

Report

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UK Heavy Metal Monitoring Network

Project Number EPG 1/3/204

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Executive Summary

General

1. The new UK heavy metal network is providing high quality measurements of a wide range of metal concentrations in precipitation, hill cloud and in air at rural locations throughout the UK.
2. The concentrations of As, Cd, Cr, Cu, Ni, Pb, Se, V, Zn, in air and precipitation are measurable at all sites and provide independent estimates of annual wet and dry deposition. In addition, the following metals are measured in the collected samples, Al, Sc, Ti, Mn, Fe, Co, Rb, Sr, Mo, Sn, Sb, Ba and W.
3. A network of Hg measurements in precipitation and air at the UK rural metal measurement stations has been established.
4. The UK spatial patterns of concentration in rain and as aerosol for most metals from the first full year of measurements in the network show the smallest values in North West Britain with the larger values in the South East, typically by factors of 2 to 4 depending on the metal.
5. The total deposition of all metals with the exception of Ni and V in the UK considerably exceeds emissions in the NAEI. In the case of Cu and Zn the total deposition, wet and dry exceeds UK emissions by approximately a factor of five. Allowing for the fraction of emissions expected to be exported out of the country by the wind and the import of metals from non-UK sources, the NAEI emissions underestimate actual emissions of some of these metals by up to an order of magnitude.
6. These total deposition values do not take account of the additional deposition very close to major sources, because they are derived from an entirely rural measurement network, and the deposition of particles larger than 10 μm which are not sampled by the aerosol instruments, furthermore, the network does not include urban sites. For these reasons the deposition values *underestimate* the total UK deposition.
7. A remaining uncertainty in the UK budget is the fraction of the measured wet deposition which derives from dry deposition to the precipitation collector, the quantification of which we see as a main priority of the next phase of the work. Current evidence suggests that this value is < 20% of the wet deposited metal.
8. For the metals considered by EMEP (Cd and Pb), deposition in the UK substantially exceeds NAEI emission values. For Cd the EMEP deposition in the UK of 7.7 tonnes annually compares with 10.3 tonnes y^{-1} from the measurements, while for Pb the EMEP value is 377 tonnes y^{-1} and the measured value is 492 tonnes y^{-1} , while Pb emissions are predicted to have decreased strongly between these two estimates.
9. Maps of concentration of a range of metals in moss provide detailed spatial patterns of accumulation with time and in the case of Pb, there are statistically significant relationships between deposition and foliar concentration which can be used to map the spatial deposition fields. For some of the other metals (As, Cd, Cu, Ni, V and Zn), there appears to be very useful information in the mapped data, but further work is necessary to improve the correlation with measured deposition.
10. The fractionation of total deposition of metals in the UK between wet and dry deposition varies between the different metals but dry deposition is typically 30% of the total. These data show that dry deposition is a very important fraction of the total and needs to be measured to quantify the total deposition.
11. For most of the metals, current concentration and deposition values are smaller than those in earlier measurements, by between 20% to 60% relative to values in the mid 1990s.
12. The new network of (TGM) mercury measurements is operating satisfactorily, and the continuously operating site for speciated mercury has operated at CEH Edinburgh in 2003, and more recently at Auchencorth Moss.

13. Elemental mercury makes up over 97% of the total atmospheric mercury burden. The remaining amount consists of Reactive Gaseous Mercury (RGM) and Particulate Mercury (Hg^{P}). Hourly averages of these mercury species are measured at Auchencorth Moss in Southern Scotland and show for RGM and Hg^{P} concentrations of 2.7 pg m^{-3} and 2.8 pg m^{-3} respectively. However, due to the non-reactivity of elemental mercury, deposition to terrestrial surface is believed to be dominated by the reactive gaseous and particulate phases. The continuous mercury measurements reveal peaks due to polluted air of local origin, but most of the peaks occur in air from sources in continental Europe.
14. Concentrations of Total Gaseous Mercury measured at network stations are consistent with a background of approximately 1.5 ng m^{-3} , widely quoted in the literature, and with slightly larger values in the South East of the UK due to the influence of more polluted continental air in these areas.

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1. Introduction

Measurements of heavy metals in air and precipitation in the UK have been made by a range of university research groups and institutes during the last two decades. However, the monitoring stations were too few in number for the production of national maps of heavy metal deposition, and inconsistent methodologies were used. A limited rural network of samplers of metals in precipitation and in aerosols has provided important measurements to quantify metal (and other trace elements) deposition to terrestrial surfaces in the UK, and to the North Sea (Baker 1999, Playford and Baker 2000, respectively). The number of measurement stations for this work was small, and operated with three Rural Trace Element (RTE) sites at Chilton, Styrrup and Wraymires, and three North Sea Network (NSN) sites at Banchory, High Muffles and East Ruston. These sites alone were not sufficient to define the broad concentration and deposition patterns of heavy metal deposition in the UK. In addition, there was evidence that local sources were contaminating some of the RTE and NSN measurements. The measurements of metal concentrations in precipitation at Wraymires for example, showed concentrations of copper which were substantially larger (a factor of 7) than at a nearby site in the Duddon valley in the Lake District. Measurements at Great Dun Fell, which is generally more polluted than sites further west, showed copper concentrations smaller by a factor of 3. The NETCEN team note in their report that concentrations of copper at Chilton, Styrrup and Wraymires were 3-7 times the values measured for their North Sea sites (1995-1999). The values were also larger in the previous measurement period, 1992-1996. The report noted that the high values for the RTE sites were “not easily explained”.

Part of the current problems in metal deposition measurement is a consequence of the substantial reduction in emissions and the resulting decline in concentrations in air and precipitation. Thus local contamination of collector sites by re-suspended soil or dust from roads or tracks make a much larger contribution to the collected samples than was the case a decade ago. At the same time, declining concentrations need to be met by improved analytical techniques to avoid values below the detection limit, which have affected the NS and RTE sites in the past.

Metal deposition in England and Wales: Measurements by the University of Reading (for MAFF)

More recently, a substantial monitoring network of 35 sites in England and Wales was used to quantify the deposition of a wide range of metals (Alloway et al 1998). In principle, these sites should be suitable for mapping the spatial metal deposition patterns for England and Wales and maps of total metal deposition have been produced (Nemitz et al 2000). The measurements provided an excellent resource for research on trace elements in the UK, but as with the RTE network, there were significant problems interpreting the measurements. The mapped wet and dry deposition for England and Wales from these data, showed much larger total deposition values for the major heavy metals than either the modelled metal deposition or the estimates based on moss sampling (Table 1). The modelled and measured values differed appreciably, in part due to uncertainties in the emission estimates for the model, and to uncertainties in the calibration of the moss based estimates. However, it was also clear that the technique used for sampling with an inverted ‘frisbee’ collector has led to appreciably larger values for metal deposition than values from the networks in the vicinity. Comparing the metal deposition at Redesdale, close to the Scotland–England border with values at Auchencorth Moss, in the Scottish Borders, a site with similar annual precipitation, deposition values were substantially larger for the ‘frisbee’ network by between 30% and a factor of two, depending on the metal. A six-month comparison at Auchencorth Moss of a wet only collector and the ‘frisbee’ collector confirmed these results. The most likely cause of the larger values from the ‘frisbee’ collector was the capture of locally re-suspended particulate matter, which was not sampled so efficiently by the wet collector. Due to their aerodynamic characteristics, the capture efficiency of the ‘frisbee’ collectors for coarse particles probably exceeded that of vegetation.

Table 1: Summary of the total emission and deposition (t y^{-1}) for the UK ,as well as England and Wales only derived by the three methods. Also included are the EMEP model results for 1998 (Ilyin et al., 2005).

	United Kingdom				England & Wales			
	Cd	Pb	Cu	Zn	Cd	Pb	Cu	Zn
EMISSIONS								
NAEI 1995	15.7	1648	83.6	1207				
NAEI 1998	13.0	1033	58.8	1047				
CEH 1997	18.8	1087	88.9	796				
DEPOSITION								
Moss 96/97	13.0	587	1574	6191	9.3	427	1098	4591
Moss 2000	8.0	659	783	3855	6.3	518	570	2985
Frisbee network	-	-	-	-	55.7	1473	1320	5552
EMEP 1998	7.9	478						
CEH model 1997	11.0	567	59.3	435	9.1	446	53.5	389

2. Heavy Metals Data Collection

2.1. Introduction

The work packages described were designed to satisfy the objectives outlined in Table 2. In the case of heavy metals there are particular measurement and analytical problems. From earlier work it was clear that the various data sets for metal deposition in the UK, prior to the current contract, were too uncertain to provide satisfactory deposition maps or validation of the emission inventories of UK emissions (Dore et al. 2004).

The differences between the various measurement approaches for some metals indicated substantial uncertainties in the measurement approaches. The current contract has now provided a full, validated data set for wet and dry deposition of 9 heavy metals and concentrations of 26 heavy metals for 2004. These deposition maps allow for the first time, a comparison with the emission inventories in the knowledge that the deposition estimates are of a sufficient quality to be confident that they are sufficiently accurate for such validation. The deposition for all metals, with the exception of Vanadium and Nickel, exceed emissions, and in some cases by a factor of 5 (for Zn and Cu). Earlier work shows that emissions from the UK should exceed deposition and for most metals, the fraction deposited within the UK is expected to be between 30% and 60% of emissions (Nemitz et al. 2006).

The CEH process work on dry deposition of aerosols has been used directly to quantify the dry deposition of metals, and the current network data combined with the process modelling of dry deposition shows that 15 - 30% of the metal deposition is dry deposition. Thus to achieve high quality total deposition, dry deposition estimates are very important and these need to be specific for the individual metals and different land uses.

Table 2: Outline of work packages for monitoring of heavy metals in the UK

Work Package 1	Production of UK Maps of Metal Deposition
Work Package 2	Heavy Metals Data Collection
Work Package 3	Derivation of relationships between metal deposition and metal concentrations in moss in the UK
Work Package 4	Monitoring at Upland Cloud Water Sites
Work Package 5	Speciated Mercury Measurements at a Single Site
Work Package 6	Total Gaseous mercury (TGM) and mercury in precipitation at up to 10 Heavy Metal data collection sites

2.2 New UK rural metals network

The UK rural heavy metals monitoring network consists of 15 sites across the UK (Figure 1). Banchory is the only site that is a continuation from the old Rural Trace Element Network (RTE). All other sites in the old network have been moved a short distance for scientific reasons. Penallt is positioned intentionally to capture the plume from the metal processing industry at Avonmouth and in South Wales.

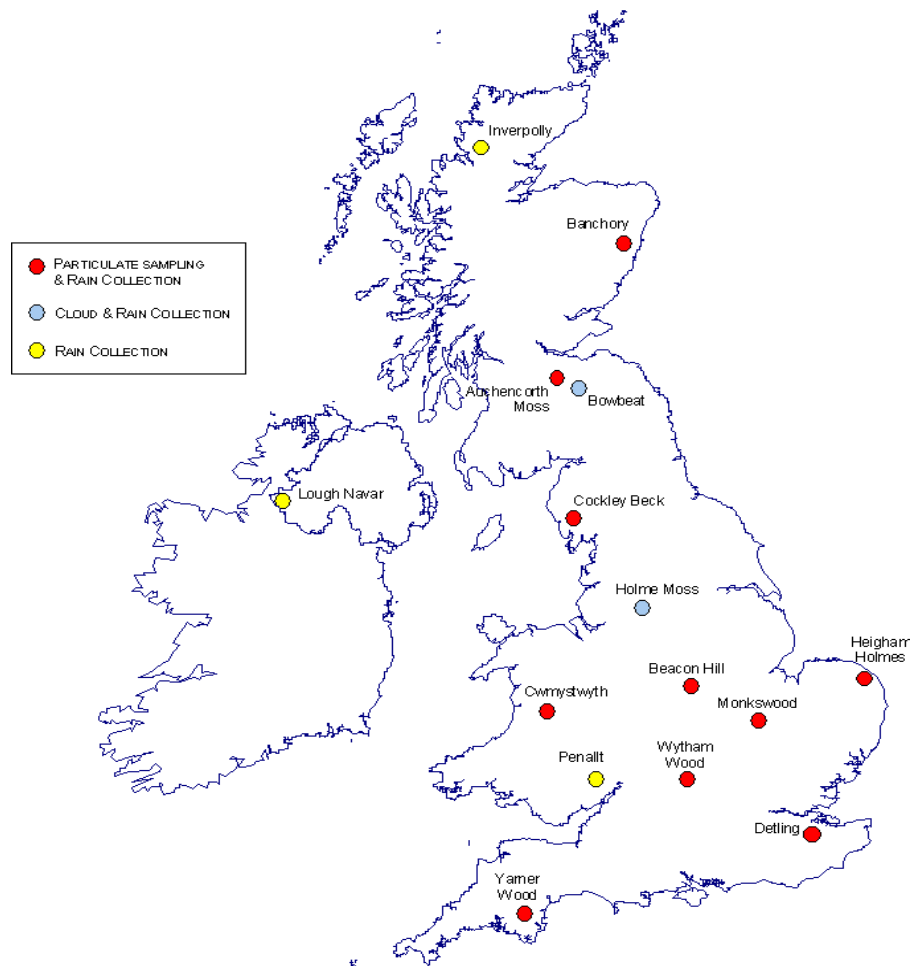


Figure 1: The UK Rural Heavy Metals Monitoring Network

There are 10 sites using particulate samplers to measure metal concentrations contained in PM_{10} . The samplers were made by ESM Anderson in Germany and supplied by Thermo Electron, and there are 2 types in use: a single sampler (FH95), and a sequential sampler (FH95 SEQ). Weekly samples are taken at all sites; however, in principle, the FH95 SEQ only requires attention 4-weekly.

All sites have a bulk collector to collect precipitation. The collectors at rain only sites and cloud collection sites are changed monthly. At sites with a single sampler, the collectors are changed weekly. At sites with a sequential sampler, the collectors are changed on a 4-weekly basis.

There are 2 sites (Bowbeat and Holme Moss) situated on high ground in the Scottish Borders and West Yorkshire respectively, which focus on sampling metal concentrations in cloud droplets captured by passive impaction on strings set above the collecting funnel collectors. These measurements provide information on occult deposition of cloud water and the enhancement of concentrations in orographic cloud relative to that in rain.

2.3 Establishment of 10 new sites for measuring heavy metal particulates in air

10 sites were established to collect heavy metal particulates in air and are shown in Figure 1.

Two types of samplers are used to collect heavy metal particulate matter. The FH95 and the FH95 SEQ are shown in Figure 2 and Figure 3. In both samplers, a pump sucks ambient air into the instrument at 16.67 litres per minute through a size-selecting inlet (10 micron), and then through a filter paper mounted in a plastic cassette. The particulate matter remains on the surface of the filter. The FH95, referred to as the single particulate sampler, contains one filter that must be changed manually. The FH95 SEQ, referred to as the sequential particulate sampler, contains a magazine of up to 16 filter cassettes that can be programmed to change automatically. The sampling period is normally one week and the filters are removed and sent to CEH Lancaster for analysis.



Figure 2: FH95 single sampler at Yarner Wood



Figure 3: FH95SEQ sequential sampler at Wytham Wood

2.4 Establishment of 15 new sites for measuring heavy metals in precipitation

At all 10 particle sampling sites, the 3 rain only sites and the 2 rain and cloud upland sites, collectors were set up for bulk precipitation (Figure 4) and continuous rainfall recorded using a tipping bucket gauges (Figure 5).

The single sampler sites collect bulk precipitation on a weekly basis, whilst the sequential sampler sites collect bulk precipitation on a 4-weekly basis, as this coincides with a site operator visit to attend to the sequential sampler. The rain only sites collect bulk precipitation at monthly intervals. The high altitude sites at Bowbeat and Holme Moss are designed to monitor concentration in cloud droplets and precipitation.



Figure 4 Bulk Precipitation collector at Heigham Holmes with cable tie bird scarer ring.



Figure 5 ARG 100 Tipping Bucket Rain gauge at Auchencorth

The tipping bucket dataloggers were upgraded to the DT2 version (Environmental Measurements Ltd) during the course of this project to protect the data from battery failure, as these improved units had non-volatile memory. Bird scarers for all precipitation samplers were essential to prevent contamination and at the remote sites of Lough Navar and Inverpolly ‘bird strikes’ are still presenting problems.

Table 3: Sampling Intervals at each site

SITE	Sampling Interval			
	Heavy metals in Particles	Heavy metals in Precipitation	Hg in Air	Hg in Precipitation
Auchencorth Moss	1-Week	1-Week	2-Week	1-Month
Banchory	1-Week	1-Week	2-Week	1-Month
Monkswood	1-Week	1-Week	2-Week	1-Month
Yarner Wood	1-Week	1-Week	2-Week	1-Month
Cockley Beck ¹	1-Week	1-Week	2-Week	1-Month
Cwmystwyth	1-Week	4-Week	2-Week	1-Month
Wytham Wood ¹	1-Week	4-Week	2-Week	1-Month
Heigham Holmes ²	1-Week	4-Week	2-Week	1-Month
Detling ²	1-Week	4-Week	2-Week	1-Month
Beacon Hill ¹	1-Week	4-Week	2-Week	1-Month
Bowbeat ³		4-Week		
Holme Moss ³		4-Week		
Inverpolly		1-Month		
Penallt		1-Month		
Lough Navar		1-Month		

¹ Replaced Rural Trace Element (RTE) site, ² Replaced North Sea Network (NS) site, ³ Cloud and Precipitation high altitude sites.

2.5 Comparison of results from new network protocols and current methods at 5 sites (3 RTE, 2 NS)

Prior to the establishment of the Rural Heavy Metals monitoring network, there had been two other networks operating. Of these previous monitoring locations, only Banchory was regarded as being acceptable for the new Rural Heavy Metal Monitoring Network. The close proximity of buildings/works, agricultural activities and other potential contaminants excluded the other locations. Alternative equivalent locations are detailed in Table 4.

Table 4 Previous Heavy Metal Monitoring Networks and sites with the equivalent locations in the new Rural Heavy Metal Monitoring Network.

The Rural Trace Element (RTE)	Heavy Metals Rural monitoring network
Chilton	Wytham Wood
Styrrup	None
Wraymires	Cockley Beck
The North Sea (NS) Network	
East Ruston	Heigham Holmes
High Muffles	None
Banchory	Banchory

Figure 6-Figure 19 illustrate the published, long term data for these four site comparisons from 1994 to 2005, for the elements, As, Cd, Cr, Cu, Ni, Pb and Zn, in both air and in rain.

Although the data for air has been more variable, in most cases there has been a discernable reduction in both air and rain concentrations. The 70-80% reductions for the higher concentration elements of Pb and Zn are convincing but the elements Cr and Ni do not illustrate any very obvious trends. However, Cr and Ni are only present in low concentrations and their variable data probably reflects how close these are to the detection limits of the sampling and analysis protocol.

Arsenic: Between 1994 and 2002 reported emissions have reduced by approx. 55%, from 54 to 24 tonnes yr⁻¹ (Vincent 2006). This level of reduction has not been observed consistently at any of the four sites. Air concentrations at Chilton/Wytham Wood (1.10ngm⁻³ - 0.70 ngm⁻³) and Wraymires/Cockley Beck (0.65ngm⁻³ - 0.40 ngm⁻³) have followed this rate of reduction but the other two sites showed an increase by 20%. Concentrations in rain however are the opposite with only East Ruston/Heigham Holmes (0.28ugl⁻¹ - 0.15ugl⁻¹) and Banchory (0.23ugl⁻¹ - 0.14ugl⁻¹) following the trend.

Cadmium: Cadmium emissions have reduced sharply since 1994 by approx. 70% from 13 to 4 tonnes yr⁻¹ (Vincent 2006). All four sites reflected this reduction both in air and rain concentrations but only when the 2004 - 2005 data is included. If the dataset is restricted to the 2002 end date there is no downward trend except for rain concentration at East Ruston/Heigham Holmes (0.17ugl⁻¹ - 0.035ugl⁻¹).

Nickel: Between 1994 and 2002 emissions reduced rapidly by approx. 72% from 370 to 100 tonnes yr⁻¹ (Vincent 2006). With the exception of East Ruston/Heigham Holmes for concentrations in air and Chilton/Wytham Wood for concentrations in rain which both increased over this period the other site combinations all exhibited variable degrees of reduction. The lowest rate of reduction was for Chilton/Wytham Wood concentration in air (1.50ngm⁻³ - 1.20 ngm⁻³) and the highest was for East Ruston/Heigham Holmes concentration in rain (1.50ugl⁻¹ - 0.30ugl⁻¹).

Lead: Lead emissions have fallen consistently from 1825 tonnes yr⁻¹ in 1994 to a low level of 150 tonnes yr⁻¹ in 2000 and then levelled off at this value through to 2002. The concentration in air fell in parallel with this general trend with the greatest reduction recorded at Chilton/Wytham Wood (26.50ngm⁻³ - 6.00 ngm⁻³) and the smallest reduction was at recorded at Banchory (5.00ugl⁻¹ - 0.50ugl⁻¹). All sites, with the exception of Chilton/Wytham Wood, had a reduction in concentration in rainfall with the greatest at East Ruston/Heigham Holmes (5.20ugl⁻¹ - 2.00ugl⁻¹) and the lowest being Wraymires/Cockley Beck (1.20ugl⁻¹ - 0.90ugl⁻¹).

In all element/site combinations, with the exception of Arsenic, Chromium and Lead in rain for Chilton/Wytham Wood, the inclusion of the 2004 - 2005 data from the new Heavy Metal Rural Monitoring Network resulted in a strengthened reduction in concentration indicating that for most elements at most sites the current concentrations in both air and rain are lower than the published 2002 values.

The published emissions data appear to show a consistent reduction over the ten years between 1992 and 2002 that has not resulted in a similar reduction in concentration in either air or rain samples. Even though the new Heavy Metal Rural Monitoring Network concentrations are lower they only just start to bring the reduction trend into line with the reduction in emissions.

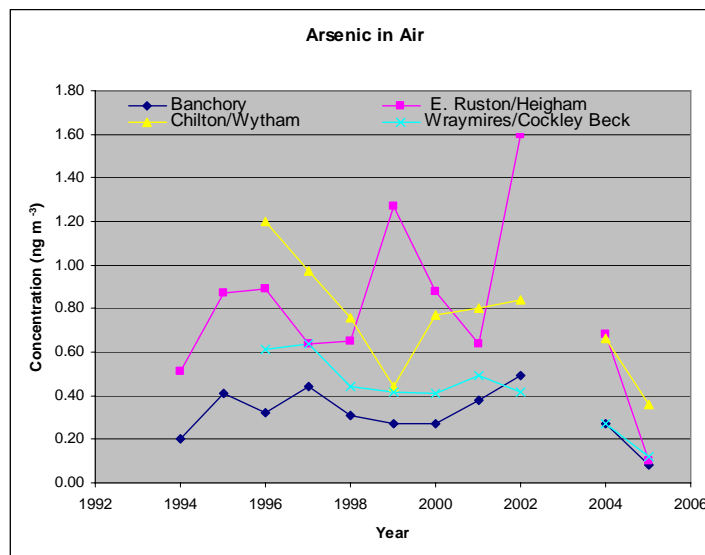


Figure 6: Long term comparisons of Arsenic air concentrations (ngm^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

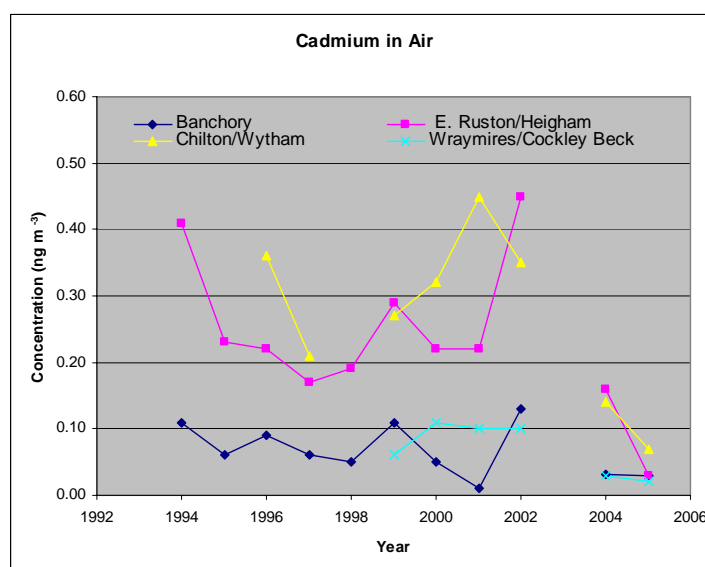


Figure 7: Long term comparisons of Cadmium air concentrations (ngm^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

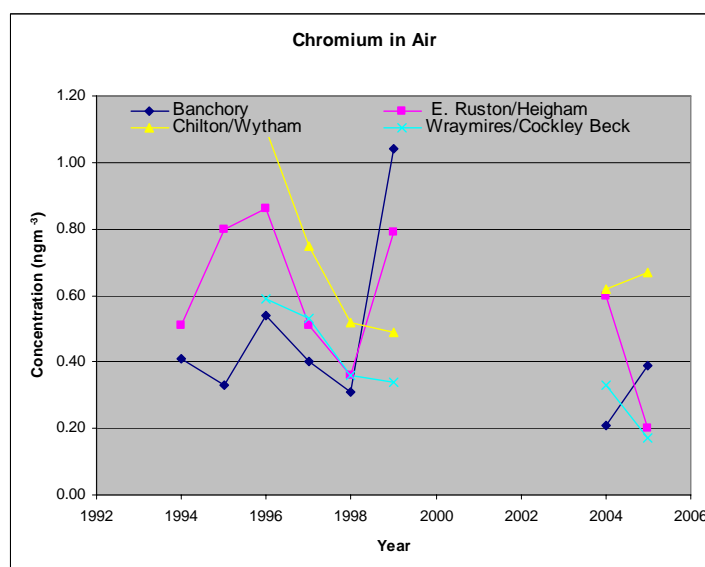


Figure 8: Long term comparisons of Chromium air concentrations (ngm^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

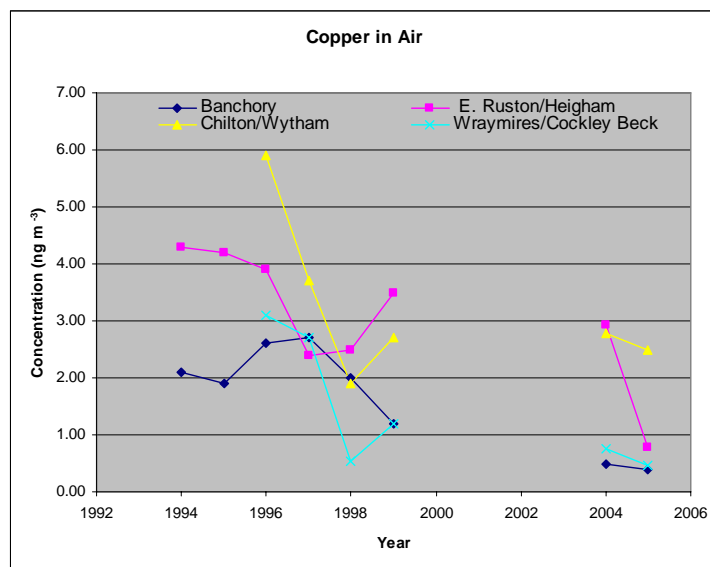


Figure 9: Long term comparisons of Copper air concentrations (ngm^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

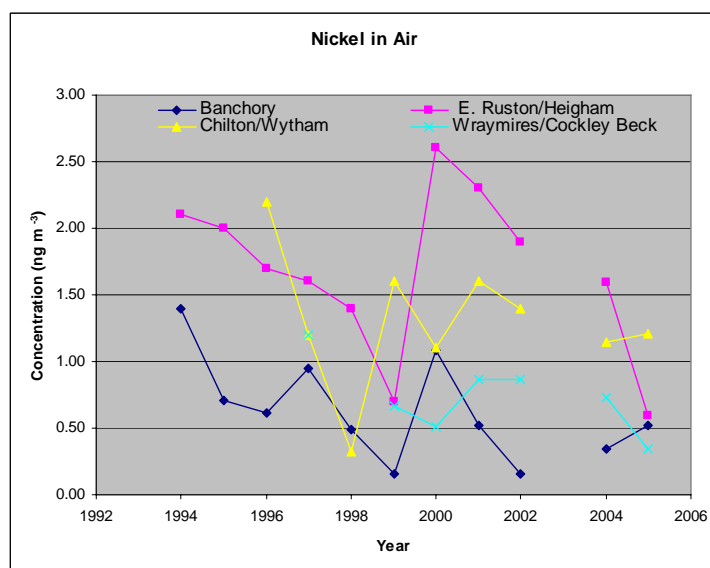


Figure 10: Long term comparisons of Nickel air concentrations (ngm^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

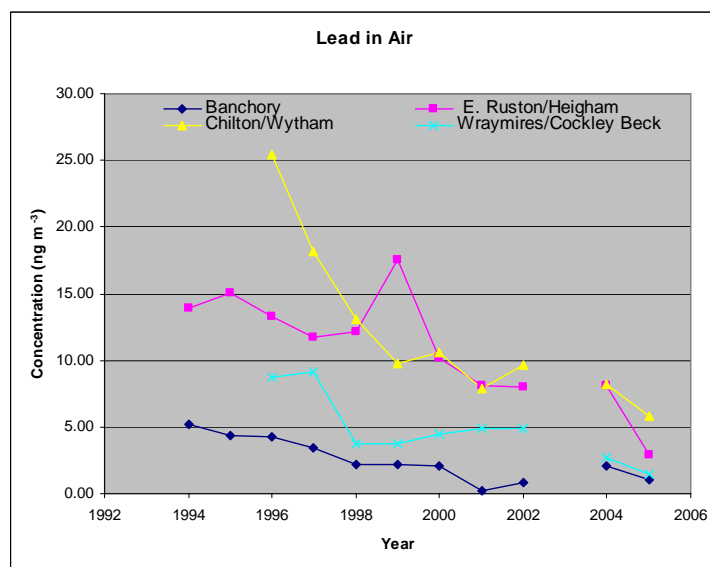


Figure 11: Long term comparisons of Lead air concentrations (ngm^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

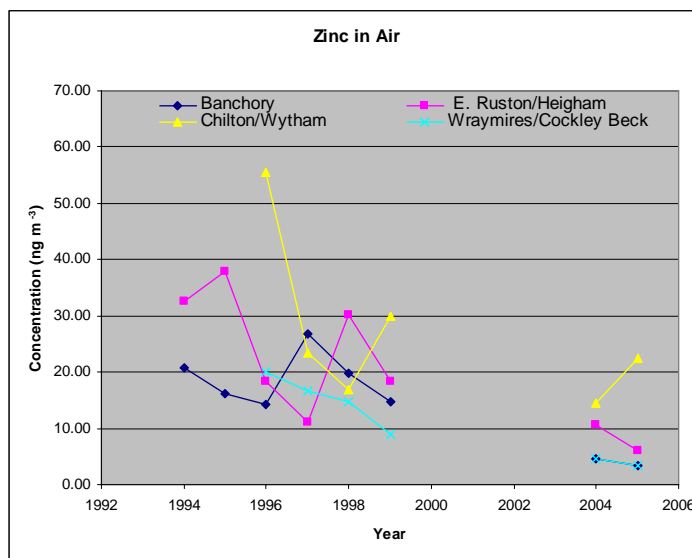


Figure 12: Long term comparisons of Zinc air concentrations (ng m^{-3}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

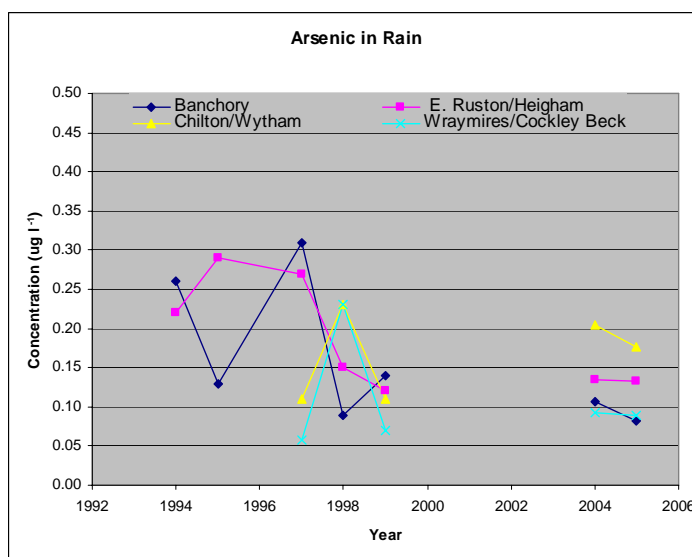


Figure 13: Long term comparisons of Arsenic rain concentrations ($\mu\text{g l}^{-1}$) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005.

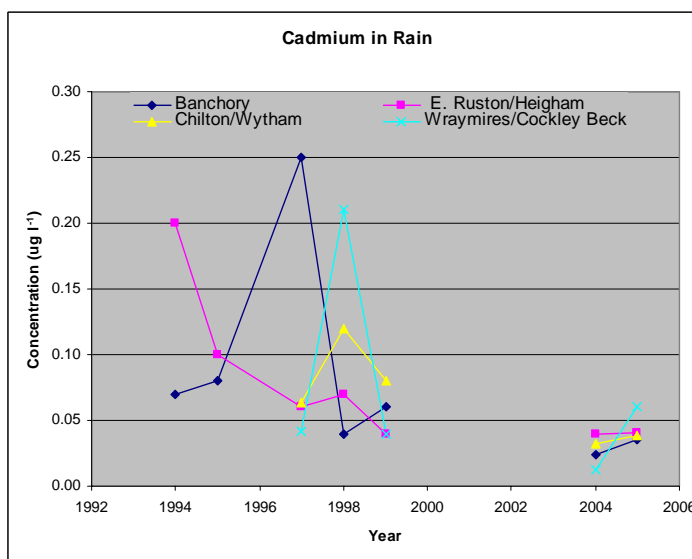


Figure 14: Long term comparisons of Cadmium rain concentrations ($\mu\text{g l}^{-1}$) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005

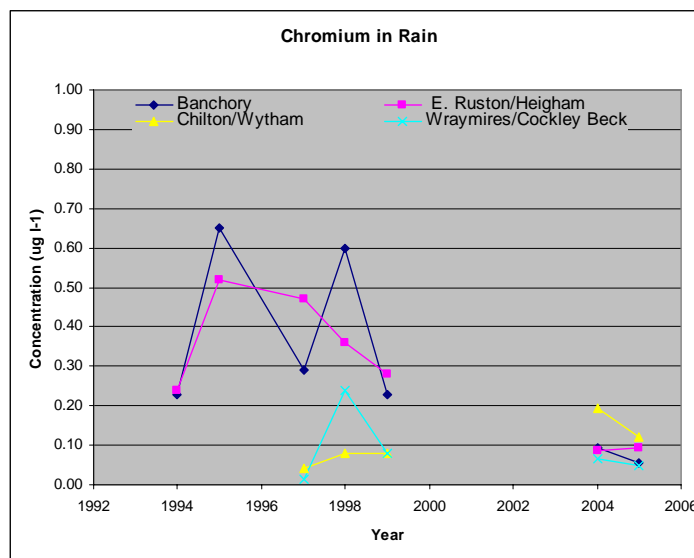


Figure 15: Long term comparisons of Chromium rain concentrations (ug l^{-1}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005

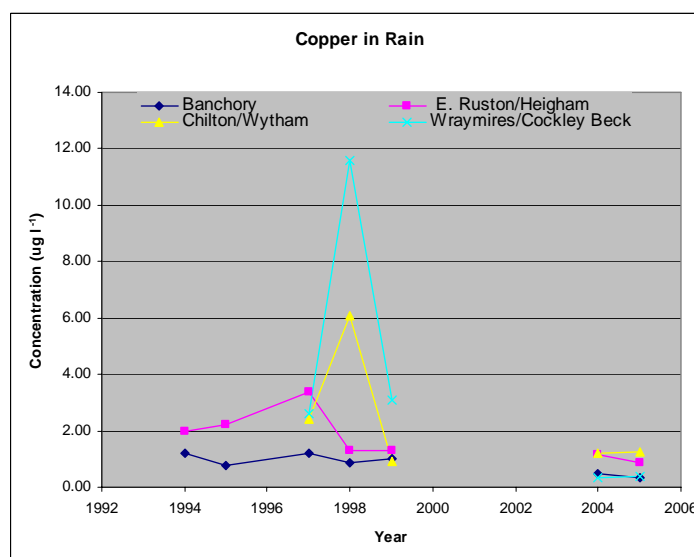


Figure 16: Long term comparisons of Copper rain concentrations (ug l^{-1}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005

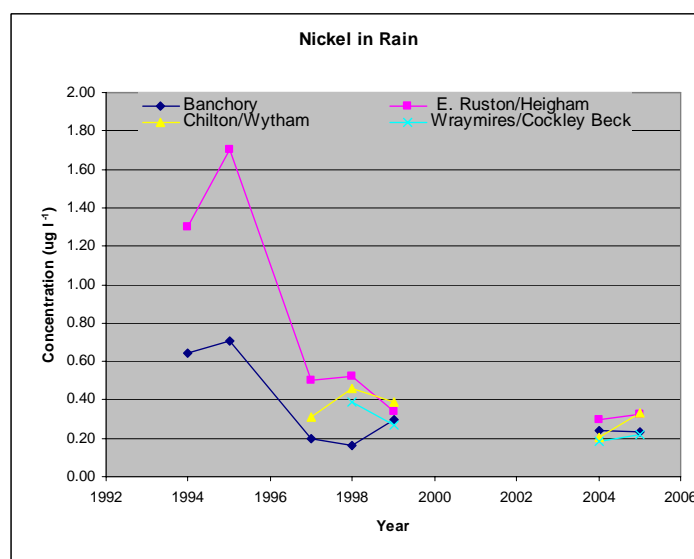


Figure 17: Long term comparisons of Nickel rain concentrations (ug l^{-1}) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005

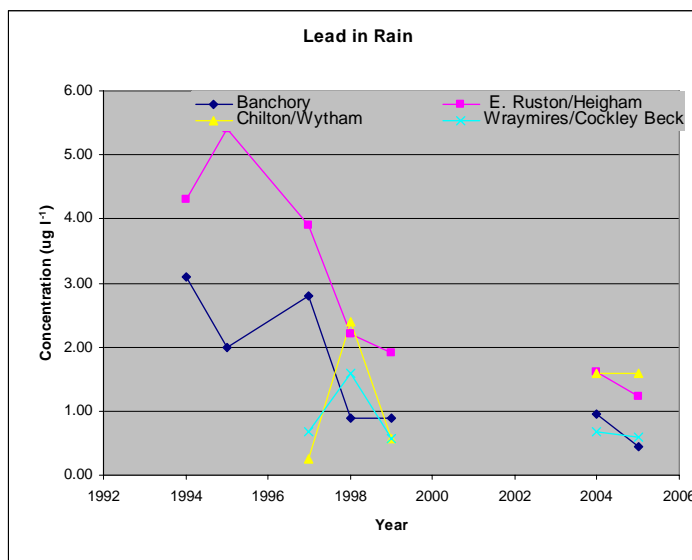


Figure 18: Long term comparisons of Lead rain concentrations ($\mu\text{g l}^{-1}$) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005

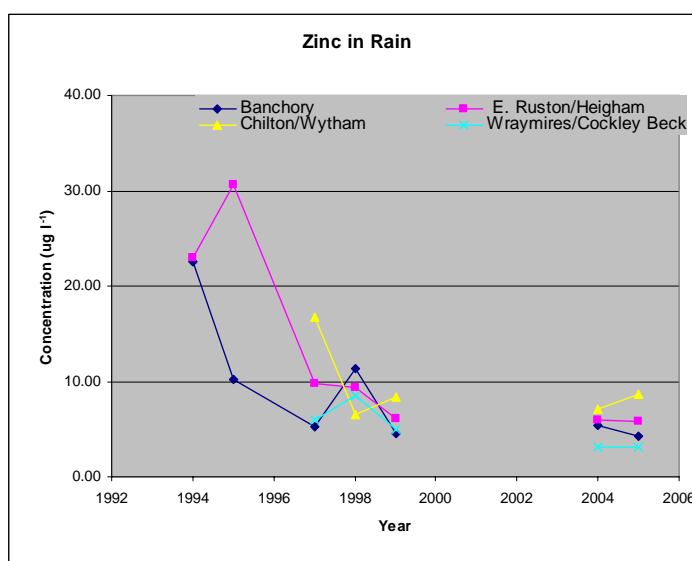


Figure 19: Long term comparisons of Zinc rain concentrations ($\mu\text{g l}^{-1}$) for Banchory, Chilton/Wytham Wood, East Ruston/Heigham Holmes and Wraymires/Cockley Beck between 1994 and 2005

2.6 Tabulated analytical concentration data from each site for each of the specified analytes on an annual basis, with annual averages (volume-weighted), for both particles and precipitation

Table 5: 2004 volume weighted mean rain concentrations at each site, filtered to remove outliers + or – 2 x S. Dev.

Volume Weighted Average Concentration In Rainfall (2004) ug/l									
	V	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
MONKSWOOD	0.37	0.14	0.27	0.90	6.80	0.17	0.14	0.02	1.36
COCKLEY BECK	0.28	0.07	0.19	0.32	2.69	0.09	0.16	0.01	0.68
AUCHENCORTH	0.23	0.07	0.14	0.39	3.40	0.09	0.13	0.01	0.62
BANCHORY	0.33	0.09	0.23	0.47	5.36	0.11	0.16	0.02	0.95
YARNER WOOD	0.55	0.06	0.22	0.34	3.55	0.08	0.18	0.02	0.63
WYTHAM WOOD	0.39	0.19	0.20	1.20	7.07	0.20	0.14	0.03	1.59
CWMYSTWYTH	0.23	0.05	0.10	0.28	2.31	0.08	0.16	0.01	0.35
HEIGHAM HOLMES	0.60	0.09	0.27	1.14	6.02	0.13	0.15	0.04	1.62
BEACON HILL	0.50	0.18	0.32	1.34	8.07	0.26	0.18	0.03	2.10
DETLING	0.72	0.12	0.30	2.28	9.04	0.22	0.19	0.03	2.07
INVERPOLLY	0.12	0.07	0.05	0.20	2.43	0.06	0.12	0.00	0.15
LOUGH NAVAR	0.15	0.12	0.05	0.34	1.76	0.20	0.16	0.01	0.18
PENALLT	0.39	0.10	0.18	0.53	5.78	0.17	0.14	0.03	1.37
BOWBEAT RAIN	0.59	0.13	0.38	1.65	13.33	0.16	0.42	0.10	2.72
HOLM MOSS RAIN	0.42	0.17	0.22	1.43	11.99	0.38	0.26	0.03	2.42
BOWBEAT CLOUD	1.61	0.30	1.51	2.40	12.93	0.45	1.14	0.17	3.30
HOLM MOSS CLOUD	3.00	1.36	2.65	11.15	50.71	1.41	2.74	0.27	13.04

Table 6: 2005 volume weighted mean rain concentrations at each site, filtered to remove outliers + or – 2 x S. Dev

Volume Weighted Average Concentration In Rainfall (2005) ug/l									
	V	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
MONKSWOOD	0.43	0.12	0.51	1.08	9.59	0.23	0.18	0.06	1.15
COCKLEY BECK	0.32	0.05	0.22	0.37	3.14	0.09	0.17	0.06	0.60
AUCHENCORTH	0.27	0.07	0.34	0.48	6.23	0.12	0.17	0.04	0.51
BANCHORY	0.26	0.06	0.23	0.33	4.24	0.08	0.14	0.03	0.45
YARNER WOOD	0.68	0.07	0.42	0.42	4.95	0.10	0.21	0.04	0.73
WYTHAM WOOD	0.57	0.12	0.33	1.24	8.64	0.18	0.16	0.04	1.59
CWMYSTWYTH	0.23	0.03	0.12	0.25	2.37	0.10	0.13	0.03	0.34
HEIGHAM HOLMES	0.60	0.09	0.33	0.87	5.85	0.13	0.21	0.04	1.23
BEACON HILL	0.56	0.16	0.29	1.34	10.20	0.26	0.18	0.03	2.15
DETLING	1.05	0.15	0.47	1.86	10.37	0.23	0.22	0.04	2.17
INVERPOLLY	0.12	0.02	0.19	0.29	1.43	0.06	0.19	0.02	0.07
LOUGH NAVAR	0.12	0.05	0.08	0.20	1.15	0.17	0.20	0.00	0.13
PENALLT	0.36	0.04	0.19	0.65	5.04	0.23	0.10	0.05	0.93
BOWBEAT RAIN	0.29	0.08	0.20	0.42	7.06	0.07	0.18	0.04	0.59
HOLM MOSS RAIN	0.62	0.23	0.33	1.57	12.20	0.54	0.36	0.04	2.27
BOWBEAT CLOUD	1.30	0.24	2.34	2.53	15.76	0.39	1.06	0.15	2.56
HOLM MOSS CLOUD	3.67	0.72	3.18	8.87	44.05	1.16	1.98	0.52	9.72

Table 7: 2004 volume weighted mean air concentrations at each site filtered to remove outliers + or – 2 x S. Dev

2004 AIR CONCENTRATIONS TIME WEIGHTED	MONKSWOOD	COCKLEY BECK	AUCHENCORTH	BANCHORY	YARNER WOOD	WYTHAM WOOD	CWMYSTWYTH	HEIGHAM HOLMES	BEACON HILL	DETLING
ngm ⁻³										
DATA CAPTURE %	81	88	91	68	88	74	10	36	37	6
Li	0.08	0.04	0.04	0.03	0.07	0.05	0.01	0.09	0.12	0.08
Be	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02
Al	46.79	48.34	36.82	17.96	40.50	43.19	19.81	64.64	82.65	47.59
Sc	0.16	0.15	0.14	0.14	0.15	0.15	0.15	0.15	0.15	0.15
Ti	1.44	0.92	1.12	0.70	1.06	1.36		1.92	2.75	
V	1.78	0.73	0.67	0.52	1.69	1.82	0.25	3.55	1.59	2.79
Cr	0.71	0.33	0.28	0.21	0.28	0.62	0.32	0.60	0.69	1.31
Mn	2.82	1.06	1.01	0.80	1.43	2.42	0.19	2.65	4.08	3.62
Fe	109.36	41.56	47.46	26.95	49.42	100.50	12.83	96.23	132.73	182.70
Co	0.21	0.16	0.21	0.06	0.09	0.11	0.06	0.06	0.18	0.02
Ni	1.05	0.73	0.60	0.34	1.01	1.15	0.13	1.59	0.99	2.08
Cu	3.40	0.76	1.05	0.49	1.14	2.78	0.43	2.93	3.16	5.18
Zn	13.91	4.59	5.55	4.67	5.84	14.56	2.97	10.74	11.25	10.67
As	0.77	0.27	0.26	0.27	0.52	0.66	0.07	0.68	0.73	1.00
Se	0.68	0.25	0.28	0.23	0.37	0.47	0.09	0.62	0.55	0.59
Rb	0.18	0.09	0.09	0.10	0.19	0.17	0.01	0.22	0.23	0.19
Sr	0.97	0.82	0.69	0.47	1.01	1.09	0.64	1.48	0.85	1.59
Mo	0.48	0.17	0.21	0.26	0.21	0.42	0.09	0.32	0.49	0.68
Cd	0.14	0.03	0.05	0.03	0.07	0.14	0.01	0.16	0.15	0.17
Sn	1.05	0.40	0.54	0.24	0.46	0.75	0.55	0.91	1.08	1.72
Sb	1.42	0.22	0.33	0.19	0.42	1.08	0.06	0.88	1.26	1.96
Cs	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.02	0.01	0.02
Ba	2.44	0.69	1.01	0.59	1.08	2.47	1.02	2.03	4.34	3.09
W	0.06	0.04	0.04	0.03	0.04	0.06	0.03	0.05	0.04	0.14
Pb	9.31	2.68	2.73	2.07	3.79	8.20	1.02	8.14	8.45	10.02
U	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cations										
K	0.11	0.04	0.06	0.05	0.07	0.07	0.02	0.10	0.06	0.11
Mg	0.07	0.08	0.05	0.04	0.09	0.07	0.05	0.10	0.05	0.16
Na	0.48	0.59	0.37	0.26	0.70	0.60	0.39	0.75	0.27	1.27
Ca	0.09	0.05	0.04	0.02	0.07	0.10	0.06	0.08	0.09	0.15

Table 8: 2005 volume weighted mean air concentrations at each site filtered to remove outliers + or – 2 x S. Dev

2005 AIR CONCENTRATIONS TIME WEIGHTED	MONKSWOOD	COCKLEY BECK	AUCHENCORTH	BANCHORY	YARNER WOOD	WYTHAM WOOD	CWMYSTWYTH	HEIGHAM HOLMES	BEACON HILL	DETLING
ngm-3										
DATA CAPTURE %	74	86	83	81	81	65	75	65	53	42
Li	0.06	0.03	0.03	0.03	0.04	0.06	0.04	0.02	0.05	0.04
Be	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Al	178.15	113.39	105.45	49.25	101.62	276.40	123.76	83.79	407.61	613.98
Sc	0.16	0.15	0.15	0.15	0.15	0.19	0.15	0.16	0.15	0.16
Ti	0.88		1.63	0.56	0.61	1.13	0.41	0.41	1.15	1.74
V	1.35	0.36	0.29	0.17	1.03	0.96	0.35	1.44	0.94	3.80
Cr	0.58	0.17	0.27	0.39	0.18	0.67	0.20	0.20	0.47	0.32
Mn	2.07	0.50	0.76	0.49	0.83	1.84	0.55	0.64	2.44	2.14
Fe	515.99	116.22	102.65	76.11	113.54	675.22	124.28	149.79	1083.50	
Co	0.04	0.02	0.03	0.02	0.02	0.06	0.13	0.02	0.11	0.03
Ni	0.92	0.34	0.70	0.52	0.84	1.21	0.58	0.59	1.26	1.30
Cu	2.39	0.46	0.69	0.40	0.70	2.50	0.51	0.77	2.45	3.29
Zn	13.19	3.47	4.23	3.35	7.18	22.40	4.12	5.96	27.97	16.79
As	0.39	0.12	0.12	0.08	0.20	0.36	0.09	0.10	0.31	0.29
Se	0.28	0.16	0.14	0.15	0.13	0.23	0.12	0.13	0.25	0.12
Rb	0.11	0.04	0.04	0.04	0.09	0.08	0.05	0.04	0.09	0.06
Sr	0.83	0.63	0.55	0.52	0.70	0.88	0.49	0.36	0.68	0.82
Mo	0.34	0.14	0.17	0.17	0.18	0.32	0.13	0.14	0.23	0.21
Cd	0.08	0.02	0.03	0.03	0.04	0.07	0.02	0.03	0.05	0.07
Sn	1.77	0.33	0.51	1.06	0.63	0.87	1.38	0.67	0.77	3.22
Sb	0.60	0.11	0.18	0.09	0.21	0.56	0.10	0.13	0.55	0.58
Cs	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Ba	1.56	0.45	0.59	0.47	0.57	1.76	0.48	0.49	1.97	2.29
W	0.05	0.04	0.05	0.05	0.04	0.08	0.05	0.05	0.05	0.05
Pb	6.58	1.50	1.50	1.07	2.55	5.78	1.70	2.93	8.67	11.82
U	0.02	0.01	0.02	0.02	0.02	0.02	0.02	0.01	0.01	0.02
Cations										
K	0.08	0.04	0.03	0.04	0.08	0.15	0.09	0.04	0.07	0.08
Mg	0.06	0.07	0.05	0.04	0.07	0.07	0.06	0.04	0.06	0.07
Na	0.41	0.52	0.33	0.32	0.55	0.53	0.44	0.26	0.38	0.52
Ca	0.13	0.09	0.08	0.07	0.09	0.20	0.09	0.09	0.13	0.17

2.7 Tabulated wet deposition data from measured concentrations and precipitation amounts for each analyte at each site, and annual totals.

Table 9: 2004 wet deposition at each site

WET Deposition 2004 g/ha/yr									
	V	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
MONKSWOOD	2.45	0.92	1.78	5.91	44.84	1.11	0.94	0.15	8.97
COCKLEY BECK	6.32	1.51	4.20	7.26	60.83	2.09	3.72	0.28	15.32
AUCHENCORTH	1.98	0.56	1.20	3.38	29.14	0.74	1.15	0.10	5.32
BANCHORY	2.47	0.69	1.69	3.48	39.95	0.80	1.22	0.18	7.06
YARNER WOOD	5.96	0.69	2.42	3.71	38.50	0.91	1.97	0.17	6.81
WYTHAM WOOD	2.29	1.13	1.18	7.01	41.31	1.19	0.84	0.19	9.26
CWMYSTWYTH	3.68	0.73	1.62	4.48	37.43	1.32	2.55	0.09	5.66
HEIGHAM HOLMES	2.58	0.38	1.16	4.88	25.81	0.58	0.65	0.17	6.95
BEACON HILL	4.07	1.45	2.58	10.91	65.55	2.07	1.44	0.27	17.04
DETLING	0.68	0.11	0.29	2.16	8.58	0.21	0.18	0.03	1.97
INVERPOLLY	0.88	0.48	0.36	1.45	17.77	0.41	0.90	0.03	1.08
LOUGH NAVAR	1.62	1.35	0.60	3.74	19.37	2.19	1.81	0.07	1.99
PENALLT	2.64	0.68	1.22	3.62	39.28	1.16	0.93	0.18	9.30
BOWBEAT RAIN	5.51	1.20	3.57	15.35	124.26	1.49	3.92	0.95	25.33
HOLM MOSS RAIN	5.89	2.45	3.13	20.20	168.81	5.31	3.71	0.44	34.13
BOWBEAT CLOUD	54.76	10.29	51.55	81.82	440.94	15.43	38.96	5.95	112.58
HOLM MOSS CLOUD	86.64	39.33	76.37	322.03	1463.92	40.58	79.07	7.70	376.58

Table 10: 2005 wet deposition at each site

WET Deposition 2005 g/ha/yr									
	V	Cr	Ni	Cu	Zn	As	Se	Cd	Pb
MONKSWOOD	1.94	0.57	2.30	4.93	43.64	1.05	0.81	0.27	5.24
COCKLEY BECK	6.58	1.01	4.47	7.59	63.89	1.84	3.37	1.21	12.21
AUCHENCORTH	2.12	0.55	2.73	3.85	49.53	0.96	1.37	0.34	4.06
BANCHORY	1.81	0.39	1.60	2.27	29.54	0.57	1.00	0.24	3.16
YARNER WOOD	7.18	0.72	4.39	4.46	52.32	1.04	2.19	0.46	7.73
WYTHAM WOOD	2.56	0.53	1.49	5.51	38.48	0.78	0.71	0.17	7.08
CWMYSTWYTH	3.73	0.54	1.94	4.04	38.78	1.58	2.12	0.47	5.62
HEIGHAM HOLMES	3.07	0.49	1.67	4.47	30.06	0.68	1.08	0.21	6.32
BEACON HILL	3.53	1.02	1.83	8.41	64.06	1.65	1.16	0.22	13.51
DETLING	5.86	0.82	2.66	10.45	58.17	1.31	1.22	0.24	12.16
INVERPOLLY	2.68	0.52	4.13	6.25	30.76	1.38	4.08	0.37	1.57
LOUGH NAVAR	1.35	0.56	0.92	2.18	12.60	1.81	2.17	0.03	1.43
PENALLT	2.84	0.34	1.47	5.10	39.57	1.84	0.80	0.41	7.33
BOWBEAT RAIN	2.60	0.69	1.78	3.78	62.76	0.65	1.63	0.36	5.29
HOLM MOSS RAIN	5.98	2.19	3.15	14.98	116.78	5.20	3.47	0.39	21.74
BOWBEAT CLOUD	72.47	13.56	131.03	141.53	882.07	21.97	59.30	8.29	143.06
HOLM MOSS CLOUD	238.43	46.96	206.51	576.87	2863.48	75.57	128.88	34.08	632.18

2.8 Scavenging Ratios

The scavenging ratios were calculated by dividing rain concentration by the air concentration for every sample and multiplying by a factor to convert to mass based scavenging ratios. For each metal, the scavenging ratios frequency distribution is log-normal, therefore, the medians of the scavenging ratios are the appropriate value to be considered, and are plotted in Figure 20, which shows the arithmetic mean and median of the site median values. The vertical bars represent the 5% - 95% range of the data.

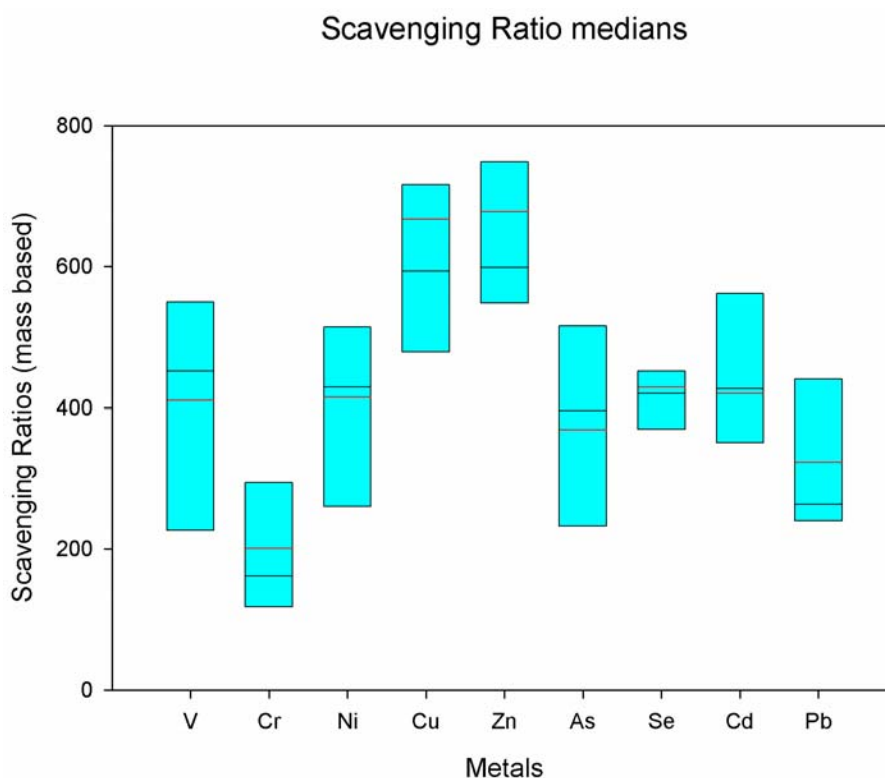


Figure 20: Box plot representing the 5% - 95% range of scavenging ratio medians at each site for each metal. The red line represents the arithmetic mean of values of the medians; the black line represents the median of the medians.

They compare reasonably well with previously reported data (Nemitz et al. 2006), though Cadmium and Nickel ratios are somewhat smaller than used previously. The network has provided significantly more data than has previously been available. We have no explanation at present for the high ratios of Copper and Zinc.

2.9 Data in appropriate format for transfer to EMEP and OSPAR networks

Data for OSPAR was provided to NETCEN as requested to fulfil the UK obligation for this database. Data was sent for Banchory, Yarner Wood, Heigham Holmes and Lough Navar, for As, Cd, Cr, Cu, Hg, Pb, Ni, Zn, for the sampling frequency at each site, in both air, and bulk precipitation.

Time weighted annual average lead concentrations for each site were also supplied to NETCEN for EU daughter directive modelling.

2.10 Summaries of quality control and quality assurance reports for both sampling and chemical analysis of particles and precipitation across the network

A brief summary of the Quality System and specific operations:

Chemical analysis of precipitation and filter samples was conducted at the new purpose-built laboratories of CEH at Lancaster. All samples were handled within the laboratory quality system and logged through the project Oracle database.

UKAS accreditation for the laboratory was awarded on 15th August 2005 (Testing Laboratory Number 2506). Methods for trace metal, cation and anion components were included within the accreditation.

Methods were validated and performance characteristics determined for each method. Estimates of uncertainty are available on request. All validation reports, analytical and QC data are archived and available for internal and external (customers and UKAS) audit.

Analytical performance was assessed within the following framework:

- Regular participation in a proficiency testing scheme for waters (see Table 11 as an example for Cd).
- Regular analysis of certified reference material for waters and filters (Figure 21).
- Checks (blanks) to evaluate whether there is contamination above background levels.
- Internal quality control samples analysed to ensure that each analytical batch is associated with valid check sample data (Figure 22).

Table 11: Aquacheck proficiency testing data for Cd in water (Group 5).

Distribution	Date	Conc (ug/l)	% Bias	Z score ¹
265	June 2004	1.97	-5.2	-0.43
269	Aug 2004	2.4	-2.7	-0.27
273	Sept 2004	4.77	-2.0	-0.2
277	Nov 2004	2.40	- 3.9	-0.39
281	Feb 2005	5.42	2.4	0.24
285	Aug 2005	3.26	-2.4	-0.24
293	Oct 2005	Missing		
301	Feb 2006	3.14	-3.82	-0.38

Note¹ Z scores below 2 indicate valid data.

Table 11 indicates that the laboratory achieved good data for the samples supplied.

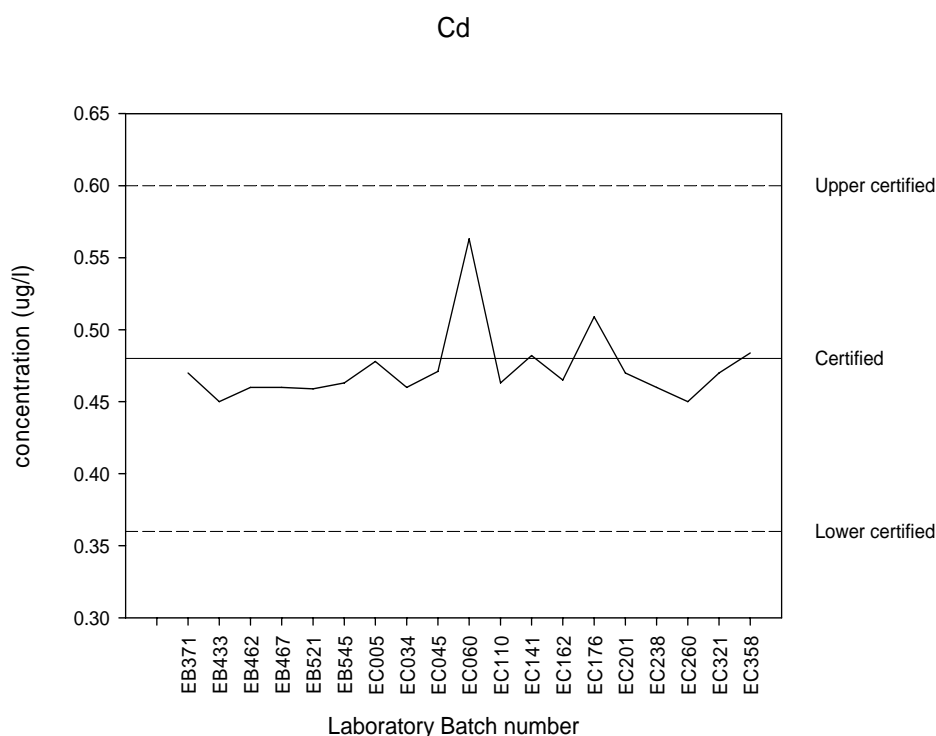


Figure 21: Shewhart control chart of Certified Reference Material TMRAIN-95 for cadmium.

Data displayed in Figure 21 confirms that the laboratory achieved reliable results for Cd over the period of the contract.

ICPMS AQC data - Cd 114

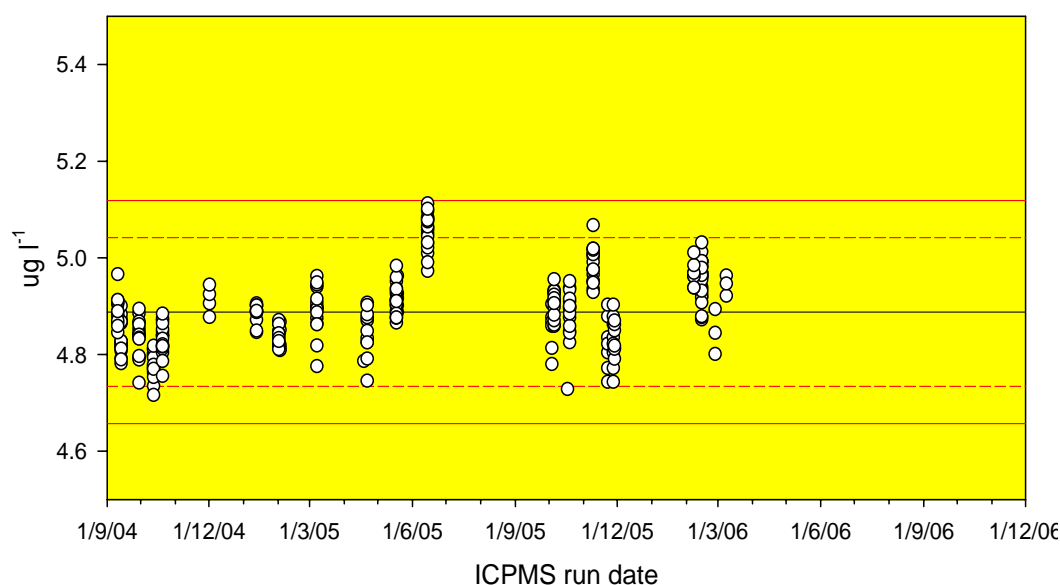


Figure 22: Performance data for cadmium derived from the AQC sample analysed with each analytical batch.

Figure 22 indicates that most of the CEH internal AQC check-sample cadmium data lies within 2σ (between the dotted red lines) of the mean and all data lies within 3σ (between the solid red lines) of the mean. We therefore conclude that the analytical process is under good control i.e. good accuracy and precision was achieved.

3. Monitoring at Upland Cloud Water Sites

3.1 Introduction

Cloud sampling sites were established at Bowbeat in the Scottish borders (580m a.s.l.), and at Holme Moss in West Yorkshire (530m a.s.l.), where cloud droplets and rainfall are collected.

The passive cloud sampler comprises a welded stainless steel frame that has been powder coated with polyurethane, supporting a polypropylene toothed edge disc. A fine filament of polypropylene (0.55mm diameter), is strung between the frame and the 168 teeth to produce an inverted cone of tensioned filaments. These filaments intercept wind driven cloud droplets which then run down via a funnel into a 5 litre collecting bottle (Figure 23).



Figure 23: Cloud collectors at Bowbeat

There have been a few occasions where these collectors have overflowed and investigations are currently in place to establish whether 20 litre collecting bottles and sub-sampling could be used without a contamination risk.

A flow diverter system, that has already been tested for rainfall could also provide an acceptable solution.

The cloud sampling sites also collect rainfall for the calculation of cloud water enrichment factors from the comparison between cloud and rainwater concentrations.

3.2 *Monthly concentrations of heavy metals in cloud and precipitation at 2 upland sites, and annual volume-weighted means.*

The weekly concentrations in rainwater and cloudwater for all 26 elements measured are given in Table 24 – 31 in Appendix 1. The annual volume weighted means filtered to remove outliers greater or less than twice the Standard Deviation of the raw data are presented in Table 12. The concentrations measured by the cloudwater collectors were typically 3 to 8 times higher than for rainwater. The design of the cloudwater collectors will intercept the fine cloud droplets but does not prevent them from capturing rainfall as well. As a consequence the concentrations presented for cloudwater will be underestimates due to ‘dilution’ by rainwater.

Table 12 Annual volume weighted means ($\mu\text{g l}^{-1}$), filtered to remove outliers greater or less than twice the Standard Deviation of the Raw data for cloudwater and rainwater at Bowbeat and Home Moss for 2004 and 2005.

	2004					2005				
	BOWBEAT		HOLME MOSS			BOWBEAT		HOLME MOSS		
	RAIN	CLOUD	RAIN	CLOUD		RAIN	CLOUD	RAIN	CLOUD	
Li	0.04	0.20	0.04	0.41		0.03	0.21	0.08	0.33	Li
Be	0.00	0.01	0.00	0.02		0.00	0.00	0.00	0.01	Be
Al	13.47	33.94	12.09	96.80		6.80	26.34	18.92	55.00	Al
Sc	0.03	0.03	0.03	0.03		0.03	0.03	0.03	0.03	Sc
Ti	0.59	1.04	0.41	2.21		0.27	0.69	0.43	1.85	Ti
V	0.59	1.61	0.42	3.00		0.29	1.30	0.62	3.67	V
Cr	0.13	0.30	0.17	1.36		0.08	0.24	0.23	0.72	Cr
Mn	2.71	6.13	1.90	18.27		1.03	4.90	2.83	10.03	Mn
Fe	22.34	70.60	19.36	141.10		7.55	33.92	23.40	90.11	Fe
Co	0.04	0.11	0.06	0.39		0.01	0.09	0.07	0.36	Co
Ni	0.38	1.51	0.22	2.65		0.20	2.34	0.33	3.18	Ni
Cu	1.65	2.40	1.43	11.15		0.42	2.53	1.57	8.87	Cu
Zn	13.33	12.93	11.99	50.71		7.06	15.76	12.20	44.05	Zn
As	0.16	0.45	0.38	1.41		0.07	0.39	0.54	1.16	As
Se	0.42	1.14	0.26	2.74		0.18	1.06	0.36	1.98	Se
Rb	0.15	0.31	0.09	0.57		0.05	0.29	0.09	0.46	Rb
Sr	3.59	9.09	1.74	15.03		1.19	8.53	2.48	11.07	Sr
Mo	0.09	0.18	0.16	2.10		0.03	0.15	0.09	0.63	Mo
Cd	0.10	0.17	0.03	0.27		0.04	0.15	0.04	0.52	Cd
Sn	0.10	0.16	0.06	0.56		0.03	0.13	0.08	0.22	Sn
Sb	0.15	0.41	0.20	1.68		0.06	0.36	0.26	1.70	Sb
Cs	0.00	0.01	0.00	0.05		0.00	0.01	0.01	0.04	Cs
Ba	2.88	5.61	1.44	15.24		0.42	5.38	1.80	11.95	Ba
W	0.01	0.02	0.02	0.22		0.03	0.05	0.02	0.19	W
Pb	2.72	3.30	2.42	13.04		0.59	2.56	2.27	9.72	Pb
U	0.00	0.01	0.00	0.04		0.00	0.01	0.00	0.02	U

3.3 *Enhancement factors (cloud/rain) of heavy metals for use in seeder-feeder modelling of wet deposition.*

Cloud enhancement factors for Bowbeat and Holme Moss were calculated by examining the ratio of concentrations in precipitation and cloud water (with the deposition due to rain in the cloud collector removed from the calculation) and are shown in Figure 24 and Figure 25, whilst the average of the 2 sites is shown in Figure 26. It should be noted that the 2003 data for Bowbeat only represents October to December 2003.

Generally, the enhancements at Holme Moss are greater than at Bowbeat (Figure 26), due to the proximity of pollutant sources to Holme Moss. Enhancements at Bowbeat are in a range between 6 and 9, whilst at Holme Moss most enhancements are in the range between 8 and 11.

Nickel, however, is an exception, as greater enhancements are found at Bowbeat, and enhancements at both sites are much higher than any other metal. This is most likely due to contamination due to Nickel leaching through the polyurethane from the stainless steel frame that holds the strings for the cloud collector, therefore, in the mapping process, lead enhancement values for were used for Nickel.

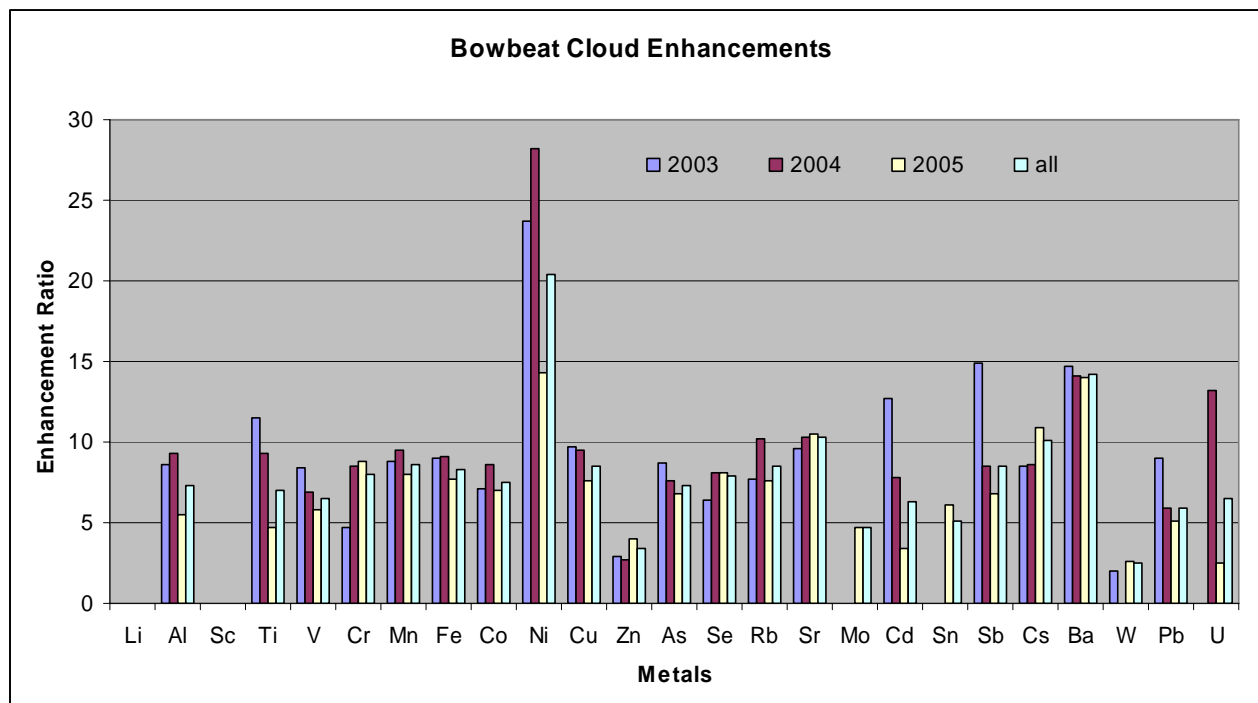


Figure 24: Cloud Enhancement values at Bowbeat for 2003, 2004, 2005, and for all sampling

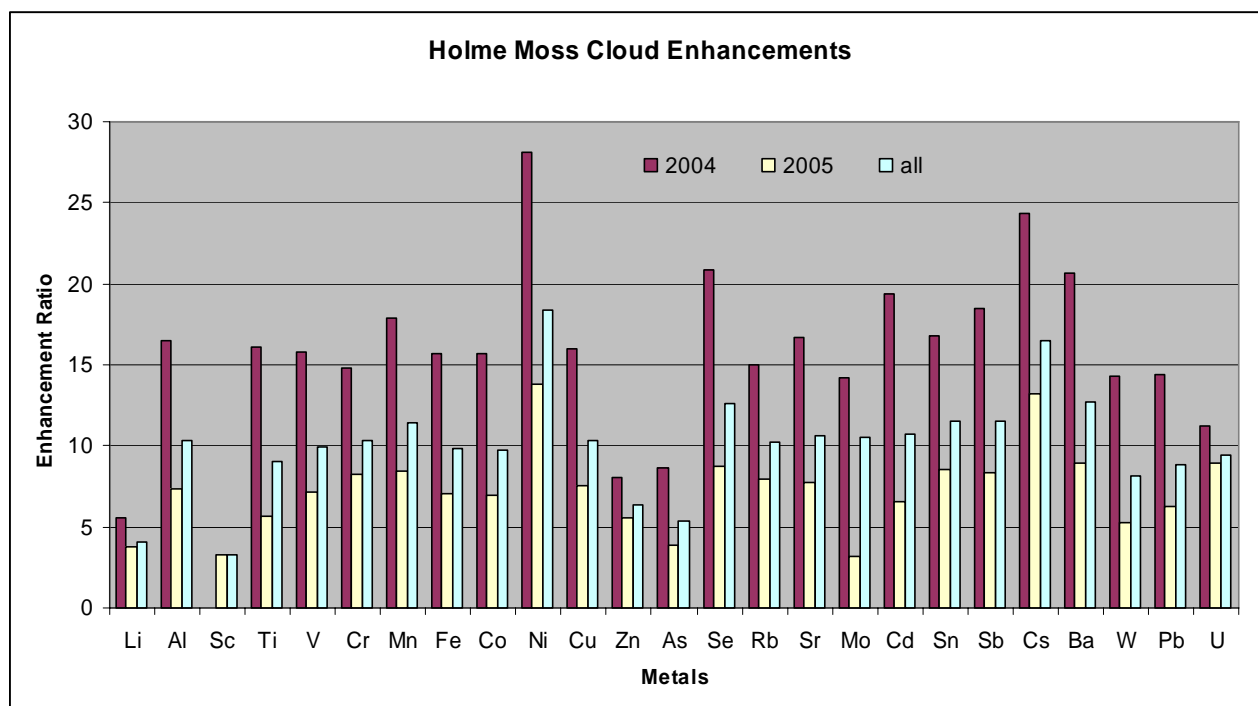


Figure 25: Cloud Enhancement values at Holme Moss for 2004, 2005, and for all sampling

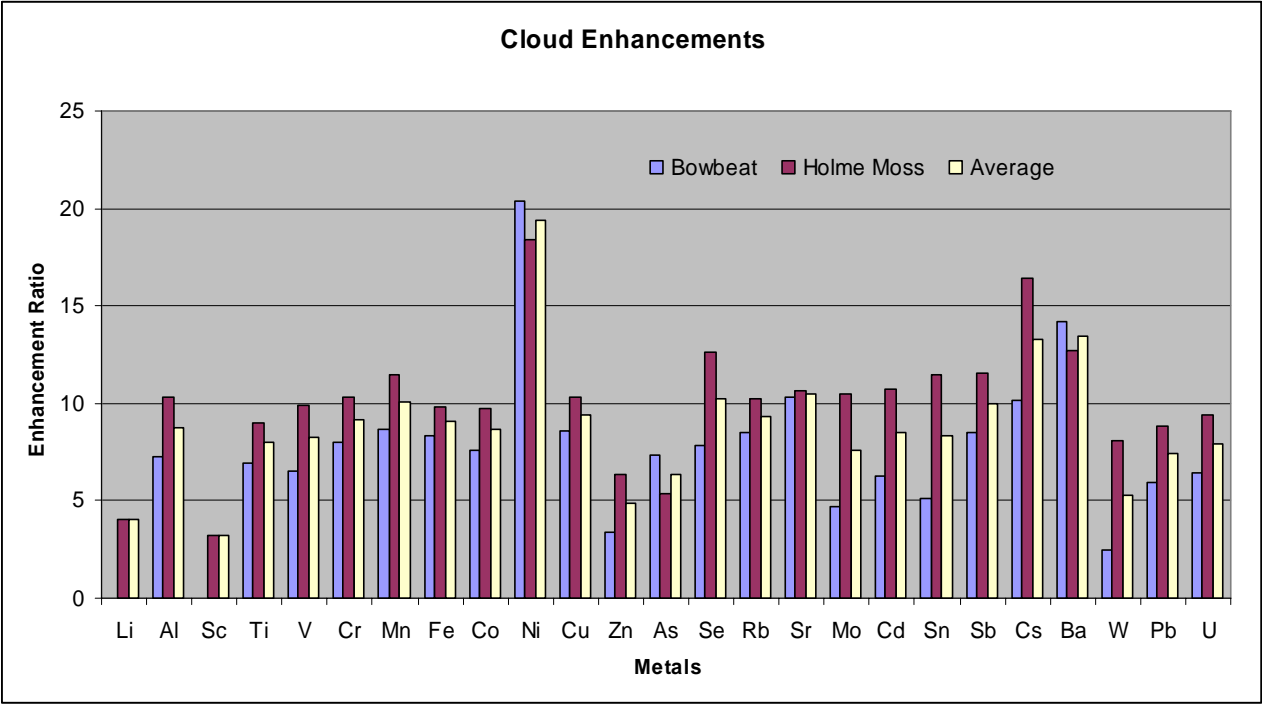


Figure 26: Average cloud enhancement values for Holme Moss, Bowbeat, and an average value of the 2 sites.

4. Production of UK Maps of Metal Deposition

4.1 *Methodology of producing maps*

4.1.1 WET DEPOSITION

To generate maps of heavy metal wet deposition, the volume-weighted annual mean rain concentration data at each of the 13 rain only sites needs to be interpolated across the UK using GIS techniques (the rain collectors at the cloud sites are not used in this process). The relatively small number of sites relative to other networks restricts the spatial detail in the concentration field that can be resolved throughout the UK.

To estimate the wet deposition, it is necessary to model the effect of orography on wet deposition to estimate the deposition on hills. The method used to calculate wet deposition in the UK uplands simulates the seeder-feeder process to take into account the enhanced deposition on upland areas. The measured metal concentrations in intercepted cloud water at both Bowbeat and Holme Moss show that the orographic cloud contains substantially larger concentrations than those in rain, by factors of 5 to 10. However, as the rainfall amounts at the two upland sites only exceed the adjacent values on lower ground by a small amount, extrapolation of the effects at these sites directly to the UK into areas with very large rainfall would lead to overestimates of the orographic enhancement. A conservative difference between the seeder and feeder cloud water concentrations of a factor of 2 has therefore been used in the wet deposition scavenging scheme. To calculate the deposition for 2004, the Met Office 2004 rain field was used, to provide a more accurate deposition field than using a 30 year average. This data is usually unavailable until approximately a year after the year end.

4.1.2 DRY DEPOSITION

The method of generating dry deposition maps is similar to that of wet deposition. The time-weighted annual mean air concentration is interpolated across the UK from the 10 key sites which monitor air concentrations using GIS techniques to create an interpolated grid at a 5km resolution for the UK.

Deposition velocities are calculated using a process model to simulate the transport to the surface. To simulate this, 5 different land use types are considered (arable, grass, moor, forest, urban), plus water, and fractional land use information is obtained from the CEH land cover map. Using wind speed and roughness length to calculate a resistance to different land uses, parameterisations from flux measurements are then used to calculate a deposition velocity to each land use type for each metal. In the case of deposition to forest only and grass only, it is assumed each grid cell is 100% forest and 100% grass respectively, and in the case of land use weighted dry deposition, the fraction of each land use type present in each cell is used to calculate the dry deposition velocity.

The annual dry deposition is calculated by multiplying the dry deposition velocity with the interpolated air concentration field.

4.1.3 CLOUD DEPOSITION

Deposition of cloud droplets accounts for very small fraction of the total metal deposition, but is included in the deposition calculations if averaged over the UK, but can make a significant contribution to heavy metal deposition locally, especially in (often sensitive) upland areas. It is therefore included in the deposition calculations. The interpolated rainfall concentrations are multiplied by cloud enhancement factors shown in Figure 26, and this is multiplied by the fraction of the number of cloud hours in a year in each grid cell. Land cover is also taken into account, as cloud droplets will deposit more efficiently onto forest than onto moor, for example. This accounts

for around 1-2% of the total UK deposition of metals, but is locally very important on the tops of mountains.

4.2 Heavy Metal Maps

Maps of concentration and deposition were produced for As, Cd, Cr, Cu, Ni, Pb, Se, V and Zn for the following:

- Interpolation of heavy metal concentrations in rain and in aerosol across the UK based on monitoring data
- Dry deposition of heavy metals in particulates across the UK for different land use (specifically moorland/grassland and forest), and weighted for different land uses, on 5 km grid
- Wet deposition of heavy metals in precipitation across the UK, enhanced for seeder-feeder effects, on 5 km grid
- Total deposition of heavy metals across the UK, on 5 km grid.

These maps are shown below and show the concentration fields generally have the expected north-west to south-east gradient, which vary by around a factor of 2 – 3, though the deposition maps, which show higher deposition to wet upland areas, have a range of roughly an order of magnitude.

Arsenic (As)

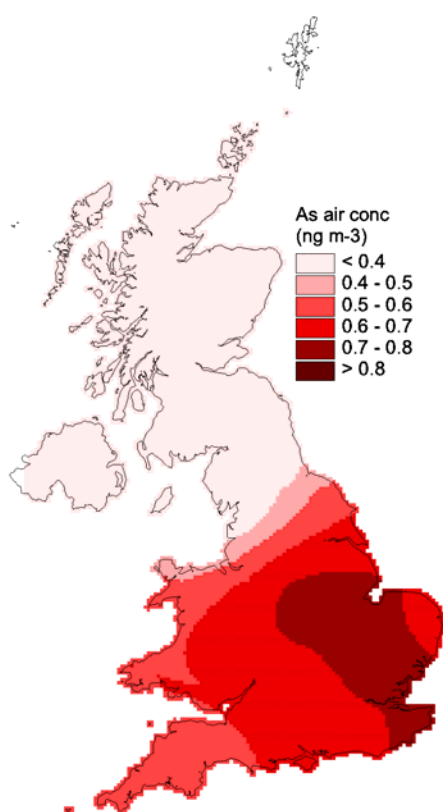


Figure 27: As concentration in air(ng m⁻³)

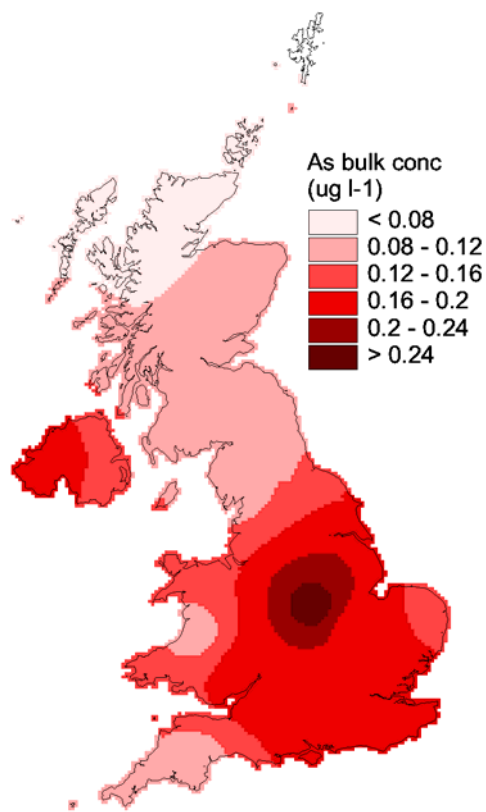


Figure 28: As concentration in precipitation(ug l⁻¹)

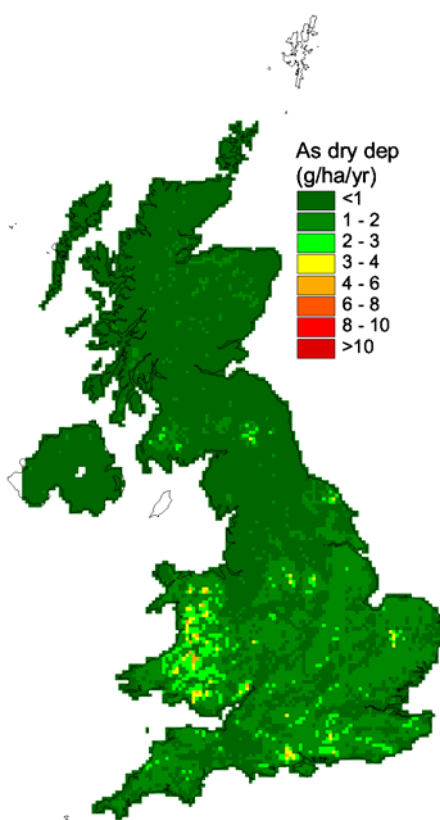


Figure 29: As dry deposition (g ha⁻¹ yr⁻¹)

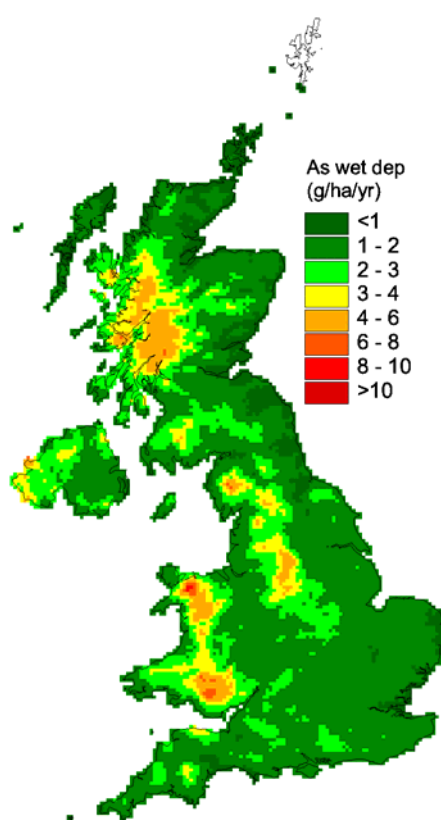


Figure 30: As wet deposition (g ha⁻¹ yr⁻¹)

Arsenic (As)

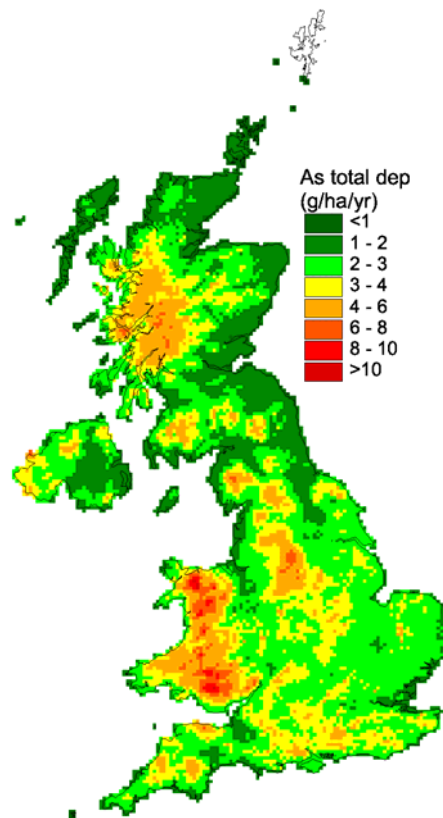


Figure 31: As total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

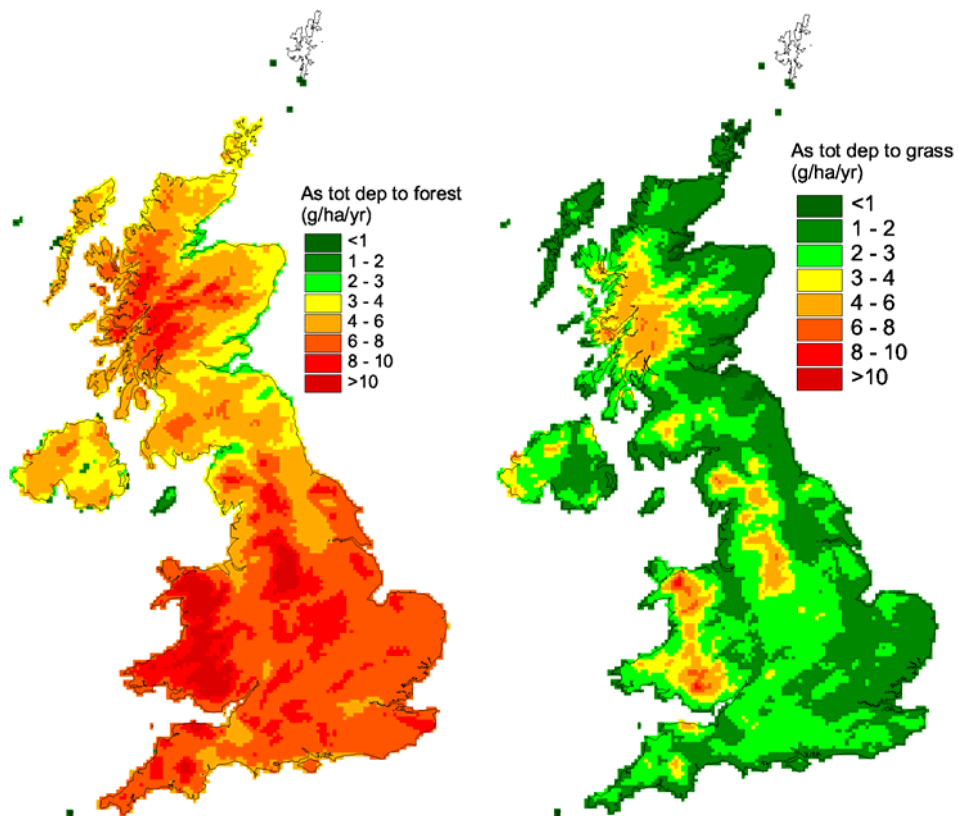


Figure 32: As total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 33: As total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Cadmium (Cd)

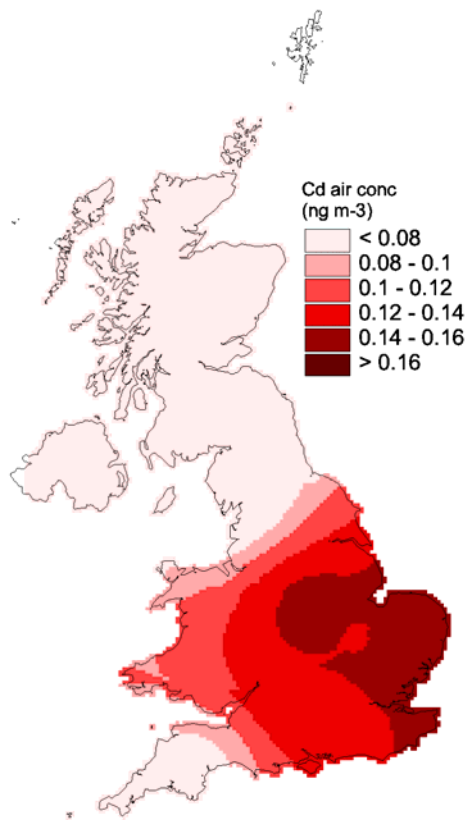


Figure 34: Cd concentration in air (ng m⁻³)

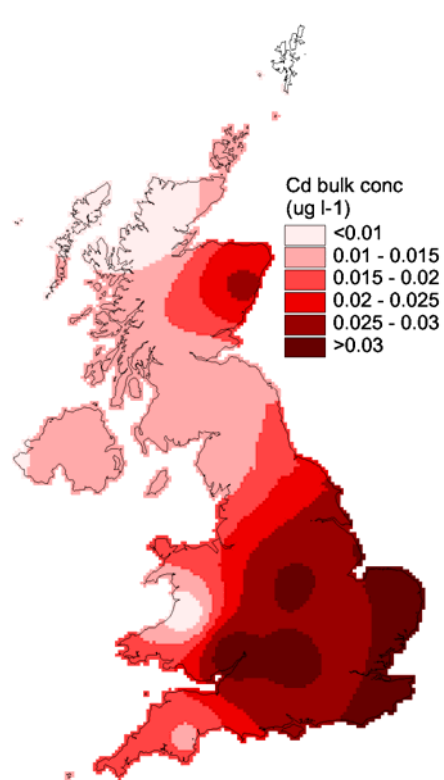


Figure 35: Cd concentration in precipitation (ug l⁻¹)

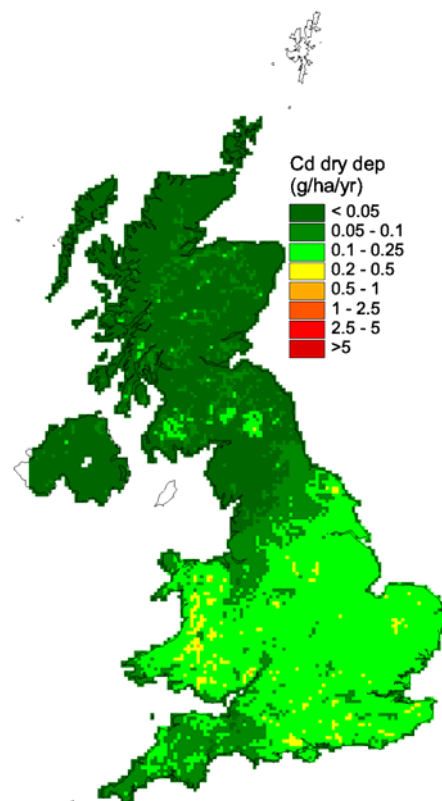


Figure 36: Cd dry deposition (g ha⁻¹ yr⁻¹)

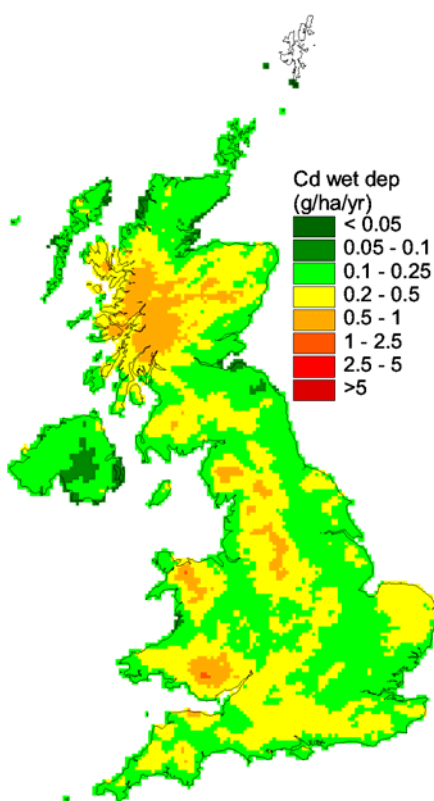


Figure 37: Cd wet deposition (g ha⁻¹ yr⁻¹)

Cadmium (Cd)

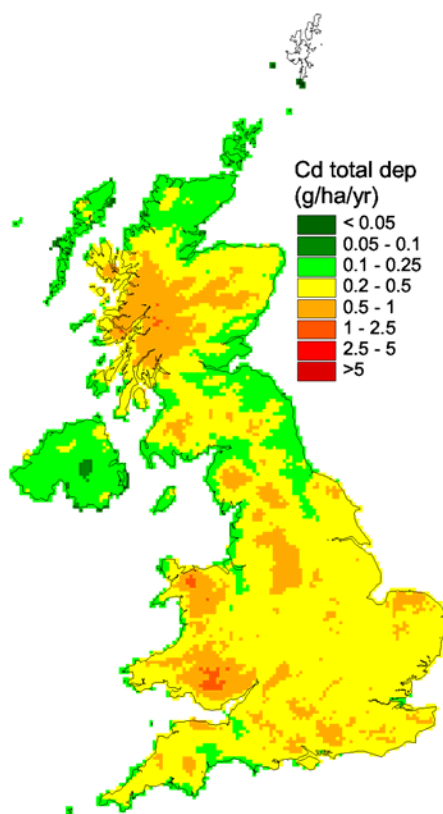


Figure 38: Cd total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

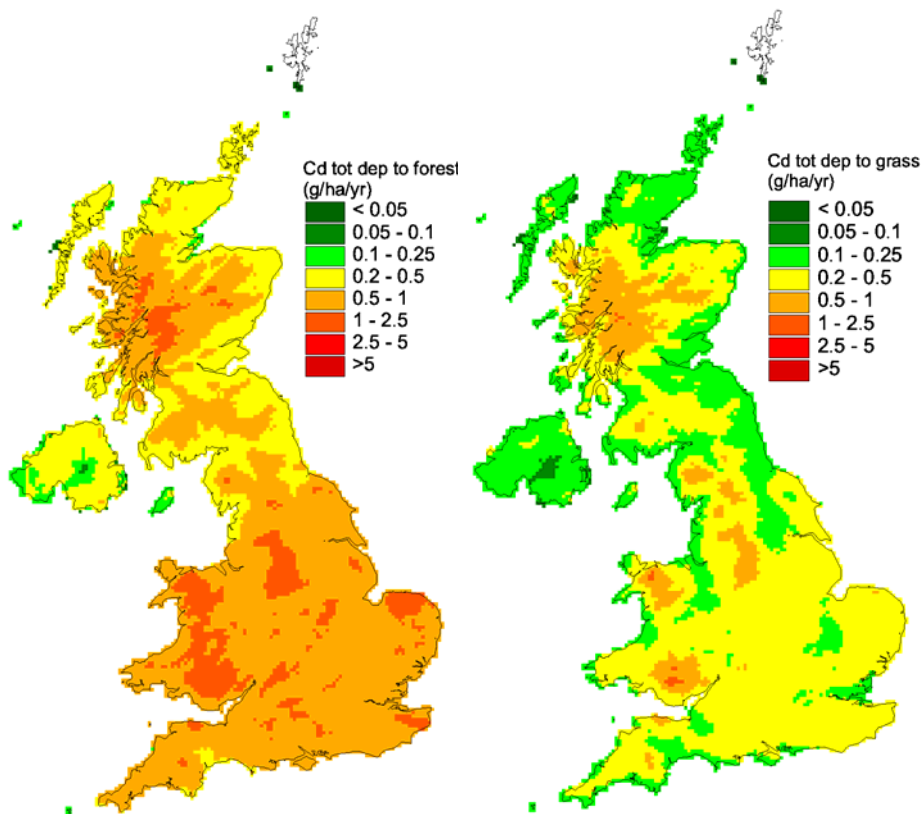


Figure 39: Cd total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 40: Cd total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Chromium (Cr)

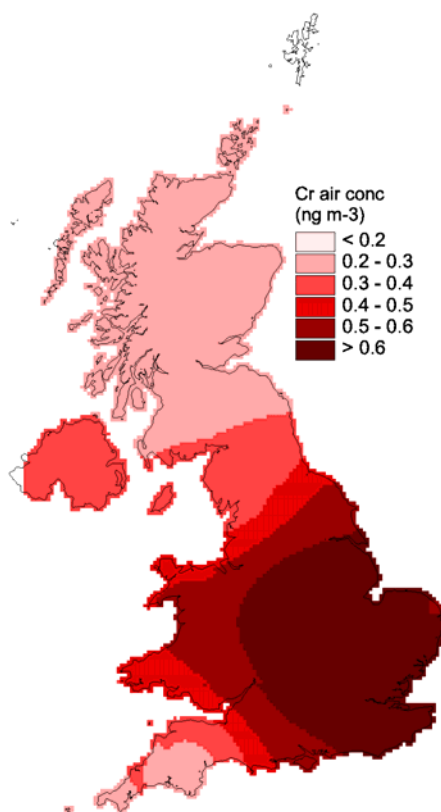


Figure 41: Cr concentration in air (ng m⁻³)

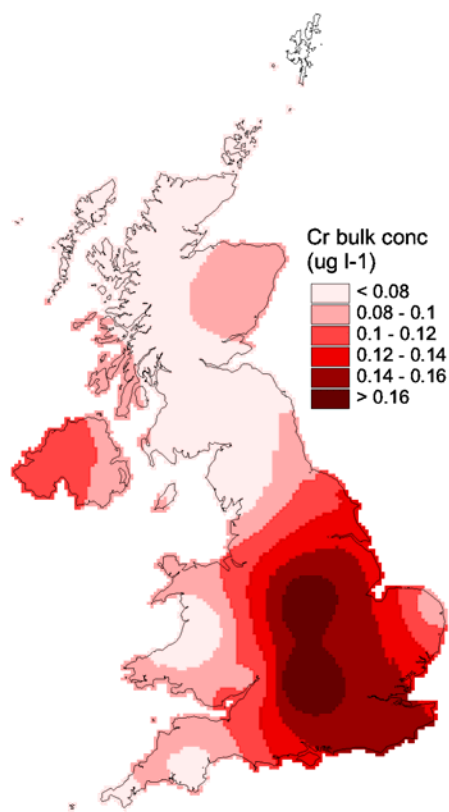


Figure 42: Cr concentration in precipitation (ug l⁻¹)

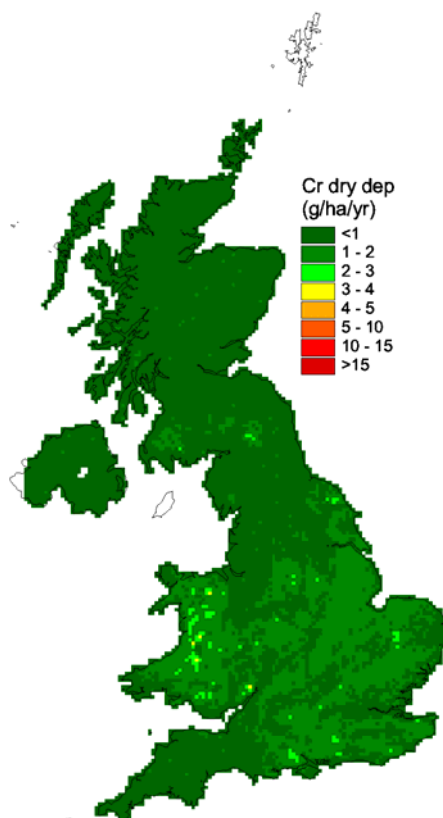


Figure 43: Cr dry deposition (g ha⁻¹ yr⁻¹)

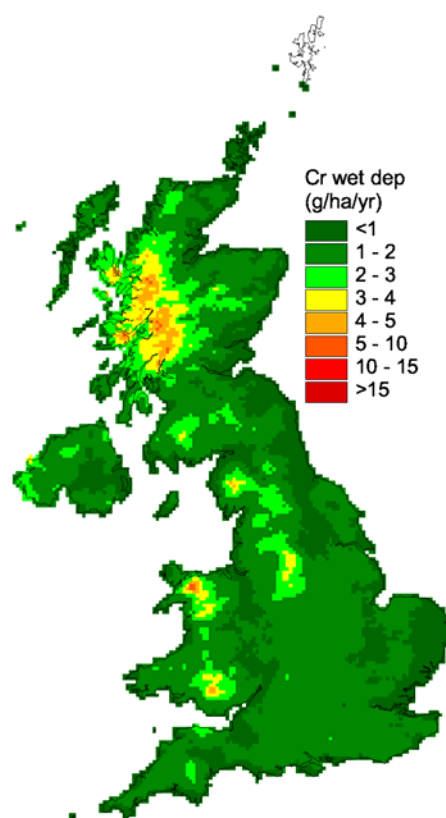


Figure 44: Cr wet deposition (g ha⁻¹ yr⁻¹)

Chromium (Cr)

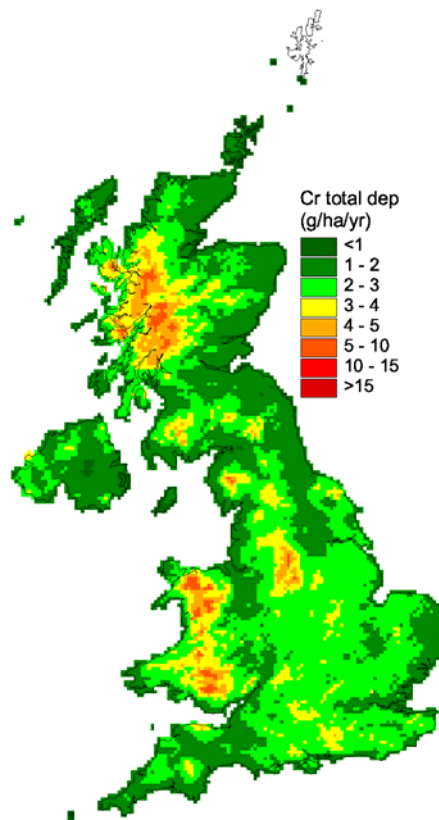


Figure 45: Cr total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

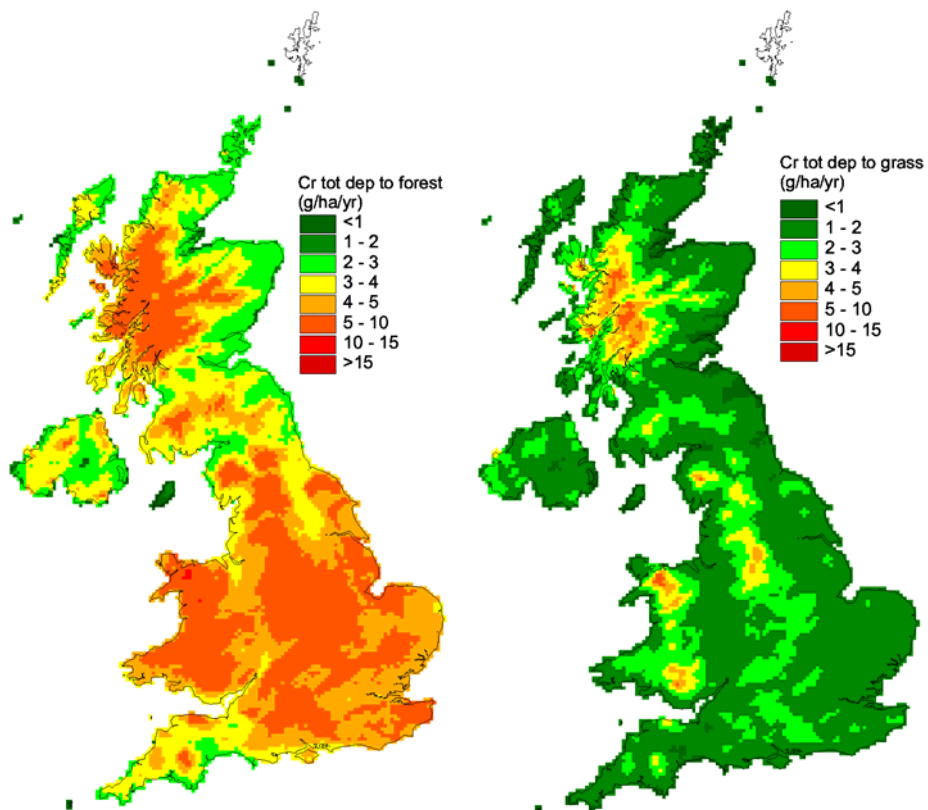


Figure 46: Cr total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 47: Cr total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Copper (Cu)

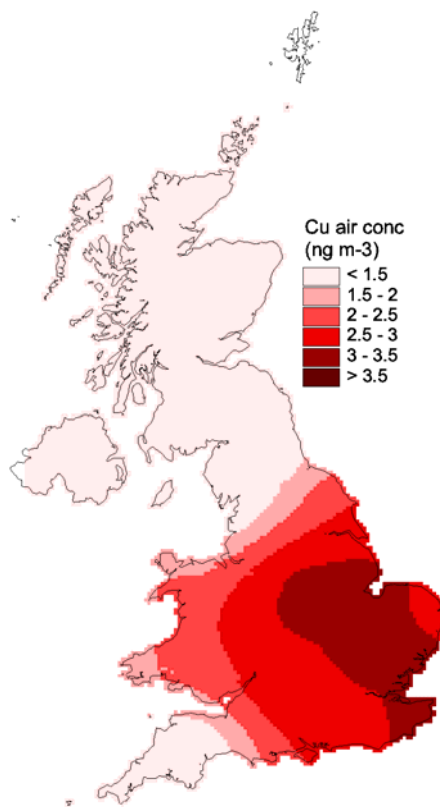


Figure 48: Cu concentration in air (ng m⁻³)

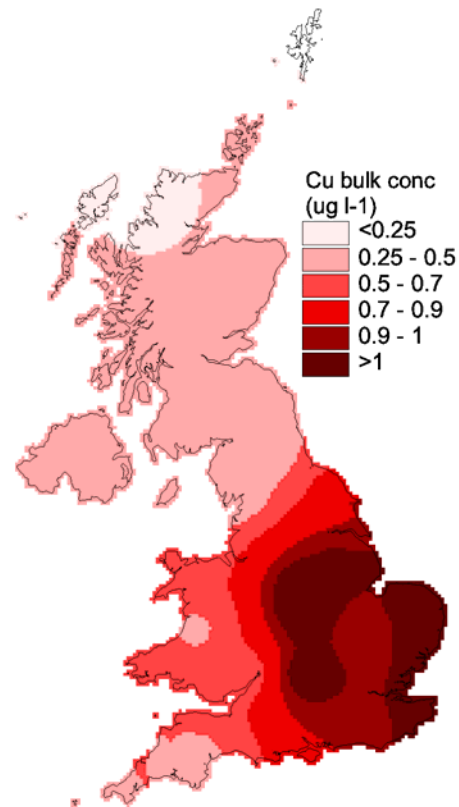


Figure 49: Cu concentration in precipitation (ug l⁻¹)

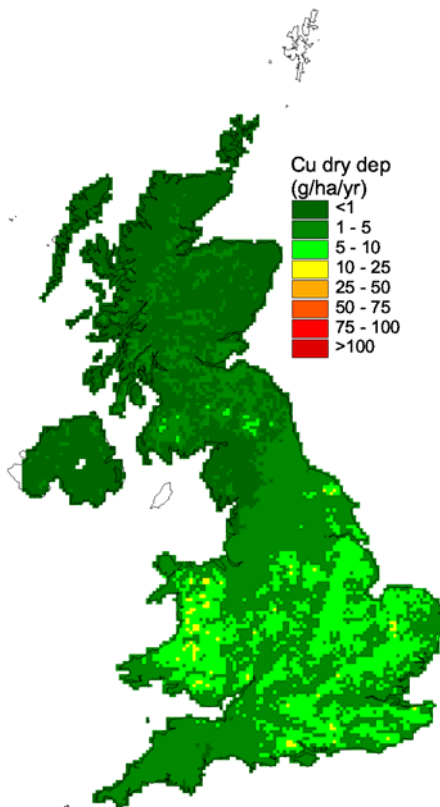


Figure 50: Cu dry deposition (g ha⁻¹ yr⁻¹)

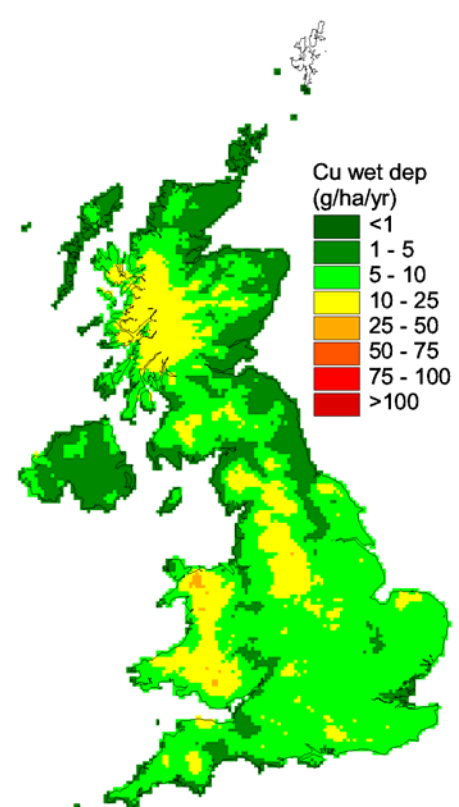


Figure 51: Cu wet deposition (g ha⁻¹ yr⁻¹)

Copper (Cu)

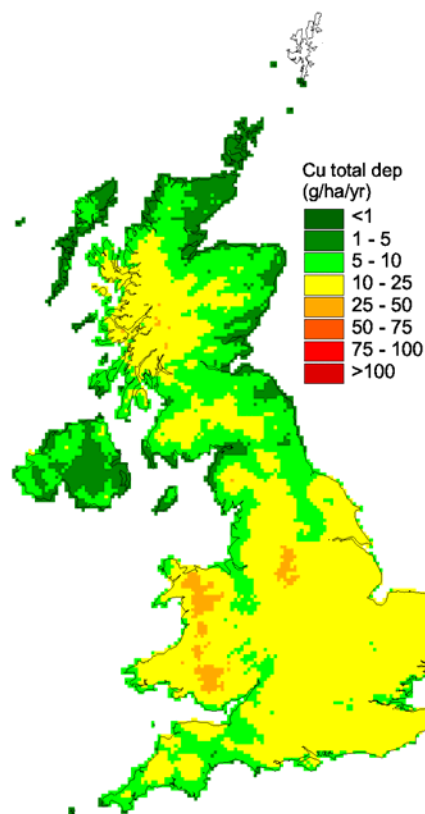


Figure 52: Cu total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

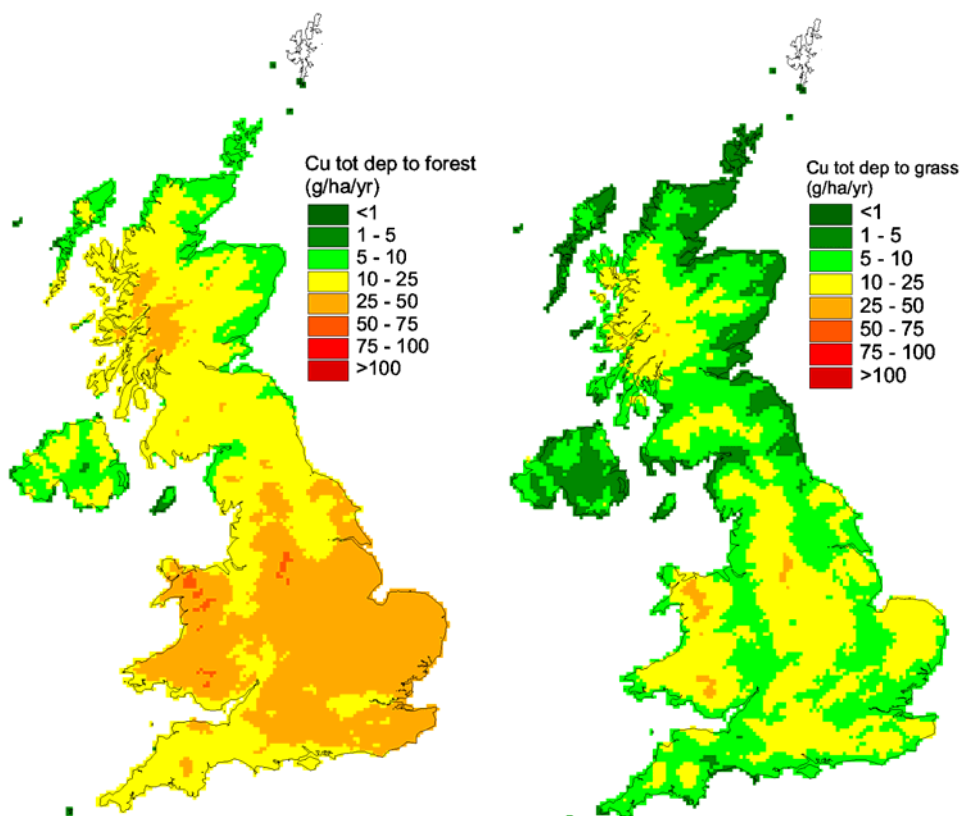


Figure 53: Cu total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 54: Cu total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Nickel (Ni)

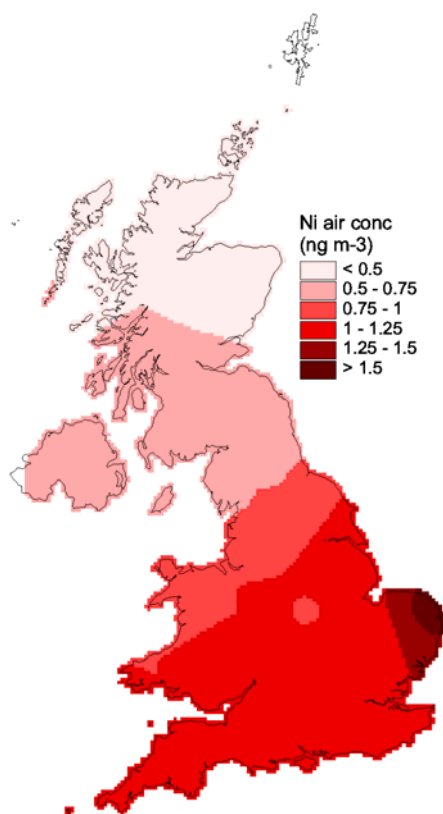


Figure 55: Ni concentration in air (ng m⁻³)

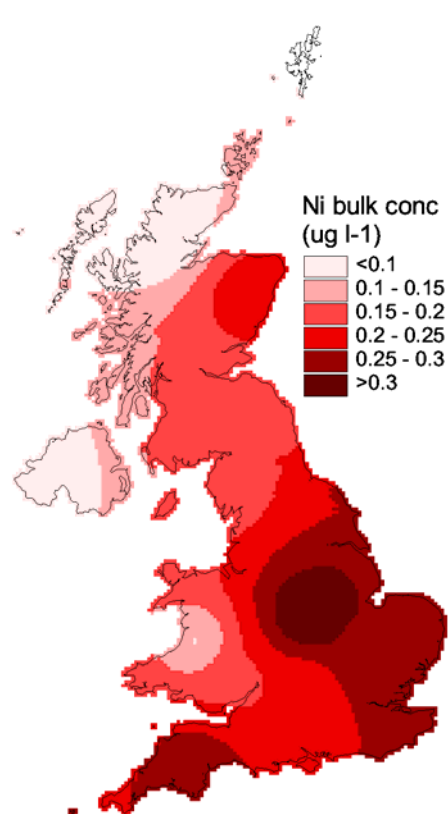


Figure 56: Ni concentration in precipitation (ug l⁻¹)

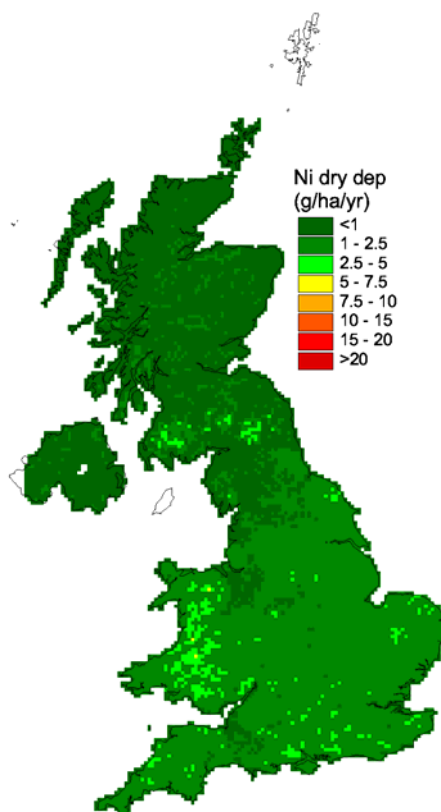


Figure 57: Ni dry deposition (g ha⁻¹ yr⁻¹)

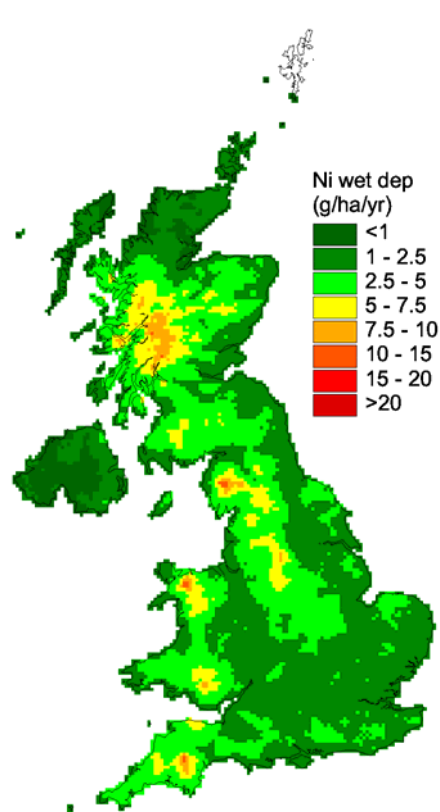


Figure 58: Ni wet deposition (g ha⁻¹ yr⁻¹)

Nickel (Ni)

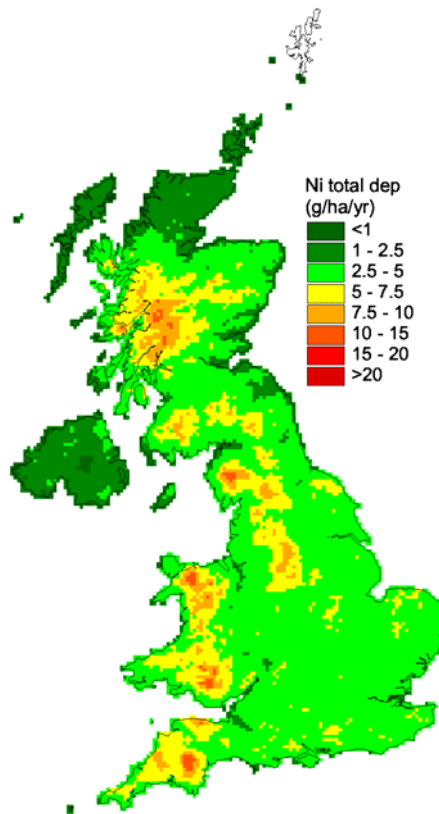


Figure 59: Ni total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

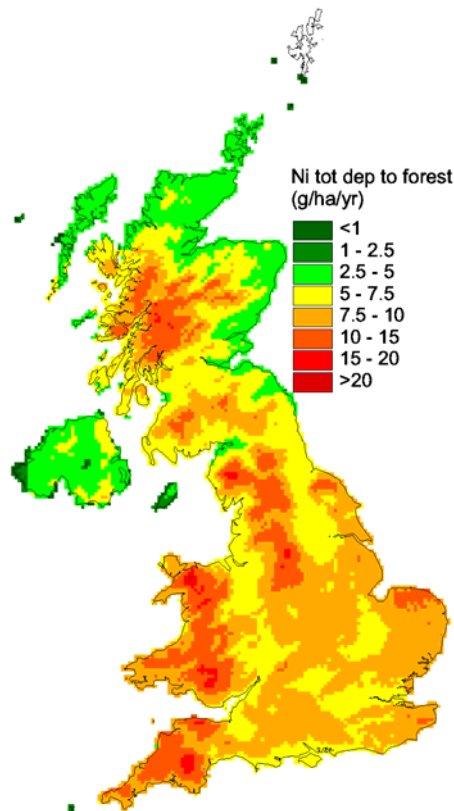


Figure 60: Ni total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

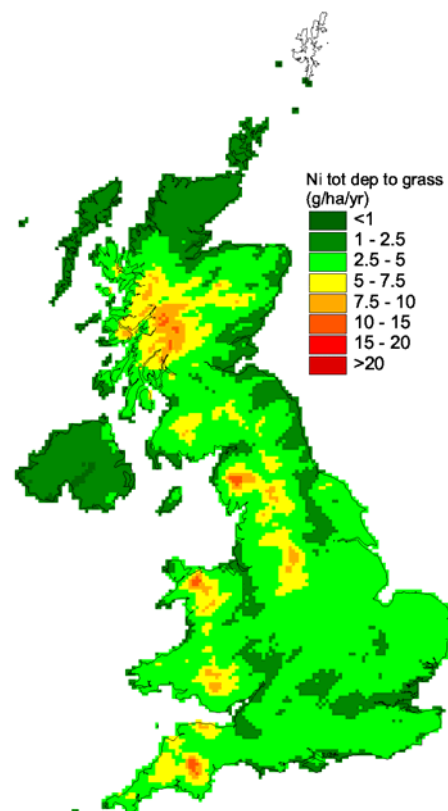


Figure 61: Ni total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Lead (Pb)

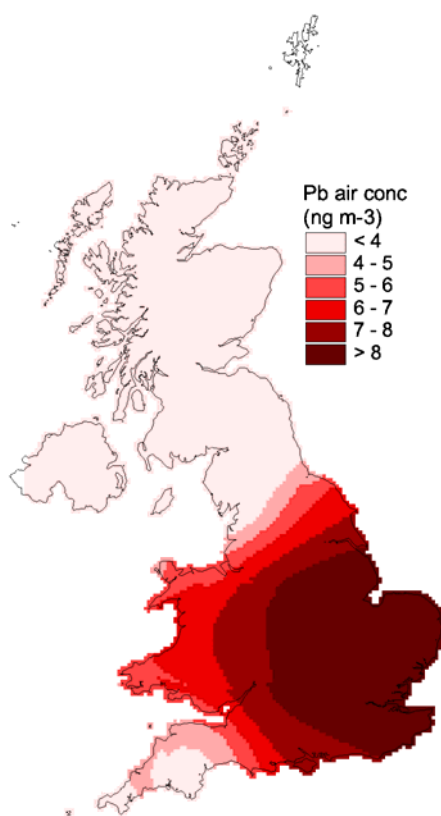


Figure 62: Pb concentration in air (ng m⁻³)

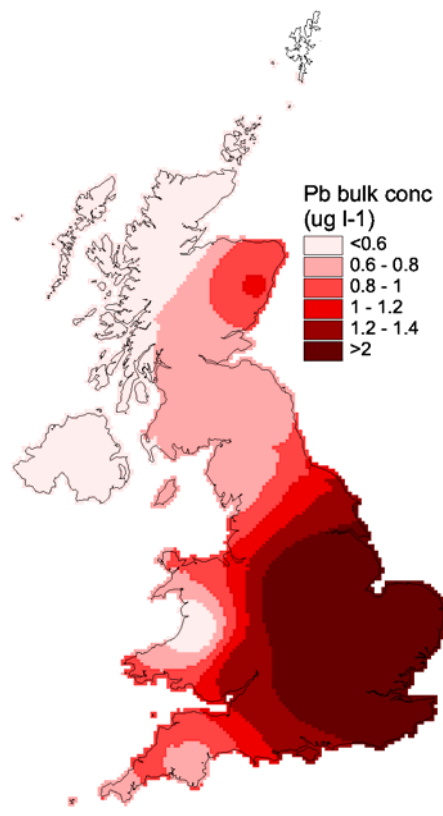


Figure 63: Pb concentration in precipitation (ug l⁻¹)

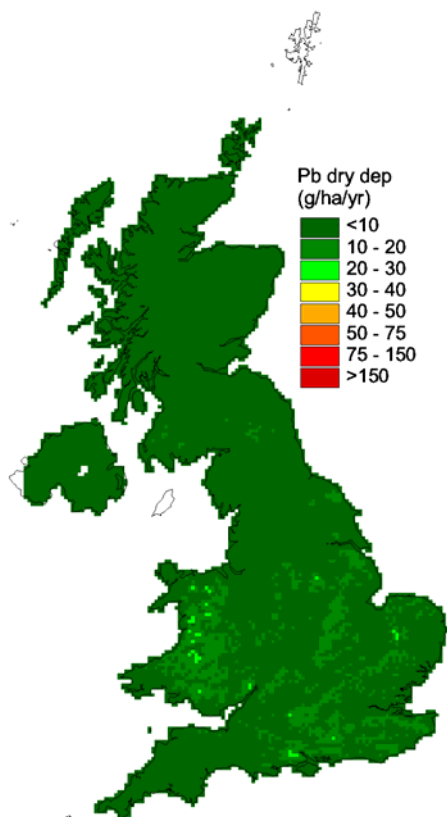


Figure 64: Pb dry deposition (g ha⁻¹ yr⁻¹)

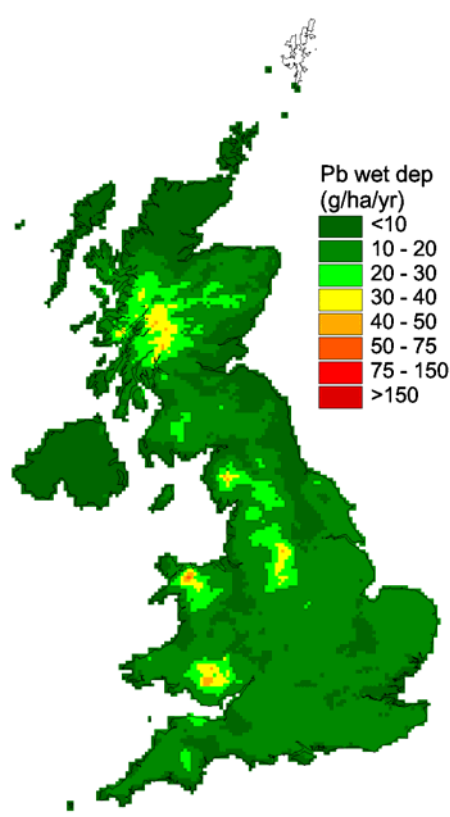


Figure 65: Pb wet deposition (g ha⁻¹ yr⁻¹)

Lead (Pb)

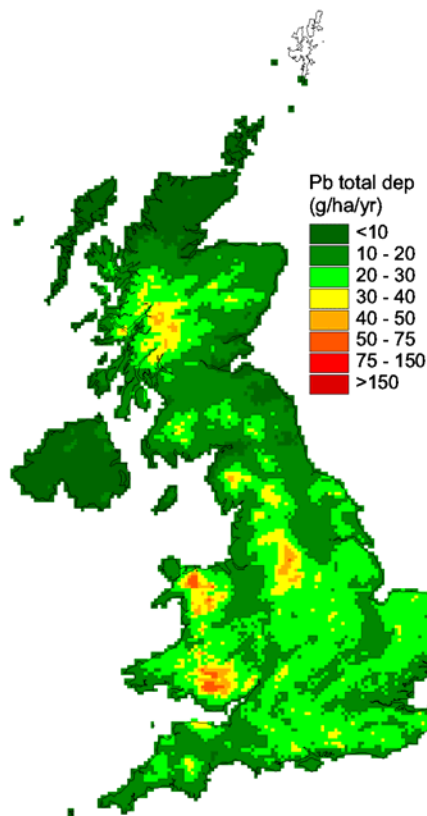


Figure 66: Pb total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

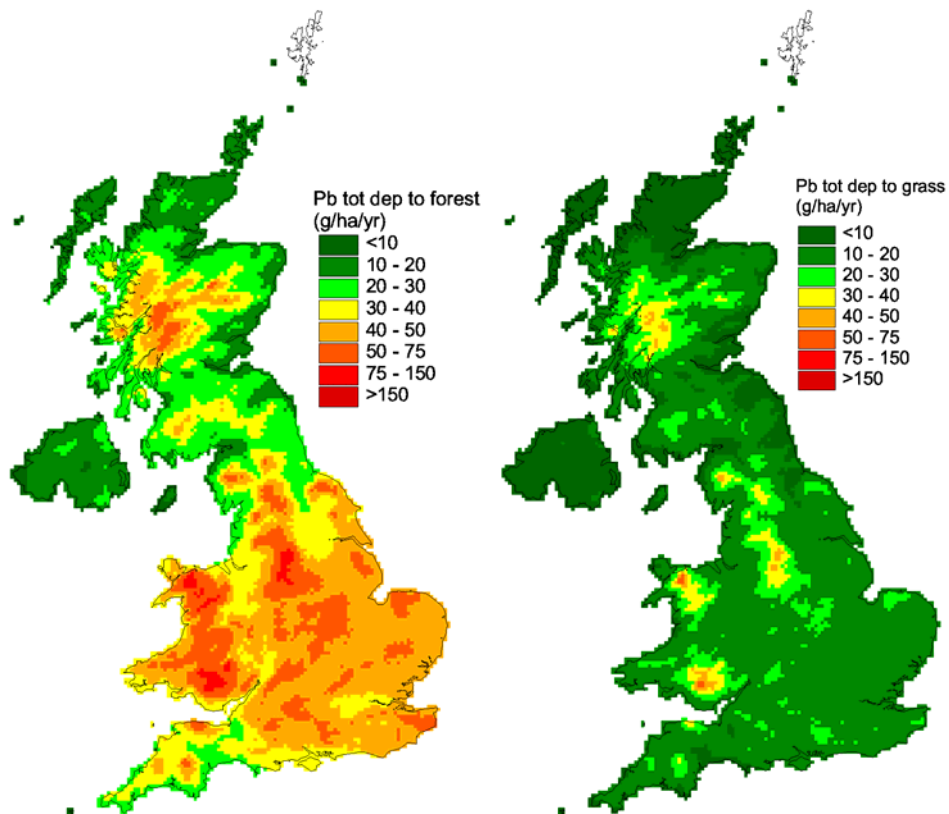


Figure 67: Pb total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 68: Pb total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Selenium (Se)

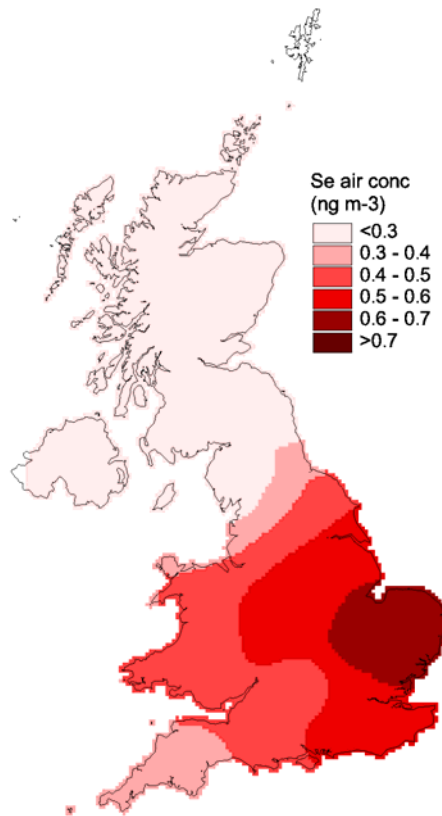


Figure 69: Se concentration in air (ng m⁻³)

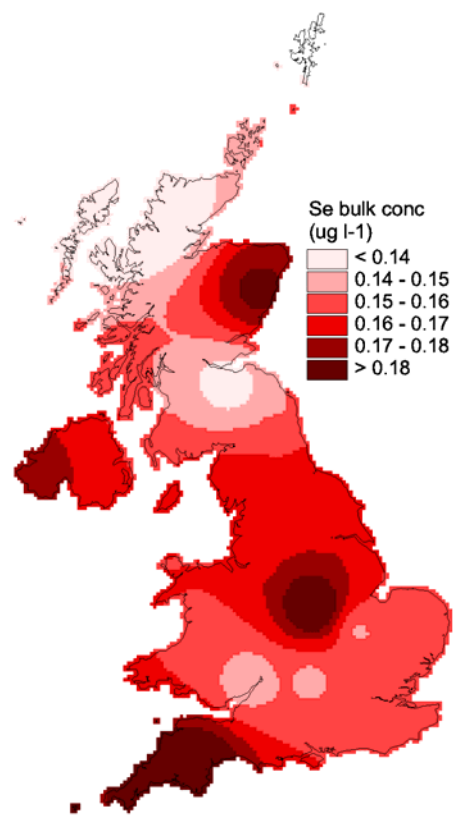


Figure 70: Se concentration in precipitation (ug l⁻¹)

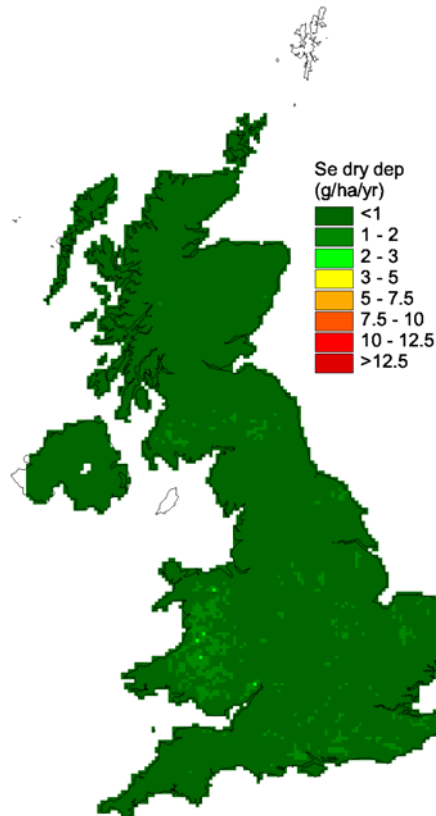


Figure 71: Se dry deposition (g ha⁻¹ yr⁻¹)

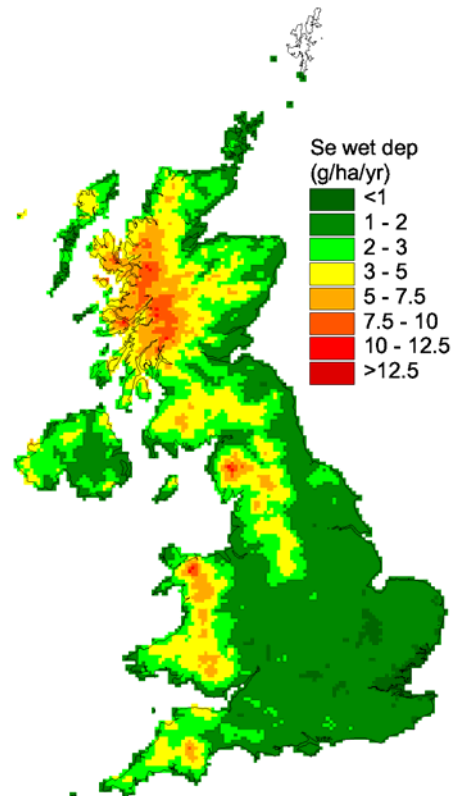


Figure 72: Se wet deposition (g ha⁻¹ yr⁻¹)

Selenium (Se)

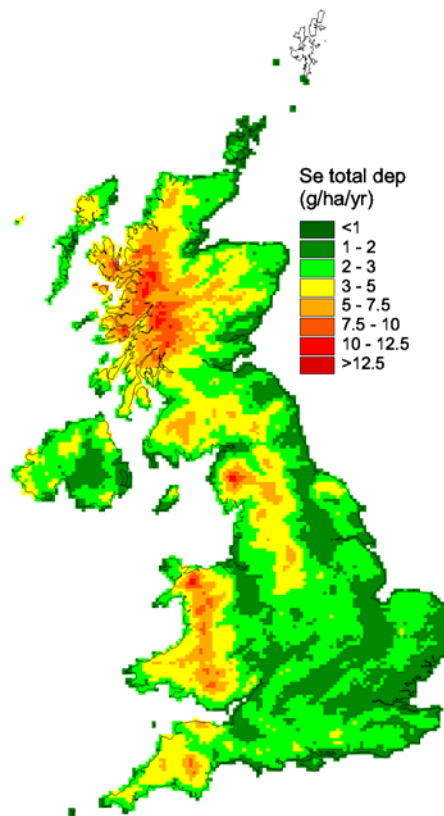


Figure 73: Se total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

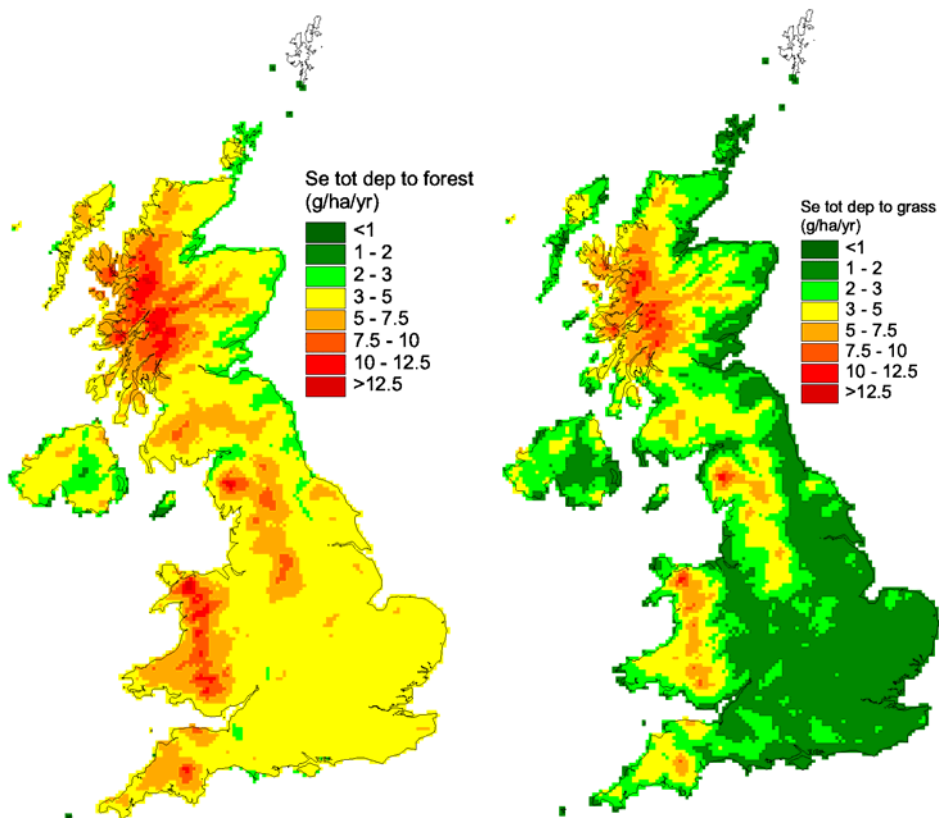


Figure 74: Se total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 75: Se total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Vanadium (V)

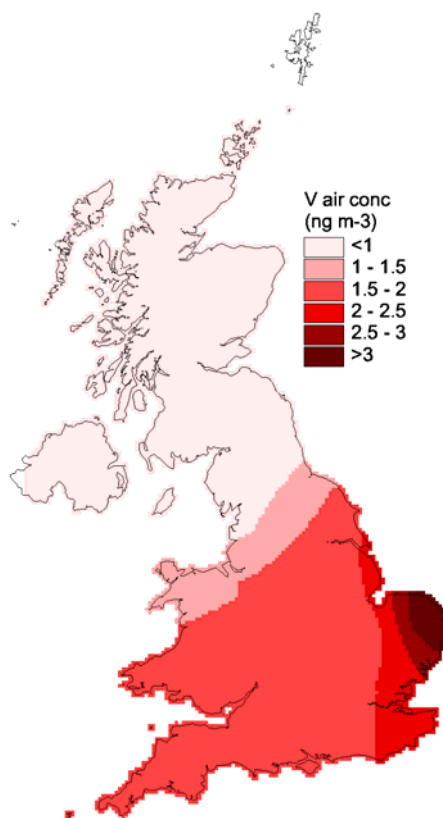


Figure 76: V concentration in air (ng m⁻³)

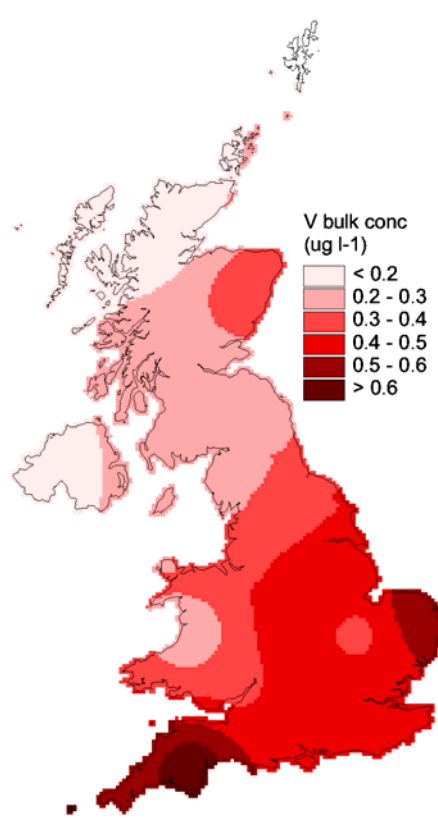


Figure 77: V concentration in precipitation (ug l⁻¹)

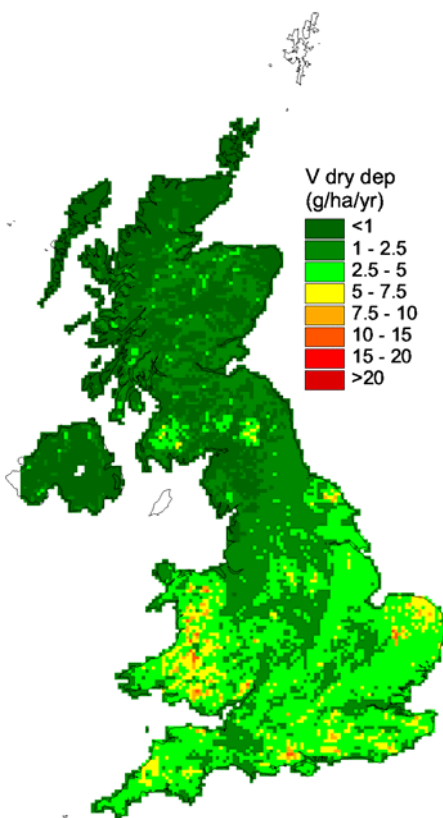


Figure 78: V dry deposition (g ha⁻¹ yr⁻¹)

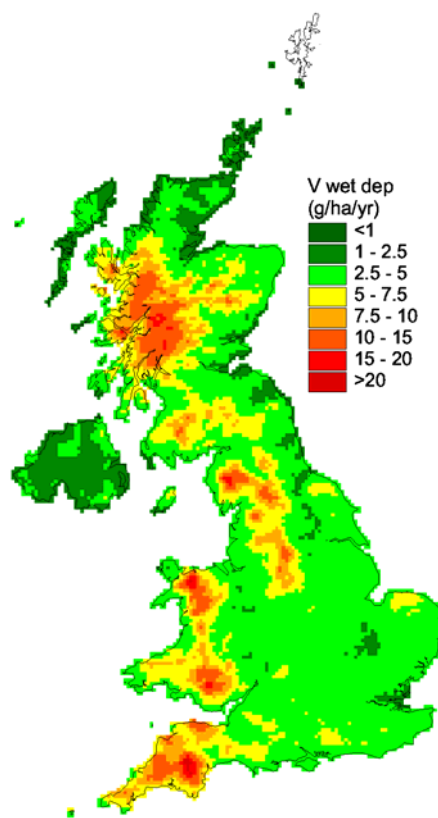


Figure 79: V wet deposition (g ha⁻¹ yr⁻¹)

Vanadium (V)

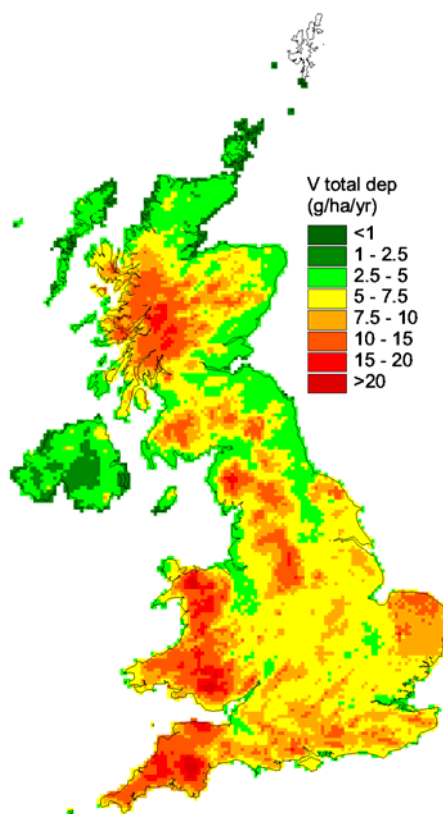


Figure 80: V total deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

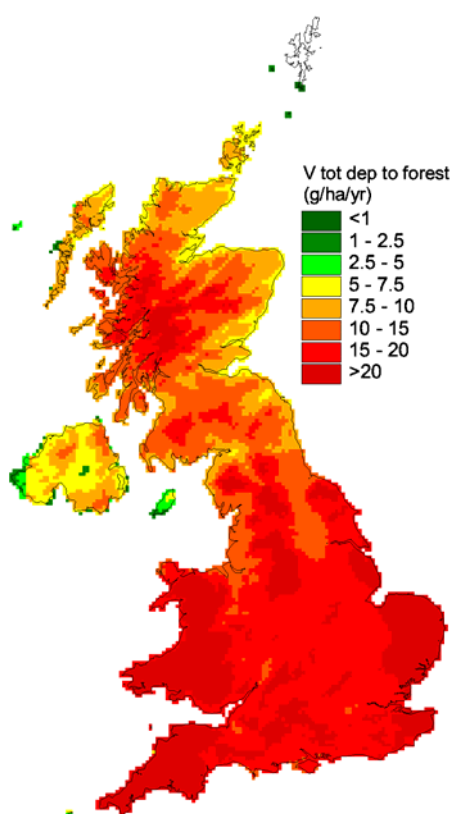


Figure 81: V total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

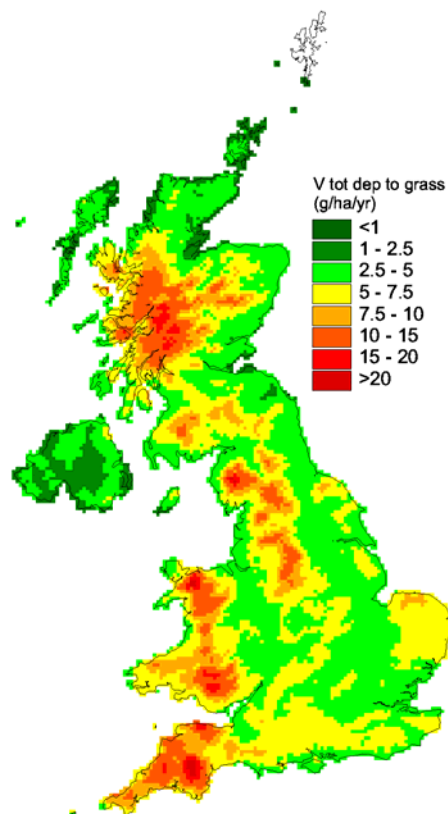


Figure 82: V total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Zinc (Zn)

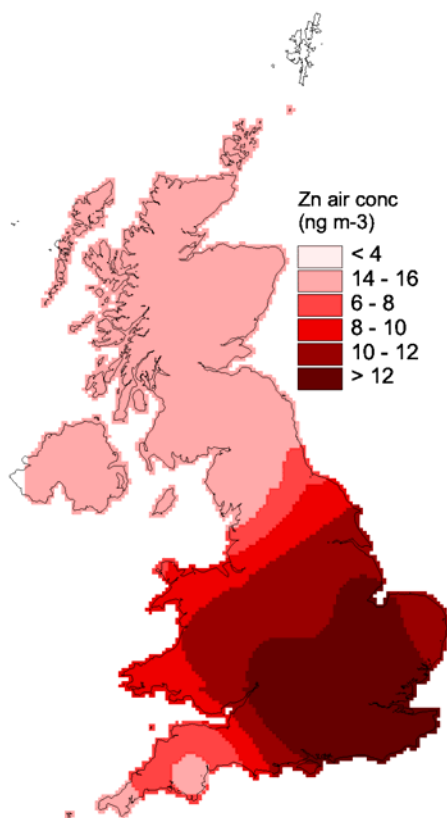


Figure 83: Zn concentration in air (ng m⁻³)

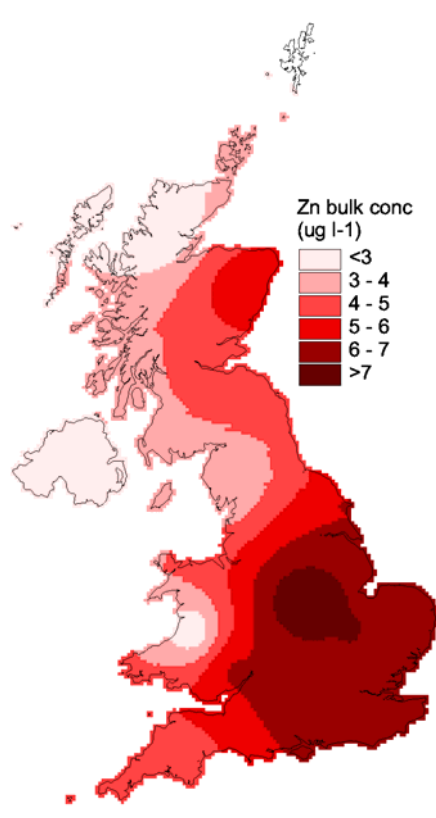


Figure 84: Zn concentration in precipitation (ug l⁻¹)

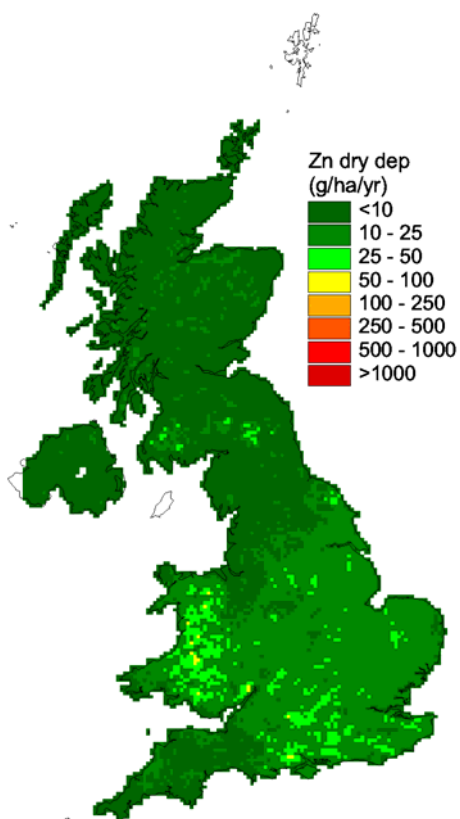


Figure 85: Zn dry deposition (g ha⁻¹ yr⁻¹)

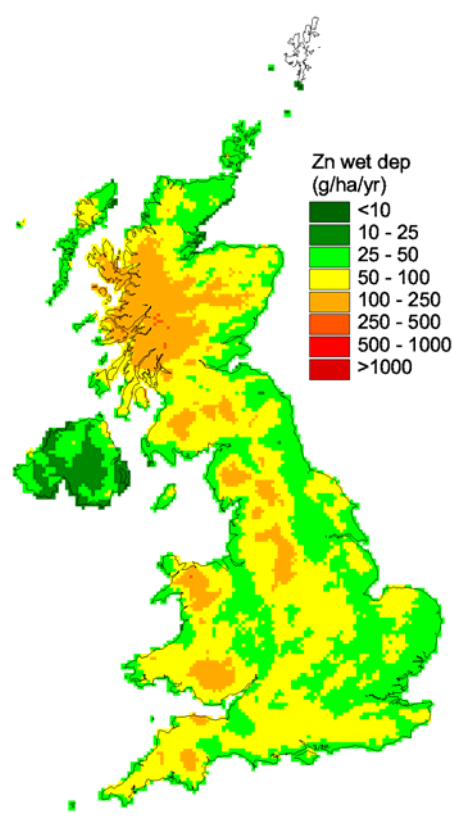


Figure 86: Zn wet deposition (g ha⁻¹ yr⁻¹)

Zinc (Zn)

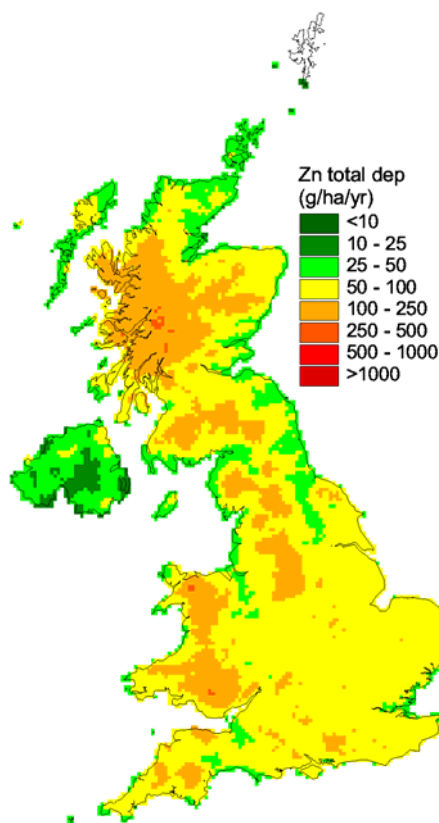


Figure 87: Zn total Deposition ($\text{g ha}^{-1} \text{ yr}^{-1}$)

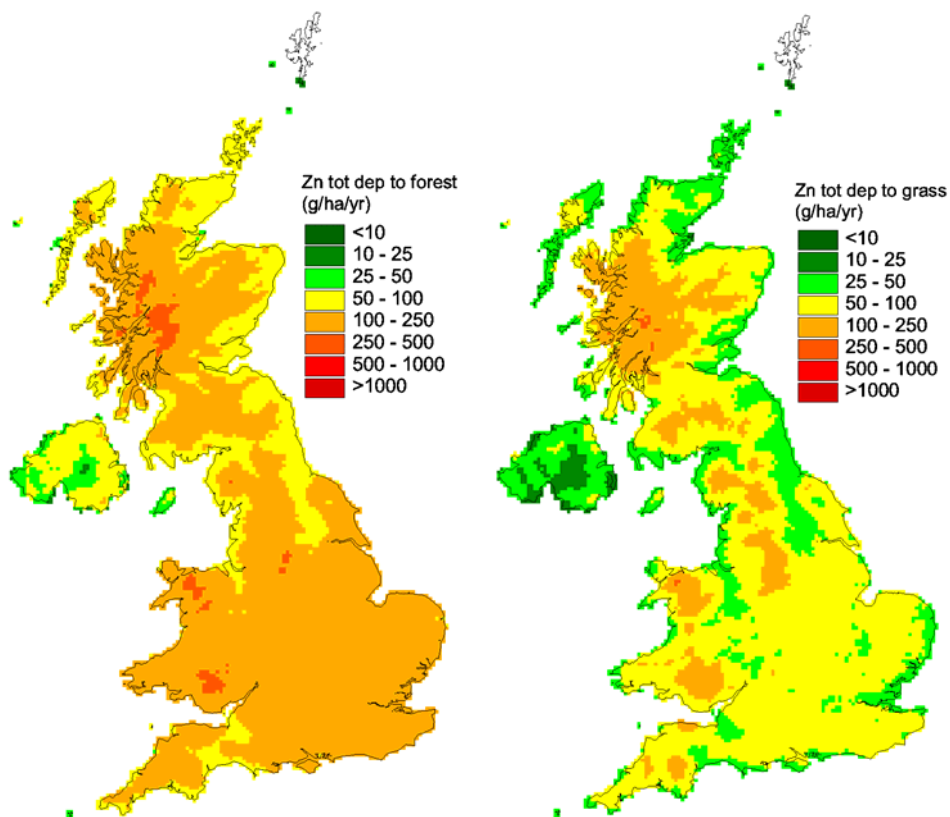


Figure 88: Zn total deposition to forest ($\text{g ha}^{-1} \text{ yr}^{-1}$)

Figure 89: Zn total deposition to grass ($\text{g ha}^{-1} \text{ yr}^{-1}$)

5. Derivation of Relationships between Metal Deposition and Concentration in Moss

5.1 Introduction

Relative concentration fields of heavy metal concentrations in mosses have long been used as a surrogate for heavy metal bulk deposition (e.g. Berg and Steinnes, 1997; Berg *et al.*, 2003; Harmens *et al.*, 2004). Several metals bio-accumulate efficiently in certain moss species and the concentration in the last (few) years' growth for a sub-selection of mosses is correlated with bulk deposition. The sampling of moss is potentially a very cost-effective method to derive measurement-based heavy metal deposition maps with a high spatial coverage. Several studies have addressed the calibration between concentration in moss and bulk deposition, in particular in Scandinavia. Significant correlations were found for selected metals (Berg and Steinnes, 1997; Berg *et al.*, 2003). However, these studies have pointed out that accumulation was reduced in coastal sites and this was attributed by displacement by sea salt-derived Na and Mg. This has potentially important implications for the validity of the moss technique to maritime UK conditions for which the Scandinavian calibrations may not be appropriate.

Objectives

1. to derive relationships between metal concentration in moss and deposition for UK;
2. to re-calculate UK deposition maps using the data from the Moss Survey 2000 applying the improved relationships, taking account of the spatial structure of wind speed, precipitation and land cover;
3. to extend the mapping to other metals.

Mosses collected and determination of their heavy metal concentration

Moss species were collected from each monitoring site as indicated in Table 13. It was not possible to select all of the necessary moss species from each monitoring site as none of the key moss species was present at all the sites. Therefore, it was decided to collect any of the five moss species indicated in Table 9 from the monitoring sites. Mosses were collected from the majority of sites in 2004 and from the remaining sites in 2005; none of the five species were present at Detling. The mosses were air dried and approximately the last year's growth was sorted: 10 mm of green shoot tip was taken from *Rhytidiadelphus squarrosus*, 10-20 mm from *Hypnum cupressiforme* and 20 mm from the other species.

The concentration of metals in mosses was determined after a hotplate digestion using nitric acid under gentle reflux followed by an ICP-MS determination at CEH Lancaster. To allow comparison of metal concentration data the digestion method was the same as that used for previous UK-wide moss surveys (1996/97 and 2000; Ashmore *et al.*, 2002). The weight of moss available for analysis was limited and therefore an analytical validation exercise was performed prior to digestion of the moss survey samples themselves. Three Certified Moss Standards (M1, M2, M3; Steinnes *et al.*, 1997) were analysed to determine the performance characteristics of the hotplate digestion/ICPMS method, and also to validate metal concentration data in relation to the aforementioned historical surveys. The analysis, mostly in triplicate, of the collected mosses described in Table 9 was completed using the validated hotplate digestion/ICP-MS method. Furthermore this analysis was monitored using in-house Analytical Quality Control solutions and the Certified Moss Standard M2(#381), analysed with each batch of hotplate digestions.

Table 13: Moss species collected at the heavy metal deposition monitoring sites; (V) indicates that a low amount of the moss species was present as contamination amongst the main species.

Year Site	<i>Pleurozium schreberi</i>	<i>Hylocomium splendens</i>	<i>Hypnum cupressiforme</i>	<i>Pseudoscle- ropodium purum</i>	<i>Rhytidiadel- phus squarrosus</i>
2004					
Auchencorth	V	V		(V)	V
Wytham				V	V
Inverpolly	(V)	V		V	(V)
Beacon Hill					V
Cockley Beck			V		V
Monks Wood				V	V
Banchory		V	V		(V)
Bowbeat	V	V			
Yarner Wood			V	V	
Cwmystwyth					V
Lough Navar	V	V			
Penallt			V	V	V
2005					
Holme Moss			V		V
Heigham Holmes			V		

In general, the recovery of metals in the Certified Moss Standard M2(#381) was between 84 and 109% (Table 14), with the exception of Co (78.8%), Cr (47.1%) and Sb (76.7%). For the majority of metals the applied method resulted in an underestimation of the certified standard values. Coefficients of variation higher than 15% were observed for Se (26.3%) and Sn (34.4%). The recovery of the metal concentration in the Certified Moss Standard M2(#381) was generally better and the coefficient of variation was generally lower than that in the UK 2000 moss survey (Table 15), when the analysis were performed at the NERC ICP-MS facility at Kingston University (Ashmore *et al.*, 2002). Only for Cr the recovery was better in the UK 2000 moss survey. Although the recovery for Pb was slightly better in the UK 2000 moss survey, this was not the case when the recovery was calculated based on the certified standard Pb values for ICP-MS only (Steinnes *et al.*, 1997).

Table 14: Performance characteristics for the hotplate digestion/ICP-MS method for the determination of metals in Certified Moss Standard M2#381. Concentrations are in $\mu\text{g g}^{-1}$ and CoV is the Coefficient of Variation ($n = 11-13$).

Metal	Certified value	Value found	CoV	Recovery (%)
Al		135	11.1	
As	0.98	0.93	4.7	94.7
Cd	0.45	0.45	2.8	99.8
Co	0.98	0.77	6.0	78.8
Cr	0.97	0.46	16.2	47.1
Cu	68.7	62.0	3.6	90.3
Fe	262	227	5.4	86.7
Mn	342	297	5.1	86.8
Ni	16.3	13.9	5.8	84.6
Pb	6.37	6.92	4.1	109
Sb	0.21	0.16	10.5	76.7
Se	0.29	0.31	26.3	102
Sn		0.18	34.4	
U		0.017	9.5	
V	1.43	1.21	5.0	84.2
Zn	36.1	34.1	13.6	94.5

Table 15: Performance characteristics for the hotplate digestion/ICP-MS method for the determination of metals in Certified Moss Standard M2#381 in the UK 2000 moss survey. Concentrations are in $\mu\text{g g}^{-1}$ and CoV is the Coefficient of Variation ($n = 8$).

Metal	Certified value	Value found	CoV	Recovery (%)
As	0.98	0.93	11.6	94.5
Cd	0.45	0.41	11.9	90.3
Cr	0.97	1.29	20.3	133
Cu	68.7	57.9	10.3	84.2
Ni	16.3	12.0	12.3	73.4
Pb	6.37	6.04	14.6	94.8
Se	0.29	0.34	21.8	115.4
V	1.43	1.13	6.3	78.8
Zn	36.1	29.6	10.3	81.9

Table 16: The relationship between metal concentrations in *Hylocomium splendens* (Hs) and *Pleurozium schreberi* (Ps), where 'Ps = constant + slope * Hs', in the current and UK 2000 moss survey.

Metal	Current moss survey (n = 3-4)			UK 2000 moss survey (n = 23-28)		
	Constant	Slope	R ²	Constant	Slope	R ²
Al	41.1	0.503	0.444			
As	-0.032	1.050	0.997	-0.017	1.243	0.919
Cd	0.098	-0.288	0.049	0.042	0.754	0.420
Co	-0.007	1.067	0.975			
Cr	-0.012	1.110	0.755	0.258	0.840	0.799
Cu	3.50	0.314	0.824	1.02	0.708	0.690
Fe	17.3	0.776	0.869			
Mn	60.3	0.731	0.714			
Ni	0.074	0.824	0.850	-0.024	1.026	0.908
Pb	0.055	0.914	0.963	0.503	0.933	0.669
Sb	0.004	0.861	0.921			
Se	0.888	-1.932	0.903	0.059	0.832	0.735
Sn	-0.048	1.139	0.770			
U	0.004	0.504	0.252			
V	0.017	0.926	0.953	0.305	0.747	0.802
Zn	37.3	0.094	0.017	9.34	0.601	0.529

5.2 Concentrations of heavy metals in moss sampled close to each of the 10 core monitoring sites

Depending on the site and the metal, species-specific accumulations were observed (Figure 90-Figure 95). *H. cupressiforme* tended to accumulate more Al, As, Cd, Co, Cr, Fe, Ni, Pb, Se, U, and V than other moss species, but this was not always true for all the sites, as at Holme Moss the concentration of metals in *H. cupressiforme* was often similar to that in *R. squarrosus*. *R. squarrosus* tends to accumulate higher levels of Cu than the other species. Although *Pseudoscleropodium purum* tended to accumulate higher levels of Al, Cd, Co, Fe, Mn, Ni, U and Zn than *R. squarrosus* at Monks Wood, the opposite was found at Penallt. In *Pleurozium schreberi* the concentration of As, and to a lesser extent Cr, was exceptionally high compared to the other species collected at Inverpolly.

Pleurozium standardisation of the metal concentrations in mosses

The moss species most commonly used for moss mapping are *Pleurozium schreberi* and *Hylocomium splendens*, and most calibrations (relationships between metal concentration in moss and bulk deposition) have been reported for these species. Despite the fact that species-specific accumulation of metals occurs, each moss species was found at an insufficient number of measurement sites of the UK Rural Heavy Metal Monitoring Network for moss specific calibrations to be derived. Hence it was decided to standardize moss concentrations for *Pleurozium* (Annexes II and III), as was done in the UK 2000 moss survey (Ashmore *et al.*, 2002) and previous studies in the literature. In the current moss sampling exercises, *Pleurozium* standardised equations could only be developed between *P. schreberi* and *H. splendens* (Table 16). However, even for these the number of data points available to determine the relationship between the metal concentration in *P. schreberi* and *H. splendens* was minimal (3 – 4). Therefore, we decided to

apply the equations established in the UK 2000 moss survey to *Pleurozium* standardise the metal concentrations in mosses, as these equations were more robust with the number of data point varying between 12 and 30 (Ashmore *et al.*, 2002).

These *Pleurozium* standardised metal concentrations were then used to map the distribution of the metal concentrations in mosses for the UK, as was done in the UK 2000 moss survey. Table 16 shows the relationship between the metal concentrations in *P. schreberi* and *H. splendens* based on the current study and the UK 2000 moss survey.

Although some highly significant linear relationships were found in the current survey, this is not the case for all metals. For example, for Cd and Se negative linear relationships were found and for Zn the relationship was not significant.

Below we provide a more detailed description per metal of the concentrations in mosses, including the mean *Pleurozium* standardised concentrations, and the spatial trends across the 14 monitoring sites. For more details regarding metal pollution sources in the UK and the observed spatial trends of metals in mosses in 2000 we refer to the UK 2000 moss survey (Ashmore *et al.*, 2002).

Aluminium (Al). Relatively high concentrations of Al were observed at Penallt and at some of the other sites in *H. cupressiforme* only (Figure 90). Relatively low concentrations were found at Inverpoll, Lough Navar and Whytham.

Antimony (Sb). Antimony, an indicator of anthropogenic pollution, was relatively high at Holme Moss and low at Inverpoll and Lough Navar (Figure 90). No big differences regarding species-specific accumulation were observed.

Arsenic (As). There was a relatively high concentration of As in *P. schreberi* at Inverpoll, in contrast to the low accumulation in other species sampled from that site (Figure 90), resulting in a relatively high mean concentration of As when data were *Pleurozium* standardised (Figure 96). The relatively high concentration of As in *R. squarrosus* at Beacon Hill became more pronounced when the data were *Pleurozium* standardised. The mean *Pleurozium* standardised As concentration was lowest in Lough Navar. Compared with the UK 2000 moss survey, the As concentrations in mosses in this study were in the low range (Ashmore *et al.*, 2002).

Cadmium (Cd). Relatively high concentrations of Cd were found in mosses at Cockley Beck, Heigham Holmes and Penallt (Figure 91, Figure 96) and 2 out of the 4 species in Inverpoll accumulated relatively high concentrations of Cd. Compared with the UK 2000 moss survey, the Cd concentrations in mosses in this study were in the low range (Ashmore *et al.*, 2002).

Chromium (Cr). As for As, a relatively high concentration of Cr was found in *P. schreberi* at Inverpoll (Figure 91). When *Pleurozium* standardised, the highest concentrations were present in mosses at Penallt, Monks Wood, Inverpoll and Beacon Hill and the lowest concentration in mosses at Lough Navar (Figure 96). The Cr concentrations reported in this study are low compared with the concentrations reported for the UK 2000 moss survey (Ashmore *et al.*, 2002). However, when correcting for the low recovery of Cr in this study (Table 10) compared with the recovery in the UK 2000 moss survey (Table 11), the Cr concentrations in this study are in the low medium range compared with the UK 2000 moss survey.

Cobalt (Co). Relatively high concentrations of Co were found in *P. purum* at Monks Wood and in two out of the three moss species sampled at Banchory and Penallt, in addition to a high concentration observed in *H. cupressiforme* at Cockley Beck. Low concentrations were present in mosses sampled at Inverpoll, Lough Navar and Whytham (Figure 91).

Copper (Cu). In contrast to many other metals, relatively high concentrations of copper were found in mosses collected at Inverpoll, in particular in *R. squarrosus* (Figure 92). In this species, relatively high levels of copper were also found at Banchory and Beacon Hill. When *Pleurozium* standardised, similar levels of copper were observed at all sites, except for the higher levels at Beacon Hill and Inverpoll (Figure 96). The Cu concentrations in mosses in this study were comparable with the concentrations reported for the UK 2000 moss survey (Ashmore *et al.*, 2002).

Iron (Fe). Relatively high levels of Fe were found in mosses at Monks Wood, Penallt, Heigham Holmes, Beacon Hill and in *H. cupressiforme* at Banchory (Figure 92). Low concentrations of Fe were found in mosses sampled at Lough Navar, Inverpoll, Whytham and Yarner Wood.

Lead (Pb). Relatively high concentrations of lead were found in mosses collected at Cockley Beck, *H. cupressiforme* in particular, Holme Moss and Penallt. As for many other metals, the lowest levels of lead were found in mosses sampled at Inverpolly and Lough Navar (Figure 92, Figure 97). In the current study the Pb concentrations in mosses was low and comparable with the concentrations in mosses found at most sites in the UK 2000 moss survey (Ashmore *et al.*, 2002).

Manganese (Mn). Relatively high levels of Mn were found in all moss species collected at Auchencorth, with similar levels being detected in *P. purum* at Monks Wood and *R. squarrosus* at Cockley Beck. The lowest concentrations of Mn were found in mosses sampled at Wytham and Heigham Holmes, with medium high concentrations being detected at Inverpolly (Figure 93).

Nickel (Ni). The relatively high level of *P. schreberi* standardized concentration of Ni at Penallt was primarily due to the high accumulation in *R. squarrosus* (Figure 93, Figure 97). A relatively high concentration of Ni was also found in *P. purum* at Monks Wood and in *H. cupressiforme* at Cockley Beck. Low levels of Ni were found at Inverpolly and Lough Navar, and at Wytham when *Pleurozium* standardised. Compared with the UK 2000 moss survey, the Ni concentrations in mosses in this study were low (Ashmore *et al.*, 2002).

Selenium (Se). Relatively high concentrations of Se were found in mosses sampled at Holme Moss and Cockley Beck (Figure 93, Figure 97). However, the *Pleurozium* standardised levels of Se were quite similar at all sites across the UK, except for the somewhat lower concentrations at Heigham Holmes. Compared with the UK 2000 moss survey, the Se concentrations in mosses in this study were in the low to medium range (Ashmore *et al.*, 2002).

Tin (Sn). Relatively high concentrations of Sn were found in both moss species collected at Holme Moss. Otherwise, there was not that much variation on the concentration of Sn in mosses (Figure 94).

Uranium (U). Relatively high levels of U were in particular found in *H. cupressiforme* collected at Banchory, Cockley Beck and Penallt (Figure 94). Low concentrations of U were detected in mosses sampled at Wytham and Yarnier Wood.

Vanadium (V). Relatively high concentrations of V were found in *H. cupressiforme* sampled at Cockley Beck, Banchory and Penallt, with the lowest levels detected in mosses collected at Inverpolly, Lough Navar and Wytham (Figure 94). Compared with the UK 2000 moss survey, the V concentrations in mosses in this study were in the low to medium range (Ashmore *et al.*, 2002).

Zinc (Zn). A relatively high concentration of Zn was found in *P. purum* sampled at Inverpolly (Figure 95). When *Pleurozium* standardised, high levels were also apparent at Beacon Hill and Cwmystwyth (Figure 97). Compared with the UK 2000 moss survey, the Zn concentrations in mosses in this study were in the low to medium range (Ashmore *et al.*, 2002).

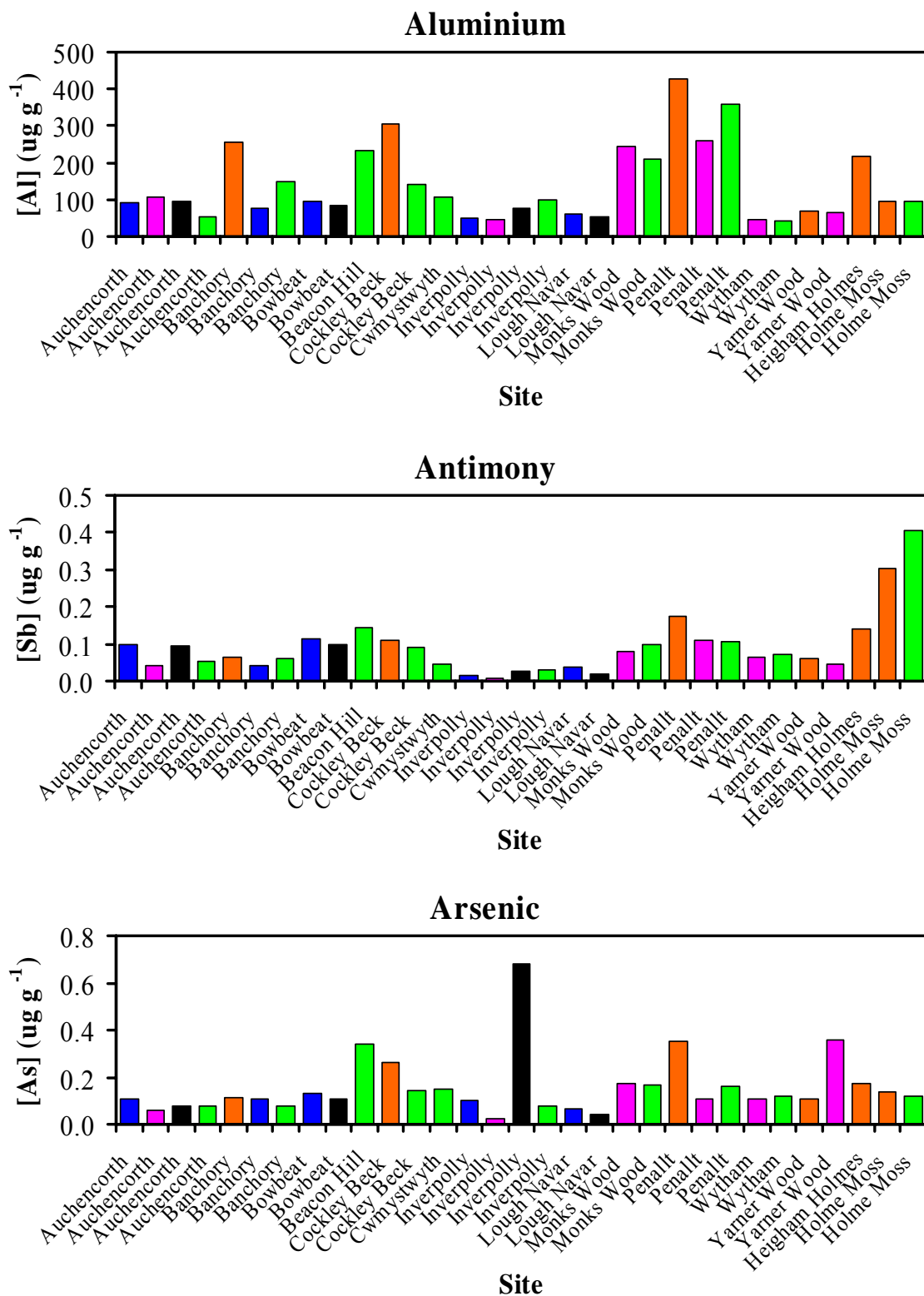


Figure 90: Concentration of aluminium, antimony and arsenic in mosses at 14 monitoring sites across the UK. Blue bars = *Hylocomium splendens*; pink bars = *Pseudoscleropodium purum*; black bars = *Pleurozium schreberi*; green bars = *Rhytidiadelphus squarrosus*; orange bars = *Hypnum cupressiforme*.

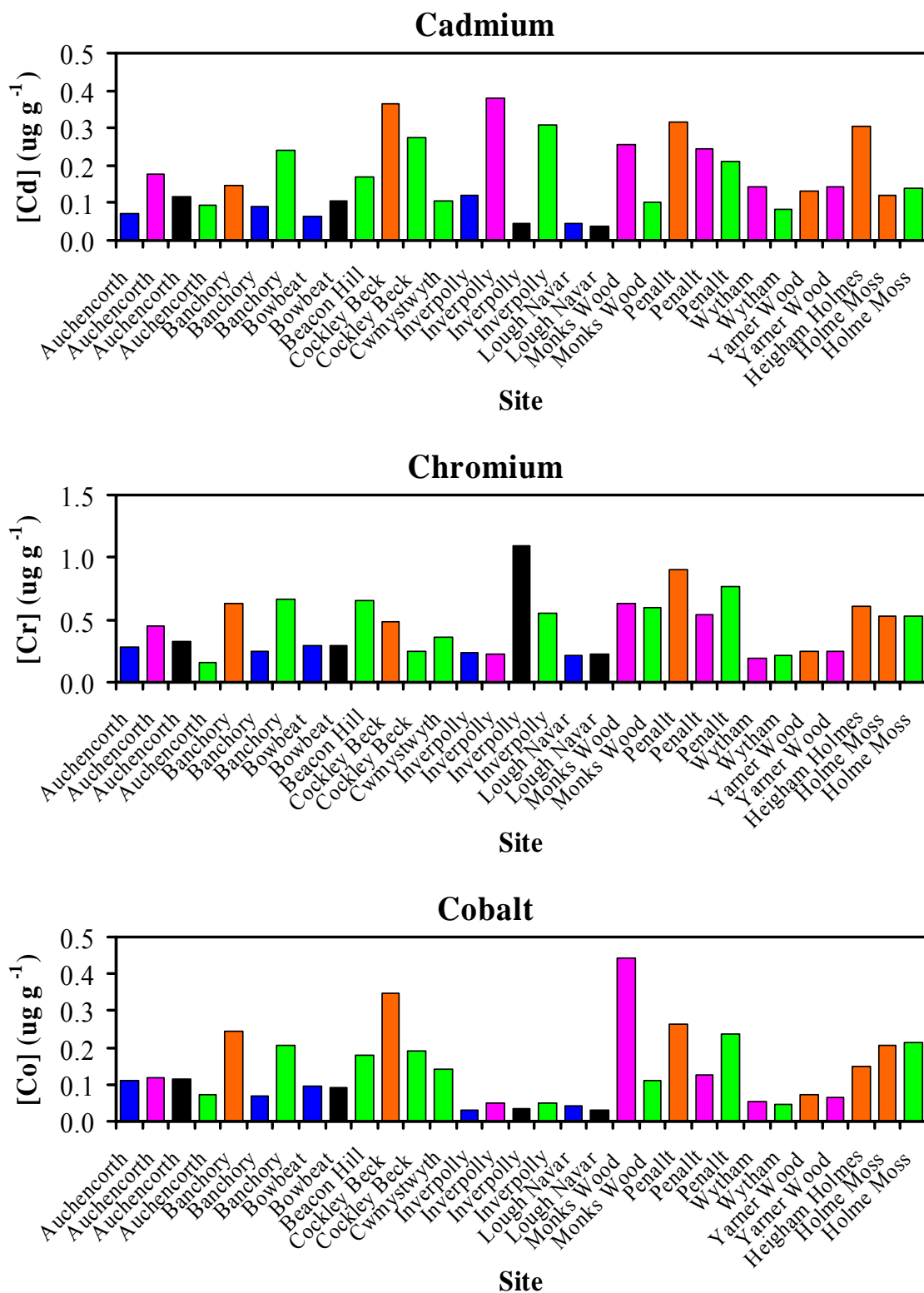


Figure 91: Concentration of cadmium, chromium and cobalt in mosses at 14 monitoring sites across the UK. Blue bars = *Hylocomium splendens*; pink bars = *Pseudoscleropodium purum*, black bars = *Pleurozium schreberi*; green bars = *Rhytidiadelphus squarrosus*; orange bars = *Hypnum cupressiforme*.

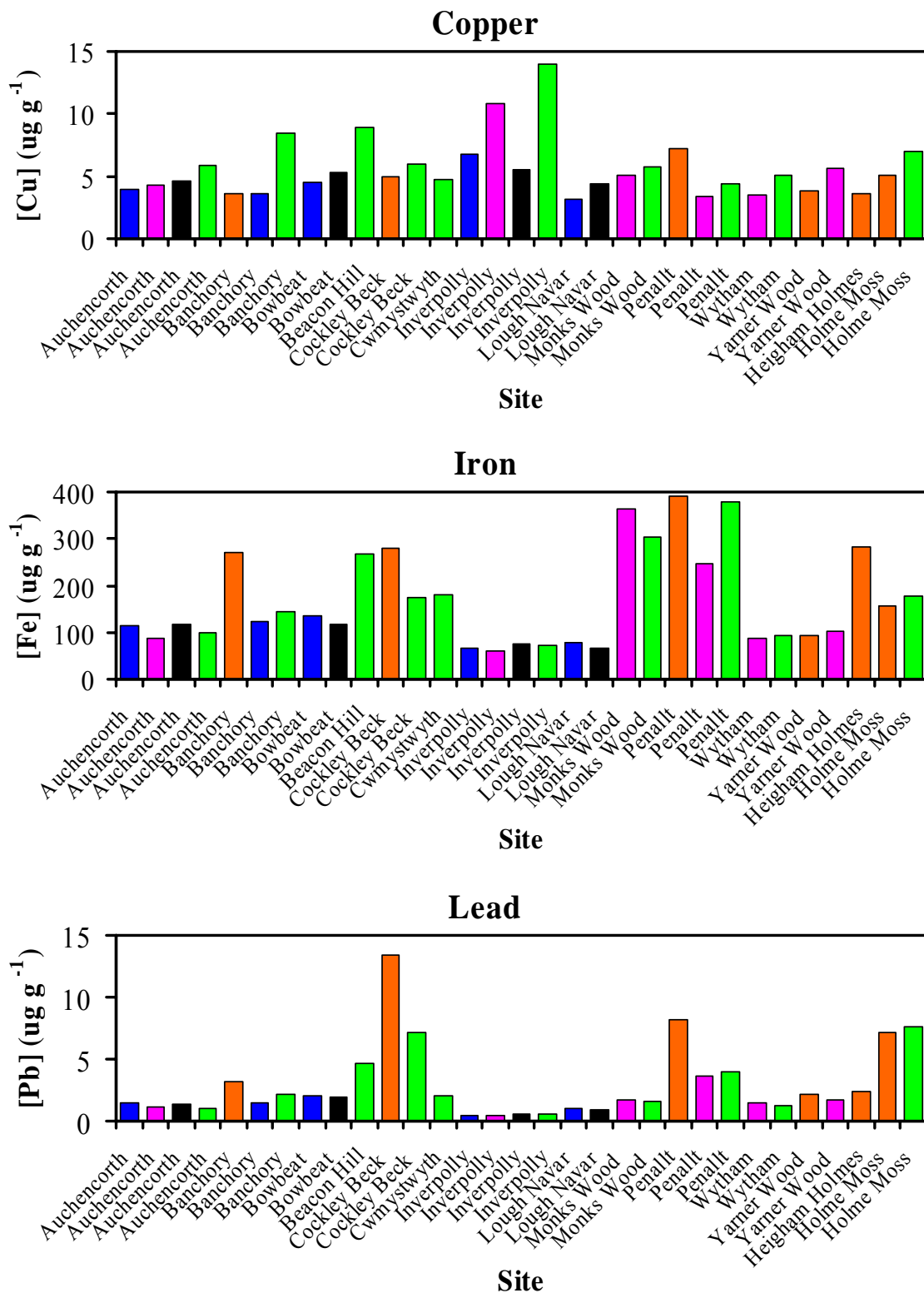


Figure 92: Concentration of copper, iron and lead in mosses at 14 monitoring sites across the UK. Blue bars = *Hylocomium splendens*; pink bars = *Pseudoscleropodium purum*, black bars = *Pleurozium schreberi*; green bars = *Rhytidiadelphus squarrosus*; orange bars = *Hypnum cupressiforme*.

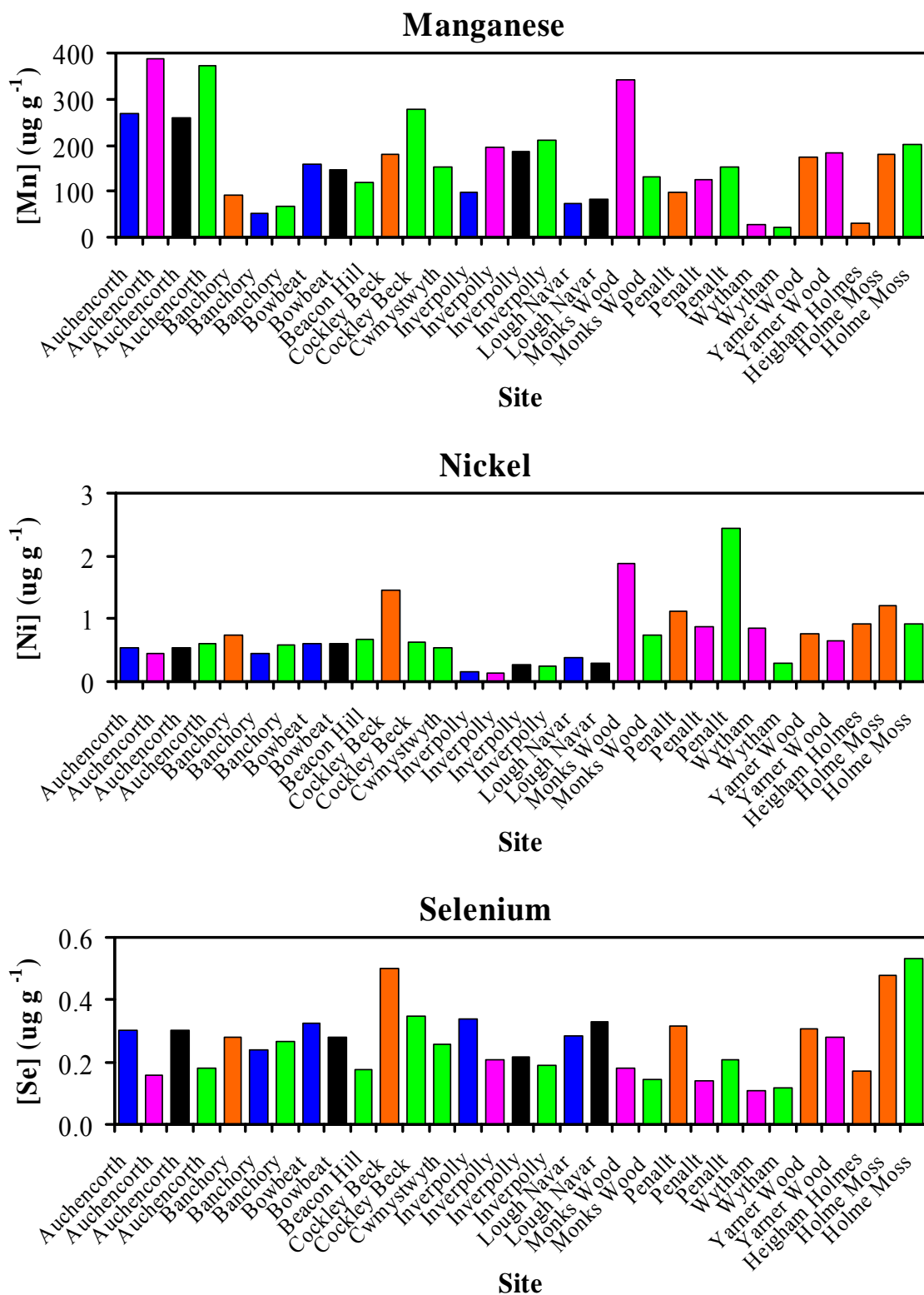


Figure 93: Concentration of manganese, nickel and selenium in mosses at 14 monitoring sites across the UK. Blue bars = *Hylocomium splendens*; pink bars = *Pseudoscleropodium purum*, black bars = *Pleurozium schreberi*; green bars = *Rhytidiadelphus squarrosus*; orange bars = *Hypnum cupressiforme*.

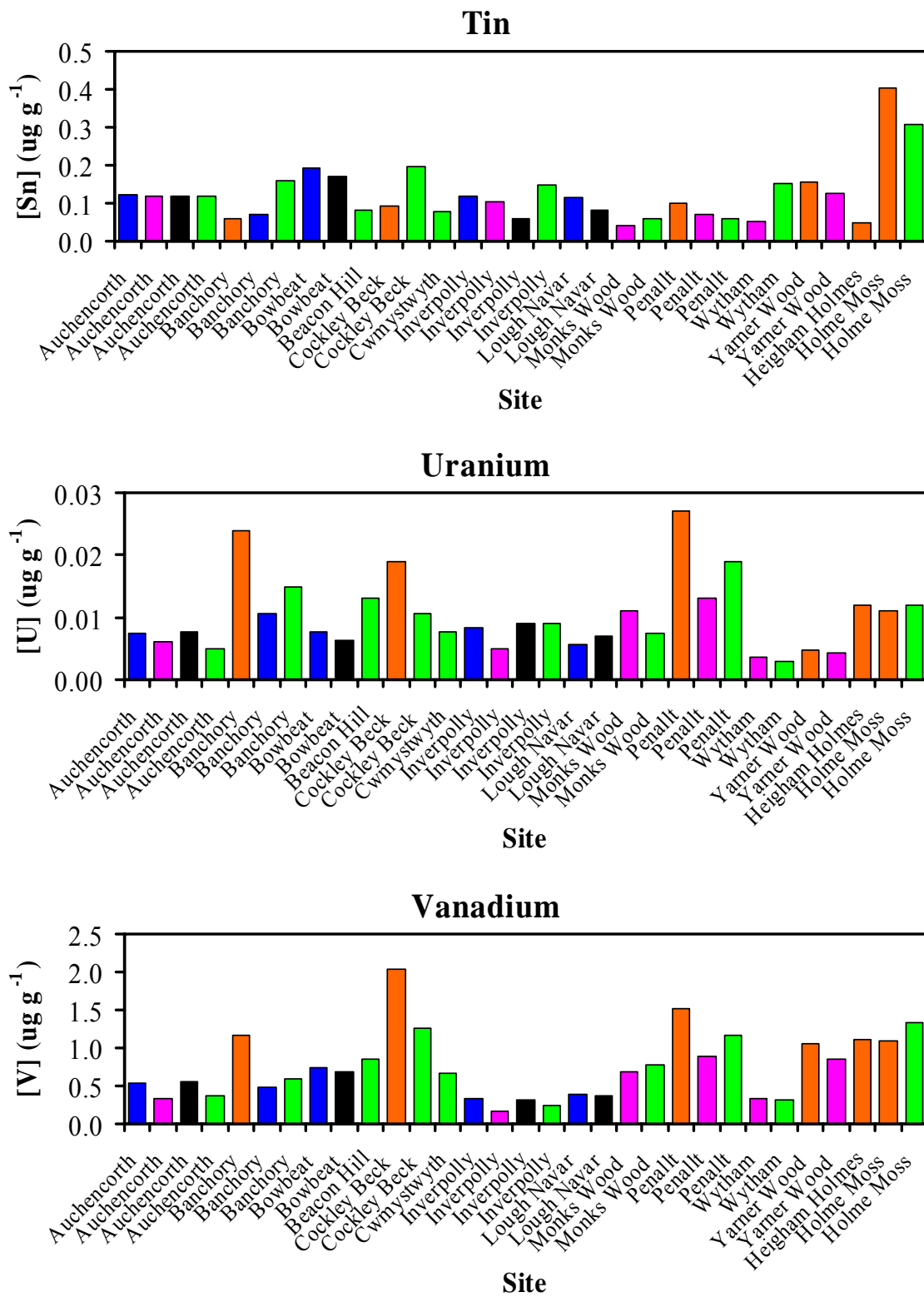


Figure 94: Concentration of tin, uranium and vanadium in mosses at 14 monitoring sites across the UK. Blue bars = *Hylocomium splendens*; pink bars = *Pseudoscleropodium purum*, black bars = *Pleurozium schreberi*; green bars = *Rhytidiadelphus squarrosus*; orange bars = *Hypnum cupressiforme*.

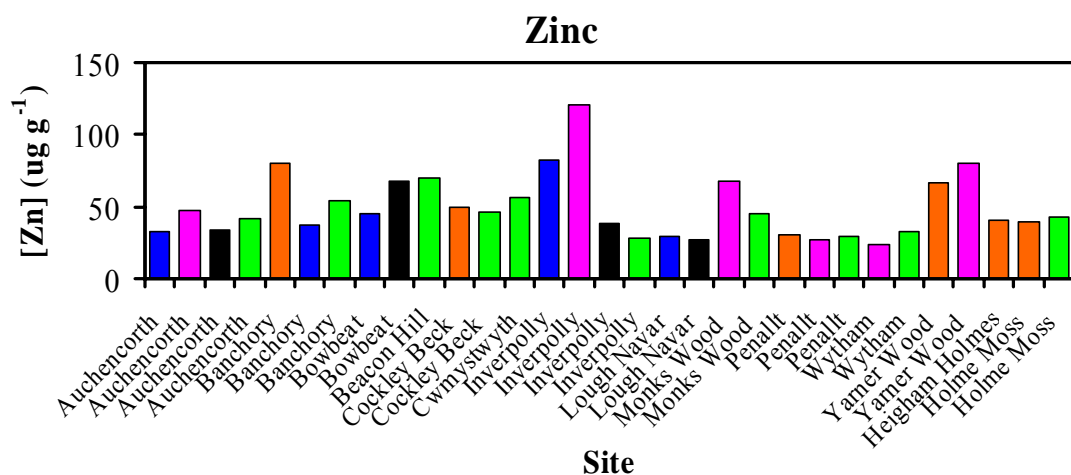


Figure 95: Concentration of zinc in mosses at 14 monitoring sites across the UK. Blue bars = *Hylocomium splendens*; pink bars = *Pseudoscleropodium purum*, black bars = *Pleurozium schreberi*; green bars = *Rhytidiadelphus squarrosus*; orange bars = *Hypnum cupressiforme*.

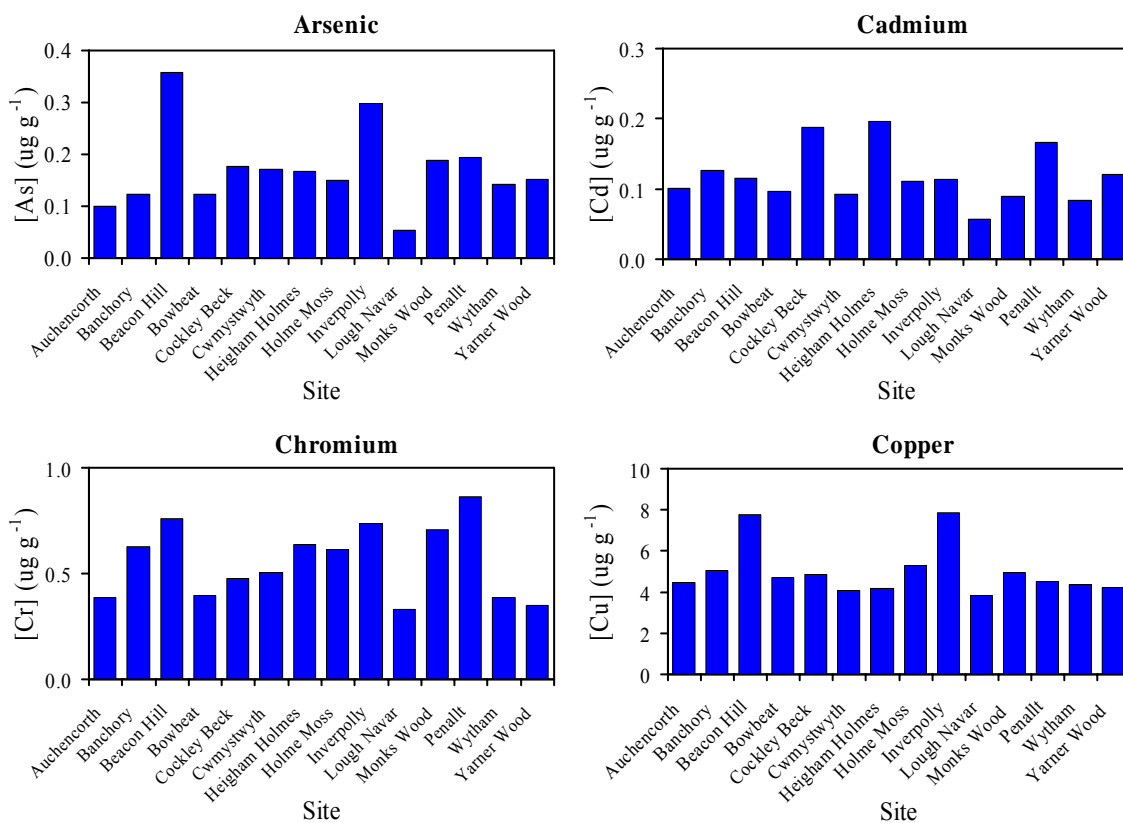


Figure 96: *Pleurozium* standardised concentrations of arsenic, cadmium, chromium and copper in mosses at 14 monitoring sites across the UK. Values were standardized for 1 – 3 species.

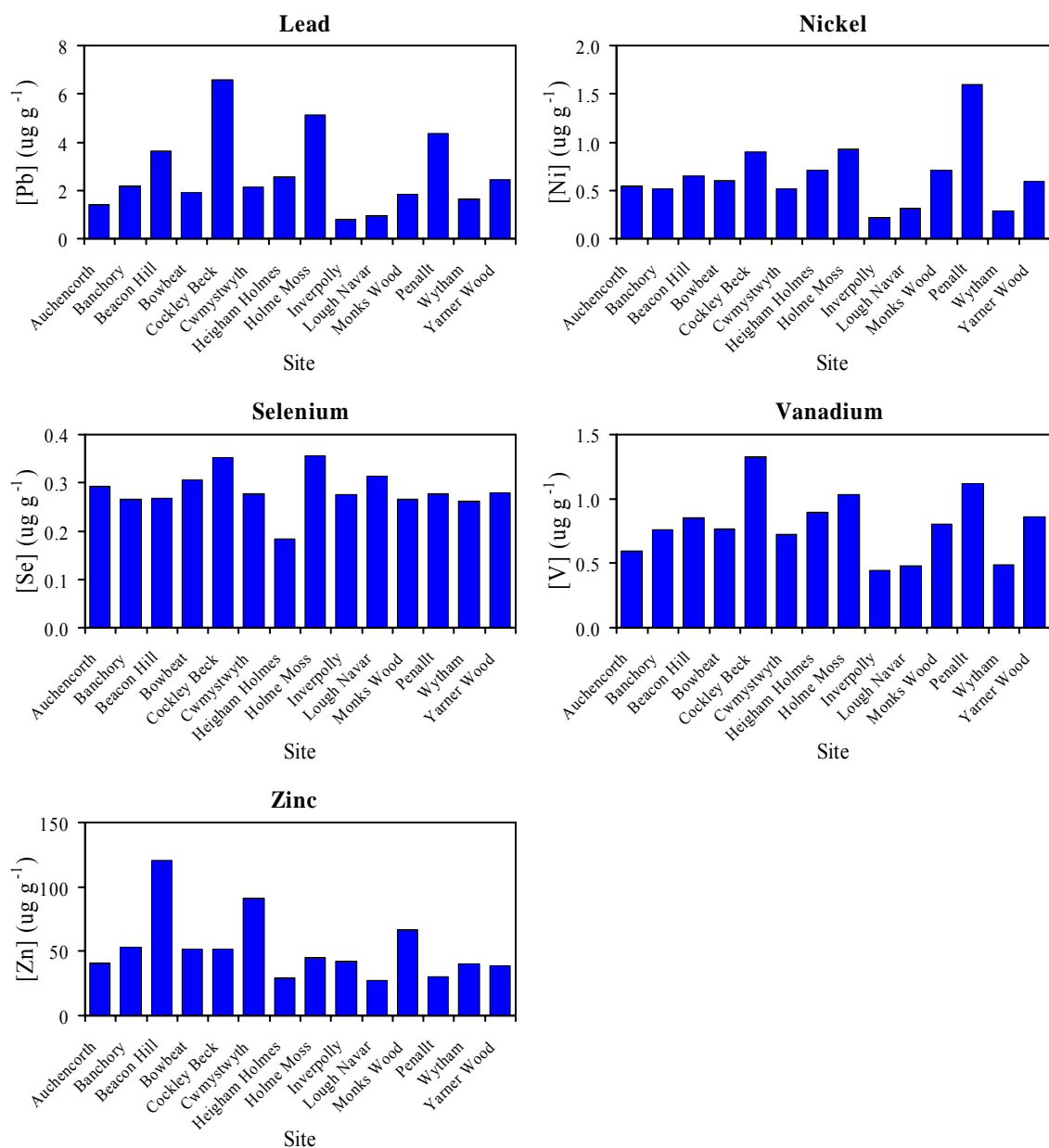


Figure 97: Pleurozium standardised concentrations of lead, nickel, selenium, vanadium and zinc in mosses at 14 monitoring sites across the UK. Values were standardized for 1 – 3 species.

5.3 Relationships between moss concentrations and measured deposition at each site

The metal concentrations of the mosses sampled in 2004/05 were compared with the annual bulk deposition measured in 2004 to derive linear relationships between the moss concentration and bulk deposition, here referred to as ‘moss calibration’. Figure 98 shows the scatter plots of heavy metal concentration in moss vs. bulk deposition for the different sites (text symbols) and moss species (colours). Here, replicate samples for the same moss have been averaged and the cloud sampling sites (Holme Moss and Bow Beat) have been omitted.

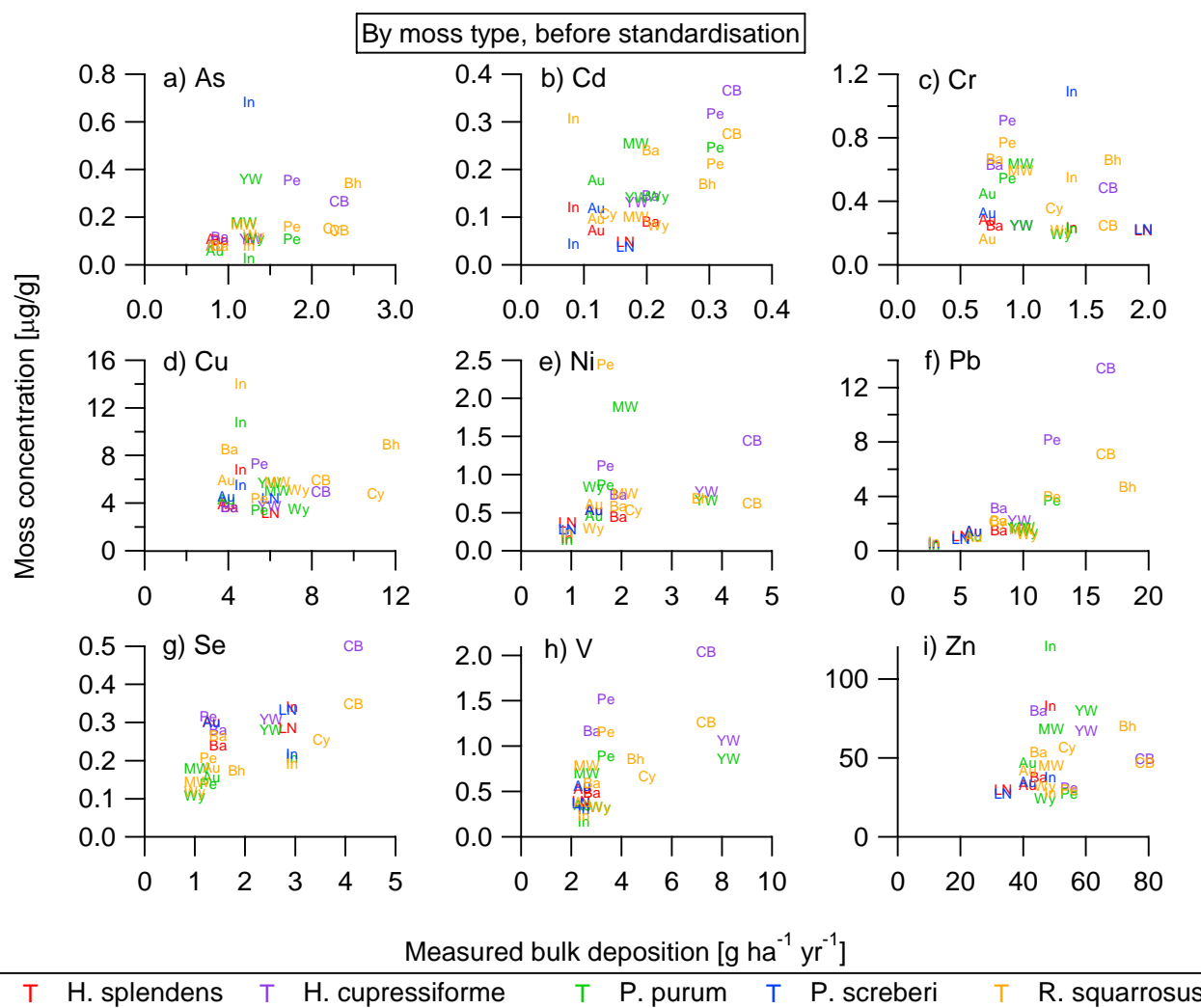


Figure 98: Relationships between heavy metal concentration in moss and bulk deposition across sites and moss species.

As described above, each sample was normalised for *P. sereberi* using the relationships from the 2000 survey (Table 16). The resulting values are shown in Figure 99. Clear outliers were removed from the dataset (e.g. As in *P. sereberi* at Inverpoll and many data points for the elevated cloud sampling sites, which are not necessarily expected to follow the standard pattern) before data across mosses were averaged for each metal at each site. From these data, linear relationships were derived, which are also shown in Figure 99, alongside relationships from the literature and those derived from previous UK measurements for the moss surveys of 1997 and 2000. The equations of the new relationships are presented in Table 17. For Pb the relationship was significant at $P < 0.01$, while for Se it just fails to be significant at $P < 0.05$. For Cr and Cu the relationships are considered to be too weak for deposition to be derived.

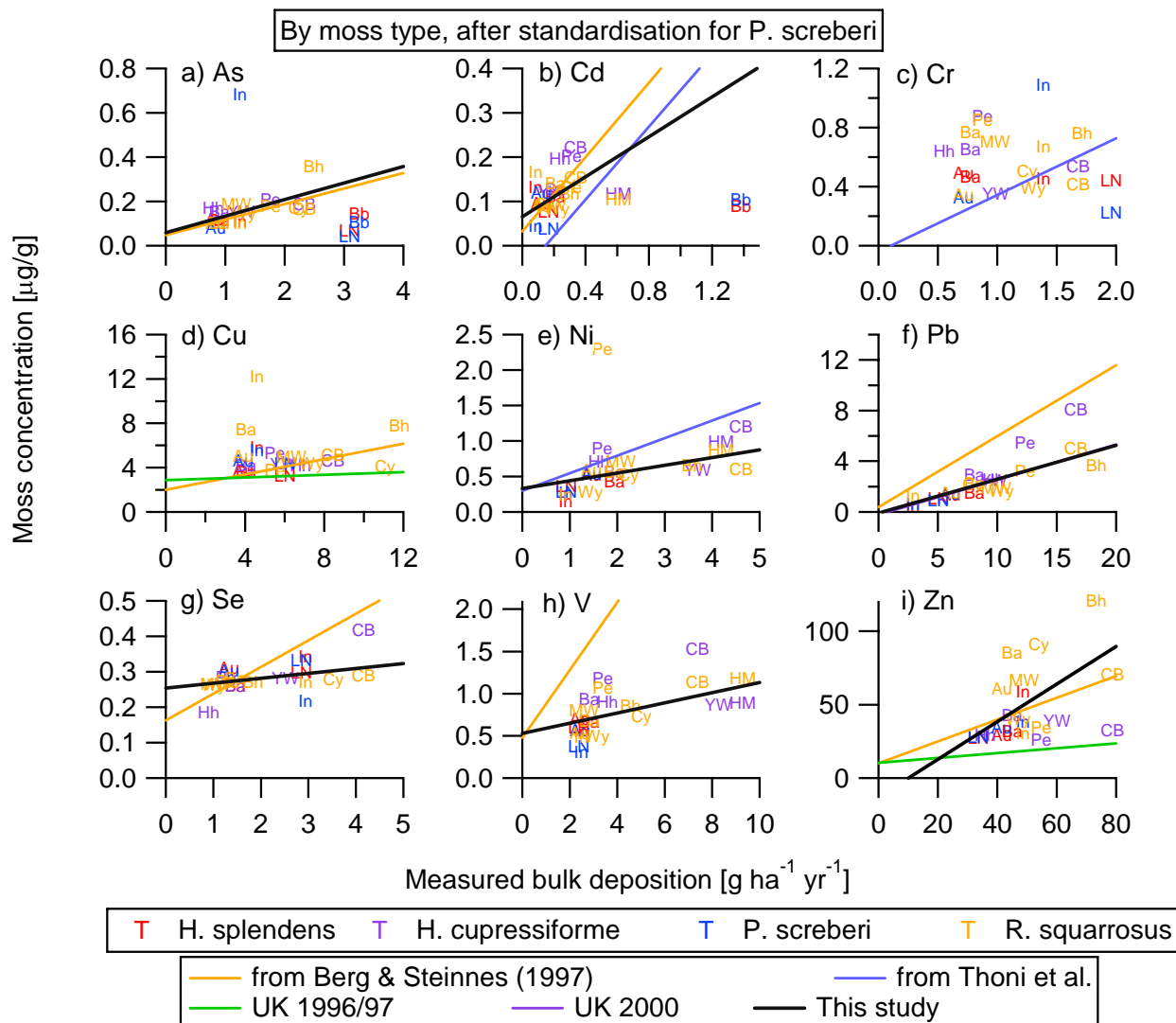


Figure 99: Relationships between heavy metal concentration in moss and bulk deposition across sites and moss species, after normalisation to *P. screberi*. Also shown are relationships from the literature and those used for the mapping of previous UK moss surveys. The new relationships derived from these new data are shown as black lines.

Table 17: The relationship between concentrations in mosses (after normalisation for *Ps*) and bulk deposition of the form $\text{conc } [\mu\text{g g}^{-1}] = m \times \text{bulk deposition } [\text{g ha}^{-1} \text{yr}^{-1}] + b [\mu\text{g g}^{-1}]$.

Metal	b	M	R ²	N	P
As	0.074	0.060	0.447	11	<0.10
Cd	0.225	0.066	0.355	11	<0.10
Cr	-0.036	0.595	0.031	14	
Cu	0.218	3.218	0.245	12	
Ni	0.109	0.331	0.367	13	<0.10
Pb	0.268	-0.088	0.691	12	<0.01
Se	0.014	0.253	0.538	11	<0.10
V	0.060	0.529	0.375	13	<0.10
Zn	1.281	-12.911	0.397	12	<0.10

As was found in previous studies, there is a high intercept for Cr, Cu, Se and V, indicating that the mosses derive a significant fraction of these metals from the soil. It should be noted that the relationship derived for Pb from the moss samples at the sites from the new network was virtually identical with the previous relationship derived from the 2000 measurements (UK 2000) in Figure 99f; the two lines are therefore not distinguishable. In addition, even after standardisation for Ps the different mosses fall into distinct populations as is most pronounced for Pb and Zn. This implies that the relationship between different moss species during the current survey was somewhat different than during the Moss Survey 2000. However, as mentioned above there were too few paired samples to derive more up-to-date moss intercalibrations.

5.4 Deposition maps for UK based on Moss Survey 2000 and new data

The deposition was mapped according to the procedure described by Ashmore *et al.* (2002). Briefly, first the calibrations of Table 17 were used to calculate the bulk deposition at the sampling sites of the Moss Survey 2000, from the Ps standardised concentration in moss. The scavenging ratios reported in Section 2 were then used to derive the air concentration at the sampling sites, which was then interpolated to calculate the air concentration map for the whole of the UK. Based on this air concentration map, total deposition was calculated for each grid cell. Dry and occult deposition was calculated, consistent with the mapping procedures of the network data, while wet deposition was calculated from the scavenging ratios. The resulting deposition fields are shown in Figure 100 to Figure 106. These deposition fields are discussed in more detail in Section 8, where they are compared to those derived from the network measurements and the FRAME-HM atmospheric transport model.

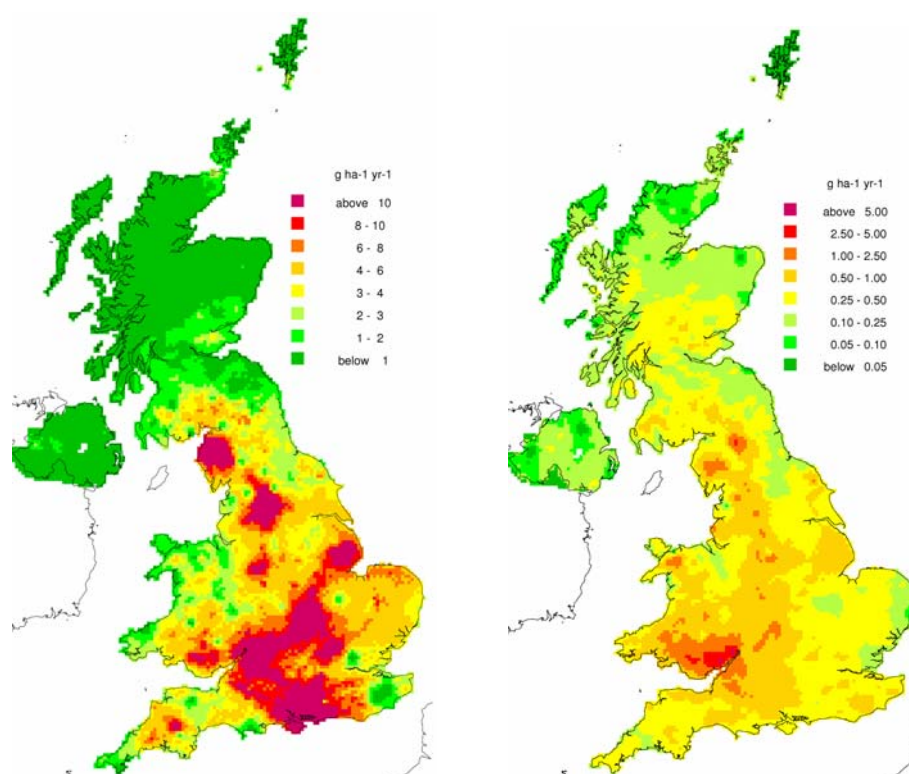


Figure 100: As from Moss Survey 2000 ($\text{g ha}^{-1} \text{yr}^{-1}$) Figure 101: Cd from Moss Survey 2000 ($\text{g ha}^{-1} \text{yr}^{-1}$)

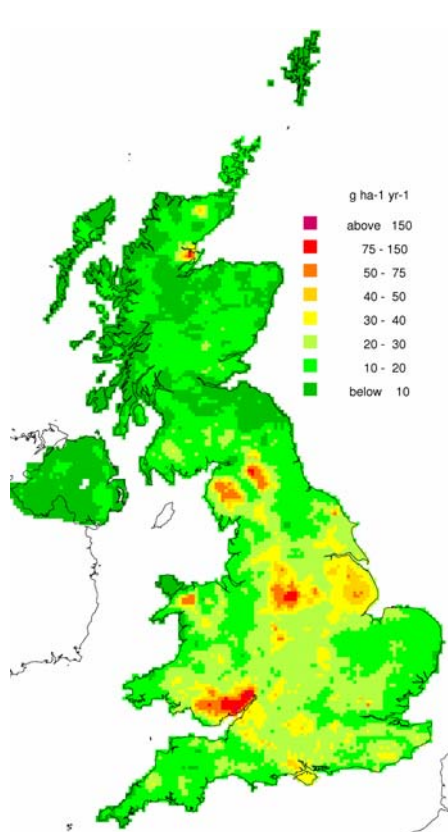


Figure 102: Pb from Moss Survey 2000 (g ha⁻¹ yr⁻¹)

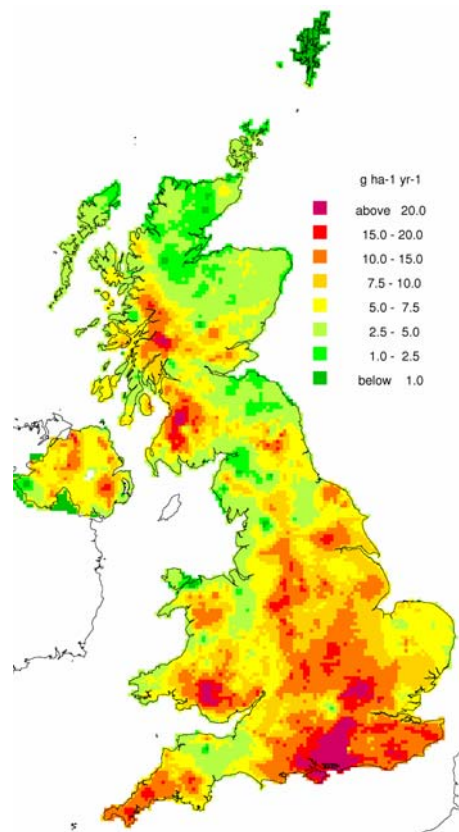


Figure 103: Ni from Moss Survey 2000 (g ha⁻¹ yr⁻¹)

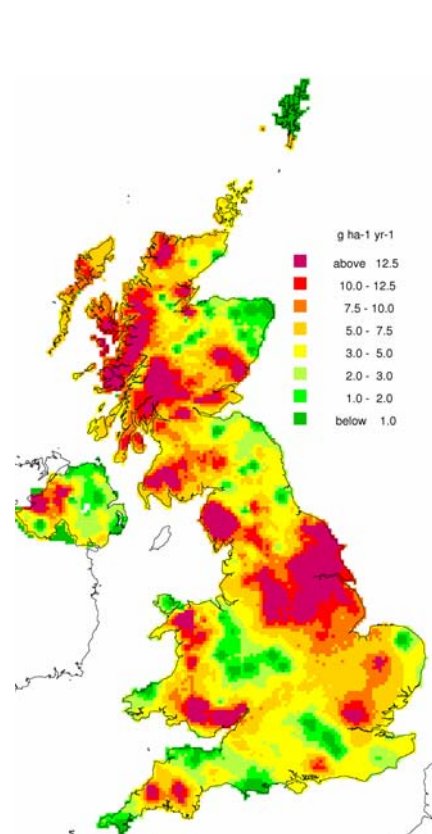


Figure 104: Se from Moss Survey 2000 (g ha⁻¹ yr⁻¹)

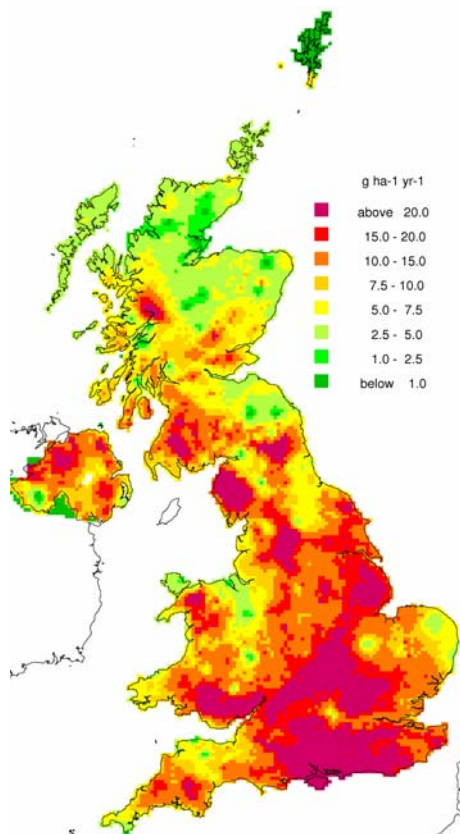


Figure 105: V from Moss Survey 2000 (g ha⁻¹ yr⁻¹)

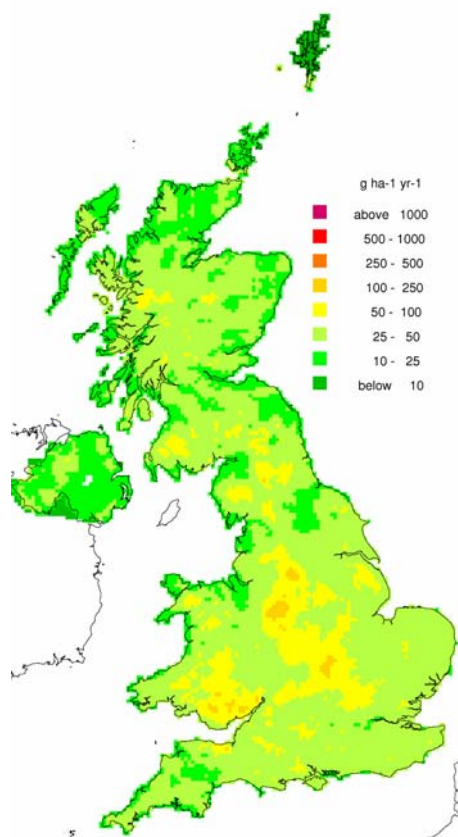


Figure 106: Zn from Moss Survey 2000 ($\text{g ha}^{-1} \text{yr}^{-1}$)

5.6 Discussion

Although for many metals the relationships between accumulated moss concentrations and bulk deposition fail to be significant at $P < 0.05$, the overall result is nevertheless encouraging. The results indicate that UK relationships are similarly 'robust' as those derived in previous studies for less maritime climates and that there is no general problem with competition of uptake of sea salt ions. More uncertainty is now introduced due to the general decline in metal deposition across Europe, leading to an absence of real hotspots in the inter-comparison data which would have strengthened the relationships.

6. Speciated Mercury Measurements at a Single Site

6.1 Introduction

Elemental mercury makes up over 97% of the total atmospheric mercury burden. The remaining amount consists of reactive gaseous mercury (RGM) and particulate mercury (Hg^{p}). Speciated measurements of mercury are made using a state-of-the-art Tekran mercury speciation system, which measures RGM, Hg^{p} and Hg^0 . As the concentration of these species is so low (in the order of pg m^{-3} for RGM and Hg^{p}), very sensitive analytical equipment is required. The detector in the Tekran 2537A analyser employs Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). Elemental mercury is sampled and analysed for one hour whilst RGM and Hg^{p} are collected on a KCl-coated denuder and particulate trap, respectively. During the following hour, the collected RGM and Hg^{p} are desorbed and analysed. Using this method, Hg^0 is analysed with a temporal resolution of 5 minutes every other hour and hourly averages of RGM and Hg^{p} concentrations are obtained every other hour.

6.2 Establishment of new 'supersite' for Hg measurements

A 'supersite' for speciated mercury measurements has been established at Auchencorth Moss, a rural site 18 km south west of Edinburgh. Measurements of speciated mercury using the Tekran system started here in October 2004 after prior testing of the equipment at Bush. The speciation system is co-located with an integrating sampler from Work Package 7 for method comparison.

6.3 Implementation, testing and calibration of new sampling and analysis equipment

The Tekran speciation system was first operated at CEH Edinburgh at Bush for the purposes of instrument familiarisation and method testing, and to ensure reliable operation at a remote location. This also enabled the validation of the new integrating samplers for Work Package 7 before they were deployed at the network sites. After successful completion of the testing, the speciation was transferred to Auchencorth Moss, where it has been running semi-continuously since. The analyser is calibrated automatically every 25 hours by an internal permeation source. This permeation source is verified annually using a mercury vapour primary calibration unit. The verification has shown negligible variation of the output of the source.

The Tekran analyser runs semi-continuously: it is taken off-line for approximately two hours every week for the analysis of the field cartridges from Work Package 7, as well as at other periods for routine maintenance.

6.4 Annual summary statistics of measurement data

Figure 107 shows hourly averages of elemental mercury from June 2003 to June 2005.

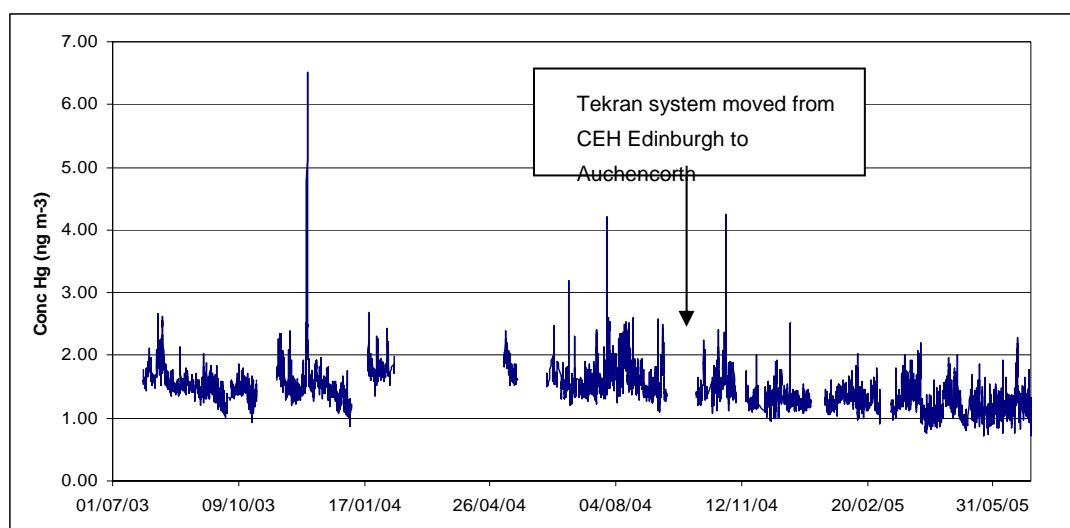


Figure 107: Hg^0 hourly averages (mg m^{-3}) from July 2003 to June 2005.

Measurements of Hg^0 show average concentrations typical of an unpolluted site in the northern hemisphere, of around 1.5 ng m^{-3} , which is in agreement with the mean value of 1.68 ng m^{-3} (with a background of 1.5 ng m^{-3}) observed in southern England. (Lee et al., 1998). The data indicate a slightly lower baseline of Hg^0 measurements at Auchencorth compared with Bush. This may be because Auchencorth is less influenced by local sources of mercury.

The background is generally stable, but is enhanced for periods of several hours during events (Figure 108, example events marked with coloured circles) in which the concentration of Hg^0 can increase almost ten-fold. The maximum hourly concentration of Hg^0 that has been observed is 6.5 ng m^{-3} . Analysis of these events shows that elevated concentrations are associated with slow-moving surface air-mass back trajectories that have travelled to Eastern Scotland from mainland Europe or industrialised regions of England. Figure 109 and Figure 110 shows two such examples, in which concentrations were elevated above 'background' levels for several hours. Lower than average concentrations are associated with clean air masses that have originated in the Arctic or the Atlantic, with minimum values around 0.8 ng m^{-3} .

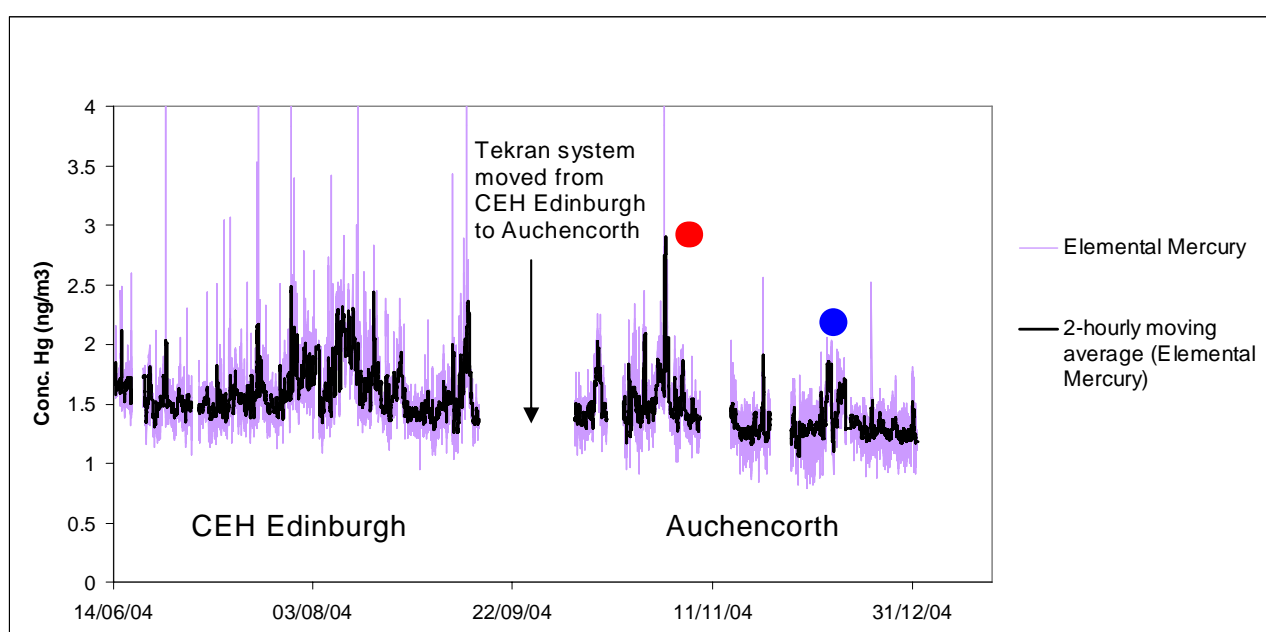


Figure 108: Concentration of elemental mercury (ng m^{-3}) in air at CEH Edinburgh and Auchencorth Moss, June – December 2004. Two example events are indicated by circles.

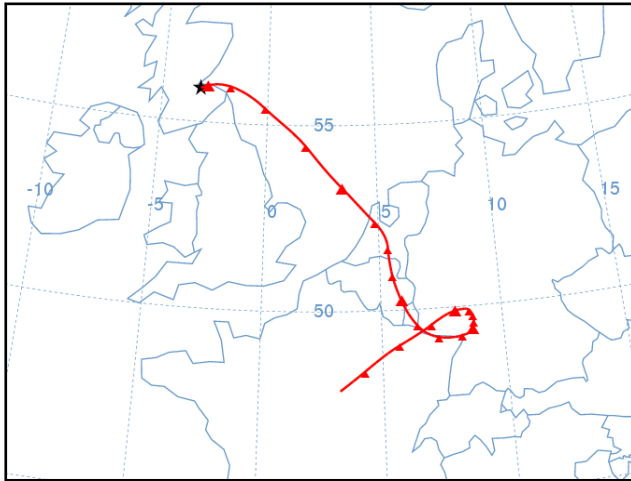


Figure 109: Air mass back trajectory (Rolph, 2003) over 5 days for air arriving at Edinburgh on 20 October 2004 (event marked by red circle in Figure 108). Tick marks are at 6 h intervals.

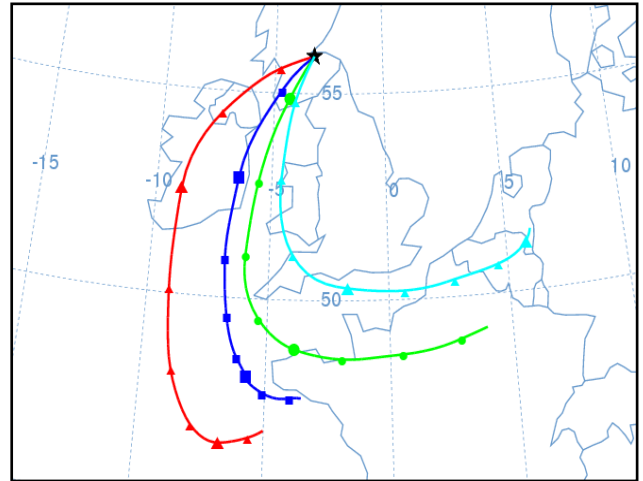


Figure 110: Air mass 48-hour back trajectories for air arriving at Edinburgh between 0900UTC on 9 December 2004 and 0900UTC on 10 December 2004, at 6-hourly intervals (event marked by blue circle in Figure 108). The sequence of the trajectories is easterly to westerly over this 24-hour period. Tick marks are at 6 h intervals.

Figure 111 and Figure 112 show hourly averages of concentrations of RGM and Hg^{P} at Auchencorth Moss. The concentration of these species is an order of magnitude lower and varies more widely than that of elemental mercury variable with hourly maxima up to 39 pg m^{-3} . Concentrations of RGM and Hg^{P} are often below the method detection limit.

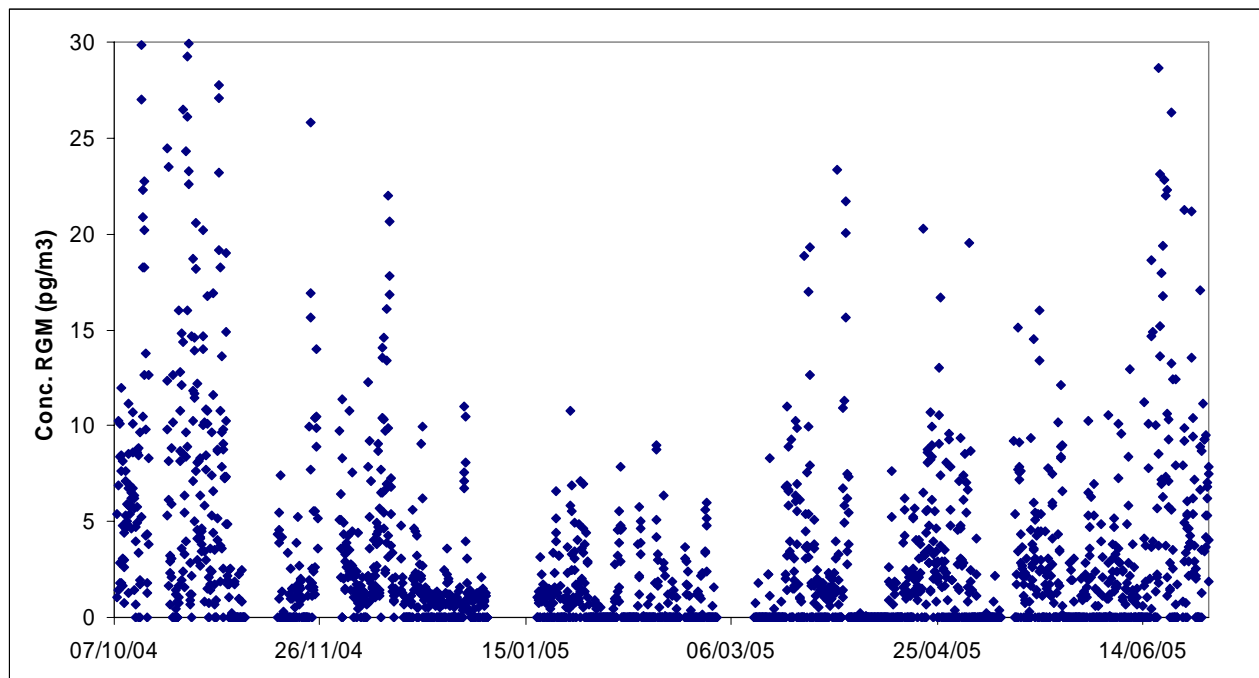


Figure 111: Hourly average concentrations of reactive gaseous mercury (RGM) at Auchencorth Moss, October 2004 – June 2005 (pg m^{-3})

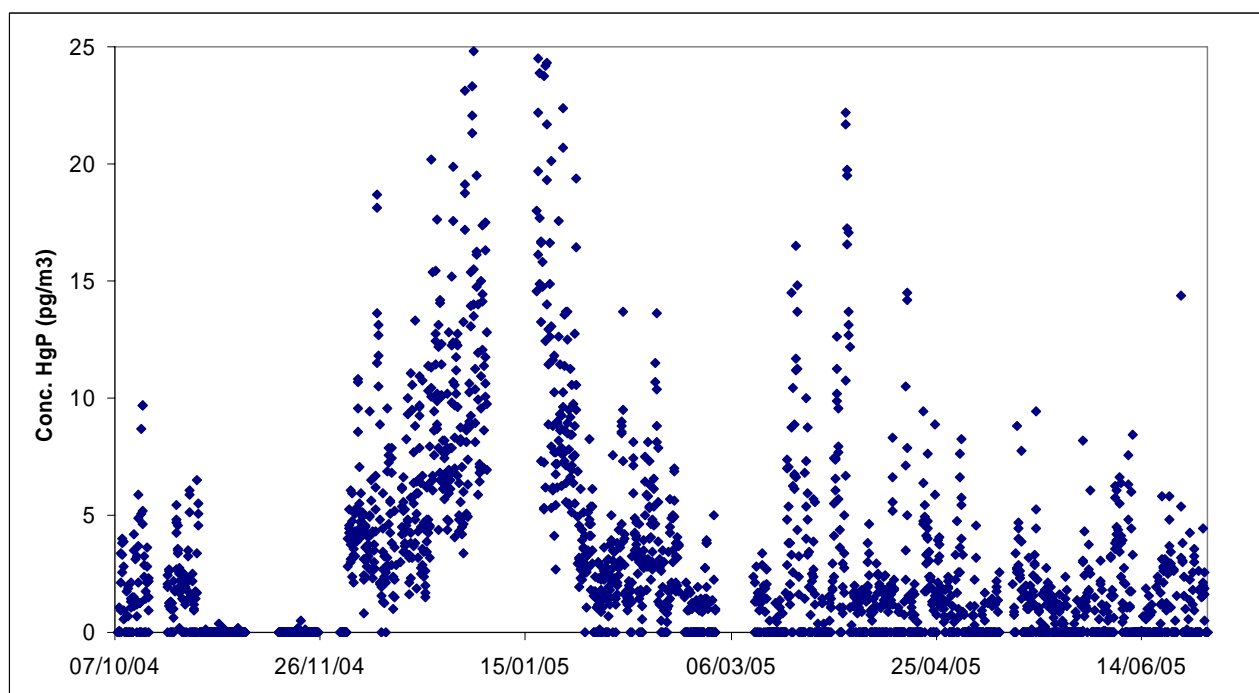


Figure 112: Hourly average concentrations of particulate mercury (Hg^{P}) at Auchencorth Moss, October 2004 – June 2005 (pg m^{-3})

Hourly average concentrations of RGM tend to decrease from autumn to winter, with a corresponding increase in the concentrations of particulate mercury. This probably reflects the different partitioning of RGM between the gaseous and particulate phase at lower temperatures. However, this general pattern hides a more complex relationship, as a positive correlation is seen between RGM and Hg^P in northerly and easterly winds, but a negative correlation is seen in south-westerly winds.

Diurnal Cycles of RGM and Hg^P

It has been found that RGM and Hg^P exhibit significant diurnal cycles, with the summer months showing the strongest cycle (Figure 113). The maximum concentrations of RGM and Hg^P are found between midday and 1500UTC. Contributing factors include photochemical reactions that both generate and consume RGM as well as the temperature dependent release of RGM from surface sources.

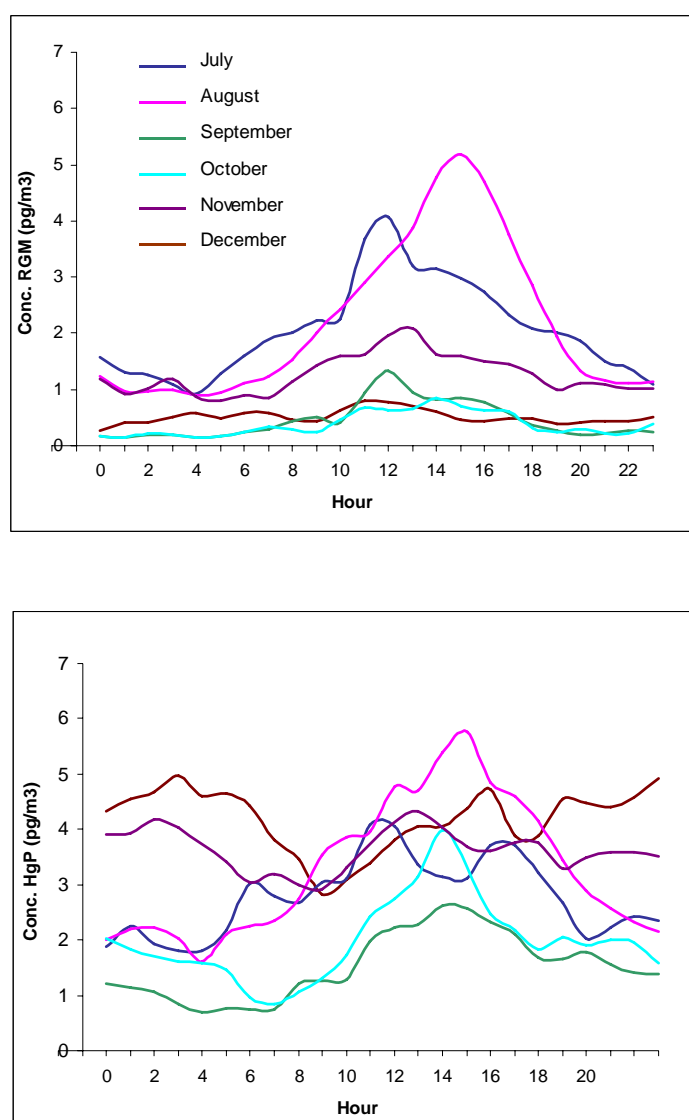


Figure 113: Diurnal cycles of RGM and Hg^P for July – December 2003 at Bush. The lines represent 2-hourly moving

Table 18 shows annual averages for elemental mercury at Bush and Auchencorth Moss. The 2003 data are from July to December and the 2005 data are from January to June.

Table 18 Annual averages for Hg⁰ at Bush and Auchencorth Moss. Note the different units for RGM and Hg^P compared with Hg⁰

Year	Bush			Auchencorth		
	Hg ⁰ /ng m ⁻³	RGM /pg m ⁻³	Hg ^P /pg m ⁻³	Hg ⁰ /ng m ⁻³	RGM /pg m ⁻³	Hg ^P /pg m ⁻³
2003	1.52	1.1	3.0			
2004	1.62	1.4	2.9	1.40	4.1	3.2
2005				1.25	2.1	2.8
Whole Period	1.57	1.2	2.9	1.33	2.7	2.8

As commented previously, the annual average concentration is lower at Auchencorth than it is at Bush. The data also show a lower annual average concentration at Auchencorth for 2005 compared with 2004, and also lower than the annual average from the Auchencorth integrating sampler (Work Package 7). Further work needs to be carried out to establish the causes of this difference. It should be noted that the average concentration from the integrating sampler for the period October – December 2004 is 1.45 ng m⁻³, which corresponds well with the Tekran average concentration over this period of 1.40 ng m⁻³.

On average, RGM concentrations are higher at Auchencorth than at Bush. There is no significant difference between Hg^P concentrations at Auchencorth and Bush.

7. Total Gaseous Mercury (TGM) in Air and Mercury in Precipitation

7.1 Introduction

Measurements of total mercury in air and rain are carried out at the 10 main network sites across the UK. The mercury in air network was set up after testing in summer 2004, and the mercury in rainfall was set up in winter 2004/2005.

7.2 Establishment of 10 new sampling sites for Hg in precipitation

The precipitation collector is based on the Iverfeldt design (Figure 114) with a long tube to reduce Hg diffusion to/from the atmosphere. We have made a few modifications in order to reduce possible contamination and improve safety. The funnel, debris filter and capillary tube is made from PTFE as per FAMS (Florida Atmospheric Monitoring Survey). The joints designed to reduce contamination and a glass bottle is used to reduce Hg⁰ diffusion. The samplers were manufactured by 'Just Plastics' and are deployed in duplicate at the 10 main network sites, pre-acidified with 1% HCl and changed on a 4-weekly basis.

The bottles are cleaned monthly according to the EMEP protocol and glassware and reagents have been rigorously tested in order to identify and reduce sources of contamination. The relatively new laboratories at CEH Lancaster have no history of previous mercury use, thus reducing the possibility of contamination from the laboratory atmosphere. The analytical detection limit is 0.8 ng l⁻¹ (99% confidence) by Cold Vapour Atomic Fluorescence Spectrometer (PSA Ltd). Controlled Reference Material NRCC-ORMS-2.

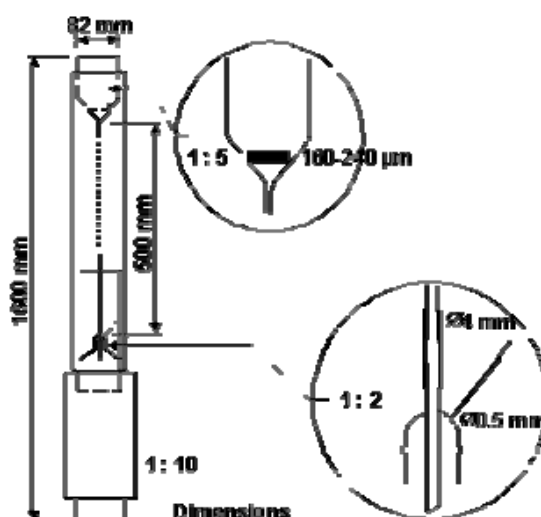


Figure 114: Iverfeldt design for sampling mercury in rain

7.3 Establishment of 10 new sampling sites for Hg in air

An integrating sampler for Total Gaseous Mercury (TGM) has been designed and tested at CEH Edinburgh (Figure 115). The samplers were tested at Bush and showed good agreement with the

Tekran analyser once each flowmeter had been individually calibrated. Ten integrating samplers have been deployed at the sites where the heavy metals particulate samplers are located. Most samplers were installed in July 2004, and the last sampler was installed in October 2004.

The flowmeters in each sampler have been individually calibrated. The flow rate is low, at 20 ml/min to prevent cartridge overloading over the two-week sample period. The cartridge assembly is heated during sampling to 100°C to drive off water and volatile organic compounds that would reduce capture efficiency. One of the integrating samplers at Auchencorth Moss runs adjacent to the Tekran analyser for method validation.

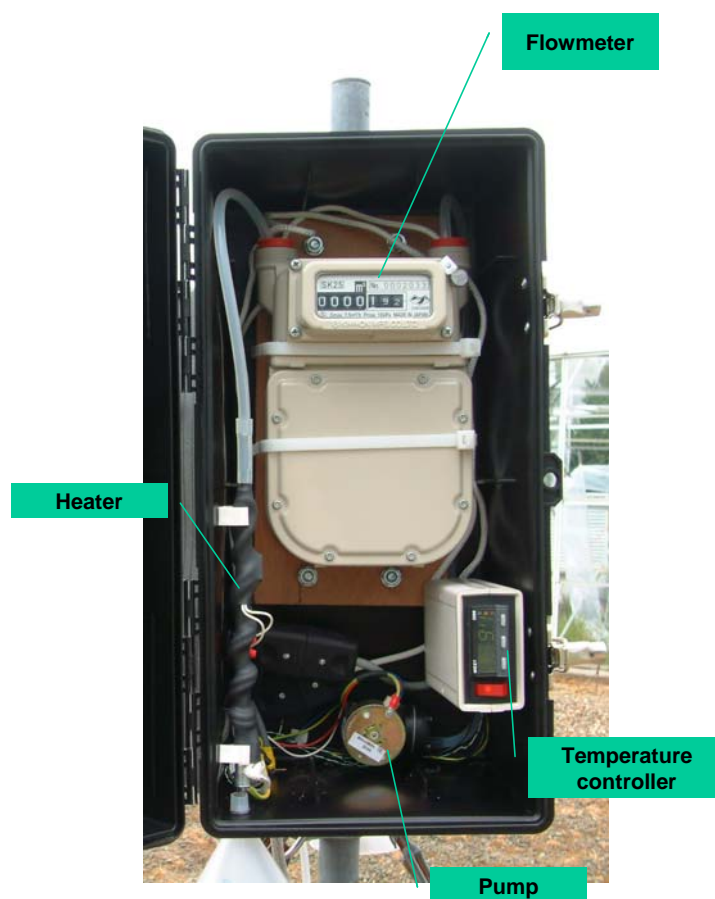


Figure 115: Integrating sampler for TGM

7.4 Development of a robust analytical method for routine measurement of Hg in air for weekly sampling frequency

Analysis of TGM is based on the system of Two-Stage Gold Amalgamation (Fitzgerald and Gill 1979). Mercury is adsorbed onto gold-coated sand contained within a quartz cartridge and is desorbed by heating the cartridge to 500°C to release the trapped mercury. Desorption is carried out using a custom-built desorption unit that interfaces with the Tekran 2537A analyser, used in off-line mode. Two cartridges are used in series to detect any breakthrough of mercury from the first cartridge, which can be analysed if the capture efficiency of the first cartridge has been reduced. Field blanks are used to analyse handling and storage contamination.

Data recovery (Table 19) has improved at all but one of the sites. The low percentage data recovery at Heigham Holmes is mainly due to site operator difficulties. There were major problems with a faulty sampler at Monks Wood, but since these were fixed at the end of May, this site has given 100% data capture. Loss of data has been caused by sampler faults, overloaded cartridges and other

site operation issues such as the breakage of cartridges. Several of the samplers were affected by a faulty temperature controller. This has now been rectified at all sites.

Overloaded cartridges can be refreshed by heating cartridges in air periodically to remove oxidisable material that may reduce capture efficiency. Unfortunately, it is not possible to predict when cartridges will become overloaded and due to the nature of the analysis, once the cartridge has been desorbed, it is not possible to re-analyse the sample. New gold-coated silica has now been purchased and the most problematic cartridges will be renewed on an ongoing basis.

Table 19: Percentage data recovery for 2005 at each of the ten TGM monitoring sites. The total number of possible samples is 26.

Site	% Data recovery
Auchencorth Moss	92
Banchory	69
Beacon Hill	65
Cockley Beck	58
Cwmystwyth	50
Detling	92
Heigham Holmes	11
Monks Wood	58
Wytham Wood	69
Yarner Wood	69

7.5 Tabulated data for monthly concentrations of Hg in air and in precipitation for 10 sites, with annual averages

7.5.1 HG IN AIR

Monthly concentrations of TGM for 2005 (Table 20) are shown graphically in Figure 116. These data show an annual average at each site in the region of 1.5 ng m^{-3} . The UK annual average from these data is 1.51 ng m^{-3} , agreeing with work by Lee *et al.* (1998). Concentrations at some sites, such as Cwmystwyth, vary more than at other sites, and this may indicate the influence of local sources. The data show no significant seasonal variation in TGM, and this is confirmed by the Tekran measurements of Hg^0 , which also show no discernible seasonal variation.

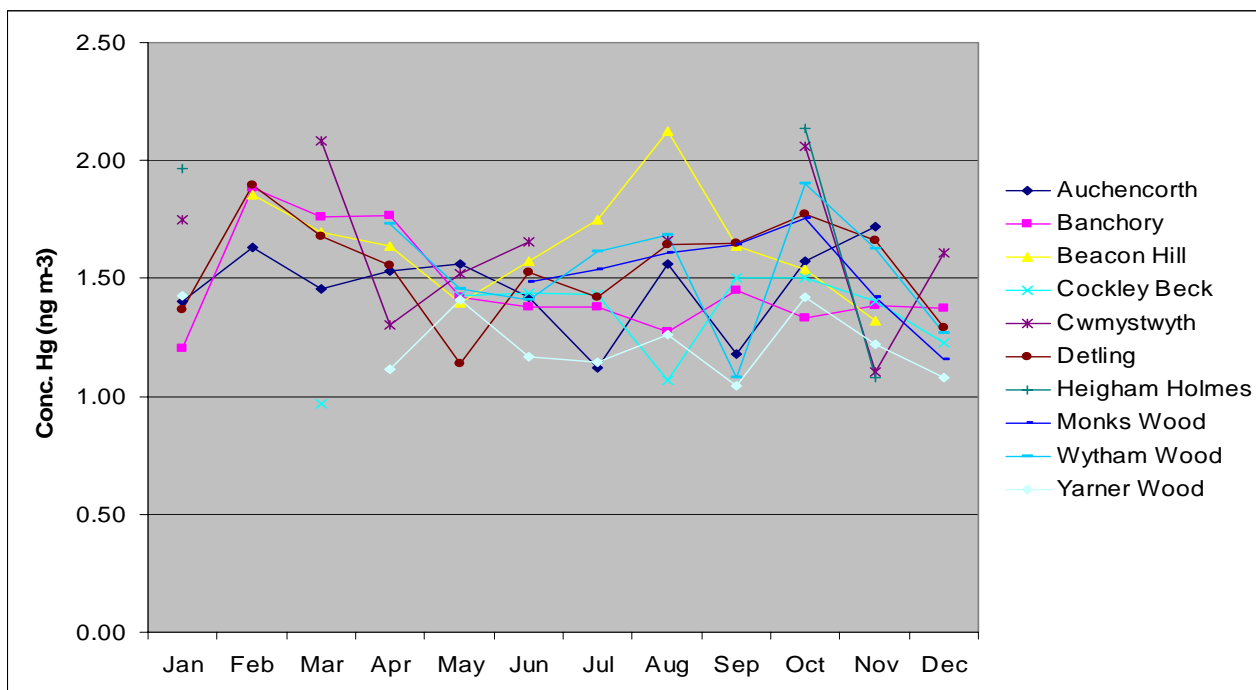


Figure 116: Monthly concentrations of TGM (ng m⁻³) for 2005 at each of the ten monitoring sites.

Table 20: Monthly and annual concentrations of TGM (ng m⁻³) for 2005 at each of the ten monitoring sites. Blank entries indicate that no valid sample was collected that month.

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual
Auchencorth	1.40	1.63	1.46	1.53	1.56	1.42	1.12	1.56	1.18	1.57	1.72		1.47
Banchory	1.20	1.89	1.76	1.77	1.42	1.38	1.38	1.27	1.45	1.33	1.38	1.38	1.43
Beacon Hill		1.86	1.69	1.64	1.40	1.58	1.75	2.12	1.64	1.54	1.32		1.66
Cockley Beck			0.97		1.42	1.44	1.43	1.07	1.50	1.50	1.40	1.23	1.36
Cwmystwyth	1.75		2.09	1.30	1.52	1.66		1.66		2.06	1.10	1.61	1.63
Detling	1.37	1.89	1.68	1.55	1.14	1.52	1.42	1.64	1.65	1.77	1.66	1.29	1.53
Heigham Holmes	1.96									2.14	1.08		1.73
Monks Wood						1.49	1.54	1.61	1.64	1.75	1.42	1.16	1.52
Wytham Wood				1.73	1.46	1.41	1.61	1.69	1.08	1.90	1.63	1.27	1.53
Yarner Wood	1.43			1.12	1.41	1.2	1.14	1.26	1.04	1.42	1.22	1.08	1.27

Wales appears to have higher mercury concentrations than may be expected for a western site. It is possible that this is due to a local source of mercury near the Cwmystwyth monitoring site, potentially the nearby house, which may burn coal. This requires further investigation. It is also possible that Beacon Hill is affected by the adjacent property, or the relatively high levels of mercury found here could be a feature of its location in a relatively urbanised area and very near the M1 motorway. The map shows higher than expected mercury concentrations for the northwest of Scotland. It is likely that if there was a monitoring site in the northwest of Scotland that it would show concentrations of mercury more akin to those found at Cockley Beck in the north west of England and Yarner Wood in the south west of England.

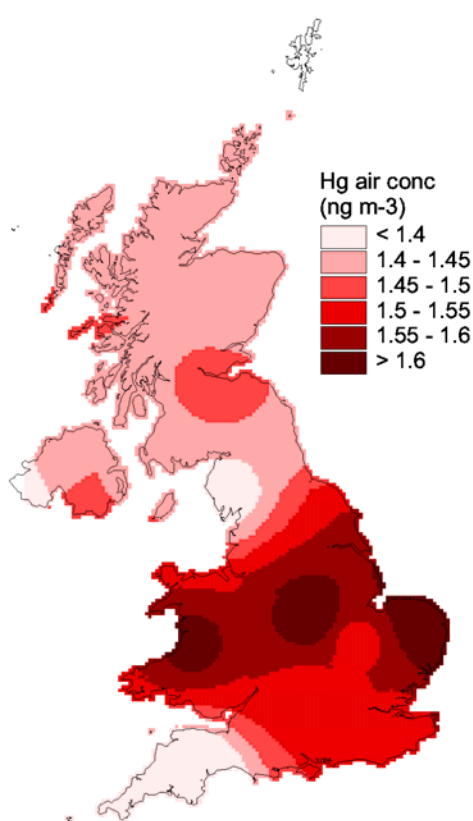


Figure 117: Concentration of mercury in air

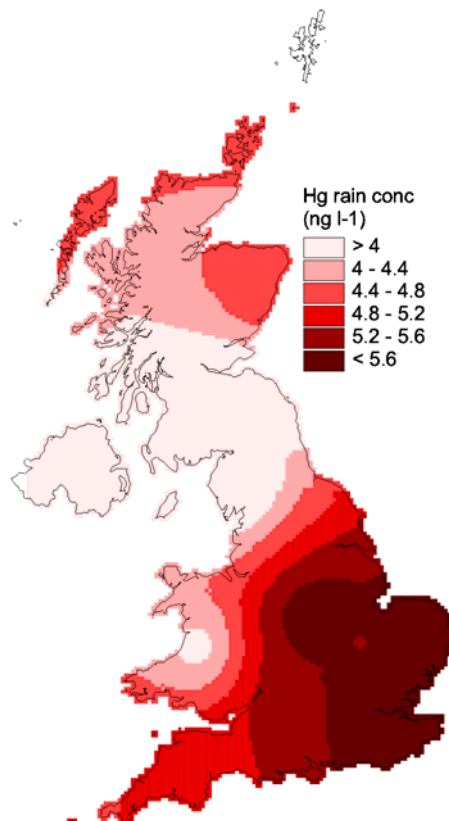


Figure 118: Concentration of mercury in rain

7.5.2 HG IN PRECIPITATION

Mercury concentrations in precipitation for 2005 at the main 10 sites are shown in Figure 118. The data collected thus far suggests a decrease in mercury concentrations in bulk deposition over the winter months. Annual mean mercury concentrations are generally higher at sites in the south-west of the UK.

Quality control checks show no correlation between bird fouling and mercury levels except at very high levels of fouling and also indicate that losses due to evaporation in the field may be greater than enhancements due to contamination therefore measured results are likely to be lower than actual concentrations. Values greater than 2 standard deviations of mean concentration were discarded.

The data collected thus far suggests a seasonal cycle as there is a decrease in mercury concentrations in bulk deposition over the winter months and an increase in the summer months. Annual mean mercury concentrations are generally higher at sites in the south-east of the UK.

Table 21: Mean 2005 concentration of mercury in precipitation (ng l⁻¹). 'm' represents missing or contaminated sample

Collection period (week no. in 2005)	1-4	5-8	9-12	13-16	17-20	21-24	25-28	29-32	33-36	37-40	41-44	45-48	49-52	Annual
Auchencorth	3.0	4.3	2.8	4.6	m	4.5	4.6	6.8	m	2.5	1.7	1.9	3.1	3.6
Banchory	0.7	m	3.0	5.4	3.8	9.6	8.4	4.6	6.2	6.8	2.4	1.9	2.4	4.6
Beacon Hill	m	4.5	7.4	6.9	m	8.6	8.0	4.9	3.3	5.3	4.6	5.9	m	5.9
Cockley Beck	1.0	6.3	6.0	5.9	4.6	3.4	3.0	3.4	1.6	3.7	1.8	2.1	m	3.6
Cwmystwyth	m	1.6	5.2	2.0	4.5	5.1	7.1	3.5	3.6	3.0	4.2	m	3.2	3.9
Detling	m	m	5.8	7.5	6.6	7.7	m	7.7	6.6	5.5	2.7	4.4	5.2	6.0
Heigham Holmes	m	m	m	m	5.6	m	m	5.7	6.7	5.2	7.1	5.1	m	5.9
Monks Wood	3.9	6.5	4.6	8.7	m	7.0	m	5.3	7.8	5.2	2.5	4.8	m	5.6
Wytham Wood	m	m	m	3.8	5.3	5.0	8.9	5.6	7.7	8.4	3.7	3.3	4.1	5.6
Yarner Wood	m	5.7	4.2	6.7	5.4	6.9	m	4.7	5.2	6.1	2.8	2.8	m	5.0

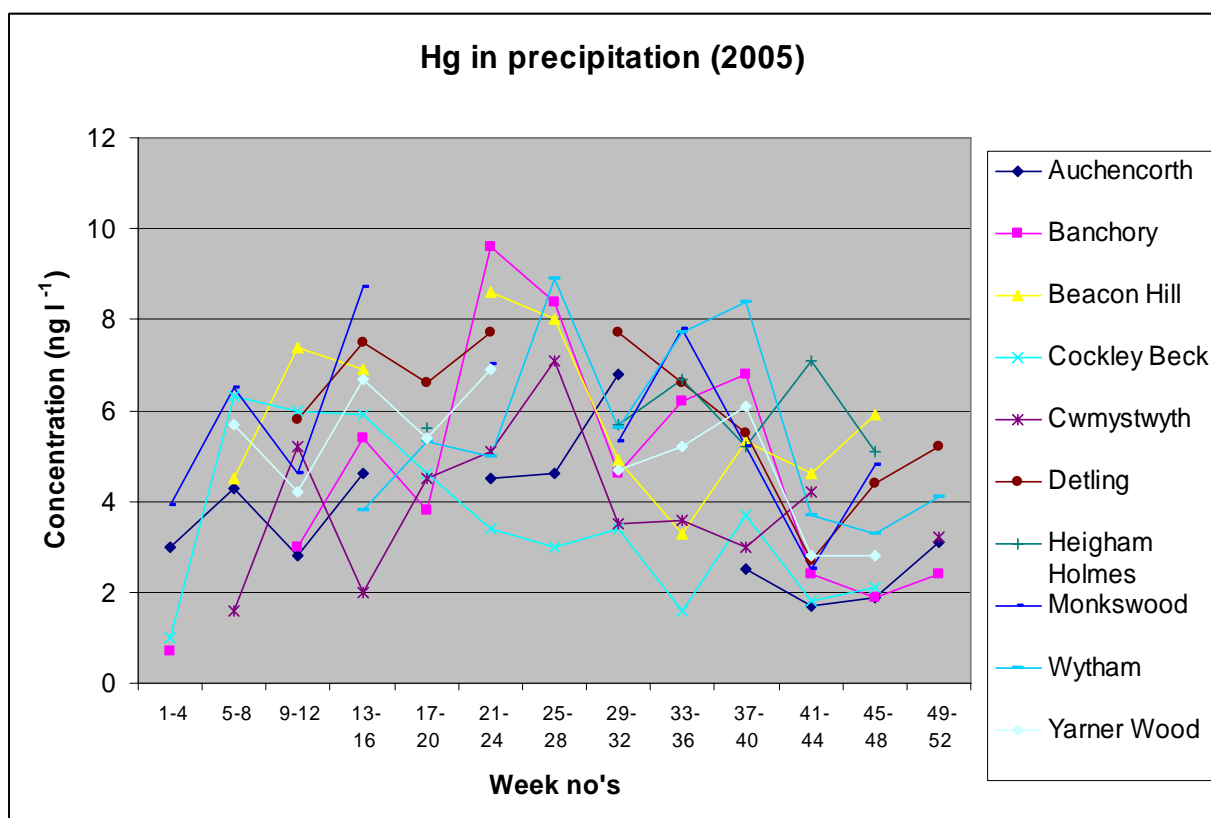


Figure 119: Mercury concentration in precipitation for 2005 at each monitoring site

8. Discussion

Introduction

The overall objective of this project was to provide high quality measurements of metal concentrations in air and precipitation throughout the UK from which the broad scale spatial patterns in concentration could be defined. These data would then be used to provide wet and dry deposition fields for the UK, e.g. as an input to the mapping of critical loads exceedances, an overall deposition budget for a range of heavy metals, and the means to check and /or validate the UK emissions inventories and the EMEP modelling of metals over the UK.

In this discussion, each of the main aspects of the measurements and derived products are considered, with the objective of showing the extent to which the objectives have been met.

The measurement network

At the beginning of the network it was recognised that in addition to the new sites to be established, it would be necessary to move some sites to avoid local sources of metals, eg from unpaved roads, arable fields and building activities. In practice, only one of the original sampling sites of the former Rural Trace Elements Network and North Sea Network was retained, at Banchory. Thus the network is largely new and meets a high specification in monitoring the background concentrations in air and precipitation. The approaches adopted have all worked, although the reliability of the sequential aerosol samplers has been poor and support from the suppliers has been weak at best. However, the 15 site network has proved adequate to measure the concentrations in air and rain of all metals required by Defra (As, Cd, Cr, Cu, Ni, Pb, Se, V and Zn). A further suite of metals has been determined in the same samples, which will considerably enhance the scientific outputs from the measurements.

The analytical methods provided adequate sensitivity and are underpinned by being accredited to ISO 17025:2005 by UKAS. The entirely new Hg network, co-located on the same sites has all been established and operates satisfactorily. In addition to the network sampling of mercury in air and precipitation, a single site at which the three components of mercury in air have also operated to quantify the concentrations of elemental gaseous mercury (Hg^0), Reactive Gaseous Mercury (RGM) and particulate mercury (Hg^p) as well as Hg in rain. All measurement methods have been successful in providing the necessary data to address the main objectives.

Spatial patterns in concentrations in air and precipitation

It is helpful to describe the general properties of the data before considering each of the metals in turn and a comparison of the maps of deposition derived by the different methods. The directly measured concentration fields for seven of the nine metals of primary interest presented in chapter 3 provide consistent patterns, with aerosol concentrations and concentrations in precipitation increasing between NW Scotland south eastwards towards SE England where concentrations are generally larger by about a factor of three. Within this general gradient over the country, which is similar to other aerosol phase pollutants such as SO_4 or NH_4 , there are areas with larger concentrations of most of the metals, and the most notable feature is a 'hot spot' in the English Midlands, with Beacon Hill often being the site with largest concentrations.

The exceptions to this generalisation are selenium and vanadium. In the case of vanadium the largest aerosol concentrations are found in SW England and in East Anglia, consistent with a substantial contribution from marine sources resulting from the combustion of residual fuel oil. For selenium, hot spots of concentration in precipitation at Beacon Hill in Leicestershire, at Banchory

in NE Scotland and in the SW of England generate a patchy distribution, which contrasts with the smoother concentration field for aerosol selenium concentrations.

Spatial patterns in the deposition of metals in the UK

By contrast with the concentration fields in air and precipitation, the deposition fields for all metals show the dominance of wet deposition, with the areas of largest deposition being the areas of largest wet deposition, and especially the areas of the country with precipitation in excess of 1500 mm annually. This spatial pattern is the consequence of removal processes dominated by precipitation scavenging and wet deposition accounts for between 60% and 70% of the total deposition of almost all the metals considered. Thus Wales, the Pennine hills, Cumbria, and the West central highlands of Scotland are the deposition hot spots of the UK for the total deposition of metals. The spatial patterns in deposition show a substantially larger range than those of the concentrations in air and precipitation, which were roughly a factor of three over the UK, whereas for deposition the maxima exceed the minima by typically an order of magnitude.

Even in the case of selenium and vanadium, which show patchy concentration fields for the UK, the deposition maps clearly illustrate the dominance of wet deposition as a scavenging mechanism. The other notable feature of the deposition fields are that because dry deposition rates are much larger on woodland than other land surfaces, the hot spots for dry deposition are generally the forests, and even in the total deposition fields, it is possible to distinguish the major UK forests (Kielder, Thetford and the New Forest for example).

Comparing the deposition maps from a range of measurement and modelling approaches.

Arsenic

Figure 120 - 123 shows the different deposition patterns for the UK from models and measurement approaches. Arsenic is the only metal for which the Frisbee network data derives smaller deposition than was measured in the new network and in the moss surveys. The hot spots from the moss survey are mainly in southern England, South Wales and in the uplands of Cumbria and the northern Pennine hills. The measured values from the new network show all high rainfall areas of the UK as the areas of greatest deposition. The map of arsenic deposition from the FRAME model shows peaks of deposition close to the main emission sources, but except in South Wales and the English Midlands the map does not reflect the measured deposition field at all well. Overall, there is little correspondence between any of the methods, and the map based on measurements from the new network, provides the best estimate of both annual deposition and the spatial distribution. It should be noted that while appropriate for the background deposition, the map based on measurements in air and precipitation is based on only 15 sites, and misses the urban areas and industry hot spots, thus the fine detail in comparisons of the methods must take account of differences in spatial resolution.

Cadmium

Figure 124 – 128 provide maps of deposition based on the different methods. The map derived from Frisbee samplers for England and Wales provides the largest values but does show similarities in spatial pattern to the map based on moss sampling in 2000. However, the values are larger by between a factor of 2 and 3. Both FRAME and EMEP models show some similarities in spatial pattern and both are based on the NAEI. However, both models substantially underestimate deposition and the spatial resolution of the EMEP model is very limited, implying that the inventories have substantially too little Cd in the emissions to reproduce the overall deposition measured by the monitoring network. The Monitoring network and moss deposition patterns are reasonably similar, and pick out the hot spot in SW England and South Wales quite well. The area of poorest comparison is the West Highlands of Scotland, where moss sampling did not pick up the

enhanced deposition in the high precipitation areas. It is important to point out that the calibration method for the moss network should couple these methods.

Chromium

The four maps, three of which are based on measurements, show different patterns of deposition. The map derived from Frisbee sampling, as in all other metals, shows the largest values, and is larger than the new monitoring data by an order of magnitude. Some of the difference is due to differences in emissions between the dates of the two sets of measurements (1995-8 and 2004), but it is important to note that when compared with the available measurements at the same time, the Frisbee sampler values were much larger. Many features of the spatial pattern in deposition are similar in the Frisbee and in the new monitoring network, especially the upland values in Wales in Northern England. FRAME-HM shows substantial Cr deposition only in parts of Northern England, and overall shows values of deposition that are substantially smaller than the measurements in the new network. The Moss sampling shows detailed structure in the deposition field, but the pattern does not seem to be related to that provided by the new measurement network or by the precipitation field in a general sense. There are areas of the country in which orography appears to influence the pattern, but this is not consistent at larger scales. It should be noted that in examining the relationship between measured deposition and concentrations in moss samples, no statistically significant relationship was found (section 5), shedding doubt on this older moss-derived Cr deposition map in general.

Overall, the best estimate of deposition is provided by the monitoring network, the models appear to be deficient in emissions and moss sampling does not provide a helpful alternative for Cr.

Copper

The spatial deposition patterns for Cu for the different measurement and modelling methods are illustrated in Figure 133 - 136. The Frisbee network produced depositions that were typically 3 times greater than the other methods with large inputs in the Central Midlands, the Severn Estuary and East Anglia. The first two regions were also evident in the FRAME-HM map but for East Anglia. The later Moss and current Monitoring Network have broadly similar distributions and significantly lower depositions and yet the Total Depositions are still 5 times higher than that presented in the NAE inventory (see Table 22). The concentrations in air and precipitation (Figure 48 and 49) clearly demonstrate a strong NW-SE gradient with the highest concentrations in the SE (Air = 3 – 3.5 ngm⁻³, Precipitation = > 1 µg l⁻¹). The gradient is still maintained in the dry deposition maps but strongly influenced by topography for the Wet Deposition (Figure 50 – 51). The reduction of smelting activities in the Severn Estuary area has clearly improved the air and precipitation quality for Copper.

Lead

This is another of the metals for which we also have EMEP deposition estimates. The Frisbee values are again largest and are related to a period with much larger emissions. The moss and new network values pick out the main areas of enhanced deposition, in the uplands of Wales and Northern England and given the statistically significant relationship between concentrations of lead in moss and measured deposition, the moss sampling network provides valuable spatial detail in the deposition field. The models highlight the areas with substantial emissions in the inventory, and urban areas in particular (urban hot spots are not detected by the new network). However, both models EMEP and FRAME contain emissions which are about an order of magnitude too small to reproduce the deposition measured by the new network. The maps from these models therefore show values of lead deposition which are much smaller than the measured values, and fail to pick up the high deposition areas of the uplands.

Overall the broad pattern of deposition across the UK is best provided by the new network but valuable additional detail is provided by the moss sampling. To provide a more complete picture of the country deposition including the urban areas, it will be necessary to incorporate the urban heavy metal monitoring data or modelled values.

Nickel

The four deposition maps for nickel deposition show some similarities to the patterns observed with lead. The moss sampling and new network values show broadly similar spatial patterns, with the uplands and orographic effects reasonably clear. The absolute values provided by the two methods are in the same range, but the moss sampling provides larger values. The modelled deposition values from FRAME have a larger range, to illustrate the urban and industrial hot spots, and this has obscured some of the orographic effects in the mapping, which are still evident, at least in England and Wales. Frisbee derived maps are again very much larger, and relate to conditions of the mid 1990s. Interestingly, the Ni deposition map is quite different from the V deposition map, although both Ni and V are thought to derive from crude oil combustion.

Overall the maps derived from the new measurements provide the best estimates of deposition across the UK, but do not reveal the additional hot spots close to sources. The FRAME modelling values are smaller in the rural areas and emissions in the model are too small to reproduce the observed patterns, but are much closer than for As, Cd, Cu Pb or Zn.

Selenium

The patterns of selenium deposition from the three methods available are unlike any of the other maps presented here. The moss derived map is similar in many respects to the new network data. The effects of orography and wet deposition seem clear and most areas of high precipitation are picked out by the two maps. There are differences especially in Yorkshire, which seems to be a moss selenium hot spot. This is consistent with the Se emissions from glass manufacture in the NAEI. The relationship between selenium in moss and deposition is not quite significant statistically, but on inspection of the two maps, there appears to be valuable additional spatial data provided by the moss sampling and further analysis of the moss data may improve the quality of the correlation with measured deposition data.

The model based map from FRAME seems entirely different, and picks out the urban centres and shows little of the broad spatial pattern in the rural landscape. Inspection of the annual budgets shows that the deposition values from measurements imply much larger sources than those in the model and therefore in the inventory, by about a factor of 4.

Vanadium

There are four maps of vanadium deposition in the UK, presented as Figure 149 - 152. The new network based map shows high deposition in many of the coastal areas and the uplands close to the west coast. The moss derived values also show some similar features, but are not supported by a really significant relationship between deposition and concentrations in the moss (section 5). Some aspects of the Frisbee based map also show similarities with the new network and the moss data. The model based map shows the hot spots close to major sources of heavy oil combustion throughout the UK, and these hot spots greatly increase the range of deposition values and obscure some of the underlying detail. It is interesting in this respect that the UK inventory for vanadium exceeds the amount deposited on the UK by about a factor five and brings the model deposition values close to the measured values for a pollutant in the aerosol phase with the majority of the

sources within the UK. The problem with this consistency is that it seems very likely that substantial vanadium is being imported from shipping emissions at varying distances from the UK coast, and it is unclear just how much of this source is included in the current inventory. Vanadium emission estimates have changed greatly over the years as the NAEI calculation algorithm has been revised, indicating just how uncertain emission factors for V are.

Zinc

There are four different maps of zinc deposition, presented as Figure 153 - 156. The moss derived map shows some of the characteristics of the new network map, and moss Zn concentrations in samples at the deposition sites show a weak correlation with the measurements ($r^2 \sim 0.4$). However, the relationship is far from robust and more needs to be done to understand the processes linking accumulation in moss and the deposition climate at the site. The new network values show the large areas of high deposition to be the uplands of Wales, Scotland and England, with broad areas of fairly uniform deposition in the lowlands. The model deposition values highlight the source areas, especially urban areas and therefore not detected by the new monitoring network. The model for Zn contains emissions from the NAEI which are about an order of magnitude too small to reproduce the measured deposition over the UK as a whole.

The UK deposition budget for metals and comparisons with the NAEI

The deposition data presented in this report can be summed over the UK to estimate the total annual deposition. These data for the different metals are presented in Table 22. Also presented in Table 22 are NAEI values for 1995 to 2003, EMEP deposition values, and derived deposition totals for the moss deposition data, the Frisbee data and the FRAME model.

There are some striking differences in the totals. The deposition totals of As, Cu, Pb and Zn in the UK are about a factor of 5 larger than the emissions in the NAEI. Allowing for the fraction of UK emissions exported and the import to the UK from other countries, the amount of the UK inventory of emissions that is expected to be deposited in the UK is of the order 20% to 40%. Thus the emissions in the NAEI, appear to be too small to account for the measured deposition, by up to an order of magnitude. While it is clear that there are sources of these metals which are not included in the NAEI, the relatively small number of sites in the new network is too small to identify individual sources. Furthermore the network does not sample urban areas, and aerosols larger than 10 μ m aerodynamic diameter. Thus the values in the deposition totals are underestimates of the actual deposition.

The most likely source of the missing emissions seems to be the resuspension of material from the surface, by vehicles and by wind for example. Data from recent NERC research into the sources and sinks of aerosols in urban areas came to similar conclusions. It is also entirely possible that combustion sources and industrial activity in general have been underestimated.

For the other five metals, three (Cd, Cr and Se) provide deposition data which imply substantially larger emissions than those in the NAEI, while for Ni and V the implied emissions for the UK from the deposition measurements are much closer to agreement, i.e. within a factor of two of the expected values.

The obvious question to the deposition data is 'is it likely that the deposition values have been substantially overestimated?' The most obvious source of overestimation is that the wet deposition values are derived from bulk collectors, which also collect some dry deposition, so there is some double counting. This is seen as a priority issue to quantify directly in the next phase of the work, however, the data from wet only rain collectors used in the Acid Deposition network in the 1980s imply quite small dry deposition of metals (Ca and Mg) onto the bulk collectors which were co-

located with the wet only collectors. Overall it is unlikely that this would lead to an error larger than 20% in the deposition totals, and we are looking for a much larger term.

The estimation of wet deposition, including the orographic enhancement process could also contribute to this difference. However, in modelling the process we have used a conservative value for the average composition of the feeder cloud relative to the seeder rain, of a factor of 2. The long term measurements of cloud water at the two upland sites provide values for the average enhancement of rainfall composition at the two sites by locally measured cloud of between a factor of 8 and 10. It is unlikely therefore that this is the cause of the difference between the emissions implied by the deposition measurements and those in the NAEI.

It seems most likely that large sources of the metals in the air over the UK are not incorporated in the emissions inventory.

Table 22: Summary of heavy metal emissions and deposition estimates using different techniques

	United Kingdom [*]									England and Wales only ⁺								
	As	Cd	Cr	Cu	Ni	Pb	Se	V	Zn	As	Cd	Cr	Cu	Ni	Pb	Se	V	Zn
Emissions[tyr⁻¹]																		
NAEI 1995	34.0	13.9	115.1	109.9	356.6	1551	60.9	1733	971	29.2	12.8	107.4	98.4	278.0	1407	50.5	1318	923
NAEI 1998	26.3	8.4	91.6	93.7	243.9	855	54.5	1361	832	22.6	7.7	85.5	83.9	190.2	776	45.2	1035	791
NAEI 1999	23.8	7.7	78.1	86.3	201.4	495	42.1	1231	675	20.4	7.1	72.9	77.2	157.0	449	34.9	936	642
NAEI 2000	20.6	7.3	76.4	81.4	168.5	164	44.2	1111	627	17.7	6.7	71.3	72.9	131.4	149	36.7	845	596
NAEI 2001	19.1	6.1	74.8	72.4	180.7	158	44.4	1203	600	16.4	5.6	69.8	64.8	140.9	143	36.9	915	571
NAEI 2003	16.1	5.5	43.5	65.2	179.7	133	42.2	1285	492	13.8	5.1	40.6	58.4	140.1	121	35	977	468
Total Deposition [tyr⁻¹]																		
Moss 96/97	315	12.8	156	854	177	548	157	140	1230	269	9.21	112	248	137	408	87.2	117	1044
Moss 2000	160	9.56	129	256	93.9	258	79.0	69.9	1075	149	7.42	83.9	175	66.1	208	47.4	53	817
Moss 2000 (UK cal.)	109	11.2	N/A	N/A	206	492	181	330	973	99	8.89	N/A	N/A	148	376	104	249	658
Frisbee Network	-	-	-	-	-	-	-	-	-	42.3	47.1	110	1197	271	1020	-	123	4536
EMEP 2003	-	7.7	-	-	-	377	-	-	-	-	N/A	-	-	-	N/A	-	-	-
CEH model (NAEI 98)	18.3	7.3	40.3	51.0	157	510	>34.8	>268	726	14.3	6.87	33.2	55.9	142	529	>28.7	>225	485
CEH model (CEH 97)	15.0	8.5	52.9	66.8	176	663	>32.2	>45.3	551	12.2	5.95	45.3	41.1	124	396	>27.6	>39.3	643
Initial network estimate – Report 8/04 - Data: 05/03 - 05/04	149	20	165	438	136	460	80.3	221	3715	81	13	96	290	87	320	44	147	2329
UK Heavy Metals Network 2004 – Data: Finalised 2004	76	10	61	325	108	493	84	194	2277	48	6.6	37	224	69	341	44	129	1328
CEH Network / NAEI	4.7	1.9	1.4	5.0	0.6	3.7	2.0	0.2	4.6	3.5	1.3	0.9	3.8	0.5	2.8	1.3	0.1	2.8

* UK Emissions estimates using UNECE Source Categories, Inventory year 2003, published by NAEI 16/8/2005

+ England and Wales emissions scaled, based on mean UK/E&W ratio (1999 and 2001) in August 2004 Report

Table 23: Summary of 2004 UK heavy metal deposition estimates as components of wet, dry and cloud. (Amount in parenthesis is percentage of total deposition.)

tonnes	As	Cd	Cr	Cu	Ni	Pb	Se	V	Zn
Total UK Deposition	75.9	10.3	61.3	324.7	107.5	492.5	84.1	193.5	2277.4
Dry Deposition	23.1 (30.4%)	2.5 (24.8%)	20.2 (32.9%)	95.6 (29.4%)	31.5 (29.3%)	146.2 (29.7%)	13.6 (16.2%)	59.5 (30.8%)	380.3 (16.7%)
Wet Deposition	51.9 (68.4%)	6.6 (73.3%)	40.1 (65.4%)	222.6 (68.6%)	74.3 (69.1%)	338.4 (68.7%)	68.4 (81.3%)	130.7 (67.5%)	1868.4 (82.0%)
Cloud Deposition	0.95 (1.3%)	0.2 (1.9%)	1.1 (1.8%)	6.5 (2.0%)	1.7 (1.6%)	7.9 (1.6%)	2.1 (2.5%)	3.3 (1.7%)	28.7 (1.3%)

Arsenic (As)

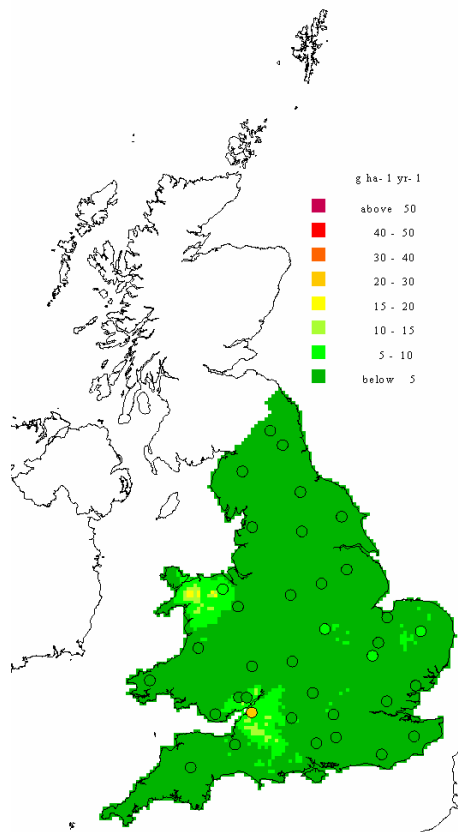


Figure 120: Frisbee Network 95-98 (g ha⁻¹ yr⁻¹)

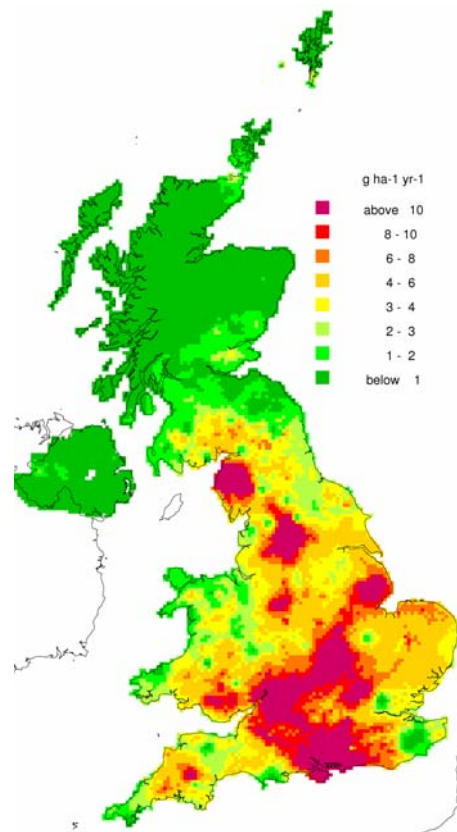


Figure 121: Moss Survey 2000, UK calibration (g ha⁻¹ yr⁻¹)

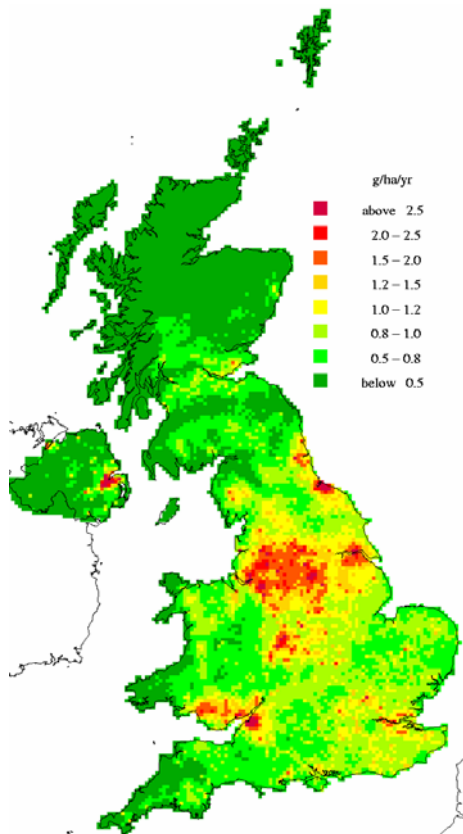


Figure 122: FRAME-HM (NAEI 1998) (g ha⁻¹ yr⁻¹)

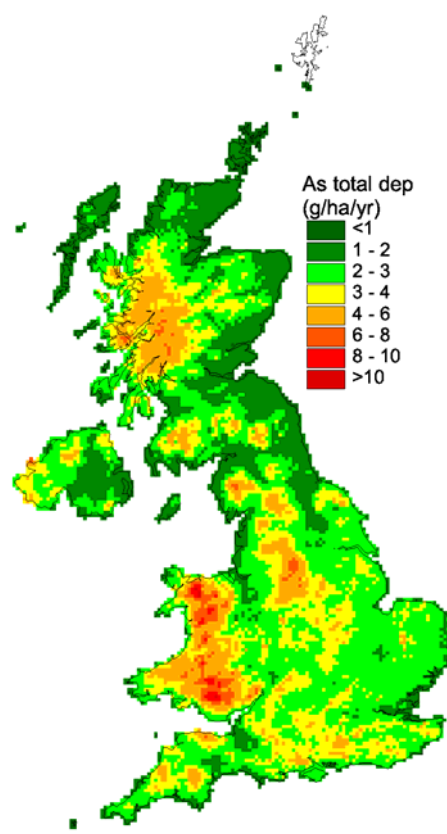


Figure 123: Monitoring Network 2004 (g ha⁻¹ yr⁻¹)

Cadmium (Cd)

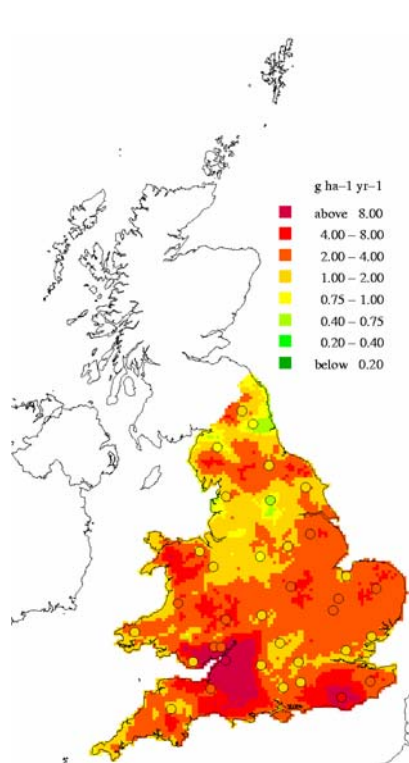


Figure 124: Frisbee Network 95-98 (g ha⁻¹ yr⁻¹)

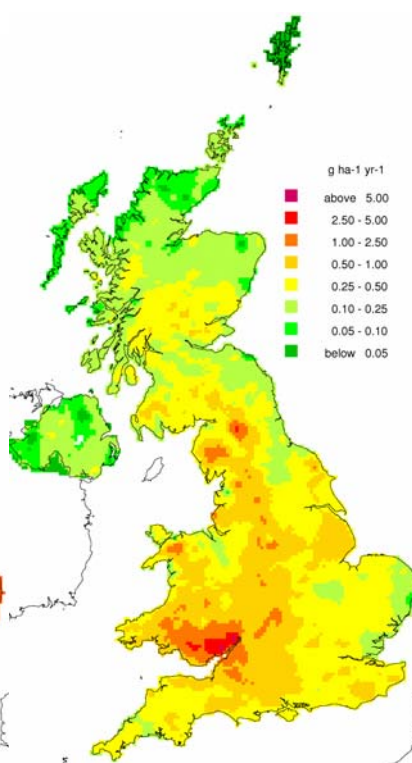


Figure 125: Moss Survey 2000, UK calibration (g ha⁻¹ yr⁻¹)

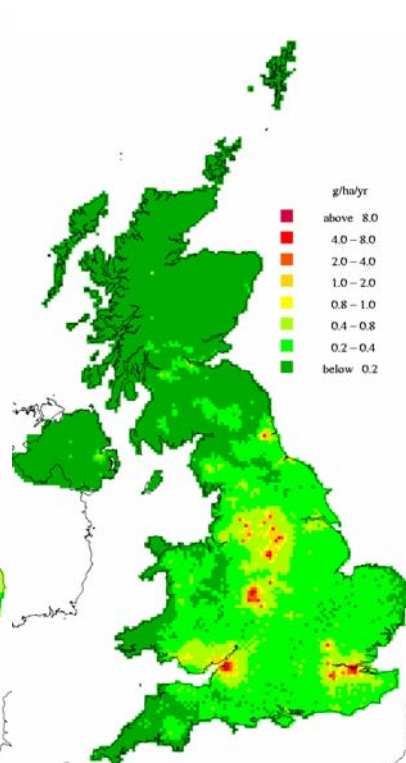


Figure 126: FRAME-HM (NAEI 1998) (g ha⁻¹ yr⁻¹)

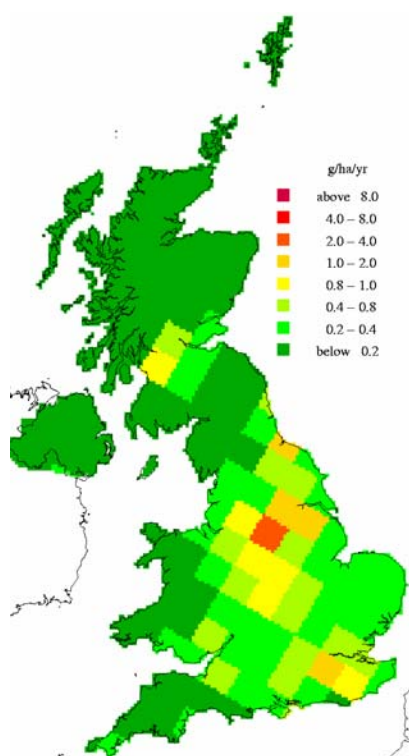


Figure 127: EMEP 1998 (g ha⁻¹ yr⁻¹)

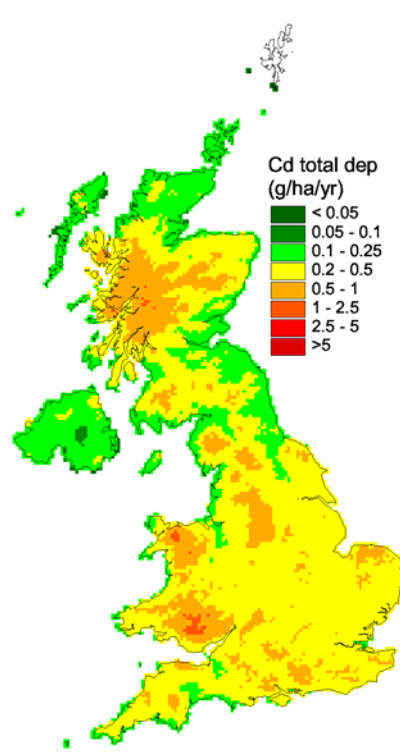


Figure 128: Monitoring Network 2004 (g ha⁻¹ yr⁻¹)

Chromium (Cr)

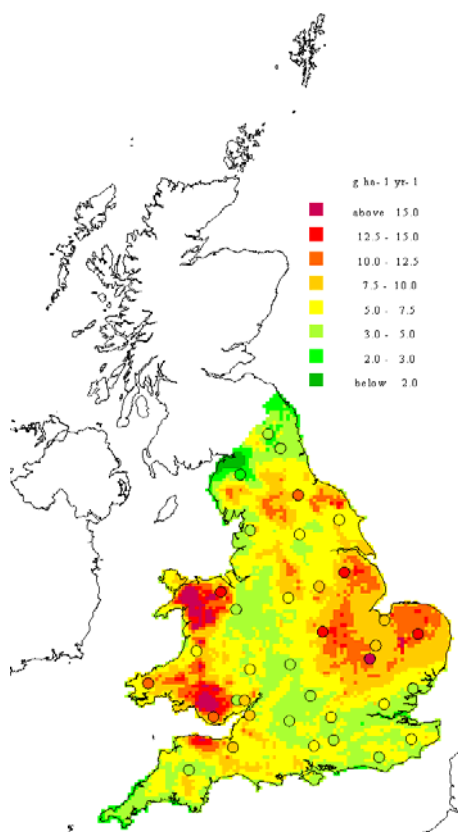


Figure 129: Frisbee Network 95-98 (g ha⁻¹ yr⁻¹)

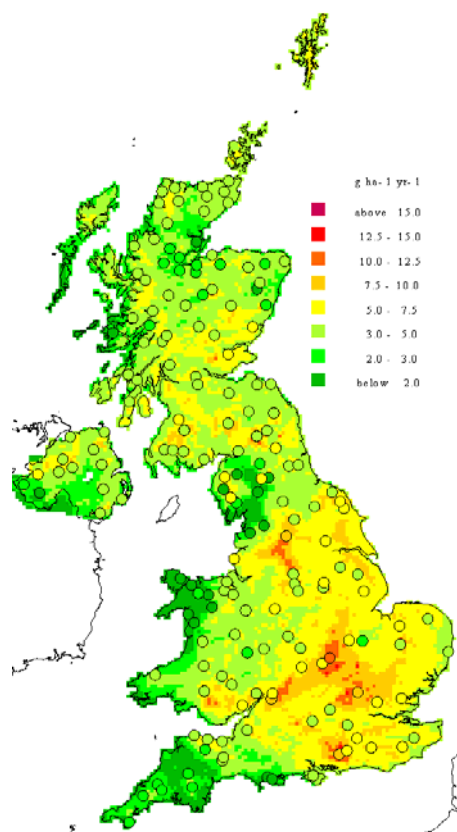


Figure 130: Moss Survey 2000, old calib. (g ha⁻¹ yr⁻¹)

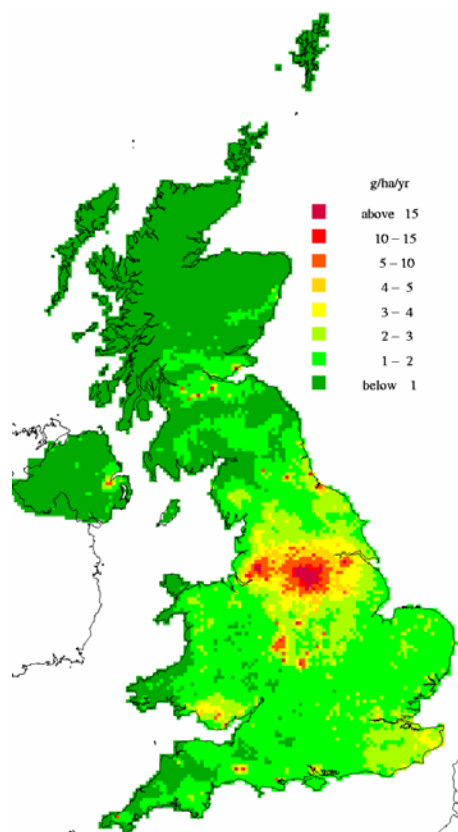


Figure 131: FRAME-HM (NAEI 1998) (g ha⁻¹ yr⁻¹)

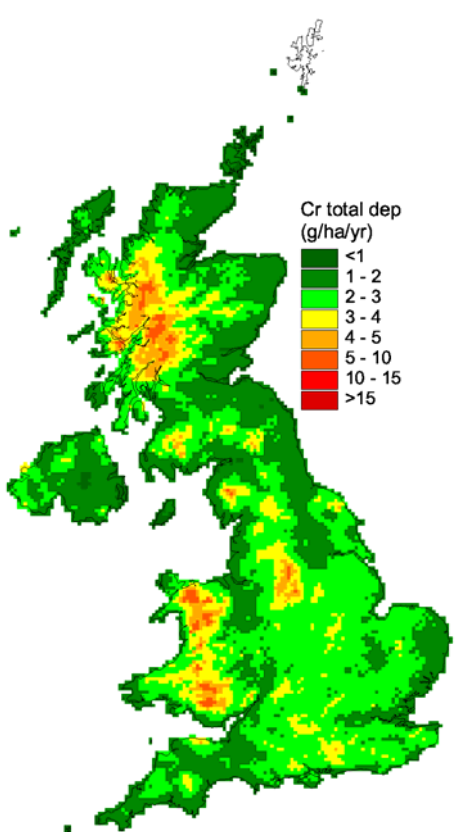


Figure 132: Monitoring Network 2004 (g ha⁻¹ yr⁻¹)

Copper (Cu)

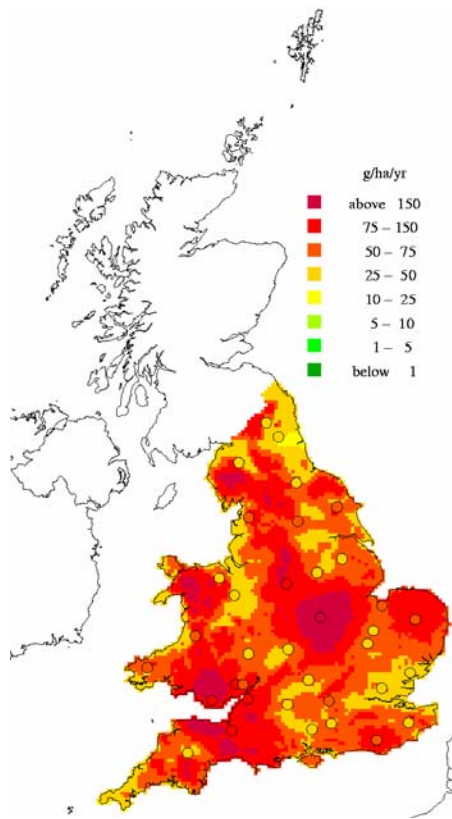


Figure 133: Frisbee Network 95-98 ($\text{g ha}^{-1} \text{yr}^{-1}$)

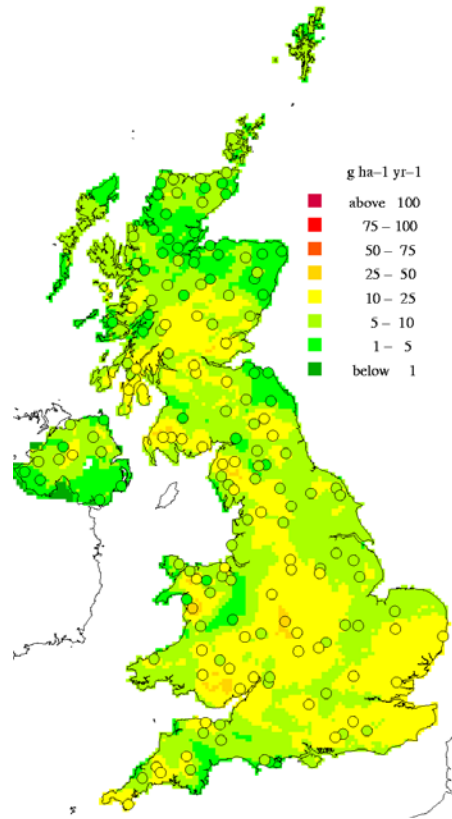


Figure 134: Moss Survey 2000, old calib. ($\text{g ha}^{-1} \text{yr}^{-1}$)

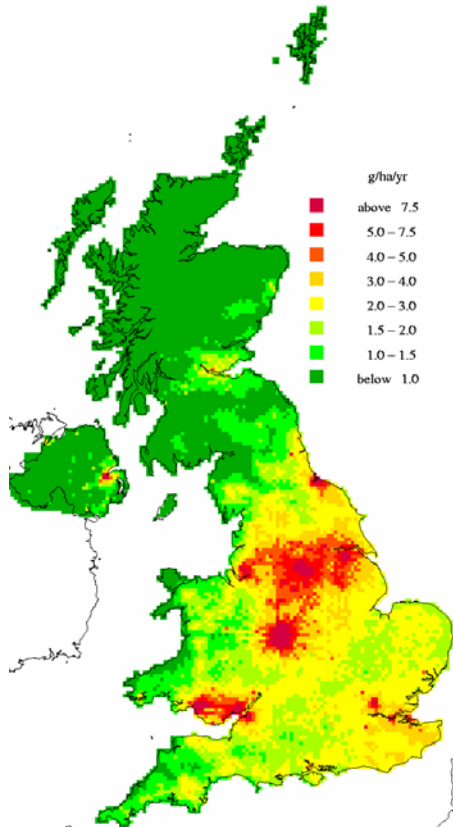


Figure 135: FRAME-HM (NAEI 1998) ($\text{g ha}^{-1} \text{yr}^{-1}$)

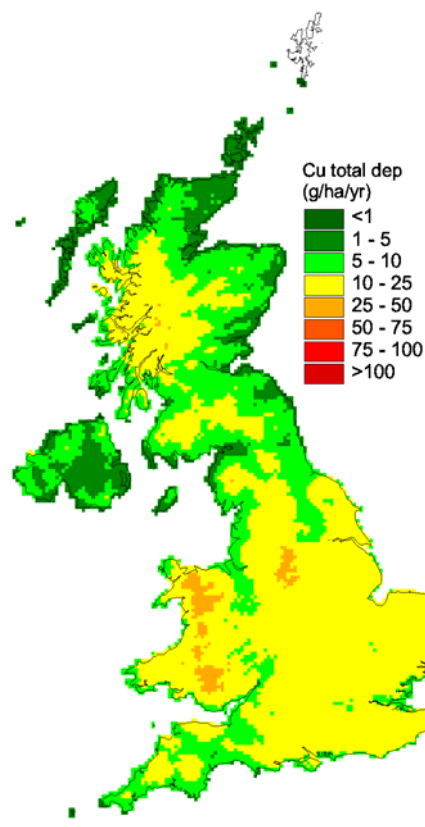


Figure 136: Monitoring Network 2004 ($\text{g ha}^{-1} \text{yr}^{-1}$)

Lead (Pb)

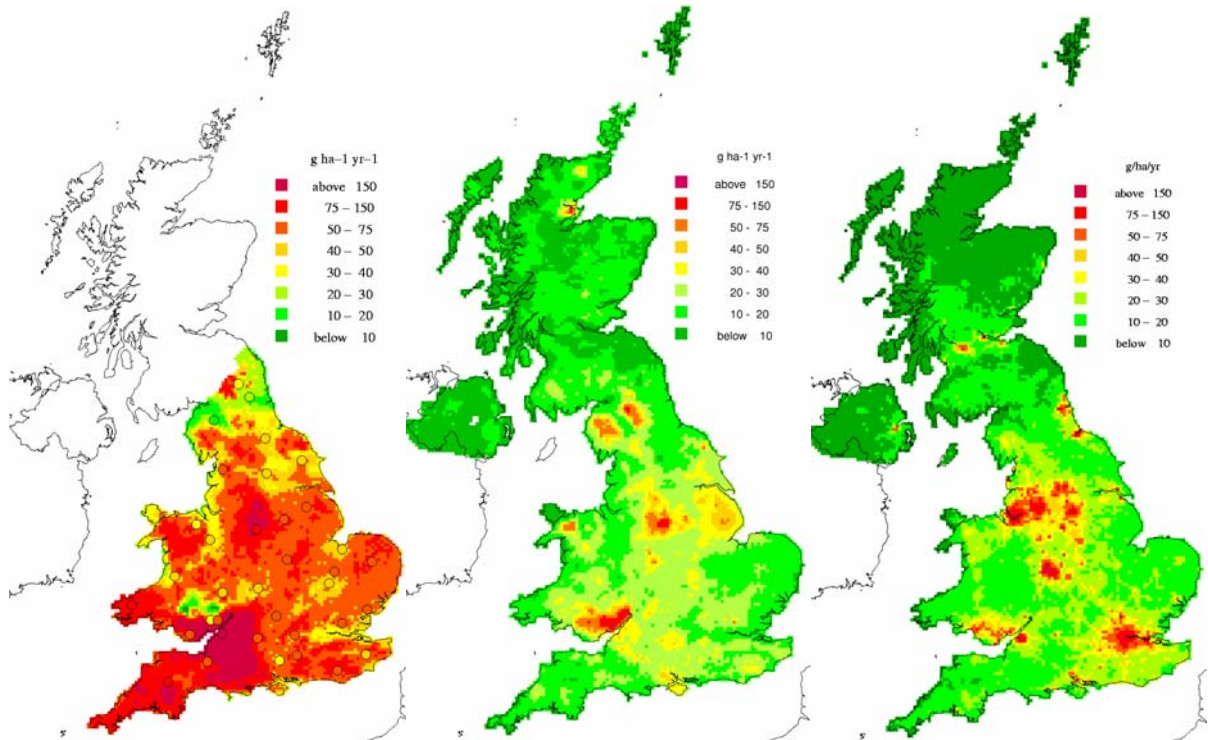


Figure 137: Frisbee Network 95-98 ($\text{g ha}^{-1} \text{yr}^{-1}$)

Figure 138: Moss Survey 2000 UK calibration ($\text{g ha}^{-1} \text{yr}^{-1}$)

Figure 139: FRAME-HM (NAEI 1998) ($\text{g ha}^{-1} \text{yr}^{-1}$)

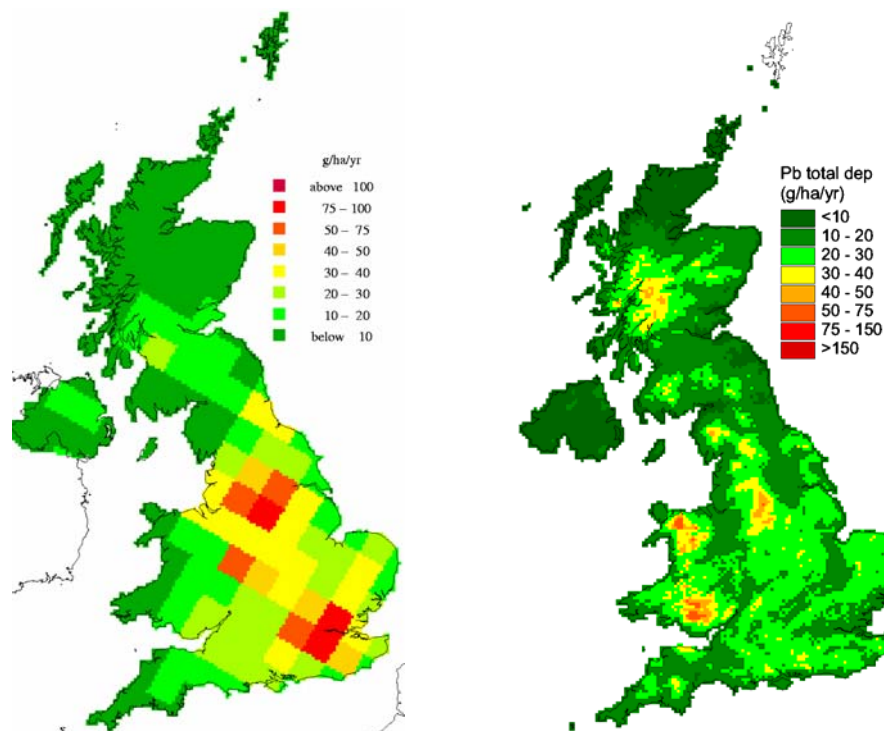


Figure 140: EMEP 1998 ($\text{g ha}^{-1} \text{yr}^{-1}$)

Figure 141: Monitoring Network 2004 ($\text{g ha}^{-1} \text{yr}^{-1}$)

Nickel (Ni)

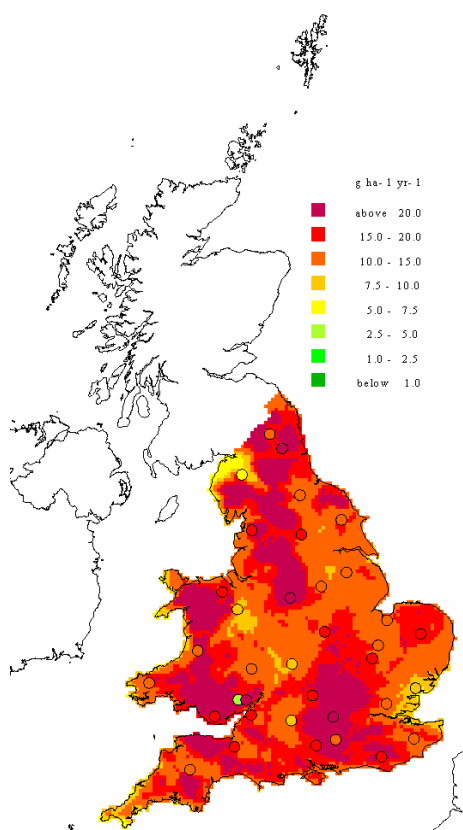


Figure 142: Frisbee Network 95-98 (g ha⁻¹ yr⁻¹)

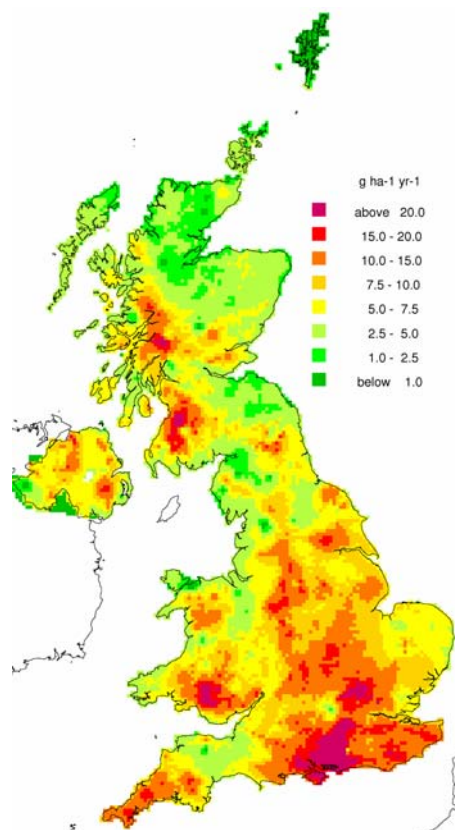


Figure 143: Moss Survey 2000, UK calib. (g ha⁻¹ yr⁻¹)

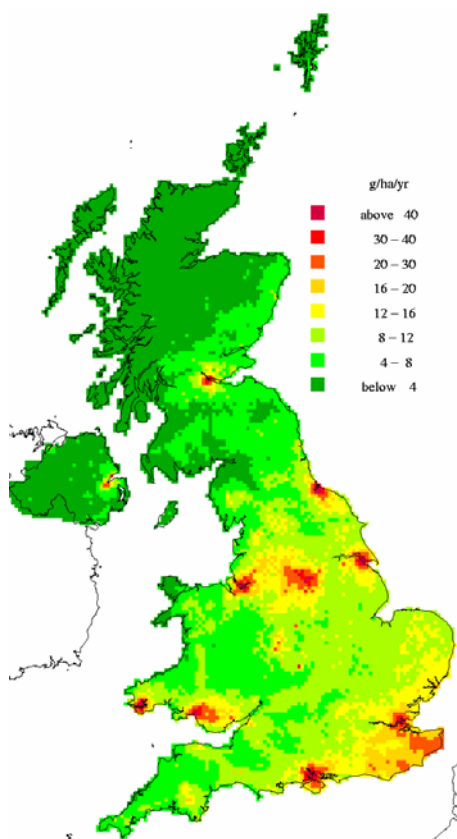


Figure 144: FRAME-HM (NAEI 1998) (g ha⁻¹ yr⁻¹)

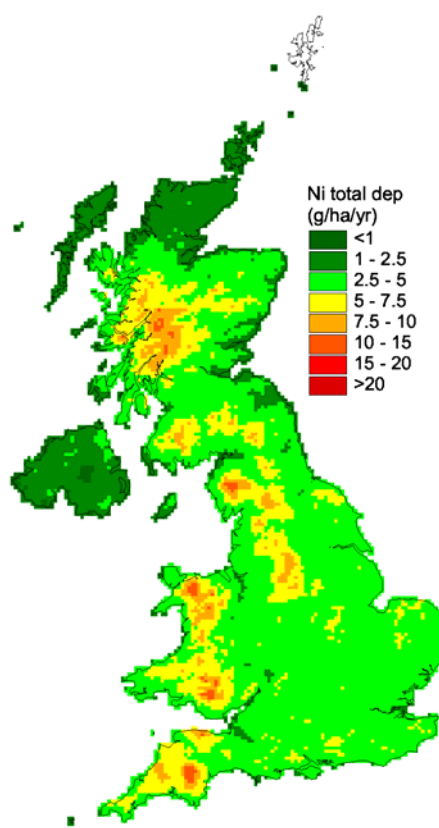


Figure 145: Monitoring Network 2004 (g ha⁻¹ yr⁻¹)

Selenium (Se)

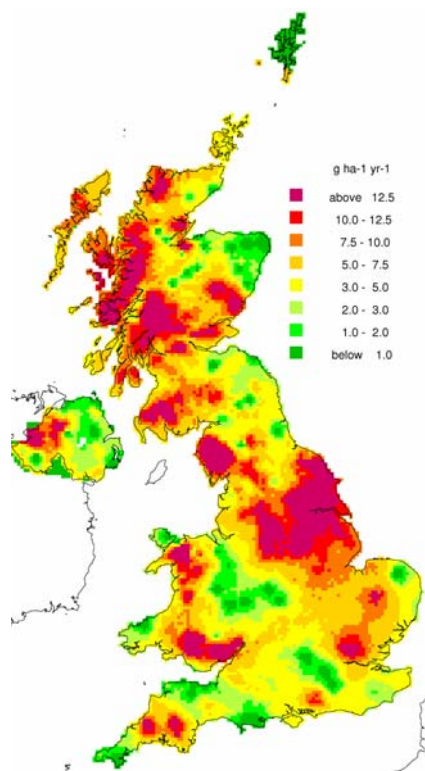


Figure 146: Moss Survey 2000, UK calibration ($\text{g ha}^{-1} \text{yr}^{-1}$)

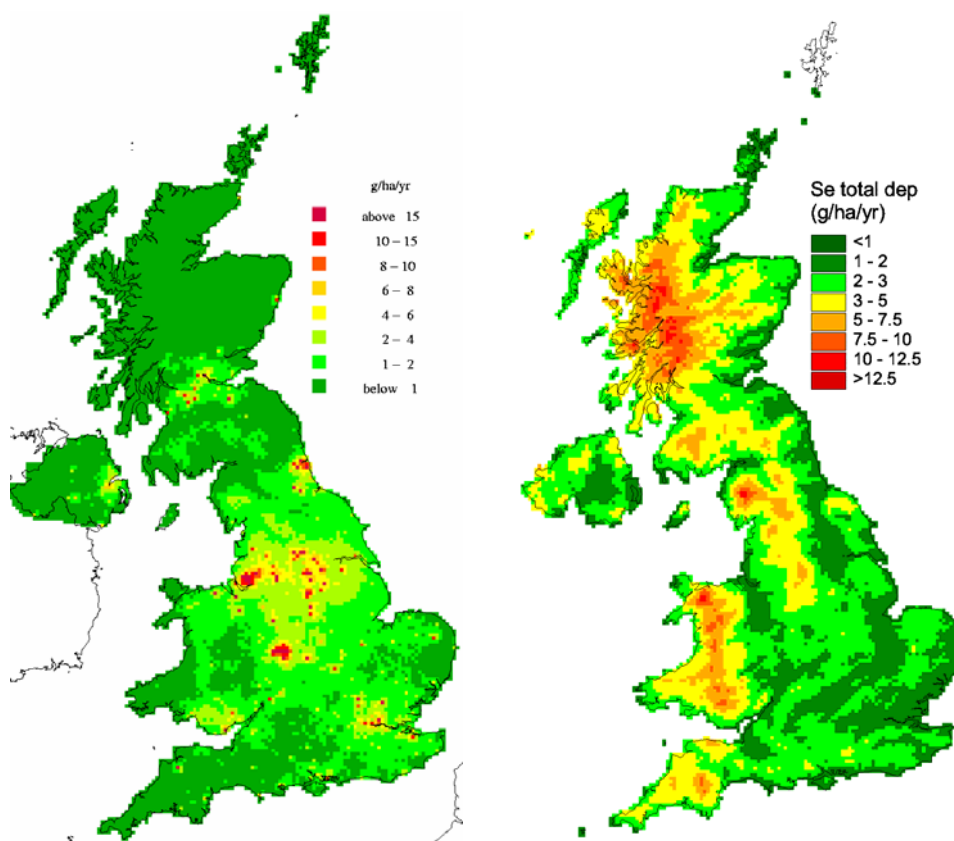


Figure 147: FRAME-HM (NAEI 1998) ($\text{g ha}^{-1} \text{yr}^{-1}$)

Figure 148: Monitoring Network 2004 ($\text{g ha}^{-1} \text{yr}^{-1}$)

Vanadium (V)

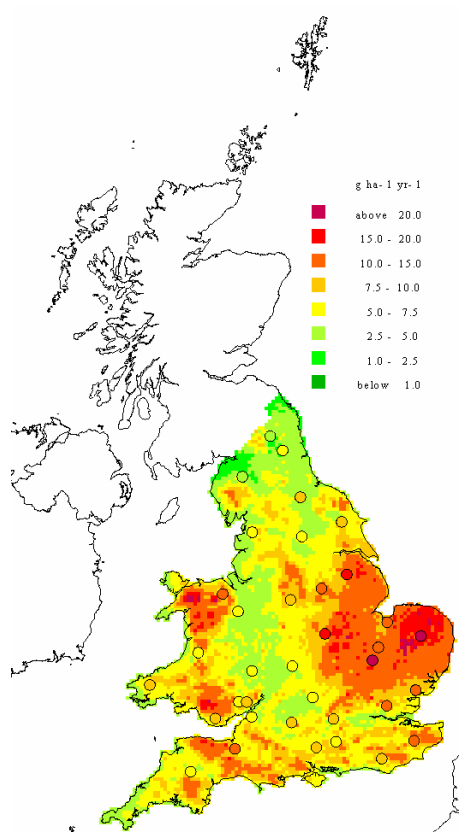


Figure 149: Frisbee Network 95-98 (g ha⁻¹ yr⁻¹)

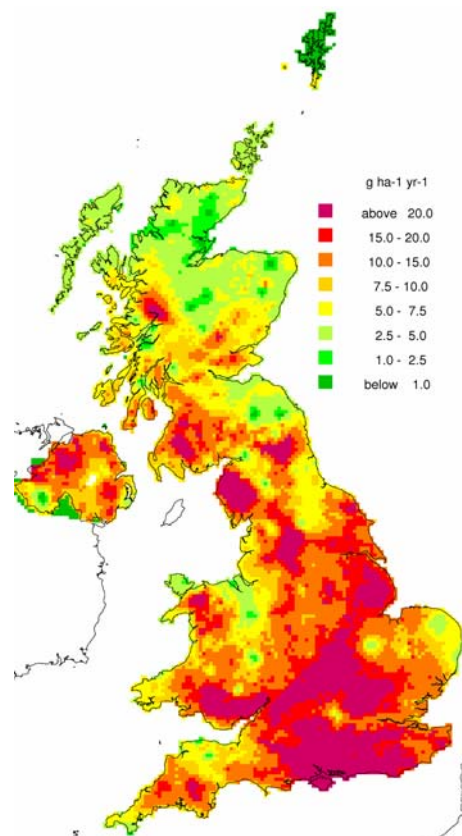


Figure 150: Moss Survey 2000, UK calib. (g ha⁻¹ yr⁻¹)

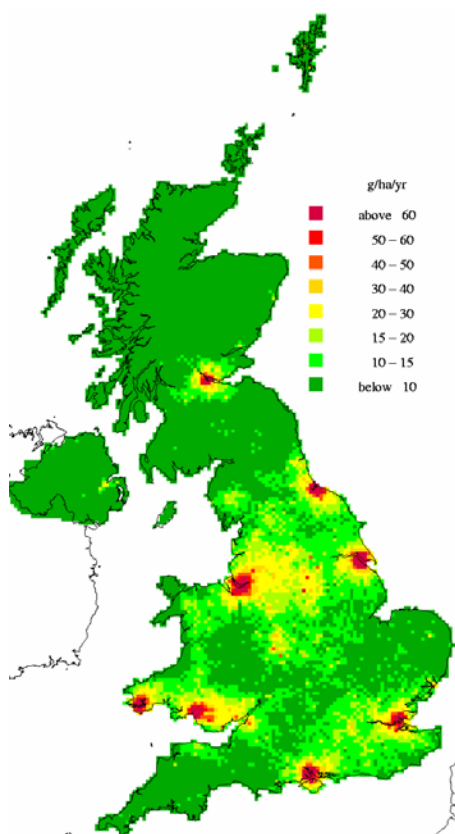


Figure 151: FRAME-HM (NAEI 1998) (g ha⁻¹ yr⁻¹)

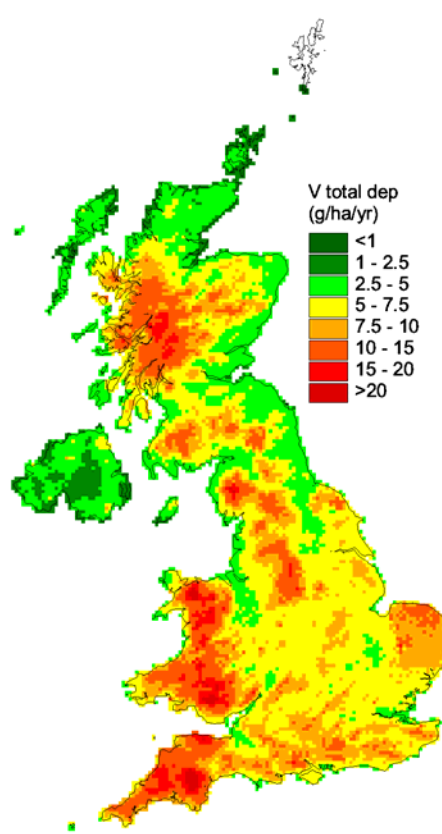


Figure 152: Monitoring Network 2004 (g ha⁻¹ yr⁻¹)

Zinc (Zn)

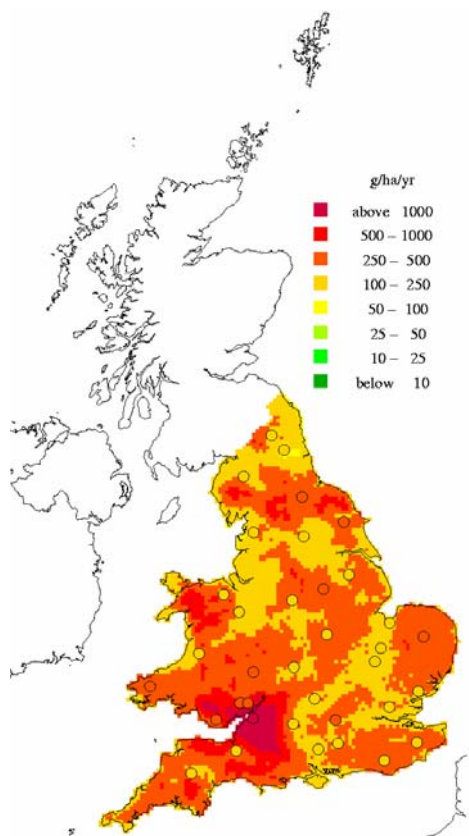


Figure 153: Frisbee Network 95-98 ($\text{g ha}^{-1} \text{yr}^{-1}$)

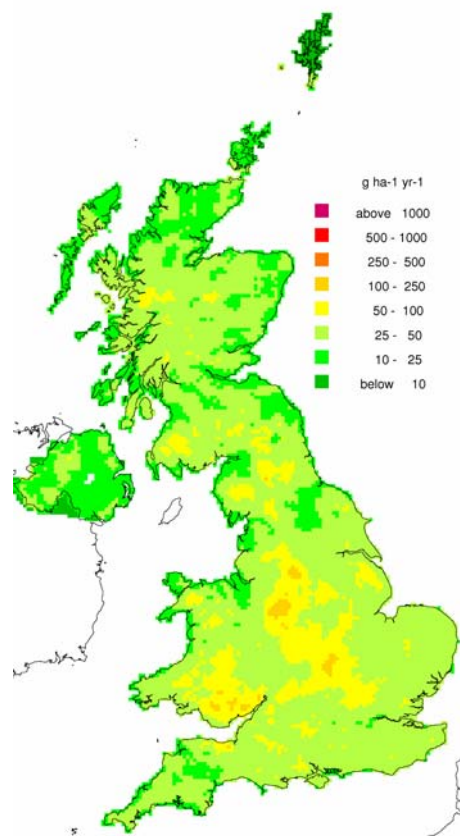


Figure 154: Moss Survey 2000, UK calib. ($\text{g ha}^{-1} \text{yr}^{-1}$)

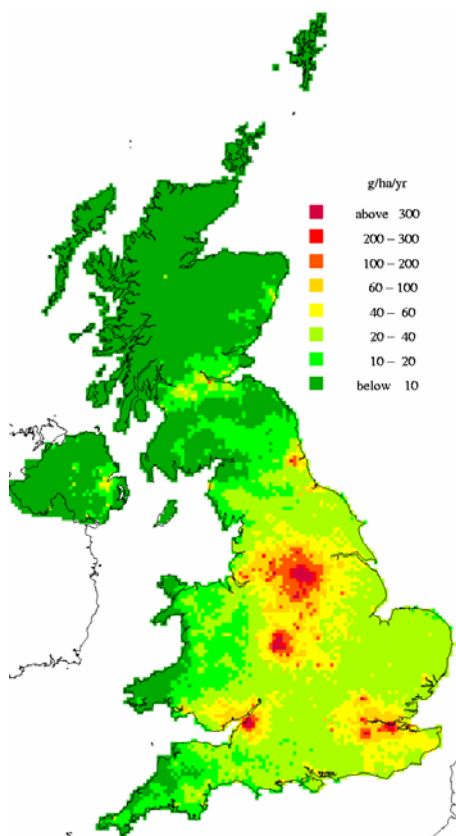


Figure 155: FRAME-HM (NAEI 1998) ($\text{g ha}^{-1} \text{yr}^{-1}$)

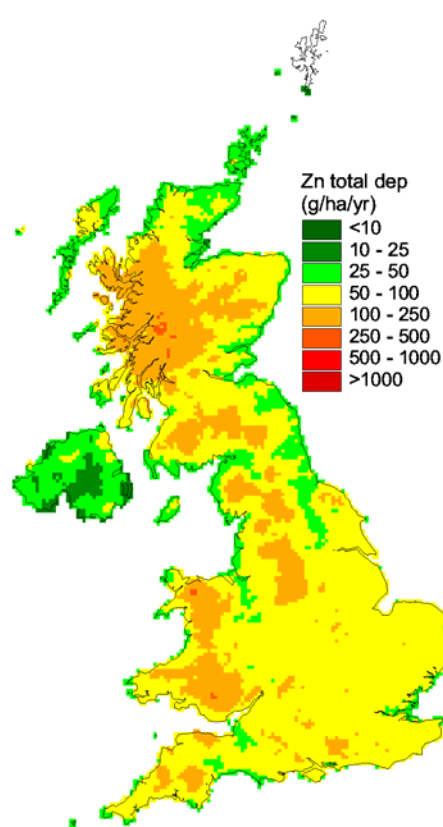


Figure 156: Monitoring Network 2004 ($\text{g ha}^{-1} \text{yr}^{-1}$)

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References

- Alloway, B.J. et al., (1998). The vulnerability of soils to pollution by heavy metals. Final project report to the UK Ministry of Agriculture, Fisheries and Food, Project OC 9325, University of Reading, Reading.
- Ashmore, M., Bell, S., Fowler, D., Hill, M., Jordan, C., Nemitz, E., Parry, S., Pugh, B., Reynolds, B., Williams, J. (2002) Survey of the UK metal content of mosses 2000. Part II of EPG 1/3/144 final contract report: development of a critical load methodology for toxic metals in soils and surface waters: stage II. University of Bradford, UK.
- Baker, S.J. 2001. Trace and major elements in the atmosphere at rural locations in the UK: summary of data for 1999. AEAT/R/ENV/0264 Issue 2, AEA Technology, NETCEN, Culham, Oxon, UK.
- Berg, T., Steinnes, E. (1997) Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitors of heavy metal deposition: from relative to absolute values, *Environ. Pollut.* 98, 61-71.
- Berg, T., Hjellbrekke, A., Rühling, Å., Steinnes, E., Kubin, E., Larsen, M.M., Piispanen, J. (2003) Absolute deposition maps of heavy metals for the Nordic countries based on the moss survey, *TemaNord* 2003:505, Nordic Council of Ministers, Copenhagen, Denmark.
- Dore, C. J., Watterson, J.D., Goodwin, J. W. L., Murrells, T.P., Passant, N.R., Hobson, M.M., Baggott, S.L., Thistlethwaite, G., Coleman, P.J., King, K.R., Adams, M.A., Cumine, P.R. (2004). UK Emissions of Air Pollutants 1970 to 2002. AEA Technology
- Fitzgerald, W. and Gill, G. (1979). Sub-Nanogram Determination of Mercury by 2-Stage Gold Amalgamation and Gas-Phase Detection Applied to Atmospheric Analysis. *Analytical Chemistry* 51 (11): 1714-1720
- Harmens, H., Buse, A., Büker, P., Norris, D., Mills, G., Williams, B., Reynolds, B., Ashenden, T.W., Rühling, Å., Steinnes, E. (2004). Heavy metal concentration in European mosses: 2000/2001 survey. *J. Atm. Chem.* 49, 425-436.
- Ilyin, I. et al., 2000. Heavy Metal Transboundary Air Pollution in Europe: Monitoring and Modelling Results for 1997 and 1998. EMEP Report 3/2000, EMEP/Meteorological Synthesizing Centre - East, Moscow.
- Ilyin, I. et al., (2005). Heavy Metals: Transboundary of the Environment. EMEP Status Report 2/2005, EMEP/Meteorological Synthesizing Centre - East, Moscow/ Chemical Co-ordinating Centre, Norway.
- Lee, D. et al., (1998). Gas-phase mercury in the atmosphere of the United Kingdom. *Atmospheric Environment* 32 (5): 855-864
- Nemitz, E., Fowler, D., McDonald, A.G., Gallagher, M.W., Dorsey, J., Harrison, R.M. and Allen, A.G. (2000). Development of critical loads methodologies for toxic metals in soils and surface waters – estimation of the UK deposition fields of Cd, Pb, Cu, Zn. *Environmental Diagnostics GST/03/1709 – Final Report.*
- Nemitz, E., McDonald, A.G., Alloway, B.J., Reynolds, B., Williams J.G., Parry, S., Ashmore, M.R. and Fowler, D. (2006). Comparison of three methods to derive high spatial resolution maps of trace metal deposition to the UK. (in press)
- Playford, K. and Baker, S.J. (2000). Atmospheric input of heavy metals to the North Sea: results for 1999, AEA Technology, NETCEN, Culham, Oxon, UK.
- Rolph, G.D. (2003). Real-time Environmental Applications and Display sYstem (READY) Website (<http://www.arl.noaa.gov/ready/hysplit4.html>). NOAA Air Resources Laboratory, Silver Spring, MD.
- Steinnes, E., Rühling, Å., Lippo, H., Mäkinen, A. (1997) Reference material for large-scale metal deposition surveys, *Accred. Qual. Assur.* 2, 243-249.

Vincent, K. and Passant, N. (2006). Assessment of Heavy Metal Concentrations in the United Kingdom. Report to the Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Executive and the Department of the Environment for Northern Ireland. AEAT/ENV/R/2013/Issue 1, AEA Technology.

Appendix 1

The series of Charts on the following pages present the concentrations in rainfall and the wet deposition for the heavy metal elements Ni, Se, Zn, Cd, Cu, Pb, As, Cr, and V at all 15 sites for 2004 and 2005.

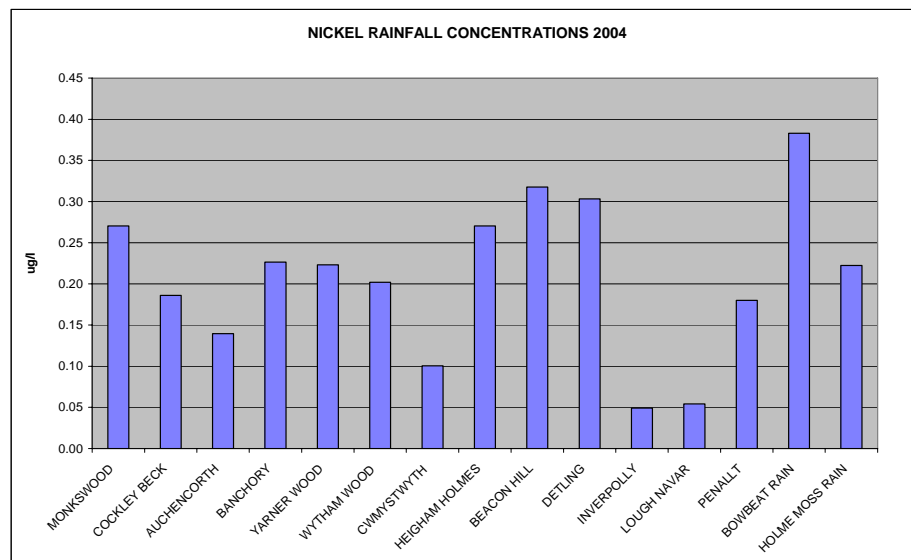


Figure 157 Nickel concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

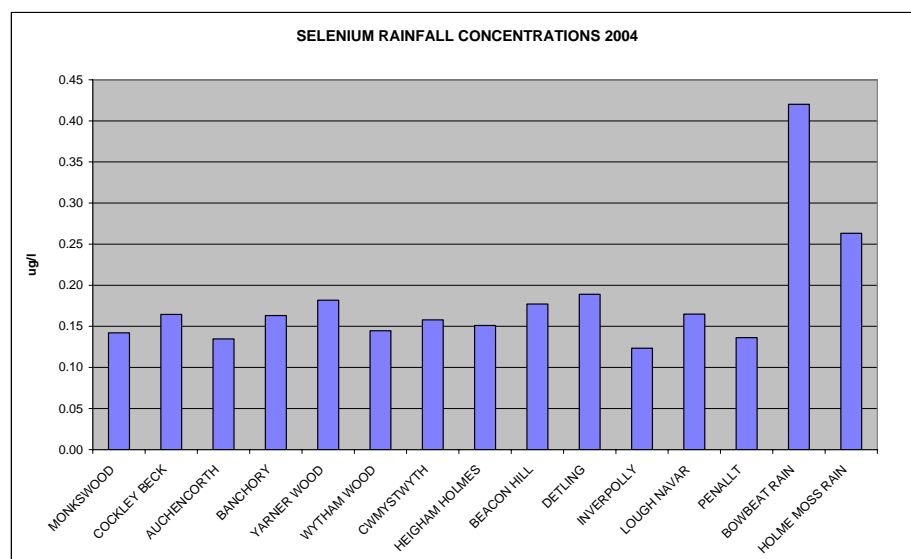


Figure 158 Selenium concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

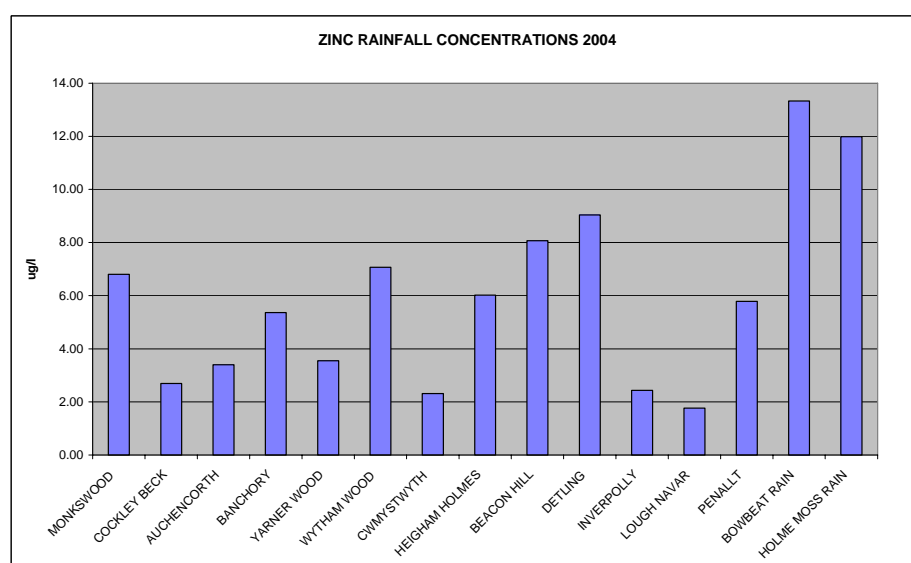


Figure 159 Zinc concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

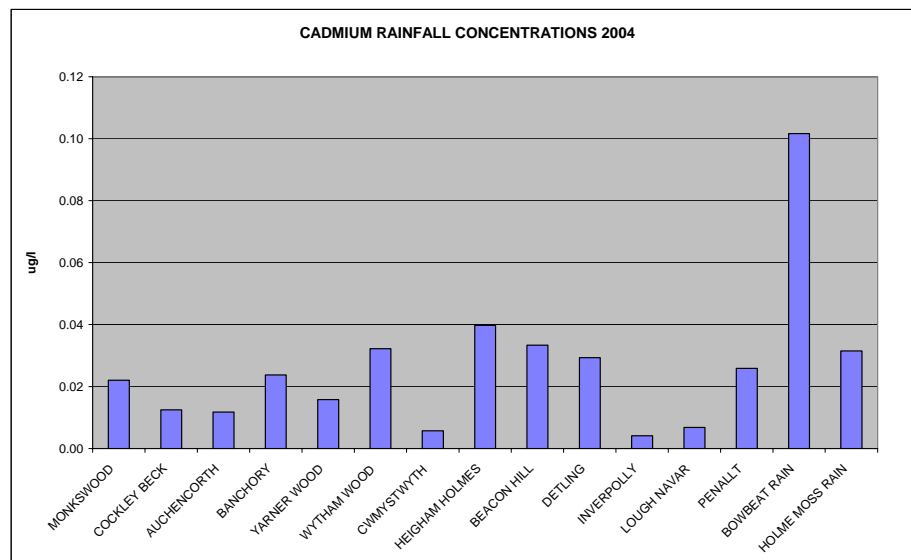


Figure 160 Cadmium concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

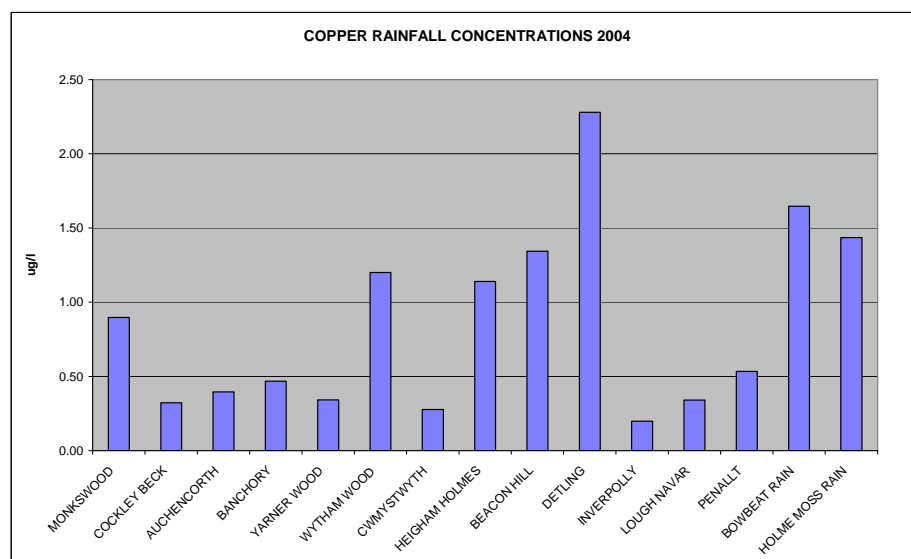


Figure 161 Copper concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

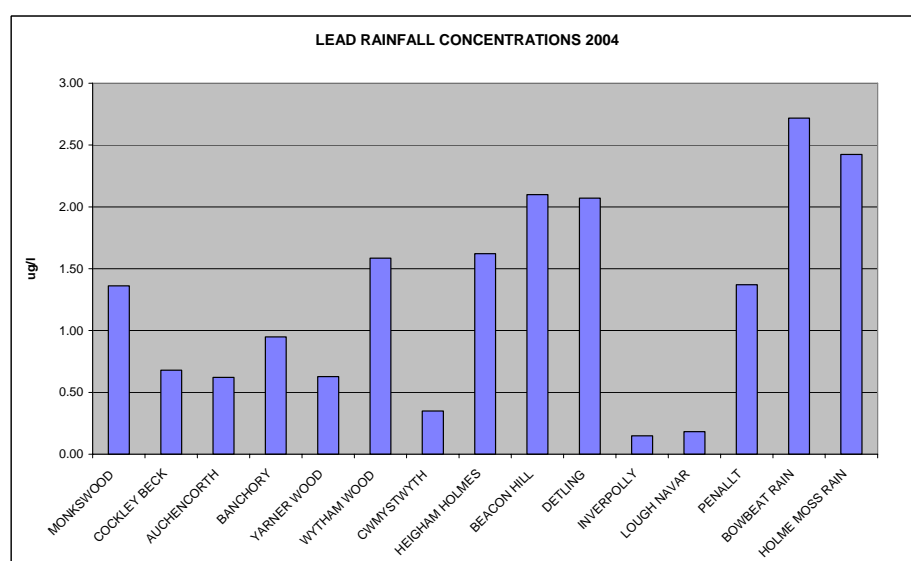


Figure 162 Lead concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

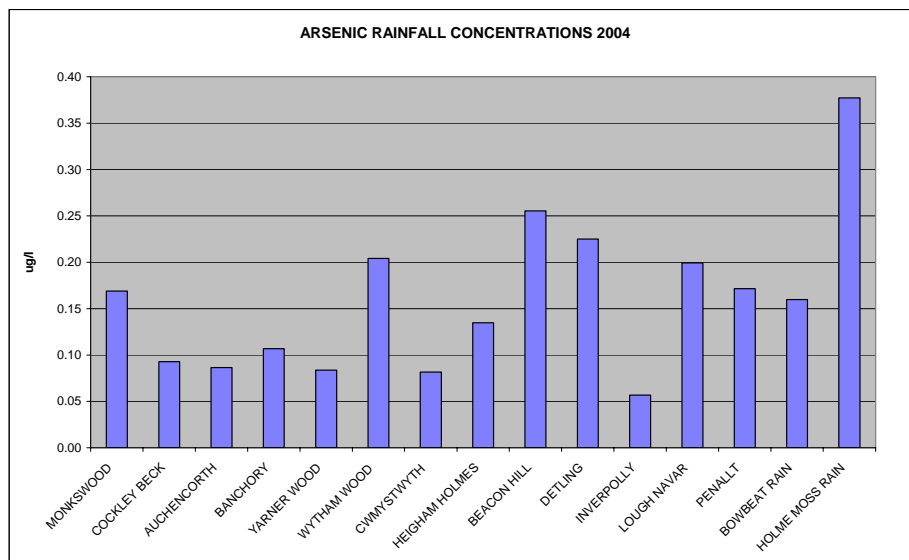


Figure 163 Arsenic concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

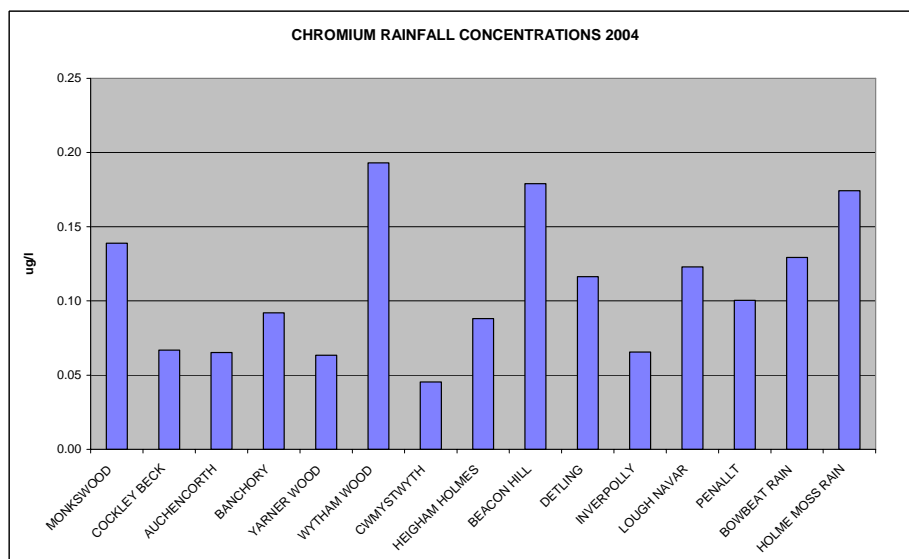


Figure 164 Chromium concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

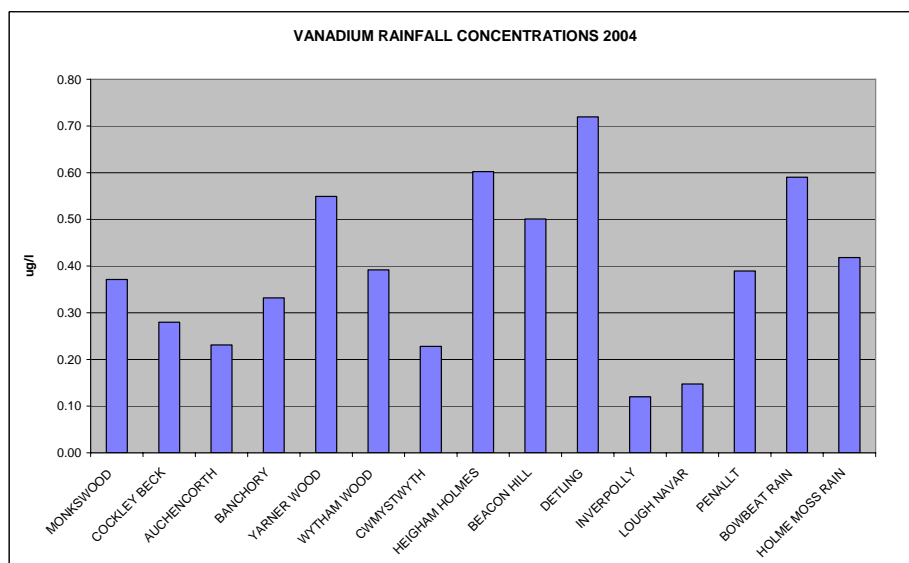


Figure 165 Vanadium concentrations in rainfall for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

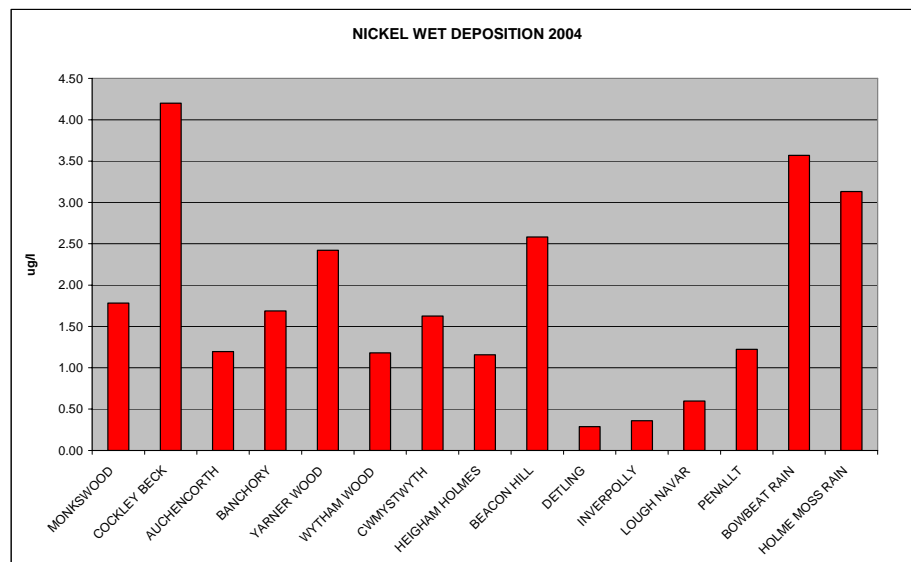


Figure 166 Nickel Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

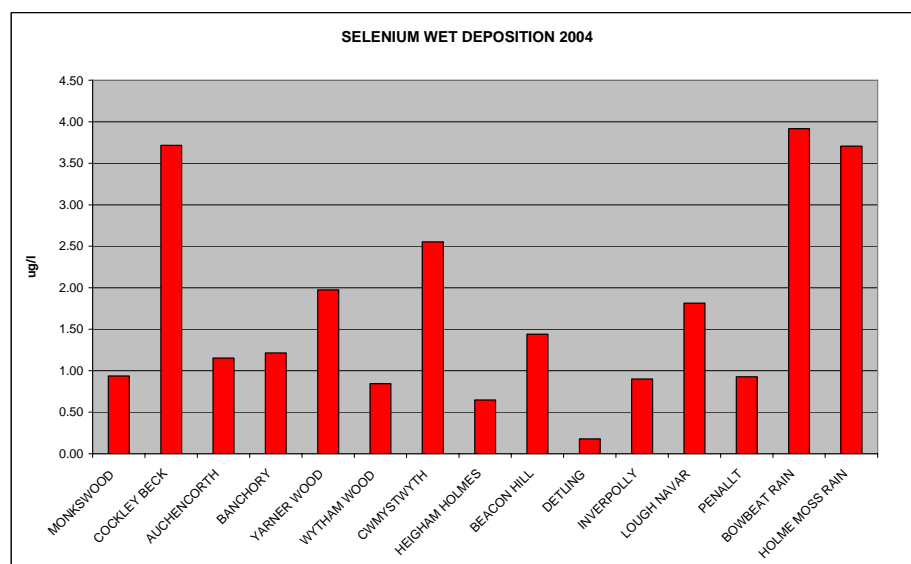


Figure 167 Selenium Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

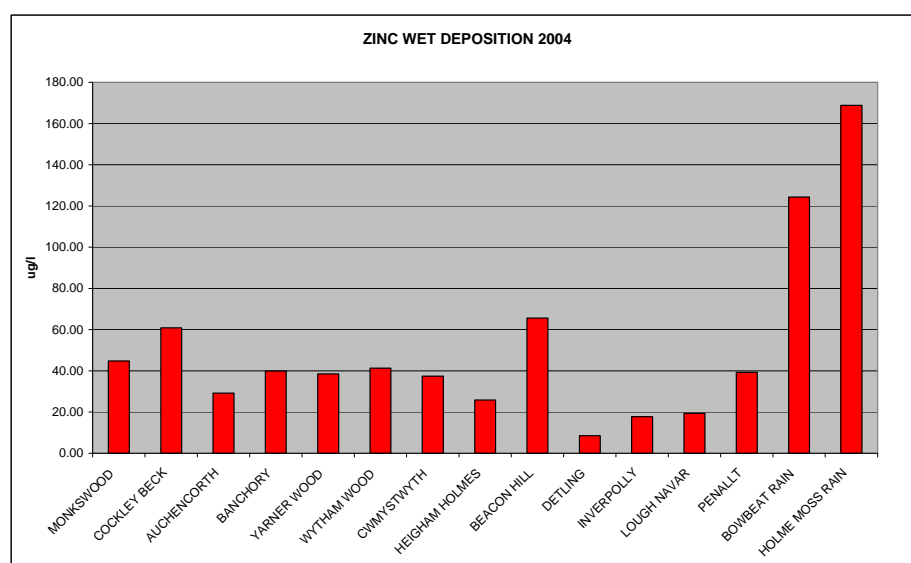


Figure 168 Zinc Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

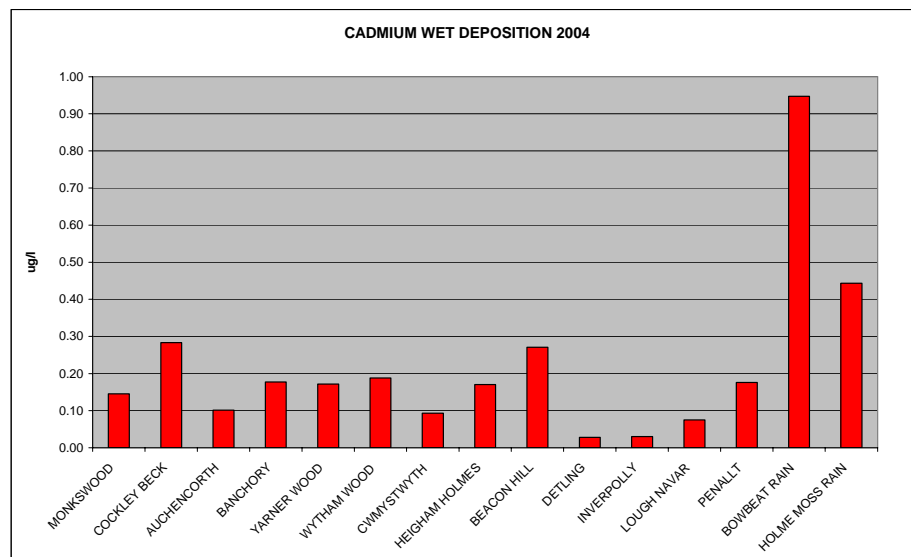


Figure 169 Cadmium Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

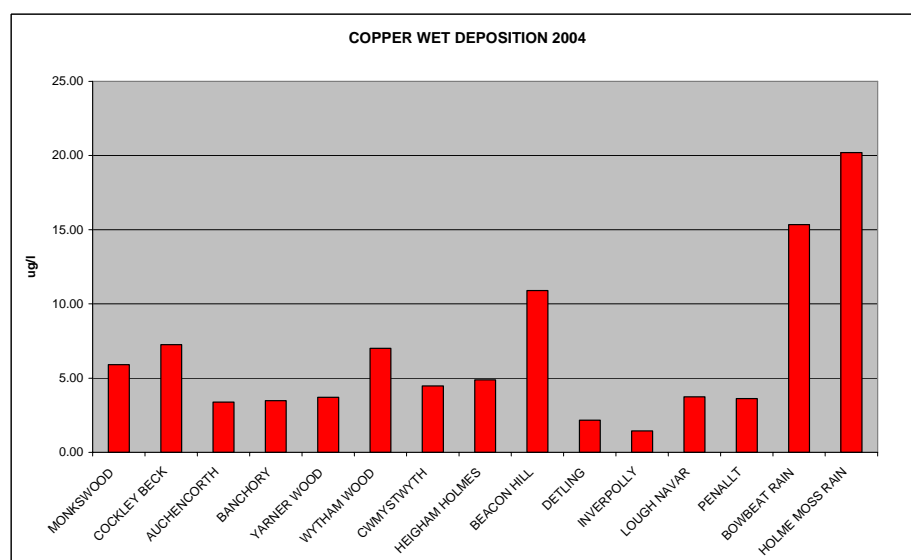


Figure 170 Copper Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

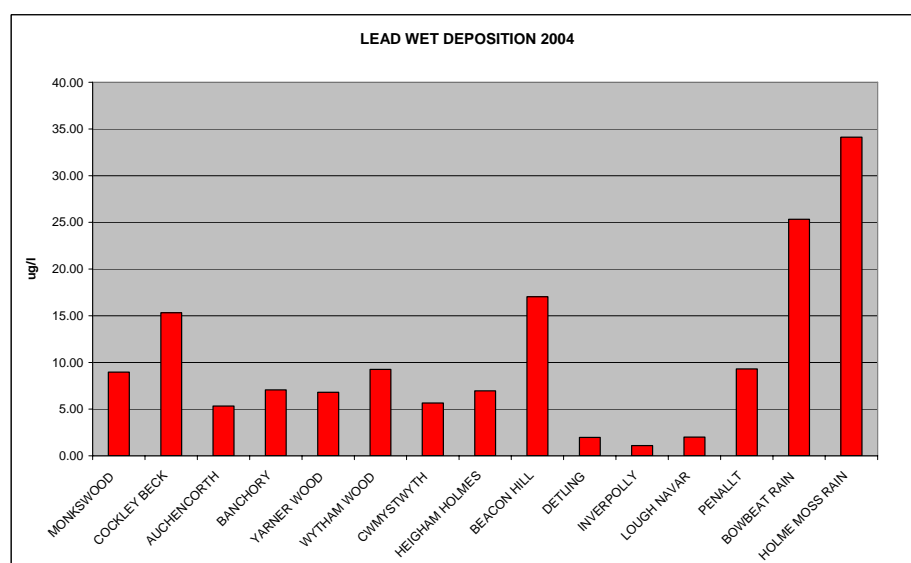


Figure 171 Lead Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

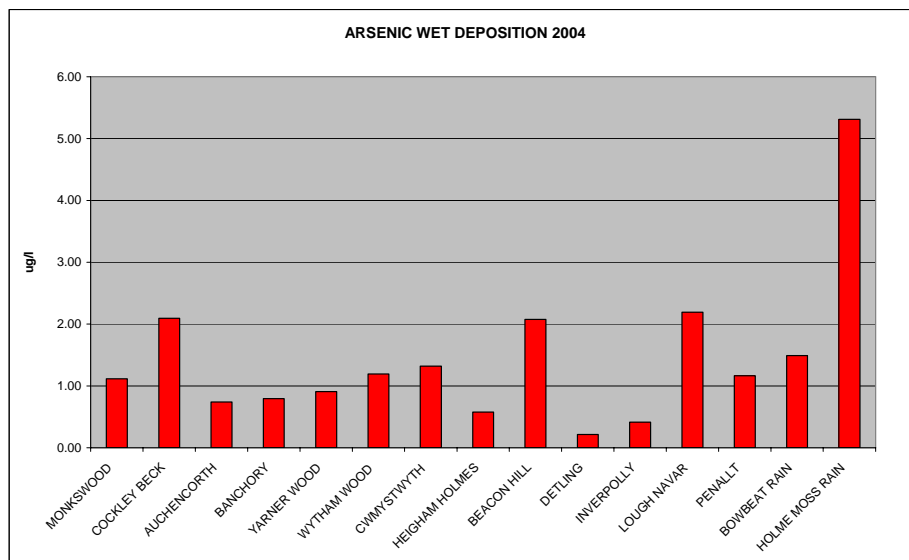


Figure 172 Arsenic Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

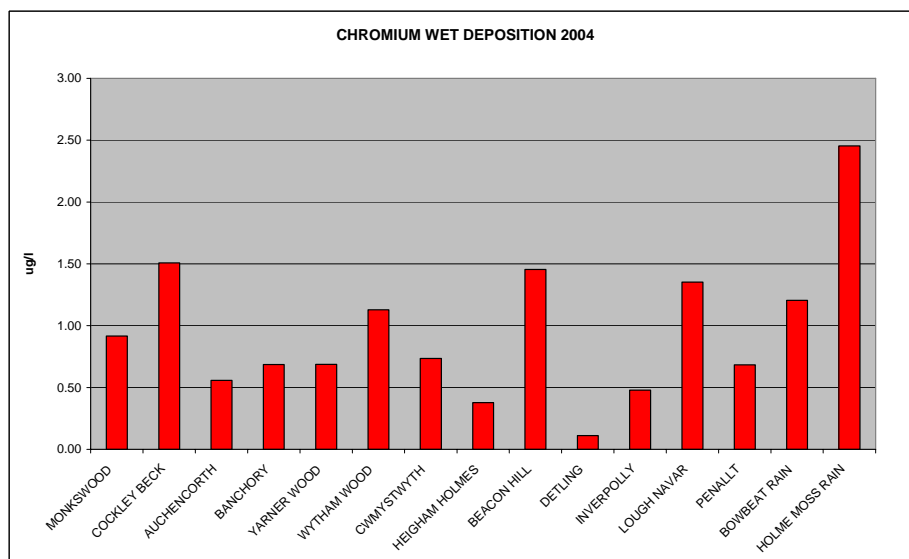


Figure 173 Chromium Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

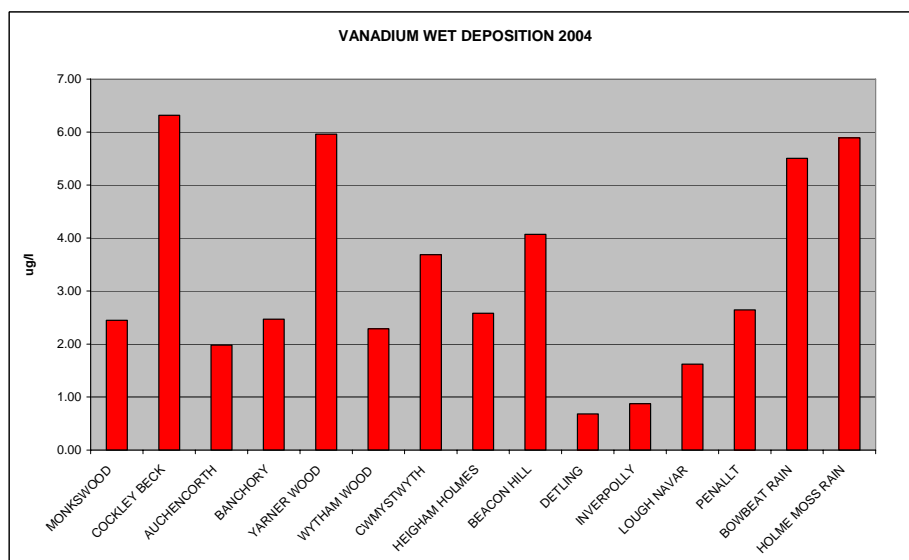


Figure 174 Vanadium Wet Deposition for 2004 at all 15 monitoring sites in the Heavy Metal Rural Network.

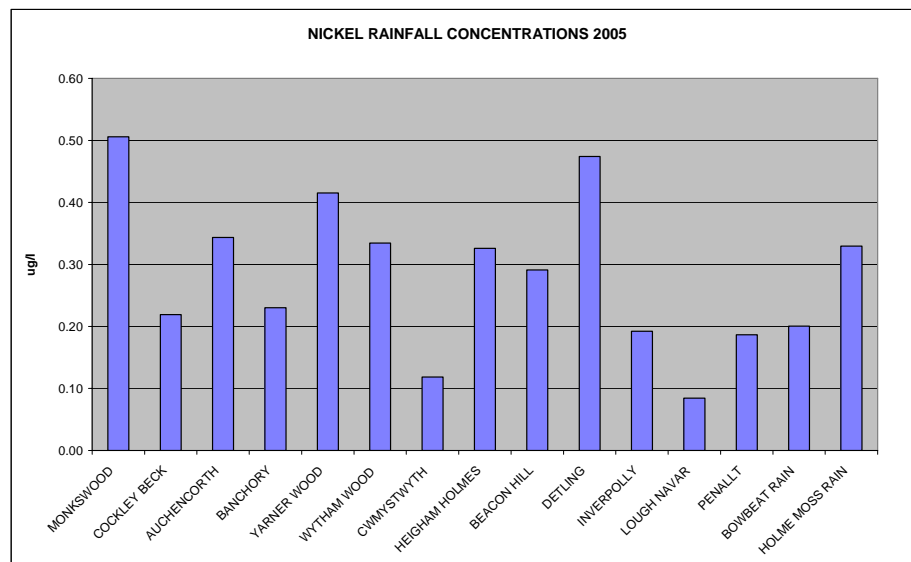


Figure 175 Nickel concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

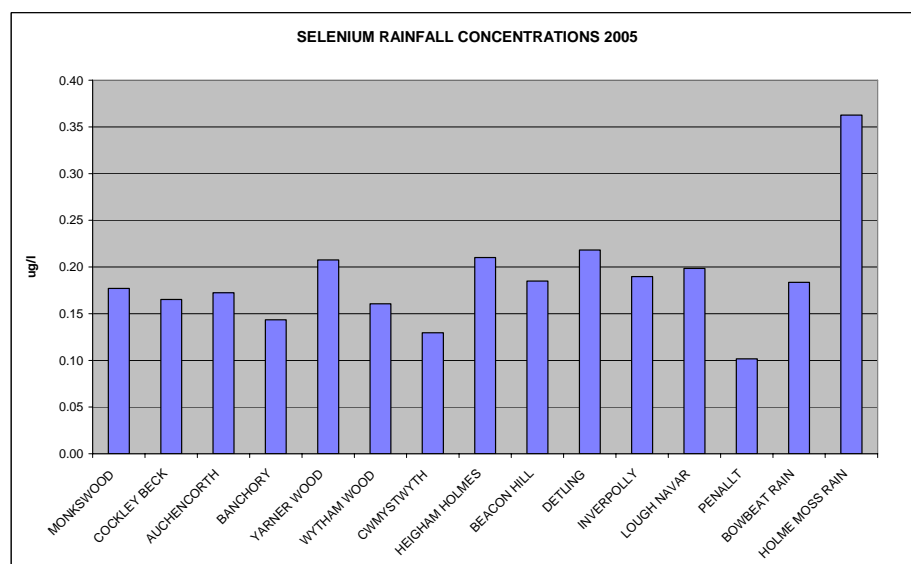


Figure 176 Selenium concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

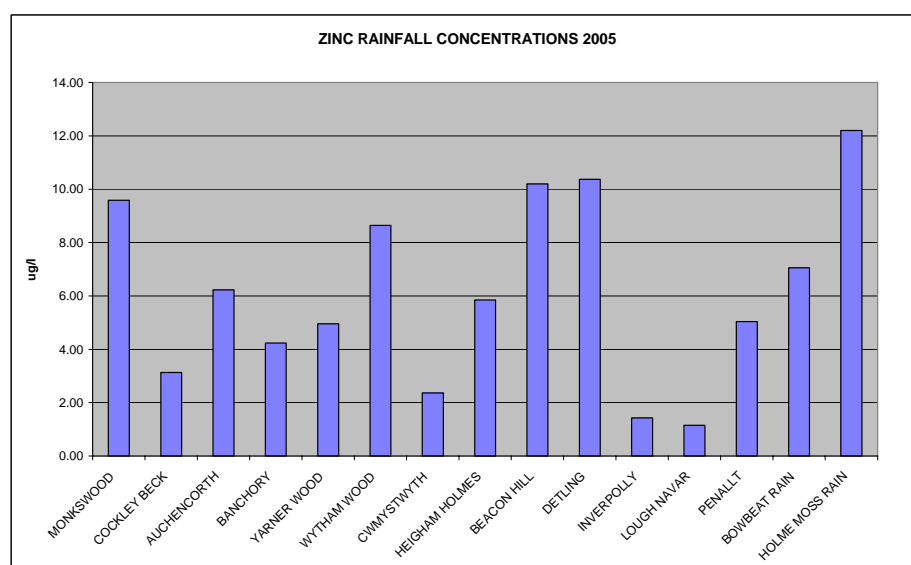


Figure 177 Zinc concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

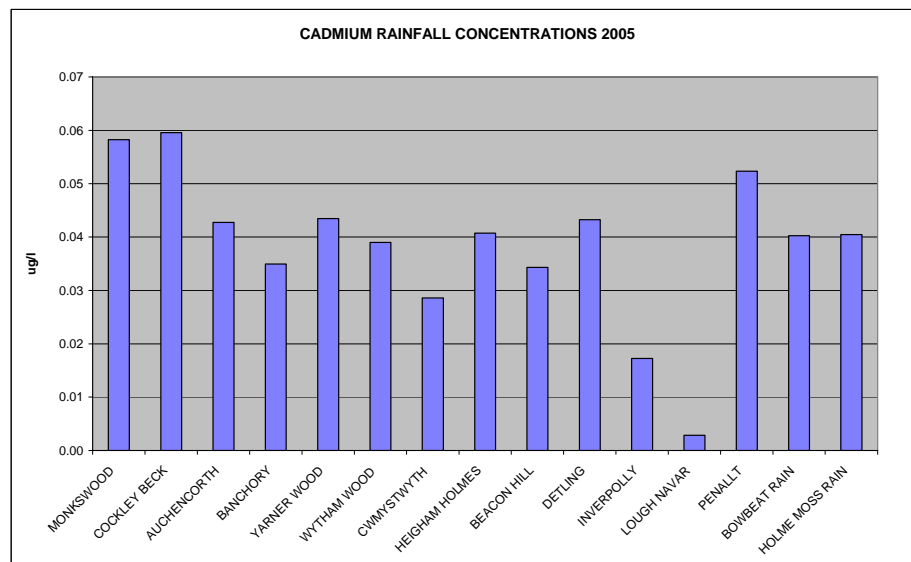


Figure 178 Cadmium concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

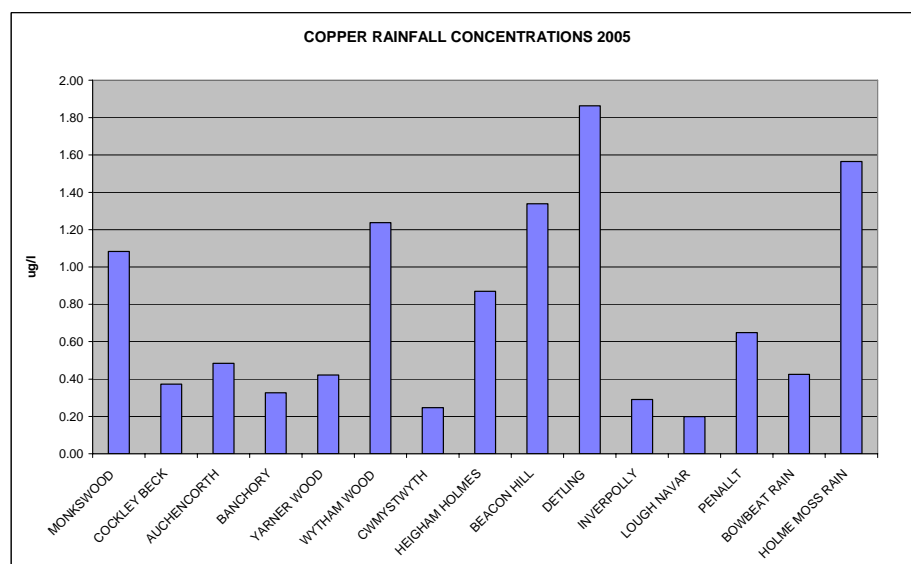


Figure 179 Copper concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

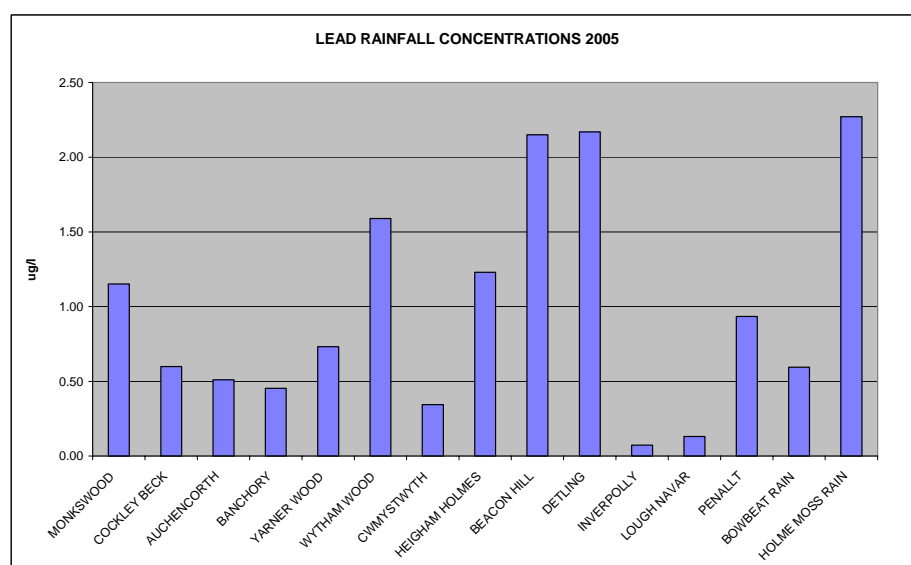


Figure 180 Lead concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

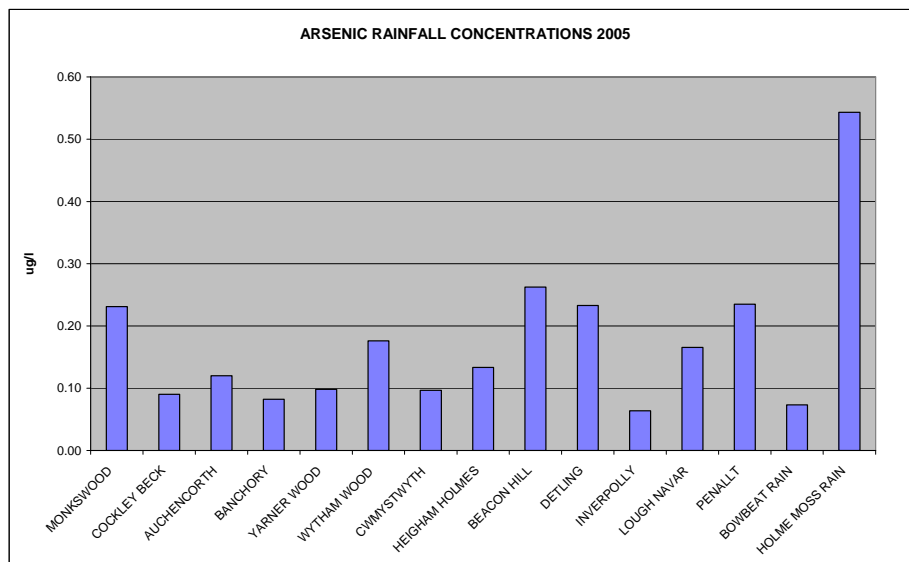


Figure 181 Arsenic concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

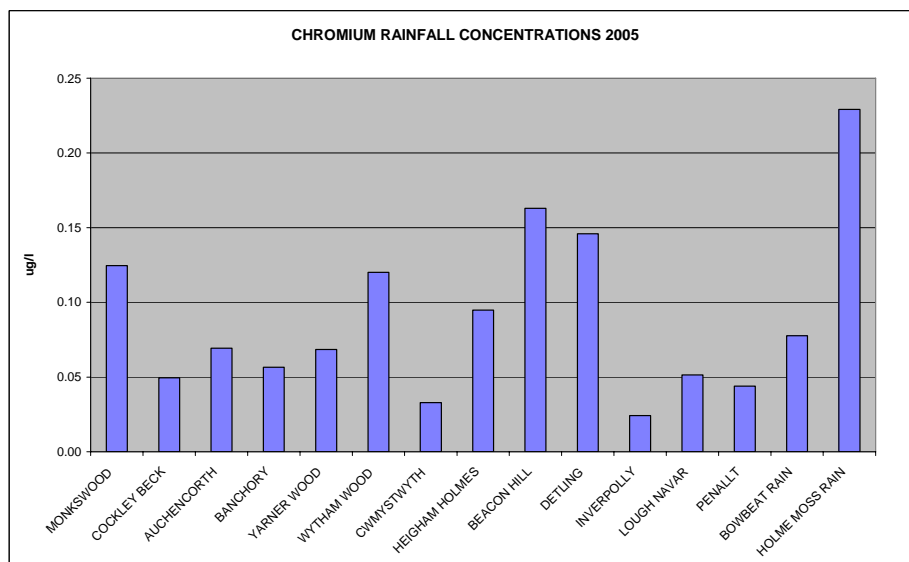


Figure 182 Chromium concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

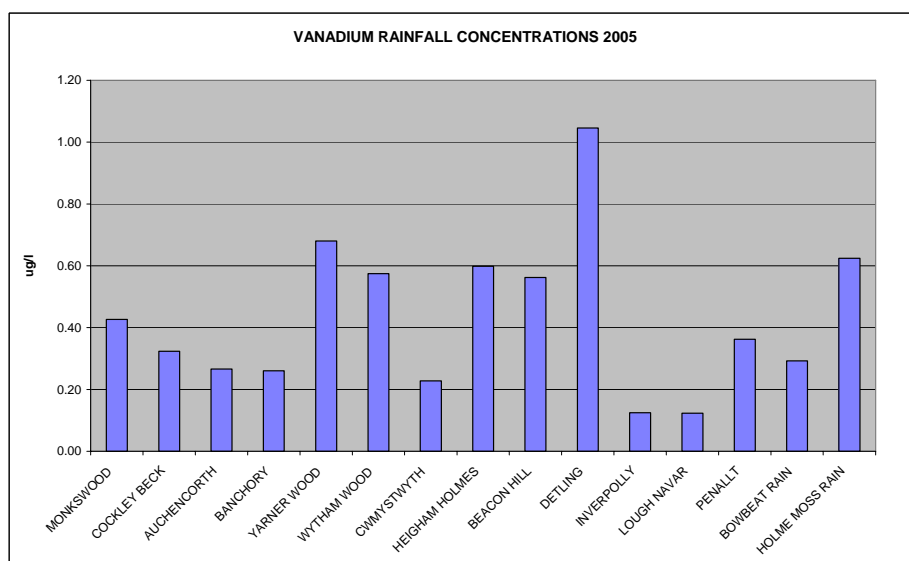


Figure 183 Vanadium concentrations in rainfall for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

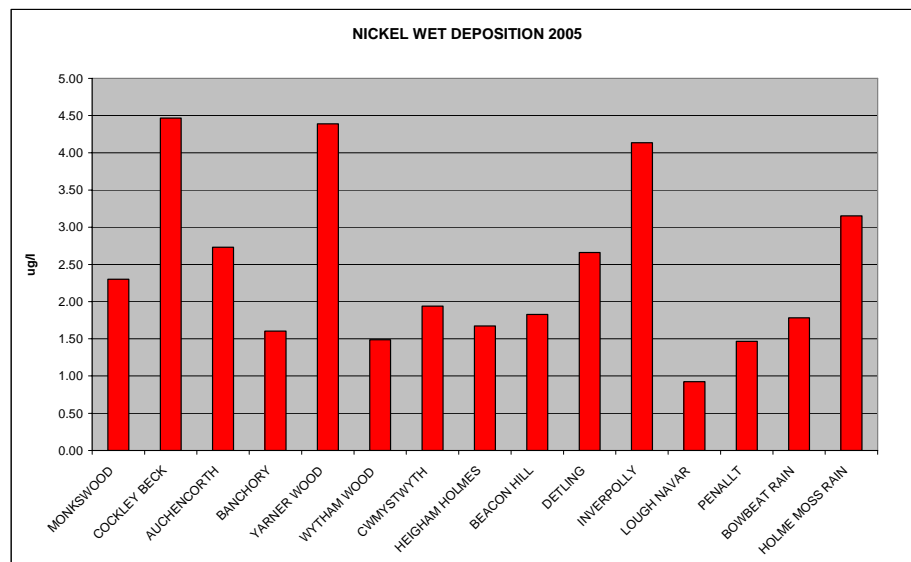


Figure 184 Nickel Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

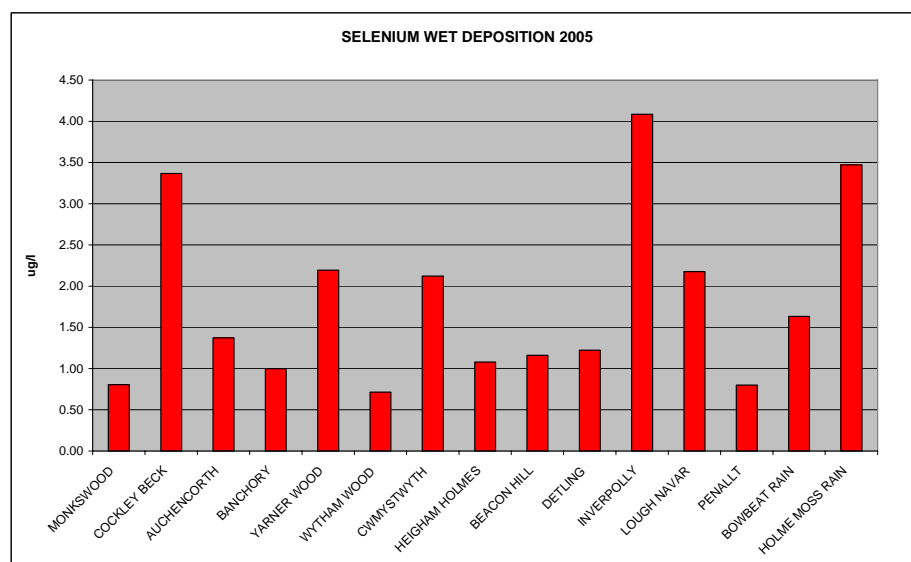


Figure 185 Selenium Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

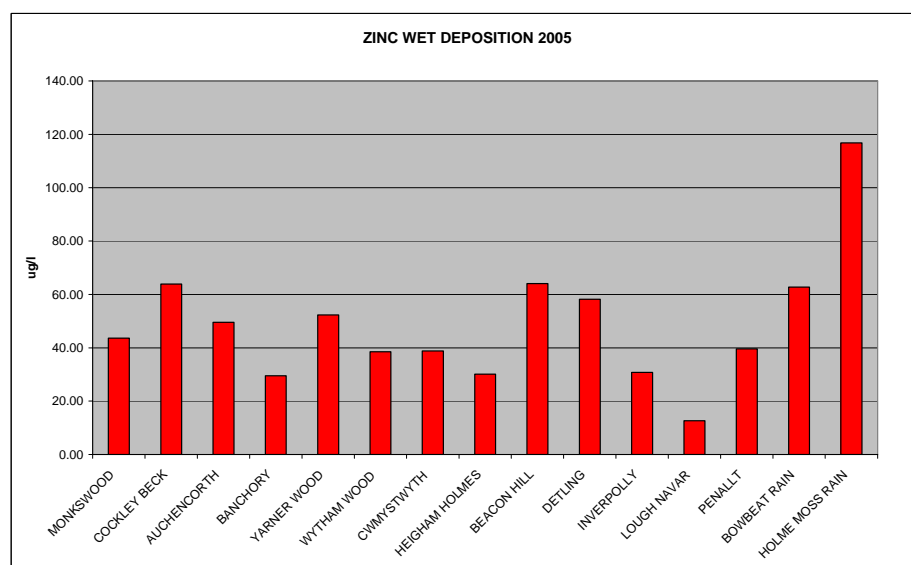


Figure 186 Zinc Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

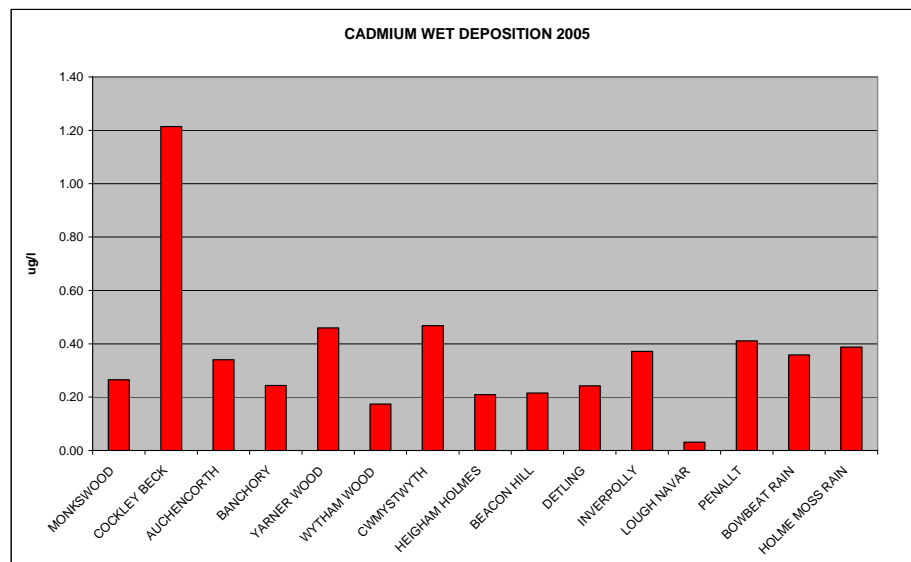


Figure 187 Cadmium Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

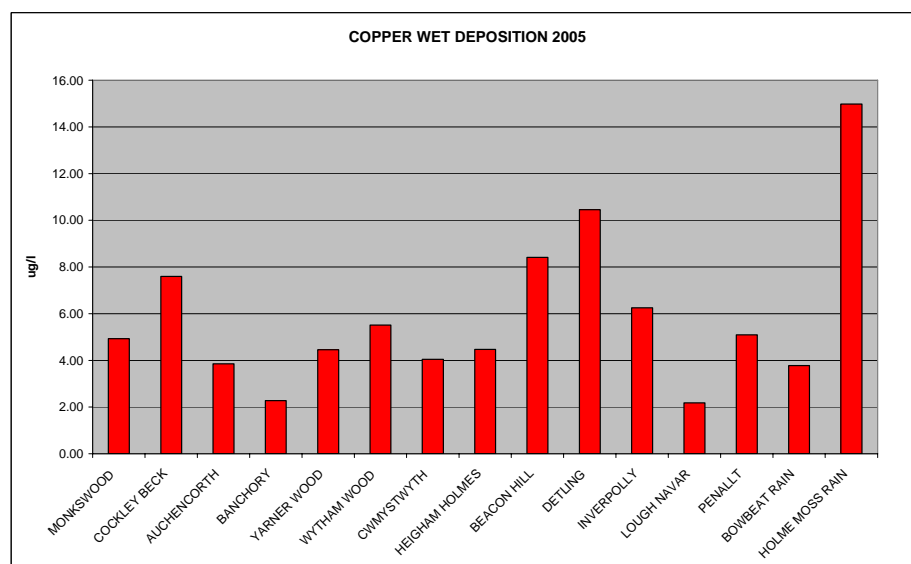


Figure 188 Copper Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

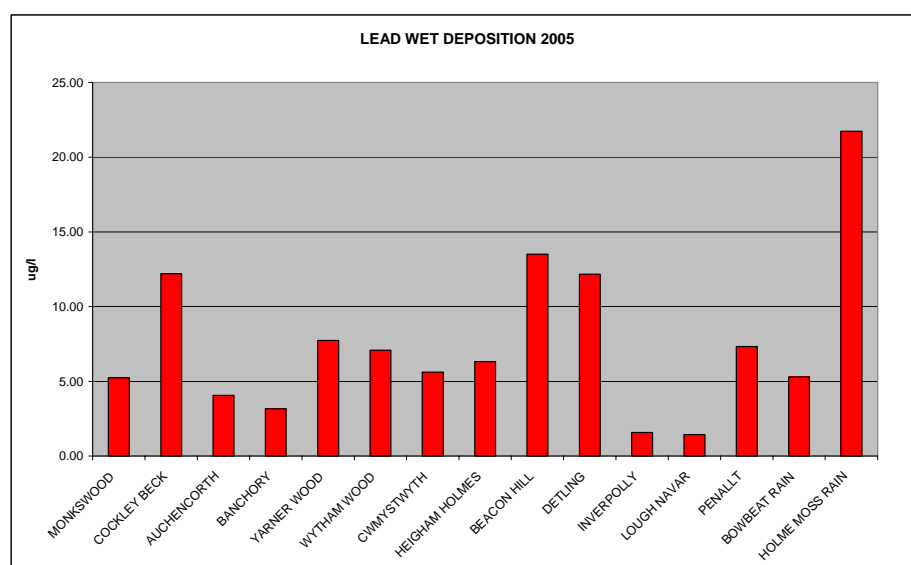


Figure 189 Lead Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

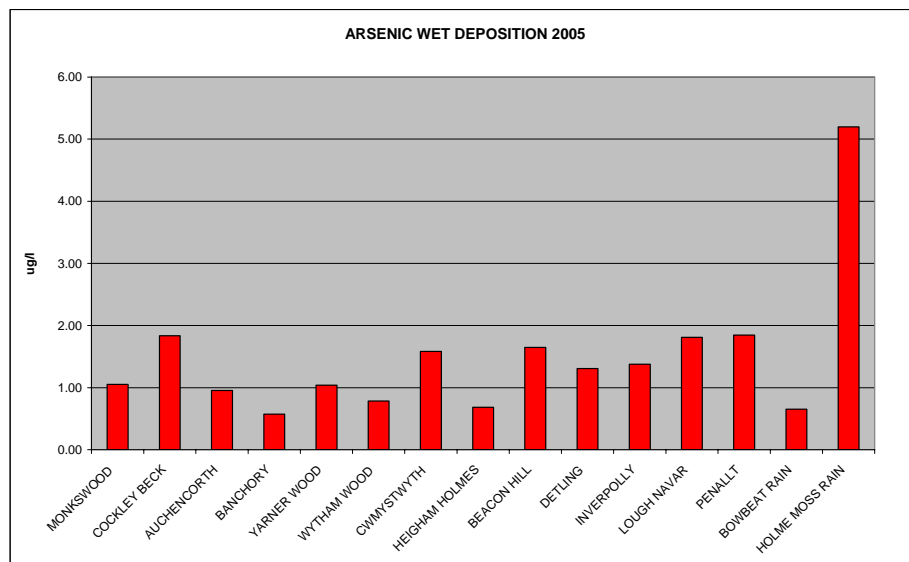


Figure 190 Arsenic Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

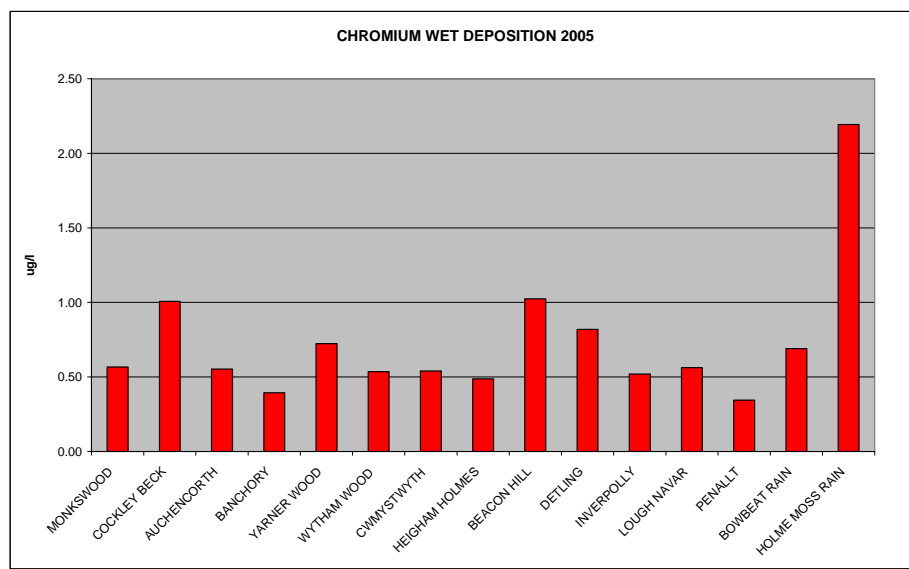


Figure 191 Chromium Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

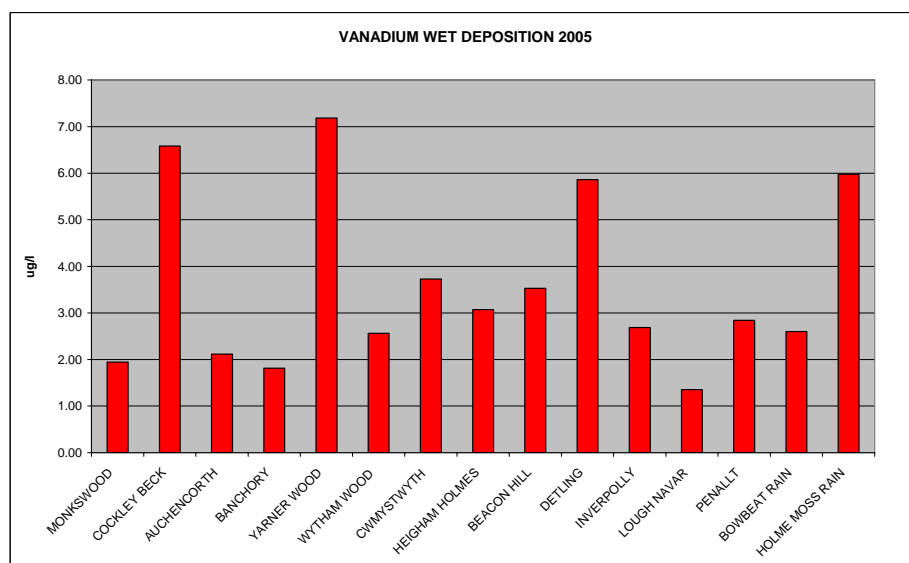


Figure 192 Vanadium Wet Deposition for 2005 at all 15 monitoring sites in the Heavy Metal Rural Network.

Table 24 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in rainwater for 2004 at Bowbeat. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2004 BOWBEAT HEAVY METAL CONCENTRATIONS IN RAINWATER $\mu\text{g/l}$																						
DATE						07/01	04/02	03/03	07/04	12/05	02/06	23/06	28/07			02/09	09/11	08/12				
volume (ml)						931	459	1305	1262	570	1247	1090	2235	-	-	3936	604	1640				MEAN v.w. 2xStDev
Li						0.02	0.06	0.03	0.02	0.05	0.01	0.11	0.26	-	-	-	-	-				0.04
Be						0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-	-	-				0.00
Al						2.53	29.77	9.57	12.15	38.26	7.65	33.80	26.20	-	-	2.89	2.98	124.00				13.47
Sc						0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	-	-	0.03	0.03	0.03				0.03
Ti						0.02	0.54	0.28	0.53	0.95	0.19	1.64	1.05	-	-	0.11	0.05	1.40				0.59
V						0.21	0.54	0.36	0.49	0.64	0.36	1.18	1.49	-	-	0.24	0.25	9.40				0.59
Cr						0.10	0.08	0.02	0.06	0.16	0.02	0.26	0.37	-	-	0.06	0.09	1.50				0.13
Mn						0.25	1.52	1.20	1.84	4.33	1.03	8.85	7.44	-	-	0.46	0.49	13.00				2.71
Fe						3.41	21.54	12.89	17.24	72.34	10.40	64.20	44.30	-	-	6.47	7.38	146.00				22.34
Co						0.01	0.05	0.02	0.02	0.08	0.02	0.10	0.08	-	-	0.01	0.01	0.51				0.04
Ni						0.09	0.19	0.13	0.20	1.05	0.18	1.10	0.97	-	-	0.09	0.13	9.40				0.38
Cu						0.28	0.36	0.57	0.56	247.27	0.35	2.67	2.21	-	-	0.27	0.34	7.80				1.65
Zn						9.93	5.34	10.29	4.35	350.50	3.35	11.20	11.40	-	-	3.90	19.00	59.00				13.33
As						0.08	0.11	0.11	0.11	0.23	0.05	0.32	0.39	-	-	0.08	0.09	1.60				0.16
Se						0.22	0.25	0.18	0.32	0.32	0.11	1.10	1.19	-	-	0.11	0.27	2.90				0.42
Rb						0.03	0.07	0.06	0.08	0.14	0.04	0.56	0.39	-	-	0.03	0.05	1.05				0.15
Sr						1.14	2.04	1.29	0.79	1.52	0.43	7.76	13.20	-	-	0.93	2.20	29.00				3.59
Mo						0.02	0.02	0.05	0.02	0.06	0.02	0.17	0.37	-	-	0.02	0.02	0.60				0.09
Cd						0.01	0.02	0.05	0.04	0.09	0.18	0.16	0.22	-	-	0.08	0.01	0.43				0.10
Sn						0.03	0.03	0.05	0.08	3.00	0.01	0.16	0.12	-	-	0.05	0.01	0.35				0.10
Sb						0.04	0.06	0.10	0.10	0.22	0.04	0.32	0.35	-	-	0.08	0.06	1.83				0.15
Cs						0.00	0.00	0.01	0.01	0.01	0.00	0.00	0.00	-	-	0.01	0.00	0.07				0.00
Ba						0.26	0.97	0.65	0.77	2.04	0.46	6.54	7.70	-	-	0.34	0.36	8.50				2.88
W						0.01	0.01	0.01	0.01	0.01	0.01	0.04	0.02	-	-	0.01	0.01	0.07				0.01
Pb						0.59	0.71	1.14	1.23	78.23	0.63	2.08	1.74	-	-	0.65	0.53	16.00				2.72
U						0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-	-	-				0.00

Table 25 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in cloudwater for 2004 at Bowbeat. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2004 BOWBEAT HEAVY METAL CONCENTRATIONS IN CLOUDWATER $\mu\text{g/l}$																						
DATE				07/01	21/01	04/02	18/02	03/03	17/03	21/04	12/05	02/06	23/06	15/07	28/07	02/09	22/09	09/11	24/11			
volume (ml)				6020	3436	3159	698	903	4287	5821	1712	5803	5041	1900	2680	2839	5781	5613	2831			MEAN v.w. 2xStDev
Li				0.16	0.29	0.54	1.09	0.53	0.37	0.17	0.27	0.10	0.09	0.00	0.00	-	-	-	-			0.20
Be				0.00	0.00	0.03	0.04	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00	-	-	-	-			0.01
Al				17.44	15.05	419.45	376.43	116.66	96.57	49.91	163.00	26.06	17.40	2.66	5.72	37.40	28.80	6.49	14.60			33.94
Sc				0.03	0.03	0.31	0.22	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03			0.03
Ti				0.40	0.63	10.39	11.28	2.45	3.18	1.47	6.01	0.69	0.88	0.15	0.14	1.00	0.49	0.26	0.42			1.04
V				0.65	1.75	3.41	5.36	5.49	3.48	2.47	2.78	1.28	1.22	0.20	0.47	1.40	1.50	0.44	1.30			1.61
Cr				0.26	0.31	0.67	1.26	1.50	0.59	0.30	0.68	0.14	0.21	0.06	0.07	0.27	0.33	0.12	0.27			0.30
Mn				1.51	1.67	15.98	30.48	22.70	13.02	8.82	19.60	6.23	4.14	0.62	1.23	10.50	4.70	0.71	2.00			6.13
Fe				28.57	35.71	293.91	539.90	213.24	169.10	71.28	322.00	39.71	33.40	6.75	5.87	61.30	27.60	17.40	41.40			70.60
Co				0.07	0.10	0.38	0.69	0.31	0.17	0.10	0.38	0.09	0.06	0.01	0.01	0.13	0.09	0.02	0.06			0.11
Ni				4.66	3.10	2.33	3.65	2.37	1.34	1.10	2.03	0.64	1.17	0.36	0.21	2.85	1.32	1.72	1.69			1.51
Cu				0.94	1.64	2.37	12.75	9.19	6.00	2.15	8.80	2.72	1.69	0.39	0.43	2.10	2.90	0.81	1.70			2.40
Zn				6.63	10.19	13.80	41.81	74.11	35.21	15.23	24.80	14.81	7.23	1.60	3.65	16.00	13.00	5.00	11.00			12.93
As				0.29	0.47	0.64	1.17	1.29	1.02	0.50	0.71	0.25	0.37	0.04	0.07	0.36	0.70	0.27	0.42			0.45
Se				0.62	1.24	1.60	2.54	2.05	1.95	0.97	1.67	0.88	1.40	0.17	0.16	1.37	1.40	0.79	1.40			1.14
Rb				0.14	0.24	0.71	1.00	0.83	0.58	0.40	0.50	0.22	0.18	0.00	0.00	0.55	0.39	0.15	0.26			0.31
Sr				6.39	12.07	18.57	42.97	20.37	13.55	5.57	9.88	3.66	6.43	0.36	0.40	21.30	12.00	7.50	12.00			9.09
Mo				0.14	0.18	0.21	0.66	0.74	0.53	0.13	0.37	0.09	0.19	0.02	0.02	0.29	0.26	0.03	0.10			0.18
Cd				0.17	0.10	0.24	0.31	0.39	0.42	0.20	0.26	0.13	0.07	0.01	0.36	0.12	0.16	0.11	0.06			0.17
Sn				0.17	0.23	0.22	0.56	0.37	0.40	0.14	0.25	0.09	0.20	0.02	0.01	0.10	0.08	0.13	0.22			0.16
Sb				0.18	0.52	0.53	1.42	1.25	1.09	0.46	0.96	0.24	0.35	0.05	0.06	0.29	0.52	0.15	0.37			0.41
Cs				0.00	0.00	0.03	0.04	0.07	0.06	0.03	0.00	0.01	0.00	0.00	0.00	0.01	0.02	0.00	0.01			0.01
Ba				2.21	3.31	11.83	20.12	8.58	8.20	8.60	10.40	6.75	4.40	0.30	0.49	5.72	9.40	1.80	2.70			5.61
W				0.01	0.02	0.01	0.06	0.16	0.07	0.01	0.11	0.02	0.01	0.01	0.01	0.07	0.04	0.01	0.01			0.02
Pb				1.47	3.04	3.49	8.41	17.27	9.76	5.04	7.55	2.22	2.21	0.31	0.85	1.40	4.70	0.64	2.90			3.30
U				0.00	0.01	0.04	0.06	0.02	0.02	0.01	0.00	0.00	0.00	0.00	0.00	-	-	-	-			0.01

Table 26 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in rainwater for 2004 at Holme Moss. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2004 HOLME MOSS HEAVY METAL CONCENTRATIONS IN RAINWATER $\mu\text{g/l}$																						
DATE						15/01	26/02	25/03	29/04	27/05	24/06	29/07	03/09	07/10	28/10	02/12						
volume (ml)						3915	1399	2355	662	2341	1773	4283	-	2145	2579	4133						MEAN v.w. 2xStDev
Li						0.06	0.12	0.06	0.05	0.04	0.00	0.00	-	-	-	-						0.04
Be						0.00	0.00	0.00	0.00	0.00	0.00	0.00	-	-	-	-						0.00
Al						13.06	16.17	17.69	30.16	14.36	12.20	6.69	-	7.68	6.12	16.90						12.09
Sc						0.03	0.03	0.03	0.03	0.03	0.03	0.03	-	0.03	0.03	0.03						0.03
Ti						0.22	0.50	0.81	0.72	0.43	0.42	0.44	-	0.28	0.15	0.45						0.41
V						0.44	0.52	0.56	0.58	0.36	0.37	0.34	-	0.38	0.41	0.88						0.42
Cr						0.18	0.26	0.19	0.26	0.13	0.18	0.11	-	0.15	0.15	0.23						0.17
Mn						1.12	3.01	2.81	6.06	2.35	2.03	2.74	-	1.30	0.88	1.50						1.90
Fe						15.09	28.11	27.16	38.64	20.88	18.10	10.20	-	13.00	13.10	29.30						19.36
Co						0.06	0.07	0.06	0.17	0.07	0.11	0.02	-	0.04	0.07	0.22						0.06
Ni						0.19	0.24	0.25	0.35	0.19	0.21	0.16	-	0.17	0.17	0.35						0.22
Cu						1.16	1.75	1.68	2.50	1.68	1.59	1.11	-	1.20	1.60	1.60						1.43
Zn						9.18	13.91	14.05	25.78	14.16	12.90	8.81	-	6.20	16.00	15.00						11.99
As						0.67	1.04	0.34	0.31	0.22	0.29	0.15	-	0.25	0.23	0.65						0.38
Se						0.27	0.38	0.28	0.24	0.28	0.23	0.23	-	0.30	0.23	0.43						0.26
Rb						0.07	0.13	0.09	0.16	0.07	0.04	0.10	-	0.06	0.05	0.14						0.09
Sr						2.53	4.43	1.97	1.95	1.36	1.60	0.64	-	1.30	1.50	6.30						1.74
Mo						0.46	0.46	0.11	0.08	0.07	0.05	0.08	-	0.12	0.05	0.07						0.16
Cd						0.03	0.04	0.04	0.06	0.03	0.03	0.02	-	0.04	0.03	0.04						0.03
Sn						0.03	0.08	0.10	0.05	0.04	0.07	0.04	-	0.10	0.09	0.14						0.06
Sb						0.16	0.22	0.24	0.23	0.21	0.18	0.11	-	0.17	0.30	0.28						0.20
Cs						0.00	0.01	0.01	0.01	0.00	0.00	0.00	-	0.01	0.00	0.01						0.00
Ba						1.06	3.78	1.84	2.16	1.94	1.78	0.98	-	0.96	1.40	1.80						1.44
W						0.01	0.02	0.02	0.04	0.01	0.05	0.01	-	0.02	0.01	0.02						0.02
Pb						1.58	2.82	2.58	4.92	2.61	1.90	1.33	-	2.00	4.30	2.90						2.42
U						0.00	0.01	0.01	0.01	0.00	0.00	0.00	-	-	-	-						0.00

Table 27 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in cloudwater for 2004 at Holme Moss. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2004 HOLME MOSS HEAVY METAL CONCENTRATIONS IN CLOUDWATER $\mu\text{g/l}$																						
DATE							30/01	26/02	25/03	29/04	27/05	24/06	29/07	03/09	07/10	28/10						
volume (ml)						5682	5698	5649	5631	4426	-	-	5695	5781	5780	5771						MEAN v.w. 2xStDev
Li						0.24	0.54	0.52	0.48	0.53	-	-	0.17	-	-	-						0.41
Be						0.00	0.02	0.01	0.02	0.03	-	-	0.01	-	-	-						0.02
Al						27.97	206.92	80.36	150.83	216.07	-	-	50.20	24.20	76.80	66.50						96.80
Sc						0.03	0.11	0.03	0.03	0.03	-	-	0.03	0.03	0.03	0.03						0.03
Ti						1.04	3.80	2.69	9.42	7.14	-	-	1.13	0.81	0.96	1.30						2.21
V						2.07	4.21	3.08	5.08	7.56	-	-	2.42	1.80	2.70	2.70						3.00
Cr						0.70	1.22	1.14	1.63	2.79	-	-	0.51	0.58	3.00	1.00						1.36
Mn						3.31	16.74	15.82	30.49	43.95	-	-	13.50	8.50	28.00	10.00						18.27
Fe						83.24	214.08	162.83	270.15	363.95	-	-	57.20	26.30	51.60	95.30						141.10
Co						0.35	0.60	0.41	0.45	1.49	-	-	0.21	0.27	0.45	0.36						0.39
Ni						1.47	2.38	6.90	3.61	4.21	-	-	1.46	2.00	4.50	1.88						2.65
Cu						8.09	11.36	9.28	14.32	19.47	-	-	7.98	4.40	9.40	18.00						11.15
Zn						27.64	44.69	53.03	67.60	90.13	-	-	32.30	33.00	48.00	69.00						50.71
As						1.26	1.69	1.47	1.74	1.91	-	-	0.80	0.92	1.30	1.70						1.41
Se						0.78	1.85	2.00	3.80	3.06	-	-	2.49	2.00	5.30	3.40						2.74
Rb						0.24	0.63	0.60	0.73	1.16	-	-	0.42	0.54	0.76	0.64						0.57
Sr						9.04	20.58	17.77	13.75	14.71	-	-	8.27	20.00	16.00	15.00						15.03
Mo						3.14	4.51	5.74	1.16	1.45	-	-	0.69	0.56	0.85	0.75						2.10
Cd						0.17	0.26	0.28	0.37	0.61	-	-	0.21	0.14	0.31	0.39						0.27
Sn						0.51	0.28	0.70	1.02	0.69	-	-	0.49	0.05	0.49	0.80						0.56
Sb						1.26	1.72	1.77	2.03	3.09	-	-	0.86	0.82	1.48	2.40						1.68
Cs						0.01	0.04	0.05	0.08	0.12	-	-	0.00	0.02	0.09	0.08						0.05
Ba						18.51	19.70	12.44	18.34	20.90	-	-	9.70	10.00	12.00	17.00						15.24
W						0.47	0.21	0.28	0.25	0.56	-	-	0.10	0.08	0.06	0.09						0.22
Pb						9.87	15.56	14.00	18.64	21.93	-	-	9.44	2.10	15.00	34.00						13.04
U						0.02	0.04	0.05	0.05	0.07	-	-	0.00	-	-	-						0.04

Table 28 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in rainwater for 2005 at Bowbeat. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2005 BOWBEAT HEAVY METAL CONCENTRATIONS IN RAINWATER $\mu\text{g/l}$																						
DATE			08/12	05/01	02/02	15/03	06/04	11/05	15/06	07/07	04/08	16/08	31/08	14/09	28/09	12/10	28/10	17/11	30/11	16/12		
volume (ml)			766	1106	726	832	1179	1828	822	628	231	510	611	453	1368	878	1043	422	626	424		MEAN v.w. 2xStDev
Li			-	-	0.05	0.03	0.06	0.07	0.02	-	0.02	0.02	0.04	0.06	0.01	0.03	0.03	0.03	0.02	0.03		0.03
Be			-	-	0.00	0.00	0.00	0.00	0.00	-	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Al			3.24	2.44	16.90	7.11	14.10	20.90	11.20	-	12.00	3.72	17.50	3.82	3.12	4.13	1.35	5.25	2.91	4.53		6.80
Sc			0.03	0.03	0.03	0.03	0.03	0.03	0.03	-	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03		0.03
Ti			0.02	0.02	1.40	0.07	0.46	0.91	0.28	-	0.32	0.12	0.30	0.14	0.06	0.07	0.17	0.13	0.25	0.25		0.27
V			0.27	0.16	0.18	0.80	0.58	0.44	0.29	-	0.25	0.10	0.37	0.21	0.11	0.36	0.16	0.33	0.37	0.31		0.29
Cr			0.07	0.08	0.61	0.02	0.06	0.12	0.02	-	0.12	0.02	0.11	0.12	0.18	0.11	0.02	0.02	0.02	0.02		0.08
Mn			0.57	0.37	4.30	0.96	1.41	2.61	1.31	-	2.05	0.90	2.20	0.73	0.25	0.75	0.26	0.27	0.37	0.31		1.03
Fe			4.69	5.41	16.30	3.51	17.60	30.60	12.30	-	20.00	6.27	14.40	5.61	3.36	4.39	2.48	4.05	2.70	4.20		7.55
Co			0.01	0.01	0.02	0.02	0.03	0.04	0.02	-	0.03	0.01	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01		0.01
Ni			0.08	0.03	1.45	0.29	0.24	0.22	0.22	-	0.29	0.14	0.21	0.16	0.25	0.21	0.21	0.25	0.26	0.22		0.20
Cu			0.23	0.22	0.57	0.52	0.55	0.80	0.33	-	0.75	0.26	0.66	0.26	0.16	0.45	0.29	0.39	0.35	0.23		0.42
Zn			15.00	14.70	3.90	9.60	3.12	6.30	5.72	-	7.22	15.40	7.10	9.00	4.30	3.90	6.10	2.70	3.80	4.70		7.06
As			0.08	0.05	0.12	0.15	0.11	0.11	0.06	-	0.09	0.03	0.06	0.05	0.03	0.10	0.05	0.11	0.08	0.06		0.07
Se			0.29	0.22	0.21	0.28	0.22	0.22	0.19	-	0.24	0.07	0.19	0.26	0.06	0.17	0.12	0.09	0.13	0.19		0.18
Rb			0.06	0.04	0.10	0.06	0.06	0.09	0.05	-	0.06	0.04	0.07	0.06	0.02	0.05	0.03	0.03	0.04	0.03		0.05
Sr			3.10	2.06	1.40	0.60	1.73	1.54	0.57	-	0.83	0.75	1.10	2.30	0.34	0.94	1.26	1.10	0.80	1.20		1.19
Mo			0.02	0.02	0.38	0.02	0.04	0.03	0.02	-	0.06	0.02	0.02	0.02	0.02	0.03	0.04	0.02	0.08	0.05		0.03
Cd			0.03	0.00	0.06	0.05	0.04	0.01	0.02	-	0.02	0.00	0.03	0.04	0.08	0.03	0.09	0.06	0.15	0.12		0.04
Sn			0.01	0.01	0.01	0.06	0.06	0.06	0.02	-	0.01	0.00	0.03	0.01	0.01	0.12	0.02	0.02	0.12	0.01		0.03
Sb			0.05	0.03	0.02	0.14	0.09	0.11	0.07	-	0.10	0.05	0.05	0.04	0.02	0.06	0.06	0.06	0.08	0.08		0.06
Cs			0.00	0.00	0.00	0.00	0.01	0.01	0.00	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00
Ba			0.26	0.22	0.49	0.53	0.88	1.37	0.60	-	1.12	0.31	0.75	0.47	0.13	0.33	0.26	0.36	0.32	0.25		0.42
W			0.01	0.01	0.01	0.02	0.01	0.01	0.01	-	0.01	0.01	-	-	-	-	0.12	0.03	0.15	0.17		0.03
Pb			0.42	0.26	0.51	1.60	1.00	1.15	0.64	-	0.79	0.28	0.42	0.22	0.24	0.67	0.39	0.63	0.77	0.45		0.59
U			-	0.00	0.00	0.00	0.00	0.00	0.00	-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		0.00

Table 29 Heavy Metal concentrations (ugl⁻¹) in cloudwater for 2005 at Bowbeat. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2005 BOWBEAT HEAVY METAL CONCENTRATIONS IN CLOUDWATER ug/l																						
DATE	21/12	05/01	25/01	02/02	15/03	06/04	20/04	11/05	15/06	07/07	20/07	04/08	16/08	31/08	14/09	28/09	12/10	28/10	17/11	30/11	16/12	
volume (ml)	5723	4156	2032	5645	5772	5673	3790	5772	4396	1680	5630	2558	1947	3748	2669	5697	5746	5780	3945	4758	4727	MEAN v.w. 2xStDev
Li	5723	4156	2032	5645	5772	5673	3790	5772	4396	1680	5630	2558	1947	3748	2669	5697	5746	5780	3945	4758	4727	0.21
Be	-	-	-	0.07	0.25	0.29	0.36	0.16	0.14	-	0.09	0.16	0.37	0.12	0.39	0.12	0.22	0.29	0.20	0.25	0.28	0.00
Al	-	-	-	0.00	0.01	0.00	0.01	0.01	0.01	-	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.01	0.00	0.00	26.34
Sc	6.71	20.30	49.70	13.30	68.40	25.00	115.00	33.30	33.40	-	15.60	39.80	11.90	29.80	25.90	13.40	35.40	11.00	31.20	32.10	18.60	0.03
Ti	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	-	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.69
V	0.18	0.34	1.59	0.50	1.00	0.91	3.61	0.96	1.02	-	0.57	1.42	0.40	0.49	0.81	0.15	0.53	0.68	0.77	0.96	0.74	1.30
Cr	0.57	1.20	1.32	0.34	4.50	1.70	3.83	1.51	1.33	-	0.92	1.17	0.85	1.30	1.40	0.55	2.30	0.87	2.40	2.50	1.30	0.24
Mn	0.19	0.20	0.33	0.02	0.35	0.11	0.65	0.53	0.27	-	0.12	0.23	0.15	0.29	0.33	0.27	0.65	0.19	0.20	0.33	0.30	4.90
Fe	1.10	3.40	3.47	0.82	9.20	5.60	16.40	7.96	9.96	-	4.04	7.13	6.55	8.90	6.30	2.70	7.80	2.32	2.90	4.00	1.80	33.92
Co	0.93	3.36	1.36	0.14	3.30	3.07	2.66	3.78	3.88	-	0.85	1.35	3.61	3.77	3.67	2.91	2.64	1.20	1.59	2.78	2.12	0.09
Ni	0.02	0.09	0.12	0.02	0.15	0.07	0.21	0.12	0.15	-	0.06	0.10	0.08	0.12	0.09	0.08	0.09	0.05	0.14	0.14	0.06	2.34
Cu	0.87	3.34	1.20	0.12	3.26	3.00	2.53	3.66	3.86	-	0.79	1.25	3.58	3.74	3.65	2.90	2.55	1.20	1.57	2.77	2.07	2.53
Zn	0.83	2.10	5.07	0.50	4.40	1.50	5.03	2.17	2.65	-	1.39	2.82	1.51	2.40	2.40	1.20	5.60	1.83	4.10	3.40	1.90	15.76
As	6.70	19.00	12.50	6.90	36.00	6.90	22.00	13.70	11.30	-	5.92	9.69	12.50	12.00	12.00	6.80	33.00	64.60	14.00	19.00	33.00	0.39
Se	0.27	0.49	0.62	0.15	0.95	0.35	0.80	0.35	0.24	-	0.17	0.38	0.28	0.23	0.39	0.16	0.74	0.49	0.60	0.63	0.34	1.06
Rb	1.10	1.50	1.50	0.24	2.10	1.20	1.42	0.98	0.78	-	0.57	1.27	1.20	0.78	1.40	0.43	1.30	0.90	1.20	1.40	0.98	0.29
Sr	0.22	0.46	0.12	0.04	0.42	0.19	0.49	0.27	0.39	-	0.21	0.28	0.45	0.26	0.47	0.17	0.46	0.32	0.19	0.30	0.24	8.53
Mo	13.00	24.00	4.69	1.70	5.30	8.00	13.00	6.35	5.77	-	3.97	6.04	14.80	5.10	16.00	5.10	11.00	18.70	6.60	8.70	12.00	0.15
Cd	0.05	0.17	0.32	0.02	0.33	0.08	0.58	0.10	0.10	-	0.07	0.16	0.12	0.11	0.13	0.05	0.22	0.14	0.17	0.37	0.23	0.15
Sn	0.13	0.16	0.33	0.04	0.40	0.10	0.18	0.03	0.03	-	0.01	0.16	0.06	0.04	0.12	0.02	0.06	0.29	0.28	0.35	0.27	0.13
Sb	0.23	0.27	0.22	0.02	0.34	0.11	0.22	0.09	0.06	-	0.04	0.07	0.10	0.09	0.09	0.05	0.19	0.09	0.18	0.23	0.11	0.36
Cs	0.24	0.41	1.08	0.06	1.03	0.24	0.74	0.32	0.28	-	0.14	0.43	0.25	0.23	0.30	0.12	0.52	0.48	0.68	0.77	0.40	0.01
Ba	0.00	0.01	0.00	0.00	0.05	0.01	0.05	0.02	0.01	-	0.01	0.01	0.01	0.02	0.01	0.01	0.05	0.01	0.01	0.02	0.01	5.38
W	2.10	2.90	7.29	0.57	5.60	4.00	10.40	9.77	6.06	-	10.20	10.60	5.84	5.90	8.80	2.50	5.90	4.75	4.40	3.80	2.80	0.05
Pb	0.03	0.07	0.12	0.01	0.07	0.01	0.08	0.01	0.02	-	0.01	0.03	0.02	-	-	-	-	0.15	0.12	0.23	0.23	2.56
U	0.65	2.40	3.56	0.83	12.00	2.60	7.06	2.21	1.67	-	0.81	1.44	0.83	1.40	1.20	1.10	6.60	2.46	5.20	4.50	2.10	0.01

Table 30 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in rainwater for 2005 at Holme Moss. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2005 HOLME MOSS HEAVY METAL CONCENTRATIONS IN RAINWATER $\mu\text{g/l}$																						
DATE			06/01	08/02	07/03	24/03	07/04	21/04	05/05	19/05	02/06	23/06	30/06	05/08	18/08	02/09	16/09	29/09	13/10			
volume (ml)			1674	1656	633	1152	949	657	407	839	958	236	1434	210	1099	1117	713	1076	1593			MEAN v.w. 2xStDev
Li			0.18	0.37	0.24	0.10	0.05	-	0.07	0.04	-	0.06	-	0.05	0.05	0.03	0.11	0.06	0.03			0.08
Be			0.00	0.01	0.01	0.00	0.00	-	0.00	0.00	-	0.01	-	0.00	0.00	0.00	0.00	0.00	0.00			0.00
Al			13.00	45.60	70.50	33.70	13.90	-	18.50	9.91	-	42.80	-	26.50	19.40	10.70	13.80	9.94	3.82			18.92
Sc			0.05	0.03	0.03	0.03	0.03	-	0.03	0.03	-	0.03	-	0.03	0.03	0.03	0.03	0.03	0.03			0.03
Ti			0.38	0.72	1.50	0.62	0.52	-	0.74	0.26	-	0.90	-	0.68	0.53	0.28	0.35	0.22	0.11			0.43
V			0.48	2.10	1.60	1.40	0.57	-	0.43	0.29	-	0.81	-	0.28	0.47	0.52	0.85	0.46	0.30			0.62
Cr			0.34	0.26	0.30	0.14	0.02	-	0.22	0.16	-	0.30	-	0.24	0.28	0.17	0.31	0.22	0.12			0.23
Mn			1.53	6.40	6.40	3.50	1.60	-	3.27	2.09	-	5.77	-	3.67	2.70	1.60	2.40	1.90	0.83			2.83
Fe			25.60	49.70	77.20	29.40	15.80	-	25.40	15.10	-	44.80	-	34.50	23.70	15.40	21.60	11.40	7.48			23.40
Co			0.13	0.43	0.46	0.13	0.06	-	0.06	0.09	-	0.08	-	0.07	0.06	0.04	0.06	0.08	0.02			0.07
Ni			0.19	2.10	1.00	0.58	0.24	-	0.30	0.14	-	0.51	-	0.39	0.29	0.28	0.47	0.28	0.18			0.33
Cu			2.03	7.20	3.50	2.20	1.10	-	1.95	0.88	-	2.02	-	2.36	1.60	1.00	1.50	1.40	0.73			1.57
Zn			13.80	37.00	21.00	14.00	5.90	-	34.90	4.85	-	10.90	-	16.10	14.00	5.10	15.00	18.00	5.80			12.20
As			0.60	0.81	0.91	0.67	0.19	-	0.23	0.58	-	0.20	-	0.38	0.63	0.16	1.00	0.63	0.26			0.54
Se			0.45	1.10	0.58	0.67	0.36	-	0.32	0.12	-	0.67	-	0.16	0.22	0.43	0.35	0.25	0.22			0.36
Rb			0.13	0.27	0.17	0.12	0.05	-	0.07	0.06	-	0.17	-	0.09	0.11	0.05	0.11	0.08	0.04			0.09
Sr			6.45	8.80	5.30	1.90	1.10	-	2.48	1.07	-	1.54	-	1.50	1.80	0.54	3.80	2.20	0.88			2.48
Mo			0.07	0.44	0.12	0.23	0.07	-	0.07	0.06	-	0.16	-	0.08	0.07	0.07	0.10	0.07	0.09			0.09
Cd			0.04	0.14	0.07	0.09	0.03	-	0.03	0.03	-	0.05	-	0.03	0.05	0.03	0.04	0.04	0.02			0.04
Sn			0.08	0.17	0.07	0.21	0.06	-	0.05	0.01	-	0.04	-	0.05	0.05	0.14	0.08	0.03	0.06			0.08
Sb			0.31	1.14	0.42	0.72	0.18	-	0.19	0.17	-	0.24	-	0.19	0.16	0.16	0.25	0.17	0.13			0.26
Cs			0.00	0.02	0.01	0.01	0.00	-	0.01	0.00	-	0.02	-	0.00	0.01	0.01	0.01	0.01	0.00			0.01
Ba			1.78	8.50	4.60	2.50	1.20	-	1.80	1.65	-	2.75	-	2.06	2.80	1.20	1.90	1.10	0.59			1.80
W			0.03	0.21	0.04	0.02	0.01	-	0.03	0.01	-	0.03	-	0.03	-	-	-	-	-			0.02
Pb			3.53	8.40	3.60	4.00	2.30	-	1.59	1.20	-	3.03	-	1.50	2.00	1.40	1.30	2.00	1.30			2.27
U			0.00	0.01	0.01	0.01	0.00	-	0.01	0.00	-	0.01	-	0.01	0.01	0.00	0.00	0.00	0.00			0.00

Table 31 Heavy Metal concentrations ($\mu\text{g l}^{-1}$) in cloudwater for 2005 at Holme Moss. Sample values and volume weighted means after filtering to remove outliers that were + or – 2 x Standard Deviation of the mean.

2005 HOLME MOSS HEAVY METAL CONCENTRATIONS IN CLOUDWATER ug/l																							
DATE	02/12	06/01	03/02	07/03	24/03	07/04	21/04	05/05	19/05	02/06	23/06	30/06	18/08	02/09	16/09	29/09	13/10	27/10	10/11	24/11	09/12	22/12	
volume (ml)	5729	5596	5602	4682	5526	5536	4176	1553	4025	5232	2324	5343	2990	5774	2567	4411	5766	5764	4735	5749	5369	5702	MEAN v.w. 2xStDev
Li	-	-	0.06	0.67	0.31	0.37	0.74	1.00	0.27	0.31	0.25	0.33	0.27	0.11	0.49	0.35	0.36	0.26	0.32	0.19	0.49	0.31	0.33
Be	-	-	0.00	0.02	0.01	0.01	0.02	0.04	0.01	0.02	0.02	0.01	0.00	0.01	0.00	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Al	147.00	35.80	5.10	267.00	68.50	61.40	287.00	291.00	60.70	62.70	94.70	36.80	61.80	31.10	67.10	69.60	83.50	32.80	46.20	25.60	66.40	24.60	55.00
Sc	0.09	0.08	0.03	0.03	0.03	0.03	0.03	0.12	0.03	0.03	0.03	0.03	0.03	0.03	0.06	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Ti	6.30	0.91	0.48	4.90	1.80	1.10	7.00	10.90	1.78	0.78	3.07	1.10	1.60	0.51	1.90	0.93	1.40	0.81	1.10	0.72	2.00	0.76	1.85
V	8.10	2.36	0.31	7.90	4.80	4.10	8.40	5.41	1.98	1.76	4.17	2.07	2.20	2.50	3.70	2.50	3.90	1.21	2.40	2.60	7.30	2.90	3.67
Cr	1.50	0.48	0.02	1.30	0.45	0.62	1.90	3.11	0.80	0.36	2.89	0.57	0.55	0.77	0.67	0.84	0.89	0.45	0.44	0.64	0.89	0.56	0.72
Mn	12.00	4.54	0.62	19.00	10.00	10.00	39.00	43.40	14.00	14.30	20.50	15.20	10.00	8.90	12.00	17.00	21.00	4.81	4.30	3.10	6.90	3.30	10.03
Fe	338.00	67.40	4.69	303.00	76.40	64.60	366.00	409.00	110.00	30.90	156.00	47.80	92.80	28.00	136.00	68.50	91.60	35.50	53.80	33.30	119.00	35.10	90.11
Co	1.50	0.45	0.02	1.70	0.25	0.38	0.51	0.52	0.79	0.38	0.28	0.21	0.23	0.19	0.29	0.48	0.30	0.24	0.82	0.25	1.60	0.42	0.36
Ni	4.31	1.46	0.15	6.62	3.31	3.77	5.93	7.92	3.40	1.98	2.51	2.94	1.30	1.94	3.99	4.31	3.06	2.58	3.40	1.95	5.04	3.60	3.18
Cu	14.00	6.34	0.53	14.00	5.90	6.00	13.00	14.80	5.96	6.92	12.40	5.77	7.80	4.00	9.10	9.50	12.00	11.80	10.00	4.80	14.00	5.50	8.87
Zn	62.00	28.90	4.30	58.00	37.00	28.00	70.00	57.00	26.80	47.70	32.70	71.10	27.00	60.00	40.00	59.00	110.00	81.60	32.00	24.00	47.00	29.00	44.05
As	2.50	1.00	0.08	1.70	1.00	1.00	1.60	1.80	0.64	1.04	0.95	0.83	0.69	0.51	0.96	1.10	1.80	1.76	1.20	1.00	1.80	0.92	1.16
Se	2.70	1.45	0.21	2.50	2.60	3.40	7.30	6.09	1.15	2.27	5.45	2.55	1.00	2.00	1.60	1.20	2.90	0.91	1.40	1.70	2.10	1.60	1.98
Rb	1.03	0.45	0.04	0.60	0.42	0.35	0.79	0.91	0.36	0.53	0.71	0.57	0.49	0.24	0.57	0.60	0.85	0.36	0.27	0.22	0.60	0.35	0.46
Sr	30.00	21.80	1.80	13.00	5.10	7.90	15.00	29.70	8.31	11.20	6.53	12.50	9.10	7.50	17.00	12.00	12.00	20.50	9.50	4.00	16.00	11.00	11.07
Mo	1.30	0.29	0.02	0.79	0.63	0.55	2.40	1.07	0.60	0.43	1.21	0.38	0.26	0.33	0.58	0.70	1.40	0.22	0.40	0.69	0.70	1.10	0.63
Cd	1.36	0.21	0.02	0.68	1.20	1.11	1.98	1.50	0.25	0.08	1.17	0.42	0.14	0.18	0.32	0.14	0.67	0.38	0.26	0.41	0.74	0.38	0.52
Sn	0.42	0.10	0.01	0.33	0.35	0.19	0.40	0.22	0.13	0.25	0.24	0.12	0.14	0.13	0.17	0.29	0.47	0.33	0.18	0.14	0.33	0.16	0.22
Sb	3.07	2.04	0.03	2.71	1.66	1.10	2.16	1.73	1.39	1.17	1.74	0.83	0.72	0.69	1.62	1.06	1.70	2.97	1.55	1.14	2.61	1.50	1.70
Cs	0.09	0.02	0.00	0.05	0.04	0.04	0.10	0.06	0.03	0.03	0.10	0.03	0.03	0.02	0.03	0.05	0.09	0.02	0.02	0.03	0.06	0.05	0.04
Ba	16.00	7.37	0.20	17.00	7.20	8.80	17.00	22.10	10.90	17.60	18.40	14.10	9.10	6.30	13.00	9.90	13.00	23.50	8.60	4.60	12.00	6.10	11.95
W	0.50	0.24	0.01	0.27	0.07	0.06	0.16	0.23	0.12	0.08	0.14	0.17	-	-	-	-	-	0.25	1.12	0.19	0.38	0.18	0.19
Pb	26.00	7.09	0.40	15.00	13.00	9.40	23.00	9.13	3.87	5.02	11.60	2.60	4.20	3.40	5.30	14.00	22.00	16.30	10.00	7.70	14.00	5.80	9.72
U	-	0.02	0.00	0.03	0.02	0.02	0.05	0.05	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.02	0.02	0.01	0.02	0.01	0.03	0.02	0.02