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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 2023 on the UK Heavy Metals Monitoring Network

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EXECUTIVE SUMMARY

The National Physical Laboratory (NPL) is contracted to manage the UK Heavy Metals (HM) air quality Network. The HM Network measures and reports concentrations of a selection of heavy metals in PM_{10} (particulate matter with an aerodynamic diameter < 10 µm) in ambient air and deposition (rain) across the UK.

This report was prepared by NPL as part of the HM Network contract with the Environment Agency, on behalf of the Department for Environment, Food and Rural Affairs and the Devolved Administrations: the Welsh Government; the Northern Ireland Executive, Department of Agriculture, Environment and Rural Affairs in Northern Ireland; and the Scottish Government.

This is the Annual Report for 2023 and contains, in particular:

- Annual mass concentrations of all metals measured at all HM Network sites and performance against relevant data quality objectives (DQOs) and the requirements of the UK Air Quality Standards Regulations (AQSR) 2010.

- Highlighting of AQSR 2010 exceedances (for lead, nickel, arsenic, and cadmium), interpretation of data and discussion of trends across the HM Network.

- A description of HM Network operation, analytical and quality assurance / quality control procedures, and notable events and changes to the HM Network during 2023.

In summary, during 2023:

- **Lead**: There were no annual average mass concentrations above the AQSR Lower Assessment Threshold (LAT) at any HM Network site. Recorded concentrations were well below the limit value set by the AQSR.

- **Nickel**: No sites had an annual average concentration recorded as above the AQSR target value. For two sites, Sheffield Tinsley and Pontardawe Tawe Terrace, the annual average concentrations were recorded as above the LAT, with Sheffield Tinsley also exceeding the Upper Assessment Threshold (UAT).

- **Arsenic and cadmium:** There were no annual average concentrations above the AQSR LAT. Recorded concentrations were well below the target values set by the AQSR.

- All DQOs specified in the AQSR were met, including time coverage, data capture, and measurement uncertainty requirements.

- In addition to the AQSR metals (lead, nickel, arsenic, and cadmium), concentrations in ambient air were also recorded 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.

- Average data capture for metals in PM during 2023 was **97 %**. For metals in deposition it was **100** %.

1 INTRODUCTION

This report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals (HM) Network contract with the Environment Agency (EA), on behalf of the Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations: the Welsh Government (WG); the Northern Ireland Executive, Department of Agriculture, Environment and Rural Affairs in Northern Ireland (DAERA); and the Scottish Government (SG).

This is the annual summary report of the HM Network for 2023, and contains:

- Annual mass concentrations of all metals measured at all HM Network sites, and performance against relevant data quality objectives (DQOs) and the requirements of the UK Air Quality Standards Regulations (AQSR) 2010[1,2,3,4], and all associated amendments, including the EU-exit amendments, which follow the requirements of the EU Air Quality Directives[5,6,7].

- Highlighting of UK AQSR 2010 exceedances, interpretation of data, and discussion of trends across the HM Network.

- Summary of HM Network operation, analytical and quality assurance / quality control (QA/QC) procedures, and a description of notable events and changes to the HM Network during 2023.

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
- 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 mass concentrations of metals in ambient air is of significant 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 lead (Pb), nickel (Ni), arsenic (As), and cadmium (Cd), allowable in the PM_{10} fraction of ambient air (particulate matter with a diameter of 10 µm or less) are limited by UK AQSR 2010[1,2,3,4], and associated amendments.

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 (NAEI)[8] has more details of anthropogenic sources and emissions of metallic pollutants in the UK. These emissions have generally declined over many years, although in recent years trends have levelled off (with the exception of increasing levels of manganese, thought to be attributable to increased biomass burning[9], and copper, which has been attributed to road vehicle engine lubricants and brake pad wear[10]).

The correlation between estimated emissions and measured ambient levels is quite strong, and a comparison between measured ambient concentrations across the HM Network and emissions has been published[11]. This has shown that an additional benefit of the HM Network is to contribute supplementary evidence to validate emissions inventory data for metals. The UK emissions since 1970 of metals relevant to those measured on the HM Network are displayed in Figure 1.

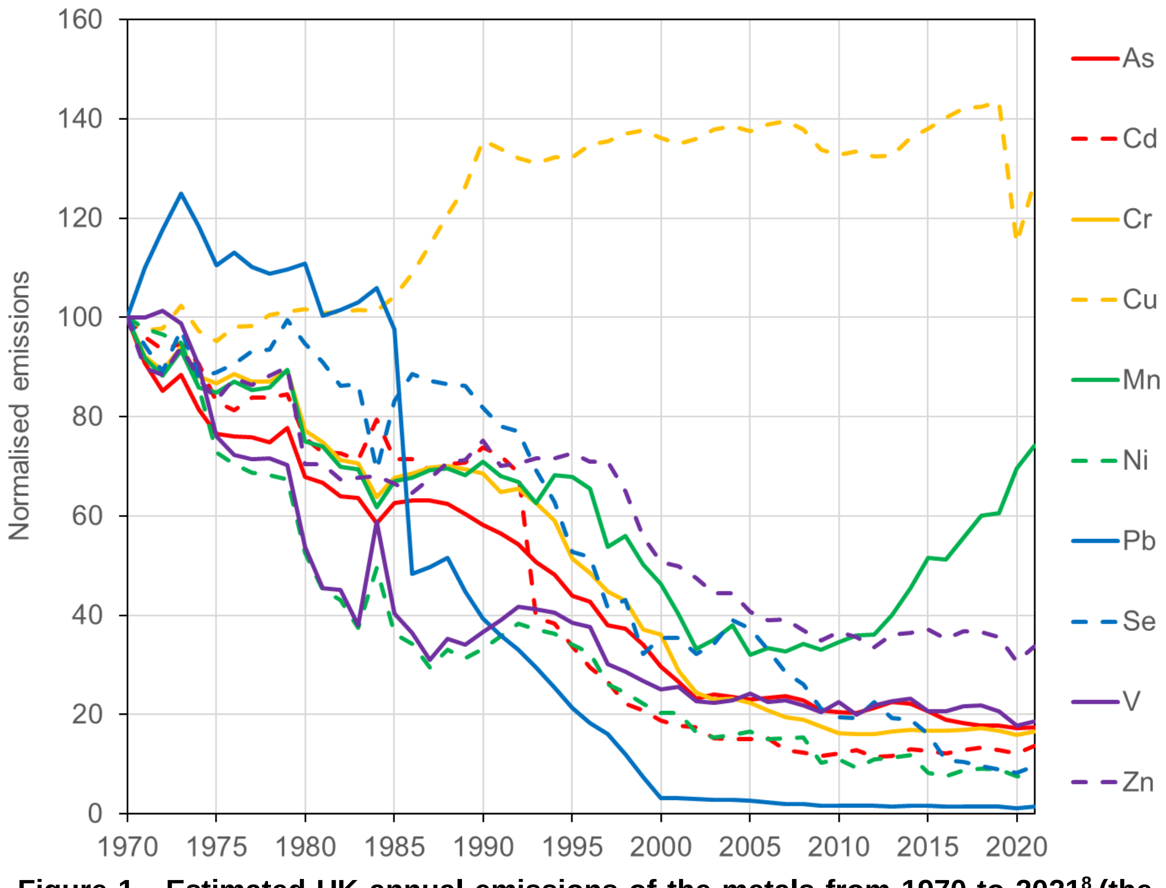

Figure 1 - Estimated UK annual emissions of the metals from 1970 to 2021[8] (the latest year for which emissions data were available at time of publication) normalised to their values in 1970. The absolute levels of emissions in 1970, in tonnes, were: As, 81; Cd, 36; Cr, 257; Cu, 431; Pb, 7493; Mn, 146; Ni, 993; Se, 93; V, 2750; and Zn, 1511. Emissions data are not available for Co or Fe.

In order to demonstrate compliance with AQSR 2010, which 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 HM Network is a regulatory air quality monitoring network that discharges the majority of the UK's obligation under AQSR 2010 relating to the monitoring of the mass concentrations of Pb, Ni, As, and Cd, in the PM_{10} phase of ambient air.

Cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), selenium (Se), vanadium (V), and zinc (Zn) concentrations are measured using the same samples to provide additional information on sources, trends, and the UK's pollution climate.

The HM Network has a number of objectives:

- To achieve compliance with monitoring requirements set out in the AQSR 2010[1,2,3,4] (and all associated amendments), and international conventions to which the UK is a signatory, including the European Monitoring and Evaluation Programme (EMEP) and the convention to protect the marine environment in the North-East Atlantic, OSPAR (named after the original Oslo and Paris conventions).

- To provide data to the UK Government on the UK's performance against the limit values, target values, and DQOs described in the relevant legislation.

- To assess impacts around 'hot spots' of metallic pollution in 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 HM Network can be found in the 2008 NPL publication that marked a quarter of a century of the nationwide monitoring of metals in ambient air[12]. A follow-up review of concentration trends was published by NPL in 2019[13]. In 2023, NPL published a paper on the novel application of the Theil-Sen robust regression method for determining the temporal trends in the concentration of heavy metals in UK ambient air over the period 2005–2020, with comparison to other regression methods[14].

2 NETWORK OPERATION

During 2023, the HM Network comprised 24 monitoring sites around the UK (14 in England, 6 in Wales, 2 in Scotland, and 2 in Northern Ireland) sampling PM_{10} and/or deposition from ambient air.

PM_{10} in ambient air is sampled onto filters at 23 of these sites; these samples are returned to NPL Teddington where they are analysed to determine the mass concentration of a suite of 12 metals in PM_{10} in ambient air. Deposition samples are taken at 5 sites; these samples are returned to UK Centre for Ecology & Hydrology (UKCEH) Lancaster where they are analysed to determine the concentration of a suite of 25 metals, with additional samples taken at 4 of the sites, to monitor mercury in deposition.

Details of the sites and pollutants measured are given in Annex 1: Details of Sites Comprising the HM Network in 2023. Relevant activity related to HM Network operation during 2023 is detailed below.

2.1 OVERVIEW

NPLs management of the HM Network in 2023 has included the following key activities:

- NPL staff audited all sites on the HM Network. This included flow calibration check and leak check of the ambient air samplers, health and safety (H&S) checks, and re-assessment of local site operators' (LSOs) performance. A second visit to each site was made during the year to perform a flow calibration check and leak check on the samplers.

- The EA Ambient Air Monitoring (AAM) service team were the appointed equipment support unit (ESU) to all HM Network sites except one, and made service visits twice during the year, which included the flow calibration of instruments. The exception was Auchencorth Moss, where Enviro Technology Services Ltd (ET) were the appointed ESU.

- Ensuring data capture has remained at a very high level for the airborne PM_{10} sampling across the HM Network (see Table 2).

2.2 SITE AUDITS

During 2023, the NPL network audit team visited all the HM Network sites twice to perform 6-monthly site audits. These audits took place during the 1st quarter (Q1, January to March) and the 3rd quarter (Q3, July to September). At these visits, the following was carried out:

- The site infrastructure, performance, and integrity were assessed, including 'In Service Inspection and Testing' (ISIT, previously known as 'Portable Appliance Testing', PAT).
- The LSOs were also audited at one of the two audit visits and received extra training where required.
- The condition of all deposition sampling equipment was assessed.
- As required by BS EN 12341[15], during each HM 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, to ensure regular maintenance of components of the sampler was being carried out as appropriate.
    - Made the following checks to ensure they were within the required limits:
        - temperature and pressure sensor readings
        - sampler clock
        - sampler flow - this data is used to correct the volumes recorded by samplers prior to the calculation of ambient concentrations.
        - leak test.

In summary:

- All the sites have been audited fully.
- Site infrastructure was assessed (including ISIT and checks of fire extinguishers), and no major or minor problems were found.
- Most samplers were found to be performing well. All except two of the flow rate checks were satisfactory (see below), and all leak checks were satisfactory.
    - Auchencorth Moss – ESU callout issued and attended with 5 days, external pressure sensor found to be faulty and replaced.
    - Swansea Coedgwilym – ESU callout issued and attended with 5 days; flow sensor recalibrated.
- The LSOs were performing their duties to a high standard.

ESU attended all sites twice in 2023 to perform services, in the 2nd quarter (Q2, April to June) and 4th quarter (Q4, October to December). The services included flow calibrations and leak checks, as detailed below.

The combination of the flow calibration data from the two NPL audits and two ESU services during the year provides the three-monthly flow and leak checks required by BS EN 14902[16].

2.3 EQUIPMENT SERVICING AND BREAKDOWNS

Twice during 2023, the EA AAM ESU team fully serviced, carried out preventative maintenance, and calibrated the flow of all the PM_{10} samplers at HM Network sites, except for Auchencorth Moss, where ET ESU carried out the two services, and Chadwell St Mary, which closed before the second service was due. These services took place during Q2 and Q4. In some cases, services were combined with emergency callouts. A total of 45 service visits were made.

In addition to the 45 service visits, NPL issued 19 additional callouts to the EA AAM ESU and ET ESU to deal with sampler faults, which in some cases included an additional service. It should be noted that this does not include the number of additional visits made by LSOs to reboot the modems, which in most cases resolved communication issues and meant ESU visits were not needed.

The key faults recorded during the year, with the remedial action taken, were:

- Failed leak checks: 2 in total
  - Eskdalemuir and Fenny Compton – perished O–ring replaced.

- Router communication issues: 3 in total
  - Eskdalemuir and Detling – router fully reset and reconfigured.
  - London Marylebone Road – router replaced under warranty.

- Software glitches causing memory or programming issues: 3 in total
  - Auchencorth Moss – full reset to resolve extra weekly filter exchange issue, and software update to resolve weekly programme pause issue.
  - Pontardawe Brecon Road – software update to fix memory issue.

- Sensor issues: 9 in total
  - Pontardawe Tawe Terrace, Scunthorpe Low Santon, Sheffield Tinsley, and Swansea Coedgwilym – flow sensor required recalibration.
  - Auchencorth Moss, Chilbolton Observatory, Heigham Holmes, and Sheffield Tinsley – faulty pressure/temperature (p/T) sensor replaced.
  - Eskdalemuir – following a series of p/T sensor issues due to water ingress, junction board replaced under warranty.

Equipment servicing is not applicable to the precipitation sample collectors for metals in deposition.

2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION

Changes to the operation of the HM Network and infrastructure issues during 2023 are detailed below:

- Chadwell St Mary – following change of use of the site, the site became unsuitable for monitoring and was subsequently closed in October 2023.
- Cwmystwyth – electrical upgrade works in January 2023.
- Heigham Holmes – swing ferry repaired in January 2023 following access issues; electrical supply building remained out of bounds for the whole year due to structural issues, but this caused no issues to the sampler operation.
- Pontardawe Brecon Road – sampler housing upgrade works in April 2023.
- Port Talbot Margam – sampler housing upgrade works in September 2023.

3 SAMPLING AND ANALYTICAL METHODOLOGY

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

3.1 SAMPLING METHODOLOGY: PARTICULATE-PHASE METALS

PM_{10} samples were taken at 23 sites in the HM Network using Digitel DPA14 instruments (Image 1), all fitted with PM_{10} heads and operating at a calibrated flow rate, nominally 1 m^3 h^{-1}, in accordance with BS EN 12341[15]. Samples were taken for a period of one week onto 47 mm diameter cellulose membrane filters.

Image 1 - Digitel DPA14 sampler at Swansea Coedgwilym Cemetery.

3.2 SAMPLING METHODOLOGY: METALS IN DEPOSITION

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

Sampling was performed by UKCEH using bulk collectors (bottle and funnel types) in accordance with BS EN 15841[17] and BS EN 15853[18].

3.3 ANALYTICAL METHODOLOGY: PARTICULATE-PHASE METALS

For most sites, data are produced as four-weekly averages of concentrations for metals in the particulate-phase, with the following exceptions that produce weekly data: Pontardawe Brecon Road, Pontardawe Tawe Terrace, Sheffield Tinsley, Swansea Coedgwilym Cemetery, and Swansea Morriston Groundhog.

Analysis for particulate-phase metals took place at NPL Teddington following NPLs analytical procedure. This procedure is accredited by UKAS to ISO 17025[19], and fully compliant with the requirements of EN 14902[16].

Upon arrival at NPL Teddington, the filters were accurately cut in half (for sites where weekly results are produced) or into quarters (where four-weekly results are produced). For sites producing weekly data, one half filter was digested separately. For sites producing four-weekly data, one quarter of each of the four filters comprising the four-week period were digested together. In both cases, the filter portion(s) were digested at temperatures up to 220 °C using an Anton Paar Multiwave 5000 microwave (Image 2, left). The digestion mixture used was 8 mL of 70 % nitric acid and 2 mL of 30 % hydrogen peroxide.

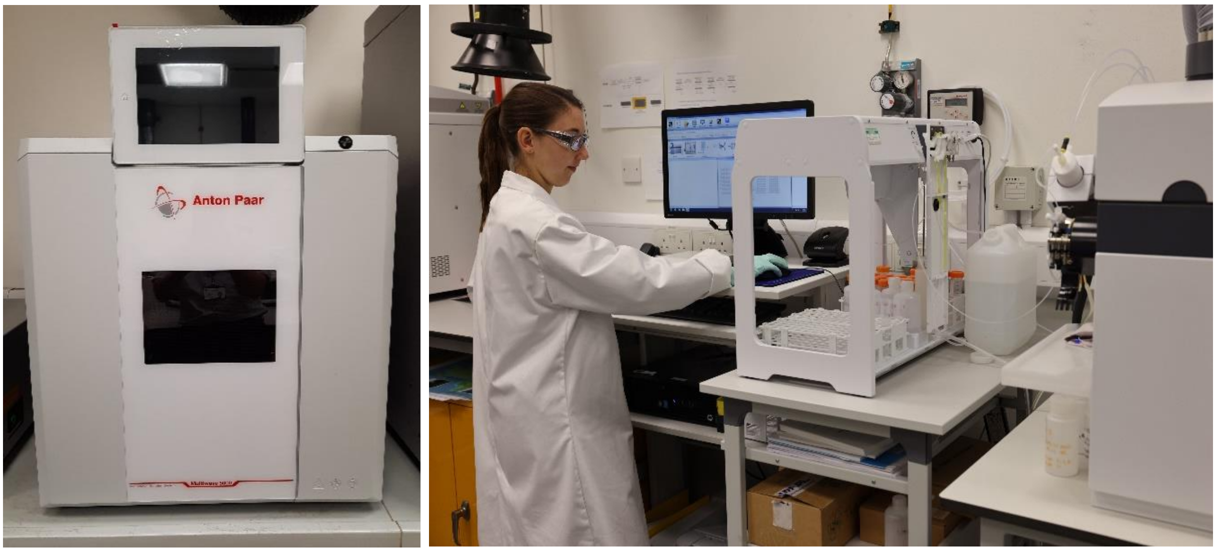

Image 2 – (left) Anton Paar Multiwave 5000 microwave used for acid digestion of the sampled filters, (right) Agilent 8800 ICP-QQQ-MS in the UK ambient metals analysis facility at NPL.

Analysis of the digested solutions was performed using Agilent 8800 (Image 2, right) and 8900 Inductively Coupled Plasma (Triple Quadrupole) – Mass Spectrometer analysers (ICP-QQQ-MS). The instrumental response was calibrated with at least four gravimetrically prepared, traceable calibration solutions. A 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. Each sample was analysed in triplicate, each analysis consisting of five replicates.

The amount of each metal in solution (and its uncertainty) was then determined by a method of generalised least squares using XLGenline (an NPL-developed program) to construct a calibration curve.

3.4 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION

For most sites, data are produced as four-weekly averages of concentrations for metals in deposition, with the following exceptions that produce weekly data: Auchencorth Moss, and Chilbolton Observatory. All samples collected for mercury analysis are collected on a four-weekly basis, with replicate samples collected at each site. During 2023, analysis of HM in deposition took place at UKCEH's Centralised Analytical Chemistry Group at Lancaster.

For the metals in deposition samples (excluding mercury), 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 5 L 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 were stored at 4 °C prior to final measurement by ICP-MS (Perkin Elmer Nexion 300D). The ICP-MS measurement used the same procedures and QA/QC checks outlined above for the measurements of particulate-phase digests at NPL. However, measurements for additional metals were made, resulting in values for a suite of 25 metals (Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, U, W, V, and Zn) being produced. The procedure was in full accordance with EN 15841[17].

For the mercury in deposition samples, the Hg collector bottles were weighed to estimate rainfall amounts and then stored at 4 °C prior to analysis. Mercury in precipitation was determined by Atomic Fluorescence Spectrometry (AFS) which used a PS Analytical Galahad analyser with pre-concentration of mercury on a gold trap to increase instrument sensitivity. This method employed a reductive desorption process. During this step, tin chloride was added to the sample being analysed in a gas–liquid separator. This reduced all the collected mercury to elemental mercury and liberated it into the gas phase using a stream of argon bubbling through the gas-liquid separator. This mercury vapour was then collected on the mercury adsorption trap, which was then heated, desorbing the mercury onto a permanent trap. Subsequent heating of this trap then desorbed the mercury onto the detector. The system was calibrated using gravimetrically prepared mercury in liquid standards. These standards are traceable to NIST mono-elemental reference materials. The procedure was in full accordance with EN 15853[18] and EN ISO 17852[20].

3.5 MEASUREMENT UNITS

Results produced by the HM Network for particulate-phase metals are calculated in accordance with ISO 11222[21] and expressed, as required by AQSR, as mass concentrations, in nanograms (of the relevant metal) per cubic metre of 'as sampled' ambient air for the particulate-phase metals: ng m^{-3}.

For metals in deposition are expressed as mass concentrations, in nanograms (of the relevant metal) per litre of 'as sampled' rain: ng L^{-1}; and deposition flux, in grams per hectare per day: g ha^{-1} d^{-1}. In this report, deposition flux is expressed in micrograms per metre squared per day: µg m^{-2} d^{-1} (which is equivalent to 0.01 g ha^{-1} d^{-1}).

3.6 MEASUREMENT UNCERTAINTY

For each result produced by the HM Network, an estimate of the uncertainty in this value is also made according to the GUM (Guide to the Expression of Uncertainty in Measurement) approach, published as ISO/IEC Guide 98-3:2008[22]. These uncertainties are used to calculate the uncertainties in the annual average values for each element and ensure that the final results meet the DQOs for uncertainty specified in the relevant legislation.

4 METHOD PERFORMANCE CHARACTERISTICS AND QC

The technical procedure used to analyse particulate-phase samples from the HM Network is accredited by UKAS to ISO 17025[19]. Limits of detection achievable using this procedure are comfortably below the requirements of EN 14902[16].

4.1 QA/QC PROCEDURES

An overview of the QA/QC procedures employed during HM Network operation to ensure the quality of the data produced are listed below:

4.1.1 Particulate-phase sampling:

- Filters are given unique IDs, which are carried through the sampling and analysis chain.
- Continued training of, and regular communication with, the LSOs. This includes assessment of performance during site audits.
- Regular despatch and analysis of field-blank filters.
- Thorough checks of the returned filters to check for damage during handling and transport. Rejection of damaged filters.
- Logging of all samples on NPLs HM Network database. Rejection of any unidentifiable samples and full investigation of any discrepancies.

4.1.2 Deposition sampling

- The mass concentration of metals found within precipitation are at the µg/l level or lower. For deposition samples (as dispatched by UKCEH), essential and rigorous protocols are used for cleaning sampling equipment (bulk collectors, bottle and funnel type) between deployments to prevent contamination within the laboratory.
- Field protocols, based on those described by EMEP, have been developed to prevent contamination of precipitation samples during re-deployment of the bulk collectors. Equipment is dispatched and transported to site in acid washed bags; multiple pairs of gloves and clean bags are provided for use at each stage of installation and removal from site.

4.1.3 Particulate-phase metals analysis (ICP-MS, by NPL):

- 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[16].
- Annual participation in an appropriate Proficiency Testing (PT) scheme to independently check the accuracy of the analysis method as a whole.
- Optimisation of the ICP-MS prior to each analysis. Comparison of the optimised parameters with pre-defined criteria.
- Regular measurement of ‘lab’ filter blanks to ensure appropriate blank subtractions are made from measured values (in addition to the ‘field-blanks’).
- 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 calibration curves must be <1.
- Ratification of all data by an NPL ‘Quality Circle’ of recognised senior NPL scientific experts independent of the analytical team.
- Regular UKAS audit of method performance, assessing analytical quality control data, is carried out.

4.1.4 Metals in deposition analysis (ICP-MS and AFS, by UKCEH):

- All analysis for metals (including mercury) in deposition is completed within two weeks of the samples arriving at the laboratory.
- All sample manipulation and processing are performed within a dedicated clean air laminar flow cabinet (ISO 5) to prevent contamination by background trace metals.
- 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 they are not submitted for analysis,
    3) following analysis, samples displaying a phosphorus:gallium (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 filter analyses at NPL during 2023 are shown in Table 1. All values are a combination of the sampling and analytical uncertainties and have been derived using full, GUM compliant, uncertainty budgets. All values are expanded uncertainties using a coverage factor of k = 2, providing a level of confidence of approximately 95 %.

The uncertainties displayed in Table 1 are representative of the range of uncertainties covering the majority of individual measurements over typical sampling periods as required by the AQSR (which refers to the EU Air Quality Directives). Most of the measurements used to compile the data in Table 1 were concentrations well below the associated target values. It is calculated that in the region of the appropriate target value – where the uncertainty DQOs apply – these relative uncertainties will be significantly lower than the maximum allowed.

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

Table 1 - The expanded uncertainty range covering the majority of filter analyses at NPL during 2023.

Analyte	Uncertainty range [%]
Arsenic (As)	9 - 11
Cadmium (Cd)	9 - 15
Cobalt (Co)	9 - 15
Chromium (Cr)	21 - 46
Copper (Cu)	9 - 14
Iron (Fe)	9 - 14
Manganese (Mn)	9 - 15
Nickel (Ni)	9 - 18
Lead (Pb)	9 - 15
Selenium (Se)	10 - 39
Vanadium (V)	9 - 17
Zinc (Zn)	9 - 16

5 DATA QUALITY

Annual data capture is calculated as the percentage of valid measurement time over the total time during which we intended to perform measurements (i.e. whole year, excluding downtime for planned calibrations). All values are stated to the nearest whole percentage.

5.1 DATA CAPTURE (PARTICULATE-PHASE)

The average data capture for PM phase metals during 2023 was **97 %**. Table 2 shows the annual data capture percentage for each site for PM data across the HM Network during 2023.

In most cases the total time intended to perform measurements is equivalent to the whole year, excluding downtime of the scheduled services and audits, i.e. annual time coverage is 100 %. Therefore, time coverage and data capture are equivalent. In a few cases, the total time intended to perform measurements is less than one year due to planned downtime. In these cases, the annual data capture has been calculated excluding this time, but the annual data capture including this time has been included in brackets.

In 2023, this applies to three sites:

- Chadwell St Mary – following change of use of the site, the site became unsuitable for monitoring and was subsequently closed in October 2023, removing 82 days from the annual time coverage.
- Pontardawe Brecon Road – due to sampler housing upgrade works, 7 days were removed from the annual time coverage.
- Port Talbot Margam – due to sampler housing upgrade works, 2 days were removed from the annual time coverage.

The AQSR requires a minimum time coverage of 50 % and minimum data capture of 90 % for fixed measurements of As, Cd, and Ni, which equates to 45 % data capture over the whole year. All sites achieved more than 50 % annual time coverage, and 45 % annual data capture, so the DQOs were met for As, Cd, and Ni.

The AQSR has no minimum time coverage specified for fixed measurements of Pb, but the minimum data capture required is 90 %. The majority of sites achieved more than 90 % data capture. Three further sites were above 85 % data capture and so can be considered to meet the same threshold, once the additional 5 % tolerance allowed in EU guidance for routine servicing and maintenance is taken into account.

This means that all sites exceed the minimum data capture requirements specified in the AQSR (as detailed in the EU Air Quality Directives).

Table 2 - PM data capture across the HM Network during 2023. Values shown exclude planned downtime (values in brackets include planned downtime).

Site Name	PM data capture [%]
Auchencorth Moss	85
Belfast Centre	100
Chadwell St Mary	100 (78)
Chesterfield Loundsley Green	100
Chilbolton Observatory	100
Cwmystwyth	89
Detling	100
Eskdalemuir	94
Fenny Compton	87
Heigham Holmes	98
London Marylebone Road	99
London Westminster	100
Pontardawe Brecon Road	96 (94)
Pontardawe Tawe Terrace	99
Port Talbot Margam	100 (99)
Scunthorpe Low Santon	100
Scunthorpe Town	100
Sheffield Devonshire Green	92
Sheffield Tinsley	100
Swansea Coedgwilym	98
Swansea Morriston	100
Walsall Pleck Park	100
Yarner Wood	98
Average across all sites	97 (96)

5.2 DATA CAPTURE (DEPOSITION)

The average data capture across all deposition analytes during 2023, excluding data loss due to lack of rain, was 100 % (including data loss due to lack of rain, it was 89 %).

The annual data capture for deposition at the sites where these measurements are made is detailed in Table 3. The values shown exclude data loss due to lack of rain. The values in brackets show the total annual data capture, i.e. including data loss due to lack of rain.

Most of the samples for the 25 metals in deposition are taken as single, weekly samples, whereas mercury samples are taken in duplicate over longer time periods (4 weeks rather than 1 week) so typically have higher data capture.

In 2023, the majority of data loss, other than lack of rain, was caused by contamination of samples by bird fouling and analysis issues. All analytical results are checked, and any analyses with lower than usual confidence in the measurement are repeated. However, this is only possible with samples of sufficient volume. Low volume samples with measured concentrations that could not be verified were excluded from reporting.

Table 3 - Data capture across the deposition sites of the HM Network during 2023.

Site Location	**Non-Hg Metals in Deposition [%]**	**Hg in Deposition [%]**
Auchencorth Moss	98 (88)	100
Chilbolton Observatory	100 (79)	99 (89)
Heigham Holmes	100	93
Lough Navar	100	N/A
Yarner Wood	100 (79)	100 (92)
Average	**100 (89)**	**98 (94)**

5.3 DATA PROCESSING AND RATIFICATION

Analysis of the HM 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 weighting these values 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 time-weighting if a site has been monitoring for less than the full year.

An NPL ‘Quality Circle’ ratifies concentration data produced by the HM Network, including deposition data provided by UKCEH. NPL personnel performing the ratification procedure are independent of the HM Network analysis 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 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 DQOs for uncertainty or time coverage for the relevant air quality regulations 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 or monthly 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.
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 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.

5.4 MEASUREMENT UNCERTAINTY OF ANNUAL AVERAGE

Data capture across the HM Network remains high (and any gaps in coverage have generally occurred evenly throughout the year), therefore the uncertainty in the annual mean values will be dominated by the analytical and sampling uncertainty.

According to the AQSR DQOs, an additional component of uncertainty due to incomplete time coverage may be determined by the procedure described in ISO 11222[21]. A 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[21], using the data capture percentage from Auchencorth Moss (the lowest site for the year). This yielded a small absolute increase in uncertainty of 7 %.

In summary, in all cases annual mean uncertainties are compliant with the AQSR uncertainty DQOs.

Exemplar expanded uncertainties, including the above component, quoted at the 95 % confidence interval, for the annual mean concentration values of the compliance metals are given in Table 4.

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

Analyte	Annual Mean Relative Expanded Uncertainty [%]	AQSR maximum [%]
As	18	40
Cd	17	40
Ni	18	40
Pb	18	25

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

6 NETWORK DATA

6.1 MEASURED CONCENTRATIONS (PARTICULATE-PHASE)

The annual time-weighted mean of measured metals concentrations in 2023, averaged over all HM Network sites (Table 5), and at individual sites (Table 6), are given below.

Table 5 also displays the maximum annual mean concentration measured at any HM Network site, and the median annual concentration across all sites.

All data, at the highest time resolution that they are produced, are available from Defra's UK-AIR website[23].

Table 5 - The 2023 annual time-weighted mean concentrations averaged over all HM Network sites, the annual median concentrations across all sites, and the maximum annual mean concentration measured at any monitoring site. The AQSR limit or target value is also listed, where applicable.

Analyte	2023 UK mean annual concentration across all sites [ng m^{-3}]	2023 UK median annual concentration across all sites [ng m^{-3}]	2023 maximum annual mean concentration at any site [ng m^{-3}]	UK limit or target value [ng m^{-3}]
As	0.58	0.63	0.89	6
Cd	0.15	0.10	0.52	5
Co	0.19	0.12	0.90	-
Cr	3.43	1.68	34.6	-
Cu	7.12	4.20	29.0	-
Fe	503	199	3298	-
Mn	10.7	4.69	70.6	-
Ni	2.55	0.89	19.0	20
Pb	6.62	4.68	34.4	500
Se	0.67	0.54	1.68	-
V	1.29	0.76	9.08	-
Zn	18.4	11.4	92.4	-

Table 6 - The 2023 annual time-weighted mean concentrations (ng m^{-3}) measured at individual HM Network sites. Colour key: red = above target or limit value; amber = above upper assessment threshold (UAT); yellow = above lower assessment threshold (LAT).

Site	Annual time-weighted mean concentrations [ng m^{-3}]											
	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
Auchencorth Moss	0.20	0.02	0.03	0.39	0.86	58.2	1.38	0.16	0.77	0.38	0.31	3.08
Belfast Centre	0.41	0.05	0.12	1.11	5.06	263	4.69	0.69	2.62	0.42	0.79	11.4
Chadwell St Mary	0.71	0.13	0.10	1.49	7.06	316	5.18	0.97	7.65	0.52	1.85	19.9
Chesterfield Loundsley Green	0.56	0.10	0.07	2.00	3.20	152	3.97	0.89	4.68	0.76	0.45	16.0
Chilbolton Observatory	0.48	0.07	0.04	0.67	2.32	98.2	2.34	0.43	2.48	0.48	0.71	8.03
Cwmystwyth	0.19	0.04	0.02	0.48	0.78	48.3	1.43	0.21	1.18	0.38	0.34	2.73
Detling	0.66	0.09	0.05	0.82	2.87	116	2.89	0.56	3.68	0.54	1.02	8.13
Eskdalemuir	0.16	0.02	0.02	0.51	0.56	30.5	0.89	0.15	0.60	0.36	0.27	1.64
Fenny Compton	0.55	0.07	0.04	0.60	1.96	96.3	2.03	0.28	2.40	0.47	0.48	7.85
Heigham Holmes	0.48	0.06	0.04	0.53	1.21	64.1	1.95	0.42	2.21	0.51	0.91	5.41
London Marylebone Road	0.74	0.10	0.22	6.54	29.0	1190	11.8	1.36	5.15	0.58	1.13	27.8
London Westminster	0.77	0.08	0.12	1.82	9.60	409	5.59	0.97	5.30	0.47	0.90	17.7
Pontardawe Brecon Road	0.52	0.17	0.17	1.05	2.91	178	3.54	2.18	4.34	0.54	0.48	9.61
Pontardawe Tawe Terrace	0.58	0.25	0.90	3.88	4.20	199	6.14	11.9	4.39	0.56	0.56	9.97
Port Talbot Margam	0.75	0.52	0.25	4.17	14.6	3300	39.2	1.09	8.38	1.06	4.13	37.4
Scunthorpe Low Santon	0.89	0.42	0.22	3.51	4.36	2110	70.6	1.19	20.0	1.31	9.08	32.4
Scunthorpe Town	0.72	0.17	0.11	1.95	4.15	595	19.2	0.80	7.88	1.10	1.78	20.3
Sheffield Devonshire Green	0.63	0.12	0.22	4.80	6.84	328	8.03	2.39	5.34	1.11	0.77	25.9
Sheffield Tinsley	0.80	0.29	0.86	34.6	14.8	575	32.3	19.0	12.5	1.68	1.07	92.4
Swansea Coedgwilym	0.67	0.22	0.33	1.68	11.0	145	3.67	6.69	34.4	0.58	0.52	9.75
Swansea Morriston	0.65	0.26	0.37	3.48	21.1	755	9.91	5.32	7.40	0.60	0.76	21.6
Walsall Pleck Park	0.80	0.22	0.13	2.34	14.4	483	7.14	0.76	7.70	0.55	0.69	31.7
Yarner Wood	0.35	0.03	0.03	0.38	0.81	49.7	1.45	0.30	1.24	0.54	0.66	3.00

6.2 MEASURED CONCENTRATIONS OF AQSR COMPLIANCE METALS IN PM

In Figure 2, the Network-wide annual time-weighted mean concentrations for the compliance metals for 2023 are compared against the relevant limit and target values from the AQSR. The annual mean concentrations for the relevant compliance metals at each HM Network site in 2023 are displayed in Figure 3.

The highest annual mean values for the compliance metals were found at the following sites:

- Arsenic: Scunthorpe Low Santon
- Cadmium: Port Talbot Margam
- Nickel: Sheffield Tinsley
- Lead: Swansea Coedgwilym

In only two instances do the measured annual mean values exceed the relevant LATs at any HM network site (percentage of target value shown in brackets). It is also noted that in one instance, one site is equal to the LAT:

- Ni at Pontardawe Tawe Terrace: exceedance of the LAT (59 %)
- Ni at Sheffield Tinsley: exceedance of the UAT (95 %)

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 very close to a metal alloy coatings plant (0.5 km). Whilst the site is usually upwind of the facility, it is very close to the source of emissions and is located on the valley floor, hence measures higher concentrations than the downwind site at Pontardawe Brecon Road, which is at an elevated position on the valley side (approximately 0.8 km from the metal alloy plant). There are also other industrial sources in the area, such as a nickel refinery (4 km downwind). Swansea Morriston is in the same area, 5 km upwind of the nickel refinery.

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

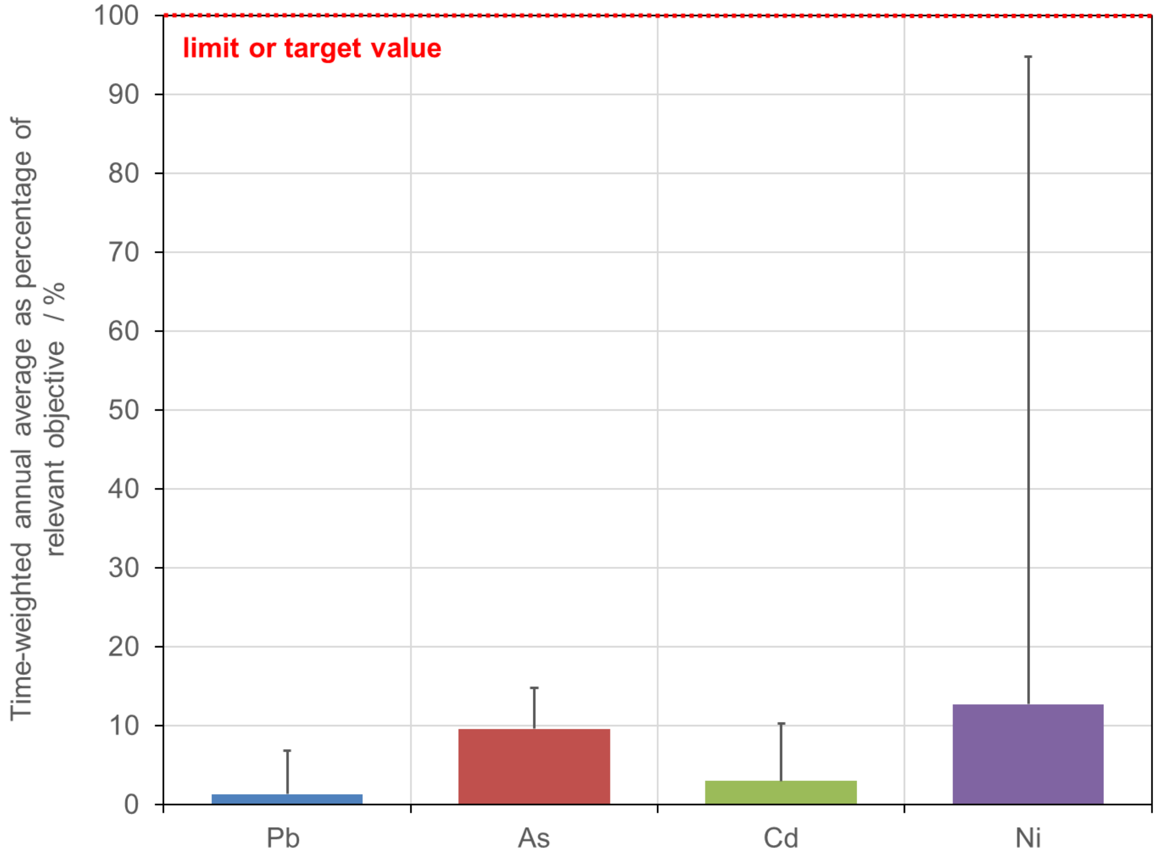

Figure 2 – The time-weighted annual mean concentrations of compliance metals relevant to the AQSR on the HM Network in 2023 as a percentage of the relevant limit or target value. The bars indicate the annual mean of all sites; the lines indicate the annual mean at the site with the highest concentrations.

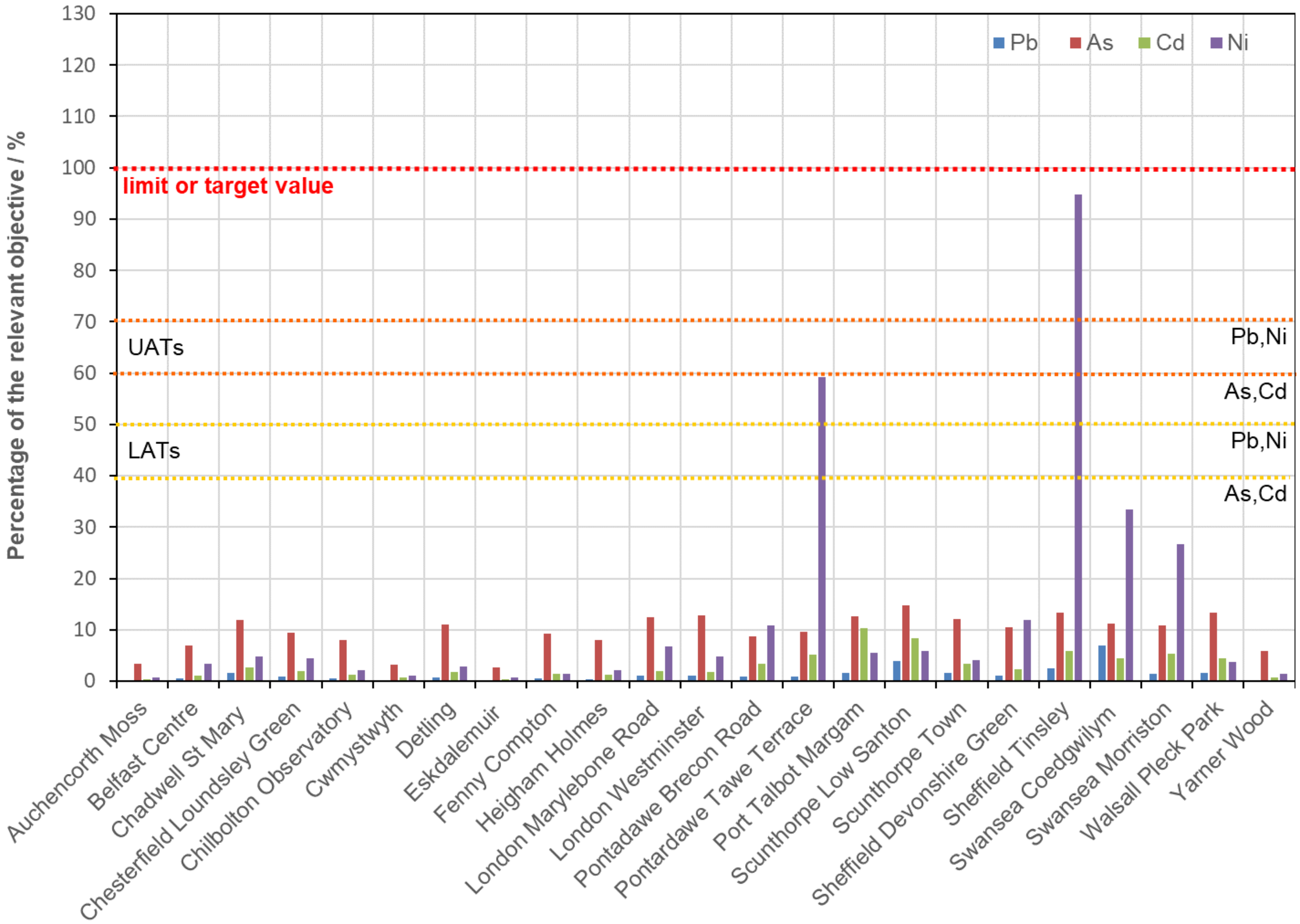

Figure 3 - The annual mean measured concentrations of the compliance metals relevant to the AQRS at all HM Network sites in 2023 as a percentage of the relevant target values shown in red, UATs in orange and LATs in yellow.

6.3 WITHIN YEAR CONCENTRATION TRENDS IM PM

Seasonal trends of air pollutant concentrations are important for understanding variations in emissions and atmospheric chemistry. Patterns seen can be influenced by anthropogenic emissions, meteorological conditions, and transport of pollutants over long and short distances. Of the metals in PM measured on the HM Network, most show variable or low seasonality, with the exception of As and V[12,24]. 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.

The ‘low in winter–high in summer’ seasonality for V is attributable to weak or non-seasonal local sources being dominated by contributions from medium and long-range transport during the summer months, when pollutant transport is more efficient[24]. The ‘high in winter–low in summer’ seasonality for As is attributable to the dominant contribution being from local primary sources, such as burning process producing larger PM sizes[24]. As is generally emitted from diffuse combustion sources, not point sources, and therefore is affected much less by meteorological conditions[12].

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 Figure 4, Figure 5, and Figure 6.

High concentration spikes 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.

High concentrations of nickel are also frequently observed at the Sheffield Tinsley monitoring site (see Figure 6). 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.

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 and the source of emissions which may result in Brecon Road not encountering any 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.

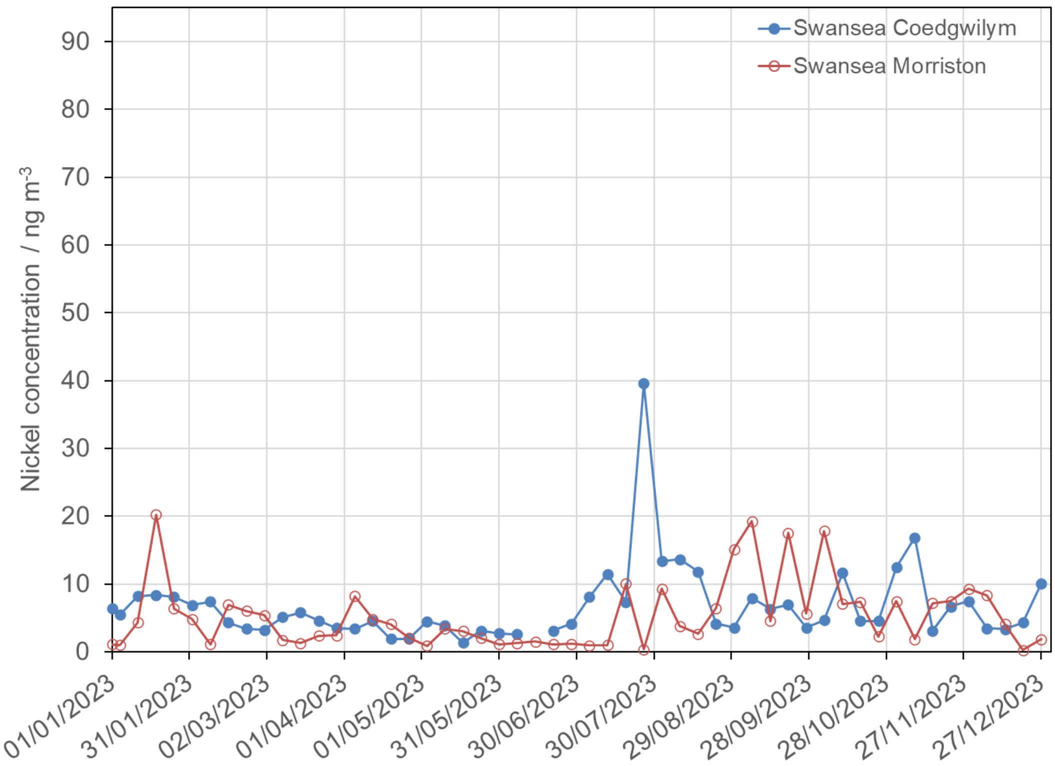

Figure 4 - Measured Ni concentrations at Swansea Coedgwilym and Swansea Morriston, in 2023 (both sampled weekly).

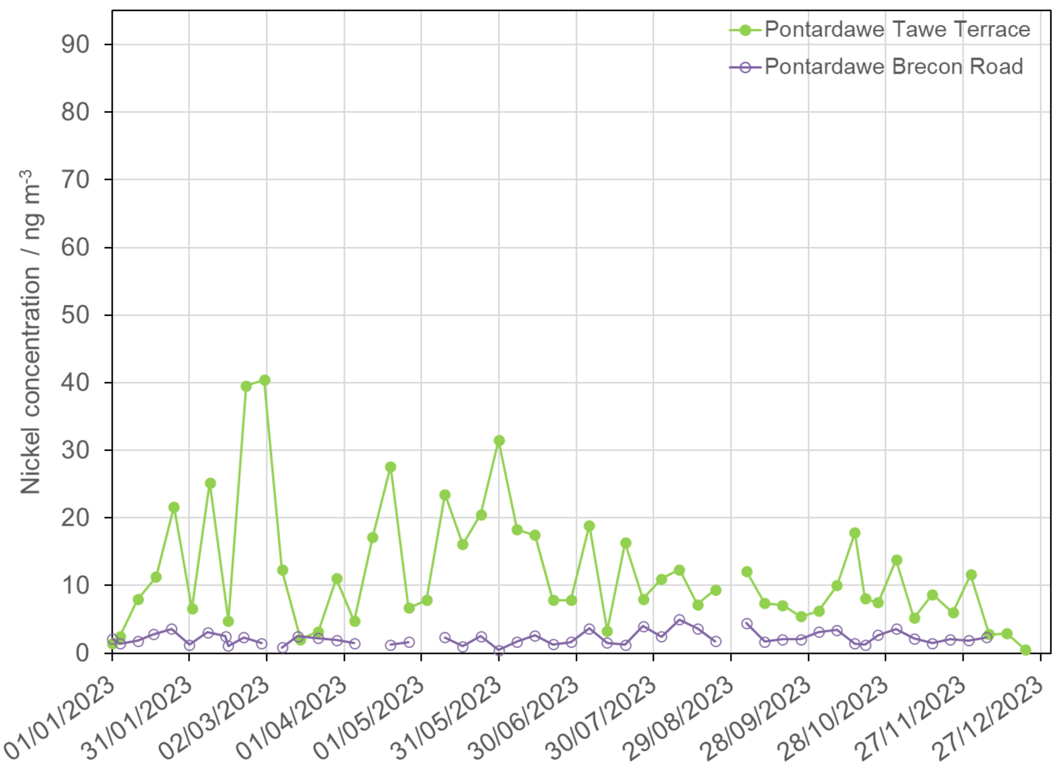

Figure 5 - Measured Ni concentrations at Pontardawe Tawe Terrace and Pontardawe Brecon Road, in 2023 (both sampled weekly).

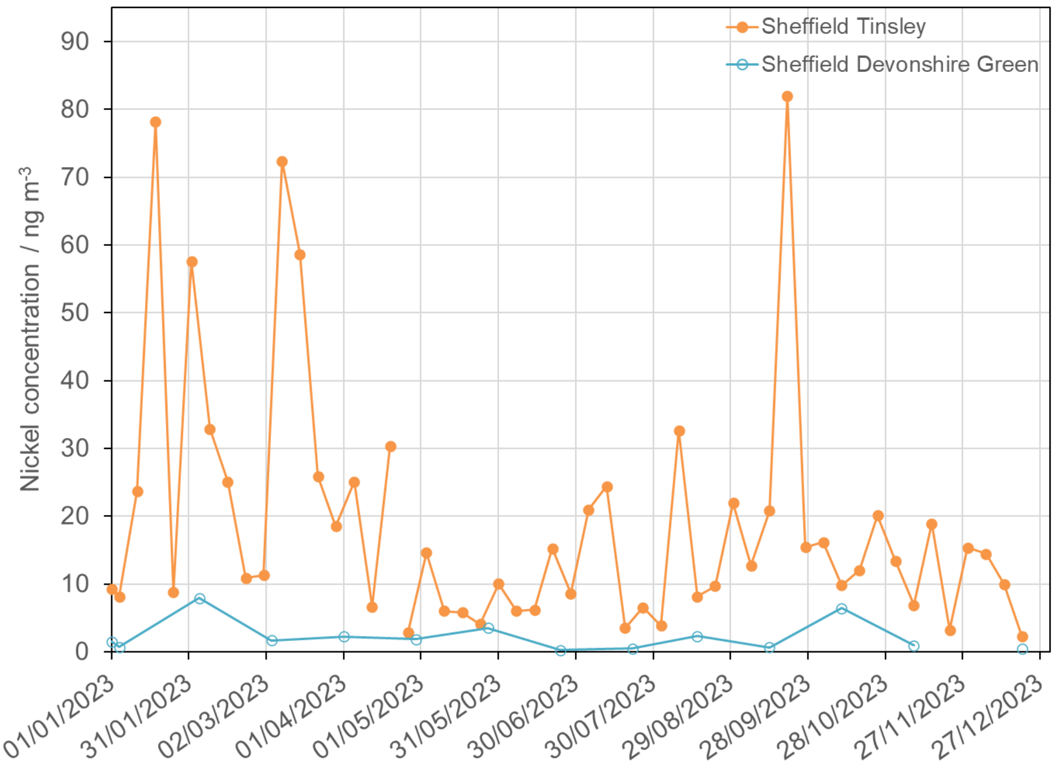

Figure 6 - Measured Ni concentrations at Sheffield Tinsley and Sheffield Devonshire Green in 2023. Results from Tinsley are weekly. Results from Sheffield Devonshire Green are averaged over four-week periods.

6.4 MEASURED CONCENTRATIONS OF NON-REGULATION METALS IN PM

Figure 7 shows the concentrations of the non-compliance metals measured across the HM Network sites, normalised to the annual median value for each metal. The annual average concentrations were given in Table 6.

High concentration values for non-compliance metals are usually pertinent 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-compliance metals, as would be expected.

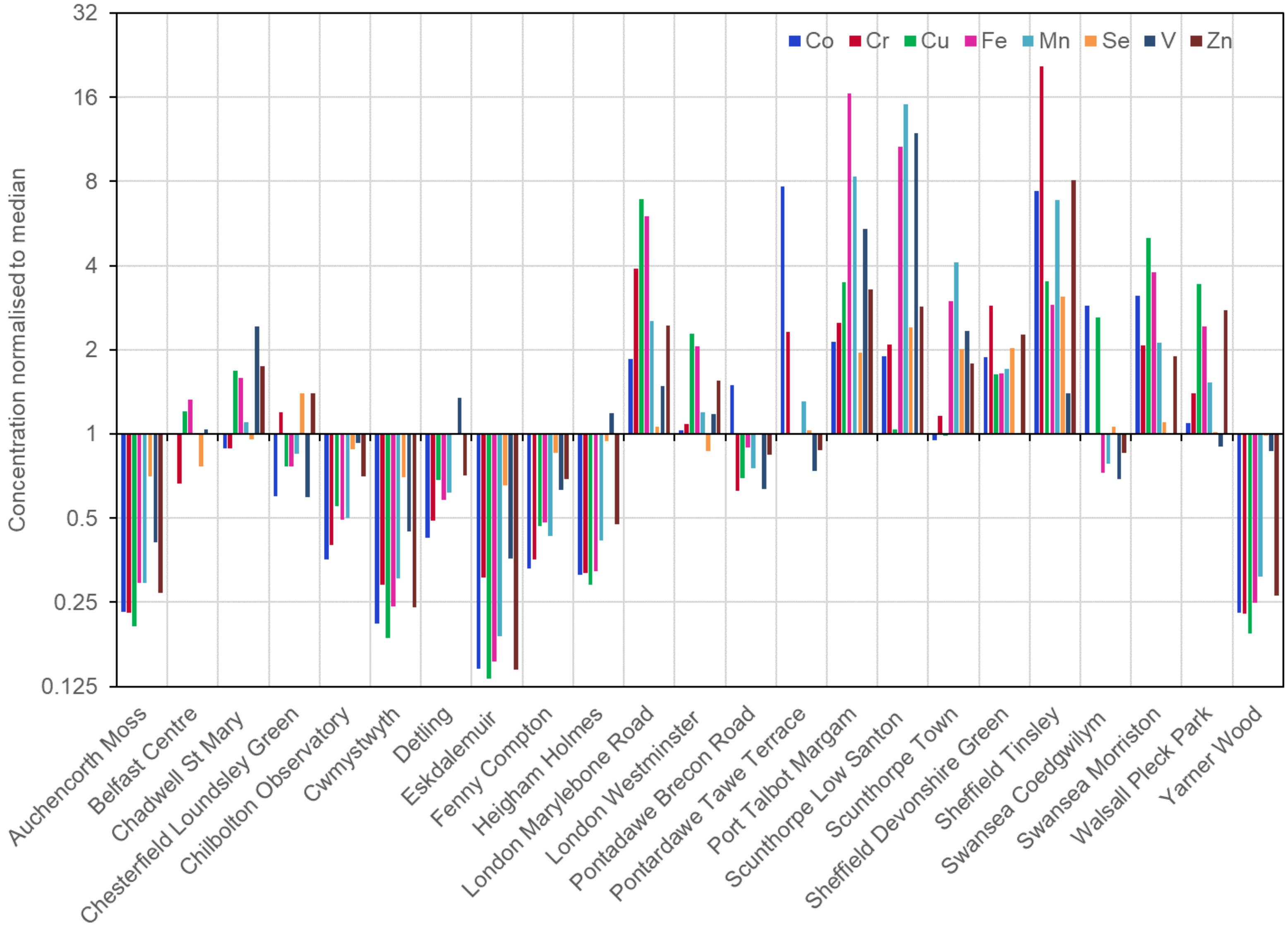

Figure 7 - The annual mean concentrations of the non-compliance metals measured at all HM network sites in 2023, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median, so it is clear which sites are above and below the median level. Note the logarithmic scale on the *y*-axis.

6.5 MEASURED CONCENTRATIONS OF METALS IN DEPOSITION

The annual mean metals deposition flux concentrations in 2023, averaged over all sites sampling metals in deposition (Table 7), and at individual sites (Table 8), are given below.

Table 7 - The 2023 annual mean, median, and maximum deposition flux measurements (in µg m^{-2} d^{-1}) averaged over all HM Network deposition monitoring sites.

Analyte	2023 UK mean annual flux across all sites [µg m^{-2} d^{-1}]	2023 UK median annual flux across all sites [µg m^{-2} d^{-1}]	2023 UK maximum annual flux at any site [µg m^{-2} d^{-1}]
Al	16.5	14.4	34.2
As	0.23	0.16	0.50
Ba	0.89	0.71	1.29
Be	0.011	0.009	0.017
Cd	0.014	0.015	0.019
Co	0.02	0.02	0.03
Cr	0.24	0.17	0.45
Cs	0.010	0.007	0.020
Cu	3.44	1.43	8.06
Fe	16.3	15.0	25.3
Hg	0.011	0.010	0.016
Li	0.14	0.13	0.20
Mn	2.56	2.32	4.17
Mo	0.05	0.05	0.06
Ni	0.19	0.21	0.30
Pb	0.12	0.09	0.25
Rb	0.43	0.25	0.92
Sb	0.08	0.07	0.11
Se	0.25	0.18	0.41
Sn	0.71	0.60	1.08
Sr	4.90	4.20	8.12
Ti	0.42	0.26	0.88
U	0.012	0.013	0.017
V	0.23	0.19	0.50
W	0.13	0.11	0.19
Zn	4.07	3.58	5.38

Table 8 - The 2023 annual mean deposition flux measurements (in µg m^{-2} d^{-1}) measured at individual deposition monitoring sites on the HM Network.

Analyte	Annual mean deposition flux measurements [µg m^{-2} d^{-1}]				
	Auchencorth Moss	**Chilbolton Observatory**	**Heigham Holmes**	**Lough Navar**	**Yarner Wood**
Al	5.36	28.62	80.7	7.93	14.0
As	0.06	0.07	0.14	0.44	0.19
Ba	0.38	1.16	3.16	0.67	0.89
Be	0.003	0.004	0.008	0.006	0.005
Cd	0.005	0.007	0.013	0.012	0.012
Co	0.010	0.030	0.09	0.015	0.021
Cr	0.13	0.11	0.22	0.28	0.23
Cs	0.003	0.004	0.006	0.005	0.01
Cu	0.28	0.80	0.81	0.51	0.74
Fe	8.30	17.9	49.2	11.5	13.6
Hg	0.008	0.007	0.008	N/A	0.008
Li	0.05	0.07	0.11	0.31	0.17
Mn	1.17	2.16	7.65	3.49	3.87
Mo	0.03	0.03	0.05	0.06	0.04
Ni	0.11	0.15	0.20	0.17	0.28
Pb	0.07	0.13	0.45	0.12	0.12
Rb	0.11	0.12	0.39	0.34	0.95
Sb	0.07	0.06	0.07	0.05	0.07
Se	0.15	0.16	0.15	0.51	0.41
Sn	0.02	0.05	0.04	0.05	0.04
Sr	1.70	2.71	4.89	11.9	6.74
Ti	0.17	0.37	0.63	0.43	0.34
U	0.002	0.003	0.009	0.005	0.004
V	0.07	0.17	0.30	0.21	0.35
W	0.015	0.011	0.03	0.03	0.02
Zn	1.65	1.82	3.30	1.94	3.15

7 TRENDS IN MEASURED CONCENTRATIONS

7.1 TRENDS IN PARTICULATE-PHASE METALS

Trends in concentrations measured over the last 44 years for the metals relevant to the legislation are summarised in Figure 8 and Figure 9, where both the UK mean and median concentrations are displayed. The trends the UK annual mean and median observed for the other metals measured by the HM Network are shown in Figure 10, Figure 11, and Figure 12.

The median has been used in addition to the mean since it is less sensitive to the effect of changes in sites measuring high concentrations and to changes in the number and location of monitoring sites making up the HM Network. 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 most elements have generally decreased over the period for which data is available. In recent years this trend has levelled off to yield lower, more stable concentrations. 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 HM Network. This generally mirrors the decrease in emissions over this period (see Figure 1). Exceptions to this are copper and manganese.

The NAEI estimated annual copper emissions have shown a gradual increase between 1990-2019, followed by a sharp decrease in 2020[8], but the measured annual mean concentration has shown a gradual decrease over this time. This increase in copper emissions has been associated with the increased use of lubricants in road vehicles (associated with 45 % of UK copper emissions in 2021). The other main source is vehicle brake pad wear (associated with 50 % of UK copper emissions in 2021). Excluding road vehicles lubricants, copper emissions from other sources have declined by 19 % since 1990, associated with the decline in metal production[10]. A possible reason that the increase in copper emissions is not reflected in the measured ambient air concentrations is because of the small number of HM Network sites directly measuring traffic emissions.

The NAEI estimated annual manganese emissions showed a decrease of almost 50 % between 1990-2000, and the measured concentrations followed this trend. Since 2000, the estimated annual emissions have shown a gradual increase up to similar levels seen in 1990 (overall 4.5 % increase, 1990 to 2021), whereas the measured concentrations have remained relatively stable at lower levels. In 2021, the main source of manganese emissions (83 %) was associated with stationary combustion such as industrial biomass and wood, which has significantly increased since 1990. The other main source in 2021 was metal production (16 %), which has significantly decreased since 1990[9]. A possible reason that the increase in manganese emissions is not reflected in the measured ambient air concentrations is because of the focus of HM Network sites measuring metal production rather than industrial biomass and wood combustion sources.

Nickel concentrations, although significantly reduced in the long-term trend, actually showed a gradual upward trend from 2010-2014, largely due to the concentration measured at monitoring sites in the Swansea and Tawe valleys. Since 2014, there has been a slight downward trend in the median, but the mean does not show a clear trend.

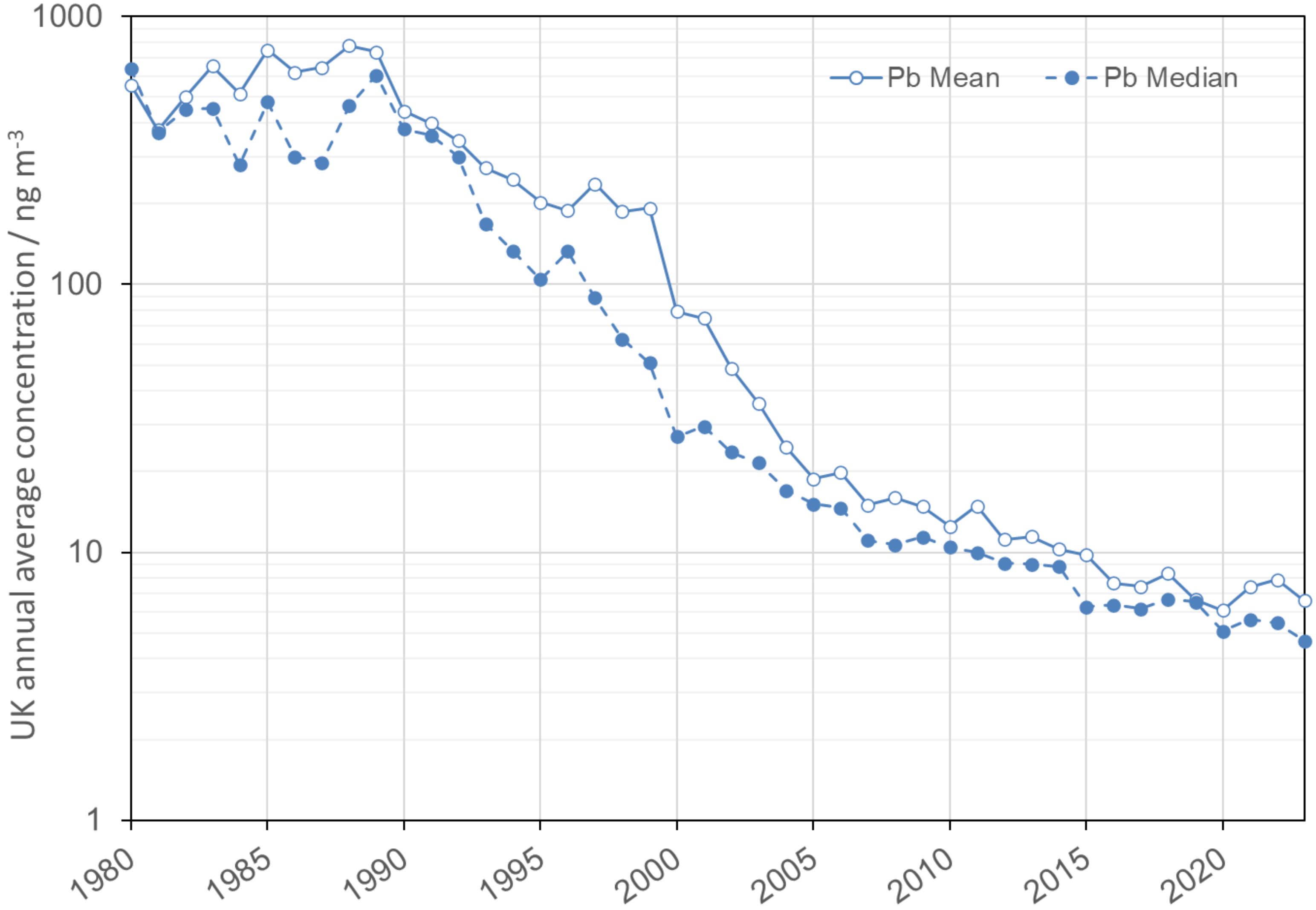

Figure 8 - The mean and median of HM Network measured annual average concentrations of Pb since 1980. The UK AQSR 2010 limit for Pb is 500 ng m^{-3}. Note the logarithmic scale on the y-axis.

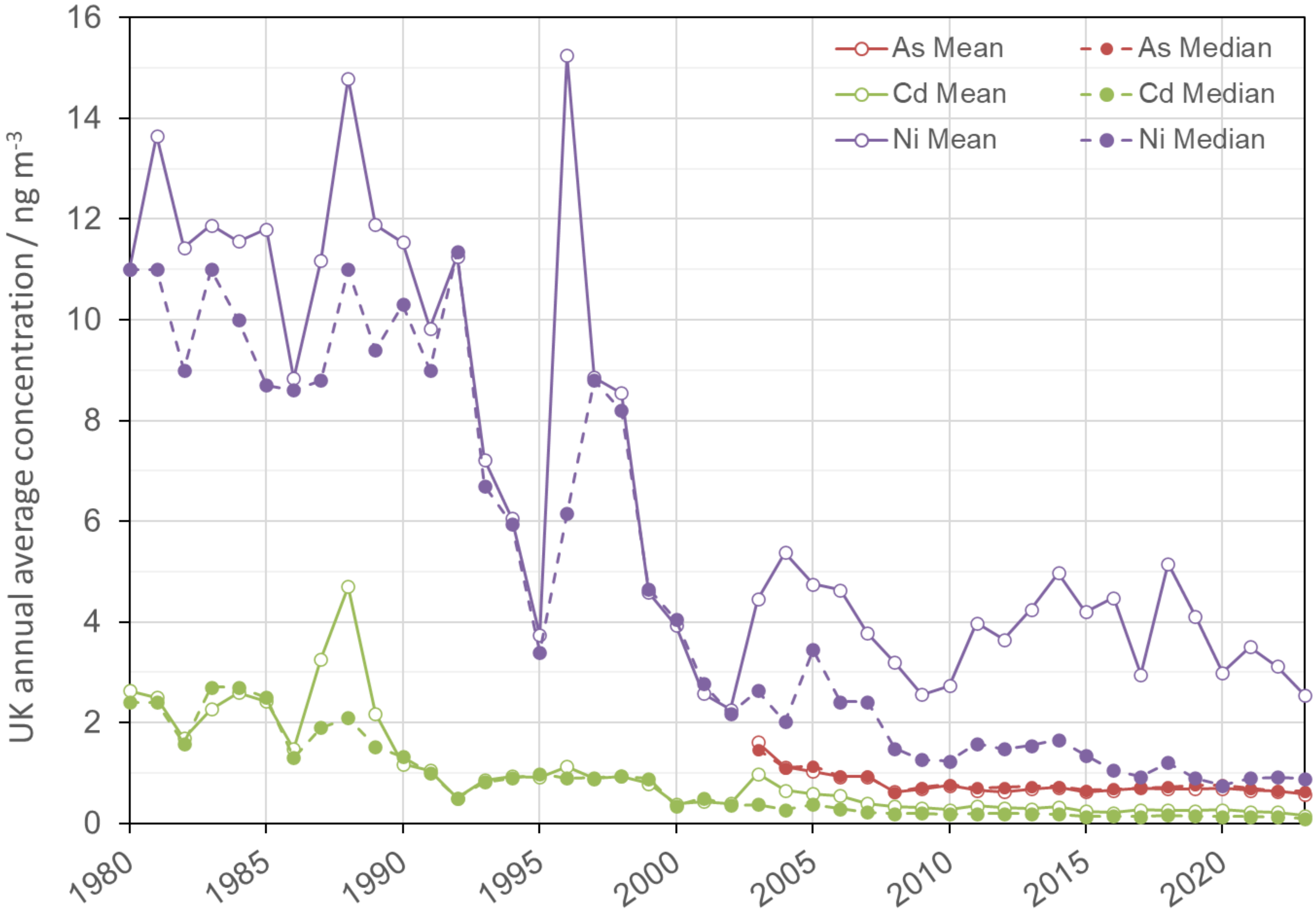

Figure 9 - The mean and median of HM network measured annual average concentrations of Ni, As, and Cd since 1980. The UK AQSR 2010 target values for Ni, As and Cd are 20 ng m^{-3}, 6 ng m^{-3} and 5 ng m^{-3} respectively.

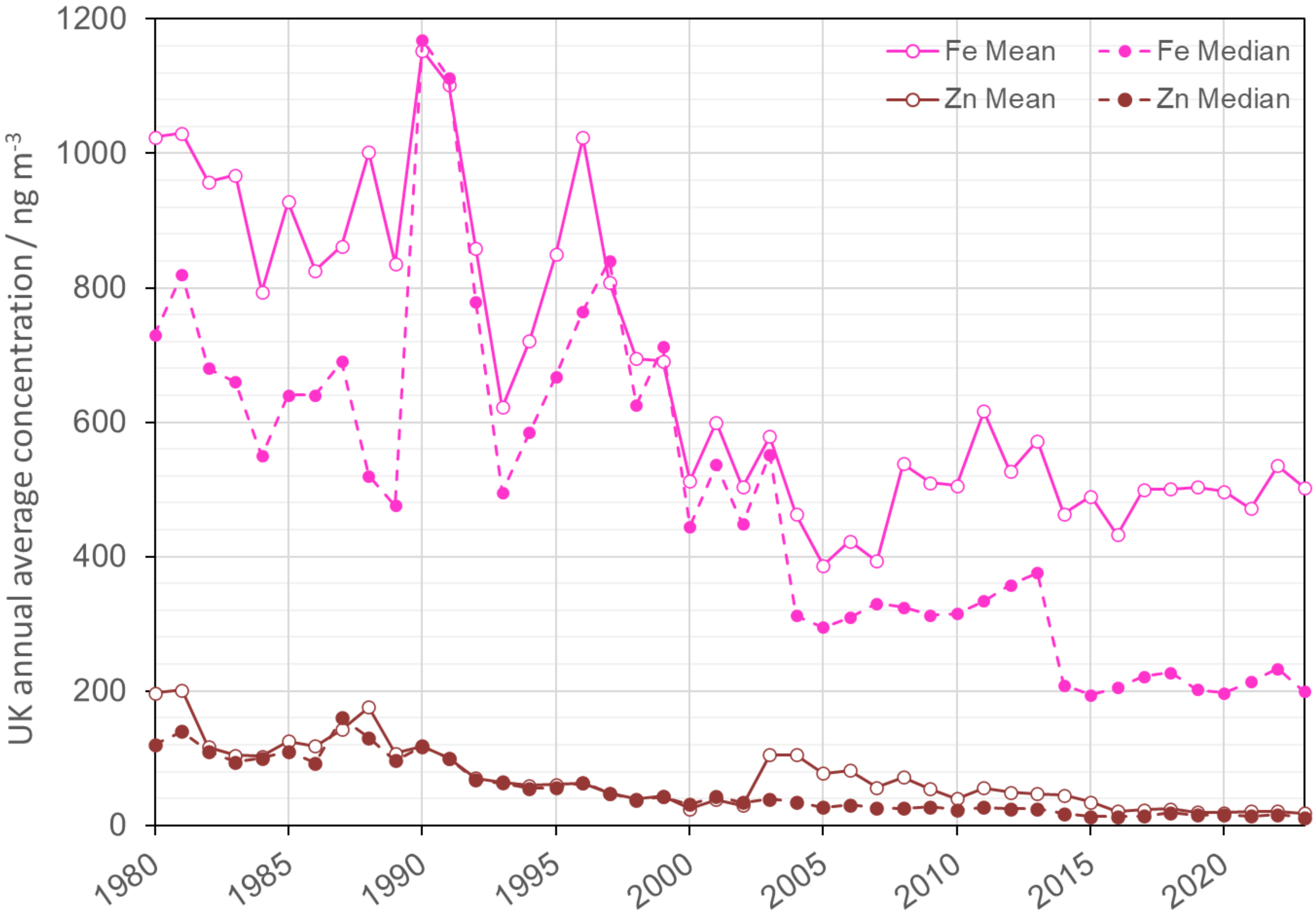

Figure 10 - The mean and median of HM Network measured annual average concentrations of Fe and Zn since 1980.

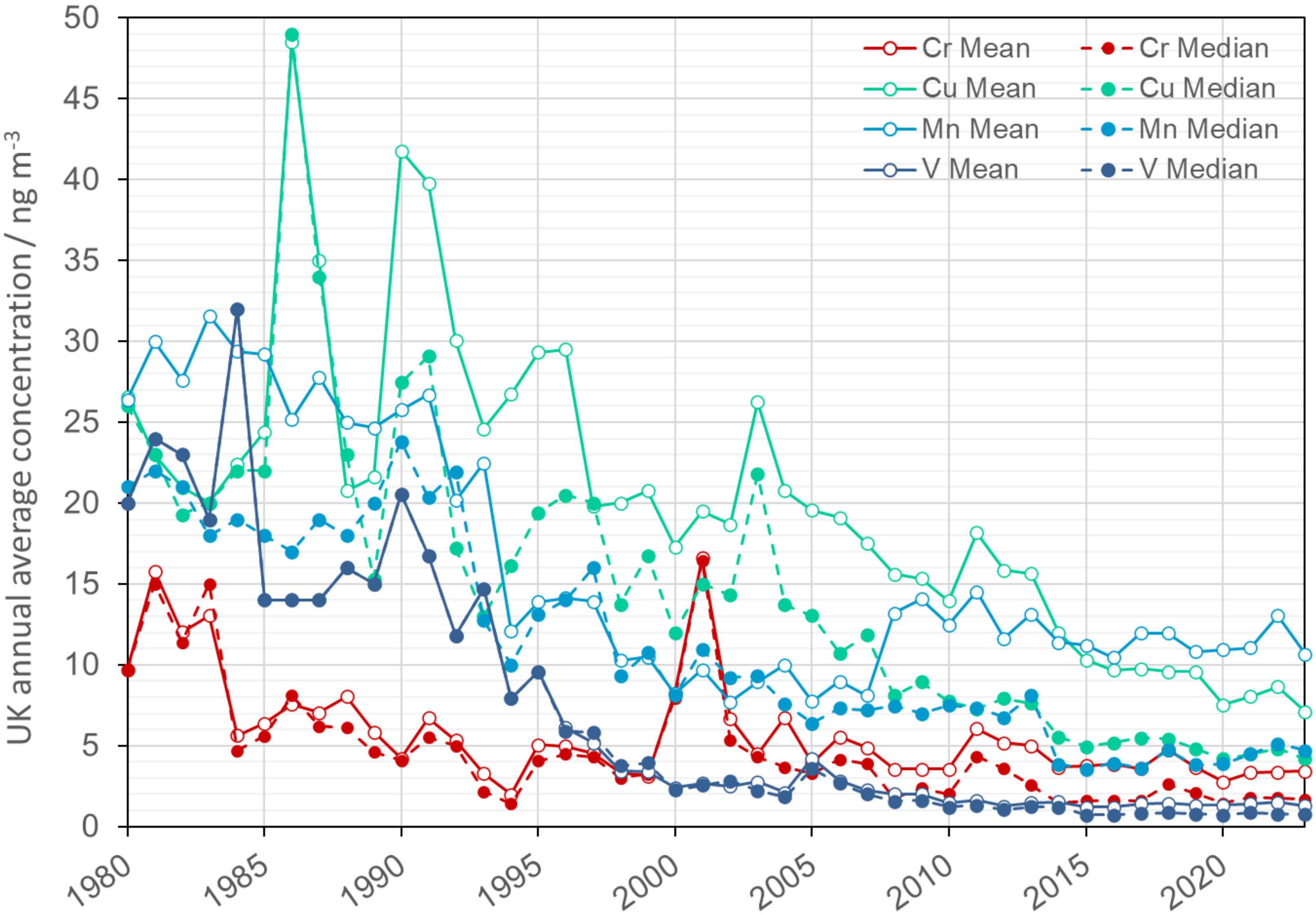

Figure 11 - The mean and median of HM Network measured annual average concentrations of Cr, Cu, Mn, and V, since 1980.

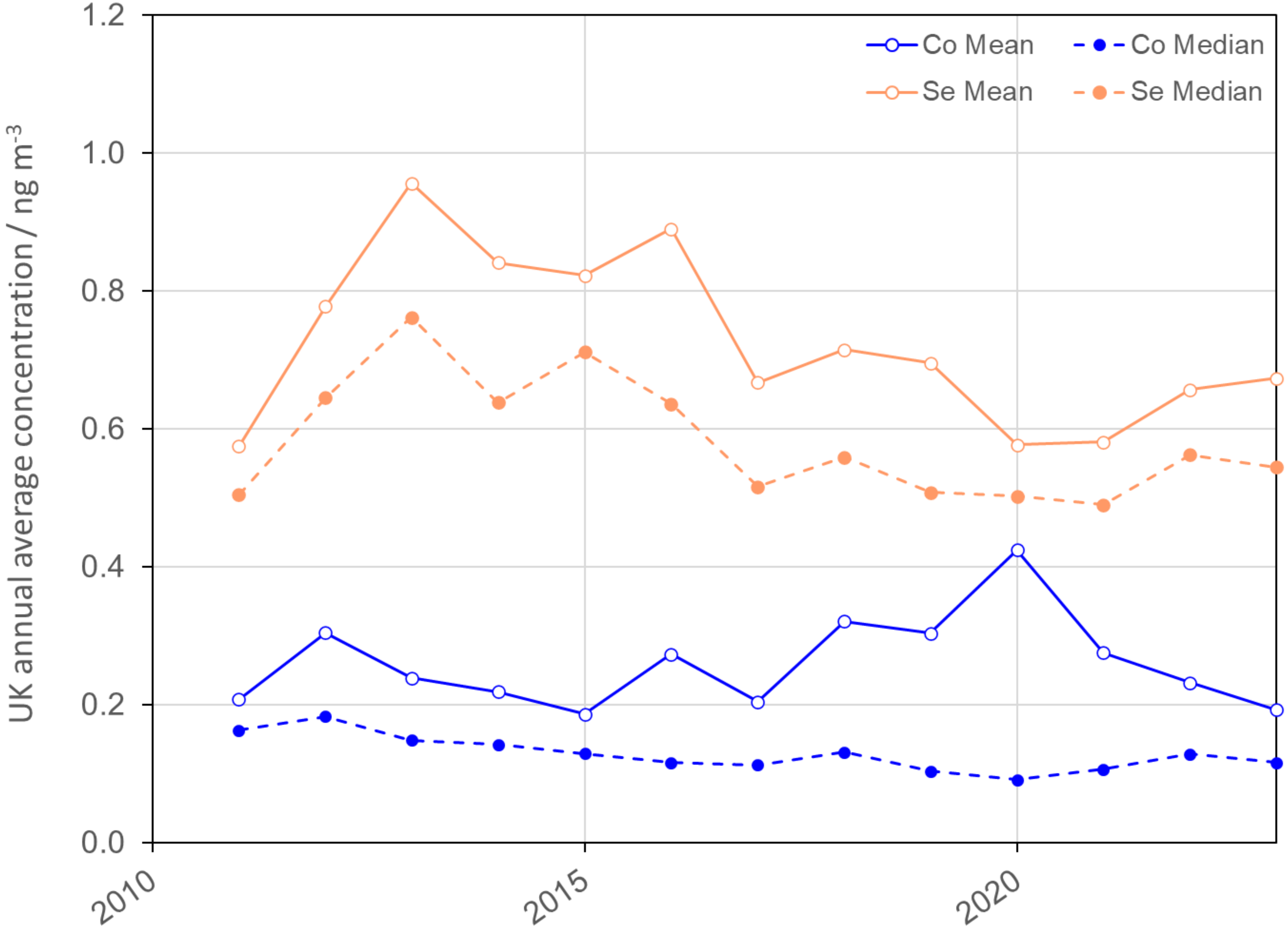

Figure 12 - The mean and median of HM Network measured annual average concentrations of Co and Se since monitoring commenced for these metals in 2011.

7.2 TRENDS IN NICKEL IN THE SWANSEA AND TAWE VALLEYS

The annual average concentration of nickel in the Swansea and Tawe valleys measured since 2003 is shown in Figure 13.

Nickel concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level. (The data for Vale Inco in 2008 – 2013, and Coedgwilym and Morriston in 2007 are courtesy of Swansea Council. The data for the Leisure Centre is courtesy of Neath Port Talbot County Borough Council). 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 the River Tawe Valley to monitor any emissions from the Vale nickel refinery situated at Clydach, about 4 km to the south-west, and a metal alloy coatings plant, approximately 1 km to the north-east.

Swansea Vale Inco (located at: Glais Primary School, School Road, Glais, Swansea, SA7 9EY) was the HM site in the Swansea area from 2003 to 2007 inclusive. It was then operated as a Swansea Council local authority site with site auditing and analysis services provided by NPL until its closure (June 2013). At the end of 2007 the local authority sites at Swansea Coedgwilym and Swansea Morriston were affiliated to the HM 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 an exceedance of the target value, again attributed to abatement issues at the industrial facility. Concentrations have since fallen, and from 2022 was less than the target value.

The trends in nickel concentrations in the Swansea and Tawe valleys were the subject of a peer-reviewed publication by NPL published in 2022, “Falling nickel concentrations in ambient air in South Wales - 50 years of progress”[25]. This paper demonstrated the effectiveness of nickel emissions abatement strategies over the last 50 years by tracking the falling air concentrations of nickel over this period. The work also showed how the monitoring network in the Swansea Valley has expanded over this time and become significantly more sensitive to nickel emissions. The data presented represents a significant public health achievement – the paper concluded that it is likely that the exposure to nickel in air of the population in the Swansea Valley has decreased more than 100-fold over the last 50 years – reflecting the progress in regulation, industrial efficiency, emissions abatement technology and air quality monitoring science achieved during this period.

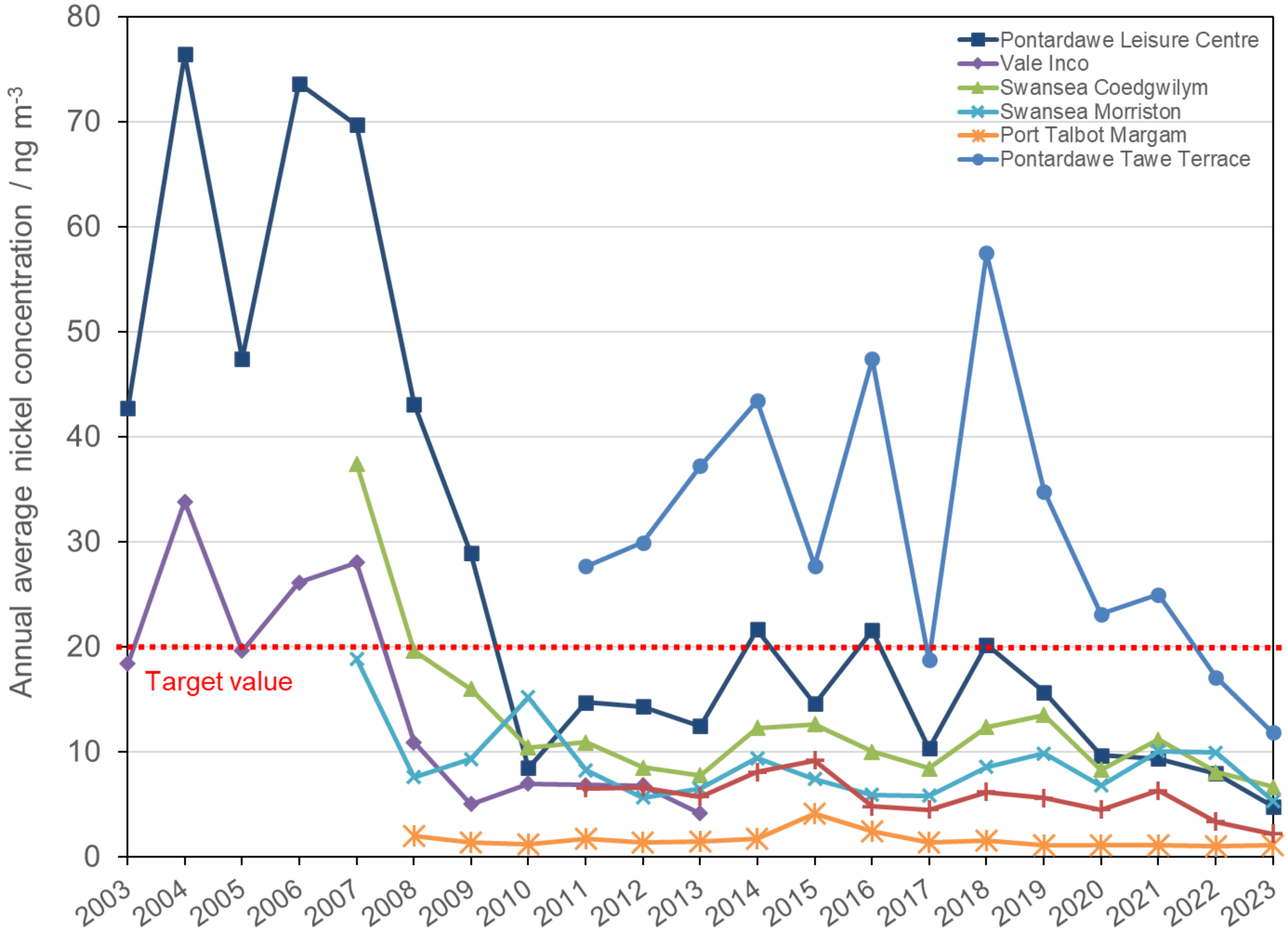

Figure 13 - The annual average nickel concentrations measured at monitoring sites in the Swansea area 2003-23. The red dotted line indicates the UK AQSR 2010 target value for nickel.

7.3 TRENDS IN DEPOSITION METALS

Trends in deposition metal concentrations measured since 2010 (the year from which data is available on UK-AIR[23]) for the metals relevant to the UK AQSR 2010 are summarised in Figure 14 to Figure 17.

The annual UK time-weighted mean concentrations (expressed in ng L^{-1}) are displayed for the current sites sampling metals in deposition. Deposition measurements were only undertaken at Chilbolton from 2015 onwards.

Although there is significant variability in measured concentrations, there is a general downward trend for Pb, Ni, and As. Concentrations for Cd and Hg are relatively low and appear stable over the time.

The tendency of Hg to bioaccumulate makes it of particular importance in deposition samples and this trend is plotted in Figure 18.

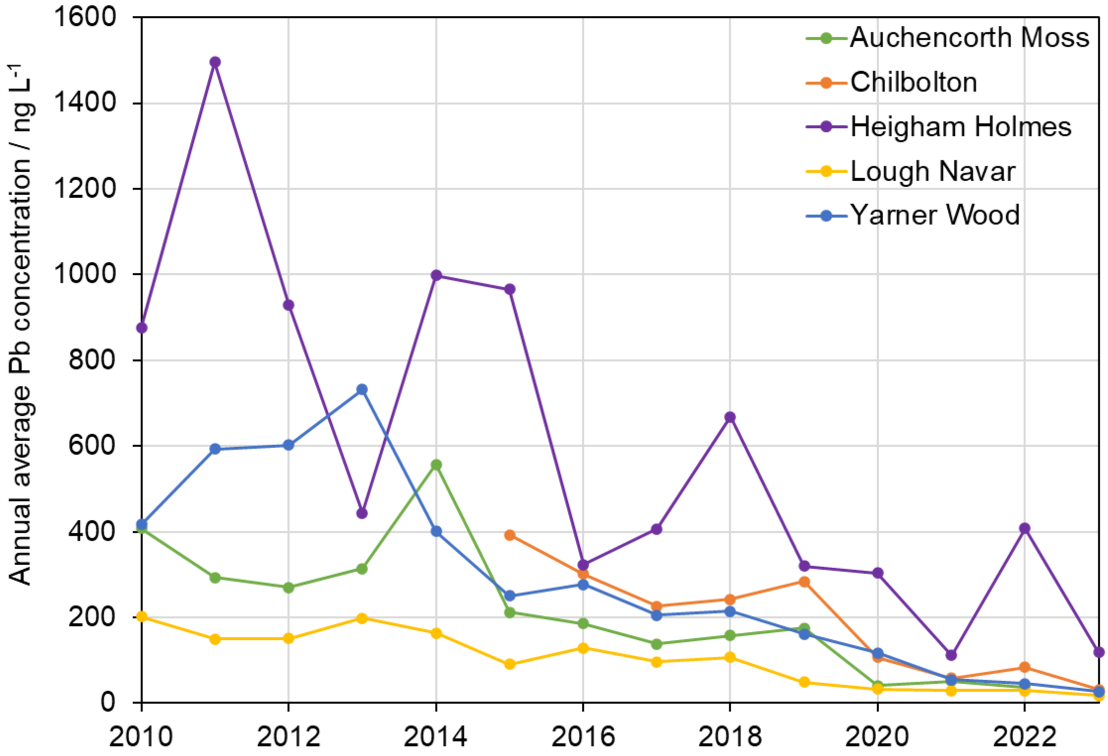

Figure 14 - The mean annual concentrations of Pb measured in deposition since 2010 at individual sites.

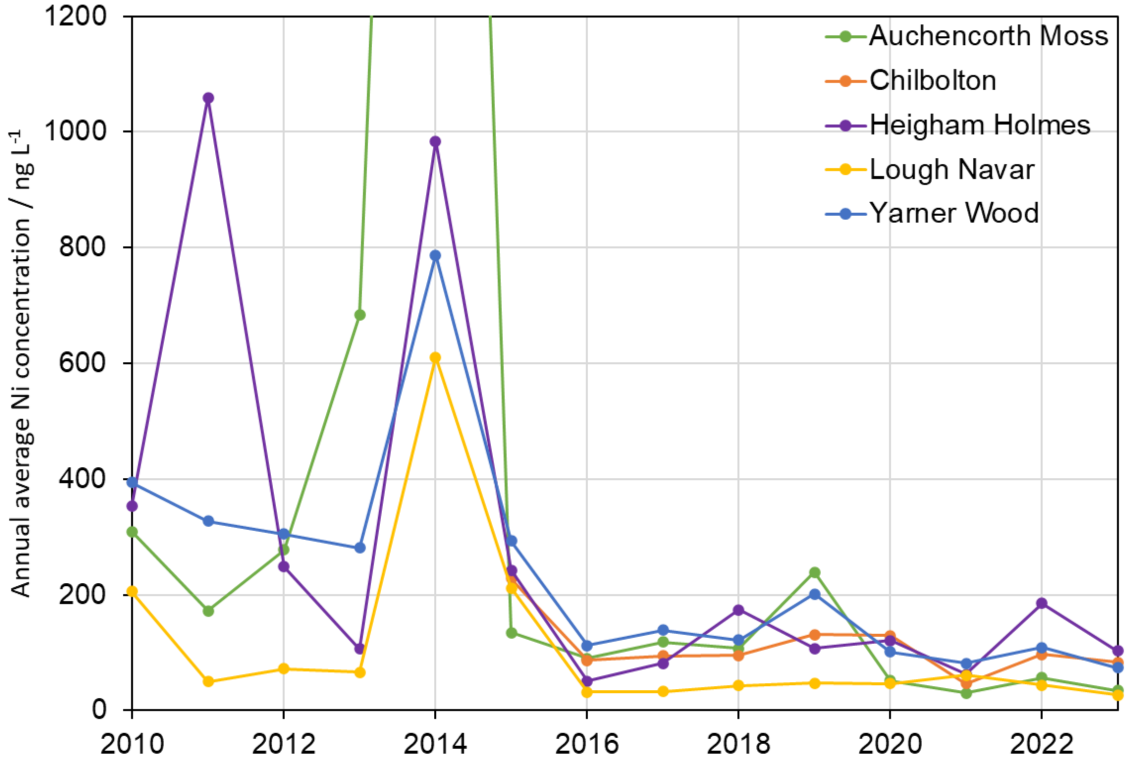

Figure 15 - The mean annual concentrations of Ni measured in deposition since 2010 at individual sites. The off-scale Auchencorth Moss point in 2014 is 3965 ng L^{-1}.

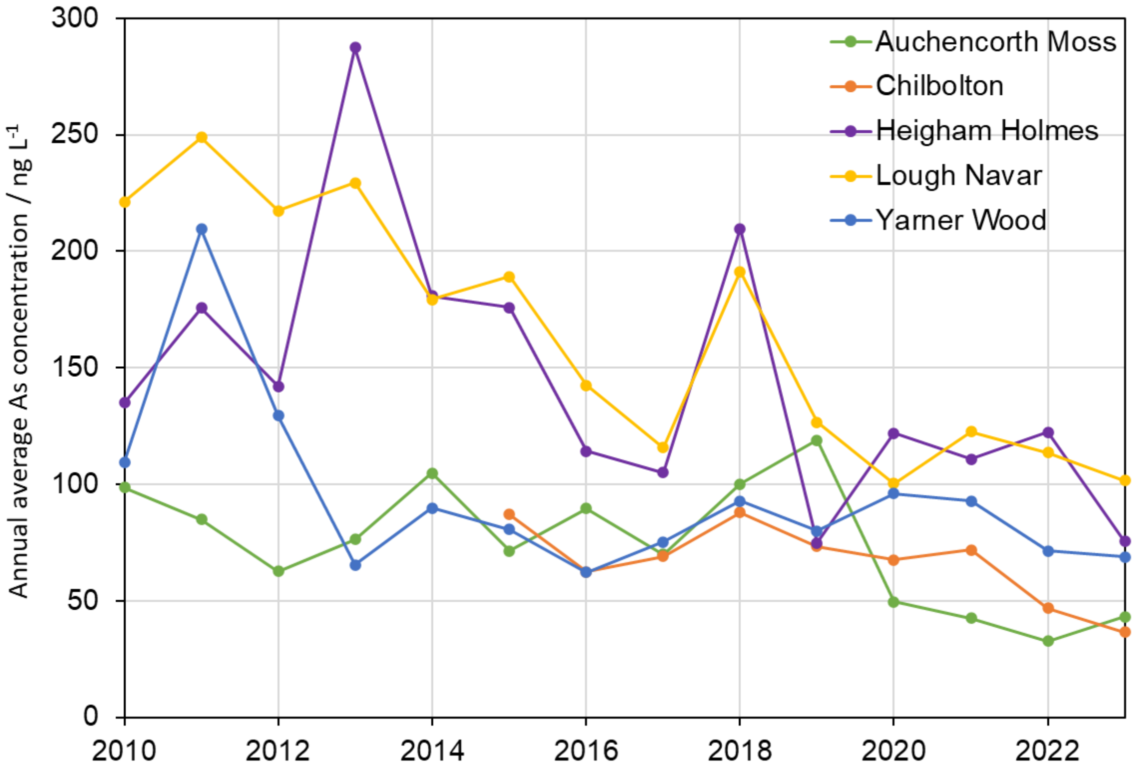

Figure 16 - The mean annual concentrations of As measured in deposition since 2010 at individual sites.

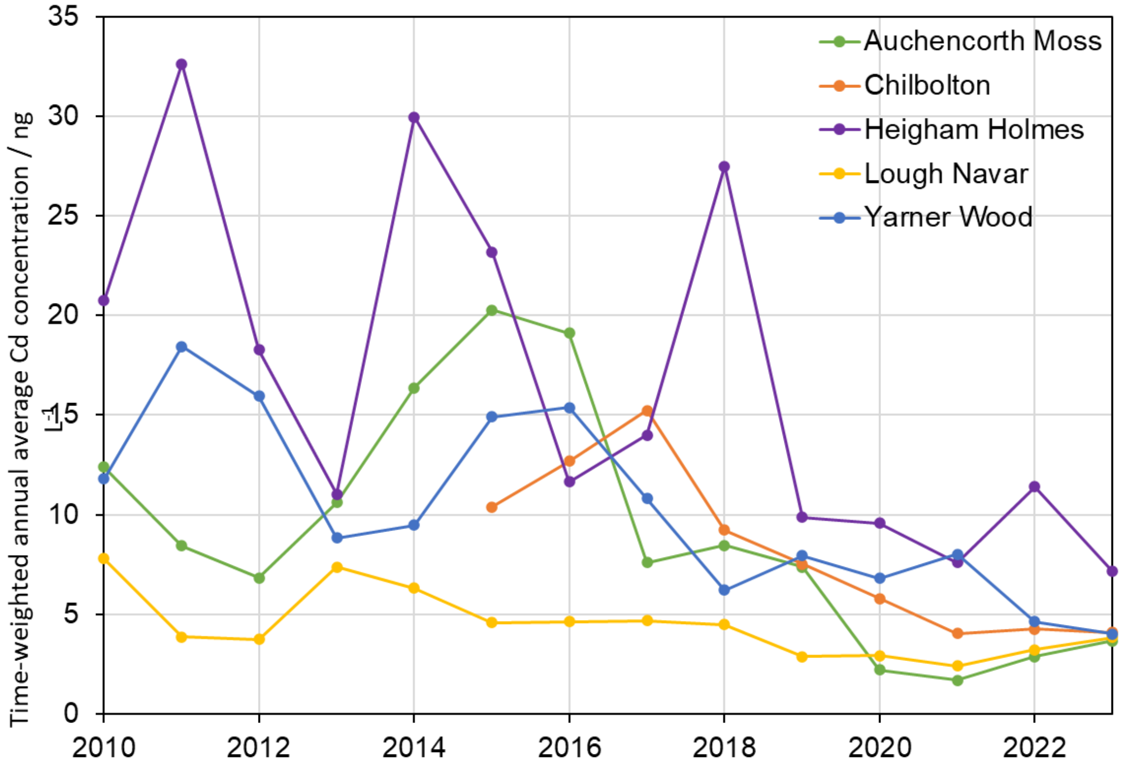

Figure 17 - The mean annual concentrations of Cd measured in deposition since 2010 at individual sites.

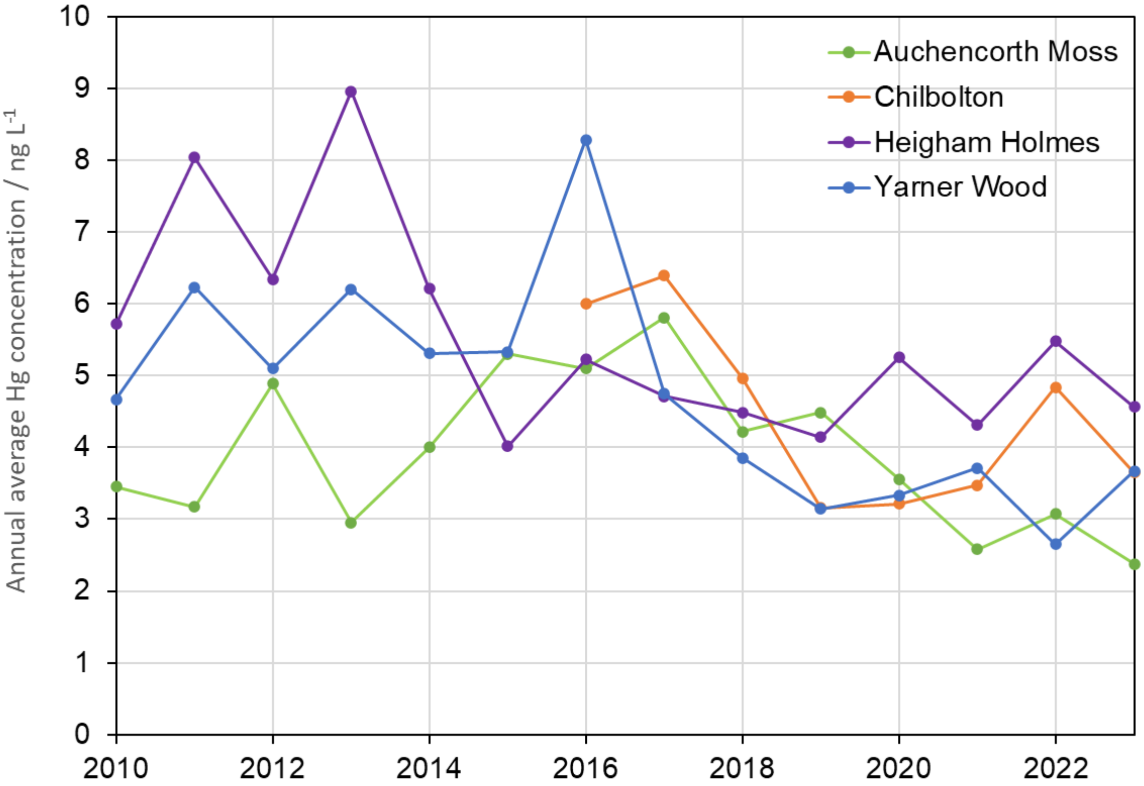

Figure 18 - The mean annual concentrations of Hg measured in deposition since 2010 at individual sites. Hg is not measured at Lough Navar.

8 ACKNOWLEDGEMENT

NPL would like to acknowledge the contribution from UKCEH (Heath Malcolm, Patrick Keenan, Hayley Guyatt, Josh Telford) for supplying the deposition data and input for associated parts of this report.

9 ANNEX 1: DETAILS OF SITES COMPRISING THE HM NETWORK IN 2023

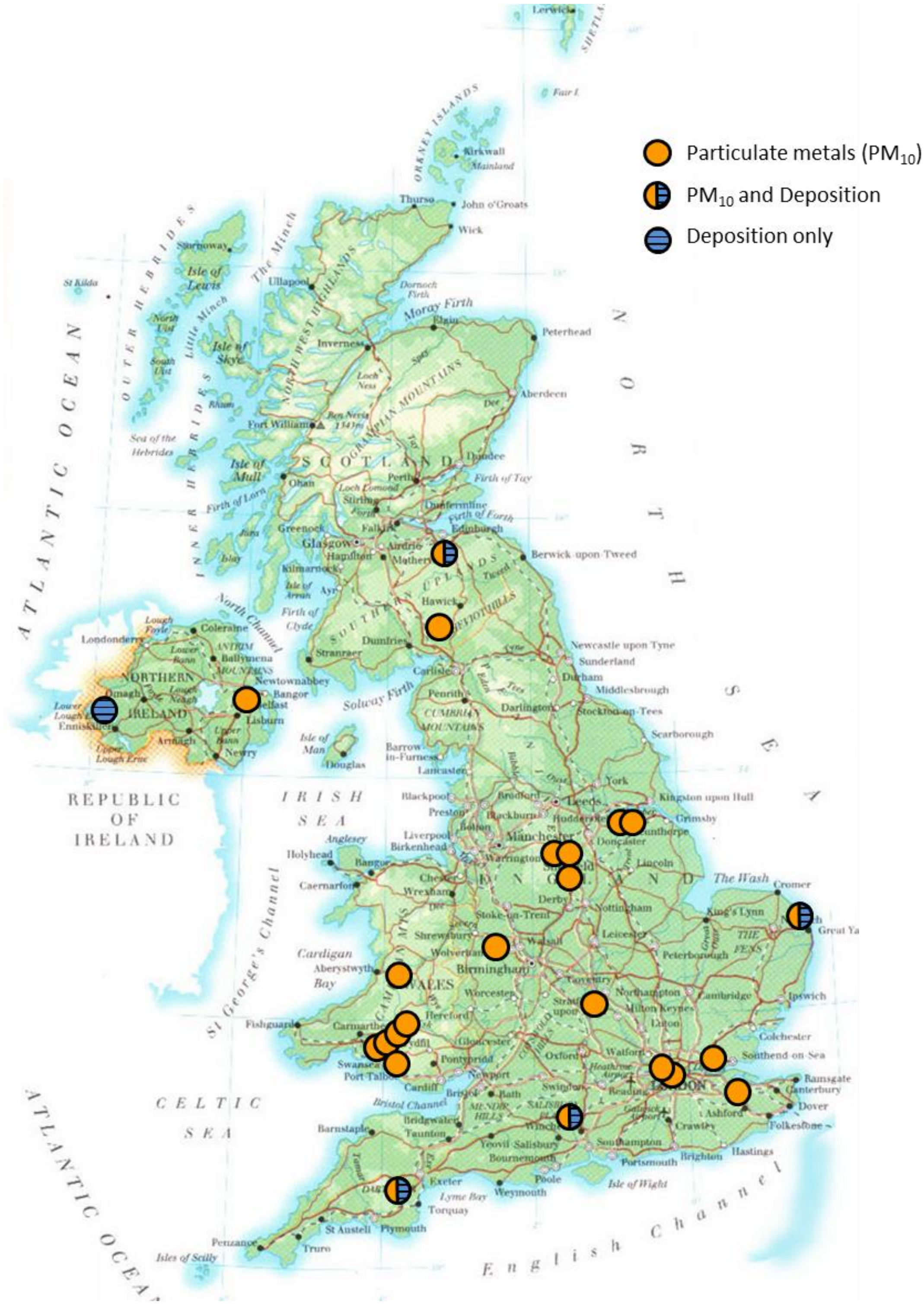

Figure 19 - Location of monitoring sites comprising the HM Network during 2023 (indicated by the coloured circles, see key) – details of which are given in Table 9 below.

Table 9 - Details of the sites comprising the HM Network in 2023, including name, location, classification, and pollutants measured.

UK-AIR Site ID	Site Name	Site Address	Site Classification [1]	PM Phase [2]	Deposition [3]
UKA00451	Auchencorth Moss	UKCEH Edinburgh, Bush Estate, Penicuik, Midlothian, EH26 0QB	RB	4-weekly	Weekly (Hg Monthly)
UKA00212	Belfast Centre	Lombard Street, Belfast, BT1 1RB	UB	4-weekly	n/a
UKA00514	Chadwell St Mary	Council Area Housing Office, Linford Road, Chadwell St Mary, Essex, RM16 4JY	UB	4-weekly	n/a
UKA00604	Chesterfield Loundsley Green	Loundsley Green, Pennine Way, Chesterfield. S40 4NG.	UB	4-weekly	n/a
UKA00614	Chilbolton Observatory	Drove Road, Chilbolton, Stockbridge, Hampshire. SO20 6BJ.	RB	4-weekly	Weekly (Hg Monthly)
UKA00325	Cwmystwyth	Cwmystwyth, Wales. Grid reference 52.352436, -3.805317	RB	4-weekly	n/a
UKA00481	Detling	Alan Day House, County Showground, Detling, Maidstone, Kent, ME14 3JF	RB	4-weekly	n/a
UKA00130	Eskdalemuir	Met Office, Eskdalemuir, Langholm, Dumfrieshire, DG13 0QW	RB	4-weekly	n/a
UKA00606	Fenny Compton	The Dassett CE Primary School, Memorial Road, Fenny Compton, Warwickshire, CV47 2XU	RB	4-weekly	n/a
UKA00461	Heigham Holmes	Gardeners Cottage, Burnley Hall, East Somerton, Great Yarmouth, Norfolk, NR29 4DZ	RB	4-weekly	Monthly (Hg Monthly)
UKA00315	London Marylebone Road	Marylebone Road (opposite Madame Tussauds), London, NW1 5LR	UT	4-weekly	n/a
UKA00435	London Westminster	Mortuary Car Park, Horseferry Road, London, SW1P 2EB	UB	4-weekly	n/a
UKA00166	Lough Navar	Lough Navar, Glennasheevar Road, Derrygonnelly, Enniskillen, Fermanagh, BT93 6AH	RB	n/a	Monthly (exc. Hg)

UK-AIR Site ID	Site Name	Site Address	Site Classification [1]	PM Phase [2]	Deposition [3]
UKA00560	Pontardawe Brecon Road	Dany Bryn Residential Care, 84 Brecon Road, Pontardawe, Swansea, SA8 4PD	IS	Weekly	n/a
UKA00557	Pontardawe Tawe Terrace	Tawe Terrace, Pontardawe, Swansea, West Glamorgan, SA8 4HA	UI	Weekly	n/a
UKA00501	Port Talbot Margam	Port Talbot Fire Station, Commercial Road, Port Talbot, West Glamorgan, SA13 1LG	UI	4-weekly	n/a
UKA00506	Scunthorpe Low Santon	Dawes Lane, Santon, Scunthorpe, North Lincolnshire, DN16 1XH	UI	4-weekly	n/a
UKA00381	Scunthorpe Town	Rowlands Road, Scunthorpe, North Lincolnshire, DN16 1TJ	UI	4-weekly	n/a
UKA00575	Sheffield Devonshire Green	Devonshire St, Sheffield, South Yorkshire. S3 7SW	UB	4-weekly	n/a
UKA00181	Sheffield Tinsley	Ingfield Avenue, Tinsley, Sheffield. S9 1WZ	UI	Weekly	n/a
UKA00520	Swansea Coedgwilym	Coedgwilym Cemetery, Pontardawe Road, Clydach, Swansea, SA6 5PB	UB	Weekly [4]	n/a
UKA00521	Swansea Morriston	Morriston Groundhog, Wychtree Street, Morriston, Swansea, SA6 8EX	UT	Weekly [4]	n/a
UKA00820	Walsall Pleck Park	Montford Road, Walsall, West Midlands. WS2 9DE	UB	4-weekly	n/a
UKA00168	Yarner Wood	Natural England, Yarner Wood, Bovey Tracey, Devon, TQ13 9LJ	RB	4-weekly	Weekly (Hg Monthly)

[1] Site Classification: RB = Rural Background; UB = Urban Background; UT = Urban Traffic; UI = Urban Industrial; IS = Industrial Suburban

[2] PM (particulate matter) phase: all sites are analysed for a suite of 12 metals: As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn; sampling is weekly for all sites, but samples are analysed in 4-weeky batches unless otherwise stated.

[3] Deposition: all sites are analysed for a suite of 26 metals: Al, Sb, As, Ba, Be, Cd, Cs, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Rb, Se, Sr, Sn, Ti, W, U, V, Zn, Hg (except for Lough Navar, which excludes Hg); sampling and analysis is weekly or monthly as stated.

[4] Weekly analysis for PM phase is subsidised by the Welsh Government.

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