UKEAP 2021 annual report

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

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Title	UKEAP 2021 annual report
Client	Environment Agency on behalf of the Department of Environment Food and Rural Affairs and the Devolved Administrations
Contract number	ECM48524
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Executive summary

This annual report for 2021 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 – 72 sites)
- **Acid Gases and Aerosol Network** (AGANet – 27 sites)
- **Precipitation chemistry Network** (Precip-Net – 41 sites)
- **Rural nitrogen dioxide (NO$_2$) diffusion tube network** (NO$_2$-Net – 23 sites)

The following report provides information on:

- Updates on network operations during 2021.
- 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 findings for 2021:

- Nitrogen dioxide reported a continued decrease in concentration across the NO$_2$ network

- Air concentrations of ammonia continue to show interannual variability in the annual average but no observable trend

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 2021. 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). 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.
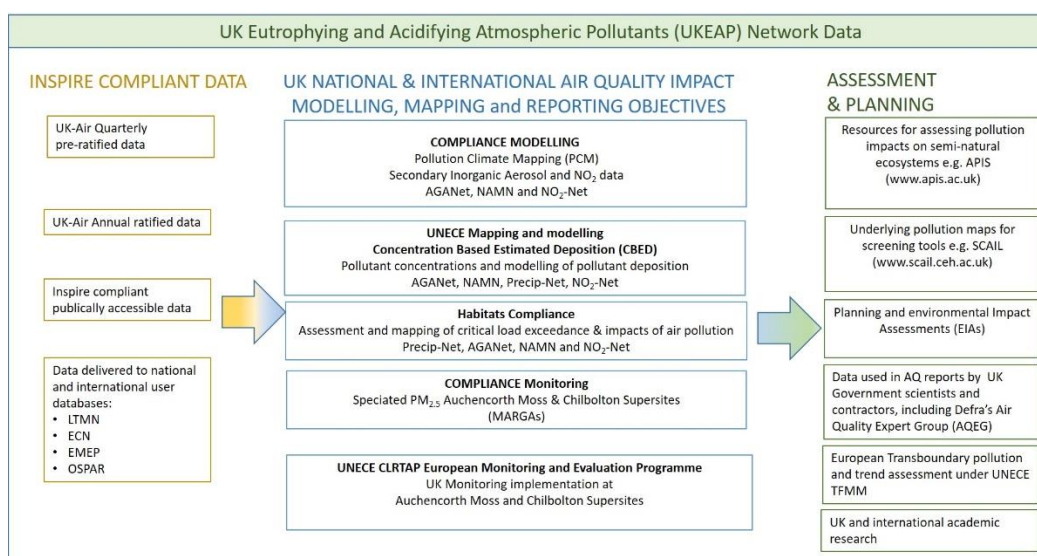

Figure 1 Summary of the data applications of the UKEAP datasets.

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. Potassium is associated with crustal sources too, but 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^+, 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 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 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 and Auchencorth Moss.
- On line mercury measurements (Chilbolton: elemental mercury; Auchencorth Moss: elemental and speciated mercury).
- Meteorological observations (barometric pressure, dewpoint, wind speed & direction, relative humidity, temperature, (total) rainfall) for Chilbolton 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 2021 (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	I	Hourly	AURN
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		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
Trace gas fluxes (O_3,)		X	III	Hourly	NERC NC[2]
NO and NO_2 (photolytic)		X	I	Hourly	NERC NC[2]

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

1.2 Scope of the report

The following annual report for 2021 contains:

- A summary of network operations including Quality Assurance (QA)/ Quality Checks (QC) results, notable events and changes to the networks during 2021.
- 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 2021 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, sulphate-S, nitrate-N, ammonium-N, sodium, chloride, calcium, magnesium, potassium, conductivity and phosphate. 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.
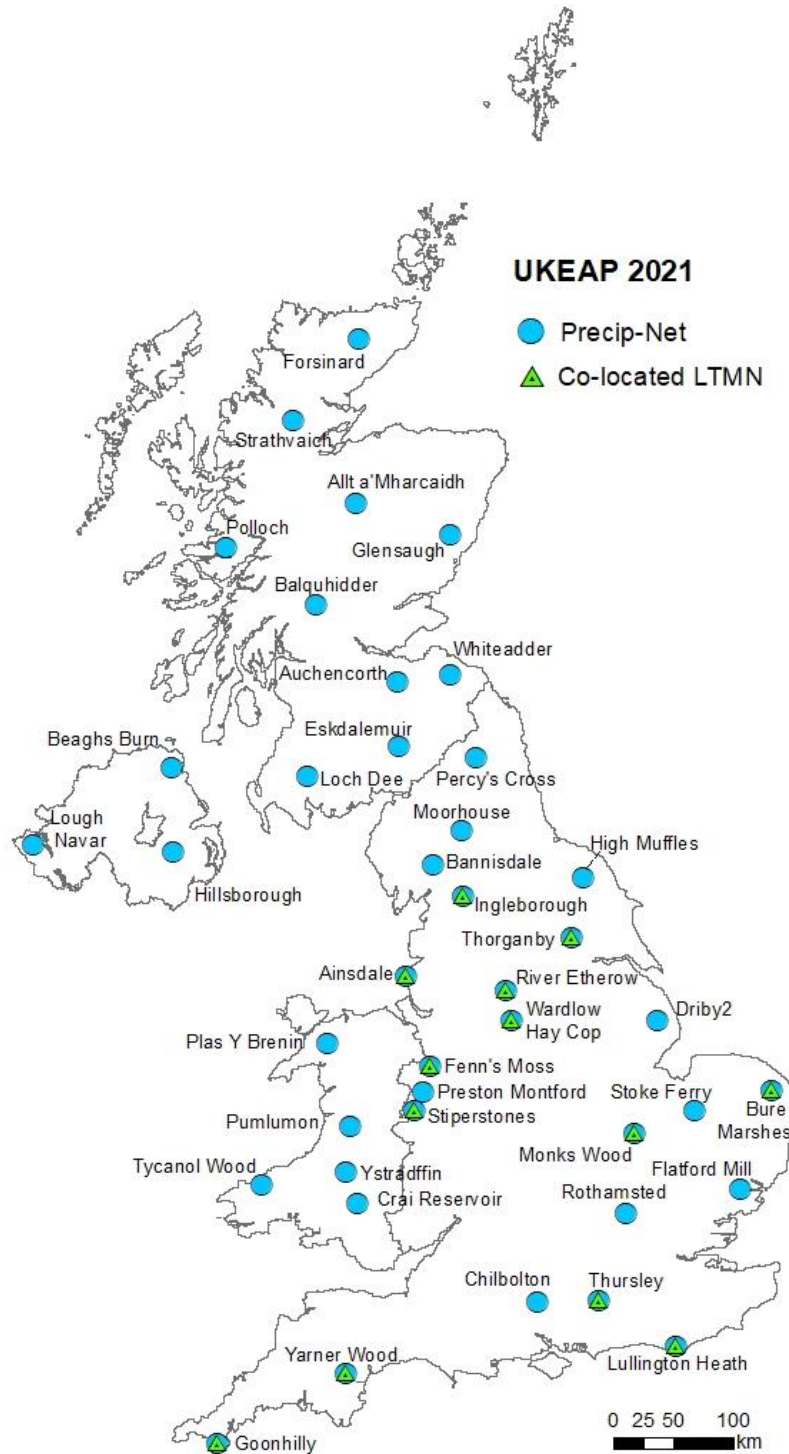

Figure 3 UK Precipitation chemistry (Precip-Net)

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 2021 are summarised in the Appendices of this report.

Due to accessibility issues, the site at Bannisdale (54.431308, -2.748991) was relocated to a new location at Bannisdale Beck (54.409225, -2.724521) in December 2021, approximately 2.9 km due south.

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 to 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 39th intercomparison is presented in Appendix 1.

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

2.2 NO₂-Net Network

The NO₂ network (NO₂-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.
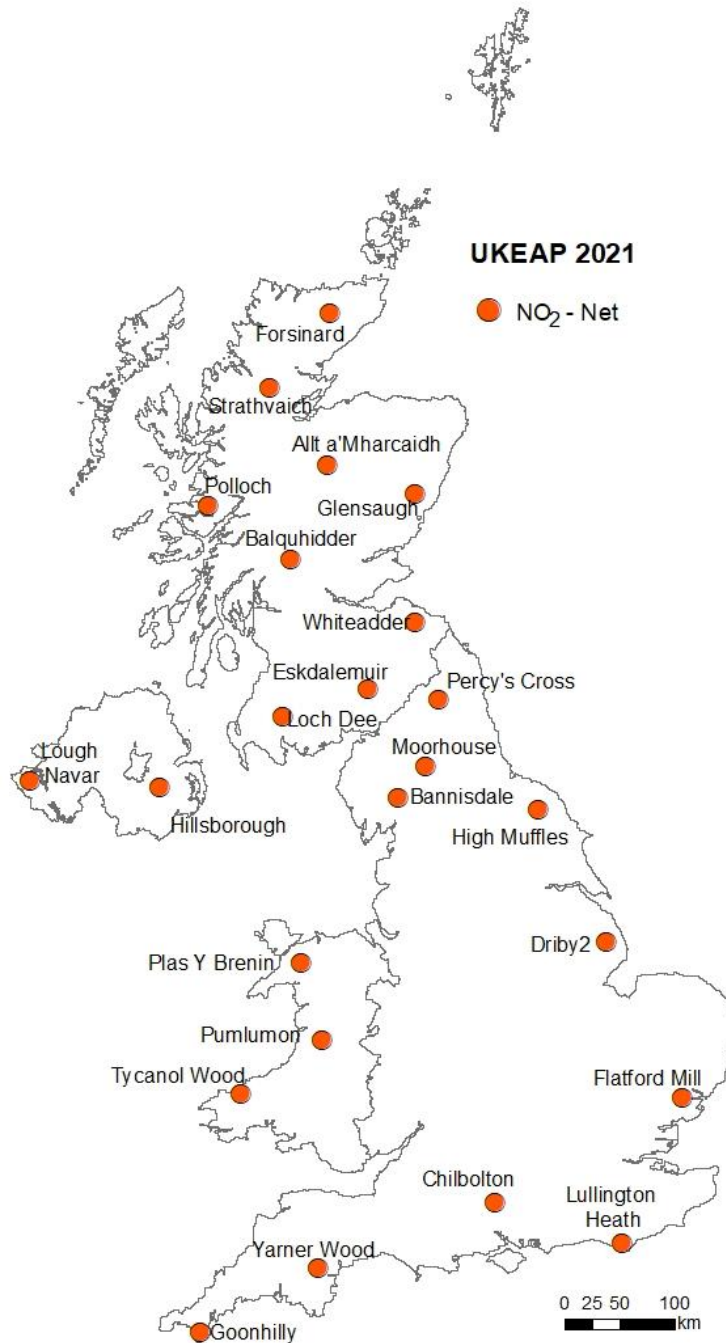

Figure 4 UK NO₂ diffusion tube (NO₂-Net) Network

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. The samplers are deployed in triplicate at twenty three monitoring locations. The supplier of the tubes is SOCOTEC, Didcot.

Due to accessibility issues, the site at Bannisdale (54.431308, -2.748991) was relocated to a new location at Bannisdale Beck (54.409225, -2.724521) in December 2021, approximately 2.9 km due south.

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 what local changes 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 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]. For those reporting periods in 2021 for which results were reported, all results, apart from AIR PT AR045, were considered satisfactory (based on z-scores less than or equal to 2). The analytical laboratory performance summarised below:

AIR PT Round	AIR PT AR042	AIR PT AR043	AIR PT AR045	AIR PT AR046
Round conducted in the period	January – February 2021	May – June 2021	July – August 2021	September – October 2021
Socotec UK Limited	100%	100%	87.50%	100%

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, Eskdalemuir, High Muffles and Yarner Wood. However, this year only Chilbolton and High Muffles were used. This was because of the poor data capture (41%) for the automatic instrument at Eskdalemuir and the automatic instrument measured higher NO_2 concentrations than the diffusion tube at Yarner Wood. The

resultant bias adjustment factor, 0.855, was applied to all other 22 diffusion tubes. The calculation of the bias adjustment factor is discussed further in Appendix 2.

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. In NAMN, some DELTA® sites report NH_3 and NH_4^+ only but these were removed at the end of 2021, whereas within AGANet the samplers report the whole suite of trace gases and aerosols, as outlined in Section 2.4.

Figure 6: DELTA® site example (Forsinard)

2.3.1 Overview of activities

During 2021 the number of NAMN sites providing monthly measurements of atmospheric NH_3 in 2021 increased from 71 to 72, summarised in Table 2.

Table 2: Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2021

Site Type	Number
UKCEH DELTA® sites sampling gaseous NH_3 (2 sites closed during 2021 refer below for details)	29
UKCEH ALPHA® sites sampling gaseous NH_3 only	52
Total number of sites	72

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 2021 the following network infrastructure changes occurred:

- Sourhope (UKA00347) and Llynclys Common (UKA00270) UKCEH DELTA® (NAMN only) ceased operation at the end of 2021. UKCEH ALPHA® samplers remain active at these sites to continue to report NH_3 as part of NAMN.
- Stanford 2 site closed (July 2021) and relocated to Thetford forest (August 2021). Thetford forest was a former NAMN ALPHA site between 2000 and January 2010.
- Co-located UKCEH ALPHA® samplers used to determine uptake rates were installed to two existing UKCEH DELTA® sites to maintain the 9 sites required for calculating uptake rate; Chilbolton and Narberth (opened Feb 22) in replacement of the Sourhope (closed Nov 21) and Llynclys Common (closed Dec 21) sites.

- A UKCEH DELTA® and ALPHA® site was opened at Allt a'Mharcaidh (opened June 21) to replace the site closed at Lagganlia (closed 2020).
- Mottey Meadows UKCEH ALPHA® site was added to both UKEAP and LTMN networks (May 2021).

Figure 7 summarises the current locations of the NAMN network. The map also shows where the NAMN provide NH_3 measurements for 15 of the LTMN network.

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 2021, the coefficient of determination (R^2) was 0.90 showing good agreement between ALPHAs and DELTAs, with the calibrated uptake rate determined as 0.0031851 m^3 hr^{-1}. When compared to historical trends, it was found that the calibrated uptake rate was within the reporting range of previous years (Figure 8). For the year 2021 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).
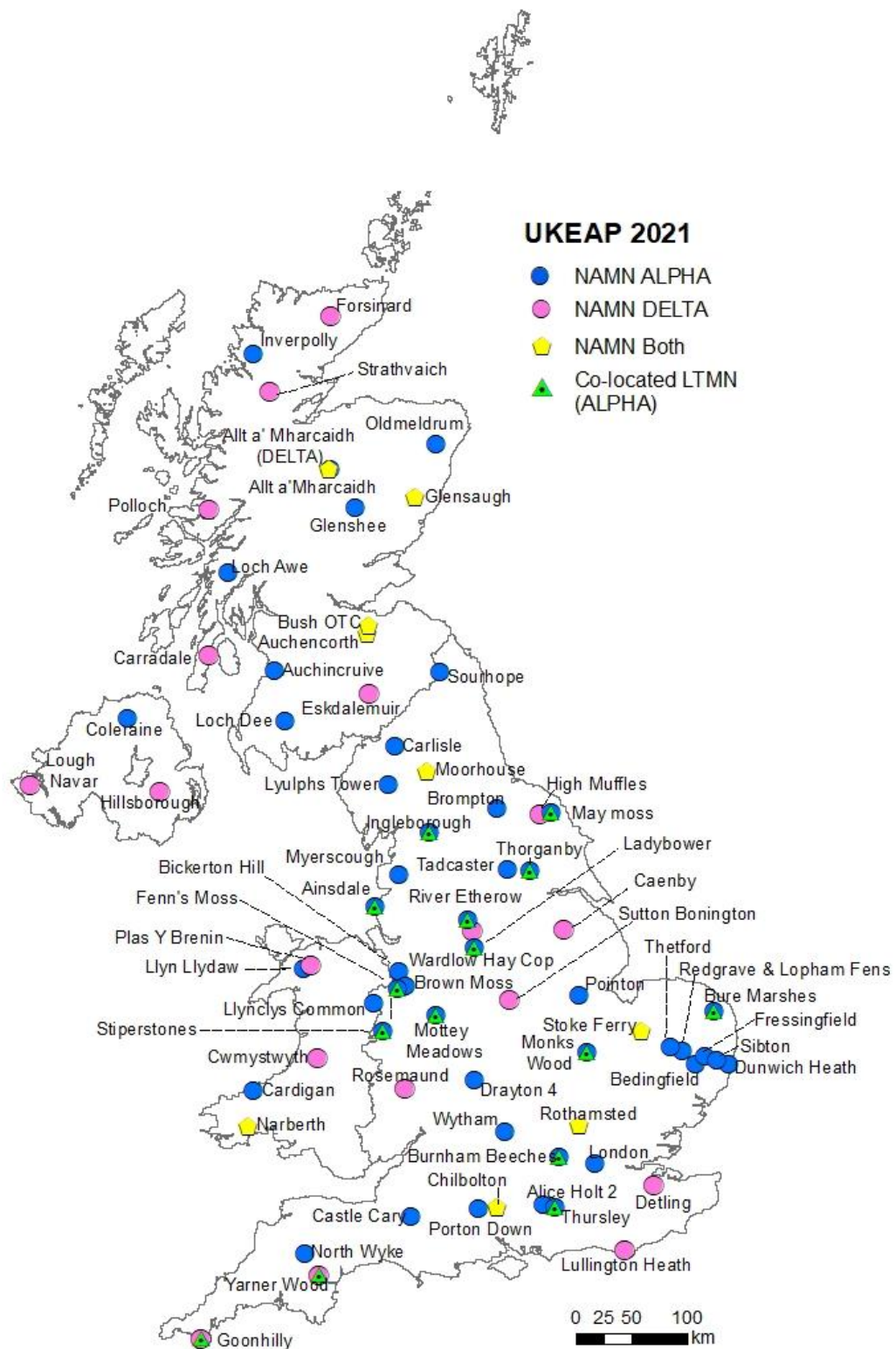
Figure 7 UK National Ammonia Monitoring Network (NAMN) and co-located LTMN sites
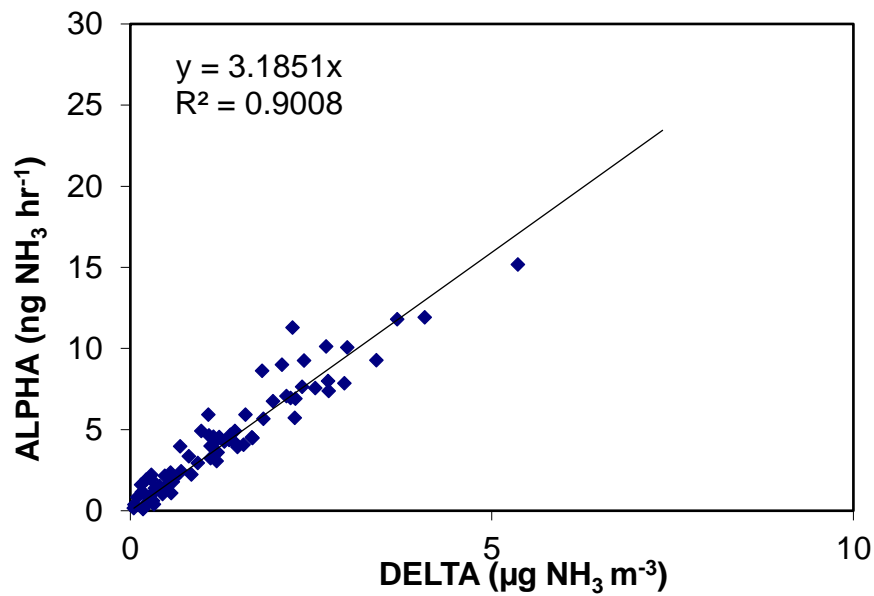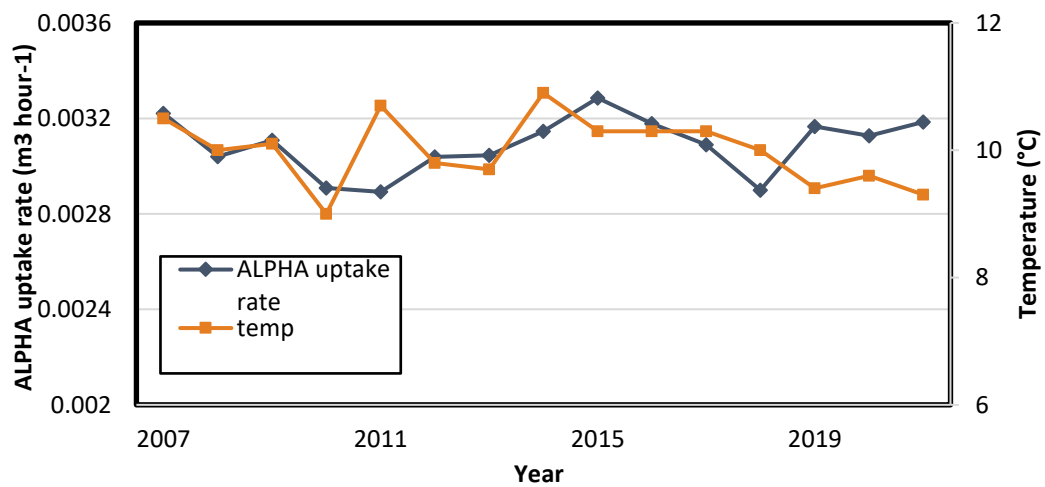
Figure 8: 2021 UKCEH ALPHA® uptake rate calibration

In the figure: $y = 3.1851x$, $R^2 = 0.9008$. Axes: ALPHA (ng NH$_3$ hr^{-1}) versus DELTA (µg NH$_3$ m^{-3}).

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)

Axes: ALPHA uptake rate (m3 hour-1) and Temperature (°C) versus Year.

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 27 sites across the UK. Measurements are carried using the DELTA® sampler as described in Section 2.3. During 2021 there were 27 sites operational within AGANet (refer to Table 3).

Table 3 Summary of the number of sites within AGANet in 2021

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+})	27
Total number of sites	27

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 2021 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 2021 calendar year was submitted to UKAIR in April 2022.

During 2021 the following network changes occurred:

- A UKCEH DELTA® was opened at Allt a'Mharcaidh (opened 2022) to replace the site closed at Lagganlia (closed 2020).

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.
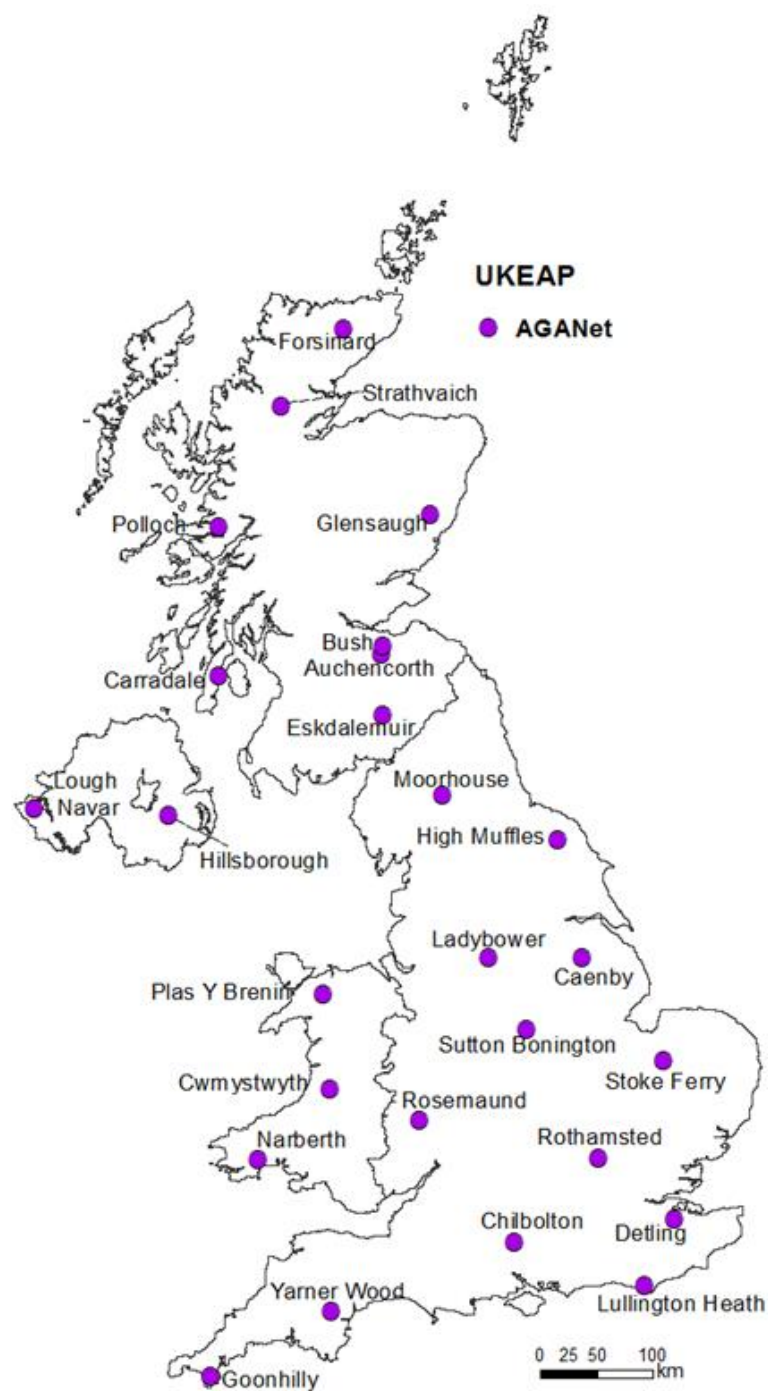
UKEAP

● **AGANet**

Forsinard

Strathvaich

Glensaugh

Polloch

Bush
Auchencorth

Carradale

Eskdalemuir

Lough
Navar

Moorhouse

High Muffles

Hillsborough

Ladybower

Caenby

Plas Y Brenin

Sutton Bonington

Stoke Ferry

Cwmystwyth

Rosemaund

Narberth

Rothamsted

Chilbolton

Detling

Yarner Wood

Lullington Heath

Goonhilly

0 25 50   100
           km

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 (Figure 11, MARGA 2S, Metrohm, NL). 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].

<u>Tekran</u>

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 report 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 flows 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 0.2μm 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 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 EMEP Supersite is operated by Ricardo summarised on UK-AIR. There were no modifications to the site infrastructure in 2021. Ricardo act as Local Site Operator for the Chilbolton (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 2021. During 2021 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 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 2021 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.

Table 4 Data capture with the Precip-Net network in 2021.

Site	Average, %	Site	Average, %
Ainsdale Dunes and Sands	83.8	Lough Navar	100.0
Allt a'Mharcaidh	96.2	Lullington Heath	96.7
Auchencorth Moss	92.3	Monks Wood	99.7
Balquhidder 2	88.5	Moorhouse	89.8
Bannisdale	66.8	Percy's Cross	92.3
Beaghs Burn	92.6	Polloch	100.0
Bure Marshes	96.2	Preston Montford	76.7
Chilbolton Observatory	88.2	Pumlumon	81.1
Crai Reservoir 2	86.0	River Etherow	80.5
Driby 2	100.0	Rothamsted	96.2
Eskdalemuir	80.5	Stiperstones	96.7
Fenn's, Whixall & Bettisfield Mosses	92.0	Stoke Ferry	96.2
Flatford Mill	84.7	Strathvaich	100.0
Forsinard RSPB	88.2	Thorganby	82.2
Glensaugh	96.2	Thursley Common 2	95.3
Goonhilly	80.0	Tycanol Wood	96.4
High Muffles	84.7	Wardlow Hay Cop	88.7
Hillsborough Forest	99.4	Whiteadder	76.7
Ingleborough	94.2	Yarner Wood	92.3
Llyn Llydaw	92.3	Ystradffin	89.6
Loch Dee	84.4	**Network Average**	**90.0**

The spatial patterns of the annual mean precipitation-weighted concentration of non-sea salt sulphate, nitrate, ammonium and hydrogen are presented in Figure 13 for 2021. 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.
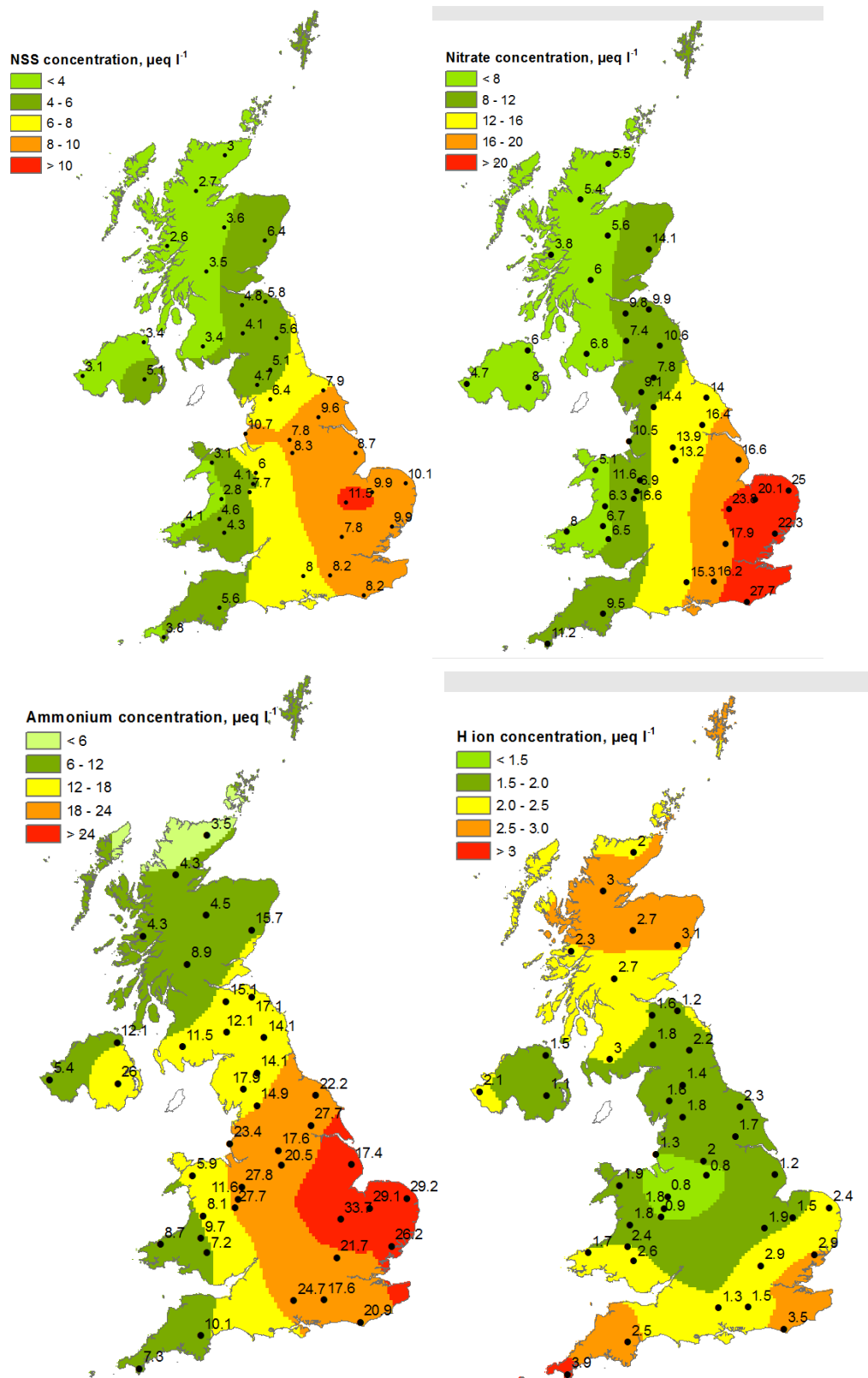
Figure 13 Interpolated concentration maps for non-sea salt sulphate, nitrate, ammonium and hydrogen ion (µeq l⁻¹)

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 ninety six percent, oxides of nitrogen emissions have decreased by about 75% and ammonia emissions have decreased by about 17%. Figure 14 also presents projected emissions for 2021, 2025 and 2030 (2040 emissions available on 15th July 2022) for the respective gases from the National Emissions Inventory (NAEI)[13].
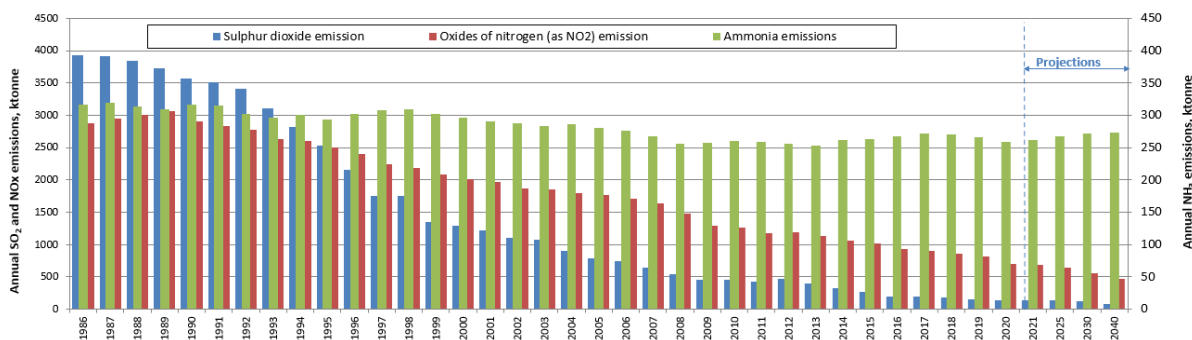
Figure 14 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986

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 non-seasalt sulphate, nitrate and ammonium, respectively. At this highly aggregated scale the rate of decrease in nitrate and ammonium concentration are smaller than that for sulphate.

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 NOx from transport emissions during the first national lock down. From 2019 to 2020 NO_X emissions from road transport were projected to decrease by about 28%. NO_X emissions from the road transport sector for 2021 are not yet available.

Network average nitrate concentrations slightly increased from 0.15 mg l^{-1} (10.5 µeq l^{-1}) in 2020 to 0.16 mg l^{-1} (11.6 µeq l^{-1}) in 2021. At the national scale, total NO_X emissions are projected to decrease by about 1 % from 2020 to 2021.

A small increase was also observed for non-sea salt sulphate which showed decreases from 0.080 mg l^{-1} (5 µeq l^{-1}) in 2020 to 0.096 mg l^{-1} (6 µeq l^{-1}) in 2021. The total sulphur dioxide emissions were projected to increase by about 4 %.

The national ammonia emission is projected to increase very slightly from 2020 to 2021 (259.2 kt to 262.68 kt) but the network average ammonium concentration in rainwater remained the same (0.22 mg l^{-1};16.0 µeq l^{-1}).
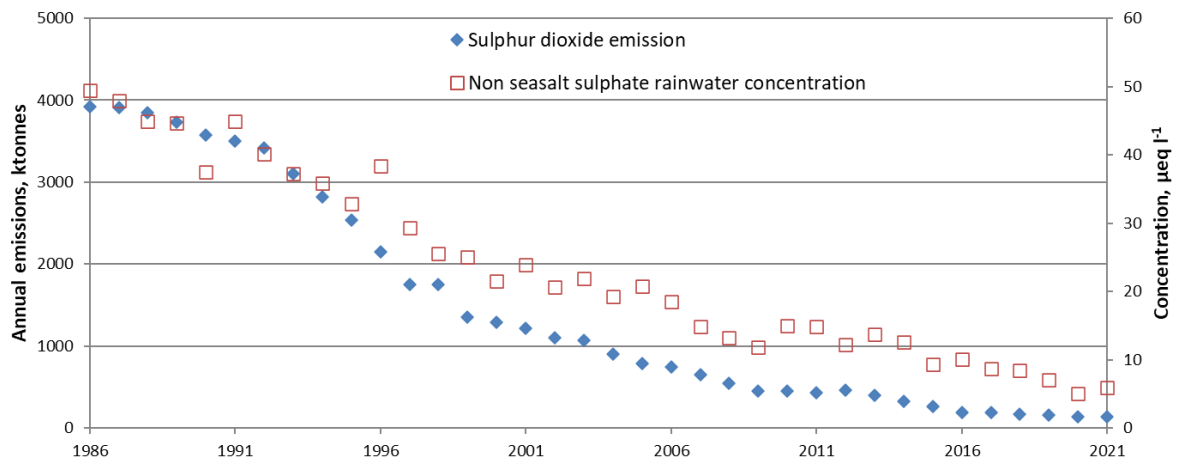
Figure 15 UK Sulphur dioxide emissions and network average sulphate concentrations in rainwater
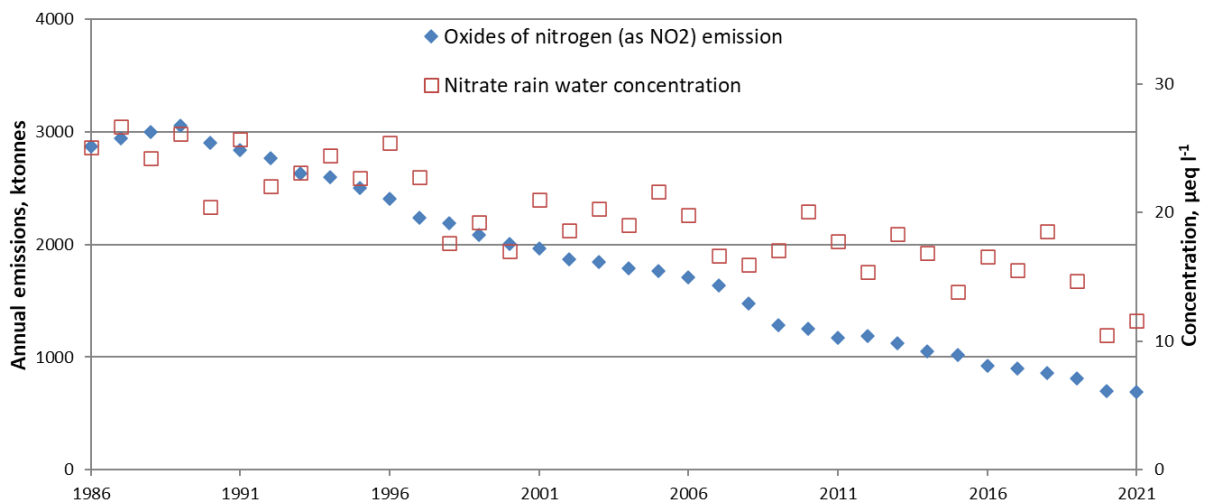

Figure 16 UK Oxides of nitrogen emissions and network average nitrate concentrations in rainwater
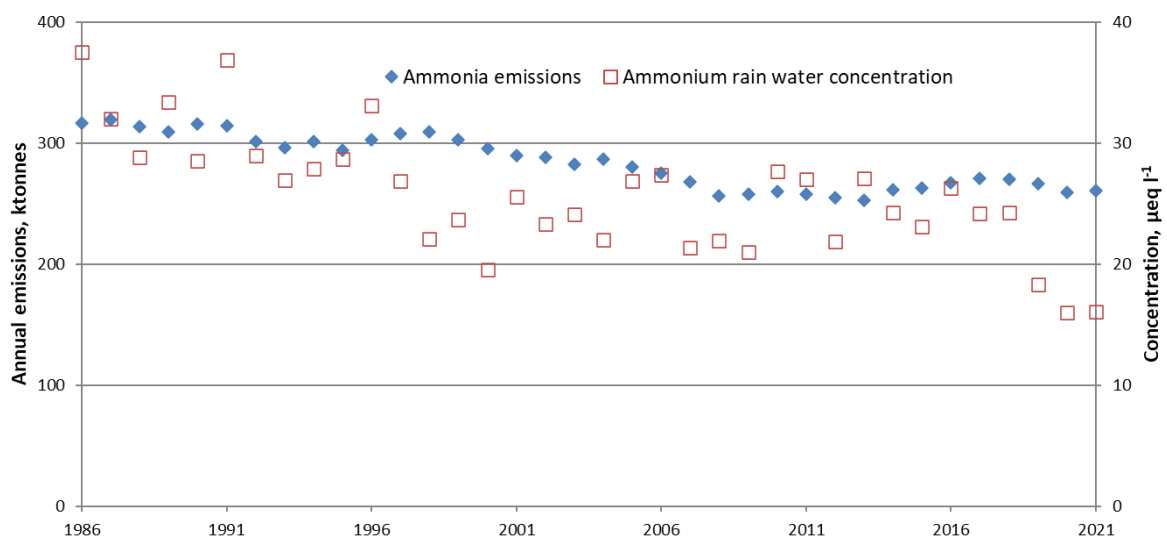
Figure 17 UK Ammonia emissions and network average ammonium concentrations in rainwater

3.2 NO$_2$-Net Network

The mean data capture of the diffusion tubes for all of the site in 2021 was 96% with 21 of the 24 sites achieving > 90% and 18 sites achieving 100% data capture.

The lowest data capture was observed at Bannisdale and was attributed to site accessibility. The site has been relocated to Bannisdale Beck.

Figure 15 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). It is apparent that 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 of the active NO$_2$-Net site over the period. More information relating to emissions in the UK can be found on the National Atmospheric Emissions Inventory (NAEI) website.

Table 5 *2021 NO$_2$ concentration from the Diffusion Tubes in the NO$_2$-Net*

Site Name	Raw 2021 concentration (µg m^{-3})	2021 concentration (µg m^{-3}) Bias Corrected (0.855)[a]	Data capture	Site Name	Raw 2021 concentration (µg m^{-3})	2021 concentration (µg m^{-3}) Bias Corrected (0.855)[1]	Data capture
Allt a'Mharcaidh	0.79	0.68	100%	Llyn Llydaw	1.77	1.51	96%
Balquhidder 2	1.25	1.07	100%	Loch Dee	1.48	1.27	100%
Bannisdale	2.48	2.12	61%	Lough Navar	1.53	1.31	100%
Chilbolton Observatory	7.78	6.30[b]	100%	Lullington Heath	9.01	7.71	100%
Driby 2	7.20	6.16	100%	Moorhouse	2.19	1.88	100%
Eskdalemuir	1.66	1.42	100%	Percy's Cross	2.61	2.23	100%
Flatford Mill	7.73	6.61	86%	Polloch	0.64	0.55	92%
Forsinard RSPB	0.98	0.84	88%	Pumlumon	1.90	1.63	100%
Glensaugh	1.79	1.53	100%	Strathvaich	0.56	0.48	100%
Goonhilly	3.86	3.30	100%	Tycanol Wood	2.47	2.11	100%
High Muffles	3.61	3.51[b]	100%	Whiteadder	2.15	1.83	90%
Hillsborough Forest	5.61	4.79	100%	Yarner Wood	3.07	2.63	100%

[a] *All sites bias adjusted by 0.855 with the exception of Chilbolton and High Muffles were corrected using co-located samplers, See appendix for details.*

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

NO$_2$ are associated with transport or industrial processes involving combustion, therefore there are smaller influences in concentrations at rural locations. The difference between the less rural site of Flatford Mill site which has an urban influence being about 50 miles from London and 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.
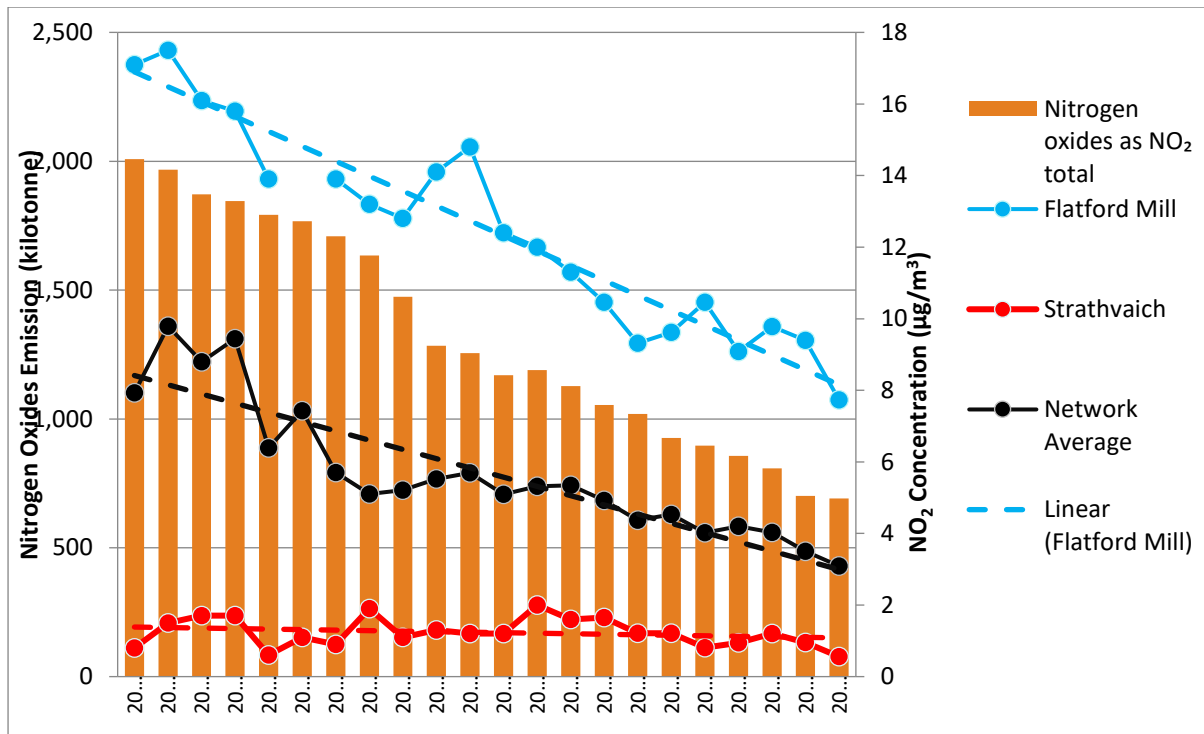
Figure 18 Long term trends where estimated emissions are plotted against selected sites in the network

The annual average uncorrected NO_2 concentrations from 2010-2021 (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.
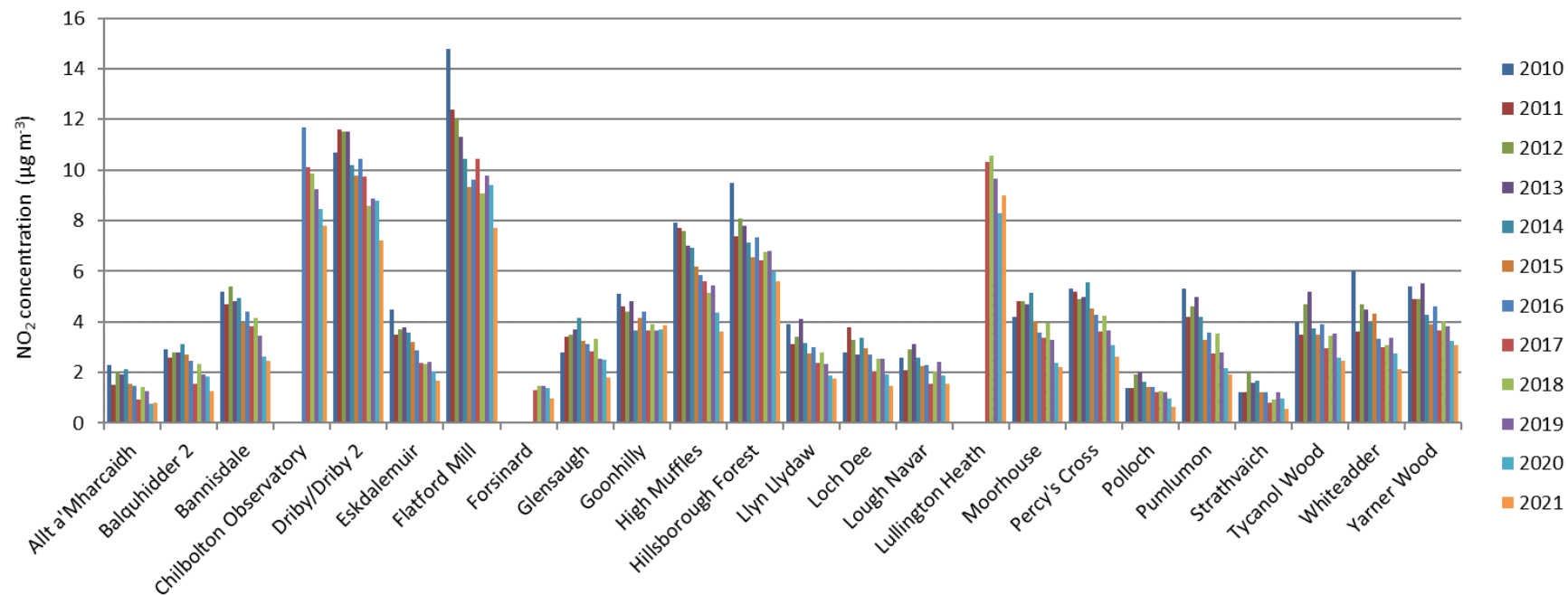
Figure 19 Annual mean NO₂ concentration (µg m⁻³) at the NO₂-Net sites 2010-2021

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 77% for NAMN.

UKCEH ALPHA® Sampler

Data capture at UKCEH ALPHA® sites was 91% in 2021 this is considered good data capture for this type of equipment. Data capture losses were primarily due to:

- Local site operator availability –some data losses (5-10%) occurred due site operator unable to change samplers
- Sampler losses – samplers lost at site either due to animal or poor weather conditions. Sites where repeated losses are observed are flagged for further action, no sites demonstrated repeated losses in 2021.

UKCEH DELTA® Sampler

Reduced data capture across UKCEH DELTA® systems (68%) was observed in 2021, this has been due to:

- COVID19 impacts increasing the time taken to discover and resolve site and LSO issues –Delays in discovering issues are due to laboratory reporting delays, delays implementing resolutions are due to parts and engineer availability external to UKCEH or Ricardo.
- Damage during transit of samplers – New transport cases were implemented from March 2022, to reduce damage to samplers.
- Water ingress –UKCEH rejected 1% of NAMN data data in 2021 due to water ingress on DELTA® samplers. It is currently being investigated by UKCEH the extent of the issue, the cause and a solution.
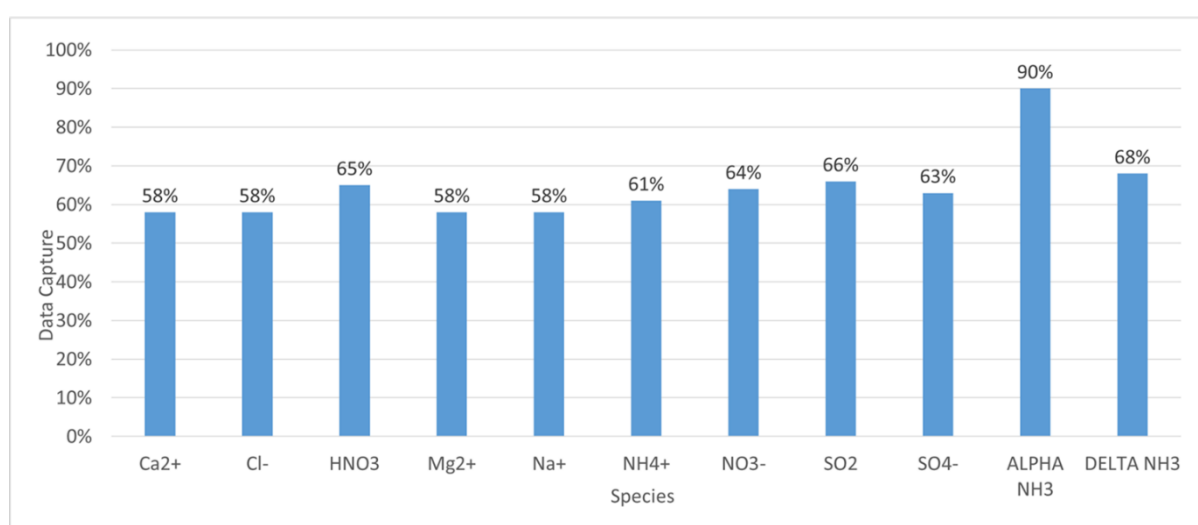

Figure 20 2021 NAMN and AGANet Percentage data capture by chemical component in 2021

NAMN Network Trends

The 2021 annual average NH_3 concentrations observed at each site in NAMN is presented in Figure 21, with the error bars showing the maximum and minima. 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 the eastern side of England (Brompton, Fressingfield and Sutton Bonnington, refer to Figure 7 and 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 dropped compared to the period 2015 to 2020, however atmospheric composition and meteorology plays an important role and therefore no conclusions should be made with this very slight drop in concentration.
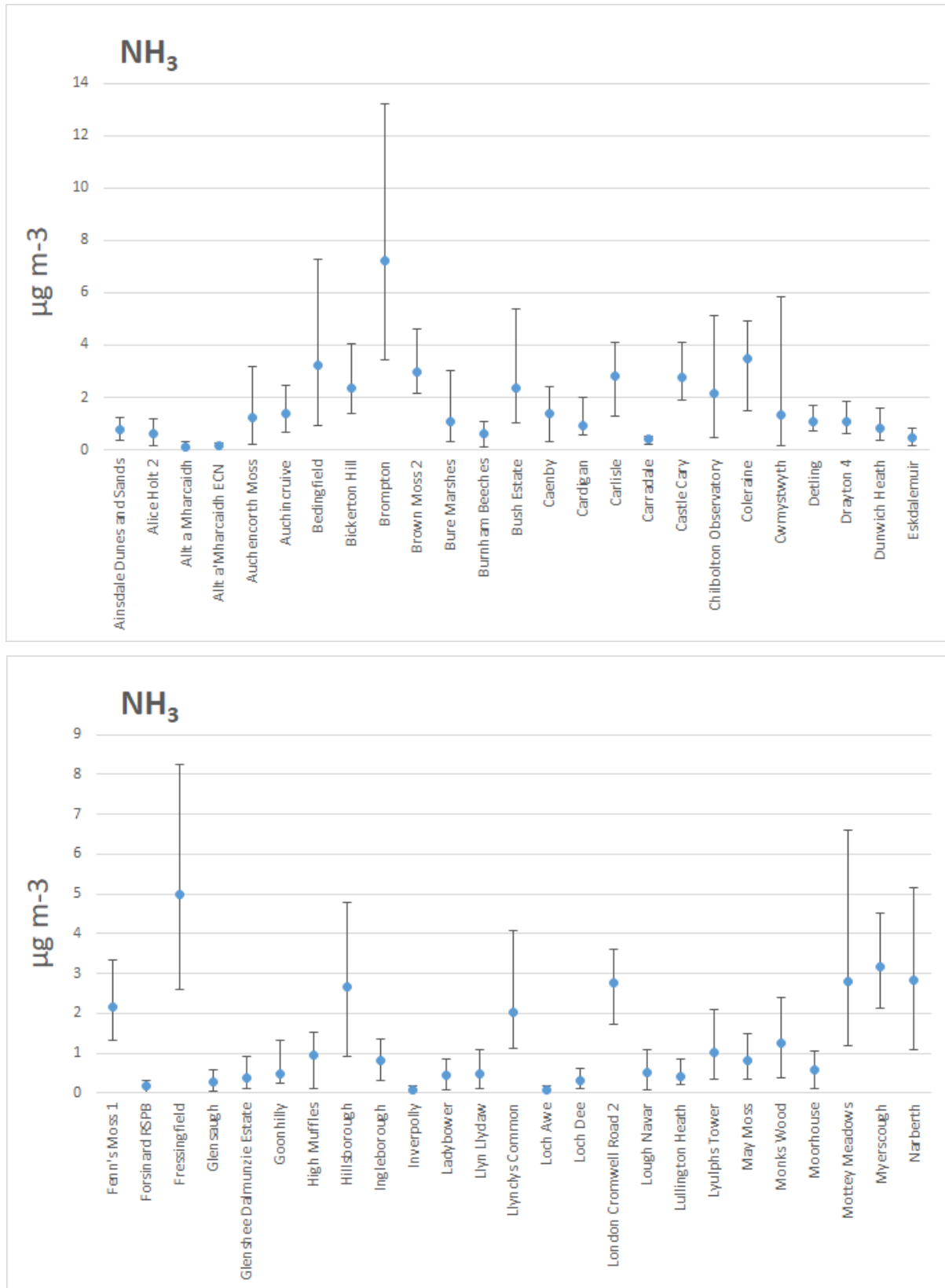
Figure 21 Annual mean concentrations of gaseous NH₃ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2021, whilst the bars show the minimum and maximum concentrations observed.
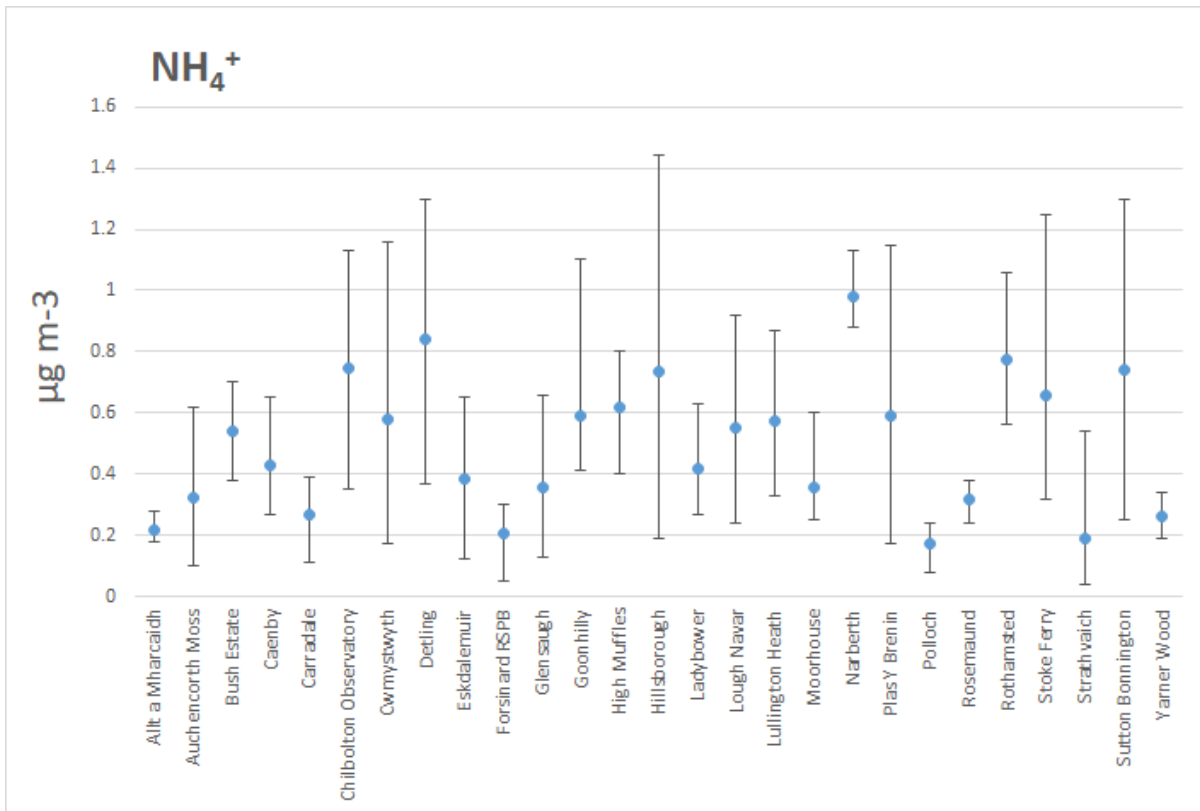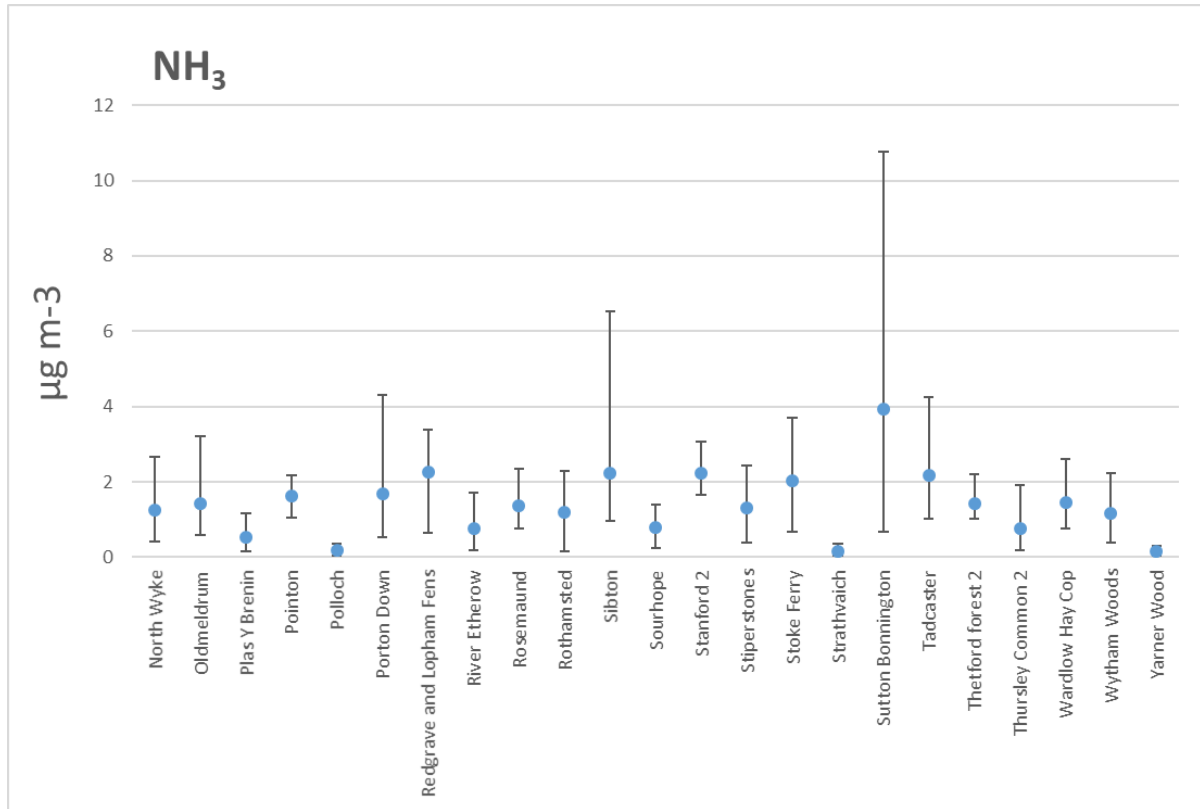
Figure 21 contd. Annual mean concentrations of gaseous NH₃ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2021, whilst the bars show the minimum and maximum concentrations observed.
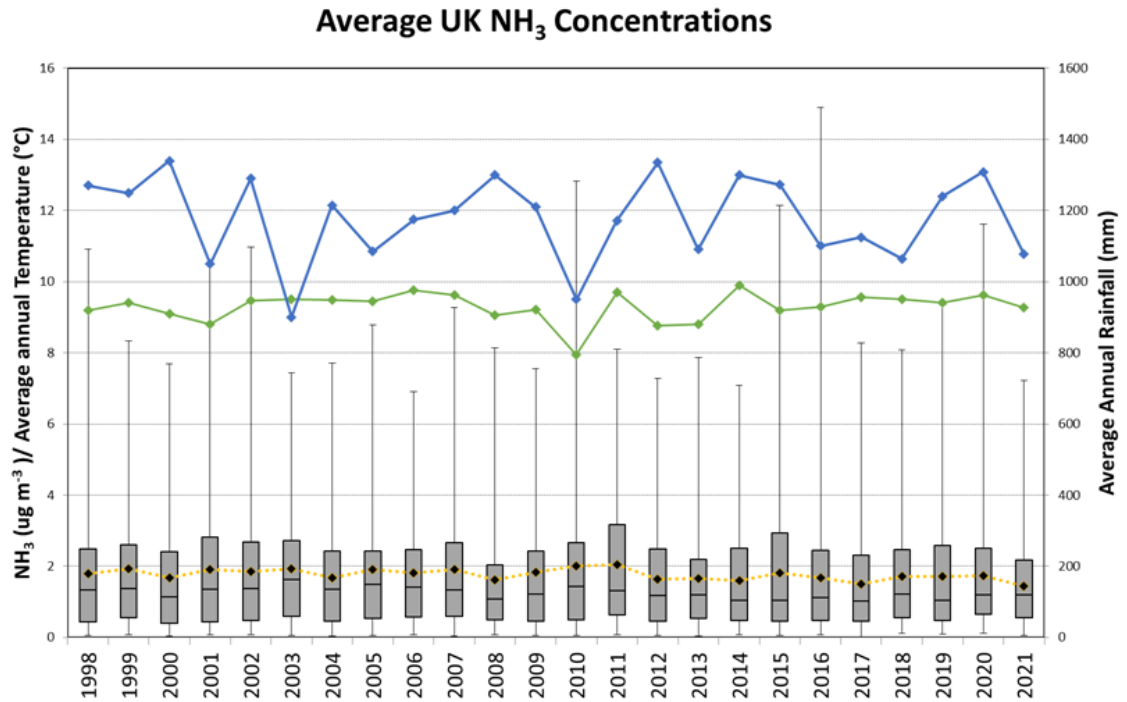
Average UK NH$_3$ Concentrations

Figure 22 Changes in atmospheric NH$_3$ averaged over all sites in NAMN operational between 1998 and 2021 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 over the past decade.
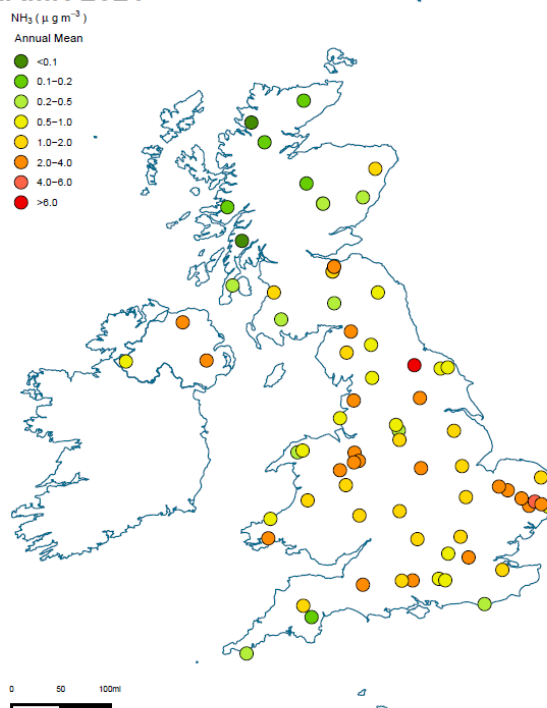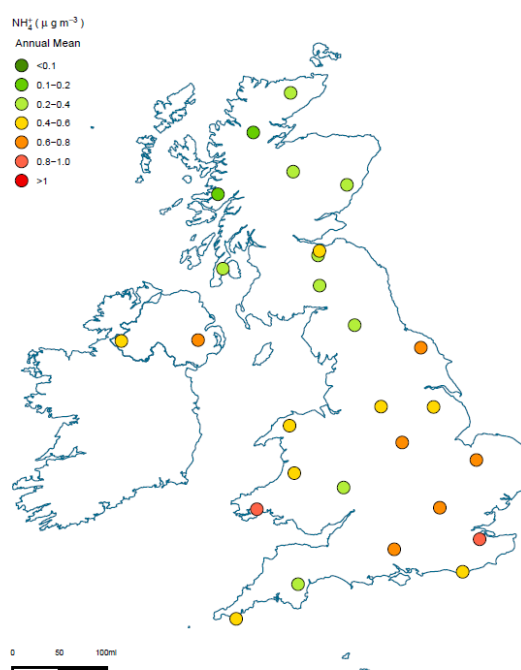
Figure 23 Spatial patterns of annual NH₃ and aerosol NH₄⁺ concentrations from monthly NAMN/AGANET measurements. Since February 2017, ammonium is measured at the 27 AGANET sites only.

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 59% for AGANet (Figure 20). This is less than reported for previous years.

UKCEH DELTA® Sampler

The reduced data capture across UKCEH DELTA® systems was observed in 2021, due to the following factors:

- COVID19 impacts increasing the time taken to discover and resolve site and LSO issues due to the following:
  - Delays in sample reporting by the laboratory due to covid restrictions.
  - Delays implementing resolutions due to parts and engineer availability external to UKCEH or Ricardo.
- Damage during transit of sample trains (14%).
  - New transport cases were implemented from March 2022 to to increase protection and reduce damage to sample trains during transport and postal exchange.
- Water ingress (5%) into samples
  - UKCEH are carrying out investigations to determine extent of the issue, cause and a solution. EA will be informed of resolution options as soon as they are available.

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, only Glensaugh and Narberth reported concentrations > 1 $\mu g\ m^{-3}$ during the year, whereas for HNO_3 only Detling reported a concentration > 1 $\mu g\ m^{-3}$. 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.
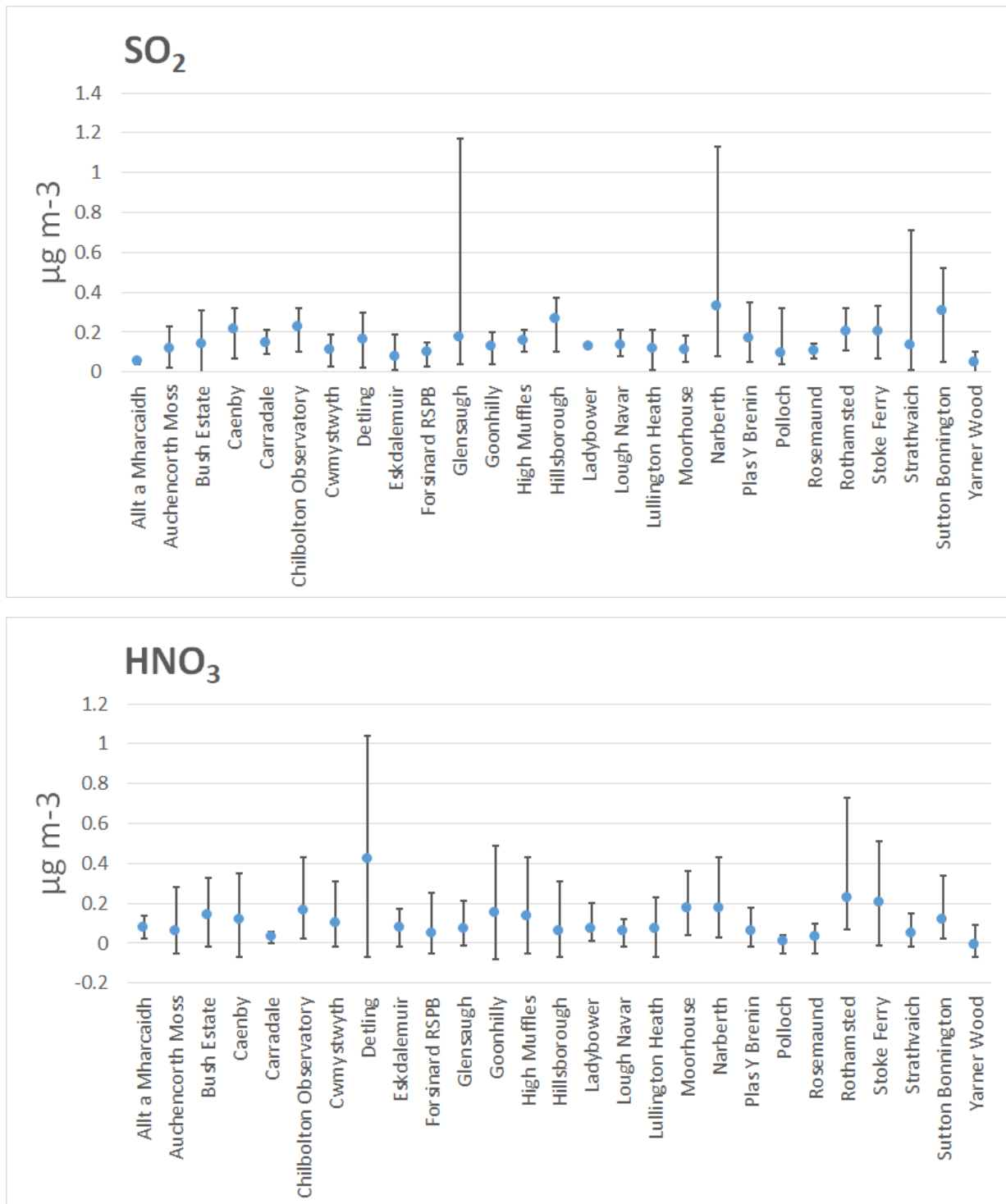
Figure 24 Mean monitored annual concentrations of gaseous HNO₃ and SO₂ at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2021, whilst the bars show the minimum and maximum concentration observed.
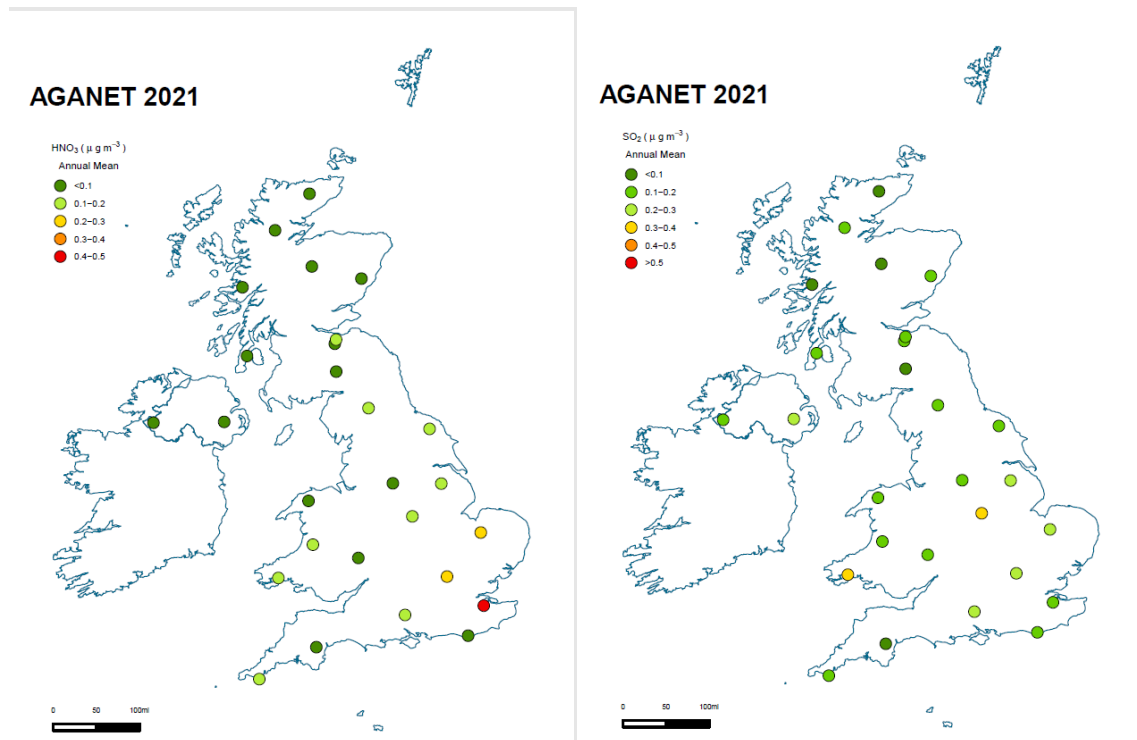
Figure 25 The annual average concentration of HNO₃ and SO₂ across the UK measured by AGANet in 2021.

Figure 26 shows the annual average, maximum and minimum of NO_3^-, SO_4^{2-}, NH_4^+ and Cl^- from each site during 2021 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). For SO_4^{-2}, this does not show the same spatial distribution in concentration and is variable across the UK (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.
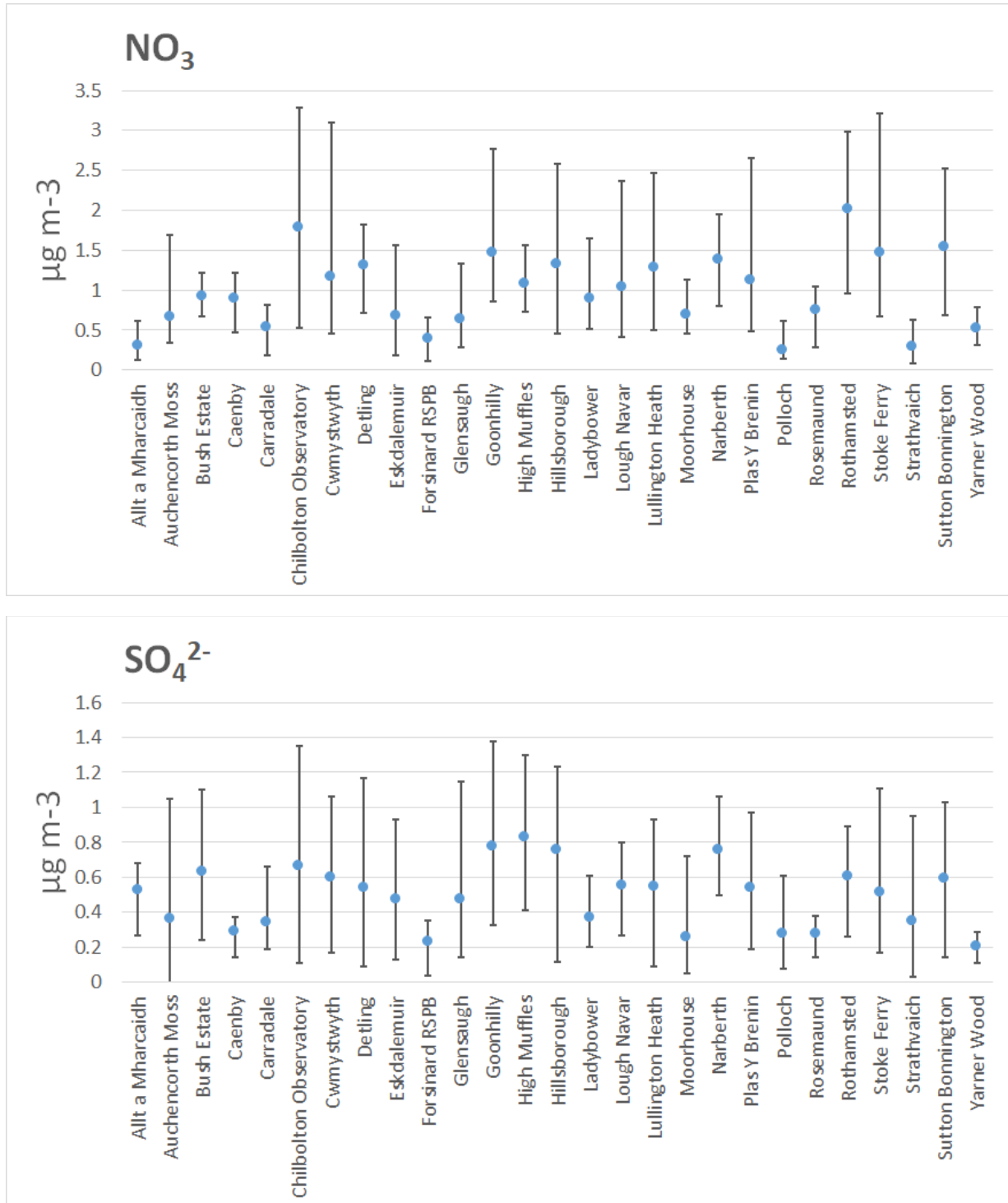
Figure 26 Mean monitored annual concentrations of particulate NO₃⁻, SO₄²⁻ , Cl⁻ and NH₄⁺ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2021, whilst the bars show the minimum and maximum concentrations observed
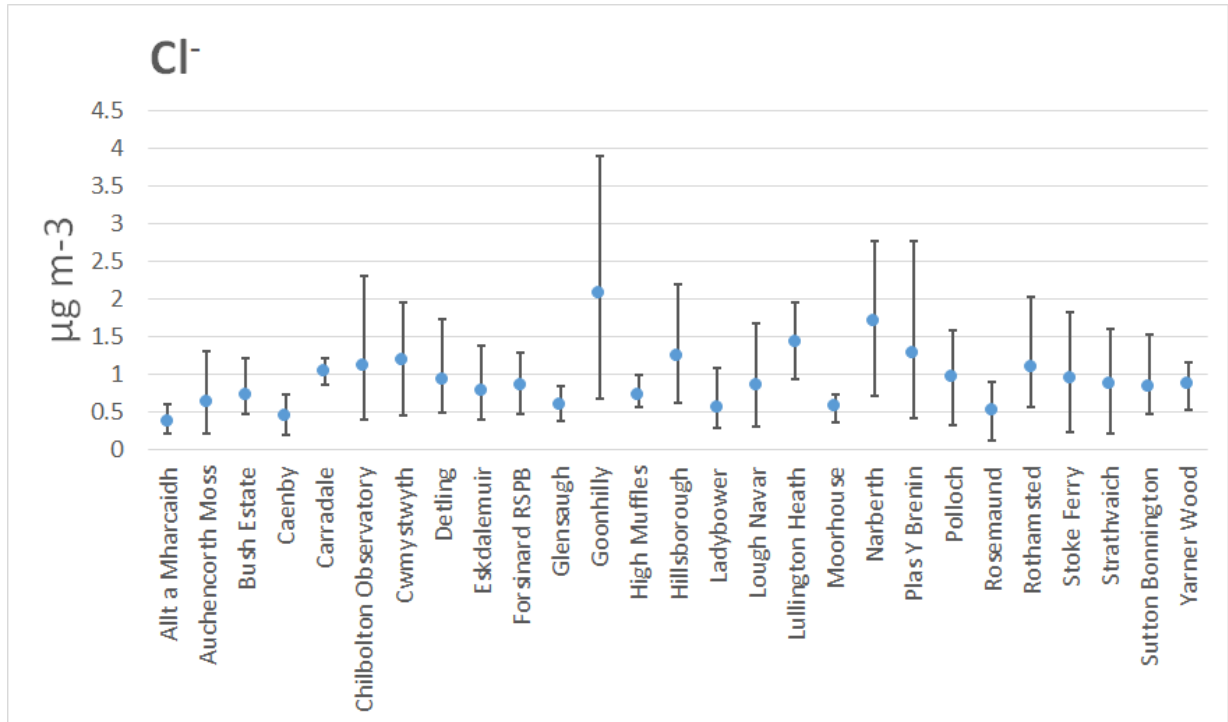
Figure 26 continued. Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-}, Cl^- and NH_4^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2021, whilst the bars show the minimum and maximum concentrations observed
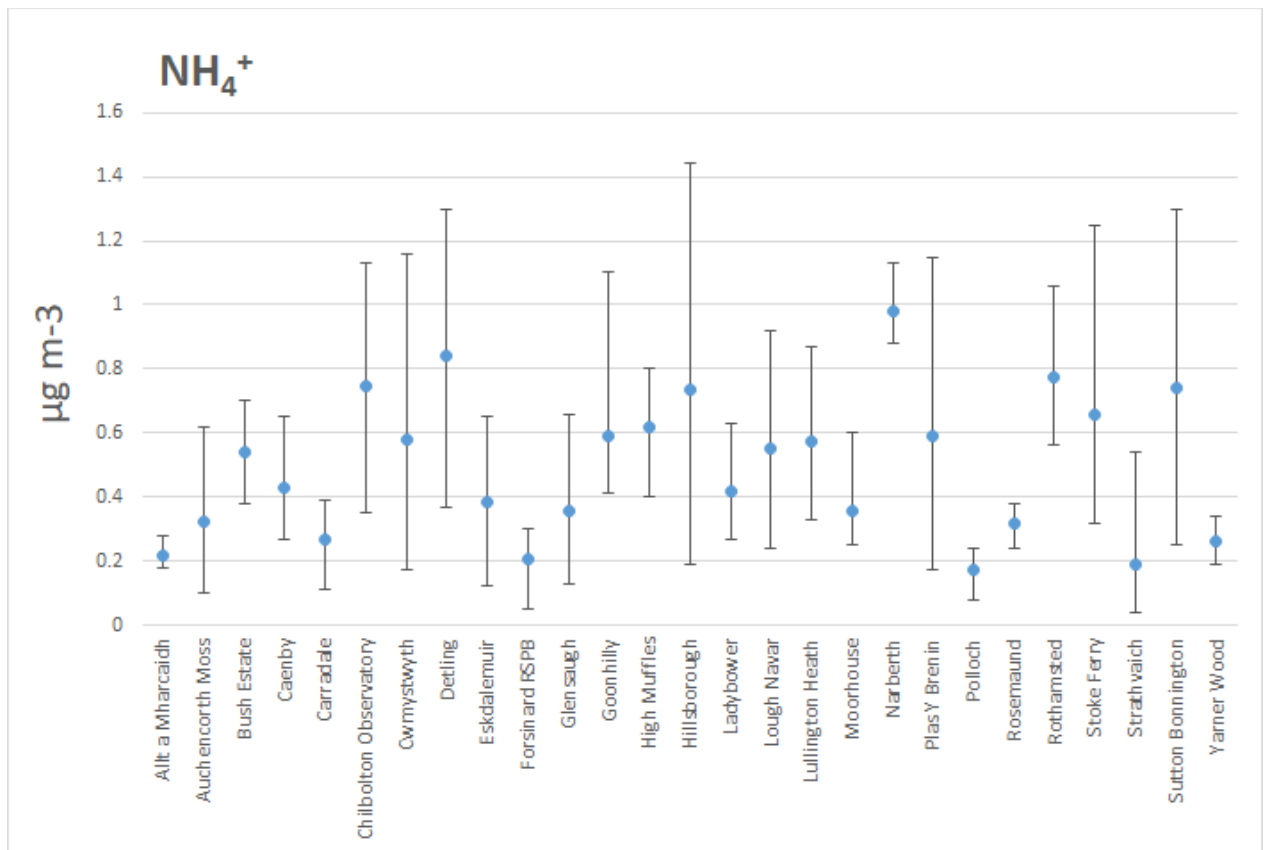
Figure 27 Annual average concentrations of NO_3^-, SO_4^{2-}, and $Cl+$ from AGANet and NH_4^+ from NAMN during 2021.

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 2021, whilst the bars show the minimum and maximum concentration
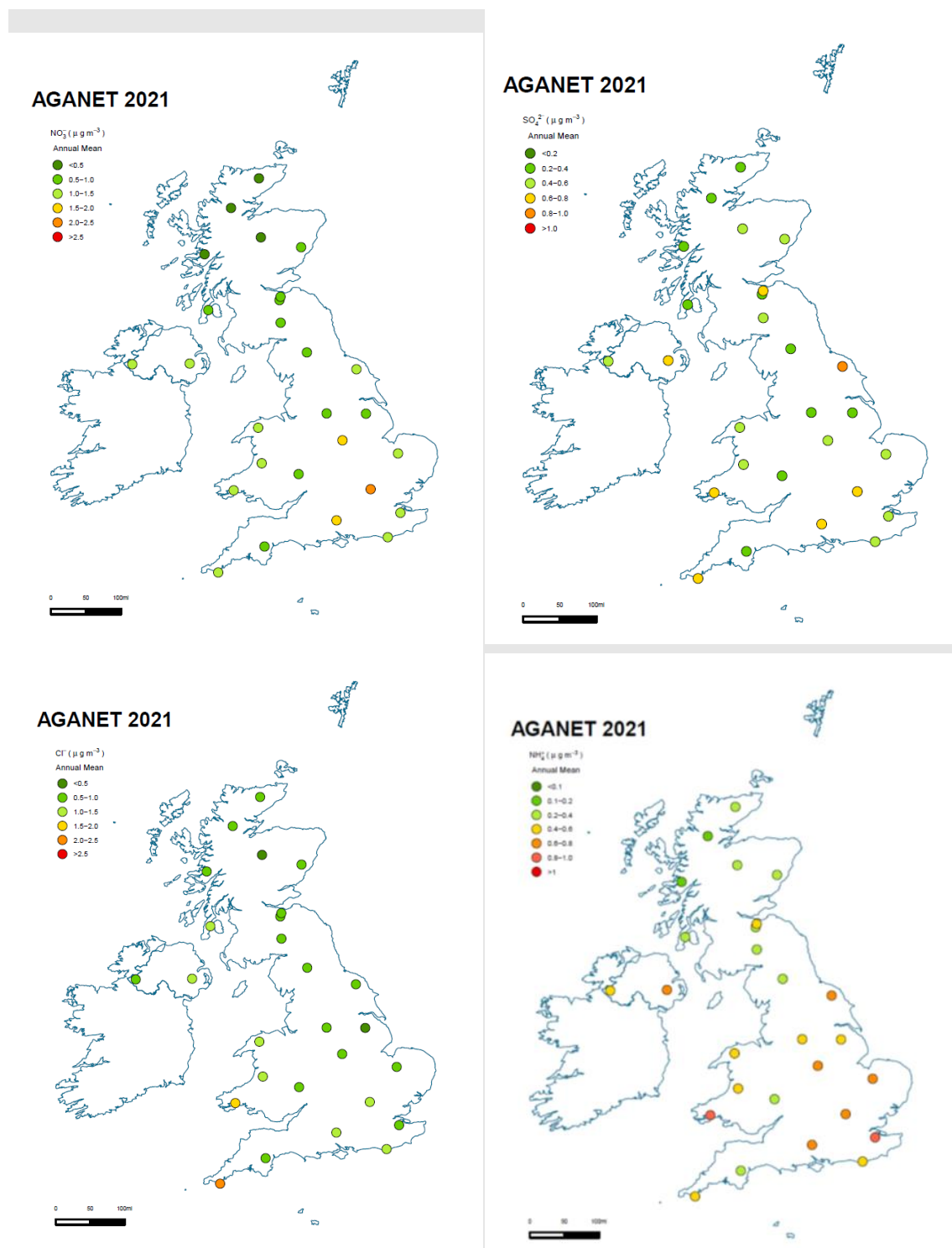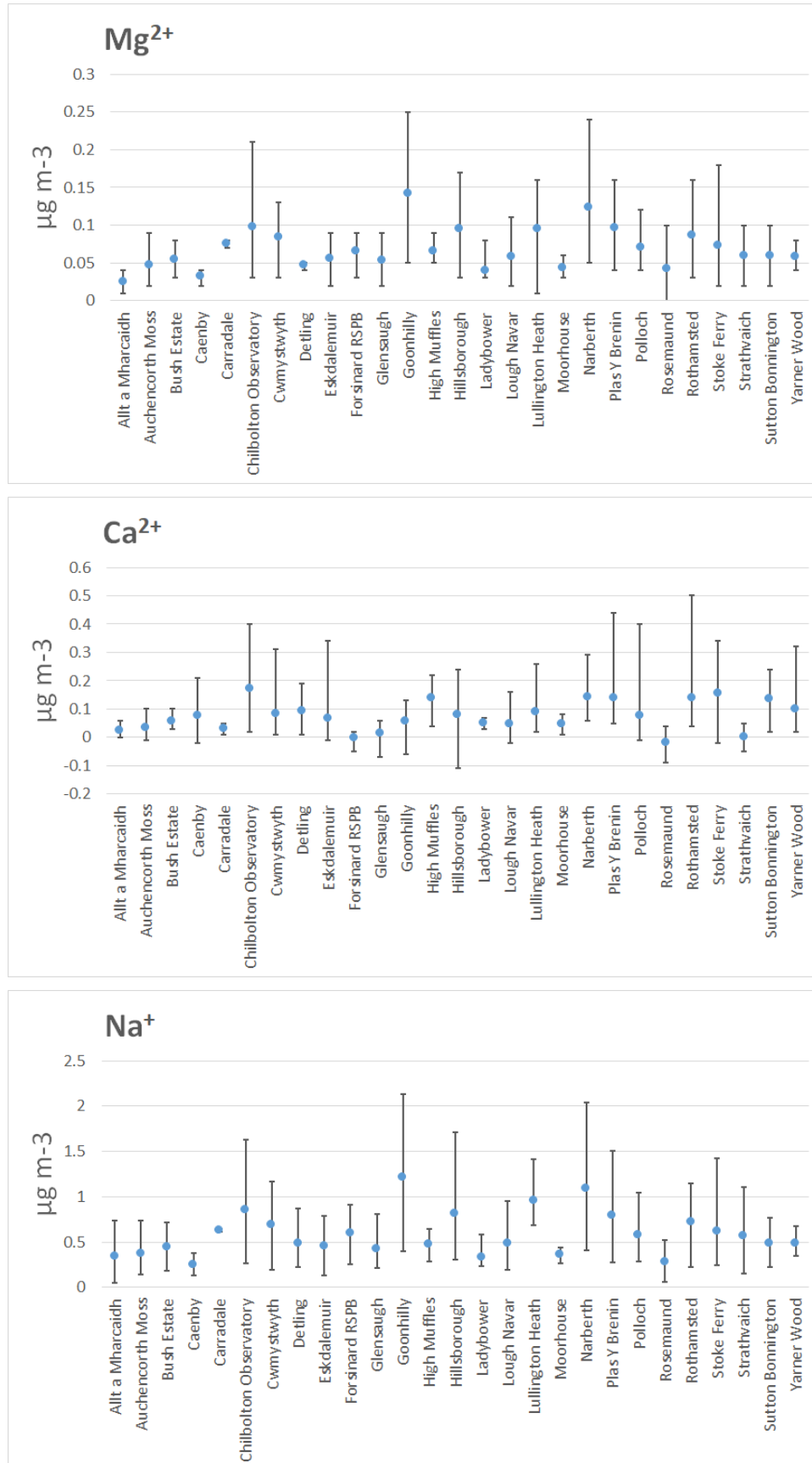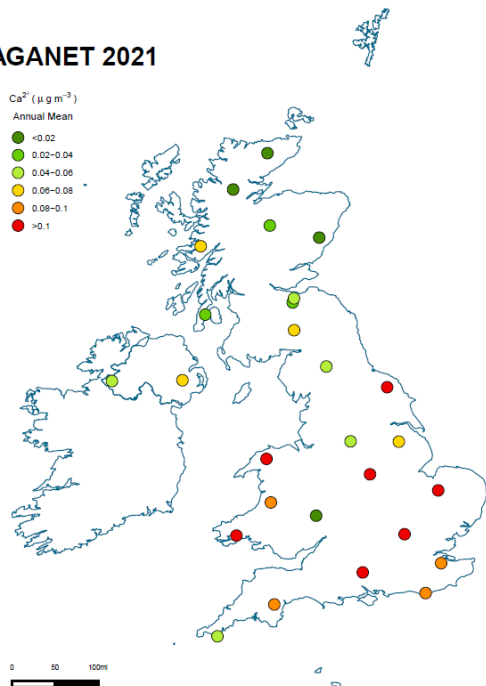
AGANET 2021

Ca²⁺ (μ g m⁻³)
Annual Mean
- <0.02
- 0.02–0.04
- 0.04–0.06
- 0.06–0.08
- 0.08–0.1
- >0.1

AGANET 2021

Mg²⁺ (μ g m⁻³)
Annual Mean
- <0.05
- 0.05–0.075
- 0.075–0.1
- 0.1–0.125
- 0.125–0.15
- >0.15
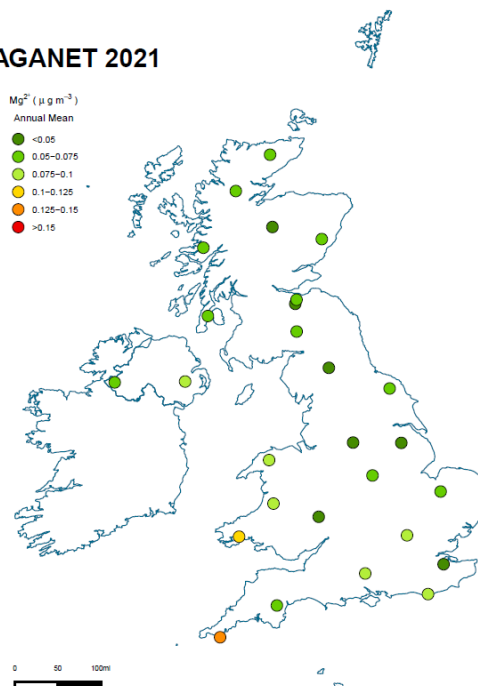
AGANET 2021

Na⁺ (μ g m⁻³)
Annual Mean
- <0.5
- 0.5–0.75
- 0.75–1.0
- 1.0–1.25
- 1.25–1.5
- >1.5
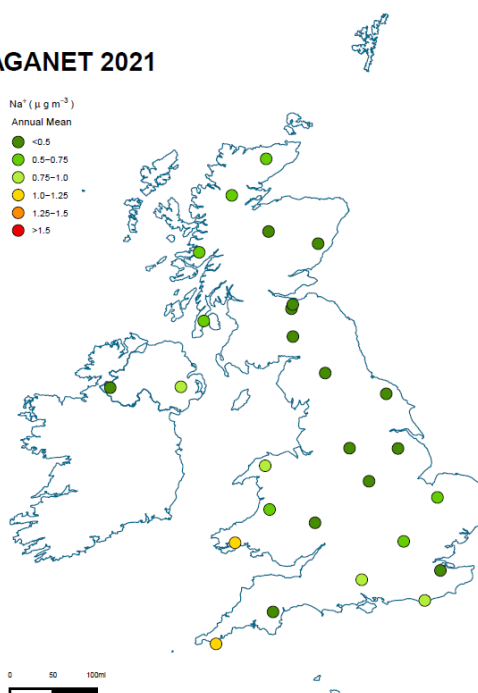
Figure 29 Annual mean monitored atmospheric base cations (Ca^{2+}, Mg^{2+} and Na$^+$) concentrations across the UK from the averaged monthly measurements made in 2021.

The long term averages for AGANet are shown in Figure 30 and Figure 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 previous UKEAP

reports for further details). 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 sudden drop in NO$_3^-$ concentration. There is no known reason to explain the observed change, however caution is advised in interpreting the result due to the low data capture in 2021 (refer to Figure 20).

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) and also the original 12 monitoring sites in the network.

Figure 31 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) and also the original 12 monitoring sites in the network.

Figure 32 compares the annual seasonal cycle (monthly averages) in 2021 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 September 2021 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 the summer of 2021 and for the majority of 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 2021.
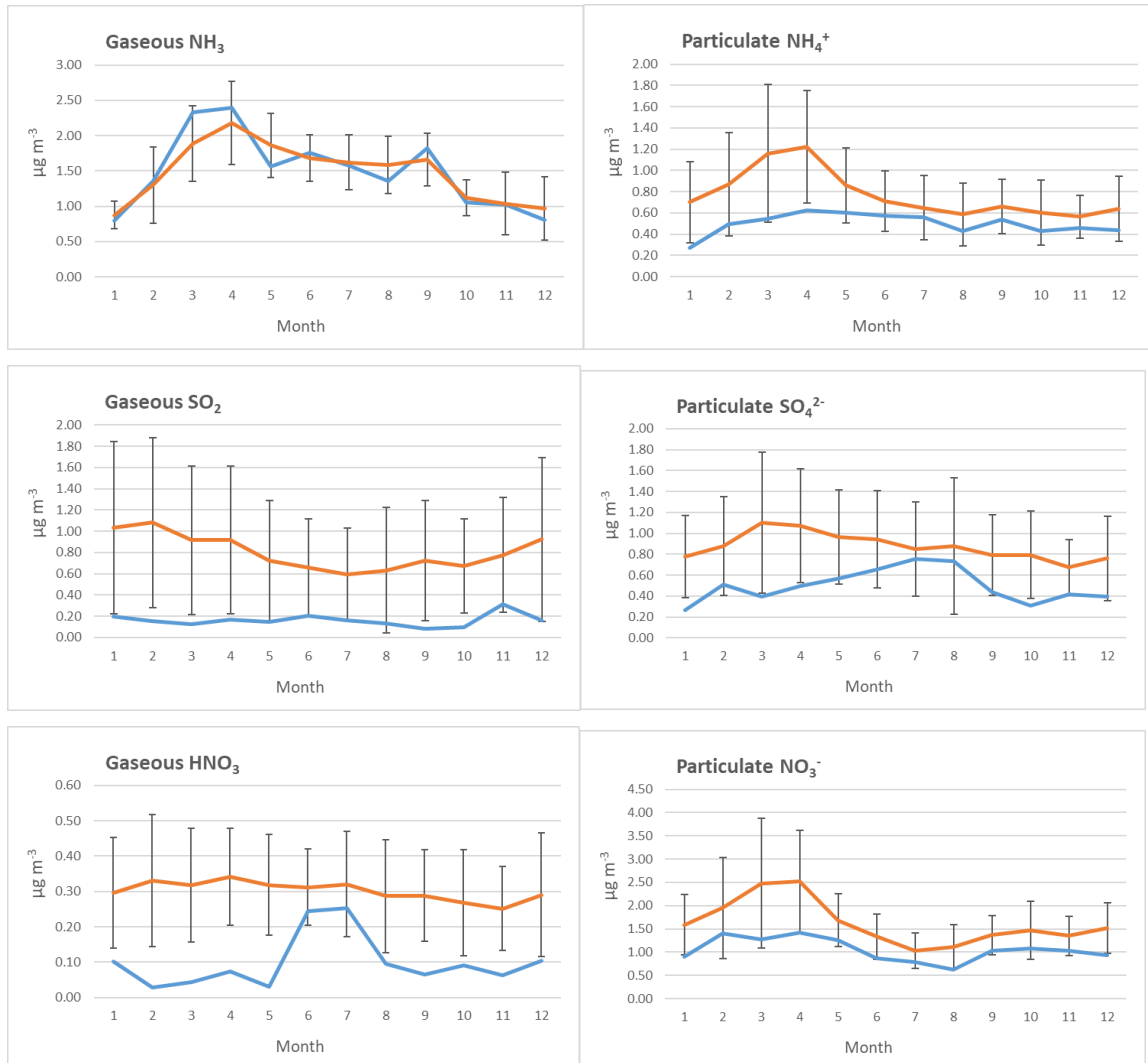
Figure 32 Monthly average of selected species from the NAMN and AGANet sites across the UK in 2021 (blue line), compared to the mean seasonal profile for year 2000-2021(orange line).Error bars are +/- standard deviation across the 27 AGANET sites in 2021

3.5 UK EMEP supersites

3.5.1 MARGA

During the year 2021, 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 Auchencorth Moss during 2021 the data capture was affected by the following operational issues:

- SJAC heater failure in January 2021.

At Chilbolton during 2021 the data capture was affected by the following operational issues:

- SJAC heater failure in January and February 2021
- degasser module failure June 2021
- anion ion chromatography (IC) pump failure in July 2021

There is more uncertainty on the Chilbolton LODs due to the lack of good blanks in most months in 2021 and limited measurement data in some months.

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

	Chilbolton		Auchencorth Moss	
Ion (PM_{10})	Annual mean (µg m^{-3})	Data capture (%)	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	0.945	47.95	0.425	81.53
Na^+	0.659	47.87	0.385	78.95
K^+	0.066	37.56	0.031	79.24
Ca^{2+}	0.149	37.76	0.040	77.47
Mg^{2+}	0.109	43.95	0.046	82.95
Cl^-	1.381	41.55	0.671	82.87
NO_3^-	2.270	41.54	0.789	80.39
SO_4^{2-}	1.322	41.30	0.668	80.19
Ion ($PM_{2.5}$)	Annual mean (µg m^{-3})	Data capture (%)	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	0.760	38.73	0.400	83.07
Na^+	0.194	44.92	0.236	78.32
K^+	0.057	42.44	0.020	80.41
Ca^{2+}	0.057	42.49	0.023	76.77
Mg^{2+}	0.056	42.64	0.026	84.16
Cl^-	0.545	40.46	0.403	84.78
NO_3^-	1.746	40.39	0.663	82.80
SO_4^{2-}	1.222	40.05	0.604	82.64
Trace Gases	Annual mean (µg m^{-3})	Data capture (%)	Annual mean (µg m^{-3})	Data capture (%)
NH_3	3.662	56.96	1.637	90.54
HCl	0.066	49.95	0.085	91.78
HNO_3	0.096	49.97	0.073	89.14
HONO	0.389	49.78	0.083	91.78
SO_2	0.063	50.03	0.047	88.58

Figure 33 to Figure 38 present the time series of the PM₁₀ (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ and SO₄²⁻), PM₂.₅ (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ and SO₄²⁻) and trace gases (NH₃, HCl, HNO₃, HONO, SO₂) reported by the MARGA at Chilbolton and Auchencorth Moss for 2021.
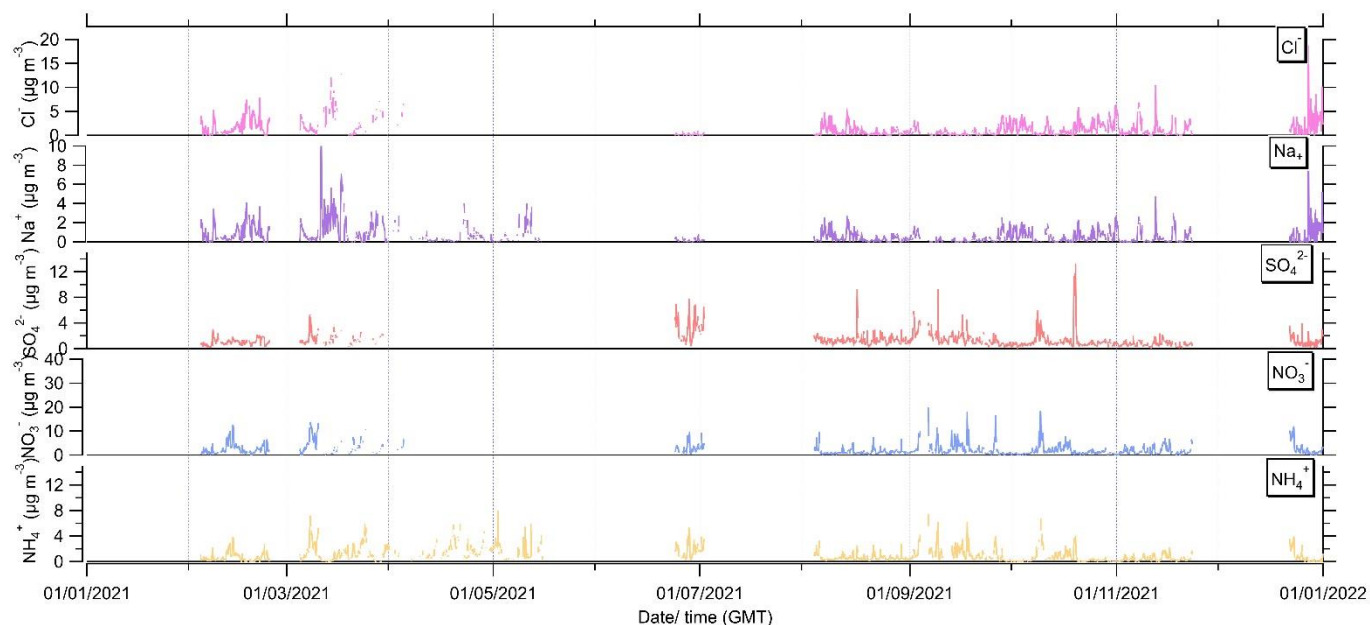
Figure 33 Ratified PM₁₀ speciated measurements by the MARGA at the Chilbolton supersite
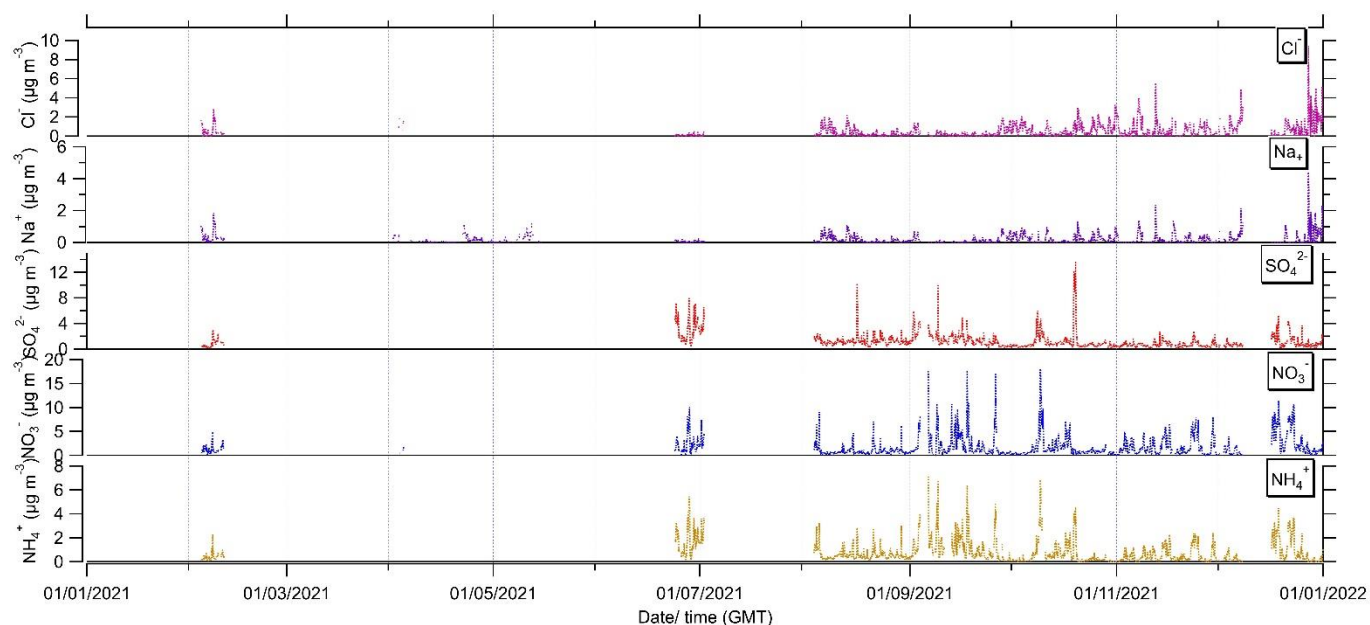
Figure 34 Ratified PM₂.₅ speciated measurements by the MARGA at the Chilbolton supersite
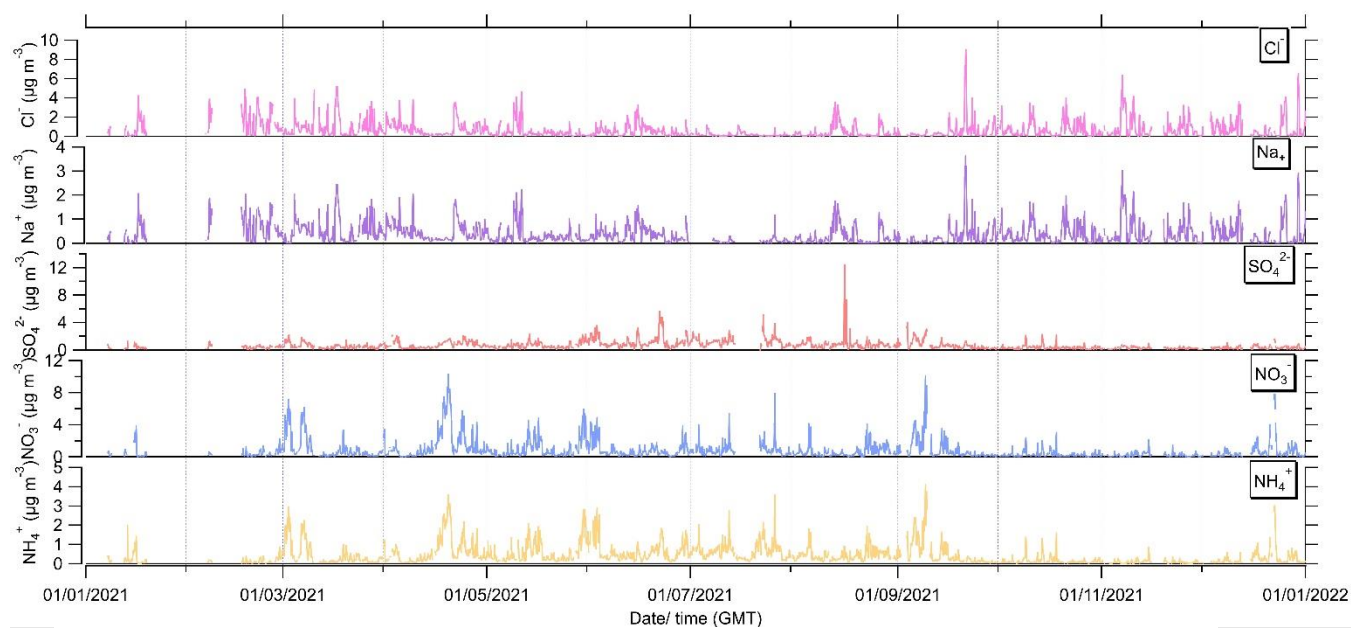
Figure 35 Ratified PM₁₀ speciated measurements by the MARGA at the Auchencorth Moss supersite
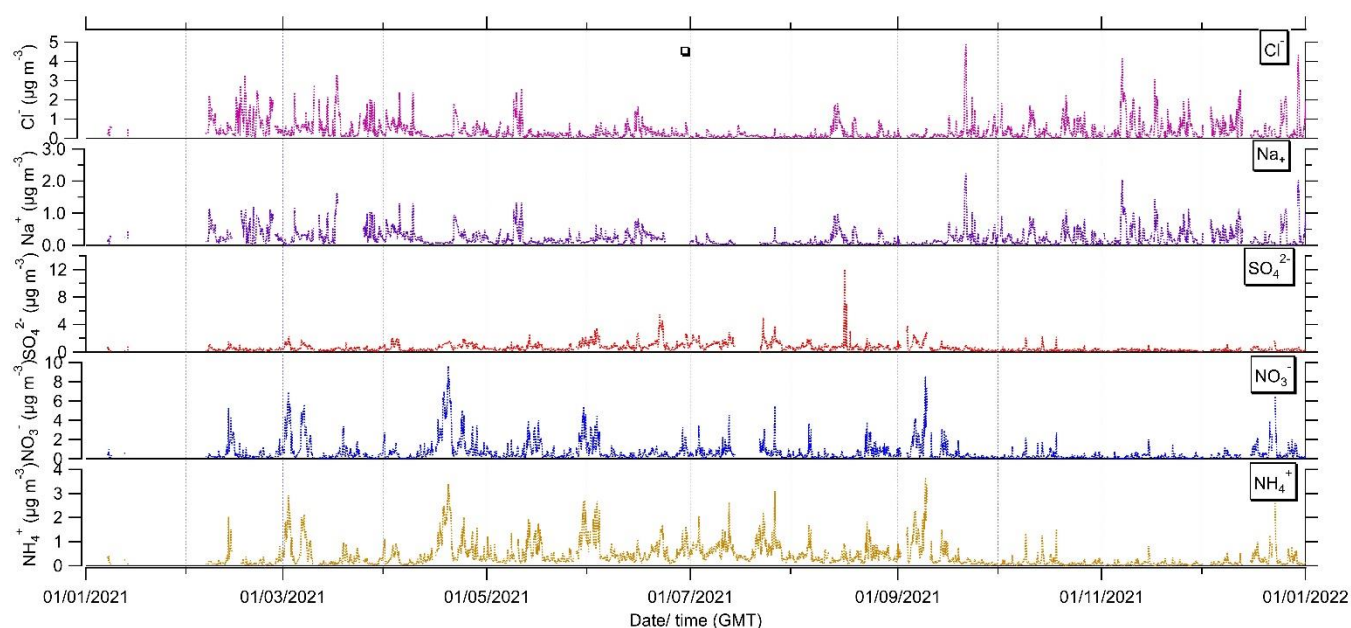
Figure 36 Ratified PM₂.₅ speciated measurements by the MARGA at the Auchencorth Moss supersite
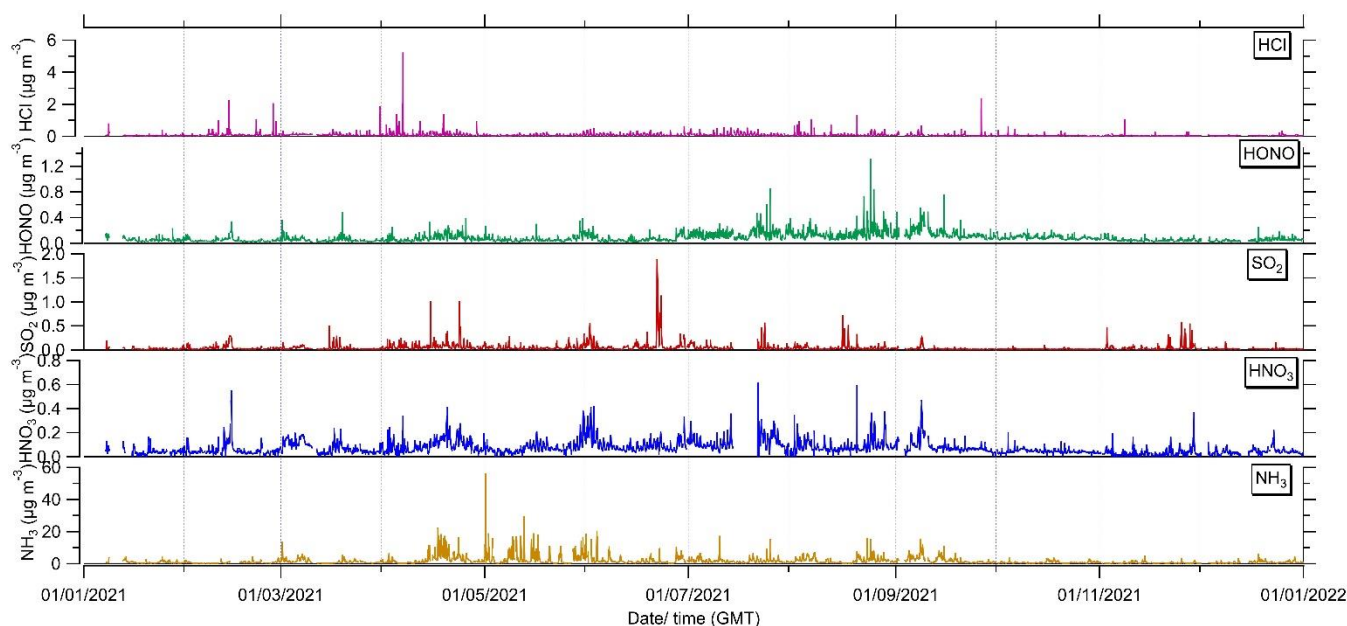
Figure 37 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite
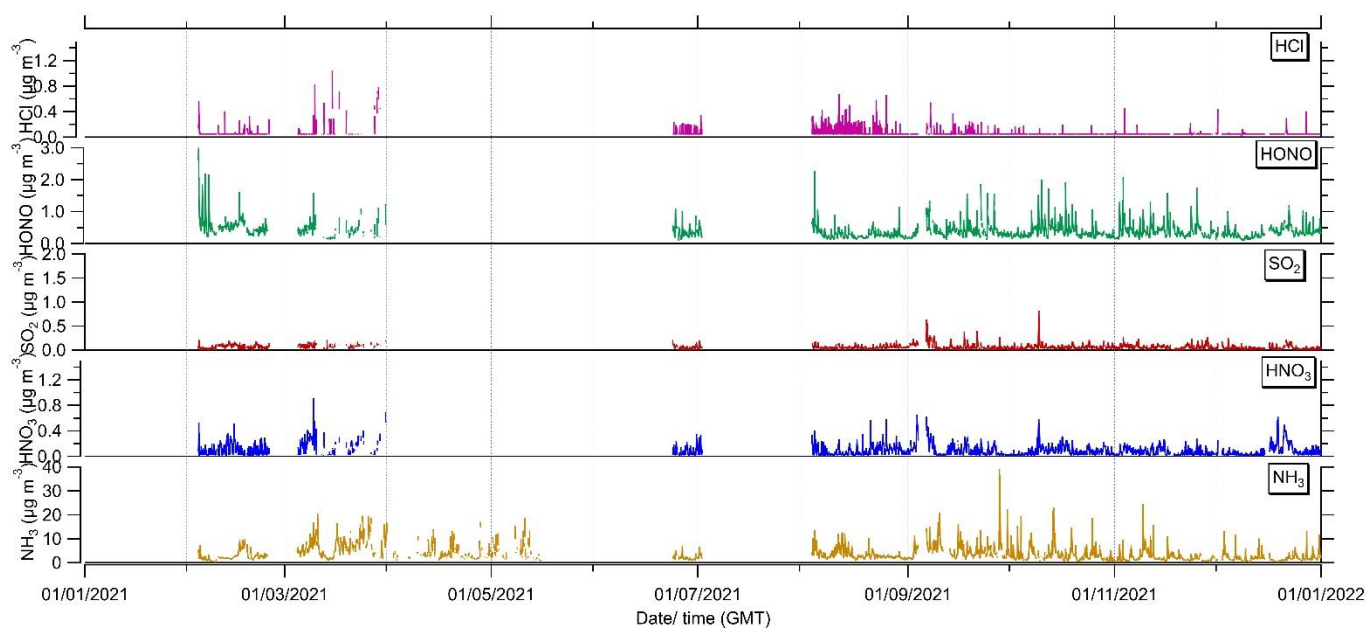
Figure 38 Ratified trace gas measurements by the MARGA at the Chilbolton supersite

Concentrations at both sites remain in usual range reported in previous annual reports. Auchencorth Moss continued to report higher concentrations of Na^+ and Cl^- compared to Chilbolton due to the dominance of Atlantic air masses (Figure 33 to Figure 36). Both sites on occasions pick up local emissions of NH_3, with concentrations reaching a maximum of 56.3 µg m^{-3} at Auchencorth Moss and 39.2 µg m^{-3} at Chilbolton, which are both attributed to local sources (Figure 37 and Figure 38). On the 16th August the aerosol became acidic due to excess sulphate. It is hypothesised that this is due to volcanic emissions from Iceland, investigations are ongoing to confirm the source (Figure 33 to Figure 36).

3.5.2 Tekran

The annual means and data capture for the 2021 ratified mercury measurements are shown below in Table 7.

Time series plots of the 2021 Auchencorth Moss measurements are shown in Figure 39. At the beginning of the year the system was only partially operational as the speciated sampling units were not collecting correctly. These were awaiting replacement due to the units being at the end of their life. As a result there is only GEM data for this period. In late April the pump module failed on the sampling system. This part was also due for replacement due to age. Without this part the instrument could not be operated leading to the loss of all data after this point until the new speciation system was installed in October. There is no data from the Chilbolton instrument as it was back in the lab undergoing fault finding and there were issues with roof access to reinstall the inlet at Chilbolton.

Table 7 Ratified mercury measurements

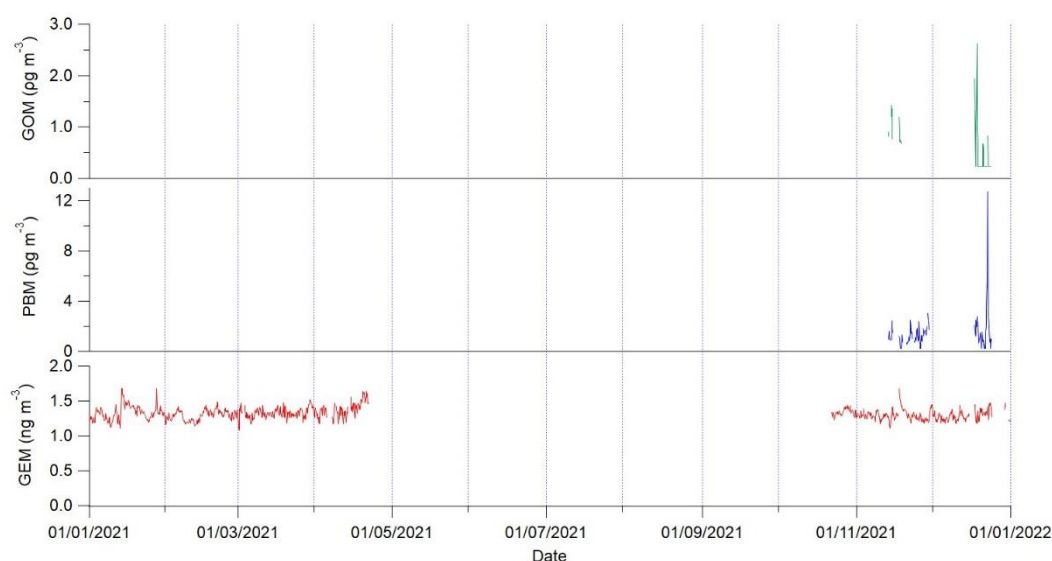|	Annual Mean	Data Capture (%)
Auchencorth Moss		
Gaseous Elemental Hg (GEM) ng m^{-3}	1.488	44.0
Gaseous Oxidised Hg (GOM) pg m-^{3}	0.596	2.1
Particulate bound Hg (PM$_{2.5}$) pg m^{-3}	1.488	4.5
Chilbolton		
Total Gaseous Hg (TGM) ng m^{-3}	N/A	

Figure 39 Ratified mercury measurements by the Tekran at the Auchencorth Moss supersite

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 2021 that have used the UKEAP network data:

ApSimon, H., Oxley, T., Woodward, H., Mehlig, D., Dore, A. and Holland, M., 2021. The UK Integrated Assessment Model for source apportionment and air pollution policy applications to PM2.5. *Environment International*, *153*, p.106515.

Berube, K., 2021. Air quality in Wales 2020. (https://orca.cardiff.ac.uk/id/eprint/147999/1/AQ-Wales-2020_English_Final.pdf)

Cao, H., Henze, D.K., Zhu, L., Shephard, M.W., Cady-Pereira, K., Dammers, E., Sitwell, M., Heath, N., Lonsdale, C., Bash, J.O. and Miyazaki, K., 2022. 4D-Var Inversion of European NH3 Emissions Using CrIS NH3 Measurements and GEOS-Chem Adjoint With Bi-Directional and Uni-Directional Flux Schemes. *Journal of Geophysical Research: Atmospheres*, *127*(9), p.e2021JD035687.

Cave, S. and Pike, J., 2021. Northern Ireland and Net Zero. (https://niopa.qub.ac.uk/bitstream/NIOPA/12789/1/1421.pdf)

Chang, C.T., Yang, C.J., Huang, K.H., Huang, J.C. and Lin, T.C., 2022. Changes of precipitation acidity related to sulfur and nitrogen deposition in forests across three continents in north hemisphere over last two decades. *Science of the Total Environment*, *806*, p.150552.

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.

Dimitriou, K., Mihalopoulos, N., Leeson, S.R. and Twigg, M.M., 2021. Sources of PM2. 5-bound water soluble ions at EMEP's Auchencorth Moss (UK) supersite revealed by 3D-Concentration Weighted Trajectory (CWT) model. *Chemosphere*, *274*, p.129979.

Ge, Y., Heal, M.R., Stevenson, D.S., Wind, P. and Vieno, M., 2021. Evaluation of global EMEP MSC-W (rv4. 34) WRF (v3. 9.1. 1) model surface concentrations and wet deposition of reactive N and S with measurements. *Geoscientific Model Development*, *14*(11), pp.7021-7046.

Kelleghan, D.B., Hayes, E.T., Everard, M., Keating, P., Lesniak-Podsiadlo, A. and Curran, T.P., 2021. Atmospheric ammonia and nitrogen deposition on Irish Natura 2000 sites: Implications for Irish agriculture. *Atmospheric Environment*, *261*, p.118611.

Kirby, B.P., Lewis, S.P. and Lewis, P.D., 2021. Do You Think Air? Public interest in Air Pollution. *Ergon. Hum. Factors*, p.8.

Mallin Martin, D. and Smedley, P.L., 2021. Baseline groundwater chemistry: the Lower Greensand aquifer of South East England. Nottingham, UK, British Geological Survey, 96pp. (OR/21/011) (https://nora.nerc.ac.uk/id/eprint/531806/)

Marais, E.A., Pandey, A.K., Van Damme, M., Clarisse, L., Coheur, P.F., Shephard, M.W., Cady-Pereira, K.E., Misselbrook, T., Zhu, L., Luo, G. and Yu, F., 2021. UK Ammonia Emissions Estimated With Satellite Observations and GEOS-Chem. *Journal of Geophysical Research: Atmospheres*, *126*(18), p.e2021JD035237.

Marchetto, A., Simpson, D., Aas, W., Fagerli, H., Hansen, K., Pihl-Karlsson, G., Karlsson, P.E., Rogora, M., Sanders, T.G., Schmitz, A. and Seidling, W., 2021. Good Agreement Between Modeled and Measured Sulfur and Nitrogen Deposition in Europe, in Spite of Marked Differences in Some Sites. *Frontiers in Environmental Science*, p.400.

Nash, J.W., Zekos, I. and Stack, M.M., 2021. Mapping of meteorological observations over the island of ireland to enhance the understanding and prediction of rain erosion in wind turbine blades. *Energies*, *14*(15), p.4555.

Saiz, E., Sgouridis, F., Drijfhout, F.P., Peichl, M., Nilsson, M.B. and Ullah, S., 2021. Chronic atmospheric reactive nitrogen deposition suppresses biological nitrogen fixation in peatlands. *Environmental Science & Technology*, *55*(2), pp.1310-1318.

Tang, Y.S., Flechard, C.R., Dämmgen, U., Vidic, S., Djuricic, V., Mitosinkova, M., Uggerud, H.T., Sanz, M.J., Simmons, I., Dragosits, U. and Nemitz, E., 2021. Pan-European rural monitoring network shows dominance of NH_3 gas and NH_4NO_3 aerosol in inorganic atmospheric pollution load. *Atmospheric Chemistry and Physics*, *21*(2), pp.875-914.

Tomlinson, S.J., Carnell, E.J., Dore, A.J. and Dragosits, U., 2021. Nitrogen deposition in the UK at 1 km resolution from 1990 to 2017. *Earth System Science Data*, *13*(10), pp.4677-4692.

Tso, C.H.M., Monteith, D., Scott, T., Watson, H., Dodd, B., Pereira, M.G., Henrys, P., Hollaway, M., Rennie, S., Lowther, A. and Watkins, J., 2022. The evolving role of weather types on rainfall chemistry under large reductions in pollutant emissions. *Environmental Pollution*, *299*, p.118905.

Vohra, K., Marais, E.A., Suckra, S., Kramer, L., Bloss, W.J., Sahu, R., Gaur, A., Tripathi, S.N., Van Damme, M., Clarisse, L. and Coheur, P.F., 2021. Long-term trends in air quality in major cities in the UK and India: a view from space. *Atmospheric Chemistry and Physics*, *21*(8), pp.6275-6296.

Vohra, K., 2022. *Application of Earth observations and chemical transport modelling to investigate air quality and health from the city to the global scale* (Doctoral dissertation, University of Birmingham).

Walker, H., 2021. *Representativeness and application of long-term trace gas and photolysis measurements for evaluating local air quality* (Doctoral dissertation, University of Edinburgh).

Worrall, F., Davies, R.J. and Hart, A., 2021. Dynamic baselines for the detection of water quality impacts–the case of shale gas development. *Environmental Science: Processes & Impacts*, *23*(8), pp.1116-1129.

3.7 Legislation and Standardisation

There were to the authors' knowledge no changes to legislation or standardisation to UKEAP network in 2021.

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.

6 References

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

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 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; Lobo-Guerrero Villegas, Juan Pablo. 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; Lobo-Guerrero Villegas, Juan Pablo. 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.

Results of the 39th EMEP Inter-comparison

The inter-comparison in 2021 was the 39th 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 ≤3 %. 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	0.095	0.094	1.1	S
C2	0.078	0.076	2.6	S
C3	0.09	0.089	1.1	S
C4	0.105	0.103	1.9	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. The improvement plan put in place by analytical laboratory has resulted in a significant improvement in the number of satisfactory results; there was only one unsatisfactory result (conductivity, G2) and four questionable results (calcium for samples G2, G4; pH for sample G2; conductivity for sample G1).

Table 9 39th EMEP Intercomparison

Species	Sample code	Reported value concentration mg l^{-1}	Expected concentration mg l^{-1}	Difference (%)	EMEP Quality Norm
SO_4^{-2}	G1	0.182	0.201	-9.5	S
	G2	0.225	0.244	-7.8	S
	G3	0.534	0.567	-5.8	S
	G4	0.63	0.688	-8.4	S
NH_4^+	G1	0.069	0.08	-13.8	S
	G2	0.21	0.227	-7.5	S
	G3	0.27	0.294	-8.2	S
	G4	0.416	0.454	-8.4	S
NO_3^-	G1	0.235	0.249	-5.6	S
	G2	0.347	0.366	-5.2	S
	G3	0.476	0.496	-4.0	S
	G4	0.741	0.738	0.4	S
Na^+	G1	0.286	0.32	-10.6	S
	G2	0.296	0.317	-6.6	S
	G3	0.885	0.948	-6.6	S
	G4	0.976	1.05	-7.0	S
Mg^{2+}	G1	0.077	0.077	0.0	S
	G2	0.086	0.088	-2.3	S
	G3	0.21	0.237	-11.4	S
	G4	0.243	0.279	-12.9	S
Cl-	G1	0.29	0.328	-11.6	S
	G2	0.364	0.367	-0.8	S
	G3	1.17	1.35	-13.3	S
	G4	1.22	1.43	-14.7	S
Ca^{2+}	G1	0.121	0.109	11.0	S
	G2	0.17	0.14	21.4	Q
	G3	0.287	0.294	-2.4	S
	G4	0.312	0.37	-15.7	Q
K^+	G1	0.248	0.289	-14.2	S
	G2	0.22	0.255	-13.7	S
	G3	0.39	0.441	-11.6	S
	G4	0.514	0.577	-10.9	S
pH*	G1	5.64	5.55	1.6	S
	G2	5.69	5.52	3.1	Q
	G3	5.56	5.48	1.5	S
	G4	5.52	5.46	1.1	S
Cond**	G1	5.41	6.73[a]	-19.6	Q
	G2	6.17	8.4[a]	-26.5	U
	G3	14.75	16.02[a]	-7.9	S
	G4	17.77	19.5[a]	-8.9	S

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

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

a.Note, these are the median conductivity values derived for all laboratories participating in the 39th EMEP intercomparison due to preparing samples with low ionic strength.

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 Harwell since 2007 (site closed at end of 2015 but replaced by Chilbolton) and at High Muffles since 2012. At each of these sites the diffusion tubes were co-located with an automatic analyser.

A comparison of the nitrogen dioxide concentrations measured by diffusion tube and automatic analyser is presented in Table 10. As was seen for the co-located samples in the national spreadsheet, concentrations measured by diffusion tube are higher than measured by the automatic analyser.

Figure 40 presents the data where data capture was greater than 75 %. The smallest concentrations are measured at Eskdalemuir and the largest at Chilbolton.

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)

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 2016); at High Muffles since 2012. These are shaded.
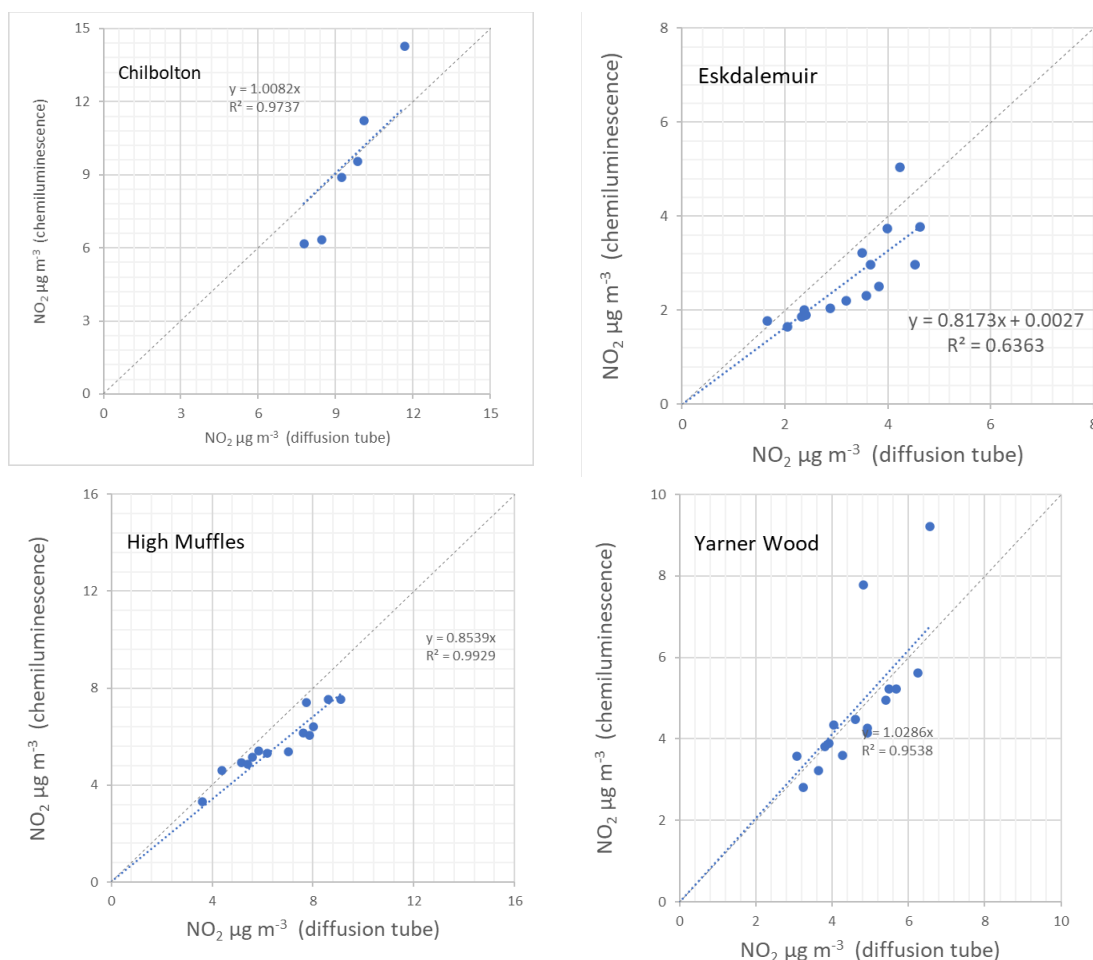
Figure 40 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each

TG16 recommends that each local authority should, if they 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 will be deriving bias adjustments each year using the collocated AURN stations and the corresponding from the Rural NO_2 Network measurements. This is because:

- the 'quality' of the measurement made by automatic analyser in the Rural NO_2 Network will always be to a "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 TG16 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. However, this year we have excluded Eskdalemuir and Yarner Wood from the bias adjustment calculation. Eskdalemuir was excluded because the NOx data capture for 2021 was low (41%). While Yarner Wood achieved the data capture target, the NO$_2$ measured by the automatic analyser was higher than that measured by the diffusion tube (3.6 µg m^{-3} and 3.1 µg m^{-3}, respectively). We have found no reason to reject the either measurement but have excluded the Yarner Wood site from the bias adjusted calculation. Therefore, this year, the bias factor is based on just two sites, High Muffles and Chilbolton.

In combining the respective B bias factors, we have followed the advice provided in TG.16 Paragraph 7.193[3]. The individual bias B factors were calculated as follows:

	High Muffles	Chilbolton
Bias factor, B	15%	35%

The average of the two values is calculated to be 17.03 % giving a bias adjustment factor of 0.855[4].

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[2] See https://laqm.defra.gov.uk/bias-adjustment-factors/local-bias.html   and Figure 7.1 of TG(16)

[3] Text from Paragraph 7.193:

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 collocation 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 2 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 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))