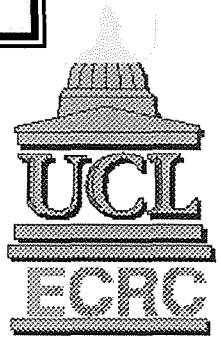
DISPLAY ONLY

ISSN 1366-7300



ENVIRONMENTAL CHANGE RESEARCH CENTRE

University College London

RESEARCH REPORT

No. 14

Fly-ash particles and heavy metals in Europe: Implications for human and environmental health

N.L. Rose, J-M Punning, J. Fott, J. Bowman, J. Watt

Progress Report 1995

FLAME Report 1/1995

March 1995

Environmental Change Research Centre
University College London
26 Bedford Way
London
WC1H 0AP

FLY-ASH PARTICLES AND HEAVY METALS IN EUROPE: IMPLICATIONS FOR HUMAN AND ENVIRONMENTAL HEALTH (FLAME).

Scientific Personnel

University College, London:	Neil Rose
	Simon Harlock
Institute of Ecology, Tallinn:	Jaan-Mati Punning
	Tiiu Alliksaar
Charles University, Prague:	Jan Fott
	Zuzana Hořická
	Jasna Vukičová
Environmental Protection Agency, Dublin:	Jim Bowman
Imperial College, London:	John Watt
	Krystyna St.Clair-Gribble

I. GENERAL AIMS AND OBJECTIVES

The main project aims are:

- to extend the mapping of carbonaceous fly-ash particles and heavy metals in lake sediments to Central Europe, Ireland and currently unstudied areas of the U.K. to identify areas of high deposition.

- to extend the present carbonaceous fly-ash particle characterisation (including coal and oil) to other major fossil-fuels used in Europe e.g. brown coal, peat and oil shale.

- to apply the developed characterisation to carbonaceous fly-ash particles extracted from lake surface sediments in Estonia, Czech Republic, Ireland and the U.K. where these fuels are used extensively and to identify possible origins for deposited particles in these countries.

- to use heavy metals from both lake surface sediments and mosses of selected species taken from within the lake catchments to assess contemporary metal loadings and to study the spatial correlation between heavy metals and deposited particles.

- to use the data gathered in this project and data already available to understand more fully how emitted pollutants are transported and deposited across Europe.

- to assess the implications for environmental and human health for the individual countries and Europe as a whole.

Additional objectives

- Experimental work in Estonia to assess the use and efficiency of *Sphagnum* peat cores to record historical trends in atmospheric fly-ash particle deposition.

II. OBJECTIVES FOR THE REPORTING PERIOD

The work programme for the project is shown in Table 1 and shows that over the reporting period progress was to be made in 7 main areas:

- Project workshops
- Collection of characterisation reference material
- Development of the characterisation scheme
- Site selection
- Sediment and moss sampling
- QA/QC procedures
- Sample analysis

III. MAIN RESULTS

Workshops

1st FLAME Workshop, London. 9-11th March 1994.

The London workshop was held within the first few weeks of the official start of the contract and was designed to decide upon sampling protocols and to familiarise those new to various aspects of the work with the analytical procedures. This meant that all techniques to be used within FLAME were standardised from the very start of the programme.

The following protocols were decided upon:

- criteria for lake site selection
- site description data requirements
- sediment core number, extrusion, preservation procedures and sample labelling
- sediment storage and analyses
- sample transport to other laboratories
- moss identification and sampling

The details of these protocols are given in Appendix A.

Table 1

PROJECT MONTH

	1 3	6	9 12	15	18	21	24
U.K. U.C.L	<--REF--> <-SITES-> <W/SHOP-> <---------- <----------	DEVELOP-- -SAMPLE---	PCS---------- ----->	---><----------	<W/SHOP> <REPORT> CP----------	ANALYSIS-	<W/SHOP> <---DATA- ----->	<REPORT><br--->
U.K. IMPERIAL	<W/SHOP-> <----------	DEVELOP--	PCS----------	---> <---------- <----------	<W/SHOP> <REPORT> SAMPLE---- METAL-----	PCS---------- ANALYSIS-	<W/SHOP> <---DATA-<br-----><br----->	<REPORT><br--->
ESTONIA	<--REF--> <-SITES-> <W/SHOP-> <----------	-SAMPLE---	----->	<-------- <----------	<W/SHOP> <REPORT> CP---------- METAL-----	ANALYSIS- ANALYSIS-	<W/SHOP> <---DATA-<br-----><br----->	<REPORT><br--->
CZECH REPUBLIC	<--REF--> <-SITES-> <W/SHOP-> <----------	-SAMPLE---	----->	<--------	<W/SHOP> <REPORT> CP----------	ANALYSIS-	<W/SHOP> <---DATA-<br----->	<REPORT><br--->
IRELAND	<--REF--> <-SITES-> <W/SHOP-> <----------	-SAMPLE---	----->		<W/SHOP> <REPORT>		<W/SHOP> <---DATA-	<REPORT><br--->

REF = Collection and preparation of reference material
SITES = Site selection
PCS = Particle Characterisation Scheme
SAMPLE = Sample Collection
DATA = Final data analysis

QA/QC of all analyses - ongoing throughout 24 months.

2nd FLAME Workshop, Prague. 8-10th February 1995.

The Prague workshop, just before the end of the first year of FLAME was used to review progress, determine immediate priorities and to set deadlines to ensure the completion of the programme within the period of the project. It was also used to discuss the format and content of this report as well as being used to sort out any analytical problems with the carbonaceous particle counting and to further the QA/QC component.

The conclusions of this workshop and the reports presented form the basis of this report, the outline timetable given in Section IV, and the data presented in Appendices B & C.

Lake site selection

35-50 lakes were selected from each country using the selection criteria outlined in Appendix A. All sites have been selected in each country and the names, locations and some basic physical data for these are given in Appendix C.

Sampling

Following the protocols, at each site 3 sediment cores were taken and the 'master core' was extruded and stored. The other two cores were sampled for surface sediments only. This enables samples to be analysed in triplicate where necessary.

U.K.

In total 74 lake sites were selected, 65 in Great Britain and 9 in Northern Ireland and the distribution of these are shown in Appendix C. This enabled are more comprehensive coverage than the original 50. Of these sites only 9 remain to be sampled. These are in the south-east of England and sampling will be completed towards the end of March 1995. Moss samples were collected at all but 14 sites and was less abundant in the southern and eastern parts of the country where many of the water bodies available to be sampled were ornamental lakes in the grounds of stately homes. The catchments of such lakes and ponds were not generally favourable for growth of the required moss species. Two additional moss samples were taken to increase coverage at Loch Laidon (NN 353 536) and just north of Glasgow (site 70a on map).

Sediment samples were taken at all sites. However, site 39, Ampfield Wood Lake proved to be unsuitable for coring and another nearby lake will be cored as a replacement.

Ireland

48 lakes were selected and sampled in Ireland and the distribution of these is shown in Appendix C. The sampling programme for Ireland is complete. Moss samples were taken from all but 4 of these sites although some of the samples obtained were not of the species required for metal analysis. The correct mosses were not available at all sites due to agricultural practices in the catchment.

Estonia

45 lakes were selected in Estonia to give a good geographical coverage and to include all landscape regions of the country. The site listing and map is shown in Appendix C. 25 sites have so far been sampled and the remaining 20 are due to be sampled in the Spring of 1995. Of the sites sampled so far, sediment cores have been obtained from all the lakes and moss samples have been collected from all but 3.

In addition a peat core was taken from a bog to the north-east of Tallinn for a study on fly-ash retention (see below).

Czech Republic

35 sites were selected in the Czech Republic and the distribution of these together with some site data is given in Appendix C. The absence of suitable natural lakes has caused a problem for sampling and reservoirs have had to be used instead. 16 sites have been cored so far and the remainder will be sampled in the Spring 1995. A problem with the use of reservoirs is the variable accumulation rate between one site and another making inter-site comparisons quite difficult. However, because the year of construction is known in every case it is hoped that an idea of sediment accumulation can be obtained and approximate particle fluxes calculated. These should be more comparable between sites.

Pleurozium schreberi was found and collected at only 7 of the sites visited so far.

QA/QC

All heavy metal analyses and carbonaceous particle characterisations are being undertaken at a single laboratory which removes the possibility of any inter-laboratory variability. Imperial College regularly participates in Quality Assurance exercises and in addition uses standard samples of known composition routinely as an intra-laboratory performance check.

Carbonaceous particle enumeration is more specialised and consequently there are no standards against which to compare. The 3 laboratories involved in this work in the FLAME project have therefore instigated a 'slide-swapping' programme whereby 5 slides from each laboratory are counted by each analyst. The results can then be compared so that any problems and differences can be identified and sorted out. Good agreement will show that particle counts between laboratories are comparable. This is an ongoing part of the research programme.

Sample analyses

This is another ongoing part of the research programme started during this reporting period. All areas of sample analysis (carbonaceous particle enumeration, heavy metal analyses and carbonaceous particle characterisation) are progressing but with sampling still incomplete this is a priority for the summer and autumn of 1995 (see Objectives for next reporting period). Preliminary carbonaceous particle results from the triplicate surface samples have shown the repeatability of the technique (coring and particle extraction and enumeration) to be of a high standard. Few results are at present available and

these will therefore not be discussed in any detail here.

The Estonian surface sediments were analysed for two particle types, carbonaceous particles and inorganic ash spheres. The reason for this is that it has been found that oil-shale produces relatively few carbonaceous particles and inorganic ash sphere data can therefore be used to supplement the carbonaceous particle concentration and characterisation results. A map of inorganic ash sphere concentration for Estonia will therefore predominantly show the impact of oil shale on the region whereas the carbonaceous particle map will mainly show impacts from transboundary pollutant deposition. The two should combine to give a great deal of information. In addition, size distributions of the two particle types are being determined. The preliminary results of this work are shown in Figure 1.

Particle characterisation reference material

33 reference samples were obtained from power plants in each country. 4 from oil shale thermal power plants in Estonia, 8 from peat-fired stations in Ireland, 7 from brown coal fired power stations in the Czech Republic, 6 from oil-fired power stations in the U.K. and Ireland and 8 from coal-fired power stations in the U.K. and Ireland. The full listing of these sites and their locations on national maps are given in Appendix B.

Fly-ashes from each were obtained from as close to the point of emission as was practicably possible. A sub-sample of each of these was then put through the carbonaceous particle extraction procedure so that each reference sample had been subjected to the same conditions as those particles extracted from the lake sediments. This technique involves the step-wise removal of unwanted sediment fractions by selective chemical attack. Further details of this technique are given in Rose (1994). Following the extraction procedure the carbonaceous particles are left as a suspension in water. These suspensions were then sent to Imperial College for EDS characterisation (see below).

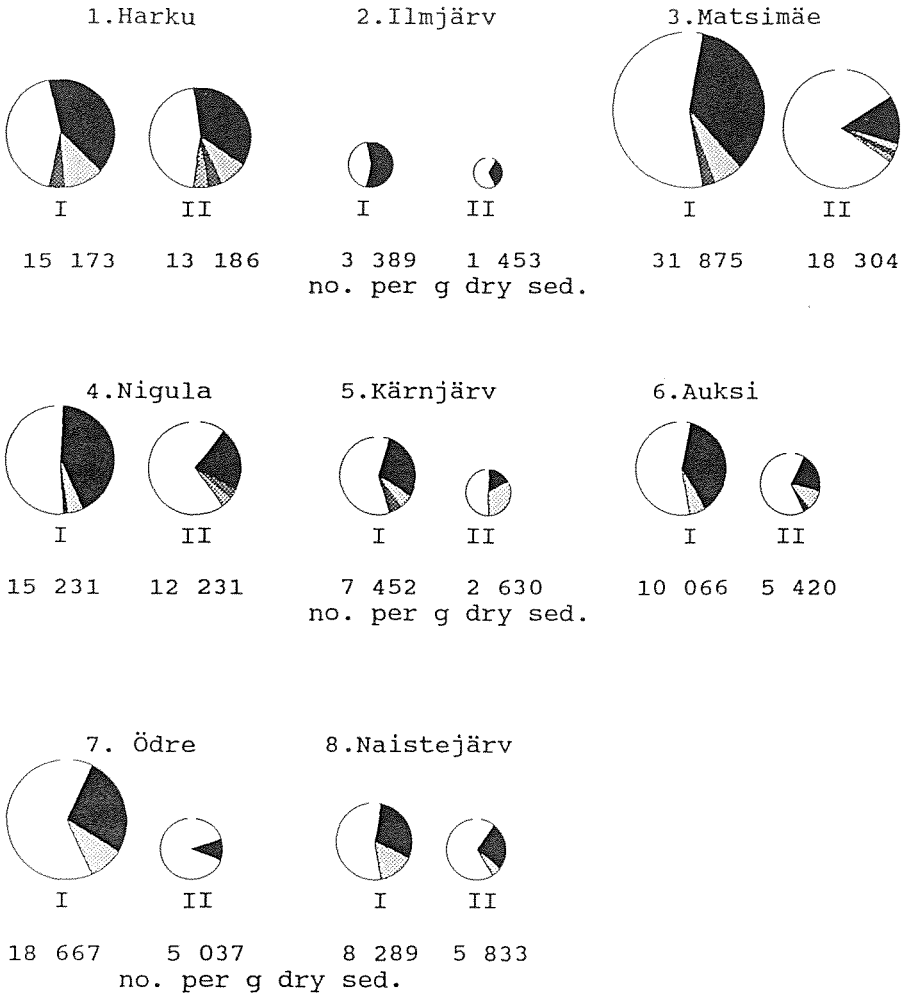
Development of the carbonaceous particle characterisation

The analysis of the extracted particles is central to this research project. Previous work (Rose et al 1994) has described the preliminary development of the technique of individual particle analysis and its potential for characterising particulate material emitted from coal and oil burning power stations, in order to differentiate between them. The aim of this project is to apply this approach to important additional fuel types used in Europe, brown coal, oil shale and peat. The first year of the contract has been concerned with the characterisation of samples taken from power stations utilising each fuel type, in order to develop a classification scheme.

<u>Background to Analysis</u>

Although many microscopy based analytical methods can be considered to be individual particle analysis techniques, the term is in this case limited to particle characterisation by computer controlled

Figure 1



I - inorganic fly-ash particles

□ - <5μm
■ - 5-10μm
▫ - 10-15μm
▪ - >15μm

II - carbonaceous fly-ash particles

□ - <20μm
■ - 20-30μm
▫ - 30-40μm
▪ - 40-50μm
▨ - >50μm

scanning electron microscopy (CCSEM). Specimen mounts are undertaken in such a way that features are separated from each other and may be analysed in isolation (chemical analysis is undertaken by energy dispersive X-ray analysis (EDX)). The particle-by-particle measurement is computer controlled by linking SEM and EDX through automated image analysis software. By identifying individual particle "types" in a sample the technique is able to resolve sources whose emission products are dissimilar at the individual particle level.

The analyses were all undertaken on the JEOL 733 Superprobe SEM in the Department of Geology, at Imperial College. Particle selection and X-ray data collection were controlled by the Link Analytical (now Oxford Instruments) programme "DIGISCAN". Initial data interpretation was mainly undertaken using the custom built programme MIDAS. This will be followed by multivariate statistical techniques undertaken at University College.

Selection of Particles.

As has been described above, particles are extracted from lake sediments using a chemical preconcentration procedure. All source samples were treated in the same way. The procedure (Rose 1994) has been shown to efficiently extract carbonaceous particles, which come from the fuel itself. Preliminary examination in the electron microscope showed that, in the case of some of the new fuel type samples, there seemed to be a number of other particle types which survived the extraction. It is possible to select different types of particle within the instrument based on their mean atomic number (roughly equivalent to a density separation) and thus the carbonaceous particles could be isolated. However, it was felt that since the other particle types from the source samples survived the extraction, that it is entirely likely that they would be visible in the sediment samples which will be analysed in the remainder of the project. Therefore the backscatter threshold (see below) was set to include the full range of particles seen. As some of these have a relatively high mean atomic number (for example we see zircons and rare earth particles), the thresholds were set to incorporate particles with a mean atomic number of about 6 (set on carbon rich material in the filter substrate) to about 82 set using a lead metal standard.

Backscatter thresholding for particle selection in the SEM.

Backscattered electrons (BSE) are high energy electrons from the incident beam of the SEM which have been diverted by a series of collision events in the target (sample). Because the output signal strength is proportional to the mean atomic number (the Z number), images derived from this signal may readily be subdivided based on useful threshold values.

The intensity of the input signal is expressed as a number (0-255) for each image pixel. The principle of particle selection is therefore very straightforward - a decision making function is generated which sets criteria for acceptance or rejection based on the measured parameter. In other words **threshold** values may be established which define the acceptability or otherwise of each pixel. This produces a binary image (eg those pixels that fall within the thresholds are given the value 1, those that do not are set to zero). It is relatively straightforward to then agglomerate sets of touching "acceptable" pixels into features for analysis (ie the beam is driven to touching 1 value pixels and skips over zero values.

Backscatter contrast may therefore be used to perform the equivalent of an on-line density separation - by the technique of BSE thresholding. By the selection of suitable upper and lower thresholds, features of any given band of mean atomic number can be isolated. The controlling image analysis program (DIGISCAN) uses this information to locate and size any features in the resulting binary image. All touching pixels in a feature are summed to give its two dimensional area. The beam is then driven back under computer control to each feature in turn for the collection of shape and X-ray information.

X-Ray Analysis.

X-rays are generated as a result of the release of energy which accompanies the movement of an electron from an outer shell to replace a dislodged secondary electron. The amount of each element in the target is given by the output of characteristic X-rays, measured by their wavelength or energy (often known as electron microprobe analysis EPMA). For the techniques and examples described here, data were gathered using energy dispersive X-ray spectroscopy (EDS). The detector used in these studies can measure any element heavier than sodium. The resulting spectra can be used to determine which elements are present in the particle as a whole, or at different points on its surface. The height of the peak is proportional to the number of X-ray photons detected and thus the relative proportion of each element present in a feature may be estimated. Thus in the case of the carbonaceous particles, they will be differentiated by estimation of amounts of associated elements, not on their carbon content.

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. Each element detectable by the system has one or more characteristic energy levels at which X-rays will be detected if it is present in the sample. A background (Bremstrahlung) radiation distribution is generated by random noise and the elements present show as peaks superimposed on this. These peaks span several channels in the multichannel analyser and a convenient way to summarise the data is to delimit a "region of interest" (often termed "to paint a window") over the channels concerned and to record the total counts in the whole region. This leads to a significant reduction in required storage space, since the counts for each element are now represented by a single number, and it is not necessary to record a value for each channel.

X-ray correction factors.

For the automated particle analysis using the DIGISCAN program, up to 25 regions of interest are defined on the spectrum, and the numbers of X-ray counts falling in each region (or "window") are stored. Several regions are defined on parts of the spectra where no elemental peaks are expected to occur. These are used to subtract the background counts from under each of the other regions of interest which are defined at the energy levels characteristic of the elements which it is desired to measure. This is known as "background correction"

In certain cases a peak for one element will overlap a peak for another. The "M" line for lead for example, falls in the same region as the "K" line for sulphur. Lead, however, has other lines (the "L series") visible in the 25KV spectrum and therefore lead is estimated from one of these regions and

the number of counts that should occur in the "M" region is predicted and subtracted from the joint peak. The remainder can be designated as sulphur. The proportion of one peak subtracted from another in this manner is termed the "overlap correction".

A final correction factor ("efficiency factor") allows a linear scaling of the elemental analysis to account for differences in detector efficiency between elements. The set of definitions of X-ray regions of interest and the correction factors to be applied to them, is stored in a separate computer file, termed a "window file", since it will be used repeatedly to correct the results for all measured features.

Normalisation.

Different sized particles of the same material will yield different absolute totals of X-ray counts in each of the specified regions of interest and so the results are normalised by expressing them as a percentage of the total sum of the counts in all the regions of interest (after correction). This normalisation procedure means that apparent values for an element may appear very similar between two features, where in fact the true percentage is very different. Thus carbon is not detectable but forms a large percentage of the chemical composition of, for example, coal fly ash particles. The remaining elements may occur as traces but appear to be major constituents once the normalisation has occurred. Thus a fully quantitative analysis by an appropriate method might give two analyses:

1 Carbon 97%, Si 1%, Al 2%
2 Si 33%, Al 25%, K 20%, Ca 22%

but a normalised analysis of the elements detectable in the current equipment would give an identical Si percentage (33%). In this type of analysis, it is the other elements on which the data is subdivided and classified.

Window files - general.

Data from DIGISCAN are not always easy to interpret at first glance. It is worth stressing therefore, that the object of the analysis is to distinguish different types of particles from each other, in order to classify and count them. It is not important to have an 'accurate' analysis for each particle defined as one that gives the 'true' percentage of each element, as long as the analysis is 'precise' in the sense that a material always gives the same result and that other materials give a different (though also constant) result.

Window files - FLAME.

The list of elements used for the X-ray measurements are given in Table 2. These have been selected to extend the previous element list with additional elements that are useful for discriminating the additional fuel types. These have been selected initially from published descriptions of fly ash compositions from these sources, complemented by careful preliminary manual analysis of the source samples. The correction factors are calculated with respect to standard materials of known composition.

Table 2.

	Window for X-rays	Background Proportion	Background Window	Overlap Proportion	Overlap Window	Efficiency Factor
Na	1	0.41	8	0	0	1
Mg	2	0.72	8	0	0	1
Al	3	1.08	8	0	0	1
Si	4	1.3	8	0	0	1
P	5	1.17	8	0	0	1
S	6	1.13	8	0	0	1
Cl	7	1.12	8	0	0	1
Cd	9	0.93	8	0.119	10	1
K	10	0.8	8	0	0	1
Ca	11	0.82	8	0.067	10	1
Ti	12	0.62	8	4.85	14	1
V	13	0.62	8	0.12	12	1
Ba	14	0.51	8	0.042	15	1
Cr	15	2.9	22	0	0	1
Mn	16	2.57	22	0.117	15	1
Fe	17	2.65	22	0.15	16	1
Co	18	2.04	22	0.06	17	1
Ni	19	1.7	22	0.024	18	1
Cu	20	1.55	22	0.018	19	1
Zn	21	1.34	22	0.008	20	1
Pb	23	1	22	0	0	1

Analysis to date.

A total of more than 65000 particles have been analysed from 30 source samples (out of 33 supplied). This has included some duplicate analyses. Details are given in Table 3.

Table 3.

Slide and Number	Power Station	Fuel type	Number of features
I1	Ahtme tpp	Oil Shale	15017*
I2	Estonian tpp	Oil Shale	1689
I3	Baltic tpp	Oil Shale	1025
I4	Kohtla-Jarve tpp	Oil Shale	631
I5	Shannonbridge	Peat	1192
I6	Ferbane	Peat	976
II1	Bellacorick	Peat	1428
II2	Rhode	Peat	1641
II3	Lanesboro	Peat	2068
II4	Money Point	Coal	1238
II5	Allenwood	Peat	4737
II6	Caherciveen	Peat	
III1	Gweedore	Peat	5975
III2	Steti	Brown Coal	582
III3	Chvaletice	Brown Coal	3152
III4	Melnik	Brown Coal	409
III5	Pocerady	Brown Coal	1756
III6	Opatovice	Brown Coal	2568
IV1	Kralupy	Brown Coal	1202
1V2	Malesice	Brown Coal	2362
1V3	Grain	Oil	943
IV4	Fawley	Oil	1082
1V5	Tarbert	Oil	3478
1V6	Ballylumford	Oil	711
V1	Pembroke	Oil	
V2	Coolkeragh	Oil	

Slide and Number	Power Station	Fuel type	Number of features
V3	Drax	Coal	1500
V4	Eggborough	Coal	2139
V5	Ironbridge	Coal	856
V6	Rugeley	Coal	1659
VI1	Tilbury	Coal	617
VI2	Fiddlers Ferry	Coal	3043
VI3	Didcot	Coal	185

* Includes repeat analyses for testing of thresholds

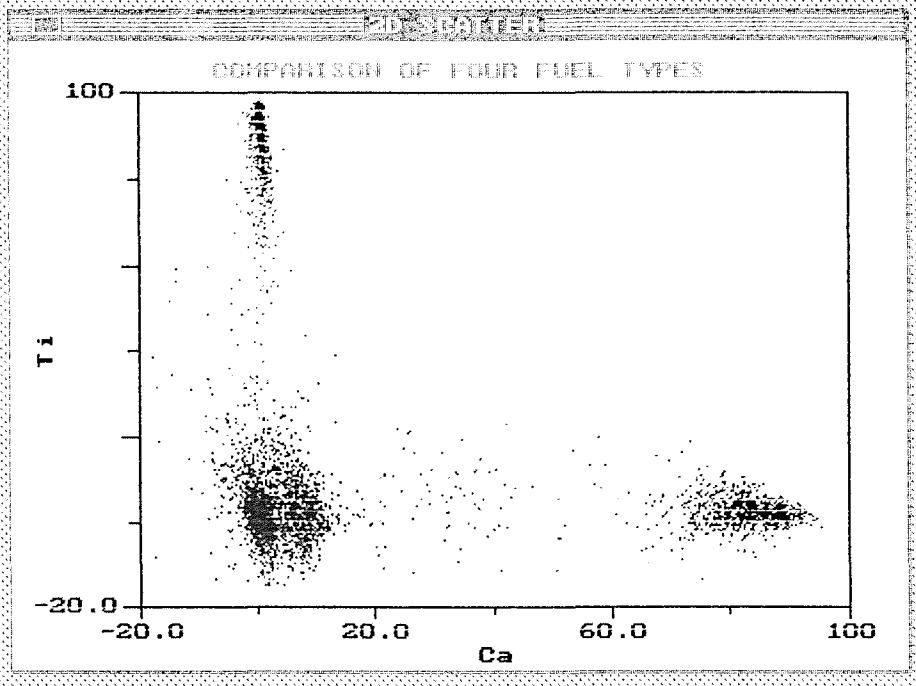
Preliminary Results.

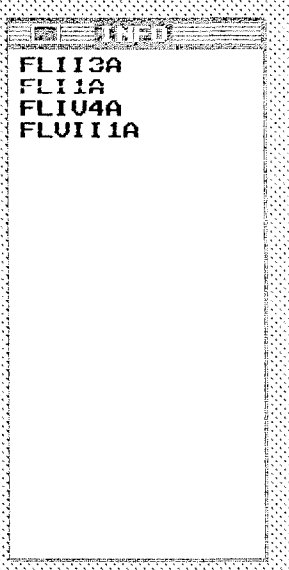
MIDAS interpretation of the above results files has revealed that there is considerable scope for differentiating the different source materials. Figure 2 shows that there are major differences in the particle types associated with some of the individual samples from different sources. Four types are plotted (Peat, FLII3 (green), Oil Shale, FLI1a (blue), Oil, FLIV4a (red) and Coal, FLVII1a (purple)). Each scatter plot shows all the values recorded for 1000 particles of each sample with respect to four parameters (Ti, Ca, Al and S). On such plots, different types of particles will cluster in different areas, so that this figure shows that we have four dissimilar types of particle.

There are also differences apparent from different samples of the same fuel type (from different power stations.) Duplicate analyses of particles from the same power station have shown a high degree of reproducibility. Multivariate examination and classification of the data is currently being undertaken and will be discussed in full in the next report.

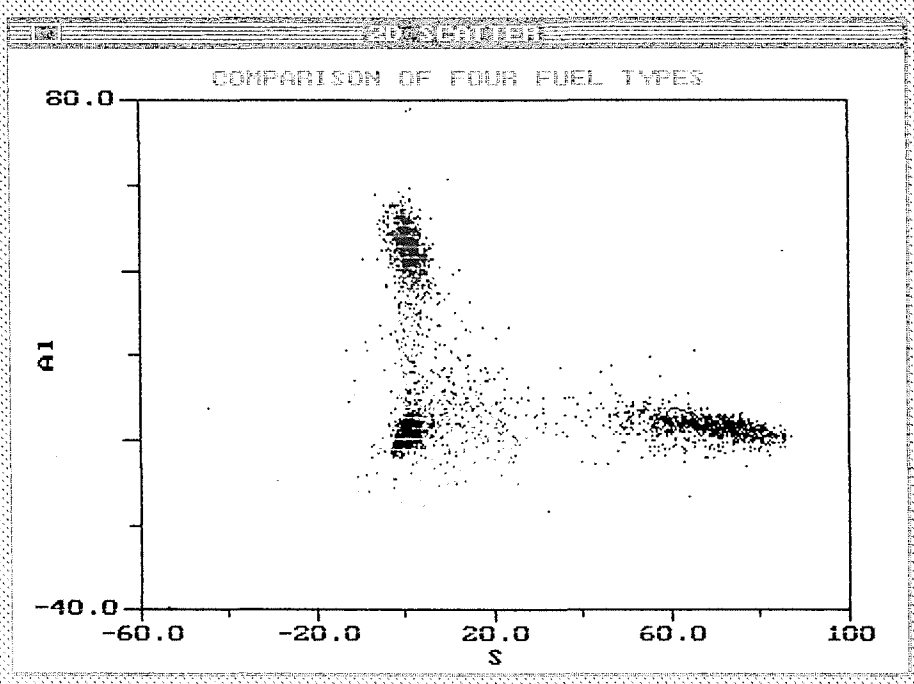
Fly-ash in Sphagnum ***peat***

Work on the retention of fly-ash particles within a *Sphagnum* peat core was undertaken experimentally in the laboratory and then applied to a peat core taken from Viru Bog to the north-east of Tallinn by the Estonian group. Experimental work conducted over 241 days showed that *Sphagnum* retained deposited fly-ash very efficiently in the surface levels of the peat, little being washed out after the equivalent of mean annual rainfall was applied over the experimental period. Analysis of the core from Viru bog showed that *Sphagnum* peat, like lake sediments, effectively stores a record of atmospheric deposition (Figure 3). In this case, the peat record closely matches the known history of oil shale combustion in the region. This work has been written up for submission to the international literature.





MIDAS FILE EDIT MODIFY GRAPHS TABLES OPTIONS



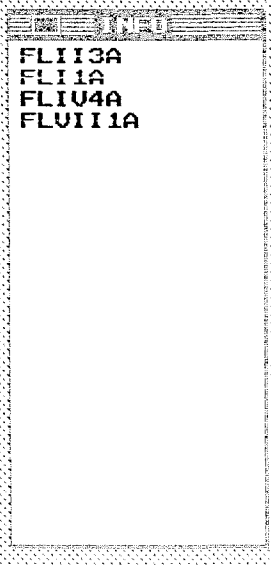
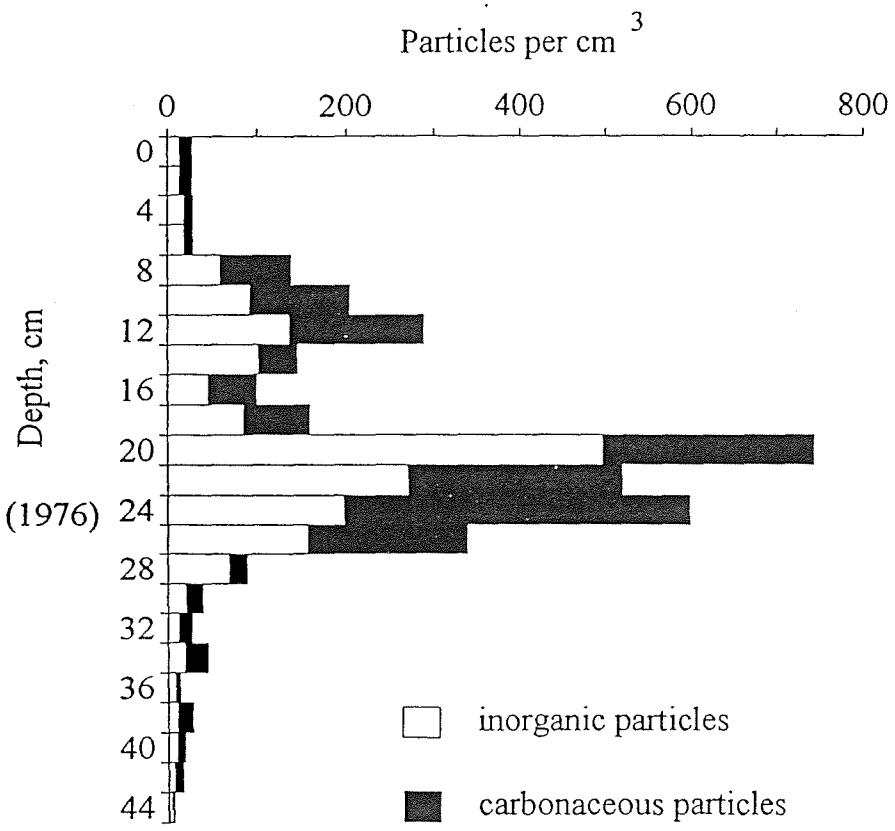


Figure 3



Distribution of fly-ash particles in the upper layers of Sphagnum peat in Viru Bog. (1976) marks the dated layer on the basis of the Pinus sylvestris tree rings

IV. OBJECTIVES FOR THE NEXT REPORTING PERIOD

FLAME is a two year project and so the objectives for the next reporting period are to complete all analyses and to interpret the data such that all the aims and objectives of the research project can be fully reported upon by the end of the programme.

With this in mind there have been a number of deadlines set within FLAME such this ultimate objective will be reached on schedule. Briefly these are as follows:

1) All lake sampling to be completed in early Spring 1995
2) All samples for metal analysis and particle characterisation to be at University College London by 1st May 1995
3) All CP concentration and heavy metals data to be at University College London by 1st October 1995
4) All CP characterisation data to be at University College London by 1st November 1995.

The final workshop for FLAME will be held in Tallinn on 8th-10th November 1995 where the final data and interpretation will be discussed and reporting format and responsibilities determined.

REFERENCES

Punning, J-M & Alliksaar, T. The fixation of fly-ash particles in accumulating *Sphagnum* peat.

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

Rose, N.L., Juggins, S., Watt, J. & Battarbee, R.W. (1994). Fuel-type characterisation of spheroidal carbonaceous particles using surface chemistry. Ambio. 23: 296-299.

Appendix A: SAMPLING AND ANALYTICAL PROTOCOLS

Sampling protocols

1) SITE SELECTION

Where possible lakes should be selected to give a good geographical coverage of the country. The number of lakes we should try and sample in each country is as follows:

U.K.	50
Estonia	50
Czech Republic	40
Ireland	50

As soon as the sites are selected, a list and a map of the sites should be sent to UCL so that individual site codes can be allocated to each site. These will then be returned to you so that you can label any samples from the site using this code. In this way, we will all be calling the sites by the same names which should hopefully avoid confusion and extensive re-labelling of samples etc.

Where possible, lakes should be small (less than 10 ha) and deep (not less than 2m) although if larger lakes are selected the minimum depth should also be greater.

2) SITE DESCRIPTION SHEET

A site description sheet should be completed for each site sampled. A suggested Site Description Sheet is attached. A copy of these sheets should be sent to UCL with your samples.

3) SEDIMENT CORING

3 cores are to be taken from within the deepest basin of each lake site.
These cores should be taken from the same anchor point, within 5-10m of each other.

Core A, the best core, is to be extruded vertically in 0.5cm slices between 0cm and 5cm depth, and 1cm slices from 5cm to the bottom of the core.

For Cores B and C only the surface sample 0-0.5cm needs to be taken.

All samples should be stored in separate plastic bags.

Core labels will need to written on each sample and included in the sample code e.g.

For the first Czech site CZ1, the sample bags will be labelled:

CZ1A 0-0.5cm, CZ1A 0.5-1cm, CZ1A 1-1.5cm and so on.
CZ1B 0-0.5cm only.
CZ1C 0-0.5cm only.

4) SEDIMENT ANALYSES

Sediment samples should be stored sealed preferably in a cold room until analyses are undertaken.

Over the period of the project it would be useful if water content, organic content and wet density determinations could be done on the core samples. The samples may then be dried and stored dry. However you will need to dry the surface levels for CP analysis and sending for metal analysis so if there is sufficient material do the water content, organic content, and wet density measurements on these first.

Water content is done by heating to 105°C and determining the % loss.
Organic content is done by heating to 550°C and determining the % loss.
Wet density is done by accurately weighing a known volume of wet sediment.

After drying the 3 surface samples the following should be done:

i) Carbonaceous Particle (CP) analysis should be done on all surface samples using the procedure outlined at the Workshop.In the first instance select a few sites for this triplicate analysis to see how it is performing.

Once you have counted the CPs on your first 5 sites send one slide from each to UCL so that we can circulate the slides for inter-comparison. We will send you slides from the other participating countries. In total there will be 15 intercomparison slides to count including your own.

After making up slides for CP counting, send a sub-sample of the final residue to UCL so that this can be forwarded for EDS analysis.

ii) Send a sub-sample of 0.5 - 1.0g dry sediment (if possible) from each surface sample to UCL so that they can be forwarded for metal analysis. Remember to keep enough for your own CP analyses.

iii) In addition, Tiiu Alliksaar has agreed to do her usual particle counting on the surface samples (in case oil shale produces too few CPs).

5) SAMPLING MOSSES FOR METAL DEPOSITION MONITORING

The following protocol is based on Ross (1990).
H.B. Ross, 1990. On the use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) for estimating trace metal deposition. Water, Air and Soil Pollution, 50: 63-76.

Moss species

Hylocomium splendens and *Pleurozium schreberi*

Field sampling

1) At each site sample at least 5 locations within 1km of the site

2) Avoid sample locations likely to be affected by throughfall

3) Samples should be of both mosses if possible

4) Wear plastic gloves during sampling and handling

5) Samples should be cleaned of litter and soil while in the field

6) Sample size approximately 1 litre,

Cleaning

1) On return to base, the mosses should be separated and dried. All traces of soil should be physically removed.

There are one or two other points we decided upon:

i) Remember only to sample the green growing shoots of both mosses.

ii) Remember to dry the moss samples as soon as possible and do not store wet.

iii) Only sample the two species that are mentioned on the list for metal analysis.

iv) We agreed to try CP analysis on the moss samples too. This is totally new so at present I cannot offer any advice. However, remember to sample plenty (i.e. 1 litre minimum) so that there is plenty of material. We also said that if the selected mosses were not present at the site we would take any moss species for CP's only. In this case do not send any moss to UCL for metals.

v) Try CPs on a few moss samples to begin with (and perhaps a few replicates to see how this method performs). The preparation should be quick - a single nitric acid attack will probably do.

vi) send only dried moss samples for metals analysis. About 2-3g dry weight should be sufficient.

vii) Moss samples should be labelled with the site code e.g. for the site CZ1 the moss sample would be labelled CZ1M.

SITE DESCRIPTION SHEET

SITE NAME: CODE:

LOCATION (e.g. grid reference)

SAMPLE DATE:

LAKE DETAILS

ALTITUDE:

LAKE AREA:

MAX. DEPTH:

MACROPHYTES:

DESCRIPTION/USE:

ESTIMATE OF RESIDENCE TIME?:

ESTIMATE OF TROPHIC STATUS:

CATCHMENT DETAILS

CATCHMENT AREA:

VEGETATION:

LAND-USE:

CORE DETAILS:

WATER DEPTH:

CORE LENGTH:

STRATIGRAPHIC CHANGES:

ROUGH SKETCH OF BATHYMETRY:

Appendix B: FLY-ASH REFERENCE SAMPLES

OIL SHALE	1	AHTME TPP (5*)	Estonia
	2	ESTONIAN TPP (1*)	Estonia
	3	BALTIC TPP (2*)	Estonia
	4	KOHTLA-JÄRVE (4*)	Estonia
PEAT	5	SHANNONBRIDGE	Ireland
	6	FERBANE	Ireland
	7	BELLACORICK	Ireland
	8	RHODE	Ireland
	9	LANESBORO	Ireland
	10	ALLENWOOD	Ireland
	11	CAHERCIVEEN	Ireland
	12	GWEEDORE	Ireland
BROWN COAL	13	ŠTĚTÍ	Czech
	14	MĚLNIK (2**) (##100)	Czech
	15	CHVALETICE	Czech
	16	POCERADY (3**) (##59)	Czech
	17	OPATOVICE (8**)	Czech
	18	KRALUPY (16**)	Czech
	19	MALESICE (23**)	Czech
OIL	20	GRAIN	UK
	21	FAWLEY	UK
	22	TARBERT	Ireland
	23	BALLYLUMFORD	UK
	24	PEMBROKE	UK
	25	COOLKERAGH	UK
COAL	26	DRAX (1#) (##14)	UK
	27	EGGBOROUGH (6#) (##50)	UK
	28	IRONBRIDGE (12#)	UK
	29	RUGELEY (8#) (##80)	UK
	30	TILBURY (18#)	UK
	31	FIDDLER'S FERRY (7#) (##41)	UK
	32	DIDCOT (9#) (##77)	UK
	33	MONEYPOINT	Ireland
	34	OSTRAVA (21**) (to be added later)	Czech

The locations of these sites are shown on the following figures.

*= Ranking in Estonian power production (see next page).

**= Ranking of SO_2 emission sources in Czech Republic (1991). Also locating numbers on Czech map.

#= Ranking of SO_2 emission sources in U.K. (1993)

##= Swedish NGO Secretariat on Acid Rain Ranking of top 100 sulphur sources in Europe (1994)

Largest power plants in Estonia

Power plant	Power production in 1971,GWh	Erected	Fuel
Estonian PP	7760	1969-73	Oil-Shale
Baltic PP	6067	1959-71	Oil-Shale
Iru CHP	522	1978-90	HFO, gas
Kohtla-Järve CHP	80	1949-86	Oil-Shale
Ahtme CHP	51	1952-57	Oil-Shale
Ulemiste CHP	25	1962-73	HFO, gas

Appendix C: SAMPLING SITES

UNITED KINGDOM: 'FLAME' SAMPLING SITES

No.	Name	Code	Grid Ref	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (ha)
1	Lough Money	NIAA	J 533 455	4.6			
2	Drumnavaddy Lough	NIAB	J 135 502	3.0			
3	Darkley Lake	NIAC	H 858 306	2.4			
4	Lough Fadden	NIAD	D 187 422	6.6			
5	Binevenagh Lough	NIAE	C 690 307	1.9			
6	The Fly Lough	NIAF	H 762 858	6.3			
7	Loughnapeast	NIAG	H 565 775	1.0			
8	Lough Skale	NIAH	H 309 442	5.8			
9	Lough Bradan	NIAI	H 259 713	10.0			
10	Brancepeth Pond	UKAA	NZ 232 380	0.5		95	
11	Debdon Lake	UKAB	NU 063 028	5.3			
12	Tindale Tarn	UKAC	NY 605 587	12.5		215	
13	Mookerkin Tarn	UKAD	NY 083 233	3.6		115	
14	Whinfell Tarn	UKAE	SD 559 980	4.0		130	
15	Gormire Lake	UKAF	SE 503 833	5.5			
16	Londsborough Park Lake	UKAG	SE 879 457	1.3		65	
17	Willow Garth Pond	UKAH	SE 333 462	2.1			
18	Wyresdale Park Lake	UKAI	SD 513 494	4.0		80	
19	Pick Mere	UKAJ	S 684 771	2.1		25	
20	Bradley Hall Pond	UKAK	SK 223 459	1.0		165	
21	Carlton Lake	UKAL	SK 585 837	0.7		35	
22	Withcote Hall Lake	UKAM	SK 797 057	1.4		135	
23	Alder Lake	UKAN	SP 378 615	2.8		120	
24	Kinver Lake	UKAO	SO 814 835	2.8		100	
25	Llyn Heilyn	UKAP	167 583	0.7		395	
26	Crose Mere	UKAQ	SJ 430 306	8.0		95	
27	Llyn Aled	UKAR	SH 917 574	14.0		375	
28	Penbrynyreglwys Pool	UKAS	SH 303 923	2.0			
29	Llyn Gwernan	UKAT	SH 705 160	8.0		175	
30	Pencarreg Lake	UKAU	SN 537 457	8.0		115	

UNITED KINGDOM: 'FLAME' SAMPLING SITES (cont.)

No.	Name	Code	Grid Ref	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (ha)
31	St. Ishmal's Lake	UKAV	SM 837 075	2.6		35	
32	Warren Mill Farm Lake	UKAW	ST 050 759	1.3		95	
33	Foxgrove Pond	UKAX	SW 636 347	1.5		70	
34	Dozmary Pond	UKAY	SX 195 745	1.0		270	
35	"Upper North Town Lake"	UKAZ	SS 498 101	2.3		110	
36	Beesands Lake	UKBA	SX 819 410	1.0		10	
37	Cothelstone Park Lake	UKBB	ST 178 319	2.1		90	
38	"Arc Lake"	UKBC	SY 856 897	1.4		50	
39	Ampfield Wood Lake	UKBD	SU 417 250	0.1		50	
40	West Woodhay Lake	UKBE	SU 386 632	2.1			
41	Upper Newton Park Lake	UKBF	ST 694 643	1.5		100	
42	Ploddy House Pond	UKBG	SO 726 227	2.5		35	
43	Moat Farm Pond	UKBH	SP 779 097	1.8		75	
44	Hemingford Lake	UKBI	TL 278 706	1.2		10	
45	Holbrook Lake	UKBJ	TM 175 364	2.1		15	
46	Childerditch Pond	UKBK	TQ 613 904	3.4		50	
47	Park Lake	UKBL	TF 368 755				
48	Thompson Water	UKBM	TL 915 949				
49	The Lake	UKBN	TG 032 309				
50	Ranworth Broad	UKBO	TG 355 154				
51	Bayfordbury Park Lake	UKBP	TL 313 102				
52	Preston Court Pool	UKBQ	TR 244 606				
53	Farthing Lake	UKBR	TQ 741 147				
54	Nutfield Priory Lake	UKBS	TQ 298 498				
55	Cranbury Park Lake	UKBT	SU 442 233				
56	Loch Cul Fraioch	CULF	NC 025 330				
57	Loch Ascaig	UKBU	NC 850 255				
58	Loch Coire nan Arr	CNA9	NG 808 422	16.0			
59	Loch nam Badan Boga	BOGA	NH 099 930				
60	Loch Achilty	UKBV	NH 434 567				

UNITED KINGDOM: 'FLAME' SAMPLING SITES (cont.)

No.	Name	Code	Grid Ref	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (ha)
61	Loch Dallas	UKBW	NJ 092 472				
62	Corby Loch	UKBX	NJ 924 145				
63	Loch Doire Bhraghaid	UKBY	NM 925 586				
64	Loch Kinnardochy	UKBZ	NN 776 552				
65	Loch Tinker	TINK	NN 445 068				
66	Loch Doire nan Sgiath	UKCA	NN 575 863				
67	Lochnagar	NAG	NO 252 859	24.0			
68	Balthayock Loch	BALT	NO 185 234				
69	Loch na Naich	UKCB	NR 743 437				
70	Woodend Loch	WOOD	NS 705 667				
71	Belston Loch	BELT	NS 475 169				
72	Hoselaw Loch	HOSE	NT 808 319				
73	Loch Eddy	EDDY	NT 282 309				
74	Loch Grannoch	UKCC	NX 541 691				

IRELAND: 'FLAME' SAMPLING SITES

No.	Name	Code	Grid Ref	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (ha)
1	Lough Fern	IRL1	C 170 230	2.0			
2	Hynestown Naul Reservoir	IRL2	O 14 59	8.0	10	60	
3	Balrothery Reservoir	IRL3	O 19 61	3.5	10	50	
4	Mullagh Lake	IRL4	N 68 86	5.3	34	121	126
5	Brackley Lough	IRL5	H 19 21	11.5	188	59	1720
6	Fenagh Lake	IRL6	H 11 07	11.5	40	67	
7	Castlefore Lough	IRL7	H 06 08	11.0	30	66	
8	Cavetown Lake	IRL8	M 82 96	12.0	80	86	
9	Nasool Lough	IRL9	G 79 07	10.0	30	100	
10	Lough Bo	IRL10	G 79 18	8.0	45	100	
11	Glen Lake	IRL11	G 94 69	7.5	30	75	
12	Bannus Lough	IRL12	H 08 66	6.5	30	72	
13	Mourne Lough	IRL13	H 07 90	6.5	100	168	
14	Mount Dalton Lough	IRL14	N 30 51	7.0	40	122	
15	Fergus Lough	IRL15	M 80 68	6.5	10	80	
16	Lough Muck	IRL16	G 29 03	10.0	25	110	
17	Lough Bunaveela	IRL17	F 98 09	17.0	50	200	
18	Pollacoppul Lough	IRL18	L 75 68	8.5	25	40	
19	Lough Inagh	IRL19	L 84 53	6.5		20	
20	Nahasleam Lough	IRL20	L 97 44	6.0	29	34	2410
21	Aunilra Lough	IRL21	L 98 24	2.0	5	20	
22	Slieveaneena Lough	IRL22	M 15 30	5.0	25	100	
23	Lough Callow	IRL23	M 71 34	2.5	25	90	
24	Pallas Lake	IRL24	N 26 19	6.0	40	80	
25	Ballykeeran Lough	IRL25	N 47 44	14.3	31	38	5960
26	Anure Lough	IRL26	B 81 16	8.0	120	38	
27	Dungloe Lough	IRL27	B 78 13	6.2	50	16	
28	Lough Barra	IRL28	B 93 12	5.0	40	91	
29	Lough Keel	IRL29	C 15 23	10.0	60	100	
30	Lough Akibbon	IRL30	C 06 18	3.0	40	70	

IRELAND: 'FLAME' SAMPLING SITES (cont.)

No.	Name	Code	Grid Ref	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (ha)
31	Lough Abisdealy	IRL31	W 13 31	12.5	25	16	
32	Lough Shreelane	IRL32	W 17 35	21.0	15	40	
33	Driminidy Lough	IRL33	W 15 43	4.5	10	80	
34	Gouganbarra Lough	IRL34	W 08 66	10.5	25	170	
35	Barfinnihy Lough	IRL35	V 84 76	18.5	15	275	
36	Lough Brin	IRL36	V 78 77	7.5	25	100	
37	Cumeenduff Lough	IRL37	V 82 80	7.5	25	80	
38	Nakirka Lough	IRL38	V 73 89	8.5	10	160	
39	Cloonsnaghta Lough	IRL39	R 21 59	5.0	10	71	
40	Lough Nammina	IRL40	R 17 70	5.0	20	170	110
41	Lough Bleach	IRL41	R 44 54	11.0	30	5	
42	Lough Gur	IRL42	R 64 41	4.0	70	81	
43	Lough Belle	IRL43	S 66 04	12.0	50	45	
44	Knockaderry Lough	IRL44	S 49 06	5.5	40	100	
45	Ballyshunnock Lough	IRL45	S 45 08	12.0	20	100	
46	Glendalough	IRL46	T 10 96	33.2	38	133	1870
47	Lough Dan	IRL47	O 15 03	36.0	80	200	
48	Lough Bray Lower	IRL48	O 13 16	47.6	29	375	1280

ESTONIA: 'FLAME' SAMPLING SITES

No.	Name	Code	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (km^2)
1	Põhjatu	EST1	4.0	0.5	7.0	0.17
2	Tihu Kolmas	EST2	1.5	4.6	15.2	3.03
3	Karujärv **	EST3	5.5	330.0	32.2	16.1
4	Koigi Naistejärv **	EST4	3.0	3.1	9.6	0.31
5	Väike Toatse	EST5	7.0	0.4	2.1	0.47
6	Veskijärv	EST6	3.0	191.8	15.2	23.5
7	Vaistu Ümarjärv	EST7			4.0	1.27
8	Klooga	EST8	3.6	135.0	11.8	5.8
9	Järveotsa	EST9	6.3	16.9	41.7	0.7
10	Harku *	EST10	2.5	1.64	0.9	50.0
11	Nigula **	EST11	3.1	17.9	53.7	2.03
12	Rummu	EST12	2.8	49.6	36.0	7.1
13	Paunküla Mustjärv **	EST13	8.0	2.6	72.0	0.47
14	Loosalu	EST14	5.0	34.1	73.2	1.6
15	Umerik **	EST15	14.0	1.6	71.3	11.3
16	Matsimäe Puhajärv **	EST16	8.1	5.5	77.0	1.53
17	Auksi **	EST17	9.8	7.3	99.5	1.81
18	Holstre Mustjärv **	EST18	6.0	1.2	89.5	0.45
19	Muti Umbjärv **	EST19	6.3	1.6	97.0	0.22
20	Udsu **	EST20	30.2	6.2	76.0	1.15
21	Viitna Linajärv	EST21	5.0	4.5	74.9	0.4
22	Neeruti Orajärv	EST22	5.1	2.8	89.2	
23	Äntu Sinijärv **	EST23	8.0	2.4	94.6	0.14
24	Prilljärv **	EST24	11.5	2.6	78.5	1.25
25	Viisaagu **	EST25	13.0	23.0	34.7	6.5
26	Otepää Kärnjärv **	EST26	11.5	5.7	146.2	0.58
27	Ödrejärv **	EST27	9.0	2.7	95.0	0.92
28	Uljaste	EST28	6.4	62.9	66.0	1.1
29	Tudu	EST29	5.0	25.7	80.2	1.1
30	Ilmjärv **	EST30	6.2	2.5	62.0	0.84

ESTONIA: 'FLAME' SAMPLING SITES (cont.)

No.	Name	Code	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (ha)
31	Vasula *	EST31	14.5	9.6	48.0	3.78
32	Piigandi Kogrejärv **	EST32	7.7	2.1	125.0	0.45
33	Väike-Palkna **	EST33	31.9	4.5	179.1	0.37
34	Jõuga Liijärv	EST34	8.3	2.2	59.0	0.17
35	Kuningvere **	EST35	7.4	24.3	55.0	3.66
36	Lahojärv **	EST36	6.0	2.7	47.0	0.57
37	Karsna **	EST37	8.1	16.3	78.1	1.41
38	Nohipalu Valgejärv **	EST38	12.5	6.3	53.9	1.12
39	Engle *	EST39	5.5	7.7	156.0	
40	Potri	EST40	6.5	0.6		
41	Mätasjärv	EST41	9.0	0.5		
42	Tuuljärv	EST42	18.0	3.5	257.0	1.95
43	Holvandi Kivijärv	EST43	18.2	5.9	58.4	0.67
44	Hüüdre	EST44	8.0	5.4	113.9	1.2
45	Kaisma	EST45			35.0	

* = sediment cores taken
** = both sediment cores and moss samples taken

CZECH REPUBLIC: 'FLAME' SAMPLING SITES

No.	Name	Code	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (km^2)
1	Prisecnice	4/1	47.0	364	734	46
2	Flaje	5/1	47.0	149	737	43.1
3	Bedrichov	7/1	14.6	42	775	4.3
4	Josefuv Dul	7/2	39.0	150	733	19.8
5	Sous	8/1	20.0	102	770	14
6	Horka	10/1	39.7	130	507	70
7	Skalka	10/2	14.0	385	444	672
8	Jesenice	10/3	18.1	746	441	407
9	Stanovice	11/1	54.0	142	518	92
10	Zlutice	11/2	23.0	161	510	216
11	Nechranice	12/1	46.0	1338	273	3590
12	Klicava	12/2	38.0	72	298	80
13	Amerika	13/1	20.0			
14	Vrchlice	14/1	33.0	102	325	101
15	Rozkos	16/1	17.0	1000	283	43
16	Lucina	20/1	22.0	80	534	105
17	Hracholusky	21/1	31.4	470	357	1610
18	Skali	22/1	20.0			
19	Drasov	23/1	8.0	6	500	
20	Luh	23/2	7.0	6	500	
21	Svihov	24/1	55.0	1670	379	1178
22	Sec	25/1	34.0	220	490	216
23	Hubenov	25/2	19.0	47	253	19
24	Vir	26/1	66.0	224	469	414
25	Kruzberk	28/1	31.0	287	431	557
26	Bystricka	29/1	27.0	38	386	64
27	Terlicko	30/1	23.0	268	278	82
28	Zermanice	30/2	28.0	248	294	45
29	Sance	30/3	62.0	335	507	164
30	Nyrsko	32/1	34.0	148	524	81

CZECH REPUBLIC: 'FLAME' SAMPLING SITES

No.	Name	Code	Maximum Depth (m)	Lake Area (ha)	Altitude (m)	Catch. Area (km^2)
31	Husinec	33/1	25.0	68	530	213
32	Rimov	34/1	43.0	211	471	489
33	Vranov	36/1	58.0	765	352	2221
34	Brnenska	37/1	19.0	259	231	1575
35	Lipno	48/1	20.0	4870	726	951

ADDITIONAL INFORMATION ON SAMPLED CZECH SITES

Name	Code	Year of Construction	Purpose	Trophic Status	Land Use	Moss Sample
Drasov	23/1	1959	D	M	Coniferous forest	PS
Flaje	5/1	1960	D,El,F	M	Coniferous forest	other
Horka	10/1	1970	D,F	M	Coniferous forest	-
Hracholusky	21/1	1964	El,In,F,Ir	E	Agric, Forest, Settlements	PS
Hubenov	25/2	1971	D	M	Agric	PS
Jesenice	10/3	1961	In,F,D	E	Agric, Forest, Settlements	other
Lucina	20/1	1974	D	M	Coniferous forest	PS
Nechranice	12/1	1968	In,El,Ir,D	E	Agric, Settlements	-
Nyrsko	32/1	1969	D,In,Ir,F	M	Coniferous forest	PS
Prisecnice	4/1	1976	D,El,F	M	Coniferous forest	-
Sec	25/1	1935	D,El,In,F	E	Agric, Forest, Settlements	PS
Skalka	10/2	1964	In,F	E	Agric, Forest, Settlements	-
Svihov	24/1	1976	D	M	Agric, Forest, Settlements	-
Vir	26/1	1958	El,D,F,In	M	Agric, Forest	PS
Vrchlice	14/1	1970	D,Ir,F	M	Agric	PS
Zlutice	11/2	1968	D,F,Ir	E	Agric, Forest, Settlements	-

D= Drinking water
El= Electricity generation
F= Flood control
In= Water for industry
Ir= Irrigation

M= Mesotrophic
E= Eutrophic

Agric= Agriculture

PS= *Pleurozium schreberi*