Heavy Metal Deposition Mapping: Concentrations and Deposition of Heavy Metals in Rural Areas of the UK

Report to the Department of Environment, Food and Rural Affairs by the Centre for Ecology and Hydrology

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1) Introduction

CEH has been monitoring the concentrations of a range of heavy metals in rural locations across the UK since 2004. This report presents the annual average concentrations and deposition of heavy metals in air and rainfall samples collected from rural locations during 2011 and it reviews the temporal and spatial trends in heavy metal concentrations and deposition between 2004 and 2011.

The monitoring network was established to measure the background concentration of a range of heavy metals in samples of airborne particulate matter (the PM_{10} fraction), rainwater and cloudwater which have been collected at rural locations which are not unduly influenced by local sources of emissions. The data are compiled to provide information of the background concentrations of these pollutants, and are used to demonstrate compliance with relevant air quality legislation. The measured concentrations are also used to calculate annual deposition of heavy metals and to produce UK maps of concentration and deposition.

The heavy metals (and metalloids) which are monitored are aluminium (Al), arsenic (As), antimony (Sb), barium (Ba), beryllium (Be), cadmium (Cd), caesium (Cs); chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), lithium (Li), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), rubidium (Rb), scandium (Sc), selenium (Se), strontium (Sr), tin (Sn), titanium (Ti), tungsten (W), uranium (U), vanadium (V) and zinc (Zn).

The network currently comprises a total of 14 monitoring sites across the UK (Figure 1). Samples of particulate matter (PM_{10}), and rain water are currently collected at the 11 sites indicated by red dots. These samples are analysed for a total of 26 heavy metals. At the other sites, only samples of cloud and rain water (blue dots) or just rainwater (yellow dots) are collected. Note that the blue dot sites are no longer in operation. At the 11 red dot sites, there is an additional analysis of mercury vapour. Details of all sampling sites are included in Annex 1.

With the exception of Harwell, all of the sites included in Figure 1 were established in 2003. The site at Harwell was established in 2008 to compliment the EMEP supersite activities which are currently undertaken there. The cloudwater site at Bowbeat was decommissioned at the end of 2008 as the orographic enhancement in rainfall at this site was insufficient to provide estimates of the average concentration of metals in rain scavenged by cloudwater, and the site at Holme Moss was decommissioned at the end of 2009 following the decision by the University of Manchester to stop their monitoring activities at this site, making the site no longer financially viable to continue monitoring for a single project.

2) Sample Collection and Analysis

2.1 Sample Collection

Each monitoring site has a designated site operator who has been trained to change the samples and post them to CEH for analysis. The methods used for the collection of precipitation, cloud water and aerosols (particulates in air) for the determination of metals and mercury are based on those adopted and described within the European Monitoring and Evaluation program (EMEP). The frequency of sample collection is listed in Table 1.

Figure 1 Location of Network Monitoring Sites. Note that the two cloud monitoring sites (blue dots) are no longer in operation, but data from them are included in this report.

SITE	Sampling Interval			
	Heavy metals in Particles	Heavy metals in Precipitation	Hg in Air	Hg in Precipitation
Auchencorth Moss[5]	1-Week	1-Week	2-Week	1-Month
Harwell[5]	1-Week	1-Week	2-Week	1-Month
Banchory[4]	1-Week	1-Week	2-Week	1-Month
Monks Wood	1-Week	1-Week	2-Week	1-Month
Yarner Wood[4]	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[1,6]	1-Week	4-Week	2-Week	1-Month
Heigham Holmes[2,4]	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[4]		1-Month		

Table 1: Sampling Intervals at each site

[1] Replaced Rural Trace Element (RTE) site, [2] Replaced North Sea Network (NS) site, [3] Cloud and Precipitation high altitude sites (no-longer in operation), [4] OSPAR Sites, [5] EMEP Supersites, [6] Co-located with EMEP site

Further details about the EMEP programme along with the EMEP manual for sampling and analysis can be found at http://www.nilu.no/projects/ccc/manual/index.html.

A summary of the equipment and protocols adopted by CEH for use within the Rural Heavy Metals Monitoring Network is given below.

2.2 Analytical Methods

The chemical analysis performed at CEH is accredited by the United Kingdom Accreditation Service (UKAS). Methods for the analysis of trace metals in precipitation and air, as well as cation and anion components of precipitation are included within the CEH Lancaster accreditation scheme (UKAS Testing Laboratory 2506; specific details can be found at http://www.ukas.com/). Each method section describing the analytical methods also outlines the performance characteristics for the instrumental methods used for the determination of trace metals in precipitation and PM_{10} filters as well as Hg in precipitation. The performance characteristics comprise: validation data obtained during the process of laboratory accreditation by UKAS, ongoing quality control and participation in proficiency testing schemes where applicable.

Analytical performance is assessed within the following framework:

- Initial instrument and method validation providing information about uncertainty (accuracy and precision),
- Participation in proficiency testing schemes for waters,
- Internal analytical quality control samples (AQC) analysed with each analytical batch and used to provide day to day measurement validation,
- Blank checks to assess contamination above background levels.

2.2.1 Bulk precipitation for trace metals

Bulk collectors, bottle and funnel type, are deployed within the deposition network for the collection of bulk precipitation. The levels of metals found within precipitation are at the µg/l level or lower. It is therefore essential that rigorous protocols are used for cleaning sampling equipment between collector deployments to prevent contamination within the laboratory. Collectors comprising 5 L polyethylene bottle, 14 cm diameter polyethylene funnel and a debris filter, are cleaned by soaking for 24 hours with 0.1 M nitric acid. Bottles, funnels and debris filters are then rinsed with ultra-pure water (> 18 MΩ cm^{-1}, Millipore) and finally dried in a filtered air drying cabinet. Bulk collectors are assembled in a dedicated laboratory, double bagged, and then sent out to field sites in flight cases along with instructions for collector changeover.

Field protocols, based on those described by EMEP, have been developed to prevent contamination of precipitation samples during re-deployment of the bulk collectors. Briefly the instructions given to site operators are as follows:

Deploying collectors (procedure to minimise trace metal contamination)
At the site remove the outer opaque plastic bag. Put on a pair of clean-room gloves (provided in the cool box) and remove the inner bag from the collector assembly. Place the collector in the housing and carefully remove the acid washed bag covering the funnel and debris filter assembly. Check that the debris filter is seated correctly. Take off the used gloves and remove the outer opaque plastic bag from the second collector. Put on a pair of fresh gloves and remove the inner bag from the second collector. Place collector in housing and carefully remove the acid washed bag covering the funnel. Check that the debris filter is seated correctly.

Replacing collectors
Firstly, remove the deployed collectors: At the site put on a pair of clean-room gloves. Remove the funnel assembly from the 5 l bottle (it will unscrew). Seal the bottle with the insert and cap provided and place in a clean plastic bag. Place the used funnel assembly in a suitably sized plastic bag and store with the 5 l bottles. Put on a new pair of gloves and repeat the process for the second collector.

All sample manipulations and processing is performed within a dedicated clean air laminar flow cabinet (*ISO 5*) to prevent contamination with background trace metals. The bulk collectors are weighed to estimate rainfall amounts then acidified with ultra-pure nitric acid (*Baker Ultrex II*) to a final strength of 1% v/v. The acidified bulk precipitation and cloud water samples are left for 24 hours to allow desorption of metals from the walls of the collector bottle and then a 50 ml sub-sample is transferred to a separate acid washed bottle. Acidified and preserved samples are stored at 4°C prior to analysis by Inductively Coupled Plasma Mass Spectrometry (ICPMS; *Perkin Elmer Elan DRC II*) for trace metals or Inductively Coupled Plasma Optical Emission Spectrometry for Na, Ca, K and Mg (*Perkin Elmer Optima DV 7300*).

2.2.2 Analytical performance for trace metal determination using ICPMS

Table 2 reports validation and quality control data for the determination of metals by ICPMS. Initial validation indicates that the instrumental method is suitable for the determination of a wide range trace metals in precipitation: accuracy and precision for a synthetic rain obtained from Environment Canada are acceptable when compared with certified values. Total uncertainty and limits of detection are also reported. The analytical quality control data for 2011, the latest complete year of data, is reported in Table 2. As part of UKAS accreditation, the laboratory is required to carry out an annual audit of method performance by assessing analytical quality control data. An assessment for the entire period of the rural metal deposition network operation (2004 to the current year, 2011) shows that the determination of trace metals by ICPMS was, and continues to be fit for purpose. Accuracy is better than ±5% and precision is, for the majority elements measured, better than ±5% of the nominal QC value. Table 2 gives summary data only; further detail is available upon request.

The performance of our laboratory in the *Aquacheck* inter-laboratory proficiency testing scheme (group 5b; low level metals) is illustrated in Table 2, using Cu, Cr, Pb, Ni, Zn, Cd and Hg as examples of typical laboratory performance. The performance of the CEH laboratory in this scheme is acceptable, with the majority of analyses receiving a z score of better than ±2, indicating excellent agreement between the CEH laboratory and a wide range of UK and worldwide testing laboratories. Table 2 gives a summary only; the performance of all metals determined for the network is tested within Aquacheck or similar schemes. Further information is available upon request.

CEH Lancaster has also participated in the EMEP 'Analytical intercomparison of heavy metals in precipitation' between 2006 and 2011. For all metals reported in 2010 (i.e. As, Cd, Cr, Cu, Pb, Ni and Zn) our laboratory met the required data quality objective (DQO) set within the scheme (see Table 3 for details). Further information about the scheme, including detailed reports relating to laboratory performance, can be found on the EMEP website at http://www.nilu.no/projects/ccc/intercomparison.html

Element	Li	Be	Al	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Mo	Cd	Sn	Sb	Cs	Ba	W	Pb	U
Atomic Mass	7	9	27	45	47	51	52	55	57	59	60	65	66	75	82	85	88	98	114	120	121	133	138	184	208	238
Instrument validation: precision and bias																										
precision, CoV, %	10.5	9.31	5.74	5.40	4.58	3.96	4.16	3.75	5.67	2.84	3.41	3.21	23.4	3.15	5.66	3.72	3.92	7.68	2.63	10.3	2.69	2.65	2.98	3.28	3.18	4.26
LoD	0.003	0.003	0.6	0.05	0.04	0.02	0.04	0.006	1.0	0.006	0.01	0.02	1.0	0.008	0.03	0.002	0.03	0.03	0.002	0.006	0.01	0.002	0.06	0.01	0.06	0.002
CRM TMRAIN 95																										
mean	0.34	0.24	1.39		0.44	0.57	0.65	5.34	19.8	0.20	0.68	5.47	13.8	0.94	0.53		1.49	0.16	0.39	0.71	0.27		0.64		0.21	0.23
σ	0.03	0.02	0.12		0.03	0.04	0.06	0.36	2.28	0.01	0.05	0.40	1.33	0.08	0.06		0.08	0.02	0.03	0.08	0.02		0.04		0.07	0.01
CoV, %	7.90	9.65	8.47		7.51	6.90	9.71	6.75	11.5	6.02	6.90	7.31	9.69	8.52	11.1		5.58	9.39	7.83	11.9	7.71		6.27		31.5	6.48
nominal	0.39	0.27	1.7		0.47	0.64	0.79	6.1	24.2	0.22	0.8	6.2	11.1	1.07	0.74		1.7	0.17	0.48	0.77	0.35		0.73		0.29	0.25
recovery, %	87	88	82		93	89	82	87	82	92	85	88	124	88	72		88	97	82	92	77		88		72	90
Routine analytical quality control (2011)																										
QC, mean	4.91	5.01	103	4.92	4.93	4.80	4.96	4.83	97.6	4.81	4.80	4.87	4.96	4.82	4.87	4.92	4.90	4.90	4.89	4.91	5.13	4.93	4.93	4.96	4.86	4.93
σ	0.21	0.15	3.31	0.13	0.16	0.11	0.12	0.11	3.27	0.10	0.12	0.18	0.37	0.10	0.14	0.10	0.12	0.22	0.10	0.17	0.18	0.09	0.11	0.13	0.09	0.12
CoV, %	4.1	3.0	3.2	2.6	3.2	2.4	2.4	2.2	3.3	2.0	2.4	3.7	7.0	2..0	2.9	2.0	2.4	4.3	2.1	3.3	3.5	1.9	2.2	2.6	1.9	2.5
nominal	5.00	5.00	100	5.00	5.00	5.00	5.00	5.00	100	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
recovery, %	98.1	100	103	98.5	98.7	95.9	99.1	96.6	97.6	96.3	96.1	97.3	99.2	96.5	97.5	98.3	98.1	98.0	97.8	98.2	103	98.5	98.5	99.2	97.3	98.7

Table 2. ICPMS validation and quality control data. Instrument validation reports precision as an estimate of the total expanded uncertainties for the ICPMS method (CoV: 100 s/mean, where s is standard deviation of the measurements). LoD is the instrumental limit of detection (LoD), where LoD = 4.03s. Note that Some LoD values changed December 2009 after reassessment: Be; 0.012, Mn; 0.024, Cu; 0.029, As; 0.044, Se; 0.044, Cd; 0.012, Sn; 0.012 and Sb; 0.13. Analytical data for the certified reference material TMRAIN-95 (Environment Canada) is reported as an estimate of bias. Analytical data for the Analytical Quality Control (QC) solutions, 2011: n = 600). Concentration values are in μg l^{-1}.

Data Quality Objective (DQO)	Concentration
25% accuracy or better	Pb, Ni, Cr, As <1 μg/l, Cd <0.5 μg/l, Zn <10 μg/l, Cu <2 μg/l
15% accuracy or better	Pb, Ni, Cr, As >1 μg/l, Cd >0.5 μg/l, Zn >10 μg/l, Cu >2 μg/l

Table 3 CEH Laboratory Performance in 2010 for EMEP 'Analytical intercomparison of heavy metals in precipitation'.

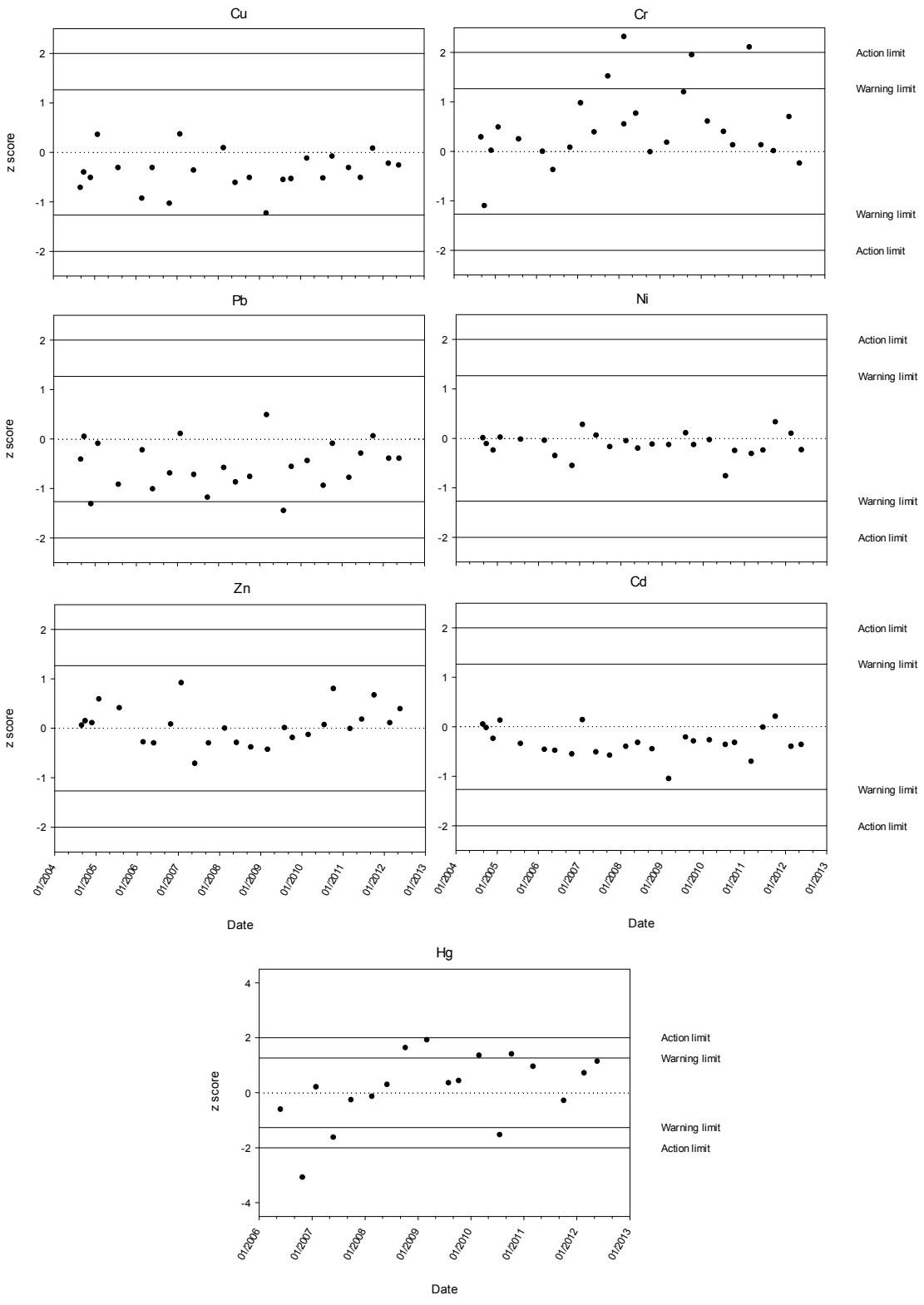


Figure 2. Laboratory performance in the Aquacheck proficiency testing scheme between 2004 and 2012 for Cu, Cr, Pb, Ni, Zn, Cd and Hg. Performance is accessed using the z score, with laboratory performance being defined, within the scheme, as being acceptable between the limits z = - 2 and z = + 2.

2.2.3 Bulk precipitation for mercury

Within the rural deposition network the EMEP protocol for sampling mercury in precipitation (EMEP, 2002) is adapted and used. The sampling equipment and cleaning protocols are specific for mercury because of this metals special characteristics i.e. it is present at ng/l levels in precipitation and is prone to background contamination. Briefly, precipitation for the determination of mercury is collected in special precipitation samplers, based on those used within the Swedish National Monitoring Program, the Iverfeldt design. The collector is designed to prevent the diffusion of gaseous Hg^0 into the collection vessel by the use of a 0.5m capillary tube between collection funnel and bottle. Sampling and analysis of bulk precipitation for mercury is particularly prone to contamination and therefore we collect duplicate bulk precipitation samples at each of the 11 network sites at which Hg is monitored.

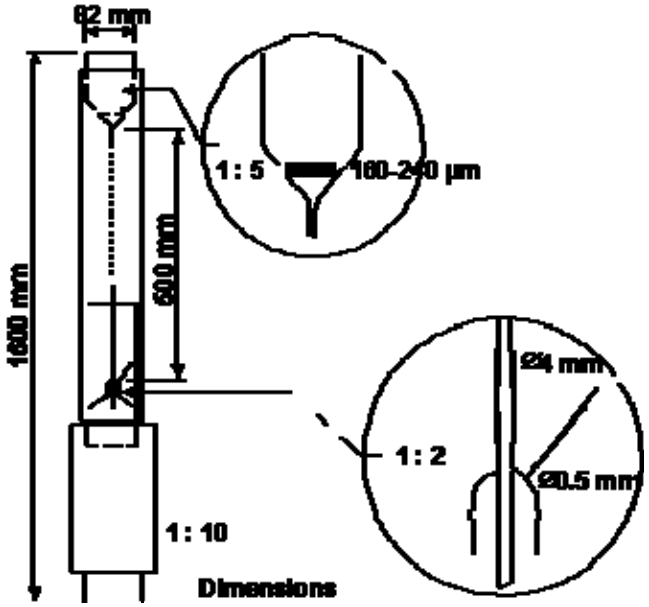


Figure 3: The Bulk Collector for the collection of precipitation for Hg, based on the Iverfeldt design.

The precipitation collector shown in Figure 3 is based on the Iverfeldt design with a long tube to reduce Hg diffusion to and from the atmosphere. A number of modifications have been made in order to reduce possible contamination and improve safety of use:

- The Funnel and tube are made in PTFE as per FAMS (Florida Atmospheric Monitoring Survey),
- The debris filter and capillary components are made of PTFE,
- The joints connecting individual components are close fitting and thus designed to reduce contamination form ingress of gaseous Hg^o,
- To reduce diffusion of gaseous Hg^o a glass bottle is used for final collection, .

Glassware and reagents are rigorously tested in order to identify and reduce sources of contamination. Bottles are cleaned on a monthly basis according to EMEP protocol by soaking in 1% nitric acid followed by bromate/bromide reagent and a final rinse with ultra pure water.

Mercury samplers are deployed, in duplicate, at the 11 main network sites, pre-acidified with hydrochloric acid as a preservative and changed on a monthly basis. The field protocols are

similar to those used for the deployment of bulk precipitation samplers and are designed to prevent sample contamination at the field sites and during transport.

On return to the laboratory Hg collector bottles are weighed to estimate rainfall amounts and stored at 4 °C prior to analysis. All analysis for Hg is completed within two weeks of the arrival within the laboratory of the first collector from the current deployment cycle. Mercury in precipitation is determined by Atomic Fluorescence Spectrometry (AFS) using a PS Analytical Galahad detector employing pre-concentration of mercury on a gold trap to increase instrument sensitivity. The analytical performance and validation of the analytical method is given in Table 4.

Element	Hg
Instrument validation: precision and bias	
Precision, CoV, %	25
LoD	1.04
CRM ORMS-3	
Mean	13.6
σ	0.71
CoV	5.2
Nominal	12.6
Recovery, %	108
Routine QC for 2011	
QC mean	10.6
σ	1.56
CoV, %	14.7
Nominal	10
Recovery, %	106

Table 4: AFS validation and quality control data for Hg. Instrument validation reports precision as an estimate of the total expanded uncertainty for the AFS method (CV: 100 s/mean, where s is standard deviation). LoD is the instrumental limit of detection (LoD = 4.03s). Analytical data (n=3) for the certified reference material ORMS-3 (Environment Canada) is reported as an estimate of bias. Analytical data for the Analytical Quality Control (QC) solutions, 2011 (n = 110). Concentration values are in ng l^{-1}.

2.2.4 Total gaseous mercury

Mercury in air is sampled using an integrated sampler using the gold amalgamation technique. A small pump pulls air at about 25 ml min^{-1} through two traps in series containing gold coated sand, onto which the mercury adsorbs by amalgamation. Two traps are used, the first to capture the bulk of the mercury, the second to catch any breakthrough that might occur with higher air concentrations or longer sampling intervals. During sampling both traps are held at 100°C using a heated sleeve, to prevent build of water vapour or organic compounds within the traps, which would impede mercury capture. A dry gas meter is used to give a quantitative concentration of mercury as mass per volume of air sampled. The adsorbed mercury is released from the traps using thermal desorption during analysis in the laboratory. A schematic of the sampler can be seen below.

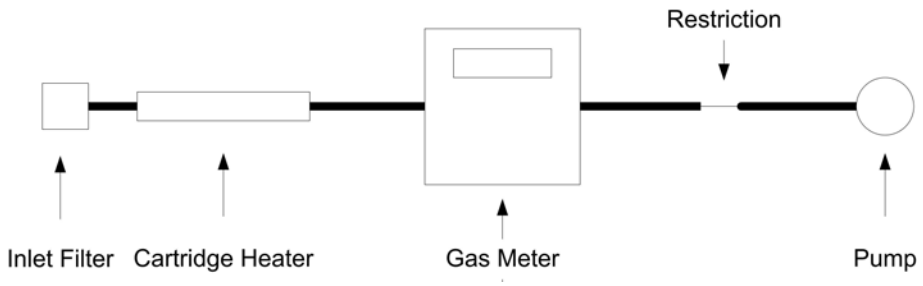


Figure 4. Schematic diagram of the mercury in air sampler.

Samplers are located at each of the 11 main network sites, and traps are changed approximately fortnightly by the local site operators. The LSOs are provided with gloves to prevent contamination of the sample traps, which, once exposed, are returned to CEH Edinburgh for analysis. Analysis is performed using a PS Analytical Millennium Merlin analyser. The sample traps are thermally desorbed in a flow of argon onto the internal trap of the analyser, which is subsequently desorbed and the mercury content analysed by Cold Vapour Atomic Fluorescence Spectroscopy.

After analysis, the traps are heated in air to clean any contamination from them before being sent out for sampling again.

2.2.5 Aerosol for trace metals

Aerosol is sampled using sequential PM_{10} samplers that are operated at a flow rate of 1 m^3 h^{-1} using 47 mm diameter Teflon or Nitrocellulose filters in FRM-style filter cassettes. Filter cassettes are assembled in a dedicated clean room and within a laminar flow cabinet (*ISO 5*) taking precautions to minimise metal contamination (i.e. using acid washed equipment and clean-room powder-free gloves). Aerosol sampler deployment and changeover of filter cassettes conforms to EMEP standards and aims to prevent contamination by providing a rigorous protocol for filter changeover and laboratory preparation prior to analysis.

Exposed filters are returned to the laboratory at CEH Lancaster and processed upon arrival: filter identifications and metadata relating to aerosol sampling are entered into a dedicated rural deposition network database (*ORACLE* and *MS Access* based) and individual PM_{10} filters are assigned codes for processing via a laboratory information management system (*LIMS*). Prior to measurement of trace metal contents the PM_{10} filters are extracted using the recommended EMEP method for filter dissolution that has been adapted for the specific equipment used at CEH Lancaster. Briefly, PM_{10} filters are extracted with 10 ml of HNO_3 (*Baker, Ultrex II*) for 12 minutes at 200°C within sealed Teflon vessels using a microwave digestion system (*CEM, MARS Express*). The method conforms to the temperature and time requirements for PM_{10} filter extraction for trace metals prescribed by EMEP, although our method uses differing equipment. The concentration of trace metals in PM_{10} filter digests is measured using ICPMS operating under standard conditions and employing matrix matched calibration standards and internal standardisation to compensate for instrument drift. Metal concentrations in air (ng m^{-3}) are calculated using EMEP methods (EMEP, 2002). The ICPMS instrument performance characteristics are detailed in Table 2.

2.2.6 Microwave digestion validation

The microwave digestion method used for determining metal contents of PM_{10} filters was validated using two standard reference materials (SRM) A2 and B2, consisting of spiked air filters, from the National Institute of Occupational Health, Norway. Furthermore, although an

appropriate and matched CRM was not available for routine ongoing quality control it was decided to certify SRM 1633b a coal fly ash from NIST using our microwave digestion method for PM_{10} filters. The aim was to provide a material that would be used for monitoring the precision of the PM10 digestion procedure over time. Note that SRM 1633b has been certified for total metal contents employing hydrofluoric acid and these values are expected to be considerably higher than those obtained using an extraction employing nitric acid only.

The certified filters, A2 and B2, NIST 1633b and a set of unexposed PM_{10} filters (to assess background contamination) were extracted using the standard microwave digestion described above. Results for the validation of the microwave digestion for the extraction of PM_{10} filters are given in Table 4. The results for SRM A2 and B2 show that the microwave digestion provides recoveries within ±10% of certified values for the majority of elements for which certified values are available.

Metal	Blank[a]	SRM A2			SRM B2			NIST 1633bb		
		cert.	found	% rec	cert.	found	% rec	cert.	found	% rec
	µg per filter							mg kg^{-1}		
Al	1.71	255	269	**105**	125	134	**107**	150500	47798	**32**
Ti	0.26	42	37	**89**	21	18	**89**	7910	1317	**17**
V	0	18	16	**91**	9	8	**92**	296	123	**42**
Cr	0.19	54	54	**99**	27	25	**93**	198	103	**52**
Mn	0.01	170	171	**101**	83	85	**102**	132	59	**45**
Fe	0	593	570	**96**	290	281	**97**	778000	46136	**6**
Co	0	42	43	**101**	21	20	**96**	50	24	**48**
Ni	0	68	64	**94**	34	32	**95**	121	58	**48**
Cu	0	85	80	**94**	42	40	**97**	113	55	**48**
Zn	0.42	256	256	**100**	125	130	**104**	210	109	**52**
As	0.01	9	8	**91**	4	4	**96**	136	110	**81**
Mo	0	43	38	**89**	21	19	**89**		13	
Cd	0	17	16	**96**	8	8	**100**	1	1	**72**
Ba	0.14	40	40	**100**	20	21	**103**	709	258	**36**
Pb	0	42	41	**97**	21	20	**100**	68	30	**43**

Table 5 Validation data for the microwave extraction of PM_{10} filters for the determination of metals. SRM A2 and B2 are spiked air filters from the National Institute of Occupational Health, Norway. NIST 1633b is a certified coal fly ash from NIST. [a] The blank is the average for 10 PM_{10} filters from 3 microwave digestion batches.[b] NIST SRM 1633b is certified for metals after a total dissolution using hydrofluoric acid. The values reported here are for extraction with nitric acid only.

2.3 Network Operation – reports of servicing, flow tests etc

Each particulate monitoring site is serviced every 6 months along with an annual site audit to assess the site infrastructure, performance and integrity. The operational conditions of each site are checked weekly, and any faults are usually rectified within a few days.

The results of the latest site audit are presented in Table 5.

2.4 Contaminated Samples

2.4.1 Precipitation Samples

Occasionally, precipitation samples will be contaminated, mainly by bird fouling. Samples with visible fouling are not submitted for analysis. In addition, samples are tested for bird fouling by determining ammonia and potassium on small sub-samples from the precipitation collectors, prior to determining metals. The sample collection equipment contains a bird-scarer to reduce the likelihood of birds perching on the equipment. Previous experience shows that such contamination varies among sites, and duplicate samples are taken at the most contaminated sites, in order to have a back-up should the first sample be contaminated.

2.4.2 Particulate samples

The aim of the monitoring scheme is to determine the background concentration and deposition of heavy metals in rural areas of the UK which are not directly affected by nearby sources of emissions. However, activities such as local bonfires occurring in the vicinity of the sampling equipment can have a transient effect on the measured concentrations of heavy metals. Where such activities are known to have occurred, the sample is excluded from contributing to the annual average means. As the sites are unmanned for the majority of the time, it is not always known when these type of activities take place. As an added precaution, any samples which exceed the mean plus two times the standard deviation for that year are also excluded from contributing to the annual average means. This gives a conservative estimation of deposition from the atmosphere. Note that all of the individual sample data are also submitted in the UK-AIR database. This database automatically calculates the annual mean of all samples, including those more than two standard deviations from the annual mean.

SPRING 2012 SERVICE – CALIBRATION AUDIT

SITE	Serial Number	Installation Date	Audit Date	Sampler Flow	Actual Flow	Difference	Difference from Set Point	Leak Test < 25mm = Pass		Filter Temperature		Compartment Temperature		Ambient Temperature		Ambient Pressure	
							16.67	mm Hg min^{-1}		°C		°C		°C		mb	
				lmin-1	lmin-1	%	%	Actual	Serviced	Sampler	Calibrated	Sampler	Calibrated	Sampler	Calibrated	Sampler	Calibrated
AUCHENCORTH	22171	21-Aug-08	30th January 2012	16.72	16.48	1.46	0.30	21	1	2.2	2.2	0.2	1.8	0.6	1.3	745	746
BANCHORY	22170	21-Aug-08	19th January 2012	16.68	16.48	1.21	0.06	9	2	5.1	5.1	5.7	5.6	4.3	4.6	740	741
BEACON HILL	22163	04-Nov-08	24th January 2012	16.68	16.70	-0.12	0.06	6	4	10.4	10.7	10.5	10.7	9.4	9.0	744	744
COCKLEY BECK	22168	20-Aug-08	01st February 2012	16.70	16.89	-1.12	0.18	4	4	3.3	1.5	2.3	0.9	2.0	0.9	756	757
CWMYSTWYTH	22166	26-Aug-08	12th January 2012	16.70	16.80	-0.60	0.18	9	2	7.7	8.4	6.4	8.3	7.2	7.2	743	748
DETLING	22164	04-Sep-08	4th April 2012	16.73	16.70	0.18	0.36	14	4	13.8	10.7	17.0	11.5	11.5	8.3	737	737
HARWELL	22165	27-Aug-08	9th February 2012	16.67	16.69	-0.12	0.00	5	5	-1.1	0.6	-0.6	0.6	-4.0	-2.0	761	768
HEIGHAM HOLMES	22167	03-Sep-08	11th April 2012	16.69	16.59	0.60	0.12	4	1	11.7	12.4	11.0	12.5	9.5	10.9	745	746
MONKSWOOD	22162	17-Feb-09	25th January 2012	16.66	16.66	0.00	-0.60	3	3	10.2	10.6	10.4	10.6	8.6	8.9	757	757
WYTHAM WOOD	22367	17-Dec-08	9th February 2012	16.68	16.55	0.79	0.06	3	3	0.8	-0.4	1.2	0.5	-0.9	-2.2	764	764
YARNER WOOD	22169	08-Sep-08	21st March 2012	16.70	16.6	0.60	0.18	11	2	12.6	12.9	12.8	13.8	11.3	11.6	761	762

Table 6: Results of Most Recent Site Audits. The delay in servicing the Heigham Holmes site was due to the site being inaccessible during the scheduled service period as a new bridge to the island was being installed.

3) Concentration data

3.1 Concentration in Air and Rainwater

The annual average concentrations of each metal analysed in air and rainwater samples collected during 2011 are presented in Table 8. To put these data into the context of the temporal trend, the annual average concentrations between 2004 and 2011 are presented in Figure 5. The ambient background concentrations of all metals are low, as would be expected in samples from rural areas which are not unduly influenced by local sources of emission. For comparative purposes, the average UK concentrations of metals which are reported in both the rural and urban / industrial heavy metals monitoring schemes are presented in Table 7. The average concentrations of all metals are higher in urban / industrial areas, and with the exception of vanadium and arsenic, the concentrations of metals are at least 3 times greater.

Metal	Rural Network ng/m^3	Urban / Industrial Network ng/m^3	Ratio of Urban / Rural Concentrations
Vanadium	1.48	2.02	1.37
Chromium	0.80	3.54	4.44
Mananese	1.85	13.20	7.15
Iron	72.60	538.00	7.41
Nickel	0.89	3.21	3.62
Copper	2.19	15.60	7.13
Zinc	8.50	71.80	8.44
Arsenic	0.44	0.63	1.42
Cadmium	0.09	0.34	3.73
Lead	3.96	16.00	4.04

Table 7 Comparison of 2008 Average Concentrations of heavy metals in the UK as measured by the two heavy metal monitoring schemes. The rural data are from this report and the urban / industrial data are from Brown et al (2009).

As there are currently only annual mean values for each year between 2004 until 2012, there are insufficient data to determine an overall temporal trend. Spatial differences in heavy metal concentration are presented in the concentration maps in Section 5. These maps have a general trend north-west to south-east gradient, with concentrations of most metals a factor of two to three times greater in the South East of England.

Auchencorth	PM10 data		2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.04	0.03	0.03	2	13
Be	0.01	0.00	0.01	1	52
Al	24.89	23.60	21.23	2	9
Sc	0.15	0.00	0.15	0	53
Ti	1.43	1.83	1.05	3	12
V	0.39	0.29	0.33	3	10
Cr	0.28	0.21	0.24	3	31
Mn	1.09	0.96	0.84	4	0
Fe	43.10	41.19	36.11	2	5
Co	0.03	0.02	0.02	3	43
Ni	0.39	0.60	0.24	3	16
Cu	0.95	0.86	0.79	2	5
Zn	4.33	2.94	3.72	2	43
As	0.23	0.21	0.19	2	3
Se	0.32	0.24	0.28	1	12
Rb	0.08	0.06	0.06	5	0
Sr	0.64	0.38	0.57	2	2
Mo	0.10	0.05	0.09	2	50
Cd	0.03	0.03	0.03	1	15
Sn	0.30	0.22	0.26	1	6
Sb	0.34	0.37	0.27	2	3
Cs	0.01	0.01	0.01	3	39
Ba	0.83	0.91	0.65	2	17
W	0.04	0.05	0.03	2	49
Pb	1.68	1.53	1.41	1	6
U	0.01	0.00	0.01	0	53
Hg	0.93	0.44	0.84	1	0
% Data Capture	97 78	metals Hg	Filters Analysed:	53 23	metals Hg

Auchencorth	Rain data			2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.06	0.03	1	0	0.39
Be	0.04	0.00	0.00	0	33	0.02
Al	0.00	10.39	4.68	5	2	53.88
Sc	5.00	0.01	0.03	0	45	0.29
Ti	0.02	0.49	0.10	3	13	1.13
V	0.15	0.10	0.10	1	0	1.09
Cr	0.09	0.05	0.04	2	24	0.41
Mn	0.04	1.82	0.61	4	0	7.06
Fe	0.69	14.57	5.52	4	3	63.63
Co	0.10	0.02	0.01	0	18	0.08
Ni	0.01	0.20	0.09	4	1	1.06
Cu	0.10	1.26	0.30	1	0	3.50
Zn	0.46	2.34	1.32	6	9	15.17
As	1.34	0.05	0.06	0	0	0.72
Se	0.07	0.08	0.09	5	7	1.04
Rb	0.10	0.16	0.05	1	0	0.57
Sr	0.05	2.40	1.16	2	0	13.37
Mo	1.69	0.44	0.03	1	30	0.36
Cd	0.05	0.01	0.00	0	9	0.05
Sn	0.01	0.06	0.02	2	17	0.24
Sb	0.03	0.04	0.04	6	4	0.48
Cs	0.04	0.00	0.00	0	30	0.02
Ba	0.00	1.87	0.30	3	1	3.43
W	0.41	0.05	0.01	0	28	0.16
Pb	0.02	0.35	0.15	5	6	1.76
U	0.18	0.00	0.00	0	35	0.01
Hg (ng/l)	2.69	1.38	2.48	1	0	0.02
mm Rainfall collected	1152 728	metals Hg	Samples Analysed	37 27	metals Hg	

Table 8a: Annual Average concentrations in air (PM10) and rainfall samples collected at Auchencorth.

Banchory		PM10 data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.03	0.03	0.02	4	18
Be	0.01	0.00	0.01	1	49
Al	18.04	24.99	12.35	4	8
Sc	0.15	0.04	0.15	1	49
Ti	1.45	2.00	1.16	3	7
V	0.35	0.31	0.32	3	10
Cr	0.34	0.42	0.25	4	30
Mn	0.89	0.66	0.80	3	0
Fe	27.67	27.29	23.45	3	6
Co	0.02	0.01	0.02	3	43
Ni	0.19	0.20	0.16	3	12
Cu	0.59	0.50	0.54	3	6
Zn	3.73	2.17	3.49	4	41
As	0.22	0.16	0.20	2	2
Se	0.25	0.18	0.23	3	19
Rb	0.11	0.07	0.11	5	0
Sr	0.52	0.26	0.50	3	1
Mo	0.09	0.04	0.09	4	46
Cd	0.03	0.03	0.03	3	11
Sn	0.16	0.15	0.16	2	10
Sb	0.21	0.14	0.21	2	3
Cs	0.01	0.01	0.01	4	39
Ba	0.54	0.46	0.48	3	17
W	0.03	0.01	0.03	1	49
Pb	1.38	1.44	1.27	1	5
U	0.01	0.01	0.01	1	48
Hg	1.36	0.94	1.14	2	0
% Data Capture	99 metals 73 Hg		Filters Analysed:	50 metals 25 Hg	

Banchory		Rain data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.03	0.04	0.03	3	37	0.22
Be	0.00	0.00	0.00	1	37	0.02
Al	8.31	29.44	8.92	3	37	63.43
Sc	0.02	0.02	0.03	1	37	0.19
Ti	0.31	1.45	0.32	2	37	2.28
V	0.17	0.17	0.18	2	37	1.29
Cr	0.04	0.07	0.05	3	37	0.33
Mn	3.04	5.13	2.58	2	37	18.38
Fe	9.62	31.69	10.29	3	37	73.20
Co	0.01	0.02	0.01	4	37	0.09
Ni	0.14	0.28	0.16	2	37	1.16
Cu	0.60	0.63	0.56	2	37	3.95
Zn	2.58	7.15	2.96	1	37	21.05
As	0.12	0.16	0.13	4	37	0.89
Se	0.12	0.15	0.13	2	37	0.92
Rb	0.36	0.70	0.34	3	37	2.39
Sr	1.04	1.32	1.09	3	37	7.75
Mo	0.04	0.06	0.04	3	37	0.25
Cd	0.01	0.03	0.01	2	37	0.10
Sn	0.03	0.08	0.04	3	37	0.27
Sb	0.05	0.07	0.05	3	37	0.35
Cs	0.00	0.00	0.00	1	37	0.03
Ba	0.55	0.75	0.60	2	37	4.24
W	0.05	0.08	0.04	2	37	0.28
Pb	0.49	0.74	0.42	2	37	2.99
U	0.00	0.01	0.00	2	37	0.02
Hg (ng/l)	4.91	2.46	4.91	0	0	0.04
mm Rainfall collected	695 metals 728 Hg		Samples Analysed	37 metals 27 Hg		

Table 8b: Annual Average concentrations in air (PM10) and rainfall samples collected at Banchory.

Beacon Hill		PM10 data		2011 Q4	Jan. 2011 - Dec. 2011
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.14	0.07	0.12	1	0
Be	0.01	0.04	0.01	1	25
Al	88.48	63.17	76.02	2	0
Sc	0.22	0.62	0.19	1	25
Ti	4.02	5.48	2.94	1	0
V	1.27	1.40	1.07	2	0
Cr	1.29	1.82	1.06	1	10
Mn	4.63	3.39	3.97	2	0
Fe	179.67	118.26	154.44	2	0
Co	0.09	0.08	0.08	2	2
Ni	1.02	1.08	0.87	2	0
Cu	4.46	2.03	3.67	2	0
Zn	14.51	12.24	12.58	1	3
As	0.78	0.37	0.68	0	0
Se	0.76	0.50	0.65	2	0
Rb	0.25	0.19	0.22	2	0
Sr	1.40	0.50	1.19	0	0
Mo	0.35	0.39	0.30	1	10
Cd	0.15	0.09	0.12	0	0
Sn	1.20	0.65	0.98	0	0
Sb	1.57	0.72	1.30	1	0
Cs	0.04	0.04	0.03	3	4
Ba	3.50	1.54	3.03	1	0
W	0.05	0.12	0.04	1	22
Pb	7.17	3.91	6.20	0	0
U	0.01	0.03	0.01	1	25
Hg	1.56	0.57	1.56	0	0
% Data Capture	41 metals 91 Hg		Filters Analysed:	32 metals 22 Hg	

Beacon Hill		Rain data		2011 Q4	Jan. 2011 - Dec. 2011
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.05	0.04	0.05	1	0	0.24
Be	0.01	0.01	0.01	1	5	0.03
Al	24.76	25.66	26.21	1	0	123.44
Sc	0.03	0.02	0.03	1	11	0.12
Ti	0.89	1.15	0.81	1	0	3.80
V	0.29	0.19	0.33	1	0	1.56
Cr	0.11	0.10	0.13	1	3	0.60
Mn	6.78	5.72	7.79	0	0	36.68
Fe	31.08	33.29	32.53	1	0	153.23
Co	0.04	0.04	0.04	1	0	0.17
Ni	0.20	0.09	0.23	2	0	1.07
Cu	1.60	1.05	1.75	1	0	8.26
Zn	7.55	5.05	8.28	1	0	39.02
As	0.21	0.12	0.24	2	0	1.11
Se	0.11	0.08	0.13	0	1	0.59
Rb	0.26	0.23	0.26	1	0	1.23
Sr	1.38	0.95	1.59	1	0	7.48
Mo	0.05	0.04	0.06	2	2	0.28
Cd	0.02	0.02	0.03	1	0	0.13
Sn	0.03	0.02	0.03	2	2	0.15
Sb	0.13	0.12	0.14	1	0	0.68
Cs	0.01	0.01	0.01	1	2	0.04
Ba	2.62	2.09	3.01	1	0	14.17
W	0.05	0.12	0.02	1	7	0.10
Pb	1.44	1.31	1.54	1	0	7.25
U	0.00	0.00	0.00	0	4	0.02
Hg (ng/l)	8.48	12.05	6.69	1	0	0.03
mm Rainfall collected	471 metals 360 Hg		Samples Analysed	12 metals 27 Hg		

Table 8c: Annual Average concentrations in air (PM10) and rainfall samples collected at Beacon Hill.

Cockley Beck	PM10 data		2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.05	0.03	0.04	2	5
Be	0.01	0.01	0.01	2	46
Al	34.80	36.28	23.61	3	4
Sc	0.19	0.08	0.15	2	46
Ti	1.79	2.95	1.12	1	9
V	0.66	0.34	0.53	1	2
Cr	0.71	1.41	0.50	3	29
Mn	1.42	1.19	1.03	2	0
Fe	49.35	40.00	34.34	3	5
Co	0.04	0.02	0.03	4	33
Ni	0.36	0.28	0.27	2	8
Cu	1.50	1.03	1.17	1	4
Zn	5.13	2.90	4.11	2	37
As	0.30	0.22	0.23	1	0
Se	0.47	0.24	0.37	3	5
Rb	0.11	0.08	0.08	3	0
Sr	1.15	0.66	0.97	1	0
Mo	0.15	0.08	0.11	2	37
Cd	0.05	0.04	0.03	2	13
Sn	0.43	0.33	0.33	3	2
Sb	0.39	0.26	0.31	1	4
Cs	0.02	0.02	0.01	1	31
Ba	1.85	18.58	0.89	1	13
W	0.05	0.04	0.04	1	42
Pb	2.37	2.42	1.94	1	4
U	0.01	0.00	0.01	2	46
Hg	1.73	0.76	1.58	2	0
% Data Capture	75 metals 93 Hg		Filters Analysed:	49 metals 23 Hg	

Cockley Beck	Rain data			2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.04	0.04	1	0	1.20
Be	0.00	0.00	0.00	2	32	0.07
Al	4.65	33.61	4.54	1	1	138.14
Sc	0.03	0.00	0.03	46	46	0.76
Ti	0.15	0.99	0.06	2	23	1.89
V	0.21	0.26	0.21	2	0	6.25
Cr	0.03	0.13	0.03	1	32	0.84
Mn	0.54	6.59	0.52	1	0	15.80
Fe	4.82	36.97	4.70	1	6	142.88
Co	0.01	0.05	0.01	1	15	0.25
Ni	0.52	1.46	0.26	2	0	7.77
Cu	0.38	1.45	0.37	1	0	11.27
Zn	1.23	5.51	1.21	1	17	36.76
As	0.08	0.08	0.08	1	0	2.35
Se	0.15	0.07	0.15	3	0	4.52
Rb	0.05	0.18	0.04	2	0	1.34
Sr	1.69	1.61	1.68	1	0	51.19
Mo	0.03	0.05	0.02	2	35	0.62
Cd	0.01	0.02	0.01	2	7	0.23
Sn	0.03	0.10	0.03	2	15	0.78
Sb	0.04	0.07	0.04	3	1	1.23
Cs	0.00	0.01	0.00	1	30	0.04
Ba	0.29	2.34	0.28	1	0	8.65
W	0.02	0.05	0.02	1	33	0.51
Pb	0.30	1.09	0.29	1	3	8.95
U	0.00	0.01	0.00	1	33	0.05
Hg (ng/l)	3.29	1.81	3.07	2		0.08
mm Rainfall collected	3040 metals 2385 Hg		Samples Analysed	46 metals 27 Hg		

Table 8d: Annual Average concentrations in air (PM10) and rainfall samples collected at Cockley Beck.

Cwmystwyth	PM10 data		2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.06	0.07	0.05	3	2
Be	0.01	0.00	0.01	1	47
Al	49.63	65.41	39.36	2	3
Sc	0.15	0.01	0.15	2	48
Ti	1.63	2.53	1.06	3	7
V	0.67	0.43	0.65	1	2
Cr	0.67	0.83	0.61	1	26
Mn	1.48	1.83	1.08	3	0
Fe	51.78	58.92	37.61	4	5
Co	0.04	0.04	0.03	3	33
Ni	0.38	0.33	0.36	1	7
Cu	2.14	5.60	1.15	2	5
Zn	5.40	4.30	4.43	4	34
As	0.27	0.24	0.24	2	0
Se	0.34	0.20	0.32	1	9
Rb	0.12	0.12	0.10	2	0
Sr	1.14	0.92	0.93	3	0
Mo	0.12	0.07	0.10	6	41
Cd	0.05	0.04	0.04	3	10
Sn	0.26	0.28	0.21	3	8
Sb	0.31	0.31	0.26	3	7
Cs	0.02	0.02	0.02	2	25
Ba	0.90	1.24	0.77	1	21
W	0.04	0.04	0.03	2	46
Pb	2.16	2.08	1.80	3	9
U	0.01	0.00	0.01	2	46
Hg	2.02	2.02	1.78	2	0
% Data Capture	91 metals 75 Hg		Filters Analysed:	48 metals 18 Hg	

Cwmystwyth	Rain data		2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.03	0.01	0.04	1	0	0.47
Be	0.00	0.00	0.00	1	6	0.02
Al	3.05	7.69	2.55	1	0	32.35
Sc	0.02	0.01	0.03	1	6	0.32
Ti	0.07	0.14	0.09	0	4	1.11
V	0.17	0.07	0.20	1	0	2.48
Cr	0.03	0.03	0.04	0	4	0.46
Mn	0.57	1.20	0.52	1	0	6.54
Fe	2.86	7.98	2.27	1	1	28.77
Co	0.01	0.01	0.01	1	4	0.06
Ni	0.11	0.17	0.09	1	0	1.10
Cu	0.17	0.19	0.21	1	0	2.64
Zn	0.79	0.95	0.98	1	4	12.40
As	0.11	0.11	0.11	1	0	1.38
Se	0.11	0.06	0.14	0	0	1.78
Rb	0.03	0.03	0.04	1	0	0.53
Sr	1.20	0.44	1.50	1	0	18.96
Mo	0.02	0.03	0.02	1	6	0.19
Cd	0.01	0.01	0.01	0	1	0.07
Sn	0.01	0.01	0.01	1	4	0.06
Sb	0.02	0.03	0.02	1	1	0.27
Cs	0.00	0.00	0.00	0	2	0.05
Ba	0.17	0.29	0.17	1	0	2.09
W	0.07	0.09	0.09	0	3	1.17
Pb	0.18	0.24	0.22	1	0	2.76
U	0.00	0.01	0.01	0	5	0.06
Hg (ng/l)	3.65	1.71	3.47	1	0	0.04
mm Rainfall collected	1268 metals 1336 Hg		Samples Analysed	7 metals 20 Hg		

Table 8e: Annual Average concentrations in air (PM10) and rainfall samples collected at Cwmystwyth.

Detling		PM10 data	2011 Q4	Jan. 2011 - Dec. 2011
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.08	0.05	0.07	4	0
Be	0.01	0.00	0.01	1	52
Al	50.45	46.94	42.09	3	0
Sc	0.15	0.00	0.15	1	52
Ti	2.19	1.94	1.76	4	0
V	2.24	1.54	1.98	3	0
Cr	0.67	0.78	0.52	4	22
Mn	3.71	2.73	3.27	3	0
Fe	133.73	73.43	121.49	3	0
Co	0.09	0.06	0.07	4	7
Ni	1.81	3.01	1.42	1	5
Cu	4.80	2.08	4.47	3	0
Zn	14.87	11.08	12.57	4	9
As	0.77	0.49	0.67	3	0
Se	0.61	0.33	0.57	3	2
Rb	0.21	0.16	0.18	4	0
Sr	1.20	0.60	1.09	3	0
Mo	0.30	0.20	0.26	3	12
Cd	0.84	3.61	0.17	2	0
Sn	1.23	0.69	1.13	3	0
Sb	1.64	1.93	1.40	1	0
Cs	0.03	0.06	0.03	1	12
Ba	2.93	1.48	2.79	1	0
W	0.05	0.09	0.04	3	45
Pb	8.71	7.03	7.77	2	0
U	0.01	0.00	0.01	4	48
Hg	0.86	0.51	0.82	1	0
% Data Capture	100	metals	Filters Analysed:	52	metals
	82	Hg		21	Hg

Detling		Rain data		2011 Q4	Jan. 2011 - Dec. 2011
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.04	0.05	1	0	0.25
Be	0.00	0.00	0.00	1	7	0.01
Al	21.70	43.38	20.79	1	0	117.10
Sc	0.03	0.02	0.03	1	11	0.14
Ti	0.52	0.94	0.51	2	0	2.87
V	0.44	0.33	0.48	1	0	2.69
Cr	0.15	0.50	0.13	1	2	0.72
Mn	4.14	8.25	3.93	1	0	22.16
Fe	21.09	34.15	20.68	1	0	116.49
Co	0.03	0.05	0.03	1	1	0.17
Ni	0.49	0.40	0.30	1	0	1.71
Cu	4.56	33.33	1.97	1	0	11.10
Zn	7.13	7.88	7.72	2	0	43.49
As	0.17	0.18	0.17	1	0	0.95
Se	0.13	0.08	0.14	0	0	0.79
Rb	0.11	0.12	0.11	1	0	0.61
Sr	1.75	1.74	1.79	1	0	10.08
Mo	0.06	0.06	0.07	0	3	0.39
Cd	0.12	0.39	0.04	1	0	0.21
Sn	0.06	0.10	0.03	1	2	0.18
Sb	0.17	0.16	0.18	1	0	1.01
Cs	0.01	0.03	0.00	1	2	0.02
Ba	1.62	2.06	1.62	1	0	9.11
W	0.02	0.03	0.02	1	6	0.10
Pb	1.38	1.34	1.50	2	0	8.43
U	0.00	0.01	0.00	2	6	0.01
Hg (ng/l)	8.74	14.36	5.36	1	0	0.03
mm Rainfall collected	563	metals	Samples Analysed	12	metals	
	525	Hg		26	Hg	

Table 8f: Annual Average concentrations in air (PM10) and rainfall samples collected at Detling.

Harwell		PM10 data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.07	0.06	0.06	3	0
Be	0.01	0.01	0.01	1	49
Al	56.66	84.64	46.13	2	0
Sc	0.15	0.15	0.15	1	49
Ti	2.11	2.33	1.63	3	1
V	1.24	0.86	1.17	3	0
Cr	0.52	0.47	0.50	2	15
Mn	2.78	2.23	2.40	3	0
Fe	110.55	84.05	99.93	2	0
Co	0.06	0.05	0.05	3	19
Ni	0.98	1.03	0.81	3	2
Cu	3.45	2.93	2.84	4	0
Zn	10.69	10.86	9.20	2	15
As	0.61	0.72	0.53	1	0
Se	0.49	0.30	0.45	3	2
Rb	0.18	0.15	0.16	3	0
Sr	1.59	1.07	1.44	2	0
Mo	0.21	0.22	0.16	6	30
Cd	0.12	0.14	0.10	2	0
Sn	0.66	0.60	0.55	4	0
Sb	1.04	1.24	0.89	1	0
Cs	0.03	0.02	0.02	3	12
Ba	17.47	22.25	12.32	4	0
W	0.04	0.06	0.04	2	44
Pb	6.32	6.82	5.53	1	0
U	0.01	0.01	0.01	1	46
Hg	1.69	0.58	1.63	2	0
% Data Capture	93 metals 85 Hg		Filters Analysed:	50 metals 23 Hg	

Harwell		Rain data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.05	0.03	0.04	2	0	0.20
Be	0.01	0.01	0.01	1	4	0.03
Al	24.53	28.43	20.02	1	0	95.45
Sc	0.03	0.02	0.03	1	10	0.12
Ti	0.72	1.01	0.57	1	1	2.73
V	0.37	0.16	0.33	0	0	1.55
Cr	0.08	0.09	0.06	1	5	0.31
Mn	3.43	4.76	2.76	1	0	13.15
Fe	23.35	30.90	18.79	1	0	89.61
Co	0.03	0.04	0.02	1	0	0.11
Ni	0.20	0.10	0.17	1	0	0.81
Cu	0.96	0.81	0.81	1	0	3.84
Zn	5.38	4.08	4.56	1	0	21.74
As	0.12	0.06	0.11	0	0	0.51
Se	0.12	0.06	0.10	0	0	0.48
Rb	0.08	0.05	0.07	1	0	0.34
Sr	3.22	2.96	2.68	1	0	12.79
Mo	0.03	0.04	0.03	1	6	0.13
Cd	0.02	0.02	0.02	1	0	0.09
Sn	0.04	0.04	0.02	1	3	0.10
Sb	0.12	0.06	0.10	0	0	0.49
Cs	0.00	0.00	0.00	0	2	0.02
Ba	43.85	67.49	34.86	1	0	166.18
W	0.03	0.03	0.02	1	6	0.09
Pb	3.11	4.50	2.48	1	0	11.81
U	0.01	0.01	0.00	1	5	0.02
Hg (ng/l)	5.47	3.10	5.47	0	0	0.03
mm Rainfall collected	477 metals 477 Hg		Samples Analysed	12 metals 26 Hg		

Table 8g: Annual Average concentrations in air (PM10) and rainfall samples collected at Harwell.

Heigham Holmes	PM10 data		2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.09	0.04	0.08	1	0
Be	0.01	0.01	0.01	1	45
Al	51.53	38.20	41.83	2	0
Sc	0.16	0.21	0.15	1	46
Ti	2.59	2.83	2.11	1	0
V	2.22	1.74	1.85	2	0
Cr	1.03	2.60	0.60	1	17
Mn	3.27	1.85	2.75	2	0
Fe	109.09	67.26	92.69	2	0
Co	0.10	0.08	0.08	2	7
Ni	1.75	1.88	1.24	2	1
Cu	2.59	1.44	2.38	2	0
Zn	11.80	8.76	10.26	1	12
As	0.58	0.38	0.55	0	0
Se	0.74	0.33	0.63	2	0
Rb	0.22	0.13	0.20	2	0
Sr	1.21	0.48	1.13	0	0
Mo	0.28	0.27	0.22	1	20
Cd	0.13	0.09	0.11	0	0
Sn	0.72	0.47	0.64	0	0
Sb	0.84	0.48	0.77	1	0
Cs	0.03	0.02	0.02	3	10
Ba	1.95	1.21	1.79	1	0
W	0.05	0.05	0.04	1	35
Pb	5.53	3.36	4.91	0	0
U	0.01	0.01	0.01	1	45
Hg	1.55	0.84	1.46	1	0
% Data Capture	84 metals 83 Hg		Filters Analysed:	48 metals 23 Hg	

Heigham Holmes	Rain data			2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.07	0.05	0.06	1	0	0.24
Be	0.01	0.01	0.00	1	8	0.01
Al	19.62	43.59	15.36	2	0	60.83
Sc	0.03	0.01	0.03	1	12	0.10
Ti	0.45	0.98	0.34	1	1	1.34
V	0.35	0.25	0.31	1	0	1.24
Cr	0.08	0.12	0.06	2	2	0.25
Mn	5.49	10.31	4.33	1	0	17.14
Fe	31.48	57.72	25.02	1	0	99.12
Co	0.04	0.07	0.03	1	0	0.13
Ni	0.75	1.61	0.45	2	0	1.77
Cu	1.24	5.31	1.11	1	0	4.40
Zn	8.58	9.15	8.07	1	0	31.95
As	0.15	0.11	0.13	1	0	0.52
Se	0.15	0.06	0.14	1	0	0.56
Rb	0.18	0.16	0.16	1	0	0.65
Sr	2.49	1.40	2.27	1	0	9.00
Mo	0.07	0.43	0.07	1	1	0.26
Cd	0.03	0.02	0.03	1	0	0.10
Sn	0.02	0.02	0.02	1	2	0.08
Sb	0.12	0.08	0.11	1	0	0.44
Cs	0.01	0.00	0.01	0	1	0.02
Ba	1.51	1.81	1.28	1	0	5.08
W	0.02	0.03	0.01	1	9	0.06
Pb	1.14	1.29	0.98	1	0	3.89
U	0.00	0.01	0.00	1	6	0.01
Hg (ng/l)	7.72	4.88	7.42	2	0	0.03
mm Rainfall collected	396 metals 402 Hg		Samples Analysed	13 metals 26 Hg		

Table 8h: Annual Average concentrations in air (PM10) and rainfall samples collected at Heigham Holmes.

Monks Wood		PM10 data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.09	0.05	0.08	4	0
Be	0.01	0.00	0.01	2	51
Al	72.66	63.41	55.86	3	0
Sc	0.16	0.01	0.15	1	53
Ti	2.59	2.32	2.15	1	0
V	1.28	0.80	1.08	2	0
Cr	0.68	0.62	0.54	1	15
Mn	3.34	1.92	2.83	3	0
Fe	144.45	73.02	122.33	2	0
Co	0.07	0.04	0.06	3	12
Ni	0.87	0.63	0.69	4	4
Cu	4.19	1.99	3.70	2	0
Zn	12.41	8.95	10.35	2	12
As	0.67	0.43	0.57	2	0
Se	0.73	0.35	0.62	2	0
Rb	0.22	0.13	0.18	4	0
Sr	1.23	0.51	1.07	1	0
Mo	0.27	0.21	0.21	3	24
Cd	0.12	0.09	0.10	3	0
Sn	0.96	0.59	0.82	2	0
Sb	1.24	0.84	1.07	1	0
Cs	0.03	0.02	0.02	3	11
Ba	2.92	1.55	2.50	2	0
W	0.04	0.03	0.03	3	46
Pb	5.94	4.22	4.94	2	0
U	0.01	0.00	0.01	2	52
Hg	1.15	0.37	1.18	1	0

% Data Capture	94	metals	Filters Analysed:	53	metals
	94	Hg		23	Hg

Monks Wood		Rain data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.04	0.04	3	0	0.13
Be	0.00	0.00	0.00	3	19	0.01
Al	20.06	24.86	15.31	2	0	50.31
Sc	0.03	0.02	0.03	2	32	0.08
Ti	0.38	0.46	0.36	4	0	1.19
V	0.26	0.25	0.24	2	0	0.78
Cr	0.08	0.08	0.08	5	6	0.26
Mn	2.51	3.16	2.02	2	0	6.63
Fe	18.94	21.10	17.69	3	0	58.16
Co	0.03	0.03	0.02	2	2	0.07
Ni	0.64	4.94	0.31	1	0	1.02
Cu	1.05	0.82	0.98	4	0	3.21
Zn	5.32	3.68	5.10	3	0	16.76
As	0.14	0.08	0.12	3	0	0.39
Se	0.12	0.09	0.11	1	4	0.35
Rb	0.10	0.08	0.10	2	0	0.32
Sr	1.37	1.22	1.17	3	0	3.84
Mo	0.05	0.06	0.04	1	18	0.12
Cd	0.02	0.02	0.02	2	0	0.06
Sn	0.09	0.46	0.04	2	5	0.13
Sb	0.12	0.07	0.11	1	0	0.37
Cs	0.01	0.01	0.00	1	10	0.01
Ba	1.21	1.17	1.00	3	0	3.28
W	0.02	0.04	0.02	2	21	0.05
Pb	0.90	0.69	0.90	1	0	2.96
U	0.00	0.00	0.00	2	17	0.01
Hg (ng/l)	7.70	6.33	7.35	2	0	0.02

mm Rainfall collected	329	metals	Samples Analysed	34	metals
	289	Hg		26	Hg

Table 8i: Annual Average concentrations in air (PM10) and rainfall samples collected at Monks Wood.

Wytham Wood		PM10 data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.07	0.05	0.06	3	1
Be	0.01	0.00	0.01	2	52
Al	50.08	40.47	39.05	3	0
Sc	0.16	0.02	0.15	2	53
Ti	2.21	2.51	1.78	1	3
V	1.23	0.75	1.02	2	0
Cr	0.41	0.36	0.32	3	26
Mn	2.65	1.86	2.14	3	0
Fe	117.16	79.37	94.78	3	0
Co	0.06	0.04	0.05	3	23
Ni	0.87	0.81	0.72	1	4
Cu	3.99	3.47	3.21	2	0
Zn	11.54	9.10	9.87	1	15
As	0.67	0.52	0.55	2	0
Se	0.57	0.31	0.48	3	1
Rb	0.19	0.12	0.15	3	0
Sr	1.27	0.79	1.04	2	0
Mo	0.23	0.19	0.16	5	31
Cd	0.12	0.09	0.09	2	0
Sn	0.79	0.61	0.65	2	0
Sb	1.12	1.06	0.92	1	0
Cs	0.03	0.03	0.02	3	9
Ba	2.63	2.32	2.18	1	0
W	0.04	0.01	0.03	3	50
Pb	6.09	5.56	5.03	1	0
U	0.01	0.00	0.01	2	51
Hg	1.01	0.34	1.01	0	0
% Data Capture	93 metals 87 Hg		Filters Analysed:	53 metals 23 Hg	

Wytham Wood		Rain data		2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.03	0.04	1	1	0.19
Be	0.00	0.01	0.00	1	1	0.01
Al	15.38	17.87	15.41	2	2	75.23
Sc	0.03	0.02	0.03	1	1	0.12
Ti	0.37	0.50	0.34	1	1	1.68
V	0.29	0.17	0.29	0	0	1.42
Cr	0.09	0.08	0.09	1	1	0.44
Mn	2.58	3.37	2.59	1	1	12.64
Fe	18.11	23.29	18.14	2	2	88.55
Co	0.02	0.03	0.02	2	2	0.12
Ni	0.18	0.13	0.18	1	1	0.89
Cu	1.21	0.97	1.21	1	1	5.90
Zn	4.74	3.80	4.75	2	2	23.20
As	0.24	0.14	0.24	1	1	1.18
Se	0.11	0.09	0.10	1	1	0.51
Rb	0.10	0.08	0.08	1	1	0.39
Sr	1.56	1.20	1.56	1	1	7.63
Mo	0.05	0.08	0.05	1	1	0.24
Cd	0.02	0.02	0.02	0	0	0.11
Sn	1.13	2.29	0.05	1	1	0.26
Sb	0.13	0.09	0.13	0	0	0.61
Cs	0.00	0.00	0.00	0	0	0.02
Ba	1.30	1.11	1.24	2	2	6.04
W	0.03	0.04	0.02	1	1	0.11
Pb	2.74	3.69	1.01	1	1	4.94
U	0.00	0.00	0.00	1	1	0.01
Hg (ng/l)	5.11	2.49	5.06	1	0	0.02
mm Rainfall collected	488 metals 387 Hg		Samples Analysed	14 metals 25 Hg		

Table 8j: Annual Average concentrations in air (PM10) and rainfall samples collected at Wytham Wood.

Yarner Wood		PM10 data		2011 Q4	Jan. 2011 - Dec. 2011
Metal	Time Weighted Annual Mean (ng/m3)	Std. Dev.	Filtered Annual Mean (ng/m3)	No. Outliers	No. Samples Below LoD
Li	0.06	0.05	0.06	3	0
Be	0.01	0.00	0.01	1	53
Al	31.24	33.21	26.72	2	3
Sc	0.15	0.02	0.15	1	53
Ti	1.22	1.51	0.87	4	10
V	1.46	1.36	1.29	2	0
Cr	0.49	0.43	0.44	2	21
Mn	1.56	1.65	1.25	3	0
Fe	52.08	57.38	41.29	3	2
Co	0.04	0.04	0.04	3	31
Ni	0.81	0.92	0.69	2	7
Cu	1.53	1.61	1.20	4	2
Zn	5.72	4.81	4.79	4	37
As	0.42	0.34	0.40	1	0
Se	0.45	0.27	0.40	4	4
Rb	0.16	0.12	0.14	4	0
Sr	1.10	0.47	1.04	3	0
Mo	0.15	0.12	0.12	4	40
Cd	0.06	0.06	0.05	4	10
Sn	0.34	0.38	0.28	4	10
Sb	0.44	0.42	0.40	2	1
Cs	0.02	0.03	0.02	2	25
Ba	0.97	0.94	0.82	3	15
W	0.03	0.01	0.03	2	52
Pb	2.38	2.26	2.08	3	6
U	0.01	0.00	0.01	2	52
Hg	1.81	0.61	1.81	0	0
% Data Capture	93 75	metals Hg	Filters Analysed:	53 21	metals Hg

Yarner Wood		Rain data		2011 Q4	Jan. 2011 - Dec. 2011
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.07	0.04	3	0	0.35
Be	0.00	0.01	0.00	3	27	0.03
Al	6.46	28.13	6.21	2	1	52.20
Sc	0.04	0.03	0.03	2	37	0.21
Ti	0.12	0.51	0.11	2	11	0.96
V	0.39	0.33	0.40	1	0	3.32
Cr	0.04	0.15	0.04	2	18	0.31
Mn	1.52	8.13	1.49	1	0	12.51
Fe	5.59	30.72	5.27	2	2	44.30
Co	0.01	0.05	0.01	2	11	0.08
Ni	0.23	0.25	0.23	3	0	1.95
Cu	0.41	1.62	0.40	2	0	3.34
Zn	2.26	6.31	2.17	3	2	18.27
As	0.10	0.32	0.09	3	0	0.77
Se	0.14	0.19	0.14	3	3	1.14
Rb	0.13	0.67	0.12	2	0	1.01
Sr	1.68	2.33	1.65	2	0	13.87
Mo	0.06	0.09	0.04	2	24	0.32
Cd	0.01	0.03	0.01	2	6	0.08
Sn	0.04	0.05	0.04	2	9	0.36
Sb	0.05	0.11	0.05	3	4	0.38
Cs	0.00	0.02	0.00	2	9	0.03
Ba	0.30	1.55	0.29	2	0	2.40
W	0.04	0.04	0.03	1	23	0.27
Pb	0.33	1.17	0.32	2	0	2.72
U	0.00	0.00	0.00	2	24	0.02
Hg (ng/l)	1.97	5.15	1.71	4	0	0.01
mm Rainfall collected	840 762	metals Hg	Samples Analysed	39 26	metals Hg	

Table 8k: Annual Average concentrations in air (PM10) and rainfall samples collected at Yarner Wood.

Inverpolly		Rain data			2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.07	0.05	0.05	0	0	1.11
Be	0.00	0.00	0.00	1	7	0.04
Al	2.56	1.55	1.87	1	0	39.05
Sc	0.03	0.00	0.03	0	11	0.52
Ti	0.20	0.16	0.13	1	2	2.77
V	0.10	0.05	0.09	0	0	1.80
Cr	0.02	0.01	0.02	1	10	0.42
Mn	0.98	0.53	0.89	0	0	18.50
Fe	2.88	1.51	2.62	0	2	54.60
Co	0.00	0.00	0.00	0	11	0.06
Ni	0.06	0.05	0.04	1	0	0.74
Cu	0.20	0.09	0.18	0	0	3.79
Zn	1.22	0.91	0.80	1	6	16.64
As	0.05	0.03	0.04	1	0	0.79
Se	0.12	0.06	0.11	0	0	2.35
Rb	0.09	0.04	0.08	0	0	1.68
Sr	2.84	2.13	2.58	0	0	53.83
Mo	0.02	0.01	0.02	1	10	0.31
Cd	0.01	0.01	0.00	1	2	0.05
Sn	0.01	0.01	0.00	1	10	0.06
Sb	0.01	0.01	0.01	0	4	0.21
Cs	0.00	0.00	0.00	1	10	0.02
Ba	0.13	0.06	0.12	0	1	2.54
W	0.06	0.10	0.02	1	7	0.49
Pb	0.11	0.11	0.09	1	4	1.95
U	0.00	0.00	0.00	1	8	0.04
Hg (ng/l)	-	-	-	-	-	-

mm Rainfall collected	2085	metals	Samples Analysed	11	metals

Table 8l: Annual Average concentrations in rainfall samples collected at Inverpolly.

Lough Navar		Rain data			2011 Q4 Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.04	0.04	0.04	1	0	0.72
Be	0.00	0.00	0.00	1	8	0.04
Al	5.63	19.71	2.39	1	1	44.70
Sc	0.02	0.00	0.03	11	11	0.47
Ti	0.16	0.16	0.13	1	3	2.43
V	0.09	0.05	0.09	1	0	1.72
Cr	0.04	0.04	0.04	1	6	0.77
Mn	0.77	0.65	0.75	1	0	14.09
Fe	2.96	5.83	2.16	1	3	40.38
Co	0.00	0.00	0.00	1	10	0.06
Ni	0.04	0.03	0.05	1	0	0.90
Cu	0.20	0.11	0.22	1	0	4.90
Zn	0.71	0.58	0.68	1	8	12.72
As	0.20	0.16	0.19	1	0	3.62
Se	0.10	0.06	0.11	0	1	2.09
Rb	0.06	0.06	0.05	1	0	0.94
Sr	1.68	1.43	1.71	1	0	32.02
Mo	0.02	0.01	0.02	1	10	0.28
Cd	0.00	0.00	0.00	1	3	0.06
Sn	0.11	0.29	0.01	1	7	0.12
Sb	0.02	0.01	0.02	1	0	0.33
Cs	0.00	0.00	0.00	1	9	0.02
Ba	0.13	0.14	0.12	1	0	2.23
W	0.07	0.11	0.05	0	0	1.01
Pb	0.12	0.09	0.13	2	0	2.36
U	0.00	0.00	0.00	1	8	0.04
Hg (ng/l)	-	-	-	-	-	-

mm Rainfall collected	1870	metals	Samples Analysed	11	metals

Table 8m: Annual Average concentrations in rainfall samples collected at Lough Navaar.

Penallt	Rain data			2011 Q4	Jan. 2011 - Dec. 2011	
Metal	Volume-Weighted Annual Mean (µg/l)	Std. Dev.	Filtered Annual Mean (ug/l)	No. Outliers	No. Samples Below LoD	Wet Deposition (g/ha/year)
Li	0.02	0.02	0.05	1	0	0.36
Be	0.00	0.00	0.00	1	2	0.02
Al	1.60	1.21	3.80	1	0	26.70
Sc	0.01	0.00	0.03	3	3	0.18
Ti	0.05	0.02	0.12	3	0	0.81
V	0.14	0.12	0.32	1	0	2.28
Cr	0.02	0.06	0.05	0	2	0.34
Mn	1.45	0.91	3.45	2	0	24.22
Fe	1.84	1.33	4.36	1	0	30.60
Co	0.00	0.01	0.01	0	1	0.06
Ni	0.09	0.09	0.21	1	0	1.44
Cu	0.27	0.32	0.63	1	0	4.43
Zn	1.54	1.78	3.65	1	0	25.62
As	0.15	0.28	0.36	0	0	2.52
Se	0.04	0.05	0.11	1	0	0.74
Rb	0.07	0.09	0.17	1	0	1.16
Sr	0.79	0.56	1.89	2	0	13.25
Mo	0.01	0.01	0.02	1	2	0.14
Cd	0.01	0.00	0.02	3	0	0.11
Sn	0.00	0.01	0.01	0	2	0.04
Sb	0.03	0.01	0.07	3	0	0.52
Cs	0.00	0.00	0.00	1	0	0.02
Ba	0.26	0.15	0.61	1	0	4.25
W	0.00	0.00	0.01	3	3	0.04
Pb	0.30	0.12	0.71	3	0	4.96
U	0.00	0.00	0.00	3	3	0.01
Hg (ng/l)	-	-	-	-	-	-
mm Rainfall collected	702	metals	Samples Analysed	3	metals	

Table 8n: Annual Average concentrations in rainfall samples collected at Penallt.

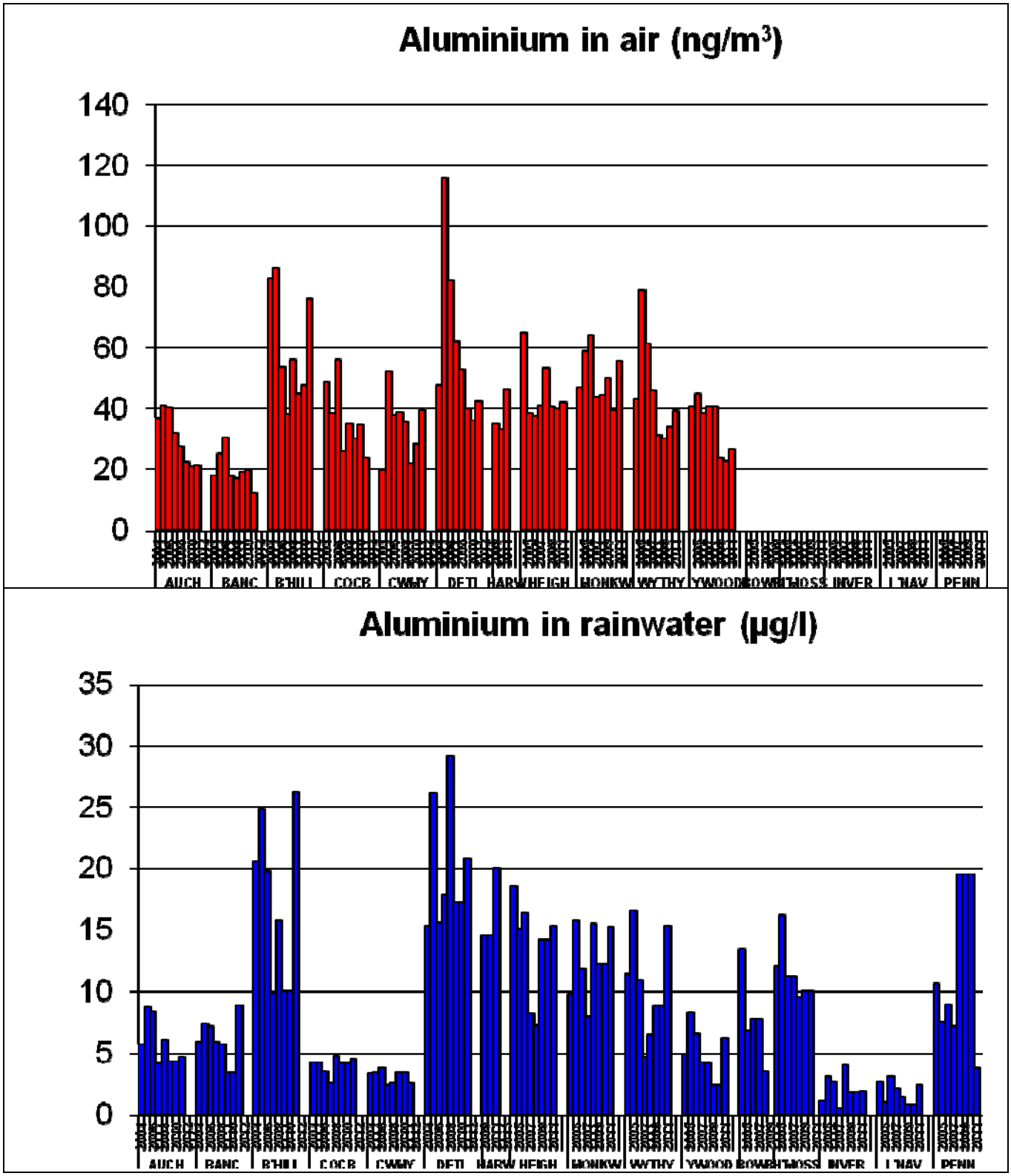


Figure 5a, Annual Average Concentration of Aluminium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

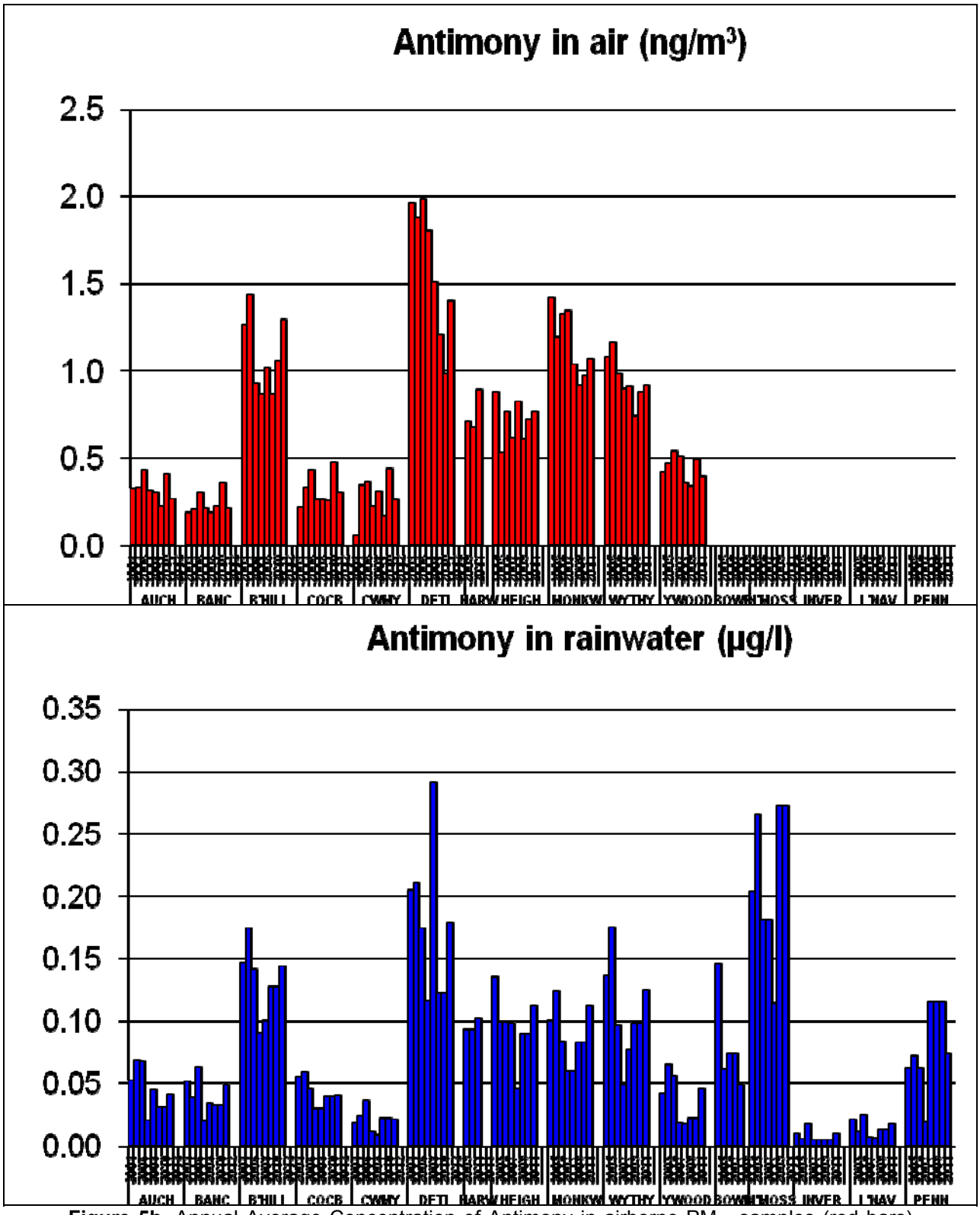


Figure 5b, Annual Average Concentration of Antimony in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

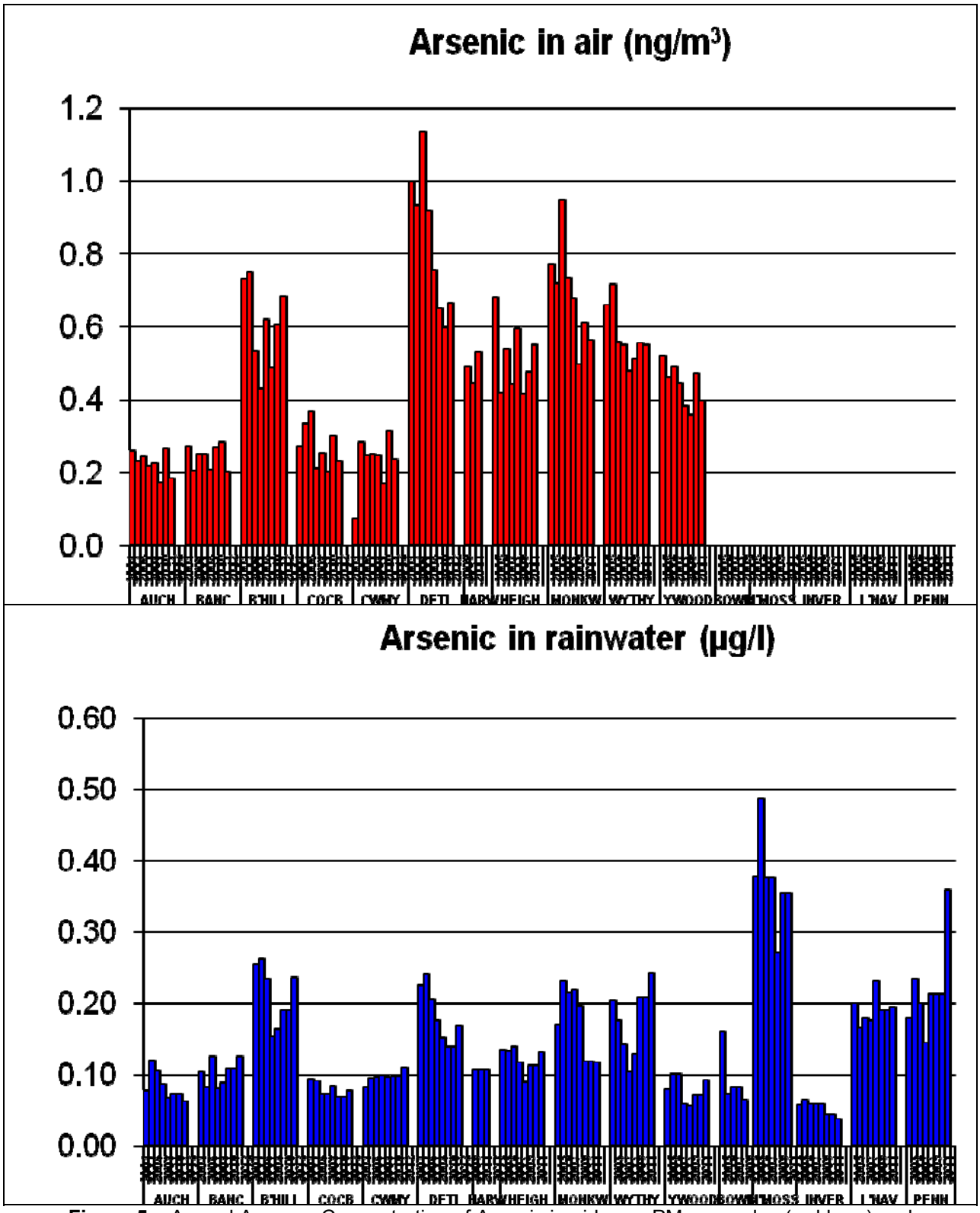


Figure 5c, Annual Average Concentration of Arsenic in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

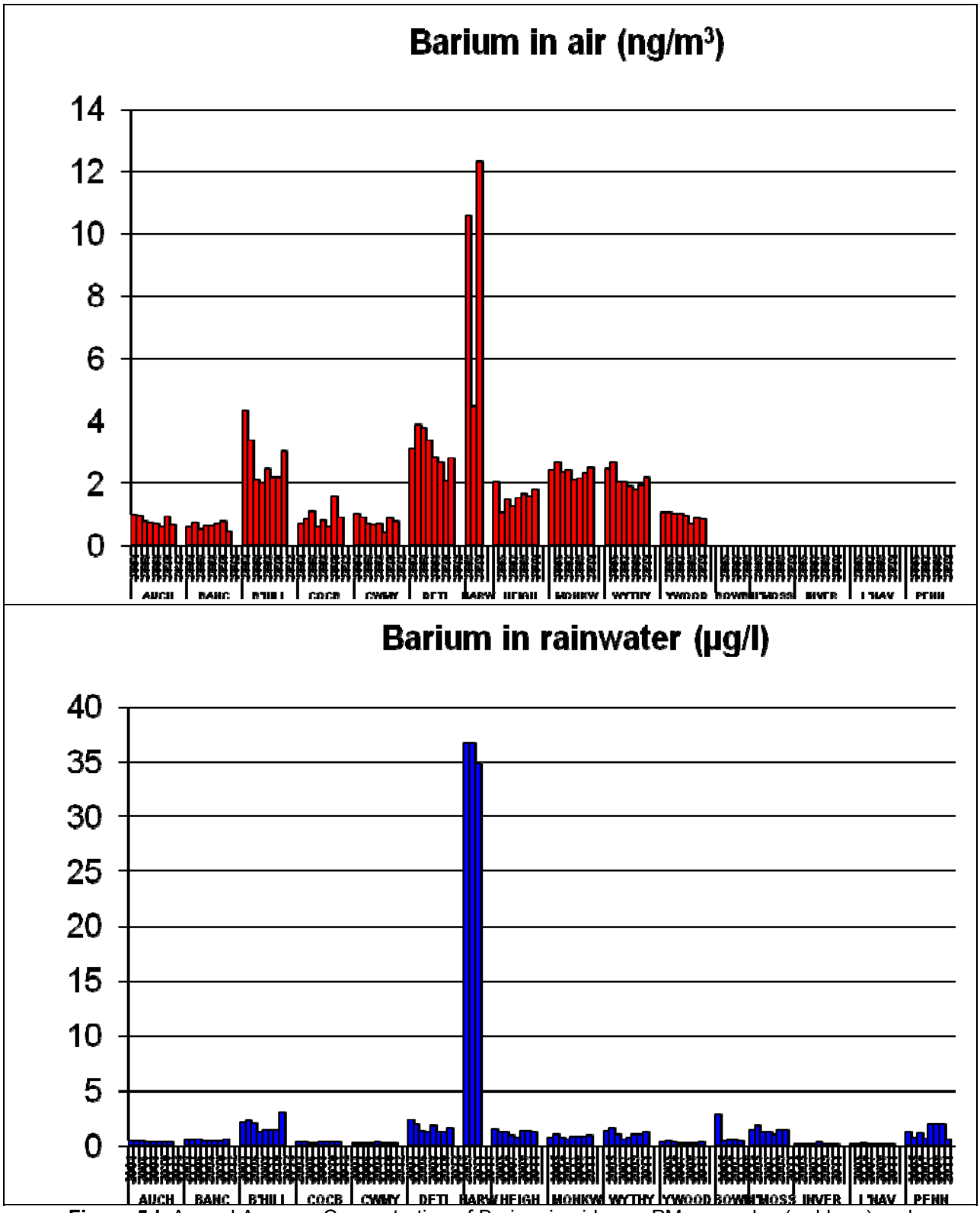


Figure 5d, Annual Average Concentration of Barium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

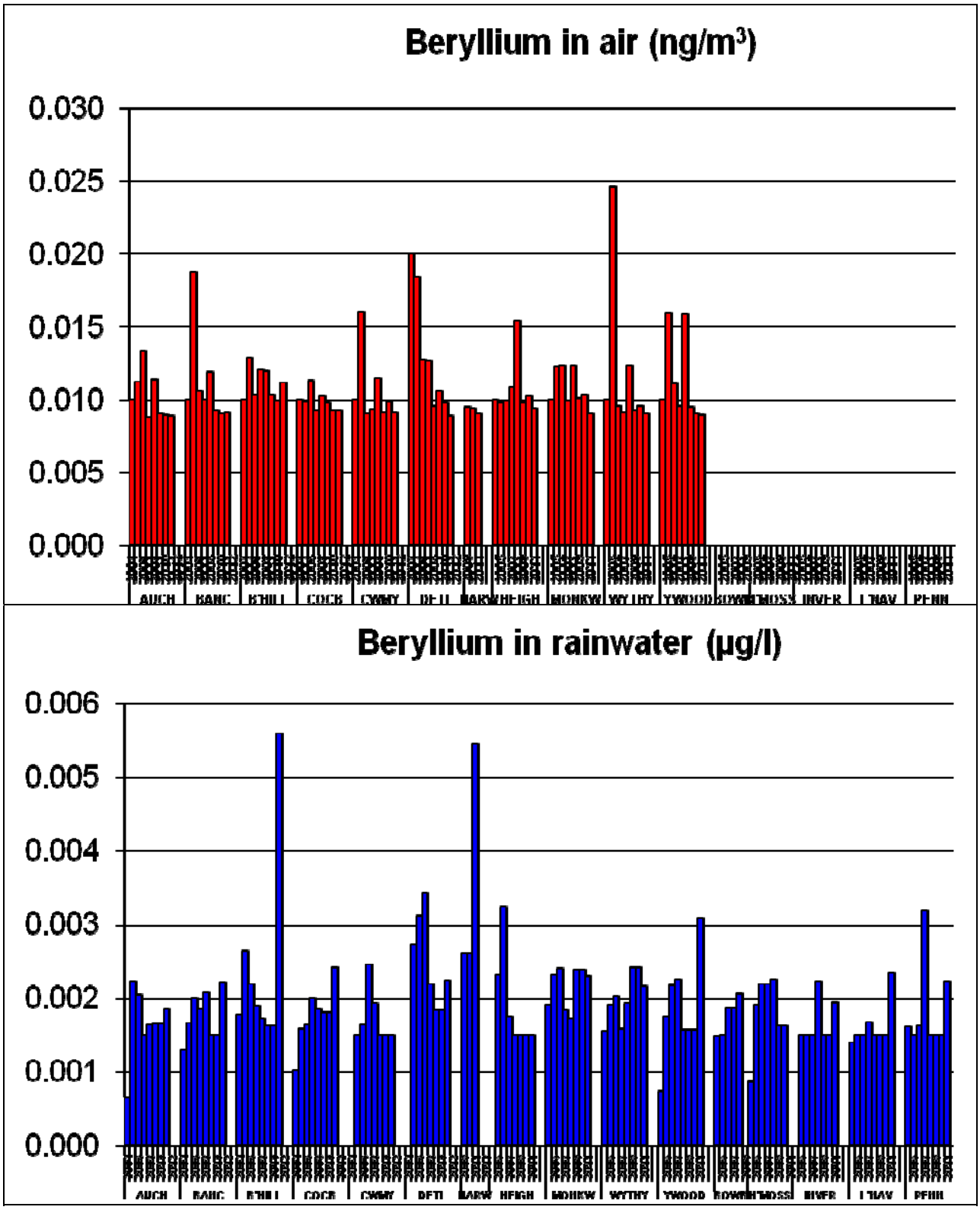


Figure 5e, Annual Average Concentration of Beryllium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

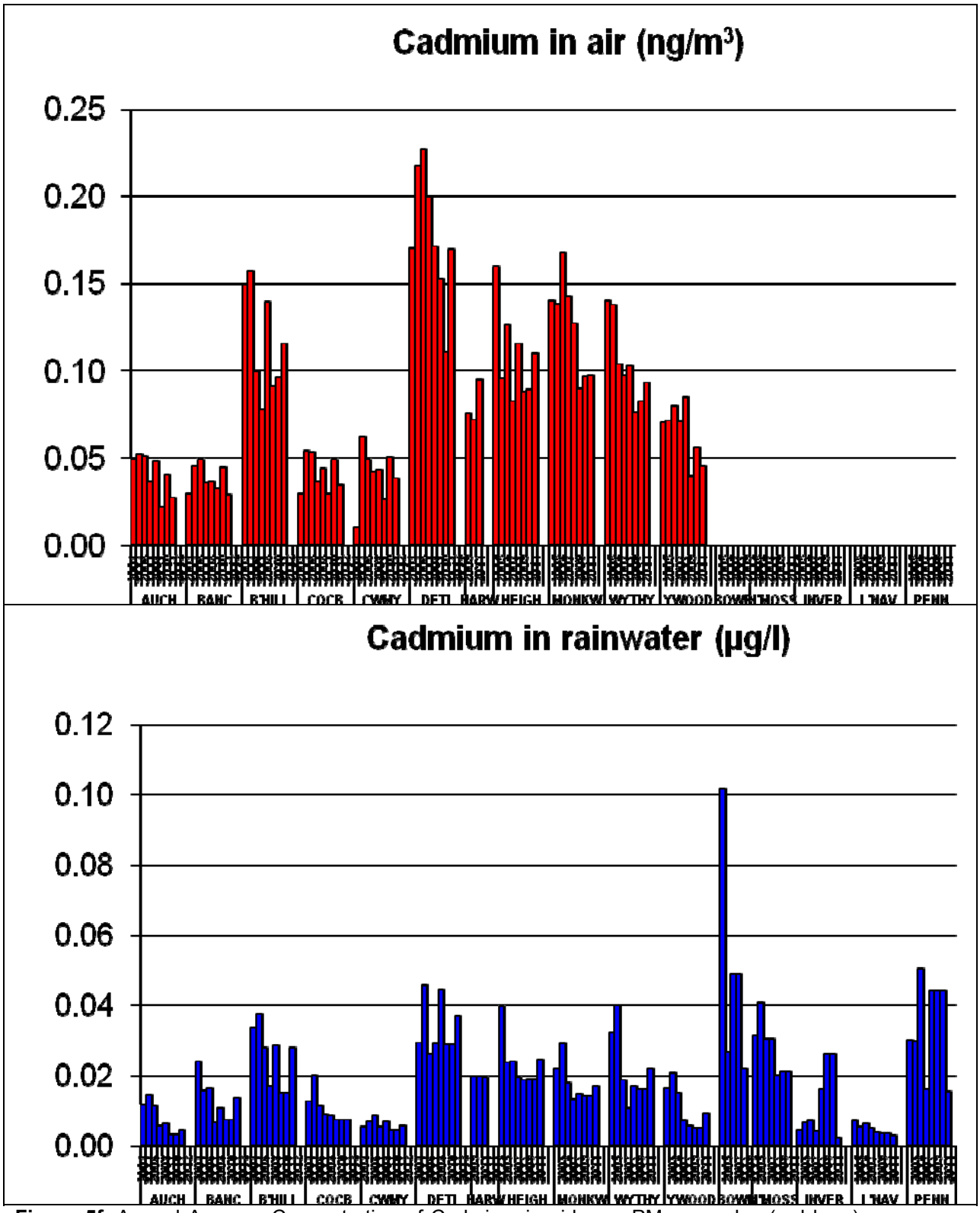


Figure 5f, Annual Average Concentration of Cadmium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

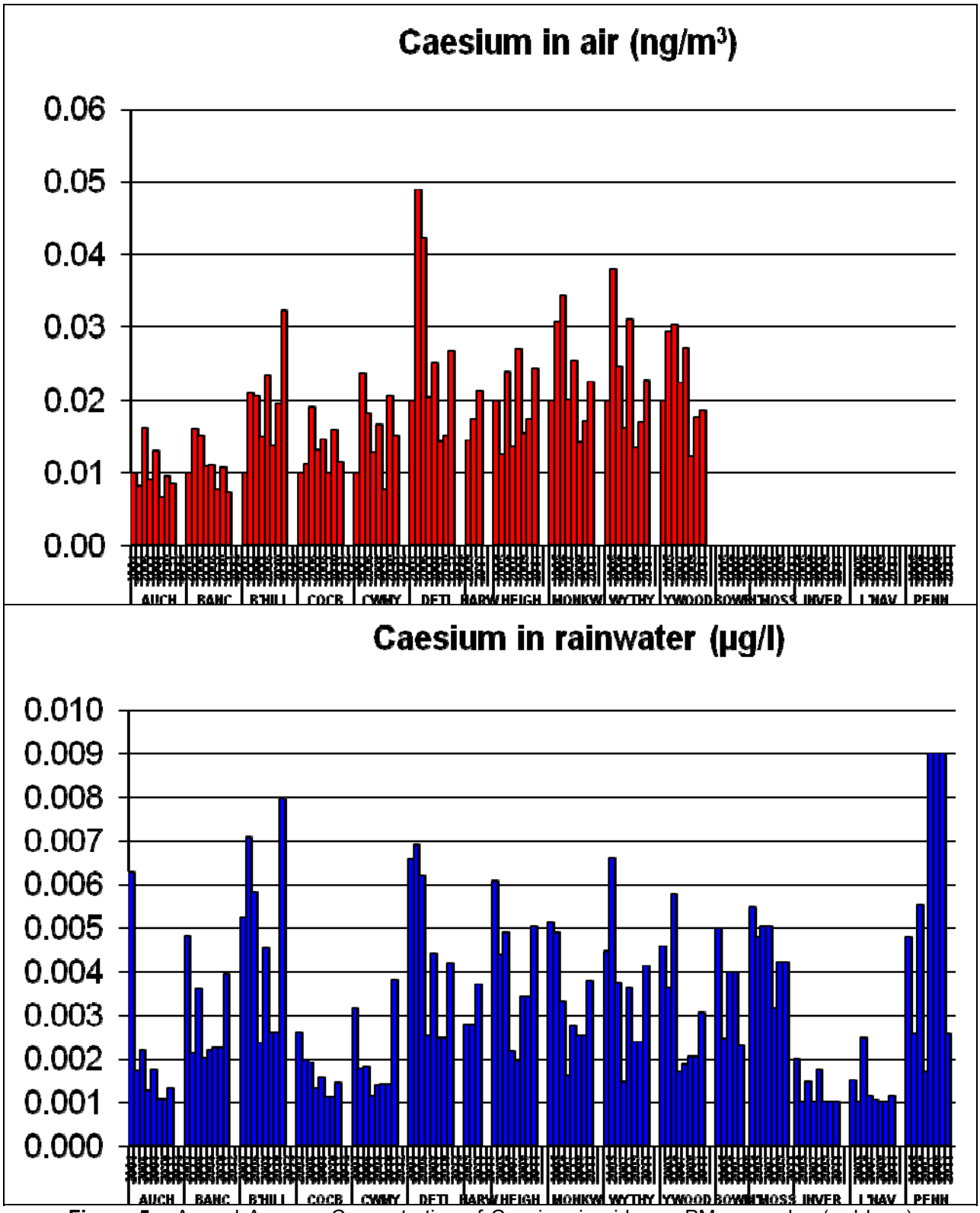


Figure 5g, Annual Average Concentration of Caesium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

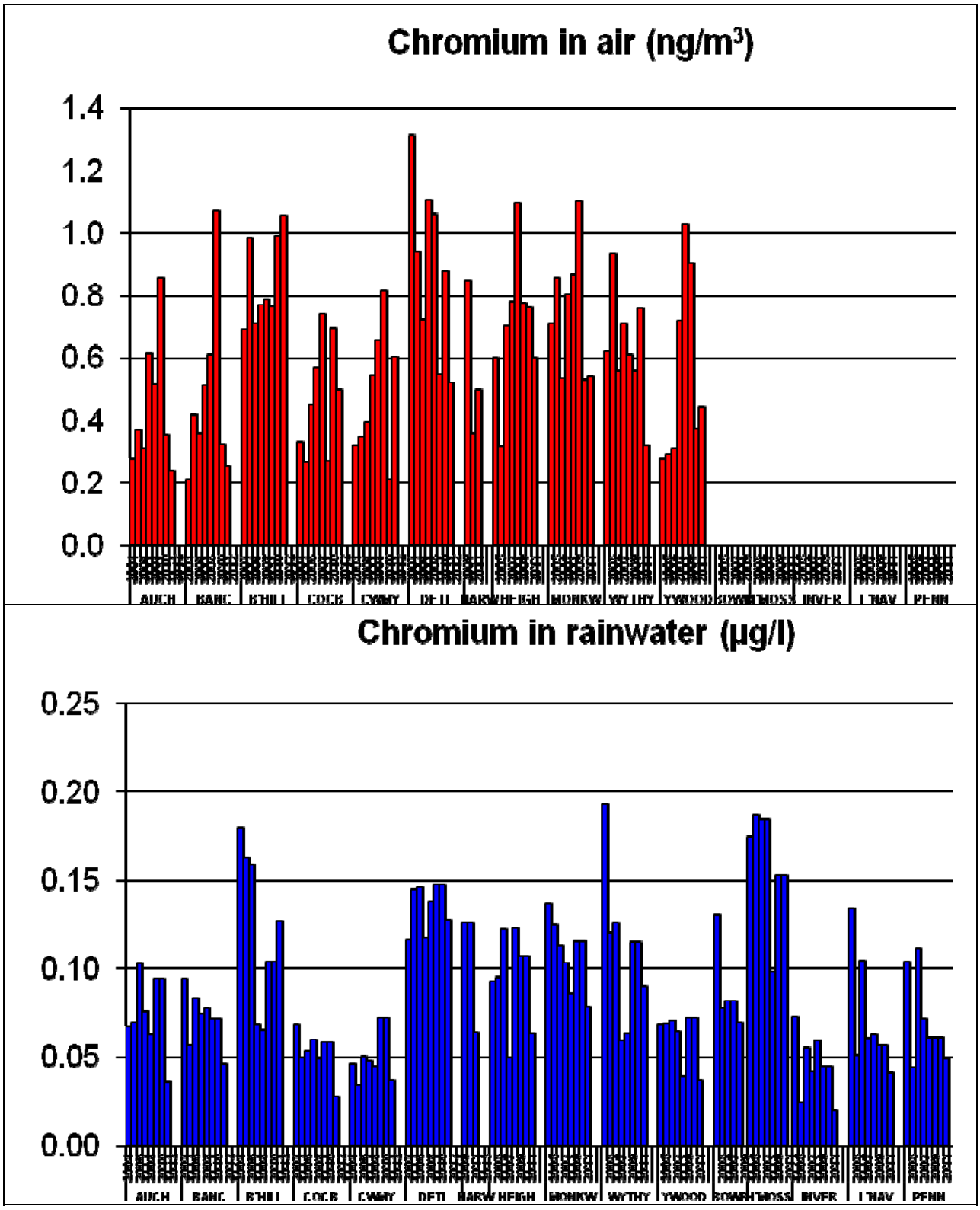


Figure 5h, Annual Average Concentration of Chromium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

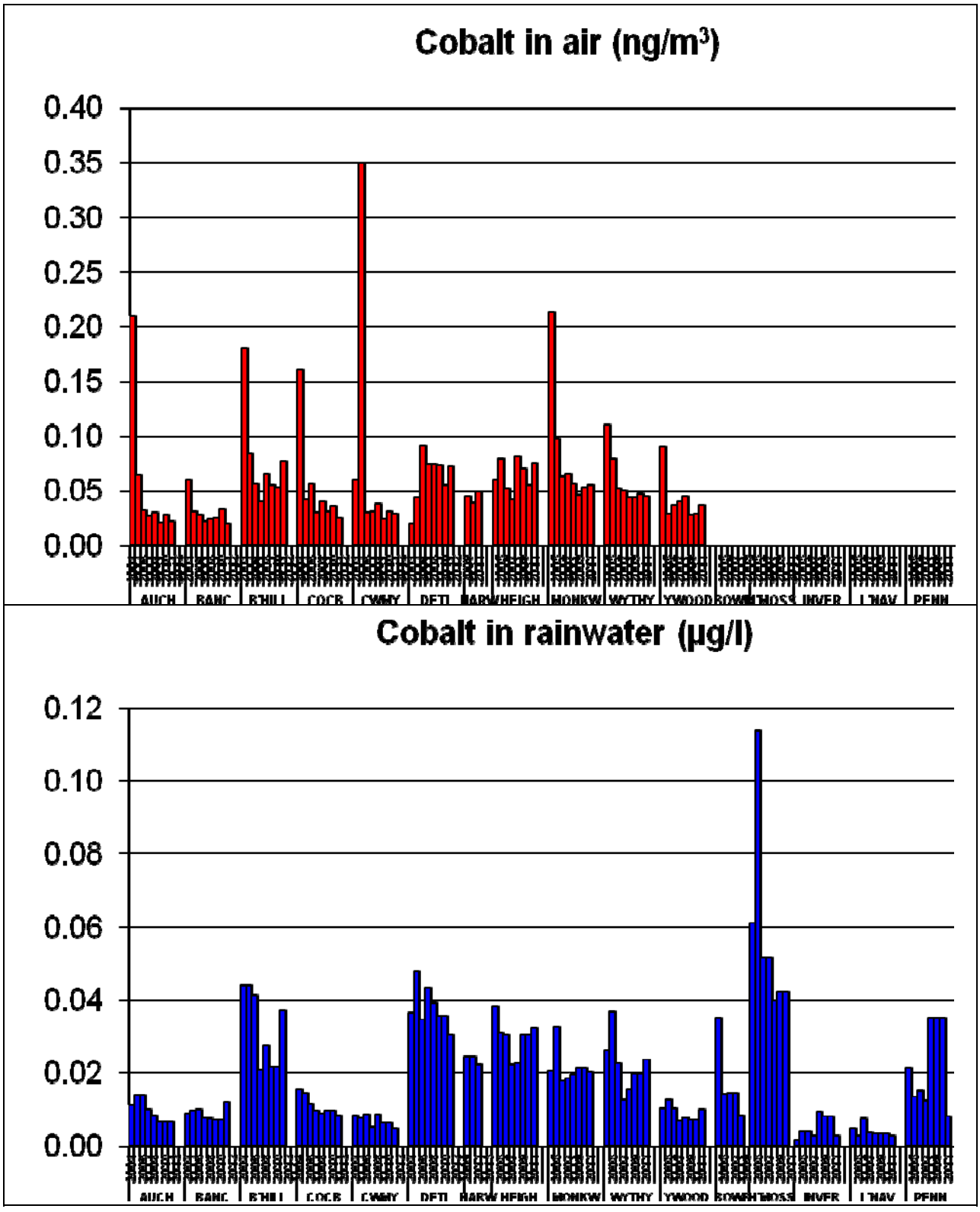


Figure 5i, Annual Average Concentration of Cobalt in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

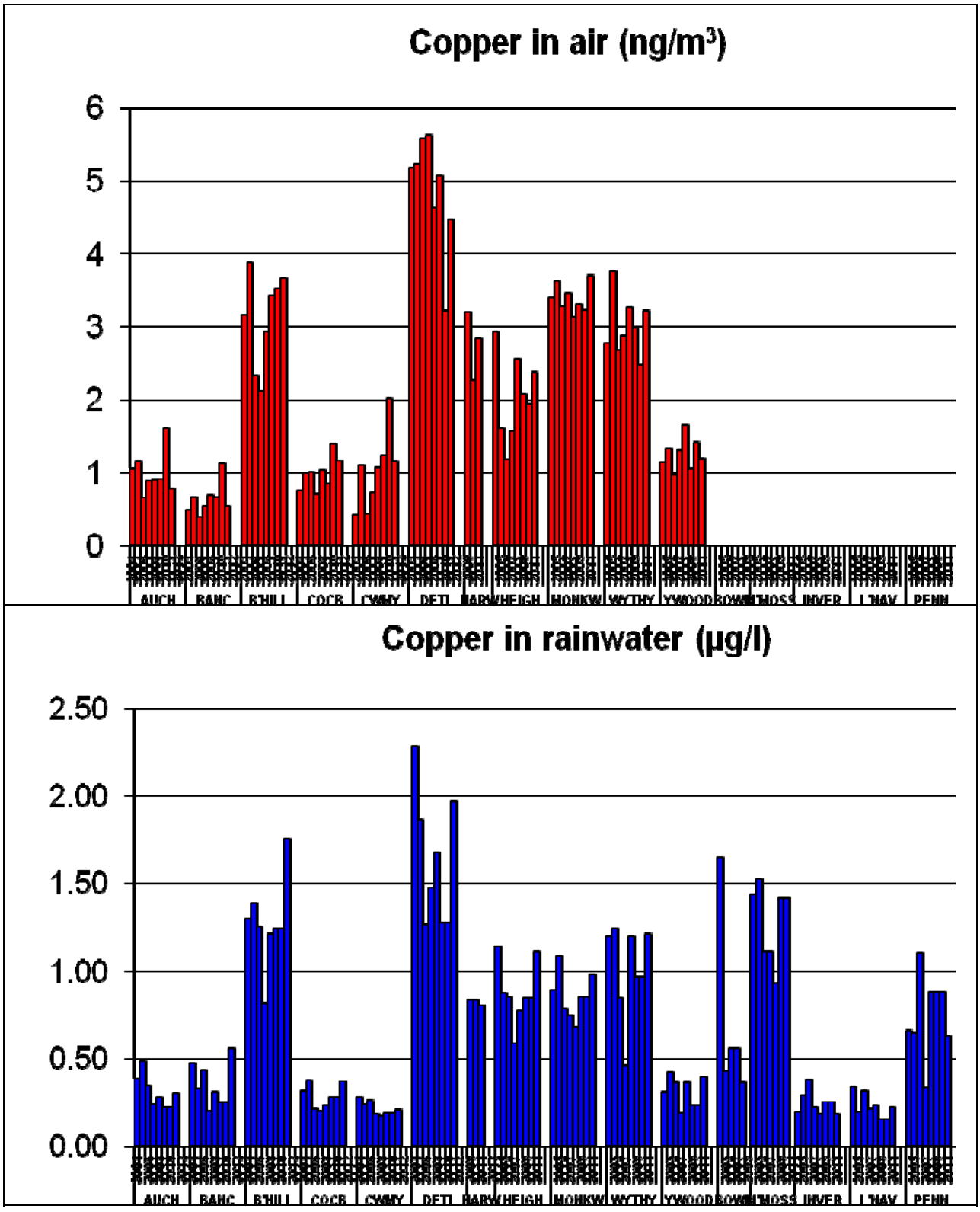


Figure 5j, Annual Average Concentration of Copper in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

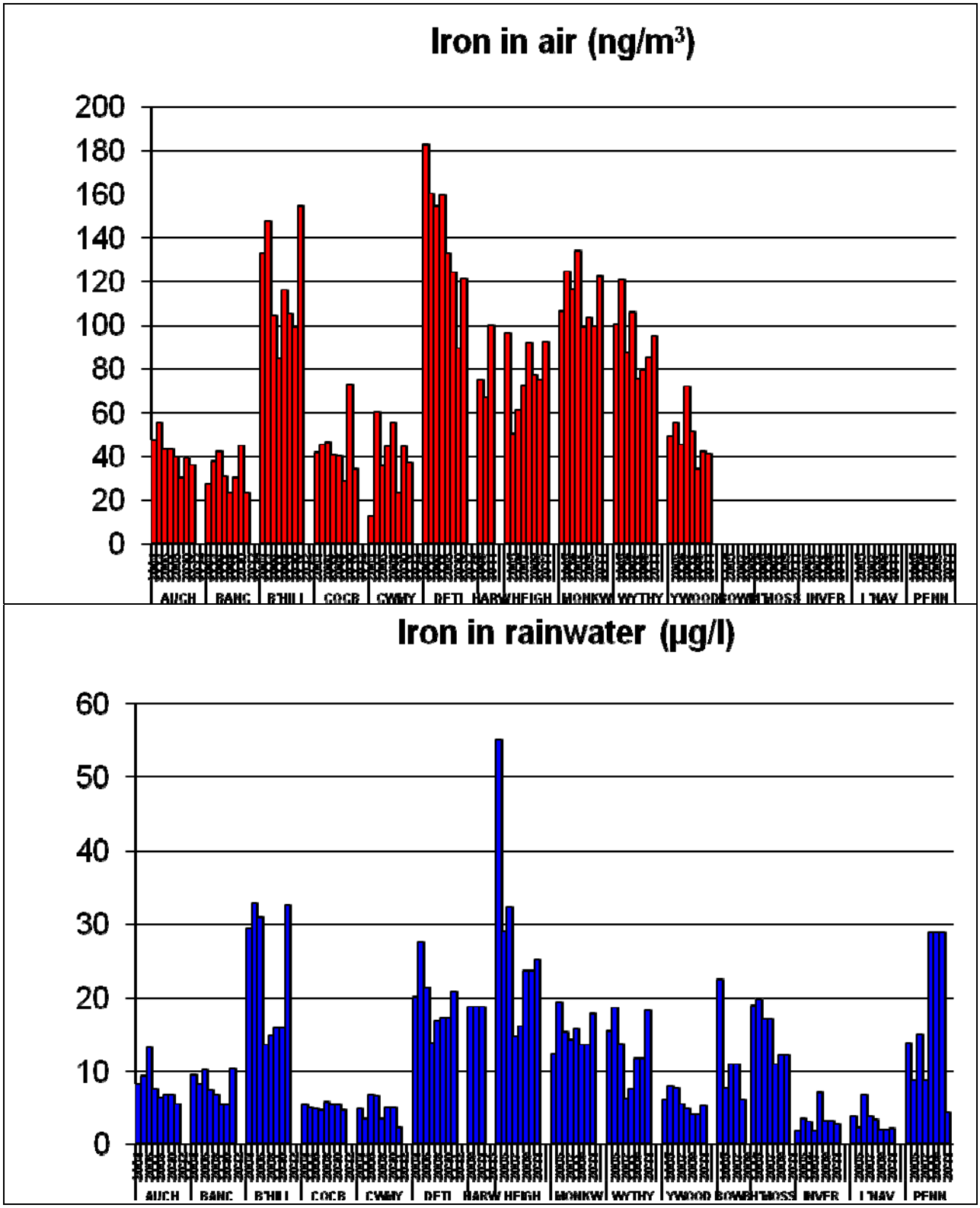


Figure 5k, Annual Average Concentration of Iron in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

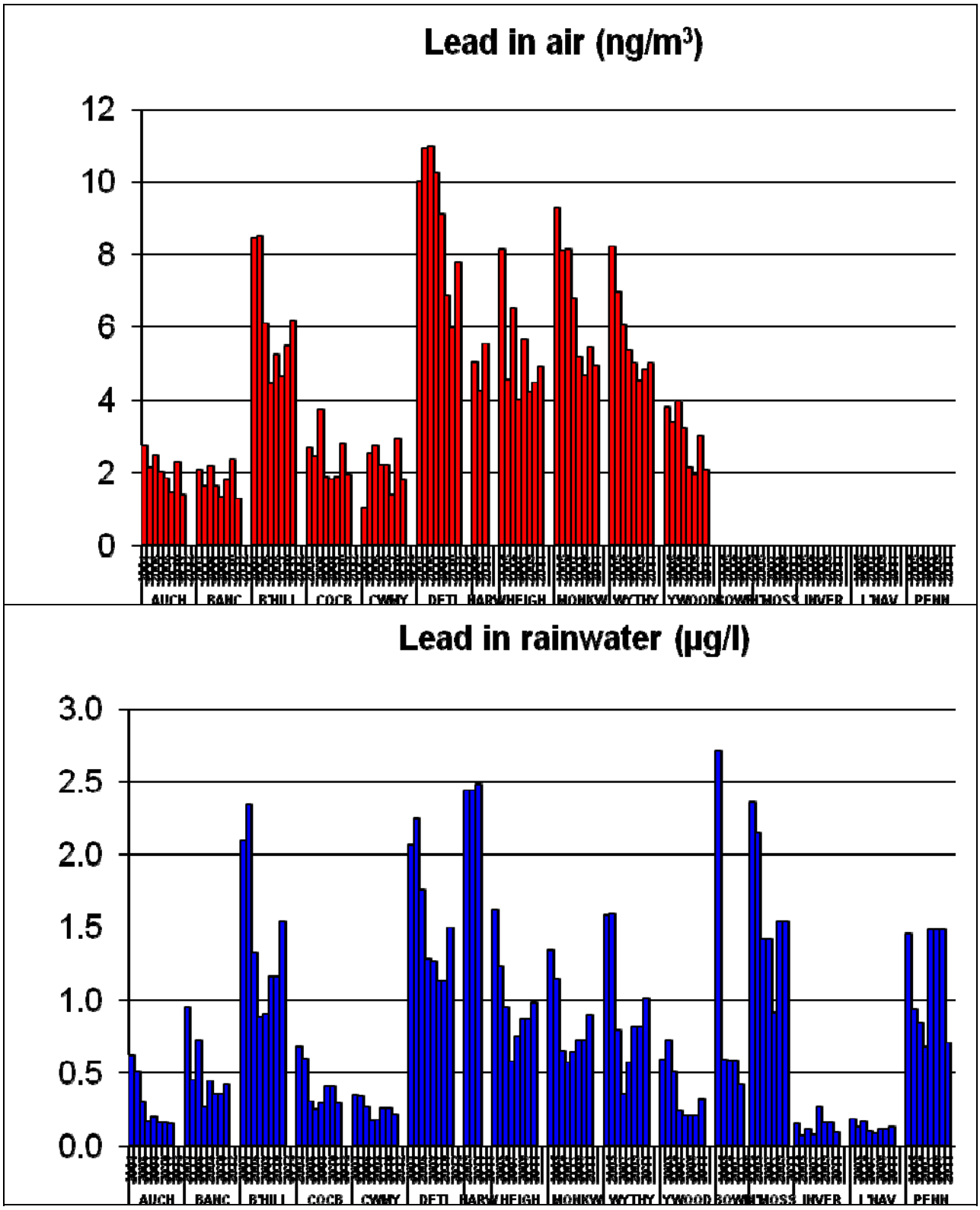


Figure 5l, Annual Average Concentration of Lead in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

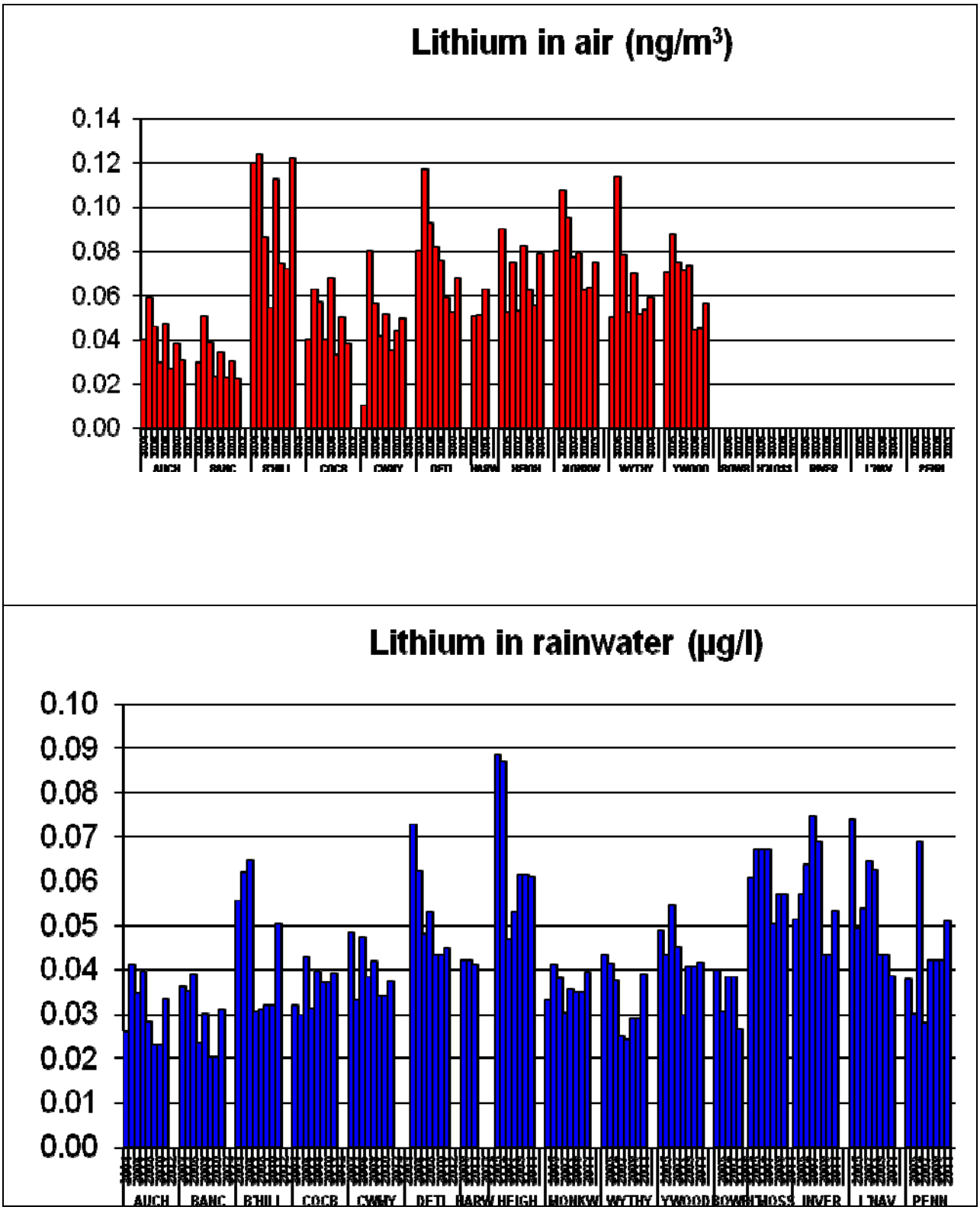


Figure 5m, Annual Average Concentration of Lithium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

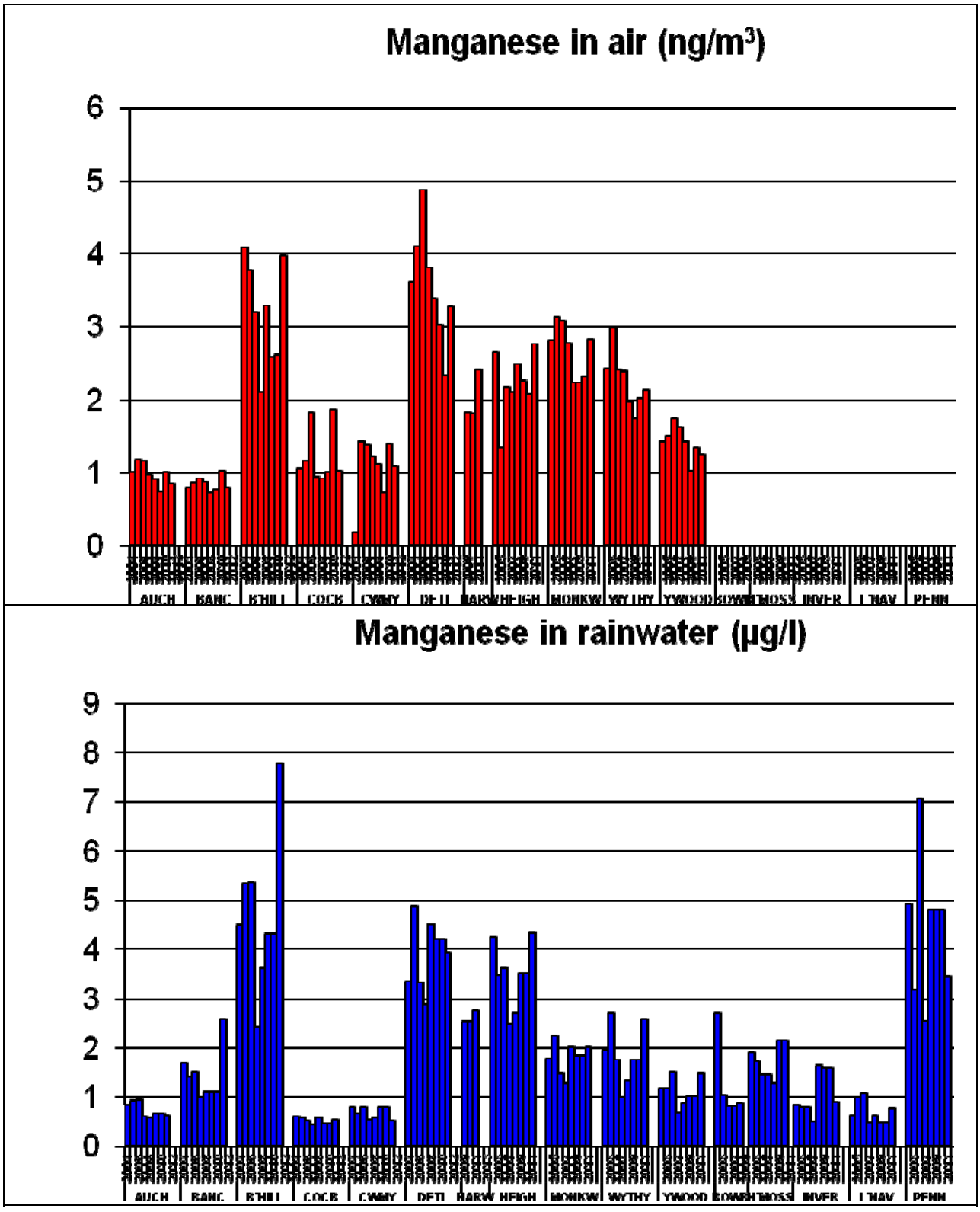


Figure 5n, Annual Average Concentration of Manganese in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

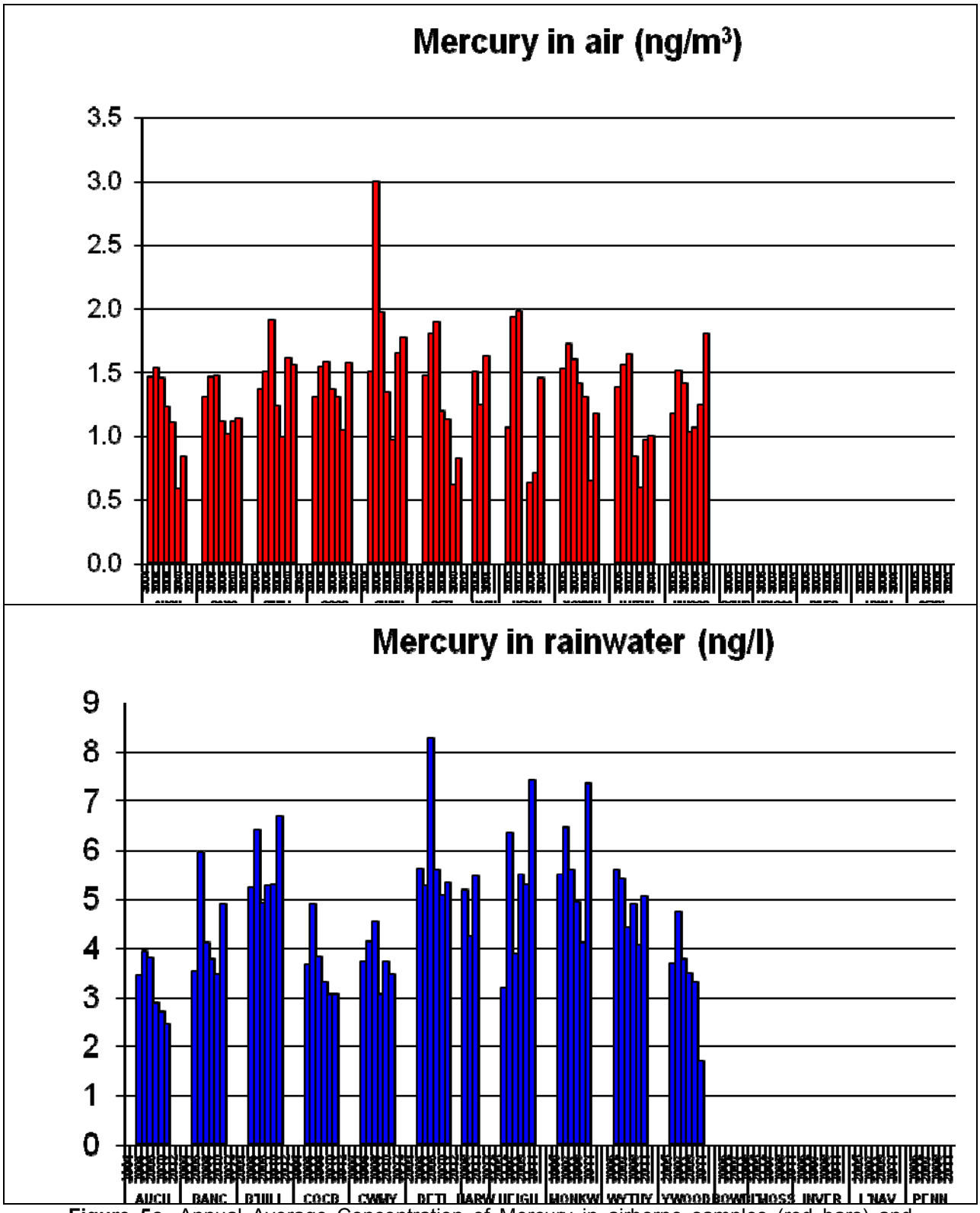


Figure 5o, Annual Average Concentration of Mercury in airborne samples (red bars) and rainwater (blue bars) between 2004 and 2011.

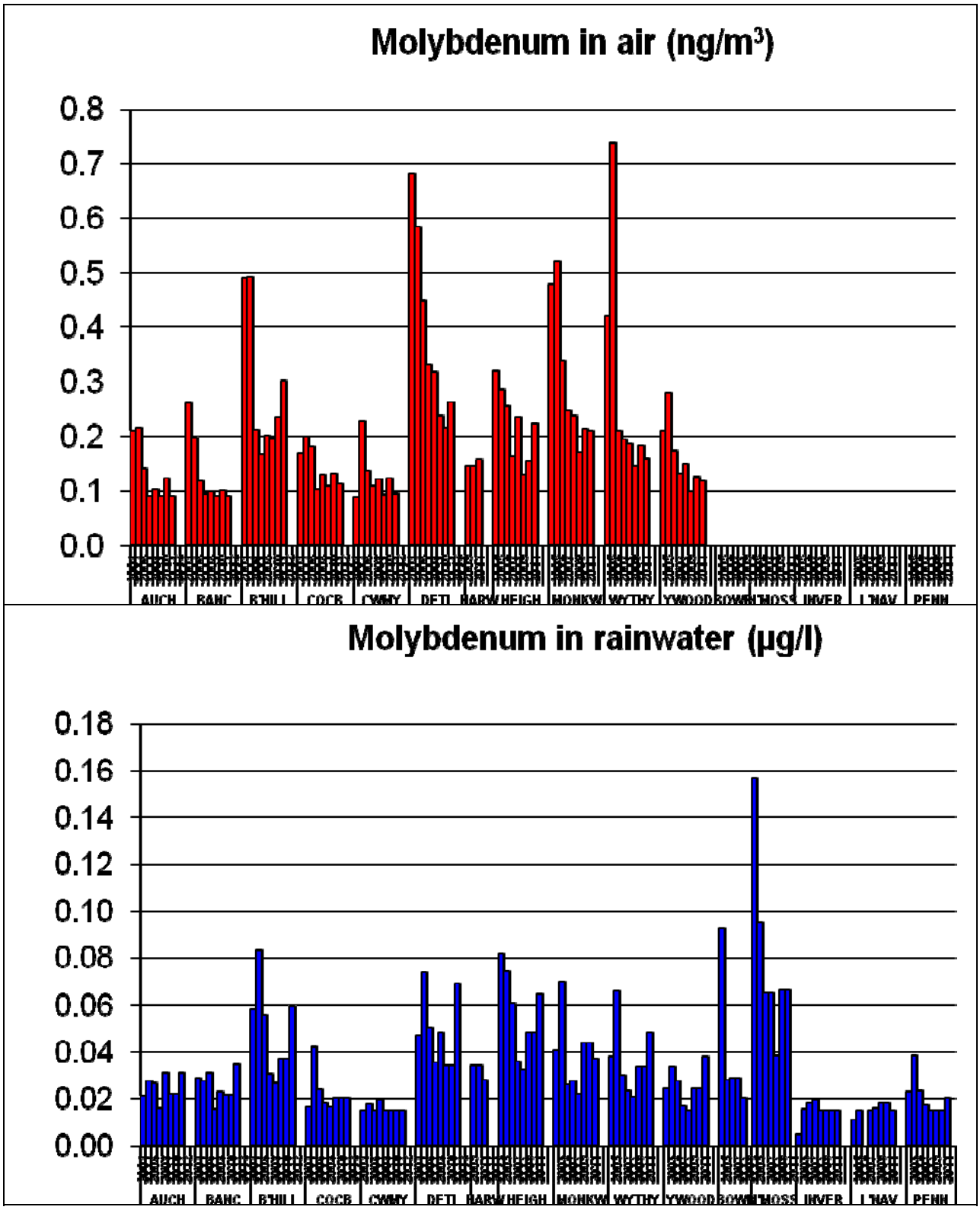


Figure 5p, Annual Average Concentration of Molybdenum in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

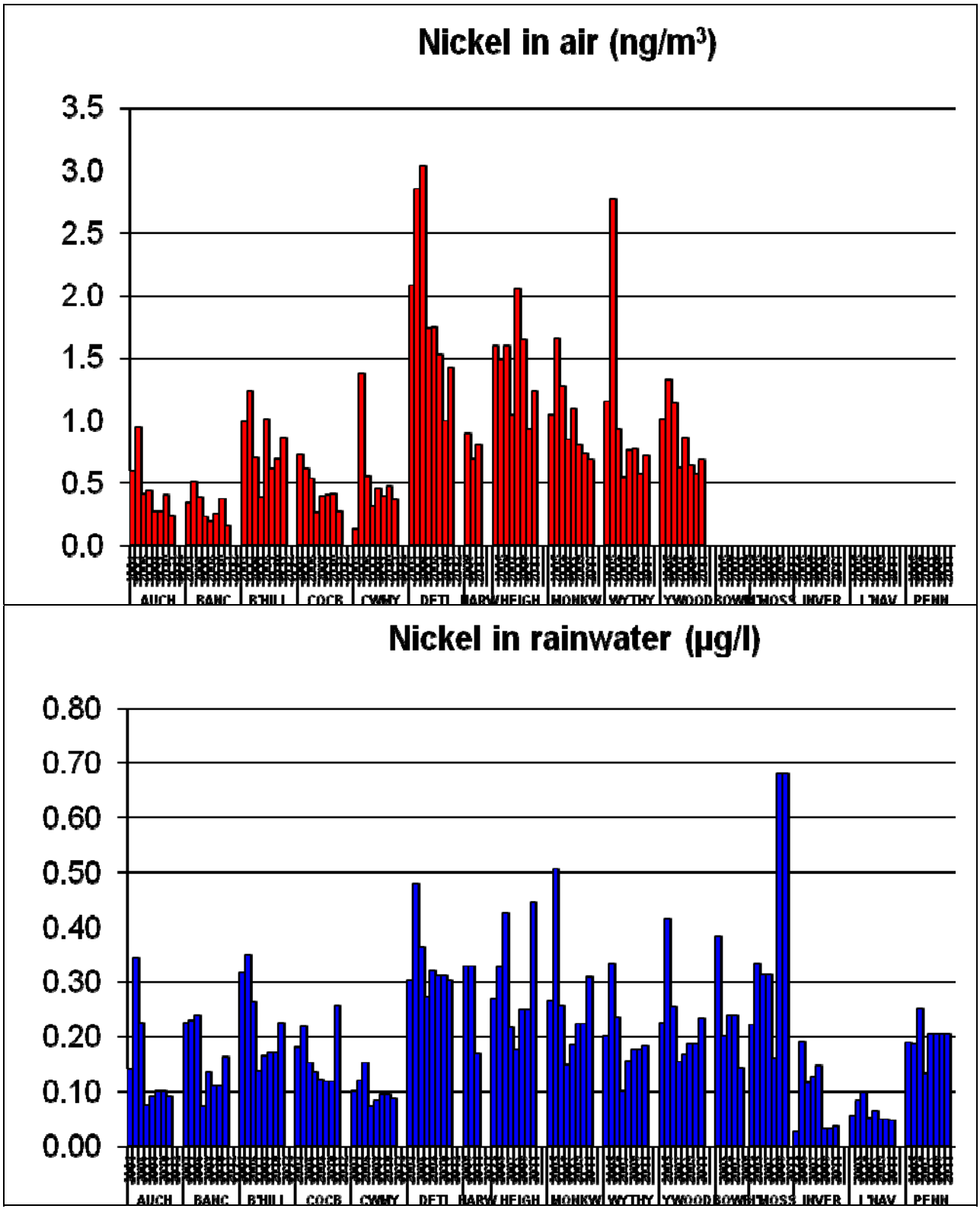


Figure 5q, Annual Average Concentration of Nickel in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

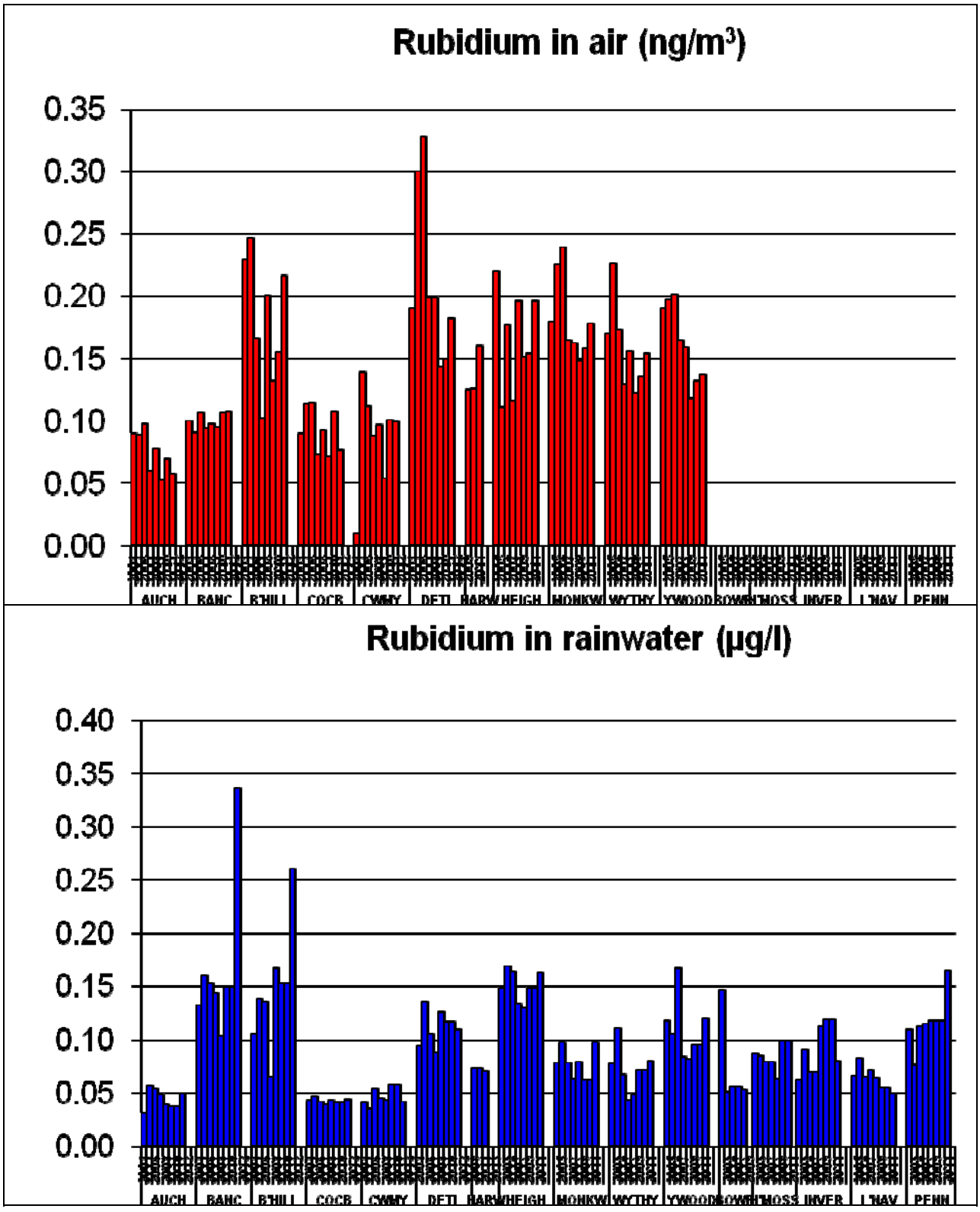


Figure 5r Annual Average Concentration of Rubidium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

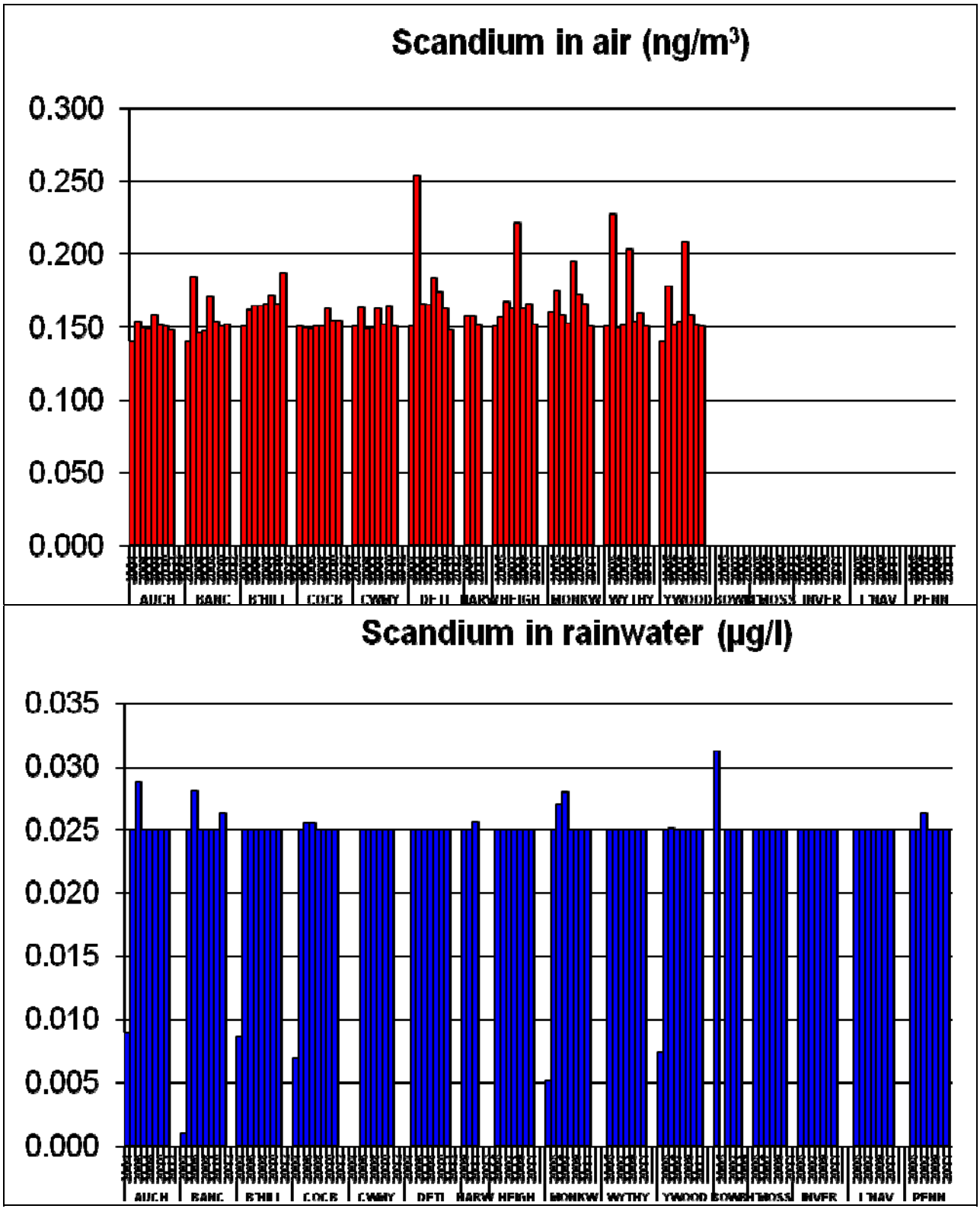


Figure 5s, Annual Average Concentration of Scandium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

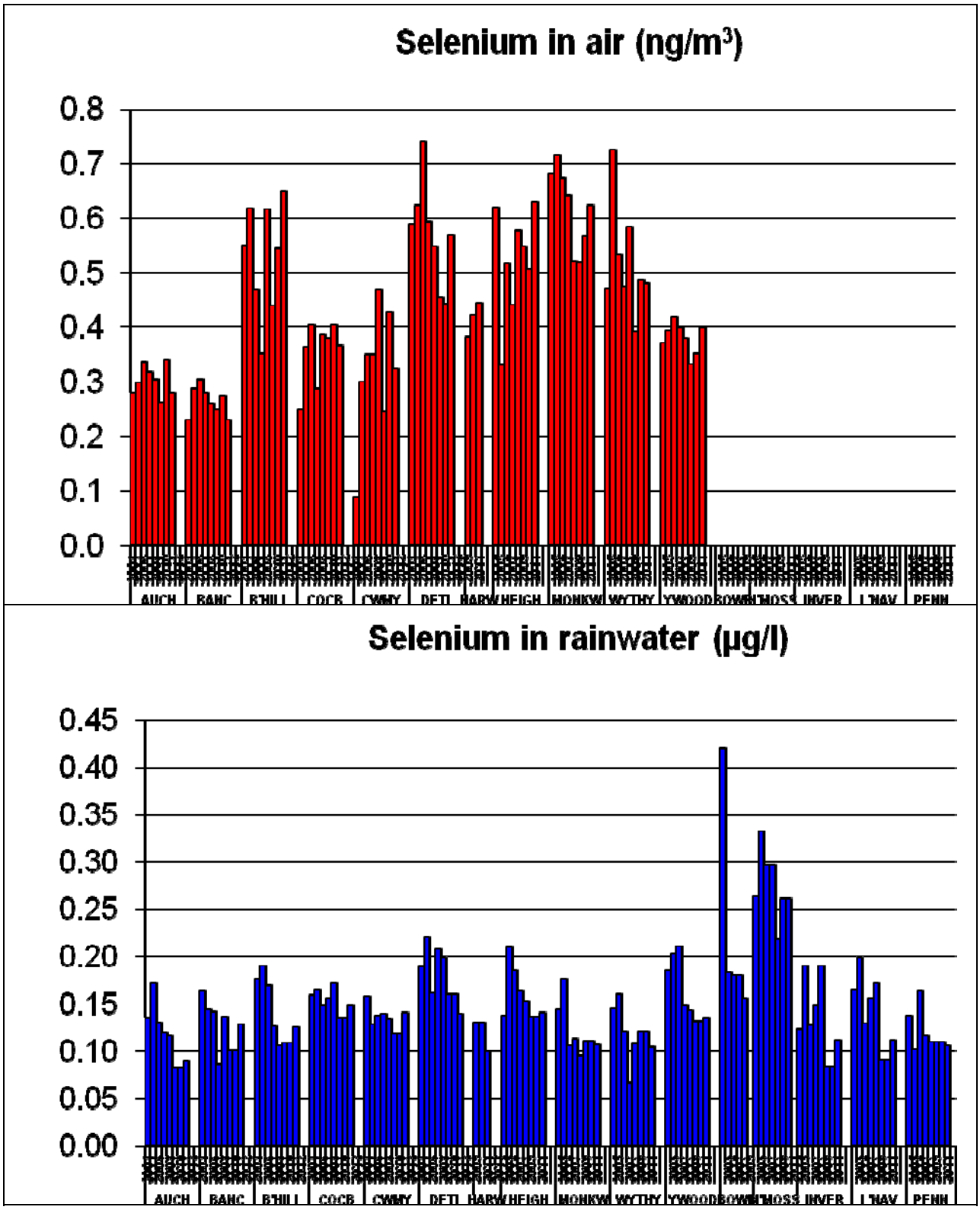


Figure 5t, Annual Average Concentration of Selenium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

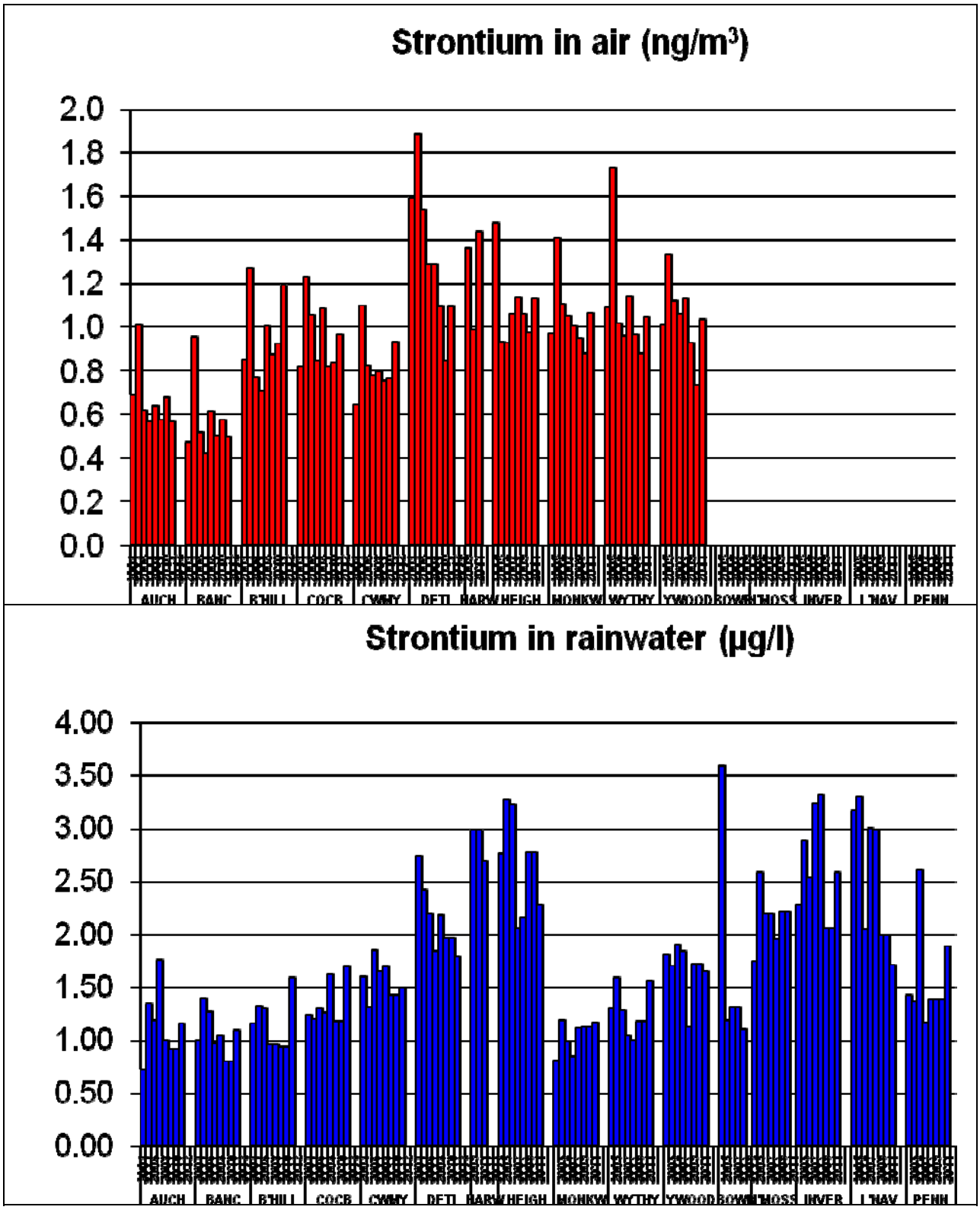


Figure 5u, Annual Average Concentration of Strontium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

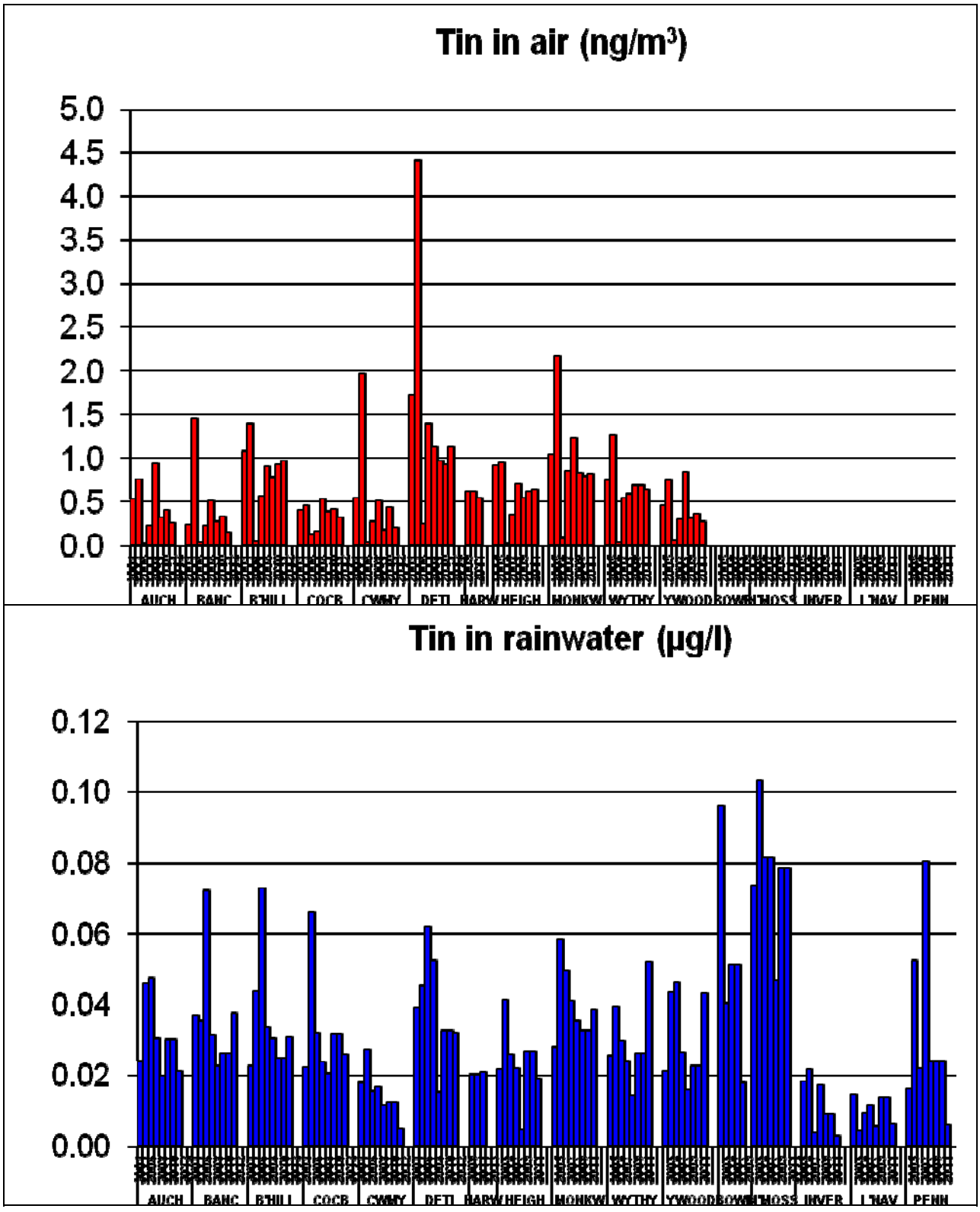


Figure 5v, Annual Average Concentration of Tin in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

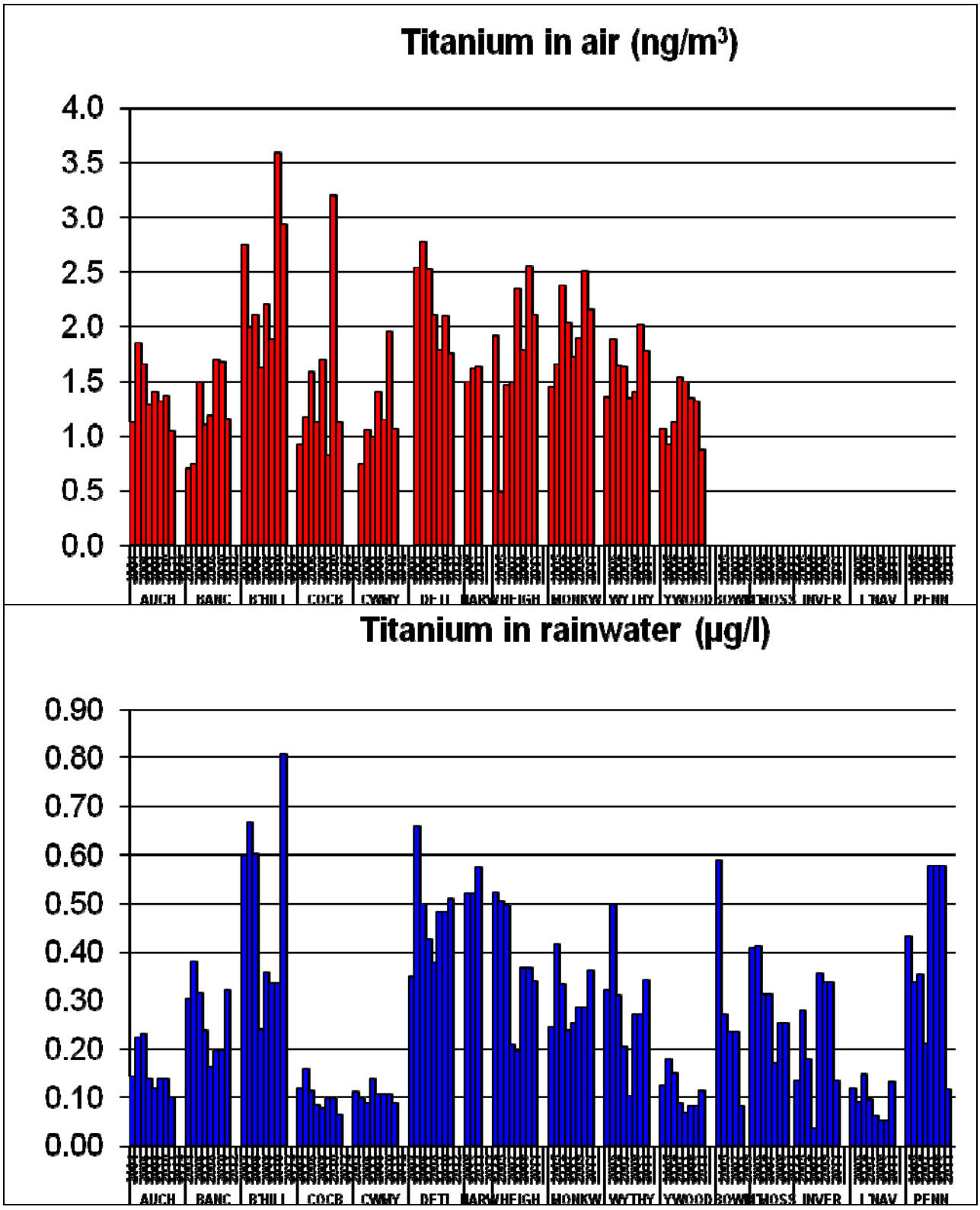


Figure 5w, Annual Average Concentration of Titanium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

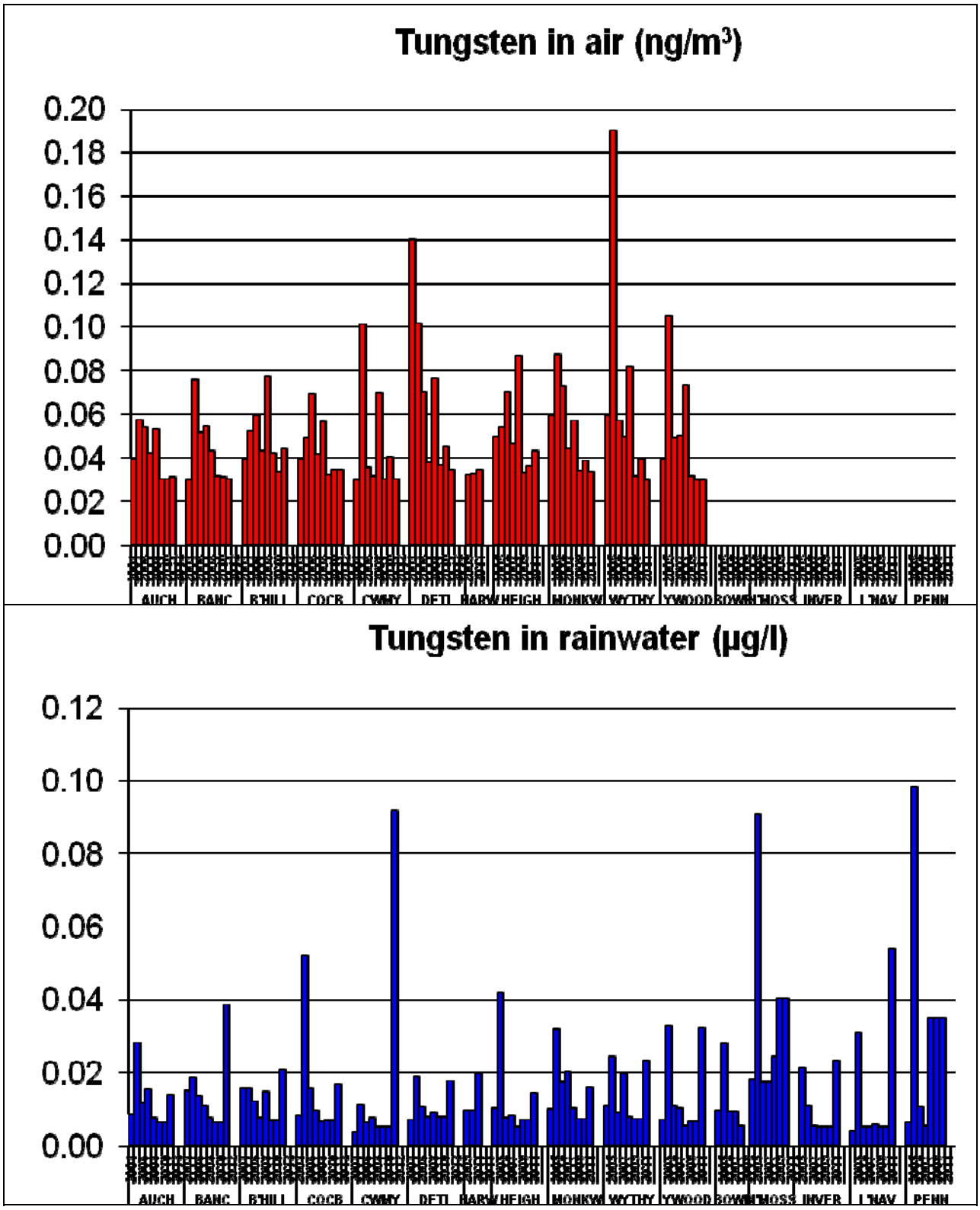


Figure 5x, Annual Average Concentration of Tungsten in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

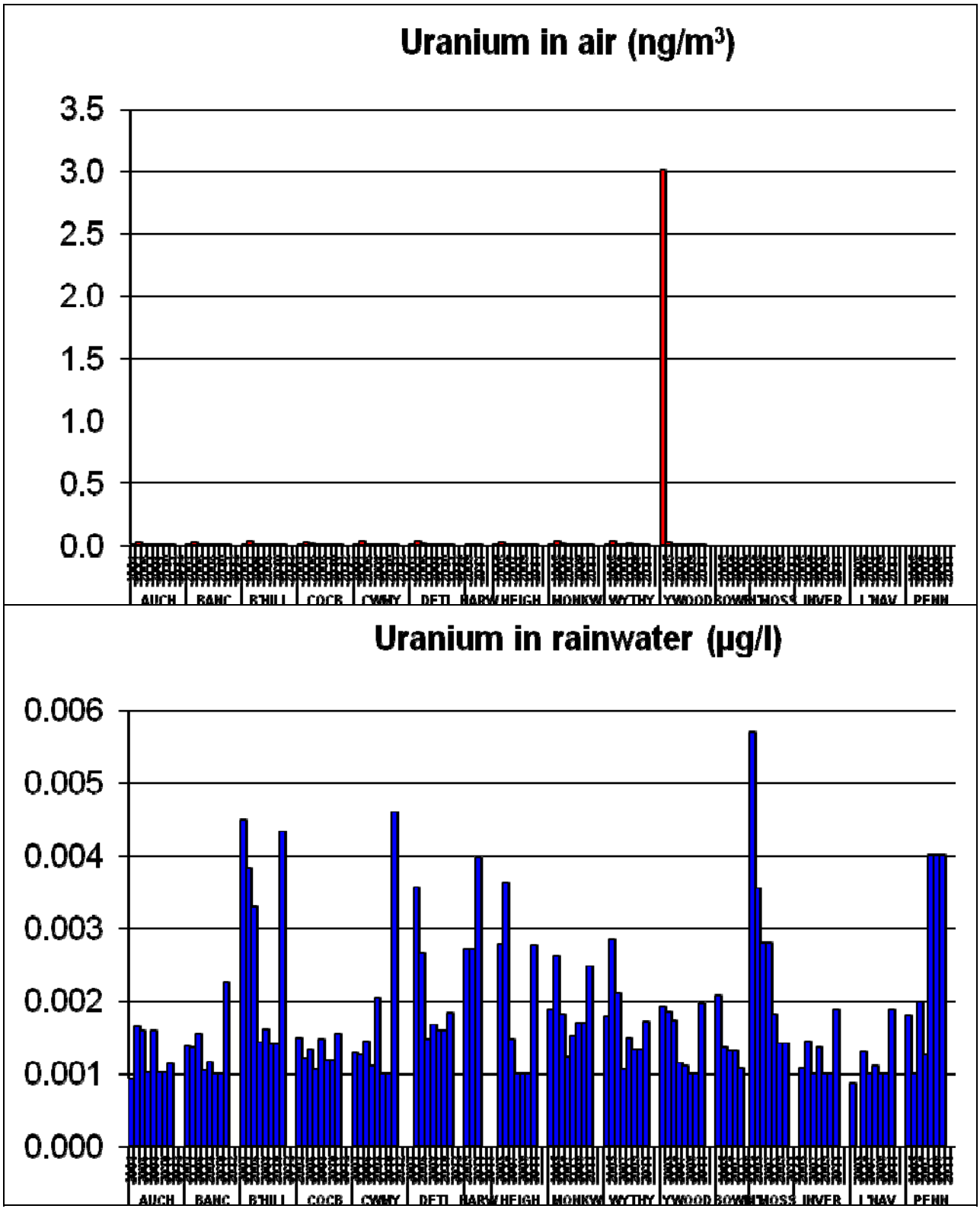


Figure 5y, Annual Average Concentration of Uranium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

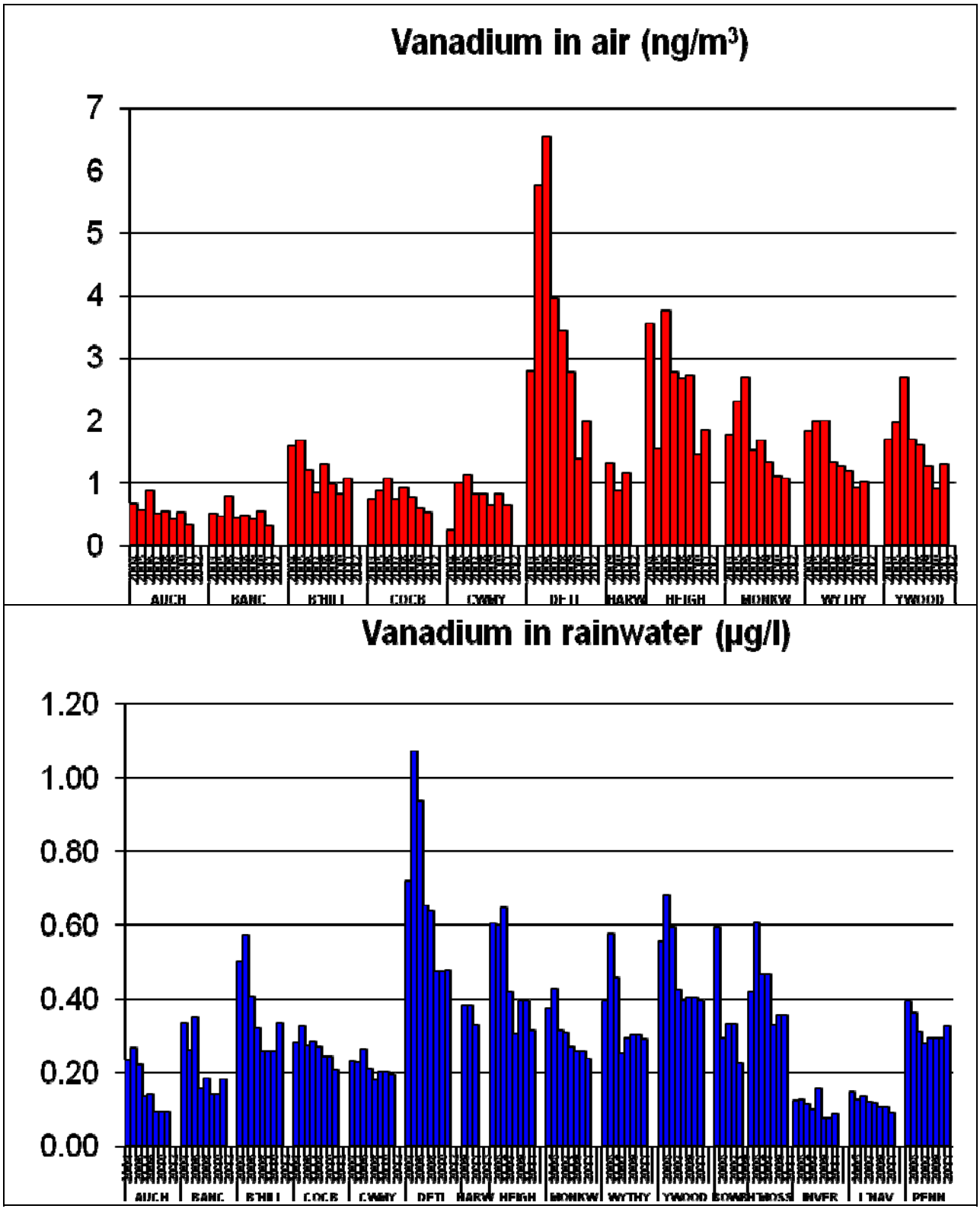


Figure 5z, Annual Average Concentration of Vanadium in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

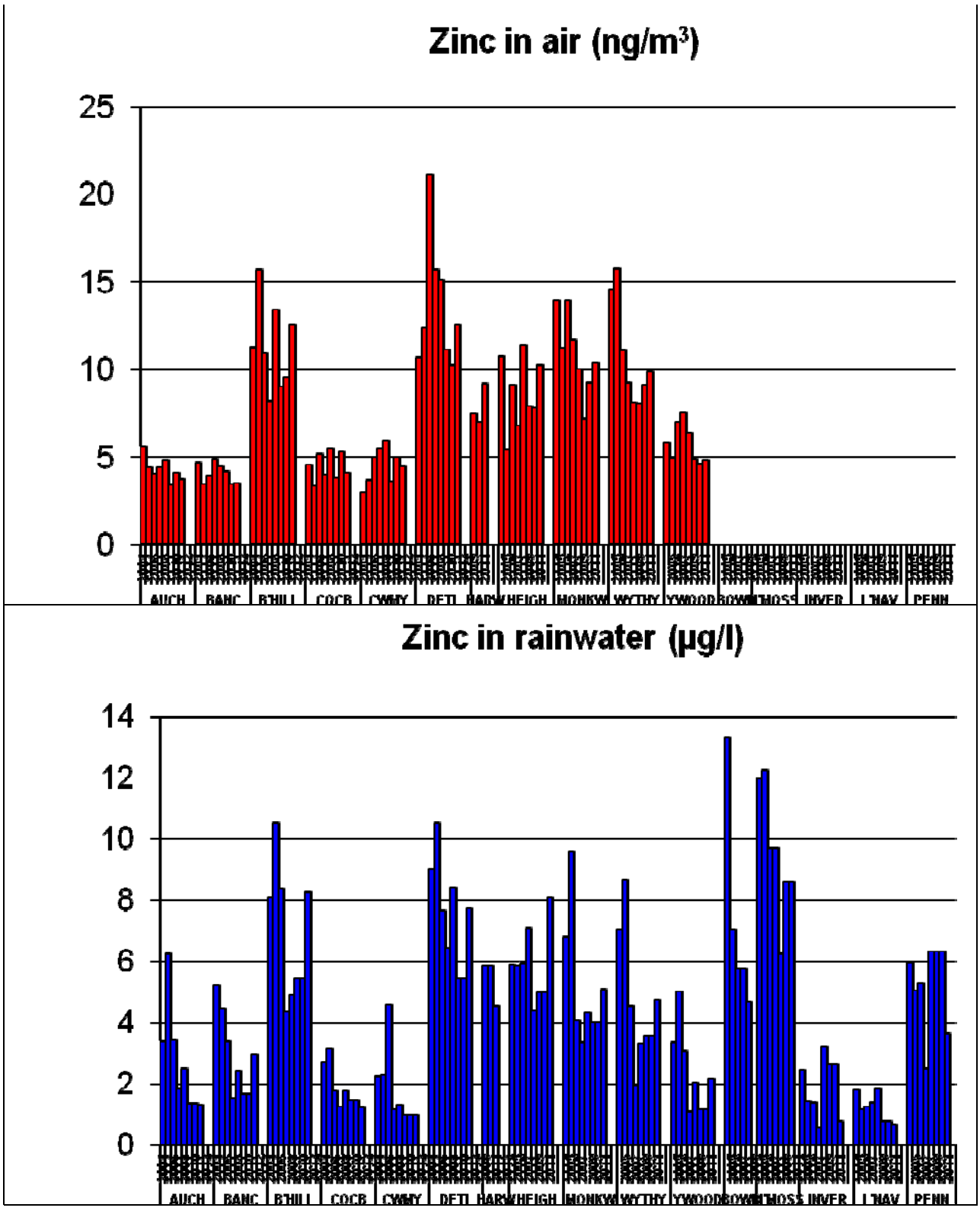


Figure 5aa, Annual Average Concentration of Zinc in airborne PM_{10} samples (red bars) and rainwater (blue bars) between 2004 and 2011.

3.2 Concentrations in Cloudwater

Samples of cloud water were collected weekly at two upland sites, Bowbeat and Holme Moss, in addition to the weekly samples of rainfall. The concentrations of metals in orographic cloud water are greater than the corresponding concentrations in rainwater, and the ratio of the two concentrations is the cloud enhancement factor. The annual mean concentrations in cloudwater and the cloud enhancement factors for both sites are presented in Table 9. The concentrations of metals in cloudwater were typically 3 to 9 times higher than the corresponding concentrations in rainwater, with similar enhancement factors for each metal at both sites. The data demonstrate that for some metals, especially aluminium, titanium, manganese, iron, cobalt, copper, barium and lead, there are clear decreases in concentrations in cloudwater at both sites. The pattern is more variable with the other metals, as inter-year variability masks any overall trend. The orographic data obtained from the cloud collection sites is used in the modelling of deposition (See Section 4). However, as the orographic enhancement between the high altitude and low altitude sites was not as large as expected, it was decided to close and decommission the cloud water sites, as sufficient data to underpin the deposition modelling had already been obtained.

Site	Year	Li	Be	Al	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Rb	Sr	Mo	Cd	Sn	Sb	Cs	Ba	W	Pb	U
Concentration (µg/l) (Bowbeat	**2004**	0.23	0.00	33.94	0.01	1.04	1.56	0.29	6.13	70.60	0.11	1.51	2.40	12.93	0.45	1.13	0.34	9.09	0.18	0.17	0.16	0.41	0.02	5.61	0.03	3.30	0.01
	2005	0.21	0.00	26.34	0.03	0.69	1.30	0.24	4.90	33.92	0.09	2.34	2.53	15.76	0.39	1.06	0.29	8.53	0.15	0.13	0.15	0.36	0.01	5.38	0.05	2.56	0.01
	2006	0.30	0.00	25.03	0.03	0.72	1.85	0.53	4.29	40.82	0.09	2.36	2.26	17.04	0.51	1.21	0.33	11.86	0.17	0.18	0.17	0.46	0.02	4.34	0.03	2.97	0.01
	2007	0.30	0.00	25.03	0.03	0.72	1.85	0.53	4.29	40.82	0.09	2.36	2.26	17.04	0.51	1.21	0.33	11.86	0.17	0.18	0.17	0.46	0.02	4.34	0.03	2.97	0.01
	2008	0.21	0.00	17.53	0.03	0.39	1.08	0.32	3.18	29.68	0.05	1.61	1.91	15.41	0.40	0.94	0.23	9.16	0.08	0.08	0.06	0.29	0.01	3.23	0.01	1.98	0.01
	mean	**0.25**	**0.00**	**25.58**	**0.02**	**0.71**	**1.53**	**0.38**	**4.56**	**43.17**	**0.09**	**2.03**	**2.27**	**15.64**	**0.45**	**1.11**	**0.30**	**10.10**	**0.15**	**0.15**	**0.14**	**0.40**	**0.02**	**4.58**	**0.03**	**2.76**	**0.01**
Concentration (µg/l) Holme Moss	**2004**	0.41	0.01	96.80	0.04	2.21	3.00	1.36	15.78	141.10	0.39	2.65	11.15	50.71	1.41	2.74	0.57	15.03	2.10	0.27	0.56	1.68	0.06	15.24	0.22	13.04	0.04
	2005	0.33	0.01	55.00	0.03	1.85	3.67	0.72	10.03	90.11	0.36	3.18	8.87	44.05	1.16	1.98	0.46	11.07	0.63	0.22	0.52	1.70	0.04	11.95	0.19	9.72	0.02
	2006	0.34	0.01	49.75	0.03	1.15	2.42	0.70	7.57	84.98	0.31	2.70	6.46	59.95	0.98	1.55	0.40	13.83	0.48	0.18	0.57	1.24	0.03	8.37	0.10	8.13	0.01
	2007	0.34	0.01	49.75	0.03	1.15	2.42	0.70	7.57	84.98	0.31	2.70	6.46	59.95	0.98	1.55	0.40	13.83	0.48	0.18	0.57	1.24	0.03	8.37	0.10	8.13	0.01
	2008	0.27	0.01	41.84	0.03	0.70	1.84	0.56	7.31	45.94	0.22	1.67	4.95	29.62	0.87	1.58	0.41	11.51	0.26	0.14	0.18	0.91	0.03	8.15	0.10	4.70	0.01
	mean	**0.34**	**0.01**	**58.63**	**0.03**	**1.41**	**2.67**	**0.81**	**9.65**	**89.42**	**0.32**	**2.58**	**7.58**	**48.85**	**1.08**	**1.88**	**0.45**	**13.05**	**0.79**	**0.20**	**0.48**	**1.35**	**0.04**	**10.42**	**0.14**	**8.75**	**0.02**
Enhancement Bowbeat	**2004**	5.67	2.52	2.52	0.36	1.76	2.64	2.23	2.26	3.16	3.09	3.95	1.46	0.97	2.83	2.68	2.30	2.53	1.92	1.72	1.70	2.80	3.83	1.94	2.60	1.21	6.47
	2005	6.85	3.01	3.88		2.56	4.43	3.12	4.75	4.49	6.16	11.68	5.96	2.23	5.35	5.77	5.71	7.20	5.32	4.73	3.66	5.76	4.12	12.77	1.74	4.30	4.64
	2006	7.83	2.57	3.20	1.03	3.05	5.62	6.46	5.36	3.77	6.30	9.83	4.03	2.95	6.21	6.75	6.03	9.12	6.08	3.66	3.40	6.21	4.60	8.78	2.90	5.06	5.07
	2007	7.83	2.57	3.20	1.03	3.05	5.62	6.46	5.36	3.77	6.30	9.83	4.03	2.95	6.21	6.75	6.03	9.12	6.08	3.66	3.40	6.21	4.60	8.78	2.90	5.06	5.07
	2008	8.01	2.37	4.91	1.00	4.77	4.84	4.64	3.68	4.95	6.12	11.33	5.30	3.30	6.18	6.04	4.31	8.32	3.93	3.89	3.20	6.05	5.59	9.51	2.43	4.67	4.92
	mean	**7.24**	**2.61**	**3.54**	**0.85**	**3.04**	**4.63**	**4.58**	**4.28**	**4.03**	**5.59**	**9.32**	**4.16**	**2.48**	**5.36**	**5.60**	**4.87**	**7.26**	**4.67**	**3.53**	**3.07**	**5.40**	**4.55**	**8.36**	**2.51**	**4.06**	**5.23**
Enhancement Holme Moss	**2004**	6.72	14.36	8.00		5.44	7.17	7.82	8.31	7.49	6.35	11.90	7.78	4.23	3.73	10.40	6.58	8.62	13.40	8.47	7.52	8.25	11.10	10.56	12.31	5.53	7.68
	2005	4.91	5.81	3.40	1.17	4.52	6.06	3.87	5.83	4.56	3.13	9.50	5.83	3.59	2.39	5.95	5.41	4.30	6.62	5.41	5.07	6.39	8.60	6.80	2.11	4.53	4.39
	2006	5.10	3.97	4.40	1.16	3.68	5.20	3.82	5.17	4.99	5.95	8.64	5.84	6.17	2.61	5.22	5.11	6.31	7.38	6.04	7.01	6.85	6.72	6.91	5.55	5.72	4.57
	2007	5.10	3.97	4.40	1.16	3.68	5.20	3.82	5.17	4.99	5.95	8.64	5.84	6.17	2.61	5.22	5.11	6.31	7.38	6.04	7.01	6.85	6.72	6.91	5.55	5.72	4.57
	2008	5.35	2.65	4.40	1.00	4.17	5.63	5.72	5.74	4.22	5.53	10.37	5.30	4.74	3.20	7.25	6.42	5.89	6.80	6.73	3.74	7.91	10.44	7.77	3.95	5.17	4.16
	mean	**5.43**	**6.15**	**4.92**	**1.12**	**4.30**	**5.85**	**5.01**	**6.05**	**5.25**	**5.38**	**9.81**	**6.12**	**4.98**	**2.91**	**6.81**	**5.73**	**6.29**	**8.32**	**6.54**	**6.07**	**7.25**	**8.71**	**7.79**	**5.90**	**5.33**	**5.07**

Table 9 Cloud Water Concentrations and Enhancement Factors for metal concentrations measured in cloud and rain water at two upland sites. The concentrations of metals in rainwater at these sites (which are used to calculate the enhancement factors) are presented in Figure 5.

4) Deposition of Heavy Metals

4.1 Calculation of Deposition

The deposition of each metal has been calculated from the annual average concentration data at each measurement site and interpolated to the whole UK, taking into account a variety of factors including orography and total rainfall data which is obtained annually from the Met Office.

Wet deposition of heavy metals is calculated by interpolating the volume-weighted annual mean rain concentration data at each of the 13 rain only sites across the UK using GIS techniques and a model which takes into account the effect of orography on rainfall to provide a more accurate estimate of wet deposition on hills. The modelling 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 lager 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.

This process allows the total wet deposition in the UK to be calculated for each metal (see Table 7), along with 5km maps of wet deposition in the UK (see section 5).

The method of calculating dry deposition is similar to that for 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 the calculated by multiplying the dry deposition velocity with the interpolated air concentration field.
This process allows the total dry deposition in the UK to be calculated for each metal (see Table 7), along with 5km maps of dry deposition, and dry deposition to grassland and forest (assuming 100% coverage of each habitat type in the UK)(see section 5).

Deposition of cloud droplets accounts for very small fraction of the total metal deposition at a UK scale. However, it can make a significant contribution to heavy metal deposition locally, especially in (often sensitive) upland areas. It is therefore included in the deposition budget calculations (see Table 7). To calculate deposition from cloud, the interpolated rainfall concentrations (used to calculate wet deposition) are multiplied by the cloud enhancement factors shown in Table 6, 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 Deposition data

The total deposition budget for the UK is presented in Table 7. This show that for all metals, with the exception of antimony and tin, the greatest deposition occurs as wet deposition, ie via rain and snow. Dry deposition generally accounts for 30 to 40% of total deposition, and deposition from cloudwater is low, although this will be more significant in localised high altitude areas.

Although the concentration data demonstrates some decreases in metal concentrations, especially at the southern and eastern sites, this trend is less evident in the deposition data which is subject to changes in both measured concentrations and meteorological conditions. There is no clear overall reduction in deposition of metals between 2004 and 2011, with inter-annual variability masking any overall temporal trend.

Metal		Deposition Budget 2004-2011								
		2004	2005	2006	2007	2008	2009 14sites	2010 14sites	2011 14sites	units
Al	dry		2291.17	2037.58	1522.51	1533.15	1273.12	1298.82	1493.71	tonnes
Al	wet		3221.47	3181.98	1992.90	3498.79	2581.50	2086.06	3096.99	tonnes
Al	cloud		86.64	76.12	47.80	75.51	62.27	63.47	79.4419	tonnes
Al	**total**		**5599.28**	**5295.68**	**3563.21**	**5107.45**	**3916.90**	**3448.35**	**4670.13**	**tonnes**
As	dry	23.07	22.01	22.46	19.00	18.97	16.48	20.02	18.4912	tonnes
As	wet	51.68	50.13	53.59	44.57	50.70	44.66	37.78	50.8772	tonnes
As	cloud	0.95	1.02	0.99	0.81	0.86	0.85	0.91	0.986598	tonnes
As	**total**	**75.70**	**73.17**	**77.04**	**64.37**	**70.52**	**62.00**	**58.70**	**70.355**	**tonnes**
Ba	dry		69.04	58.30	54.48	54.43	76.98	68.16	90.8944	tonnes
Ba	wet		223.80	237.26	163.12	261.13	818.74	388.38	713.923	tonnes
Ba	cloud		6.10	5.71	3.80	5.67	18.26	11.13	18.3467	tonnes
Ba	**total**		**298.94**	**301.26**	**221.40**	**321.23**	**913.97**	**467.67**	**823.164**	**tonnes**
Be	dry		0.64	0.47	0.42	0.51	0.41	0.40	0.395297	tonnes
Be	wet		0.72	0.83	0.85	0.86	0.71	0.57	1.04026	tonnes
Be	cloud		0.02	0.02	0.02	0.02	0.02	0.02	0.024712	tonnes
Be	**total**		**1.38**	**1.32**	**1.29**	**1.39**	**1.13**	**0.99**	**1.46028**	**tonnes**
Cd	dry	2.54	2.77	2.61	2.11	2.39	1.66	1.96	1.9551	tonnes
Cd	wet	7.49	7.00	6.74	3.87	6.76	5.79	4.37	4.33374	tonnes
Cd	cloud	0.20	0.21	0.18	0.10	0.16	0.15	0.15	0.123755	tonnes
Cd	**total**	**10.23**	**9.97**	**9.52**	**6.08**	**9.31**	**7.60**	**6.47**	**6.41259**	**tonnes**
Co	dry		4.07	1.95	1.63	1.89	1.56	1.66	1.69409	tonnes
Co	wet		5.93	6.00	4.48	6.12	5.36	4.02	4.5767	tonnes
Co	cloud		0.16	0.14	0.10	0.13	0.13	0.12	0.11765	tonnes
Co	**total**		**10.16**	**8.09**	**6.22**	**8.14**	**7.05**	**5.81**	**6.38843**	**tonnes**
Cr	dry	20.15	25.63	22.20	31.91	35.06	37.55	24.62	22.6635	tonnes
Cr	wet	39.91	25.24	38.50	27.98	29.98	32.72	13.61	19.7722	tonnes
Cr	cloud	1.09	0.78	1.05	0.78	0.77	0.94	0.48	0.571655	tonnes
Cr	**total**	**61.14**	**51.65**	**61.76**	**60.67**	**65.82**	**71.20**	**38.71**	**43.0075**	**tonnes**

Table 10 Deposition Budget of Heavy Metals in the UK, 2004 to 2011

Metal		Deposition Budget 2004-2011								
		2004	2005	2006	2007	2008	2009 14sites	2010 14sites	2011 14sites	units
Cs	dry		0.92	0.95	0.61	0.83	0.45	0.66	0.713854	tonnes
Cs	wet		1.02	1.34	0.65	1.19	0.87	0.88	1.12349	tonnes
Cs	cloud		0.03	0.03	0.02	0.03	0.02	0.03	0.029617	tonnes
Cs	**total**		**1.98**	**2.32**	**1.27**	**2.04**	**1.35**	**1.57**	**1.86696**	**tonnes**
Cu	dry	95.55	113.75	85.54	91.87	103.58	105.52	114.04	106.552	tonnes
Cu	wet	221.82	212.49	225.59	148.87	217.30	187.89	146.80	224.162	tonnes
Cu	cloud	6.51	6.87	6.49	4.14	5.72	5.47	5.40	6.98657	tonnes
Cu	**total**	**323.87**	**333.11**	**317.62**	**244.88**	**326.61**	**298.88**	**266.25**	**337.7**	**tonnes**
Fe	dry		3363.49	2807.38	2931.16	2709.08	2340.35	2724.95	2845.92	tonnes
Fe	wet		3803.96	4752.86	2971.31	4145.17	3666.45	2689.11	3527.65	tonnes
Fe	cloud		102.27	114.11	71.88	89.83	89.04	82.04	90.609	tonnes
Fe	**total**		**7269.72**	**7674.35**	**5974.35**	**6944.07**	**6095.84**	**5496.10**	**6464.17**	**tonnes**
Hg	dry		0.00	0.00	0.00	0.00	0.00	0.00	0	kg
Hg	wet		1791.00	2075.97	2518.84	2046.79	1601.66	1201.68	1779.56	kg
Hg	cloud		46.57	48.56	59.01	44.98	39.04	37.42	42.8475	kg
Hg	**total**		**1837.57**	**2124.53**	**2577.85**	**2091.76**	**1640.70**	**1239.10**	**1822.41**	**kg**
Li	dry		3.47	2.75	2.01	2.75	1.81	2.04	2.2953	tonnes
Li	wet		17.70	22.04	18.46	19.72	14.78	11.19	18.2817	tonnes
Li	cloud		0.45	0.51	0.42	0.42	0.35	0.35	0.422176	tonnes
Li	**total**		**21.62**	**25.31**	**20.89**	**22.89**	**16.94**	**13.57**	**20.9991**	**tonnes**
Mn	dry		82.73	85.61	69.78	68.19	59.44	70.59	74.2289	tonnes
Mn	wet		622.34	772.01	433.67	715.16	683.31	503.90	744.945	tonnes
Mn	cloud		16.65	18.47	10.14	15.34	16.32	15.95	19.3641	tonnes
Mn	**total**		**721.72**	**876.09**	**513.58**	**798.69**	**759.07**	**590.44**	**838.537**	**tonnes**
Mo	dry		14.59	8.36	6.18	6.73	5.38	6.36	6.27816	tonnes
Mo	wet		13.78	12.03	8.79	9.90	9.72	12.39	12.3961	tonnes
Mo	cloud		0.37	0.29	0.21	0.22	0.24	0.39	0.303924	tonnes
Mo	**total**		**28.74**	**20.68**	**15.18**	**16.84**	**15.34**	**19.14**	**18.9781**	**tonnes**
Ni	dry	31.48	50.65	32.79	20.35	26.70	23.04	21.43	20.961	tonnes
Ni	wet	73.96	102.13	88.05	49.89	64.17	54.51	57.71	64.8845	tonnes
Ni	cloud	1.74	2.58	2.06	1.10	1.36	1.30	1.75	1.57957	tonnes
Ni	**total**	**107.17**	**155.36**	**122.90**	**71.34**	**92.22**	**78.85**	**80.89**	**87.425**	**tonnes**
Pb	dry	146.16	128.49	132.07	103.65	97.01	86.56	104.45	94.8132	tonnes
Pb	wet	337.22	262.63	219.81	140.88	207.74	223.13	176.57	202.406	tonnes
Pb	cloud	7.92	6.93	5.21	3.17	4.41	5.19	5.15	5.10547	tonnes
Pb	**total**	**491.30**	**398.05**	**357.08**	**247.70**	**309.16**	**314.87**	**286.16**	**302.325**	**tonnes**
Rb	dry		6.78	6.50	4.59	5.51	4.20	5.02	5.39132	tonnes
Rb	wet		35.86	37.55	31.79	38.03	36.81	28.26	49.1057	tonnes
Rb	cloud		0.95	0.93	0.78	0.84	0.92	0.94	1.26715	tonnes
Rb	**total**		**43.59**	**44.98**	**37.16**	**44.38**	**41.94**	**34.22**	**55.7642**	**tonnes**

Table 10 (continued) Deposition Budget of Heavy Metals in the UK, 2004 to 2011.

Metal		Deposition Budget 2004-2011								
		2004	2005	2006	2007	2008	2009 14sites	2010 14sites	2011 14sites	units
Sb	dry		28.96	29.42	25.06	24.10	20.25	26.10	25.1761	tonnes
Sb	wet		24.74	26.34	12.95	21.90	19.85	20.32	22.4991	tonnes
Sb	cloud		0.67	0.63	0.30	0.47	0.48	0.62	0.571573	tonnes
Sb	**total**		**54.37**	**56.39**	**38.30**	**46.47**	**40.58**	**47.03**	**48.2467**	**tonnes**
Sc	dry		7.52	6.52	6.52	7.49	6.79	6.71	6.56477	tonnes
Sc	wet		9.90	11.38	10.96	11.68	10.46	7.26	11.1148	tonnes
Sc	cloud		0.26	0.27	0.26	0.26	0.26	0.23	0.259929	tonnes
Sc	**total**		**17.68**	**18.17**	**17.74**	**19.42**	**17.50**	**14.20**	**17.9395**	**tonnes**
Se	dry	13.64	15.41	15.44	13.55	15.30	12.37	14.54	14.4373	tonnes
Se	wet	68.04	67.38	62.37	56.98	67.46	45.12	35.02	52.3213	tonnes
Se	cloud	2.08	2.22	1.91	1.72	1.90	1.44	1.40	1.60216	tonnes
Se	**total**	**83.76**	**85.00**	**79.73**	**72.25**	**84.66**	**58.93**	**50.96**	**68.361**	**tonnes**
Sn	dry		60.78	2.76	17.92	32.29	20.15	23.19	19.6368	tonnes
Sn	wet		14.94	16.56	11.72	8.75	9.43	6.98	9.00847	tonnes
Sn	cloud		0.40	0.41	0.28	0.19	0.24	0.21	0.225589	tonnes
Sn	**total**		**76.13**	**19.73**	**29.92**	**41.23**	**29.81**	**30.39**	**28.8708**	**tonnes**
Sr	dry		52.74	37.51	34.00	39.12	35.11	33.69	39.1089	tonnes
Sr	wet		729.96	763.70	773.77	805.52	615.03	433.14	753.557	tonnes
Sr	cloud		17.94	17.66	17.54	17.04	14.58	13.45	17.0765	tonnes
Sr	**total**		**800.65**	**818.86**	**825.31**	**861.68**	**664.72**	**480.28**	**809.74**	**tonnes**
Ti	dry		58.92	71.08	60.90	68.10	62.02	90.32	63.2246	tonnes
Ti	wet		115.10	107.60	64.92	96.30	99.90	59.57	90.1851	tonnes
Ti	cloud		3.02	2.56	1.59	2.06	2.37	1.82	2.28522	tonnes
Ti	**total**		**177.04**	**181.24**	**127.42**	**166.46**	**164.30**	**151.72**	**155.695**	**tonnes**
U	dry		1.29	0.47	0.30	0.41	0.27	0.27	0.265447	tonnes
U	wet		0.67	0.76	0.49	0.75	0.56	0.42	0.934656	tonnes
U	cloud		0.02	0.02	0.01	0.02	0.01	0.01	0.02347	tonnes
U	**total**		**1.97**	**1.25**	**0.80**	**1.18**	**0.85**	**0.70**	**1.22358**	**tonnes**
V	dry	59.55	70.10	85.51	54.56	56.64	47.22	38.26	39.3941	tonnes
V	wet	130.14	129.22	131.91	98.64	106.13	85.08	65.65	83.51	tonnes
V	cloud	3.26	3.59	3.32	2.39	2.39	2.16	2.09	2.18555	tonnes
V	**total**	**192.94**	**202.91**	**220.74**	**155.60**	**165.16**	**134.45**	**106.00**	**125.09**	**tonnes**
W	dry		3.64	2.43	1.89	2.74	1.41	1.49	1.43038	tonnes
W	wet		12.25	4.92	4.32	4.16	3.34	3.19	12.6737	tonnes
W	cloud		0.32	0.12	0.10	0.09	0.08	0.10	0.319611	tonnes
W	**total**		**16.21**	**7.46**	**6.31**	**6.99**	**4.83**	**4.79**	**14.4237**	**tonnes**
Zn	dry	380.26	338.90	364.88	323.22	350.96	263.46	286.21	312.079	tonnes
Zn	wet	1861.45	1816.31	1523.14	850.49	1441.58	1098.51	875.78	1053.72	tonnes
Zn	cloud	28.74	31.59	24.01	12.87	19.98	16.79	17.11	17.6573	tonnes
Zn	**total**	**2270.44**	**2186.80**	**1912.02**	**1186.59**	**1812.52**	**1378.76**	**1179.11**	**1383.46**	**tonnes**

Table 10 (continued) Deposition Budget of Heavy Metals in the UK, 2004 to 2011.

4.2) Comparison of Measured Deposition Data with the NAEI Emissions data

UK Data on the primary emissions to the atmosphere of 13 heavy metals are reported annually as part of the National Atmospheric Emissions Inventory (NAEI) (Murrells et al., 2009). Figure 5 shows the changes in the reported emissions of the 13 metals between 1970 and 2007. The emissions are presented in the histograms, and the error bar refers to the maximum level of uncertainty in the data as reported in the 2007 Inventory. Emissions of all metals included in the NAEI have declined since their peak values in 1970 (or later for metals whose emission data was only recorded in more recent inventories). The main emission sources of these metals are summarised in Table 11. Figure 5 also shows changes in the annual deposition of metals to the UK as calculated from the Rural Heavy Metals Monitoring network, as represented by the line graph. Deposition data from this network is currently only available for the years 2004 to 2011.

Metal	Emission Sources
Arsenic	Historically, the largest source of arsenic in the UK has been the combustion of coal, with other sources being very small by comparison. More recently, with the decline in use of coal, the main source of arsenic has become the industrial combustion of timber which has been treated with chromated copper arsenate (CCA).
Beryllium	Beryllium is emitted to the atmosphere during the combustion of fossil fuels including coal and heavy liquid fuels.
Cadmium	The main sources of cadmium emissions in the UK are from industrial combustion processes including energy production, non-ferrous metal production (such as lead-zinc smelting plants and lead battery recycling plants) and the manufacture of iron and steel.
Chromium	The main sources of chromium emissions in the UK are coal combustion, the production of iron and steel in integrated works, electric arc furnaces and the production of chromium based chemicals. Emissions from the industrial combustion of timber treated with chromated copper arsenate (CCA) have been increasing in significance following a decline in coal consumption.
Copper	The main sources of copper emissions in the UK are from tyre and brake wear, metal production, industrial combustion of lubricants and the combustion of coal.
Lead	The largest source of lead emissions in the UK was traditionally from its use as an anti-knock additive in petrol. However the general sale of leaded petrol was phase dout at the end of 1999, with a subsequent decline in emissions from the road transport sector. The largest emissions of lead are now from iron and steel works, and other industrial combustion processes.
Manganese	The greatest emissions of manganese in the UK are from metal production plants, followed by production of electricity, heat production and other industrial combustion processes.
Mercury	The main sources of mercury in the UK are emissions from generation of electricity and heat production, waste incineration, the manufacture of chlorine in mercury cells and the combustion of coal and other fuels.
Nickel	The main source of nickel emissions in the UK is from the combustion of heavy fuel oil and Orimulsion. The combustion of coal was formerly the main UK source.
Selenium	The main emission sources of selenium in the UK are from glass production and combustion for the production of public electricity and heat generation. The main source of selenium in early years was coal combustion.
Tin	The main emissions sources of tin are from combustion and road transport, with emissions greatest from petroleum-based fuels.
Vanadium	The main source of vanadium emissions in the UK is from the road transport sector. Combustion of petroleum based fuels accounts for 97% of total vanadium emissions. Emissions from the combustion of coal and heavy fuel oil in industrial processes have recently declined. Emissions from iron and steel plants vary depending on the type of steel produced and its vanadium content.
Zinc	The main sources of zinc emissions in the UK are metal production and industrial combustion. Emissions from road transport, especially tyre and brake wear are also significant.

Table 11 Emissions Sources of Heavy Metals in the UK. Data taken from Murrells et al (2009)

For seven of the thirteen metals with emission data, (arsenic, copper, cadmium, lead, manganese, selenium and zinc), the calculated annual deposition amount is far greater than the maximum emission data including the highest degree of quantified uncertainty. For most of these metals, the deposition is approximately two times greater than the emissions. However, for manganese, the difference is nearly 12 times. The deposition of beryllium, mercury and vanadium are 30 to 40% of the corresponding reported emissions. Deposition of

chromium, nickel and tin are within the range of reported uncertainty of emissions. Although emissions of all metals have declined since 1990 and 2000, there has been no overall decline in total deposition. This is due to the short time series and high inter-annual variability in the deposition data.

The discrepancy between the emissions and deposition of heavy metals can partially be explained by a combination of factors. The emissions data only include primary emissions from known anthropogenic sources. They do not include unknown anthropogenic sources, fugitive emissions from known sources, natural emissions and emissions released from non-UK sources. The deposition data will include metals which are not the result of primary emissions, including the deposition of re-suspended material, ie dust and soil particles which are blown into the atmosphere from the land surface due to the action of wind and turbulence along with material imported into the UK atmosphere from foreign sources.

The deposition data are a calculated from measured concentrations of metals sampled from rural sites away from the major sources of metal emissions. If monitoring from industrial and urban areas were included in the calculation, the total deposition of the metal in the UK is likely to be higher, further increasing the discrepancy between reported emissions and calculated deposition. This is an area that warrants further investigation, as only by better quantifying the full range of emissions to the atmosphere is it likely that the discrepancy will be reduced.

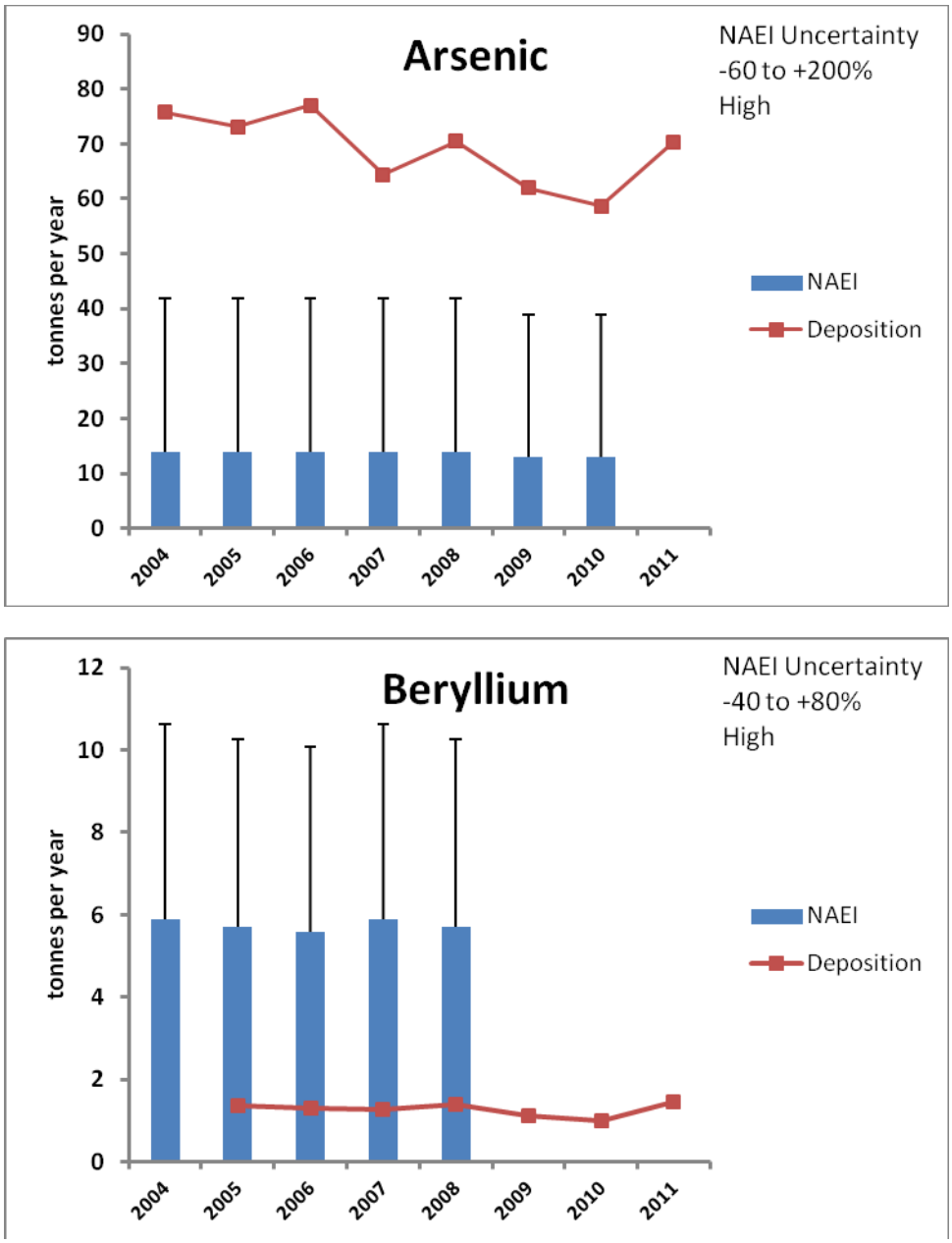


Figure 6a Comparison of the Emissions (Blue bars) and Deposition (red line) of Arsenic, and Beryllium in the UK 2004-2011

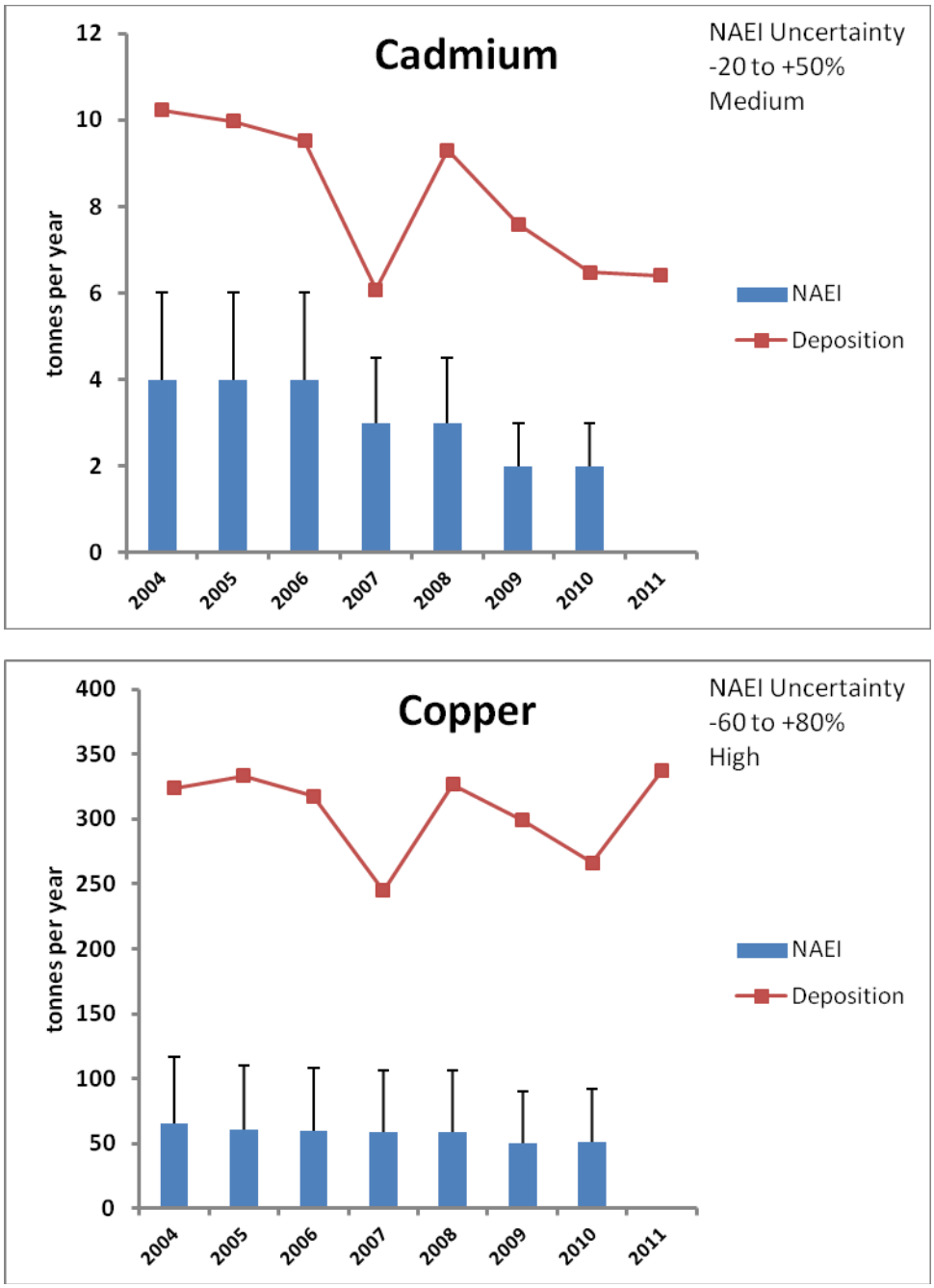
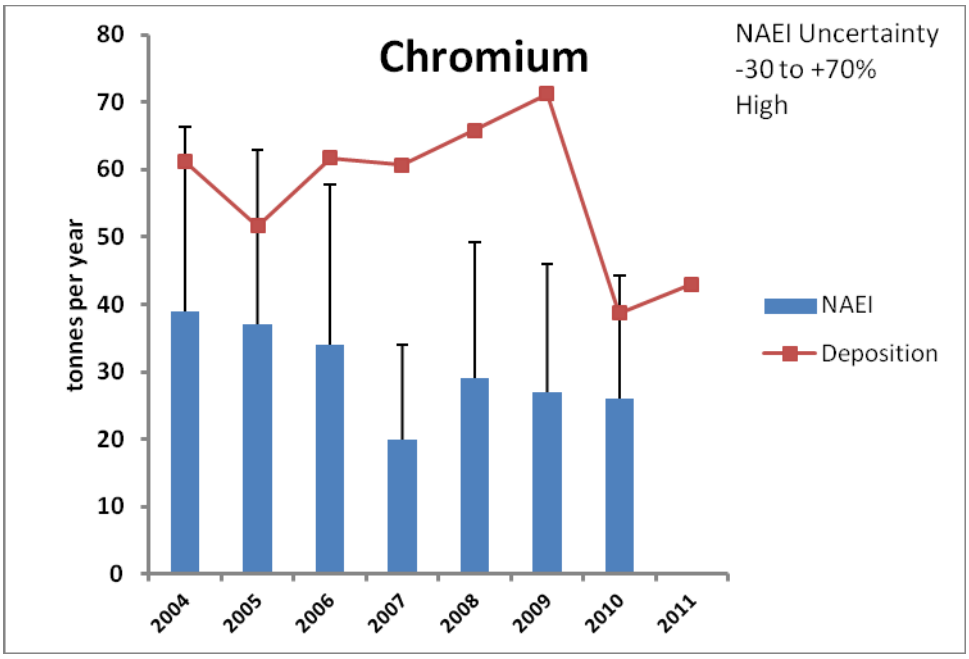


Figure 6b Comparison of the Emissions (Blue bars) and Deposition (red line) of Cadmium and Copper in the UK,2004-2011



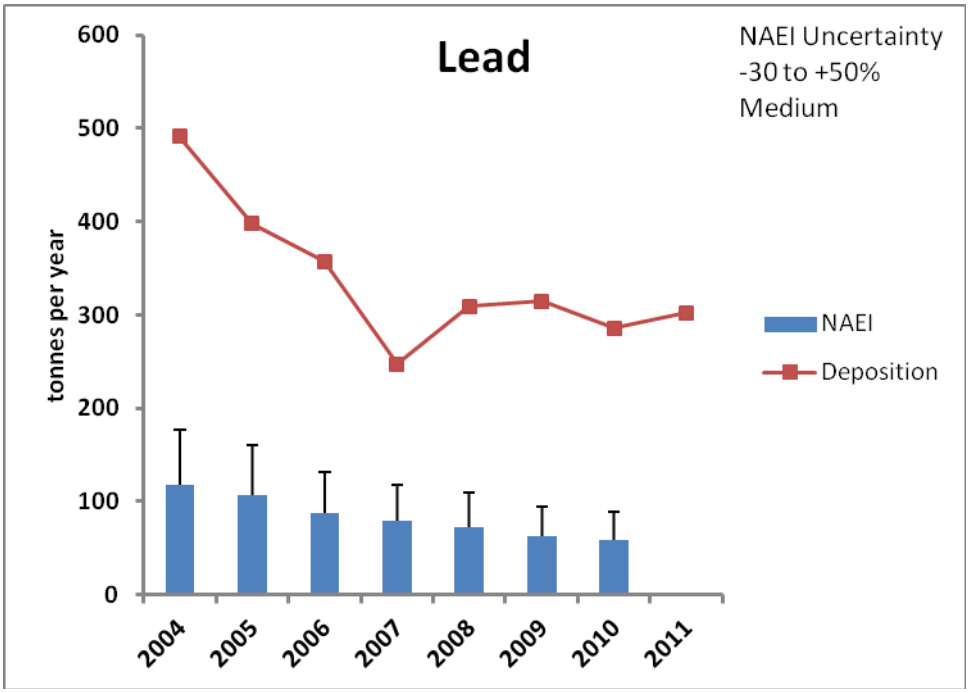


Figure 6c Comparison of the Emissions (Blue bars) and Deposition (red line) of Chromium and Lead in the UK,2004-2011

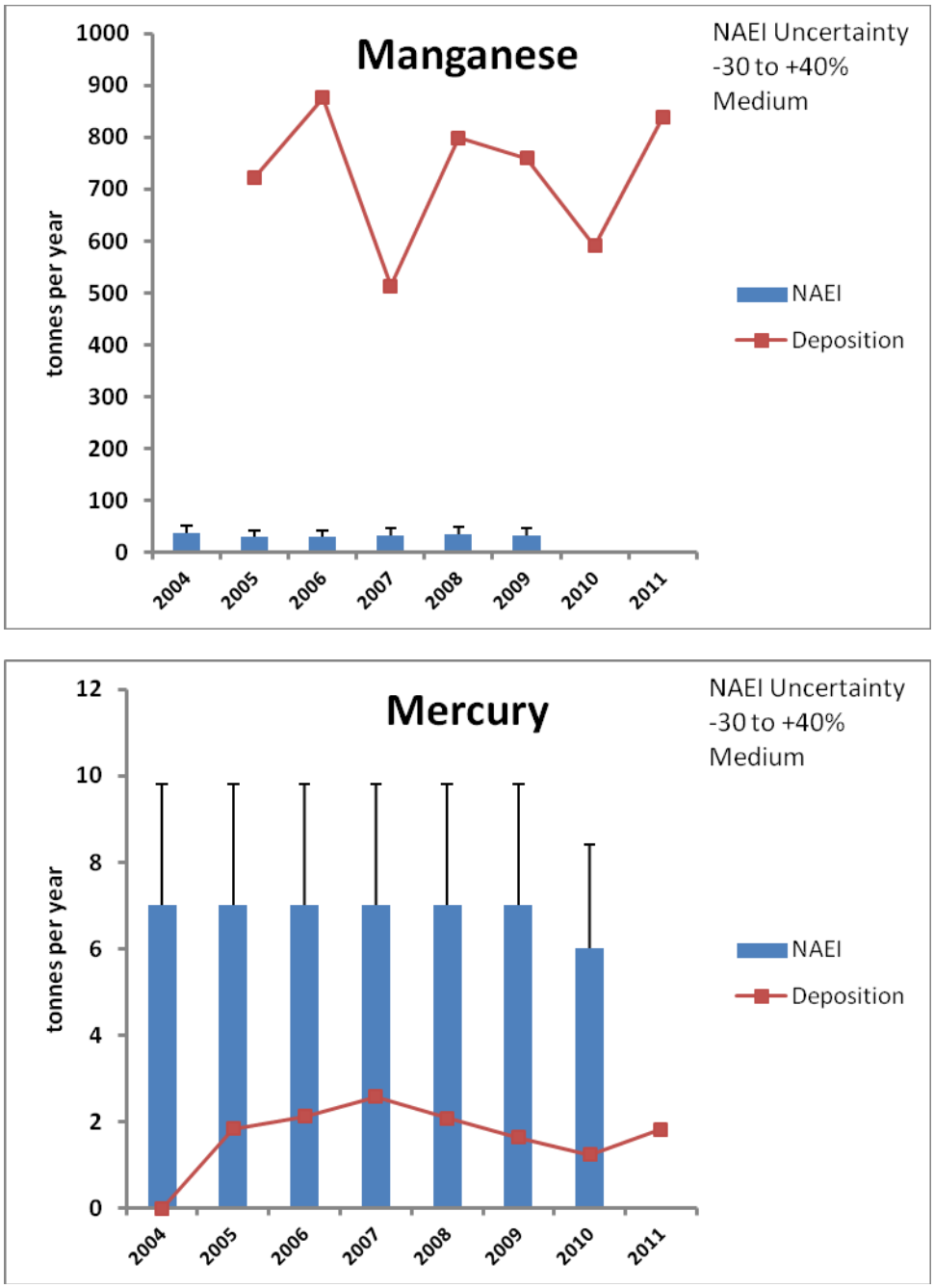


Figure 6d Comparison of the Emissions (Blue bars) and Deposition (red line) of Manganese and Mercury in the UK,2004-2011

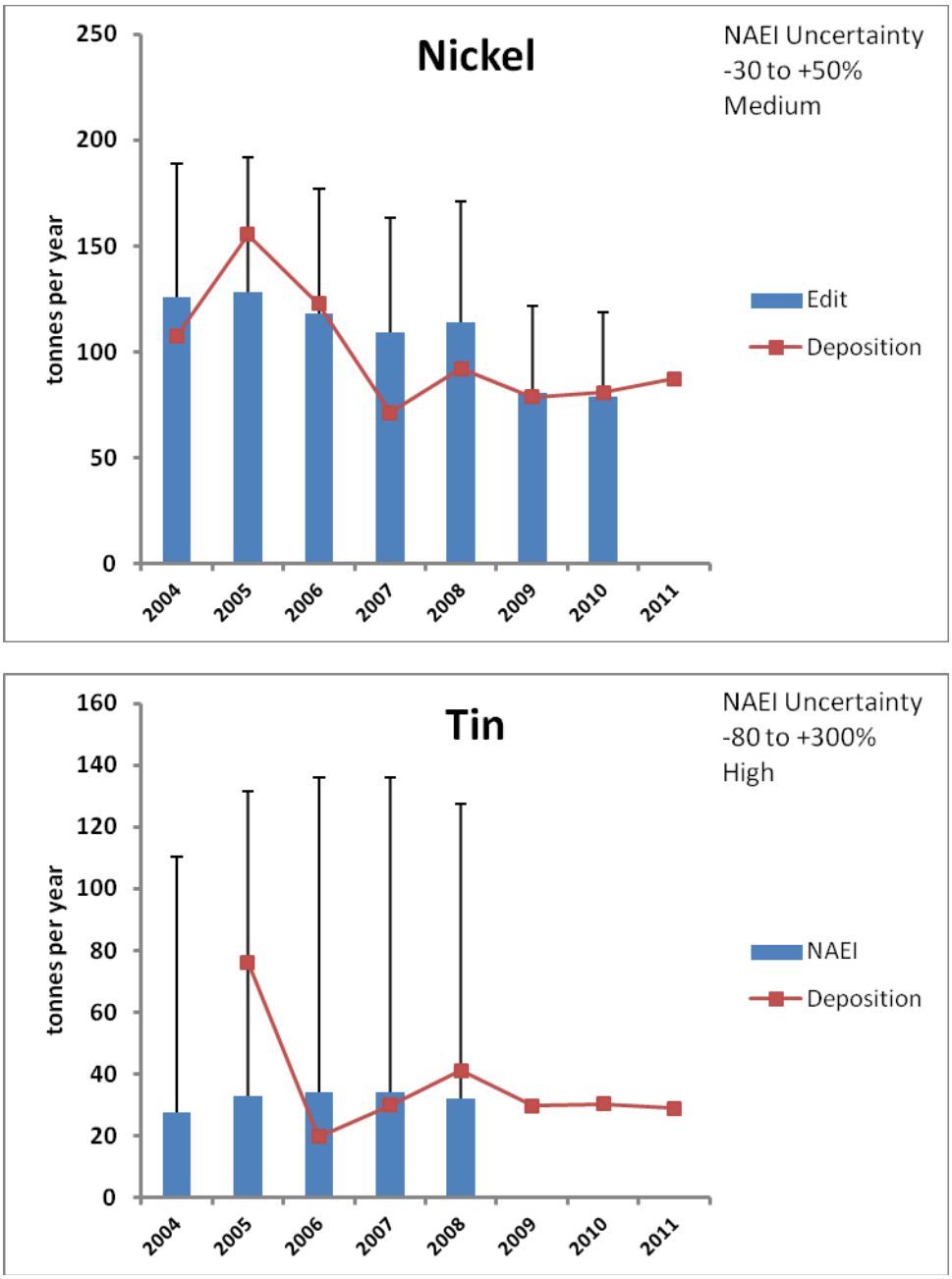


Figure 6e Comparison of the Emissions (Blue bars) and Deposition (red line) of Nickel and , Tin in the UK,2004-2011

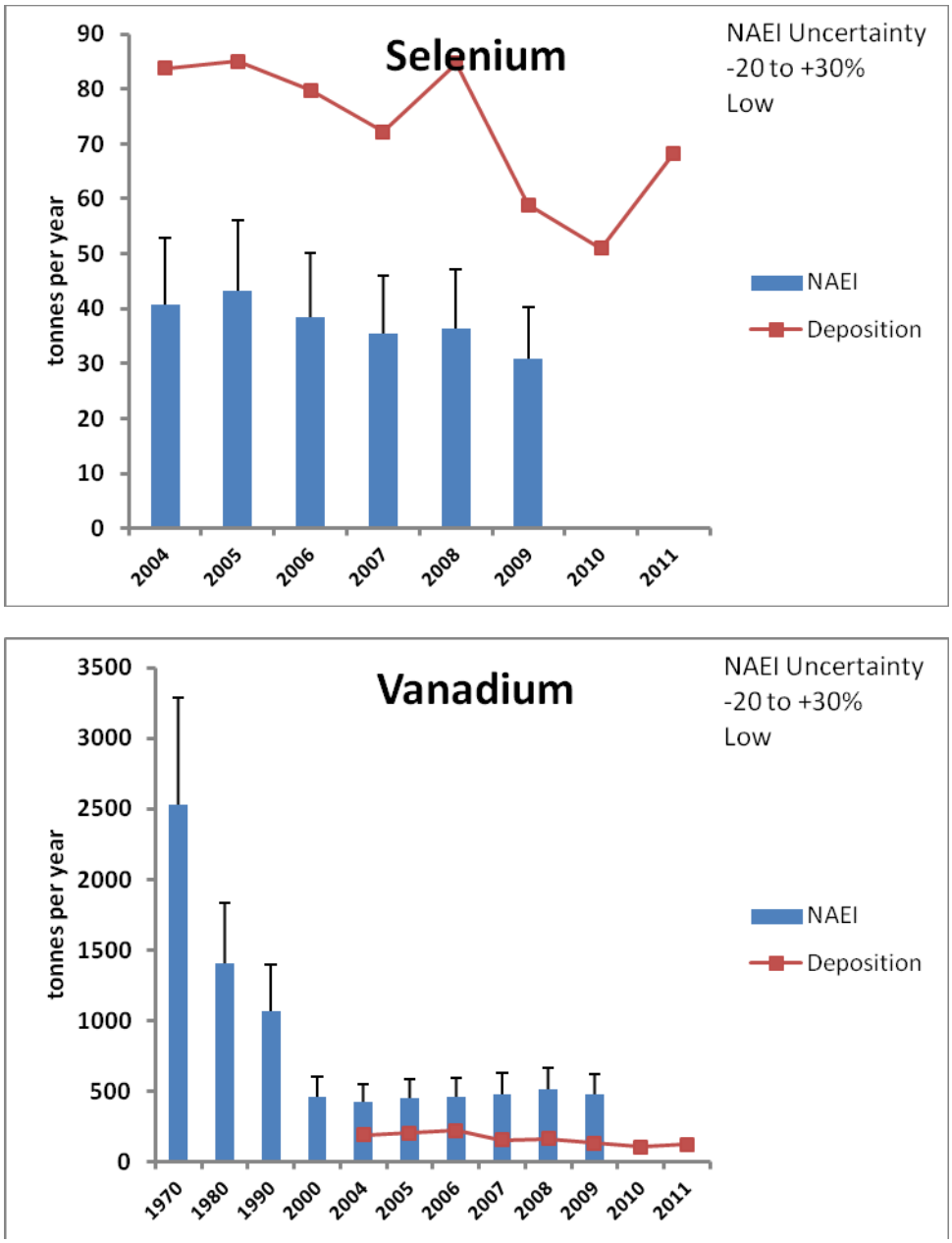


Figure 6f Comparison of the Emissions (Blue bars) and Deposition (red line) of Selenium and Vanadium in the UK,2004-2011

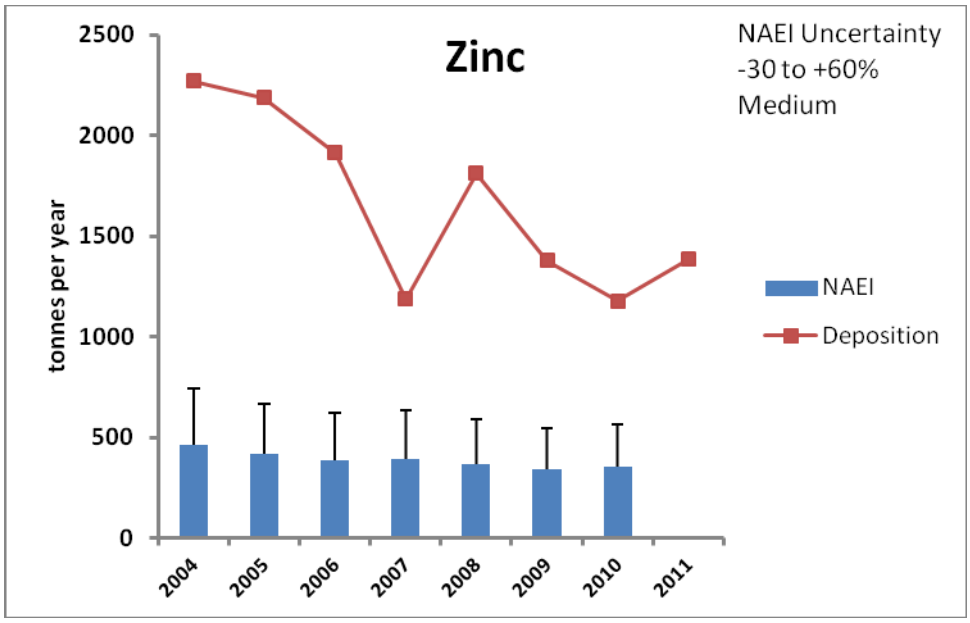


Figure 6g Comparison of the Emissions (Blue bars) and Deposition (red line) of Zinc in the UK,2004-2011

5) Maps of the Heavy Metals Data

5.1 Mapping Methodology

The data from the heavy metals monitoring network are used to produce annual maps of concentration and deposition of each metal. These are generated by taking the annual mean concentration data from each site and interpolating these values across the UK using GIS and modelling techniques. Details of the modelling procedure used to calculate wet, dry and cloud deposition are listed in sections 4.1 to 4.3.

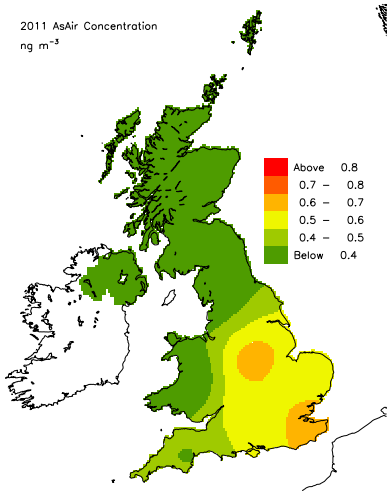
UK annual average maps for samples collected in 2011 (using the ratified 2011 rainfall data supplied by the Met Office) are presented in Figure 7. Maps have been produced for arsenic, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, vanadium and zinc as follows:

Concentration in air (ng/m^3)
Concentration in rain (µg/l)
Total Deposition (g/ha/year)
Dry Deposition (g/ha/year)
Wet Deposition (g/ha/year)
Cloud Deposition (g/ha/year)
Deposition to grassland (g/ha/year)
Deposition to moorland (g/ha/year)

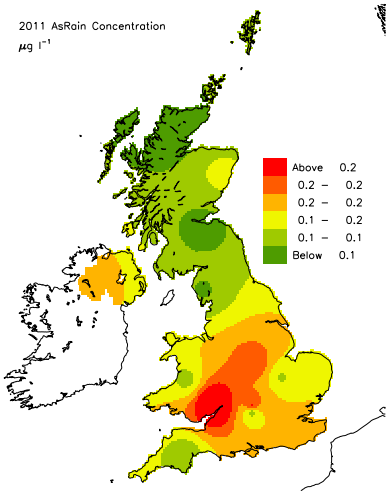
In addition, maps of 2010 emissions of heavy metals as reported in the National Atmospheric Emissions Inventory (NAEI, 2012) are also included.

Metal: Arsenic **Year 2011**

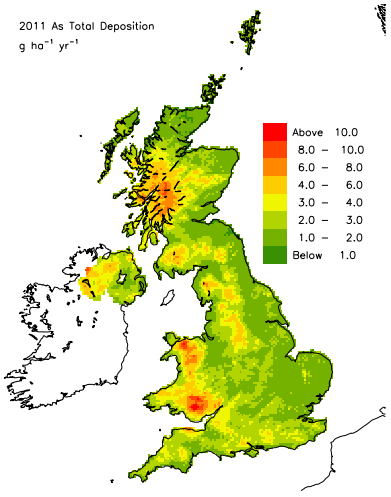
Concentration in air



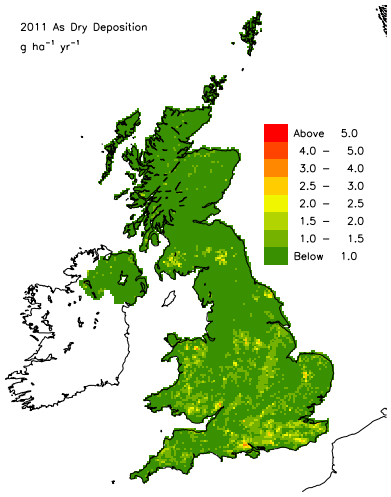
Concentration in rain



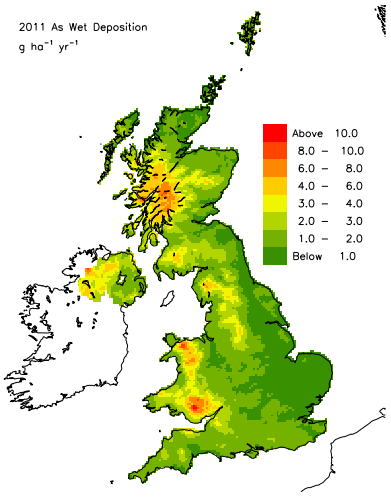
Total Deposition



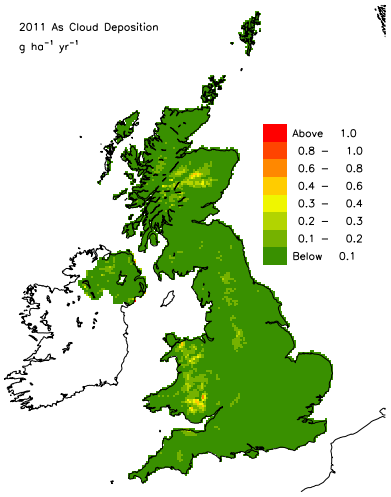
Dry Deposition



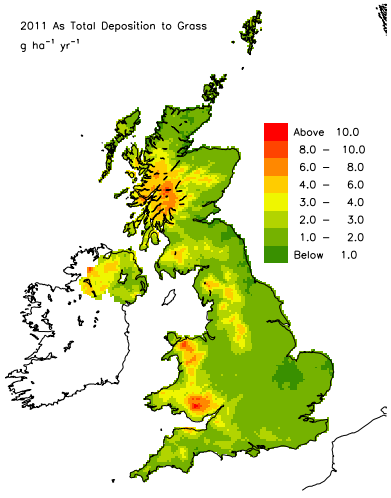
Wet Deposition



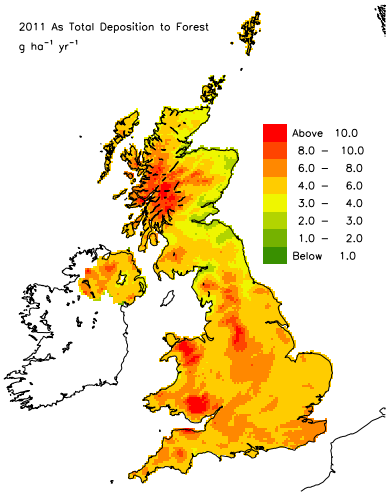
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions 2010

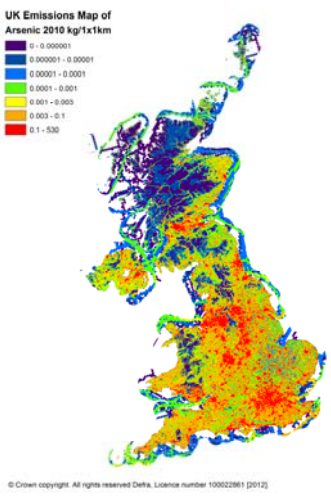
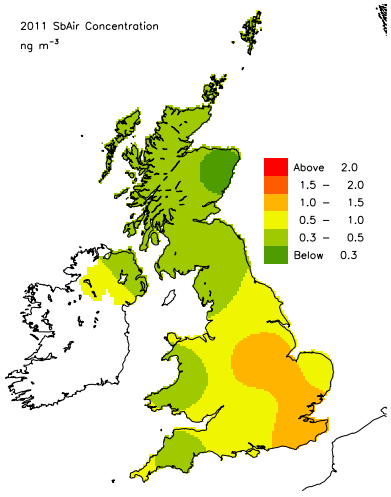


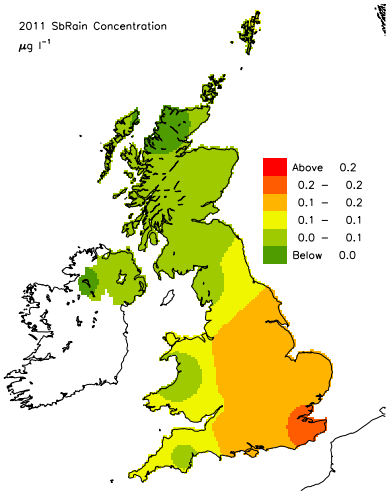
Figure 7a Maps of Arsenic Concentration, Deposition and Emission

Metal: Antimony **Year: 2011**

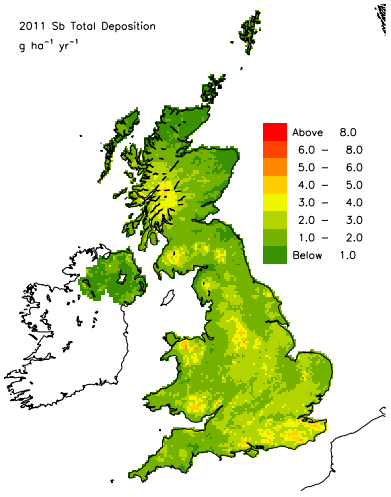
Concentration in air



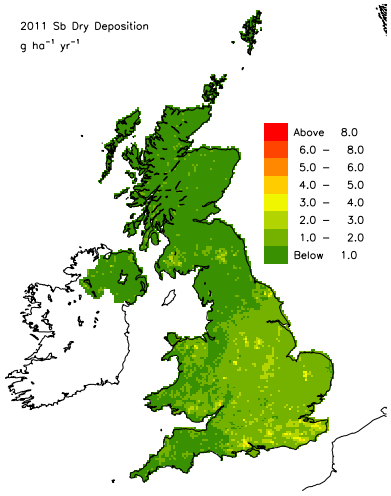
Concentration in rain



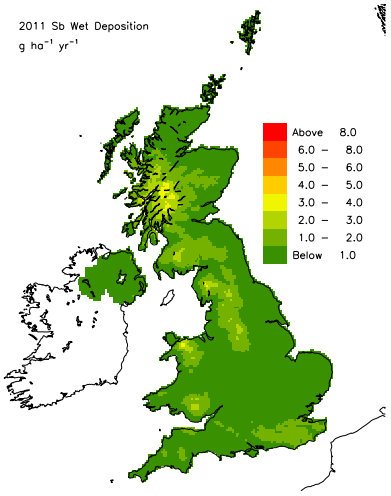
Total Deposition



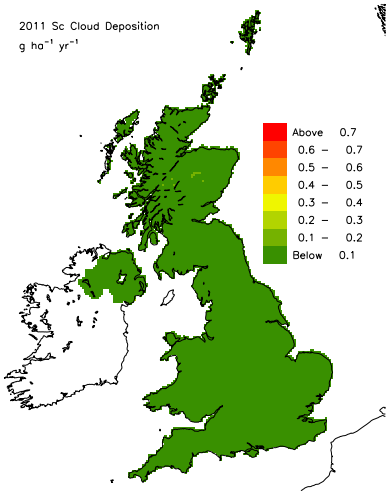
Dry Deposition



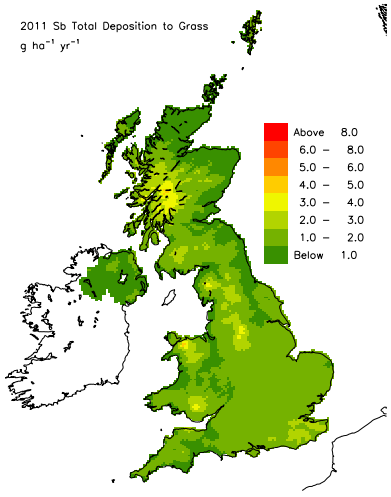
Wet Deposition



Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest

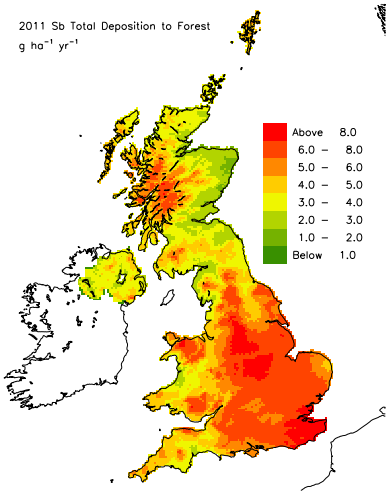
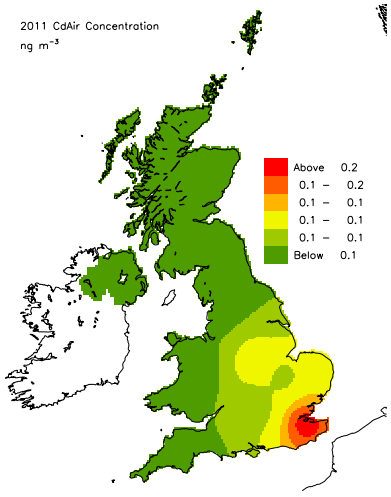


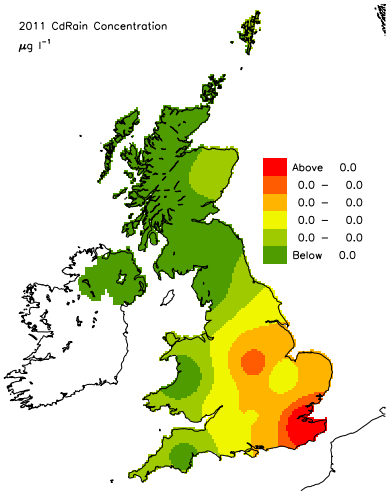
Figure 7b Maps of Antimony Concentration and Deposition

Metal: Cadmium **Year 2011**

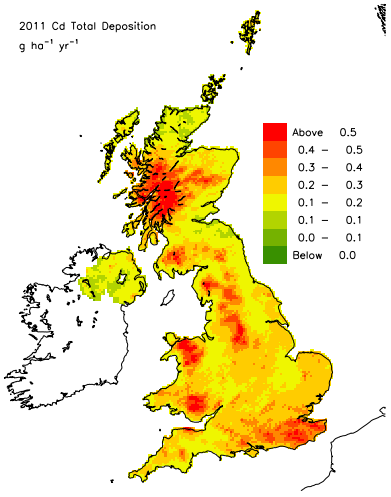
Concentration in air



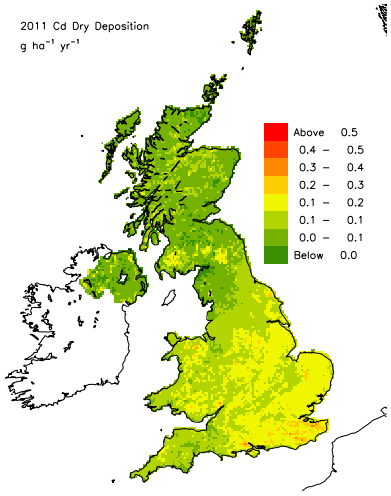
Concentration in rain



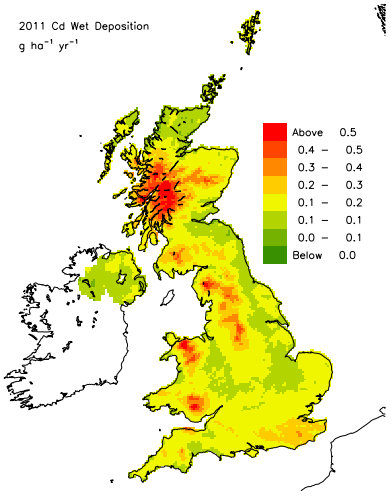
Total Deposition



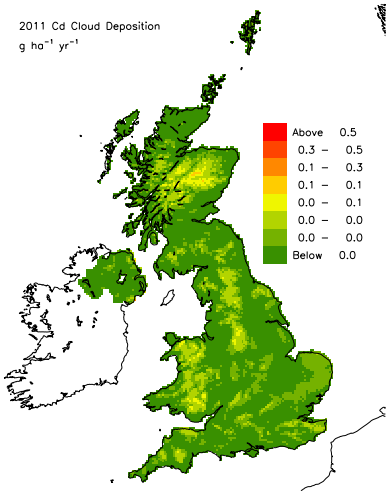
Dry Deposition



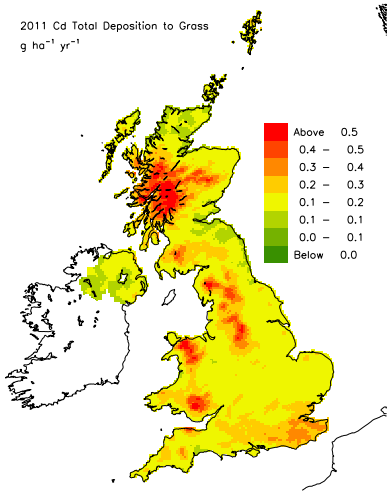
Wet Deposition



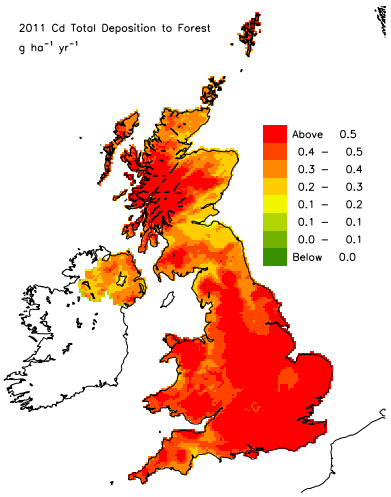
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

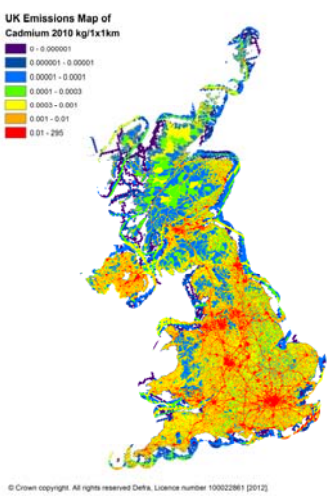
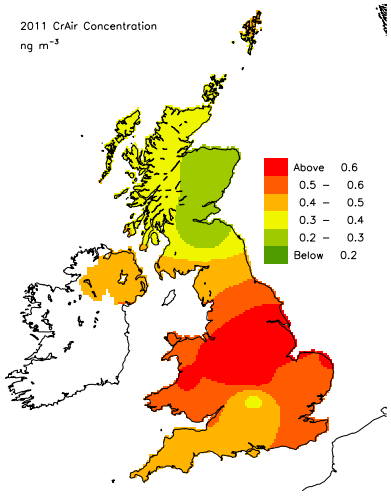


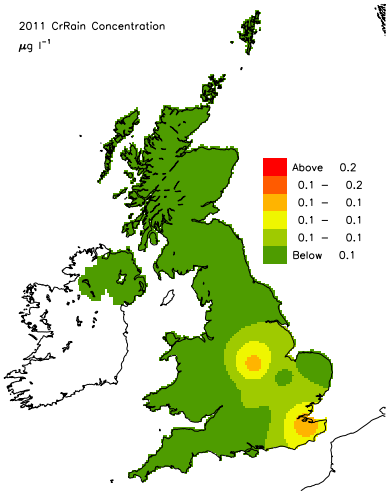
Figure 7c Maps of Cadmium Concentration, Deposition and Emission

Metal: Chromium **Year: 2011**

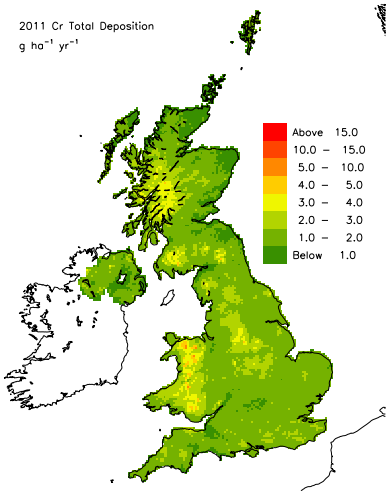
Concentration in air



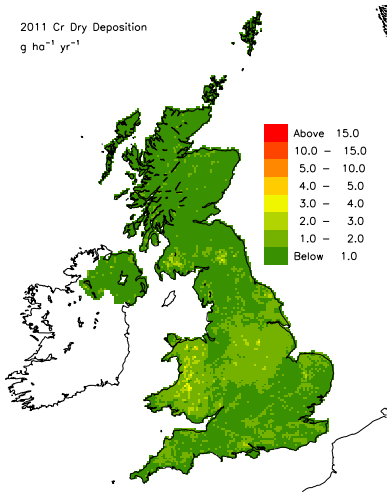
Concentration in rain



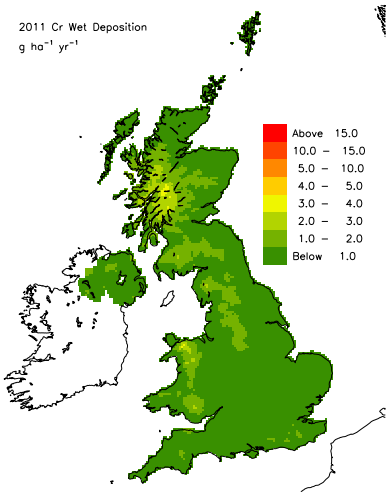
Total Deposition



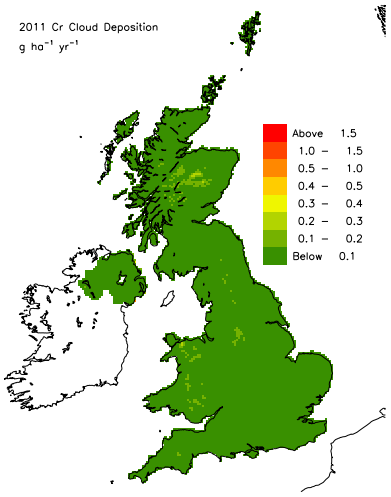
Dry Deposition



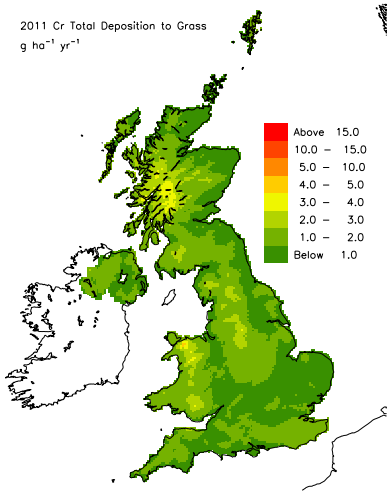
Wet Deposition



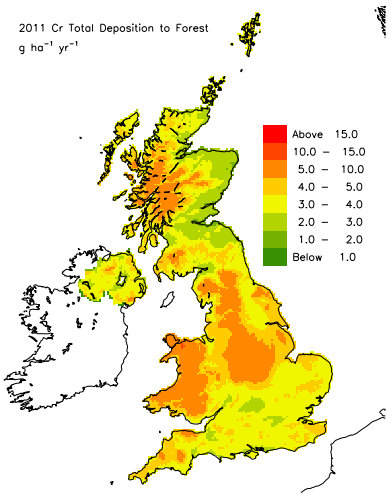
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

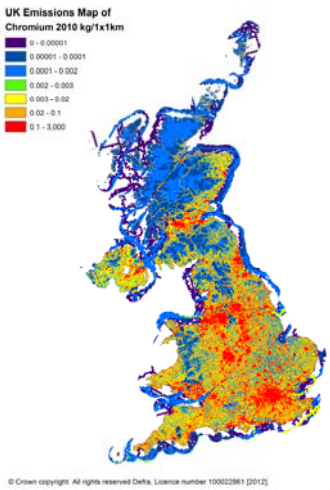
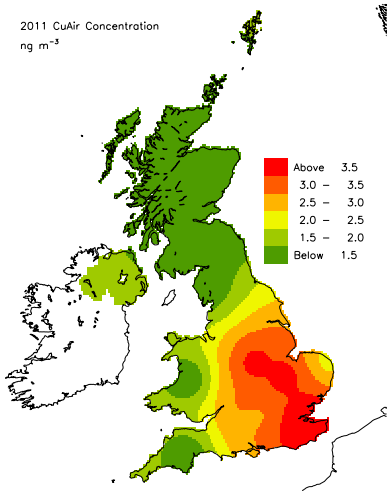


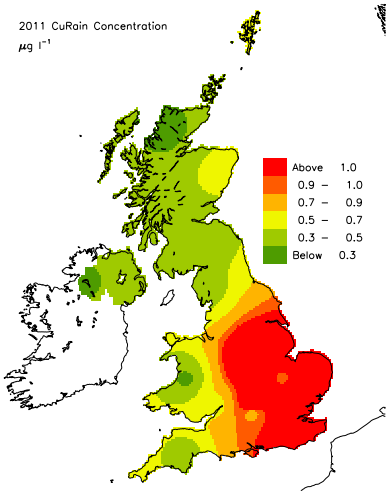
Figure 7d Maps of Chromium Concentration, Deposition and Emission

Metal: Copper **Year: 2011**

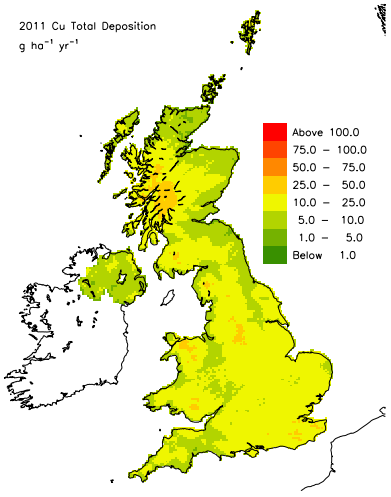
Concentration in air



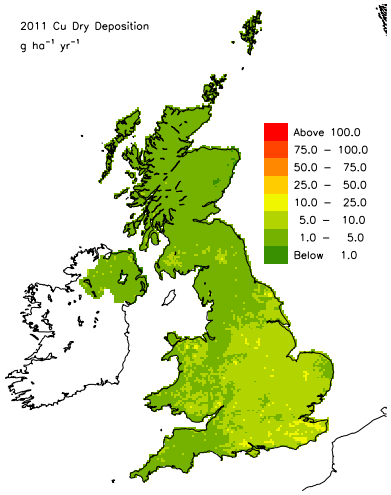
Concentration in rain



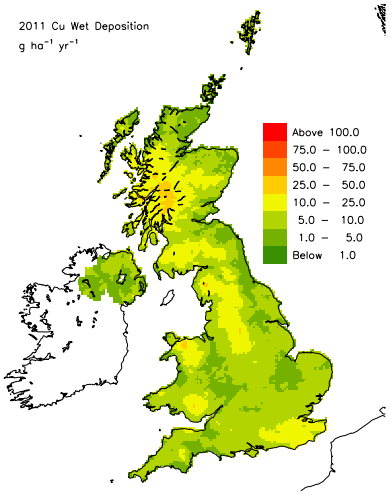
Total Deposition



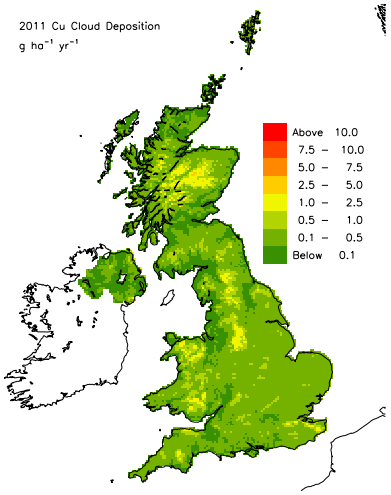
Dry Deposition



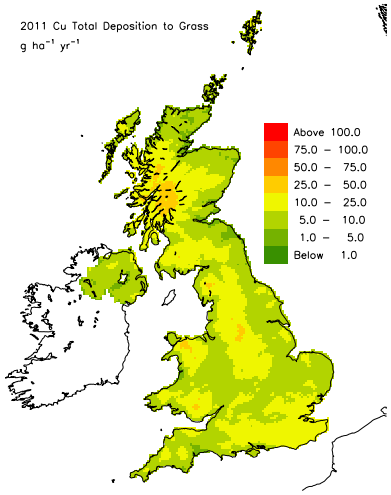
Wet Deposition



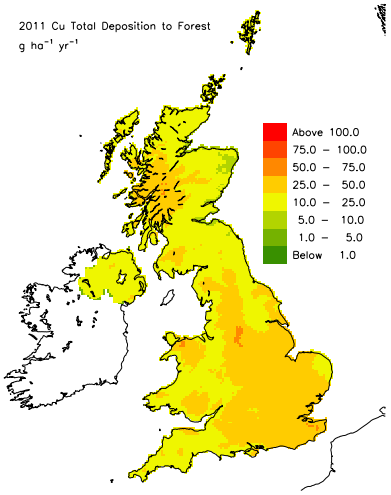
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

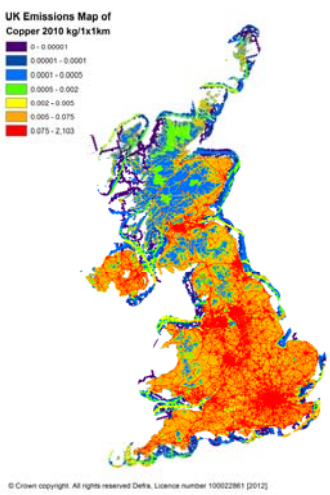
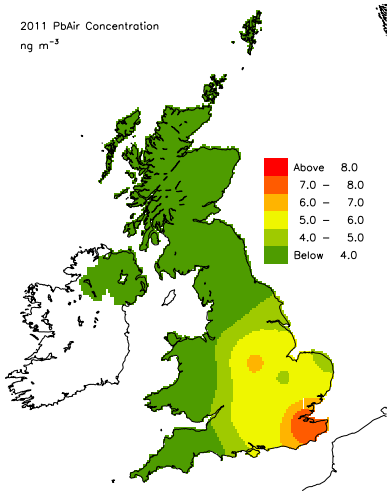


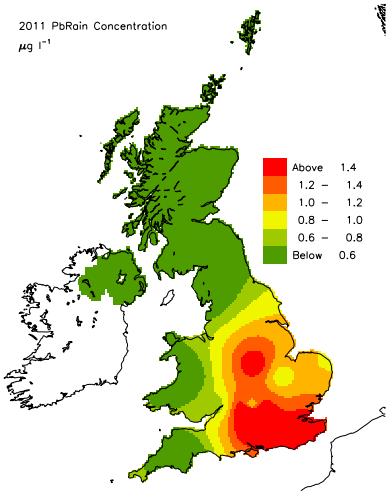
Figure 7e Maps of Copper Concentration, Deposition and Emission

Metal: Lead **Year: 2011**

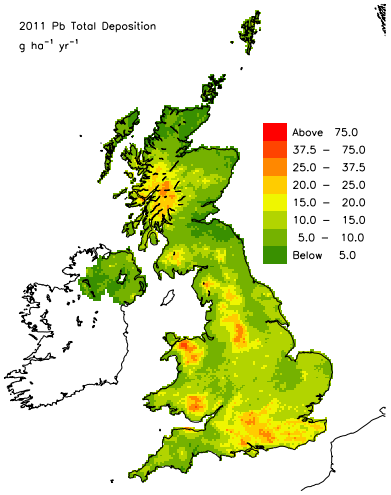
Concentration in air



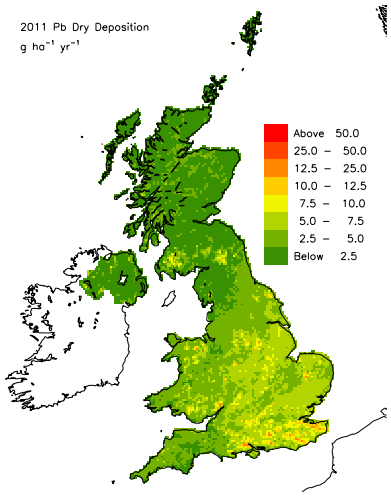
Concentration in rain



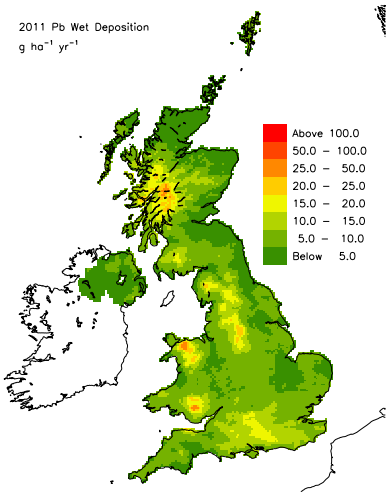
Total Deposition



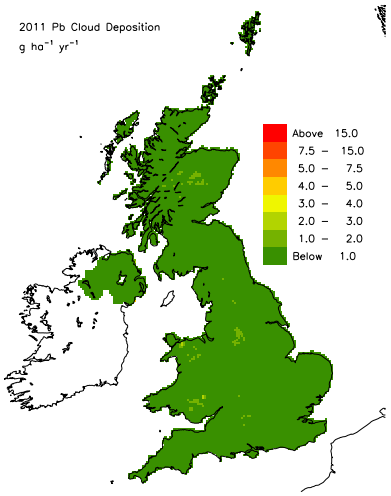
Dry Deposition



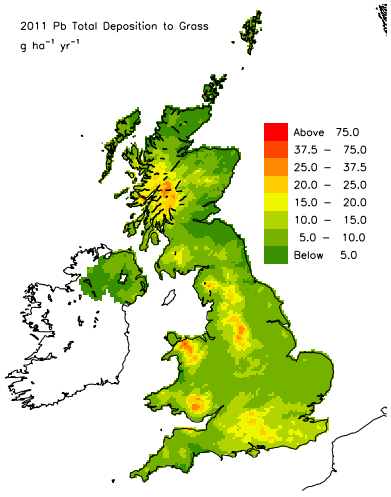
Wet Deposition



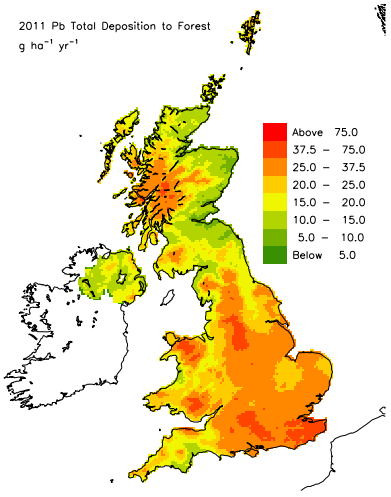
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

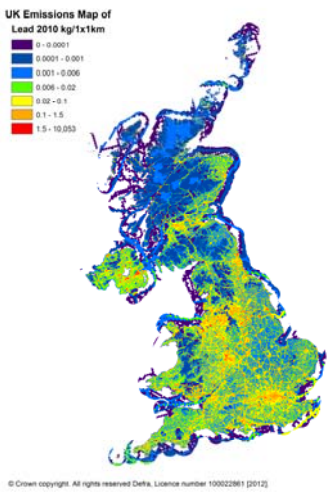
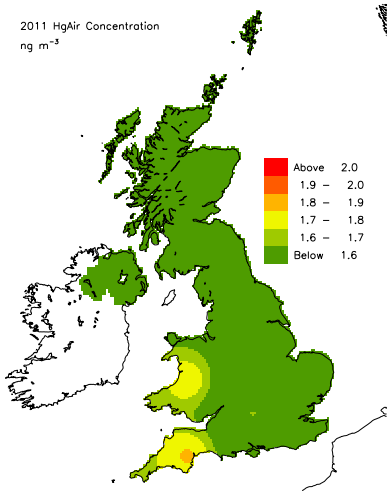


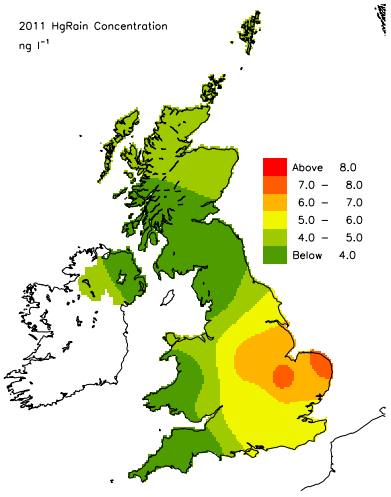
Figure 7f Maps of Lead Concentration, Deposition and Emission

Metal: Mercury **Year: 2011**

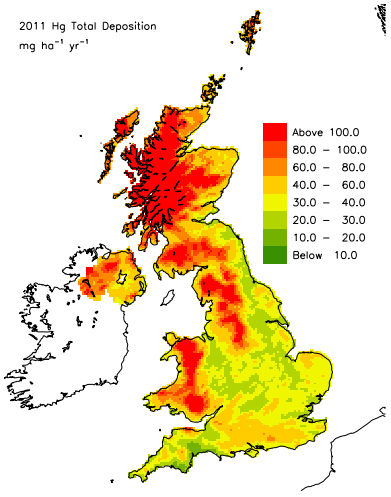
Concentration in air



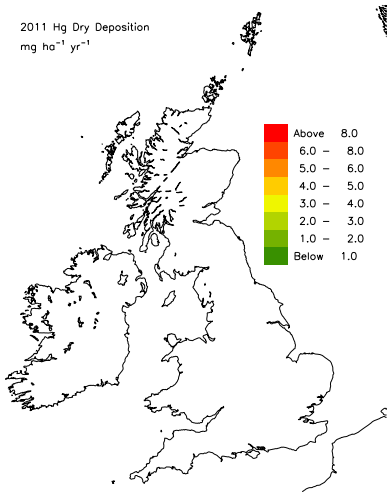
Concentration in rain



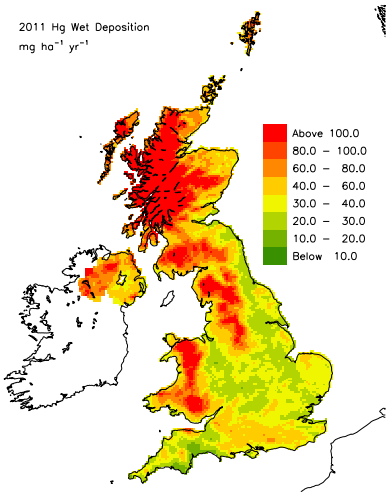
Total Deposition



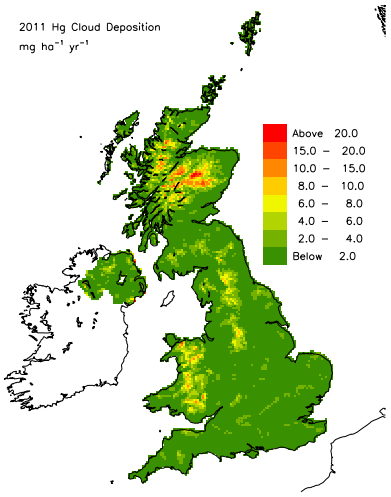
Dry Deposition



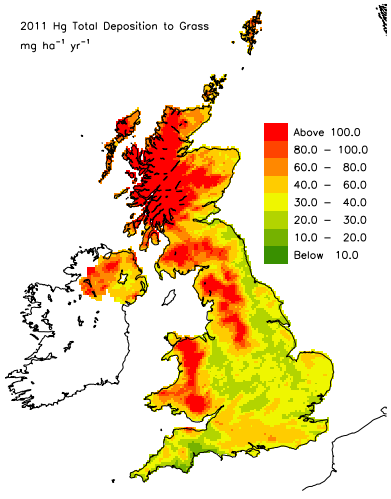
Wet Deposition



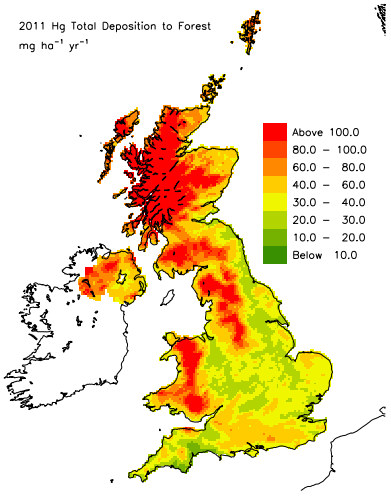
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

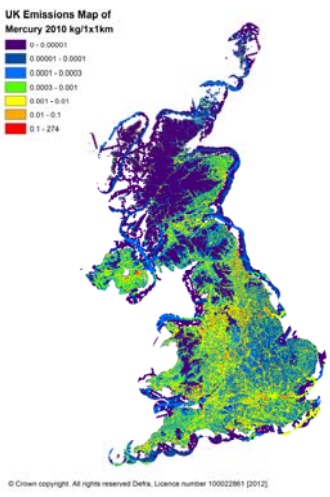
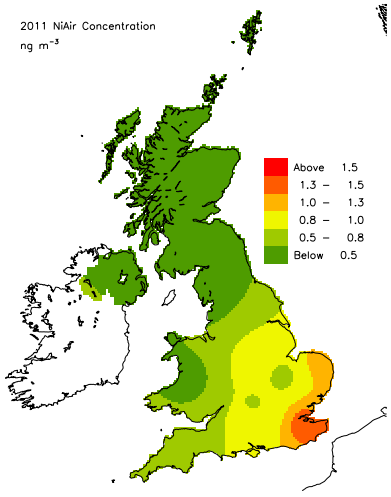


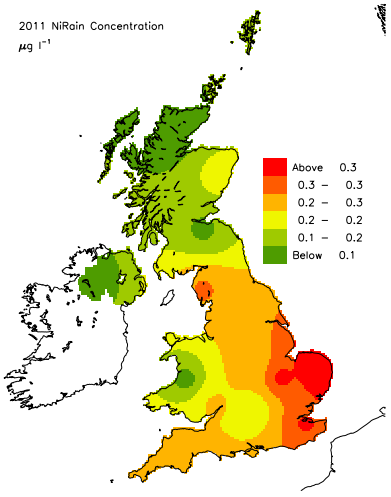
Figure 7g Maps of Mercury Concentration, Deposition and Emission

Metal: Nickel **Year: 2011**

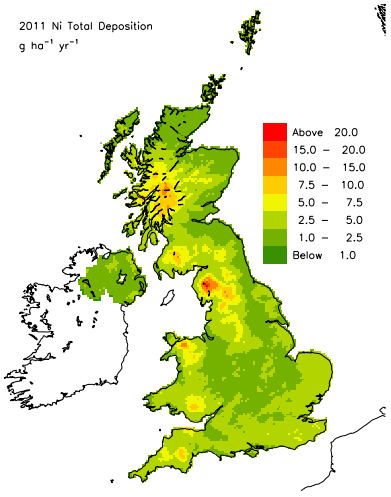
Concentration in air



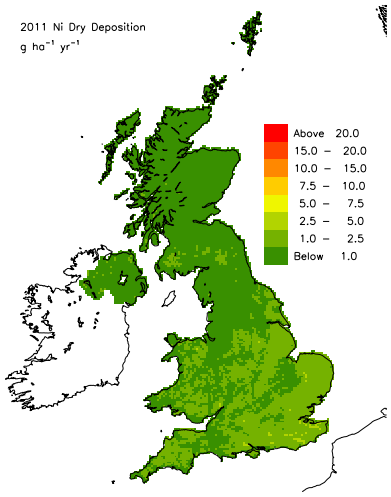
Concentration in rain



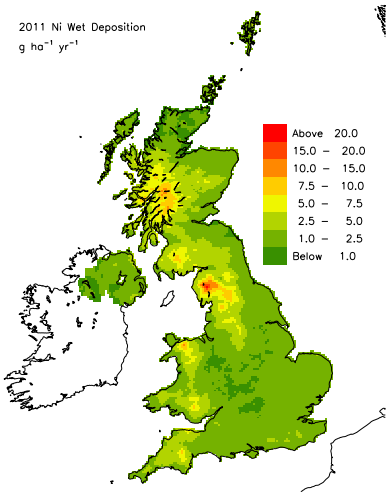
Total Deposition



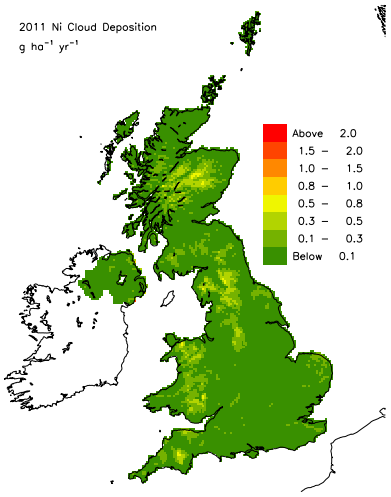
Dry Deposition



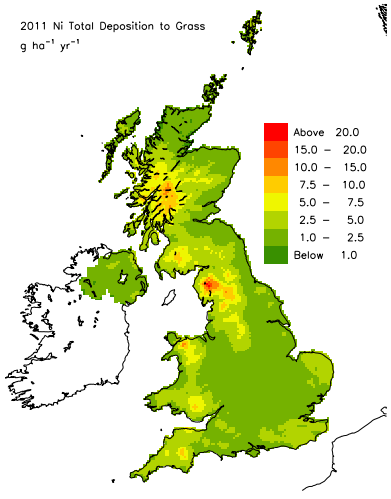
Wet Deposition



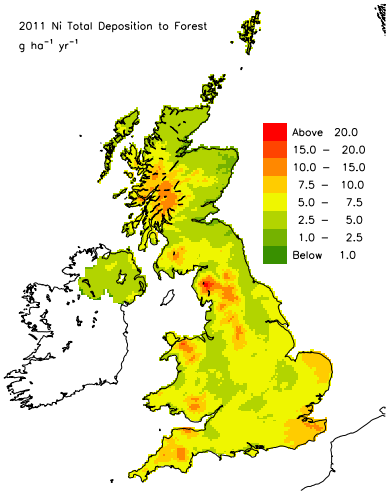
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions In 2010

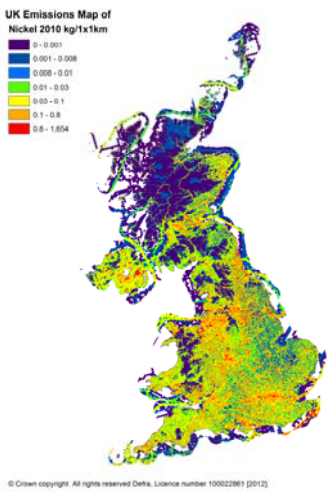
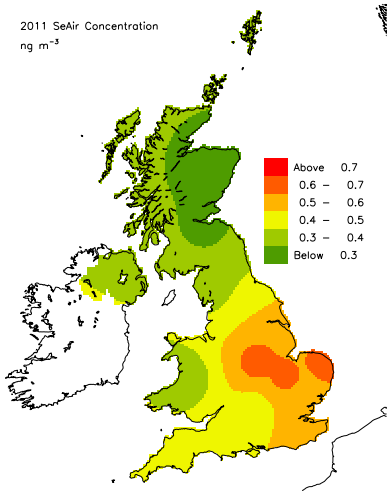


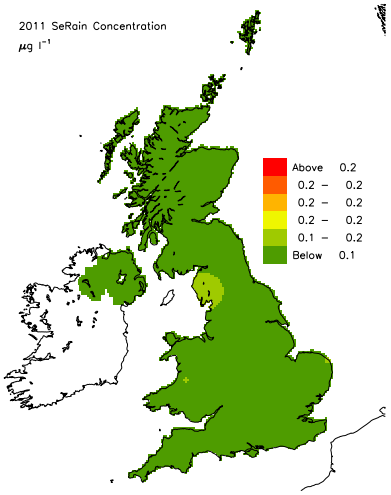
Figure 7h Maps of Nickel Concentration, Deposition and Emission

Metal: Selenium **Year: 2011**

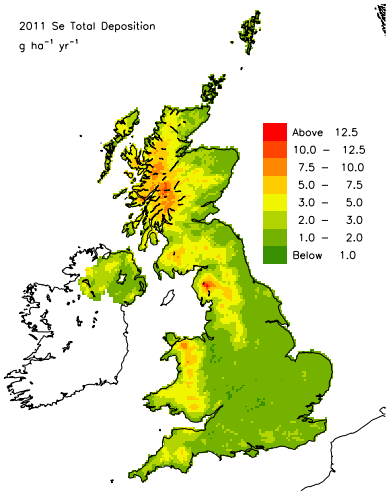
Concentration in air



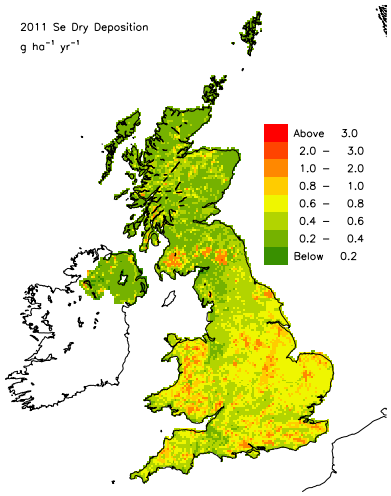
Concentration in rain



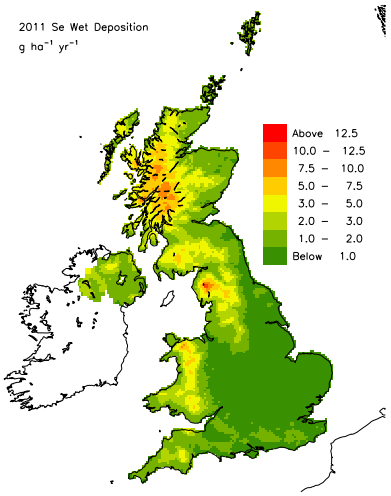
Total Deposition



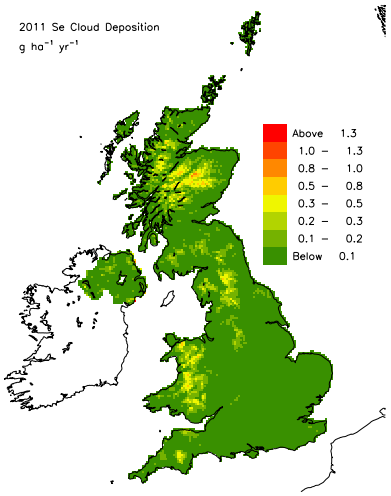
Dry Deposition



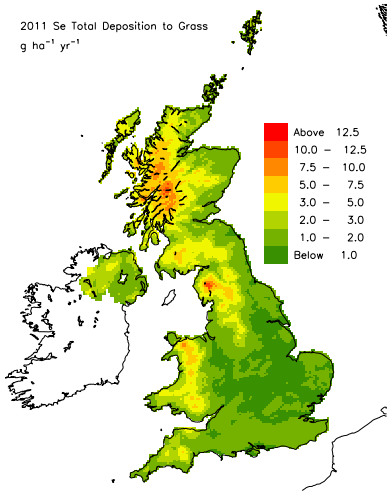
Wet Deposition



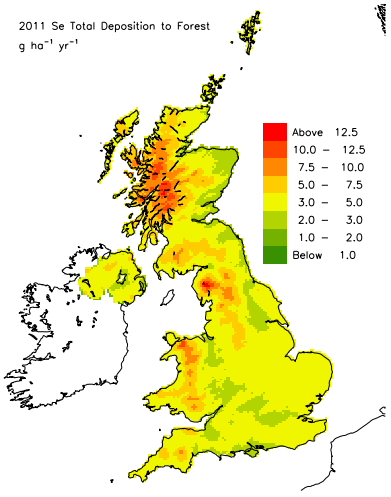
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

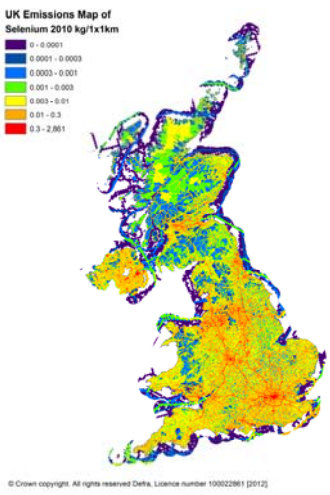
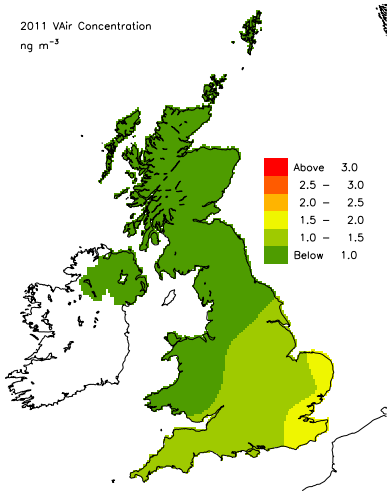


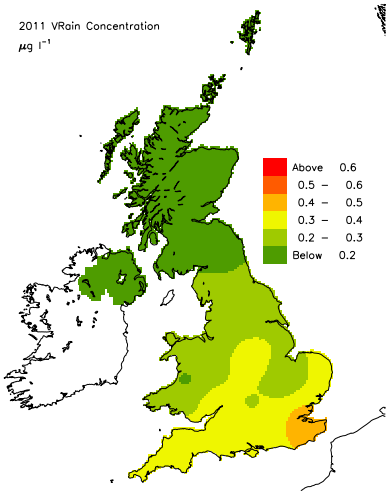
Figure 7i Maps of Selenium Concentration, Deposition and Emission

Metal: Vanadium **Year: 2011**

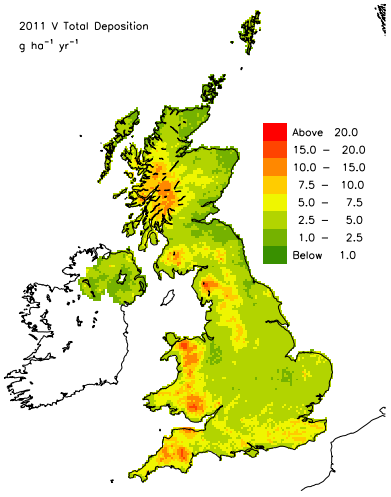
Concentration in air



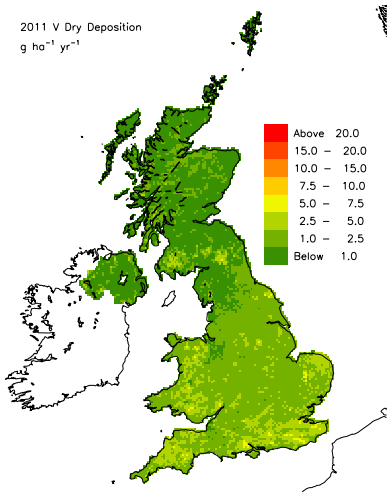
Concentration in rain



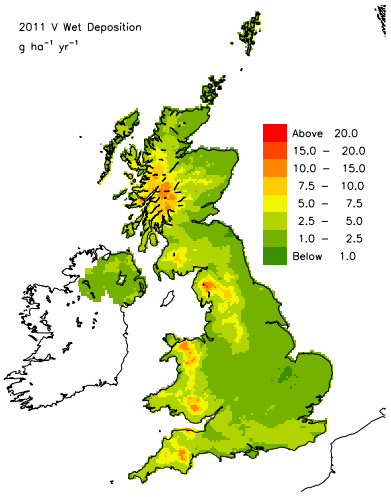
Total Deposition



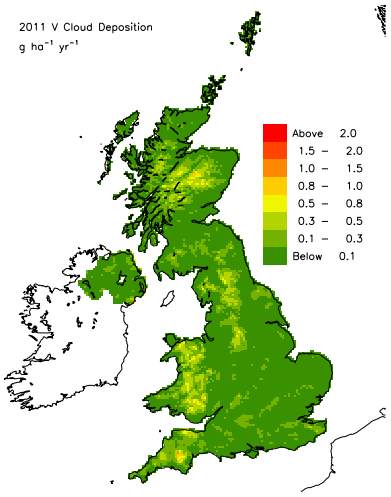
Dry Deposition



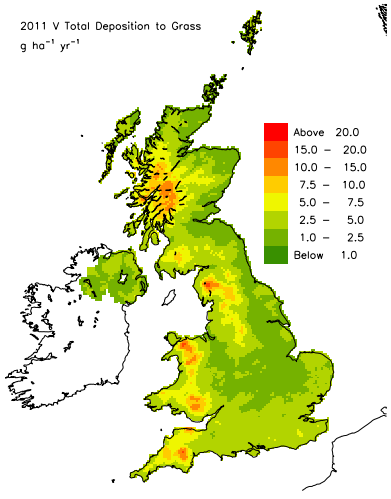
Wet Deposition



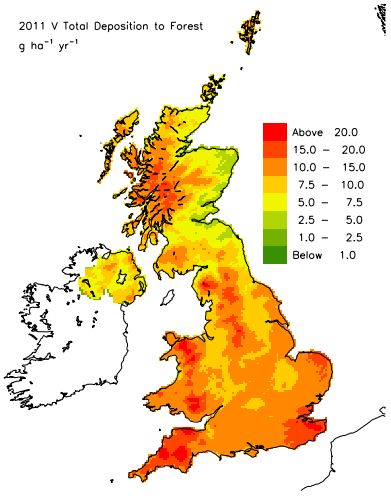
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

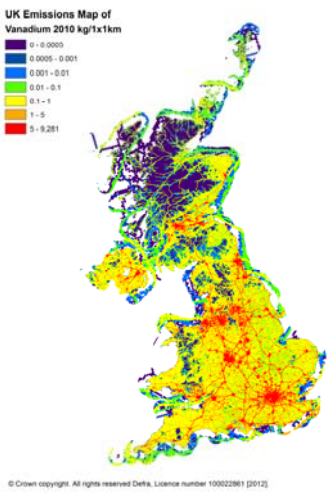
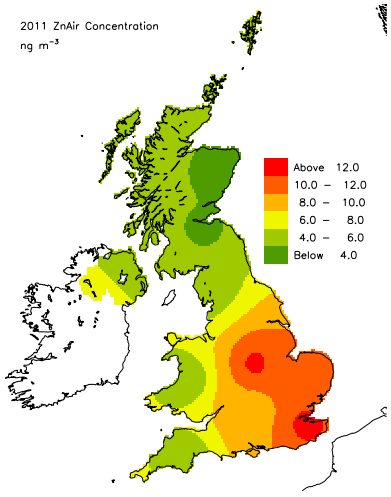


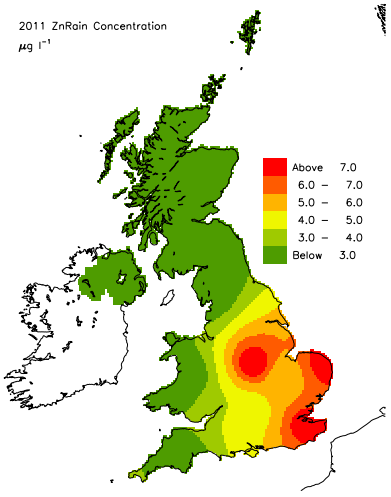
Figure 7j Maps of Vanadium Concentration, Deposition and Emission

Metal: Zinc **Year: 2011**

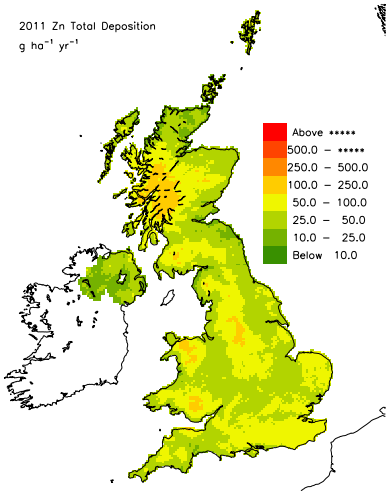
Concentration in air



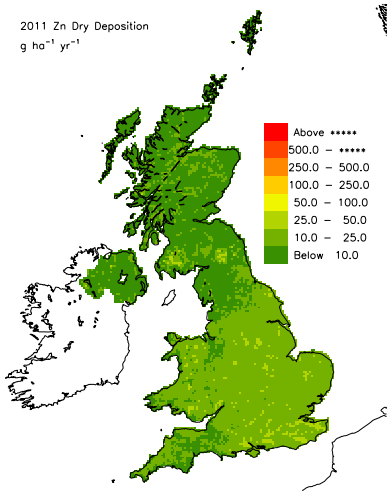
Concentration in rain



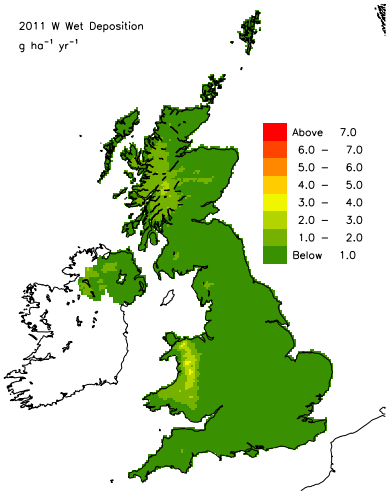
Total Deposition



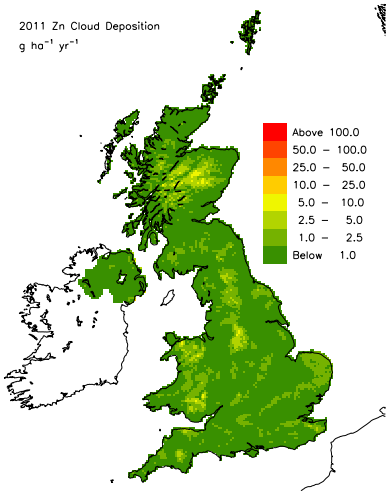
Dry Deposition



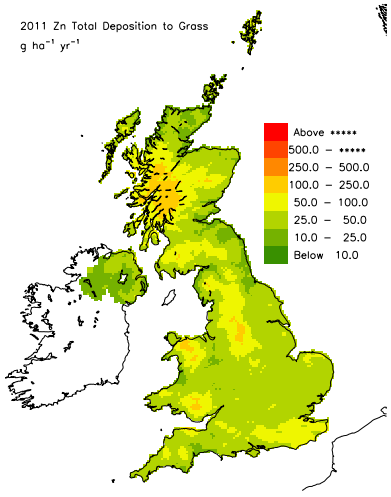
Wet Deposition



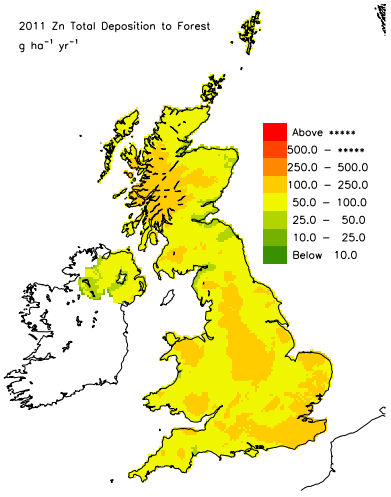
Cloud Deposition



Total Deposition to Grassland



Total Deposition to Forest



Total Emissions in 2010

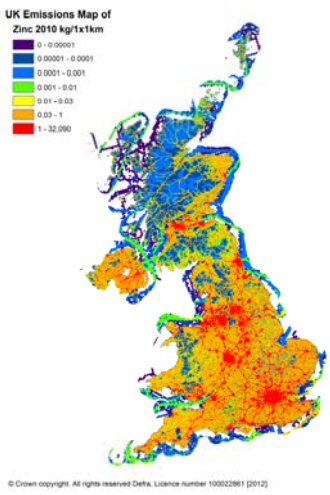


Figure 7k Maps of Zinc Concentration, Deposition and Emission

6) Concentrations of Metals in Mosses and Their Relationship to Deposition

Relative concentrations of heavy metals in moss samples have long been used as a surrogate for heavy metal bulk deposition. The previous report (Fowler et al., 2006) included an analysis of moss samples collected from each monitoring site in the network to determine any differences in the relationship between moss concentration and deposition that was established from the UK 2000 Moss Survey (Ashmore et al., 2002). Analysis of mosses from the network monitoring sites is undertaken to compliment the European Moss Surveys which are regularly undertaken as part of the *International Cooperative Programme ion Effects of Air Pollution on natural Vegetation and Crops* (Harmens et al., 2008).

Samples of moss were collected from all sites during 2008 and analysed for heavy metals. As with the previous sampling regime, different species were collected from each site (Table 12), and there were mosses available for sampling at Detling. The concentrations of 9 metals (arsenic, cadmium, chromium, copper, lead, nickel, selenium, vanadium and zinc) in each moss species sampled were standardised to the reference species *Pleurozium schreberi*. Figure 8 presents the standardised concentration at each monitoring from both this survey (pink bars) and the 2004/05 survey (blue bars).

For most metals, the standardised concentrations in mosses are generally consistent between the two sampling years. However, there are some outliers which concentrations increasing at some sites, such as Beacon Hill (arsenic, chromium, lead, nickel, vanadium), Cockley Beck (arsenic), Penallt (arsenic, cadmium, chromium, lead and vanadium) and Wytham Wood (arsenic, chromium, nickel and vanadium).

	Pleurozium schreberi	*Hylocomium splendens*	Hypnum cupressiforme	Pseudoscleropodium purum	Rhytidiadelphus squarrosus	Total
Auchencorth Moss	✓	✓			✓	**3**
Banchory		✓	✓		✓	**3**
Beacon Hill					✓	**1**
Bowbeat	✓	✓				**2**
Cockley Beck					✓	**1**
Cwmystwyth	✓	✓		✓	✓	**4**
Heigham Holmes			✓			**1**
Holme Moss			✓		✓	**2**
Inverpolly	✓	✓			✓	**3**
Lough Navar		✓	✓			**2**
Penallt			✓			**1**
Wytham Wood				✓	✓	**2**
Yarner Wood				✓		**1**
Total	**4**	**6**	**5**	**3**	**8**	**26**

Table 12 Species Composition of Moss Samples Collected from each monitoring site

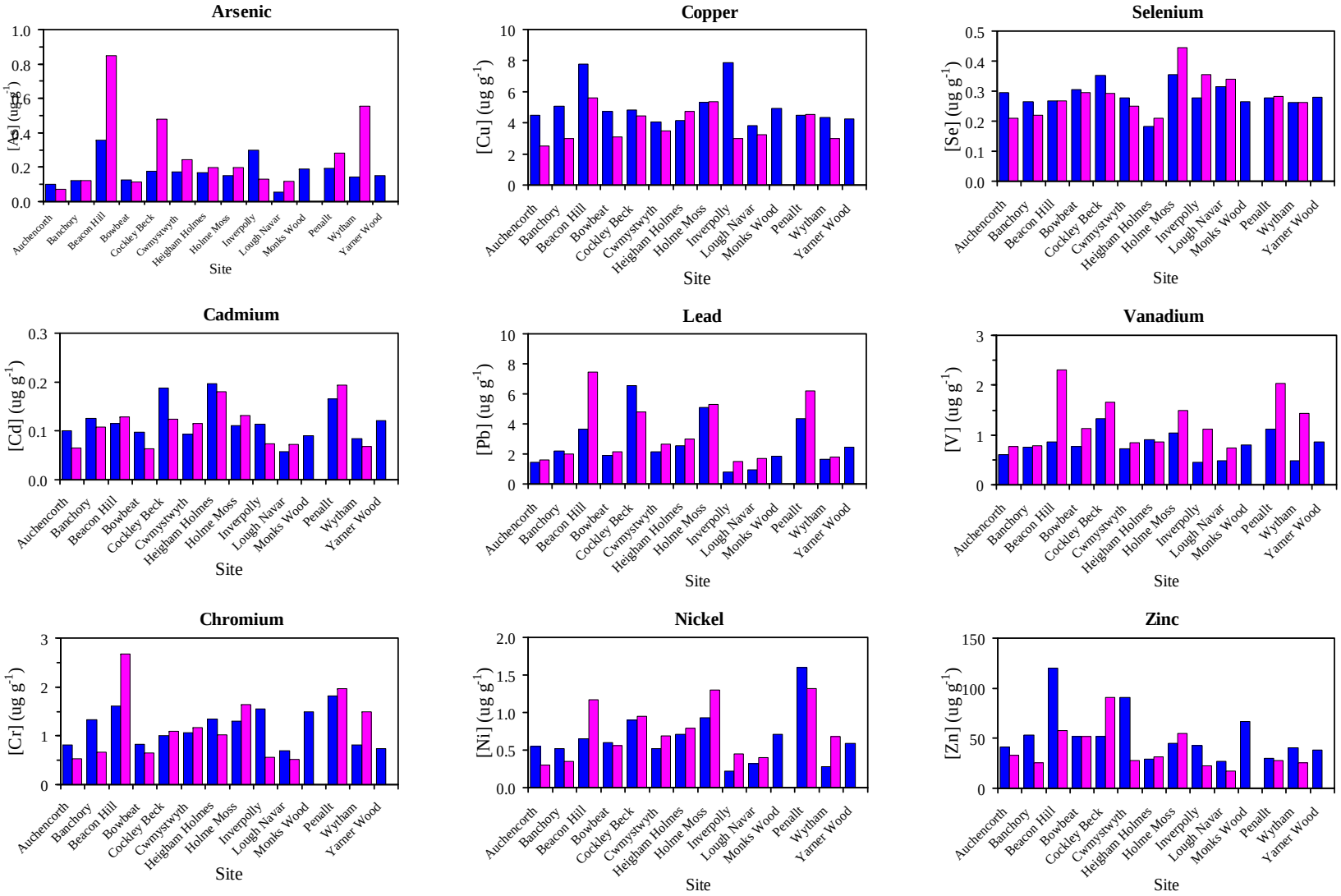


Figure 8 Concentrations of metals in moss samples, standardised to *Pleurozium schreberi*. Blue bars refer to samples collected in 2004/05, pink bars refer to samples collected in 2008

7) Speciated Mercury Measurements at EMEP Supersites

7.1 Introduction

Elemental mercury (Hg^0) makes up over 97% of the total atmospheric mercury burden, with the remaining fraction consisting 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 Hg^0, RGM and Hg^P. As the concentrations of these species are 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 uses Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS). Elemental mercury is sampled and analysed for one hour with simultaneous RGM and Hg^P collection on a KCl-coated denuder and particulate trap respectively. During the following hour, the collected RGM and Hg^P are desorbed and analysed. This method allows for measurements of Hg^0 at a 5-minute temporal resolution and concentrations of RGM and Hg^P every other hour.

7.2 Establishment of 'supersite' for Hg measurements

A 'supersite' for speciated mercury measurements was established at Auchencorth Moss, a rural site 18 km south west of Edinburgh. Measurements of speciated mercury using the Tekran system started at Auncencorth in October 2004 after prior testing of the equipment under field conditions at CEH Bush.

7.3 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 mercury sampling before they were deployed at the other sites in the network (see Figure 1). After successful completion of the testing, the speciation sampler and analyser were 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 internal source.

The Tekran analyser runs semi-continuously: it was taken off-line for approximately three hours every fortnight for the analysis of the field cartridges from the integrated samplers from other sites, as well as at other periods for routine maintenance. Since January 2009, analysis of the field cartridges has been carried out on a separate analyser at CEH Edinburgh, so the Tekran has been running continuously, except for calibrations and maintenance.

7.4 Major problems affecting data

Three major problems have beset the continuous monitoring of mercury at Auchencorth. The largest problem was the passivation of the internal gold cartridges in the 2537A, which led to an apparent steady decline in observed mercury levels over a period of 2.5 years, at least between July 2007 and January 2009. Data affected by this problem, which was identified as being caused by increasing noise levels in the raw signal (Swartzendruber et al., 2009), were subjected to a linear back correction to adjust for this decline and are shown in green in Figure 8A. The problem was subsequently rectified by installing new cartridges and a new maintenance routine for the analyser.

The second problem concerned the Hg^P particulate trap, which repeatedly suffered from power interruptions as it tripped to ground. This resulted in the unit twice being returned to

North America for lengthy periods to try to resolve the problem. As of 2011, this has now been solved.

During spring 2011, the mercury speciation system was relocated to achieve a better sampling inlet height. A new scaffold was erected at Auchencorth, on to which the RGM denuder and HgP trap are mounted. This improved the inlet height from 0.9 metres, with the potential for significant losses of mercury species to surfaces, to a height of 4 metres, which should give more representative background concentrations. The 2537A analyser and pump module are located at the base of the tower in a weatherproof cabinet. This relocation resulted in a significant period of downtime for the system in early 2011, with the speciated systems not being operational again until 2012 owing to various teething problems.

7.5 Summary statistics of measurement data

Hourly averages of elemental mercury from January 2004 to December 2011 are presented in Figure 9. Annual averages for elemental mercury at CEH Edinburgh and Auchencorth Moss are shown in Table 13. For the 2004 data, measurements were made at CEH Edinburgh from January to September and at Auchencorth from October to December.

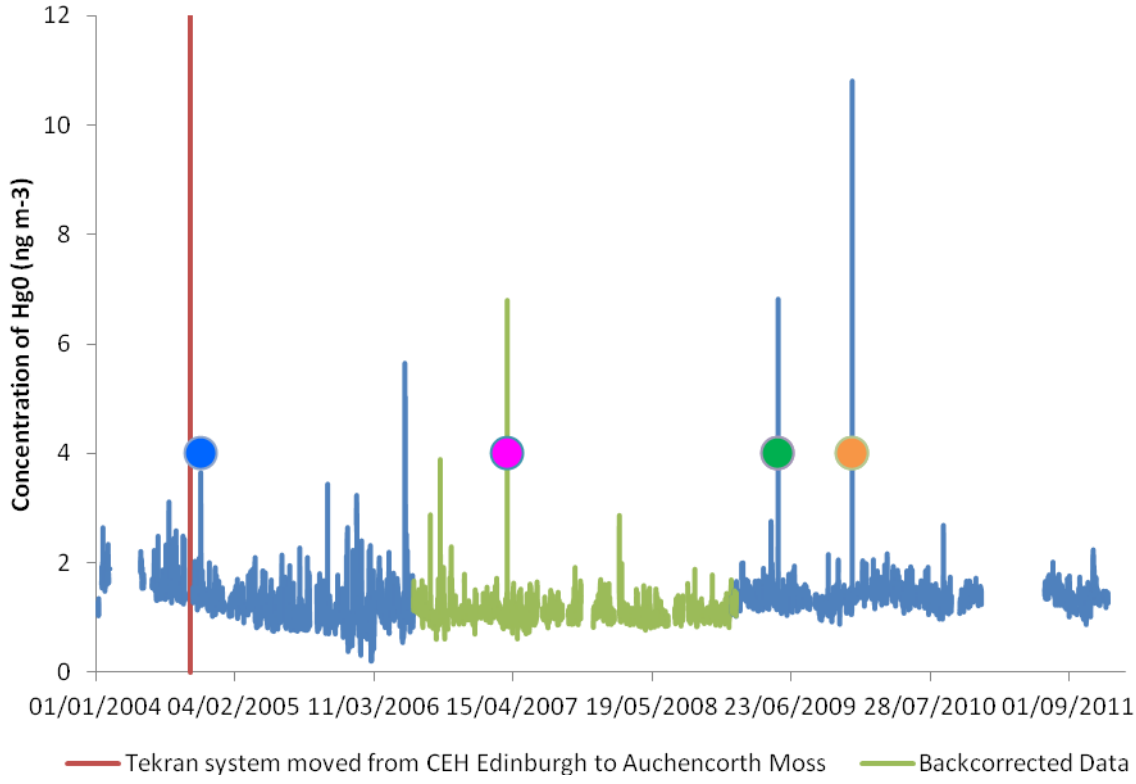


Figure 9: Hg^0 hourly averages (ng m^{-3}) from January 2004 to December 2011. Coloured dots indicate events that are shown in Figures 9 and 10.

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Year	CEH Edinburgh			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}
2004 (part year)	1.63	1.29	3.02	1.40	4.14	3.19
2005				1.14	3.20	2.62
2006				1.15	0.42	0.79
2007				1.10	0.11	0.86
2008				1.08	0.21	1.12
2009				1.39	0.30	3.63
2010				1.45	0.57	0.68
2011				1.38	-	-

Table 13: Annual average for Hg^0 at CEH Edinburgh and Auchencorth Moss. Note the units for RGM and Hg^P are different from those for Hg^0

Measurements of Hg^0 between 2005-8 show an average concentration of 1.13 ng m^{-3}, due to experimental difficulties with cartridge passivation described earlier. The co-located integrated sampler at Auchencorth shows an average of 1.44 ng m^{-3} for the same period, suggesting a more likely average mercury level and one which is consistent with the Tekran data for 2009-10 of 1.42 ng m^{-3}. However, this value is still lower that other published data for the south of England (1.68 ng m^{-3} (with a background of 1.5 ng m^{-3}), Lee et al, 1998). The average concentration for the northern hemisphere is around 1.5-1.7 ng m^{-3} (Ebinghaus et al, 2002) These data indicate a lower baseline at Auchencorth, probably due to its remote location and less influence from local sources.

The background is generally stable, but is enhanced for periods of several hours during events in which the concentration of Hg^0 can increase almost seven-fold. The maximum hourly concentration of Hg^0 that has been observed is 10.8 ng m^{-3}. Analysis of these events shows that elevated concentrations are generally associated with slow-moving surface air-mass back trajectories that have travelled to Eastern Scotland from mainland Europe or industrialised regions of England. Figures 9 and 10 show four such examples, in which concentrations were elevated above 'background' levels for several hours. Lower than average concentrations are generally associated with clean air masses that have originated in the Arctic or the Atlantic.

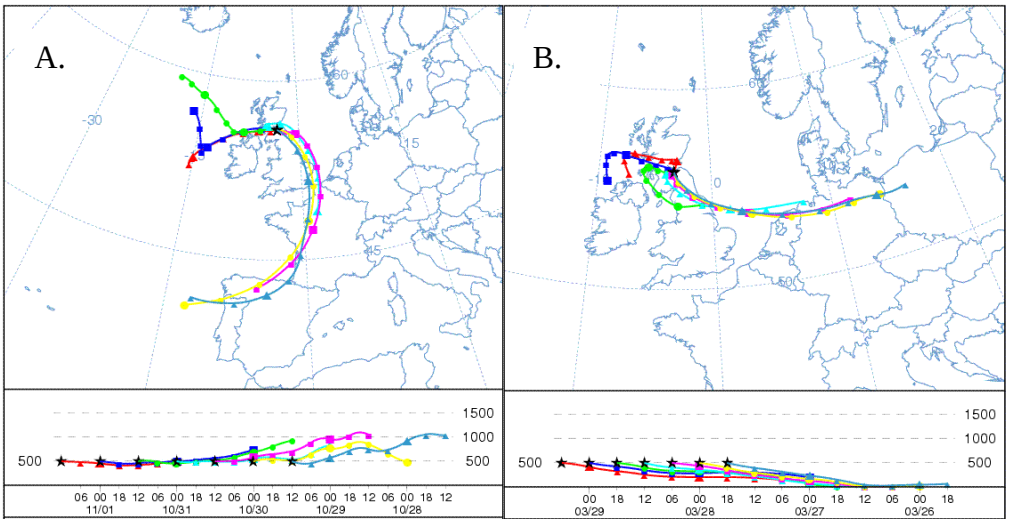

Figure 10: Air mass back trajectory for air arriving at Auchencorth Moss between A) the 29th October and 1st November 2004 and B) 18th and 19th August 2006. (Event marked by blue circle and pink circle respectively in Figure 8.) Tick marks are at 6h intervals.

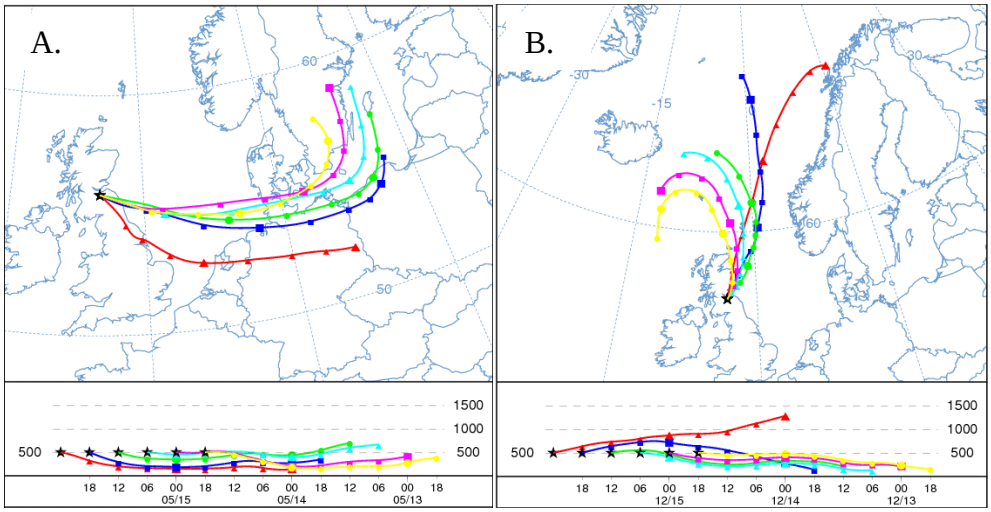

Figure 11: Air mass back trajectory over 2 days for air arriving at Auchencorth Moss between A) the 13th – 16th May 2009 and B) the 13th – 16th December 2009. (Events marked by green and orange circles respectively in Figure 8.) Tick marks are at 6h intervals.

Figures 12 and 13 show hourly averages of concentrations of RGM and Hg^P at Auchencorth Moss. The concentration of these species is at least an order of magnitude lower and varies more widely than that of elemental mercury variable with hourly maxima up to 127 pg m^{-3}. Concentrations of RGM and Hg^P are often below the method detection limit.

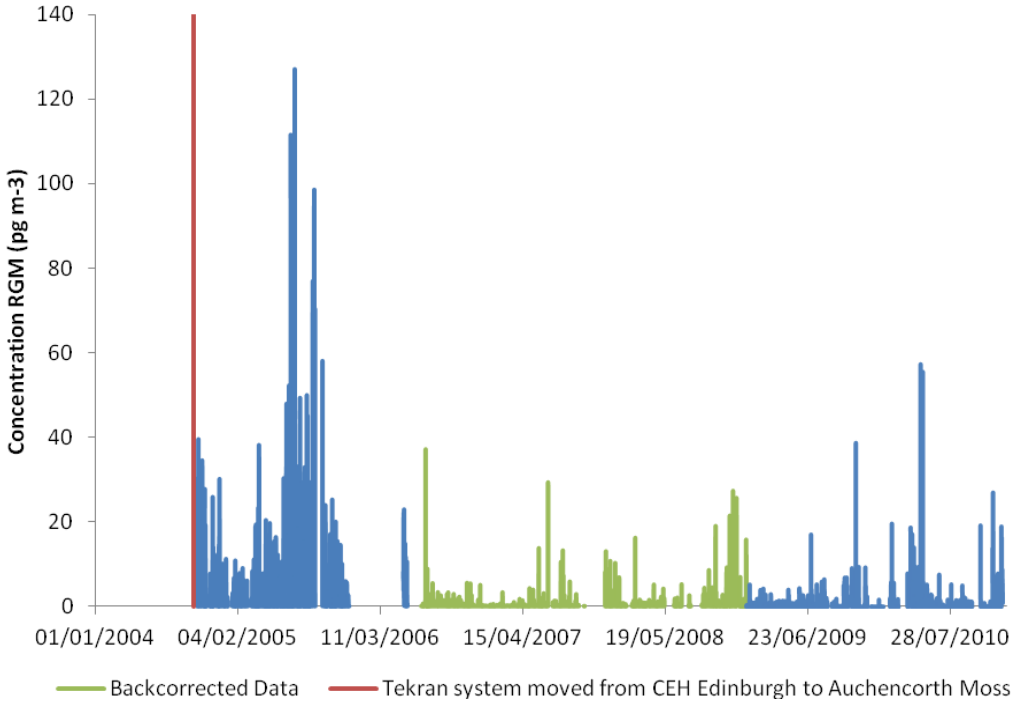

Figure 12: Hourly concentrations of reactive gaseous mercury (RGM), January 2004 – December 2010 (pg m^{-3})

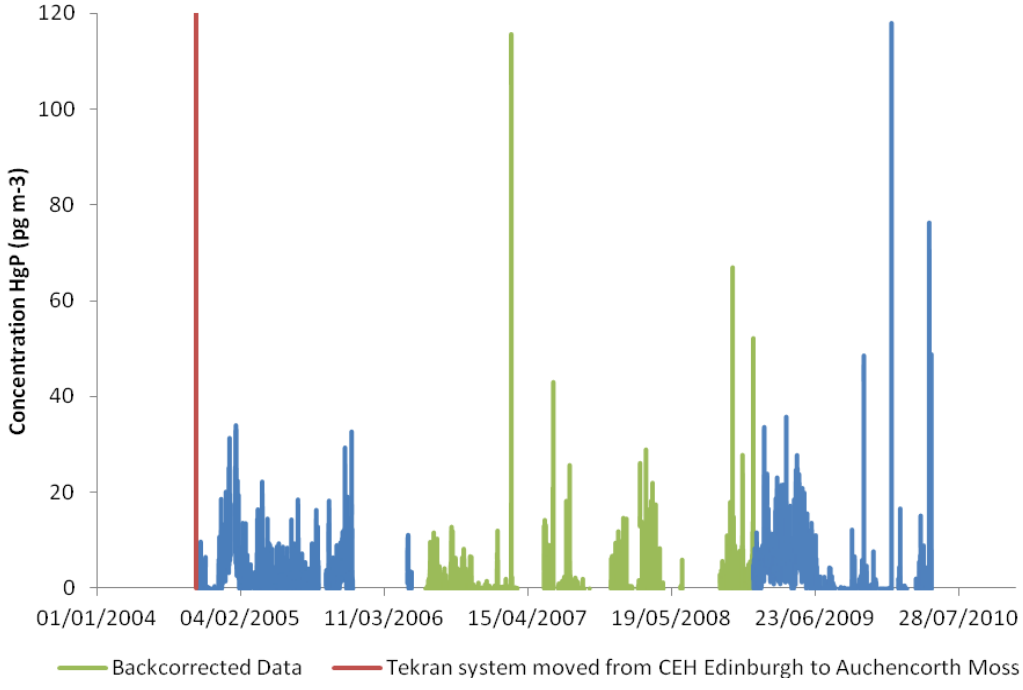

Figure 13: Hourly concentrations of particulate mercury (Hg^P), January 2004 – December 2010 (pg m^{-3})

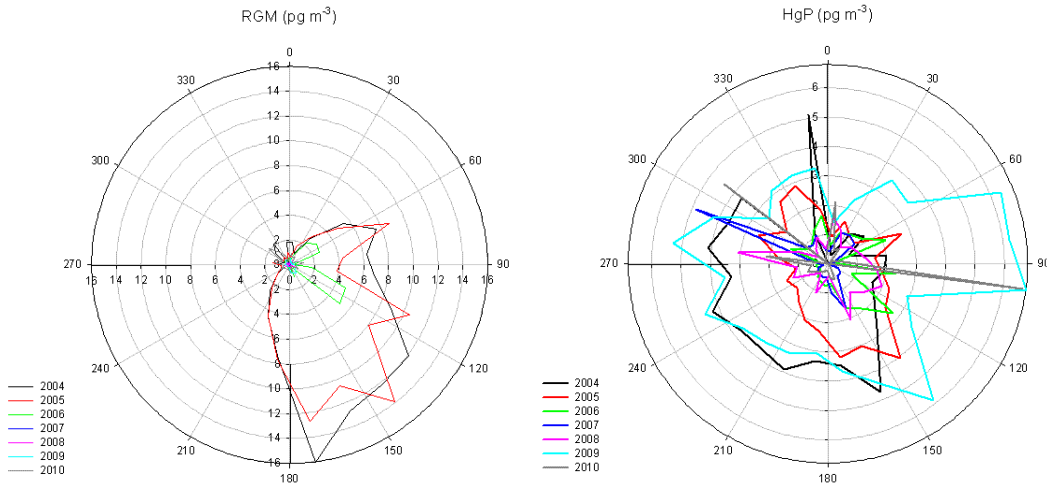

Figure 14: Distribution of average RGM and Hg^P concentrations (pg m^{-3}) by wind direction for the years 2004 – 2008.

Figure 14 shows the spatial distribution of average RGM and Hg^P data for each of the years 2004 – 2010. This clearly shows that during 2004 and 2005, RGM was particularly prevalent from the south-east, dwindling in 2006 to the lower levels observed in 2007 through to 2010. This prevalence is most likely due to contaminated air masses moving in from continental Europe. This contamination can also be seen in the data from the Hg^P plot, which also shows higher concentrations from the south-east. The Hg^P data also shows a series of spikes in the north-west sector between 270° and 320°, which are likely the result of emissions from the Longannet coal fired power station. Similarly, emissions to the north east, between 60° and 90°, are likely from the Cockenzie coal fired power station.

Seasonal and Diurnal Patterns of Hg^0, RGM and Hg^P concentrations

Figure 15A shows the daily plots of average elemental mercury in which a clear diurnal pattern is noticeable (Figure 15B), with a peak between midday and 3pm and a trough between 3 and 6am. The two larger peaks in these plots are the influence of the two large peaks identified in Figure 8 (Green and Orange dots). Figure 14C shows the seasonal trend in Hg^0, with a springtime maxima and autumnal minima as seen in other studies. Figure 14D shows the daily averages, with Hg^0 peaking mid-week, which we speculate to be the influence of activity in the city of Edinburgh and possibly related to the influence of the city crematoria.

Figure 15E shows a directionally dependent plot of the daily diurnal cycle. Midnight is at the centre of the ring and midday is in the middle. This again clearly shows the diurnal cycle, but also shows the strong influence of higher concentrations from the north-east (Edinburgh) and lower concentrations from the south-west (prevailing wind direction).

The diurnal cycle seen in Hg0 as well as RGM and Hg^P (Figure 15) would be controlled through the temperature dependent release of mercury species from surface sources, with concentrations of RGM and Hg^P being significantly controlled through photochemical processes that both generate and consume RGM in the atmosphere. There is also a noticeable difference between the hourly concentrations of RGM and Hg^P according to season. RGM concentrations tend to decrease in the winter and spring, coinciding with a corresponding increase in the concentrations of Hg^P. This likely reflects the partitioning of RGM between its gaseous and particulate bound phases at lower temperatures.

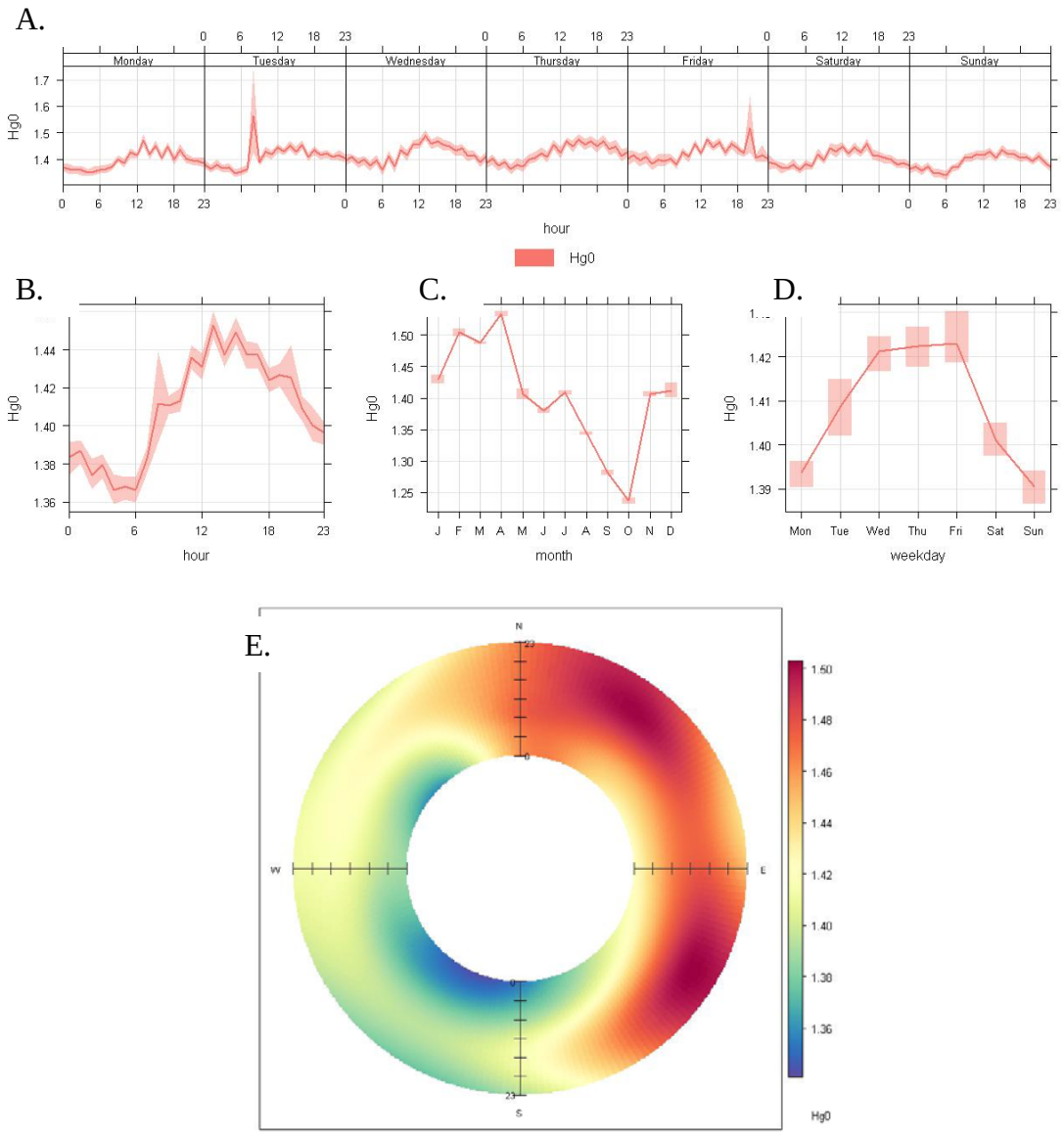

Figure 15: Temporal and direction trends in Hg^0 between January 2009 and December 2010. A) Daily trend, B) Diurnal trend, C) Seasonal trend, D) Weekly trend, E) Directional dependence and diurnal cycle. (Average concentrations at midnight are on the inside of the ring and midday at the centre.) *Plot uses openair software (www.openair-project.org).*

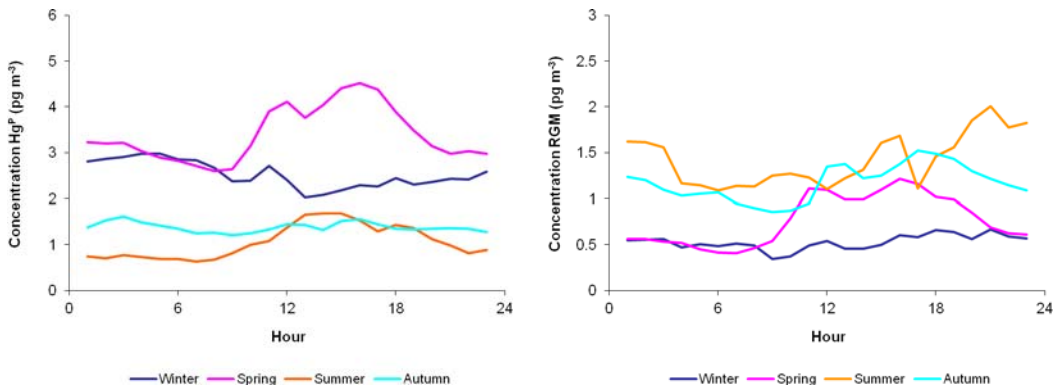

Figure 16: Concentration of RGM and Hg^P by season for October 2004 – December 2010 at Auchencorth Moss. The lines represent 2-hourly moving average.

8) Comparison of data from Wytham Wood and Harwell

Monitoring of heavy metals at the Harwell site, Oxfordshire, commenced in August 2008 with the aim of complimenting the existing monitoring activities at this EMEP supersite. As Harwell is only 10 miles from the site at Wytham Wood, it was originally proposed by Defra that the Harwell site should replace the Wytham site in Rural Heavy Metals Monitoring Network. The decision to decommission Wytham would only be made if it can be demonstrated that this will not have an effect on the calculations of the annual UK budgets of heavy metal deposition.

There are now over three calendar years worth of data from both sites as presented in Table 14.

A full statistical analysis will also be conducted, including the effect on the overall UK budget, so that Defra have the full information available before making a long term decision on the future of the Wytham Wood monitoring site.

		Annual Air Concentrations (ng/m3)		Annual Rain Concentrations (µg/l, ng Hg/l)		Wet Deposition (g/ha/year)	
		Harwell	Wytham Wood	Harwell	Wytham Wood	Harwell	Wytham Wood
Al	2009	34.807 ± 30.306	30.324 ± 24.023	14.555 ± 52.080	8.791 ± 25.272	102.279	53.408
Al	2010	33.238 ± 36.722	33.826 ± 33.760	13.574 ± 22.963	8.258 ± 13.870	82.026	44.082
Al	2011	46.126 ± 84.638	39.046 ± 33.209	20.019 ± 28.430	12.018 ± 16.128	95.449	54.902
As	2009	7.452 ± 7.079	8.060 ± 6.558	0.106 ± 0.136	0.208 ± 0.099	0.748	1.264
As	2010	6.989 ± 5.823	9.104 ± 11.916	4.640 ± 3.322	3.619 ± 2.692	28.039	19.317
As	2011	9.195 ± 10.856	9.867 ± 4.812	4.561 ± 4.078	4.496 ± 3.899	21.744	20.540
Ba	2009	0.014 ± 0.010	0.013 ± 0.011	36.697 ± 188.884	1.016 ± 1.321	257.878	6.175
Ba	2010	0.017 ± 0.025	0.017 ± 0.034	0.002 ± 0.003	0.003 ± 0.003	0.013	0.015
Ba	2011	0.021 ± 0.023	0.023 ± 0.027	0.004 ± 0.003	0.004 ± 0.004	0.018	0.018
Be	2009	0.009 ± 0.003	0.009 ± 0.002	0.003 ± 0.008	0.002 ± 0.002	0.018	0.015
Be	2010	0.009 ± 0.005	0.010 ± 0.034	0.003 ± 0.003	0.002 ± 0.002	0.016	0.009
Be	2011	0.009 ± 0.009	0.009 ± 0.001	0.005 ± 0.006	0.002 ± 0.006	0.026	0.010
Cd	2009	0.145 ± 0.110	0.144 ± 0.092	0.020 ± 0.070	0.016 ± 0.015	0.139	0.098
Cd	2010	0.145 ± 0.147	0.183 ± 0.351	0.026 ± 0.190	0.037 ± 0.177	0.154	0.197
Cd	2011	0.159 ± 0.222	0.160 ± 0.117	0.028 ± 0.035	0.047 ± 0.086	0.134	0.216
Co	2009	0.925 ± 2.409	0.785 ± 0.518	0.025 ± 0.062	0.020 ± 0.040	0.172	0.121
Co	2010	0.817 ± 0.949	0.703 ± 0.540	0.277 ± 0.246	0.188 ± 0.195	1.674	1.003
Co	2011	0.959 ± 1.092	0.826 ± 0.959	0.179 ± 0.139	0.178 ± 0.160	0.853	0.814
Cr	2009	0.847 ± 1.074	0.559 ± 0.994	0.126 ± 0.162	0.115 ± 0.094	0.884	0.700
Cr	2010	0.357 ± 1.129	0.758 ± 1.085	0.044 ± 0.078	0.048 ± 0.050	0.265	0.256
Cr	2011	0.499 ± 0.474	0.317 ± 0.427	0.064 ± 0.092	0.078 ± 0.075	0.305	0.357
Cs	2009	0.709 ± 0.661	0.746 ± 0.764	0.003 ± 0.006	0.002 ± 0.003	0.019	0.015
Cs	2010	0.680 ± 0.512	0.878 ± 0.504	0.103 ± 0.069	0.123 ± 0.077	0.623	0.657
Cs	2011	0.891 ± 1.239	0.916 ± 0.415	0.102 ± 0.062	0.122 ± 0.097	0.487	0.558

Table 14: Comparison of annual mean data at the Harwell and Wytham Wood sites.

		Annual Air Concentrations (ng/m3)		Annual Rain Concentrations (µg/l, ng Hg/l)		Wet Deposition (g/ha/year)	
		Harwell	Wytham Wood	Harwell	Wytham Wood	Harwell	Wytham Wood
Cu	2009	0.893 ± 2.407	0.770 ± 0.519	0.834 ± 1.537	0.968 ± 0.955	5.857	5.883
Cu	2010	0.694 ± 0.907	0.571 ± 0.417	0.217 ± 0.214	0.191 ± 0.192	1.311	1.017
Cu	2011	0.807 ± 1.030	0.721 ± 0.915	0.169 ± 0.102	0.174 ± 0.136	0.805	0.793
Fe	2009	74.795 ± 55.268	79.002 ± 46.357	18.703 ± 55.009	11.751 ± 32.790	131.427	71.392
Fe	2010	67.008 ± 68.218	85.600 ± 76.236	12.735 ± 27.890	9.996 ± 20.585	76.955	53.359
Fe	2011	99.931 ± 84.045	94.784 ± 57.378	18.794 ± 30.903	13.557 ± 21.365	89.606	61.931
Hg	2009	1.503 ± 2.175	0.600 ± 0.593	5.196 ± 4.361	4.903 ± 3.190	0.025	0.021
Hg	2010	1.247 ± 0.404	0.970 ± 0.495	4.251 ± 3.159	4.081 ± 2.557	0.019	0.017
Hg	2011	1.628 ± 0.578	1.006 ± 0.337	5.466 ± 3.099	5.058 ± 2.488	0.026	0.020
Li	2009	0.051 ± 0.030	0.051 ± 0.027	0.042 ± 0.061	0.029 ± 0.033	0.296	0.175
Li	2010	0.051 ± 0.039	0.053 ± 0.042	0.034 ± 0.036	0.030 ± 0.024	0.205	0.160
Li	2011	0.063 ± 0.057	0.059 ± 0.046	0.041 ± 0.033	0.038 ± 0.031	0.196	0.172
Mn	2009	1.819 ± 1.203	1.754 ± 0.928	2.510 ± 8.114	1.755 ± 3.980	17.636	10.662
Mn	2010	1.801 ± 1.926	2.026 ± 1.515	1.681 ± 3.939	1.811 ± 2.966	10.160	9.669
Mn	2011	2.399 ± 2.226	2.135 ± 1.646	2.759 ± 4.759	1.964 ± 3.168	13.152	8.972
Mo	2009	1.358 ± 1.301	0.964 ± 0.992	0.034 ± 0.043	0.034 ± 0.029	0.240	0.205
Mo	2010	0.987 ± 0.605	0.878 ± 0.735	1.707 ± 2.398	1.181 ± 0.967	10.314	6.303
Mo	2011	1.435 ± 1.070	1.044 ± 0.474	2.683 ± 2.964	1.528 ± 1.246	12.794	6.979
Ni	2009	0.045 ± 0.032	0.044 ± 0.036	0.328 ± 0.239	0.177 ± 0.127	2.302	1.073
Ni	2010	0.039 ± 0.039	0.047 ± 0.072	0.019 ± 0.035	0.020 ± 0.023	0.117	0.107
Ni	2011	0.050 ± 0.046	0.045 ± 0.041	0.022 ± 0.037	0.017 ± 0.029	0.105	0.078
Pb	2009	0.032 ± 0.026	0.032 ± 0.017	2.442 ± 12.868	0.810 ± 0.814	17.157	4.923
Pb	2010	0.033 ± 0.019	0.040 ± 0.131	0.011 ± 0.105	0.006 ± 0.006	0.068	0.030
Pb	2011	0.035 ± 0.057	0.030 ± 0.006	0.020 ± 0.034	0.025 ± 0.042	0.094	0.112

Table 14 Continued) Comparison of annual mean data at the Harwell and Wytham Wood sites.

		Annual Air Concentrations (ng/m3)		Annual Rain Concentrations (µg/l, ng Hg/l)		Wet Deposition (g/ha/year)	
		Harwell	Wytham Wood	Harwell	Wytham Wood	Harwell	Wytham Wood
Rb	2009	0.381 ± 0.234	0.391 ± 0.241	0.073 ± 0.087	0.071 ± 0.070	0.515	0.431
Rb	2010	0.421 ± 0.260	0.486 ± 0.365	0.116 ± 0.100	0.121 ± 0.089	0.700	0.646
Rb	2011	0.445 ± 0.296	0.481 ± 0.266	0.100 ± 0.056	0.103 ± 0.094	0.479	0.472
Sb	2009	0.619 ± 0.625	0.687 ± 0.944	0.093 ± 0.135	0.099 ± 0.085	0.652	0.602
Sb	2010	0.622 ± 2.532	0.690 ± 0.635	0.031 ± 0.021	0.017 ± 0.040	0.185	0.091
Sb	2011	0.550 ± 0.604	0.645 ± 0.381	0.021 ± 0.039	0.056 ± 2.374	0.099	0.256
Sc	2009	0.157 ± 0.056	0.154 ± 0.094	0.025 ± 0.021	0.025 ± 0.000	0.176	0.152
Sc	2010	0.157 ± 0.088	0.159 ± 0.566	0.025 ± 0.000	0.025 ± 0.000	0.000	0.133
Sc	2011	0.151 ± 0.146	0.150 ± 0.017	0.026 ± 0.018	0.025 ± 0.019	0.122	0.114
Se	2009	0.491 ± 0.520	0.511 ± 0.416	0.130 ± 0.093	0.120 ± 0.059	0.916	0.731
Se	2010	0.445 ± 0.348	0.554 ± 0.341	0.118 ± 0.103	0.196 ± 0.115	0.712	1.047
Se	2011	0.529 ± 0.719	0.548 ± 0.336	0.107 ± 0.064	0.243 ± 0.141	0.510	1.112
Sn	2009	0.076 ± 0.083	0.076 ± 0.066	0.020 ± 0.065	0.026 ± 0.024	0.142	0.159
Sn	2010	0.072 ± 0.073	0.083 ± 0.053	0.019 ± 0.011	0.019 ± 0.011	0.115	0.099
Sn	2011	0.095 ± 0.137	0.093 ± 0.057	0.019 ± 0.020	0.021 ± 0.016	0.093	0.097
Sr	2009	0.125 ± 0.065	0.123 ± 0.065	2.979 ± 6.653	1.180 ± 0.908	20.933	7.166
Sr	2010	0.126 ± 0.105	0.135 ± 0.076	0.052 ± 0.088	0.067 ± 0.090	0.315	0.359
Sr	2011	0.160 ± 0.145	0.154 ± 0.116	0.071 ± 0.054	0.080 ± 0.051	0.337	0.365
Ti	2009	1.503 ± 1.574	1.405 ± 1.191	0.520 ± 1.749	0.271 ± 0.602	3.655	1.647
Ti	2010	1.615 ± 2.930	2.011 ± 5.415	0.325 ± 0.693	0.157 ± 0.472	1.962	0.840
Ti	2011	1.632 ± 2.328	1.777 ± 1.506	0.574 ± 1.011	0.279 ± 0.475	2.734	1.274
U	2009	5.050 ± 5.445	4.534 ± 4.389	0.003 ± 0.010	0.001 ± 0.003	0.019	0.008
U	2010	4.248 ± 3.852	4.818 ± 3.168	1.797 ± 2.627	0.784 ± 0.620	10.858	4.183
U	2011	5.529 ± 6.822	5.032 ± 2.260	2.478 ± 4.496	0.947 ± 3.838	11.814	4.326

Table 14 Continued) Comparison of annual mean data at the Harwell and Wytham Wood sites.

		Annual Air Concentrations (ng/m3)		Annual Rain Concentrations (µg/l, ng Hg/l)		Wet Deposition (g/ha/year)	
		Harwell	Wytham Wood	Harwell	Wytham Wood	Harwell	Wytham Wood
V	2009	1.310 ± 0.768	1.195 ± 0.662	0.382 ± 0.380	0.302 ± 0.187	2.683	1.838
V	2010	0.880 ± 1.445	0.931 ± 0.720	0.294 ± 0.225	0.258 ± 0.152	1.779	1.377
V	2011	1.170 ± 0.860	1.020 ± 1.355	0.326 ± 0.164	0.276 ± 0.169	1.553	1.262
W	2009	10.564 ± 17.533	1.797 ± 2.845	0.010 ± 0.026	0.007 ± 0.011	0.068	0.045
W	2010	4.472 ± 12.220	1.916 ± 1.672	16.492 ± 43.492	1.088 ± 0.862	99.655	5.808
W	2011	12.322 ± 22.250	2.183 ± 0.935	34.855 ± 67.491	1.136 ± 1.120	166.182	5.191
Zn	2009	3.204 ± 3.410	2.992 ± 6.544	5.870 ± 9.322	3.560 ± 3.795	41.251	21.629
Zn	2010	2.278 ± 2.060	2.481 ± 1.405	0.681 ± 0.654	0.930 ± 0.682	4.114	4.967
Zn	2011	2.840 ± 2.927	3.211 ± 1.607	0.806 ± 0.806	1.125 ± 0.971	3.841	5.141

Table 14 Continued) Comparison of annual mean data at the Harwell and Wytham Wood sites.

9) Discussion

The concentrations of all metals measured in airborne particulate matter, rainfall and cloudwater are low, as would be expected in samples collected from rural areas. The concentrations are 1.5 to 8.5 times lower than the national average as reported in the Urban and Industrial Heavy Metals Monitoring network (see Table 5 for comparison).

The main legislation governing the concentrations of heavy metals in ambient air in the UK is EC Directive 96/62/EC on Ambient Air Quality Assessment and Management (the Framework Directive) which established a common strategy to define and set objectives for ambient air quality. Heavy Metals are covered in two associated Daughter Directives, namely Directive 1999/30/EC (the first Daughter Directive, AQDD1) which set a limit value for lead of 0.5µg/m^3, and Directive 2004/107/EC (the fourth Daughter Directive AQDD4) which set target values for arsenic, cadmium and nickel of 6, 5 and 20 ng/m^3, respectively. Mercury is also covered by the Fourth Daughter Directive, although no limit or target value was set.

The mean annual concentration of nickel, arsenic, cadmium and lead between 2004 and 2011 at each of the monitoring sites was calculated and expressed as a percentage of the relevant target or limit value as defined in the Air Quality Framework Directive (Figure 17). Concentrations of cadmium and lead are generally less than 5% of their respective target and limit values. Although the relative concentrations of nickel and arsenic are slightly higher at up to 15% of the target values, these values are still considerably below the lower assessment thresholds (equivalent to 50% and 40% respectively), where the legislation requires initial action to be undertaken.
As the Rural Heavy Metals Monitoring Network has only been in operation since 2004, the 5 years' worth of data is currently insufficient to determine any overall temporal trends in concentration or deposition of heavy metals in rural areas. Although the reported emissions of heavy metals in the UK have declined considerably from their industrial peak in the 1970s, and more recently during the 1990s, the inter-year variability in measured concentrations do not allow any corresponding temporal trends in measured concentrations to be established. For the majority of metals analysed, there are also large discrepancies between the reported UK emissions and the amount of metal deposited in the UK. This discrepancy needs further investigation, including improvements being made to the way that metal emission are produced, and the quantification of the amount of re-suspended material that is being picked up by the monitoring networks, as has been modelled by Yap et al (2009). The heavy metal concentrations do show a spatial gradient between lower concentrations in the north west of Scotland and higher concentrations in the south east of England. Further source apportionment analysis is required to determine the significance of variations in metal concentrations at each site.

When the metal deposition data are examined, it is clear that for all metals, the majority deposition occurs via wet deposition. This means that areas with the highest rainfall, such as the north west of Scotland, and upland areas have the highest deposition of heavy metals.

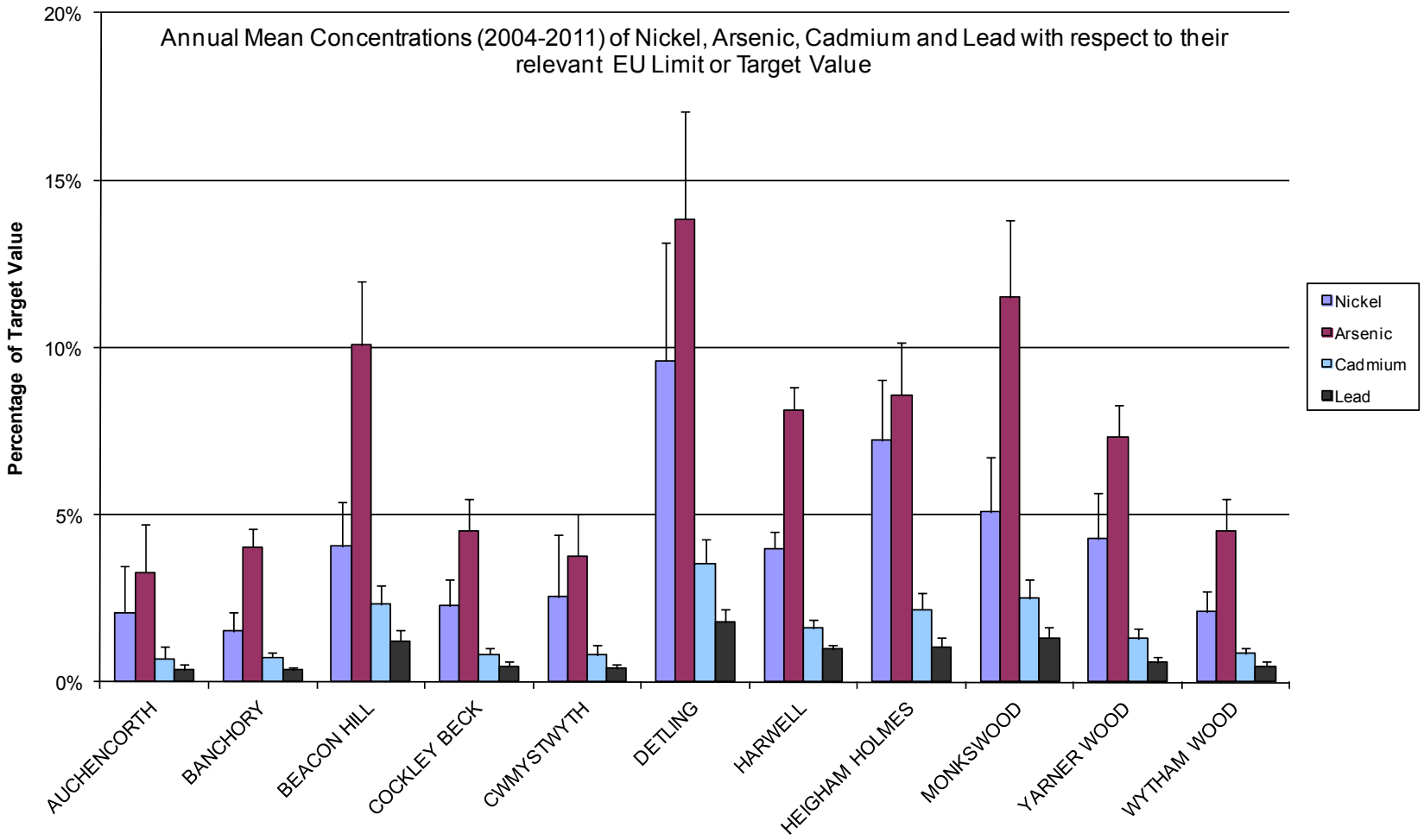

Figure 17 Annual Mean Concentrations of Nickel, Arsenic, Cadmium and Lead with respect to their relevant Limit or Target Value. Data based upon annual average concentration between 2004 and 2011.

10) References

Ashmore, M., Bell, S., Fowler, D., Hill, M., Jordan, C., Nemitz, E., Parry, S., Pugh, B., Reynolds, B., and 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 Bardford, UK.

Brown, R., Butterfield, D., Goddard, S., Muhunthan, D., Brown, A.S., and Williams, M. (2009): Annual Report for 2008 on the UK Heavy Metals Monitoring Network, pp. 67

Ebinghaus, R., Kock, H.H., Coggins, A.M., Spain, T.G., Jennings, S.G., and Temme, C. (2002): Long-term measurements of atmospheric mercury at Mace Head, Irish west coast, between 1995 and 2001. *Atmospheric Environment* **36** (34), 5267-5276.

EMEP (2002): Manual for Sampling and Analysis. EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe, pp. 303 Available at: http://www.nilu.no/projects/ccc/manual/index.html

Fowler, D., McDonald, A., Crossley, A., Nemitz, E., Leaver, D., Cape, J.N., Smith, R.I., Anderson, D., Rowland, P., Ainsworth, G., Lawlor, A.J., Guyatt, H., and Harmens, H. (2006): UK Heavy Metal Monitoring Network, pp. 120, Report to Defra by the Centre for Ecology and Hydrology Available at: http://www.uk-pollutantdeposition.ceh.ac.uk/sites/uk-pollutantdeposition.ceh.ac.uk/files/UK_HeavyMetals_Final_report_2006_final_version.pdf

Harmens, H., Norris, D., and the participants of the moss survey (2008): Spatial and temporal trends in heavy metal accumulation in mosses in Europe (1990-2005), pp. 51, Programme Coordination Centre for the ICP Vegetation, Centre for Ecology & Hydrology, Bangor. Available at: http://icpvegetation.ceh.ac.uk

Lee, D.S., Dollard, G.J., and Pepler, S. (1998): Gas-phase mercury in the atmosphere of the United Kingdom. *Atmospheric Environment* **32** (5), 855-864.

Murrells, T., Passant, N., Thistlethwaite, G., Wagner, A., Li, Y., Bush, T., Norris, J., Coleman, P., Walker, C., Stewart, R., Tsagatakis, I., Conolly, C., Brophy, N., and Okamura, S. (2009): UK Emissions of Air Pollutants 1970 to 2007, pp. 172, AEA Technology Energy & Environment

NAEI (2012) National Atmospheric Emissions Inventory 2010 Emissions Maps. Available at http://naei.defra.gov.uk/mapping/mapping_2010.php

Swartzendruber, P.C., Jaffe, D.A., and Finley, B. (2009): Improved fluorescence peak integration in the Tekran 2537 for applications with sub-optimal sample loadings. *Atmospheric Environment* **43** (22-23), 3648-3651.

Yap, F.W., Kent, A.J., Stedman, J.R., Grice, S., and Vincent, K.J. (2009): UK Air Quality Modelling for Annual Reporting 2008 on Ambient Air Quality Assessment under Council Directives 96/62/EC, 1999/30/EC and 2004/107/EC. Report to the Department for Environment, Food and Rural Affairs, Welsh Assembly Government, the Scottish Government and the Department of the Environment for Northern Ireland, pp. 57, AEA Technology plc

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Annex One: Details of Monitoring Sites

Site	Measurements	Grid References
Auchencorth	Particulate sampling – all metals including Hg Rain water – all metals including Hg Speciated Hg measurements	OS X (Eastings) 322050 OS Y (Northings) 656250 Nearest Post Code EH26 8PR Lat (WGS84) N55:47:36 (55.793236) Long (WGS84) W3:14:41 (-3.244782) LR NT220562 mX -361207 mY 7481998 Altitude 265m
Banchory	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 367650 OS Y (Northings) 798750 Nearest Post Code AB31 4BY Lat (WGS84) N57:04:43 (57.078620) Long (WGS84) W2:32:07 (-2.535274) LR NO676987 mX -282225 mY 7740307 Altitude 130m
Beacon Hill	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 451950 OS Y (Northings) 314150 Nearest Post Code LE12 8SR Lat (WGS84) N52:43:21 (52.722513) Long (WGS84) W1:13:56 (-1.232279) LR SK519141 mX -137176 mY 6897811 Altitude 200m
Bowbeat	Rain water - all metals excluding Hg Cloud water -all metals excluding Hg **Note**: site closed 31/12/2008	OS X (Eastings) 328289 OS Y (Northings) 647302 Nearest Post Code EH45 8PN Lat (WGS84) N55:42:50 (55.713821) Long (WGS84) W3:08:35 (-3.142947) LR NT282473 mX -349871 mY 7466323 Altitude 580m
Cockley Beck	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 324750 OS Y (Northings) 501550 Nearest Post Code LA20 6EQ Lat (WGS84) N54:24:14 (54.403825) Long (WGS84) W3:09:39 (-3.160733) LR NY247015 mX -351851 mY 7212239 Altitude 220m
Cwmystwyth	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 277150 OS Y (Northings) 274250 Nearest Post Code SY23 4AB Lat (WGS84) N52:21:09 (52.352509) Long (WGS84) W3:48:19 (-3.805145) LR SN771742 mX -423586 mY 6830261 Altitude 260m

Site	Measurements	Grid References
Detling	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 580150 OS Y (Northings) 159750 Nearest Post Code ME14 3HD Lat (WGS84) N51:18:30 (51.308351) Long (WGS84) E0:34:60 (0.583246) LR TQ801597 mX 64926 mY 6642647 Altitude 185m
Harwell	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 447502 OS Y (Northings) 186247 Nearest Post Code OX11 0QX Lat (WGS84) N51:34:23 (51.573097) Long (WGS84) W1:18:58 (-1.315973) LR SU475862 mX -146493 mY 6689805 Altitude TBC m
Heigham Holmes	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 644150 OS Y (Northings) 320550 Nearest Post Code NR29 4RG Lat (WGS84) N52:43:39 (52.727440) Long (WGS84) E1:36:52 (1.614388) LR TG441205 mX 179712 mY 6898714 Altitude 5m
Holme Moss	Rain water - all metals excluding Hg Cloud water -all metals excluding Hg	OS X (Eastings) 409550 OS Y (Northings) 404050 Nearest Post Code HD9 2QH Lat (WGS84) N53:31:59 (53.533020) Long (WGS84) W1:51:27 (-1.857391) LR SE095040 mX -206763 mY 7047820 Altitude 530m
Inverpolly	Rain water - all metals excluding Hg	OS X (Eastings) 218750 OS Y (Northings) 908950 Nearest Post Code IV27 4HH Lat (WGS84) N58:01:57 (58.032568) Long (WGS84) W5:04:17 (-5.071375) LR NC187089 mX -564542 mY 7937881 Altitude 230m
Lough Navar	Rain water - all metals excluding Hg	OS X (Eastings) 17655 OS Y (Northings) 520876 Nearest Post Code Lat (WGS84) N54:26:20 (54.438915) Long (WGS84) W7:53:59 (-7.899622) LR NV176208 mX -879381 mY 7218937 Altitude 190m

Site	Measurements	Grid References
Monks Wood 	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 520150 OS Y (Northings) 279950 Nearest Post Code PE28 2LS Lat (WGS84) N52:24:16 (52.404377) Long (WGS84) W0:14:07 (-0.235281) LR TL201799 mX -26191 mY 6839696 Altitude 35m
Penallt 	Rain water - all metals excluding Hg	OS X (Eastings) 352350 OS Y (Northings) 209450 Nearest Post Code NP25 4AP Lat (WGS84) N51:46:54 (51.781673) Long (WGS84) W2:41:32 (-2.692126) LR SO523094 mX -299686 mY 6727152 Altitude 205m
Wytham Wood 	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 446150 OS Y (Northings) 208150 Nearest Post Code OX2 8QQ Lat (WGS84) N51:46:12 (51.770130) Long (WGS84) W1:19:57 (-1.332593) LR SP461081 mX -148343 mY 6725081 Altitude 155m
Yarner Wood 	Particulate sampling – all metals including Hg Rain water – all metals including Hg	OS X (Eastings) 278650 OS Y (Northings) 79150 Nearest Post Code TQ13 9LJ Lat (WGS84) N50:35:58 (50.599420) Long (WGS84) W3:42:58 (-3.716019) LR SX786791 mX -413665 mY 6517701 Altitude 120m