

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

**Annual Report for 2005 on
the UK Heavy Metals
Network**

Richard J. C. Brown
Melanie Williams
David Butterfield
Rachel E. Yardley
Dharsheni Muhunthan
Peter T. Woods

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

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

Annual Report for 2005 on the UK Heavy Metals Network

Executive Summary

This Report was prepared by NPL as part of the 2004-2007 UK Heavy Metals Monitoring contract with the Department for the Environment, Food and Rural Affairs. This is the Annual Summary Report for 2005 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.
- Policy update on relevant areas.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events during 2005.

In summary, during 2005:

- No annual average site levels above the First Daughter Directive Lower Assessment Threshold for lead were recorded.
- Two annual average site levels above the Fourth Daughter Directive Upper Assessment Threshold for nickel were recorded.
- One annual average site level above the Fourth Daughter Directive Upper Assessment Threshold for cadmium was recorded.
- No annual average site levels above the Fourth Daughter Directive Lower Assessment Threshold for arsenic were recorded.
- Measured levels of total mercury across the Network remain low (with the exception of the site at Weston Point, Runcorn).
- The downward trend in annual concentration values has continued. However, values for vanadium have increased during the last year.
- NPL continue to provide a total of 56 extra measurement results per week, for elements not previously measured at 6 sites until September 2004, to provide a more comprehensive and robust data set.
- All First, and Fourth, Daughter Directive data quality objectives were met, including their measurement uncertainty requirements.
- Data capture across the Network was 93% for the year.

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Introduction

This Report was prepared by NPL as part of the 2004-2007 UK Heavy Metals Monitoring 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 2005 and contains:

- A summary of Network Operation for 2005
- A description of analytical methods used including QA/QC procedures used by NPL
- 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.
- Highlighting of exceedences, interpretation of data and discussion of trends
- Policy update on relevant areas

Network Operation

Overview

NPL's management of the UK Heavy Metals Network in 2005 has included a great deal of activity. Particular highlights have been:

- The ESU contract was re-tendered in the early part of 2005. The new contract was won by Air Monitors, who replaced Casella ETI as the ESU from April.
- NPL staff visited and fully audited all sites on the Network. This included the calibration and basic maintenance of the Partisol and mercury vapour samplers and re-assessment of LSOs' procedures.
- All network sites have either been, or are scheduled to be, tested for electrical safety.
- The ESU has made service visits to all Network sites. As part of these service visits all Partisol pumps on the Network have been fully overhauled.
- NPL is trialing a new mercury pump in Brent, in parallel with the current system. The new pump is expected to suffer less frequent breakdowns than the current pump.
- The work done as part of the UK Heavy Metals Network has received publicity in both trade¹ and learned journals² during the year, and also in Defra's Air Quality Networks newsletter³.
- NPL have identified possible new monitoring sites which may need to be commissioned in future to meet the requirement of the EU's Fourth Daughter Directive.

Site audits

During 2005 NPL visited all the sampling sites of the Metals Network. The site infrastructure, performance and its integrity were assessed. The LSOs were also audited and received extra training where required. A list of sites on the Network, with location and site code, 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 PM₁₀ sampling head and impactor plate;
- Calibrated the flows of both the particulate (for volumetric and standard flow), and vapour phase (volumetric flow), monitoring equipment;
- Leak tested both the particulate, and vapour phase, monitoring equipment;
- Calibrated the site rotameter (used by the LSO for determining the flow rate of the mercury vapour sampling line).

¹ Brown, R J C, "Heavy metals monitoring network aids UK meet target values", Local Authority Waste and Environment, 2005, 13, (9), 28.

² Brown, R J C, "Benford's law and the screening of analytical data: the case of pollutant concentrations in ambient air", Analyst, 2005, 130, 1280-1285.

³ Brown, R J C, "Monitoring ambient metals: UK response to fourth daughter directive", Network: The newsletter for the UK Air Quality Monitoring Network, 2005, (9), 1-2

The dates of individual site audits and the flow data recorded at each site may be found in Annexes 2, 3 and 4. In summary:

- All of the sites have been audited and are performing well.
- The site infrastructure was assessed at all sites and no problems were found. All of the sites are currently being inspected for the electrical safety of the installation, after the problems found at Hallen earlier in the year. Defra is aware of the faults found at the Hallen site. The findings of the electrical inspection will be presented in a separate report.
- Nearly all of the LSOs audited were carrying out all of their functions correctly. There were a couple of cases where the flow through the mercury vapour adsorption tube was measured and adjusted at the end of a sampling period and was not rechecked when a new adsorption tube was inserted in to the sampling system. It cannot be assumed that a new tube will allow the same flow rate as the old tube. All of the LSOs who made this error have been instructed in the correct procedure.
- A comparison between the ESU flow calibrator and the NPL flow calibrator was performed at NPL and it was found that both calibrators agreed with each other to within 2% at ambient conditions and better than 1% at standard temperature and pressure.

Equipment servicing and breakdowns

During 2005 the ESU visited, and fully serviced, every Network site twice at 6-month intervals.

During 2005 NPL and the ESU carried out a programme of additional preventative maintenance to replace the flow controllers of all the Partisol samplers in order to reduce the rate of future breakdowns and to increase data capture across the Network.

NPL is currently trialling a new type of mercury vapour pump, in parallel with the current system, in Brent. The trial started in September 2005 and will last 6 months. The new mercury pump should reduce the rate of breakdowns across the Network and increase data capture. If the two mercury pumps produce comparable results, the new mercury pumps will be rolled out across the Network, with agreement from Defra.

During 2005, NPL has called-out the ESU to deal with sampler failures at: BZL Avonmouth (water ingress into Partisol), Brent (keypad failure), Cardiff (twice for low recorded flows), London Cromwell Road (low recorded valid hours), BZL Hallen (screen malfunction), Leeds (low recorded flows), Manchester (low recorded flow and screen malfunction), ICI Western Point (electrical fault) and Sheffield (four times for repeated whole-unit failure).

Repeated failure of the Partisol in Sheffield during May meant that it was not possible to record any data for this month.

During 2005 NPL has replaced failed mercury pumps at: Cardiff, Motherwell (three times), Eskdalemuir (twice), Glasgow (twice), Newcastle, London Cromwell Road (twice), London Horseferry Road, Leeds, Manchester (twice), IMI Walsall and ICI Western Point.

This notwithstanding the Network has functioned well during the last quarter and Partisol down-times have decreased dramatically since the new ESU contract.

ESU

The ESU contract was re-tendered in the early part of 2005. The new contract was won by Air Monitors, who replaced Casella ETI as the ESU from April.

Electrical Safety

During a routine service visit to the BZL Hallen site in June 2005, it was discovered that the Partisol unit had been incorrectly installed, with the electrical supply cable bypassing the isolator unit, resulting in the unit remaining 'live' even when turned off. This was logged as a near miss incident with NPL's Health and Safety department. Following discussion with Defra a campaign of electrical safety testing for all network sites was initiated. All sites have now either been, or have a scheduled date to be, tested for electrical safety. The findings of the electrical inspection will be presented in a separate report.

Site 70: Newcastle (Elswick 6)

Due to the previously raised issue of the health and safety implications of working at heights to service and maintain the Elswick 6 monitoring site, the Newcastle Centre AURN site was inspected with the view to installing the Partisol and mercury vapour samplers at this location. It was concluded that the samplers would have to be mounted in a cage on the outside of the existing hut due to space limitations inside the hut. There is currently enough space around the hut to install the samplers safely. NPL have submitted these findings, along with several other options for the future of the site, to Defra for consideration.

Sampling and Analytical Methodology

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

Sampling Methodology: Particulate-phase metals

Particulate samples were taken at all sites in the Network using Partisol 2000 instruments (fitted with PM₁₀ heads) operating at a calibrated flow rate of 1m³.h⁻¹. Samples were taken for a period of one week onto 47 mm diameter GN Metrical membrane filters.

Sampling Methodology: Vapour-phase mercury

Sampling for vapour-phase mercury took place at 13 of the 17 Network sites, using an SKC low volume pump (calibrated annually by NPL). Air was pumped through Amasil (gold-coated silica) tubes at a rate of 100 ml.min⁻¹ for either one week or four weeks, depending on the specific site. A schematic diagram of the sampling set-up is given in Figure 1.

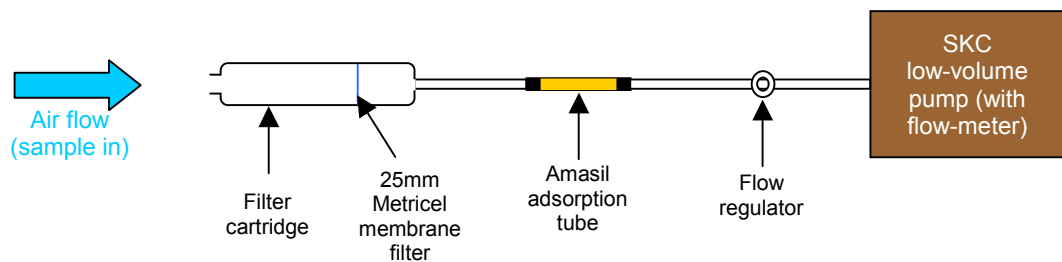


Figure 1. Schematic diagram of vapour-phase mercury sampling apparatus. The 25 mm diameter filter was used to trap any particulate material

Analytical Methodology: Particulate-phase metals

Analysis for particulate-phase metals took place in-house at NPL using a PerkinElmer Elan DRC II ICP-MS, following NPL's UKAS-accredited procedure.

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 is mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS is corrected for by use of an internal standards mixture (containing Y, In, Bi, Sc, Ga & Rh) continuously added to the all samples by 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.

Analytical Methodology: Vapour-phase mercury

Analysis of vapour-phase mercury samples took place at NPL using a PS Analytical Sir Galahad II analyser with a fluorescence detector. 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. Mercury vapour analysis method parameters

To overcome problems associated with instrumental drift, a novel calibration procedure was developed. Before the analysis of each tube, the drift of the detector was characterised by the analysis of a known amount of injected mercury vapour. The application of this drift-correction procedure significantly improves the accuracy of the analysis.

Data quality

Limits of Detection: Particulate-phase metals

Indicative detection limits achieved by NPL using UKAS-accredited ICP-MS methods, fully compatible with EN 14902, in are shown in Table 2. The solution limits of detection were calculated using the method outlined in EN14902, repeatedly analysing of a typical acid blank solution and taking into account the variability between individual instrumental readings. Values for the limits of detectors have been calculated assuming a solution mass of 53 g and a volume of sampled air of 168 m³ (equivalent to seven days sampling at 1.0 m³.h⁻¹).

Analyte	Limit of Detection		
	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.

Limits of Detection: Vapour-phase mercury

The limit of detection routinely achievable for analysis of vapour-phase mercury at NPL is 0.03 ng per tube, equivalent to an air concentration of approximately 0.03 ng.m⁻³ (assuming a volume of sampled air of 1.01 m³, equivalent to one week's sampling at 100 ml.min⁻¹). 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).

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.

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 limit specified by prEN14902.
- 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 standard-corrected 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.

Vapour-phase 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.
- 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.

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%.

It should be noted that the measurement uncertainty requirements given in the Fourth Daughter Directive refer to that of a 'single measurement'. This has been interpreted at present by NPL in its most stringent form.

Analyte	Expanded relative uncertainty	
	Single measurement	Daughter Directive maximum
As	30%	40%
Cd	26%	40%
Cr	16%	-
Cu	17%	-
Fe	15%	-
Mn	15%	-
Ni	20%	40%
Pb	16%	25%
Pt	n/a [†]	-
V	21%	-
Zn	14%	-
Hg (particulate)	40%*	-
Hg (vapour)	23%	-

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.

* Relatively high uncertainty recorded for Hg due to its measured low levels in ambient air.

[†] 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 anticipated that in the region of the appropriate target value - where the Daughter Directive uncertainty data quality objectives apply – these uncertainties will be significantly lower.

Network data

Data capture

Data capture across the entire Network during 2005 was **93%**.

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

Location	Data Capture / %	
	Particulate phase	Vapour phase
Whole Network	92	96
IMI Walsall	100	98
BZL Hallen	94	N/A
Swansea	100	N/A
BZL Avonmouth	100	N/A
Sheffield	85	N/A
ICI Western Point	85	92
London Brent	92	100
London Cromwell Rd	92	100
London Horseferry Rd	92	100
Leeds	94	92
Glasgow	88	92
Eskdalemuir	90	100
Motherwell	94	100
Manchester	90	98
Cardiff	90	83
Brookside Metals	98	100
Newcastle	90	93

Table 4. Data capture across the UK Heavy Metals Network during 2005

Data processing and ratification

Analysis of the Network samples produces individual concentration values for weekly, or monthly (for some mercury tubes) 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 uncertainty-weighted 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 across the individual sites.

An NPL QA/QC circle (the 'quality circle') ratifies ambient concentration data produced by the UK Heavy Metals 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 80% 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, and 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. (vapour phase 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 be detected using a Benford's Law analysis).
- 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 relevant to EC Directives.

Uncertainty

Since the data capture across the Network has been high (and 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 insignificant uncertainty contributions due to lack of 100% time coverage.

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:

Analyte	Expanded Relative Uncertainty	
	Annual Mean	Daughter Directive maximum
As	31%	40%
Cd	27%	40%
Ni	22%	40%
Pb	18%	25%

Table 5. Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant (First and Fourth) Daughter Directive metals.

Measured Concentrations

The annual mean measured metals concentrations, average over all sites are displayed in the table below.

Analyte	2005 Annual Mean Concentration / ng.m⁻³
As	1.03
Cd	0.59
Cr	3.94
Cu	19.6
Fe	386
Mn	7.73
Ni	4.75
Pb	18.8
Pt	0.02
V	4.21
Zn	77.8
Hg (p)	0.64
Hg (v)	4.60

Table 6. 2005 annual mean concentrations averaged over all site on the UK Heavy Metals Network. Hg (p) and Hg (g) and particulate phase mercury, and vapour phase mercury, respectively.

The individual annual mean values from the seventeen sites on the UK Heavy Metals Network are given in the table below:

2005 Annual Mean Concentration / ng.m ⁻³													
Site	Analyte												
	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg (p)	Hg (g)
IMI Walsall	1.18	0.64	2.51	15.00	294	8.52	2.82	16.7	0.03	3.30	71.0	0.54	1.79
BZL Avonmouth	1.09	0.48	2.17	5.01	217	5.00	4.13	15.2	0.04	4.18	52.6	1.16	N/A
Swansea	1.18	0.38	4.17	6.20	133	4.08	19.62	17.9	0.01	17.24	17.8	0.46	N/A
BZL Hallen	0.97	1.06	1.21	5.90	185	5.86	3.51	15.0	0.04	2.89	35.0	0.36	N/A
Sheffield	1.53	0.63	18.86	16.63	444	26.15	14.26	29.0	0.03	4.15	142.7	0.46	N/A
ICI Western Point	0.73	0.28	1.13	9.19	142	3.28	2.34	13.5	0.01	3.53	21.2	2.00	40.21
London Brent	1.41	0.55	4.32	24.12	532	7.56	3.45	23.5	0.02	4.19	25.2	0.62	1.16
London Cromwell	1.14	0.36	5.53	41.82	876	10.06	4.46	14.6	0.02	6.34	32.7	0.81	1.71
London Horseferry	1.26	0.37	2.37	22.40	439	6.40	3.47	15.9	0.02	3.69	26.5	0.16	2.37
Leeds	1.15	0.38	3.29	11.46	305	8.28	2.61	18.2	0.00	3.72	24.3	0.90	1.28
Glasgow	0.81	0.21	1.66	13.06	287	4.37	2.11	12.9	0.05	1.58	22.7	0.20	1.67
Eskdalemuir	0.15	0.09	3.27	1.42	37	1.00	1.53	2.9	0.02	1.23	4.4	0.19	1.39
Motherwell	0.81	0.28	3.33	8.47	242	5.52	3.34	6.8	0.01	2.23	15.3	0.25	1.06
Manchester	1.01	0.31	5.30	52.99	1008	11.66	3.86	12.6	0.02	3.01	46.2	0.34	1.38
Cardiff	1.22	0.50	3.84	41.91	833	12.43	1.89	20.8	0.02	3.57	77.2	1.20	1.46
Brookside Metals	1.26	3.33	3.49	48.14	396	8.51	5.51	76.3	0.02	4.08	691.2	0.44	1.85
Newcastle	0.75	0.23	1.87	8.89	197	4.41	2.75	9.1	0.02	2.43	20.7	0.92	1.78

Table 7. 2005 annual mean concentrations measured at individual sites on the UK Heavy Metals Network. The monthly measured metals concentrations from all Network sites are summarised in the tables in Annex 5. Hg (p) and Hg (g) and particulate phase mercury, and vapour phase mercury, respectively.

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:

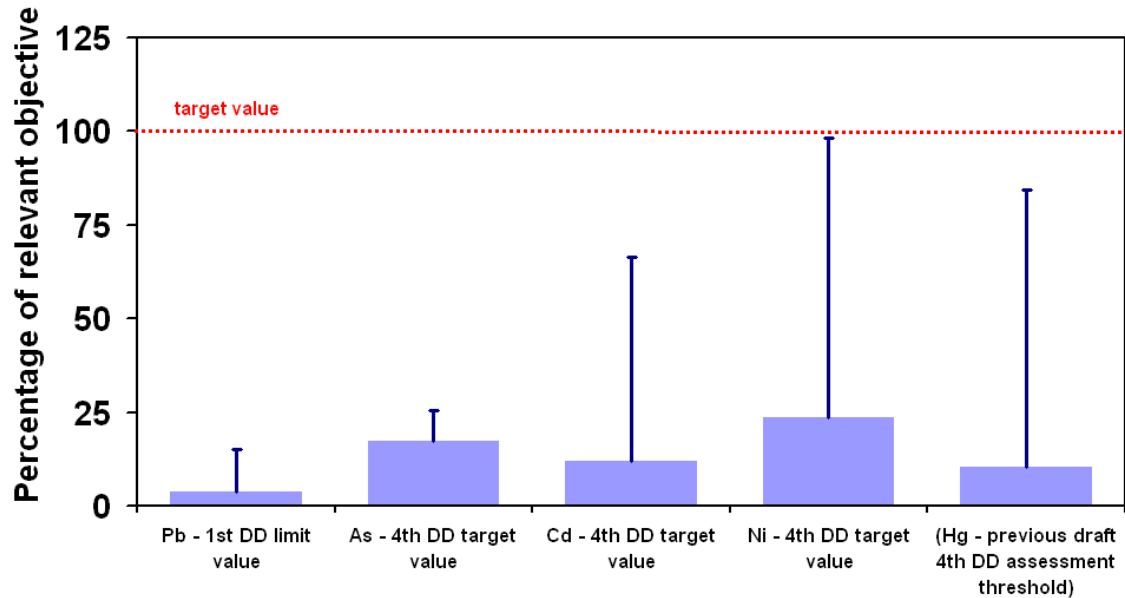


Figure 2. A summary of the annual mean measured concentrations of the heavy metals relevant to the First and Fourth Daughter Directives on the UK Heavy Metals Network in 2005 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the annual means at the site with the highest concentrations. The mercury objective is taken from a threshold value quoted in a draft of the Fourth DD. Mercury refers to the sum of the vapour phase and particulate phase concentrations.

In all cases the annual mean values are well below the limit and target values. In no cases 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:

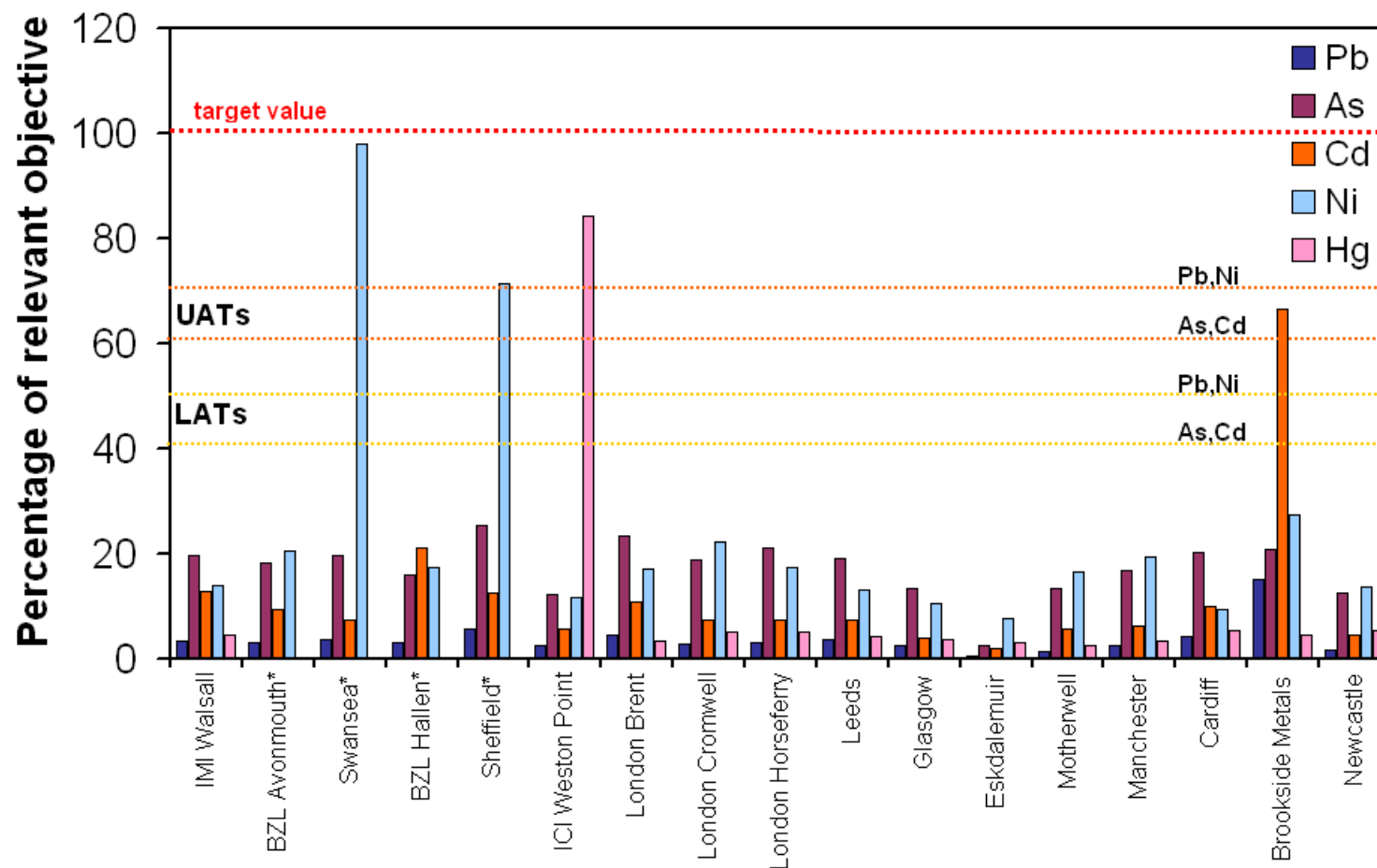


Figure 3. A summary of the annual mean measured concentrations of the heavy metals relevant to the 1st and 4th Daughter Directives (DD) at all site on the UK Heavy Metals Network in 2005 as a percentage of the relevant target values, lower assessment thresholds (LAT) and upper assessment thresholds (UAT). The mercury objective originates from a threshold value quotes in a draft of the Fourth DD. Site numbers with asterisks indicate that these are sites measuring particulate phase mercury only. Mercury refers to the sum of the vapour phase and particulate phase 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 (Sheffield). The highest annual mean value for 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 Upper Assessment Threshold:

- Nickel at Site 49 (INCO Europe, Swansea): 98% of the target value.
- Nickel at Site 58 (Avesta Steel, Sheffield): 71% of the target value.
- Cadmium at Site 69 (Brookside Metals, Walsall): 67% of the target value.

All three of these sites are located next to active industrial plants where metals levels would be expected to be high.

However, the annual average nickel concentration at Swansea has decreased by almost 50% compared to the 2004 value. It is possible that this is owing to a change in Network contractor (9 months of 2004's data was produced by the previous contractor), or to differences in the average wind conditions between 2004 and 2005, or simply to changes in the amount of nickel present in the ambient surroundings of the site. Since intercomparison results during the handover period showed very good agreement between NPL and the previous contractor, it is thought that the first explanation for this drop in concentration is the least likely. Therefore, as a route to providing greater value to the interpretation of metals data, NPL plan, in future reports, to assess the metals concentration levels at point source locations in combination with metrological data. This will be especially useful for the interpretation of trends at sites such as Sheffield, Swansea, Brookside Metals, and ICI Weston Point, Runcorn:

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

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

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

Although there is no target value for mercury, the measured annual mean mercury level at Site 59 (ICI Weston Point, Runcorn) is approximately 80% of a target value quoted in an early draft of the 4th DD.

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

Trends in measured concentrations

Changes in the annual average metals concentrations measured, across the Network, over the past 25 years are shown in the table below:

Analyte	Changes in measured concentrations during the:			
	Last 25 Years	Last 10 Years	Last 5 Years	Last Year
As	not measured	not measured	not measured	-7%
Cd	-78%	-36%	55%	-9%
Cr	-59%	-21%	-51%	-41%
Cu	-26%	-33%	+13%	-6%
Fe	-62%	-55%	-25%	-16%
Hg (part)	not measured	not measured	not measured	-9%
Hg (vap)	not measured	not measured	not measured	22%
Mn	-70%	-44%	-5%	-22%
Ni	-56%	+29%	+22%	-11%
Pt	not measured	not measured	not measured	+100%
V	-79%	-56%	+74%	+98%
Zn	-60%	+28%	+214%	-26%
Pb	-97%	-92%	-76%	-24%

Table 8. Trends in the measured annual average concentrations of metals measured by the UK Heavy Metals Network

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:

During the third year of network-wide **arsenic** measurement, the concentrations have fallen with respect to previous values, and remain low across the whole Network.

Cadmium concentrations continue to fall and remain low across the Network.

Chromium concentrations have fallen in 2005 following a relatively high 2004. They have exhibited a slow, but steady decrease over the last 25 years.

Copper concentrations are relatively low across the Network and continue to decrease slowly following high recorded concentrations in 2003.

Iron concentrations continue to show a rapid downward trend across the Network, and have more than halved over the last 10 years.

Particulate phase **mercury** concentrations decreased in 2005 and still remain very low across the Network. Vapour phase **mercury** showed an 22% increase in 2005. However trends, and average recorded concentrations, for mercury are strongly influenced by the very high levels at Site 59 (ICI Weston Point, Runcorn). These are over 15 times as high as the next highest site.

Manganese values showed a slight decrease in 2005, but have remained relatively constant and low over the last 5 years.

Nickel values fell by 11% in 2005. The high values recorded at sites 49 and 58 (INCO 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⁻³). In 2005 NPL ceased the previous practice of using “<limit of detection” to report very low platinum concentrations. Instead the actual measurement result is quoted with an enlarged measurement uncertainty, as appropriate. Concentrations measured for platinum are the lowest, by an order of magnitude, of any of the metals monitored across the Network.

Vanadium levels increased in 2005, but remain generally low and have more than halved over the last 10 years. The high values recorded at sites 49 (INCO Swansea) have a very large influence on trends, and average recorded concentrations, for this element across the Network

Zinc levels have decreased in 2005 following relatively high measured concentrations in 2003 and 2004. Trends, and average recorded concentrations, for this element across the Network are influenced substantially by the high measured concentrations at Sites 58 and 69 (Sheffield and Brookside Metals, respectively).

Lead concentrations continue to fall sharply across the Network. All sites exhibit concentrations that are less than 15% of the First Daughter Directive Limit Value.

Concentration trends over the last 25 years are summarised in the graphs below:

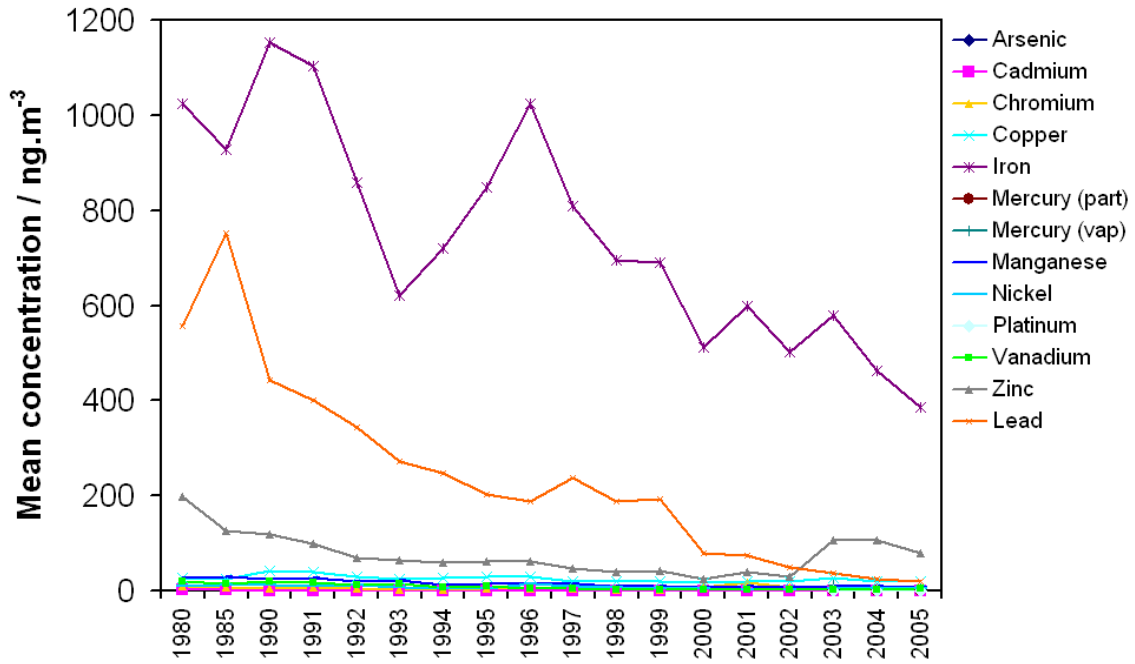


Figure 4. The annual mean concentration of metals measured on the UK Heavy Metals Network over the last 25 years.

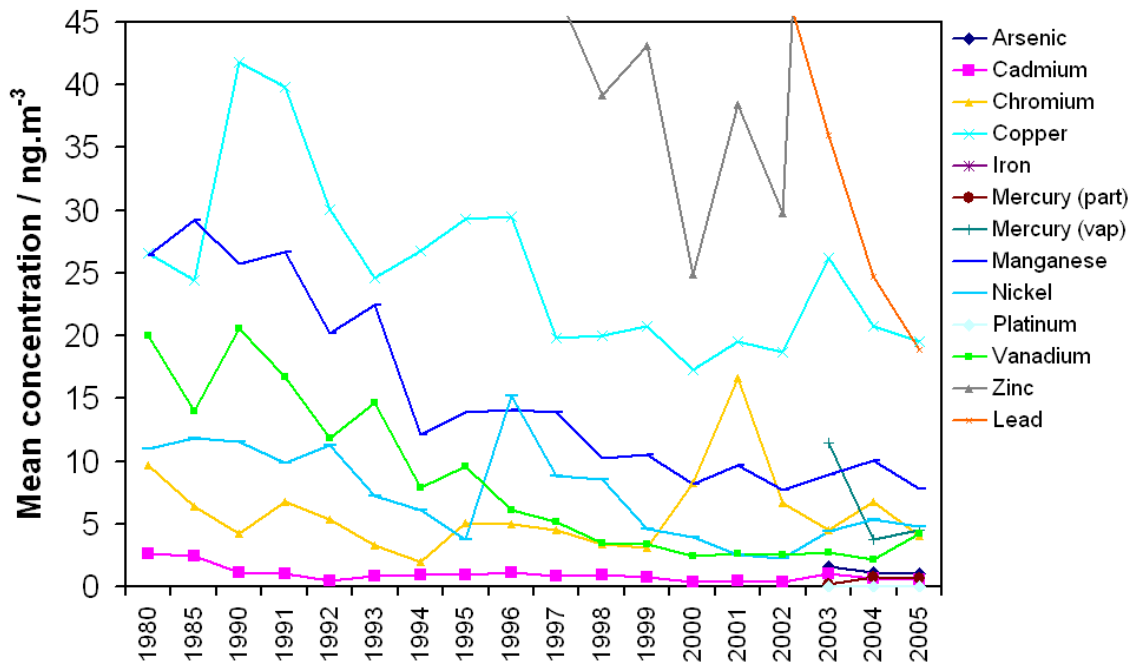


Figure 5. The annual mean concentration of metals measured on the UK Heavy Metals Network over the last 25 years – enlarged to elucidate trends at lower concentrations.

Policy Update

CEN TC264 WG14 – Measurement of Heavy Metals in Ambient Air

After major revision at CEN enquiry stage, lead by NPL, this standard was approved following the formal vote among the Member States and was recently published as *BS EN 14902:2005 “Ambient air quality - Standard method for the measurement of Pb, Cd, As and Ni in the PM10 fraction of suspended particulate matter”*. NPL is, in this contract, working fully in conformance with all the requirements and provisions of this published standard and also, as recommended in this standard, all the analytical measurements carried out for the Defra Network are covered by accreditation to ISO/EN 17025.

CEN TC264 WG20 – Deposition of Heavy Metals

The laboratory and field validation work in this working group was tendered in accordance with the new CEN guidelines. WG20 was the first working group to follow this procedure. All of the laboratory and field validation work has now been allocated on an individual workpackage basis, (in some case to laboratories who were not originally members of the working group). The laboratory tests have now been completed, and the field validation work has started, with two sites in Europe sampling concurrently for six months, followed by two further sites in the second half of 2006.

CEN TC264 WG25 – Mercury

This working group met in early October 2005, and produced a draft document calling for tenders for the group’s mandated laboratory and field validation work. The working group was due to meet in January 2006 to finalise the document, but the Commission now requires the document by the end of the year, so final adjustments were made by e-mail circulation. NPL has been working hard to ensure that UK instrument manufacturers are properly represented during the field validation work. The next WG25 meeting is scheduled for March 2006.

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



Site Code	Site Address	Site Classification	Pollutants measured
46: IMI Refiners Ltd, Walsall	74 Primley Avenue, Walsall, WS2 9UW	Industrial Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
47: BZL Ltd, Avonmouth	Avonmouth Medical Centre, Collins Street, Bristol, BS11 9JJ	Industrial Background	As, Cd, Cr, Cu, Fe, Hg[Part], Mn, Ni, Pb, Pt, V, Zn
49: INCO Europe, Swansea	Glais Primary School, School Road, Glais, Swansea, SA7 9EY	Industrial Background	As, Cd, Cr, Cu, Fe, Hg[Part], Mn, Ni, Pb, Pt, V, Zn
56: BZL Ltd, Avonmouth (Hallen Village)	West Country Caravans Ltd., Moorhouse Lane, Hallen, Bristol, BS10 7RU	Background	As, Cd, Cr, Cu, Fe, Hg[Part], Mn, Ni, Pb, Pt, V, Zn
58: Avesta Steel, Sheffield	BOC Gases, Bawtry Road, Brinsworth, Sheffield.	Industrial Background	As, Cd, Cr, Cu, Fe, Hg[Part], Mn, Ni, Pb, Pt, V, Zn
59: ICI Weston Point, Runcorn	Weston Point County Primary School, Caster Avenue, Weston Point, Runcorn, WA7 4EQ	Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
60: London Brent, North Circular	Tesco Superstore, North Circular Road, Brent, London	Roadside	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
61: London, Cromwell Road	Natural History Museum, Cromwell Road, London	Roadside	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
62: London, Horseferry Road	Mortuary Car Park, Horseferry Road, London	Urban Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
63: Leeds, Old Market Buildings	Old Market Building, Vicar Lane, Leeds, LS11	Urban Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
64: Glasgow, St Annes Primary School	St Annes Primary School, 37 David Street, Glasgow, G40 2UN	Urban Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
65: Eskdalemuir, Met Office	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	Rural	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
66: Motherwell, Civic Centre	Civic Centre	Urban Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
67: Manchester M56, Junction 4	Junction 4, M56, Newhall Green, Wythenshaw, Manchester	Roadside	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
68: Cardiff, Waungron Road	Cleansing Depot, Waungron, Fairwater, Cardiff, CF5 2JJ	Roadside	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
69: Brookside Metals, Bilston Lane	Adult Training Centre, Bilston Lane, Shepwell Green, Willenhall, Walsall	Industrial Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn
70: Elswick 6, Newcastle Upon Tyne	Telewest Arena, Arena Way, Newcastle Upon Tyne	Industrial Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part], Mn, Ni, Pb, Pt, V, Zn

Annex 2 - Site Audit reports

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

Site	Date	Partisol 2000 Serial Numbers	Mercury Vapour Serial Numbers	LSO audited
Avesta Steel, Sheffield	19/10/2005	2000A204719901	Not Measured	Andy Hawkins
Brookside Metals, Bilston Lane	21/09/2005	2000A204649811	404949	Liz Riley, Mick Clews
BZL Ltd, Avonmouth	29/06/2005	2000A205009902	Not Measured	-
BZL Ltd, Hallen	29/06/2005	200A205049902	Not Measured	-
Cardiff, Waungron Road	28/06/2005	2000A204919902	733232	-
Elswick 6, Newcastle Upon Tyne	31/08/2005	2000A205069902	508289	David Donnelly
Eskdalemuir	31/08/2005	2000A204909902	508290	Ian Dawson
Glasgow, St Annes	30/08/2005	2000A204899902	404948	Dominic Callahan
ICI Weston Point	18/10/2005	2000A205079902	404947	John Carrington
IMI Refiners Ltd, Walsall	21/09/2005	2000A204989902	508291	Liz Riley, Mick Clews
INCO Europe	28/06/2005	2000A205089902	Not Measured	-
Leeds, Old Market Buildings	18/10/2005	2000A204739901	508289	April Wood
London Brent	23/09/2005	2000A204999902	508774	Dharsheni Velumylyum
London Cromwell Road	04/10/2005	2000A205059902	672736	Colin Gilham
London Horseferry Road	04/10/2005	2000A204969902	508775	Colin Gilham
Manchester M56, Jn 4	18/10/2005	2000A204959902	404946	Mike Concannon
Motherwell, Civic Centre	31/08/2005	2000A204979902	404950	Pat Docherty

LSOs for Avonmouth, Hallen, INCO and Cardiff were unavailable at the time of audit, but were audited last year.

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. The Vol-U-Meter is 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, Walsall	17.14	+2.6	Passed
BZL Avonmouth	16.91	+1.9	Passed
BZL Hallen	16.72	+0.7	Passed
Cardiff	17.11	+3.1	Passed
Eskdalemuir	16.72	+0.1	Passed
Glasgow	16.84	+1.4	Passed
ICI Weston Point	16.81	+0.7	Passed
IMI Refiners Ltd, Walsall	16.71	+0.7	Passed
Leeds	16.85	+0.9	Passed
London Brent	16.86	+0.4	Passed
London Cromwell Road	16.54	-0.9	Passed
London Horseferry Road	16.99	+2.3	Passed
Manchester	16.83	+0.8	Passed
Motherwell	16.30	-2.4	Passed
Newcastle	16.82	+1.3	Passed
Sheffield	16.69	-0.1	Passed
Swansea INCO	18.18	+8.8	Passed

The uncertainty in the flow measurements, expressed with a level of uncertainty of 95%, is 6%.

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.

Annex 4 - Results of Mercury Vapour Phase 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. The Vol-U-Meter is 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, Walsall	100	95.48	-4.5	Passed
Cardiff	90	98.15	+9.1	Passed
Eskdalemuir	N/A	-	-	Passed
Glasgow	100	97.46	-2.5	Passed
ICI Weston Point	N/A	-	-	Passed
IMI Refiners Ltd, Walsall	100	98.94	-1.1	Passed
Leeds	100	107.46	+7.5	Passed
London Brent	100	95.18	-4.8	Passed
London Cromwell Road	100	100.63	+0.6	Passed
London Horseferry Road	100	98.84	-1.2	Passed
Manchester	100	134.90	+34.9	Passed
Motherwell	108	111.32	+3.1	Passed
Newcastle	100	130.34	+30.3	Passed

The uncertainty in the measured flow rates, expressed with a level of uncertainty of 95%, is 6%.

The difference from set point determined from the audits of the mercury vapour samplers is used at ratification to adjust the volume recorded by the LSO for each sample. There is no threshold for remedial action on the mercury vapour samplers 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

Site	Month	Concentration ng.m ⁻³												Hg Vap
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	
IMI Refiners, Walsall 46	Jan	0.60	0.47	2.71	9.96	254	6.94	4.25	19.7	0.06	2.73	62.5	0.12	1.85
	Feb	0.96	0.24	1.27	4.09	101	3.45	1.55	8.3	0.00	5.05	22.5	0.09	1.43
	Mar	1.08	0.49	2.05	14.04	353	11.72	4.78	26.2	0.00	2.95	108.9	0.09	1.71
	Apr	1.82	1.06	1.28	11.63	277	7.37	4.14	21.3	0.00	4.24	126.1	0.17	2.20
	May	0.66	0.56	1.97	10.19	237	8.70	0.19	14.2	0.00	1.22	44.0	0.08	2.10
	Jun	0.84	0.41	1.01	18.47	271	8.16	0.59	14.9	0.00	2.08	61.1	0.05	1.85
	Jul	0.64	0.41	1.54	14.17	264	7.03	0.36	12.2	0.02	2.20	67.9	0.11	1.61
	Aug	1.30	0.36	2.80	15.14	311	6.57	1.32	14.0	0.02	8.98	39.1	0.18	1.03
	Sep	1.72	0.47	7.44	19.59	426	12.10	7.43	11.5	0.02	4.96	85.8	0.69	0.56
	Oct	1.03	0.39	2.71	13.29	286	9.38	2.16	16.5	0.01	2.76	49.1	3.99	1.99
	Nov	2.36	1.12	3.34	31.21	446	11.74	4.33	12.4	0.03	0.85	106.0	0.27	3.27
	Dec	1.18	1.70	1.97	18.16	314	9.03	2.74	29.3	0.17	1.56	78.5	0.62	1.87

Site	Month	Concentration ng.m ⁻³												Hg Vap
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	
BZL Ltd., Avonmouth 47	Jan	1.64	0.64	0.63	4.28	265	4.98	1.93	19.0	0.40	5.65	48.2	0.27	N/A
	Feb	1.41	1.30	2.04	4.84	236	6.40	4.30	27.3	0.00	4.31	48.1	0.40	N/A
	Mar	0.82	0.24	1.88	3.37	162	4.46	2.73	10.0	0.00	5.86	29.2	0.17	N/A
	Apr	0.85	0.27	1.66	3.81	208	5.33	4.25	12.1	0.00	6.98	33.5	0.35	N/A
	May	0.77	0.57	2.58	5.06	217	4.75	6.14	17.6	0.00	4.97	71.6	0.19	N/A
	Jun	1.78	0.25	11.35	5.23	90	3.38	6.50	5.4	0.00	2.81	20.9	0.27	N/A
	Jul	0.63	0.20	0.06	4.43	175	5.19	2.40	12.8	0.00	3.36	37.7	1.71	N/A
	Aug	1.60	0.30	3.87	5.57	302	6.49	4.99	13.0	0.00	4.79	36.6	3.18	N/A
	Sep	0.50	0.44	0.10	4.70	171	4.13	7.84	13.3	0.00	3.81	192.3	1.25	N/A
	Oct	0.91	0.33	0.15	4.18	167	3.32	0.95	16.2	0.00	1.94	20.4	2.80	N/A
	Nov	1.37	0.81	0.31	8.83	384	6.68	4.57	19.8	0.00	1.93	43.1	2.23	N/A
	Dec	0.81	0.39	1.35	5.86	235	4.85	2.97	15.2	0.08	3.80	49.5	1.14	N/A

Site	Month	Concentration ng.m ⁻³												Hg Vap
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	
Swansea 49	Jan	0.60	0.25	6.90	4.84	73	1.84	18.82	22.5	0.08	48.40	16.7	0.05	N/A
	Feb	4.17	2.23	9.92	24.18	84	9.23	26.76	98.2	0.00	2.88	34.9	0.16	N/A
	Mar	0.78	0.19	1.16	3.20	113	3.08	18.02	7.6	0.00	2.68	14.2	0.08	N/A
	Apr	0.69	0.25	5.33	2.60	121	3.75	20.24	7.1	0.00	31.67	13.1	0.09	N/A
	May	2.35	0.10	8.75	1.83	92	3.53	7.11	5.3	0.00	84.79	7.4	0.88	N/A
	Jun	0.44	0.11	1.21	3.50	98	3.25	9.52	6.0	0.00	2.78	26.8	0.09	N/A
	Jul	0.52	0.23	1.71	4.19	171	3.87	33.38	8.2	0.02	1.65	18.0	0.21	N/A
	Aug	0.50	0.15	5.88	3.99	154	4.37	23.17	6.4	0.02	23.99	7.0	0.26	N/A
	Sep	0.58	0.28	3.81	5.11	151	5.32	16.65	12.6	0.00	2.80	27.4	0.07	N/A
	Oct	0.85	0.29	1.84	4.10	162	3.87	11.81	10.2	0.00	1.86	16.5	2.64	N/A
	Nov	1.38	0.23	2.25	10.63	162	3.44	21.46	17.3	0.02	0.43	15.5	0.69	N/A
	Dec	1.30	0.21	1.28	6.20	215	3.38	28.48	13.4	0.04	2.93	16.5	0.28	N/A

Site	Month	Concentration ng.m ⁻³												Hg Vap
		As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	
BZL Ltd., Hallen Village 56	Jan	1.66	0.64	0.64	4.33	268	5.04	1.95	19.2	0.40	5.72	48.8	0.28	N/A
	Feb	1.43	1.31	2.06	4.90	239	6.47	4.35	27.7	0.00	4.36	48.7	0.41	N/A
	Mar	1.16	0.38	2.28	5.94	179	6.12	1.79	17.2	0.00	3.72	29.1	0.17	N/A
	Apr	1.09	1.18	1.86	6.59	192	8.72	3.24	22.0	0.00	3.54	50.0	0.30	N/A
	May	0.52	0.22	2.10	9.43	278	6.84	15.40	7.9	0.00	2.30	24.1	0.08	N/A
	Jun	0.31	1.71	1.06	4.25	97	4.15	0.98	13.7	0.00	2.30	39.2	0.10	N/A
	Jul	0.45	2.96	1.00	4.99	97	5.77	0.90	11.8	0.01	1.64	24.5	0.18	N/A
	Aug	1.26	0.33	0.61	6.19	184	6.56	4.31	8.1	0.01	1.95	20.9	0.19	N/A
	Sep	0.36	1.12	1.54	4.68	96	2.67	2.88	4.8	0.00	3.41	16.5	0.46	N/A
	Oct	0.67	2.15	0.11	9.13	127	4.39	0.18	13.4	0.01	1.71	31.3	1.29	N/A
	Nov	2.11	0.59	1.32	6.42	400	12.10	5.84	29.2	0.00	2.63	70.5	0.57	N/A
	Dec	0.60	0.14	0.01	3.92	72	1.52	0.35	5.5	0.01	1.38	15.8	0.27	N/A

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		Concentration ng.m ⁻³													
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap	
Sheffield 58	Jan	1.38	0.73	36.76	13.12	491	43.49	25.10	41.3	0.07	3.19	168.8	0.71	N/A	
	Feb	1.42	0.88	35.84	13.61	425	36.01	19.83	42.4	0.00	3.64	171.3	0.08	N/A	
	Mar	1.28	0.51	18.50	10.94	395	29.08	9.73	34.3	0.00	3.55	85.7	0.14	N/A	
	Apr	2.11	0.70	10.34	18.03	553	34.77	7.37	49.3	0.00	7.73	140.2	0.24	N/A	
	May	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
	Jun	1.15	0.45	29.68	6.46	407	19.27	20.31	17.8	0.00	2.17	47.0	0.09	N/A	
	Jul	0.81	0.26	6.28	12.04	336	13.15	10.55	10.7	0.05	3.06	48.2	0.14	N/A	
	Aug	1.30	0.39	17.33	28.05	352	18.21	19.80	14.8	0.03	5.53	97.7	0.10	N/A	
	Sep	1.34	0.91	17.23	15.99	409	27.10	10.77	16.9	0.00	6.79	376.1	2.53	N/A	
	Oct	0.57	0.37	1.38	11.09	275	3.72	1.28	7.6	0.00	1.70	111.5	0.43	N/A	
	Nov	3.01	0.98	18.21	26.19	495	30.74	13.01	48.4	0.04	3.03	179.3	0.36	N/A	
	Dec	2.46	0.78	15.90	27.36	748	32.08	19.11	34.9	0.09	5.30	143.6	0.19	N/A	

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Weston Point, Runcorn 59	Jan	1.51	1.08	1.47	16.19	229	5.46	1.90	45.7	0.00	5.06	37.3	3.57	30.07
	Feb	1.08	0.56	0.31	7.06	67	2.68	1.85	22.3	0.00	2.83	26.0	0.06	23.83
	Mar	0.83	0.21	1.10	7.52	127	3.62	1.04	11.6	0.00	4.09	17.3	1.14	66.78
	Apr	0.58	0.16	1.20	4.76	105	3.38	3.69	9.1	0.00	3.11	12.8	0.86	25.13
	May	0.36	0.15	0.56	6.47	97	2.30	2.93	4.5	0.00	2.11	12.6	0.35	26.39
	Jun	0.29	0.09	1.52	8.48	148	3.29	1.74	6.7	0.00	2.47	13.0	0.20	29.34
	Jul	0.48	0.16	2.25	12.05	177	3.81	3.05	9.9	0.02	7.04	49.8	0.67	38.41
	Aug	0.27	0.12	0.00	5.73	123	2.32	3.99	7.1	0.02	7.99	10.3	7.69	41.96
	Sep	0.89	0.18	1.94	8.60	211	4.10	4.80	8.2	0.00	2.23	21.0	0.61	63.03
	Oct	0.66	0.21	0.92	5.43	117	2.44	1.01	7.6	0.00	1.50	11.5	6.47	44.80
	Nov	0.70	0.20	0.92	11.71	113	2.23	0.73	12.5	0.07	1.49	15.8	1.54	79.51
	Dec	1.14	0.28	1.36	16.25	190	3.76	1.33	17.3	0.03	2.42	26.7	0.78	13.27

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
London Brent 60	Jan	2.36	0.92	5.77	27.03	597	8.33	3.69	40.2	0.12	1.87	28.1	0.11	0.00
	Feb	3.03	1.70	7.93	23.00	333	7.43	6.60	69.4	0.00	2.79	27.2	0.05	1.75
	Mar	3.62	1.69	10.21	35.43	684	13.05	8.11	66.6	0.00	7.34	52.6	0.23	2.12
	Apr	1.27	0.44	3.94	24.31	699	10.66	10.96	15.9	0.00	9.16	33.5	0.32	1.41
	May	0.80	0.20	3.07	19.11	586	7.77	0.39	11.1	0.00	3.84	17.7	0.10	2.27
	Jun	0.47	0.12	4.22	31.81	658	7.89	0.81	8.3	0.00	3.65	18.2	0.15	1.11
	Jul	0.80	0.20	7.32	42.53	918	10.45	3.85	14.3	0.00	3.24	27.2	2.09	0.99
	Aug	1.12	0.24	5.44	29.25	659	7.80	1.27	8.9	0.00	5.79	20.4	1.21	0.11
	Sep	1.16	0.34	1.62	27.83	643	7.40	3.03	10.8	0.02	7.13	22.0	0.16	1.34
	Oct	0.47	0.21	0.00	1.30	314	4.02	0.60	7.1	0.02	1.55	13.4	0.69	0.11
	Nov	0.70	0.20	0.92	11.68	113	2.22	0.73	12.5	0.07	1.48	15.7	1.54	1.78
	Dec	1.13	0.28	1.36	16.20	190	3.75	1.32	17.2	0.03	2.42	26.6	0.78	0.88

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
London Cromwell 61	Jan	0.93	0.39	5.39	42.30	897	8.79	4.94	12.4	0.06	3.58	27.8	0.16	1.64
	Feb	0.80	0.47	4.75	37.14	730	8.17	1.23	12.0	0.00	10.65	26.8	0.09	2.03
	Mar	1.05	0.50	7.98	35.52	756	9.36	8.43	14.3	0.00	15.23	36.4	0.23	1.39
	Apr	1.33	0.76	11.90	50.73	1067	14.83	5.49	20.7	0.00	20.11	50.8	0.34	1.28
	May	0.66	0.10	5.36	33.68	676	7.16	1.48	7.3	0.00	2.94	15.6	0.09	1.36
	Jun	0.74	0.19	5.19	30.07	803	11.22	3.34	13.9	0.00	5.20	23.8	0.24	1.50
	Jul	0.78	0.17	2.36	42.52	738	7.73	1.99	6.5	0.00	3.68	20.5	0.27	1.12
	Aug	0.79	0.20	2.98	35.14	567	6.06	9.02	4.3	0.00	2.08	24.2	0.19	0.68
	Sep	1.26	0.25	3.30	55.37	890	9.13	4.04	4.7	0.00	5.21	27.8	2.85	4.24
	Oct	1.05	0.29	3.66	19.03	1007	9.77	4.40	17.4	0.02	2.76	29.5	0.39	1.08
	Nov	2.48	0.70	8.75	61.94	1014	16.20	6.49	35.5	0.09	2.43	70.1	4.37	1.54
	Dec	1.80	0.35	4.72	58.43	1370	12.36	2.71	26.7	0.07	2.17	38.8	0.47	2.67

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
London Horseferry 62	Jan	2.08	0.82	3.50	15.67	331	4.42	2.94	27.3	0.06	2.63	18.1	0.12	1.24
	Feb	2.41	0.96	4.80	25.37	494	8.36	4.14	40.3	0.00	3.20	34.2	0.08	1.89
	Mar	1.18	0.36	3.95	20.64	589	7.78	2.42	14.8	0.00	2.52	28.5	0.26	1.79
	Apr	0.80	0.52	2.10	9.78	261	7.37	1.33	9.6	0.00	4.70	58.1	0.14	2.70
	May	0.66	0.11	1.82	14.56	380	5.23	1.11	7.4	0.00	3.79	11.8	0.11	1.60
	Jun	0.62	0.17	2.36	21.89	453	6.16	5.44	9.6	0.01	3.41	18.0	0.08	2.64
	Jul	0.89	0.18	1.95	24.59	472	5.97	1.78	8.9	0.02	3.97	24.1	0.06	4.08
	Aug	1.10	0.31	4.16	24.03	514	6.21	6.85	9.7	0.06	6.88	17.2	0.06	3.00
	Sep	1.28	0.25	0.59	26.83	476	6.38	2.99	9.4	0.01	6.28	23.5	0.00	0.15
	Oct	1.60	0.29	1.87	32.39	500	9.01	3.42	20.9	0.02	2.96	44.1	0.40	1.83
	Nov	1.27	0.20	1.30	29.50	349	4.70	0.06	19.0	0.06	1.08	16.2	0.39	5.85
	Dec	1.24	0.29	0.00	23.49	458	5.21	9.21	13.8	0.02	2.88	24.0	0.25	1.66

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		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Leeds 63	Jan	1.10	0.25	3.52	8.51	247	5.42	2.79	14.7	0.01	2.16	27.3	0.09	1.86
	Feb	3.10	1.71	7.22	20.72	391	10.64	6.29	63.9	0.00	4.40	43.2	0.07	1.69
	Mar	0.95	0.25	3.04	7.82	253	8.06	0.55	12.7	0.00	2.79	24.9	0.12	1.19
	Apr	1.06	0.30	3.56	8.03	266	9.32	4.03	14.2	0.00	4.33	25.5	0.15	1.32
	May	0.66	0.15	3.62	6.69	253	8.25	0.86	9.8	0.00	1.81	14.0	0.07	1.07
	Jun	0.52	0.16	0.96	7.78	232	6.75	0.00	10.3	0.00	1.39	17.9	1.54	1.87
	Jul	0.35	0.13	0.05	7.21	202	6.17	2.37	8.5	0.02	9.17	11.9	0.17	0.20
	Aug	0.74	0.21	3.13	8.45	300	6.35	6.05	10.8	0.00	6.84	14.8	0.08	0.48
	Sep	0.97	0.23	8.12	11.19	360	6.81	1.26	10.5	0.00	5.75	24.7	1.99	0.03
	Oct	1.26	0.33	3.27	13.13	353	9.22	3.47	16.5	0.00	1.84	27.2	4.43	2.33
	Nov	1.34	0.35	0.84	19.45	363	10.79	1.85	25.9	0.00	0.73	31.4	1.76	1.60
	Dec	1.75	0.44	2.15	18.53	443	11.54	1.82	20.3	0.03	3.42	29.1	0.29	1.70

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Glasgow 64	Jan	0.41	0.15	2.71	8.38	204	2.73	1.58	8.3	0.31	0.50	20.7	0.14	1.41
	Feb	0.73	0.22	0.92	8.60	212	3.74	0.63	10.7	0.00	0.95	27.3	0.06	1.28
	Mar	0.97	0.15	1.25	10.44	331	5.47	1.46	12.7	0.00	1.45	22.0	0.08	1.15
	Apr	0.55	0.13	1.48	9.79	258	4.39	1.81	5.7	0.00	2.88	15.9	0.12	1.42
	May	0.56	0.36	2.05	7.04	208	3.69	1.96	15.1	0.00	1.03	21.5	0.09	1.35
	Jun	0.38	0.07	0.54	7.23	175	2.91	1.43	6.5	0.00	1.89	18.9	0.02	5.60
	Jul	0.38	0.12	0.29	8.18	184	3.74	1.03	5.9	0.02	2.99	17.5	0.05	3.42
	Aug	0.56	0.19	1.17	7.39	137	2.51	0.09	6.6	0.05	0.74	12.7	0.03	1.22
	Sep	0.65	0.20	0.85	9.77	195	3.56	2.61	9.1	0.05	1.50	14.3	0.03	1.12
	Oct	0.57	0.17	0.52	8.25	384	4.91	3.47	17.7	0.08	1.24	24.7	0.90	0.10
	Nov	2.84	0.43	5.39	27.87	419	6.31	6.02	26.0	0.06	1.50	35.5	0.52	N/A
	Dec	1.13	0.30	2.80	43.78	746	8.51	3.25	30.8	0.02	2.21	41.5	0.40	0.26

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Eskdalemuir 65	Jan	0.00	0.02	5.98	0.00	21	0.36	0.70	0.0	0.02	0.05	1.6	0.33	N/A
	Feb	0.03	0.02	0.10	1.19	8	0.49	0.05	0.5	0.00	1.71	1.3	0.05	1.86
	Mar	0.50	0.41	1.14	2.94	29	1.54	1.07	12.1	0.00	1.71	6.8	0.06	1.31
	Apr	0.35	0.10	0.00	1.03	64	1.24	2.20	1.9	0.00	2.52	5.2	0.08	2.43
	May	0.02	0.04	1.82	0.36	26	0.68	1.65	0.6	0.00	0.64	6.4	0.12	0.94
	Jun	0.13	0.16	8.45	0.60	89	2.23	5.52	1.4	0.03	1.31	9.7	0.06	0.97
	Jul	0.07	0.01	0.18	0.25	15	1.15	0.37	1.3	0.01	1.37	1.0	0.32	0.91
	Aug	0.00	0.01	0.90	0.38	15	0.55	0.56	1.1	0.02	1.19	1.1	0.19	1.38
	Sep	0.06	0.09	8.84	1.59	77	1.06	2.35	3.8	0.00	2.00	6.2	0.11	1.24
	Oct	0.34	0.10	11.48	2.75	47	1.30	2.96	4.2	0.00	1.41	5.7	0.24	1.94
	Nov	0.21	0.05	0.10	0.42	4	0.67	0.10	4.2	0.05	0.49	3.0	0.31	1.27
	Dec	0.11	0.13	0.20	5.51	56	0.76	0.81	3.6	0.09	0.41	4.7	0.43	1.02

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Motherwell 66	Jan	0.91	0.15	1.59	5.31	141	2.85	6.08	7.0	0.00	1.36	15.0	0.44	1.18
	Feb	0.62	0.58	0.84	6.12	319	6.24	2.61	4.6	0.00	2.94	10.8	0.07	2.41
	Mar	0.65	0.13	14.46	5.01	435	7.77	1.27	5.7	0.00	5.65	8.8	0.07	1.95
	Apr	0.33	0.16	3.34	3.83	268	6.05	2.78	4.6	0.00	2.56	10.6	0.11	0.73
	May	0.53	0.15	0.35	6.35	230	6.38	7.39	4.5	0.00	2.93	7.8	0.06	0.47
	Jun	0.34	0.65	0.00	12.39	202	4.04	0.00	3.5	0.00	2.19	6.5	0.11	1.32
	Jul	1.46	0.50	0.00	8.61	164	3.59	1.10	3.6	0.00	1.25	5.5	0.15	0.67
	Aug	0.27	0.08	1.28	6.21	117	2.04	0.56	3.0	0.00	0.69	6.7	0.56	0.16
	Sep	0.18	0.03	1.09	5.13	113	1.76	1.63	3.6	0.01	1.91	3.8	0.15	0.44
	Oct	1.47	0.56	12.68	15.97	408	18.37	11.27	12.6	0.03	3.06	79.0	0.43	1.47
	Nov	2.02	0.24	1.72	12.66	299	4.67	0.68	14.0	0.06	1.02	15.5	0.41	1.57
	Dec	0.93	0.18	2.82	14.08	207	2.49	4.71	14.7	0.06	1.24	13.5	0.41	0.38

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Manchester 67	Jan	0.65	0.16	12.92	25.40	572	5.90	12.13	7.9	0.10	1.53	24.6	0.15	1.13
	Feb	1.13	0.28	3.32	44.33	948	10.72	9.59	14.9	0.00	11.61	37.7	0.07	1.44
	Mar	0.83	0.27	5.48	41.58	1018	12.10	2.00	12.8	0.00	3.67	42.8	0.10	1.64
	Apr	1.07	0.25	4.13	48.06	1073	13.42	2.33	13.9	0.00	3.22	50.9	0.15	1.20
	May	0.55	0.13	3.58	36.15	828	10.09	1.00	9.5	0.00	1.86	27.4	0.18	1.30
	Jun	1.43	0.33	5.48	120.35	2276	28.01	1.09	21.1	0.00	4.02	77.2	0.16	1.19
	Jul	0.70	0.16	3.40	51.19	893	8.99	1.50	6.0	0.00	1.79	31.1	1.72	1.78
	Aug	0.94	0.29	5.71	49.79	856	8.15	1.36	5.6	0.00	1.32	25.8	0.43	0.20
	Sep	1.03	0.17	2.34	53.60	977	8.56	3.77	8.0	0.02	1.02	24.8	0.25	2.01
	Oct	0.79	0.34	2.77	52.64	980	10.09	9.84	11.6	0.02	1.83	29.1	0.19	1.44
	Nov	1.62	1.05	11.42	60.60	705	14.50	0.97	24.2	0.06	0.83	152.7	0.40	1.07
	Dec	1.36	0.30	3.10	52.21	970	9.43	0.80	15.6	0.03	3.35	30.2	0.26	2.12

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		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Cardiff 68	Jan	3.62	1.77	10.61	42.22	744	12.93	1.76	63.1	0.01	2.80	36.2	0.09	2.14
	Feb	0.79	0.26	2.09	29.69	721	10.18	1.76	16.2	0.00	2.93	37.6	0.09	1.72
	Mar	0.90	0.21	3.07	26.74	792	9.53	0.49	14.39	0.00	3.45	35.9	1.93	1.75
	Apr	0.86	0.28	2.95	34.02	856	13.06	1.03	13.4	0.00	3.42	46.5	0.16	1.75
	May	0.68	0.39	3.21	38.80	894	12.30	3.02	13.30	0.00	3.48	47.2	0.00	1.44
	Jun	0.66	0.67	4.05	24.74	666	11.20	0.49	14.4	0.00	2.34	67.2	0.14	1.12
	Jul	0.74	0.21	2.39	45.13	984	17.75	1.32	12.2	0.01	12.87	46.7	4.51	2.06
	Aug	1.08	0.22	5.40	47.78	862	12.61	3.42	8.2	0.07	3.31	29.8	0.98	1.30
	Sep	0.98	0.65	2.15	50.06	923	11.41	2.18	10.0	0.00	2.63	204.8	0.57	1.19
	Oct	1.29	0.35	6.78	81.99	727	13.38	1.12	36.3	0.00	2.93	130.1	4.38	0.07
	Nov	1.90	0.63	1.48	43.81	949	14.37	3.43	31.8	0.00	1.07	108.9	0.89	1.80
	Dec	1.10	0.32	1.89	37.99	883	10.40	2.63	15.7	0.17	1.61	135.4	0.62	1.15

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Brookside Metals 69	Jan	1.00	4.42	5.06	37.64	350	9.24	4.75	81.3	0.05	1.98	844.3	0.19	1.45
	Feb	0.87	0.30	1.55	6.45	143	2.56	0.13	8.6	0.00	2.82	54.3	0.23	2.05
	Mar	1.76	4.08	4.34	73.26	426	13.92	1.65	128.9	0.00	3.45	1315.6	0.18	3.72
	Apr	0.91	1.19	3.33	35.23	303	8.34	0.99	35.5	0.00	2.97	754.7	0.16	2.00
	May	1.42	5.31	4.88	60.93	279	8.99	8.46	163.4	0.00	1.58	1165.1	0.10	1.79
	Jun	0.78	1.03	1.33	25.08	330	5.55	1.70	41.0	0.00	2.39	142.7	0.08	1.83
	Jul	0.45	1.92	3.86	27.87	1108	6.78	5.83	25.9	0.05	10.09	304.0	0.09	2.04
	Aug	0.71	0.92	3.02	31.88	341	5.15	4.03	25.7	0.05	10.51	155.3	0.06	0.84
	Sep	0.86	4.95	4.39	94.65	391	11.30	9.10	56.2	0.00	6.14	723.1	0.10	0.21
	Oct	2.68	4.83	4.74	59.64	430	11.13	7.42	82.4	0.00	3.05	603.5	3.45	2.15
	Nov	1.82	7.68	2.76	79.20	231	9.22	13.81	185.1	0.03	0.63	1592.7	0.40	2.17
	Dec	1.83	3.32	2.65	45.86	424	9.89	8.18	81.6	0.02	3.34	639.0	0.23	2.01

		Concentration ng.m ⁻³												
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg	Hg Vap
Newcastle 70	Jan	0.79	0.24	0.96	15.25	113	2.79	3.67	6.9	0.07	2.98	11.5	0.09	0.55
	Feb	0.46	0.11	0.79	4.45	137	2.97	0.00	7.0	0.00	4.11	11.2	0.08	2.02
	Mar	0.67	0.23	1.72	6.47	204	5.11	1.49	10.9	0.00	2.85	28.0	0.17	5.24
	Apr	0.86	0.21	1.73	7.64	228	6.23	3.19	8.8	0.00	3.21	29.5	0.40	2.22
	May	0.35	0.56	0.16	3.69	113	3.33	0.00	8.3	0.00	1.44	27.6	0.00	1.79
	Jun	0.33	0.17	0.69	5.80	125	3.15	0.21	5.7	0.00	1.23	19.8	0.18	1.73
	Jul	0.28	0.10	2.29	6.94	187	3.98	5.98	4.4	0.00	1.52	15.1	0.11	2.32
	Aug	0.71	0.19	0.99	6.70	157	2.95	2.51	6.5	0.00	3.63	12.8	2.03	1.20
	Sep	0.74	0.10	5.50	7.70	194	3.95	4.39	6.5	0.02	2.47	14.5	1.30	1.09
	Oct	0.89	0.21	0.88	10.45	267	5.23	4.56	9.1	0.02	2.16	25.5	3.95	0.46
	Nov	1.26	0.35	2.01	14.65	213	5.09	2.43	19.1	0.06	1.31	23.2	2.60	1.23
	Dec	1.64	0.36	4.73	16.90	427	8.17	4.59	16.4	0.09	2.19	30.1	0.12	1.49