

**THE UK HEAVY METALS MONITORING NETWORK:
ANNUAL REPORT 2024**

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Approved on behalf of NPLML by
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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 the PM₁₀ (particulate matter with an aerodynamic diameter < 10 µm) fraction of ambient air and deposition (precipitation) 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 (Defra) 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 2024 annual report contains:

- A summary of the HM Network structure, operation, and quality procedures.
- Annual mass concentrations of metals measured at all HM Network sites.
- Performance against relevant data quality objectives (DQOs) and requirements of the UK Air Quality Standards Regulations (AQSR) 2010.
- Highlighting of AQSR 2010 exceedances (for lead, nickel, arsenic, and cadmium in PM₁₀), interpretation of data, and discussion of trends across the HM Network.

In 2024, the HM Network operated ambient air and deposition samplers across the UK at 23 monitoring sites with a mixture of site classifications: rural (background), suburban (industrial), and urban (background, traffic, and industrial). Thirteen of the sites were in England, six in Wales, two in Scotland, and two in Northern Ireland. In 2024, the HM Network reported data for:

Analyte	Instrument(s)	Frequency	Sites
Metals in PM ₁₀ (As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Se, V, Zn)	Ambient air sampler and inductively-coupled plasma mass spectrometer	Weekly or four-weekly	22
Metals in deposition (Al, As, Ba, Be, Cd, Co, Cr, Cs, Cu, Fe, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, U, W, V, Zn)	Deposition collector and inductively-coupled plasma mass spectrometer	Weekly or monthly	5
Mercury in deposition	Precipitation collector and atomic fluorescence analyser	Monthly	4

In summary for 2024:

- Metals in PM₁₀
 - **Lead:** There were no annual average mass concentrations above the AQSR 2010 lower assessment threshold (LAT) at any HM Network site. Recorded concentrations were well below the limit value set by the AQSR 2010.
 - **Nickel:** No sites had an annual average mass concentration above the AQSR 2010 target value. For two sites, Sheffield Tinsley and Pontardawe Tawe Terrace, the annual average concentrations were above the LAT, with Sheffield Tinsley also exceeding the upper assessment threshold (UAT).

- **Arsenic and cadmium:** There were no annual average mass concentrations above the AQSR 2010 LAT. Recorded concentrations were well below the target values set by the AQSR 2010.
 - DQOs regarding time coverage, data capture, and measurement uncertainty requirements specified in the AQSR 2010 were met for all sites except for one - Heigham Holmes, where an electrical fault meant the site was not operational for most of the year. DQOs for number of sampling points were met for all zones and agglomerations, except for two - Eastern and Northwest & Merseyside. However modelled data suggests concentrations remain low in these zones.
 - Average data capture for metals in PM₁₀ during 2024 was **93 %**.
 - In addition to the AQSR 2010 metals (lead, nickel, arsenic, and cadmium), concentrations in PM₁₀ were also recorded for cobalt, chromium, copper, iron, manganese, selenium, vanadium, and zinc.
- **Metals in Deposition**
 - As required by AQSR 2010, European monitoring and evaluation programme (EMEP) and the convention to protect the marine environment in the North-East Atlantic (OSPAR), concentrations of arsenic, cadmium, chromium, copper, lead, nickel, mercury, and zinc in deposition were monitored at five sites during 2024, including one coastal site.
 - DQOs regarding time coverage, data capture, and measurement uncertainty requirements specified in the AQSR 2010 were met for all sites.
 - Average data capture for metals in deposition it was **98 %**.
 - In addition to the AQSR 2010, EMEP, and OPSAR metals concentrations in deposition were also recorded for a larger suite of metals, as listed in the table above.

Fully ratified data from the HM Network can be downloaded from the Defra UK-AIR air information resource website¹

1 INTRODUCTION

1.1 OVERVIEW

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

This annual report for the HM Network for 2024 contains a summary of:

- Network operation, management, and notable changes
- Analytical methodology and quality assurance / quality control (QA/QC) procedures
- Performance against relevant data quality objectives (DQOs) and requirements of the UK Air Quality Standards Regulations (AQSR) 2010^{2,3,4,5}, and all associated amendments
- Annual mass concentrations of all metals measured at all HM Network sites for metals in the PM₁₀ (particulate matter with an aerodynamic diameter < 10 µm) fraction of ambient air and deposition (precipitation)
- Highlighting of AQSR 2010 limit value exceedances and discussion of trends

1.2 BACKGROUND

The HM Network has a number of objectives:

- Achieve compliance with monitoring requirements set out in the UK AQSR 2010^{2,3,4,5} (and all associated amendments), and international conventions to which the UK is a signatory, including EMEP and OSPAR
- Provide data to government on the UK's performance against the limit values, target values, and DQOs described in the relevant legislation
- Assess impacts around 'hot spots' of metallic pollution in air, particularly industrial areas
- Produce accurate and reliable data for dissemination to the general public and for use by scientific and medical researchers and the air quality community
- Provide background concentrations as a baseline for air quality modelling
- Provide accurate ambient concentration data to benchmark against emissions inventory estimates

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 to the general public, inform other scientific endeavours (for example climate change research), and provide an infrastructure that can respond to new and 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 mass concentration levels of arsenic (As), cadmium (Cd), nickel (Ni), and lead (Pb) allowable in the PM₁₀ fraction of ambient air are limited by AQSR 2010, and associated amendments. In order to demonstrate compliance with AQSR 2010, the total mass concentration levels of ambient metals need to be measured at multiple sites nationwide. 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 As, Cd, Ni, and Pb in the PM₁₀ fraction of ambient air.

Further to this, the Air Quality Strategy for England, Scotland, Wales and Northern Ireland 2007⁶ also sets out a lower objective for Pb of 250 ng m⁻³; half that of the AQSR 2010 limit value (500 ng m⁻³).

For metals in deposition, AQSR 2010 requires monitoring of As, Cd, Ni, and mercury (Hg). In addition to these four, the European monitoring and evaluation programme⁷ (EMEP) and the convention to protect the marine environment in the North-East Atlantic⁸, OSPAR (named after the original Oslo and Paris conventions) require monitoring of Pb, chromium (Cr), copper (Cu), and zinc (Zn).

A larger suite of metals in PM₁₀ and deposition are measured using the same samples to provide additional information on sources, trends, and the UK's pollution climate.

The AQSR 2010 (and all associated amendments) follow the requirements of the 2004 and 2008 EU Air Quality Directives (and all associated amendments)^{9,10}. The new 2024 European Air Quality Directive¹¹ combines and updates the previous directives.

With regards to metals in PM₁₀ and in deposition, there are no major differences to most of the requirements in the new 2024 European Directive. The regulated pollutants and target/limit values are the same, except Pb is now also a requirement for deposition, whereas previously it was only requirement under OSPAR. The DQOs are largely the same - the maximum uncertainty (for fixed measurements), minimum data capture, and reference methods are the same, except for deposition where the minimum data capture has decreased slightly, and the uncertainty requirements have been removed and replaced with a reference to EMEP requirements.

Some key differences to note are that pollutants previously assigned "target values" have now also been assigned "limit values", however these are currently the same, so it is only a nominal change; the lower and upper assessment thresholds (either 40 % and 60 %, or 50 % and 70 %) have been consolidated into a single assessment threshold of 50 %; and number of sampling points has changed. However, it is outside the remit of this report to fully assess the differences.

Emissions of metals in the UK arise from a variety of sources including in particular:

- Industrial, domestic, and public power combustion
- Metals and chemical processing industries
- Road transport
- Waste incineration
- Iron and steel industry
- Break and tyre wear from road vehicles

The National Atmospheric Emissions Inventory (NAEI)¹² 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 (Mn), attributed to increased biomass burning¹³, and Cu, which has been attributed to road vehicle engine lubricants and brake pad wear¹⁴.

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 published¹⁵. This has shown an additional benefit of the HM Network is to contribute supplementary evidence to validate emissions inventory data. The past 50 years of UK metals emissions relevant to those measured on the HM Network are displayed in Figure 1.

Further information on the history of the HM Network can be found in a 2008 NPL publication that marked a quarter of a century of the nationwide monitoring of metals in ambient air¹⁶. A follow-up review of concentration trends was published by NPL in 2019¹⁷. Additionally, 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 methods¹⁸.

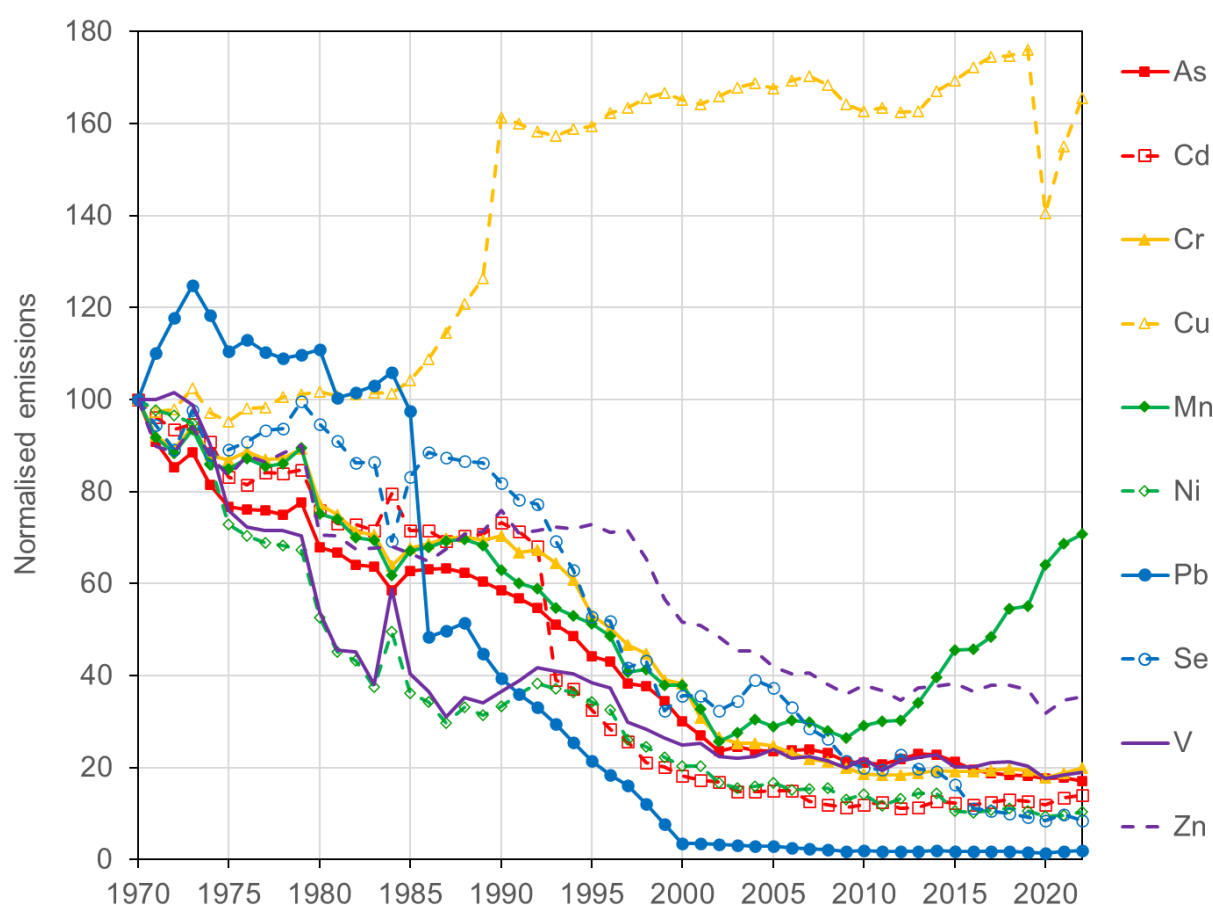


Figure 1 - Estimated UK annual emissions of the metals from 1970 to 2022¹² (the most recent year for which data were available at time of publication) normalised to their values in 1970. The absolute levels of emissions in 1970, in tonnes, were: As, 81; Cd, 36; Cr, 257; Cu, 431; Pb, 7493; Mn, 146; Ni, 993; Se, 93; V, 2750; and Zn, 1511. Emissions data are not available for Co or Fe.

2 NETWORK INFRASTRUTURE AND OPERATION

2.1 OVERVIEW

In 2024, the HM Network was structured and managed in the same way as the previous year. Details about site locations, network management, and notable changes are given below.

2.2 NETWORK SITES

During 2024, the HM Network comprised 23 monitoring sites around the UK (13 in England, six in Wales, two in Scotland, and two in Northern Ireland) sampling PM₁₀ in ambient air and/or deposition as detailed in Figure 2 and Table 1.



Figure 2 - Map of monitoring sites comprising the HM Network during 2024.
Key: purple = PM₁₀ only; yellow = deposition only, orange = both PM₁₀ and deposition;
number = multiple sites within region.

Table 1 - Details of the sites comprising the HM Network in 2024, including name, region, classification, and pollutants measured.

Site Name	Region	UK-AIR Site ID ¹	Site Type [1]	PM ₁₀ [2]	Deposition [3]
Auchencorth Moss	Scotland - Central Scotland	UKA00451	RB	Four-weekly	Weekly (Hg monthly)
Belfast Centre	Northern Ireland	UKA00212	UB	Four-weekly	-
Chesterfield Loundsley Green	England - East Midlands	UKA00604	UB	Four-weekly	-
Chilbolton Observatory	England - South-east	UKA00614	RB	Four-weekly	Weekly (Hg monthly)
Cwmystwyth	Wales - South	UKA00325	RB	Four-weekly	-
Detling	England - South-east	UKA00481	RB	Four-weekly	-
Eskdalemuir	Scotland - Scottish Borders	UKA00130	RB	Four-weekly	-
Fenny Compton	England - West Midlands	UKA00606	RB	Four-weekly	-
Heigham Holmes	England - East	UKA00461	RB	Four-weekly	Monthly (Hg monthly)
London Marylebone Road	England - London	UKA00315	UT	Four-weekly	-
London Westminster	England - London	UKA00435	UB	Four-weekly	-
Lough Navar	Northern Ireland	UKA00166	RB	-	Monthly
Pontardawe Brecon Road	Wales - South	UKA00560	IS	Weekly	-
Pontardawe Tawe Terrace	Wales - South	UKA00557	UI	Weekly	-
Port Talbot Margam	Wales - South	UKA00501	UI	Four-weekly	-
Scunthorpe Low Santon	England - Yorkshire & Humberside	UKA00506	UI	Four-weekly	-
Scunthorpe Town	England - Yorkshire & Humberside	UKA00381	UI	Four-weekly	-
Sheffield Devonshire Green	England - Yorkshire & Humberside	UKA00575	UB	Four-weekly	-
Sheffield Tinsley	England - Yorkshire & Humberside	UKA00181	UI	Weekly	-

Site Name	Region	UK-AIR Site ID ¹	Site Type [1]	PM ₁₀ [2]	Deposition [3]
Swansea Coedgwilym	Wales - South	UKA00520	UB	Weekly [4]	-
Swansea Morriston	Wales - South	UKA00521	UT	Weekly [4]	-
Walsall Pleck Park	England - West Midlands	UKA00820	UB	Four-weekly	-
Yarner Wood	England - South-west	UKA00168	RB	Four-weekly	Weekly (Hg monthly)

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

[2] PM₁₀: 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-weekly 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 metals in PM₁₀ is subsidised by the Welsh Government.

2.3 NETWORK MANAGEMENT

The day-to-day operation of the HM Network is set up to mirror that of the Automatic Urban and Rural Network (AURN), which includes a central management and control unit (CMCU) and a quality assurance and quality control (QA/QC) unit. In 2024, NPL continued its role as the main CMCU and QA/QC unit.

CMCU activities include management of equipment, consumables, and health and safety (H&S); management of subcontractors such as local site operators (LSOs) and the equipment support unit (ESU); collection and storage of data; reporting; and providing technical advice to the Environment Agency.

QA/QC activities include ensuring adherence to the appropriate technical standards; training and auditing LSOs; managing equipment services and calibrations; and data ratification and submission to the data dissemination unit (DDU).

NPL continued to undertake dispatch and analysis of the PM₁₀ samples, including associated CMCU and QA/QC activities. UK Centre for Ecology & Hydrology (UKCEH) remained the subcontractor of all deposition samples and were responsible for the associated CMCU and QA/QC activities.

NPL audited all sites on the HM Network. This included a flow calibration check and leak check of the ambient air samplers, H&S checks, and re-assessment of LSO performance. A second visit to each site was made during the year to perform a flow calibration check and leak check on the samplers. Further details can be found in section 2.5.

The Environment Agency Ambient Air Monitoring (AAM) service team were the appointed (ESU and carried out the two 6-monthly service visits (including flow calibration) and all ad-hoc callouts at each operational site during the year, except Auchencorth Moss, where Enviro Technology Services Ltd (ET) were the appointed ESU between January and October 2024, and therefore carried out the first of the two 6-monthly service visits and any callouts during this period. Further details can be found in section 2.6.

2.4 NOTABLE CHANGES

Changes to the operation of the HM Network and infrastructure issues during 2024 are detailed below:

- Beccles – following the closure of the Chadwell St. Mary site in October 2023, a location for a new site in Beccles is being sought.
- Detling – as of 1 November 2024, the Environment Agency took over the lease for the site.
- Heigham Holmes – the electrical supply for the PM₁₀ sampler tripped on 1 May 2024, but due to structural issues with the building housing the trip switch, no access was possible to resolve issue directly. The site owner has approved installation of a new power cable and relocation of sampler as a long-term solution. This work is currently in progress. The site has continued to collect deposition samples throughout.
- Yarner Wood – replacement of sampler power supply cable in March 2024.

2.5 SITE AUDITS

During 2024, the NPL network audit team visited all the operational HM Network sites twice to perform six-monthly site audits. These audits took place during the first quarter (Q1, January to March) and the third quarter (Q3, July to September). At these visits, the following was carried out:

- Assessment of site infrastructure, performance, and integrity.
- Auditing of LSO competency during one of the two audit visits, and extra training if required.
- Assessment of the condition of all deposition sampling equipment.
- Assessment of the condition of all PM sampling equipment, including the requirements of BS EN 12341¹⁹:
 - In-service inspection and testing (ISIT, previously known as Portable Appliance Testing, PAT)
 - Assessment of the condition of the sampler, including the condition of the PM₁₀ sampling head and impactor plate, to ensure regular maintenance of components of the sampler was being carried out as appropriate.
 - Checks to ensure components were operating within the required limits:
 - pressure and temperature (p/T) 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; the LSOs were performing their duties to a high standard; and most samplers were found to be performing well - all except three of the flow rate checks and leak checks were satisfactory, the exceptions were:

- London Westminster – difference between measured and set flow rate close to limit, ESU corrected within five days of requested callout.
- Auchencorth Moss – difference between measured and set flow rate outside of limit, ESU (ET) corrected within 10 days of requested callout.
- Auchencorth Moss – leak check outside of required limit, ESU (ET) attended within five days and replaced deteriorated O-ring.

In addition to six-monthly NPL audits during 2024 Q1 and Q3, the ESU carried out six-monthly services during the second quarter (Q2, April to June) and fourth quarter (Q4, October to December) of 2024. In some cases, additional services were carried out in the event of sampler breakdown. All services included flow calibrations and leak checks, as detailed in section 2.6. The combination of the flow data from the NPL audits and ESU services during the year provides the minimum three-monthly flow and leak checks required by BS EN 14902²⁰.

2.6 EQUIPMENT SERVICING AND BREAKDOWNS

During Q2 and Q4 2024, the AAM team fully serviced, carried out preventative maintenance, and calibrated the flow of all PM₁₀ samplers at HM Network sites. Exceptions were Auchencorth Moss, where ET carried out the Q2 service, and Heigham Holmes, which was not operational from May 2024 onwards so missed both 2024 service rounds. In some cases, services were combined with emergency callouts. A total of 42 service visits were made to the 22 operational samplers during 2024.

Further to the scheduled service visits, NPL issued 12 additional ESU callouts to deal with issues, which in some cases included an additional service. This does not include a number of additional visits made by LSOs to reboot the sampler/modem or perform troubleshooting with remote ESU guidance, which in many cases resolved issues without an ESU visit.

The key issues dealt with during 2024 service visits or emergency callouts for the PM₁₀ samplers are summarised below in Table 2.

Further to these issues, there was a general ongoing issue with remote communications during 2024 which did not result in callouts. In summary, eight of the 20 sites with remote communications had extended periods of communication downtime (>1 week). The ESU took several actions either remotely or during service visits in order update software and improve router security and robustness.

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

Table 2 - Summary of issues with PM₁₀ samplers during 2024 identified and/or resolved during ESU services or callouts.

Issue	Sites	Action	Occurrences
P/T sensor issues	Chilbolton Observatory, Eskdalemuir, Swansea Coedgwilym, Yarner Wood	New p/T sensor installed	4
Software glitches causing memory or programming issues	Scunthorpe Low Santon, Sheffield Devonshire Green (x2)	Software update	3
Comms issues	Scunthorpe Town, Chesterfield Loundsley Green, Yarner Wood	New router	3
Leak test fail	Auchencorth Moss, Yarner Wood (x2)	O–ring replaced	3
High flow deviation	London Westminster, Auchencorth Moss	Flow recalibration	2
Broken filter stuck in sampling chamber	Swansea Morriston	Pieces of broken filter removed	1
Component issues – Fuse	London Westminster	Fuse blown in control unit, fuse replaced	1
Component issues - Screen	Port Talbot Margam	Display screen frozen, screen replaced	1
Electrical issue	Yarner Wood	Power supply cable replacement organised by site manager	1

3 SAMPLING AND ANALYTICAL METHODOLOGY

3.1 OVERVIEW

An overview of the sampling and analytical procedures used to analyse the PM₁₀ and deposition samples from the HM Network is given below.

3.2 SAMPLING METHODOLOGY: METALS IN PM₁₀

In 2024, PM₁₀ samples were taken at all HM Network sites using Digitel DPA14 instruments (Figure 3), all fitted with PM₁₀ heads and operating at a calibrated flow rate, nominally 1 m³ h⁻¹, in accordance with BS EN 12341¹⁹. Samples were taken for a period of one week onto 47 mm diameter cellulose membrane filters.



Figure 3 - Digitel DPA14 sampler at Swansea Coedgwilym.

3.3 SAMPLING METHODOLOGY: METALS IN DEPOSITION

Sampling for metals in deposition took place at five 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 15841²¹ and BS EN 15853²². Due to different analytical requirements, samples for Hg are collected separately and in duplicate.

3.4 ANALYTICAL METHODOLOGY: METALS IN PM₁₀

Analysis for metals in PM₁₀ took place at NPL Teddington (UKAS accredited testing laboratory No. 0002), following NPLs analytical procedure for determining the mass concentration of metals in PM₁₀ on filters. This procedure is accredited by UKAS to ISO 17025²³, and fully compliant with the requirements of EN 14902²⁰.

For most sites, data were produced as four-weekly averages of concentrations for metals in PM₁₀, with the following exceptions that produced weekly data: Pontardawe Brecon Road, Pontardawe Tawe Terrace, Sheffield Tinsley, Swansea Coedgwilym, and Swansea Morriston.

Upon arrival at NPL Teddington, the filters were cut in half (for sites where weekly results were produced) or into quarters (where four-weekly results were produced). For sites producing weekly data, each half filter was digested individually. 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 portions were digested at temperatures up to 220 °C using an Anton Paar Multiwave 5000 microwave (Figure 4). The digestion mixture used was nitric acid (8 mL, 70 %) and hydrogen peroxide (2 mL, 30 %).

The samples were analysed for As, Cd, Ni, and Pb (as required by AQSR 2010) as well as Co, Cr, Cu, Fe, Mn, Se, V, Zn. Analysis of the digested solutions was performed using Agilent 8800 (Figure 4) and 8900 Inductively Coupled Plasma (Triple Quadrupole) – Mass Spectrometer (ICP-QQQ-MS) analysers. 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, with each analysis consisting of five replicate measurements.

The amount of each metal in solution (and its uncertainty) was then determined by a method of generalised least squares using XLGenline²⁴ (an NPL-developed program) to construct a calibration curve.

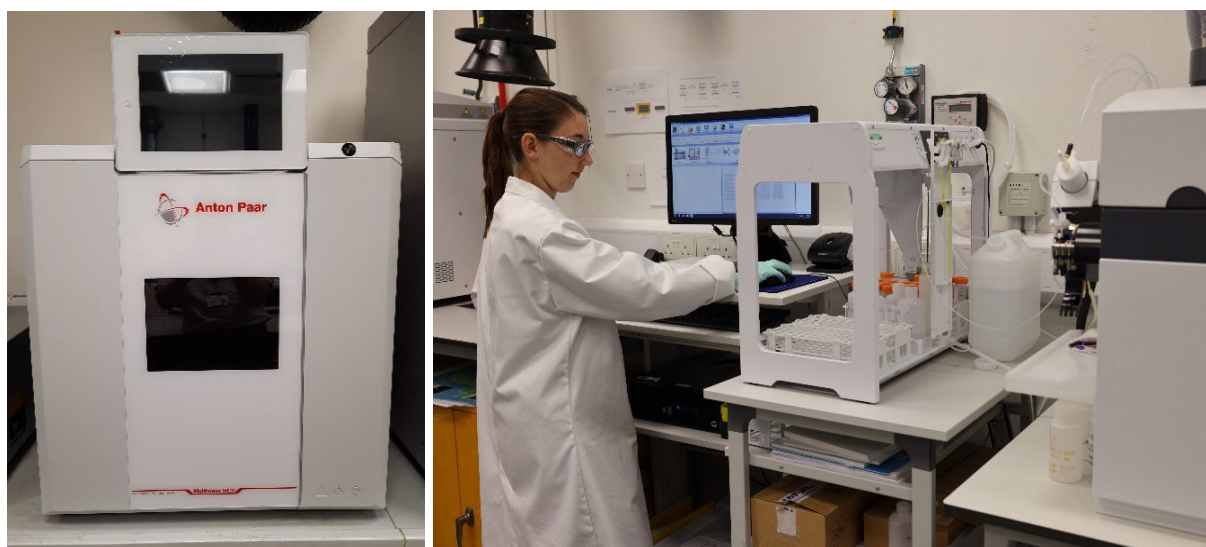


Figure 4 - (left) Anton Paar Multiwave 5000 microwave used for acid digestion of sampled filters, (right) Agilent 8800 ICP-QQQ-MS in the UK ambient metals analysis facility at NPL.

3.5 ANALYTICAL METHODOLOGY: METALS IN DEPOSITION

3.5.1 Metals (excluding mercury)

Analysis of metals in deposition took place at UKCEH's Centralised Analytical Chemistry Group at Lancaster (UKAS accredited testing laboratory No. 2506), following UKCEH's analytical procedures for trace metals in surface waters. This procedure is accredited by UKAS to ISO 17025²³, and fully compliant with the requirements of EN 15841²¹. Not all analytes are covered by the UKAS accreditation scope, as specified below.

For most sites, data were produced as four-weekly averages of concentrations for metals in deposition, with the following exceptions that produce weekly data: Auchencorth Moss and Chilbolton Observatory. The sample bulk collectors were weighed to estimate rainfall amounts then acidified with ultra-pure nitric acid (Baker Ultrex II) to a final volume concentration of 1 %. 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 for the measurements of PM₁₀ samples at NPL in section 3.4. The samples were analysed for a total of 25 metals, 19 of which were within UKAS scope: As, Cd, Ni (as required by AQSR 2010); Cr, Cu, Pb, Zn (as required by EMEP and OSPAR), as well as Al, Ba, Be, Co, Fe, Li, Mn, Mo, Sb, Se, Sr, and V; and six outside of UKAS scope Cs Rb, Sn, Ti, U, and W.

3.5.2 Mercury

Analysis of Hg in deposition also took place at UKCEH Lancaster (UKAS accredited testing laboratory No. 2506), following UKCEH's analytical procedure for mercury in surface waters. This procedure is accredited by UKAS to ISO 17025²³, and fully compliant with the requirements of EN 15853²² and EN ISO 17852²⁵.

All samples for mercury analysis were collected on a four-weekly basis, with duplicate samples taken at each site. The Hg collector bottles were weighed to estimate rainfall amounts and then stored at 4 °C prior to analysis.

Hg 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 were traceable to NIST mono-elemental reference materials.

3.6 MEASUREMENT UNITS

Results produced by the HM Network for metals in PM₁₀ are calculated in accordance with ISO 11222²⁶. They are expressed, as required by AQSR 2010, as mass concentrations in nanograms (of the relevant metal) per cubic metre of 'as sampled' ambient air for the metals in PM₁₀: ng m⁻³.

For metals in deposition, results 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).

3.7 MEASUREMENT UNCERTAINTY CALCULATION

For each result produced by the HM Network, an estimate of the uncertainty is also made according to the Guide to the Expression of Uncertainty in Measurement (GUM) approach, published as ISO/IEC Guide 98-3:2008²⁷. These uncertainties are propagated to 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

4.1 QA/QC PROCEDURES

The technical procedure used to analyse metals in PM₁₀ samples from the HM Network is accredited by UKAS to ISO 17025²³. Limits of detection achievable using this procedure are comfortably below the requirements of EN 14902²⁰.

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 Metals in PM₁₀ sampling

- Filters are given unique ID numbers, 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 (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 Metals in PM₁₀ 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 14902²⁰.
- Annual participation in an appropriate proficiency testing 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 drift-corrected measured intensities of each analysis of each sample.
- The XLGeline maximum absolute weighted residual for calibration curves must be <2.
- 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 analyses for metals (including mercury) in deposition are 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 lab and field blank gauges (one per quarter per site).
- Regular UKAS audit of method performance, assessing analytical quality control data.
- 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.
- Ratification of all data by a recognised senior scientific expert independent of the analytical team.

4.2 MEASUREMENT UNCERTAINTY

The range of uncertainties for individual mass concentrations of metals in PM₁₀ during 2024 are shown in Table 3. 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 %.

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 for each metal in PM₁₀ at each site will be dominated by the analytical and sampling uncertainty.

According to the AQSR 2010 DQOs, an additional component of uncertainty due to incomplete time coverage may be determined by the procedure described in ISO 11222²⁶. 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 11222²⁶, using the data capture percentage from Fenny Compton (the lowest eligible site for the year, i.e. excluding Heigham Holmes). This yielded a small absolute increase in uncertainty of 4 %.

These relative uncertainties for both individual measurements, and the annual means are lower than the maximum allowed (40 % for As, Cd, Ni and 25 % for Pb), and therefore all PM₁₀ measurements made in 2024 meet the AQSR 2010 DQO for uncertainty values for fixed (and indicative) measurements of As, Cd, Ni, and Pb.

Uncertainties for metals in deposition are approximately 25 % for individual measurements and 35 % for the annual mean values, both significantly less than the limit of 70 % specified in the AQSR 2010 DQOs.

Table 3 - The expanded uncertainty range covering the majority of filter analyses at NPL during 2024, and relevant regulatory limits.

Analyte	Uncertainty range / %	AQSR 2010 limit / %
As	9 – 18	40
Cd	9 – 27	40
Co	9 – 32	-
Cr	9 – 24	-
Cu	9 – 20	-
Fe	9 – 21	-
Mn	9 – 15	-
Ni	9 – 20	40
Pb	9 – 15	25
Se	10 – 40	-
V	9 – 17	-
Zn	9 – 46	-

5 DATA QUALITY

5.1 OVERVIEW

Annual data capture is calculated as the percentage of valid measurement time over the total time during which we intended to perform measurements. All data capture values are stated to the nearest whole percentage.

5.2 DATA CAPTURE: METALS IN PM₁₀

The average data capture for metals in PM₁₀ during 2024 was 93 %. Table 4 shows the annual data capture for each site for PM data across the HM Network during 2024. Table 5 gives a summary of the reasons for data loss and mitigations.

In most cases the total time intended to perform measurements is the whole year excluding downtime due to 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 unavoidable maintenance activities. In these cases, in Table 4, the annual data capture has been calculated excluding this time (annual data capture including this time is in brackets).

In 2024, this applies to one site:

- Yarner Wood – due to sampler power cable upgrade works, 11 days were removed from the annual time coverage.

Table 4 – PM₁₀ data capture across the HM Network during 2024. Values shown exclude planned downtime (values in brackets include planned downtime).

Site Name	PM ₁₀ data capture / %
Auchencorth Moss	100
Belfast Centre	98
Chesterfield Loundsley Green	100
Chilbolton Observatory	98
Cwmystwyth	99
Detling	98
Eskdalemuir	90
Fenny Compton	85
Heigham Holmes	31
London Marylebone Road	100
London Westminster	94
Pontardawe Brecon Road	98
Pontardawe Tawe Terrace	98
Port Talbot Margam	100
Scunthorpe Low Santon	100
Scunthorpe Town	96
Sheffield Devonshire Green	96
Sheffield Tinsley	100
Swansea Coedgwilym	89
Swansea Morriston	89
Walsall Pleck Park	99
Yarner Wood	92 (89)
Average across all sites	93 (93)

Table 5 - A summary of the issues that account for the bulk of the data loss for metals in PM₁₀ across the HM Network in 2024.

Issue	Data loss / %	Description	Mitigation
Heigham Holmes non- operational	3.1	See section 2.4	Sampler and electrical supply are being relocated.
Broken filter	1.0	An increase in brittle filters resulted in holes in filters, invalidating samples, and in some cases invalidating subsequent filters.	Filter support grids are now used to minimise this issue.
Unknown issue	0.7	Two sets of four filters were returned blank despite all evidence suggesting the filters had sampled.	The situation has been thoroughly investigated and discussed with the sampler manufacturer. Most likely they were isolated incidents, but will continue to be closely monitored.
Programming / user error	0.5	Incorrect settings used, or filters loaded late.	Information and training provided where required. All samplers monitored weekly to minimise these issues.
Power cuts	0.4	Short / intermittent power cuts at sites.	Electrical checks and maintenance carried out regularly; infrastructure replaced where necessary.
Filters lost	0.4	Filter lost in transit.	LSOs are required to send filters using tracked postage.
P/T sensor errors	0.3	P/T sensor errors causing invalid or low sampling time.	Weekly checks on sampler log files to identify deteriorating sensors; deteriorating sensors replaced pre-emptively; p/T sensors kept in stock by ESU for quick replacement; sensor covers installed at some sites.

For As, Cd, and Ni, the AQSR 2010 requires a minimum time coverage of 50 % and minimum data capture of 90 % for fixed measurements, which equates to 45 % data capture over the whole year. All sites, except for Heigham Holmes, achieved more than 50 % annual time coverage, and 45 % annual data capture, and therefore met the AQSR 2010 data capture DQO for fixed measurements of As, Cd, and Ni.

For Pb, the AQSR 2010 does not specify a minimum time coverage for fixed measurements other than to note indicative measurements must exceed 14 % time coverage (distributed evenly across the year, with uncertainty value including a component for random sampling still lower than the threshold of 25 %). Both fixed and indicative measurements require a minimum data capture of 90 %, equating to minimum of 13% data capture for the whole year. All sites, except for Heigham Holmes, achieved more than 14 % annual time coverage, and 13 % annual data capture, and therefore met the AQSR 2010 data capture DQO for fixed measurements of Pb.

Heigham Holmes only sampled for the first four months of 2024, so does not meet the time coverage requirements to be considered as fixed or indicative measurements.

5.3 NUMBER OF SAMPLING POINTS: METALS IN PM₁₀

The target number of sites required by the AQSR 2010, based on modelled concentrations, as summarised in Defra's 2023 air quality monitoring regime assessment: compliance network status (2016-2020)²⁸, was met or exceeded for all zones and agglomerations in 2024, except for the Eastern and Northwest & Merseyside zones.

For the Northwest & Merseyside zone, the assessment threshold classification for As, based on modelled concentrations between 2016-18, meant that one site was required. However, given that concentrations had dropped below the LAT during 2019-20, the report recommended waiting for the next assessment to ascertain if the drop of concentration had been maintained²⁸. The current available compliance data suggests that the area has remained below the LAT during 2020-23²⁹.

For the Eastern zone, the assessment threshold classification for Ni means that one site was required, but since the removal of Chadwell St Mary in 2023, and the non-operation of Heigham Holmes for most part of 2024, the requirement was not met in 2024. However, the current available compliance data suggests that the area has remained below the LAT during 2022-23²⁹.

5.4 DATA CAPTURE: METALS IN DEPOSITION

The average data capture across all deposition analytes during 2024, excluding data loss due to lack of precipitation, was 98 %. If including data loss due to lack of precipitation, the data capture was 91 %.

The annual data capture for deposition at the sites where these measurements are made is detailed in Table 6. 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 (four weeks rather than one week) so typically have higher data capture.

In 2024, 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.

For deposition, the AQSR 2010 requires a minimum time coverage of 50 % and minimum data capture of 90 % for fixed measurements, of which equates to 45 % data capture over the whole year. All sites, achieved more than 50 % annual time coverage and 45 % annual data capture, and therefore met the AQSR 2010 data capture DQO for fixed deposition measurements.

Table 6 - Data capture across the deposition sites of the HM Network during 2024.

Site Location	Non-Hg Metals in Deposition / %	Hg in Deposition / %
Auchencorth Moss	90	90
Chilbolton Observatory	100 (79)	98
Heigham Holmes	100	100
Lough Navar	100	N/A
Yarner Wood	100 (87)	100
Average	98 (91)	97

5.5 NUMBER OF SAMPLING POINTS: METALS IN DEPOSITION

To summarise the requirement of sampling points for deposition for AQSR 2010, EMEP, and OSPAR, the UK requires at least two (ideally four) background sites, including at least one coastal site (<10 km from coastline). In 2024, this was met, with Heigham Holmes as the coastal site.

5.6 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 for the metals in PM₁₀ samples. 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.

UKCEH follow a similar procedure for the concentration data produced for the metals in deposition samples. NPL carry out sensibility checks on the deposition data before submission.

6 NETWORK DATA

6.1 MEASURED CONCENTRATIONS: METALS IN PM₁₀

Table 7 summarises the measured concentrations of each metal in PM₁₀ for 2024, and the UK limit or target value (where appropriate). Due to low data capture, measurements from Heigham Holmes have been excluded from these calculations.

Table 7 - 2024 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 2010 limit or target and AQ Strategy 2007 objective values are listed where applicable. Heigham Holmes has been excluded from all calculations.

Analyte	2024 UK mean annual concentration across all sites / (ng m⁻³)	2024 UK median annual concentration across all sites / (ng m⁻³)	2024 maximum annual mean concentration at any site / (ng m⁻³)	UK limit or target value [objective] / (ng m⁻³)
As	0.58	0.63	0.94	6
Cd	0.15	0.10	0.43	5
Co	0.20	0.14	0.96	-
Cr	4.05	2.34	30.7	-
Cu	7.08	4.48	25.6	-
Fe	516	186	2596	-
Mn	10.6	4.40	68.8	-
Ni	2.56	1.15	14.7	20
Pb	6.51	4.92	25.2	500 [250]
Se	0.68	0.55	1.58	-
V	1.14	0.68	7.32	-
Zn	20.1	10.8	87.2	-

Table 8 shows the annual time-weighted mean of measured metals concentrations in 2024 at individual sites, highlighting any exceedances of target/limit values or associated upper and lower thresholds. Measurements from Heigham Holmes have been included for indicative purposes but cannot be considered as representative of the whole year.

All data, at the highest time resolution that they are produced, are available from Defra's UK-AIR website¹.

Table 8 - The 2024 annual time-weighted mean concentrations 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); grey = indicative only.

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	0.04	0.02	0.99	0.90	51.2	1.27	0.26	0.86	0.40	0.26	2.87
Belfast Centre	0.41	0.06	0.10	1.91	4.69	261	4.40	0.85	2.57	0.48	0.81	10.6
Chesterfield Loundsley Green	0.94	0.09	0.07	2.88	3.57	162	4.11	1.37	4.58	0.69	0.49	17.2
Chilbolton Observatory	0.46	0.06	0.03	1.10	1.84	86.1	2.09	0.50	2.34	0.45	0.68	6.61
Cwmystwyth	0.18	0.04	0.02	0.84	0.88	38.9	1.14	0.31	0.99	0.37	0.30	2.68
Detling	0.63	0.09	0.05	1.30	2.93	119	2.60	0.73	4.03	0.44	0.98	8.89
Eskdalemuir	0.20	0.05	0.02	1.04	0.80	44.1	1.20	0.37	0.86	0.45	0.28	3.04
Fenny Compton	0.56	0.07	0.04	0.96	2.09	106	2.21	0.37	2.78	0.47	0.50	10.8
Heigham Holmes	0.40	0.06	0.03	1.02	2.02	66.5	1.59	0.54	2.32	0.45	0.66	6.22
London Marylebone Road	0.73	0.10	0.23	7.62	25.6	1190	11.9	1.42	5.49	0.54	1.16	29.1
London Westminster	0.73	0.10	0.20	2.77	9.28	500	6.71	1.80	5.41	0.51	1.13	17.5
Pontardawe Brecon Road	0.49	0.17	0.19	1.81	3.65	186	3.73	2.37	4.92	0.55	0.49	9.87
Pontardawe Tawe Terrace	0.49	0.17	0.96	4.21	3.52	173	4.75	10.6	4.18	0.65	0.49	9.81
Port Talbot Margam	0.66	0.43	0.19	5.27	15.4	2380	34.1	1.15	6.45	0.94	3.09	39.8
Scunthorpe Low Santon	0.90	0.38	0.27	4.09	5.95	2600	68.8	1.52	20.0	1.38	7.32	49.1
Scunthorpe Town	0.69	0.17	0.11	2.34	4.48	694	17.5	0.87	9.10	1.02	1.47	26.7
Sheffield Devonshire Green	0.64	0.14	0.14	4.60	7.62	312	7.02	1.73	5.42	0.99	0.72	20.9
Sheffield Tinsley	0.78	0.25	0.56	30.7	12.5	523	27.1	14.7	12.7	1.58	1.22	87.2
Swansea Coedgwilym	0.53	0.18	0.34	2.28	9.39	146	3.71	5.85	25.2	0.63	0.52	9.88
Swansea Morriston	0.77	0.25	0.46	4.10	19.9	737	8.90	5.39	8.01	0.65	0.67	20.5
Walsall Pleck Park	0.75	0.17	0.21	3.15	12.5	459	7.03	0.94	9.41	0.58	0.72	33.3
Yarner Wood	0.37	0.05	0.03	1.04	1.11	60.7	1.71	0.57	1.39	0.43	0.65	4.97

6.2 MEASURED CONCENTRATIONS OF COMPLIANCE METALS IN PM₁₀

In Figure 5, the network-wide annual time-weighted mean concentrations (excluding Heigham Holmes) for the compliance metals for 2024 are compared against the relevant limit and target values from the AQSR 2010. The annual mean concentrations for the relevant compliance metals at each HM Network site in 2024 are displayed in Figure 6; Heigham Holmes has been included for indicative purposes only.

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

- As: Chesterfield Loundsley Green
- Cd: Port Talbot Margam
- Ni: Sheffield Tinsley
- Pb: 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):

- Ni at Pontardawe Tawe Terrace: exceedance of the LAT (53 %)
- Ni at Sheffield Tinsley: exceedance of the UAT (74 %)

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 Ni refinery (4 km downwind). Swansea Morriston is in the same area, 5 km upwind of the Ni 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.

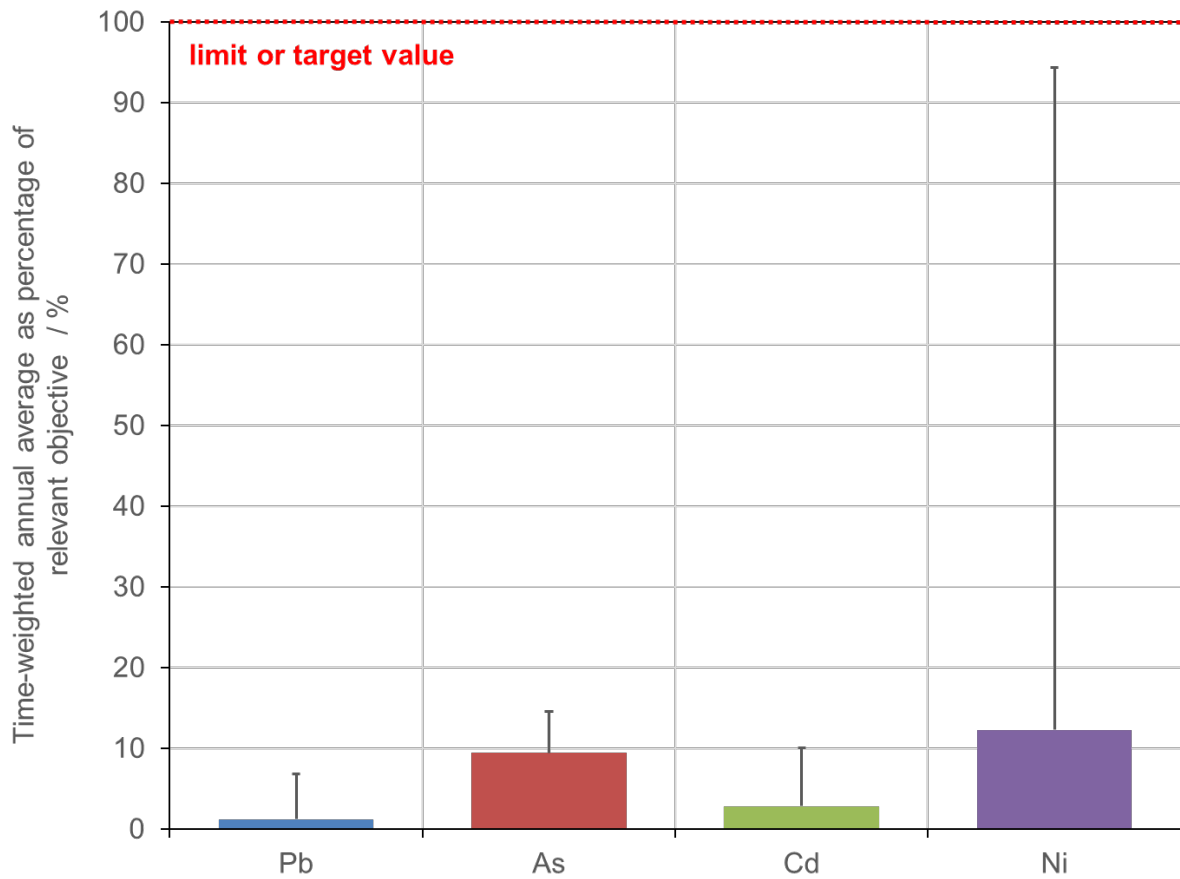


Figure 5 – The time-weighted annual mean concentrations of compliance metals relevant to the AQSR 2010 on the HM Network in 2024 (excluding Heigham Holmes) as a percentage of the relevant limit or target value. The bars indicate the annual mean of all sites; the lines indicate the annual mean at the site with the highest concentrations.

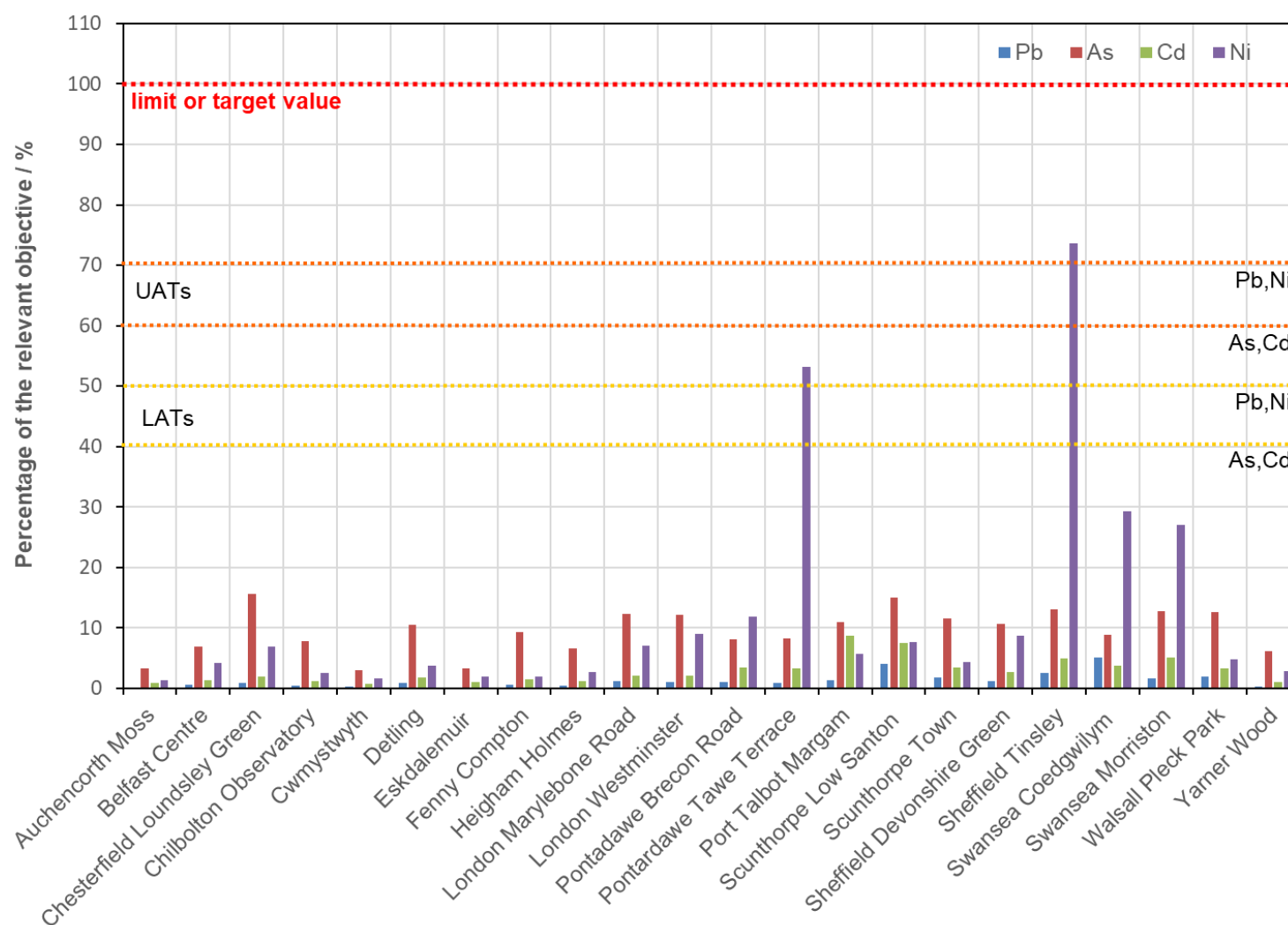


Figure 6 - The annual mean measured concentrations of the compliance metals relevant to the AQSR at all HM Network sites in 2024 as a percentage of the relevant target values shown in red, UATs in orange and LATs in yellow. Heigham Holmes should be considered as indicative.

6.3 WITHIN YEAR CONCENTRATION TRENDS IN PM₁₀

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 PM₁₀ measured on the HM Network, most show variable or low seasonality, with the exception of As and V^{16,30}. 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 efficient³⁰. 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 sizes³⁰. As is generally emitted from diffuse combustion sources, not point sources, and therefore is affected much less by meteorological conditions¹⁶.

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 7 to Figure 9.

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 Ni 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 Ni are also frequently observed at the Sheffield Tinsley monitoring site (see Figure 9). The emissions landscape is much more complex in Sheffield than South Wales, as there are numerous potential industrial sources of Ni emissions in the Sheffield area. The local Environment Agency works closely with industrial facilities in Sheffield to highlight processes that could contribute to Ni 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.

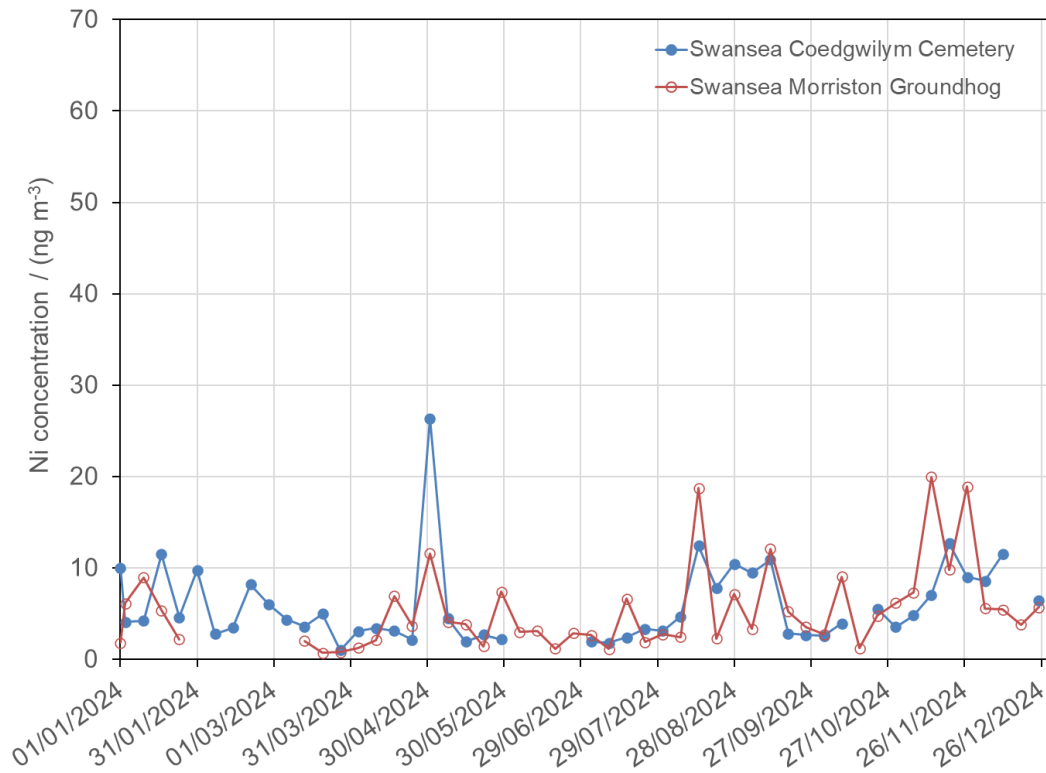


Figure 7 - Measured Ni concentrations at Swansea Coedgwilym and Swansea Morryston in 2024 (both sampled weekly). Data points mark the start date of the weekly sampling period.

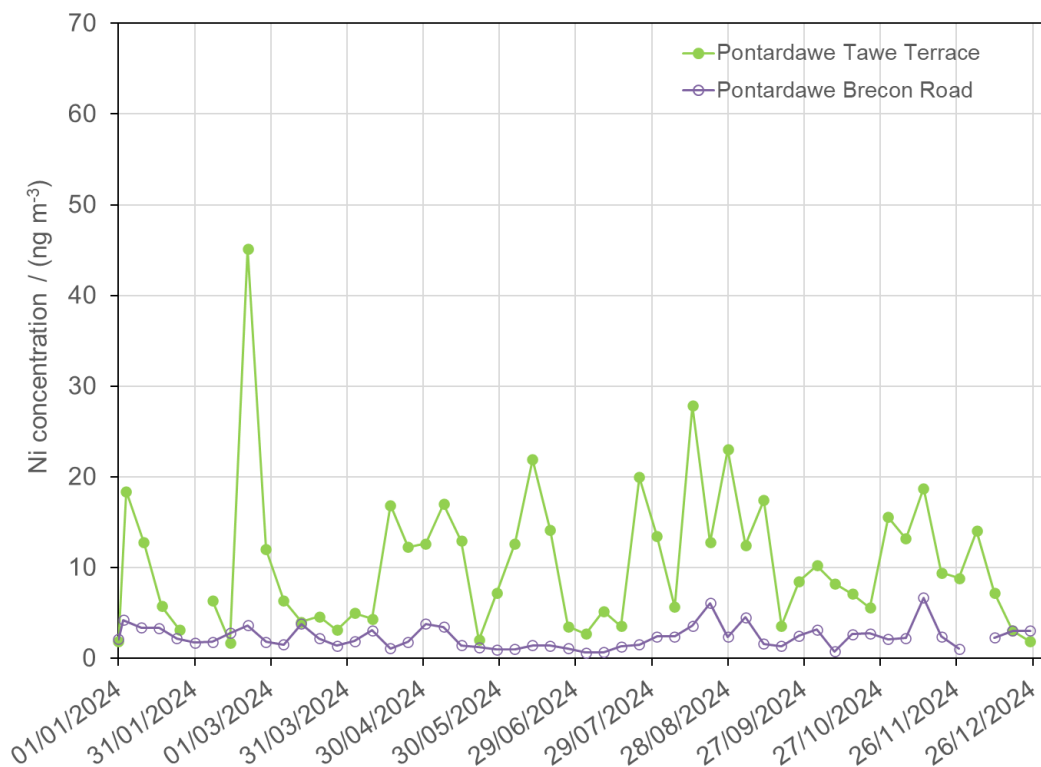


Figure 8 - Measured Ni concentrations at Pontardawe Tawe Terrace and Pontardawe Brecon Road in 2024 (both sampled weekly). Data points mark the start date of the weekly sampling period.

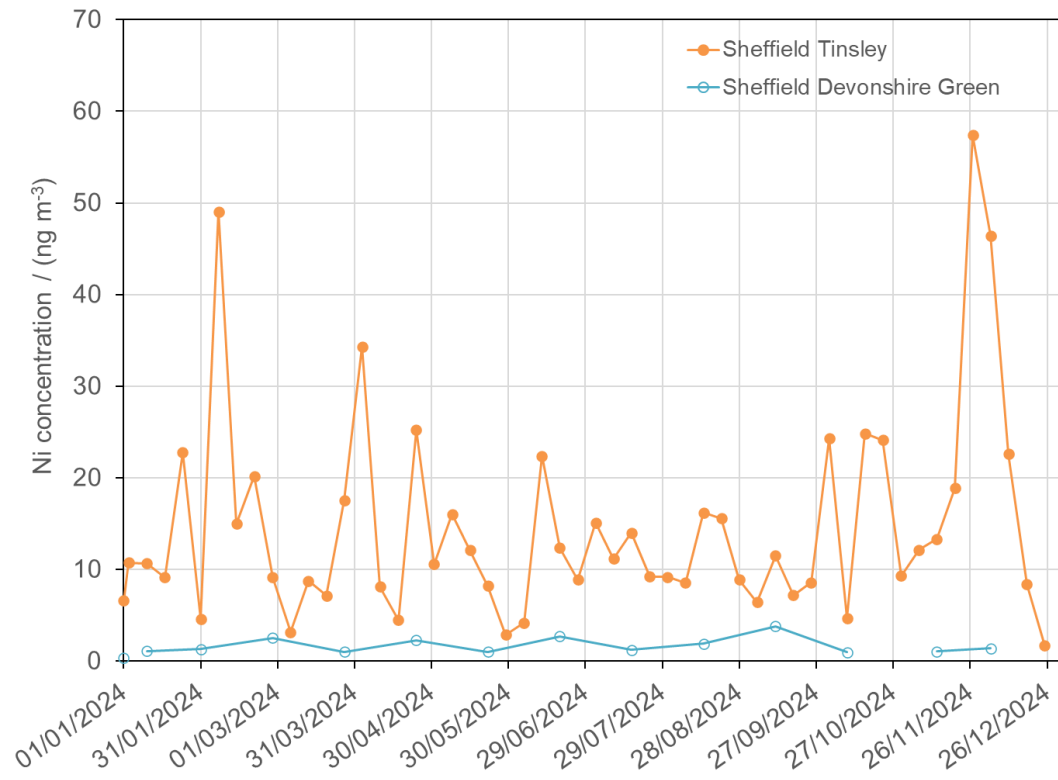


Figure 9 - Measured Ni concentrations at Sheffield Tinsley and Sheffield Devonshire Green in 2024. Results from Tinsley are weekly. Results from Sheffield Devonshire Green are averaged over four-week periods. Data points mark the start date of the sampling period.

6.4 MEASURED CONCENTRATIONS OF NON-COMPLIANCE METALS IN PM₁₀

Figure 10 shows the concentrations of the non-compliance metals measured across the HM Network sites, normalised to the annual median value for each metal. Heigham Holmes has been included for indicative purposes, but excluded from the median calculation.

High concentration values for non-compliance metals are usually pertinent to specific processes close to the monitoring sites concerned. For instance:

- Cu and Fe at roadside sites such as London Marylebone Road from non-exhaust emissions and re-suspension.
- Fe and Mn at Port Talbot Margam and Scunthorpe Low Santon, near to steel works.
- Co, Cr, Cu, Mn, Se, and Zn at Sheffield Tinsley near to a steel processing facility.
- Co, Cr, and Se at Pontardawe Tawe Terrace close to a Ni-Co alloy production process.

The rural sites all report low concentrations for non-compliance metals, as would be expected

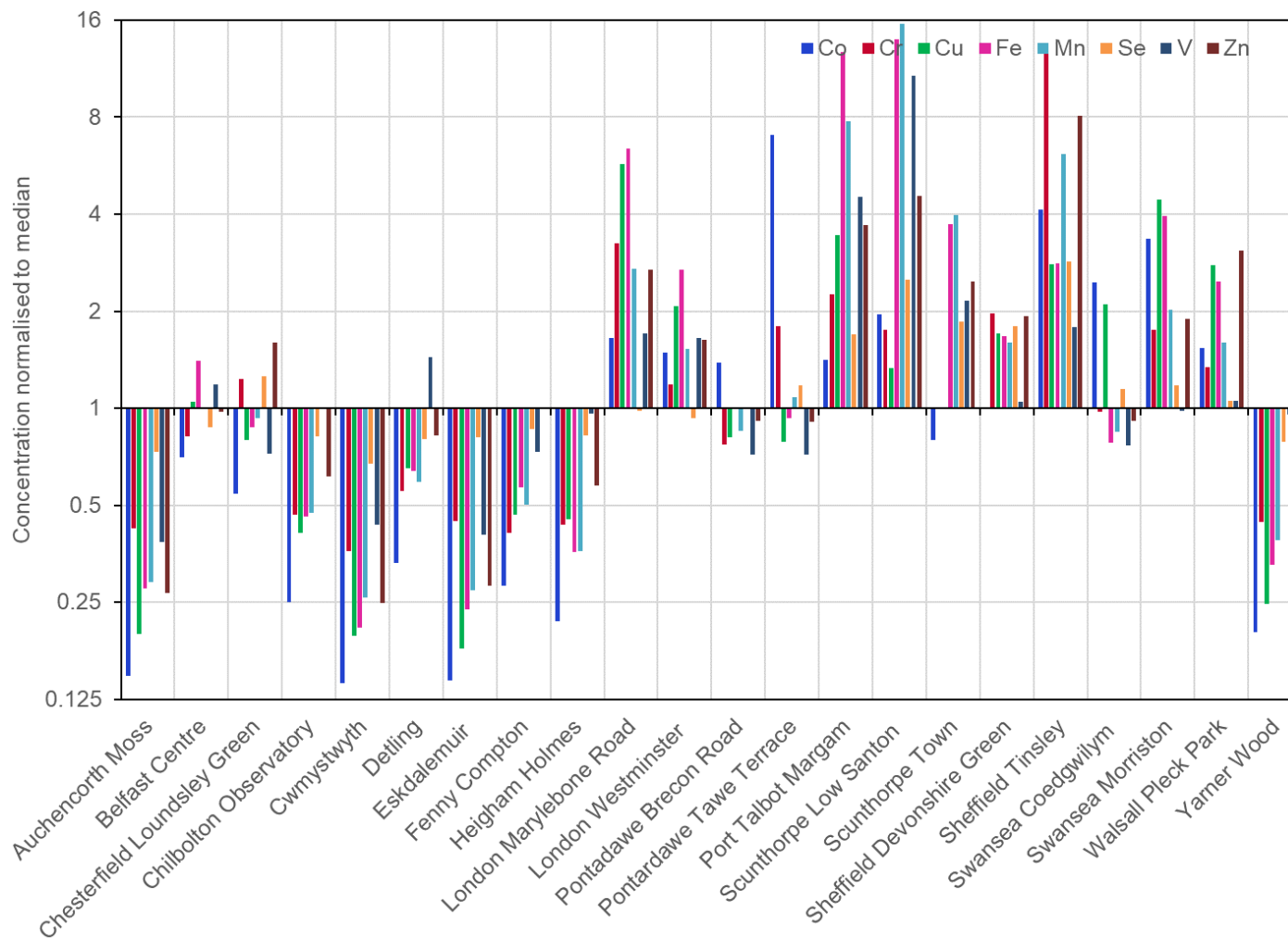


Figure 10 - The annual mean concentrations of the non-compliance metals measured at all HM Network sites in 2024, normalised to the UK annual median concentration for the relevant element. These values are plotted with respect to the median, so it is clear which sites are above and below the median level. Note the logarithmic scale on the y-axis. Heigham Holmes has been included for indicative purposes only, and excluded from the median calculation.

6.5 MEASURED CONCENTRATIONS: METALS IN DEPOSITION

The annual mean metals deposition flux concentrations in 2024, averaged over all sites sampling metals in deposition (Table 9), and at individual sites (Table 10), are given below.

Table 9 - 2024 annual mean, median, and maximum deposition flux measurements averaged over all HM Network deposition monitoring sites.

Analyte	2024 UK mean annual flux across all sites [$\mu\text{g m}^{-2} \text{ d}^{-1}$]	2024 UK median annual flux across all sites [$\mu\text{g m}^{-2} \text{ d}^{-1}$]	2024 UK maximum annual flux at any site [$\mu\text{g m}^{-2} \text{ d}^{-1}$]
Al	17.0	16.7	33.3
As	0.21	0.18	0.37
Ba	0.94	0.97	1.26
Be	0.012	0.011	0.016
Cd	0.022	0.019	0.031
Co	0.023	0.024	0.038
Cr	0.30	0.25	0.43
Cs	0.013	0.012	0.020
Cu	0.64	0.57	0.98
Fe	19.7	12.6	42.6
Hg	0.010	0.009	0.015
Li	0.15	0.14	0.22
Mn	3.17	2.76	4.42
Mo	0.067	0.063	0.085
Ni	0.35	0.27	0.55
Pb	0.15	0.16	0.27
Rb	0.34	0.30	0.59
Sb	0.086	0.083	0.114
Se	0.27	0.26	0.40
Sn	0.37	0.35	0.52
Sr	5.70	5.59	9.31
Ti	0.56	0.42	1.01
U	0.012	0.012	0.016
V	0.70	0.65	0.97
W	0.12	0.10	0.16
Zn	3.03	2.82	4.56

Table 10 - 2024 annual mean deposition flux measurements measured at individual deposition monitoring sites on the HM Network.

Analyte	Annual mean deposition flux measurements [$\mu\text{g m}^{-2} \text{d}^{-1}$]				
	Auchencorth Moss	Chilbolton Observatory	Heigham Holmes	Lough Navar	Yarner Wood
Al	7.05	16.7	18.9	9.17	33.3
As	0.18	0.12	0.17	0.37	0.22
Ba	0.88	0.97	1.02	0.59	1.26
Be	0.011	0.010	0.007	0.015	0.016
Cd	0.019	0.019	0.014	0.026	0.031
Co	0.017	0.024	0.025	0.013	0.038
Cr	0.24	0.20	0.25	0.43	0.39
Cs	0.012	0.010	0.007	0.016	0.02
Cu	0.36	0.35	0.94	0.57	0.98
Fe	8.45	11.3	42.6	12.6	23.8
Hg	0.0094	0.0091	0.0076	-	0.0149
Li	0.14	0.10	0.10	0.22	0.17
Mn	1.81	2.65	4.42	2.76	4.22
Mo	0.063	0.055	0.059	0.073	0.085
Ni	0.25	0.55	0.13	0.27	0.54
Pb	0.05	0.18	0.27	0.09	0.16
Rb	0.20	0.12	0.30	0.49	0.59
Sb	0.075	0.083	0.072	0.085	0.114
Se	0.26	0.19	0.17	0.40	0.34
Sn	0.35	0.33	0.20	0.47	0.52
Sr	5.59	2.75	4.00	9.3	6.86
Ti	0.20	0.42	1.01	0.30	0.88
U	0.016	0.009	0.006	0.012	0.015
V	0.65	0.57	0.41	0.90	0.97
W	0.10	0.10	0.07	0.15	0.16
Zn	2.82	2.13	4.08	1.57	4.56

7 TRENDS IN MEASURED CONCENTRATIONS

7.1 TRENDS IN METALS IN PM₁₀

Trends in concentrations measured over the last 45 years for regulated metals are summarised in Figure 11 and Figure 12, 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 13, Figure 14, and Figure 15.

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 is 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 recently have tended to come from either meteorological variability or from changes in the configuration of the HM Network. This generally mirrors the decrease in emissions over this period (see Figure 1). Exceptions to this are Cu and Mn.

The NAEI estimated annual Cu emissions have shown a gradual increase between 1990-2019, followed by a sharp decrease in 2020 and then a sharp increase across 2021-22, back to similar levels estimated for 1990¹², but the measured annual mean concentration has shown a gradual decrease over this time. This increase in estimated Cu emissions has been associated with the increased use of lubricants in road vehicles (37 % of UK Cu emissions in 2022). The other main source is vehicle brake pad wear (59 % of UK Cu emissions in 2022). Excluding road vehicles lubricants, Cu emissions from other sources have declined by 7 % since 1990, associated with the decline in metal production¹⁴. A possible reason that the increase in Cu 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 Mn 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 12.5 % increase, 1990 to 2022), whereas the measured concentrations have remained relatively stable at lower levels. In 2022, the main source of Mn emissions (81 %) was associated with fuel combustion activities, with 49 % specifically related to industrial biomass and wood combustion, which has significantly increased since 1990. The other main source in 2022 was metal production (18 %), which has decreased since 1990¹³. A possible reason that the increase in Mn 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.

Ni 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.

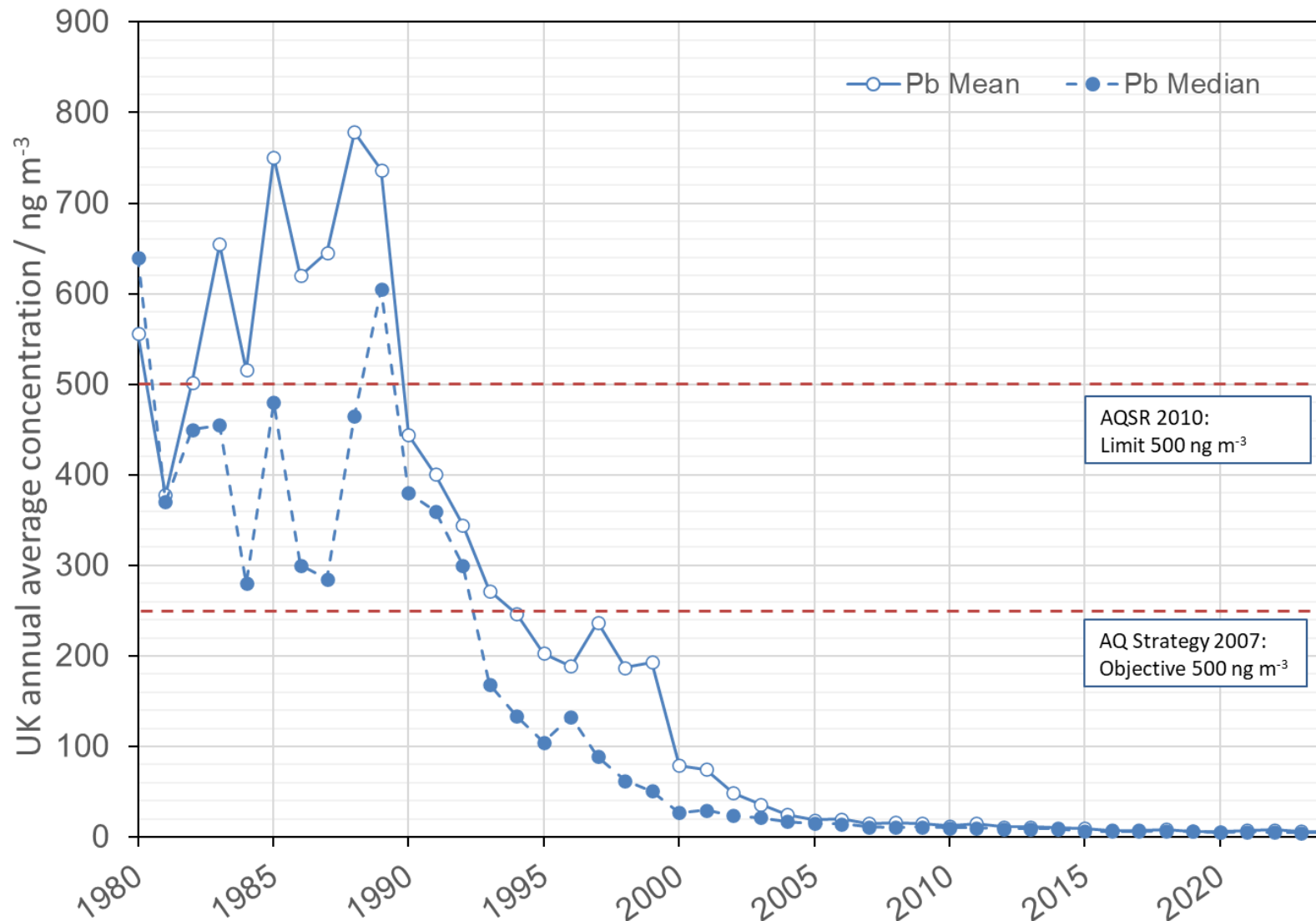


Figure 11 - The mean and median of HM Network measured annual average concentrations of Pb, 1980 - 2024. The UK AQSR 2010 limit for Pb is 500 ng m⁻³, and the UK AQ Strategy 2007 objective is 250 ng m⁻³.

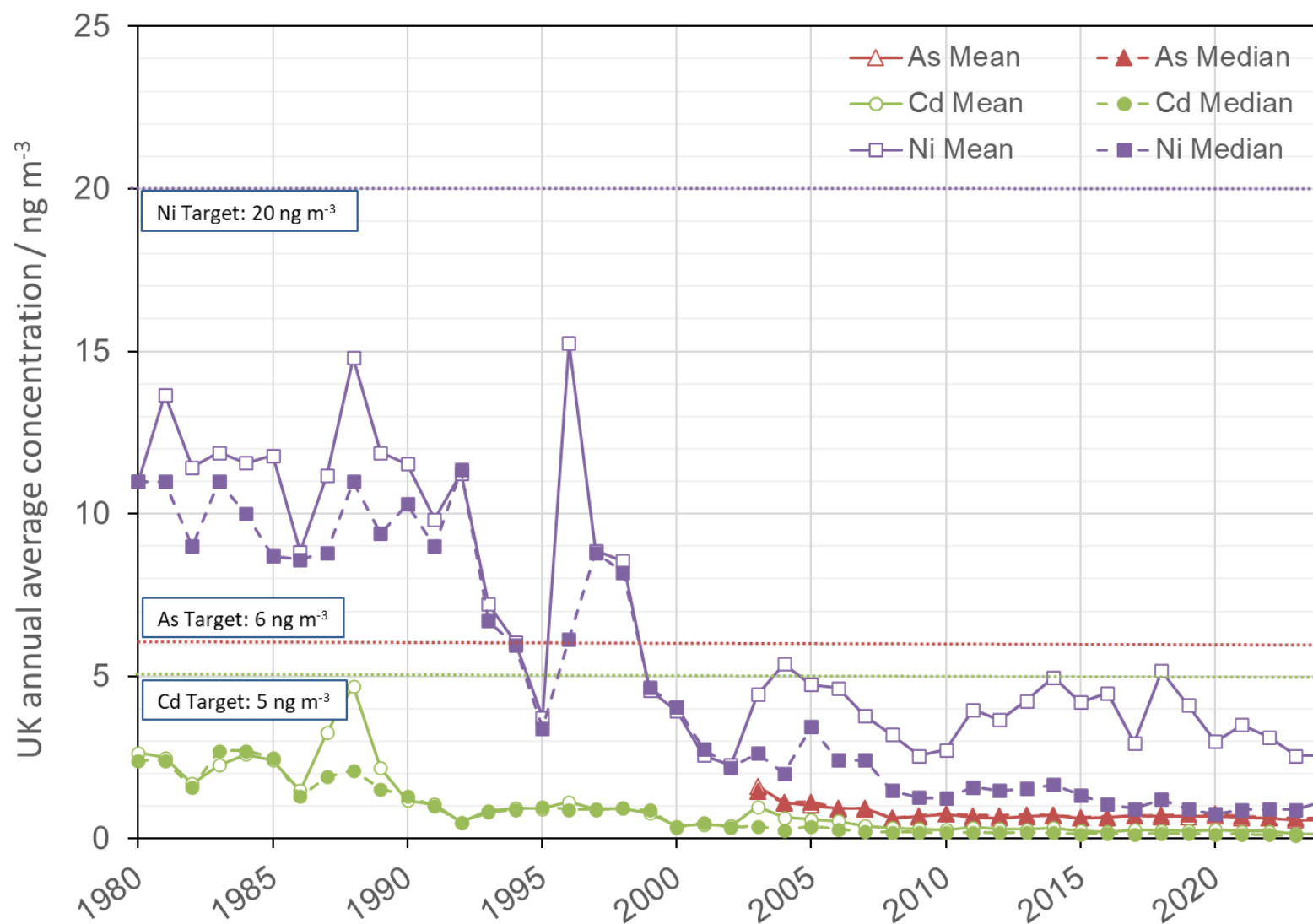


Figure 12 - The mean and median of HM network measured annual average concentrations of Ni, As, and Cd, 1980 - 2024. The UK AQSR 2010 target values for Ni, As and Cd are 20 ng m^{-3} , 6 ng m^{-3} and 5 ng m^{-3} respectively.

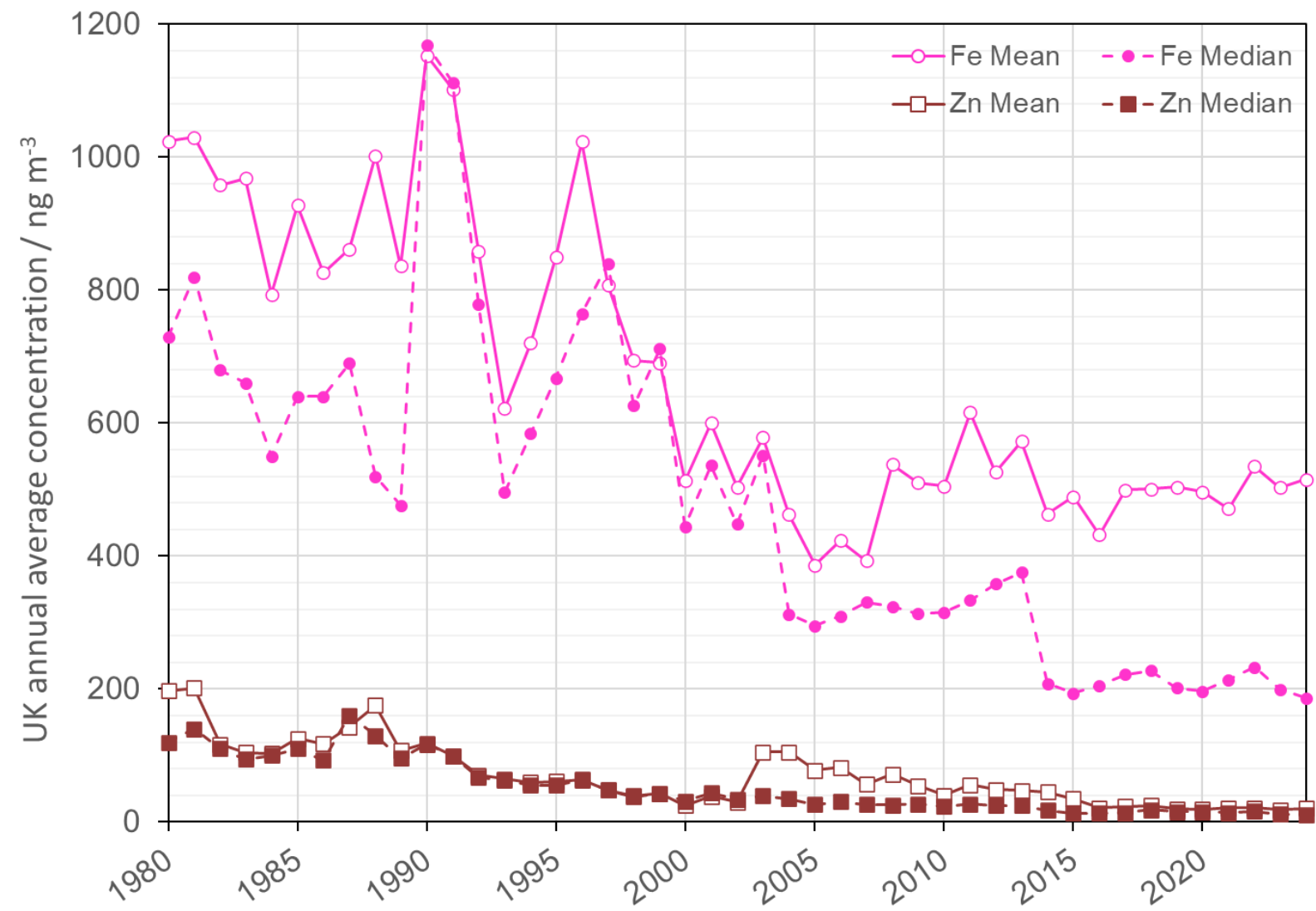


Figure 13 - The mean and median of HM Network measured annual average concentrations of Fe and Zn, 1980 - 2024.

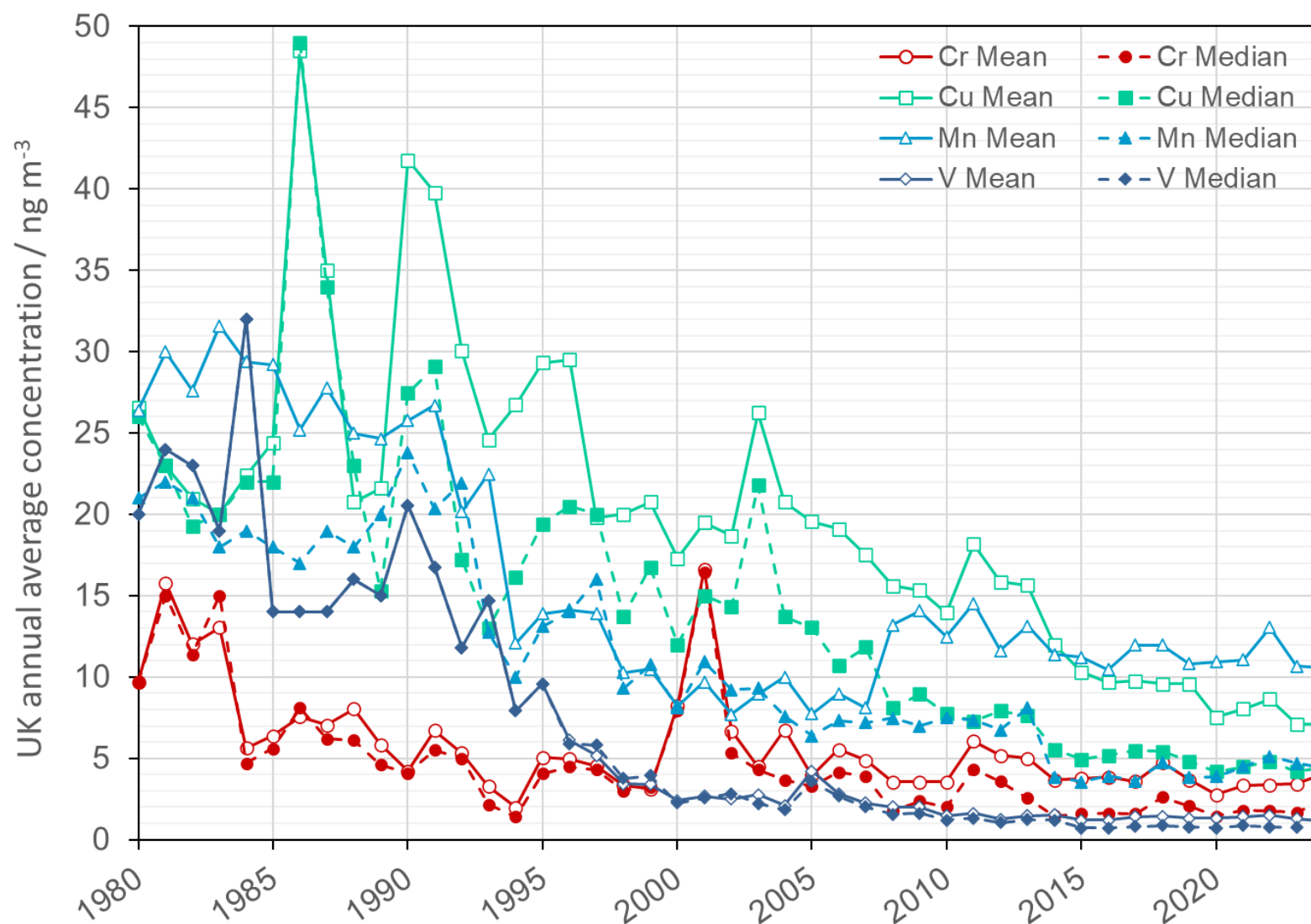


Figure 14 - The mean and median of HM Network measured annual average concentrations of Cr, Cu, Mn, and V, 1980 - 2024.

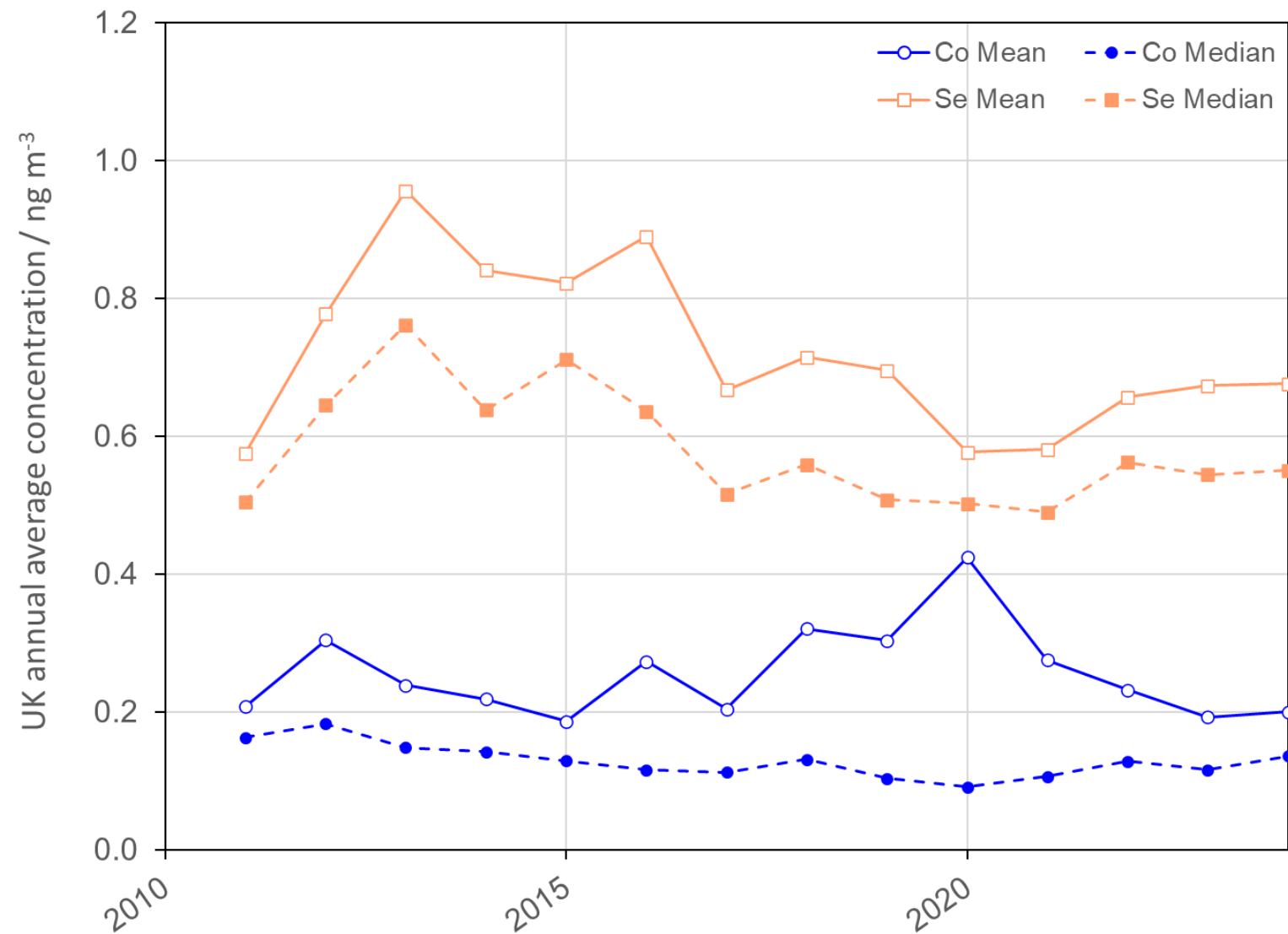


Figure 15 - The mean and median of HM Network measured annual average concentrations of Co and Se, 2011 – 2024, since monitoring commenced for these metals in 2011.

7.2 TRENDS IN NICKEL IN PM₁₀ IN THE SWANSEA AND TAW VALLEYS

The annual average concentration of Ni in the Swansea and Tawe valleys measured since 2003 is shown in Figure 16. Ni concentrations at Port Talbot (since monitoring began in 2008) have also been included to indicate the regional background level.

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 Ni 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 Network 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 Ni 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 Ni 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. Ni concentrations have since fallen, and, from 2022 onwards, have been less than the target value.

The trends in Ni concentrations in the Swansea and Tawe valleys were the subject of a peer-reviewed publication by NPL published in 2022³¹. This paper demonstrates the effectiveness of Ni emissions abatement strategies over the last 50 years by tracking the falling air concentrations of Ni over this period. The work also shows how the monitoring network in the Swansea Valley has expanded over this time and become significantly more sensitive to Ni emissions. The data presented represents a significant public health achievement – the paper concluded that it is likely that the exposure to Ni 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.

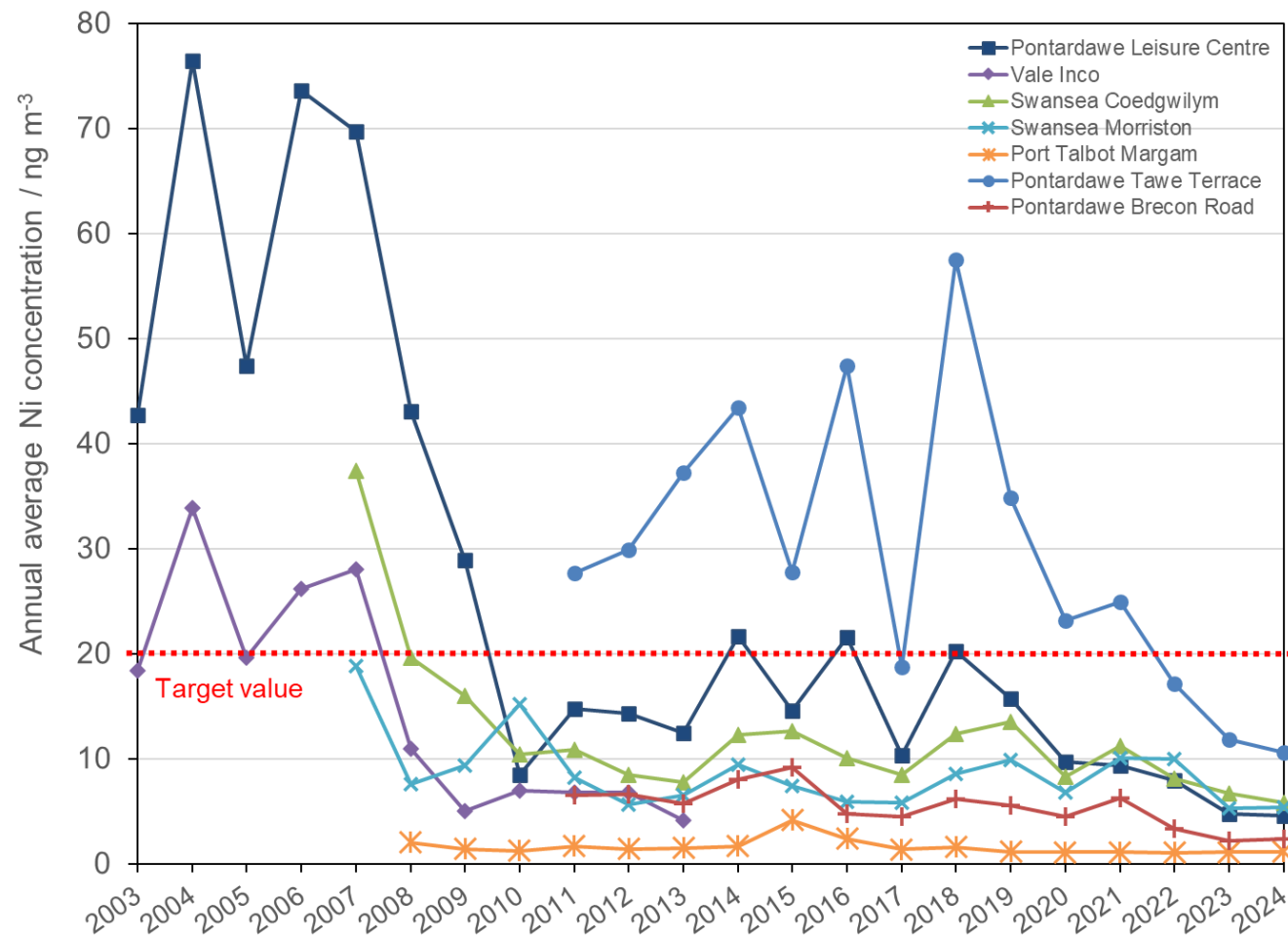


Figure 16 - The annual average Ni concentrations measured at monitoring sites in the Swansea area 2003-24. The red dotted line indicates the UK AQSR 2010 target value for nickel. The data for Vale Inco in 2008 – 2013, and Coedgwilym and Morriston in 2007 are courtesy of Swansea Council. The data for the Leisure Centre is courtesy of Neath Port Talbot County Borough Council. The Vale Inco data for 2013 was only based on 19 % data capture.

7.3 TRENDS IN METALS IN DEPOSITION

Trends in deposition metal concentrations measured since 2010 (the year from which data is available on UK-AIR¹) for the metals relevant to the UK AQSR 2010 (As, Cd, Ni, Hg) are summarised in Figure 17 to Figure 20.

Trends in deposition metal concentrations measured since 2010 for the metals relevant to the EMEP and OSPAR (Pb, Cr, Cu, Zn) are summarised in Figure 21 to Figure 24.

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.

It should be noted that the limit of detection (LoD) for some analytes has increased since 2023, meaning a higher percentage of results were less than the LoD and therefore reported as half the LoD. In some cases this means the value of half the LoD dominates the calculated annual mean concentration, so trend analysis should be treated with caution. This is particularly evident for Cd in Figure 17 to Figure 24, where only 11 % of measurements were higher than the LoD in 2024.

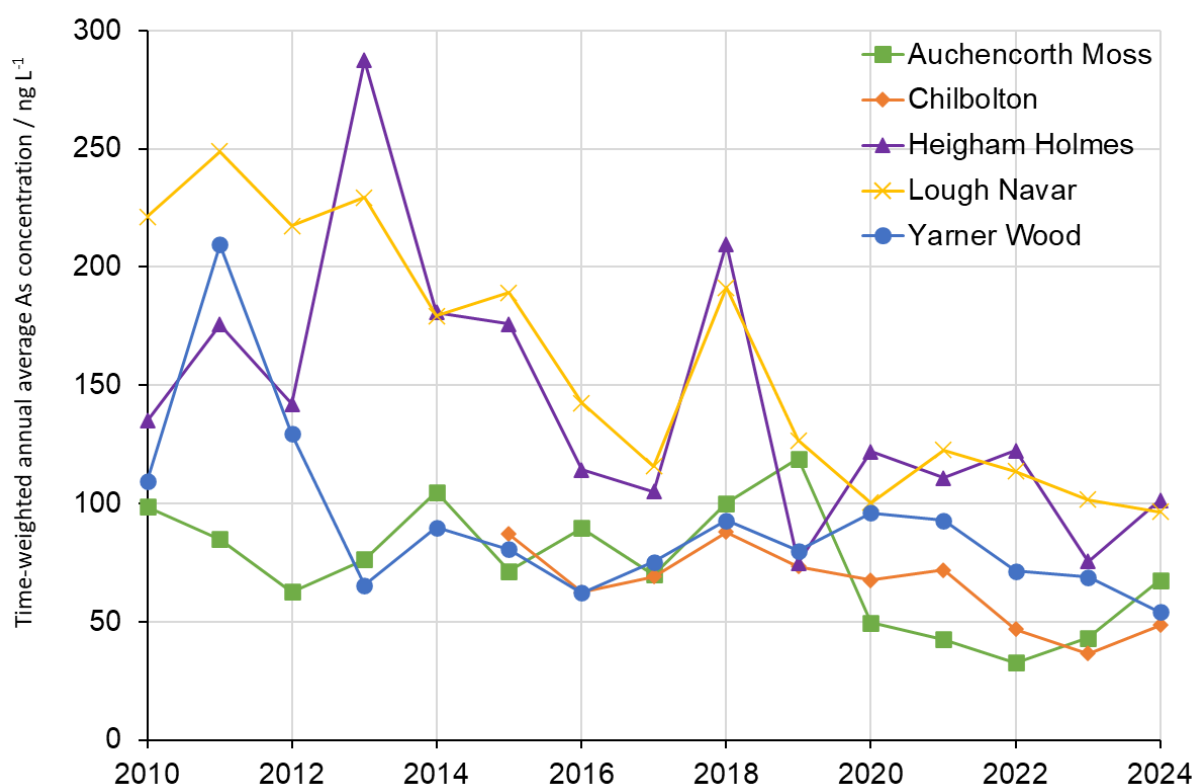


Figure 17 - The mean annual concentrations of As measured in deposition since 2010 at individual sites.

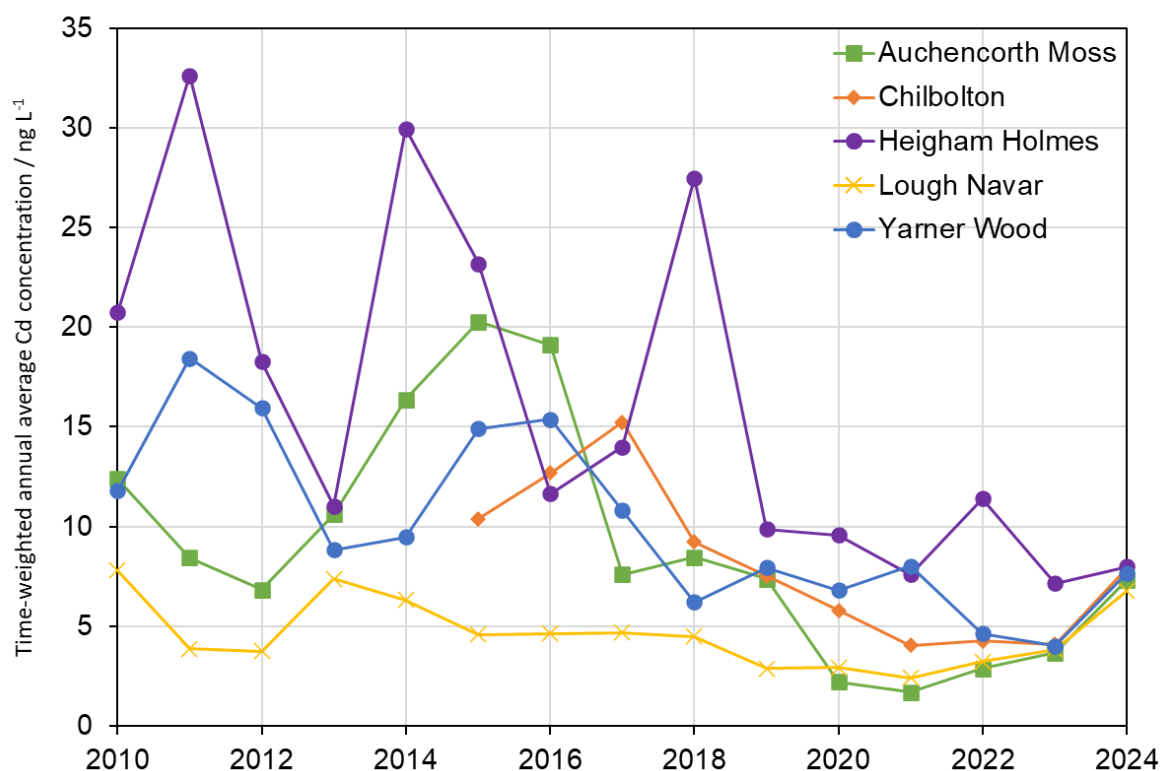


Figure 18 - The mean annual concentrations of Cd measured in deposition since 2010 at individual sites.

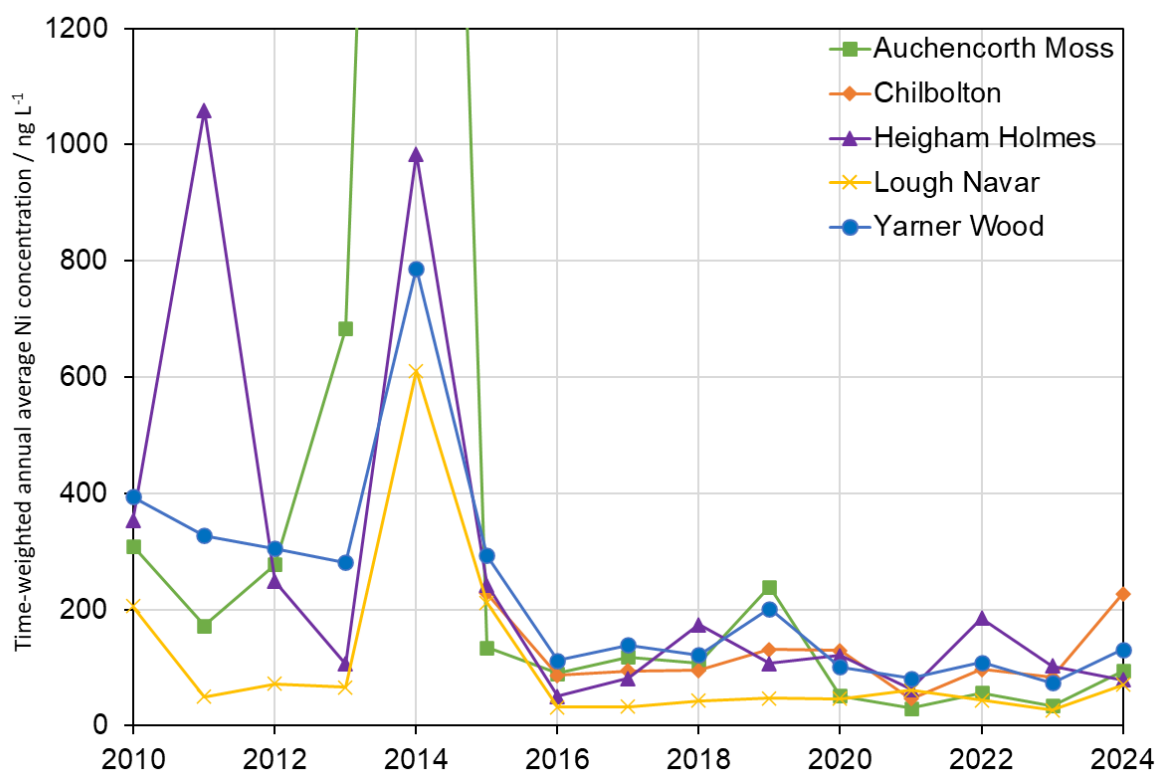


Figure 19 - The mean annual concentrations of Ni measured in deposition since 2010 at individual sites. The off-scale Auchencorth Moss point in 2014 is 3965 ng L⁻¹.

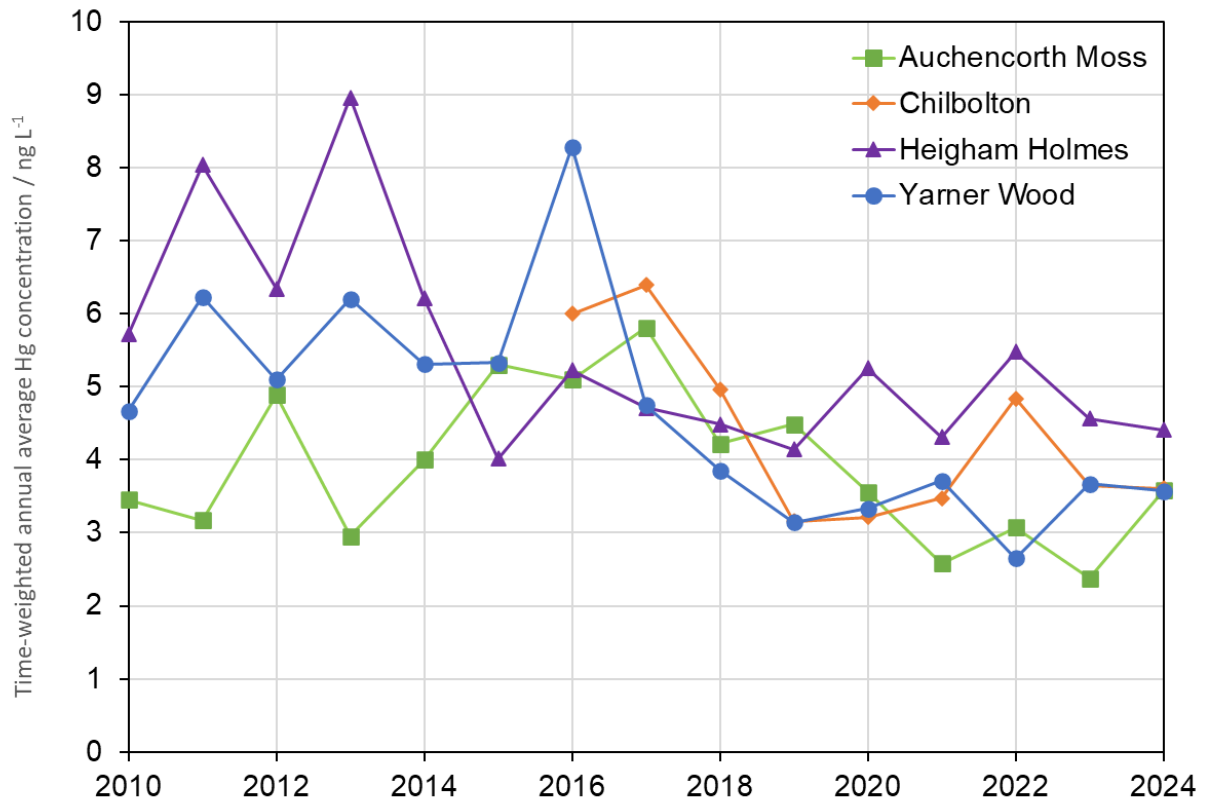


Figure 20 - The mean annual concentrations of Hg measured in deposition since 2010 at individual sites. Hg is not measured at Lough Navar.

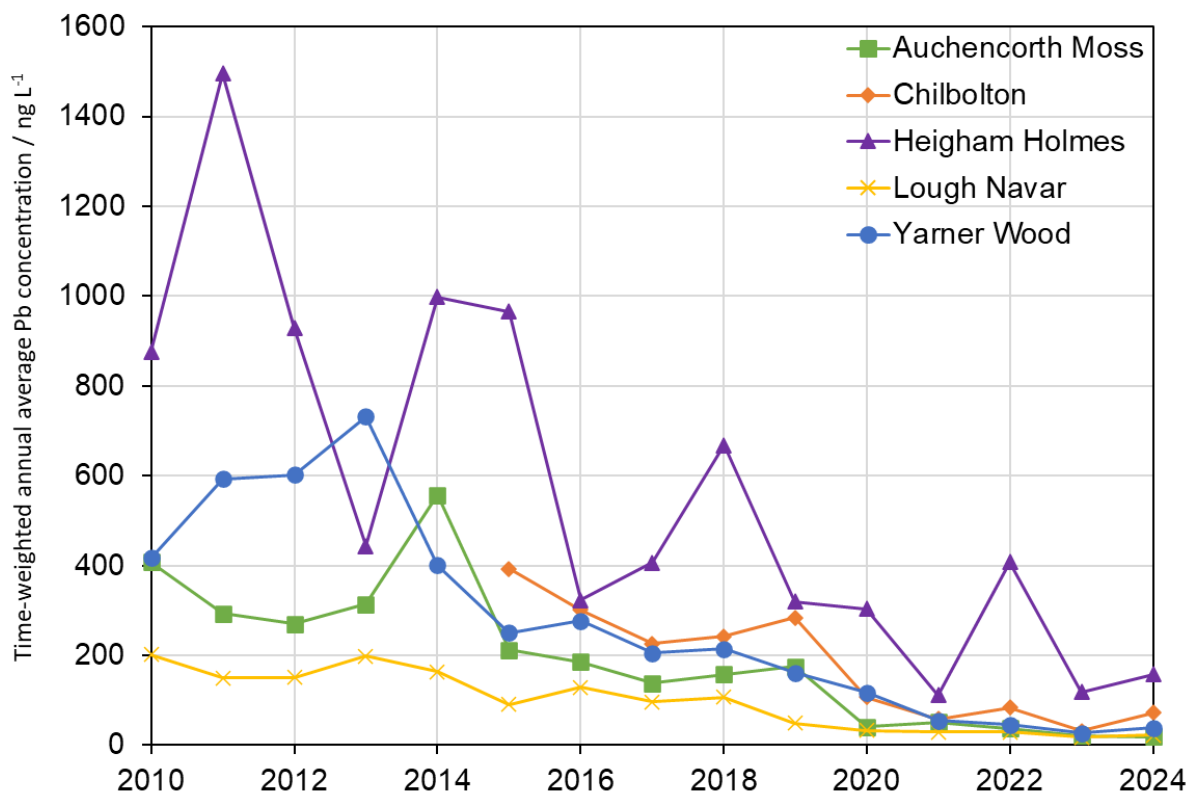


Figure 21 - The mean annual concentrations of Pb measured in deposition since 2010 at individual sites.

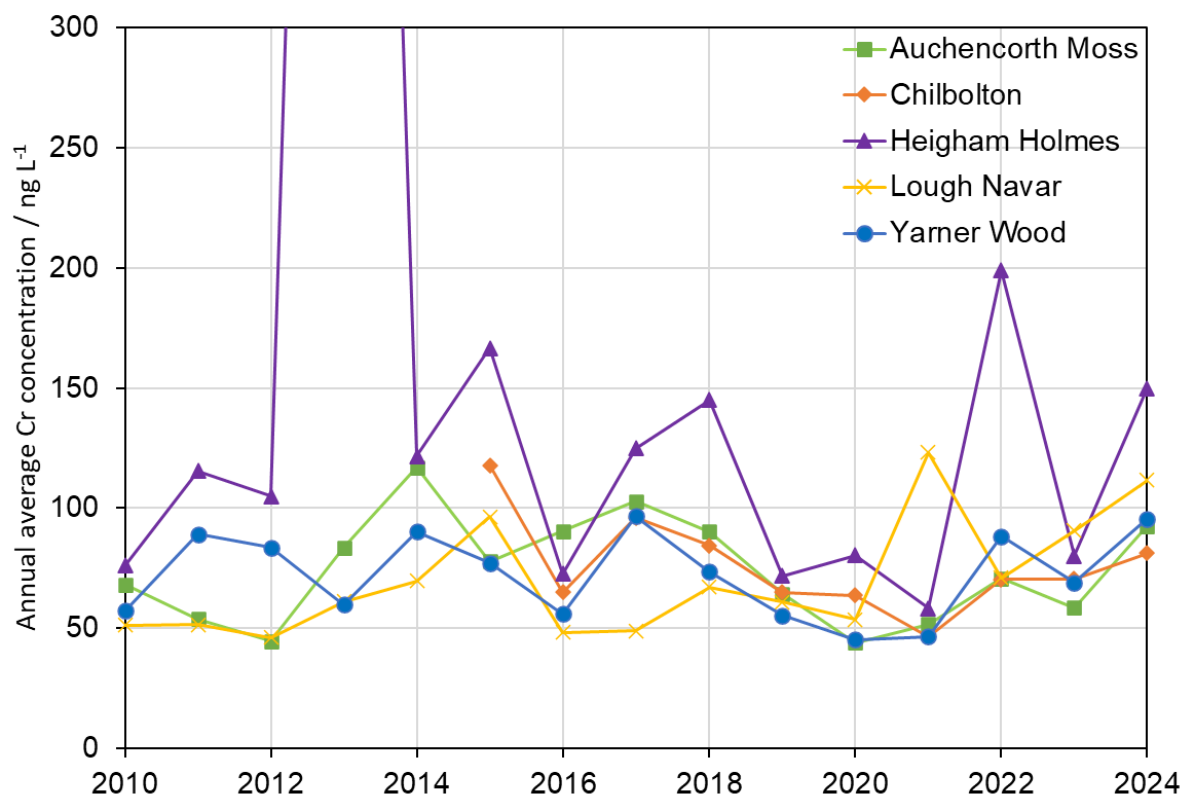


Figure 22 - The mean annual concentrations of Cr measured in deposition since 2010 at individual sites. The off-scale Heigham Holmes point in 2013 is 1058 ng L⁻¹.

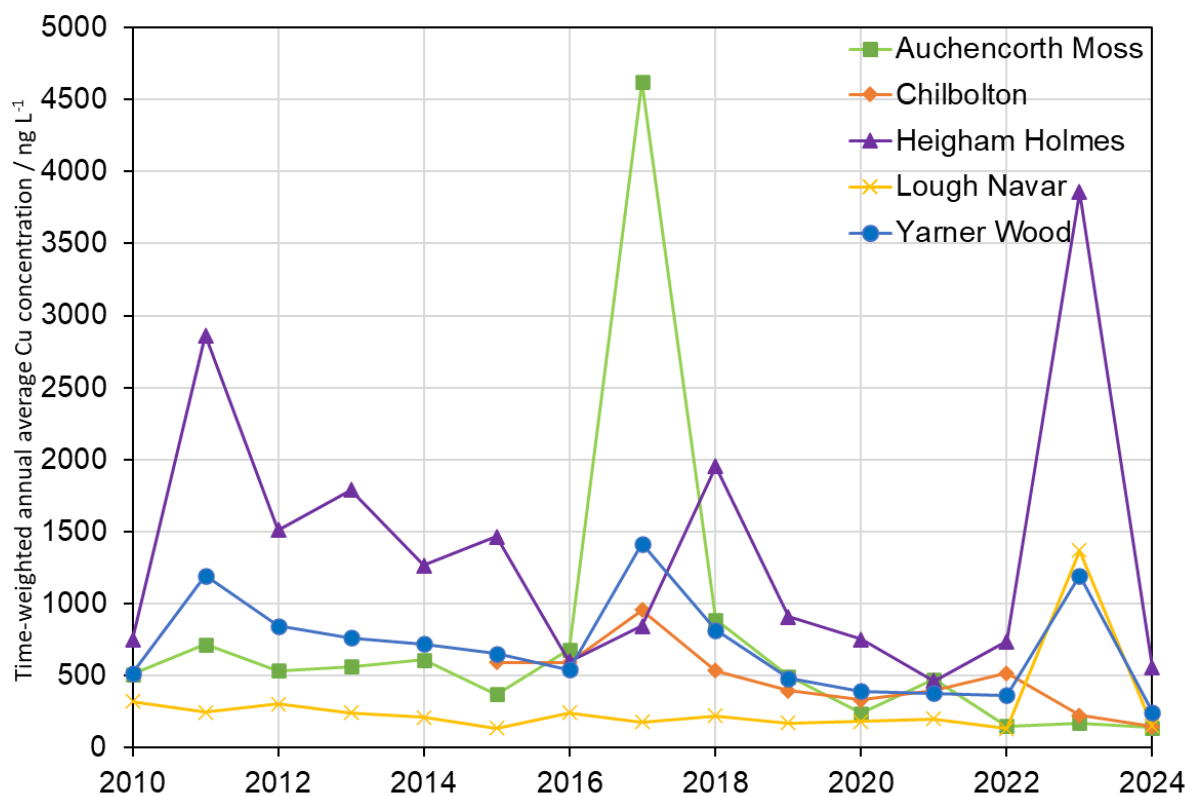


Figure 23 - The mean annual concentrations of Cu measured in deposition since 2010 at individual sites.

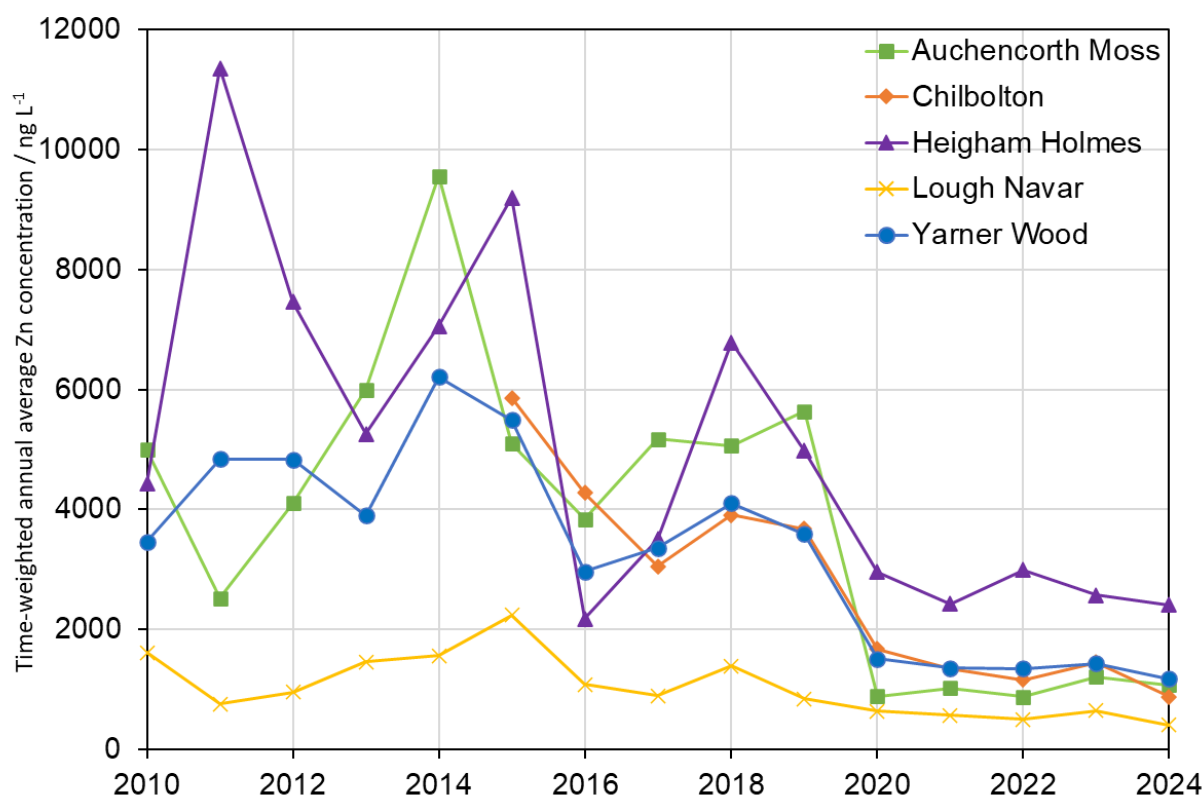


Figure 24 - The mean annual concentrations of Zn measured in deposition since 2010 at individual sites.

8 PEER-REVIEW PUBLICATIONS

Recent peer-review papers that used samples or data from the HM data are listed below. A summary of the first few sentences of the abstract of each paper is also provided for context.

1. *Air-quality networks collect environmental DNA with the potential to measure biodiversity at continental scales*³²

Quantifying biodiversity and monitoring continual change is difficult but ever more relevant with the accelerating loss of biodiversity threatening ecosystems. This study tests whether airborne environmental DNA is captured on filter samples produced by the UK Heavy Metals Network.

2. *PM₁₀-bound trace elements in pan-European urban atmosphere*³³

This paper presents a comprehensive assessment of concentrations for 20 trace elements in PM₁₀ at 55 monitoring sites in seven European countries (Switzerland, Spain, France, Greece, Italy, Portugal, UK) during 2013-22, including data from the UK Heavy Metals Network rural background monitoring sites.

9 ACKNOWLEDGEMENT

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- ¹³ National Atmospheric Emissions Inventory - Pollutant Information: Manganese https://naei.beis.gov.uk/overview/pollutants?pollutant_id=53
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