

Characterisation and Distribution of Carbonaceous Particles in Lake Sediments

Abstract

Spheroidal carbonaceous particles produced by high temperature combustion of coal and oil are found in high concentrations in the surface levels of lake sediments in areas of high acid deposition. The sediment record of these particles showing the onset of industrialisation correlates well with the record of acidification as indicated by diatom analysis.

To find sources of the atmospheric deposition affecting a lake and its catchment, characterisation of the carbonaceous particles is necessary. A reference data set of particle chemistries from coal and oil power stations was produced for 17 elements using energy dispersive spectroscopy (EDS). Using stepwise discriminant analysis and principal components analysis, the most important elements for the coal/oil separation were identified and incorporated into a linear discriminant function which allocates particles to their fuel type with 97 % accuracy.

Application of this technique to surface sediments in Scotland shows the influence of oil burning from outside the region, higher oil areas located on the east coast and in the south-west of the country. When applied to a full sediment core, the history of coal and oil combustion affecting the lake is seen and this correlates well with known fossil fuel consumption figures.

The technique has been extended to include peat particles and could potentially be used on those from brown coal and lignite combustion.

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 and Goldberg, 1981 ; Renberg and Wik, 1984). Sites in the United Kingdom show close correlation between the onset of atmospheric contamination as indicated by carbonaceous particles and heavy

metals 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, spheroidal 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 spheroidal carbonaceous particles. Those produced from peat combustion have an amorphous appearance, many still retaining some cellular structure.

The inorganic ash spheres have not been characterised because, being fused mineral inclusions their chemistry is independent of fuel type, and they are almost exclusively coal in origin.

METHODS

The sediment cores were taken using a variety of methods (e.g. Livingstone, 1955; Kajak, 1966; Mackereth, 1969) and the particles were extracted from the sediments using selective chemical attack to remove unwanted fractions as described in Rose (1990).

The EDS analysis of the particle chemistries was undertaken at Imperial College using a JEOL 733 Superprobe linked to a Scanning Electron Microscope (SEM). These data were gathered using a fully automated technique as described in Watt (1990). Initial handling of these data used the MIDAS program before being transferred for further statistical analysis. Hampstead Heath core was dated in the University of Liverpool Environmental Radiometric Laboratory using gamma spectrometry to analyse for ^{210}Pb , ^{226}Ra , ^{137}Cs and ^{241}Am (Appleby *et al.*, 1986).

A REFERENCE DATA SET

In order to construct a classification scheme for carbonaceous particles, reference samples of fly-ashes were needed from the various potential 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.

Ten stations were selected, 5 coal and 5 oil to produce a reference data set of particle chemistries 'typical' of these fuel types. One peat station was also included in the characterisation study to show that the scheme can be extended to include other fuel types. 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, first to subject the reference material to the same chemical treatments as the particles extracted from sediments and secondly to remove the inorganic ash spheres from the coal ash samples.

EDS was performed on these samples as described by Watt (1991 ; this volume), for the following elements : Na, Mg, Al, Si, S, P, Cl, Ca, K, Ti, V, Cr, Mn, Fe, Ni, Cu and Zn. Outliers were removed where extreme values occurred for several elements on a single particle. These often had very low total X-ray counts, showing them to be 'lacy' particles with very little surface area remaining after combustion. Once these outliers had been removed from the analysis, over 5500 particles remained upon which to base a classification scheme.

CHARACTERISATION

Principal components analysis (PCA) and stepwise discriminant analysis (SDA) were used to determine the most important elements in the separation. PCA transforms the original data into a series of principal components. The first principal component is the line of maximum variability passing through the data cluster, the second principal component is the line of maximum variability perpendicular to the first and so on. Each principal component has a loading from each element, and by seeing which elements have the highest loading it is possible to see which elements explain most of the variance in the data (i.e. best separate the fuel types). Table 1 shows the loadings on the first principal component for (a) the reference data set (coal and oil only), (b) the reference data set with peat data and (c) the reference data set with data from 1500 'fossil' particles extracted from lake sediments.

The two most important elements are sulphur and aluminium and these appear to be highly negatively correlated (Pearson's coefficient = -0.694). Sulphur has a slightly higher loading than aluminium in each case, and when the fossil particles are added to the analysis the difference between the loadings is increased. This seems to suggest that sulphur is the more important element when trying to separate fossil coal and oil particles.

SDA can also be used to determine the most important elements in fuel type separations. SDA produces an F statistic for each element which is a measure of how well that variable will separate the groups. The element with the highest F statistic is added to the classification function and then the F statistics are recalculated omitting the added element, but taking into account the separation already possible by its presence in the function.

TABLE 1. — LOADINGS ON 1ST PRINCIPAL COMPONENTS FOR PCA ON (A) THE REFERENCE DATA SET, (B) REFERENCE DATA + PEAT AND (C) REFERENCE DATA + FOSSIL PARTICLES.

Element	(a) coal + oil	(b) + peat	(c) + fossil
Na	0.377	0.319	0.188
Mg	0.167	0.074	- 0.037
Al	- 0.461	- 0.468	- 0.331
Si	- 0.392	- 0.408	- 0.363
P	0.078	0.017	- 0.009
S	0.465	0.500	0.496
Cl	- 0.271	- 0.303	- 0.387
K	- 0.099	- 0.126	- 0.311
Ca	0.146	- 0.047	- 0.234
Ti	- 0.081	- 0.068	- 0.157
V	0.127	0.156	0.177
Cr	- 0.077	- 0.069	- 0.058
Mn	- 0.098	- 0.091	- 0.092
Fe	0.194	0.216	0.246
Ni	0.104	0.127	0.100
Cu	- 0.148	- 0.136	- 0.130
Zn	- 0.167	- 0.157	- 0.142

Consequently, highly correlated variables (either positively or negatively), are reduced in importance once one has been added to the function. (i.e. The inclusion of two perfectly correlated variables is equivalent to including the same variable twice, and no extra separation is achieved.) Aluminium and sulphur have the highest initial F statistics, but being highly correlated sulphur becomes relatively unimportant once aluminium has been added to the function and vice versa. Depending on which one is selected first, two element rankings are achieved :

Al > Cl > Na > Si > K > V > Ti > Zn > Fe > S > Mg > Cr > Mn > Ni > P > Ca > Cu
 S > V > Fe > Mg > Cl > Ti > Cr > Al > K > Si > Na > Mn > Ni > P > Zn > Ca > Cu

There is very little to choose between the two, in terms of fuel type separation, and little improvement is made to the number of particles correctly allocated after the first 6 elements have been added in each case.

Discriminant function analysis (DFA) differs from SDA in that the elements for the separation are pre-selected, rather than joining the classification function on the calculated F statistic criterion. The elements in the rankings shown above were selected for DFA in turn (i.e. Al only, then Al + Cl, then Al, Cl + Na etc... followed by S only, S + V). At each stage the discriminant function containing sulphur correctly allocated more particles than the one containing aluminium, but again little improvement was achieved after the first six elements had been included.

From the results of these analyses, it was concluded that the most efficient fuel type separation was achieved when the first six elements from the sulphur ranking were included in the linear discriminant function produced from the DFA. This correctly allocates over 94 % of the particles.

Each particle is also given a probability of allocation to each fuel type. A threshold for this probability can be set so that only those particles with a probability higher than the threshold are allocated to a fuel type. Those falling below the threshold go into a group called 'other'. This procedure increases the confidence that unknown particles allocated to a fuel type have been allocated correctly. If the threshold is set too low, many mis-allocated particles remain in the analysis, and if set too high, many correctly allocated particles fall into the group 'other'. The threshold setting which removes the highest number of misallocated particles from the analysis whilst minimising the number of legitimate particles falling into the unclassified group is 0.8. (i.e only those particles with a probability of allocation > 0.8 will be allocated a fuel type).

Using the linear discriminant function containing S, V, Fe, Mg, Cl & Ti only, and a probability threshold of 0.8, of the 94 % of the particles allocated a fuel type, over 97 % of them are allocated correctly.

SPATIAL DISTRIBUTION OF CHARACTERISED PARTICLES

To study the impact of the combustion of different fossil-fuels on Scottish lochs, the carbonaceous particles extracted from the surface levels of 17 Scottish sediment cores were characterised using the methods described above.

As might be expected in a country where there are now no oil fired power stations, the results show that coal is the dominant fossil-fuel, with over 87 % of the characterised particles allocated to coal at every site. However, the east coast and south-west of Scotland appear to be areas where there is a higher oil influence. Figure 1 shows a contour map of percentage oil particles interpolated from the above data. The high point around Glasgow is due to the value for Loch Tinker. This may be higher than expected, because it is from a core taken in June 1985, at a time when the Inverkip oil-fired power station in Glasgow was still functional, only 40km away. Inverkip closed down in 1987 and it may be that characterisation of particles extracted from the surface level of a core taken from Loch Tinker now, would show a lower oil value. Apart from these areas there appears to be very little oil influence (less than 3 %) over the rest of the country.

The oil particles deposited in these higher (5-12 %) oil areas must have their origins outside the country. Oil percentage contours decline to the

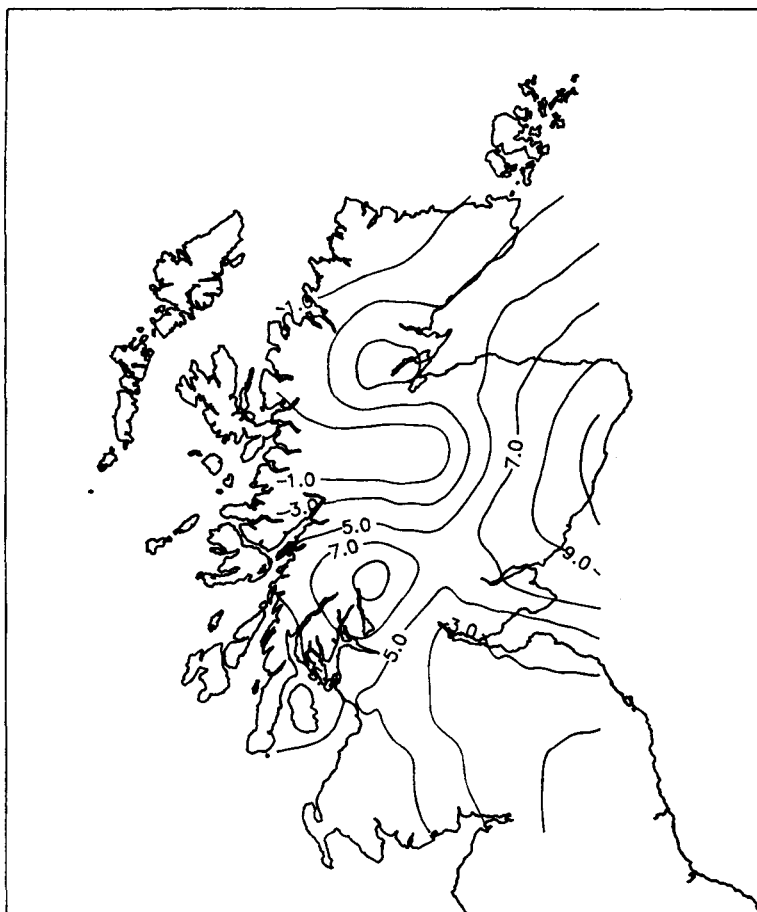


Fig. 1. Percentage of carbonaceous particles of oil origin in surface sediments from Scottish lochs.

south of Galloway with the value for Whitfield Lough in the North Pennines being only 0.22% and this suggests that they are not being transported northwards from England. The furthest north oil-fired power station in England is Ince 'B' on Merseyside about 200 km away, and even this is not a major plant. The alternative sources for the south-western oil particles are the oil-fired power stations at Coolkeragh and Ballylumford in Northern Ireland.

Sources for the east coast oil particles are not so clear. Although Scotland contains no oil-fired power stations, this coast is the terminus for many of the pipelines from the North Sea oil-fields and the burning off of wastes may produce some particles, although whether they would be in sufficient quantity to account for these results is doubtful. The only other possible source for oil particles transported from the east would be

Scandinavia, where oil is the major fossil-fuel consumed in power generation and other industries. It should be remembered however, that these results are only generated by 17 points, and although there are several sites with 'high' oil in each of these regions, the map is far from conclusive. A further 20 sites concentrated around these two areas are in the process of being characterised and it is hoped that these extra sites will help to confirm these results.

TEMPORAL DISTRIBUTION OF CHARACTERISED PARTICLES

The characterisation technique was then applied to carbonaceous particles extracted from a sediment core taken from the Men's Bathing Pond on Hampstead Heath in North London. This site was selected as there were many particles present at all levels, which maximises EDS efficiency and also there has been a change from exclusively coal to some oil burning in this region since the 1920's (*i.e.* the base of the core). 7504 carbonaceous particles from 18 levels were characterised as described above. The results are shown in Table 2 and Figure 2.

TABLE 2. — FUEL TYPE ALLOCATION FOR THE HAMPSTEAD HEATH CORE

Depth (cm)	Date	% coal	% oil	% other
0-1	1987	63.8	22.8	13.4
1-2	1987	79.0	9.3	11.7
2-3	1986	72.6	13.0	14.4
3-4	1986	72.5	14.7	12.8
5-6	1986	65.4	19.3	15.3
7-8	1985	67.1	18.4	14.5
9-10	1984	68.9	14.6	16.5
14-15	1982	88.5	7.4	4.1
19-20	1980	80.9	11.9	7.2
24-25	1978	76.1	17.1	6.8
29-30	1976	82.6	12.4	5.0
34-35	1974	79.6	15.6	4.8
39-40	1971	77.6	14.1	8.3
49-50	1967	78.0	17.4	4.6
59-60	1962	84.7	9.3	6.0
79-80	1952	92.4	3.3	4.3
99-100	1941	94.7	2.1	3.2
119-120	1929	99.8	0.0	0.2

These results fit very well with the known combustion histories of coal and oil. Before the 1920's fossil-fuel consumption in Britain was almost exclusively coal based, although from this time onwards the use of oil

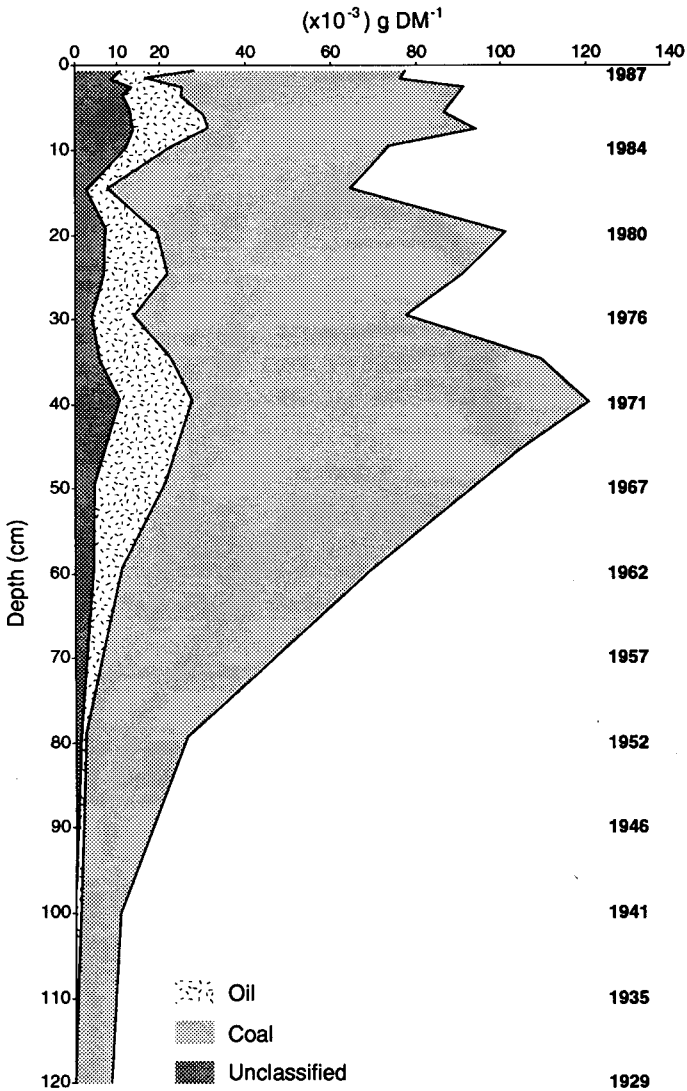


Fig. 2. The carbonaceous particle concentration profile for the Men's Bathing Pond, Hampstead Heath, divided into coal, oil and unclassified groups.

increased rapidly from 3 million tonnes in 1920 to 160 million tonnes in 1972. This was principally due to an influx of cheap fuel oil after the Second World War and as a response to this the first major power station specifically designed to be oil-fired was opened in 1952 on the River Thames at Bankside. Oil consumption increased rapidly in the late 1950's/early 1960's and continued to increase until the oil crisis in 1974. Since then, there has been a general decrease in oil consumption, with the exception of the miners strike in 1984/85, and coal has remained the dominant fuel

throughout. Despite the limited number of data points, most of these events can be seen in figure 2. There are very few oil particles until the 1950's, a sharp increase at the end of that decade, and a steady increase until the mid-1970's, when the number generally decreases except for a peak at about 1985.

CONCLUSIONS

Carbonaceous particles from coal and oil combustion can be readily separated using the elemental chemistry data produced by EDS analysis of the particle surfaces. A linear discriminant function involving six elements enables this separation to be done with over 97 % of the particles allocated to a fuel type being allocated correctly.

This technique has been applied to both surface sediments to study spatial distribution and to a dated sediment core to study changes through time and the results correlate well with known combustion distributions and histories.

Other work (Rose, unpub. data) has shown that the possibility of taking this particle characterisation a stage further to power station level seems very unlikely, but extending the scheme to include fuel types commonly used in other parts of Europe seems highly plausible. Only a preliminary study using peat data has been undertaken, but the results suggest that an effective characterisation including peat could be produced. The work of Mejstrik and Svacha (1988) shows that fly-ashes produced from power stations burning brown coal and lignite in Czechoslovakia are enriched in Co, Zn, Cr, Ni and Cd. If this is true of all brown coal and lignite ashes then there should be few problems in including these fuel types in a future characterisation scheme.

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