UKEAP 2022 annual report

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

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Contents

Executive summary

This annual report for 2022 was prepared by UK Centre for Ecology & Hydrology and Ricardo Energy and Environment 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 network:

- **UK Environmental Monitoring and Evaluation Program (EMEP) monitoring supersites** (Chilbolton Observatory and Auchencorth Moss)
- **National Ammonia Monitoring Network** (NAMN – 97 sites, Dec 2022)
- **Acid Gases and Aerosol Network** (AGANet – 28 sites, Dec 2022)
- **Precipitation chemistry Network** (Precip-Net – 41 sites)
- **Rural nitrogen dioxide (NO_2) diffusion tube network** (NO_2-Net – 24 sites)

The following report provides information on:

- Updates on network operations during 2022.
- Annual concentrations.
- Interpretation of data and discussion of trends across the network.
- A brief summary of the scientific research, publications and other activities related to the network.

Key changes for 2022:

- In April 2022, 25 sites were added to NAMN and 1 site was added to AGANet. The additional sites to the monitoring networks are located in Northern Ireland.

1 Introduction

The Defra, Environment Agency and Devolved Administrations rural air pollutant monitoring networks project, UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP), is operated jointly between Ricardo Energy & Environment and the UK NERC 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 2022. 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). In addition, during 2022 a network already operational in Northern Ireland, was embedded into the 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, where the EU reporting objectives will continue as its transposed into UK law following EU exit.

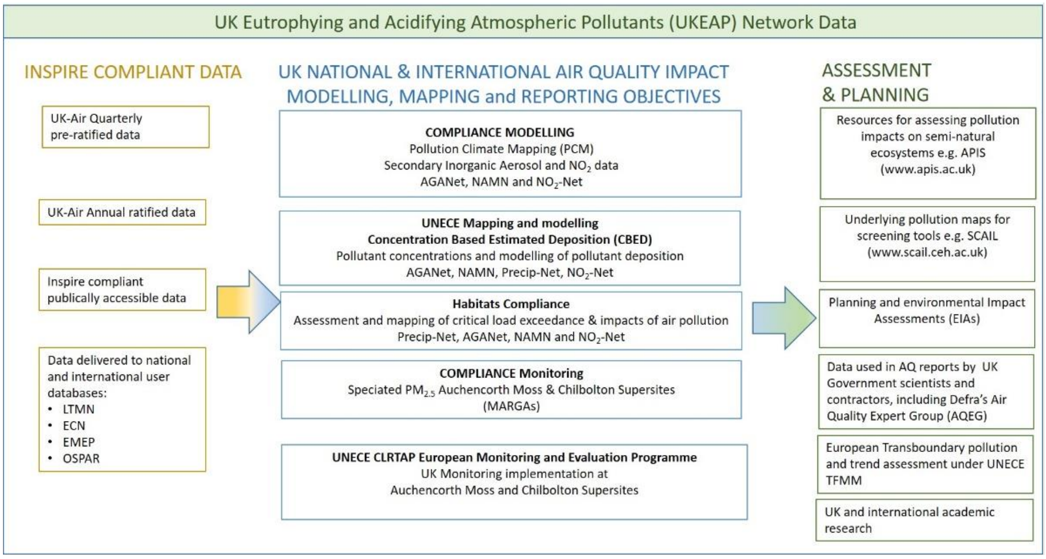


Figure 1 Summary of the data applications of the UKEAP datasets.

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 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 monitoring networks have been in operation much longer in 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 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. Examples of the data use can be found in 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. Further details of the use of the data can be found in section 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 to Pollution Climate Mapping (PCM) and modelling (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 2021 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 assumed to be now implemented under the Air Quality Standards Regulations[1]. 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 2022 (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**	**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 Scope of the report

The following annual report for 2022 contains:

- A summary of network operations including Quality Assurance (QA)/ Quality Checks (QC) results, notable events and changes to the networks during 2022.
- Measured annual concentrations from all monitoring sites for each network.
- Interpretation of data and discussion of trends across the network.
- A brief 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 2022 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.

Samples are collected at fortnightly intervals at each of the 41 sites in the network (see Figure 3).

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

The network also incorporates eight sites (Ainsdale Dunes and Sands, Bure Marshes, Fenns, Whixall and Bettisfield Mosses, Ingleborough, Lullington Heath, Monks Wood, Stiperstones and Thursley Common 2) which form part of the Natural England's Long Term Monitoring Network (LTMN).

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.

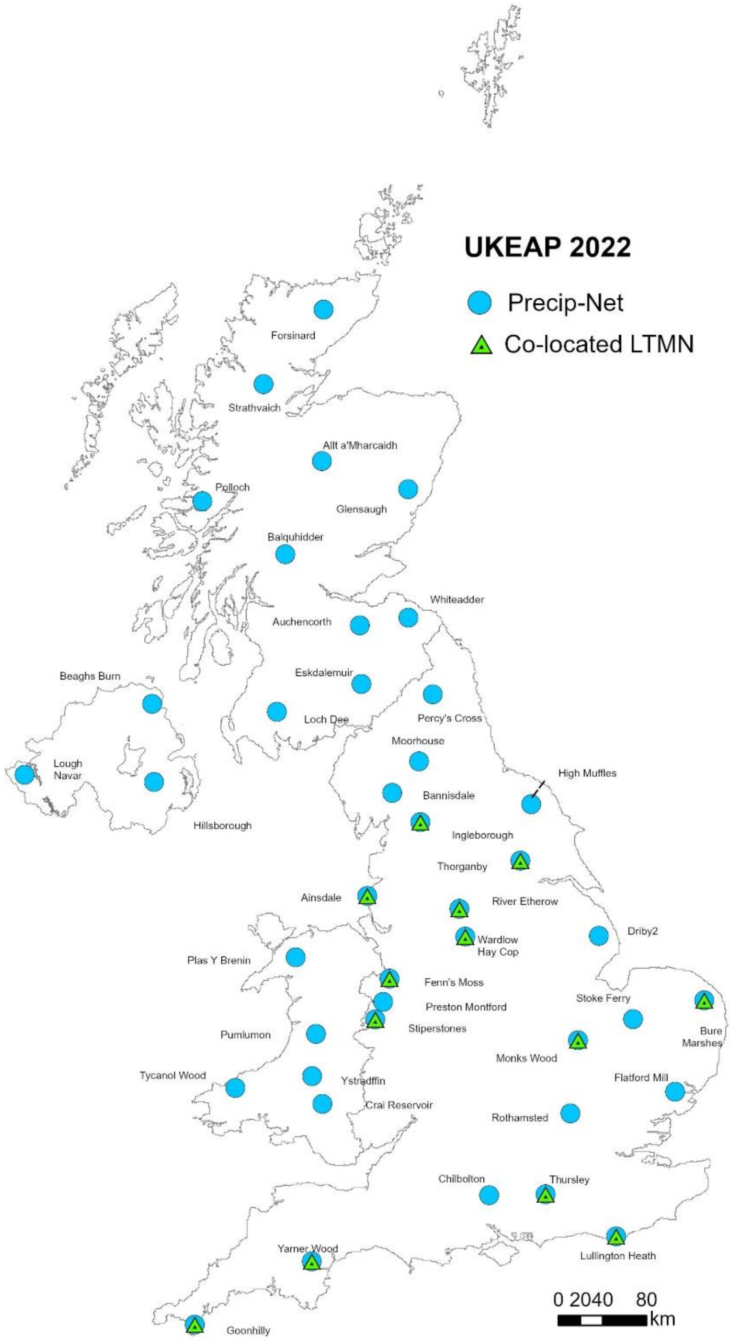


Figure 3 UK Precipitation chemistry Network (Precip-Net) in 2022

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 2022 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 around samplers is maintained during these visits.

All analysed samples undergo an ion balance check. Samples are submitted for reanalysis if the difference in ion balance is greater than 15%, 30% or 60% depending on the ion strength. 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 accredited. Details can be found under the analytical laboratory's accreditation.

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 40th intercomparison is presented in Appendix 2.

[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. Diffusion tubes consist 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. In this case, the absorbent is a solution of 50% triethanolamine and acetone.

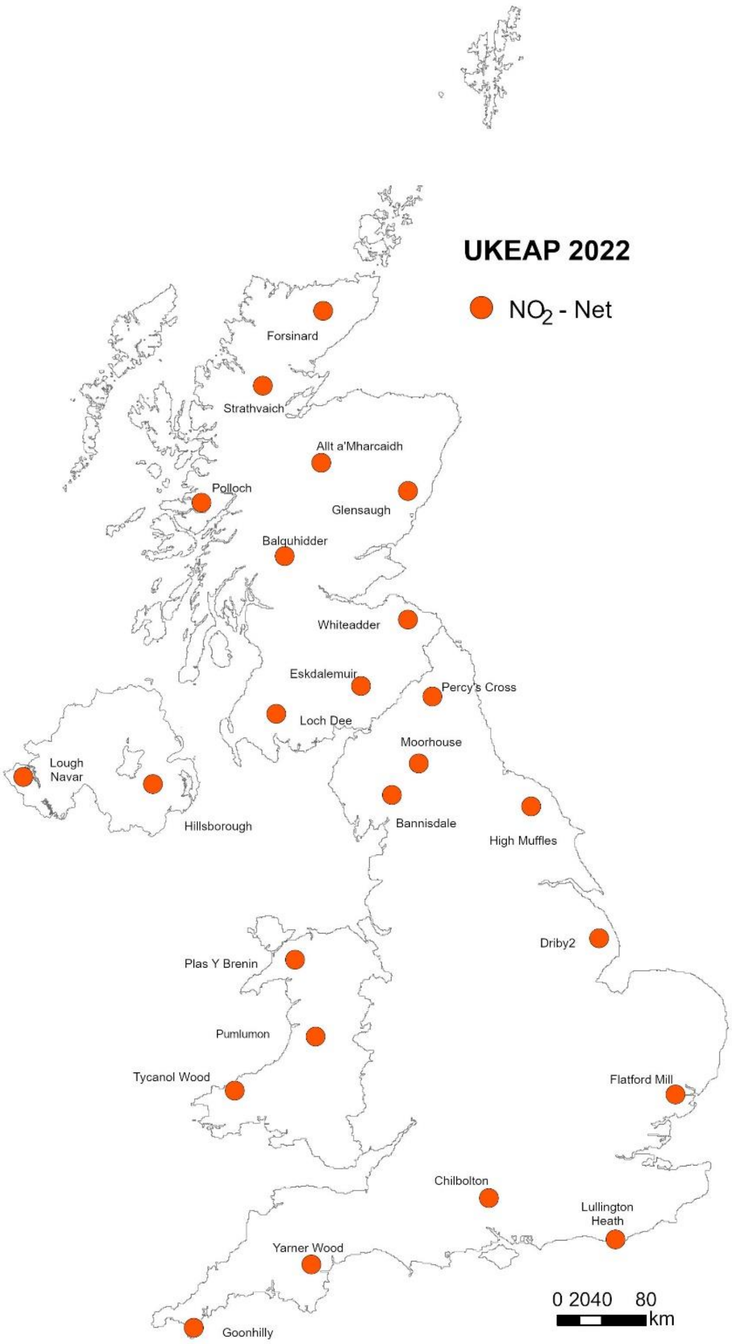


Figure 4 UK NO_2 diffusion tube (NO_2-Net) Network in 2022

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 supplier of the tubes is SOCOTEC, Didcot.

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.

During 2022, co-located wind capped tubes that are used in the UK Urban NO_2 Network (UUNN) were also deployed at the UKEAP sites to assess their performance however the results are not published or discussed within this report. The results will be published in a separate report at a later date.

2.2.2 Accreditation, analytical proficiency testing (PT) and intercomparisons

The analytical method used to measure the concentrations of NO_2 using diffusion tubes is UKAS accredited. Details can be found under the analytical laboratory's accreditation.

The analytical laboratory 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]. All recent results apart from AIR PT AR053 of the were considered satisfactory. The failures for within AR053 were not due any aspects of the analysis related to the UKEAP network. The analytical laboratory performance summarised below:

AIR PT Round	AIR PT AR049	AIR PT AR050	AIR PT AR052	AIR PT AR053	AIR PT AR054
Period	January– February 2022	June– July 2022	September – October 2022	November – December 2022	May– June 2023
Socotec UK Limited	100.00%	100.00%	90.30%	70%*	100%

* Failures were due to BTEX analysis on Tenax tubes method ASC/SOP/211 (all 12 samples for this method this round which constitutes 30% of the samples failed)

In addition to this each year the analytical laboratory participates 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 1.

2.2.3 Bias adjustment

Diffusion tubes tend to overestimate NO_2 concentrations due to shortening of the path length within the tube by the wind. Hence, a bias adjustment is required. Normally this is derived from the four collocated automatic analysers and diffusion tubes at Chilbolton Observatory, Eskdalemuir, High Muffles and Yarner Wood. Due to the need for a new electrical cable at Eskdalemuir there was no automatic analyser operating during 2022. The resultant bias adjustment factor, 0.943, was applied to all other 21 diffusion tubes. The calculation of the bias adjustment factor is discussed further in Appendix 3.

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 2022 the number of NAMN sites providing monthly measurements of atmospheric NH_3 increased from 72 to 98, summarised in Table 2Table 2.

Table 2: Summary of National Ammonia Monitoring Network (NAMN) monitoring site types in December 2022

Site Type	Number
UKCEH DELTA® sites sampling gaseous NH_3 (2 sites closed during 2021 refer below for details)	28
UKCEH ALPHA® sites sampling gaseous NH_3 only	78
Total number of sites	97

Note: 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. 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 2022.

During 2022 the following network infrastructure changes occurred:

- 25 sites were added to the network in Northern Ireland (Figure 7). The sites added are listed below.
    - U of Ulster met station (UKA00938)
    - Castle Enigan (UKA00939)
    - Beaghs Burn (UKA00383)

- Slieve Beagh (UKA00940)
- Moninea Bog (UKA00941)
- Seekinore (UKA00942)
- Lisbellaw (UKA00943)
- Glenwherry COSMOS (UKA00944)
- UWMN Bencrom River (UKA00945)
- Blackwatertown (UKA00946)
- Ratarnet Rd (UKA00947)
- Inch Abbey 4 (UKA00948)
- Belfast centre (UKA00212)
- Ballylinney Church (UKA00949)
- West of Crumlin (UKA00950)
- Loughmore River (UKA00951)
- Caldanagh Bog (UKA00952)
- Cloughmills (UKA00953)
- Caddy Rd (UKA00954)
- Turmennan Rd (UKA00955)
- Carrowbane Rd (UKA00956)
- Creggan (UKA00957)
- Corramore Rd (UKA00958)
- Ballynahone Bog (UKA00959)
- Drumclamph 2 (UKA00960)

- The Carradale site (UKA00389) was closed in May 2022 and a new site opened in May 2022 at Carradale Distillery (UKA00961), however due to a fault at this site no data was collected at the new site in 2022.

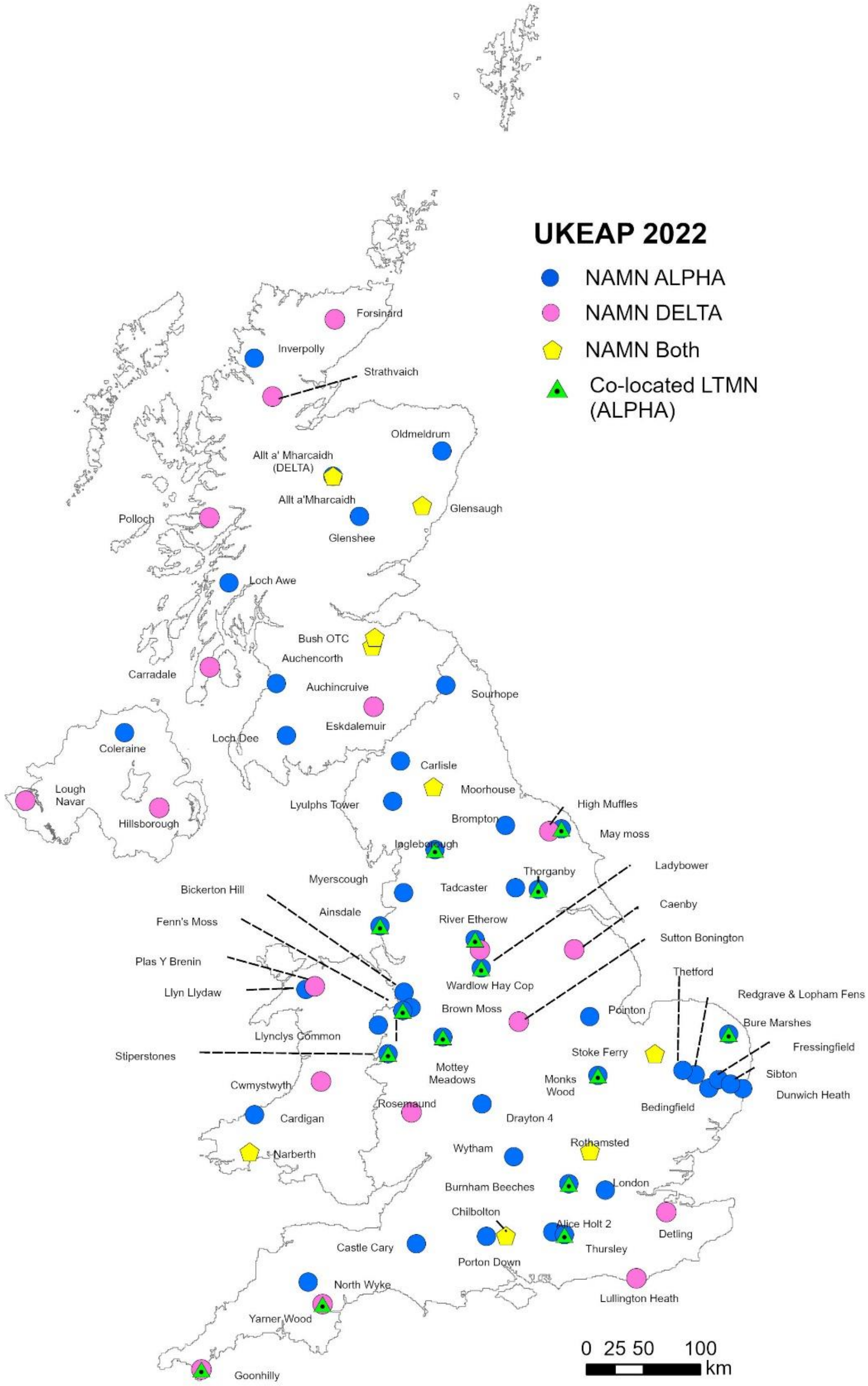


Figure 7 a) UK National Ammonia Monitoring Network (NAMN) and co-located LTMN sites.

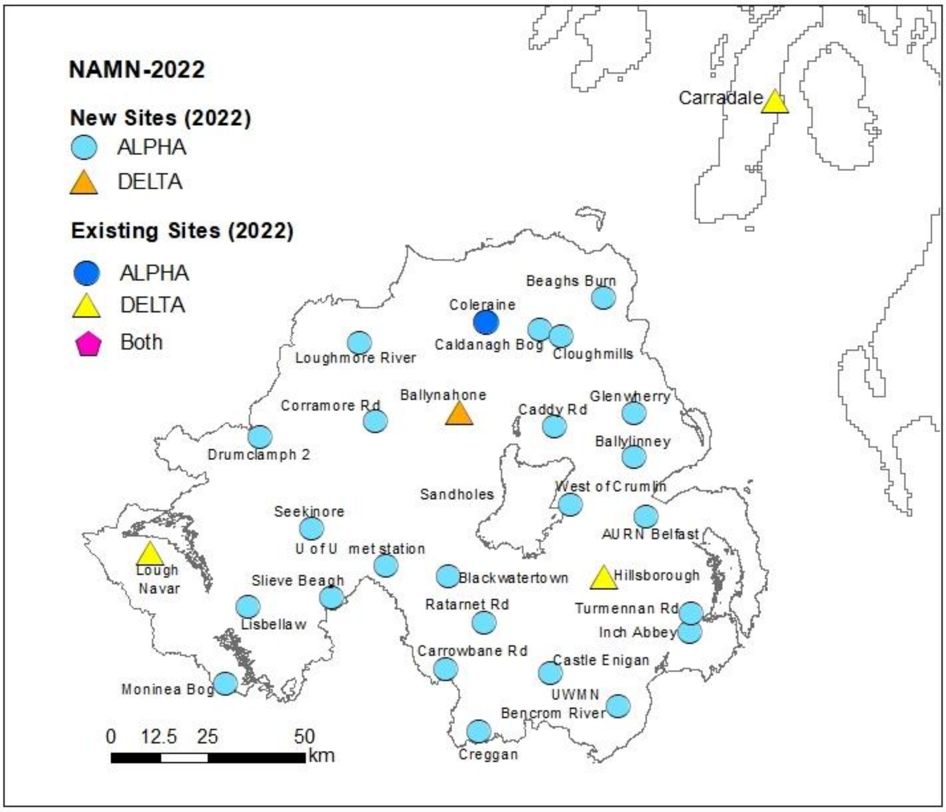


Figure 7 b) NAMN sites added to the network in Northern Ireland in 2022.

Figure 7 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 (LTMN, 15 sites) and the new sites from the Northern Ireland Network (NI Network, 25 sites, 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 2022, the coefficient of determination (R^2) was 0.92 showing good agreement between ALPHAs and DELTAs, with the calibrated uptake rate determined as 0.0037884 m^3 hr^{-1} (Figure 9). When compared to historical trends, it was found that the calibrated uptake rate was higher than the reporting range of previous years (Figure 10). For the year 2022 the calculated uncertainty of the UKCEH ALPHA® system is 12% 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. Replicate UKCEH ALPHA® samplers were used for each measurement (triplicate samplers) and were only accepted when they were within 15% (Coefficient of Variance, CV).

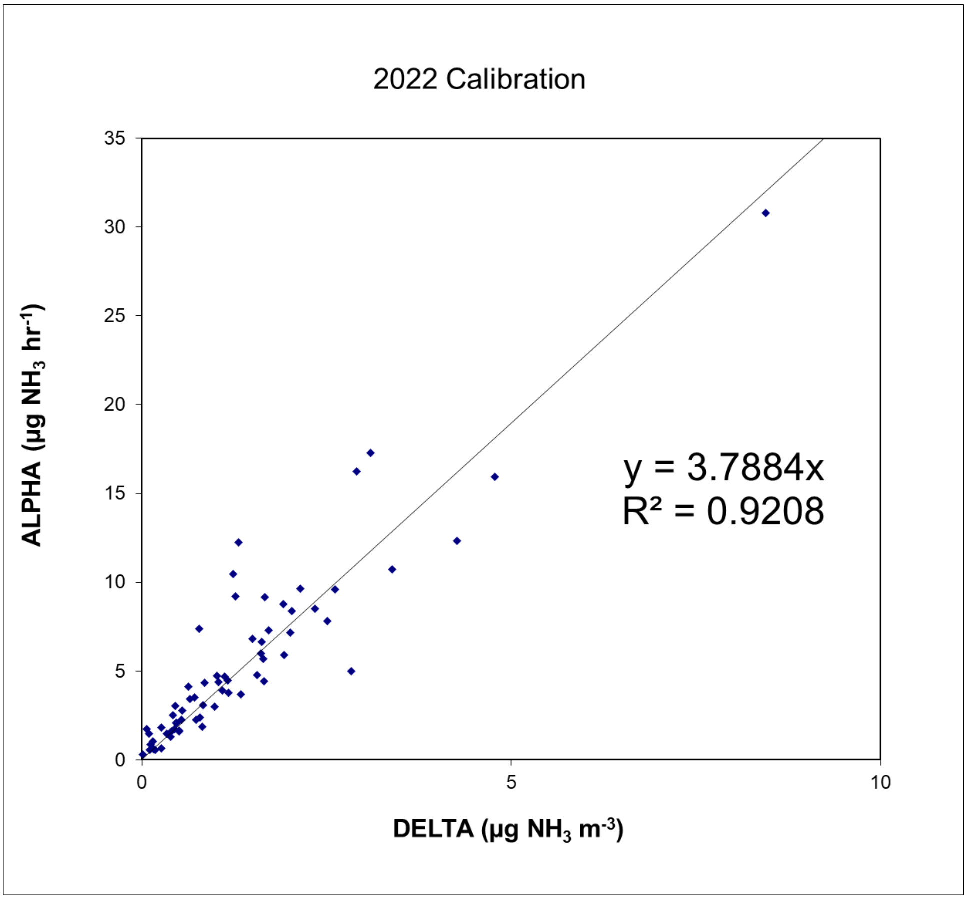


Figure 8: 2022 UKCEH ALPHA® uptake rate calibration

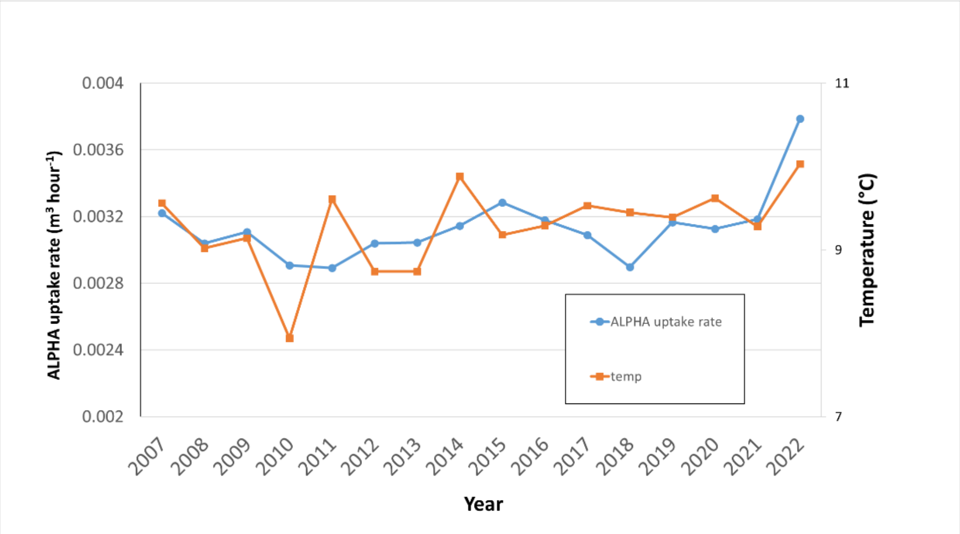


Figure 9: Historical UKEAP uptake rate for ALPHA samplers and UK annual average temperature (source: https://www.metoffice.gov.uk/research/climate/maps-and-data/summaries/index)

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. At the start of 2022 there were 27 sites operational within AGANet (refer to Table 3) by December 2022 there were 28 sites operational.

Table 3 Summary of the number of sites within AGANet in December 2022

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 2022 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 2022 calendar year was submitted to UKAIR in April 2023.

During 2022 the following network changes occurred:

- The Ballynahone Bog (UKA00959) site was added to the network in April 2022, increasing the network from 27 sites to 28 sites.
- An issue with DELTA heating in the sample holder was identified in October 2022 and as a precaution DELTA® did not operate with heaters from this point. A design adaptation to ensure future safety and climate resilience is being implemented in 2023.

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.

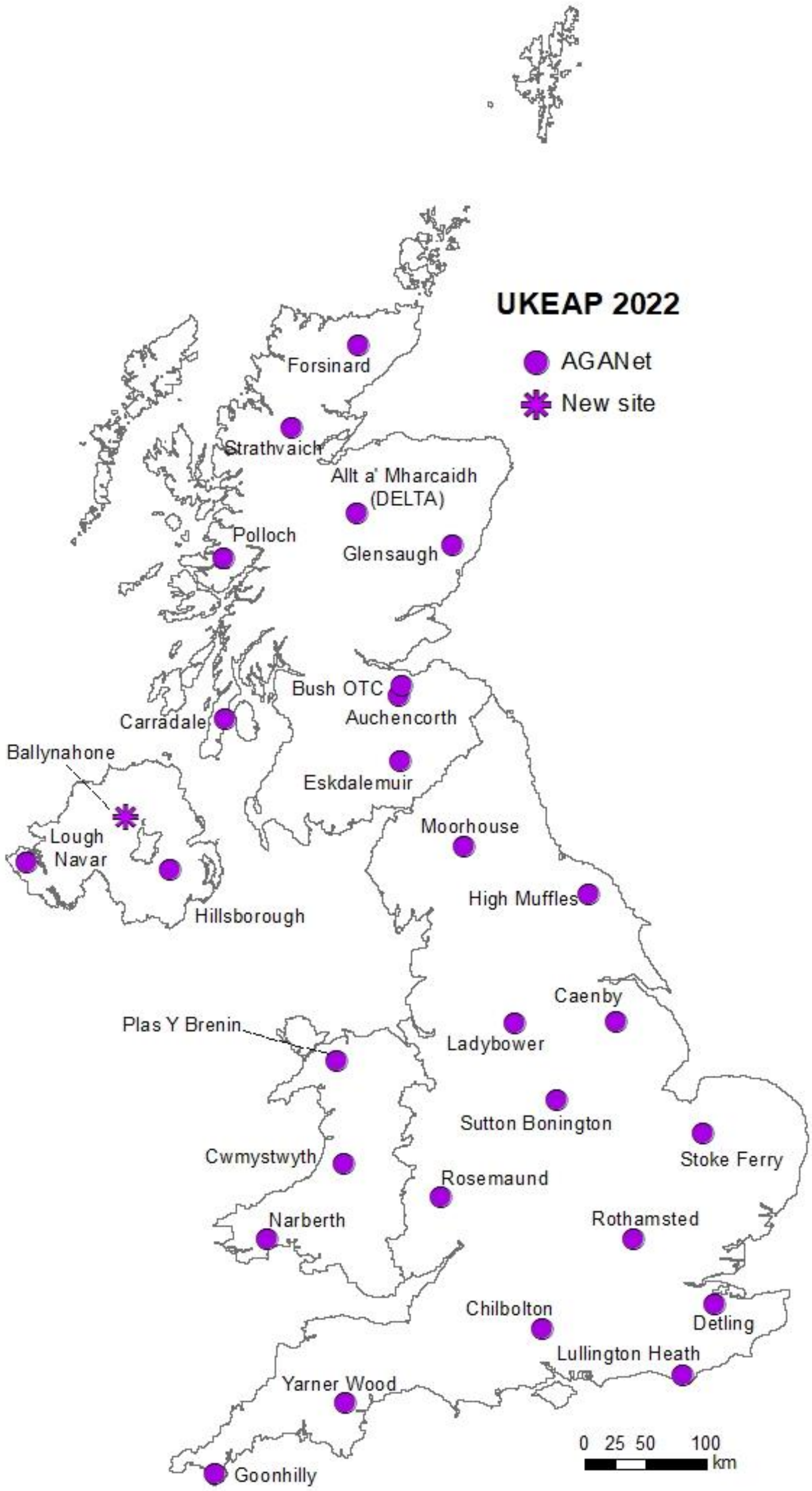


Figure 10 UK Acid Gases and Aerosol Network (AGANet).

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, Teledyne, 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. These 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 remaining 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 2022. During 2022 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 2022 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 was a considerable number of samples lost at Loch Dee due to bird strike in 2022. We review the bird deterrents at this site during the site service in 2023.

Table 4 Data capture with the Precip-Net network in 2022.

Site	Average, %	Site	Average, %
Ainsdale Dunes and Sands	72.6	Lough Navar	100.0
Allt a'Mharcaidh	80.2	Lullington Heath	86.4
Auchencorth Moss	87.6	Monks Wood	78.8
Balquhidder 2	93.9	Moorhouse	98.2
Bannisdale Beck	93.9	Percy's Cross	90.3
Beaghs Burn	99.7	Polloch	100.0
Bure Marshes	91.4	Preston Montford	76.7
Chilbolton Observatory	91.4	Pumlumon	61.9
Crai Reservoir 2	92.9	River Etherow	76.4
Driby 2	84.4	Rothamsted	94.4
Eskdalemuir	83.8	Stiperstones	87.9
Fenn's, Whixall and Bettisfield Mosses	89.6	Stoke Ferry	69.9
Flatford Mill	80.7	Strathvaich	93.9
Forsinard RSPB	79.9	Thorganby	75.5
Glensaugh	73.2	Thursley Common 2	77.5
Goonhilly	80.2	Tycanol Wood	91.4
High Muffles	96.2	Wardlow Hay Cop	96.7
Hillsborough Forest	84.8	Whiteadder	90.9
Ingleborough	95.9	Yarner Wood	61.4
Llyn Llydaw	84.8	Ystradffin	91.5
Loch Dee	46.0	Network average	85.0

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 Figure 13 for 2022. 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.

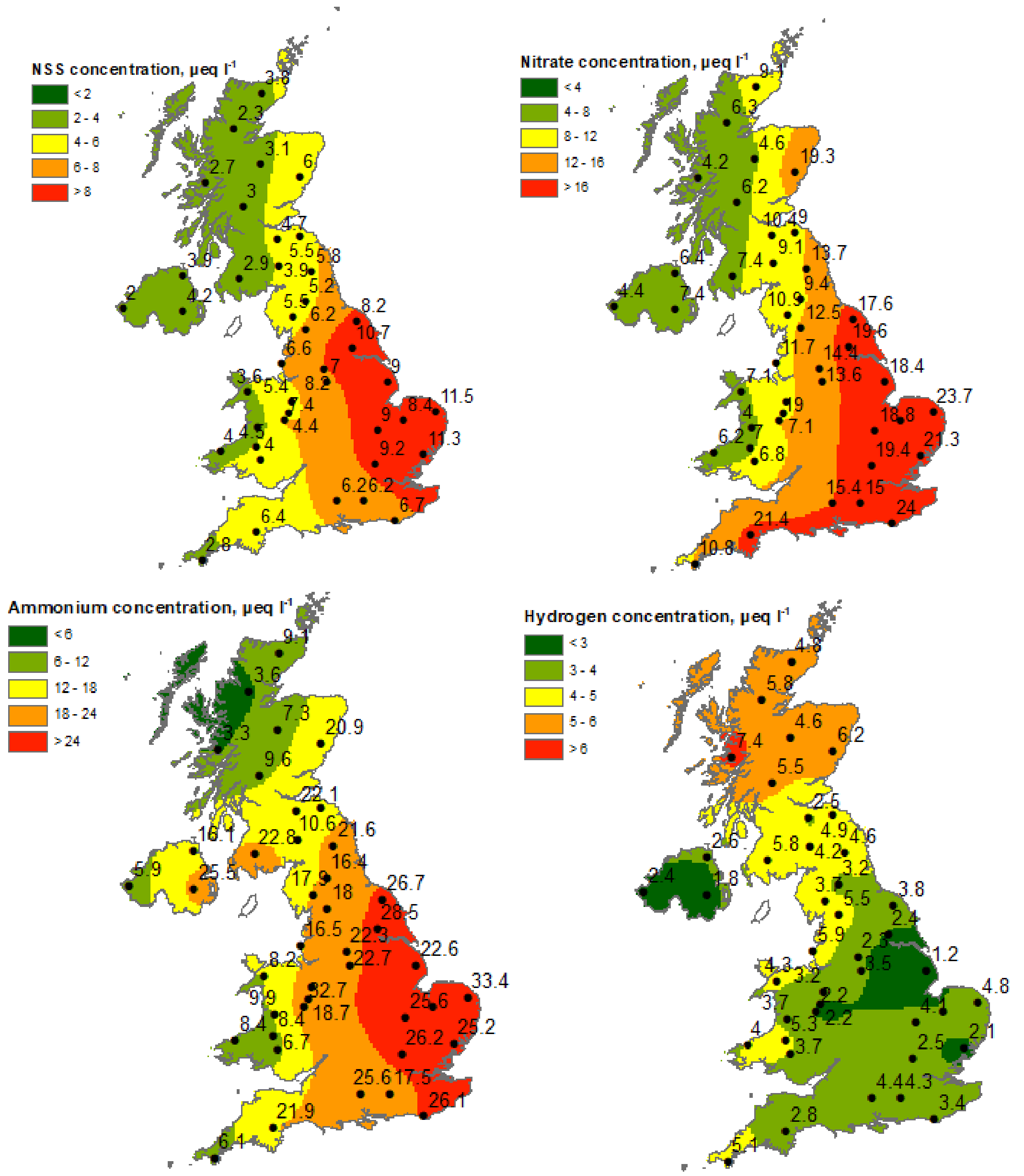


Figure 13 Interpolated concentration maps for nss-SO_4^{2-}, NO_3^-, NH_4^+ and H^+ ion (μeq l^{-1})

Figure 14 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 77% and ammonia emissions have decreased by about 16%. Figure 14 Also presents projected emissions for 2022, 2025 and 2030 (2040 emissions available on 13th July 2023) for the respective gases from the National Emissions Inventory (NAEI)[13].

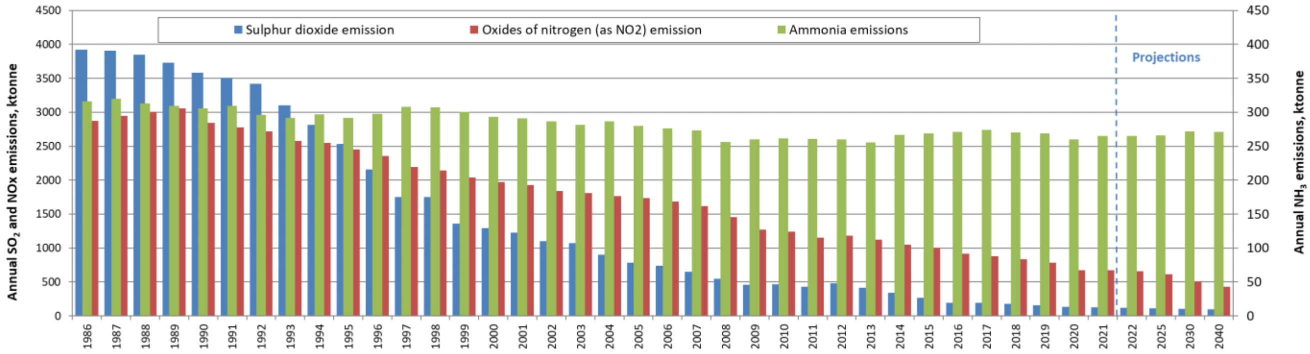


Figure 14 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986

Figure 15, Figure 16 and Figure 17 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^+ concentration are smaller than that for SO_4^{2-}.

The impact of Covid-19 on transport and consequently on NO_X emissions has been well documented (Lewis et al. 2020)[14] with significant reductions in NO_X from transport emissions during the first national lock down. From 2019 to 2020 NO_X emissions from road transport decreased by about 26%. NO_X emissions from the road transport sector have not yet returned to pre Covid levels- the increase from 2020 to 2021 was less than 1 %.

Network average NO_3^- concentrations increased slightly from 0.16 mg l^{-1} (11.7 µeq l^{-1}) in 2021 to 0.17 mg l^{-1} (12.3 µeq l^{-1}) in 2022. At the national scale, total NO_X emissions are projected to decrease by about 2 % from 2021 to 2022.

A small decrease was observed for nns-SO_4^{2-} which decreased from 0.096 mg l^{-1} (6 µeq l^{-1}) in 2021 to 0.092 mg l^{-1} (5.7 µeq l^{-1}) in 2022. The total sulphur dioxide emissions were projected to decrease by about 3 %.

The nationalNH_3 emission is projected to increase very slightly from 2021 to 2022 (265.02 kt to 265.26 kt). There was an increase in the network NH_4^+ average from 0.22 mg l^{-1} (16.0 µeq l^{-1}) in 2021 to 0.25 mg l^{-1} (18.0 µeq l^{-1}) in 2022.

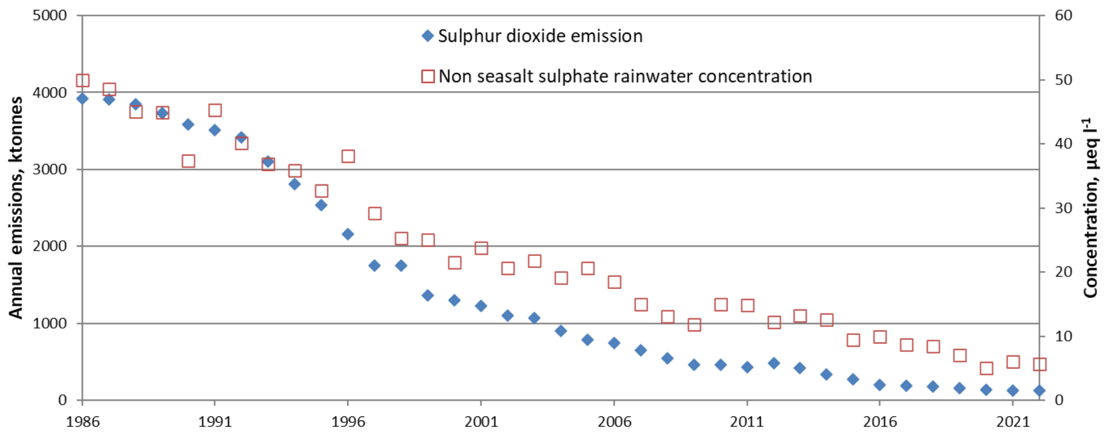


Figure 15 UK sulphur dioxide emissions and network average sulphate concentrations in rainwater

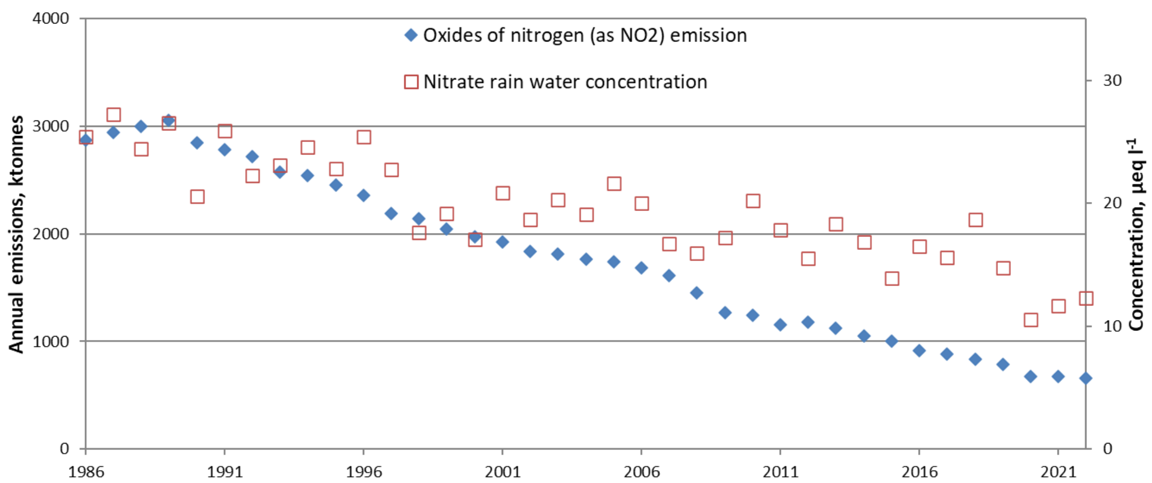


Figure 16 UK oxides of nitrogen emissions and network average nitrate concentrations in rainwater

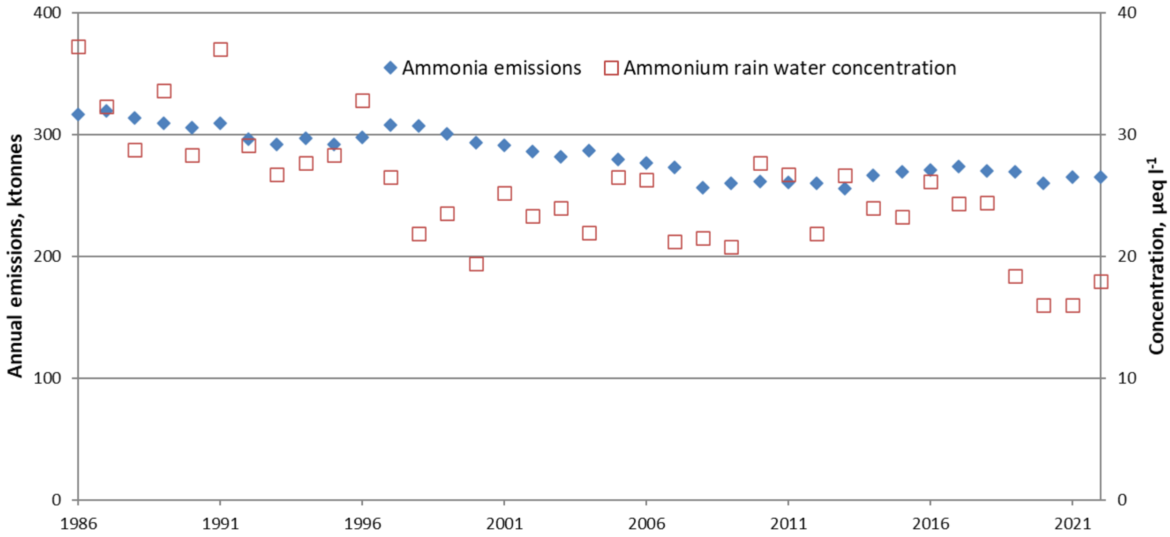


Figure 17 UK ammonia emissions and network average ammonium concentrations in rainwater

3.2 NO_2-Net Network

The mean data capture of the diffusion tubes for all of the site in 2022 was 96% with 18 of the 24 sites achieving > 90% and 17 sites achieving 100% data capture.

The lowest data capture was observed at Flatford Mill and was attributed to lost tubes and local site operation issues causing the 78% 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 2022 NO_2 concentration from the Diffusion Tubes in the NO_2-Net

Site Name	Raw 2022 concentration (µg m^{-3})	2022 concentration (µg m^{-3}) Bias Corrected (0.943)[a]	Data capture	Site Name	Raw 2022 concentration (µg m^{-3})	2022 concentration (µg m^{-3}) Bias Corrected (0.943)[1]	Data capture
Allt a’Mharcaidh	0.65	0.62	100%	Llyn Llydaw	1.9	1.8	87%
Balquhidder 2	1.4	1.3	85%	Loch Dee	1.7	1.6	100%
Bannisdale Beck	3	2.8	85%	Lough Navar	1.3	1.2	100%
Chilbolton Observatory	7.7	7.1	100%	Lullington Heath	9.9	9.3	100%
Driby 2	6.1	5.8	92%	Moorhouse	2.2	2.1	100%
Eskdalemuir	1.6	1.6	100%	Percy’s Cross	2.9	2.7	100%

Site Name	Raw 2022 concentration (µg m⁻³)	2022 concentration (µg m⁻³) Bias Corrected (0.943)[a]	Data capture	Site Name	Raw 2022 concentration (µg m⁻³)	2022 concentration (µg m⁻³) Bias Corrected (0.943)[1]	Data capture
Flatford Mill	7.9	7.4	78%	Polloch	0.52	0.49	100%
Forsinard RSPB	0.98	0.92	88%	Pumlumon	1.8	1.7	100%
Glensaugh	2.4	2.3	100%	Strathvaich	0.42	0.39	100%
Goonhilly	3.6	3.4	100%	Tycanol Wood	2.6	2.4	100%
High Muffles	3.8	4.3	100%	Whiteadder	2.1	2	100%
Hillsborough Forest	5.1	4.8	87%	Yarner Wood	3.1	3.1	100%

[a] All sites bias adjusted by 0.943 with the exception of Chilbolton Observatory, High Muffles and Yarner Wood were corrected using co-located samplers, See appendix for details.

[b] bias adjusted using collocated automatic analyser. See appendix for details.

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.

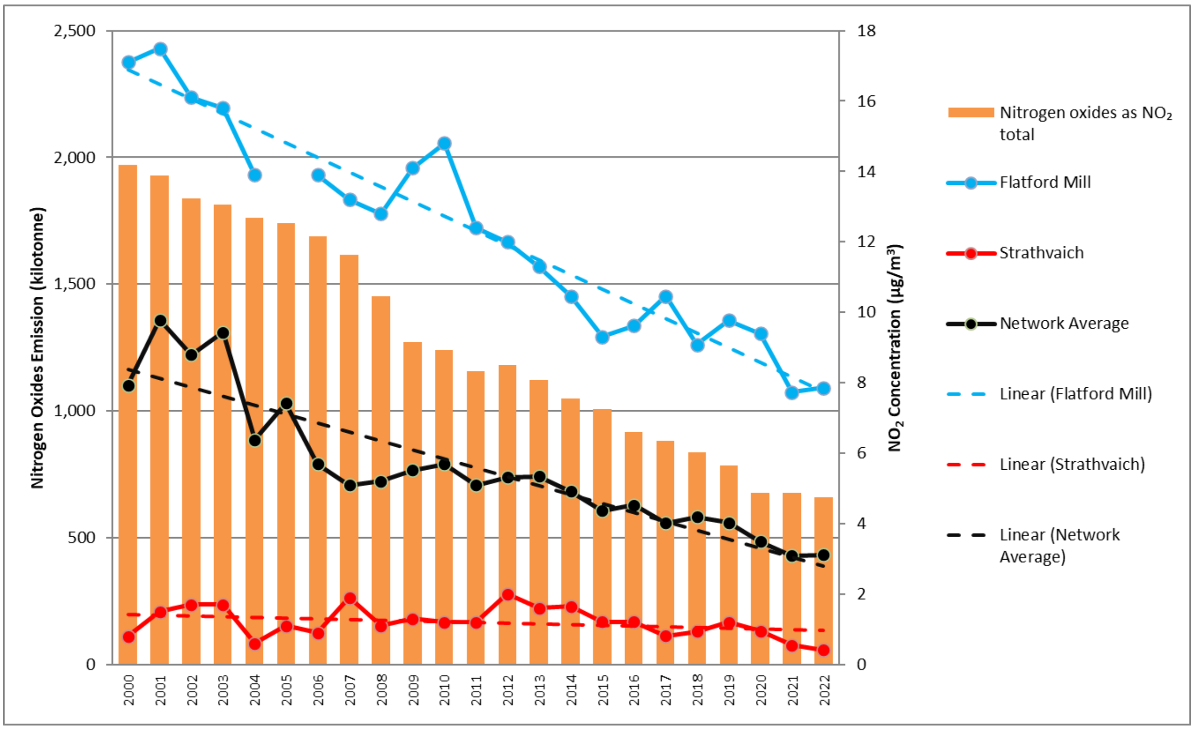


Figure 18 Long term trends where estimated emissions are plotted against selected sites in the network

The annual average uncorrected NO_2 concentrations from 2010-2022 (Figure 19) 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.

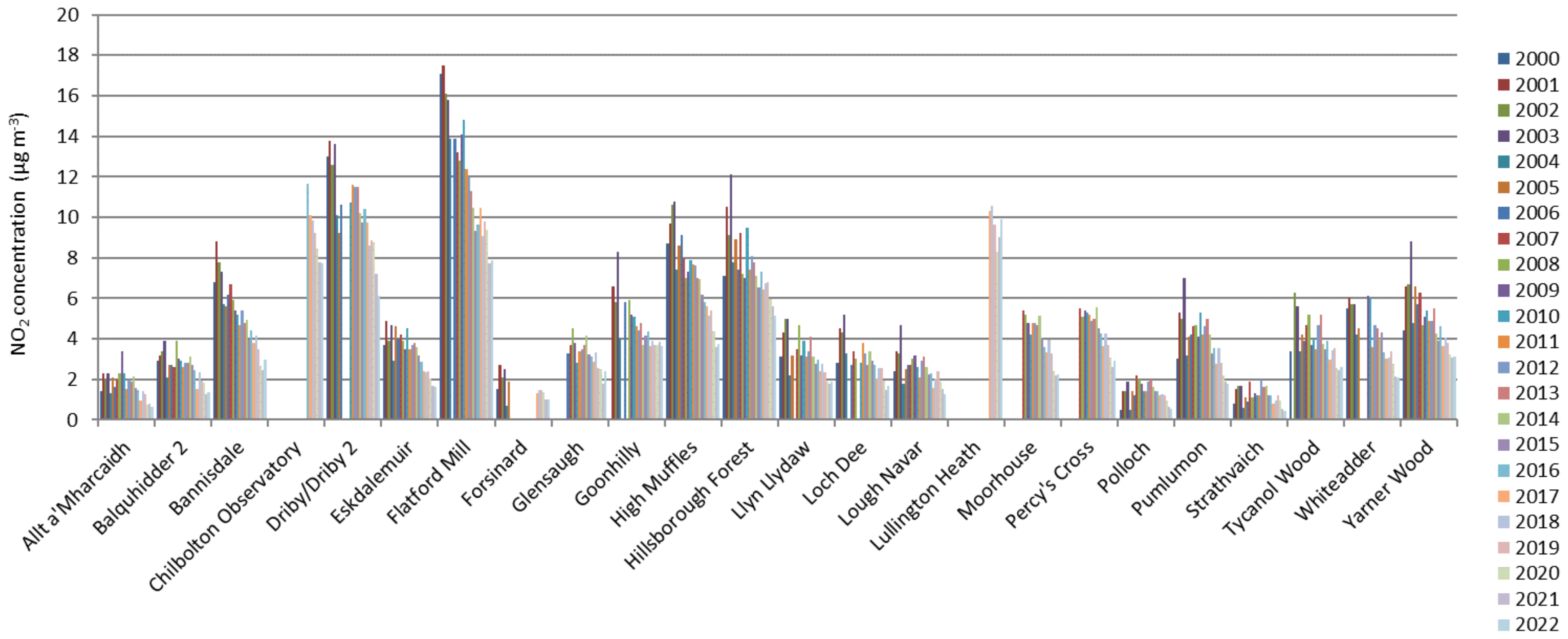


Figure 19 Annual mean NO_2 concentration (µg m^{-3}) at the NO_2-Net sites 2000-2022

3.3 National Ammonia Monitoring Network (NAMN)

NAMN Performance and Data capture

Figure 20 contains the average percentage data capture across all sites for each chemical of interest. Average data capture was 79% for NAMN.

UKCEH ALPHA® Sampler

Data capture at UKCEH ALPHA® sites was 93% in 2022. 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 2022.

UKCEH DELTA® Sampler

Data capture across UKCEH DELTA® systems was 66% in 2022. Data capture losses were primarily due to:

- Flow issues which are picked up during the first stage quality assurance and scheduling of operational field repairs. A modified system will be implemented in 2023.
- 2% DELTA data capture losses attributed to issues during transport in 2022 (note that this has been reduced from 14% in 2021 by use of new transport cases)

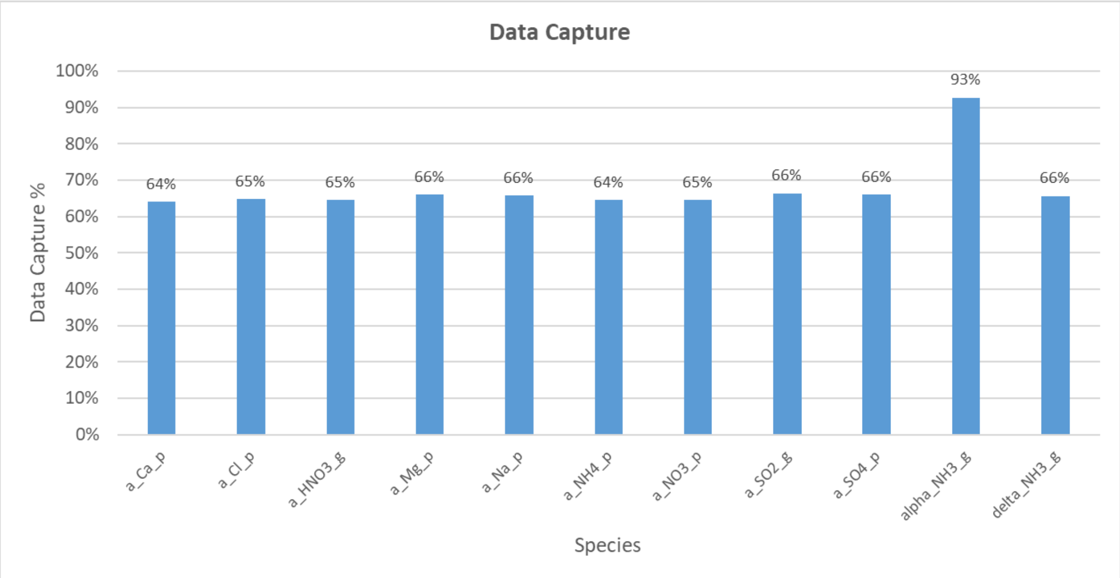
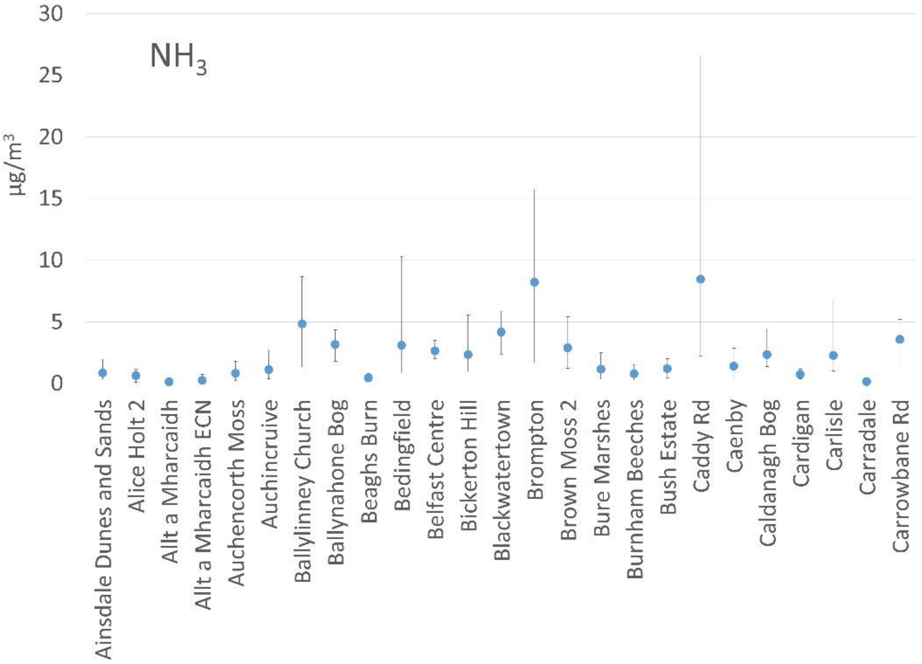


Figure 20 NAMN and AGANet percentage data capture by chemical component in 2022

NAMN Network Trends

The 2022 annual average NH_3 concentrations observed at each site in NAMN is presented in Figure 21 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 and the eastern side of England (Brompton, Caddy Rd, Drumclamph, Inch Abbey, Lisbellaw, Ratarnat Rd, U of Ulster Met station. refer to Figure 21.

Historical changes in the annual average NH_3 concentrations can be seen in Figure 22. The annual average across the network is similar to the range previously reported across the period. It is noted that maximum reported concentration had increased compared to the period 2015 to 2020, however this is attributed to new sites in Northern Ireland which have reported the largest monthly averages concentrations.



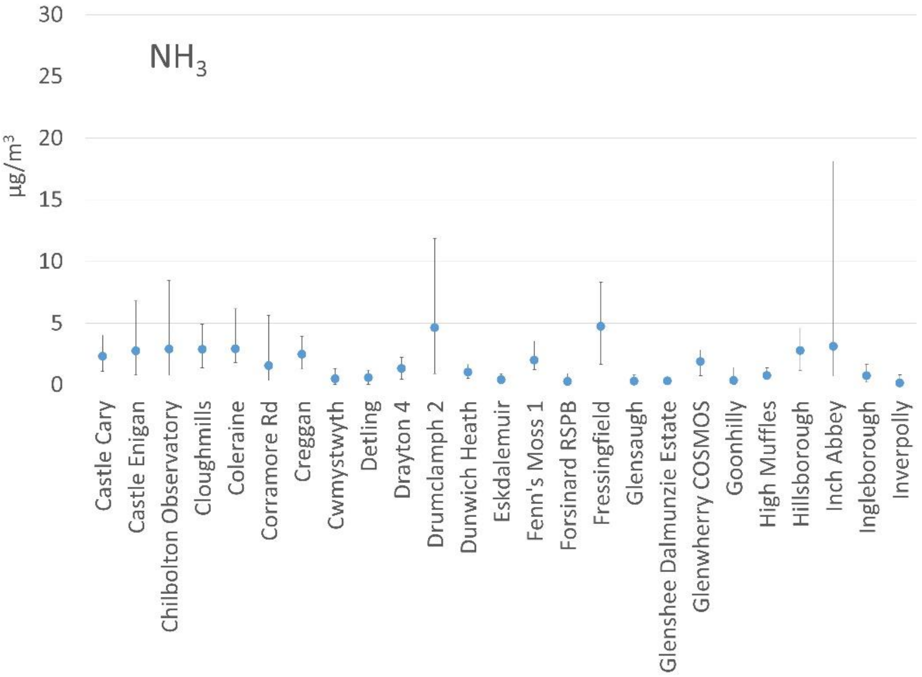
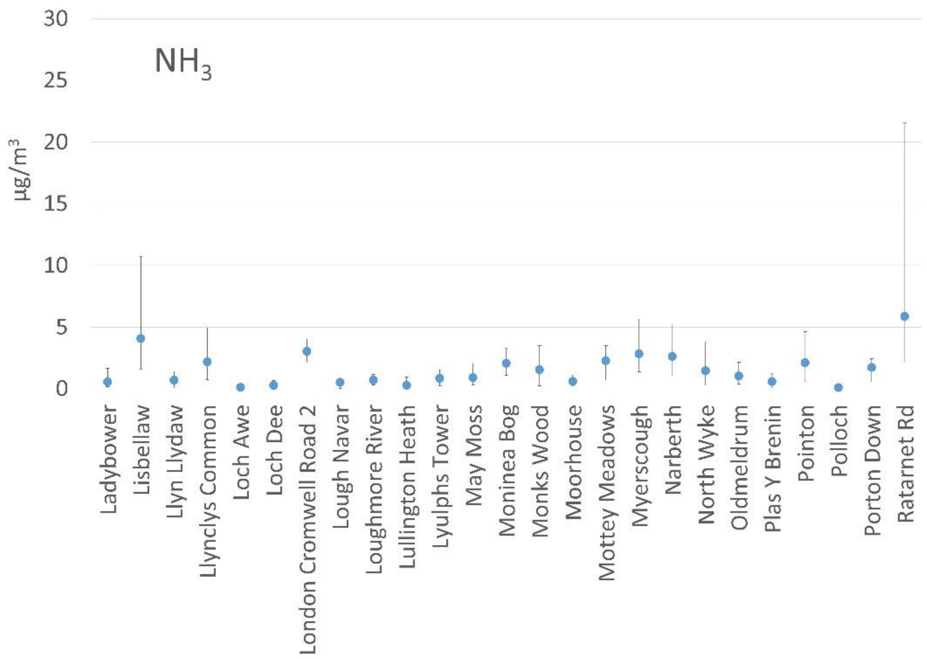


Figure 21 Annual mean concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentrations observed.



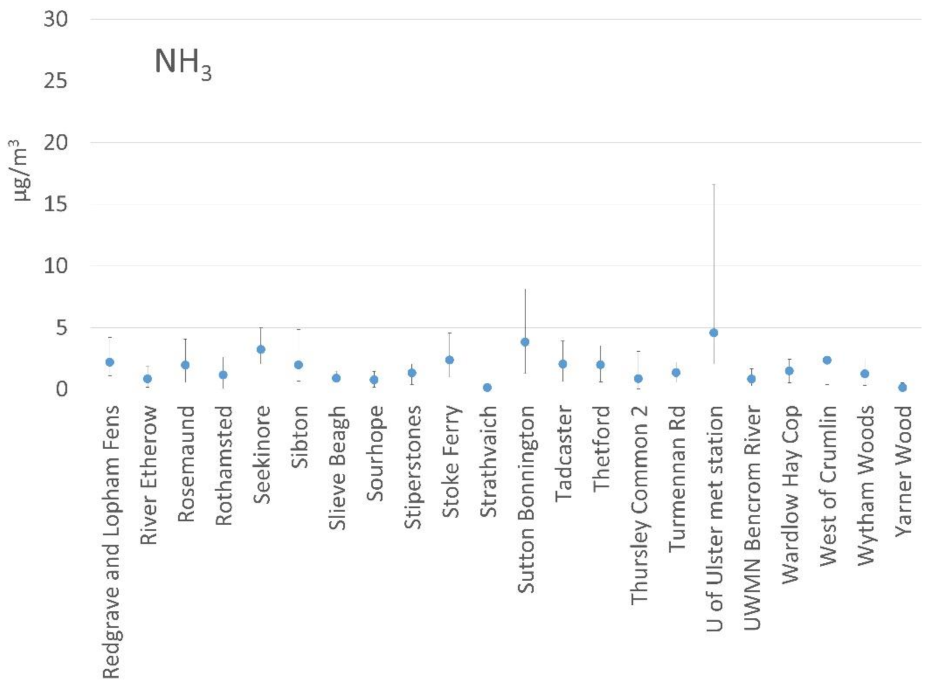


Figure 21 contd. Annual mean concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentrations observed.

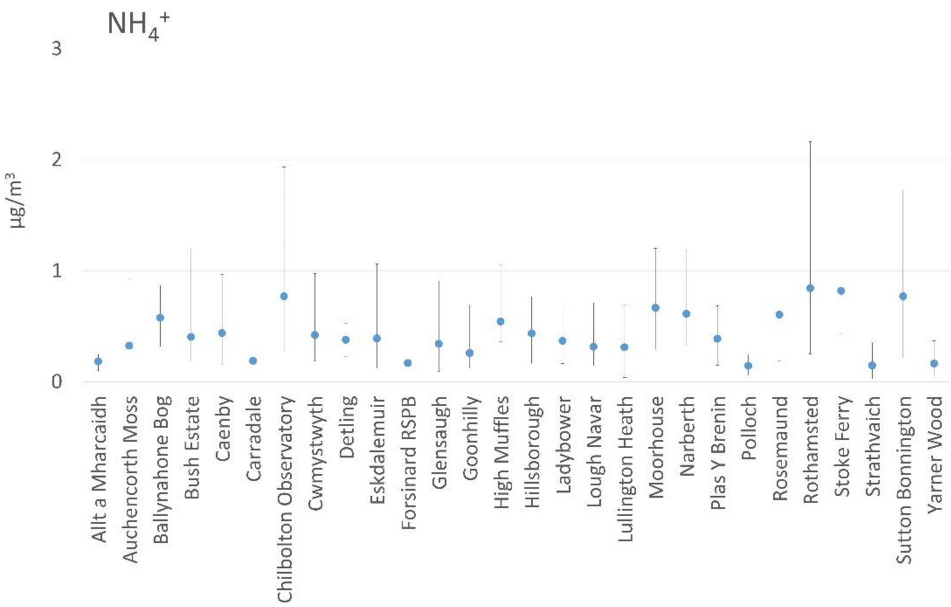


Figure 21 contd Annual mean concentrations of NH_4^+ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentrations observed.

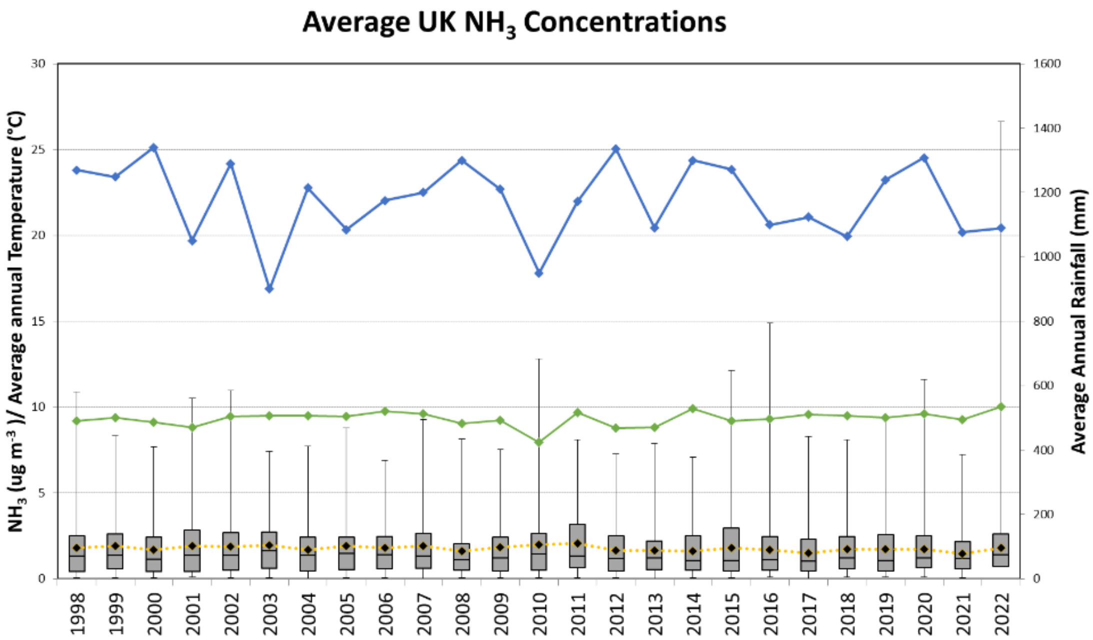


Figure 22 Changes in atmospheric NH_3 averaged over all sites in NAMN operational between 1998 and 2022 summarised in a box plot. The whiskers show the absolute max and min and the diamond is the mean annual concentration. Meteorological data is also displayed for comparison. The green line is the average 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 23. For NH_3, lower concentrations (green markers), as previously stated, are primarily located in the North of Scotland, with some locations in the south coast of England. Similarly NH_4^+ concentrations are lowest in northern England and Scotland, and highest on the eastern side of England. High ammonia air concentration values are also observed across the south and north-east of Northern Ireland.

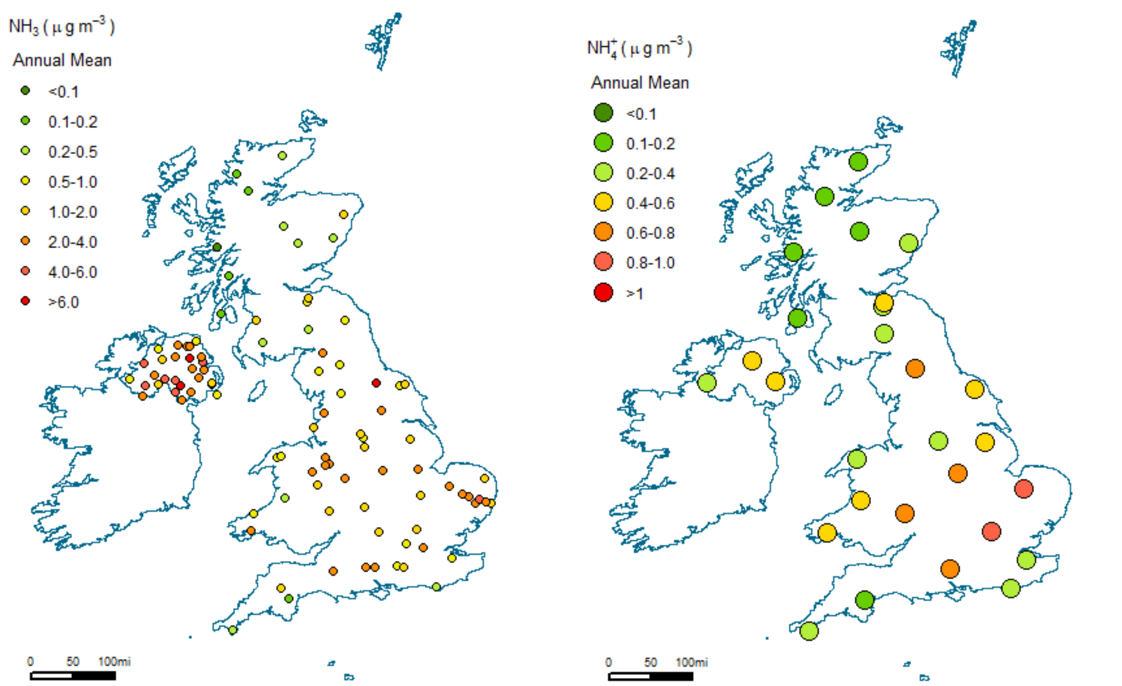


Figure 23 Spatial patterns of annual NH_3 and aerosol NH_4^+ concentrations from monthly NAMN/AGANET measurements. Since February 2017, ammonium is measured at the 27 (28 from April 2022) AGANET sites only.

3.4 Acid Gas and Aerosol Network (AGANet)

AGANet Performance and Data capture

Figure 20 contains the average percentage data capture across all sites for each chemical of interest. The average data capture was 65% for AGANet (Figure 20).

Data capture losses were primarily due to:

- Flow issues which are picked up during the first stage quality assurance and scheduling of operational field repairs. A modified system will be implemented in 2023.
- 2% DELTA data capture losses attributed to issues during transport in 2022 (note that this has been reduced from 14% in 2021 by use of new transport cases)

AGANet Network Trends

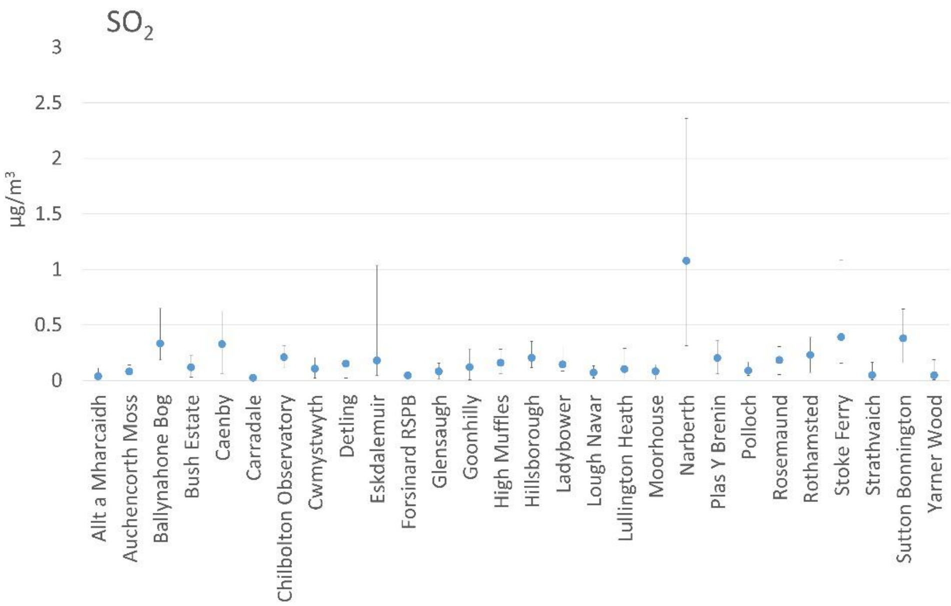
Figure 24 presents the annual average concentrations, with the minimum and maximum of SO_2 and HNO_3 reported at the sites within AGANet. For SO_2 and HNO_3 Eskdalemuir, Narberth and Stoke Ferry reported concentrations > 1 µg m^{-3} during the year. The spatial distribution of the annual average concentration for both species can be found in Figure 25, where it is observed that higher HNO_3 concentrations generally occur in the South-East of the UK.

Figure 26 shows the annual average, maximum and minimum of NO_3^-, SO_4^{2-}, NH_4^+ and Cl^- from each site during 2022 reported by AGANet. Like NH_4^+ in the NAMN network the lowest reported concentrations are from sites in the North of Scotland for NO_3^- (Figure 26 and Figure 27) and SO_4^{-2} (Figure 26 and Figure 27). For Cl^- (Figure 26 and Figure 27) and Na^+ (Figure 28 and Figure 29) there is a more distinct variability in the observed concentrations, with the south west 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 28 and Figure 29) as it is also found in sea salt, whereas Ca^{2+} concentrations are highly variable across the UK.

The long-term averages for AGANet are shown in Figure 30 to 31. It is observed for HNO_3 that the annual average concentration continues to fall, as has SO_2. Ammonia, on the other hand, still shows high inter-annual variability in the annual average with no obvious trend. Particulate NO_3^-, SO_4^{2-}, Ca^+ had a clear step change in 2016 with an increase in concentration which is attributed to the method change which resulted in increased capture of the components (refer to UKEAP annual report 2016 for further details[15]). Since this method change, a similar inter-annual variability is qualitatively 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 which continued in 2022. It is noted that there was a concurrent decrease in the 2021 and 2022 HNO_3, NO_2-Net NO_2 and Precip-Net nitrate levels (see Figures 18, 19 and 30). The data in 2023 will be reviewed to understand if this is a short-term variability or the beginning of a significant decrease. It is noted that there was a step change in Ca^{2+} in 2022, in reviewing the data it was determined that the source of the step change was due to high concentrations of Ca^{2+} at Stoke Ferry. In removing Stoke Ferry from the annual average it is seen that a similar magnitude to previous years is observed (Figure 32).

Figure 33 compares the annual seasonal cycle (monthly averages) in 2022 compared to previous years for selected species in NAMN and AGNet. In general, the species follow similar temporal patterns. Ammonia though it follows a similar temporal profile to previous years, it is noted that in August 2022 the concentration is above the long term average standard deviation. Nitric acid did not follow the long-term temporal pattern, as it appeared to have a clear increase in concentration in March and the summer of 2022 and the year was below the standard deviation of the long-term trend. Caution is given in over interpretation of the results due to the low data capture in 2022 and interannual variability.



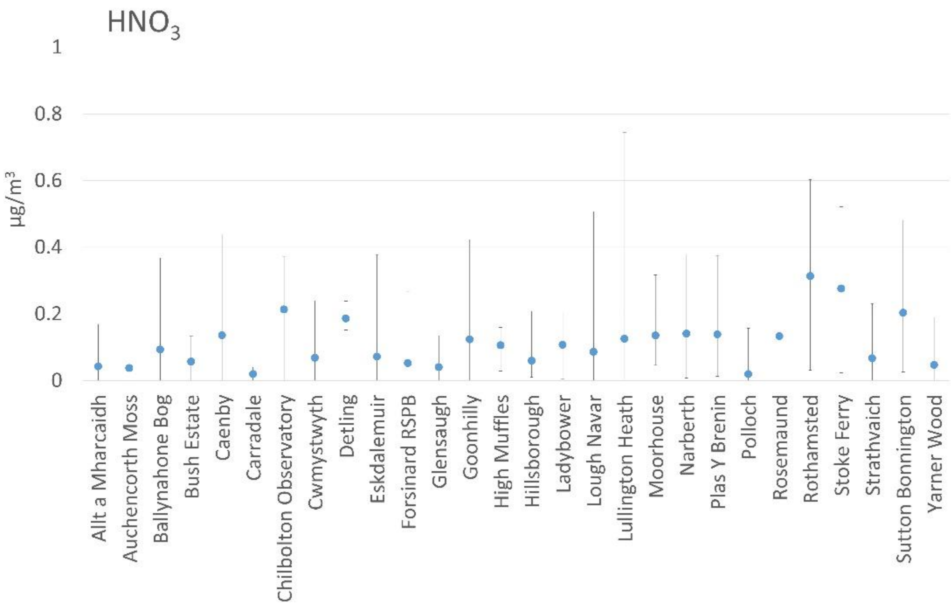


Figure 24 Mean monitored annual concentrations of gaseous HNO_3 and SO_2 at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentration observed.

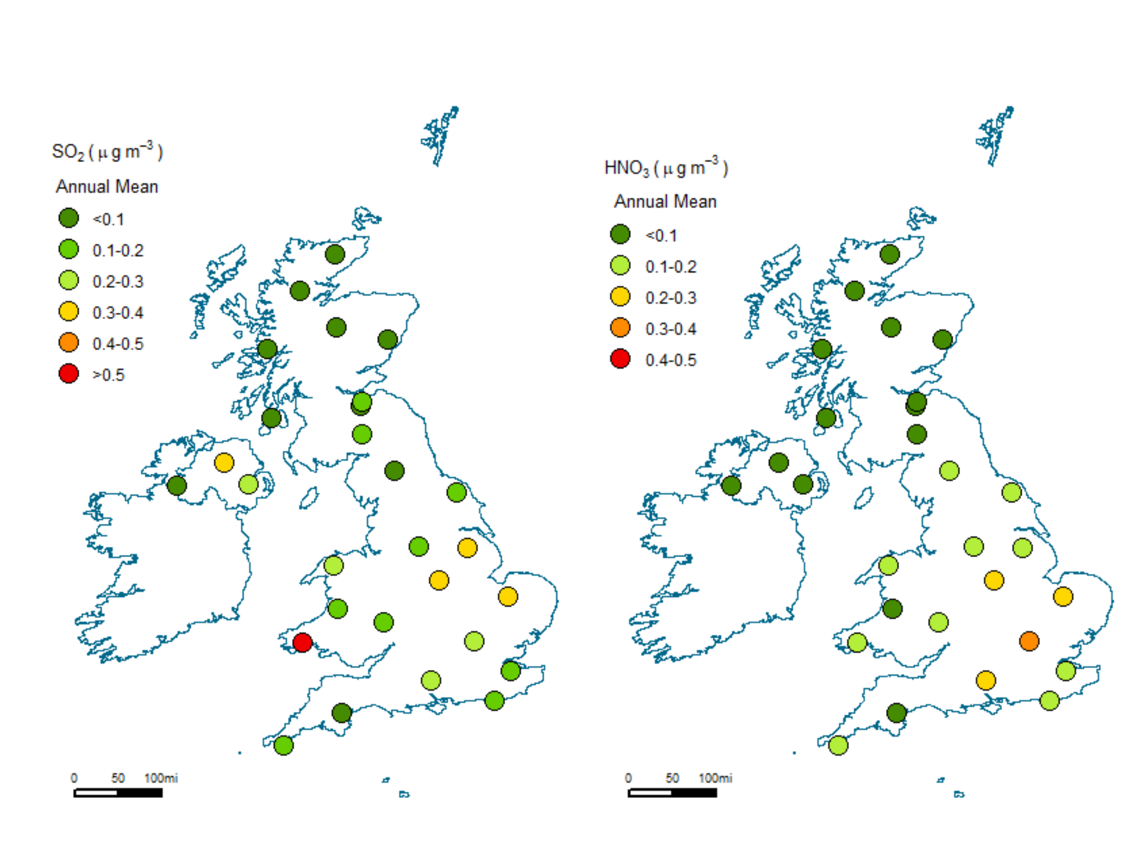
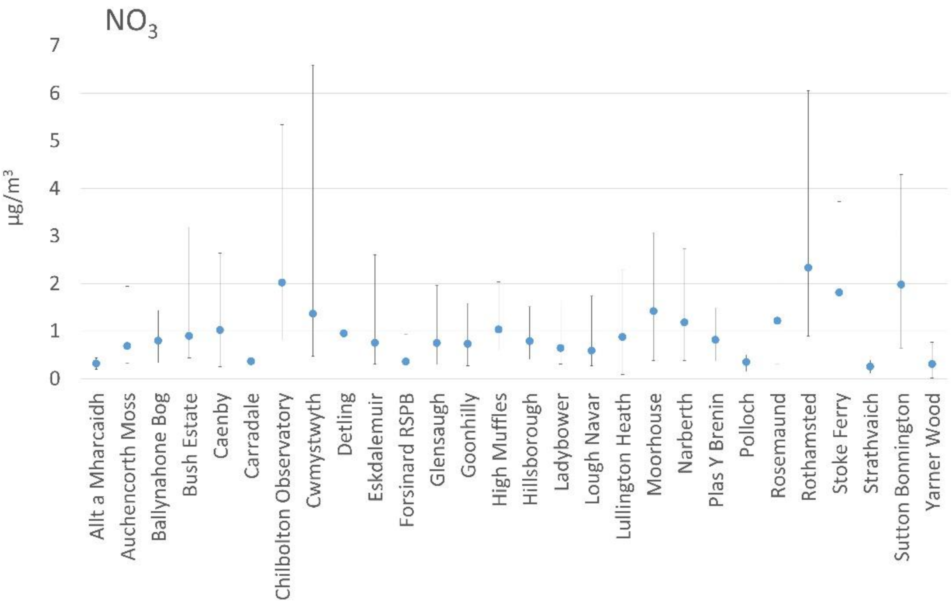


Figure 25 The annual average concentration of HNO_3 and SO_2 across the UK measured by AGANet in 2022.



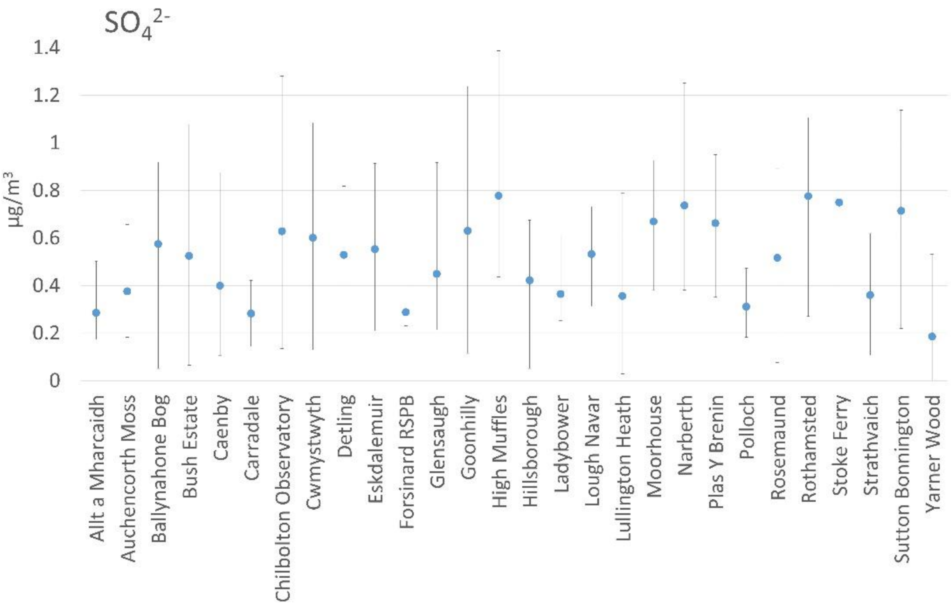
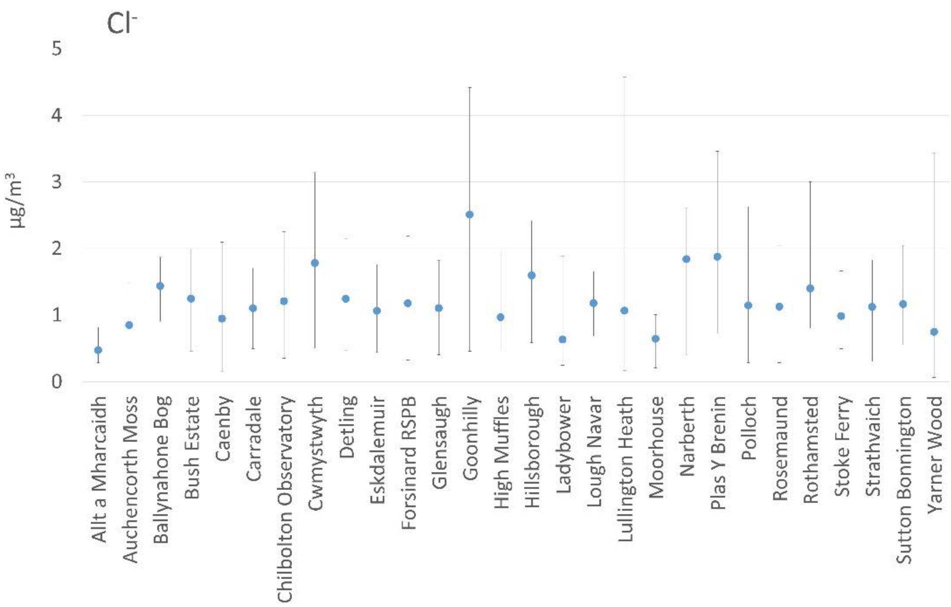


Figure 26 Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-} , Cl^- and NH_4^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentrations observed



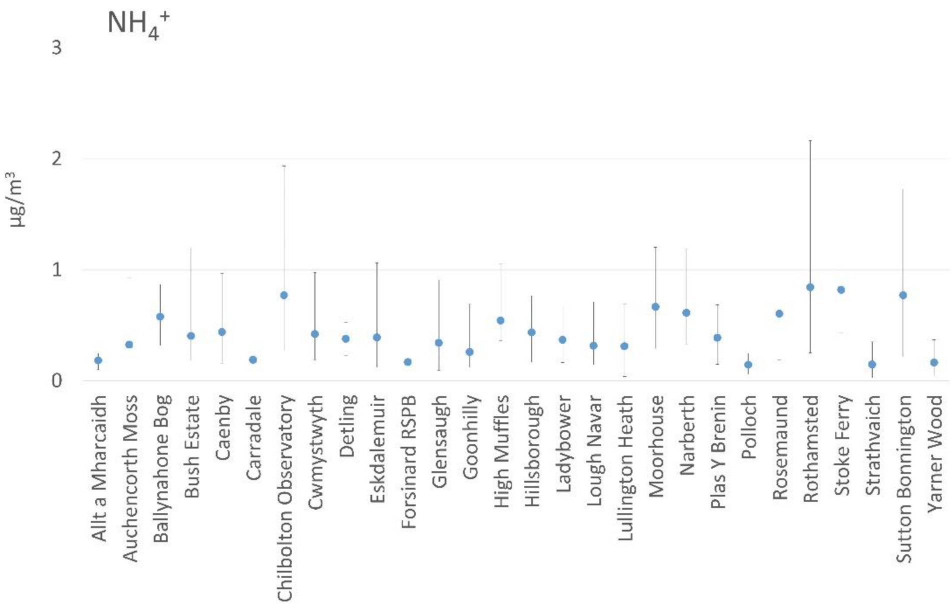


Figure 26 continued. Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-} , Cl^- and NH_4^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentrations observed

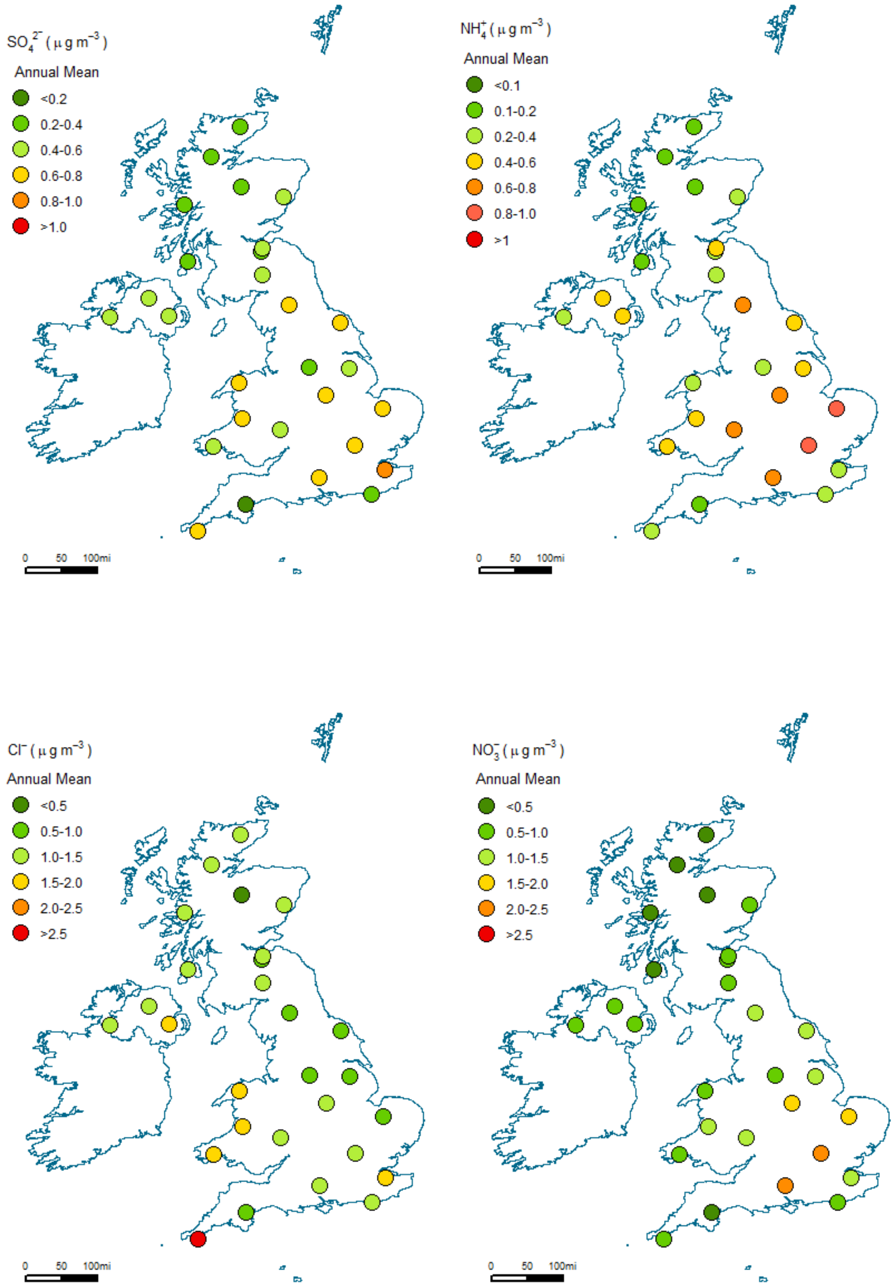


Figure 27 Annual average concentrations of NO_3^-, SO_4^{2-}, and Cl+ from AGANet and NH_4^+ from NAMN during 2022.

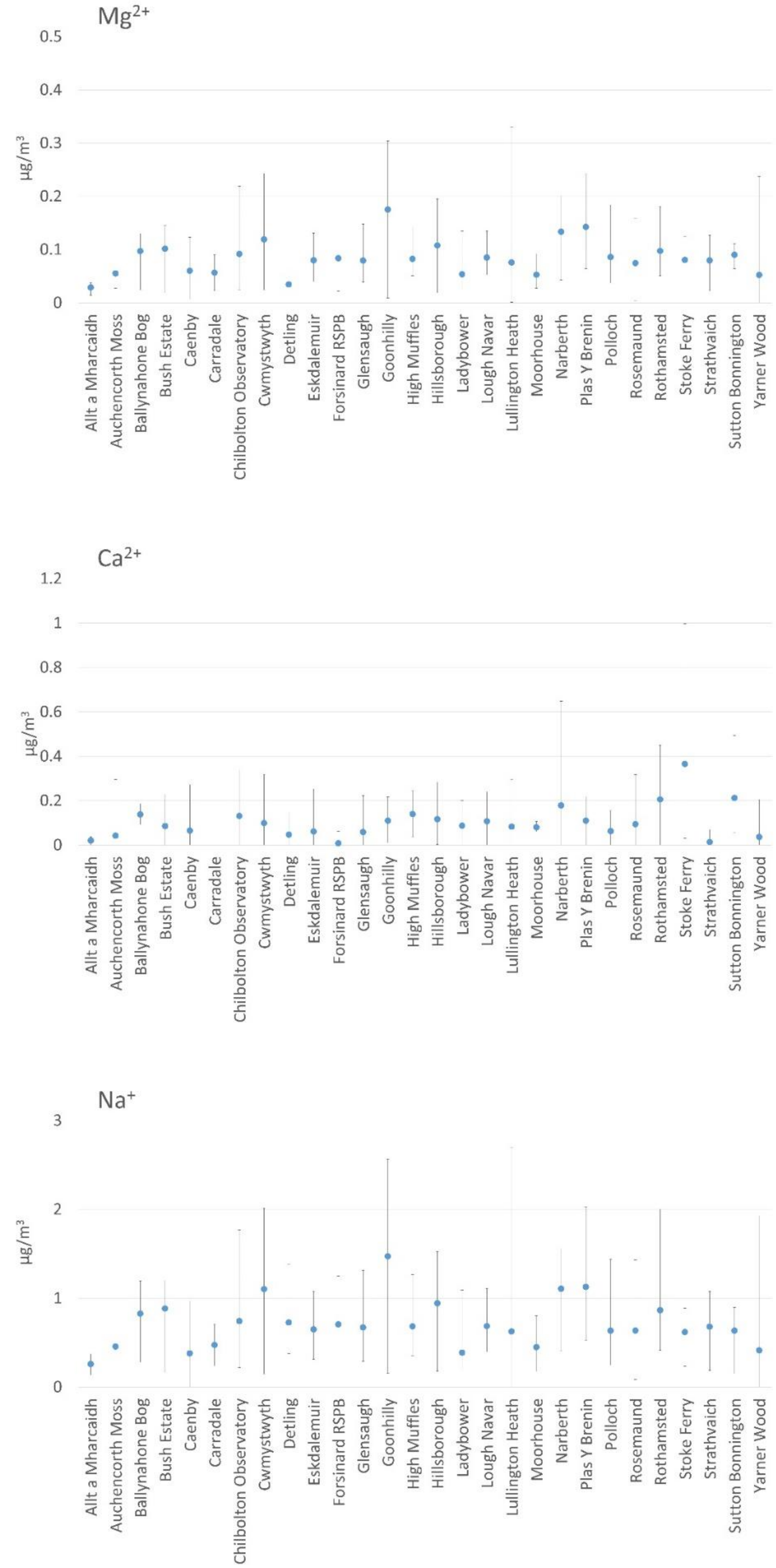


Figure 28 Mean monitored annual concentrations of particulate Mg, Ca and Na at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2022, whilst the bars show the minimum and maximum concentration

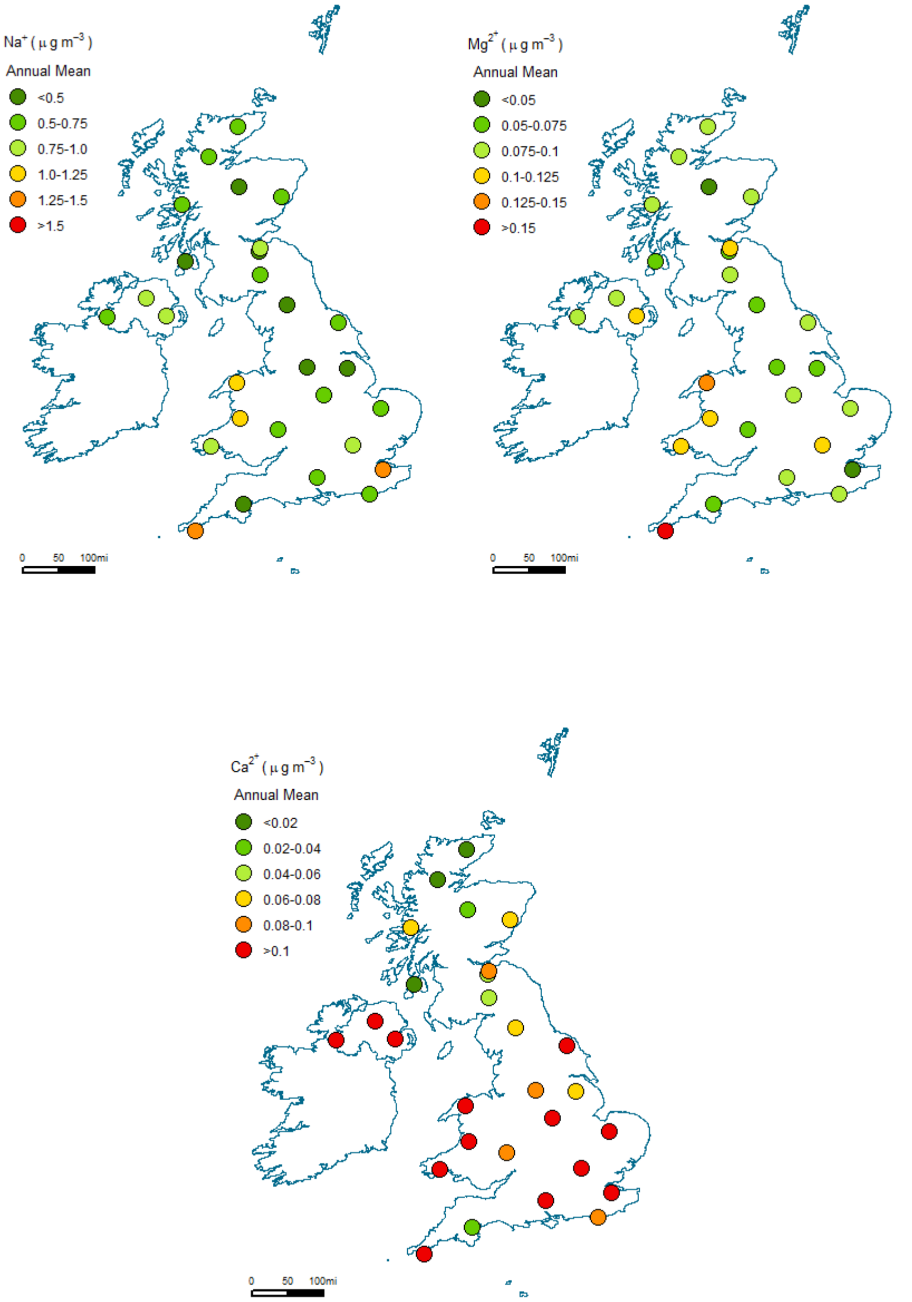


Figure 29 Annual mean monitored atmospheric base cations (Ca^{2+}, Mg^{2+} and Na^{+}) concentrations across the UK from the average monthly measurements made in 2022.

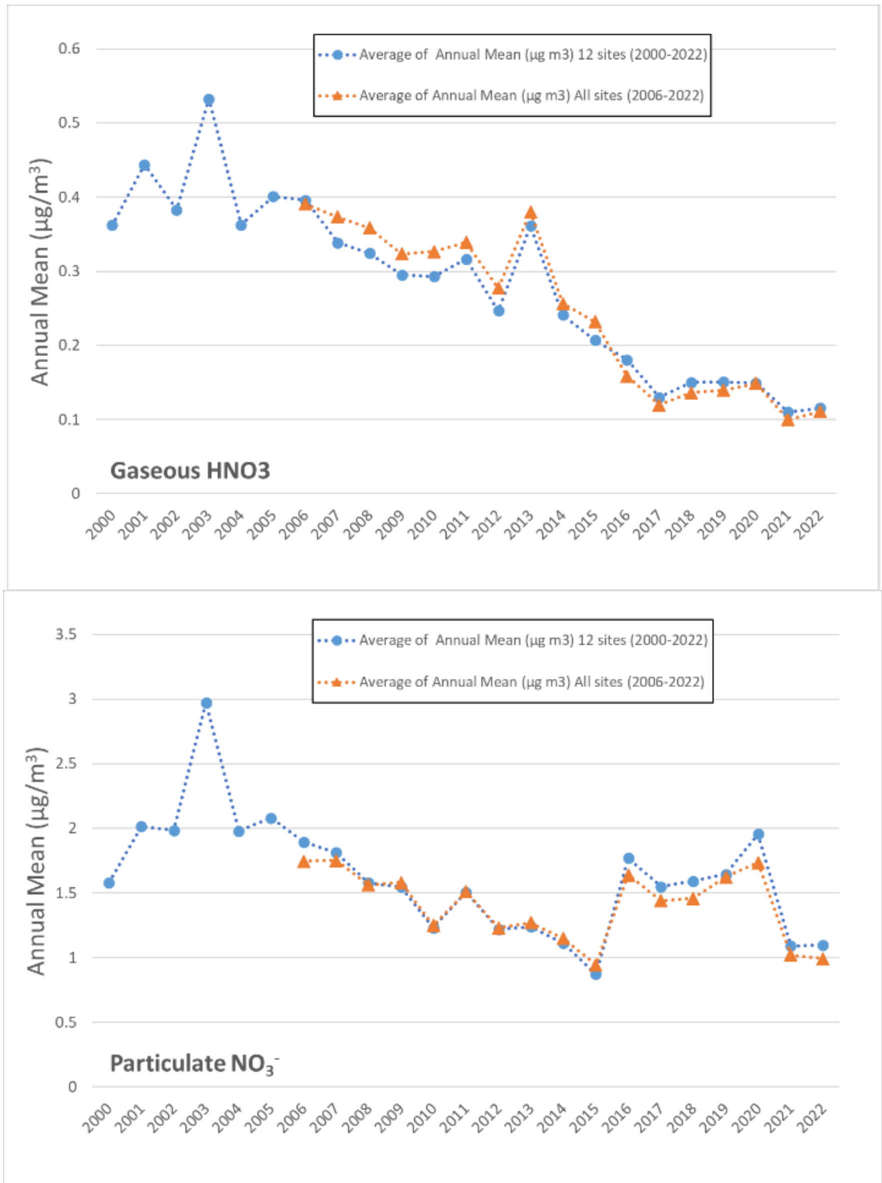
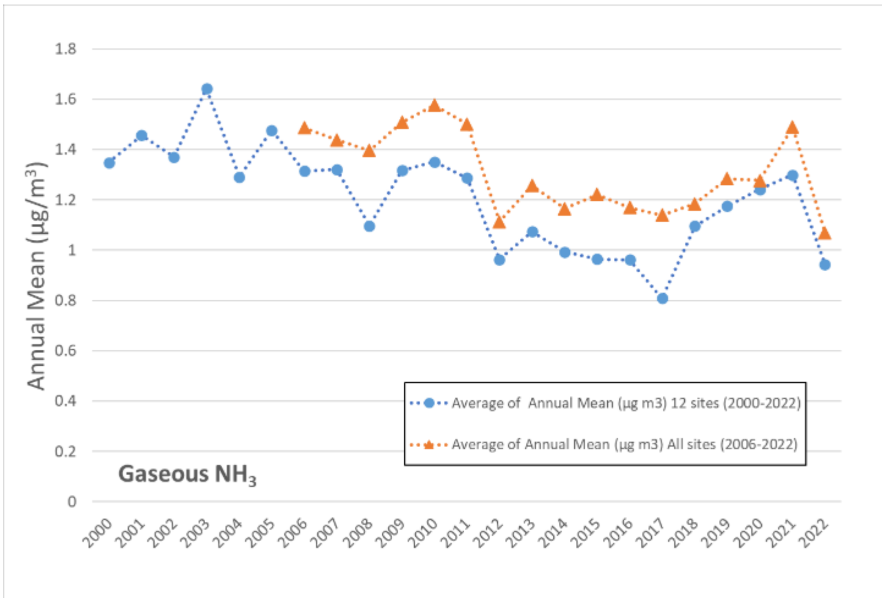


Figure 30 Long-term trend in annual mean concentrations of HNO_3, NH_3, SO_2, NO_3^-, NH_4^+ and SO_4^{2-} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original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



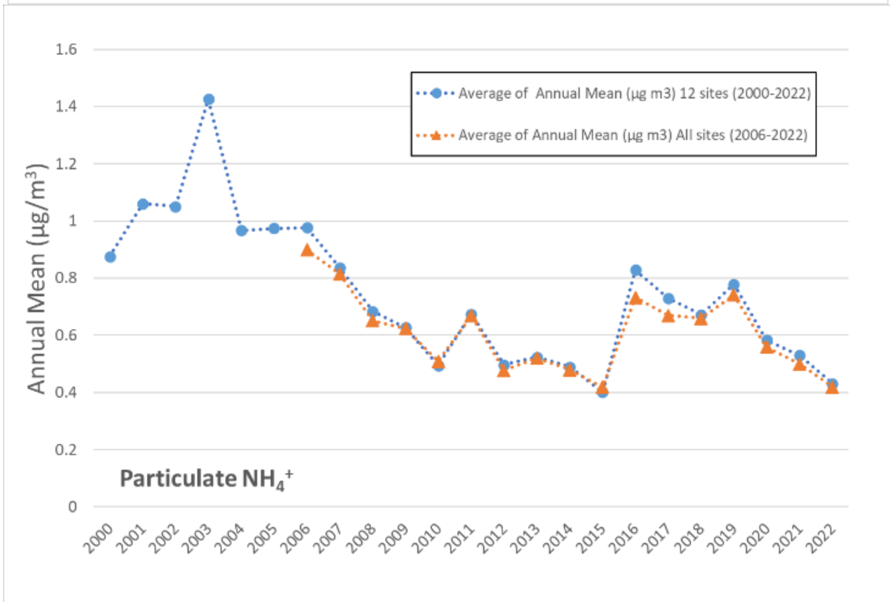
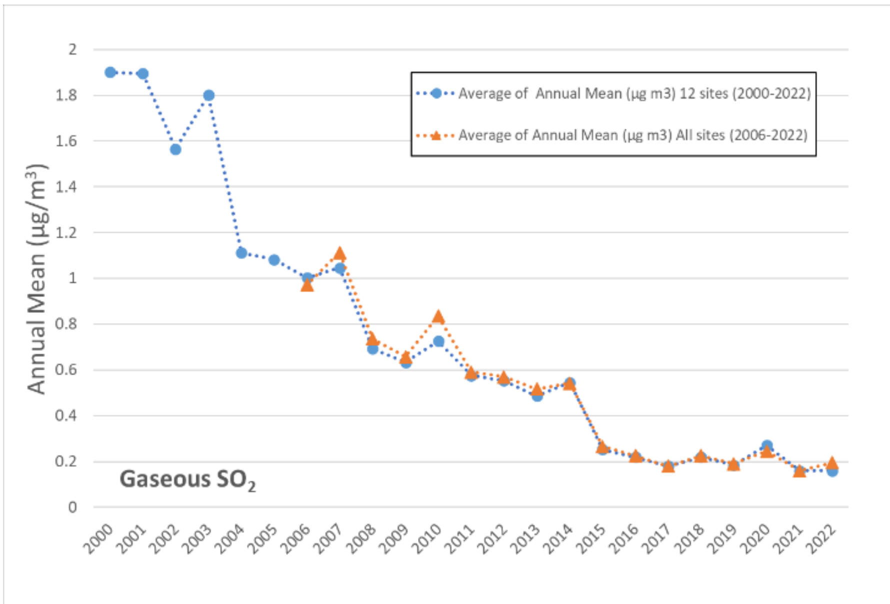


Figure 30 contd. Long-term trend in annual mean concentrations of HNO_3, NH_3, SO_2, NO_3^-, NH_4^+ and SO_4^{2-} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the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



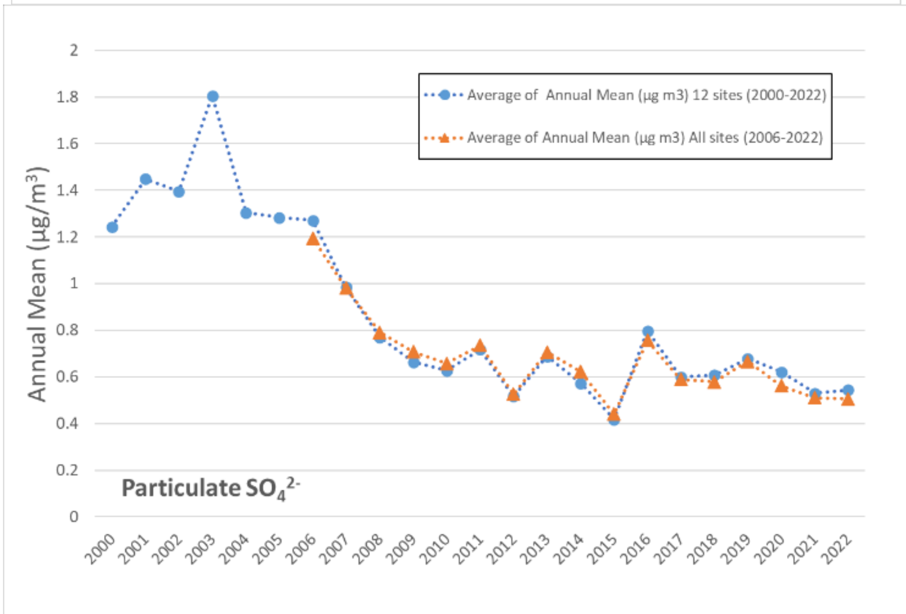


Figure 30 contd. Long-term trend in annual mean concentrations of HNO_3, NH_3, SO_2, NO_3^-, NH_4^+ and SO_4^{2-} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the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

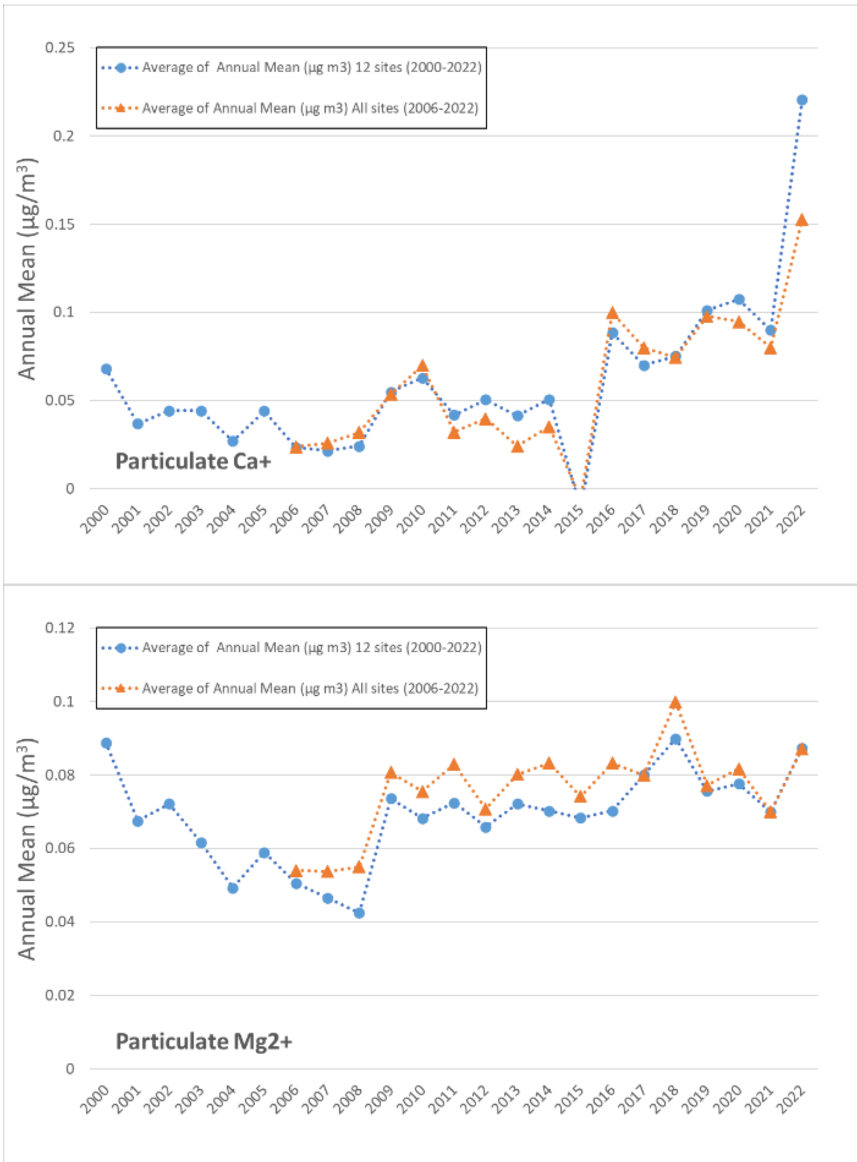
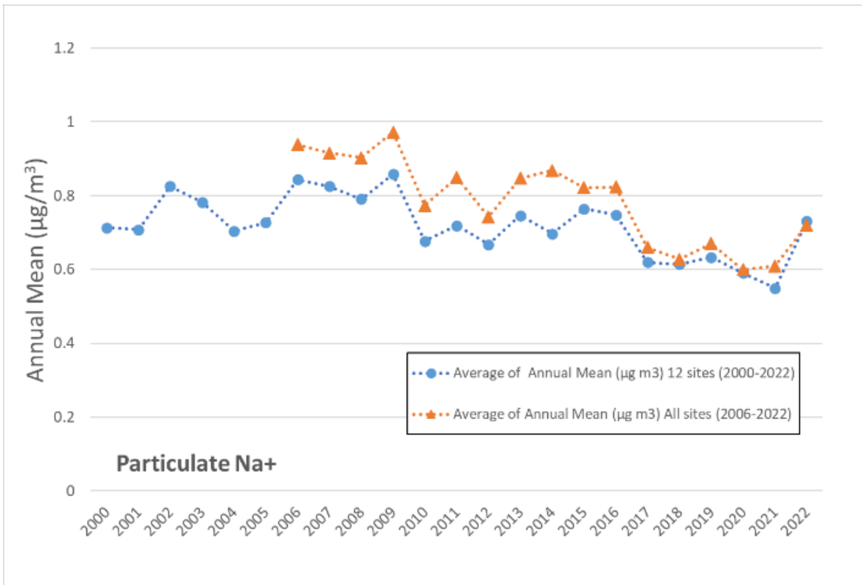


Figure 31 Long-term trend in annual mean concentrations of Ca^{2+}, Mg^{2+}, Na^{+} and Ca^{2+} monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.



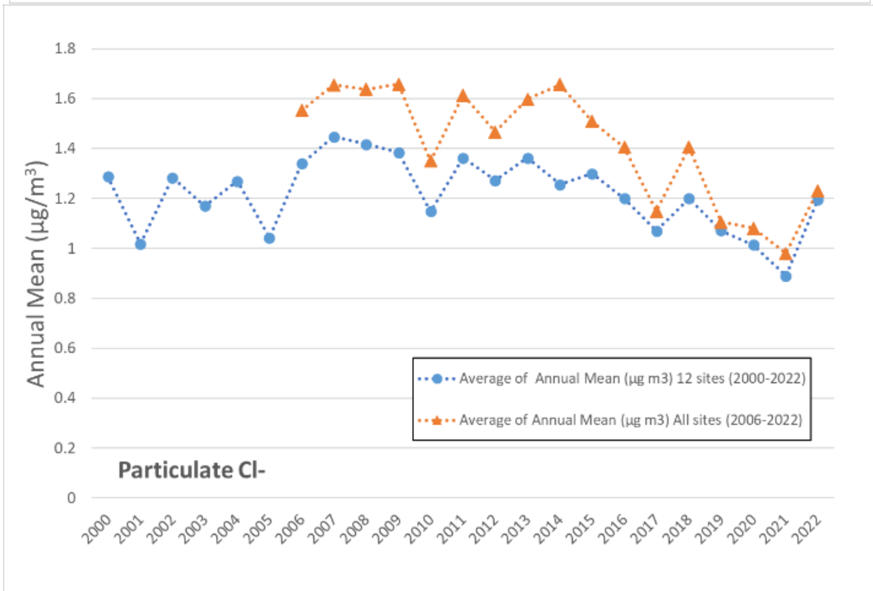


Figure 31 contd. Long-term trend in annual mean concentrations of Ca2+, Mg2+, Na+ and Ca2+ monitored in AGANET. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.

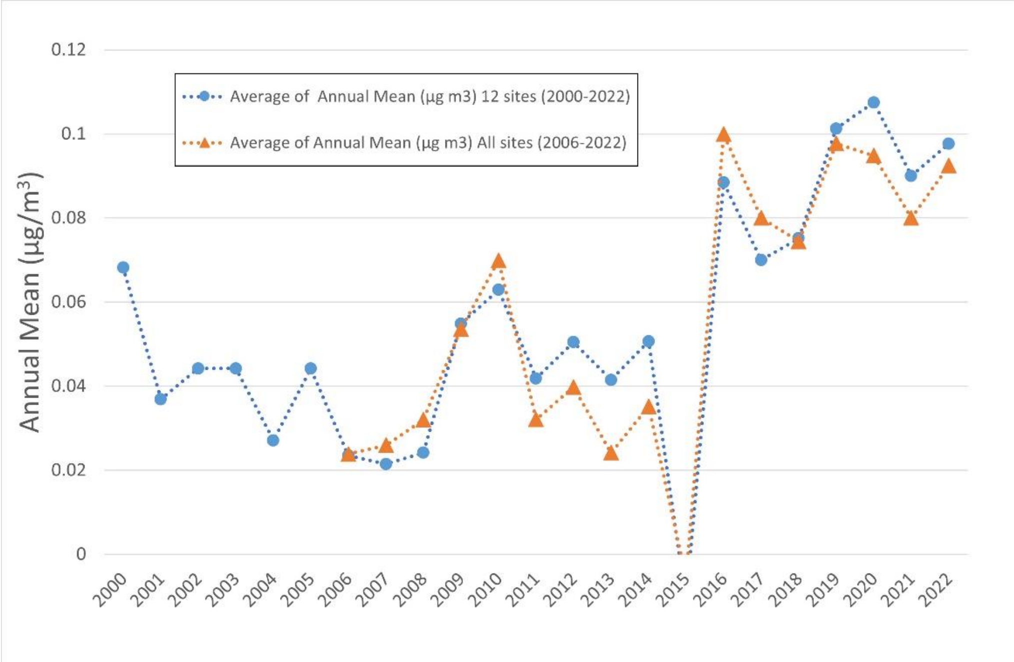


Figure 32 Long-term trend in annual mean concentrations of Ca^{2+} in AGANET, excluding Stoke Ferry. Each data point represents the time-weighted average annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites, from April 2022 =28 sites) and also the original 12 monitoring sites in the network.

Figure 33 Monthly average of selected species from the NAMN and AGANet sites across the UK in 2022 (blue line), compared to the mean seasonal profile for year 2000-2022 (orange line). Error bars are +/- standard deviation across the 27 AGANET sites (from April 2022 28 sites) in 2022.

3.5 UK EMEP supersites

3.5.1 MARGA

During the year 2022, both sites met the minimum data capture of 14% required under the UK regulations for speciated $PM_{2.5}$ (refer to Table 6 for data capture).

At Chilbolton Observatory during 2022 the data capture was affected by the following operational issues:

- Denude seals March 2022
- faulty cation and anion columns

Table 6 Summary of the ratified speciated PM10 and PM2.5 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^+	0.961	78.09	0.396	88.50
Na^+	0.764	78.07	0.503	83.21
K^+	0.083	78.03	0.037	90.43
Ca^{2+}	0.157	77.85	0.052	86.42
Mg^{2+}	0.110	77.95	0.068	90.43
Cl^-	1.597	79.41	1.001	85.59
NO_3^-	2.798	79.35	0.858	91.39
SO_4^{2-}	1.320	79.35	0.631	91.39
Ion ($PM_{2.5}$)	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_4^+	0.744	69.93	0.360	89.25
Na^+	0.350	69.97	0.285	83.81
K^+	0.061	69.83	0.020	90.35
Ca^{2+}	0.046	69.76	0.026	88.17
Mg^{2+}	0.054	69.83	0.037	90.34
Cl^-	0.821	72.79	0.557	88.89
NO_3^-	1.936	72.68	0.699	90.83
SO_4^{2-}	1.043	72.36	0.552	90.83
Trace Gases	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_3	3.897	85.35	1.333	91.82
HCl	0.038	86.27	0.139	87.21
HNO_3	0.142	86.28	0.071	92.96
HONO	0.402	86.38	0.066	92.96
SO_2	0.094	86.38	0.053	92.96

Figure 34 to Figure 39 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 2022.

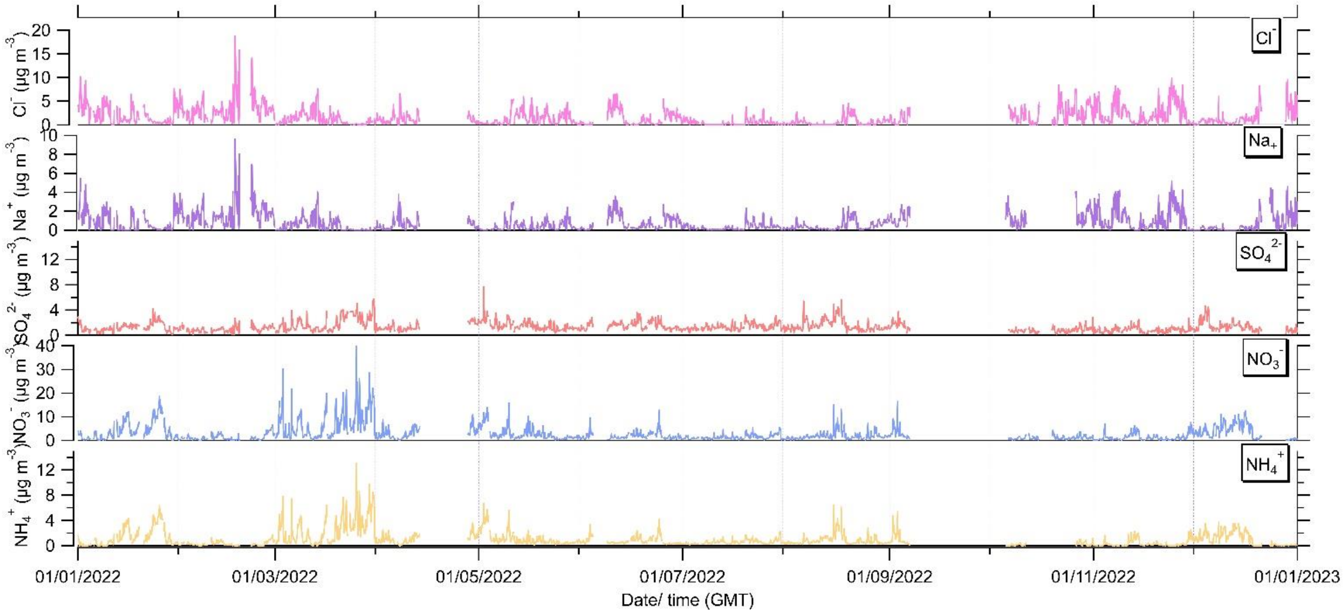


Figure 34 Ratified PM_{10} speciated measurements by the MARGA at the Chilbolton Observatory supersite

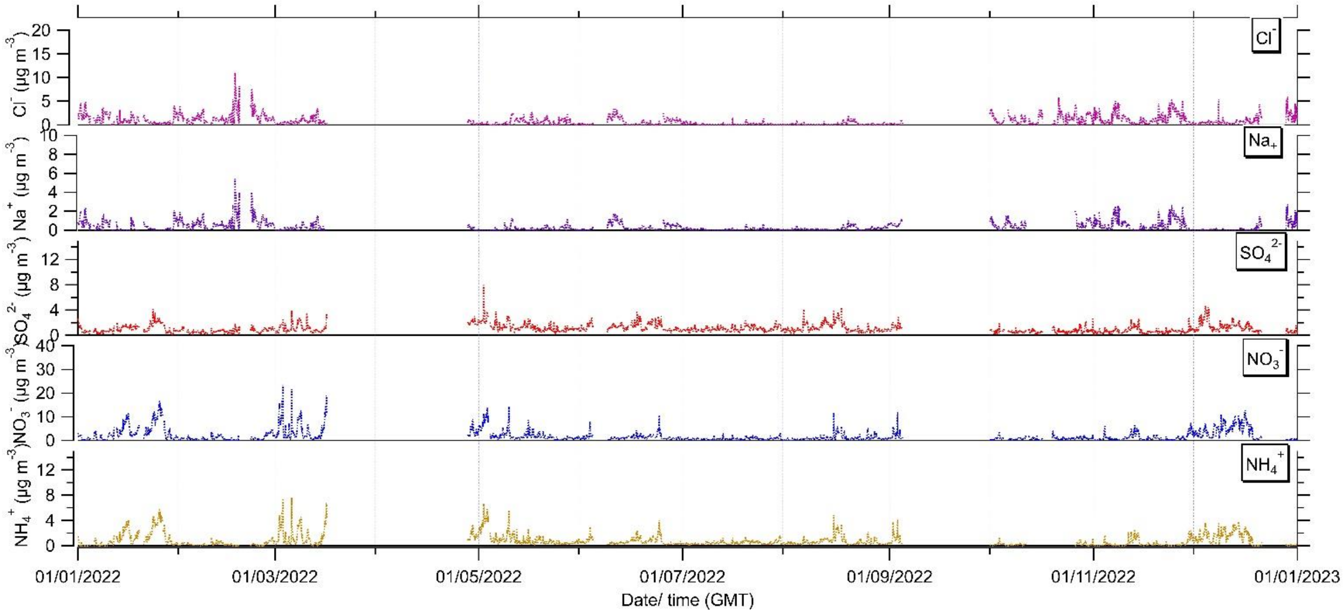


Figure 35 Ratified $PM_{2.5}$ speciated measurements by the MARGA at the Chilbolton Observatory supersite

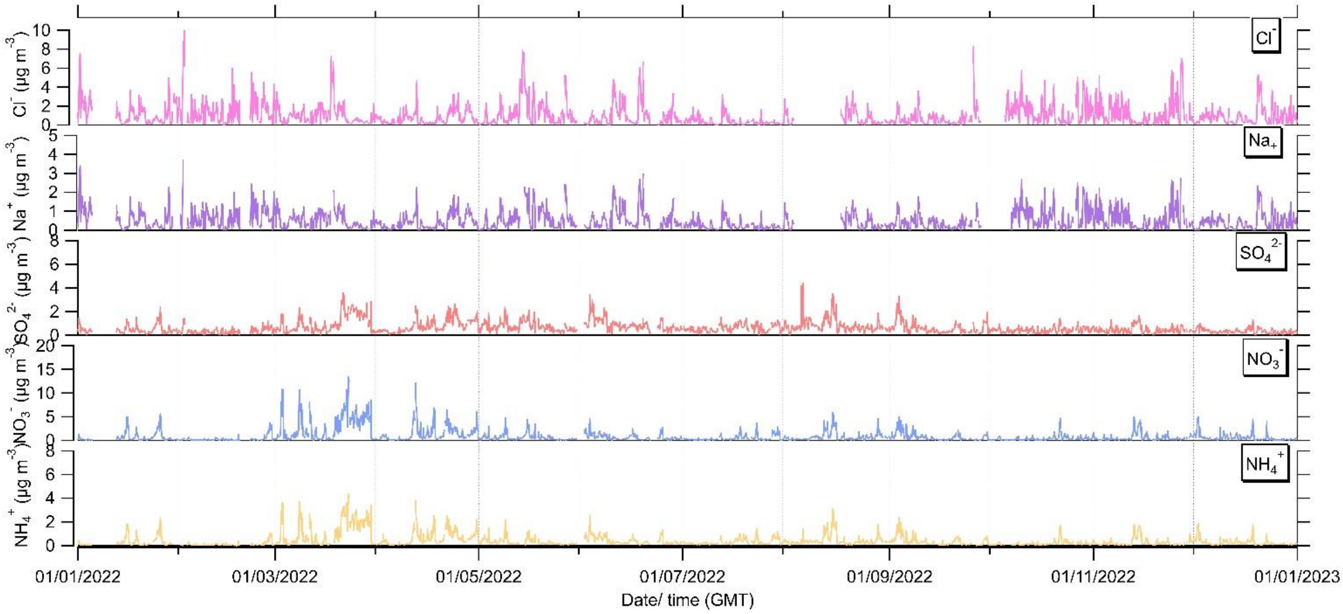


Figure 36 Ratified PM_{10} speciated measurements by the MARGA at the Auchencorth Moss supersite

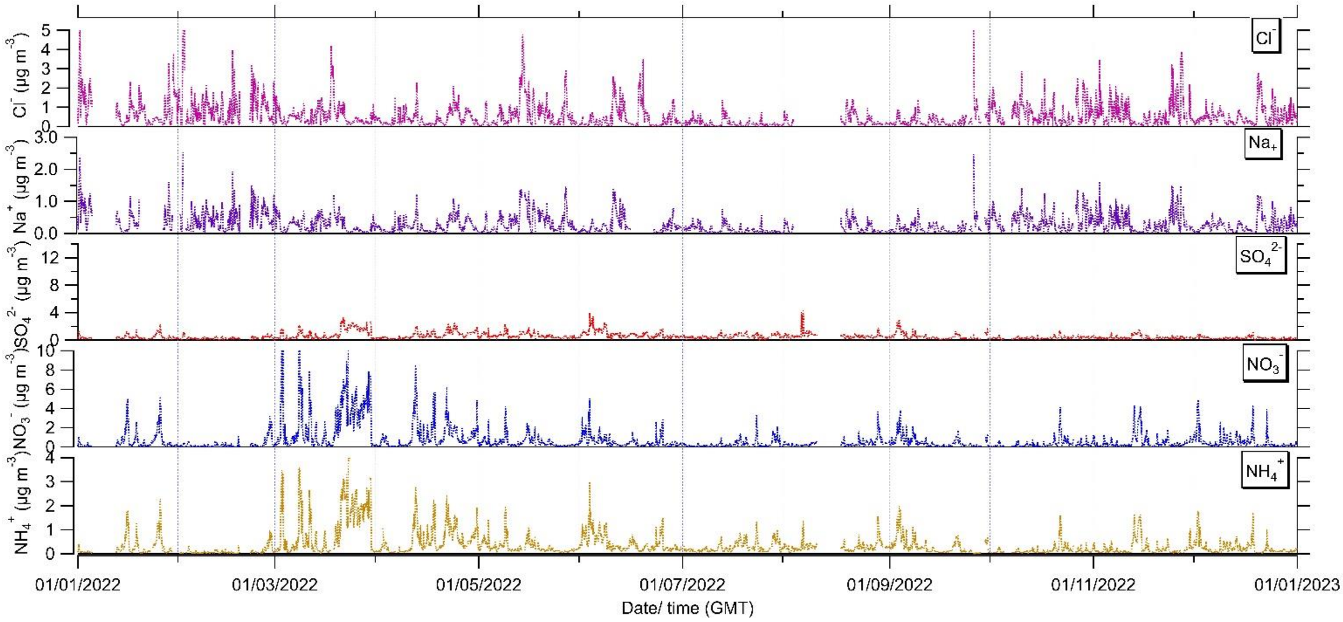


Figure 37 Ratified $PM_{2.5}$ speciated measurements by the MARGA at the Auchencorth Moss supersite

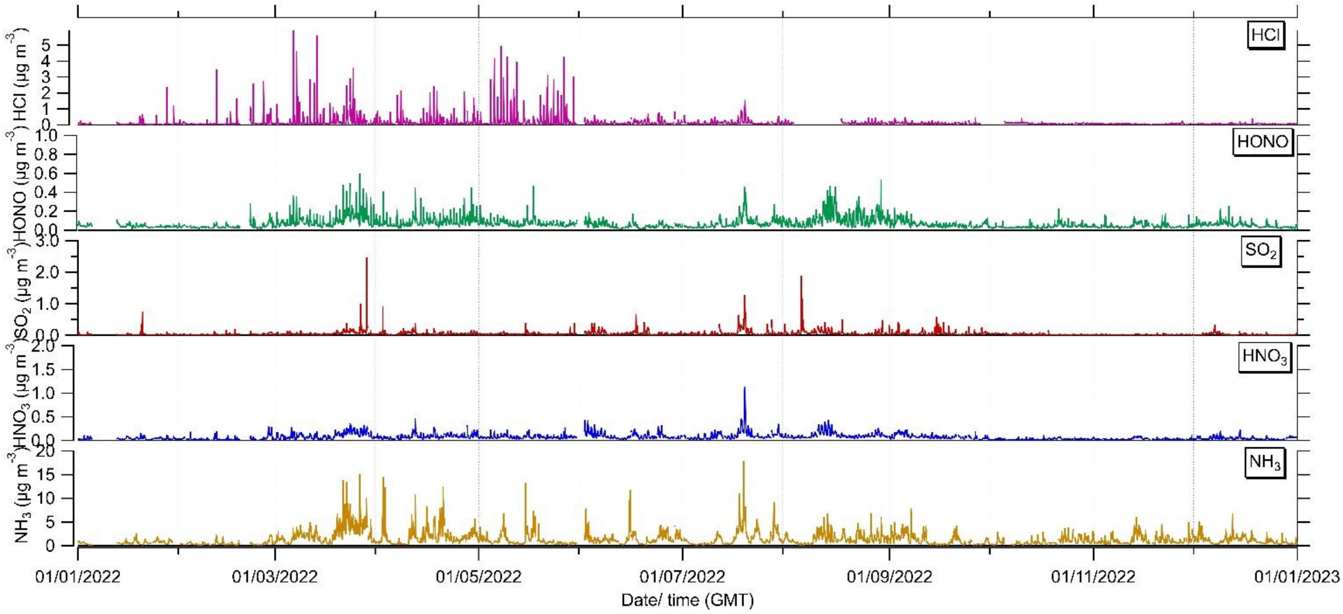


Figure 38 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite

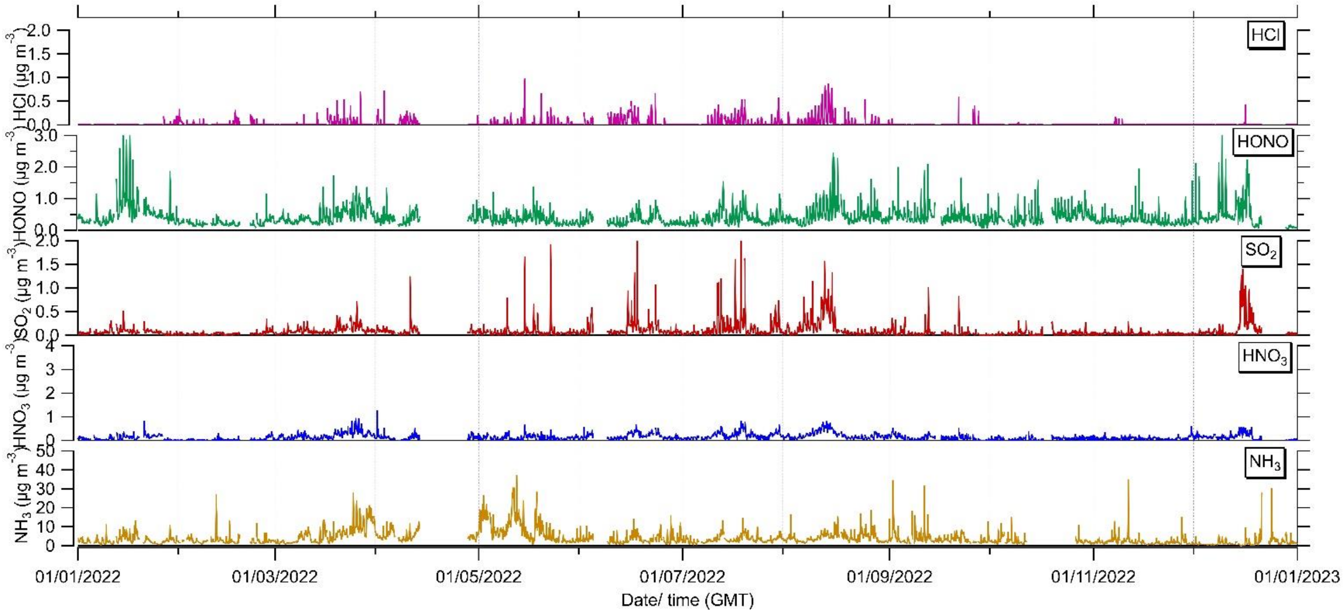


Figure 39 Ratified trace gas measurements by the MARGA at the Chilbolton Observatory supersite

Annual average concentrations at both sites (Table 6) were similar to that reported in previous years with the exception of HCl at Auchencorth Moss which was reported a higher annual average (0.139 µg m^{-3}) compared to 2021 (0.085 µg m^{-3}). Investigations will be undertaken to identify the potential source of the increase in concentration of HCl at the Auchencorth Moss. As observed in previous years, both Auchencorth Moss and the Chilbolton Observatory reported elevated NH_4^+ and NO_3^- concentrations in spring 2022 (March).

3.5.2 Tekran

The annual means and data capture for the 2022 ratified mercury measurements are shown below in Table 7.

The time series of the Auchencorth Moss measurements are shown in Figure 40. The system had reduced data capture for the following reasons

- March 2022 there was a leak in the system.
- April 2022 there was a failure of the air conditioning unit and the pump module within the instrument developed an electronic fault.
- Summer 2022 - Reduced data capture because of a temporary air conditioning unit not performing well during unusually high ambient temperatures. This resulted in poor performance of the instrument.
- Winter 2022 - Data was invalidated at the end of the year due to a leak causing the instrument not to achieve zero on the desorb cycles.

The 2022 data from the Chilbolton Observatory site is shown in Figure 41. Data is missing from the beginning of the year due to the baseline being too 'noisy'. This was found to be that the photodiode on the lamp control board had failed. Over the summer months the cabin temperature was too warm causing it to impact on the readings from the analyzer's detector.

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}	1.317	55.53
Gaseous Oxidised Hg (GOM) pg m-^{3}	0.649	46.46
Particulate bound Hg ($PM_{2.5}$) pg m^{-3}	1.727	48.91
Chilbolton Observatory		
Total Gaseous Hg (TGM) ng m^{-3}	1.534	68.23

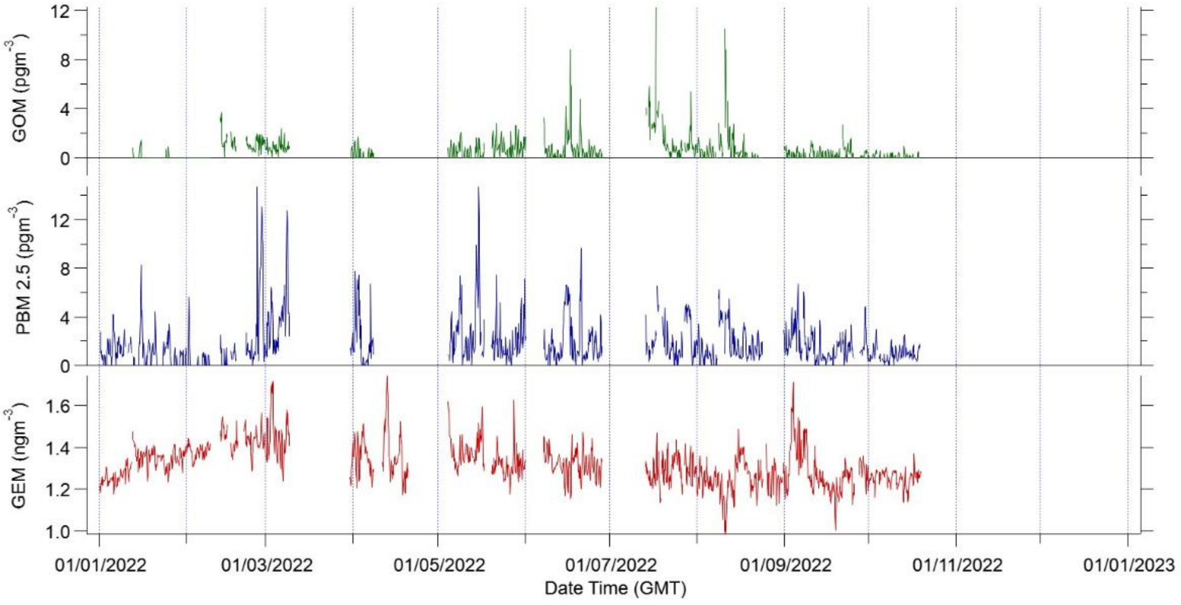


Figure 40 Ratified mercury measurements by the Tekran at the Auchencorth Moss supersite

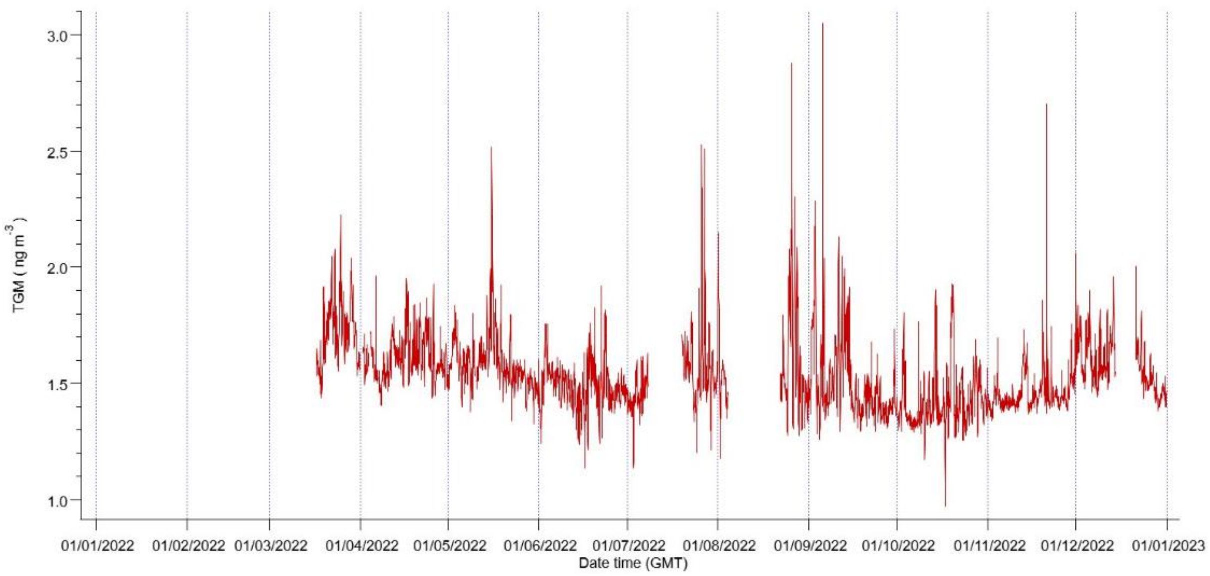


Figure 41 Ratified mercury measurements by the Tekran at the Chilbolton observatory

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 2022 that have used the UKEAP network data:

Atmospheric ammonia assessments on six designated sites in Northern Ireland. Year 1: June 2020 – May 2021' ' - NERC Open Research Archive, [online] Available from: https://nora.nerc.ac.uk/id/eprint/533585/ (Accessed 11 July 2023a), n.d.

How well are aerosol-cloud interactions represented in climate models? Part 1: Understanding the sulphate aerosol production from the 2014–15 Holuhraun eruption, [online] Available from: https://egusphere.copernicus.org/preprints/2023/egusphere-2023-619/ (Accessed 11 July 2023b), n.d.

Application of Earth observations and chemical transport modelling to investigate air quality and health from the city to the global scale, [online] Available from: http://etheses.bham.ac.uk/id/eprint/12425 (Accessed 11 July 2023c), n.d.

UK Upland Waters Monitoring Network data interpretation 1988-2019' ' - NERC Open Research Archive, [online] Available from: https://nora.nerc.ac.uk/id/eprint/534034/ (Accessed 11 July 2023d), n.d.

Chang, C.-T., Yang, C.-J., Huang, K.-H., Huang, J.-C. and Lin, T.-C.: Changes of precipitation acidity related to sulfur and nitrogen deposition in forests across three continents in north hemisphere over last two decades., Sci. Total Environ., 806(Pt 1), 150552, doi:10.1016/j.scitotenv.2021.150552, 2022.

Cowan, N., Nemitz, E., Walker, J. T., Fowler, D., Finnigan, J. J., Webster, H. N., Levy, P., Twigg, M., Tang, S. Y., Bachiller-Jareno, N., Trembath, P., Kinnersley, R. P. and Braban, C. F.: Review of methods for assessing deposition of reactive nitrogen pollutants across complex terrain with focus on the UK, Environ. Sci.: Atmos., 2(5), 829–851, doi:10.1039/D2EA00012A, 2022.

Crittenden, P. D., Ellis, C. J., Smith, R. I., Wanek, W. and Thornton, B.: Loss of nitrogen fixing capacity in a montane lichen is linked to increased nitrogen deposition, J. Ecol., 111(2), 280–299, doi:10.1111/1365-2745.14056, 2023.

Dajnak, D., Kitwiroon, N., Assareh, N., Stewart, G., Evangelopoulos, D., Wood, D., Walton, H. and Beevers, S.: Pathway to WHO: achieving clean air in the UK. Modelling air quality costs and benefits., Unpublished, doi:10.13140/rg.2.2.11242.80323, 2022.

Fisher, L. V. and Barron, A. R.: Effect of functionalized and unfunctionalized basic oxygen steelmaking slag on the growth of cereal wheat (Triticum aestivum), Resources, Conservation & Recycling Advances, 15, 200092, doi:10.1016/j.rcradv.2022.200092, 2022.

Harrison, R. M., Beddows, D. C. S., Tong, C. and Damayanti, S.: Non-linearity of secondary pollutant formation estimated from emissions data and measured precursor-secondary pollutant relationships., npj Clim. Atmos. Sci., 5(1), 71, doi:10.1038/s41612-022-00297-9, 2022.

Jarvis, A. P., Gandy, C. J. and Webb, J. A.: Controls on the Generation and Geochemistry of Neutral Mine Drainage: Evidence from Force Crag Mine, Cumbria, UK, Minerals, 13(5), 592, doi:10.3390/min13050592, 2023.

Kelly, J. M., Marais, E. A., Lu, G., Obszynska, J., Mace, M., White, J. and Leigh, R. J.: Diagnosing domestic and transboundary sources of fine particulate matter (PM2.5) in UK cities using GEOS-Chem, City and Environment Interactions, 18, 100100, doi:10.1016/j.cacint.2023.100100, 2023.

Manninen, S., Jääskeläinen, K., Stephens, A., Iwanicka, A., Tang, S. and van Dijk, N.: NH3 concentrations below the current critical level affect the epiphytic macrolichen communities - Evidence from a Northern European City., Sci. Total Environ., 877, 162877, doi:10.1016/j.scitotenv.2023.162877, 2023.

Monteith, D. T., Henrys, P. A., Hruška, J., de Wit, H. A., Krám, P., Moldan, F., Posch, M., Räike, A., Stoddard, J. L., Shilland, E. M., Pereira, M. G. and Evans, C. D.: Long-term rise in riverine dissolved organic carbon concentration is predicted by electrolyte solubility theory., Sci. Adv., 9(3), eade3491, doi:10.1126/sciadv.ade3491, 2023.

Oxley, T., Vieno, M., Woodward, H., ApSimon, H., Mehlig, D., Beck, R., Nemitz, E. and Reis, S.: Reduced-form and complex ACTM modelling for air quality policy development: A model inter-comparison., Environ. Int., 171, 107676, doi:10.1016/j.envint.2022.107676, 2023.

Walker, H. L., Heal, M. R., Braban, C. F., Leeson, S. R., Simmons, I., Jones, M. R., Kift, R., Marsden, N. and Twigg, M. M.: The Importance of Capturing Local Measurement-Driven Adjustment of Modelled j(NO2), Atmosphere, 13(7), 1065, doi:10.3390/atmos13071065, 2022a.

Walker, H. L., Heal, M. R., Braban, C. F., Whalley, L. K. and Twigg, M. M.: Evaluation of local measurement-driven adjustments of modelled cloud-free atmospheric photolysis rate coefficients, Environ. Sci.: Atmos., 2(6), 1411–1427, doi:10.1039/D2EA00072E, 2022b.

3.7 Legislation and Standardisation

There were to the authors' knowledge no changes to legislation or standardisation to UKEAP network in 2022.

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.

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and Department of Agriculture, Environment and Rural Affairs in Northern Ireland, 2020).

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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 Energy & Environment

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 Energy & Environment

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., Van Dijk, N., Jones, M.R., Stephens, A.C.M., Braban, C.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. 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

Stephens, Amy; Tang, Yuk; Braban, Christine; Dos Santos Pereira, Gloria; Tanna, Binoti; Hunt, Alexander; Keenan, Patrick; Guyatt, Hayley; Thacker, Sarah; Salisbury, Edward; Smith, Hannah; Shield, Julian; Leaver, David; Twigg, Marsailidh UKEAP (UK Eutrophying and Acidifying Atmospheric Pollutants) 2020 dataset: Acid Gas and Aerosol Network (AGANet). April 2021, https://uk-air.defra.gov.uk/data/

National Ammonia Monitoring Network (NAMN)

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

Stephens, Amy; Tang, Yuk; Braban, Christine; Dos Santos Pereira, Gloria; Keenan, Patrick; Tanna, Binoti; Salisbury, Edward; Hunt, Alexander; Guyatt, Hayley; Thacker, Sarah; Smith, Hannah; Shield, Julian; Leaver, David; Twigg, Marsailidh *UKEAP (UK Eutrophying and Acidifying Atmospheric Pollutants) 2020 dataset: National Ammonia Monitoring Network (NAMN).* April 2021, https://uk-air.defra.gov.uk/data/

Precipitation Network (Precip-Net)

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo Energy & Environment

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 Energy & Environment

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 Inter-comparison

EMEP Inter-comparison

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.

The analytical laboratory used with the Precip Network is SOCOTEC's Advanced Chemistry and Research laboratory. They are accredited to ISO17025 and participate in an external international PT scheme.

Results of the 40th EMEP Inter-comparison

The inter-comparison in 2022 was the 40th time such an inter-comparison took place.

Nitrogen dioxide absorbing solution

The results of the nitrogen dioxide absorbing solution are shown below in Table 8. The results of this intercomparison are excellent with absolute mean difference all ≤1.5 %. They are within the criteria for satisfactory reported by EMEP which is the highest rating for the EMEP quality norm. The analytical laboratory has been made aware of the performance to they are aware their performance meets expectations.

Table 8 Comparison of Reported and Measured Nitrogen Dioxide Concentrations in Absorbing Solution

Sample code	Reported concentration µg NO_2-N/ml	Expected concentration µg NO_2-N/ml	Difference (%)	EMEP quality norm
C1	0.073	0.074	-1.4%	S
C2	0.11	0.111	-0.9%	S
C3	0.186	0.185	0.5%	S
C4	0.244	0.241	1.2%	S

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

Synthetic Rainwater Samples

The results of the intercomparison for the synthetic rainwater samples are shown in

Table 9. A number of the results for calcium, magnesium and pH require improvement as were not satisfactory and potassium and sulphate also need improvement as a number of the results were questionable.

Table 9 40th EMEP Intercomparison

Species	Sample code	Reported value concentration mg l^{-1}	Expected concentration mg l^{-1}	Difference (%)	EMEP Quality Norm
$SO4^{-2}$	G1	0.608	0.663	-8%	S
	G2	0.423	0.477	-11%	Q
	G3	0.332	0.375	-11%	Q
	G4	0.2	0.235	-15%	Q
NH_4^+	G1	0.212	0.241	-12%	S
	G2	0.238	0.254	-6%	S
	G3	0.173	0.187	-7%	S
	G4	0.158	0.174	-9%	S
NO_3^-	G1	0.482	0.462	4%	S
	G2	0.518	0.501	3%	S
	G3	0.36	0.346	4%	S
	G4	0.356	0.343	4%	S
Na^+	G1	0.597	0.644	-7%	S
	G2	0.673	0.751	-10%	S
	G3	0.416	0.456	-9%	S
	G4	0.532	0.574	-7%	S
Mg^{2+}	G1	0.167	0.32	-48%	U
	G2	0.163	0.196	-17%	Q
	G3	0.12	0.155	-23%	Q
	G4	0.083	0.093	-11%	S
Cl-	G1	0.727	0.772	-6%	S
	G2	0.893	0.965	-7%	S
	G3	0.542	0.579	-6%	S
	G4	0.684	0.734	-7%	S
Ca^{2+}	G1	0.195	0.268	-27%	U
	G2	0.158	0.243	-35%	U
	G3	0.121	0.192	-37%	U
	G4	0.073	0.115	-37%	U
K^+	G1	0.332	0.374	-11%	S
	G2	0.402	0.475	-15%	Q
	G3	0.244	0.306	-20%	Q
	G4	0.262	0.306	-14%	S
pH*	G1	4.99	5.43	-8%	U
	G2	5.02	5.45	-8%	U
	G3	5.11	5.51	-7%	U
	G4	5.1	5.48	-7%	U
Cond**	G1	12.8	14.16	-10%	S
	G2	12.2	13.68	-11%	S
	G3	8.96	9.76	-8%	S
	G4	8.43	9.13	-8%	S

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

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

The analytical laboratory was made aware of the analytical performance, and this led to the investigation of the performance of these methods. A review has taken place to identify corrective actions needed. These are summarised below.

pH improvements

Calibration standards with lower ionic strength will be used to better match the synthetic rainwater and ambient samples. In addition, the calibration range of standards was changed to align better with the current ambient pH range.

Ion chromatography improvements

The magnesium, calcium and potassium ions are more susceptible to changes in the baseline and are close to the detection limits meaning they are more uncertain.

The analyst discussed with service engineers the best way to increase the signal to noise ratio.

System suitability checks have been tightened which improves system performance in the short term. In addition, the analysts have invested in a new ion chromatography system due for delivery and commissioning in summer 2023. The analysts expected it to have a lower measurement uncertainty.

Appendix 3 Locally derived adjustment factors: co-location of UKEAP diffusion tubes within AURN.

Triplicate diffusion tubes have been located at Eskdalemuir and Yarner Wood since 2006, at High Muffles since 2012 and at Chilbolton Observatory since 2016. At each of these sites the diffusion tubes were co-located with an automatic analyser. However, due to an issue with electricity supply throughout 2022 at Eskdalemuir, it was not possible to measure NO_2 using the automatic analyser, hence only NO_2 measured by diffusion tubes are available in 2022.

A comparison of the nitrogen dioxide concentrations measured by diffusion tube and automatic analyser is presented in Table 10 and displayed in Figure 42. For most years the concentrations measured by diffusion tube are higher than measured by the automatic analysed. The lowest concentrations are measured at Eskdalemuir and the largest at Chilbolton Observatory.

Table 10 Annual mean nitrogen dioxide concentrations (µg m^{-3}) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis)

	Chilbolton Observatory		Eskdalemuir		Harwell		High Muffles		Yarner Wood	
	DT	CM	DT[b]	CM	DT	CM	DT[b]	CM	DT[b]	CM
2003			4.7			15.7(87)	10.8	14.4(18)	8.8	10.7(29)
2004			2.9	5.7(6)		12.0(96)	7.4	9.0(70)	4.8	7.8(99)
2005			4.6	3.8(93)		11.6(91)	8.6	7.5(89)	6.6	9.2(82)
2006			4.0	3.7(89)		11.5(93)	9.1	7.5(88)	5.7	5.2(88)
2007			4.2	5.0(78)		12.2(91)	8.0	6.4(98)	6.3	5.6(91)
2008			[a]	5.1(93)	[a]	10.1(98)	[a]	6.6(98)	[a]	5.3(82)
2009			[a]	4.3(94)	[a]	10.0(98)	[a]	7.5(56)	[a]	4.3(87)
2010			4.5(100)	3.0(98)	15.1(100)	11.9(97)	7.9(95)	6.1(92)	5.4(100)	4.9(98)
2011			3.5(100)	3.2(92)	12.2(100)	10.3(97)	7.7(100)	7.4(95)	4.9(100)	4.1(85)
2012			3.7(100)	3.0(99)	11.6(100)	10.1(97)	7.6(100)	6.2(97)	4.9(100)	4.3(97)
2013			3.8(92)	2.5(97)	12.4(100)	12.5(50)	7.0(100)	5.4(96)	5.5(99)	5.2(85)
2014			3.6(92)	2.3(99)	10.5(100)	8.0(97)	6.9(100)	5.4(89)	4.3(100)	3.6(92)
2015			3.2(100)	2.2(98)	9.0(100)	7.7(97)	6.2(100)	5.3(92)	3.9(100)	3.9(99)
2016	11.7(96)	14.3(88)	2.9(100)	2.0(97)			5.8(100)	5.4(91)	4.6(100)	4.5(93)
2017	10.1(100)	11.2(97)	2.4(100)	2.0(93)			5.6(100)	5.1(79)	3.6(100)	3.2(89)
2018	9.9(100)	9.5(99)	2.3(100)	1.9(97)			5.1(100)	4.9(95)	4.0(83)	4.3(98)
2019	9.2(100)	8.9(87)	2.4(100)	1.9(97)			5.4(100)	4.9(99)	3.8(100)	3.8(98)
2020	8.5(100)	6.3(99)	2.0(100)	1.7(85)			4.4(100)	4.6(47)	3.3(100)	2.8(96)
2021	7.8(100)	6.2(99)	1.7(100)	1.8(41)			3.6(100)	3.3(99)	3.1(100)	3.6(90)
2022	7.7(100)	6.8(96)	1.6(100)	- (0)			3.8 (100)	4.1(98)	3.1(100)	3.2(94)

Notes: [a] Data were downloaded from Archive database. The database does not yet contain the annual mean concentrations as measured by diffusion tube for 2008 and 2009; [b] Data captures were not calculated for diffusion tubes concentrations archived before 2010. Diffusion tubes were sampling in triplicate at Yarner Wood and Eskdalemuir since 2006; at Harwell since 2007 (replaced by Chilbolton Observatory 2016); at High Muffles since 2012. These are shaded.

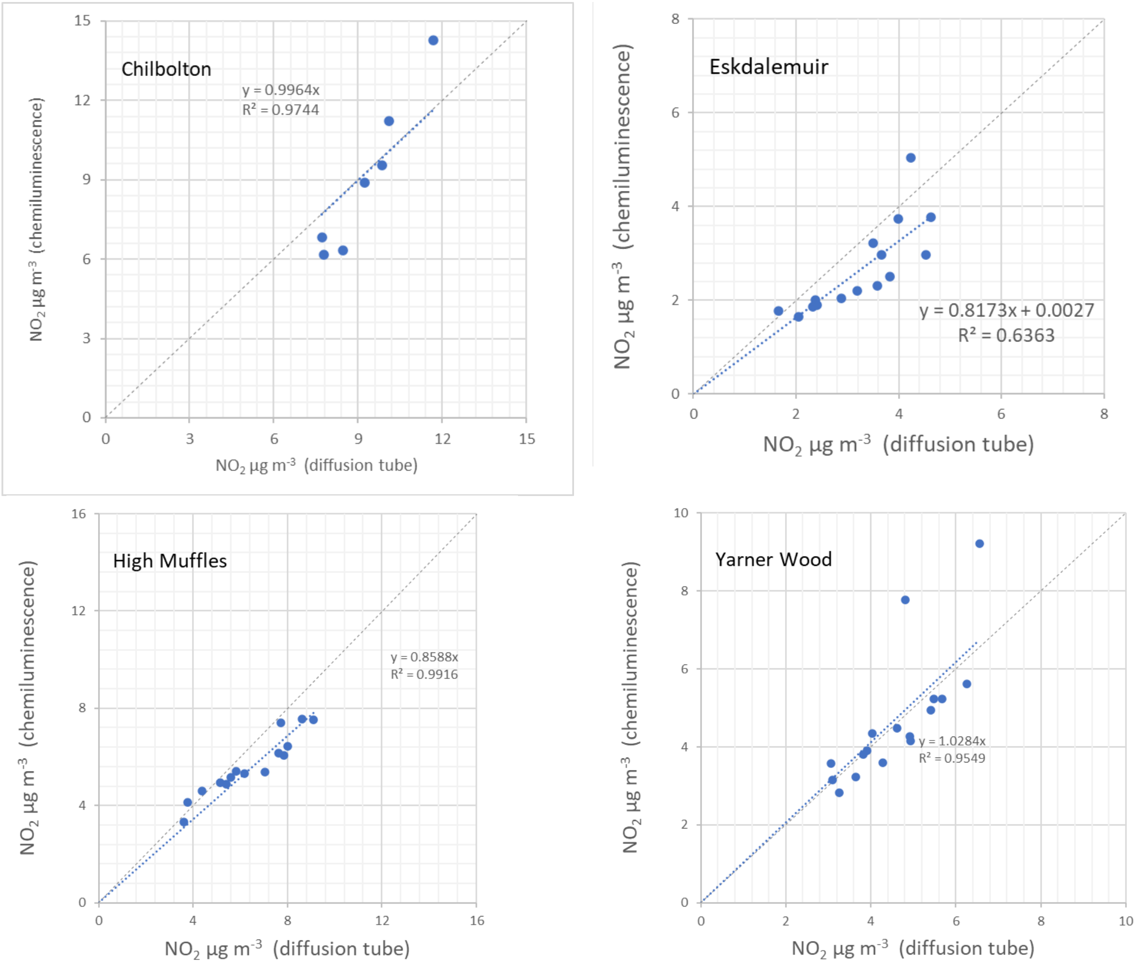

Figure 42 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each

TG22 recommends that each local authority should, if they have been involved in a co-location study, present both the local and national bias adjustment bias spreadsheet and justify which value should be used in the final bias adjustment. In line with this approach, we have derived bias adjustments each year using the collocated automatic and diffusion tube measurements. This is because:

- the ‘quality’ of the measurement made by automatic analyser in the AURN has been considered as “reference” standard;
- the measurement environment will be always rural background whereas the national study will comprise a range of environments most of which will be roadside or urban background;
- Samples are dispatched, handled and exposed in a consistent way.

Raw and bias corrected data are made available via UKAIR.

Calculation of average bias factor for the co-located NO_2 sampling sites

Following the guidance provided in TG22 we have calculated monthly mean NO_2 concentrations for the automatic analysers corresponding to the periods the diffusion tubes were exposed. We have also updated the calculation spreadsheet[2] to allow for time weighting the mean concentrations and bias adjustment factors. As collocated data was not available at Eskdalemuir, the bias correction factor was based on data collected at the other sites.

In combining the respective B bias factors, we have followed the advice provided in TG22 Paragraph 7.222[3]. The individual bias B factors were calculated as follows:

	Yarner Wood	High Muffles	Chilbolton Observatory
Adjustment factor (A)	1.004	1.138	0.917
Bias factor B	7%	-8%	19%

The average of the two values is calculated to be 6.09 % giving a bias adjustment factor of 0.943[4].

We also note that the NO_2 concentrations measured by the automatic analysis at Yarner Wood and High Muffles in 2022 are marginally higher than that measured by diffusion tubes. 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 NO_y species.

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[2] See https://laqm.defra.gov.uk/bias-adjustment-factors/local-bias.html and Figure 7.1 of TG(22)

[3] LAQM-TG22-August-22-v1.0.pdf (defra.gov.uk) Text from Paragraph 7.222:

Two bias factors are output, A and B, and in this example they are 0.78 and 28% respectively. The Bias factor A is the local bias correction factor. If there is more than one local co-location study, then the A factors should not be averaged. Instead, a reasonable approximation can be derived by averaging the B values. For example, if there were two studies of 22% and 28%, then the average would be 25%. This is then expressed as a factor, e.g. 25% is 0.25. Next add 1.00 to this value, e.g. 0.25 + 1.00 = 1.25. Finally, take the inverse to give the bias adjustment factor, e.g. 1/1.25 = 0.80.

[4] Calculated as (1 / (bias average+1))

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