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Trace element measurements within London and across the UK with particular emphasis on mercury

Preliminary Report to the Department of Environment

Contract No. EPG 1/3/159

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TRACE ELEMENT MEASUREMENTS WITHIN LONDON AND ACROSS THE UK WITH PARTICULAR EMPHASIS ON MERCURY.

A preliminary report to the Department of the Environment, Transport and the Regions.
Contract No. EPG 1/3/159

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Introduction

EC Directive 96/62/EC on ambient air quality assessment and management, the 'Air Quality Framework Directive', and its associated Air Quality Daughter Directives will have an important impact on UK air quality policy and the UK Air Quality Strategy (DETR, 1999). The first Daughter Directive, adopted in April 1999, established legally binding limit values for lead to be achieved by 1st January 2005 and 2010.

The Heavy Metals Protocol, signed in 1998, addresses atmospheric emissions of cadmium, lead and mercury with the provision for adding other metals and controls in future if international action is required. This Protocol will need to be taken into account in setting objectives for heavy metals covered by future Air Quality Daughter Directives. The European Commission is now developing proposals for Daughter Directives to include cadmium, arsenic, nickel and mercury.

However, despite these requirements and the current interest in developing a critical loads approach to metals deposition within Europe (UNECE LRTAP Task Force on Mapping, 1998) there is a paucity of trace metals data for the UK.

In a review for the DETR on the state of metals monitoring within the UK, Henderson (1999) found very few long-term (> 2 years) multi-element studies covering more than one site. In the absence of such direct monitoring data lake sediments have been found to be useful as natural archives and can cover hundreds or thousands of years enabling current deposition patterns to be put into their correct historical perspective (e.g. Brannvall et al., 1999).

The aim of this project is to provide additional contemporary metals (especially mercury) data to that currently available and to place this in a temporal context on both a short time scale (annual variability in depositional values) and, using lake sediments, decadal scales within London and still longer scales (centuries) at selected sites across the UK.

This report includes a summary of work in progress (January - March 2000) and those data available at the end of March 2000. It also includes retrospective mercury data for deposition in London for the period January - December 1999. A final report, including data interpretation, will be produced upon completion of the entire work programme.

Objectives

1. Monitoring mercury concentrations in deposition in London over the period of a year (1999 - 2000) and selected metals over the period January - March 2000.

2. Determining the spatial distribution of mercury and selected metals across London using lake surface sediments

3. Identifying temporal patterns of mercury and selected metals over the last century using a lake sediment core from London

4. Identifying temporal patterns of mercury and selected metals over 350+ years using lake sediment cores from five sites across the UK.

Results

1. Mercury and selected metals in deposition in London (January 1999 - March 2000).

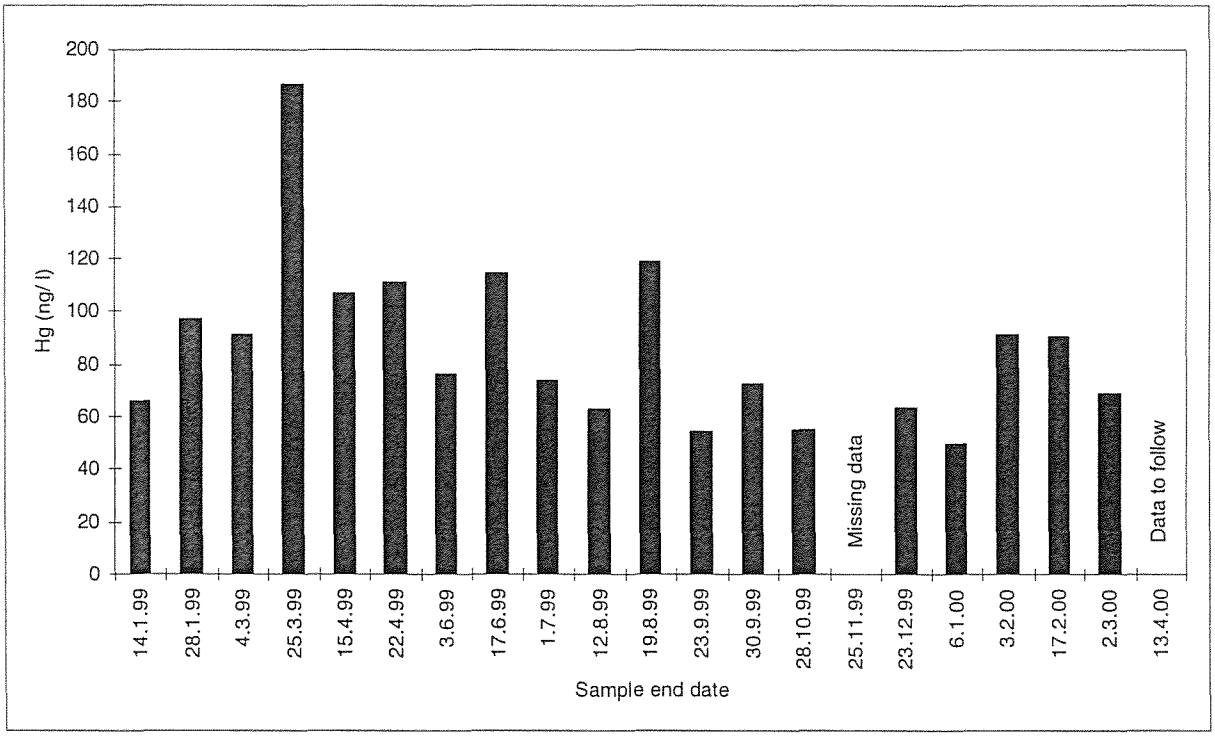
In January 1999,a standard deposition collector suitable for mercury sampling (as recommended by the Norwegian Institute for Air Research - NILU) was established on the roof of the Geography Department, University College London. This location is secure and sufficiently elevated (c. 25m) to be

removed from contamination by re-suspended road dusts and vehicular emissions. Samples were collected weekly although if insufficient sample was collected over this period the sampling was extended for a further week.

All equipment and PTFE collecting bottles in contact with samples were cleaned following NILU protocols. This involved acid soaking in HNO_3 overnight followed by three rinses in deionised water. Samples were acidified with concentrated HNO_3 (suprapure) to a total acid concentration of 1% (v/v). Acidified samples were stored at 5°C prior to analysis. Samples were sent to NILU for analysis by cold vapour atomic fluorescence spectroscopy (CV-AFS). Detection limits were in the region of 1 ng l^{-1}. The results for the available Hg data are shown in Figure 1.

For the period January - March 2000 a sub-sample of the acidified sample was taken and stored at 5°C for analysis of Pb, Cd, As, Cr, Mn, Ni, Cu, Zn, Pt, Pd, Rh, V, Be, Se, Sn by ICP-MS.

Figure 1. Mercury in deposition for central London.



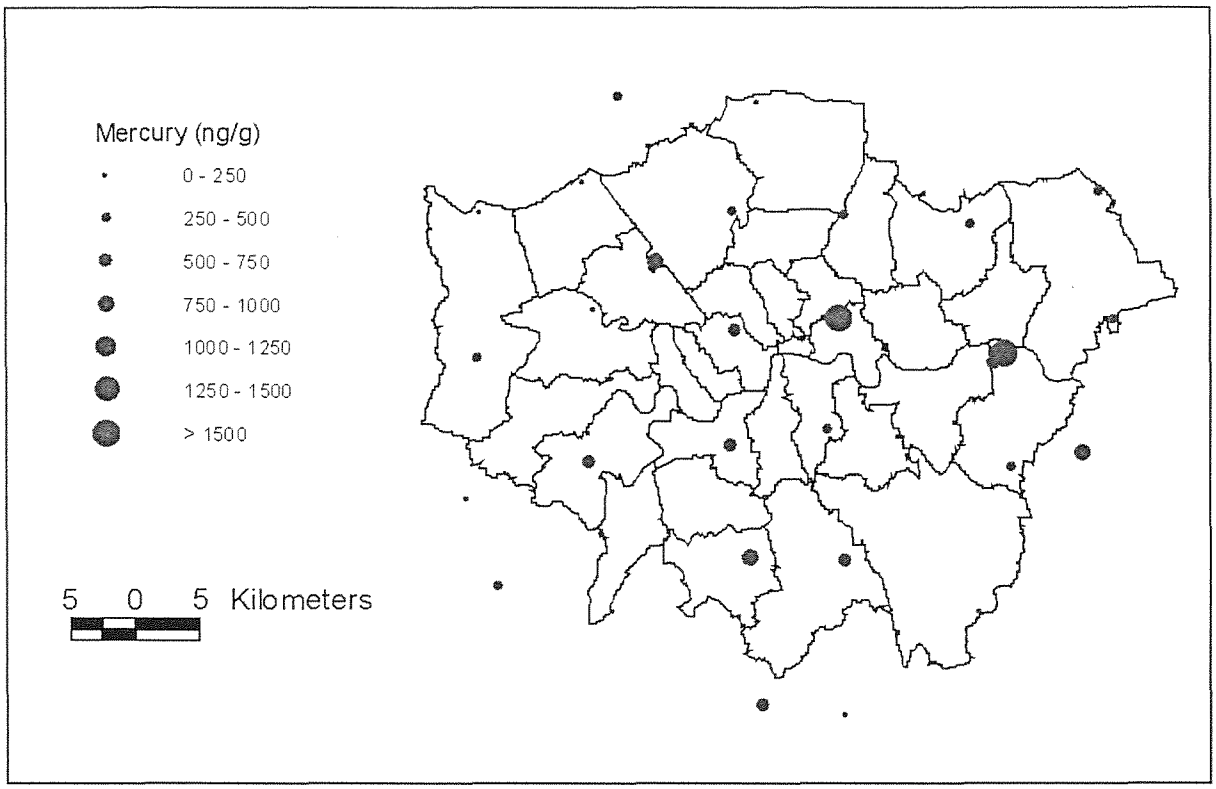
Mercury data for the final sample and the remaining metals data for the samples from January to March 2000 remain outstanding.

2. Spatial distribution of mercury and selected metals across London using lake surface sediments

As they accumulate, lake sediments store a record of atmospherically deposited pollutants falling onto the lake surface and the immediate catchment. Lake surface sediments can therefore provide a reliable indication of recent deposition and the analysis of a number of surface sediments from across a region can provide information on deposition gradients and 'hot-spots'. Such information is therefore very important in highly populated areas where it can quickly and easily identify areas where further sampling and monitoring should take place. From within the M25, surface sediments from 27 lakes were taken between June and August 1998 to provide a regular grid across London. These were analysed for mercury using cold-vapour atomic absorption spectroscopy (CV-AAS) at the University of Liverpool. These preliminary, unvalidated Hg results are shown in Figure 2.

The other selected metals, Pb, Cd, Cr, Mn, Ni, Cu, Zn, V, As, Be, Se, Pt, Pd, Rh, Sn (+ Si, Ti, Fe, Ca, K, S, Rb, Sr, Zr) are to be analysed using a combination of AES, ICP-MS and XRF techniques at the University of Liverpool and University College London. These data are currently outstanding.

Figure 2. Mercury concentrations in surface sediments across London (unvalidated).



3. Temporal patterns of mercury and selected metals over the last century using a lake sediment core from London

In order to put contemporary sediment concentrations into their correct historical context, analysis of full sediment cores needs to be undertaken. In London, sediment records are often very short due to site disturbance such as sediment dredging. It is rare to find sites where the sediment record has been undamaged for any reasonable period of time. The sediment core BANB5 from Banbury Reservoir, Walthamstow, (NGR: TQ 361 914) is therefore of great interest as the site was built in 1895 and the sediment record is thought to be intact since this time. BANB5 has been analysed for Na, Mg, Ba, Co, Cr and Ni by AES, Cd by AAS, Si, Al, Ti, Ca, K, Fe, Mn, S, Pb, Zn, Cu, Zr, Rb, Sr and Br by XRF, Hg by CV-AAS and is currently being dated using a radionuclide chronology. Although not part of this current project it is hoped that this dating will be available for the final report. Figure 3 shows the available metals data for the Banbury Reservoir core along with the lithostratigraphic information % dry weight and % loss-on-ignition (at 550°C) and wet and dry density measurements. Data for the requested elements V, As, Be, Se, Pt, Pd, Rh and Sn are currently outstanding and will be measured by ICP-MS at University College London.

Total storage densities for Hg, Pb, Cu, Zn and Cd, for the period 1895 to 1998 calculated from these sediment profiles are 43.2 mg m^{-2}, 23.1 g m^{-2}, 9.8 g m^{-2}, 28.6 g m^{-2} and 1.2 g m^{-2} respectively.

Figure 3. Lithostratigraphic and metals data for the Banbury Reservoir core (BANB5).

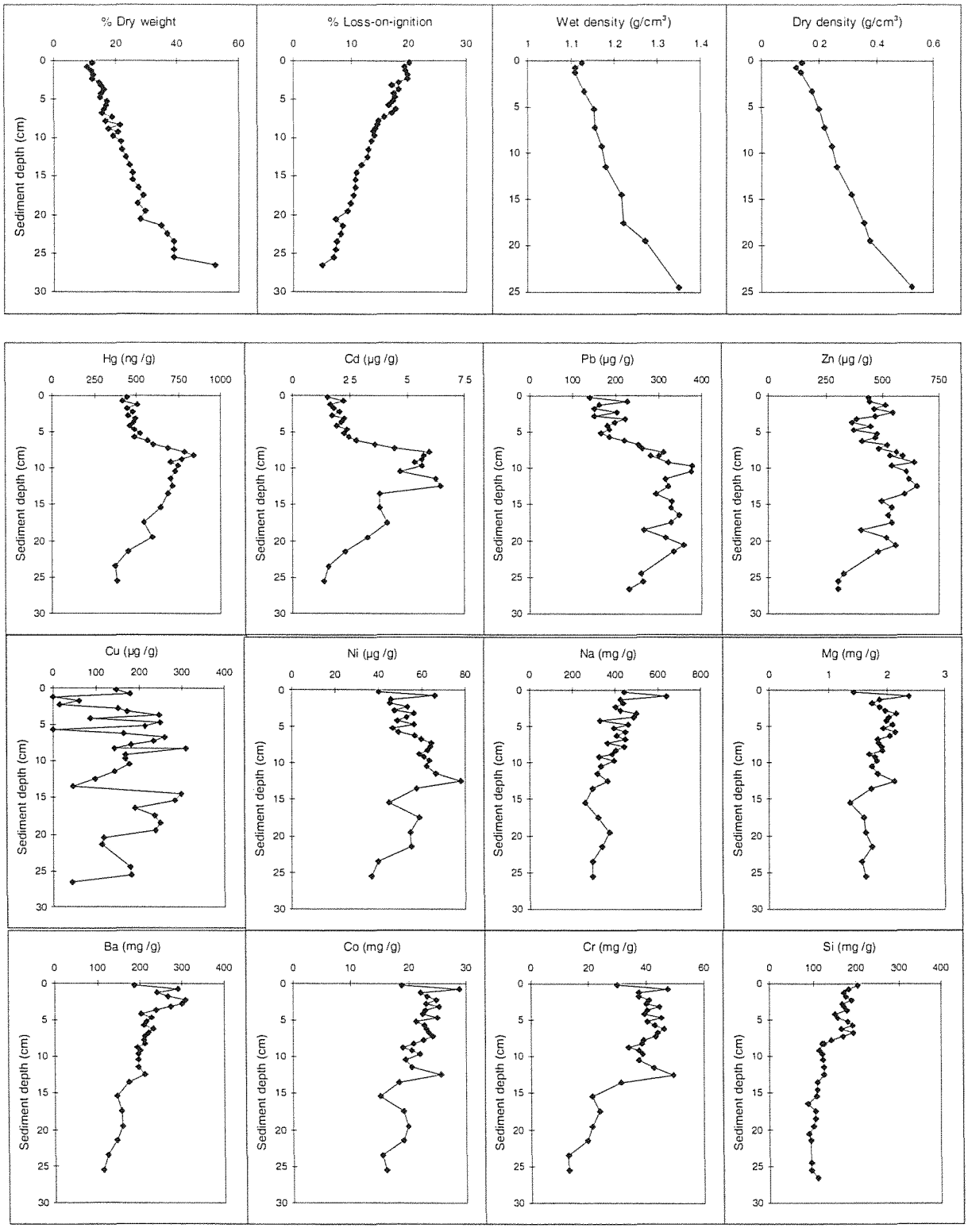
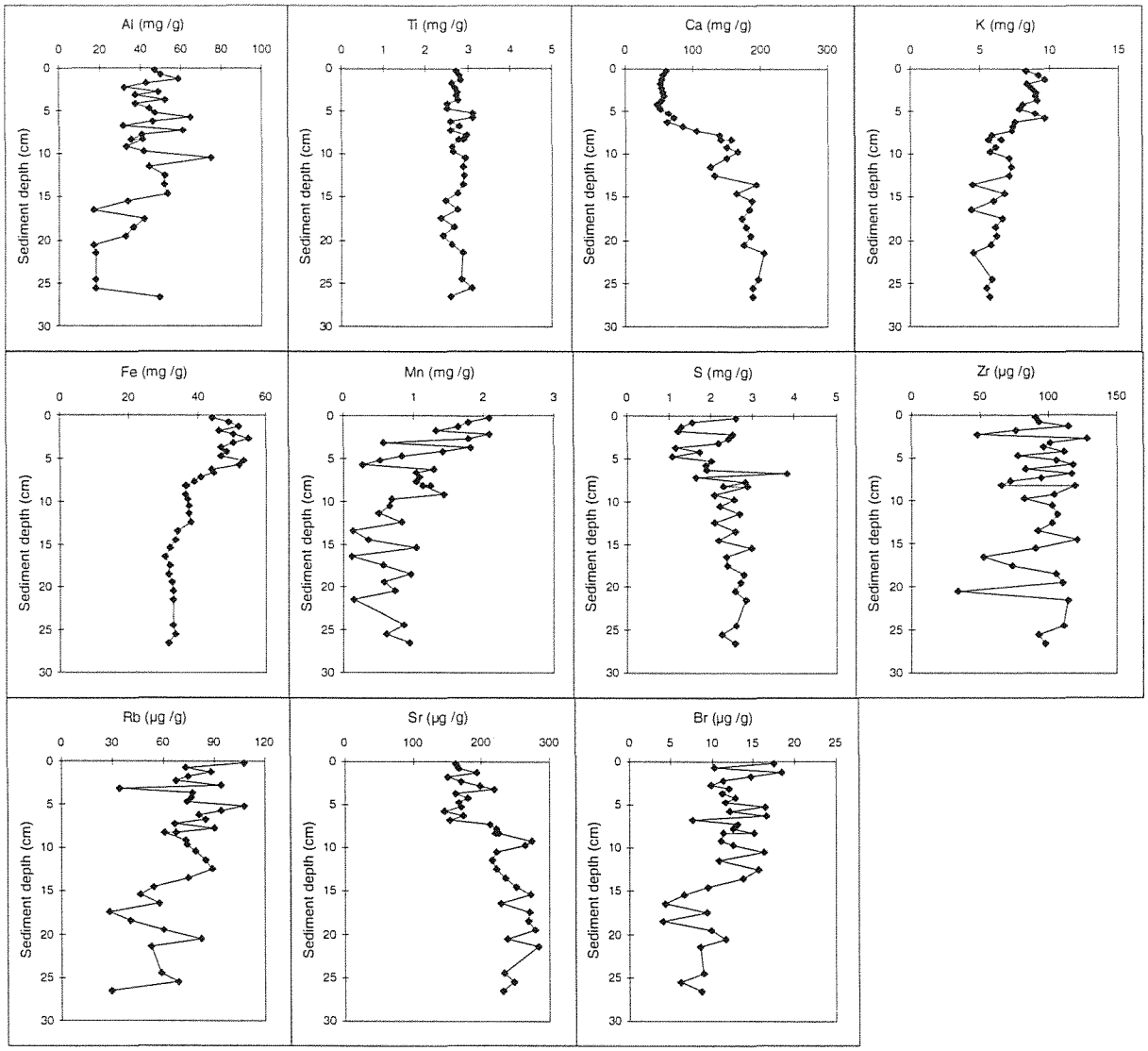


Figure 3 (cont)



4. Historical patterns of mercury and selected metals across the UK.

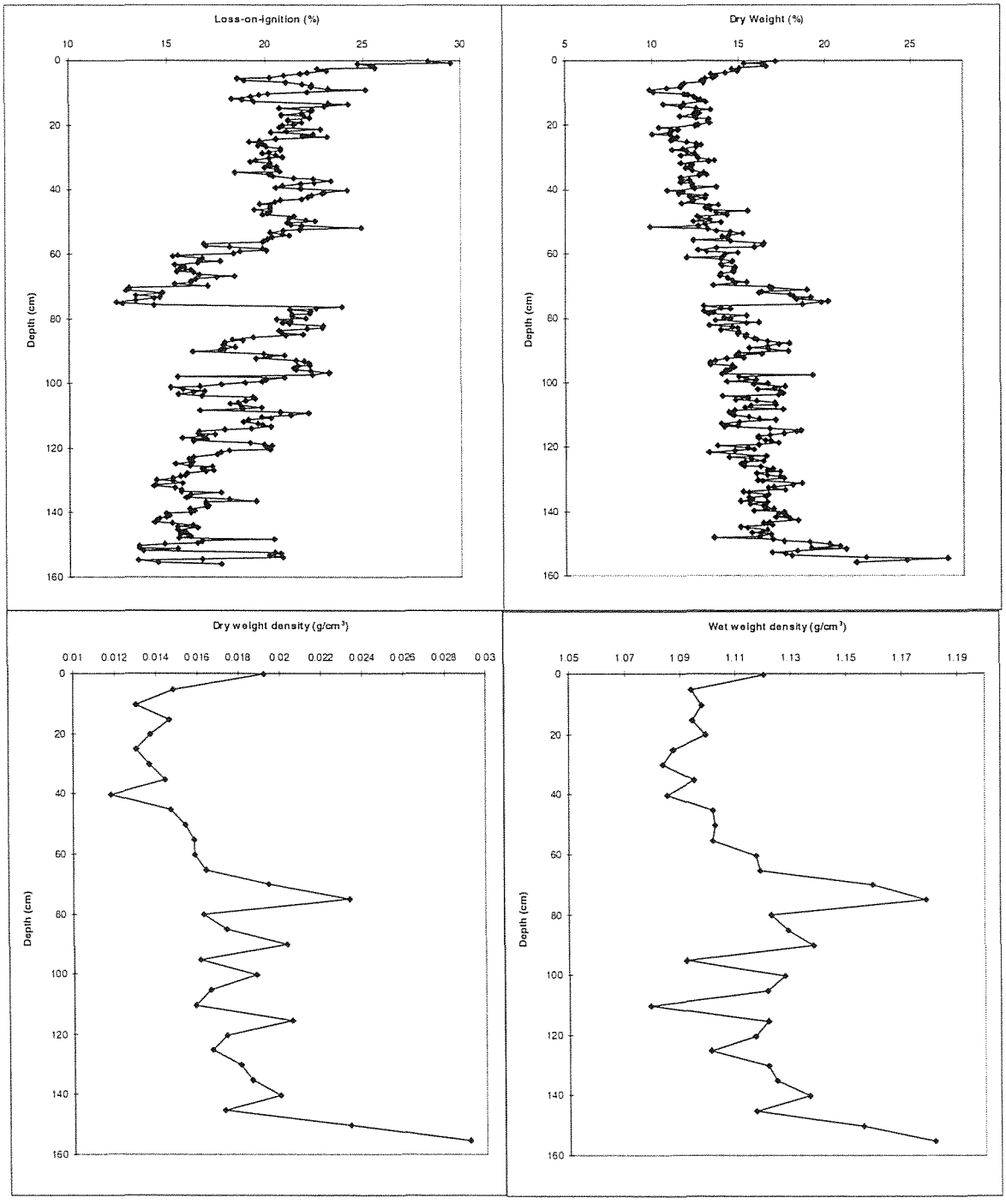
Although undisturbed sediment records of 100 years are rare in London, across the UK, many lakes contain records dating back hundreds or thousands of years. Most sites with undisturbed records such as this are in upland areas. Five lakes were selected for coring in order to gain a sediment record covering the full industrial and a significant pre-industrial period (i.e. at least 350 years). As there are no resources for sediment dating within this current project, sites were selected which had been cored and dated by the ECRC before and at which we therefore had an idea of sediment accumulation rate and hence an idea of how long a core was needed to cover the required time period. The five sites were also UK Acid Waters Monitoring Network sites. A great deal is known now about the lakes in the Network and this will help interpretation of the data produced in this project.

The sites were: Lochnagar, Loch Chon and Loch Grannoch in Scotland, Burnmoor Tarn in the English Lake District and Llyn Llagi in the Snowdonia region of Wales. For further details about the UKAWMN and these sites see the web-site at http://www.geog.ucl.ac.uk/ukawmn

Loch Chon, Loch Grannoch, Burnmoor Tarn and Llyn Llagi were cored in March 2000 using a mini-Mackereth corer. This produced cores 85 - 90 cm long for each site and these, extrapolating from previous dated cores, should cover in the region of at least 800 - 900 years, 350 years, 350 years and 600 years respectively.

A longer core of 156cm (NAG29) was taken from Lochnagar using a tapper corer. Comparison with other cores from the site dated using AMS ^{14}C dates and confirmed using pollen analysis suggests that this core could cover in the region of 8000 years, almost the full Holocene record. Figure 4 shows the results of the lithostratigraphic analyses (% dry weight, % loss-on-ignition, wet and dry densities) from this core. These measurements remain to be done on the cores from Loch Chon, Loch Grannoch, Burnmoor Tarn and Llyn Llagi as do the analyses for the full suite of elements (Hg, Pb, Cd, Cr, Mn, Ni, Cu, Zn, V, As, Be, Se, Pt, Pd, Rh, Sn, Si, Ti, Fe, Ca, K, S, Rb, Sr and Zr) on all the cores. These are to be undertaken using a combination of AES, ICP-MS and XRF techniques at the University of Liverpool and University College London on 50 levels from each core.

Figure 4. Lithostratigraphic analyses from Lochnagar core NAG29.



Work in progress

1. Mercury and selected metals in deposition in London (January 1999 - March 2000).

- The Hg data from the final sample remains to be received from NILU.
- The samples from January - March 2000 remain to be analysed for Pb, Cd, As, Cr, Mn, Ni, Cu, Zn, Pt, Pd, Rh, V, Be, Se, Sn.

2. Spatial distribution of mercury and selected metals across London using lake surface sediments

- The Hg data remain to be fully validated.
- The 27 surface samples remain to be analysed for Pb, Cd, Cr, Mn, Ni, Cu, Zn, V, As, Be, Se, Pt, Pd, Rh, Sn, Si, Ti, Fe, Ca, K, S, Rb, Sr, Zr.

3. Temporal patterns of mercury and selected metals over the last century using a lake sediment core from London

- The Banbury Reservoir core (BANB5) remains to be analysed for V, As, Be, Se, Pt, Pd, Rh and Sn.

4. Historical patterns of mercury and selected metals across the UK.

- Lithostratigraphic analyses remain to be completed on the cores from Loch Chon, Loch Grannoch, Burnmoor Tarn and Llyn Llagi. These analyses for the Lochnagar core NAG29 are complete.
- Analysis of Hg, Pb, Cd, Cr, Mn, Ni, Cu, Zn, V, As, Be, Se, Pt, Pd, Rh, Sn, Si, Ti, Fe, Ca, K, S, Rb, Sr and Zr remain to be done on 50 levels from each core. These are to be undertaken using a combination of AES, ICP-MS and XRF techniques at the University of Liverpool and University College London.

5. Reporting.

- A final interpretative report will be produced by Autumn 2000.

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