

Report

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

Annual Report for 2004 on the UK Heavy Metals Network

Richard J. C. Brown Neil J. Harrison Andrew S. Brown Rachel E. Yardley Dharsheni Velummylum

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Our vision for NPL is to be the National Measurement Institute that delivers the highest economic and social impact, through excellent and responsive science.

We will deliver this through:

- Excellence in science
- Increased exploitation of that science to boost UK competitiveness and quality of life
- Integrity and independence as a national asset
- Enhanced international standing

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Quality of Life Division

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National Physical Laboratory Hampton 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 2004 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 2004 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 2004.

In summary, during 2004:

- No levels above the First Daughter Directive Lower Assessment Threshold for lead were recorded.
- Two exceedences of the Fourth Daughter Directive Limit Value for Nickel were recorded.
- One level above the Fourth Daughter Directive Upper Assessment Threshold for cadmium was recorded.
- No levels above the Fourth Daughter Directive Lower Assessment Threshold for arsenic were recorded.
- Measured levels of mercury across the Network remain low.
- The downward trend in annual concentration values has continued. Values for platinum and particulate phase mercury have increased slightly after September, most probably owing to a more rigorous digestion procedure employed by NPL, as compared to the previous contractor.
- From September, NPL provided a total of 56 extra measurement results per week, for elements not previously measured at 6 sites, 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 90% for the year (with NPL achieving 96% from October to December).

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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.

During 2004 the contractor operating the UK Heavy Metals Network, on behalf of Defra, changed. From January to August, Casella Stanger operated the Network. September was the handover month, during which, Casella Stanger gradually handed over all Network responsibilities to the National Physical Laboratory. From October to December, the National Physical Laboratory operated the Network.

This is the Annual Summary Report for the UK Heavy Metals Network for 2004 and contains:

- A summary of Network Operation (from NPL's period of management, September 2004-)
- 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

This report follows NPL's recent Network Compliance Report (December 2004), which fully assessed the current state of the UK Metals Network with respect to the requirements of the First Daughter Air Quality Directive (1st DD) (for Lead) and the proposed Fourth Daughter Air Quality Directive (4th DD) (for Nickel, Arsenic, Cadmium and Mercury) for the relevant heavy metal target analytes.

Network Operation

Overview

NPL took over operation of the UK Heavy Metals Network from Casella Stanger in September 2004. The first quarter of NPL's management of the Heavy Metals Network encompassed a great deal of activity:

- A generally smooth handover from the previous contractors during September and part of October.
- NPL renewed all LSO contracts with the exception of Brent where NPL has taken over as LSO.
- NPL issued a 6-month extension to the Equipment Support Unit (ESU) contract.
- 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, assessment of LSOs' procedures, improvements to Network operation in several cases.
- NPL produced updated procedure manuals that were distributed to all LSOs.
- NPL introduced filter field blanks into the operation of the Network to ensure the robustness of measurement results.
- NPL produced a report assessing the compliance of the Network with the First and Fourth Daughter Air Quality Directive, and the current operating state of the Network. This was delivered to Defra in December 2004.
- NPL expanded the analysis of Network samples to include all metals at all sites.

Site audits

Since Network handover on 1st September 2004 NPL has 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:

- Assessed each site against the micro-scale siting requirements of the Fourth DD;
- Audited the procedures of the LSO on-site;
- 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).

During the site audits, some deficiencies in Network Operation and current LSO procedures were discovered which were corrected by NPL's site auditors. When instruments were found to be faulty at the audit, NPL staff attempted to repair them. If the repair was not possible then the ESU was called out.

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

- In 6 out of the 17 sites NPL auditors were able to make minor on-the-spot improvements to Network operation, such as: correcting LSOs' procedures for measuring flow, or cleaning of the samplers.
- In 4 cases NPL auditors were able to make significant improvements to Network Operation, such as: identifying and acting on health and safety issues, identifying faulty equipment and requesting a service visit, or providing vital measuring equipment that was previously missing.
- The majority of sites reported never having received an audit visit previously, or having received routine service visits, during the previous contract.

Equipment failures and servicing

During the first quarter of NPL's operation of the Network, the sites at Glasgow, Motherwell, Leeds, London (Brent), London (Horseferry Road) and Sheffield have received routine service visits from the ESU.

Additionally, during this period, NPL has called-out the ESU to deal with sampler failures at Runcorn (twice), Brent, Leeds and Manchester (three times) as a result of low flows being reported by NPL site auditors or LSOs. Notwithstanding this the Network has functioned well during the last quarter.

NPL has agreed with Defra 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.

LSOs and ESU

NPL has renewed all LSO contracts, with the exception of Brent, where NPL has taken over as LSO.

NPL has issued a 6-month contract extension to the current ESU contractor. NPL is currently in the process of arranging a new ESU contract after this period by means of competitive tender.

Siting problems at Newcastle

As a result of revised health and safety procedures, the current ESU deem that the Newcastle site is currently unsafe to service. As a result, no service visits or emergency callouts will be made to Newcastle until this situation is resolved. Any future equipment failures will, therefore, severely affect time coverage at this site.

NPL have made Defra aware of this situation. NPL judge that it is not possible or practical to make the required safety reparations to the current site. The land-owners at the current site have already stated that they do not want the sampler sited at ground level near to its current position. A siting change is required. Therefore NPL are proposing re-installing the sampler at a different site, possible in the city centre.

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 PM_{10} heads) operating at a calibrated flow rate of $1m^3.h^{-1}$ Samples were taken for a period of one week onto 47 mm diameter GN Metricel 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.

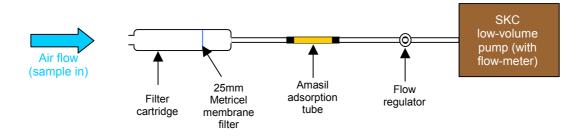


Figure 1. Schematic diagram of vapour-phase mercy sampling apparatus. The 25 mm diameter filter was used to trap any particulate material

Analytical Methodology: Particulate-phase metals

Analysis for particulate-phase metals took place in-house at NPL using a PerkinElmer Elan 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

The limits of detection achieved at NPL in November 2004 using UKAS-accredited ICP-MS methods in are shown in Table 2. The solution limits of detection were calculated using the method outlined in PrEN14902, 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) respectively.

	Limit of Detection			
Analyte	Solution (ng.g ⁻¹)	Filter (ng)	Air (ng.m⁻³)	
As	0.081	4.3	0.026	
Cd	0.003	0.003 0.16		
Cr	0.077	4.1	0.024	
Cu	0.068	0.068 3.6		
Fe	0.99	52	0.31	
Mn	0.009	0.48	0.0028	
Ni	0.033	1.7	0.010	
Pb	0.037	2.0	0.012	
Pt	0.004	0.21	0.0013	
V	0.007	0.37	0.0022	
Zn	0.20	11	0.063	
Hg	0.035	1.9	0.011	

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:

- Dispatch and analysis of one filed blank filter and one blank adsorption tube per site per four months.
- Thorough checks of the filters and adsorption tubes and before despatch 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.
- 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.

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. This will be discussed in future by NPL if a clarification of what is meant by a single measurement is obtained.

	Expanded relative uncertainty		
Analyte	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 permissibleuncertainty 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.

NPL are currently considering, in collaboration with DG Environment, whether the uncertainties mentioned above are applicable to the annual mean values.

Network data

Data capture

Data capture across the entire Network during 2004 is displayed in the table below:

Data	Jan-Sept (Casella Stanger)	Oct-Dec (NPL)	Overall 2004
capture	88%	96%	90%

Table 4. Data capture across the UK Heavy Metals Network during 2004

Data processing

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.

Uncertainty

Since the data capture across the Network has been so 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:

	Expanded Relative Uncertainty	
Analyte	Annual Mean	Daughter Directive maximum
As	31%	40%
Cd	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	2004 Annual Mean Concentration / ng.m ⁻³
As	1.12
Cd	0.65
Cr	6.76
Cu	20.8
Fe	463
Mn	10.0
Ni	5.38
Pb	24.7
Pt	<0.06
v	2.12
Zn	105
Hg (part)	0.71
Hg (vap)	3.70

Table 6. 2004 annual mean concentrations averaged over all site on the UKHeavy Metals Network.

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

46 47 49 56 58 59 60 61 62 63 64 1.54 1.01* 0.77* 1.53 1.67 0.81* 1.53 1.15 1.38 1.05 0.82 0.89 0.71 0.28* 1.44 0.67 0.24* 0.33 0.29 0.26 0.21 0.18 2.86* 1.92* 1.78* 60.1* 4.06* 4.90 5.68 4.31 3.20 2.36 18.7* 8.46* 5.09* 6.63* 20.1* 13.7* 30.1 46.3 20.8 9.71 10.5 338* 258* 114* 280* 649* 216* 870 987 598 312 294 12.3* 6.83* 20.1* 13.7* 30.1 46.3 20.8 4.33 2.12 10.5 10.5 294 12.3* 258* 11.3 13.7 30.1 46.3 20.8 312 294			2004 Annua	_	ean Cor	ncentrat	Mean Concentration / ng.m ⁻³	l.m ⁻³						
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2.86* 1.92* 1.29* 1.78* 60.1* 4.06* 4.90 5.68 4.31 3.20 2.36 18.7* 8.46* 5.09* 6.63* 20.1* 13.7* 30.1 46.3 20.8 9.71 10.5 338* 258* 114* 280* 649* 216* 870 987 598 312 294 12.3* 6.83* 4.33* 7.60* 47.1* 4.53* 11.3 10.4 7.20 8.10 4.33 12.3* 6.83* 4.33* 7.60* 47.1* 4.53* 11.3 10.4 7.20 8.10 4.33 12.3* 6.83* 4.33* 7.60* 47.1* 4.53* 11.3 10.4 7.20 8.10 4.33 2.02 11.75* 33.8 2.12 20.5 8.73* 4.26 2.97 1.90 1.93 13.7 2.010* 0.06* 0.05* 0.07* 0.16* 3.18 19.5 16.8 1.31 13.7 32.4 25.5* 18.8* 19.5 16.8 <th>0.71 0.28*</th> <th></th> <th>0.24*</th> <th>0.33</th> <th>0.29</th> <th>0.26</th> <th>0.21</th> <th>0.18</th> <th>0.04</th> <th>0.14</th> <th>0.21</th> <th>0.27</th> <th>4.72</th> <th>0.21</th>	0.71 0.28*		0.24*	0.33	0.29	0.26	0.21	0.18	0.04	0.14	0.21	0.27	4.72	0.21
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338* 258* 114* 280* 649* 216* 870 987 598 312 294 12.3* 6.83* 4.33* 7.60* 47.1* 4.53* 11.3 10.4 7.20 8.10 4.33 2.02 1.75* 33.8 7.60* 47.1* 4.53* 11.3 10.4 7.20 8.10 4.33 2.02 1.75* 33.8 2.12 20.5 8.73* 4.26 2.97 1.90 0.98 1.31 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 1.31 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 1.31 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 1.31 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 1.7.3 13.7 1.41* 3.13* 1.28* 2.51* 2.95* 3.45 3.89 1.67 1.29 1.41* <t< th=""><th>8.46* 5.09*</th><th></th><th></th><th>30.1</th><th>46.3</th><th>20.8</th><th>9.71</th><th>10.5</th><th>0.53</th><th>6.50</th><th>45.6</th><th>41.3</th><th>61.0</th><th>7.57</th></t<>	8.46* 5.09*			30.1	46.3	20.8	9.71	10.5	0.53	6.50	45.6	41.3	61.0	7.57
12.3* 6.83* 4.33* 7.60* 47.1* 4.53* 11.3 10.4 7.20 8.10 4.33 2.02 1.75* 33.8 2.12 20.5 8.73* 4.26 2.97 1.90 0.98 1.31 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 15.0 14.3 13.7 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 15.0 14.3 13.7 0.10* 0.06* 0.05* 0.07* 0.16* <0.07 <0.06 <0.07 <0.06 <0.07 14.3 13.7 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.55* 51.6* 161* 2.55* 34.8 34.2 27.9 35.9 1.08* 114* 3.90*	258* 114*		216*	870	987	598	312	294	23.8	218	966	1013	438	289
2.02 1.75* 33.8 2.12 20.5 8.73* 4.26 2.97 1.90 0.98 1.31 32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 15.0 14.3 13.7 0.10* 0.06* 0.05* 0.07* 0.16* <0.07 <0.06 <0.05 14.3 13.7 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 108* 114* 15.5* 51.6* 161* 2.55* 34.8 34.2 27.9 35.9 0.38 0.61* 0.11* 3.90* 2.13* 2.56 0.48 0.27 0.06 0.04 0.02 0.38 0.61* 0.11* 3.90* 2.13* 2	6.83* 4.33*			11.3	10.4	7.20	8.10	4.33	0.69	3.67	10.2	13.5	12.4	5.84
32.4 25.5* 16.8* 44.6 33.8 18.8* 19.5 16.8 15.0 14.3 13.7 0.10* 0.06* 0.05* 0.03* 0.07* 0.16* <0.07 <0.06 <0.07 <0.05 <0.04 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.08* 114* 15.5* 51.6* 161* 2.55* 34.8 34.2 27.9 35.9 0.38 0.61* 0.11* 3.90* 2.13* 2.56* 34.8 0.27 0.06 0.04 0.02 0.34 0.61* 0.11* 3.90* 2.13* 2.56 7.40 7.84 7.83 7.83 7.83 7.83 7.83 7.83 7.83 7.83 <	1.75* 33.8		8.73*	4.26	2.97	1.90	0.98	1.31	1.77	0.70	1.51	2.70	2.51	1.84
0.10* 0.06* 0.05* 0.07* 0.16* <0.07 <0.06 <0.05 <0.05 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 1.29 108* 114* 15.5* 51.6* 161* 25.5* 34.8 34.2 27.9 35.9 0.38 0.61* 0.11* 3.90* 2.13* 2.58 0.48 0.27 0.06 0.04 0.02 0.38 0.61* 0.11* 3.90* 2.13* 2.58 0.48 0.27 0.06 0.04 0.02	25.5* 16.8*		18.8*	19.5	16.8	15.0	14.3	13.7	2.23	8.38	15.6	17.04	106	19.4
1.41* 3.13* 1.28* 2.51* 2.92* 1.71* 3.89 3.45 3.89 1.67 108* 114* 15.5* 51.6* 161* 25.5* 34.8 34.2 27.2 27.9 0.38 0.61* 0.11* 3.90* 2.13* 2.58 0.48 0.27 0.06 0.04 2.44 0.11* 3.90* 2.13* 2.58 0.48 0.27 0.06 0.04	0.06* 0.05*			<0.07	<0.06	<0.07	<0.05	<0.04	<0.02	<0.03	<0.06	<0.06	<0.02	<0.04
108* 114* 15.5* 51.6* 161* 25.5* 34.8 34.2 27.2 27.9 0.38 0.61* 0.11* 3.90* 2.13* 2.58 0.48 0.27 0.06 0.04 2.44 0.74 0.74 0.74 0.74 1.83	3.13* 1.28*			3.89	3.45	3.89	1.67	1.29	0.62	0.91	1.83	1.83	1.68	2.00
0.38 0.61* 0.11* 3.90* 2.13* 2.58 0.48 0.27 0.06 0.04	114* 15.5*		25.5*	34.8	34.2	27.2	27.9	35.9	4.83	17.0	38.8	52.1	1018	25.5
2 11 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	0.61* 0.11*			0.48	0.27	0.06	0.04	0.02	0.06	0.03	0.35	0.20	0.16	0.65
	4	1	23.5	2.49	1.84	2.34	1.83	2.53	2.40	0.44	1.81	2.34	1.86	2.33

Table 7. 2004 annual mean concentrations measured at individual sites on the UK Heavy Metals Network. (A list of site code identifiers can be found in Annex 1). The asterisks indicate that measurements were only taken from September onwards.

These values include measurements for additional elements at sites, 46, 47, 49, 56, 58 and 59 from September, when NPL took over responsibility for the analysis of samples. The monthly measured metals concentrations from all Network sites are summarised in the tables in Annex 4.

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:

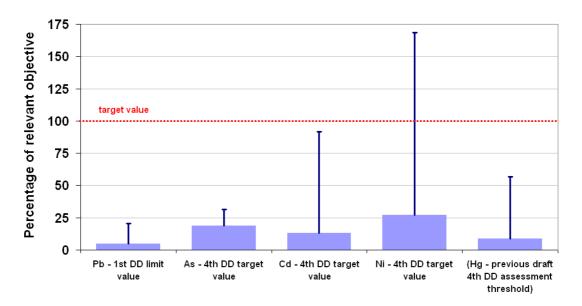


Figure 2. A summary of the annual mean measured concentrations of the heavy metals relevant to the First and Fourth Daughter Directives on the UK Heavy Metals Network in 2004 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the 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. For only one element, Nickel, does the highest annual average at an individual site exceed the target value.

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

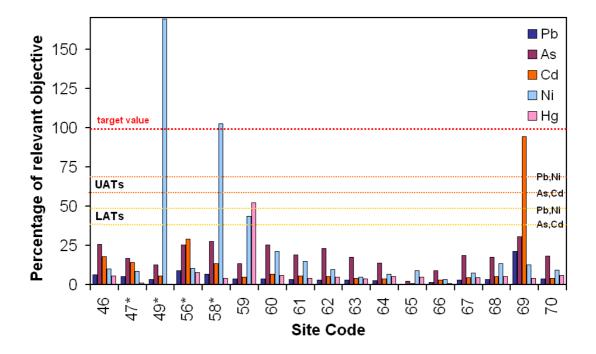


Figure 3. A summary of the annual mean measured concentrations of the heavy metals relevant to the 1st and 4th Daughter Directives (DD) at all site on the UK Heavy Metals Network in 2004 as a percentage of the relevant target values, lower assessment thresholds (LAT) and upper assessment thresholds (UAT). 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 arsenic, cadmium and lead are found at site 69 (Brookside Metals, Walsall). 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 Target Value:

- Nickel at Site 49 (INCO Europe, Swansea): 169% of the target value.
- Nickel at Site 58 (Avesta Steel, Sheffield): 102% of the target value.

Annual Mean Concentrations above the Upper Assessment Threshold:

• Cadmium at Site 69 (Brookside Metals, Walsall): 94% 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.

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.

The macroscale siting requirements of the First and Fourth Daughter Directive, with relevance to the monitoring of industrial sources, require that site selection should fulfil several criteria:

- sampling points should provide data on areas within zones and agglomerations where the population is likely to be directly or indirectly exposed to the highest concentrations averaged over a calendar year
- sampling points should be chosen so as to avoid measuring very small microenvironments in their immediate vicinity
- where contributions from industrial sources are to be assessed, at least one sampling point shall be installed downwind of the source in the nearest residential area

These three monitoring sites where exceedences have been recorded during 2004 may be unnecessarily close to the direct industrial process emissions that they are monitoring and therefore these sites maybe measuring very small microenvironments. Consequently the metals concentrations at these sites may be disproportionately high. The macroscale siting requirements of the Daughter Directive would be more closely followed if the sites were located further away from the industrial plants in question, within the nearest agglomerations. This would provide data more representative of population exposure, and may well decrease measured concentration values.

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 24 years are shown in the table below:

	Changes	in measured c	in measured concentrations during the:		
Analyte	Last 24 Years	Last 10 Years	Last 5 Years Last Yea		
As	not measured	not measured	not measured	-30.6%	
Cd	-75.3%	-30.2%	-17.3%	-33.9%	
Cr	-30.3%	+240%	+117%	+50.4%	
Cu	-21.9%	-22.4%	0.0%	-20.9%	
Fe	-54.8%	-35.8%	-33.0%	-20.0%	
Hg (part)	not measured	not measured	not measured	+287%	
Hg (vap)	not measured	not measured	not measured	-67.6%	
Mn	-62.1%	-17.2%	-4.6%	+11.8%	
Ni	-51.1%	-11.3%	+17.3%	+20.9%	
Pt	not measured	not measured	not measured	0.0%	
v	-89.4%	-73.2%	-37.7%	-23.1%	
Zn	-46.6%	+77.7%	+144.0%	+0.1%	
Pb	-95.6%	-90.0%	-87.2%	-31.4%	

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:

In only the second year of widespread **arsenic** measurement, the concentrations have fallen with respect to the 2003 value, and remain low across the whole network.

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

Chromium concentrations have shown an increase on the 2003 value. This is in part due to high concentrations being recorded at sites where, until September, only Fourth Daughter Directive species were measured, e.g. Sheffield. However, overall concentrations remain low and down over 50% from the maximum recorded value in 2001.

Copper concentrations remain low and have shown a tendency to decrease slowly with time.

Iron concentrations have continued to fall across the Network and have almost halved since 1980. However, iron still accounts for over 70% of the total mass of all metals measured across the Network in 2004.

Mercury has only been measured across the Network for two years and therefore the deduction of trends is difficult. Particulate phase mercury concentrations increased in 2004 but still remain very low across the Network. There was an increase in recorded values at industrial locations after September. After noticing this increase, extensive in-house checks and validation procedures were carried out to ensure the validity of the data, including a review of the available literature on digestion procedures for particulate bound mercury. This investigation, and further method validation by the repeated digestion of certified reference materials, showed that NPL's data were robust. This suggests that the previous contractor may not have been using the correct methodology to extract all particulate bound mercury prior to this date. Data from 2005 will confirm whether this is the case.

Vapour phase mercury decreased in 2004. The average value across the Network would decrease by a further 40% if the very high values recorded at Runcorn were excluded. Vapour phase mercury accounts for 95% of the total mercury measured across the Network.

Manganese values showed a slight increase in 2004, probably owing to the relatively high levels at sites where, until September, only Fourth Daughter Directive species were measured, e.g. Sheffield.

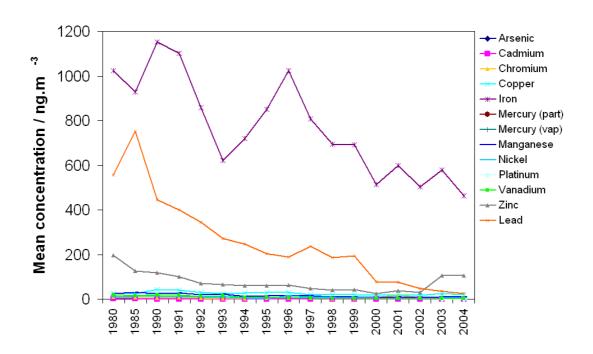
Nickel values rose slightly in 2004 but still remain very low across the Network, except at the sites in Swansea (where the measured concentration doubled in 2004) and Sheffield. Relatively high values have also been recorded at the site in Runcorn since monitoring for nickel began there in September.

Platinum values remain extremely low across all Network sites, although increased values since September indicate that the previous contractor may not have been using the correct methodology to extract all particulate bound platinum prior to this date. Additionally, improved detection limits for the measurement of platinum, since NPL took over analysis of Network samples, means that it has been possible to report low level Pt concentrations more accurately; instead of using: "*limit of detection*".

Vanadium values continue to decrease and remain very low across the entire Network.

Zinc values have remained constant in 2004 despite relatively high levels at sites where, until September, only Fourth Daughter Directive species were measured, e.g. Sheffield. However, average levels are higher than 10 years ago following a sharp increase in measured concentration during 2003.

Lead concentrations continue to fall across the whole Network year upon year. This trend continued with a 34% decrease in 2004. The only measured concentration above 50 ng.m⁻³ (10% of the First Daughter Directive Limit Value) in the Network was at Brookside Metals (106 ng.m⁻³)



Concentration trends over the last 24 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 24 years.

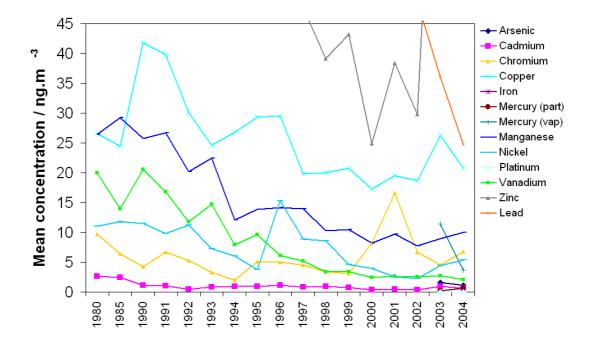


Figure 5. The annual mean concentration of metals measured on the UK Heavy Metals Network over the last 24 years – enlarged to elucidate trends at lower concentrations.

Mercury vapour to particulate concentration ratio

The ratio of the vapour phase mercury concentration to the particulate phase mercury concentrations, at Network sites where both are measured, is usually very high. The calculated values are displayed in the graph below:

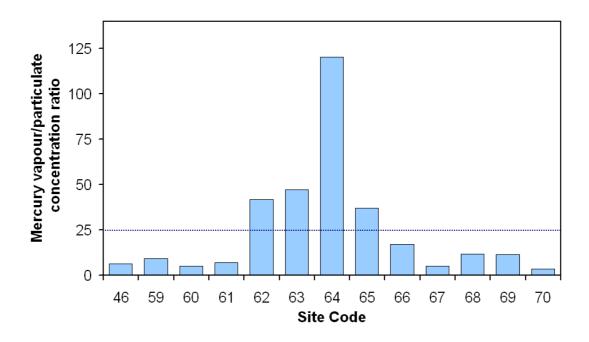


Figure 6. The average vapour phase mercury to particulate phase mercury concentration ratios during 2004, at sites where both quantities are measured. The dotted blue line represents the average vapour phase mercury to particulate phase mercury concentration ratio across the entire Network.

The average mercury vapour to particulate concentration ratio is about 25, but ranges between 4 (at the Newcastle site) and 120 (at the Glasgow site).

The distribution of the ratios seems, where, until September, only Fourth Daughter Directive species were measured, empirically, to fall into two categories: Low (0-15); and High (>15). Sites in the 'Low' category all have 'Roadside' or 'Industrial Background' classifications. Sites in the 'High' category all have 'Urban Background or 'Rural' classifications. This observation suggests different sources of local mercury emission are associated with the different site classifications, or that chemical conversions take place with time.

At sites where both quantities are measured, vapour phase concentrations account for over 95% of the total ambient mercury concentrations.



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

Sito Codo	Sito Addrace	Site	Dollistante
		Classification	
46: IMI Refiners Ltd,	74 Primley Avenue, Walsall, WS2 9UW	Industrial	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Walsall		Backaround	Mn. Ni, Pb, Pt, V, Zn
47: BZL Ltd, Avonmouth	Avonmouth Medical Centre, Collins Street, Bristol,	Industrial	As, Cd, Cr, Cu, Fe, Hg[Part], Mn,
	BS11 9JJ	Background	Ni. Pb. Pt. V. Zn
49: INCO Europe,	Glais Primary School, School Road, Glais, Swansea,	Industrial	As, Cd, Cr, Cu, Fe, Hg[Part], Mn,
Swansea	SA7 9EY	Background	Ni, Pb, Pt, V, Zn
56: BZL Ltd, Avonmouth	West Country Caravans Ltd., Moorhouse Lane,	Background	As, Cd, Cr, Cu, Fe, Hg[Part], Mn,
(Hallen Village)	Hallen, Bristol, BS10 7RU		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,	Weston Point County Primary School, Caster Avenue,	Background	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Runcorn	Weston Point, Runcorn, WA7 4EQ		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	Mortuary Car Park, Horseferry Road, London	Urban	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Road		Background	Mn, Ni, Pb, Pt, V, Zn
63: Leeds, Old Market	Old Market Building, Vicar Lane, Leeds, LS11	Urban	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Buildings		Background	Mn, Ni, Pb, Pt, V, Zn
64: Glasgow, St Annes	St Annes Primary School, 37 David Street, Glasgow,	Urban	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Primary School	G40 2UN	Background	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	Civic Centre	Urban	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Centre		Background	Mn, Ni, Pb, Pt, V, Zn
67: Manchester M56,	Junction 4, M56, Newhall Green, Wythenshaw,	Roadside	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Junction 4	Manchester		Mn, Ni, Pb, Pt, V, Zn
68: Cardiff, Waungron	Cleansing Depot, Waungron, Fairwater, Cardiff, CF5	Roadside	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Road	2JJ		Mn, Ni, Pb, Pt, V, Zn
69: Brookside Metals,	Adult Training Centre, Bilston Lane, Shepwell Green, Willenhall, Walsall	Industrial	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Bilston Lane		Background	Mn, Ni, Pb, Pt, V, Zn
70: Elswick 6, Newcastle	Telewest Arena, Arena Way, Newcastle Upon Tyne	Industrial	As, Cd, Cr, Cu, Fe, Hg[Vap + Part],
Upon Tyne		Background	Mn, Ni, Pb, Pt, V, Zn

Site Name	Site Number	Mean Volumetric Flow (l.min ⁻¹)	Difference from Set Point (16.67 l.min ⁻¹), %
BZL Avonmouth	47	17.44	4.6
INCO Europe	49	16.56	-0.6
BZL Hallen Village	56	16.50	-1.0
Avesta Steel	58	16.93	1.6
ICI Weston Point ¹	59	14.28	-14.4
London Brent	60	16.08	-3.6
Cromwell Road	61	15.94	-4.4
Horseferry Road	62	15.97	-4.2
Leeds Old Market Buildings	63	16.49	-1.1
Manchester M56 ¹	67	15.57	-6.6
Cardiff, Waungron Road	68	17.46	4.8
IMI Refiners Ltd, Walsall	46	16.56	-0.6
Brookside Metals, Bilston Lane	69	16.74	0.4
Eskdalemuir	65	16.65	-0.1
Glasgow, St Anne's	64	16.65	-0.1
Elswick 6, Newcastle Upon Tyne	70	17.26	3.5
Motherwell, Civic Centre	66	16.41	-1.5

Annex 2 - Results of Particulate Metal Samplers Flow Audits

¹ Partisol found to be leaking

Site Name	Site Number	Set Point, ml.min ⁻¹	Mean Volumetric Flow, ml.min ⁻¹	Difference from Set Point, %
ICI Weston Point	59	80	89.6	+12.1
London Brent	60	98	111.5	+13.8
Cromwell Road	61	98	109.5	+11.7
Horseferry Road	62	100	101.3	+1.3
Leeds Old Market Buildings	63	98	117.0	+19.4
Manchester M56	67	100	133.5	+33.5
Cardiff, Waungron Road	68	110	110.9	+0.9
IMI Refiners Ltd, Walsall	46	100	105.1	+5.1
Brookside Metals, Bilston Lane	69	100	107.6	+7.6
Eskdalemuir	65	120	121.4	+1.2
Glasgow, St Anne's	64	100	144.1	+44.1
Elswick 6, Newcastle Upon Tyne	70	100	120.9	+20.9
Motherwell, Civic Centre ²	66	As found, no rotameter	335.7	+235
Motherwell, Civic Centre	66	100	131.8	+31.8

Annex 3 - Results of Mercury Vapour Phase Flow Audits

² Set point of 100 is assumed for calculation

Annex 4 – Average monthly measured metals concentrations at all Network sites

							Conce	ntratior	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
IMI Refiners, Walsall														
46	Jan	1.88	0.95					1.53	44.43				0.07	1.71
	Feb	1.68	0.84					1.53	41.37				0.07	2.28
	Mar	3.16	1.03					2.99	49.03				0.10	2.19
	Apr	2.19	2.98					2.65	29.97				0.08	2.47
	May	1.28	0.56					1.40	23.49				0.03	3.33
	Jun	0.81	0.67					1.13	25.68				0.03	1.33
	Jul	0.99	0.92					1.01	45.19				0.05	2.38
	Aug	1.61	0.64					1.51	26.84				0.07	5.71
	Sep	1.10	0.48	2.82	14.04	390	17.32	0.92	20.62	0.001	1.51	116.7	0.02	2.93
	Oct	1.67	0.49	3.14	15.40	441	14.10	3.47	25.89	0.043	1.62	115.6	4.09	1.87
	Nov	1.32	0.91	4.65	39.89	327	12.22	2.40	44.59	0.140	1.52	153.0	0.00	1.46
	Dec	0.83	0.25	0.83	5.36	194	5.37	3.67	11.85	0.218	1.00	46.6	0.00	1.57
	Yearly Average	1.54	0.89	2.86	18.67	338	12.25	2.02	32.41	0.100	1.41	108.0	0.38	2.44

							Conce	ntration	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
BZL Ltd., Avonmouth														· ·
47	Jan		0.29											N/A
	Feb		1.61											N/A
	Mar		0.86											N/A
	Apr		0.70											N/A
	May		0.86											N/A
	Jun		0.35											N/A
	Jul		1.17											N/A
	Aug		0.61											N/A
	Sep	0.60	0.27	1.63	3.32	255	6.64	1.54	13.80	0.002	4.85	35.7	0.10	N/A
	Oct	1.13	0.55	1.58	4.60	229	5.13	1.39	19.69	0.001	3.97	35.1	0.62	N/A
	Nov	1.05	0.15	1.79	5.00	168	3.68	1.43	18.22	0.025	2.30	39.0	0.14	N/A
	Dec	1.25	1.05	2.69	20.91	381	11.86	2.64	50.31	0.194	1.40	345.6	1.58	N/A
	Yearly Average	1.01	0.71	1.92	8.46	258	6.83	1.75	25.50	0.055	3.13	113.8	0.61	

							Conce	ntration	ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Swansea														
49	Jan							22.73						N/A
	Feb							25.47						N/A
	Mar							26.65						N/A
	Apr							36.68						N/A
	May							52.67						N/A
	Jun							54.91						N/A
	Jul							45.38						N/A
	Aug							35.74						N/A
	Sep	0.41	0.12	0.12	5.41	84	3.26	26.52	5.03	0.003	1.33	4.0	0.05	N/A
	Oct	0.61	0.15	2.77	2.87	103	6.86	20.19	8.94	0.000	1.08	18.6	0.00	N/A
	Nov	0.70	0.14	0.88	5.21	102	1.99	33.98	10.33	0.000	1.08	11.8	0.37	N/A
	Dec	1.36	0.71	1.40	6.88	169	5.18	25.05	42.70	0.180	1.62	28.2	0.00	N/A
	Yearly Average	0.77	0.28	1.29	5.09	114	4.33	33.83	16.75	0.046	1.28	15.6	0.11	

							Conce	ntration	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
BZL Ltd., Hallen Village														· ·
56	Jan	1.70	0.95					1.40	39.87					N/A
	Feb	2.95	1.56					1.84	41.78					N/A
	Mar	1.46	0.55					1.68	27.94					N/A
	Apr	1.31	0.62					2.11	26.08					N/A
	May	1.47	3.80					1.69	88.48					N/A
	Jun	1.44	2.71					2.40	74.77					N/A
	Jul	1.44	3.01					2.17	83.94					N/A
	Aug	1.47	1.92					2.73	53.88					N/A
	Sep	0.76	0.57	1.15	4.10	182	5.23	2.06	21.08	0.000	2.23	39.6	0.10	N/A
	Oct	0.87	1.06	0.91	4.32	152	3.97	0.59	21.14	0.002	1.73	36.1	1.64	N/A
	Nov	2.21	0.29	2.63	8.10	443	10.29	3.67	38.22	0.093	3.53	85.3	6.88	N/A
	Dec	1.30	0.28	2.42	10.01	344	10.91	3.15	17.88	0.005	2.54	47.3	6.96	N/A
	Yearly Average	1.53	1.44	1.78	6.63	280	7.60	2.12	44.59	0.025	2.51	52.1	3.90	

							Conce	ntration	ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Sheffield														1
58	Jan	1.73	0.72					38.20	25.15					N/A
	Feb	1.80	0.72					27.82	29.61					N/A
	Mar	1.76	0.93					16.33	38.87					N/A
	Apr	2.08	0.72					14.22	32.64					N/A
	May	1.58	0.69					10.51	26.88					N/A
	Jun	1.09	0.47					10.78	23.32					N/A
	Jul	1.26	0.83					14.49	47.24					N/A
	Aug	1.14	0.49					15.47	25.01					N/A
	Sep	1.24	0.51	95.42	19.73	674	56.22	32.00	37.12	0.002	2.19	172.1	0.11	N/A
	Oct	1.38	0.86	89.19	17.72	531	65.93	28.08	40.29	0.052	2.09	205.0	0.39	N/A
	Nov	2.78	0.48	21.54	22.30	621	25.41	18.30	49.34	0.000	2.90	140.3	7.63	N/A
	Dec	2.15	0.63	36.43	20.87	770	40.82	19.49	30.31	0.208	4.50	126.5	0.38	N/A
I	Yearly Average	1.67	0.67	60.65	20.15	649	47.10	20.47	33.82	0.065	2.92	161.0	2.13	

							Conce	ntration	ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Weston Point, Runcorn														
59	Jan												0.41	18.75
	Feb												1.38	22.86
	Mar												0.92	33.04
	Apr												0.49	14.11
	May												0.76	14.55
	Jun												0.92	44.46
	Jul												0.44	19.64
	Aug												0.27	19.46
	Sep	0.46	0.20	2.91	11.58	188	4.95	2.34	8.52	0.000	2.00	17.6	0.77	38.04
	Oct	0.71	0.21	1.66	7.73	162	3.80	0.94	19.62	0.095	2.34	23.6	3.89	22.30
	Nov	0.98	0.23	3.34	12.47	258	4.83	12.02	23.07	0.318	1.19	25.0	14.48	11.15
	Dec	1.09	0.31	8.34	23.02	254	4.57	19.60	24.16	0.217	1.29	34.5	6.21	23.05
	Yearly Average	0.81	0.24	4.06	13.70	216	4.53	8.73	18.84	0.158	1.71	25.2	2.58	23.45

	1						Conce	ntration	ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
London Brent														
60	Jan	1.44	0.27	4.64	21.56	559	7.22	1.38	16.74	<0.01	2.41	27.3	0.08	3.87
	Feb	1.68	0.26	5.75	23.52	758	10.51	3.69	15.19	<0.01	3.22	28.0	0.04	4.22
	Mar	1.79	0.43	6.07	29.48	924	12.35	2.64	18.10	<0.01	4.19	41.6	0.05	2.90
	Apr	1.81	0.46	5.42	35.32	1074	15.15	3.85	25.26	<0.04	5.63	54.8	0.03	4.39
	May	1.55	0.39	3.74	26.33	860	12.53	2.57	18.90	<0.04	4.46	36.7	0.02	3.16
	Jun	1.08	0.20	3.45	22.35	788	11.63	1.91	13.10	< 0.03	3.24	24.8	0.02	2.20
	Jul	0.86	0.22	3.31	20.91	604	8.87	1.49	18.79	<0.02	2.89	25.2	0.02	1.32
	Aug	1.26	0.26	3.95	30.25	861	12.34	3.48	18.00	<0.02	6.56	27.7	0.03	1.23
	Sep	1.05	0.22	3.18	29.80	900	11.99	2.32	16.30	0.012	5.59	33.1	0.02	2.78
	Oct	0.91	0.17	7.56	50.66	1114	11.06	2.85	11.80	0.120	2.87	27.3	3.26	1.81
	Nov	2.20	0.43	4.11	27.24	524	6.77	2.17	30.91	0.231	2.54	34.8	0.00	1.80
	Dec	2.72	0.62	7.59	47.53	1470	15.19	22.78	31.14	0.347	3.07	56.6	2.15	0.20
	Yearly Average	1.53	0.33	4.90	30.41	870	11.30	4.26	19.52	<0.07	3.89	34.8	0.48	2.49

							Conce	ntratior	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
London Cromwell	Í													
61	Jan	1.09	0.26	6.24	43.71	947	9.75	1.57	15.61	<0.01	2.22	30.5	0.05	1.79
	Feb	1.45	0.34	6.02	43.58	991	11.06	1.72	18.62	<0.01	2.65	37.5	0.07	2.06
	Mar	1.23	0.42	7.75	52.88	1109	11.88	2.50	18.94	<0.01	4.19	45.1	0.05	2.15
	Apr	1.62	0.53	4.78	49.79	1062	12.20	2.84	21.30	<0.01	4.86	41.6	0.04	1.88
	May	1.13	0.32	4.18	40.55	863	9.99	2.05	14.67	<0.01	3.58	29.9	0.02	1.88
	Jun	0.84	0.17	5.46	47.45	963	9.70	1.68	11.83	<0.01	2.57	27.4	0.02	1.88
	Jul	0.86	0.20	5.04	44.63	921	9.58	2.38	18.00	<0.01	4.70	30.7	0.05	2.24
	Aug	1.06	0.19	3.55	40.42	860	8.23	2.64	13.23	<0.01	5.16	26.8	0.03	1.88
	Sep	0.85	0.16	6.46	58.45	1195	12.14	2.36	13.38	0.014	3.56	37.6	0.05	2.11
	Oct	1.10	0.15	6.72	31.78	768	8.33	7.63	11.43	0.135	2.21	25.0	2.63	1.86
	Nov	0.81	0.22	4.97	42.23	868	8.86	4.00	18.52	0.201	3.34	28.1	0.15	1.34
	Dec	1.76	0.48	7.00	60.41	1296	13.37	4.34	25.81	0.347	2.34	49.9	0.05	1.06
	Yearly Average	1.15	0.29	5.68	46.32	987	10.42	2.97	16.78	<0.06	3.45	34.2	0.27	1.84

	1						Conce	ntratior	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
London Horseferry	İ													i .
62	Jan	1.06	0.14	3.83	15.89	407	4.74	0.93	11.27	<0.01	1.97	23.9	0.05	1.97
	Feb	1.74	0.21	6.03	21.01	693	8.03	2.02	16.04	<0.02	5.34	29.5	0.06	2.27
	Mar	1.48	0.18	5.35	19.65	570	7.03	2.12	13.98	<0.05	4.50	24.6	0.08	-
	Apr	2.01	0.54	3.27	26.03	732	9.97	3.46	21.88	<0.06	6.52	42.4	0.06	2.07
	May	1.15	0.31	4.34	23.18	631	7.26	1.46	15.51	<0.10	3.02	25.3	0.04	2.47
	Jun	0.83	0.15	3.06	19.30	558	6.17	1.43	11.34	<0.04	2.00	17.6	0.05	-
	Jul	0.75	0.16	2.46	18.55	478	5.80	1.45	12.91	<0.03	2.76	21.7	0.04	1.88
	Aug	1.13	0.22	2.28	20.38	547	7.04	3.12	15.17	<0.01	7.26	24.6	0.07	3.36
	Sep	0.53	0.13	3.25	18.23	508	7.23	1.88	11.07	0.004	3.07	20.8	0.03	2.82
	Oct	0.89	0.14	1.67	17.93	414	5.22	0.59	12.42	0.000	2.07	20.1	0.03	1.31
	Nov	1.88	0.33	3.18	29.83	636	7.78	2.21	28.68	0.251	1.81	35.9	0.08	1.97
	Dec	1.96	0.50	2.84	29.78	710	9.57	4.78	29.44	0.238	2.31	51.9	0.13	2.55
	Yearly Average	1.38	0.26	4.31	20.84	598	7.20	1.90	15.00	<0.07	3.89	27.2	0.06	2.34

							Conce	ntratior	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Leeds														· ·
63	Jan	1.27	0.18	4.61	10.66	367	8.17	1.06	15.06	<0.01	1.75	28.5	0.06	1.76
	Feb	1.19	0.24	5.02	10.14	334	9.85	1.18	16.75	<0.02	1.82	34.7	0.07	1.59
	Mar	1.32	0.30	3.56	11.34	346	9.88	1.32	16.63	<0.03	1.95	34.8	0.07	1.76
	Apr	0.99	0.23	2.47	9.88	330	8.96	1.09	14.08	<0.04	1.96	23.3	0.02	1.59
	May	0.75	0.17	1.78	8.12	249	5.86	0.62	11.50	< 0.05	1.26	22.9	0.01	1.76
	Jun	0.75	0.17	1.78	8.12	249	5.86	0.62	11.50	< 0.01	1.26	22.9	0.01	1.34
	Jul	0.79	0.19	2.62	9.38	293	7.50	0.84	13.85	< 0.01	1.27	25.4	0.05	2.18
	Aug	1.07	0.26	2.39	9.45	349	9.65	1.89	15.03	<0.01	3.65	28.2	0.07	2.68
	Sep	0.70	0.22	2.53	11.15	376	11.47	0.93	16.78	0.000	1.02	25.0	0.00	2.57
	Oct	0.64	0.17	2.15	9.92	305	7.60	0.63	14.72	0.000	2.26	23.2	0.00	1.50
	Nov	1.83	0.34	3.04	15.22	343	8.16	0.68	44.08	0.205	1.33	43.6	0.00	1.02
	Dec	2.14	0.61	8.64	23.76	880	20.03	4.35	66.24	0.243	2.53	124.6	0.85	0.09
	Yearly Average	1.05	0.21	3.20	9.71	312	8.10	0.98	14.26	<0.05	1.67	27.8	0.04	1.83

							Conce	ntration	n ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Glasgow														
64	Jan	0.94	0.19	3.08	11.88	235	2.82	0.53	13.98	<0.01	0.64	30.2	0.03	14.16
	Feb	1.60	0.44	5.47	22.40	669	9.83	2.49	22.44	<0.01	2.04	53.1	0.05	-
	Mar	0.63	0.17	4.05	8.04	301	4.81	1.29	8.76	<0.01	1.32	22.9	0.03	0.14
	Apr	0.51	0.15	1.28	6.42	204	2.94	0.63	6.57	<0.01	1.24	19.4	0.03	0.28
	May	0.64	0.11	1.47	8.07	303	5.17	1.02	7.52	<0.01	1.63	19.0	0.02	0.00
	Jun	0.60	0.38	1.28	7.86	186	2.92	0.59	31.04	<0.01	0.95	133.7	0.02	0.00
	Jul	0.45	0.08	1.20	6.75	228	3.34	1.08	7.11	<0.01	0.69	17.3	0.02	4.37
	Aug	0.43	0.07	1.08	6.44	204	3.06	0.89	7.10	<0.01	0.72	17.5	0.02	0.42
	Sep	0.71	0.15	1.62	9.24	254	4.14	1.70	9.19	<0.01	2.32	21.7	0.04	-
	Oct	0.82	0.12	1.35	11.26	293	3.97	0.21	12.43	0.000	0.78	33.1	0.00	3.98
	Nov	1.03	0.12	1.93	14.81	281	4.23	2.33	16.76	0.121	1.29	31.0	0.00	1.97
	Dec	1.54	0.19	4.48	12.27	374	4.73	2.90	21.32	0.240	1.79	32.6	0.00	0.00
	Yearly Average	0.82	0.18	2.36	10.45	294	4.33	1.31	13.68	<0.04	1.29	36.0	0.02	2.53

							Conce	ntration	ng.m ⁻³					
Site	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Eskdalemuir														
65	Jan	0.14	0.01	1.01	0.38	8	0.56	0.19	1.31	<0.01	0.34	2.8	0.01	2.37
	Feb	0.21	0.02	2.67	0.55	17	1.36	0.30	2.74	<0.01	0.68	6.9	0.03	1.98
	Mar	0.28	0.07	3.12	0.74	34	0.95	0.68	4.01	<0.01	1.08	9.7	0.04	2.17
	Apr	0.20	0.04	0.59	0.40	25	0.38	0.17	1.44	<0.01	0.72	2.6	0.02	2.47
	May	0.25	0.05	0.73	0.74	56	1.19	0.30	2.69	<0.01	0.83	4.9	0.02	1.78
	Jun	0.13	0.03	0.71	0.44	26	0.59	0.17	2.13	<0.01	0.67	4.0	0.01	3.76
	Jul	0.11	0.02	1.00	0.44	15	0.27	0.10	1.23	<0.01	0.46	2.5	0.01	1.88
	Aug	0.09	0.02	1.03	0.36	13	0.12	0.04	0.81	<0.01	0.36	2.9	0.01	3.95
	Sep	0.12	0.03	0.38	0.45	23	0.90	0.13	0.79	0.003	0.70	6.2	0.11	2.99
	Oct	0.06	0.05	0.77	1.11	18	0.80	0.54	3.93	0.000	1.29	5.7	0.17	
	Nov	0.02	0.01	0.79	0.00	13	0.34	1.72	2.07	0.000	0.09	1.1	0.00	1.33
	Dec	0.11	0.10	4.96	0.70	37	0.84	16.90	3.65	0.145	0.20	6.8	0.34	1.72
	Yearly Average	0.14	0.04	1.48	0.53	24	0.69	1.77	2.23	<0.02	0.62	4.7	0.06	2.40

Site							Conce	ntratior	n ng.m ⁻³					
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Motherwell														
66	Jan	0.92	0.14	2.75	10.27	291	4.75	0.95	11.73	<0.01	0.88	13.1	0.06	0.00
	Feb	0.85	0.15	1.11	8.35	267	4.01	0.78	14.05	<0.01	1.00	22.1	0.03	0.00
	Mar	0.50	0.12	3.75	7.08	256	4.25	0.47	8.34	<0.01	1.07	19.8	0.03	0.00
	Apr	0.68	0.11	3.74	4.97	231	3.61	0.68	5.22	<0.01	1.11	12.0	0.02	0.00
	May	0.88	0.18	1.84	6.96	256	4.70	0.84	8.10	<0.01	1.30	13.1	0.02	0.00
	Jun	0.53	0.27	1.24	6.57	206	3.38	0.62	17.38	<0.01	0.83	67.0	0.02	0.00
	Jul	0.37	0.06	1.42	6.06	232	3.57	0.78	5.91	<0.01	0.69	9.6	0.02	0.92
	Aug	0.57	0.12	1.50	6.43	236	4.42	0.98	7.95	<0.01	2.11	12.7	0.03	1.46
	Sep	0.12	0.01	0.26	3.04	82	1.65	0.00	2.84	0.000	0.14	2.6	0.00	0.84
	Oct	0.48	0.49	1.58	6.34	220	4.44	0.00	8.42	0.000	0.49	15.8	0.00	0.37
	Nov	0.25	0.00	1.38	6.51	195	2.90	0.91	4.84	0.000	0.76	7.4	0.09	0.80
	Dec	0.40	0.09	1.00	5.36	150	2.34	1.38	5.83	0.292	0.51	9.0	0.00	0.85
l	Yearly Average	0.55	0.14	1.80	6.50	218	3.67	0.70	8.38	<0.03	0.91	17.0	0.03	0.44

Site							Conce	ntratior	n ng.m ⁻³					
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Manchester														
67	Jan	1.16	0.23	5.85	32.67	753	6.99	0.89	26.88	<0.01	1.23	28.9	0.15	1.95
	Feb	1.60	0.29	7.49	53.11	1223	12.78	1.55	19.90	<0.01	2.04	50.3	0.13	2.25
	Mar	1.42	0.28	8.02	51.66	1122	12.48	1.88	16.97	<0.01	2.15	55.2	0.07	2.85
	Apr	1.25	0.23	4.54	48.34	1123	11.63	1.58	14.91	<0.01	2.15	40.8	0.07	2.25
	May	1.31	0.31	5.43	59.58	1160	13.99	2.09	21.99	<0.01	2.19	48.3	0.08	2.55
	Jun	0.76	0.15	3.89	46.70	882	9.53	1.37	12.43	<0.01	1.52	32.4	0.04	1.95
	Jul	1.03	0.26	4.69	50.10	996	10.29	1.47	13.50	<0.01	1.76	38.8	0.07	1.80
	Aug	1.31	0.23	4.02	42.84	938	9.15	1.65	12.08	<0.01	2.17	38.0	0.06	1.50
	Sep	0.60	0.12	3.87	43.57	904	9.70	1.27	9.20	0.020	1.43	27.6	3.38	0.10
	Oct	0.64	0.10	4.92	36.07	758	8.42	0.51	9.75	0.061	1.02	29.3	0.10	1.42
	Nov	1.30	0.23	4.42	42.94	868	8.48	2.40	15.14	0.284	1.88	38.5	0.00	1.50
	Dec	1.05	0.15	4.44	40.11	867	9.38	1.48	13.94	0.266	2.36	37.3	0.05	1.57
1	Yearly Average	1.12	0.21	5.13	45.64	966	10.24	1.51	15.56	<0.06	1.83	38.8	0.35	1.81

Site							Conce	ntratior	n ng.m ⁻³					
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Cardiff														
68	Jan	1.23	0.21	5.88	36.57	836	10.28	1.31	15.76	<0.01	1.49	37.4	0.11	2.98
	Feb	1.63	0.32	5.77	40.72	1049	15.61	2.07	25.88	<0.01	2.31	67.0	0.06	4.66
	Mar	1.29	0.31	6.75	41.06	1040	16.95	2.13	21.16	<0.01	2.17	79.2	0.06	2.28
	Apr	1.41	0.29	5.00	44.45	1011	15.21	2.16	17.77	<0.01	2.30	53.8	0.06	2.18
	May	1.64	0.40	4.63	47.81	1192	19.52	3.28	31.30	0.030	2.76	102.1	0.05	3.37
	Jun	0.54	0.13	3.14	34.97	899	10.63	1.79	9.59	<0.01	1.48	25.4	0.05	3.27
	Jul	0.81	0.23	4.16	44.87	1095	12.78	2.37	15.68	<0.01	2.38	46.4	0.08	1.59
	Aug	0.65	0.25	3.18	38.06	959	11.02	1.80	14.61	<0.01	1.85	44.2	0.06	2.68
	Sep	0.70	0.11	8.13	38.24	910	10.96	6.84	7.55	0.006	0.75	19.4	0.02	1.71
	Oct	0.84	0.18	5.44	45.06	1042	11.82	2.68	11.76	0.069	1.42	40.1	0.12	1.50
	Nov	0.77	0.44	5.98	44.67	1178	14.99	3.16	15.73	0.268	1.79	44.4	0.00	0.00
	Dec	1.07	0.32	4.55	38.65	941	12.40	2.77	17.74	0.253	1.29	60.5	1.75	1.84
	Yearly Average	1.05	0.27	5.22	41.26	1013	13.51	2.70	17.04	<0.06	1.83	51.7	0.20	2.34

Site	Concentration ng.m ⁻³													
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Brookside Metals														
69	Jan	2.09	4.62	8.58	58.85	278	9.25	1.17	78.89	<0.01	0.90	1041.5	0.06	2.04
	Feb	3.12	3.12	5.25	54.07	627	15.23	1.52	83.77	<0.01	2.05	393.7	0.09	1.86
	Mar	1.89	1.26	4.49	25.57	450	12.08	2.45	38.52	<0.01	1.76	186.6	0.07	1.49
	Apr	2.12	4.89	2.74	52.22	481	12.35	1.90	103.04	<0.01	2.29	602.7	0.05	1.86
	May	1.64	1.67	2.43	28.36	457	10.79	1.43	69.45	0.030	2.08	266.2	0.04	1.21
	Jun	1.29	3.09	2.90	56.27	467	10.66	2.36	82.13	<0.01	1.45	641.9	0.05	0.74
	Jul	2.35	5.98	2.94	60.67	454	10.50	2.67	85.31	<0.01	1.85	403.9	0.07	1.49
	Aug	2.33	5.92	3.38	88.17	395	11.61	2.51	133.22	<0.01	1.93	1475.1	0.10	1.95
	Sep	1.26	11.07	2.57	82.87	395	16.69	2.44	239.17	0.001	1.61	3660.6	0.04	2.33
	Oct	1.47	6.48	3.60	56.64	428	13.05	1.29	105.73	0.007	1.23	1409.8	0.08	1.80
	Nov	0.89	1.13	12.45	93.07	338	10.91	5.48	139.39	0.000	1.07	993.9	0.84	1.70
	Dec	1.58	7.40	4.35	75.58	485	15.11	4.93	114.18	0.185	1.91	1134.2	0.46	3.88
	Yearly Average	1.84	4.72	4.64	61.03	438	12.35	2.51	106.07	<0.02	1.68	1017.5	0.16	1.86

Site							Conce	ntration	n ng.m ⁻³					
	Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg	Hg Vap
Newcastle	l l													
70	Jan	0.66	0.11	3.65	4.47	165	3.17	0.50	12.01	<0.01	0.74	12.7	0.06	1.99
	Feb	0.63	0.15	4.33	6.59	304	5.21	1.04	8.57	<0.01	1.13	15.6	0.19	2.15
	Mar	0.91	0.19	5.98	9.06	332	6.62	1.46	15.24	<0.01	1.81	25.2	0.12	2.73
	Apr	0.92	0.23	3.07	8.21	328	5.86	1.51	22.83	<0.01	2.24	26.7	0.11	2.23
	May	0.86	0.27	2.54	8.36	353	7.34	1.54	18.30	0.030	1.88	22.4	0.17	2.32
	Jun	0.72	0.25	2.32	5.97	244	5.11	1.43	48.74	<0.01	1.66	20.4	0.05	2.32
	Jul	0.79	0.23	3.37	6.69	276	5.83	2.11	35.27	<0.01	1.90	28.7	0.11	2.23
	Aug	0.97	0.16	2.73	7.55	291	5.98	2.45	10.97	<0.01	4.04	28.3	0.40	2.07
	Sep	0.29	0.12	1.11	6.92	234	5.24	1.20	8.10	0.003	0.63	24.8	0.11	2.60
	Oct	1.02	0.14	3.80	8.18	241	5.30	2.39	13.31	0.051	1.33	33.5	3.59	1.99
	Nov	2.77	0.28	4.93	8.14	271	5.81	3.16	13.52	0.000	3.43	32.2	1.31	2.11
	Dec	2.69	0.44	6.20	10.64	429	8.67	3.25	25.39	0.330	3.25	34.6	1.53	3.21
l	Yearly Average	1.10	0.21	3.67	7.57	289	5.84	1.84	19.35	<0.04	2.00	25.4	0.65	2.33