

# Report

NPL REPORT DQL-AS 036

Report to the Department of Environment, Food and Rural Affairs by the National Physical Laboratory:

# Annual Report for 2006 on the UK Heavy Metals Monitoring Network

Richard J. C. Brown Melanie Williams David M. Butterfield Rachel E. Yardley Dharsheni Muhunthan Sharon L. Goddard

NOT RESTRICTED

March 2007

Report to the Department of Environment, Food and Rural Affairs by the National Physical Laboratory:

# Annual Report for 2006 on the UK Heavy Metals Monitoring Network

Richard J. C. Brown Melanie Williams David M. Butterfield Rachel E. Yardley Dharsheni Muhunthan Sharon L. Goddard

#### © Crown copyright 2007

#### Reproduced by permission of the Controller of HMSO and Queen's Printer for Scotland

#### ISSN 1744-0602

#### National Physical Laboratory Queens Road, Teddington, Middlesex, TW11 0LW

Extracts from this report may be reproduced provided the source is acknowledged and the extract is not taken out of context

Approved on behalf of Managing Director, NPL By S Windsor, Business Leader, Division of Quality of Life

# Annual Report for 2006 on the UK Heavy Metals Monitoring Network

#### **Executive Summary**

This Report was prepared by NPL as part of the 2004-2007 UK Heavy Metals Monitoring Network contract with the Department for the Environment, Food and Rural Affairs. This is the Annual Summary Report for 2006 and contains, in particular:

- Measured monthly concentration levels of all metals at all sites and performance against relevant data quality objectives and the requirements of the First and Fourth EC Air Quality Daughter Directives (DDs).
- Highlighting of exceedences, interpretation of data and discussion of trends.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events during 2006.
- Policy update on relevant areas.

In summary, during 2006:

- Lead: No annual average site levels above the First Daughter Directive Lower Assessment Threshold were recorded.
- **Nickel**: One annual average site level above the Fourth Daughter Directive Target Value, and one annual average site level above the Fourth Daughter Directive Lower Assessment Threshold were recorded.
- **Cadmium**: One annual average site level above the Fourth Daughter Directive Upper Assessment Threshold was recorded.
- **Arsenic**: No annual average site levels above the Fourth Daughter Directive Lower Assessment Threshold were recorded.
- **Total gaseous mercury**: Measured levels across the Network remain low (with the exception of the site at ICI Weston Point, Runcorn).
- The general downward trend in annual average concentration values has continued.
- All First, and Fourth, Daughter Directive data quality objectives were met, including time coverage, data capture and measurement uncertainty requirements.
- Data capture across the Network was 94% for the year.

### **Table of Contents**

Executive Summary4					
Table of Contents5					
1. Introduction					
2. Network Operation72.1 Overview72.2 Site audits72.3 Equipment servicing and breakdowns82.4 Site infrastructure and other issues10					
<ul> <li>3. Sampling and Analytical Methodology</li></ul>					
4Data quality					
5Network data.185.1Data capture - 4th Quarter 2006185.2Data capture - 2006185.3Data processing and ratification205.4Measurement Uncertainty of Annual Average215.5Measured Concentrations225.6Measured concentrations with respect to the requirements of theFirst and Fourth Daughter Directives245.7Correlation with metrological conditions265.8Contribution of individual sites to the annual average28					
6 Trends in measured concentrations					
7 Policy Update					
Annex 1 - Location and details of sites on the UK Heavy Metals Network35 Annex 2 - Site Audit reports					

#### 1. Introduction

This Report was prepared by NPL as part of the 2004-2007 UK Heavy Metals Monitoring Network contract (RMP 2387) with the Department for the Environment, Food and Rural Affairs.

This is the Annual Summary Report for the UK Heavy Metals Network for 2006 and contains:

- A summary of Network operation and performance during 2006.
- A description of analytical methods, including QA/QC procedures used by NPL.
- A summary of Network data quality statistics.
- Measured monthly concentration levels of all metals at all sites and performance against relevant data quality objectives and the requirements of the First and Fourth EC Air Quality Daughter Directives (DDs).
- Highlighting of exceedences, interpretation of data and discussion of trends.
- Policy update on relevant areas.

#### 2. Network Operation

#### 2.1 Overview

NPL's management of the UK Heavy Metals Monitoring Network (the 'Network') in 2006 has covered a great deal of activity. In summary:

- NPL staff visited and fully audited all sites on the Network. This included the calibration and basic maintenance of the Partisol and total gaseous mercury samplers and re-assessment of LSOs' procedures.
- All network sites have now been tested for electrical safety, and any remedial work required is now well underway.
- The Equipment Support Unit (ESU) has made service visits to all Network sites twice throughout the year. This has included the flow calibration of instruments. This has resulted in a substantial decrease in the number of instrument breakdowns, and smaller uncertainties on sampled volumes.
- NPL has rolled out a new type of total gaseous mercury sampling pump across the Network. Installation of this system, which was first trialled over a six-month period in Brent, has resulted in a significantly reduced breakdown rate.
- Data capture has increased across the Network.
- The UK Heavy Metals Monitoring Network and the data it produces has received exposure in both trade<sup>1</sup> and learned journals<sup>2</sup>.
- NPL are providing metals analysis at two extra sites (that are not currently part of the Network) for the local authority in Swansea. These sites are being used to assess the same point source as the current Metals Network site in the area.

#### 2.2 Site audits

During 2006 NPL visited all the Network sites. The site infrastructure, performance and integrity were assessed. The LSOs were also audited and received extra training where required. A list of sites on the Network, with locations, site codes, site names and abbreviated site names is displayed in Annex 1.

During each site visit NPL has:

- Audited the procedures of the LSO on-site, and encouraged LSOs to feed-back into the running of the Network;
- Assessed the current condition of all on-site equipment, including the condition of the PM<sub>10</sub> sampling head and impactor plate;
- Calibrated the flows of both the particulate (for volumetric and standard flow), and gaseous phase (volumetric flow), monitoring equipment;

<sup>&</sup>lt;sup>1</sup> Brown, R J C, "A breath of fresh air", Environmental Measures, No. 2, Summer 2006, 6, NPL, UK,.

<sup>&</sup>lt;sup>2</sup> Brown, R J C, "The use of Zipf's law in the screening of analytical data: a step beyond Benford", Analyst, 2007, DOI: 10.1039/b618255k.

- Leak tested both the particulate, and gaseous phase, monitoring equipment;
- Calibrated the site rotameter (used by the LSOs for determining the flow rate through the total gaseous mercury sampling line).

The dates of individual site audits and the flow data recorded at each site may be found in Annexes 2, 3 and 4. A detailed report on the findings of the audits is available<sup>3</sup>, but in summary:

- All of the sites have been audited and are performing well.
- The site infrastructure was assessed at all sites and no significant problems were found.
- Following electrical safety tests on all of the Network sites, the details of which are available in a separate report<sup>4</sup>, NPL is in the process of performing the identified remedial actions.
- Nearly all of the LSOs audited were carrying out all of their functions correctly. However, there were a couple of cases where the flow through the total gaseous mercury adsorption tube was measured and adjusted at the end of a sampling period and was not rechecked when a new adsorption tube was inserted into the sampling system. It cannot be assumed that the new tube will have the same flow rate as the old tube. All of the LSOs who made this error have been instructed in the correct procedure.
- Additionally, at one site, the LSO was not measuring the flow through the mercury adsorption tube at the end of the sampling period. This is essential to allow the average flow through the tube over the sampling period to be calculated. Again remedial action has been taken to ensure this does not reoccur.

#### 2.3 Equipment servicing and breakdowns

During 2006 the ESU visited, fully serviced, and calibrated the Partisol samplers at every Network site twice, at 6-month intervals.

During 2006, NPL has called-out the ESU to deal with sampler failures at: Swansea (low flow); Motherwell (low flow); and London Horseferry Road (split washer). None of these callouts occurred in the final quarter of 2006.

As a result of a new, and more rigorous servicing programme, agreed between NPL and the ESU, and the installation of new pumps and mass-flow controllers in the Partisol instruments during 2005, the number of call-outs of the ESU to failed instruments has decreased from 13, in 2005, to 3, in 2006.

During 2006 NPL has replaced failed total gaseous mercury sampling pumps at: Motherwell (twice), Eskdalemuir, Glasgow, Newcastle, London Brent,

<sup>&</sup>lt;sup>3</sup> Butterfield, D M, and Yardley, R E, NPL Report DQL-AS (RES) 020, "UK Heavy Metals Monitoring Network Audit Report For 2006", NPL, August 2006.

<sup>&</sup>lt;sup>4</sup> Butterfield, D M, NPL Report DQL-AS (RES) 019, "UK Heavy Metals Monitoring Network Electrical Safety Inspection Report", NPL, August 2006.

London Cromwell Road, London Horseferry Road, Leeds, and Manchester (twice). None of these callouts occurred in the final quarter of 2006.

Following the successful trial of the new pumps for sampling total gaseous mercury at London Brent<sup>5</sup>, and the agreement of Defra, these new pumps were installed at all Network sites at the end of August. The comparison of the concentration of total gaseous mercury measured using these pumps is shown in Figure 1.



**Figure 1**. Comparison of average total gaseous mercury concentrations, measured monthly, over 6 months at London Brent, using the old and new types of pump.

Figure 1 shows the excellent comparability between the measured total gaseous mercury values using the current and new pumps. In addition, the uncertainty of the measurement performed using the new pump is less than with the old pump. This is because the new pump exhibits much more stable flow characteristics. Since the installation of these new pumps there have been no breakdowns of total gaseous mercury sampling apparatus anywhere on the Network. This is illustrated in Figure 2.

<sup>&</sup>lt;sup>5</sup> Williams, M, and Brown, R J C, "Defra UK Heavy Metals Monitoring Network: NPL's Quarterly Report for January-March (inclusive) 2006", NPL, April 2006.





#### 2.4 Site infrastructure and other issues

#### Site 46: IMI Walsall

This sampler is located in the garden of a council-owned property. New tenants took up residence in this property at the end of October 2006, and began to switch off the sampler after the LSO had visited. This resulted in the partial loss of November December's samples. The sampler has since been moved to the next door property and the situation has been resolved.

#### Sites 46: IMI Walsall; and Site 69: Brookside Metals

The LSO has been supplied with a ladder stay to improve safety when climbing on to the roofs where the samplers are located. Arrangements for its installation have been made with the LSO.

#### Sites 47 and 56: BZL Avonmouth and BZL Hallen

The LSO has been supplied with a ladder stay to improve safety when climbing onto the roof where the sampler is located. Arrangements for its installation have been made with the LSO.

#### Site 49: Swansea

The site has had additional scaffolding installed next to the sampler. This has been erected for roof repairs, but it also improves the access to the site for the LSO. The scaffolding will be in place for nearly a year.

#### Site 59: Weston Point

The LSO has been supplied with a ladder stay to improve safety when climbing on to the school roof where the sampler is located. Arrangements for its installation have been made with the LSO.

#### Site 61: London Cromwell Road

During NPL's audit it was found that foliage was becoming increasingly dense around the sampler on two sides. The LSO has cut back the foliage and will maintain a clear area around the sampling head.

#### Site 70: Newcastle

The Partisol sampler has been moved to the centre of the roof at this location to minimise the risk of falling from the roof while working on the sampler. The sampler is now at least 2 metres from all edges of the roof. Access across the roof is also now a lot clearer than in previous years.

#### 3. Sampling and Analytical Methodology

An overview of the sampling and analytical procedures used to analyse samples from the Network is given below.

#### 3.1 Sampling Methodology: Particulate-phase metals

Particulate samples were taken at all sites in the Network using Partisol 2000 instruments (fitted with  $PM_{10}$  heads) operating at a calibrated flow rate of 1 m<sup>3</sup>-.h<sup>-1</sup> in accordance with EN 12341:1998. Samples were taken for a period of one week onto 47 mm diameter GN Metricel membrane filters.

#### 3.2 Sampling Methodology: Total gaseous mercury

Sampling for total gaseous mercury took place at 13 of the 17 Network sites, using a low-volume pump (calibrated annually by NPL). Air was pumped through Amasil (gold-coated silica) tubes at a rate of 100 ml.min<sup>-1</sup> for either one week or four weeks, depending on the specific site and the expected ambient concentrations. A schematic diagram of the sampling set-up is given in Figure 3.



**Figure 3**. Schematic diagram of the total gaseous mercury sampling apparatus. The 25 mm diameter filter was used to remove any particulate material.

#### 3.3 Analytical Methodology: Particulate-phase metals

Analysis for particulate-phase metals took place at NPL using a PerkinElmer Elan DRC II ICP-MS, following NPL's UKAS accredited procedure, which is fully complaint with the requirements of EN 14902:2005.

Upon arrival at NPL, the filters were cut accurately in half, and each portion digested at temperatures up to 220°C using a CEM Mars X microwave. The digestion mixtures used were:

- Hg & Pt: 5 ml of nitric acid and 5 ml hydrochloric acid.
- All other metals: 8 ml of nitric acid and 2 ml hydrogen peroxide.

ICP-MS analysis of the digested solutions took place using at least four gravimetrically-prepared calibration solutions. A QA standard was repeatedly analysed (after every two solutions), and the change in response of the QA standard was mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS was corrected for by use of an internal standards mixture (containing Y, In, Bi, Sc, Ga & Rh) continuously added to the all samples via a mixing block. Each sample is analysed in triplicate, each analysis consisting of five replicates.

The amount of each metal in solution (and its uncertainty) was then determined by a method of generalised least squares using XGenline (an NPL-developed program) to construct a calibration curve.

#### 3.4 Analytical Methodology: Total gaseous mercury

Analysis of total gaseous mercury samples took place at NPL using a PS Analytical Sir Galahad II analyser with a fluorescence detector, using NPL's UKAS accredited procedure which is based on the standard method currently being developed by CEN TC264 WG25 'Mercury'. The instrument was calibrated by use of a gas-tight syringe, making multiple injections of known amounts of mercury vapour onto the permanent trap of the analyser.

Sampled adsorption tubes were placed in the remote port of the instrument and heated to 900°C, desorbing the mercury onto a permanent trap. Subsequent heating of this trap then desorbed the mercury onto the detector. The full heating program used is shown in Table 1:

Stage	Adsorption Tube	Permanent Trap
Delay time	30s	30s
Heating period	60s	15s
Cooling period	200s	120s
Transfer delay time	60s	-

**Table 1.** Total gaseous mercury analysis method parameters

#### 4 Data quality

#### 4.1 Limits of Detection: Particulate-phase metals

Indicative detection limits achieved by NPL using a UKAS accredited ICP-MS method, fully compatible with EN 14902:2005, are shown in Table 2. The solution limits of detection were calculated using the method outlined in EN14902:2005, repeatedly analysing a typical acid blank solution and taking into account the variability between individual instrumental readings. Values for the limits of detection have been calculated assuming a solution mass of 53 g and a volume of sampled air of 168 m<sup>3</sup> (equivalent to seven days sampling at 1.0 m<sup>3</sup>.h<sup>-1</sup>).

	Limit of Detection					
Analyte	Solution (ng.g⁻¹)	Filter (ng)	Air (ng.m⁻³)			
As	0.08	4.2	0.03			
Cd	0.003	0.16	0.001			
Cr	0.08	4.1	0.02			
Cu	0.07	3.6	0.02			
Fe	1.0	50	0.3			
Mn	0.009	0.5	0.003			
Ni	0.03	1.7	0.01			
Pb	0.04	2.0	0.01			
Pt	0.004	0.2	0.001			
V	0.007	0.4	0.002			
Zn	0.2	11	0.06			
Hg	0.03	1.9	0.01			

**Table 2.** Limits of detection for particulate-phase metals.

#### 4.2 Limits of Detection: Total gaseous mercury

The limit of detection routinely achievable for analysis of total gaseous mercury at NPL using its UKAS accredited procedure, which is consistent with the draft standard method being developed by CEN TC264 WG25, is 0.03 ng per tube, equivalent to an air concentration of approximately 0.03 ng.m<sup>-3</sup> (assuming a volume of sampled air of 1.01 m<sup>3</sup>, equivalent to one week's sampling at 100 ml.min<sup>-1</sup>). This value was calculated using a minimum detectable peak height of three times the baseline noise (with the instrument detector being operated at its usual sensitivity setting).

#### 4.3 QA/QC Procedures

The quality assurance and quality control procedures used during the sampling and analysis process are listed below:

Sampling:

- Despatch and analysis of one field-blank filter and one field-blank adsorption tube per site per quarter.
- Thorough checks of the returned filters and adsorption tubes to check for damage during transport. Rejection of damaged filters or tubes.
- Logging of all samples on NPL's Network database. Rejection of any unidentifiable samples and full investigation of any discrepancies.
- Continued training of, and regular communication with, the LSOs. This includes assessment of performance during site audits.

Particulate phase metals (ICP-MS analysis):

- Optimisation of the ICP-MS prior to each set of analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular extraction of an appropriate certified reference material (e.g. NIST SRM 1648) to check the recovery of the digestion method. Recoveries must be within the limits specified by EN14902.
- Regular measurement of filter blanks to ensure appropriate blank subtractions are made from measured values.
- Maximum levels for the standard deviation of the five internal standardcorrected measured intensities of each analysis of each sample.
- The XGenline goodness-of-fit for all calibration curves must be less than 2.
- Ratification of all data by an NPL Quality Circle of recognised NPL scientific experts independent of the analytical team.

Total gaseous mercury (atomic fluorescence analysis):

- Regular recovery tests carried out by analysing tubes spiked with a known quantity of mercury. Recoveries of between 95% and 105% must be achieved.
- Control limits on changes in instrument sensitivity between analyses.
- Analysis of clean tubes to ensure that blank levels are sufficiently low.
- Ratification of all data by an NPL Quality Circle of recognised NPL scientific experts independent of the analytical team.

#### 4.4 Measurement uncertainty

The average uncertainty from the analyses of single filters and tubes at NPL are shown in Table 3. All figures are a combination of the analytical and sampling uncertainties and have been derived using full, GUM compliant,

uncertainty budgets. All values are stated to a coverage factor of k = 2, providing a level of confidence of approximately 95%.

	Expanded relative uncertainty				
Analyte	Single measurement average	Daughter Directive maximum			
As	28%	40%			
Cd	18%	40%			
Cr	20%	-			
Cu	11%	-			
Fe	10%	-			
Mn	11%	-			
Ni	21%	40%			
Pb	11%	25%			
Pt	n/a <sup>†</sup>	-			
V	15%	-			
Zn	10%	-			
Hg(p)	33%	-			
Hg(v)	22%	50%			

**Table 3.** Typical measurement uncertainties achieved at NPL. The 'Daughter Directive maximum' column shows the maximum permissible uncertainty permitted by the relevant (First or Fourth) Daughter Directive. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

<sup>†</sup> The majority of Pt measurements are below the limit of detection.

The measurement uncertainties displayed in Table 3 are representative of individual measurements averaged over a typical sampling period (here, one week), as required by the First and Fourth Daughter Directives. The vast majority of the measurements used to compile the data in Table 3 were of ambient concentrations well below the appropriate target values. It is calculated that in the region of the appropriate target value - where the Daughter Directive's uncertainty data quality objectives apply (except for Hg(v) where there is no target value) – these uncertainties will be significantly lower.

A comparison of these uncertainties with the measured annual means shows the expected empirical Horwitz relationship, with uncertainty of measurement increasing as concentration decreases.



**Figure 4.** The relationship between the average uncertainties of the analytical measurements for each element and their annual mean measured concentrations. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

#### 5 Network data

#### 5.1 Data capture – 4<sup>th</sup> Quarter 2006

During the final quarter of 2006 the overall data capture across the Network was 93%, of which:

- Particulate phase data capture was 95%;
- Total gaseous mercury data capture was 86%.

The Network sites at Brookside Metals, BZL Avonmouth, BZL Hallen, Cardiff, Eskdalemuir, Glasgow, Weston Point, Swansea, Leeds, London Horseferry Road, Manchester and Motherwell achieved 100% data capture for 4<sup>th</sup> Quarter of 2006.

Data capture at the other Network sites during the reporting period was as follows: London Brent, 94%; London Cromwell Road, 94%; Sheffield, 92%; Newcastle, 80%; and IMI Walsall, 50%.

Particular operational issues occurred at Newcastle, IMI Walsall and Weston Point during the 4<sup>th</sup> Quarter:

- Newcastle 4 mercury adsorption tubes were lost in the postal system.
- IMI Walsall This sampler is located in the garden of a council owned property. New tenants took up residence at the end of October, and began to switch off the sampler after the LSO had visited. This resulted in the partial loss of November and December's samples. The sampler has since been moved to the next door property and the situation has been resolved.
- Weston Point Several power cuts at this site affected data capture during the final quarter of 2006.

#### 5.2 Data capture – 2006

All data capture figures are based on a target time coverage of 100%.

Data capture across the entire Network during 2006 was 94%.

The breakdown of this figure between the particulate and gaseous phase, and at each site is displayed in the table below:

	Data Capture / %				
Location	Particulate phase	Gaseous phase			
Whole Network	93	95			
IMI Walsall	79	94			
BZL Hallen	96	N/A			
Swansea	98	N/A			
BZL Avonmouth	98	N/A			
Sheffield	98	N/A			
Weston Point	89	98			
London Brent	95	90			
London Cromwell Rd	94	100			
London Horseferry Rd	90	100			
Leeds	98	93			
Glasgow	91	93			
Eskdalemuir	100	93			
Motherwell	92	100			
Manchester	91	81			
Cardiff	90	93			
Brookside Metals	96	92			
Newcastle	98	87			

**Table 4**.Data capture across the UK Heavy Metals MonitoringNetwork during 2006

The quarterly data capture achieved by the Network over the last three years is displayed in Figure 5.



Figure 5. Network data capture from 2004-2006 (inclusive).

NPL continues to provide a total of 56 extra measurement results per week, for elements not previously measured at 6 sites until the final quarter of 2004, to provide a more comprehensive and robust data set.

#### 5.3 Data processing and ratification

Analysis of the Network samples produces individual concentration values for weekly, or for some mercury adsorption tubes, monthly periods. These individual measurement results each have a stated measurement uncertainty, quoted at the 95% confidence level, associated with them.

Monthly concentrations at each site are then calculated as uncertaintyweighted means of weekly measurement data. Annual means at each site are produced by calculating the means of the monthly values. Network-wide annual means are then produced by averaging annual means from the individual sites.

An NPL QA/QC circle (the 'quality circle') ratifies ambient concentration data produced by the UK Heavy Metals Monitoring Network. NPL personnel performing the ratification procedure are independent of the analysis process.

It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place in accordance with several guidelines, outlined below: 1) Only data where the valid sampling hours are greater or equal to 75% of the total sampling hours will be eligible to produce valid concentration data, and count towards the total data capture percentage.

2) Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.

3) Upon production, weekly data for each element at each site is plotted in a time series, or displayed as a continuous list of values which may be easily compared. (total gaseous, and particulate phase, mercury should be plotted, or listed separately).

4) In the first instance these data are assessed visually for any obvious discrepancies with due regard to long terms trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data. (Detection of gross errors or systematic transcription of data entry faults may also be detected using chemometric methods).

5) If valid reasons for obviously discrepant values are found (e.g. incorrect calculation, low exposure time, non-valid exposure volume, analytical error) these values may be either excluded or corrected (depending on the nature of the error).

6) As part of the internal quality and technical auditing procedures, a selection of ambient air concentrations calculated each month are thoroughly audited by a party independent of the analysis procedure. For these samples, the sample number, target analyte, auditor, audit date and status of the data should be recorded in the designated Excel spreadsheet after auditing. These audits concentrate most heavily on Ni, As, Cd, Pb and Hg analyses, as these are directly relevant to EC Directives.

#### 5.4 Measurement Uncertainty of Annual Average

Since the data capture across the Network has been high (and any gaps in coverage have occurred evenly throughout the year) the uncertainty in the annual mean values will be dominated by the analytical uncertainty, with only small uncertainty contributions due to less than 100% time coverage. These contributions are calculated using the method described in ISO 11222:2002 "Air quality - Determination of the uncertainty of the time average of air quality measurements".

In all cases annual mean uncertainties are compliant with the data quality objectives for uncertainty in the First and Fourth Daughter Directives. Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant First and Fourth Daughter Directive metals are given in the table below:

	Expanded Relative Uncertainty				
Analyte	Annual Mean	Daughter Directive maximum			
As	29%	40%			
Cd	19%	40%			
Ni	23%	40%			
Pb	13%	25%			
Hg(v)	23%	50%			

**Table 5.** Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Daughter Directive metals. Hg(v) refers to total gaseous mercury.

#### 5.5 Measured Concentrations

The annual mean measured metals concentrations, averaged over all sites (Table 6), and at individual sites (Table 7), are given below:

Analyte	2006 Annual Mean Concentration / ng.m <sup>-3</sup>
As	0.93
Cd	0.55
Cr	5.53
Cu	19.1
Fe	423
Mn	8.99
Ni	4.63
Pb	19.9
Pt	0.02
V	2.82
Zn	82.2
Hg(p)	0.40
Hg(v)	4.71

**Table 6**. 2006 annual mean concentrations averaged over all sites on the UK Heavy Metals Monitoring Network. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

2006 Annual Mean Concentration / ng.m <sup>-3</sup>													
Sito		Analyte											
Site	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg (p)	Hg (v)
IMI Walsall	1.19	0.88	5.01	25.93	413	10.81	3.50	30.9	0.02	2.48	168.1	0.32	2.39
BZL Avonmouth	0.71	0.35	2.80	5.57	250	6.64	2.45	18.7	0.02	4.60	43.1	0.42	N/A
Swansea	0.92	0.21	3.50	6.56	205	4.68	26.13	13.2	0.03	2.01	18.4	0.52	N/A
BZL Hallen	1.05	0.42	3.62	7.53	224	6.91	3.72	18.0	0.04	3.33	45.0	0.33	N/A
Sheffield	1.21	0.61	23.56	16.57	486	30.34	12.18	34.1	0.02	3.23	109.8	0.34	N/A
Weston Point	0.82	0.23	3.86	9.37	208	4.42	3.08	10.5	0.01	3.50	16.6	1.46	31.10
London Brent	1.08	0.22	4.17	25.14	681	8.39	2.18	14.7	0.02	3.64	26.9	0.29	2.54
London Cromwell	0.98	0.24	5.27	47.61	1030	11.31	2.14	17.3	0.02	4.65	33.7	0.36	3.13
London Horseferry	0.95	0.28	3.16	18.74	450	6.30	2.07	14.1	0.01	4.15	27.2	0.20	2.02
Leeds	0.89	0.25	6.13	10.21	305	9.30	1.77	16.9	0.01	2.00	30.1	0.26	2.61
Glasgow	0.68	0.50	3.92	10.74	259	4.18	1.69	8.4	0.01	1.90	20.5	0.18	2.04
Eskdalemuir	0.38	0.12	3.71	3.33	42	2.57	1.13	2.8	0.01	1.25	7.7	0.24	1.69
Motherwell	0.91	0.53	5.49	6.28	195	3.40	0.68	6.2	0.02	1.26	10.7	0.28	2.50
Manchester	0.80	0.28	5.73	43.18	1012	11.23	2.41	10.3	0.02	2.22	31.3	0.46	1.96
Cardiff	1.09	0.35	5.76	28.21	756	13.96	3.76	18.7	0.02	2.68	49.7	0.34	2.61
Brookside Metals	1.20	3.64	4.90	50.60	369	11.01	7.56	92.3	0.03	1.97	727.5	0.32	1.96
Newcastle	0.94	0.29	3.46	9.09	309	7.31	2.33	12.2	0.02	3.11	30.4	0.51	3.01

**Table 7**. 2006 annual mean concentrations measured at individual sites on the UK Heavy Metals Monitoring Network. The monthly measured metals concentrations from all Network sites are summarised in the tables in Annex 5. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

# 5.6 Measured concentrations with respect to the requirements of the First and Fourth Daughter Directives

The annual mean concentrations are compared against the relevant limit and target values, contained within the First and Fourth Daughter Directives, in the graph below:



**Figure 6**. A summary of the annual mean measured concentrations of the heavy metals relevant to the First and Fourth Daughter Directives on the UK Heavy Metals Monitoring Network in 2006 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the annual means at the site with the highest concentrations. Hg(v) refers to the total gaseous mercury concentrations. The mercury objective is taken from a threshold value quoted in a draft of the Fourth DD.

In all cases the annual mean values are well below the limit and target values. In only one case does the highest annual average at an individual site exceed the target values.

Annual mean concentration values for the relevant First and Fourth Daughter Directive metals at all Network sites are displayed in the graph below:



**Figure 7.** A summary of the annual mean measured concentrations of the heavy metals relevant to the First and Fourth DDs at all site on the UK Heavy Metals Monitoring Network in 2006 as a percentage of the relevant target values, lower assessment thresholds (LATs) and upper assessment thresholds (UATs). The mercury objective originates from a threshold value quoted in a draft of the Fourth DD. Sites with asterisks indicate that sites do not measure total gaseous mercury. Hg(v) refers to the total gaseous mercury concentrations.

The highest annual mean value for nickel has been found at site 49 (INCO Europe, Swansea). The highest annual mean values for cadmium and lead are found at site 69 (Brookside Metals, Walsall). The highest mean value for arsenic has been found at site 58 (Avesta Steel, Sheffield). The highest annual mean value for total gaseous mercury has been found at site 59 (ICI Weston Point, Runcorn).

In only three instances do the measured annual mean values exceed the relevant lower assessment thresholds:

#### Annual Mean Concentrations above the Target Values:

• Nickel at Site 49 (INCO Europe, Swansea): 131% of the target value.

#### Annual Mean Concentrations above the Upper Assessment Threshold:

• Cadmium at Site 69 (Brookside Metals, Walsall): 73% of the target value.

#### Annual Mean Concentrations above the Lower Assessment Threshold:

• Nickel at Site 58 (Avesta Steel, Sheffield): 61% of the target value.

#### Other notable Concentrations:

• Total gaseous mercury at Site 59 (ICI Weston Point, Runcorn). The measured concentration represents 62% of the target value of 50 ng.m<sup>-3</sup> quoted in a draft version of the Fourth DD.

The site at Swansea is situated near to a nickel refinery, producing speciality nickel products and nickel-coated materials.

The site at Sheffield is located next to a steel rolling mill and processing plant producing specialist steel strip, and coil, products.

The site at Bilston Lane, in Walsall, is close to the UK's largest producer of gunmetal, brass, bronze and other copper alloy ingots.

All other annual mean values at all sites for Ni, As, Cd, Pb and Hg are below the relevant Lower Assessment Thresholds.

The total gaseous mercury to particulate phase mercury concentration ratio is in the range 4 to 11 for all sites, except Site 59 (ICI Weston Point, Runcorn) where the ratio is 21.

#### 5.7 Correlation with metrological conditions

An analysis of the correlations between the individual pollutant concentrations in excess of target values or assessment thresholds and the wind conditions local to the sites at which these levels occurred has been performed (no wind data was available at Brookside Metals).

This has involved plotting the monthly metals concentrations, against the percentage of that month for which the wind was blowing from a direction that would carry emissions from the point sources in question to the monitoring locations. The results of these analyses for nickel at Swansea and Sheffield, and for total gaseous mercury at Weston Point are shown in Figure 8.





**Figure 8.** Measured monthly concentrations in 2006 of pollutants above the LAT at three monitoring locations, against the percentage of time the wind was blowing from a direction that would carry emissions from the point sources in question to these monitoring locations.

Figure 8 shows that there is a correlation between wind direction and measured concentration for the pollutant in question at these sites. This indicates that the likely origins of the majority of the measured metals at these sites are from the stationary sources they are intended to measure. These relationships also indicate the importance of sampler location in order to capture realistic upwind and downwind samples from stationary sources. Moreover it is clear that changes in prevailing meteorological conditions over monitoring periods can significantly affect measured concentrations. Small changes in average annual prevailing conditions can in part account for the often relatively large changes observed in annual concentrations at sites from year to year.

#### 5.8 Contribution of individual sites to the annual average

For some elements a small number of point source sites can have a disproportionate effect on the annual average concentration across all sites. These sites have necessarily been set up to measure in areas close to point sources where exposure of the general population to a particular element, or elements, is expected to be high. For these elements, annual average values over all sites may be sensitive to the events that occur at a few point source sites. The contribution of individual sites to the annual average over all sites during 2006 is shown in Figure 9.



**Figure 9.** The percentage contribution from interval monitoring sites to the annual average concentration over all sites for each element across the Network (Pt excluded) in 2006. In each case the contributions for each element are sorted into order of size from largest (bottom) to smallest (top), with each differently shaded part of the bar represented an individual monitoring site. (Therefore bars of the same colour in different columns do not necessarily represent the same monitoring site). Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. The total Hg(v) contribution has 13 component sites, all the other elements have 17.

It can be seen that the first few elements on the left hand side of Figure 9 have annual averages over all sites dominated by the measured concentrations at one or two sites, whereas those elements to the right have annual average contributions spread more evenly across all sites and are not dominate by individual sites. The effect of this is that the interpretation of any nationwide annual average trends for Hg(v), Zn, Cd, and to a lesser extent Ni and Pb must take this into account to ensure that annual average trends are not simply reflections of changes in concentrations levels at one site (for instance the annual average increase in Zn over all sites in 2003 following the introduction of a point source site in the Walsall area).

#### 6 Trends in measured concentrations

Changes in the annual average metals concentrations measured, across the Network, over the past 26 years are shown in the table below:

	Changes in measured concentrations during the:					
Analyte	Last 26 Years	Last 10 Years	Last 5 Years	Last Year		
As	not measured	not measured	not measured	-10.6%		
Cd	-79.0%	-51.0%	26.1%	-6.7%		
Cr	-43.0%	+11.4%	-66.7%	+37.7%		
Cu	-28.2%	-35.3%	-2.1%	-2.4%		
Fe	-58.7%	-58.7%	-29.5%	+9.4%		
Hg(p)	not measured	not measured	not measured	-38.0%		
Hg(v)	not measured	not measured	not measured	+1.1%		
Mn	-66.0%	-36.4%	-7.5%	+14.8%		
Ni	-57.9%	-69.6%	80.1%	-3.5%		
Pt	not measured	not measured	not measured	0%		
V	-85.9%	-53.9%	5.9%	-32.7%		
Zn	-58.3%	+30.8%	+114.1%	+5.3%		
Pb	-96.4%	-89.5%	-73.3%	+5.7%		

**Table 8**. Trends in the measured annual average concentrations of metals measured by the UK Heavy Metals Monitoring Network. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

Measurements of annual mean concentrations for all elements have generally fallen year upon year over the period for which data is available. This trend has, in the most part, continued over the last year. The trends for individual elements are investigated in more detail below:

**Arsenic**: Arsenic has now been measured for four years across the Network; levels are low and are continuing to fall.

**Cadmium:** Concentrations continue to fall and remain low across the Network, with the exception of one site (Brookside Metals).

**Chromium:** Concentrations have risen in 2006, but remain low across the Network. The average UK concentration is similar to that recorded ten years ago.

**Copper**: Recorded concentrations continue to fall gradually across the Network and are now below 20 ng.m<sup>-3</sup>.

**Iron:** Concentrations have increased slightly in 2006 but continue to show an overall downward trend over the last quarter of a century, halving in the last 20 years.

**Particulate phase mercury:** Concentrations decreased in 2006 and remain very low across the Network.

**Total gaseous mercury:** Concentrations showed little change over the last year. Trends, and average recorded concentrations, for mercury are strongly influenced by the very high levels at Site 59 (ICI Weston Point, Runcorn).

**Manganese:** Concentrations are low across the Network and show signs of levelling off after more than halving in the 1990s.

**Nickel:** Concentrations decreased slightly in 2006. The high values recorded at sites 49 and 58 (Swansea and Sheffield, respectively) have a large influence on trends, and average recorded concentrations, for this element across the Network.

**Platinum:** Values remain extremely low across all Network sites (annual average: 0.02 ng.m<sup>-3</sup>). Concentrations measured for platinum remain the lowest, by an order of magnitude, of any of the metals monitored across the Network.

**Vanadium:** Concentrations decreased in 2006, and remain generally low across the Network. They have decreased by almost an order of magnitude over the last 16 years.

**Zinc:** Concentrations showed a small increase in 2006. Trends, and average recorded concentrations, for this element across the Network are influenced substantially by the high measured concentrations at Site 69 (Brookside Metals).

**Lead:** Concentrations rose slightly in 2006 but remain low across the Network. All sites exhibit concentrations that are less than 7% of the First Daughter Directive Limit Value (except at Site 69 (Brookside Metals): 18%).

Concentration trends over the last 26 years for the metals relevant to the First and Fourth DDs are summarised in the graph below:



**Figure 10.** The annual mean concentration of Pb, As, Cd, Ni, and Hg(v) measured on the UK Heavy Metals Monitoring Network over the last 26 years.

#### 7 Policy Update

A brief description of progress of activities relevant to this Network:

#### CEN TC264 WG25 – Mercury

WG25 last met in September 2006 in Rende, Italy. This meeting was preceded by a workshop on instrument operation for those laboratories chosen to operate the field validation sites, after which the first field trial was started at the Rende air quality monitoring site. At the full working group meeting NPL delivered a presentation on a proposed methodology to estimate the uncertainty of mercury measurements in ambient air and in deposition that complies with the requirements of CEN and the EU. This proposal was accepted by the working group and will form the basis of the uncertainty section of the draft standard. NPL will also lead the statistical evaluation of the field trial data.

The field trial in Italy has now been completed and the instruments have been shipped to Spain where the second part of the field trial is scheduled to take place.

The next WG25 meeting will be in Brussels in April 2007.

#### CEN TC264 WG20 – Deposition of Heavy Metals

WG20 last met in October 2006 in Copenhagen. The results of the first round of field trials in Germany and France were presented, and discussion of the draft standard was initiated. It seems that initial results from the different sampling apparatus agree reasonably well. An NPL presentation on calculation of uncertainty for ambient air quality measurements was circulated, and is being adopted, together with prEN ISO 20988, as a model for use in the WG20 standard. The second round of field trials is now underway in Denmark and Norway.

The next WG20 meeting will be in Oslo in June 2007.

#### Certified Reference Materials (CRMs) for Heavy Metals and PAHs

During the 8th AQUILA meeting in June 2006 it was announced that JRC-IRMM has selected five materials as potential candidates for the future production and certification of CRMs for heavy metals and PAHs content in a  $PM_{10}$  matrix.

These materials are two existing CRMs: BCR-605 (urban dust certified for trimethyllead) and BCR-723 (road dust certified for Pd, Pt and Rh); and three materials specifically collected for this purpose: tunnel dust (collected from the walls of a road tunnel), winter filter dust, and summer filter dust. The filter dust material was collected off filters from the ventilation systems of the JRC-IRMM buildings.

A feasibility study to evaluate these materials for analyte content, microhomogeneity and particle size distribution is planned for the second quarter of 2007. NPL is participating in the heavy metals content evaluation of these materials.

#### JRC-IES Heavy Metals Intercomparison

JRC-IES is currently organising an intercomparison exercise for heavy metals, to be carried out in the first quarter of 2007. The objectives of this exercise are:

- To assess whether the data quality objectives of the First and Fourth DDs are met;
- To evaluate the repeatability and reproducibility of methods of measurement;
- To investigate the main sources of uncertainty and analytical deviation.

Each participating laboratory is to receive: a liquid CRM sample, a solution of a digested certified dust sample, a certified dust sample, a solution prepared by the digestion of an exposed filter, and a blank and exposed filter to be digested by the participating laboratory.

NPL is participating in the intercomparison, and has also provided JRC-IES with some of the materials to be used in the study.



Annex 1 - Location and details of sites on the UK Heavy Metals Network

Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Classification	Pollutants measured
46: IMI Refiners Ltd, Walsall (IMI Walsall)	74 Primley Avenue, Walsall, WS2 9UW	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
47: BZL Ltd, Avonmouth (BZL Avonmouth)	Avonmouth Medical Centre, Collins Street, Bristol, BS11 9JJ	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
49: INCO Europe, Swansea	Glais Primary School, School Road, Glais,	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
(Swansea)	Swansea, SA7 9EY		Pb, Pt, V, Zn
56: BZL Ltd, Avonmouth, Hallen	West Country Caravans Ltd., Moorhouse Lane,	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
Village (BZL Hallen)	Hallen, Bristol, BS10 7RU		Pb, Pt, V, Zn
58: Avesta Steel, Sheffield (Sheffield)	BOC Gases, Bawtry Road, Brinsworth, Sheffield, S60 5NT	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
59: ICI Weston Point, Runcorn	Weston Point County Primary School, Caster	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
(Weston Point)	Avenue, Weston Point, Runcorn, WA7 4EQ		Pb, Pt, V, Zn, Hg(v)
60: London Brent, North Circular	Tesco Superstore, North Circular Road, Brent,	Roadside	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
(London Brent)	London, NW10 0TL		Pb, Pt, V, Zn, Hg(v)
61: London, Cromwell Road (London Cromwell (Rd))	Natural History Museum, Cromwell Road, London, SW7 5BD	Roadside	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
62: London, Horseferry Road	Mortuary Car Park, Horseferry Road, London,	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
(London Horseferry (Rd))	SW1P 2EB		Pb, Pt, V, Zn, Hg(v)
63: Leeds, Old Market Buildings (Leeds)	Old Market Buildings, Vicar Lane, Leeds, LS1	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
64: Glasgow, St Annes Primary	St Annes Primary School, 37 David Street,	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
School (Glasgow)	Glasgow, G40 2UN		Pb, Pt, V, Zn, Hg(v)
65: Eskdalemuir, Met Office (Eskdalemuir)	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	Rural	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
66: Motherwell, Civic Centre (Motherwell)	Civic Centre, Motherwell, Lanarkshire ML1 1TW	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
67: Manchester M56, Junction 4	Junction 4, M56, Newhall Green, Wythenshaw,	Roadside	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
(Manchester)	Manchester		Pb, Pt, V, Zn, Hg(v)
68: Cardiff, Waungron Road (Cardiff)	Cleansing Depot, Waungron, Fairwater, Cardiff, CF5 2JJ	Roadside	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
69: Brookside Metals, Bilston Lane,	Adult Training Centre, Bilston Lane, Shepwell	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
Walsall (Brookside Metals)	Green, Willenhall, Walsall, WV13 2QJ		Pb, Pt, V, Zn, Hg(v)
70: Elswick 6, Newcastle Upon Tyne	Metro Radio Arena, Arena Way, Newcastle Upon	Industrial Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni,
(Newcastle)	Tyne, NE4 7NA		Pb, Pt, V, Zn, Hg(v)

#### Annex 2 - Site Audit reports

The following table details the dates of the audits, what equipment and which LSOs were audited.

Site	Date	Partisol 2000 Serial Numbers	Mercury Vapour Serial Numbers	LSO audited
Sheffield	26/06/06	2000A204719901	N/A	Andy Hawkins
Brookside Metals	02/08/06	2000A204649811	404949	Alison Humphreys, Mick Clews
BZL Avonmouth	10/05/06	2000A205049902	N/A	Steve Carter
BZL Hallen	10/05/06	2000A205009902	N/A	Steve Carter
Cardiff	09/05/06	2000A204919902	508289	Phil Jones
Newcastle	28/06/06	2000A205069902	508291	Colin Bird
Eskdalemuir	28/06/06	2000A204909902	Sampler being repaired	lan Dawson
Glasgow	27/06/06	2000A204899902	404950	David Cardigan
Weston Point	27/06/06	2000A205079902	508292	Ken McGrath
IMI Walsall	02/08/06	2000A204989902	508775	Alison Humphreys, Mick Clews
Swansea	09/05/06	2000A205089902	N/A	-
Leeds	26/06/06	2000A204739901	404948	Chris Hill
London Brent	04/07/06	2000A204999902	672736	Dharsheni Muhunthan
London Cromwell Road	04/07/06	2000A205059902	733232	Colin Gilham
London Horseferry Road	04/07/06	2000A204969902	404946	Colin Gilham
Manchester	26/06/06	2000A204959902	508774	Mike Concannon
Motherwell	28/06/06	2000A204979902	Sampler being repaired	Pat Docherty

- The LSO for the Swansea site was unavailable at the time of audit.
- The total gaseous mercury sampling pump at Motherwell was not operational at the time of the audits.

#### Annex 3 - Results of Partisol 2000 Particulate Metal Samplers Flow Audits

The sample flow for each sampler was measured using a BIOS Flow Calibrator, which was previously calibrated at NPL against a Brooks Vol-U-Meter, traceable to national standards. The reported flow is measured and reported at ambient conditions. A leak test was also performed on each sampler. The following table details the results of the Partisol 2000 audits.

Site	Measured flow, litres per minute	Difference from set point, %	Leak Test
Brookside Metals	16.93	+2.0	Passed
BZL Avonmouth	16.93	+2.0	Passed
BZL Hallen	16.63	-0.4	Passed
Cardiff	17.13	+2.6	Passed
Eskdalemuir	17.00	+1.8	Passed
Glasgow	17.16	+2.8	Passed
Weston Point	17.09	+3.0	Passed
IMI Walsall	17.05	+2.7	Passed
Swansea	17.19	+3.6	Passed
Leeds	18.19	+8.9	Passed
London Brent	17.17	+3.1	Passed
London Cromwell Road	17.22	+3.1	Passed
London Horseferry Road	16.62	-0.5	Passed
Manchester	17.03	+2.0	Passed
Motherwell	16.61	-0.5	Passed
Newcastle	16.83	+0.8	Passed
Sheffield	17.77	+6.4	Passed

The expanded uncertainty (k=2) in the flow measurements is 5.8% expressed at the 95% confidence interval. The average difference between the measured flows and the set point is 2.6%. This is within the uncertainty of the measurement. The difference from set point determined from the audits of the Partisol 2000s is used at ratification to adjust the volume recorded by the Partisol for each sample. If the difference from set point is greater than 10% then remedial action would be taken, for example calling out the Equipment Support Unit (ESU).

#### Annex 4 - Results of Total Gaseous Mercury Pump Flow Audits

The sample flow for each sampler was measured using a BIOS Flow Calibrator, which was previously calibrated at NPL against a Brooks Vol-U-Meter, traceable to national standards. The reported flow is measured and reported at ambient conditions. A leak test was also performed on each sampler.

Site	Set point, ml per minute	Measured flow, ml per minute	Difference from set point, %	Leak Test
Brookside Metals	76	81.4	+7.2	Passed
Cardiff	103	104.3	+1.2	Passed
Eskdalemuir	100	102.2	+2.2	Passed
Glasgow	100	98.5	-1.5	Passed
Weston Point	100	101.4	+1.4	Passed
IMI Walsall	99	96.4	-2.7	Passed
Leeds	105	114.3	+8.8	Passed
London Brent	100	99.5	-0.5	Passed
London Cromwell Road	100	105.0	+5.0	Passed
London Horseferry Road	100	99.3	-0.7	Passed
Manchester	150	151.2	+0.8	Passed
Motherwell	N/A	N/A	N/A	Not tested
Newcastle	112	110.2	-1.9	Passed

The expanded uncertainty (k=2) in the flow measurements is 5.8% expressed at the 95% confidence interval.

The average difference between the measured flows and the set point is 2.8%. This is within the uncertainty of the measurement.

Although Eskdalemuir's total gaseous mercury sampling pump was being repaired, a travelling audit pump was used to calibrate the on-site rotameter and leak check the pipe work.

The difference from set point determined from the audit of the total gaseous mercury sampling pumps is used at ratification to adjust the volume recorded by the LSO for each sample. There is no threshold for remedial action on the total gaseous mercury sampling pumps as the flow is adjusted by the LSO on a weekly basis and the flow can drift by more than 10% in one week.

# Annex 5 – Average monthly measured metals concentrations at all Network sites

							Conce	ntratior	n ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
IMI Refiners, Walsall														
46	Jan	1.37	1.10	4.15	28.59	575	7.76	1.33	19.1	0.15	1.43	57.8	0.37	4.10
	Feb	1.60	2.95	7.75	66.55	733	17.96	4.24	110.9	0.05	3.31	722.0	0.29	1.69
	Mar	1.59	0.46	5.22	53.99	491	10.68	1.87	15.6	0.03	4.32	335.1	0.23	4.64
	Apr	1.90	1.04	6.59	20.56	348	8.01	7.69	24.5	0.01	2.80	249.1	0.52	2.51
	May	1.07	0.81	3.30	12.11	298	7.43	2.66	15.2	0.01	2.77	65.6	0.47	2.44
	Jun	0.96	0.36	12.09	14.43	417	8.65	1.17	19.8	0.01	4.53	45.3	0.55	2.83
	Jul	0.75	0.57	4.98	18.55	321	9.17	7.57	26.6	0.00	3.09	63.7	0.14	2.35
	Aug	0.56	0.61	2.21	13.51	221	7.01	1.23	20.1	0.00	0.44	47.6	0.25	1.91
	Sep	0.76	0.56	4.12	19.52	453	13.65	2.59	28.8	0.00	2.52	115.3	0.35	2.45
	Oct	0.98	0.43	7.75	16.83	347	13.76	5.22	20.2	0.00	1.69	90.4	0.44	2.48
	Nov	0.60	0.38	1.96	17.30	305	13.19	6.08	22.0	0.00	0.95	75.1	0.01	N/A
	Dec	2.10	1.23	0.01	29.23	452	12.44	0.38	47.5	0.00	1.97	150.8	0.20	1.22

							Conce	ntration	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
BZL Ltd., Avonmouth														
47	Jan	0.69	0.23	1.42	4.38	121	1.70	2.56	9.6	0.10	4.23	46.0	2.02	N/A
	Feb	1.23	0.58	7.68	9.78	317	9.93	3.34	40.1	0.12	5.90	68.1	0.55	N/A
	Mar	0.39	0.62	4.34	4.19	170	5.86	2.23	18.8	0.02	6.90	55.1	0.18	N/A
	Apr	0.41	0.20	0.89	3.16	220	5.54	0.83	10.1	0.00	5.05	28.5	0.01	N/A
	May	0.33	0.12	1.25	2.61	164	4.88	0.42	8.6	0.01	5.03	26.5	0.16	N/A
	Jun	0.43	0.23	1.53	4.26	348	8.42	1.43	18.9	0.01	3.30	55.9	0.32	N/A
	Jul	0.58	0.32	5.64	5.03	509	11.69	4.75	22.6	0.00	6.02	52.2	0.21	N/A
	Aug	0.16	0.11	0.19	2.64	169	5.72	2.49	9.1	0.00	3.06	43.0	0.56	N/A
	Sep	0.68	0.25	1.53	5.15	305	6.81	2.10	12.6	0.00	3.96	31.4	0.38	N/A
	Oct	0.85	0.18	1.80	5.69	210	5.63	1.30	14.9	0.00	3.21	36.7	0.34	N/A
	Nov	1.09	0.65	5.51	14.27	314	10.78	5.42	51.4	0.00	3.73	52.0	0.22	N/A
	Dec	1.66	0.68	1.77	5.63	147	2.70	2.50	7.2	0.00	4.80	22.3	0.10	N/A

							Conce	entration	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Swansea														
49	Jan	1.14	0.29	0.62	7.43	234	4.79	30.86	16.9	0.02	1.65	21.4	2.29	N/A
	Feb	1.44	0.33	6.90	22.54	668	9.37	15.76	21.6	0.00	3.77	37.2	0.23	N/A
	Mar	0.52	0.19	5.20	2.96	107	2.82	24.35	6.2	0.15	2.40	11.3	0.64	N/A
	Apr	0.41	0.11	2.98	3.49	82	2.18	26.86	5.4	0.01	1.66	13.9	0.25	N/A
	May	0.72	0.14	3.28	4.62	196	4.69	18.68	7.6	0.01	3.00	16.9	0.26	N/A
	Jun	0.38	0.20	1.91	5.15	229	6.50	20.04	9.3	0.10	2.12	16.6	0.52	N/A
	Jul	0.71	0.24	2.12	5.02	274	6.91	18.98	12.5	0.00	3.52	16.3	0.17	N/A
	Aug	0.36	0.14	1.51	3.42	91	2.90	27.42	7.5	0.00	0.78	9.0	0.24	N/A
	Sep	0.39	0.21	6.22	4.43	183	6.22	18.19	8.6	0.01	1.13	20.2	0.68	N/A
	Oct	0.84	0.15	1.97	3.94	100	3.35	32.60	9.4	0.00	1.73	15.1	0.63	N/A
	Nov	2.73	0.34	5.84	10.41	168	3.83	27.72	34.5	0.00	0.85	24.8	0.18	N/A
	Dec	1.39	0.24	3.45	5.34	124	2.61	52.09	18.5	0.00	1.51	18.5	0.12	N/A

							Conce	ntration	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
BZL Ltd., Hallen Village														
56	Jan	1.82	0.45	3.36	13.59	462	14.45	5.83	23.6	0.01	3.33	56.7	0.68	N/A
	Feb	1.70	0.79	0.01	6.81	195	5.88	1.81	21.7	0.22	1.69	43.8	0.27	N/A
	Mar	0.64	0.63	0.68	9.63	334	15.46	1.18	40.3	0.00	1.86	125.6	0.07	N/A
	Apr	0.51	0.33	3.04	3.98	192	5.47	1.19	13.2	0.07	4.80	36.2	0.66	N/A
	May	1.79	0.31	14.18	4.65	185	6.19	3.54	11.8	0.04	6.66	44.2	0.10	N/A
	Jun	0.77	0.26	3.39	5.59	238	6.52	4.90	12.5	0.00	4.70	30.4	0.37	N/A
	Jul	0.71	0.36	3.12	5.85	281	8.04	4.51	16.5	0.14	5.41	39.9	0.30	N/A
	Aug	0.22	0.16	0.73	2.98	145	4.23	6.39	8.0	0.00	1.38	19.5	0.19	N/A
	Sep	0.40	0.17	0.81	5.32	184	4.96	1.34	8.7	0.00	2.86	37.8	0.26	N/A
	Oct	0.81	0.19	4.74	5.11	142	4.20	3.90	8.9	0.00	1.96	27.1	0.27	N/A
	Nov	0.92	0.62	5.50	12.87	185	4.85	5.81	40.1	0.00	1.61	41.2	0.24	N/A
	Dec	2.29	0.80	3.89	13.97	146	2.71	4.19	10.4	0.00	3.70	37.5	0.56	N/A

							Conce	ntration	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Sheffield														
58	Jan	2.07	0.73	17.98	32.50	700	30.72	9.84	41.0	0.09	5.56	109.1	0.42	N/A
	Feb	1.23	0.59	17.44	17.19	491	34.43	18.66	53.7	0.06	3.88	175.3	0.55	N/A
	Mar	1.39	0.57	16.78	15.18	477	32.31	8.83	43.5	0.04	6.76	192.2	0.17	N/A
	Apr	0.47	0.30	14.73	8.04	350	24.62	6.40	19.3	0.01	2.51	72.0	0.15	N/A
	May	0.92	0.44	25.17	11.39	464	30.23	18.22	28.9	0.01	2.72	74.2	0.10	N/A
	Jun	1.10	0.52	24.27	14.59	681	35.21	10.14	45.4	0.01	3.93	117.2	0.12	N/A
	Jul	0.69	0.31	31.05	12.35	490	29.33	8.08	24.7	0.00	2.06	83.1	0.88	N/A
	Aug	0.59	0.20	14.06	10.09	335	14.82	6.64	13.2	0.02	0.95	58.3	0.69	N/A
	Sep	0.99	1.86	24.49	13.89	518	28.66	11.16	29.7	0.00	2.40	60.2	0.37	N/A
	Oct	1.09	0.35	28.85	27.65	409	29.81	12.11	30.5	0.00	1.80	121.3	0.15	N/A
	Nov	2.66	0.97	29.38	19.44	443	33.84	14.31	32.8	0.00	2.53	146.2	0.21	N/A
	Dec	1.28	0.45	38.51	16.50	472	40.10	21.78	46.2	0.01	3.70	108.1	0.21	N/A

							Conce	ntration	n ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Weston Point, Runcorn														
59	Jan	1.75	0.32	3.58	11.95	223	4.89	4.31	22.5	0.01	2.65	25.8	1.04	9.97
	Feb	0.90	0.36	0.91	11.77	193	3.95	2.99	14.3	0.01	1.99	17.7	2.45	16.32
	Mar	0.61	0.20	1.85	5.23	132	3.37	0.87	8.8	0.01	2.85	15.0	0.98	23.38
	Apr	0.26	0.24	5.71	4.08	183	5.47	4.98	9.6	0.01	6.68	23.4	0.93	25.64
	May	0.99	0.19	5.59	20.07	493	7.17	2.92	9.8	0.01	6.50	21.7	1.69	14.98
	Jun	0.51	0.15	2.46	6.50	279	4.62	0.78	10.1	0.01	2.81	15.7	0.43	20.55
	Jul	0.36	0.10	1.48	5.61	146	2.99	2.54	5.6	0.00	2.27	8.2	1.10	34.25
	Aug	0.91	0.14	2.59	7.80	223	5.25	1.19	7.8	0.01	3.30	11.1	1.30	37.27
	Sep	0.46	0.20	3.64	9.47	178	4.55	1.27	9.2	0.02	3.09	15.1	1.41	45.82
	Oct	0.66	0.16	1.59	9.61	138	3.16	3.28	9.9	0.00	1.45	14.9	1.75	29.27
	Nov	1.10	0.30	6.20	8.62	126	3.42	6.77	8.0	0.00	1.76	12.1	2.28	69.74
	Dec	1.28	0.34	10.70	11.69	185	4.16	5.06	11.0	0.00	6.66	17.9	2.21	45.97

							Conce	ntration	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
London Brent														
60	Jan	2.17	0.36	2.19	35.54	920	11.33	1.87	26.9	0.02	5.48	42.0	0.27	1.16
	Feb	0.67	0.19	1.39	21.31	548	6.38	0.78	10.2	0.05	1.71	24.0	0.43	4.09
	Mar	0.61	0.16	2.08	16.34	471	6.35	1.28	9.2	0.03	2.00	22.3	0.21	0.30
	Apr	0.59	0.13	11.29	15.38	508	5.82	3.40	8.8	0.05	2.06	19.4	0.29	1.98
	May	0.87	0.19	3.31	21.90	644	7.76	3.08	10.9	0.01	5.99	18.8	0.28	3.53
	Jun	0.71	0.23	4.38	25.83	804	10.88	2.20	12.7	0.01	7.35	28.1	0.11	0.17
	Jul	0.60	0.19	3.28	22.15	744	10.40	5.40	10.7	0.10	7.60	21.3	0.85	0.28
	Aug	0.37	0.09	2.13	15.76	490	6.02	1.29	6.0	0.00	1.78	16.9	0.22	0.14
	Sep	0.90	0.24	4.07	31.12	899	11.17	3.24	14.3	0.00	3.71	35.8	0.24	2.93
	Oct	0.72	0.16	6.75	32.44	739	9.20	1.31	15.6	0.00	2.64	29.0	0.16	11.01
	Nov	1.86	0.48	5.92	40.13	850	9.57	1.10	33.7	0.00	1.36	41.2	0.20	2.31
	Dec	2.87	0.20	3.24	23.79	554	5.86	1.17	17.0	0.00	2.02	23.6	0.18	N/A

							Conce	ntration	n ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
London Cromwell														
61	Jan	1.15	0.21	6.06	66.76	1171	10.62	2.18	13.6	0.07	5.21	28.7	0.90	2.56
	Feb	0.59	0.23	2.88	48.27	944	8.62	1.26	11.0	0.01	2.49	28.9	0.09	3.68
	Mar	1.50	0.30	2.96	36.36	816	9.31	2.82	16.1	0.00	4.12	38.0	0.59	2.42
	Apr	0.05	0.20	6.36	38.48	1313	18.66	2.78	10.2	0.01	4.75	28.3	0.05	2.19
	May	0.73	0.20	6.53	39.34	927	10.56	3.50	13.0	0.01	10.94	29.0	0.01	0.99
	Jun	0.94	0.29	6.29	69.10	1569	17.73	2.63	17.6	0.01	9.27	41.2	0.22	1.87
	Jul	0.57	0.27	3.57	27.31	739	9.17	2.70	12.5	0.00	5.95	42.7	0.22	6.24
	Aug	0.42	0.10	3.08	30.24	602	7.48	0.56	8.3	0.02	1.58	13.9	0.61	3.17
	Sep	0.82	0.19	4.11	46.48	1027	11.86	1.88	14.8	0.05	4.47	35.7	1.30	0.97
	Oct	0.91	0.17	5.78	47.75	974	9.98	2.35	15.7	0.00	2.95	32.7	0.07	9.74
	Nov	2.73	0.56	9.09	70.34	1192	11.86	1.48	49.8	0.00	1.53	54.2	0.07	1.60
	Dec	1.33	0.21	6.58	50.95	1084	9.84	1.56	24.9	0.00	2.51	31.6	0.16	2.15

							Conce	ntratior	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
London Horseferry														
62	Jan	1.35	0.29	3.11	26.03	654	8.97	4.03	24.8	0.01	6.81	42.2	0.11	0.53
	Feb	0.53	0.22	1.50	18.51	392	4.65	0.90	11.1	0.00	2.65	19.8	0.12	2.71
	Mar	0.62	0.48	0.60	21.76	496	7.40	6.65	13.6	0.00	3.96	29.6	0.49	1.68
	Apr	0.23	0.11	2.43	9.51	294	3.57	0.55	6.3	0.01	2.85	11.5	0.06	1.42
	May	0.06	0.07	3.69	7.61	202	2.52	0.17	3.7	0.01	3.69	14.3	0.01	1.89
	Jun	0.61	0.26	3.27	23.73	643	9.88	1.80	13.0	0.01	7.98	25.4	0.27	1.31
	Jul	0.55	0.28	6.97	16.00	505	7.95	3.99	10.3	0.00	7.00	44.3	0.38	1.57
	Aug	0.26	0.11	1.10	13.05	321	4.18	0.12	5.6	0.01	1.25	13.7	0.24	2.43
	Sep	0.87	0.34	1.54	22.40	624	10.18	1.72	16.9	0.00	5.16	41.3	0.34	3.75
	Oct	1.80	0.20	3.47	21.77	466	6.46	2.78	17.2	0.01	3.63	27.9	0.17	2.79
	Nov	2.91	0.51	5.23	28.21	453	5.89	0.88	34.5	0.01	1.76	38.2	0.12	2.25
	Dec	1.61	0.54	5.04	16.31	355	3.90	1.25	11.9	0.00	3.06	17.9	0.08	1.95

							Conce	ntratior	n ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Leeds														
63	Jan	1.19	0.23	2.98	9.48	242	5.20	3.39	13.5	0.04	1.53	20.0	0.24	1.96
	Feb	0.54	0.26	2.79	10.10	284	6.45	0.39	11.2	0.01	2.10	60.1	0.38	2.62
	Mar	0.76	0.25	0.01	7.75	250	6.80	1.89	14.1	0.01	1.79	33.2	0.11	1.22
	Apr	0.98	0.29	17.07	5.78	204	4.97	3.23	12.5	0.01	0.76	16.5	0.16	1.99
	May	1.15	0.23	23.12	6.13	260	6.95	2.40	8.7	0.01	2.47	17.9	0.30	1.68
	Jun	0.55	0.18	3.87	6.77	288	10.85	1.19	11.8	0.01	2.97	24.8	0.23	2.19
	Jul	0.67	0.24	3.13	9.03	366	12.62	2.61	13.4	0.00	3.49	38.4	0.22	N/A
	Aug	0.53	0.13	3.27	6.88	194	4.65	0.53	7.7	0.00	1.19	19.1	0.27	6.86
	Sep	0.96	0.32	5.92	14.39	472	13.09	2.61	21.1	0.01	3.58	36.3	0.87	2.34
	Oct	0.85	0.19	3.02	12.77	331	10.55	1.40	13.7	0.00	1.77	30.2	0.05	2.34
	Nov	1.33	0.48	4.95	18.56	395	10.36	0.95	54.8	0.00	0.67	41.5	0.19	2.58
	Dec	1.13	0.26	3.45	14.88	370	19.06	0.61	19.9	0.00	1.62	23.8	0.14	2.88

							Conce	ntration	ng.m <sup>-3</sup>					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Glasgow														
64	Jan	0.73	2.19	2.16	9.41	231	3.00	1.64	8.5	0.01	1.06	16.8	0.04	2.22
	Feb	0.75	1.72	1.00	15.99	380	5.37	1.92	11.4	0.01	1.58	28.5	0.43	1.19
	Mar	0.38	0.29	2.77	12.43	307	4.51	0.82	8.4	0.01	1.37	19.5	0.04	1.42
	Apr	0.34	0.12	2.92	8.59	184	3.06	0.06	5.7	0.01	2.09	21.8	0.04	1.42
	May	1.42	0.19	23.89	8.11	179	2.55	1.59	3.8	0.01	5.50	14.9	0.42	0.49
	Jun	0.52	0.20	1.53	8.63	239	4.31	2.70	6.7	0.01	2.88	18.6	0.01	1.35
	Jul	0.48	0.14	1.39	8.73	276	5.11	2.73	9.0	0.10	2.76	22.0	0.33	2.21
	Aug	0.25	0.13	1.62	6.90	208	3.74	0.73	5.9	0.00	0.81	16.3	0.29	1.77
	Sep	0.51	0.13	1.36	10.61	253	4.55	3.73	8.2	0.00	1.06	17.6	0.26	7.21
	Oct	0.79	0.20	3.80	17.28	408	6.72	2.88	14.1	0.00	1.12	24.8	0.06	1.53
	Nov	1.26	0.56	4.66	12.35	235	4.09	1.39	9.5	0.00	1.59	24.1	0.12	2.11
	Dec	0.68	0.09	0.01	9.84	203	3.17	0.14	9.1	0.00	1.01	21.5	0.11	1.58

	Concentration ng.m <sup>-3</sup>													
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Eskdalemuir														
65	Jan	0.76	0.16	5.44	16.45	61	6.55	5.17	8.8	0.11	0.43	16.4	0.61	0.52
	Feb	0.01	0.01	0.47	0.31	38	0.61	0.01	1.4	0.00	0.44	2.2	0.00	1.51
	Mar	0.01	0.69	4.06	4.66	90	1.25	0.20	2.5	0.01	1.96	11.6	0.04	1.82
	Apr	0.09	0.08	1.44	0.01	4	0.52	0.01	0.4	0.01	0.84	4.3	0.04	1.69
	May	0.49	0.24	15.68	14.04	76	5.88	1.44	6.5	0.01	5.89	20.7	0.04	1.89
	Jun	0.13	0.03	0.11	0.35	21	1.35	0.01	1.5	0.00	1.40	5.9	0.20	1.77
	Jul	0.59	0.01	2.10	0.35	45	1.58	0.01	0.9	0.00	0.68	4.0	0.25	1.64
	Aug	0.02	0.01	0.12	0.43	50	1.14	2.78	1.1	0.00	0.87	4.1	0.50	1.89
	Sep	0.07	0.08	2.77	1.07	76	3.45	2.02	2.5	0.00	0.25	6.1	0.38	1.91
	Oct	0.53	0.10	4.42	1.02	41	1.37	1.32	5.0	0.00	1.22	10.5	0.55	1.83
	Nov	0.16	0.05	3.09	1.03	1	1.87	0.61	1.9	0.00	0.47	5.3	0.22	N/A
	Dec	1.68	0.02	4.88	0.22	1	5.28	0.01	1.0	0.00	0.47	1.7	0.09	2.07

	Concentration ng.m <sup>-3</sup>													
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Motherwell														
66	Jan	0.81	0.20	1.66	9.98	240	4.26	1.75	11.5	0.05	1.39	17.0	0.45	7.48
	Feb	0.52	3.29	0.00	8.27	246	5.58	0.69	8.0	0.00	1.62	20.8	0.13	2.01
	Mar	0.19	0.10	1.50	4.70	203	1.80	1.01	3.7	0.00	1.14	4.6	0.40	1.06
	Apr	2.23	1.27	29.11	6.04	230	2.08	0.00	3.4	0.01	0.37	7.4	0.15	1.56
	May	1.02	0.24	15.48	6.17	295	6.13	1.57	4.9	0.14	1.15	14.3	0.25	2.07
	Jun	1.04	0.10	4.39	5.42	210	4.37	0.16	7.3	0.01	2.59	9.7	0.20	3.37
	Jul	0.35	0.14	0.97	4.34	197	3.97	1.62	5.3	0.00	1.71	5.5	0.41	2.55
	Aug	0.08	0.08	1.56	4.30	152	2.52	0.01	2.5	0.00	0.37	7.1	0.29	2.08
	Sep	0.32	0.10	0.24	5.67	123	2.71	1.00	3.6	0.06	0.74	13.3	0.71	1.86
	Oct	0.47	0.20	4.05	5.62	132	2.74	0.01	7.3	0.00	0.99	10.4	0.13	1.86
	Nov	1.98	0.11	5.59	9.25	213	3.17	0.01	11.4	0.00	0.56	9.4	0.16	1.81
	Dec	1.96	0.52	1.31	5.63	100	1.44	0.35	6.0	0.00	2.53	8.9	0.10	2.33

Site	Concentration ng.m <sup>-3</sup>													
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Manchester														
67	Jan	1.56	0.32	5.60	47.62	1531	9.89	3.37	13.7	0.08	3.30	31.5	0.59	2.29
	Feb	1.11	0.28	5.41	43.26	1003	11.20	3.87	13.3	0.06	3.44	36.6	0.49	2.20
	Mar	0.56	0.20	9.78	38.65	880	10.19	1.34	9.1	0.05	2.09	38.9	1.87	1.33
	Apr	0.00	0.29	6.85	45.82	1122	12.59	1.52	9.6	0.01	2.55	36.4	0.43	1.53
	May	0.77	0.26	6.87	41.79	988	11.47	1.89	10.3	0.01	3.04	31.3	0.60	0.91
	Jun	0.69	0.14	7.54	56.49	1175	16.42	3.86	11.8	0.05	2.36	36.1	0.29	2.16
	Jul	0.42	0.13	2.66	42.79	1213	19.34	7.97	9.5	0.01	2.68	17.0	0.14	3.38
	Aug	0.61	0.13	6.52	39.88	848	8.72	1.41	8.2	0.00	1.04	26.4	0.39	2.61
	Sep	0.59	0.19	3.42	46.94	1049	11.26	0.75	9.4	0.00	2.29	39.2	0.28	3.39
	Oct	1.04	0.20	5.15	45.89	916	9.58	1.06	10.3	0.00	1.49	31.0	0.14	0.01
	Nov	1.14	0.93	4.42	35.62	722	7.30	0.32	7.8	0.00	1.30	27.1	0.14	1.84
	Dec	1.12	0.32	4.49	33.48	697	6.82	1.63	10.4	0.00	1.03	24.7	0.12	1.89

		Concentration ng.m <sup>-3</sup>													
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap	
Cardiff															
68	Jan	1.38	0.45	3.88	19.63	575	29.82	5.35	22.0	0.11	4.06	78.8	1.40	6.77	
	Feb	0.88	0.25	3.71	28.29	734	10.97	5.60	14.5	0.08	1.82	42.7	0.20	3.72	
	Mar	0.74	0.24	3.18	27.41	741	12.01	2.40	13.0	0.01	2.65	41.9	0.48	3.09	
	Apr	0.99	0.20	7.06	19.53	603	13.84	4.54	13.0	0.01	1.96	40.4	0.01	4.11	
	May	1.36	0.33	4.23	24.41	704	14.94	4.79	18.5	0.01	3.14	60.0	0.18	1.26	
	Jun	0.64	0.15	13.94	26.79	735	12.71	3.28	11.4	0.01	3.00	34.8	0.28	1.24	
	Jul	0.90	0.31	3.59	27.53	847	15.58	3.15	18.6	0.00	5.12	47.0	0.15	1.54	
	Aug	0.41	0.20	7.79	30.93	800	10.82	4.78	8.7	0.00	1.03	37.4	0.21	1.83	
	Sep	0.50	0.21	3.09	33.91	873	11.61	2.09	10.9	0.00	2.59	43.8	0.18	1.85	
	Oct	1.34	0.40	6.62	33.14	864	13.90	3.06	25.8	0.00	2.17	74.8	0.34	1.86	
	Nov	1.73	0.67	6.92	39.11	866	12.02	4.00	51.2	0.00	1.05	51.0	0.15	2.01	
	Dec	2.14	0.86	5.16	27.85	726	9.34	2.13	17.0	0.00	3.53	43.4	0.48	2.03	

	Concentration ng.m <sup>-3</sup>													
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Brookside Metals														
69	Jan	2.87	5.98	1.73	57.42	296	8.02	5.72	144.7	0.21	3.49	1065.6	0.45	1.81
	Feb	1.21	1.53	1.82	34.77	440	12.38	8.06	45.2	0.12	6.01	259.4	0.62	1.71
	Mar	0.44	0.22	4.32	9.59	238	7.43	4.07	11.2	0.01	0.97	45.9	0.08	3.37
	Apr	1.37	2.62	5.98	50.38	349	9.45	1.26	81.3	0.01	1.63	482.2	0.19	1.60
	May	1.33	4.96	6.56	58.14	464	12.61	6.16	114.5	0.01	3.02	839.9	0.95	1.40
	Jun	0.55	0.93	1.86	22.43	279	8.24	5.79	39.5	0.01	1.35	245.4	0.30	1.89
	Jul	0.64	1.80	9.99	53.33	366	9.91	9.61	65.8	0.00	1.61	497.5	0.23	1.95
	Aug	0.63	1.31	3.43	25.77	248	5.89	9.76	41.5	0.01	0.37	263.6	0.23	1.35
	Sep	1.05	5.28	5.76	66.78	536	14.36	21.71	172.6	0.03	1.99	954.5	0.32	2.32
	Oct	1.71	6.10	3.89	74.03	444	13.73	7.79	193.0	0.00	1.55	1377.5	0.15	2.25
	Nov	1.80	8.50	6.42	90.60	470	21.63	8.18	124.5	0.00	1.00	1568.8	0.09	1.53
	Dec	0.84	4.50	7.03	63.93	300	8.45	2.56	73.9	0.00	0.69	1129.6	0.17	2.35

Site		Concentration ng.m <sup>-3</sup>												
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Newcastle														
70	Jan	1.73	0.79	2.57	20.58	419	11.65	3.98	28.9	0.10	3.16	72.7	0.14	1.91
	Feb	0.90	0.14	2.57	6.38	208	4.59	0.91	7.5	0.01	1.52	15.4	0.07	4.60
	Mar	0.88	0.45	4.80	9.26	347	6.96	2.40	11.5	0.05	6.22	40.1	0.71	5.05
	Apr	0.78	0.20	3.58	6.49	293	6.18	2.26	9.6	0.02	5.29	22.6	1.68	3.18
	May	0.87	0.14	2.74	6.31	286	6.28	2.46	6.4	0.01	4.50	19.2	1.85	2.52
	Jun	0.89	0.19	3.22	11.35	463	10.46	2.55	17.7	0.01	5.42	42.3	0.23	1.80
	Jul	0.73	0.16	4.67	8.59	378	8.64	4.59	16.0	0.00	3.55	35.7	0.60	4.59
	Aug	0.32	0.10	3.13	5.65	214	4.67	1.55	8.2	0.00	0.75	14.2	0.23	0.55
	Sep	0.81	0.16	4.61	7.65	281	7.70	2.95	8.9	0.00	2.46	25.5	0.31	2.66
	Oct	0.87	0.24	3.53	12.68	393	10.30	2.50	11.6	0.00	1.69	41.1	0.13	2.50
	Nov	1.03	0.26	3.33	7.05	213	5.21	0.51	10.2	0.00	1.36	15.9	0.09	2.71
	Dec	1.47	0.60	2.76	7.07	219	5.08	1.34	9.9	0.00	1.46	19.8	0.03	4.12