

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 2021 on the UK Heavy Metals Monitoring Network

**Katie R. Williams
Sharon L. Goddard
Emma C. Braysher
Richard J. C. Brown
David M. Butterfield
Chris C. Robins
Adam Lilley
Chris Bradshaw
Bryan Sweeney
Andrew S. Brown**

JUNE 2023

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 2021 on the UK Heavy Metals Monitoring Network

Katie R. Williams, Sharon L. Goddard, Emma C. Braysher,
Richard J. C. Brown, David M. Butterfield, Chris Robins, Adam Lilley,
Chris Bradshaw, Bryan Sweeney, Andrew S. Brown

Atmospheric Environmental Science Department

© NPL Management Limited, 2023

ISSN 2059-6030

<https://doi.org/10.47120/npl.ENV49>

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

Extracts from this report may be reproduced provided the source is acknowledged
and the extract is not taken out of context.

Approved on behalf of NPLML by
Andrew Sims, Group Leader – Air Quality & Aerosol Metrology

CONTENTS

EXECUTIVE SUMMARY

1	INTRODUCTION.....	1
1.1	BACKGROUND	1
2	NETWORK OPERATION.....	4
2.1	OVERVIEW.....	4
2.2	SITE AUDITS	5
2.3	EQUIPMENT SERVICING AND BREAKDOWNS.....	6
2.4	SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION	6
3	SAMPLING AND ANALYTICAL METHODOLOGY	7
3.1	SAMPLING METHODOLOGY: PARTICULATE-PHASE METALS	7
3.2	SAMPLING METHODOLOGY: METALS IN DEPOSITION	7
3.3	ANALYTICAL METHODOLOGY: PARTICULATE-PHASE METALS.....	8
3.4	ANALYTICAL METHODOLOGY: METALS IN DEPOSITION	9
3.5	MEASUREMENT UNITS.....	10
3.6	MEASUREMENT UNCERTAINTY	10
4	METHOD PERFORMANCE CHARACTERISTICS AND QUALITY CONTROL.....	11
4.1	QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) PROCEDURES	11
4.2	MEASUREMENT UNCERTAINTY	12
5	DATA QUALITY.....	13
5.1	DATA CAPTURE (PARTICULATE PHASE)	13
5.2	DATA CAPTURE (DEPOSITION)	14
5.3	DATA PROCESSING AND RATIFICATION	15
5.4	MEASUREMENT UNCERTAINTY OF ANNUAL AVERAGE	15
6	NETWORK DATA.....	17
6.1	MEASURED CONCENTRATIONS (PM PHASE)	17
6.2	MEASURED CONCENTRATIONS WITH RESPECT TO THE REQUIREMENTS OF THE EU AIR QUALITY DIRECTIVES.....	19
6.3	WITHIN YEAR CONCENTRATION TRENDS	22
6.4	MEASURED CONCENTRATIONS OF NON-DIRECTIVE METALS	25
6.5	MEASURED CONCENTRATIONS OF METALS IN DEPOSITION	27
7	TRENDS IN MEASURED CONCENTRATIONS	29
7.1	TRENDS IN PARTICULATE-PHASE METALS	29
7.2	TRENDS IN NICKEL IN THE SWANSEA AND Tawe VALLEYS.....	35
7.3	TRENDS IN DEPOSITION METALS.....	37
ANNEX 1: LOCATION AND DETAILS OF SITES COMPRISING THE UK HEAVY METALS NETWORK IN 2021		40
REFERENCES.....		43

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 2021 and contains, in particular:

- Annual concentrations of all metals measured at all monitoring sites and performance against relevant data quality objectives and the requirements of the European Commission (EC) Air Quality Directives, implemented through the Air Quality regulations.
- Highlighting of Air Quality Directive exceedances (for lead, nickel, arsenic, and cadmium), interpretation of data and discussion of trends across the Network.
- A description of Network operation, analytical and quality assurance / quality control (QA/QC) procedures and notable events and changes to the Network during 2021.
- A brief summary of scientific research, publications, international representation, and other activities related to the Network.

In summary, during 2021:

- **Lead:** There were no annual average concentrations above the Ambient Air Quality Directive's Lower Assessment Threshold at any Network site. Recorded concentrations were therefore well below the limit value set by the Directive.
- **Nickel:** At one site, Pontardawe Tawe Terrace, the annual average concentration was recorded as above the Target Value. At three sites, Sheffield Tinsley, Swansea Coedgwilym and Swansea Morriston, the annual average concentration was recorded as above the Lower Assessment Threshold.
- **Arsenic and Cadmium:** There were no annual average concentrations above the Fourth Daughter Directive's 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 (for lead, nickel, arsenic, and cadmium), concentrations in ambient air were 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.
- Data capture for metals in the PM phase during 2021 was **98%**. For metals in deposition it was **84%**.

1 INTRODUCTION

This report was prepared by the National Physical Laboratory (NPL) as part of the UK Heavy Metals Monitoring Network contract with the Environment Agency, for the Department for Environment, Food and Rural Affairs (Defra) and the Devolved Administrations: the Welsh Government; the Northern Ireland Executive, represented by the Department of the Environment Northern Ireland (DOENI); and the Scottish Government, represented by the Scottish Government Environment and Forestry Directorate.

This is the Annual Summary Report for the UK Heavy Metals Monitoring Network (the 'Network') for 2021 and contains:

- Annual concentrations of all metals measured at all monitoring sites included in the Network and performance against relevant data quality objectives and the requirements of the relevant Air Quality Directives:
 - the Ambient Air Quality Directive (2008/50/EC¹) for lead;
 - the Fourth Air Quality Daughter Directive (2004/107/EC²) for nickel, arsenic, and cadmium;
 - the Commission Directive (EU) 2015/1480³ amending several annexes to Directives 2008/50/EC and 2004/107/EC;
 - and the Air Quality Strategy for England, Scotland, Wales, and Northern Ireland⁴ for lead.
- Highlighting of Air Quality Directive exceedances, interpretation of data and discussion of trends across the Network.
- Summary of Network operation, analytical and quality assurance/quality control (QA/QC) procedures and a description of notable events and changes to the Network during 2021.
- 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
- 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 of metals in ambient air is of great importance within this framework.

NOTE: The term 'concentration' is used in this report to refer to mass concentration.

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 Cd, allowable in the PM₁₀ fraction of ambient air (particles with an equivalent aerodynamic diameter of 10µm 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 (NAEI) has more details of anthropogenic sources and emissions of metallic pollutants in the UK⁵. 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 levelled off (with the exception of the increasing levels of manganese, thought to be attributable to increased biomass burning, and copper, which has been attributed to road vehicle engines lubricants and brake pad wear⁵). The correlation between these two data sets is quite strong, and a comparison between measured ambient concentrations across the Network and emissions has been published⁶. 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 Air Quality Directives relating to the monitoring of the mass concentrations of Pb, Ni, As and Cd, in the PM₁₀ phase of ambient air.

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

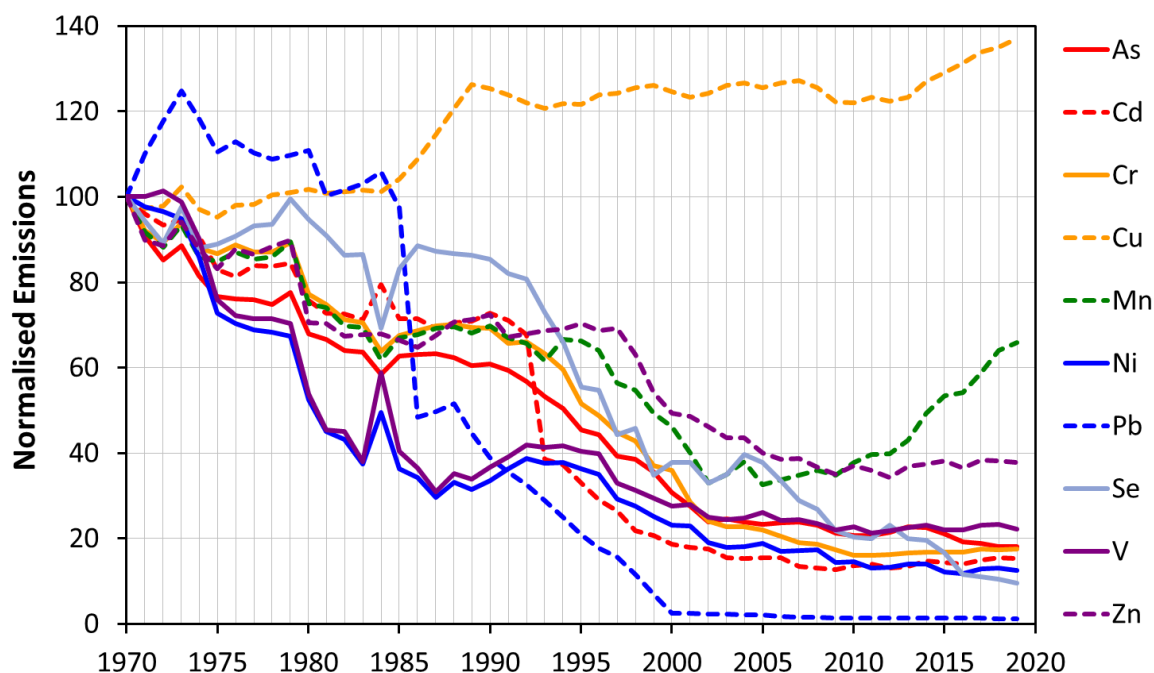


Figure 1 Estimated UK annual emissions of the metals from 1970 to 2019⁵ (the latest year for which emissions data were available at time of publishing) normalised to their values in 1970. The absolute levels of emissions in 1970, in tonnes, were: As, 81; Cd, 36; Cr, 257; Cu, 431; Mn, 146; Ni, 993; Pb, 7493; Se, 93; V, 2750; and Zn, 1511. Emissions data are not available for Co or Fe.

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 the European Monitoring and Evaluation Programme (EMEP) and the convention to protect the marine environment in the North-East Atlantic, OSPAR (from 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 data quality objectives 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 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 air⁷. A follow-up review of concentration trends was also published in 2019⁸.

2 NETWORK OPERATION

At the end of 2021 the UK Heavy Metals Monitoring Network comprised 24 monitoring sites around the UK (14 in England, 6 in Wales, 2 in Scotland, and 2 in Northern Ireland) sampling PM₁₀ and/or deposition from ambient air. Details of the sites are given in Annex 1. The PM₁₀ is sampled onto filters. These are returned to NPL where they are analysed to determine the content of various metals in the particulate matter, in order to produce concentration values for these metals in ambient air. Metals in deposition are monitored at 5 sites, 4 of which also monitor mercury in deposition. Relevant activity related to Network operation during 2021 is detailed below.

2.1 OVERVIEW

The ongoing Coronavirus (COVID-19) pandemic posed operational challenges throughout 2021. However, network operations were able to continue largely as normal.

NPL's management of the UK Heavy Metals Monitoring Network in 2021 has included the following key activities:

- NPL staff visited and fully audited all sites on the Network. This included the calibration checks and basic maintenance of the ambient air samplers, and re-assessment of local site operators' (LSOs') performance. A further visit to each site was made during the year to perform a flow calibration and leak check on the samplers.
- The Environment Agency's Ambient Air Monitoring (AAM) service team were the appointed Equipment Support Unit (ESU) and made service visits to all Network sites at least once during the year, and this included the flow calibration of instruments. In a normal year, the ESU would fulfil two service rounds. However, due to the installation of new samplers, only one visit was necessary at some sites.
- During September to December 2021, Partisol (models 2000 and 2025) samplers were replaced with Digitel (model DPA14) samplers at 18 of the 23 sites where ambient air sampling occurs.
- Ensuring data capture has remained at a very high level for the airborne PM₁₀ sampling across the Network (see Table 2).

2.2 SITE AUDITS

During 2021, the NPL Network Audit team visited all the network sites twice to perform 6-monthly site audits. These audits took place during the 1st quarter (January to March), except for Belfast Centre which was delayed until May due to COVID-19 travel restrictions, and the 3rd quarter (July to September). 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 2021, with locations, site codes, site names, and site designations, is given in Annex 1.

As required by EN 12341⁹, during each Network site audit visit NPL:

- Assessed the current condition of all on-site equipment, including the condition of the PM₁₀ sampling head and impactor plate.
- Assessed the current condition of all deposition sampling equipment.
- Check and calibration of the flow rate of the particulate monitoring equipment (for volumetric and standard flow).
- Leak tested the particulate monitoring equipment.

In summary:

- All the sites have been audited fully and were found to be performing well.
- Site infrastructure was assessed (including PAT testing and checks of fire extinguishers), and no major or minor problems were found.
- Audits of the flow-rate of the samplers were satisfactory and no remedial action was required. This flow calibration data is used to correct the volumes recorded by samplers prior to the calculation of ambient concentrations.
- The LSOs were performing their duties to a high standard.

The ESU attended all sites at least once in 2021 to perform services. The services included flow calibrations and leak checks. In a normal year, the ESU would fulfil two service rounds, in 2nd quarter (April to June) and 4th quarter (October to December). However, due to the installation of new Digitel samplers, some sites were only visited once.

Usually, the combination of the flow calibration data from the two NPL audits and two ESU services during the year supplies the three-monthly flow and leak checks required by EN14902¹⁰. In 2021, due to the installation of new Digitel samplers, the initial installation report confirming the initial flow rates constituted one of the four checks.

2.3 EQUIPMENT SERVICING AND BREAKDOWNS

- During 2021, the ESU fully serviced, carried out preventative maintenance and calibrated the flow of the samplers at least once at all Network sites. Where a new sampler had recently been installed, the second service was deemed unnecessary.
- During 2021, NPL called out the ESU to deal with sampler faults at: Pontardawe Brecon Road; Eskdalemuir; Belfast Centre; and Walsall Pleck Park.

2.4 SITE INFRASTRUCTURE AND NETWORK RE-ORGANISATION

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

- Walsall Pleck Park: Following the closure of the Walsall Bilston Lane in 2018, monitoring commenced at Walsall Pleck Park in January 2021.
- Swansea Coedgwilym: In accordance with AURN upgrades, a ladder restraint system was installed at Swansea Coedgwilym in January 2021.
- During September to December 2021, Enviro Technology (ET) Ltd replaced the Partisol 2000/2025 samplers with Digitel DPA14 samplers at 18 of the 23 sites where ambient air sampling occurs: Belfast Centre, Chadwell St Mary, Chesterfield Loundsley Green, Cwmystwyth, Detling, Eskdalemuir, Fenny Compton, Heigham Holmes, London Westminster, Pontardawe Brecon Road, Pontardawe Tawe Terrace, Port Talbot Margam, Scunthorpe Low Santon, Scunthorpe Town, Sheffield Devonshire Green, Sheffield Tinsley, Swansea Morriston Groundhog, and Yarnier Wood. The replacement at Swansea Coedgwilym and installation at Walsall Pleck Park took place in December 2020, and the replacement at the remaining three sites, Chilbolton Observatory, Auchencorth Moss and London Marylebone Road, is due to take place in early 2022.
- Detling: following a power cut and corrupted data in July 2021, an issue with degraded cable housing was identified causing electrical faults with the sampler. The cable was immediately replaced as a temporary fix, and an issue with the fence supporting part of the cable was also identified. Both the fence and cable housing were replaced. All works were completed by March 2022.
- Heigham Holmes: in January 2021 there was a planned preventative maintenance visit that identified some required electrical remedial work. In June 2021 this work was completed, and the electrical installation condition report (EICR) was carried out. The EICR identified some remaining C3 issues (improvement recommended, but not dangerous). During the process of obtaining quotes for these issues, asbestos was found in the building that houses the electrical supply for the sampler. The site owner commissioned a survey and resolved the asbestos issue in early 2022, however now structural issues have been identified, which still need to be resolved. None of these issues has affected the normal operation of the sampler.
- Cwmystwyth: In November 2021, when the new sampler was installed, it was identified that the insulated power cable has started to degrade. NPL are working with local contractors to replace the cable.

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 23 sites in the Network using Partisol 2000B, Partisol 2025A/B or Digitel DPA14 instruments (see Image 1), all fitted with PM₁₀ heads and operating at a calibrated flow rate, nominally 1 m³ h⁻¹, in accordance with EN 12341⁹. Samples were taken for a period of one week onto 47 mm diameter cellulose membrane filters.



Image 1 The Digitel DPA14 sampler at the network monitoring site at Swansea Coedgwilym.

3.2 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 Yarnier Wood. Mercury in deposition was not monitored at Lough Navar.

Sampling was performed by the UK Centre for Ecology & Hydrology (UKCEH) using bulk collectors (bottle and funnel types) in accordance with EN 15841¹¹ and EN 15853¹².

3.3 ANALYTICAL METHODOLOGY: PARTICULATE-PHASE METALS

Data are produced as four-weekly averages of concentrations for metals in the particulate phase at all sites except for the following sites that produce weekly data: Sheffield Tinsley, Swansea Coedgwilym, Swansea Morriston, Pontardawe Tawe Terrace and Pontardawe Brecon Road.

Analysis for particulate-phase metals took place at NPL following NPL's analytical procedure. This procedure is accredited by UKAS to ISO 17025¹³, and fully compliant with the requirements of EN 14902¹⁰.

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 or Multiwave 5000 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 70% nitric acid and 2 mL of 30% hydrogen peroxide.



Image 2 Anton Paar Multiwave 3000 (left) and Multiwave 5000 (right) microwaved used for acid digestion of the sampled filters.

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.

3.4 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION

During 2021, 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 UKCEHs 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 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 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, Be, Cd, Cs, Cr, Co, Cu, Fe, Pb, Li, Mn, Mo, Ni, Rb, Se, Sr, Sn, Ti, W, V and Zn being produced. The procedure is in full accordance with EN 15841¹¹.

For the mercury in deposition samples, also analysed at UKCEH 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 with pre-concentration of mercury on a gold trap to increase instrument sensitivity. This method employs a reductive desorption process. 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 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 is calibrated using gravimetrically prepared mercury in liquid standards. These standards are traceable to NIST mono-elemental reference materials. The procedure is in full accordance with EN 15853¹² and EN ISO 17852¹⁴.

3.5 MEASUREMENT UNITS

Results produced by the Network for particulate phase metals are calculated in accordance with ISO 11222¹⁵ 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: ng m^{-3} .

Results produced by the Network 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: $\text{g ha}^{-1} \text{d}^{-1}$. In this report, deposition flux is expressed in micrograms per metre squared per day: $\mu\text{g m}^{-2} \text{d}^{-1}$ (which is equivalent to $0.01 \text{ g ha}^{-1} \text{d}^{-1}$).

3.6 MEASUREMENT UNCERTAINTY

For each result produced by the Network an estimate of the uncertainty in this value is also made according to an ISO GUM (Guide to the Expression of Uncertainty in Measurement) approach, published as ISO/IEC Guide 98-3:2008¹⁶. 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 procedure used to analyse samples from the Network (metals in the particulate phase by ICP-MS) was last audited by UKAS in 2021 and retained UKAS accreditation to ISO 17025¹³. Limits of detection achievable using this procedure are comfortably below the requirements of EN 14902¹⁰.

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.
- Thorough checks of the returned filters to check for damage during transport. Rejection of damaged filters.
- 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 UKCEH), 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 14902¹⁰.
- 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 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.

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

- 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 they 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 filter analyses at NPL during 2021 are shown in Table 1. All values are a combination of the analytical and sampling uncertainties and have been derived using full, GUM compliant uncertainty budgets. All values are stated to a coverage factor of $k = 2$, providing a level of confidence of approximately 95%.

Table 1 The uncertainty range covering the majority of filter analyses at NPL during 2021.

Analyte	Uncertainty range
Arsenic (As)	10 - 16%
Cadmium (Cd)	9 - 15%
Cobalt (Co)	9 - 25%
Chromium (Cr)	10 - 35%
Copper (Cu)	9 - 14%
Iron (Fe)	10 - 13%
Manganese (Mn)	9 - 16%
Nickel (Ni)	10 - 20%
Lead (Pb)	10 - 16%
Selenium (Se)	11 - 32%
Vanadium (V)	9 - 16%
Zinc (Zn)	9 - 14%

The measurement 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 EU Air Quality Directives, which is implemented under the UK Air Quality Standards Regulations. 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 Air Quality Directive's uncertainty data quality objectives apply – 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 (PARTICULATE PHASE)

All data capture percentages 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 2021 was **98%**. Of the data lost, the majority was owing to equipment failure, site operation problems or the changeover to new samplers.

The breakdown of the overall data capture in the particulate phase and at each site is displayed in Table 2. All sites achieved more than 90% data capture for the year. This means that all sites exceed the minimum data capture requirements specified in the Ambient Air Quality Directive (2008/50/EC¹) and Fourth Air Quality Daughter Directive (2004/107/EC²).

Table 2 Particulate phase data capture across the UK Heavy Metals Monitoring Network during 2021.

Site Number: Site Location	Particulate phase data capture
62: London Westminster	99%
65: Eskdalemuir	98%
100: Swansea Coedgwilym	91%
101: Swansea Morriston	100%
103: Belfast Centre	96%
104: Port Talbot Margam	99%
106: Scunthorpe Town	100%
107: Scunthorpe Low Santon	100%
110: Chadwell St Mary	99%
113: Pontardawe Tawe Terrace	99%
114: London Marylebone Road	99%
115: Pontardawe Brecon Road	98%
117: Sheffield Tinsley	99%
119: Sheffield Devonshire Green	100%
202: Auchencorth Moss	100%
203: Yarnier Wood	98%
204: Cwmystwyth	100%
206: Heigham Holmes	100%
208: Detling	100%
209: Fenny Compton	97%
210: Chesterfield Loundsley Green	96%
211: Chilbolton Observatory	100%
213: Walsall Pleck Park	93%
Average across all sites	98%

5.2 DATA CAPTURE (DEPOSITION)

Data capture for deposition monitoring during 2021 was 84%. Deposition data capture at the sites where these measurements are made is detailed in Table 3.

Data capture is generally lower for these measurements than for others made by the Network because of a number of external factors, for example: lack of rain during sampling periods and contamination by bird fouling.

Mercury samples are taken in duplicate and over longer time periods (4 weeks rather than 1 week) so typically have higher data capture.

Table 3 Data capture across the deposition sites of the UK Heavy Metals Monitoring Network during 2021.

Site Location	Metals in Deposition	Hg in Deposition
Auchencorth Moss	85%	100%
Chilbolton	60%	92%
Heigham Holmes	85%	92%
Lough Navar	91%	N/A
Yarner Wood	65%	85%

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 time-weighting if a site has been monitoring for less than the full year.

An NPL 'Quality Circle' ratifies ambient concentration data produced by the UK Heavy Metals Monitoring Network, including deposition data provided by UKCEH. 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.
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 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 Air Quality Directives^{1,2} an additional component of uncertainty due to incomplete time coverage may be determined by the procedure described in ISO 11222¹⁵. 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 11222¹⁵, using the data capture percentage from Swansea Coedgwilym (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 Air Quality Directives. Exemplar expanded uncertainties, quoted at the 95% confidence interval, for the annual mean concentration values of the relevant Air Quality Directives 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 Directive metals in particulate matter, averaged across the Network.

Analyte	Annual Mean Relative Expanded Uncertainty	Directive maximum
As	13%	40%
Cd	11%	40%
Ni	13%	40%
Pb	13%	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 Directives.

6 NETWORK DATA

6.1 MEASURED CONCENTRATIONS (PM PHASE)

The annual mean measured metals concentrations in 2021, 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 website¹⁷.

Table 5 The 2021 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.

Analyte	2021 UK Mean Annual Concentration across all sites (ng m ⁻³)	2021 UK Median Annual Concentration across all sites (ng m ⁻³)	2021 Maximum Annual Mean Concentration at any site (ng m ⁻³)	EC limit or target value [UK objective] (ng m ⁻³)
As	0.66	0.69	1.02	6
Cd	0.23	0.13	0.99	5
Co	0.28	0.11	2.90	-
Cr	3.36	1.79	32.7	-
Cu	8.05	4.49	34.2	-
Fe	472	214	2633	-
Mn	11.1	4.48	82.9	-
Ni	3.50	0.90	25.0	20
Pb	7.42	5.61	21.8	500 [250]
Se	0.58	0.49	1.66	-
V	1.40	0.86	9.60	-
Zn	21.3	13.8	85.2	-

Table 6 The 2021 annual mean concentrations (ng m⁻³) measured at individual sites on the UK Heavy Metals Monitoring Network.

Site	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
62: London Westminster	0.79	0.12	0.08	1.83	10.3	388	5.22	0.77	5.82	0.45	1.07	17.0
65: Eskdalemuir	0.15	0.02	0.02	0.36	0.73	47.6	1.22	0.26	0.77	0.23	0.26	2.59
100: Swansea Coedgwilym	0.71	0.30	0.46	2.02	16.4	161	3.85	11.2	21.8	0.50	0.51	12.3
101: Swansea Morriston	1.02	0.37	0.35	3.42	25.5	732	9.25	10.1	9.98	0.57	0.75	25.1
103: Belfast Centre	0.45	0.06	0.11	0.81	5.22	215	3.47	0.84	3.12	0.39	0.96	12.7
104: Port Talbot Margam	0.85	0.99	0.21	3.64	13.6	2633	29.3	1.12	8.24	0.74	3.77	48.2
106: Scunthorpe Town	0.69	0.33	0.11	1.79	4.49	600	21.5	0.94	12.5	0.89	1.65	22.7
107: Scunthorpe Low Santon	0.73	0.80	0.23	3.57	4.18	1918	82.9	1.17	21.0	1.02	9.60	33.8
110: Chadwell St Mary	0.88	0.18	0.09	1.22	8.09	334	5.39	1.31	11.4	0.46	3.02	22.7
113: Pontardawe Tawe Terrace	0.67	0.28	2.90	5.62	4.45	214	6.32	25.0	5.88	0.54	0.59	13.8
114: London Marylebone Road	0.87	0.13	0.17	6.30	34.2	1295	12.4	1.33	5.61	0.49	1.23	30.8
115: Pontardawe Brecon Road	0.69	0.25	0.38	1.59	4.85	200	3.86	6.29	5.61	0.49	0.52	13.8
117: Sheffield Tinsley	0.98	0.35	0.65	32.7	15.9	593	34.6	13.6	14.2	1.66	1.22	85.2
119: Sheffield Devonshire Green	0.63	0.25	0.16	4.82	7.40	318	7.56	2.20	14.8	0.94	0.69	46.1
202: Auchencorth Moss	0.19	0.02	0.02	0.46	0.79	49.0	1.26	0.14	0.80	0.23	0.23	3.21
203: Yarner Wood	0.40	0.06	0.03	0.41	1.10	64.8	1.87	0.43	1.66	0.37	0.89	5.35
204: Cwmystwyth	0.25	0.05	0.02	0.37	0.71	49.5	1.40	0.25	1.33	0.33	0.35	3.62
206: Heigham Holmes	0.54	0.08	0.04	0.37	1.51	78.2	2.41	0.55	2.87	0.50	1.18	8.06
208: Detling	0.74	0.13	0.06	0.61	3.38	130	3.49	0.68	5.37	0.42	1.17	11.8
209: Fenny Compton	0.81	0.09	0.04	0.52	2.22	111	2.46	0.34	3.22	0.46	0.53	9.45
210: Chesterfield Loundsley Green	0.59	0.10	0.07	2.04	3.52	158	4.48	0.90	4.64	0.67	0.46	17.3
211: Chilbolton Observatory	0.61	0.09	0.04	0.46	2.08	98.1	2.37	0.42	3.03	0.41	0.86	8.38
213: Walsall Pleck Park	0.83	0.22	0.12	2.30	14.5	460	7.86	0.85	7.03	0.61	0.65	35.2

Colour key: **red = above target value**; **orange = above upper assessment threshold**; **yellow = above lower assessment threshold**.

6.2 MEASURED CONCENTRATIONS WITH RESPECT TO THE REQUIREMENTS OF THE EU AIR QUALITY DIRECTIVES

In Figure 2, the annual mean concentrations are compared against the relevant limit and target values from the EU Air Quality Directives. Annual mean concentrations for the relevant Air Quality Directives metals at all Network sites in 2021 are displayed in Figure 3.

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

- Nickel: Pontardawe Tawe Terrace
- Cadmium: Port Talbot Margam
- Lead: Scunthorpe Low Santon
- Arsenic: Swansea Morriston.

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

- Nickel at Pontardawe Tawe Terrace: exceedance of the target value (125%)
- Nickel at Sheffield Tinsley: exceedance of the LAT value (68% of the target value)
- Nickel at Swansea Coedgwilym: exceedance of the LAT value (56% of the target value)
- Nickel at Swansea Morriston: exceedance of the LAT value (50% 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 a nickel alloy production facility. Whilst the site is usually 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 an elevated position on the valley side. There are also other industrial sources in the area.

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.

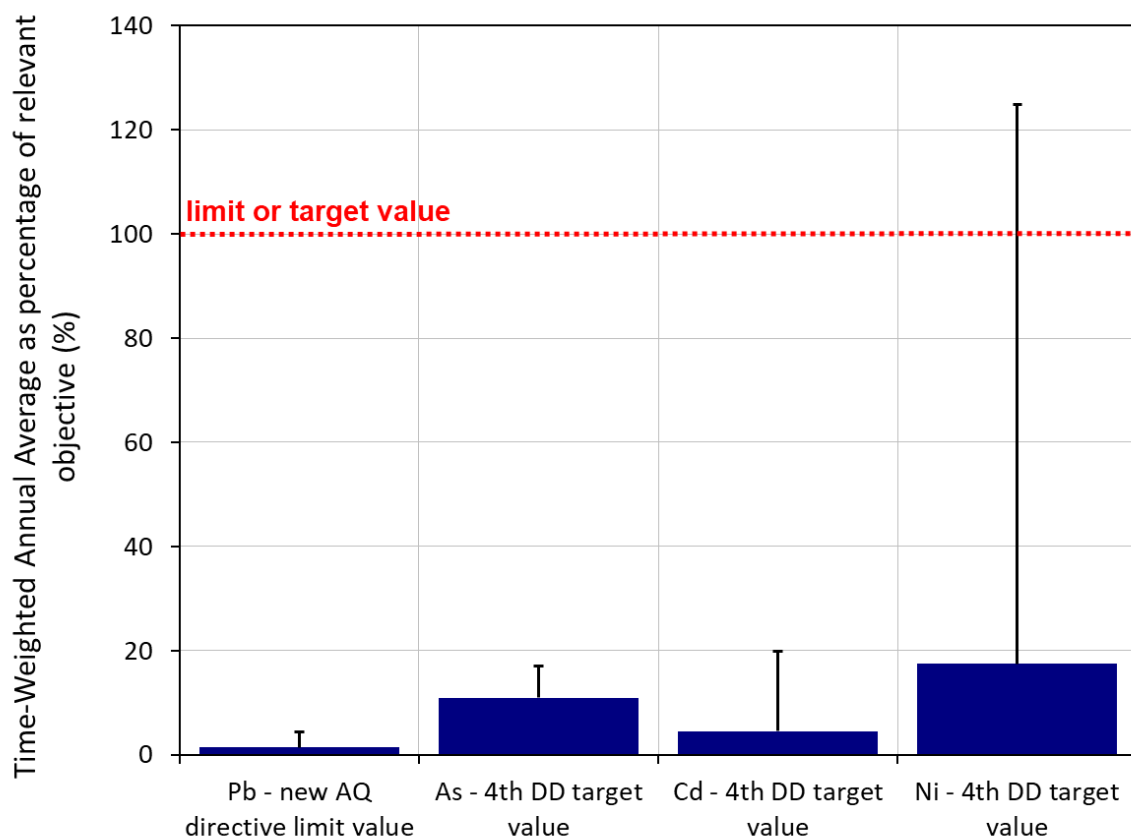


Figure 2 A summary of the annual mean concentrations of the heavy metals relevant to the Ambient Air Quality Directive and Fourth DD measured on the Network in 2021 as a percentage of the relevant air quality objectives. The bars indicate the annual mean of all sites; the lines indicate the annual mean at the site with the highest concentrations.

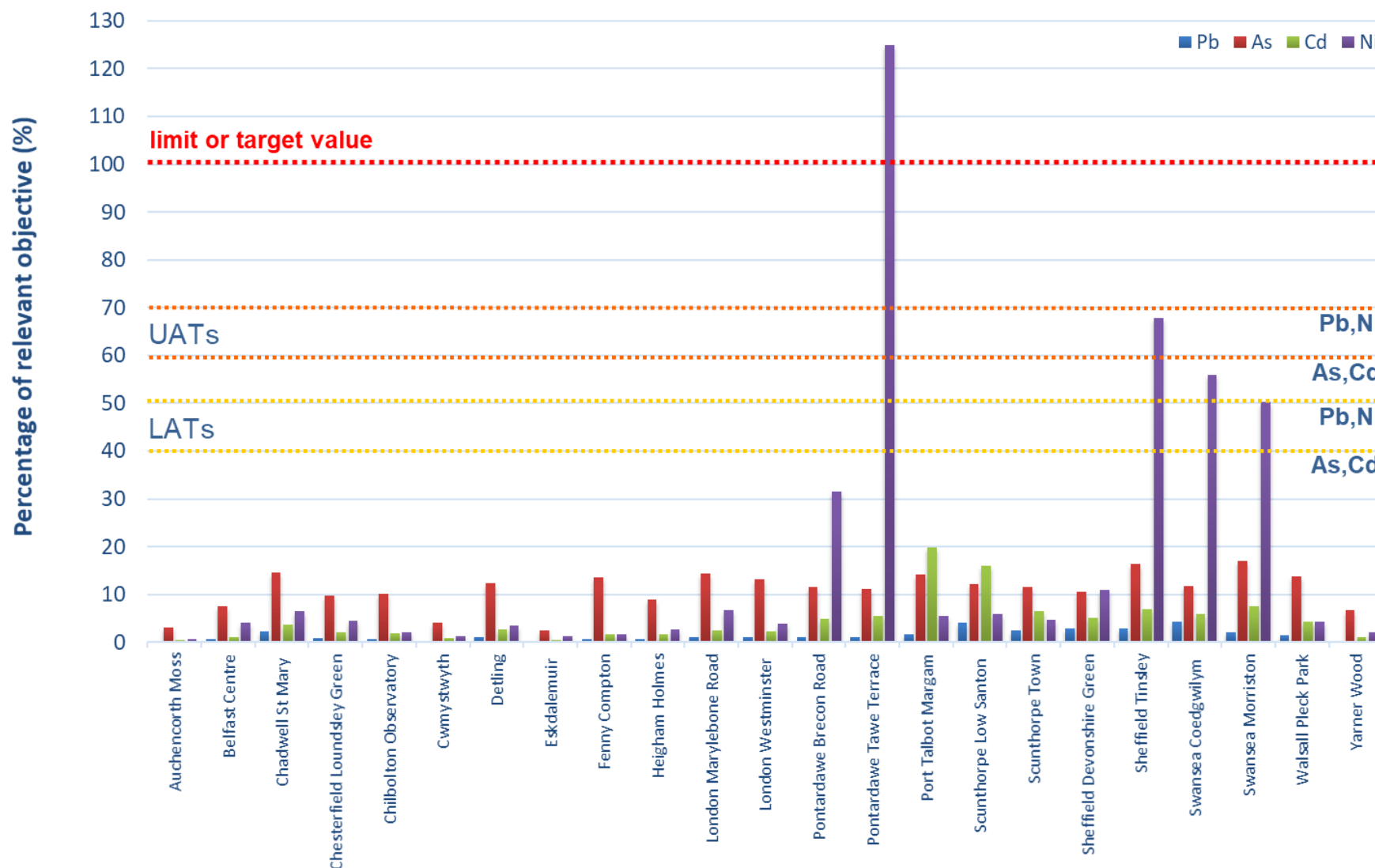


Figure 3 A summary of the annual mean measured concentrations of the heavy metals relevant to the New Air Quality Directive and Fourth DD at all sites on the UK Heavy Metals Monitoring Network in 2021 as a percentage of the relevant target values shown in red, upper assessment thresholds (UATs) in orange and lower assessment thresholds (LATs) in yellow.

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 arsenic⁷, 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 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.

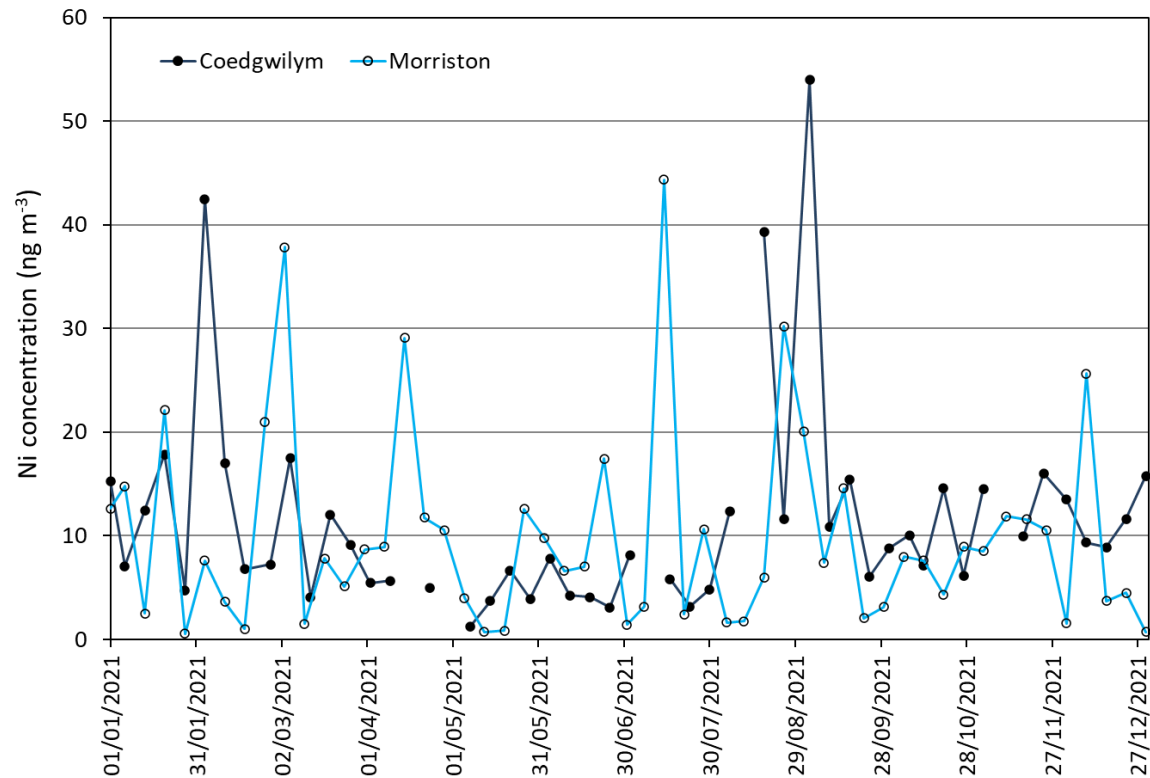


Figure 4 Measured Ni concentrations at Site 100: Swansea Coedgwilym and Site 101: Swansea Morryston, in 2021 (both sampled weekly).

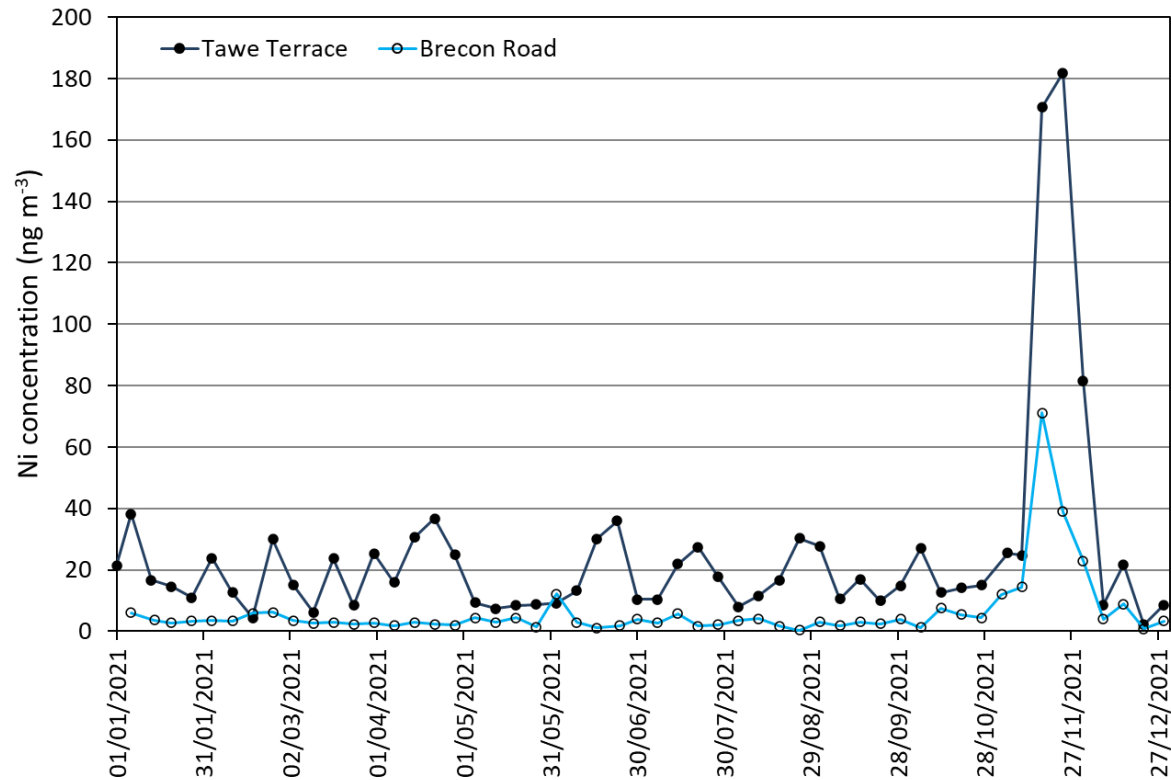


Figure 5 Measured Ni concentrations at Site 113: Pontardawe Tawe Terrace and Site 115: Pontardawe Brecon Road, in 2021 (both sampled weekly).

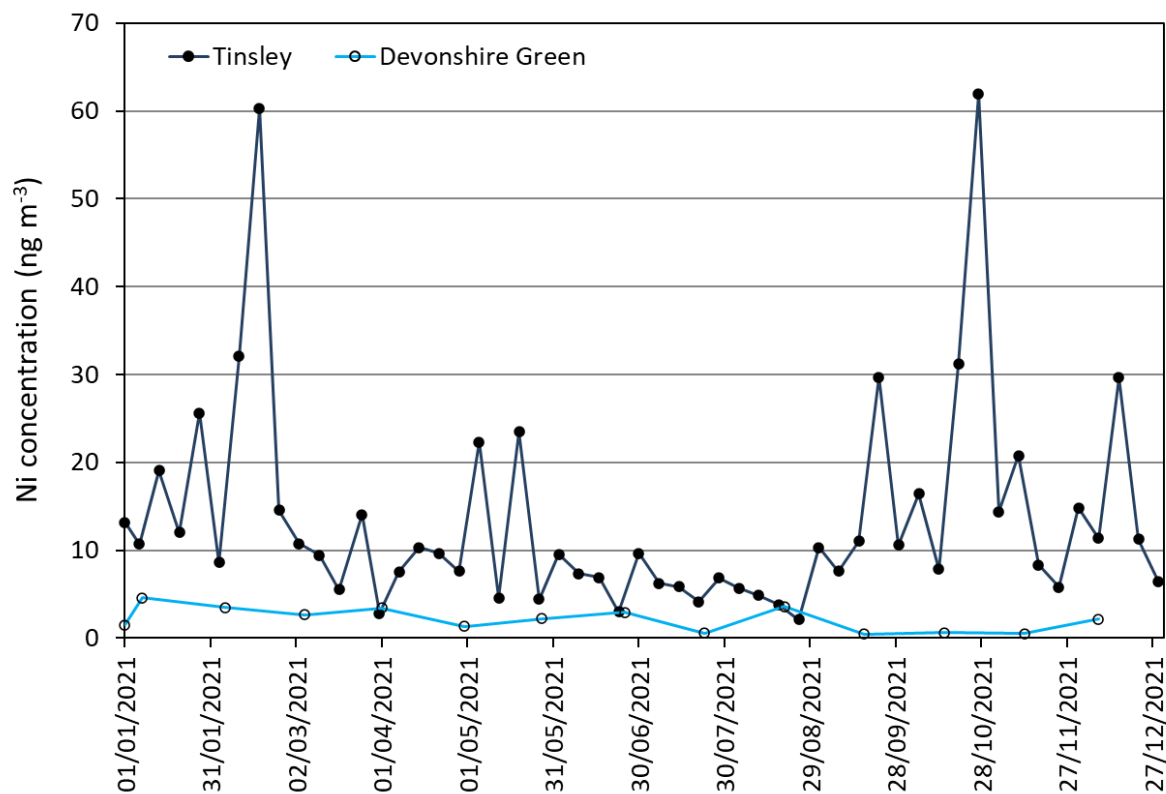


Figure 6 Measured Ni concentrations at Site 117: Sheffield Tinsley and Site 119: Sheffield Devonshire Green in 2021. Sampling at Tinsley is weekly. Results from Sheffield Devonshire Green are averaged over four-week periods.

6.4 MEASURED CONCENTRATIONS OF NON-DIRECTIVE METALS

Figure 7 shows the concentrations of the non-Directive metals normalised to the annual median value for each metal across all sites. The annual average concentrations were given in Table 6.

High concentration values for non-directive 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-Directive metals, as would be expected.

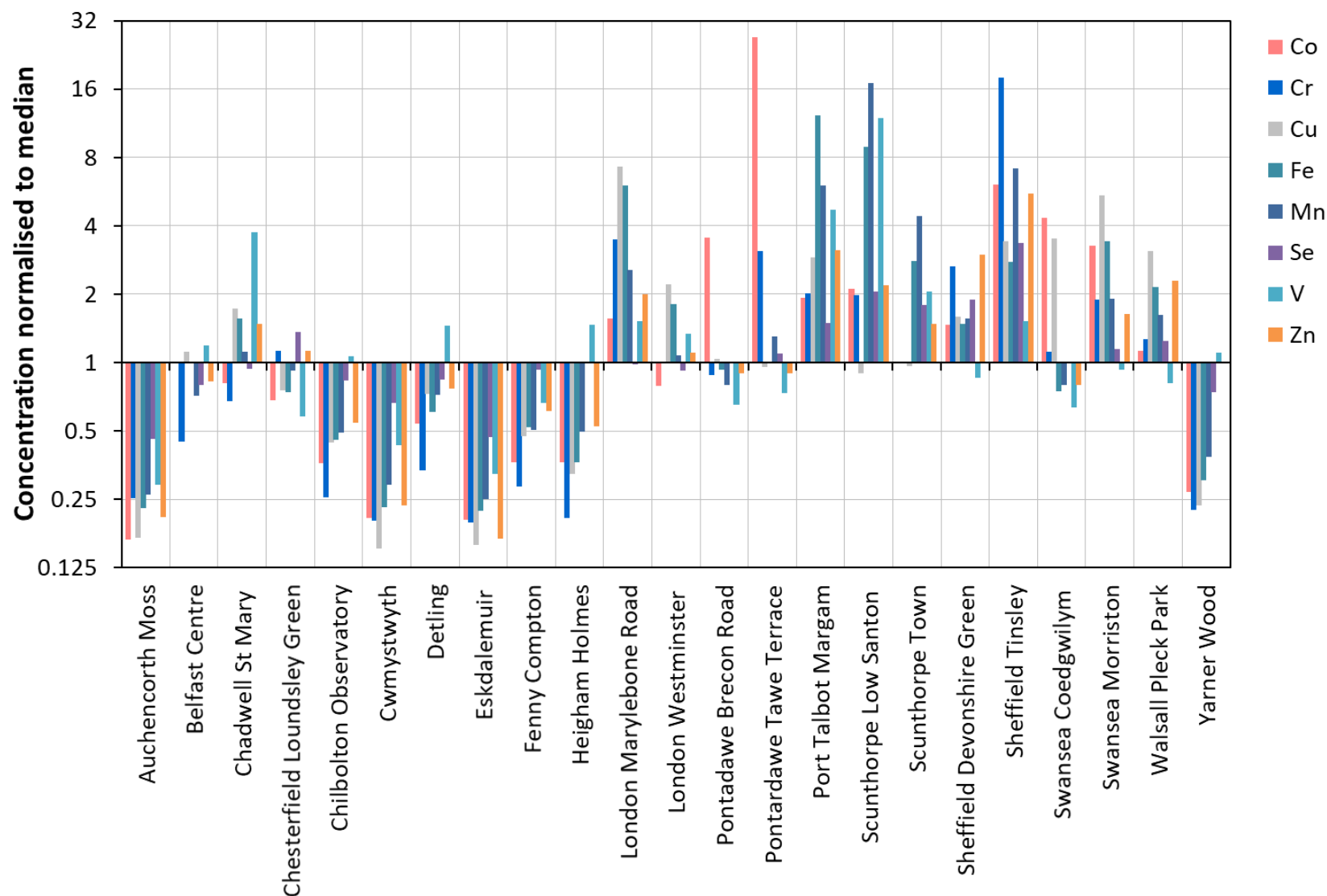


Figure 7 A summary of the annual mean measured concentrations of the non-directive metals at all sites on the UK Heavy Metals Monitoring Network in 2021, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median, so it is clear which 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 2021, averaged over all sites sampling metals in deposition (Table 7), and at individual sites (Table 8), are given below.

Table 7 The 2021 annual mean, median and maximum deposition flux measurements (in $\mu\text{g m}^{-2} \text{d}^{-1}$) averaged over all deposition monitoring sites on the UK Heavy Metals Monitoring Network.

Analyte	2021 UK Mean Annual Flux across all sites ($\mu\text{g m}^{-2} \text{d}^{-1}$)	2021 UK Median Annual Flux across all sites ($\mu\text{g m}^{-2} \text{d}^{-1}$)	2021 UK Maximum Annual Flux at any site ($\mu\text{g m}^{-2} \text{d}^{-1}$)
Al	8.1	5.2	21.8
As	0.22	0.14	0.48
Ba	0.66	0.78	1.00
Be	0.004	0.003	0.007
Cd	0.01	0.01	0.02
Co	0.01	0.01	0.02
Cr	0.18	0.11	0.48
Cs	0.006	0.003	0.016
Cu	0.81	0.76	1.07
Fe	10.6	9.4	14.6
Hg	0.007	0.006	0.011
Li	0.09	0.08	0.18
Mn	2.02	1.59	3.91
Mo	0.06	0.04	0.14
Ni	0.14	0.08	0.25
Pb	0.13	0.12	0.17
Rb	0.30	0.19	0.92
Sb	0.07	0.07	0.08
Se	0.25	0.20	0.40
Sn	0.05	0.03	0.17
Sr	3.85	3.23	7.75
Ti	0.26	0.20	0.63
U	0.005	0.003	0.017
V	0.28	0.20	0.70
W	0.03	0.02	0.11
Zn	2.78	2.24	4.29

Table 8 The 2021 annual mean deposition flux measurements (in $\mu\text{g m}^{-2} \text{d}^{-1}$) measured at individual deposition monitoring sites on the UK Heavy Metals Monitoring Network.

Analyte	Auchencorth Moss	Chilbolton	Heigham Holmes	Lough Navar	Yarner Wood
Al	5.37	5.21	4.80	3.46	21.8
As	0.09	0.11	0.14	0.48	0.28
Ba	0.31	0.80	0.78	0.39	1.00
Be	0.003	0.002	0.002	0.007	0.006
Cd	0.004	0.006	0.010	0.009	0.025
Co	0.008	0.008	0.009	0.015	0.022
Cr	0.11	0.07	0.07	0.48	0.14
Cs	0.003	0.003	0.003	0.004	0.02
Cu	1.03	0.60	0.59	0.76	1.07
Fe	9.40	6.33	9.40	14.6	13.3
Hg	0.006	0.006	0.006	N/A	0.011
Li	0.03	0.04	0.08	0.18	0.14
Mn	0.86	0.94	1.59	2.81	3.91
Mo	0.03	0.03	0.04	0.14	0.06
Ni	0.07	0.07	0.08	0.24	0.25
Pb	0.11	0.09	0.14	0.12	0.17
Rb	0.07	0.08	0.19	0.23	0.92
Sb	0.06	0.07	0.08	0.06	0.07
Se	0.16	0.13	0.20	0.35	0.40
Sn	0.02	0.02	0.03	0.17	0.04
Sr	0.99	1.66	3.23	7.75	5.61
Ti	0.13	0.13	0.24	0.20	0.63
U	0.002	0.002	0.003	0.017	0.003
V	0.08	0.20	0.17	0.23	0.70
W	0.01	0.01	0.02	0.11	0.02
Zn	2.24	2.01	3.12	2.22	4.29

7 TRENDS IN MEASURED CONCENTRATIONS

7.1 TRENDS IN PARTICULATE-PHASE METALS

Trends in concentrations measured over the last 41 years for the metals relevant to the Air Quality Directives are summarised in Figure 8 and Figure 9, where both the UK mean and median concentrations are displayed.

The trends in both the UK annual mean and median observed for the other metals measured by the 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 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. This generally mirrors the decrease in emissions over this period (see Figure 1). 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.

One exception to this is copper. The annual mean concentration has shown a decrease between 1990-2019 (latest data available), but the estimated annual emissions have shown a gradual increase⁵. This increase in emissions has been associated with the increased use of lubricants in road vehicles (a source which was retrospectively added to the emissions estimation in 2019). Lubricant use in road vehicles currently contributes 50% of UK copper emissions. The other major source is vehicle brake pad wear, which contributed 45% in 2019. Excluding road vehicles lubricants, emissions from other sources have declined by 11% since 1990, due to the decline in metal production¹⁸. A possible reason that the increase in copper emissions is not reflected in increased ambient air concentrations is because of the small number of network sites directly measuring traffic emissions.

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 gradual downward trend in the median.

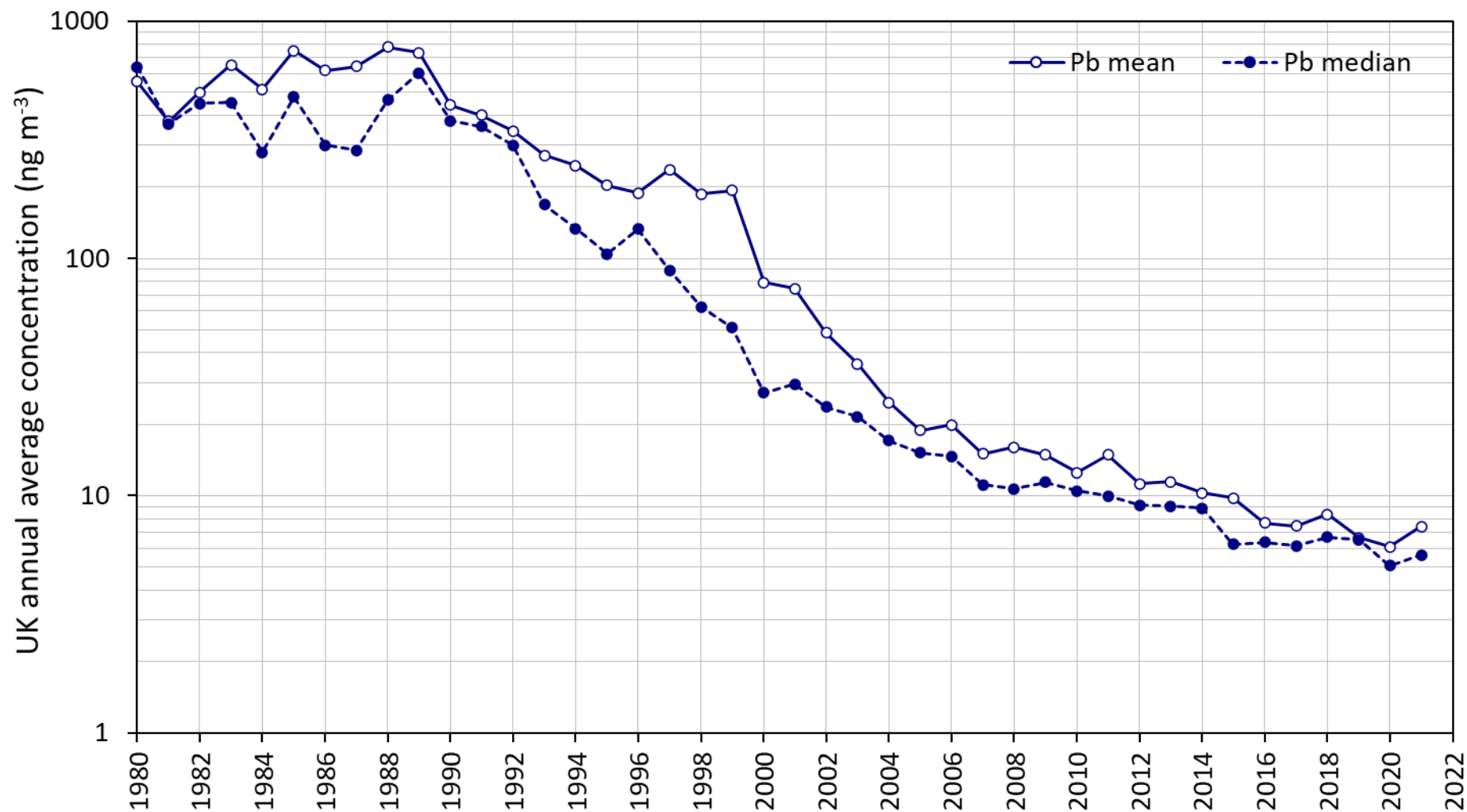


Figure 8 The mean and median of site annual average concentrations of Pb measured on the UK Heavy Metals Monitoring Network over the last 41 years. The EC limit value for lead is 500 ng m^{-3} and the UK Air Quality Objective for lead is 250 ng m^{-3} . Note the logarithmic scale on the y-axis.

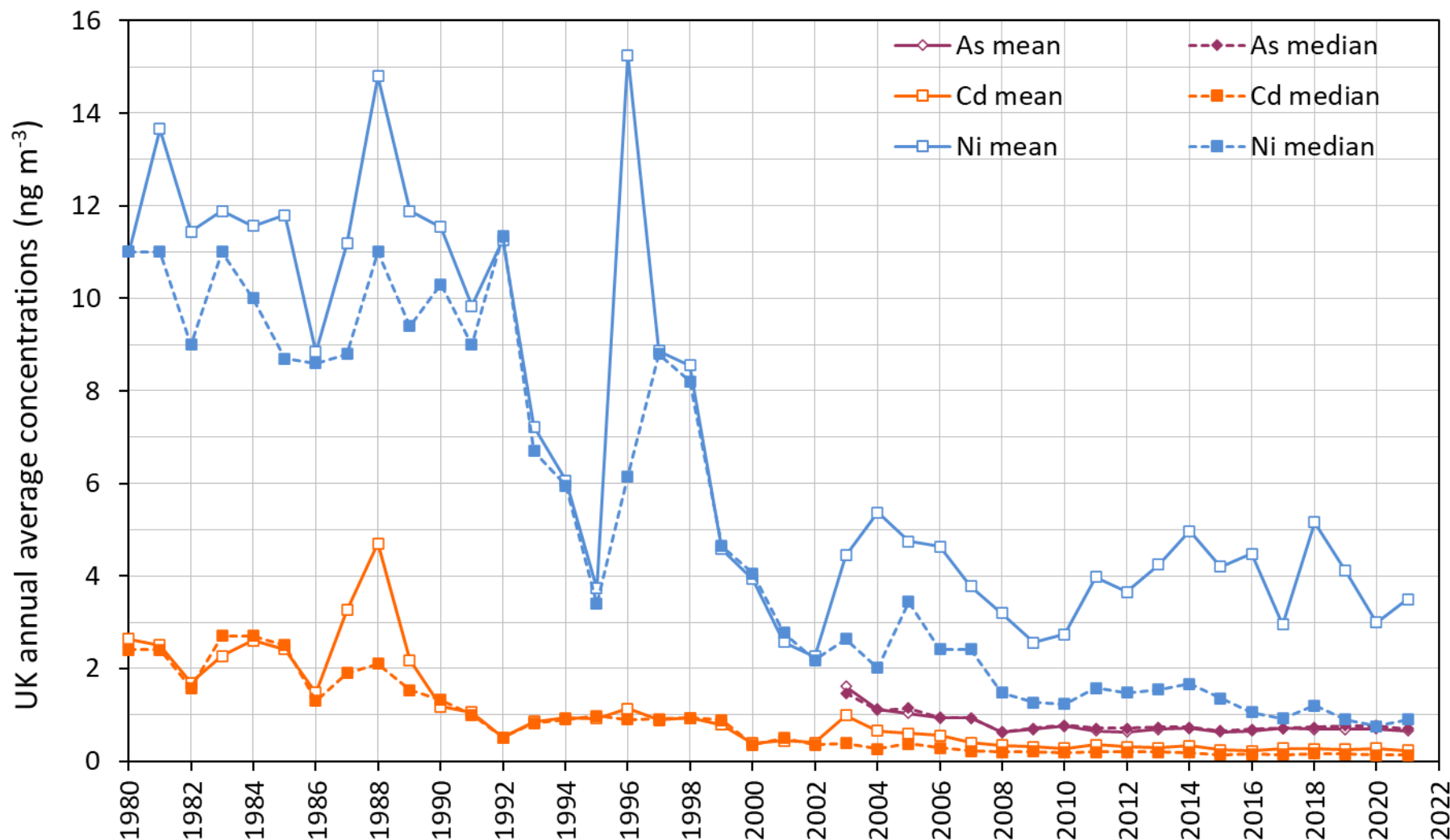


Figure 9 The mean and median of site annual average concentrations of Ni, As, and Cd measured on the UK Heavy Metals Monitoring Network over the last 41 years. The EC target values for Ni, As and Cd are 20 ng m⁻³, 6 ng m⁻³ and 5 ng m⁻³ respectively.

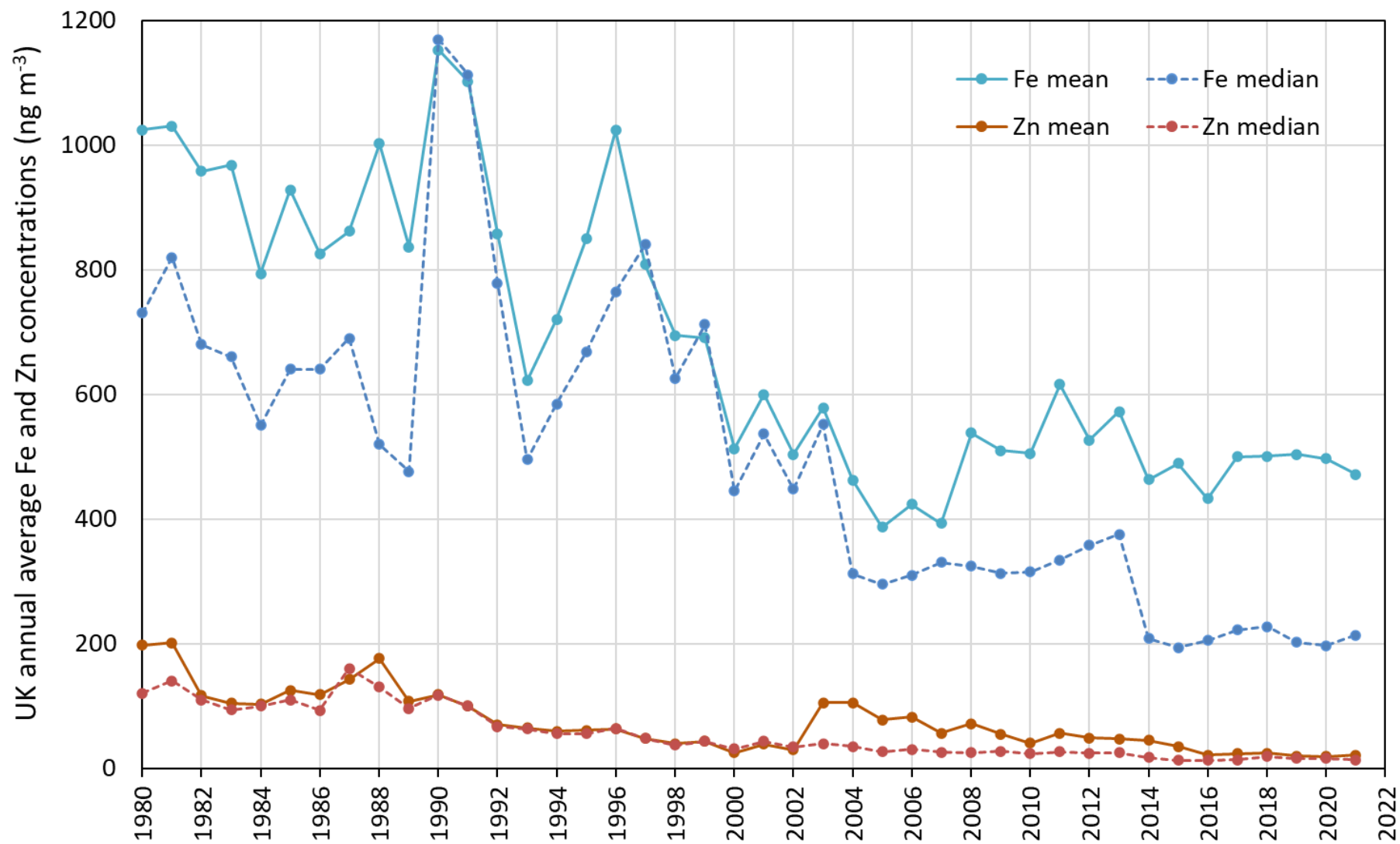


Figure 10 The mean and median of site annual average concentrations of Fe and Zn measured on the UK Heavy Metals Monitoring Network over the last 41 years.

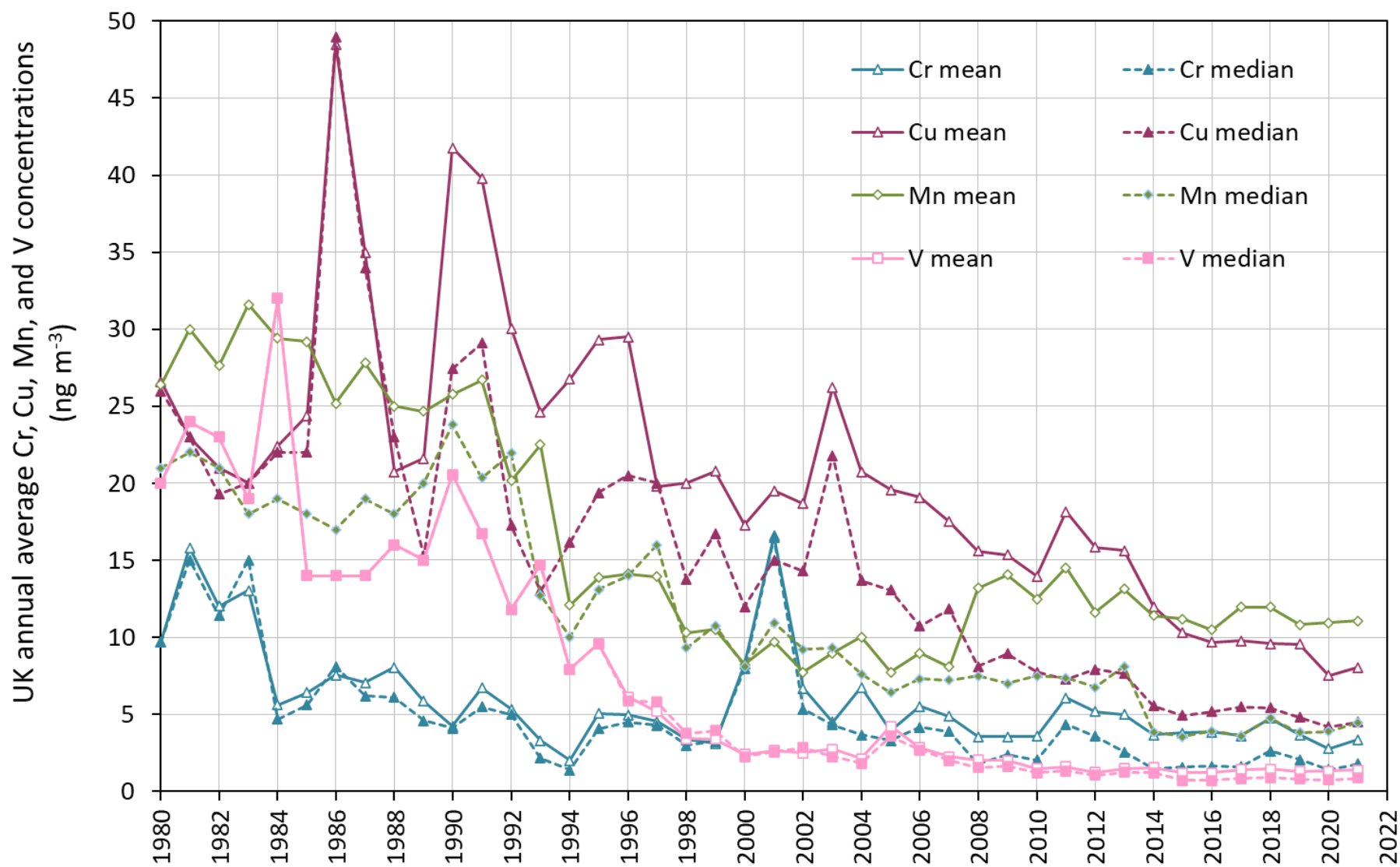


Figure 11 The mean and median of site annual average concentrations of Cr, Cu, Mn, and V measured on the UK Heavy Metals Monitoring Network over the last 41 years.

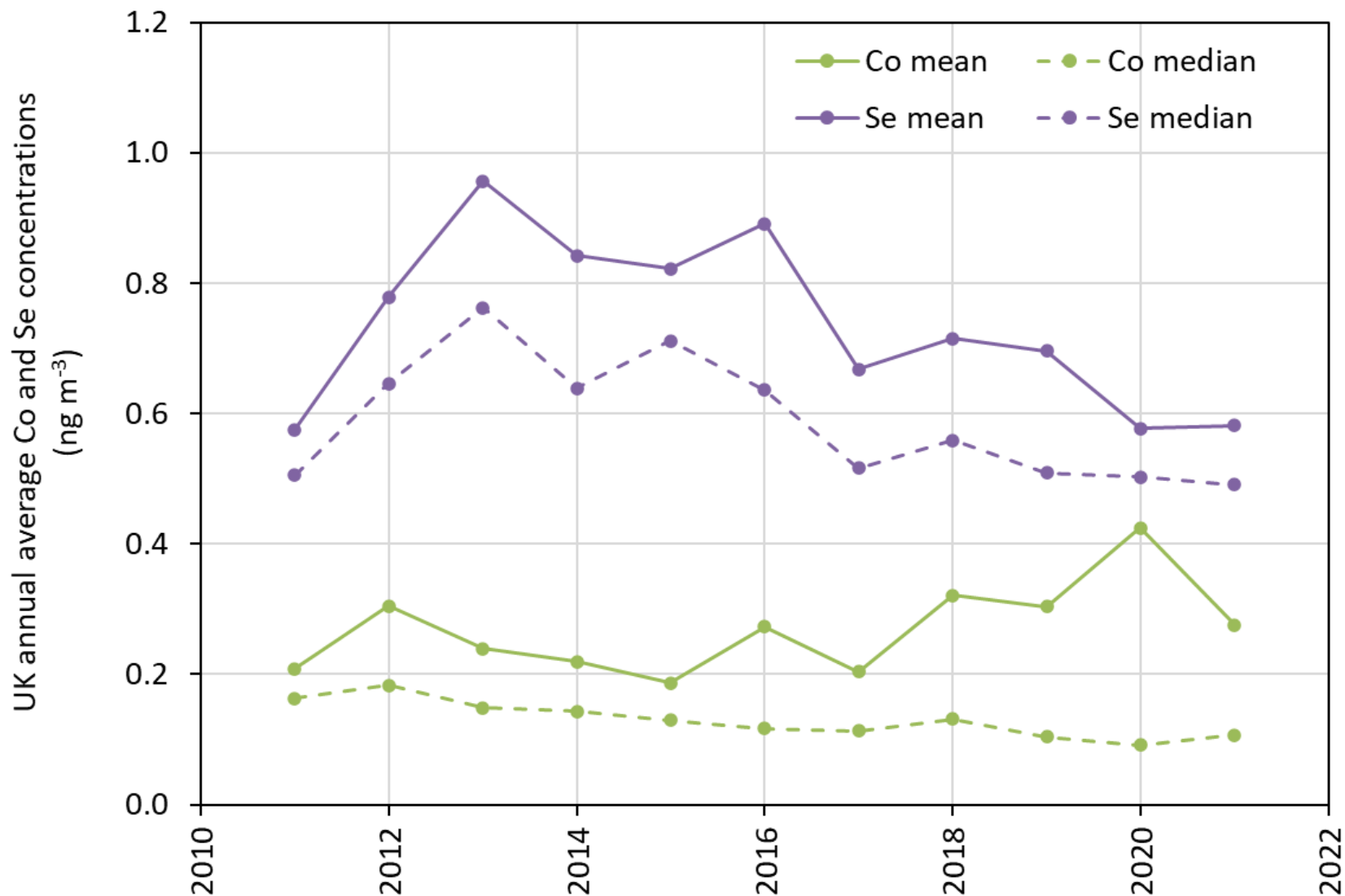


Figure 12 The mean and median of site annual average concentrations of Co and Se measured on the UK Heavy Metals Monitoring Network since monitoring commenced for these metals in 2011.

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 18 years 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 UK Heavy Metals Monitoring 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 (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 an exceedance of the target value, again attributed to abatement issues at the industrial facility. Concentrations have since fallen although have continued to exceed the target value.

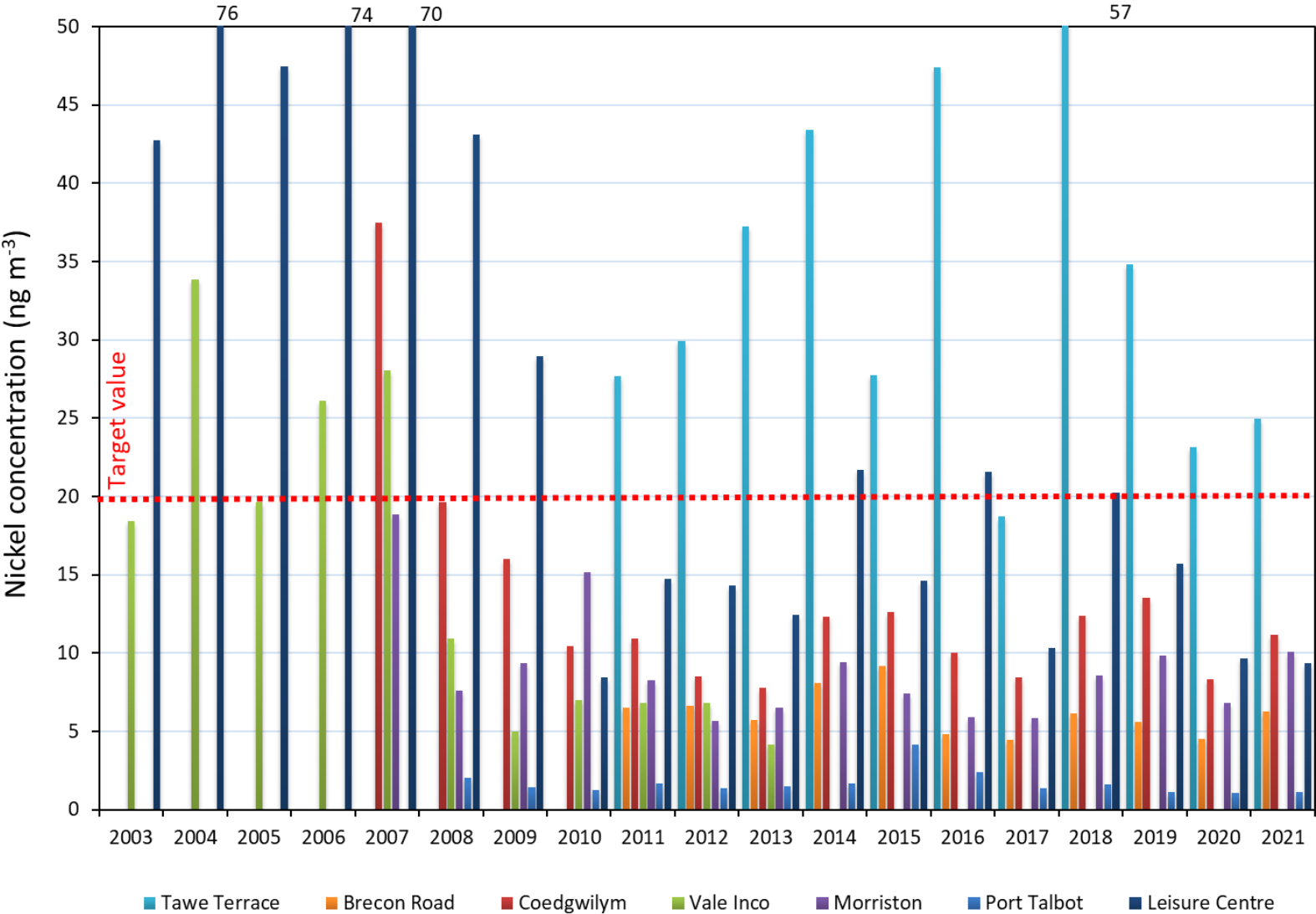


Figure 13 The annual average nickel concentrations measured at monitoring sites in the Swansea area 2003-21. The red dotted line indicates the Fourth DD target value for nickel.

7.3 TRENDS IN DEPOSITION METALS

Trends in deposition metal concentrations measured since 2010 (the year from which data is available on UK-AIR¹⁷) for the metals relevant to the Air Quality Directives 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. Please note, 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 mercury to bio-accumulate makes it of particular importance in deposition samples, so this trend is plotted in Figure 18.

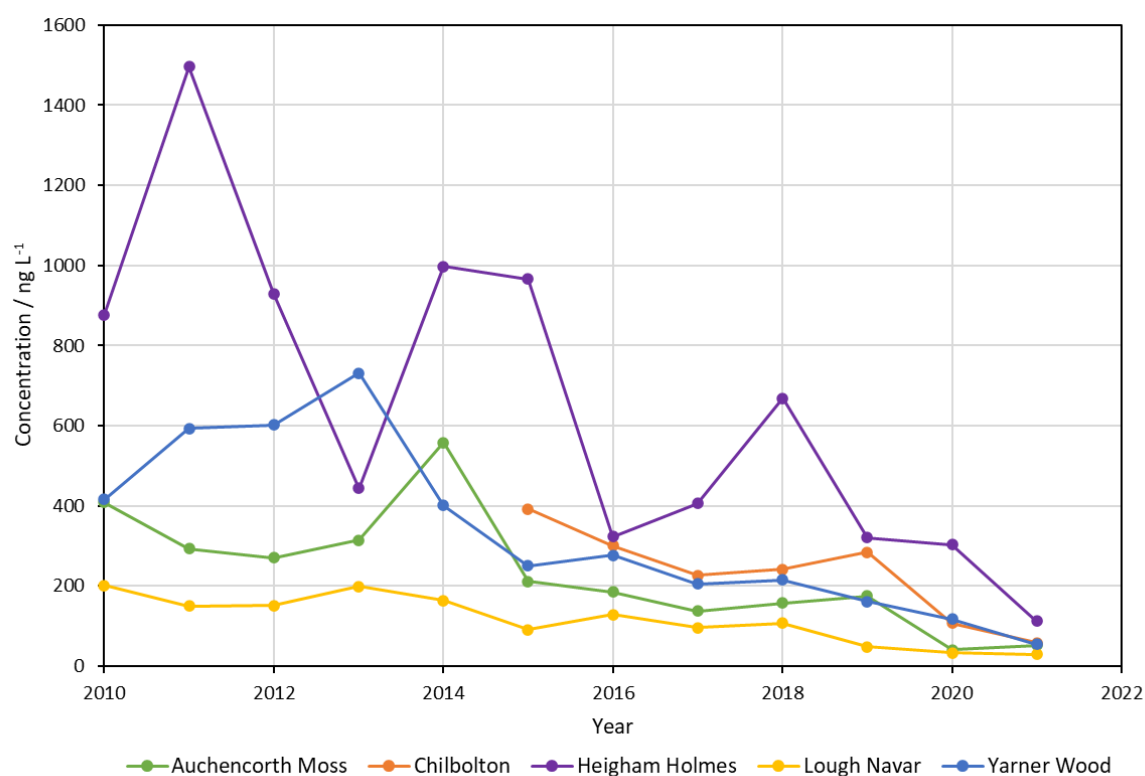


Figure 14 The mean annual concentrations of Pb measured in deposition since 2010 at individual sites.

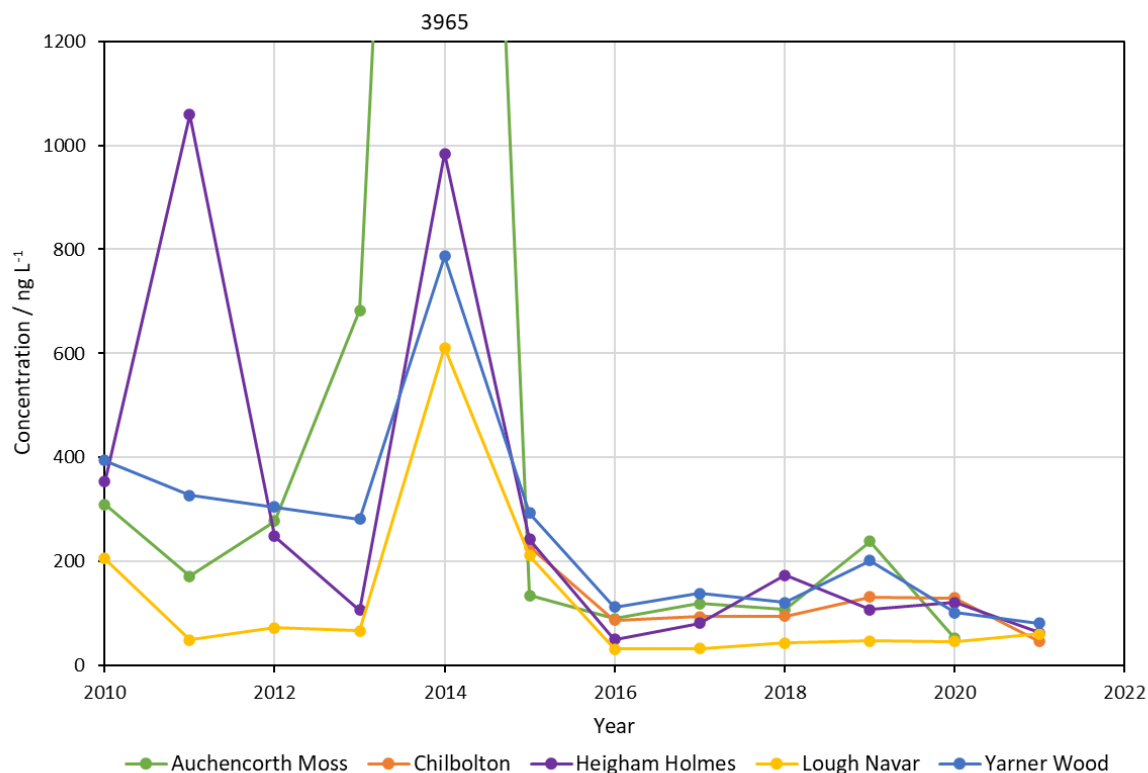


Figure 15 The mean annual concentrations of Ni measured in deposition since 2010 at individual sites.

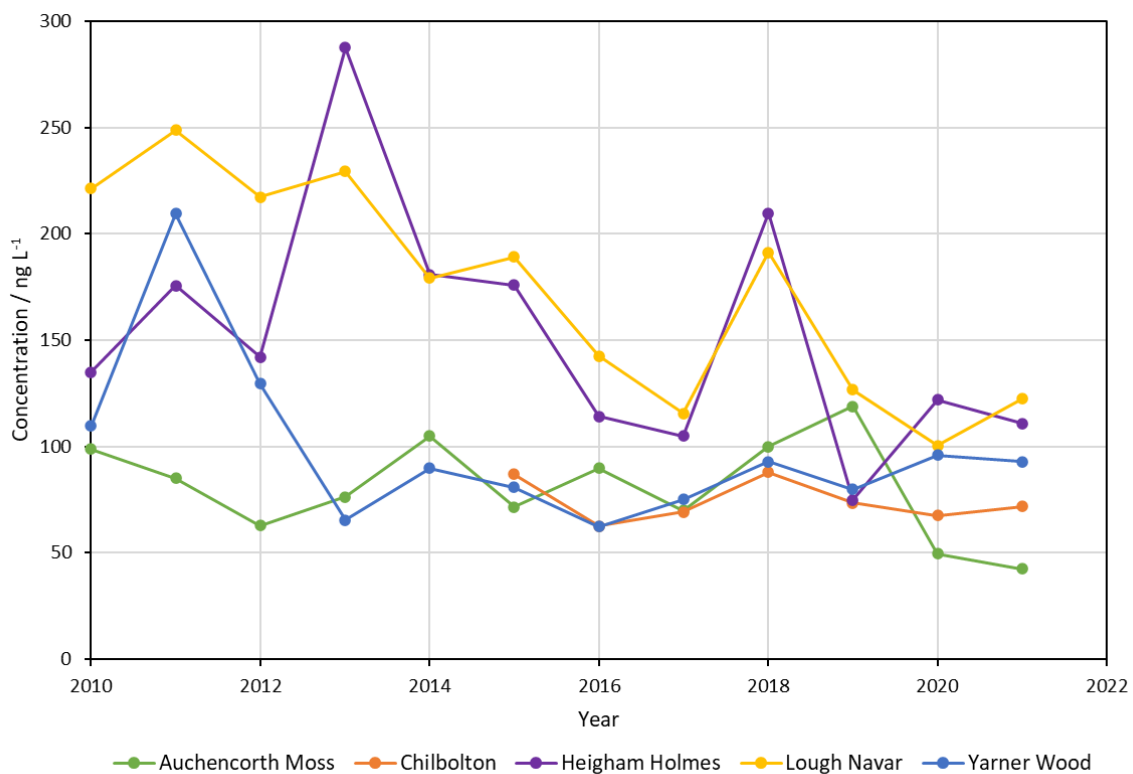


Figure 16 The mean annual concentrations of As measured in deposition since 2010 at individual sites.

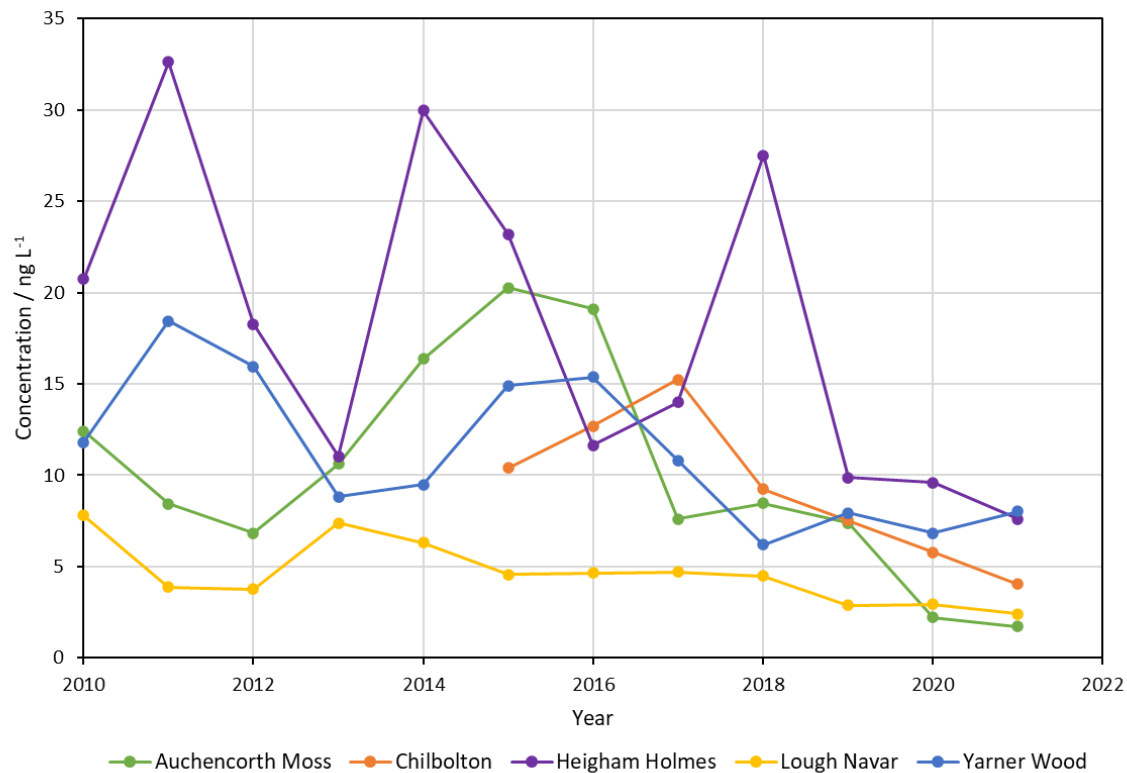


Figure 17 The mean annual concentrations of Cd measured in deposition since 2010 at individual sites.

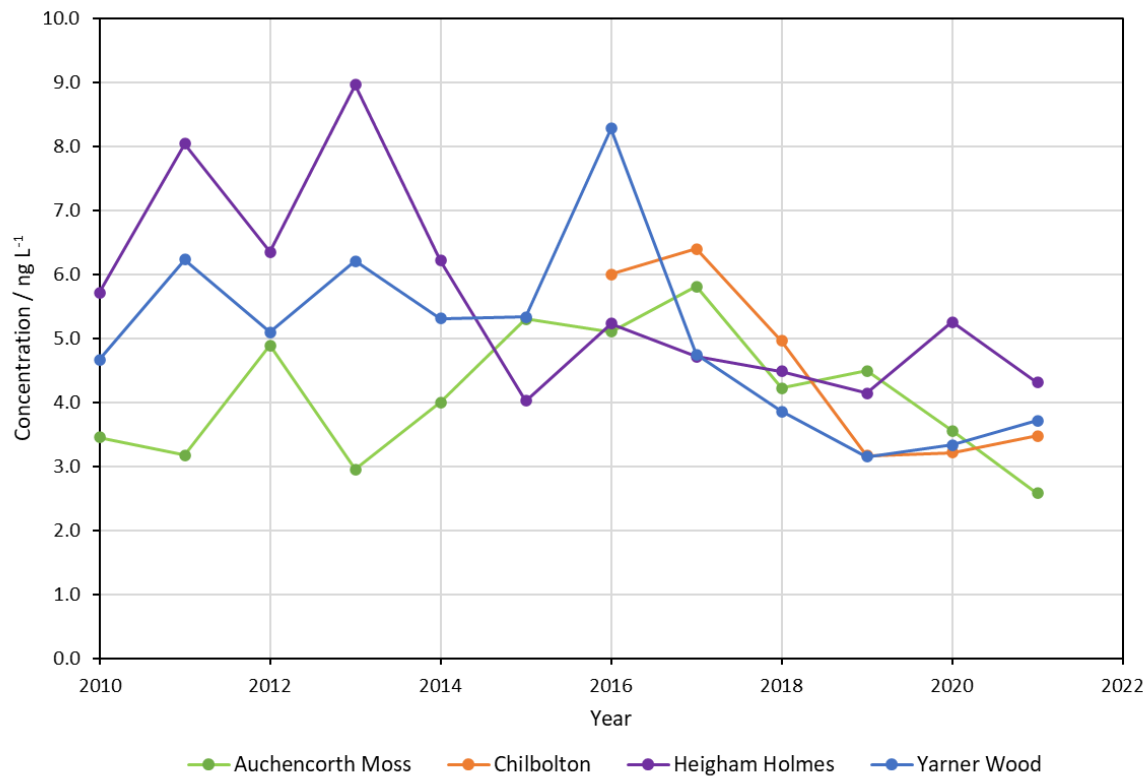


Figure 18 The mean annual concentrations of Hg measured in deposition since 2010 at individual sites. Hg is not measured at Lough Navar.

ANNEX 1: LOCATION AND DETAILS OF SITES COMPRISING THE UK HEAVY METALS NETWORK IN 2021



Figure 19 Location of monitoring sites comprising the UK Heavy Metals Monitoring Network during 2021 (indicated by the coloured circles, see key) – details of which are given in Table 9 below.

Table 9 Details of the sites comprising the UK Heavy Metals Monitoring Network, including: name, location, classification, and pollutants measured – (p) denotes metals in particulate matter (PM), (d) denotes metals in deposition.

Site Code: Site Name	Site Address	Site Classification	Pollutants measured
62: London Westminster	Mortuary Car Park, Horseferry Road, London, SW1P 2EB	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
65: Eskdalemuir	Met Office, Eskdalemuir, Langholm, Dumfriesshire, DG13 0QW	Rural Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
100: Swansea Coedgwilym	Coedgwilym Cemetery, Pontardawe Road, Clydach, Swansea, SA6 5PB	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
101: Swansea Morriston	Morriston Groundhog, Wychtree Street, Morriston, Swansea, SA6 8EX	Urban Traffic	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
103: Belfast Centre	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 Fire Station, Commercial Road, Port Talbot, West Glamorgan, SA13 1LG	Urban Industrial	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
106: Scunthorpe Town	Rowlands Road, Scunthorpe, North Lincolnshire, DN16 1TJ	Urban Industrial	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
107: Scunthorpe Low Santon	Dawes Lane, Santon, Scunthorpe, North Lincolnshire, DN16 1XH	Urban Industrial	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
110: Chadwell St Mary	Council Area Housing Office, Linford Road, Chadwell St Mary, Essex, RM16 4JY	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
113: Pontardawe Tawe Terrace	Tawe Terrace, Pontardawe, Swansea, West Glamorgan, SA8 4HA	Urban Industrial	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
114: London 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	Dany Bryn Residential Care, 84 Brecon Road, Pontardawe, Swansea, SA8 4PD	Industrial Suburban	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
117: Sheffield Tinsley	Ingfield Avenue, Tinsley, Sheffield. S9 1WZ	Urban Industrial	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
119: Sheffield Devonshire Green	Devonshire St, Sheffield, South Yorkshire. S3 7SW	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn

Site Code: Site Name	Site Address	Site Classification	Pollutants measured
202: Auchencorth Moss	UKCEH Edinburgh, Bush Estate, Penicuik, Midlothian, EH26 0QB	Rural Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d): 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
203: Yarner Wood	Natural England, Yarner Wood, Bovey Tracey, Devon, TQ13 9LJ	Rural Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d): 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
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	Gardeners Cottage, Burnley Hall, East Somerton, Great Yarmouth, Norfolk, NR29 4DZ	Rural Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d): 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
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 Dasset CE Primary School, Memorial Road, Fenny Compton, Warwickshire, CV47 2XU	Rural background	(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	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn (d): 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
213: Walsall Pleck Park	Montford Road, Walsall, West Midlands. WS2 9DE	Urban Background	(p): As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn
UKA00166: Lough Navar	Lough Navar, Glennasheevar Road, Derrygonnelly, Enniskillen, Fermanagh, BT93 6AH	Rural Background	(d): 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

REFERENCES

- ¹ 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.
- ² 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.
- ³ Commission Directive (EU) 2015/1480 of 28 August 2015 amending several annexes to Directives 2004/107/EC and 2008/50/EC of the European Parliament and of the Council laying down the rules concerning reference methods, data validation and location of sampling points for the assessment of ambient air quality, *Official Journal L 226*, 29/8/2015 P. 0004–0011.
- ⁴ Air Quality Strategy for England, Scotland, Wales and Northern Ireland, 2007, Cmd paper No 7169 NIA 61/06-07.
- ⁵ National Atmospheric Emissions Inventory, www.naei.org.uk
- ⁶ 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.
- ⁷ 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.
- ⁸ Concentration trends of metals in ambient air in the UK: a review. Goddard, S. L., *et al*, *Environmental Monitoring and Assessment*, **106**, Article number: 683 (2019)
- ⁹ European standard, EN 12341:2014. *Ambient air - Standard gravimetric measurement method for the determination of the PM₁₀ or PM_{2.5} mass concentration of suspended particulate matter.*
- ¹⁰ European standard, EN 14902:2005. *Ambient air quality - Standard method for the measurement of Pb, Cd, As and Ni in the PM₁₀ fraction of suspended particulate matter.*
- ¹¹ European Standard, EN 15841:2009. *Ambient air quality - Standard method for determination of arsenic, cadmium, lead and nickel in atmospheric deposition.*
- ¹² European Standard, EN 15853:2010. *Ambient air quality - Standard method for the determination of mercury deposition.*
- ¹³ International standard, ISO/IEC 17025:2017. *General requirements for the competence of testing and calibration laboratories.*
- ¹⁴ International standard, ISO 17852:2008. *Water quality - Determination of mercury. Method using a combined preservation and digestion step followed by atomic fluorescence spectrometry.*
- ¹⁵ International standard, ISO 11222:2002. *Air quality - Determination of the uncertainty of the time average of air quality measurements.*
- ¹⁶ International standard, ISO/IEC GUIDE 98-3:2008. *Uncertainty of measurement. Guide to the expression of uncertainty in measurement.*
- ¹⁷ UK AIR, Air Information Resource, <https://uk-air.defra.gov.uk/>
- ¹⁸ National Atmospheric Emissions Inventory - Pollutant Information: Copper https://naei.beis.gov.uk/overview/pollutants?pollutant_id=13