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

Final report to the Department of the Environment, Transport and the Regions, Department of the Environment Northern Ireland, National Assembly for Wales and the Scottish Executive.
Contract No. EPG 1/3/159

H. Yang, N.L. Rose and A. Berry
ENSIS - Environmental Change Research Centre, University College London, 26 Bedford Way,London, WC1H 0AP.

January 2001

SUMMARY

- Bulk deposition samples have been collected in London since 7th January 1999 and analysed for Hg concentration using cold vapour atomic fluorescence spectrometry (CV-AFS). Since 26th November 1999, sub-samples from these deposition samples have been taken in order to measure lead (Pb), cadmium (Cd), copper (Cu), zinc (Zn), chromium (Cr), manganese (Mn), nickel (Ni), arsenic (As), platinum (Pt), palladium (Pd), rhodium (Rh), vanadium (V), beryllium (Be), selenium (Se) and tin (Sn) using inductively coupled plasma - mass spectrometry (ICP-MS).

- Mercury (Hg) concentrations in London deposition samples were found to be in the range 45 - 187 ng/l with a mean of 81.5 ng/l. Similarly, Pb had a range of 4.58 - 35.2 μg/l with a mean of 17.9 μg/l and Cd a range of 0.04 - 0.40 μg/l with a mean of 0.16 μg/l.

- Whilst no temporal trends were observed in the metal deposition data, some elements such as Cu, Pb and Ni were seen to co-vary over the period of sampling.

- The rainfall in London from 7th January 1999 to 6th January 2000 was 612 mm, about one third that at Lochnagar, a mountain lake site in Scotland where similar monitoring is being undertaken. Despite this low rainfall, the yearly Hg deposition flux in London is 47.01 $\mu g/m^2$, higher than that at Lochnagar, and this is due to the high Hg concentration.

- Surface sediment samples from 29 lakes and ponds across London (within the M25) and sediment cores from 5 lakes and 1 reservoir (Loch Chon - Trossachs; Loch Grannoch - Galloway; Lochnagar- Grampians; Llyn Llagi – Snowdonia; Burnmoor Tarn – Lake District; Banbury Reservoir – London) across the UK were taken. These samples were analysed for lithostratigraphic parameters such as dry weight, loss-on-ignition and wet density, and analysed for Hg, Pb, Zn, Cd, Cu, Cr, Ni, Mn, As, V, Be, Se, Sn, Pt, Pd, aluminium (Al), silicon (Si), iron (Fe), titanium (Ti), rubidium (Rb), strontium (Sr), zirconium (Zr), and niobium (Nb) using a combination of CV-AAS, XRF, and ICP-MS. In Nag29, the sediment core taken from Lochnagar, stable Pb isotopes ^{206}Pb and ^{207}Pb have also been measured using ICP-MS.

- London surface sediments show large ranges in concentrations for Hg, Pb, Zn, Cd, Cu, Cr, Ni, As, V, Se and Sn. Sites close to industrial areas, roads or commercial areas usually have high concentrations of these elements.

- Sediment cores show that sites across the UK have been contaminated by Hg, Pb, Zn, Cd, Cu, Cr, Ni, As, V, Se and Sn. In Nag29, it appears that Hg concentrations increase from c. 6000 years ago to the present. This increase is much earlier than observed elsewhere. There is a rapid increase in Hg concentration during the last 200 years or so at all rural sites. In the 95 year record from Banbury Reservoir in London the sediments show high Hg concentrations throughout.

- The provenance of the Hg in the sediments varies and catchment in-wash influences Hg loading to the sediments. Catchment contributions result in a sharp peak (1606 ng/g) in the Hg concentration profile in the core Chon14 taken from Loch Chon in the Trossachs region of Scotland. Considering Hg concentrations and predicted sediment accumulation rates, it appears that the Hg accumulation rates for these UK sites, except Lochnagar, would fall into the upper range for Europe. However without dating, it is not possible to say with any certainty.

- Pb, Zn, Cd, Cu and Sn profiles in the cores taken from rural areas are similar to the Hg profiles in individual cores, whilst As, V, Se, Cr and Ni profiles show different temporal patterns. These profiles show that the lakes have been contaminated by these elements, and the sources of these elements are varied. Be, Pd, Zr, Rb, Sr and Nb are mainly from mineral material. In Banbury Reservoir, the sediments show high concentrations of Hg, Pb, Zn, Cu, Cr, Ni and Sn. This may reveal the history of local industrial development over the last c.100 years.

- Lead isotopes may be used to trace the influence of anthropogenic deposition. Lead from anthropogenic sources has a lower $^{206}Pb/^{207}Pb$ isotopic ratio than mineral lead and hence ratio changes through time indicate the extent to which the site has been impacted. In Nag29, the trend in lead isotope ratio is more significant than the Pb concentration profile alone. There are two major conclusions. First, that the isotope ratio, and hence human impact, has been declining slightly since c. 5000 years ago, and second, that this impact has significantly accelerated in the top 25cm of the core.

Contents

1 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, addressed atmospheric emissions of cadmium, lead and mercury with the provision for adding other metals and controls in future if international action is required. 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 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).

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.

However, in order to put contemporary sediment concentrations into an 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. Although records of 100 years or more 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 in previous studies and at which, therefore, there was an idea of sediment accumulation rate. The five sites were also UK Acid Waters Monitoring Network sites.

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 deposition values) and, using lake sediments, decadal scales within London and still longer scales (centuries) at the selected sites across the UK.

2 THE STUDY SITES AND METHODS

2.1 The study sites

2.1.1 The sites in London

On 7th January 1999, a standard mercury deposition collector (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 direct vehicular emissions. There are no major industries within the immediate location although a concrete and cement batching plant is located in the King’s Cross area 700 – 800m to the north (Rickard *et al.*, 1999). The site is in Bloomsbury, a fairly residential area of London with the University College London campus, hotels and offices in the immediate vicinity as well as many parks and public gardens. The road above which the monitor is sited has a typical traffic flow of c.10,000 vehicles a day (London Borough of Camden; pers. comm.). However, the site is surrounded by major traffic routes, Euston Road (A501) is 350m to the north (60,000 vehicles a day (Rickard *et al.*, 1999)), Oxford Street (A40) is 650m to the south, Tottenham Court Road and Gower Street (both A400) are 400m and 200m to the west respectively and Southampton Row (A4200) is 150m to the east.

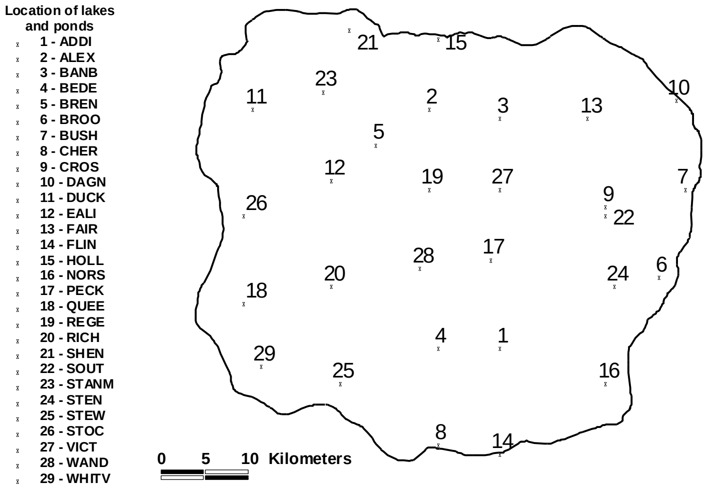
Surface lake sediment samples were taken from 29 sites within the M25 between June and August 1998 to provide a regular grid across Greater London. The names and grid references for these sites are shown in Table 1 and the sites mapped in Figure 1.

As mentioned above, undisturbed sediment records within London are rare. The sediment core Banb5 from Banbury Reservoir, Walthamstow, (NGR: TQ 361 914) (Site 3 in Figure 1) is therefore of great interest as the site was built in 1903 and the sediment record is thought to be intact since this time. This was the only sediment core from within the London area to be analysed in this project.

Table 1. The sites for surface sediment sampling in London

Number	Site Name	Short Name	Grid Reference
1	Addiscombe Scouts Club	ADDI	5361 1648
2	Alexandra Park Conservation Pond	ALEX	5275 1916
3	Banbury Reservoir	BANB	5361 1914
4	Grange Park Lake	BEDE	5289 1651
5	Brent Reservoir	BREN	5217 1877
6	Brooklands Lake	BROO	5544 1731
7	Bramble Farm	BUSH	5568 1833
8	Lake at Gatton Bottom	CHER	5289 1537
9	Crosmere Sewage Works Lake	CROS	5484 1807
10	Dagnam Park	DAGN	5557 1932
11	The Riverside Club	DUCK	5080 1916
12	Ealing Pond	EALI	5168 1841
13	Fairlop Waters	FAIR	5458 1907
14	Flint Hall Farm	FLIN	5361 1530
15	Holly Bush Farm	HOLL	5294 2001
16	Norstead Manor Farm	NORS	5464 1609
17	Peckham Rye Park Lake	PECK	5349 1749
18	Queen Mary Storage Reservoir	QUEE	5071 1697
19	Regents Park Boating Lake	REGE	5278 1825
20	Infilled pit in Richmond	RICH	5165 1724
21	Shenley Pond	SHEN	5188 2005
22	Southmere Lake	SOUT	5476 1800
23	Stanmore Common Lake	STANM	5161 1940
24	Stenhil Fishing Lake	STEN	5489 1720
25	Stew Pond	STEW	5183 1609
26	Stockley Park	STOC	5079 1804
27	Victoria Park	VICT	5356 1834
28	Wandsworth Pond	WAND	5274 1737
29	Whitely Village	WHITV	5094 1628

Figure 1. The sites for surface lake sediment sampling in London



2.1.2 Other study sites across the UK

The other sites selected for this project are: 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

Site description

Lochnagar:

Lochnagar is a corrie loch and lies at an altitude of 785 m in the centre of the granitic massif which comprises much of Balmoral Forest. No distinguishable inflow feeds the loch but it drains to the north-east through a series of small pools to the Lochnagar Burn which feeds the Gelder Burn, a south-bank tributary of the River Dee. The geology is composed of biotite granite overlain in places by blanket peat. Of the localised areas of peat in the catchment, certain areas, notably along the eastern shore, are severely eroded. At over 700 m the catchment lies above the limit of summer sheep grazing in the region and there is no evidence for any land-use change or active land-management within the catchment. Any anthropogenic pollutants are derived solely from atmospheric deposition.

Table 2. Lochnagar site characteristics

Grid reference	NO252859
Lake altitude	785 m
Maximum depth	26 m
Mean depth	8.4 m
Volume	8.2×10^5 m^3
Lake area	9.8 ha
Catchment area (excl. lake)	91.9 ha
Catchment : lake ratio	9.37
Catchment geology	granite
Catchment soils	peats
Catchment vegetation	alpine - moorland 100%
Net relief	370 m

Loch Chon:

Loch Chon lies at an altitude of 100 m in the Trossachs region of central Scotland with a surface area of 100 ha. It is fed by several small streams and drains to the south via Loch Ard and the River Forth. The geology consists of metamorphosed sediments of the Dalradian group (Cambrian), with bands of rocks containing high proportions of calcium and magnesium. Catchment soils consist of peaty gleys, peaty podsols and humus iron podsols. Most of the lower areas of the Loch Chon catchment are planted with coniferous forest. There is a small farm at the north end of Loch Chon, but in recent years the intensity of land-management in this area has declined. A small road passes through the catchment on the east side of the loch and a subterranean aqueduct, built in the nineteenth century to carry water from Loch Katrine to Glasgow, passes along the west side of the loch.

Table 3. Loch Chon site characteristics

Grid reference	NN 421051
Lake altitude	100 m
Maximum depth	25 m
Mean depth	7.6 m
Volume	7.3×10^6 m^3
Lake area	100 ha
Catchment area (excl. lake)	1570 ha
Catchment : lake ratio	15.7
Catchment geology	mica schists and grits
Catchment soils	peaty gleys, peaty podzols
Catchment vegetation	conifers - 44% moorland - 52% recently felled - 4%
Net relief	500 m

Loch Grannoch:

Loch Grannoch is a large elongated lake which lies at 210 m altitude in the Galloway region of south-west Scotland. Small streams feed the loch, and it drains to the north into the River Dee. The catchment of the loch forms part of the Cairnmore of Fleet granite intrusion. Catchment soils comprise blanket peat, peaty podsols and gleys with skeletal soils and bare rock on the highest ground. The catchment is largely afforested (70%) with conifers. Planting occurred in 1962 and 1977-1978.

Table 4. Loch Grannoch site characteristics

Grid reference	NX 542700
Lake altitude	210 m
Maximum depth	20.5 m
Mean depth	6.4 m
Volume	7.4×10^6 m^3
Lake area	114.3 ha
Catchment area (excl. lake)	1287 ha
Catchment : lake ratio	11.3
Catchment geology	granite
Catchment soils	peats, peaty podsols, peaty gleys, skeletal soils
Catchment vegetation	conifers - 70% moorland - 30%
Net relief	391 m

Burnmoor Tarn:

Burnmoor Tarn is the largest “tarn” in the English Lake District. It lies in a moraine hollow on the uplands between Wastwater and Eskdale. There are four main inflow streams to the north and north-west. The outflow at the eastern end joins the Hardrigg Beck which drains the slopes of Scafell and, in times of high flow, is partly diverted into the lake across a braided delta. To the north and west of the lake the bedrock is Ordovician andesite lava of the Borrowdale Volcanic series, to the south and east it is granite. There are thick till deposits in the catchment, notably on the southern side of the lake and the catchment soils are characterised by podsols and shallow peat rankers.

Table 5. Burnmoor Tarn site characteristics

Grid reference	NY 184044
Lake altitude	252 m
Maximum depth	13 m
Mean depth	5.1 m
Volume	8.9×10^5 m^3
Lake area	24 ha
Catchment area (excl. lake)	226 ha
Catchment : lake ratio	9.4
Catchment geology	andesite lava and granite
Catchment soils	podsols, shallow peat, rankers
Catchment vegetation	moorland - 100%
Net relief	350 m

Llyn Llagi:

Llyn Llagi occupies a north-facing corrie in the central area of the Snowdonia region of North Wales. The lake lies at 380 m beneath a steep backwall. The primary inflow consitutes the outflow stream from Llyn yr Adar which lies above the backwall. The lake drains to the north-west to the Nanmor Valley. The catchment geology consists primarily of Ordovician slates and shales of the Glanarfon series. The backwall is composed of a large doleritic intrusion with small intrusions of fine microgranites and volcanic tuff. Away from the precipitous bare rock of the backwall the catchment soils are chiefly stagnopodsols and gleys, interspersed with blanket peats. The catchment vegetation is characterised by acid moorland species and grazed at a low intensity by sheep but there is no other contemporary land-management.

Table 6. Llyn Llagi site characteristics

Grid reference	SH 649483
Lake altitude	380 m
Maximum depth	16.5 m
Mean depth	5.8 m
Volume	3.3×10^5 m^3
Lake area	5.67 ha
Catchment area (excl. lake)	157 ha
Catchment : lake ratio	27.7
Catchment geology	ordivcian slates and shales, dolerite and volcanic intrusions
Catchment soils	stagnopodsols, stagnohumic gleys, banket peat
Catchment vegetation	moorland - 100%
Net relief	298 m

2.2 Methods

2.2.1 Sampling

2.2.1.1 Deposition sampling

Bulk deposition samples were collected weekly unless insufficient sample was collected. In this case the sampling was extended for a further week.

The rack of the collector is made of black polyethylene, whereas all parts of the collector in contact with the sample (funnel, filter, capillary, and bottle) are made of borosilicate glass. The bulk sampler is protected from collecting wind-blown litter and insects by a capillary attached to the funnel and a filter placed in the bottom of the funnel. The collection bottle is fitted with a wide black polyethylene collar to protect against sunlight penetration. All equipment, and Teflon 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 HCl (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 fluoresence spectroscopy (CV-AFS). The detection limit for the method is 0.3 ng/l.

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

2.2.1.2 Sediment sampling

Core Banb5 was taken from Banbury Reservoir in August 1998 using a Glew Corer (Glew, 1991). An investigation of sediment thickness at the sampling site revealed that the core reached the sediment bottom, and therefore this core covers 95 years, the period since the formation of the reservoir. The core was sliced using a stainless steel slicer at 0.5 cm intervals from the surface to 10 cm depth, and then at 1 cm intervals from 10 cm to the bottom of the core.

A core of 156 cm (NAG29) was taken from Lochnagar using a tapper corer in September 1999. 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 6000 years, i.e. most of the Holocene record. This core was sliced at 0.5 cm from the surface to the bottom. Loch Chon (Chon14), Loch Grannoch (Gran5), Burnmoor Tarn (Burn3) and Llyn Llagi (Lag4) 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, 300 years, 300 years and 600 years respectively. These sediment cores were also sliced at 0.5 cm from the surface to the bottom.

During sediment coring and extrusion, plastic gloves were worn in order to avoid sample contamination.

2.2.2 Methods of elemental analyses

All the sediment samples were freeze-dried after measuring percentage dry weight (105°C), percentage loss-on-ignition (at 550°C), and wet density. Again, plastic gloves were worn at all time when the sediments were handled.

2.2.2.1 Digestion

The method for sediment digestion used in this study was to heat the samples at 100°C for one hour with 8 ml Aristar HNO_3. The procedure is described fully in Yang (2000). For Hg analysis, the method was slightly changed, as the Hg was measured by cold vapour atomic absorption spectrometry (CV-AAS). Again full details are described in Yang (2000).

2.2.2.2 Elemental analyses

Hg in deposition samples were analysed by cold vapour atomic fluorescence spectrometry (CV-AFS) at the Norwegian Institute for Air Research. The method reduces dissolved Hg^{2+} to elemental Hg (Hg^0) vapour by using tin chloride ($SnCl_2$) solution in a reaction vessel, and Hg^0 is then analysed by CV-AFS. The detection limit for the method is 0.3 ng/l which is lower than for ICP-MS. Analytical uncertainties lie within ±20% of the measured level. Since 26th November 1999, Pb, Cd, As, Cr, Mn, Ni, Cu, Zn, Pt, Pd, Rh, V, Be, Se, and Sn in deposition samples were measured by inductively coupled plasma mass spectrometry (ICP-MS) at University College London.

Hg in digested sediment solutions was measured by cold vapour atomic adsorption spectrometry (CV-AAS) at the University of Liverpool following reduction of Hg in the digested sample to its elemental state by 2 ml fresh $SnCl_2$ (10% in 20% (v/v) HCl) (Engstrom & Swain, 1997). During digestion and measurement, reference material (Buffalo River sediment 2704) and sample blanks were analysed every twenty samples. Measured mean concentrations of Hg were 93 ng/g in Buffalo River sediment ($n = 12$; relative standard deviation (RSD) = 8.6 ng/g; certified value = 100 ng/g). The standard solution was measured every five samples to monitor measurement stability. Calibration was made using the standard solution.

The Metorex Xmet920 X-ray fluorescence (XRF) spectrometer, run by the software DECONV, was used to measure Pb, Zn, S, Fe, Mn, Al, Ca, K, Si, Ti, Zr, Rb, Sr and Nb in the sediment samples. This was also at the University of Liverpool. The instrument was calibrated using Buffalo River Standard Sediment and has a reasonable accuracy for these elements (Boyle, 2000). In practice, DECONV uses Buffalo River sediment to monitor and correct for changes in the instrument. During measurement, Buffalo River sediment (NIST2704), stream sediment (GBW 7309) and pond sediment (NIES No.2) were run every ten samples, giving an opportunity to evaluate the accuracy of the measurements.

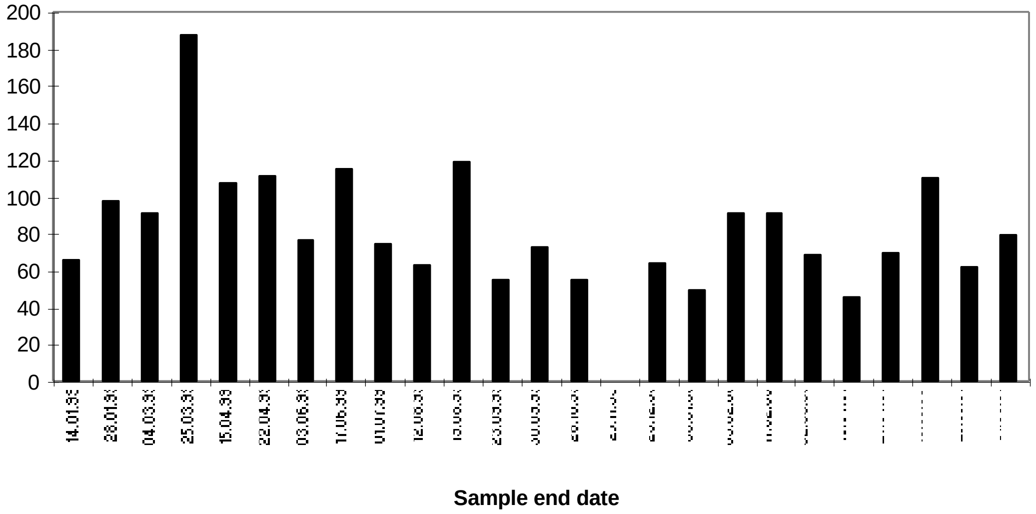
Pb, Cd, As, Cr, Mn, Ni, Cu, Zn, Pt, Pd, Rh, V, Be, Se and Sn in digested solutions were measured by ICP-MS at University College London. Reference material (Buffalo River sediment 2704) and sample blanks were analysed every twenty samples during digestion and measurement.

3 RESULTS AND DISCUSSION

3.1 Deposition in London

The concentration of Hg in deposition for central London from 7th January 1999 to 1st June 2000 are shown in Figure 2 and are seen to vary between 45 and 187 ng/l. Although it is difficult to interpret data from such short sampling periods it seems that Hg concentration in deposition during spring is higher than that during autumn, and Hg concentrations in the spring of 1999 are higher than those in the spring of 2000. This may be affected by the amount of rainfall. The mean concentration of Hg in central London deposition samples is 81.5 ng/l, which is more than three times that collected over the same period at Lochnagar (collected under the Critical Loads of Acidity and Metals project; CLAM). On a global scale, the dominant anthropogenic sources of atmospheric Hg are manufacturing, coal combustion, waste incineration, and non-ferrous metal smelting. The Hg in the deposition collected over the sampling period in London is likely to be a variable combination of these sources.

Figure 2. Hg concentrations (ng/l) in the deposition samples collected in London



By using data from the London Weather Centre, Holborn, the amounts of rainfall during the individual sampling periods were calculated as were the amounts of Hg deposition. The sum of rainfall between 7th January 1999 and 6th January 2000 was 612.3 mm and the sum of Hg deposition was 47.01 μg/m^2/year. At Lochnagar, the rainfall between 8th October 1997 and 7th October 1998 was 1655.5 mm, which is much higher than that in London, but the yearly Hg bulk deposition over this period was 35.87 μg/m^2/year, lower than that in London. This is due to the high Hg concentration in London deposition.

Other element concentrations in the deposition samples collected in London are shown in Table 7. Compared to the element concentration in Lochnagar deposition samples (Yang, 2000) and the data from the Rural Deposition Network monitoring site in Banchory (Oslo and Paris Commission, 1997), the concentrations of Cr, Ni, Zn and Pb in London deposition samples are generally 10 to 100 times higher.

Lead isotopes may be used to trace the influence of anthropogenic deposition. Lead from anthropogenic sources has a lower ^{206}Pb/^{207}Pb isotopic ratio than mineral lead and hence ratio changes through time indicate the extent to which the site has been impacted. Isotope ratios of ^{206}Pb/^{207}Pb in the London surface samples are very low suggesting anthropogenic Pb sources are very important contributors (see section 3.4). However, these data still require calibration.

As the samples collected for measuring these elements cover a relatively short period, it is not possible to interpret these trends further. However, it should be noted that some elements such as Cu, Pb and Ni were seen to co-vary over the period of sampling. A longer period of sampling is required to identify any temporal trend in these elemental depositions.

Table 7. Element concentrations (μg/l) in the deposition samples collected in London

Sampling period	Be	V	Cr	Mn	Ni	Zn	Cu	As	Se	Cd	Pb	^{206}Pb/^{207}Pb
26/11/99-23/12/99	0.018	n.d.	19.9	11.2	6.34	4.57	16.38	n.d.	3.16	0.15	24.6	0.931
24/12/99-06/01/00	0.006	n.d.	19.0	4.19	2.62	48.83	5.07	0.64	2.99	0.04	9.27	0.944
07/01/00-03/02/00	0.018	0.93	40.2	14.5	18.4	n.d.	17.96	n.d.	6.43	0.20	25.2	0.941
04/02/00-17/02/00	0.027	1.35	45.7	17.7	19.8	5.42	23.83	n.d.	5.11	0.18	35.2	0.931
18/02/00-02/03/00	0.012	n.d.	36.5	9.41	8.96	11.12	10.34	n.d.	3.47	0.17	14.5	0.947
03/03/00-13/04/00	0.017	n.d.	25.7	12.3	6.68	2.14	9.15	0.09	3.59	0.12	9.59	0.940
14/04/00-27/04/00	0.013	n.d.	26.0	10.5	8.86	1.01	9.53	n.d.	3.18	0.08	15.2	0.950
28/04/00-18/05/00	0.024	0.69	46.0	20.2	10.9	0.30	15.11	n.d.	4.37	0.21	17.3	0.910
19/05/00-25/05/00	0.011	n.d.	24.8	8.33	8.54	16.37	8.55	n.d.	4.11	0.09	15.0	0.950
26/05/00-01/06/00	0.003	n.d.	28.6	3.55	5.69	28.32	2.80	n.d.	4.45	0.05	4.58	0.951
02/06/00-29/06/00	0.042	n.d.	40.4	31.4	15.7	6.69	28.91	n.d.	6.23	0.40	32.1	0.946
30/06/00-13/07/00	0.010	n.d.	23.5	9.17	4.97	9.21	10.32	1.22	3.28	0.19	12.5	0.933

n.d.: not detected

3.2. Element distribution in London surface sediments

The distributions for Hg, Pb, Zn, S, Cd, Cu, Cr, Ni, Sn, Se, V, As and Be elements in London surface sediments are shown in Figures 3 to 15 and their concentrations can be seen to vary greatly over the region showing differences in contamination. The concentrations for the other measured elements in the surface sediments are given in Table 8. Generally, these elements have similar patterns of distribution. A few sites have high concentrations for most of these elements, but these are located in diverse areas and hence do not form a ‘hot-spot’. For example, CROS (site 9) is a lake within the Crosmere sewage work complex, close to Belvedere power station and CRODA

Resins Ltd; Victoria Park Lake (27) is in Victoria Park, in the middle of a dense residential and commercial area, but close to a number of roads with some industrial works to the east and a major rail depot to the north-east; Brent Reservoir is fed by Silk Stream. It is very close to a number of roads including the M1 motorway and is mostly surrounded by residential areas and parkland; Grange Park Lake is a small urban boating lake in Beddington Park, South London. A sewage works and some other industry are within 1 km to the north-east.

Figure 3. Hg concentrations in the surface sediments in London

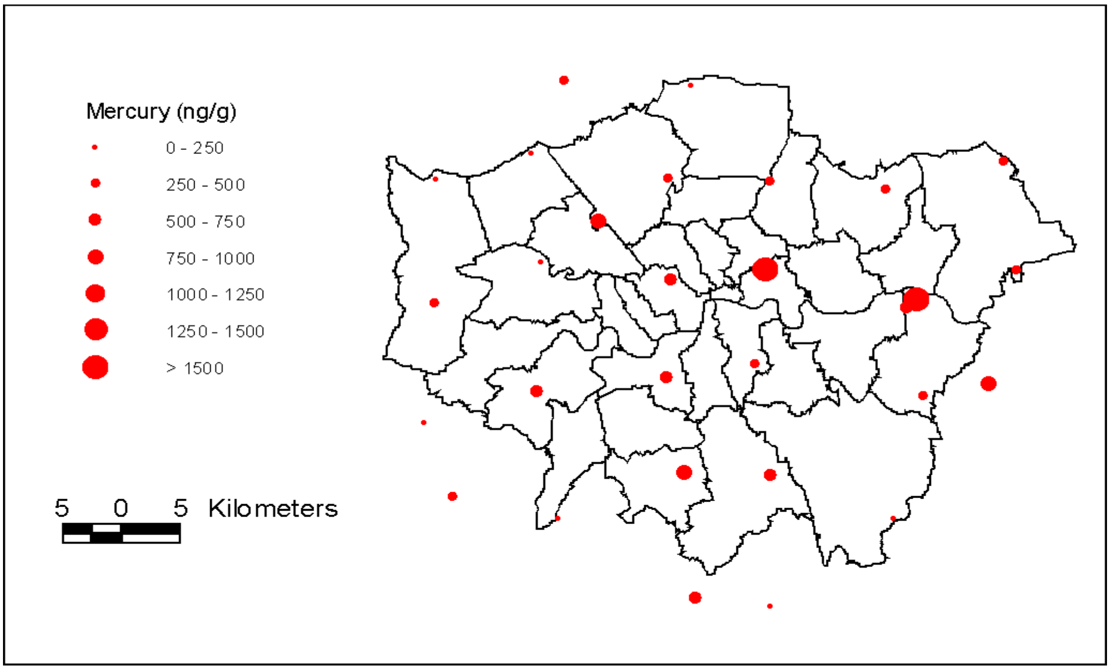


Figure 4. Pb concentrations in the surface sediments in London. (Boundary line denotes the M25).

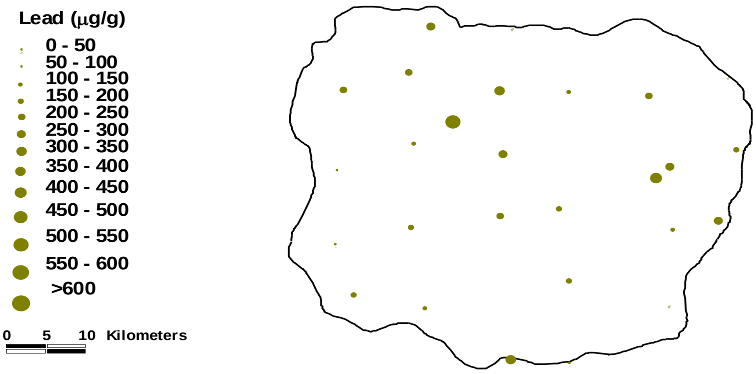


Figure 5. Zn concentrations in the surface sediments in London

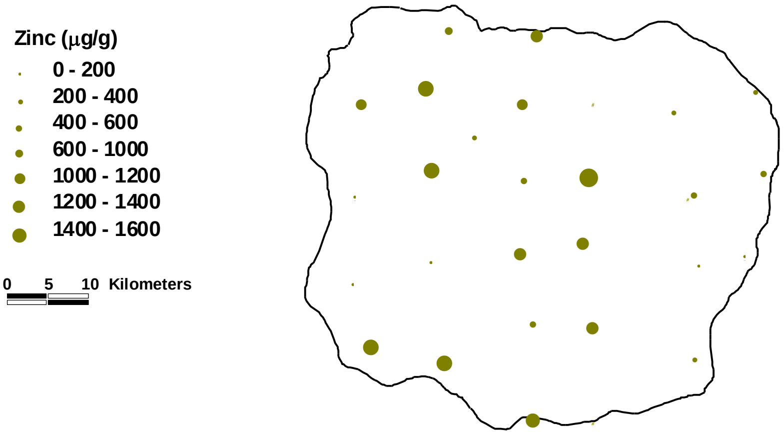


Figure 6. S concentrations in the surface sediments in London

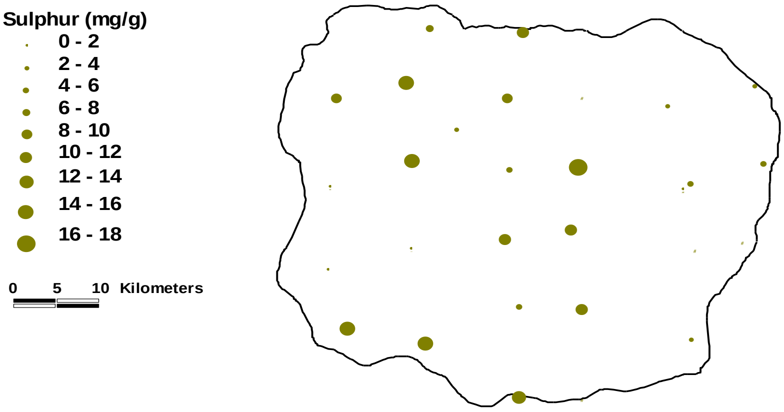


Figure 7. Cd concentrations in the surface sediments in London

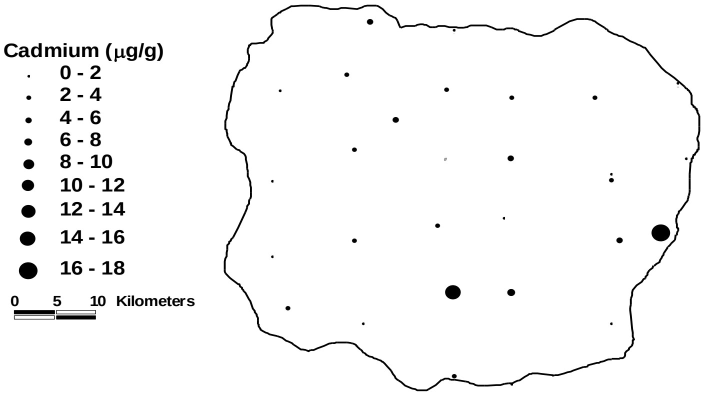


Figure 8. Cu concentrations in the surface sediments in London

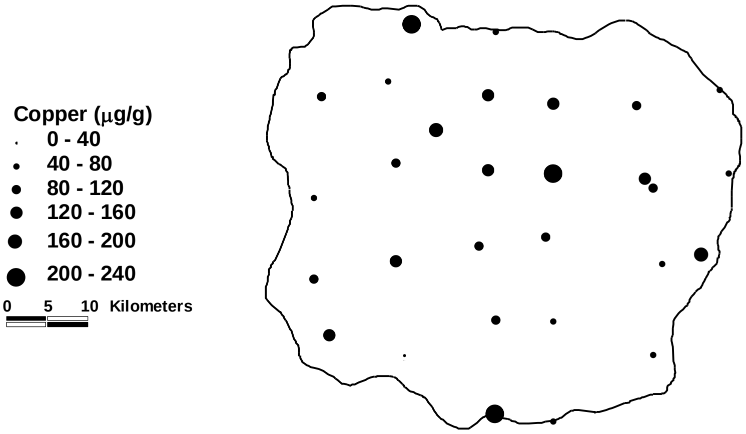


Figure 9. Cr concentrations in the surface sediments in London

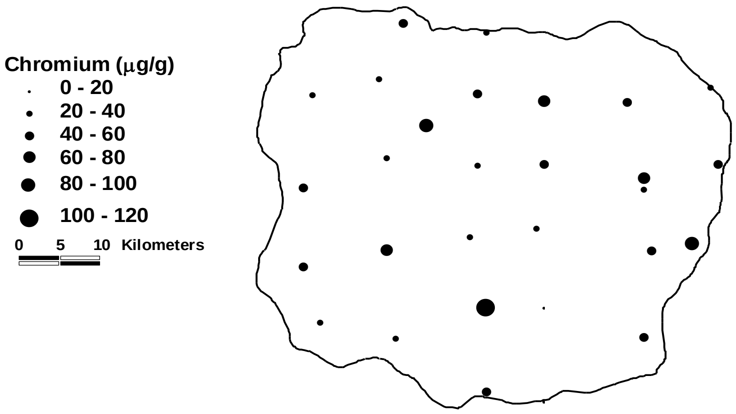


Figure 10. Ni concentrations in the surface sediments in London

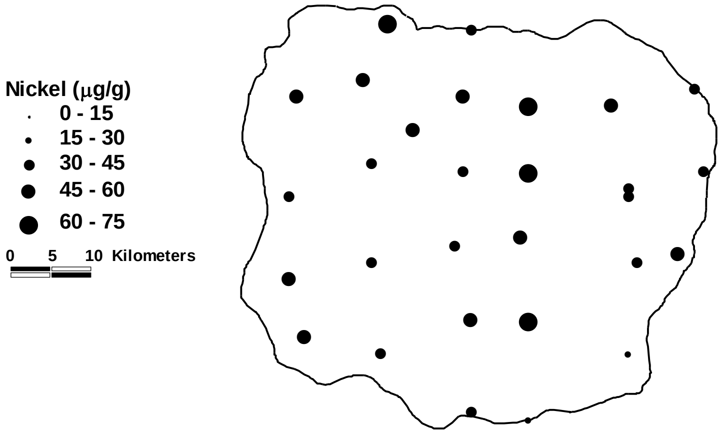


Figure 11. Sn concentrations in the surface sediments in London

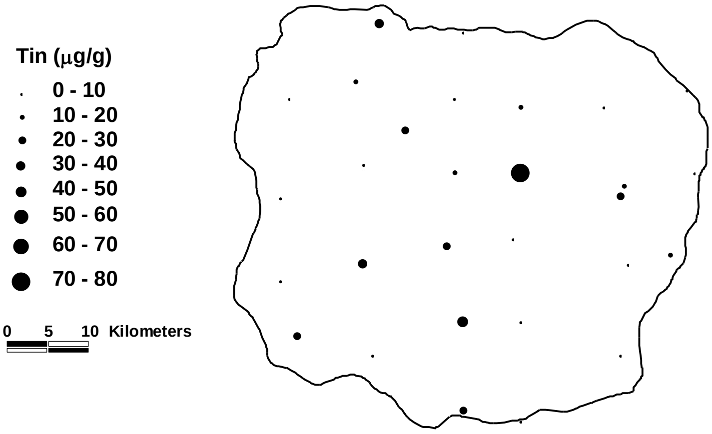


Figure 12. Se concentrations in the surface sediments in London

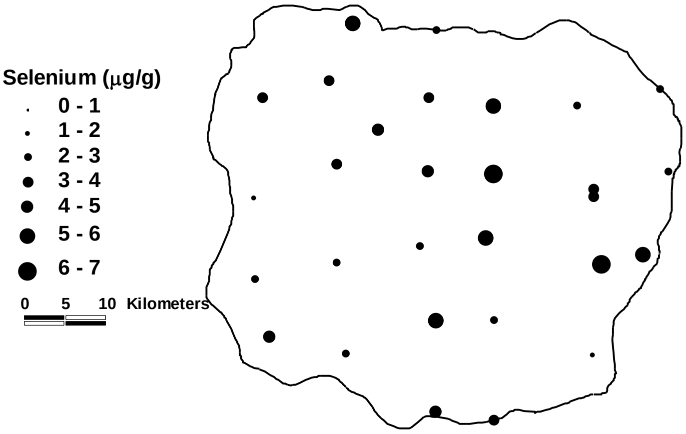


Figure 13. V concentrations in the surface sediments in London

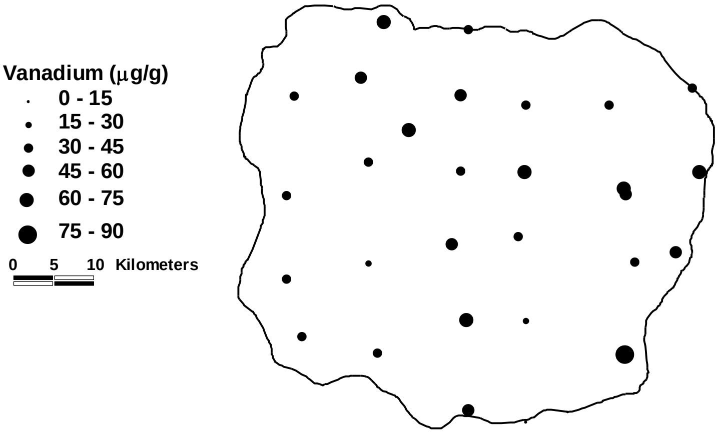


Figure 14. As concentrations in the surface sediments in London

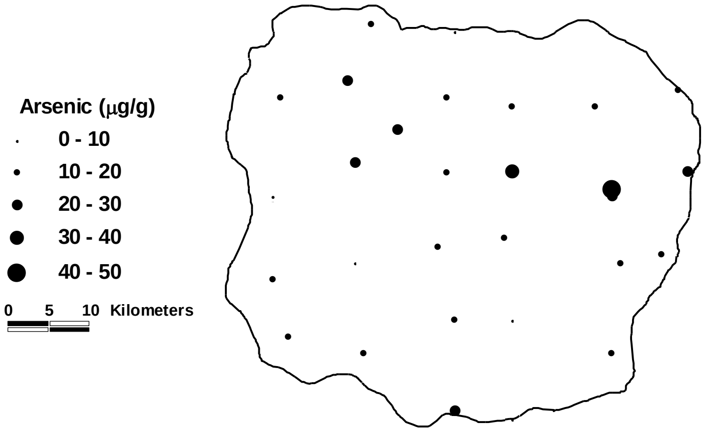


Figure 15. Be concentrations in the surface sediments in London

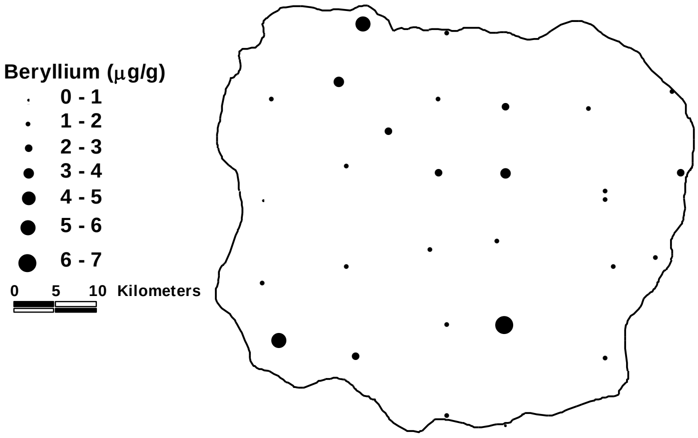


Table 8. Other element concentrations in the London surface sediments (Si, Al, Ti, Ca, K, Fe, Mn in mg/g; Pd, Pt, Zr, Rb, Sr in μg/g)

	Si	Al	Ti	Ca	K	Fe	Mn	Pd	Pt	Zr	Rb	Sr
Addiscombe Scouts Club	301	121.6	3.78	7.67	11.3	24	0.12	2.32	0.26	311	45	78
Alexandra Park Conservation Pond	216	103.9	4.52	24.1	22.5	39	0.20	2.08	0.31	128	106	141
Banbury Reservoir	219	106.5	2.24	64.7	25.0	46	1.15	1.87	0.34	85	92	180
Grange Park Lake	184	97.9	2.26	91.9	27.4	30	0.16	4.70	0.25	150	63	188
Brent Reservoir	208	118.0	4.45	30.0	23.3	52	0.26	3.34	0.26	132	119	167
Brooklands Lake	215	110.8	0.37	135	32.8	20	0.10	4.57	0.23	229	23	185
Bramble Farm	238	120.5	3.80	15.3	17.6	48	0.24	1.93	0.21	248	115	84
Lake at Getton Bottom	156	84.6	1.77	84.1	28.2	30	0.15	1.93	0.33	79	86	213
Crosmere Sewage Works Lake	233	120.6	3.64	45.2	27.6	36	0.18	1.51	0.21	201	101	182
Dagnam Park	246	123.0	3.43	42.5	27.4	29	0.15	1.41	0.25	190	116	84
The Riverside Club	212	99.2	3.75	36.9	23.7	35	0.18	1.76	0.54	181	130	132
Ealing Pond	197	106.5	2.95	37.9	23.0	32	0.41	1.88	0.32	75	73	44
Fairlop Waters	252	118.4	4.69	21.9	22.6	43	0.22	1.82	0.19	193	131	118
Flint Hall Farm	146	76.2	0.10	185	35.2	13	0.15	0.67	0.18	99	33	273
Holly Bush Farm	220	115.3	4.28	13.0	19.2	37	0.19	1.44	0.28	133	82	98
Norstead Manor Farm	226	115.8	3.94	5.7	11.7	46	0.23	1.98	0.22	221	95	59
Peckham Rye Park Lake	185	100.2	3.46	36.9	23.0	33	0.17	1.48	0.30	130	66	160
Queen Mary Storage Reservoir	246	132.1	3.09	80.2	32.9	46	0.23	1.53	0.22	177	62	154
Regents Park Boating Lake	170	111.2	2.59	78.1	31.4	38	0.36	1.52	0.20	122	84	324
Infilled pit in Richmond	208	108.7	2.69	72.0	28.7	38	0.20	1.63	0.24	138	62	209
Shenley Pond	195	110.0	3.73	11.0	13.3	35	0.18	2.37	0.52	94	55	54
Southmere Lake	126	73.4	0.10	146	32.8	41	0.41	1.86	0.25	53	71	288
Stanmore Common Lake	185	99.6	2.99	10.8	11.3	64	0.32	1.81	0.24	107	46	126
Stenhil Fishing Lake	209	129.3	0.10	173	38.3	25	0.39	1.75	0.15	207	46	150
Stew Pond	241	125.7	4.97	2.7	14.9	46	0.23	1.70	0.27	147	123	30
Stockley Park	188	97.2	2.01	100	33.7	30	0.15	1.43	0.16	96	71	249
Victoria Park Lake	196	111.2	3.47	16.8	15.4	40	0.20	2.59	0.39	174	76	105.
Wandsworth Pond	215	95.86	3.28	24.1	17.8	38	0.43	1.36	0.19	276	60	114
Whitely Village	231	97.1	3.38	8.36	14.5	41	0.21	1.80	0.43	93	81	44

3.3 Historical patterns of elements across the UK

3.3.1 Lithostratigraphic analyses of the sediment cores

Dry weight, organic content measured as loss-on-ignition (LOI), wet and dry densities have been analysed for the sediment cores. The profiles are shown in Figures 16 to 21. The LOI values in Nag29 and Chon14 are in the region of 12 - 30% with a dramatic decrease in Nag29 at 78 cm. The LOI values in Chon4, Gran5, Burn3 and Lag4 are higher than 20%. The catchment soils have a high organic matter content and catchment soil erosion is the most likely source of the high organic content of these sediment cores.

Core Banb5 (Figure 21) is brown clay throughout. The dry weight, wet density and dry density decline steadily from the bottom to the surface of the core, whilst the LOI value increases steadily from 5% at the bottom to 20% at the surface of the core. These profiles suggest that the sediment in this core has probably not been disturbed.

Figure 16. Lithostratigraphic profiles for Nag29 from Lochnagar.

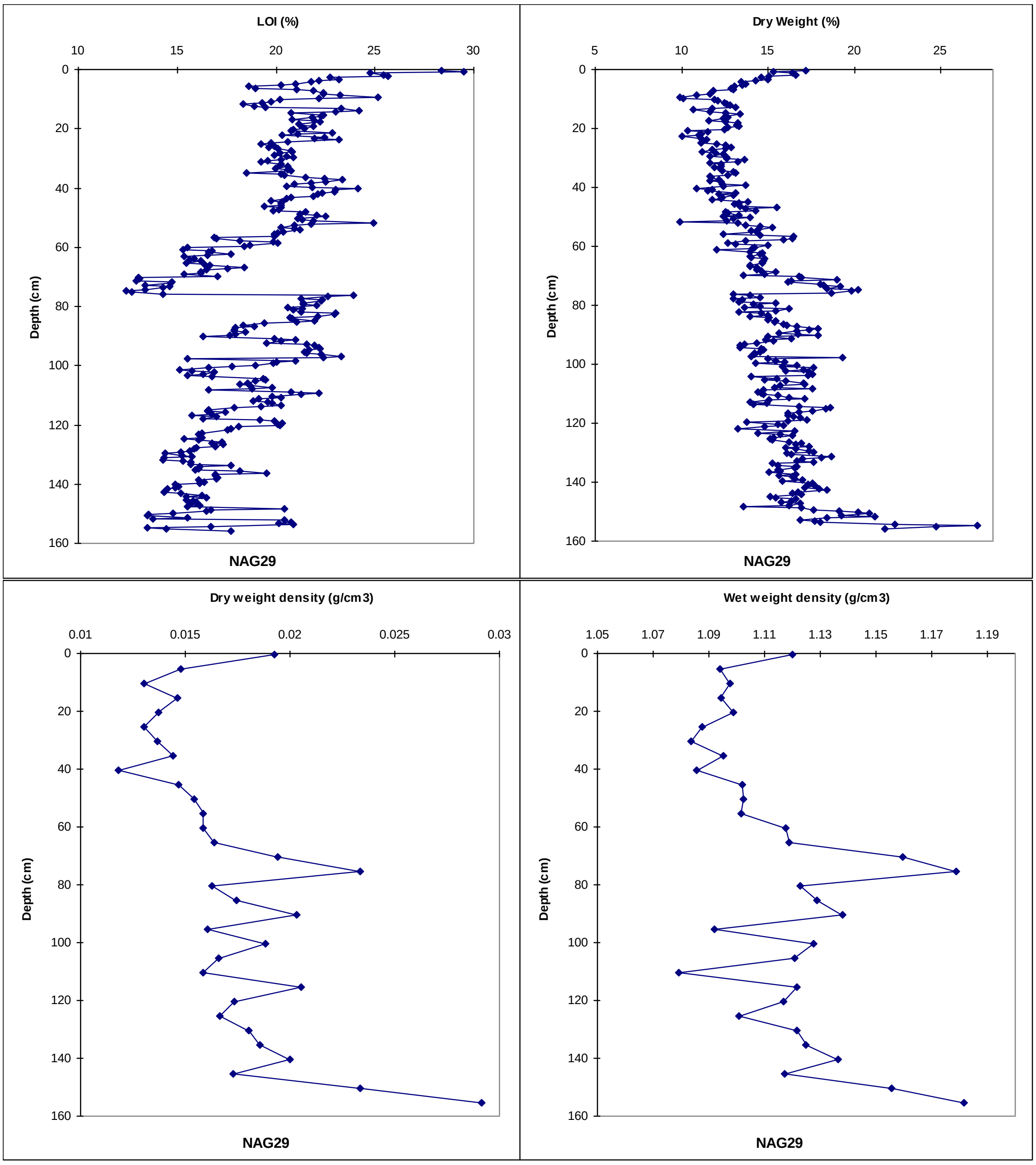


Figure 17. Lithostratigraphic profiles for Chon14 from Loch Chon.

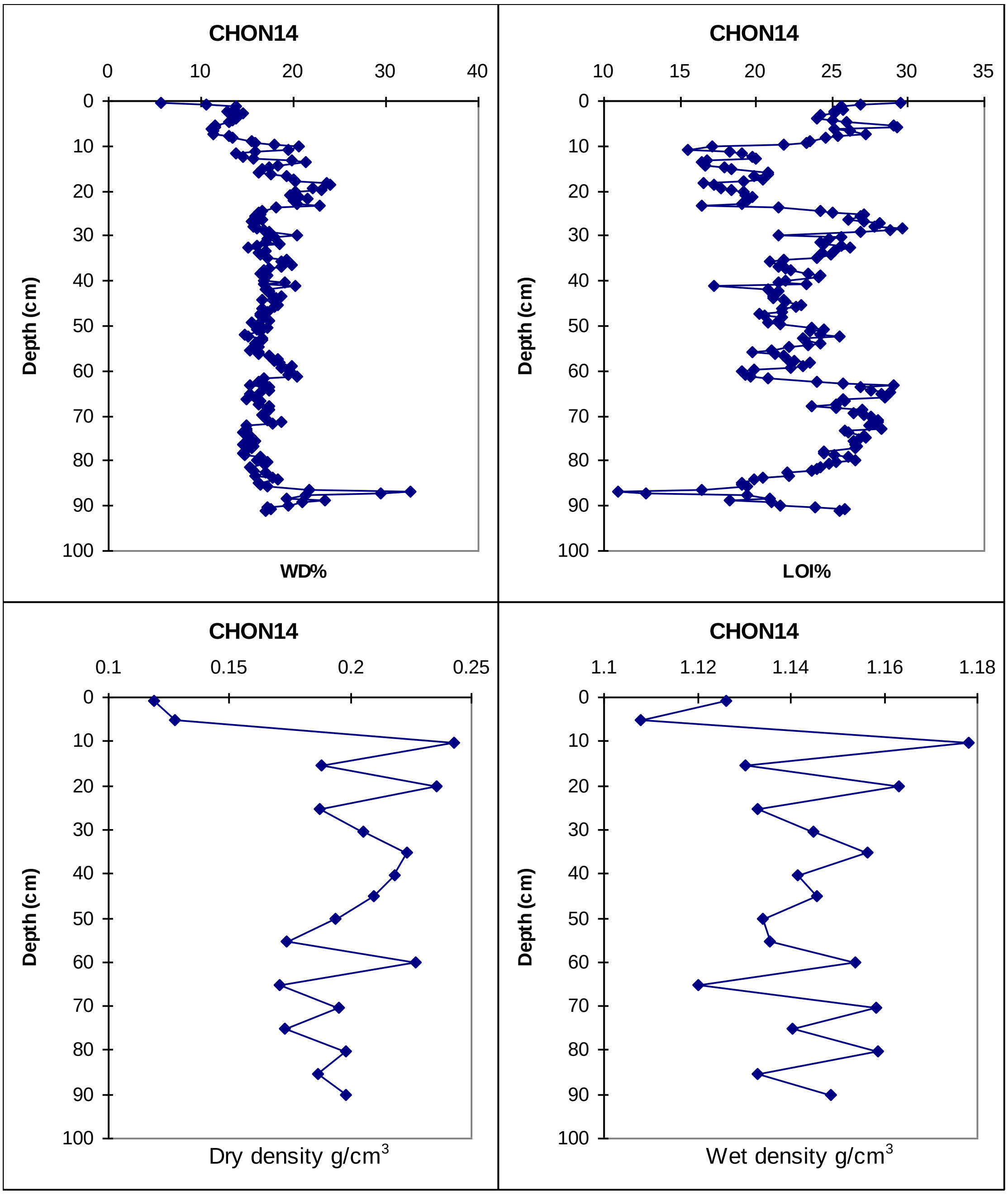


Figure 18. Lithostratigraphic profiles for Gran5 from Loch Grannoch.

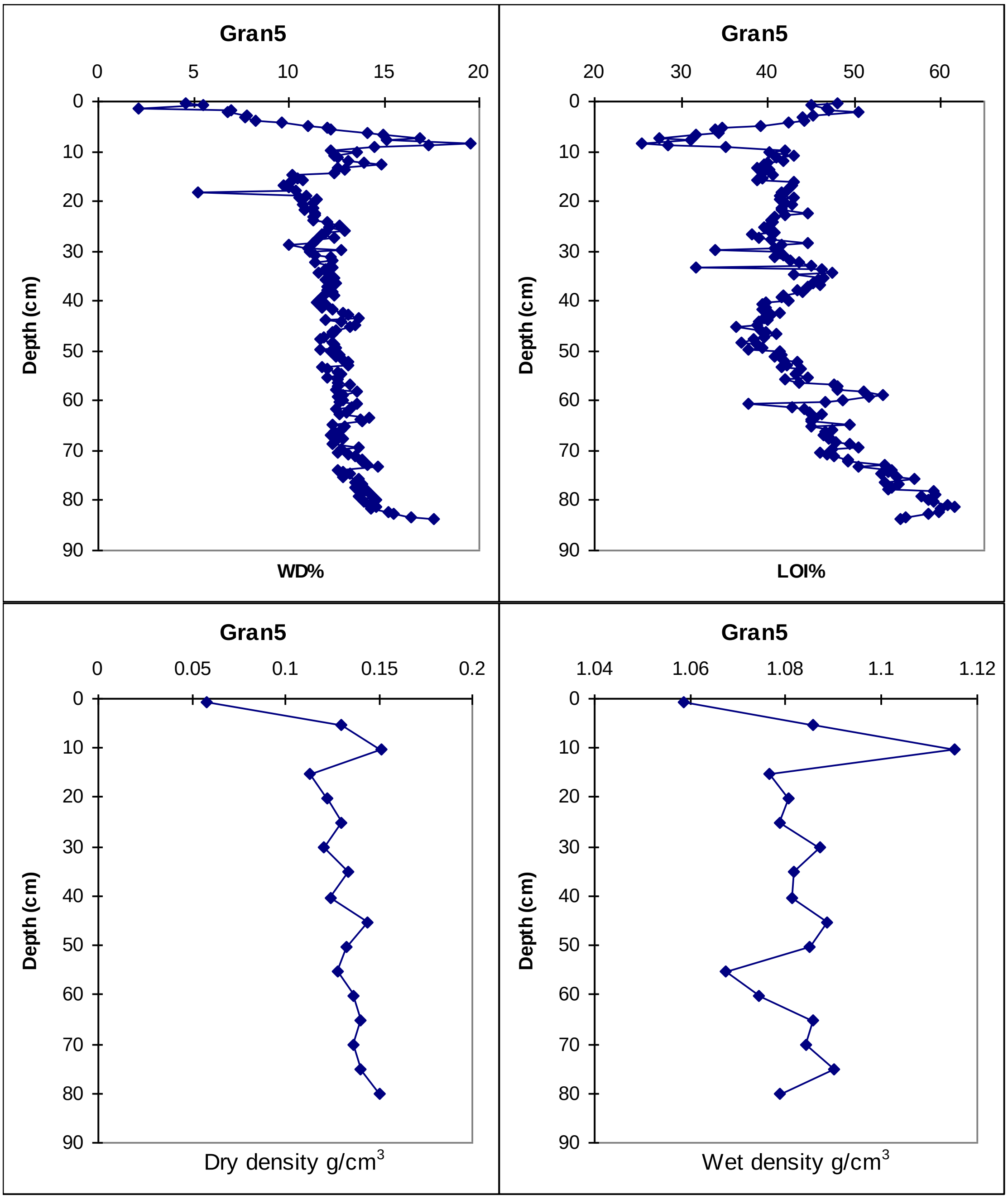


Figure 19. Lithostratigraphic profiles for Burn3 from Burnmoor Tarn

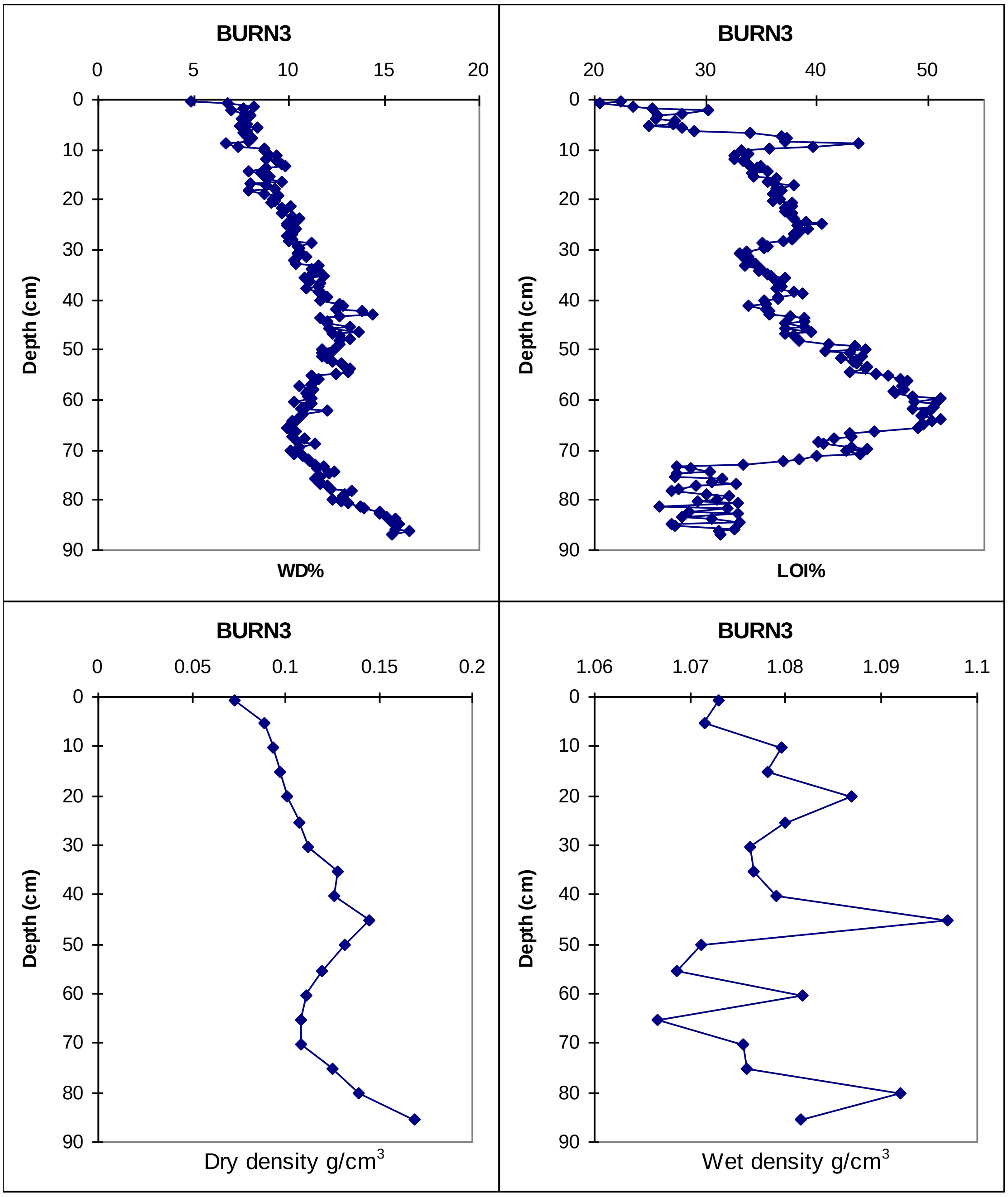


Figure 20. Lithostratigraphic profiles for Lag4 from Llyn Llagi

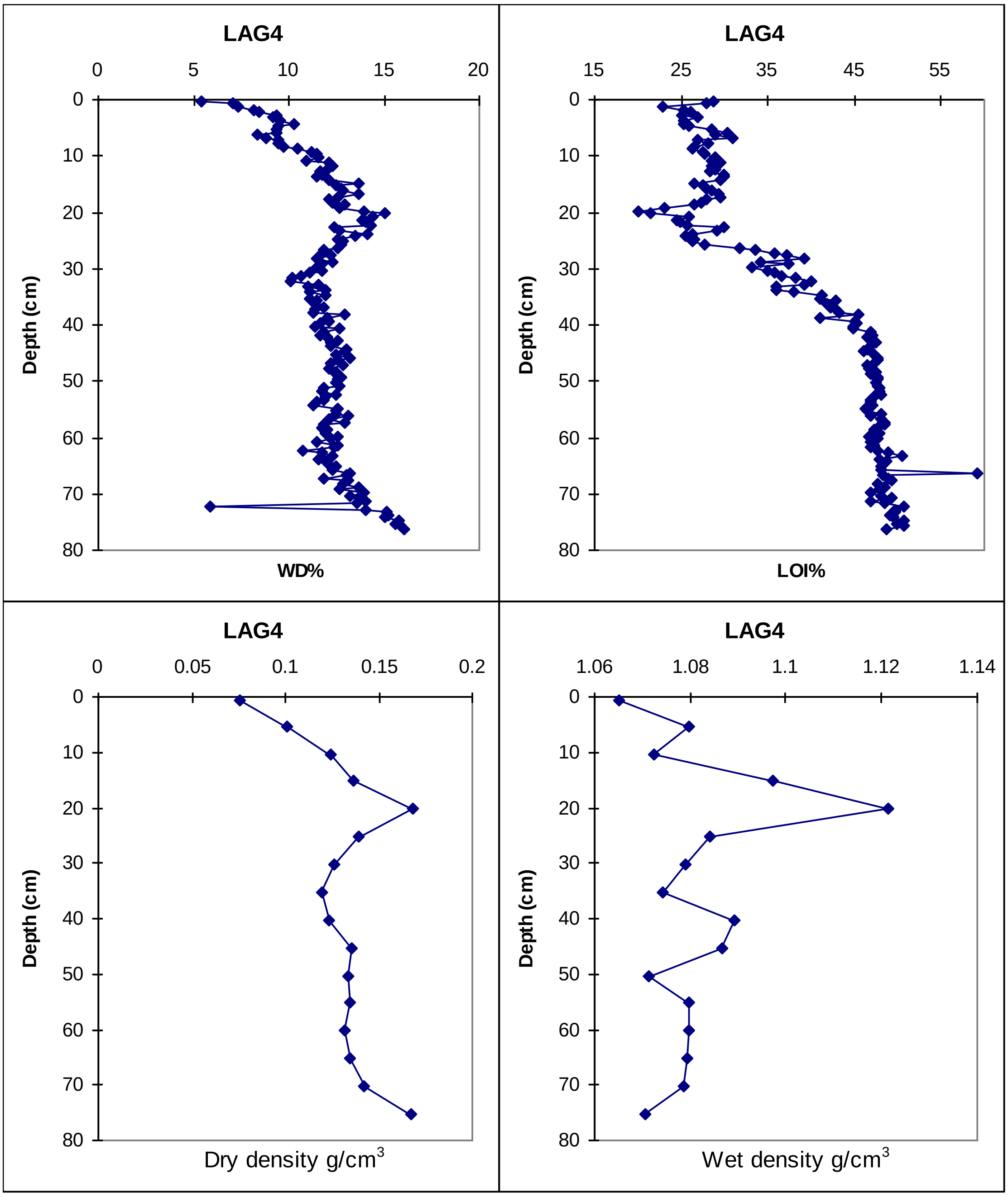
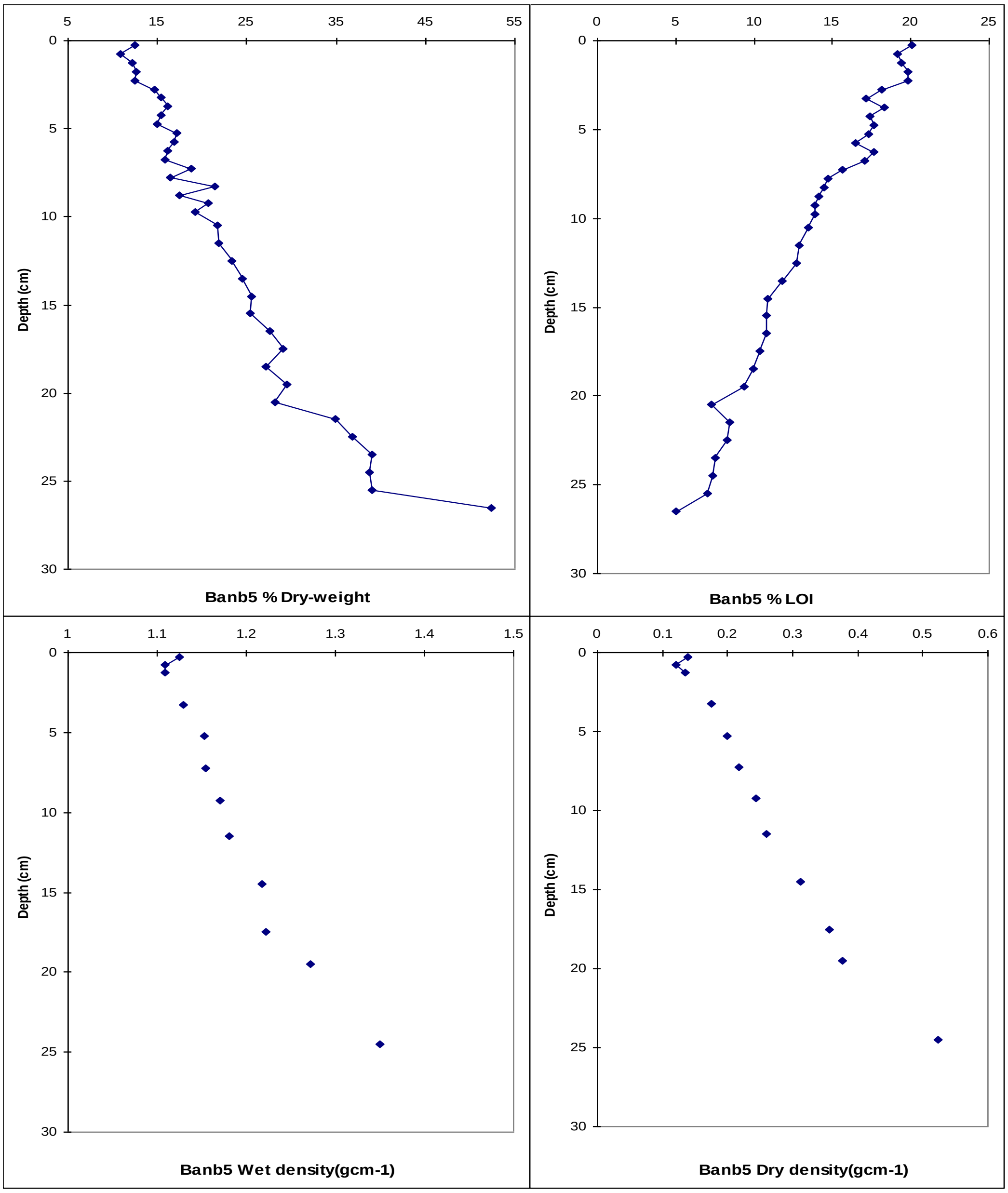


Figure 21. Lithostratigraphic profiles for Banb5 from Banbury Reservoir



3.3.2 Historical patterns of geochemical elements in individual cores

The Si concentration in Nag29 is higher than that in the cores taken from the other sites (Figures 22 to 26) and this corresponds to the Si concentration in Lochnagar lake water being higher than in the other sites (Patrick *et al*, 1991, no data available for Banbury Reservoir). The trends in Si concentration in Nag29 appear to be opposite to those of Ti, K, Fe, Zr and Rb in the same core.

Generally speaking, Ti, K, Zr, Rb and Sr concentration profiles follow similar patterns in the cores from the different sites. Ti normally exists in the form of rutile (TiO_2) and, as rutile is a particularly stable mineral, Ti has been used as a conservative metal in sediment studies. K, Zr, Rb and Sr concentration profiles are similar to the Ti concentration profile in these cores and this suggests that these elements mainly exist in the mineral fraction. Fe and Mn concentrations have a rapid increase in the surface sediments in cores Nag29, Chon14, Burn3 and Lag4 and this may be due to a redox change at the interface beween the sediments and the water (Belzile *et al*., 2000).

In Banb5 (Figure 27), the content of calcium carbonate is high, and Ca declines from the bottom to the surface, especially from 8 cm to the surface, whilst Si and organic matter contents increase from the bottom to the surface. The concentrations of Mn and Fe are higher in the upper part than the lower part. There is a significant increase from 8 cm to 5 cm in the Fe concentration, and this then remains relatively stable to the surface. As XRF data are total concentrations it is unlikely that the change in Fe concentration is due to the redox change in the interface of the sediments and the water. This suggests that the accumulation rate of Fe to the upper part of the core may be higher than in the lower part. Since we have no chronological data for this core this accumulation rate change is currently unconfirmed.

Figure 22. Historical patterns of geochemical elements in Nag29

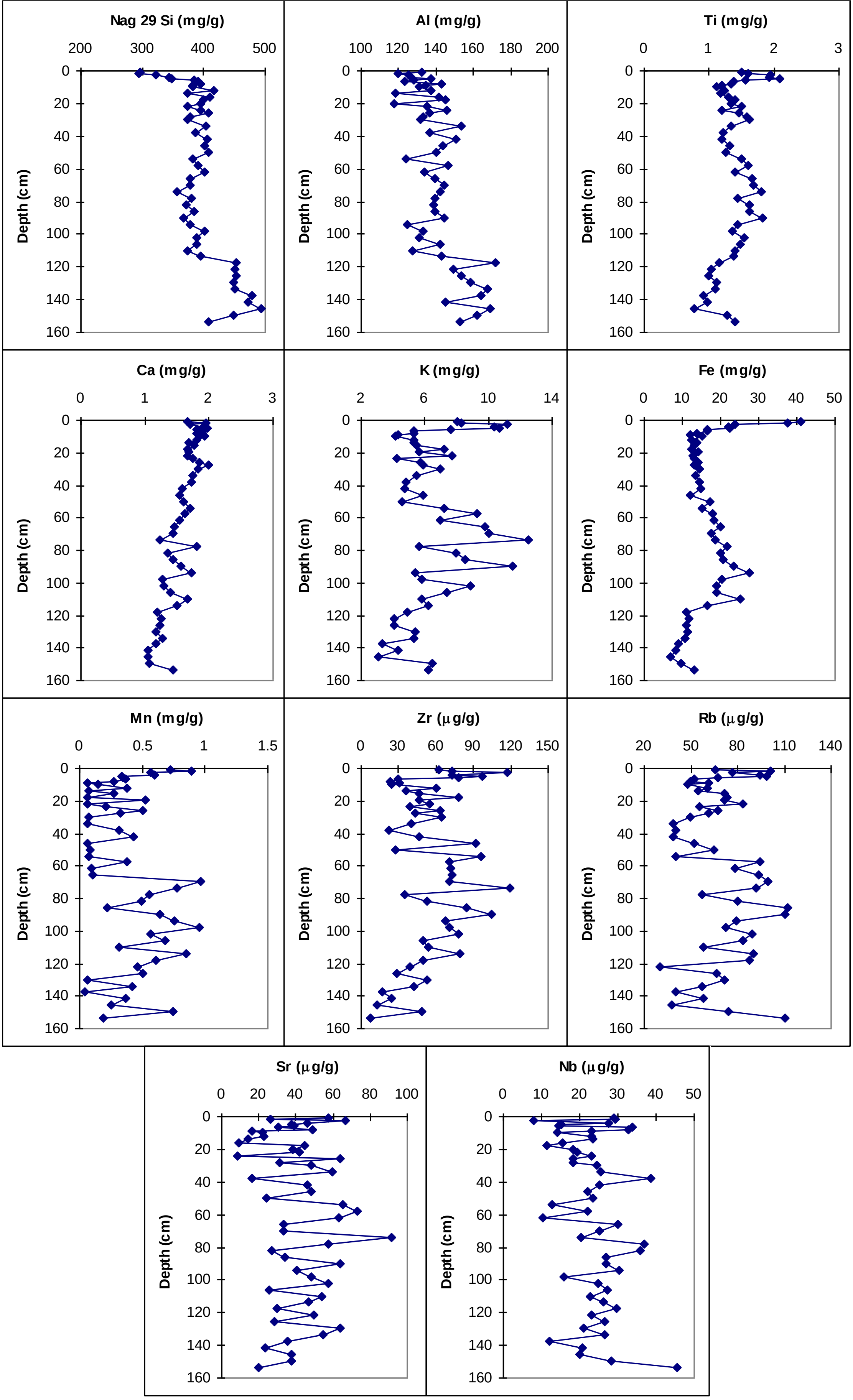


Figure 23. Historical patterns of geochemical elements in Chon14

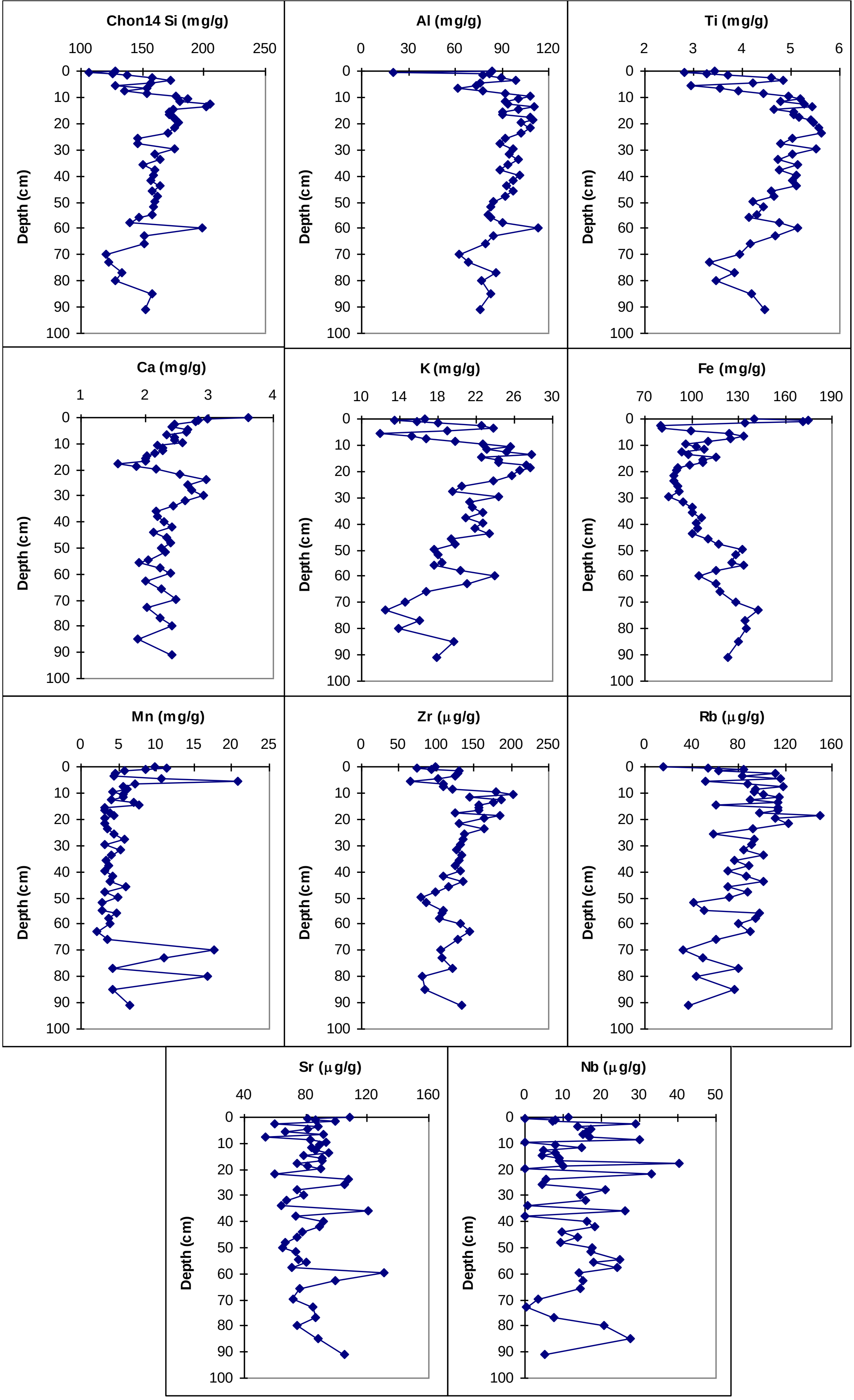


Figure 24. Historical patterns of geochemical elements in Gran5

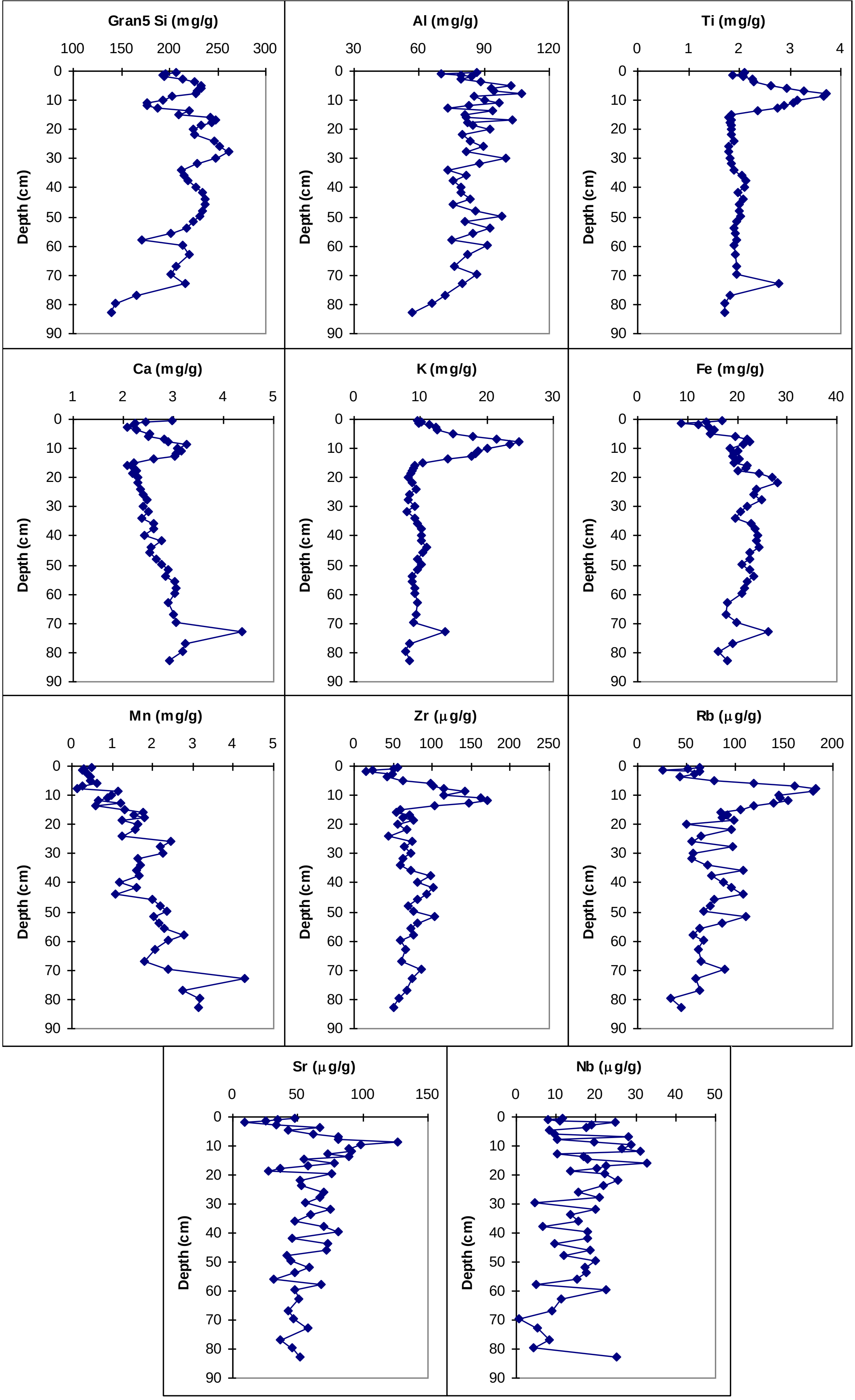


Figure 25. Historical patterns of geochemical elements in Burn3

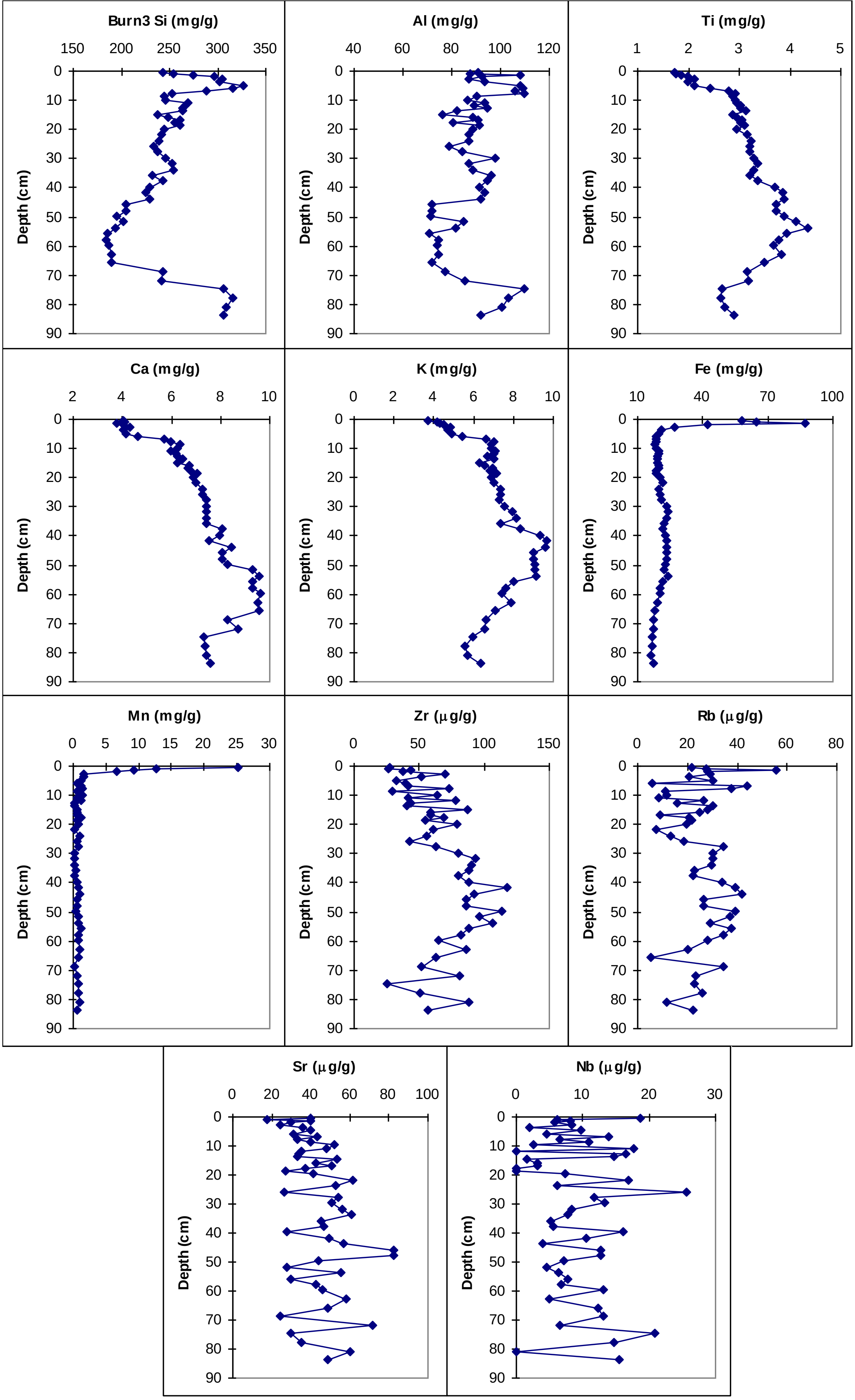


Figure 26. Historical patterns of geochemical elements in Lag4

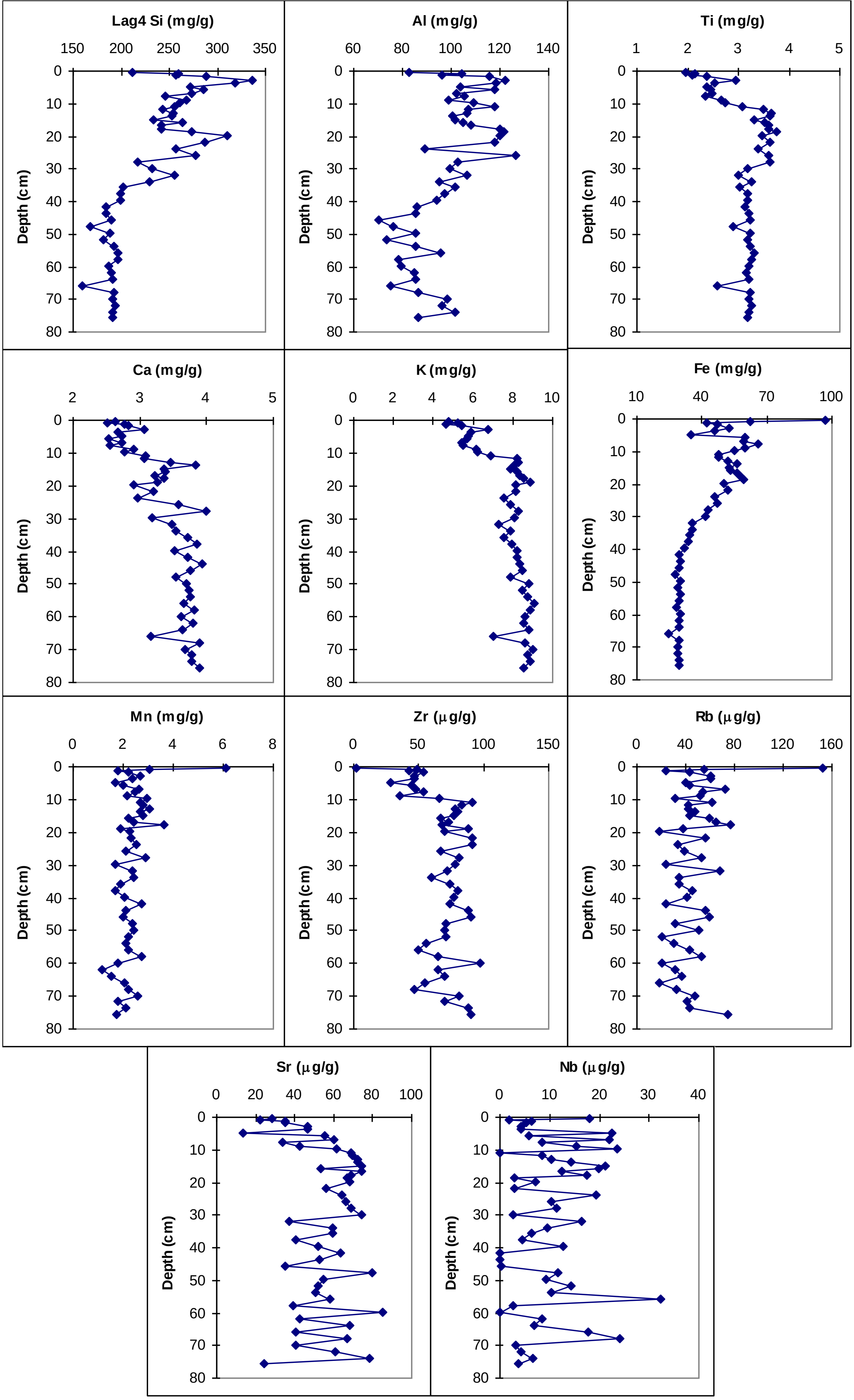
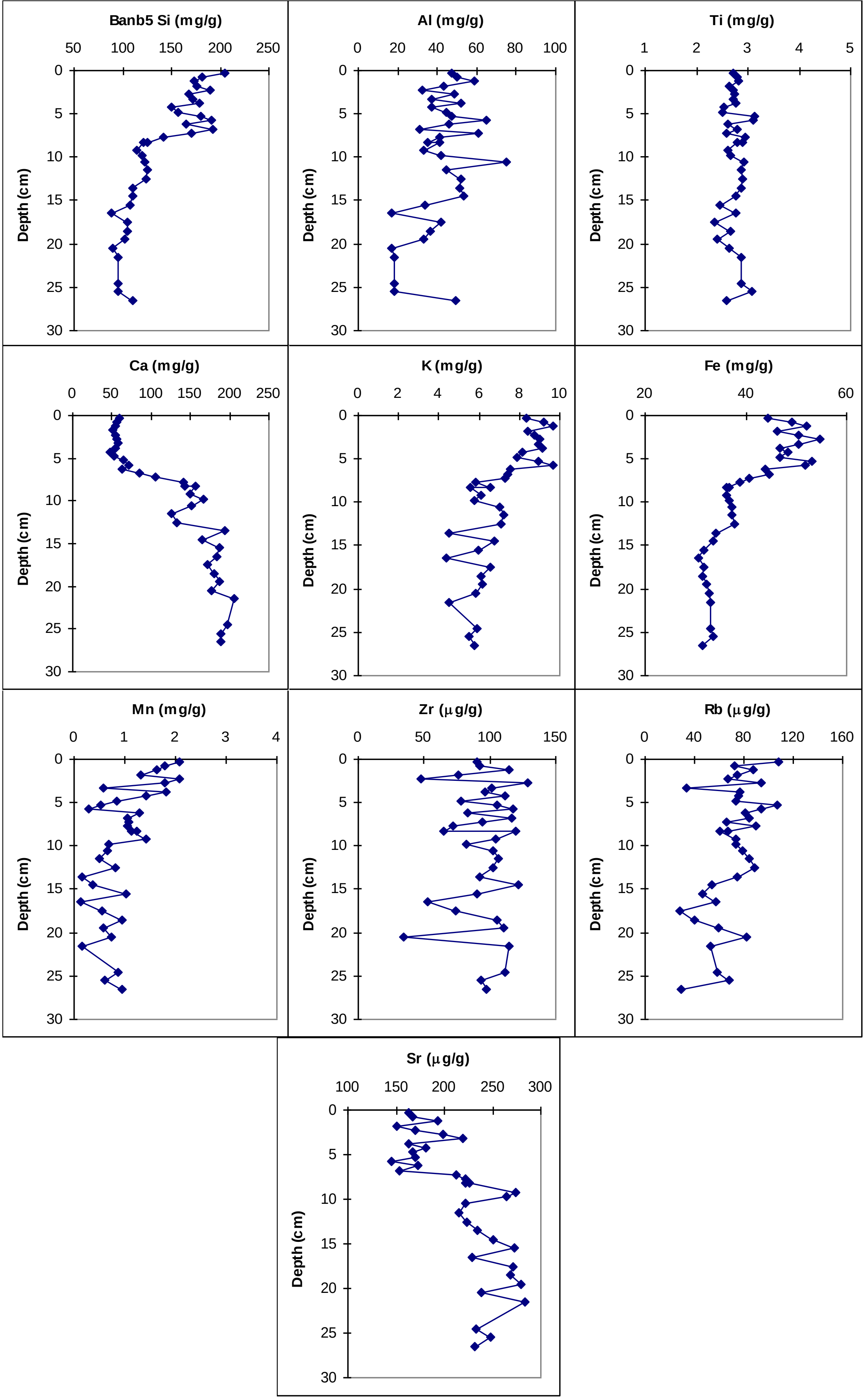


Figure 27. Historical patterns of geochemical elements in Banb5

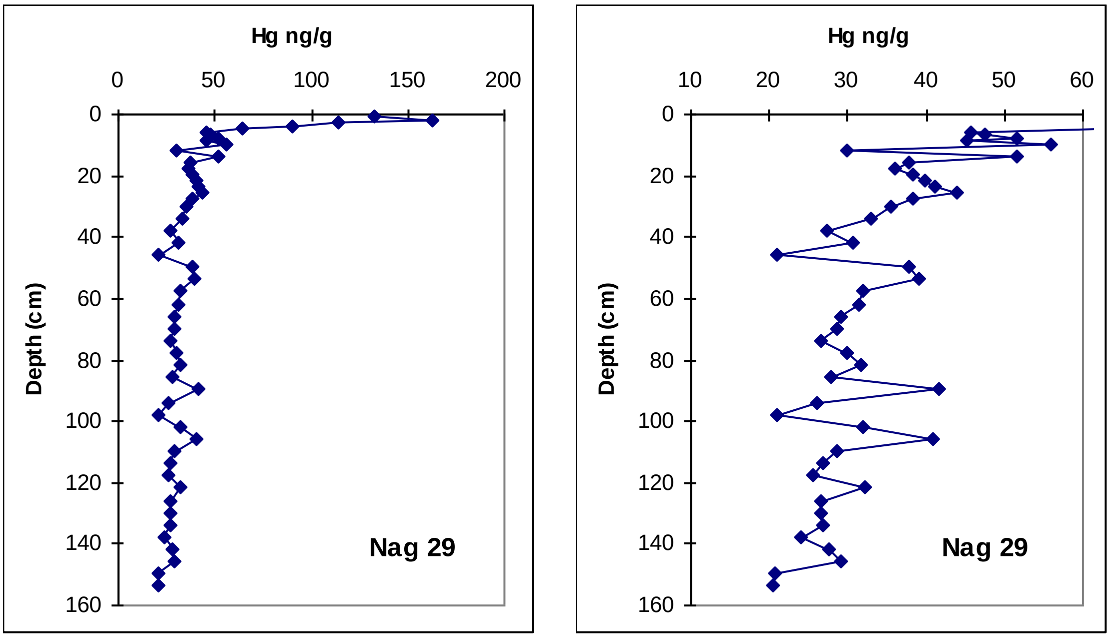


3.3.3 Historical patterns of Hg, Pb, Zn, S, Cu, Cd, Cr, Ni, Sn, As, V, Se, Be, Pd and Pt across the UK

3.3.3.1 Historical pattern of Hg across the UK

Hg concentration profiles for Nag29, Chon14, Gran5, Burn3 and Lag4 are shown in Figures 28 to 30 and provide historical patterns for the different sites across the UK. The Hg profile for Nag29 from Lochnagar is shown in Figure 29A. Plotting this on an expanded scale (Figure 29B) shows that Hg concentration increases slowly but steadily from about 20 ng/g at the bottom to 40 ng/g at about 20 cm in the core followed by a rapid increase to 162 ng/g at 0.75 cm and a decline to 130 ng/g at the sediment surface. This peak value is typical for the site (150 - 250 ng/g; Yang, 2000) .

Figure 28. Hg concentration profiles for Nag29 (AAS results)


A.

B.

Hg is of increasing concern due to its toxicity and its ubiquitous contamination of the environment. When studying Hg pollution history, it is usual to take the ‘pre-industrial’ level (150 - 200 years ago) as background values (Engstrom & Swain, 1997; Klein & Jacobs, 1995; Grondin *et al.* 1995; Verta *et al.* 1989), even though it has been suggested that Hg contamination via silver refining may have had local effects since the 15th century (Nriagu, 1993) and Martinez-Cortizas *et al* (1999) have found that Hg concentrations have increased in a peat bog since c.1500 before present (B.P.).

In Lochnagar, pollen data from correlated cores suggest that the 150 cm of Nag29 covers a c.6000 year period, which means that Hg concentrations appear to have increased at the site since c.4000 BC. If this is a real signal, this has a special significance for the debate on the true definition of “background” in the UK. The Nag29 core also shows a few small peaks in the Hg profile between 20 and 157 cm and the peaks between 20 and 60 cm may correspond to Roman and Medieval periods. However, as this core has not been dated we cannot interpret these peaks further. The Nag29 core was sliced at 0.5 cm intervals and therefore only 50 of the 314 samples have so far been analysed providing only a low resolution to the Hg profile. ^{14}C dating and analysis of the remainder of the samples are required before complete interpretation of the Hg temporal trends can be undertaken.

Hg concentrations in the Loch Chon core (Chon14) show a very slow increase from the bottom to 15 cm followed by a sharp increase to a peak concentration of 1603 ng/g at 9.25 cm (Figure 29). This then rapidly declines to the sediment surface. This peak concentration is higher than has been observed in any rural lake site in the UK, and is of the same order as the Hg concentrations in the surface sediment samples taken from the Crosness lake (sewage works complex; Site 9 - Figure 1) and Victoria Park Lake (Site 27) in London, the two highest Hg concentrations in the surface sediment dataset (Figure 3). Previous sediment studies would suggest that the sediment accumulation rate in Loch Chon is about 1 mm / year and hence this 90 cm core should cover c.900 years. This puts the Hg peak at the beginning of the 20th century which is probably quite unlikely. However, the site is afforested and previous studies have shown that the sediment accumulation rate has increased as a result of catchment inputs following forestry activities. Therefore, the peak is probably more recent, but as the core has not been dated, its provenance is currently uncertain.

There is a sharp peak in some other element concentration profiles in this core, for example Pb, Zn, Se, V, Ni, Sn and S. The peak in the Pb profile is at 6.75 cm and the peak in Zn is at 7.75 cm whilst the peaks of Se, S, V, Ni and Sn are a little more shallow than the Hg peak depth (see Figures 32 to 45 for these element profiles). It would appear that these peaks are caused by the same disturbance and that this happened at the same time, but this cannot be due to direct atmospheric deposition as the peaks are not at the same depth in the sediments. Although the catchment could be an important source of trace metals for the lake (Yang, 2000), transport for different metals from the catchment to the lake is not always the same (Xue *et al*., 2000). The catchment of Loch Chon is relatively large and it would appear that the material forming these peaks is derived from a catchment source. Differential storage and re-mobilisation of these metals from catchment soils (a sort of metal ‘chromatography’) may have caused the observed results, but the difference in the sediment peak depths for the different elements would suggest that if this is the cause, then it has occurred over some considerable time. Sediment dating would be required in order to interpret this further.

The pattern of the Hg concentration profile for Loch Grannoch (Gran5) is different from the other cores. The Hg concentration slowly increases from the bottom to 45 cm followed by a rapid increase to a peak concentration (about 330 ng/g) at 20 cm. There is a broad peak from 20 to 15 cm followed by a decline to 8 cm, and an increase once more to the sediment surface. From previous studies, Gran5 is thought to cover c.300 years and hence the rapid increase in Hg concentration at about 45 cm probably dates from c. 1830 - 1840s and the peak at 20 - 15 cm from 1930s - 1950s. However, these dates could vary as the Loch Grannoch catchment is afforested and, as with Loch Chon, forestry activities could have resulted in high catchment inputs to the lake and have lead to an increase in the sediment accumulation rate. If these forestry activities occurred before the formation of the Hg peak concentration, the dates for the peak could be more recent. By contrast, peaks in the Ti, K, Zr, Rb and Sr profiles occur at about 8 cm, which may correspond to a mineral in-wash caused by forest planting in 1962 and/or 1977-1978. If this is the case, then the dates for the Hg increase and peak could be earlier. Without independent dating of the sediment core it is not possible to confirm the peak date with any certainty. However, the peak Hg concentration in Loch Grannoch is almost double that of Lochnagar and, from previous studies, the sediment accumulation rate is also much higher. Therefore, the total Hg input to the site is likely to be much higher than for Lochnagar.

Burn3 taken from Burnmoor Tarn shows the peak Hg concentration to be intermediate to those of Lochnagar and Loch Grannoch. This 84 cm core is also thought to cover about 300 years. The rapid increase in this core is at about 12 cm which probably dates to about the 1950s. This would agree with the period of rapid increase in coal consumption in the UK. If this is the case then the peak concentration, 275 ng/g, at 4.5 - 5 cm would appear to occur in the early 1980s.

The Hg concentration profile in Lag4 taken from Llyn Llagi shows similar trends to those of Burn3 with a similar peak concentration. However, the background concentration of Hg in this core is about two times that of Burn3 and hence Hg enrichment would appear to be lower (Table 9). The core is thought to cover c.550 years and therefore, if the sediment accumulation rate is correct and constant, the increase in Hg would date to the 1930s which would be slightly earlier than that estimated for Burn3. Again, without dating it is not possible to be certain.

Figure 29. Hg concentration profiles for Chon14 and Gran5

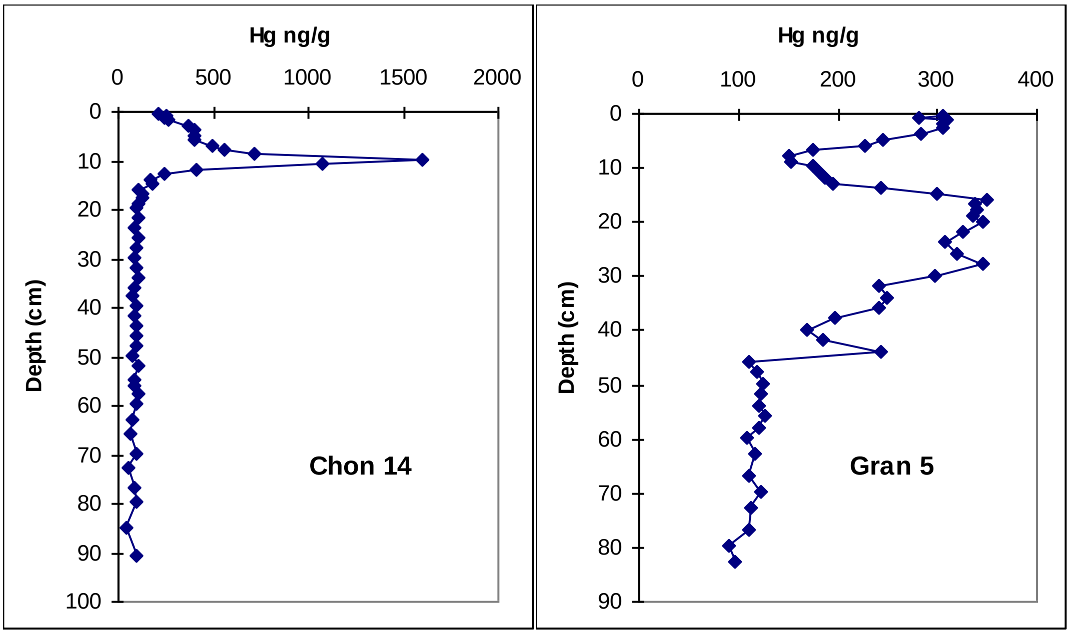
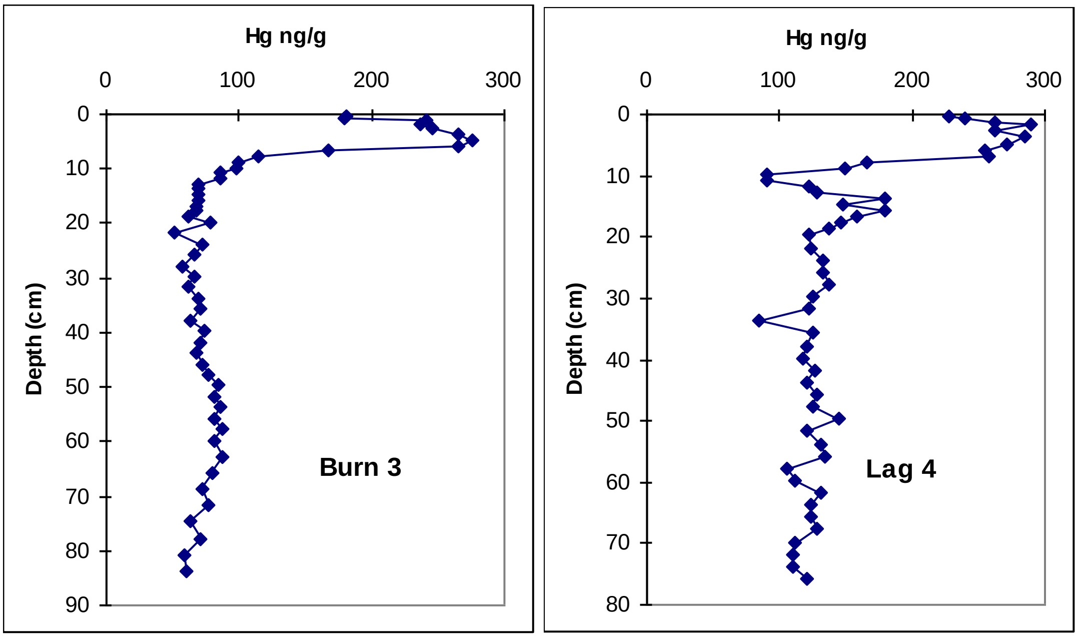
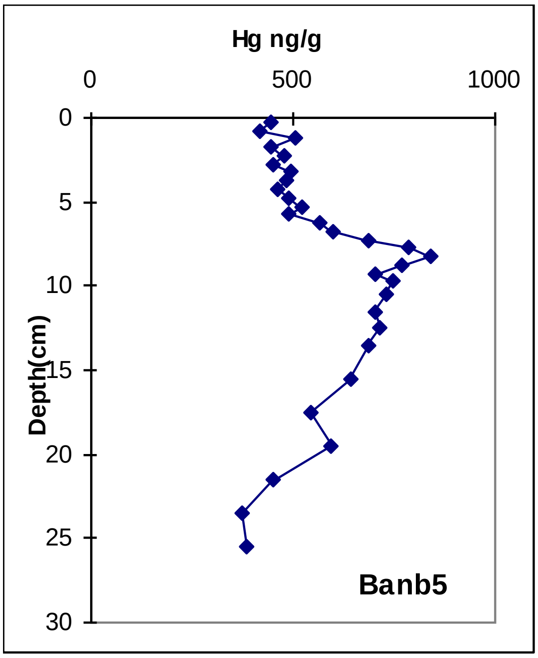


Figure 30. Hg concentration profiles for Burn3 and Lag4



The Hg profile of Banb5 is shown in Figure 31. Hg concentrations in this core generally increase from 380 ng/g at the bottom to 840 ng/g, reaching this peak at 8.5 cm, and then declining steadily to 420-450 ng/g at the surface. The reservoir was constructed in 1903 and hence the accumulation rate is likely to be about 0.3 cm / year. This would place the peak at the end of the 1960s or the beginning of the 1970s. Hg concentrations in Banb5 are higher by a factor of 2 - 5 than the surface sediments taken from Lochnagar (Yang, 2000). The high peak concentration and the rapid accumulation rate in Banb5 suggest that Hg inputs at the site have been very high though declining steadily in recent years.

Figure 31. Hg concentration in Banb5 taken from Banbury Reservoir in London



In all of the Hg concentration profiles in these cores, there is a slow increase from the bottom upwards, suggesting the concentrations at the bottom of the cores ("background" concentrations) are not real natural values. Certainly, at only 95 years old, the oldest sediments in Banbury Reservoir would never have approached a natural background value. However, the peak and the "background" concentrations are shown in Table 9 for comparison.

Table 9. Peak and the "background" concentration of Hg (ng/g) in the sediment cores across the UK

Core	Nag29	Chon14	Gran5	Burn3	Lag4	Banb5
Peak concentration	162	1602	339	275	289	840
Background concentration	20	60	90	60	110	380
Enrichment	8.1	26.7	3.8	6.3	2.6	2.2

The differences in background concentrations between the sites (expect Banbury Reservoir) may mainly arise from differences in sediment accumulation rate. Hg accumulation rates are therefore a more comparable way of assessing background levels (Fitzgerald *et al.* 1998) although dating is required for this. For the same reason, Hg accumulation rates in the contaminated layers are also a more reliable way of assessing pollution status. Although there are few reported Hg data for sediments in Europe, considering Hg concentrations and the predicted sediment accumulation rates, our data would suggest that the Hg accumulation rates for these sites, except Lochnagar, would fall into the upper range within Europe.

3.3.3.2 Historical patterns of other elements across the UK

Generally speaking, the Pb and Zn concentration profiles follow similar trends to the Hg concentration profiles in each individual core (Figures 32 and 33). In Gran5, Pb concentrations rapidly increase from the bottom of the core, earlier than the depth at which the rapid increase starts in the Hg concentration profile. The peak Pb concentrations, between 15 and 30 cm in Gran5 (maximum is 978 μg/g at 27.75 cm) are about 3 or 4 times those of the surface sediments, whilst the Hg peak concentrations between 15 and 30 cm are about 1.1 times the surface values.

Comparing the profiles in the top 50 cm of Hg, Pb and Zn in Gran5, all three show a decline from the peak to about 10 cm, after which Pb and Zn concentrations remain relatively stable, whilst Hg concentrations increase again to the surface. Therefore, if the high concentrations between 15 and 40 cm for Hg, Pb and Zn have a similar source, e.g. atmospheric deposition and/or forestry activities, the increase in Hg concentration in the upper 10cm is likely to be due to some other reason. The high concentrations of Hg, Pb and Zn may mainly be caused by atmospheric deposition and/or forestry activities, but since the main planting in 1962 and 1977-1978 the catchment has been relatively stable. Therefore, the increase in Hg concentration in the surface sediments is more likely to be caused by an increase in Hg deposition. It is unlikely that catchment in-wash has caused an increase in Hg, but not in Pb and Zn.

Coal burning and waste incineration are two of the main sources of S as well as Hg and Pb and the S profiles in the cores (Figure 34) are usually similar to their respective Hg and Pb profiles. However, the S profile in Burn3 shows the same trends as the LOI profile, whilst the S profile in Gran5 shows a broad, high concentration period between 15 and 40 cm similar to the as Hg, Pb and Zn profiles. These suggest that organic matter in-wash and forestry activities also contribute to the S record in the lake sediments.

Cd, Cu, Sn (except Banb5), Se, Cr and Ni (except Gran5) patterns (Figures 35 - 42) are also similar to the Hg and Pb profiles. In Gran5, Cr and Ni concentrations increase from the bottom to the surface, whilst some other element profiles such as Hg have a wide peak between 15 and 40 cm. Comparison of Cr and Ni concentrations in the catchment soils with those in the sediments may help identify the sources of these elements. Furthermore, this would help interpret the influence of forestry activities on the Hg profiles in the core.

Few long-term trends are observable in the As profiles (Figure 40). Concentrations in Nag29 are the lowest but show a rapid and dramatic increase in the surface sediments. The As concentrations in Banb5 are of a similar order to those of the other cores, except Nag29. However, for V (Figure 41) Banb5 concentrations are lower than those in Chon14, Gran5, Burn3 and Lag4 with surface sediment concentrations 2 - 3 times lower. Only Nag29 concentrations are lower than the London core. The reasons for this are currently unclear. Combustion, especially oil, is the dominant contributor of V to the environment and it is difficult to conclude that the London site is less impacted by oil combustion than the other sites. It maybe that the rapid sediment accumulation rate is diluting the signal at the site.

The patterns of Be and Pd (Figures 43 and 44) in Gran5, Burn3 and Lag4 are similar with that of their respective Al concentration profiles but opposite to the LOI profiles. This suggests that Be and Pd are mainly derived from mineral material. Figure 45 shows a significant change in Pt concentration at c. 25cm (estimated to c. 1900) in the Burn3 core. This is presumably due to the introduction of a new atmospheric source, probably industrial, influencing this area of northern England.

In the Banb5 core, Pb concentrations increase from the bottom (232 µg/g) to 20 cm (320 µg/g) followed by fluctuation to 10 cm, then a rapid decline to 6 cm (220 µg/g). In the top 6 cm, Pb concentrations fluctuate around 200 µg/g. Also in this core, there is an undulating increase in Zn concentration from the bottom (304 µg/g) to 10 cm (641 µg/g) followed by a rapid decline to 5 cm (373 µg/g), and an increase to the surface. Cu and Cd concentrations in Banb5 are a factor of 3-10 times the concentration of the contaminated sediment layers in Lochnagar (Yang, 2000). Lochnagar surface sediments also show contamination by Hg, Pb, Zn, Cu and Cd, but comparison of the two sites emphasises the magnitude of the pollution status at the London site.

The peak in the Hg profile of Banb5 is at 8.5 cm whilst the peaks in Pb and Zn are at 10 cm, and the Cd profile shows a broad peak between 7.5 and 13 cm. The shapes of the profiles and the positions of the peaks suggest that the times for the inputs of these metals reaching their maxima at the site are similar. This is estimated to be in the 1960s. The Sn profile generally increases from about 3 μg/g at the bottom to about 24 μg/g in the surface of the core and the Cr profile increases from the bottom to 13 cm followed by a slow decline to the surface.

Banbury Reservoir has a single inflow and outflow and local drainage is thought to have affected metal loadings to the site. Therefore, the profiles in Banb5 may reveal the history of industrial development around Banbury Reservoir over the last century. As this core has not been dated, it is difficult to calculate the loading rates of Hg, Pb, Cu, Zn and Cd to the sediments at different times. However, Table 10 shows the total storage densities for these metals for the period 1903 to 1998 calculated from the sediment profiles.

Table 10. Total storage densities of trace metals in Banbury Reservoir sediments since its formation (Note Hg unit)

Hg mg/m^2	Pb g/m^2	Cu g/m^2	Zn g/m^2	Cd g/m^2
43.23	23.1	9.82	28.64	1.222

Figure 32. Historical patterns of Pb across the UK

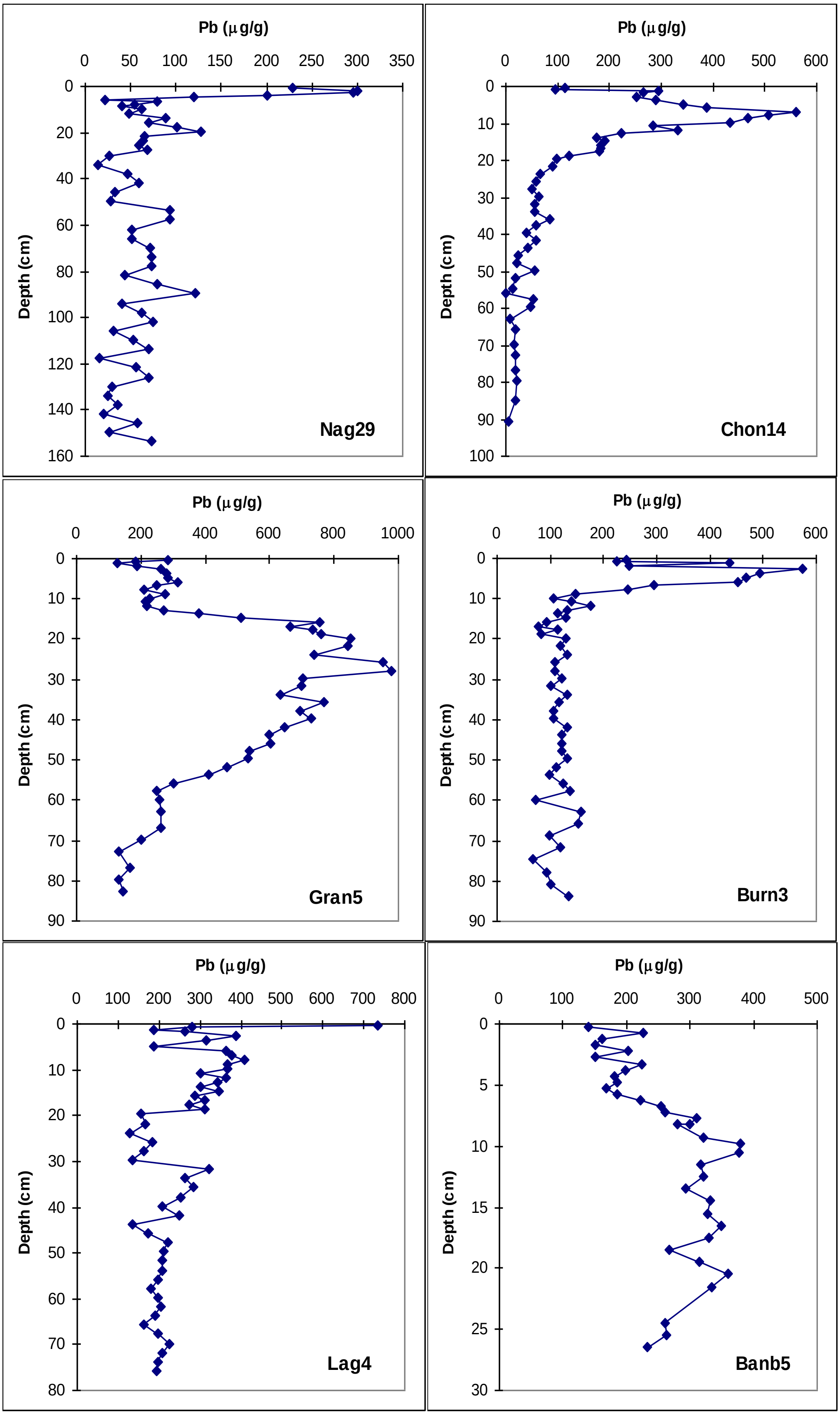


Figure 33. Historical patterns of Zn across the UK

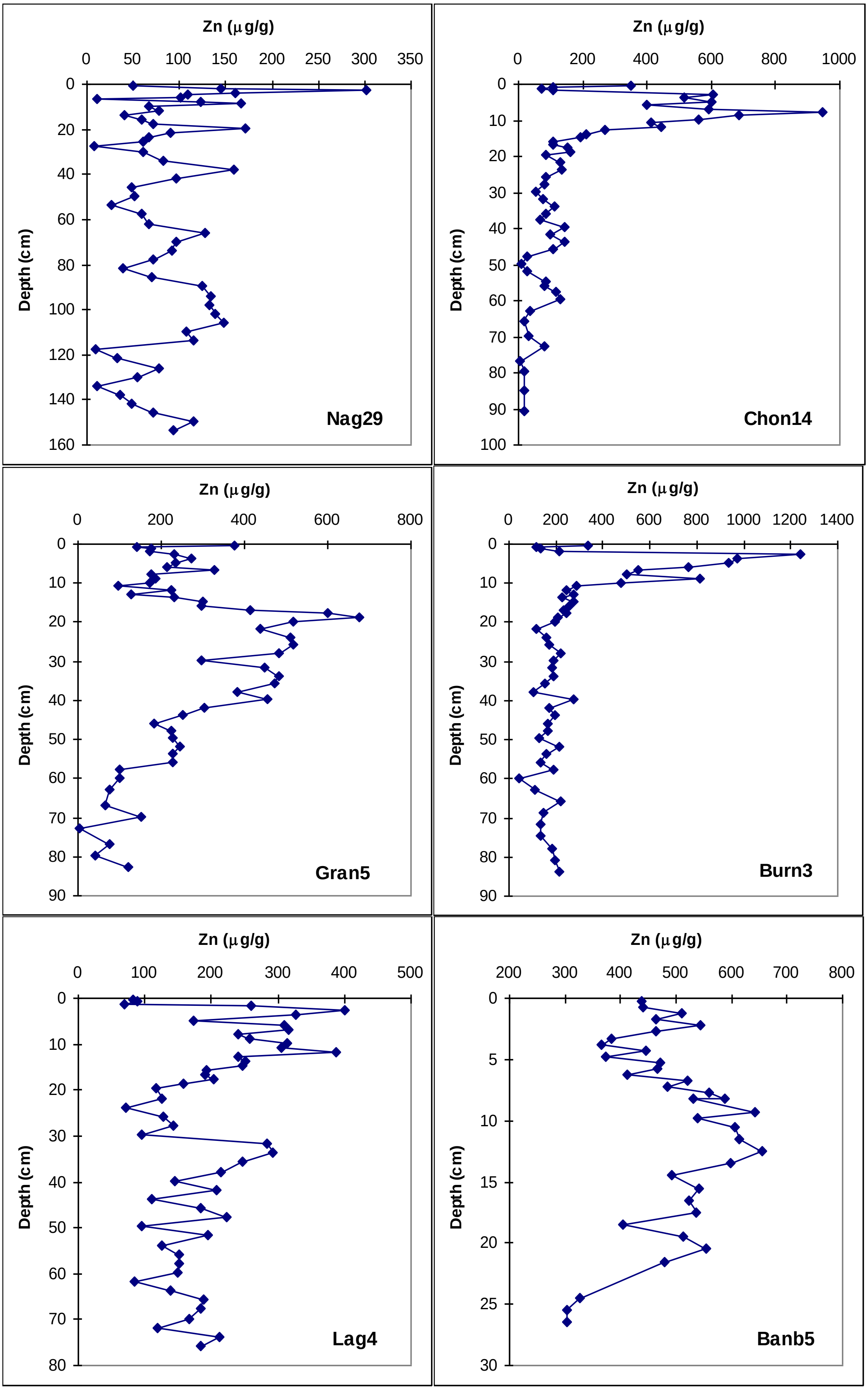


Figure 34. Historical patterns of S across the UK

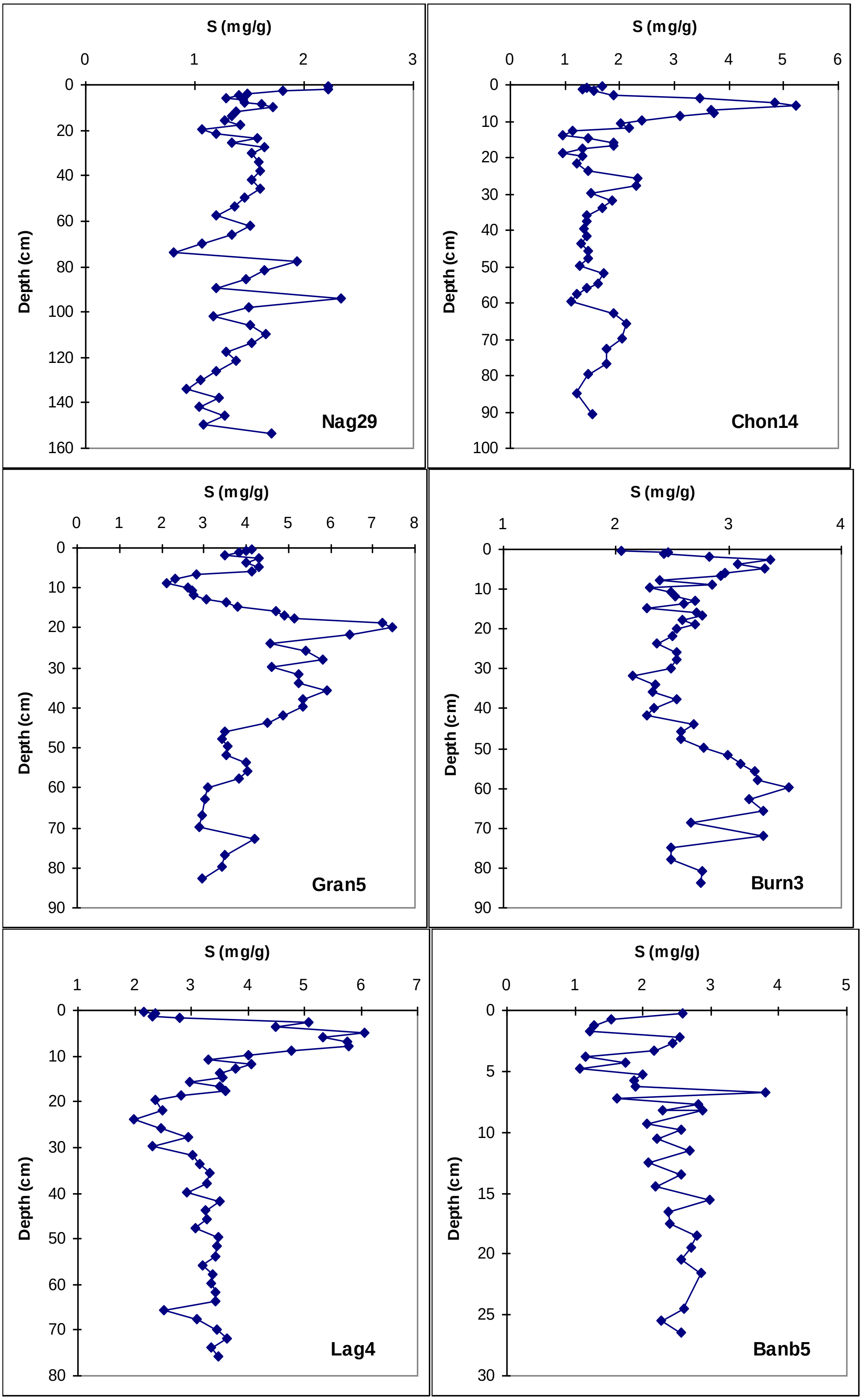


Figure 35. Historical patterns of Cu across the UK

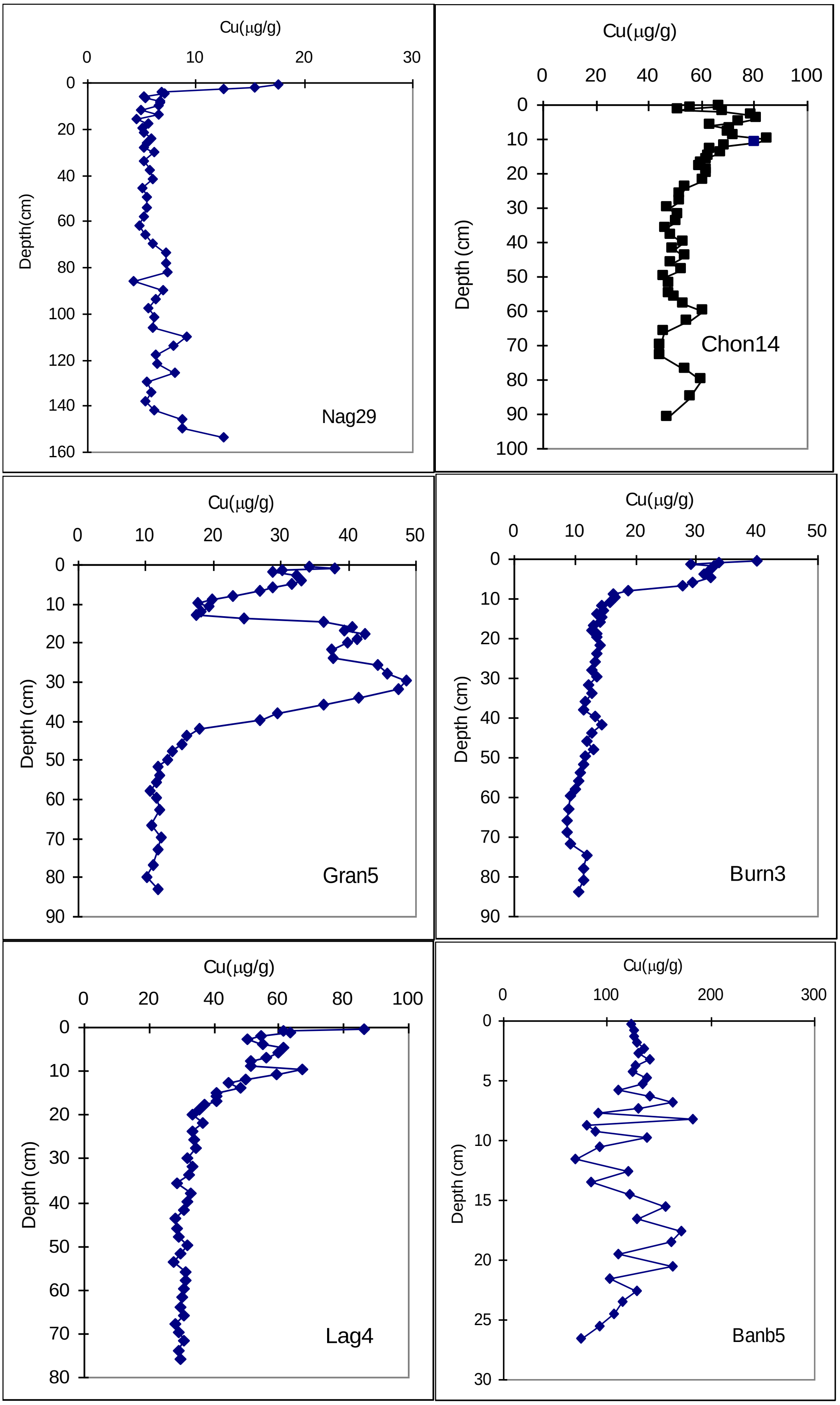


Figure 36. Historical patterns of Cd across the UK

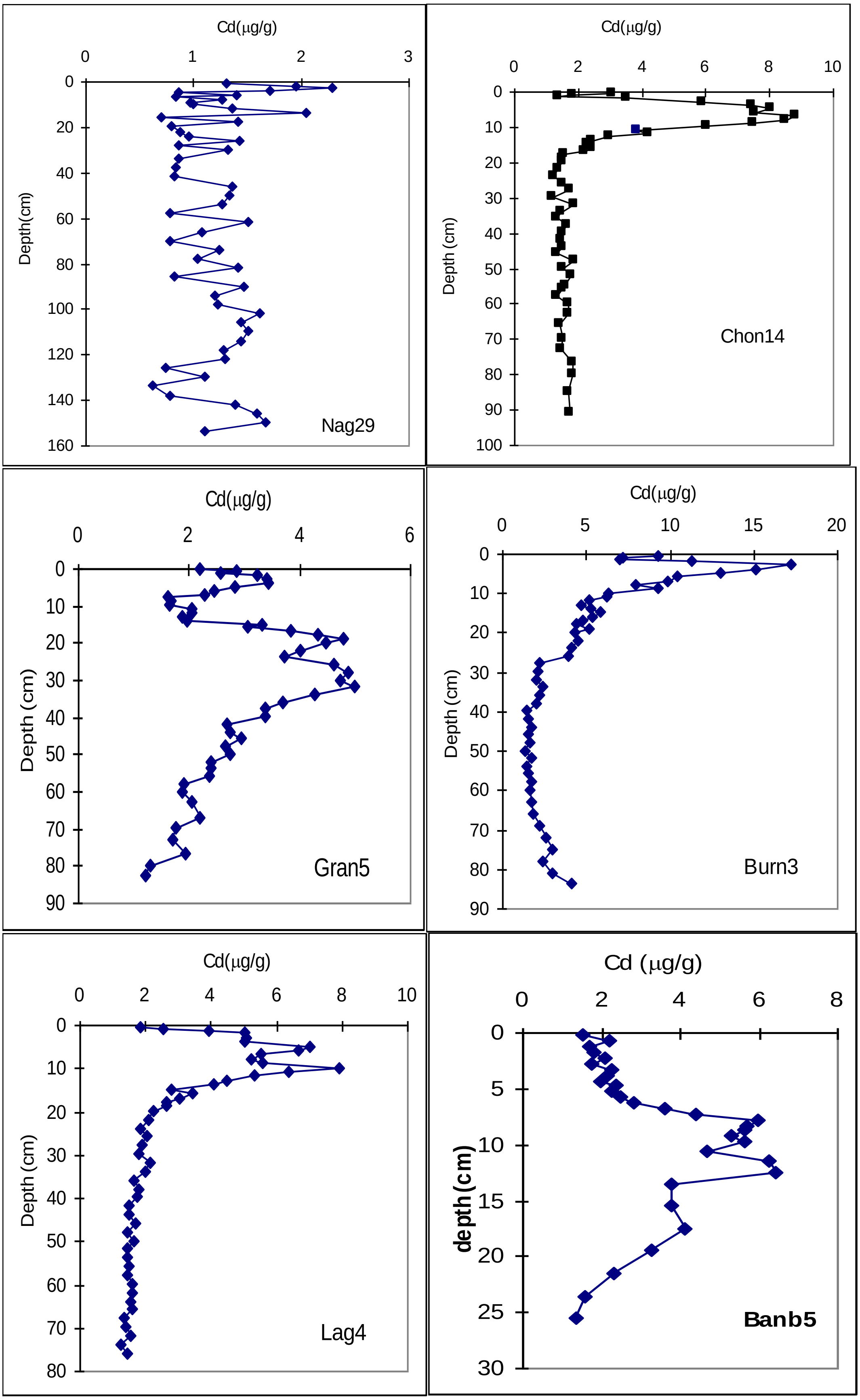


Figure 37. Historical patterns of Cr across the UK

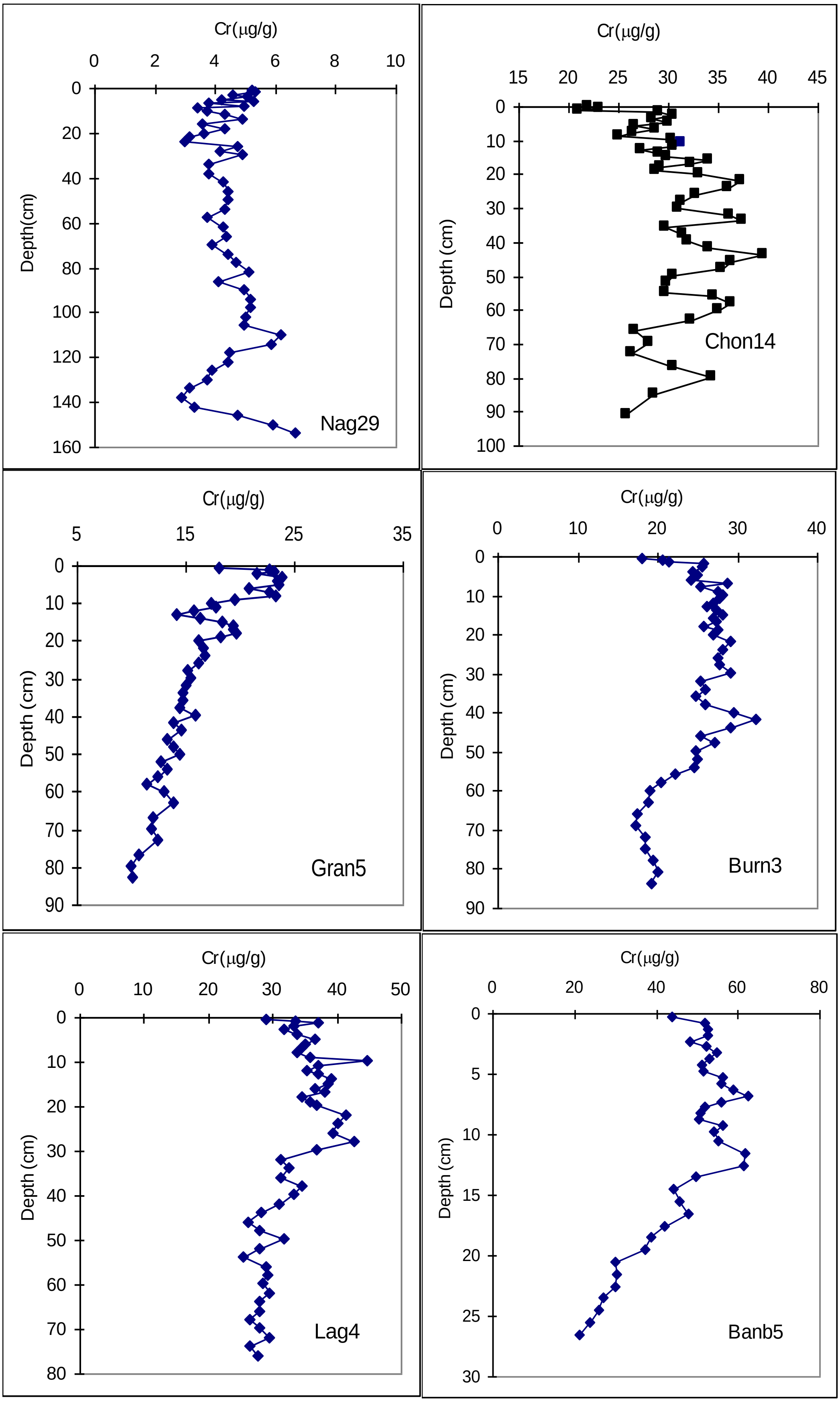


Figure 38. Historical patterns of Ni across the UK

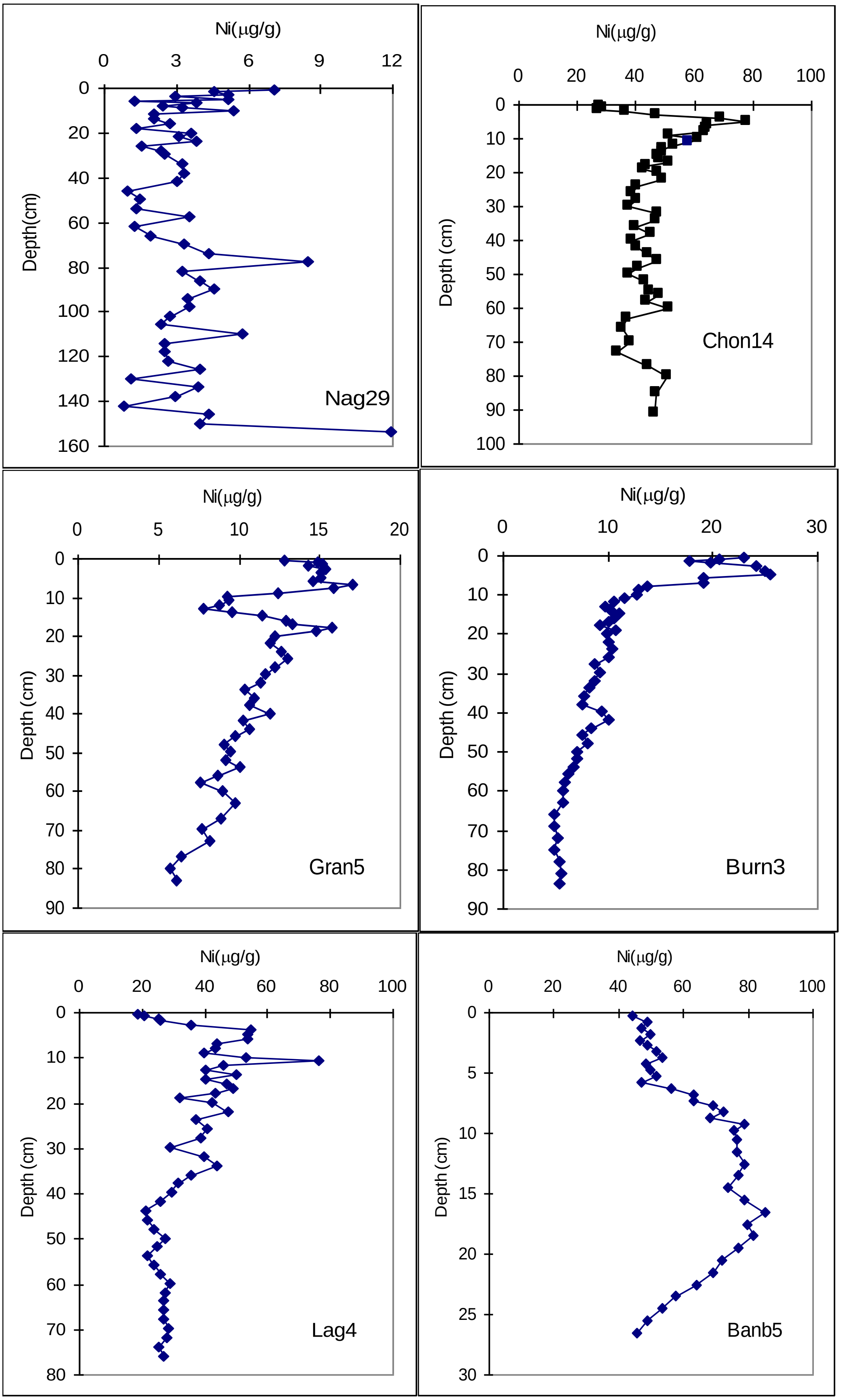


Figure 39. Historical patterns of Sn across the UK

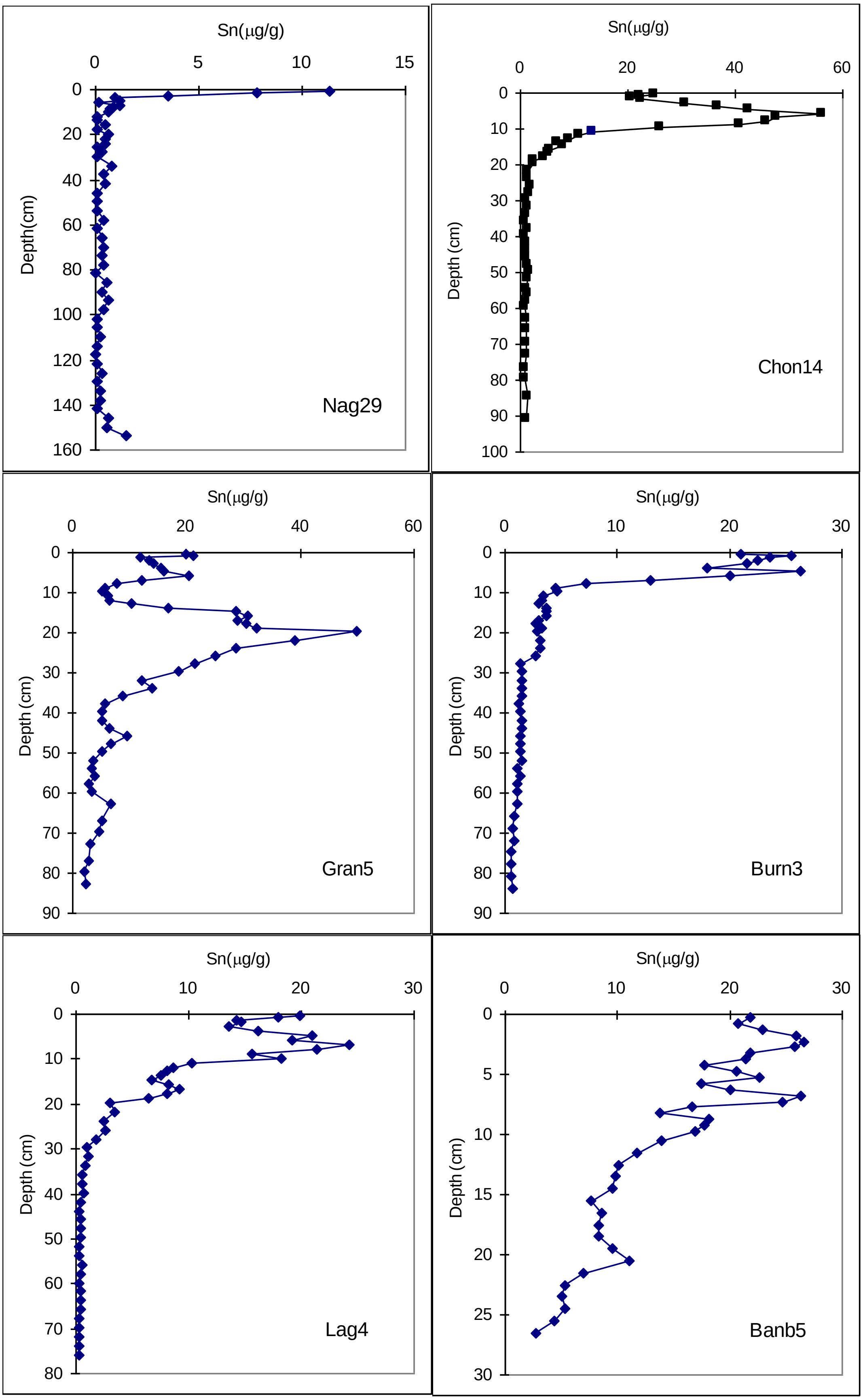


Figure 40. Historical patterns of As across the UK

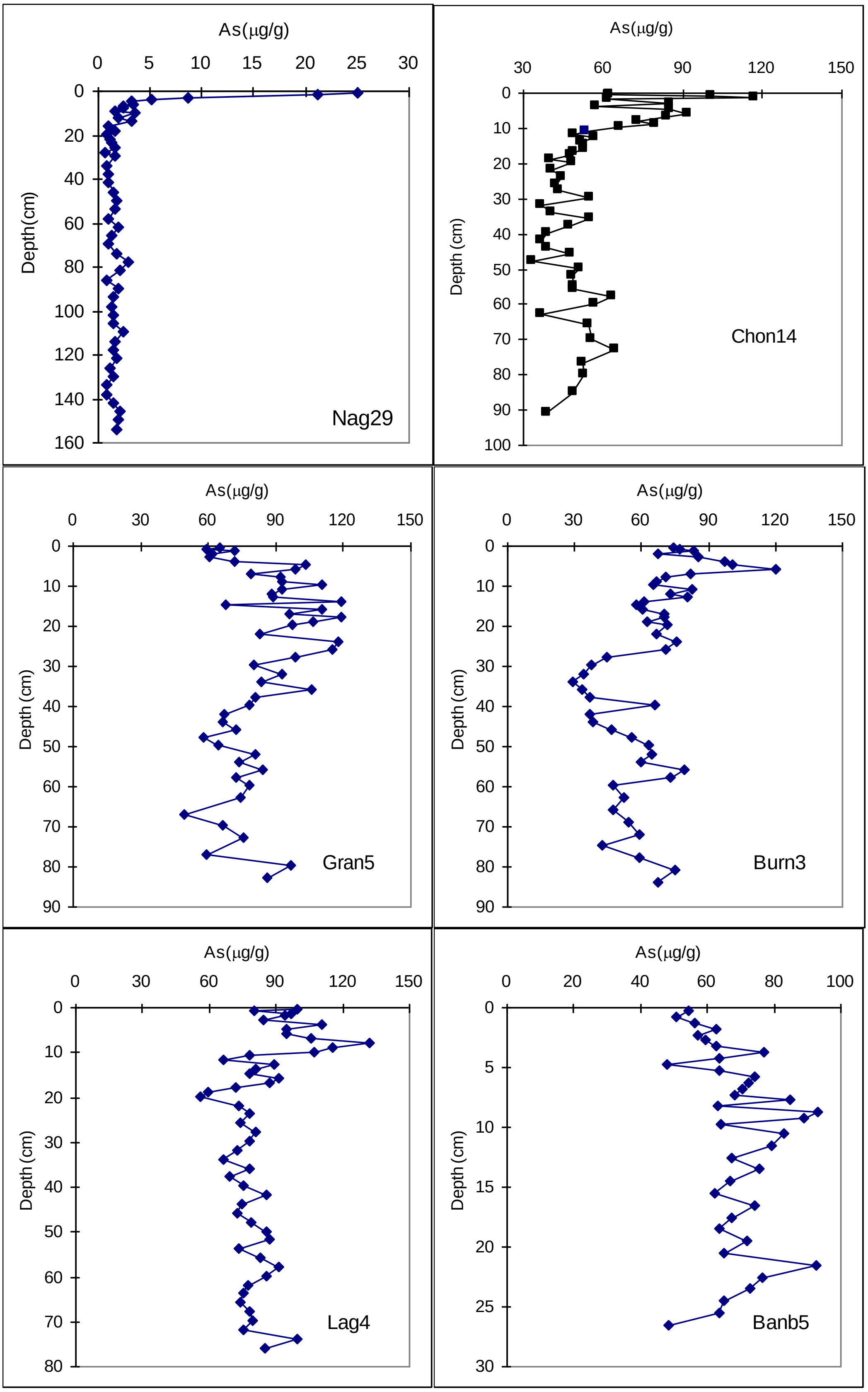


Figure 41. Historical patterns of V across the UK

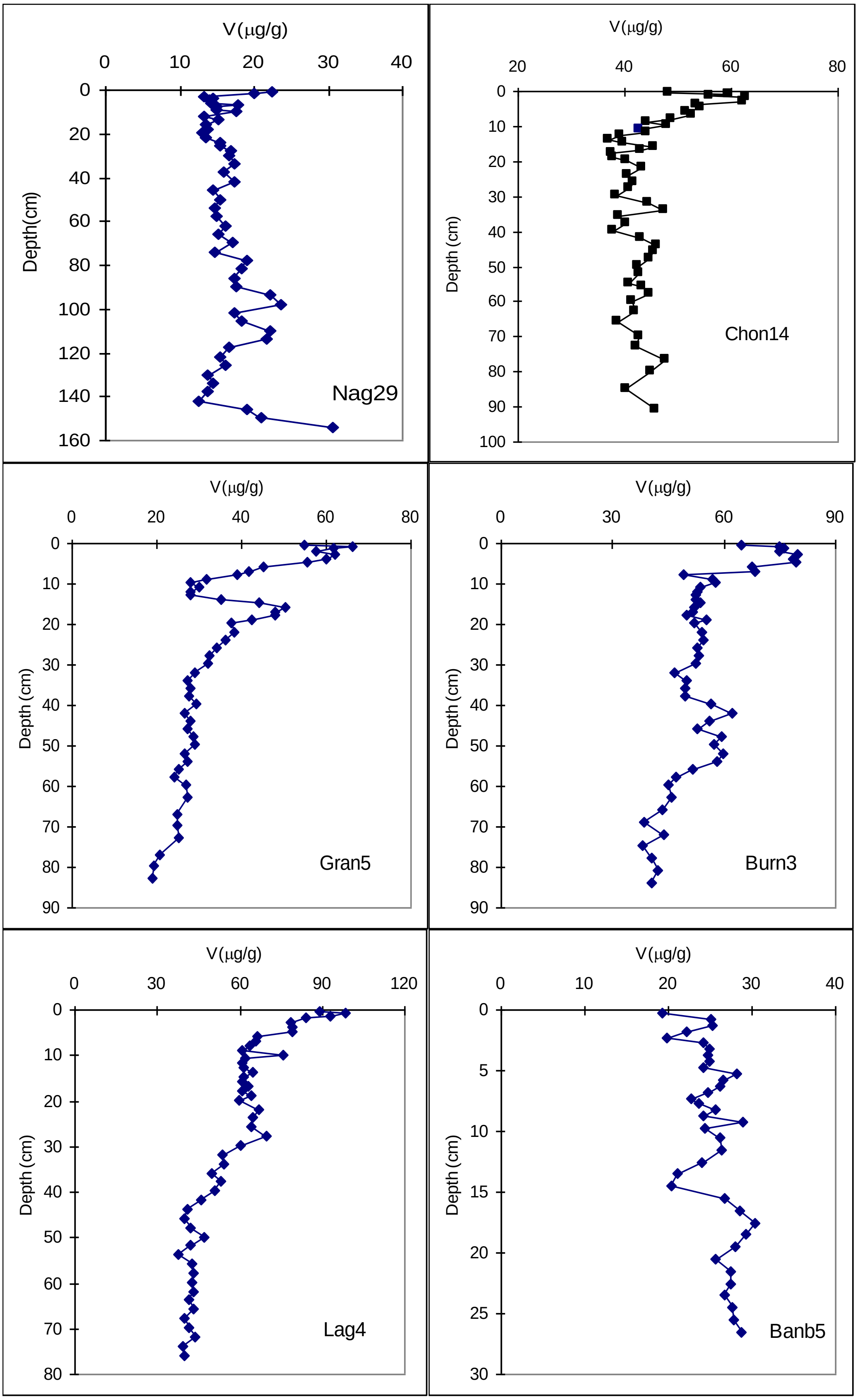


Figure 42. Historical patterns of Se across the UK

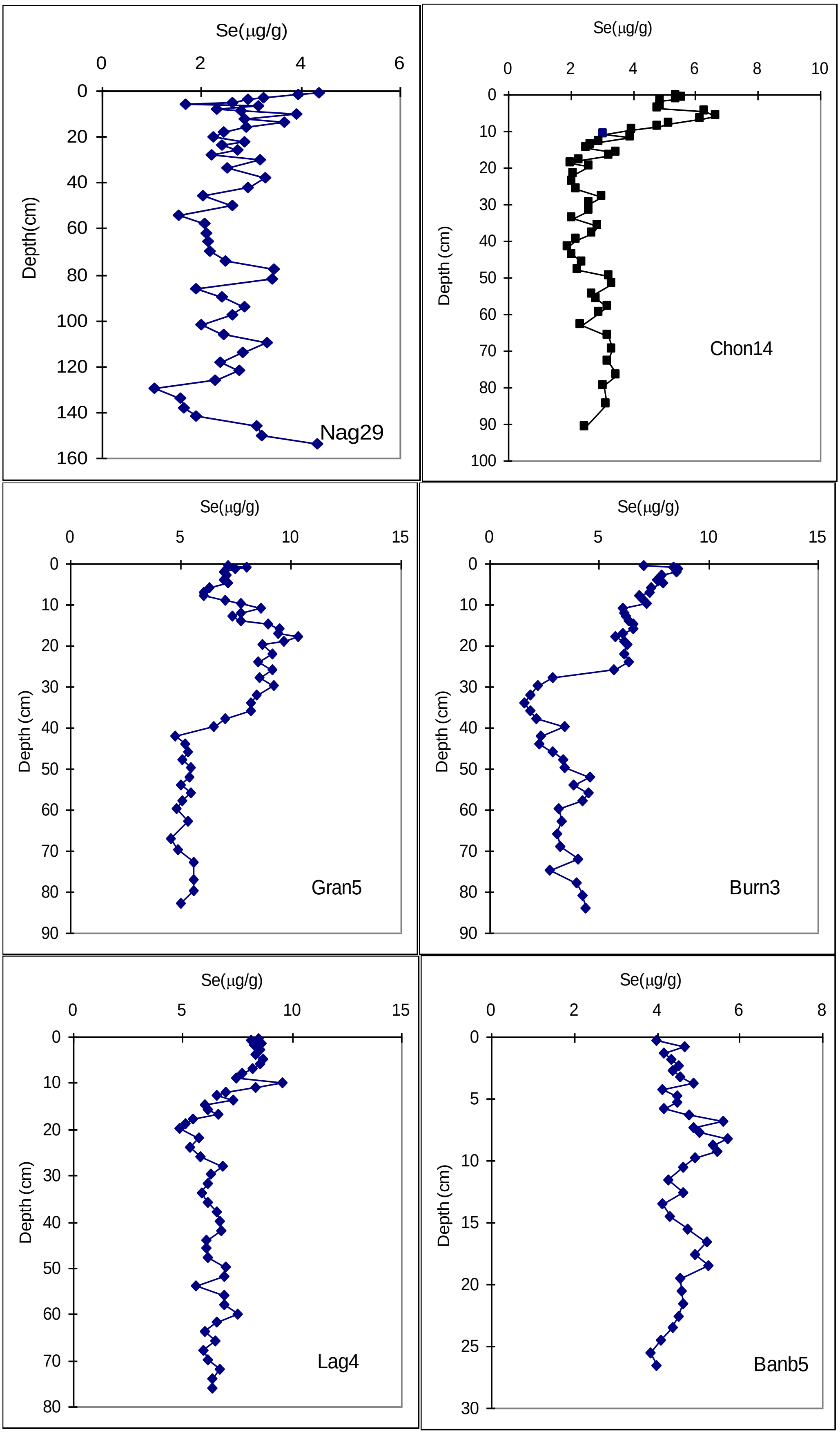


Figure 43. Historical patterns of Be across the UK

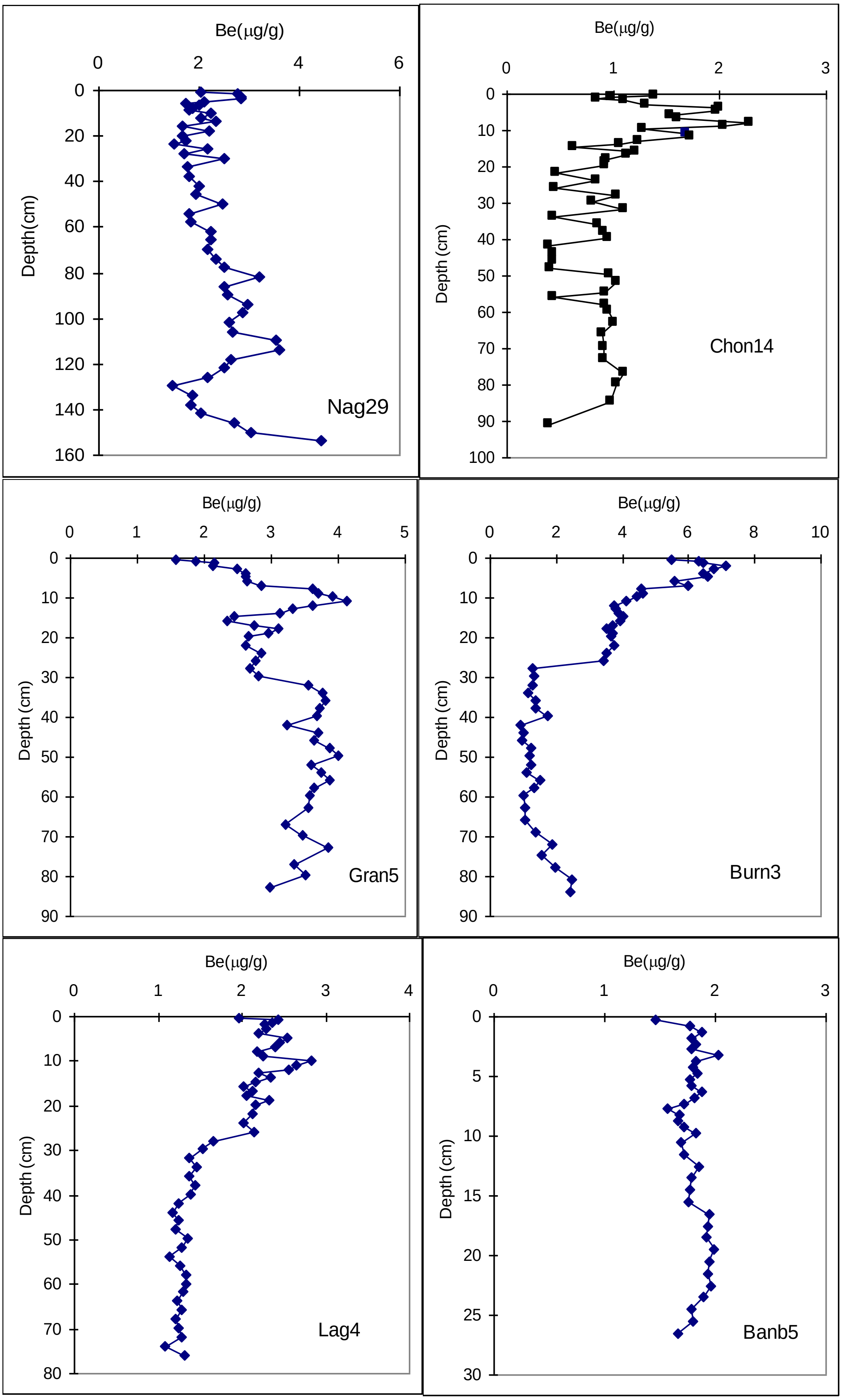


Figure 44. Historical patterns of Pd across the UK

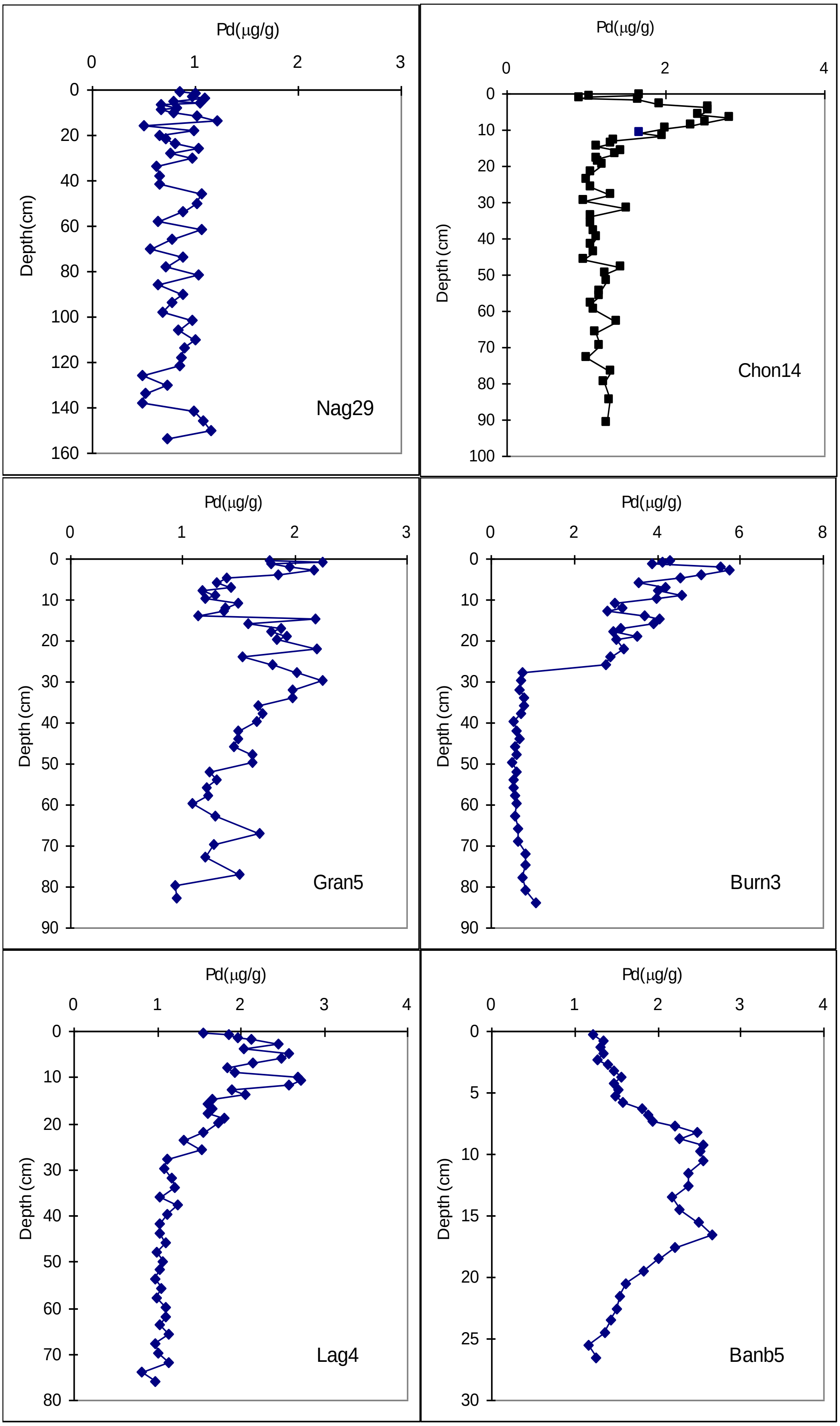
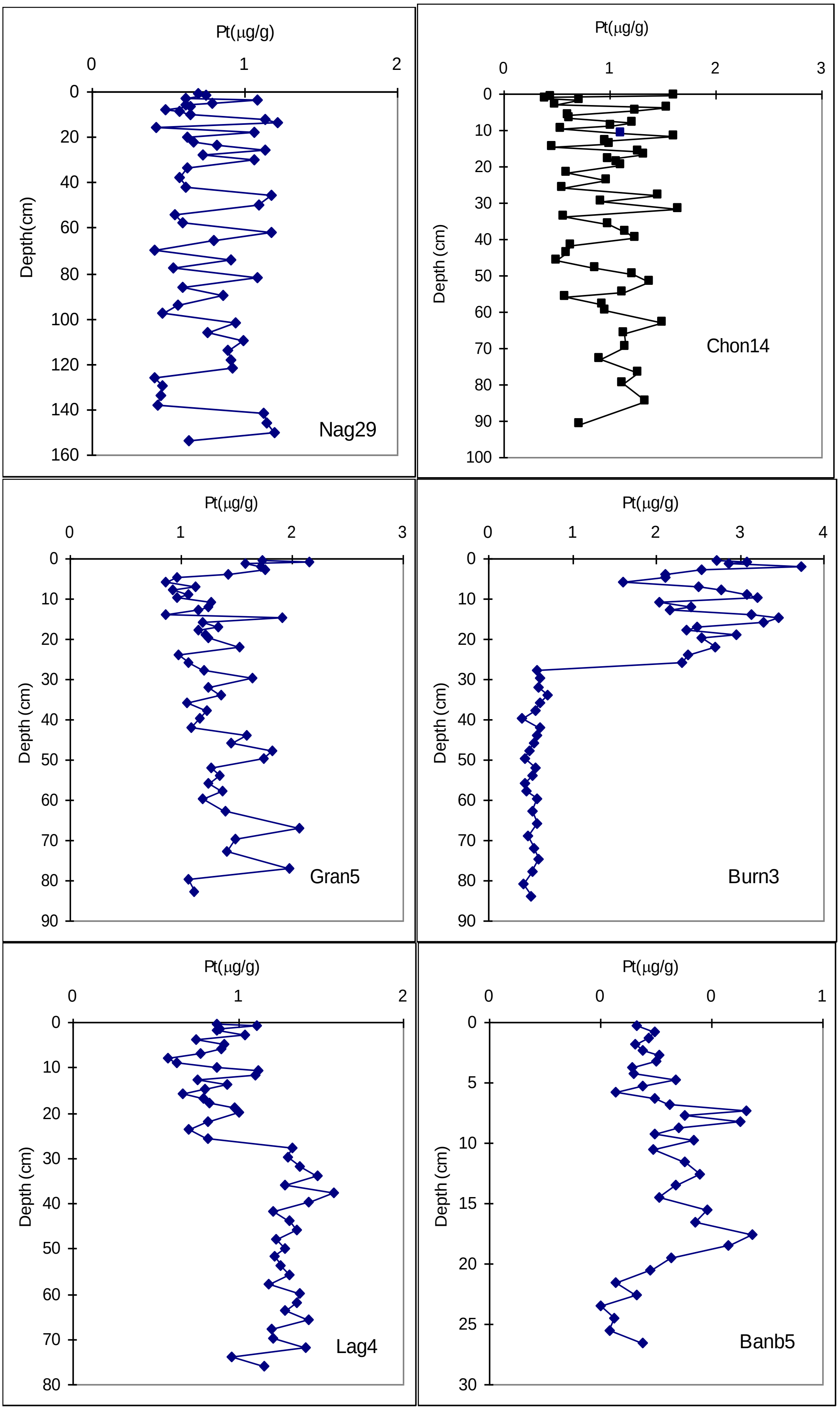


Figure 45. Historical patterns of Pt across the UK

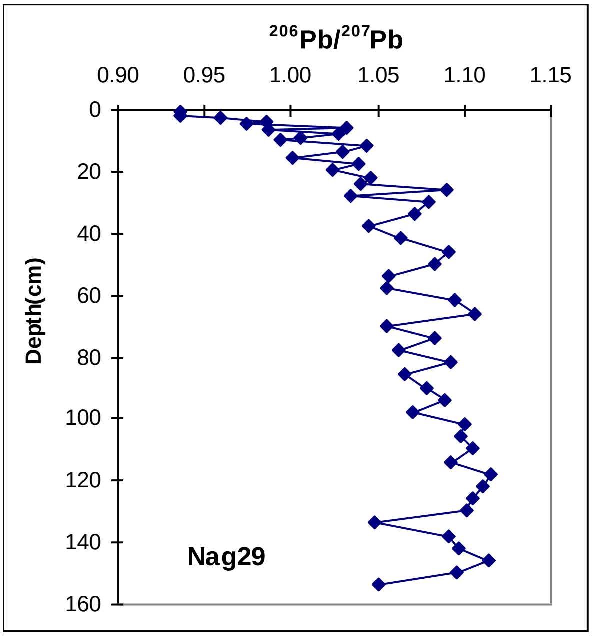


3.4 Stable Pb isotopes in Nag29

The stable Pb isotopes ^{206}Pb and ^{207}Pb were measured in Nag29 by ICP-MS and the isotope ratio (^{206}Pb/^{207}Pb) profile is shown in Figure 46. Stable Pb isotope analysis has been used to trace emission sources, particularly to assess spatial and temporal changes of recent Pb pollution originating from Pb smelters, industry and from the use of alkyl-lead in petrol. Lead from anthropogenic sources has a lower ^{206}Pb/^{207}Pb isotopic ratio than mineral lead and hence ratio changes through time indicate the extent to which a site has been impacted. Low ratios in recent sediments, peats and surface soils are therefore caused by deposition and accumulation of atmospheric Pb pollution. The very large differences in Pb isotope ratios between natural soil-derived Pb and atmospheric pollution Pb has made analysis of Pb isotopes a powerful tool in detecting the influx of pollution Pb to the environment in Sweden, Switzerland (Brannvall *et al.* 1999; Bindler *et al.* 1999; Weiss *et al.* 1999) and the UK (Farmer *et al.*, 1996) The stable Pb isotope ratio (^{206}Pb/^{207}Pb) profile in Nag29 shows that the ^{206}Pb/^{207}Pb ratio is relatively stable from the bottom to 120 cm depth followed by a slow, steady decline from 120 cm to about 30 cm, and then a rapid decline in the ratio from 30 cm to the sediment surface. According to pollen data, 120 cm depth in this core could date to c. 5000 years BP and therefore Lochnagar could have been contaminated by anthropogenic Pb since this time.

Trends in the ^{206}Pb/^{207}Pb isotope ratios of Nag29, are in good agreement with other UK data from the Lake District (Farmer *et al.,* 1996) although our data, measured by the ICP-MS system at University College London, are low compared to other results (Brannvall *et al.* 1999; Bindler *et al.* 1999; Farmer *et al.*, 1996; Weiss *et al.* 1999; Monna *et al.* 1997), and the values need to be confirmed. However, the change of trends in the ^{206}Pb/^{207}Pb profile is clearer and more significant than that of the Pb concentration profile in Nag29. Again, the profile is low resolution and it will be worthwhile confirming these trends by further analysis. This may reveal Roman and Medieval periods and the lake restoration processes from these periods of contamination. In Lochnagar, as the catchment soils are very organic, they store relatively high amounts of trace metals such as Hg, Pb and Zn, derived from anthropogenic sources. The catchment is, and will continue to be, the most important source of these metals to the lake for many years to come (Yang, 2000). In many other sites across the UK including Loch Chon, Loch Grannoch, Burnmoor Tarn and Llyn Llagi, catchment soils are also very organic and therefore may also store relatively high amounts of atmospherically deposited trace metals. Hence an investigation into the restoration processes of the lake ecosystems from Roman and Medieval periods has a special significance for predicting and managing the restoration of these sites from their current contaminated status.

Figure 46. Stable lead isotope ratio ($^{206}Pb/^{207}Pb$) profile in Nag29



4 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

4.1 Conclusions

Bulk deposition samples have been collected in London since 7th January 1999 and analysed for Hg concentration using cold vapour atomic fluorescence spectrometry (CV-AFS). Since 26th November 1999, sub-samples from the deposition samples have been taken for measuring Pb, Cd, Cu, Zn, Cr, Mn, Ni, As, Pt, Pd, Rh, V, Be, Se and Sn using inductively coupled plasma - mass spectrometry (ICP-MS). Hg concentrations in London deposition samples were found to be in the range 45 - 187 ng/l with a mean of 81.5 ng/l. Similarly, Pb had a range of 4.58 - 35.2 µg/l with a mean of 17.9 µg/l and Cd a range of 0.04 - 0.40 µg/l with a mean of 0.16 µg/l. Whilst no temporal trends were observed in these metal deposition data, some elements such as Cu, Pb and Ni were seen to co-vary over the period. The rainfall in London from 7th January 1999 to 6th January 2000 was 612 mm, about one third that at Lochnagar. Despite this, the yearly Hg deposition in London is 47.01 $\mu g/m^2$, higher than that at Lochnagar, and this is due to the high Hg concentration in London.

Surface sediment samples from 29 lakes and ponds across London (within the M25) and sediment cores from 5 lakes and 1 reservoir across the UK were taken. These samples were analysed for lithostratigraphic parameters such as dry weight, loss-on-ignition, wet density, and analysed for Hg, Pb, Zn, Cd, Cu, Cr, Ni, Mn, Al, Si, Fe, Ti, As, V, Be, Se, Sn, Pt, Pd, Rb, Sr, Zr, and Nb using CV-AAS, XRF, and ICP-MS. London surface sediments show large ranges in concentrations for Hg, Pb, Zn, Cd, Cu, Cr, Ni, As, V, Se and Sn. Sites close to industrial areas, roads or commercial areas usually have high concentrations of these elements.

Sediment cores show that sites across the UK have been contaminated by Hg, Pb, Zn, Cd, Cu, Cr, Ni, As, V, Se and Sn. In Nag29, it appears that Hg concentrations increase from c. 6000 years ago up to the present. This increase is much earlier than observed elsewhere but is supported by Pb stable isotope data. There is a rapid increase in Hg concentration during the last 200 years or so at all sites. In the 95 year record from Banbury Reservoir in London the sediments show high Hg concentrations throughout.

The provenance of the Hg in the sediments varies and catchment in-wash influences Hg loading to the sediments. Catchment contributions result in a sharp peak (1606 ng/g) in the Hg concentration profile at 9.25 cm in the core Chon14 taken from Loch Chon in the Trossachs region of Scotland. Considering Hg concentrations and predicted sediment accumulation rates, it appears that the Hg accumulation rates for these UK sites, except Lochnagar, would fall into the upper range for Europe. However, without dating the sediment cores, it is not possible to confirm this. Pb, Zn, Cd, Cu and Sn profiles in the cores taken from rural areas are similar to the Hg profile in individual cores, whilst As, V, Se, Cr and Ni profiles in these cores have different temporal patterns. These profiles show that the lakes have been contaminated by these elements, and the sources of these elements are varied. Be, Pd, Zr, Rb, Sr and Nb are mainly from mineral material. In Banbury Reservoir, the sediments show high concentrations of Hg, Pb, Zn, Cu, Cr, Ni and Sn. This may reveal the history of local industrial development over the last c.100 years.

In Nag29, the sediment core taken from Lochnagar, stable Pb isotopes ^{206}Pb and ^{207}Pb were also measured using ICP-MS. The ratios of these isotopes allow the trends in inputs of anthropogenically derived Pb to be observed. The change of trends in the ^{206}Pb/^{207}Pb profile in Nag29 is clearer and more significant than that of the Pb concentration profile and suggests that Lochnagar has been contaminated by anthropogenic Pb since c.5000 years ago.

4.2 Recommendations for further work

There are several topics addressed within this report which clearly require further study.

Long-term monitoring of deposition

Hg data in London has shown considerable inter-annual and intra-annual variability. The short dataset for the other elements also shows considerable variability. In order to determine more significant trends in the deposition of these elements, especially with respect to human health studies, it is recommended that monitoring is continued, and furthermore, expanded to other sites in order to gain an insight into spatial variability.

Dating of sediment cores

Although concentration data, as reported here, are useful indicators of long-term trends in metals, the timing of any changes (and hence an indication of cause) and perhaps more importantly the rates of change require a sediment chronology. Although beyond the scope of this present study, both in terms of finance and time, dating of the cores using independent means such as ^{210}Pb or ^{14}C (in the case of the long Lochnagar core) are required for better interpretation of the data.

Long core analysis of Hg pollution.

There is an apparent increasing trend throughout the full length of the Hg concentration profile in Nag29, and this core is thought to cover c.6000 years. This long-term contamination of the site is supported by the stable Pb isotope data. However, so far only 50 of the 314 samples have been analysed and any interpretation of these data is restricted by this low resolution. Full analysis of the remaining samples may reveal the impact, on this remote site, of Roman and Medieval metal emissions. More importantly a detailed analysis of these periods may allow a better understanding of the lake restoration processes following periods of contamination. Such knowledge may help in our understanding of how we might expect lakes to ‘recover’ from the current levels of contamination following the implementation of present and possible future emission reduction policies.

Stable Pb isotopes analyses

The data from the stable Pb isotope analysis suggests that the $^{206}Pb/^{207}Pb$ ratio may be used to assess Pb pollution histories in the lake sediments of the UK. Further, this may provide clearer evidence of anthropogenic impact than the profiles of Pb concentration alone. This work needs to be confirmed at other sites.

Further sediment core and catchment soil analyses for trace metals

The data presented here show that pollution histories vary both spatially and temporally across the UK. However, there are still large gaps in our knowledge both in terms of the regional impact of metal deposition on freshwater sites and the role that catchments play in both the storage of metals and as sources of secondary metals (i.e. originally atmospherically deposited but stored in soils) for the lake.

Further analyses need to be undertaken, especially in those areas which have so far been neglected, so that we have a full picture of temporal trends across the UK. Twinned analyses of lake sediment and catchment soil cores would enable the importance of the catchment to lakes to be estimated as well as an identification of all the factors that may influence metal contamination of UK lakes. This work may become more important as the impact of a changing climate is considered with respect to metals in freshwaters, in particular, the potential for release of the vast store of anthropogenically derived metals currently bound in catchment soils.

5 ACKNOWLEDGEMENTS

We gratefully acknowledge the funding for this project by the Department of the Environment, Transport and the Regions, Department of the Environment Northern Ireland, National Assembly for Wales and the Scottish Executive. (Contract No. EPG 1/3/159). We would like to thank colleagues from the Environmental Change Research Centre, University College London for their help in the field and the laboratory. Thanks also go to Irene Cooper and John Boyle for access to the Metorex Xmet 920 XRF system and Unicam 939 AAS system at the Geography Department, Liverpool University, Torunn Berg for Hg measurements in deposition samples at the Norwegian Institute for Air Research (NILU) and Spiros Pergantis at the Chemistry Department, University College London and Birkbeck College.

6 REFERENCES

Belzile, N., Chen, Y.-W. and Xu, R., 2000. Early diagenetic behaviour of selenium in freshwater sediments, *Applied Geochemistry*, **15**: 1439-1454.

Bindler, R., Brannvall, M.-L., Renberg, I., Emteryd, O. and Grip, H., 1999. Natural lead concentrations in pristine boreal forest soils and past pollution trends: a reference for critical load models. *Environ. Sci. Technol.* **33**: 3362-3367.

Boyle, J. F., 2000. Rapid element analysis of sediment samples by isotope source XRF, *J. Paleolimnology*, **23**: 213-221.

Brannvall, M.-L., Bindler, R., Renberg, I., Emteryd, O., Bartnicki, J. and Billstrom, K., 1999. The Medieval metal industry was the cradle of modern large-scale atmosheric laed pollution in Northern Europe. *Environ. Sci. Technol.* **33**: 4391-4395.

Department of the Environment, Transport and Regions, 1999. *The air quality strategy for England, Scotland, Wales and Northern Ireland. A consultation document*, DETR, London.122pp.

Engstrom, D. R. and Swain, E. B., 1997. Recent declines in atmospheric mercury deposition in the Upper Midwest. *Environ. Sci. Technol.* **31**: 960-967.

Farmer, J. G., Eades, L. J., Mackenzie, A. B., Kirika, A. And Bailey-Watts, T.E., 1996. Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. *Environ. Sci. Technol.* **30**: 3080-3083.

Fitzgerald, W. F., Engstrom, D. R., Mason, R. P. and Nater, E.A., 1998. The case for atmospheric mercury contamination in remote areas. *Environ. Sci. Technol.* **32**: 1-7.

Glew, J. R., 1991. Miniature gravity corer for recovering short sediment cores. *J. Paleolimnology*, **5**: 285-287.

Grondin, A., Lucotte, M., Mucci, A. and Fortin, B., 1995. Mercury and lead profiles and Burdens in soils of Quebec (Canada) before and after flooding. *Can. J.Fish. Aquat. Sci.*, **52**: 2493-2506.

Henderson, P. A., 1999. *Atmospheric deposition of heavy metals: An assessment of monitoring in the UK with reference to critical loads and forthcoming legislation*. A scoping study produced for DETR as part of the Critical Loads of Acidity and Metals programme (Contract No. EPG 1/3/117 [AQ 17/8/307]). Environmental Change Research Centre / ENSIS Ltd, University College London.

Klein, S. M. and Jacobs, L. A., 1995. Distribution of mercury in the sediments of Onondaga Lake, N.Y. *Water Air Soil Pollut.*, **80**: 1035 -1038.

Martinez-Corizas, A., Pontevedra-Pombal, X., Garcia-Rodeja, E., Novoa-Munoz, J. C. and Shotyk, W., 1999. Mercury in a Spanish peat bog: archive of climate change and atmospheric metal deposition. *Science*, **284**: 939-942.

Monna, F., Lancelot, J., Croudace, I. W., Cundy, A. B. and Lewis, J. T., 1997. Pb isotopic composition of airborne particulate material from France and the southern United Kingdom: Implications for pollution sources in urban areas. *Environ. Sci. Technol.* **31**: 2277-2286.

Nriagu, J. O., 1993. Legacy of mercury pollution. *Nature*, **363**: 589.

Oslo and Paris Coventions for the Prevention of Marine Pollution, Environmental Monitoring and Assessment (ASMO), 1997. *Draft Data Report og CAMP Measurements Made at Coastal Stations in 1995.*

Patrick, S., Waters, D., Juggins, S. and Jenkins, A., 1991. *The United Kingdom Acid Waters Monitoring Network: Sites and Methodology report*. ENSIS Publishing, London. 63pp.

Rickard, A., Millikan, C. and Neville, S., 1999. The mass concentration and size distribution of particles in central London using non-continuous gravimetric sampling techniques. *Clean Air*, **29**, 14-20.

UNECE Convention on Long-range Transboundary Air Pollution, Task Force on Mapping, 1998. *Proceedings of a Workshop on Critical Limits and Effect Based Approaches for Heavy Metals and Persistent Organic Pollutants*. Bad Harzburg, Germany, 3 - 7 November 1997. Pub: Federal Environment Agency, Berlin. Texte 5/98.

Verta, M., Tolonen, K. and Simdla, H., 1989. History of heavy metal pollution in Finland as recorded by lake sediments. *Sci. Total Environ*. **87/88**: 1-18.

Weiss, D., Shotyk, W., Appleby, P. G., Kramers, J. D. and Cheburkin, A. K., 1999. Atmospheric Pb deposition since the industrial revolution recorded by five Swiss peat profiles: enrichment factors, fluxes, isotopic composition, and sources. *Environ. Sci. Technol.* **33**: 1340-1352.

Xue, H., Sigg, L. and Gachter, R., 2000. Transport of Cu, Zn and Cd in a small agricultural catchment. *Wat. Res*. **34**: 2558-2568.

Yang, H., 2000. *Trace Metal Storage in Lake System and its Relationship with Atmospheric Deposition with Particular Reference to Lochnagar, Scotland.* PhD unpublished thesis, University of London.