THE USE OF FLY-ASH PARTICLES FOR DATING LAKE SEDIMENTS

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Abstract

Fly-ash particles comprise two particle types, spheroidal carbonaceous particles (SCP) and inorganic ash spheres (IAS). In lake sediments, these particles form an unambiguous record of atmospheric deposition of industrial pollutants. The main temporal trends of these sediment records have been found to be remarkably consistent over wide geographical areas and these features can be used to ascribe dates to cores undated by other means. SCP are the main particle type used in this way as they are easier to extract and enumerate. IAS are morphologically similar to some natural particles (volcanic, meteoritic) and therefore show a natural background concentration at all pre-Industrial sediment depths. Apart from this background temporal trends are similar to SCP and IAS could be used for dating in the same way. Gaining an indication of fuel-type change, either from IAS:SCP ratio or chemical characterisation of SCP enables additional dates to be added to sediment cores through comparison with documentary evidence. In the future, as ^{210}Pb becomes progressively unable to date the post-Industrial sediment record, dating using fly-ash techniques may become increasingly important.

Introduction

As lake sediments accumulate they store an historical record of atmospheric pollutants deposited on to the lake and its catchment. These pollutants include fly-ash particles produced from the high temperature combustion of fossil-fuels. Fly-ash consists of two types of particle, spheroidal carbonaceous particles (SCPs) (Fig. 1) formed from the incomplete combustion of the fuel, and inorganic ash spheres (IAS) (Fig. 2) formed by the fusing of mineral inclusions. Fly-ash particle analyses on lake sediment cores and surface sediments

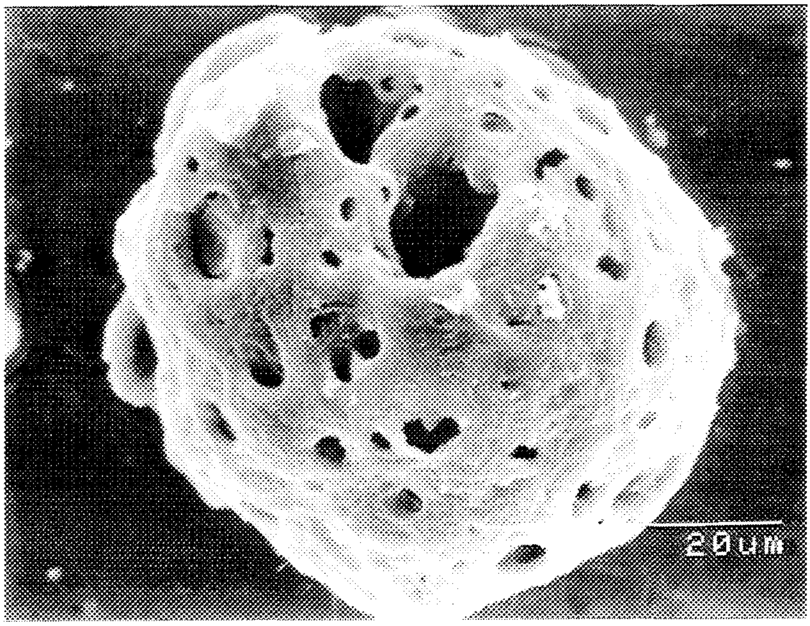

Figure 1. Spheroidal carbonaceous particle (SCP) from the incomplete combustion of fossil-fuel extracted from a lake sediment core.

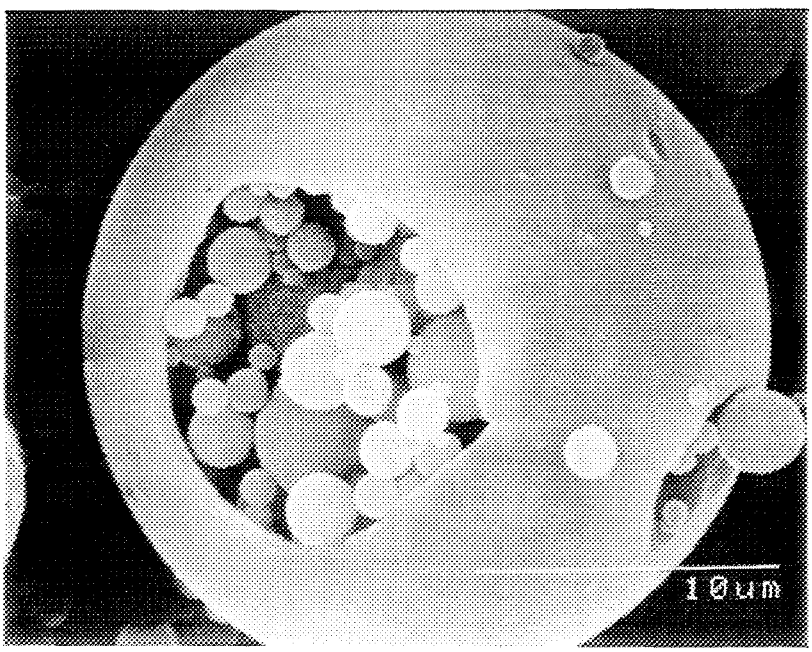

Figure 2. Inorganic ash sphere (IAS) containing enclosed plerospheres. Such particles are formed by inconsistencies in melting the mineral grain.

provide a temporal and spatial record of the impact of fossil-fuel combustion on a region.

Although physically fragile, SCP are chemically robust and so strong mineral acids (HF, HNO_3 & HCl) can be used in their extraction from sediments (Rose, 1994). In addition, they are morphologically characteristic, have no natural sources and therefore in lake sediments form unambiguous indicators of atmospheric deposition from industrial sources. IAS, however, are mainly composed of aluminosilicates and therefore have to be extracted using less rigorous means. This results in a less complete extraction and consequently IAS are more difficult to enumerate than SCP. They are also morphologically similar to volcanic microspherules and micro-meteorites. Most palaeolimnological studies have therefore used SCP in preference to IAS although some additional information is obtainable from the use of both particle types. Studies on the chemical characterisation of fly-ash particles (for source apportionment studies) also utilise SCP rather than IAS. This is because the SCP chemistries reflect the fuel from which they were derived whereas the IAS chemistries reflect their mineral origins rather than being fuel-specific. Results from particle characterisation can also be used to ascribe additional dates to sediment cores.

Background

The first carbonaceous particle profile for lake sediments was produced by Griffin and Goldberg (1981). This was a profile of percentage carbon by weight for a core taken from Lake Michigan using infra-red techniques on the >38μm fraction. A carbon record was present at all sediment levels due to domestic wood burning and natural fire sources and the industrial fossil-fuel record began at around 1900. This was shown by an increase in carbon levels and a change in particle morphology towards a more spherical nature. Carbon concentrations were shown to double in the periods 1900-1930 and 1930-1960 followed by a decline. It was concluded that particles found in lake sediments produced by the high temperature combustion of fossil-fuels were characteristically spheroidal, and that the change in concentrations of this type of particle reflected the changes in fossil-fuel consumption and the introduction and improvement of particle-arresting techniques at the combustion sources.

The first European profiles of SCP concentrations were produced for Swedish lakes (Renberg & Wik, 1984, 1985a & 1985b). These were also seen to reflect the historical development of coal and oil burning with the beginning of particle deposition seen to be around the middle of the 19th century due to increased coal burning in the Industrial Revolution. This was followed by a steady rise in concentration and, after the Second World War, a sharp increase in particle concentration caused by increased oil consumption. A peak concentration occurred around 1970 followed by a general decline in particle concentration. This pattern emerged so consistently that it became possible to use these SCP profiles as a dating method for sediment cores in Sweden (Renberg & Wik, 1985b).

The first SCP profile for a U.K. lake sediment core was produced for the Round Loch of Glenhead by Darley and was shown to be correlated strongly with the history of fossil-fuel combustion in the U.K. (Darley, 1985). Rose *et al.* (1995) later used this approach to (a) date lake sediment cores from the U.K. and Ireland, and (b) to show that there are regional differences within countries which must be taken into account when attributing dates. SCP profiles have now been produced extensively within Europe and the main temporal patterns remain consistent from Svalbard to the Sierra Nevada in southern Spain and from western Ireland to the Tatra Mountains in Slovakia and Poland (Rose *et al.*, in prep.) SCP profiles have also been determined for lake sites in many parts of the world including China, USA, Siberia and Tasmania and the principles of dating apply equally well in all locations.

SCP Profiles

The technique of dating sediment cores using fly-ash particle concentration profiles relies, in the first instance, on dating the first few profiles in a region using independent dating means such as ^{210}Pb chronologies or varve counting. Once the main features of the particle profile have had reliable dates attributed to them then subsequent profiles in that region can themselves be used for dating.

In most SCP profiles there are three main features that are used for dating purposes (Fig. 3). These are the start of the particle record (A), the rapid increase in SCP concentration (B) and the SCP sub-surface maximum (C). These features occur in most sediment profiles, except where sediment accumulation rate or variability obscures them, and can usually be related to major events in industrial development or pollution control strategy in the main source areas.

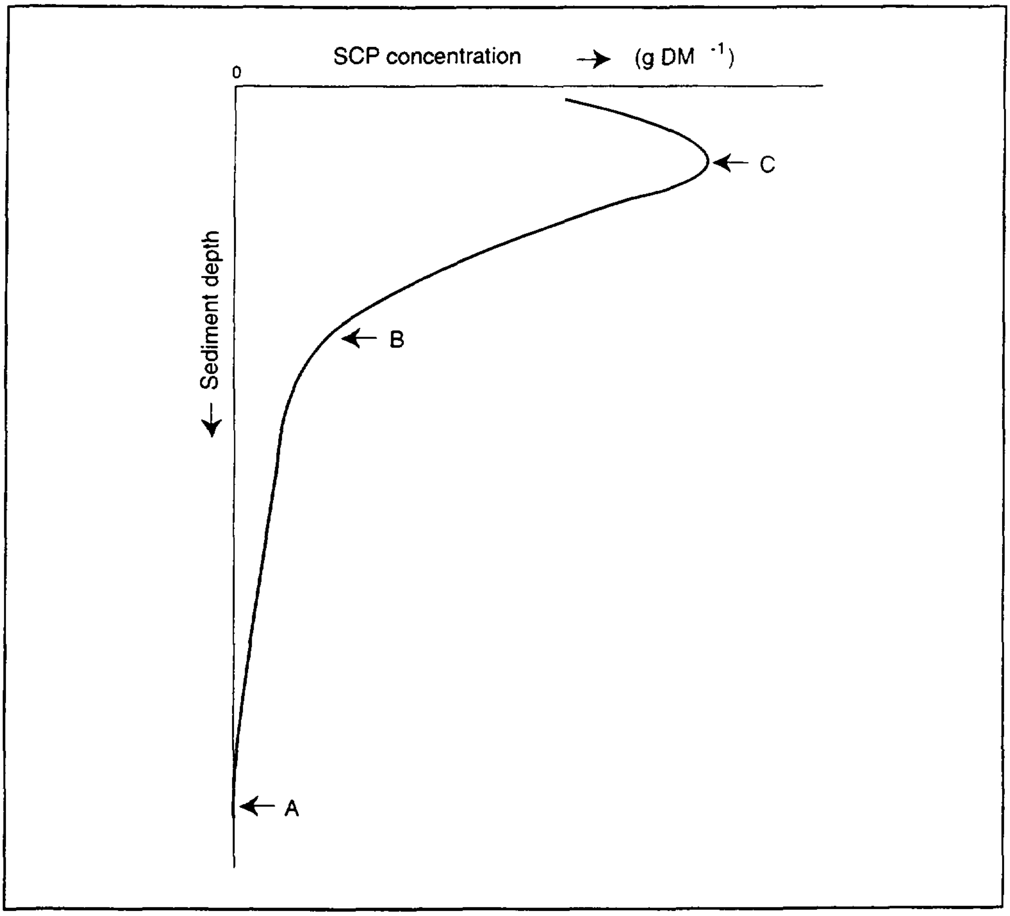

Figure 3. *A schematic SCP profile showing the three profile features used for dating:* ***A*** *- the start of the particle record,* ***B*** *- the rapid increase in concentration - defined by the change in slope of the two parts of the profile,* ***C*** *- the SCP concentration peak. (Figure taken from Rose et al., 1995)*

It should be stressed that SCP are found in areas far removed from sources suggesting there is a possible 'northern hemispherical background' of SCP deposition. However, in most regions this background has regional or local deposition patterns superimposed upon it and it is these patterns that are most useful in profile interpretation and dating.

The start of the record

Using the U.K. as an example, the start of the SCP record is generally seen to occur in the middle of the 19th century and this is generally attributed to developments in the Industrial Revolution and the combustion of larger quantities of coal at higher temperatures. The Industrial Revolution in Britain began in the early years of the eighteenth century with the development of a pumping engine by Savery, Papin and Newcomen, but it was not until the late nineteenth century and the work of Faraday and Gramme that the industrial generation of electricity finally became practicable. The first fossil-fuelled power station supplying electricity to the public was situated at Holborn Viaduct in London and began generation on 12th January 1882, and by the end of the century most large towns had their own electricity generating stations. The start of the SCP record in lake sediments therefore pre-dates the first power generating station and therefore during this period reflects the combustion of coal in industry as a whole. This may account for the variability in the start of the particle record both within and between regions, as local industries would have had a large impact on atmospheric deposition especially as industrial chimney heights were generally low at this time.

The dates for the start of the SCP record cover the largest range of the dating and so can be attributed to nothing more accurate than 'the mid-19th century' although the 1860s appear to be the most common decade. In Ireland, there is also a wide range of dates but these are generally later than for the U.K. and cover the late 19th and early 20th centuries. The same is true of many areas of Europe, but at remote sites the start of the record is often seen to be much later. This is probably because concentrations are much lower and so the start of the record at these sites becomes the date at which the SCP concentration first exceeds the detection limit of the technique rather than the true first date. In these cases the start of the record appears to show reasonable agreement with the rapid increase feature in more polluted lakes in the region.

Although such a wide margin may appear to limit the usefulness of this feature as a dating tool, it should be noted that errors on ^{210}Pb dates for this period are frequently ± 15-20 years and sometimes more (e.g. 1896 ± 24 is the earliest date available for a Loch Uisge, Scotland core) making the dating margin for both of similar magnitude.

The rapid increase feature

From the 1920s and 1930s onwards, the consumption of coal in the U.K. continued to increase, and this accelerated after the Second World War due to a considerable increase in total energy demand. An abundance of cheap fuel-oil also became available at this time and led to the commissioning of the first oil-fired power station in the U.K. at Bankside, London in 1952. During this period of expansion and increased consumption in the power generation industry there was a substantial reduction in coal consumption in other industrial markets and the railways. Particle emission legislation was also limited at this time as the Clean Air Act was not passed until 1956.

The SCP record for this period shows a rapid increase in most U.K. sediment cores and it seems probable that this mainly reflects the increased fuel consumption of the electricity generation industry. Although this feature usually dates to the 1950s or 1960s it also varies with region and is present in virtually every analysed core both within U.K. and throughout Europe (Wik & Natkanski, 1990; Cameron *et al*, 1993; Toro *et al.*, 1993, Rose *et al.*, in prep.).

The sub-surface maximum

Coal consumption throughout the U.K. continued to increase until the late 1970s. Since this time, consumption has remained reasonably steady in England and Wales (Electricity Council, 1988) although in Scotland it decreased from about 8 million tonnes in the late 1970s to about 3 million tonnes in 1985 mainly due to the reduction in heavy industry. Oil consumption throughout the U.K. increased from the 1950s until 1973 when the massive price increases imposed by OPEC (Organisation of Petroleum Exporting Countries) and the oil shortage caused by the Arab oil embargo of 1973-1974, caused consumption to decrease again.

Starting in the 1930s, the Central Electricity Board (C.E.B.), (later to become the Central Electricity Authority (C.E.A.) and then the Central Electricity Generating Board (C.E.G.B.)) continued a policy of creating fewer, larger and more efficient power stations. In addition, following the Clean Air Act of 1956 (and subsequent amendments and extensions) all new power stations were fitted with dust extraction equipment. The increase in particle removal efficiency and the implementation of more rigorous pollution control legislation meant that despite the continued increase in fuel consumption the increase in particulate emissions slowed down and from the mid 1970s started to decrease.

The particle record in lake sediments for the post-War period shows a continued increase in concentration to a peak, usually dating to the late 1970s / early 1980s followed by a decline in SCP concentration to most recent times. This recent reduction in the number of SCPs reaching lake sediments throughout the British Isles is therefore probably due to a combination of two factors. Firstly, the small decrease in fossil-fuel consumption (probably more significant in Scotland than elsewhere) and secondly, improvements in the removal of particulates from flue gases and to the more widespread use of these techniques, caused by the implementation of more stringent air pollution legislation.

This last feature is the best defined of the three and in the U.K. can normally be ascribed with an accuracy of ± 3-4 years (Rose *et al.*, 1995). As with the other two features the date for the SCP peak varies between the different regions. In this particular case, however, the range of dates is narrower and the difference between regions is only a few years. Most recent cores in Europe show this feature except those with very low sediment accumulation rates (Cameron *et al.*, 1993, Rose *et al.*, in prep.) Regional dating variations for all profile features are to be expected due to variations in emission histories across Europe. However, how localised these variations are has not been studied except in parts of the U.K. and Ireland (Rose *et al.*, 1995).

Further, more detailed, dating using SCP data may be possible using cumulative SCP profiles. This is especially the case where the dates to be transferred are between multiple cores taken from a single lake. Although only limited data exist, cumulative SCP profiles appear to show much closer agreement than multiple SCP concentration profiles and it may be that more dates can be ascribed to sediment profiles between lakes using this approach in addition to using the `traditional' three SCP features (Rose *et al.*, in press).

IAS profiles and IAS:SCP ratios

As IAS are also produced from fossil-fuel combustion, the post-Industrial sediment record shows similar trends to those of SCP. However, there are two points of note when comparing the profiles. First, IAS shows a continuous background concentration at all pre-industrial levels, and second, there can be significant differences in concentration depending on where the sediment core is taken with respect to deposition sources (e.g. Fig. 4).

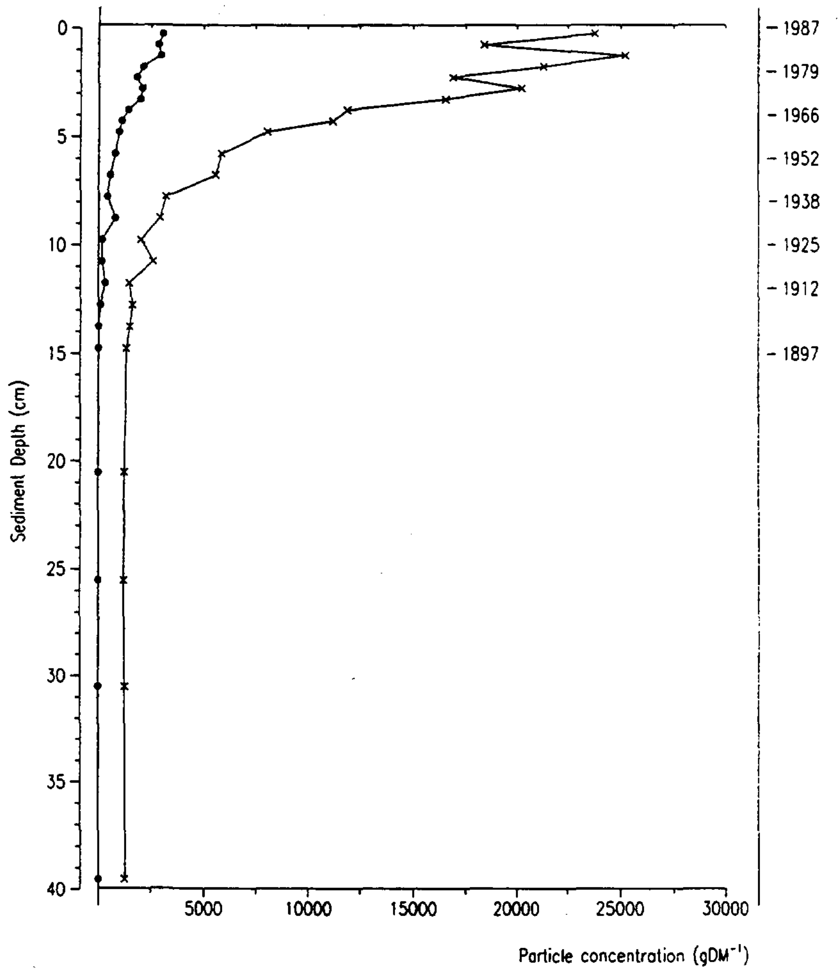

Figure 4. IAS and SCP profiles for Loch Teanga in the Outer Hebrides, Scotland. • = SCP, x = IAS. (Figure taken from Rose, 1996)

The continuous background is due to naturally produced IAS either from volcanic microspherules (Lefèvre *et al.*, 1986) or possibly micrometeorites (Wohletz & McQueen, 1984). These appear morphologically identical to the IAS under the light microscope and the particle types cannot be distinguished in this way (Rose, 1996). Meteoritic spheres could be isolated by chemical means but volcanic particles may still not be distinguishable. If this background concentration is removed from all sediment levels then the IAS profile begins at the same date as the SCP profile. In a country where the dominant fuel is coal (such as the U.K.) then the other profile features are similar to those of SCP and dates can be attributed in the same way.

The second point of interest is the difference in sediment concentration of IAS and SCP. For many Scottish lochs, IAS concentrations are higher than SCP concentrations with a surface ratio of these particle concentrations (the IAS:SCP ratio) of greater than 5.0. For sites in the south-east of England however, the concentrations of both particle types are approximately equal at the surface. For one site in London, on Hampstead Heath, there is a ratio minimum in the mid 1970s but prior to this there is a steady decrease in ratio since the 1920s.

Fossil-fuel combustion in Scotland at the time these cores were taken was almost solely coal except one oil-fired power station situated at Peterhead near Aberdeen, and another at Inverkip in Glasgow which closed in 1987. It is known that pulverised coal fly-ash typically contains greater than 95% inorganic material and so the fly-ash particles emitted and deposited in Scotland should be predominantly IAS rather than SCP. The south-east of England however, has a much higher proportion of oil-fired stations and within a 40km radius of London there is 5,700 MW capacity of oil-fired electricity generation and 4,790 MW of coal. Oil fly-ash is predominantly composed of SCP and so it might be expected that the IAS:SCP ratio at a London site would be much lower than those from Scotland. The period between the mid 1950s and the oil crisis of the mid 1970s was a time of rapid expansion in the use of oil in the U.K. and it is interesting to note that this is the only period for the Hampstead Heath site where SCP concentrations are greater than those of IAS (Fig. 5).

An alternative explanation may be that as IAS generally have a smaller diameter than SCP they can travel further in air streams and it is distance from source that is the main criterion explaining IAS and SCP variability. However, Loch Tinker, only 45km from Glasgow shows a high ratio throughout the

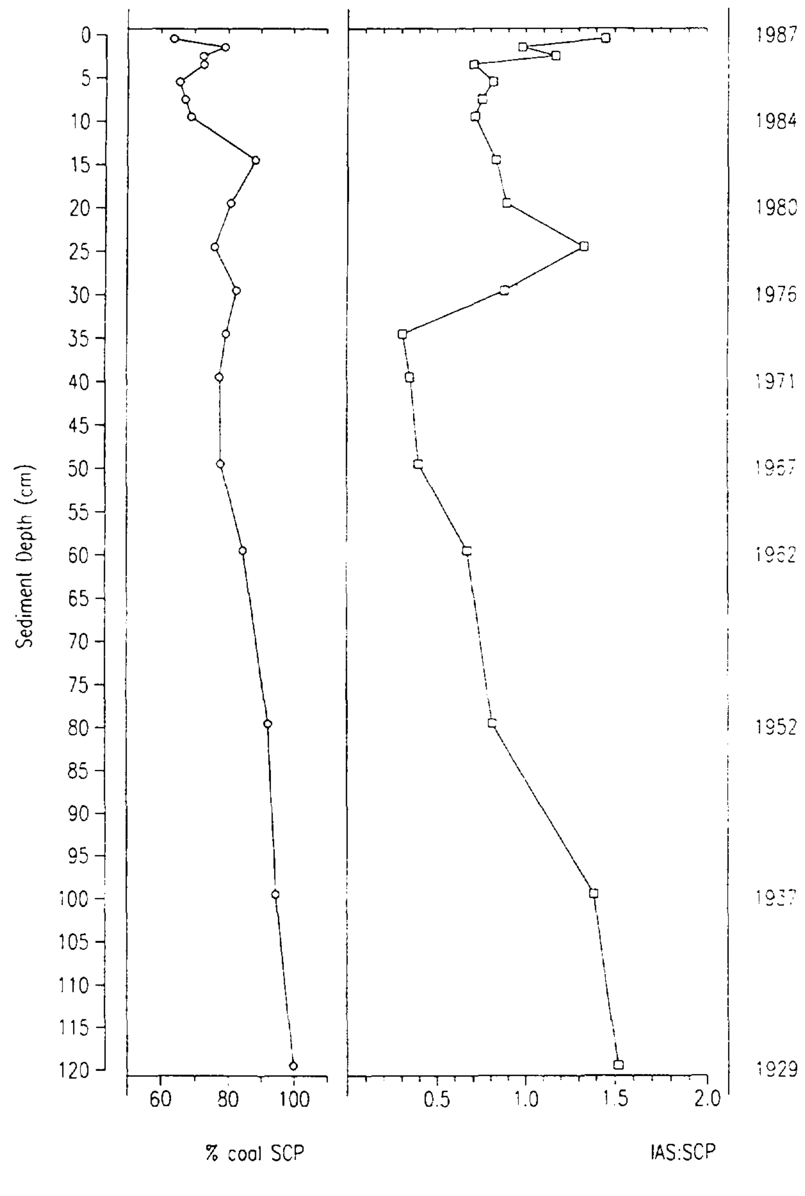

***Figure 5.** IAS:SCP ratio and particle characterisation data for a sediment core taken from Hampstead Heath, north London, U.K.*
*(Figure taken from Rose, **1996**)*

profile (> 5.0) and therefore it seems unlikely that distance from source alone explains the difference between the IAS:SCP ratios. Regional fuel-use is therefore the most likely factor explaining this difference and therefore it may be possible to use IAS:SCP ratios to gain an idea of the relative impacts and temporal changes in the combustion of coal and oil on atmospheric depositions at a lake site in the U.K. This information, in combination with a historical documentary knowledge of combustion within that region, allows the possibility of ascribing additional dates to the sediment profile.

Dates from SCP characterisation

All the above dating approaches have used sediment particle concentration data only, but further information is available from SCP if they are characterised to their fuel-type using their elemental chemistries (Rose *et al.*, 1996). A technique has now been developed which allows sediment extracted SCP of coal, oil, peat, brown coal and oil shale origin to be allocated with high levels (>80%) of confidence. This approach is more accurate at determining fuels than the particle ratio technique and allows historical records of specific fuels to be used. It therefore provides more specific information from a sediment core. However, for regions such as the U.K., where there are only two main fuel-types, coal and oil, the two approaches provide similar information, albeit that the characterisation technique is more reliable. The advantage of the chemical approach becomes more obvious when making comparisons between countries. For example, particle ratios in Estonia will be similar to those in the U.K. despite the fuels being very different, and this is because oil shale, like coal, produces large numbers of IAS compared to SCP. In regions where such fuel-types overlap the particle ratio approach would be of limited use although the chemical characterisation approach may still be useful.

In areas where there has not been significant fuel-type changes through time, both particle ratio and chemical characterisation techniques will be of limited use. The 'traditional' profile dating approach will, however, still be useful.

Conclusions & the future

The use of fly-ash particle profiles allows a cheap and quick method for allocating dates to sediment cores, but allocatable dates are few and accuracy is perhaps not as good as more established techniques such as ^{210}Pb and varve counting. However, in sites without varves the future of SCP dating is perhaps more assured.

Over the last 10-15 years ^{210}Pb dating has proved very useful in many palaeolimnological studies concerned with surface water acidification and pollutant deposition. This is because the half-life of ^{210}Pb enables a chronology to be constructed for the past 100-150 years, spanning the major part of the period since the Industrial Revolution. In future years this will cease to be the case as the early years of this period progressively fall below the ^{210}Pb dating horizon. Since there is no indication that SCPs are mobile within the sediment column (except possibly for some surficial mixing in the initial stages) or that they degrade with time, the start of the particle record may become one of the few ways of dating the early part of this period. The other features of the SCP profile (B and C in Figure 1) will be of increasing value in providing a relatively quick and cheap means of determining approximate core dates that can be used on their own, or as a means of increasing the reliability of more detailed ^{210}Pb chronologies. Therefore unless new techniques are developed, fly-ash dating will become increasingly more important in future years and, in combination with ^{210}Pb, will ensure that the entire post-Industrial period remains accessible to palaeolimnologists through the use of the lake sediment record.

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