AEAT/R/ENV/0264 Issue 2

Trace and Major Elements in the Atmosphere at Rural Locations in the UK: Summary of Data for 1999

A report produced for Department of the Environment, Transport and the Regions; the Scottish Executive; the National Assembly for Wales and the Department of the Environment in Northern Ireland

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Executive Summary

Information on the long-term trends of trace and major elements is required to assess the impact of changes in emissions control policies on air quality in the United Kingdom. AEA Technology's National Environmental Technology Centre has operated a long-term sampling and measurement programme at rural locations in England; the Rural Trace Elements (RTE) network. The measurement programme commenced in 1972.

Atmospheric particulate material and rainwater (bulk deposition) have been sampled continuously at three locations, i.e. Chilton (Oxfordshire), Styrrup (Nottinghamshire) and Wraymires (Cumbria). The concentrations of 35 elements have been measured in atmospheric particulate material. In rainwater, the concentrations of 25 elements, nitrate and sulphate have been measured (in the soluble fraction only).

This report provides a summary of data obtained during the year 1999. These data have been compared both with recent and with more historical data. The on-going investigation into long-term changes in concentrations of trace elements in air particulate and in atmospheric deposition in the UK rural environment in relation to changes in methods of energy production, energy consumption and emissions control policy, has been updated.

Concentrations of potentially toxic metals, e.g. As, Cd, Cr, Cu, Ni, Pb and Zn, in air and rainwater are comparable with measurements at other rural locations in the UK. From these measurements, current 'rural UK background' concentration ranges of these metals in air and rainwater have been established. These have been compared with measurements of airborne metals at urban locations in the UK. Up to 7-fold increases were found at the urban sites.

Insufficient monitoring of heavy metals is currently undertaken at rural locations in the UK to enable all the spatial variance in average air concentrations or in the deposition of heavy metals to be defined. However, from the limited data available there appears to be a north-south gradient for many heavy metals, with the lowest values observed in the northern UK.

Road transport is still the largest source of Pb emissions in the UK and is thought to be the major source of Pb at in the atmosphere at rural locations. During 1999, average air concentrations have continued to fall. The maximum annual mean air concentration was 26 ng m^{-3}. This represents only ~5% of the proposed limit value (0.5 μg m^{-3}) under the forthcoming EU Air Quality Daughter Directive or ~10% of the annual mean value recommended by EPAQS as an air quality standard for the UK.

Both atmospheric concentrations and depositions of Pb at rural sites were well correlated with estimated UK emissions to the atmosphere between 1972 and 1998. Restrictions on the use of Pb additives in petrol have substantially reduced the concentrations of airborne Pb in the rural environment. Reductions in annual mean air concentrations and annual mean depositions of 80% - 90% have occurred since the 1970s. In more recent years (since 1988), the increased usage of unleaded petrol has also contributed to these reductions.

Decreases in atmospheric concentrations of As, Cr, Ni, V and Zn have been measured between the periods 1972-1979 and 1994-1998. The major source of the emissions of these metals is the combustion of fossil fuels. The percentage reductions in the annual mean air concentrations of these metals recorded at Chilton, Styrrup and Wraymires were between ~60% and ~80%. The changes in annual mean air concentrations were well correlated (although less so for Zn) with the changes in estimated annual total UK emissions to the atmosphere between 1972 and 1998. It is likely that estimates for Zn emissions are more uncertain than for the other metals. For Zn the proportion emitted from fossil fuel combustion is lower, with larger contributions from other sources for which the emission estimates have greater uncertainty such as ferrous and non-ferrous metals production processes, road transport (tyre wear) and waste incineration.

Considerable reductions in both annual mean air concentrations and depositions of the predominantly soil-derived or ‘crustal’ elements (Al, Fe, Mn and Sc) have been measured at all three rural sites since the 1970s. These decreases were of a similar magnitude to those recorded for the anthropogenically-derived heavy metals. Reductions in fly-ash emissions, brought about by long-term changes in fossil fuel combustion for power generation, industrial requirements and domestic and industrial space heating, together with improved abatement technology in power generation and industry, are the likely explanation. Average annual mean air concentrations of Ca, K and Mg have declined similarly, by ~60% - 80%. Although these elements are thought to be mainly soil-derived (and have a marine-aerosol source also), the large decreases observed are attributed to decreases in emissions of fly ash.

To complement the routine measurements programme, two additional pieces of work were undertaken during 2000.

(1) An intercomparison of the analysis of air filters for arsenic, cadmium, lead and nickel. The objective was to compare the determination of these metals using two different sample digestion techniques, i.e. open and closed vessel digestions. A working group of the European Committee for Standardisation, CEN 264/Working Group 14, is developing a reference method for determining concentrations of As, Cd, Pb and Ni in ambient air. This will almost certainly be adopted as the reference method for the forthcoming EU Daughter Directives for these compounds. The intercomparison exercise undertaken here has provided information on the procedure used to analyse air filters from the RTE monitoring network in future.

(2) To improve the existing RTE network dataset for measurement of Cd in airborne particulate material, archived air filter samples from the three long-term sampling stations have been analysed retrospectively. Data on quarterly and annual Cd concentrations in air at the RTE network sites are now available for the period 1979-1999. As found previously for other trace and major elements, air concentrations of Cd have exhibited a seasonal variability. Higher concentrations have tended to be measured in the ‘winter’ quarters, January to March and October to December.

The long-term reductions in air concentrations of Cd have been consistent at all three RTE network sampling locations. Comparing the periods 1979-1982 and 1995-1998, the reductions in annual mean air concentrations were in the range 69%-79%. The corresponding reduction in estimated emissions to the atmosphere in the UK was only 44%. The discrepancy (like that observed for Zn) is attributed to the uncertainty in emissions estimates. However, between 1979 and 1998 the measured average annual air concentrations of Cd were significantly correlated with estimates of emissions.

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1 Introduction

AEA Technology, on behalf of the Air and Environment Quality Division of the Department of the Environment Transport and the Regions (DETR); the Scottish Executive; the National Assembly for Wales; and the Department of the Environment in Northern Ireland, has operated three long-term sampling stations for trace elements in the atmosphere in rural environments in England since the early 1970s (the Rural Trace Elements network). The overall aims of this programme of measurements are to quantify and follow changes at rural locations in air particulate and atmospheric deposition with respect to inorganic species, and to examine any variation in relation to changes in methods of energy production, energy consumption and emissions control policy.

The objectives of the present study were as follows:

(i) to maintain the existing measurements programme;
(ii) to determine the long-term changes in elemental concentrations in air and rainwater at rural locations and deposition to soil;
(iii) to provide comparison with urban air quality.

This report provides a comprehensive summary of data obtained for the year 1999. The data obtained between 1992 and 1998 has been reviewed and reported previously (Baker, 1997 and Baker, 1999). These data were compared with the historical data to investigate long-term changes in concentrations of trace elements in air particulate and atmospheric deposition. A review of the data obtained during the period 1972-1991 was undertaken by Cawse et al. (1995).

To complement the routine measurements programme, two additional studies were undertaken during 2000. These were:

- **An intercomparison of the analysis of air filters for arsenic, cadmium, lead and nickel**. The objective was to compare the determination of these metals using two different sample digestion techniques.

- **The retrospective analysis of samples of historical air filters for cadmium**. The objective was to improve the existing dataset for measurements of cadmium in airborne particulate material at the three long-term sampling sites.

The results of these studies are also presented in this report.

2 Methods of Sampling and Analysis

2.1 SAMPLING LOCATIONS

The three long-term sampling stations are situated at the locations shown in Figure 1. Details of the sampling sites are as follows.

Chilton, Oxfordshire (National Grid Reference: SU 468861, altitude 130 m). This site is in central southern England, about 90 km from the English Channel. The sampling equipment is situated on site at AEA Technology's Harwell Laboratory. The surroundings are predominantly rural, with large areas devoted to cereal cultivation.

Styrrup, Yorkshire. In 1982, the sampling station was re-located to Sandbeck Park (National Grid Reference SK 561906), altitude 15 m). This site is 4-5 km to the west of the original site at Styrrup (National Grid Reference SK 606898, altitude 15 m). For reasons of continuity, the original name of the station has been retained. The station is in a rural area with some arable farming in the immediate surrounding area. There are some industrial influences, e.g. Sheffield, with its steel industry lies some 25 km to the west.

Wraymires, Cumbria (National Grid Reference SD 362974, altitude 84 m). This is a rural site adjacent to Esthwaite Water, near Lake Windermere. It is approximately 25 km from the Irish Sea and is ~30 km to the north-east of Barrow-in-Furness, where there is some shipbuilding industry. Approximately 40 km to the south of Wraymires is the Heysham oil refinery. The station is rural with a moderate maritime influence and relatively high annual rainfall. There is little arable farming in the area which might give rise to resuspension of local soil dust.

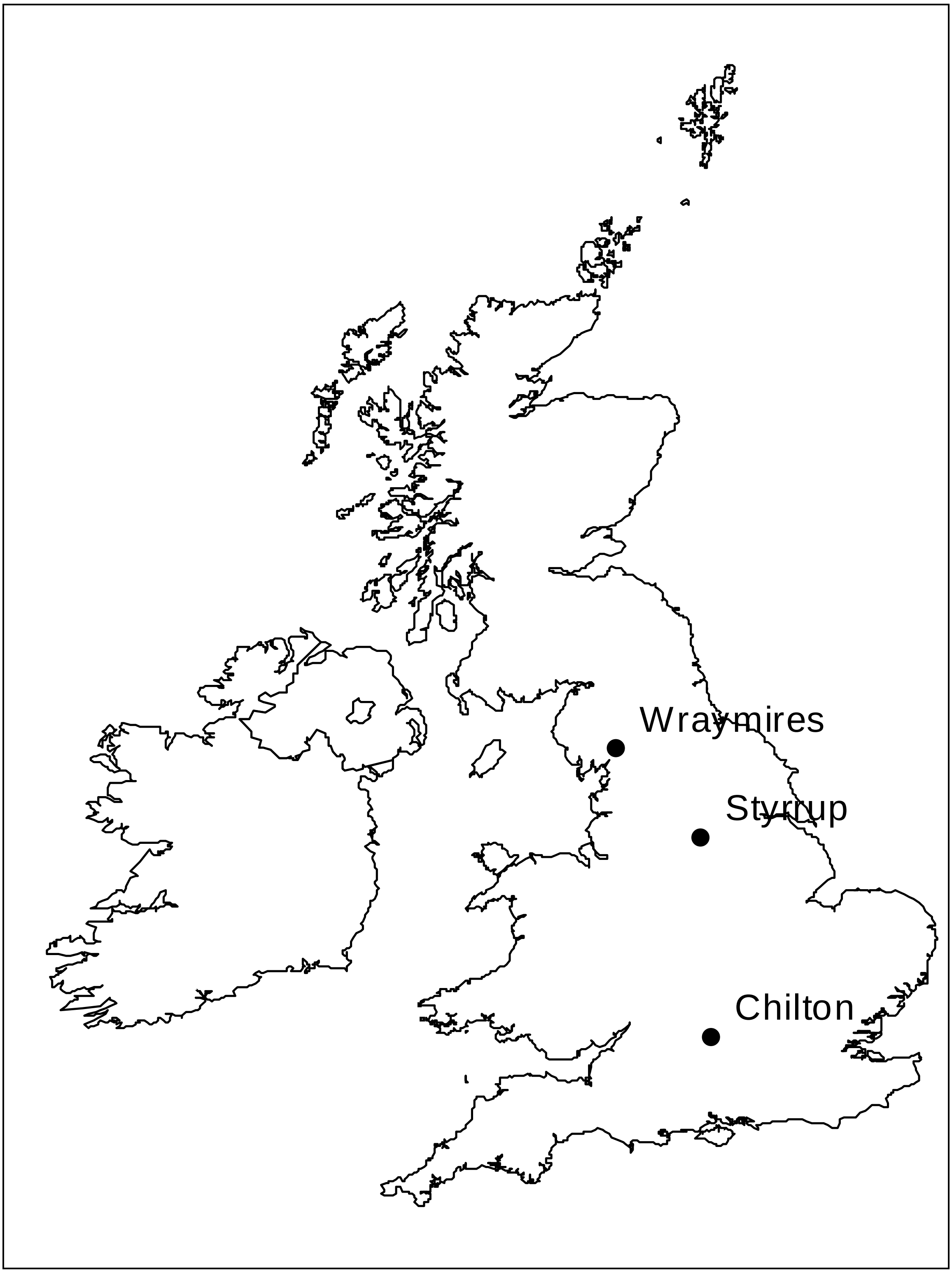


Figure 1
Location of sampling sites

2.2 SAMPLING OF ATMOSPHERIC PARTICULATE AND RAINWATER

Atmospheric particulate material and rainwater is sampled continuously. The sample collectors (described below) are changed each month by local site operators. The samples are sealed prior to their despatch to the National Environmental Technology Centre (NETCEN). All samples are collected at 1.5 m above ground level to reduce contamination by soil splashing during heavy rainfall. The sampling equipment and methods used were chosen to obtain continuous, trouble-free operation that required a minimum of attention. Each sampling station is subject to an annual maintenance and calibration visit.

Airborne particulate material is sampled by drawing air through a cellulose filter (Whatman 40 grade paper, 6 cm diameter) held in a polypropylene duct. The inlet nozzle faces downwards to avoid the intake of rain. A plastic backing disc (1.5 mm mesh) prevents the collapse of the filter paper. Air is drawn through the filter paper by an electrically driven pump. The volume of air sampled (~250 m^3 per month) is measured by a calibrated gas meter. The sampling characteristics, e.g. collection efficiency, have been established experimentally (Pattenden and Wiffen, 1976) and has been briefly described in Cawse et al. (1995). Although they do not conform to a PM_{10} specification, these air samplers tend not to collect large particles efficiently and are therefore reasonable surrogates for respirable particle samplers. The filter papers are oven-dried and pre-weighed to allow determination of the total suspended particulate (TSP) in air. It should be noted that the recorded TSP will exclude volatile components, especially NH_4NO_3 and NH_4Cl, since the exposed filter papers are oven-dried before they are weighed.

Rainwater is collected each month using a polythene funnel and bottle. The collecting funnel contains a polythene debris filter (0.5 mm mesh) to exclude insects. The bottle is enclosed in black polythene to prevent the growth of algae in the collected rainwater sample. The collector retains the bulk deposition, i.e. the wet deposition, plus the dry deposit that falls upon the funnel and is washed into the bottle by subsequent rain. In contrast to the restrictions on particle size collected by the air sampler, the bulk precipitation collector may retain larger particles in the atmosphere. The monthly rainfall at each site is recorded by a standard Meteorological Office rain gauge at 0.3 m above ground level.

During the autumn of 1999, a maintenance visit was made to each of the three sampling stations. All sampling apparatus was overhauled, e.g. gas meters and pumps were replaced and calibrated as appropriate. Safety checks (e.g. electrical testing of pumps and power leads) were carried out on all sampling equipment.

2.3 SAMPLE PREPARATION AND ANALYSIS

2.3.1 Air Filters

Representative portions of each monthly air filter are bulked to obtain quarterly (i.e. three-monthly) samples for analysis. To avoid contamination by trace and major elements, sample processing is carried out in a laminar air-flow cabinet. Air filter holders are only opened to remove the filter paper under these conditions. Polythene gloves and polythene apparatus are used for sample handling to avoid contamination, e.g. by metals. All apparatus is cleaned with

5% v/v acetic acid AR grade, then rinsed with demineralised water before use. A portion of each monthly sample is retained for retrospective analysis, if required.

The following 35 elements are analysed in atmospheric particulate material. Ag, Al, As, Au, Br, Ca, Cd, Ce, Cl, Co, Cr, Cs, Cu, Eu, Fe, Hg, I, In, K, La, Mg, Mn, Mo, Na, Ni, Pb, Rb, Sb, Sc, Se, Sm, Ti, V, W and Zn. Historically, instrumental neutron activation analysis (INAA) was the preferred technique for the majority of these analytes and is still currently used. The exceptions were Cd, Cu, Ni and Pb which, between 1995 and 1998, have been determined by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The samples collected in 1999 were analysed by inductively-coupled plasma mass spectrometry (ICP-MS), a more sensitive technique than ICP-AES for these metals, since in recent years air concentrations of Cd and Ni were found to be close to or below analytical limits of detection (LODs). Historically, Cu, Ni and Pb were analysed by x-ray fluorescence (XRF). It should be noted that the sampling method only collects non-volatile particulate material and will not truly represent elemental mercury and volatile mercury compounds. Appropriate ‘blank’ samples are also analysed.

Errors in analysis by INAA are based on 1σ counting statistics. Detection limits are based on the rejection of errors >30%. A Standard Reference Material, i.e. National Bureau of Standards (NBS) citrus leaves, is also analysed for Quality Control (QC) purposes.

Uncertainty in the measurements made by ICP-MS is estimated to be ± 20% for results that were an order of magnitude greater than the Limit of Determination (LOD). For each element, the analytical LOD was determined at the time of analysis. Higher uncertainties are associated with measurements that fall within an order of magnitude of the LOD. An independent QC standard is measured during the analysis of samples using this technique. The reported detection limit varies between samples analysed at the same time as it is a function both of the LOD and the air volume sampled.

2.3.2 Rainwater/Bulk Deposition

Monthly rainwater samples are bulked, according to rainfall amount each month, to obtain a quarterly sample for analysis. All monthly samples are stored at -5 °C upon receipt until they are bulked into quarterly samples. A portion of each monthly sample is stored frozen, should retrospective analysis be required. The quarterly rainwater samples are filtered (using Whatman 42 grade cellulose filter paper) to separate the soluble and insoluble fractions. Filtered samples are then concentrated prior to their analysis.

ICP-AES and inductively-coupled plasma mass spectrometry (ICP-MS) techniques are used to determine the following 25 analytes in the soluble fraction of the rainwater samples; Ag, Al, As, Au, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Ti, V, W and Zn. The soluble fraction is known to contain a higher percentage of potentially toxic elements, whereas the insoluble component contains a high proportion of elements derived from the soil, e.g. Al, Ce, Fe and Sc (Cawse et al, 1995). Uncertainties in the measurements made by ICP-AES/ICP-MS are described above (section 2.3.1).

Nitrate and sulphate were also analysed in the filtered rainwater samples using Ion Chromatography. The pH of both the monthly samples as received, and the bulked quarterly samples, is measured by a standard pH electrode and meter.

3 Results for 1999

The quarterly mean concentrations of 35 elements and TSP measured in air at Chilton, Styrrup and Wraymires during 1999 are tabulated in Appendix 1. These tables also include the annual mean air concentrations for each year.

The quarterly and annual mean concentrations of 25 elements, nitrate and sulphate measured in the soluble fraction of rainwater at these three locations during 1999 are also listed in tables in Appendix 1. The annual mean concentrations are precipitation-weighted. Quarterly and annual deposition data have also been derived, from the rainwater concentrations and the measured rainfall at each site, and are also listed in the tables in Appendix 1.

3.1 AIR CONCENTRATIONS

The annual mean air concentrations of many of the 35 elements, measured at each of the three sites during 1999, have been compared to the measurements made over the preceding three years. These measurements (1996-1998), reported in Baker (1999), have been summarised in Table 1. Those elements whose annual mean concentrations were frequently below analytical detection limits have been omitted from this summary.

The elements can be broadly classified into the following groups according to average air concentrations that were usually recorded:

(i) Concentrations >1000 ng m^{-3}: **Cl**.

(ii) Concentrations between 100 - 1000 ng m^{-3}: **Ca, Fe, K, Mg** and **Na** (concentrations of **Al** at Styrrup fell within this range).

(iii) Concentrations between 10 - 100 ng m^{-3}:**Al, Pb** and **Zn** (concentrations of **Fe** at Wraymires fell within this range).

(iv) Concentrations between 1 - 10 ng m^{-3}: **Br, Cu, I, Mn, Ni, V** (concentrations of **Pb** at Wraymires fell within this range). Concentrations of Ti were generally <10 ng m^{-3} at Chilton and Wraymires and between 10 and 20 ng m^{-3} at Styrrup.

(v) Concentrations of <1 ng m^{-3}: **Ag, Au, Cd, Ce, Co, Cs, Eu, Hg, In, La, Mo, Rb, Sc, Sm** and **W.**

Air concentrations of **As, Cr, Sb** and **Se** fell into groups (iv) or (v) depending on location. Concentrations of these elements were generally ~1 ng m^{-3} at Chilton or >1 ng m^{-3} at Styrrup, with concentrations of <1 ng m^{-3} recorded at Wraymires (Table 1).

Table 1
Summary of Annual Mean Air Concentrations of Elements at Chilton, Styrrup and Wraymires (1996-1999)

Annual Mean Air Concentration (ng m^{-3})												
Element	**Chilton**				**Styrrup**				**Wraymires**			
	1996	1997	1998	**1999**	1996	1997	1998	**1999**	1996	1997	1998	**1999**
Al	117	110	91.6	68.3	174	145	137	114	53.8	58.2	66.6	48.5
As	1.2	0.97	0.76	0.44	4.2	3.4	3.0	2.4	0.61	0.64	0.44	0.42
Br	8.7	8.4	6.7	4.2	13.1	13.9	10.6	10.2	<5	7.2	6.4	6.9
Ca	507	487	234	176	429	490	320	296	185	370	176	128
Cd	0.36	0.21	<0.1	0.27	0.57	0.29	<0.2	0.28	<0.2	<0.08	<0.1	0.06
Ce	0.23	0.21	0.14	0.11	0.40	0.32	0.32	0.22	0.12	0.14	0.11	0.10
Cl	1618	1569	1568	979	1913	2146	1732	1763	852	1359	1457	1849
Co	0.14	0.13	0.12	0.093	0.24	0.23	0.22	0.19	0.076	0.097	0.067	0.070
Cr	1.1	0.75	0.52	0.49	4.9	4.3	3.6	4.3	0.59	0.53	0.36	0.34
Cs	0.060	0.050	0.035	0.024	0.069	0.051	0.042	0.039	0.028	0.023	0.019	0.020
Cu	5.9	3.7	1.9	2.7	8.2	8.0	4.6	4.4	3.1	2.7	0.54	1.2
Fe	164	144	108	96	248	236	211	190	65	69.3	56.0	52.1
Hg	0.18	0.07	0.22	0.11	0.37	<0.2	0.72	0.28	0.23	0.19	0.49	0.24
I	1.8	1.9	1.4	0.89	2.4	2.0	1.5	1.4	1.1	1.7	1.2	1.1
K	238	250	219	104	262	297	252	196	<140	262	230	<99
Mg	171	153	157	106	239	213	197	219	82	116	128	164
Mn	5.2	5.0	3.2	2.4	11.8	12.9	9.9	11.3	2.0	2.2	1.7	1.6
Na	777	894	909	503	786	927	784	857	467	769	900	1028
Ni	2.2	1.2	0.32	1.6	3.5	3.1	1.6	2.2	<1	1.2	<0.1	0.67
Pb	25.4	18.2	13.1	9.8	37.9	36.1	29.1	25.8	8.7	9.1	3.7	3.7
Sb	1.1	1.1	0.86	0.78	2.3	1.9	2.0	1.9	0.58	0.67	0.54	0.38
Sc	0.026	0.022	0.017	0.013	0.038	0.032	0.029	0.023	0.013	0.012	0.012	0.0095
Se	1.1	0.79	0.61	0.40	2.8	2.7	2.5	1.9	0.65	0.81	0.63	0.51
V	3.9	3.6	2.6	1.5	4.6	4.0	3.0	3.2	1.5	1.8	1.3	1.3
Zn	55.4	23.4	16.9	30.0	100	152	43.8	64.8	20.1	16.7	14.8	9.0

For a given site, the annual mean concentrations measured in 1999 were similar to the annual means recorded in the years 1996, 1997 and 1998 (Table 1). Further, the plots of quarterly mean air concentrations of a number of heavy metals for the period 1992-1999 at all three locations indicate that the levels measured during 1999 were typical of recent years (Figure 2). Over the last five years, air concentrations of Cd and Ni at Wraymires were mainly below the analytical limits of detection (typically <0.1 and <1 ng m^{-3}, respectively). However, a change to the use of the more sensitive ICP-MS analytical technique in 1999 (section 2.3.1) has enabled quarterly mean Cd and Ni air concentrations to be determined at this site (Table A1.3, Appendix 1).

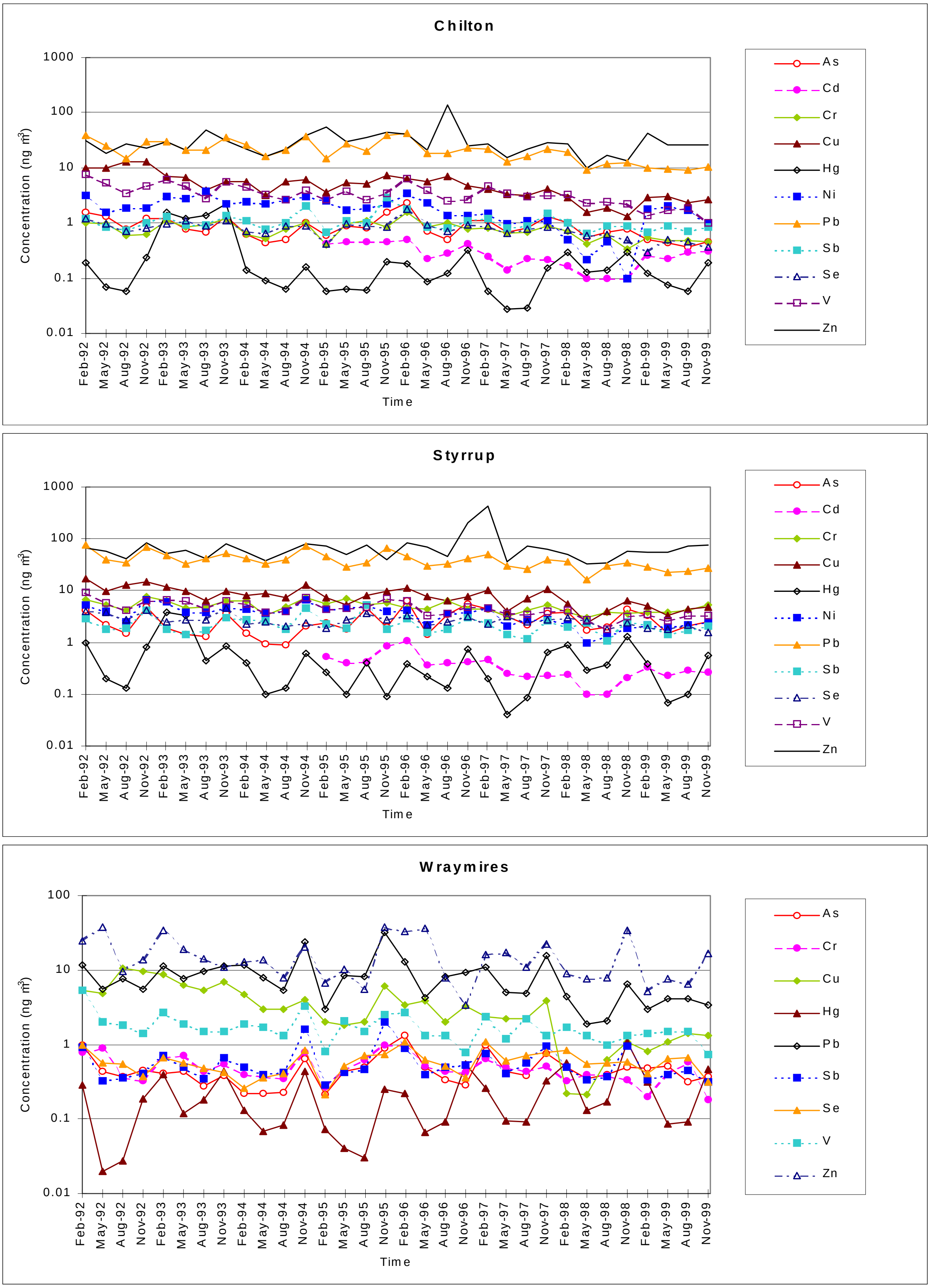


Figure 2
Quarterly mean concentrations of heavy metals in air at Chilton, Styrrup and Wraymires (1992-1999)

For each element, where the air concentrations were above the analytical LOD, the lowest annual mean concentrations during 1999 continued to be measured at Wraymires, with highest values found at Styrrup (Table 1). Historically, with few exceptions air concentrations of the elements have followed the order Styrrup>Chilton>Wraymires. The Styrrup location is known to be influenced by the nearby South Yorkshire industrial region (Baker, 1999 and Cawse et al., 1995). In 1999, annual mean air concentrations of many anthropogenically-derived heavy metals (e.g. As, Cd, Cr, Ni, Pb, Sb, Se, V and Zn) were ~3 to ~7-fold greater (and ~10-fold greater for Cr) at Styrrup compared to Wraymires.

Quarterly mean air concentrations of lead at Chilton and Styrrup have continued to fall. Those measured in 1999 were among the lowest measured during the 1990s (Figure 2). The 1999 annual mean concentrations measured at each location were the lowest ever, whilst the low levels recorded at Wraymires during 1998 continued to be measured in 1999 (Figure 2, Table 1). The highest annual mean air concentration of Pb in 1999 was measured at Styrrup (26 ng m^{-3}). This represents only 5% of the new ambient air quality limit value for Pb of 0.5 $\mu g\ m^{-3}$ proposed by the European Council (EC) Framework Directive on Ambient Air Quality Assessment and Management (96/62/EC) or 10% of the air quality standard for Pb in the UK of 0.25 $\mu g\ m^{-3}$ recommended by EPAQS as an annual average (DETR, 1998).

For other heavy metals no ambient air quality standards exist in the UK. Under the EC Framework Directive (96/62/EC) further daughter Directives are being developed which will set limit values for some metal pollutants, i.e. As, Cd, Ni and Hg. The World Health Organisation (WHO) has produced guideline values, with regard to air pollution, for a variety of compounds, including some metals (WHO, 1987). For example, for Cd in air at rural locations, the levels present in 1987 (<1 - 5 ng m^{-3} as an annual mean concentration) should not be allowed to increase. At Chilton, Styrrup and Wraymires, the 1999 annual mean air concentrations were all below 0.3 ng m^{-3}. As, Cr and Ni are also referred to in the WHO publication. However, no WHO guideline values for these metals are given, due to their carcinogenicity and no safe levels are recommended.

The potential effects of Hg upon human health were reviewed by the WHO. Although they were unable to recommend a guideline value, a concentration of 1 $\mu g\ m^{-3}$ as an annual average was considered to be a level which should adequately protect human health (WHO, 1987). Hg is present in the atmosphere in the gaseous phase and attached to particulate material. The above WHO value applies to both forms of Hg. The sampling method used in this network will collect only the particulate-bound Hg (section 2.3.1). During the period 1999, the maximum annual mean air concentration of Hg (0.28 ng m^{-3} recorded at Styrrup, Table 1) represents only 0.03% of the WHO recommended value.

However, gaseous Hg is the dominant form present in the atmosphere. Measurements of total gaseous mercury (TGM) were made at the Chilton site between June 1995 and April 1996 (Lee et al., 1996). The average air concentration of TGM over this period was 1.68 ng m^{-3}, compared with a particulate-bound Hg concentration of ~0.1 ng m^{-3}, i.e. > 90% of the atmospheric Hg measured at this site was found to be TGM. If this were also true at the Styrrup location in 1999, then the total atmospheric Hg present would still only be 0.3% of the WHO value recommended above.

3.1.1 Air concentrations of heavy metals at rural locations in the UK

Air concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn are routinely measured at three other rural locations in the UK as part of DETR's North Sea network (Playford and Baker, 1999). These data are now available up to 1999 (Playford and Baker, 2000). These sites are located on the east coast of the UK at East Ruston (Norfolk), High Muffles (North Yorkshire) and Banchory (Aberdeenshire). The data from these locations, together with those from Chilton, Styrrup and Wraymires, can be used to derive 'current' air concentrations of these metals at rural locations in the UK.

In Table 2 the average, maximum and minimum values for the annual mean air concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn over the last five years (1995-1999) are listed. Anomalously high quarterly mean concentrations of Zn measured at Styrrup and High Muffles were excluded in calculating the means that are summarised in Table 2.

Table 2
Annual Mean Air Concentrations of Heavy Metals
at Rural Locations in the UK (1995-1999)

Location		Annual Mean Air Concentration (ng m^{-3})						
		As	Cd	Cr	Cu	Ni	Pb	Zn
Chilton	Mean	0.86	0.28	0.73	3.9	1.5	18	33
	Max	1.2	0.45	1.1	5.9	2.2	25	55
	Min	0.44	<0.1	0.49	1.9	0.32	10	17
Styrrup	Mean	3.1	0.37	4.6	6.6	3.0	35	58
	Max	4.2	0.57	5.9	8.2	4.6	44	66
	Min	2.4	<0.2	3.6	4.4	1.6	26	44
Wraymires	Mean	0.52	<0.1	0.48	2.1	0.7	7.6	15
	Max	0.64		0.59	3.1	1.3	13	20
	Min	0.42		0.34	0.54	0.36	3.7	9
East Ruston	Mean	0.87	0.22	0.66	3.3	1.5	14	23
	Max	1.3	0.29	0.86	4.2	2.0	17	38
	Min	0.64	0.17	0.36	2.4	0.66	12	11
High Muffles	Mean	0.60	0.14	0.74	4.1	1.3	8.7	30
	Max	0.76	0.16	1.2	6.3	1.8	12	40
	Min	0.40	0.10	0.19	2.7	0.70	6.6	20
Banchory	Mean	0.35	0.07	0.51	2.1	0.58	3.3	18
	Max	0.44	0.11	1.0	2.7	0.95	4.3	27
	Min	0.27	0.05	0.31	1.2	0.16	2.2	14

Notes
(i) Annual mean concentrations of Cd at Wraymires were mainly below analytical limits of detection.

The annual mean air concentrations of Pb, Cd, As and Ni at UK rural locations for the period 1995-1999 are shown in Figure 3a; corresponding values for Cu, Cr and Zn are illustrated in Figure 3b. Air concentrations of all seven metals measured at Chilton and Wraymires were of a similar order to values reported for the three east coast sites (Table 2, Figures 3a and 3b). At Styrrup, average concentrations of the metals (particularly Pb, As, Ni, Cu, Cr, and Zn) exceeded those measured at East Ruston, High Muffles and Banchory over the last five years (Figures 3a and 3b). The exceedances are attributed to regional influences, e.g. industrial activity and greater consumption of coal for domestic and light commercial industrial combustion, in South Yorkshire and the East Midlands.

Pb concentrations have also been measured in air at two other rural locations in the UK, Cottered (Hertfordshire) and Eskdalemuir (Dumfries and Galloway). These sampling sites form part of DETR's Lead in Petrol Monitoring network. For the period 1995-1999, the following annual mean air concentrations of Pb were recorded at these sites (DETR 2000; DETR's National Air Quality Information Archive: at the following Website (http://www.environment.detr.gov.uk/airq/aqnfo.htm).

Cottered:	Mean 21 ng $m^{-3,}$, range 16 -25 ng m^{-3}.
Eskdalemuir:	Mean 8 ng m^{-3}, range 5 - 10 ng m^{-3}.

These annual average concentrations of Pb fall within the ranges listed in Table 2.

The spatial distribution of the average annual mean air concentrations of Pb, Cd, As and Ni for the period 1995-1999 is shown in Figure 3a (including data for Cottered and Eskdalemuir sites). These metals are of particular interest since a limit value either exists (for Pb) or is likely to be set for Cd, As and Ni in future EC daughter Directives under the Framework Directive on Ambient Air Quality Assessment and Management (96/62/EC).

There are insufficient data to define all the spatial variance in the annual mean air concentrations of these metals. However, in the broad spatial pattern a north-south gradient is apparent with the smallest values being observed at Banchory in eastern Scotland. The highest values were observed at Styrrup where regional influences prevail as discussed above. Since UK emissions of Pb are dominated by those from road transport, air concentrations of Pb would be expected to be largest in and around southern Britain, as with other traffic-related pollutants such as NO_2. Industrial source of Pb are generally of local importance to air quality. As leaded petrol was withdrawn at the end of 1999 it will be interesting to see trends in future years.

Similarly, air concentrations of other metals would be expected to follow this pattern since they are emitted from centres of UK population and industrial sources. This is illustrated for Cd, As and Ni in Figure 3a and Cu, Cr and Zn (Figure 3b).

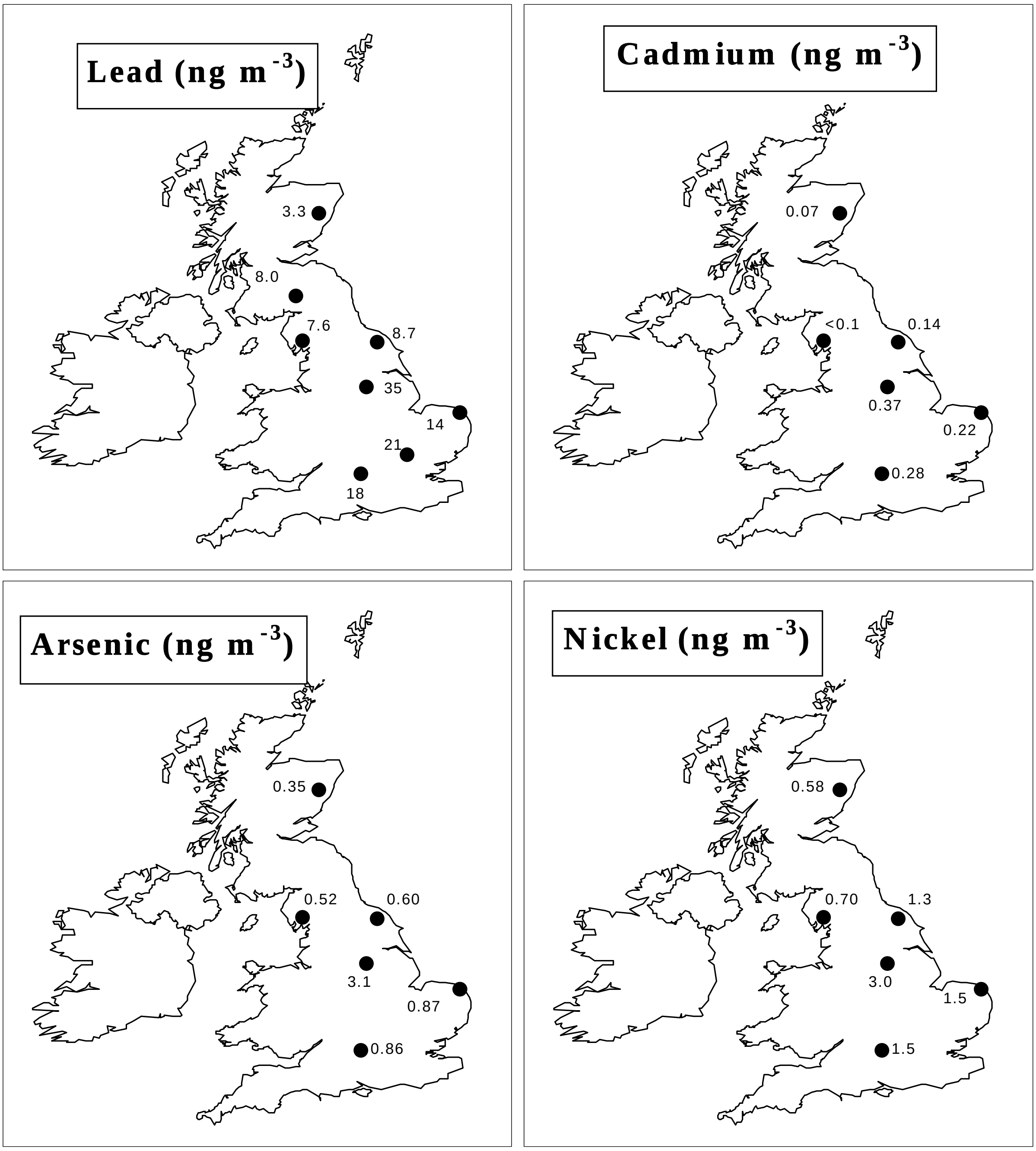
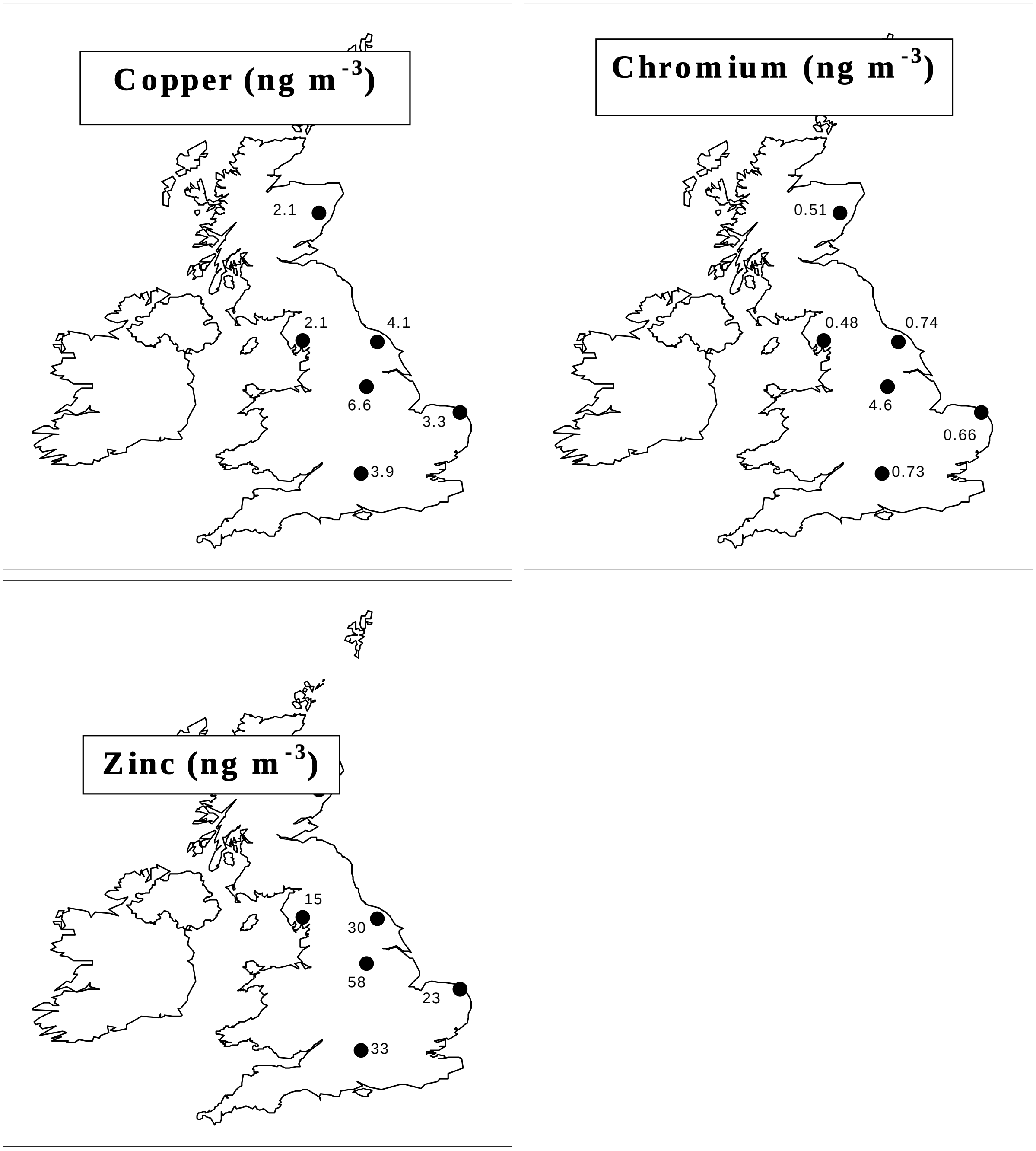


Figure 3a
Average annual mean air concentrations of Pb, Cd, As and Ni at rural locations in the UK (1995-1999)


Copper (ng m^{-3})

Chromium (ng m^{-3})

Zinc (ng m^{-3})

Figure 3b
Average annual mean air concentrations of Cu, Cr and Zn at rural locations in the UK (1995-1999)

3.1.2 Comparison of rural and urban air concentrations of heavy metals in the UK

Urban and rural air concentrations of heavy metals can be compared to help assess what proportion of urban airborne trace metals are due to regional scale transport and how much is locally derived.

Gee (1998) has reported the 1997 annual mean air concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn at five urban locations in the UK. These are Motherwell, Glasgow, Leeds, Brent and Central London. The corresponding data for 1998 (DETR, 2000) and 1999 (Carrington, 2000) are available. The data for the period 1997 to 1999 are summarised for comparison with corresponding data from the rural sites (see section 3.1.1) in Table 3. The average, maximum and minimum annual mean concentrations, averaged for all five urban sites, together with corresponding data from the six UK rural locations, are shown in Table 3.

Table 3
Comparison of Annual Mean Air Concentrations of Heavy Metals at Rural and Urban Locations in the UK (1997-1999)

Annual Mean Air Concentration (ng m^{-3}) (1997-1999)									
Rural sites(1)									
	Cd	Cr	Cu	Fe(a)	Mn(a)	Ni	Pb	V(a)	Zn
Mean	0.16	1.2	3.3	129	5.6	1.2	12	2.5	28
Max	0.29	4.3	8.0	236	13	3.1	36	4.0	65
Min	0.05	0.19	0.54	52	1.6	<0.1	2.2	1.3	9
Urban sites(2)									
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
Mean	0.92	3.5	16	659	11	8.8	43	3.9	43
Max	1.0	8.4	25	1180	17	9.8	89	7.4	75
Min	0.77	1.7	8	291	5.0	7.6	16	1.7	19

Notes
(1) Rural sites are at Chilton, Styrrup, Wraymires and data include East Ruston, High Muffles and Banchory except where indicated by (a).
(2) Urban sites are at Central London, Brent, Leeds, Motherwell and Glasgow (Gee, 1998).

The greatest differences between average rural and urban air concentrations during the period 1997-1999 were seen for Cd, Cu, Fe and Ni. Average urban concentrations of these metals were generally ~5 to ~7-fold greater. Average Cr and Pb air concentrations at the urban sites were ~3 to ~4-fold greater, while urban airborne levels of Mn, V and Zn were ~2-fold in excess of those measured at the rural locations over the last three years.

3.2 RAINWATER CONCENTRATIONS AND DEPOSITION OF ELEMENTS

The annual precipitation-weighted mean concentrations of the 25 trace elements, nitrate and sulphate measured at each of the three sites during 1999 are listed in Table 4. For comparison, the corresponding data for the previous three years are also presented in Table 4.

The elements can be broadly classified, according to rainwater concentrations (soluble fraction only) that were usually measured:

(i) Concentrations >1000 μg l^{-1}: **Na** (and **Ca** at Chilton) (also **nitrate** and **sulphate**).

(ii) Concentrations between 100 - 1000 μg l^{-1}: **Ca**, **K**, **Mg**.

(iii) Concentrations between 10 - 100 μg l^{-1}: **Zn**.

(iv) Concentrations between 1 - 10 μg l^{-1}: **Cu**, **Fe**, **Mn**, **Pb**, (and **Zn** at Wraymires).

(v) Concentrations of <1 μg l^{-1}: **As**, **Cd**, **Co, Cr**, **Mo**, **Se**, **V**, **W**.

Rainwater concentrations of **Al** fell into groups (iii) or (iv) depending on location. Concentrations of **Ni**, **Sb** and **Ti** fell into groups (iv) or (v) depending on location (Table 4). The rainwater concentrations of the remaining four elements that are routinely measured were frequently below analytical limits of detection (see Table 4).

The quarterly mean rainwater concentrations of certain elements for the period 1994-1999 have also been plotted. The heavy metals As, Cd, Co, Cu, Pb and Zn at Chilton, Styrrup and Wraymires are shown in Figure 4a. Ni and V were omitted since some quarterly concentrations were below prevailing analytical limits of detection, particularly during 1995 and 1996. Figure 4b shows the corresponding concentrations of Al, Ca, Fe, K, Mg, Mn and Na.

As observed in the air concentrations of many elements for a given site (section 4.1), the precipitation-weighted annual mean concentrations in rainwater measured in 1999 were similar to those measured in recent years, although the rainwater concentrations tended to be more variable (Table 4). This is also shown in the plots of quarterly mean air concentrations of a number of heavy metals and base cations for the period 1992-1999 at all three locations (Figures 4a and 4b)

The high annual rainfall at Wraymires, about three times greater than at both Chilton and Styrrup, should be noted when making comparisons between concentrations of elements in rainwater at the three sites. Hence at Wraymires a lower rain concentration would be found for a given air concentration of pollutant. However the total deposition would probably be greater given the higher washout likely to be experienced. Also, it should be remembered that any dry deposition to the collecting funnel will be washed into the rain bottle.

The annual deposition of some elements, together with nitrate and sulphate has been estimated for 1999. The estimates were based on rainwater concentrations and measurements of rainfall. These data are summarised in Table 5 which also includes the annual deposition estimates for

Table 4
Annual Precipitation-Weighted Mean Concentrations of Elements, Nitrate and Sulphate in Rainwater at Chilton, Styrrup and Wraymires (1996-1999)

Element	Annual Mean Concentration in Rainwater ($\mu g\ l^{-1}$)											
	Chilton				Styrrup				Wraymires			
	1996	1997	1998	1999	1996	1997	1998	1999	1996	1997	1998	1999
Ag	< 0.005	0.0009	0.0055	< 0.001	< 0.006	0.0003	0.012	< 0.002	< 0.006	< 0.0009	0.011	< 0.01
Al	< 15	5.7	< 6	< 4	46.4	28.7	< 23	14	< 48	8.2	< 4	< 4
As	0.41	0.11	0.23	0.11	0.78	0.22	0.57	0.27	0.18	0.058	0.23	0.07
Au	< 0.01	< 0.0007	< 0.002	< 0.06	< 0.01	< 0.0005	< 0.002	< 0.06	< 0.01	< 0.0006	< 0.002	< 0.06
Ca	2053	2414	2042	538	1150	713	509	724	222	381	231	223
Cd	0.18	0.064	0.12	0.08	0.61	0.32	0.21	0.09	0.25	0.042	0.21	0.04
Co	0.10	0.031	0.077	0.04	0.20	0.052	0.18	0.07	0.040	0.019	0.064	0.03
Cr	< 0.7	0.040	0.080	0.08	< 0.7	0.084	0.43	0.15	< 0.8	0.014	0.24	0.08
Cu	10.8	2.4	6.1	0.9	14.1	2.1	10.7	2.3	11.2	2.6	11.6	3.1
Fe	2.8	< 3	3	3	8.4	6.9	8.0	4	3.0	2.3	6.4	2
Hg	< 0.1	< 0.005	< 0.006	< 0.01	< 0.1	< 0.008	< 0.006	< 0.01	< 0.1	0.009	< 0.006	< 0.01
In	< 0.003	0.00008	0.0022	< 0.04	< 0.003	0.00025	0.0062	< 0.04	< 0.004	0.0001	0.011	< 0.04
K	281	229	103	81	250	143	128	143	227	117	86	130
Mg	428	418	185	163	607	291	225	237	260	335	237	385
Mn	6.0	2.3	3.6	2.7	12.5	3.3	8.3	8.0	1.3	0.75	1.7	1.3
Mo	0.10	0.030	0.061	0.05	0.52	0.10	0.37	0.16	< 0.05	0.012	0.045	0.02
Na	3304	3193	1480	1166	2759	1222	1205	1039	2141	1690	2169	3061
Ni	< 2	0.31	0.46	0.39	< 2	0.42	1.4	1.3	< 5	< 0.07	0.39	0.27
Pb	1.1	0.26	2.4	0.57	4.5	1.5	7.7	1.4	2.4	0.67	1.6	0.57
Sb	0.29	0.10	0.25	0.13	27.9	14.0	1.2	0.65	0.52	0.53	0.45	0.15
Se	0.49	0.11	0.12	0.07	0.28	0.12	0.32	0.1	< 0.1	0.07	0.27	0.08
Ti	< 1	3.8	0.08	0.08	< 1	1.5	0.26	0.1	< 1	0.75	0.14	0.07
V	< 2	0.31	0.58	0.34	< 2	0.41	1.1	0.41	< 2	0.24	0.51	0.30
W	0.052	0.020	0.025	< 0.07	0.20	0.043	0.066	< 0.07	< 0.007	< 0.001	0.021	< 0.07
Zn	46.7	16.7	6.5	8.3	53.8	32.8	21.0	35.0	18.4	6.0	8.5	4.9
NO_3^-	5898	4043	3011	1945	5008	2279	2656	2212	2243	1768	1590	1125
SO_4^{2-}	5665	3868	2194	1733	5877	3664	3444	3029	2568	2293	1960	1978
Annual Rainfall (mm)	468	645	783	778	474	705	635	659	1537	1731	2453	1998

Note Only the soluble fraction of the rainwater samples was analysed.

Table 5
Summary of Estimated Annual Deposition of Elements, Nitrate and Sulphate at Chilton, Styrrup and Wraymires (1996-1999)

Element	Estimated Annual Deposition (μg m^{-2})											
	Chilton				**Styrrup**				**Wraymires**			
	1996	1997	1998	1999	1996	1997	1998	1999	1996	1997	1998	1999
Al	< 7.09E+03	3.68E+03	< 5.07E+03	< 3.11E+03	2.20E+04	2.02E+04	1.45E+04	9.23E+03	< 7.34E+04	1.42E+04	< 1.02E+04	< 7.99E+03
As	1.90E+02	7.01E+01	1.82E+02	8.60E+01	3.69E+02	1.54E+02	3.63E+02	1.76E+02	2.71E+02	1.01E+02	5.75E+02	1.33E+02
Ca	9.61E+05	1.56E+06	1.60E+06	4.19E+05	5.45E+05	5.03E+05	3.23E+05	4.77E+05	3.42E+05	6.59E+05	5.66E+05	4.45E+05
Cd	8.47E+01	4.12E+01	9.65E+01	6.29E+01	2.89E+02	2.30E+02	1.34E+02	5.75E+01	3.87E+02	7.22E+01	5.14E+02	8.60E+01
Co	4.93E+01	2.04E+01	6.01E+01	3.07E+01	9.48E+01	3.71E+01	1.17E+02	4.58E+01	6.10E+01	3.32E+01	1.58E+02	5.38E+01
Cu	5.06E+03	1.52E+03	4.78E+03	6.63E+02	6.68E+03	1.47E+03	6.79E+03	1.51E+03	1.73E+04	4.42E+03	2.84E+04	6.11E+03
Fe	1.29E+03	< 1.63E+03	2.05E+03	2.50E+03	3.97E+03	4.87E+03	5.06E+03	2.41E+03	4.55E+03	3.99E+03	1.56E+04	4.15E+03
K	1.32E+05	1.48E+05	8.09E+04	6.30E+04	1.19E+05	1.01E+05	8.15E+04	9.45E+04	3.50E+05	2.02E+05	2.11E+05	2.60E+05
Mg	2.00E+05	2.69E+05	1.45E+05	1.27E+05	2.88E+05	2.05E+05	1.43E+05	1.56E+05	4.00E+05	5.80E+05	5.81E+05	7.70E+05
Mn	2.83E+03	1.50E+03	2.84E+03	2.11E+03	5.92E+03	2.34E+03	5.25E+03	5.30E+03	1.98E+03	1.29E+03	4.05E+03	2.54E+03
Na	1.55E+06	2.06E+06	1.16E+06	9.07E+05	1.31E+06	8.62E+05	7.65E+05	6.85E+05	3.29E+06	2.93E+06	5.32E+06	6.12E+06
Ni	< 1.03E+03	1.98E+02	3.61E+02	3.07E+02	< 1.15E+03	2.97E+02	8.68E+02	8.68E+02	< 7.16E+03	< 1.22E+02	9.65E+02	5.38E+02
Pb	4.97E+02	1.68E+02	1.92E+03	4.43E+02	2.14E+03	1.03E+03	4.88E+03	9.33E+02	3.69E+03	1.14E+03	5.76E+03	1.14E+03
Sb	1.37E+02	6.45E+01	1.96E+02	1.01E+02	1.32E+04	9.88E+03	7.86E+02	4.28E+02	8.03E+02	9.20E+02	1.12E+03	2.93E+02
V	1.03E+03	2.01E+02	4.57E+02	2.68E+02	< 1.05E+03	2.89E+02	6.67E+02	2.68E+02	< 3.37E+03	4.12E+02	1.25E+03	5.97E+02
Zn	2.18E+04	1.08E+04	5.10E+03	6.44E+03	2.55E+04	2.31E+04	1.35E+04	2.33E+04	2.82E+04	1.04E+04	2.09E+04	9.79E+03
NO_3^-	2.76E+06	2.61E+06	2.36E+06	1.51E+06	2.37E+06	1.61E+06	1.69E+06	1.46E+06	3.45E+06	3.06E+06	3.90E+06	2.25E+06
SO_4^{2-}	2.65E+06	2.50E+06	1.72E+06	1.35E+06	2.79E+06	2.58E+06	2.19E+06	2.00E+06	3.95E+06	3.97E+06	4.81E+06	3.95E+06
Annual Rainfall (mm)	468	645	783	778	474	705	635	659	1537	1731	2453	1998

Notes

(i) Only the soluble fraction of the rainwater sample was analysed.
(ii) The estimated annual deposition of some elements is not derived where the majority of annual mean rainwater concentrations are below the analytical limits of detection.

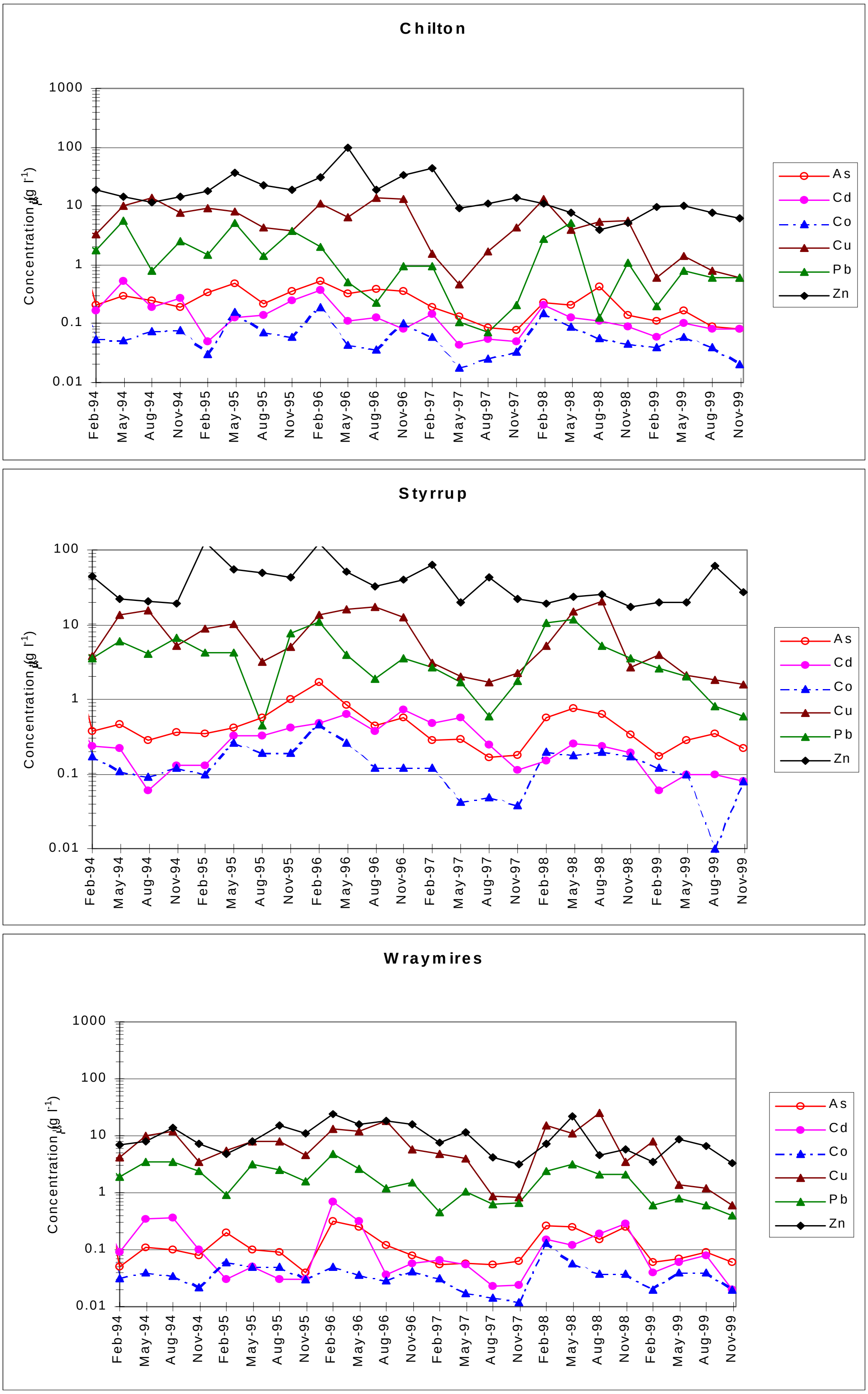


Figure 4a
Quarterly mean concentrations of heavy metals in rainwater At Chilton, Styrrup and Wraymires (1994-1999)

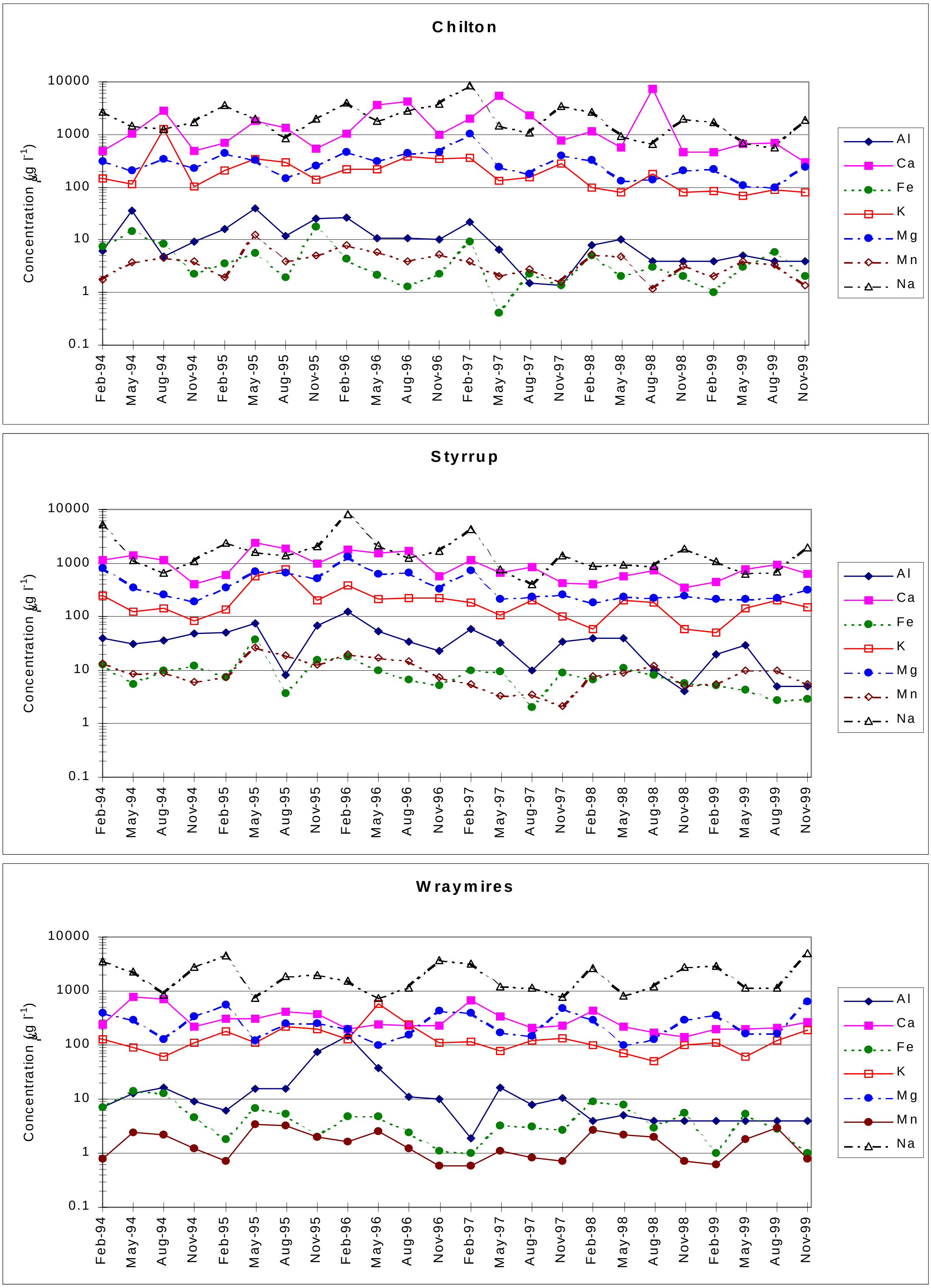


Figure 4b
Quarterly mean concentrations of Al, Ca, Fe, K, Mg, Mn and Na in rainwater At Chilton, Styrrup and Wraymires (1994-1999)

each of the years 1996, 1997 and 1998 for comparison. Of all the elements that are routinely measured, only those elements whose annual mean concentrations were regularly above analytical detection limits have been included in this summary.

3.2.1 Concentrations of heavy metals in rainwater at rural locations in the UK

Several of the heavy metals which are monitored in rainwater in the Rural Trace Elements network are also routinely measured in rainwater at the three east coast locations (East Ruston, High Muffles and Banchory). The average, maximum and minimum precipitation-weighted annual mean concentrations in rainwater, measured at these sites for the period 1995-1999, are compared with those from Chilton, Styrrup and Wraymires in Table 6. These concentrations (Playford and Baker, 2000) are for bulk deposition (and include the insoluble rainwater fraction).

Table 6
Annual Precipitation-Weighted Mean Concentrations of Heavy Metals in Rainwater at Rural Locations in the UK (1995-1999)

Location		Annual Mean Rainfall (mm)	Annual Mean Rainwater Concentration (µg l^{-1})						
			As	Cd	Cu	Cr (b)	Ni	Pb	Zn
Chilton	Mean	696	0.24	0.15	5.8	0.07	0.85	1.4	20
	Max	805	0.41	0.18	10.8	0.08	2.0	2.5	47
	Min	468	0.11	0.06	0.90	0.04	0.31	0.26	6.5
Styrrup	Mean	593	0.48	0.30	7.3	0.22	1.8	4.0	44
	Max	705	0.78	0.61	14.1	0.43	3.8	7.7	79
	Min	474	0.22	0.09	2.1	0.08	0.42	1.4	21
Wraymires	Mean	1894	0.13	0.11	6.9	0.11	(c)	1.3	9.2
	Max	2453	0.23	0.25	11.6	0.24		2.4	18
	Min	1537	0.06	<0.03	2.6	0.014		0.57	4.9
East Ruston [(a)]	Mean	713	0.21	0.07	2.1	0.41	0.77	3.4	14
	Max	914	0.29	0.10	3.4	0.52	1.7	5.4	31
	Min	598	0.12	0.04	1.3	0.28	0.34	1.9	6.1
High Muffles [(a)]	Mean	839	0.27	0.08	1.5	0.36	0.45	3.4	15
	Max	997	0.33	0.13	2.1	0.57	1.0	4.4	28
	Min	617	0.20	0.05	1.0	0.16	0.18	2.5	7.4
Banchory [(a)]	Mean	937	0.17	0.11	1.0	0.44	0.33	1.6	7.7
	Max	1040	0.31	0.25	1.2	0.63	0.66	2.8	11
	Min	880	0.09	0.04	0.85	0.23	0.16	0.89	4.6

Notes

(a) Measurements exclude 1996.

(b) In 1995 and 1996, the annual mean concentrations of Cr at Chilton, Styrrup and Wraymires were below analytical limits of detection (<0.8 µg l^{-1}). These have been excluded in the above summary.

(c) The majority of the annual mean concentrations of Ni at Wraymires were below analytical limits of detection (typically <0.1 µg l^{-1}). Therefore, these data have been excluded from the above summary.

The average precipitation-weighted annual mean rainwater concentrations of these seven metals for the period 1995-1999 at these rural locations are also shown in Figures 5a and 5b.

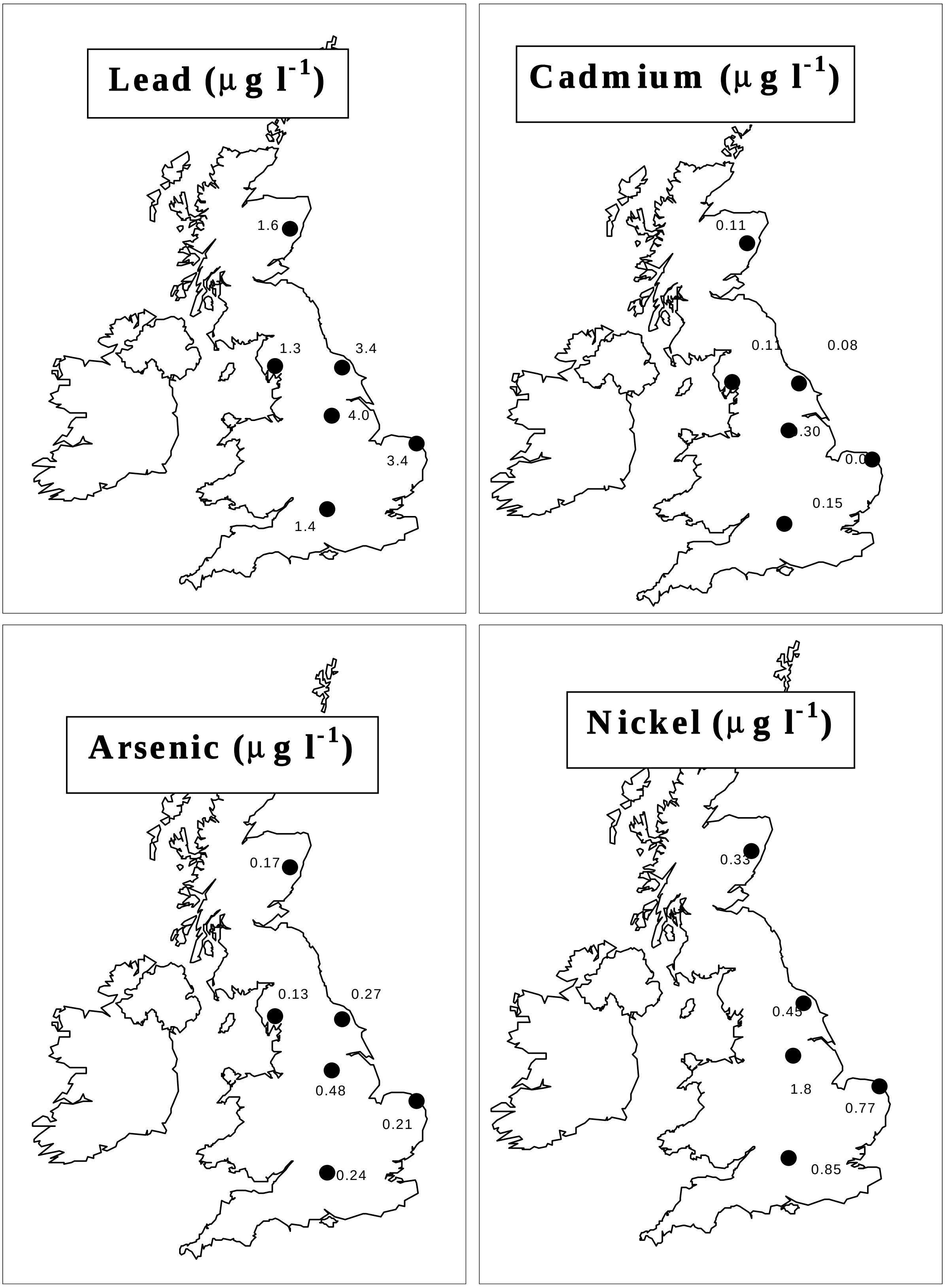


Figure 5a
Average annual precipitation-weighted concentrations of Pb, Cd, As and Ni in rainwater at rural locations in the UK (1995-1999)

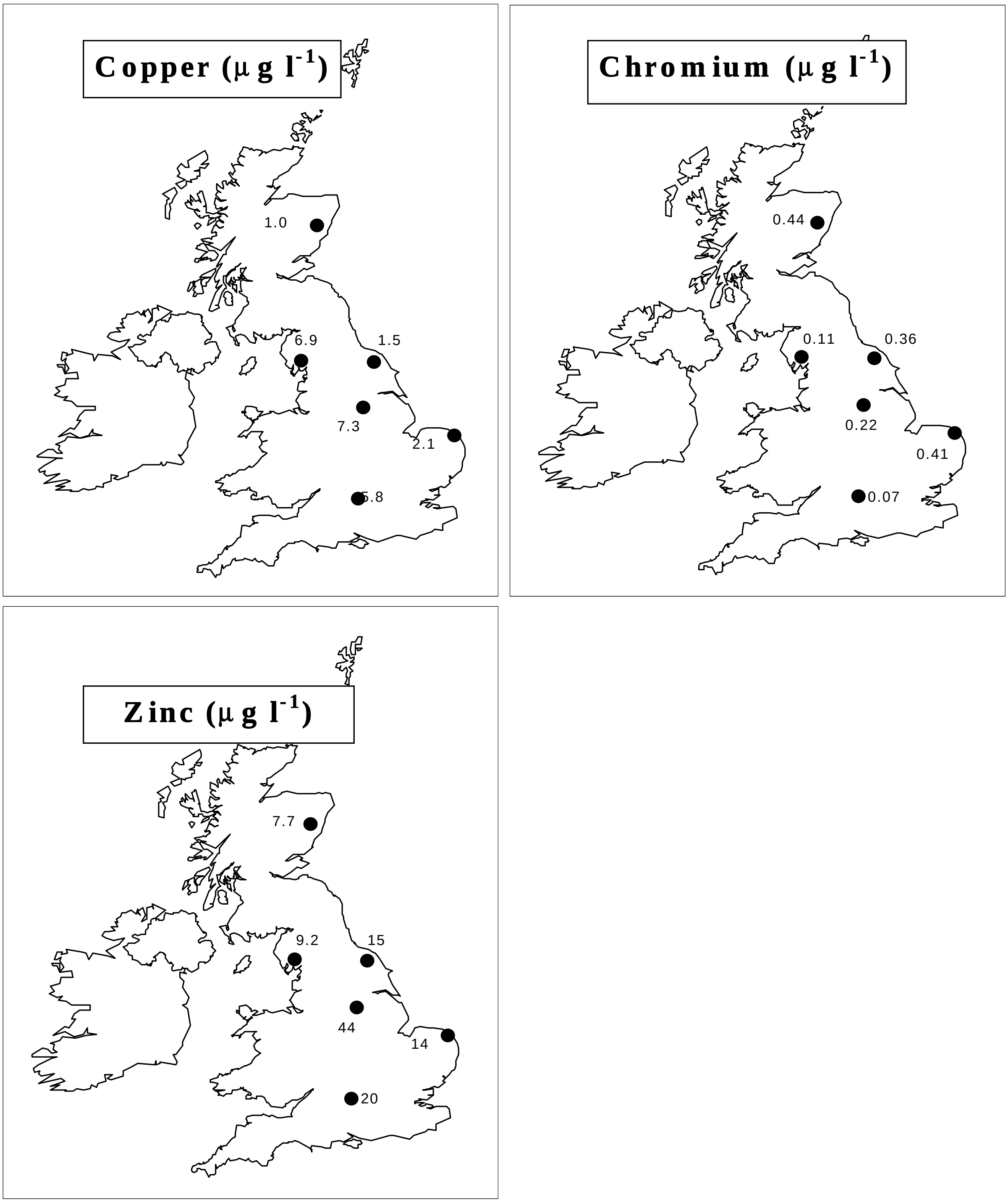


Figure 5b
Average annual precipitation-weighted concentrations of Cu, Cr and Zn in rainwater at rural locations in the UK (1995-1999)

Over the last five years, the average annual mean rainwater concentrations of As, Cd, and Pb at Chilton and Wraymires were similar to those at the three east coast locations. Average Ni concentrations at Chilton were also of a similar order. Average concentrations of these four metals were slighted elevated at Styrrup in comparison (Table 6, Figures 5a). At Wraymires, annual mean concentrations of Ni were mainly below analytical detection limits (i.e <0.1 μg l^{-1}).

For Cr, due to the presence of some data (from Chilton, Styrrup and Wraymires for 1995 and 1996) that were below the prevailing analytical detection limits (typically <0.8 μg l^{-1}), a comparison with the other three locations was more limited (Table 6). Average annual mean rainwater concentrations were lower at the inland locations (Figure 5b). However, the highest concentrations of Cr measured at Chilton, Styrrup and Wraymires were of the same order as those recorded at Banchory, East Ruston and High Muffles; the lowest were an order of magnitude lower at the inland sites (Table 6).

The concentrations of Cu in rainwater measured at Chilton, Styrrup and Wraymires during the period 1995-1999 have been consistently similar at all three of these locations (Table 6). The average concentrations at these sites were typically 3 to 4-fold higher than those measured at East Ruston and Banchory and up to 7 times greater than those at Banchory (Figure 5b).
Elevated concentrations (2 to 3 times greater) were measured at Chilton, Styrrup and Wraymires relative to the three coastal sites during the period 1992-1996. Also, the annual mean concentrations for the period 1987-1991 at Chilton, Styrrup and Wraymires were consistent with those for 1992-1996 (Baker, 1997). Therefore, the increased Cu concentrations in rainwater at Chilton, Styrrup and Wraymires relative to the other three rural sites is not easily explained.

4 Long-term Trends

4.1 LONG-TERM CHANGES IN CONCENTRATIONS OF ELEMENTS IN AIR

The changes in the atmospheric concentrations of selected trace elements at rural locations, for the period 1972-1998, have been reported previously (Baker, 1999). The long-term trends in changes in air quality, with respect to the anthropogenically-derived metals As, Cr, Ni, V, Zn and Pb together with Br, were investigated. Cl and Na (of mainly marine origin) and Ce and Sc (mainly soil-derived) were also included for comparison. Data for 1999 have now been included.

The annual mean concentrations of As, Cr, Ni, Se, V and Zn in air at Chilton for the period 1972-1999 are shown in Figure 6a, with annual mean air concentrations for Pb, Br, Cl, Na, Ce and Sc at Chilton shown in Figure 6b. Corresponding data for Styrrup and Wraymires are plotted in Figures 6c to 6f, respectively. In each of these time-series plots (Figures 6a to 6f) a regression against time is also shown to indicate the direction of any trend. The data were found to fit better to an exponential rather than linear trend line. Also, a linear regression trend line implies that air concentrations of an element will reach zero at some future date, which is very unlikely to be the case.

Regression analysis is often used to determine whether measurements of concentration or deposition have a significant upward or downward trend with time. There are limitations to this technique, as discussed by Lee et al. (1994), due to autocorrelation. Essentially, although the rate of decline can be assessed by regression analysis, the significance attributed to the decline may be overestimated. However, this is unlikely to be a severe limitation with annual data, for which the autocorrelation in error terms is less important than for shorter period data. Nevertheless, the statistical significance of the trends in air concentrations of elements has not been assessed in the current work.

The downward trends in annual mean air concentrations of the mainly anthropogenically-derived metals As, Cr, Ni (at Chilton and Styrrup only), V and Zn are quite apparent (although less so for Se) at all three locations. Downward trends are also evident for Ce and Sc, which are thought to be predominantly associated with material of direct terrestrial origin (Cawse, 1987). For Na and Cl (mainly marine-derived) a decline in average air concentrations was less apparent at all three locations, except for Cl at Styrrup.

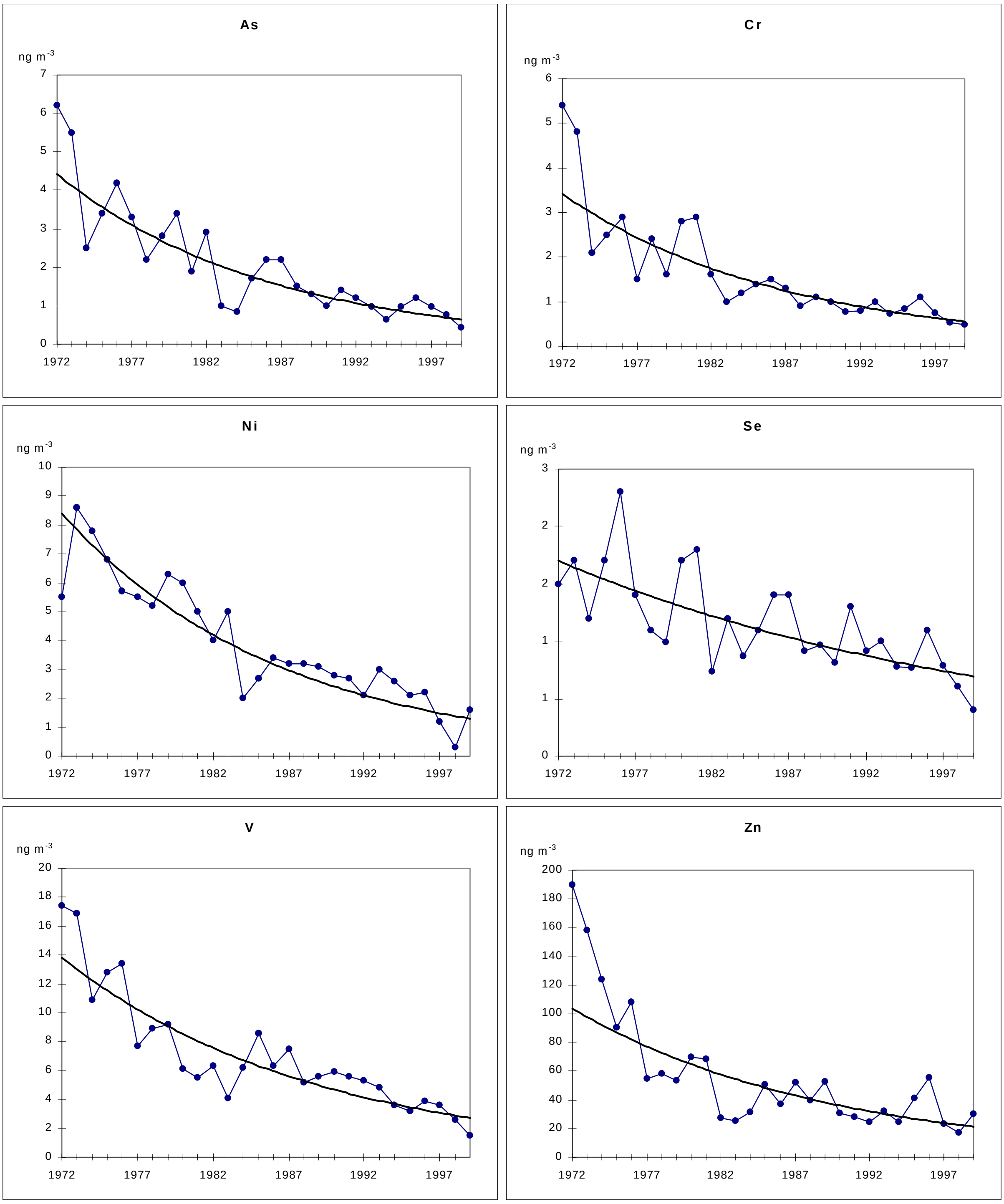


Figure 6a
Changes in annual mean concentrations of As, Cr, Ni, Se, V and Zn in air at Chilton (1972-1999)

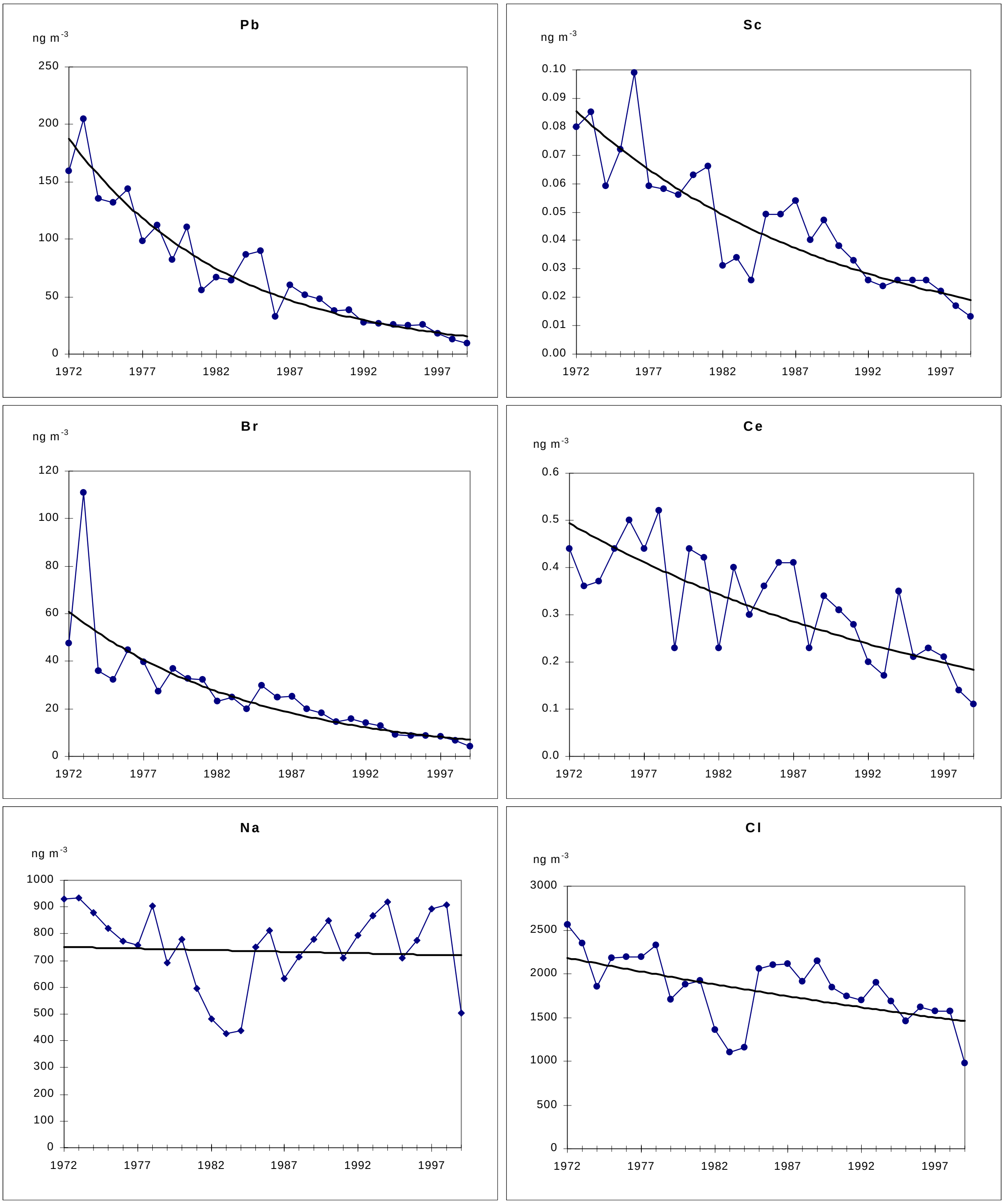


Figure 6b
Changes in annual mean concentrations of Pb, Br, Sc, Ce, Na and Cl in air at Chilton (1972-1999)

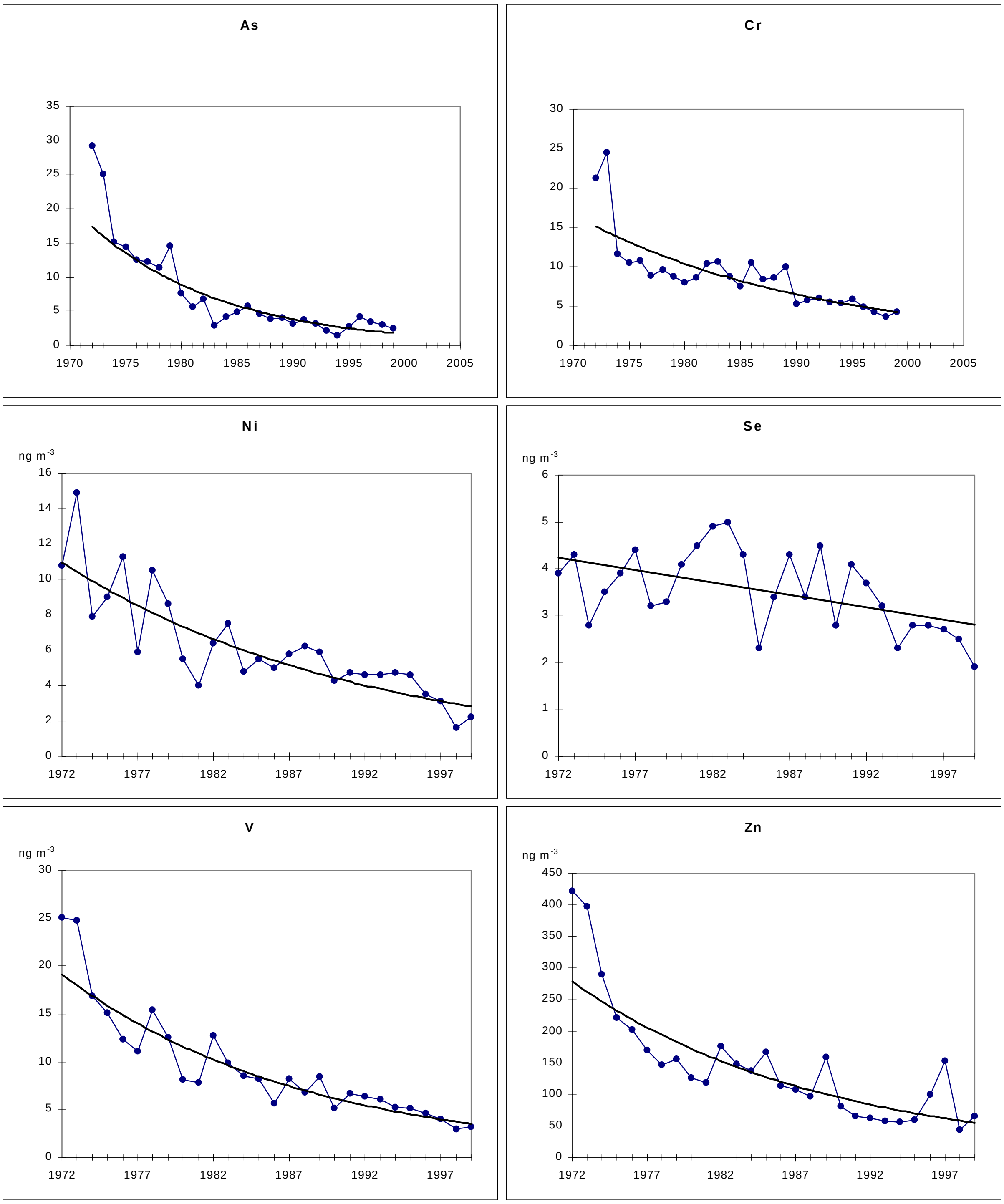


Figure 6c
Changes in annual mean concentrations of As, Cr, Ni, Se, V and Zn in air at Styrrup (1972-1999)

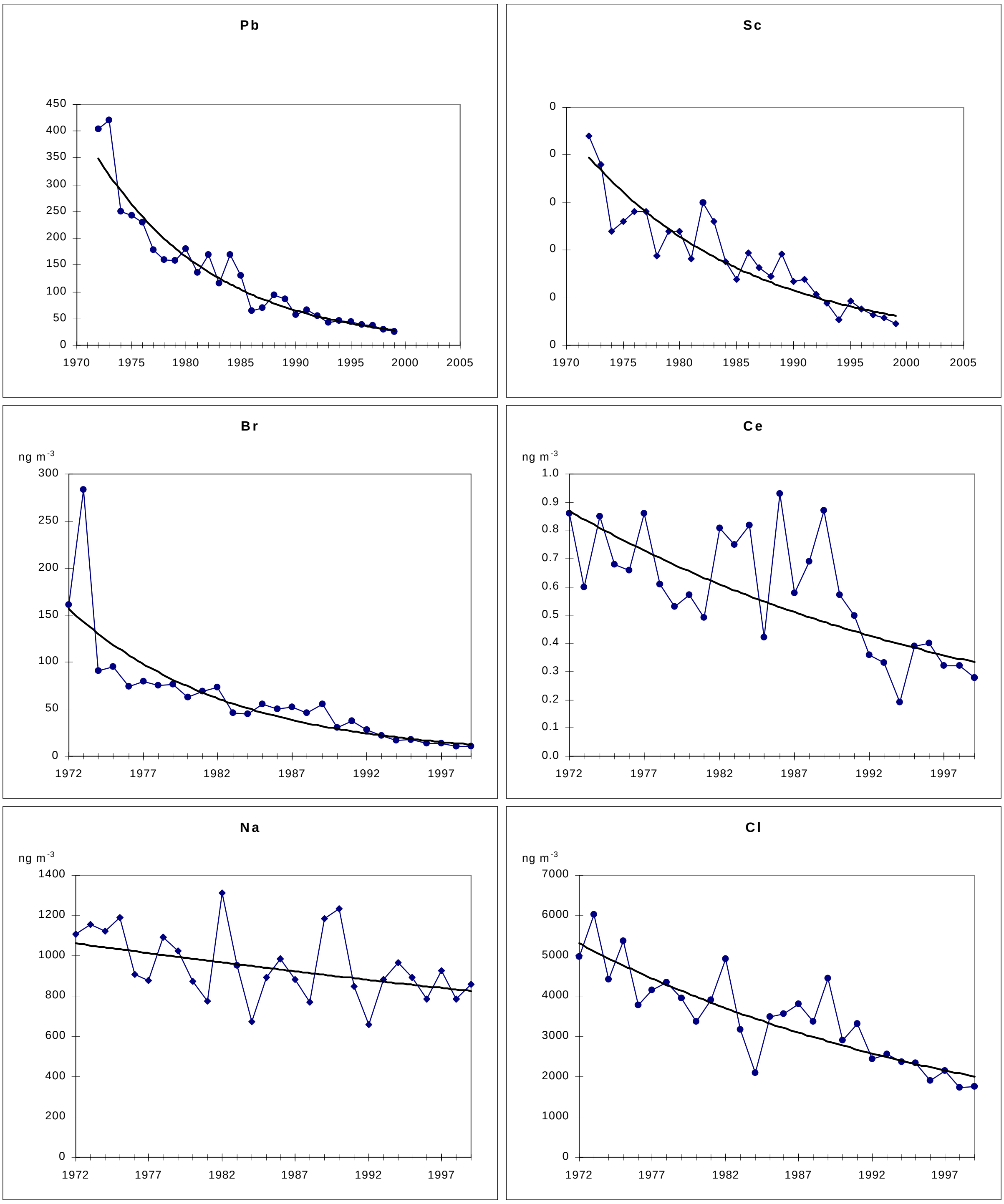


Figure 6d
Changes in annual mean concentrations of Pb, Br, Sc, Ce, Na and Cl in air at Styrrup (1972-1999)

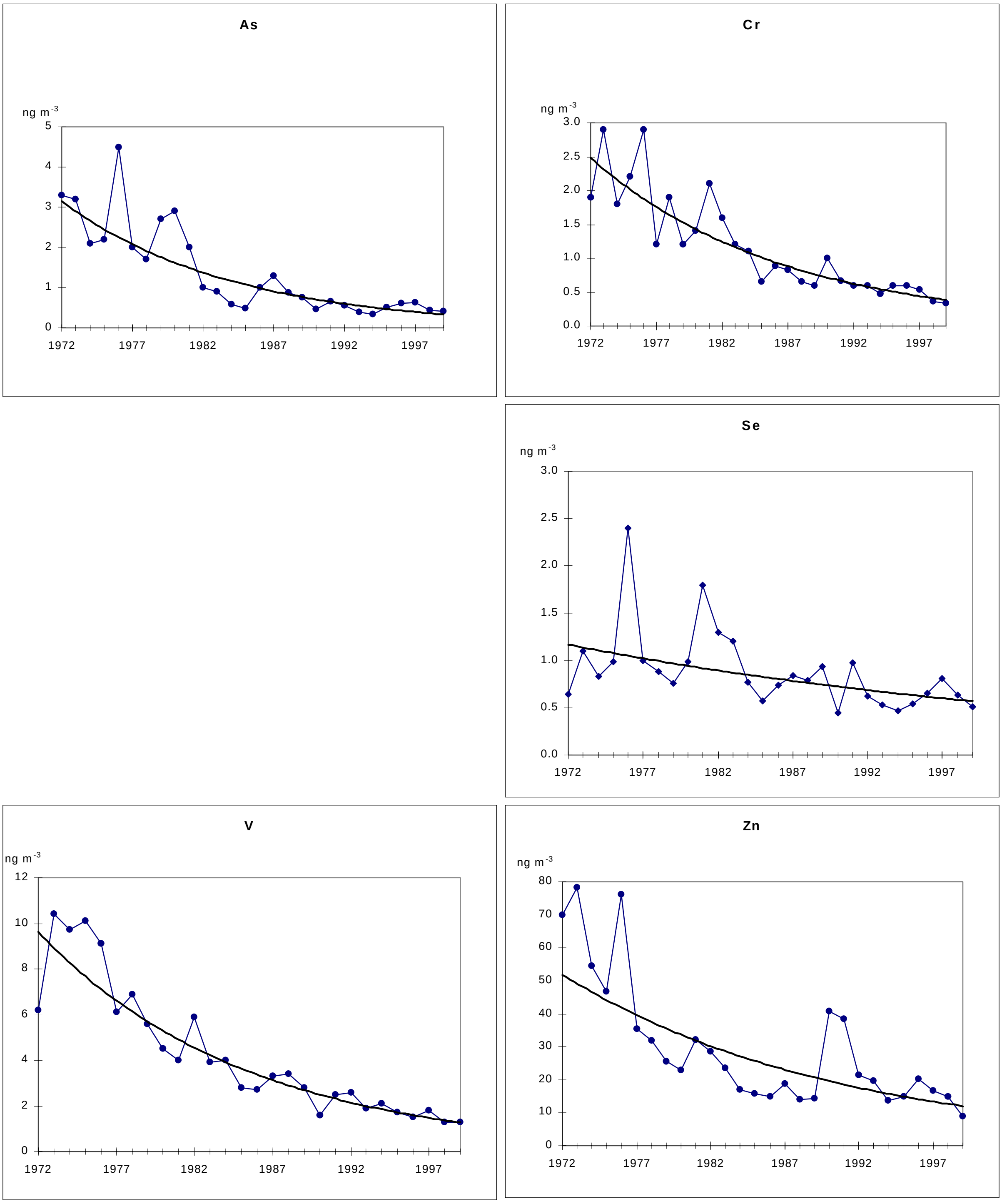


Figure 6e
Changes in annual mean concentrations of As, Cr, Se, V and Zn in air at Wraymires (1972-1999)

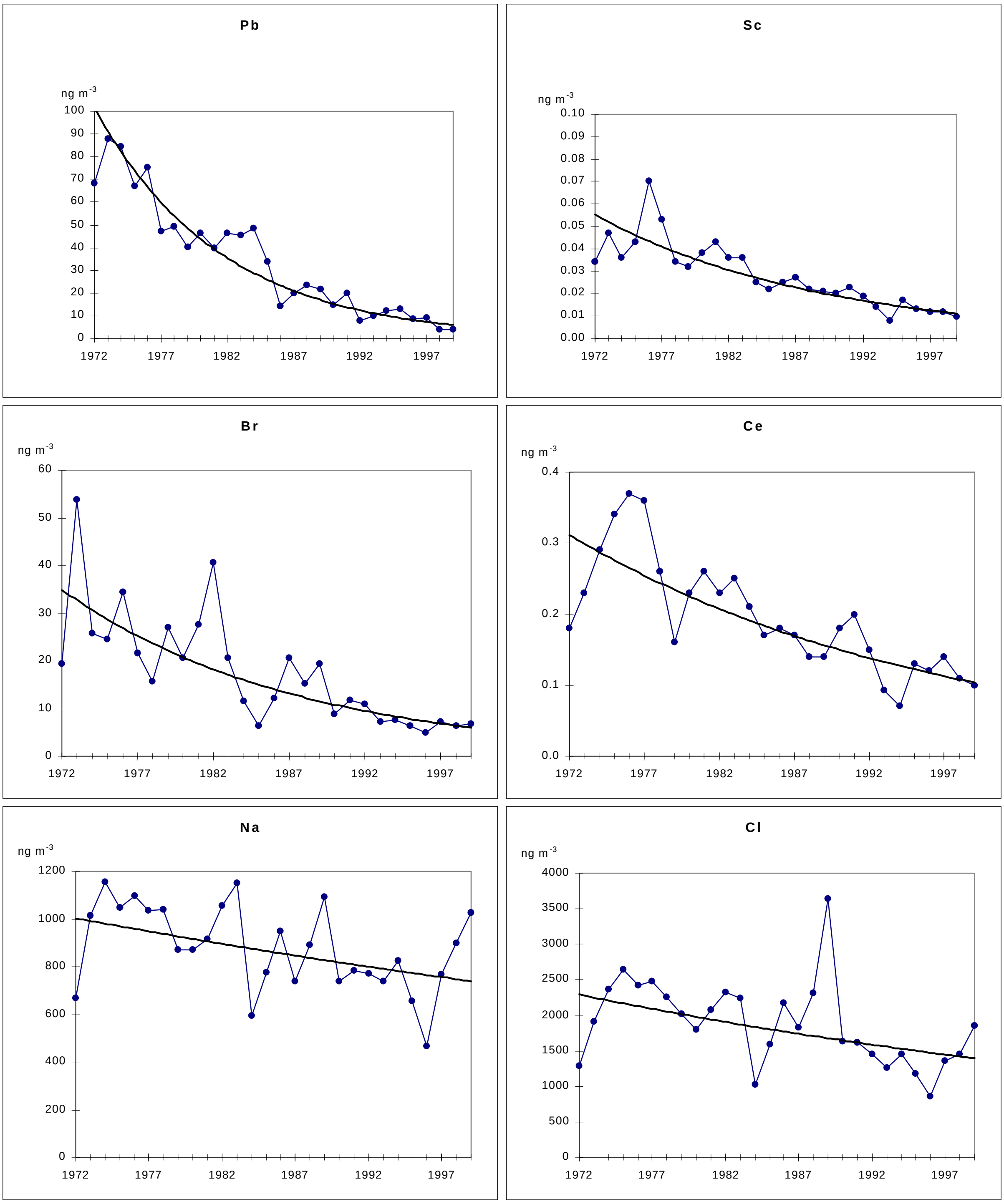


Figure 6f
Changes in annual mean concentrations of Pb, Br, Sc, Ce, Na and Cl in air at Wraymires (1972-1999)

The long-term changes in average atmospheric concentrations of elements at Chilton, Styrrup and Wraymires have been quantified by comparison of their annual mean air concentrations for the periods 1972-1979, 1980-1989 and 1990-1999. The percentage reduction in the annual mean, relative to the period mean for 1972-1979 has been calculated for each element at each sampling location. These reductions, for the 12 elements shown in Figures 6a to 6f and for 10 other elements are shown in Figure 7. Those elements whose quarterly concentrations (and therefore annual mean concentrations) were frequently below analytical detection limits were excluded from this summary. In Figure 7, Ni has been excluded at Wraymires since many annual mean air concentrations of Ni (particularly in more recent years) were below analytical LODs at this site. Also, for the elements Ca, Cu K and Mg, the percentage reductions in annual mean air concentrations are relative to the period mean for 1975-1979; also data for the period 1980-1989 are excluded as annual mean concentrations were frequently below LODs during the 1980s.

Where both the period means for 1980-1989 and 1990-1999 could be compared with 1972-1979, the majority of the elements showed an increase in the percentage reduction in annual mean air concentration with time (Figure 7). The greatest reductions (70% or greater) were recorded at two or more sites for As, Br, Cr, Cu, K, Mn, Pb, V and Zn when the 1990s were compared to the 1970s. Corresponding reductions of between 60-70% for Al, Ca, Co, Cs, Fe, Mg, Ni, Sc and V were seen at least at two of the sites. The smallest reductions (<60%) tended to occur for Ce, Cl, Na, Sb and Se.

The considerable reductions in air concentrations of Sc (and to a lesser extent Ce), together with Al, Fe and Mn, that were recorded between the 1970s and the 1990s, may seem unexpected at first since these elements are thought to be of mainly crustal origin. However, they may also be emitted as fly ash from the combustion of coal and as dust from mining and other mineral-related activities (Lee et al., 1994). Consequently, the observed reductions can be explained by reductions in fly-ash emissions caused by reductions in coal and fuel oil combustion by industry and changes in domestic energy sources for space heating, e.g. from coal to gas.

The percentage reductions in average air concentrations of Na and Cl were among lowest observed (Figure 7). Also, the trends in their air concentrations (particularly for Na) were not as apparent as for the industrially-derived heavy metals at Chilton, Styrrup and Wraymires (Figures 6a to 6f). This indicates that little change in concentrations of marine-derived aerosols has occurred at any of the rural locations since the 1970s.

The decline in air concentrations of Ca, K and Mg between the 1970s and the end of 1993 at Chilton, Styrrup and Wraymires was discussed by Lee et al. (1995). The major source of these elements has commonly and long been assumed to be soil dust. However, sources of Ca have been identified to include fly-ash from coal and fuel oil combustion, with other industrial emissions from cement manufacture and quarrying of limestone (Lee et al., 1995). The large long-term reductions in air concentrations of Ca, K and Mg are similar to those for Sc (Figure 7), another element thought to be of predominantly crustal origin, but present in fly-ash. Therefore, Lee et al. (1995) concluded that the decline in air concentrations of Ca, K and Mg at these three rural locations could be, at least in part, explained by reductions in fly-ash emissions.

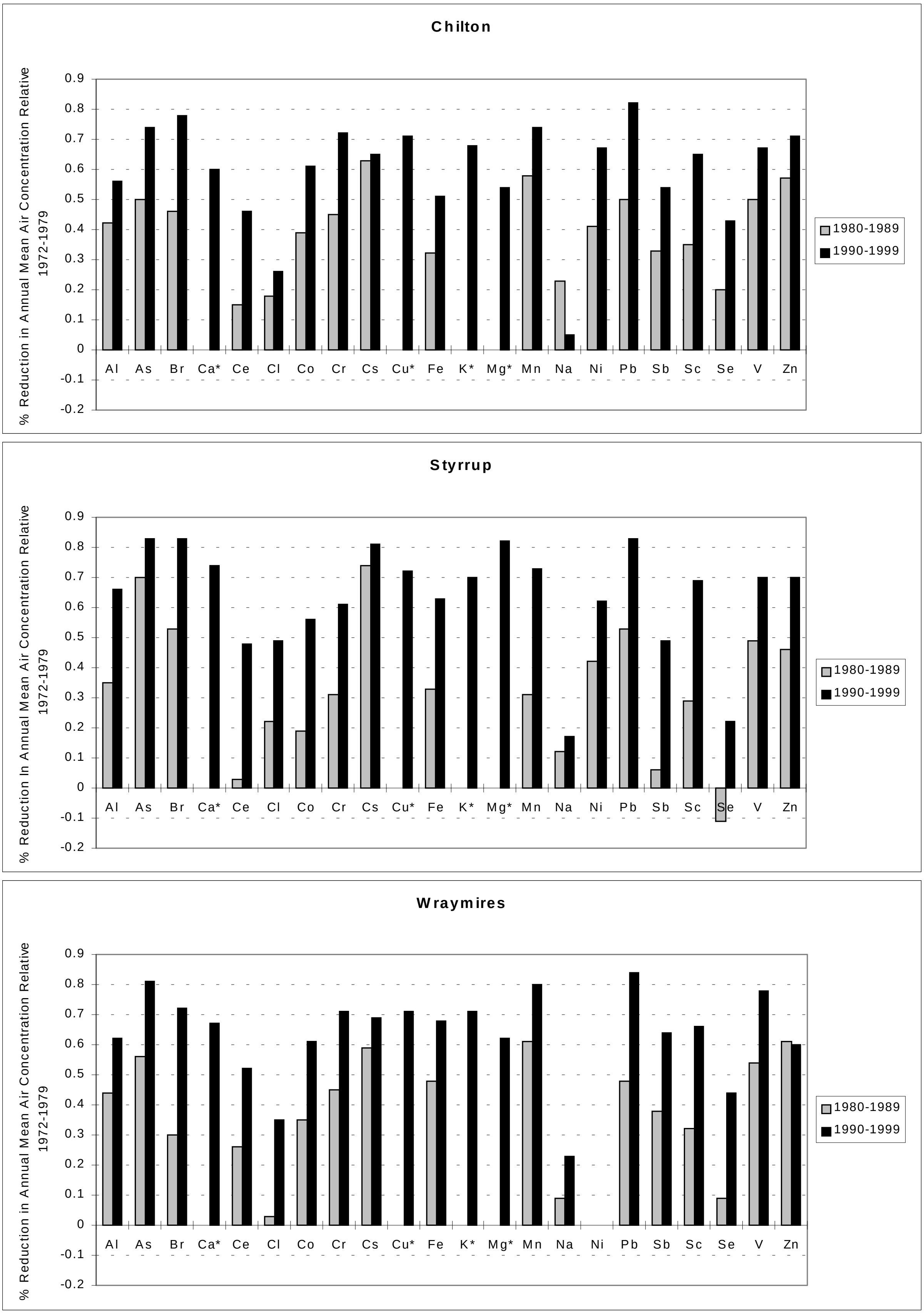


Figure 7
Reductions in annual mean air concentrations of elements relative to the period 1972-1979 at Chilton, Styrrup and Wraymires

4.1.1 Long-term changes in rural air concentrations of heavy metals and in their estimated emissions to the atmosphere

The National Atmospheric Emissions Inventory (NAEI) has compiled emissions inventories for several heavy metals in the UK for the years between 1970 and 1999 (Goodwin et al 2000). The estimations of emissions are subject to uncertainties and these are discussed in the above report. Nevertheless, these data are useful in quantifying industrial outputs of heavy metals to the atmosphere.

The long-term changes in the annual mean air concentrations of As, Cr, Ni, Pb, V and Zn at the three rural locations, have been compared to corresponding changes in the estimated annual atmospheric emissions of these metals by industry (Goodwin et al., 1999) during the period 1972-1997 (Baker, 1999). Cd and Cu were excluded since many historical measurements of Cd and Cu (particularly during the 1980s) were frequently below the limits of detection achievable by the analytical technique used at the time (section 2.3.1).

The NAEI has revised the data for heavy metal emissions since the above comparison was made and also data for estimated emissions for 1998 are now available (Goodwin et al., 2000). The main changes were the use of EA Pollution Inventory data for waste incineration, coke ovens and cement. Also some new sources, for example, copper refining and other non-ferrous metal processes were added to the inventories.

The revised emissions data for As, Cr, Ni, Pb, Se, V and Zn (Goodwin et al., 2000) have now been compared with the changes in their annual average air concentrations at Chilton, Styrrup and Wraymires for the period 1972 to 1998 (Figures 8, 9a, 9b and 9c). Data for As, Cr, Se and Zn from Styrrup (Figure 9b) have been plotted separately to the data from Chilton and Wraymires (Figure 9a) for clarity.

The percentage reduction in the annual mean air concentrations of these metals, for the period 1994-1998 relative to 1972-1979 together with the corresponding reductions in their estimated annual emissions are presented in Table 7.

Table 7
Temporal Changes in Annual Mean Air Concentrations and Estimated UK Atmospheric Emissions of Heavy Metals at Rural Locations, (1972-1998)

Annual Mean Air Concentration (ng m^{-3})	**As**	**Cr**	**Ni**	**Pb**	**Se**	**V**	**Zn**
				CHILTON			
1972-1979	3.8	2.9	6.4	134	1.5	12.2	105
1994-1998	0.91	0.79	1.7	21.4	0.81	3.4	32.4
% reduction	**76%**	**73%**	**73%**	**84%**	**46%**	**72%**	**69%**
				STYRRUP			
1972-1979	16.8	13.2	9.9	256	3.7	16.6	250
1994-1998	2.9	4.8	3.5	38.8	2.6	4.4	82.4
% reduction	**83%**	**64%**	**65%**	**85%**	**30%**	**73%**	**67%**
				WRAYMIRES			
1972-1979	2.7	2.0	4.5	65.0	1.1	8.0	52.2
1994-1998	0.51	0.51	(a)	9.3	0.62	1.7	16.0
% reduction	**81%**	**74%**	**-**	**86%**	**44%**	**79%**	**69%**
Annual Mean Estimated Total UK Atmospheric Emissions (t) (b)	**As**	**Cr**	**Ni**	**Pb**	**Se**	**V**	**Zn**
1972-1979	162	172	1075	8589	153	3504	1687
1994-1998	64	87	327	1609	94	999	1183
% reduction	**60%**	**49%**	**73%**	**82%**	**39%**	**71%**	**30%**

Notes
(a) Not derived as many annual mean concentrations were below analytical limits of detection.
(b) Derived from data from Goodwin et al. (2000).

In addition, the annual mean air concentrations (ng m^{-3}) of these metals have been plotted against annual estimates of total emissions (t) at each location (Figures 8 to 10c). The significances of the respective correlation coefficients are listed in Table 8.

Table 8
Correlations between Annual Mean Air Concentrations at Rural Locations and Estimated Annual Total Atmospheric Emissions of Heavy Metals in the UK
(1972-1998)

		Chilton	Styrrup	Wraymires
As	r	0.857	0.865	0.799
	p	<0.001	<0.001	<0.001
Cr	r	0.656	0.665	0.739
	p	<0.001	<0.001	<0.001
Ni	r	0.909	0.853	(a)
	p	<0.001	<0.001	-
Pb	r	0.865	0.825	0.910
	p	<0.001	<0.001	<0.001
Se	r	0.616	0.477	0.372
	p	<0.001	<0.02	<0.1
V	r	0.888	0.921	0.901
	p	<0.001	<0.001	<0.001
Zn	r	0.498	0.510	0.535
	p	<0.01	<0.01	<0.01

Notes
(a) Not derived as many annual mean concentrations were below analytical limits of detection.

4.1.1.1 Lead in air

The temporal changes in annual mean air concentrations of Pb at these three rural locations are plotted, along with estimated annual total atmospheric emissions for the UK, during the period 1972-1998 in Figure 8. It is apparent that the decreases in air concentrations of Pb at Chilton, Styrrup and Wraymires were consistent with corresponding decreases in estimated emissions during this period.

The percentage reductions in the annual mean air concentrations at these three sites, between the periods 1972-1979 and 1994-1998, were in the range 84% - 86% compared with an 82% reduction in estimated annual emissions (Table 7). Also, annual average air concentrations of Pb at all three locations were highly significantly correlated with estimated emissions (Table 8). UK atmospheric emissions of Pb have been dominated by road transport (from anti-knock lead additives in petrol) which in 1998 contributed to 57% of total UK emissions (Goodwin et al., 2000). As a result lead is better quantified than other pollutants (Salway et al., 1996 and Goodwin et al., 2000). The step change in estimated emissions (when the last reduction in the limit on the Pb content of petrol was introduced) is clearly seen between 1985 and 1986 (Figure 8). This is reflected in the plots of annual mean air concentrations, both against time and estimated annual emissions, for each of the three sites. Also, since 1987 sales of unleaded petrol have increased particularly as a result of the increased use of cars fitted with catalytic converters and fiscal measures encouraging older vehicles to switch fuels(Goodwin et al., 2000). Consequently, atmospheric emissions of Pb have fallen further still during the 1990s, as have annual mean air concentrations at rural locations in the UK (Figure 8).

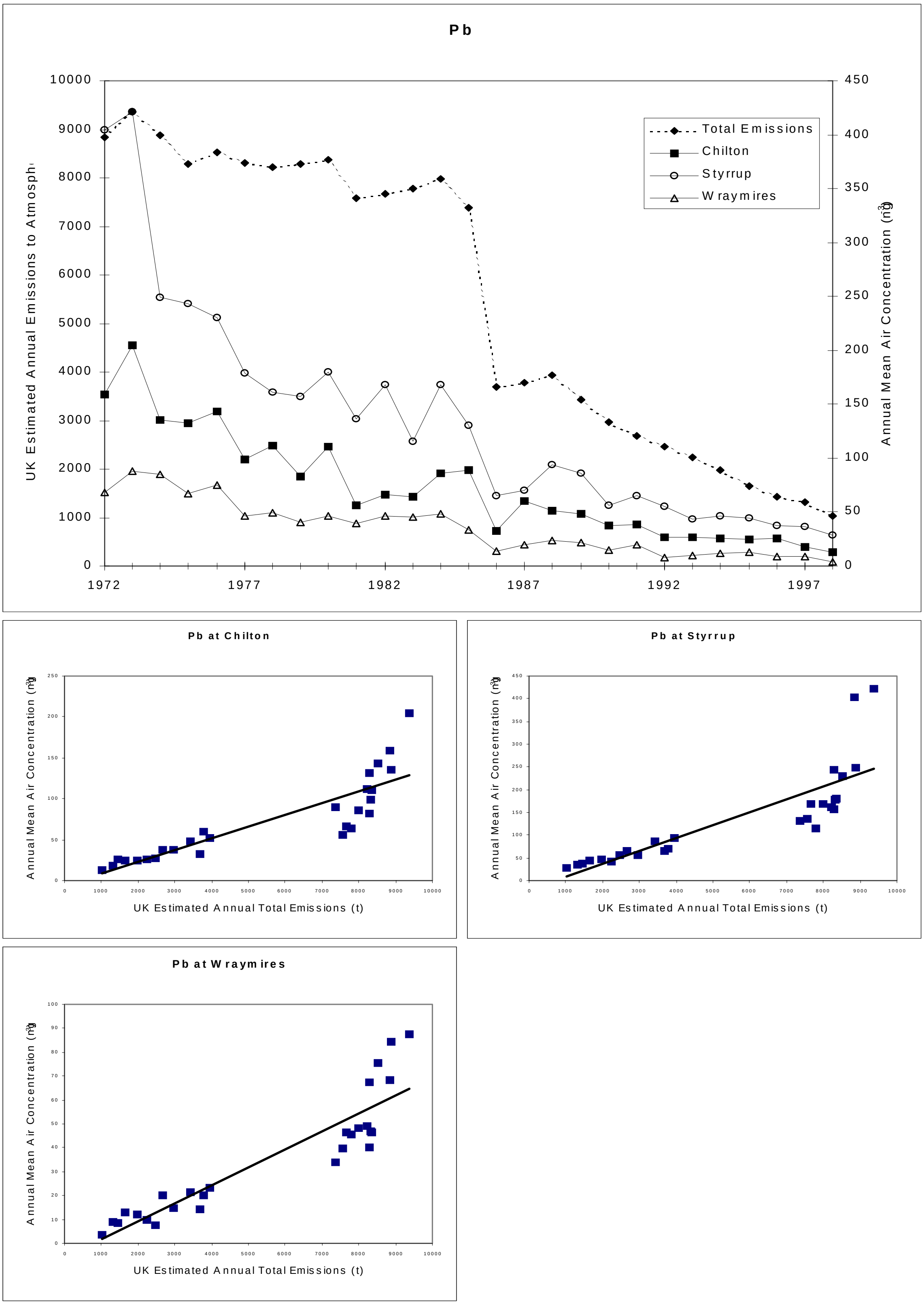


Figure 8
Comparison of annual mean air concentrations of Pb at rural locations with the estimated annual total UK emissions to the atmosphere (1972-1998)

Similar reductions have been reported for other rural locations (i.e. East Ruston, High Muffles and Banchory) in the UK (Playford and Baker, 2000). The percentage reductions in average air concentrations of Pb were in the range 58% - 72% between 1987-1990 and 1996-1999; these compare well with a reduction in estimated UK emissions of 62% between 1987-1990 and 1995-1998. At all these locations, the changes in annual mean air concentrations were highly significantly correlated with changes in estimated emissions of Pb between 1987 and 1998.

4.1.1.2 Arsenic, chromium, selenium and zinc in air

The major source of As and Cr emissions in the UK is coal combustion, with other notable contributions from industrial production processes, e.g. iron and steel production processes for Cr (Goodwin et al., 2000). The reduction in emissions of these metals that have been estimated since the 1970s are thought to be attributable in the main to the decline in coal use in favour of natural gas use, together with improvements in abatement technology.

At the three Rural Trace Element network sites, the percentage reductions in annual mean air concentrations of As (76% - 83%) and Cr (64% - 74%) since the 1970s were in excess of corresponding reductions in atmospheric emissions estimates, i.e. 60% and 49%, respectively (Table 7). However, the average air concentrations of both metals were significantly correlated with their estimated emissions between 1972 and 1998 (Table 8, Figure 10a).

At Chilton and Wraymires (Figure 9a) and at Styrrup (Figure 9b), it is apparent that the pattern in annual mean air concentrations of As follows that of the estimated emissions, particularly since the mid-1980s. For Cr, this feature is not so apparent (Figures 9a and 9b). However, reductions in annual mean air concentrations of Cr at East Ruston and High Muffles (1987-1990 to 1996-1999) were 22% and 54%, respectively (Playford and Baker, 2000) and were comparable to reductions in Cr emissions (45%) for the period 1987-1990 to 1995-1998. As was not measured at these locations over the whole 10 year period.

It is possible that analytical uncertainties in the historical air concentrations data were greater than in the more recent data. However, estimates of emissions of these metals are less well quantified and are more uncertain than say for Pb (predominantly of motor vehicular origin) (Goodwin et al., 2000). These uncertainties in the data may be responsible for the discrepancies between the percentage reductions, calculated for air concentrations and for estimated emissions, of As and Cr shown in Table 7.

The main source of Se emissions was coal combustion for public power generation and industry in earlier years. As for As and Cr, emissions have reduced over the period considered because of the decline in coal use in favour of natural gas combustion. Glass production is now thought to be the dominant source (Goodwin et al., 2000).

Annual average air concentrations of Se have decreased at Chilton (46%), Styrrup (30%) and Wraymires (44%), 1994-1998 relative to 1972-1979 and are very comparable to the corresponding reduction (39%) in estimated UK atmospheric emissions (Table 7). At Styrrup and Wraymires, the average air concentrations of Se were less significantly correlated with estimated annual emissions between 1972 and 1998, than As and Cr (Table 8, Figure 10b). However, the significance of these correlations for Se has improved since the last comparison of measured air concentrations with estimated atmospheric emissions (Baker, 1999).

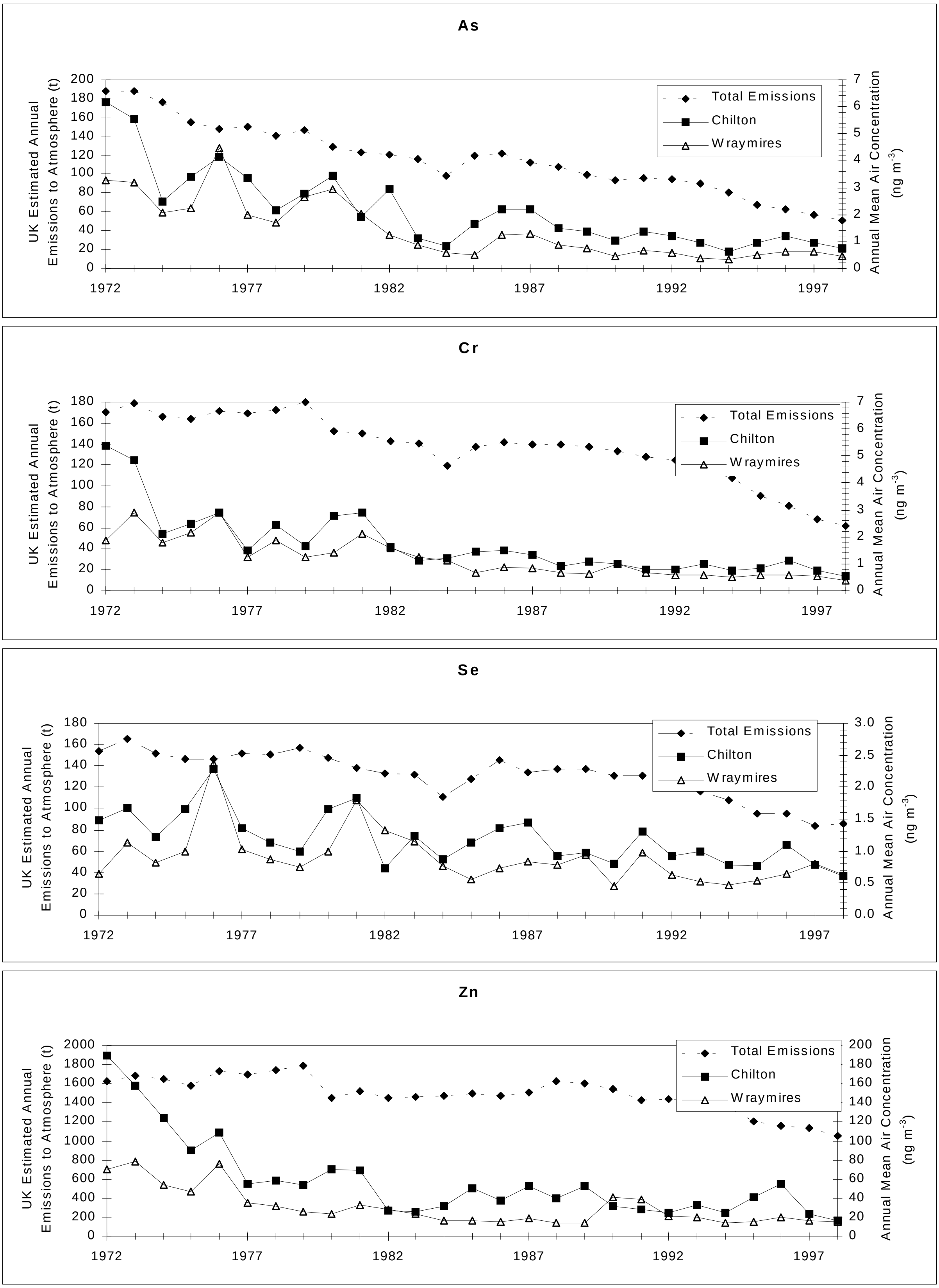


Figure 9a
Changes in annual mean air concentrations of As, Cr, Se and Zn at Chilton and Wraymires compared with changes in their estimated annual total UK emissions to the atmosphere (1972-1998)

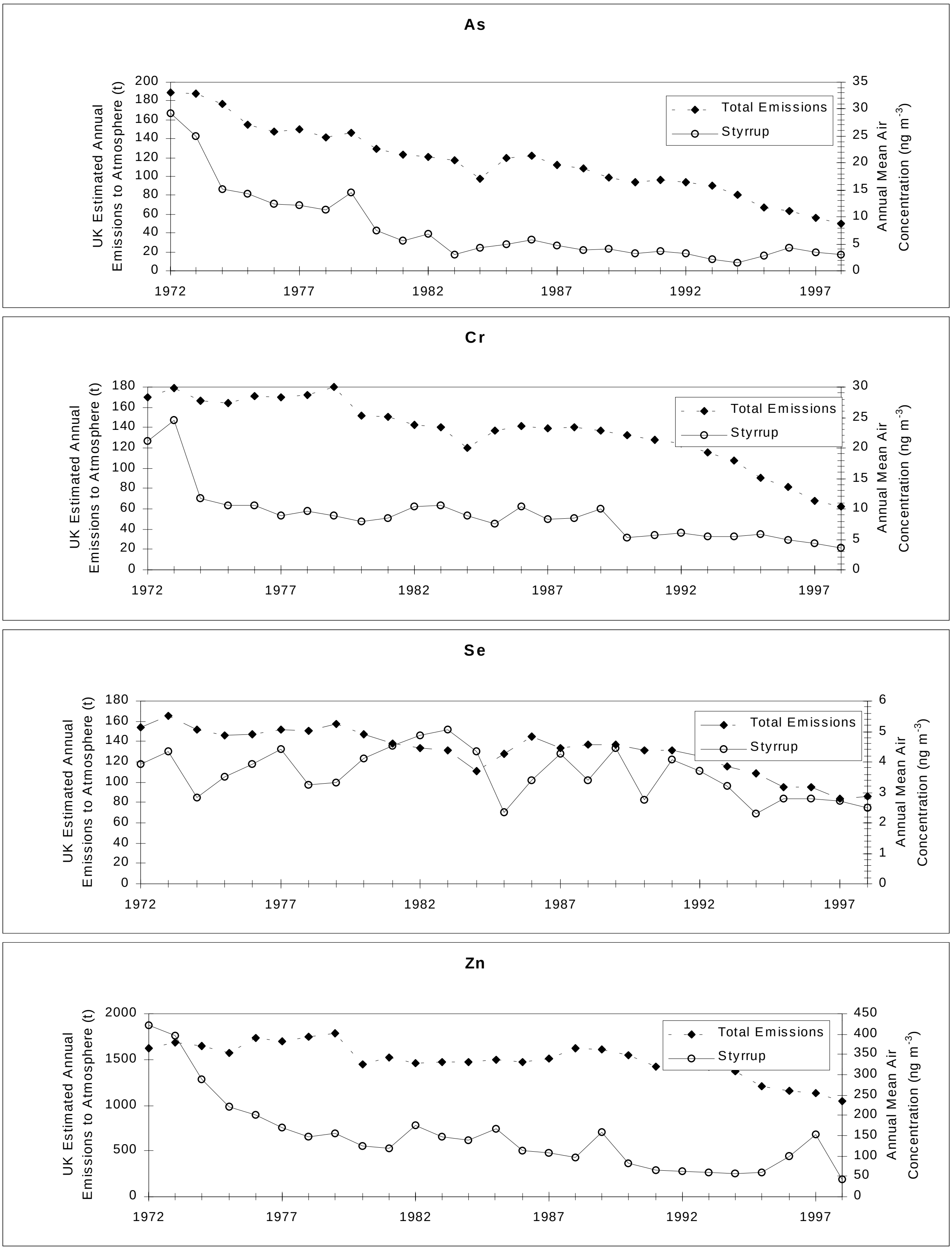


Figure 9b Changes in annual mean air concentrations of As, Cr, Se and Zn at Styrrup compared with changes in their estimated annual total UK emissions to the atmosphere (1972-1998)

Correlations between Zn concentrations in air at Chilton, Styrrup and Wraymires and its estimated emissions to the atmosphere in the UK are also less significantly correlated than is the case for the other metals (Table 8, Figure 10b). However, as found for Se, the significance of the correlation was found to be greater than reported in Baker (1999). The reduction in estimated emissions was only 30% between the 1970s and 1994-1998, while corresponding reductions in annual mean air concentrations of Zn were consistent (67-69%) at the three sampling sites (Table 7). At the east coast rural site of High Muffles the decrease in average annual air concentrations since the late1980s (concentrations have been halved), was also greater than the corresponding reduction in estimated emissions of Zn (28%). However, typical air concentrations at East Ruston have reduced by a comparable 33% (Playford and Baker, 2000). In neither case was there any strong correlation between measured annual mean air concentrations and estimated emissions of Zn.

The contribution of coal combustion to the total emissions is much less for Zn, compared to the other metals, with Zn contributions from other sources. The main sources are iron and steel production, non-ferrous metals manufacture and road transport (almost entirely from tyre wear). Again, the uncertainty in the emissions data for Zn could be the cause of the discrepancy between reductions in measured rural air concentrations and national emissions. It may also be that emissions from such sources, while significant to the UK as a whole, were not as important as local sources at these sites during the 1970s.

4.1.1.3 Nickel and vanadium in air

The temporal changes in annual mean air concentrations of Ni at Chilton and Styrrup are plotted along with the estimated annual total atmospheric emissions of Ni for the UK, during the period 1972-1998 in Figure 9c. In recent years the annual mean concentrations of Ni at Wraymires have been below analytical limits of detection and therefore the plot for Ni at this site is excluded. Corresponding data for V at all three locations is also plotted in Figure 9c.

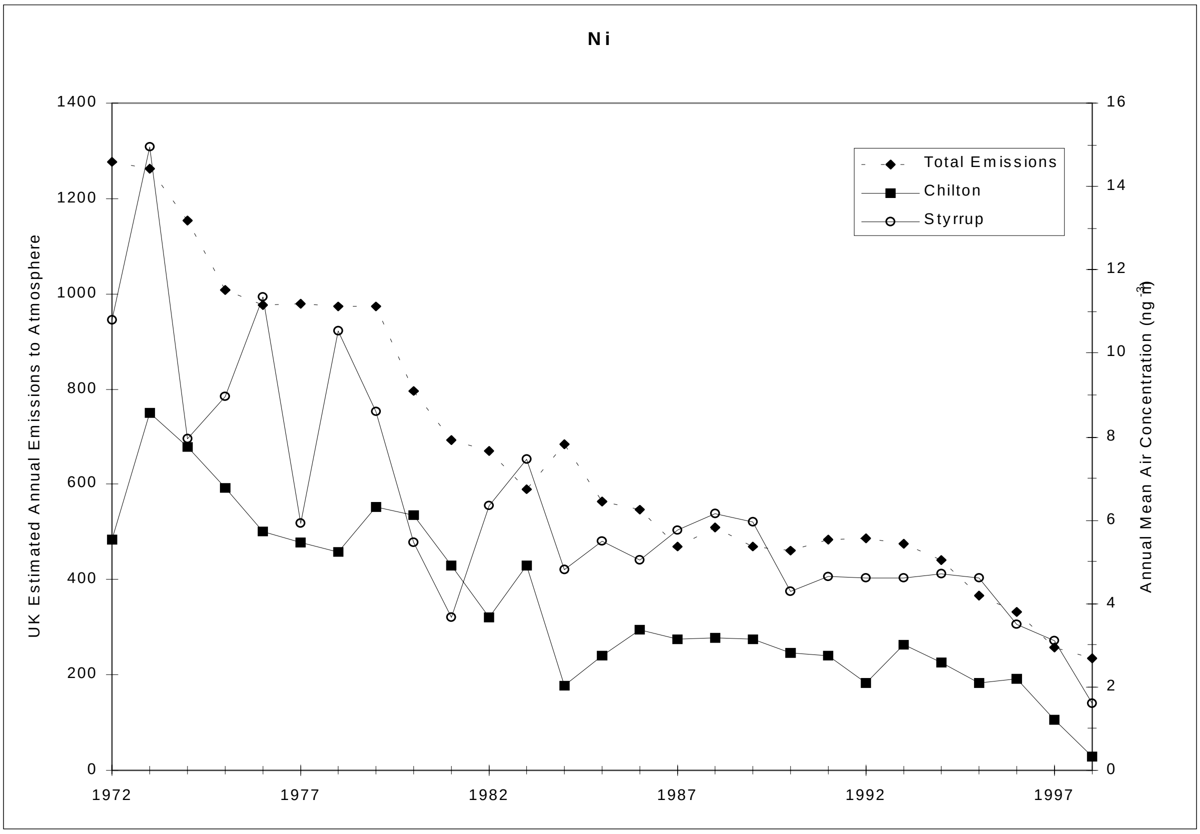
The percentage reductions in the annual mean air concentrations of Ni at Chilton and Styrrup, between the periods 1972-1979 and 1994-1998, were 73% and 65%, respectively. These reductions were very consistent with the 73% reduction in annual emissions that has been estimated since the 1970s (Table 7). Also, annual average air concentrations of Ni at these locations were highly significantly correlated with estimated emissions (Table 8, Figure 10c).

Similar observations have been made at other rural locations in the UK. Between the periods 1987-1990 and 1996-1999, the reductions in average air concentrations of Ni at East Ruston (41%) and High Muffles (47%) (Playford and Baker, 2000) were comparable to the estimated decrease in UK emissions between 1987-1990 and 1995-1998 (37%).

For V, reductions in annual average air concentrations of V at all three rural locations have followed the changes in estimated atmospheric emissions in the UK since the 1970s (Figure 9c). The percentage reductions in the annual mean air concentrations of V were very consistent at all three rural locations (72% - 79%), compared with a 71% reduction in estimated annual emissions, 1994-1998 relative to 1972-1979 (Table 7). At all three sites, annual mean air concentrations of V were very significantly correlated with estimated annual emissions between 1972 and 1998 (Table 8, Figure 10c).

The main sources of both Ni and V emissions are the combustion of coal and heavy fuel oil (for V, liquid fuels contributed almost 90% of estimated emissions in 1998). The reduction in emissions of both metals reflects the decline in the use of fuel oils by the electricity supply industry, industry in general and the domestic sector in favour of natural gas (Goodwin et al., 2000). It is interesting to note the slight peak in both emissions and UK rural air concentrations of both Ni and V that occurred around the late 1980s and early 1990 (Figure 9c). Since 1989 some heavy fuel oil use was replaced for a time by Orimulsion (an emulsion of bitumen in water) in some power stations although this has now been discontinued. The Ni and V content of Orimulsion was higher than that of heavy fuel oil and hence resulted in higher emissions.

It may be considered surprising that there is a very good agreement between estimated emissions and measured air concentrations of V, given that emission data for V is scarce and so the estimates are very uncertain (Goodwin et al., 2000). Nevertheless, it is apparent that the magnitude of the reduction in estimated emissions is quite accurate, assuming that the measured reductions in rural air concentrations carry a relatively low uncertainty.



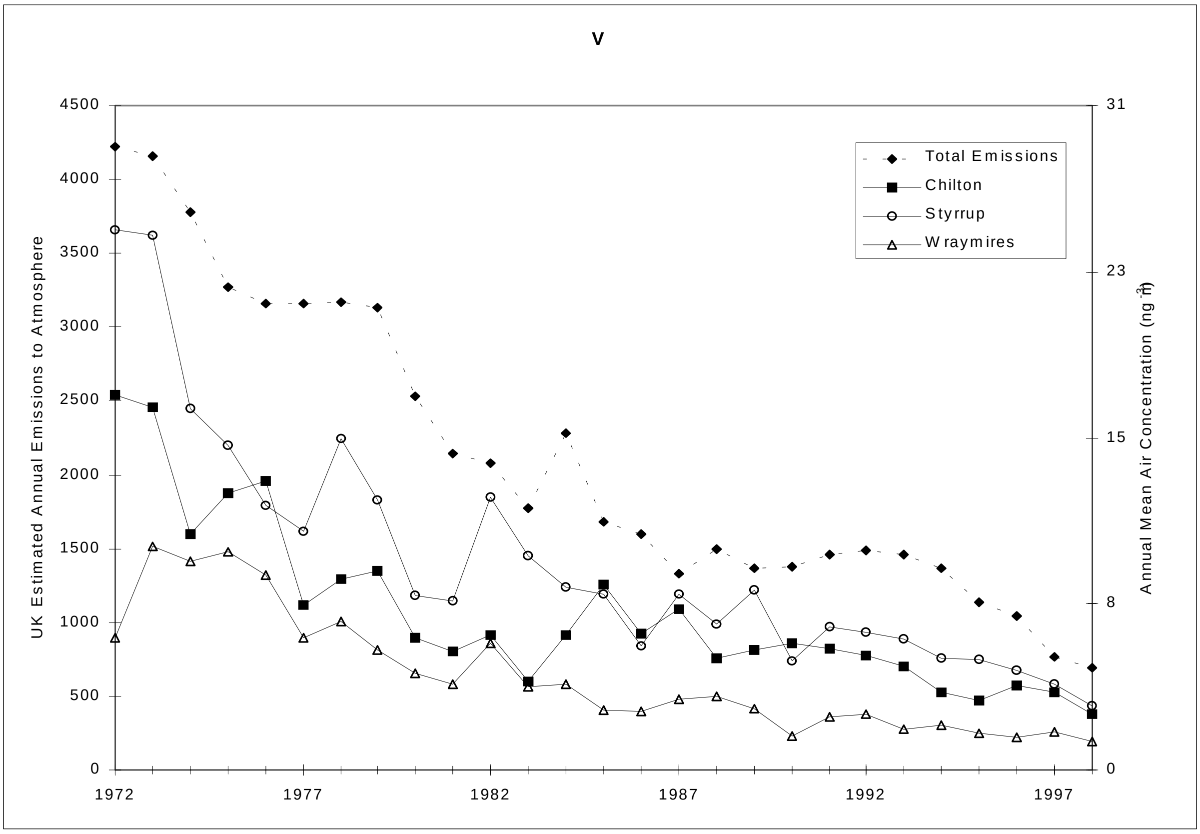


Figure 9c
Changes in annual mean air concentrations of Ni and V at rural locations compared with changes in their estimated annual total UK emissions to the atmosphere (1972-1998)

4.2 LONG-TERM CHANGES IN THE DEPOSITION OF ELEMENTS

The long-term trends in the annual bulk depositions of Cu, Ni, Pb, V, Zn and Na at the three rural locations were previously investigated for the period 1972-1998 (Baker, 1999). The time-series plots produced then have now been updated to include the 1999 data. In the time-series plots a regression analysis (as for the air concentrations, section 3.3) has been used to indicate the direction of the trend in annual deposition since the 1970s. (Figures 11a to 11c). In recent years, many quarterly mean concentrations of Ni in rainwater at Wraymires were below analytical limits of detection (section 3.2). Other anthropogenically-derived metals, e.g. As, Cd and Cr could not be included since many of the historical measurements were below analytical LODs. Over the last 28 years, downward trends in the deposition of the anthropogenically-derived metals Cu, Ni, Pb, V and Zn were evident. However, for Na the downward trend was less marked with even an upward trend shown at Wraymires (Figures 11a to 11c).

The long-term changes in average annual bulk depositions of these six metals, together with several others which are routinely monitored at Chilton, Styrrup and Wraymires, have been quantified by comparison of their average annual means for the periods 1972-1979, 1980-1989 and 1990-1999. The percentage reduction in the annual mean, relative to the period 1972-1979 was calculated for each element at each sampling location. These changes are plotted in Figure 12. Those elements whose quarterly concentrations (and therefore annual mean concentrations) were frequently below analytical detection limits were excluded from this summary.

All the elements, except Na (and Mg at Wraymires), showed an increase in the percentage reduction in annual mean deposition with time (Figure 12). As was noted for air concentrations of Na (section 4.1), the changes in the deposition of Na were not as clearly seen as were those for the metals of anthropogenic origin. This reflects the relatively unchanging contribution of marine-derived aerosols at all three locations. Further, the deposition of Mg at Wraymires has hardly changed since the 1970s (Figure 12). Inputs of Mg at this site are primarily marine-derived.

It is apparent that for each element investigated, the long-term reductions in their deposition were less at Wraymires than at the other two sites (Figure 12). The annual rainfall at Wraymires is about 3 to 4 times greater than that at Chilton and Styrrup and also experiences larger variations in rainfall (Baker, 1999). These influences appear to have reduced the magnitude of the long-term changes in the deposition of elements at this site, relative to the other two.

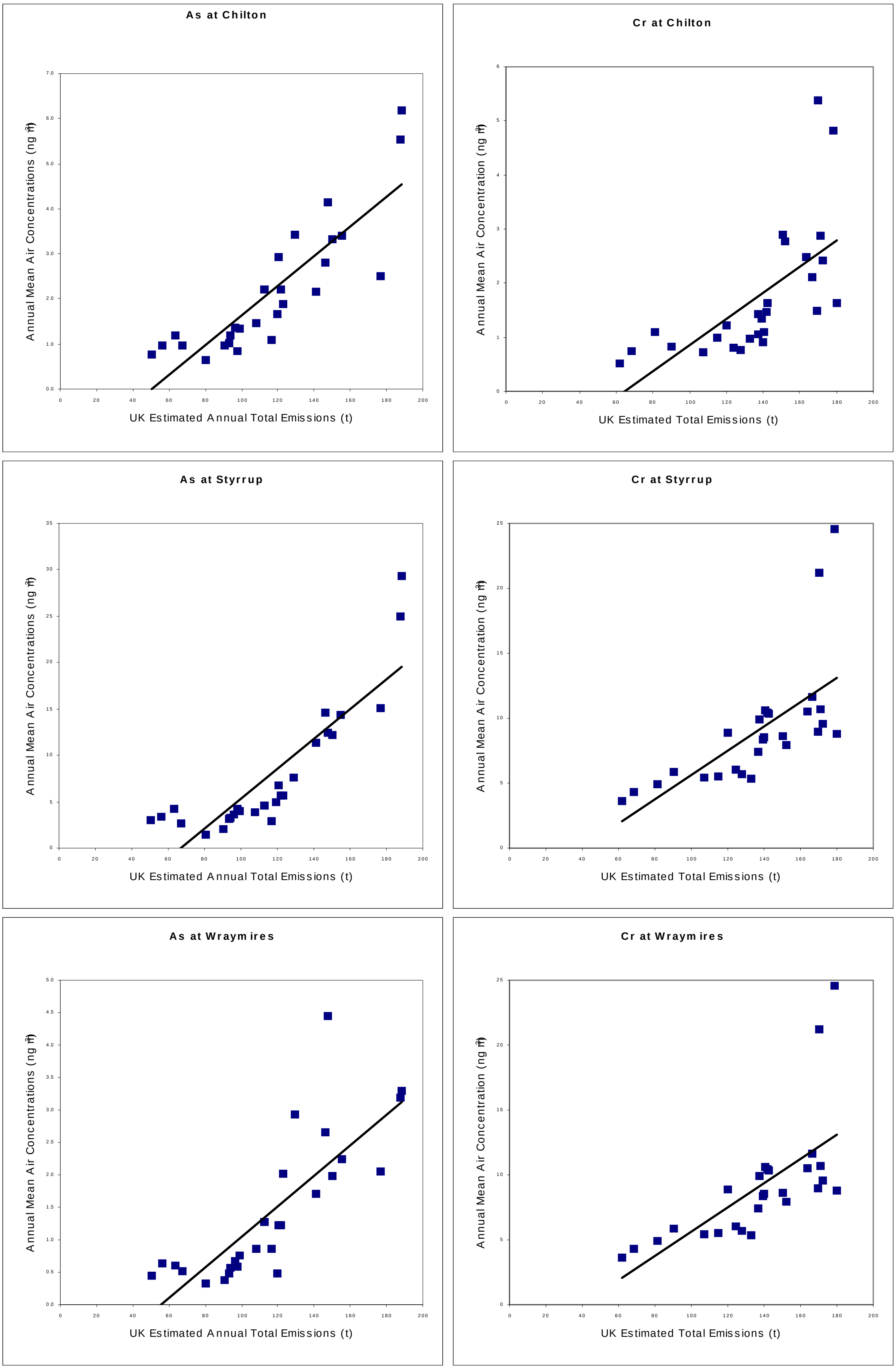
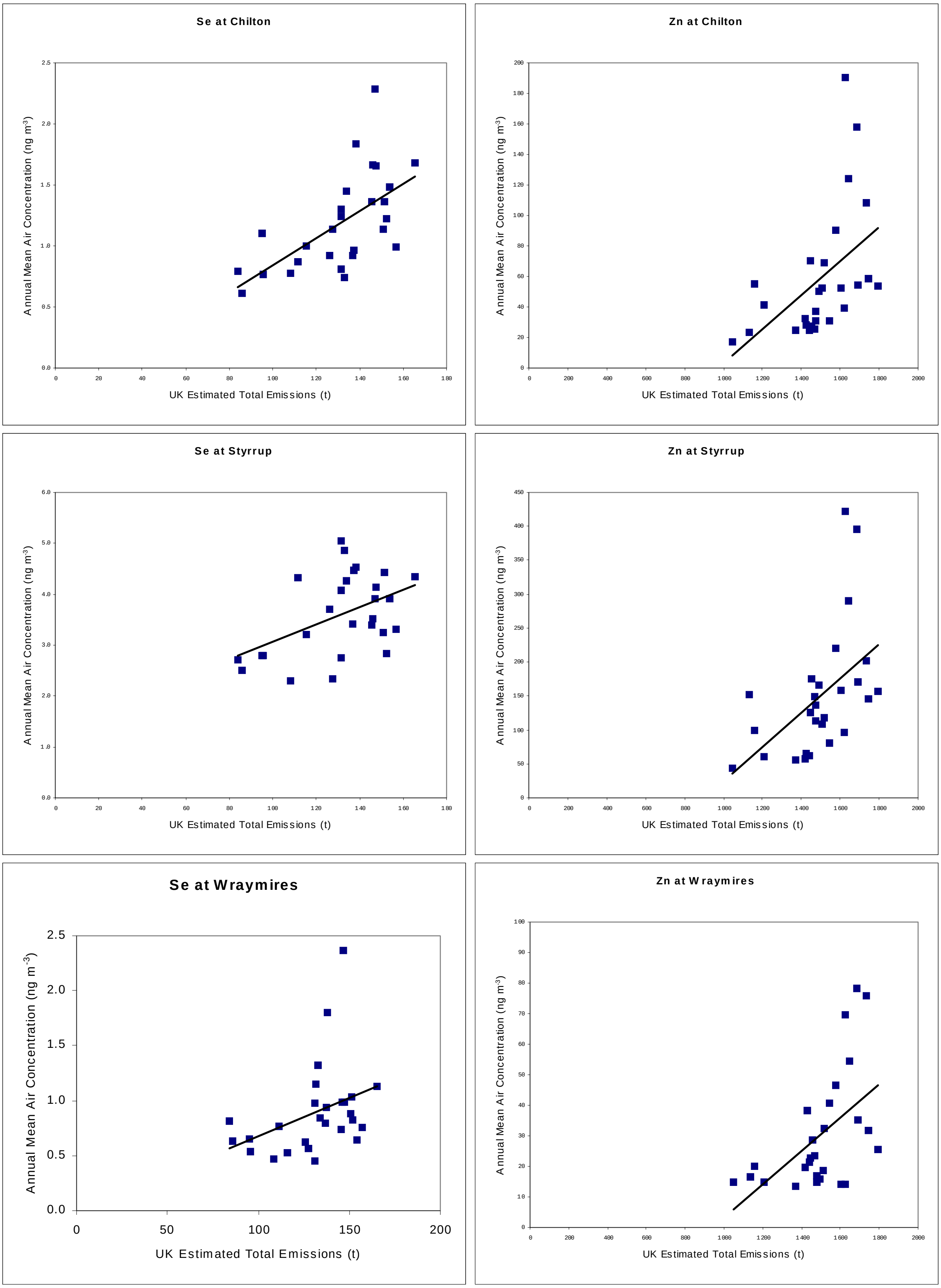


Figure 10a Annual Mean Concentrations of As and Cr against total UK emissions


Se at Chilton

Zn at Chilton

Se at Styrrup

Zn at Styrrup

Se at Wraymires

Zn at Wraymires

Figure 10b Annual Mean Concentrations of Se and Zn against total UK emissions

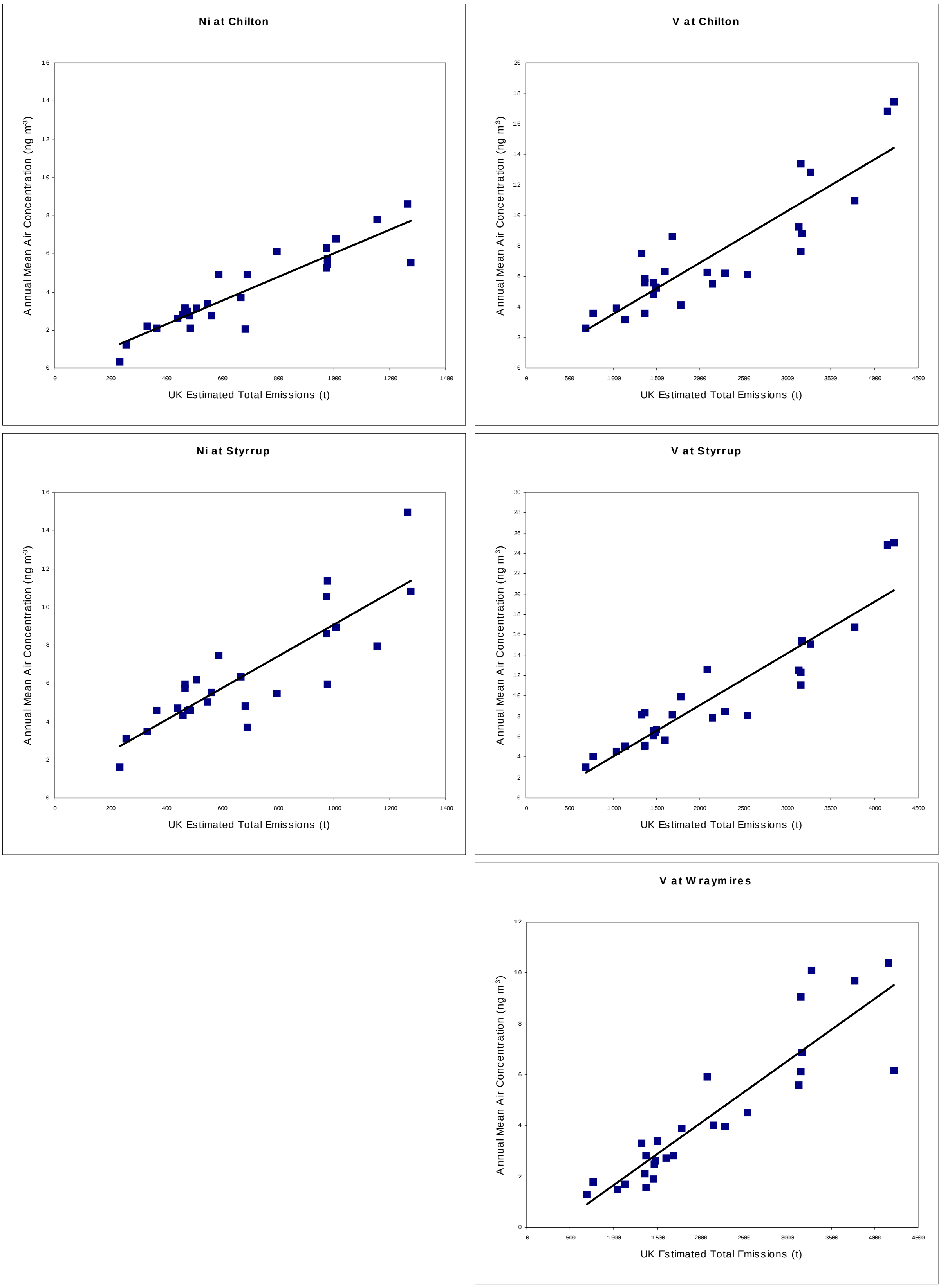


Figure 10c Annual Mean Concentrations of Ni and V plotted total UK emissions

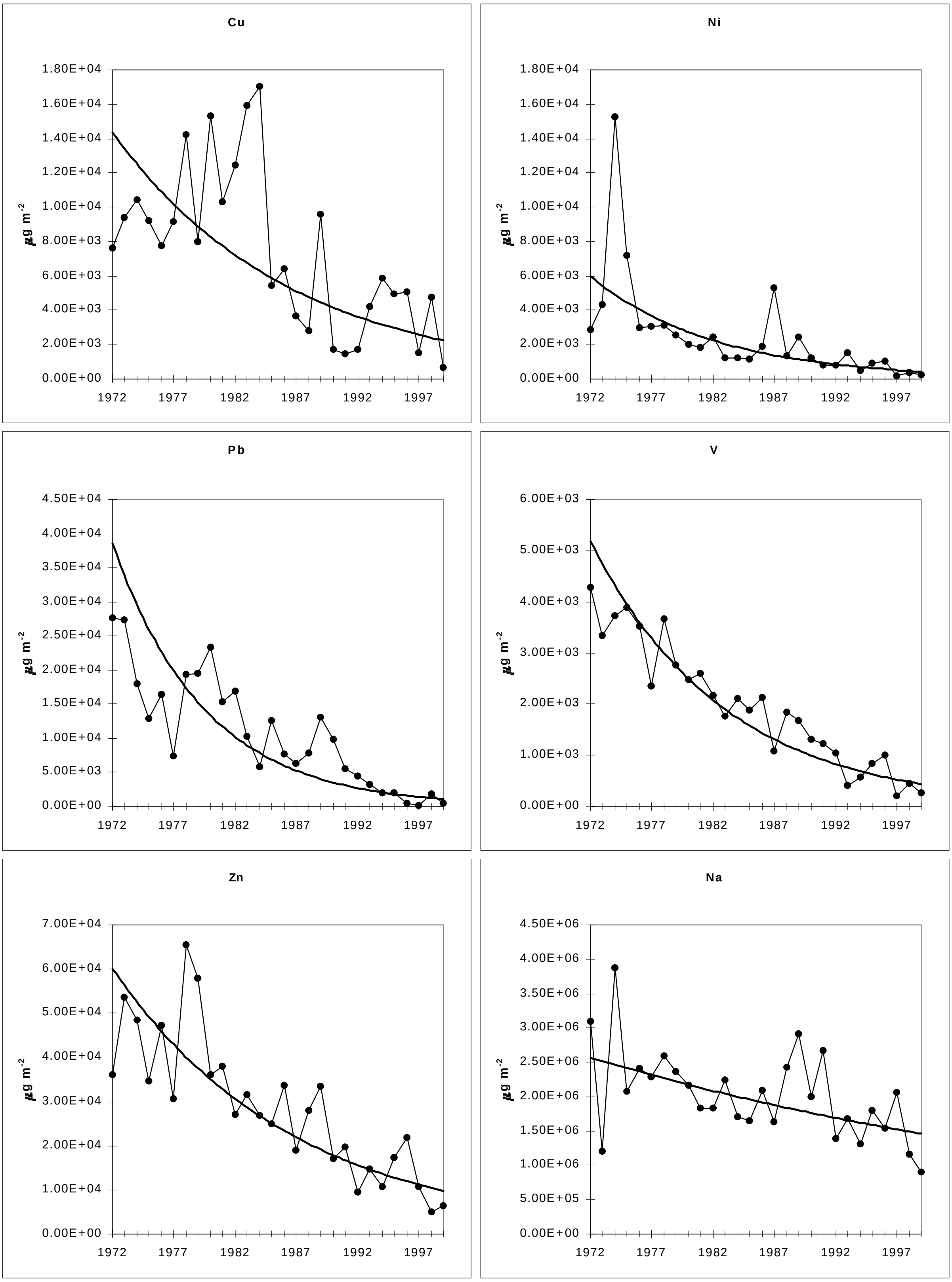


Figure 11a
Changes in annual mean depositions of Cu, Ni, Pb, V, Zn and Na at Chilton (1972-1999)

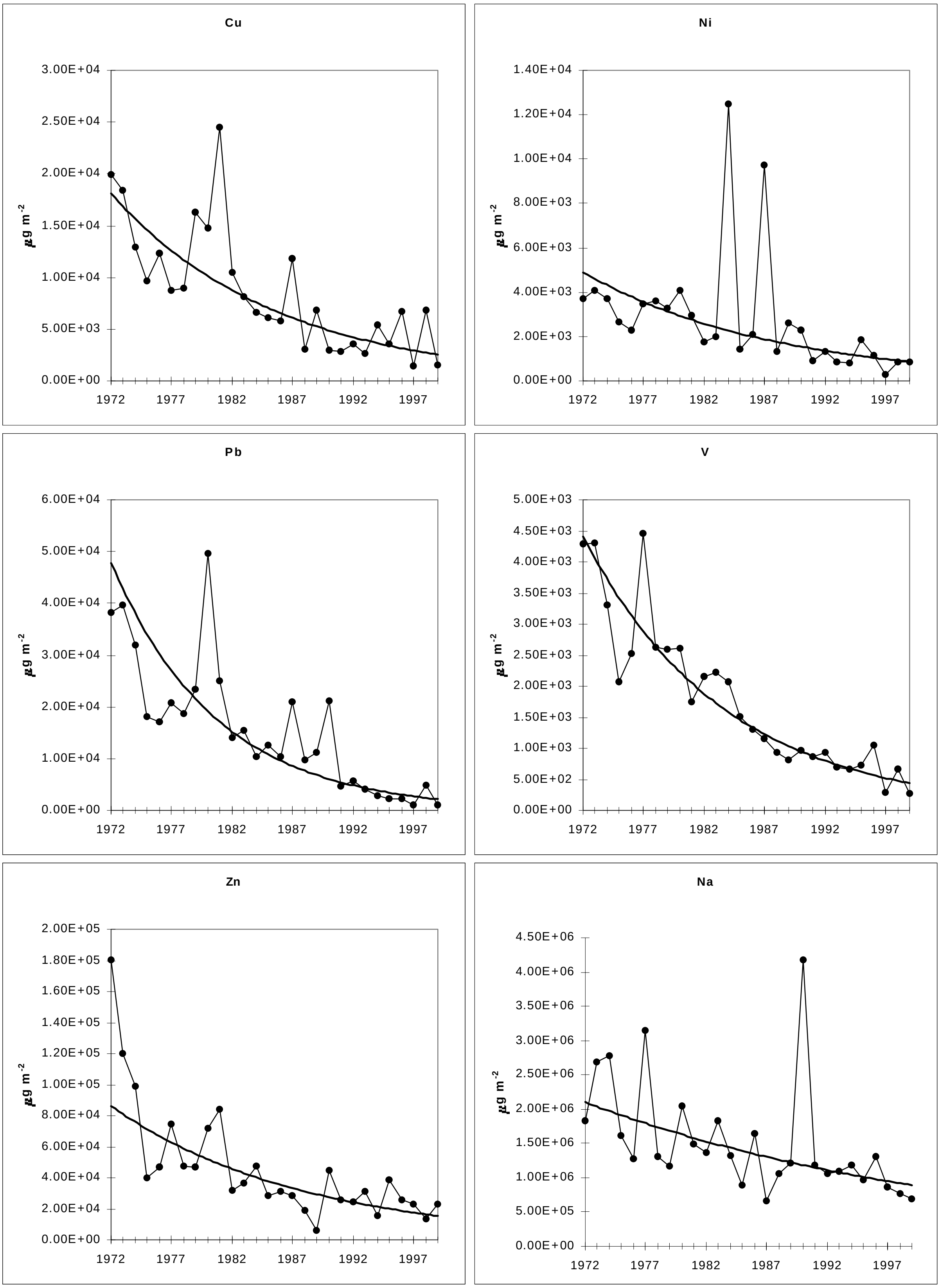


Figure 11b
Changes in annual mean depositions of Cu, Ni, Pb, V, Zn and Na at Styrrup (1972-1999)

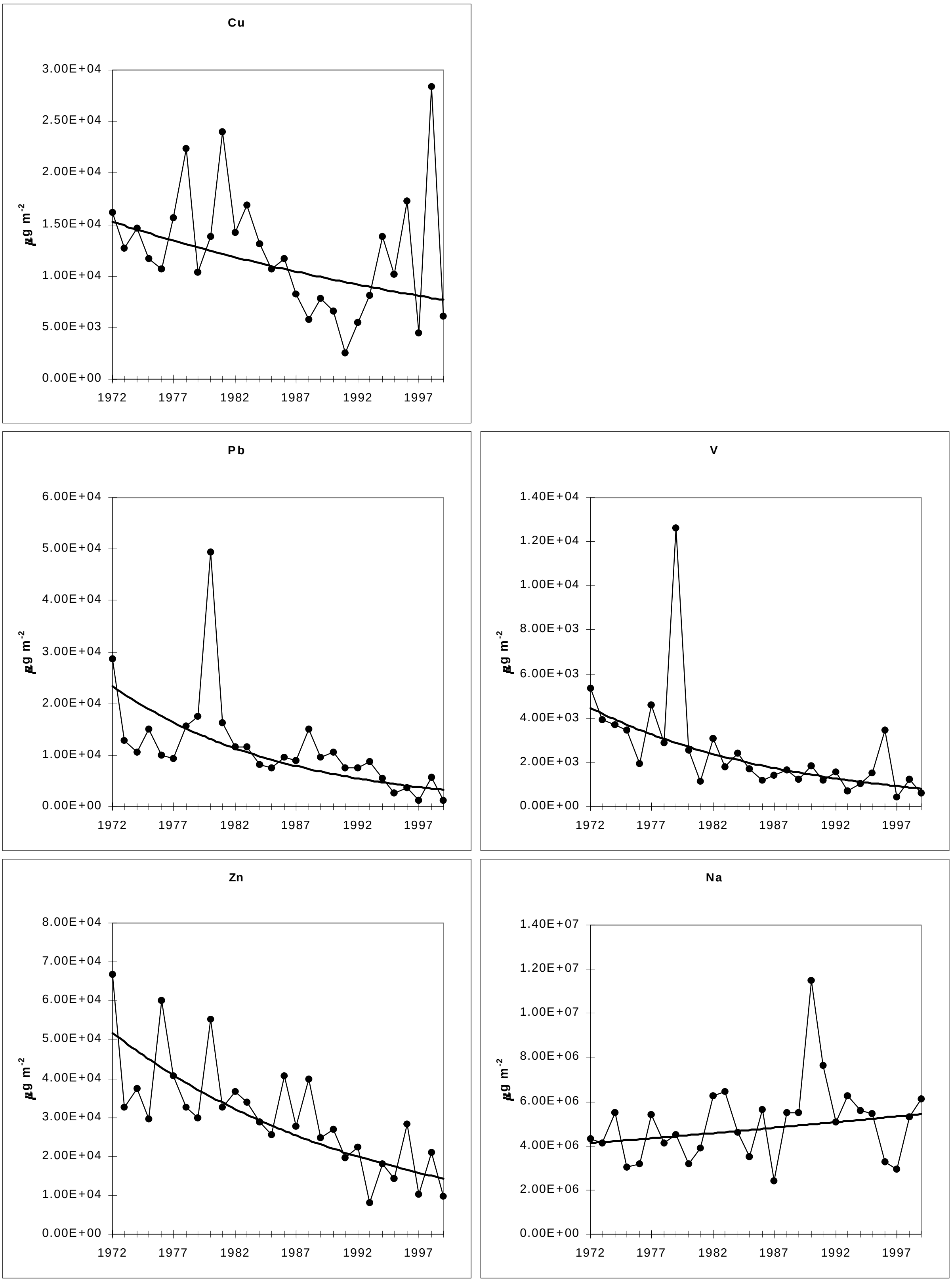


Figure 11c
Changes in annual mean depositions of Cu, Ni, Pb, V, Zn and Na at Wraymires (1972-1999)

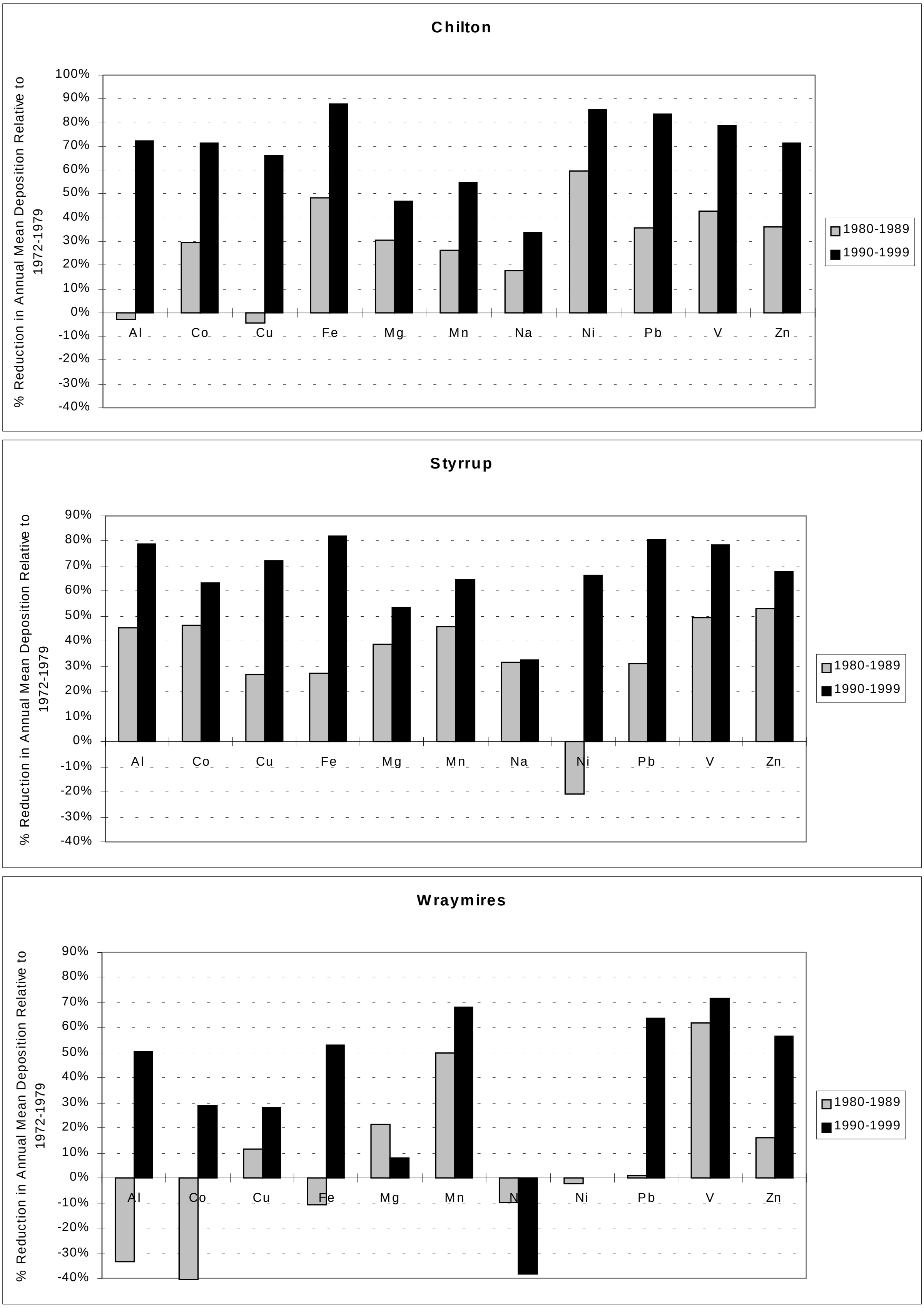


Figure 12 Percentage reductions in annual mean deposition of elements relative to the period 1972-1979 at Chilton, Styrrup and Wraymires

Considerable reductions in air concentrations of Al, Fe and Mn have occurred between the 1970s and the 1990s, with >60% reductions in annual means being measured at all three sites during this time (section 4.1). At Chilton and Styrrup, similar reductions in their annual mean depositions have occurred (1990-1999 relative to 1972-1979) (Figure 12). Again, the long-term decrease in emissions of fly ash is the likely explanation (see section 4.1).

For the predominantly industrially-derived metals and Pb, large reductions (>60%) in their deposition have occurred relative to the 1970s at Chilton, Styrrup and Wraymires (Figure 12). The long-term reductions in the deposition of Cu, Ni, Pb, V and Zn at these rural locations are discussed, in relation to corresponding changes in atmospheric emissions in the UK in section 4.2.1.

4.2.1 Long-term changes in the deposition of heavy metals at rural locations and in their estimated emissions to the atmosphere

The long-term changes in the annual depositions of Pb, Ni (Chilton and Styrrup only), V, Cu and Zn for the period 1972-1998 are compared with corresponding changes in atmospheric emissions which have been revised (Goodwin et al., 2000) since a similar assessment was last made (Baker, 1999). The temporal changes are shown in Figures 13a to 13e, in which the annual mean depositions ($\mu g\ m^{-2}$) of these metals are also plotted against annual estimates of total emissions (t) at each location.

The percentage reduction in the annual mean depositions of these metals, for the period 1994-1998 relative to 1972-1979 together with the corresponding reductions in their estimated annual emissions are presented in Table 9. For each metal at each location, these two parameters have also been correlated. The significances of the respective correlation coefficients are listed in Table 10.

Table 9

Temporal Changes in Annual Mean Annual Depositions and Estimated UK Atmospheric Emissions of Heavy Metals at Rural Locations, (1972-1998)

Annual Mean Deposition ($\mu g\ m^{-2}$)	**Cu**	**Ni**	**Pb**	**V**	**Zn**
			CHILTON		
1972-1979	9.47E+03	5.17E+03	1.86E+04	3.44E+03	4.67E+04
1994-1998	4.44E+03	5.96E+02	1.33E+03	6.12E+02	1.31E+04
% reduction	**53%**	**88%**	**93%**	**82%**	**72%**
			STYRRUP		
1972-1979	1.34E+04	3.34E+03	2.60E+04	3.27E+03	8.19E+04
1994-1998	4.78E+03	9.95E+02	2.65E+03	6.79E+02	2.34E+04
% reduction	**64%**	**70%**	**90%**	**79%**	**72%**
			WRAYMIRES		
1972-1979	1.43E+04	7.17E+03	1.49E+04	3.70E+03	4.12E+04
1994-1998	1.48E+04	(a)	3.78E+03	1.54E+03	1.84E+04
% reduction	**-3%**	**-**	**75%**	**58%**	**55%**

Annual Mean Estimated Total UK Atmospheric Emissions (t) (b)

	Cu	**Ni**	**Pb**	**V**	**Zn**
1972-1979	164	1075	8589	3504	1687
1994-1998	76	327	1609	999	1183
% reduction	**54%**	**73%**	**82%**	**71%**	**30%**

Notes

(a) Not derived as many annual mean concentrations were below analytical limits of detection.

(b) Derived from data from Goodwin et al. (2000).

Table 13

Correlations between Annual Mean Depositions at Rural Locations and Estimated Annual Total Atmospheric Emissions of Heavy Metals in the UK (1972-1997)

		Chilton	Styrrup	Wraymires
Cu	r	0.463	0.655	0.041
	p	<0.02	<0.001	not significant
Ni	r	0.592	0.285	(a)
	p	<0.01	not significant	-
Pb	r	0.823	0.748	0.530
	p	<0.001	<0.001	<0.01
V	r	0.924	0.922	0.801
	p	<0.001	<0.001	<0.001
Zn	r	0.786	0.421	0.533
	p	<0.001	<0.05	<0.01

Notes

(a) Not derived as many annual mean concentrations were below analytical limits of detection.

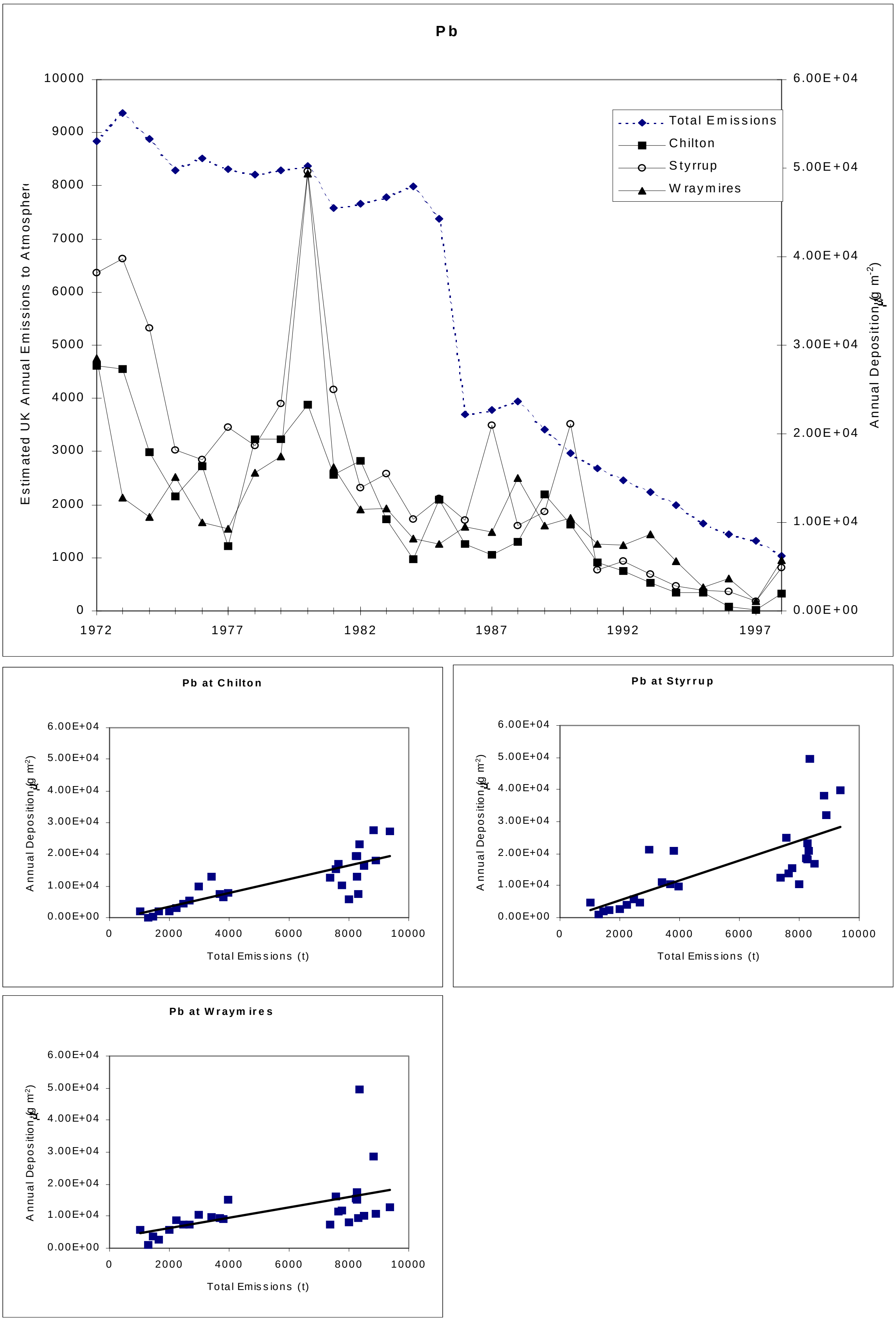


Figure 13a

Comparison of annual mean depositions of Pb at Chilton, Styrrup and Wraymires with the estimated annual total UK emissions to the atmosphere (1972-1998)

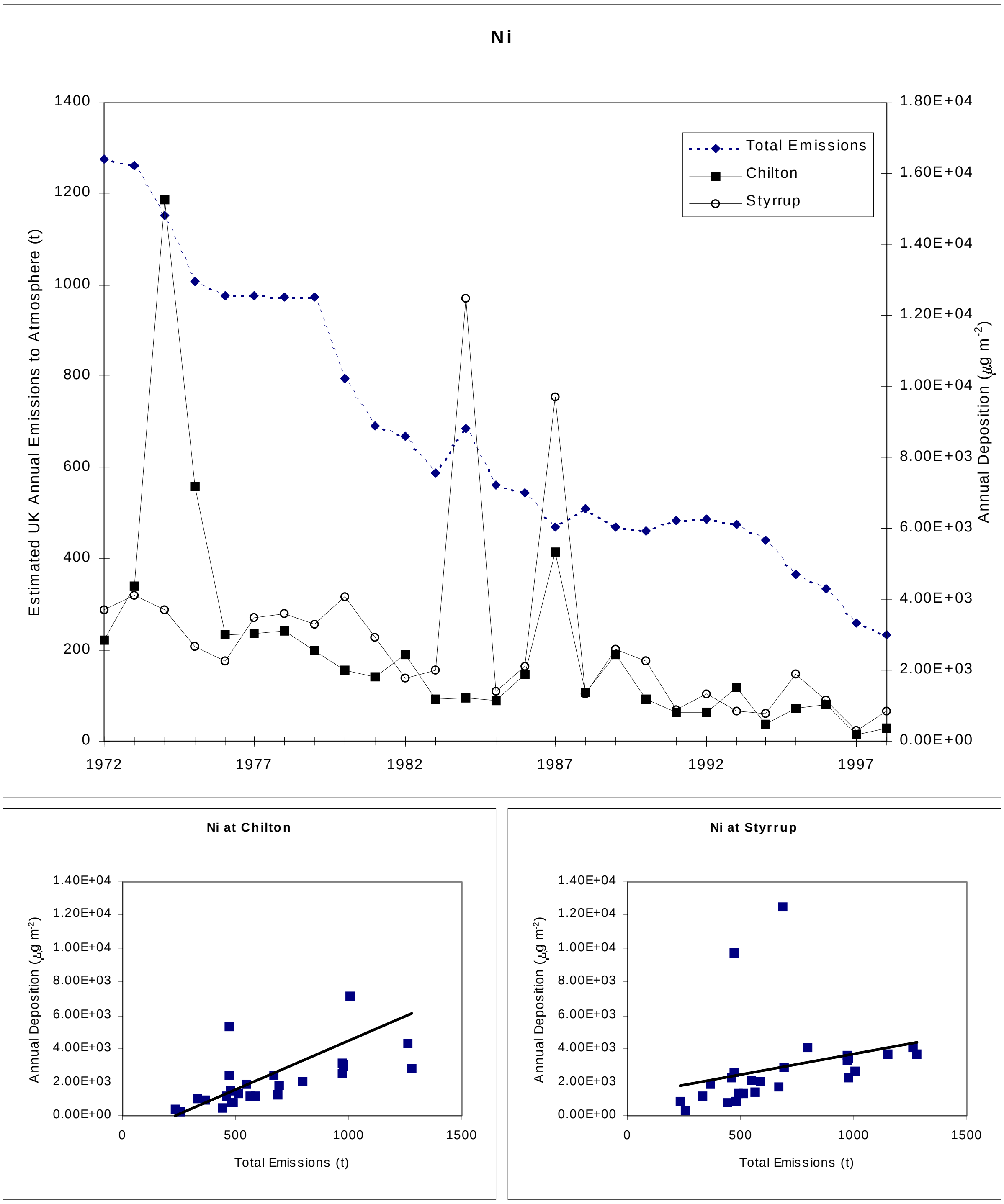


Figure 13b
Comparison of annual mean depositions of Ni at Chilton and Styrrup with the estimated annual total UK emissions to the atmosphere (1972-1998)

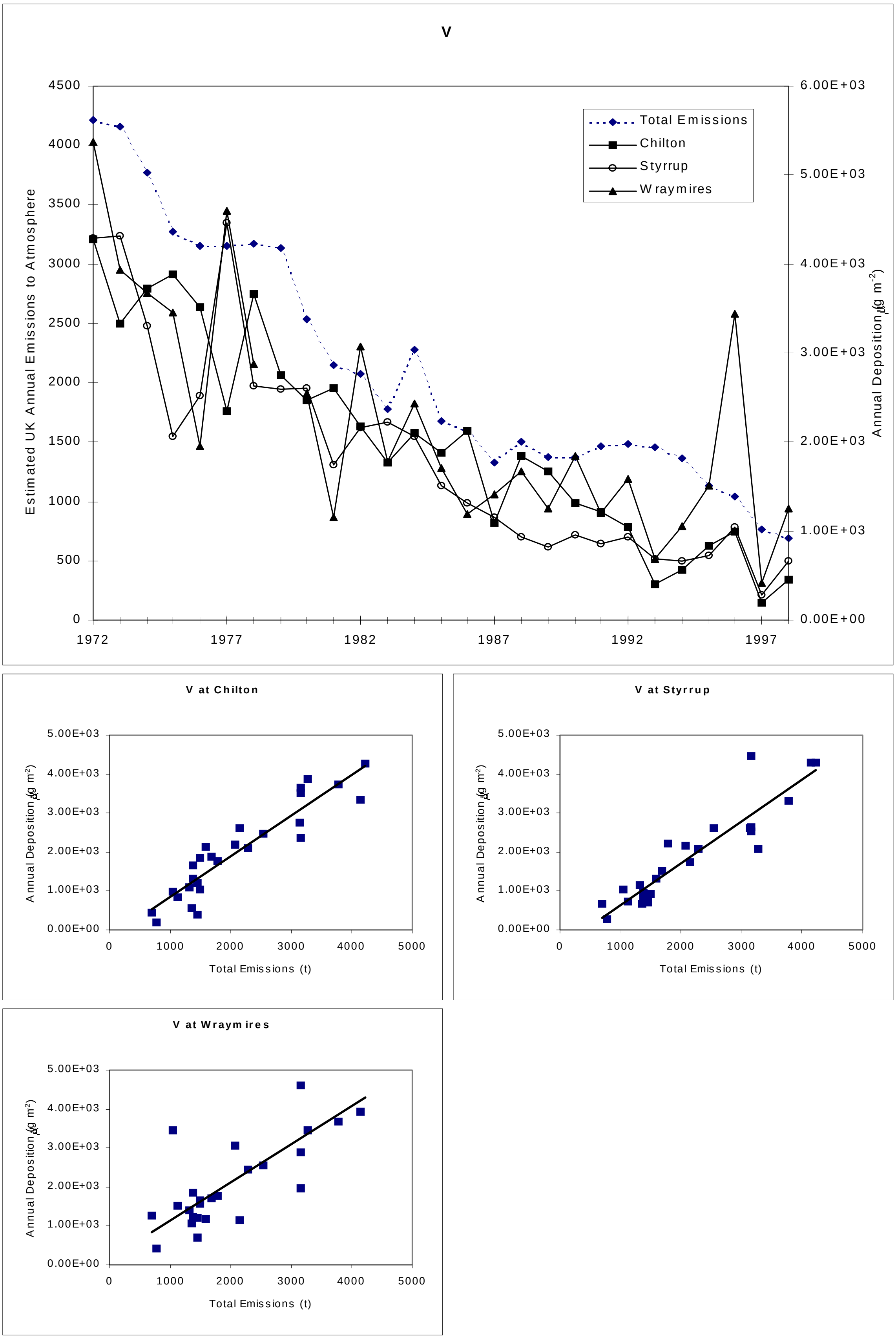


Figure 13c
Comparison of annual mean depositions of V at Chilton, Styrrup and Wraymires with the estimated annual total UK emissions to the atmosphere (1972-1998)

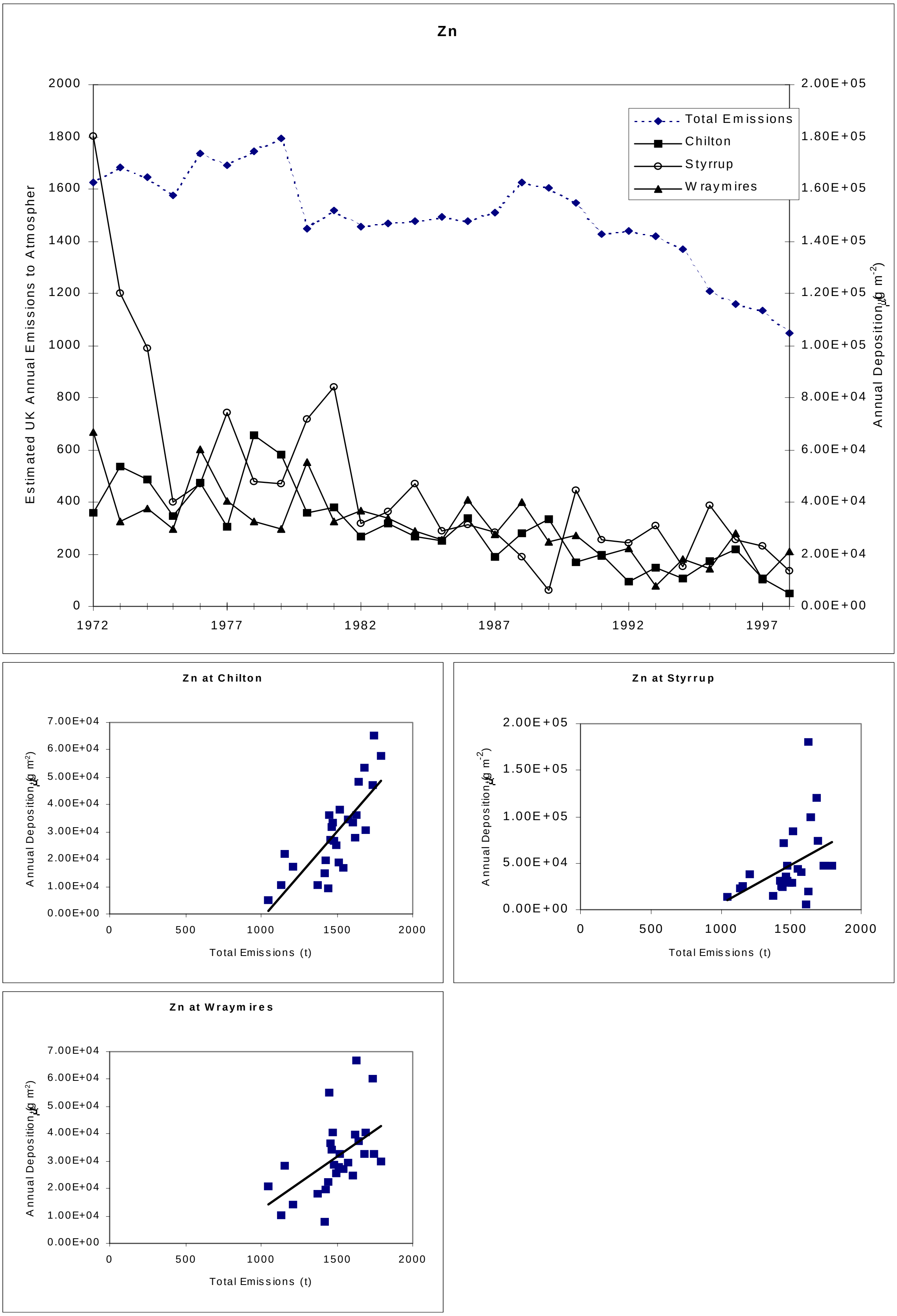


Figure 13d

Comparison of annual mean depositions of Zn at Chilton, Styrrup and Wraymires with the estimated annual total UK emissions to the atmosphere (1972-1998)

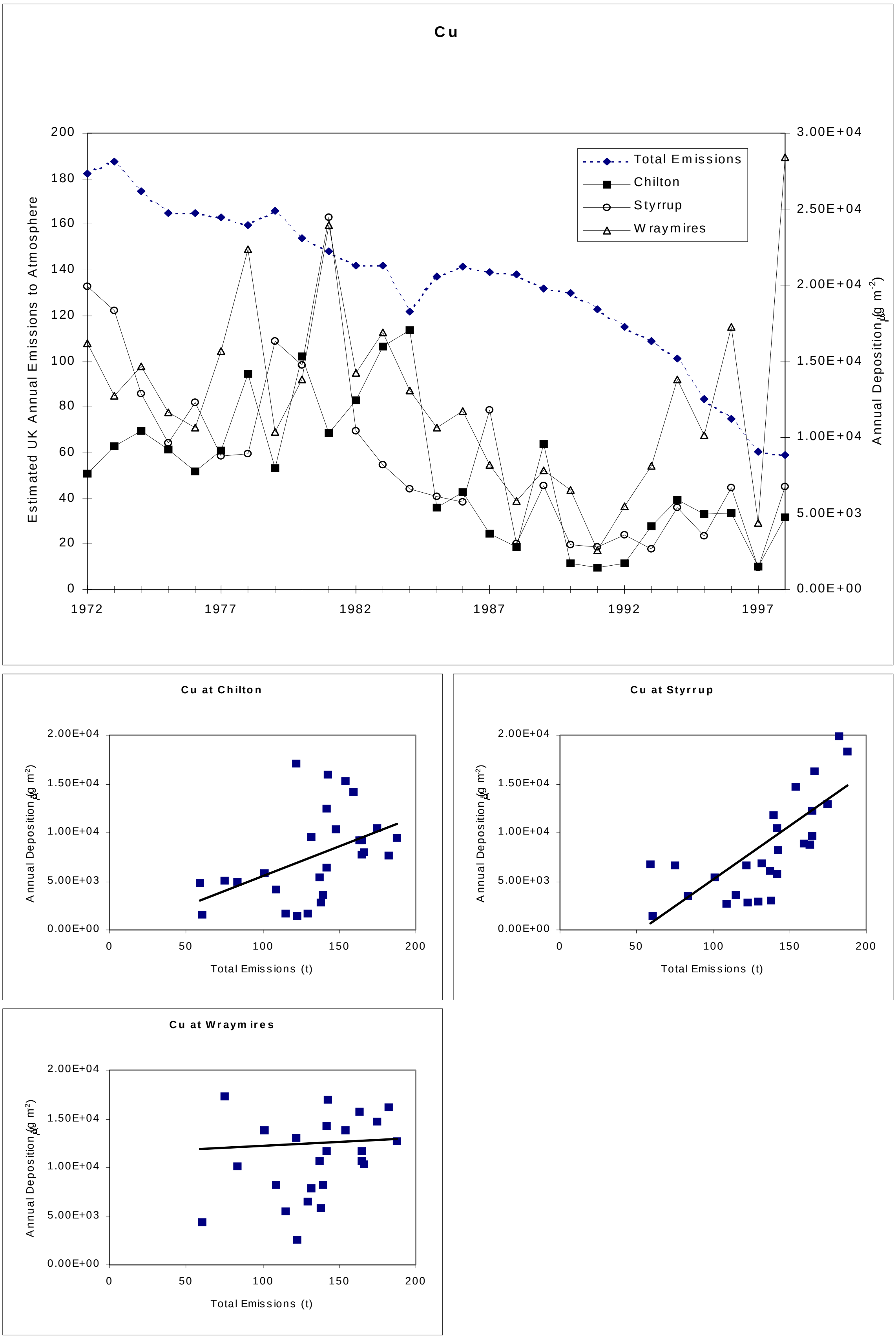


Figure 13e

Comparison of annual mean depositions of Cu at Chilton, Styrrup and Wraymires with the estimated annual total UK emissions to the atmosphere (1972-1998)

4.2.1.1 Deposition of lead

The reductions in the annual mean depositions of Pb between 1972-1979 and 1994-1998 ranged from 75% to 93% at the three rural locations, which was comparable to the corresponding reduction in estimated annual emissions (82%) (Table 9). Further, the temporal changes in the annual deposition of Pb at Chilton and Styrrup were highly significantly correlated with the changes in emissions, although the significance was less at Wraymires (Table 10, Figure 13a).

A sharp reduction in annual mean air concentrations of Pb, which corresponded with the reduction in the Pb content of petrol between 1985 and 1986 was clearly seen at all three sites (Figure 8) (section 4.1.1.1). No such discernible step change in the annual deposition of Pb was apparent at any of the sites (Figure 13a). However from the end of the 1980s to 1998, Pb deposition has clearly fallen below the levels that were recorded pre-1986 at all three sites. This is attributed to the increase in the use of unleaded petrol since 1988. Sales of unleaded petrol accounted for over 70% of the market in 1997 (DETR, 1998). Further, in the plots of Pb deposition against atmospheric emissions the points clearly fall into two groups, pre- and post-1986. At all three locations, the majority of the lower measurements of annual mean deposition fall within the post-1986 group (Figure 13a). The influence of vehicle emissions on Pb in bulk deposition at rural locations is shown by these data.

Over the period 1972-1999, the annual depositions of Pb were highly significantly correlated with annual mean air concentrations at all three sites. The correlations were highly significant at Chilton ($r = 0.851$, $p < 0.001$) and Styrrup ($r = 0.776$, $p < 0.001$), but less so at Wraymires ($r = 0.435$, $p < 0.01$).

4.2.1.2 Deposition of Ni

Reductions in the depositions of Ni at both Chilton and Styrrup were comparable with the corresponding reductions in emissions. Compared to that for the 1970s, the annual mean for Ni during the period 1994-1998 was reduced by 88% at Chilton and 70% at Styrrup. The reduction in emissions was estimated to be 73% (Table 9). Annual mean air concentrations of Ni were highly significantly correlated (at the 99.9% level) with estimated annual emissions between 1972 and 1998 (section 4.1.1.3). However, the correlations between annual deposits and annual emissions appears to be less significant (at the 99% level) at Chilton and not significant at Styrrup (Table 10).

From the plots of annual deposition against annual emissions, it is clear that one data point at Chilton and two data points at Styrrup appear anomalous and but for these both correlations would be highly significant (Figure 13b). During 1984 (Styrrup only) and 1987, unusually high quarterly concentrations of Ni in rainwater were recorded at both sites and these have given rise to the anomalously high depositions seen in Figure 13b. Exclusion of these data points increases the significance of the correlations at both sites. At Chilton, the correlation coefficient, r, becomes 0.625 ($p < 0.001$) while that for Styrrup increases to 0.848 ($p < 0.001$), compared to the values listed in Table 10. Further, if these data are excluded then depositions of Ni are highly significantly correlated with corresponding air concentrations measured at both Chilton ($r = 0.691$, $p < 0.001$) and Styrrup ($r = 0.689$, $p < 0.001$) since 1972.

4.2.1.3 Deposition of vanadium

The reductions in estimated atmospheric emissions of V over the last 27 years are reflected in the corresponding decreases in V deposition at all three rural sites (Figure 13c). Annual mean emissions fell by 71% between 1972-1979 and 1994-1998, while the reductions in annual mean depositions were in the range 58% to 82% (Table 9). In addition, annual emissions estimates were highly significantly correlated (at the 99.9% level) with annual depositions at Chilton, Styrrup and Wraymires between 1972 and 1998 (Table 10). Further, the annual deposition of V was highly significantly correlated with annual mean concentrations between 1972 and 1998 at Chilton ($r = 0.855$, $p < 0.001$) and Styrrup ($r = 0.862$, $p < 0.001$); at Wraymires the significance was less ($r = 0.438$, $p < 0.05$).

4.2.1.4 Deposition of zinc

Like the Zn concentrations in air (section 4.1.1.2), the reductions in the annual mean depositions between 1972-1979 and 1994-1998 (range 55-72%) exceeded the corresponding reduction in atmospheric emissions (30%) (Table 9). Nevertheless, the measured annual depositions at all three rural locations were significantly correlated (although to varying degrees) with atmospheric emissions between 1972 and 1998 (Table 10, Figure 13d). Further, annual mean air concentrations and depositions of Zn were highly significantly correlated at Chilton ($r = 0.592$, $p < 0.001$) and Styrrup ($r = 0.822$, $p < 0.001$) but less so at Wraymires ($r = 0.588$, $p < 0.01$).

4.2.1.5 Deposition of copper

The reduction in the mean estimated annual atmospheric emissions of Cu between the periods 1972-1979 and 1994-1998 was 54%. This reduction was well reflected by the corresponding changes in annual depositions at Chilton (53%) and Styrrup (64%) (Table 9). Also, at these locations annual Cu emissions were well correlated with the measured depositions between 1972 and 1998, particularly at Styrrup (Table 10, Figure 13e). The relationship between annual mean air concentrations and depositions of Cu could not be investigated as undertaken for Pb, Ni, V and Zn (sections 4.2.1.1 to 4.2.1.4). Some historical measurements of Cu in air were below prevailing analytical LODs.

The main sources of atmospheric emissions of Cu are coal combustion, iron and steel manufacture and non-ferrous metals production. Emissions have declined over the period due to the decline in coal combustion and to a lesser extent the combustion of heavy fuel oil (Goodwin et al., 2000). Therefore it is possible that the better correlation between emissions and deposition observed at Styrrup is attributable to its relative proximity to the major power stations and the metals industries, e.g. iron and steel in South Yorkshire.

At Wraymires, it is apparent that average annual depositions of Cu in recent years were similar to those estimated during the 1970s and 1980s (Figure 13d). The average annual deposition over the last five years was very similar to that of the 1970s (Table 9). Consequently, there is no correlation between emissions and the deposition of Cu at this site (Table 10, Figure 13d). The quarterly concentrations of Cu measured at all three sites in recent years have been very variable, with order of magnitude differences being reported. These variations have occurred between years and have occurred at all three sites (Figure 4a, section 3.2). Consequently, the estimated annual deposits have varied considerably too, depending on the rainfall at a given site. Since the annual average rainfall at Wraymires is about three times that at the other sites (section 3.2), the effect of the relatively high Cu concentrations measured in recent years on the estimated deposition has been magnified at this location. Historical samples are stored deep-frozen in an archive and could be retrospectively analysed as a check on the Cu concentrations reported at all three sites in recent years.

5 Additional Studies

5.1 INTERCOMPARISON OF ANALYSIS OF AIR FILTERS FOR ARSENIC, CADMIUM, LEAD AND NICKEL USING DIFFERENT DIGESTION TECHNIQUES

5.1.1 Background

A working group of the European Committee for Standardisation, CEN 264/Working Group 14, is developing a reference method for determining concentrations of As, Cd, Pb and Ni in ambient air. This will almost certainly be adopted as the reference method for the forthcoming EU Daughter Directives for these compounds. A working draft of the standard, which covers sampling methods and analysis of filter material, is currently available.

The current draft standard details several methods of filter digestion and analysis, without recommending any particular method. However, CEN 264/Working Group 10 on stack sampling of heavy metals has opted for closed vessel digestion, since open digestion has been shown to underestimate the metal content of collected particulate matter, particularly for the more volatile metals such as As. Working Group 10 has validated closed vessel digestion using a mixture of nitric acid and hydrofluoric acid, to ensure total digestion of filters and the particulate matrix (especially the silicate material). Within Working Group 14 (ambient sampling), most members seem to be moving towards accepting the closed vessel system for analysis of ambient samples.

In recent years, as part of the operations of the Rural Trace Elements network, Cd, Pb and Ni in ambient air were determined by ICP-AES after open vessel digestion of the air filter, while As is determined by INAA (section 2.3.1). Over the last few years air concentrations of Cd and Ni at the sampling sites (particularly Wraymires) were close to analytical limits of detection. Therefore it was proposed to analyse the 1999 air filter samples using ICP-MS. At the same time, an investigation into possible differences in reported concentrations of As, Cd, Pb and Ni, after digestion of the air filter samples by both open and closed vessel techniques was also proposed. If any significant differences were found between results determined by the two digestion methods, then recent (and ultimately historical) measurements made by this monitoring network could be re-assessed. Historically, considerable variations in average air concentrations of these metals have been recorded between the three sites. Therefore, this intercomparison exercise would also cover any possible effects that may be dependent on variations in air concentrations.

5.1.2 Methodology

Since two air filter samples are routinely collected on a monthly basis at each sampling location, the second air filter was used for this intercomparison exercise (the first being used for routine multi-element analysis by INAA). Representative portions of each monthly filter collected in 1999 at each of the three sampling sites were bulked together to obtain quarterly (i.e. three-monthly) samples for analysis. Two sets of samples were prepared. In addition, one blank sample was prepared for each set; these comprised representative portions (equivalent to the samples) of three blank filter papers.

One batch of samples (plus blank) was digested using a nitric acid/perchloric acid mixture in an open vessel. The second batch and blank, were prepared using a microwave digestion procedure with nitric acid in a closed digestion vessel. Analyte concentrations in all digests were then measured using ICP-MS. Three standard reference materials (SRMs) were subjected to the same digestion and measurement procedures with the two batches of samples.

The standard reference materials were National Institute of Standards and Technology (NIST) SRM 3087a and two SRMs, A2 and B2, produced by the Norwegian National Institute of Occupational Health. All three were 37 mm diameter cellulose ester type membrane filter papers that were spiked or impregnated with an aqueous solution containing a range of metal elements including As, Cd, Ni and Pb. More appropriate SRMs, i.e. containing particulate material trapped on filter paper, were not available. The SRMs used in this programme of work were the closest matrix (to the actual samples of particulate material on cellulose filter paper) available to the analysts.

5.1.3 Results

Air concentrations of As, Cd, Ni and Pb for the 1999 air filter samples have been derived from the blank-corrected results from both analytical methods. These data are presented in Table A2.1, Appendix 2. The results of the analysis of the SRMs are listed in Table A2.2, Appendix 2.

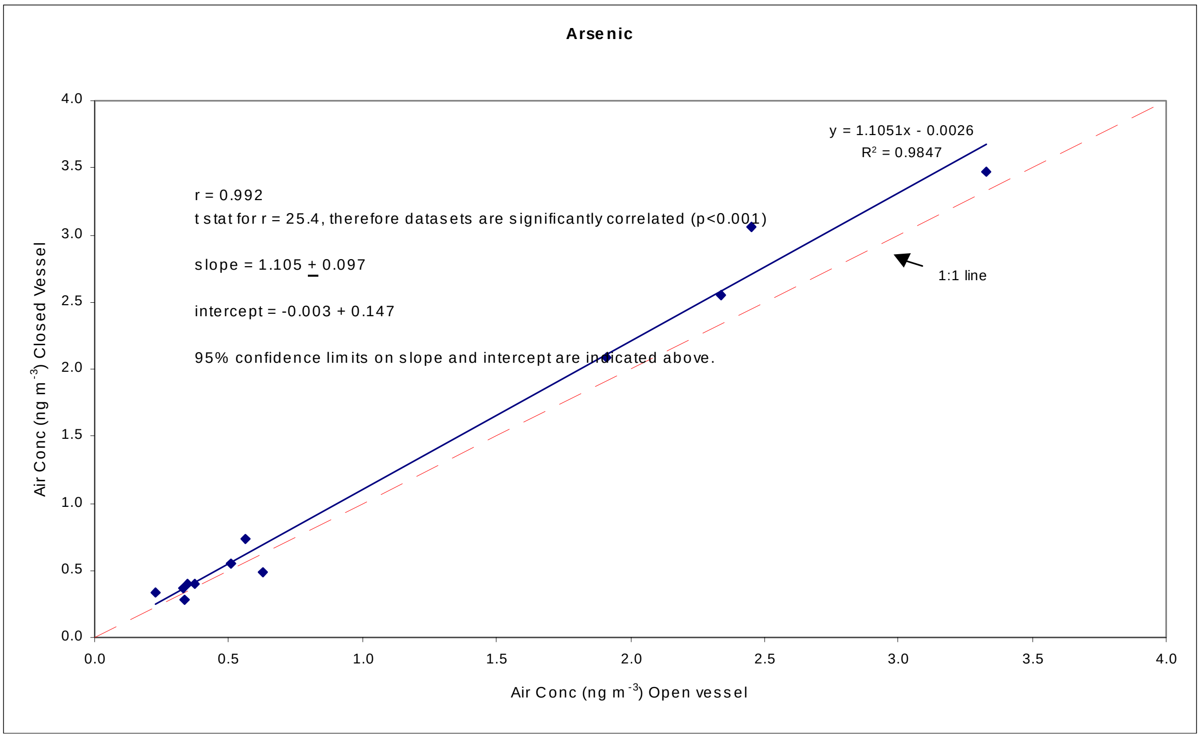
For each metal analyte the air concentrations obtained from the two different filter paper digestion techniques were compared by plotting them against each other and a linear regression line shown (Figures 14a to 14d). A 1:1 line is also plotted which represents the ‘ideal’ situation, i.e. where the two analytical methods used yield the same air concentration result. The slope, intercept and 95% confidence limits on both, together with the correlation coefficient is also shown in each of Figures 14a to 14d.

Also shown in each of these figures is a summary of the corresponding results for the three SRMs, which compares them with expected values for a given analyte in each SRM. These results are also listed in Table 14. The accuracy of the mean analytical results was investigated; for a given SRM the differences between the mean result given by the analyses using a particular technique ($\bar{x}$) and the expected value (μ) were tested for any statistical significance using the equation:

$$t = (\bar{x} - \mu)\sqrt{n/s}$$, where s = standard deviation of n analytical results.

The test statistic t was compared with the critical value of t at the 95% significance level for $n - 1$ degrees of freedom.

Further, a *two-tailed F-test* was undertaken on the analytical results obtained for each metal analyte using the open and closed vessel digestion techniques to test whether the methods



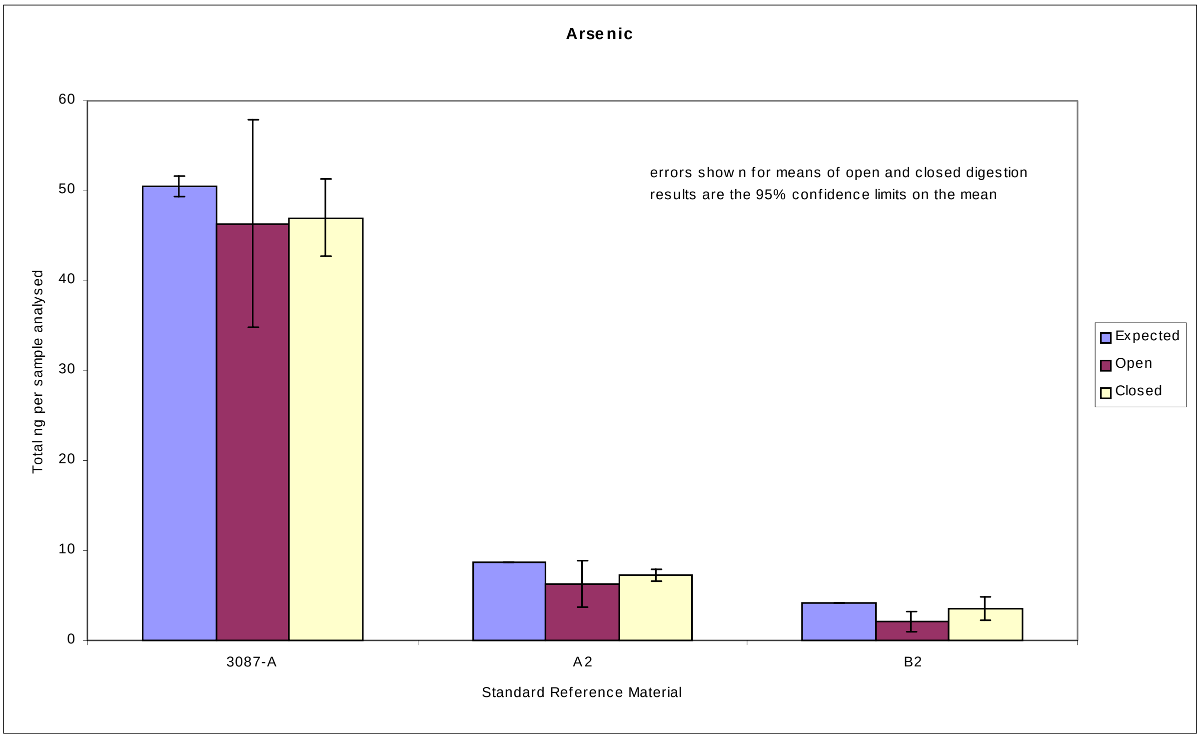
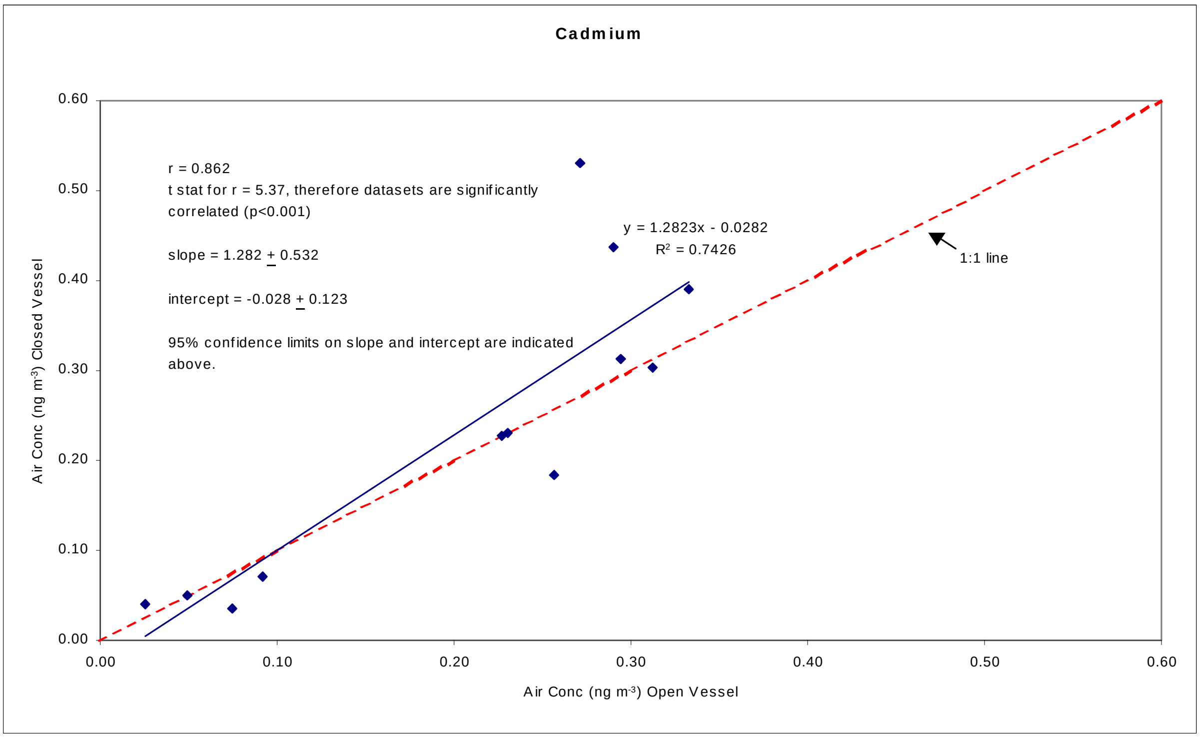


Figure 14a
Comparison of analysis of air filter samples and standard reference materials for As by ICP-MS following open and closed vessel digestion techniques



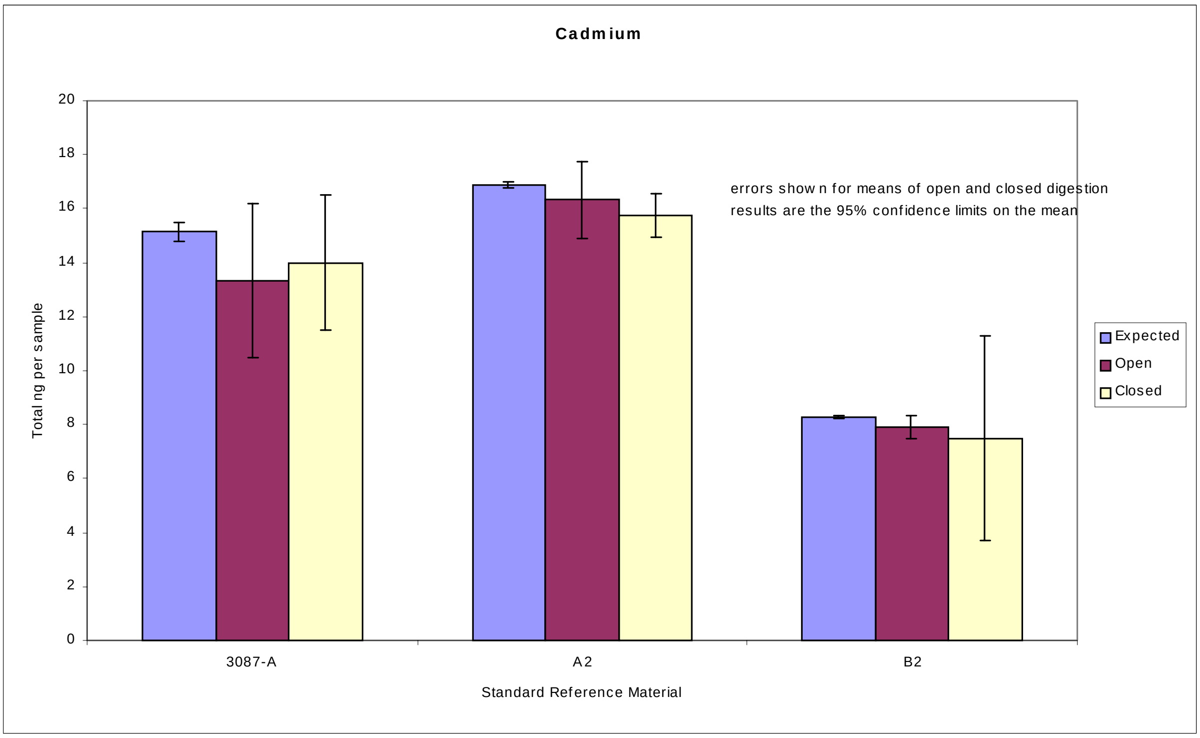
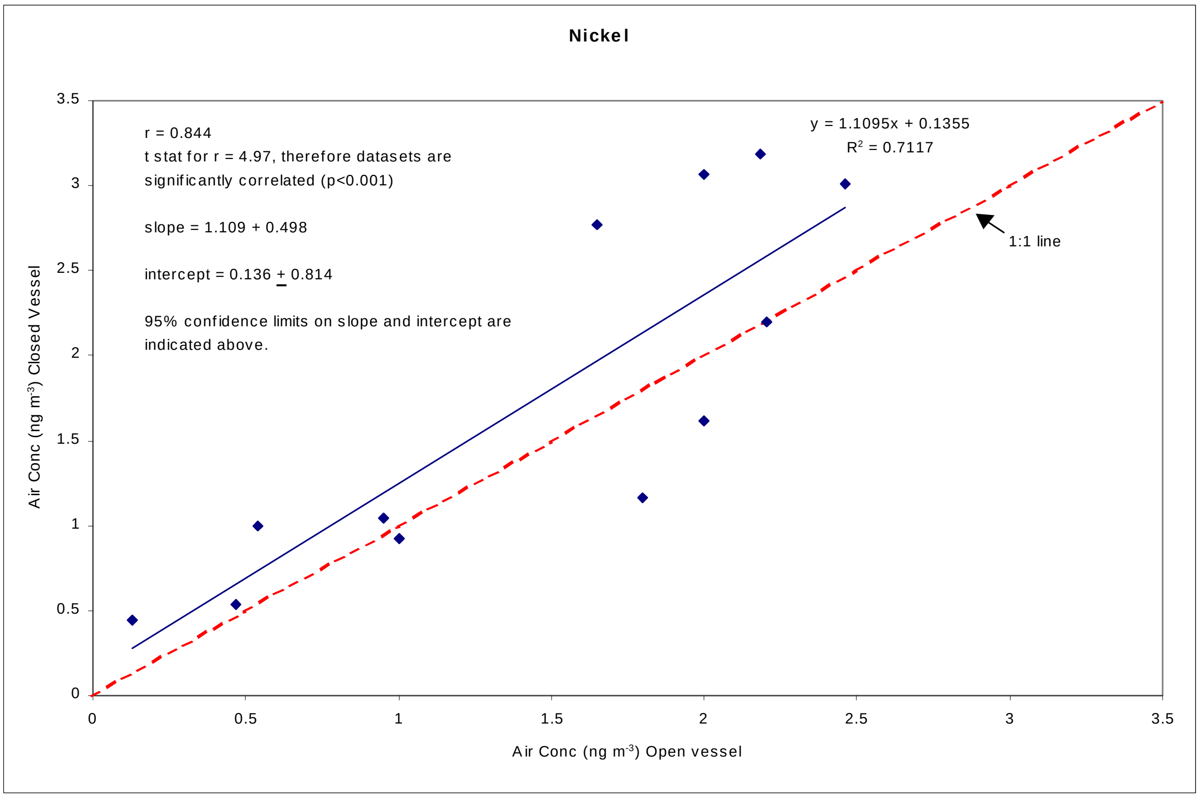


Figure 14b
Comparison of analysis of air filter samples and standard reference materials for Cd by ICP-MS following open and closed vessel digestion techniques



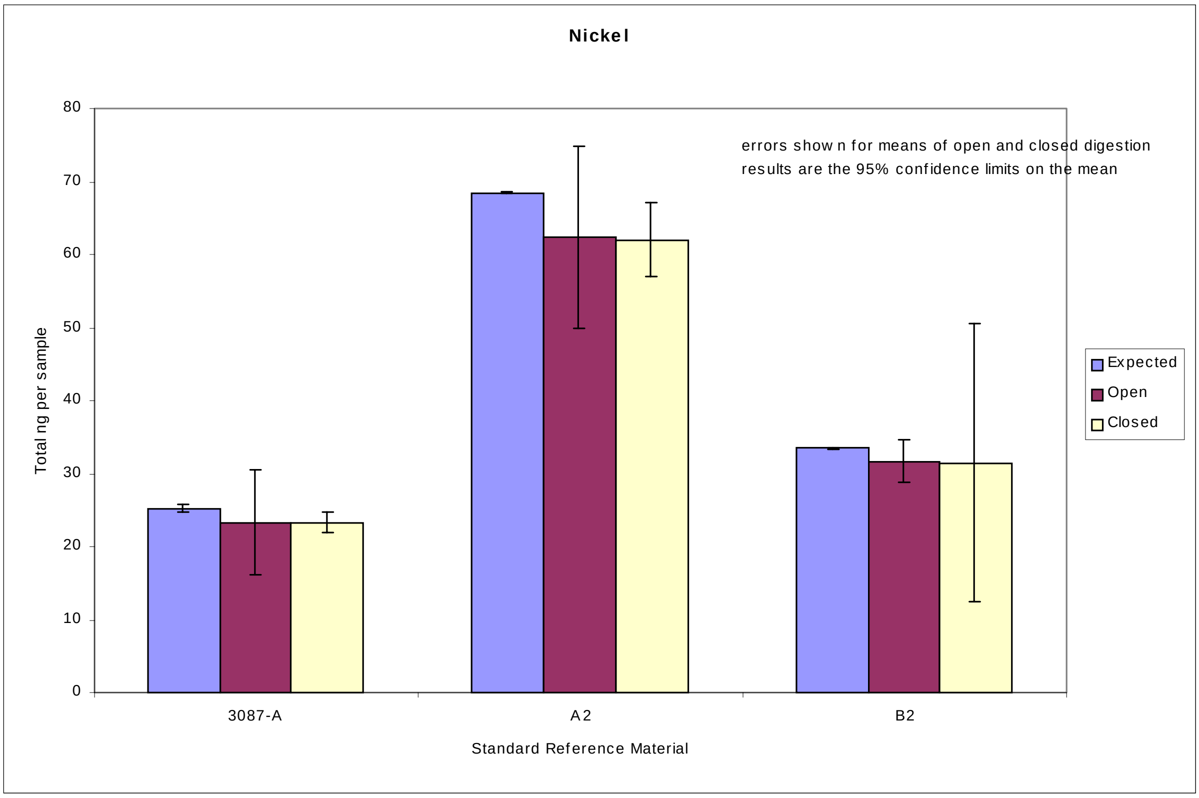
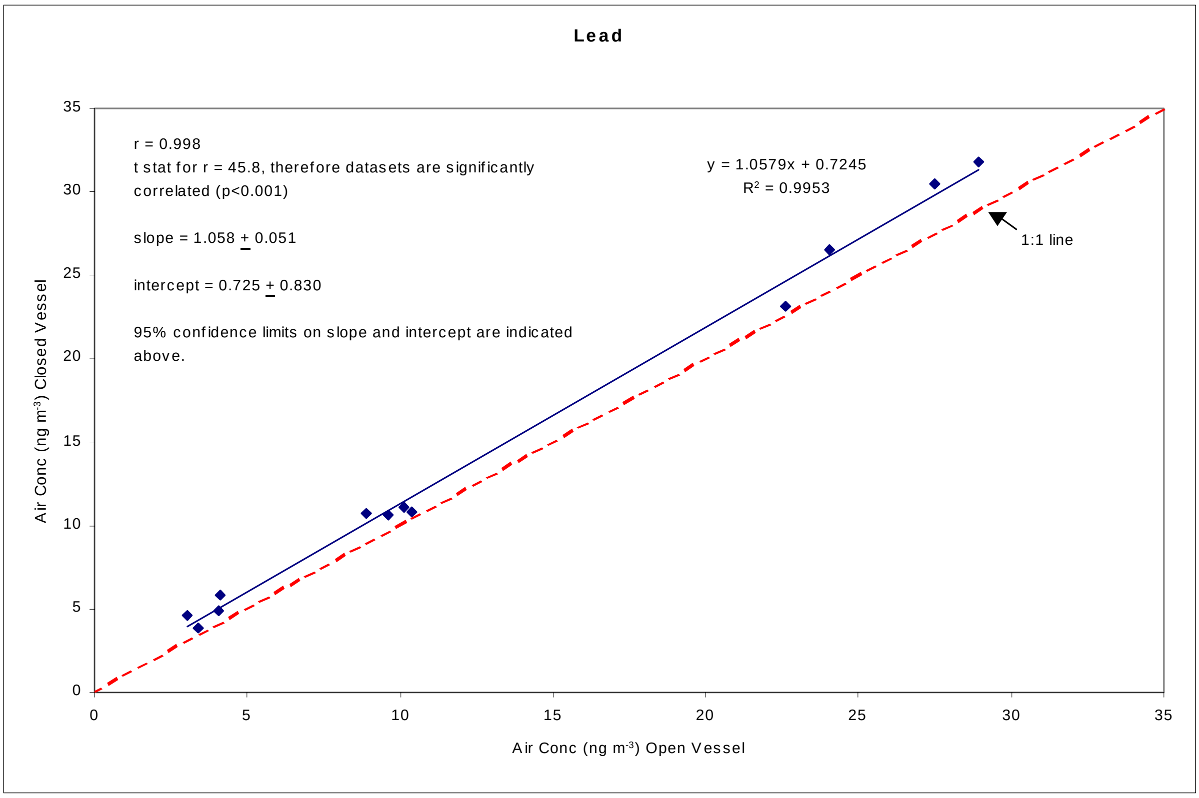


Figure 14c

Comparison of analysis of air filter samples and standard reference materials for Ni by ICP-MS following open and closed vessel digestion techniques



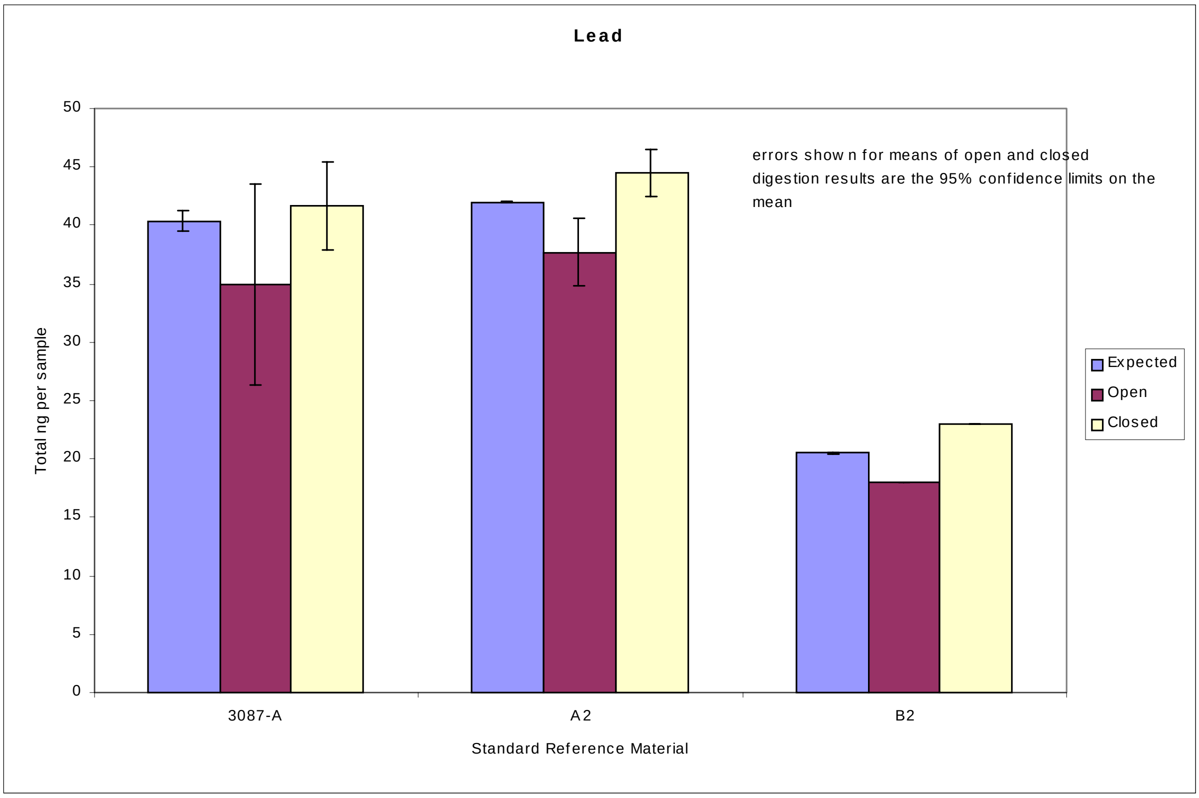


Figure 14d

Comparison of analysis of air filter samples and standard reference materials for Pb by ICP-MS following open and closed vessel digestion techniques

differed in their precision, before the mean results of the two methods were compared using a *two-tailed Student's t-test*. The results of these statistical tests are summarised in Table 14.

Table 14
Summary of the results of the analysis of samples of standard reference materials by ICP-MS following open or closed vessel digestion techniques

Standard Reference Material	**Expected Result (ng sample^{-1})**	**Mean Analytical Result (ng sample^{-1}) (coefficient of variation is shown in parentheses)**		**F-test between Analytical Results ***	**t-test between Analytical Results****
		Open vessel digestion	**Closed vessel digestion**		
ARSENIC					
3087-A	50.48 ± 1.16	46.33 ± 11.57 (10%)	47.00 ± 4.30 (4%)	x	x
A2	8.68 ± 0.02	6.30 ± 2.59 (17%)	7.30 ± 0.65 (6%)	x	x
B2	4.25 ± 0.01	2.13 ± 1.15 (22%)	3.60 ± 1.27 (4%)	x	✓
CADMIUM					
3087-A	15.14 ± 0.35	13.33 ± 2.87 (9%)	14.00 ± 2.48 (7%)	x	x
A2	16.9 ± 0.1	16.33 ± 1.43 (4%)	15.75 ± 0.80 (3%)	x	x
B2	8.29 ± 0.05	7.90 ± 0.43 (2%)	7.50 ± 3.81 (6%)	x	x
NICKEL					
3087-A	25.24 ± 0.54	23.33 ± 7.17 (12%)	23.33 ± 1.43 (2%)	✓	x
A2	68.4 ± 0.1	62.33 ± 12.50 (8%)	62.00 ± 5.03 (5%)	x	x
B2	33.5 ± 0.1	31.67 ± 2.87 (4%)	31.50 ± 19 (7%)	x	x
LEAD					
3087-A	40.38 ± 0.92	35.00 ± 8.60 (10%)	41.67 ± 3.79 (4%)	x	✓
A2	42.0 ± 0.1	37.67 ± 2.87 (3%)	44.50 ± 2.05 (3%)	x	✓
B2	20.5 ± 0.1	18.00 ± 0.00 (0%)	23.00 ± 0.00 (0%)	-	-

Notes
1) Where the mean analytical result is significantly different from the expected result, the analytical result is highlighted in grey.
2) ***** The F-test compares the standard deviation (and variances) of each set of analytical results (open v closed vessel digestion). ✓ indicates a significant difference between variances was found and that a difference in precision between the methods was apparent.
3) ****** The t-test compares the means of each set of analytical results (open v closed vessel digestion). ✓ indicates a significant difference between the means was found.

5.1.3.1 Arsenic

For the air filter samples from the RTE network sites the air concentrations of As reported using both digestion methods were highly significantly correlated. There was a tendency for higher As concentrations to be reported by the closed vessel digestion technique. However, the 95% confidence limits on the slope and intercept of the regression line indicate that these parameters do not differ significantly from the 'ideal' values of 1 and 0, respectively.

For the SRM samples, higher levels of As were reported after closed vessel digestion, although both methods tended to 'under-recover', with mean results for the A2 and B2 SRMs being significantly different from the expected values (Figure 14a, Table 14). There was also a significant difference between the mean results of the analysis of SRM B2. It appears (although not proven to be statistically significant) that more consistent and precise results were obtained using the closed vessel digestion method, with results also nearer to the expected values for all three SRMs (Figure 14a, Table 14). Therefore, it is recommended that air filters obtained from the RTE network in future should be digested using the closed vessel technique prior to analysis for As by ICP-MS.

5.1.3.2 Cadmium

The results obtained using the open and close vessel digestion for Cd in the RTE network air filter samples were in good agreement (significantly correlated). However, for the higher levels of Cd that can be recorded by this particular monitoring network (0.3 ng m^{-3} or higher), higher concentrations were reported using the closed vessel technique (Figure 14b).

The analysis for Cd in the SRM samples was more accurate than in the case of As, with greater recoveries of the analyte apparent (Table A2.2, Appendix 2). Only the result obtained using the closed vessel digestion technique was significantly different from the expected value (Table 14). There was no significant difference between the precision of either method. Further, the differences between the mean results obtained by each were not significant, with neither method consistently reporting the lower or higher analytical results (Table 14, Figure 14b). Therefore, based on the results of this exercise, it is difficult to conclude that either digestion method is more suitable for the RTE network air filter samples for Cd analysis.

5.1.3.3 Nickel

The air concentrations of Ni that were obtained by the two methods were significantly correlated but higher concentrations tended to be reported following sample digestion in a closed vessel, particularly where higher levels of Ni were present(<2 ng m^{-3}) (Figure 14c).

In the analysis of the SRMs for Ni, digestion of the sample in an open vessel appeared to give the more accurate results since only significant differences between the mean results from the closed vessel technique and the expected values were found (Table 14). However, the closed vessel results were more precise (Figure 14c), certainly for the SRM 3087A (Table 14) although this was not the case for SRM B2 (Figure 14c).

Overall, no significant differences between the mean values for the SRMs using either of the two methods were apparent, however the closed method was either more precise or gave more consistent results for the SRMs. Based on this observation, combined with the tendency for higher values of Ni to be reported for the actual air filter samples using the closed digestion method, the closed method of digestion is recommended in the analysis of RTE network air filter samples for Ni.

5.1.3.4 Lead

The results obtained for the RTE network air filter samples were significantly correlated (Figure 14d). For all 12 samples the higher Pb concentrations were reported for the closed vessel digestion method (Figure 14d). The 95% confidence limits on the slope and intercept of the regression line indicate that the values for the slope and intercept do not differ significantly from 1 and 0, respectively.

In the analyses of the SRMs, the results from both digestion method techniques at first appear to be accurate and compare well with expected values; only the open vessel result for A2 was found to be significantly different from the true value. There was also no apparent difference between the precision of both methods (table 14, Figure 14d). However, when the mean results of both methods were compared, a statistically significant difference was found (Table 14). Although the closed vessel digestion technique consistently gave the higher Pb values, this method also consistently ‘over-recovered’ the Pb in the SRMs (Figure 14d and Table A2.2, Appendix 2). This ‘over-recovery’ suggests that some Pb contamination was present in the determinations using the closed vessel technique. This may be the reason why consistently higher air concentrations of Pb were reported for the actual filter samples by the closed vessel method. However, if a contamination problem is identified but could be overcome, then perhaps the closed vessel technique would be the preferred digestion method, prior to analysis by ICP-MS, in the analysis for Pb in RTE network air filter samples.

4)

5.2 RETROSPECTIVE ANALYSIS OF HISTORICAL AIR FILTERS FOR CADMIUM

5.2.1 Background

In an EU Draft Position Paper on ambient air pollution by As, Cd and Ni compounds, Member States have contributed information on current and long-term trends in ambient air concentrations of these metals. Although the recent annual mean concentrations of these metals that have been measured at rural locations in the UK were included in the Draft Position Paper, no information on long-term trend trends in air concentrations at rural sites in the UK were included.

The long-term datasets from the Rural Trace Element network exist for As and Ni for the period 1972-1999. However, due to the relatively poor sensitivity of INAA for Cd only a limited dataset for Cd is available; many historical measurements of Cd in air were below the prevailing analytical LOD. In order to improve the existing dataset for Cd, thus providing more accurate information on long-term trends in air concentrations, it was proposed to retrospectively analyse portions of archived historical air filters from the Rural Trace Element network for Cd.

5.2.2 Methodology

Historical air filter samples for the period 1979 to 1994 inclusive were obtained from AEA Technology's storage archive. Samples from Chilton, Styrrup and Wraymires were prepared for analysis on a quarterly basis by bulking together representative portions of monthly samples (as described in sections 2.3.1 and 5.1.2. A total of 192 samples were prepared for analysis.

No conclusive evidence was found to suggest that RTE network air filter samples should be digested using either the open or closed vessel techniques (section 5.1.3.2). However, this investigation did imply that for the other metals, e.g. the more volatile As, Ni and Pb, the microwave digestion in a closed vessel technique might be more suitable for their determination in RTE network air filter samples. Therefore, it was decided to use this technique in the retrospective determination of Cd in archived historical air filter samples from this network. The digests of the samples that were prepared could then be retained and stored appropriately should any further retrospective analyses for other volatile metals be required. These digests are now stored.

The samples were digested using the closed vessel microwave technique described in section 5.1.2. Concentrations of Cd were then measured using ICP-MS. The samples were analysed in batches and a number of blanks and standard reference materials were also analysed with each batch as described in section 5.1.2.

5.2.3 Results

The quarterly air concentrations of Cd (ng m^{-3}) for the period 1979-1994 at Chilton, Styrrup and Wraymires are listed in Tables A3.1 to A3.3, Appendix 3, respectively. These have been derived from the analytical results for Cd in the historical air filter samples and corresponding records of the volumes of air that were sampled. An annual mean has also been calculated for each year, based on the quarterly data, and is also listed in Tables A3.1 to A3.3, Appendix 3. The results for Cd in the SRMs that were also analysed along with the air filter samples are summarised in Table A3.4, Appendix 3.

The results for the SRMs provide a good measure of confidence in the data from this programme of retrospective analysis of archived air filter samples (Table A3.4, Appendix 3). The recovery of Cd in the analyses ranged between 95% and 106%. The accuracy of the analyses was good, i.e. no statistically significant differences between the average result for each of the three SRMs and the corresponding expected values was found. Also, the precision (or repeatability) of the analyses was good with low coefficients of variation (3 –6%) calculated for the analysis of each SRM.

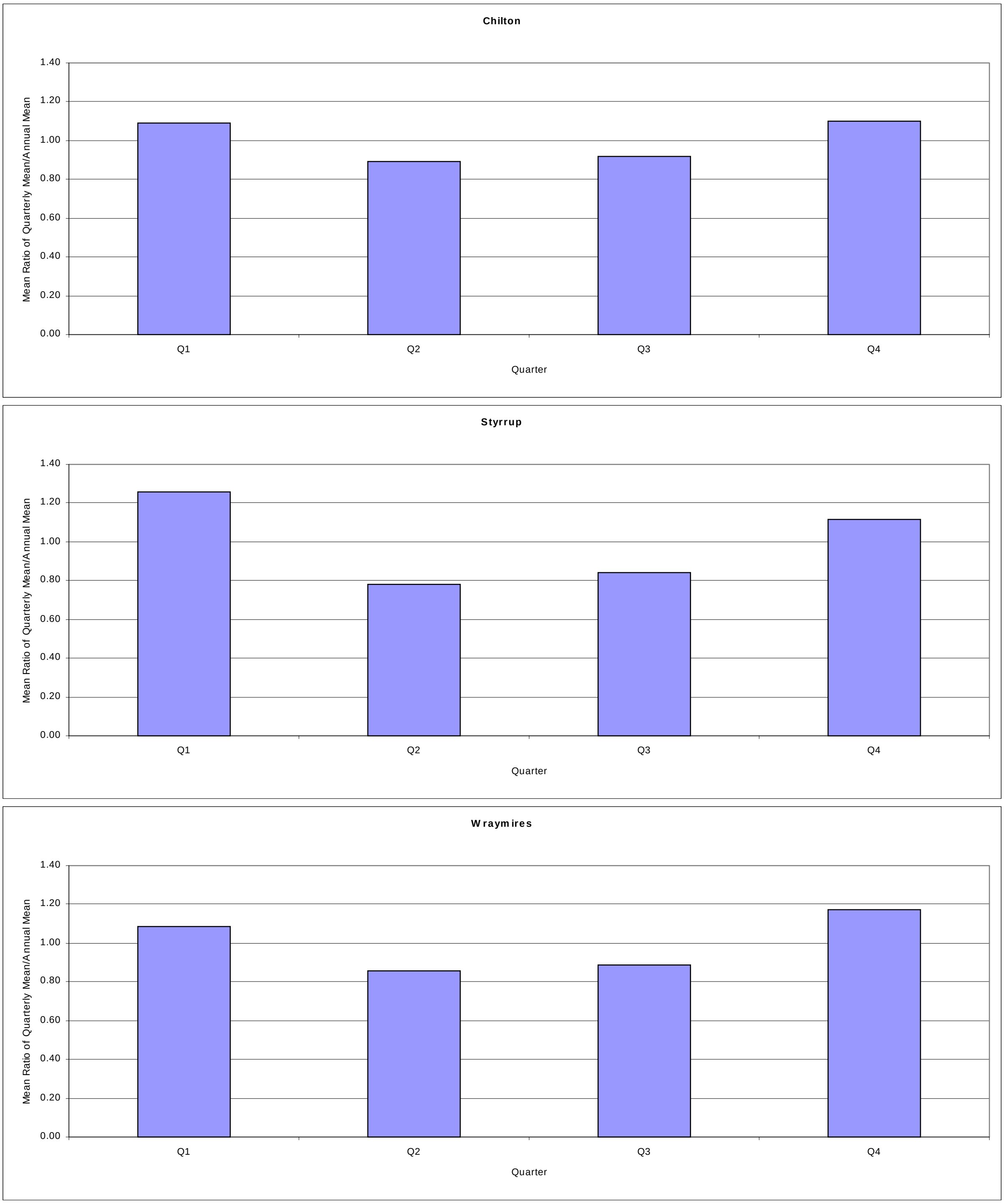


Figure 15
Seasonal variability in air concentrations of Cd
At Chilton, Styrrup and Wraymires (1979-1999)

5.2.3.1 Seasonal variability in the concentrations of cadmium in air

Historically, air concentrations of many of the elements have shown a seasonal variability (Cawse et al., 1995; Baker, 1997 and Baker, 1999). Now that the dataset for air concentrations of Cd has been improved, the seasonal variations during the period 1979-1999 has been investigated. The average ratio of the quarterly mean to annual mean during each of the four quarters has been derived and is shown, for each location, in Figure 15. At all three locations the highest ratios have tended to occur during the 'winter' quarters 1 and 4. In recent years (1992-1998) other anthropogenically-derived heavy metals such as As, Ni, Pb and V have also displayed similar seasonal variations (Baker, 1999). The 'winter' increases are attributed to the increased combustion of fossil fuels, together with the persistence of inversion layers in the atmosphere that decrease the dispersion of pollutants.

5.2.3.2 Long-term changes in rural air concentrations of cadmium

In section 4.1.1 the long-term changes in air concentrations of certain heavy metals at rural locations in the UK have been compared to corresponding changes in their atmospheric emissions. This comparison has now been made for Cd over the 20 year period 1979-1998.
The temporal changes in annual mean air concentrations of Cd at Chilton, Styrrup and Wraymires are plotted for the period 1979-1999 in Figure 16. The estimated annual total atmospheric emissions for the UK, during the period 1972-1998 are also plotted (Figure 16). In addition, the annual mean air concentrations (ng m^{-3}) of Cd have been plotted against annual estimates of total emissions (t) at each location (Figures 16).

Currently the main sources of Cd emissions to the atmosphere are non-ferrous metal production and iron and steel manufacture, with other contributions from fossil fuel combustion for electricity generation for public and industrial power needs. Since the 1970s the decline in Cd emissions is a result of the general fall in coal combustion and the decline in fuel oil combustion in power generation (Goodwin et al., 2000). A large decrease in estimated emissions has occurred post-1994 (Figure 16). Prior to 1994, waste incineration was one of the larger emission sources for Cd. The closure of many of the existing incinerators as a result of the implementation of the relevant EU directive and the implementation of stricter emission controls on those in continued use and built since is the main reason for the sudden decrease in estimated emissions in the late 1990s.

For other heavy metals the percentage reduction in the annual mean air concentrations of these metals, for the period 1994-1998 relative to 1972-1979 have been compared with the corresponding reductions in their estimated annual emissions (section 4.1.1). The available dataset for air concentrations of Cd is from 1979 only so a corresponding comparison cannot be made for Cd. Therefore, bearing in mind the sudden step-change in estimated emissions described above, the percentage reduction in emissions and air concentrations of Cd has been calculated for the period 1995-1998, relative to the four year period 1979-1982.

The reductions in the measured air concentrations were consistent at all three RTE network monitoring sites. These were 69%, 79% and 71% at Chilton, Styrrup and Wraymires, respectively. The corresponding reduction in estimated emissions was only 44%. Such a discrepancy was also apparent for Zn and the uncertainty in emissions estimates (Goodwin et al., 2000), which was thought to be the main cause (section 4.1.1.2).

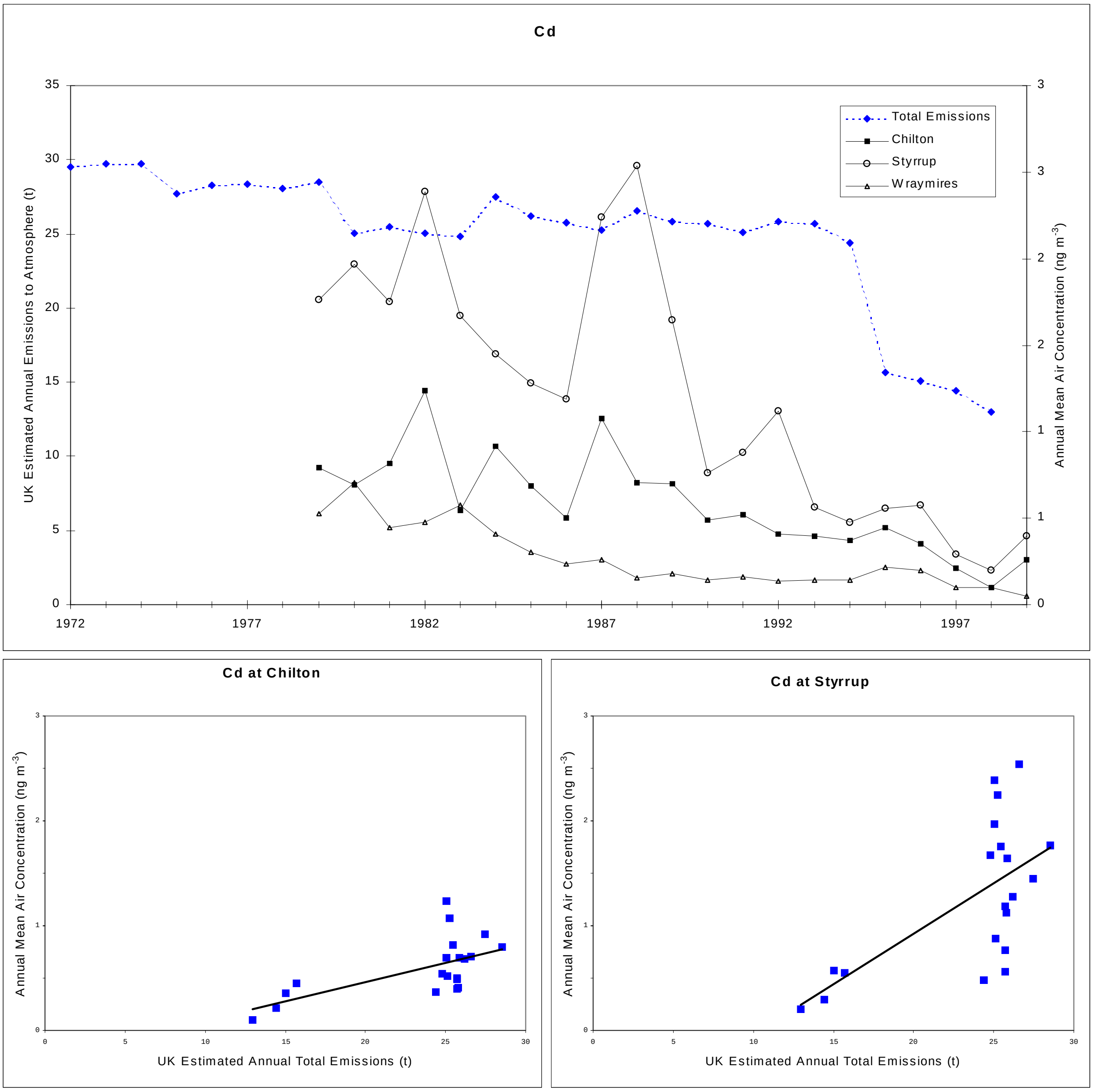


Figure 16
Comparison of annual mean air concentrations of Cd at rural locations with the estimated annual total UK emissions to the atmosphere (1979-1998)

However, for the period 1979-1998, annual mean air concentrations of Cd were significantly correlated with annual emissions, particularly at Chilton ($r = 0.620$, $p < 0.01$) and Styrrup ($r = 0.637$, $p < 0.01$), but less so at Wraymires ($r = 0.385$, $p < 0.1$). The post-1994 step change in emissions has not been exactly mirrored in rural air concentrations but levels of Cd in air over the last three years do appear to have fallen when compared with measurements in the earlier part of the 1990s. This observation is more apparent at Chilton and Styrrup than at Wraymires (Figure 16).

Similar reductions in air concentrations have also been recorded at other rural locations in the UK. The reductions in annual mean air concentrations between 1987-1990 and 1996-1999 were 45% at Banchory, 52% at East Ruston and 78% at High Muffles/Staxton Wold, compared with a 44% reduction in annual mean estimated total emissions of Cd in the UK between 1987-1990 and 1995-1998. Measured air concentrations at these east coast sites were also significantly correlated with emissions during the period 1987-1998 (Playford and Baker, 2000).

6 Conclusions

A long-term programme of measurements of trace and major elements, in airborne particulate material and rainwater at ground level at three rural locations in England, the Rural Trace Elements (RTE) network, has been continued during 1999. Concentrations of 35 elements in air and 25 elements in rainwater (plus nitrate and sulphate) have been measured on a quarterly basis during this year.

These measurements have been compared with earlier data from the 1990s. They have also been incorporated with corresponding historical data, compiled since the early 1970s, to update an on-going investigation into long-term changes in the UK rural environment in relation to changes in methods of energy production, energy consumption and emissions control policy.

The main conclusions are:

- Concentrations of many of the trace (including heavy metals) and major elements measured in air and rainwater at each of the three RTE network sites during 1999 were similar to those recorded in the preceding three years.

- Recent annual mean concentrations of heavy metals in air and rainwater at two sites, Chilton and Wraymires, are similar to those measured at other rural locations in the UK. At Styrrup, both air and rainwater concentrations were slightly elevated in comparison, owing to regional power generation and industrial influences. Over the last five years (1995-1999 inclusive), the average annual mean concentrations of these metals at rural locations in the UK are in the following ranges:

  Air (ng m^{-3})

  As (0.3 - 0.9); ~3 at Styrrup.
  Cd (0.1 - 0.4).
  Cr (0.5 - 0.7); ~5 at Styrrup.
  Cu (2 - 4); ~7 at Styrrup.
  Ni (0.6 – 1.5); ~4 at Styrrup.
  Pb (3 - 18); ~35 at Styrrup.
  Zn (15 - 33);~58 at Styrrup.

  Rainwater (µg l^{-1})

  As (0.1 - 0.3); ~0.5 at Styrrup.
  Cd (0.07 - 0.3);
  Cr (0.07 - 0.4).
  Cu (1 - 2); 6 - 7 at Chilton, Styrrup and Wraymires.
  Ni (0.3 – 0.9); ~2 at Styrrup.
  Pb (1 - 4).
  Zn (9 - 20);~45 at Styrrup.

- Insufficient data exist to enable all the spatial variance in average air concentrations of heavy metals to be defined. However, in the broad spatial distribution in the UK a north-south gradient is apparent, with the lowest values observed in north-eastern Scotland.

- The current annual average air concentrations of several heavy metals at urban sites in the UK exceed those at rural locations. ~5 to ~7-fold increases in concentrations of Cd, Cu, Fe and Ni were seen, while those for Cr and Pb were 3 to 4 times greater. Urban airborne levels of Mn, V and Zn were twice those at rural locations.

- Average air concentrations of Pb have continued to fall at rural locations in the UK. In 1999 the highest annual mean air concentration of Pb (26 ng m^{-3}) that was measured was only 5% of the ambient air quality limit value of 0.5 $\mu g\ m^{-3}$ proposed by the EC Framework Directive on Ambient Air Quality Assessment and Management (96/62/EC) or 10% of the 0.25 $\mu g\ m^{-3}$ recommended by EPAQS as an air quality standard for Pb for the UK.

- The main source of atmospheric Pb is vehicle emissions. Restrictions, imposed since 1972, on the use of Pb additives in petrol have substantially reduced the concentrations of airborne Pb in the UK rural environment. The effect of the restrictions was particularly noticeable after the most recent regulation in January 1986. The increase in the use of unleaded petrol since 1988 has contributed to further reductions in concentrations of Pb in air and rainwater at rural UK sites. Comparison of the periods 1972-1979 and 1990-1999 shows that reductions in annual mean air concentrations and depositions of Pb of between 80% and 90 % have been recorded. The percentage reductions in annual mean air concentrations of Pb, between the periods 1972-1979 and 1994-1998, were consistent all the three RTE network sites (84%-86%) and compared well with the corresponding reduction in estimated atmospheric emissions in the UK (82%). Similar reductions in the deposition of Pb at these sites were also observed (75%-93%).

- Annual mean air concentrations of Cd at rural locations in the UK during 1999 were below 0.3 ng m^{-3} and were within the WHO range of guideline values, i.e. <1 - 5 ng m^{-3}.

- Substantial decreases in air concentrations of the heavy metals, As, Cr, Cu, Ni, V and Zn have been measured since the 1970s. The reductions in their average annual mean concentrations between 1972-1979 and 1990-1999 were around 60% - 80%. Similar reductions in the deposition of Cu, Ni, V and Zn have also been recorded. The decreases in rural annual mean air concentrations of As, Cr, Ni, Se and V have closely followed corresponding decreases in their estimated emissions to the atmosphere in the UK since the 1970s. The reductions in the average annual mean air concentrations of these metals (particularly Ni, Se and V), between the periods 1972-1979 and 1994-1998, were very similar to the corresponding reduction in estimated emissions. This was also true for the deposition of Ni and V.

- Percentage reductions between 1972-1979 and 1994-1998 for Zn in both air and rainwater were very consistent (mainly between 67% - 72%) at rural locations. However, the corresponding reduction in estimated emissions was only 30%. This reflects the higher uncertainty in the estimates for Zn emissions compared to other metals such as Ni and V. The proportion from fossil fuel combustion is also estimated to be much less for Zn, with larger contributions from other sources such as ferrous and non-ferrous metals production, waste incineration and road transport (tyre wear).

- The major source of airborne As, Cr, Cu, Se and in particular Ni and V, in the UK is the combustion of fossil fuels for public power generation and industrial energy requirements. Therefore, the beneficial impact that changes in methods of energy production and associated abatement technology has had on rural air quality with respect to heavy metals in the UK, is illustrated by this long-term measurements programme.

- Considerable reductions in both air concentrations and in the deposition of Al, Fe, Mn and Sc (elements thought to be predominantly soil-derived origin) were apparent since the 1970s. The decreases in their average annual mean concentrations and deposition (not Sc) between 1972-1979 and 1990-1999 were around 60% - 80%, i.e. similar to those for heavy metals of predominantly anthropogenic origin. Consequently, reductions in fly-ash emissions from changes in fossil fuel combustion and abatement technology described above can probably explain the long-term decreases in airborne Al, Fe, Mn and Sc at rural locations in the UK.

- Air concentrations of Ca, K and Mg have also declined by a similar magnitude since the 1970s. Soil dust has long been assumed to be a major source of these elements, together with a contribution from marine-derived aerosols. However as for Al, Fe, Mn and Sc, the large long-term reductions in air concentrations of Ca, K and Mg are likely to be due to decreases in fly-ash emissions. The corresponding decreases in the annual mean deposition of Mg were much less marked and were more similar to those recorded for Na of marine-aerosol origin (particularly at Wraymires); Less reliable historical measurements of deposits of Ca and K prevented their investigation. This suggests that the main source of Mg in bulk deposition is marine aerosols. Differences in the sizes of particles (and therefore their source) that are sampled by the air sampler and bulk deposition collector can account for the apparent difference in the long-term changes for Mg in air and in bulk deposition.

To complement the routine measurements programme, two additional pieces of work were undertaken during 2000. These were:

(1) An intercomparison of the analysis of air filters for arsenic, cadmium, lead and nickel. The objective was to compare the determination of these metals in using two different sample digestion techniques, i.e. open and closed vessel digestions.

In the analysis of RTE network air filters for As, Cd, Ni and Pb, the digestion of the filter samples should in future be undertaken in a closed vessel, using a microwave digestion procedure. More consistent and precise results, particularly for the more volatile As and for Ni, were obtained following closed vessel digestion compared to use of an open vessel. Results for Cd and Pb were less conclusive. However, since these analytes are currently determined on the same samples as Ni, then the closed vessel method will be used in their determinations.

(2) The retrospective analysis of samples of historical air filters for cadmium. The objective was to improve the existing dataset for measurements of cadmium in airborne particulate material at the three long-term sampling sites.

- The retrospective analysis of archived air filter samples from the RTE monitoring network for Cd has been successfully achieved. A closed vessel digestion method was used prior to analysis by ICP-MS. Simultaneous analysis of appropriate Standard Reference Materials has confirmed the integrity of the analysis of historical air filter samples.

- Data on quarterly and annual Cd concentrations in air at RTE network sites are now available for the period 1979 to 1999.

- Over the last 21 years, air concentrations of Cd at rural locations in the UK, have exhibited a seasonal variability. The higher concentrations have tended to be measured during the ‘winter’ quarters, January to March and October to December. Such seasonal variations have previously been observed for other heavy metals and major elements.

- The long-term reductions in air concentrations of Cd have been consistent at all three RTE network sampling locations. Comparing the periods 1979-1982 and 1995-1998, the reductions in annual mean air concentrations were in the range 69%-79%. The corresponding reduction in estimated emissions to the atmosphere in the UK was only 44%. The discrepancy is attributed to the uncertainty in emissions estimates. However, between 1979 and 1998 the measured average annual air concentrations of Cd were significantly correlated with estimates of emissions.

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Appendix 1

Tables of quarterly and annual mean concentrations of elements in air and rainwater at Chilton, Styrrup and Wraymires in 1999

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TABLE A1.1 QUARTERLY AND ANNUAL MEAN CONCENTRATIONS OF ELEMENTS IN AIR AT CHILTON (1999).

Element	Quarterly Mean Concentration of Element in Air (ng/m^3)				Annual Mean Concentration in Air (ng/m^3)	Annual Mean Air Particulate Enrichment Factor
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec		
Ag	0.053	0.053	0.039	0.057	0.051	277
Al	58.5	90.4	78.7	45.7	68.3	0.5
As	0.50	0.43	0.37	0.46	0.44	39
Au	< 0.01	< 0.01	< 0.02	< 0.08	< 0.03	-
Br	4.0	4.5	3.8	4.6	4.2	458
Ca	159	167	291	< 86	176	6.9
Cd	0.26	0.23	0.29	0.31	0.27	2437
Ce	0.10	0.14	0.12	0.086	0.11	1.2
Cl	1250	869	800	998	979	5380
Co	0.14	0.10	0.070	0.060	0.093	6.5
Cr	0.54	0.48	0.47	0.45	0.49	2.7
Cs	0.023	0.026	0.025	0.021	0.024	2.1
Cu	2.9	3.0	2.3	2.7	2.7	72
Eu	0.0030	0.0057	0.0030	0.0036	0.0038	5.3
Fe	90.2	119	98.5	75.7	96	1.4
Hg	0.12	0.074	0.059	0.19	0.11	1981
I	0.90	0.87	0.79	1.0	0.89	96
In	< 0.009	< 0.003	< 0.004	< 0.007	< 0.006	-
K	121	66.3	143	85.7	104	4.0
La	< 0.2	< 0.1	0.27	< 0.1	< 0.2	-
Mg	107	110	112	93.0	106	11.4
Mn	2.1	2.4	3.1	1.8	2.4	1.5
Mo	< 1	< 1	< 1	< 3	< 2	-
Na	536	459	475	540	503	43
Ni	1.8	2.0	1.7	0.95	1.6	21.8
Pb	10.1	9.6	8.9	10.4	9.8	536
Rb	< 0.1	0.38	0.40	< 0.1	< 0.2	-
Sb	0.67	0.89	0.71	0.83	0.78	60
Sc	0.011	0.018	0.015	0.0081	0.013	1.0
Se	0.30	0.49	0.46	0.36	0.40	1068
Sm	0.0080	0.0082	0.010	< 0.007	0.0083	0.02
Ti	5.5	7.4	7.3	4.4	6.2	0.7
V	1.4	1.7	1.9	1.0	1.5	8
W	0.68	0.34	< 0.1	0.34	0.37	201
Zn	41.6	26.3	25.6	26.4	30.0	325
TSP (µg/m^3)	11	12	13	4	10	

Note

(i) Air particulate enrichment factors are normalised to scandium. These are not derived where the annual mean concentration of an element is below the limit of detection.

TABLE A1.2 QUARTERLY AND ANNUAL MEAN CONCENTRATIONS OF ELEMENTS IN AIR AT STYRRUP (1

Element	Quarterly Mean Concentration of Element in Air (ng/m^{3}				Annual Mean Concentration in Air (ng/m^{3})	Annual Mean Air Particulate Enrichment Factor
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec		
Ag	0.11	0.080	0.10	0.12	0.10	318
Al	100	112	157	87.9	114	0.5
As	3.3	1.5	2.1	2.5	2.4	119
Au	< 0.004	< 0.003	< 0.01	< 0.02	< 0.01	-
Br	13.4	6.5	7.7	13.1	10.2	623
Ca	286	298	294	307	296	6.6
Cd	0.33	0.23	0.29	0.27	0.28	1416
Ce	0.22	0.19	0.26	0.21	0.22	1.3
Cl	2102	1231	1166	2551	1763	5474
Co	0.24	0.14	0.18	0.19	0.19	7.4
Cr	3.8	3.8	4.1	5.4	4.3	13.3
Cs	0.043	0.039	0.045	0.030	0.039	2.0
Cu	5.0	3.3	4.3	4.8	4.4	65
Eu	0.0065	0.0037	0.0056	0.0053	0.0053	4.2
Fe	194	161	223	183	190	1.5
Hf	0.026	0.022	0.028	0.019	0.024	1.2
Hg	0.39	0.067	0.10	0.57	0.28	2849
I	1.5	1.3	1.3	1.5	1.4	86
In	0.026	< 0.004	0.022	0.029	0.020	196
K	160	122	231	269	196	4.3
La	0.18	0.16	0.28	0.18	0.20	2.0
Mg	212	178	222	262	219	13.4
Mn	11.5	10.7	11.9	11.2	11.3	4.1
Mo	2.7	1.6	1.8	2.0	2.0	304
Na	912	644	573	1298	857	41
Ni	2.2	2.0	2.2	2.5	2.2	17
Pb	28.9	22.6	24.1	27.5	25.8	800
Rb	0.61	0.56	0.73	0.67	0.64	2
Sb	2.2	1.4	1.7	2.1	1.9	80
Sc	0.022	0.022	0.031	0.017	0.023	1.0
Se	1.9	1.8	2.2	1.6	1.9	2811
Ti	7.4	11.2	15.8	14.6	12.3	0.8
V	3.4	2.6	3.3	3.3	3.2	9.8
W	1.1	0.50	0.55	0.83	0.75	231
Zn	55.4	54.8	72.6	76.5	64.8	397
TSP (µg/m^{3})	17	20	16	9	16	

Note

(i) Air particulate enrichment factors are normalised to scandium. These are not derived where the annual mean concentration of an element is below the limit of detection.

TABLE A1.3 QUARTERLY AND ANNUAL MEAN CONCENTRATIONS OF ELEMENTS IN AIR AT WRAYMIRES

Element	Quarterly Mean Concentration of Element in Air (ng/m^3				Annual Mean Concentration in Air (ng/m^3)	Annual Mean Air Particulate Enrichment Factor
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec		
Ag	0.020	0.035	0.031	0.029	0.029	216
Al	31.0	73.7	66.6	22.6	48.5	0.5
As	0.48	0.52	0.31	0.37	0.42	51
Au	< 0.01	< 0.01	< 0.01	< 0.005	< 0.01	-
Br	8.7	5.7	4.7	8.6	6.9	1027
Ca	145	122	116	129	128	6.9
Cd	0.03	0.07	0.05	0.09	0.06	734
Ce	0.071	0.13	0.12	0.063	0.10	1.4
Cl	2666	1448	946	2334	1849	13898
Co	0.059	0.088	0.073	0.060	0.070	6.7
Cr	0.20	0.40	0.58	0.18	0.34	2.6
Cs	0.015	0.021	0.036	0.0095	0.020	2.5
Cu	0.80	1.1	1.4	1.3	1.2	42
Eu	0.0015	0.0037	0.0029	< 0.001	0.0023	4.4
Fe	35.1	79.3	68.6	25.5	52.1	1.0
Hf	0.0053	0.0084	0.0095	0.0039	0.0068	0.8
Hg	0.31	0.087	0.090	0.47	0.24	5857
I	1.2	1.0	0.85	1.2	1.1	158
In	< 0.007	< 0.006	< 0.005	< 0.007	< 0.006	-
K	< 97	97.1	102	< 100	< 99	5.2
La	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	-
Mg	195	154	122	183	164	24.2
Mn	1.0	2.2	2.2	0.81	1.6	1.4
Mo	< 2	< 1	< 2	< 2	< 2	-
Na	1448	797	576	1290	1028	120
Ni	0.68	0.54	0.47	1.0	0.67	12
Pb	3.0	4.1	4.1	3.4	3.7	274
Rb	< 0.1	< 0.1	< 0.1	< 0.5	< 0.2	-
Sb	0.34	0.40	0.45	0.32	0.38	40
Sc	0.0058	0.014	0.013	0.0051	0.0095	1.0
Se	0.41	0.65	0.67	0.31	0.51	1851
Ti	< 7	7.2	< 7	< 7	< 7	-
V	1.4	1.5	1.5	0.74	1.3	9.7
W	< 0.3	< 0.2	< 0.1	< 0.2	< 0.2	-
Zn	5.2	7.6	6.6	16.7	9.0	134
TSP (μg/m^3)	9	13	12	6	10	

Note

(i) Air particulate enrichment factors are normalised to scandium. These are not derived where the annual mean concentration of an element is below the limit of detection.

TABLE A1.4 QUARTERLY AND ANNUAL MEAN CONCENTRATIONS AND DEPOSITION OF ELEMENTS IN RAINWATER AT CHILTON (1999).

Element	Quarterly Mean Concentration in Rainwater (µg/l)				Total Annual Rainfall (mm)	Annual Mean Concentration in Rainwater (µg/l)	Quarterly Deposition (µg/m^2)				Annual Deposition (µg/m^2)
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec			Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	
Rainfall (mm)	153	188	227	210	778						
Ag	< 0.001	< 0.001	< 0.001	< 0.001		< 0.001	< 1.53E-01	< 1.88E-01	< 2.27E-01	< 2.10E-01	< 7.78E-01
Al	< 4	< 4	< 4	< 4		< 4	< 6.12E+02	< 7.52E+02	< 9.08E+02	< 8.40E+02	< 3.11E+03
As	0.11	0.17	0.09	0.08		0.11	1.68E+01	3.20E+01	2.04E+01	1.68E+01	8.60E+01
Au	< 0.06	< 0.06	< 0.06	< 0.06		< 0.06	< 9.18E+00	< 1.13E+01	< 1.36E+01	< 1.26E+01	< 4.67E+01
Ca	460	660	710	300		538	7.04E+04	1.24E+05	1.61E+05	6.30E+04	4.19E+05
Cd	0.06	0.10	0.08	0.08		0.08	9.18E+00	1.88E+01	1.82E+01	1.68E+01	6.29E+01
Co	0.04	0.06	0.04	0.02		0.04	6.12E+00	1.13E+01	9.08E+00	4.20E+00	3.07E+01
Cr	0.06	0.08	0.12	0.04		0.08	9.18E+00	1.50E+01	2.72E+01	8.40E+00	5.99E+01
Cu	0.6	1.4	0.8	0.6		0.9	9.18E+01	2.63E+02	1.82E+02	1.26E+02	6.63E+02
Fe	1	3	6	2		3	1.53E+02	5.64E+02	1.36E+03	4.20E+02	2.50E+03
Hg	< 0.01	< 0.01	< 0.01	< 0.01		< 0.01	< 1.53E+00	< 1.88E+00	< 2.27E+00	< 2.10E+00	< 7.78E+00
In	< 0.04	< 0.04	< 0.04	< 0.04		< 0.04	< 6.12E+00	< 7.52E+00	< 9.08E+00	< 8.40E+00	< 3.11E+01
K	84	70	89	80		81	1.29E+04	1.32E+04	2.02E+04	1.68E+04	6.30E+04
Mg	220	110	97	240		163	3.37E+04	2.07E+04	2.20E+04	5.04E+04	1.27E+05
Mn	2.0	3.9	3.4	1.4		2.7	3.06E+02	7.33E+02	7.72E+02	2.94E+02	2.11E+03
Mo	0.04	0.04	0.06	0.04		0.05	6.12E+00	7.52E+00	1.36E+01	8.40E+00	3.57E+01
Na	1680	680	560	1880		1166	2.57E+05	1.28E+05	1.27E+05	3.95E+05	9.07E+05
Ni	0.40	0.60	0.40	0.20		0.39	6.12E+01	1.13E+02	9.08E+01	4.20E+01	3.07E+02
Pb	0.20	0.80	0.60	0.60		0.57	3.06E+01	1.50E+02	1.36E+02	1.26E+02	4.43E+02
Sb	0.12	0.18	0.14	0.08		0.13	1.84E+01	3.38E+01	3.18E+01	1.68E+01	1.01E+02
Se	0.06	0.05	0.08	0.08		0.07	9.18E+00	9.40E+00	1.82E+01	1.68E+01	5.35E+01
Ti	0.06	0.1	0.1	< 0.06		0.08	9.18E+00	1.88E+01	2.27E+01	< 1.26E+01	6.33E+01
V	0.39	0.40	0.40	0.20		0.34	5.97E+01	7.52E+01	9.08E+01	4.20E+01	2.68E+02
W	< 0.07	< 0.07	< 0.07	< 0.07		< 0.07	< 1.07E+01	< 1.32E+01	< 1.59E+01	< 1.47E+01	< 5.45E+01
Zn	9.5	10.3	7.7	6.2		8.3	1.45E+03	1.94E+03	1.75E+03	1.30E+03	6.44E+03
NO_3^-	1910	2790	2040	1110		1945	2.92E+05	5.25E+05	4.63E+05	2.33E+05	1.51E+06
SO_4^{2-}	1770	2130	1650	1440		1733	2.71E+05	4.00E+05	3.75E+05	3.02E+05	1.35E+06
pH	5.0	4.9	5.7	5.1							

Note

(i) Only the soluble fraction of the rainwater samples was analysed.

TABLE A1.5 QUARTERLY AND ANNUAL MEAN CONCENTRATIONS AND DEPOSITION OF ELEMENTS IN RAINWATER AT STYRRUP (1999).

Element	Quarterly Mean Concentration in Rainwater (µg/l)				Total Annual Rainfall (mm)	Annual Mean Concentration in Rainwater (µg/l)	Quarterly Deposition (µg/m^2)				Annual Deposition (µg/m^2)
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec			Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	
Rainfall (mm)	139	154	222	144	659						
Ag	0.004	0.001	< 0.001	< 0.001		< 0.002	5.56E-01	1.54E-01	< 2.22E-01	< 1.44E-01	< 1.08E+00
Al	20	30	5	5		14	2.78E+03	4.62E+03	1.11E+03	7.20E+02	9.23E+03
As	0.17	0.28	0.35	0.22		0.27	2.36E+01	4.31E+01	7.77E+01	3.17E+01	1.76E+02
Au	< 0.06	< 0.06	< 0.06	< 0.06		< 0.06	< 8.34E+00	< 9.24E+00	< 1.33E+01	< 8.64E+00	< 3.95E+01
Ca	440	750	950	620		724	6.12E+04	1.16E+05	2.11E+05	8.93E+04	4.77E+05
Cd	0.06	0.10	0.10	0.08		0.09	8.34E+00	1.54E+01	2.22E+01	1.15E+01	5.75E+01
Co	0.12	0.10	0.01	0.08		0.07	1.67E+01	1.54E+01	2.22E+00	1.15E+01	4.58E+01
Cr	0.12	0.15	0.14	0.20		0.15	1.67E+01	2.31E+01	3.11E+01	2.88E+01	9.97E+01
Cu	4.0	2.1	1.8	1.6		2.3	5.56E+02	3.23E+02	4.00E+02	2.30E+02	1.51E+03
Fe	5	4	3	3		4	6.95E+02	6.16E+02	6.66E+02	4.32E+02	2.41E+03
Hg	< 0.01	< 0.01	< 0.01	< 0.01		< 0.01	< 1.39E+00	< 1.54E+00	< 2.22E+00	< 1.44E+00	< 6.59E+00
In	< 0.04	< 0.04	< 0.04	< 0.04		< 0.04	< 5.56E+00	< 6.16E+00	< 8.88E+00	< 5.76E+00	< 2.64E+01
K	50	140	200	150		143	6.95E+03	2.16E+04	4.44E+04	2.16E+04	9.45E+04
Mg	210	210	220	320		237	2.92E+04	3.23E+04	4.88E+04	4.61E+04	1.56E+05
Mn	5.6	9.9	10	5.4		8.0	7.78E+02	1.52E+03	2.22E+03	7.78E+02	5.30E+03
Mo	0.12	0.14	0.20	0.18		0.16	1.67E+01	2.16E+01	4.44E+01	2.59E+01	1.09E+02
Na	1080	640	680	1980		1039	1.50E+05	9.86E+04	1.51E+05	2.85E+05	6.85E+05
Ni	1.2	1.7	1.2	1.2		1.3	1.67E+02	2.62E+02	2.66E+02	1.73E+02	8.68E+02
Pb	2.6	2.0	0.8	0.6		1.4	3.61E+02	3.08E+02	1.78E+02	8.64E+01	9.33E+02
Sb	0.40	0.60	1.0	0.40		0.65	5.56E+01	9.24E+01	2.22E+02	5.76E+01	4.28E+02
Se	0.1	0.1	0.1	0.1		0.1	1.39E+01	1.54E+01	2.22E+01	1.44E+01	6.59E+01
Ti	0.1	0.1	0.1	0.1		0.1	1.39E+01	1.54E+01	2.22E+01	1.44E+01	6.59E+01
V	0.32	0.50	0.40	0.40		0.41	4.45E+01	7.70E+01	8.88E+01	5.76E+01	2.68E+02
W	< 0.07	< 0.07	< 0.07	< 0.07		< 0.07	< 9.73E+00	< 1.08E+01	< 1.55E+01	< 1.01E+01	< 4.61E+01
Zn	20	20	61	27		35	2.78E+03	3.08E+03	1.35E+04	3.89E+03	2.33E+04
NO_3^-	1820	2970	2530	1290		2212	2.53E+05	4.57E+05	5.62E+05	1.86E+05	1.46E+06
SO_4^{2-}	2610	3450	3270	2610		3029	3.63E+05	5.31E+05	7.26E+05	3.76E+05	2.00E+06
pH	4.3	4.3	5.4	5.1							

Note

(i) Only the soluble fraction of the rainwater samples was analysed.

TABLE A1.6 QUARTERLY AND ANNUAL MEAN CONCENTRATIONS AND DEPOSITION OF ELEMENTS IN RAINWATER AT WRAYMIRES (1999).

Element	Quarterly Mean Concentration in Rainwater (µg/l)				Total Annual Rainfall (mm)	Annual Mean Concentration in Rainwater (µg/l)	Quarterly Deposition (µg/m^2)				Annual Deposition (µg/m^2)
	Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec			Jan-Mar	Apr-Jun	Jul-Sep	Oct-Dec	
Rainfall (mm)	605	381	312	700	1998						
Ag	< 0.01	< 0.01	< 0.01	< 0.01		< 0.01	< 6.05E+00	< 3.81E+00	< 3.12E+00	< 7.00E+00	< 2.00E+01
Al	< 4	< 4	< 4	< 4		< 4	< 2.42E+03	< 1.52E+03	< 1.25E+03	< 2.80E+03	< 7.99E+03
As	0.06	0.07	0.09	0.06		0.07	3.63E+01	2.67E+01	2.81E+01	4.20E+01	1.33E+02
Au	< 0.06	< 0.06	< 0.06	< 0.06		< 0.06	< 3.63E+01	< 2.29E+01	< 1.87E+01	< 4.20E+01	< 1.20E+02
Ca	200	200	210	260		223	1.21E+05	7.62E+04	6.55E+04	1.82E+05	4.45E+05
Cd	0.04	0.06	0.08	0.02		0.04	2.42E+01	2.29E+01	2.50E+01	1.40E+01	8.60E+01
Co	0.02	0.04	0.04	0.02		0.03	1.21E+01	1.52E+01	1.25E+01	1.40E+01	5.38E+01
Cr	0.07	0.14	0.06	0.06		0.08	4.24E+01	5.33E+01	1.87E+01	4.20E+01	1.56E+02
Cu	7.9	1.4	1.2	0.6		3.1	4.78E+03	5.33E+02	3.74E+02	4.20E+02	6.11E+03
Fe	1	5	3	1		2	6.05E+02	1.91E+03	9.36E+02	7.00E+02	4.15E+03
Hg	< 0.01	< 0.01	< 0.01	< 0.01		< 0.01	< 6.05E+00	< 3.81E+00	< 3.12E+00	< 7.00E+00	< 2.00E+01
In	< 0.04	< 0.04	< 0.04	< 0.04		< 0.04	< 2.42E+01	< 1.52E+01	< 1.25E+01	< 2.80E+01	< 7.99E+01
K	110	60	120	190		130	6.66E+04	2.29E+04	3.74E+04	1.33E+05	2.60E+05
Mg	360	160	160	630		385	2.18E+05	6.10E+04	4.99E+04	4.41E+05	7.70E+05
Mn	0.60	1.8	3.0	0.80		1.3	3.63E+02	6.86E+02	9.36E+02	5.60E+02	2.54E+03
Mo	0.02	0.02	0.02	0.03		0.02	1.21E+01	7.62E+00	6.24E+00	2.10E+01	4.70E+01
Na	2880	1180	1180	5080		3061	1.74E+06	4.50E+05	3.68E+05	3.56E+06	6.12E+06
Ni	0.20	0.40	0.40	0.20		0.27	1.21E+02	1.52E+02	1.25E+02	1.40E+02	5.38E+02
Pb	0.60	0.80	0.60	0.40		0.57	3.63E+02	3.05E+02	1.87E+02	2.80E+02	1.14E+03
Sb	0.30	0.10	0.10	0.06		0.15	1.82E+02	3.81E+01	3.12E+01	4.20E+01	2.93E+02
Se	0.08	0.06	0.08	0.10		0.08	4.84E+01	2.29E+01	2.50E+01	7.00E+01	1.66E+02
Ti	< 0.06	0.08	0.08	0.07		0.07	< 3.63E+01	3.05E+01	2.50E+01	4.90E+01	1.41E+02
V	0.40	0.40	0.20	0.20		0.30	2.42E+02	1.52E+02	6.24E+01	1.40E+02	5.97E+02
W	< 0.07	< 0.07	< 0.07	< 0.07		< 0.07	< 4.24E+01	< 2.67E+01	< 2.18E+01	< 4.90E+01	< 1.40E+02
Zn	3.5	8.6	6.7	3.3		4.9	2.12E+03	3.28E+03	2.09E+03	2.31E+03	9.79E+03
NO_3^-	1370	1370	1370	670		1125	8.29E+05	5.22E+05	4.27E+05	4.69E+05	2.25E+06
SO_4^{2-}	1830	1860	1800	2250		1978	1.11E+06	7.09E+05	5.62E+05	1.58E+06	3.95E+06
pH	4.5	4.6	4.5	4.8							

Note

(i) Only the soluble fraction of the rainwater samples was analysed.

Appendix 2

Intercomparison of analysis of air filter samples for As, Cd, Ni and Pb using open and closed vessel digestion techniques

CONTENTS

Table A2.1 Quarterly air concentrations of As, Cd, Ni and Pb at Chilton, Styrrup and Wraymires in 1999 following the digestion of air filter papers using open and closed vessel techniques.

Table A2.2 Results for the determination of As, Cd, Ni and Pb in Standard Reference Materials, 3087-A, A2 and B2.

Table A2.1 Quarterly air concentrations of As, Cd, Ni and Pb at Chilton, Styrrup and Wraymires in 199 following the digestion of air filter papers using open and closed vessel techniques.

	Air Concentration (ng m^{-3})							
	Open Vessel Digestion				Closed Vessel Digestion			
	As	Cd	Ni	Pb	As	Cd	Ni	Pb
Chilton								
Jan-Mar	0.63	0.26	1.8	10.1	0.48	0.18	1.2	11.1
Apr-Jun	0.51	0.23	2.0	9.6	0.55	0.23	1.6	10.6
Jul-Sep	0.33	0.29	1.7	8.9	0.37	0.31	2.8	10.7
Oct-Dec	0.56	0.31	0.95	10.4	0.74	0.30	1.0	10.8
Styrrup								
Jan-Mar	3.3	0.33	2.2	28.9	3.5	0.39	3.2	31.8
Apr-Jun	1.9	0.23	2.0	22.6	2.1	0.23	3.1	23.1
Jul-Sep	2.5	0.29	2.2	24.1	3.1	0.44	2.2	26.6
Oct-Dec	2.3	0.27	2.5	27.5	2.5	0.53	3.0	30.5
Wraymires								
Jan-Mar	0.23	0.03	0.13	3.0	0.33	0.04	0.44	4.7
Apr-Jun	0.37	0.07	0.54	4.1	0.40	0.04	1.0	5.8
Jul-Sep	0.34	0.05	0.47	4.1	0.28	0.05	0.53	4.9
Oct-Dec	0.35	0.09	1.0	3.4	0.40	0.07	0.92	3.8

Table A2.2 Results for the determination of As, Cd, Ni and Pb in Standard Reference Materials, 3087-A, A2 and

Open digestion					Closed digestion				
		(Total ng/sample)		%			(Total ng/sample)		%
Analyte	Sample	Measured	Expected	Recovery	Analyte	Sample	Measured	Expected	Recovery
As	3087-A	41	50.48	81%	**As**	3087-A	49	50.48	97%
	3087-A	49	50.48	97%		3087-A	46	50.48	91%
	3087-A	49	50.48	97%		3087-A	46	50.48	91%
	A2-793	5.6	8.68	65%		A2-789	7.6	8.68	88%
	A2-783	7.5	8.68	86%		A2-788	7.7	8.68	89%
	A2-784	5.8	8.68	67%		A2-790	7.0	8.68	81%
	B2-1448	2.4	4.25	56%		A2-791	6.9	8.68	79%
	B2-1454	2.4	4.25	56%		B2-1451	3.7	4.25	87%
	B2-1455	1.6	4.25	38%		B2-1446	3.5	4.25	82%
Cd	3087-A	12	15.14	79%	**Cd**	3087-A	15	15.14	99%
	3087-A	14	15.14	92%		3087-A	14	15.14	92%
	3087-A	14	15.14	92%		3087-A	13	15.14	86%
	A2-793	16	16.9	95%		A2-789	16	16.9	95%
	A2-783	17	16.9	101%		A2-788	16	16.9	95%
	A2-784	16	16.9	95%		A2-790	16	16.9	95%
	B2-1448	7.8	8.29	94%		A2-791	15	16.9	89%
	B2-1454	8.1	8.29	98%		B2-1451	7.8	8.29	94%
	B2-1455	7.8	8.29	94%		B2-1446	7.2	8.29	87%
Ni	3087-A	20	25	80%	**Ni**	3087-A	49	50.48	97%
	3087-A	25	25	100%		3087-A	46	50.48	91%
	3087-A	25	25	100%		3087-A	23	25	92%
	A2-793	57	68.4	83%		A2-789	64	68.4	94%
	A2-783	67	68.4	98%		A2-788	65	68.4	95%
	A2-784	63	68.4	92%		A2-790	61	68.4	89%
	B2-1448	31	33.5	93%		A2-791	58	68.4	85%
	B2-1454	33	33.5	99%		B2-1451	33	33.5	99%
	B2-1455	31	33.5	93%		B2-1446	30	33.5	90%
Pb	3087-A	31	40.38	77%	**Pb**	3087-A	42	40.38	104%
	3087-A	37	40.38	92%		3087-A	40	40.38	99%
	3087-A	37	40.38	92%		3087-A	43	40.38	106%
	A2-793	37	42	88%		A2-789	45	42	107%
	A2-783	39	42	93%		A2-788	46	42	110%
	A2-784	37	42	88%		A2-790	44	42	105%
	B2-1448	18	20.5	88%		A2-791	43	42	102%
	B2-1454	18	20.5	88%		B2-1451	23	20.5	112%
	B2-1455	18	20.5	88%		B2-1446	23	20.5	112%

Appendix 3

Retrospective analysis of historical air filter samples (1979-1994 inclusive) from Chilton, Styrrup and Wraymires for Cd

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Table A3.1 Quarterly and annual mean air concentrations of cadmium at Chilton (1979-1994)
Table A3.2 Quarterly and annual mean air concentrations of cadmium at Styrrup (1979-1994)
Table A3.3 Quarterly and annual mean air concentrations of cadmium at Wraymires (1979-1994)
Table A3.4 Results of analysis of Standard Reference Materials for cadmium

Table A3.1 Quarterly and annual mean air concentra
of cadmium at Chilton (1979 - 1994).

Year	Quarter	Air Concentration of Cd (ng/m3)	Annual Mean (ng/m3)
1979	Jan-Mar	0.85	
	Apr-Jun	0.65	
	Jul-Sep	0.75	
	Oct-Dec	0.91	0.79
1980	Jan-Mar	0.77	
	Apr-Jun	0.54	
	Jul-Sep	0.55	
	Oct-Dec	0.90	0.69
1981	Jan-Mar	0.67	
	Apr-Jun	0.85	
	Jul-Sep	0.71	
	Oct-Dec	1.02	0.81
1982	Jan-Mar	1.17	
	Apr-Jun	2.52	
	Jul-Sep	0.62	
	Oct-Dec	0.64	1.24
1983	Jan-Mar	0.65	
	Apr-Jun	0.24	
	Jul-Sep	0.21	
	Oct-Dec	1.09	0.55
1984	Jan-Mar	1.14	
	Apr-Jun	0.83	
	Jul-Sep	1.03	
	Oct-Dec	0.67	0.92
1985	Jan-Mar	1.17	
	Apr-Jun	0.53	
	Jul-Sep	0.48	
	Oct-Dec	0.57	0.69
1986	Jan-Mar	0.53	
	Apr-Jun	0.49	
	Jul-Sep	0.72	
	Oct-Dec	0.26	0.50
1987	Jan-Mar	1.17	
	Apr-Jun	1.07	
	Jul-Sep	0.71	
	Oct-Dec	1.35	1.07
1988	Jan-Mar	0.37	
	Apr-Jun	0.55	
	Jul-Sep	0.80	
	Oct-Dec	1.10	0.71
1989	Jan-Mar	0.55	
	Apr-Jun	0.67	
	Jul-Sep	0.89	
	Oct-Dec	0.67	0.70
1990	Jan-Mar	0.37	
	Apr-Jun	0.48	
	Jul-Sep	0.47	
	Oct-Dec	0.63	0.49
1991	Jan-Mar	0.66	
	Apr-Jun	0.37	
	Jul-Sep	0.43	
	Oct-Dec	0.62	0.52
1992	Jan-Mar	0.53	
	Apr-Jun	0.37	
	Jul-Sep	0.41	
	Oct-Dec	0.32	0.41
1993	Jan-Mar	0.48	
	Apr-Jun	0.33	
	Jul-Sep	0.36	
	Oct-Dec	0.41	0.39
1994	Jan-Mar	0.40	
	Apr-Jun	0.26	
	Jul-Sep	0.28	
	Oct-Dec	0.53	0.37

Table A3.2 Quarterly and annual mean air concentra of cadmium at Styrrup (1979 - 1994).

Year	Quarter	Air Concentration of Cd (ng/m3)	Annual Mean (ng/m3)
1979	Jan-Mar	1.67	
	Apr-Jun	1.76	
	Jul-Sep	1.81	
	Oct-Dec	1.80	1.76
1980	Jan-Mar	3.93	
	Apr-Jun	1.41	
	Jul-Sep	1.32	
	Oct-Dec	1.21	1.97
1981	Jan-Mar	1.37	
	Apr-Jun	1.61	
	Jul-Sep	1.63	
	Oct-Dec	2.40	1.75
1982	Jan-Mar	2.50	
	Apr-Jun	1.48	
	Jul-Sep	2.83	
	Oct-Dec	2.73	2.39
1983	Jan-Mar	2.02	
	Apr-Jun	1.54	
	Jul-Sep	2.19	
	Oct-Dec	0.94	1.67
1984	Jan-Mar	2.61	
	Apr-Jun	1.20	
	Jul-Sep	1.39	
	Oct-Dec	0.57	1.45
1985	Jan-Mar	1.53	
	Apr-Jun	0.93	
	Jul-Sep	0.97	
	Oct-Dec	1.68	1.28
1986	Jan-Mar	1.39	
	Apr-Jun	0.99	
	Jul-Sep	1.30	
	Oct-Dec	1.08	1.19
1987	Jan-Mar	3.19	
	Apr-Jun	1.05	
	Jul-Sep	1.40	
	Oct-Dec	3.32	2.24
1988	Jan-Mar	3.77	
	Apr-Jun	1.50	
	Jul-Sep	1.28	
	Oct-Dec	3.60	2.54
1989	Jan-Mar	1.22	
	Apr-Jun	1.52	
	Jul-Sep	1.25	
	Oct-Dec	2.58	1.64
1990	Jan-Mar	0.67	
	Apr-Jun	0.92	
	Jul-Sep	0.63	
	Oct-Dec	0.83	0.76
1991	Jan-Mar	0.92	
	Apr-Jun	0.76	
	Jul-Sep	0.64	
	Oct-Dec	1.19	0.88
1992	Jan-Mar	1.42	
	Apr-Jun	0.82	
	Jul-Sep	0.84	
	Oct-Dec	1.40	1.12
1993	Jan-Mar	0.81	
	Apr-Jun	0.39	
	Jul-Sep	0.48	
	Oct-Dec	0.56	0.56
1994	Jan-Mar	0.40	
	Apr-Jun	0.35	
	Jul-Sep	0.37	
	Oct-Dec	0.79	0.48

Table A3.3 Quarterly and annual mean air concentra of cadmium at Wraymires (1979 - 1994).

Year	Quarter	Air Concentration of Cd (ng/m3)	Annual Mean (ng/m3)
1979	Jan-Mar	0.54	
	Apr-Jun	0.30	
	Jul-Sep	0.43	
	Oct-Dec	0.83	0.53
1980	Jan-Mar	0.91	
	Apr-Jun	0.35	
	Jul-Sep	1.13	
	Oct-Dec	0.44	0.71
1981	Jan-Mar	0.65	
	Apr-Jun	0.44	
	Jul-Sep	0.27	
	Oct-Dec	0.42	0.45
1982	Jan-Mar	0.66	
	Apr-Jun	0.34	
	Jul-Sep	0.48	
	Oct-Dec	0.42	0.48
1983	Jan-Mar	0.26	
	Apr-Jun	0.41	
	Jul-Sep	0.38	
	Oct-Dec	1.25	0.57
1984	Jan-Mar	0.54	
	Apr-Jun	0.30	
	Jul-Sep	0.31	
	Oct-Dec	0.48	0.41
1985	Jan-Mar	0.45	
	Apr-Jun	0.17	
	Jul-Sep	0.22	
	Oct-Dec	0.37	0.30
1986	Jan-Mar	0.40	
	Apr-Jun	0.22	
	Jul-Sep	0.17	
	Oct-Dec	0.15	0.23
1987	Jan-Mar	0.16	
	Apr-Jun	0.20	
	Jul-Sep	0.17	
	Oct-Dec	0.50	0.26
1988	Jan-Mar	0.17	
	Apr-Jun	0.15	
	Jul-Sep	0.12	
	Oct-Dec	0.17	0.15
1989	Jan-Mar	0.07	
	Apr-Jun	0.13	
	Jul-Sep	0.17	
	Oct-Dec	0.36	0.18
1990	Jan-Mar	0.12	
	Apr-Jun	0.20	
	Jul-Sep	0.11	
	Oct-Dec	0.13	0.14
1991	Jan-Mar	0.24	
	Apr-Jun	0.06	
	Jul-Sep	0.13	
	Oct-Dec	0.22	0.16
1992	Jan-Mar	0.18	
	Apr-Jun	0.17	
	Jul-Sep	0.11	
	Oct-Dec	0.10	0.14
1993	Jan-Mar	0.23	
	Apr-Jun	0.15	
	Jul-Sep	0.12	
	Oct-Dec	0.08	0.14
1994	Jan-Mar	0.14	
	Apr-Jun	0.08	
	Jul-Sep	0.29	
	Oct-Dec	0.07	0.14

Table A3.4 Results of analysis of Standard Reference Materials for cadmium.

	(Total ng/sample)			%
Sample	Measured	Expected	+/-	Recovery
3087a	16	15.14	0.35	106%
3087a	15			99%
3087a	15			99%
mean	15.33	+/-	1.43	101%
s.d	0.58			
coeff. of variation	4%			
t test for systematic error	0.58	No significant difference between mean and expected value.		
A2-731	17	16.9	0.1	101%
A2-734	17			101%
A2-735	17			101%
A2-736	17			101%
A2-737	16			95%
mean	16.80	+/-	0.56	99%
s.d	0.45			
coeff. of variation	3%			
t test for systematic error	-0.50	No significant difference between mean and expected value.		
B2-1011	8.0	8.29	0.05	97%
B2-1012	9.4			113%
B2-1013	8.3			100%
B2-1015	8.7			105%
B2-1416	7.3			88%
B2-1420	8.6			104%
B2-1450	8.3			100%
B2-1453	8.3			100%
B2-1014	8.2			99%
B2-1016	8.4			101%
B2-1017	8.5			103%
B2-1018	8.2			99%
mean	8.35	+/-	0.31	101%
s.d	0.49			
coeff. of variation	6%			
t test for systematic error	0.43	No significant difference between mean and expected value.		

Notes

(1) Uncertainty on the mean analytical result is the 95% confidence limit on the mean.