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**FLY-ASH PARTICLES IN LAKE SEDIMENTS:
EXTRACTION AND CHARACTERISATION**

A REPORT TO THE C.E.G.B.

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AIMS OF THE STUDY

In recent years the occurrence of fly-ash particles in lake sediments has been increasingly used to indicate the historical and spatial impact of acid deposition on freshwater lakes. A number of papers have shown correlations between increasing carbonaceous particle concentrations and increasing acidity of surface waters. However these early carbonaceous particle studies used relatively primitive techniques for extraction, enumeration and characterisation of particles. Consequently, the project we report on here had the following four aims:

- i) to develop improved extraction methods for carbonaceous particles and new extraction methods for inorganic ash spheres from lake sediments.
- ii) to develop an effective fuel type characterisation for the carbonaceous particles.
- iii) to apply the extraction techniques to two lake sites in Scotland, a low acid deposition site, Loch Teanga, in the Outer Hebrides and a high acid deposition site, Loch Tinker, just north of Glasgow.
- iv) to apply the extraction and characterisation techniques to a sediment core from a pond on Hampstead Heath in North London.

EXECUTIVE SUMMARY

1. Fly-ash particles are produced by high temperature combustion of coal and oil. They are dispersed widely in the environment, despite the presence of electrostatic precipitators on coal-fired station chimneys.
2. Two types of particle are produced, spheroidal carbonaceous particles, from both coal and oil, and inorganic ash spheres, produced predominantly from coal combustion.
3. The history of fly-ash particle deposition is recorded in lake sediments.
4. Methods for the extraction of carbonaceous particles and inorganic ash spheres from lake sediments have been developed giving repeatable and accurate results when applied to sediment cores. For the carbonaceous particles this is an improvement on those methods to be found in the literature, and for the ash spheres is the first chemical extraction described.
5. A characterisation, based on reference particles from modern power stations, for differentiating between coal and oil carbonaceous particles has also been developed using the surface chemistry of 17 elements identified by EDAX. There is over 95% correct fuel-type allocation using this technique.
6. Application of these techniques to lake sediments gives information on the deposition history of fly-ash particles on a lake and its catchment. This technique has been applied to both modern surface sediments in Scotland and a historical record in a dated sediment core taken from a pond in North London. In both cases, fossil fuel combustion records support the results obtained.
7. The methods can be developed further to include additional fuel types e.g. brown coals and lignite, and the present results can be used to address environmental problems associated with fly-ash particle contamination.

1. INTRODUCTION.

Lake sediments provide a record of atmospheric contamination and so have been important in recent studies of surface water acidification. Carbonaceous particles derived from fossil-fuel combustion are found in considerable numbers in upper levels of sediment cores taken from areas with high acid deposition (Griffin & Goldberg, 1981; Renberg & Wik, 1984). Sites in the United Kingdom show close correlation between the onset of atmospheric contamination as indicated by carbonaceous particles and the acidification of lakes as indicated by diatom analysis (Battarbee *et al.*, 1988).

The particulate emissions from high temperature fossil fuel combustion can be divided into two groups, carbonaceous particles, which are composed mainly of elemental carbon (Goldberg, 1985), and inorganic ash spheres, which are formed by the fusing of inorganic minerals within the fuel (Raask, 1984). Of the fossil fuels commonly used in Britain, only coal and oil produce spherical carbonaceous particles. Those produced from peat combustion have an amorphous appearance, many still retaining some cellular structure.

1.1 Historical Perspective: Methods.

Smith *et al.* (1975), first produced a method for the extraction of elemental carbon from marine sediments. An acid treatment with hydrofluoric and hydrochloric acids was used to remove some mineral species and a basic peroxide treatment was used if organic material was present. The remaining carbon material was ground up and infra-red spectroscopy used to determine quantitatively the elemental carbon levels. This was used by Griffin & Goldberg (1975) for coastal marine sediments, where there was a higher organic content, and again I-R spectroscopy was used to determine elemental carbon fluxes. This carbonaceous material was thought to be principally from forest fires, as concentrations increased on a latitudinal basis; particles being transported by the major wind systems. However, it was also suggested that the more spherical and perforated particles might have been formed by high temperature fossil fuel combustion. Griffin & Goldberg (1979), then turned to the freshwater sediments of Lake Michigan. The elemental carbon particles were extracted and compared against oil, coal and wood fly-ash. It was concluded that forest and grass burning could contribute a significant amount of carbonaceous material to the atmosphere, but the concentration of the "spherical" carbon particles reflected the history of fossil fuel combustion in the area. Similar results were obtained at Green Lake, New York, (Kothari & Wahlen, 1984), where a similar digestion technique to that of Griffin and Goldberg, was employed. Goldberg *et al.* (1981), showed that the concentration of certain trace elements such as tin, chromium, nickel, lead, copper, cobalt, cadmium, zinc and iron had a similar profile in the sediment to carbonaceous particles. Magnetic mineral ash spherules, which were formed by the oxidation of iron minerals in the furnace to haematite (Fe_2O_3) and magnetite (Fe_3O_4), were also correlated.

In Sweden, an alternative method of carbonaceous particle concentration determination was developed, using hydrogen peroxide (H_2O_2) to remove organic material, followed by direct counting of a small fraction of the residue to obtain the number of particles per gram dry weight of sediment. This was used as an indirect dating method by matching concentration levels with that of a core previously dated by ^{210}Pb , ^{137}Cs or varve counting (Renberg & Wik, 1985a). As for Lake Michigan (Griffin & Goldberg, 1975, 1979, 1983; Goldberg *et al.*, 1981) and Green Lake (Kothari & Wahlen, 1984), the elemental carbon

concentrations were found to reflect the increase of industrial activity and the fossil fuel combustion history of the twentieth century (Wik *et al.*, 1986). Apart from this temporal distribution of carbonaceous particles, there was also seen to be a spatial distribution which reflected the industrial regions of Sweden. This was seen in both lake sediments (Renberg & Wik, 1985b) and forest soils (Wik & Renberg, 1987).

Until the present study, work on carbonaceous particles in British lake sediments has used the Renberg and Wik method. The lakes involved have been principally in Scotland (Darley, 1985; Wik *et al.*, 1986; Battarbee *et al.*, 1988) and Wales (Battarbee *et al.*, 1988; Fritz *et al.*, 1989). Here also, the carbonaceous particle record follows the history of fossil-fuel burning. The record begins in the mid-nineteenth century at the onset of the Industrial Revolution in Britain, and a sharp increase in concentration occurs after about 1940 which reflects the expansion of the power generation industry since World War 2 (Darley, 1985).

1.2 Historical Perspective: Characterisation.

In order to determine possible sources for carbonaceous particles found in lake sediments, it is necessary to be able to characterise particles to fuel type. Characterisation to individual power stations would be ideal, but power stations use many types of fuel from differing sources and it seems unlikely that each station will produce particles with an individual signature, be it morphological or chemical.

In certain instances fuel type characterisation may locate sources. For example, particles of coal-fired origin found in the lake sediments of western Ireland should be derived from the Moneypoint station on the River Shannon, the only coal-fired station in the country. Similarly, oil derived particles found in the Galloway region of Scotland are most likely to have come from the stations at Ballylumford or Coolkeeragh in Northern Ireland, since there are no oil-fired stations in Scotland or northern England. On an international scale, there are no coal-fired stations in Sweden and so any coal derived particles in lakes there, must have been transported from other countries.

No attempt has been made to characterise inorganic ash spheres for two reasons. Firstly, they are almost entirely of coal origin, and secondly, they are formed from the fusing of inorganic inclusions within the fuel rather than from the fuel itself and so their chemistry is independent of fuel type (Hulett *et al.*, 1980; Ramsden & Shibaoka, 1982).

1.2.1 External Morphology.

The morphological characteristics of carbonaceous particles have been studied using light and electron microscopy. Fisher *et al.* (1978), used light microscopy, to differentiate between 11 morphological types of coal fly-ash, using shape and opacity to separate the classes. Griffin & Goldberg (1981) used electron microscopy to separate carbonaceous particles into nine classes, the main separator between coal and oil being the convoluted or layered patterns seen on the surface of the oil particles. Not all oil derived particles show this surface contouring, however, and many particles of both oil and coal origin have very little surface area, being highly porous or 'lacy' (Lightman & Street, 1968). This makes surface features of limited use in a classification, and this group of particles are left out of the Griffin & Goldberg characterisation.

Size distribution studies (Shen *et al.*, 1976), indicate that particulates emitted from coal fired boiler stacks generally have a higher mean diameter than those from oil fired boilers.

There is such an overlap however, that there would be little confidence in a size separation when trying to classify an individual particle into fuel type using size criteria alone.

Particles from different coal combustion techniques also appear to show morphological and size differences due to the temperatures the coal encounters in the furnace (McCrone & Delly, 1973; Falster & Jacobsen, 1981). Spreader stokers and fluidized bed plants produce the largest particles and pulverised fuel and drop tube furnaces the smallest. Pulverised fuel is the only coal combustion technique now used in the British power generation industry and so when studying modern carbonaceous particles these size differences are no longer important.

1.2.2 Internal structure using thin sectioning.

When embedded in resin and thin sectioned, oil particles appear spherical with extensive and regular cross partitioning (Raask & Street, 1978), and in cross-polarised light they are anisotropic (i.e they give incomplete extinction upon rotation).

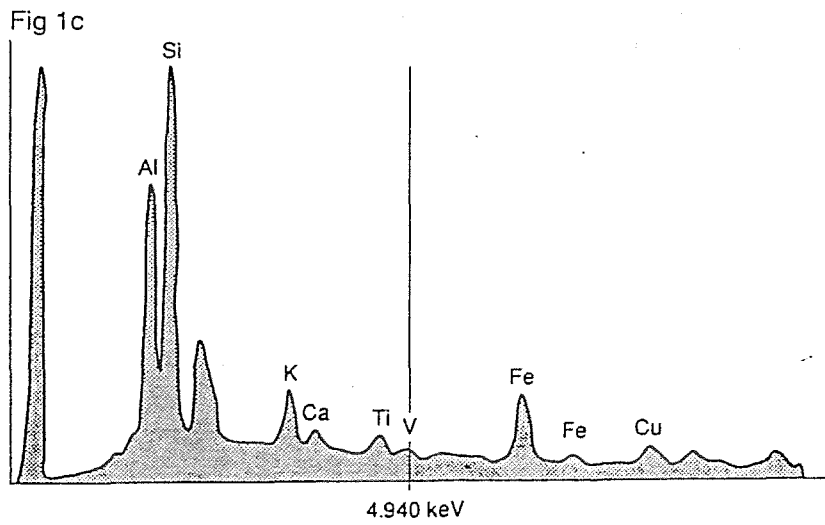
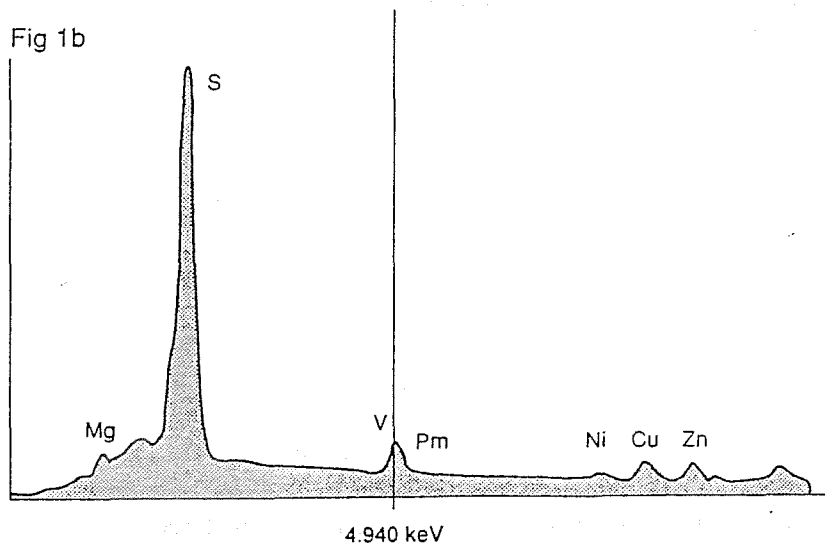
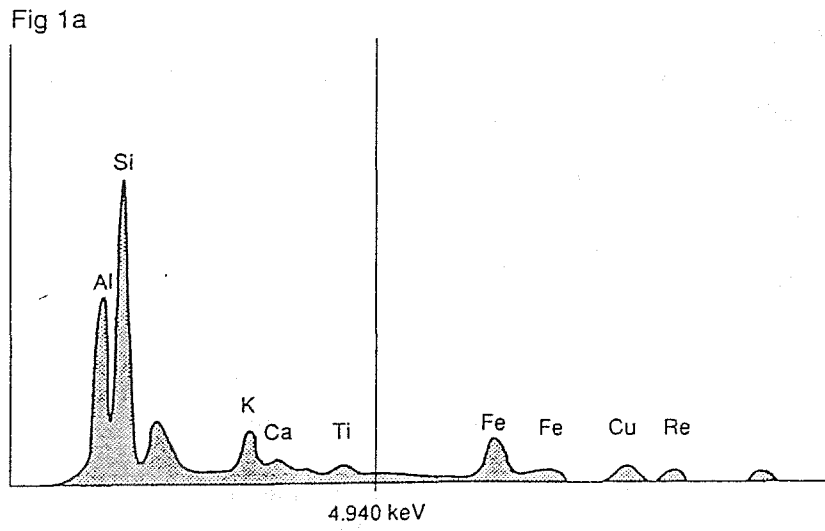
There are four different types of coal derived particle (Lightman & Street, 1968): solid, produced from the fusain maceral, 'balloons,' with thin walls and a single large cavity, 'C' shaped particles, with thick walls and a large pore opening to the surface, and 'lacy' particles, with many internal partitions similar to those from oil combustion. In cross-polarised light, low rank coals are isotropic (i.e. give complete extinction upon rotation) and mid- to high-rank coals are anisotropic (Griest & Harris, 1985).

This classification has been used with a high degree of success (80-90%) using power station ash (Street, pers. comm.). When using particles extracted from lake sediments, however, the number of particles available to embed in the resin is orders of magnitude lower and this limits the usefulness of thin sectioning in the present study especially as the 'lacy' particles remain unclassified.

1.2.3 Chemical parameters.

Further characterisation is possible using particle surface chemistry. Elemental analysis on particulates from many different sources including car emissions, incinerators, and cigarettes, have been published as well as from coal and oil fired power stations (McCrone & Delly, 1973). The results from this and other studies (Shen *et al.*, 1976; Cheng *et al.*, 1976) show that the major elements present in power station emission particulates are, for oil: V, Fe, Si, S, and Ca, and for coal: Fe, Ti, Si, S, K, and Ca. Hence, the distinguishing elements traditionally used to separate coal particles from oil are titanium and vanadium. These elements are good indicators of origin, but both oil and coal are heterogeneous materials and one or both of these elements may or may not be found in any individual particle. Figures 1a and 1b show EDAX spectra of typical coal and oil carbonaceous particles respectively and here, titanium and vanadium could be used to distinguish between the two types. However, figure 1c shows the EDAX spectrum of a carbonaceous particle from the same coal ash as figure 1a, and shows the presence of both elements. The use of a single chemical parameter is, therefore limited as a classification tool.

Figure 1. Typical EDAX spectra of carbonaceous particles from (a) coal combustion, (b) oil combustion, and (c) coal, showing the presence of both vanadium and titanium.



1.3 Methods.

Methods were developed for the extraction of carbonaceous particles and inorganic ash spheres using material from a sediment core taken from Loch Tinker. Reference material was obtained from power stations and examined using EDAX to produce a fuel type characterisation for coal and oil carbonaceous particles. The methods developed were applied to the sediments of cores taken from Loch Tinker, Loch Teanga and the Men's Bathing Pond, Hampstead Heath. These cores were taken using a mini-Mackereth corer (Mackereth, 1969) and dated using ^{210}Pb techniques at the University of Liverpool.

2. A METHOD FOR THE EXTRACTION OF CARBONACEOUS PARTICLES FROM LAKE SEDIMENT.

This method is summarised in Rose (1990a).

The aim of this work was to develop a sensitive technique for extracting carbonaceous particles from lake sediments, suitable for use even at low carbonaceous particle concentrations, by removing unwanted sediment by selective chemical attack. Neither of the two methods in the literature were perfectly suitable for these requirements.

The Renberg and Wik method, due to the amount of residue left at the end of the digestion, is insensitive at low particle concentrations and low magnification counting at $\times 50$ misses particles in the $<10\mu\text{m}$ fraction.

The method used by Griffin & Goldberg (1975), deals with all charcoal, not just spheroidal particles produced from high temperature combustion and so the results are expressed in per cent carbon by weight, rather than by particle concentration. Also, only the $>38\mu\text{m}$ fraction is considered, which excludes many smaller particles and preferentially those which are oil derived. However, this method reduces 10g of dried Lake Michigan sediment to 10-30mg of some of the more persistent minerals, primarily pyrite (FeS_2), rutile (TiO_2) and zircon ($\text{Zr}(\text{SiO}_4)$), but most importantly elemental carbon. It involves a more complete digestion than that of Renberg and Wik and was therefore adopted as the basis of the method used here.

2.1 Laboratory procedure.

1) Place 0.2g of dried sediment in a covered 250ml beaker. Add 30ml 6M KOH and 4ml 30% H_2O_2 . Leave overnight, centrifuge at 2000rpm for 5 minutes and then wash the residue with distilled water and return to the beaker.

This stage breaks up the sediment for further reaction and removes some of the organic and humic fractions.

The use of 10g of dried sediment and large quantities of reagents is unnecessary. As replicate digestions were to be done, an arbitrary value of 0.2g of dried sediment was used and the reagent quantities reduced to match. Griffin and Goldberg used ultrasonic dispersion to break up the sediment in the early stages of their digestion. However, carbonaceous particles are physically fragile and ultrasounding can cause fragmentation. As the eventual residue was ground up for infra-red analysis, this was not important, but for the present study, the particles are required whole and so ultrasonic dispersion was not used. It was found that this first basic peroxide treatment breaks up the sediment satisfactorily.

2) Add 30ml 6M HCl to the residue. Heat on a hotplate at 80°C for 2 hours. When cool, centrifuge and wash as before.

This stage removes the HCl soluble salts, such as carbonates and bicarbonates, and removes the soluble materials which may form insoluble fluorides in the next step.

3) Transfer the residue to PTFE beakers (with PTFE lids). Add 20ml 40% HF and heat

on a hotplate at 150°C for 3 hours. Wash as before.

This stage breaks down the siliceous minerals and removes the silicon as SiF₄. The time was reduced by changing this step from 6 days at room temperature to 3 hours at 150°C, effectively halving the length of the whole procedure.

4) Return the residue to the 250ml beakers. Add 30ml 6M HCl and heat on a hotplate at 80°C for 2 hours. Wash the residue again.

This step removes any fluorides formed in the last step.

5) Add 20ml 6M KOH and 25ml 30% H₂O₂ in 5ml aliquots, to the residue. Leave overnight in an oven at 55°C. Cool and wash the residue.

6) Transfer the residue to a 25ml beaker and add 4ml 6M KOH and 1ml 30% H₂O₂. Leave overnight in an oven at 55°C. When the reaction is complete, cool and wash again.

Steps 5 & 6 remove the remaining organic and humic matter.

7) Add 10ml 6M HCl and heat on a hotplate for 2 hours at 80°C. Wash again. Transfer the residue to storage vessel.

[N.B. All containers should be kept covered to stop possible atmospheric contamination. The presence of carbonaceous particles in laboratory dust shows the need for this precaution.]

2.2 Density separations.

Further extraction of the material by density separation was considered. However, due to the high variability of the 'apparent' density of the carbonaceous particles (due to varying pore size, internal gas pockets), this idea was discarded. Also, although the minerals remaining at the end of the digestion have a higher density than that of elemental carbon, there is a sufficiently small amount of them that it is not worth the extra time and potential loss of recovery to include a density separation in the standard digestion technique.

2.3 Filtration.

After completing the digestion there is occasionally fine, amorphous, black material present in some layers which can cause problems in the counting stage by obscuring the shapes of the particles. This material does not always follow the same trends as the carbonaceous particle record as there is sometimes little in the surface layers. Therefore, it seems that it does not have the same origin as the particles. It has been thought it may be a precipitation product of the digestion technique itself (Renberg pers. commun.), or a product of some other form of combustion (domestic burning, engine exhausts etc.).

As this material is fine, it may be removed by filtration. This will enable a higher fraction of the residue to be counted, increasing repeatability, as well as making counting easier. However, filtration also removes the smaller carbonaceous particles, 10µm and 5µm filters reducing the recovery rate to 40% and 65% respectively. As carbonaceous particles from oil combustion are usually smaller than those from coal, this approach may selectively

remove oil particles from the residue, making filtration of limited use.

2.4 Effects of the method on the carbonaceous particles.

In order to see the effect of the method on the chemistry and morphology of the carbon particles, a sediment sample was spiked with some material from an oil fired power station. In this way, the particle characteristics could be compared before and after digestion. Using SEM and EDAX, it was seen that the digestion had no apparent effect on particle morphology or surface chemistry.

2.5 Counting.

A known fraction of the remaining residues were evaporated onto coverslips. These were then mounted using 'Naphrax' diatom mountant, and the whole of each coverslip counted at x400 using a light microscope. Random views were not used, as at the bottom of the particle record, where there was either one or zero particles to be counted on the whole coverslip, this raised the limit of detection. The method of adding a known amount of polystyrene microspheres and calculating the number of carbonaceous particles from the ratio (Battarbee & Kneen, 1982) was found to have higher errors, especially at low concentrations.

2.6 Repeatability.

To see if separate digestions of a sediment sample would give the same particle concentrations, 5 replicate digestions were done from 3 different sediment levels, followed by triplicate counts from each digestion. This then gives 15 concentrations for each level from which the standard deviation and 95% confidence limits on the statistical counting error can be calculated. The results are shown in Table 1.

Table 1. Means, standard deviations and 95% confidence limits on the statistical counting error for carbonaceous particle counts from three different sediment levels in Loch Tinker. All values as concentrations per gram dry mass of lake sediment.

Level	Mean	S.D.	95% Confidence
0.0-0.5cm	70073	6398	48418 - 86168
4.5-5.0cm	45947	4933	26000 - 62771
11.5-12cm	8303	1021	3715 - 15140

2.7 Recovery rate.

A suspension of known carbonaceous particle concentration was made by adding a small amount of oil-fired residue from a power station to water and homogenising the solution. A known fraction was then removed and counted at x400 under a light microscope. The concentration of the solution could then be calculated. A known number of particles from this solution were added to a sediment sample before digestion. This sample was from below the start of the particle record in a core from Loch Tinker and it could be assumed that no carbonaceous particles were present within it. After the digestion, the number of particles was counted as before and compared with the number added to give a recovery rate. These digestions were done in triplicate and the recovery range was from 93.9% -

100.1%, showing that very few particles are lost during the digestion. This is confirmed by examining the supernatant fraction using SEM. The residue showed no particles of any size to be present in this fraction at any stage of the digestion.

Blank digestions involving no sediment were also performed to check on atmospheric contamination and cross contamination from other digestions. These showed that as long as the digestion vessels are kept covered and reasonable precautions taken in manipulating the digestion material, no atmospheric or cross contamination occurs.

One potential source of contamination is from the smearing of surface sediments down the inside of the core tube upon coring. This pushes sediment from layers rich in carbonaceous particles down into pre-industrial depths. Carbonaceous particles have been seen in very old sediment and as these particles are not formed by any 'natural' processes, this seems to be the only explanation. This was tested by preparing digestions from a sediment layer just below the start of the carbonaceous particle record, (e.g. 30-31cm depth in Loch Tinker). Duplicate digestions were performed on samples taken from the middle of the sediment slice and from around the edges. For the 'within slice' digestion, only one particle was found in four separate counts (a value of about 8 particles per gram dry mass) but particles resulting in a value of about 200 particles gDM⁻¹ were counted on the 'slice edge' samples. This shows smearing does take place, and could have a significant effect on particle number calculations in the lower levels of a sediment profile, demonstrating the need for 'trimming' core slices.

2.8 Detection limit.

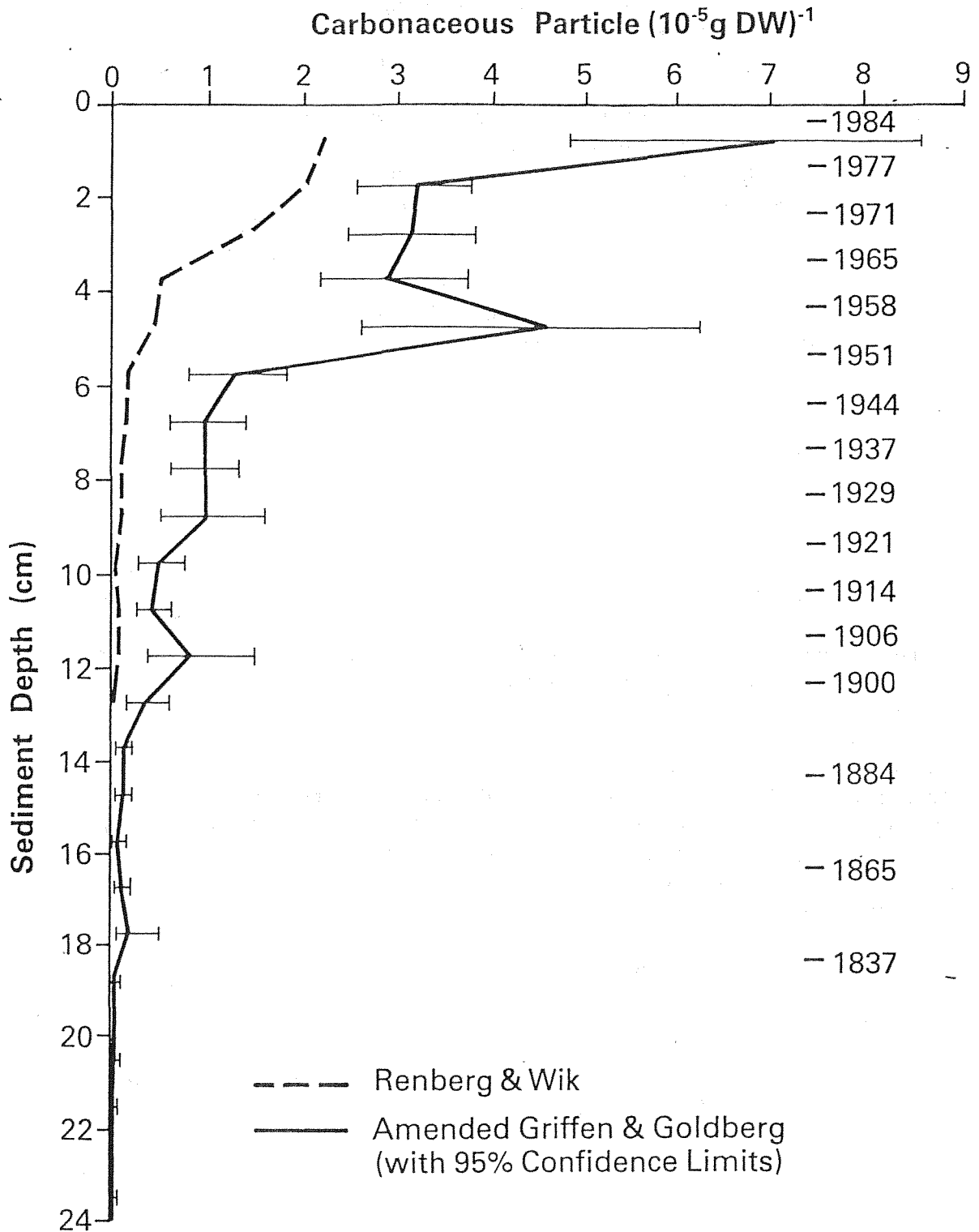
The Renberg and Wik method, removing as it does, only the organic fraction from the sediment, leaves a large amount of material at the end of a digestion. Therefore, unless a very long time is spent counting each sample, only a small fraction of the residual material will be counted and hence the limit of detection is quite high i.e. if only 1 particle is counted in the residual sample fraction, the result is a value of 80-100 particles per gram dry weight.

Using the method described above, the material remaining after digestion is predominantly carbonaceous. Therefore, at the bottom of the particle record, very little material remains and if so desired, 100% of this material could be counted in a short space of time. As approximately 0.2g of dried sediment is used for the digestion, if only 1 particle is counted, this will give a detection limit of approximately 5 particles per gram dry weight, at least a ten-fold improvement on the older method.

2.9 Application to a sediment core.

This digestion method was then applied to a sediment core taken from Loch Tinker in the Trossachs region of Western Scotland. The carbonaceous particle record has previously been analysed using the Renberg and Wik method so a comparison between the two methods can be drawn. The core was also dated using ²¹⁰Pb and the results are shown in figure 2.

Figure 2. Carbonaceous particle profile of Loch Tinker, comparing the two extraction methods



There are several points to note:

i) The basic trends are the same for both methods, i.e. the carbonaceous particle record begins in the early 1800's and there is a large rise in concentration after the 1940's.

ii) As the method described above removes more unwanted material, after digestion, a higher percentage of the original sediment is available to be counted, and this improves particle counting accuracy. Using a higher magnification, x400 as opposed to x50 in the Renberg and Wik method, means that carbonaceous particles down to $1\mu\text{m}$ are included. Using x50 magnification, only particles down to $10\mu\text{m}$ can be counted (Renberg & Wik, 1984, 1985a, 1985b; Wik & Renberg, 1987; Darley, 1985), and because of this, at the top of the core, particle concentrations using the method described are higher than those when using the Renberg & Wik method.

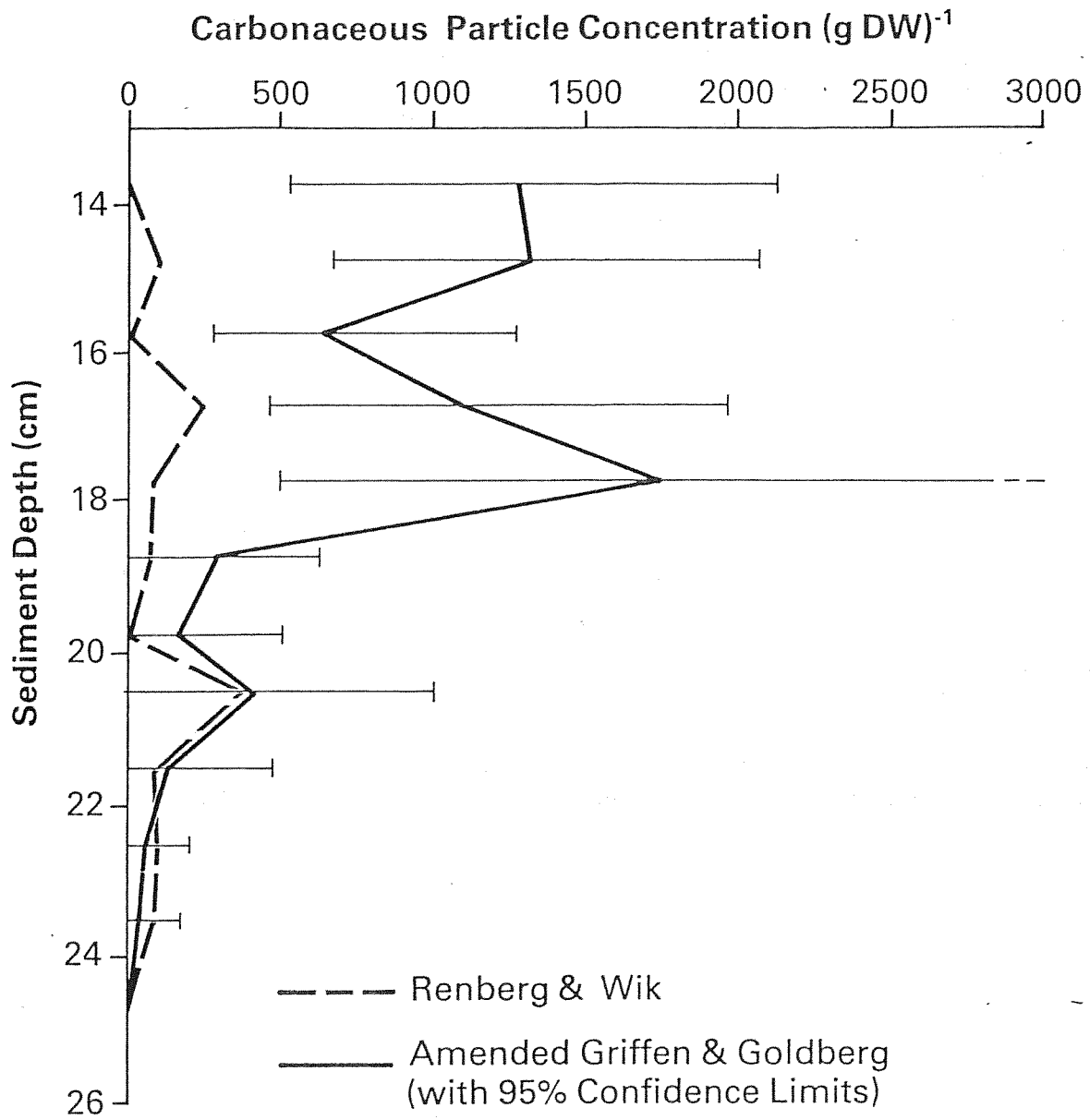
Lower down, at and below the point where the limit of detection for the Renberg & Wik method is reached, the particle concentrations using the method above become lower, due to better sensitivity. This is best illustrated in an expanded bottom section of the sediment profile (figure 3).

2.10 Discussion

The method described has a number of advantages over previous methods used to extract carbonaceous particles from sediments. It is more accurate and has a lower detection limit than the Renberg and Wik method previously used on British lakes, and it is quicker and involves less risk of fragmentation of the particles than the Griffin and Goldberg method upon which it is based.

Although the majority of the residue at the end of the digestion is carbonaceous material, some minerals do survive albeit in low concentrations. This includes some silicates, and even one or two siliceous spheres may appear in the residue, due to particles being washed in from the beaker walls after the hydrofluoric acid digestion step. This is not particularly important as the remaining non-carbonaceous material is sufficiently different both chemically and morphologically, that the counting and EDAX procedures will not be confused by their presence.

Figure 3. Expanded bottom section of the carbonaceous particle profiles for Loch Tinker (figure 2), to compare the detection limits of the two methods.



3. AN EXTRACTION TECHNIQUE FOR INORGANIC ASH SPHERES FROM LAKE SEDIMENTS.

This extraction method is summarised in Rose (1990b).

Except for the magnetic fraction, no extraction techniques for inorganic ash spheres appear in the literature, for either soils or sediments. These ash spheres are formed from the inorganic component present in the original fuel and so they are mostly aluminosilicate in composition with varying amounts of iron giving the spheres colours from yellow to dark brown and black. This means that they have a similar chemistry to many of the lake sediment minerals from which they are to be extracted and this restricts the range of reagents that can be used. For example hydrofluoric acid (HF), used in the carbonaceous particle extraction to remove silicates, is very effective at dissolving the silicate ash and even at low concentrations such as a 1% solution, will etch the surface of the spheres to reveal the underlying structure (Hullett & Weinberger, 1980). However, it is possible to remove some fractions of the sediment without damaging the inorganic ash spheres.

3.1 Organic material.

This can be removed by using 30% hydrogen peroxide (H_2O_2), at about 50-60°C until effervescence ceases. Basic peroxide (a mixture of 6M KOH and 30% H_2O_2) and nitric acid are more effective oxidants than H_2O_2 alone, but these also damage the ash particles.

3.2 Biogenic silica.

Biogenic silica (that which is biologically incorporated e.g. diatom frustules and chrysophyte cysts) can be removed from other forms of silica, such as mineral silica and non-crystalline or amorphous silica (including inorganic ash) by preferential digestion. Wet alkaline extractions are best for this purpose (Krausse *et al.*, 1983), as other methods such as fusion and mineral acid attacks are not selective for different forms of silica.

Trials performed on lake sediment spiked with coal-fired power station ash (to ascertain the extent of etching on the spheres), compared the effectiveness of different concentrations of sodium carbonate (Na_2CO_3) and sodium hydroxide (NaOH) at dissolving biogenic silica. Silicate analyses (Goltermann *et al.*, 1970) were performed on sub-samples removed at intervals from the digestion supernate. When the dissolved silicate concentration stopped increasing, this represented the end of biogenic silica dissolution. In most cases, interference from mineral sources is insignificant compared to the quantity of biogenic silica (Krausse *et al.*, 1983), but were this not the case, the dissolved silicate concentration would keep increasing with time rather than levelling off. It was found that 0.3M NaOH at 100°C, was the most effective solution and dissolved silica concentrations levelled off after about 2 hours. No etching of the ash particles occurred until after 6 hours and so 2½ hours was the time selected for the extraction technique.

3.3 Carbonates.

The strongest acid attack that dissolves carbonates (CO_3^{2-}) and bicarbonates (HCO_3^-), but leaves the ash spheres unaffected was found to be 3M HCl at 80°C for 2 hours.

3.4 Mineral silica.

Various techniques were tried to remove silicate mineral species from the inorganic ash. Fluorosilicic acid (H_2SiF_6), preferentially removes feldspars and certain other minerals from quartz, but this also severely etched the ash spheres. Pyrosulphate ($\text{Na}_2\text{S}_2\text{O}_7$) fusions (Chapman *et al.*, 1969; Kiely & Jackson, 1965), digested the ash spheres as well as the minerals leaving only quartz grains, but as a 2M solution there was no effect on either ash spheres or silicate minerals. The same occurred for pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) digestion attempts. No satisfactory separation was achieved for mineral silicate and the ash spheres.

3.5 Magnetic separation.

This can be achieved either by repeatedly swirling a covered magnet in a solution of the sediment, until no more magnetic particles are removed (Nriagu & Bowser, 1969), or by using a more sophisticated technique, such as an automated self-circulating magnetic separator (Munro & Papamarinopoulos, 1978). Both methods, however, only give a partial extraction, as not all ash particles contain ferrite ($\text{Fe}_{2.3}\text{Al}_{0.7}\text{O}_4$) the magnetic component of fly-ash (Hulett *et al.*, 1980).

3.6 Density separations.

Inorganic ash spheres found in lake sediments have a density of greater than $1\text{g}/\text{cm}^3$. Density studies of ash from power stations (Watt & Thorne, 1965) show that virtually no particles have a density greater than $2.9\text{g}/\text{cm}^3$ and so heavy minerals can be separated by using heavy liquids such as 1,1,2,2-tetrabromoethane (TBE) [$(\text{CHBr}_2)_2$] or sodium polytungstate [$3\text{Na}_2\text{WO}_4 \cdot 9\text{WO}_3 \cdot \text{H}_2\text{O}$]. The greater than $2.9\text{g}/\text{cm}^3$ fraction removed from lake sediment, when viewed under SEM reveals large angular mineral grains. No spheres were noted at all.

Sodium polytungstate has the advantages over TBE of being non-toxic and non-corrosive. Its density is adjustable up to $3.1\text{g}/\text{cm}^3$, it is neutral in aqueous solution and is stable in the pH range 2-14. It is very easy to handle, but quite viscous at higher densities and so a centrifuge is required for effective separation.

3.7 Laboratory procedure

The digestion is in four steps:

- 1) Place 0.2g of dried sediment in a 250ml beaker and add 50ml 30% H_2O_2 . Once the initial reaction has died down, place in an oven at 55°C and leave overnight. If, after this, there is still effervescence, add another 10ml H_2O_2 and return to the oven. Once reaction is complete, cool, centrifuge at 2000 r.p.m. for 5 minutes to settle the residue, and wash in distilled deionised water.

- 2) Return the residue to the beaker and add 50ml 0.3M NaOH. Heat at 100°C for $2\frac{1}{2}$ hours (including heating up time). Cool, centrifuge and wash as before.

3) Density separation.

a) with TBE. (density = 2.96 g/cm³)

- i) Wash the residue with acetone to remove the water, as water and TBE are immiscible. Remove as much of the supernate as possible.
- ii) Add 2ml TBE to a glass centrifuge tube and carefully add the sediment residue.
- iii) Centrifuge at 500 r.p.m. for 2 minutes.
- iv) Discard the >2.96 fraction.
- v) Wash the <2.96 fraction in acetone to remove the TBE and then in water to remove the acetone.

b) with sodium polytungstate (density adjusted to 2.95g/cm³)

- i) Remove as much supernatant water from the residue as possible.
- ii) Add 2ml polytungstate to a centrifuge tube and carefully add the residue.
- iii) Centrifuge at 500 r.p.m. for 2 minutes.
- iv) Discard the >2.95 fraction.
- v) Wash the lighter fraction in distilled deionised water.

NB. Both TBE and polytungstate are recoverable from these methods.

- 4) Transfer the residue to a 100ml beaker, add 30ml 3M HCl and heat for 2 hours at 80°C. Wash and centrifuge.

3.8 Counting.

A known fraction of the final residue is evaporated onto a coverslip, mounted with Naphrax (a diatom mountant) and the particles on the whole coverslip counted at x400 using a light microscope. Polystyrene microspheres (Battarbee & Kneen, 1982) were not used due to their similar appearance to the ash spheres. A known concentration of exotic spores could be added to count in this way, but due to low concentrations, large errors would be introduced lower down the core.

3.9 Effects of the method on the inorganic ash spheres.

At each stage of the development of the method, samples were checked under the SEM to see the extent of etching on the particles. There is no visible effect on the particles from any stage.

3.10 Repeatability.

The repeatability was tested in the same way as for the carbonaceous particle extraction method above. The results are shown in Table 2.

Table 2. Means, standard deviations and 95% confidence limits on the statistical counting error for mineral ash sphere counts from three different sediment levels in Loch Tinker. All values as concentrations per gram dry weight of lake sediment.

Level	Mean	S.D.	95% Confidence
4.5-5.0cm	257300	21500	250500 - 262360
11-11.5cm	56700	2760	53460 - 59350
22-23.0cm	12530	1250	11320 - 13780

3.11 Recovery rate.

A suspension of known inorganic ash sphere concentration was made up by adding a small amount of coal-fired residue from a power station to water. After homogenisation a known fraction was then removed and counted at x400 under a light microscope, to calculate the concentration of the suspension. A known volume of the homogenised suspension was then added to a sediment sample before digestion. The sediment sample was from 100-101cm depth of Loch Tinker, a level which had been previously counted and had only a 'background' value of ash spheres. After the digestion, the particle concentrations were counted as before and the value compared with the number of particles added to give a percentage recovery. These digestions were done in triplicate and the recovery range was 82% - 102%. Blank digestions show that no atmospheric or cross contamination from other digestions need occur as long as reasonable precautions are taken. Petri-dishes left in the open laboratory show that atmospheric contamination could cause false results at low concentrations. One source of contamination could again be core smearing, but as before this can be avoided by core trimming.

3.12 Detection limit.

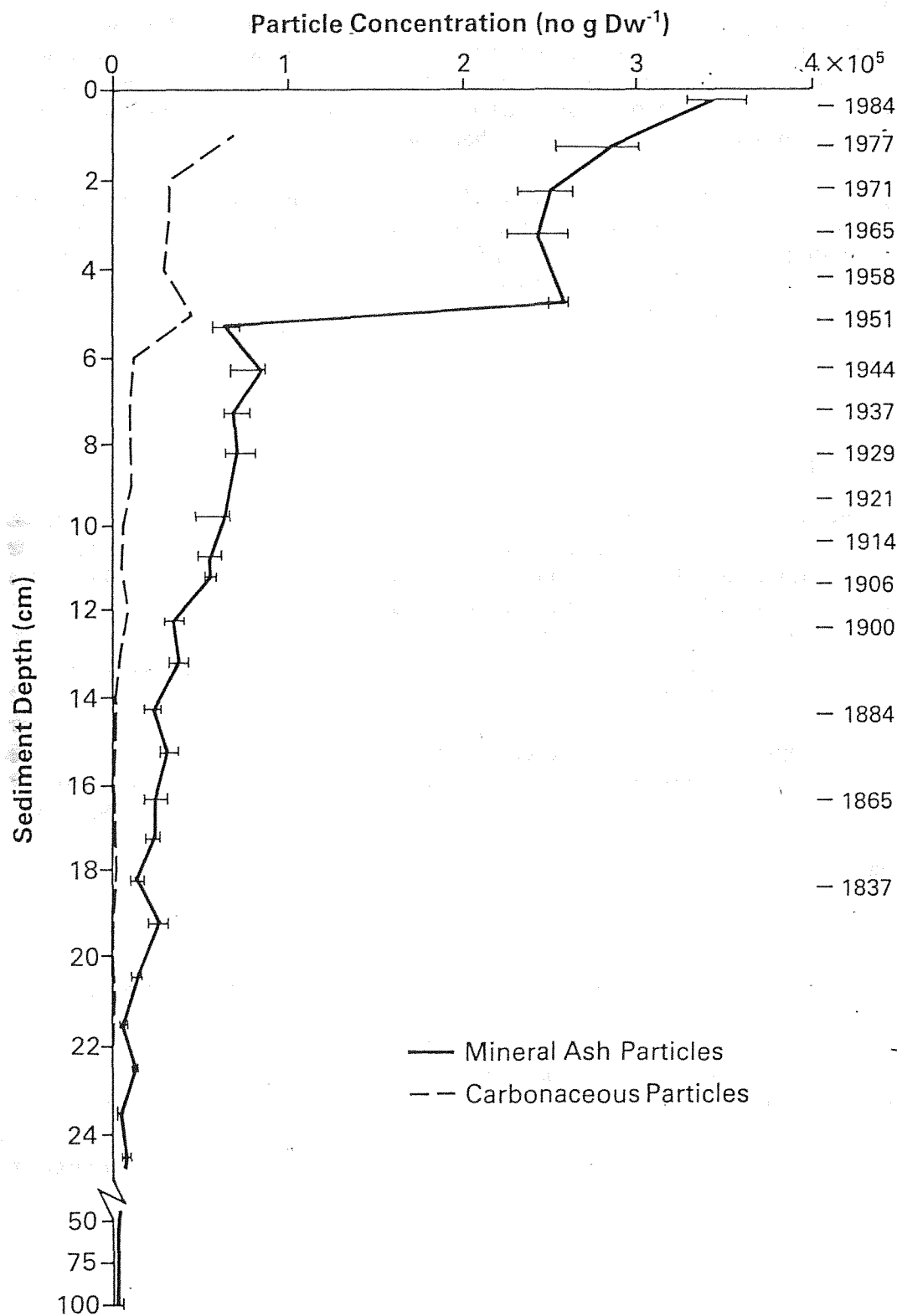
Due to the reagent restrictions outlined above, at the end of the digestion there is still quite a lot of material present, only a fraction of which is made up of the inorganic ash spheres. Consequently, the limit of detection for this method is quite high at about 180-200 particles gDM⁻¹, although particle numbers rarely get this low, due to non-industrial input of spheres.

3.13 Application of the method to a sediment core.

The technique was then applied to a sediment core taken from Loch Tinker. The basic trend of the profile is similar to that of the carbonaceous particle profile produced for Loch Tinker, especially in the top 5cm. The two profiles are compared in figure 4. The main difference between the profiles is the continuous background value of the inorganic ash, whereas the carbonaceous particle record falls to zero at about 24-25cm depth. Below this, the mineral ash record is fairly uniform and low, at 2000-3500 particles gDM⁻¹. If this record is attributable to a constant background flux from non-industrial sources through time, the start of the "industrial" ash sphere record can be identified and occurs at approximately the same depth/date as the carbonaceous particle record.

Marked changes in the pre-industrial background concentration of particles may be related to significant changes in sediment accumulation (causing dilution), or to changes in atmospheric flux e.g. following a volcanic eruption. The identification of such events using this technique may be of additional palaeoecological or chronological value.

Figure 4. Inorganic ash concentration profile for Loch Tinker.



4. CHARACTERISATION OF CARBONACEOUS PARTICLES USING ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX).

Once carbonaceous particles could be efficiently extracted from lake sediments a technique was needed for characterisation of these particles into fuel type. Because size and surface morphology are ambiguous variables attempts at characterisation were based on surface chemistry using EDAX. Consequently, particles of known origin from various coal and oil fired power stations were obtained to set up a dataset of reference surface chemistry. This could then be used to develop a multi-element discrimination and hence classify sediment extracted particles into their fuel type.

Energy Dispersive X-Ray Analysis (EDAX), permits the detection and simultaneous display of all mid-energy X-rays collected during a single analysis, and so many elements may be studied at any one time. EDAX systems are also readily linked to electron microscopes enabling selection of individual particles of interest and the combination of morphological and chemical data.

The EDAX analysis was performed by John Watt at the Royal School of Mines, Imperial College, London.

4.1. Sample preparation.

At the end of the carbonaceous particle extraction (section 2 above), the particles are left as a suspension in water. A few drops of this suspension are added to the top of a column of alcohol and allowed to spread for a few seconds before being drawn through a 0.4 μ m Nuclepore filter. These filters provide an excellent substrate for this type of analysis because the particles are retained on the surface, rather than being absorbed into the filter. Also, the organic composition of the filter does not add any detectable X-ray peaks to spectrum produced.

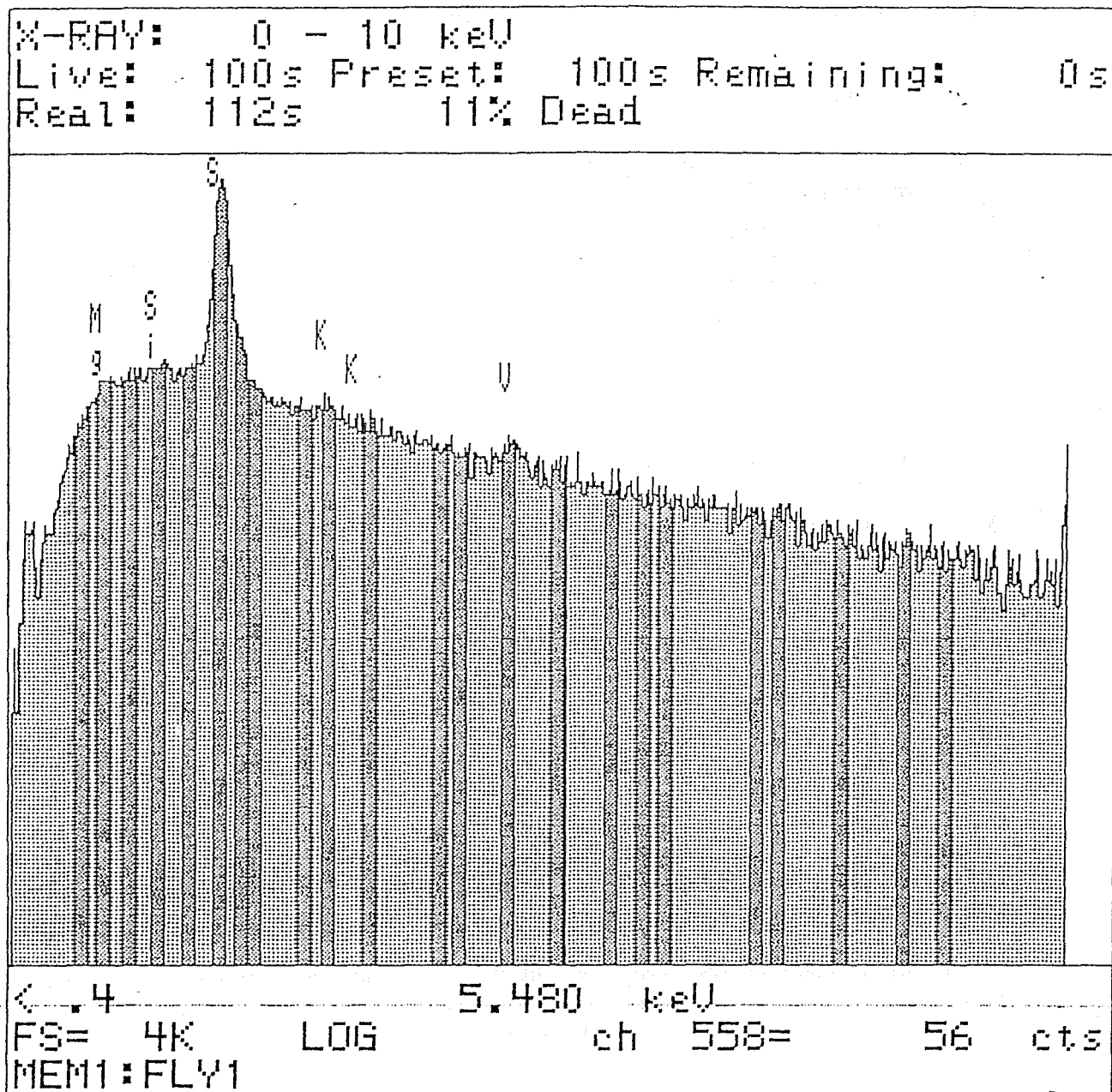
The filter samples are mounted onto glass slides using colloidal graphite paint and coated with a thin layer of carbon by evaporation in a vacuum. This forms a conducting layer over the particles and prevents the build-up of charge on the specimen in the SEM. Carbon is used rather than a metal coating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

4.2 EDAX - principles.

When an electron beam is focused onto a specimen a number of signals result. The JEOL 733 Superprobe used in this study makes use of three of these:

- Secondary electrons are emergent electrons with an energy less than 50eV, produced by the interaction of primary and backscattered electrons with weakly bound surface electrons.
- Backscattered electrons are electrons which are elastically scattered through a large angle. The yield of these electrons increases with atomic number.

Figure 5. EDAX spectrum of a carbonaceous particle showing delimited regions of interest or 'windows'



- X-rays are a form of electromagnetic radiation. The energy dispersive X-ray spectrum is represented as a histogram of the total X-ray photons counted by each channel of the multi-channel analyser in the detection system. This spectrum is composed of X-rays of two origins. Continuum X-rays (or bremsstrahlung radiation), which form much of the background underlying the peaks of the energy spectrum, and characteristic X-rays, produced during the interaction of incident electrons with the orbital electrons of an atom, and form the peaks superimposed on the background (figure 5).

When an incident electron interacts with an atomic orbital electron, ejection of the atomic electron may result, leaving a vacancy. The atom is now unstable and stability is restored by an electron from a higher energy level, dropping down to fill the vacancy. The excess energy is emitted as an X-ray photon. If the vacancy was created on the innermost electron or 'K' shell, these are designated K X-rays, and L and M X-rays are generated in a similar way. The vacancy can be filled by electrons from different higher energy levels, giving rise to e.g. $K\alpha$ (from L level) and $K\beta$ (from M level) lines in the spectrum. Hence, each element detectable by the system has one or more characteristic X-ray lines which will be produced if it is present in the sample.

4.3 Element selection.

Elements for the EDAX analysis of carbonaceous particles were selected from elemental studies of mainly coal-fired power station ash available in the literature (e.g McCrone & Delly, 1973; Davison *et al.*, 1974; Cheng *et al.*, 1976; Block & Dams, 1976; Coles *et al.*, 1979; Mamane *et al.*, 1986 etc.). Although very many elements exist in fly-ash (Klein *et al.*, 1975) a short list of 17 was finally produced for analysis: Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu & Zn. Other studies since have confirmed that most of these elements are also the common ones in oil fly-ashes (Raeymaekers *et al.*, 1988).

4.4 Automated data acquisition.

The development of image analysis software has made it possible for computers to perform some parts of the analysis. The advantages of this are that it allows large amounts of data to be collected in short periods of time and the analysis is less dependent on the skill of the operator. The ability to create large data sets means that multivariate statistical techniques can then be used to examine trends that may not be apparent in smaller, potentially biased samples.

The controlling image analysis program, DIGISCAN, locates any features present which fall between operator selected threshold values. This means the computer will count only those pixels (points on the image) which fall within these thresholds. The image is then scanned and the location of each of these pixels noted. The beam is then moved under computer control to each selected feature in turn for the collection of size (all touching pixels are summed to give the two dimensional area of a feature) and X-ray information.

4.5 X-ray corrections.

The characteristic X-ray peaks produced span several channels in the multichannel analyser and a convenient way to summarise the data, is to delimit a region of interest (or window) over the channels concerned (see figure 5) and then to record the total counts in the whole region. This leads to a reduction in data storage since the counts for each

element are now represented by a single number, rather than a number for each channel.

Using the DIGISCAN program, up to 25 windows can be defined on the spectrum and the numbers of X-ray counts falling in each are stored. Most of these windows are defined at the energy levels characteristic of the elements to be measured, but several other regions are also defined on parts of the spectra where no elemental peaks are expected to occur. These are then used to subtract background counts from each of the other windows. The background channel selected and the proportion subtracted from each window form the Background Correction.

In certain cases a peak for one element will overlap a peak for another. For example, the major elemental line for Ca, ($K\alpha$), is overlapped by a minor line for K ($K\beta$). Where this occurs, one of the elements can be estimated from lines appearing elsewhere in the spectrum. The number of counts that should occur in the first region can then be calculated, and subtracted from the joint peak. The remainder can then be allocated to the overlapping element. The proportion of one peak subtracted from another in this way, is termed the Overlap Correction. A final Efficiency Correction allows a linear scaling of the elemental analysis to account for differences in detector efficiency between elements.

The set of definitions of X-ray windows and the correction factors to be applied to them is stored in a separate 'window file', since it will be used repeatedly to correct the results for all measured features. For results of analyses to be fully comparable they must have been obtained using the same window file (Watt, 1990).

Table 3. *The window file created for the analysis of carbonaceous particles*

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

Different sized particles of the same composition will give different totals of X-ray counts in each of the specified windows, and so the results are normalised by expressing them as a percentage of the total sum of the corrected counts from all the windows. As carbon is undetectable using EDAX, in the analysis of carbonaceous particles, normalisation has the effect of making the remaining trace elements appear as major chemical constituents. However, this lack of carbon detection, may in fact be an advantage, as it

enables the trace elements to be studied in more detail, and it is these which will separate the different fuel types, if such a separation is possible, and not the uniformly large carbon component.

4.6 Power station reference material.

4.6.1. Sources

In order to construct a classification for carbonaceous particles, reference samples of fly-ash were obtained from the various sources. 32 power station ashes were obtained, from the Central Electricity Generating Board, the South of Scotland Electricity Board, the Northern Ireland Electricity Board and the Electricity Supply Board of Ireland. Of these ashes, 23 were from coal-fired stations, 7 from oil and 2 from peat (see Table 4). Although peat does not produce spheroidal carbonaceous particles, its inclusion in the characterisation study is to show that the scheme can be extended to include other fuel types. The reference material supplied by the Electricity Boards, is taken from the various flue gas particle extraction systems fitted to the stations. Consequently, although the reference samples are chemically the same as the particles emitted to the atmosphere, they may be morphologically slightly different, larger particles being more easily extracted from the flue gases.

Table 4. *Power station ash reference collection : Fuel type and sources.*

1.	FAWLEY	OIL	CEGB
2.	PEMBROKE	OIL	"
3.	CARRINGTON	COAL	"
4.	PADIHAM	COAL	"
5.	FIDDLERS FERRY	COAL	"
6.	USKMOUTH	COAL	"
7.	DIDCOT	COAL	"
8.	ABERTHAW	COAL	"
9.	IRONBRIDGE	COAL	"
10.	KINGSNORTH	COAL	"
11.	BLYTH	COAL	"
12.	EGGBOROUGH	COAL	"
13.	THORPE MARSH	COAL	"
14.	WEST THURROCK	COAL	"
15.	RUGELEY	COAL	"
16.	DRAX	COAL	"
17.	AGECROFT	COAL	"
18.	WEST BURTON	COAL	"
19.	DRAKELOW	COAL	"
20.	GRAIN	OIL	"
21.	TILBURY	COAL	"
22.	METHIL	COAL	SSEB
23.	LONGANNET	COAL	"
24.	COCKENZIE	COAL	"
25.	COOLKERAGH	OIL	NIEB
26.	KILROOT	OIL	"
27.	BELFAST WEST 'B'	COAL	"
28.	BALLYLUMFORD	OIL	"

29.	MONEYPOINT	COAL	ESB
30.	TARBERT	OIL	"
31.	GWEEDORE	PEAT	"
32.	BELLACORRICK	PEAT	"

4.6.2. EDAX of reference material.

Ten power stations were selected from the 32 reference samples, to produce a carbonaceous particle calibration set on which to base a characterisation scheme. These were:

Coal	Oil
Blyth	Ballylumford
Drax	Fawley
Eggborough	Isle of Grain
Ironbridge	Pembroke
Rugeley	Tarbert

The Gweedore peat-fired station was also selected. A sample of the reference material from each of these stations was then put through the carbonaceous particle extraction technique. This was for two reasons, firstly, so that the reference material had been subjected to the same chemical treatments as the lake extracted particles, and secondly to remove the inorganic ash spheres from the coal ash samples.

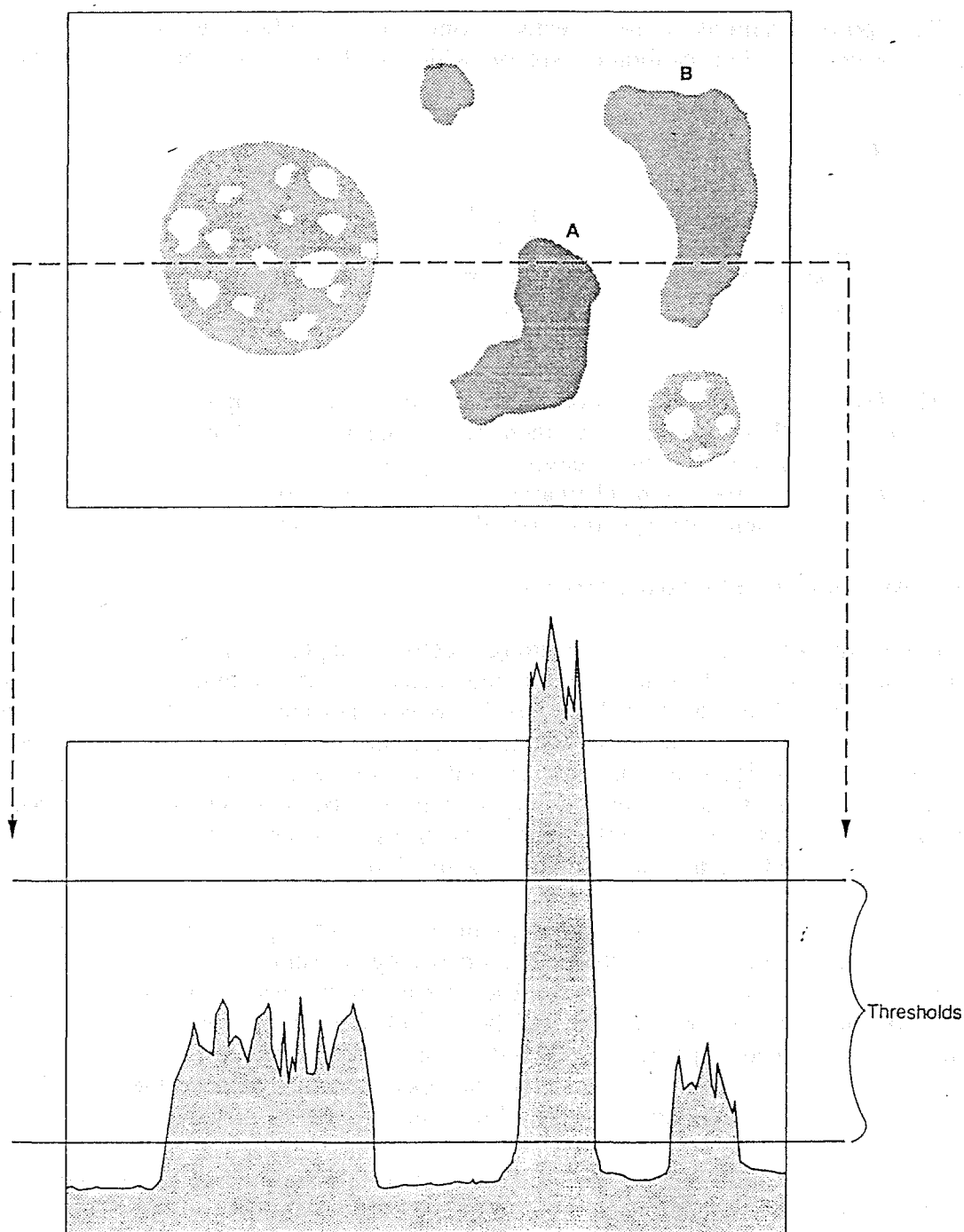
4.7. Analysis of individual particles.

Using the wave form of the scanning electron image, signal thresholds are set so that carbonaceous material is included in the analysis, but remaining fragments of mineral matter are not. The setting of these thresholds is important, as any feature (over 600 pixels joined together) that is included within these limits in the field of view will be analysed. For example, in figure 6, mineral fragment A will be excluded from the analysis, as its wave-form exceeds the threshold. Fragment B will be included however, along with the carbonaceous particles as it falls within the thresholds set. Such extra features will have to be removed at a later stage of the data manipulation.

The wave-form of a carbonaceous particle does not register greatly above that of the background and this causes problems upon setting threshold levels. If the lower threshold is set high, this excludes most of the background from subsequent analysis, but also some parts of the carbonaceous particle will be excluded. If the lower threshold is set too low, all the carbonaceous particle is included, but also many extra unwanted features are included in the analysis. Consequently, the operator must balance these levels to include as much carbonaceous particle, but as little background as possible.

The final threshold setting will therefore alter the number of pixels recorded for the carbonaceous particle and hence the size of the particle as seen by the EDAX. This makes size data (cross-sectional areas, diameters, aspect ratios etc.) generated by the EDAX of doubtful quality and should be treated with caution.

Figure 6. The setting of the threshold levels using the wave form of a SEM image will determine the features that are analysed. Those particles falling within the threshold range (the carbonaceous particles and mineral fragment B) will be included, but mineral fragment A will not as its waveform exceeds the threshold. Unwanted analyses such as that of fragment B must be removed at a later stage of data manipulation.



4.8 Data manipulation.

The morphological and chemical data produced is transferred from the EDAX for analysis. Initially this is done using MIDAS, a package with the ability to handle large amounts of data and locate discrete groupings of particles with similar chemistry, as well as being able to look at the individual data of any single particle in the data set.

Preliminary subdivisions are made by examination of the distribution of single elements using quantile plots and pairs of elements using scatter plots. In each case the value obtained for the element in every particle in a data set, or combination of data sets, is plotted. Use is made of any obvious clusters in the scatter plots (figure 7a) and discontinuities shown by breaks in slope on the quantile plots (figure 7b), to split the data into various groups. These subsets of the data can then be examined to assess the homogeneity of the groups and to split them further if necessary. If no further subdivisions are apparent, the group description is added to the classification scheme.

When this is done using particles of known origin from the reference material, particles of a single fuel type may form discrete clusters. These can be temporarily removed from the analysis and further clusters of a single fuel type located using other elements. When no further subdivisions occur, there will be a number of groups with an individual chemistry range, each allocated a fuel type.

Coal/oil, oil/peat and coal/peat separations were carried out in this way and the three amalgamated to form a single classification scheme. This is shown in figure 8. Here, there are 12 groups within the population, and each has been allocated a single fuel type. There is one group, however, labelled coal/oil for which no further split was achieved. These particles show low X-ray counts and probably represent some of the 'lacy' particles, with little surface area. Even with this 'unclassified' group, the classification scheme correctly allocates 85% of the particles.

4.9 Multivariate analysis on EDAX generated data.

4.9.1 Preliminary Analysis.

Although the classification scheme described above, provides a fairly good separation, the use of multivariate statistical techniques should be able to improve this further.

A preliminary study, using a stepwise discrimination procedure, on 1400 particles from one coal and one oil-fired power station, shows a very good separation between fuel types. This is shown graphically in figure 9. This discrimination uses all the EDAX generated data and the morphological variables appear to be important. In order of importance, the top variables are:

- Aluminium
- Maximum diameter
- Cross-sectional area
- Chlorine
- Sodium
- Aspect ratio
- Silicon

Figure 7. Preliminary particle separations (a) Scatter plot showing particle clusters, and (b) quantile plot showing breaks in slope which indicate different particle sub-populations

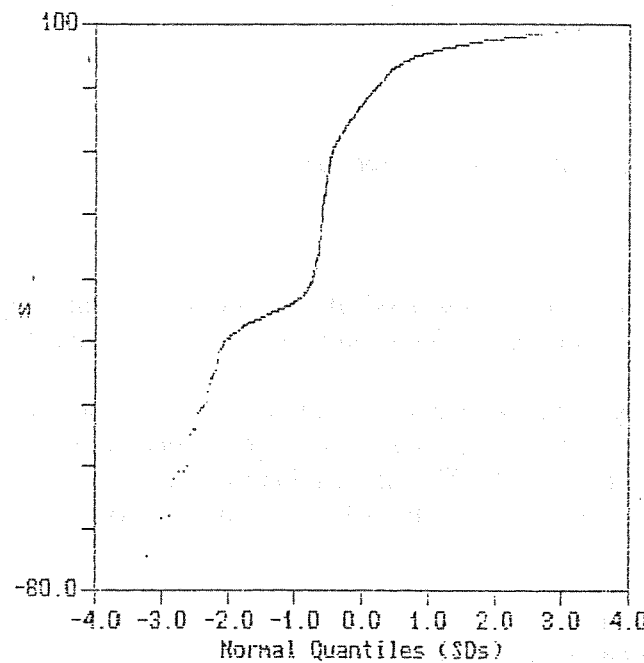
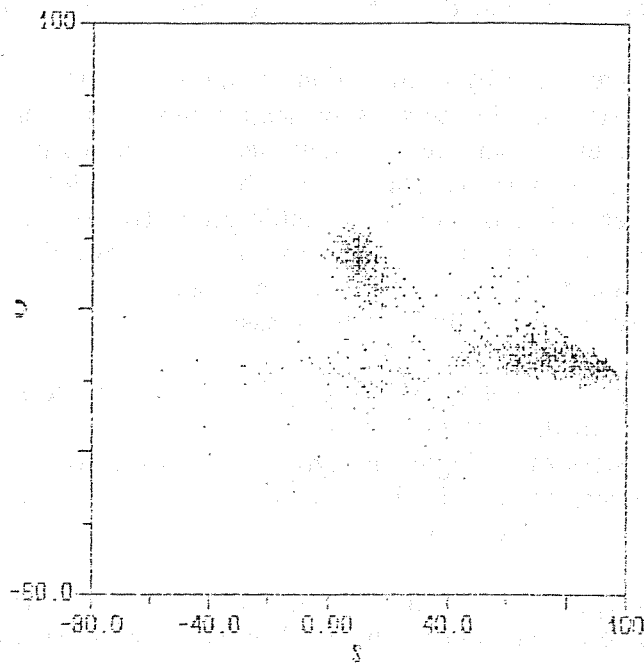
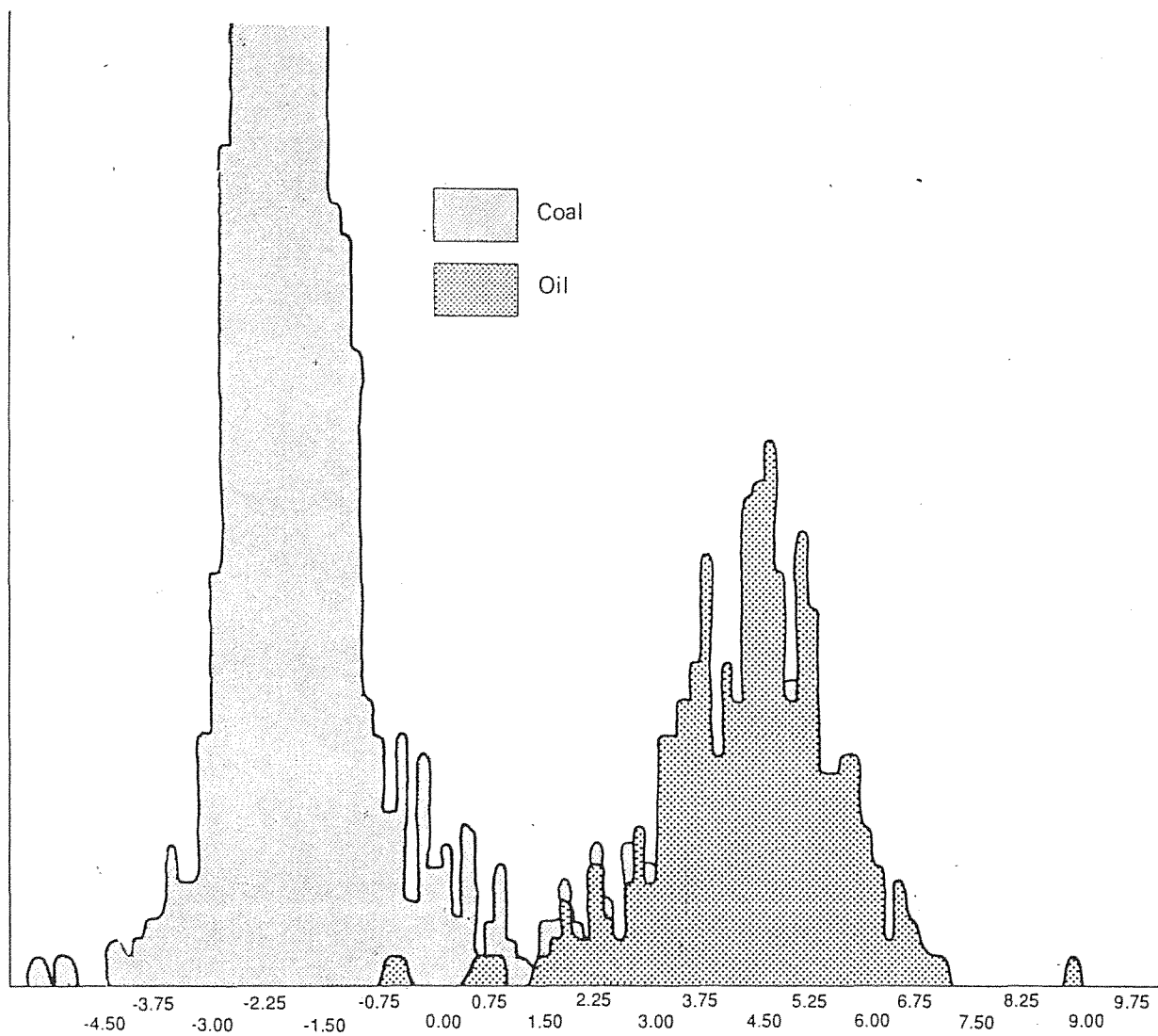


Figure 9. Graphical representation of a preliminary stepwise discrimination.



This discrimination is encouraging, as it correctly assigns over 90% of the particles and shows that an effective separation is possible. Due to the factors outlined in section 3.7 however, size variables should be treated with caution and further analyses performed using chemical data alone.

4.9.2. A reference data set.

The EDAX analyses of 5565 particles from the ten selected power stations were brought together to be used as the particle reference data set. This could then be used to develop and test any future allocation procedure.

Within this data set there are small number of outliers which should be removed. When studying the distribution of single elements in the population, the same particles showed extreme values, well outside the normal range shown by the rest of the population. When this was exhibited by more than one element in a given particle, this particle was removed from the analysis. The general trend was for the removed particles to be extremely negative in elements such as sodium, magnesium, and silicon, and either very high in copper, nickel and zinc, showing them to be mineral fragments, or have very low total electron counts, showing them to be highly porous carbonaceous material. The cut-off ranges are shown in Table 5. When this selection is applied to the reference set, it reduces the population to 5539 particles.

Table 5. *Cut-off ranges to remove outliers from particle reference set.*

Element	Range	Element	Range
Na	>-100	Mg	>-100
Al	>-40	Si	>-40, <90
P	>-50	S	>-35
Cl	>-35	K	>-30
Ca	>-30	Ti	>-30
V	>-20	Cr	>-20
Mn	>-25	Fe	>-20
Ni	>-20	Cu	< 20
Zn	>-15, <15		

Stepwise discrimination analysis was performed on the chemical data of 500 particles (250 coal and 250 oil), selected at random from the data set. This was done twice, using different random selections and gave two different sets of element rankings:

Analysis 1: S > V > Fe > Mg > Ti > Cl

Analysis 2: Al > Cl > Si > V > Mg > K

There is very little to choose between the two discriminations, both producing over 95% correct particle allocation. Sulphur and aluminium appear to be inversely correlated and depending on the individual particles selected either will be the dominant element.

To achieve a single element ranking, a test set of more than 500 is needed and so a stepwise discrimination was performed on the 5539 particles in the population. Table 6 shows the element ranking, the percentage correct allocation using the added element and Wilks' Lambda, a test statistic for multivariate analyses.

Table 6. *Percent correct allocations and Wilks' Lambda for ranked elements*

Rank No.	Selected Element	% Correctly Allocated	Wilks' Lambda
1	Aluminium	83.9	0.5963
2	Chlorine	90.4	0.4231
3	Sodium	92.2	0.3715
4	Silicon	93.3	0.3433
5	Potassium	93.8	0.3178
6	Vanadium	94.2	0.3005
7	Titanium	94.4	0.2909
8	Zinc	94.8	0.2844
9	Iron	94.9	0.2807
10	Sulphur	95.0	0.2759
11	Magnesium	95.1	0.2729
12	Chromium	95.2	0.2708
13	Manganese	95.3	0.2697
14	Nickel	95.4	0.2680
15	Phosphorus	95.4	0.2671
16	Calcium	95.5	0.2671
17	Copper	95.5	0.2671

These values are also shown in figure 10. Best separation is achieved at the optimal Wilks' Lambda in this case using all 17 elements. However, very little improvement is caused by adding elements after zinc and a cut-off might be considered here in the interests of speed during an analysis. It can be seen that it is very easy and requires only four or five elements to achieve a 94-95% correct particle allocation, and use of all 17 elements does not improve the separation significantly.

4.10 Misallocated Particles.

The discrimination procedures described above used SAS, a computer statistics package. Different outputs can be selected for each discrimination, one of which is a probability of allocation for each particle. A post-probability level can also be set, and this is the minimum a particle must achieve to be allocated into a group. For example, with only two groups, if the post-probability is set at 0.5, then all the particles will be allocated into one or the other (in this case coal or oil). However, some features will have been analysed which are not particles, but mineral fragments surviving the extraction procedures (see section 3.7), and raising the post-probability may help remove these from the analysis. Figure 11 shows the probability that a given particle in the reference data set is allocated 'coal'. There are two main peaks, the 0.0 - 0.1 peak representing the majority of the oil particles and the 0.9 - 1.0 peak representing the majority of coal particles. Consequently, the post-probability can be set quite high (0.8 or 0.9) and most of the particles will still be included. Those particles with probabilities falling below the set level are allocated a group called 'other'.

Figure 10. Graph showing the improvement of Wilks' Lambda and % correct allocation of particles with the addition of successive elements to the analysis.

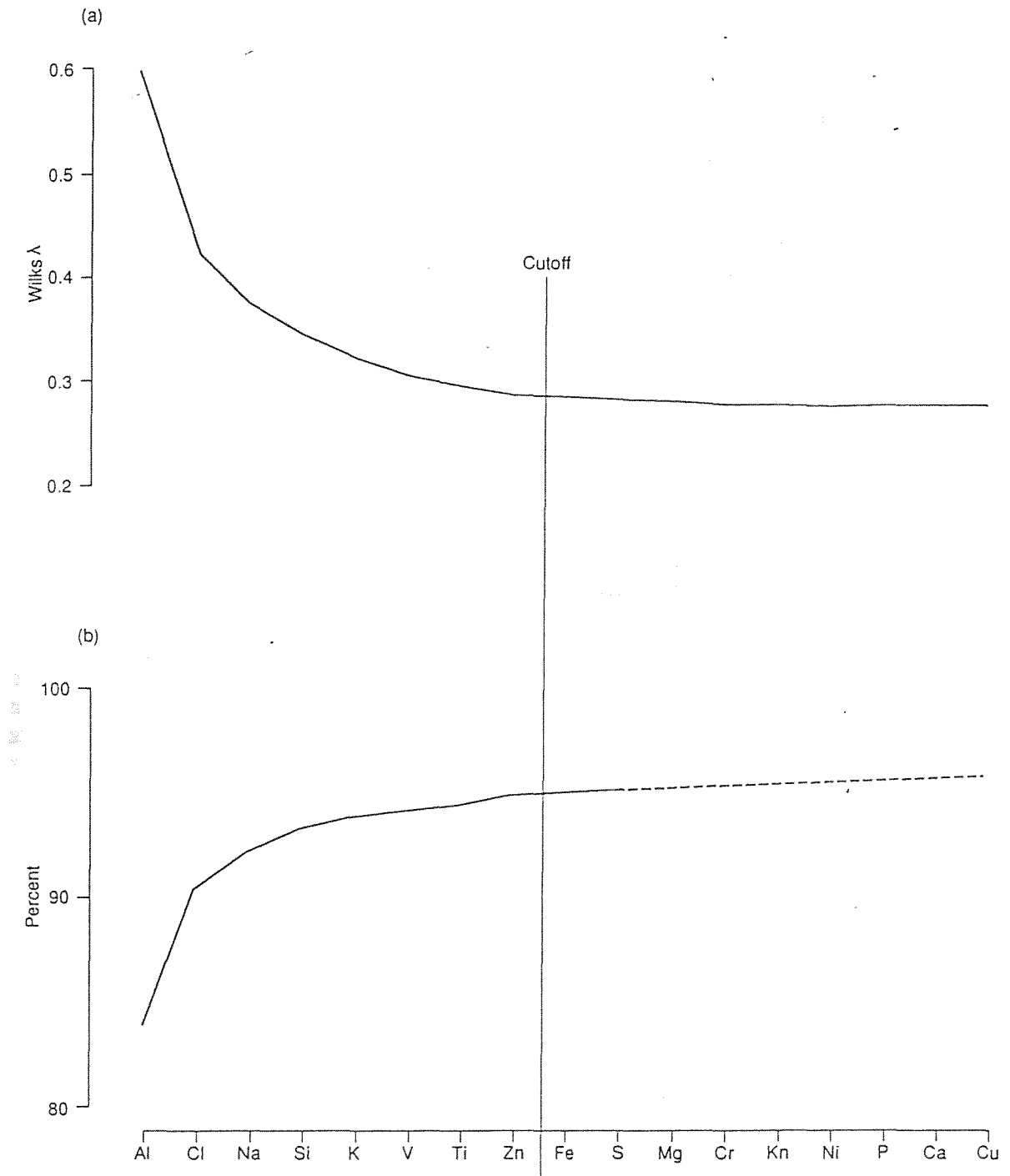
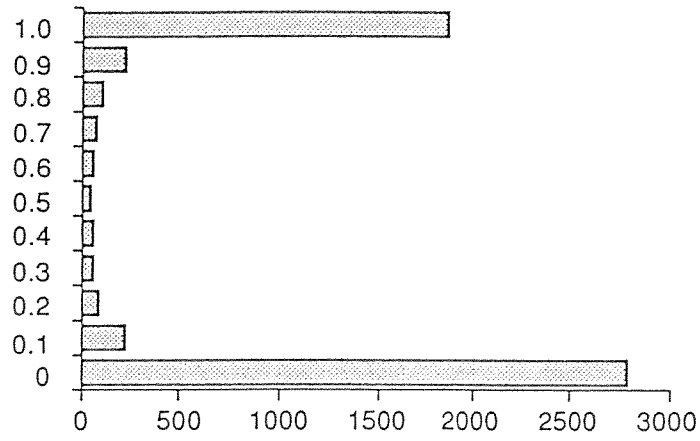
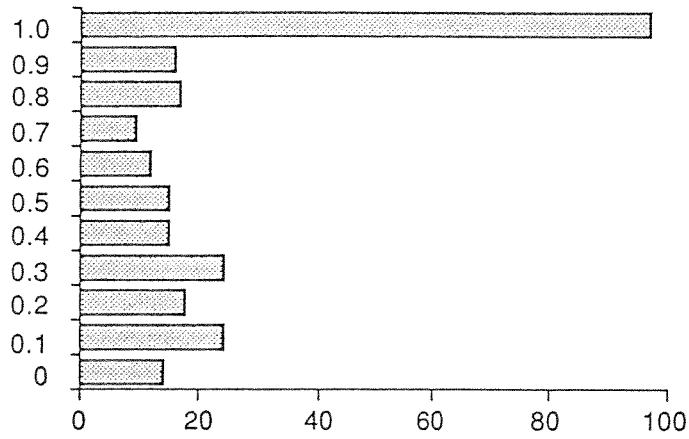


Figure 11. (a) Probability of allocating particles in the reference set to 'coal', and (b) the probability of allocation of mis-allocated particles

a.



b.



However, Figure 11a shows the probability of allocation of all the misallocated particles and this also shows that the majority have a probability of over 0.9, and so the setting of the post-probability at a higher level would still include most of the misallocated particles. Setting the post-probability at various levels and running the analysis, gives the following results:

Post-Probability	No. Misallocated	No. in 'other'	No. Misallocated in 'other'
0.5	261 (4.7%)	0	0
0.6	216 (4.0%)	96	45
0.7	171 (3.2%)	209	90
0.8	147 (2.9%)	331	114
0.9	125 (2.5%)	588	136

Therefore, if the post-probability is set at 0.9, of the particles allocated a fuel type (90% of the population), 97.5% are allocated correctly.

4.11 Power Station Allocation

A tentative characterisation of the particles to power station level was attempted. About 150 particles from seven power stations (Blyth, Drax, Eggborough, Ironbridge, Pembroke, Rugeley & Tarbert) were randomly selected, and a discrimination using the full chemical data run. Initially, no threshold was set, the particle being allocated to the station with the highest probability. The results (see Table 7a) are quite good and most of the particles are allocated to their correct power station, although there is some overlap between some stations within a fuel type (e.g. Blyth and Drax).

Table 7b shows the same discrimination but with the post-probability set at 0.5 (only probabilities >0.5 are allocated). There are one or two stations which show remarkably good separations, Eggborough, Pembroke and Tarbert all having over 70% correct allocation. Rugeley has 41% correct, but the remaining stations show very poor allocation, most of their particles being allocated into 'other'. Blyth has none of its particles correctly allocated.

Table 7. Probabilities of power station allocation.

a) No post-probability

From Stn.	Percent Classified into Station.						
	blyt	drax	eggb	iron	pemb	ruge	tarb.
blyt	31.71	24.39	6.10	17.07	0.61	18.90	1.22
drax	14.55	49.70	4.85	10.91	1.21	11.52	7.27
eggb	4.35	6.83	77.64	6.83	0.62	2.48	1.24
iron	26.85	21.48	6.71	21.48	0.67	17.45	5.37
pemb	0.00	5.68	0.00	1.70	71.02	0.57	21.02
ruge	11.03	15.17	1.38	15.17	0.00	52.41	4.83
tarb	0.74	2.22	2.96	2.22	1.48	0.00	90.37

b) Post-probability = 0.5

From Stn.	Percent classified into Station							
	blyt	drax	eggb	iron	pemb	ruge	tarb	other
blyt	0.00	4.88	2.44	0.00	0.61	10.98	0.61	80.49
drax	0.00	7.88	2.42	0.00	1.21	9.09	1.21	78.18
eggb	0.00	0.62	70.81	0.00	0.00	1.24	0.00	27.33
iron	0.00	4.03	5.37	2.01	0.67	10.74	2.68	74.50
pemb	0.00	1.14	0.00	0.00	70.45	0.00	17.61	10.80
ruge	0.00	0.69	0.69	0.00	0.00	41.38	1.38	55.86
tarb	0.00	0.00	2.96	0.00	1.48	0.00	84.44	11.11

It must be remembered, however, that the particles from to undertake this separation were produced over a short period of time, and presumably from one fuel source. To proceed with a power station characterisation, a number of ashes from each station covering a long period of time would need to be collected and studied together, so that a characterisation based on station differences rather than fuel source differences would be produced, if this is indeed possible. Even then, in the end it may prove that there are no discernible differences between one coal-fired (or oil-fired) station and another.

5. APPLICATION TO LAKE SEDIMENTS

5.1 A comparison of particle concentrations for two Scottish lochs.

5.1.1 Site selection and coring.

Two lochs were selected for the study of particle deposition history in low and high acid deposition areas of Scotland. The 'clean' site was chosen as Loch Teanga, on South Uist in the Outer Hebrides, a location remote from any major power generation or large city sources. The 'dirty' site was selected as Loch Tinker, in the Trossachs region of west central Scotland, a site about 40km north of Glasgow (see figure 12).

Loch Tinker was cored before the present study, in June 1985, using a modified piston corer. The sediment had already been analysed for carbonaceous particles using the Renberg & Wik method (see section 2.9) and so was an ideal core with which to test the new methods. Loch Teanga was cored in October 1987, again using a modified piston corer. Both cores were dated using ^{210}Pb measurements.

5.1.2 Carbonaceous particle analysis.

The results of the comparison between the Renberg & Wik method and the new method for Loch Tinker appear in section 2.9. Carbonaceous particle analysis of the Loch Teanga core was done using the new method and the results appear in figure 13.

The trends exhibited by the two profiles are generally the same. A slow increase in concentration from the start of the particle record and accelerating from the 1940/1950's to the time of coring. The obvious differences are in particle concentration, Loch Tinker showing a surface concentration over 20 times that of Loch Teanga, and in the start of the particle record, the more remote site in the Hebrides not having a particle record until the early 20th century compared with the 1820/1830's for Loch Tinker. These results both support the low and high acid deposition labels previously given to these sites.

5.1.3 Inorganic ash sphere analysis.

Analysis for inorganic ash spheres was performed by the method described in section 2.2. The results for Loch Tinker and Loch Teanga appear in figures 4 and 14 respectively.

Again the trends for both profiles are the same, a low continuous background probably due to natural inputs (e.g. volcanic) until the start of the industrial record, as indicated by the carbonaceous particle profile. At this point there is a steady increase in particle concentration until the 1950's when there is a sharp increase. This may be due to the introduction of new large power stations in the 1950's in Scotland, the first new stations there since the 1920's. These were all coal-fired and so their presence would show up more in the inorganic ash profiles than the carbonaceous particle profiles. This increase is followed by some degree of levelling off until the time of coring. Again there is over an order of magnitude difference in particle concentration at the surface.

Figure 12. Location map of Loch Tinker and Loch Teanga, and isolines of sulphur deposition ($g S m^{-2} yr^{-1}$).

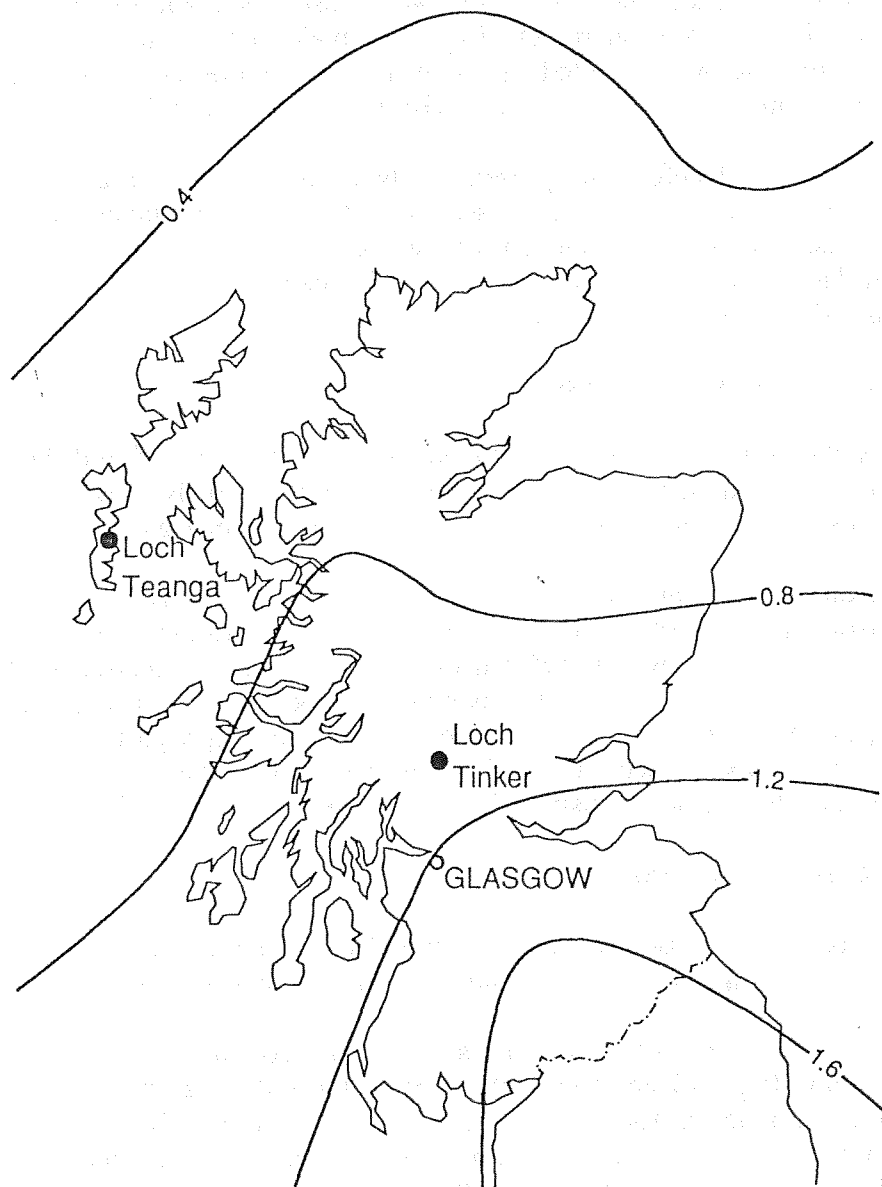


Figure 13. Carbonaceous particle profile of Loch Teanga

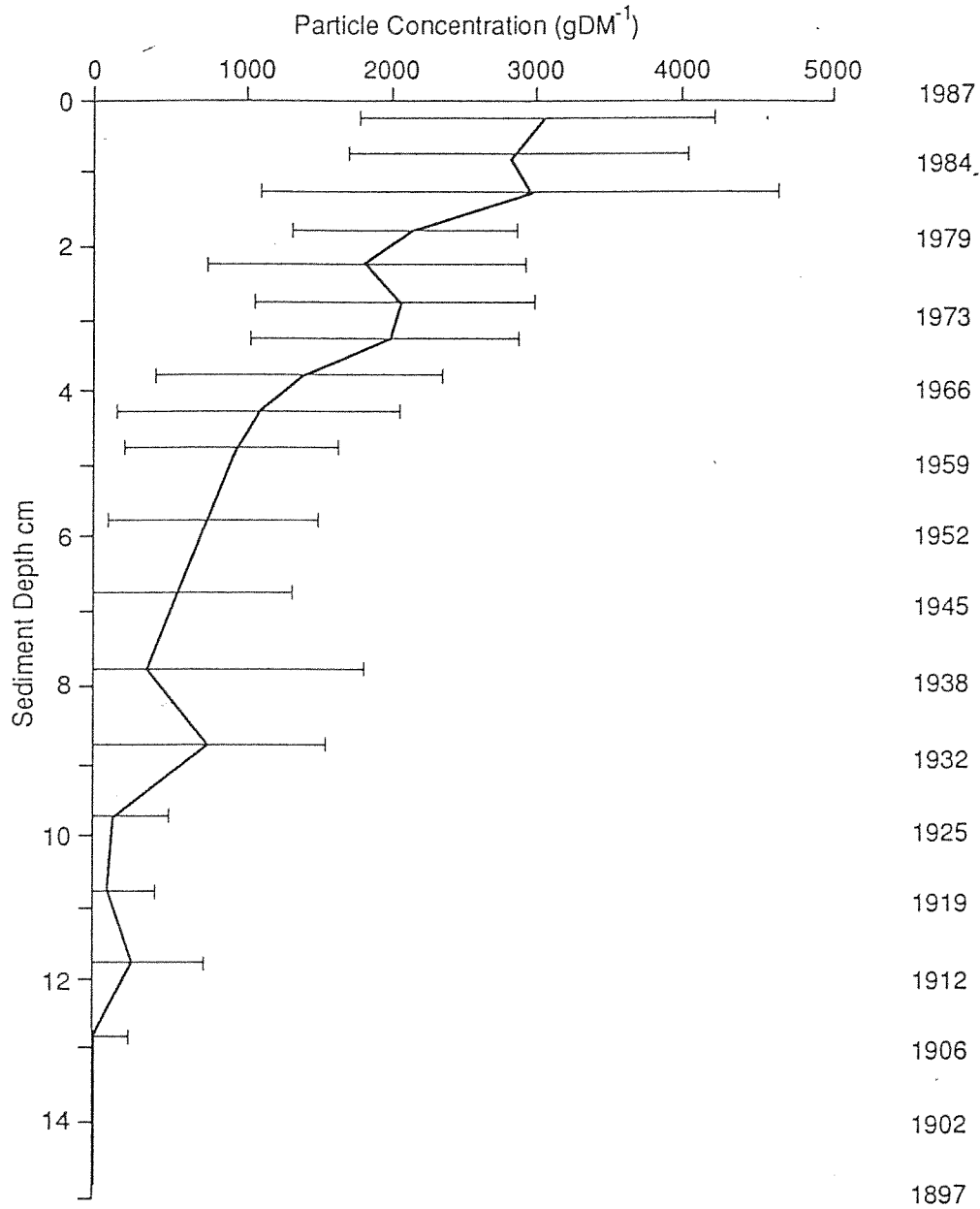
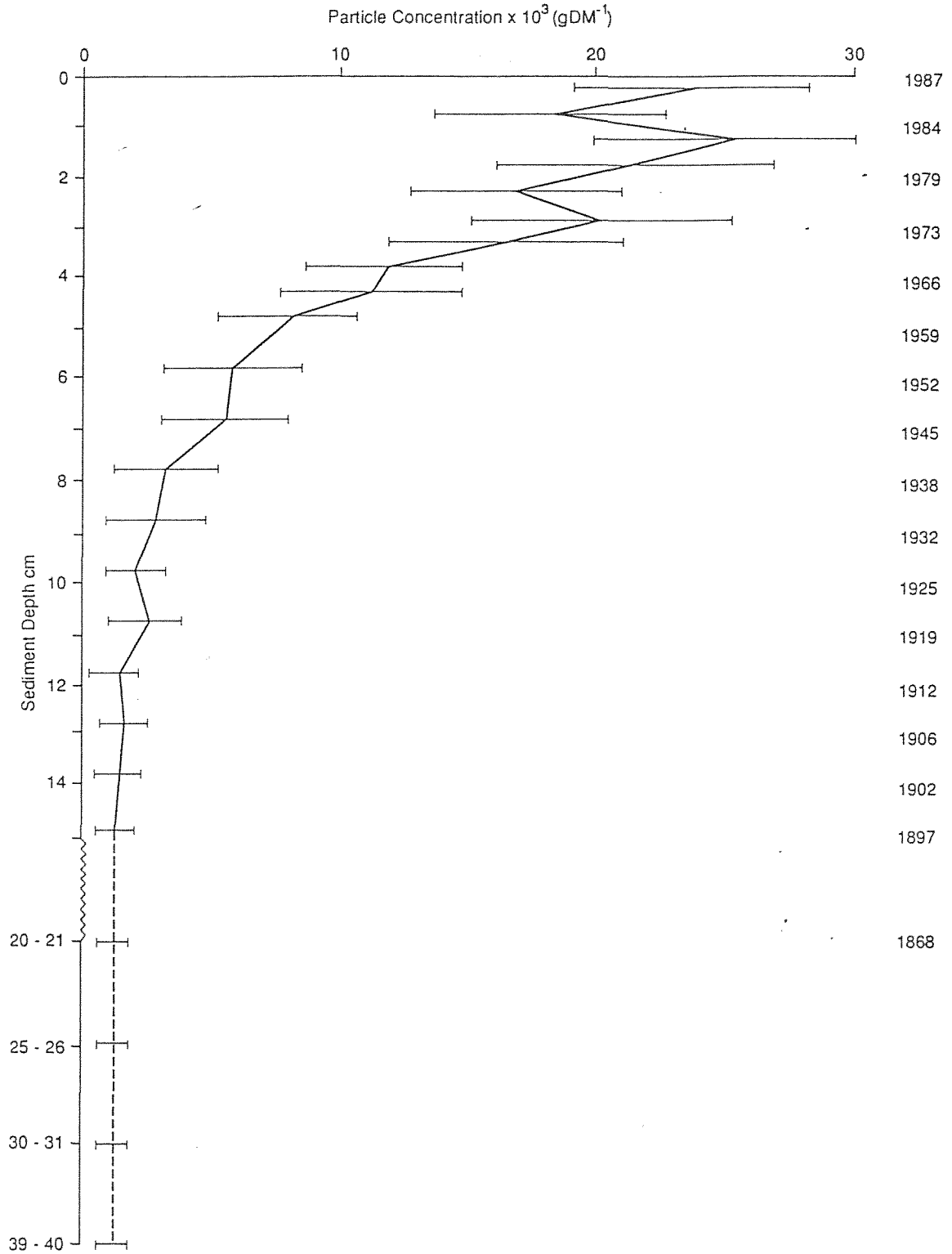


Figure 14. Inorganic ash sphere profile for Loch Teanga.



5.2 Application of EDAX to Loch Tinker surface sediments.

With a few exceptions, fossil-fuel combustion in Scotland has been almost exclusively coal based, and so a characterisation of carbonaceous particles in Scottish sediments should show a bias towards coal origin. The surface sediments (0.0 - 0.5cm and 1.5 - 2.0cm) of Loch Tinker were chosen to test this, as the carbonaceous particle analyses showed a high concentration, giving abundant particles for the analysis.

The 5539 particles of the reference data set were used to produce the discrimination and then 2217 particles from the 0.0 - 0.5cm layer and 554 particles from the 1.5 - 2.0cm layer were characterised, using different post-probabilities. The results were as follows:

0.0 - 0.5cm (1985)

Post-prob	% coal	% oil	% other
0.50	89.1	10.9	0.0
0.75	88.5	9.8	1.7
0.90	88.1	9.2	2.7

1.5 - 2.0cm (1975)

Post-prob	% coal	% oil	% other
0.50	82.3	17.7	0.0
0.75	81.0	16.8	2.2
0.90	79.8	14.8	5.4

The different settings of the post-probability make little difference to the fuel-type allocations, and so the confidence that these results are correct can be fairly high. They also support the hypothesis that coal-burning would cause the major impact on the loch, as does the high inorganic ash sphere: carbonaceous particle ratio.

5.3 Application of extraction and characterisation methods to a sediment core.

5.3.1 Site selection and coring.

A site was needed to study the change in coal and oil use through time using EDAX characterisation. To maximise EDAX efficiency a site with many particles at all levels is most suitable, in an area where there has been a significant change in fuel type. London having been the area of much of the early development of the power generation industry in this country, has a long record of coal burning up until the 1950's. Since then, increasingly more of London's power has been generated outside the city, some of which is by oil-fired generating stations at, for example, the Isle of Grain and Belverdere plants. The ponds on Hampstead Heath in North London (see figure 15) therefore fulfil the criteria, and the Men's Bathing Pond was selected for coring. This was done by means of a modified piston corer, in October 1987.

Figure 15. Location map of the Men's Bathing Pond, Hampstead Heath, London

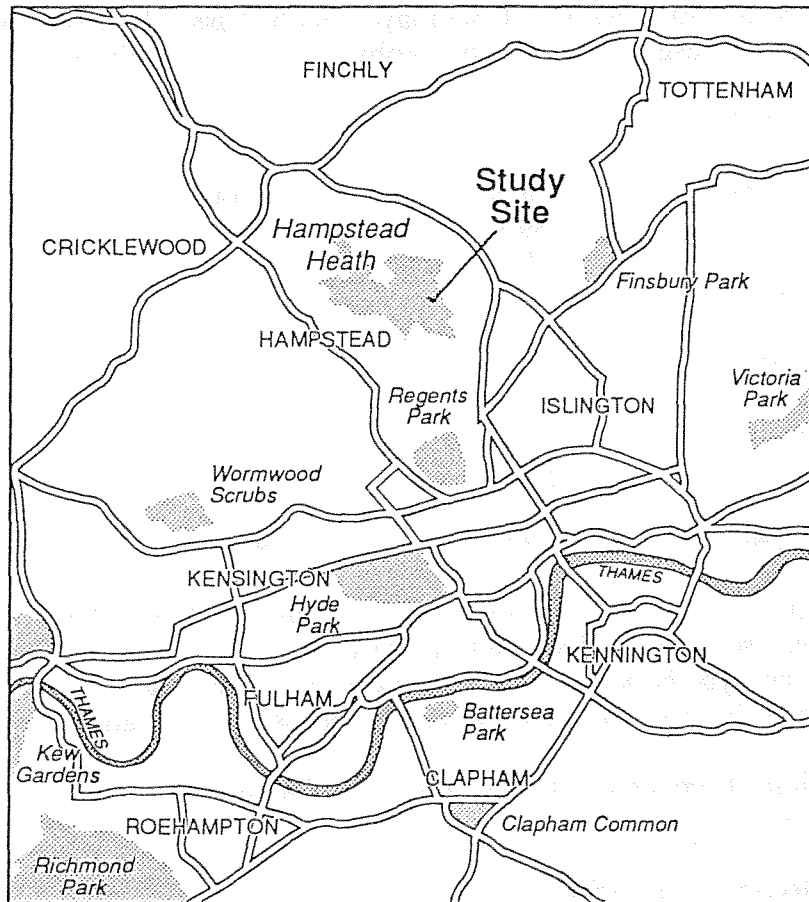
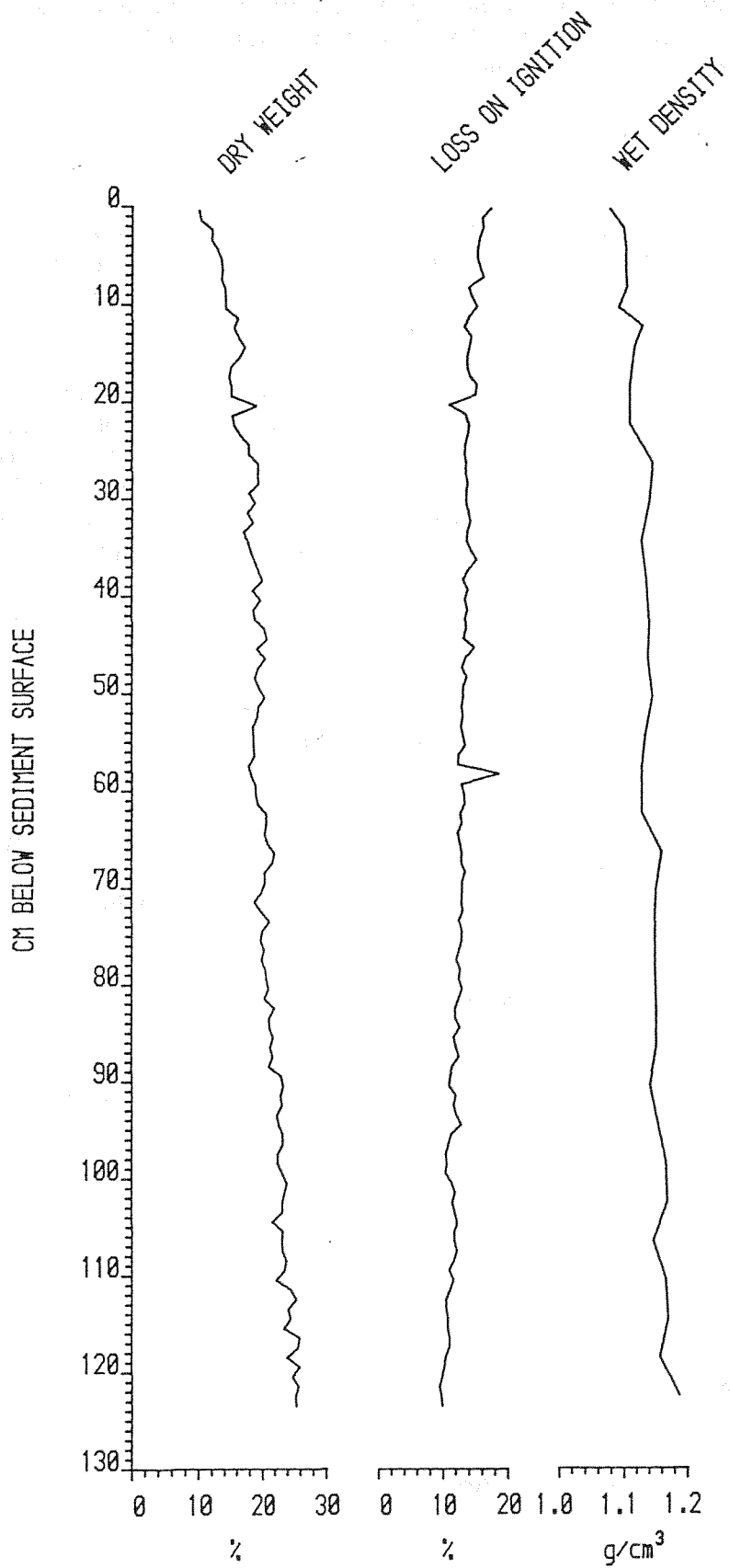


Figure 16. Loss on ignition, dry weight and wet density profiles for the Hampstead Heath core.



5.3.2 Sediment description.

The percentage dry weight and wet density profiles (figure 16), show only minor downcore variations and both decline in the top few centimetres, indicating increased water content in the top surface sediments. The loss-on-ignition profile also exhibits little variation, and with the exception of one or two spikes increases steadily towards the surface.

5.3.3 Dating

Sediment samples from the Hampstead Heath Bathing Pond core were analysed for ^{210}Pb , ^{226}Ra , ^{137}Cs , and ^{241}Am by gamma spectrometry using a well-type coaxial low background intrinsic germanium detector fitted with a NaI(Tl) escape suppression shield (Appleby et al., 1986).

^{210}Pb dates calculated using the CRS (constant rate of supply) model and CIC (constant initial concentration) ^{210}Pb dating models (Appleby & Oldfield, 1978) both suggest that the entire core consists of very recent sediment, post-dating 1920 and indicate a rapid accumulation of sediment. The mean value of the sedimentation rates given by the two models is $0.462 \text{ gcm}^{-2}\text{yr}^{-1}$, and dates calculated using this mean value are given in Table 8. These do not differ from those given in the CRS model by more than a year. The ^{210}Pb inventory of the core is 24.0 pCig^{-1} , and this corresponds to a mean ^{210}Pb flux of $0.75 \text{ pCicm}^{-2}\text{yr}^{-1}$. This is well in excess of expected atmospheric flux, and suggests that the core site may be subject to extensive sediment focusing.

Because of the rapid accumulation rate, the ^{137}Cs activity in the core appears to provide an accurate record of the fallout from atmospheric testing of nuclear weapons. A well-defined maximum exists at 52.5cm and can be presumed to record the 1963 fallout maximum. The onset of ^{137}Cs activity in the core between 80cm and 60cm can be presumed to mark the onset of fallout in 1954. A small peak present at 4-5cm probably represents the fallout from Chernobyl in 1986 as London was not greatly effected by this incident. These dates are in good agreement with the ^{210}Pb results, which put 1963 at a depth of 55cm, 1954 at 75cm and 1986 at 5cm.

Table 8. ^{210}Pb chronology of Hampstead Heath core.

Depth (cm)	Cum Dry Mass (gcm^{-2})	Chronology Date	Chronology Age	Sedimentation rate ($\text{gcm}^{-2}\text{yr}^{-1}$)	Sedimentation rate (cmyr^{-1})
0.0	0.0000	1987	0	↑	↑ 2.50 ↓
5.0	0.6295	1986	1±2		
10.0	1.3846	1984	3±2		
15.0	2.2560	1982	5±2		
20.0	3.1275	1980	7±2		
25.0	4.1162	1978	9±2		
30.0	5.1180	1976	11±2		
35.0	6.1587	1974	13±2		
40.0	7.2036	1971	16±2		
45.0	8.3089	1969	18±2		
50.0	9.4208	1967	20±2		
55.0	10.5005	1964	23±3		

60.0	11.5802	1962	25±3	0.462	2.11
65.0	12.7356	1959	28±3	↓	↓
70.0	13.8909	1957	30±3		↓
75.0	15.0463	1954	33±3		↑
80.0	16.2017	1952	35±3		↑
85.0	17.4624	1949	38±3		↑
90.0	18.7347	1946	41±3		↑
95.0	20.0071	1944	43±3		↑
100.0	21.3135	1941	46±3		1.74
105.0	22.6994	1938	49±3		↓
110.0	24.0852	1935	52±3		↓
115.0	25.4710	1932	55±3		↓
120.0	26.856	1929	58±4		↓

5.3.4 Carbonaceous particle and inorganic ash analysis

Carbonaceous particle and inorganic ash sphere concentration profiles were produced as described in sections 2 and 3. The results are shown in figures 17 and 18 respectively.

With a core such as this with a fast accumulation rate, there is a danger of over-interpretation, trying to assign an event to every peak and trough in the profile. The 95% confidence levels give some indication, especially for the inorganic ash, that the particle concentration profiles may be smoother than they appear in the figures. However, the surface values of the carbonaceous particle profile do show that there is a good deal of variation within a short period of time. The ten values in the 0 - 10cm region only cover a period of 3 - 4 years and it would be easy to over-interpret the spikiness in this region as high winter values and low summer values depending on the amount of electricity produced for heating and lighting.

Some of the basic trends seen in the Scottish cores are present here too. The steady increase in carbonaceous particle concentration until the 1950's and then a sharp increase. Here though, a peak occurs in the mid to late 1960's, possibly due to the introduction of electrostatic precipitators or perhaps the power station closure programme, which reduced the number of stations in the south-east region from 73-46 between the years 1964 and 1972 (CEGB Annual reports). There is a general trend in carbonaceous particle concentration from the late 1960's to the present.

The inorganic ash profile, also shows an increase in concentration up to the 1950's, but whereas the carbonaceous particle profile goes on to peak, the inorganic ash profile drops away again up to the early 1970's when there is a sharp increase and a peak in the mid to late 1970's. Inorganic ash particles result mainly from coal combustion and this profile could be interpreted by looking at fossil fuel consumption during this period. Coal consumption peaked in 1968/69 and then dropped during the early 1970's whilst oil consumption rose over the same period. Then following the oil crisis consumption decreased while coal consumption increased to peak in 1979/80 (All coal and oil statistics from Handbook of Electricity Supply Statistics, The Electricity Council). Again there is a danger of over interpretation, but as figure 19 shows there is a close similarity over this period.

Figure 17. Carbonaceous particle profile for the Men's Bathing Pond core.

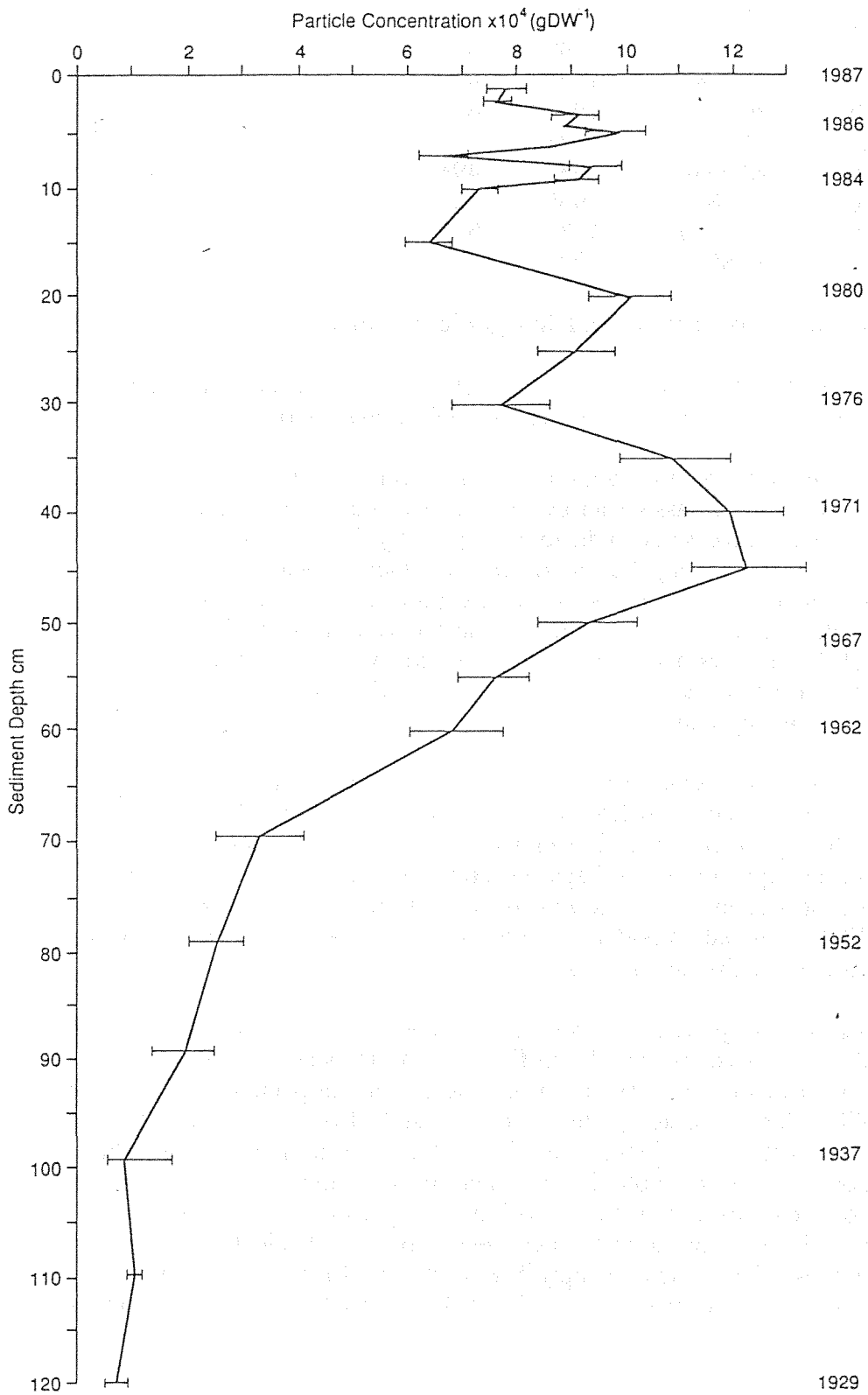


Figure 18. Inorganic ash sphere profile for the Men's Bathing Pond core.

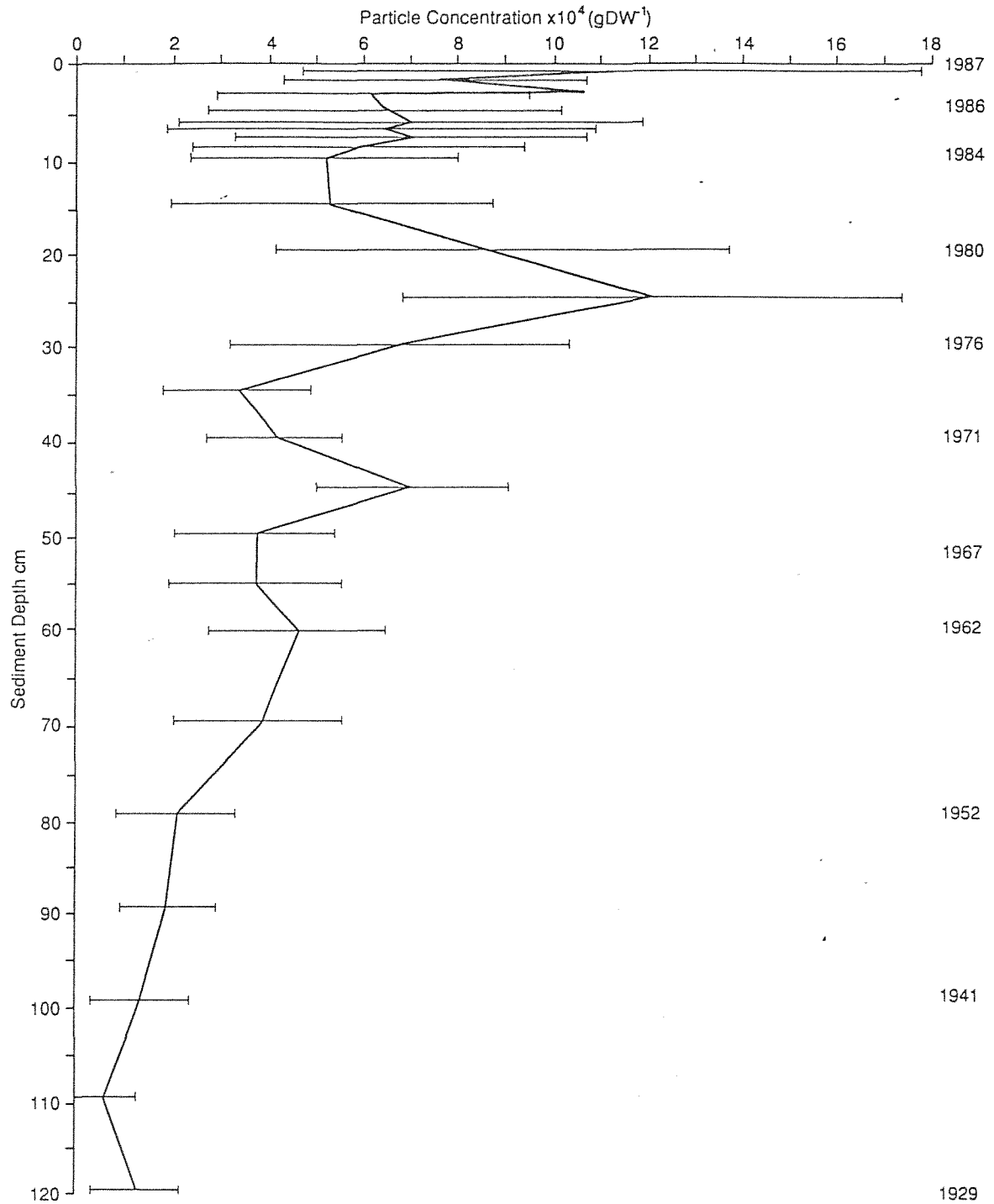
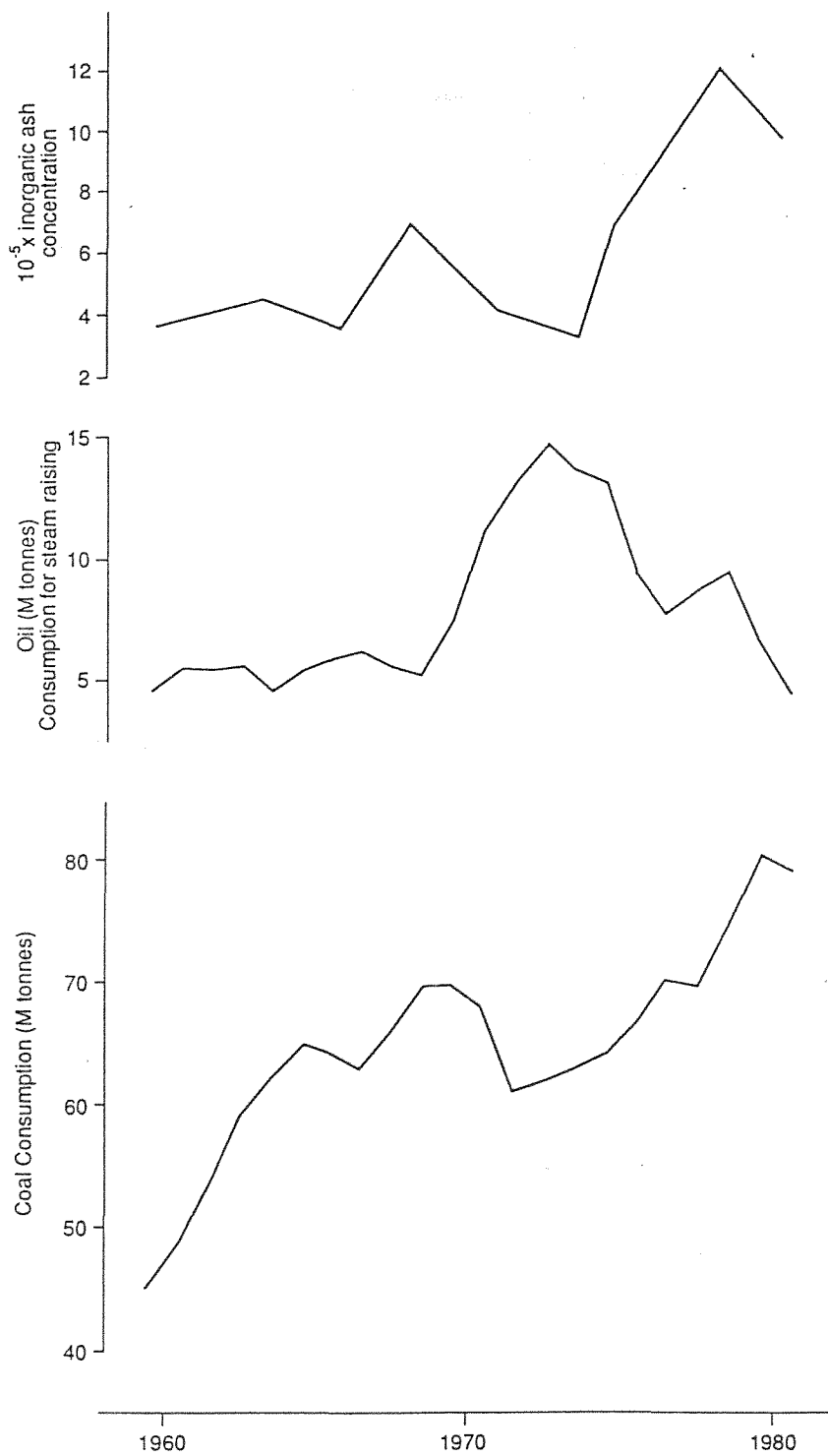


Figure 19. Comparison of inorganic ash sphere concentration in the Men's Bathing Pond core, and coal and oil consumption in U.K. between 1960 and 1980.



5.3.5 Particle Characterisation.

Between 150 and 400 extracted particles from 15 levels were characterised using the methods described above. Again the discrimination was produced using the 5539 particles of the reference data set. The results are shown in Table 9.

Table 9. *Fuel type allocation for Hampstead Heath core.*

Depth (cm)	Post-Probability = 0.5		Post-probability = 0.9		
	% coal	% oil	% coal	% oil	% other
0-1	69.9	30.1	56.5	16.7	26.8
1-2	86.3	13.7	74.4	8.4	17.2
2-3	78.8	21.2	67.1	8.9	24.0
3-4	78.9	21.1	59.9	12.8	27.3
5-6	73.5	26.5	58.9	15.4	25.7
7-8	72.1	27.9	55.7	15.2	29.1
9-10	77.8	22.2	63.9	12.3	23.8
14-15	89.7	10.3	85.6	5.4	9.0
19-20	83.6	16.4	78.3	9.9	11.8
24-25	78.8	21.2	74.4	16.0	9.6
29-30	83.8	16.2	78.1	9.8	12.1
34-35	80.4	19.6	76.8	15.2	8.0
39-40	78.7	21.3	74.7	13.0	12.3
49-50	80.3	19.7	76.2	14.2	9.6
59-60	87.1	12.9	81.5	7.3	4.2

These show that the influence of oil-fired particulates on the Hampstead Heath Pond has increased since the 1950's. It would be expected that earlier levels would exhibit up to 100% coal influence, and levels at 79-80cm, 99-100cm and 119-120cm are at present being analysed although the data are not yet available.

The increase in oil particles in the surface levels of the core is also shown by a decrease in inorganic ash sphere concentration in those levels. Although it is not possible to get an accurate prediction of one from the other, as the error margins in the inorganic ash profile are quite large, the trends in the two are similar.

It should be noted however, that this type of historical reconstruction is probably over-optimistic, as the calibration discrimination uses modern reference material. As oil burning power stations are relatively modern however, the classification of these particles should be better.

6. CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK.

- i) Methods for the extraction of carbonaceous particles and inorganic ash spheres from lake sediments have been developed giving repeatable and accurate results when applied to sediment cores. For the carbonaceous particles this, is an improvement on those methods to be found in the literature, and for the ash spheres is the first chemical extraction described.
- ii) A characterisation for differentiating between coal and oil carbonaceous particles has been developed using the surface chemistry of 17 elements. There is over 95% correct fuel-type allocation using this technique.
- iii) Application of these techniques to lake sediments gives information on the impact that different fuel combustion sources have on a lake and its catchment. This has been applied to both modern surface sediments and a historical record in a dated sediment core.
- iv) Although partial success was achieved upon attempting to characterise different power station sources using this chemical technique, much more work needs to be done to see if it is possible to do this separation with any degree of confidence.

There are two directions in which this work can be taken further. Firstly, using the methods in their present form to give information on history and distribution of particles and secondly to develop the methods still further to include new particle types and sources. For example:

- i) To assess the impact of future pollution control measures on an area. For example, the effect on particle deposition in lakes and ponds surrounding the Drax power station after the addition of FGD.
- ii) To use the extraction methods to produce a map of surface concentrations covering the country, to use the particles as a sulphur surrogate in areas where this is not measured directly.
- iii) To pinpoint sources as described in section 1.2. i.e. coal particles in Norway and Sweden, oil particles in Galloway etc.
- iv) Brown coals and lignite commonly burnt in central and eastern Europe could be characterised. These fuels contain elevated concentrations of certain trace elements, for instance, cobalt, zinc, chromium, nickel and cadmium (Mejstrik & Svacha, 1988). As these elements are low in coal, oil and peat, characterisation should prove possible and the long range transport of material to Britain and Scandinavia could be traced (e.g. Davies *et al.*, 1984)
- v) Use could be made of the inorganic ash spheres as geochronological markers of volcanic eruptions. The method described in section 3, has been used on a peat core taken from an Irish bog and a faint peak was found at the time of the Hekla III eruption, where other methods had failed to locate it. However, further work is needed in areas with well documented eruption histories to gain more confidence in the technique.

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