National Physical Laboratory

NPL REPORT ENV 1

Report by the National Physical Laboratory to the Department for Environment, Food and Rural Affairs, the Welsh Government, the Department of the Environment in Northern Ireland and the Scottish Government:

Annual Report for 2013 on the UK Heavy Metals Monitoring Network

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EXECUTIVE SUMMARY

This Report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Department for Environment, Food and Rural Affairs, the Welsh Government, the Department of the Environment Northern Ireland and the Scottish Government.

This is the Annual Report for 2013 and contains, in particular:

- Measured annual concentrations of all metals at all monitoring sites and performance against relevant data quality objectives and the requirements of the EC Air Quality Directives.
- Highlighting of exceedances, interpretation of data and discussion of trends across the Network.
- Summary of Network operation, analytical and QA/QC procedures and a description of notable events and changes to the Network during 2013.
- A brief summary of scientific research, publications, international representation and other activities related to the Network.

In summary, during 2013:

- There was **one** exceedance of a target or limit value across the Network: Nickel, at Pontardawe Tawe Terrace.

- **Lead**: No annual average site concentrations above the Air Quality Directive's Lower Assessment Threshold were recorded.

- **Nickel**: One annual average site concentration above the Fourth Daughter Directive's target value; one annual average site concentration above the Fourth Daughter Directive's upper assessment threshold and one annual average site concentration above the Fourth Daughter Directive's lower assessment threshold were recorded.

- **Cadmium**: No annual average site concentration above the Fourth Daughter Directive's Lower Assessment Threshold was recorded.

- **Arsenic**: No annual average site concentrations above the Fourth Daughter Directive's Lower Assessment Threshold were recorded.

- **Total gaseous mercury**: Measured concentrations across the Network remain close to background concentration levels with the exception of the site at Runcorn Weston Point.

- The annual average concentrations measured across the Network have not changed significantly in the last few years.

- 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 **97.6%** for the year.

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1 INTRODUCTION

This report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Department for Environment, Food and Rural Affairs and the Devolved Administrations[1] (the Welsh Government, the Department of the Environment in Northern Ireland and the Scottish Government).

This is the Annual Summary Report for the UK Heavy Metals Monitoring Network (the 'Network') for 2013 and contains:

- Measured annual concentrations of all metals at all monitoring 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/EC[2]) for lead, and the Fourth Air Quality Daughter Directive (DD) (2004/107/EC[3]) for nickel, arsenic, cadmium, and total gaseous mercury, and the Air Quality Strategy for England, Scotland, Wales and Northern Ireland[4] for lead.

- Highlighting of exceedances, interpretation of data and discussion of trends across the Network.

- Summary of Network operation, analytical and QA/QC procedures and a description of notable events and changes to the Network during 2013.

- A brief summary of scientific research, publications, international representation and other activities related to the Network.

1.1 BACKGROUND

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.

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

1 The Devolved Administrations are in detail: the Welsh Government, the Northern Ireland Executive, represented by the Department of the Environment in Northern Ireland (DoENI), and the Scottish Government, represented by the Scottish Government Enterprise and Environment Directorate.
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.
5 The term 'concentration' is used in this report to refer to mass concentration.

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 and Cd, allowable in the PM_{10} fraction of ambient air (particles with an equivalent aerodynamic diameter of 10 µm or less) are limited by European legislation.

Human exposure to toxic air pollutants at sufficient concentrations and over long enough time periods may increase chances of serious health effects including cancer. Such health effects can include damage to the immune, reproductive and respiratory systems and developmental and neurological impairment. In addition to exposure from breathing in these pollutants, some pollutants such as mercury may also deposit from the air onto the earth or water, where they may enter the terrestrial and aquatic food chains, eventually resulting in human exposure through ingestion of contaminated food.

Emissions of metals in the UK 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 UK [6]. These emissions have declined over many years and this has generally been mirrored by the decrease in measured ambient levels, although in recent years both trends have flattened out. The correlation between these two data sets is quite strong, and indeed measured ambient concentrations across the Network have recently been compared against emissions[7]. This has shown that an additional benefit of the Network is to contribute supplementary evidence to show that trends in emissions inventory data for metals are correct. The UK emissions since 1970 of metals relevant to those measured on the Network are displayed in Figure 1.

In order to demonstrate compliance with legislation that provides limit and target values relating to ambient air and to measure human and environmental exposure, 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 majority of the UK's obligation under the EC Air Quality Directives relating to the monitoring of the mass concentrations of Pb, Ni, As and Cd, in the PM_{10} phase of ambient air, and total gaseous mercury [referred to as: Hg(v)].

6 www.naei.org.uk
7 Comparison of estimated annual emissions and measured annual ambient concentrations of metals in the UK 1980–2007, R J C, Brown, *J. Environ. Monit*., 2010, **12**, 665-671.

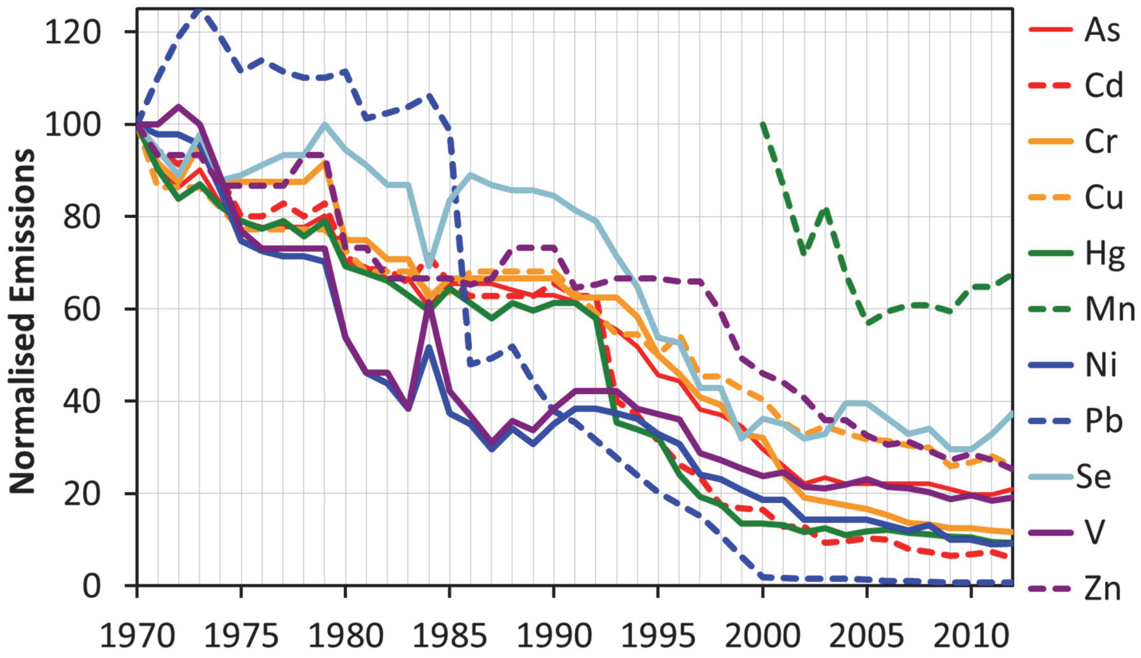

Figure 1. Estimated UK annual emissions of the metals from 1970 to 2012, normalised to their values in 1970 such that 1970 = 100 (except for Mn where values are only available since 2000 and therefore have been normalised to this year). The absolute levels of emissions in 1970, in tonnes, were: As, 81; Cd, 35; Cr, 240; Cu, 220; Ni, 910; Pb, 7900; Se 91; V, 2600; and Zn, 1500. The absolute level of Mn emissions in 2000 was 74 tonnes. Emissions data are not available for Co, Fe and Pt, although these are measured by the Network.

The Network has a number of objectives:

- To achieve compliance with monitoring requirements set out in European legislation;
- To provide data to the UK Government and European Commission on the UK's performance against the limit values, target values, and data quality objectives described in the relevant legislation;
- To assess impacts around 'hot spots' of metallic pollution to air, particularly in industrial areas;
- To produce 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 an NPL publication that marked a quarter of a century of the nationwide monitoring of metals in ambient air[8].

8 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.

2 NETWORK OPERATION

The UK Heavy Metals Monitoring Network in 2013 comprised 27 monitoring sites around the country (17 in England, 7 in Wales, 2 in Scotland, and 1 in Northern Ireland) sampling in the PM_{10} phase of ambient air onto filters (see Annex 1). These filters are then returned to NPL where they are analysed to determine the content of various metals in the particulate matter, in order to produce concentration values for these metals in ambient air. Total gaseous mercury is additionally sampled onto adsorption tubes at 14 of these Network sites (8 in England, 3 in Wales, 2 in Scotland, and 1 in Northern Ireland). These absorption tubes are then analysed at NPL to produce concentration values for total gaseous mercury in ambient air. Relevant activity related to Network operation during 2013 is detailed below.

2.1 OVERVIEW

NPL's management of the UK Heavy Metals Monitoring Network in 2013 has included the following key activities:

- 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. A further visit to each site was made during the year to perform a flow calibration and leak check on the Partisol samplers.

- The Equipment Support Unit (ESU) made service visits to all Network sites twice during the year, and this has included the flow calibration of instruments.

- Data capture has remained at a very high level across the Network and is at its highest level since NPL began operating the Network (see Figure 3).

2.2 SITE AUDITS

During 2013 NPL visited all the Network sites to perform annual site audits. At these visits the site infrastructure, performance and integrity were assessed. The LSOs were also audited and received extra training where required.

A list of sites comprising the Network as of the end of 2013, with locations, site codes, site names, site designations, identified point sources in the vicinity, where applicable, is given in Annex 1.

During each Network site audit visit NPL carried out the following duties:

- 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 PM_{10} 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).

This flow calibration data are used to correct the volumes recorded by the Partisol instruments and mercury vapour sampling equipment prior to the calculation of ambient concentrations. In summary:

- All of the sites have been audited fully and were found to be performing well.
- Site infrastructure was assessed and no major or minor problems were found.
- Audits of the flow-rate of the Partisol samplers and the mercury vapour sampling equipment were satisfactory and no remedial action was required.
- The LSOs were performing their duties to a high standard. Some small issues were identified and rectified during the audits in order to improve performance even further.

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 +1.4 %, which is well within the uncertainty of the flow measurement itself.

NPL visited each site a second time during the year to perform a flow calibration and leak check of the samplers. Together with the two flow calibrations and leak checks performed by the ESU during the year this meets the requirement for a three-monthly flow and leak check required by EN 14902.

2.3 EQUIPMENT SERVICING AND BREAKDOWNS

- During 2013 the ESU twice fully serviced, carried out preventative maintenance and calibrated the flow of the Partisol samplers at all Network sites.

- During 2013, NPL called-out the ESU to deal with Partisol sampler faults at: Scunthorpe Town, Manchester Wythenshawe, Walsall Centre.

- During 2013, failed or failing mercury vapour sampling pumps were replaced at: London Cromwell Road, Eskdalemuir, Cardiff Llandaff.

2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION

Changes to the operation of the Network during the year are detailed below:

- Site 117: Sheffield Tinsley began monitoring on 28th February 2013. The station was run in parallel with the Sheffield Brinsworth station that did not meet the siting requirements of the directive to verify equivalence between the concentrations measured at the two stations, before the Sheffield Brinsworth station was decommissioned on 11th September 2013.

- On 2nd September 2013 the power was disconnected at 105: Sheffield Centre station, prior to the move of all sampling equipment located there to the proposed new Sheffield Devonshire Green site.

- On 29th October 2013 site 119: Sheffield Devonshire Green began sampling.

3 SAMPLING AND ANALYTICAL METHODOLOGY

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

3.1 SAMPLING METHODOLOGY: PARTICULATE-PHASE METALS

Particulate samples were taken at all sites in the Network using Partisol 2000B instruments (fitted with PM_{10} heads) operating at a calibrated flow rate, nominally of 1 m^3 h^{-1}, in accordance with EN 12341 (see Image 1). Samples were taken for a period of one week onto 47 mm diameter GN Metricel membrane filters.

Image 1. The Partisol 2000 sampler at the Network monitoring site at Eskdalemuir. The grey box attached to the side of the sampler contains the mercury vapour sampling equipment (the particulate pre-filter can just be seen protruding from the bottom right of the box.)

3.2 SAMPLING METHODOLOGY: TOTAL GASEOUS MERCURY

Sampling for total gaseous mercury took place at 13 of the 24 Network sites using a low-volume pump (calibrated annually by NPL). Air was pumped through Amasil (gold-coated silica) tubes at a rate of 100 ml min^{-1} for either one week or four weeks, depending on the specific site and the required resolution of data. The mercury vapour sampling equipment is housed in a specially designed box on the side of the Partisol 2000B samplers (see Image 1). A schematic diagram of the mercury vapour sampling equipment is given in Figure 2.

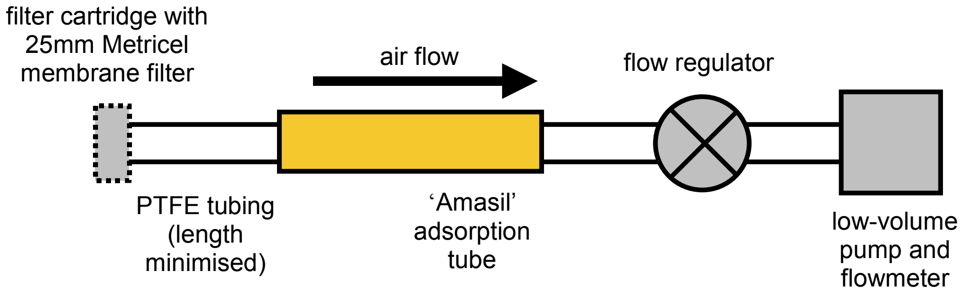

Figure 2. Schematic diagram of the total gaseous mercury sampling apparatus. The 25 mm diameter filter was used to remove any particulate material.

3.3 ANALYTICAL METHODOLOGY: PARTICULATE-PHASE METALS

Data are produced as four-weekly averages for metals in the particulate phase at all sites except: Sheffield Brinsworth (closed to be replaced by Sheffield Tinsley on 11th September 2013), Sheffield Tinsley, Walsall Bilston Lane, Swansea Coedgwilym, Swansea Morriston, Pontardawe Tawe Terrace and Pontardawe Brecon Road where weekly data are produced.

Analysis for particulate-phase metals took place at NPL using PerkinElmer Elan DRC II and Elan 9000 ICP-MSs, following NPL's procedure, accredited by UKAS to ISO 17025, which is fully compliant with the requirements of EN 14902 (see Image 3). Upon arrival at NPL, the filters were cut accurately in half (for sites where weekly results are produced) and into quarters (where four weekly results are produced). For the sites producing weekly data each portion is digested at temperatures up to 220°C using an Anton Parr Multiwave 3000 microwave. For the sites producing four-weekly data one quarter of each of the four filters comprising the four week period are digested. 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 all the 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.

3.4 ANALYTICAL METHODOLOGY: TOTAL GASEOUS MERCURY

Mercury vapour results are reported as four-weekly averages at all sites except for Walsall Bilston Lane, Walsall Centre and Runcorn Weston Point where data are reported weekly.

Analysis of total gaseous mercury samples took place at NPL using a PS Analytical Sir Galahad II analyser with a fluorescence detector, using NPL's procedure, accredited by UKAS to ISO 17025, which is in accordance with the published reference method EN 15852 (see

Image 3). (The manual variant of EN 15852 used on the Network has been recently shown to be equivalent to the automatic reference method within the uncertainty of the analytical determination[9].) 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.

3.5 MEASUREMENT UNITS

Results produced by the Network are expressed as required by the relevant air quality Directives as mass concentrations, in nanograms (of the relevant metal) per cubic metre of 'as sampled' ambient air for the particulate phase metals, and per cubic meter of air under the reference conditions given in EN 15852 for total gaseous mercury (a temperature of 293.15 K and pressure of 101.325 kPa). The units used in both cases are: ng m^{-3}.

3.6 MEASUREMENT UNCERTAINTY

For each result produced by the Network an estimate of the uncertainty in this value is also made according to an ISO GUM (Guide to the Expression of Uncertainty in Measurement) approach. These uncertainties are used to calculate the uncertainties in the annual average values for each element and ensure that the final results meet the data quality objectives for uncertainty specified in the relevant legislation.

Image 2: (Far left) One of two dedicated ICP-MS instruments comprising the UK ambient metals analysis facility at NPL.

Image 3: (Near left) One of two thermal desorption-atomic fluorescence analysers comprising the UK total gaseous mercury analysis facility at NPL.

9 Field comparison of manual and semi-automatic methods for the measurement of total gaseous mercury in ambient air and assessment of equivalence. R J C Brown, et al., *Journal of Environmental Monitoring*, 2012, **14** (2), 657-665.

4 METHOD PERFORMANCE CHARACTERISTICS AND QUALITY CONTROL

The application 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) was last audited by UKAS in 2013, and both retained accreditation to ISO 17025 from UKAS with no mandatory corrective actions. Limits of detection achievable using NPL's UKAS accredited methods are comfortably below the requirements of EN 14902 (for particulate phase metals) and EN 15852 (total gashouse mercury).

4.1 QA/QC PROCEDURES

A sub-set of the quality assurance and quality control procedures employed during Network operation to ensure the quality of the data produced are listed below:

Sampling:

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

Particulate phase metals (ICP-MS analysis):

- Optimisation of the ICP-MS prior to each set of analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular extraction of an appropriate certified reference material (e.g. NIST SRM 1648a) 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 standard-corrected measured intensities of each analysis of each sample.
- The XLGenline maximum absolute weighted residual for all calibration curves must be less than 1.
- 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.
- Novel 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.

4.2 MEASUREMENT UNCERTAINTY

The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2013 are shown in Table 2. All figures are a combination of the analytical and sampling uncertainties and have been derived using full, ISO GUM compliant, uncertainty budgets. All values are stated to a coverage factor of *k* = 2, providing a level of confidence of approximately 95%.

Analyte	**Expanded relative uncertainty**	
	Single measurement range	EC Directive maximum
As	16 - 26 %	40 %
Cd	13 - 20 %	40 %
Co	18 - 38 %	-
Cr	14 - 32 %	-
Cu	11 - 15 %	-
Fe	12 - 17 %	-
Mn	11 - 15 %	-
Ni	10 - 14 %	40 %
Pb	8 - 13 %	25 %
Pt	40 - 50 % ‡	-
Se	20 - 35 %	-
V	11 - 16 %	-
Zn	10 - 14 %	-
Hg(p)	20 - 40 %	-
Hg(v)	13 - 20 %	50 %

Table 2. The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2013. The 'EC Directive maximum' column shows the maximum permissible uncertainty at the target value allowed by the relevant EU Air Quality Directive. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. ‡ Many Pt measurements are below the limit of detection, the uncertainty quoted refers to those measurements that are above the detection limit.

The measurement uncertainties displayed in Table 2 are representative of the range of uncertainties covering the majority of individual measurements 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 relative uncertainties will be significantly lower.

5 DATA QUALITY

5.1 DATA CAPTURE

All data capture figures are based on a target time coverage of 100 %. (The Fourth DD requires time coverage of only 50 % for fixed measurements of As, Ni and Cd.) Therefore any lost time coverage has a direct and equal effect on the data capture achieved. This is the most stringent way by which to calculate data capture percentages and represents the absolute percentage of all available time during the year for which valid data has been produced.

Data capture across the entire Network during 2013 was **97.6%**. Of the data lost the majority was owing to equipment failure or site operation problems.

The breakdown of the overall data capture between the particulate and gaseous phase, and at each site, is displayed in Table 3. The quarterly data capture, and the rolling annual average data capture, achieved by the Network over the last seven years are displayed in Figure 3. The yearly average data capture is currently at its highest level since NPL began operating the Network.

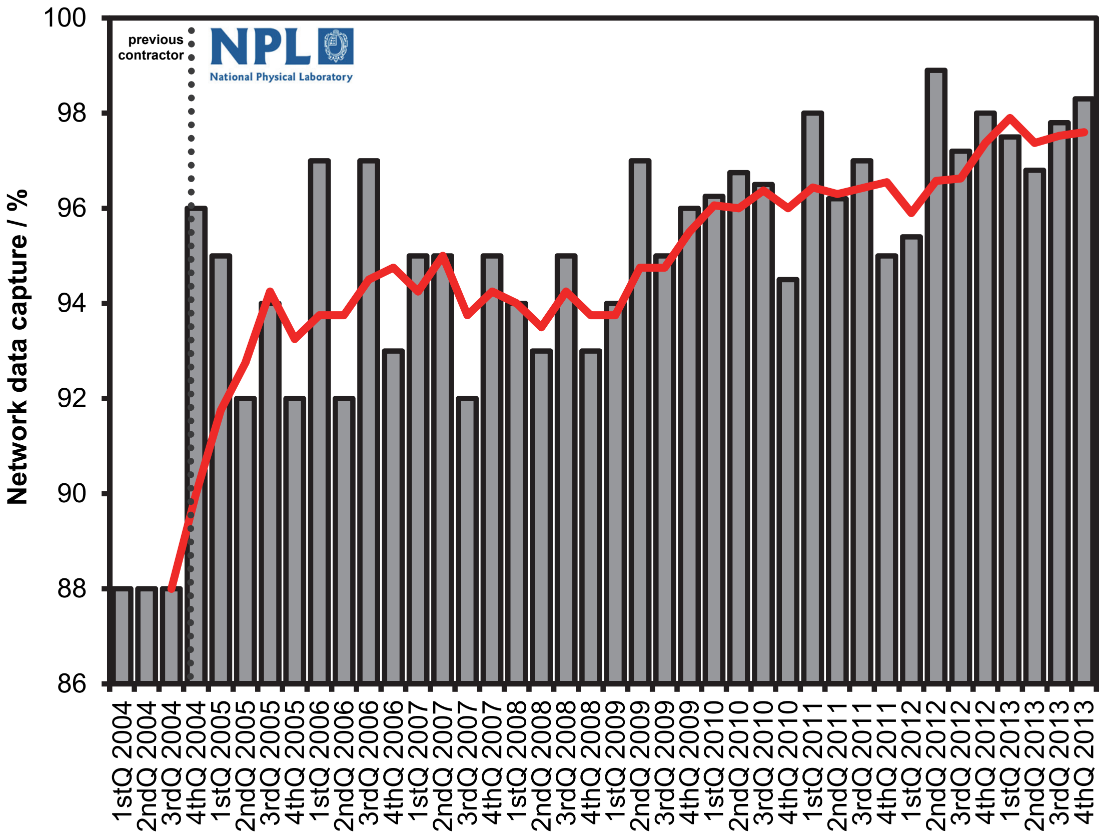

Figure 3. Network data capture from 2004-2013 (inclusive). Quarterly data capture is indicated by the grey bars, whilst the rolling annual average data capture is given by the red line. Data to the right of the dotted vertical line is associated with NPL's current operation of the Network; data to the left of the dotted line is associated with the previous contractor's operation of the Network.

Site Number: Site Location	Data Capture / %	
	Particulate phase	Gaseous phase
Whole Network	**98.1%**	**96.9%**
46: Walsall Centre	90.7%	100.0%
58: Sheffield Brinsworth *	100.0%	N/A
59: Runcorn Weston Point	97.8%	98.1%
61: London Cromwell Road 2	98.1%	91.8%
62: London Westminster	100.0%	100.0%
65: Eskdalemuir	98.3%	100.0%
66: Motherwell South	100.0%	96.3%
67: Manchester Wythenshawe	96.2%	100.0%
68: Cardiff Llandaff	100.0%	80.8%
69: Walsall Bilston Lane	99.6%	96.1%
100: Swansea Coedgwilym	100.0%	N/A
101: Swansea Morriston	100.0%	100.0%
103: Belfast Centre	94.5%	96.2%
104: Port Talbot Margam	100.0%	100.0%
105: Sheffield Centre*	100.0%	100.0%
106: Scunthorpe Town	96.2%	N/A
107: Scunthorpe Low Santon	90.4%	N/A
109: Cardiff Rumney	100.0%	N/A
110: Chadwell St Mary	100.0%	N/A
111: Redcar Normanby	98.1%	N/A
112: Dartford Bean	98.5%	N/A
113: Pontardawe Tawe Terrace	98.0%	N/A
114: London Marylebone Road	98.1%	N/A
115: Pontardawe Brecon Road	97.6%	N/A
116: Redcar Dormanstown	100.0%	N/A
117: Sheffield Tinsley*	97.0%	N/A
119: Devonshire Green*	100.0%	N/A

Table 3. Data capture across the UK Heavy Metals Monitoring Network during 2013. * Data capture refers only to the period of the year when the following stations were operational: Sheffield Brinsworth was closed 12th September 2013; Sheffield Centre closed 30th August 2013; Sheffield Tinsley was opened 28th February 2013; Devonshire Green was opened 20th November 2013.

Of the stations not achieving 90 % data capture for the year:

- Cardiff Llandaff (Hg vapour only): 4 weeks of sampling was lost due to repeated mercury pump failure.

5.2 DATA PROCESSING AND RATIFICATION

Analysis of the Network samples produces individual concentration values for four-weekly or weekly periods. These individual measurement results each have a stated measurement uncertainty, quoted at the 95% confidence level, associated with them. Annual means at each site are produced by calculating the means of these values, weighted according to the data capture during each period. Network-wide annual means are then produced by averaging annual means from the individual sites, again using appropriate weighing if a site has been monitoring for less than the full year.

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.
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, including the use of powerful chemometric techniques[10].
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 are 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.

10 Using principal component analysis to detect outliers in ambient air monitoring studies, Brown, R J C, Goddard, S L, Brown, A S, *International Journal of Environmental Analytical Chemistry*, 2010, **90,** 761–772.

5.3 MEASUREMENT UNCERTAINTY OF ANNUAL AVERAGE

ISO 11222 “Air quality - Determination of the uncertainty of the time average of air quality measurements” is used to determine the uncertainty in the annual mean for each element at each sampling location. This is easily done since NPL produce a statement of uncertainty with each measurement result.

Data capture across the Network remains 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 and sampling uncertainty, with only small uncertainty contributions due to less than 100% time coverage. (The effect of these contributions is calculated using the method described in ISO 11222 “Air quality - Determination of the uncertainty of the time average of air quality measurements”.)

In all cases annual mean uncertainties are compliant with the data quality objectives for uncertainty in the 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:

Analyte	**Relative Expanded Uncertainty**	
	Annual Mean	**EC Directive maximum**
As	20 %	40 %
Cd	12 %	40 %
Ni	18 %	40 %
Pb	11 %	25 %
Hg(v)	17 %	50 %

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

6 NETWORK DATA

6.1 MEASURED CONCENTRATIONS

The annual mean measured metals concentrations in 2013, averaged over all sites (Table 5), and at individual sites (Table 6), are given below. Table 5 also displays the maximum annual mean concentration measured at any monitoring site across the Network and the median annual concentration across all sites. In addition all data, at the highest time resolution that they are produced, are available from Defra's UK-AIR website: http://uk-air.defra.gov.uk/data/.

Analyte	2013 UK Mean Annual Concentration / ng m^{-3}	2013 UK Median Annual Concentration / ng m^{-3}	2013 Maximum Annual Mean Concentration / ng m^{-3}	EC limit or target value (UK objective) / ng m^{-3}
As	0.68	0.74	0.96	6
Cd	0.29	0.19	1.92	5
Co	0.24	0.15	1.31	-
Cr	5.01	2.55	31.9	-
Cu	15.7	7.63	84.2	-
Fe	573	376	3005	-
Mn	13.1	8.10	73.8	-
Ni	4.25	1.55	37.2	20
Pb	11.5	9.04	59.4	500 (250)
Pt	0.00	0.00	0.01	-
Se	0.96	0.76	2.63	-
V	1.47	1.23	5.89	-
Zn	47.7	24.8	481	-
Hg (p)	0.04	0.02	0.45	-
Hg (v)	3.71	2.08	23.5	-

Table 5. The 2013 annual mean concentrations averaged over all sites on the UK Heavy Metals Monitoring Network, the annual median concentrations across all sites, and the maximum annual mean concentration measured at any monitoring site. Hg(p) and Hg(v) are particulate phase mercury and total gaseous mercury, respectively. The EC limit or target value (and/or UK objective, in brackets) is also listed, where applicable.

Site	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Pt	Se	V	Zn	Hg (p)	Hg (v)
46: Walsall Centre	0.96	0.32	0.09	2.12	12.6	285	8.23	1.07	10.8	0.002	0.68	0.90	47.3	0.020	1.94
58: Sheffield Brinsworth	0.77	0.32	0.82	31.9	14.2	566	28.3	12.9	21.4	0.003	2.63	1.98	87.8	0.066	N/A
59: Runcorn Weston Point	0.63	0.11	0.22	1.83	5.62	206	4.02	1.55	6.06	0.001	1.58	1.61	12.8	0.449	23.5
61: London Cromwell Road 2	0.87	0.15	0.13	3.47	35.2	853	8.74	1.78	9.05	0.007	0.69	1.51	24.8	0.017	3.02
62: London Westminster	0.83	0.16	0.10	1.83	16.0	453	5.85	1.38	9.04	0.004	0.62	1.53	23.1	0.015	3.28
65: Eskdalemuir	0.12	0.03	0.04	1.38	0.68	28	0.85	0.32	1.08	0.001	0.24	0.39	2.63	0.003	1.96
66: Motherwell South	0.30	0.09	0.05	1.35	4.06	111	2.35	0.56	2.59	0.001	0.32	0.53	6.77	0.005	2.10
67: Manchester Wythenshawe	0.74	0.12	0.16	4.09	43.9	1137	11.6	1.48	6.29	0.007	0.79	1.20	31.2	0.016	2.05
68: Cardiff Llandaff	0.69	0.21	0.14	2.19	19.9	633	8.77	1.10	7.75	0.004	0.56	1.06	31.7	0.014	2.55
69: Walsall Bilston Lane	0.94	1.92	0.24	4.25	84.2	445	12.2	2.22	59.4	0.001	1.78	1.16	481	0.046	2.21
100: Swansea Coedgwilym	0.62	0.22	0.26	1.90	3.71	164	3.69	7.78	10.5	0.001	1.42	0.89	16.8	0.020	N/A
101: Swansea Morriston	0.83	0.51	0.26	2.49	22.9	553	8.10	6.51	15.4	0.002	1.36	1.12	31.7	0.015	1.65
103: Belfast Centre	0.37	0.10	0.06	1.48	6.47	197	3.13	1.04	3.94	0.007	0.34	1.83	14.5	0.006	1.47
104: Port Talbot Margam	0.58	0.89	0.14	2.55	7.63	3005	39.7	1.50	12.0	0.002	0.83	2.31	91.8	0.016	2.10
105: Sheffield Centre	0.58	0.18	0.21	5.88	10.5	376	14.4	3.23	12.5	0.002	1.01	1.27	34.4	0.028	2.05
106: Scunthorpe Town	0.69	0.14	0.12	2.85	5.18	625	21.6	1.26	10.5	0.002	0.90	1.54	22.0	0.018	N/A
107: Scunthorpe Low Santon	0.74	0.20	0.20	2.84	4.63	1680	73.8	1.65	15.0	0.002	1.17	5.89	28.8	0.019	N/A
109: Cardiff Rumney	0.74	0.23	0.10	1.79	6.11	221	6.02	0.83	8.51	0.001	0.62	1.00	31.5	0.018	N/A
110: Chadwell St Mary	0.80	0.21	0.15	1.66	8.69	258	4.51	1.97	10.8	0.002	0.70	2.59	19.7	0.013	N/A
111: Redcar Normanby	0.39	0.12	0.03	1.60	2.17	167	4.14	0.51	4.34	0.002	0.52	0.65	12.0	0.011	N/A
112: Dartford Bean	0.71	0.16	0.08	0.93	7.14	195	3.59	1.53	9.02	0.004	0.66	1.85	15.4	0.013	N/A
113: Pontardawe Tawe Terrace	0.58	0.24	1.31	10.2	5.65	222	5.08	37.2	7.40	0.001	1.27	0.86	17.2	0.099	N/A
114: London Marylebone Road	0.84	0.17	0.19	6.58	61.5	1499	14.0	2.23	8.77	0.009	0.76	1.68	32.5	0.019	N/A
115: Pontardawe Brecon Road	0.89	0.19	0.23	4.00	5.19	213	4.00	5.72	7.08	0.001	1.17	0.83	15.7	0.022	N/A
116: Redcar Dormanstown	0.76	0.38	0.12	3.62	2.95	559	22.6	2.39	15.5	0.001	0.55	1.23	66.8	0.012	N/A
117: Sheffield Tinsley	0.84	0.32	0.51	27.8	17.8	567	30.6	14.1	17.9	0.005	2.21	1.69	74.7	0.043	N/A
119: Devonshire Green	0.69	0.11	0.51	2.62	9.12	244	5.14	0.86	7.60	0.001	0.47	0.66	14.4	0.012	2.07

Table 6. The 2013 annual mean concentrations (in ng/m^3) measured at individual sites on the UK Heavy Metals Monitoring Network. Hg(p) and Hg(v) are particulate phase mercury, and total gaseous mercury, respectively. Colour coding for concentrations: **above target value**, **above upper assessment threshold**, **above lower assessment threshold**, **below lower assessment threshold.**

6.2 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:

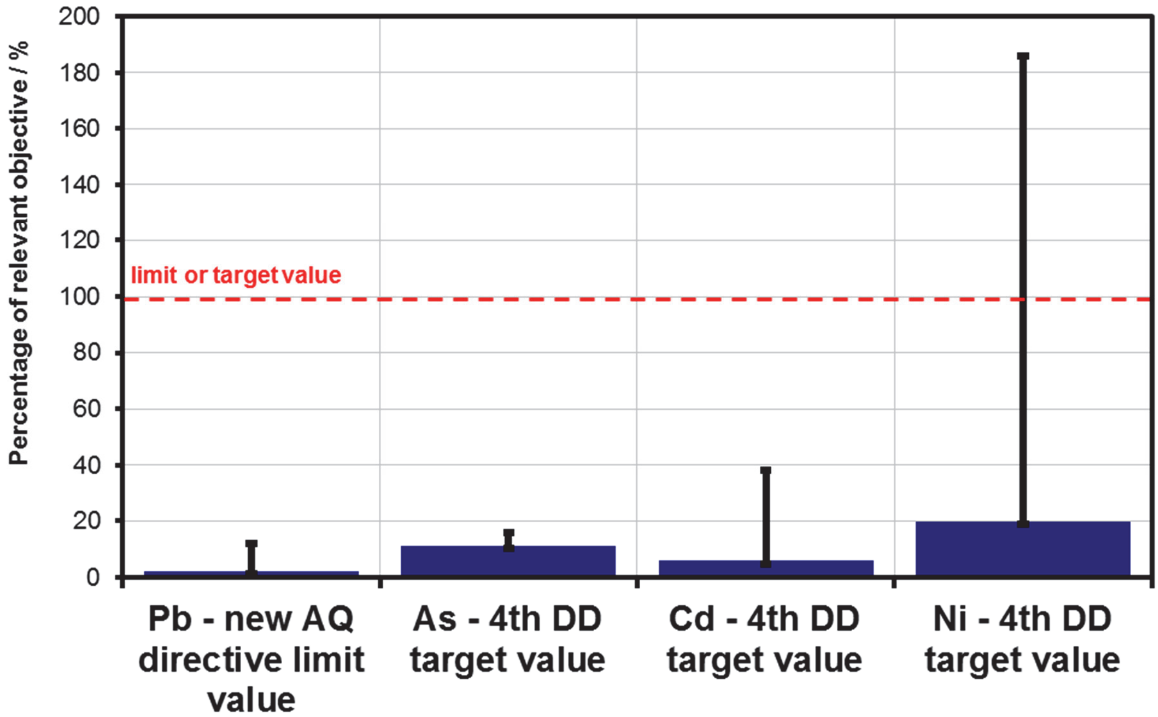

Figure 4. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth Daughter Directives on the UK Heavy Metals Monitoring Network in 2013 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the annual mean at the site with the highest concentrations.

Annual mean concentration values for the relevant EC Air Quality Directives metals at all Network sites are displayed in Figure 5.

The highest annual mean value for nickel has been found at Site 113: Pontardawe Tawe Terrace. The highest annual mean values for cadmium, arsenic and lead are found at Site 69: Walsall Bilston Lane.

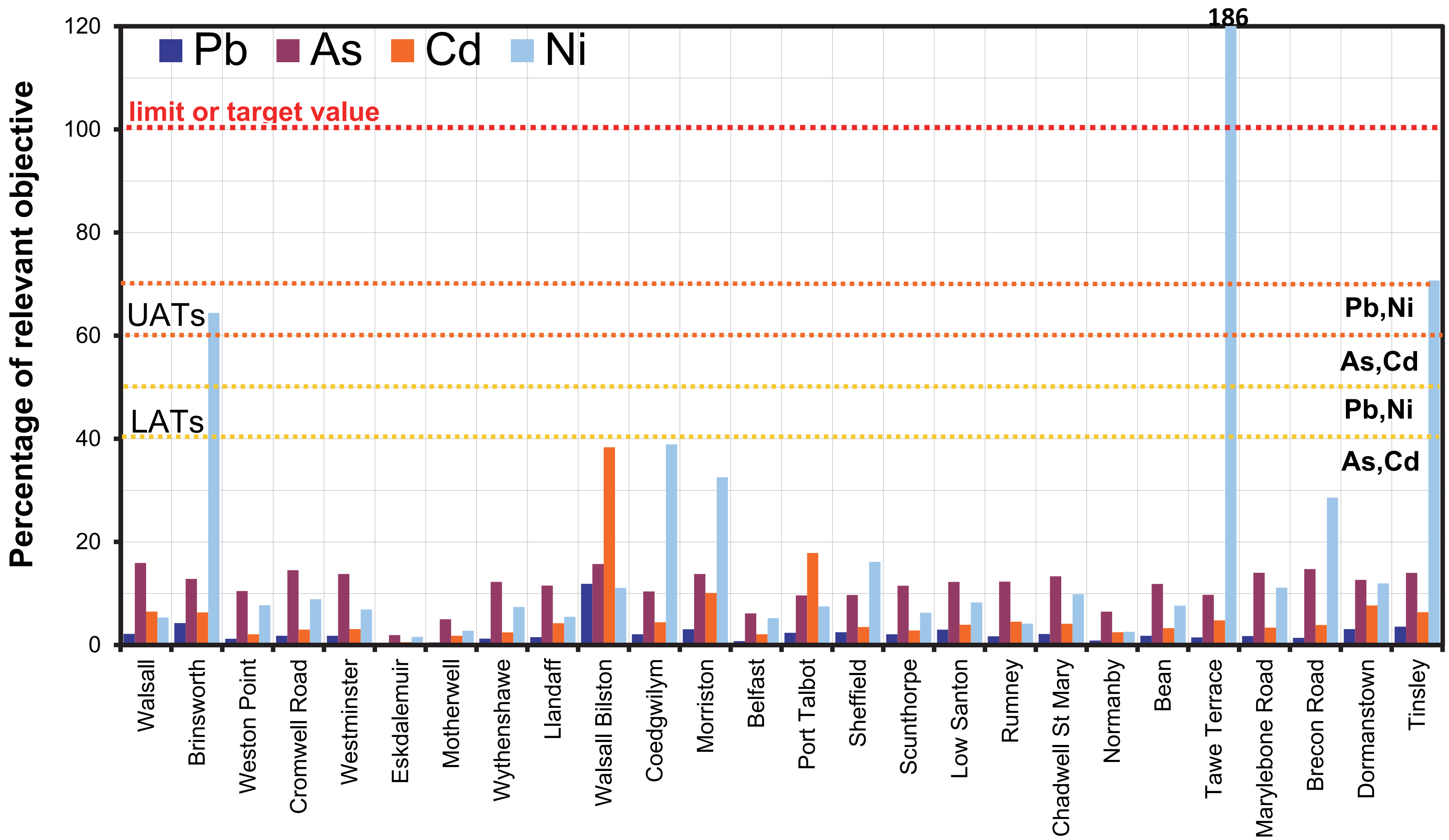

Figure 5. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2013 as a percentage of the relevant target values, lower assessment thresholds (LATs) and upper assessment thresholds (UATs).

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

Annual Mean Concentrations above Target or Limit Values:

- Nickel at Site 113: Pontardawe Tawe Terrace: 186 % of the target value.

Annual Mean Concentrations above the Upper Assessment Threshold:

- Nickel at Site 117: Sheffield Tinsley: 70 % of the target value (based on monitoring for 81.5 % of the year).

Annual Mean Concentrations above the Lower Assessment Threshold:

- Nickel at Site 58: Sheffield Brinsworth: 65 % of the target value (based on monitoring for 69.7 % of the year).

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

The site at Pontardawe Tawe Terrace is situated close to the Wall Colmonoy nickel alloy production facility in Pontardawe. Whilst the Tawe Terrace site is nominally upwind of the facility it is very close to the source of nickel emissions and is located on the valley floor and hence measures higher concentrations than the downwind site at Pontardawe Brecon Road which is at several metres elevation up the valley.

The site at Sheffield Brinsworth is located next to the Outokumpu steel melt shop, continuous casting operations, bar finishing facility and rod mill, producing specialist steel strip, and coil, products.

The site at Sheffield Tinsley replaced the Brinsworth site when it closed, so is also located next to the Outokumpu facility.

6.3 WITHIN YEAR CONCENTRATION TRENDS

Seasonal trends are rarely observed for metals concentrations on the Network. This is not because there is no seasonality in the emissions of metals but more that the seasonality is small compared to the random effects of variability in the local meteorological conditions and uncertainty in the analysis of the samples. However distinct seasonality has been observed for arsenic[11], which is generally emitted from diffuse combustion sources, not point sources, and therefore is affected much less by meteorological conditions.

Weekly measurements provide an opportunity to examine the within year variability and trends of measured concentrations. This has been done for the stations and metals where weekly data are available and where these concentrations are likely to be significant, together with data from appropriate paired sites, in the Figures below.

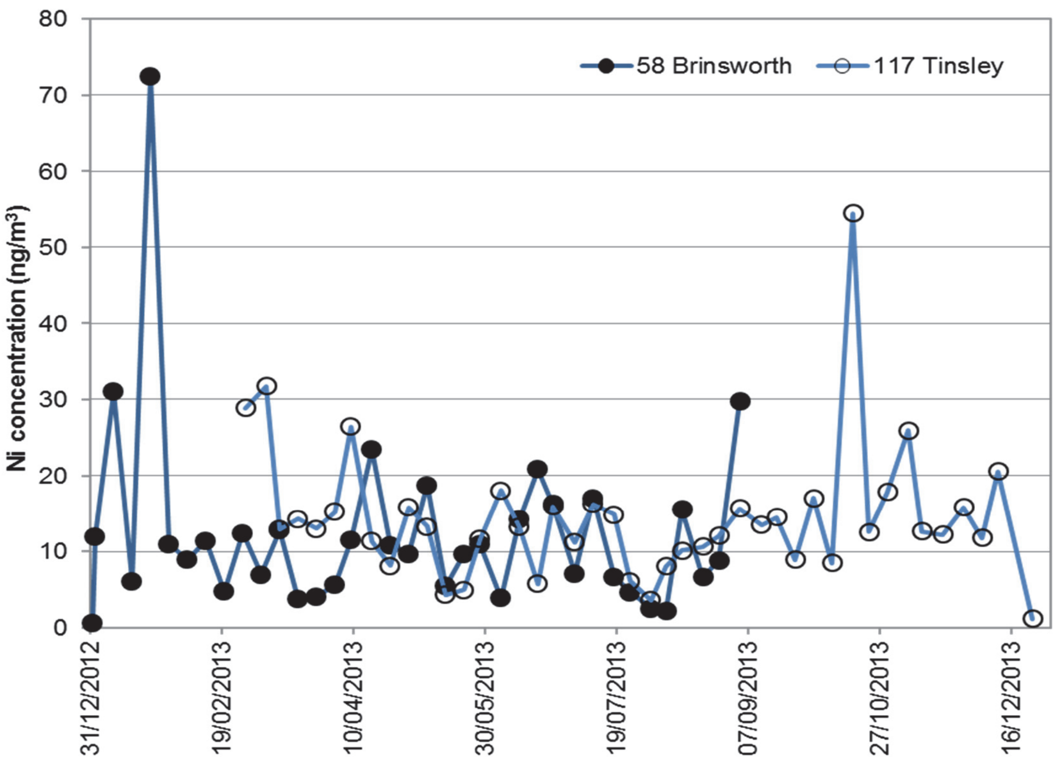

Figure 6. Measured Ni concentrations at Site 58: Sheffield Brinsworth and Site 117: Sheffield Tinsley in 2013 (both sampled weekly). The Sheffield Tinsley station began monitoring on 28th February 2013 as a replacement for the Sheffield Brinsworth site that did not meet the siting criteria of the Fourth Duaghter Directive. The site was run in parallel with the Sheffield Brinsworth station for six months to verify equivalence between the concentrations measured at the two stations. Sheffield Brinsworth ceased sampling on 11th September 2013.

11 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.

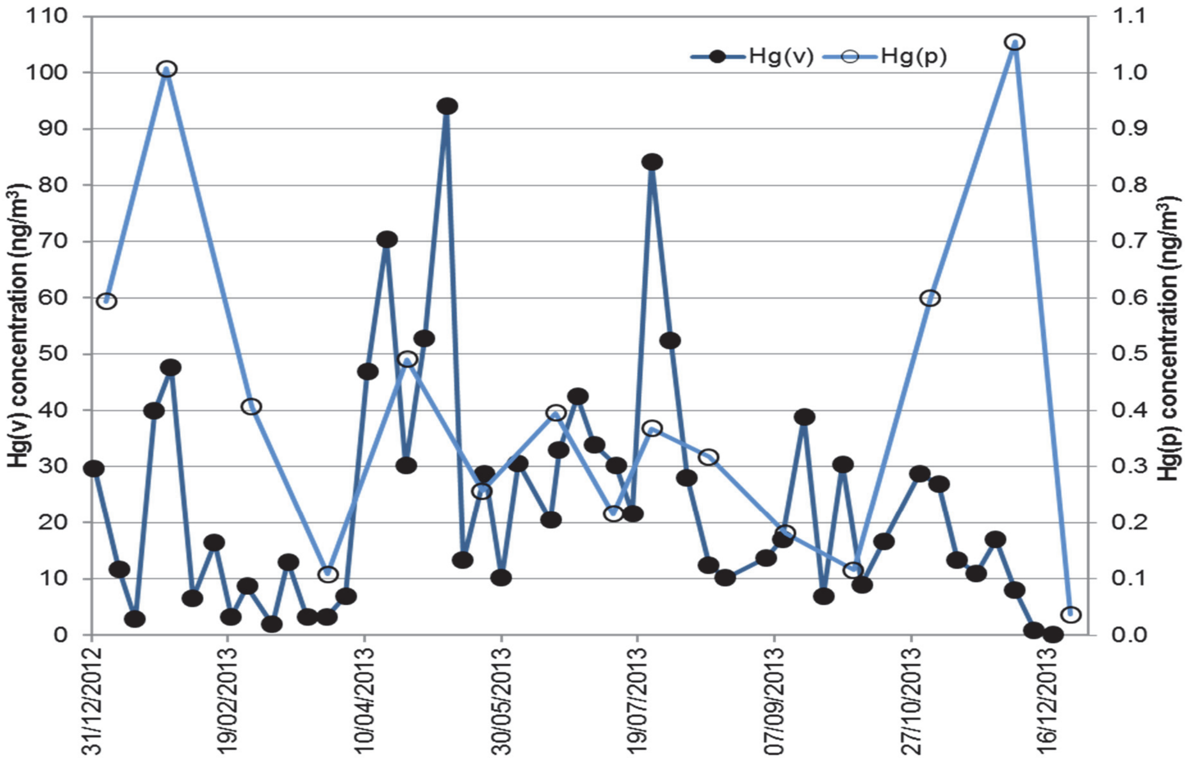

Figure 7. Measured weekly Hg(v) and four-weekly Hg(p) concentrations at Site 59: Runcorn Weston Point, in 2013. The values are displayed at the centre of the sampling period to which they refer.

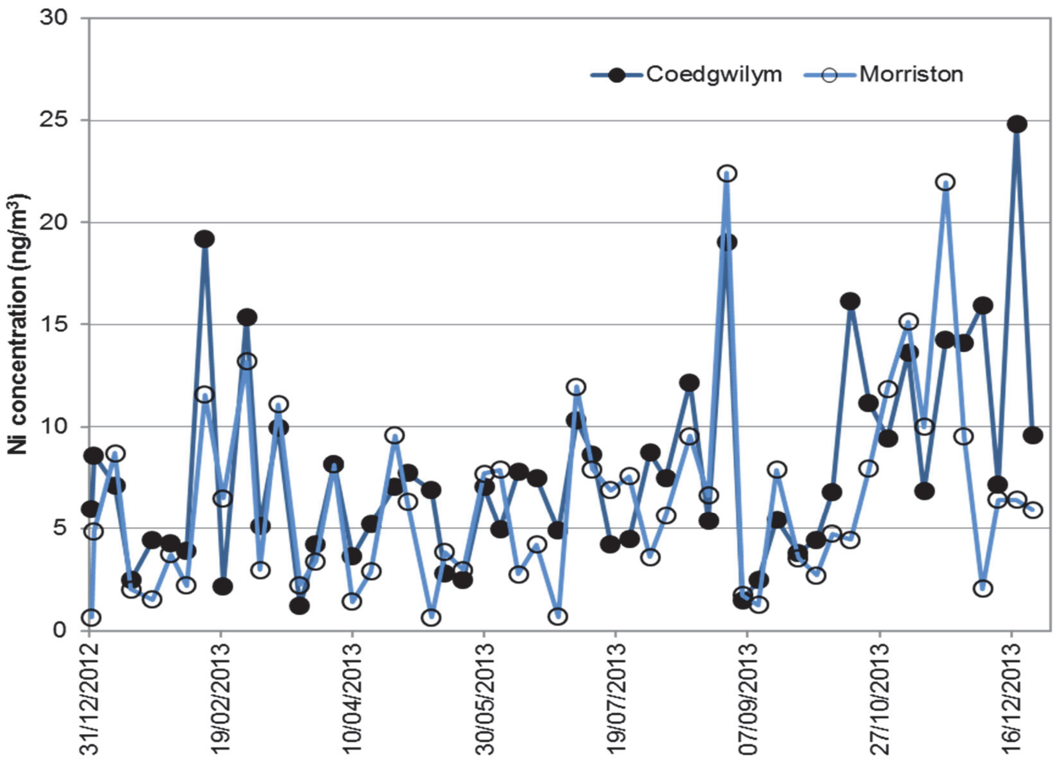

Figure 8. Measured Ni concentrations at Site 100: Swansea Coedgwilym and Site 101: Swansea Morriston, in 2013 (both sampled weekly).

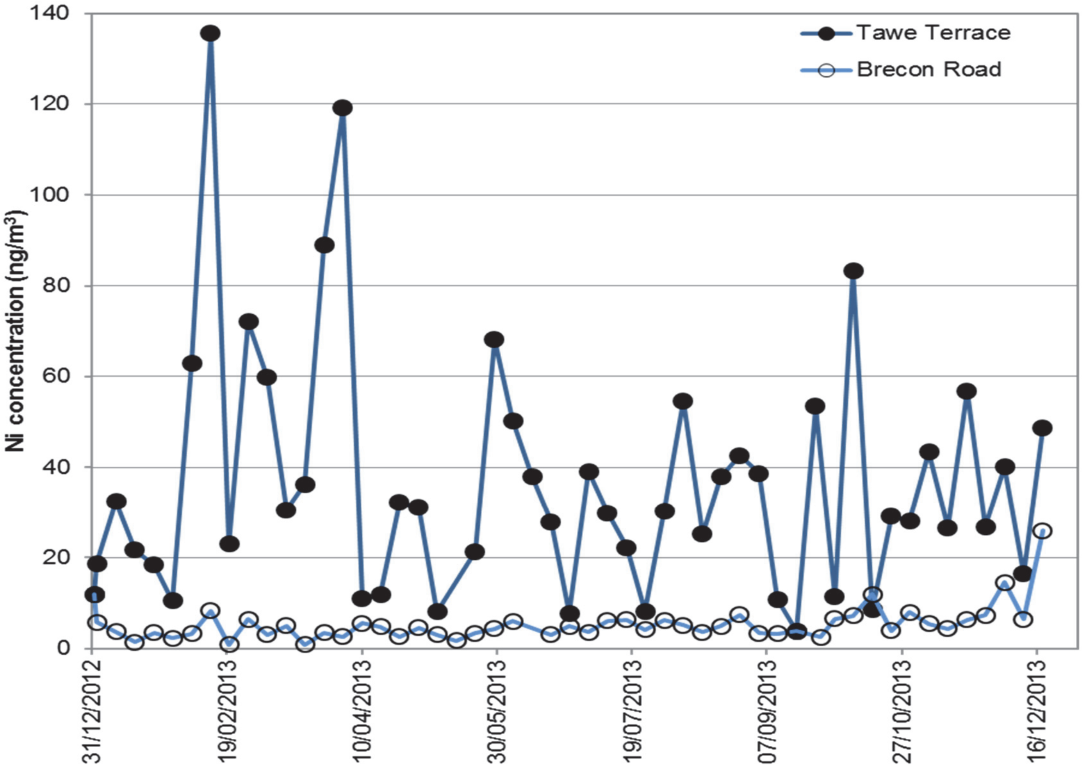

Figure 9. Measured Ni concentrations at Site 113: Pontardawe Tawe Terrace and Site 115: Pontardawe Brecon Road, in 2013 (both sampled weekly).

It is clear from these Figures 6 to 9 that the variability in measured concentrations from week to week is often large – much more so than when these values are averaged over a monthly period.

High concentration spikes often make a significant contribution to the annual average. A good example of this is the high Ni concentrations in January and October at Sheffield Brinsworth and Sheffield Tinsley respectively. Determining the origin of these high concentration events and how they relate to the industrial process being monitored and the local meteorological conditions can be a crucial part to reducing concentrations in the long term. For the stations in South Wales, where there is significant interest in these weekly values from both regulators and industry as part of the Swansea Nickel Working Group chaired by the Welsh Government, it is often possible to correlate high concentration spikes with specific industrial processes or events.

As expected, downwind sites all exhibit higher measured concentrations than their respective upwind site pairs (except for the Tawe Terrace and Brecon Road pair, as explained in Section 6.2). This continues to provide extra confidence that the direction of the prevailing weather conditions has been correctly assessed at each location and that the monitoring site pairs have been properly located. However, the concentrations recorded to date at these new sites are well below those predicted in the report[12] 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.

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

6.4 MEASURED CONCENTRATIONS OF NON-DIRECTIVE METALS

Figure 10 shows the concentrations of the other non-directive metals normalised to the annual median value for each metal.

High concentration values for non-Directive metals are usually owing to specific processes close to the monitoring sites concerned. For instance:

- Copper and iron at roadside sites such as London Cromwell Road, London Marylebone Road, Swansea Morriston and Manchester Wythenshawe from non-exhaust emissions and re-suspension;
- Iron and Manganese at Port Talbot Margam and Scunthorpe Low Santon, near to steel works;
- Chromium, manganese and zinc at Sheffield Brinsworth near to a steel processing facilities;
- Particulate phase mercury at Runcorn Weston Point close to a chemical plant and probable contributions from re-suspension and volatilisation from contaminated land;
- Copper and zinc at Walsall Bilston Lane close to a metal refining works;
- Cobalt at Pontardawe Tawe Terrace close to a nickel-cobalt alloy production process;
- Elevated vanadium at Scunthorpe Low Santon and Chadwell St Mary, possibly owing to the steel works and nearby metals refining processes, respectively;

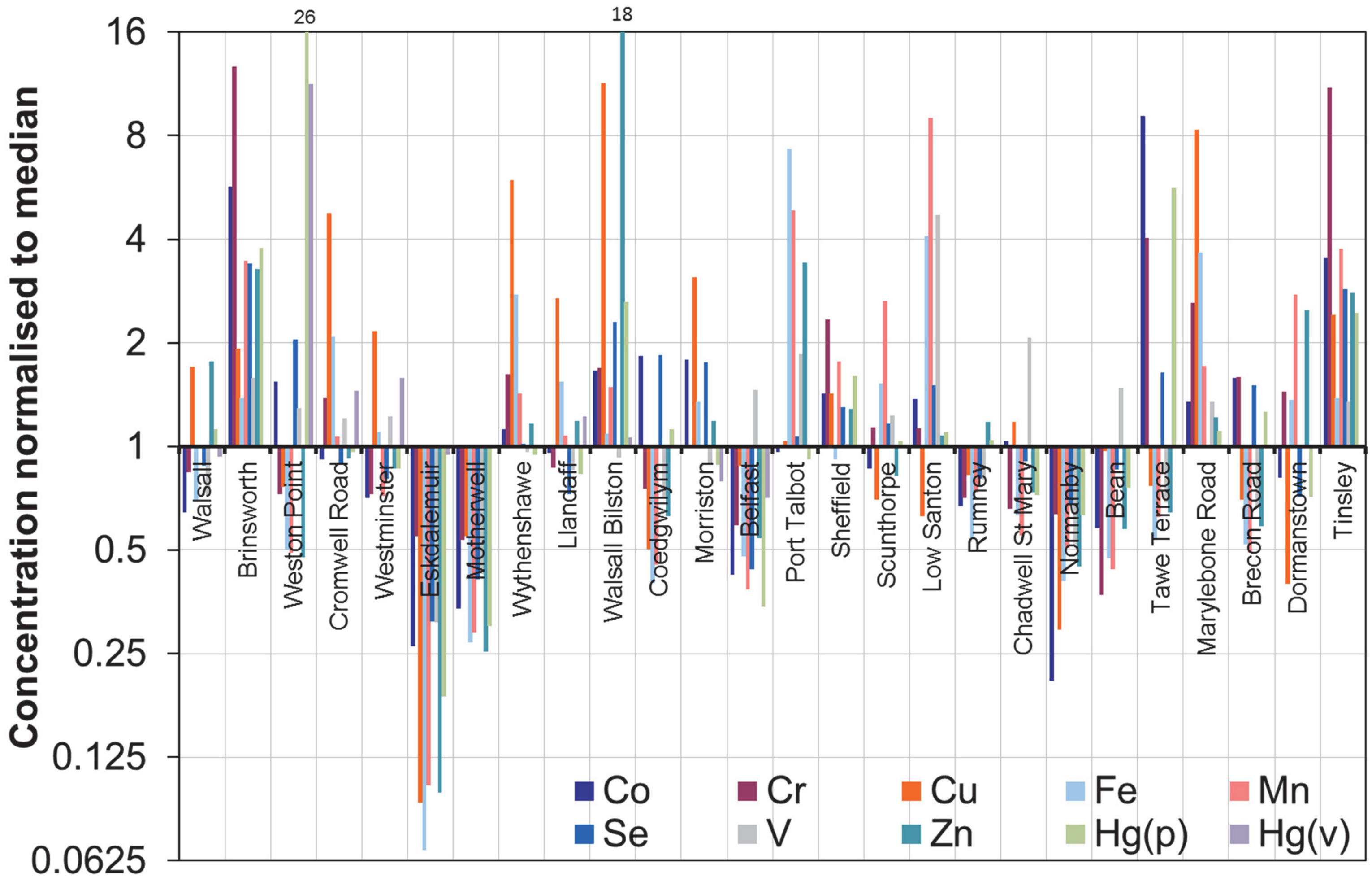

Figure 10. A summary of the annual mean measured concentrations of the non-directive metals at all sites on the UK Heavy Metals Monitoring Network in 2013, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median so it is clear which stations are above and below the median level. Bars that are off scale at the top of the chart have their values indicated. Hg(p) and Hg(v) refers to particulate phase mercury and vapour phase mercury, respectively.

6.5 RATIO OF TOTAL GASEOUS MERCURY TO PARTICULATE PHASE MERCURY

Figure 11 shows the relationship between particulate and vapour phase mercury measurements during 2013 where these are measured together on the Network.

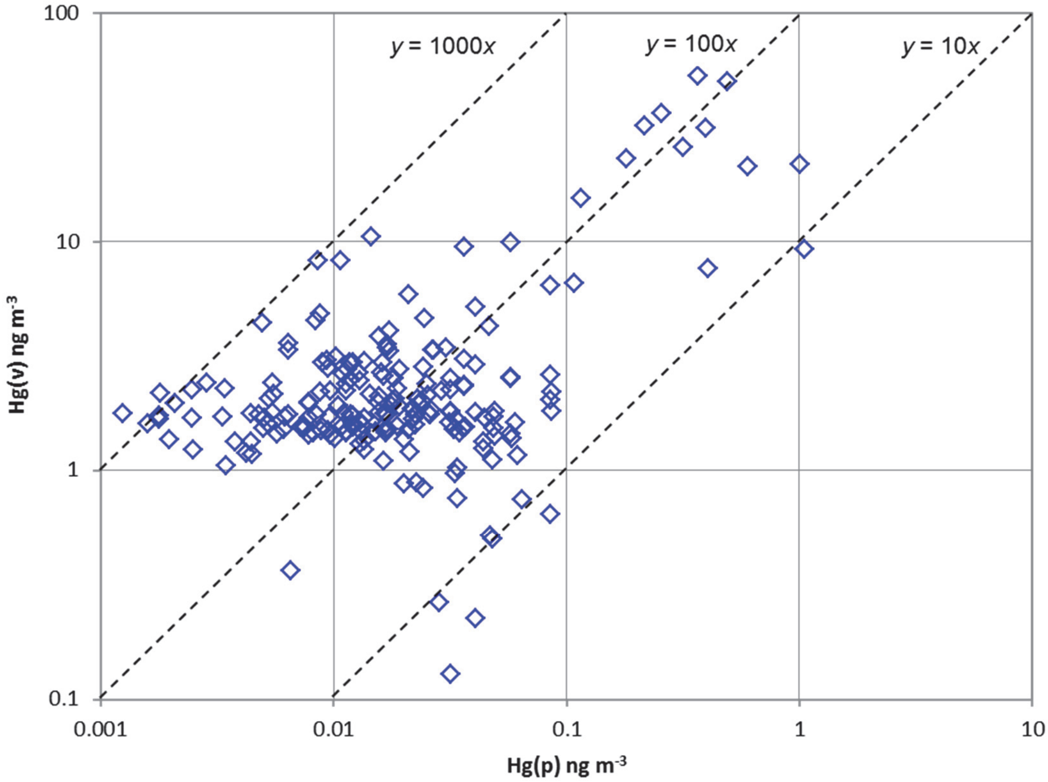

Figure 11. The relationship between monthly particulate [Hg(p)] and total gaseous [Hg(v)] mercury measurements during 2013 where these are made together. The dotted diagonal lines represent the locus of points for which the total gaseous mercury concentration (*y*) are 10, 100 and 1000 times greater than the measured particulate phase mercury concentrations (*x*), as indicated.

Figure 11 shows that in almost all cases the total gaseous to particulate mercury concentration ratio during 2013 was greater than 10 (97.5 % of all data points), with the majority of measurements displaying a ratio of between 10 and 100 (56 % of all data points) or between 100 and 1000 (38 % of all data points). Some ratios (about 3 % of all values) are in excess of 1000. This demonstrates that the overwhelming majority of mercury in ambient air is present in the gaseous phase, at sites where these are measured together. The overall average total gaseous to particulate mercury concentration ratio during 2013 was 244. From 2014 onwards, monitoring of particulate phase mercury will cease at all network stations, and vapour phase monitoring will be discontinued at all sites aside from Runcorn Weston Point and London Westminster.

The table below shows the annual average total gaseous mercury to particulate phase mercury ratio at each site on the Network measuring both species.

Site	Annual average Hg(v) to Hg(p) ratio
Runcorn Weston Point	85
Walsall Bilston Lane	86
Sheffield Centre	97
Walsall Centre	113
Swansea Morriston	144
Port Talbot	151
Manchester Wytheshawe	185
Cardiff Llandaff	191
London Cromwell Rd	229
London Westminster	269
Belfast Centre	343
Motherwell South	597
Eskdalemuir	1038

Table 7. The 2013 annual average total gaseous mercury to particulate phase mercury ratio at each station on the Network which measures both species.

It is clear that there is some correlation between site type and the ratio observed. In general total gaseous mercury levels are similar across the country because of the long-range transport and relatively long atmospheric lifetime of this species compared to particulate bound metal species. (Although more recently elevated mercury vapour concentrations have been observed in urban centres.) In contrast, particulate bound mercury concentrations will be strongly related to distance from significant emissions sources. Hence industrially impacted sites such as Runcorn Weston Point (where both Hg(v) and Hg(p) are very high), Sheffield Centre, Walsall Centre, and Walsall Bilston Lane, show low ratios because of their relatively high Hg(p) levels. Sites impacted mostly by traffic emissions, such as London Cromwell Road, London Westminster, Manchester Wythenshawe, Cardiff Llandaff and Swansea Morriston, with intermediate Hg(p) levels show intermediate ratios. Sites in rural locations, such as Eskdalemuir, or in urban areas not close to significant traffic emissions, such as Belfast Centre and Motherwell South, show the highest ratios.

7 TRENDS IN MEASURED CONCENTRATIONS

7.1 UK TRENDS

Trends in concentrations measured over the last 33 years for the metals relevant to the EU Air Quality Directives are summarised in Figures 11 and 12, where both the UK mean and UK median concentrations are displayed. The median has been used in addition to the mean since it is less sensitive to the effect of significant changes in sites measuring high concentrations, and to changes in the number and location of monitoring stations making up the Network.

The trends in both the UK annual mean and median observed for the other metals measured by the Network are shown in Figures 13 and 14. (Co and Se are not included since they have only been measured for two years. Pt is excluded since many concentrations are below the detection limit).

Where mean values are significantly higher than median values, this indicates that that there are a small number of sites with very high concentration levels whose measured values and variability have a disproportionate effect on the overall mean. Under these circumstances the median value may give a more representative reflection of the long-term concentration trends.

Annual mean concentrations for all elements have generally fallen over the period for which data are available – this generally mirrors the decrease in emissions over this period (see Figure 1).

In recent years this trend has levelled off to yield more stable concentrations. Indeed the largest influences from year to year in recent years have tended to come from either meteorological variability or from changes in the composition of the Network. For instance the increase in the mean nickel concentration from 2010 to 2011 as a result of the replacement of the two stations in Avonmouth recording background nickel concentrations with the two stations in Pontardawe recording elevated nickel concentrations; and the increase in copper concentrations from 2010 to 2011 as a result of the inclusion of London Marylebone Road which, as a station with heavy traffic influence, records very high copper concentrations.

Since 2008 a gradual increase in Fe and Mn concentrations has occurred. This is correlated with the incorporation onto the Network at this time of stations close to steel processing facilities, particularly Port Talbot, Scunthorpe Town, Scunthorpe Low Santon, Redcar Normanby and Redcar Dormanstown.

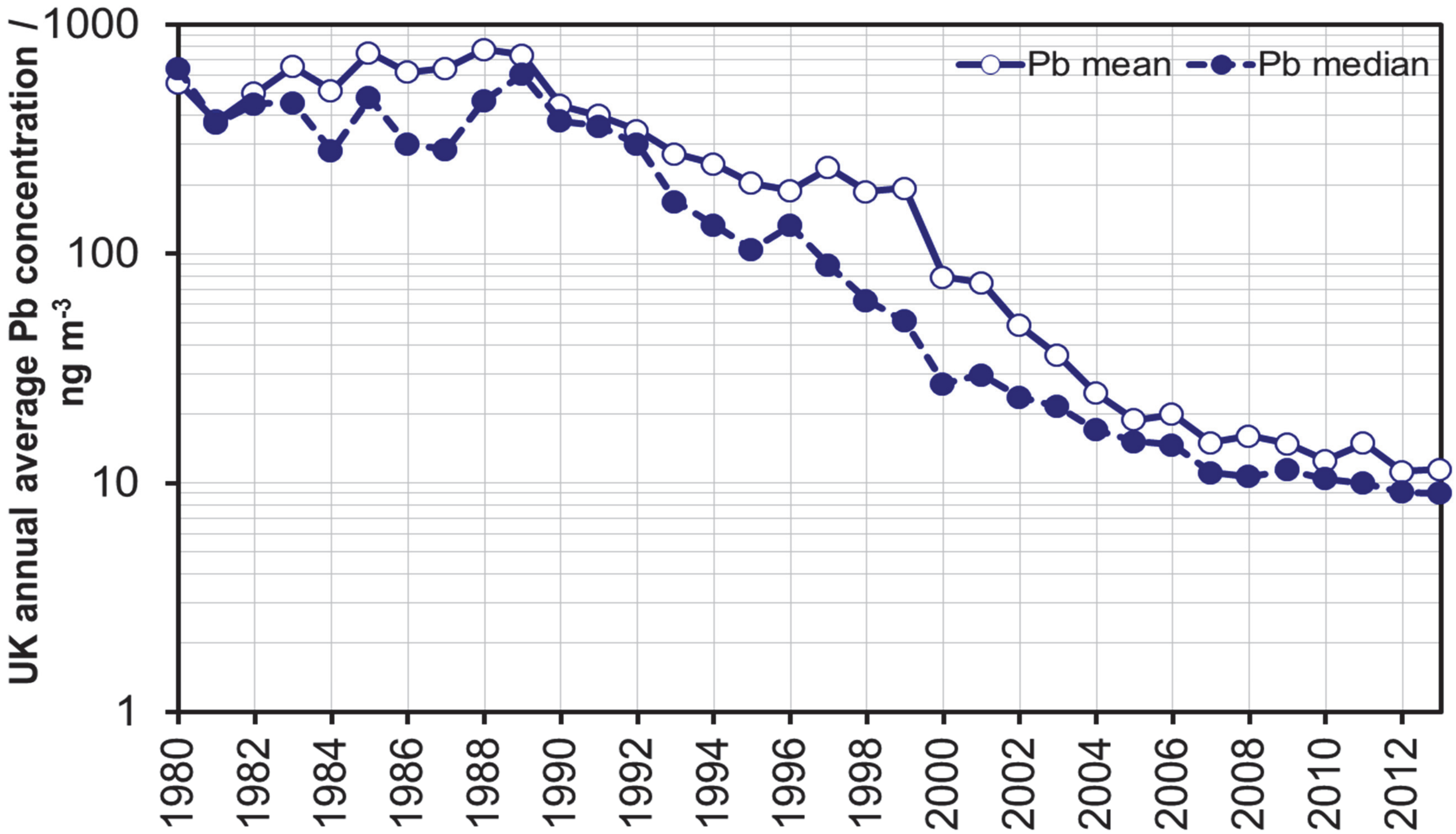

Figure 11. The mean and median of station annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 34 years. The EC limit value for lead is 500 ng m^{-3} and the UK Air Quality Objective for lead is 250 ng m^{-3}. Note the logarithmic scale on the *y*-axis.

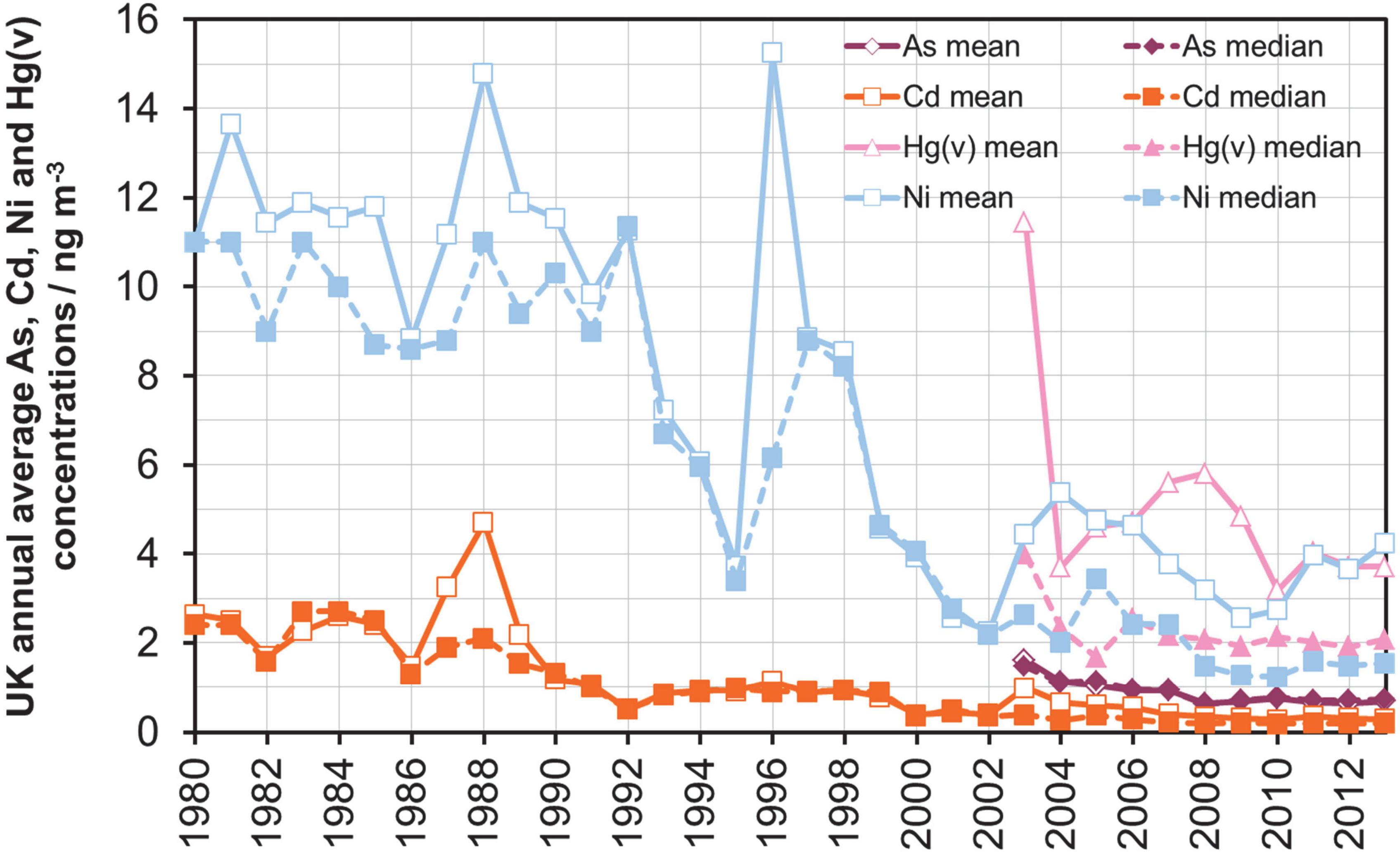

Figure 12. The mean and median of station annual average concentrations of Ni, As, Cd and total gaseous mercury [Hg(v)] measured on the UK Heavy Metals Monitoring Network over the last 34 years. The EC targets values for Ni, As and Cd are 20 ng m^{-3}, 6 ng m^{-3} and 5 ng m^{-3} respectively.

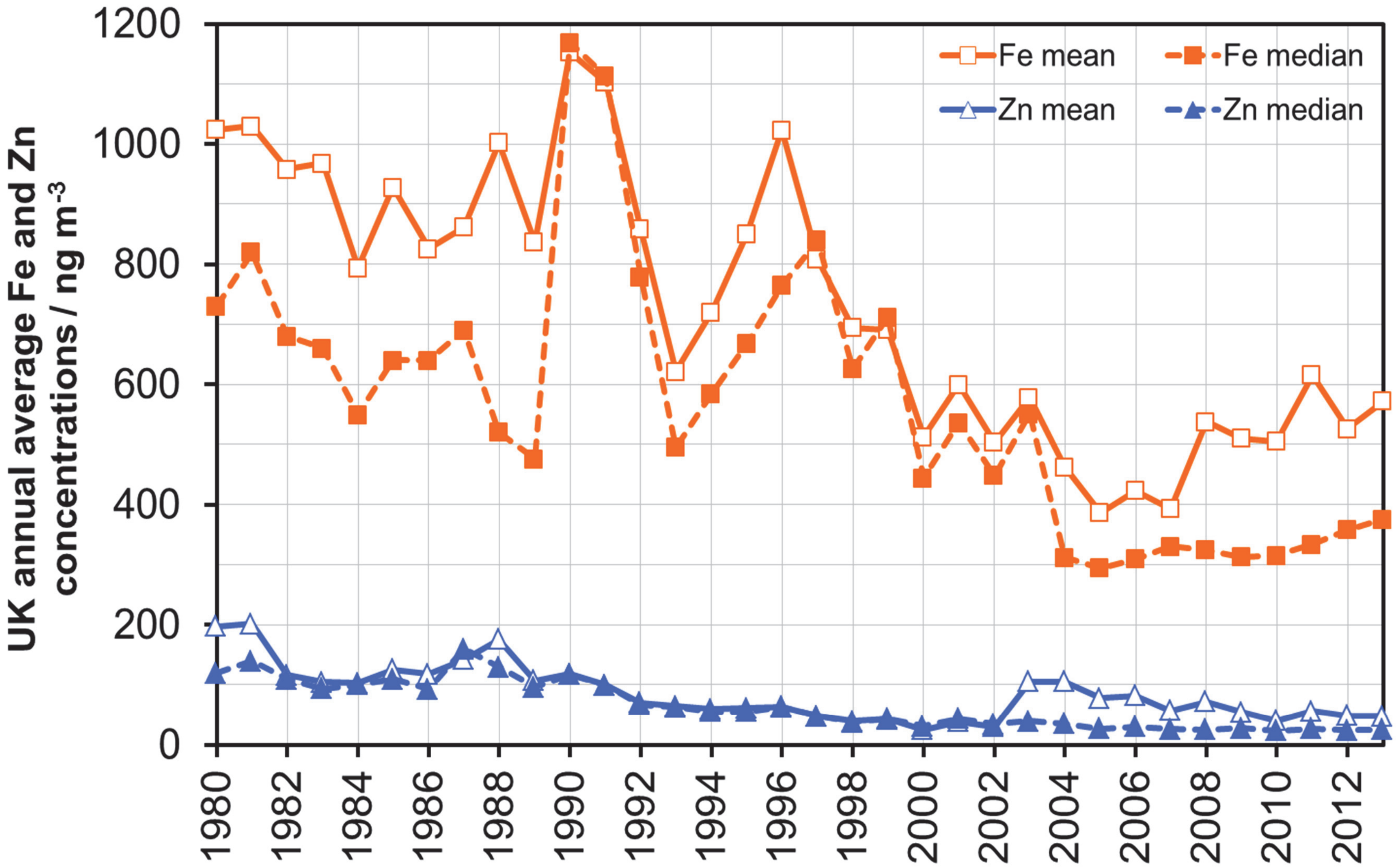

Figure 13. The mean and median of station annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 34 years.

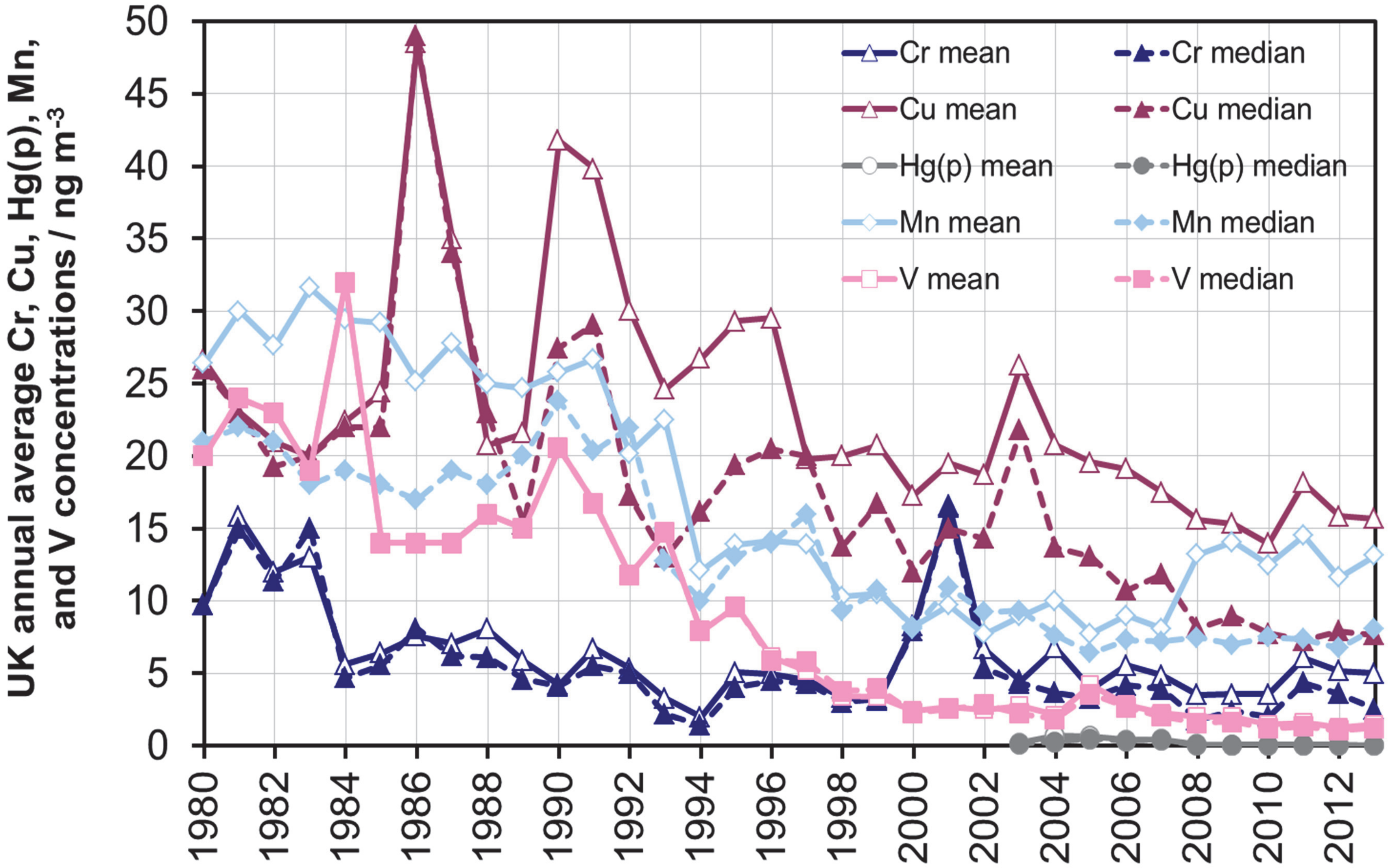

Figure 14. The mean and median of station annual average concentrations of Cr, Cu, Hg(p), Mn and V measured on the UK Heavy Metals Monitoring Network over the last 34 years.

7.2 TRENDS IN NICKEL IN THE SWANSEA AND TAWE VALLEYS

The annual average concentration of Nickel at in the Swansea and Tawe valleys measured over the last 10 years is shown in Figure 15.

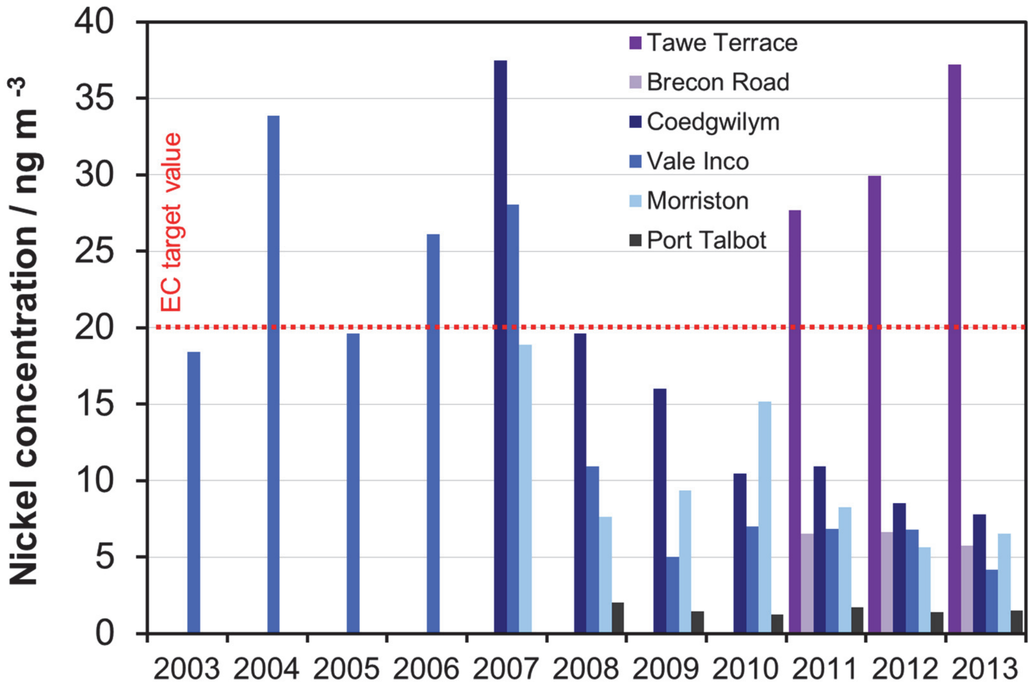

Figure 15. The annual average nickel concentrations measured at monitoring sites in the Swansea area (indicated by the key) 2003 - 2013. Nickel concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level. The red dotted line indicates the Fourth DD target value for nickel. (The data for Vale Inco in 2008 – 2013, and Coedgwilym and Morriston in 2007 are courtesy of the City and County of Swansea). Note: the Vale Inco data for 2013 was only based on 18.8% data capture.

Swansea Vale Inco (located at: Glais Primary School, School Road, Glais, Swansea, SA7 9EY) was the UK Heavy Metals Monitoring site in the Swansea area from 2003 to 2007 inclusive: it was then operated as a City and County of Swansea local authority site with site auditing and analysis services provided by NPL until it's closure (5th June 2013). At the end of 2007 the local authority sites at Swansea Coedgwilym and Swansea Morriston were affiliated to the Network.

The Swansea valley stations (i.e. excluding Pontardawe Tawe Terrace and Brecon Road) have shown a decrease in measured concentrations from 2007 onwards. This correlates with abatement technologies being installed in late 2007 in order to reduce particle emissions from the point source in question. According to information from the operators presented at the 'Nickel in South Wales Working Group', in 2013 the industrial point source in the Swansea valley experienced its highest production since 2008, whilst also achieving a 70% reduction in emissions over the same period. The network monitoring results appear to support this figure, although the data for the Vale Inco station in 2013 was only based on 18.8% data capture, so should be viewed with caution.

Another City and County of Swansea local authority site for which NPL provide the auditing and analytical service, YGG Gellionnen (location: YGG Gellionnen School, Gellionnen Road, Clydach, Pontardawe, SA6 5LB), has shown similar concentration trends over this period. Moreover, the relative concentrations between these sites continue to be broadly as predicted by NPL's modelling study of the area in 2009[13].

In the Tawe valley the concentrations at Pontardawe Tawe Terrace have shown a year upon year increase from 2011 to 2103. Abatement processes at the industrial facility impacting on the Pontardawe Tawe Terrace station were introduced in November 2013. This was too late to have any significant influence on the 2013 annual average, but from 2014 onwards should have a positive effect in reducing local Ni concentrations.

13 NPL Report AS 30, "Atmospheric Dispersion Modelling of Nickel in the Swansea Area", Hayman, G, February 2009

8 SCIENTIFIC RESEARCH, PUBLICATIONS AND RELATED ACTIVITIES

8.1 PUBLICATIONS

NPL has produced a number of articles in learned journals during 2013 that feature the data, analytical procedures and operation of the Network and research relevant to Network objectives – especially the calculation of annual average and mitigation of the effects of missing data. These articles are listed below:

- Data loss from time series of pollutants in ambient air exhibiting seasonality: consequences and strategies for data prediction, Brown, R J C, *Environmental Science: Processes & Impacts*, 2013, **15**, 545-553.

This paper studied the effect of data loss on annual average concentrations of seasonal and non-seasonal pollutants in ambient air. The annual average concentration values produced with and without the use of predicted data have been compared to the actual annual averages in the absence of data loss.

- Improved strategies for calculating annual averages of ambient air pollutants in cases of incomplete data coverage, Brown, R J C; Harris, P M; Cox, M G, *Environmental Science: Process & Impacts*, 2013, **15**, 904-911.

This paper discussed the consequences of missing data during air quality monitoring activities and the calculation of the annual average mass concentration of ambient pollutants. A mathematical description of a preferred method for the determination of annual average concentration using the simple mean, and not using time weighting to account for missing data, is justified. It is hoped this discussion paper will provoke debate in the air quality community about the best way to assess measured concentrations of ambient pollutants against legislative values.

- A temperature-based approach to predicting lost data from highly seasonal pollutant data sets, Brown, R J C; Brown, A S; Kim, K H, *Environmental Science: Process & Impacts*, 2013, **15**, 1256-1263.

A new technique to predict concentrations of seasonal pollutants in ambient air during periods of lost data was developed and tested. The annual average concentration values produced with and without the use of predicted data have been compared to the actual annual averages in the absence of any data loss. The use of predicted data are a significant improvement when compared with the averages produced in the absence of any data prediction and outperforms previous prediction strategies associated with intra-year trends.

8.2 LEGISLATION AND STANDARDISATION

There has been little recent activity in the standardisation arena relevant to this Network. However, NPL has been active, via AQUILA, in inputting into the document "Guidance on the Commission Implementing Decision laying down rules for Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council as regards the reciprocal exchange of information and reporting on ambient air (Decision 2011/850/EU)" – the IPR Guidance – and on the supplementary AQUILA document giving further guidance on the reporting of measurement uncertainties, especially where this relates to metals and PAH concentrations in ambient air.

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 during 2013 (indicated by the orange circles) – details of which are given in Table A1 below.

NEW Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Area and Classification (with identified point source, where applicable)	Pollutants measured
46: Walsall Centre (Walsall)	74 Primley Avenue, Walsall, WS2 9UW	Urban Industrial (IMI Refiners Ltd, Walsall)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
58: Sheffield Brinsworth (Brinsworth)	BOC Gases, Bawtry Road, Brinsworth, Sheffield, S60 5NT	Urban Industrial (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
59: Runcorn Weston Point (Weston Point)	Weston Point County Primary School, Caster Avenue, Weston Point, Runcorn, WA7 4EQ	Urban Industrial (INEOS Enterprises Ltd, Weston Point)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
61: London Cromwell Road 2 (Cromwell Road)	Natural History Museum, Cromwell Road, London, SW7 5BD	Urban Traffic	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
62: London Westminster (Westminster)	Mortuary Car Park, Horseferry Road, London, SW1P 2EB	Urban Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
65: Eskdalemuir (Eskdalemuir)	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	Rural Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
66: Motherwell South (Motherwell)	Our Lady's High School, Dalzell Drive, Motherwell, North Lanarkshire, ML1 2DG	Urban Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
67: Manchester Wythenshawe (Wythenshawe)	Junction 4, M56, Newhall Green, Wythenshawe, Manchester, M22 8	Urban Traffic	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
68: Cardiff Llandaff (Llandaff)	Cleansing Depot, Waungron, Fairwater, Cardiff, CF5 2JJ	Urban Traffic (Celsa UK Ltd, Tremorfa)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
69: Walsall Bilston Lane (Walsall Bilston)	Adult Training Centre, Bilston Lane, Shepwell Green, Willenhall, Walsall, WV13 2QJ	Urban Industrial (Brookside Metals Ltd, Willenhall)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
100: Swansea Coedgwilym (Coedgwilym)	Coedgwilym Cemetery, Pontardawe Road, Clydach, Swansea, SA6 5PB	Urban Background (Vale Ltd, Swansea)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
101: Swansea Morriston (Morriston)	Morriston Groundhog, Wychtree Street, Morriston, Swansea, SA6 8EX	Urban Traffic (Vale Ltd, Swansea)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
103: Belfast Centre (Belfast)	Lombard Street, Belfast, BT1 1RB	Urban Background	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
104: Port Talbot Margam (Port Talbot)	Port Talbot Fire Station, Commercial Road, Port Talbot, West Glamorgan, SA13 1LG	Urban Industrial (Corus Group Ltd, Port Talbot)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
105: Sheffield Centre (Sheffield)	Charter Square, Sheffield, S1 4JD	Urban Background (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)
106: Scunthorpe Town (Scunthorpe)	Rowlands Road, Scunthorpe, North Lincolnshire, DN16 1TJ	Urban Industrial (Corus Group Ltd, Scunthorpe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn

NEW Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Classification (with identified point source, where applicable)	Pollutants measured
107: Scunthorpe Low Santon (Low Santon)	Dawes Lane, Santon, Scunthorpe, North Lincolnshire, DN16 1XH	Urban Industrial (Corus Group Ltd, Scunthorpe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
109: Cardiff Rumney (Rumney)	Greenway Primary School, Llanstephen Road, Rumney, Cardiff, CF3 3JG	Urban Background (Celsa UK Ltd, Tremorfa)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
110: Chadwell St Mary (Chadwell St Mary)	Council Area Housing Office, Linford Road, Chadwell St Mary, Essex, RM16 4JY	Urban Background (Britannia Refined Metals, Gravesend)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
111: Redcar Normanby (Normanby)	Tees, Esk and Wear Valleys NHS Trust, Flatts Lane, Normanby, Middlesbrough, TS6 0SZ	Urban Background (Corus Group Ltd, Redcar)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
112: Dartford Bean (Bean)	Bean Primary School, Bean, Dartford, Kent, DA2 8AW	Urban Background (Britannia Refined Metals, Gravesend)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
113: Pontardawe Tawe Terrace (Tawe Terrace)	Tawe Terrace, Pontardawe, Swansea, West Glamorgan, SA8 4HA	Urban Industrial (Wall Colmonoy, Pontardawe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
114: London Marylebone Road (Marylebone Road)	Marylebone Road (opposite Madame Tussauds), London, NW1 5LR	Urban Traffic	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
115: Pontardawe Brecon Road (Brecon Road)	Dany Bryn Residential Care, 84 Brecon Road, Pontardawe, Swansea, SA8 4PD	Industrial Suburban (Wall Colmonoy, Pontardawe)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
116: Redcar Dormanstown (Dormanstown)	Price Road, Dormanstown, Redcar, TS10 5LY	Suburban Background (Corus Group Ltd, Redcar)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
117: Sheffield Tinsley (Tinsley)	Ingfield Avenue, Tinsley, Sheffield. S9 1WZ	Urban Industrial (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn
119: Sheffield Devonshire Green (Devonshire Green)	Devonshire St, Sheffield, South Yorkshire. S3 7SW	Urban Background (Outokumpu Stainless Ltd, Sheffield)	As, Cd, Co, Cr, Cu, Fe, Hg(p), Mn, Ni, Pb, Pt, Se, V, Zn, Hg(v)

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

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Image 4. The head of the Partisol sampler at London Westminster appears above the wall of the Westminster Public Mortuary on Horseferry Road.