

Report by the National Physical Laboratory to the Environment Agency, 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 2016 on the
UK Heavy Metals Monitoring Network**

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ISSN 2059-6030

<https://doi.org/10.47120/npl.ENV31>

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Approved on behalf of NPLML by
Ian Severn, Head of Chemical, Medical and Environmental Department

EXECUTIVE SUMMARY

This Report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Environment Agency, 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 2016 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 2016.
- A brief summary of scientific research, publications, international representation and other activities related to the Network.

In summary, during 2016:

- **Lead:** No annual average site concentrations above the Ambient Air Quality Directive's Lower Assessment Threshold were recorded. Recorded concentrations were therefore well below the limit value set by the Directive.
- **Nickel:** Two annual average site concentrations, at Pontardawe Tawe Terrace and Sheffield Tinsley, were recorded above the Fourth Daughter Directive's target value. One further annual average site concentration above the lower assessment threshold was recorded.
- **Arsenic and cadmium:** no sites recorded annual average concentrations above the lower assessment threshold. Recorded concentrations were therefore well below the target values set by the Fourth Daughter Directive.
- All data quality objectives specified in the Ambient Air Quality Directive and Fourth Daughter Directive were met, including time coverage, data capture and measurement uncertainty requirements.
- Concentrations in ambient air were recorded for gaseous mercury, as required by the Fourth Daughter Directive, and also for cobalt, chromium, copper, iron, manganese, selenium, vanadium and zinc. Concentrations for a larger range of metals were recorded for the sites monitoring metals in deposition.
- Data capture for metals in the PM phase during 2016 was **95.8 %**. For gaseous phase mercury and metals in deposition it was 96.6 % and 87.3 % respectively.

CONTENTS

EXECUTIVE SUMMARY
1 INTRODUCTION	1
1.1 BACKGROUND	1
2 NETWORK OPERATION.....	4
2.1 OVERVIEW	4
2.2 SITE AUDITS.....	4
2.3 EQUIPMENT SERVICING AND BREAKDOWNS.....	5
2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION.....	5
3 SAMPLING AND ANALYTICAL METHODOLOGY	6
3.1 SAMPLING METHODOLOGY: PARTICULATE-PHASE METALS	6
3.2 SAMPLING METHODOLOGY: TOTAL GASEOUS MERCURY	6
3.3 ANALYTICAL METHODOLOGY: PARTICULATE-PHASE METALS.....	7
3.4 ANALYTICAL METHODOLOGY: TOTAL GASEOUS MERCURY (TGM).....	8
3.5 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION	9
3.6 MEASUREMENT UNITS	10
3.7 MEASUREMENT UNCERTAINTY	10
4 METHOD PERFORMANCE CHARACTERISTICS AND QUALITY CONTROL	11
4.1 QA/QC PROCEDURES	11
4.2 MEASUREMENT UNCERTAINTY	12
5 DATA QUALITY	14
5.1 DATA CAPTURE (PM AND GASEOUS PHASE MERCURY).....	14
5.2 DATA CAPTURE (DEPOSITION)	16
5.3 DATA PROCESSING AND RATIFICATION.....	16
5.4 MEASUREMENT UNCERTAINTY OF ANNUAL AVERAGE	17
6 NETWORK DATA	19
6.1 MEASURED CONCENTRATIONS (PM AND GASEOUS PHASE MERCURY).....	19
6.2 MEASURED CONCENTRATIONS WITH RESPECT TO THE REQUIREMENTS OF THE EU AIR QUALITY DIRECTIVES	27
6.3 WITHIN YEAR CONCENTRATION TRENDS.....	30
6.4 MEASURED CONCENTRATIONS OF NON-DIRECTIVE METALS.....	34
6.5 MEASURED CONCENTRATIONS OF METALS IN DEPOSITION.....	36
7 TRENDS IN MEASURED CONCENTRATIONS.....	38
7.1 UK TRENDS	38
7.2 TRENDS IN NICKEL IN THE SWANSEA AND TAW VALLEYS.....	43
8 SCIENTIFIC RESEARCH, PUBLICATIONS AND RELATED ACTIVITIES	45

8.1 PUBLICATIONS.....45

8.2 LEGISLATION AND STANDARDISATION45

**ANNEX 1 LOCATION AND DETAILS OF SITES COMPRISING THE UK HEAVY METALS
NETWORK.....46**

1. INTRODUCTION

This report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Environment Agency, the Department for Environment, Food and Rural Affairs and the Devolved Administrations¹ (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 2016 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 Ambient Air Quality Directive (2008/50/EC²) for lead; the Fourth Air Quality Daughter Directive (DD) (2004/107/EC³) for nickel, arsenic, cadmium, and total gaseous mercury; the Commission Directive (EU) 2015/1480 amending several annexes to Directives 2004/107/EC and 2008/50/EC; and the Air Quality Strategy for England, Scotland, Wales and Northern Ireland⁴ 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 2016.
- 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; and 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 concentrations⁵ 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 Northern Ireland (DOENI), and the Scottish Government, represented by the Scottish Government Environment and Forestry 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 PM₁₀ fraction of ambient air (particles with an equivalent aerodynamic diameter of 10 µm or less) are limited by European Directives and adopted into UK 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 a comparison between measured ambient concentrations across the Network and emissions has been published⁷. 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 PM₁₀ phase of ambient air, and total gaseous mercury [referred to as: Hg(v)].

Co, Cr, Cu, Fe, Mn, Se, V and Zn concentrations are measured using the same samples to provide additional information on sources and trends.

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.

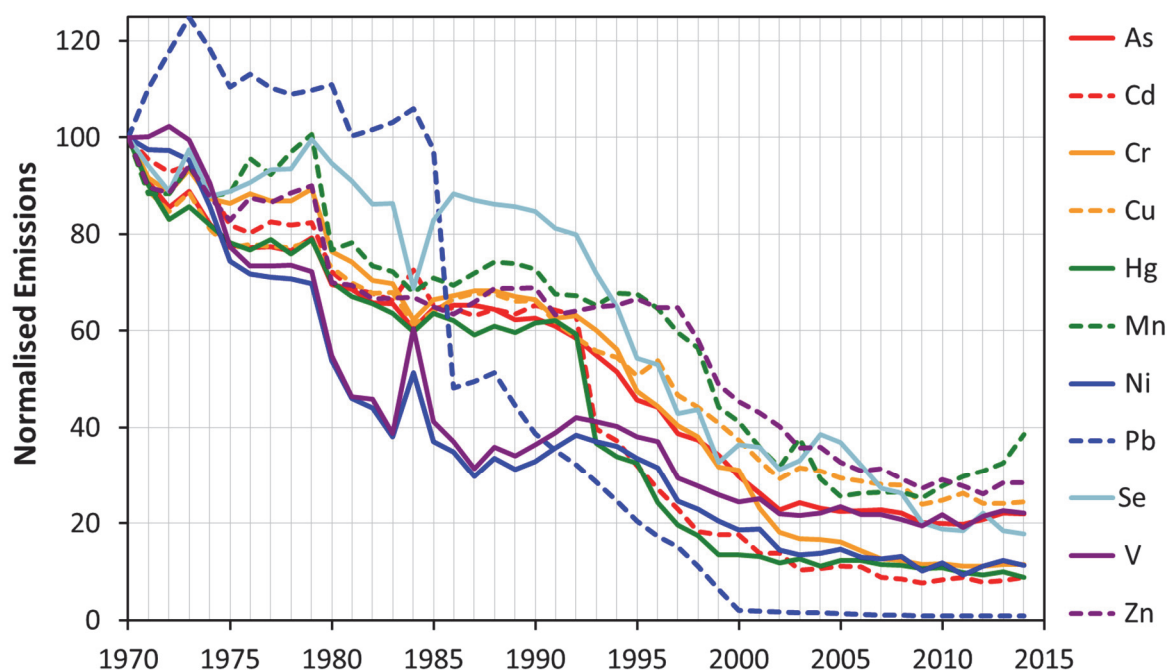


Figure 1. Estimated UK annual emissions of the metals from 1970 to 2014 (the latest year for which emissions data were available at time of publishing) normalised to their values in 1970. The absolute levels of emissions in 1970, in tonnes, were: As, 81; Cd, 35; Cr, 241; Cu, 217; Mn, 188; Ni, 912; Pb, 7472; Hg, 61; Se, 91; V, 2595; and Zn, 1544. Emissions data are not available for Co or 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 air⁸.

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 2016 comprised 25 monitoring sites around the UK (15 in England, 6 in Wales, 2 in Scotland, and 2 in Northern Ireland) sampling PM₁₀, mercury vapour and/or deposition phases of ambient air. Details of the sites are given in Annex 1. The PM₁₀ is sampled onto filters. These are 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 2016 is detailed below.

2.1 OVERVIEW

NPL's management of the UK Heavy Metals Monitoring Network in 2016 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 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 2016 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 2016, 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 PM₁₀ sampling head and impactor plate;
- Assessed the current condition of all deposition sampling equipment;
- 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.

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 2016 the ESU twice fully serviced, carried out preventative maintenance and calibrated the flow of the Partisol samplers at all Network sites.
- During 2016, NPL called-out the ESU to deal with Partisol sampler faults at: Chesterfield, Chilbolton, Marylebone Road, Swansea Morriston, Brecon Road, Sheffield Devonshire Green, Sheffield Tinsley and Yarnier Wood.

2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION

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

- On 11th January 2016 sampling ceased at site 205: Harwell. The site was relocated to site 211: Chilbolton, which commenced sampling on the 20th January 2016.
- From 19th August 2015 – 3rd February 2016, filter sampling and analysis at site 113: Pontardawe Tawe Terrace was performed on a daily basis (before and after this period sampling and analysis was performed weekly). This was undertaken for a study to provide higher time resolution measurements to aid the understanding of sources in the Pontardawe area. The data were also compared with the data collected by King's College London using a real-time XPS analyser⁹.
- From 25th February – 10th August 2016, filter sampling and analysis at site 117: Sheffield Tinsley was performed on a daily basis (before and after this period sampling and analysis was performed weekly). This was undertaken for a study to provide higher time resolution measurements to aid the understanding of sources in the Sheffield area¹⁰.

9 NPL Report ENV (RES) 010 "Analysis of Daily Heavy Metals Measurements at Tawe Terrace, Pontardawe, 19th August 2015 – 31st January 2016", Butterfield et al. 2016

10 Department for Environment, Food and Rural Affairs report "Report on measures for 2014 exceedance of the Target Value for Nickel in Sheffield Urban Area agglomeration zone (UK0007)." DEFRA, November 2016.

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 24 sites in the Network using Partisol 2000B or 2025A/B instruments (fitted with PM₁₀ heads) operating at a calibrated flow rate, nominally of 1 m³ 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 Runcorn Weston Point. The inlet for the mercury vapour sampling equipment is located on the bottom left, below the white hood.

3.2 SAMPLING METHODOLOGY: TOTAL GASEOUS MERCURY

Sampling for total gaseous mercury took place at 2 of the 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 for the following sites that produce weekly data: Sheffield Tinsley (except for the period 25th February – 10th August 2016, when daily sampling was implemented), Walsall Bilston Lane, Swansea Coedgwilym, Swansea Morriston, Pontardawe Tawe Terrace (except for the period 19th August 2015 – 3rd February 2016, when daily sampling was implemented) and Pontardawe Brecon Road.



Image 2: Anton Parr Multiwave 3000 microwave used for acid digestion of the sampled filters.

Analysis for particulate-phase metals took place at NPL following NPL's analytical procedure. This procedure is accredited by UKAS to ISO 17025, and fully compliant with the requirements of EN 14902.

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 (see Image 2). 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 was performed using Agilent 8800 (see Image 3) and Elan 9000 ICP-MSs. The instrumental response was calibrated with 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.

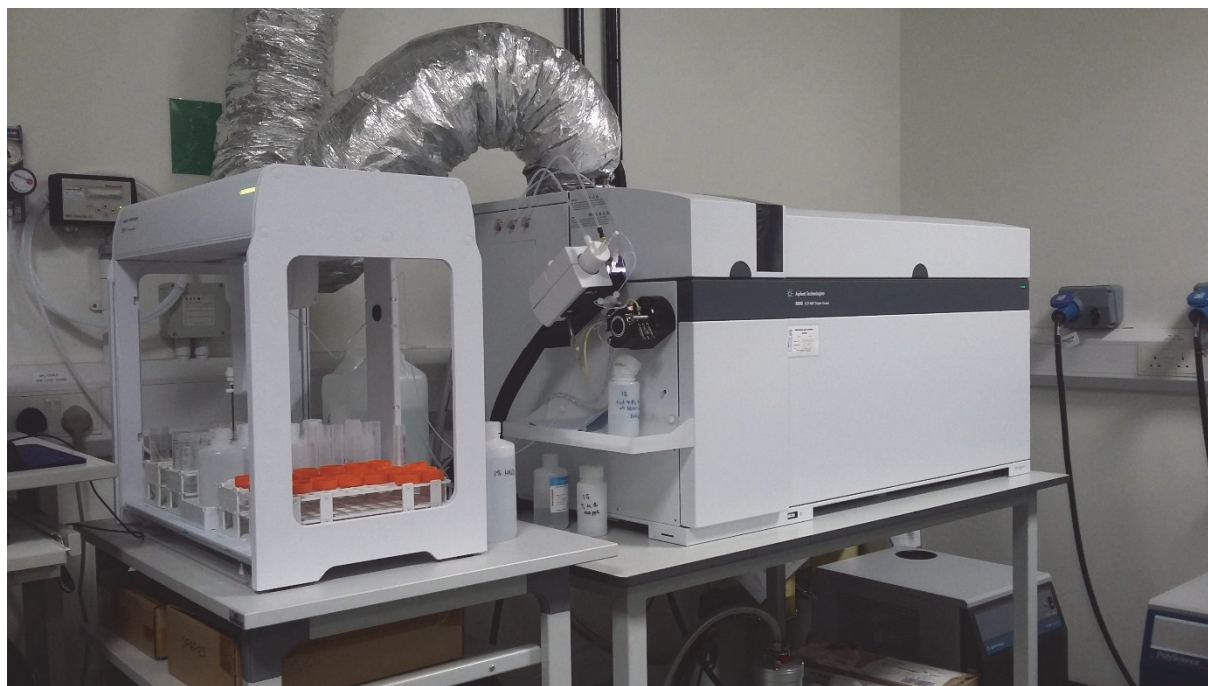


Image 3: Agilent 8800 ICP-MS in the UK ambient metals analysis facility at NPL.

3.4 ANALYTICAL METHODOLOGY: TOTAL GASEOUS MERCURY (TGM)

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 4). (The manual variant of EN 15852 used on the Network has been shown to be equivalent to the automatic reference method within the uncertainty of the analytical determination¹¹.) 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.

¹¹ 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.

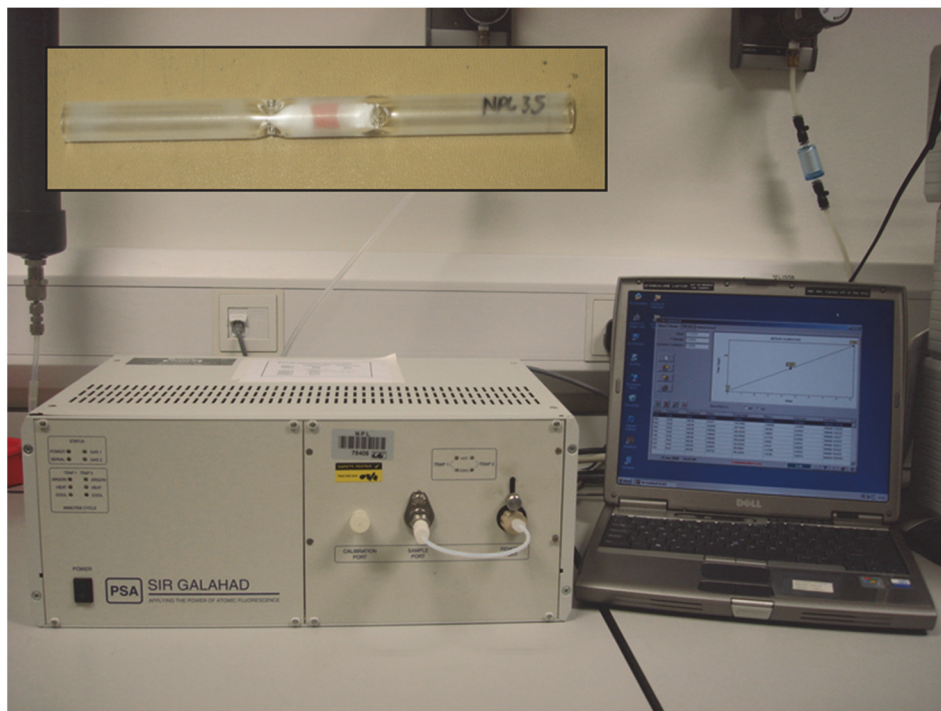


Image 4: One of two thermal desorption-atomic fluorescence analysers comprising the UK total gaseous mercury analysis facility at NPL.

The inset image shows one of the Amasil gold-coated silica adsorption tubes used for total gaseous mercury sampling.

3.5 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION

During 2016, monitoring of heavy metals and mercury in deposition was undertaken by the Network at Auchencorth Moss, Harwell/Chilbolton, Yarner Wood, Cwmystwyth, Heigham Holmes and Detling. Metals in deposition excluding mercury were also monitored 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 (ICP-MS; 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 values for Al, Sb, As, Ba, Cd, Cr, 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 calculated in accordance with ISO 11222 and 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: (µg/m²)/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, published as ISO/IEC Guide 98-3:2008. 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 2015, and both retained accreditation to ISO 17025 from UKAS. 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 gaseous mercury).

4.1 QA/QC PROCEDURES

An overview 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 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 85% and 105%¹² 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.

¹² Statistical fluctuations and uncertainty of measurement (see section 4.2) mean that recoveries exceeding 100% are possible.

- 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 2016 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	Uncertainty range
As	8 - 22 %
Cd	8 - 12 %
Co	8 - 17 %
Cr	9 - 22 %
Cu	8 - 18 %
Fe	8 - 20 %
Mn	8 - 25 %
Ni	8 - 21 %
Pb	8 - 21 %
Se	11 - 22 %
V	8 - 25 %
Zn	8 - 25 %
Hg(v)	10 - 20 %

Table 1. The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2016. 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 Directives.

5 DATA QUALITY

5.1 DATA CAPTURE (PM AND GASEOUS PHASE MERCURY)

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 represents the absolute percentage of all available time during the year for which valid data has been produced.

Data capture for metals in the PM phase during 2016 was **95.8 %**. For gaseous phase mercury it was 96.6 %. 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 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.

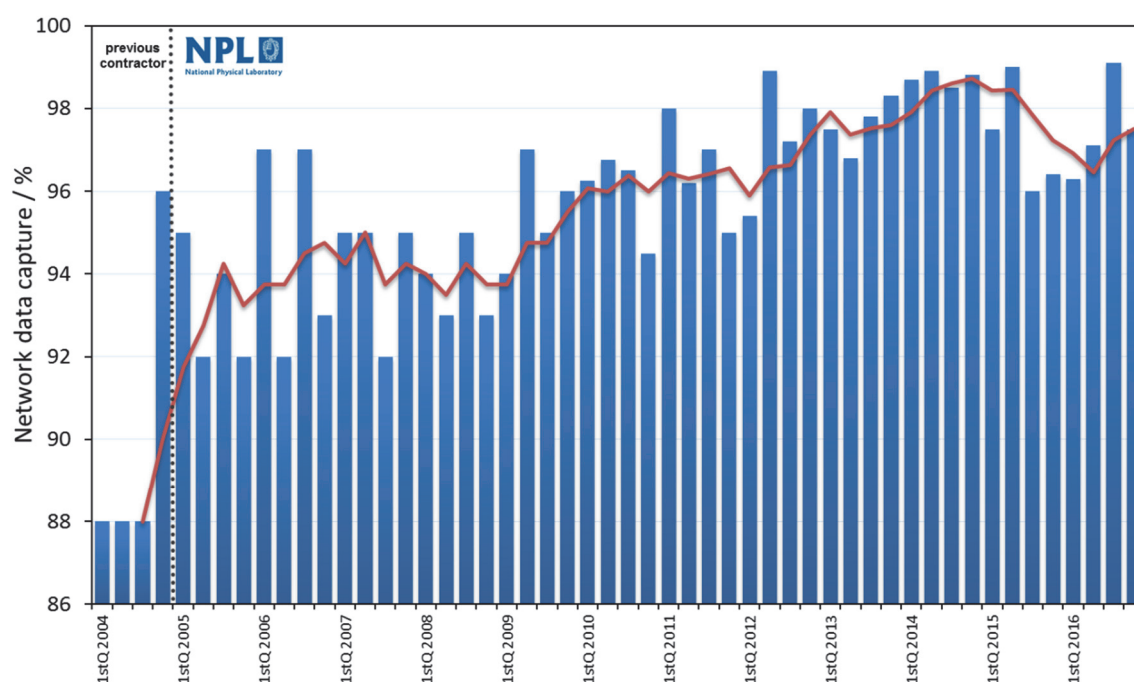


Figure 3. Network data capture from 2004-2016 (inclusive) for particulate and gaseous phase measurements. Quarterly data capture is indicated by the blue bars, whilst the rolling annual average data capture is given by the red line. Data to the right of the dotted vertical line is associated with NPL's 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	95.8%	96.6%
59: Runcorn Weston Point	94.6%	97.8%
62: London Westminster	99.8%	95.4%
65: Eskdalemuir	97.5%	N/A
69: Walsall Bilston Lane	97.3%	N/A
100: Swansea Coedgwilym	99.9%	N/A
101: Swansea Morriston	93.2%	N/A
103: Belfast Centre	99.9%	N/A
104: Port Talbot Margam	97.9%	N/A
106: Scunthorpe Town	97.7%	N/A
107: Scunthorpe Low Santon	99.6%	N/A
110: Chadwell St Mary	99.7%	N/A
113: Pontardawe Tawe Terrace	96.8%	N/A
114: London Marylebone Road	84.6%	N/A
115: Pontardawe Brecon Road	99.7%	N/A
117: Sheffield Tinsley	88.9%	N/A
119: Devonshire Green	97.7%	N/A
202: Auchencorth Moss	98.7%	N/A
203: Yarner Wood	95.1%	N/A
204: Cwmystwyth	99.9%	N/A
205: Harwell*	83.3%	N/A
206: Heigham Holmes	92.1%	N/A
208: Detling	89.7%	N/A
209: Fenny Compton	99.6%	N/A
210: Chesterfield	96.7%	N/A
211: Chilbolton*	94.6%	N/A

Table 2. Data capture across the UK Heavy Metals Monitoring Network during 2016.

*Data capture refers only to the period of the year when the following stations were operational: Harwell was closed 11th January 2016. Chilbolton was opened 20th January 2016.

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

- London Marylebone Road: Filters sampled 4th May – 29th June were lost in the post on return to NPL. All LSOs have since been reminded to return all filters using a tracked method of delivery.
- Sheffield Tinsley: There was a power cut affecting the site 9th – 16th March. On 14th July the ESU removed the sampler from site to investigate issues with the software freezing. Sampling resumed 27th July with a spare replacement sampler. On 14th September the replacement sampler also had to be removed from site having experienced similar problems. This was replaced with a further spare unit.

- Harwell: Harwell was closed 11th January 2016. The last filter stopped sampling early due to a sampler error.
- Detling: Little actual sampling time was missed at this site. However, due to its location this site is prone to certain weather conditions (particularly in winter) that cause flow problems, and thus result in low data coverage.

5.2 DATA CAPTURE (DEPOSITION)

Data capture for deposition monitoring during 2016 was 87.3 %. Data capture is generally lower for these measurements than for others 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	83.4%	100.0%
Chilbolton	65.7%	100.0%
Heigham Holmes	70.2%	100.0%
Lough Navar	90.7%	N/A
Yarner Wood	63.3%	100.0%

Table 3. Data capture across the deposition sites of the UK Heavy Metals Monitoring Network during 2016.

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 Phosphorus to Gallium (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 techniques¹³.
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.) 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	22 %	40 %
Cd	19 %	40 %
Ni	10 %	40 %
Pb	13 %	25 %
Hg(v)	16 %	50 %

Table 4. Relative expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Directive metals in particulate

¹³ 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.

matter, 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.

6 NETWORK DATA

6.1 MEASURED CONCENTRATIONS (PM AND GASEOUS PHASE MERCURY)

The annual mean measured metals concentrations in 2016, 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	2016 UK Mean Annual Concentration / ng m^{-3}	2016 UK Median Annual Concentration / ng m^{-3}	2016 Maximum Annual Mean Concentration / ng m^{-3}	EC limit or target value (UK objective) / ng m^{-3}
As	0.65	0.68	1.12	6
Cd	0.21	0.15	0.89	5
Co	0.27	0.12	3.06	-
Cr	3.85	1.63	31.3	-
Cu	9.68	5.18	54.0	-
Fe	432	205	2364	-
Mn	10.5	3.90	93.3	-
Ni	4.48	1.06	47.4	20
Pb	7.68	6.37	22.2	500 (250)
Se	0.89	0.64	2.69	-
V	1.20	0.71	9.23	-
Zn	20.9	13.0	110	-
Hg (v)	8.91	8.91	15.3	-

Table 5. The 2016 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 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	0.12	0.14	1.12	6.03	186	3.27	1.09	5.93	1.73	0.96	12.6	15.3
62: London Westminster	0.85	0.14	0.12	1.63	15.6	468	5.70	0.84	8.56	0.50	0.71	19.9	2.52
65: Eskdalemuir	0.08	0.02	0.01	1.36	0.46	29.0	0.77	0.40	0.79	0.31	0.31	1.57	N/A
69: Walsall Bilston Lane	1.01	0.89	0.28	2.81	23.5	494	9.38	1.51	22.2	1.47	0.79	110	N/A
100: Swansea Coedgwilym	0.57	0.21	0.51	2.69	4.09	133	2.69	10.0	5.89	1.33	0.64	9.54	N/A
101: Swansea Morriston	0.74	0.32	0.30	2.85	26.8	577	7.29	5.91	11.4	1.41	0.94	19.7	N/A
103: Belfast Centre	0.39	0.15	0.11	1.38	6.62	259	3.90	1.12	4.07	0.39	1.42	14.1	N/A
104: Port Talbot Margam	0.69	0.70	0.19	4.18	8.62	2364	29.5	2.40	9.08	0.78	2.97	35.6	N/A
106: Scunthorpe Town	0.71	0.17	0.11	1.57	4.91	491	18.2	0.94	11.2	0.94	1.30	22.5	N/A
107: Scunthorpe Low Santon	0.70	0.30	0.19	2.78	4.32	1680	93.3	1.27	16.6	1.12	9.23	24.7	N/A
110: Chadwell St Mary	1.00	0.25	0.12	1.59	10.6	330	5.50	0.88	11.4	0.54	0.99	20.4	N/A
113: Pontardawe Tawe Terrace	0.68	0.28	3.06	12.1	7.06	207	4.91	47.4	7.89	1.31	0.70	13.0	N/A
114: London Marylebone Road	1.12	0.17	0.21	8.91	54.0	1545	14.1	1.76	11.9	0.64	1.01	33.6	N/A
115: Pontadawe Brecon Road	1.08	0.20	0.26	1.95	5.45	205	3.31	4.80	6.01	1.23	0.66	10.8	N/A
117: Sheffield Tinsley	0.90	0.57	0.60	31.3	33.4	585	30.15	23.6	17.7	2.69	1.21	83.3	N/A
119: Devonshire Green	0.68	0.14	0.23	4.62	9.23	325	8.55	2.67	7.80	1.30	0.76	22.7	N/A
202: Auchencorth Moss	0.14	0.02	0.02	1.28	0.79	42.3	0.98	0.25	1.13	0.28	0.31	2.41	N/A
203: Yarnar Wood	0.48	0.05	0.02	1.23	1.14	45.7	1.29	0.68	2.23	0.45	0.62	4.27	N/A
204: Cwmystwyth	0.19	0.04	0.02	1.53	0.75	41.5	1.11	0.42	1.52	0.38	0.44	3.05	N/A
205: Harwell	0.28	0.03	0.07	1.43	1.15	198	3.18	0.64	1.85	0.35	1.18	3.11	N/A
206: Heigham Holmes	0.46	0.08	0.04	1.63	1.81	74.4	2.18	0.78	3.58	0.55	0.64	7.43	N/A
208: Detling	0.85	0.15	0.05	1.49	4.67	140	3.42	0.58	6.78	0.54	0.59	11.9	N/A
209: Fenny Compton	0.81	0.11	0.04	1.49	3.04	120	2.44	0.39	5.53	0.52	0.54	10.5	N/A
210: Chesterfield	0.62	0.12	0.09	1.99	5.18	172	4.42	1.06	6.37	1.01	0.57	17.3	N/A
211: Chilbolton	0.64	0.10	0.03	1.40	2.98	94.4	2.22	0.69	4.53	0.50	0.58	8.67	N/A

Table 6. The 2016 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:

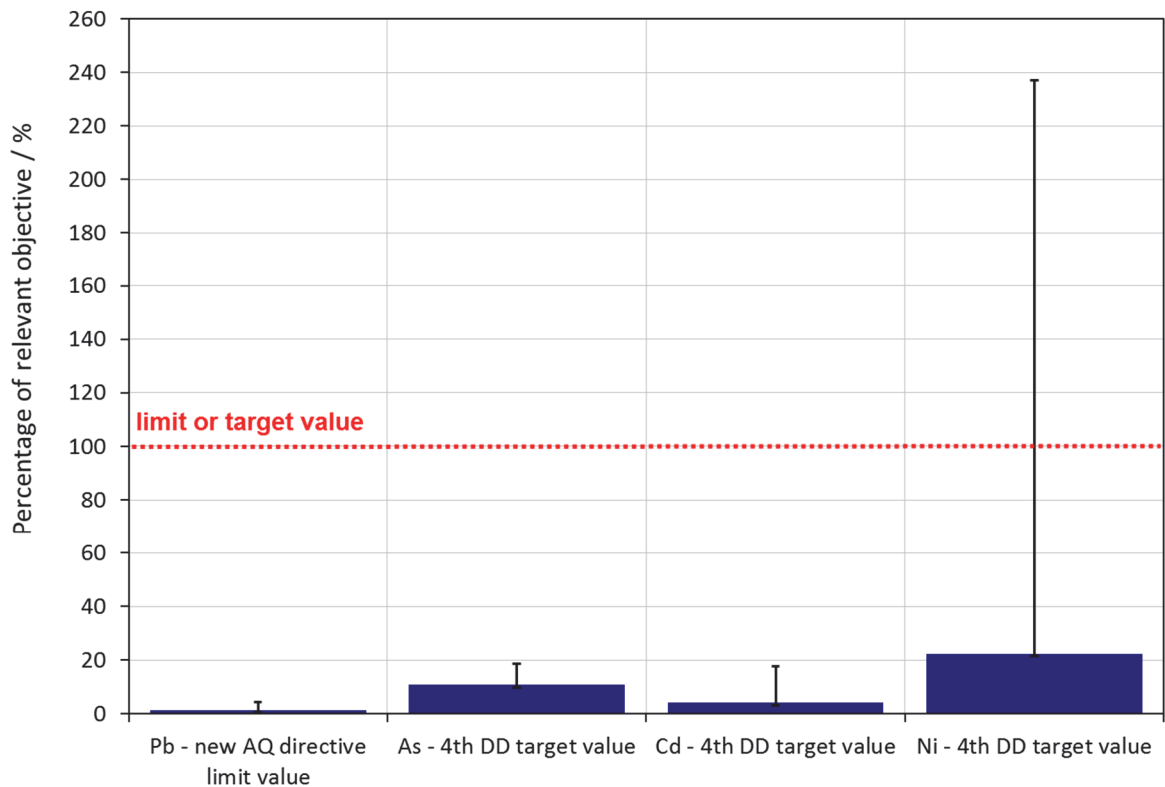


Figure 4. A summary of the annual mean measured concentrations of the heavy metals relevant to the Ambient Air Quality Directive and Fourth Daughter Directive on the UK Heavy Metals Monitoring Network in 2016 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of 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 and lead are found at Site 69: Walsall Bilston Lane. The highest annual mean value for arsenic has been found at Site 114: London Marylebone Road.

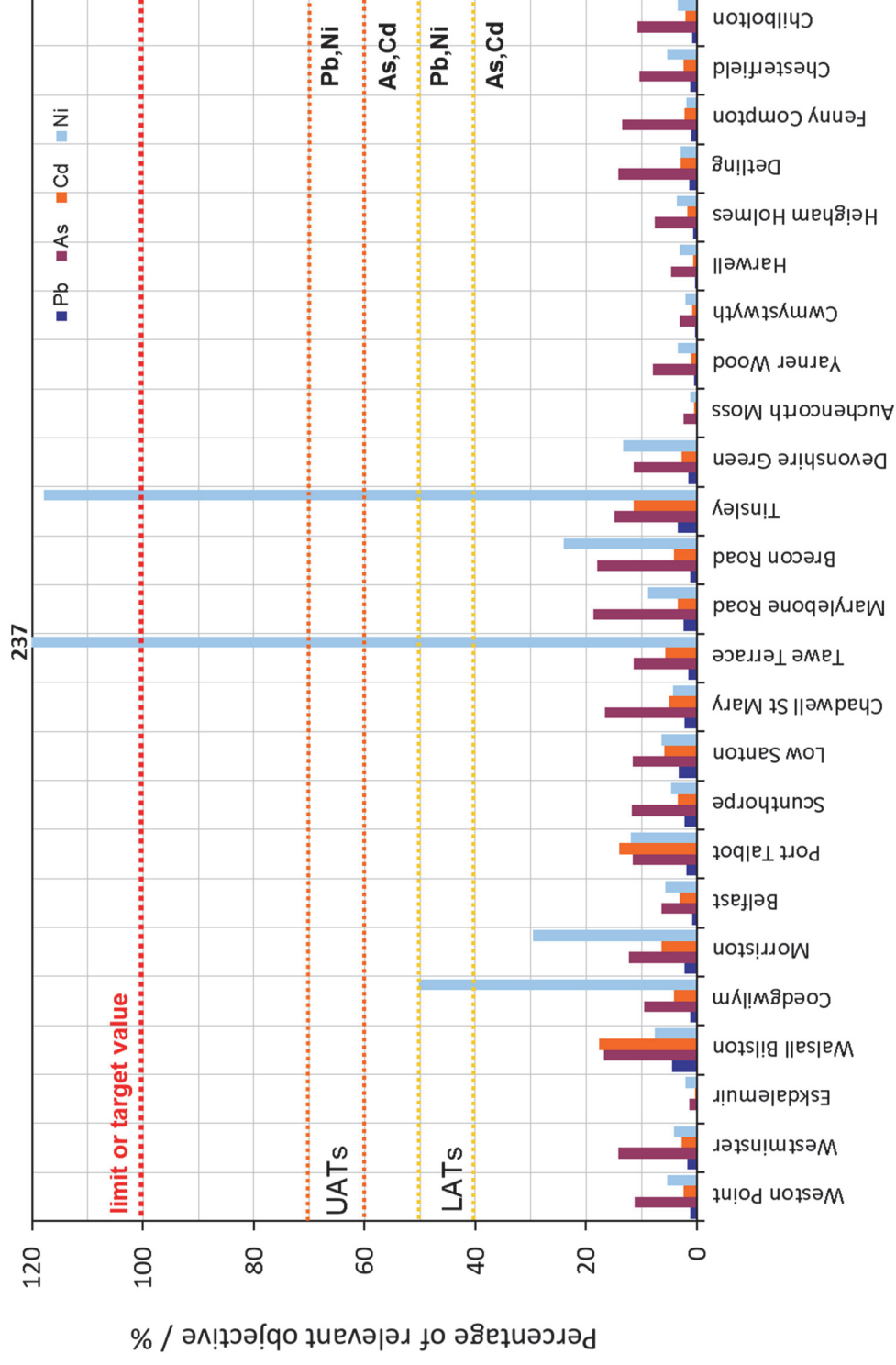


Figure 5. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2016 as a percentage of the relevant target values shown in red, lower assessment thresholds (LATs) in yellow and upper assessment thresholds (UATs) in orange.

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: 237 % of the target value.
- Nickel at Site 117: Sheffield Tinsley: 118 % of the target value.

Annual Mean Concentrations above the Lower Assessment Threshold:

- Nickel at Site 100: Coedgwilym Cemetery: 50.1 % 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.

Chilbolton

The new site at Chilbolton began sampling on 20th January 2016. This site location was selected to replace the monitoring site at Harwell. Concentrations for all Directive metals were below the Lower Assessment Thresholds for the sampling period available.

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 because 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 arsenic¹⁴, which is generally emitted from diffuse combustion sources, not point sources, and therefore is affected much less by meteorological conditions.

Weekly measurements provide a better 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.

Daily measurements were undertaken at Sheffield Tinsley from 25th February – 10th August 2016. The daily results have been compared to the calculated weekly averages in Figure 9 for this period to show how weekly results can inadequately reflect the magnitude of short-lived pollution episodes.

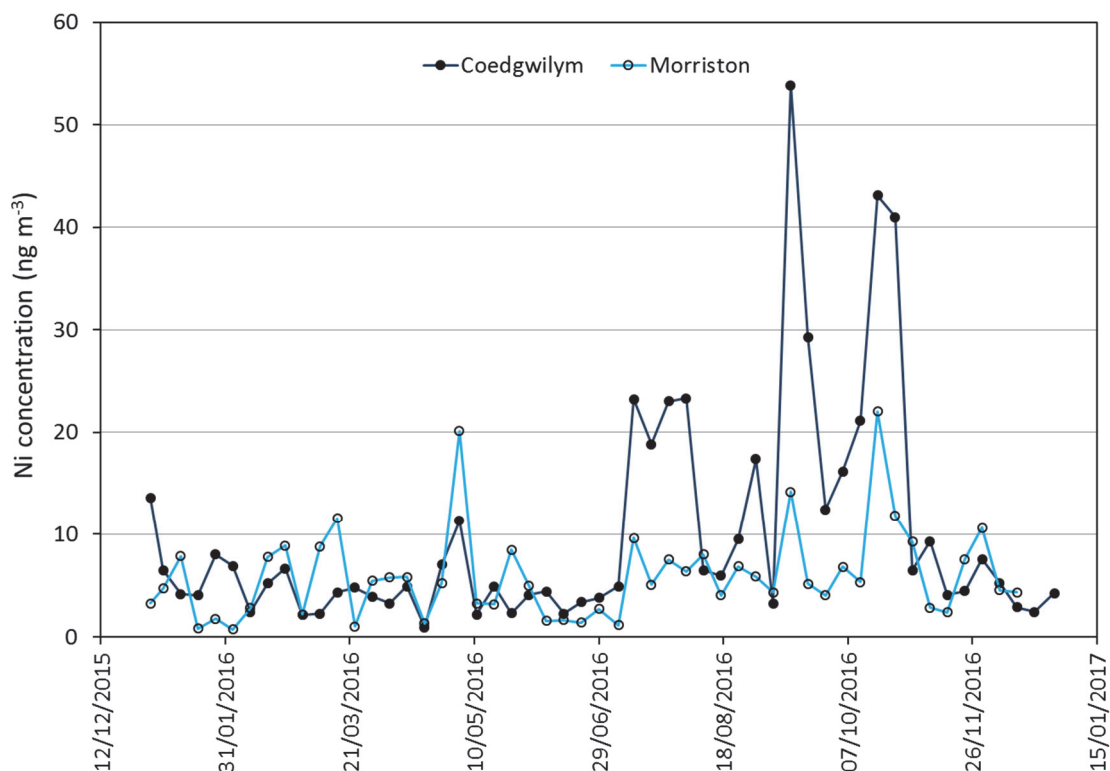


Figure 6. Measured Ni concentrations at Site 100: Swansea Coedgwilym and Site 101: Swansea Morryston, in 2016 (both sampled weekly).

¹⁴ 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.

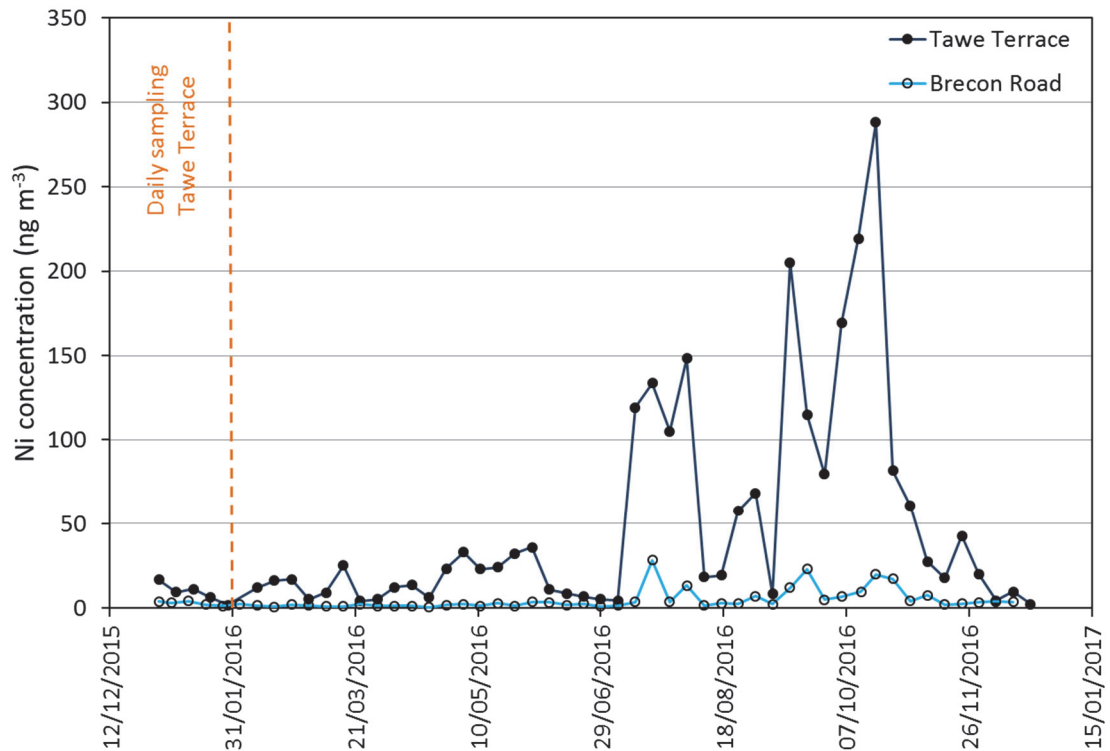


Figure 7. Measured Ni concentrations at Site 113: Pontardawe Tawe Terrace and Site 115: Pontardawe Brecon Road, in 2016. Both sites were sampled weekly except Pontardawe Tawe Terrace which was sampled daily from 19th August 2015 – 3rd February 2016. For the period 1st January - 3rd February 2016, weekly averages of the daily results have been plotted.

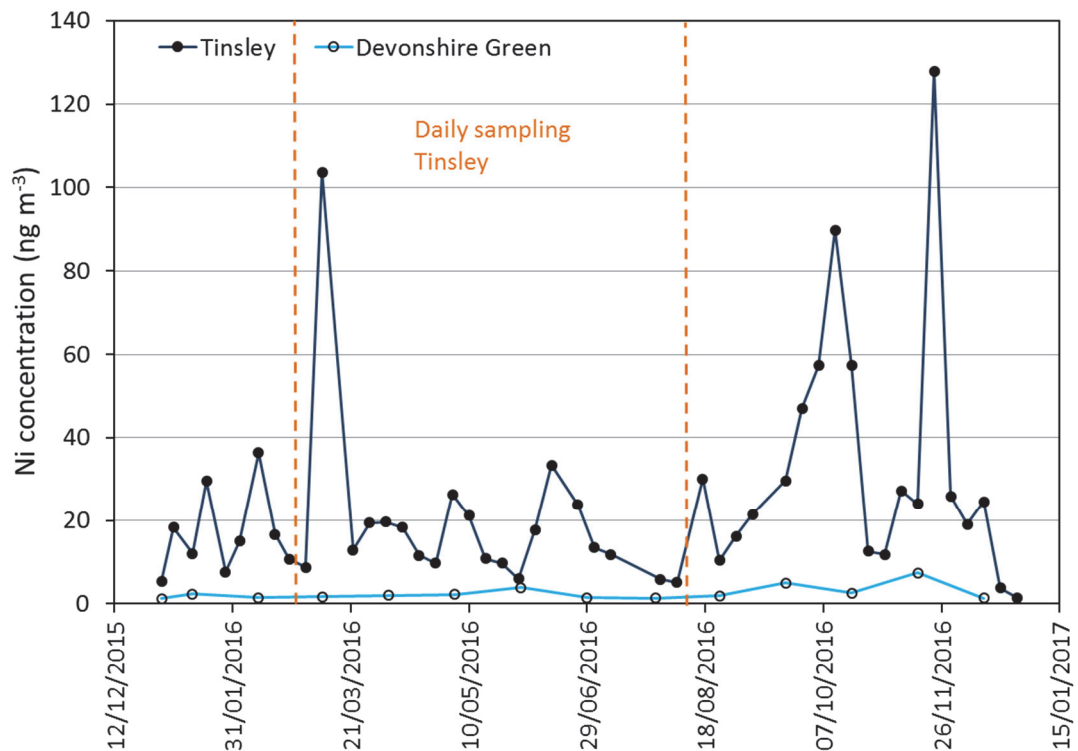


Figure 8. Measured Ni concentrations at Site 117: Sheffield Tinsley and Site 119: Sheffield Devonshire Green in 2016. Sampling at Tinsley is weekly, except for the period 25th February – 10th August 2016, when daily sampling was

implemented. For this period weekly averages of the daily results have been plotted. Results from Sheffield Devonshire Green are averaged over 4-weekly periods.

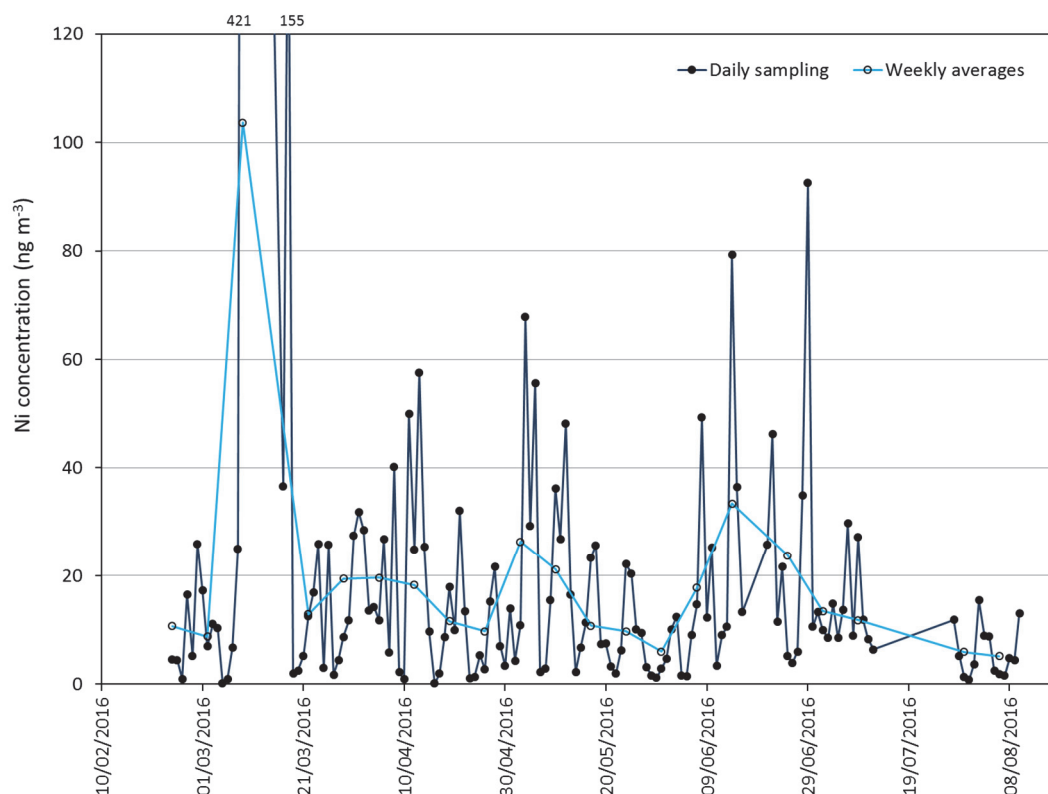


Figure 9. Comparing daily results and calculated weekly averages at Site 117: Sheffield Tinsley from 25th February – 10th August 2016.

The additional value of increased sampling time resolution is clear from Figures 6 to 9. The variability in measured concentrations decreases considerably from daily to weekly to 4-weekly sampling.

In the case of Sheffield Tinsley where daily results were available from 25th February – 10th August, it is clear to see how the peak concentration of short-term pollution events on single days would have been significantly underestimated with weekly sampling (see Figure 9).

High concentration spikes often make a significant contribution to the annual average. 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 Brecon Road, although nominally downwind of a local industrial source, is at an elevated position compared to Tawe Terrace which may result in Brecon Road not

encountering the emission plume). 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 non-directive metals normalised to the annual median value for each metal. The annual average concentrations were given in Table 6.

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 from non-exhaust emissions (e.g. emissions from brake wear) and re-suspension (e.g. from erosion of the road surface or road furniture);
- Iron and manganese at Port Talbot Margam and Scunthorpe Low Santon, near to steel works;
- Cobalt, chromium, copper, manganese, selenium and zinc at Sheffield Tinsley near to a steel processing facility;
- Copper and zinc at Walsall Bilston Lane close to a metal refining works;
- Cobalt, chromium and selenium at Pontardawe Tawe Terrace close to a nickel-cobalt alloy production process;
- Elevated vanadium at Scunthorpe Low Santon and Port Talbot, possibly owing to neighbouring steel works.

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

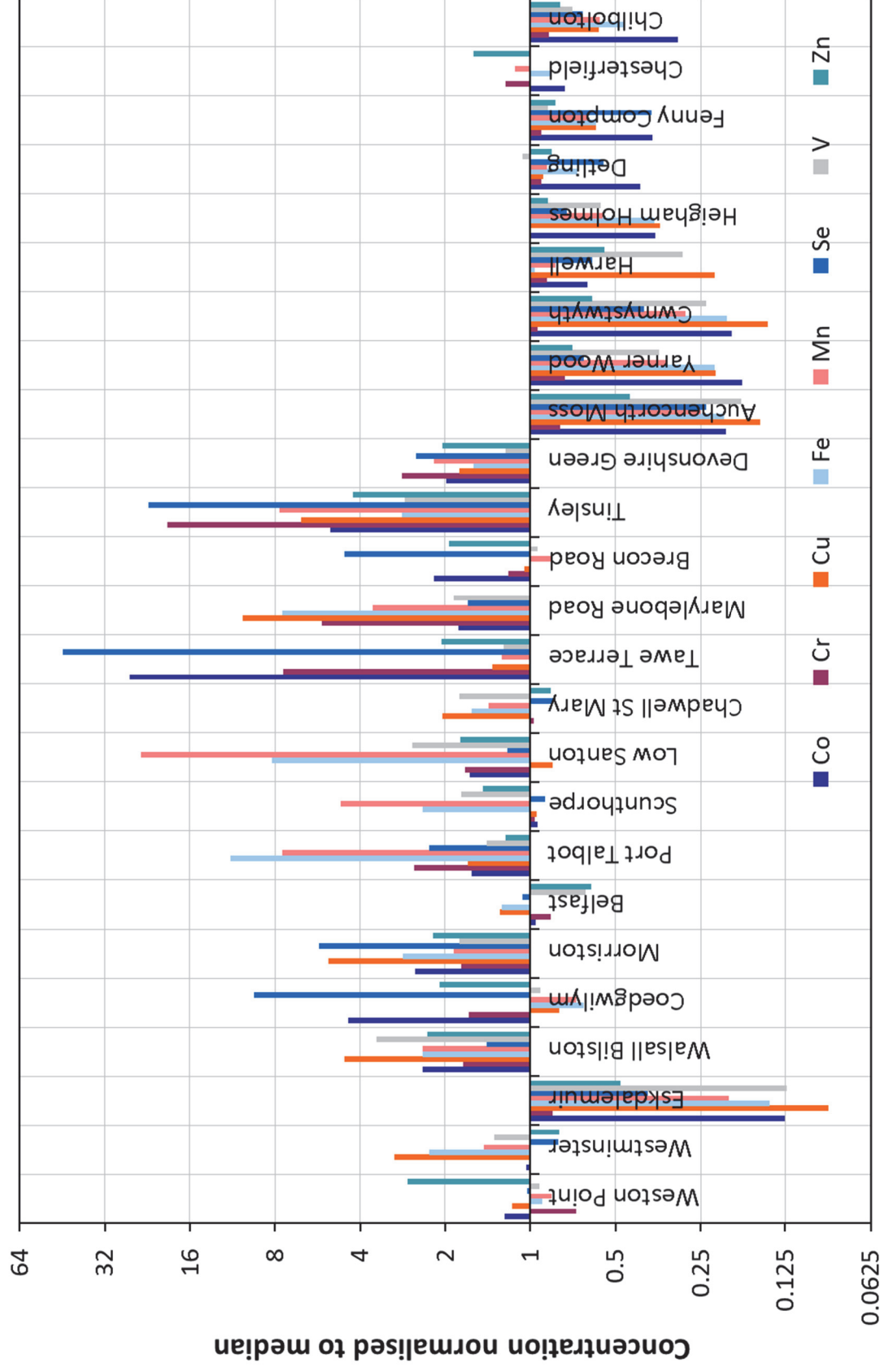


Figure 10. A summary of the annual mean measured concentrations of the non-directive metals at all sites on the UK Heavy Metals Monitoring Network in 2016, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median so it is clear which stations are above and below the median level. Note the logarithmic scale on the y-axis.

6.5 MEASURED CONCENTRATIONS OF METALS IN DEPOSITION

The annual mean metals deposition flux concentrations in 2016, averaged over all sites sampling metals in deposition (Table 8), and at individual sites (Table 9), are given below.

Analyte	2016 UK Mean Annual Flux / $\mu\text{g m}^{-2} \text{d}^{-1}$	2016 UK Median Annual Flux / $\mu\text{g m}^{-2} \text{d}^{-1}$	2016 UK Maximum Annual Flux / $\mu\text{g m}^{-2} \text{d}^{-1}$
Al	20.8	20.0	25.9
As	0.23	0.14	0.58
Ba	1.28	1.36	1.81
Be	0.01	0.004	0.02
Cd	0.02	0.02	0.04
Co	0.02	0.02	0.03
Cr	0.13	0.12	0.18
Cs	0.004	0.004	0.01
Cu	0.95	0.86	1.20
Fe	15.5	16.3	19.7
Hg	0.01	0.01	0.01
Li	0.12	0.09	0.24
Mn	2.24	2.16	2.72
Mo	0.04	0.04	0.06
Ni	0.14	0.14	0.23
Pb	0.44	0.42	0.72
Rb	0.16	0.14	0.25
Sb	0.08	0.08	0.10
Se	0.22	0.19	0.36
Sn	0.06	0.06	0.10
Sr	4.94	4.39	10.2
Ti	0.38	0.37	0.54
U	0.01	0.005	0.02
V	0.42	0.30	0.64
W	0.01	0.01	0.02
Zn	4.69	4.40	6.45

Table 8. The 2016 annual mean, median and maximum deposition flux measurements (in $\mu\text{g m}^{-2} \text{d}^{-1}$) averaged over all deposition monitoring sites on the UK Heavy Metals Monitoring Network.

	Annual Average Deposition Flux ($\mu\text{g m}^{-2} \text{d}^{-1}$)				
Analyte	Auchencorth Moss	Chilbolton	Heigham Holmes	Lough Navar	Yarner Wood
Al	25.9	18.1	19.5	20.6	20.0
As	0.17	0.12	0.14	0.58	0.14
Ba	1.36	1.81	0.82	0.91	1.48
Be	0.02	0.003	0.002	0.01	0.004
Cd	0.04	0.02	0.01	0.02	0.01
Co	0.03	0.02	0.02	0.02	0.01
Cr	0.18	0.11	0.09	0.17	0.12
Cs	0.003	0.004	0.004	0.01	0.01
Cu	1.20	1.15	0.76	0.86	0.78
Fe	18.6	16.3	19.7	14.0	8.71
Hg	0.01	0.01	0.01	N/A	0.01
Li	0.09	0.05	0.09	0.24	0.12
Mn	2.04	2.35	2.16	2.72	1.94
Mo	0.04	0.03	0.02	0.06	0.04
Ni	0.15	0.14	0.08	0.11	0.23
Pb	0.30	0.72	0.43	0.42	0.33
Rb	0.09	0.10	0.14	0.25	0.21
Sb	0.07	0.10	0.10	0.08	0.04
Se	0.19	0.14	0.13	0.36	0.29
Sn	0.10	0.06	0.02	0.07	0.06
Sr	2.42	2.25	4.39	10.2	5.50
Ti	0.46	0.33	0.37	0.54	0.19
U	0.02	0.003	0.002	0.01	0.005
V	0.27	0.30	0.27	0.64	0.59
W	0.01	0.01	0.01	0.02	0.02
Zn	5.12	6.45	3.77	3.68	4.40

Table 9. The 2016 annual mean deposition flux measurements (in $\mu\text{g m}^{-2} \text{d}^{-1}$) 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 36 years for the metals relevant to the EC 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 six years.)

Where mean values are significantly higher than median values, this indicates 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 lower, 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 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, and so these are no longer comparable datasets for the purposes of plotting long term trends. Consequently, the average and median Hg(v) values are equal and are dominated by Runcorn Weston Point.

Nickel concentrations although significantly reduced in the 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.

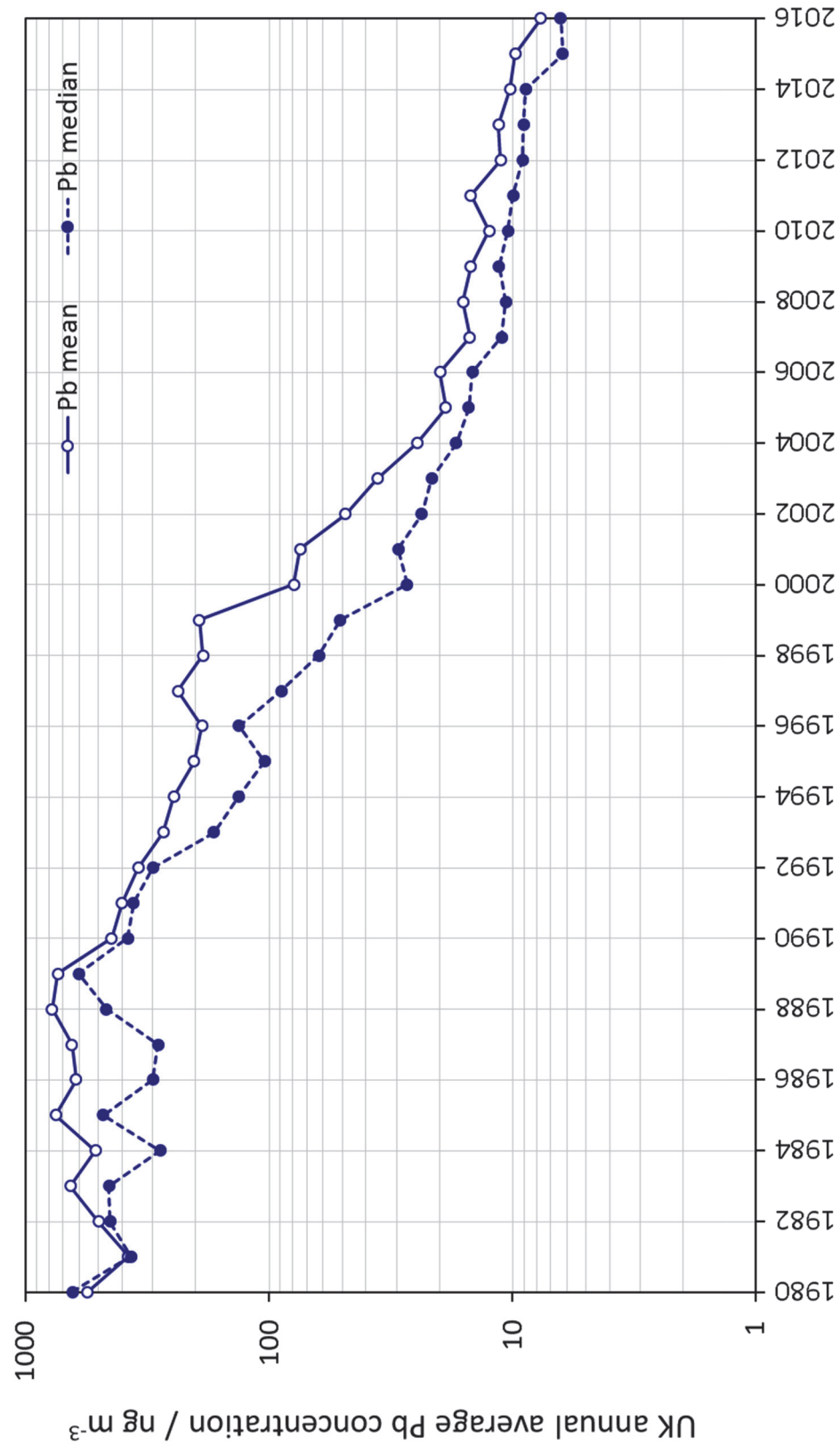


Figure 11. The mean and median of station annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 36 years. The EC limit value for lead is 500 ng m^{-3} and the UK Air Quality Objective for lead is 250 ng m^{-3} . Note the logarithmic scale on the y-axis.

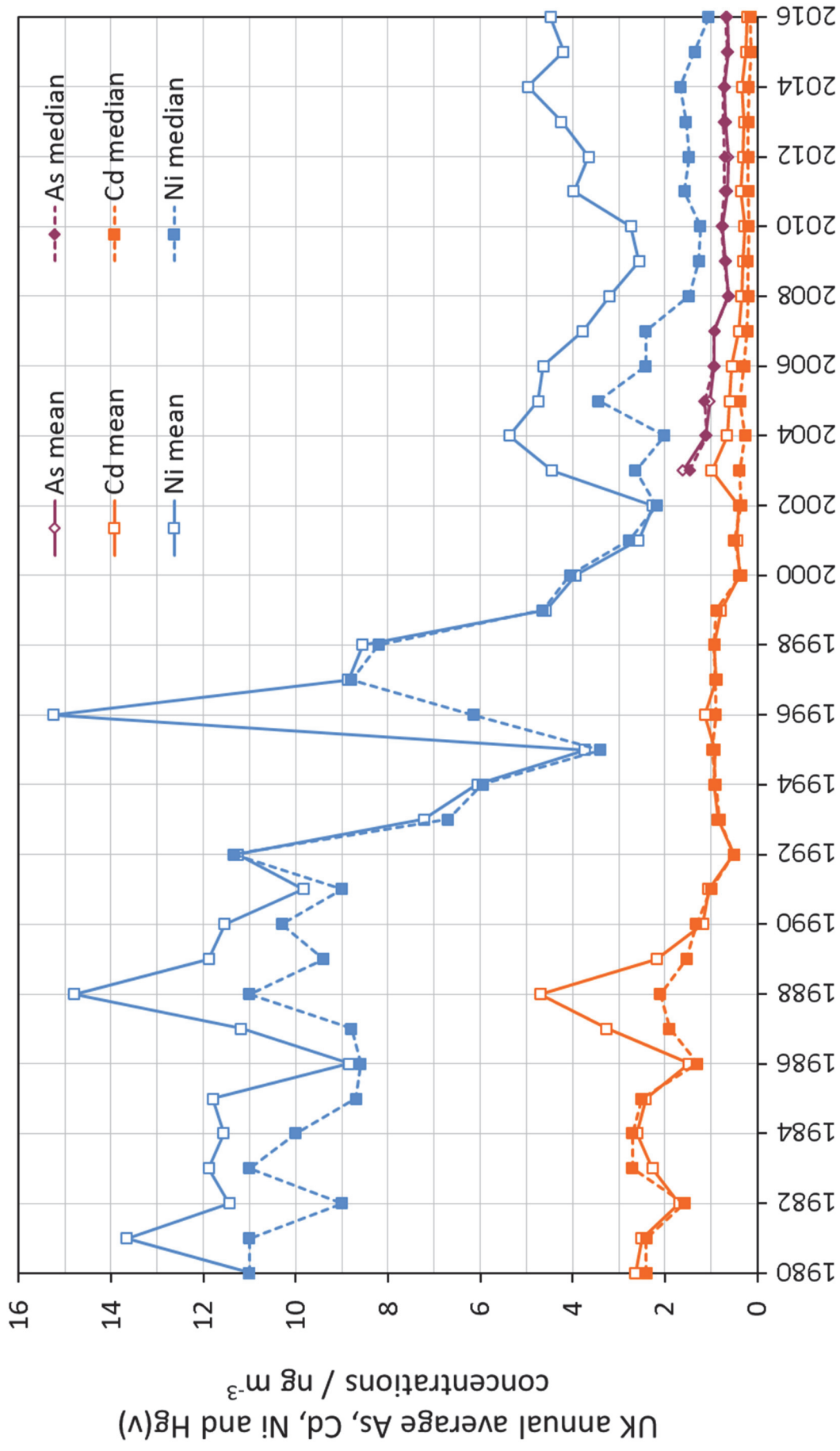


Figure 12. The mean and median of station annual average concentrations of Ni, As and Cd measured on the UK Heavy Metals Monitoring Network over the last 36 years. The EC target values for Ni, As and Cd are 20 ng m⁻³, 6 ng m⁻³ and 5 ng m⁻³ respectively.

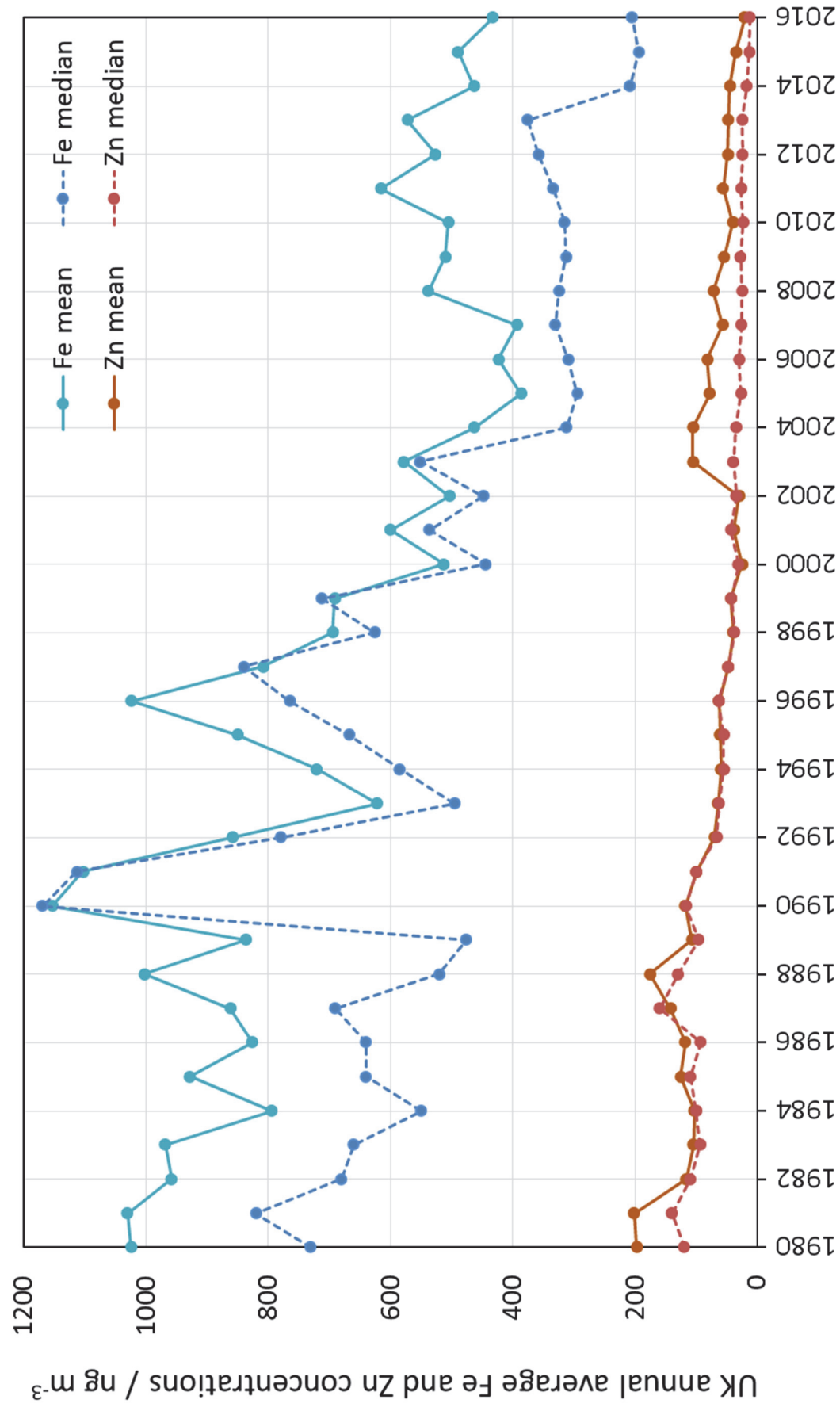


Figure 13. The mean and median of station annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 36 years.

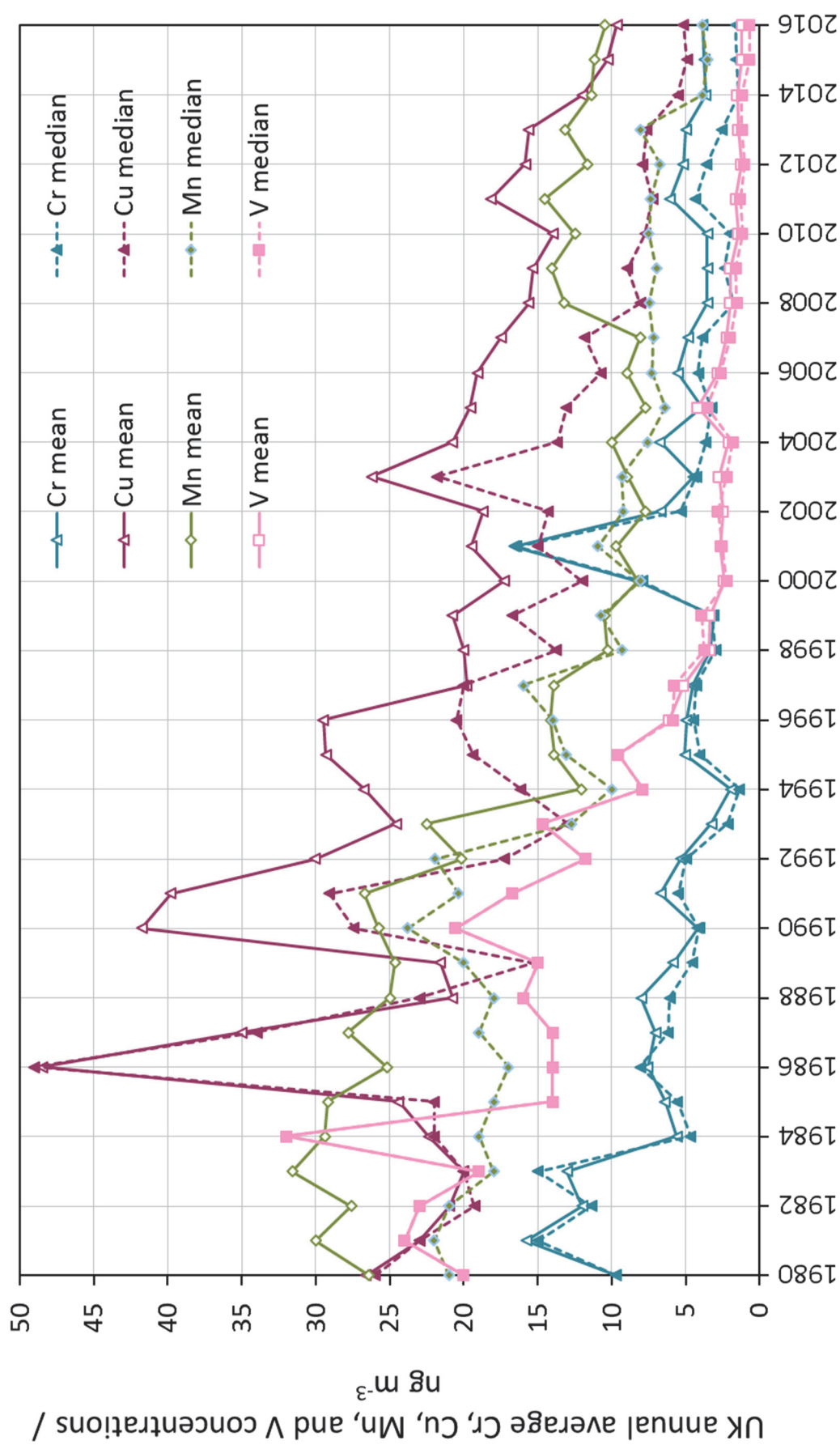


Figure 14. The mean and median of station annual average concentrations of Cr, Cu, Mn and V measured on the UK Heavy Metals Monitoring Network over the last 36 years.

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 12 years is shown in Figure 15.

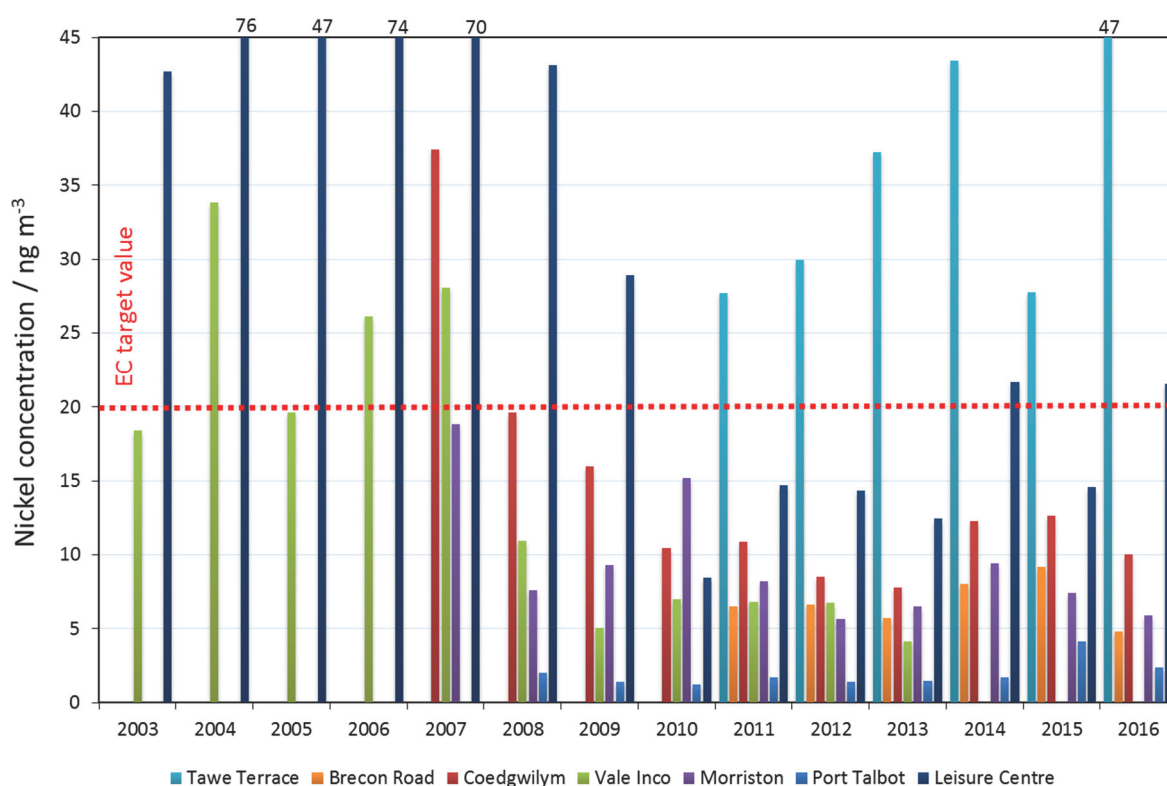


Figure 15. The annual average nickel concentrations measured at monitoring sites in the Swansea area (indicated by the key) 2003 - 2016. Nickel concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level. The red dotted line indicates 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. The data for the Leisure Centre is courtesy of Neath Port Talbot County Borough Council.) Note: the Vale Inco data for 2013 was only based on 18.8% data capture.

The sampling at the Pontardawe Leisure Centre is operated by NPL on behalf of Neath Port Talbot County Borough Council. The site is positioned in a semi-rural location, in the River Tawe Valley to monitor any emissions from the Vale nickel refinery situated at Clydach, about 4 km to the south-west, and the Wall Colmonoy metal alloy coatings plant, approximately 1 km to the north-east¹⁵.

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 its closure (5th June 2013). At the end of

¹⁵ NPL Report ENV (RES) 032 "Measurement of Heavy Metals in PM₁₀ at Pontardawe Leisure Centre in 2016: Report for Neath Port Talbot County Borough Council", Goddard et al. 2017

2007 the local authority sites at Swansea Coedgwilym and Swansea Morriston were affiliated to the Network.

With the exception of Pontardawe Tawe Terrace, the other Swansea and Tawe valley stations showed significant decreases in measured nickel 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.

In the Tawe valley the concentrations at Pontardawe Tawe Terrace showed a year upon year increase from 2011 to 2014, followed by a decrease in 2015. Abatement processes at the industrial facility impacting on the Pontardawe Tawe Terrace station were introduced in November 2013. Concentrations continued to increase in 2014, then decreased in 2015 to levels equivalent to those observed in 2011, the first year of monitoring at Tawe Terrace. However in 2016 concentrations rose again to a new high for the site. It is considered likely that problems with abatement at the industrial facility during the second half of the year contributed significantly to the high annual average. The 'South Wales Nickel Working Group' continues to work to investigate and agree actions to reduce these concentrations in future.

8 SCIENTIFIC RESEARCH, PUBLICATIONS AND RELATED ACTIVITIES

8.1 PUBLICATIONS

NPL has produced a number of articles in learned journals during 2016 that feature the data, analytical procedures and operation of the Network and research relevant to Network objectives. These articles are listed below:

- Determination of beryllium in ambient air quality filter samples.
Sharon L Goddard, Richard J C Brown, Baljit K Ghatora (Kingston University).
Atmospheric Environment, 2016, 147, 320-329

This paper used the spare filter portions available following network analysis to assess ambient concentrations of beryllium at the UK Heavy Metals Network sites. The concentrations found were compared to a guideline level of 0.2 ng m⁻³ specified by the Expert Panel on Air Quality Standards (EPAQS) in a report produced for Defra¹⁶. All concentrations were significantly below the EPAQS guideline level, giving reassurance that beryllium emissions are not a significant problem for UK ambient air quality overall. However the highest levels were measured at sites monitoring industrial point sources, suggesting a strong possibility that beryllium is being emitted by these facilities. Targeted monitoring at confirmed industrial point sources (especially coal-fired power stations) and roadside locations would be advantageous to establish potential hot-spots of beryllium emissions that would not have been apparent at the existing network sites.

- Temperature dependence of Hg vapour mass concentration at saturation in air: new SI traceable results between 15 and 30 °C
Quétel, C R; Zampella, M; Brown, R J C
Trends in Analytical Chemistry, 2016, 85B, 81–88.

This paper proposes a new model for calibrating measurements of mercury vapour using an improved vapour pressure equation, and should reduce the uncertainty of ambient measurements of mercury vapour in future.

- The contributions to long-term health-relevant particulate matter at the UK EMEP supersites: quantifying the mitigation challenge
Malley, C S; Heal, M R; Braban, C F; Kentisbeer, J; Leeson, S R; Malcolm, H; Lingard, J J N; Ritchie, S; Maggs, R; Beccaceci, S; Quincey, P; Brown, R J C; Twigg, M M
Environment International, 2016, 95, 98-111

This paper provides a statistical analysis of the conditions that contribute to annual average PM₁₀ and PM_{2.5}, the metrics currently recommended by the World Health Organization for quantification of long-term health-relevant PM, at the UK EMEP supersites (Harwell and Auchencorth Moss). Data from the Heavy Metals Network was utilised in the analysis.

8.2 LEGISLATION AND STANDARDISATION

There were no changes to legislation or standardisation relevant to the UK Heavy Metals Monitoring Network in 2016

¹⁶ EPAQs (2008) Consultation on guidelines for metals and metalloids in ambient air for the protection of human health, May 2008, Defra.

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

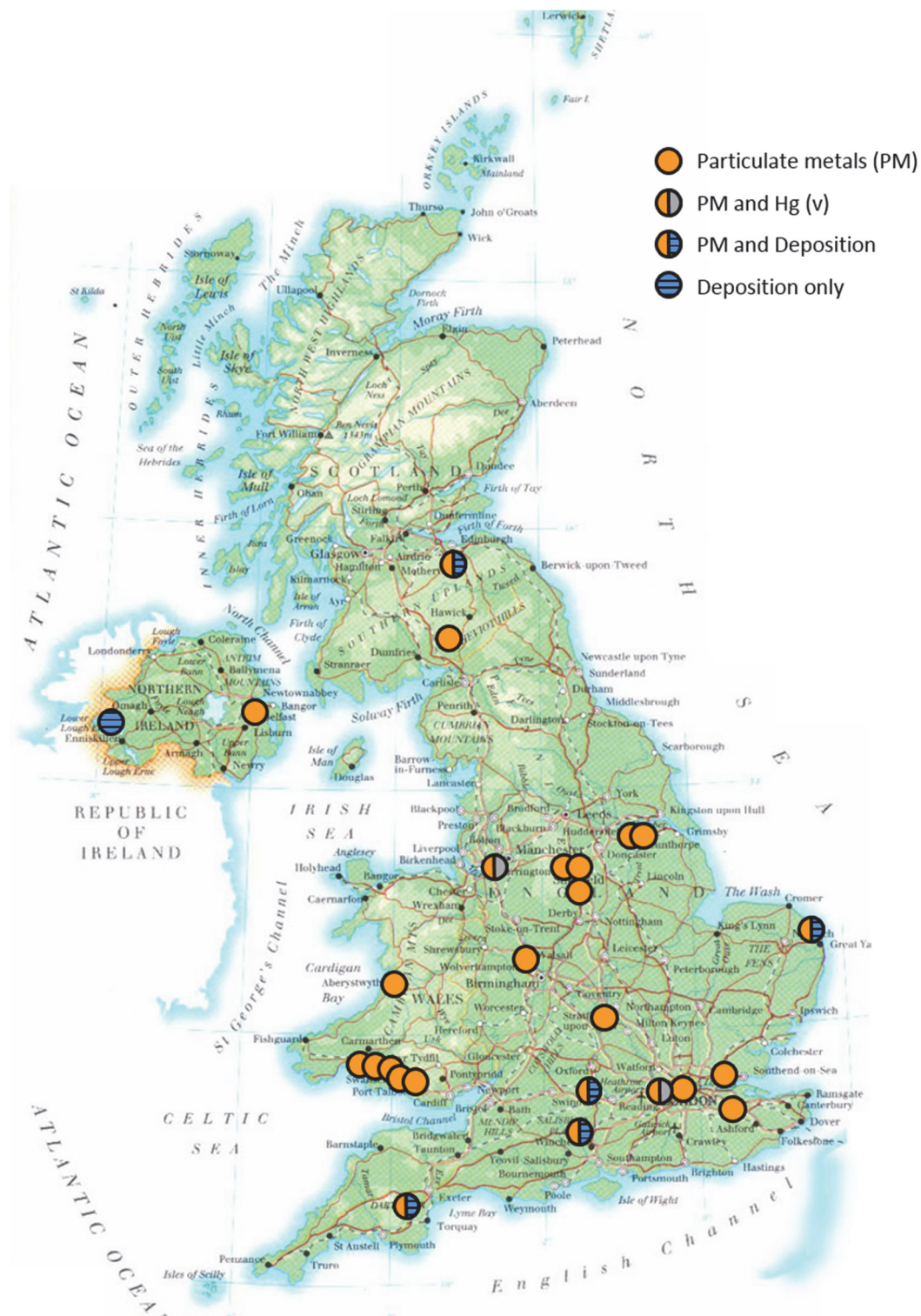


Figure A1. Location of monitoring sites comprising the UK Heavy Metals Monitoring Network during 2016 (indicated by the coloured circles, see key) – details of which are given in Table A1 below.

NPL Report ENV 31

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, Dumfriesshire, 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 Background, 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: Yarnier Wood (Yarnier Wood)	Natural England, Yarnier Wood, Bovey Tracey, Devon, TQ13 9LJ	Rural Background, 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 Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
205: Harwell (Harwell) (closed January 2016)	Ricardo-AEA, Gemini Building, Fermi Avenue, Harwell campus, Didcot, Oxon, OX11 0QR	Rural Background, 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 Background, 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 Background	(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
210: Chesterfield	Loundsley Green, Pennine Way, Chesterfield. S40 4NG.	Urban Background	p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
211: Chilbolton	Drove Road, Chilbolton, Stockbridge, Hampshire. SO20 6BJ.	Rural Background, 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
UKA00166: Lough Navar	Lough Navar, Glennasheevan Road, Derrygonnelly, Enniskillen, Fermanagh, BT93 6AH	Rural Background, 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 5. Samplers at Chilbolton, Metals Partisol in the background on the left.

