

Report

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

Annual Report for 2008 on the UK Heavy Metals Monitoring Network

Richard J. C. Brown David M. Butterfield Sharon L. Goddard Dharsheni Muhunthan Andrew S. Brown Melanie Williams

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March 2009

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Approved on behalf of Managing Director, NPL by M Sene, Director, Quality of Life Division

Annual Report for 2008 on the UK Heavy Metals Monitoring Network

Executive Summary

This Report was prepared by NPL as part of the 2004-2009 UK Heavy Metals Monitoring Network contract (an extension until September 2009 was granted in September 2007) with the Department for the Environment, Food and Rural Affairs and the Devolved Administrations. This is the Annual Report for 2008 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 EC Air Quality Directives.
- Highlighting of exceedences, interpretation of data and discussion of trends across the Network.
- Details and outcomes of the Network re-organisation required to meet the requirements of the Fourth Daughter Directive.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events during 2008.
- The Network's science profile.

In summary, during 2008:

- **Lead**: No annual average site levels above the New Air Quality Directive's Lower Assessment Threshold were recorded.
- Nickel: One annual average site level above the Fourth Daughter Directive Upper Assessment Threshold, and one annual average site level above the Fourth Daughter Directive Lower Assessment Threshold were recorded.
- Cadmium: One annual average site level above the Fourth Daughter Directive Lower Assessment Threshold was recorded.
- Arsenic: No annual average site levels above the Fourth Daughter Directive Lower Assessment Threshold were recorded.
- Total gaseous mercury: Measured levels across the Network remain low (with the exception of the site at Runcorn Weston Point).
- The general slow downward trend in annual average concentration values has continued.
- All data quality objectives specified in the New Air Quality Directive and Fourth Daughter Directive were met, including time coverage, data capture and measurement uncertainty requirements.
- Data capture across the Network was 93% for the year.

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1 Introduction

This Report was prepared by NPL as part of the 2004-2009 UK Heavy Metals Monitoring Network contract (an extension until September 2009 was granted in September 2007) with the Department for the Environment, Food and Rural Affairs and the Devolved Administrations¹.

This is the Annual Summary Report for the UK Heavy Metals Monitoring Network (the 'Network) for 2008 and contains:

- Measured monthly concentration levels of all metals at all sites and performance against relevant data quality objectives and the requirements of the relevant EC Air Quality Directives the New Air Quality Directive (2008/50/EC²) for lead, and the Fourth Air Quality Daughter Directive (DD) (2004/107/EC³) for nickel, arsenic, cadmium, and total gaseous mercury, and the Air Quality Strategy for England, Scotland, Wales and Northern Ireland⁴ for lead.
- Highlighting of exceedences, interpretation of data and discussion of trends across the Network.
- Details and outcomes of the Network re-organisation required to meet the requirements of the Fourth Daughter Directive.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events during 2008.
- The Network s science profile.

1.1 General Context

Several requirements drive the need for air quality measurements, including: measuring the exposure of the general population to a variety of toxic compounds; assessing compliance with legislative limits or similar target values; informing policy development and assessing the effectiveness of abatement strategies. In addition there is a need to provide air quality information for the general public and to inform other scientific endeavours (for example, climate change research), and to provide an infrastructure that can readily respond to new and rapidly changing requirements, such as the specification of new pollutants requiring measurement, or assessment of episodes, such as local, regional or trans-boundary pollution events.

¹ The devolved administrations are as follows: the National Assembly for Wales (NAW), the Northern Ireland Executive, represented by the Department of the Environment in Northern Ireland (DoENI), and the Scottish Executive, represented by the Scottish Executive Environment and Rural Affairs Department (SEERAD).

² Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, *Official Journal L* **152**, 11/06/2008 P. 0001 - 0044

³ Directive 2004/107/EC of the European Parliament and of the Council of 15 December 2004 relating to arsenic, cadmium, mercury, nickel and polycyclic aromatic hydrocarbons in ambient air, *Official Journal* **L 023**, 26/01/2005 P. 0003 - 0016

⁴ Air Quality Strategy for England, Scotland, Wales and Northern Ireland, 2007, Cmd paper No 7169 NIA 61/06-07

The determination of the total concentrations 5 of metals in ambient air is of great importance within this framework. The general public and the environment can be exposed to several classes of hazardous compounds containing metallic elements, which occur naturally or are released by domestic or industrial processes. The total concentration levels of Pb, Ni, As, Cd and Hg, allowable in the PM₁₀ fraction of ambient air (particles with an aerodynamic diameter of 10 μ m or less), are now limited by European legislation. Emissions of metals in the UK continue to arise from a variety of sources including in particular:

- Industrial combustion:
- Domestic combustion:
- Public power combustion;
- Metals processing industry;
- Road transport:
- Waste incineration:
- Chemical industry processes;
- Iron and steel industry.

The National Atmospheric Emissions Inventory has more details of anthropogenic sources and emissions of metallic pollutants in the UK⁶. These emissions have declined consistency over many years and this has generally been mirrored by the decrease in measured ambient levels.

In order to enable the enforcement of legislation, to measure human and environmental exposure, and to show compliance with limit and target values, the total concentration levels of ambient metals, at multiple sites on nationwide air quality monitoring networks, need to be measured. The UK Heavy Metals Monitoring Network is a regulatory air quality monitoring network that discharges the UK s obligation under the EC Air Quality Directives relating to the monitoring of the mass concentrations of Pb, Ni, As, Cd, and total gaseous mercury [Hg(v)], in the PM_{10} phase of ambient air. The Network has a number of objectives:

- Compliance with monitoring requirements set out in European legislation;
- Provision of data to the European Commission on the UK's performance against the limit values, target values, and data quality objectives described in the relevant legislation;
- Assessing impacts around 'hot spots of metal pollution, particularly in industrial areas:
- Producing accurate and reliable data for dissemination to the general public and for use by scientific and medical researchers and the air quality community.

Further information on the history of the UK Heavy Metals Monitoring Network can be found in: "Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends, Brown, R J C, et al, Environmental Monitoring and Assessment, 2008, **142**, 127-140.

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⁵ The term 'concentration is used in this report to refer to mass concentration.

⁶ www.<u>naei.org.uk</u>

2 Network Operation

2.1 Overview

NPLs management of the UK Heavy Metals Monitoring Network in 2008 has involved a great deal of activity. In summary:

- The Network has completed an extensive reorganisation (that began in 2007) with 11 completely new Network sites becoming operational and the total number of monitoring sites across the UK increasing from 17 to 24.
- NPL staff visited and fully audited all sites on the Network. This included the calibration and basic maintenance of the Partisol and total gaseous mercury samplers and re-assessment of local site operators (LSOs) procedures.
- The Equipment Support Unit (ESU) has made service visits to all Network sites twice during the year, and this has included the flow calibration of instruments. This has resulted in a substantial decrease in the number of instrument breakdowns, and smaller uncertainties on sampled volumes.
- Data capture has remained at a very high level across the Network.
- The UK Heavy Metals Monitoring Network and the data it produces has received extensive exposure in learned journals^{7,8,9,10,11,12} during 2008. The publication resulting from work undertaken to ensure the accuracy and traceability of mercury vapour measurements made by the Network won the 2008 CITAC (Cooperation on International Traceability in Analytical Chemistry) Award for the most important paper on metrology in chemistry. More details are given in Section 9.

2.2 Site Audits

During 2008 NPL visited all the Network sites to perform annual site audits. This year this included start-up audits of newly installed Network sites.

During these visits the site infrastructure, performance and integrity were assessed. The LSOs were also audited and received extra training where required. LSOs at

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⁷ A practical uncertainty budget for ambient mercury vapour measurement. Brown, R J C, Brown, A S, Yardley, R E, Corns, W T, Stockwell, P B, *Atmos. Environ.*, 2008, **42**, (10), 2504-2517

⁸ Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends. Brown, R J C, Yardley, R E, Muhunthan, D, Butterfield, D M, Williams, M, Woods, P T, Brown, A S, Goddard, S L, *Environ. Monit. Assess.*, 2008, **142**, (1-3), 127-140

<sup>3), 127-140

&</sup>lt;sup>9</sup> On the optimum sampling time for the measurement of pollutants in ambient atmospheres. Brown, R J C, Hood, D, Brown, A S, *J. Autom. Meth. Manag. Chem.*, **2008**, Article ID: 814715

¹⁰ Accurate calibration of mercury vapour measurements. Brown, R J C, Brown, A S, *Analyst*, 2008, **133**, (11), 1611-1618

¹¹ The Effect of Isotopic Composition on the Uncertainty of Routine Metal Mass Concentration Measurements in Ambient Air, Brown, R J C, Goddard, S L, Brown, A S, Yardley, R E, *J. Autom. Meth. Manag. Chem.*, **2008**, Article ID: 504092

¹² Establishing SI traceability for measurements of mercury vapour Brown, A S, Brown, R J C, Corns, W T, Stockwell, P B, *Analyst*, 2008, **133**, (7), 946-953

sites where new Network sites had been installed additionally received full introductory training to the operation and maintenance of the equipment.

A list of sites comprising the Network as of the end of 2008, with locations, site codes, site names, site designations, identified point sources in the vicinity where applicable, is given in Annex 1. Following the reorganisation of the Network during 2008 (the details of which are described in detail later) the names of some sites changed to ensure consistency and avoid confusion, and to adopt the names of sites co-located with existing monitoring sites the details of these changes, listing old and new site names, are also given in Annex 1.

During each Network site audit visit NPL:

- Audited the procedures of the LSO on-site, giving introductory training where necessary, 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 gaseous phase (volumetric flow), monitoring equipment;
- Leak tested both the particulate, and gaseous phase, monitoring equipment;
- Calibrated the site rotameter (used by the LSOs for determining the flow rate through the total gaseous mercury sampling line).

The audit data recorded at each site may be found in Annexes 2 and 3. This flow data is used to correct the flows recorded by the Partisol instruments prior to the calculation of ambient concentrations. A detailed report on the findings of the audits is available ¹³, but in summary:

- All of the sites have been audited, including the 11 sites new to the Network, and are performing well.
- No problems were found with site infrastructure, and all of the new samplers had been correctly installed.
- Audits of the flow-rate on the Partisol samplers and the mercury vapour sampling equipment were satisfactory and no remedial action was required.
 The difference from set point determined at the audit visit is used at the data ratification stage to adjust the volume of air recorded for each sample.
- Nearly all of the LSOs audited were carrying out all of their functions correctly.
 However, there were a few cases where the audit procedure found that best practice was not being followed and corrective action was recommended:
 - At two locations the Partisol PM₁₀ head impactor plate was found to be very dirty and required cleaning. The LSOs were reminded of the need to clean the impactor plate monthly and the accelerator quarterly.
 - At two locations there was excessive grease on the two o-rings that seal the Partisol PM_{10} head onto the sampler. This resulted in a build up of grease on the inside of the main sampling orifice, which can remove particles from the sample air stream. The grease was removed and the LSO was instructed to remove regularly any grease build up in future.

¹³ NPL Report AS (RES) 020, "UK Heavy Metals Monitoring Network Audit Report For 2008, Butterfield, D M, Beccaceci, S, NPL, January 2009.

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- At one location the Partisol sampler was operating in standard flow control mode rather than volumetric flow control mode. This was corrected during the audit visit.

The auditing of the sampler flow rates also allowed a comparison of the ESU and NPL flow calibrators. (The ESU recorded the sampler flow rate during their service visits.) The flow measurements were in good agreement with an average difference of only 0.3%, which is well within the uncertainty of the flow measurement itself.



Image 1. A site audit in progress at the Redcar AURN Network site in May 2008. The Partisol 2000 sampler is visible in the cage on the top of the monitoring cabin.

2.3 Equipment Servicing and Breakdowns

During 2008 the ESU visited, fully serviced, and calibrated the Partisol samplers at the Network sites twice.

During 2008, NPL called-out the ESU to deal with Partisol sampler failures at:

- Bristol Avonmouth (faulty sampler replaced);
- London Horseferry Road three times (flow controller replaced after low valid hours reported; pump capacitor and cooling fan replaced; repair of software crash);
- London Cromwell Road (cooling fan replaced);
- Scunthorpe Town AURN (flow controller and temperature probe replaced);

- Scunthorpe Santon (unit replaced, after screen failure);
- Cardiff Rumney (flow sensor and temperature sensor replaced);
- Runcorn Weston Point (repair to vandalised wiring);
- Redcar AURN (flow controller replaced);
- Cardiff Llandaff (cooling fan replaced);
- Redcar Normanby (failure of volumetric control).

In addition, a corrupt display on the Partisol at Dartford Bean was resolved over the phone, and a cracked rain jar on the Partisol at Bristol Hallen was replaced.

During 2008, failed mercury vapour sampling pumps at Belfast Centre AURN, Walsall Centre and Walsall Willenhall were replaced by NPL.

Following the installation of new pumps for sampling total gaseous mercury across the Network in 2006, there have only been 3 failures of mercury vapour sampling pumps in the last 30 months.

2.4 Site Infrastructure and Other Issues

Site 67: Manchester Wythenshawe

Power was lost to the site in early October. The Highways Agency investigated the cause of the failure and power was restored in early November.

Site 68: Cardiff Llandaff

Operation at the Network site at Cardiff Llandaff was suspended in mid-February owing to building works that affected the power supply to the sampler. The shutdown was expected to be for one month only, so no plan for alternative power was made. However, this shutdown continued for longer than was expected, and the operation of this site was not restored until September.

3 Network Re-organisation to Meet the Requirements of the Fourth Daughter Directive

Following a comprehensive assessment of the sites monitoring heavy metals against the requirements of the European Directives (the full details of which can be found elsewhere 14), proposals were made to re-organise the Network to ensure compliance with these requirements. The proposed changes were agreed with Defra in the fourth quarter of 2007, and the activities of re-organisation began shortly afterwards. The actions taken to reorganise the Network in 2007-2008 and the timeline over which these occurred are detailed below.

3.1 Timeline and Activities

Overall the reorganisation of the Network involved the number of sites on the Network increasing from 17 to 24. The period of reorganisation encompassed the final quarter of 2007 and the first half of 2008. A detailed report of the changes to the Network are available in NPLs report on the subject¹⁵.

To summarise the changes made, the timeline of Network reorganisation in terms of changes to the number of Network sites is summarised in the figure below.

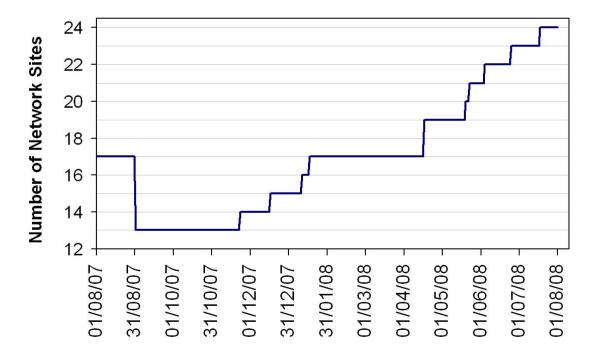


Figure 1. The timeline detailing Network re-organisation, and how the number of sites operating on the Network has varied between August 2007 and August 2008.

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¹⁴ AEAT Report AEAT/ENV/2243 "Preliminary Assessment of PAH and heavy metal levels in the UK, Bush, T, AEAT, February 2007.

¹⁵ NPL Report AS 28: "UK Heavy Metals Network Expansion Report for Defra, Butterfield, D, Lipscombe, B, Brown, R J C, Williams, M.

A detailed description of the activities as part of the re-organisation of the Network in 2007 and during 2008 is given below:

- 31st August 2007: 17 Network Sites were operational.
- 1st September 2007: The Network sites at London Brent (in operation, at two locations, since 1980), Leeds (in operation since 1980), Newcastle (in operation, at various locations, since 1989), and Glasgow (in operation since 1980) were closed. The Partisol samplers at these locations were redistributed for use at new Network sites. 13 Network sites were operational.
- 23rd November 2007: The local authority sites at Swansea (Morriston) and Swansea (Coedgwilym) were assimilated on the Network. NPL had been providing the analysis for samples from these sites for the previous 18 months. The Network site at Swansea (INCO) was devoleved into local authority control. 14 Network sites were operational.



Image 2. The new Network site at Swansea Morriston. The Partisol 2000 sampler is located in the tall cage on top of the green monitoring cabin in the centre of the picture.

 17th December 2007: A new Network site at Belfast (Belfast Centre) was installed. 15 Network sites were operational.

- 11th January 2008: A new Network site at Port Talbot (Port Talbot Margam AURN) was installed. 16 Network sites were operational.
- 17th January 2008: A new Network site at Sheffield (Sheffield Centre AURN) was installed. 17 Network sites were operational.
- 17th April 2008: Two new Network sites at Scunthorpe (Scunthorpe Town and Scunthorpe Santon) were installed. *19 Network sites were operational.*
- 20th May 2008: A new Network site at Redcar (Redcar AURN) was installed. *20 Network sites were operational.*
- 23rd May 2008: A new Network site in Cardiff (Cardiff Rumney) was installed.
 21 Network sites were operational.
- 4th June 2008: A new Network site around the Thames Estuary (Chadwell St Mary) was installed. 22 Network sites were operational.
- 25th June 2008: A new Network site around the Thames Estuary (Dartford Bean) was installed. 23 Network sites were operational.
- 18th July 2008: A new Network site at Redcar (Redcar Normanby) was installed. *24 Network sites were operational.*

3.2 New Site Locations

The majority of new sites installed on the Network during 2007-2008 were pairs of monitoring stations to provide upwind and downwind measurements of identified point source emitters. The description of the new Network sites, and their intended monitoring purpose is given below:

- The new site in Belfast is an Urban Background site for the Belfast Metropolitan Urban Area.
- The two new sites in Swansea represent a relocation of the single existing site to provide a more representative downwind measurement of the local nickel refining plant, and an additional upwind site. Additionally, these sites were the subject of a modelling study to ensure they were correctly located see Section 3.3 for details.
- The new site in Port Talbot provides a downwind site for emissions from the local steel works.
- The new site in Sheffield provides an upwind site to compliment the existing downwind site measuring emissions from the local steel works.
- The two new sites in and around Scunthorpe provide upwind and downwind monitoring locations for the local steel works.
- The two new sites in and around Redcar provide upwind and downwind monitoring locations for the local steel works.

- The two new sites around the Thames Estuary provide upwind and downwind monitoring locations for the metals refinery at Gravesend.
- The new site in Cardiff provides a downwind monitoring location to pair with the existing upwind site surrounding the local steel works.

Additional mercury vapour monitoring has been started at Belfast and Swansea (Morriston) to replace the mercury vapour monitoring lost at the four sites that closed in 2007. Monitoring for mercury vapour will also be initiated at Sheffield Centre and Bristol Hallen by the middle of 2009, in order to bring the number of sites monitoring for mercury vapour back up to 13.

The Network sites at Bristol Avonmouth and Hallen have assumed an Urban Background classification as the point source they were monitoring has now been closed for more than 5 years.

Figure 2 demonstrates the impact of the re-organisation of the distribution on Network sites across the UK between August 2007 and August 2008.

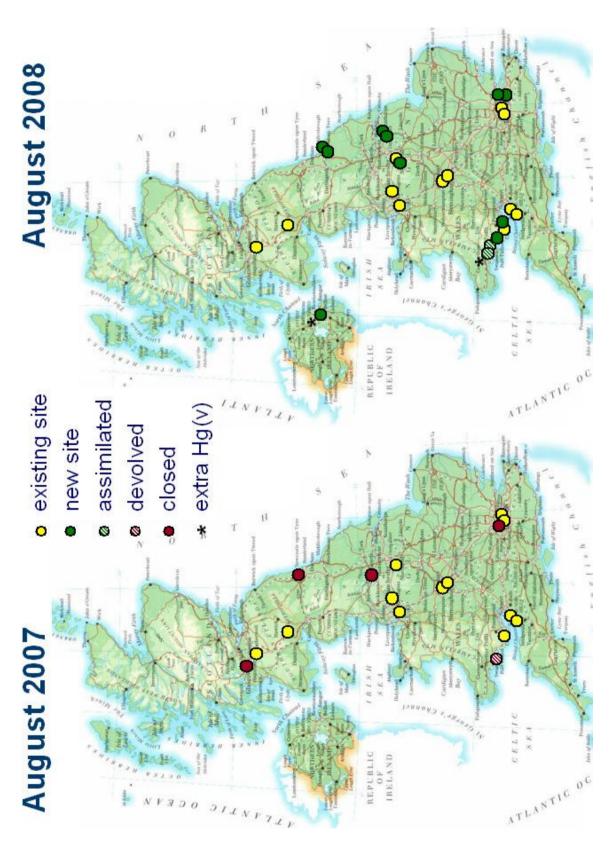


Figure 2. Location of sites on the UK Heavy Metals Network in August 2007 (left) and in August 2008 (right). The key displays the fate or origin of the Network sites.

3.3 Modelling of the Sites Around the Swansea Area

In order to gauge the effect of a point source on the concentrations measured locally it is important that the relevant monitoring sites are correctly positioned. The requirement is for the concentrations measured at the upwind site to have little or no contribution from the point source in question and that the downwind site is positioned so as to measure the maximum ground concentrations resulting from the emissions of the point source.

These conditions are not usually possible to meet entirely, given the variability of meteorological conditions, especially wind direction. However, sites should be placed so that, given the prevailing weather conditions, these requirements are best satisfied. Equally, it is not always possible to place monitoring sites in the most desirable locations for a number of reasons such as: lack of easily accessible power supply, the property owner not giving consent, lack of planning permission, or poor accessibility of sampler for maintenance and filter changing (e.g. in a secure compound, or location not continuously occupied).

These considerations are particularly important in the Swansea area as this continues to be a location of high nickel concentrations, which are regularly close to, or above, the target value. Therefore correct positioning of sites around this point source is essential to ensure the maximum ground concentrations in the vicinity are being detected, relative to a sound upwind background location, to ensure that the risk to the population is properly assessed and that any statements about comparison of measured levels with the target value can be made defensibly and with confidence.

The site reorganisation in the Swansea area was performed in collaboration with an air quality modelling study carried out by NPL to ensure that the new sites were located in the correct positions to best meet the requirements for upwind and downwind sampling locations mentioned above. The results of this exercise are shown in Figure 3. Even though the recorded nickel values are lower in 2008 at the Swansea Coedgwilym that they were at the previous Swansea site, this gives confidence that the new Network sites are located at ideal upwind and downwind locations to assess the effect of the point source in the Swansea area—the local nickel refinery.

In the long run this will provided greater certainty that the concentration levels measured at this site are representative of the likely maximum values in the local area. Moreover, the new locations are a substantial improvement on the previous Network site at Swansea INCO (the easternmost of the two local authority sites) and the other local authority site that was an additional possible location for a New Network site. Full details of the study may be found in the relevant NPL report¹⁶.

 $^{^{16}}$ NPL Report AS 30, "Atmospheric Dispersion Modelling of Nickel in the Swansea Area , Hayman, G, February 2009

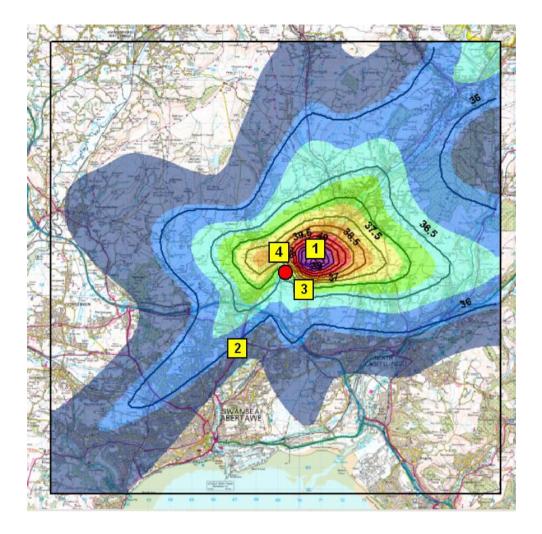


Figure 3. The results of the air quality modelling study around Swansea. The point source is shown as the red circle, the yellow boxes indicate the following sites: 1: Swansea Coedgwilym (Network site); 2: Swansea Morriston (Network site); 3: Swansea INCO (local authority site former Network site 49: Glais Primary School, Glais, SA7 9EY); 4: Swansea YGG Gellionnen (local authority site: YGG Gellionnen School, Clydach, SA6 5LB). The predicated nickel concentrations decrease from the centre of the picture outwards, in colour order: purple > red > orange > yellow > green > cyan > blue. The Ordnance Survey map is © Crown Copyright (2008).

3.4 Changes in Observed UK Wide Concentrations

It is desirable following reorganisation of Network sites to ensure that the annual average values do not exhibit a step-change owing to the different composition of the Network and the processes that are being monitored. This is especially important for the metals that are limited by European legislation (Pb, Ni, As, Cd). This is not particularly easy to assess, as annual average concentrations are not stable even when the composition of the Network is invariant. Most metals have showed a steady decrease in measured concentration over the last 25 years.

Therefore, the best way to gauge whether the changing composition of the Network has had any affect on measured values is to look not at absolute concentrations, but to assess whether there has been any significant change in the rate of decrease of measured concentrations following reorganisation. The results of this analysis are displayed in Figure 4, which displays the change in the annual average concentration of the metals measured by the Network (excluding Hg and Pt which are regularly below the detection limit) between 2004 and 2006 (when the Network composition was unchanged), and between 2006 and 2008 (during which time period the Network underwent reorganisation).

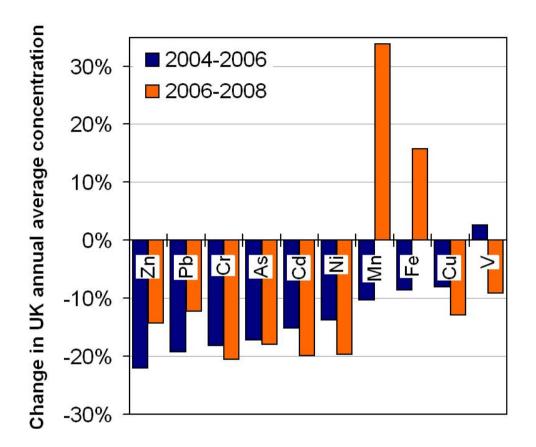


Figure 4. Graph displaying the change in the annual average concentration of the metals measured by the Network (excluding Hg and Pt which are regularly below the detection limit) between 2004 and 2006 (when the Network composition was unchanged), and between 2006 and 2008 (during which time period the Network underwent reorganisation).

As can be seen, there is no significant variation in the rate of decrease of metals concentrations, with the exception of Fe and Mn which have shown significant increases. The reason for this is that a subset of the new monitoring sites are targeted specifically at emissions from steel works where recorded PM_{10} levels are also very high¹⁷. This notwithstanding, Figure 4 demonstrates that the Network reorganisation has not significantly affected the measured annual average values and the trends in these annual averages, especially for the metals that are the subject of European legislation.

¹⁷ www.airguality.co.uk

4 Sampling and Analytical Methodology

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

4.1 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, nominally of 1 m³.h⁻¹, in accordance with EN 12341. Samples were taken for a period of one week onto 47 mm diameter GN Metricel membrane filters.

4.2 Sampling Methodology: Total Gaseous Mercury

Sampling for total gaseous mercury took place at 9 of the 17 Network sites at the start of the year, rising to 11 by the year end, using a low-volume pump (calibrated annually by NPL). Air was pumped through Amasil (gold-coated silica) tubes at a rate of 100 ml.min⁻¹ for either one week or four weeks, depending on the specific site and the expected ambient concentrations. A schematic diagram of the bespoke sampling set-up is given in Figure 5.

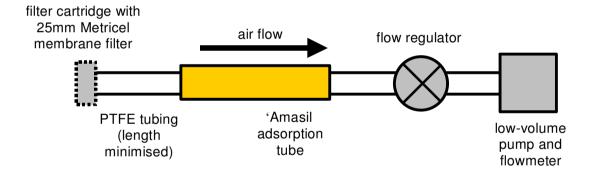


Figure 5. Schematic diagram of the total gaseous mercury sampling apparatus. The 25 mm diameter filter was used to remove any particulate material.

4.3 Analytical Methodology: Particulate-phase Metals

Analysis for particulate-phase metals took place at NPL using a PerkinElmer Elan DRC II ICP-MS, following NPLs procedure, accredited by UKAS to ISO 17025, which is fully compliant with the requirements of EN 14902.

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 quality assurance (QA) standard was repeatedly analysed (after every two solutions), and the change in response of the QA standard was mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS was corrected for by use of an internal standards mixture (containing Y, In, Bi, Sc, Ga & Rh) continuously added to the all samples via a mixing block. Each sample was 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 XLGenline (an NPL-developed program) to construct a calibration curve.



Image 3: One of two dedicated ICP-MS instruments comprising the UK ambient metals analysis facility at NPL.

4.4 Analytical Methodology: Total Gaseous Mercury

Analysis of total gaseous mercury samples took place at NPL using a PS Analytical Sir Galahad II analyser with a fluorescence detector, using NPLs procedure, accredited by UKAS to ISO 17025, which is based on the draft standard method prEN 15852. 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.



Image 4: One of two thermal desorption-atomic fluorescence analysers comprising the UK total gaseous mercury analysis facility at NPL

4.5 Measurement Units

Results produced by the Network are expressed as mass concentrations, in nanograms (of the relevant element) per cubic metre (of ambient air sampled): ng.m⁻³.

5 Method Performance Characteristics and Quality Control

UKAS carried out a surveillance assessment visit to NPL in November 2008. Both of the technical procedures used to analyse samples from the Network (metals in the particulate phase by ICP-MS, and mercury vapour by atomic fluorescence spectroscopy) were audited by UKAS, and both retained accreditation to ISO 17025 with no mandatory corrective actions.

5.1 Limits of Detection: Particulate-phase Metals

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

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

Table 1. Indicative limits of detection for particulate-phase metals.

5.2 Limits of Detection: Total Gaseous Mercury

The limit of detection routinely achievable for analysis of total gaseous mercury at NPL using its UKAS accredited procedure, which is consistent with the draft standard prEN 15852, is 0.02 ng per tube, equivalent to an air concentration of approximately 0.02 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).

5.3 QA/QC Procedures

Some of the quality assurance and quality control procedures used during Network operation 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 NPLs Network database. Rejection of any unidentifiable samples and full investigation of any discrepancies.
- Continued training of, and regular communication with, the LSOs. This
 includes assessment of performance during site audits.

Particulate phase metals (ICP-MS analysis):

- Optimisation of the ICP-MS prior to each set of analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular extraction of an appropriate certified reference material (e.g. NIST SRM 1648a or NIES No.8) to check the recovery of the digestion method. Recoveries must be within the limits specified by EN 14902.
- Regular measurement of filter blanks to ensure appropriate blank subtractions are made from measured values.
- Maximum levels for the standard deviation of the five internal standardcorrected measured intensities of each analysis of each sample.
- The XLGenline goodness-of-fit for all calibration curves must be less than 2.
- Ratification of all data by an NPL Quality Circle of recognised senior NPL scientific experts independent of the analytical team.

Total gaseous mercury (atomic fluorescence analysis):

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

5.4 Measurement Uncertainty

The average uncertainty from the analyses of single filters and tubes at NPL during 2008 are shown in Table 2. 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%.

		d relative tainty
Analyte	Single measurement average	EC Directive maximum
As	25%	40%
Cd	16%	40%
Cr	28%	-
Cu	10%	-
Fe	10%	-
Mn	11%	-
Ni	15%	40%
Pb	11%	25%
Pt	50%	-
V	16%	-
Zn	11%	-
Hg(p)	25%	-
Hg(v)	18%	50%

Table 2. Average measurement uncertainties achieved at NPL during 2008. The 'EC Directive maximum column shows the maximum permissible uncertainty permitted by the relevant EU Air Quality Directive. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. The majority of Pt measurements are below the limit of detection, the 50% uncertainty refers to those measurements which are above the detection limit.

The measurement uncertainties displayed in Table 2 are representative of individual measurements averaged over a typical sampling period (here, one week), as required by the EU Air Quality Directives. The vast majority of the measurements used to compile the data in Table 2 were of ambient concentrations well below the appropriate target values. It is calculated that in the region of the appropriate target value where the EU Air Quality Directive's uncertainty data quality objectives apply (except for Hg(v) where there is no target value) these uncertainties will be significantly lower.

6 Network Data Quality

6.1 Data Capture in 2008

All data capture figures are based on a target time coverage of 100 %. (The Fourth DD requires a time coverage of only 50 % for fixed measurements of As, Ni and Cd.)

Data capture across the entire Network during 2008 was 93 %.

Of the data lost approximately:

- 45 % was excluded because the minimum number of valid sampling hours was not achieved during the sampling period;
- 50 % was lost owing to equipment failure or site operation problems, and;
- 5 % was excluded at the analytical stage (owing to contamination of sample, instrument failure, exclusion during data ratification).

The breakdown of the overall data capture between the particulate and gaseous phase, and at each site, is displayed in the table below:

Location	Data Cap	ture / %
Location	Particulate phase	Gaseous phase
Whole Network	93 %	91 %
46: Walsall Centre	96 %	100 %
47: Bristol Avonmouth	96 %	N/A
56: Bristol Hallen	96 %	N/A
58: Sheffield Brinsworth	94 %	N/A
59: Runcorn Weston	90 %	85 %
61: London Cromwell Road	90 %	92 %
62: London Horseferry Road	83 %	92 %
65: Eskdalemuir	100 %	100 %
66: Motherwell Centre	88 %	92 %
67: Manchester Wythenshawe	90 %	75 %
68: Cardiff Llandaff *	96 %	100 %
69: Walsall Willenhall	96 %	85 %
100: Swansea Coedgwilym	100 %	N/A
101: Swansea Morriston	87 %	100 %
103: Belfast Centre AURN	92 %	80 %
104: Port Talbot Margam AURN	98 %	N/A
105: Sheffield Centre AURN	92 %	N/A
106: Scunthorpe Town AURN	91 %	N/A
107: Scunthorpe Santon	80 %	N/A
108: Redcar AURN	89 %	N/A
109: Cardiff Rumney	91 %	N/A
110: Chadwell St Mary	97 %	N/A
111: Redcar Normanby	75 %	N/A
112: Dartford Bean	92 %	N/A

Table 3. Data capture across the UK Heavy Metals Monitoring Network during 2008. Data capture for new monitoring sites is counted from the start of monitoring. * Instrument down time at Cardiff Llandaff owing to the planned power outage has not been counted against lost data capture.

The quarterly data capture, and the rolling annual average data capture, achieved by the Network over the last four years is displayed in Figure 6.

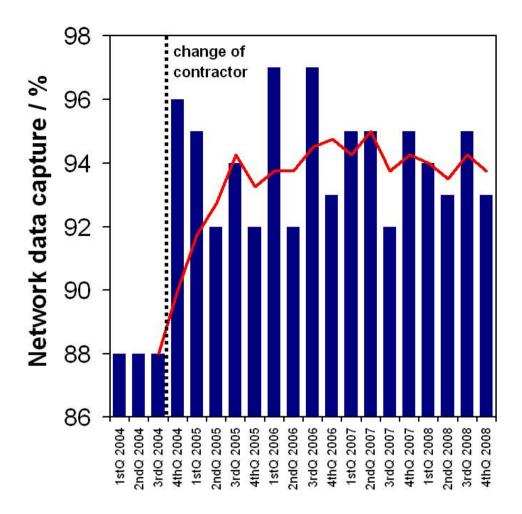


Figure 6. Network data capture from 2004-2008 (inclusive). Quarterly data capture is indicated by the blue bars, whilst the rolling annual average data capture is given by the red line.

6.2 Data Processing and Ratification

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

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

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

It is the aim of the ratification procedure to distinguish between changing ambient concentrations (including long terms trends, seasonal variation and single pollution events), and analytical discrepancies within the large amount of Network data. Ratification takes place in accordance with several guidelines, outlined below:

- 1) Only data where the valid sampling hours are greater or equal to 75% of the total sampling hours will be eligible to produce valid concentration data, and count towards the total data capture percentage.
- 2) Data not meeting the data quality objectives for uncertainty or time coverage for the relevant air quality directive are not eligible to produce concentration data and is counted as lost data capture.
- 3) Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.
- 4) Upon production, weekly data for each element at each site is plotted in a time series, or displayed as a continuous list of values which may be easily compared. (Total gaseous, and particulate phase, mercury should be plotted, or listed separately).
- 5) In the first instance these data are assessed visually for any obvious discrepancies with due regard to long terms trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data. (Detection of gross errors or systematic transcription of data entry faults may also be detected using chemometric methods).
- 6) 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).
- 7) 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 is recorded in the designated Excel spreadsheet after auditing. These audits concentrate most heavily on Ni, As, Cd, Pb and Hg vapour analyses, as these are directly relevant to EC Air Quality Directives.

6.3 Measurement Uncertainty of Annual Average

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

New sites that have been monitoring for less than the full year have had their contribution to the UK annual average and annual uncertainty weighted accordingly in proportion to the fraction of the year for which they have produced data.

In all cases annual mean uncertainties are compliant with the data quality objectives for uncertainty in the EC Air Quality Directives. Expanded uncertainties, quoted at

the 95% confidence interval, for the annual mean concentration values of the relevant EC Air Quality Directives metals are given in the table below:

		d Relative tainty
Analyte	Annual Mean	Daughter Directive maximum
As	28 %	40 %
Cd	18 %	40 %
Ni	17 %	40 %
Pb	13 %	25 %
Hg(v)	21 %	50 %

Table 4. Expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Daughter Directive metals. Hg(v) refers to total gaseous mercury. For Hg(v) there is no limit or target value stated in the 4^{th} DD at which this maximum allowable uncertainty applies.

7 Network Data

7.1 Measured Concentrations

The annual mean measured metals concentrations, averaged over all sites (Table 5), and at individual sites (Table 6), are given in the table below.

The UK annual mean concentration for each element has been calculated as the mean of all sites on Network, using appropriate weighting factors for new sites which have not been monitoring for the entire year, in order to decrease their contribution to the annual mean proportionally.

Analyte	2008 UK Annual Mean Concentration / ng.m ⁻³	EC limit or target value (UK objective) / ng.m ⁻³
As	0.63	6
Cd	0.34	5
Cr	3.54	-
Cu	15.6	-
Fe	538	-
Mn	13.2	-
Ni	3.21	20
Pb	16.0	500 (250)
Pt	<0.01	-
٧	2.02	-
Zn	71.8	-
Hg(p)	0.10	-
Hg(v)	5.80	-

Table 5. 2008 annual mean concentrations averaged over all sites on the UK Heavy Metals Monitoring Network. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. The EC limit or target value (or UK objective) is also listed, where applicable.

The UK monthly mean concentrations of each element during 2008 are shown in Figure 7. Monthly data for each element at each monitoring site are given in Annexes 4 and 5. The higher concentrations observed across the Network in February correlate strongly with the high PM_{10} concentrations measured across the whole UK during this month¹⁸.

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¹⁸ www.airquality.co.uk

				2008	Annual Mea	2008 Annual Mean Concentration / ng.m ⁻³	ration / ng.	m ⁻³				-	
Site	As	PO	Cr	no	Fe	Mn	ï	Pb	Pt	۸	Zn	(d) bH	Hg (v)
46: Walsall Centre	86'0	0.48	1.46	15.7	326	9.0	1.47	19.3	<0.01	1.35	101.6	0.03	4.31
47: Bristol Avonmouth	0.64	0.38	1.27	6.1	322	6.7	2.45	12.8	<0.01	5.66	34.7	0.07	N/A
56: Bristol Hallen	85.0	0.33	1.43	2.2	191	3.4	1.17	8.2	<0.01	1.79	17.6	0.04	N/A
58: Sheffield Brinsworth	1.01	0.46	30.87	16.1	468	34.6	12.31	27.2	0.01	1.76	81.3	0.11	N/A
59: Runcorn Weston Point	0.71	0.19	0.57	6.4	168	3.4	1.24	9.2	<0.01	1.82	18.4	1.03	32.0
61: London Cromwell Road	69'0	0.20	3.98	41.1	9/8	9.4	1.65	11.6	0.01	2.71	25.6	0.05	2.05
62: London Horseferry Road	92'0	0.20	1.57	18.8	4/4	6.5	1.84	10.4	0.01	3.16	21.7	0.04	2.08
65: Eskdalemuir	90'0	0.04	0.41	1.1	31	6.0	0.34	1.2	<0.01	0.33	2.8	0.02	1.61
66: Motherwell Centre	6.33	0.12	0.59	8.3	208	3.4	0.35	9.9	<0.01	79'0	11.9	0.02	2.23
67: Manchester Wythenshawe	9'0	0.15	3.52	34.3	292	8.2	0.93	7.4	0.01	1.06	25.3	0.04	1.74
68: Cardiff Llandaff	99'0	0.21	2.46	27.7	723	9.2	1.37	13.4	<0.01	1.22	26.3	0.01	1.91
69: Walsall Willenhall	1.15	2.24	3.38	60.4	364	9.5	1.66	88.1	<0.01	1.32	841.1	90'0	3.19
100: Swansea Coedgwilym	0.49	0.17	2.83	4.5	141	3.2	19.61	8.0	<0.01	1.00	13.3	0.04	N/A
101: Swansea Morriston	0.51	08.0	2.06	31.0	299	8.3	7.60	20.5	<0.01	1.30	36.5	60.03	1.58
103: Belfast Centre AURN	68'0	60'0	06:0	8.3	592	4.2	1.08	0.9	0.01	2.50	14.7	0.04	2.41
104: Port Talbot Margam AURN	0.62	0.31	1.58	6'2	2936	33.9	2.03	11.9	<0.01	2.17	52.5	0.03	N/A
105: Sheffield Centre AURN	09'0	0.17	4.11	6.6	290	10.2	1.98	11.0	<0.01	1.20	21.8	90.0	N/A
106: Scunthorpe Town AURN	0.58	0.18	1.99	5.4	650	25.7	1.61	18.1	<0.01	1.78	25.8	0.04	N/A
107: Scunthorpe Santon	0.85	0.24	3.52	6.8	2050	111.3	1.18	33.1	<0.01	4.48	44.6	0.06	N/A
108: Redcar AURN	0.40	0.19	2.97	3.6	443	25.3	0.92	9.1	<0.01	1.22	33.2	0.03	N/A
109: Cardiff Rumney	0.61	0.18	0.70	8.4	245	5.8	0.72	6.7	<0.01	1.07	25.0	0.02	N/A
110: Chadwell St Mary	0.62	0.34	1.06	10.1	270	4.3	2.43	12.5	<0.01	4.86	20.6	0.03	N/A
111: Redcar Normanby	0.21	0.11	2.98	2.5	143	5.6	0.42	5.0	<0.01	0.71	14.1	0.01	N/A
112: Dartford Bean	0.61	0.16	0.47	7.9	190	3.0	1.49	8.2	<0.01	2.47	15.2	0.01	N/A

Table 6. The 2008 annual mean concentrations measured at individual sites on the UK Heavy Metals Monitoring Network. The monthly measured metals concentrations from all Network sites are summarised in the tables in Annex 5. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

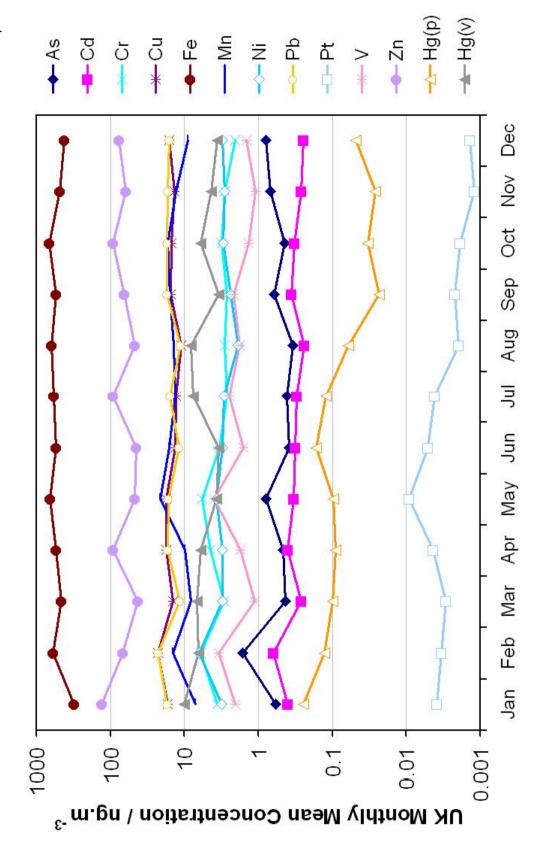


Figure 7. The measured UK monthly mean concentrations of each element during 2008. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively.

7.2 Measured Concentrations with Respect to the Requirements of the EU Air Quality Directives

The annual mean concentrations are compared against the relevant limit and target values, contained within the EU Air Quality Directives, in the figure below:

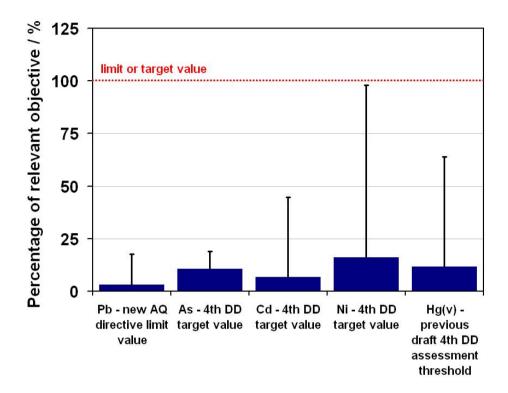


Figure 7. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth Daughter Directives on the UK Heavy Metals Monitoring Network in 2008 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the annual means at the site with the highest concentrations. Hg(v) refers to the total gaseous mercury concentrations. The mercury objective is taken from a threshold value quoted in a draft of the Fourth DD.

In all cases the annual mean values are well below the limit and target values. Additionally the highest annual average at an individual site does not exceed any target or limit values.

Annual mean concentration values for the relevant EC Air Quality Directives metals at all Network sites are displayed in Figure 8.

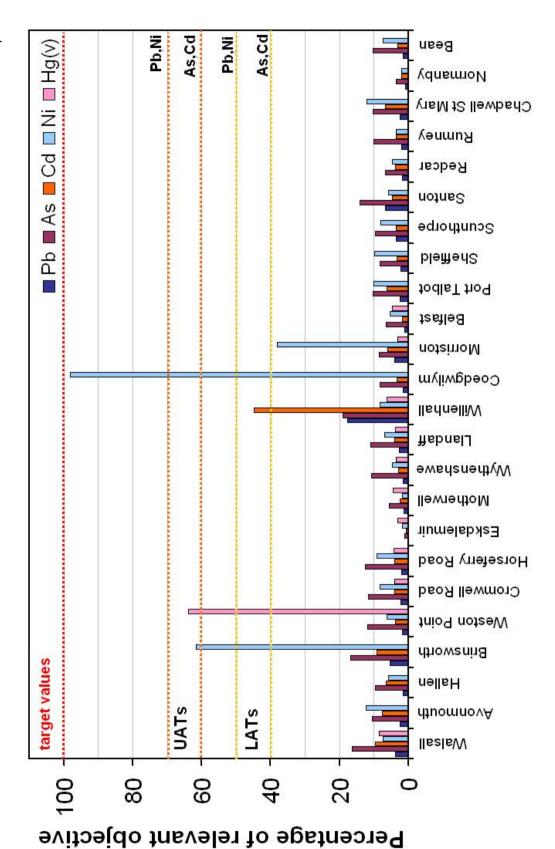


Figure 8. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2008 as a percentage of the relevant target values, lower assessment thresholds (LATs) and upper assessment thresholds (UATs). The mercury objective originates from a threshold value quoted in a draft of the Fourth DD. Hg(v) represents total gaseous mercury

The highest annual mean value for nickel has been found at Site 100: Swansea Coedgwliym. The highest annual mean values for arsenic, cadmium and lead are found at Site 69: Walsall Willenhall. The highest annual mean value for total gaseous mercury has been found at Site 59: Runcorn Weston Point.

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 100: Swansea Coedgwliym: 98 % of the target value.

Annual Mean Concentrations above the Lower Assessment Thresholds:

- Cadmium at Site 69 Walsall Willenhall: 45 % of the target value.
- Nickel at Site 58: Sheffield Brinsworth: 62 % of the target value.

Other Notable Concentrations:

Total gaseous mercury at Site 59: Runcorn Weston Point. The measured concentration represents 64% of the target value of 50 ng.m⁻³ quoted in a draft version of the Fourth DD.

The site at Swansea Coedgwliym is situated near to the Vale Inco nickel refinery, producing speciality nickel products and nickel-coated materials. The site at Sheffield Brinsworth is located next to the Outokumpu steel rolling mill and processing plant producing specialist steel strip, and coil, products. The site at Walsall Willenhall, is close to Brookside Metal Company the UK's largest producer of gunmetal, brass, bronze and other copper alloy ingots.

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

Figure 9 shows the concentrations of the other non-directive metals normalised to the annual average for each metal.

Figure 10 shows the relationship between particulate and vapour phase mercury measurements during 2008 where these are measured together.

As expected, the new downwind sites all exhibit higher measured concentrations than their respective new upwind site pairs. Nevertheless, this provides extra confidence that the direction of the prevailing weather conditions has been correctly assessed at each location and that the monitoring sites have been properly located. However, the concentrations recorded to date at these new sites are well below those predicted in the report¹⁹ that recommended the locations of these sites based on modelled exceedences of lower assessment thresholds in the vicinity of point sources. This may be because the model over-estimated fugitive emissions around these point sources.

¹⁹ AEAT Report AEAT/ENV/2243 "Preliminary Assessment of PAH and heavy metal levels in the UK, Bush, T, AEAT, February 2007.

Figure 9. A summary of the annual mean measured concentrations of the non-directive at all sites on the UK Heavy Metals Monitoring Network in 2008, normalised to the UK annual average concentration for the relevant element. Bars that are off-scale have their values indicated at the top of the chart.

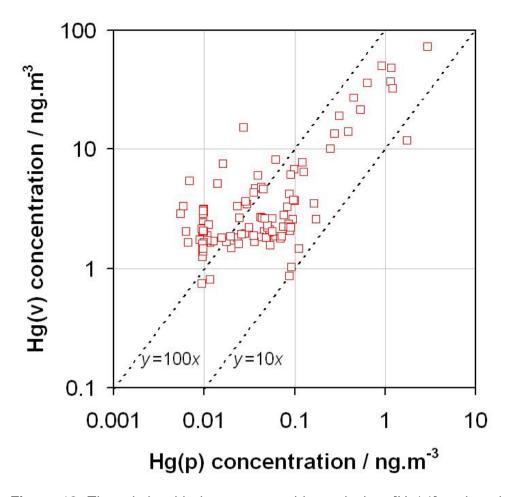


Figure 10. The relationship between monthly particulate [Hg(p)] and total gaseous [Hg(v)] mercury measurements during 2008 where these are made together. The dotted diagonal lines represent the locus of points for which the total gaseous mercury concentration are 10 (y = 100x) and 100 (y = 100x) times greater than the measured particulate phase mercury concentrations, as indicated.

Figure 10 shows that in almost all cases the total gaseous to particulate mercury concentration ration during 2008 was greater than 10, with the majority of measurements displaying a ratio of between 10 and 100. A significant number of measurements displayed ratios of in excess of 100. This demonstrates that the overwhelming majority of mercury in ambient air is present in the gaseous phase, at sites where these are measured together.

8 Trends in Measured Concentrations

8.1 UK Trends

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

	Changes	in measured c	oncentrations	over the:
Analyte	Last 25 Years	Last 10 Years	Last 5 Years	Last Year
As	not measured	not measured	-61 %	-32 %
Cd	-85 %	-64 %	-66 %	-15 %
Cr	-73 %	+6 %	-21 %	-27 %
Cu	-44 %	-23 %	-41 %	-11 %
Fe	-44 %	-23 %	-7 %	+37 %
Hg(p)	not measured	not measured	-45 %	-77 %
Hg(v)	not measured	not measured	-49 %	+4 %
Mn	-58 %	+28 %	+47 %	+63 %
Ni	-73 %	-63 %	-28 %	-15 %
Pt	not measured	not measured	N/A*	N/A*
V	-89 %	-41 %	-27 %	-10 %
Zn	-31 %	+83 %	-32 %	+27 %
Pb	-98 %	-91 %	-56 %	+7 %

Table 7. Trends in the measured annual average concentrations of metals measured by the UK Heavy Metals Monitoring Network. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. *Since monitoring for Pt began in 2003, average annual concentrations levels have remained below the detection limit.

Measurements of annual mean concentrations for all elements have generally fallen year upon year over the period for which data is available this generally mirrors the decrease in emissions over this period. Further details and interpretation of these data and trends is available²⁰. This trend has, in the most part, continued over the last year. The trends for individual elements are disussed in more detail below:

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²⁰ Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends. Brown, R J C, *et al*, *Environ. Monit. Assess.*, 2008, **142**, (1-3), 127-140

Arsenic: Levels continue to fall and are uniformly low across the Network.

Cadmium: Concentrations are low across the Network, with the exception of Walsall Willenhall, and show signs of a continuing slight decrease.

Chromium: Concentrations remain low across the Network, and are similar to those seen 10 years ago. The annual average is dominated by the levels measured at Sheffield Brinsworth.

Copper: Copper levels have decreased for the fifth year in a row, and have halved over the last 15 years. The highest values tend to be recorded at roadside sites.

Iron: Concentrations have increased in 2008, primarily because the Network reorganisation has encompassed a large number of point sources located around steel plants.

Particulate phase mercury: Concentrations remain very low across the Network and have decreased in 2008.

Total gaseous mercury: Concentrations have shown a very small increase over the last year, but remain low. Trends, and average recorded concentrations, for total gaseous mercury are strongly influenced by the very high levels at Runcorn Weston Point.

Manganese: Concentrations have increased in 2008, primarily because the Network re-organisation has encompassed a large number of point sources located around steel plants.

Nickel: Concentrations showed a decrease in 2008. The high values recorded at Swansea Coedgwilym and Sheffield Brinsworth have a large influence on trends, and average recorded concentrations, for this element across the Network. Recorded concentrations at the Swansea Coedgwilym were lower that those recorded at the old Swansea Network site in 2007.

Platinum: Average annual values remain below the detection limit across all Network sites. Concentrations measured for platinum remain the lowest, by an order of magnitude, of any of the metals monitored across the Network. The highest concentrations are recorded at roadside sites.

Vanadium: Concentrations decreased slightly in 2008, and remain generally low across the Network. Levels have decreased significantly over the last quarter of a century.

Zinc: Concentrations increased in 2008, but levels at most locations remain low. Trends, and average recorded concentrations, for this element across the Network are influenced substantially by the high measured concentrations at Walsall Willenhall.

Lead: Lead levels showed a slight increase 2008 but remain low across the Network. Over the last 10 years levels have approximately halved.

Concentration trends over the last 28 years for the metals relevant to the EU Air Quality Directives are summarised in Figures 11 and 12. The trends observed for the other metals measured by the Network are shown in Figures 13 and 14. Pt has been omitted from these graphs as its levels are routinely below detection limits.

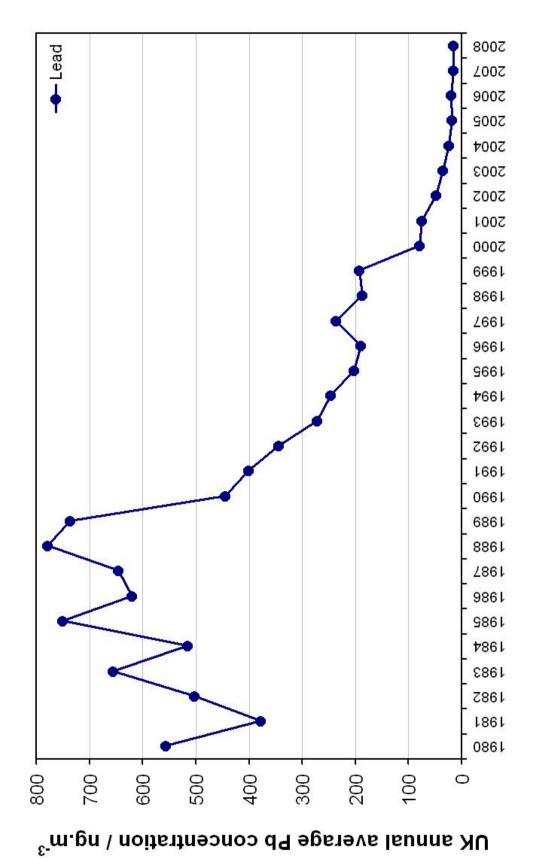


Figure 11. The UK annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 28 years. The EC limit value for lead is 500 ng.m⁻³ and the UK Air Quality Objective for lead is 250 ng.m⁻³

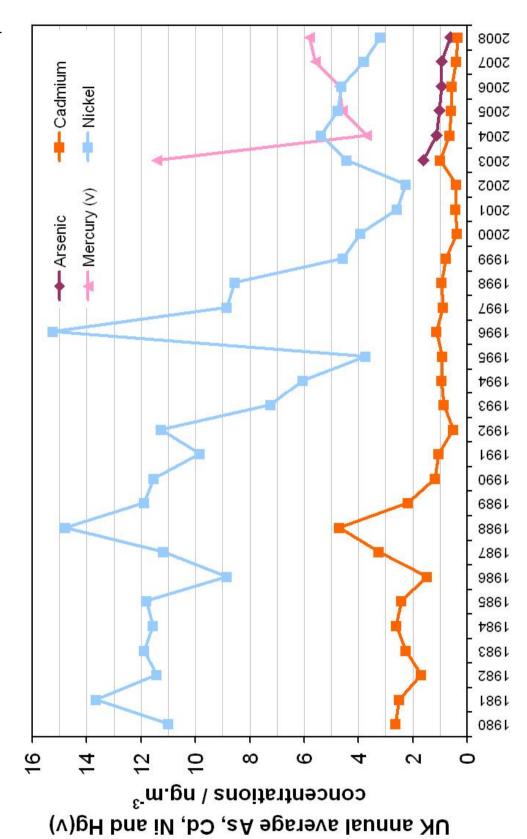


Figure 12. The UK annual average concentrations of Ni, As, Cd and total gaseous mercury [Hg(v)] measured on the UK Heavy Metals Monitoring Network over the last 28 years. The EC targets values for Ni, As and Cd are 20 ng.m⁻³, 6 ng.m⁻³ and 5 ng.m⁻³ respectively

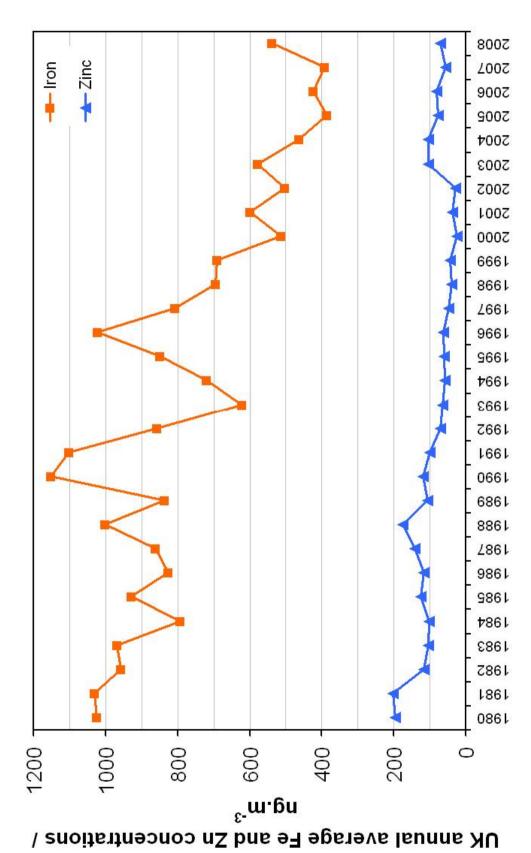


Figure 13. The UK annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 28 years.

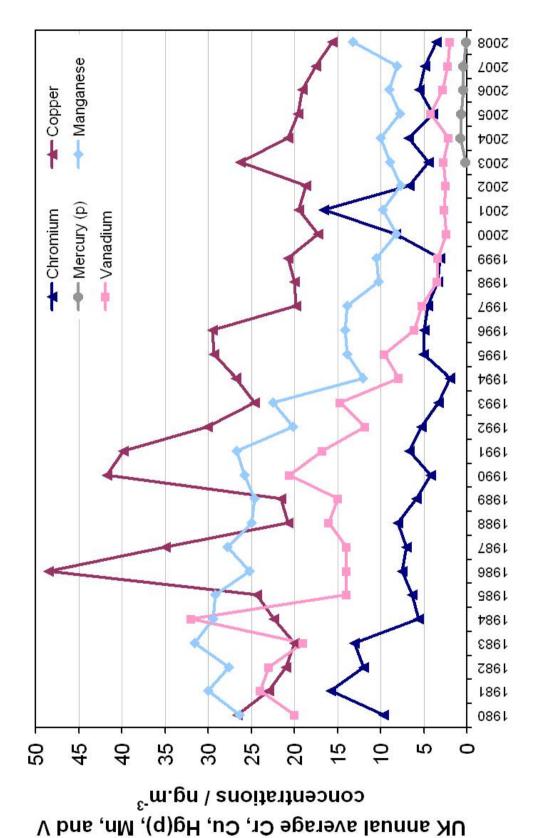


Figure 14. The UK annual average concentrations of Cr, Cu, Hg(p), Mn and V measured on the UK Heavy Metals Monitoring Network over the last 28 years.

8.2 Trends at Swansea

The annual average concentration of Nickel at Swansea measured over the last 6 years is shown in Figure 15.

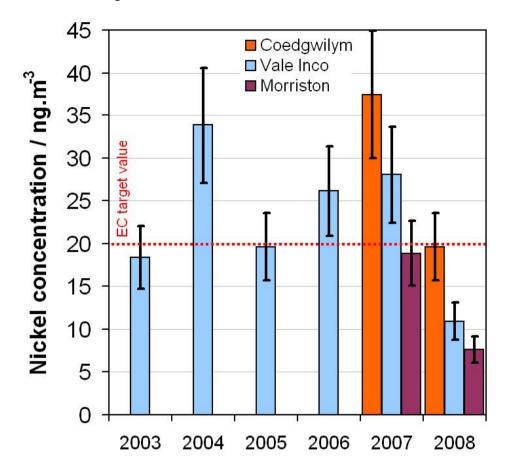


Figure 15. The annual average nickel concentration measured at monitoring sites in the Swansea area (indicated by the key) over the last 6 years, with the error bars indicated the expanded uncertainty in these values at the 95 % confidence level. The red dotted line indicated the 4th DD target value for nickel. The location of these sites is given in Figure 3. Swansea Vale Inco was the UK Heavy Metals Monitoring site from 2003 to 2007 inclusive; in 2008 the Network monitoring sites moved to Swansea Coedgwilym and Swansea Morriston. (The data for Vale Inco in 2008, and Coedgwilym and Morriston in 2007 is courtesy of Tom Price and the City and County of Swansea. However the sampled filters have been analysed at NPL using the methods described In Section 4, under a separate contract).

All sites showed a significant decrease in measured concentrations from 2007 to 2008. This correlates with bag filters being installed in late 2007 in order to reduce particle emissions from the point source in question. Moreover the Vale Inco site, for which there is the longest time series of data, and which has produced concentrations consistently around or above the EC target value, recorded the lowest value since measurements began at that location just over 50 % of the target value. This reinforces the benefits of the changes of sites location in the Swansea area as discussed in Section 3.3, and also suggests that nickel concentrations in this area may be starting to decrease.

9 Science Profile of the Network

9.1 Publications

NPL has produced six articles during 2008 that feature the data, analytical procedures and operation of the Network. These articles are detailed below:

 "Establishing SI traceability for measurements of mercury vapour Brown, A S, Brown, R J C, Corns, W T, Stockwell, P B Analyst, 2008, 133, (7), 946-953

This paper describes novel work undertaken to remove the dependency of the measurement of mercury vapour on empirical vapour pressure equations by providing a direct link between mercury vapour measurements and standards of mass. This work has therefore demonstrated SI traceability for measurements of mercury vapour for the first time. The most commonly used empirical mercury vapour pressure equation has been shown to be valid within the uncertainty of the measurement. By introducing an underpinning traceability framework for these measurements, this work will have a large impact in shaping the confidence and comparability in results taken on the UK Network, and worldwide, in the future.

The importance of this work was recognised by the award of the 2008 CITAC²¹ Award for the Most Important Paper on Metrology in Chemistry.

- "A practical uncertainty budget for ambient mercury vapour measurement, Brown, R J C, Brown, A S, Yardley, R E, Corns, W T, Stockwell, P B, Atmos. Environ., 2008, 42, (10), 2504-2517
- "Accurate calibration of mercury vapour measurements, Brown, R J C, Brown, A S, *Analyst*, 2008, **133**, (11), 1611-1618

These two papers have made a large contribution to the way that total gaseous mercury measurements are made around Europe. For the first time, a full uncertainty budget has been presented for these measurements, describing the contribution of all relevant experimental parameters. Additionally, the part of the measurement procedure highlighted as the most sensitive in terms of contributing to the uncertainty of the overall method, the calibration method using the so-called 'bell-jar apparatus, has been described in detail. The *Analyst* paper discusses the thermodynamic and kinetic considerations that must be taken into account when using the bell-jar apparatus, provides the theoretical basis for understanding the operation of the bell-jar, and presents experimental data demonstrating the systematic biases which may be obtained if the bell-jar is used incorrectly.

Both these papers will be included as references in the forthcoming CEN TC264 WG25 standard method for total gaseous mercury measurement: prEN 15852, ensuring that the UK has taken a leading role in ensuring measurement comparability across European air quality networks.

 "Twenty-five years of nationwide ambient metals measurement in the United Kingdom: concentration levels and trends, Brown, R J C, Yardley, R E, Muhunthan, D, Butterfield, D M, Williams, M, Woods, P T, Brown, A S, Goddard, S L, *Environ. Monit. Assess.*, 2008, 142, (1-3), 127-140

²¹ CITAC is the Co-operation on International Traceability in Analytical Chemistry; www.citac.cc

This paper provides a novel and critical examination of Network operations, measured concentration levels, and trends, over the last guarter of a century. Following the extensive media coverage generated when this paper was published on-line, hardcopy publication occurred in 2008, following which the work was highlighted in the European Commission DG Environment's News Alert Service: 'Science for Environment Policy 22.

- "On the optimum sampling time for the measurement of pollutants in ambient atmospheres . Brown, R J C. Hood, D. Brown, A S. Journal of Automated Methods and Management in Chemistry, 2008, Article ID: 814715
- "The Effect of Isotopic Composition on the Uncertainty of Routine Metal Mass Concentration Measurements in Ambient Air, Brown, R J C, Goddard, S L, Brown, A S. Yardley, R E. Journal of Automated Methods and Management in Chemistry, 2008, Article ID: 504092

These two papers have highlighted improvements to measurement techniques as a result of the work carried out in the operation of the Network. The first paper discusses the optimum sampling time for pollutants such as mercury vapour, and how a balance between measurement uncertainty and the time resolution of data must be accommodated. The second paper highlights the effect that uncertainty in the isotopic composition of samples and calibration standards can have on the overall uncertainty of the analytical measurement. It is shown that in most cases this is negligible, but is worth considering for lead measurements.

Both papers have been published in an open access chemistry journal to increase the visibility, access and impact of this work within the relevant scientific community.

9.2 **International Activity**

In 2008, NPL continued to represent the interests of the Network and the UK on relevant CEN standardisation committees, in particular: CEN TC264 WG25 "Mercury measurement methods in ambient air and deposition, CEN TC264 WG20 "Deposition measurements of heavy metals, and CEN TC264 WG15 "Reference gravimetric method for particulate matter.

In addition NPL has continued to host and provide the secretariat for BSI committee EH/002/03 "Ambient Atmospheres which is the UK mirror group shadowing the development of ambient and indoor air standards within CEN and ISO, in particular, CEN TC264 'Air Quality and ISO TC146 'Air Quality .

In 2008 the report on the EC-JRC-IES organised intercomparison exercise for heavy metals in PM10 was published²³. NPL s performance was in the top three Air Quality Reference Laboratories across the whole of Europe.

NPL continues to be involved in the EC-JRC-IRMM led development of a European certified reference material for PAHs and metals in PM₁₀ and, during 2009, will be a key partner in the interlaboratory comparison to characterise the candidate material.

²² http://ec.europa.eu/environment/integration/research/newsalert/pdf/118na5.pdf

²³ Intercomparison exercise for heavy metals in PM10, Gerboles, M, Buzica, D, EUR 23219 EN 2008.

http://ies.jrc.ec.europa.eu/uploads/fileadmin/Documentation/Reports/Emissions and Health/E UR 2006-2007/EUR 23219 EN.pdf

Annex 1 Location and Details of Sites Comprising the UK Heavy Metals Network

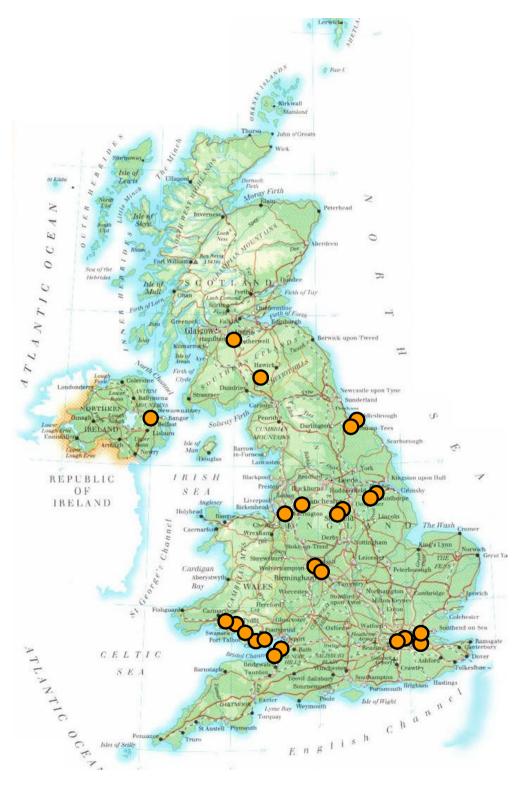


Figure A1. Location of monitoring sites comprising the UK Heavy Metals Monitoring Network (indicated by the orange circles) at the end of 2008 details of which are given in Table A1 below.

NEW Site Code: Site Name (Abbreviated Site Name)	OLD Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Classification (with identified point source, where applicable)	Pollutants measured
46: Walsall Centre (Walsall)	46: IMI Refiners Ltd, Walsall (IMI Walsall)	74 Primley Avenue, Walsall, WS2 9UW	Industrial Background (IMI Refiners Ltd, Walsall)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
47: Bristol Avonmouth (Avonmouth)	47: BZL Ltd, Avonmouth (BZL Avonmouth)	Avonmouth Medical Centre, Collins Street, Bristol, BS11 9JJ	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
56: Bristol Hallen (Hallen)	56: BZL Ltd, Avonmouth, Hallen Village (BZL Hallen)	West Country Caravans Ltd., Moorhouse Lane, Hallen, Bristol, BS10 7RU	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
58: Sheffield Brinsworth (Brinsworth)	58: Avesta Steel, Sheffield (Sheffield)	BOC Gases, Bawtry Road, Brinsworth, Sheffield, S60 5NT	Industrial Background (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
59: Runcorn Weston Point (Weston Point)	59: ICI Weston Point, Runcorn (Weston Point)	Weston Point County Primary School, Caster Avenue, Weston Point, Runcorn, WA7 4EQ	Industrial Background (INEOS Enterprises Ltd, Weston Point)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
61: London Cromwell Road (Cromwell Road)	61: London, Cromwell Road (London Cromwell)	Natural History Museum, Cromwell Road, London, SW7 5BD	Roadside	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
62: London Horseferry Road (Horseferry Road)	62: London, Horseferry Road (London Horseferry)	Mortuary Car Park, Horseferry Road, London, SW1P 2EB	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
65: Eskdalemuir (Eskdalemuir)	65: Eskdalemuir, Met Office (Eskdalemuir)	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	Rural	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
66: Motherwell Centre (Motherwell)	66: Motherwell, Civic Centre (Motherwell)	Civic Centre, Motherwell, Lanarkshire ML1 1TW	Urban Background	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
67: Manchester Wythenshawe (Wythenshawe)	67: Manchester M56, Junction 4 (Manchester)	Junction 4, M56, Newhall Green, Wythenshawe, Manchester, M23 2ZQ	Roadside	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
68: Cardiff Llandaff (Llandaff)	68: Cardiff, Waungron Road (Cardiff)	Cleansing Depot, Waungron, Fairwater, Cardiff, CF5 2JJ	Roadside / Urban background (Celsa UK Ltd, Tremorfa)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
69: Walsall Willenhall (Willenhall)	69: Brookside Metals, Bilston Lane, Walsall (Brookside Metals)	Adult Training Centre, Bilston Lane, Shepwell Green, Willenhall, Walsall, WV13 2QJ	Industrial Background (Brookside Metals Ltd, Willenhall)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
100: Swansea Coedgwilym (Coedgwilym)	100: Coedgwilym Cemetery (Swansea)	Coedgwilym Cemetery, Pontardawe Road, Clydach, Swansea, SA6 5PB	Industrial Background (Vale Inco Ltd, Swansea)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
101: Swansea Morriston (Morriston)	101: Morriston Groundhog (Swansea)	Morriston Groundhog, Wychtree Street, Morriston, Swansea, SA6 8EX	Urban Background (Vale Inco Ltd, Swansea)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
103: Belfast Centre AURN (Belfast)	103: Belfast Centre (Belfast)	Lombard Street, Belfast, BT1 1RB	Urban Centre (Belfast Metropolitan Urban Area)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn, Hg(v)
104: Port Talbot Margam AURN (Port Talbot)	104: Port Talbot	Port Talbot Fire Station, Commercial Road, Port Talbot, West Glamorgan, SA13 1LG	Industrial Background (Corus Group Ltd, Port Talbot)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn

NEW Site Code: Site Name (Abbreviated Site Name)	OLD Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Classification (with identified point source, where applicable)	Pollutants measured
105: Sheffield Centre AURN (Sheffield)	105: Sheffield Centre (Sheffield)	Charter Square, Sheffield, S1 4JD	Urban Centre (Outokumpu Stainless Ltd, Sheffiled)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
106: Scunthorpe Town AURN (Scunthorpe)	106: Scunthorpe Town	Rowlands Road, Scunthorpe, North Lincolnshire, DN16 1TJ	Urban Background (Corus Group Ltd, Scunthorpe)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
107: Scunthorpe Santon (Santon)	107: Santon	Dawes Lane, Saunton, Scunthorpe, North Lincolnshire, DN16 1XH	Industrial Background (Corus Group Ltd, Scunthorpe)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
108: Redcar AURN (Redcar)	108: Redcar	Further Education Centre, Corporation Road, Redcar, TS10 1HA	Industrial Background (Corus Group Ltd, Redcar)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
109: Cardiff Rumney (Rumney)	109: Cardiff Rumney	Greenway Primary School, Llanstephen Road, Rumney, Cardiff, CF3 3JG	Industrial Background (Celsa UK Ltd, Tremorfa)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
110: Chadwell St Mary (Chadwell St Mary)	110: Chadwell St Mary	Council Area Housing Office, Linford Road, Chadwell St Mary, Essex, RM16 4JY	Industrial Background (Britannia Refined Metals, Gravesend)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
111: Redcar Normanby (Normanby)	111: Redcar Flatts Lane	Tees, Esk and Wear Valleys NHS Trust, Flatts Lane, Normanby, Middlesbrough, TS6 0SZ	Urban Background (Corus Group Ltd, Redcar)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn
112: Dartford Bean (Bean)	112: Bean	Bean Primary School, Bean, Dartford, Kent, DA2 8AW	Urban Background (Britannia Refined Metals, Gravesend)	As, Cd, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, V, Zn

Table A1. Details of the sites comprising the UK Heavy Metals Monitoring Network at the end of 2008, including: site names, abbreviated site names, site name changes, site locations, site classification, point source monitored (where applicable) and pollutants measured.

Annex 2 Results of Partisol 2000 PM₁₀ Sampler Flow Audits

The sample flow for each sampler was measured using a BIOS Flow Calibrator, which was previously calibrated at NPL against weight loss from a cylinder, thus giving direct traceability to national standards. The reported flow rate 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 PM₁₀ sampler flow audits.

Site	Measured flow, I.min ⁻¹	Difference from set point (16.67 l.min ⁻¹)	Leak Test
Belfast Centre AURN	17.09	2.4 %	Passed
Bristol Avonmouth	16.56	-0.2 %	Passed
Bristol Hallen	17.07	2.9 %	Passed
Cardiff Rumney	16.11	-3.5 %	Passed
Cardiff, LLandaff	16.78	1.1 %	Passed
Chadwell St Mary	17.35	4.5 %	Passed
Dartford Bean	17.15	2.7 %	Passed
Eskdalemuir	17.44	4.4 %	Passed
London Cromwell Road	16.78	0.5 %	Passed
London Horseferry Road	17.08	2.9 %	Passed
Manchester Wythenshawe	17.49	4.7 %	Passed
Motherwell Centre	17.12	2.5 %	Passed
Port Talbot Margam AURN	17.18	2.9 %	Passed
Redcar AURN	17.02	1.9 %	Passed
Redcar Normanby	16.73	0.2 %	Passed
Runcorn Weston Point	17.14	2.7 %	Passed
Scunthorpe Santon	17.06	2.8 %	Passed
Scunthorpe Town AURN	17.13	2.6 %	Passed
Sheffield Brinsworth	17.17	2.8 %	Passed
Sheffield Centre	17.01	1.9 %	Passed
Swansea Coedgwilym	17.59	5.9 %	Passed
Swansea Morriston	17.26	3.3 %	Passed
Walsall Centre	16.63	-0.4 %	Passed
Walsall Willenhall	17.46	4.5 %	Passed

Table A2. Results of Partisol 2000 PM_{10} sampler flow audits for 2008.

The expanded uncertainty (k=2) in the flow measurements is 5.8 % expressed at the 95 % confidence interval. The average difference between the measured flows and the set point was 2.4 %. This is within the uncertainty of the measurement. The difference from set point determined from the audits of the Partisol 2000 samplers is used at ratification to adjust the volume recorded by the Partisol for each sample. If the difference from set point is greater than 10 % then remedial action would be taken, for example calling out the Equipment Support Unit (ESU).

Annex 3 Results of Total Gaseous Mercury Pump Flow Audits

The sample flow for each total gaseous mercury pump was measured using a BIOS Flow Calibrator, which was previously calibrated at NPL against weight loss from a cylinder, thus giving direct traceability to national standards. The reported flow rate is measured and reported at ambient conditions. A leak test was also performed on each sampler. The following table details the results of the total gaseous mercury pump flow audits.

Site	Set point / ml.min ⁻¹	Measured flow / ml.min ⁻¹	Difference from set point	Leak Test
Belfast Centre AURN	100	98.8	-1.2 %	Passed
Cardiff Llandaff	104	101.8	-2.1 %	Passed
Eskdalemuir	93	91.3	-1.9 %	Passed
London Cromwell Road	100	105.9	5.9 %	Passed
London Horseferry Road	100	103.0	3.0 %	Passed
Manchester Wythenshawe	110	129.0	17.3 %	Passed
Motherwell Centre	110	116.5	5.9 %	Passed
Runcorn Weston Point	100	105.0	5.0 %	Passed
Swansea Morriston	110	108.2	-1.7 %	Passed
Walsall Centre	113	113.7	0.5 %	Passed
Walsall Willenhall	104	104.3	0.1 %	Passed

Table A3. Results of total gaseous mercury pump flow audits for 2008.

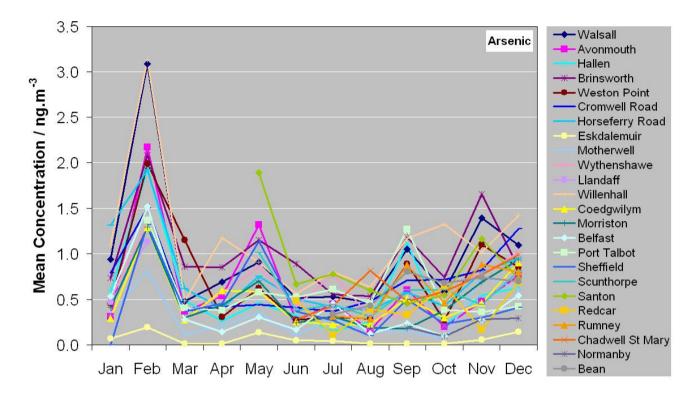
The expanded uncertainty (k=2) in the flow measurements is 5 % expressed at the 95 % confidence interval.

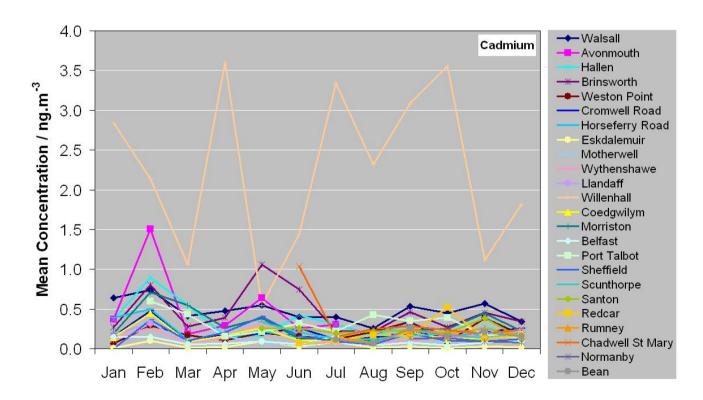
The average difference between the measured flows and the set point was 2.9 %.

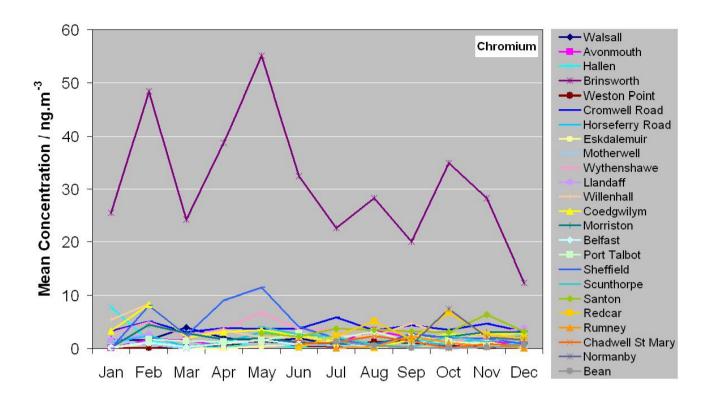
The difference from set point determined from the audits of the mercury vapour sampler pumps is used at ratification to adjust the volume recorded by the LSO for each sample. There is no threshold for remedial action on the mercury vapour samplers as the flow is adjusted by the LSO on a weekly basis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

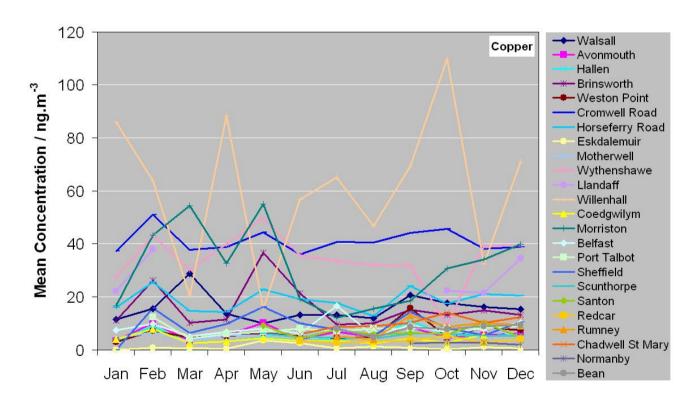
Annex 4 Average Monthly Metals Concentrations Measured for Each Element

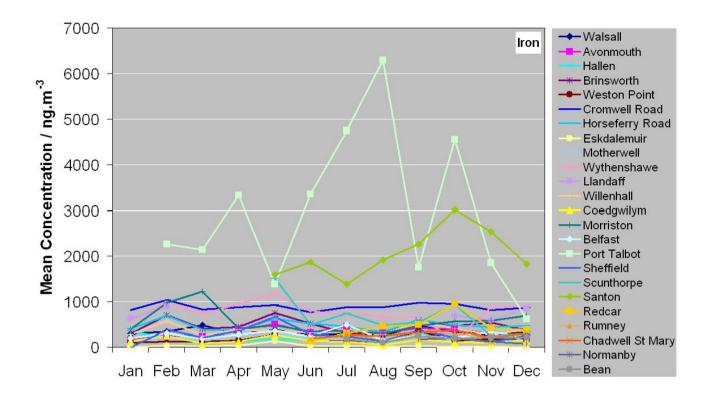
The following figures display the average monthly concentrations of each metal (as indicated in the top right-hand corner of each plot) measured at each site during 2008.

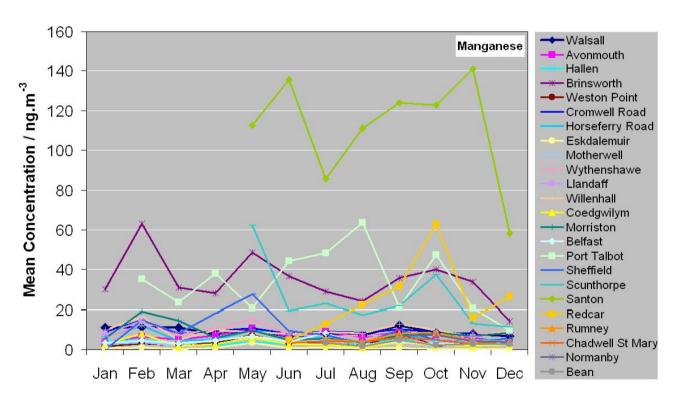


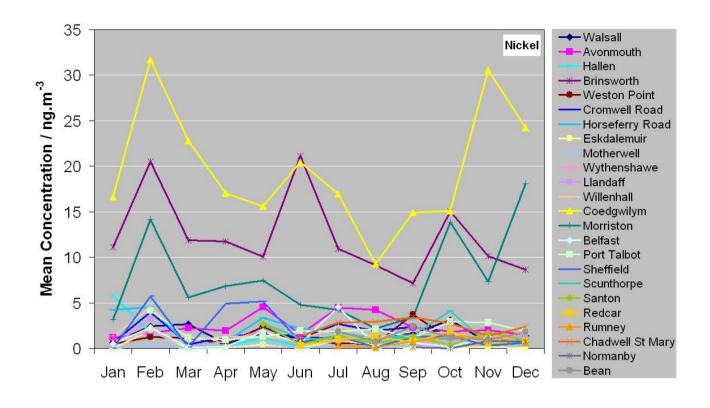


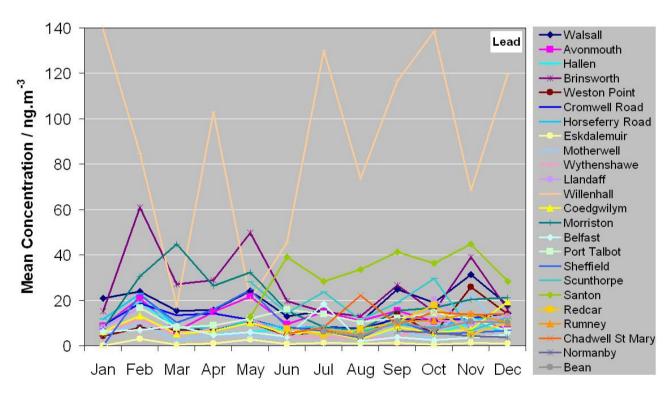


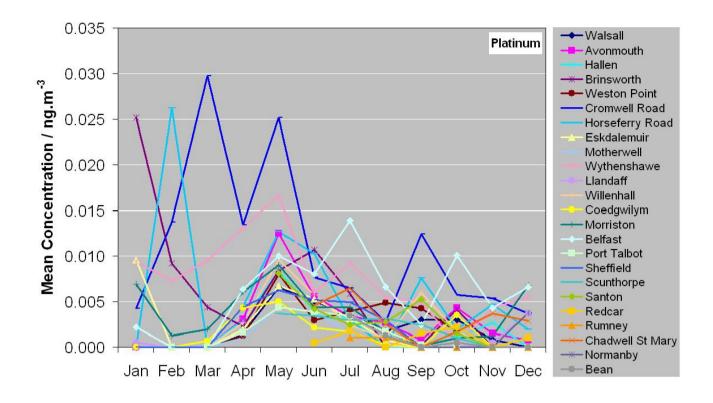


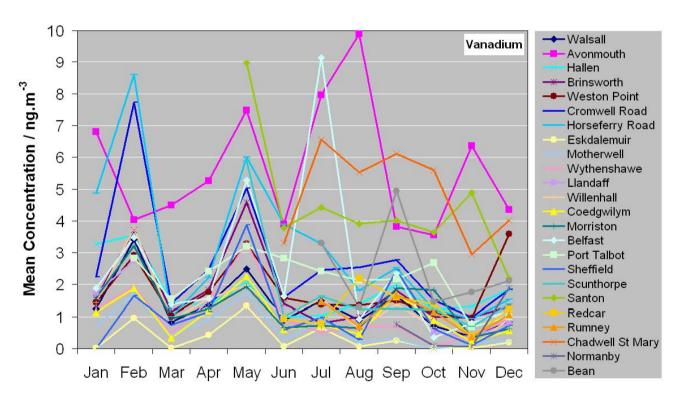


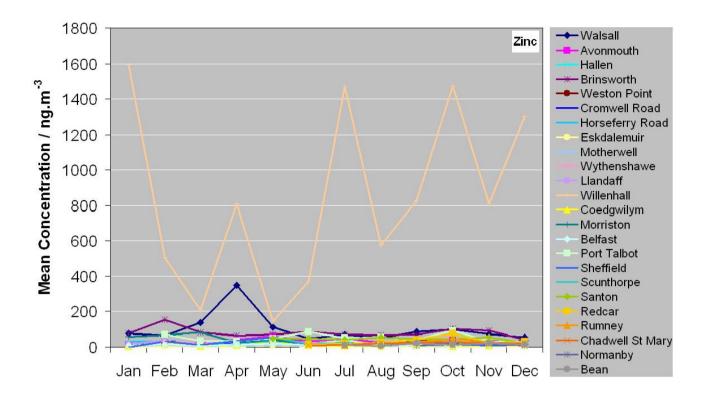


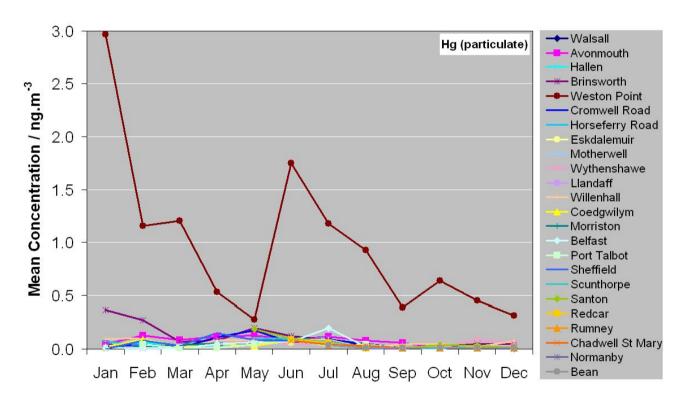


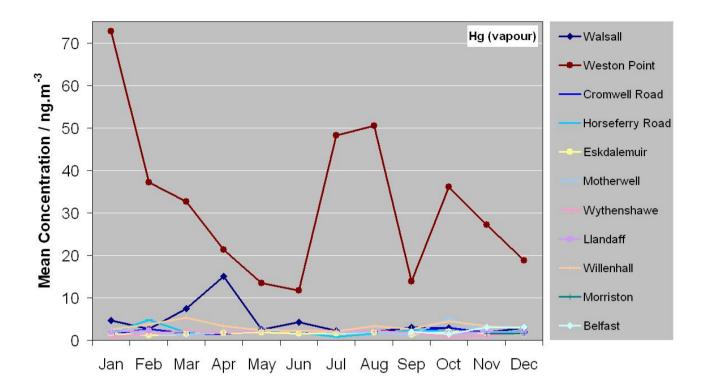












Annex 5 Average Monthly Metals Concentrations Measured at Each Network Site

The following tables display the average monthly concentrations measured at each site (as indicated at the top of each table) for each element during 2008.

Site 46: Walsall Centre

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.94	0.64	1.71	11.5	280	11.2	0.61	21.0	0.00	1.24	75.9	0.04	4.68
Feb	3.09	0.74	1.64	15.6	341	11.3	2.42	23.8	0.00	3.42	63.4	0.02	2.66
Mar	0.48	0.41	3.94	28.8	469	11.0	2.68	15.4	0.00	0.84	137.5	0.02	7.47
Apr	0.69	0.47	2.03	13.6	284	7.7	0.52	15.8	0.00	1.36	347.3	0.03	15.10
May	0.91	0.55	1.18	10.1	371	10.1	1.66	24.1	0.01	2.48	112.5	0.06	2.60
Jun	0.52	0.40	1.95	13.3	257	6.5	1.30	13.0	0.01	0.90	47.5	0.09	4.23
Jul	0.53	0.40	0.61	13.2	283	7.9	0.97	15.3	0.00	1.50	69.0	0.09	2.22
Aug	0.47	0.26	0.44	12.0	253	7.0	1.23	10.4	0.00	0.89	50.9	0.03	1.96
Sep	1.05	0.53	1.81	20.7	454	12.1	1.62	24.9	0.00	1.64	86.2	0.01	3.12
Oct	0.58	0.44	0.28	17.6	332	8.6	3.08	19.0	0.00	0.72	99.0	0.01	2.94
Nov	1.40	0.57	0.77	16.2	262	8.0	0.60	31.4	0.00	0.37	74.8	0.01	1.87
Dec	1.10	0.34	1.21	15.4	329	6.9	0.99	17.8	0.00	0.84	55.7	0.01	2.86
Annual Average	0.98	0.48	1.46	15.7	326	9.0	1.47	19.3	0.00	1.35	101.6	0.03	4.31

Site 47: Bristol Avonmouth

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg(p)	Hg(v)
Jan	0.31	0.37	0.10	3.4	168	3.7	1.15	8.8	0.00	6.81	16.9	0.05	N/A
Feb	2.17	1.51	1.68	10.1	262	6.5	1.68	21.0	0.00	4.04	29.1	0.13	N/A
Mar	0.37	0.18	1.63	3.5	219	5.0	2.21	6.6	0.00	4.50	24.0	0.09	N/A
Apr	0.53	0.29	0.40	5.5	368	7.1	1.92	15.0	0.00	5.26	40.6	0.12	N/A
May	1.32	0.64	1.43	10.1	499	10.7	4.54	21.7	0.01	7.48	59.5	0.13	N/A
Jun	0.27	0.26	0.91	3.9	317	6.6	1.53	9.4	0.01	3.89	32.0	0.09	N/A
Jul	0.45	0.30	1.07	6.8	451	9.2	4.45	14.8	0.00	7.96	47.4	0.12	N/A
Aug	0.16	0.16	3.46	5.0	314	6.3	4.20	11.0	0.00	9.89	26.8	0.08	N/A
Sep	0.61	0.33	1.99	8.4	410	8.8	2.31	15.4	0.00	3.82	42.7	0.06	N/A
Oct	0.20	0.16	0.37	4.7	388	7.4	1.85	10.8	0.00	3.55	40.2	0.01	N/A
Nov	0.48	0.21	1.29	5.5	297	6.0	1.99	11.0	0.00	6.37	38.5	0.01	N/A
Dec	0.76	0.17	0.88	6.1	176	3.3	1.52	7.7	0.00	4.36	18.3	0.02	N/A
Annual Average	0.64	0.38	1.27	6.1	322	6.7	2.45	12.8	0.00	5.66	34.7	0.07	N/A

Site 56: Bristol Hallen

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.58	0.37	7.77	3.3	327	3.9	5.86	9.0	0.00	3.26	14.5	0.03	N/A
Feb	1.93	0.90	1.51	9.0	222	5.2	1.74	19.1	0.00	3.55	24.9	0.06	N/A
Mar	0.48	0.55	0.10	2.5	123	2.8	0.12	8.1	0.00	1.45	17.0	0.03	N/A
Apr	0.26	0.17	0.36	3.3	126	2.4	0.31	5.1	0.00	1.35	12.7	0.05	N/A
May	0.46	0.16	1.19	4.6	184	3.9	1.15	5.9	0.01	2.08	14.0	0.04	N/A
Jun	0.32	0.42	0.16	3.7	146	2.8	0.25	7.5	0.00	0.99	15.5	0.10	N/A
Jul	0.15	0.31	1.53	3.9	133	2.6	0.90	5.1	0.00	1.03	13.3	0.10	N/A
Aug	0.26	0.15	1.07	4.9	170	2.8	0.26	6.2	0.00	1.39	15.5	0.01	N/A
Sep	1.12	0.32	1.99	10.8	304	5.6	1.17	11.9	0.00	1.99	27.2	0.01	N/A
Oct	0.21	0.13	0.17	5.7	234	2.9	1.29	4.9	0.00	1.21	15.8	0.01	N/A
Nov	0.54	0.27	0.23	5.0	152	3.3	0.39	10.0	0.00	1.31	26.4	0.02	N/A
Dec	0.63	0.15	1.17	6.0	173	2.3	0.54	5.8	0.00	1.85	14.6	0.01	N/A
Annual Average	0.58	0.33	1.44	5.2	191	3.4	1.17	8.2	0.00	1.79	17.6	0.04	N/A

Site 58: Sheffield Brinsworth

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.74	0.27	25.42	11.0	291	30.1	11.16	15.1	0.03	1.56	77.8	0.37	N/A
Feb	2.08	0.80	48.37	26.2	692	63.0	20.54	61.0	0.01	3.71	153.0	0.27	N/A
Mar	0.86	0.28	24.19	10.3	397	31.1	11.90	27.1	0.00	1.16	82.4	0.07	N/A
Apr	0.86	0.39	38.66	11.6	433	28.3	11.75	28.8	0.00	1.83	63.4	0.08	N/A
May	1.15	1.06	55.07	36.6	748	48.7	10.06	49.7	0.01	4.58	70.4	0.20	N/A
Jun	0.89	0.75	32.38	21.2	511	36.6	21.15	19.8	0.01	1.41	85.2	0.12	N/A
Jul	0.56	0.22	22.57	9.6	303	29.0	10.96	15.0	0.01	0.80	70.5	0.08	N/A
Aug	0.54	0.21	28.26	10.1	291	24.2	9.16	12.9	0.00	0.99	67.6	0.01	N/A
Sep	1.18	0.46	20.01	15.1	588	35.9	7.16	26.7	0.00	1.81	70.3	0.01	N/A
Oct	0.74	0.27	34.88	13.2	462	40.0	15.04	14.9	0.00	0.99	102.1	0.02	N/A
Nov	1.66	0.45	28.28	15.0	529	33.8	10.14	39.0	0.00	0.98	92.1	0.05	N/A
Dec	0.84	0.34	12.35	13.3	367	14.3	8.67	16.0	0.00	1.32	41.2	0.01	N/A
Annual Average	1.01	0.46	30.87	16.1	468	34.6	12.31	27.2	0.01	1.76	81.3	0.11	N/A

Site 59: Runcorn Weston Point

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	0.45	0.06	0.08	2.9	94	1.8	0.48	4.3	0.00	1.43	4.4	2.97	72.7
Feb	1.99	0.29	0.07	7.2	121	3.0	1.26	7.9	0.00	2.92	11.3	1.15	37.1
Mar	1.15	0.17	0.28	4.7	120	2.3	1.14	6.9	0.00	1.03	12.8	1.21	32.6
Apr	0.31	0.10	0.60	5.0	153	3.3	0.52	7.2	0.00	1.76	13.3	0.53	21.3
May	0.62	0.20	1.27	6.5	268	7.3	2.39	10.2	0.01	3.28	21.4	0.28	13.5
Jun	0.28	0.15	0.56	5.0	138	2.9	0.73	4.5	0.00	1.58	23.0	1.75	11.8
Jul	0.31	0.12	0.35	4.4	137	3.0	0.56	6.4	0.00	1.36	11.0	1.18	48.2
Aug	0.28	0.21	1.24	4.8	124	1.9	0.50	3.8	0.00	1.36	8.0	0.93	50.4
Sep	0.89	0.34	1.10	15.8	352	7.9	3.71	13.8	0.00	1.49	43.3	0.39	13.9
Oct	0.27	0.09	0.59	4.8	154	1.9	0.97	5.1	0.00	1.12	22.5	0.64	36.1
Nov	1.10	0.38	0.21	8.5	169	2.9	1.01	25.8	0.00	0.96	29.7	0.45	27.2
Dec	0.85	0.18	0.45	7.5	181	2.6	1.65	13.9	0.00	3.58	20.4	0.31	18.8
Annual Average	0.71	0.19	0.57	6.4	168	3.4	1.24	9.2	0.00	1.82	18.4	0.98	32.0

Site 61: London Cromwell Road

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.79	0.16	3.30	37.2	805	8.9	0.65	9.0	0.00	2.24	16.3	0.02	1.48
Feb	1.50	0.48	5.09	51.0	1031	14.8	3.99	18.6	0.01	7.73	33.8	0.04	2.69
Mar	0.37	0.09	3.04	37.7	818	8.0	0.45	13.3	0.03	1.41	20.5	0.01	1.64
Apr	0.42	0.18	3.88	38.9	864	9.3	1.22	14.2	0.01	2.46	28.2	0.11	1.46
May	0.44	0.19	3.73	44.2	925	10.9	1.65	11.4	0.03	5.03	33.8	0.17	2.59
Jun	0.41	0.26	3.73	36.1	759	7.8	1.03	7.5	0.01	1.59	18.4	0.06	1.84
Jul	0.37	0.11	5.85	40.7	868	9.1	2.67	8.4	0.01	2.46	21.5	0.09	2.07
Aug	0.48	0.14	3.38	40.5	873	8.6	1.93	7.5	0.00	2.54	22.0	0.05	2.03
Sep	0.71	0.21	4.38	44.2	968	10.4	2.38	12.0	0.01	2.76	29.5	0.01	2.25
Oct	0.71	0.15	3.54	45.5	947	8.7	1.53	11.0	0.01	1.52	24.3	0.01	2.97
Nov	0.82	0.21	4.67	38.2	807	7.7	0.98	12.1	0.01	0.98	25.1	0.01	1.69
Dec	1.28	0.26	3.17	38.7	853	8.5	1.34	14.1	0.00	1.86	34.0	0.01	1.89
Annual Average	0.69	0.20	3.98	41.1	876	9.4	1.65	11.6	0.01	2.71	25.6	0.05	2.05

Site 62: London Horseferry Road

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	1.32	0.39	1.16	16.0	398	6.6	4.25	11.8	0.00	4.87	33.0	0.07	1.79
Feb	1.92	0.50	2.45	25.6	689	12.1	4.57	22.8	0.03	8.60	32.5	0.04	4.81
Mar	0.62	0.12	0.27	14.7	367	4.5	0.27	8.3	0.00	1.00	11.4	0.02	1.82
Apr	0.40	0.13	1.04	14.3	372	5.0	0.73	7.4	0.00	2.23	16.5	0.05	1.80
May	0.75	0.22	3.04	22.8	620	9.8	3.37	10.9	0.01	6.01	31.0	0.05	2.00
Jun	0.51	0.14	2.71	19.2	509	7.6	2.18	7.8	0.01	3.90	21.4	0.07	1.86
Jul	0.42	0.13	1.69	17.6	442	5.9	1.76	8.4	0.00	3.28	16.7	0.09	0.86
Aug	0.38	0.11	0.60	12.9	318	4.0	1.03	6.3	0.00	1.82	12.7	0.02	1.66
Sep	0.58	0.20	1.44	24.0	596	7.6	1.33	9.4	0.01	2.53	24.6	0.01	2.42
Oct	0.43	0.11	0.69	17.4	477	4.4	0.96	8.0	0.00	1.20	17.7	0.01	2.11
Nov	0.80	0.19	2.17	21.2	434	5.0	0.63	11.9	0.00	0.95	21.8	0.01	1.76
Dec	0.95	0.22	1.63	20.4	461	5.2	0.99	11.6	0.00	1.53	21.5	0.01	2.14
Annual Average	0.76	0.20	1.57	18.8	474	6.5	1.84	10.4	0.01	3.16	21.7	0.04	2.08

Site 65: Eskdalemuir

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.07	0.01	0.10	0.0	1	0.7	0.01	0.1	0.01	0.01	0.0	0.01	1.57
Feb	0.20	0.10	0.96	8.0	40	1.1	1.99	2.9	0.00	0.96	3.2	0.01	1.24
Mar	0.01	0.01	0.10	0.7	30	0.4	0.01	0.5	0.00	0.01	1.9	0.01	1.41
Apr	0.01	0.02	0.01	0.3	36	0.8	0.09	1.0	0.00	0.43	2.9	0.01	1.69
May	0.14	0.09	0.38	3.6	132	3.3	0.43	2.7	0.01	1.33	8.6	0.04	1.83
Jun	0.05	0.03	0.86	2.5	26	0.8	0.05	0.7	0.01	0.07	2.6	0.05	1.57
Jul	0.04	0.09	0.64	0.7	27	1.2	0.84	1.1	0.00	0.65	2.6	0.04	1.66
Aug	0.01	0.02	0.29	1.4	14	0.5	0.37	0.9	0.00	0.07	1.8	0.02	1.80
Sep	0.01	0.03	0.29	0.8	25	0.8	0.01	1.3	0.00	0.25	2.9	0.01	1.39
Oct	0.01	0.01	0.01	0.3	15	0.2	0.09	0.4	0.00	0.01	1.2	0.01	2.04
Nov	0.05	0.03	1.25	1.0	17	0.3	0.13	1.3	0.00	0.01	3.5	0.01	1.68
Dec	0.14	0.02	0.01	0.6	5	0.2	0.06	1.0	0.00	0.20	2.6	0.01	1.46
Annual Average	0.06	0.04	0.41	1.1	31	0.9	0.34	1.2	0.00	0.33	2.8	0.02	1.61

Site 66: Motherwell Centre

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.35	0.17	1.47	4.5	141	2.6	0.01	4.8	0.00	0.71	7.2	0.01	2.86
Feb	0.81	0.34	0.79	6.6	194	3.6	0.39	9.7	0.00	1.71	13.6	0.01	1.65
Mar	0.11	0.04	0.01	3.5	119	2.1	0.01	2.3	0.00	0.45	5.6	0.01	1.39
Apr	0.21	0.16	1.03	5.6	315	5.2	0.18	4.6	0.00	0.90	11.1	0.03	1.93
May	0.36	0.08	0.92	5.6	321	6.6	0.60	4.1	0.00	1.74	12.2	0.04	2.64
Jun	0.11	0.05	0.72	5.1	179	3.0	0.01	3.2	0.00	0.24	10.8	0.05	2.12
Jul	0.30	0.09	0.52	8.5	174	2.8	0.37	9.1	0.00	0.91	10.9	0.04	1.88
Aug	0.15	0.06	0.57	5.6	142	2.1	0.03	2.5	0.00	0.20	6.3	0.02	1.86
Sep	0.15	0.06	0.22	6.0	277	4.0	0.22	6.6	0.00	0.31	9.9	0.01	1.38
Oct	0.08	0.07	0.01	4.9	152	1.9	0.01	3.1	0.00	0.01	6.2	0.01	5.15
Nov	0.75	0.25	0.17	8.9	369	5.1	1.00	22.2	0.00	0.16	35.1	0.01	2.18
Dec	0.62	0.12	0.65	4.6	118	2.3	1.34	6.6	0.00	0.27	14.1	0.01	1.72
Annual Average	0.33	0.12	0.59	5.8	208	3.4	0.35	6.6	0.00	0.64	11.9	0.02	2.23

Site 67: Manchester Wythenshawe

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.51	0.12	2.96	27.4	566	6.5	0.78	5.9	0.01	1.26	18.0	0.01	0.80
Feb	1.33	0.27	5.05	43.1	980	12.4	1.85	11.6	0.01	1.94	32.1	0.02	1.61
Mar	0.27	0.07	2.19	30.2	721	7.4	0.18	4.6	0.01	0.48	22.9	0.01	2.14
Apr	0.57	0.13	3.70	39.9	943	10.4	0.72	7.8	0.01	1.47	31.2	0.05	1.81
May	0.86	0.32	6.68	49.6	1168	15.2	2.02	11.8	0.02	3.31	41.8	0.08	2.22
Jun	0.42	0.08	3.60	35.9	779	7.8	0.45	4.3	0.01	0.93	25.4	0.05	2.19
Jul	0.78	0.08	3.61	33.4	710	6.9	0.84	3.7	0.01	0.52	20.6	0.05	2.28
Aug	0.30	0.09	3.55	31.9	662	7.0	1.02	3.4	0.01	0.67	20.8	0.01	2.33
Sep	0.32	0.09	3.39	31.8	664	7.1	0.89	3.5	0.00	0.71	20.3	0.01	1.72
Oct	0.66	0.17	0.83	9.3	148	1.6	0.19	11.1	0.00	0.09	13.0	0.01	0.74
Nov	0.78	0.16	2.82	39.3	869	8.3	0.60	10.4	0.00	0.40	28.6	0.09	1.02
Dec	1.02	0.17	3.87	39.5	877	8.1	1.64	10.4	0.01	0.96	28.8	0.06	2.04
Annual Average	0.65	0.15	3.52	34.3	757	8.2	0.93	7.4	0.01	1.06	25.3	0.04	1.74

Site 68: Cardiff Llandaff

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.46	0.18	1.65	22.1	621	8.1	0.29	7.8	0.00	1.72	15.7	0.01	2.02
Feb	1.13	0.32	2.71	38.0	880	14.4	3.25	16.7	0.00	2.75	38.7	0.03	2.21
Mar	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
Apr	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
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
Jun	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
Jul	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
Aug	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
Sep	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
Oct	0.36	0.15	2.15	22.4	688	7.8	0.88	20.4	0.00	0.47	22.8	0.01	1.64
Nov	0.44	0.16	1.96	21.6	583	6.6	1.17	9.1	0.00	0.37	27.3	0.01	2.04
Dec	0.91	0.22	3.82	34.5	844	9.1	1.25	12.9	0.00	0.80	27.1	0.01	1.66
Annual Average	0.66	0.21	2.46	27.7	723	9.2	1.37	13.4	0.00	1.22	26.3	0.01	1.91

Site 69: Walsall Willenhall

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	v	Zn	Hg(p)	Hg(v)
Jan	1.10	2.85	5.39	85.9	277	10.0	1.37	139.3	0.00	1.43	1595.7	0.10	2.58
Feb	3.14	2.14	8.47	63.7	576	16.5	4.50	84.8	0.00	3.77	506.7	0.10	3.69
Mar	0.48	1.06	2.02	20.4	244	4.7	0.82	17.4	0.00	0.89	207.1	0.01	5.36
Apr	1.18	3.60	3.39	88.2	381	9.9	1.33	102.9	0.00	1.55	808.1	0.08	3.27
May	0.91	0.55	2.10	15.5	348	8.8	1.28	20.3	0.01	1.98	145.5	0.09	2.34
Jun	0.56	1.45	2.10	56.8	316	8.0	0.96	45.6	0.01	0.99	372.2	0.09	2.22
Jul	0.80	3.34	2.45	65.0	344	8.7	2.46	130.0	0.00	1.55	1470.3	0.09	2.19
Aug	0.63	2.32	2.35	46.7	276	8.2	1.15	73.5	0.00	0.63	576.0	0.01	3.30
Sep	1.17	3.08	4.64	69.3	564	12.9	1.86	116.6	0.01	1.39	827.8	0.05	2.63
Oct	1.32	3.56	2.58	109.7	402	10.0	1.67	138.6	0.00	0.67	1475.1	0.05	4.59
Nov	1.02	1.12	2.03	32.5	268	6.5	0.44	68.4	0.00	0.10	809.0	0.02	3.33
Dec	1.43	1.82	3.04	71.0	369	9.6	2.01	119.7	0.00	0.92	1299.8	0.08	2.79
Annual Average	1.15	2.24	3.38	60.4	364	9.5	1.66	88.1	0.00	1.32	841.1	0.06	3.19

Site 100: Swansea Coedgwilym

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	0.29	0.14	3.31	4.1	135	2.9	16.66	6.2	0.00	1.14	7.0	0.02	N/A
Feb	1.29	0.44	8.32	7.8	244	7.9	31.69	13.1	0.00	1.88	24.7	0.09	N/A
Mar	0.27	0.09	1.98	2.5	83	1.7	22.79	5.2	0.00	0.34	6.9	0.03	N/A
Apr	0.60	0.16	3.14	3.3	129	2.9	17.02	6.5	0.00	1.20	11.7	0.05	N/A
May	0.58	0.26	3.51	4.4	279	6.1	15.61	10.3	0.00	2.25	25.3	0.03	N/A
Jun	0.26	0.10	2.33	3.4	135	2.9	20.43	5.2	0.00	0.61	13.7	0.08	N/A
Jul	0.23	0.12	1.34	3.4	119	2.5	17.00	6.3	0.00	0.74	9.8	0.07	N/A
Aug	0.23	0.06	0.09	2.5	55	1.1	9.28	2.8	0.00	0.47	6.0	0.01	N/A
Sep	0.51	0.21	1.69	4.3	161	3.7	14.92	8.3	0.00	1.71	15.7	0.01	N/A
Oct	0.30	0.12	2.70	2.7	112	2.2	15.13	5.6	0.00	0.89	7.6	0.01	N/A
Nov	0.46	0.14	2.70	5.8	96	1.9	30.56	7.2	0.00	0.21	10.9	0.01	N/A
Dec	0.90	0.15	2.85	10.0	145	2.5	24.26	19.4	0.00	0.57	20.1	0.01	N/A
Annual Average	0.49	0.17	2.83	4.5	141	3.2	19.61	8.0	0.00	1.00	13.3	0.04	N/A

Site 101: Swansea Morriston

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	0.41	0.19	0.22	16.7	385	5.6	3.16	7.5	0.01	1.59	56.7	0.01	N/A
Feb	1.29	0.71	4.43	43.3	970	19.2	14.20	30.7	0.00	3.22	66.6	0.02	N/A
Mar	0.30	0.54	2.92	54.3	1223	14.5	5.57	44.9	0.00	0.93	83.1	0.04	N/A
Apr	0.44	0.27	1.69	32.5	399	6.0	6.81	26.3	0.01	1.25	24.4	0.05	N/A
May	0.70	0.38	1.87	54.9	471	9.7	7.49	32.5	0.01	1.93	41.9	0.05	N/A
Jun	0.24	0.13	1.13	19.1	331	5.0	4.81	15.3	0.00	0.65	17.5	0.11	N/A
Jul	0.31	0.12	0.89	12.1	348	5.7	4.24	8.1	0.00	0.72	17.2	0.05	N/A
Aug	0.18	0.09	0.82	15.5	285	3.6	2.20	6.9	0.00	0.64	12.1	0.01	N/A
Sep	0.18	0.24	2.40	18.7	463	7.0	3.40	15.3	0.00	1.88	32.8	0.01	N/A
Oct	0.38	0.25	2.20	30.8	556	8.5	13.89	16.6	0.00	1.82	26.9	0.01	N/A
Nov	0.69	0.45	3.12	34.1	568	6.7	7.36	20.4	0.00	0.35	26.3	0.01	1.55
Dec	0.94	0.22	3.08	39.9	686	8.6	18.11	21.2	0.01	0.62	32.0	0.01	1.61
Annual Average	0.51	0.30	2.06	31.0	557	8.3	7.60	20.5	0.00	1.30	36.5	0.03	1.58

Site 103: Belfast Centre AURN

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	0.54	0.15	0.22	7.5	194	3.5	0.48	6.1	0.00	1.89	11.0	0.01	N/A
Feb	1.52	0.15	1.19	9.9	300	4.5	2.32	6.9	0.00	3.49	15.1	0.01	N/A
Mar	0.28	0.05	0.35	5.1	188	3.1	0.12	8.6	0.00	1.39	10.5	0.01	N/A
Apr	0.15	0.07	0.85	6.9	277	4.6	0.20	4.6	0.01	1.56	13.4	0.05	N/A
May	0.31	0.09	1.63	8.0	354	6.8	1.85	6.1	0.01	5.28	18.5	0.06	N/A
Jun	0.17	0.05	0.73	6.1	231	3.8	0.58	4.0	0.01	1.63	12.6	0.07	N/A
Jul	0.45	0.16	1.39	16.7	481	8.2	4.52	18.4	0.01	9.14	42.5	0.20	N/A
Aug	0.13	0.04	0.14	5.2	151	2.5	0.31	1.9	0.01	0.93	7.3	0.02	N/A
Sep	0.24	0.08	2.67	9.4	249	4.0	0.62	3.8	0.00	2.34	12.6	0.01	2.06
Oct	0.10	0.05	0.96	6.5	213	3.0	0.20	2.5	0.01	0.36	9.6	0.01	1.47
Nov	0.27	0.07	0.61	8.1	325	3.3	1.27	3.6	0.00	0.80	11.8	0.01	3.09
Dec	0.54	0.10	0.10	10.2	227	3.1	0.44	4.9	0.01	1.17	11.9	0.01	3.01
Annual Average	0.39	0.09	0.90	8.3	266	4.2	1.08	6.0	0.01	2.50	14.7	0.04	2.41

Site 104: Port Talbot Margam AURN

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	N/A	N/A											
Feb	1.37	0.59	1.75	12.5	2261	35.2	4.15	16.7	0.00	2.82	71.0	0.04	N/A
Mar	0.41	0.44	1.42	4.4	2140	23.5	1.16	7.9	0.00	1.54	34.3	0.01	N/A
Apr	0.38	0.16	1.27	6.0	3331	38.1	0.93	9.1	0.00	2.42	35.0	0.01	N/A
May	0.58	0.21	1.51	6.9	1376	20.7	1.30	12.0	0.00	3.20	48.8	0.05	N/A
Jun	0.52	0.32	2.91	8.2	3363	44.2	1.95	15.8	0.00	2.83	84.8	0.09	N/A
Jul	0.61	0.22	1.80	7.0	4744	48.4	1.90	13.9	0.00	2.41	52.0	0.03	N/A
Aug	0.46	0.43	3.25	8.1	6302	63.6	2.11	10.5	0.00	2.14	54.1	0.04	N/A
Sep	1.27	0.35	1.18	8.1	1755	21.1	1.17	12.2	0.00	2.16	41.8	0.01	N/A
Oct	0.39	0.39	1.24	8.2	4561	47.4	2.95	14.4	0.00	2.69	91.6	0.01	N/A
Nov	0.36	0.17	1.00	8.2	1858	20.7	2.84	11.8	0.00	0.68	32.5	0.01	N/A
Dec	0.42	0.18	0.07	8.9	609	9.6	1.86	6.4	0.00	1.00	32.2	0.01	N/A
Annual Average	0.62	0.31	1.58	7.9	2936	33.9	2.03	11.9	0.00	2.17	52.5	0.03	N/A

Site 105: Sheffield Centre AURN

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	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
Feb	1.32	0.36	8.14	15.8	375	14.9	5.74	22.4	0.00	1.65	31.2	0.08	N/A
Mar	0.37	0.10	2.49	6.3	216	8.2	0.13	10.3	0.00	0.75	13.5	0.03	N/A
Apr	0.46	0.21	9.11	9.7	346	18.1	4.91	16.0	0.00	1.16	36.3	0.15	N/A
May	1.14	0.41	11.48	16.2	655	27.6	5.19	24.5	0.01	3.87	53.8	0.08	N/A
Jun	0.37	0.15	4.00	10.1	275	9.5	0.68	8.3	0.01	0.58	16.7	0.08	N/A
Jul	0.27	0.09	1.96	7.6	234	7.4	1.40	6.5	0.00	0.97	14.1	0.07	N/A
Aug	0.10	0.06	0.38	5.3	138	3.2	0.11	3.4	0.00	0.29	7.8	0.01	N/A
Sep	0.50	0.19	2.78	14.2	366	9.9	1.26	11.3	0.00	2.46	28.8	0.01	N/A
Oct	0.23	0.10	2.07	8.3	211	4.8	1.34	5.1	0.00	0.63	15.4	0.01	N/A
Nov	0.30	0.09	1.92	5.5	111	2.8	0.34	5.8	0.00	0.12	10.0	0.01	N/A
Dec	0.41	0.12	0.86	10.4	264	6.0	0.64	6.8	0.00	0.72	12.0	0.01	N/A
Annual Average	0.50	0.17	4.11	9.9	290	10.2	1.98	11.0	0.00	1.20	21.8	0.05	N/A

Site 106: Scunthorpe Town AURN

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
May	1.01	0.33	4.06	6.2	1501	62.1	2.75	28.1	0.00	5.88	53.0	0.11	N/A
Jun	0.38	0.21	2.65	4.8	491	19.4	1.15	14.4	0.00	1.00	19.4	0.10	N/A
Jul	0.45	0.12	2.10	4.6	728	22.9	0.98	23.5	0.00	1.63	25.1	0.07	N/A
Aug	0.31	0.12	0.77	4.3	476	17.2	1.09	11.5	0.00	1.22	19.1	0.01	N/A
Sep	0.61	0.17	0.23	6.2	533	22.0	1.49	19.0	0.00	1.25	24.0	0.01	N/A
Oct	0.61	0.18	2.39	6.1	935	37.4	4.08	29.6	0.00	1.21	30.0	0.01	N/A
Nov	0.44	0.13	1.24	5.4	241	12.9	0.51	6.7	0.00	0.70	17.6	0.01	N/A
Dec	0.81	0.20	2.46	5.3	296	11.5	0.79	11.9	0.00	1.39	18.5	0.01	N/A
Annual Average	0.58	0.18	1.99	5.4	650	25.7	1.61	18.1	0.00	1.78	25.8	0.04	N/A

Site 107: Scunthorpe Santon

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
May	1.89	0.26	2.86	9.2	1594	112.5	2.70	12.7	0.01	8.97	48.9	0.19	N/A
Jun	0.67	0.26	2.27	4.3	1865	135.5	0.43	39.1	0.00	3.78	48.9	0.10	N/A
Jul	0.78	0.20	3.73	7.8	1378	85.6	1.38	28.4	0.00	4.42	41.2	0.06	N/A
Aug	0.60	0.22	3.49	5.7	1909	111.2	0.57	33.5	0.00	3.91	53.7	0.01	N/A
Sep	0.46	0.24	3.16	6.3	2257	123.9	1.29	41.4	0.01	4.01	44.4	0.01	N/A
Oct	0.55	0.20	3.10	6.0	3023	122.7	0.40	36.2	0.00	3.65	44.5	0.04	N/A
Nov	1.16	0.39	6.38	10.3	2540	140.9	1.74	44.8	0.00	4.88	53.3	0.03	N/A
Dec	0.73	0.13	3.20	4.6	1831	58.2	0.94	28.2	0.00	2.19	21.4	0.01	N/A
Annual Average	0.85	0.24	3.52	6.8	2050	111.3	1.18	33.1	0.00	4.48	44.6	0.06	N/A

Site 108: Redcar AURN

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
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
Jun	0.49	0.07	0.25	3.4	131	4.9	0.30	7.4	0.00	0.93	15.6	0.09	N/A
Jul	0.11	0.10	2.38	2.7	300	12.7	0.97	4.8	0.00	0.79	17.7	0.06	N/A
Aug	0.39	0.17	5.17	3.3	453	22.3	1.28	7.3	0.00	2.19	27.0	0.01	N/A
Sep	0.33	0.16	1.73	3.6	479	31.6	0.70	10.4	0.00	1.59	40.3	0.01	N/A
Oct	0.65	0.52	6.74	5.4	949	62.8	1.86	18.0	0.00	1.39	76.5	0.01	N/A
Nov	0.17	0.13	2.56	2.7	409	16.0	0.56	5.1	0.00	0.40	23.8	0.01	N/A
Dec	0.68	0.17	1.97	4.1	376	26.5	0.79	10.3	0.00	1.23	31.2	0.01	N/A
Annual Average	0.40	0.19	2.97	3.6	443	25.3	0.92	9.1	0.00	1.22	33.2	0.03	N/A

Site 109: Cardiff Rumney

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
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
Jun	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
Jul	0.32	0.14	0.06	5.2	292	5.1	0.31	7.3	0.00	1.47	12.0	0.04	N/A
Aug	0.29	0.08	0.35	4.1	147	4.0	0.14	4.9	0.00	0.72	18.1	0.02	N/A
Sep	0.88	0.23	2.30	13.1	310	8.4	0.73	10.4	0.00	1.66	27.7	0.01	N/A
Oct	0.46	0.19	1.03	8.7	299	8.6	1.31	11.3	0.00	1.15	45.4	0.01	N/A
Nov	0.89	0.26	0.42	10.1	201	4.5	1.22	14.1	0.00	0.38	28.5	0.01	N/A
Dec	0.80	0.16	0.07	9.3	223	3.9	0.60	10.2	0.00	1.06	18.4	0.01	N/A
Annual Average	0.61	0.18	0.70	8.4	245	5.8	0.72	9.7	0.00	1.07	25.0	0.02	N/A

Site 110: Chadwell St. Mary

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
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
Jun	0.28	1.04	0.85	6.0	190	3.3	1.29	5.3	0.00	3.31	9.9	0.08	N/A
Jul	0.43	0.15	1.21	8.7	261	4.2	2.88	8.2	0.01	6.55	14.3	0.04	N/A
Aug	0.82	0.25	2.40	8.9	246	4.0	2.91	22.1	0.00	5.52	22.1	0.03	N/A
Sep	0.48	0.28	1.39	10.3	323	6.0	3.41	9.1	0.00	6.11	24.3	0.01	N/A
Oct	0.59	0.23	0.12	14.0	358	4.9	2.75	14.9	0.00	5.59	29.1	0.01	N/A
Nov	0.77	0.19	0.89	10.2	214	3.2	1.35	13.7	0.00	2.94	21.5	0.01	N/A
Dec	0.99	0.24	0.56	12.4	299	4.4	2.38	13.8	0.00	4.01	23.1	0.01	N/A
Annual Average	0.62	0.34	1.06	10.1	270	4.3	2.43	12.5	0.00	4.86	20.6	0.03	N/A

Site 111: Redcar Normanby

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	V	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
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
Jun	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
Jul	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
Aug	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
Sep	0.19	0.12	0.77	2.5	177	6.8	0.12	6.5	0.00	0.77	11.0	0.01	N/A
Oct	0.09	0.13	7.42	2.8	204	7.5	0.00	5.7	0.00	0.10	16.4	0.01	N/A
Nov	0.28	0.09	2.12	2.8	120	4.4	0.82	4.2	0.00	0.06	20.1	0.01	N/A
Dec	0.29	0.08	1.62	1.9	69	3.6	0.74	3.7	0.00	1.90	9.0	0.01	N/A
Annual Average	0.21	0.11	2.98	2.5	143	5.6	0.42	5.0	0.00	0.71	14.1	0.01	N/A

Site 112: Dartford Bean

Month	As	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Pt	٧	Zn	Hg(p)	Hg(v)
Jan	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
Feb	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
Mar	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
Apr	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
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
Jun	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
Jul	0.33	0.11	1.29	8.1	177	3.5	1.84	6.3	0.00	3.30	12.3	0.04	N/A
Aug	0.43	0.06	0.49	4.6	96	1.6	0.76	4.3	0.00	1.29	7.6	0.01	N/A
Sep	0.80	0.25	0.10	8.6	253	4.7	2.41	10.6	0.00	4.93	20.8	0.01	N/A
Oct	0.68	0.16	0.10	7.9	190	2.3	1.18	7.3	0.00	1.46	13.2	0.01	N/A
Nov	0.74	0.20	0.24	8.8	213	2.8	0.95	10.6	0.00	1.75	21.3	0.01	N/A
Dec	0.70	0.15	0.59	9.4	211	2.9	1.80	10.1	0.00	2.11	16.3	0.01	N/A
Annual Average	0.61	0.16	0.47	7.9	190	3.0	1.49	8.2	0.00	2.47	15.2	0.01	N/A

Note:

Any Pt concentrations stated as 0.00 ng.m⁻³ should be considered as <0.01 ng.m⁻³.

