimnological studies of the history and effects of acid precipitation."
Maine, May 1984.
Organized by S. A. Norton.

48. NRIAGU, J.O. (ed) (1979) - "Copper in the environment".
        (Wiley - Interscience publication).

49. NRIAGU, J.O. (ed) (1980) - "Zinc in the environment".
        (Wiley - Interscience publication).

50. NRIAGU, J.O. (ed) (1978) - "The biogeochemistry of lead in the
        environment."
        (Elsevier/North Holland Biomedical Press).

51. NRIAGU, J.O. (1984) - "Dynamics of particular metals in lakes
        of Northern Ontario."
        Proceedings of a workshop on palaeolimnological studies
        of the history and effects of acid precipitation."
        Maine, May 1984.
        Organized by S.A. Norton.

52. NRIAGU, J.O., KEMP, A.L.W., WONG, H.K.T. and HARPER, N. (1979) -
        "Sedimentary record of heavy metal pollution in Lake Erie."
        Geochim. Cosmochim. Acta 43 p 247 - 258

53. NRIAGU, J.O., WONG, H.K.T. and COKER, R.D. (1982) -
        "Deposition and chemistry of pollutant metals in lakes
        around the smelters at Sudbury, Ontario."
        Env. Sci. and Technol. 16 (9) p 551 - 560

53. OCHSENBEIN, U., DAVISON, W., HILTON, J and HAWORTH, E.Y. (1983) -
        "The geochemical records of major cations and trace metals
        in a productive lake."
        Arch. Hydrobiol. 98 (4) p 463 - 488

54. OLDFIELD, F., BANOSKY, C., LEOPOLD, E.F. and SMITH, J.P. (1983) -
        Mineral magnetic studies on lake sediments. A brief review."
        Hydrobiologia 103 p 37 - 44

55. OLDFIELD, F. et. al. (1984) - "Magnetic measurements of atmospheric
        particulates and ombrotrophic peat : a review."
        Preceedings of a workshop on Palaeolimnology.
        Studies of the history and effects of acidic precipitation.
        Maine, May 1984.
        Organized by S.A. Norton.

56. PEIRSON, D.H. and CAWSE, P.A. (1979) - "Trace elements in the
        atmosphere."
        Phil. Trans. R. Soc. Lond. B 288 p 41 - 49.

57. RIPPEY, B., MURPHY, R.J. and STIRK KYLE (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. & Technol. 16 (1) p 23 - 30

58. ROYAL SOCIETY OF LONDON DISCUSSION (1979) - "Pathways of Pollutants
         in the atmosphere."
         Phil. Trans. R. Soc. Lond. A 290 p 467 - 637

59. SCHLESINGER, W.H., REINERS, W.A. and KNOPMAN, D.S. (1974) -
         "Heavy metal concentrations and deposition in bulk precipitation
         in Montane ecosystems in New Hampshire, U.S.A."
         Env. Pollution 6 p 39 - 47.

60. SICCAMA, T.G. and SMITH, W.H. (1980) - "Changes in lead, zinc,
         copper, dry weight and organic matter content of the forest
         floor of white pine stands in central Massachusetts over
         16 years."
         Env. Sci. Technol. 14 p 54 - 56

61. SMITH, W.H. (1981) - "Air pollution and forests."
         (Springer-Verlag).

62. SMITH, W.H. and SICCAMA, T.G. (1980) - "The Hubbard Brook Ecosystem
         Study ; Biogeochemistry of Pb in the northern hardwood
         forest."
         J. Env. Quality 9 p 116 - 121

63. THOMPSON, K.C. (1980) - "Atomic Absorption Spectrophotometry
         1979 version. An essay review."
         (London, Her Majesty's Stationary Office).

64. THOMPSON, K.C. and REYNOLDS, R.J. (1982, 2nd. ed.) - "Atomic
         Absorption, Fluorescence & Flame Emission Spectroscopy.
         A practical approach."
         (Charles Griffin & Co. Ltd.)

65. TROUTMAN, D. and PETERS, N. (1980) - "Comparison of lead, manganese
         and zinc transport in three Adirondack Lake watersheds,
         New York."
         Drablos, D. and Tollan, A. (eds.)
         Proceedings of an International Conference.
         "The Ecological Impact of Acid Precipitation."
         Norway, March 1980.
         SNSF project.

66. WONG, H.K.T., NRIAGU, J.O. and COKER, R.D. (1984) - "Atmospheric
         input of heavy metals chronicled in lake sediments of the
         Algonquin Provincial Park, Ontario, Canada."
         Chem. Geol. 44 p 187 - 201.

*   HANSON, D.W., NORTON, S.A. and WILLIAMS, J.S. (1982) -
         "Modern and palaeolimnological evidence for accel-
         erated leaching and metal accumulation in soils in
         New England, caused by atmospheric deposition."
         Watwr, Air and Soil Pollution 18 p 227 - 239

Appendix

Table (i) RLGH 3 Percentage Dry Weight and LOI

Depth		% Dry wt.	% LOI	Depth		% Dry wt.	% LOI
0.0	0.5	2.54	42.11	66.0	67.0	13.34	25.24
1.0	1.5	6.79	37.68	68.0	69.0	13.15	25.15
2.0	2.5	7.19	38.25	70.0	71.0	13.12	26.83
3.0	3.5	7.84	37.50	72.0	73.0	12.86	27.69
4.0	4.5	8.79	35.37	74.0	75.0	13.27	29.10
5.0	5.5	8.54	37.37	76.0	77.0	12.09	35.46
6.0	6.5	8.46	37.87	78.0	79.0	15.27	25.99
7.0	7.5	8.87	38.01	80.0	81.0	14.43	24.87
8.0	8.5	8.62	41.54	82.0	83.0	14.91	22.54
9.0	9.5	8.55	45.28	84.0	85.0	14.87	22.35
10.0	10.5	8.80	40.30	86.0	87.0	14.53	24.49
11.0	11.5	8.62	43.92	88.0	89.0	13.99	29.33
12.0	12.5	9.02	42.01	90.0	91.0	14.74	26.70
13.0	13.5	8.98	40.10	92.0	93.0	15.44	22.36
14.0	14.5	9.34	40.72	94.0	95.0	14.57	25.71
15.0	15.5	9.43	42.92	96.0	97.0	15.23	21.11
16.0	16.5	9.38	43.75	98.0	99.0	14.70	21.67
17.0	17.5	9.65	43.52	100.0	101.0	15.16	21.78
18.0	19.5	10.03	44.12	102.0	103.0	15.40	22.20
19.0	19.5	9.77	44.49	104.0	105.0	15.54	20.77
20.0	20.5	9.89	45.45	106.0	107.0	14.61	19.94
21.0	21.5	10.03	44.84	108.0	109.0	14.65	21.78
22.0	22.5	9.68	45.20	110.0	111.0	15.59	23.59
23.0	23.5	9.47	46.69	112.0	113.0	16.15	24.74
24.0	24.5	9.64	47.69	114.0	115.0	16.78	23.45
25.0	25.5	9.49	48.26	116.0	117.0	16.57	23.34
26.0	26.5	9.50	47.03	118.0	119.0	20.19	22.03
27.0	27.5	10.37	47.00	120.0	121.0	16.29	27.05
28.0	28.5	10.46	47.56	122.0	123.0	19.80	21.99
29.0	29.5	9.84	52.14	124.0	125.0	18.29	21.77
30.0	31.0	9.78	50.00	126.0	127.0	16.61	25.36
31.0	32.0	9.67	45.09	128.0	129.0	16.37	27.73
32.0	33.0	10.21	45.35	130.0	131.0	17.95	20.96
33.0	34.0	9.13	45.61	134.0	135.0	18.79	19.67
34.0	35.0	9.29	46.22	136.0	137.0	18.77	21.05
35.0	36.0	9.19	47.76	138.0	139.0	19.57	18.85
36.0	37.0	9.08	48.36	140.0	141.0	21.44	18.79
37.0	39.0	9.12	48.00	142.0	143.0	18.32	21.09
38.0	39.0	7.79	49.40	144.0	145.0	22.62	17.46
39.0	40.0	9.41	48.84	146.0	147.0	17.97	20.73
40.0	41.0	9.33	48.79	148.0	149.0	16.55	23.60
41.0	42.0	9.24	48.06	150.0	151.0	16.12	24.17
42.0	43.0	9.27	47.47	152.0	153.0	16.37	24.04
43.0	44.0	9.84	45.83	154.0	155.0	16.32	24.03
44.0	45.0	10.05	43.40	156.0	157.0	17.44	24.89
45.0	46.0	9.97	43.02	158.0	159.0	16.77	24.89
46.0	47.0	10.34	41.88	160.0	161.0	16.57	26.79
47.0	48.0	10.91	38.71	162.0	163.0	17.62	24.72
48.0	49.0	11.42	34.46	164.0	165.0	16.46	26.98
49.0	50.0	11.59	31.20	166.0	167.0	15.94	27.03
50.0	51.0	12.09	29.87	168.0	169.0	15.92	28.46
52.0	53.0	12.84	26.84	170.0	171.0	15.75	27.75
54.0	55.0	13.07	26.61	172.0	173.0	17.04	26.47
56.0	57.0	13.26	27.17	174.0	175.0	17.26	26.02
58.0	59.0	13.55	26.19	176.0	177.0	16.43	25.40
60.0	61.0	13.25	26.94	178.0	179.0	16.69	25.93
62.0	63.0	13.16	26.18	180.0	181.0	14.45	31.75
64.0	65.0	13.45	25.30	182.0	183.0	14.36	30.00

Table (i) cont.

Depth		% Dry wt.	% LOI
184.0	185.0	14.53	30.25
186.0	187.0	14.72	31.17
188.0	189.0	14.56	33.02
190.0	191.0	14.59	32.24
192.0	193.0	14.61	32.94
194.0	195.0	14.09	33.85
196.0	197.0	13.83	33.89
198.0	199.0	14.45	31.78
200.0	201.0	14.99	28.93
202.0	203.0	15.25	27.91
204.0	205.0	15.72	24.03
206.0	207.0	15.74	25.10
208.0	209.0	17.29	26.39
210.0	211.0	17.00	29.03
212.0	213.0	17.94	22.92
214.0	215.0	17.90	22.65
216.0	217.0	17.67	24.04
218.0	219.0	20.45	19.53
220.0	221.0	21.98	17.05
222.0	223.0	18.79	20.91
224.0	225.0	17.94	22.59
225.0	226.0	21.07	17.87
226.0	227.0	26.10	13.47
227.0	228.0	28.64	11.64
228.0	229.0	43.35	5.91
229.0	230.0	60.71	3.49
230.0	231.0	72.02	2.36
231.0	232.0	75.69	1.83
232.0	233.0	77.63	1.59
233.0	234.0	77.97	1.44
236.0	237.0	59.77	4.58
238.0	239.0	63.29	4.35
240.0	241.0	63.47	4.82
242.0	243.0	50.75	6.19
243.0	244.0	27.80	15.91
244.0	245.0	16.91	26.12
246.0	247.0	16.97	30.11
248.0	249.0	20.94	19.71
250.0	251.0	21.54	17.69
252.0	253.0	18.55	23.15
253.0	254.0	19.08	21.94
254.0	255.0	22.21	18.23
255.0	256.0	23.85	15.76
256.0	257.0	33.30	9.71
257.0	258.0	37.80	7.79
258.0	259.0	45.67	6.03
259.0	260.0	51.57	4.96
260.0	261.0	50.32	4.44

Table (iii)   RLGH3 Zn, Cu and Pb values   corrected for organic matter ($\mu g.g^{-1}$ om)

Depth	Zn	Cu	Pb	Depth	Zn	Cu	Pb
0	1798.9	94.9	681.5	63	337.9	61.7	123.7
1	300.2	85.7	573.5	67	244.7	65.5	70.6
2	281.8	117.4	760.4	71	184.5	54.6	64.6
3	385.6	109.6	941.3	75	180.6	47.4	49.3
4	517.4	108.0	869.1	79	447.5	70.0	73.7
5	631.3	101.9	773.6	83	440.5	91.3	103.4
6	857.1	114.1	876.2	87	216.8	60.4	93.5
7	505.4	104.8	741.1	91	325.1	73.3	296.6
8	614.6	93.9	781.4	95	359.7	114.1	362.2
9	646.9	86.6	952.7	99	432.6	95.3	113.1
10	529.0	84.9	1004.9	103	487.6	112.1	47.5
11	360.4	71.3	814.9	107	407.0	73.6	71.4
12	330.9	71.6	912.6	111	373.6	50.9	90.6
13	373.1	65.3	708.9	115	302.5	61.7	35.6
14	320.5	59.4	879.9	119	239.6	53.8	49.7
15	269.1	47.5	823.9	123	320.4	54.7	152.9
16	250.1	47.1	689.4	127	258.5	46.2	43.6
17	264.5	50.3	559.9	131	518.6	83.5	116.3
18	250.9	24.9	632.1	135	420.4	85.5	60.4
19	191.5	26.7	450.0	139	401.2	81.0	37.7
20	180.2	18.9	443.1	143	392.3	66.4	11.9
21	193.1	14.3	446.2	147	379.9	86.8	6.0
22	197.1	17.9	554.4	151	123.6	43.7	9.3
23	157.9	20.3	486.9	155	121.4	45.8	21.8
24	139.4	20.1	390.2	159	110.3	54.0	23.5
25	136.3	22.1	360.1	163	63.6	51.7	2.7
26	152.7	23.6	388.1	167	116.8	25.2	3.5
27	146.4	18.7	465.1	171	111.8	46.7	7.0
28	95.9	17.2	243.2	175	143.5	47.4	6.3
29	94.6	14.8	241.4	179	107.8	43.3	7.9
30	94.7	15.6	273.8	183	97.2	51.1	101.2
31	104.5	16.0	260.9	187	79.2	36.1	124.6
32	104.1	16.9	302.5	191	75.5	31.3	101.5
33	103.9	16.4	219.9	195	76.9	31.0	85.4
34	101.9	18.2	225.4	199	89.4	38.2	98.3
35	101.3	18.2	214.0	203	121.7	43.5	163.2
36	97.2	17.0	203.5	207	142.9	54.7	124.3
37	86.9	17.5	168.3	211	150.3	51.2	131.3
38	83.4	13.8	146.4	215	273.3	56.1	128.0
39	92.5	17.0	112.0	219	331.3	79.8	153.3
41	73.4	16.0	60.5	223	308.0	63.0	151.3
43	95.3	26.8	79.9	227	561.9	121.1	264.6
45	89.2	34.9	91.6	231	3147.5	1000.0	1067.2
47	114.7	31.5	91.7	235	1255.4	327.5	1292.6
49	154.8	35.9	96.2	239	1237.9	543.7	1061.1
51	210.4	55.0	111.5	243	293.5	160.3	260.8
53	214.4	50.9	134.3	247	187.5	79.1	181.6
55	219.3	46.8	143.9	251	315.3	159.3	307.7
57	232.7	37.5	143.9	255	1002.0	506.0	927.9
59	304.6	42.5	167.5	259	1293.7	674.9	1051.8

Table (iv)   RLGH 3 Bulk Densities

Depth Top	Bot	Bulk Density	Depth Top	Bot	Bulk Density
0.0	0.5	0.027	41.0	42.0	0.098
1.0	1.5	0.072	42.0	43.0	0.099
2.0	2.5	0.076	43.0	44.0	0.105
3.0	3.5	0.083	44.0	45.0	0.108
4.0	4.5	0.094	45.0	46.0	0.104
5.0	5.5	0.091	46.0	47.0	0.112
6.0	6.5	0.090	47.0	48.0	0.117
7.0	7.5	0.095	48.0	49.0	0.124
8.0	8.5	0.091	49.0	50.0	0.125
9.0	9.5	0.091	50.0	51.0	0.133
10.0	10.5	0.094	52.0	53.0	0.140
11.0	11.5	0.092	54.0	55.0	0.144
12.0	12.5	0.096	56.0	57.0	0.146
13.0	13.5	0.096	58.0	59.0	0.149
14.0	14.5	0.099	60.0	61.0	0.145
15.0	15.5	0.101	62.0	63.0	0.145
16.0	16.5	0.100	64.0	65.0	0.148
17.0	17.5	0.103	66.0	67.0	0.147
18.0	18.5	0.107	68.0	69.0	0.144
19.0	19.5	0.105	70.0	71.0	0.144
20.0	20.5	0.105	72.0	73.0	0.140
21.0	21.5	0.107	74.0	75.0	0.145
22.0	22.5	0.103	76.0	77.0	0.141
23.0	23.5	0.102	78.0	79.0	0.149
24.0	24.5	0.103	80.0	81.0	0.160
25.0	25.5	0.102	82.0	83.0	0.166
26.0	26.5	0.101	84.0	85.0	0.165
27.0	27.5	0.111	86.0	87.0	0.161
28.0	28.5	0.112	88.0	89.0	0.154
29.0	29.5	0.105	90.0	91.0	0.143
30.0	31.0	0.105	92.0	93.0	0.174
31.0	32.0	0.103	94.0	95.0	0.162
32.0	33.0	0.109	96.0	97.0	0.169
33.0	34.0	0.096	98.0	99.0	0.164
34.0	35.0	0.099	100.0	101.0	0.169
35.0	36.0	0.098	102.0	103.0	0.172
36.0	37.0	0.098	104.0	105.0	0.173
37.0	38.0	0.096	106.0	107.0	0.163
38.0	39.0	0.083	108.0	109.0	0.163
39.0	40.0	0.100	110.0	111.0	0.175
40.0	41.0	0.100	112.0	113.0	0.181
			114.0	115.0	0.189

Table (v)

Excess flux of Zn, Cu and Pb to RLGH3

(minus figure indicates average background concentration
has been reached).

Depth (cm)   Flux ($\mu g.cm^{-2}.yr^{-1}$)

	Zn	Cu	Pb
0 - 0.5	22.2	0.8	7.9
1 - 1.5	4.5	1.4	15.0
2 - 2.5	4.2	2.7	22.8
3 - 3.5	8.3	2.6	30.7
4 - 4.5	13.7	2.6	29.6
5 - 5.5	18.9	2.5	26.8
6 - 6.5	28.1	2.9	31.0
7 - 7.5	14.8	2.8	27.1
8 - 8.5	21.0	2.6	30.6
9 - 9.5	25.0	2.4	42.0
10 - 10.5	17.0	2.1	40.5
11 - 11.5	10.6	1.8	24.9
12 - 12.5	9.0	1.7	38.9
13 - 13.5	10.1	1.3	27.7
14 - 14.5	8.3	1.1	37.1
15 - 15.5	6.6	0.6	37.8
16 - 16.5	5.8	0.7	30.9
17 - 17.5	3.5	0.8	24.8
18 - 18.5	6.4	- 0.5	30.2
19 - 19.5	3.1		19.8
20 - 20.5	2.7		19.9
21 - 21.5	2.8		20.2
22 - 22.5	3.5		25.6
23 - 23.5	0.5		19.4
24 - 24.5	0.8		17.7
25 - 25.5	0.7		16.0
26 - 26.5	1.1		17.0
27 - 27.5	1.2		23.4
28 - 28.5	- 1.9		10.1
29 - 29.5			11.9
30 - 31			9.6
31 - 32			9.4
32 - 33			11.6
33 - 34			6.8
34 - 35			7.6
35 - 36			7.2
36 - 37			4.7
37 - 38			3.7
38 - 39			3.2
39 - 40			0.6
41 - 42			- 1.3