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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 2014 on the UK Heavy Metals Monitoring Network

Sharon L. Goddard
Richard J. C. Brown
David M. Butterfield
Elizabeth A. McGhee
Chris Robins
Andrew Brown
Sonya Beccaceci
Adam Lilley
Chris Bradshaw
Stuart Brennan

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Environment Division

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

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Approved on behalf of NPLML by
Jane Burston, Head of Environment Division

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 2014 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 2014.
- A brief summary of scientific research, publications, international representation and other activities related to the Network.

In summary, during 2014:

- There were two exceedances of a target or limit value across the Network: Nickel, at Pontardawe Tawe Terrace and Sheffield Tinsley.

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

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

- **Cadmium**: One 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.

- 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 **95.7 %** 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 2014 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 2014.

- 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 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

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.

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)].

At the beginning of 2014, the former UK Urban and Industrial Heavy Metals Monitoring Network and Rural Heavy Metals Monitoring Network were merged to form one network: the UK Heavy Metals Monitoring Network. All national heavy metals monitoring sites now operate under the auspices of this single network.

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.

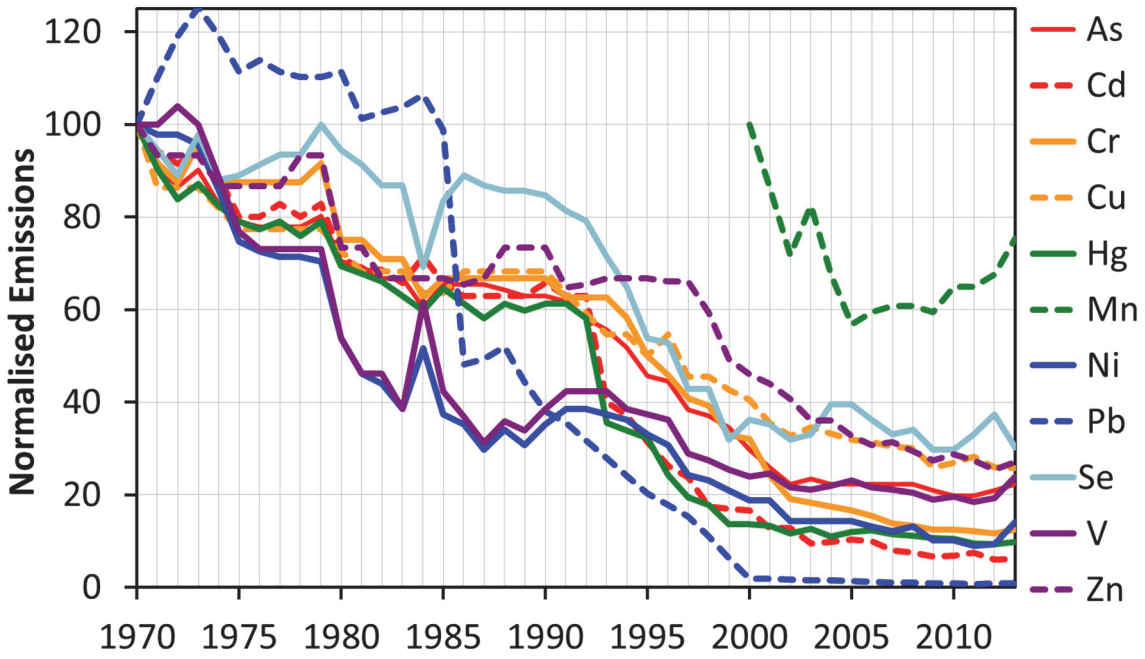

Figure 1. Estimated UK annual emissions of the metals from 1970 to 2013 normalised to their values in 1970 such that 1970 = 100 (except for Mn where values are only available since 2000 and therefore have been normalised to this year). The absolute levels of emissions in 1970, in tonnes, were: As, 81; 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, 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 and international conventions to which the UK is a signatory (including EMEP and OSPAR);
- 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;
- To provide background concentrations as a baseline for air quality modelling;
- To provide accurate ambient concentration data to benchmark against emissions inventory estimates.

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 at the end of 2014 comprised 23 monitoring sites around the UK (13 in England, 6 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 2 of these Network sites. These adsorption tubes are then analysed at NPL to produce concentration values for total gaseous mercury in ambient air. In addition, metals in deposition are monitored at 5 sites, 4 of which also monitor mercury in deposition. Relevant activity related to Network operation during 2014 is detailed below.

2.1 OVERVIEW

NPL's management of the UK Heavy Metals Monitoring Network in 2014 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 (see Figure 3).

2.2 SITE AUDITS

During 2014 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 2014, 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:

- 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 is 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 2014 the ESU twice fully serviced, carried out preventative maintenance and calibrated the flow of the Partisol samplers at all Network sites.

- During 2014, NPL called-out the ESU to deal with Partisol sampler faults at: Belfast, Detling, Eskdalemuir and Scunthorpe Low Santon.

2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION

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

- The Network underwent significant reorganisation in 2014. At the beginning of 2014 the Urban and Industrial Heavy Metals Monitoring Network merged with the Rural Heavy Metals Monitoring Network to produce a combined UK Heavy Metals Monitoring Network.

- The following eight stations, previously part of the Rural Metals Network, were affiliated to this Network: Auchencorth Moss (PM and deposition), Beacon Hill (PM only), Cwmystwyth (PM only), Detling (PM only), Lough Navar (deposition only), Harwell (PM and deposition), Heigham Holmes (PM and deposition), Yarner Wood (PM and deposition).

- At the end of 2013 nine Network stations closed: Cardiff Llandaff, Cardiff Rumney, Dartford Bean, London Cromwell Road, Manchester Wythenshawe, Motherwell, Redcar Dormanstown, Redcar Normanby, Walsall Centre.

- These changes were made in order to focus network resources on the sites with the highest concentrations. The sites that were closed had historically monitored low levels of metals (below the LAT) and were therefore not required for the purposes of

compliance assessment with the Fourth Daughter Directive and were not deemed important to be retained for the purposes of inputting into the national compliance assessment modelling. A Fourth Daughter Directive Regime Review report will be published on Defra's UK Air Website during 2015 detailing this assessment.

- From the beginning of 2014, Pt and Hg are no longer measured in PM_{10} at any station, and vapour phase mercury is only measured at Runcorn (only station with concentrations significantly above background levels due to industrial sources) and London Westminster (highest roadside concentration).

- On 20th March 2014 site 207: Beacon Hill station ceased monitoring and was closed. A replacement site is being identified.

- On 2nd December 2014 site 209: Fenny Compton 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 or 2025A/B 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 2 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.

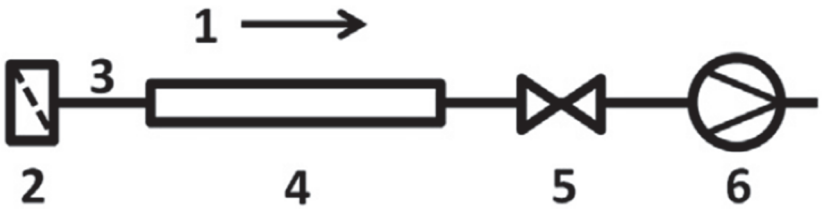

Figure 2. Schematic diagram of the total gaseous mercury sampling apparatus, where: 1 - direction of air flow, 2 - inlet particulate filter, 3 - PTFE tubing (with length minimised between the inlet particulate filter and 'Amasil' adsorption tube to fewer than 10 cm), 4 - 'Amasil' adsorption tube, 5 - flow restrictor, 6 - pump.

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 Tinsley, Walsall Bilston Lane, Swansea Coedgwilym, Swansea Morriston, Pontardawe Tawe Terrace and Pontardawe Brecon Road where weekly data is 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 2). 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 mixture used was 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) 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 a four-weekly average for London Horseferry Road and weekly for Runcorn Weston Point.

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.

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.

3.5 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION

Following the reorganisation of the Network on 1st January 2014, measurement of heavy metals and mercury in deposition are also being undertaken by the Network at Auchencorth Moss, Harwell, Yarner Wood, Cwmystwyth, Heigham Holmes and Detling. Measurement of heavy metals only in deposition (not including mercury) is additionally being undertaken at Lough Navar.

For the metals in deposition samples, analysis took place at CEH's Centralised Analytical Chemistry Group at Lancaster. The bulk collectors were weighed to estimate rainfall amounts then acidified with ultra-pure nitric acid (Baker Ultrex II) to a final strength of 1% v/v. The acidified 5L bulk precipitation samples were left for 24 hours to allow desorption of metals from the walls of the collector bottle and then a 50 ml sub-sample was transferred to a separate acid washed bottle. Acidified and preserved samples are stored at 4°C prior to final measurement by Inductively Coupled Plasma Mass Spectrometry (ICPMS; Perkin Elmer Nexion 300D). The ICP-MS measurement uses the same procedures and QA/QC checks outlined above for the measurements of particulate phase digests at NPL. However measurements for additional metals are made, resulting in a values for Al, Sb, As, Ba, Cd, Cr,

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.

Co, Cu, Fe, Pb, Mn, Mo, Ni, Rb, Sc, Se, Sr, Sn, Ti, W, V and Zn being produced. The procedure is in full accordance with EN 15841.

For the mercury in deposition samples, also analysed at CEH Lancaster, the Hg collector bottles are weighed to estimate rainfall amounts and then stored at 4 °C prior to analysis. Mercury in precipitation was determined by Atomic Fluorescence Spectrometry (AFS) using a PS Analytical Galahad analyser using pre-concentration of mercury on a gold trap to increase instrument sensitivity. This method is almost identical to the method described above for the analysis of TGM samples by NPL, but includes an additional step employing reductive desorption. During this step, tin chloride is added to the sample being analysed in a gas–liquid separator. This reduces all the collected mercury to elemental mercury and liberates this into the gas phase using a stream of argon bubbling through the gas-liquid separator. This mercury vapour is then collected on the trap mercury adsorption trap and analysis proceeds as per the method described above to TGM using the same quality control criteria. The only additional difference is the use of gravimetrically prepared mercury in liquid standards for calibration of the method, rather than gas phase injection. These standards are traceable to NIST mono-elemental reference materials. The procedure is in full accordance with EN 15853 and EN ISO 17852 (the analytical standard called upon with EN 15853).

3.6 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}.

Results produced by the Network for metals in deposition flux are reported as a mass of metal per unit area per unit time. In this report results are expressed in units of micrograms per square meter per day: ($\mu g/m^2$)/d.

3.7 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.

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 2014, 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.
- For deposition samples (as dispatched by our sub-contractor CEH), rigorous protocols are used for cleaning sampling equipment between collector deployments to prevent contamination.

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.

Metals and mercury in deposition (ICP-MS and AFS, CEH):

- All analysis for metals and mercury in deposition is completed within two weeks of the samples arriving at the laboratory.
- Regular extraction of an appropriate certified reference material, e.g. synthetic rain CRM obtained from Environment Canada.
- Regular measurement of blank gauges and field blank gauges (one per quarter per site).
- An annual UKAS audit of method performance, assessing analytical quality control data, is carried out.
- Three separate checks to test for bird-fouling to ensure samples are valid: 1) samples with visible fouling are not submitted for analysis. 2) samples are tested for bird fouling by determining ammonia and potassium on sub-samples from the precipitation collectors, prior to determining metals content - if these are in excess of normal thresholds samples are not submitted for analysis, and 3) following analysis, samples displaying a P: Ga ratio in excess of 0.6 are likely to have been contaminated and these are flagged as invalid.

4.2 MEASUREMENT UNCERTAINTY

The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2014 are shown in Table 1. 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	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 %
Se	20 - 35 %	-
V	11 - 16 %	-
Zn	10 - 14 %	-
Hg(v)	13 - 20 %	50 %

Table 1. The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2014. The 'EC Directive maximum' column shows the maximum permissible uncertainty at the target value allowed by the relevant EU Air Quality Directive. Hg(v) refers to total gaseous mercury.

The measurement uncertainties displayed in Table 1 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 1 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.

Uncertainties for individual deposition measurements are around 25 %, significantly less than the limit of 70 % specified in the air quality Directives.

5 DATA QUALITY

5.1 DATA CAPTURE (PM AND GASEOUS PHASE)

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.) 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 2014 was **97 %**. 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 2. 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.

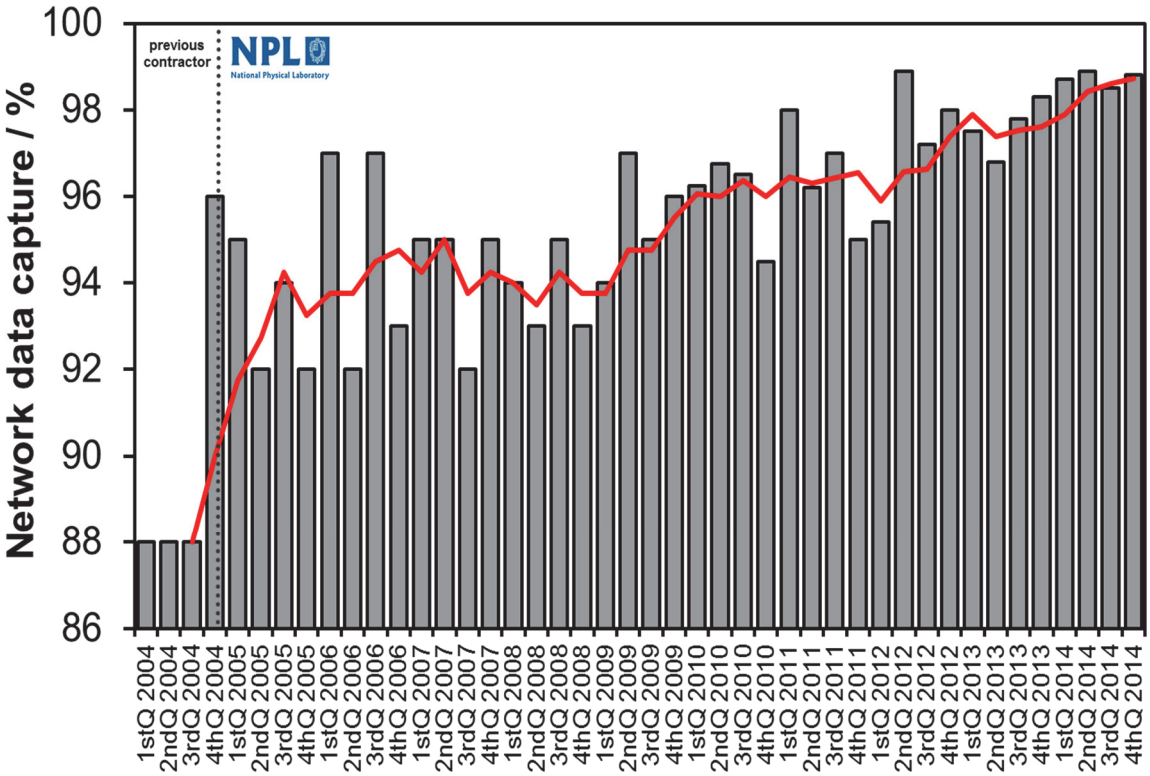

Figure 3. Network data capture from 2004-2014 (inclusive) for particulate and gaseous phase measurements. Quarterly data capture is indicated by the grey bars, whilst the rolling annual average data capture is given by the red line. Data to the right of the dotted vertical line is associated with NPL's 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
Across all stations	**97.2**	**94.2**
59: Runcorn Weston Point	98.2	88.3
62: London Westminster	97.2	100
65: Eskdalemuir	97.4	N/A
69: Walsall Bilston Lane	94.0	N/A
100: Swansea Coedgwilym	100	N/A
101: Swansea Morriston	100	N/A
103: Belfast Centre	100	N/A
104: Port Talbot Margam	99.9	N/A
106: Scunthorpe Town	95.1	N/A
107: Scunthorpe Low Santon	92.5	N/A
110: Chadwell St Mary	100	N/A
113: Pontardawe Tawe Terrace	99.7	N/A
114: London Marylebone Road	95.7	N/A
115: Pontadawe Brecon Road	96.1	N/A
117: Sheffield Tinsley	96.1	N/A
119: Devonshire Green	99.0	N/A
202: Auchencorth Moss	99.6	N/A
203: Yarner Wood	91.7	N/A
204: Cwmystwyth	98.0	N/A
205: Harwell	96.8	N/A
206: Heigham Holmes	93.9	N/A
207: Beacon Hill*	100	N/A
208: Detling	94.4	N/A

Table 2. Data capture across the UK Heavy Metals Monitoring Network during 2014. *Data capture refers only to the period of the year when the following stations were operational: Beacon Hill was closed 20th March 2014. Fenny Compton was only opened 2nd December 2014; data capture to end of 2014 was 100 %.

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

- Runcorn Weston Point (Hg vapour only): 6 weeks of sampling was lost due to repeated mercury pump failure.

5.2 DATA CAPTURE (DEPOSITION)

Data capture for deposition monitoring is generally lower than for other measurements made by the Network because of a number of external factors, for example: lack of rain during

sampling periods and contamination by bird fouling. Deposition data capture at the stations where these measurements are made is detailed in the Table below.

Site Location	Metals in Deposition / %	Hg in Deposition / %
Auchencorth Moss	94.2	100
Harwell	80.6	100
Heigham Holmes	89.8	100
Lough Navar	100	N/A
Yarner Wood	80.4	100

Table 3. Data capture across the deposition sites of the UK Heavy Metals Monitoring Network during 2014.

5.3 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, including deposition data provided by CEH. 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. For deposition samples, results are only classed as valid if tests for bird-fouling are negative, i.e. visual test and ammonia and potassium determinations prior to determining metals content. If these are in excess of normal thresholds samples are not submitted for analysis. Following analysis, samples displaying a P: Ga ratio in excess of 0.6 are likely to have been contaminated and these are flagged as invalid.
3. 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.
4. Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.
5. 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.
6. 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].

7. 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).
8. 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.

5.4 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 (p)	20 %	40 %
Cd (p)	12 %	40 %
Ni (p)	18 %	40 %
Pb (p)	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 in particulate matter (p), 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.

Uncertainties for the annual average value of metals in deposition are approximately 35 %, around half the maximum allowable limit specified in the air quality Directives.

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

6 NETWORK DATA

6.1 MEASURED CONCENTRATIONS (PM AND GASEOUS PHASE)

The annual mean measured metals concentrations in 2014, 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	2014 UK Mean Annual Concentration / ng m^{-3}	2014 UK Median Annual Concentration / ng m^{-3}	2014 Maximum Annual Mean Concentration / ng m^{-3}	EC limit or target value (UK objective) / ng m^{-3}
As	0.70	0.68	1.21	6
Cd	0.34	0.19	2.46	5
Co	0.23	0.14	1.47	-
Cr	3.79	1.61	35.2	-
Cu	12.4	5.56	80.3	-
Fe	481	216	2938	-
Mn	11.9	4.03	77.0	-
Ni	5.18	1.68	43.4	20
Pb	10.5	9.15	56.7	500 (250)
Se	0.87	0.72	2.45	-
V	1.58	1.26	7.10	-
Zn	46.8	17.4	510	-
Hg (v)	9.60	9.60	15.4	-

Table 5. The 2014 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. 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	Se	V	Zn	Hg (v)
59: Runcorn Weston Point	0.68	0.13	0.16	1.34	5.82	184	3.52	1.24	6.49	1.58	1.28	12.8	15.4
62: London Westminster	0.99	0.15	0.14	1.26	16.2	462	5.88	1.91	9.35	0.55	1.59	24.2	3.79
65: Eskdalemuir	0.16	0.04	0.03	0.75	0.71	35.0	0.99	0.54	1.32	0.25	0.48	3.57	N/A
69: Walsall Bilston Lane	1.21	2.46	0.29	3.75	80.3	459	12.5	2.30	56.7	1.75	1.15	510	N/A
100: Swansea Coedgwilym	0.65	0.26	0.33	3.06	4.13	173	3.70	12.3	9.15	1.16	0.88	17.1	N/A
101: Swansea Morriston	0.79	0.48	0.29	2.51	23.5	576	8.20	9.43	16.9	1.22	1.12	38.1	N/A
103: Belfast Centre	0.38	0.09	0.09	0.95	6.67	201	3.08	1.04	3.43	0.36	1.60	12.7	N/A
104: Port Talbot Margam	0.66	0.90	0.20	1.79	8.61	2938	43.3	1.70	15.1	0.79	3.14	121	N/A
106: Scunthorpe Town	0.82	0.33	0.14	1.61	5.53	558	22.5	1.36	11.7	1.02	1.78	23.9	N/A
107: Scunthorpe Low Santon	0.85	0.51	0.22	2.46	5.31	1656	77.0	1.68	16.5	1.33	7.10	30.8	N/A
110: Chadwell St Mary	0.96	0.25	0.13	1.13	9.24	270	4.75	2.02	10.5	0.54	2.67	21.9	N/A
113: Pontardawe Tawe Terrace	0.63	0.32	1.47	10.7	5.56	223	5.24	43.4	9.47	1.17	0.86	18.9	N/A
114: London Marylebone Road	1.09	0.19	0.23	8.28	62.4	1589	14.5	2.56	8.56	0.72	1.86	32.4	N/A
115: Pontadawe Brecon Road	1.03	0.24	0.28	2.11	5.93	216	4.03	8.06	9.60	1.14	0.84	17.4	N/A
117: Sheffield Tinsley	1.06	0.60	0.73	35.2	22.1	628	37.6	20.7	19.0	2.45	1.60	104	N/A
119: Devonshire Green	0.81	0.23	0.15	3.20	9.37	377	13.0	2.62	11.8	1.18	1.26	32.2	N/A
202: Auchencorth Moss	0.23	0.04	0.03	0.73	0.86	38.2	0.96	0.53	1.37	0.23	0.42	4.04	N/A
203: Yarner Wood	0.42	0.06	0.04	0.77	0.97	39.9	1.16	0.69	2.00	0.38	0.96	4.53	N/A
204: Cwmystwyth	0.21	0.06	0.03	0.87	0.77	44.3	1.23	0.48	2.13	0.29	0.57	4.40	N/A
205: Harwell	0.63	0.10	0.05	0.86	2.80	91.3	2.09	0.82	4.64	0.38	0.95	9.53	N/A
206: Heigham Holmes	0.52	0.11	0.08	0.82	1.81	71.7	2.00	1.42	4.18	0.53	1.76	8.45	N/A
207: Beacon Hill	0.60	0.09	0.05	2.07	2.77	110	2.21	0.64	4.44	0.44	0.70	10.8	N/A
208: Detling	0.82	0.19	0.08	0.90	4.43	129	3.24	1.65	7.39	0.46	1.88	12.7	N/A

Table 6. The 2014 annual mean concentrations (in ng/m^3) measured at individual sites on the UK Heavy Metals Monitoring Network. 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:

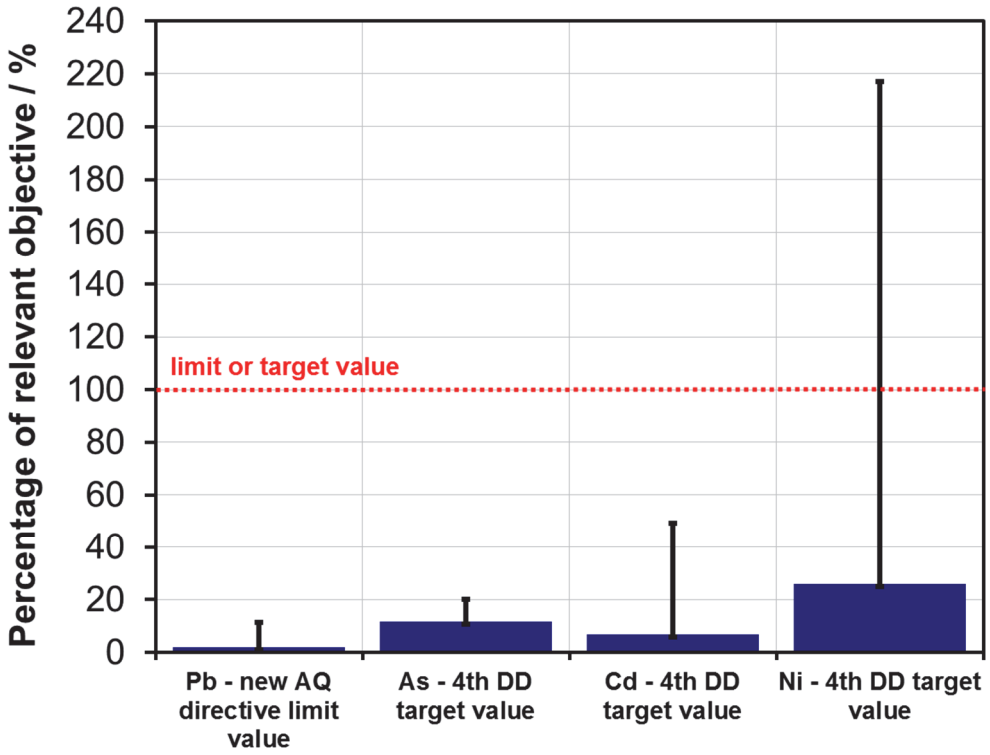

Figure 4. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth Daughter Directives on the UK Heavy Metals Monitoring Network in 2014 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all 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.

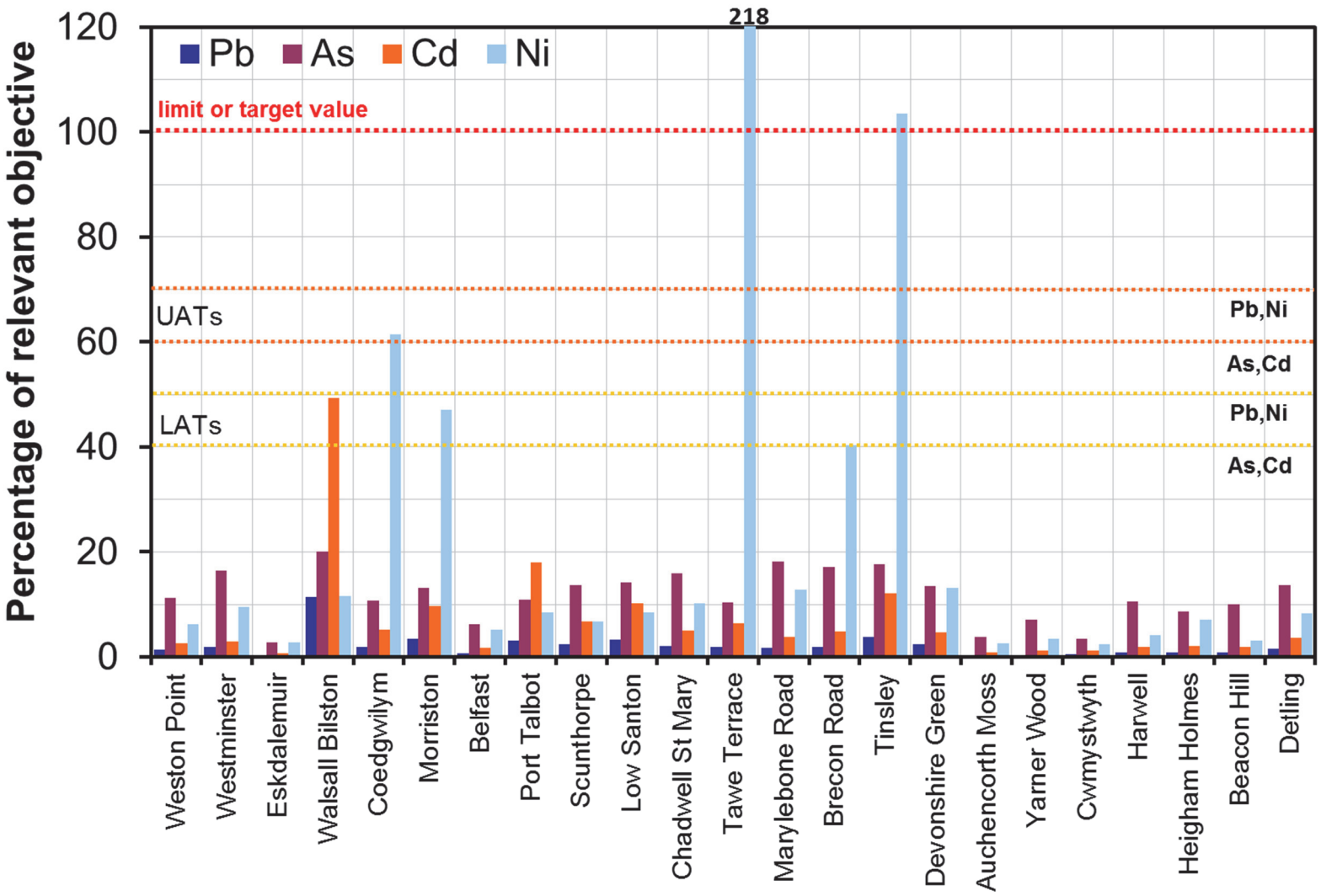

Figure 5. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2014 as a percentage of the relevant target values, lower assessment thresholds (LATs) and upper assessment thresholds (UATs).

In only four 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: 218 % of the target value.
- Nickel at Site 117: Sheffield Tinsley: 104 % of the target value.

Annual Mean Concentrations above the Lower Assessment Threshold:

- Nickel at Site 100: Coedgwilym Cemetery: 62 % of the target value.
- Cadmium at Site 69: Walsall Bilston Lane: 49 % of the target value.

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 Tinsley 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 Coedgwilym Cemetery is located approximately 2.7 km to the southwest of the Wall Colmonoy facility in Pontardawe and 1.2 km northeast of the Vale Europe facility in Clydach.

Fenny Compton

The new site at Fenny Compton only began sampling on 2nd December 2014. This site location was selected to measure re-suspended arsenic in soil and from nearby motorways in response to exceedances of the lower assessment threshold predicted by Defra's modelling contractor. Concentrations for all Directive metals were below the Lower Assessment Thresholds for the limited sampling period available. The mean concentrations measured are outlined in the table below.

Analyte	Mean concentration / ng/m^3
As	0.85
Cd	0.08
Co	0.03
Cr	0.88
Cu	1.86
Fe	55.2
Mn	1.23
Ni	0.17
Pb	4.55
Se	0.27
V	0.27
Zn	6.73

Table 7. The mean concentrations (in ng/m^3) measured at Fenny Compton, sampling period 2nd – 31st December 2014.

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 is available and where these concentrations are likely to be significant, together with data from appropriate paired sites, in the Figures below.

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.

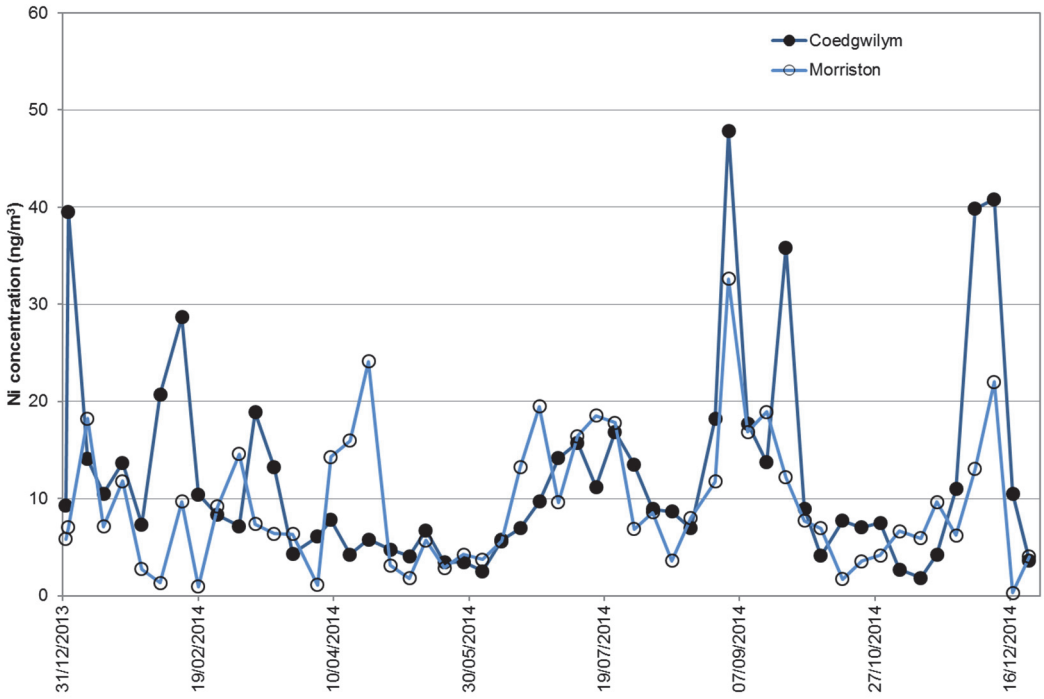

Figure 6. Measured Ni concentrations at Site 100: Swansea Coedgwilym and Site 101: Swansea Morriston, in 2014 (both sampled weekly).

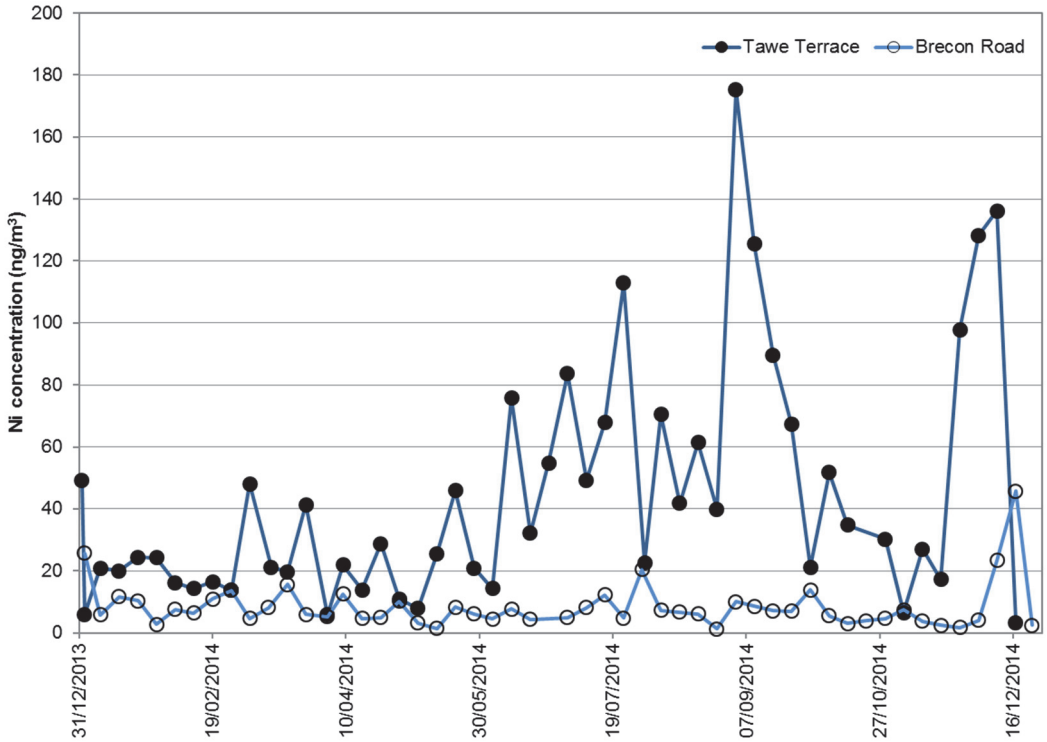

Figure 7. Measured Ni concentrations at Site 113: Pontardawe Tawe Terrace and Site 115: Pontardawe Brecon Road, in 2014 (both sampled weekly).

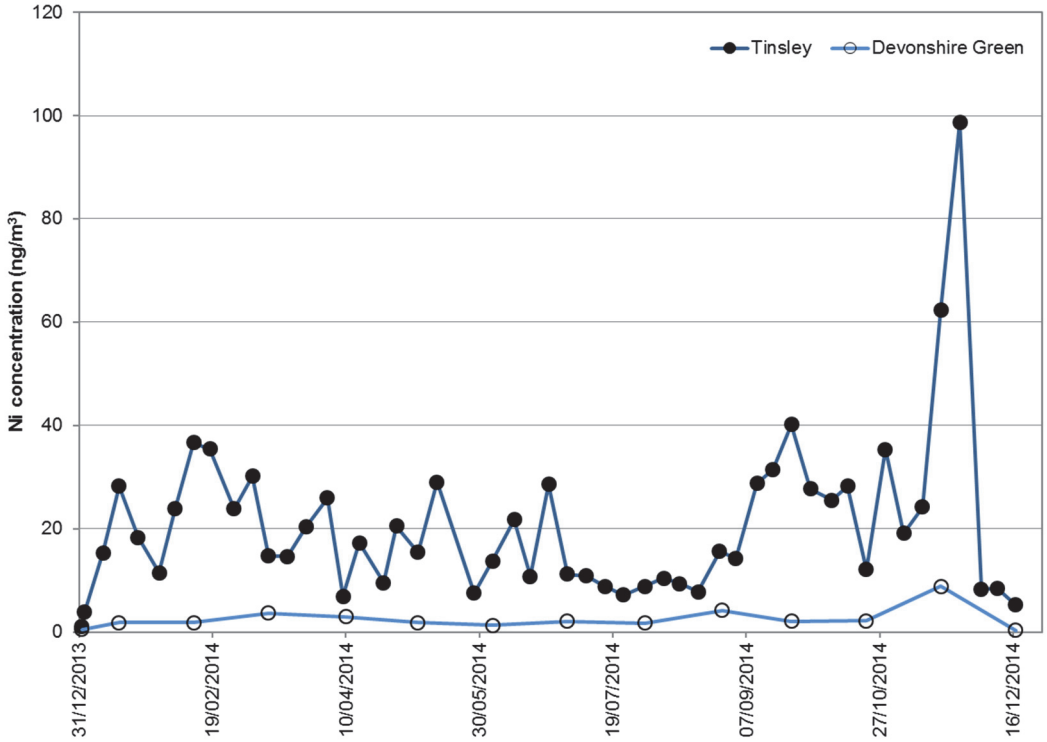

Figure 8. Measured Ni concentrations at Site 117: Sheffield Tinsley (sampled weekly) and Site 119: Sheffield Devonshire Green (results averaged over 4-weekly periods), in 2014.

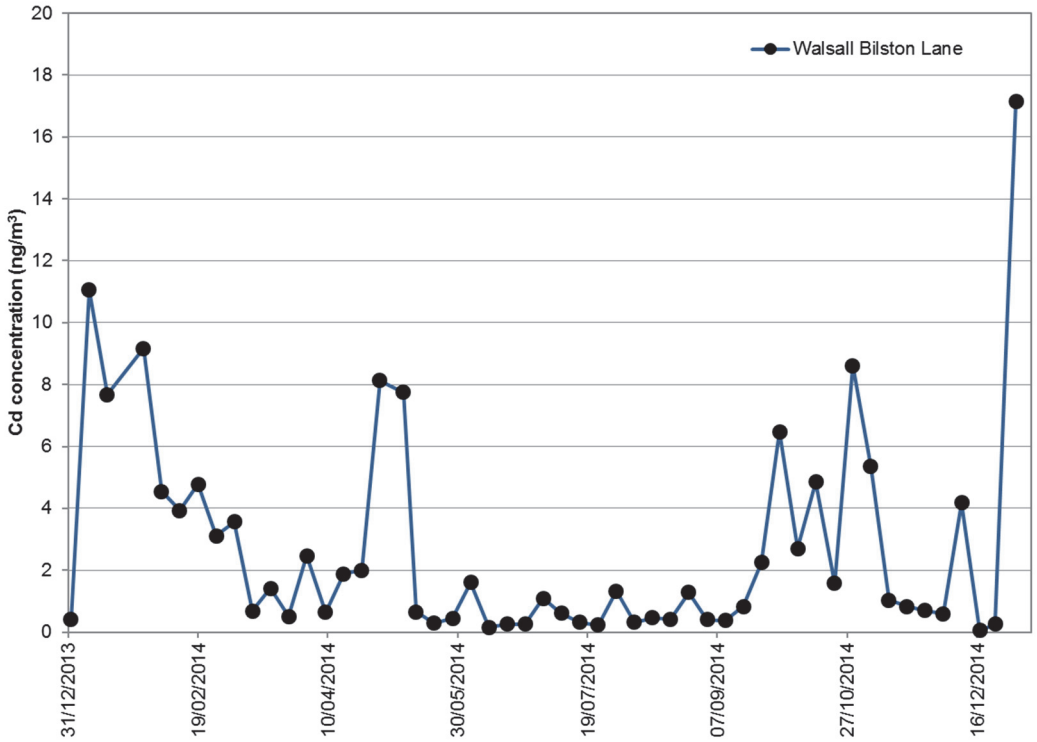

Figure 9. Measured Cd concentrations at Site 69: Walsall Bilston Lane (sampled weekly) in 2014.

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 November and December at Sheffield Tinsley and high Cd concentration spikes throughout the year at Walsall Bilston Lane. 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.

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 Marylebone Road and Swansea Morriston 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 Tinsley near to a steel processing facility;
- 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;

The former rural network stations all display low concentration values for non-Directive metals, as would be expected.

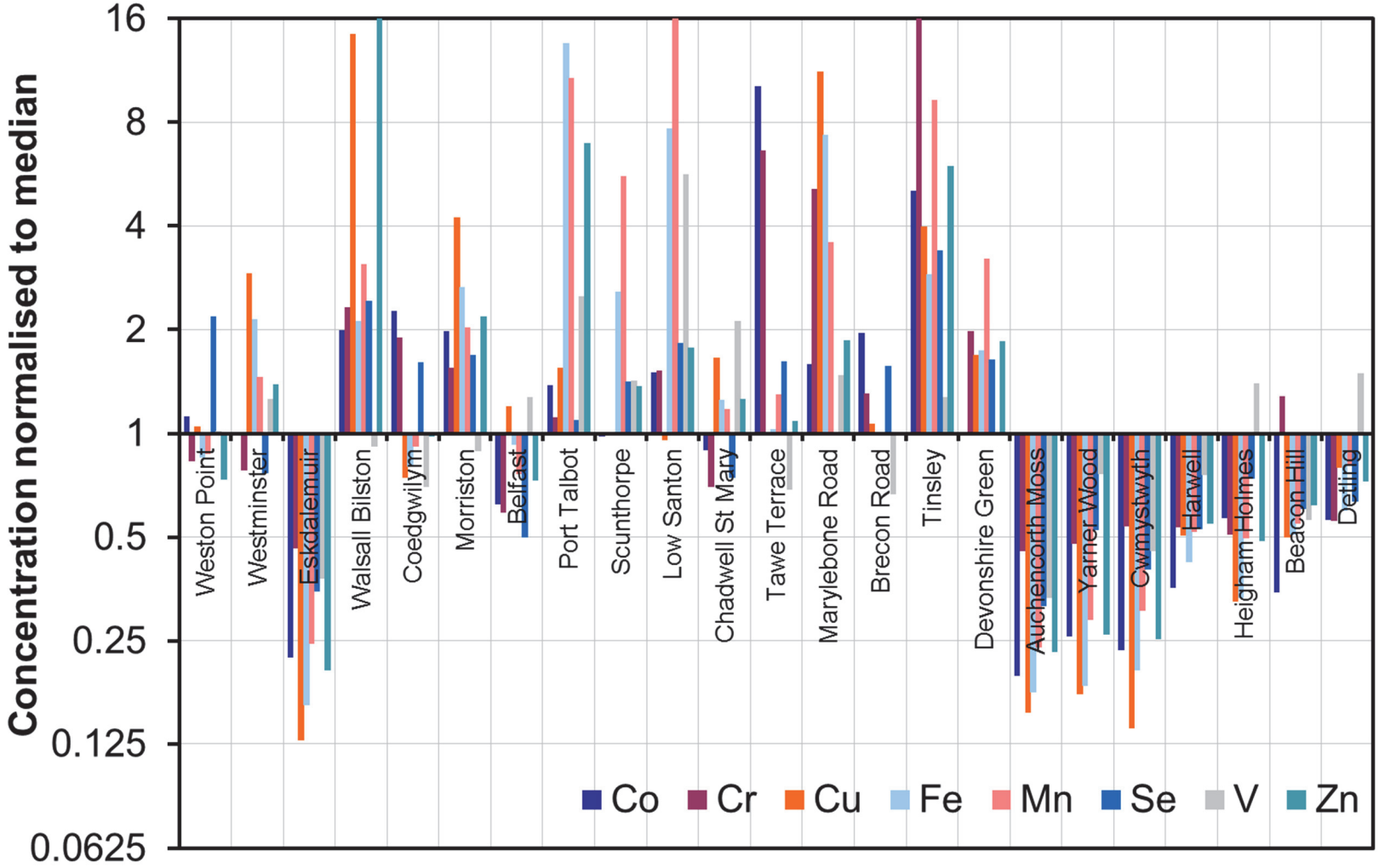

Figure 10. A summary of the annual mean measured concentrations of the non-directive metals at all sites on the UK Heavy Metals Monitoring Network in 2014, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median so it is clear which stations are above and below the median level. Bars that are off scale at the top of the chart have their values indicated.

6.5 MEASURED CONCENTRATIONS OF METALS IN DEPOSITION

The annual mean metals deposition flux concentrations in 2014, averaged over all sites sampling metals in deposition (Table 8), and at individual sites (Table 9), are given below.

Analyte	2014 UK Mean Annual Flux / µg m^{-2} d^{-1}	2014 UK Median Annual Flux / µg m^{-2} day^{-1}	2014 UK Maximum Annual Flux / µg m^{-2} d^{-1}
Al	23.8	23.2	31.4
As	0.36	0.22	0.81
Ba	2.72	1.26	8.72
Be	0.005	0.005	0.01
Cd	0.03	0.03	0.04
Co	0.03	0.04	0.04
Cr	0.25	0.23	0.34
Cs	0.01	0.01	0.02
Cu	1.43	1.39	2.44
Fe	26.0	28.3	33.5
Hg	0.01	0.01	0.02
Li	0.16	0.09	0.28
Mn	4.57	5.11	5.89
Mo	0.05	0.06	0.07
Ni	2.76	2.11	5.42
Pb	1.05	0.95	1.91
Rb	0.34	0.19	0.80
Sb	0.11	0.10	0.17
Se	0.33	0.23	0.53
Sn	0.07	0.07	0.15
Sr	6.30	3.64	11.3
Ti	0.57	0.58	0.67
U	0.004	0.004	0.01
V	0.67	0.50	1.15
W	0.02	0.01	0.02
Zn	11.4	11.7	13.7

Table 8. The 2014 annual mean, median and maximum deposition flux measurements averaged over all deposition monitoring sites on the UK Heavy Metals Monitoring Network.

	Annual Average Deposition Flux (µg m^{-2} day^{-1})				
Analyte	**Auchencorth Moss**	**Harwell**	**Heigham Holmes**	**Lough Navar**	**Yarner Wood**
Al	**31.4**	**30.0**	**23.2**	**12.1**	**22.3**
As	**0.19**	**0.22**	**0.21**	**0.81**	**0.36**
Ba	**1.26**	**8.72**	**1.68**	**0.77**	**1.18**
Be	**0.005**	**0.005**	**0.004**	**0.01**	**0.01**
Cd	**0.03**	**0.04**	**0.03**	**0.02**	**0.02**
Co	**0.04**	**0.04**	**0.04**	**0.02**	**0.03**
Cr	**0.23**	**0.23**	**0.15**	**0.30**	**0.34**
Cs	**0.01**	**0.01**	**0.01**	**0.01**	**0.02**
Cu	**0.85**	**1.72**	**1.39**	**0.74**	**2.44**
Fe	**28.3**	**31.1**	**33.5**	**14.2**	**23.0**
Hg	**0.01**	**0.01**	**0.01**	**N/A**	**0.02**
Li	**0.09**	**0.08**	**0.09**	**0.28**	**0.26**
Mn	**2.76**	**3.90**	**5.89**	**5.11**	**5.21**
Mo	**0.04**	**0.06**	**0.05**	**0.07**	**0.06**
Ni	**5.42**	**1.35**	**0.83**	**4.09**	**2.11**
Pb	**0.81**	**1.91**	**1.05**	**0.54**	**0.95**
Rb	**0.14**	**0.17**	**0.19**	**0.38**	**0.80**
Sb	**0.10**	**0.17**	**0.12**	**0.09**	**0.08**
Se	**0.22**	**0.23**	**0.20**	**0.53**	**0.48**
Sn	**0.07**	**0.15**	**0.02**	**0.04**	**0.07**
Sr	**3.32**	**3.35**	**3.64**	**11.3**	**9.88**
Ti	**0.49**	**0.64**	**0.67**	**0.48**	**0.58**
U	**0.004**	**0.004**	**0.003**	**0.01**	**0.004**
V	**0.39**	**0.50**	**0.46**	**0.86**	**1.15**
W	**0.01**	**0.01**	**0.01**	**0.02**	**0.02**
Zn	**11.7**	**12.0**	**9.88**	**10.0**	**13.7**

Table 9. The 2014 annual mean deposition flux measurements (in µg m^{-2} day^{-1}) measured at individual sites on the UK Heavy Metals Monitoring Network.

7 TRENDS IN MEASURED CONCENTRATIONS

7.1 UK TRENDS

Trends in concentrations measured over the last 34 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 three years.

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 is 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. In 2014, the incorporation of the former Rural Network sites into the Network appears to have resulted in a change in the balance between urban and rural stations included in the network. This has produced reductions in the mean and median values for many metals, in particular Fe, Cr, Cu and Mn. In contrast, the values for Hg(v) have significantly increased due to the reduction in sites monitoring Hg(v), from 13 sites down to 2 sites. Consequently, the average and median Hg(v) values are equal and are dominated by Runcorn Weston Point.

Nickel concentrations although reduced significantly as a long term trend, have shown a gradual upward trend since 2010, largely due to the concentration of monitoring sites in the Swansea and Tawe valleys.

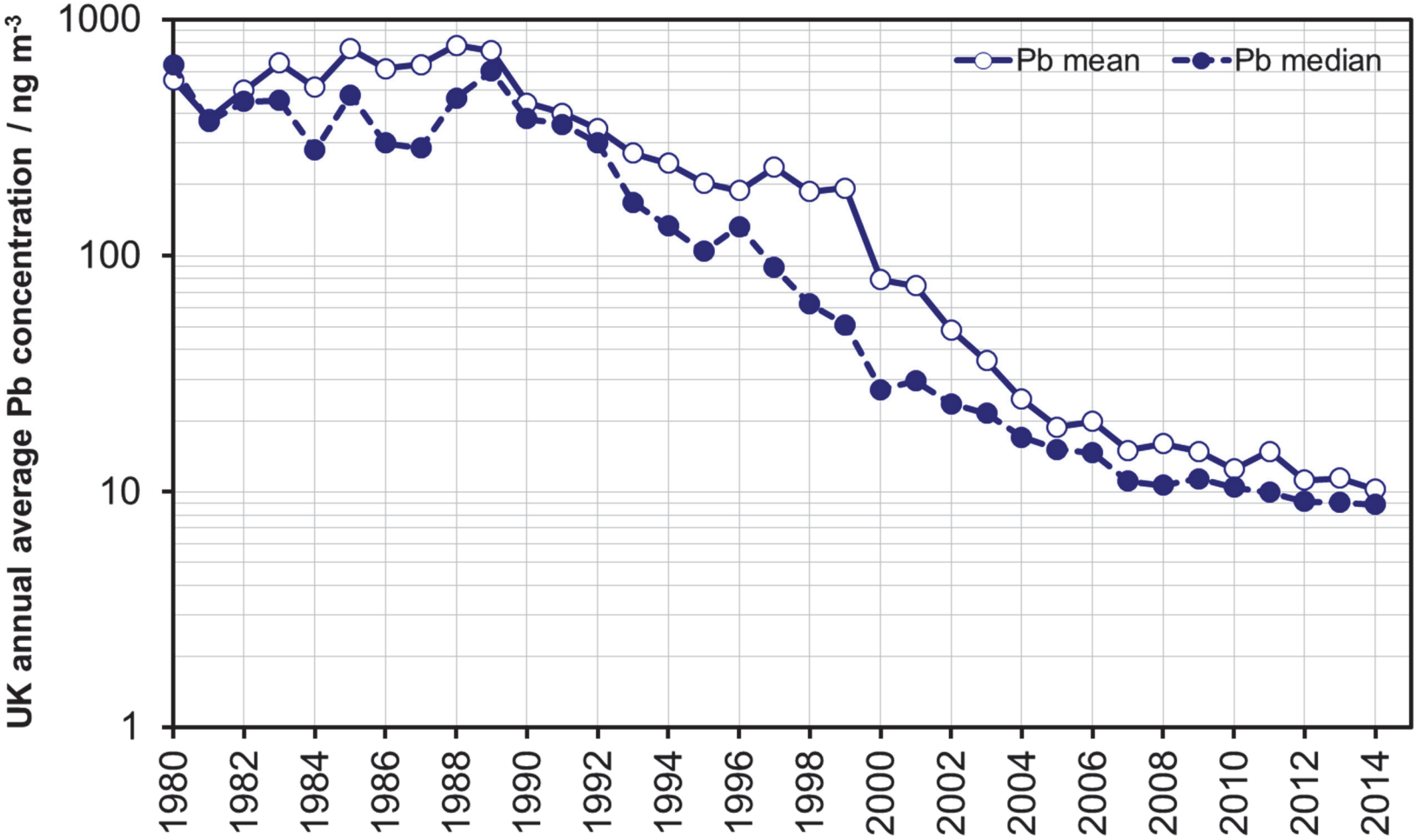

Figure 11. The mean and median of station annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 34 years. The EC limit value for lead is 500 ng m^{-3} and the UK Air Quality Objective for lead is 250 ng m^{-3}. Note the logarithmic scale on the *y*-axis.

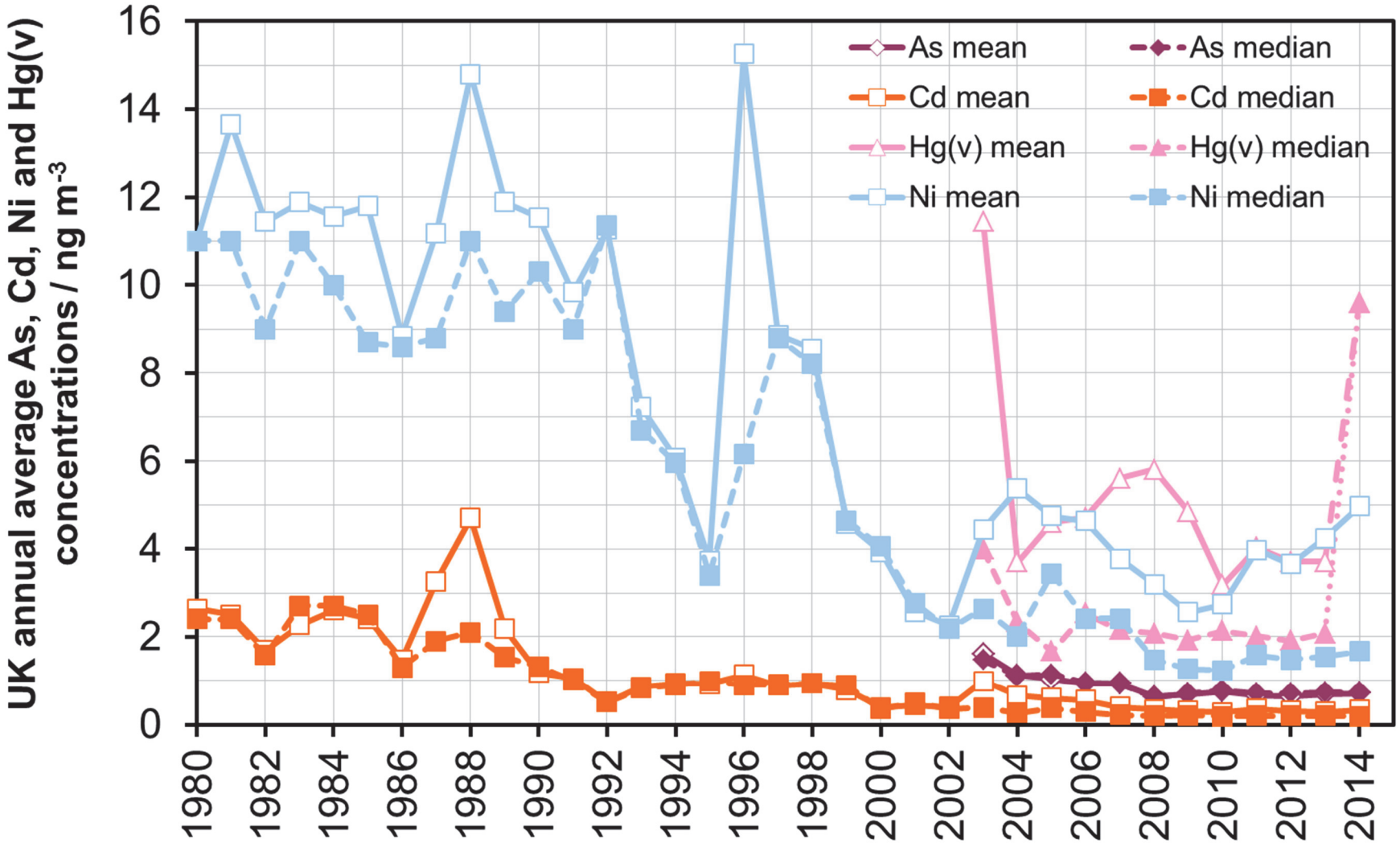

Figure 12. The mean and median of station annual average concentrations of Ni, As, Cd and total gaseous mercury [Hg(v)] measured on the UK Heavy Metals Monitoring Network over the last 34 years. The EC targets values for Ni, As and Cd are 20 ng m^{-3}, 6 ng m^{-3} and 5 ng m^{-3} respectively.

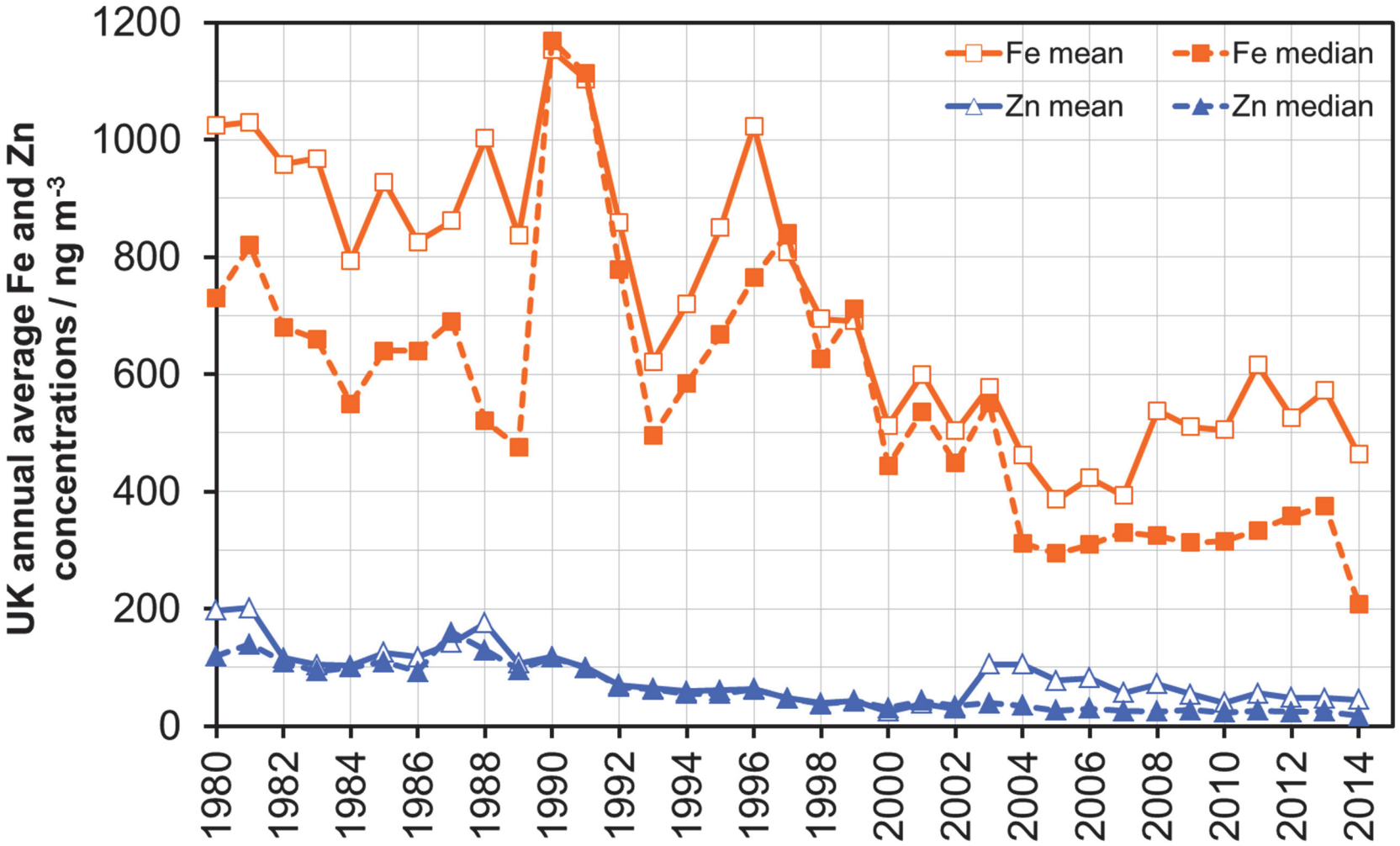

Figure 13. The mean and median of station annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 34 years.

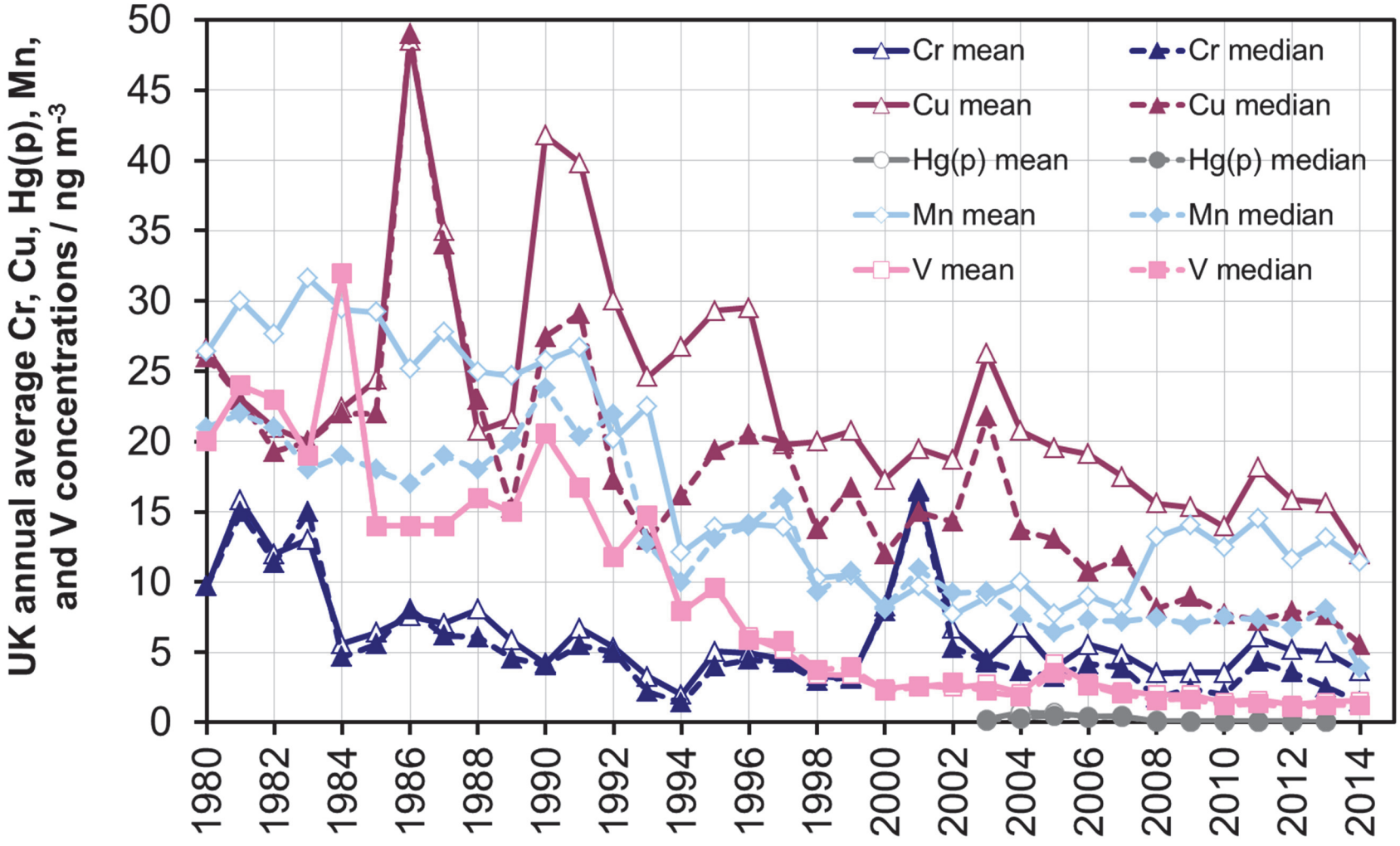

Figure 14. The mean and median of station annual average concentrations of Cr, Cu, Mn and V measured on the UK Heavy Metals Monitoring Network over the last 34 years.

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 11 years is shown in Figure 15.

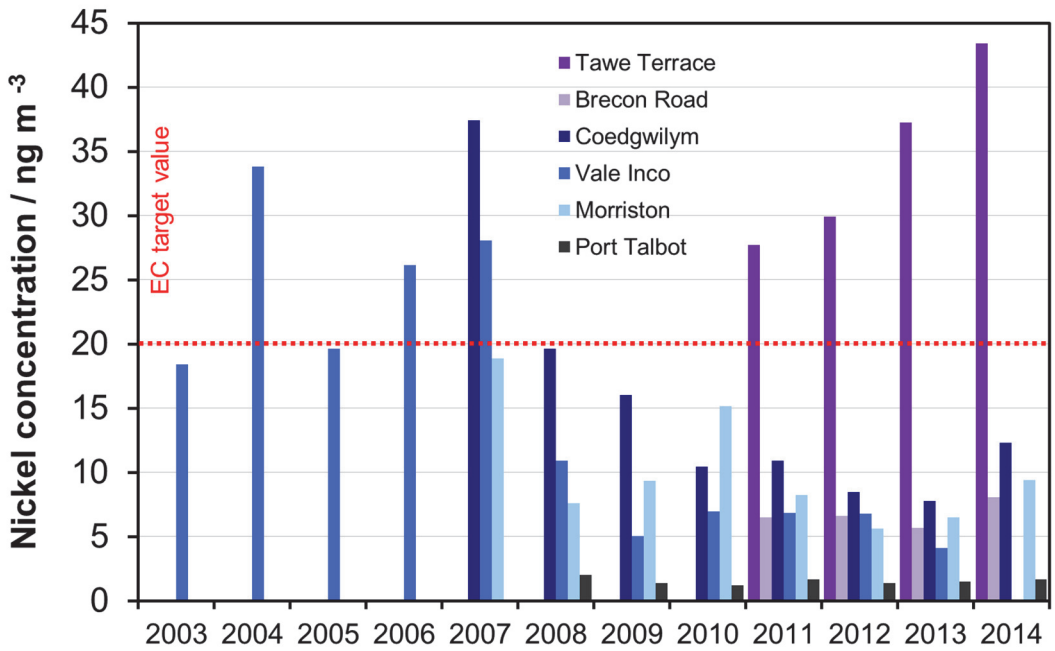

Figure 15. The annual average nickel concentrations measured at monitoring sites in the Swansea area (indicated by the key) 2003 - 2014. Nickel concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level. The red dotted line indicates 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), showed similar concentration trends until its closure (13th February 2014). Moreover, the relative concentrations between these sites continue to be broadly as predicted by NPL's modelling study of the area in 2009[12].

In the Tawe valley the concentrations at Pontardawe Tawe Terrace have shown a year upon year increase from 2011 to 2014. Abatement processes at the industrial facility impacting on the Pontardawe Tawe Terrace station were introduced in November 2013. Concentrations showed a further increase in 2014, but at this stage it is not clear whether this is due to changes in industrial processes and emissions or meteorological investigations. The 'South Wales Nickel Working Group' continues to work to investigate and agree actions to reduce these concentrations in future.

12 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 2014 that feature the data, analytical procedures and operation of the Network and research relevant to Network objectives. These articles are listed below:

- UK concentrations of chromium and chromium (VI), measured as water soluble chromium, in PM_{10}. Richard J C Brown, Sivan Van Aswegen, William R Webb, Sharon L Goddard: Atmospheric Environment, 2014, **99**, 385-391.

This paper described the changing concentrations of total chromium measured by the Network across the UK since 1980 and also provided a novel analysis of the proportion of the more toxic chromium oxidation state, Cr (VI), present in the total chromium.

- Ten years of mercury measurement at urban and industrial air quality monitoring stations in the UK. Richard J C Brown, Sharon L Goddard, David M Butterfield, Andrew S Brown, Chris Robins, Chantal L Mustoe, Elizabeth A McGhee: Atmospheric Environment, 2015, **109**, 1-8

This paper presented concentrations and trends from a decade of measurements of total gaseous mercury and particulate phase mercury at a number of monitoring stations on the UK Network. The ratio between gaseous and particulate phase mercury was described, indicating the dominance of gaseous mercury in the atmosphere across the UK

8.2 LEGISLATION AND STANDARDISATION

The EH/2/3 committee for ambient atmospheres (which NPL chairs) reapproved the EN 15841 standard 'Ambient air quality. Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition' at the end of 2014.

The committee has also voted to reapprove the EN 14902 standard 'Ambient air quality. Standard method for the measurement of Pb, Cd, AS, and Ni in the PM_{10} fraction of suspended particulate matter'. Confirmation of this is expected shortly.

ANNEX 1 LOCATION AND DETAILS OF SITES COMPRISING THE UK HEAVY METALS NETWORK

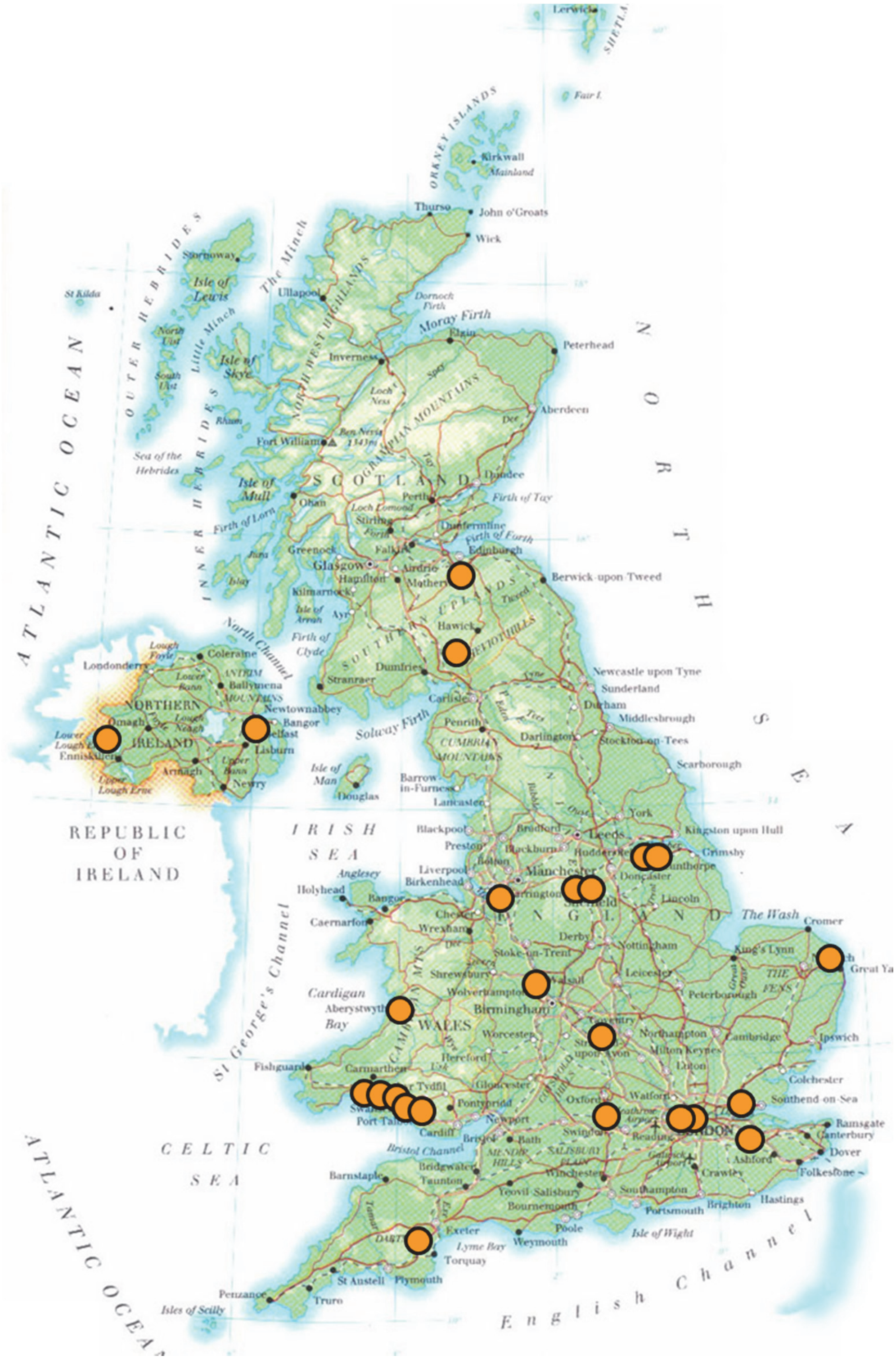

Figure A1. Location of monitoring sites comprising the UK Heavy Metals Monitoring Network during 2014 (indicated by the orange circles) – details of which are given in Table A1 below.

NEW Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Area and Classification (with identified point source, where applicable)	Pollutants measured
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)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn & Hg(v)
62: London Westminster (Westminster)	Mortuary Car Park, Horseferry Road, London, SW1P 2EB	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn & Hg(v)
65: Eskdalemuir (Eskdalemuir)	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	Rural Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
69: Walsall Bilston Lane (Walsall Bilston)	Adult Training Centre, Bilston Lane, Shepwell Green, Willenhall, Walsall, WV13 2QJ	Urban Industrial (Brookside Metals Ltd, Willenhall)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
100: Swansea Coedgwilym (Coedgwilym)	Coedgwilym Cemetery, Pontardawe Road, Clydach, Swansea, SA6 5PB	Urban Background (Vale Ltd, Swansea)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
101: Swansea Morriston (Morriston)	Morriston Groundhog, Wychtree Street, Morriston, Swansea, SA6 8EX	Urban Traffic (Vale Ltd, Swansea)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
103: Belfast Centre (Belfast)	Lombard Street, Belfast, BT1 1RB	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
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)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
106: Scunthorpe Town (Scunthorpe)	Rowlands Road, Scunthorpe, North Lincolnshire, DN16 1TJ	Urban Industrial (Corus Group Ltd, Scunthorpe)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
107: Scunthorpe Low Santon (Low Santon)	Dawes Lane, Santon, Scunthorpe, North Lincolnshire, DN16 1XH	Urban Industrial (Corus Group Ltd, Scunthorpe)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, 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)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
113: Pontardawe Tawe Terrace (Tawe Terrace)	Tawe Terrace, Pontardawe, Swansea, West Glamorgan, SA8 4HA	Urban Industrial (Wall Colmonoy, Pontardawe)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
114: London Marylebone Road (Marylebone Road)	Marylebone Road (opposite Madame Tussauds), London, NW1 5LR	Urban Traffic	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, 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)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
117: Sheffield Tinsley (Tinsley)	Ingfield Avenue, Tinsley, Sheffield. S9 1WZ	Urban Industrial (Outokumpu Stainless Ltd, Sheffield)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
119: Sheffield Devonshire Green (Devonshire Green)	Devonshire St, Sheffield, South Yorkshire. S3 7SW	Urban Background (Outokumpu Stainless Ltd, Sheffield)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn

NEW Site Code: Site Name (Abbreviated Site Name)	Site Address	Site Area and Classification (with identified point source, where applicable)	Pollutants measured
202: Auchencorth Moss (Auchencorth)	CEH Edinburgh, Bush Estate, Penicuik, Midlothian, EH26 0QB	Rural, deposition	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d) : Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Rb, Sc, Se, Sr, Sn, Ti, W, V, Zn, Hg
203: Yarner Wood (Yarner Wood)	Natural England, Yarner Wood, Bovey Tracey, Devon, TQ13 9LJ	Rural, deposition	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d) : Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Rb, Sc, Se, Sr, Sn, Ti, W, V, Zn, Hg
204: Cwmystwyth (Cwmystwyth)	Cwmystwyth, Wales. Grid reference 52.352436, -3.805317	Rural	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
205: Harwell (Harwell)	Ricardo-AEA, Gemini Building, Fermi Avenue, Harwell campus, Didcot, Oxon, OX11 0QR	Rural, deposition	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d) : Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Rb, Sc, Se, Sr, Sn, Ti, W, V, Zn, Hg
206: Heigham Holmes (Heigham)	Gardeners Cottage, Burnley Hall, East Somerton, Great Yarmouth, Norfolk, NR29 4DZ	Rural, deposition	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d) : Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Rb, Sc, Se, Sr, Sn, Ti, W, V, Zn, Hg
208: Detling (Detling)	Alan Day House, County Showground, Detling, Maidstone, Kent, ME14 3JF	Rural	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
209: Fenny Compton	The Dassett CE Primary School, Memorial Road, Fenny Compton, Warwickshire, CV47 2XU	Rural background (re-suspended arsenic)	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
UKA00166: Lough Navar	Lough Navar, Glennasheevar Road, Derrygonnelly, Enniskillen, Fermanagh, BT93 6AH	Rural, deposition	(d) : Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Rb, Sc, Se, Sr, Sn, Ti, W, V, Zn

Table A1. Details of the sites comprising the UK Heavy Metals Monitoring Network, including: site names, abbreviated site names, site locations, site area and classification, point source monitored (where applicable) and pollutants measured – (p) denotes metals in particulate matter (PM), (d) denotes metals in deposition.

Next page:
Image 4. The Partisol sampler at Runcorn Weston Point.