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UKEAP 2023 annual report

Prepared for the Environment Agency, the Department of Environment Food and Rural Affairs and the Devolved Administrations

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Glossary of Abbreviations

AGANet	Acid Gases and Aerosol Network
ALPHA	Adapted Low-cost High Absorption sampler
APIS	Air Pollution Information System (https://www.apis.ac.uk/)
CEDA	Centre for Environmental Data Analysis (https://www.ceda.ac.uk/)
CLRTAP	Convention on Long-range Transboundary Air Pollution
Defra	Department for Environment, Food and Rural Affairs (UK)
DELTA	DEnuder for Long-Term Atmospheric sampling
ECN	UK Environmental Change Network (https://ecn.ac.uk/)
EMEP	European Monitoring and Evaluation Programme
LSO	Local site operator
LTMN	Long Term Monitoring Network (https://publications.naturalengland.org.uk/category/5316639066161152)
MARGA	Monitor for AeRosols and Gases in Ambient air
NAMN	National ammonia monitoring network
NERC	Natural Environment Research Council
NO2-Net	Nitrogen dioxide network (rural)
OSPAR	Mechanism by which 15 Governments and the EU cooperate to protect the marine environment of the North-East Atlantic (Details here: https://www.ospar.org/about)
PCM	Pollution Climate Mapping (https://uk-air.defra.gov.uk/research/air-quality-modelling?view=modelling)
Precip-Net	Precipitation Network
SCAIL	Simple Calculation of Atmospheric Impact Limits (https://www.scail.ceh.ac.uk/)
STFC	Science and Technology Facilities Council
TFMM	Task Force for Measurement and Modelling
UNECE	United Nations Economic Commission for Europe
UKEAP	UK Eutrophying and Acidifying Atmospheric Pollutants

Executive summary

This annual report for 2023 was prepared by UK Centre for Ecology & Hydrology and Ricardo for the Environment Agency, the Department of Environment and Rural Affairs, the Department of Environment Northern Ireland, the Welsh Government and the Scottish Government.

The Defra rural air pollutant monitoring networks project, (2021 – 2024: ECM48524), **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)** comprises the following measurement networks:

- **UK Environmental Monitoring and Evaluation Program (EMEP) monitoring supersites** (Chilbolton Observatory and Auchencorth Moss)
- **National Ammonia Monitoring Network** (NAMN – 113 sites, Dec 2023)
- **Acid Gases and Aerosol Network** (AGANet – 28 sites, Dec 2023)
- **Precipitation chemistry Network** (Precip-Net – 48 sites)
- **Rural nitrogen dioxide (NO_2) diffusion tube network** (NO_2-Net – 24 sites)

The report provides information on:

- Updates on network operations during 2023.
- Annual concentrations.
- Interpretation of data and discussion of trends across the network.
- A summary of the scientific research, publications and other activities related to the network.

Key network changes for 2023:

- In spring 2023, 16 sites were added to NAMN and 7 sites were added to Precip-Net. The additional sites were embedded Natural England’s Long Term Monitoring Network (LTMN).

1. Introduction

The UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network is commissioned by Defra, the Environment Agency, and the Devolved Administration and is jointly operated by Ricardo and the UK Centre for Ecology and Hydrology (UKCEH). UKEAP measurements are undertaken to allow improvements in understanding of the chemical composition, deposition and removal processes of inorganic air pollutants and to allow validation of atmospheric transport models. This report summarises operation and monitoring data under the UKEAP contract for 2023. UKEAP is comprised of the following measurement networks:

- **UK EMEP Supersites** (Chilbolton Observatory and Auchencorth Moss)
- **National Ammonia Monitoring Network** (NAMN)
- **Acid Gases and Aerosol Network** (AGANet)
- **Precipitation chemistry Network** (Precip-Net)
- **Rural NO_2 diffusion tube network** (NO_2-Net)

Embedded within the NAMN and Precip-Net networks are the air quality measurements of Natural England's Long Term Monitoring Network (LTMN) and a network in Northern Ireland as part of NAMN and AGANet. The data from the UKEAP measurements underpins UK rural air quality modelling and mapping which feeds into policy. In addition, data from the networks within UKEAP are used both within the UK and internationally. Figure 1 highlights the most significant data applications both in the UK and internationally.

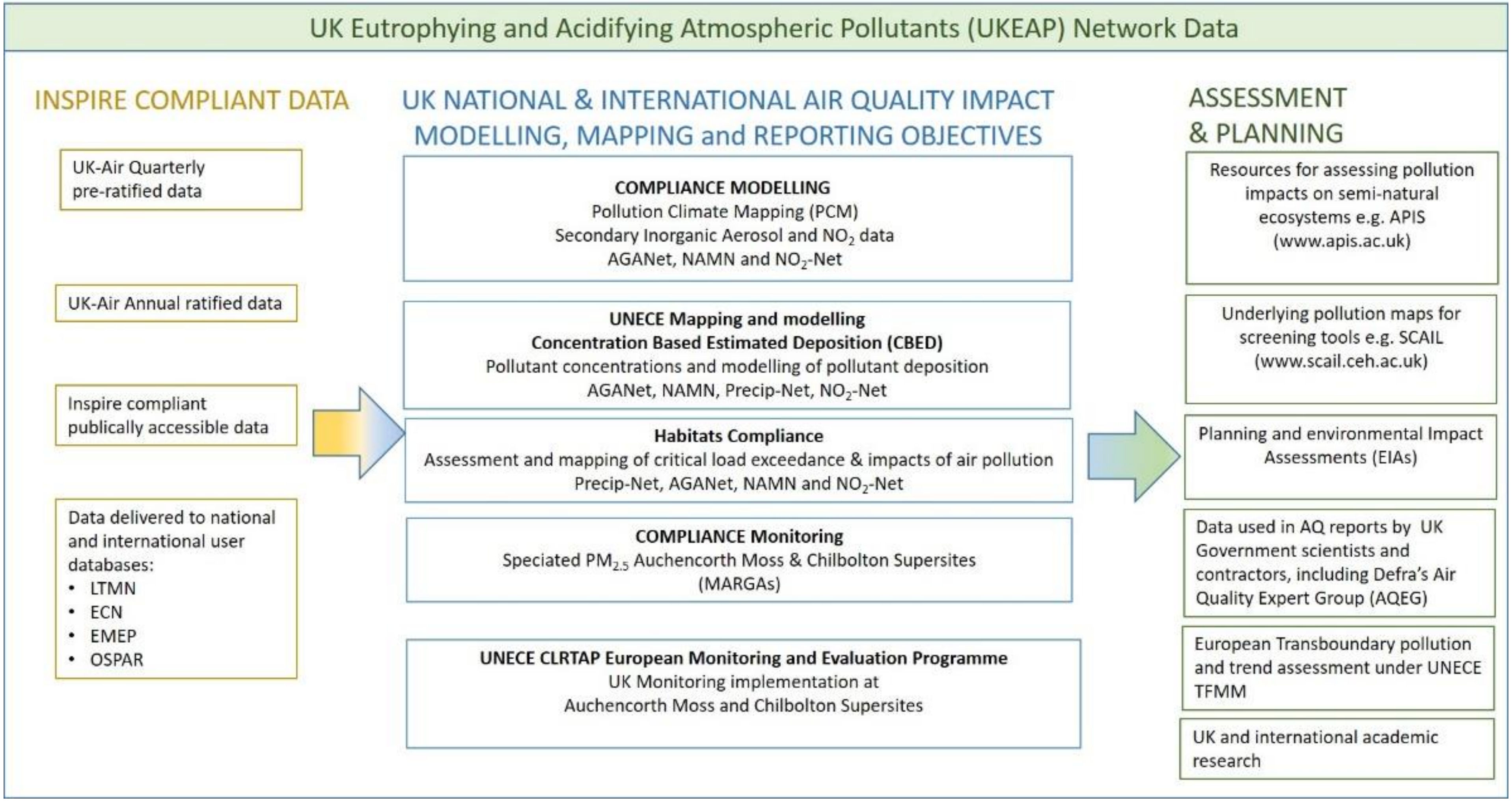

Figure 1 Summary of the data applications of the UKEAP datasets.

1.1 Background

The UKEAP measurements are in place to support compliance on estimates of secondary aerosol for $PM_{2.5}$, assess exceedances of critical loads (https://uk-air.defra.gov.uk/data/critical-load) and the risks to ecosystem, as well as to inform policy development on measures to reduce concentrations and deposition of atmospheric pollutants. UKEAP has been in place since 2012, however the 5 individual monitoring networks have been in operation much longer under separate contracts. The following section provides a brief background summary of the measurements and objectives of each network.

1.1.1 NAMN

The National Ammonia Monitoring Network (NAMN) has been in operation since 1996, and reports ammonia (NH_3) gas and ammonium (NH_4^+) aerosol. Ammonia is an air pollutant which is a precursor to secondary inorganic aerosol found in particulate matter of < 2.5 μm in diameter ($PM_{2.5}$), which is known to be detrimental to human health. In addition, deposition of NH_3 can cause damage to sensitive ecosystems directly through the eutrophication and indirectly through acidification. The objective of this network is to understand the long term spatial and temporal trends in concentrations across the UK, as well as providing information on the gas/aerosol partitioning of NH_3 to NH_4^+. The data is used to examine the changes in agricultural practices and allow assessment of the compliance to legislation, as well as to support deposition modelling (refer to Figure 1).

1.1.2 AGANet

The Acid Gases and Aerosol Network (AGANet) has been in operation since 1999 and provides information on the spatial concentrations of acid gases; nitric acid (HNO_3), sulphur dioxide (SO_2) and aerosols including chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), sodium (Na^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}). Nitric acid is a secondary pollutant produced from the photochemical reaction of nitrogen dioxide (NO_2) and is the precursor of NO_3^- aerosol. Sulphur dioxide is a primary pollutant, with the main anthropogenic source being the combustion of fossil fuels and major biogenic source being volcanic emissions. It is also the precursor to some SO_4^{2-} found in $PM_{2.5}$ and PM_{10}, which can also be found in sea salt. Sodium is predominantly from sea salt, whereas Ca^{2+} and Mg^{2+} also found in sea salt can be from other crustal sources such as soil resuspension and Saharan Sand. Aerosol potassium is associated with crustal sources and is also a marker for biomass burning. The objective of this network is to provide information on the long-term rural trends of pollutants that contribute to the acidification and eutrophication of ecosystems within the UK (refer to Figure 1).

1.1.3 Precip-Net

The Precipitation Network (Precip-Net) started monitoring in 1986. It provides information on the chemical composition of the precipitation across the UK. Specifically, the network reports the following parameters in precipitation: Ca^{2+}, Cl^-, Mg^{2+}, K^+, phosphate (PO_4^{3-}), NH_4^+, NO_3^-, SO_4^{2-} and Cl^-, as well as pH, conductivity and rainfall amount. The objective of this network is to provide information on the long-term trends of wet deposition of pollutants that are responsible for eutrophication and acidification of ecosystems (refer to Figure 1).

1.1.4 NO_2 - Net

The nitrogen dioxide network (NO_2-Net) started monitoring in 1993. The network provides a long-term monitoring of nitrogen dioxide within the rural environment and the gathered measurements provide measurement input data for national compliance modelling undertaken using the Pollution Climate Mapping (PCM) model. The model uses NO_2 measurement data from NO2-net to calculate the background NO_x concentration field (refer to Figure 1).

1.1.5 EMEP supersites

EMEP is the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe operates under the UNECE Convention on Long Range Transboundary Air Pollutants). There are two UK EMEP supersites, Auchencorth Moss has operated as an atmospheric observatory for long term measurements since 1995 and became EMEP Supersite in 2006, whereas Chilbolton Observatory completed its first year of measurements in 2016, following a relocation from Harwell (2006-2015) due to decommissioning of the site. Measurements made at the supersites in 2023 are summarised in Table 1.

The sites in addition provide the **required coverage**, of at least one station every 100,000 km^2, to determine the composition of $PM_{2.5}$ at rural background locations which were required under Annex IV of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe, which is now implemented under the Air Quality Standards Regulations[1] (Refer to section 1.2 further details). The chemical composition of $PM_{2.5}$ is determined for the following species:

- Elemental carbon (EC) and organic carbon (OC), from the UK Particle Concentrations and Numbers Monitoring Network.
- Inorganic species (K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}), from the MARGA instrument.

The UK Particle Concentrations and Numbers Monitoring Network provide the OC and EC, whereas UKEAP provides the inorganic species required. The high-resolution data is sufficient to allow comparison with atmospheric models and back-trajectory source apportionment.

EMEP supersite measurements funded under the UKEAP contract are specifically:

- Trace gas (HCl, HONO, HNO_3, NH_3, SO_2) and PM_{10} and $PM_{2.5}$ aerosol concentrations (K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}), Chilbolton Observatory and Auchencorth Moss.
- Online mercury measurements (Chilbolton Observatory: elemental mercury; Auchencorth Moss: elemental and speciated mercury).
- Meteorological observations (barometric pressure, dewpoint, wind speed & direction, relative humidity, temperature, (total) rainfall) for Chilbolton Observatory and are reported to EMEP. Auchencorth Moss meteorological measurements are instead funded by NERC National Capability UKSCAPE project. Data are from Auchencorth Moss are available on request and archived on STFC Centre for Environmental Data Analysis (CEDA, https://www.ceda.ac.uk/)

Table 1 Pollutants measured at the UK EMEP Supersites during 2023 (Highlighted in bold are those reported under the UKEAP contract)

Pollutant	CHO[1]	AUC[1]	EMEP Level	Averaging period	Monitoring network (CHO/AUC)
SO_2, HCl, HNO_3, HONO, NH_3 (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**
$PM_{2.5}$ K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**
PM_{10} K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**
Elemental mercury (GEM)		**X**	**III**	**Hourly**	**UKEAP**
Particulate mercury (PBM)		**X**	**III**	**Hourly**	**UKEAP**
Reactive mercury (GOM)		**X**	**III**	**Hourly**	**UKEAP**
Total gaseous mercury (TGM) in air	**X**		**II**	**Hourly**	**UKEAP**
Meteorological parameters (WS, WD, T, RH, rainfall)	**X**	***X*[2]**	**I**	**Hourly**	**UKEAP/UKCEH**
Precipitation chemistry	**X**	**X**	**I**	**Daily**	**UKEAP**
NO and NO_2 (thermal converter)	X	X[2]	I	Hourly	AURN/UKCEH
Sulphur dioxide	X		I	Hourly	AURN
Ozone	X	X	I	Hourly	AURN/UKCEH
Particulate matter $PM_{2.5}$, PM_{10}	X	X	I	Hourly	AURN
VOCs in air	X	X	II	Hourly	Automated HC Network
PAH in PM_{10}, air and rain	X	X	I	Monthly	PAH
Black carbon	X	X	II	Hourly	Particle numbers
Particle counts (>7 nm)	X	X[2]	II	Hourly	Particle numbers/UKCEH
Particle size distribution	X	X[2]	II	Hourly	Particle numbers
PM_{10} carbon-content (elemental carbon, EC, organic carbon, OC, total carbon, TC)	X	X	II	Weekly	Particle numbers
DELTA sampler (particulate-phase ions: Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NH_4^{2+}, NO_3^-, SO_4^{2-})	**X**	**X**	**I**	**Monthly**	**UKEAP**
Trace gases (HCl, HNO_3, NH_3, and SO_2)	**X**	**X**	**I**	**Monthly**	**UKEAP**
Heavy metals in precipitation	X	X	I	Monthly	Heavy Metals
Mercury in precipitation	X	X		Monthly	Heavy Metals
Heavy metals in PM_{10}	X	X	II	Weekly	Heavy Metals
Persistent Organic Pollutants (POPs) in air	X	X	I	Monthly	TOMPS
CO_2 measurements		X	III	Hourly	ICOS
NO and NO_2 (photolytic)		X	I	Hourly	NERC NC[2]

[1]CHO: Chilbolton Observatory; AUC: Auchencorth Moss; [2]NERC UKCEH National capability funded

1.2 UK Air Quality Legislation

The Ambient Air Quality Directive (2008/50/EC) and Fourth Daughter Directive (2004/107/EC) set standards such as statutory limit values and target values for the concentration of pollutants in ambient air. They also define monitoring and reporting obligations. In the UK, responsibility for meeting air quality targets and limit values is the Secretary of State in England but also devolved to the administrations in Scotland, Wales and Northern Ireland. These Directives were transposed by respective Air Quality Standard Regulations (as detailed below):

- The Air Quality Standards Regulations 2010 in England (UK Government, 2010), and their December 2016 and January 2019 amendments (UK Government, 2016 and 2019)
- The Air Quality Standards (Scotland) Regulations 2010 in Scotland (Scottish Government, 2010), and their December 2016 amendment (Scottish Government, 2016)
- The Air Quality Standards (Wales) Regulations 2010 in Wales (Welsh Government, 2010) and their February 2019 amendment (Welsh Government, 2019).
- The Air Quality Standards Regulations (Northern Ireland) 2010 (DAERA, 2010), and their December 2016, December 2018 and November 2020 amendments (DAERA, 2017, 2018 and 2020)

The Secretary of State for Environment, Food and Rural Affairs has responsibility for meeting the limit values and target values as defined through the Air Quality Standards Regulations 2010 for England and the Department for Environment, Food and Rural Affairs (Defra) co-ordinates assessment for the UK as a whole.

International relations are reserved to the UK Government; therefore Defra retains overall policy responsibility for the formulation of international air quality policy. Defra continues to represent the UK internationally, which reflects that while new domestic legislation is a devolved responsibility the overall compliance with international agreements will remain the responsibility of the UK Government.

The UK Environment Act (2021) (UK Government, 2021) established a duty for the UK Government to set a legally mandatory target in England to reduce $PM_{2.5}$, alongside at least one further long-term target on air quality. Within this framework, the Environmental Targets (Fine Particulate Matter) (England) Regulations (2023) (UK Government, 2023) came into force in January 2023. The Environmental Targets (fine particulate matter) (England) Regulations 2023 set two $PM_{2.5}$ targets to be met by 2040, these provide:

- A legal target to reduce population exposure to $PM_{2.5}$ by 35% in 2040 compared to 2018 levels

- A legal target to require a maximum annual mean concentration of 10 micrograms of PM2.5 per cubic metre (µg/m3) by 2040

The current UKEAP contract reports water-soluble $PM_{2.5}$ inorganic ions (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Mg^{2+} and Ca^{2+}) from the two EMEP supersites. The data is used to support the understanding of the composition and sources of total $PM_{2.5}$ at rural background locations in the UK but does not directly provide the total $PM_{2.5}$ mass concentrations.

1.3 Scope of the report

The following annual report for 2023 contains:

- A summary of network operations including Quality Assurance (QA)/ Quality Checks (QC) results, notable events and changes to the networks during 2023.
- Measured annual concentrations from all monitoring sites for each network.
- Interpretation of data and discussion of trends across the network.
- A summary of the scientific research and publications.
- A brief summary other activities using data from the network.

2. Methodologies

The following section outlines the methodologies used in each network and outlines information on site activities, calibrations or testing that is of note in 2023 to each network.

2.1 Precipitation Network (Precip-Net)

Bulk precipitation samples are collected using a bulk deposition collector. The bulk sampler consists of a funnel that collects the rain into a 3-litre sampling bottle. The sample bottle is protected by a stainless heat shield. An example bulk collector is shown in Figure 2.

Figure 2 An example of a bulk rain collector (Driby 2)

Samples are collected at fortnightly intervals at each of the 48 sites in the network (see Figure 3).

The network also incorporates fifteen sites (Ainsdale Dunes and Sands, Bure Marshes, Fenns, Whixall and Bettisfield Mosses, Ingleborough, Lullington Heath, Monks Wood, Stiperstones and Thursley Common 2, Braunton Burrows, Finglandrigg Woods, Lindisfarne, Saltfleetby-Theddlethorpe Dunes, Malham Tarn, Roudsea Wood & Mosses and Dersingham Bog) which form part of the Natural England's Long Term Monitoring Network (LTMN). The latter seven sites started operating in 2023.

All major ions in the rainwater samples are analysed including pH, S in sulphate (SO_4^{2-}—S), N in nitrate (NO_3^{-}—N), N in ammonium (NH_4^+-N), Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+, conductivity and PO_4^{3-}. Samples are deemed to be contaminated by bird strike if phosphate concentration is greater than 0.10 mg l^{-1}. Rainwater water volume is also measured. Derived parameters include sulphate derived from non-sea salt (anthropogenic) sources, hydrogen ion and rainfall height.

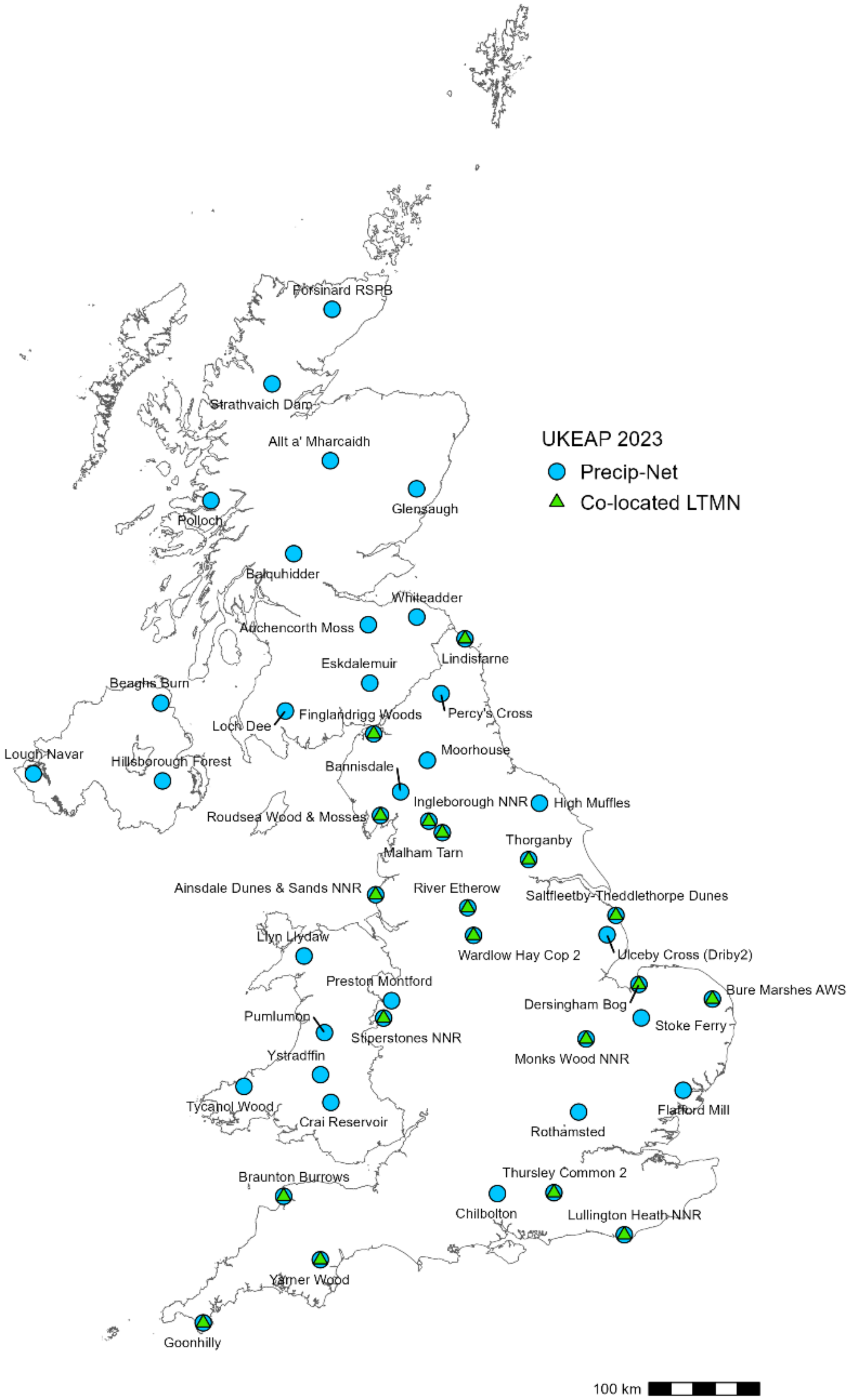

Figure 3 UK Precipitation chemistry Network (Precip-Net) in 2023

2.1.1 Overview of activities (Site Changes/services/audits/data ratification)

Local Sites Operators (LSOs) are used to undertake the site operation including replacing rain collection bottles, cleaning funnels, replacing debris filters and making observations at the site. LSOs also ensure the return of the collected rain samples. Quality assurance and laboratory intercomparison results from 2023 are summarised in the Appendix 2.

All sites are inspected and serviced during the summer months.

Maintenance and servicing of equipment at UKEAP network sites is undertaken across the UK with responsibility shared between Ricardo and UKCEH. The site maintenance and service visits are an opportunity to discuss with the LSO what local changes have occurred and provide training to LSOs where necessary. Vegetation surrounding the samplers is trimmed back during these visits.

All analysed samples undergo an ion balance check which involves comparing the total concentration of positive ions (cations) with the total concentration of negative ions (anions) in a sample. Samples are submitted for reanalysis if the difference in ion balance is greater than 15%, 30% or 60% depending on the ion strength of the sample. Samples are also submitted for reanalysis if the difference between the measured and theoretical conductivity is greater than 30%. Typically, 10-20% of samples are submitted for reanalysis.

2.1.2 Certification, testing and calibration

The analytical methods used to measure the concentrations of anions and cations, pH and conductivity in the rainwater samples are UKAS ISO/IEC 17025:2017 accredited. Details can be found under the analytical laboratory's accreditation at https://www.ukas.com.

Each year the analytical laboratory participates in a laboratory intercomparison exercise managed by the Norwegian Institute for Air Research (NILU)[1]. This involves the analysis of four synthetic rainwater samples typical of concentrations currently measured in Europe. A discussion of the performance for the 41st intercomparison is presented in Appendix 2. Most results were satisfactory, however the low concentration measurements for calcium, magnesium and potassium required improvement and the analysts are investigating how the analysis can be improved.

[1] https://projects.nilu.no/ccc/intercomparison/index.html

2.2 NO_2-Net Network

The NO_2 network (NO_2-Net) consists of 24 sites (see Figure 4) at which diffusion tubes (7.1 cm long, open inlet), in triplicate, were exposed for approximately 4-week exposure periods. Up until 2021 diffusion tubes consisted of a polypropylene tube (7.1 cm in length), on one end of which is a low-density polyethylene cap. Two stainless steel grids impregnated with the absorbent chemical are mounted within this cap. At the other end the cap was left open during sampling. The absorbent is a solution of 50% triethanolamine in acetone.

Since 2022 an additional set of triplicate tubes similar to those used in the UK Urban NO_2 Network[2] was introduced into the network. These tubes have a wind protection cap that maintains the diffusion path length and hence reduces the positive sampling bias. After two years of parallel sampling the open diffusions were discontinued and only the diffusion tubes with wind protection caps are used. The absorbent is a solution of 20% triethanolamine in water.

The decision to discontinue the diffusion tubes without the wind protection caps was based on an evaluation of nitrogen dioxide concentrations measured by diffusion tubes with and without wind protection caps (see Appendix 3). This evaluation was carried out for samples over 14 four-week periods, from December 2021 until December 2022 and showed that the diffusion tubes with wind protection caps measured on average a nitrogen dioxide concentration about 0.9 µg m^{-3} less than that measured by those diffusion tubes without wind protection caps.

The coefficient of variation for the triplicate tubes was also shown to be much lower for the tubes with wind protection caps compared to those without wind protection caps, with values of 5.2 % and 12.4 %, respectively. This suggests that the tubes with wind protection caps are more consistent.

The evaluation also compared the NO_2 concentrations measured by the chemiluminescence analysers at the three sites (Chilbolton, High Muffles and Yarner Wood) within the AURN where diffusion tubes are collocated. For each sampling period, the chemiluminescence analyser measured a higher nitrogen dioxide concentration than that measured by the diffusion tubes with the wind protection tubes. One of the reasons for the higher measurements could be attributed to the oxidation of total reactive nitrogen during the chemiluminescent measurement process (this is also described further in Appendix 3). Bias adjustment using the chemiluminescent analysers may not be appropriate for diffusion tubes with wind protection caps at the low concentrations found at the rural locations in the UKEAP network.

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[2] https://uk-air.defra.gov.uk/assets/documents/reports/cat09/2309281201_UUNN_Public_Annual_Report_2022.pdf

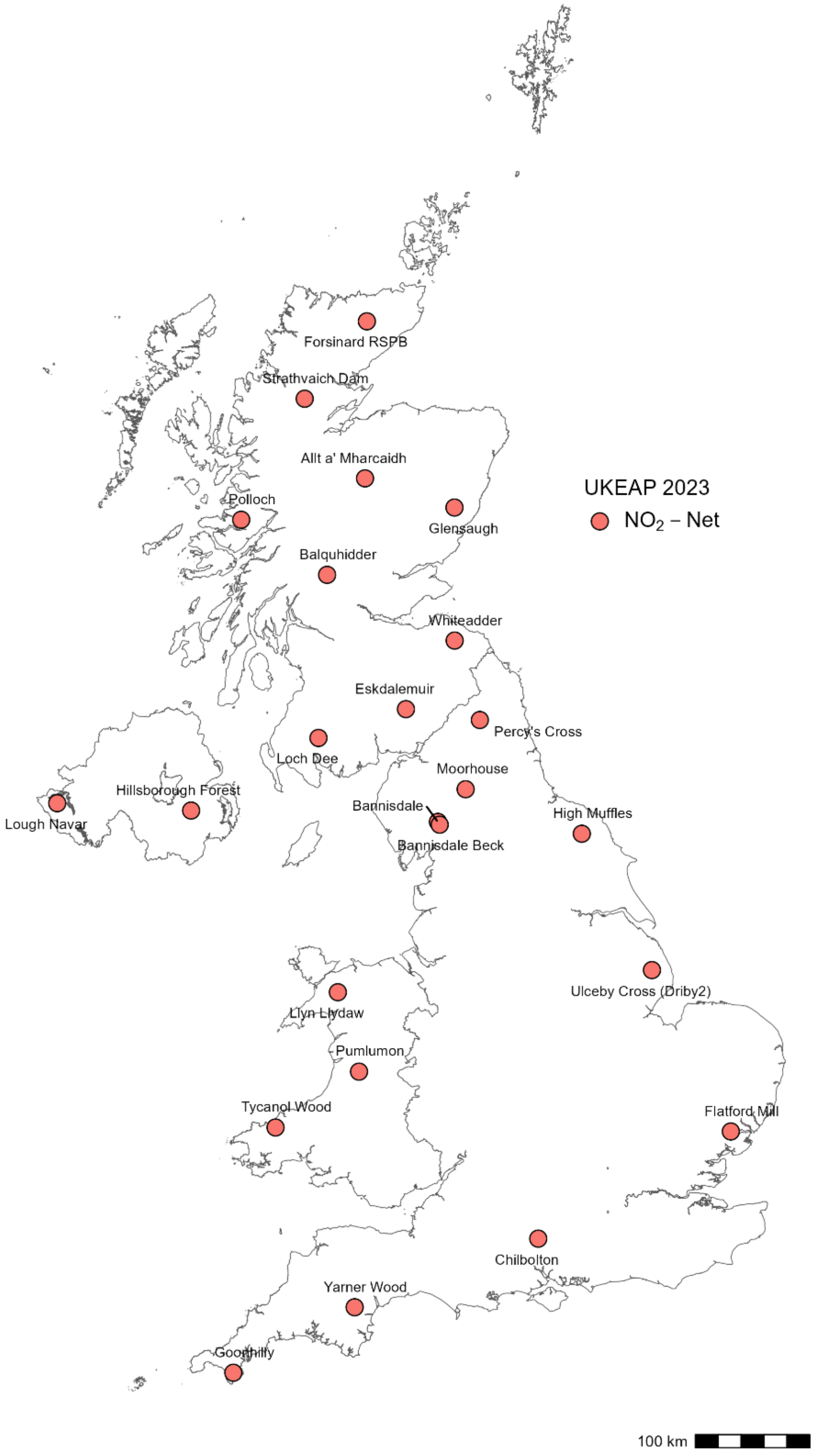


Figure 4 UK NO_2 diffusion tube (NO_2-Net) Network in 2023

2.2.1 Overview of activities (site changes/ services/audits, data ratification)

The NO_2 measured is used to generate a background nitrogen oxides (NO_X) concentration field for Defra's Pollution Climate Mapping (Figure 1). The samplers are deployed in triplicate at the monitoring locations. The open tubes and wind protected tubes were supplied by SOCOTEC and Gradko respectively.

All sites are inspected during the summer months with responsibility shared between Ricardo and UKCEH. The site maintenance and service visits are an opportunity to discuss with the LSO local changes that have occurred and provide training to LSOs where necessary. Vegetation around samplers is maintained during these visits.

2.2.2 Accreditation, analytical proficiency testing (PT) and intercomparisons

The analytical methods used by Socotec and Gradko to measure the concentrations of NO_2 using diffusion tubes are both UKAS accredited. Details of each analytical laboratory's accreditation can be found at https://www.ukas.com.

Both analytical laboratories also participate in the AIR-PT analysis scheme[2]. This is an independent analytical proficiency-testing scheme, operated by LGC Standards and supported by the Health and Safety Laboratory (HSL). Defra and the Devolved Administrations advise that diffusion tubes used for Local Air Quality management (LAQM) should be obtained from laboratories that have demonstrated satisfactory performance in the AIR NO_2 PT scheme[2]. Results for recent analytical laboratory performance are summarised below:

AIR PT Round	AIR PT AR053	AIR PT AR055	AIR PT AR056	AIR PT AR058	AIR PT AR059
Period	September – October 2022	January – February 2023	May – June 2023	July – August 2023	September – October 2023
Socotec UK Limited	100%	100%	100%	100%	100%
Gradko International Ltd	100%	100%	100%	100%	100%

In addition, Socotec also participated in the EMEP laboratory intercomparison exercise managed by NILU[3]. This involves the analysis of four absorbing solution samples. A discussion of the performance for the most recent intercomparison is presented in Appendix 2.

2.2.3 Bias adjustment

As discussed above in Section 2.2 diffusion tubes with no wind protection caps were discontinued from 2024 onwards and only diffusion tubes with wind protection caps will be employed going forward and they will be reported without bias adjustment.

Measurements of open diffusion tubes between 2020 and 2022 were biased corrected using the collocated diffusion tubes and chemiluminescence analysers at Chilbolton Observatory, Eskdalemuir, High Muffles and Yarner Wood.

2.3 National Ammonia Monitoring Network (NAMN)

NAMN measurements continue to be made with a mixture of active DELTA® (NH_3 and NH_4^+) systems and passive ALPHA® samplers (NH_3 only)[4]. Details for the two methods are described below.

ALPHA®

The ALPHA® (Adapted Low-cost High Absorption) sampler (Figure 5) is a badge type diffusive sampler designed by the UK Centre for Ecology & Hydrology[5] for the long-term sampling of NH_3 concentrations. The samplers are deployed in triplicate at each monitoring location, with uptake rates calculated annually by collocating samplers with DELTAs at 9 sites around the UK. The sampling protocol used is based on the EN17346:2020 standard[6] with samplers changed on a monthly basis by local site operators (LSOs).

Figure 5: ALPHA® Site Example (Carlisle)

DELTA®

The DELTA® (**DE**nuder for **L**ong-**T**erm **A**tmospheric sampling, Figure 6)[7] is a low-volume denuder filter pack method designed for time integrated monitoring of trace gases (NH_3, HNO_3, SO_2) and aerosols (NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca_2^+ and Mg^{2+})[8]. Samplers are changed on a monthly basis as per the UKEAP protocols.

Figure 6: DELTA® site example (Forsinard)

2.3.1 Overview of activities

During 2023 the number of NAMN sites providing monthly measurements of atmospheric NH_3 increased from 97 to 113, summarised in Table 2.

Table 2: Summary of National Ammonia Monitoring Network (NAMN) monitoring site types in December 2023

Site Type	Number
UKCEH DELTA® sites sampling	28
UKCEH ALPHA® sites sampling	94
Total number of sites	113*

*9 sites were co-located ALPHA and DELTA sites for calibration

All NAMN sites (UKCEH ALPHA® and UKCEH DELTA®) had site visits conducted as stated in the protocols. This included a visual audit of all ALPHA sites in NAMN in 2023, with any remedial action identified and discussed with LSOs. Data from the NAMN network have been submitted according to the agreed project deadlines, unratified data was submitted to UK-AIR quarterly and ratified data for the entire year was submitted to UKAIR in April 2024.

During 2023 the following network infrastructure changes occurred:

- 16 (UKCEH ALPHA) sites were added to the network (Figure 7a). The sites added are listed below:

1. UKA00969 Braunton Burrows
2. UKA01032 Chippenham Fen
3. UKA01031 Chobham Common
4. UKA00970 Dersingham Bog
5. UKA01033 Downton Gorge
6. UKA01028 Epping Forest
7. UKA00971 Finglandrigg Woods
8. UKA00972 Lindisfarne
9. UKA01030 Lower Derwent Valley
10. UKA00974 Malham Tarn
11. UKA01035 North Walney
12. UKA01034 Old Winchester Hill
13. UKA00975 Roudsea Wood & Mosses
14. UKA00973 Saltfleetby-Theddlethorpe Dunes
15. UKA01036 Woodwalton Fen
16. UKA01029 Wyre Forest

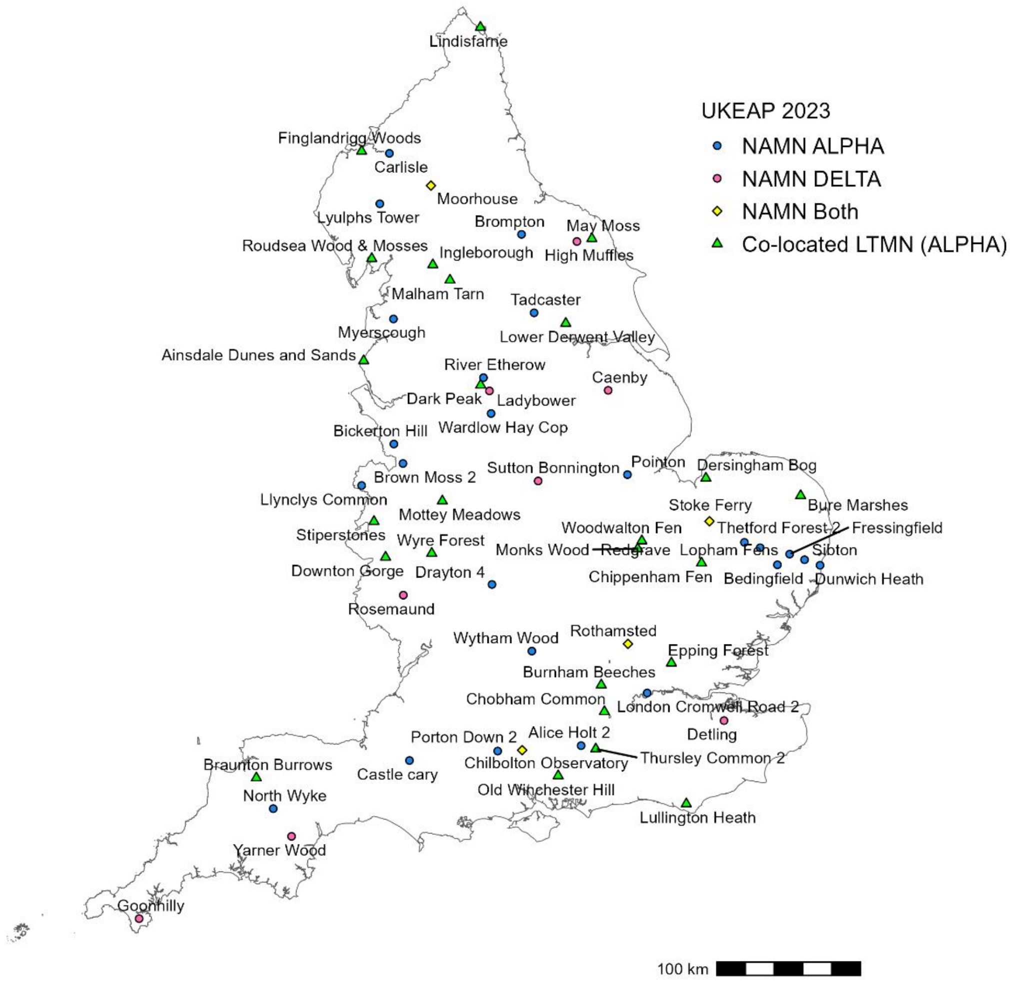
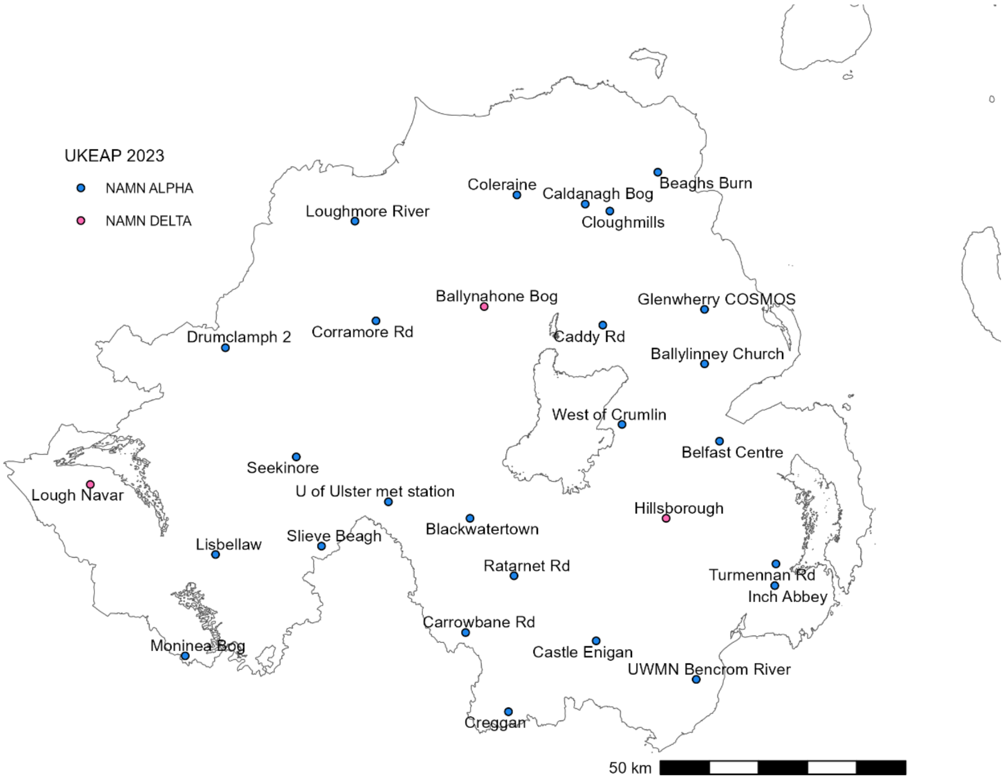


Figure 7a) UK National Ammonia Monitoring Network (NAMN) and co-located LTMN sites in England. NAMN both – sites which have co-located ALPHA® and DELTA® samplers.



Fig*ure 7b) UK National Ammonia Monitoring Network (NAMN) in Northern Ireland. NAMN both – sites which have co-located ALPHA® and DELTA® samplers.*

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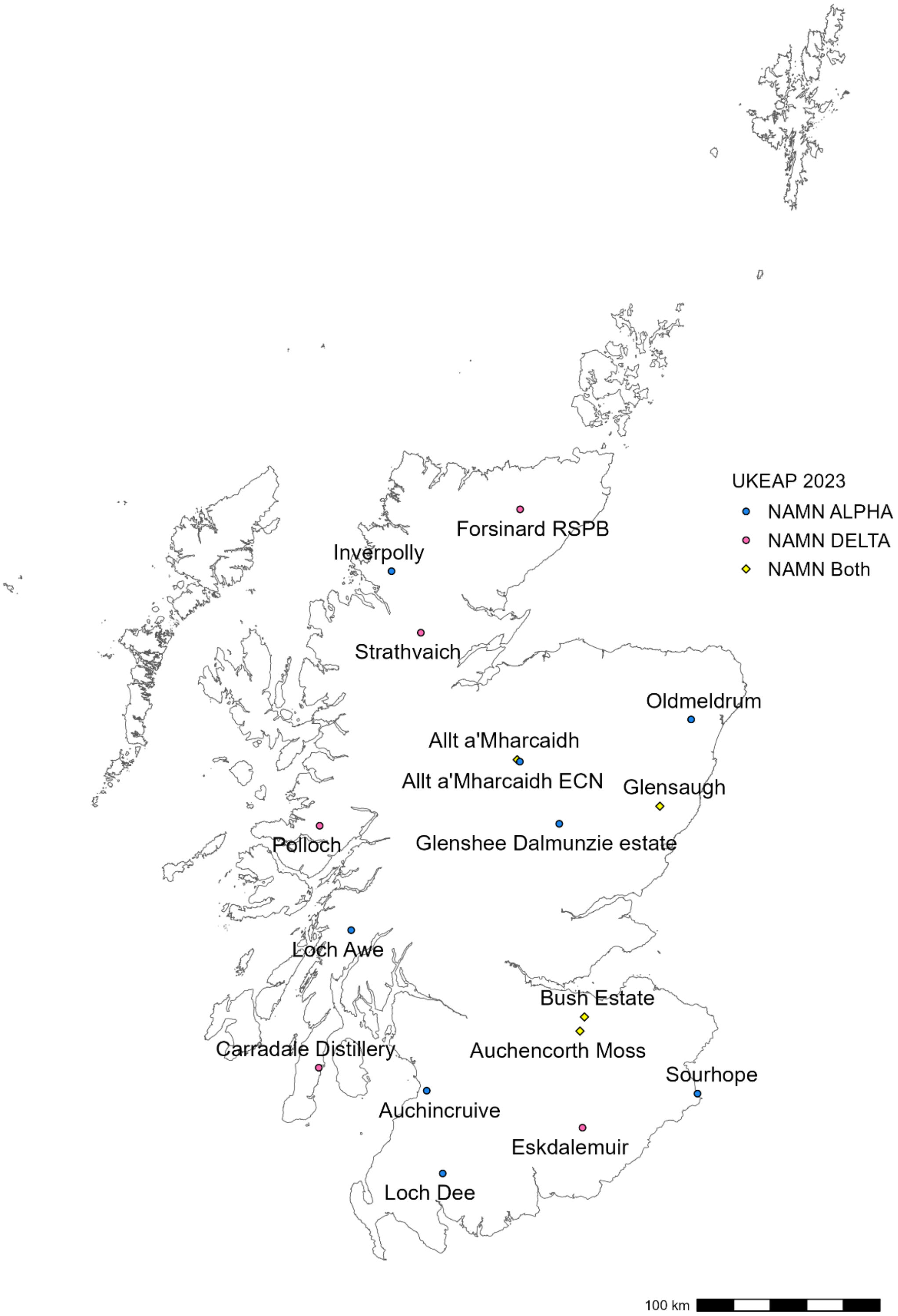


Figure 7c) UK National Ammonia Monitoring Network (NAMN) in Scotland. NAMN both – sites which have co-located ALPHA® and DELTA® samplers.

Figure 7d) UK National Ammonia Monitoring Network (NAMN) in Wales. NAMN both – sites which have co-located ALPHA® and DELTA® samplers.

Figure 7a to d summarises the current locations of the NAMN network. The map also shows where the NAMN sites are embedded in the Natural England Long Term Monitoring Network (Figure 7a) LTMN, 31 sites) and the sites from the Northern Ireland Network (NI Network, 25 sites added in 2022, Figure 7b)

2.3.2 Certification, testing and calibration

At 9 NAMN sites around the UK, parallel measurements are made with both the UKCEH DELTA® systems and passive UKCEH ALPHA® samplers to 1) determine the annual uptake rate of the ALPHA® as per the EN17346:2020 standard[6] and 2) to ensure that no bias is introduced into the sampling and to maintain the validity of long-term trends. For the year 2023, the coefficient of determination (R^2) was 0.89 showing as normal linearity between ALPHAs and DELTAs, with the calibrated uptake rate determined as 0.0043698 m^3 hr^{-1} (Figure 8). When compared to historical trends, it was found that the calibrated uptake rate was higher than the reported range for previous years (Figure 9). The higher the uptake rate applied, the lower the ammonia concentration reported. Studies are being undertaken to investigate this increase in the calculated uptake rate. For the year 2023 the calculated uncertainty of the UKCEH ALPHA® system is 11% which is comparable to the results found in Martin *et al.* (2019)[9] for passive samplers.

Laboratory Quality Assurance

Preparation and analysis of both the UKCEH ALPHA® and UKCEH DELTA® sampler was conducted by UKCEH Lancaster Laboratories. These laboratories operate and are certified to ISO 17025:2017 for the analysis relating to the UKCEH ALPHA® and DELTA® systems. Details of the laboratory accreditation can be found at https://www.ukas.com. Replicate UKCEH ALPHA® samplers were used for each measurement (triplicate samplers) and were only accepted when they were within 15% (Coefficient of Variance, CV).

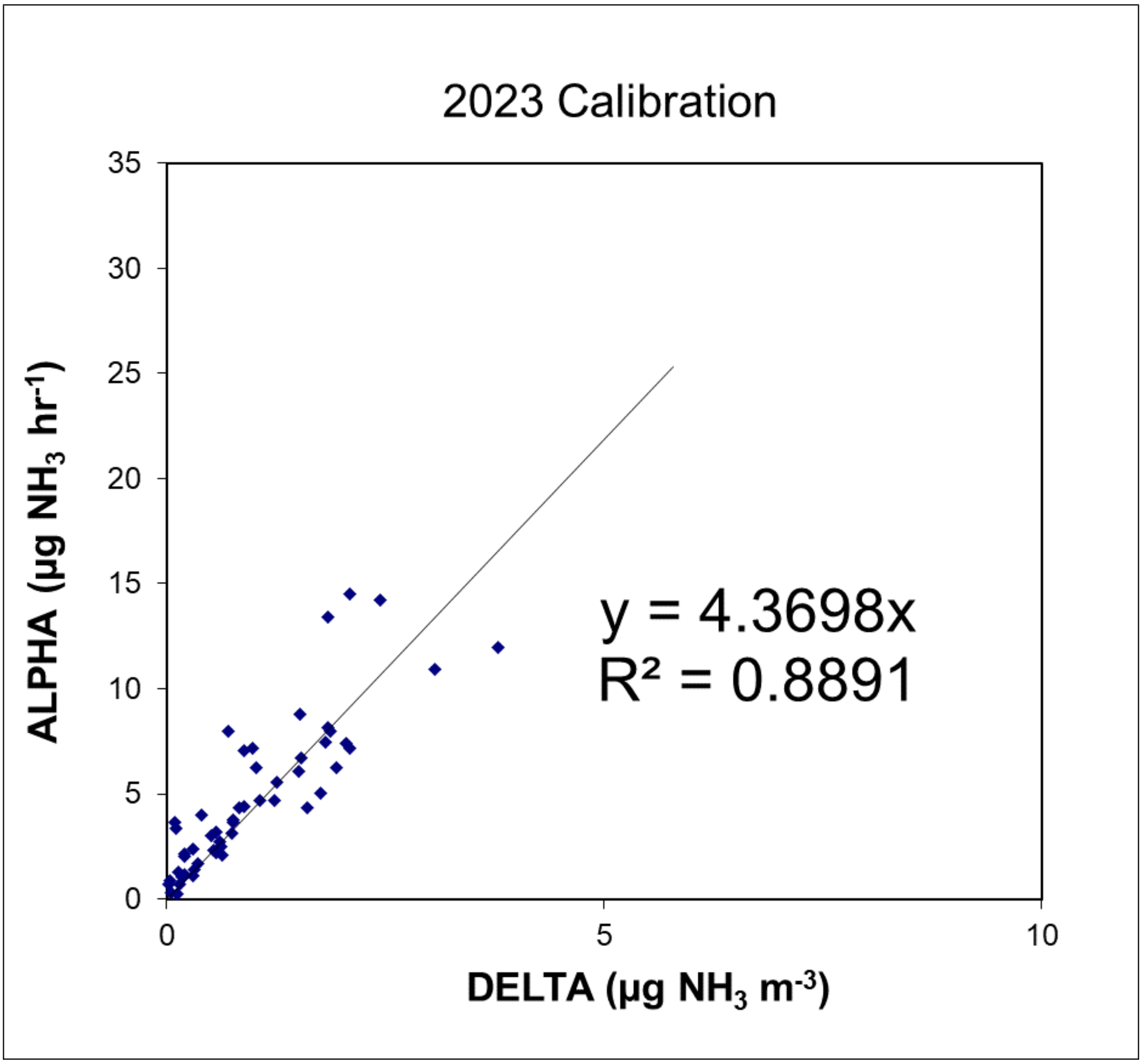


Figure 8: 2023 UKCEH ALPHA® uptake rate calibration

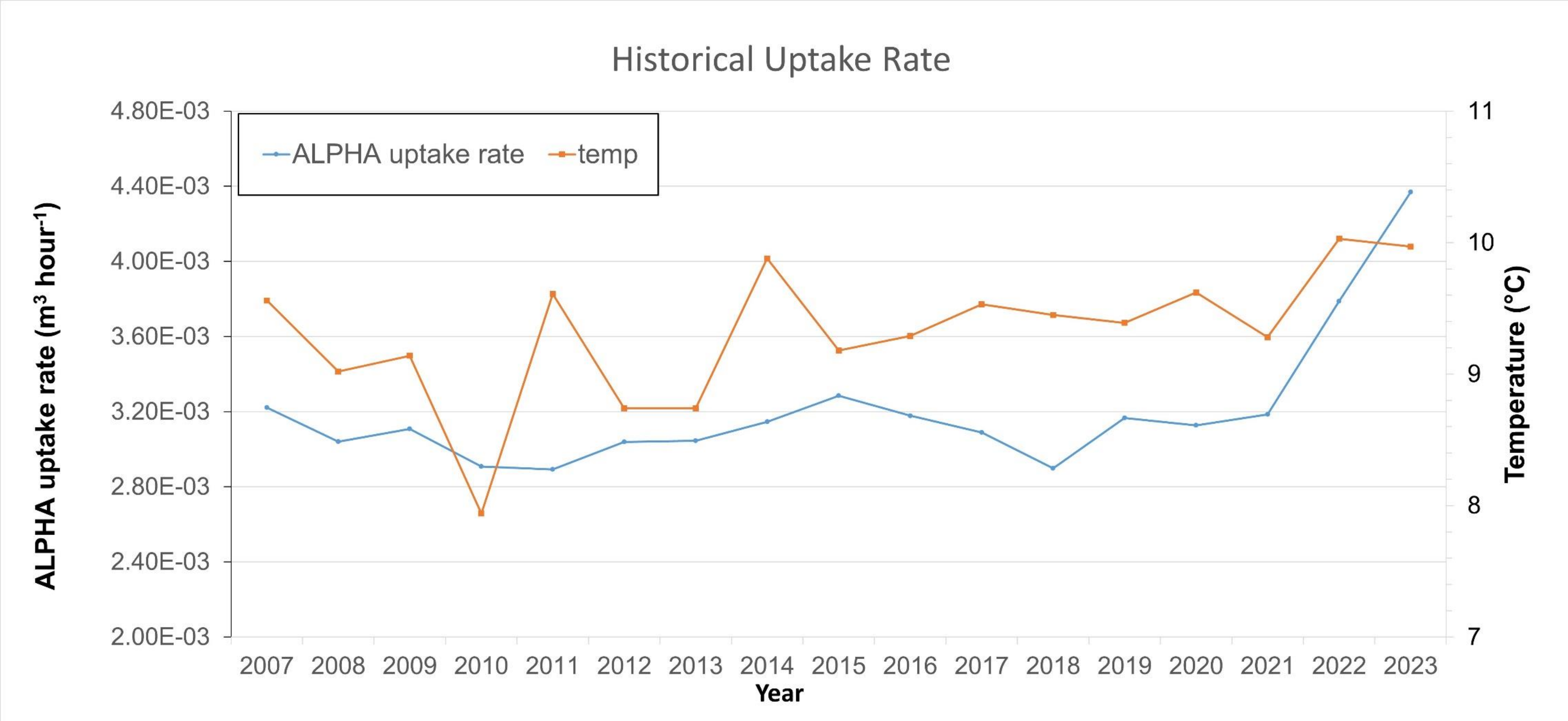


Figure 9: UKEAP uptake rate for ALPHA samplers and UK annual average temperature (source: https://www.metoffice.gov.uk/research/climate/maps-and-data/summaries/index)

2.4 Acid Gas and Aerosol Network (AGANet)

The UK Acid Gas and Aerosol Network (AGANet) provides monthly speciated measurements of atmospheric reactive gases (HNO_3, SO_2) and aerosols (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, Ca^{2+}, Mg^{2+}) at 28 sites across the UK (Figure 10). Measurements are carried using the DELTA® sampler as described in Section 2.3.

Table 3 Summary of the number of sites within AGANet in December 2023

Site Type	Number
AGANET UKCEH DELTA® sites (sampling gaseous NH_3, HNO_3, SO & aerosol NH_4^+, NO_3^-, SO_4^2, Cl^-, Na^+, Ca^{2+}, Mg^{2+})	28
Total number of sites	28

2.4.1 Overview of activities

All AGANet sites had LSO and annual site visits conducted according to project protocols. There are currently no outstanding actions from the 2023 service round. Data from the AGANet was submitted according to the agreed project deadlines. Unratified data was submitted to UKAIR quarterly and annual ratified data for the 2023 calendar year was submitted to UKAIR in April 2024. During 2023 there were no changes to the network.

2.4.2 Certification, testing and calibration

Laboratory Quality Assurance

Preparation and analysis of both the UKCEH ALPHA® and UKCEH DELTA® sampler was conducted by UKCEH Lancaster Laboratories. These laboratories operate and are certified to ISO 17025:2017 for the analysis relating to the UKCEH ALPHA® and DELTA® systems. Details of the laboratory accreditation can be found at https://www.ukas.com.

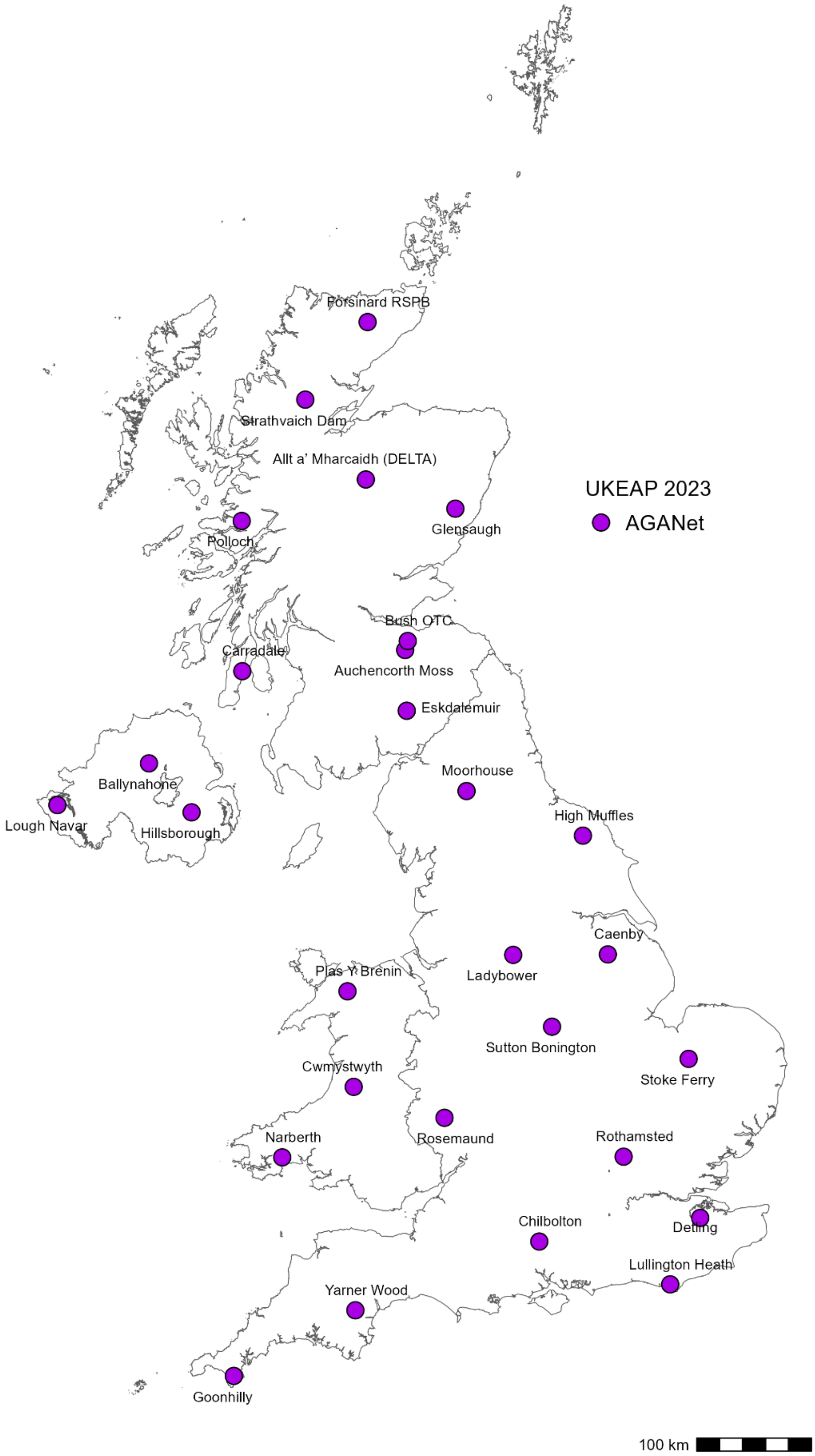


Figure 10 UK Acid Gases and Aerosol Network (AGANet).

2.5 UK EMEP supersites

The instrumentation used under UKEAP as part of the reporting to EMEP is summarised below.

Monitor for Aerosols and Gases in Ambient air (MARGA)

Measurements of water soluble inorganic cations and anions in PM_{10} and $PM_{2.5}$: sulphate (SO_4^{2-}), nitrate (NO_3^-), sodium ion (Na^+), potassium ion (K^+), ammonium ion (NH_4^+), chloride ion (Cl^-), calcium ion (Ca^{2+}), and magnesium ion (Mg^{2+}) were measured by the **M**onitor for **A**e**R**osols and **G**ases in ambient **A**ir monitor (MARGA 2S, Metrohm, NL, Figure 11). In addition, the MARGA measure ammonia (NH_3), nitric acid (HNO_3), nitrous acid (HONO), hydrochloric acid (HCl) and sulphur dioxide (SO_2).

Figure 11 Photo of the MARGA 2S in operation at Auchencorth Moss

The MARGA 2S operates by sampling the ambient air through a PM_{10} size-selective inlet head at a nominal flow rate of 2 m^3 hr^{-1}. The air stream is then split as there are two sample boxes, which both contain a wet rotating annular denuder (WRD) and a steam jet aerosol collector (SJAC). One sample box reports PM_{10} and the trace gases, whereas the second sample box reports the $PM_{2.5}$. The $PM_{2.5}$ fraction is separated from the sampled PM_{10} by means of a cyclone separator fitted at the inlet to the $PM_{2.5}$ sample box. On entering the sample box, the WRD removes water-soluble gases from the sampled air stream. Particles (PM) pass through the denuder unsampled and are activated by steam (generated at ~120°C) into droplets in the SJAC and are removed via a cyclone. The solutions of dissolved gases and aerosol species are then analysed on-line, and in near real-time, by ion chromatography. Parallel IC systems are used for the detection of the cation and anion species. An internal standard of lithium bromide (LiBr) is used for on-going calibration purposes. Further details can be found in Twigg et al. (2015)[10].

Tekran

Both sites use a Tekran 2537X (Figure 12, Tekran Instruments, USA) to measure the mercury in ambient air. The analyser uses an automated dual channel amalgamation technique and Cold Vapour Atomic Fluorescence Spectroscopy (CVAFS, 253.7nm) to detect gaseous elemental mercury (GEM). The Tekran 2537X reports everything as GEM however different sampling set-ups can change the mercury species reported.

At the Auchencorth Moss site there are extra instruments (Tekran 1130 and 1135, Teledyne, USA) running alongside the Tekran 2537X. The units separate the sample prior to analysis resulting in speciated mercury measurements. The sampled air (10 l min^{-1}) first passes through a $PM_{2.5}$ impactor and through onto a coated denuder which capturers the gaseous oxidised mercury (GOM) species. The air then flows through a filter to capture any particle bound mercury (PBM). The remaining air goes straight to the Tekran 2537X, where any mercury is reported as gaseous elemental mercury (GEM). The system operates on a 3-hour cycle. For the first 2 hours it collects the GOM and PBM, while the GEM is measured every 5 minutes. In the third hour, zero air is flowed through the sample train and the denuder and filter are heated in sequence giving results for the GOM and PBM, from the 2-hour sampling period.

At the Chilbolton Observatory site there is only the Tekran 2537X. This has a 0.2 µm filter on a heated inlet line sampling a 1 l min^{-1}. Due to its difference in set-up it reports total gaseous mercury (TGM), as the particulate is removed by the filter leaving the sample made up of GEM and GOM.

Both Tekran 2537X instruments perform a calibration from a perm source every 25 hours. Annually as part of the maintenance service a manual multipoint perm source verification is carried out. Full details of the Chilbolton Observatory set-up can be found in Kentisbeer et al. (2015)[11], whereas the Auchencorth Moss set-up is described in Kentisbeer et al. (2014)[12].

Figure 12 Photo of the Tekran set-up at Auchencorth Moss

2.5.1 Overview of activities

The Chilbolton Observatory EMEP Supersite is operated by Ricardo summarised on UK-AIR. There were no modifications to the site infrastructure in 2022. Ricardo act as Local Site Operator for the Chilbolton Observatory (CHO) EMEP Supersite measurements for all measurements except those conducted by the National Physical Laboratory (NPL). The Auchencorth Moss (AUC) EMEP Supersite is operated by UKCEH, summarised on UK-AIR. UK CEH is LSO for all measurements at Auchencorth Moss. No instruments were changed during 2023. During 2023 no health and safety incidents occurred that require action by UKCEH or Ricardo at either site in relation to the operation of the EMEP Supersites.

2.5.2 Certification, testing and calibration

The MARGA's detection system was continuously calibrated by the use of an internal standard, containing ions not normally present in ambient air. At Auchencorth Moss the solutions are: stock solution: Li^+ 28 mg/L and Br^- 325 mg/L, working solution: Li^+

70 ppb Br^- 800 ppb. The Chilbolton Observatory instrument's working solution was made-up periodically by diluting) a high concentration stock solution of LiBr. The nominal concentration of Li^+ in the stock and work solutions were 320000 ppb and 320 ppb, respectively, and 3680 mg L^{-1} and 3.68 mg L^{-1} (1 mg L^{-1} = 1 ppm) of Br^-.

Sub-samples of the internal standard used at both sites were analysed by UKCEH to ensure that both the stock and working solutions contained the correct, within ±20%, concentrations of Li^+ and Br^- when compared to the nominal concentrations. Spot samples of the stock and working solution were sent once a quarter via mail-out and analysed retrospectively. The Li^+ and Br^- concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC), respectively. As part of the data ratification process, MARGA measurements were rejected if the measured concentrations of Li^+ and Br^-, in the internal standard, deviated by more than ± 20% of the nominal concentration.

A regular maintenance scheme is in place on the MARGA instrument includes monthly calibration of the 2 mass flow controllers in the instrument, to ensure the correct flow rate through a steam jet aerosol collector (SJAC), which has been designed to operate at 1 m^3/hr. The frequency of calibration is increased if the positions of annular denuders in the system are altered. As part of the MARGAs ongoing QC a monthly blank. As well as being used to identify any potential contamination in the system, it was used in the calculation of a detection limit for certain species which is used in the ratifying process.

2.5.3 Data Quality objectives

For the supersites the MARGA has a legal obligation to report speciated $PM_{2.5}$ by the MARGA. In 2023 the $PM_{2.5}$ time coverage by MARGA instruments met the minimum time coverage requirement of 14% which is required under compliance of the Air Quality Standard Regulations, refer to Section 3.5.1 for further details.

3. Results & Discussion

3.1 Precipitation Network (Precip-Net)

The data capture measured as an average of all measured components for each site is presented in Table 4. Data capture has been defined as the percentage of samples with valid data. Reasons why samples have invalid sample include contamination, usually by bird strike, extended sampling times or loss or damage of samples during transit. There continues to be a considerable loss of samples at Loch Dee. We will investigate the options for bird deterrents at Loch Dee the during the site service in 2024 however, several measures are already in place.

The spatial patterns of the annual mean precipitation-weighted concentration of non-sea salt sulphate (nss-SO_4^{2-}), NO_3^-, NH_4^+ and H^+ are presented in Figures 13 and 14 for 2023. These are prepared using kriging. The maps show that: the non-sea salt sulphate and nitrate concentrations tend to be highest on the eastern seaboard where the rainwater volume is smallest. Ammonium concentrations are highest in the areas of the UK where intensive livestock activity is highest. There is no clear pattern in the hydrogen ion concentration.

Figure 15 summarises the National Emissions Inventory (NAEI) estimated annual emission of precursor gases since the inception of the Precip-Net network in 1986. All of the emission estimates have decreased though the rate of decrease for sulphur dioxide was greater than that for oxides of nitrogen and ammonium. Sulphur dioxide emissions have decreased by about 97%, oxides of nitrogen emissions have decreased by about 78% and ammonia emissions have decreased by about 18%. Figure 15 also presents projected emissions for 2022, 2025 and 2030 (2040 emissions available on 11th July 2024) for the respective gases from the National Emissions Inventory (NAEI)[13].

Table 4 Data capture with the Precip-Net network in 2023.

Site	UKAIR ID	Average, %	Site	UKAIR ID	Average, %
Ainsdale Dunes and Sands	UKA00635	91.7	Loch Dee	UKA00107	47.7
Allt a'Mharcaidh	UKA00086	86.7	Lough Navar	UKA00166	92.3
Auchencorth Moss	UKA00451	96.2	Lullington Heath	UKA00152	84.4
Balquhidder 2	UKA00239	96.2	Malham Tarn	UKA00974	94.5
Bannisdale Beck	UKA00936	99.3	Monks Wood	UKA00639	92.3
Beaghs Burn	UKA00383	92.1	Moorhouse	UKA00357	92.6
Braunton Burrows	UKA00969	77.6	Percy's Cross	UKA00504	90.6
Bure Marshes	UKA00641	90.1	Polloch	UKA00180	92.3
Chilbolton Observatory	UKA00614	91.4	Preston Montford	UKA00110	84.2
Crai Reservoir 2	UKA00657	83.6	Pumlumon	UKA00173	77.3
Dersingham Bog	UKA00970	95.2	River Etherow	UKA00391	95.3
Driby 2	UKA00550	97.5	Rothamsted	UKA00275	91.4
Eskdalemuir	UKA00130	94.0	Roudsea Wood & Mosses	UKA00975	87.0
Fenn's, Whixall and Bettisfield Mosses	UKA00642	79.9	Saltfleetby-Theddlethorpe Dunes	UKA00973	95.4
Finglandrigg Woods	UKA00971	89.5	Stiperstones	UKA00640	95.3
Flatford Mill	UKA00103	76.5	Stoke Ferry	UKA00317	89.3
Forsinard RSPB	UKA00607	82.5	Strathvaich	UKA00162	100.0
Glensaugh	UKA00348	83.8	Thorganby	UKA00112	90.6
Goonhilly	UKA00056	91.9	Thursley Common 2	UKA00588	86.3
High Muffles	UKA00169	92.3	Tycanol Wood	UKA00113	96.9
Hillsborough Forest	UKA00293	84.4	Wardlow Hay Cop	UKA00119	89.9
Ingleborough	UKA00637	94.5	Whiteadder	UKA00123	88.3
Lindisfarne	UKA00972	84.0	Yarner Wood	UKA00168	61.6
Llyn Llydaw	UKA00268	91.6	Ystradffin	UKA00505	77.2
			Network average		88.2

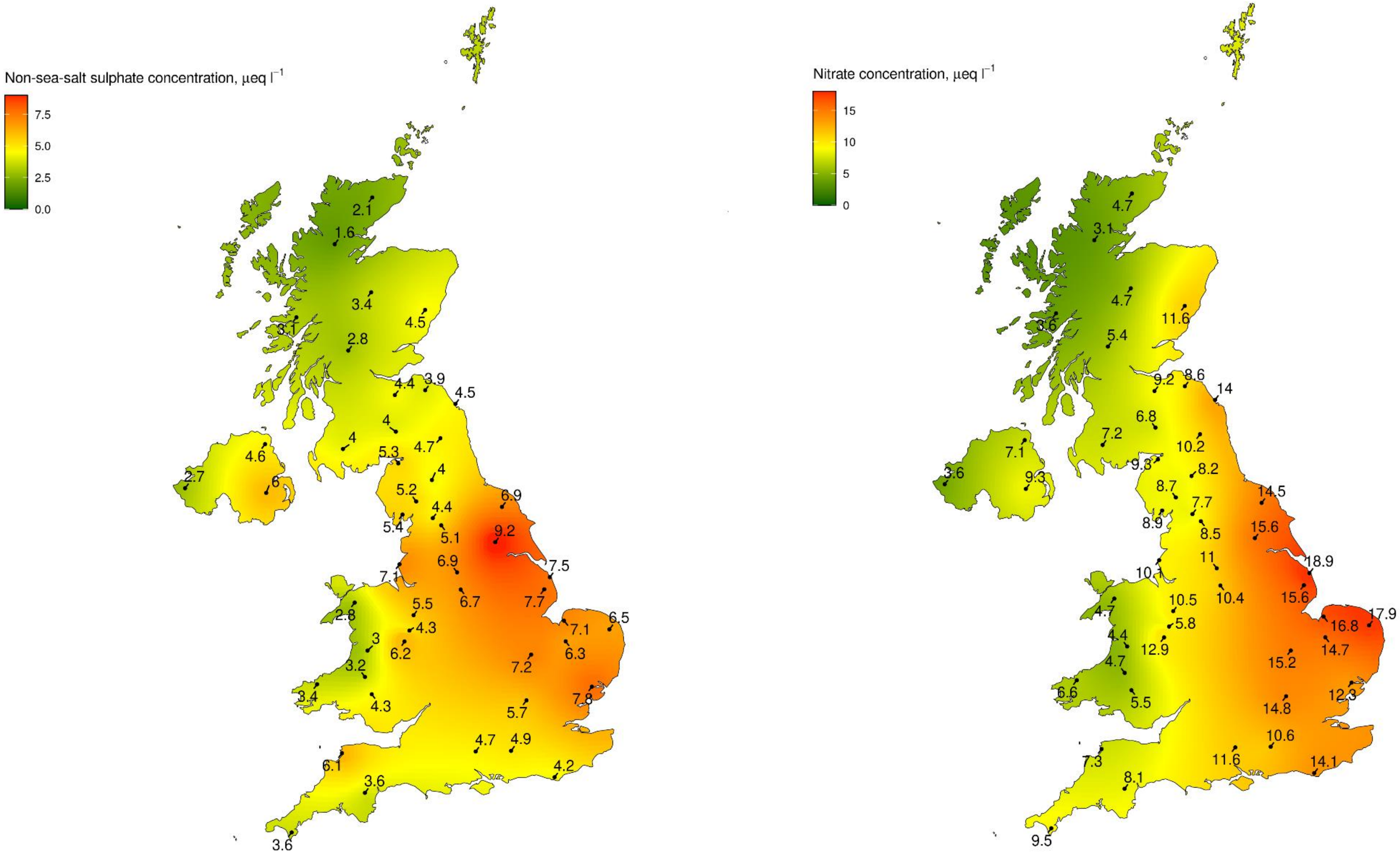


Figure 13 Interpolated concentration maps for nss-SO_4^{2-} and NO_3^- (µeq l^{-1})

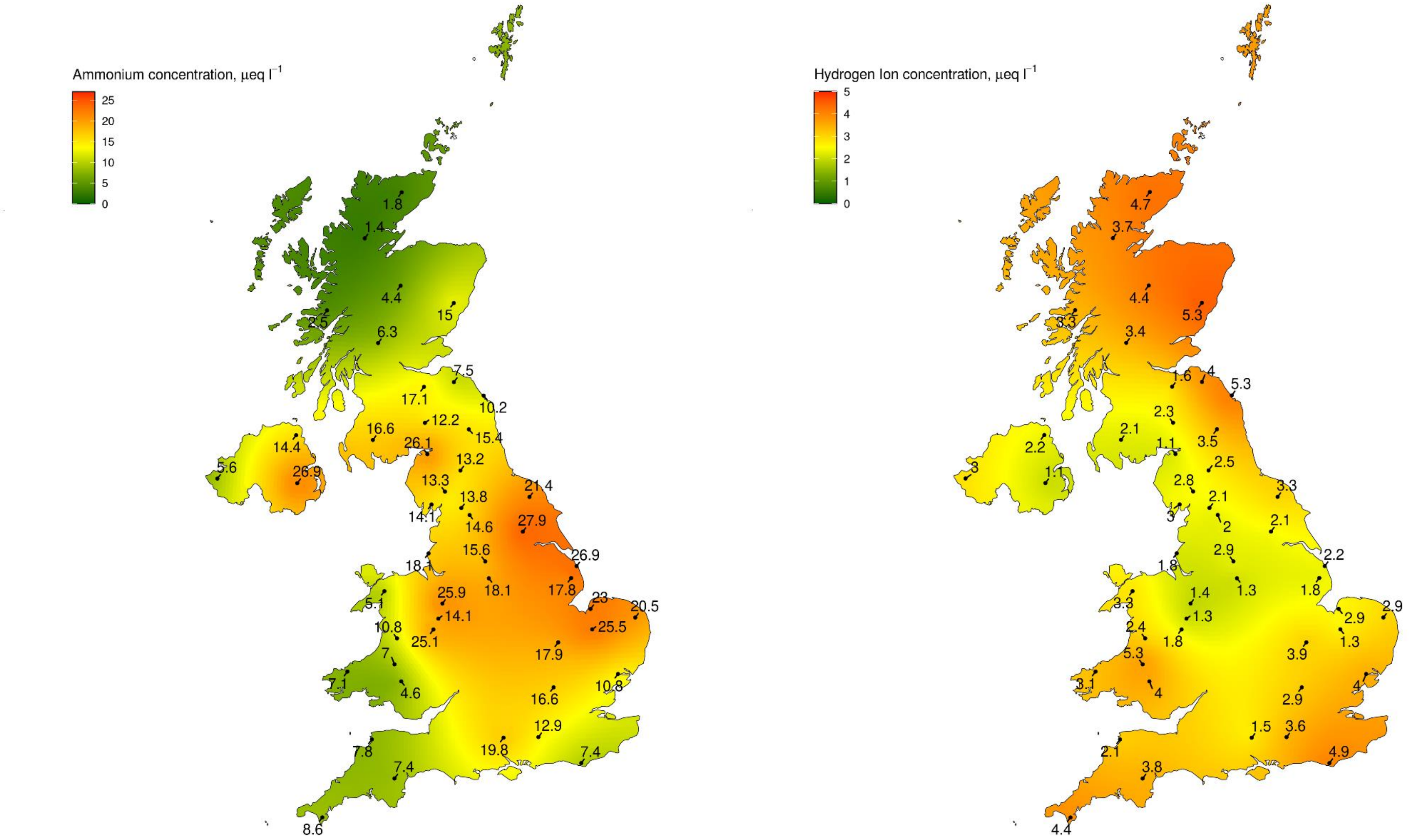


Figure 14 Interpolated concentration maps for NH4+ and H+ ion (μeq l-1)

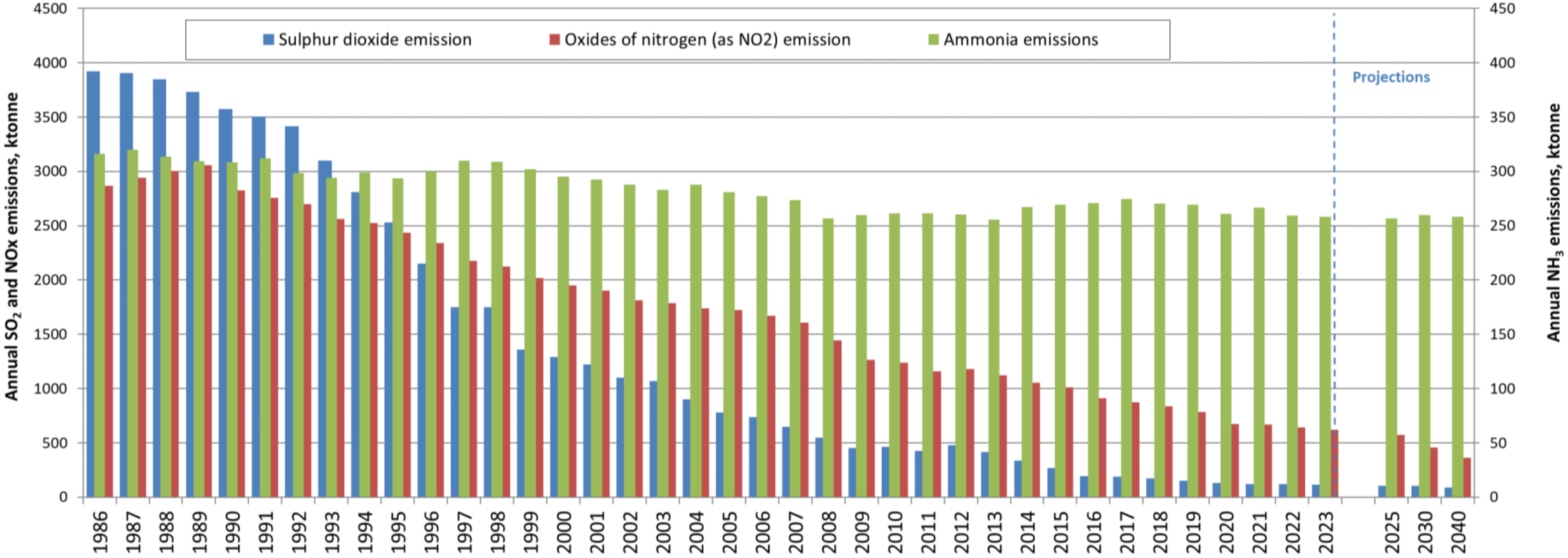


Figure 15 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986

Figure 16, Figure 17 and Figure 18 compare the total sulphur dioxide, oxides of nitrogen and ammonium emissions for the UK with the Precip-Net national average concentrations for nss-SO_4^{2-}, NO_3^- and NH_4^+, respectively. At this highly aggregated scale the rate of decrease in NO_3^- and NH_4^+ concentrations are smaller than that for SO_4^{2-}. At the national scale, total NO_X emissions were projected to decrease by about 3 % from 2022 to 2023. Whereas there was a larger decrease in the network average NO_3^- concentrations from 0.17 mg l^{-1} (12.3 µeq l^{-1}) in 2022 to 0.14 mg l^{-1} (9.7 µeq l^{-1}) in 2023.

The total sulphur dioxide emissions were projected to decrease by about 4 %. A small decrease was observed for nss-SO_4^{2-} which decreased from 0.092 mg l^{-1} (5.7 µeq l^{-1}) in 2022 to 0.080 mg l^{-1} (5.0 µeq l^{-1}) in 2023.

The national NH_3 emission is projected to decrease very slightly (0.4 %) from 2022 to 2023 (259.3 kt to 258.5 kt). There was a decrease in the network NH_4^+ average from 0.25 mg l^{-1} (18.0 µeq l^{-1}) in 2022 to 0.20 mg l^{-1} (14.1 µeq l^{-1}) in 2023.

The relatively large decrease in measured concentrations may, in part be attributed to inter year variability.

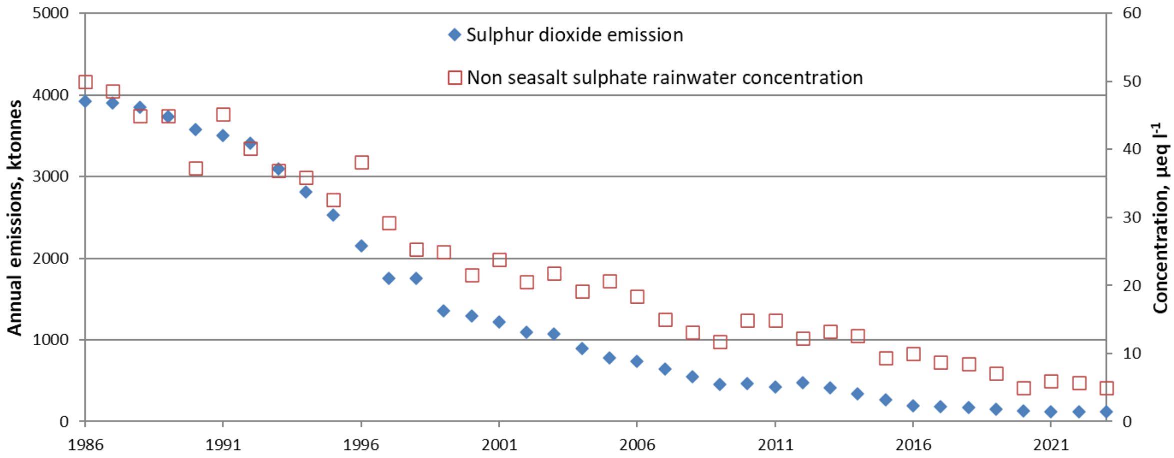


Figure 16 UK sulphur dioxide emissions and network average sulphate concentrations in rainwater

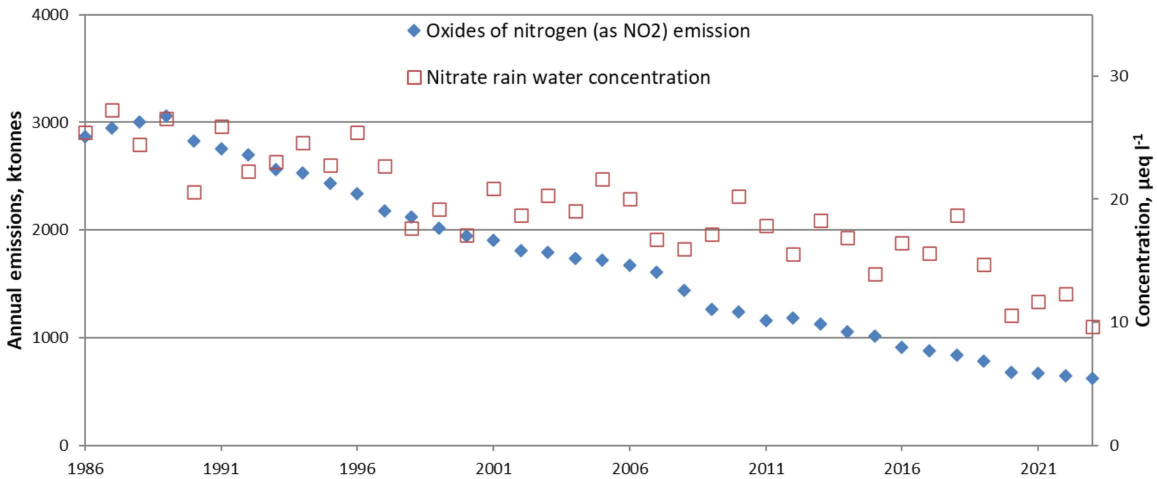


Figure 17 UK oxides of nitrogen emissions and network average nitrate concentrations in rainwater

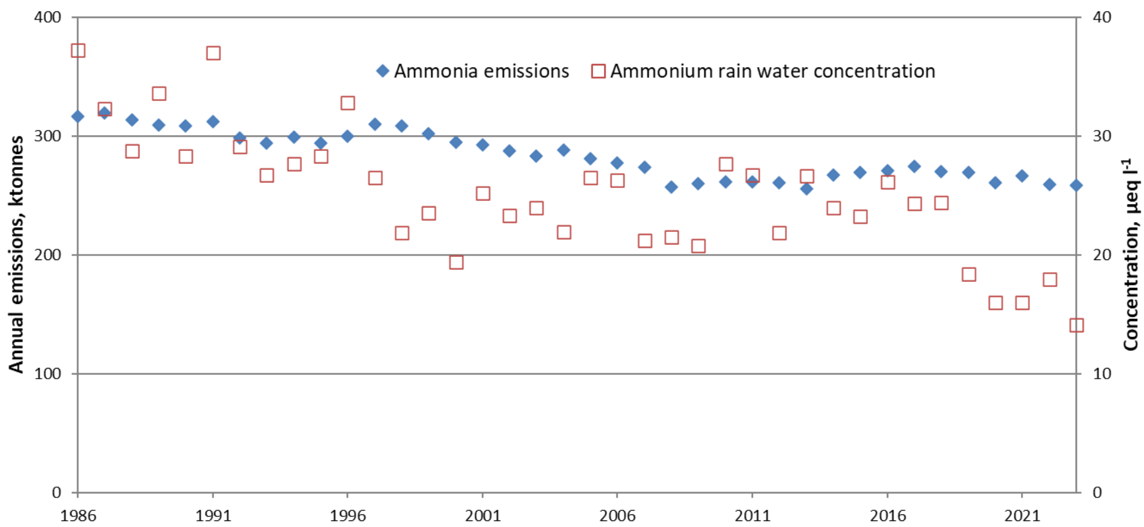


Figure 18 UK ammonia emissions and network average ammonium concentrations in rainwater

3.2 NO_2-Net Network

The mean data capture of the diffusion tubes for all of the site in 2023 was 90% with 16 of the 24 sites achieving > 90% and 14 sites achieving 100% data capture.

The lowest data capture was observed at Llyn Llydaw and was attributed to local site operation issues causing the 53 % data capture.

Figure 18 shows the trend in emissions of NO_X and NO_2 concentrations measured by the diffusion tubes in the network as a network average, very rural site (Strathvaich) and less rural site (Flatford Mill). The estimated emissions of NO_X in the UK as a whole show a reduction over the period shown and there is also a reduction in the average concentrations of all the active NO_2-Net site over the same period. More information relating to emissions in the UK can be found on the National Atmospheric Emissions Inventory (NAEI) website.

Table 5 2023 NO_2 concentration from the Diffusion Tubes in the NO_2-Net

Site Name	NO_2 concentration, µg m^{-3}	Data capture, %	Site Name	NO_2 concentration, µg m^{-3}	Data capture, %
Allt a'Mharcaidh	0.6	100	Llyn Llydaw	1.3	53
Balquhidder 2	1.3	87	Loch Dee	1.2	85
Bannisdale Beck	2.8	65	Lough Navar	1.4	100
Chilbolton Observatory	4.8	92	Lullington Heath	4.9	100
Driby 2	4.2	85	Moorhouse	1.3	100
Eskdalemuir	1.2	100	Percy's Cross	1.7	100
Flatford Mill	8.4	64	Polloch	0.6	100
Forsinard RSPB	0.8	100	Pumlumon	1.3	100
Glensaugh	1.3	100	Strathvaich	0.6	86
Goonhilly	2.2	63	Tycanol Wood	1.6	100
High Muffles	2.9	100	Whiteadder	2.0	100
Hillsborough Forest	4.0	93	Yarner Wood	2.4	100

NO_2 emissions are associated with transport or industrial processes involving combustion, therefore there are smaller influences in concentrations at rural locations.

There is an observable difference in trends in concentrations at the Flatford Mill when compared to the more rural site of Strathvaich. The difference between the less rural site of Flatford Mill site which has an urban influence being about 50 miles from London located between Colchester and Ipswich and the more rural Strathvaich site located in the north of Scotland can also be seen in the plot. The trend in concentrations at the Strathvaich site does not appear to show any observable reduction in NO_2 concentration whereas the Flatford Mill sites shows a similar rate of reduction to that of the NAEI estimated.

The annual average uncorrected NO_2 concentrations from 2010-2023 (Figure 22) indicates the differing NO_2 concentrations at rural locations across the UK. Most of the sites show some reduction between 2010 and 2021 but the larger decreases being seen at the sites that are closer to the sources of NO_X.

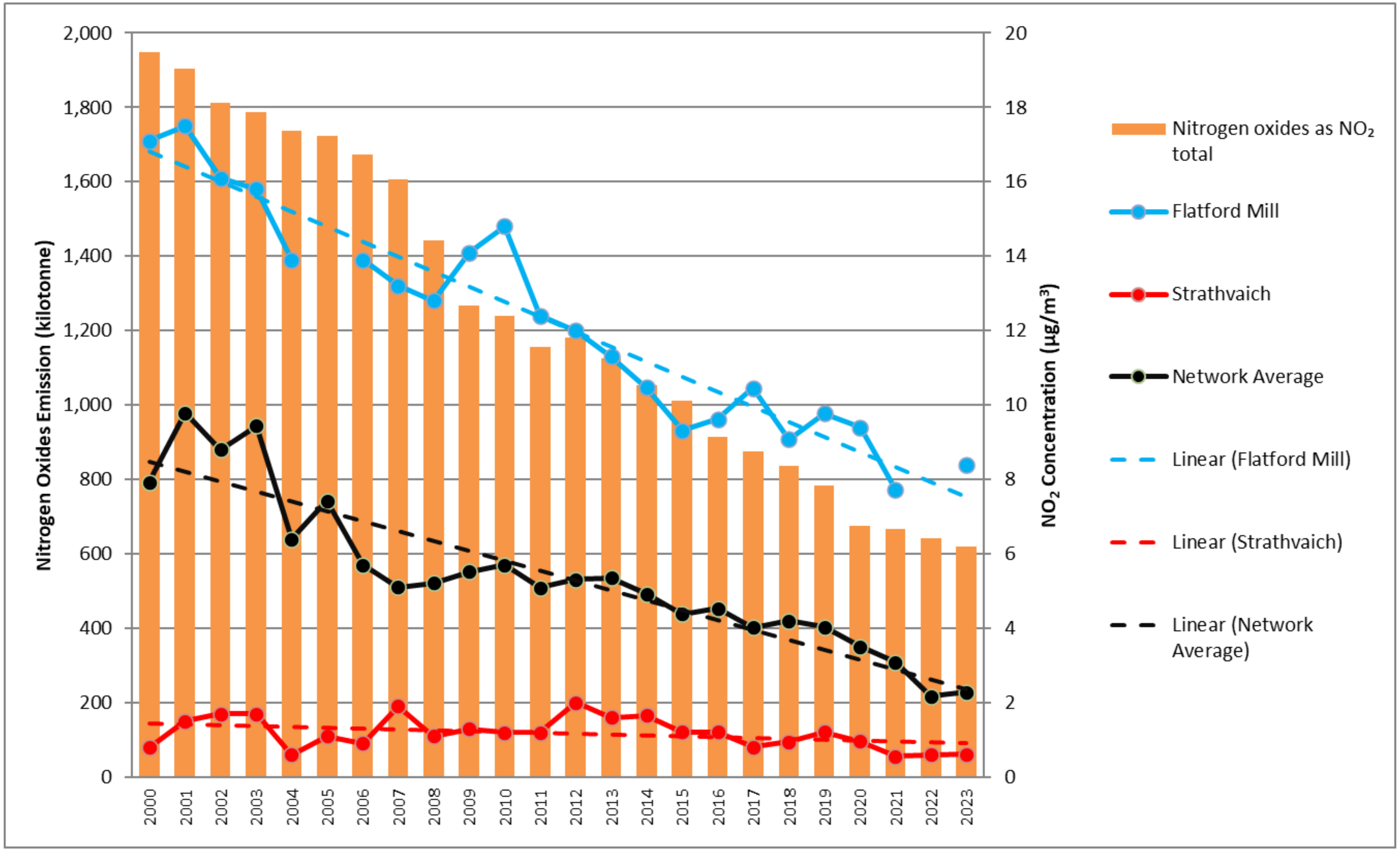


Figure 19 Long term trends where estimated emissions are plotted against selected sites in the network

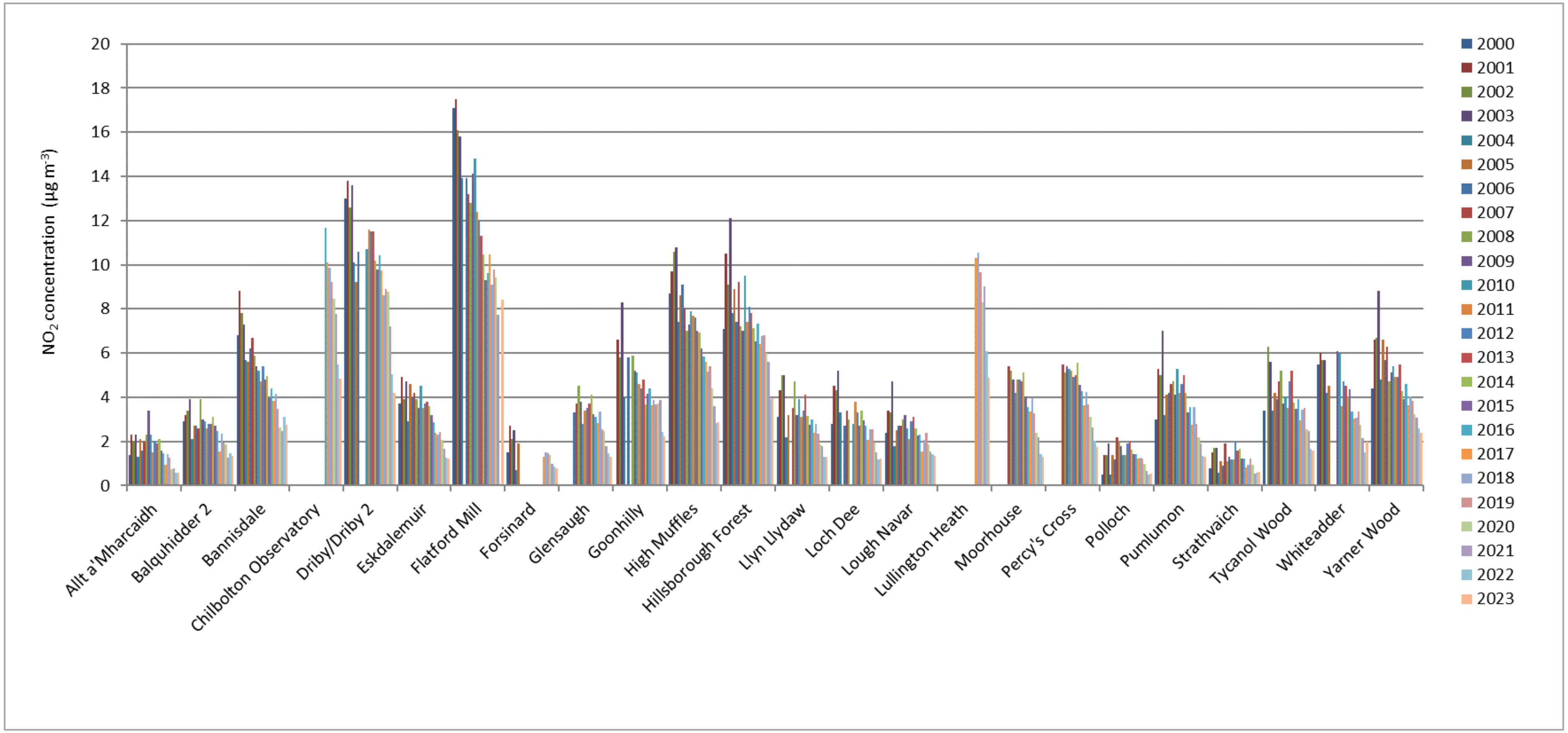


Figure 20 Annual mean NO2 concentration (µg m^{-3}) at the NO2-Net sites 2000-2023

3.3 National Ammonia Monitoring Network (NAMN)

NAMN Performance and Data capture

Figure 21 contains the average percentage data capture across all sites for each chemical of interest. Average data capture was 76% for NAMN.

UKCEH ALPHA® Sampler

Data capture at UKCEH ALPHA® sites was 87% in 2023. Data capture losses were primarily due to:

- Local site operator availability.
- Sampler losses either due to animal or poor weather conditions. No sites demonstrated repeated losses in 2023.

UKCEH DELTA® Sampler

DELTA systems data capture was lower than previous years, with a data capture of 62%. Data losses were a result of:

- 18% of the reported losses were attributed to water ingress being identified in samples and so failed QA/QC processes.
  - Remedial action has been implemented, and it expected that data capture from the network should improve from June 2024.
- Damage on shipment – 7%
  - New transport boxes were implemented in 2022 and there was an reduction in data loss observed (reduced from 14% in 2021 to 2% in 2022). The losses appear to have increased again in 2023. UKCEH is continuing to evaluate shipment losses on an ongoing basis and seeking further solutions.
- Equipment Failure – 3%
- Site Issues – 3%

Measures are being taken to resolve the DELTA system performance:

- DELTA hardware upgrades (completed in June 2024).
- Revisions of LSO procedures and engagement exercise (March 2024)
- Review of annual servicing protocols and training provision to DELTA service engineers (March 2024).

UKCEH are continuing to undertake a review to identify areas of improvement in the DELTA system and network operations management to reduce data capture losses going forward.

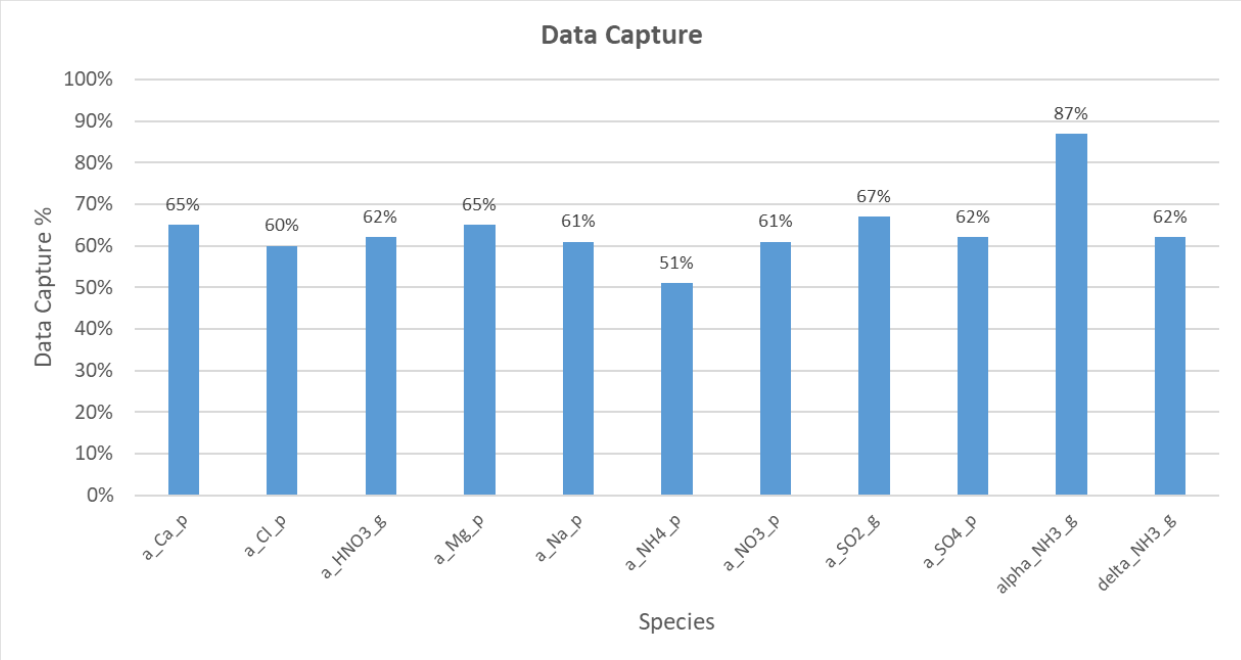


Figure 21 NAMN and AGANet percentage data capture by chemical component in 2023.

NAMN Network Trends

The 2023 annual average NH_3 concentrations observed at each site in NAMN is presented in Figure 22 with the bars showing the maximum and minimum concentration in the year at that site. It was found there is high spatial variability in NH_3 concentrations across the UK, with seasonal variability across each site. The sites in the north of Scotland, which are typically remote rural sites, reported the lowest annual concentrations (Allt a'Mharcaidh, Inverpolly and Loch Awe). The highest reported concentrations were generally reported from Northern Ireland (Caddy Rd, Drumclamph 2, Inch Abbey, Lisbellaw, Ratarnet Rd.) and the eastern side of England (Brompton, Fressingfield) as seen in Figure 22.

Historical changes in the annual average NH_3 concentrations can be seen in Figure 23. The annual average across the full network is similar to the range previously reported across the measurement period. It should be noted, however, that the network sites have changed with time, including over the past two years.

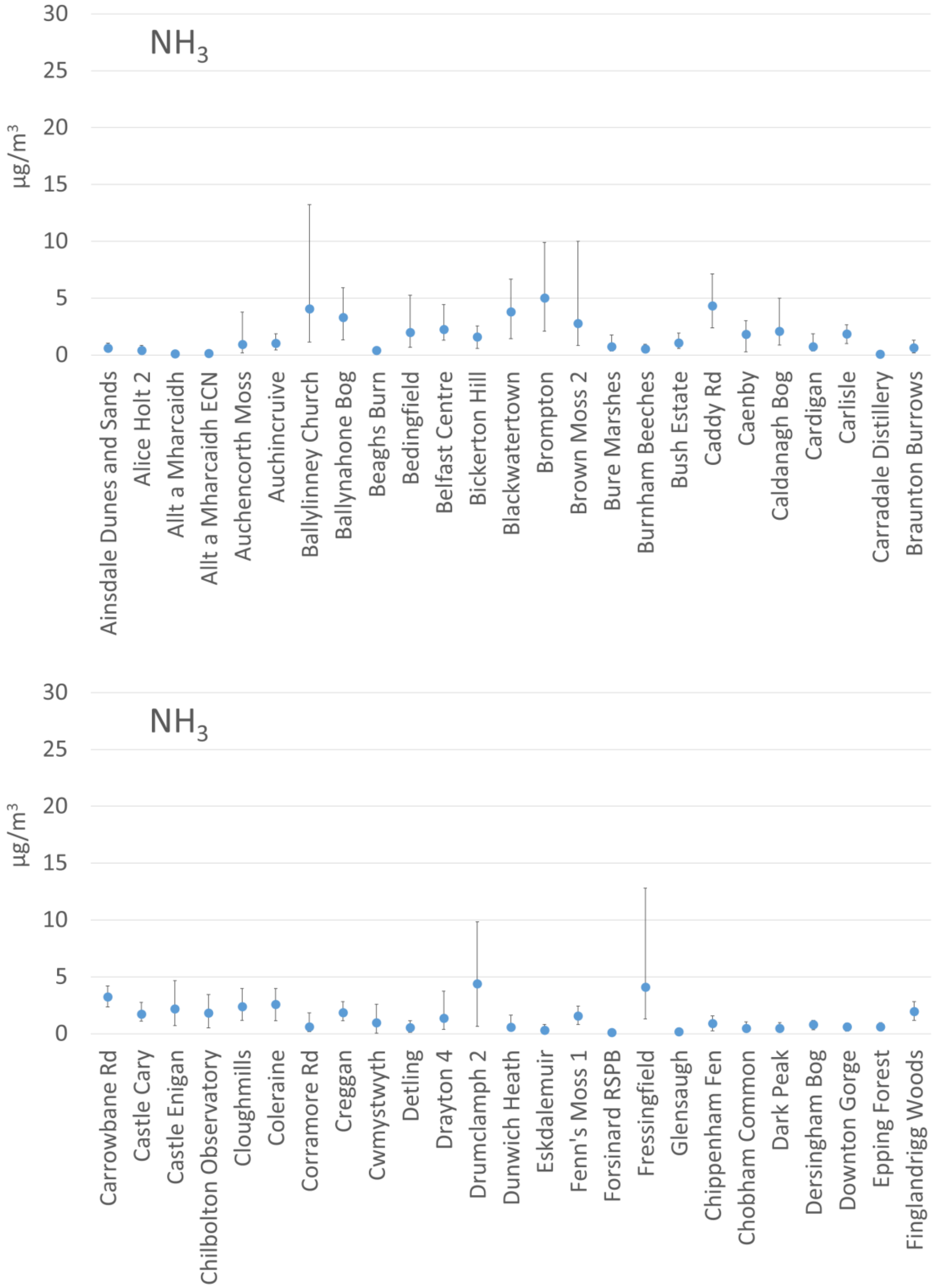
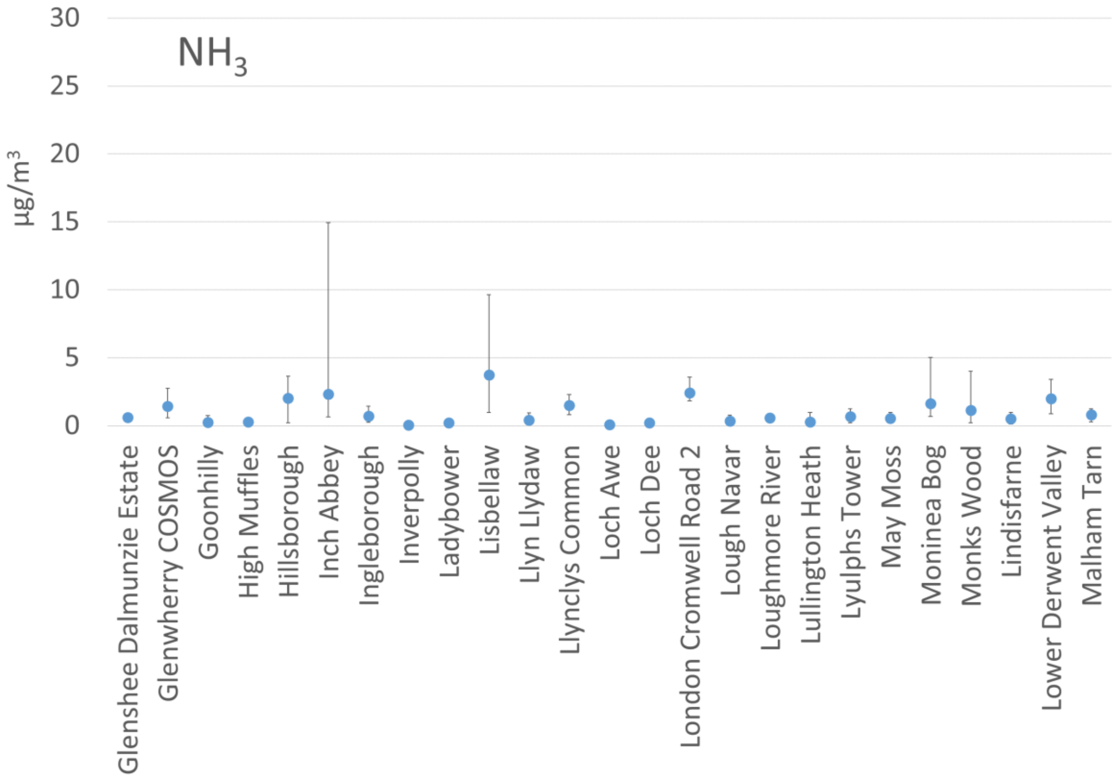


Figure 22 Annual mean concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentrations observed.



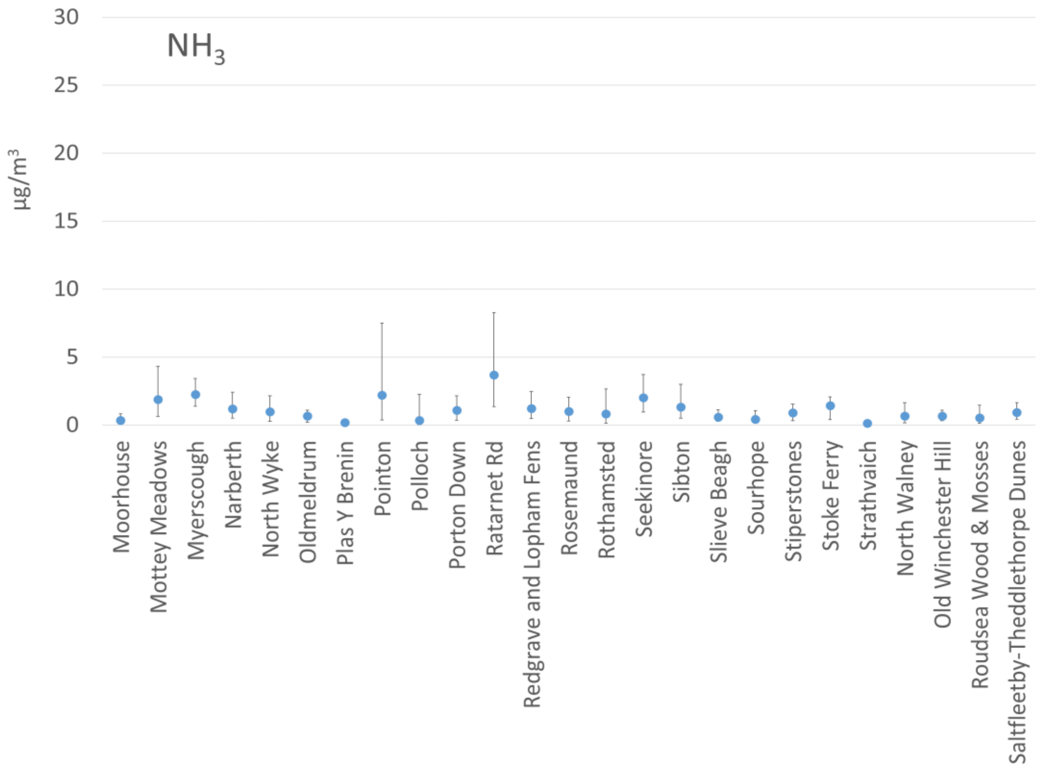


Figure 22 contd. Annual mean concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentrations observed.

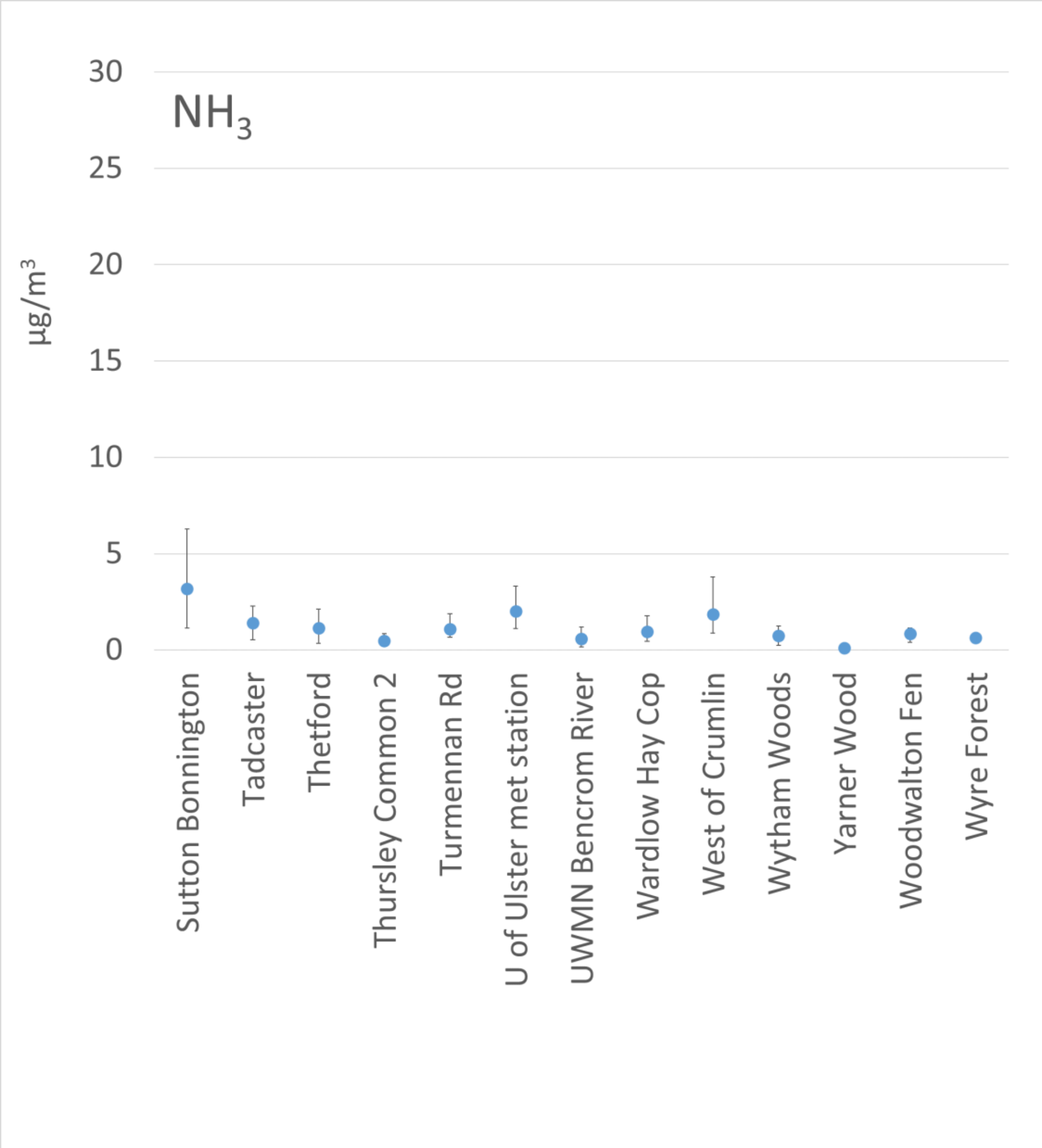


Figure 22 contd. Annual mean concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentrations observed.

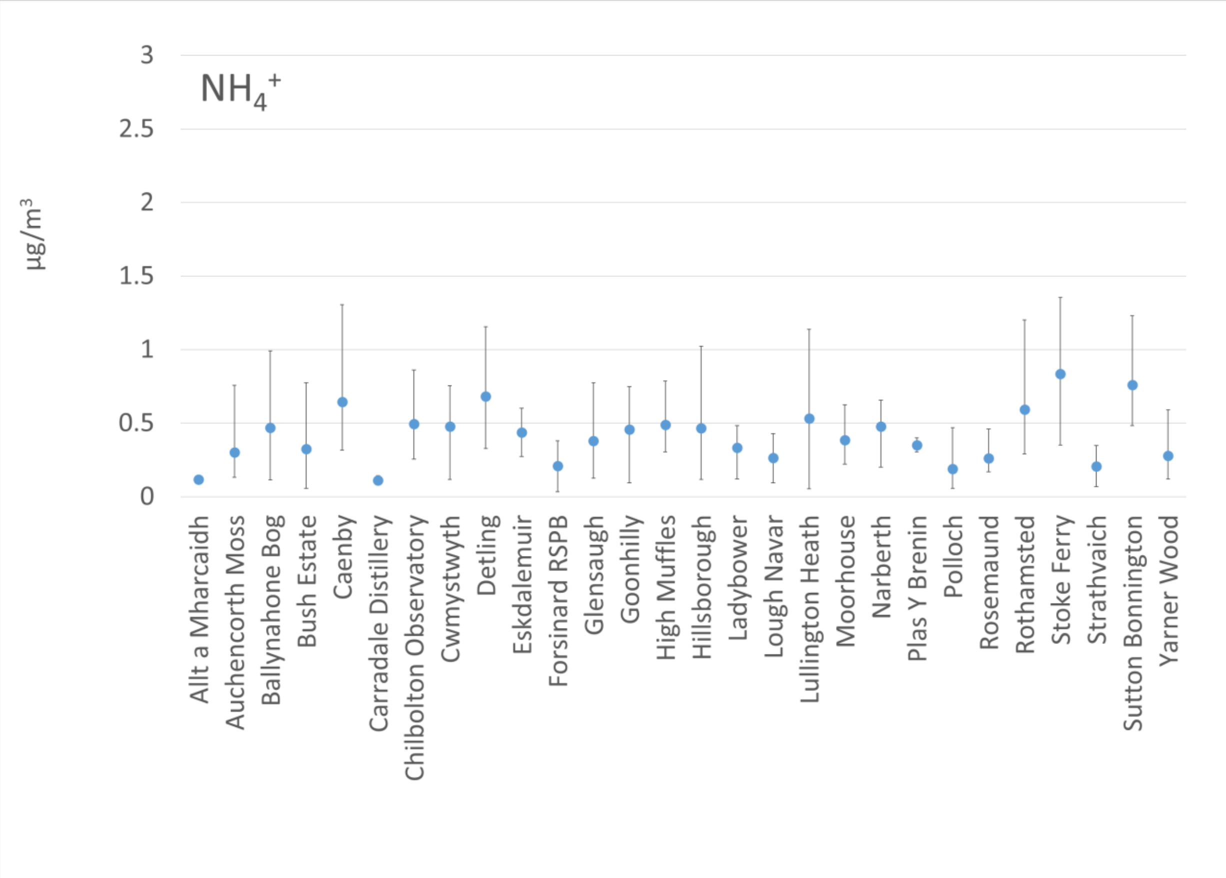


Figure 22 contd Annual mean concentrations of NH_4^+ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentrations observed.

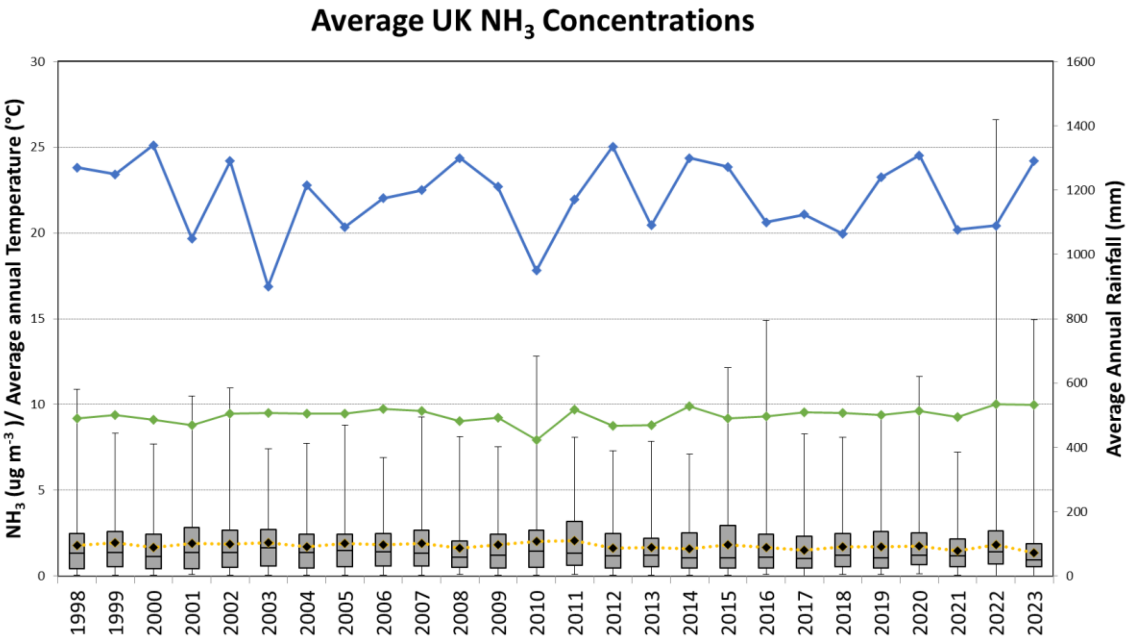


Figure 23 Changes in atmospheric NH_3 averaged over all sites in NAMN operational between 1998 and 2023 summarised in a box plot. The whiskers show the absolute max and min and the diamond is the mean annual concentration. Meteorological data is also displayed for comparison. The green line is the average annual temperature and the blue line the annual average rainfall (data source: https://www.metoffice.gov.uk/research/climate/maps-and-data/summaries/index).

The spatial variability of the annual concentration of NH_3 and NH_4^+ are presented in Figure 24 and Figure 25, respectively. For NH_3, lower concentrations primarily located in the North of Scotland, with some locations in the south coast of England. High ammonia air concentration values are also observed in Northern Ireland. For NH_4^+, the lowest concentrations are found in northern England and Scotland, while the highest concentrations occur on the south east of England.

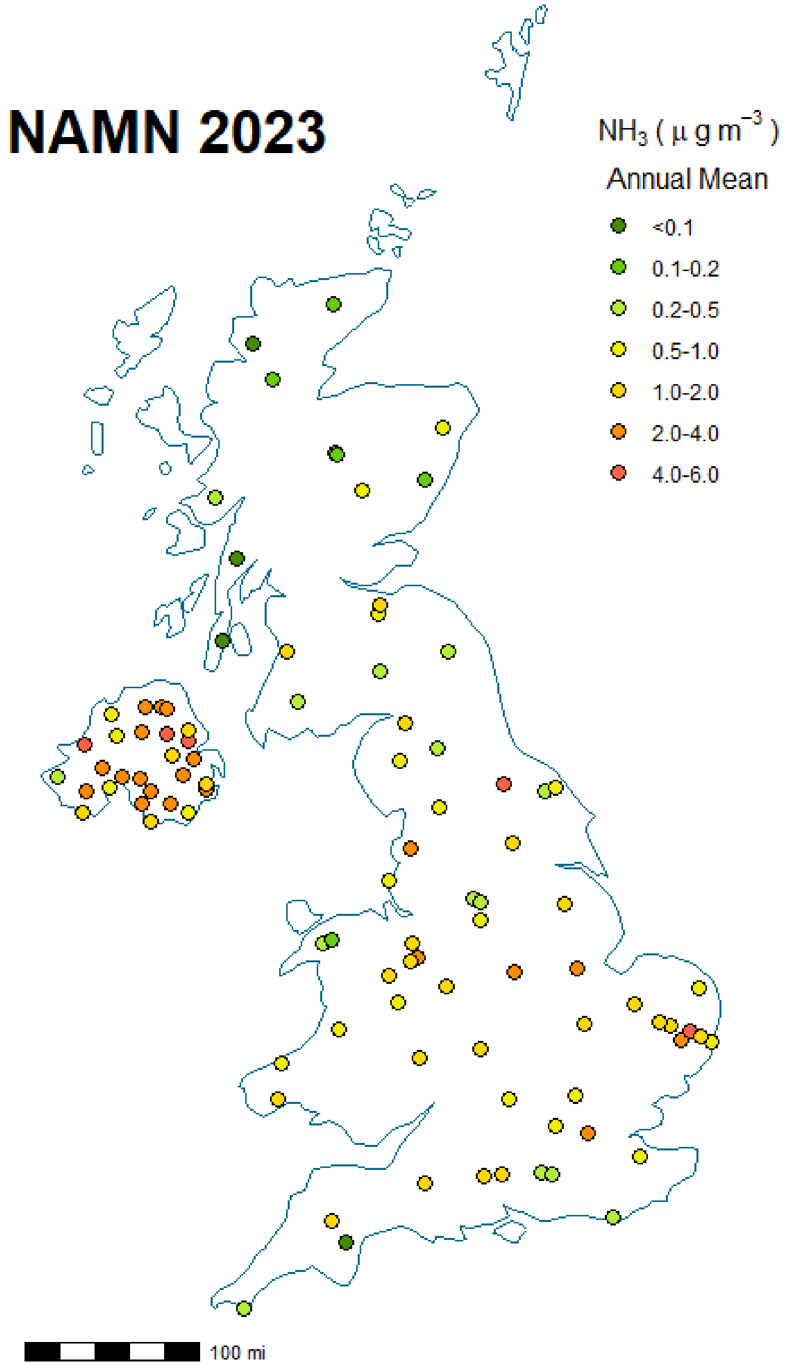


Figure 24 Spatial patterns of annual NH_3 concentrations from monthly NAMN/AGANET measurements.

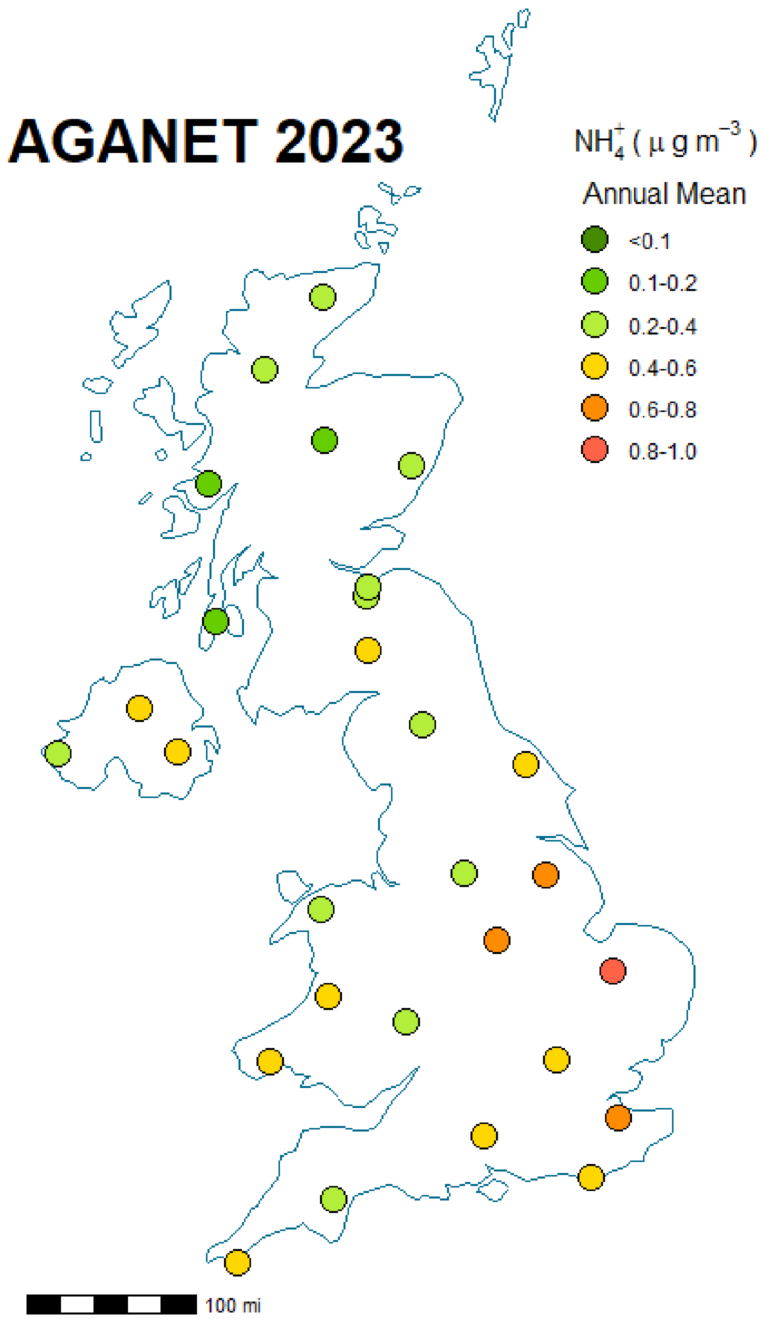


Figure 25 Spatial patterns of annual aerosol NH_4^+ concentrations from monthly NAMN/AGANET measurements

3.4 Acid Gas and Aerosol Network (AGANet)

AGANet Performance and Data capture

Figure 21 contains the average percentage data capture across all sites for each chemical of interest. The average DELTA systems data capture was lower than previous years, with 62% for AGANet, as explained in Section 3.2

Data losses were a result of:

- 18% of the reported losses were attributed to water ingress being identified in samples and so failed QA/QC processes.
- Damage on shipment – 7%
- Equipment Failure – 3%
- Site Issues – 3%

AGANet Network Trends

Figure 26 presents the annual average concentrations, with the minimum and maximum of SO_2 and HNO_3 reported at the sites within AGANet. None of the sites surpassed annual average concentrations over 1 µg m^{-3} in 2023, although Ballynahone Bog showed unusual high HNO_3 concentrations during the summer months over 1 µg m^{-3}. The spatial distribution of the annual average concentration for both species can be found in Figure 27 and Figure 28, where it is observed that higher HNO_3 concentrations generally occur in the south-east of the England.

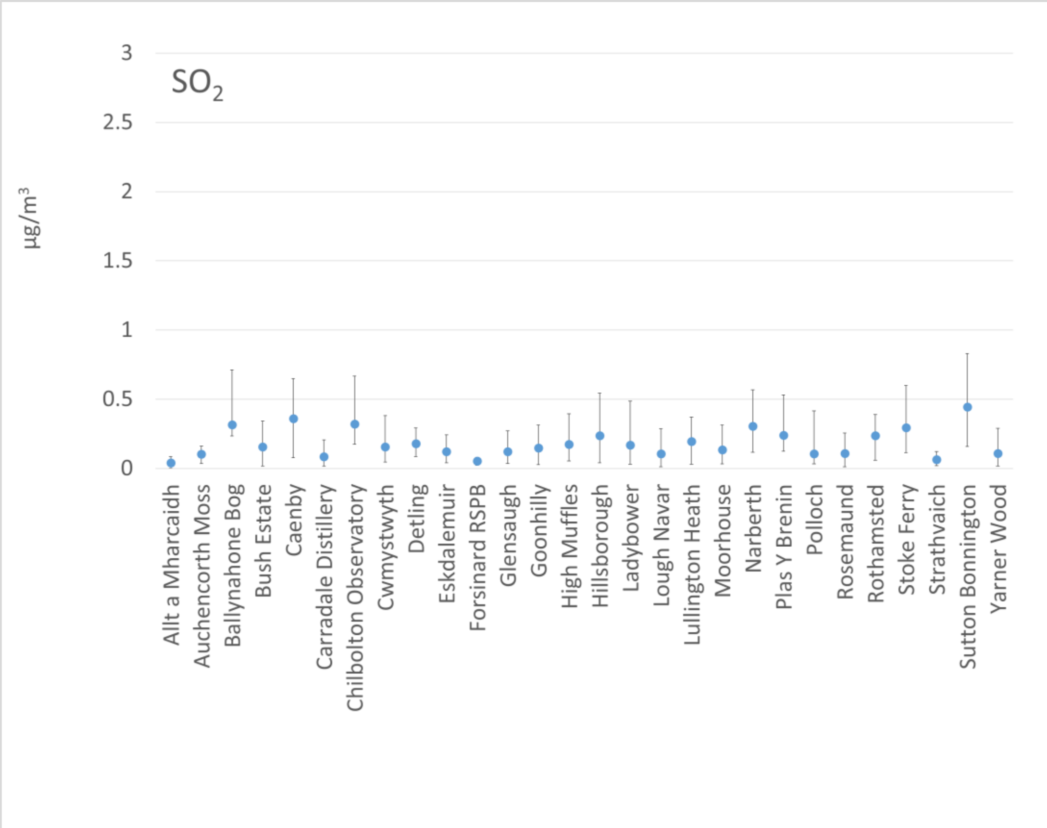
Figure 29 shows the annual average, maximum and minimum of NO_3^-, SO_4^{2-}, NH_4^+ and Cl^- from each site during 2023 reported by AGANet. Like for NH_4^+ in the NAMN network, the lowest reported concentrations are from sites in the North of Scotland for NO_3^- and SO_4^{-2} (Figure 29 and Figure 30). For Cl^- (Figure 29 and Figure 30) and Na^+ (Figure 32 and Figure 33) there is a more distinct variability in the observed concentrations, with the southwest coast of the UK observing the higher average concentrations due Na^+ and Cl^- primarily being originating from sea salt. A similar spatial pattern is found for Mg^{2+} (Figure 31 and Figure 33) as it is also found in sea salt, whereas Ca^{2+} concentrations are low and highly variable across the UK.

The long-term averages for AGANet are shown in Figure 34 to 35. There is a small observable increase of HNO_3 compared to 2021 and 2022, however the longer-term trend is a decrease in concentration. The average NH_3 concentrations has decreased for the second year running at 28 AGANet sites, unlike in the full NAMN time series, currently at 113 sites (Figure 23). This apparent inconsistency is being investigated with respect to changes in the network sites and changes in calibration for the ALPHA uptake rate (Section 2.3.2). The SO_2 annual average concentration has remained stable around 0.2 µg m^{-3} since 2016.

Particulate NO_3^- and Ca^{2+} show an observable step change in 2016 with an increase in concentration that is attributed to the method change resulting in the increased capture of the aerosol components (refer to UKEAP annual report 2016 for further details[14]). Since this method change, an inter-annual variability is observed with concentrations relatively stable within ±0.5 µg m^{-3} between 2016 and 2020 for all components. In 2021, however, there was a decrease in NO_3^- concentration and this has remained at a similar level 2023. It is noted that observed changes in NO_3^- concentrations are concurrent with an observed decreases in HNO_3, NO_2 and NO_3^- in precipitation (refer to Figures 34, 19 and 17, respectively). Indications are the HNO_3 concentrations are continuing to remain at the same levels in 2023, however caution is advised in over interpretation due to the reduced data capture.

Figure 36 compares the annual seasonal cycle (monthly averages) in 2023 compared to previous years for the inorganic precursors gases and their particulate counterparts. Most species show low concentration levels through 2023 compared to the long-term monthly average concentrations. Ammonia shows an unusually high concentration in February. During the rest of the year, the temporal pattern of NH_3 deviates from the long-term averages, especially in the spring months. For ammonium concentrations in 2023 are also consistently lower compared to the long-term averages, following a similar temporal pattern with the exceptions of March and July months.

Nitic acid concentrations are very low all year around except in June and September, when concentrations are of a similar magnitude as the long-term values. In the winter months, the reported concentrations are below the long-term average standard deviation, however caution is required in over interpretation of the results due to the low data capture in 2023 from the DELTA. Nitrate concentration and temporal patterns follow the same pattern as particulate NH_4^+, reflecting the dominance of NH_4NO_3 in the SIA. The SO_2 concentrations in 2023 did not show a strong temporal pattern and remained very low throughout the year. Particulate SO_4^{2-} on the other side shows higher concentration levels during the summer months, when temperature and photochemical activity may enhance SO_4^{2-} formation.



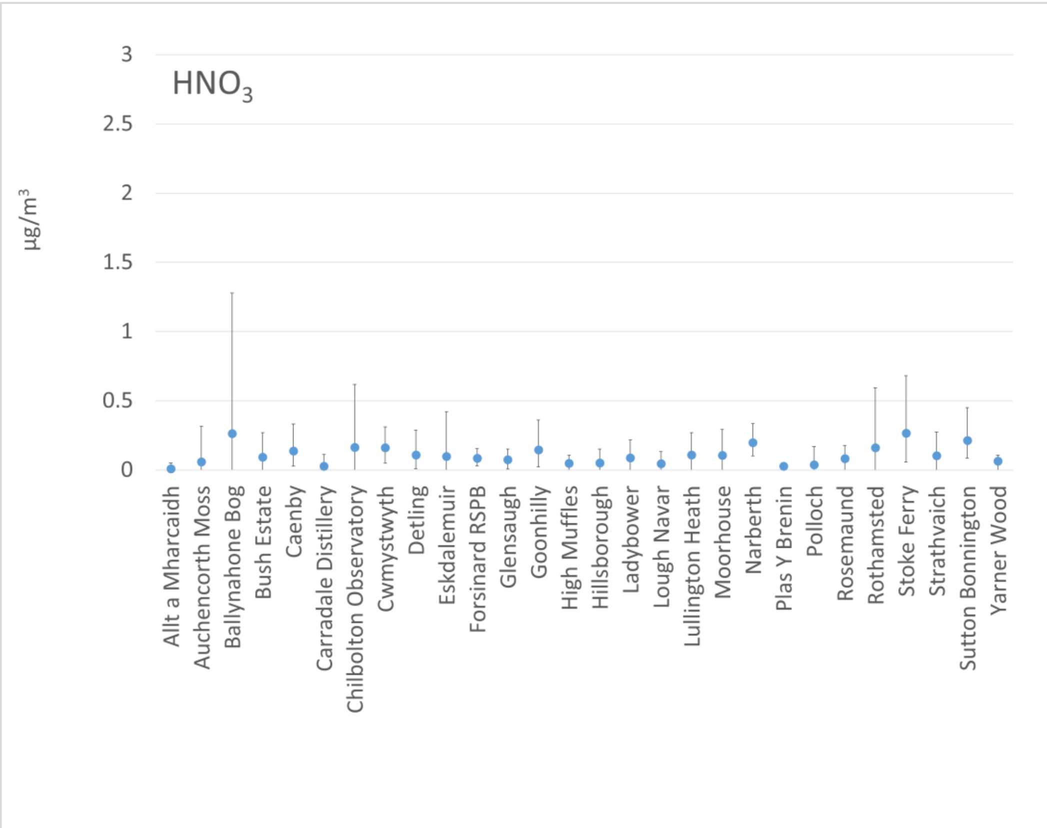


Figure 26 Mean monitored annual concentrations of gaseous HNO_3 and SO_2 at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentration observed.

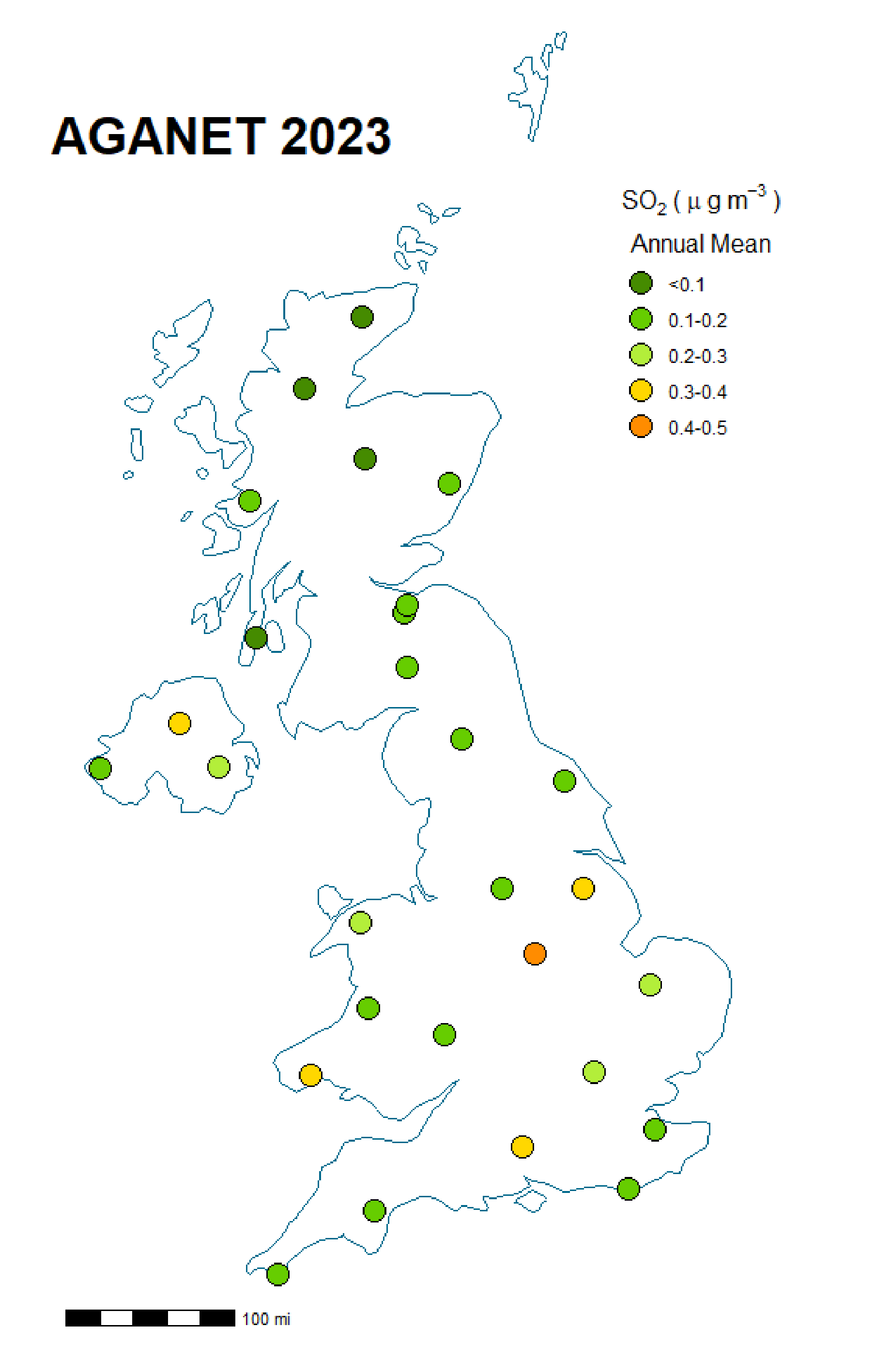


Figure 27 The annual average concentration of SO2 across the UK measured by AGANet in 2023.

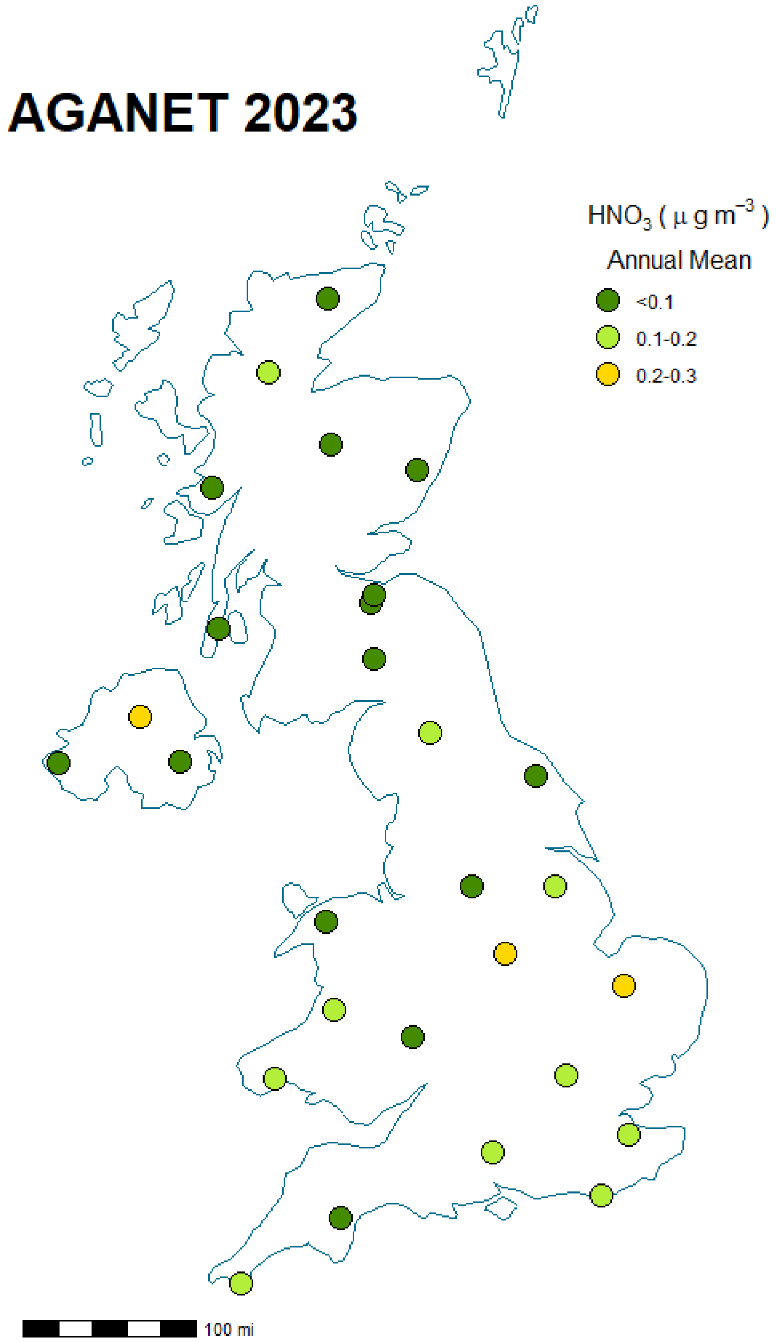
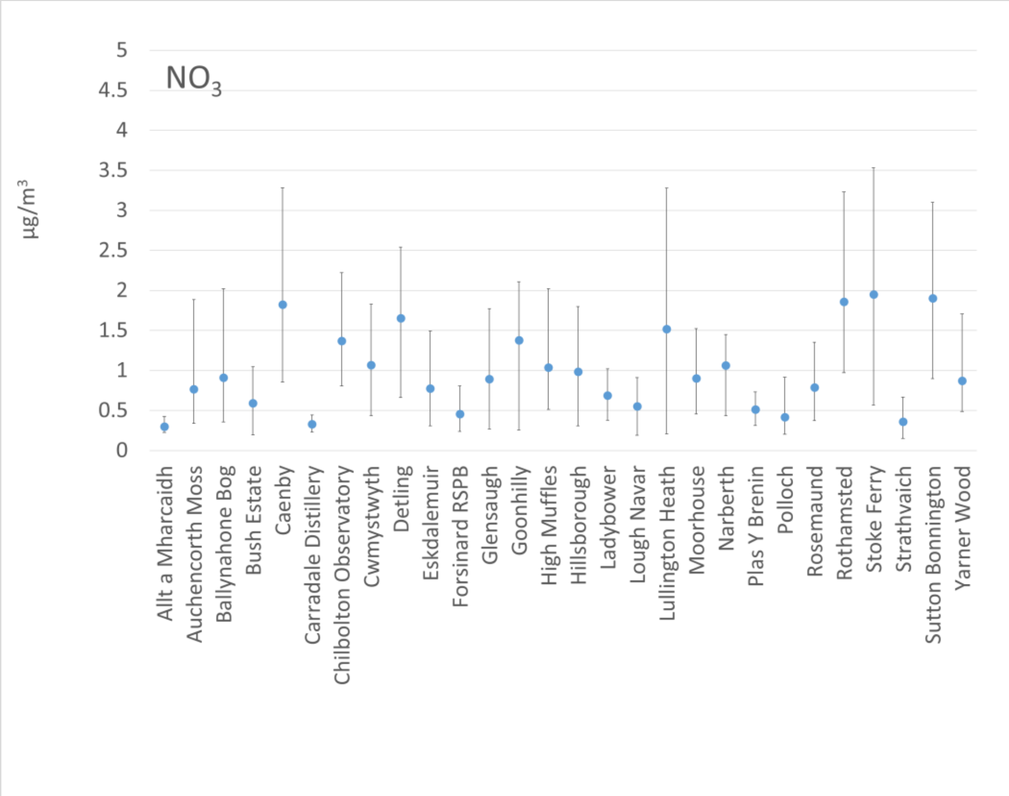


Figure 28 The annual average concentration of HNO_3 across the UK measured by AGANet in 2023.



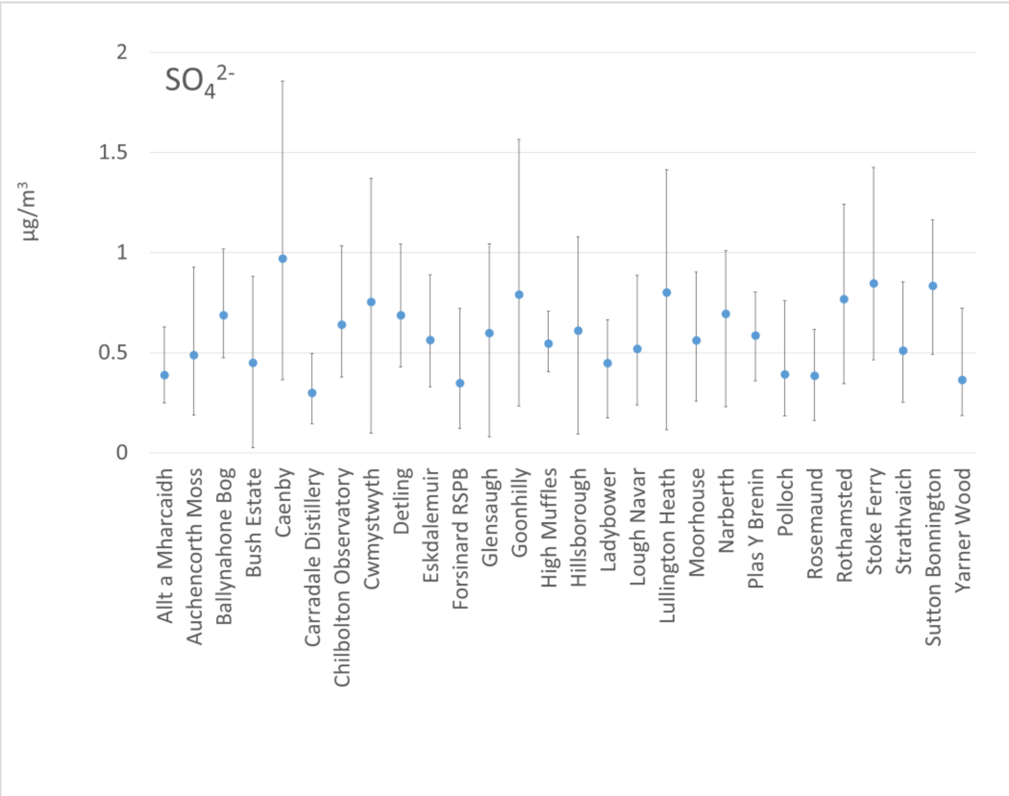
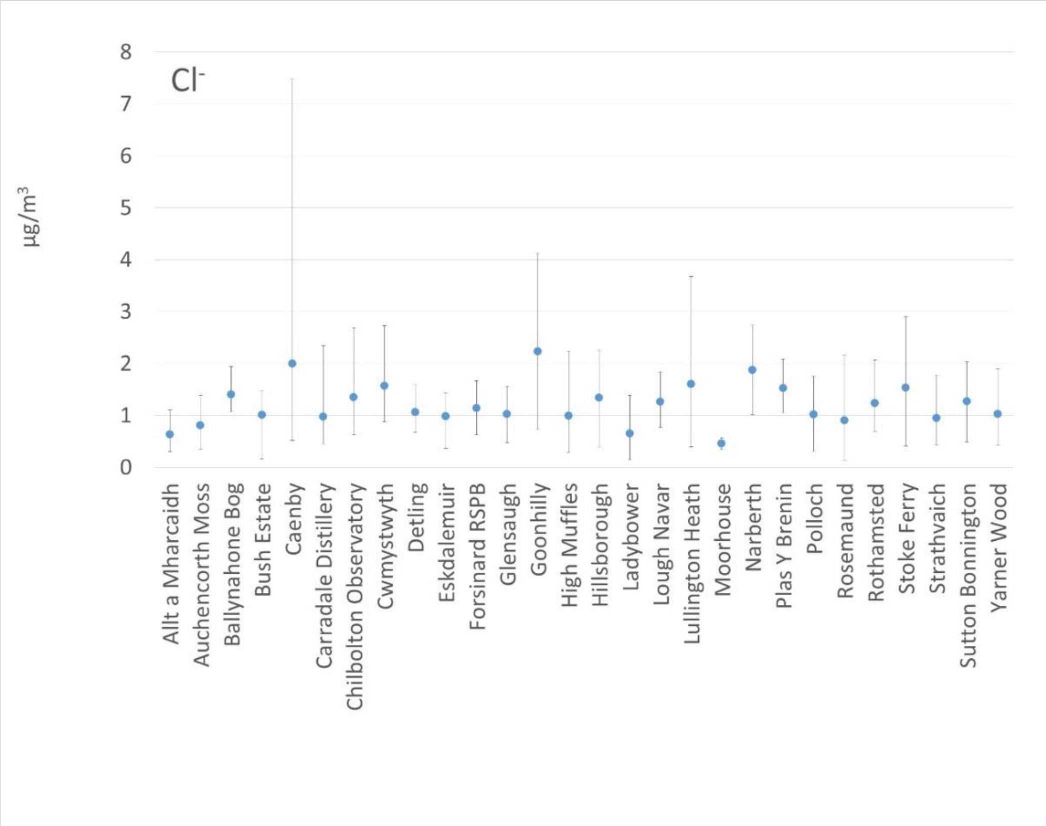


Figure 29 Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-} , Cl^- and NH_4^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentrations observed.



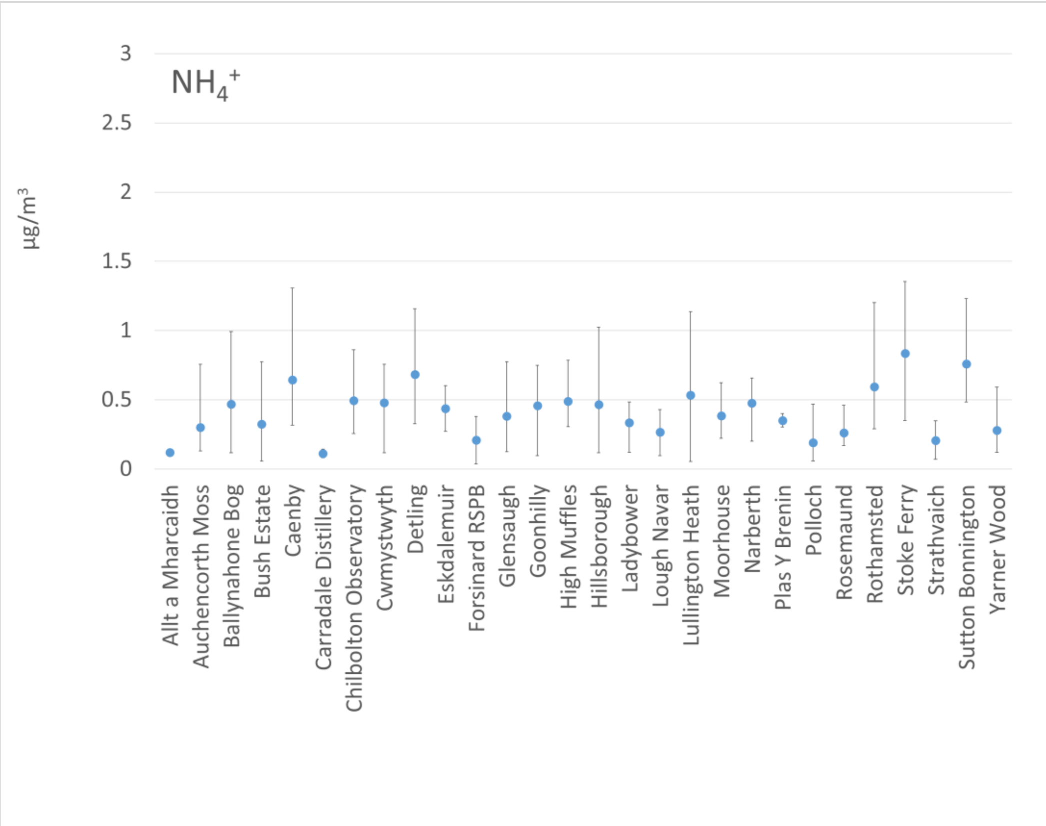


Figure 29 continued. Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-} , Cl^- and NH_4^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentrations observed

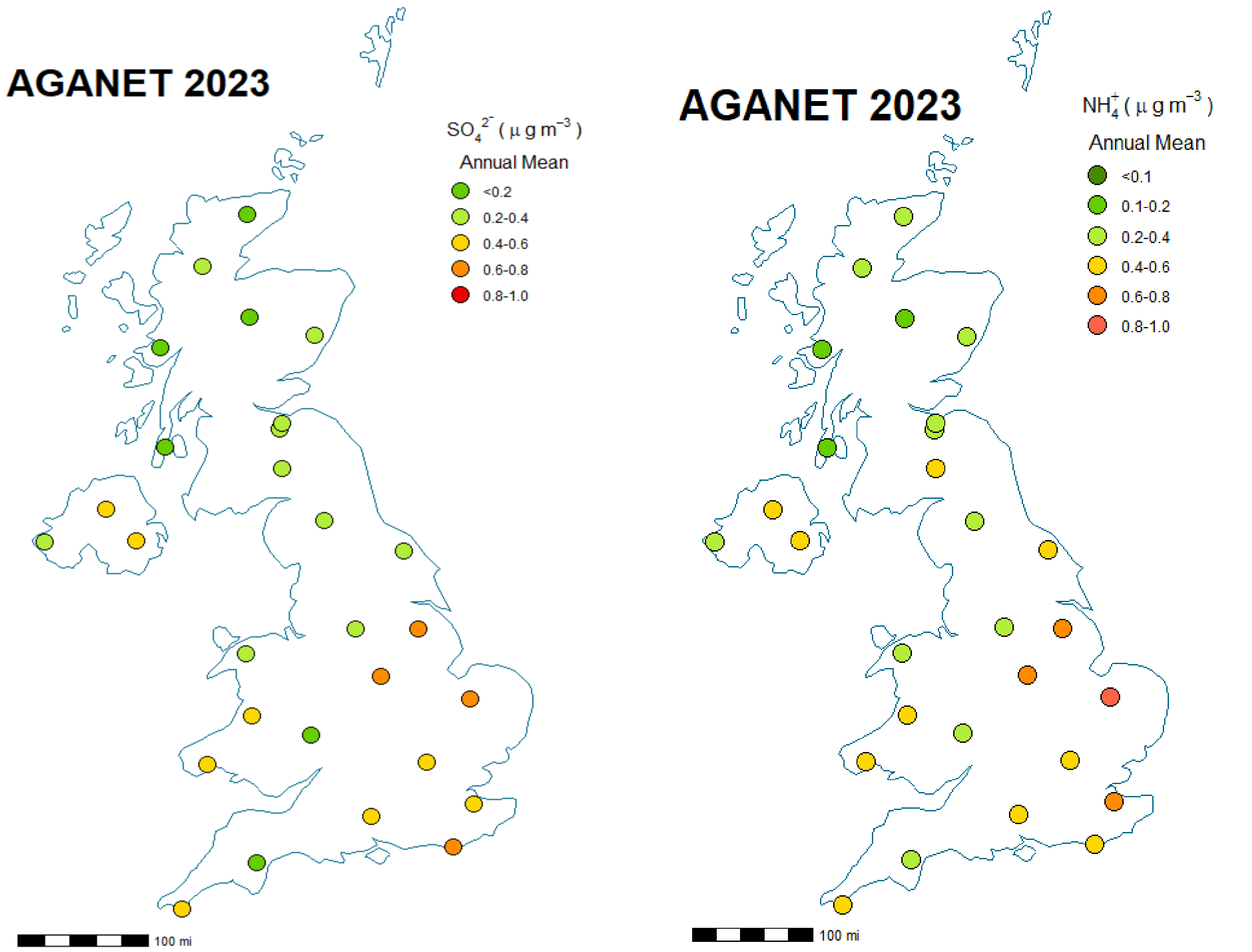


Figure 30a Annual average concentrations of SO_4^{2} from AGANet and NH_4^+ from NAMN during 2023

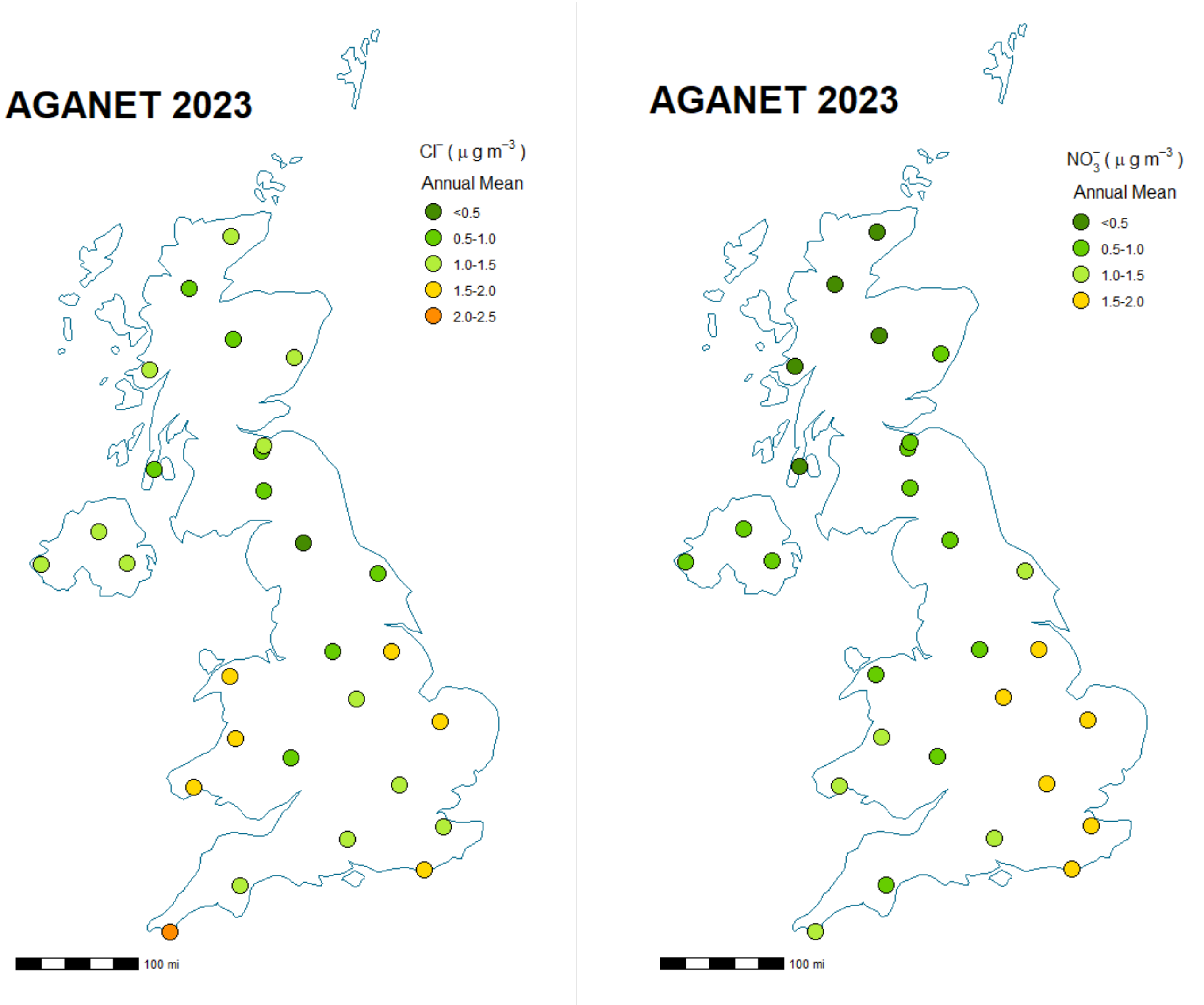
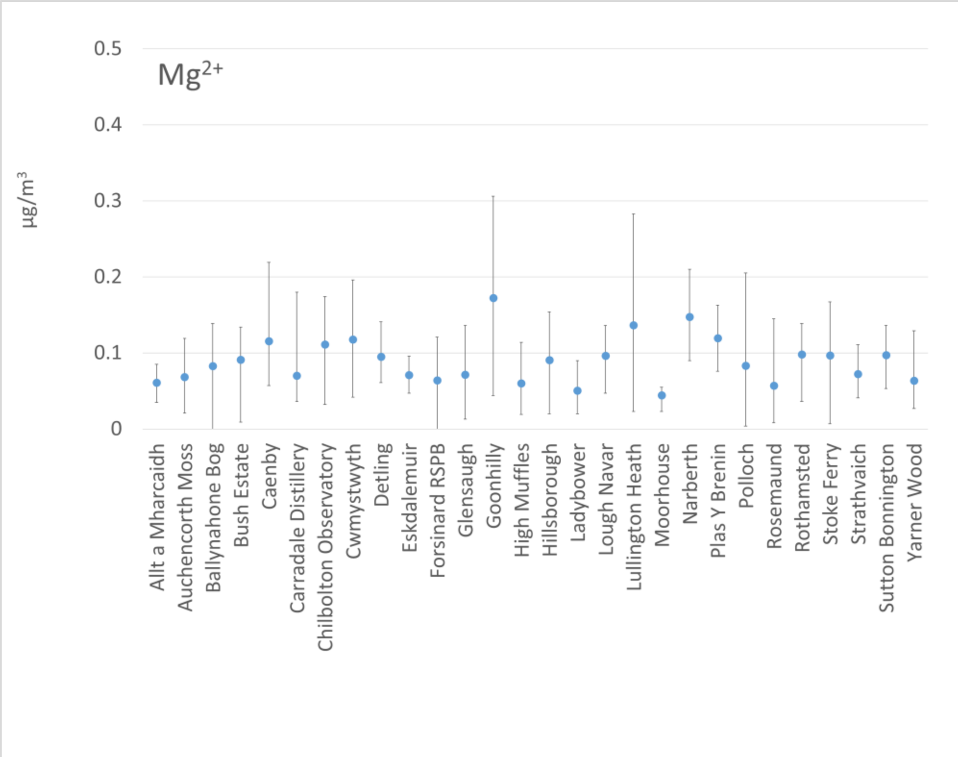


Figure 30b Annual average concentrations of NO_3^- and Cl^- from AGANet during 2023.



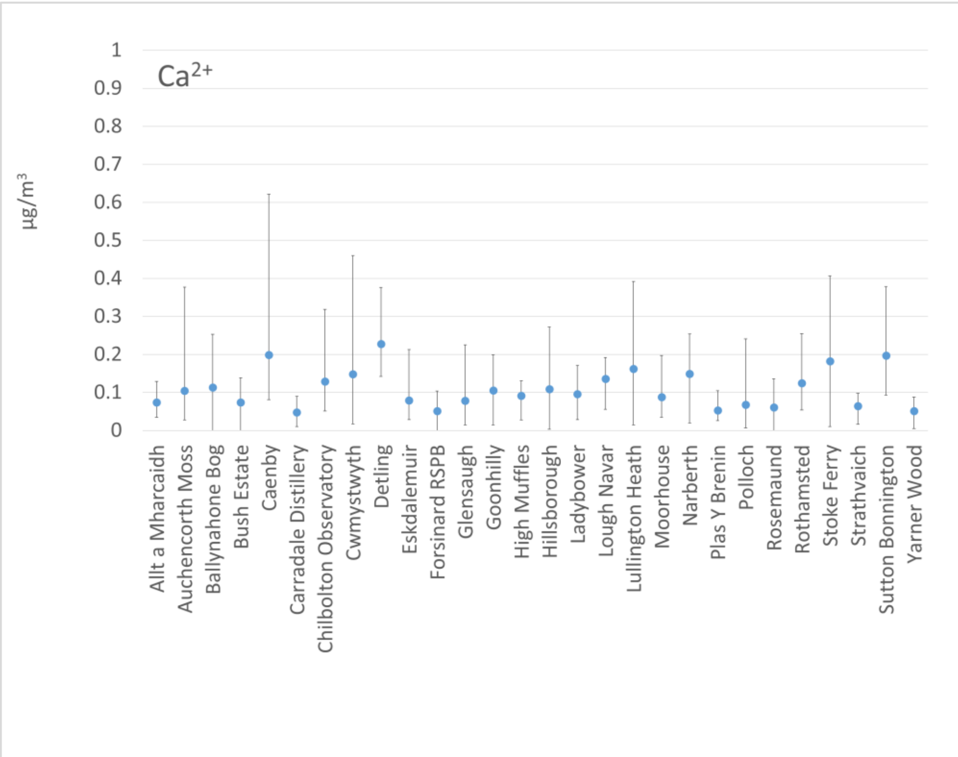


Figure 31 Mean monitored annual concentrations of particulate Mg^{2+} and Ca^{2+} at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentration.

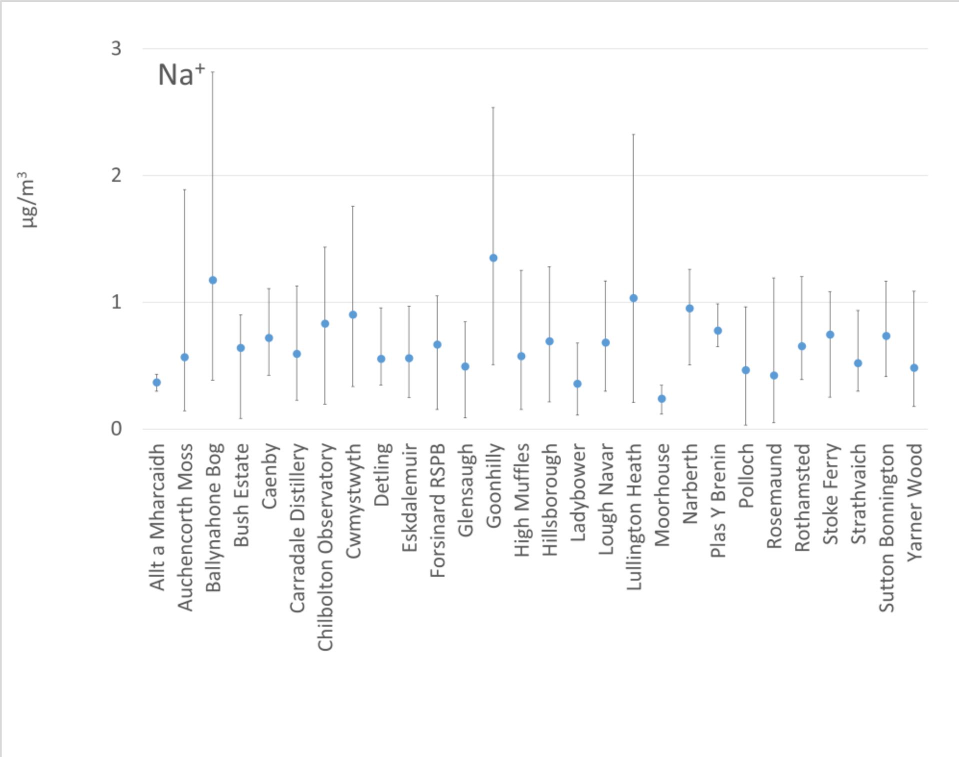


Figure 32. Mean monitored annual concentrations of particulate Na^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2023, whilst the bars show the minimum and maximum concentration.

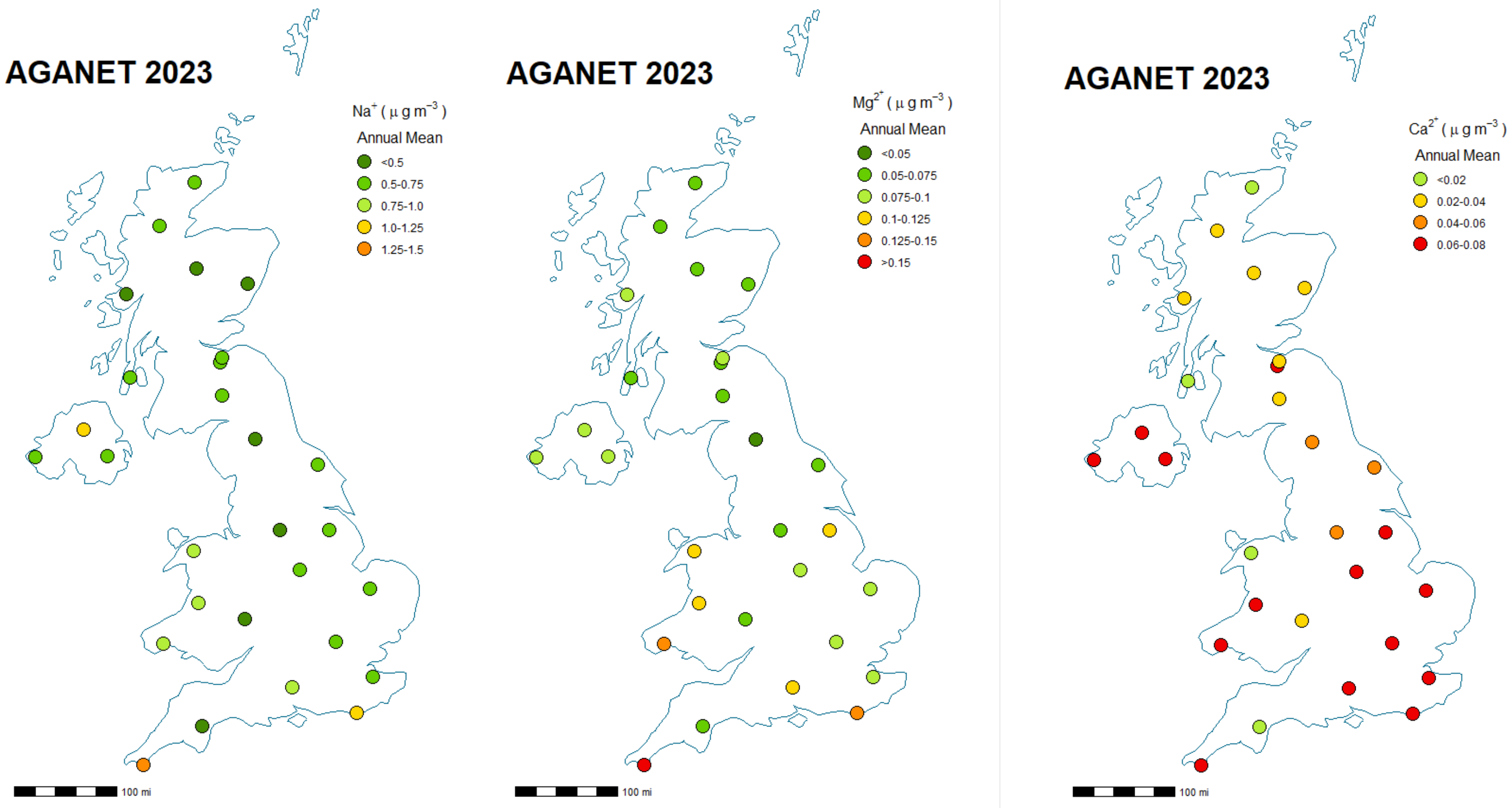
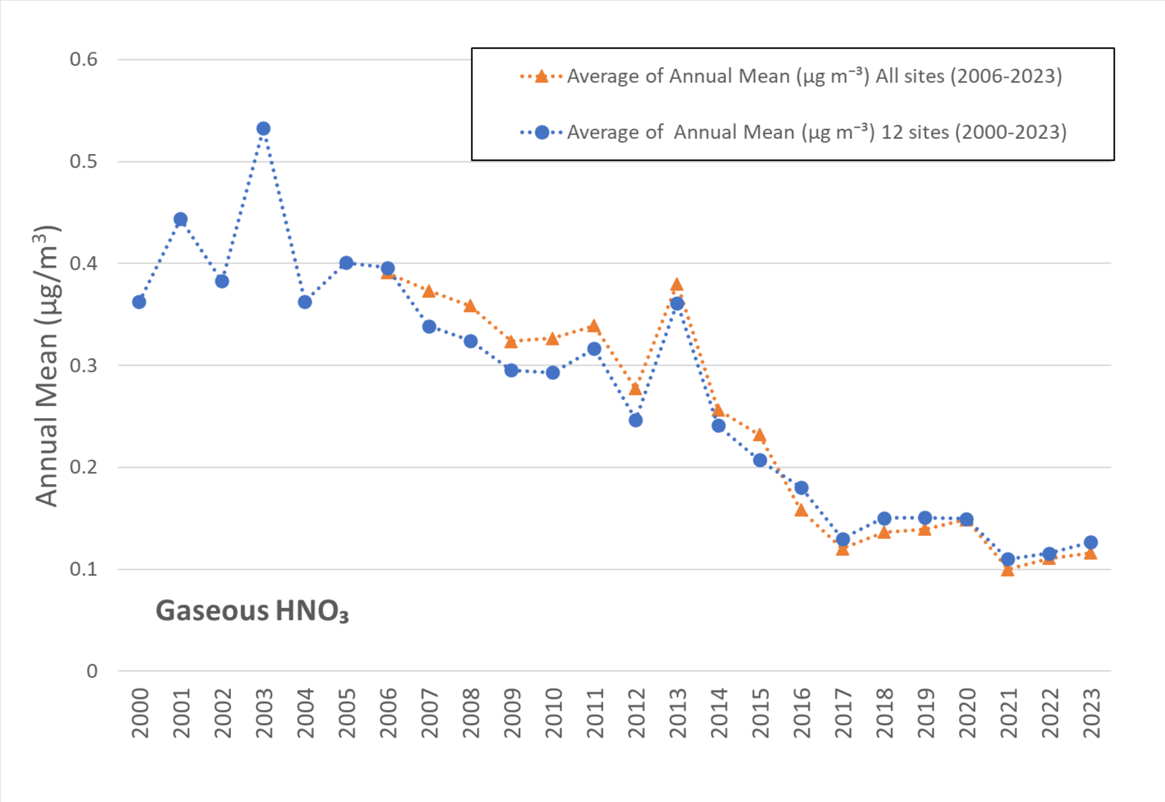


Figure 33 Annual mean monitored atmospheric base cations (Ca^{2+}, Mg^{2+} and Na^{+}) concentrations across the UK from the average monthly measurements made in 2023.



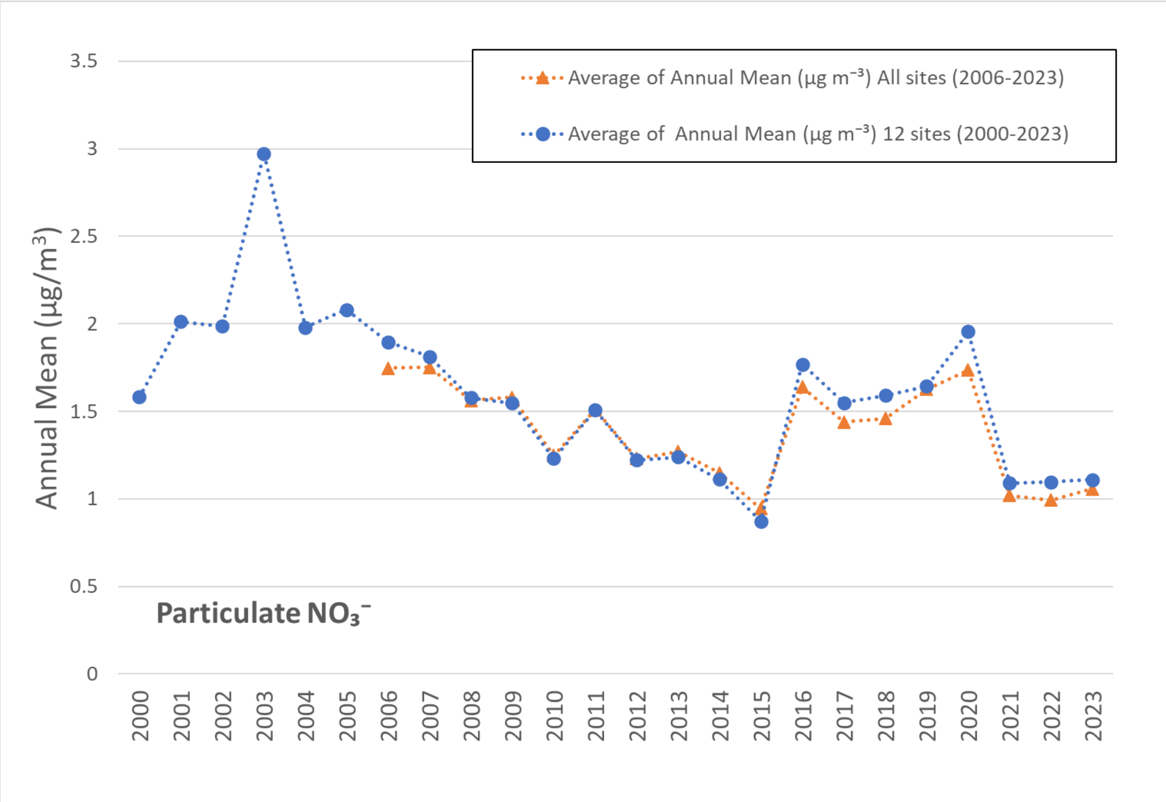
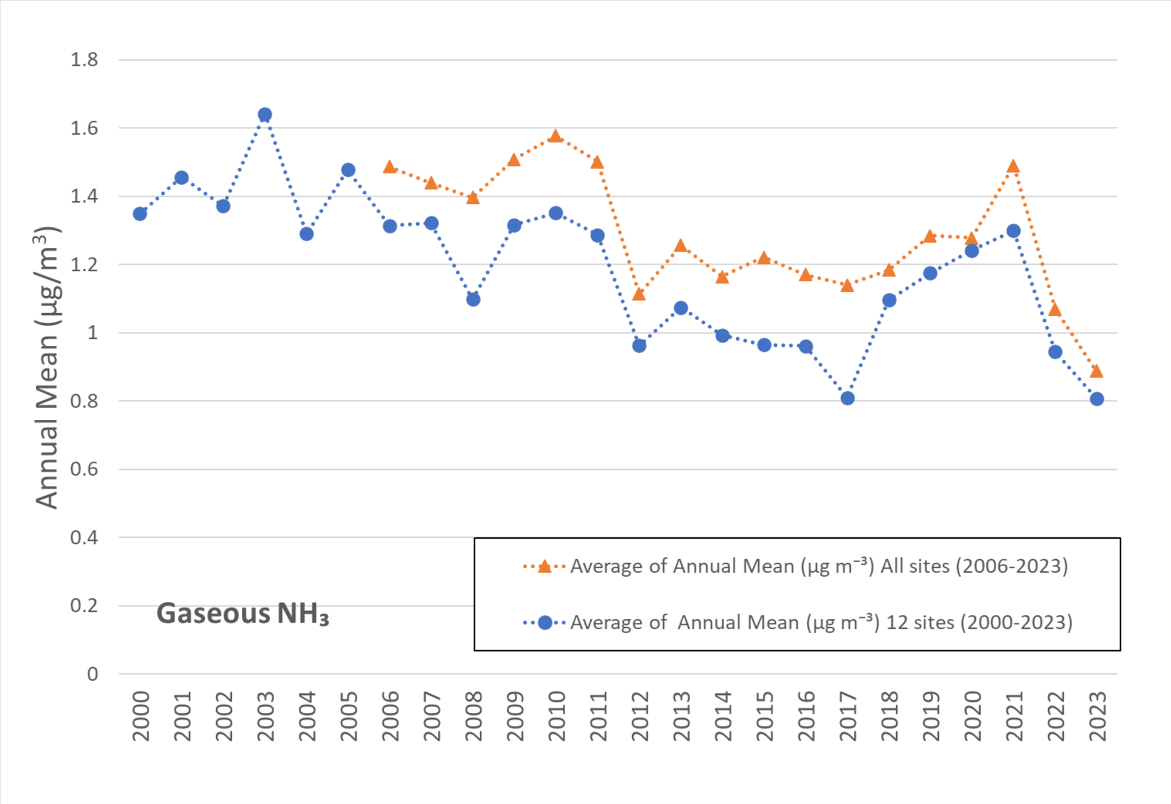


Figure 34 Long-term trend in annual mean concentrations of HNO_3, NH_3, SO_2, NO_3^-, NH_4^+ and SO_4^{2--} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.



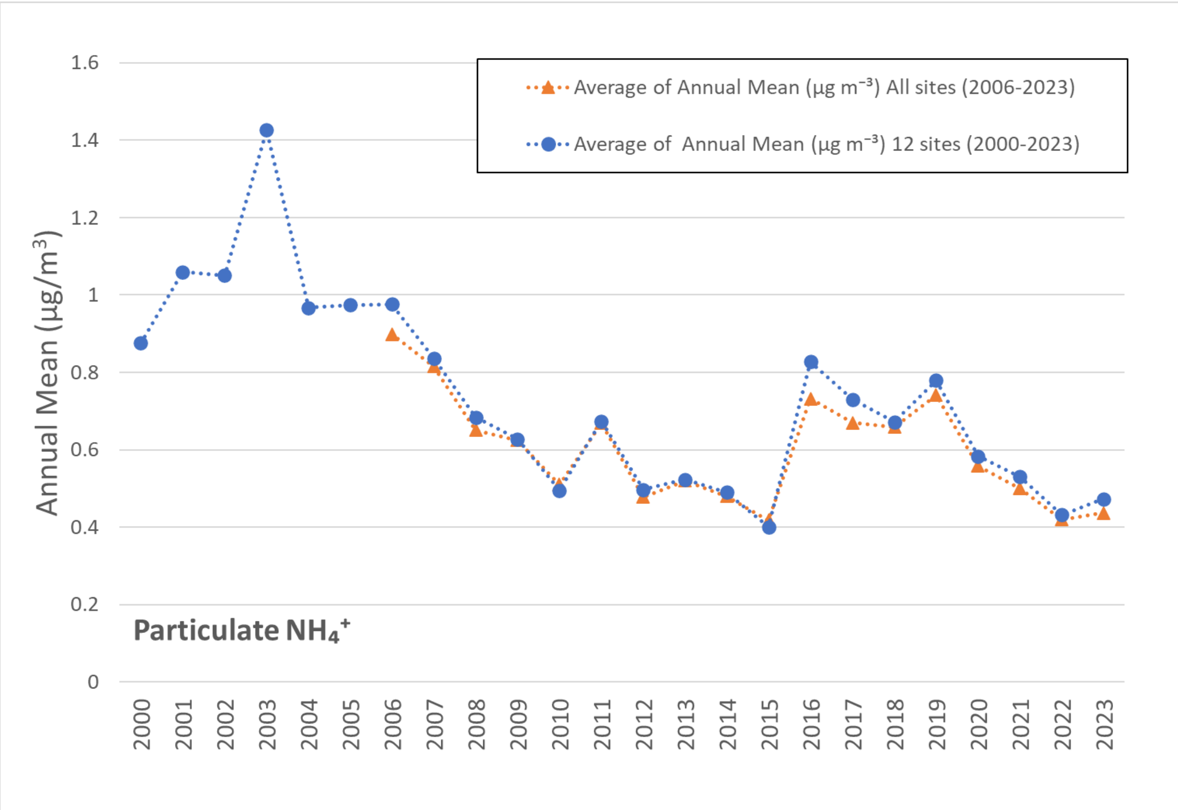
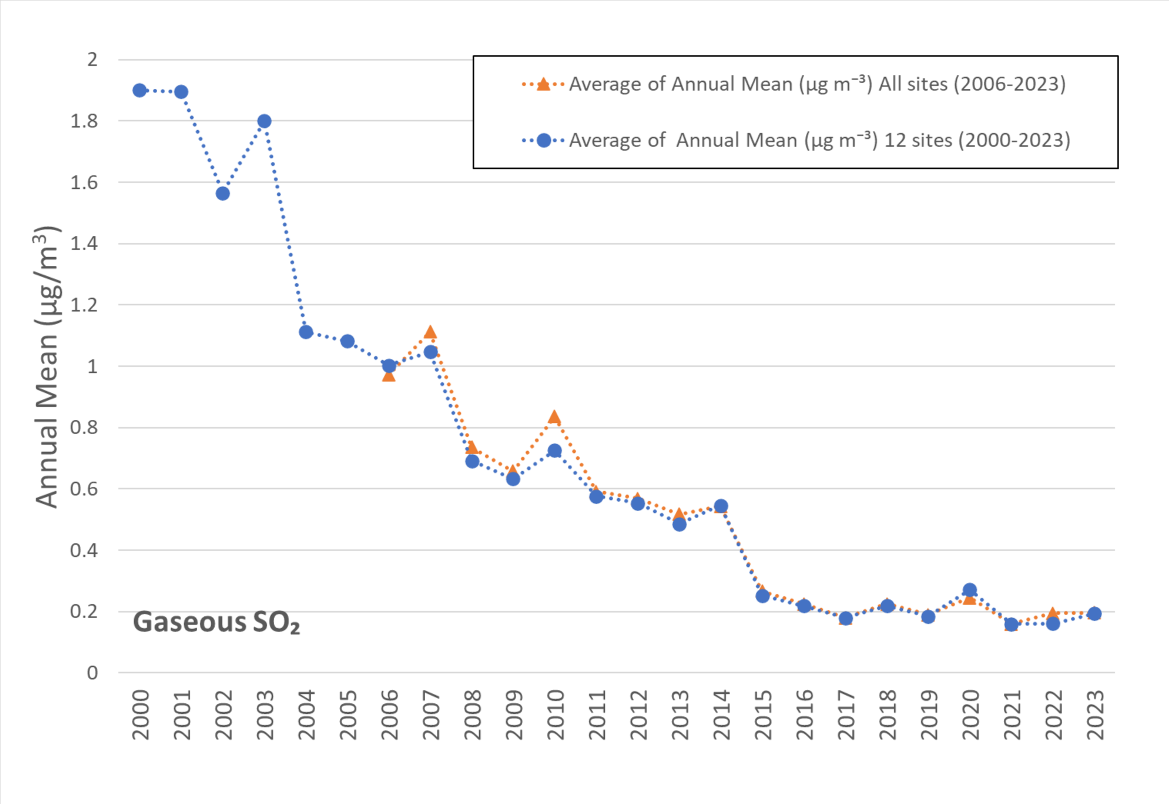


Figure 34 contd. Long-term trend in annual mean concentrations of HNO_3, NH_3, SO_2, NO_3^-, NH_4^+ and SO_4^{2-} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.



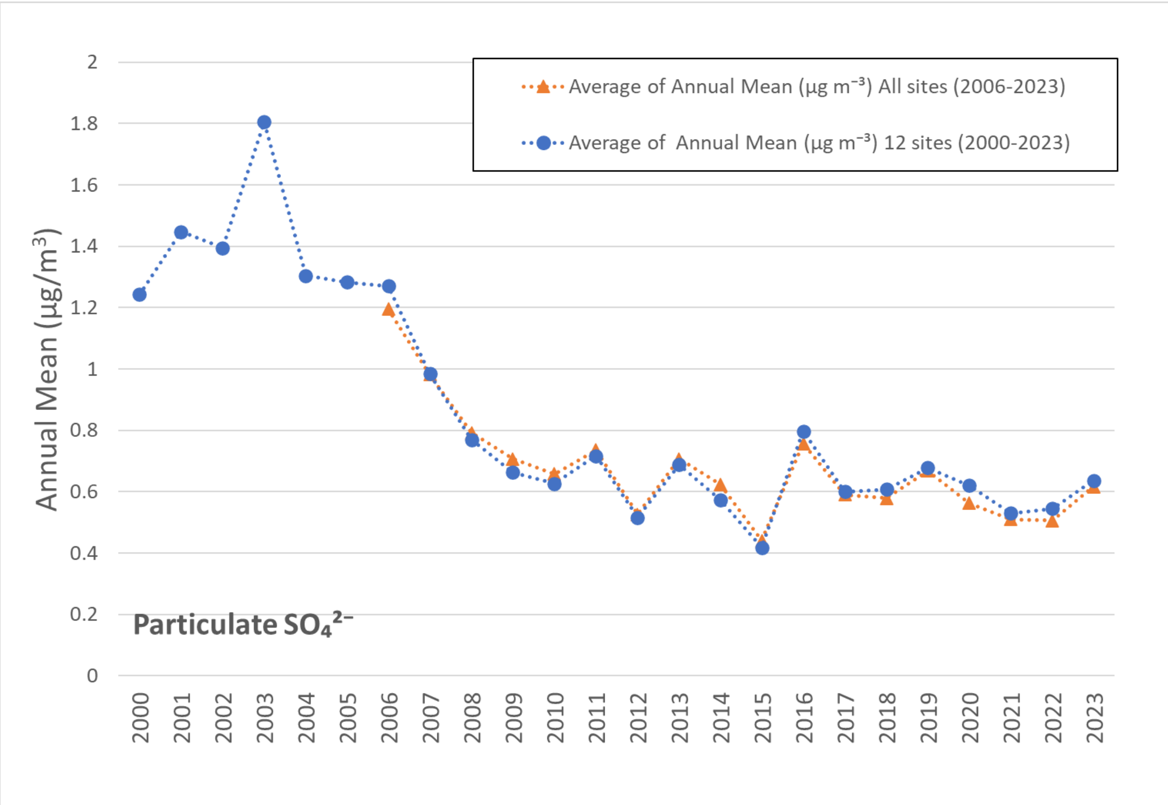


Figure 34 contd. Long-term trend in annual mean concentrations of HNO_3, NH_3, SO_2, NO_3^-, NH_4^+ and SO_4^{2-} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.

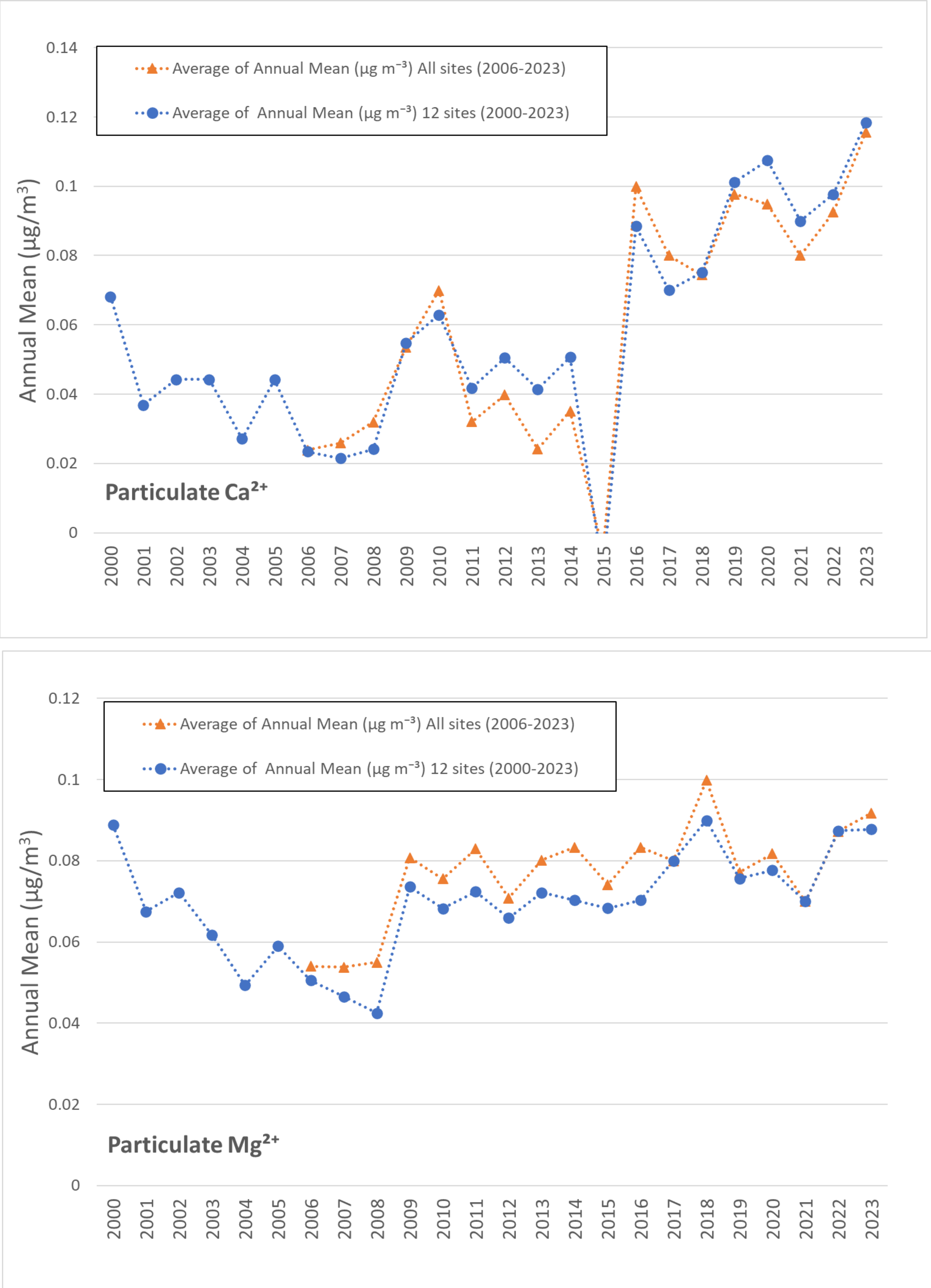
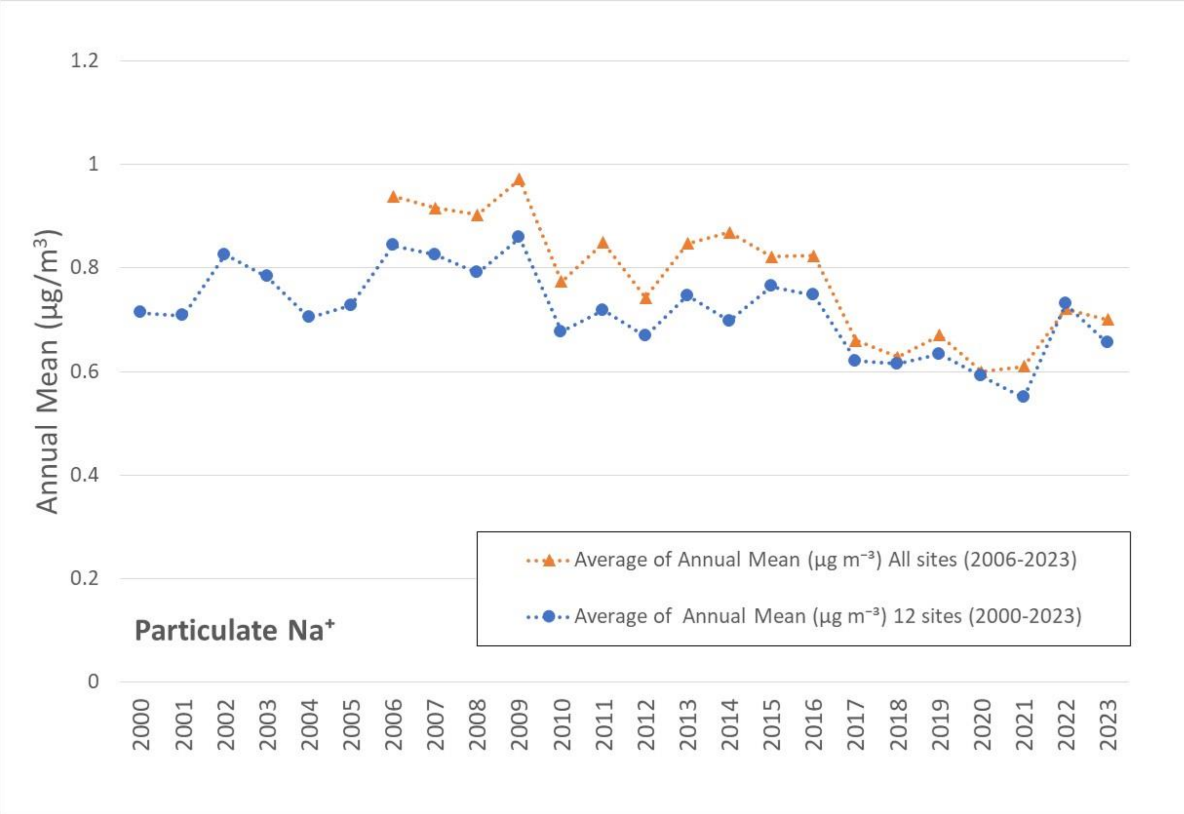


Figure 35 Long-term trend in annual mean concentrations of Ca^{2+}, Mg^{2+}, Na^{+} and Ca^{2+} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.



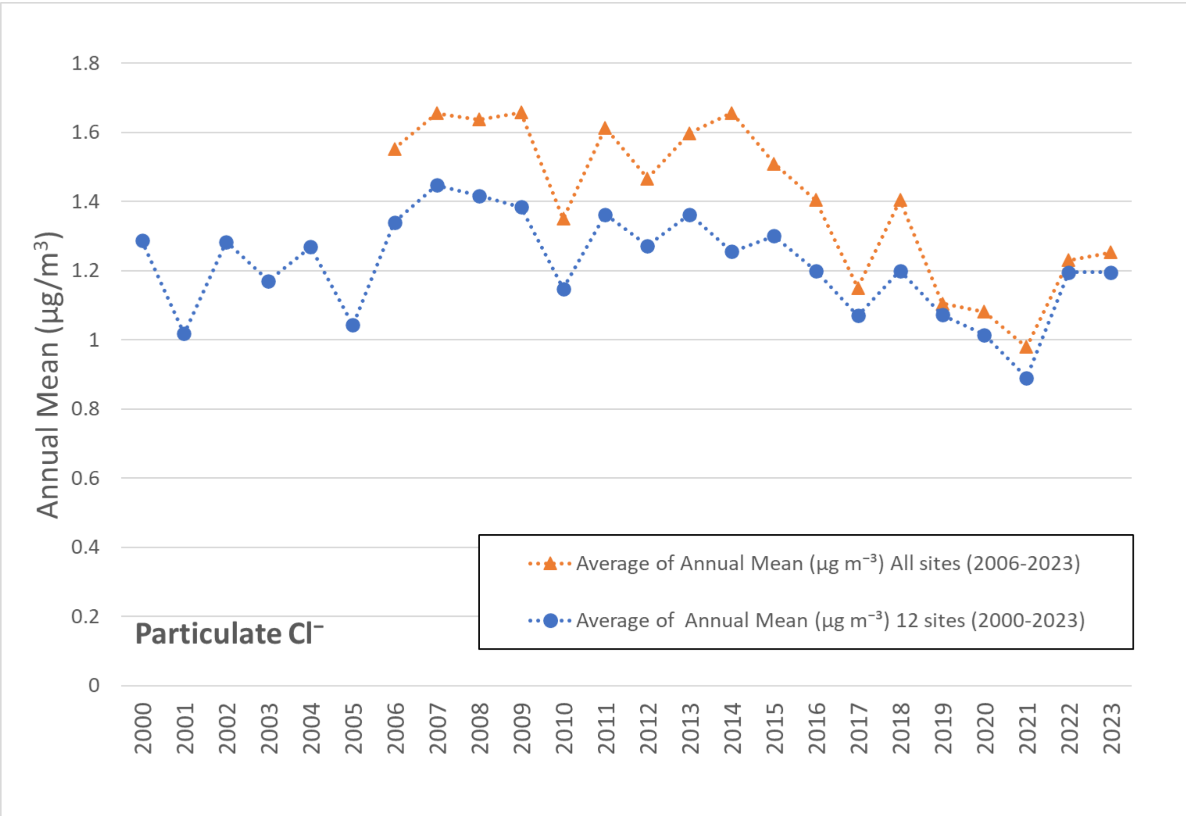


Figure 35 contd. Long-term trend in annual mean concentrations of Ca2+, Mg2+, Na+ and Ca2+ monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.

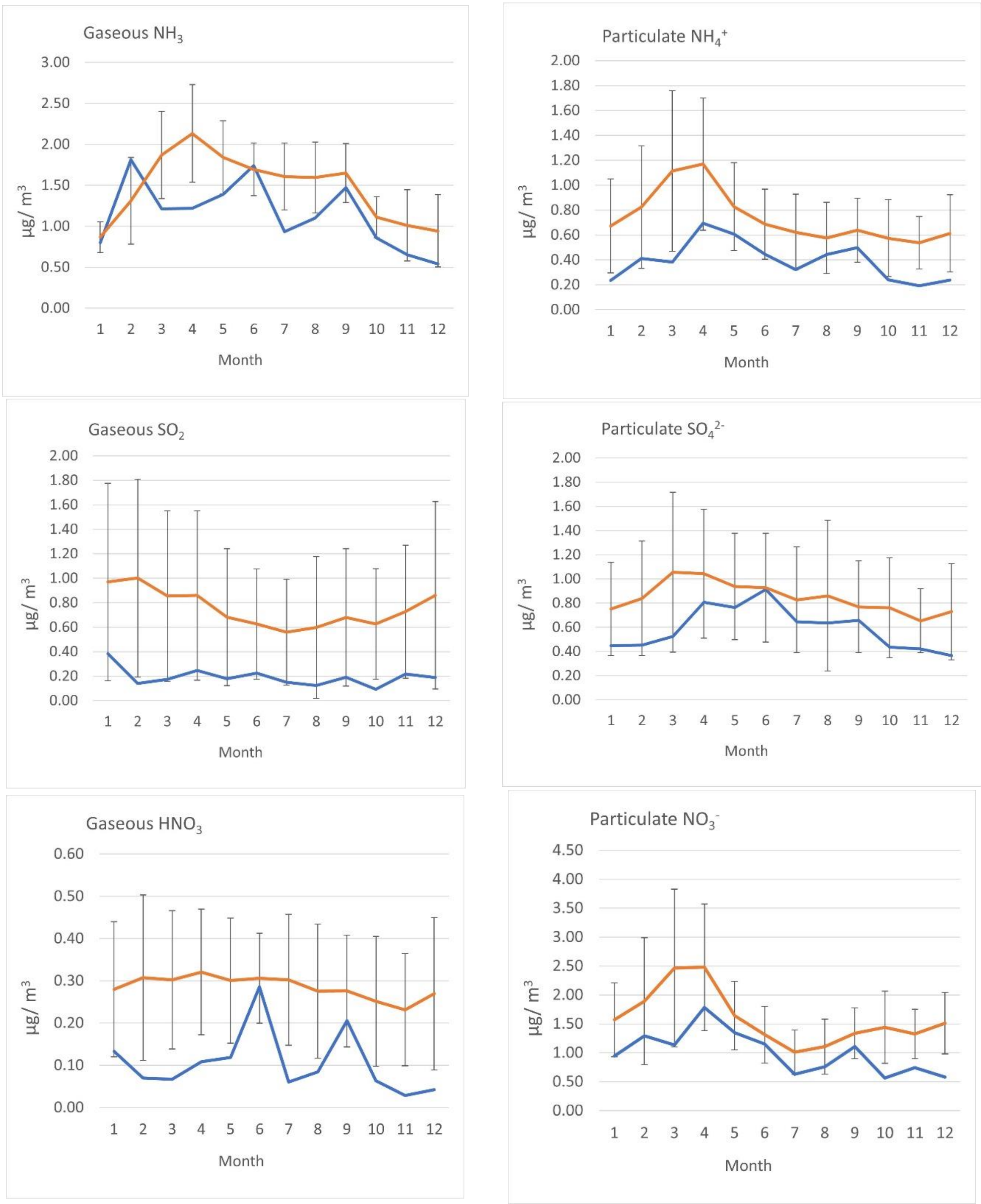


Figure 36 Monthly average of selected species from the NAMN and AGANet sites across the UK in 2023 (blue line), compared to the mean seasonal profile for year 2000-2023 (orange line). Error bars are +/- standard deviation across the 27 AGANET sites (from April 2022 28 sites) in 2023.

3.5 UK EMEP supersites

3.5.1 MARGA

Annual average concentrations from the MARGA at Auchencorth Moss continued to report lower concentrations to that of Chilbolton Observatory (Table 6).

At Auchencorth Moss the 2023 data capture was lower than previous years as data failed QA/QC processes due to contamination. The source of the contamination has been identified and remedial action implemented.

Table 6 Summary of the ratified speciated PM_{10} and $PM_{2.5}$ and trace gases of annual mean concentrations and data capture for Auchencorth Moss and Chilbolton Observatory

	Chilbolton Observatory		Auchencorth Moss	
Ion (PM_{10})	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_4^+	0.633	76.46	0.348	74.14
Na^+	0.729	81.32	0.517	74.02
K^+	0.100	79.73	0.041	75.77
Ca^{2+}	0.144	78.41	0.068	75.77
Mg^{2+}	0.167	77.73	0.063	75.77
Cl^-	1.760	81.16	0.859	72.88
NO_3^-	1.935	81.86	0.727	75.58
SO_4^{2-}	1.145	82.03	0.593	75.58
Ion ($PM_{2.5}$)	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_4^+	0.574	76.51	0.308	74.52
Na^+	0.303	77.01	0.262	70.51
K^+	0.076	76.96	0.016	75.16
Ca^{2+}	0.045	75.87	0.035	66.55
Mg^{2+}	0.084	75.59	0.029	75.16
Cl^-	0.848	74.95	0.429	73.55
NO_3^-	1.593	77.12	0.549	74.98
SO_4^{2-}	0.991	76.61	0.497	74.98
Trace Gases	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_3	2.832	87.30	1.273	82.98
HCl	0.042	86.72	0.093	80.24
HNO_3	0.112	86.63	0.064	83.51
HONO	0.278	87.03	0.056	81.63
SO_2	0.123	87.63	0.048	83.51

Figure 37 to Figure 42 present the time series of the PM_{10} (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}), $PM_{2.5}$ (NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^- and SO_4^{2-}) and trace gases (NH_3, HCl, HNO_3, HONO, SO_2) reported by the MARGA at Chilbolton Observatory and Auchencorth Moss for 2023.

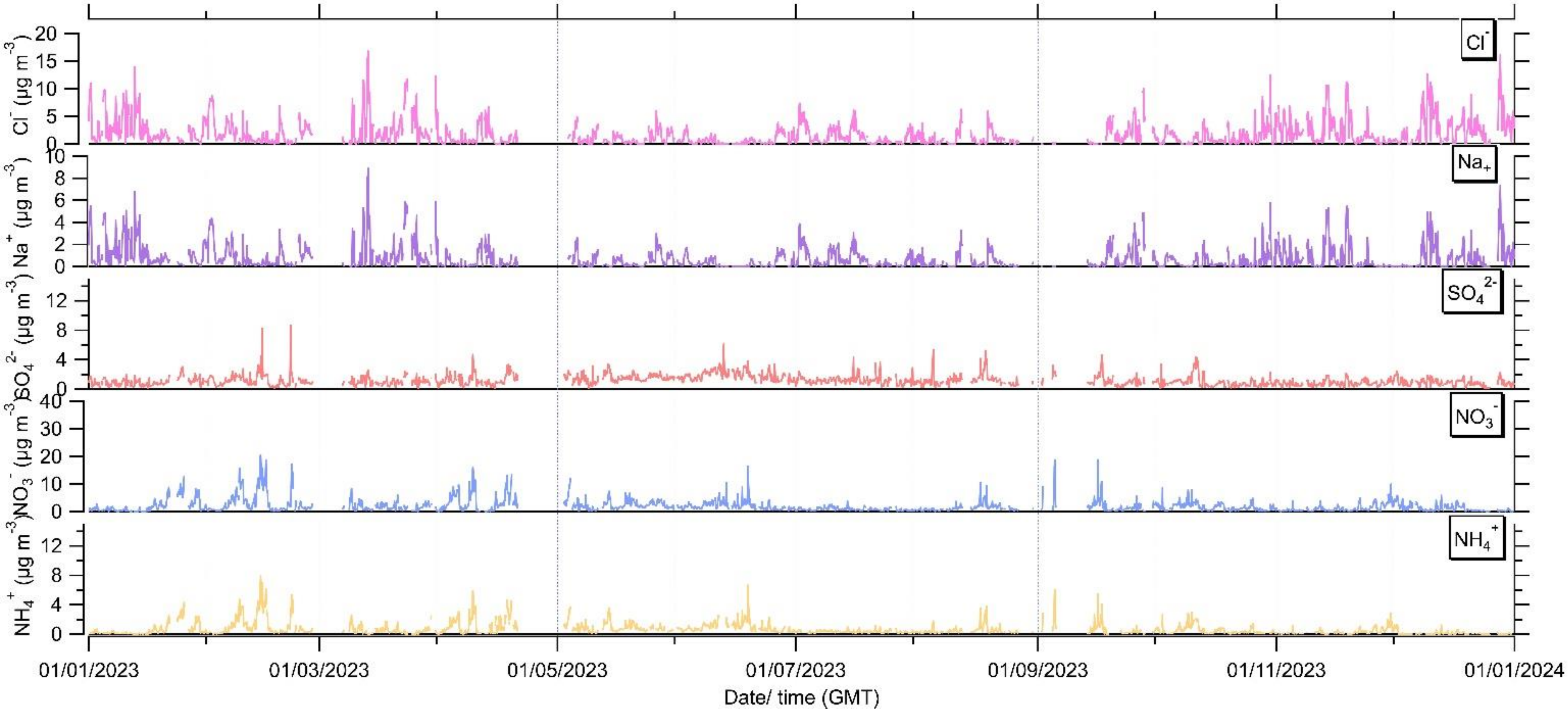


Figure 37 Ratified PM_{10} speciated measurements by the MARGA at the Chilbolton Observatory supersite

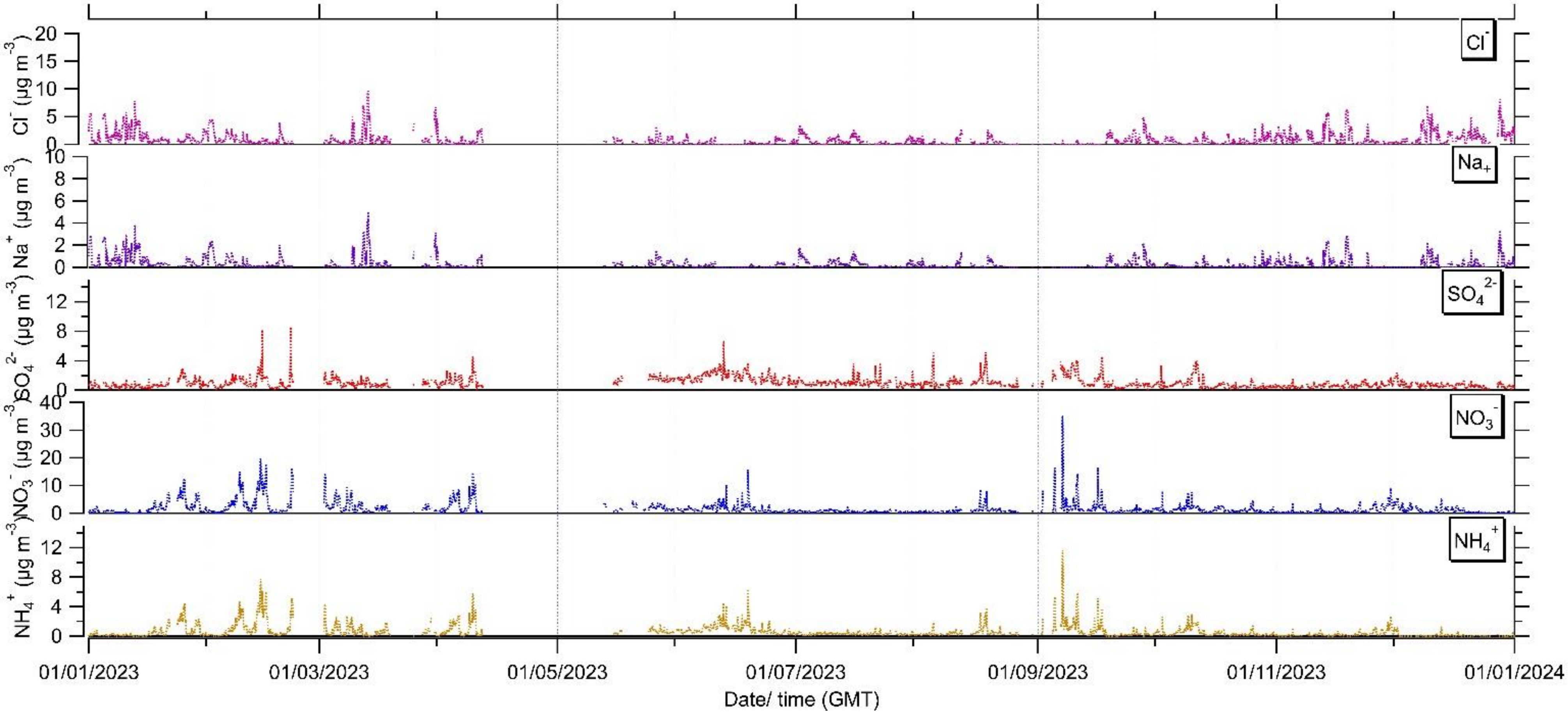


Figure 38 Ratified $PM_{2.5}$ speciated measurements by the MARGA at the Chilbolton Observatory supersite

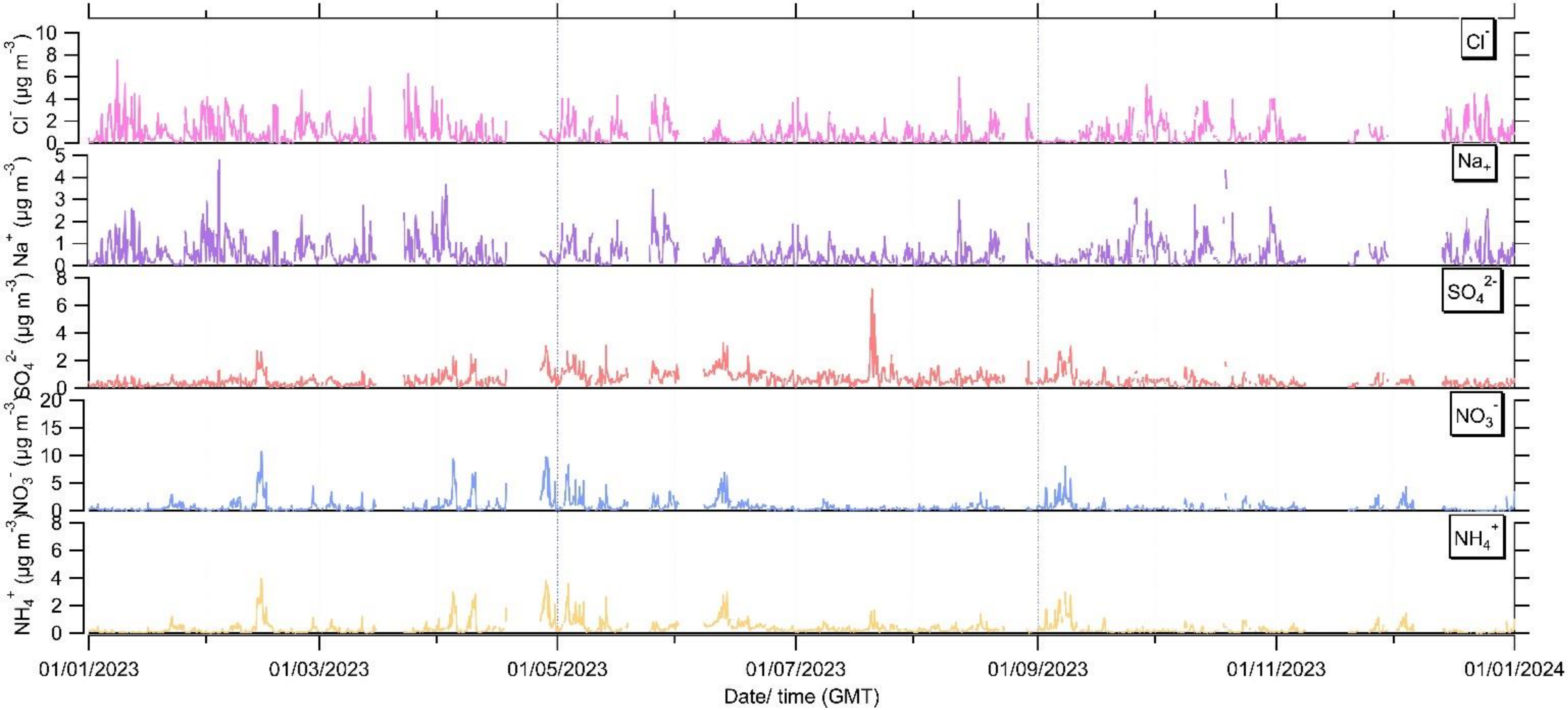


Figure 39 Ratified PM_{10} speciated measurements by the MARGA at the Auchencorth Moss supersite

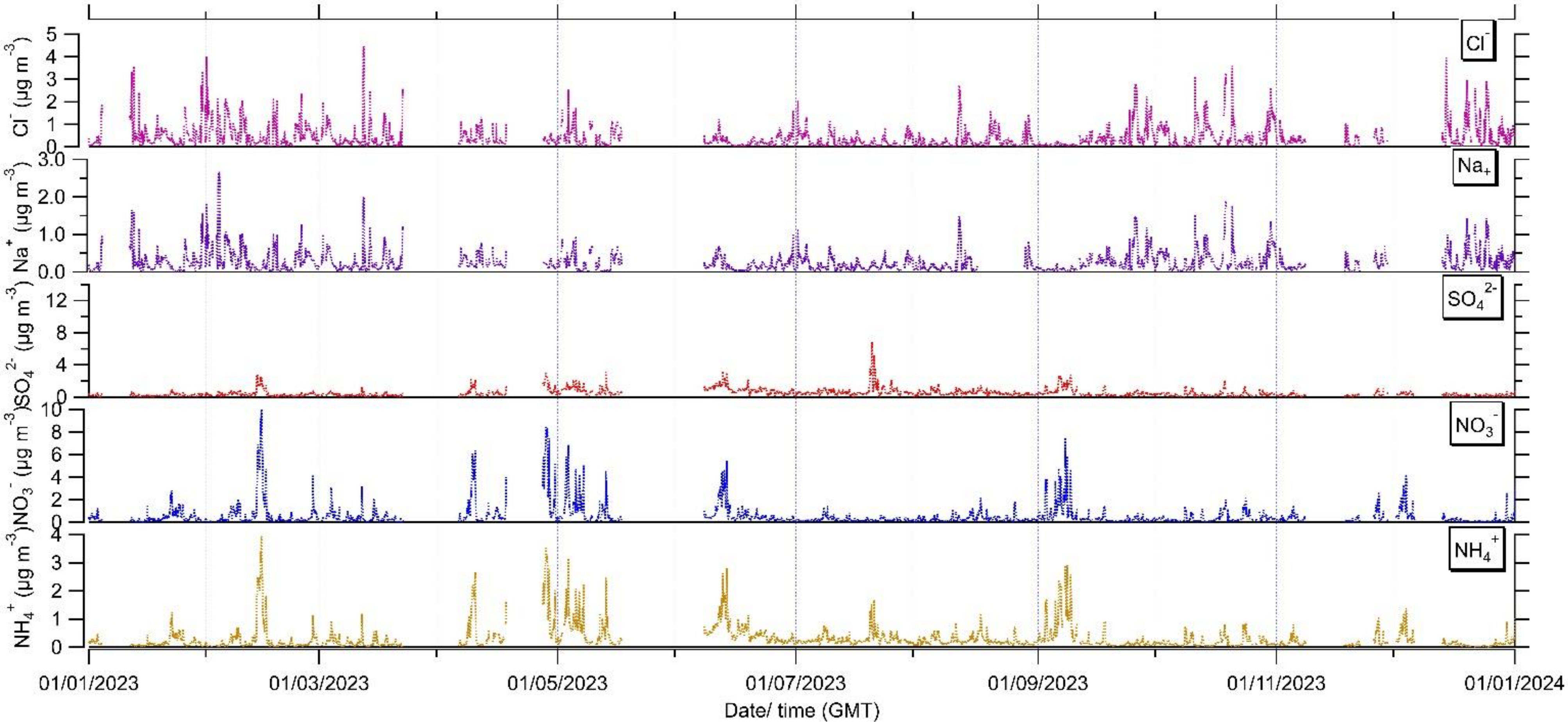


Figure 40 Ratified $PM_{2.5}$ speciated measurements by the MARGA at the Auchencorth Moss supersite

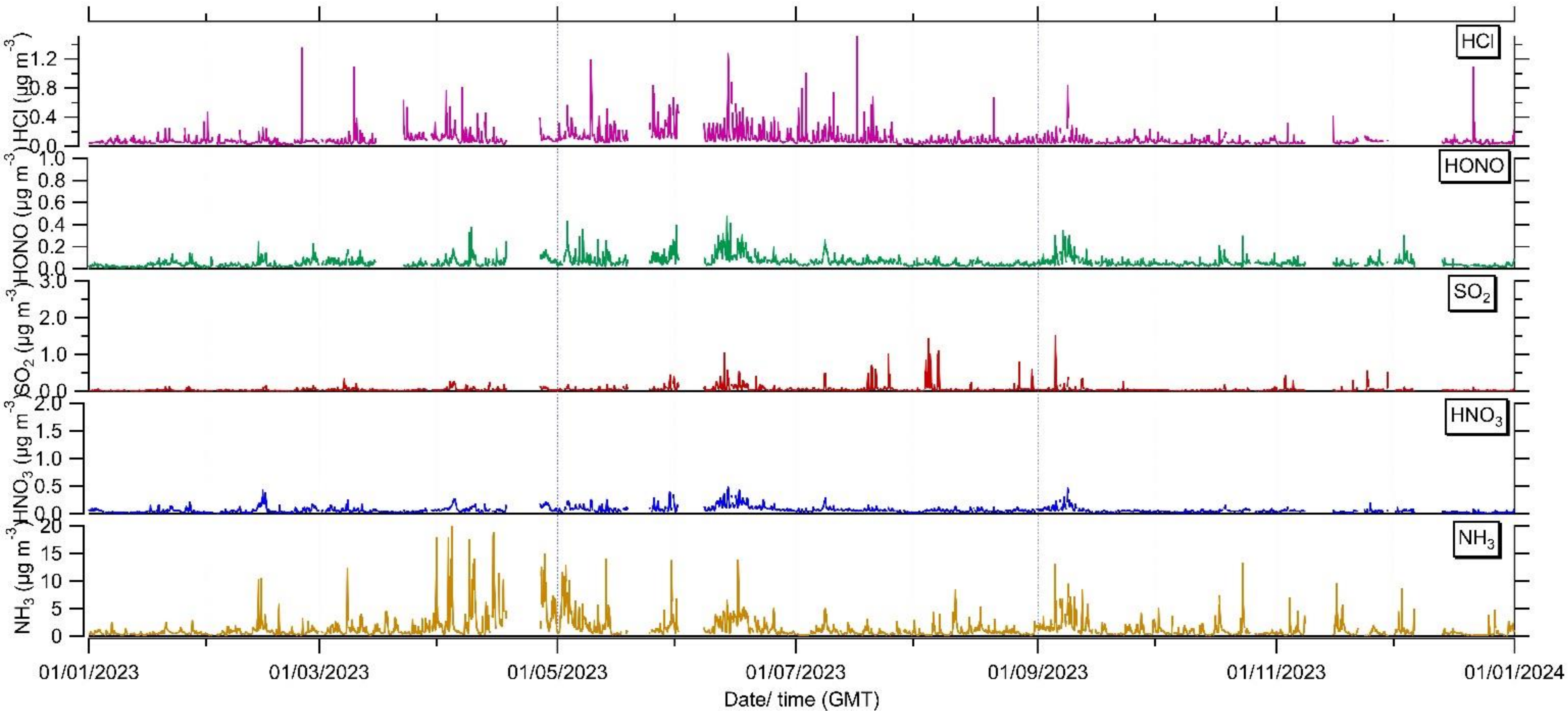


Figure 41 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite

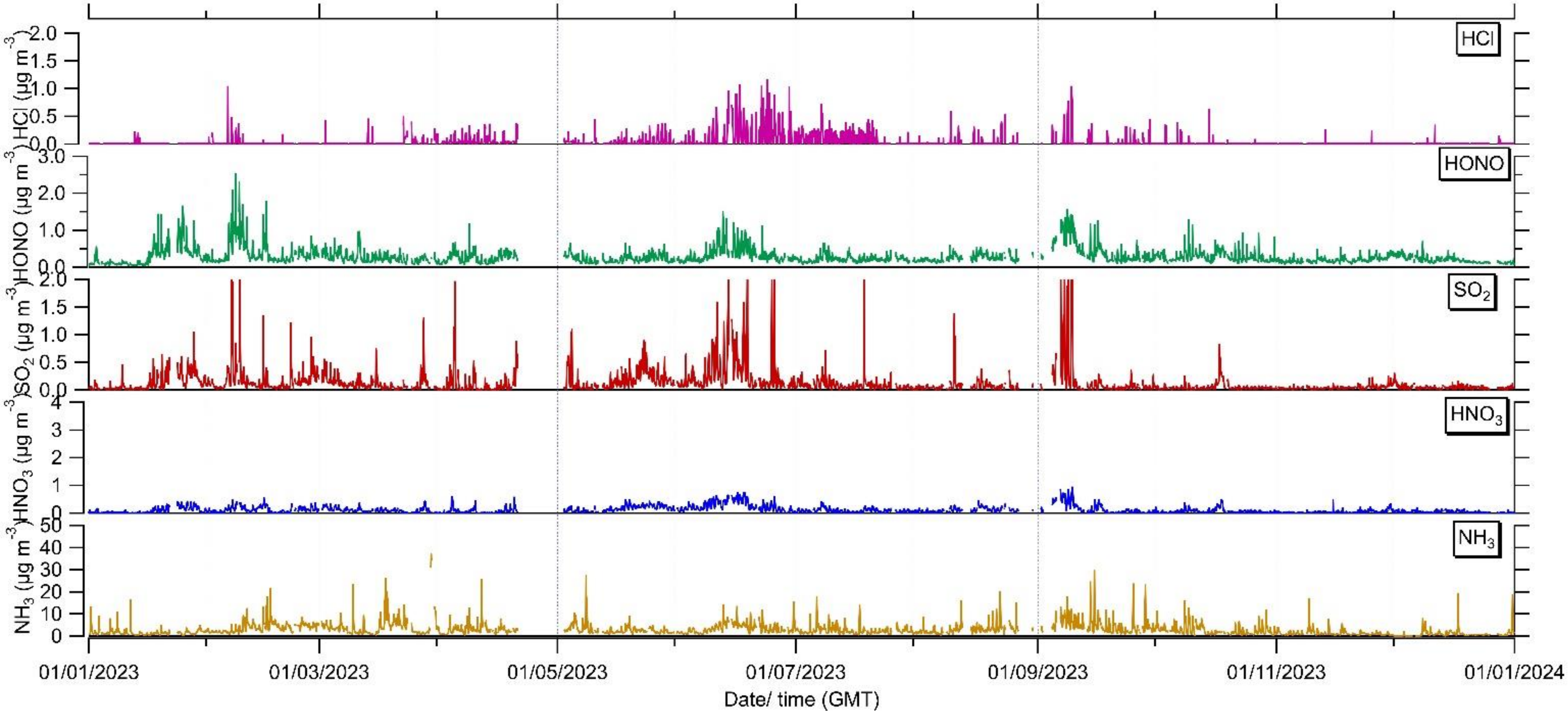


Figure 42 Ratified trace gas measurements by the MARGA at the Chilbolton Observatory supersite

3.5.2 Tekran

The annual means and data capture for the 2023 ratified mercury measurements are shown below in Table 7.

The time series of the Auchencorth Moss measurements are shown in Figure 43. The system had reduced data capture due to the following reasons:

- January – February 2023 - contamination in sample line.
- May 2023 – Failed argon supply valve on 2537X.
- June – July 2023 – issues with Hg speciation system oven and heating controls.

The 2023 data from the Chilbolton Observatory site is shown in Figure 44. Data is missing from mid-May to August due to the lamp control board failing. This has now been upgraded to a newer version board.

Table 7 Ratified mercury measurements at the Auchencorth Moss and Chilbolton Observatory field sites.

	Annual Mean	**Data Capture (%)**
Auchencorth Moss		
Gaseous Elemental Hg (GEM) ng m^{-3}	1.298	49.21
Gaseous Oxidised Hg (GOM) pg m-^{3}	0.425	39.34
Particulate bound Hg ($PM_{2.5}$) pg m^{-3}	1.700	39.34
Chilbolton Observatory		
Total Gaseous Hg (TGM) ng m^{-3}	1.457	72.35

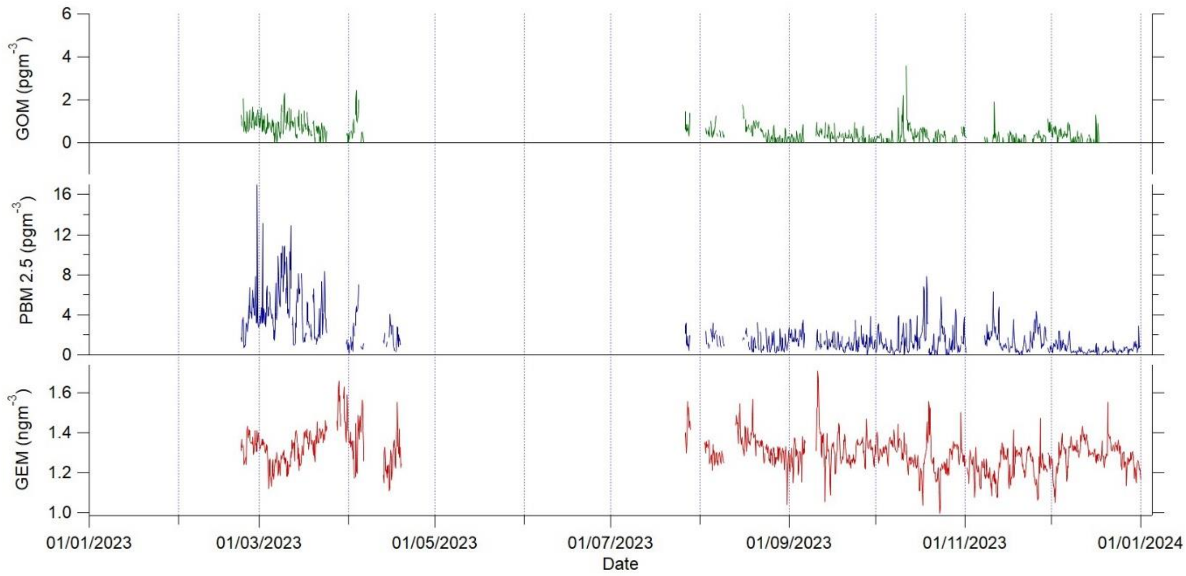


Figure 43 Ratified mercury measurements by the Tekran at the Auchencorth Moss supersite

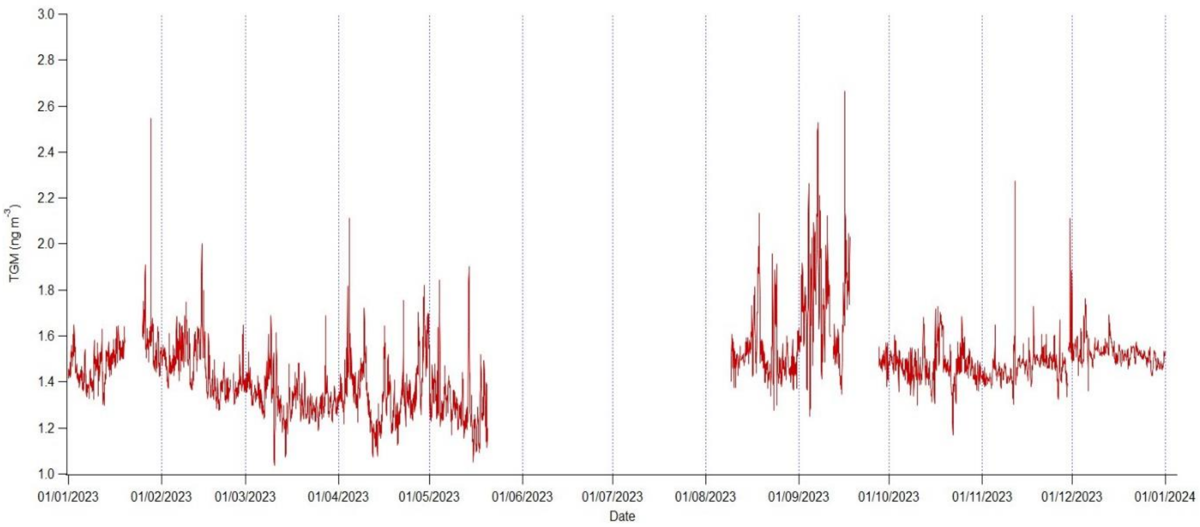


Figure 44 Ratified mercury measurements by the Tekran at the Chilbolton observatory

3.6 Publications and related activities

The UKEAP data is used to allow improvements in understanding of the chemical composition, deposition and removal processes of inorganic air pollutants and to allow validation of atmospheric transport models. It is however also used by a number of different organisations beyond the reporting required for Defra and the devolved administrations.

Below is a summary of the publications identified to have been published since 2023 that have used the UKEAP network data:

Bourin, A., Espina-Martin, P., Font, A., Crunaire, S., Twigg, M.M., Braban, C.F. and Sauvage, S., 2023. Atmospheric ammonia in-situ long-term monitoring: review worldwide strategies and recommendations for implementation. EGU General Assembly 2023.

Cowan, N., Twigg, M.M., Leeson, S.R., Jones, M.R., Harvey, D., Simmons, I., Coyle, M., Kentisbeer, J., Walker, H. and Braban, C.F., 2024. Assessing the bias of molybdenum catalytic conversion in the measurement of NO_2 in rural air quality networks. Atmospheric Environment, 322, p.120375.

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3.7 Legislation and Standardisation

There were to the authors’ knowledge no changes to legislation or standardisation to UKEAP network in 2023.

4. Where to find out more

All datasets are submitted to UK-Air. To access the data use the UK-Air tool found at: https://uk-air.defra.gov.uk/data/. Provisional data is available on a quarterly basis and ratified data is made available on an annual basis in the proceeding year.

Information on the sites within the UKEAP network can be found using the interactive map on UK-Air here: https://uk-air.defra.gov.uk/interactive-map

Data are also submitted to the_*OSPAR* and *EMEP* databases. UKEAP Team members at Ricardo and UKCEH are available to give information on the measurements when requested (please refer to Appendix 1).

5. Acknowledgements

The measurements in the UKEAP network would not be possible without the dedicated support of Local Site Operators across the UK throughout the year.

UKCEH, Ricardo, the Environment Agency, Defra and the Devolved Administrations thank them for their hard work and support, noting the appreciation that many of these sites can be challenging to access.

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Appendix 1 Guide to UKEAP data and Data usage

Please contact UK Centre for Ecology and Hydrology or Ricardo for guidance or discussion regarding authorship of multi-year datasets.

Chilbolton Observatory EMEP Supersite

Trace gas and aerosols (MARGA) Contact: Mr Chris Conolly, Ricardo

Sanocka, A., Ritchie, S., Conolly, C. UK Eutrophying and Acidifying Atmospheric Pollutant project's Monitoring instrument for AeRosols and reactive Gases (MARGA), Harwell Supersite (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (Data user ***insert date of data receipt***)

Mercury measurements: Contact: Ms Sarah Leeson, UK Centre for Ecology and Hydrology

Leeson, S.R., Ritchie, S. UK Eutrophying and Acidifying Atmospheric Pollutant project's mercury instrument, Auchencorth Supersite(Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (Data user **insert date of data receipt**)

Meteorological Data: Contact Mr Chris Conolly Ricardo

Auchencorth Moss EMEP Supersite

MARGA: Contact: Dr Marsailidh Twigg, UK Centre for Ecology and Hydrology

Twigg, M.M., Leeson, S.R., Simmons, I, Harvey, D., Yeung, K. Jones, M.R., A. Iwanicka, Duarte, F., UK Eutrophying and Acidifying Atmospheric Pollutant project's Monitoring instrument for AeRosols and reactive Gases (MARGA), Auchencorth Supersite(Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (Data user **insert date of data receipt**)

Mercury: Contact: Ms Sarah Leeson, UK Centre for Ecology and Hydrology

Leeson, S.R. J., Harvey, D. Yeung, K. UK Eutrophying and Acidifying Atmospheric Pollutant project's Tekran instrument, Auchencorth Supersite(Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (Data user **insert date of data receipt**)

Acid Gas and Aerosol Network (AGANet)

Contact: Dr Marsailidh Twigg and Ms Amy Stephens, UK Centre for Ecology and Hydrology

ACM Stephens, P. Espina Martin, A. Iwanicka, F. Duarte, D Leaver, C Andrews, CF Braban, S Thacker, PO Keenan, M.G Pereira, H Guyatt, A Hunt, E Salisbury, N Chetiu , F Cook, A Warwick, D Rylett, S Teagle, W Lord, G. Bannister & MM Twigg.UK Eutrophying and Acidifying Atmospheric Pollutants. (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK AGANet, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (Data user **insert date of data receipt**)

National Ammonia Monitoring Network (NAMN)

Contact: Dr Marsailidh Twigg and Ms Amy Stephens, UK Centre for Ecology and Hydrology

ACM Stephens, P. Espina Martin, A. Iwanicka, F. Duarte, D Leaver, C Andrews, CF Braban, S Thacker, PO Keenan, M.G Pereira, H Guyatt, A Hunt, E Salisbury, N Chetiu , F Cook, A Warwick, D Rylett, S Teagle, W Lord, G. Bannister & MM Twigg. UK Eutrophying and Acidifying Atmospheric Pollutants. (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK AGANet, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (Data user **insert date of data receipt**)

Precipitation Network (Precip-Net)

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo

Conolly, C., Collings, A., Knight, D., Vincent, K., Donovan, B., UK Eutrophying and Acidifying Atmospheric Pollutant project's Precipitation Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, Precip-Net, http://uk-air.defra.gov.uk/networks/network-info?view=ukeap), Date received: (***insert date of data receipt***)

NO_2-Network

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo

Conolly, C., Collings, A., Knight, D., Vincent, K., Donovan, B., UK Eutrophying and Acidifying Atmospheric Pollutant project's rural NO_2-Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, NO_2-Net, http://uk-air.defra.gov.uk/networks/network-info?view=ukeap), Date received: (***insert date of data receipt***)

Appendix 2 Precip-Net: EMEP and WMO Inter-comparisons

EMEP and WMO Inter-comparisons

An important data quality assessment is organised annually by the EMEP Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research (NILU). Each year, samples are sent to over sixty analytical laboratories in Europe, and to other internationally recognised analytical laboratories. The inter-comparison exercise is required as part of the EMEP monitoring programme – such a fundamental check on analytical performance is essential if response to emission reductions can be observed consistently throughout Europe.

Another analytical intercomparison exercises that will be discussed in this section is the World Meteorological Organisation's intercomparison exercise.

The analytical laboratory used with the Precipitation Network (Precip-net) is Socotec's Advanced Chemistry and Research laboratory. They are accredited to ISO17025 and participate in the EMEP and WMO intercomparisons.

Results of the 41st EMEP Inter-comparison

The inter-comparison in 2023 was the 41st time such an inter-comparison took place.

Synthetic Rainwater Samples

The results of the intercomparison for the synthetic rainwater samples are shown in Appendix 2 Table 1. Satisfactory results were obtained for all anions, ammonium, sodium, pH and conductivity. Three of the four results for calcium were not satisfactory- the fourth was questionable. The magnesium and potassium results were considered questionable.

Appendix 2 Table 1 41st EMEP Intercomparison

Species	Sample code	Reported value concentration mg l^{-1}	Expected concentration mg l^{-1}	Difference (%)	EMEP Quality Norm
$SO4^{-2}$	G1	0.286	0.314	-8.9	S
	G2	0.3	0.326	-8.0	S
	G3	0.272	0.298	-8.7	S
	G4	0.236	0.26	-9.2	S
NH_4^+	G1	0.114	0.134	-14.9	S
	G2	0.139	0.16	-13.1	S
	G3	0.129	0.147	-12.2	S
	G4	0.103	0.12	-14.2	S
NO_3^-	G1	0.222	0.238	-6.7	S
	G2	0.317	0.342	-7.3	S
	G3	0.315	0.343	-8.2	S
	G4	0.255	0.276	-7.6	S
Na^+	G1	0.855	0.948	-9.8	S
	G2	0.767	0.855	-10.3	S
	G3	0.673	0.737	-8.7	S
	G4	0.768	0.851	-9.8	S
Mg^{2+}	G1	0.087	0.114	-23.7	Q
	G2	0.111	0.145	-23.4	Q
	G3	0.081	0.103	-21.4	Q
	G4	0.066	0.083	-20.5	Q
Cl-	G1	1.24	1.35	-8.1	S
	G2	0.954	1.04	-8.3	S
	G3	0.814	0.888	-8.3	S
	G4	1.03	1.12	-8.0	S
Ca^{2+}	G1	0.13	0.179	-27.4	U
	G2	0.106	0.14	-24.3	Q
	G3	0.122	0.166	-26.5	U
	G4	0.113	0.153	-26.1	U
K^+	G1	0.133	0.162	-17.9	Q
	G2	0.162	0.195	-16.9	Q
	G3	0.219	0.26	-15.8	Q
	G4	0.175	0.21	-16.7	Q
pH*	G1	5.52	5.47	0.05	S
	G2	5.5	5.46	0.04	S
	G3	5.49	5.41	0.08	S
	G4	5.48	5.42	0.06	S
Cond**	G1	10.75	11	-2.3	S
	G2	10.36	10.9	-5.0	S
	G3	9.72	10.3	-5.6	S
	G4	9.63	10.1	-4.7	S

* pH as pH units, **Cond, conductivity, units: µS/cm

[1] EMEP quality norm given as Satisfactory (S), Questionable (Q) or Unsatisfactory (U)

Since the 40th intercomparison, the pH calibration standards with lower ionic strength to match both the synthetic and ambient rain samples have resulted in the pH measurements being satisfactory.

Work is on-going with the analyst to quantify the calcium, magnesium and potassium concentrations at the relatively low concentrations. Since last year the signal to noise ratio has increased.

The analyst also participates in the World Meteorological Organisations analytical intercomparison. The result from the most recent is shown in Appendix 2 Table 2. Using the same quality norm as used in the EMEP intercomparison, all apart from one sample for both calcium and magnesium are satisfactory.

Appendix 2 Table 2 WMO 700130 Intercomparison

	Sample	Reported value, mg/l	Mean value, mg/l	Difference, %	Quality norm
SO_4^{2-}	1	1.777	1.932	-8.0	S
	2	2.314	2.518	-8.1	S
	3	3.997	4.373	-8.6	S
NH_4^+	1	0.913	0.957	-4.6	S
	2	0.575	0.614	-6.4	S
	3	0.696	0.801	-13.1	S
NO_3^-	1	2.144	2.334	-8.1	S
	2	1.701	1.849	-8.0	S
	3	2.005	2.174	-7.8	S
Na^+	1	0.407	0.437	-6.9	S
	2	0.384	0.414	-7.2	S
	3	2.135	2.28	-6.4	S
Mg^{2+}	1	0.106	0.129	-17.8	Q
	2	0.089	0.097	-8.2	S
	3	0.218	0.252	-13.5	S
Cl^-	1	0.823	0.879	-6.4	S
	2	0.733	0.779	-5.9	S
	3	3.391	3.658	-7.3	S
Ca^{2+}	1	0.392	0.515	-23.9	Q
	2	0.301	0.34	-11.5	S
	3	0.549	0.621	-11.6	S
K^+	1	0.107	0.12	-10.8	S
	2	0.111	0.126	-11.9	S
	3	0.344	0.394	-12.7	S
pH	1	5.85	5.83	0.020	S
	2	4.64	4.63	0.010	S
	3	4.63	4.6	0.030	S
Cond	1	15.7	16	-1.9	S
	2	21.6	22	-1.8	S
	3	37.5	38.2	-1.8	S

Appendix 3: Diffusion tube intercomparison

CONTENTS

1. Introduction

1.1 Why intercomparison is required

Diffusion tubes without wind protection caps have been used to measure nitrogen dioxide concentrations at rural locations within the United Kingdom since 1993. The nitrogen dioxide concentrations are used to produce the national NO_2 compliance maps in support of the requirements of The Air Quality Standards Regulations, 2010[3]. Whilst it has always been was recognised that these tubes may overread, the nitrogen dioxide concentrations have always been made available without bias adjustment. Since 2020 the rural NO_2 concentrations measured by diffusion tubes have been biased adjusted using the method provided in the Defra's technical guidance document TG22[4].

However, since the introduction of diffusion tubes fitted with wind protection caps into the UK Urban NO_2 Network (UUNN) late in 2020 there has been an interest in using these tubes in the UK Rural NO_2 Network. These tubes have been shown to reduce the positive bias and have a relatively low reported measurement uncertainty.

To understand how diffusion tubes with and without wind protection caps would compare an intercomparison exercise was planned and put in place at the end of 2021. At each of the twenty-four sites in the Rural NO_2 Network, diffusion tubes with wind protection caps were collocated on the heat shield of the rain stand. In addition, the nitrogen dioxide concentrations measured by each set of diffusion tubes are compared with results from the UK's Automatic Urban and Rural Network (AURN) analysers at Chilbolton Observatory, High Muffles and Yarner Wood.

The AURN provides NO2 measurements made by the Standard Reference Method (SRM) defined in EN14221 (2012), using chemiluminescent NOx instruments that have been type-approved and are operated in line with the quality control requirements of the standard.

This report presents the results of the intercomparison from the start of sampling until the end of 2022 however sampling is currently ongoing and funded until June 2023.

The report is structured as follows:

- A review recent literature related to diffusion tube measurement uncertainty
- A short review of the impact of NOz compounds on measured NO_2 concentrations
- A comparison of all nitrogen dioxide concentrations measured by both sets of diffusion tubes
- A comparison of repeatability for both sets of tubes using the coefficient of variation (COV)
- A comparison with NO_2 concentration measured at three locations where the tubes are collocated with the automatic analysers sites.

[3] https://www.legislation.gov.uk/uksi/2010/1001/contents/made

[4] https://laqm.defra.gov.uk/wp-content/uploads/2022/08/LAQM-TG22-August-22-v1.0.pdf

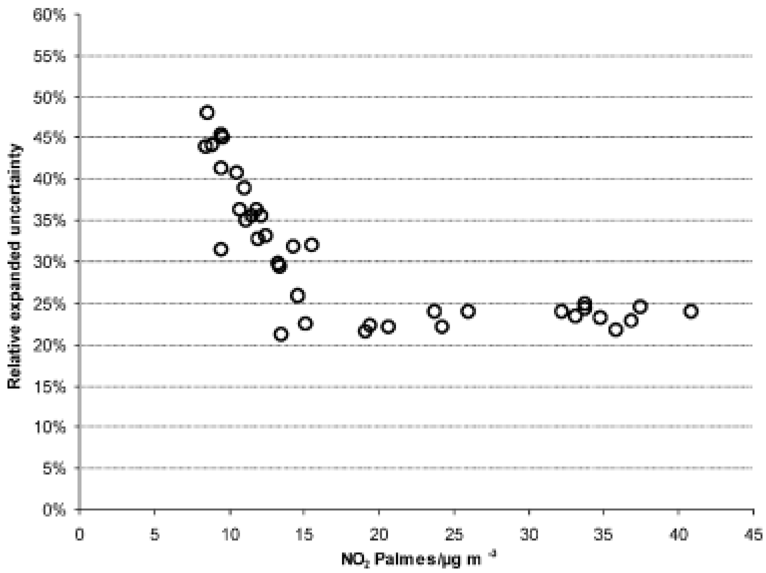
Recommendations to the Environment Agency have been made on the basis of the findings.

1.2 literature review

1.2.1 Diffusion tube measurement uncertainty

Given the widespread use of the diffusion tube as a low-cost sampler there have been many studies over the years[5,6,7] that have aimed to characterise their performance and which environmental factors will impact the accurate determination of concentration most. Buzica *et al*., (2004) ranked wind speed, humidity and temperature, in that order, as the three most important factors influencing the update rate. In fact, their parameterisation of a model to predict update rates based on wind speed fulfilled the 25 % accuracy requirement for 'indicative' NO_2 measurements. They also showed that under laboratory conditions that the relative expanded uncertainty was lower than 25 % when the NO_2 concentration was greater than 16 µg m^{-3} (see Appendix 3 Figure 1). The increase in relatively expanded uncertainty at concentrations less than 16 µg m^{-3} was attributed to the dependency on the uncertainty of the factors affecting uptake rate.

Appendix 3 Figure 1 Relative expanded uncertainty of the NO_2 concentration measured with the open diffusion tube versus the NO_2 concentration. Buzica et al., (2004)



Martin *et al.*, (2014) tested a range of materials to reduce the impact of wind shortening including PTFE and metal meshes, polyethylene filter and two types of woven stainless steel wire cloth. The testing was carried out using a controlled atmospheric test facility

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[5] Buzica, D.,Gerboles, M., Amantini, L., Pérez Ballesta, P. and De Saeger, E. (2005), Modelling of the uptake rate of the nitrogen dioxide Palmes diffusive sampler based on the effect of environmental factors. Journal of Environmental Monitoring 7 169- 174

[6] Martin, N.A, Helmore, J.J., White, S., Ieuan L. Barker Snook, I.L., Parish, A and Gates L.S. (2014). Measurement of nitrogen dioxide diffusive sampling rates for Palmes diffusion tubes using a controlled atmosphere test facility (CATFAC) Atmospheric Environment 94 (2014) 529 - 537

[7] Mathew R. Heal, M.R., Duncan P. H. Laxen, D.P.H and Marner, B.B. (2019). Biases in the Measurement of Ambient Nitrogen Dioxide (NO_2) by Palmes Passive Diffusion Tube: A Review of Current Understanding Atmosphere 2019, 10, 357

(CATFAC). The work concluded that the polyethylene filter provided by Gradko and the two types woven stainless steel wire cloth, provided by ESG (now SOCOTEC) improved the repeatability of measurements and hence the uncertainty. Diffusion tubes ‘capped’ by the polyethylene filters were subsequently chosen for the UK Urban NO_2 Network (UUNN).

A review of the biases impacting the measurement of NO_2 was carried out by Heal *et al.*, 2019. A summary of factors influencing bias is provided in Appendix 3 Table 1.

Appendix 3 Table 1 Potential factors influencing accuracy of quantification of ambient NO_2 by passive diffusion tube (PDT). Heal et al., (2019)

Stage in the Methodology	Origin of Potential Bias	Direction of Potential Bias
PDT preparation	Choice of solvent for application of triethanolamine (TEA) to grids	−(presumed) **a**
	Application of TEA by pipetting or by dipping grids in solution	−(presumed) **a**
	Insufficient TEA applied to grids leading to saturation of the TEA by absorbed NO2 during exposure	−
	Shelf-life of prepared PDT	−
Quantification of absorbed nitrite (NO_2^-)	Failure to extract all absorbed NO_2^- into solution	−
	Ratio and absolute concentrations of the sulphanilamide and N-1-naphthyl ethylene diamine dihydrochloride (NEDD) added to the solution of extracted NO_2^-	−(presumed) **a**
	Pre-mixing or sequential addition of sulphanilamide and NEDD solutions	−(presumed) **a**
	Differential degradation of chromophore intensity because of different times from addition of colour reagent to absorbance measurement between standard and sample solutions	+ or −
The influence of factors during PDT exposure	Ambient nitrous acid (HONO) and peroxyacetyl nitrate (PAN) gases as source of trapped NO_2-	+
	Variability in ambient NO_2 concentrations breaking an assumption in Fick’s first law of diffusion	+
	Non-stoichiometric conversion of NO_2 to extractable NO_2^- ion at the absorbent	−
	Effects of ambient humidity and temperature during exposure	+ or −
	Wind at open end of tube leading to turbulent rather than molecular transport of NO_2 into the first part of the tube	+
	Within-tube chemical reaction ($NO + O_3 \rightarrow NO_2 + O_2$) creating additional NO_2, the rate of which is determined by the ambient concentrations of NO and O3 during exposure	+
	Degradative loss of the absorbed NO_2^- during exposure	−
	Calculation of average ambient NO_2 from the quantified NO_2	−
	Inaccurate value for the diffusion coefficient of NO_2 in air	+ or −
Comparison of PDT NO_2 with chemiluminescence analyser NO_2	Inaccuracy in the chemiluminescence analyser	+ or −
	Not reporting PDT and chemiluminescence analyser NO_2 concentrations to the same pressure and temperature (p,T) reporting conditions	+ or −
	Differential interferences from ambient HONO and PAN between PDT and chemiluminescence analyser measurements	+ or −

a Biases from these sources, if present, are presumed to be negative on the basis that it is not possible for these aspects of PDT preparation and analysis to yield more NO_2^- than is present as NO_2 in the sampled air.

More recently Butterfield *et al.*, (2021)[8] calculated the uncertainty for those diffusion tubes used in the National Bias Adjustment Database[9]. They wanted to check to what extent the diffusion tubes used in Local Authority Review and Assessment (LAQM) could be classified as providing "indicative" measurements. Here indicative is defined as having an uncertainty better than 25 %. Data (both as monthly and annual averages) from a five-year period (2014 to 2019) were examined and the impact of different diffusion tube preparations (either 20 % triethanolamine (TEA) in water or 50 % TEA in acetone) and excluding the busy Marylebone Road site assessed. The method to calculate the equivalence of the different types of diffusion tube measurement to the chemiluminescence analyser was calculated according to the guide to the demonstration of equivalence of ambient air monitoring methods, 2010[10]. The tool used to carry out the equivalence assessment was the Equivalence Tool, Version 3.1[11]

The results are presented in Appendix 3 Table 2 and show:

- The 'as measured' uncertainty for the annual NO_2 concentrations is less than that for the monthly NO_2 concentration
- Excluding the higher concentrations at Marylebone Road significantly reduced the uncertainty
- The 20 % TEA in water recipe also tended to have a lower uncertainty.

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[8] Butterfield, D., Martin, N.A., Coppin, G. and Fryer, D.E., (2021). Equivalence of UK nitrogen dioxide diffusion tube data to the EU reference method. Atmospheric Environment 262 118614

[9] The annual NO_2 concentrations measured by both the diffusion tubes and automatic analysers are available from the Excel workbook *Database_Diffusion_Tube_Bias_Factors_v03_23-FINAL.xlsx* downloadable from https://laqm.defra.gov.uk/air-quality/air-quality-assessment/national-bias/ (Accessed 17/05/2023)

[10] Equivalence Report Jan 2010 (europa.eu) (Accessed 17th May 2023)

[11] This tool was developed by David Harrison of Bureau Veritas for CEN/TC264/WG 15. A version of this tool (Equivalence Tool V3.1 020720.xlsb) will be used in Section 3 to assess the equivalence of both the diffusion tubes with and without wind protection caps.

Appendix 3 Table 2 Uncertainty calculated for diffusion tubes in National bias adjustment database (2015 to 2019)

Diffusion tube recipe/excluding Marylebone Road	Monthly uncertainty compared to reference method, %	Number of data points	Annual uncertainty compared to reference method, %	Number of data points
All tubes	±49.7	9498	±42.1	835
All tubes – Marylebone Road excluded	±36.4	8532	±32.6	757
20% TEA in water – all tubes	±48.3	5048	±39.3	443
50% TEA in acetone – all tubes	±51.3	4450	±45.3	392
20% TEA in water – excluding Marylebone Road	±33.2	4499	±28.8	399
50% TEA in acetone – excluding Marylebone Road	±40.4	4033	±37.4	358

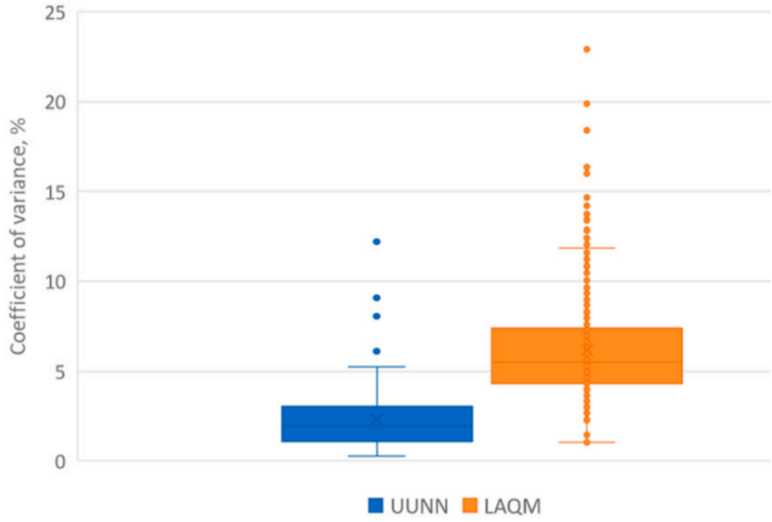
The uncertainties presented in Appendix 3 Table 2 are the 'as measured' uncertainties, that is, those applied without any calibration or bias adjustment. Butterfield *et al.,* (2021) also calculated the uncertainties for calibrated and bias adjusted data and showed that the uncertainties for the annual data are significantly improved and will meet the data quality objective of 25 %.

In addition, Butterfield *et al.,* (2021) calculated the uncertainty for the diffusion tubes used UUNN network in 2020 using the same equivalence method to be ± 13.3 %.

Butterfield *et al.,* (2021) also presented a summary of the coefficient of variance[12] (COV) for the monthly diffusion tubes in the UUNN and those in the National diffusion tube network (LAQM). The average COV for the UUNN and LAQM tubes were calculated to be 2.3 % and 6.2 %, respectively, which they considered as suitable improvement in repeatability to justify the use of the diffusion tubes with caps compared to those with no caps. A box and whisker plot comparing the two data sets is shown in Appendix 3 Figure 2.

[12] Coefficient of variation is calculated for each triplicate set of diffusion tubes by dividing the standard deviation of the NO_2 concentration measured by the three tubes by arithmetic mean of the NO_2 concentrations, expressed as a percentage.

Appendix 3 Figure 2 Spread of COV % for UUNN and conventional LAQM diffusion tubes (Butterfield et al., 2021)



As part of ad-hoc studies to inform decisions regarding affiliation and data validation for the UUNN, BV[13] assessed the impact of storage and calculated the expanded uncertainty of three types of diffusion tubes:

- UUNN – This method represents tubes deployed following the same method as the UUNN. Tubes were sent from the laboratory to the LSO in vials and included an end cap with a filter. The tube was deployed with the end cap (with filter) on. Upon collection the end cap with filter was left on the tube and the tube was placed back into the vial. The tube inside the vial was then sent back to the laboratory for analysis.
- UUNN+ – This method represented an approach similar to the UUNN, but replacing the end cap following collection. Tubes were sent from the laboratory to the LSO in vials and included an end cap with a filter. The tube was deployed with the end cap (with filter) on. Upon collection the end cap with filter was replaced with a sealed rubber end cap. Following this the tube was not placed back in the vial. The tube was then sent back to the laboratory for analysis.
- LAQM – This method represented tubes deployed following the same methodology as LAQM tubes currently are. Tubes were sent from the laboratory to the LSO, not in vials, but included a sealed end cap (without a filter). The tube was deployed without the sealed end cap. Upon collection the sealed end cap (without a filter) was replaced. The tube was then sent back to the laboratory for analysis.

Tubes were exposed at four locations (Stoke, Birmingham, Marylebone Road and St Helens) for two sampling periods (August and September 2021) and stored for three different sampling periods (5, 19 and 39 days). Due to vandalism and low data capture, there were 18 samples in the dataset. The uncertainties are presented in Appendix 3

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[13] Bureau Veritas (2021). UK Urban NO2 Network - Diffusion Tube Ad-hoc Studies. Work Package 5 Report December 2021

Table 3 and show that replaced the filter cap with a sealed cap after sampling significantly improves the measurement uncertainty. The uncertainty for the LAQM tubes is much greater than that presented above in Appendix 3 Table 2 and may reflect the impact of increased storage time on uncertainty.

Appendix 3 Table 3 Equivalence analysis of three different tube types (BV, 2021)

Tube Type	n	Expanded uncertainty (no correction)	Slope	Intercept
UUNN	18	13.2 %	0.91	5.5
UUNN+	18	8.6 %	0.92	4.1
LAQM	18	76.3 %	1.44	-2.5

1.2.2 Impact of other nitrogen/oxygen compounds measured in rural locations using chemiluminescence analysers

It has long been recognised[14] that using a conventional chemiluminescent is likely to overestimate the NO_2 concentrations due to the oxidation of total reactive nitrogen, NOy, (sum of NOx, nitrous acid, nitric acid, organic nitrates and peroxyacetyl nitrate) and where NOz = NOy – NOx.

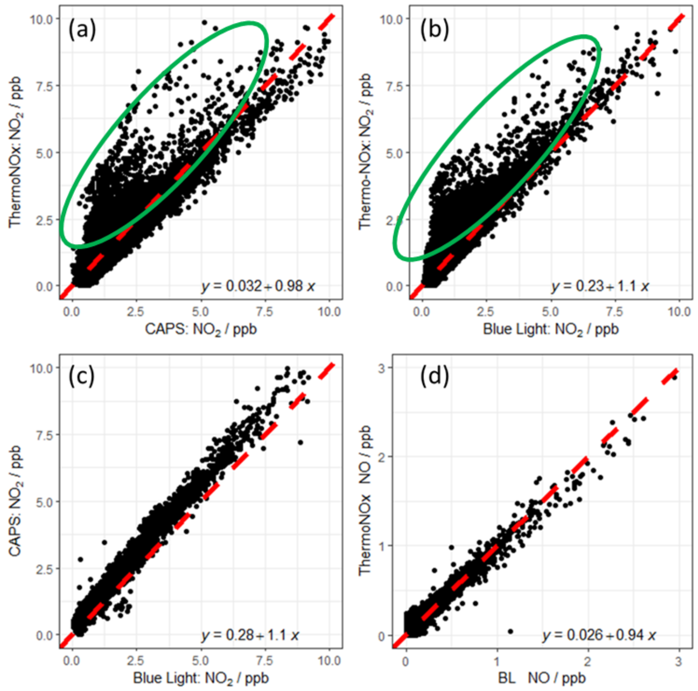
There are a number of analysers that measure NO_2 directly, but they are not deployed in significant numbers in national UK monitoring networks. UKCEH have been running an intercomparison of different NO_2 analysers since 2019. These include:

- Thermo 42c; Chemiluminescent; Molybdenum Conversion; detection limit 0.4 ppb
- Teledyne CAPS T200U; UV Absorption Spectroscopy (CAPS); detection limit 0.05 ppb
- Teledyne T200P; Chemiluminescent: Photolytic Conversion (Blue Light); detection limit 0.1 ppb

The top two panels in Appendix 3 Figure 3 compares the NO_2 concentration measured by the Thermo 32 vs the CAPS and Blue light respectively. The green shape highlights the apparent excess NO_2 measured by the Thermo 32. The lower left panel shows a relatively linear relationship for both samplers that measure NO_2 directly.

[14] USEAP (2013) https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=280753&Lab=NERL Direct and Indirect Methods for the Measurement of Ambient Nitrogen Dioxide Extended Abstract # 57

Appendix 3 Figure 3 A comparison of hourly NO_2 and NO concentrations measured by Thermo 42, CAPS and Blue Light instruments. (Nick Cowen et al., 2024)[15]



Quantification of the contribution of NOy to excess NO_2 has been quantified by various researchers. For example. Dunlea *et al*.[16], undertook a study in Mexico City, comparing a chemiluminescence NOx analyser with a tuneable laser diode analyser and an Opsis-type open path spectrometer. They found that, during some afternoons, NOz concentrations could contribute up half of the reported NO_2 by the chemiluminescence analyser, driven mostly by HNO_3 interference. For one specific period, this was as much as 20ppb. Ge et al.[17], undertook a study in Beijing with chemiluminescence and Cavity Attenuated Phase Shift (CAPS) analysers. They found that the CL analyser could overestimate NO_2 concentrations by up to 20%, regularly as much as 10ppb. They found a significant diurnal profile in NOz concentrations, peaking at 15ppb in the early afternoon.

Adams, T in a PhD research study carried out at the University of Leicester in 2014 compared the NO_2 measured by the chemiluminescence analyser at the AURN site (urban background) with a collocated highly sensitive spectroscopic technique of broadband cavity enhanced absorption spectroscopy (BBCEAS). This technique uses a high finesse optical cavity to make absorption measurements over extended path lengths within a compact instrument and over wavelength ranges that are sufficiently broad to enable several overlapping absorbers to be quantified simultaneously. Appendix 3 Figure 4 compares the 15-minute NO_2 concentrations over a single day (13th March 2014). The

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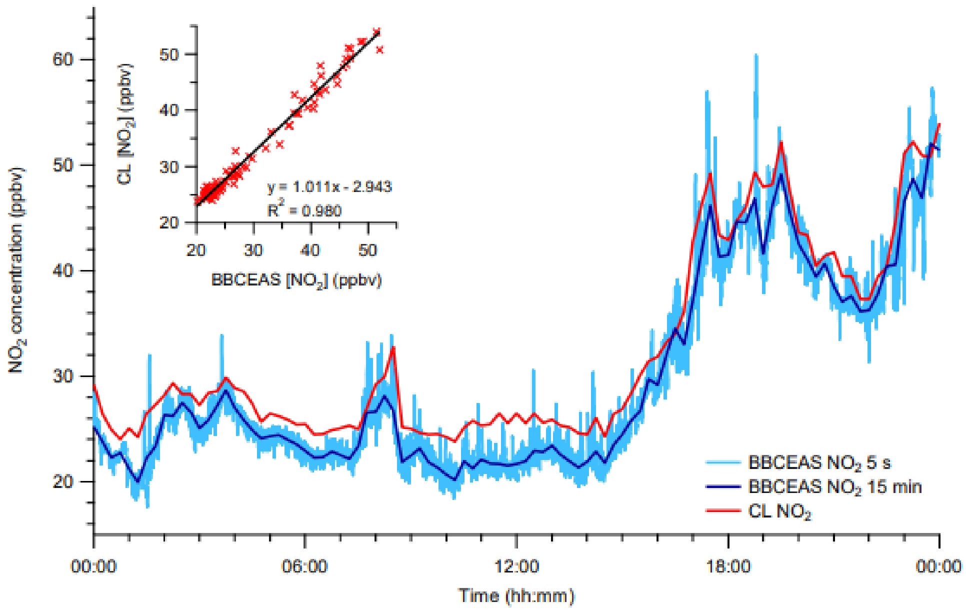
[15] Cowan, N, Twigg, M.M., Leeson, S.R., Jones, M.R., Harvey, D. Ivan Simmons, I. Coyle, M., Kentisbeer J., Walker, H., and Braban, C. F. Assessing the bias of molybdenum catalytic conversion in the measurement of NO2 in rural air quality networks Atmospheric Environment 322 (2024) 120375

[16] (Atmos. Chem. Phys., 7, 2691–2704, 2007)

[17] (https://doi.org/10.1002/jgrd.50757)

enhancement of NO_2 is variable in the range of about 0 to 4 ppb with the enhancement peaking about midday.

Appendix 3 Figure 4 BBCEAS and CL NO_2 concentration time series obtained on 13-03-2014 showing the interpolation of BBCEAS 5 s data onto a common 15 min time resolution provided by the CL instrument and the subsequent statistical comparison (inset). Adams, T. PhD thesis.



1.3 Implementation

In late 2021 guidance for the site operators was prepared and provided to each of the UKEAP local site operators. The guidance provided information on how to install and deploy the additional set of tubes.

At most sites sampling began sometime during the week beginning Monday 6th December 2021 and all sites, with the exception of Bannisdale Beck, started by Thursday 16th December. Bannisdale Beck started sampling 4th January 2022. In February 2022 the sampling protocol was updated so that the wind protection cap was replaced by a sealed cap upon collection (UUNN+ tubes).

Due to the incorrect deployment of the tubes with the wind protection caps at Flatford Mill there were no valid data collected in 2022.

1.4 Diffusion tube suppliers

Diffusion tubes were supplied by the existing suppliers for the Rural NO_2 and Enhanced Urban NO_2 Network.

These together with the absorbents and detection limits are presented in Appendix 3 Table 4.

Appendix 3 Table 4 Diffusion tube suppliers, absorbent and detection limits

Tube type	Analyst	Absorbent	Detection limit, per mesh, µg	Detection limit, mass concentration, µg m^{-3}
No Wind Protection Cap	Socotec	50 % triethanolamine and acetone	0.03	0.5 to 0.9
Wind Protection Cap	Gradko	20 % triethanolamine and water		

Each diffusion tube supplier takes part in a proficiency test[18]. This is an independent analytical proficiency-testing scheme, operated by LGC Standards and supported by the Health and Safety Laboratory (HSL). Defra and the Devolved Administrations advise that diffusion tubes used for LAQM should be obtained from laboratories that have demonstrated satisfactory performance in the AIR NO_2 PT scheme.

The analytical laboratory performance for each lab is summarised in Appendix 3 Table 5 for a period just before and for two periods in 2022. All results were considered satisfactory (based on z-scores less than or equal to 2).

Appendix 3 Table 5 Scores for recent AIR NO_2 PT rounds

AIR PT Round	AIR PT46	AIR PT49	AIR PT50
Round conducted in the period	Sep – Oct 2021	Jan – Feb 2022	May – Jun 2022
Socotec UK Limited	100	100	100
Gradko	100	100	100

[18] https://laqm.defra.gov.uk/wp-content/uploads/2022/07/LAQM-NO2-Performance-data_Up-to-June-2022_V2.1.pdf

2. Results

2.1 Nitrogen dioxide concentrations measured by each type of diffusion tubes

Altogether over the period December 2021 to December 2022 there were approximately 330 scheduled sampling periods. The arithmetic mean NO_2 concentration were calculated for each set of triplicates which then were in turn averaged for the whole data set. The statistical summary is presented in Appendix 3 Table 6. All individual sample concentrations are presented in Appendix 3 I with a graphical presentation in Appendix 3 II.

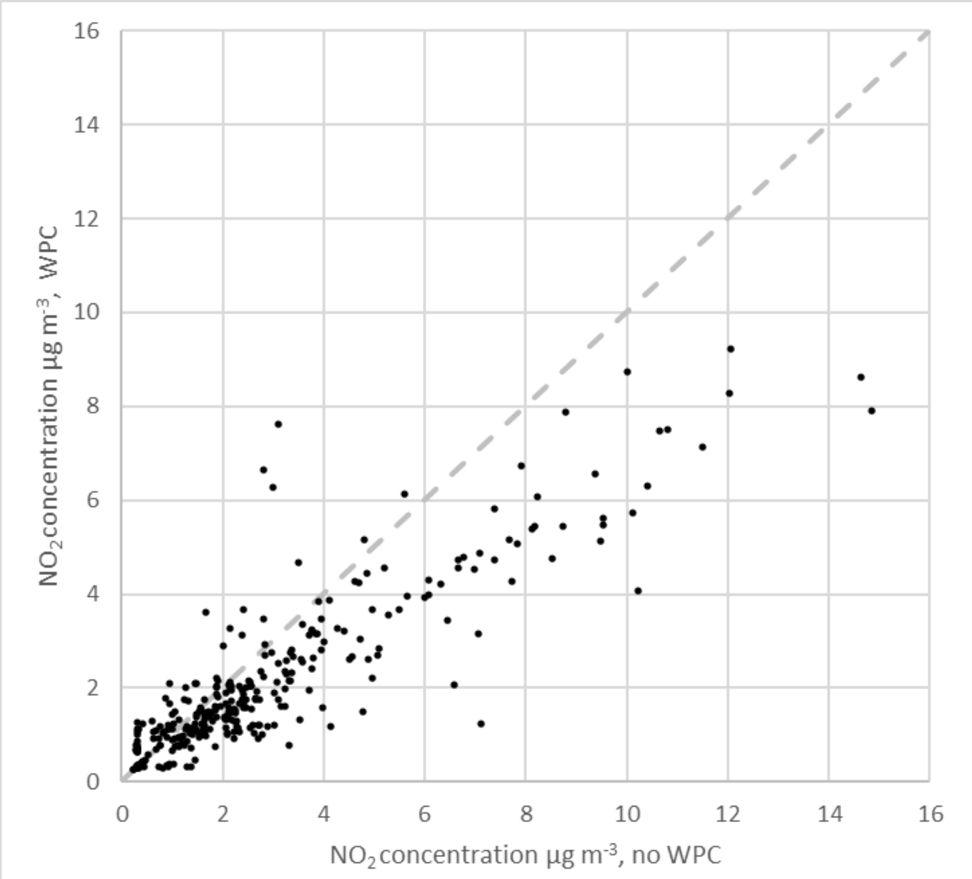
As expected, the diffusion tubes with no wind protection cap measured higher NO_2 concentration than those with no caps. On average the diffusion tubes with no caps are measuring about 0.9 µg m^{-3} more NO_2 than those tubes with the wind protection caps.

Appendix 3 Table 6 Summary statistics for nitrogen dioxide over sampling period from December 2021 to December 2022

Statistic	No wind protection cap	With wind protection cap
Arithmetic mean NO_2 concentration, µg m^{-3}	3.11	2.18
Standard deviation, µg m^{-3}	2.82	1.79
Count	323	308
R^2	0.904	

When plotted on an individual sampling period basis (Appendix 3 Figure 5), some variation can be seen but in the main the tubes with no caps are measuring higher. The R^2 value was 0.904 indicating reasonable agreement between each set of results.

Appendix 3 Figure 5 Measured nitrogen dioxide concentrations by each type of diffusion tube



2.2 coefficient of variance (COV)

In addition to calculating the arithmetic mean for each set of triplicate tubes, the coefficient of variance[19] was also obtained. This provides a useful estimate of the performance of each type of tube in terms of the sampler's precision. To make the comparison, the COV for each type of tube were then sorted into bins of 5 % intervals (< 5, 5 to 10, 10 to 15 etc). Appendix 3 Table 7 compares the ranges for both sets of tubes. The precision of the WPC tubes can be seen to be significantly more precise than the tubes with no WPC. For samples, 70 % of the WPC tubes have a precision better than 5 %, whereas as for the tubes with no WPC this is only 33 %. If an acceptability criterion of tube was set to a precision of 20%, then only 4 % of the WPC tubes would fail this criterion compared to 19 % of the no WPC tubes.

[19] Coefficient of variation is calculated as the standard deviation divided by arithmetic mean, expressed as a percentage.

Appendix 3 Table 7 Coefficient of variance measured for tubes without and with wind protector caps

Coefficient of variance, %	No wind protector cap	With wind protector cap	No wind protector cap, %	With wind protector cap, %
< 5	107	215	33	70
5 - 10	76	58	24	19
10 - 15	51	13	16	4
15 - 20	27	9	8	3
20 - 25	20	4	6	1
25 - 30	14	1	4	0
30 - 35	6	1	2	0
35 - 40	5	3	2	1
40 - 45	4	1	1	0
45 - 50	3	1	1	0
> 50	9	1	3	0

3. Comparison with AURN Instruments

At Chilbolton Observatory, High Muffles, and Yarner Wood the diffusion tubes are collocated with AURN chemiluminescent NOx instruments which are measuring NO2 in compliance with the Standard Reference Method (SRM) defined in EN14221 (2012).

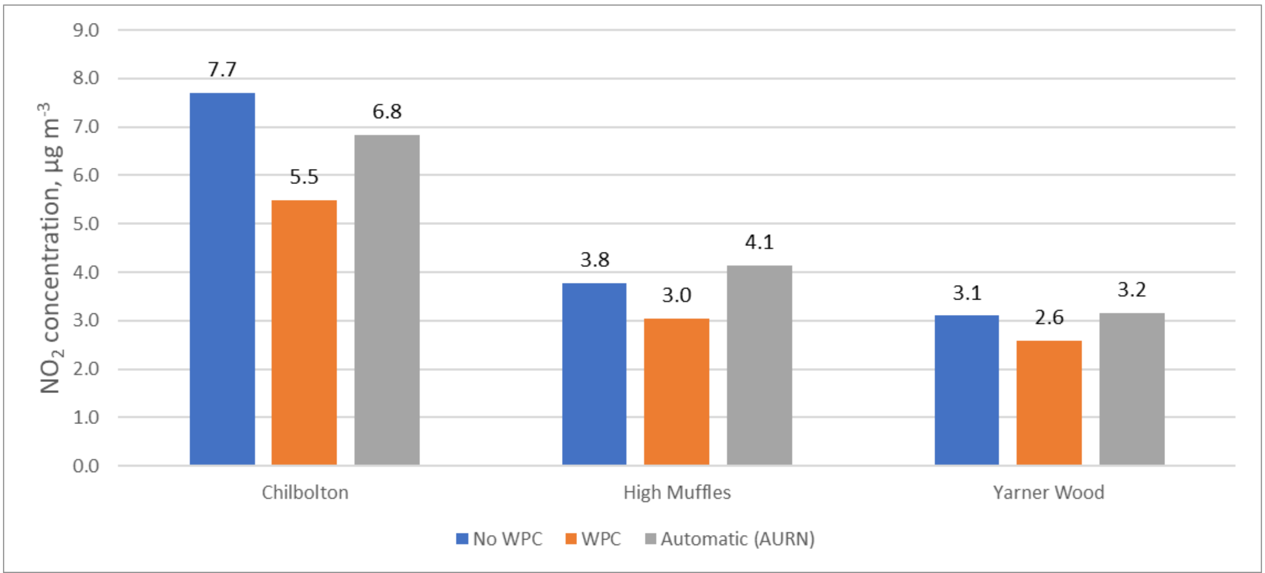
The annual mean concentrations for 2022 are presented in Appendix 3 Figure 6. The highest NO_2 concentration is measured at Chilbolton, then High Muffles, then Yarner Wood.

At Chilbolton the diffusion tubes with no WPC measured the highest concentration (7.7 µg m^{-3}) followed by the automatic analyser (6.8 µg m^{-3}) then the diffusion tube WPC (5.5 µg m^{-3}).

At High Muffles, the automatic analyser measured the highest concentration (4.1 µg m^{-3}) followed by the diffusion tube no WPC (3.8 µg m^{-3}) then the diffusion tube WPC (3.0 µg m^{-3}).

Likewise, at Yarner Wood, the automatic analyser measured the highest concentration (3.2 µg m^{-3}) followed by the diffusion tube no WPC (3.1 µg m^{-3}) then the diffusion tube WPC (2.6 µg m^{-3}).

Appendix 3 Figure 6 Annual mean concentrations measured by each sampler at Chilbolton, High Muffles and Yarner Wood

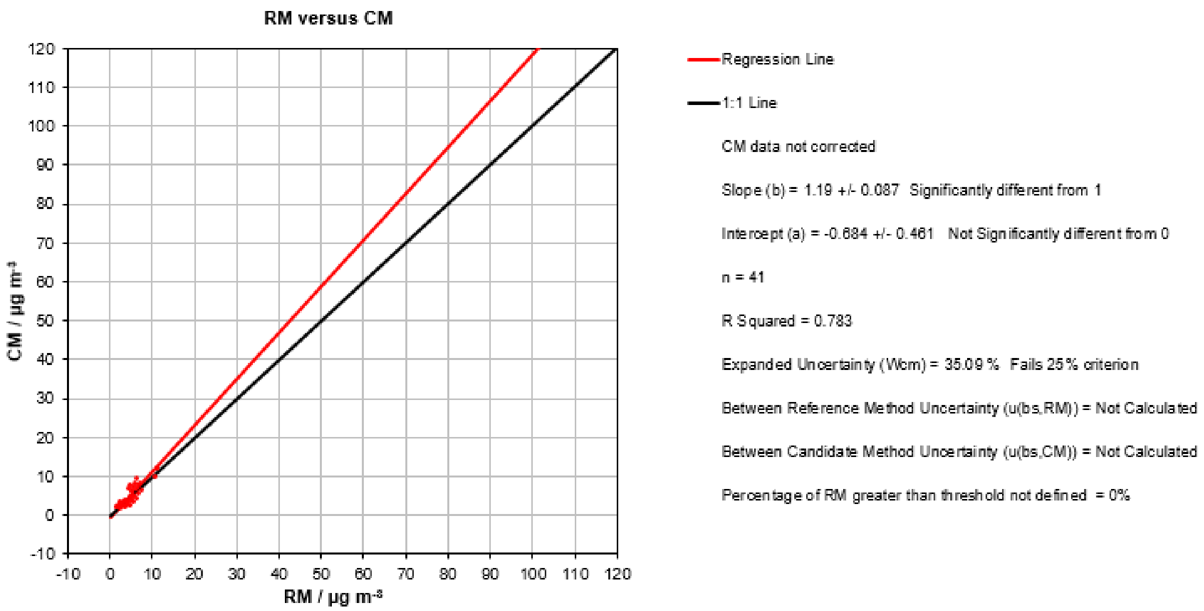


While it is assumed that the diffusion tubes with no wind protection cap measures higher NO_2 concentration than the diffusion tube with a wind protection cap, it was less expected that the automatic analyser measured the highest concentration at High Muffles and Yarner Wood. Reasons for this may be that the chemiluminescence analyser is measuring close to its detection limit (each site has an API 200 analyser with a detection limit of 2.3 µg m^{-3}) and the measurement is hence very uncertain and/or it may be measuring an unknown amount of NOy species.

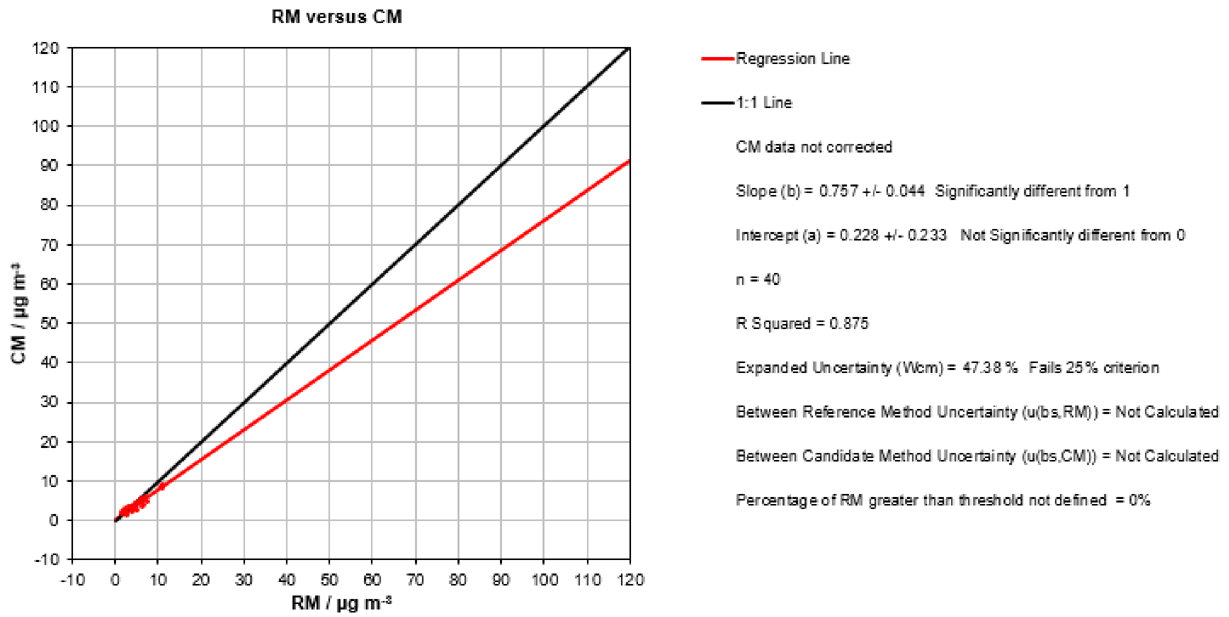
The equivalence tool employed in the UUNN and discussed in Section 1.2.1 was used to estimate the expanded uncertainty. The chemiluminescence analyser was assumed to be reference method and respective diffusion tubes the candidate methods. The monthly concentrations at the three sites were combined to give a total of about 40 measurement pairs. Appendix 3 Figure 7 shows the chemiluminescence vs the diffusion tubes no wind protection cap. The expanded uncertainty was calculated to be 35%.

Appendix 3 Figure 8 shows the chemiluminescence vs the diffusion tubes with wind protection cap. The expanded uncertainty was calculated to be 47 %. That the uncertainty for the diffusion tubes with a wind protection cap is higher than that for the diffusion tubes with no wind protection cap wasn't expected. This may because the equivalence tool is not configured to work at such low concentrations. Further work would be needed to understand why this occurred.

Appendix 3 Figure 7 Scatter plot with equivalence calculations, AURN (Reference Method, RM) vs diffusion tube no WPC (Candidate Method, CM)



Appendix 3 Figure 8 Scatter plot with equivalence calculations, AURN (Reference Method, RM) vs diffusion tube WPC (Candidate Method, CM)



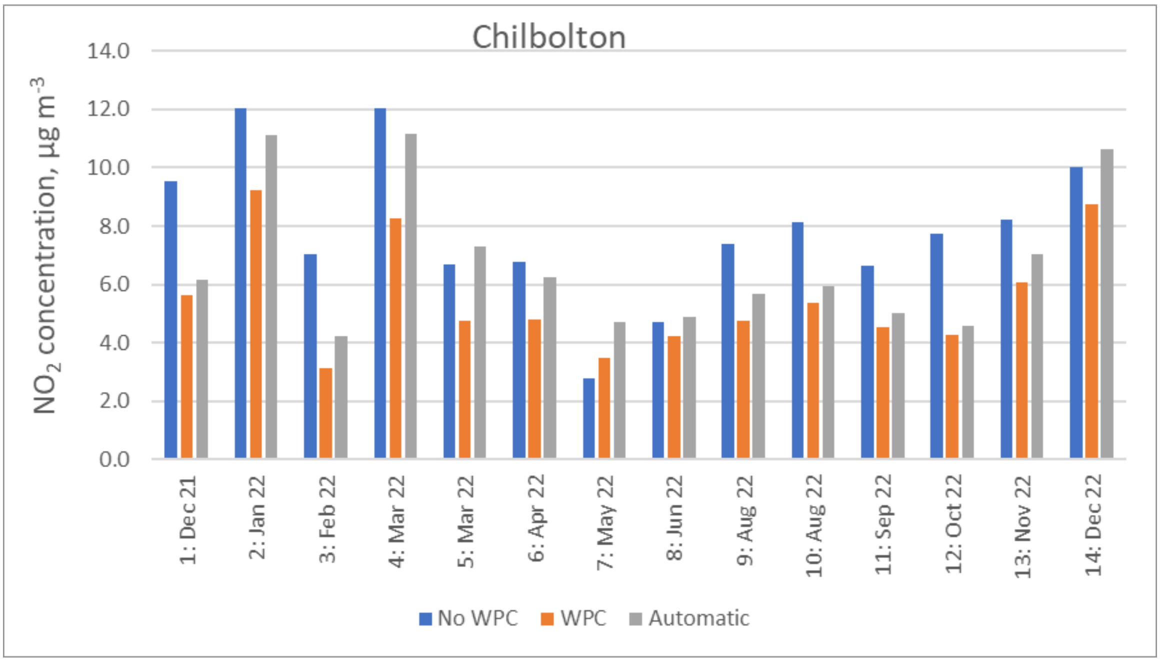
3.1 Chilbolton

The NO_2 concentrations measured at Chilbolton are presented in Appendix 3 Table 8 and displayed graphically in Appendix 3 Figure 9. All samplers tend to show a minimum NO_2 concentration in the summer months. As shown in the annual average concentrations the diffusion tubes with no wind protection caps measured the highest concentration.

Appendix 3 Table 8 Nitrogen dioxide concentration measured by each sampler at Chilbolton

Start date	End date	NO_2 concentration, µg m^{-3} No WPC	NO_2 concentration, µg m^{-3} WPC	NO_2 concentration, µg m^{-3} Automatic
08/12/2021	05/01/2022	9.5	5.6	6.1
05/01/2022	02/02/2022	12.1	9.2	11.1
02/02/2022	02/03/2022	7.1	3.2	4.2
02/03/2022	30/03/2022	12.0	8.3	11.2
30/03/2022	27/04/2022	6.7	4.7	7.3
27/04/2022	25/05/2022	6.8	4.8	6.2
25/05/2022	22/06/2022	2.8	3.5	4.7
22/06/2022	20/07/2022	4.7	4.2	4.9
20/07/2022	17/08/2022	7.4	4.7	5.7
17/08/2022	14/09/2022	8.1	5.4	6.0
14/09/2022	12/10/2022	6.7	4.6	5.0
12/10/2022	09/11/2022	7.7	4.3	4.6
09/11/2022	07/12/2022	8.2	6.1	7.0
07/12/2022	04/01/2023	10.0	8.7	10.6

Appendix 3 Figure 9 Graphical presentation of NO_2 measured by each sampler at Chilbolton



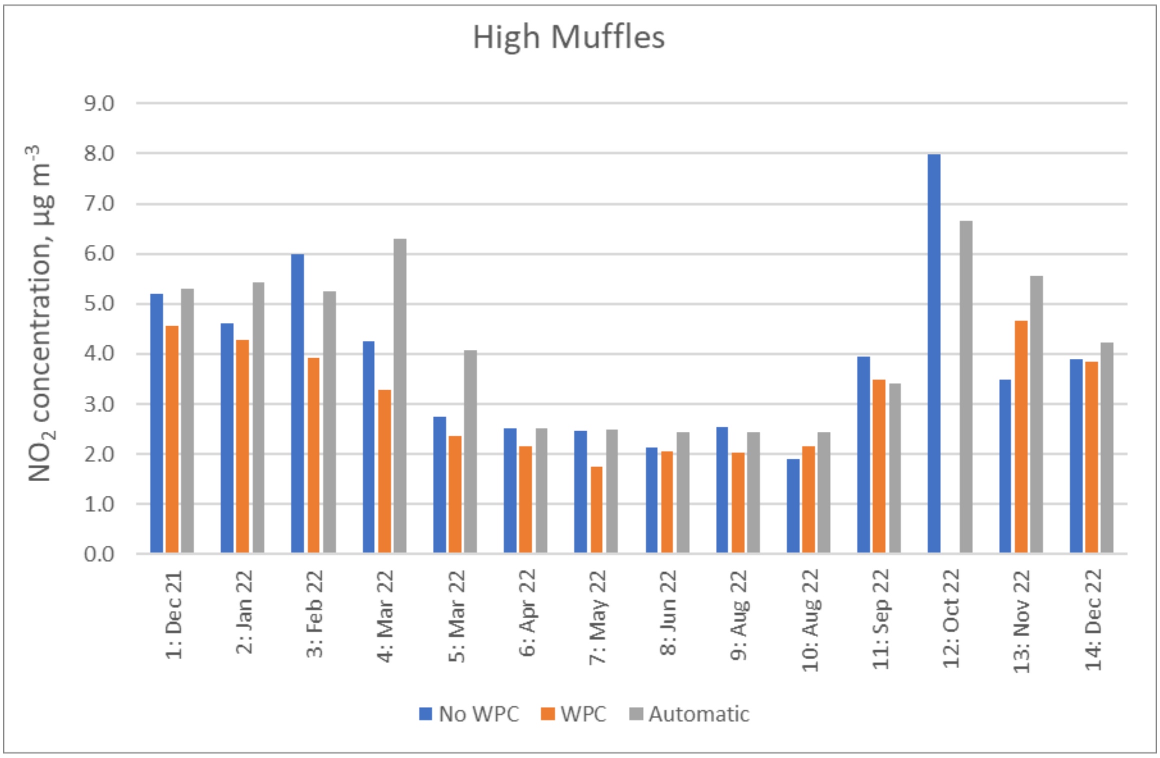
3.2 High Muffles

The NO_2 concentrations measured at High Muffles are presented in Appendix 3 Table 9 and displayed graphically in Appendix 3 Figure 10. All samplers tend to show a minimum NO_2 concentration in the summer months. As shown in the annual average concentrations the automatic analyser typically measured the highest concentration.

Appendix 3 Table 9 Nitrogen dioxide concentration measured by each sampler at High Muffles

Start date	End date	NO_2 concentration, µg m^{-3} No WPC	NO_2 concentration, µg m^{-3} WPC	NO_2 concentration, µg m^{-3} Automatic
15/12/2021	12/01/2022	5.2	4.6	5.3
12/01/2022	09/02/2022	4.6	4.3	5.4
09/02/2022	09/03/2022	6.0	3.9	5.3
09/03/2022	06/04/2022	4.3	3.3	6.3
06/04/2022	04/05/2022	2.8	2.4	4.1
04/05/2022	01/06/2022	2.5	2.2	2.5
01/06/2022	29/06/2022	2.5	1.8	2.5
29/06/2022	27/07/2022	2.1	2.1	2.4
27/07/2022	24/08/2022	2.5	2.0	2.4
24/08/2022	21/09/2022	1.9	2.1	2.4
21/09/2022	19/10/2022	4.0	3.5	3.4
19/10/2022	16/11/2022	8.0		6.7
16/11/2022	18/12/2022	3.5	4.7	5.6
18/12/2022	11/01/2023	3.9	3.8	4.2

Appendix 3 Figure 10 Graphical presentation of NO_2 measured by each sampler at High Muffles



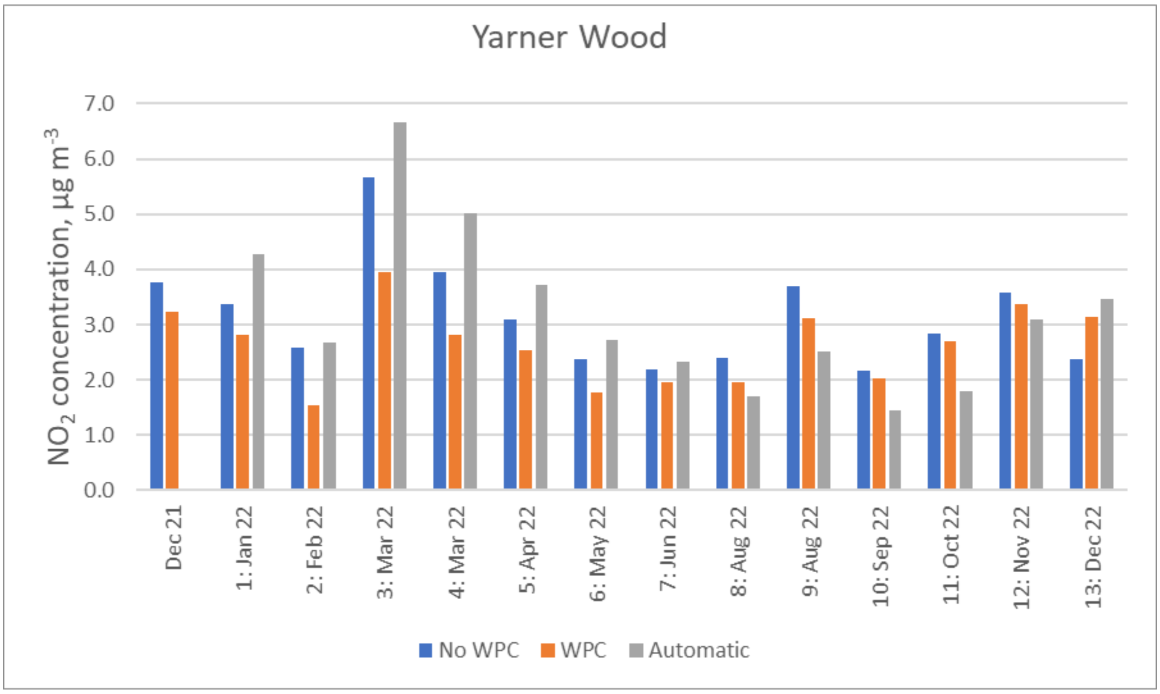
3.3 Yarner Wood

The NO_2 concentrations measured at High Muffles are presented in Appendix 3 Table 10 and displayed graphically in Appendix 3 Figure 11. All samplers tend to show a minimum NO_2 concentration in the summer months. However, for the first eight sampling periods the highest concentration was measured by the automatic analyser, for the remaining periods of the year the diffusion tubes with no WPC measured the highest NO_2 concentration.

Appendix 3 Table 10 Nitrogen dioxide concentration measured by each sampler at Yarner Wood

Start date	End date	NO_2 concentration, µg m^{-3} No WPC	NO_2 concentration, µg m^{-3} WPC	NO_2 concentration, µg m^{-3} Automatic
08/12/2021	05/01/2022	3.8	3.2	
05/01/2022	02/02/2022	3.4	2.8	4.3
02/02/2022	02/03/2022	2.6	1.5	2.7
02/03/2022	30/03/2022	5.7	4.0	6.7
30/03/2022	27/04/2022	4.0	2.8	5.0
27/04/2022	25/05/2022	3.1	2.5	3.7
25/05/2022	22/06/2022	2.4	1.8	2.7
22/06/2022	20/07/2022	2.2	2.0	2.3
20/07/2022	17/08/2022	2.4	2.0	1.7
17/08/2022	14/09/2022	3.7	3.1	2.5
14/09/2022	19/10/2022	2.2	2.0	1.5
19/10/2022	09/11/2022	2.8	2.7	1.8
09/11/2022	07/12/2022	3.6	3.4	3.1
07/12/2022	04/01/2023	2.4	3.1	3.5

Appendix 3 Figure 11 Graphical presentation of NO_2 measured by each sampler at Yarner Wood



APPENDICES 3 I AND 3 II

APPENDIX 3 I DIFFUSION TUBE NO_2 CONCENTRATIONS

APPENDIX 3 II PLOTS OF NO_2 CONCENTRATIONS FOR DIFFUSION TUBES WITH & WITHOUT WPC

APPENDIX I DIFFUSION TUBE NO_2 CONCENTRATIONS

Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Eskdalemuir	05-Dec-21	05-Jan-22	1.3	1.7	1	1	11.7	5.2
Eskdalemuir	05-Jan-22	02-Feb-22	1.9	1.5	1	1	10.4	5.2
Eskdalemuir	02-Feb-22	02-Mar-22	2.3	1.1	1	1	4.9	1.2
Eskdalemuir	02-Mar-22	30-Mar-22	3.2	2.0	1	1	8.8	1.7
Eskdalemuir	30-Mar-22	27-Apr-22	1.3	1.2	1	1	29.7	4.3
Eskdalemuir	27-Apr-22	30-May-22	1.2	0.9	1	1	13.5	3.5
Eskdalemuir	30-May-22	22-Jun-22	1.1	1.0	1	1	13.5	4.3
Eskdalemuir	22-Jun-22	03-Aug-22	1.6	1.0	1	1	25.4	5.2
Eskdalemuir	03-Aug-22	17-Aug-22	1.6	1.3	1	1	27.4	0
Eskdalemuir	17-Aug-22	14-Sep-22	0.8	1.2	1	1	16.9	2.9
Eskdalemuir	14-Sep-22	12-Oct-22	1.4	1.1	1	1	17.2	7.5
Eskdalemuir	12-Oct-22	09-Nov-22	2.2	1.3	1	1	5.1	3.9
Eskdalemuir	09-Nov-22	07-Dec-22	1.8	1.6	1	1	58.7	19.3
Eskdalemuir	07-Dec-22	04-Jan-23	1.1	1.3	1	1	33.2	6.3
Goonhilly	10-Dec-21	07-Jan-22	4.6	2.7	1	1	5.9	2.6
Goonhilly	07-Jan-22	03-Feb-22	3.4	2.7	1	1	9.7	3.5
Goonhilly	03-Feb-22	08-Mar-22	3.1	7.6	1	1	3.4	14.2
Goonhilly	08-Mar-22	03-Apr-22	6.5	3.4	1	1	1.4	2.7
Goonhilly	03-Apr-22	03-May-22	4.8	5.2	1	1	7.1	35.7
Goonhilly	03-May-22	27-May-22	3.6	2.6	1	1	14.8	1.6
Goonhilly	27-May-22	22-Jun-22	3.2	1.6	1	1	3.3	6.1
Goonhilly	22-Jun-22	25-Jul-22	3.3	2.3	1	1	2.8	1.3
Goonhilly	25-Jul-22	18-Aug-22	3.1	2.1	1	1	3.8	2.2
Goonhilly	18-Aug-22	14-Sep-22	3.8	2.6	1	1	4.7	0.9
Goonhilly	14-Sep-22	13-Oct-22	2.5	2.1	1	1	2.5	1
Goonhilly	13-Oct-22	14-Nov-22	5.1	2.7	1	1	7	4.2
Goonhilly	14-Nov-22	07-Dec-22	1.9	2.2	1	1	59.4	3.7
Goonhilly	07-Dec-22	14-Jan-23	2.4	1.9	1	1	22.6	2.6
Lough Navar	06-Dec-21	03-Jan-22	1.9	2.0	1	1	11.2	3.8
Lough Navar	03-Jan-22	31-Jan-22	1.9	1.9	1	1	10.8	2.4
Lough Navar	31-Jan-22	28-Feb-22	1.6	1.0	1	1	17.2	1.3
Lough Navar	28-Feb-22	28-Mar-22	2.8	2.3	1	1	3.5	2
Lough Navar	28-Mar-22	25-Apr-22	1.5	1.5	1	1	11.5	6.5
Lough Navar	25-Apr-22	30-May-22	0.8	1.1	1	1	20.7	6.5
Lough Navar	30-May-22	20-Jun-22	1.1	0.9	1	1	22.9	3.7
Lough Navar	20-Jun-22	18-Jul-22	0.3	0.8	3	1	0.6	3.3
Lough Navar	18-Jul-22	15-Aug-22	1.2	1.0	1	1	7.8	11.4
Lough Navar	15-Aug-22	18-Sep-22	0.6	1.3	1	1	6.7	4.6
Lough Navar	18-Sep-22	10-Oct-22	0.4	1.2	3	1	0	3.5

Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Lough Navar	10-Oct-22	07-Nov-22	1.9	1.4	1	1	42.5	12.6
Lough Navar	07-Nov-22	05-Dec-22	1.5	2.1	1	1	7.8	1.6
Lough Navar	05-Dec-22	02-Jan-23	1.0	2.1	1	1	35.9	2.5
Yarner Wood	08-Dec-21	05-Jan-22	3.8	3.2	1	1	0.9	4.4
Yarner Wood	05-Jan-22	02-Feb-22	3.4	2.8	1	1	4.2	1.5
Yarner Wood	02-Feb-22	02-Mar-22	2.6	1.6	1	1	9.8	13.3
Yarner Wood	02-Mar-22	30-Mar-22	5.7	4.0	1	1	8.8	2.6
Yarner Wood	30-Mar-22	27-Apr-22	4.0	2.8	1	1	0.7	3
Yarner Wood	27-Apr-22	25-May-22	3.1	2.5	1	1	9.2	5.8
Yarner Wood	25-May-22	22-Jun-22	2.4	1.8	1	1	6.7	3.8
Yarner Wood	22-Jun-22	20-Jul-22	2.2	2.0	1	1	1.2	1.3
Yarner Wood	20-Jul-22	17-Aug-22	2.4	2.0	1	1	6.4	8.7
Yarner Wood	17-Aug-22	14-Sep-22	3.7	3.1	1	1	14.6	6.2
Yarner Wood	14-Sep-22	19-Oct-22	2.2	2.0	1	1	5.5	0.5
Yarner Wood	19-Oct-22	09-Nov-22	2.8	2.7	1	1	0.5	1.9
Yarner Wood	09-Nov-22	07-Dec-22	3.6	3.4	1	1	26.6	0.4
Yarner Wood	07-Dec-22	04-Jan-23	2.4	3.1	1	1	32.7	3.1
High Muffles	15-Dec-21	12-Jan-22	5.2	4.6	1	1	15.6	2
High Muffles	12-Jan-22	09-Feb-22	4.6	4.3	1	1	10.5	2.7
High Muffles	09-Feb-22	09-Mar-22	6.0	3.9	1	1	9.3	0.9
High Muffles	09-Mar-22	06-Apr-22	4.3	3.3	1	1	8.3	0.7
High Muffles	06-Apr-22	04-May-22	2.8	2.4	1	1	4.1	7.9
High Muffles	04-May-22	01-Jun-22	2.5	2.2	1	1	1.1	9.9
High Muffles	01-Jun-22	29-Jun-22	2.5	1.8	1	1	3.2	1.5
High Muffles	29-Jun-22	27-Jul-22	2.1	2.1	1	1	21.4	12.6
High Muffles	27-Jul-22	24-Aug-22	2.5	2.0	1	1	0.4	4.8
High Muffles	24-Aug-22	21-Sep-22	1.9	2.1	1	1	4.5	1.2
High Muffles	21-Sep-22	19-Oct-22	4.0	3.5	1	1	7.4	6.5
High Muffles	19-Oct-22	16-Nov-22	8.0	-999.0	1	-1	0.8	0
High Muffles	16-Nov-22	18-Dec-22	3.5	4.7	1	1	69.2	1.1
High Muffles	18-Dec-22	11-Jan-23	3.9	3.8	1	1	4.1	9.3
Strathvaich	10-Dec-21	29-Dec-21	0.5	0.5	3	3	0	0
Strathvaich	29-Dec-21	04-Feb-22	0.2	0.3	3	3	0	0
Strathvaich	04-Feb-22	26-Feb-22	0.4	0.4	3	3	0	0
Strathvaich	26-Feb-22	05-Apr-22	0.9	1.1	1	1	2.2	15.9
Strathvaich	05-Apr-22	06-May-22	0.3	0.7	3	1	0	1.7
Strathvaich	06-May-22	29-May-22	0.4	0.4	3	3	0	0
Strathvaich	29-May-22	29-Jun-22	0.3	0.7	3	1	0	2.9
Strathvaich	29-Jun-22	05-Aug-22	0.2	0.3	3	3	0	5.4
Strathvaich	05-Aug-22	26-Aug-22	0.4	0.4	3	3	0	0
Strathvaich	26-Aug-22	12-Sep-22	0.5	0.6	3	3	0	0

Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Strathvaich	12-Sep-22	12-Oct-22	0.3	0.3	3	3	0	0
Strathvaich	12-Oct-22	02-Nov-22	0.4	0.4	3	3	3.8	5.1
Strathvaich	02-Nov-22	06-Dec-22	0.6	0.9	1	1	7.9	2
Strathvaich	06-Dec-22	06-Jan-23	0.3	0.3	3	3	0	0
Flatford Mill	09-Dec-21	24-Jan-22	0.8	0.6	-1	-1	44.1	#N/A
Flatford Mill	24-Jan-22	03-Feb-22	10.5	3.1	1	-1	40.2	#N/A
Flatford Mill	03-Feb-22	05-Mar-22	12.6	0.3	1	-1	2.5	#N/A
Flatford Mill	05-Mar-22	29-Mar-22	11.6	0.4	1	-1	3.8	#N/A
Flatford Mill	29-Mar-22	26-Apr-22	7.8	0.4	1	-1	3.9	#N/A
Flatford Mill	26-Apr-22	22-Jun-22	4.7	0.7	-1	-1	2.8	#N/A
Flatford Mill	22-Jun-22	20-Jul-22	5.0	2.6	1	-1	10.6	#N/A
Flatford Mill	20-Jul-22	18-Aug-22	4.6	3.5	1	-1	1.4	#N/A
Flatford Mill	18-Aug-22	21-Sep-22	5.0	0.9	1	-1	5.7	#N/A
Flatford Mill	21-Sep-22	13-Oct-22	5.9	0.5	1	-1	4.6	#N/A
Flatford Mill	13-Oct-22	23-Nov-22	9.7	1.1	1	-1	1.7	#N/A
Flatford Mill	23-Nov-22	07-Dec-22	3.8	0.8	1	-1	68.3	#N/A
Flatford Mill	07-Dec-22	06-Jan-23	9.4	0.3	1	-1	5.3	#N/A
Allt a'Mharcaidh	06-Dec-21	06-Jan-22	0.3	0.8	3	1	0	18.7
Allt a'Mharcaidh	06-Jan-22	31-Jan-22	0.4	0.4	3	3	0	0
Allt a'Mharcaidh	31-Jan-22	28-Feb-22	0.9	0.3	1	3	11.7	0
Allt a'Mharcaidh	28-Feb-22	28-Mar-22	1.5	1.1	1	1	6.3	3.6
Allt a'Mharcaidh	28-Mar-22	26-Apr-22	0.8	0.8	1	1	32.1	4.8
Allt a'Mharcaidh	26-Apr-22	23-May-22	0.9	0.4	1	3	30.4	0
Allt a'Mharcaidh	23-May-22	20-Jun-22	0.3	0.3	3	3	0	0
Allt a'Mharcaidh	20-Jun-22	18-Jul-22	0.3	0.4	3	3	0	0
Allt a'Mharcaidh	18-Jul-22	15-Aug-22	0.7	0.3	1	3	18.8	0
Allt a'Mharcaidh	15-Aug-22	12-Sep-22	0.3	0.4	3	3	0	0
Allt a'Mharcaidh	12-Sep-22	10-Oct-22	0.3	0.3	3	3	0	0
Allt a'Mharcaidh	10-Oct-22	07-Nov-22	0.7	0.7	1	1	4.8	3.7
Allt a'Mharcaidh	07-Nov-22	07-Dec-22	1.0	1.1	1	1	14.1	4.9
Allt a'Mharcaidh	07-Dec-22	04-Jan-23	0.3	0.7	3	1	0	7.5
Whiteadder	16-Dec-21	06-Jan-22	1.5	1.2	1	1	35.6	7
Whiteadder	06-Jan-22	03-Feb-22	2.4	1.6	1	1	38.2	2.2
Whiteadder	03-Feb-22	03-Mar-22	4.1	1.2	1	1	42.1	5.5
Whiteadder	03-Mar-22	30-Mar-22	3.3	2.1	1	1	14.2	2.2
Whiteadder	30-Mar-22	28-Apr-22	2.1	1.3	1	1	15.2	3.4
Whiteadder	28-Apr-22	25-May-22	1.7	1.1	1	1	9.4	18.1
Whiteadder	25-May-22	23-Jun-22	1.7	1.0	1	1	7.8	7.4
Whiteadder	23-Jun-22	21-Jul-22	1.6	1.2	1	1	3.1	9.6
Whiteadder	21-Jul-22	18-Aug-22	2.3	1.5	1	1	18	4.1
Whiteadder	18-Aug-22	15-Sep-22	1.6	1.6	1	1	14.9	0

Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Whiteadder	15-Sep-22	14-Oct-22	1.5	1.5	1	1	6.7	1.7
Whiteadder	14-Oct-22	10-Nov-22	1.9	1.8	1	1	3.8	3.9
Whiteadder	10-Nov-22	15-Dec-22	2.0	2.9	1	1	14.9	3.1
Whiteadder	15-Dec-22	05-Jan-23	1.0	1.7	1	1	10.3	1.8
Loch Dee	14-Dec-21	12-Jan-22	2.3	1.5	1	1	8.7	4.9
Loch Dee	12-Jan-22	01-Feb-22	1.7	1.5	1	1	8.6	3.2
Loch Dee	01-Feb-22	01-Mar-22	2.2	0.9	1	1	3.3	9.8
Loch Dee	01-Mar-22	30-Mar-22	2.7	1.8	1	1	9.9	6.9
Loch Dee	30-Mar-22	27-Apr-22	1.3	1.1	1	1	18.9	36
Loch Dee	27-Apr-22	25-May-22	1.7	1.0	1	1	9.1	1.3
Loch Dee	25-May-22	22-Jun-22	1.1	0.8	1	1	24.6	6.1
Loch Dee	22-Jun-22	20-Jul-22	1.9	0.8	1	1	11.4	6.9
Loch Dee	20-Jul-22	17-Aug-22	3.3	0.8	1	1	15.6	6.1
Loch Dee	17-Aug-22	14-Sep-22	0.9	1.1	1	1	19.2	21.8
Loch Dee	14-Sep-22	12-Oct-22	0.7	0.9	1	1	14.8	1.4
Loch Dee	12-Oct-22	10-Nov-22	1.7	1.2	1	1	1.1	8.9
Loch Dee	10-Nov-22	07-Dec-22	1.5	2.1	1	1	51.9	2.9
Loch Dee	07-Dec-22	17-Jan-23	0.8	1.0	1	1	27	1.7
Tycanol Wood	09-Dec-21	05-Jan-22	3.8	2.4	1	1	27.7	4
Tycanol Wood	05-Jan-22	31-Jan-22	3.4	2.2	1	1	1.9	0.6
Tycanol Wood	31-Jan-22	02-Mar-22	2.7	0.9	1	1	12.8	3.9
Tycanol Wood	02-Mar-22	29-Mar-22	5.0	2.2	1	1	18.1	0.6
Tycanol Wood	29-Mar-22	28-Apr-22	2.7	1.9	1	1	4.8	3.9
Tycanol Wood	28-Apr-22	28-May-22	2.0	1.6	1	1	24.5	19.1
Tycanol Wood	28-May-22	21-Jun-22	2.2	1.7	1	1	14.2	0
Tycanol Wood	21-Jun-22	20-Jul-22	2.1	1.4	1	1	4.8	1.8
Tycanol Wood	20-Jul-22	18-Aug-22	2.1	1.3	1	1	2.7	3.2
Tycanol Wood	18-Aug-22	14-Sep-22	2.1	1.6	1	1	5.4	0
Tycanol Wood	14-Sep-22	12-Oct-22	1.6	1.3	1	1	6.8	2.6
Tycanol Wood	12-Oct-22	09-Nov-22	2.6	1.1	1	1	8.3	28
Tycanol Wood	09-Nov-22	08-Dec-22	3.2	2.4	1	1	17.6	1.4
Tycanol Wood	08-Dec-22	04-Jan-23	2.1	1.7	1	1	21.4	6.4
Hillsborough	10-Dec-21	04-Jan-22	6.1	4.3	1	1	7.9	2.8
Hillsborough	04-Jan-22	07-Feb-22	6.3	4.2	1	1	7.6	0
Hillsborough	07-Feb-22	01-Mar-22	6.6	2.1	1	1	9.6	3.1
Hillsborough	01-Mar-22	29-Mar-22	7.1	4.9	1	1	14.9	2.4
Hillsborough	29-Mar-22	26-Apr-22	5.3	3.6	1	1	4.6	3.5
Hillsborough	26-Apr-22	24-May-22	3.3	2.6	1	1	5.1	10.2
Hillsborough	24-May-22	23-Jun-22	3.3	2.8	1	1	1.2	7.1
Hillsborough	23-Jun-22	18-Jul-22	3.2	-999.0	1	-1	11.9	107.1
Hillsborough	18-Jul-22	02-Sep-22	4.7	-999.0	-1	-1	3.8	28.7

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Hillsborough	02-Sep-22	29-Sep-22	4.9	-999.0	1	-1	5.3	68.5
Hillsborough	29-Sep-22	11-Oct-22	3.6	-999.0	1	-1	10.6	67.4
Hillsborough	11-Oct-22	08-Nov-22	4.7	3.0	1	1	4.1	3.3
Hillsborough	08-Nov-22	12-Dec-22	5.6	6.1	1	1	45.2	0.2
Hillsborough	12-Dec-22	09-Jan-23	7.4	5.8	1	1	10.7	1.2
Pumlumon	09-Dec-21	06-Jan-22	2.1	2.0	1	1	26.1	4.6
Pumlumon	06-Jan-22	02-Feb-22	1.4	1.3	1	1	16	4.6
Pumlumon	02-Feb-22	03-Mar-22	2.9	1.2	1	1	6.9	2.6
Pumlumon	03-Mar-22	30-Mar-22	3.7	2.0	1	1	8	2.9
Pumlumon	30-Mar-22	27-Apr-22	2.2	1.5	1	1	9.5	2.3
Pumlumon	27-Apr-22	25-May-22	1.3	1.0	1	1	9.8	3.3
Pumlumon	25-May-22	22-Jun-22	1.4	1.0	1	1	13.8	0
Pumlumon	22-Jun-22	20-Jul-22	1.0	0.9	1	1	4.3	5.2
Pumlumon	20-Jul-22	17-Aug-22	2.1	1.2	1	1	3.2	5
Pumlumon	17-Aug-22	14-Sep-22	1.6	1.5	1	1	11.1	2.2
Pumlumon	14-Sep-22	13-Oct-22	1.2	0.9	1	1	61.8	2.7
Pumlumon	13-Oct-22	09-Nov-22	2.1	1.5	1	1	2.3	5.7
Pumlumon	09-Nov-22	07-Dec-22	1.3	2.0	1	1	60.3	4
Pumlumon	07-Dec-22	04-Jan-23	1.0	1.5	1	1	12.2	2.3
Polloch	07-Dec-21	04-Jan-22	0.3	0.6	3	1	0	2
Polloch	04-Jan-22	01-Feb-22	0.4	0.3	3	3	16.9	#DIV/0!
Polloch	01-Feb-22	01-Mar-22	1.0	0.7	1	1	2.6	0
Polloch	01-Mar-22	29-Mar-22	1.4	0.5	1	3	9.5	1.4
Polloch	29-Mar-22	26-Apr-22	0.3	0.7	3	1	0	0
Polloch	26-Apr-22	24-May-22	1.0	0.4	1	3	36.2	13.7
Polloch	24-May-22	21-Jun-22	0.3	0.3	3	3	0.6	0
Polloch	21-Jun-22	19-Jul-22	0.3	0.4	3	3	7.5	0
Polloch	19-Jul-22	17-Aug-22	0.3	0.3	3	3	11.2	0
Polloch	17-Aug-22	14-Sep-22	0.3	0.4	3	3	0	0
Polloch	14-Sep-22	12-Oct-22	0.4	0.3	3	3	47.7	0
Polloch	12-Oct-22	09-Nov-22	0.3	0.7	3	1	0	4
Polloch	09-Nov-22	07-Dec-22	0.3	1.1	3	1	0	8.5
Polloch	07-Dec-22	04-Jan-23	0.3	0.7	3	1	0	5.2
Balquhidder 2	15-Dec-21	12-Jan-22	1.0	1.4	1	1	43.3	3.9
Balquhidder 2	12-Jan-22	09-Feb-22	0.3	0.7	3	1	2.5	1.8
Balquhidder 2	09-Feb-22	09-Mar-22	2.3	1.2	1	1	2.9	3.9
Balquhidder 2	09-Mar-22	07-Apr-22	2.1	1.5	1	1	2.3	5.8
Balquhidder 2	07-Apr-22	04-May-22	1.9	2.0	1	1	5.3	42.8
Balquhidder 2	04-May-22	29-Jun-22	-9999.0	-999.0	-1	-1	#DIV/0!	#N/A
Balquhidder 2	29-Jun-22	28-Jul-22	0.7	1.1	1	1	2.6	13.9
Balquhidder 2	28-Jul-22	24-Aug-22	1.1	0.8	1	1	86.6	7.8

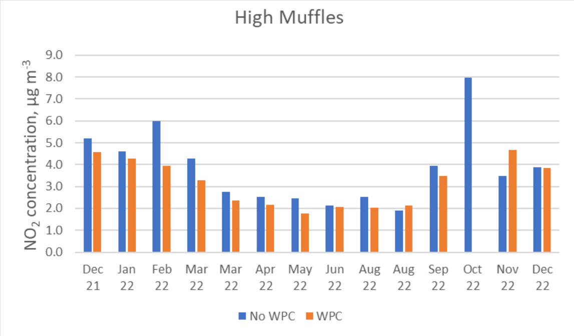
Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Balquhidder 2	24-Aug-22	21-Sep-22	0.6	1.1	1	1	0	4.8
Balquhidder 2	21-Sep-22	19-Oct-22	0.9	1.0	3	1	12.1	2.7
Balquhidder 2	19-Oct-22	16-Nov-22	2.1	1.9	1	1	12.1	5.6
Balquhidder 2	16-Nov-22	14-Dec-22	2.4	3.7	1	1	20.8	13.8
Balquhidder 2	14-Dec-22	11-Jan-23	0.9	1.8	1	1	23.6	0.7
Llyn Llydaw	16-Feb-22	16-Mar-22	3.0	1.2	1	1	0.9	2.8
Llyn Llydaw	16-Mar-22	13-Apr-22	3.0	1.9	1	1	6.6	0.7
Llyn Llydaw	13-Apr-22	11-May-22	2.0	1.4	1	1	18	5.7
Llyn Llydaw	11-May-22	08-Jun-22	1.6	1.1	1	1	25.6	4.2
Llyn Llydaw	08-Jun-22	06-Jul-22	1.4	0.7	1	1	26.5	3.1
Llyn Llydaw	06-Jul-22	03-Aug-22	1.7	1.4	1	1	15.3	53
Llyn Llydaw	03-Aug-22	31-Aug-22	1.5	1.4	1	1	11.1	7
Llyn Llydaw	31-Aug-22	28-Sep-22	0.3	1.3	3	1	0	17.7
Llyn Llydaw	28-Sep-22	26-Oct-22	2.7	1.2	1	1	8.1	3.8
Llyn Llydaw	26-Oct-22	24-Nov-22	2.1	1.0	1	1	5.4	21.4
Llyn Llydaw	24-Nov-22	19-Dec-22	2.2	2.1	1	1	26.5	3.6
Llyn Llydaw	19-Dec-22	18-Jan-23	0.3	-999.0	3	-1	0	0
Glensaugh	15-Dec-21	12-Jan-22	0.9	1.2	1	1	27.4	1.1
Glensaugh	12-Jan-22	09-Feb-22	1.3	0.9	1	1	15.2	2.6
Glensaugh	09-Feb-22	09-Mar-22	4.0	1.6	1	1	9.1	2.4
Glensaugh	09-Mar-22	06-Apr-22	3.1	1.8	1	1	20.8	6.7
Glensaugh	06-Apr-22	04-May-22	2.7	1.8	1	1	4.2	0.7
Glensaugh	04-May-22	01-Jun-22	1.5	1.1	1	1	20.7	4.3
Glensaugh	01-Jun-22	29-Jun-22	2.3	1.2	1	1	9.6	2.9
Glensaugh	29-Jun-22	27-Jul-22	1.4	1.2	1	1	3.2	3
Glensaugh	27-Jul-22	23-Aug-22	2.2	1.1	1	1	12.6	5.8
Glensaugh	23-Aug-22	21-Sep-22	1.0	1.2	1	1	20.9	4.4
Glensaugh	21-Sep-22	20-Oct-22	2.7	1.2	1	1	14.3	2.1
Glensaugh	20-Oct-22	16-Nov-22	5.1	2.9	1	1	3.7	4.9
Glensaugh	16-Nov-22	13-Dec-22	2.4	1.7	1	1	80.9	18.3
Glensaugh	13-Dec-22	11-Jan-23	2.3	1.7	1	1	24.2	2
Moorhouse	16-Dec-21	05-Jan-22	2.5	2.0	1	1	25.9	7.3
Moorhouse	05-Jan-22	02-Feb-22	2.0	1.4	1	1	10.5	2.8
Moorhouse	02-Feb-22	02-Mar-22	2.8	1.0	1	1	6.5	0
Moorhouse	02-Mar-22	30-Mar-22	4.9	2.6	1	1	0.5	7.8
Moorhouse	30-Mar-22	27-Apr-22	2.3	1.3	1	1	8.8	3.6
Moorhouse	27-Apr-22	25-May-22	1.8	1.3	1	1	7.7	14.8
Moorhouse	25-May-22	22-Jun-22	1.2	0.8	1	1	8.6	1.6
Moorhouse	22-Jun-22	20-Jul-22	1.2	1.0	1	1	10.4	4.7
Moorhouse	20-Jul-22	17-Aug-22	2.1	1.0	1	1	11	4.5
Moorhouse	17-Aug-22	14-Sep-22	1.7	1.7	1	1	14.9	39.4

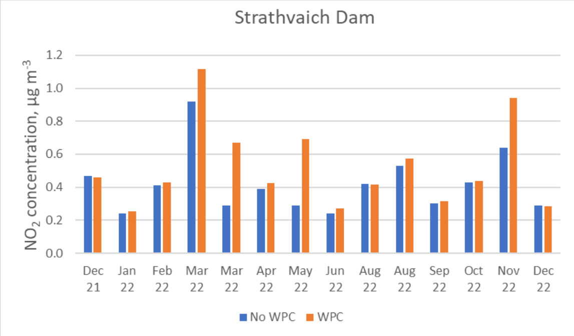
Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Moorhouse	14-Sep-22	12-Oct-22	2.5	1.1	1	1	7.4	10.9
Moorhouse	12-Oct-22	08-Nov-22	2.6	1.8	1	1	1.1	10.9
Moorhouse	08-Nov-22	07-Dec-22	2.3	2.1	1	1	20.9	6.7
Moorhouse	07-Dec-22	05-Jan-23	1.8	1.4	1	1	18.5	32.2
Percy's Cross	08-Dec-21	05-Jan-22	3.8	3.2	1	1	14.9	1.4
Percy's Cross	05-Jan-22	02-Feb-22	2.5	1.6	1	1	22.9	2.2
Percy's Cross	02-Feb-22	02-Mar-22	3.5	1.3	1	1	10.3	4.8
Percy's Cross	02-Mar-22	29-Mar-22	5.5	3.7	1	1	4.4	4.1
Percy's Cross	29-Mar-22	27-Apr-22	2.2	1.5	1	1	13.4	1.7
Percy's Cross	27-Apr-22	25-May-22	1.8	1.5	1	1	6.9	1.5
Percy's Cross	25-May-22	22-Jun-22	1.5	1.0	1	1	30.8	1.4
Percy's Cross	22-Jun-22	20-Jul-22	2.2	1.3	1	1	16.4	5.1
Percy's Cross	20-Jul-22	17-Aug-22	2.6	1.2	1	1	12.4	49.3
Percy's Cross	17-Aug-22	14-Sep-22	2.6	2.1	1	1	17.4	2.5
Percy's Cross	14-Sep-22	12-Oct-22	3.1	1.6	1	1	2.3	0.8
Percy's Cross	12-Oct-22	09-Nov-22	3.4	2.3	1	1	23	4.8
Percy's Cross	09-Nov-22	07-Dec-22	4.1	3.9	1	1	18.7	2
Percy's Cross	07-Dec-22	05-Jan-23	2.8	2.9	1	1	14.6	1.9
Driby 2	06-Dec-21	03-Jan-22	10.8	7.5	1	1	3.6	3.7
Driby 2	02-Feb-22	02-Mar-22	8.5	4.8	1	1	11	0.3
Driby 2	02-Mar-22	30-Mar-22	10.6	7.5	1	1	1.4	1.8
Driby 2	30-Mar-22	27-Apr-22	6.1	4.0	1	1	4.7	6.5
Driby 2	27-Apr-22	25-May-22	5.0	3.7	1	1	9.8	1.6
Driby 2	25-May-22	21-Jun-22	3.6	2.6	1	1	1	2.3
Driby 2	21-Jun-22	20-Jul-22	3.9	3.2	1	1	0.5	1.4
Driby 2	20-Jul-22	17-Aug-22	4.4	3.2	1	1	4.2	7
Driby 2	17-Aug-22	14-Sep-22	4.9	4.4	1	1	3	20.6
Driby 2	14-Sep-22	12-Oct-22	7.0	4.5	1	1	12	0.7
Driby 2	12-Oct-22	09-Nov-22	7.8	5.1	1	1	4.5	2.2
Driby 2	09-Nov-22	07-Dec-22	2.8	6.6	1	1	31.3	0.2
Driby 2	07-Dec-22	04-Jan-23	8.8	7.9	1	1	10.4	1.2
Chilbolton	08-Dec-21	05-Jan-22	9.5	5.6	1	1	4.7	2
Chilbolton	05-Jan-22	02-Feb-22	12.1	9.2	1	1	5.2	0.6
Chilbolton	02-Feb-22	02-Mar-22	7.1	3.2	1	1	6.1	5.2
Chilbolton	02-Mar-22	30-Mar-22	12.0	8.3	1	1	16.5	3.7
Chilbolton	30-Mar-22	27-Apr-22	6.7	4.7	1	1	8.8	1.9
Chilbolton	27-Apr-22	25-May-22	6.8	4.8	1	1	8.7	1.3
Chilbolton	25-May-22	22-Jun-22	2.8	3.5	1	1	9.9	2.3
Chilbolton	22-Jun-22	20-Jul-22	4.7	4.2	1	1	18.5	4.7
Chilbolton	20-Jul-22	17-Aug-22	7.4	4.7	1	1	10.5	2.1
Chilbolton	17-Aug-22	14-Sep-22	8.1	5.4	1	1	5.2	1

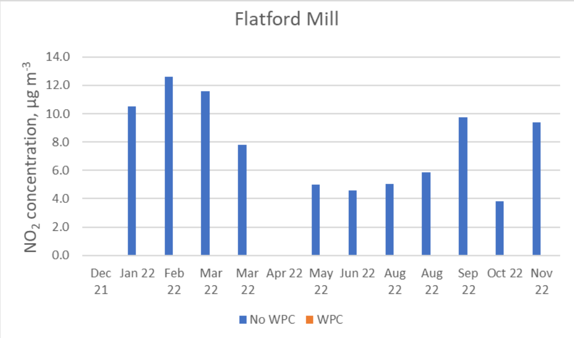
Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Chilbolton	14-Sep-22	12-Oct-22	6.7	4.6	1	1	10.4	0
Chilbolton	12-Oct-22	09-Nov-22	7.7	4.3	1	1	7.5	7
Chilbolton	09-Nov-22	07-Dec-22	8.2	6.1	1	1	21.2	11.7
Chilbolton	07-Dec-22	04-Jan-23	10.0	8.7	1	1	29.5	1.2
Forsinard RSPB	06-Dec-21	06-Jan-22	0.8	0.8	1	1	6.8	4
Forsinard RSPB	06-Jan-22	31-Jan-22	1.0	0.4	1	3	22.1	0
Forsinard RSPB	31-Jan-22	02-Mar-22	1.4	0.3	1	3	18.9	0
Forsinard RSPB	02-Mar-22	28-Mar-22	2.2	1.6	1	1	8.2	3.9
Forsinard RSPB	28-Mar-22	25-Apr-22	1.3	0.8	1	1	12	6
Forsinard RSPB	25-Apr-22	24-May-22	0.3	0.9	3	1	0	0
Forsinard RSPB	24-May-22	20-Jun-22	0.8	0.3	1	3	21.9	0
Forsinard RSPB	20-Jun-22	18-Jul-22	0.3	1.1	3	1	0	16.8
Forsinard RSPB	18-Jul-22	15-Aug-22	1.3	0.3	1	3	37.4	0
Forsinard RSPB	15-Aug-22	12-Sep-22	0.3	1.1	3	1	6.3	24.5
Forsinard RSPB	12-Sep-22	25-Oct-22	1.5	0.7	-1	1	39	3.3
Forsinard RSPB	25-Oct-22	07-Nov-22	1.9	1.5	1	1	16.2	3.7
Forsinard RSPB	07-Nov-22	06-Dec-22	1.2	1.8	1	1	47.3	2.9
Forsinard RSPB	06-Dec-22	03-Jan-23	0.3	1.0	3	1	0	4.4
Lullington Heath	08-Dec-21	05-Jan-22	10.4	6.3	1	1	#N/A	4.4
Lullington Heath	05-Jan-22	02-Feb-22	11.5	7.1	1	1	3.8	6.1
Lullington Heath	02-Feb-22	02-Mar-22	10.2	4.1	1	1	5.3	4.5
Lullington Heath	02-Mar-22	30-Mar-22	14.8	7.9	1	1	5	2.4
Lullington Heath	30-Mar-22	27-Apr-22	10.1	5.7	1	1	7.6	2.6
Lullington Heath	27-Apr-22	25-May-22	8.7	5.4	1	1	18	3.7
Lullington Heath	25-May-22	22-Jun-22	8.2	5.4	1	1	9.7	2.5
Lullington Heath	22-Jun-22	20-Jul-22	7.7	5.2	1	1	2.3	1
Lullington Heath	20-Jul-22	17-Aug-22	9.5	5.5	1	1	10.1	0.6
Lullington Heath	17-Aug-22	16-Sep-22	7.9	6.7	1	1	5.7	2.5
Lullington Heath	16-Sep-22	12-Oct-22	7.1	1.3	1	1	4.4	0
Lullington Heath	12-Oct-22	10-Nov-22	9.5	5.1	1	1	7.2	6.9
Lullington Heath	10-Nov-22	07-Dec-22	9.4	6.6	1	1	28.6	3.2
Lullington Heath	07-Dec-22	04-Jan-23	14.6	8.6	1	1	2.1	2
Bannisdale Beck	03-Jan-22	31-Jan-22	4.0	3.0	1	1	20.4	2.6
Bannisdale Beck	31-Jan-22	02-Mar-22	4.5	2.6	1	1	3.5	3.8
Bannisdale Beck	02-Mar-22	30-Mar-22	4.4	-999.0	1	-1	4.7	#N/A
Bannisdale Beck	30-Mar-22	27-Apr-22	1.7	1.5	1	1	8	9.1
Bannisdale Beck	27-Apr-22	25-May-22	1.7	3.6	1	1	8.7	9.7
Bannisdale Beck	25-May-22	22-Jun-22	1.0	0.8	1	1	8.6	16.9
Bannisdale Beck	22-Jun-22	20-Jul-22	3.0	6.3	1	1	4.8	9.2
Bannisdale Beck	20-Jul-22	31-Aug-22	2.1	3.3	1	1	10.1	5.8
Bannisdale Beck	31-Aug-22	14-Sep-22	4.8	1.5	1	1	9	3.8

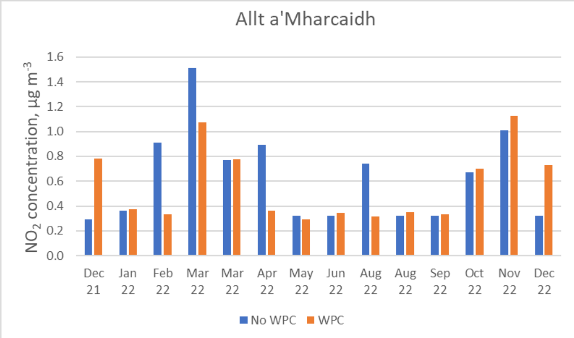
Site name	Start date	End date	No WPC NO_2, µg m^{-3}	Validity flag	COV, %	WPC NO_2, µg m^{-3}	Validity flag	COV, %
Bannisdale Beck	14-Sep-22	12-Oct-22	3.9	3.2	1	1	5	3.5
Bannisdale Beck	12-Oct-22	09-Nov-22	3.0	2.8	1	1	19.1	9.7
Bannisdale Beck	09-Nov-22	21-Dec-22	2.4	3.7	-1	1	86.9	7.5
Bannisdale Beck	21-Dec-22	18-Jan-23	0.3	-999.0	-1	-1	0	#N/A

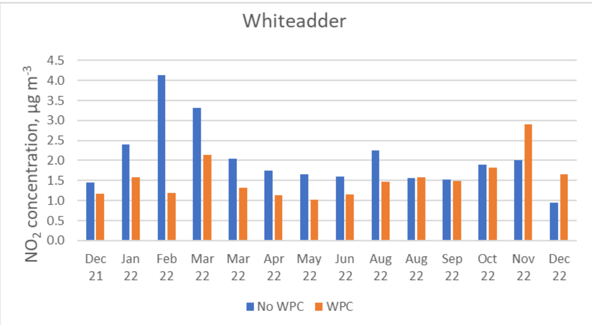
APPENDIX II PLOTS OF NO_2 CONCENTRATIONS FOR DIFFUSION TUBES WITH & WITHOUT WPC

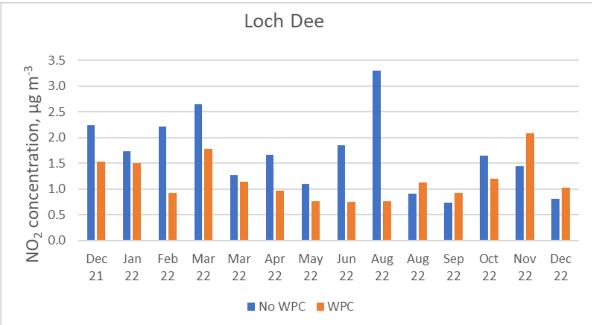


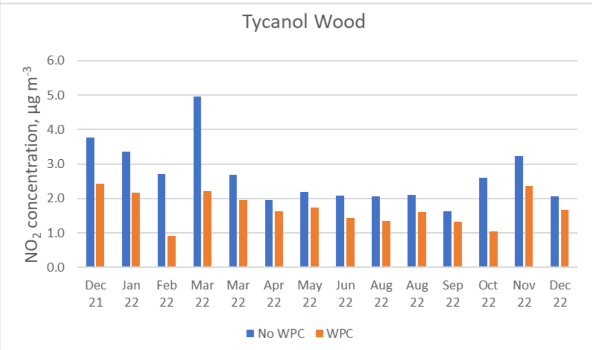


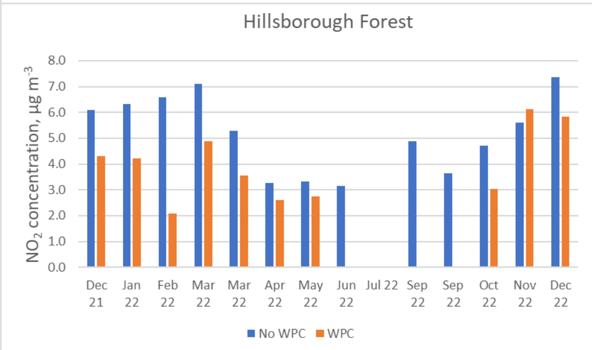


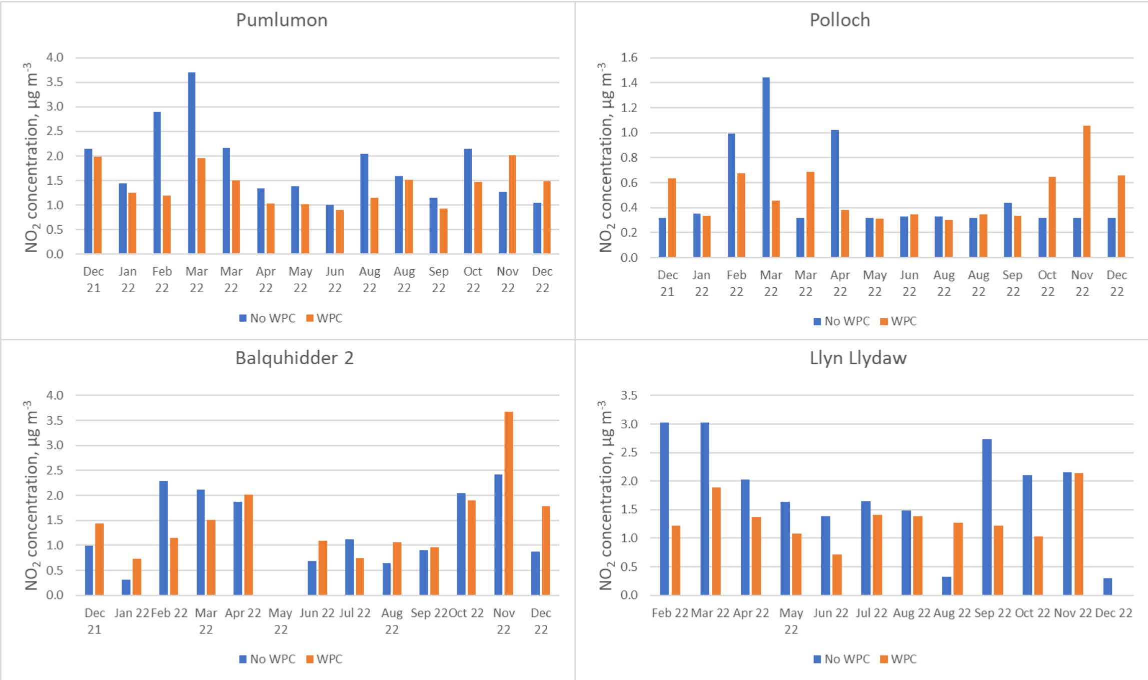


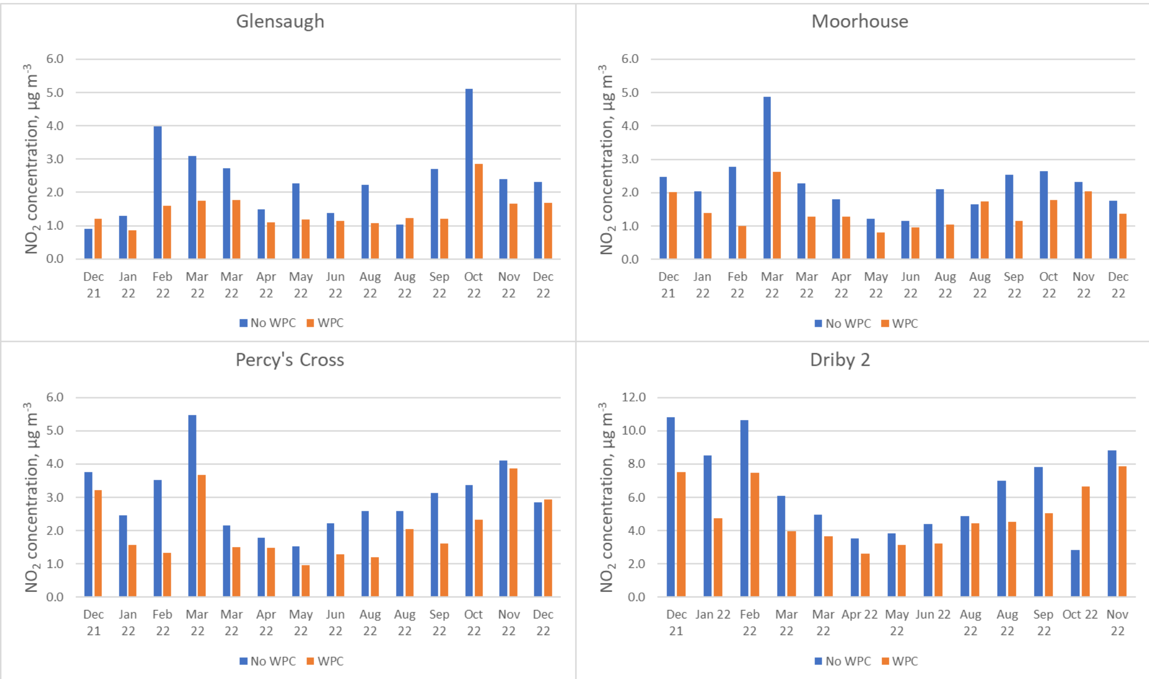


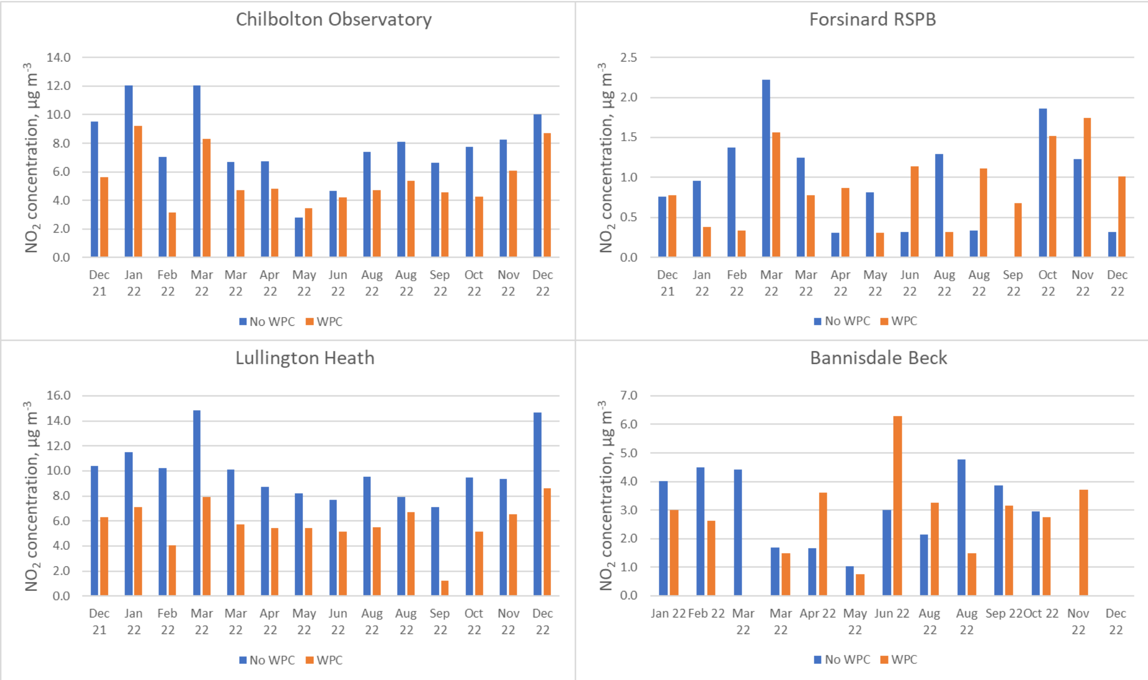







Pumlumon
Polloch
Balquhidder 2
Llyn Llydaw
NO2 concentration, µg m-3
No WPC
WPC


Glensaugh
Moorhouse
Percy's Cross
Driby 2
NO2 concentration, µg m-3
No WPC
WPC


Chilbolton Observatory
Forsinard RSPB
Lullington Heath
Bannisdale Beck
NO2 concentration, µg m-3
Dec 21
Jan 22
Feb 22
Mar 22
Apr 22
May 22
Jun 22
Aug 22
Sep 22
Oct 22
Nov 22
Dec 22
No WPC
WPC

RICARDO

UK CEH