NPL
National Physical Laboratory

NPL REPORT ENV 29

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

Annual Report for 2018 on the UK Heavy Metals Monitoring Network

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EXECUTIVE SUMMARY

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

This is the Annual Report for 2018 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 2018.

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

In summary, during 2018:

- **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.

- **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.

- In addition to the Directive metals, concentrations in ambient air were recorded for cobalt, chromium, copper, iron, manganese, selenium, vanadium and zinc. Gaseous phase mercury was also monitored at two sites until August. 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 2018 was **97.9 %**. For gaseous phase mercury and metals in deposition it was 100 % and 76.1 % respectively.

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Approved on behalf of NPLML by
Robert Smith, Head of Environment Department

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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 Administrations[1] (the Welsh Government, the Department of Agriculture, Environment and Rural Affairs in Northern Ireland, and the Scottish Government).

This is the Annual Summary Report for the UK Heavy Metals Monitoring Network (the 'Network') for 2018 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/EC[2]) for lead; the Fourth Air Quality Daughter Directive (DD) (2004/107/EC[3]) for nickel, arsenic, and cadmium; 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 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 2018.

- 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, 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

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1 The Devolved Administrations are in detail: the Welsh Government, the Northern Ireland Executive, represented by the Department of Agriculture, Environment and Rural Affairs in Northern Ireland (DAERA)), and the Scottish Government.
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 Directives and adopted into UK legislation.

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 published[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)].

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.

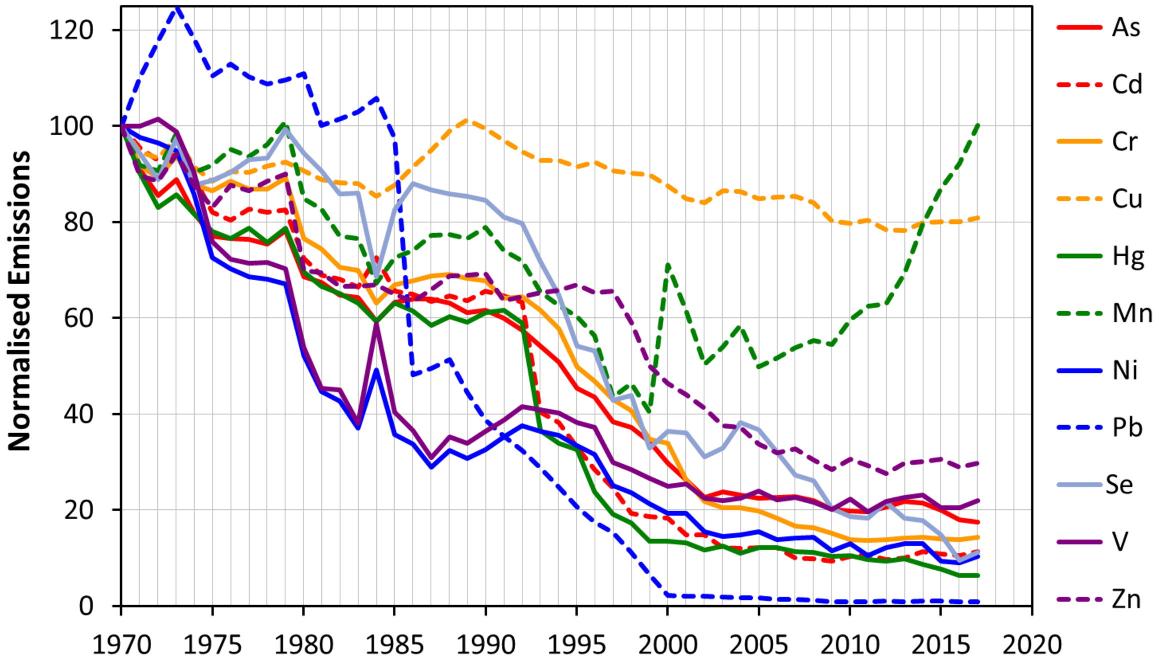

Figure 1. Estimated UK annual emissions of the metals from 1970 to 2016 (the latest year for which emissions data were available at time of writing) normalised to their values in 1970. The absolute levels of emissions in 1970, in tonnes, were: As, 83; Cd, 36; Cr, 250; Cu, 226; Mn, 136; Ni, 991; Pb, 7495; Hg, 62; Se, 92; V, 2751; and Zn, 1566. 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 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 2018 comprised 25 monitoring sites around the UK (15 in England, 6 in Wales, 2 in Scotland, and 2 in Northern Ireland) sampling PM_{10}, total gaseous mercury and/or deposition from ambient air. Details of the sites are given in Annex 1. The PM_{10} 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. Metals in deposition are monitored at 5 sites, 4 of which also monitor mercury in deposition. Total gaseous mercury was additionally monitored at 2 of these network sites by sampling onto adsorption tubes (until monitoring ceased on until 31st July). These adsorption tubes were then analysed at NPL to produce concentration values for total gaseous mercury in ambient air. Relevant activity related to Network operation during 2018 is detailed below.

2.1 OVERVIEW

NPL's management of the UK Heavy Metals Monitoring Network in 2018 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 2018, NPL visited all the network sites twice to perform 6 monthly site audits. At these visits the site infrastructure, performance and integrity were assessed. The LSOs were also audited at one of the two audit visits and received extra training where required.

A list of sites comprising the network as of the end of 2018, 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:

- Assessed the current condition of all on-site equipment, including the condition of the PM_{10} 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 where applicable (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 gaseous mercury 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 gaseous mercury sampling equipment were satisfactory and no remedial action was required.
- The LSOs were performing their duties to a high standard.

The ESU also attended all sites twice in 2018 to perform 6 monthly Partisol services. The services included flow calibrations and leak checks.

In combination, the flow calibration data from the NPL audits and ESU services during the year supplies the three-monthly flow and leak checks required by EN 14902.

2.3 EQUIPMENT SERVICING AND BREAKDOWNS

- During 2018, the ESU fully serviced, carried out preventative maintenance and calibrated the flow of the Partisol samplers twice at all Network sites.

- During 2018, NPL called out the ESU to deal with Partisol sampler faults at: Walsall Bilston Lane, Eskdalemuir, Fenny Compton, Swansea Coedgwilym, Scunthorpe Town and Yarner Wood.

2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION

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

- Monitoring for total gaseous mercury ceased at London Westminster on 14th August and Runcorn Weston Point on 10th August due to a reduction in the scope of the network.

- Sampling was stopped at Walsall Bilston Lane on 23rd August due to health and safety concerns regarding roof access. The sampler was removed to storage by the ESU on 14th November and the electrics were made safe on 12th February 2019. Alternative locations for a site in the area are being considered.

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 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 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) until monitoring ceased on in August. 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 at Runcorn Weston Point and London Westminster (see Image 1). A schematic diagram of the mercury vapour sampling equipment is given in Figure 2.

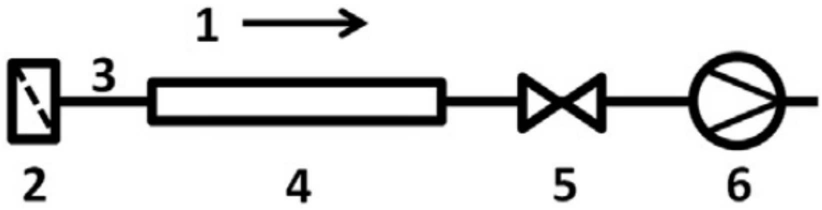

Figure 2. Schematic diagram of the total gaseous mercury sampling apparatus, where: 1 - direction of air flow, 2 - inlet particulate filter, 3 - PTFE tubing (with length minimised between the inlet particulate filter and ‘Amasil’ adsorption tube to fewer than 10 cm), 4 - ‘Amasil’ adsorption tube, 5 -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

3.3 SAMPLING METHODOLOGY: METALS IN DEPOSITION

Sampling for metals in deposition took place at 5 of the network sites: Auchencorth Moss, Chilbolton, Heigham Holmes, Lough Navar and Yarner Wood. Mercury in deposition was not monitored at Lough Navar.

Sampling was performed by CEH using bulk collectors (bottle and funnel types) in accordance with EN 15841 and EN 15853.

3.4 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, Walsall Bilston Lane (until the site was closed on 23rd August), Swansea Coedgwilym, Swansea Morriston, Pontardawe Tawe Terrace and Pontardawe Brecon Road.

Image 2: Anton Paar 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 Paar 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.

Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) analysis of the digested solutions was performed using Agilent 8800 (see Image 3) and 8900 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) 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-QQQ-MS in the UK ambient metals analysis facility at NPL.

3.5 ANALYTICAL METHODOLOGY: TOTAL GASEOUS MERCURY (TGM)

Mercury vapour results are reported as a four-weekly average for London Westminster 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 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.

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.

Image 4: Thermal desorption-atomic fluorescence analysers comprising the UK total gaseous mercury analysis facility at NPL.

3.6 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION

During 2018, monitoring of heavy metals and mercury in deposition was undertaken by the Network at Auchencorth Moss, Chilbolton, Heigham Holmes and Yarner Wood. 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 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 monoelemental reference materials. The procedure is in full accordance with EN 15853 and EN ISO 17852 (the analytical standard called upon with EN 15853).

3.7 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/m^2)/d.

3.8 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 AFS was last audited by UKAS in 2018, 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 QUALITY ASSURANCE/QUALITY CONTROL (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 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% 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 2018 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	7 - 16 %
Cd	7 - 16 %
Co	7 - 15 %
Cr	7 - 25 %
Cu	7 - 25 %
Fe	7 - 16 %
Mn	7 - 18 %
Ni	7 - 15 %
Pb	7 - 15 %
Se	8 - 26 %
V	7 - 16 %
Zn	7 - 13 %
Hg(v)	10 - 20 %

Table 1. The range of uncertainties covering the majority of analyses of single filters and tubes at NPL during 2018. 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 2018 was **97.9 %**. For gaseous phase mercury it was 100 %. 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 fifteen years are displayed in Figure 3.

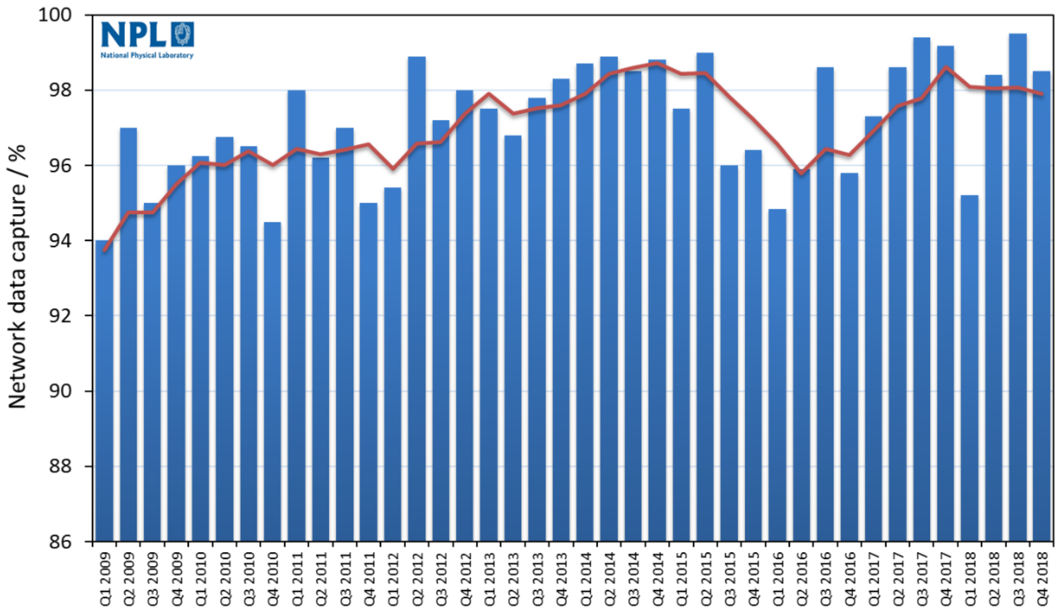

Figure 3. Network data capture from the last 10 years (2009-2018 inclusive) for particulate and gaseous phase measurements. Quarterly data capture is indicated by the blue bars, whilst the rolling annual average data capture is given by the red line.

Site Number: Site Location	Data Capture / %	
	Particulate phase	Gaseous phase
Across all sites	**97.9**	**100.0**
59: Runcorn Weston Point	97.7%	100.0^
62: London Westminster	99.9%	100.0^
65: Eskdalemuir	92.9%	N/A
69: Walsall Bilston Lane	87.2% *	N/A
100: Swansea Coedgwilym	99.6%	N/A
101: Swansea Morriston	100.0%	N/A
103: Belfast Centre	95.9%	N/A
104: Port Talbot Margam	99.9%	N/A
106: Scunthorpe Town	95.0%	N/A
107: Scunthorpe Low Santon	98.1%	N/A
110: Chadwell St Mary	99.9%	N/A
113: Pontardawe Tawe Terrace	99.9%	N/A
114: London Marylebone Road	99.7%	N/A
115: Pontadawe Brecon Road	98.0%	N/A
117: Sheffield Tinsley	99.7%	N/A
119: Devonshire Green	99.9%	N/A
202: Auchencorth Moss	99.6%	N/A
203: Yarner Wood	99.4%	N/A
204: Cwmystwyth	99.9%	N/A
206: Heigham Holmes	97.4%	N/A
208: Detling	96.6%	N/A
209: Fenny Compton	99.9%	N/A
210: Chesterfield	95.6%	N/A
211: Chilbolton	98.8%	N/A

Table 2. Data capture across the UK Heavy Metals Monitoring Network during 2018.
* Covers the period 1 Jan – 29 Aug prior to site closure.
^ • This Data Capture figure represents from 1 January - 14 August at London Westminster and 1 January – 10 August at Runcorn Weston Point Due to cessation of sampling at both of these sites.

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

- Walsall Bilston Lane: Results from 10 – 31 January were invalid due to low valid hours. A callout by the ESU identified and replaced a faulty flow controller. This site then ceased sampling on 29 August due to health and safety concerns regarding the roof access.

5.2 DATA CAPTURE (DEPOSITION)

Data capture for deposition monitoring during 2018 was 76.1 %. 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. Mercury samples are taken in duplicate so typically have higher data capture. Deposition data capture at the sites where these measurements are made is detailed in the Table below.

Site Location	Metals in Deposition / %	Hg in Deposition / %
Auchencorth Moss	86.4%	100.0%
Chilbolton	66.7%	100.0%
Heigham Holmes	55.8%	100.0%
Lough Navar	100.0%	N/A
Yarner Wood	67.8%	100.0%

Table 3. Data capture across the deposition sites of the UK Heavy Metals Monitoring Network during 2018.

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. Data not meeting the data quality objectives for uncertainty or time coverage for the relevant air quality directive are not eligible to produce concentration data and is counted as lost data capture.
3. Data excluded following the ratification procedure will also not be eligible to produce valid concentration data, or count towards the total data capture percentage.
4. Upon production, weekly data for each element at each site is plotted in a time series, or displayed as a continuous list of values which may be easily compared.
5. In the first instance these data are assessed visually for any obvious discrepancies with due regard to long terms trends, short term variability and seasonal variation. Then outlier tests are performed to detect any potentially discrepant data, including the use of powerful chemometric techniques[10].
6. If valid reasons for obviously discrepant values are found (e.g. incorrect calculation, low exposure time, non-valid exposure volume, analytical error) these values may be either excluded or corrected (depending on the nature of the error).
7. As part of the internal quality and technical auditing procedures, a selection of ambient air concentrations calculated each month are thoroughly audited by a party independent of the analysis procedure. For these samples, the sample number, target analyte, auditor, audit date and status of the data 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

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.

According to the EC Air Quality Directives[2,3] an additional component of uncertainty due to incomplete time coverage may be determined by the procedure described in ISO 11222. A

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.

worse-case scenario for this year's data has been assessed by combining analytical uncertainties with a component for incomplete time coverage, calculated in accordance with ISO 11222, using the data capture figure from Walsall Bilston Lane (the lowest site for the year). This yielded only a very small increase in uncertainty (approximately 1 % absolute).

To conclude, in all cases annual mean uncertainties are compliant with the data quality objectives for uncertainty in the EC Air Quality Directives. Exemplar 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	10 %	40 %
Cd	9 %	40 %
Ni	10 %	40 %
Pb	10 %	25 %

Table 4. Exemplar relative expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Directive metals in particulate matter, averaged across the Network.

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 2018, 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	2018 UK Mean Annual Concentration across all sites / ng m^{-3}	2018 UK Median Annual Concentration across all sites / ng m^{-3}	2018 Maximum Annual Mean Concentration at any site / ng m^{-3}	EC limit or target value (UK objective) / ng m^{-3}
As	0.68	0.73	1.04	6
Cd	0.26	0.17	1.18	5
Co	0.32	0.13	3.10	-
Cr	4.75	2.62	39.0	-
Cu	9.59	5.42	53.6	-
Fe	501	227	2870	-
Mn	12.0	4.74	92.9	-
Ni	5.16	1.20	57.5	20
Pb	8.35	6.69	19.8	500 (250)
Se	0.72	0.56	2.09	-
V	1.45	0.88	9.84	-
Zn	24.4	18.5	96.1	-
Hg (v)	9.39	9.39	16.0	-

Table 5. The 2018 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	0.09	0.39	1.72	5.12	165	3.21	0.83	4.67	2.09	0.97	14.5	16.0
62: London Westminster	0.81	0.13	0.12	3.02	15.3	522	6.74	0.94	6.66	0.51	0.92	22.8	2.79
65: Eskdalemuir	0.17	0.02	0.03	1.02	0.60	37.1	1.01	0.26	0.98	0.26	0.35	3.12	N/A
69: Walsall Bilston Lane	0.72	0.62	0.22	3.63	18.1	455	10.1	1.78	19.1	0.99	0.92	74.1	N/A
100: Swansea Coedgwilym	0.63	0.32	0.46	2.82	3.27	161	3.69	**12.4**	5.32	0.54	0.71	11.9	N/A
101: Swansea Morriston	0.83	0.50	0.30	4.18	23.3	717	9.60	8.56	10.5	0.60	1.05	26.9	N/A
103: Belfast Centre	0.45	0.10	0.11	1.72	7.13	271	3.88	1.28	19.8	0.37	1.72	21.9	N/A
104: Port Talbot Margam	0.82	1.18	0.23	4.44	14.8	2870	34.9	1.60	7.81	0.74	4.70	45.7	N/A
106: Scunthorpe Town	0.77	0.33	0.13	2.83	6.13	662	21.6	1.18	16.5	0.94	1.60	28.5	N/A
107: Scunthorpe Low Santon	0.73	0.64	0.21	4.50	5.66	1830	92.9	1.26	18.6	1.06	9.84	29.8	N/A
110: Chadwell St Mary	0.93	0.26	0.13	2.22	10.6	349	5.86	1.14	11.7	0.58	1.46	24.8	N/A
113: Pontardawe Tawe Terrace	0.74	0.33	3.10	14.9	5.40	232	6.79	**57.5**	6.27	0.61	0.78	14.0	N/A
114: London Marylebone Road	0.87	0.16	0.22	8.81	53.6	1640	15.3	1.69	6.73	0.54	1.07	38.9	N/A
115: Pontadawe Brecon Road	1.03	0.29	0.40	2.43	4.78	222	4.04	6.17	5.35	0.53	0.73	12.8	N/A
117: Sheffield Tinsley	1.04	0.43	0.92	39.0	25.6	656	35.6	**20.1**	18.5	1.66	1.67	96.1	N/A
119: Devonshire Green	0.69	0.17	0.18	5.75	9.83	339	9.73	2.25	8.39	1.09	0.84	30.9	N/A
202: Auchencorth Moss	0.20	0.03	0.08	0.89	0.87	46.4	1.12	0.23	1.03	0.25	0.32	3.59	N/A
203: Yarner Wood	0.49	0.06	0.04	0.81	1.35	65.3	1.77	0.45	2.27	0.43	0.71	6.35	N/A
204: Cwmystwyth	0.25	0.06	0.03	1.17	0.90	56.6	1.61	0.39	1.72	0.40	0.54	4.71	N/A
206: Heigham Holmes	0.50	0.10	0.07	0.97	1.99	98.4	2.87	0.81	4.21	0.59	1.01	9.93	N/A
208: Detling	0.93	0.19	0.06	1.47	4.52	154	3.62	0.71	8.13	0.51	0.79	15.1	N/A
209: Fenny Compton	0.80	0.10	0.12	1.23	3.24	156	3.18	0.55	5.62	0.50	0.65	11.7	N/A
210: Chesterfield	0.67	0.14	0.13	3.35	5.44	196	5.44	1.23	7.01	0.89	0.64	28.9	N/A
211: Chilbolton	0.63	0.09	0.05	1.13	2.76	113	2.68	0.51	3.58	0.47	0.75	9.50	N/A

Table 6. The 2018 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:

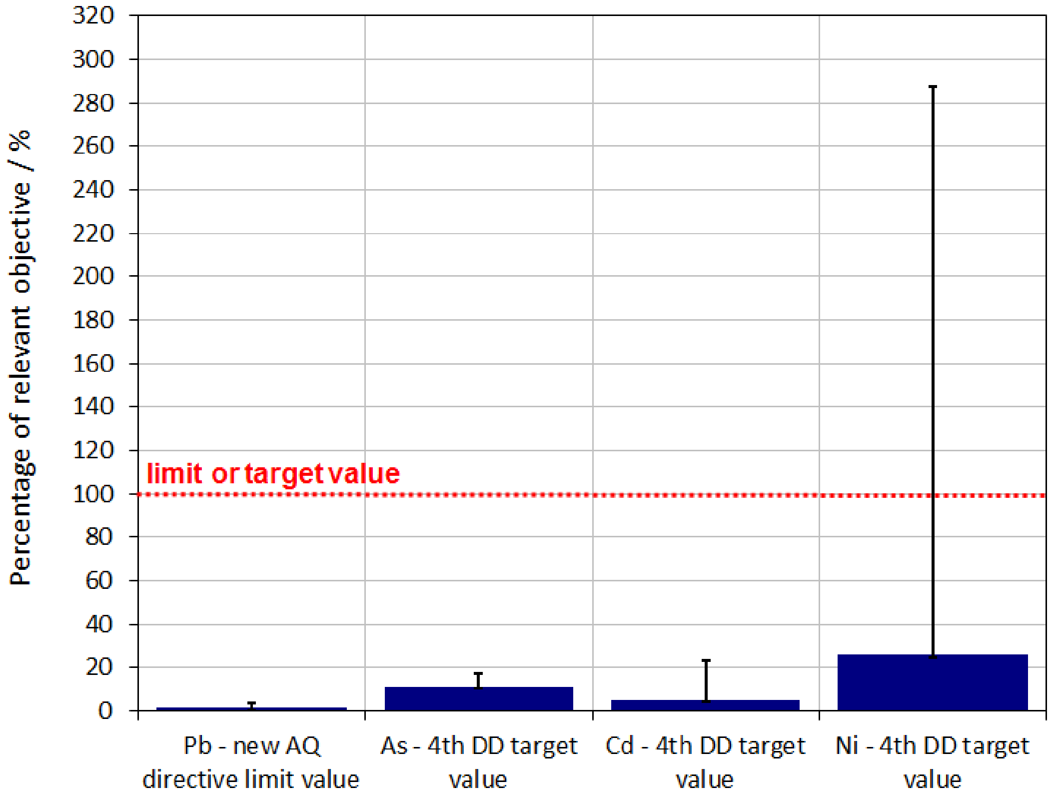

Figure 4. A summary of the annual mean measured concentrations of the heavy metals relevant to the Ambient Air Quality Directive and Fourth Daughter Directive on the UK Heavy Metals Monitoring Network in 2018 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of 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 value for cadmium was found at Site 104: Port Talbot. The highest annual mean value for lead was found at Site 103: Belfast Centre. The highest annual mean value for arsenic was found at Site117: Sheffield Tinsley.

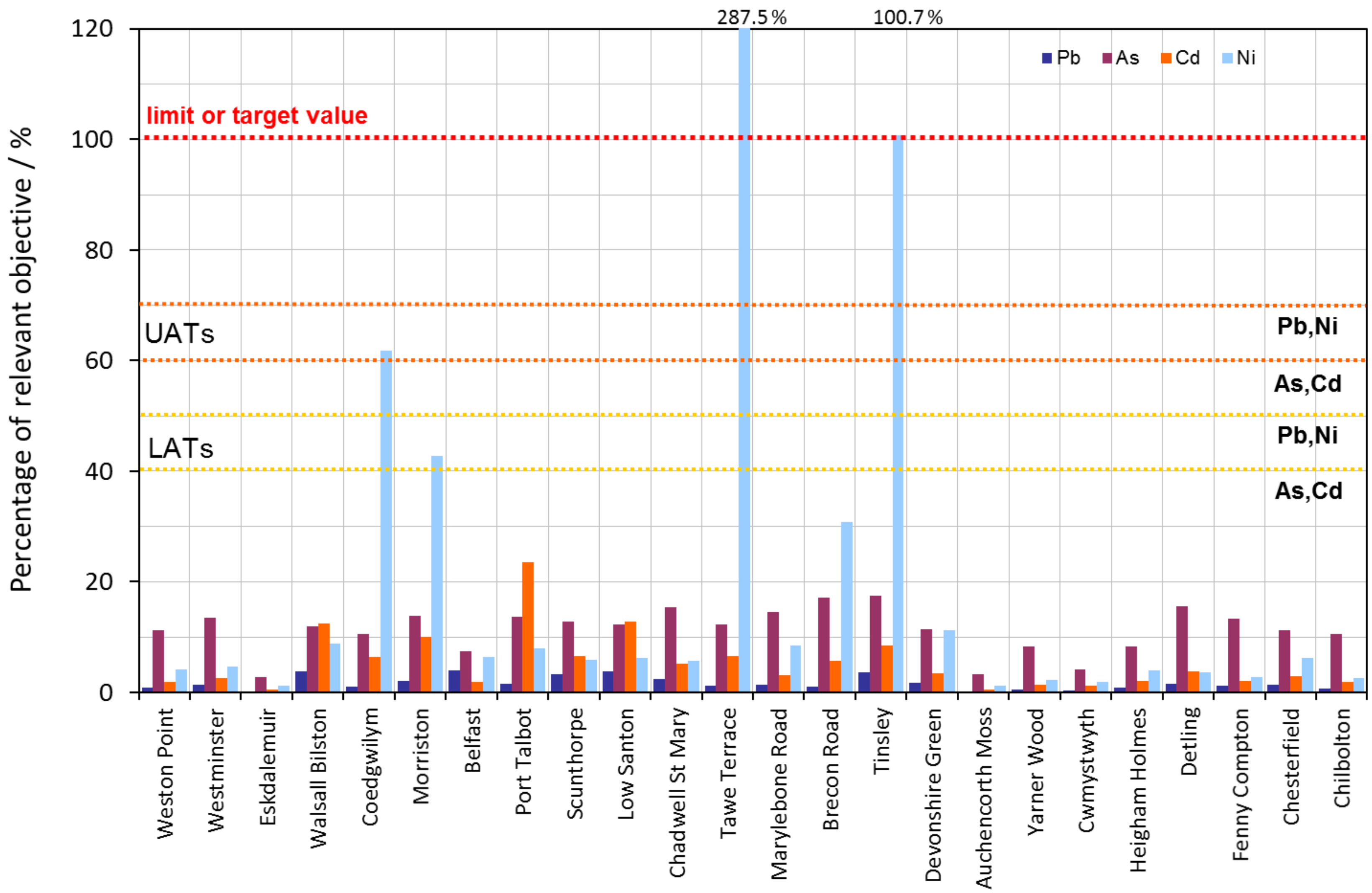

Figure 5. A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2018 as a percentage of the relevant target values shown in red, upper assessment thresholds (UATs) in orange and lower assessment thresholds (LATs) in yellow.

In only three instances do the measured annual mean values exceed the relevant Lower Assessment Thresholds (LATs):

Annual Mean Concentrations above the Target Value:

- Nickel at Pontardawe Tawe Terrace: exceedance of the target value (287.5 %)
- Nickel at Sheffield Tinsley: exceedance of the target value (100.7 %)
- Nickel Swansea Coedgwilym: exceedance of the LAT (61.8 % of the target value)

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

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. There are other industrial sources in the area.

The site at Sheffield Tinsley is located near a variety of industrial sources, including the Outokumpu steel melt shop, continuous casting operations, bar finishing facility and rod mill, producing specialist steel strip, and coil products.

The site at Swansea Coedgwilym is located near the Vale Nickel Refinery and may also receive emissions from Wall Colmonoy in certain wind conditions.

The annual average lead concentration at Belfast Centre, although significantly below the LAT, was uncharacteristically high at 19.8 ng/m^3. This was due to a measured concentration of 212 ng/m^3 for the period 22 August – 19 September (concentrations for all other four-weekly periods were < 5 ng/m^3). A major fire started on 28 August at a commercial property in Belfast city centre and continued to burn for three days[11]. Although not confirmed it is possible that lead components on the roof of the historic building that caught fire caused the high lead concentrations.

11 https://www.bbc.co.uk/news/uk-northern-ireland-45376563

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 arsenic[12], 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 sites and metals where weekly data are available and where these concentrations are likely to be significant, together with data from appropriate paired sites, in the Figures below.

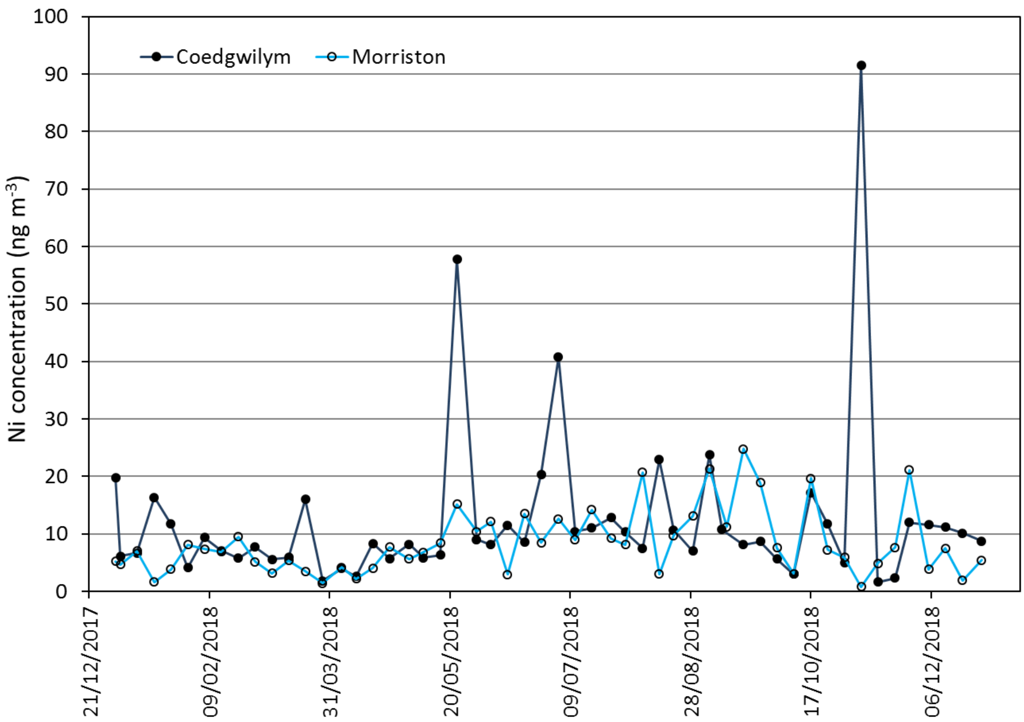

Figure 6. Measured Ni concentrations at Site 100: Swansea Coedgwilym and Site 101: Swansea Morriston, in 2018 (both sampled weekly).

12 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.

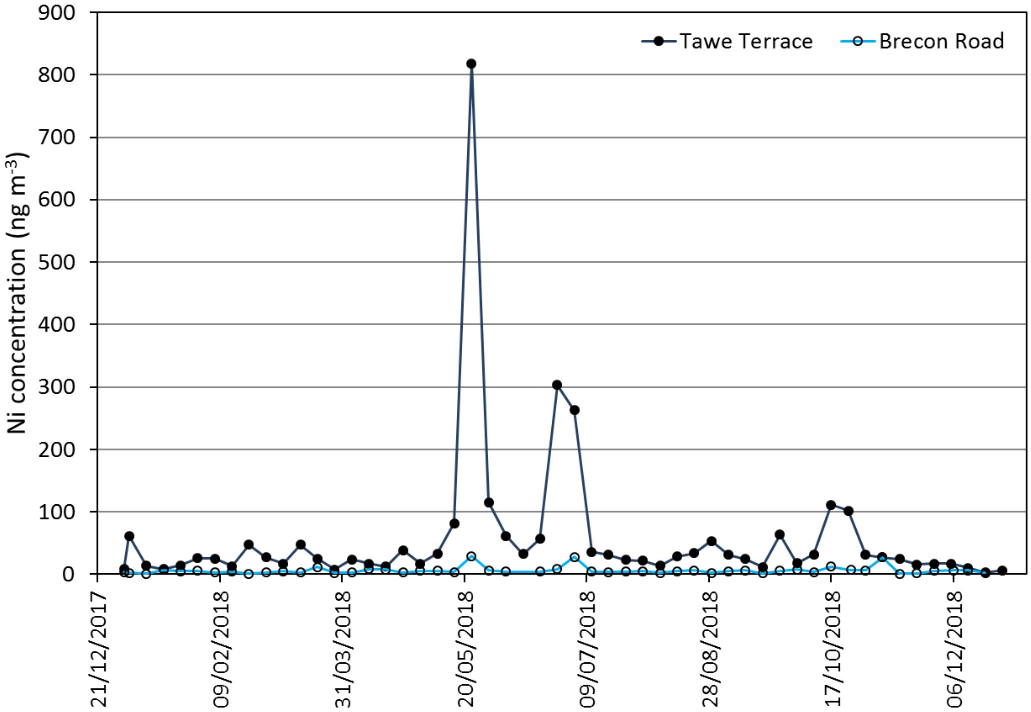

Figure 7. Measured Ni concentrations at Site 113: Pontardawe Tawe Terrace and Site 115: Pontardawe Brecon Road, in 2018 (both sampled weekly).

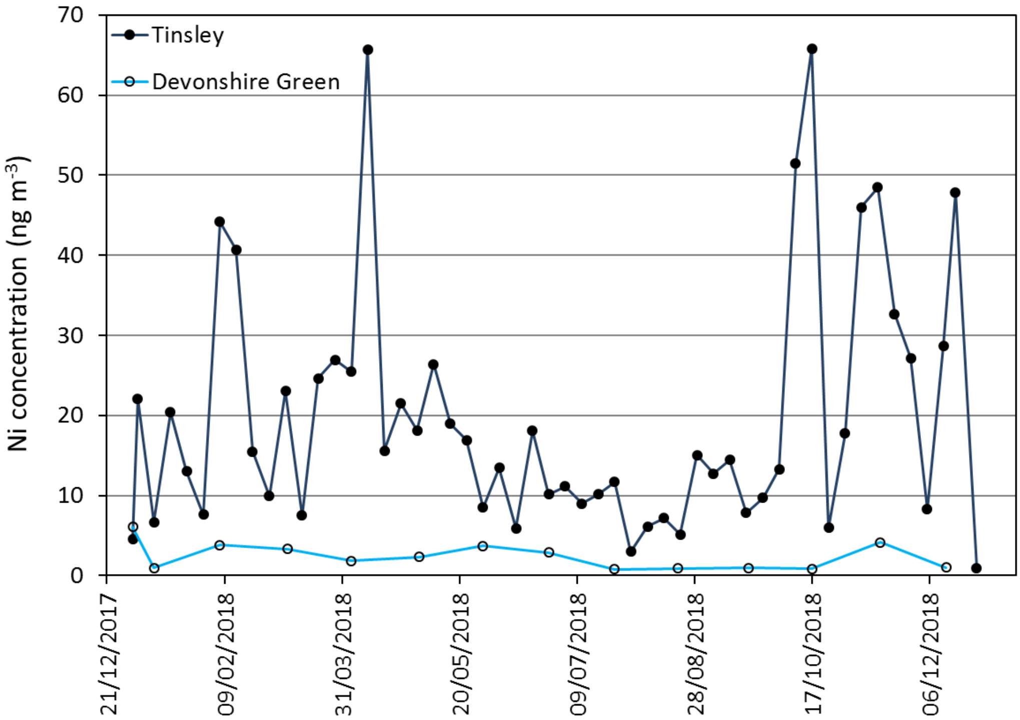

Figure 8. Measured Ni concentrations at Site 117: Sheffield Tinsley and Site 119: Sheffield Devonshire Green in 2018. Sampling at Tinsley is weekly. Results from Sheffield Devonshire Green are averaged over 4-weekly periods.

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 processes being monitored and the local meteorological conditions can be a crucial part to reducing concentrations in the long term.

For the sites 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. Wall Colmonoy reported issues with abatement throughout the year, so provide the most likely cause of these concentration spikes throughout 2018 [13].

Another working group monitors the situation regarding nickel concentrations at the Sheffield sites. The emissions landscape is much more complex in Sheffield than South Wales, as there are numerous potential industrial sources of nickel emissions in the Sheffield area. The local Environment Agency works closely with industrial facilities in Sheffield to highlight processes that could contribute to nickel emissions and improve working practices to reduce them. Further daily monitoring campaigns in Sheffield may be worthwhile in future to assess the impact of changes in industrial processes.

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.

13 NPL Report ENV (RES) 001 "Measurement of Heavy Metals in PM_{10} at Pontardawe Leisure Centre in 2018: Report for Neath Port Talbot County Borough Council", Goddard et al. 2019

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 and re-suspension;
- 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;
- Cobalt, chromium and selenium at Pontardawe Tawe Terrace close to a nickel-cobalt alloy production process;

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

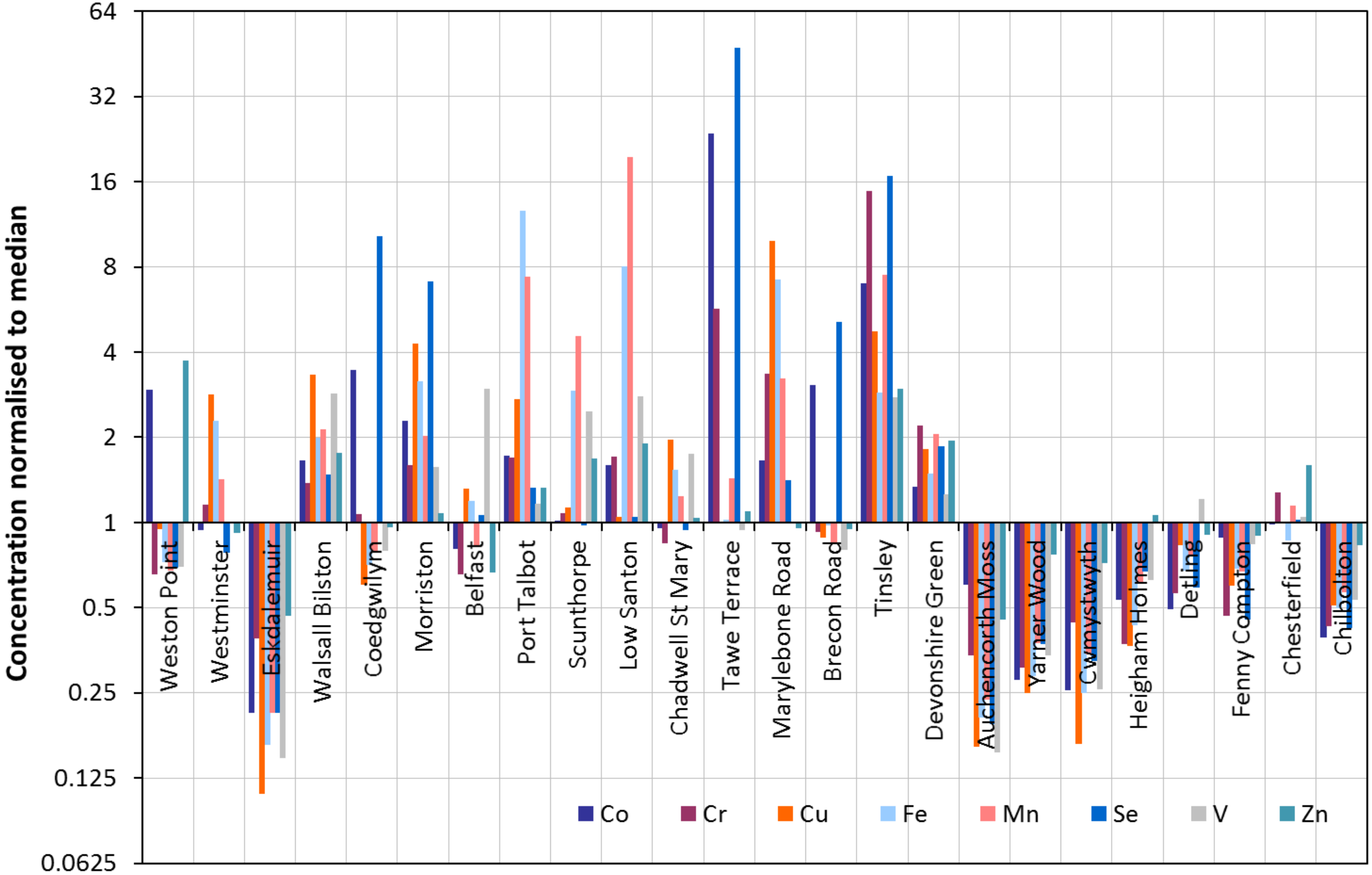

Figure 10. A summary of the annual mean measured concentrations of the non-directive metals at all sites on the UK Heavy Metals Monitoring Network in 2018, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median so it is clear which sites 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 2018, averaged over all sites sampling metals in deposition (Table 8), and at individual sites (Table 9), are given below.

Analyte	2018 UK Mean Annual Flux across all sites / µg m^{-2} d^{-1}	2018 UK Median Annual Flux across all sites / µg m^{-2} d^{-1}	2018 UK Maximum Annual Flux at any site / µg m^{-2} d^{-1}
Al	29.8	18.9	67.1
As	0.30	0.19	0.73
Ba	1.60	1.46	3.05
Be	0.004	0.003	0.01
Cd	0.02	0.02	0.03
Co	0.02	0.02	0.03
Cr	0.18	0.16	0.26
Cs	0.01	0.01	0.01
Cu	1.29	1.34	1.78
Fe	14.8	13.0	25.6
Hg	0.01	0.01	0.02
Li	0.10	0.12	0.17
Mn	2.84	2.50	4.33
Mo	0.05	0.04	0.06
Ni	0.20	0.17	0.34
Pb	0.46	0.41	0.61
Rb	0.16	0.13	0.29
Sb	0.08	0.08	0.09
Se	0.21	0.16	0.31
Sn	0.12	0.12	0.20
Sr	4.61	5.35	7.4
Ti	0.33	0.31	0.49
U	0.004	0.004	0.01
V	0.42	0.33	0.72
W	0.02	0.02	0.02
Zn	7.31	6.55	9.34

Table 8. The 2018 annual mean, median and maximum deposition flux measurements (in µg m^{-2} d^{-1}) averaged over all deposition monitoring sites on the UK Heavy Metals Monitoring Network.

	Annual Average Deposition Flux (µg m^{-2} d^{-1})				
Analyte	**Auchencorth Moss**	**Chilbolton**	**Heigham Holmes**	**Lough Navar**	**Yarner Wood**
Al	35.6	18.9	67.1	11.5	15.9
As	0.18	0.15	0.19	0.73	0.26
Ba	2.26	1.46	3.05	0.54	0.71
Be	0.003	0.003	0.002	0.01	0.004
Cd	0.02	0.02	0.03	0.02	0.02
Co	0.02	0.02	0.03	0.02	0.02
Cr	0.16	0.14	0.13	0.26	0.21
Cs	0.004	0.003	0.01	0.01	0.01
Cu	1.60	0.90	1.78	0.84	1.34
Fe	13.6	11.8	25.6	10.3	13.0
Hg	0.01	0.01	0.02	N/A	0.01
Li	0.05	0.04	0.12	0.17	0.12
Mn	1.98	1.98	3.39	4.33	2.50
Mo	0.04	0.03	0.04	0.06	0.06
Ni	0.19	0.16	0.16	0.17	0.34
Pb	0.28	0.40	0.61	0.41	0.60
Rb	0.08	0.08	0.13	0.23	0.29
Sb	0.07	0.09	0.08	0.08	0.08
Se	0.14	0.11	0.16	0.31	0.31
Sn	0.14	0.09	0.06	0.12	0.20
Sr	2.15	2.24	5.35	7.4	5.90
Ti	0.27	0.25	0.49	0.31	0.32
U	0.003	0.002	0.004	0.004	0.01
V	0.22	0.29	0.33	0.55	0.72
W	0.02	0.01	0.01	0.02	0.02
Zn	9.15	6.55	6.17	5.34	9.34

Table 9. The 2018 annual mean deposition flux measurements (in µg m^{-2} d^{-1}) measured at individual sites on the UK Heavy Metals Monitoring Network.

7 TRENDS IN MEASURED CONCENTRATIONS

7.1 TRENDS IN PARTICULATE-PHASE METALS

Trends in concentrations measured over the last 38 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 sites 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 to 15.

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 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 sites 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 (therefore a Hg(v) trend plot has not been included in this report). Consequently, the average and median Hg(v) values are equal and are dominated by Runcorn Weston Point.

Monitoring of Co and Se commenced in 2011 (Figure 15). Measured concentrations have remained low (< 1 $ng.m^{-3}$) and relatively stable.

Nickel concentrations although significantly reduced in the long-term trend, actually showed a gradual upward trend from 2010 - 2014, largely due to the concentration of monitoring sites in the Swansea and Tawe valleys. Data from 2015 onwards indicated a downward trend until the 2018 data point where there is an increase visible in Figure 12.

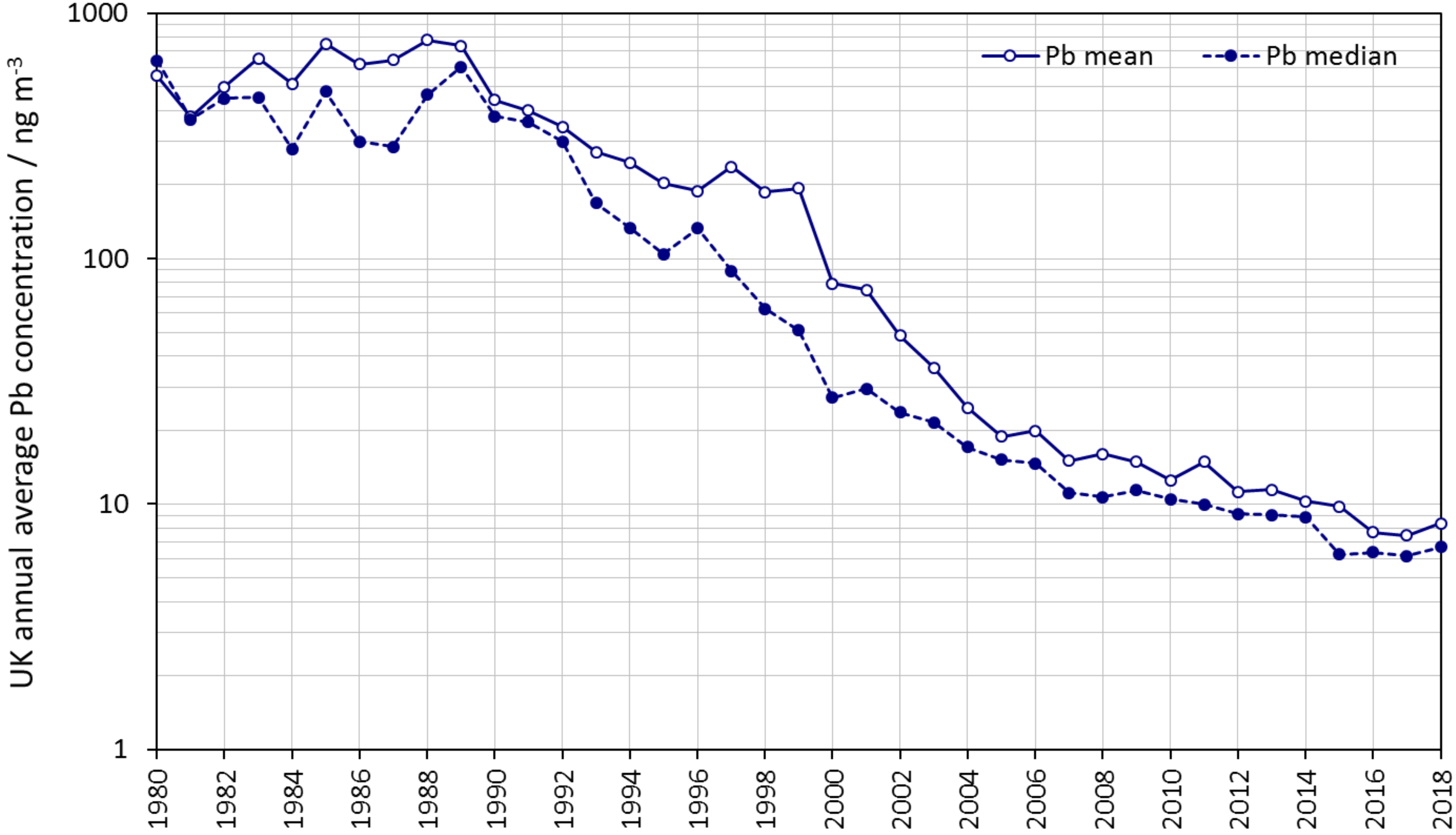

Figure 11. The mean and median of site annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 38 years. The EC limit value for lead is 500 ng m^{-3} and the UK Air Quality Objective for lead is 250 ng m^{-3}. Note the logarithmic scale on the *y*-axis.

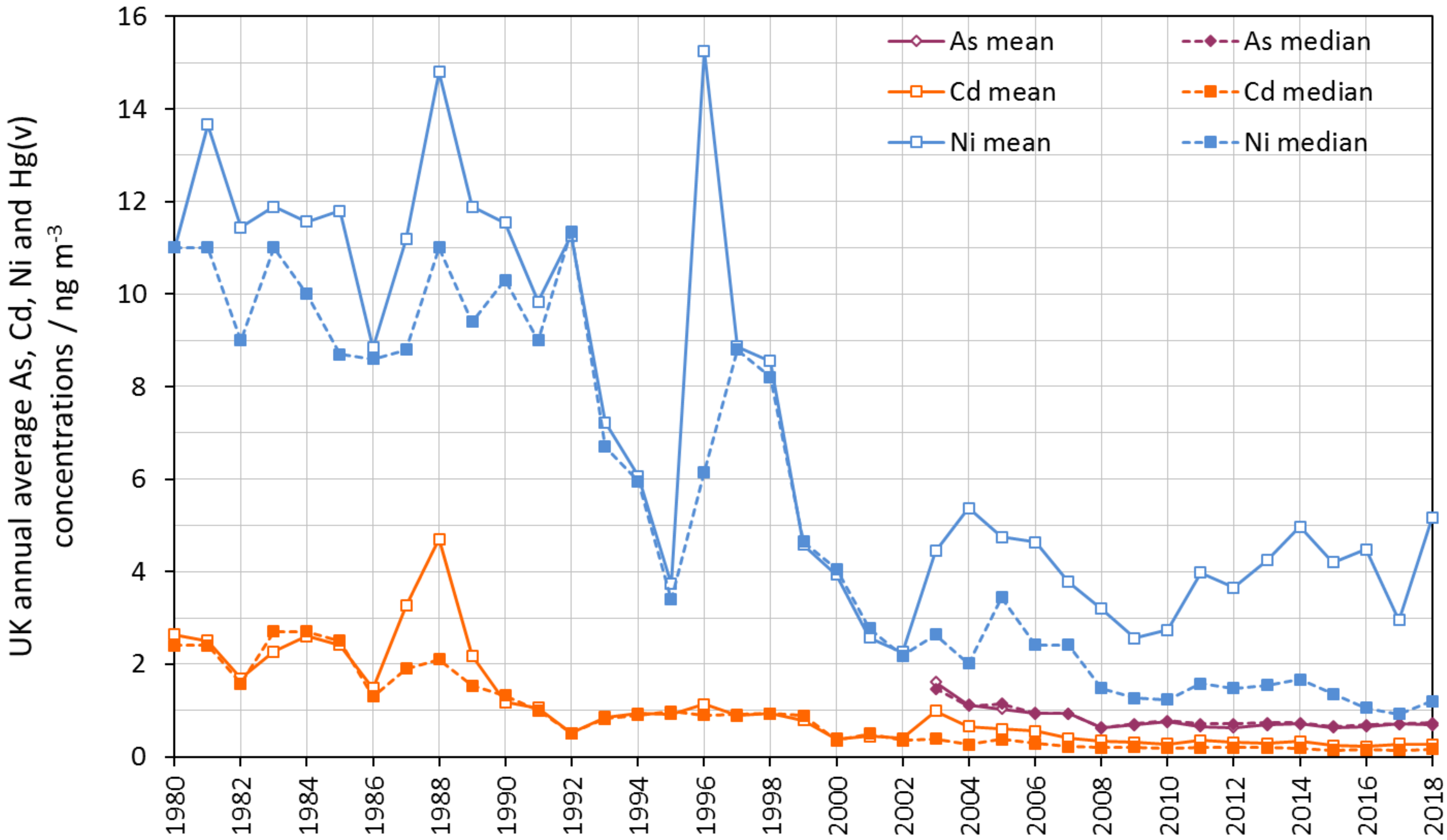

Figure 12. The mean and median of site annual average concentrations of Ni, As and Cd measured on the UK Heavy Metals Monitoring Network over the last 38 years. The EC target values for Ni, As and Cd are 20 ng m^{-3}, 6 ng m^{-3} and 5 ng m^{-3} respectively.

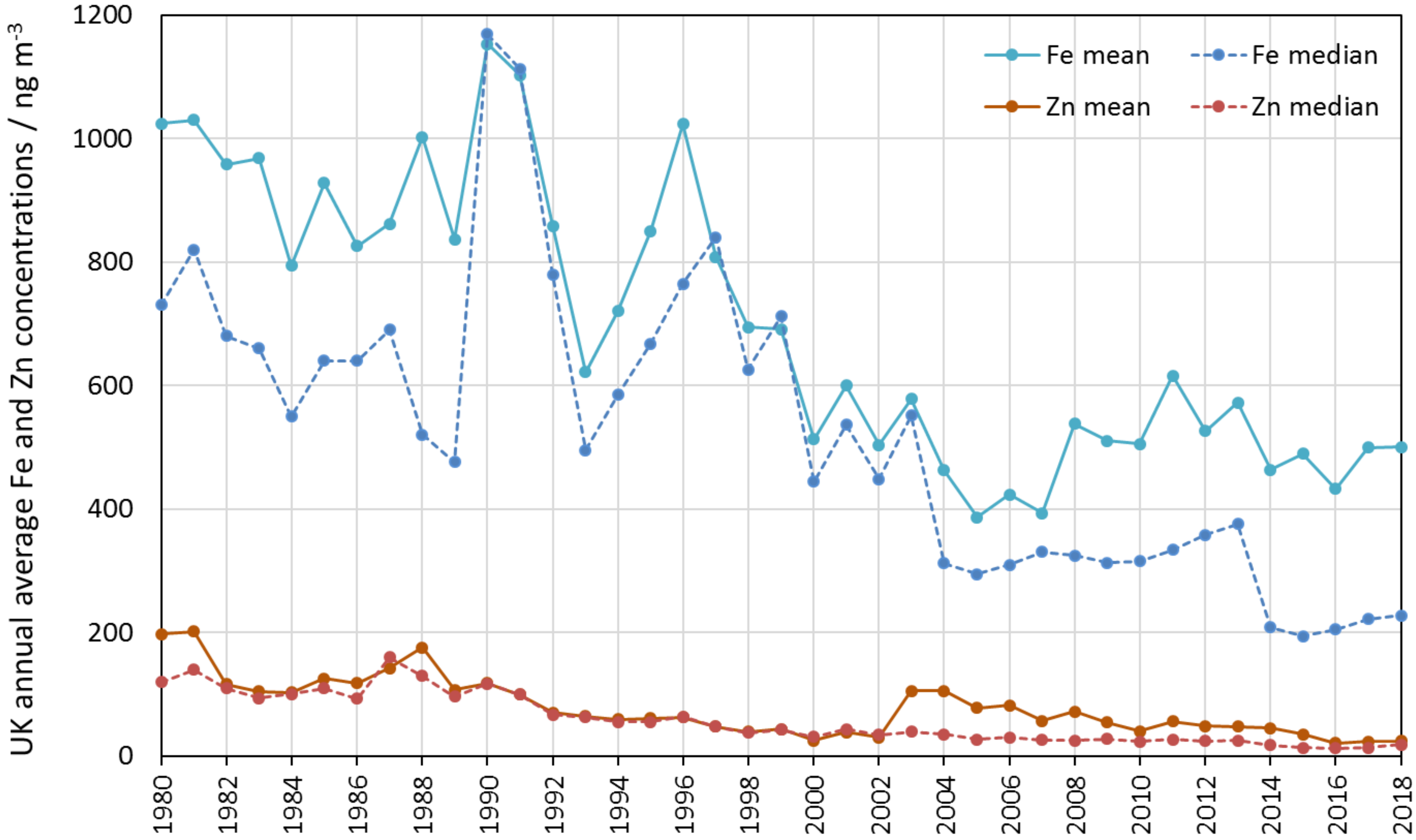

Figure 13. The mean and median of site annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 38 years.

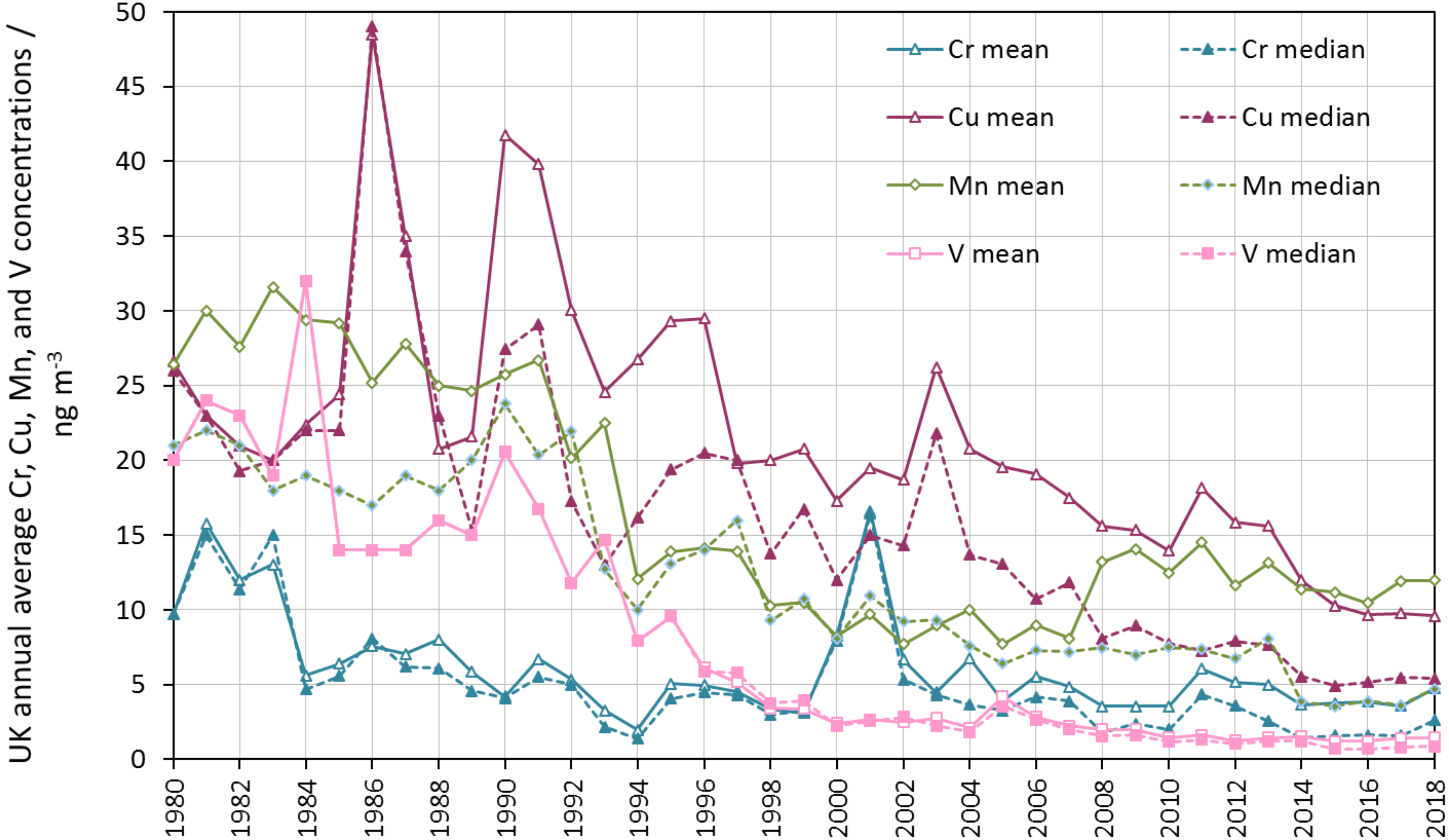

Figure 14. The mean and median of site annual average concentrations of Cr, Cu, Mn and V measured on the UK Heavy Metals Monitoring Network over the last 38 years.

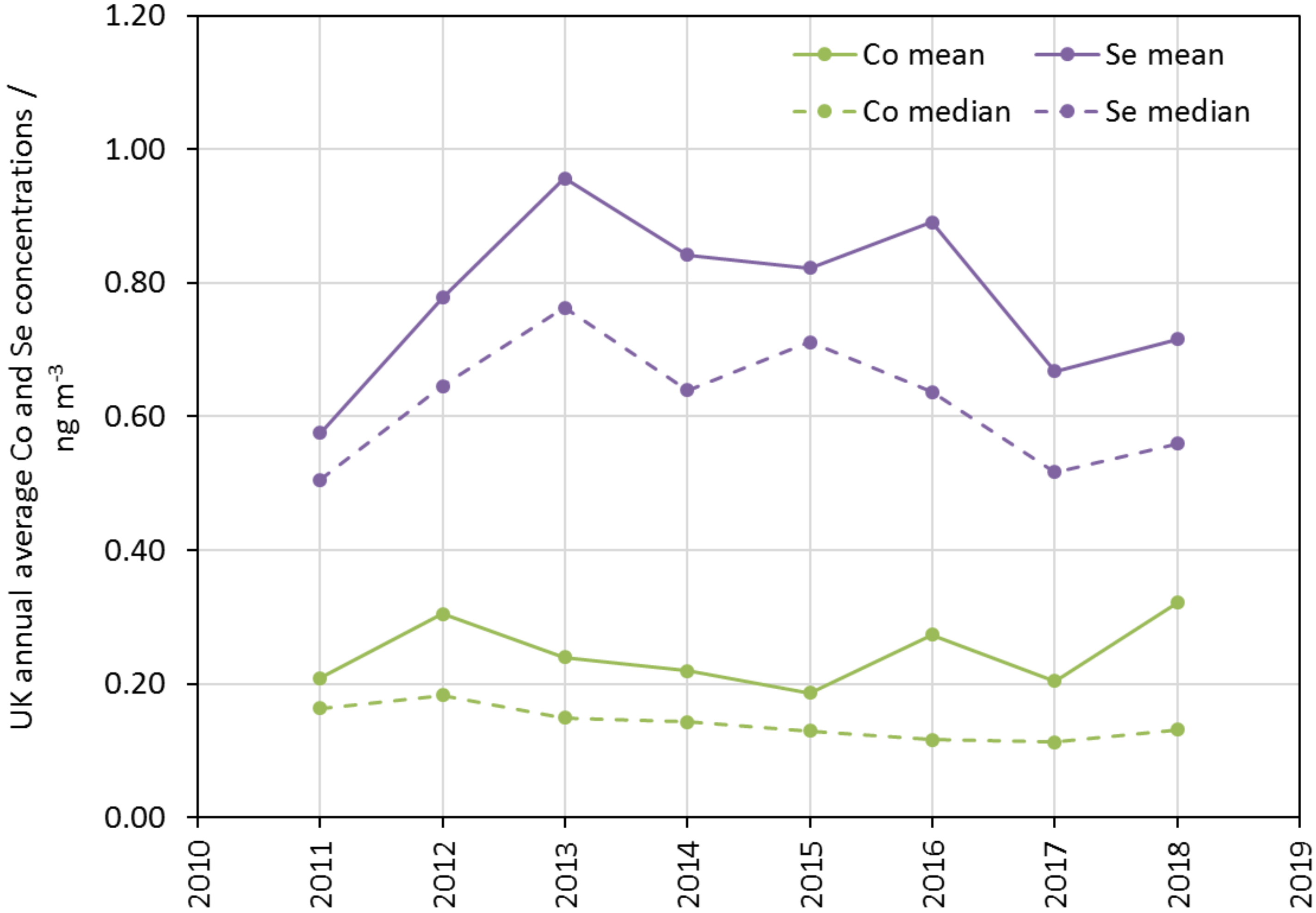

Figure 15. The mean and median of site annual average concentrations of Co and Se measured on the UK Heavy Metals Monitoring Network since monitoring commenced for these metals in 2011.

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 15 years is shown in Figure 16.

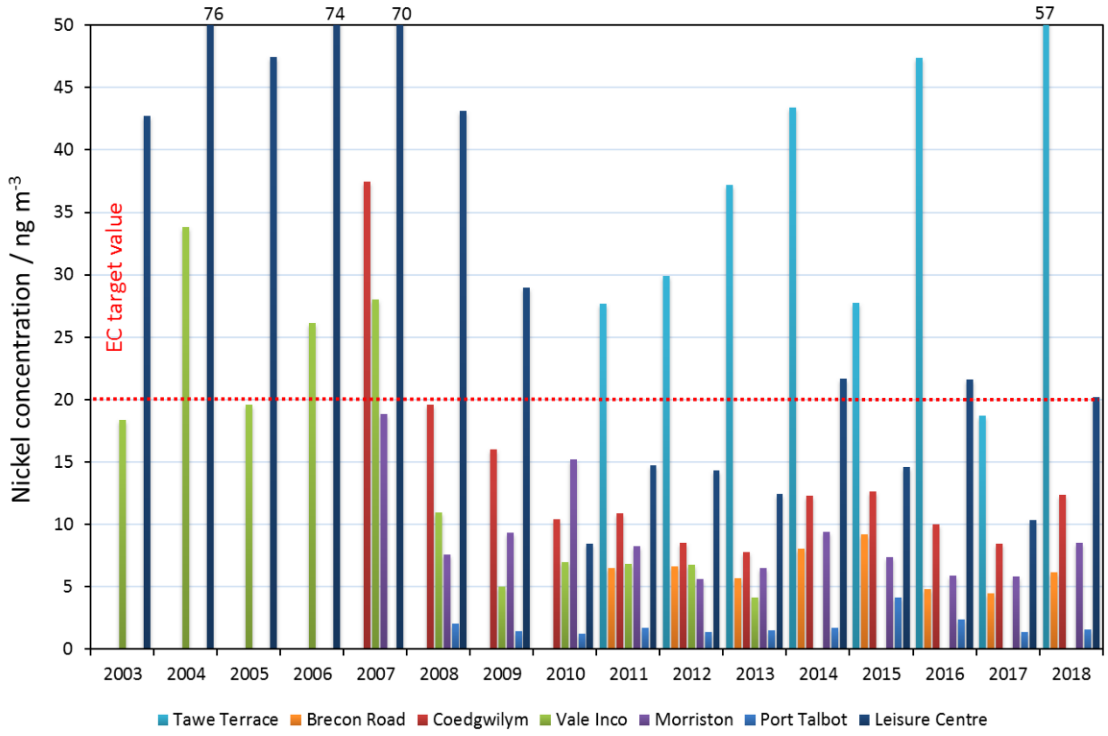

Figure 16. The annual average nickel concentrations measured at monitoring sites in the Swansea area (indicated by the key) 2003 - 2018. Nickel concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level. The red dotted line indicates 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-east [12].

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 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 sites 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. In 2016 concentrations rose again. It is considered likely that problems with abatement at the industrial facility during the second half of 2016 contributed significantly to the high annual average. In 2017 the average nickel concentration fell below the target value for the first time since the site opened, but this was followed in 2018 by a new high annual average for the site, again attributed to abatement issues at the industrial facility.

7.3 TRENDS IN DEPOSITION METALS

Trends in deposition metal concentrations measured since 2010 [14] (the year from which data is available on UK-AIR) for the metals relevant to the EC Air Quality Directives are summarised in Figures 17 to 20. The tendency of mercury to bio-accumulate makes it of particular importance in deposition samples, so this trend is plotted in Figure 21.

The annual UK mean concentrations are displayed for the current sites sampling metals in deposition. Please note, deposition measurements were only undertaken at Chilbolton from 2015 onwards.

Although there is significant variability in measured concentrations, there is some evidence of downward trends for Pb, Ni and As. Concentrations for Cd and Hg are relatively low and appear stable over the time period.

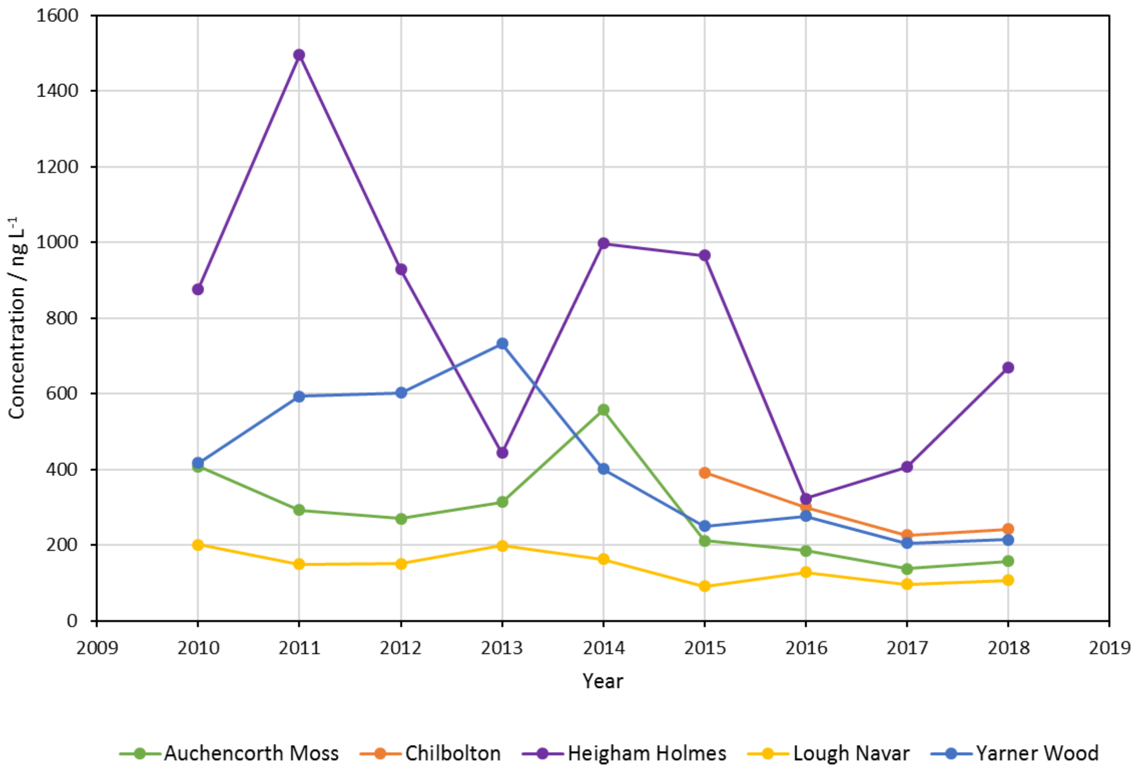

Figure 17. The mean annual concentrations of Pb measured in deposition since 2010 at individual sites.

14 https://uk-air.defra.gov.uk/

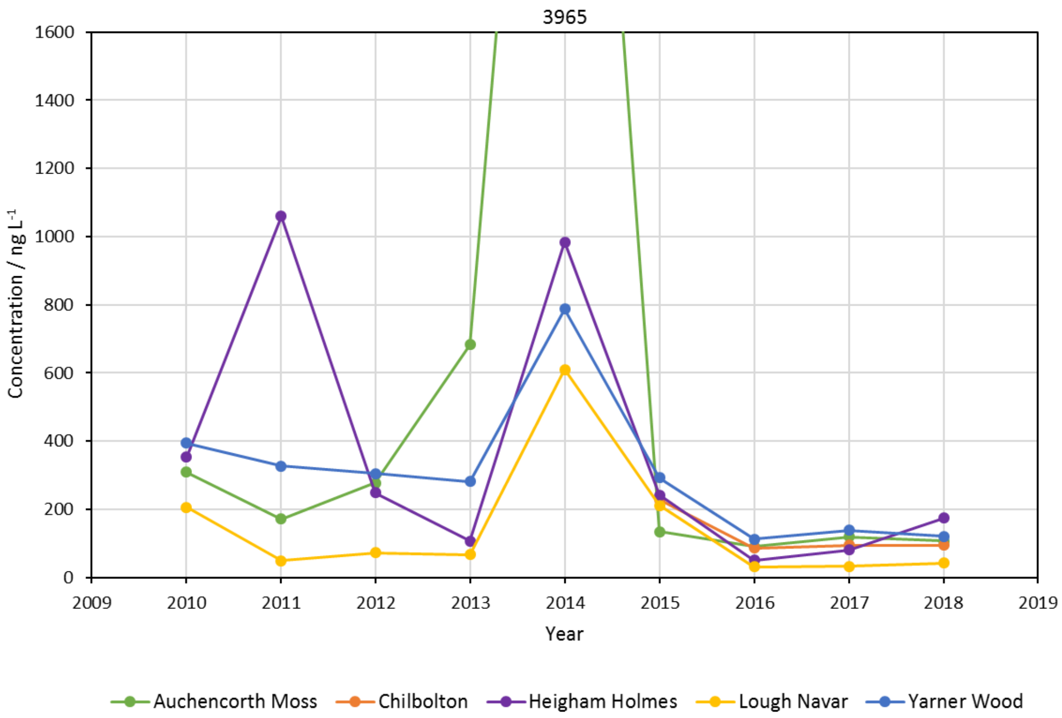

Figure 18. The mean annual concentrations of Ni measured in deposition since 2010 at individual sites.

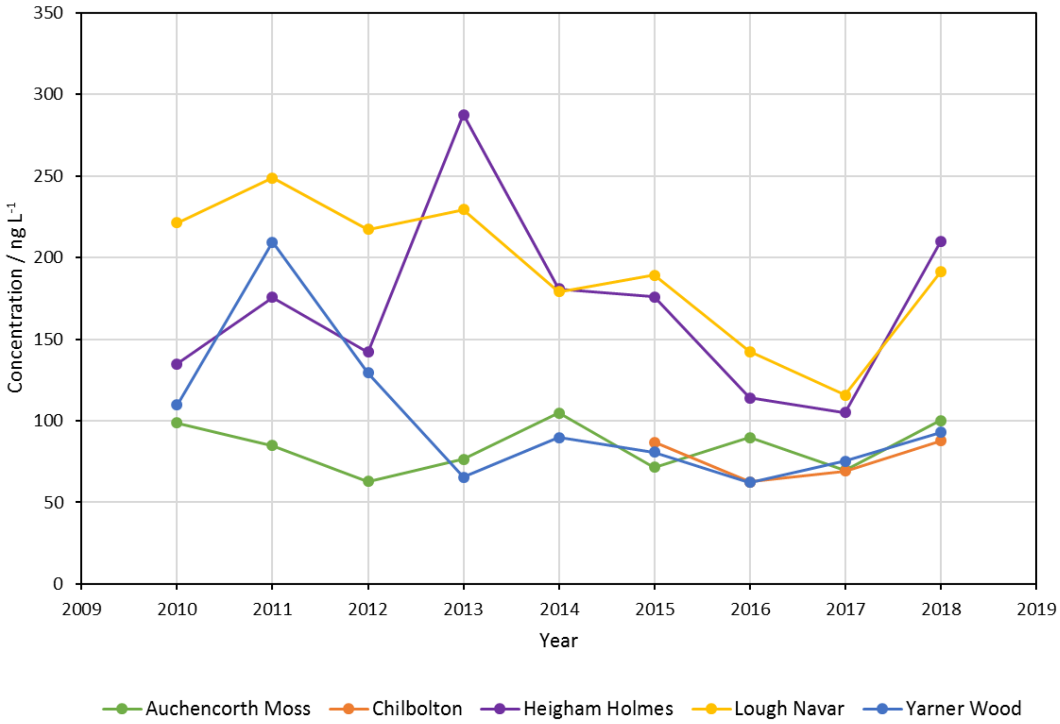

Figure 19. The mean annual concentrations of As measured in deposition since 2010 at individual sites.

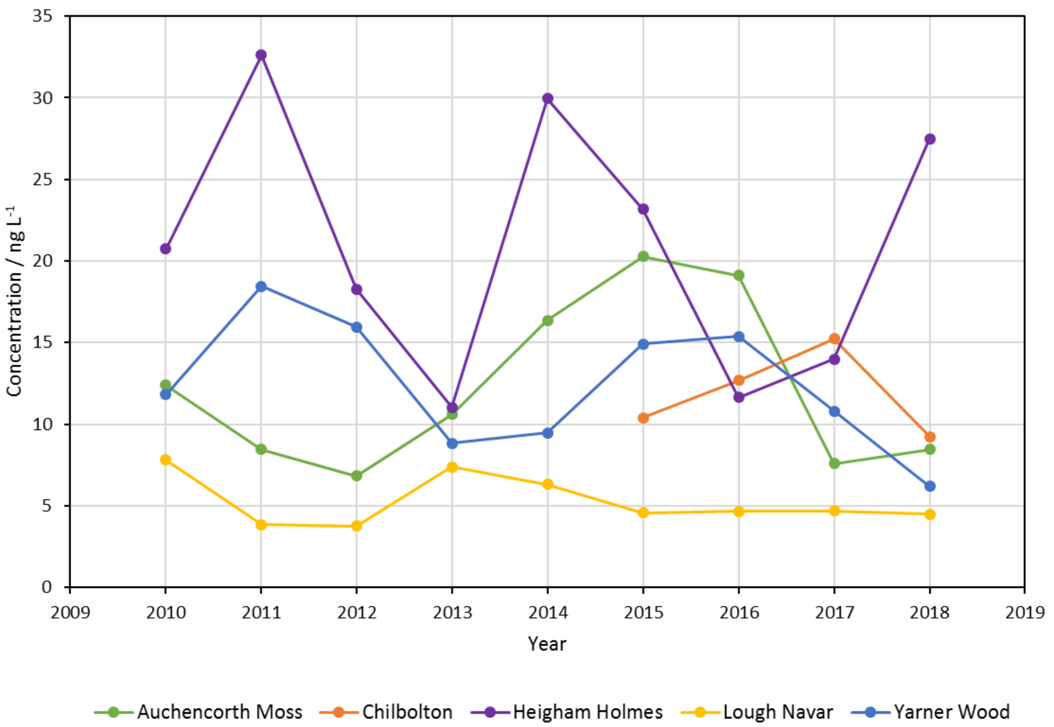

Figure 20. The mean annual concentrations of Cd measured in deposition since 2010 at individual sites.

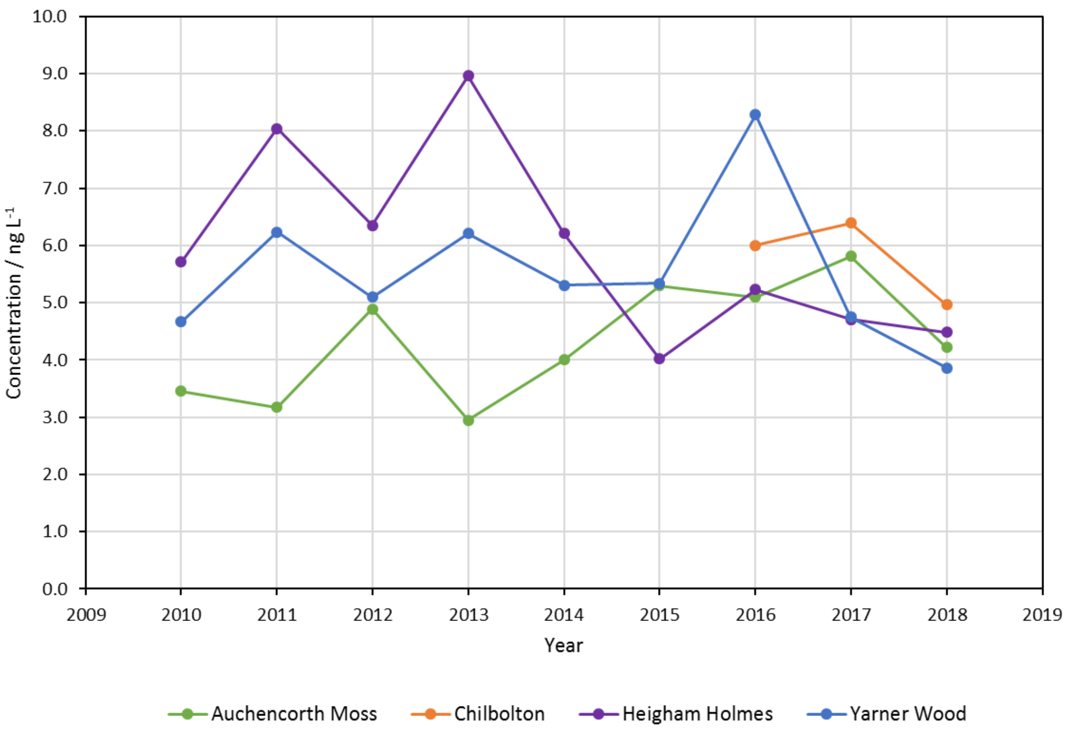

Figure 21. The mean annual concentrations of Hg measured in deposition since 2010 at individual sites. Please note: Hg is not measured at Lough Navar.

8 SCIENTIFIC RESEARCH, PUBLICATIONS AND RELATED ACTIVITIES

8.1 PUBLICATIONS

- Field and laboratory evaluation of a high time resolution x-ray fluorescence instrument for determining the elemental composition of ambient aerosols.
  Tremper, Anja H. (King's College London); Font, Anna (KCL); Priestman, Max (KCL); Hamad, Samera H.(University of Maryland, USA) ; Chung, Tsai-Chia (Royal Holloway University of London); Pribadi, Ari (KCL) ; Brown, Richard J. C. (NPL); Goddard, Sharon L. (NPL); Grassineau, Nathalie (RHUL); Petterson, Krag (Cooper Environmental Services, Orlando USA); Kelly, Frank J. (KCL); Green, David C. (KCL)
  Atmospheric Measurement Techniques, 2018, **11,** 6, pp 3541-3557.

This paper considered XRF as an alternative technique for determining elemental composition, including metals, in air quality samples.

8.2 LEGISLATION AND STANDARDISATION

There were no changes to legislation or standardisation relevant to the UK Heavy Metals Monitoring Network in 2018.

ANNEX 1: LOCATION AND DETAILS OF SITES COMPRISING THE UK HEAVY METALS NETWORK IN 2018

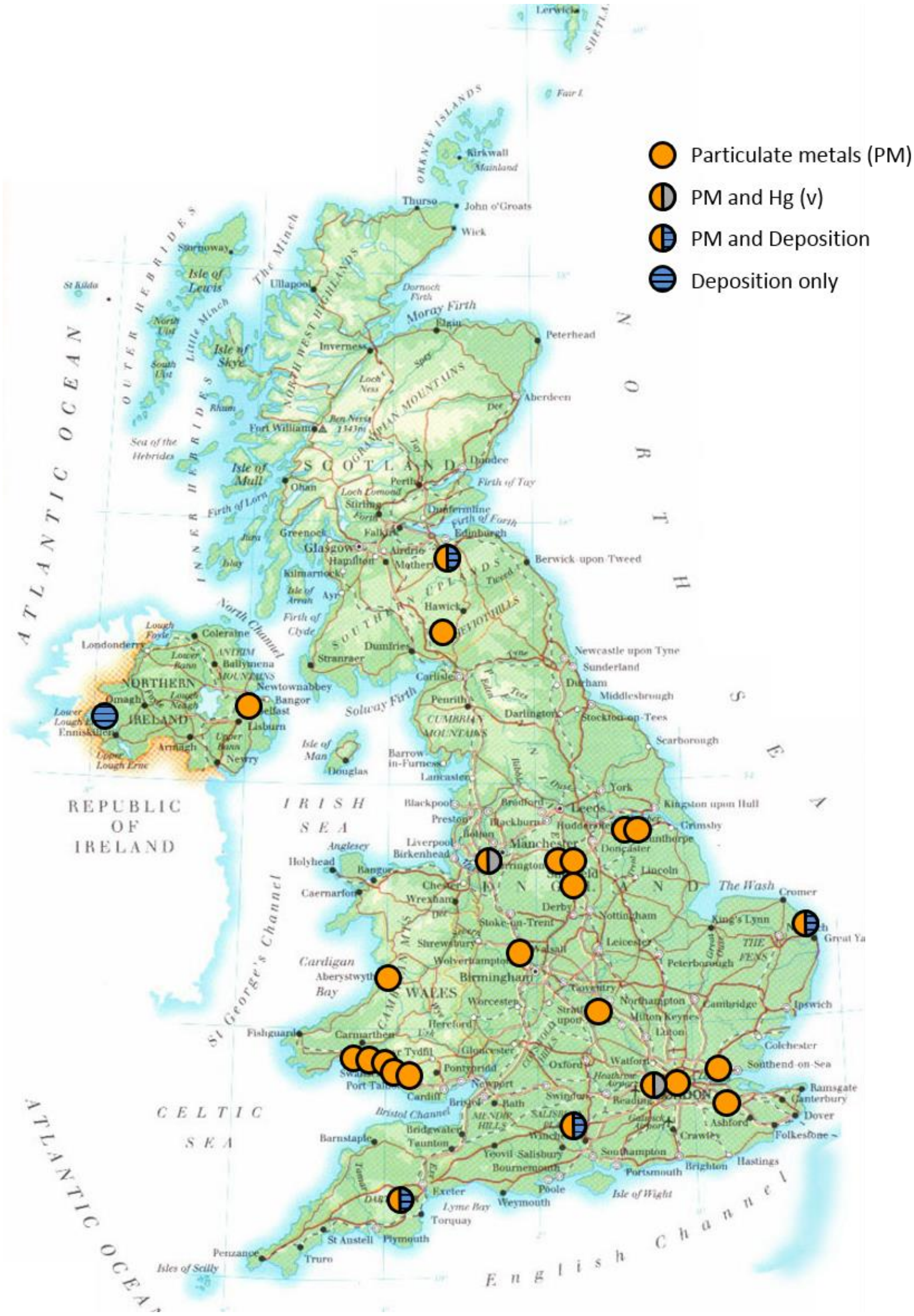

Figure A1. Location of monitoring sites comprising the UK Heavy Metals Monitoring Network during 2018 (indicated by the coloured circles, see key) – details of which are given in Table A1 below. Monitoring for Hg(v) ceased in August 2018. Monitoring at Walsall Bilston Lane also ceased in August 2018.

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) **Hg(v) monitoring ceased 10th August 2018**	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) **Hg(v) monitoring ceased 14th August 2018**	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	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) **All monitoring ceased 23rd August 2018**	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)	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: Yarner Wood	Natural England, Yarner 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, Wales. Grid reference 52.352436, -3.805317	Rural Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
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	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, Glennasheevar 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. Please note: sampling ceased on 23rd August at site 69: Walsall Bilston Lane.

Next page:
Image 5. Partisol sampler at Runcorn Weston Point.