

# UKEAP 2019 Annual Report

Prepared for the Environment Agency

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Defra

And the Devolved Administrations

By

NERC Centre for Ecology & Hydrology

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Ricardo Energy & Environment

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# 1. Summary

## 1.1 Overview

The Defra rural air pollutant monitoring networks project, (2017-2020: ECM48524), **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)** comprises the following measurement activities:

- **UK EMEP monitoring supersites** (Chilbolton and Auchencorth)
  - **National Ammonia Monitoring Network (NAMN)**
  - **Acid Gases and Aerosol Network (AGA-Net)**
  - **Precipitation chemistry Network (Precip-Net)**
  - **Rural NO<sub>2</sub> diffusion tube network (NO<sub>2</sub>-Net)**
- The air quality measurements of Natural England’s Long Term Monitoring Network are embedded in NAMN and Precip-Net
  - The UKEAP network data underpins UK rural air quality modelling and mapping.
  - The diagram below highlights the most significant data applications in the UK and internationally (Figure 1).
  - The UKEAP network is operated by the UK Centre for Ecology and Hydrology and Ricardo Energy and Environment.
  - Measurements would not be possible without the dedicated support of Local Site Operators across the UK through the year

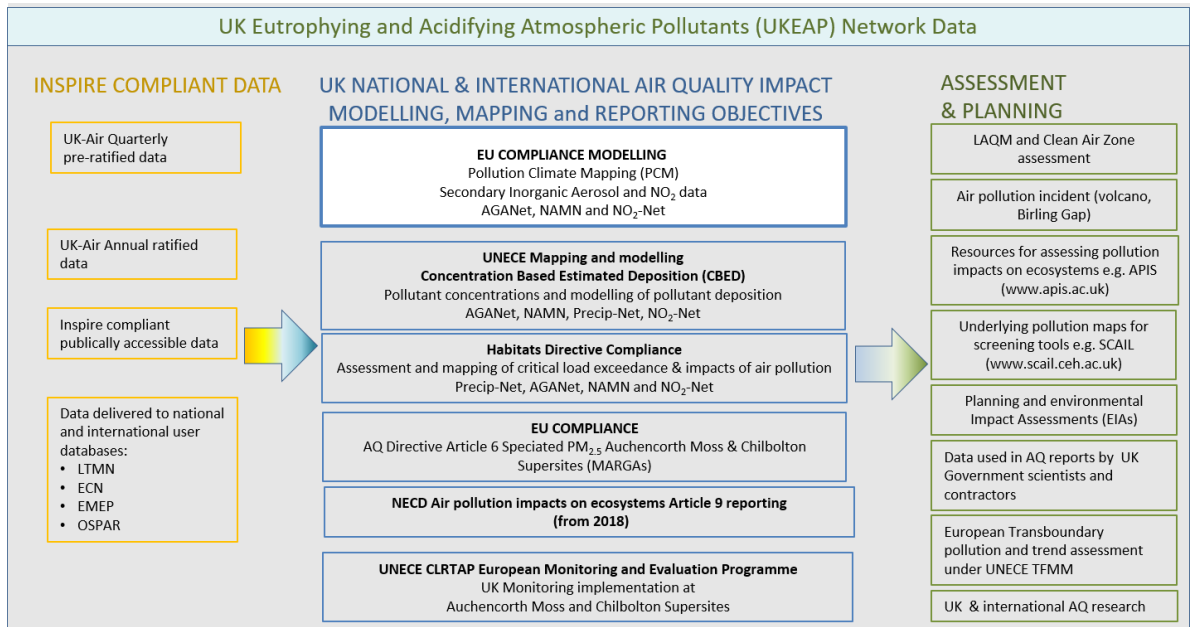


Figure 1. Summary of the data applications of the UKEAP datasets prior to the UKs EU exit. (Note: It is assumed that EU reporting objectives will continue and be transposed into UK law.)

## 1.2 Evidence and Policy Use of UKEAP Measurement data

Measurement data from the UKEAP networks are in place to support compliance assessment, assess exceedance of critical levels and loads, as well as inform policy development. A summary of on-going activities is presented below:

### Modelling Ambient Air Quality (MAAQ)

- Ambient concentrations of sulphate, nitrate and ammonium measured within the AGA-Net and NAMN networks are used to produce maps of the secondary inorganic aerosol components of PM<sub>2.5</sub> and PM<sub>10</sub>.
- The Rural NO<sub>2</sub>-Net is used to produce the rural background NO<sub>x</sub> concentration field in the Pollutant Climate Mapping compliance modelling process.

Further details of how these measurements are used in compliance assessment modelling can be found on <http://uk-air.defra.gov.uk> ([here](#)).

### Mapping and Modelling of Critical Loads and Levels

#### **Concentration Based Estimated Deposition (CBED):**

- UKEAP Precip-Net, AGA-Net, NAMN and NO<sub>2</sub>-Net data used to produce annual concentration & surface deposition maps of nitrogen and sulphur pollutants, separating wet and dry components.
- Long term trends and impact assessment.

Further details of this work may be found on <http://www.cldm.ceh.ac.uk/uk-national-focal-centre> ([here](#)).

#### **Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME)**

- NAMN data used with the model for calculating ammonia concentrations in the UK at 5 km and 1 km resolution and assessing critical level exceedance.

Further details of this work may be found on <http://www.pollutantdeposition.ceh.ac.uk/frame> ([here](#)).

#### **UK Critical Loads and Levels mapping:**

Maps from CBED and FRAME are used to assess:

- Impacts on UK ecosystems from sulphur and nitrogen.
- UK trends in ecosystems exceeding critical loads **headline indicator (B5a)** for Defra, JNCC and the Devolved Administrations.
- CBED calcium and base cation deposition used to derive UK acidity critical loads.
- UK critical loads submitted to the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) Working group for abatement strategy development.

Further details of this work may be found on <http://www.cldm.ceh.ac.uk/> ([here](#))

### **Support for National Air Pollution Control Strategies**

- Source-receptor data is calculated with FRAME to input to the UK Integrated Assessment Model and used to support national policy on strategies for control of air pollution, as well as for source attribution of Sulphur and Nitrogen deposition in APIS. See [here](#) for further details

### **Air Pollution Information System (APIS) (SEPA, JNCC, EA, NE, NRW, NIEA and SNH)**

- Resource for UK agencies, local authorities, SMEs and the public for information on air pollution related to ecosystem effects; uses UKEAP, CBED and Critical Loads maps.
- Searchable site relevant critical loads and source attribution.
- Assessment by habitat, ecosystem or species and literature database.

### **Habitats Directive assessments ([JNCC](#) and others)**

- Assessments based on critical loads exceedance for habitats which are sensitive to nitrogen
- Assessment of pressures and threats from air pollution as part of the conservation status assessments for Annex I habitats for the Article 17.
- Assessments used to inform judgements of conservation status.

### **Article 6 and [Annex IV](#) of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe**

The Air Quality Directive requires the speciation of PM<sub>2.5</sub> at rural background locations with a spatial coverage of 1 station per 100,000 km<sup>2</sup>. This sampling is coordinated with the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) through the two supersites at Chilbolton and Auchencorth Moss.

### **National Emission Ceiling Directive Article 9**

The NECD Article 9 requires the submission of site based monitoring of air pollution impacts on ecosystems. UKEAP data from NAMN, AGANet, Precip-Net and NO<sub>2</sub>-Net sites which are co-located with Defra, Natural England, Forest Research and other UKRI National Capability-ecosystem long-term monitoring networks are provided for the UK data collation and submission.

### **Direct public provision of air quality data**

*All the UKEAP data is managed through a centralised database and is available for download through the [UK-AIR](#) web site. 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.*

## 1.3 Publications

*Reports and research papers published in 2019 and 2020 using UKEAP site air quality data, maps derived from UKEAP data or science supported at UKEAP sites*

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**UKEAP data is freely available to download from UK-AIR and EMEP databases. Appendix 1 suggests citations formats for users. Data use is not tracked on the databases; the list collated above represents a non-exhaustive search of the literature.**

## 2. 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 and to allow validation of atmospheric transport models. This report summarises operation and monitoring data for 2019.

**UKEAP is comprised of:**

- **National Ammonia Monitoring Network** (NAMN – 74 sites)
- **Acid Gases and Aerosol Network** (AGA-Net – 27 sites)
- **Precipitation chemistry Network** (Precip-Net – 41 sites)
- **Rural NO<sub>2</sub> diffusion tube network** (NO<sub>2</sub>-Net – 24 sites)
- **UK EMEP Supersites** (Chilbolton Observatory and Auchencorth Moss)

The geographical distribution of the NAMN and AGANet networks are shown in Figure 2 and Figure 3 respectively, Precip-Net and NO<sub>2</sub>-Net in Figure 4. Natural England **Long Term Monitoring Network** air quality measurements are embedded in UKEAP networks Precip-Net and NO<sub>2</sub>-Net.

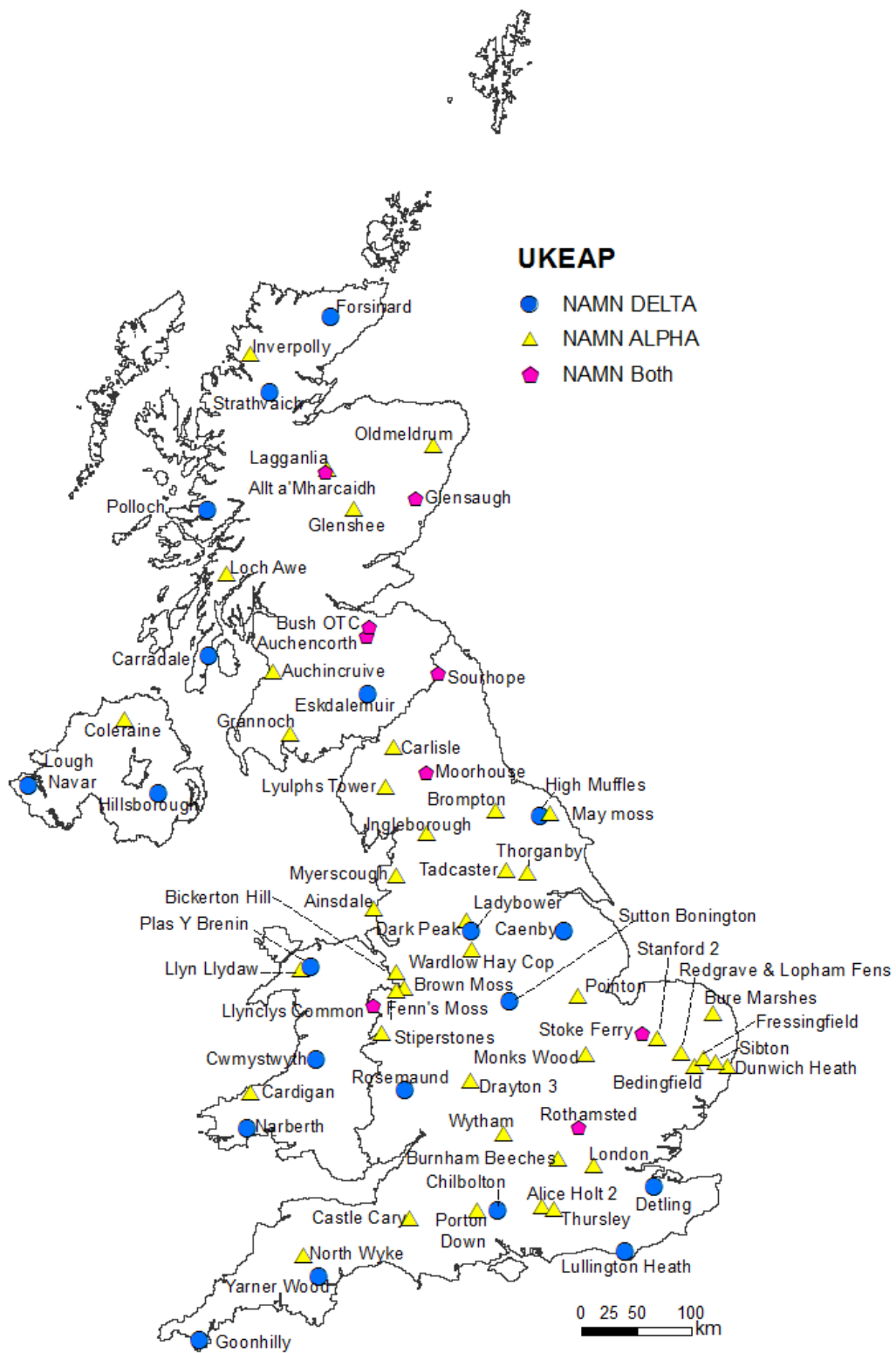


Figure 2 UK National Ammonia Monitoring Network (NAMN)

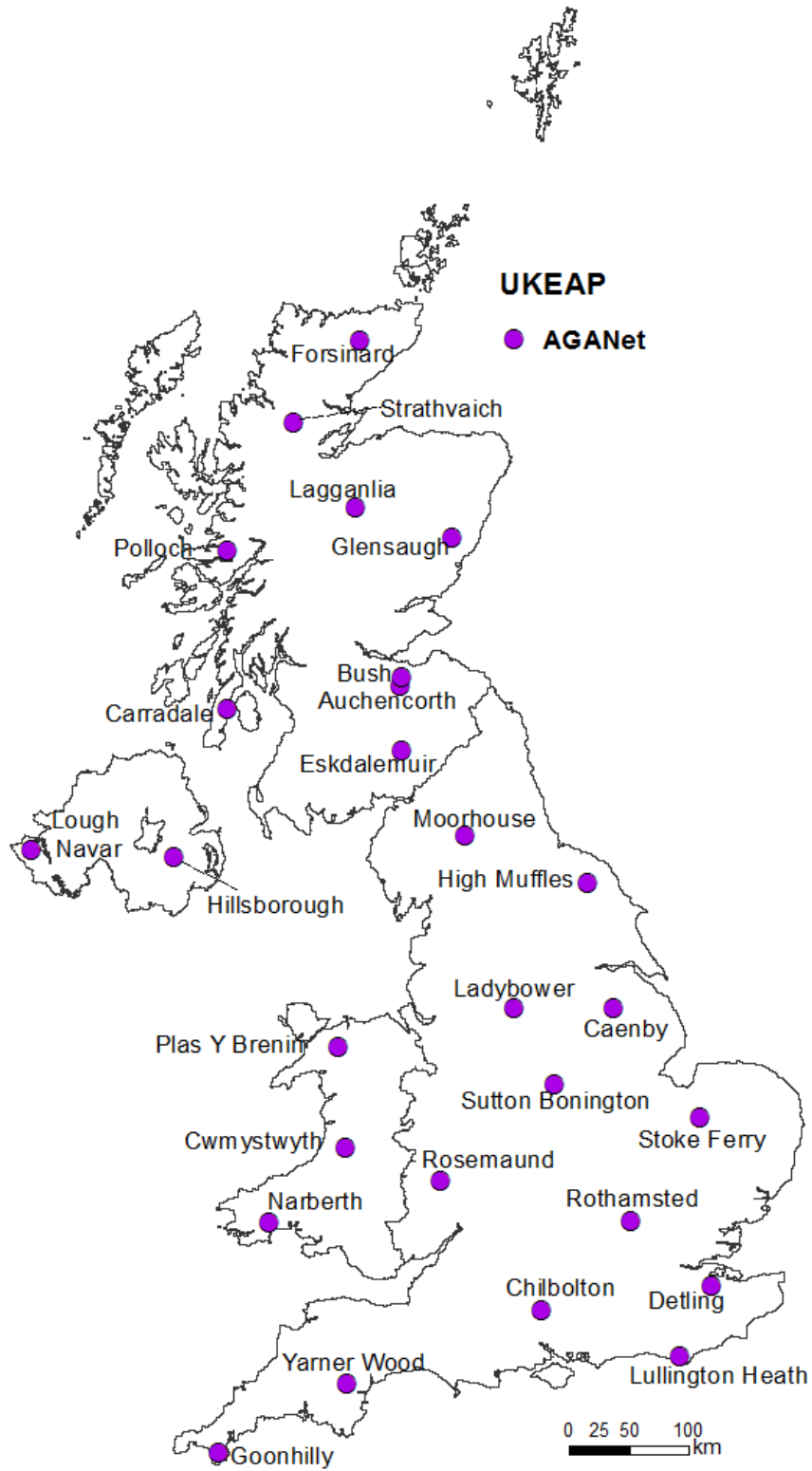


Figure 3 UK Acid Gases and Aerosol Network (AGANet)

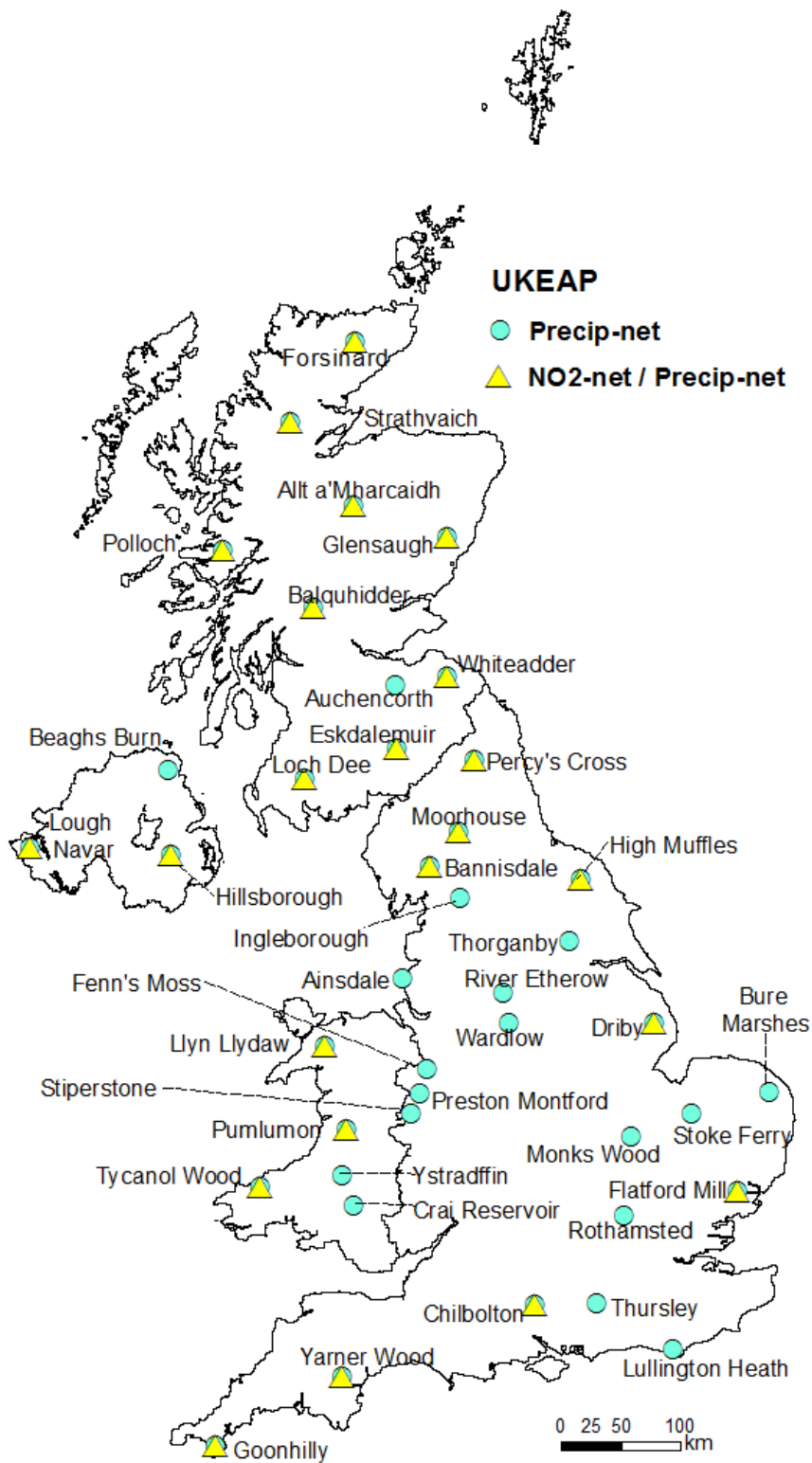


Figure 4 UK Precipitation chemistry (Precip-Net) and NO<sub>2</sub> diffusion tube (NO<sub>2</sub>-Net) Network

## 2. UKEAP Networks Reports

### 2.1 Precipitation Network (Precip-Net)

Precip-Net operated without major change in 2019. Samples continued to be collected 41 fortnightly bulk rain monitoring sites and 2 daily wet only (DWOC) collectors in operation throughout the year.

Bulk precipitation samples are collected using bulk deposition collectors (Figure 5 Bulk rain sampler (Bannisdale)) at fortnightly intervals, details of which can be found in previous reports. Precip-Net sites are located across the UK (Figure 4) and consists of both new Natural England Long Term Monitoring Network (LTMN) sites and those which were part of the original 1985-2016 network prior to the 2016 network review (Figure 6 and Figure 7 Precip-Net monitoring network respectively).

Unratified quarterly monitoring data are made available publically quarterly and the annual ratified data made available through the [UK-AIR website](#). Measurement data is supported by site specific information such as site location, co-location of other air quality networks and site metadata (e.g. altitude and location photos).

Two daily collection of precipitation sampler using Daily Wet Only Collectors (DWOC) are operated at two sites: Auchencorth Moss and Chilbolton sites which deliver to UK contribution to the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP).

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 2019 are summarised in the Appendices of this report.



Figure 5 Bulk rain sampler (Bannisdale)



Figure 6 LTMN sites forming part of the Precip-Net monitoring network (eight sites)



Figure 7 Precip-Net monitoring network



The spatial pattern of ammonia, nitrate and acidity and non-seasalt sulphate are shown in Figure 8. The spatial pattern has low concentrations of pollutants in the western seaboard and north west of Scotland. As expected concentrations of nitrate and ammonium is significantly higher than sulphate.

Figure 9 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 more than 71 % and ammonia emissions have decreased by about 14 %. Figure 9 also presents projected emissions for the respective gases from the National Emissions Inventory (NAEI).

As in previous years the concentration of pollutants in rain are generally in line with the variability of emissions (Figure 9 and Figure 10-12), however the interannual variability means that a direct correlation with annual changes is not observable in the simple timeline plots and detail statistical analysis with both meteorology and emissions would be needed for causal changes to be identified, particularly in the case of  $\text{NO}_3^-$  in rain given small changes in annual emissions. For most sites non-sea salt sulphate is generally less than  $10 \mu\text{eq.l}^{-1}$ , nitrate and ammonium concentrations are on average approximately  $20 \mu\text{eq.l}^{-1}$ .

Figures 13-15 summarise the long term time series trends in non-sea salt sulphate, nitrate and ammonium at Precip-Net sites across the UK. The figures illustrated the large spatial variability of trends and the different patterns of change.

Non-sea salt sulphate is decreasing across most Precip-Net sites, however at a few sites, the rate of decrease has slowed in the past 5 years (e.g. Eskdalemuir, Beagh's Burnand Loch Dee) whereas others are still continuing a similar rate of decrease (e.g. Yarner Wood, Goonhilly, River Etherow). From an atmospheric chemistry perspective, "natural" non-sea salt sulphate would be driven by volcanic emissions globally and non-anthropogenic biomass burning.

Nitrate in precipitation is decreasing at most Precip-Net sites on an interannual basis with the rate of decrease slowed in the past 5 years (in line with emissions rate decrease). For some cleaner sites, there is an interannual variability as large as the magnitude of the concentration (e.g. Ystraffdin and Hillsborough Forest amongst several) therefore care needs to be taken in interpreting the changes in concentration overtime.

For ammonium in precipitation, although a trendline has been fitted, there is a significant level of noise in the interannual data over the decadal timescale, likely due to the strong impact of meteorology on ammonia emissions and atmospheric processing prior to wet deposition.

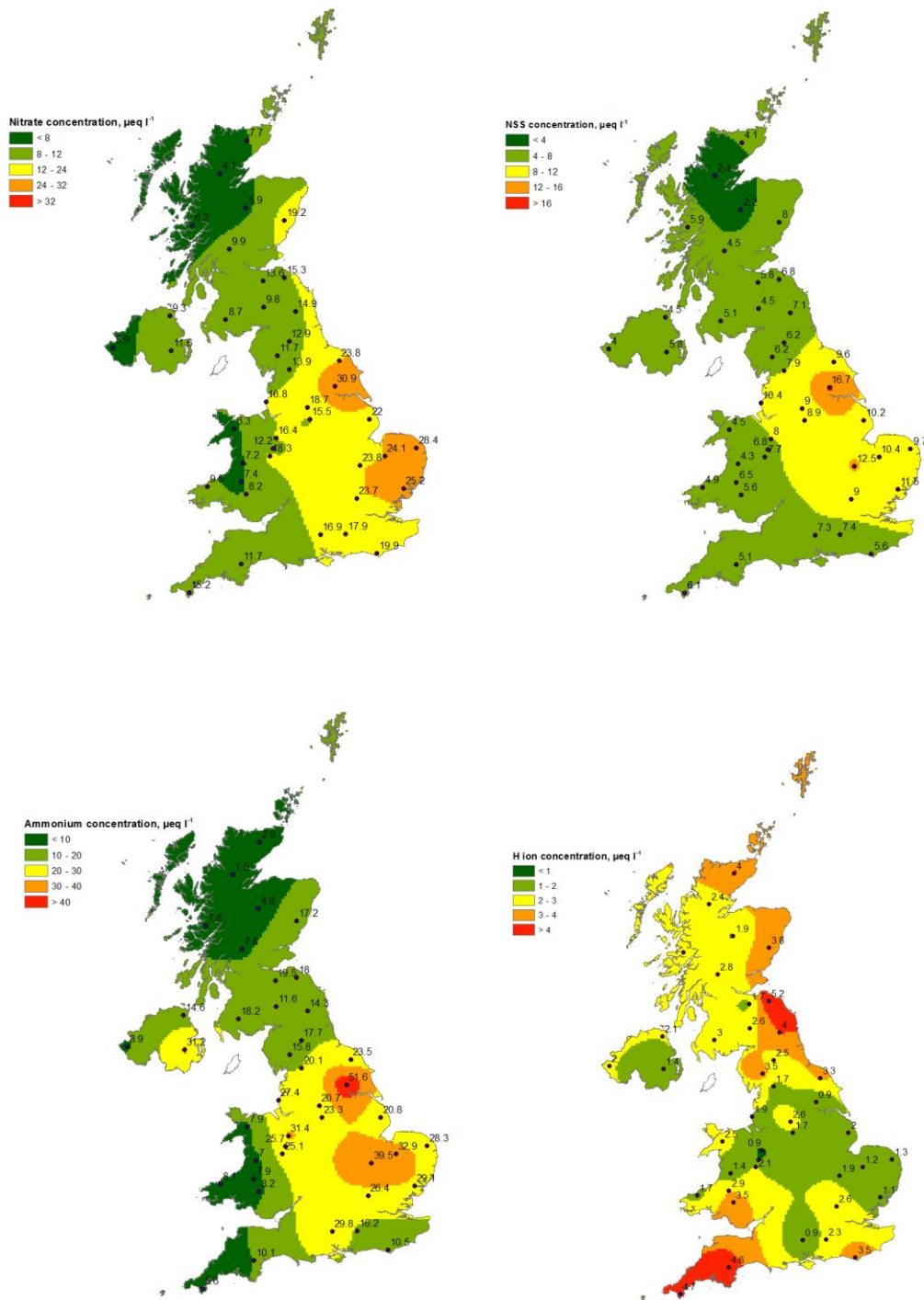


Figure 8 Interpolated concentration maps for non-sea salt sulphate, nitrate, ammonium and hydrogen ion ( $\mu\text{eq l}^{-1}$ )

1)

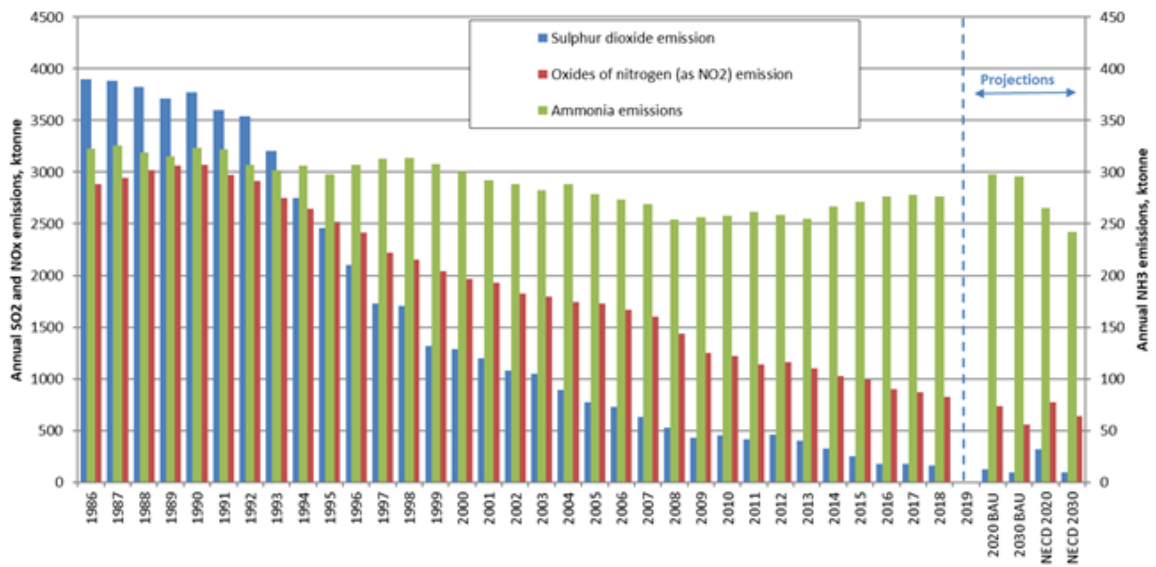


Figure 9 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986

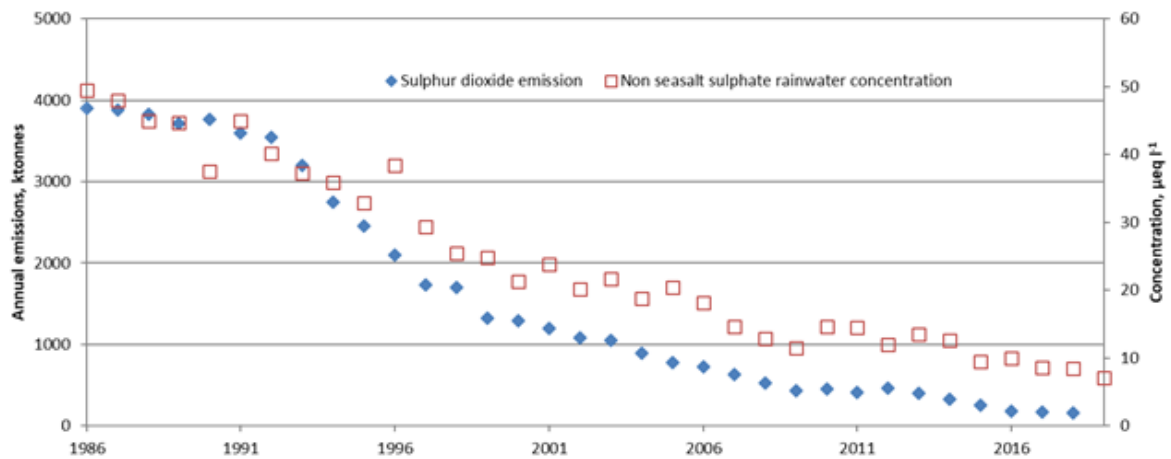


Figure 10 Sulphur dioxide emissions and sulphate concentrations in rainwater

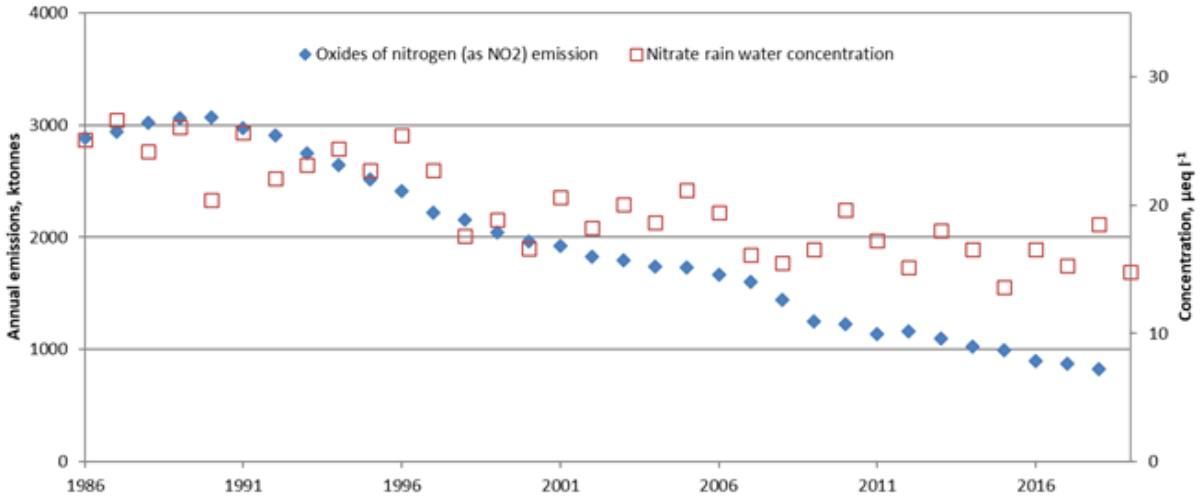


Figure 11 Oxides of nitrogen emissions and nitrate concentrations in rainwater

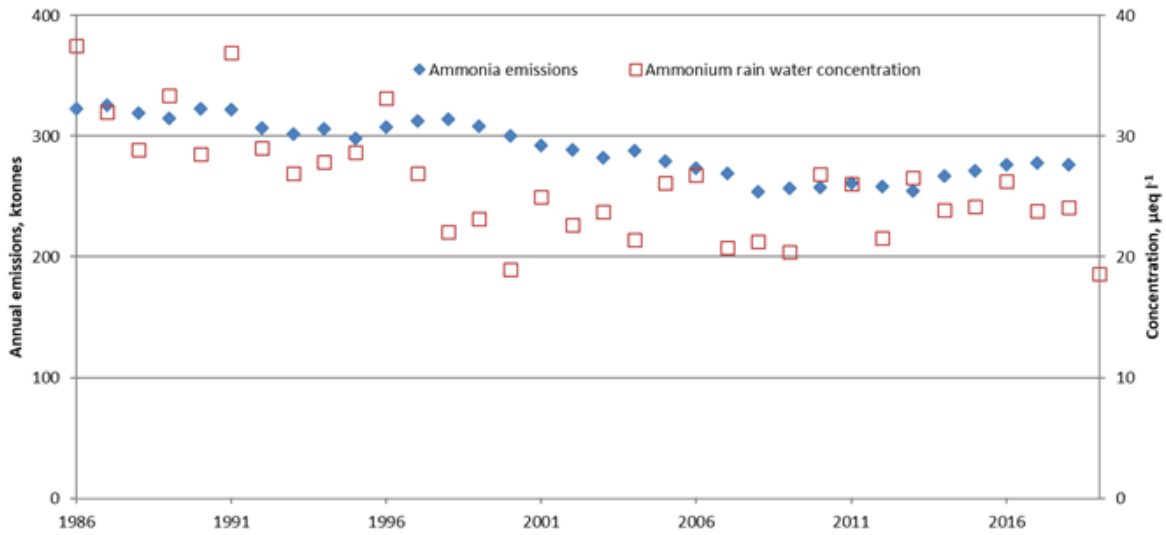


Figure 12 Ammonia emissions and ammonium concentrations in rainwater

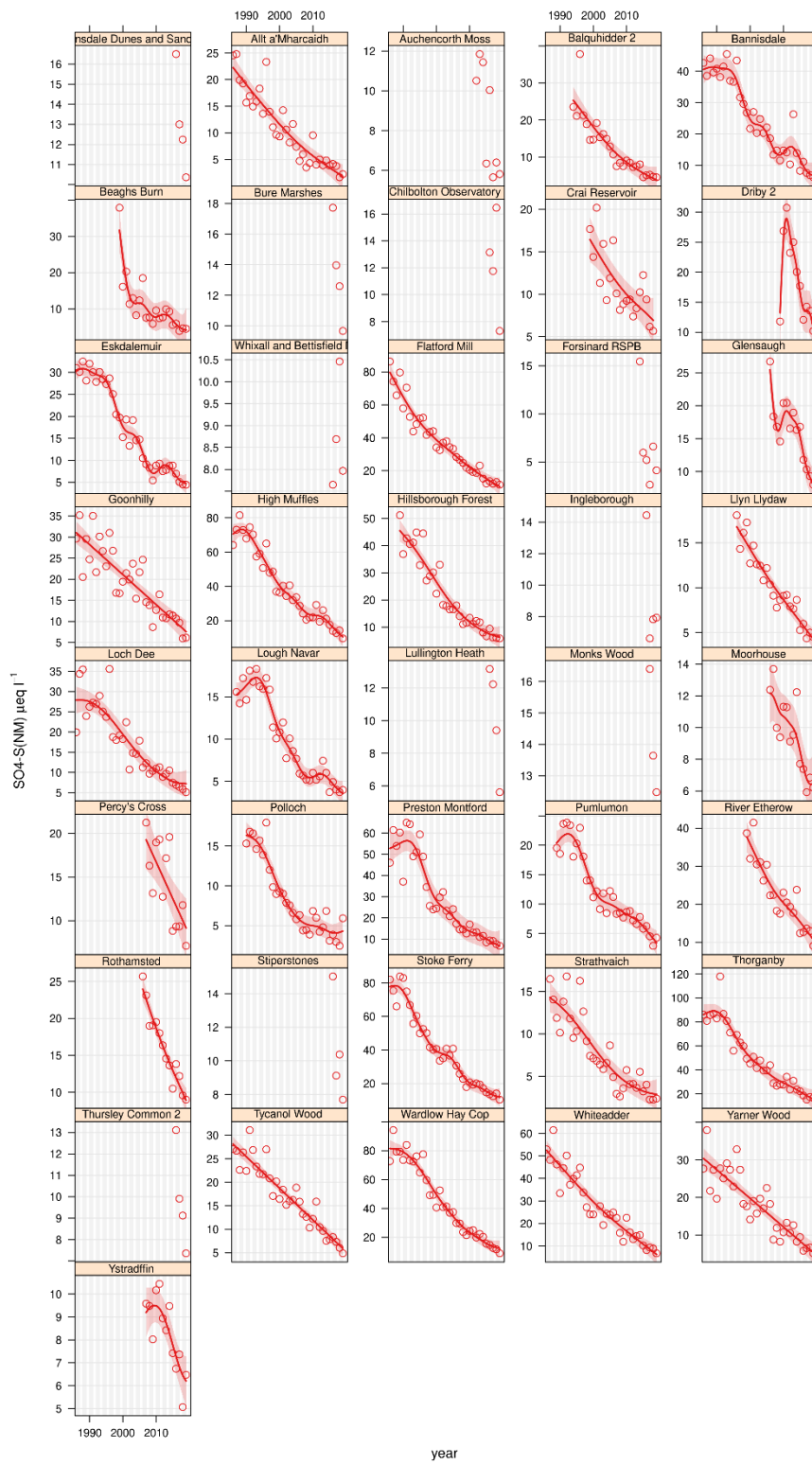


Figure 13 Non-sea salt sulphate concentrations measured at sites with the Precip-Net since 1986

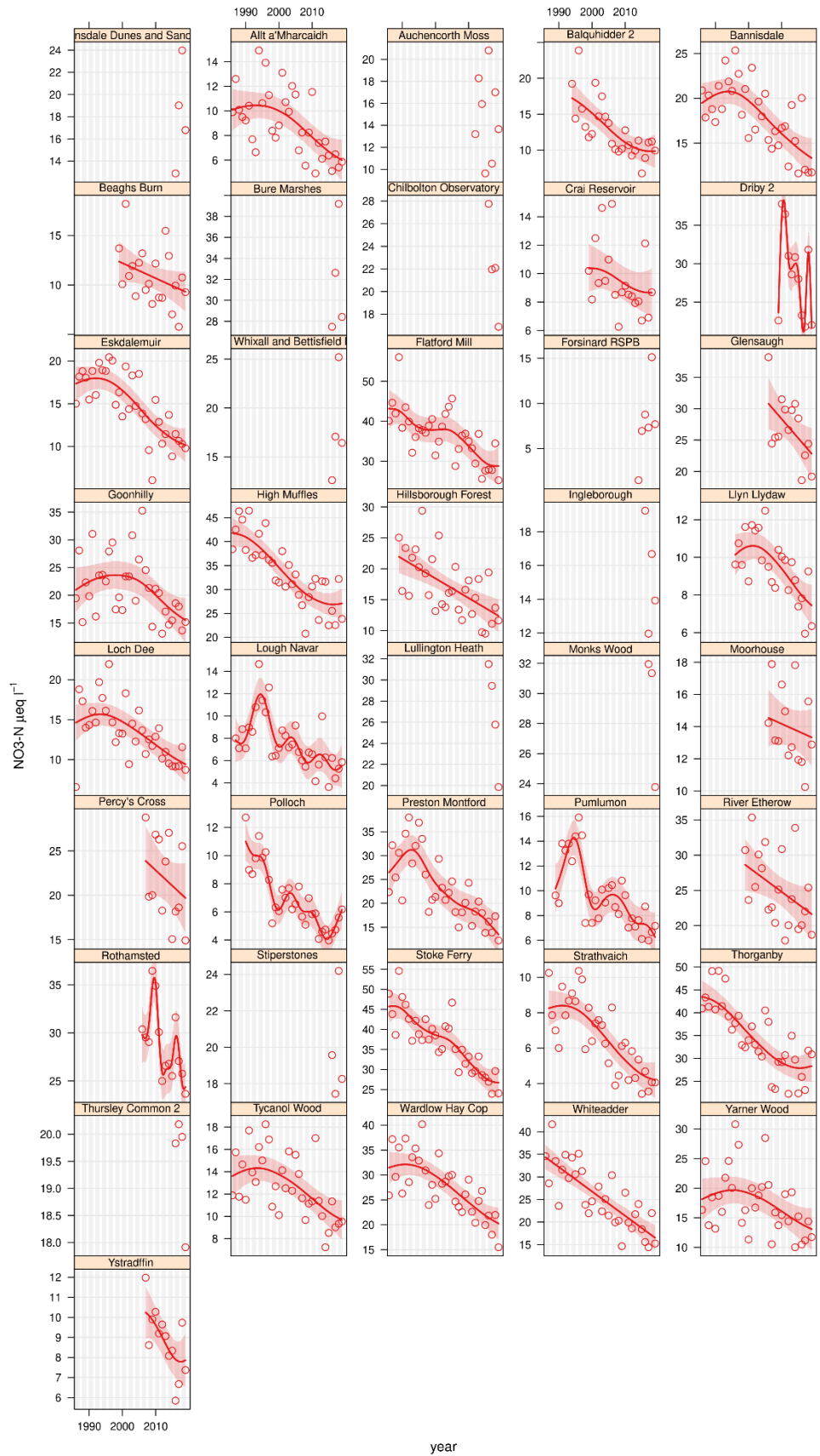


Figure 14 Nitrate concentrations measured at sites with the Precip-Net network since 1986

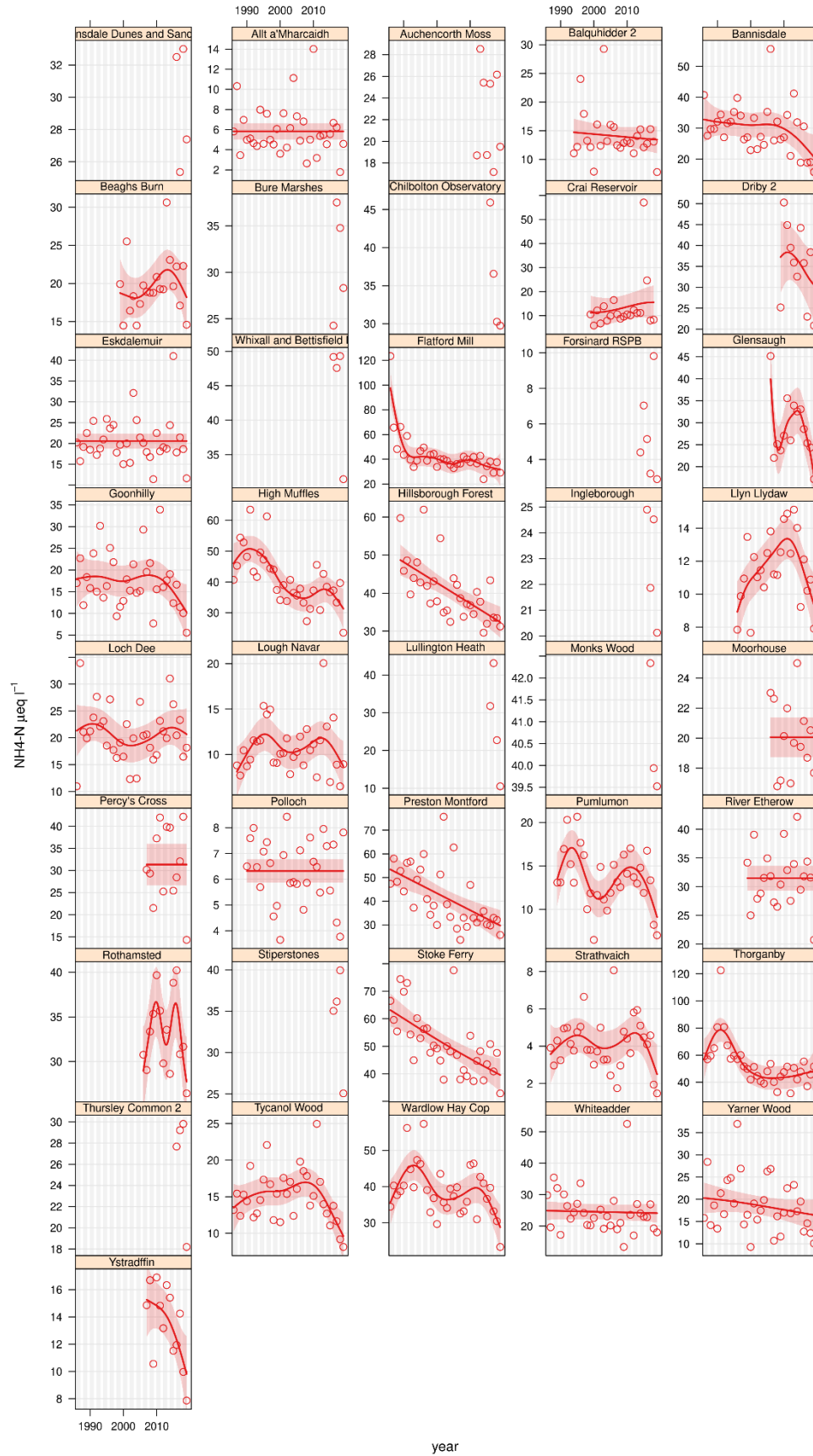


Figure 15 Ammonium concentrations measured at sites with the Precip-Net network since 1986

## 2.2 NO<sub>2</sub>-Net Network

The NO<sub>2</sub> network (NO<sub>2</sub>-Net) consists of 24 sites at which diffusion tubes, in triplicate, were exposed for approximately 4-week exposure periods. The annual average NO<sub>2</sub> measured at each site, together with data capture, are shown in [Table 1](#). 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 triethanolamine and acetone.

The mean data capture of the diffusion tubes for all of the site in 2019 was 94% with 19 of the 24 sites achieving > 90% and 17 sites achieving 100% data capture. There were various reasons for the lower data capture at Balquidder 2 and Llyn Llydaw such as local site operator availability and extended tube exposure.

**Table 1 2019 NO<sub>2</sub> concentration from the Diffusion Tubes in the NO<sub>2</sub>-Net**

Site Name	Raw 2019 concentration (µg m <sup>-3</sup> )	2019 concentration Bias Corrected (0.828) <sup>1</sup>	Data capture	Site Name	Raw 2019 concentration (µg m <sup>-3</sup> )	2019 concentration Bias Corrected (0.828) <sup>1</sup>	Data capture
Allt a'Mharcaidh	1.25	1.03	100%	Llyn Llydaw	2.35	1.95	47%
Balquidder 2	1.93	1.60	62%	Loch Dee	2.54	2.10	100%
Bannisdale	3.46	2.87	100%	Lough Navar	2.40	1.99	100%
Chilbolton Observatory	9.22	8.44	100%	Lullington Heath	9.65	7.99	100%
Driby 2	8.89	7.36	100%	Moorhouse	3.29	2.72	100%
Eskdalemuir	2.42	1.99	100%	Percy's Cross	3.67	3.04	100%
Flatford Mill	9.78	8.10	92%	Polloch	1.22	1.01	100%
Forsinard RSPB	1.47	1.22	100%	Pumlumon	2.79	2.31	100%
Glensaugh	2.54	2.10	100%	Strathvaich	1.20	1.00	76%
Goonhilly	3.67	3.04	85%	Tycanol Wood	3.53	2.92	100%
High Muffles	5.42	5.08	100%	Whiteadder	3.37	2.79	87%
Hillsborough Forest	6.82	5.64	100%	Yarner Wood	3.82	3.83	100%

<sup>1</sup> All sites bias adjusted by 0.828 with the exception of Chilbolton, Eskdalemuir, High Muffles and Yarner Wood which were corrected using co-located samplers, See appendix for details.

Figure 16 shows the trend in emissions of NO<sub>x</sub> and NO<sub>2</sub> 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<sub>x</sub> 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<sub>2</sub>-



Net site over the period. More information relating to emissions in the UK can be found on the National Atmospheric Emissions Inventory (NAEI) [website](#).

NO<sub>2</sub> 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<sub>2</sub> concentration whereas the Flatford Mill sites shows a similar rate of reduction to that of the NAEI estimated.

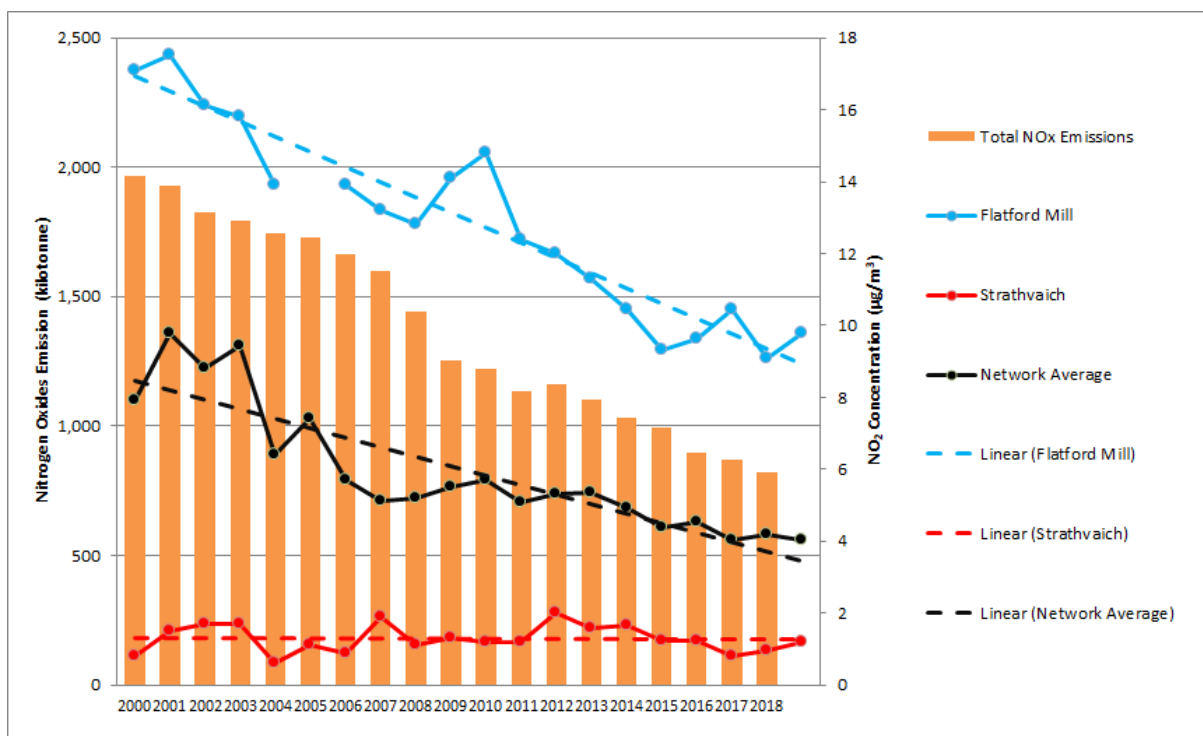


Figure 16 Long term trends where estimated emissions are plotted against selected sites in the network

The annual average uncorrected NO<sub>2</sub> concentrations from 2010-2019 (Figure 17) indicates the differing NO<sub>2</sub> concentrations at rural locations across the UK. Most of the sites show some reduction between 2010 and 2019 but the larger decreases being seen at the sites that are closer to the sources of NO<sub>x</sub>.

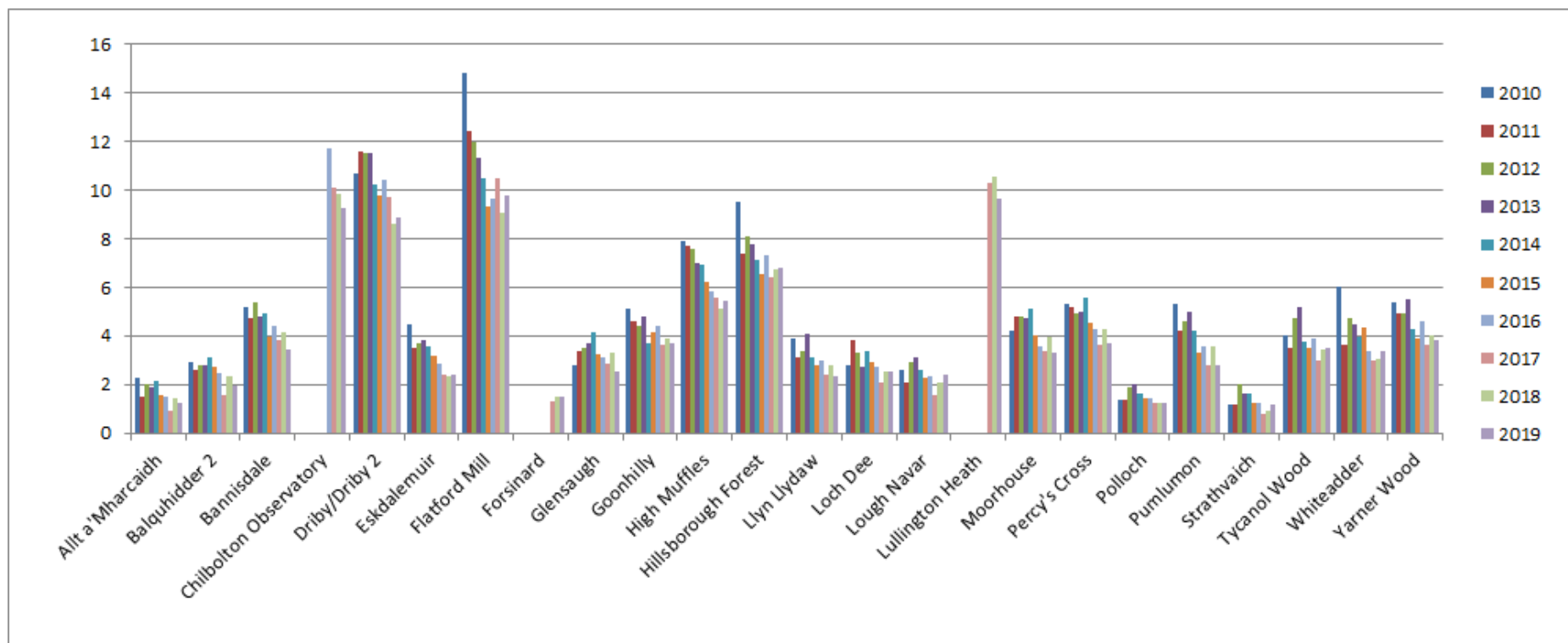


Figure 17 Annual mean NO<sub>2</sub> concentration (µg m<sup>-3</sup>) at the NO<sub>2</sub>-Net sites 2010-2019

## 2.3 National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly measurements of atmospheric NH<sub>3</sub> in 2019 was 71, summarised in Figure 2. The LTMN site at North Derwent Valley/Thorganby was not operational and removed from the network. The 2019 annual NAMN results are summarised by the average and range of annual NH<sub>3</sub> concentrations observed at each site in Figure 18. There is high spatial variability in NH<sub>3</sub> concentrations across the UK and significant seasonal variability. This reflects the large heterogeneity of NH<sub>3</sub> sources in the rural countryside and variability in levels of NH<sub>3</sub> emissions (see [Tang et. 2018](#) for a more detailed discussion). During 2019 average data capture across NAMN was 76.9%. (QC criteria summarised in the Appendix of this report).

Table 2 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2019

Site Type	Number
DELTA sites sampling gaseous NH <sub>3</sub>	29
AGANET DELTA sites (sampling gaseous NH <sub>3</sub> , HNO <sub>3</sub> , SO <sub>2</sub> , HCl & aerosol NH <sub>4</sub> <sup>+</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> , Cl <sup>-</sup> , Na <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> )	27
ALPHA sites sampling gaseous NH <sub>3</sub> only	51
Intercomparison sites with both DELTA & ALPHA	9
Total number of sites	71

2019 annual mean concentrations of ammonia across all NAMN sites are shown in Figure 18. Annual average concentrations range between <0.1 µg.m<sup>-3</sup> at the cleaner background sites (e.g. Inverpolly and Strathvaich Dam) to just under 10 µg.m<sup>-3</sup> at the highest concentration sites (Brompton A). As a network average (Figure 19) the ammonia concentration was within variability from the previous two years. The spatial variability for both ammonia and ammonium (NH<sub>4</sub><sup>+</sup>) (Figure 20), the lowest concentrations can be seen in the west of Scotland with most sites being in the range of 0.5-5 µg.m<sup>-3</sup> across the UK.

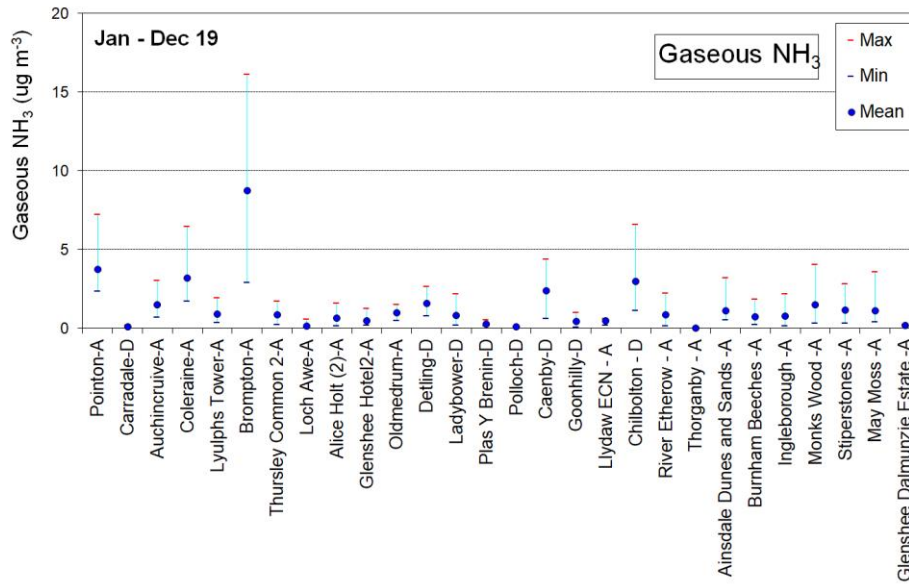
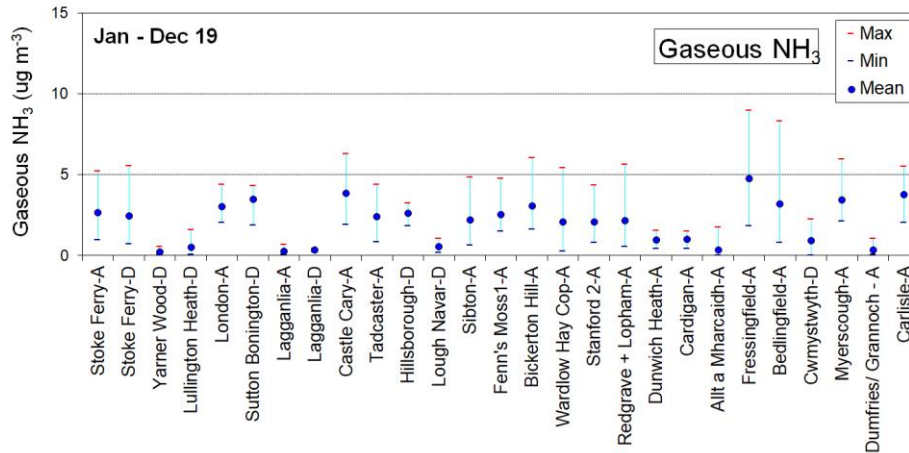
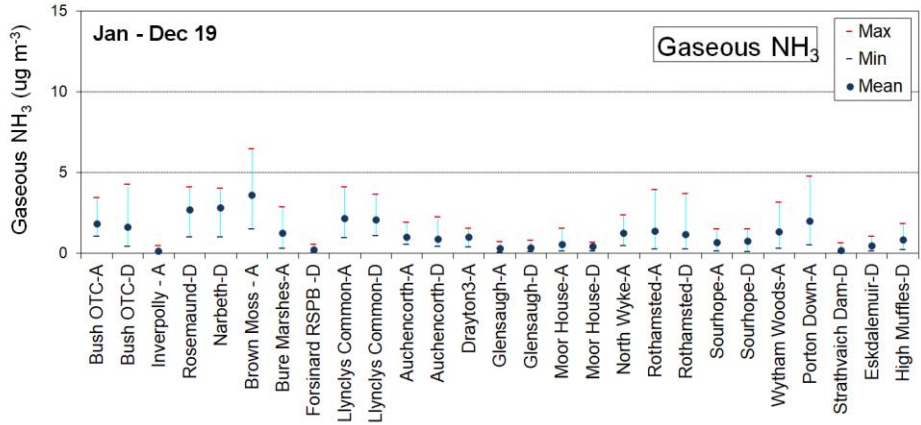


Figure 18 Annual mean concentrations of gaseous NH<sub>3</sub> in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations observed (A = ALPHA sampler; D=DELTA)

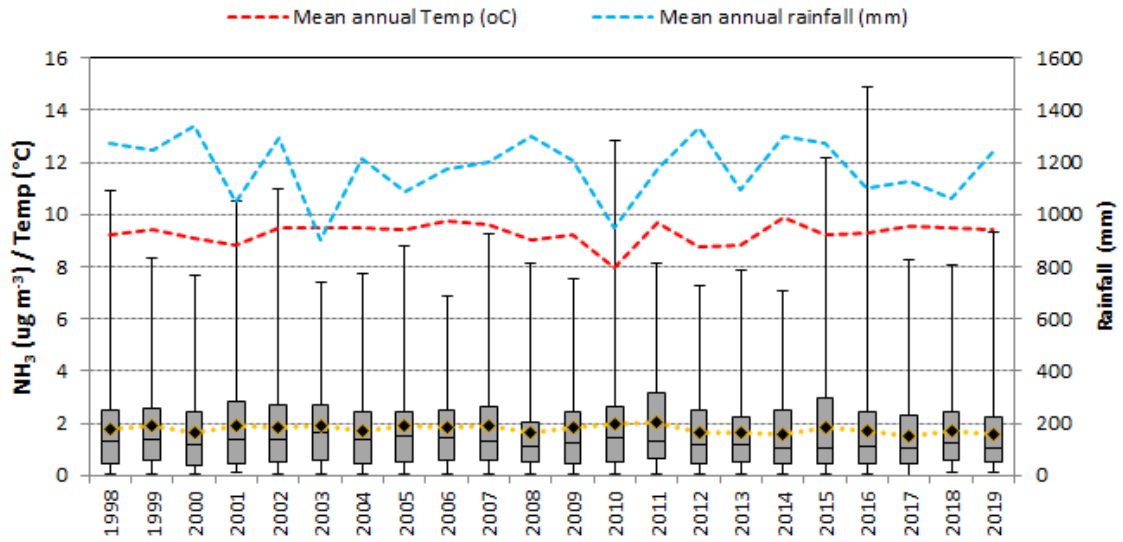


Figure 19: Changes in atmospheric  $\text{NH}_3$  averaged over all sites in NAMN operational between 1998 and 2019 summarised in a box plot. The whiskers show the absolute max and min and the diamond is the mean annual concentration. Annual mean UK meteorological data (source <http://www.metoffice.gov.uk/>) are plotted on top to illustrate the relationship between inter-annual variability in  $\text{NH}_3$  concentrations with changing temperature and rainfall.

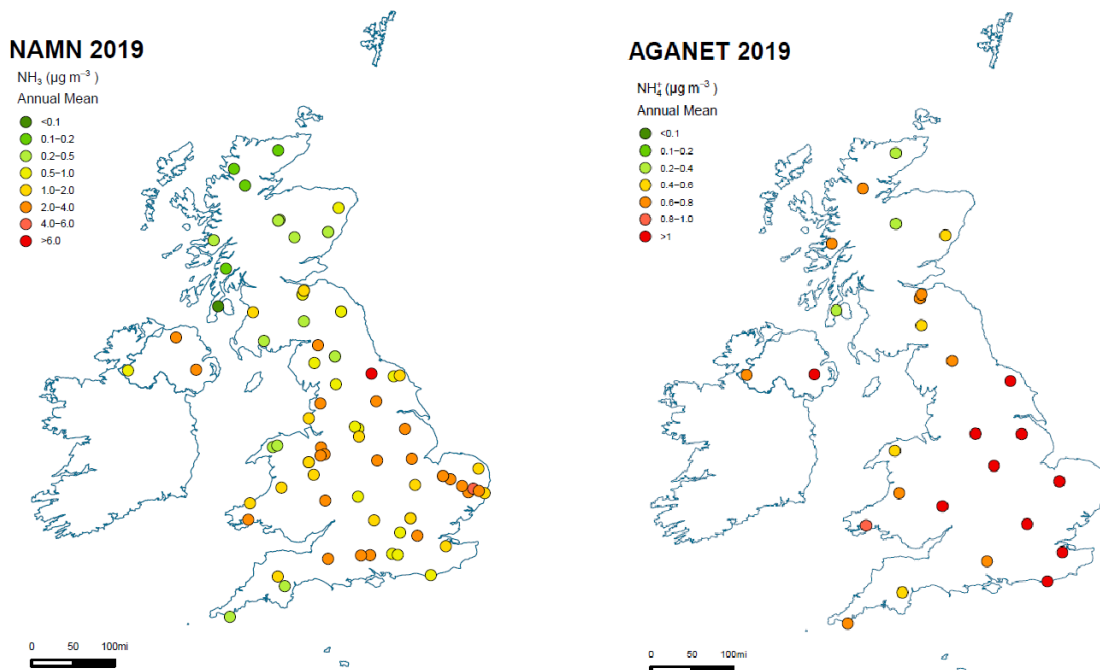


Figure 20: Spatial patterns of annual  $\text{NH}_3$  and aerosol  $\text{NH}_4^+$  concentrations from monthly NAMN/AGANET measurements. Since February 2017, ammonium is measured at the 27 AGANET sites only.

## 2.4 Acid Gas and Aerosol Network (AGANET)

The UK Acid Gas and Aerosol Network (AGANET) provides monthly speciated measurements of atmospheric reactive gases ( $\text{HNO}_3$ ,  $\text{SO}_2$ ) and aerosols ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) at 27 sites across the UK. The spatial distributions of acid gases and aerosol ions, which are primarily anthropogenic in origin, in particular  $\text{HNO}_3/\text{NO}_3^-$  and  $\text{SO}_2/\text{SO}_4^{2-}$ , have the highest concentrations in the south and east of the UK. Atmospheric gases including  $\text{SO}_2$  and  $\text{HNO}_3$  are somewhat more spatially variable than aerosol species, reflecting the longer atmospheric residence time of the latter. Although on the UK scale with only 27 sites the higher spatial variability in gaseous species can be seen.

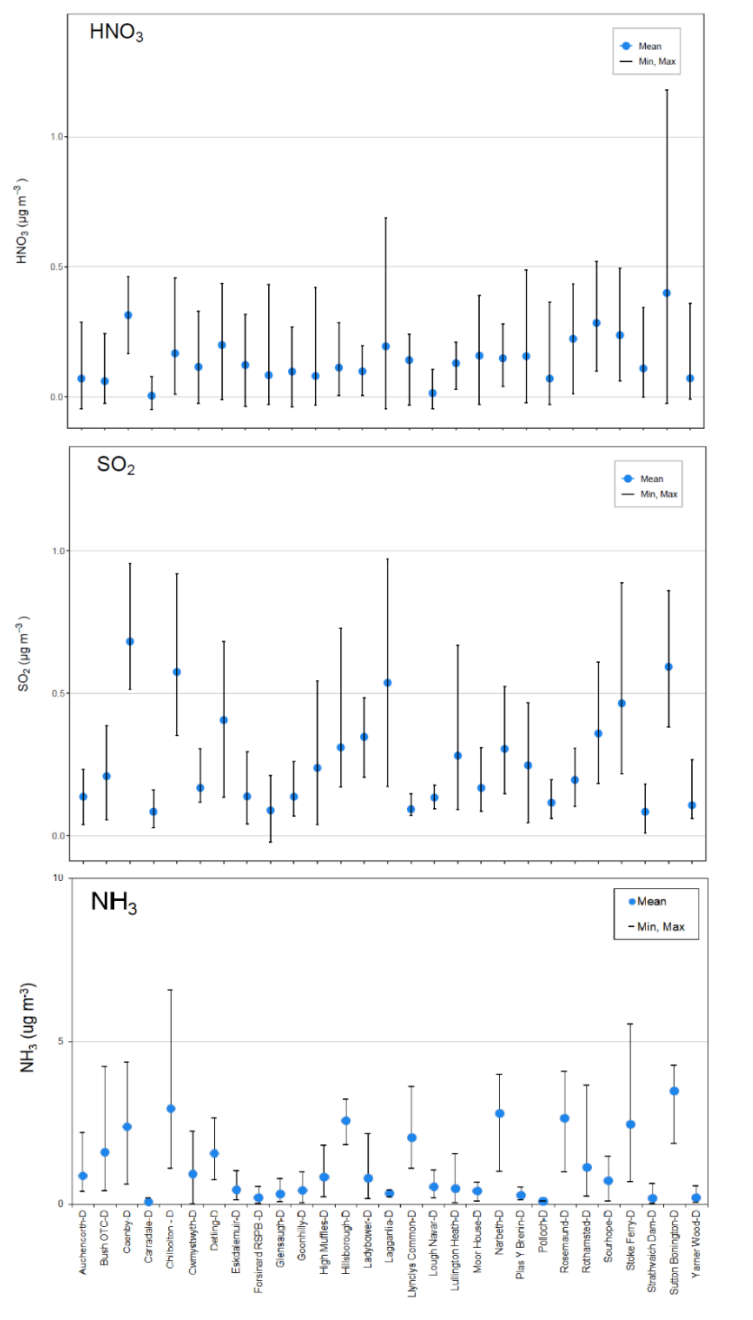


Figure 21: Mean monitored annual concentrations of gaseous  $\text{HNO}_3$  and  $\text{SO}_2$  at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations observed. Data for gaseous  $\text{NH}_3$  measured under NAMN is also shown for comparison.

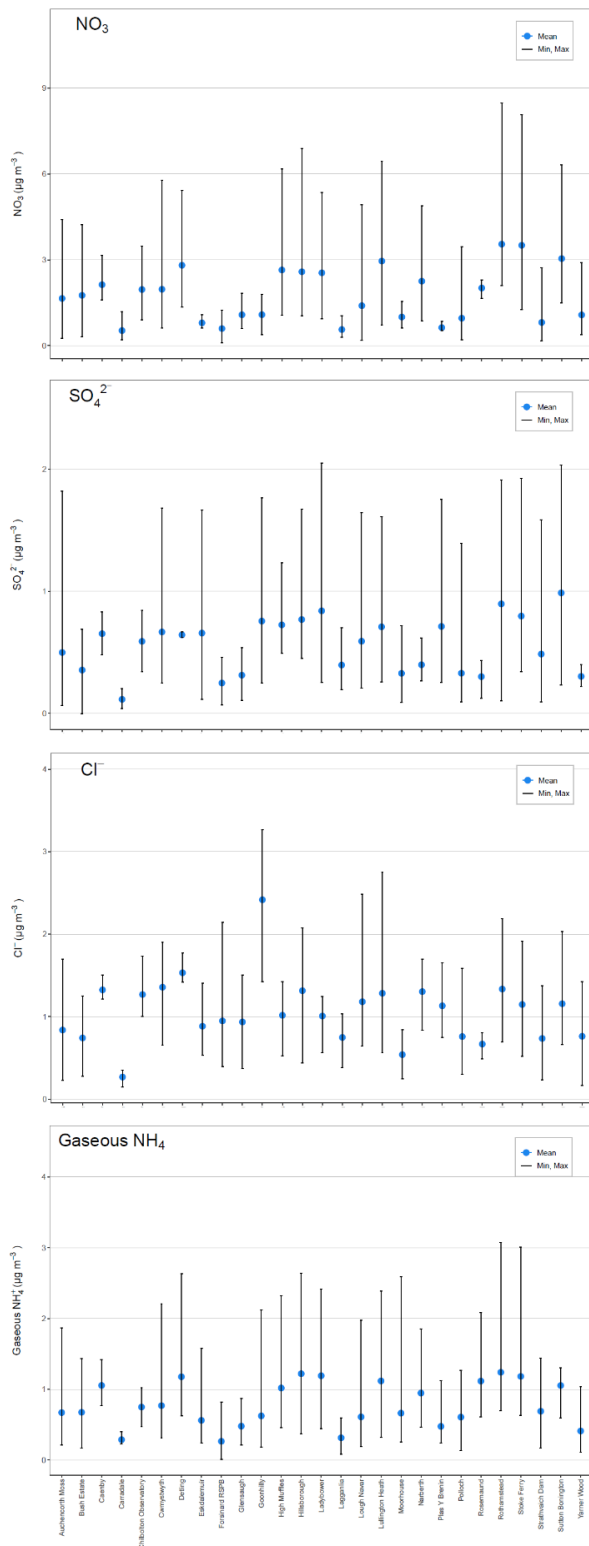


Figure 22: Mean monitored annual concentrations of particulate NO<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup> and NH<sub>4</sub><sup>+</sup> at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations observed.

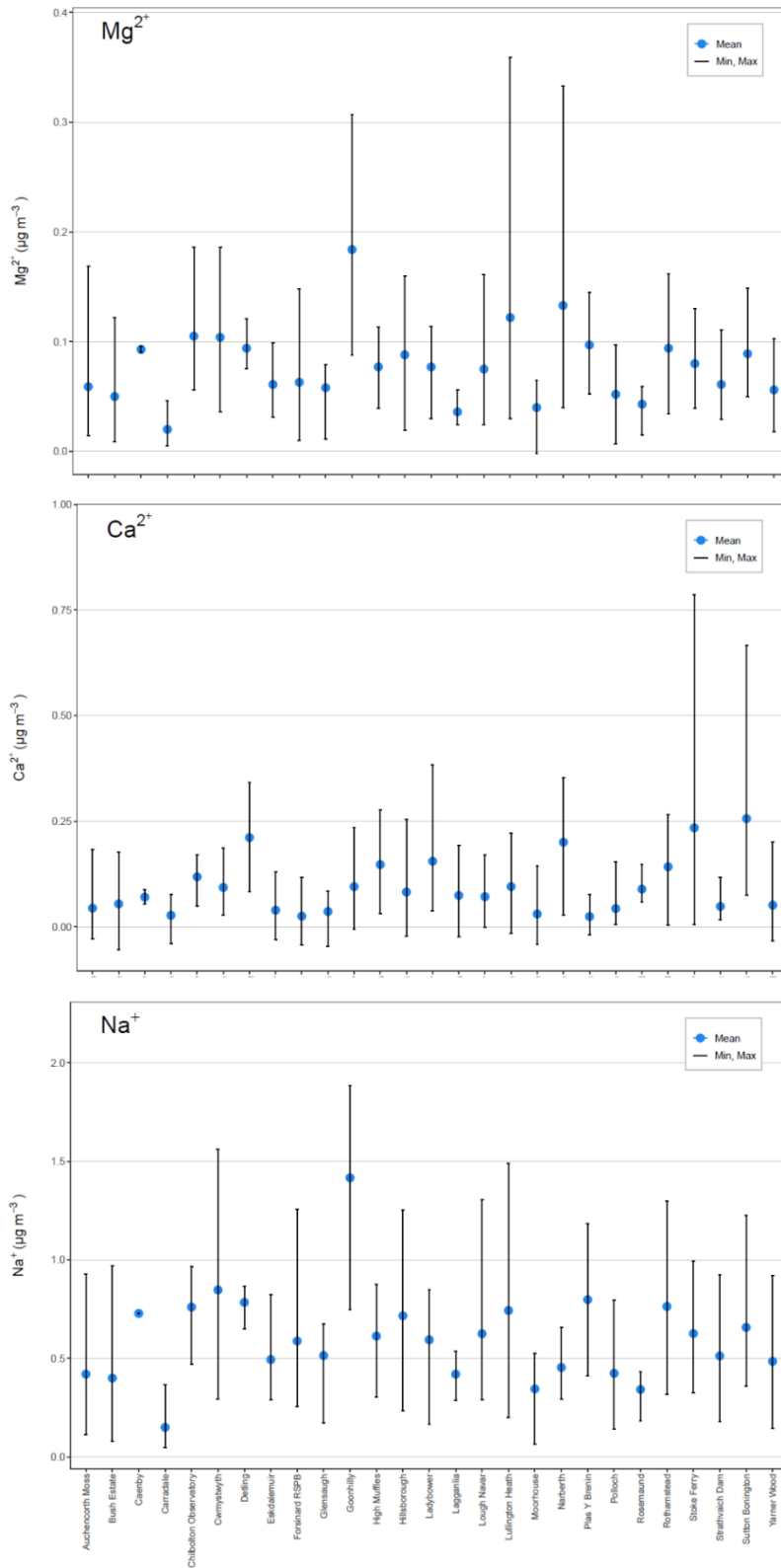


Figure 23 Mean monitored annual concentrations of particulate Mg, Ca and Na at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations



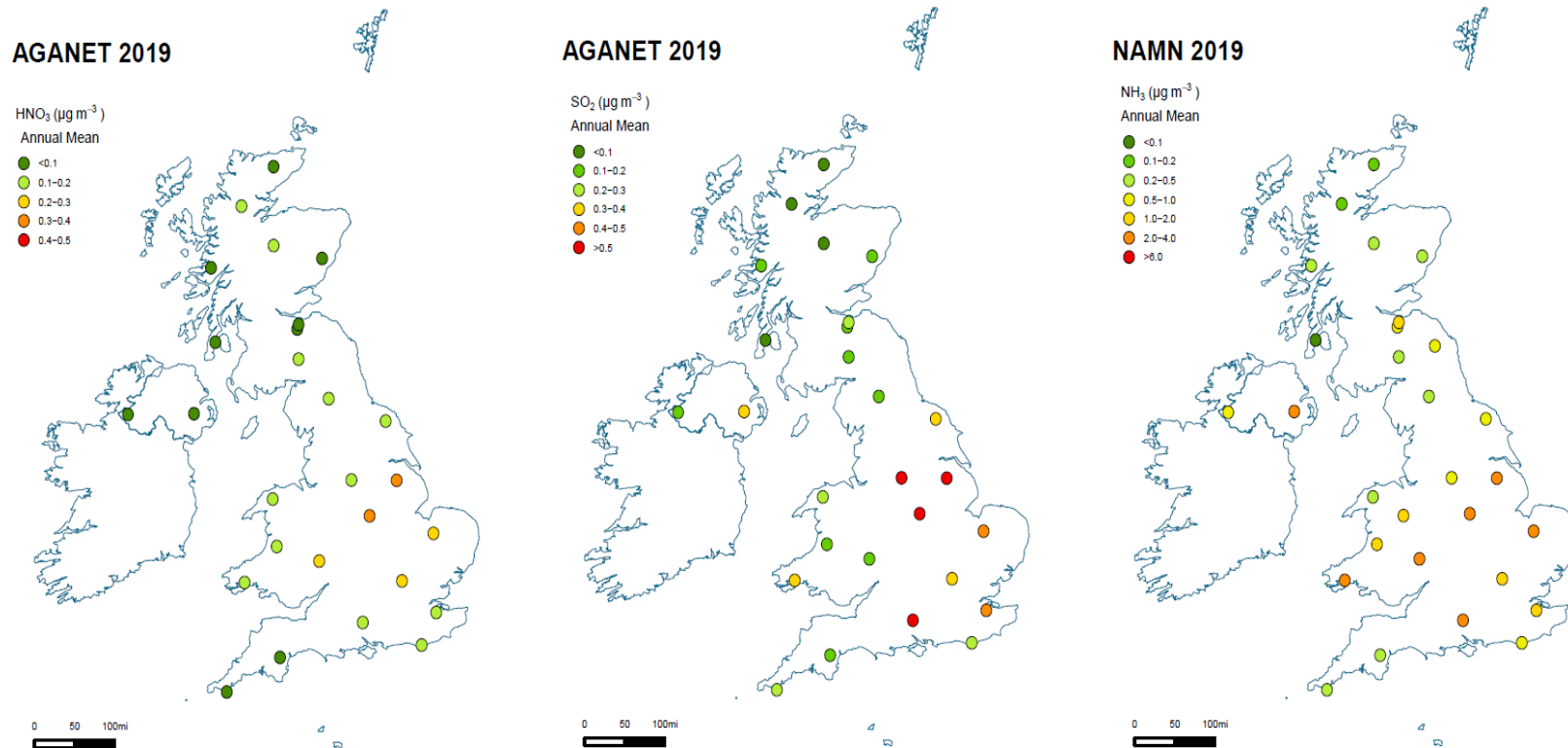


Figure 24 Annual mean monitored atmospheric reactive gas concentrations ( $\text{HNO}_3$  and  $\text{SO}_2$  from AGANET and  $\text{NH}_3$  from NAMN) across the UK from annual averaged monthly measurements made in 2019.

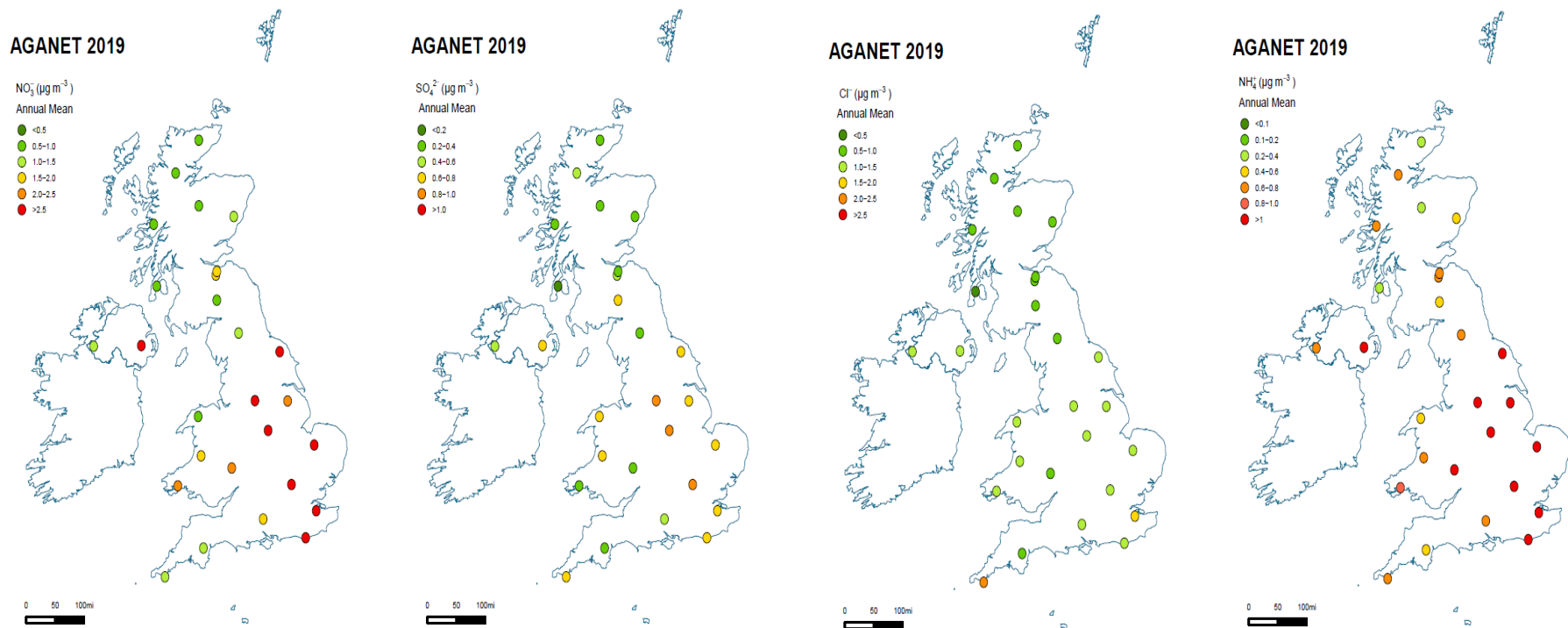


Figure 25: Annual mean monitored atmospheric aerosols (particulate  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  from AGANET and  $\text{NH}_4^+$  from NAMN) concentrations across the UK from averaged monthly measurements made in 2019.

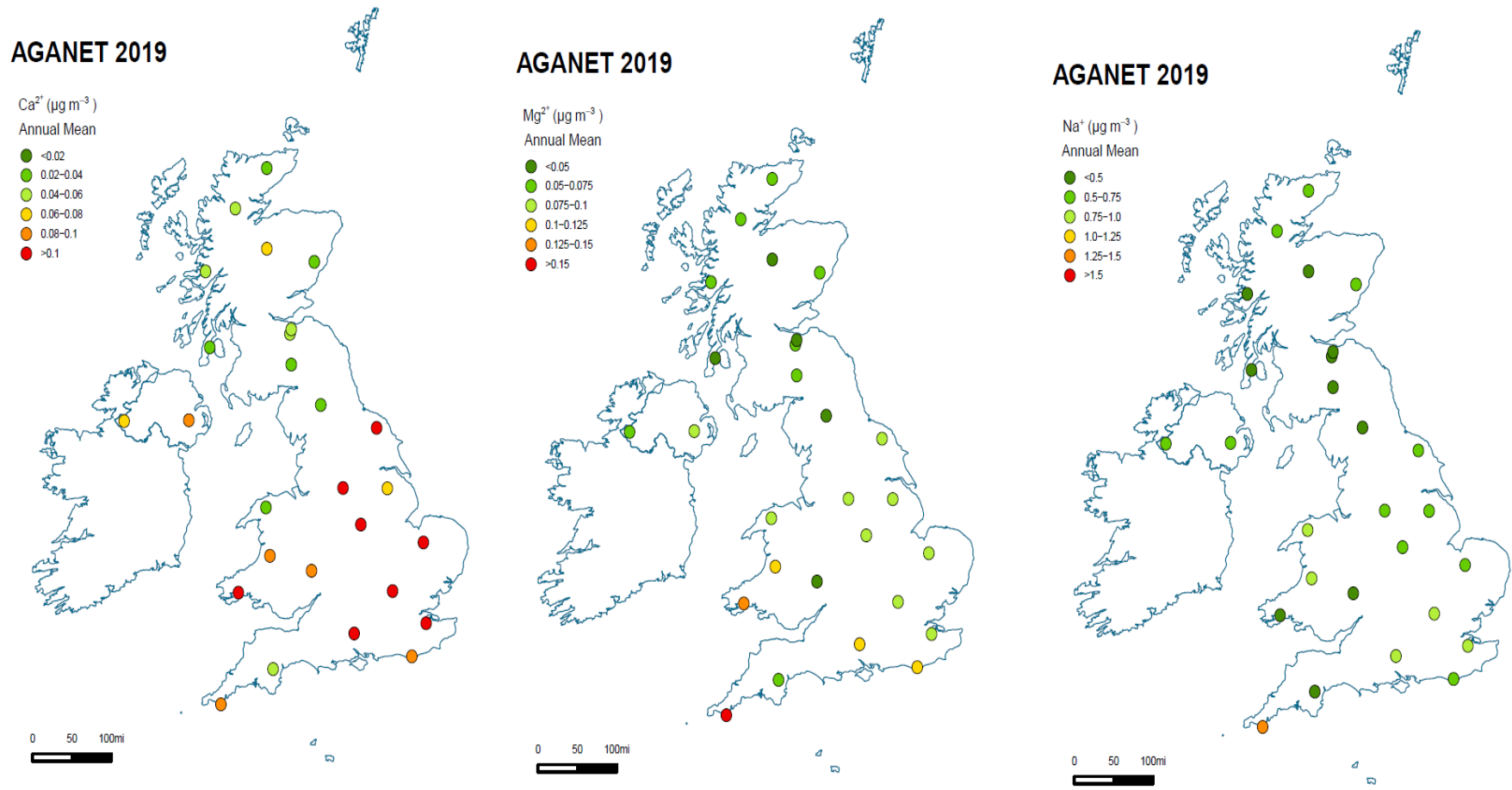


Figure 26: Annual mean monitored atmospheric base cation (Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup>) concentrations across the UK from the averaged monthly measurements made in 2019.

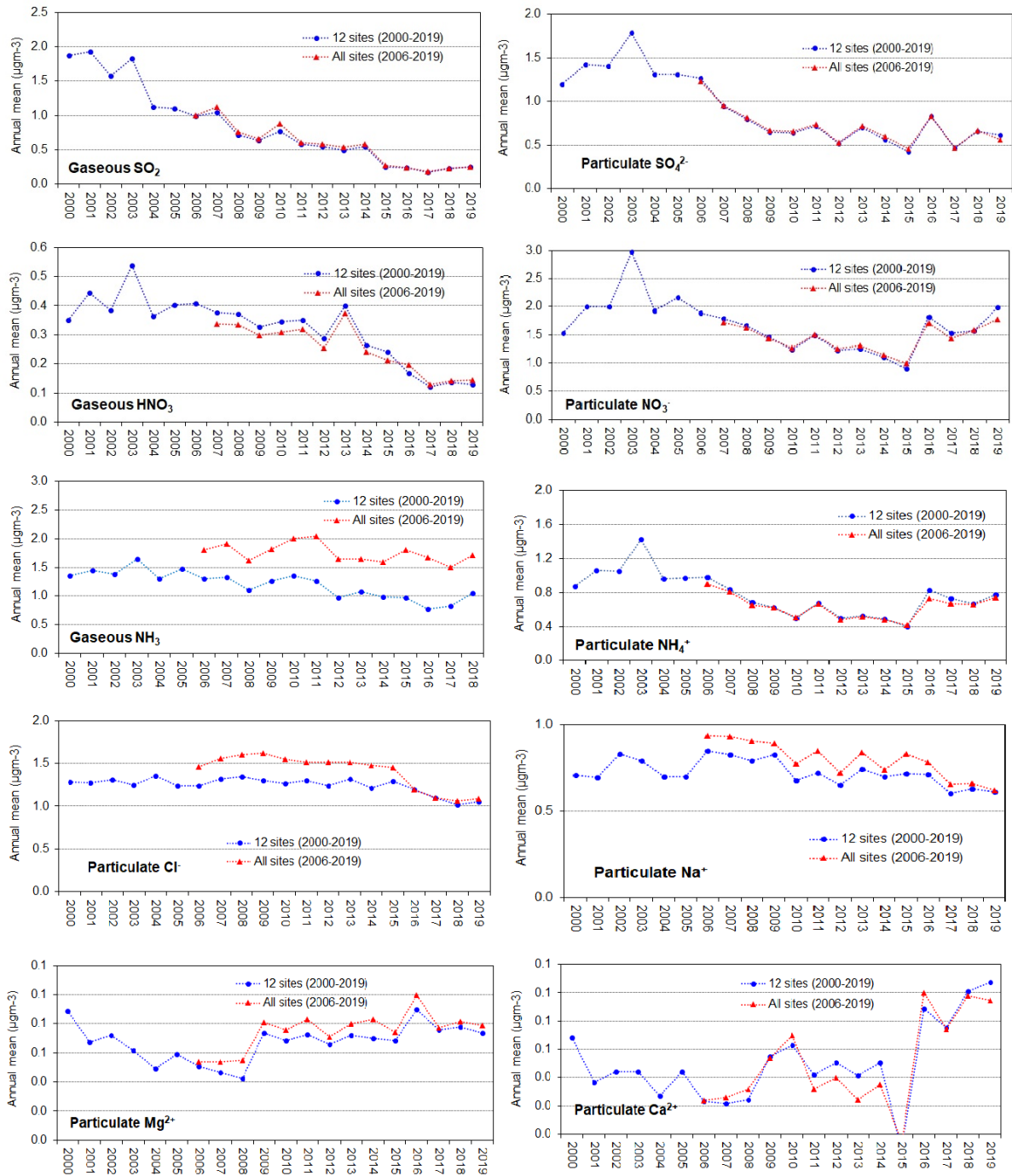


Figure 27: Long-term trend in annual mean concentrations of gases and aerosols monitored in AGANET. Each data point represents the time-weighted averaged annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites) and also the original I2 monitoring sites in the network. Since 2016, HCl is no longer measured in the new DELTA sampling train configuration. NAMN NH<sub>3</sub> data for AGANET sites are also shown, for comparison.

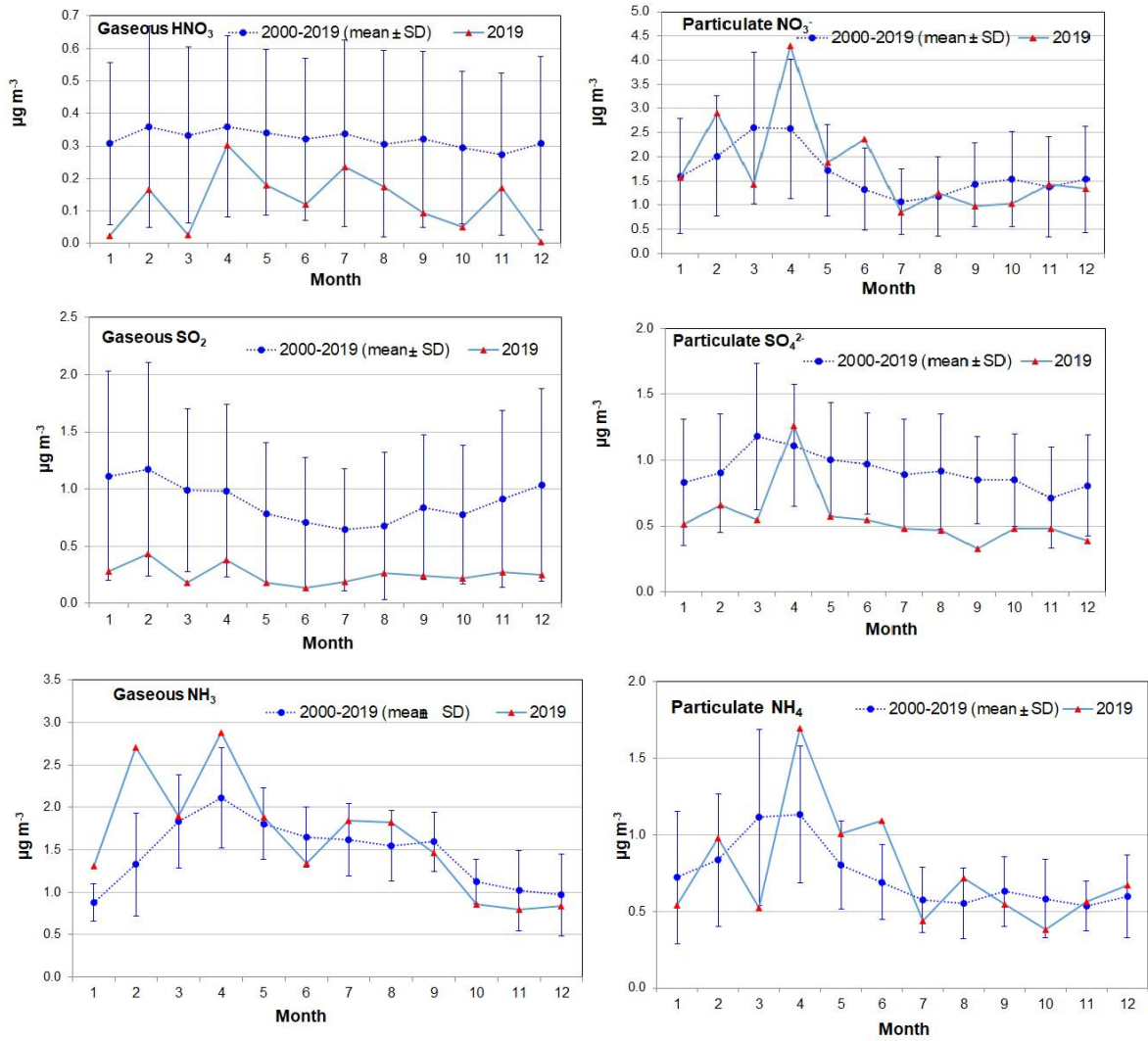


Figure 28: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (2000-2019: mean +/- SD of 27 AGANET sites) against year 2019.

### 3. UK EMEP Supersites 2019 measurement overview

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. EMEP – 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). Measurements made at the supersites in 2018 are summarised in Table 3.

Both EMEP Supersites are rural sites. The sites provide the **required coverage**, of at least once station every 100,000 km<sup>2</sup>, to determine the composition of PM<sub>2.5</sub> at rural background locations as required under Annex IV of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe. The chemical composition of PM<sub>2.5</sub> 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<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), from the MARGA instrument.

The PM<sub>2.5</sub> time coverage at both EMEP Supersites exceeds the *minimum* time coverage (14%) specified in the Directive for indicative PM<sub>2.5</sub> measurements. The high resolution data is sufficient to allow comparison with atmospheric models and back-trajectory source apportionment.

Auchencorth and Chilbolton are part of all major UK air quality measurement networks including Defra's Automated Urban and Rural Network (AURN), the UK-wide network providing evidence for the UK for compliance with the EU Ambient Air Directives and the Gothenberg Protocol of automatic air quality monitoring stations measuring oxides of nitrogen (NO<sub>x</sub>), nitrogen dioxide (NO<sub>2</sub>), sulphur dioxide (SO<sub>2</sub>), ozone (O<sub>3</sub>), carbon monoxide (CO) and atmospheric particulate matter (PM<sub>10</sub> and PM<sub>2.5</sub>).

Non-automatic measurements of (rural) heavy metal concentrations in PM<sub>10</sub> and precipitation; particulate-phase base cations, anions and trace gases; polycyclic aromatic hydrocarbons (PAHs) in PM<sub>10</sub>, air and precipitation were also made at the site. Automated real-time measurements of total particle number and soot (also termed "Black Carbon") were made at the site as part of the UK Particle Concentrations and Numbers Monitoring Network.

UK Particle Concentrations and Numbers Monitoring Network also provided a daily assessment of the contribution of Organic Carbon (OC), Elemental Carbon (EC), and Total Carbon (TC), to the airborne ambient PM<sub>10</sub> and PM<sub>2.5</sub> mass concentration at the site. All the above air pollutant measurement activities were funded by Defra. This report summarises the measurements made between January and December 2019. The statistics reported on UK-AIR are those reported to the Commission to demonstrate compliance with the air quality Directives.

Measurements funded under this project and described here are specifically:

- Meteorological observations (barometric pressure, dewpoint, wind speed & direction, relative humidity, temperature, (total) rainfall): **Chilbolton reported here, Auchencorth available on request and archived on CEDA**
- Trace gas (HCl, HONO, HNO<sub>3</sub>, NH<sub>3</sub>, SO<sub>2</sub>) and PM<sub>10</sub> and PM<sub>2.5</sub> aerosol concentrations (K<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>), **Chilbolton and Auchencorth Moss.**
- On line mercury measurements (Chilbolton: elemental mercury; Auchencorth Moss: elemental and speciated mercury).

Table 3 Pollutants measured at the UK EMEP Supersites during 2019

Pollutant	CHO <sup>1</sup>	AUC <sup>1</sup>	EMEP Level	Averaging period	Monitoring network (Ha/Au)	Contract holder
SO <sub>2</sub> , HCl, HNO <sub>3</sub> , HONO, NH <sub>3</sub> (MARGA)	X	X	II	Hourly	UKEAP	CEH/Ricardo E&E
PM <sub>2.5</sub> K <sup>+</sup> , Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> (MARGA)	X	X	II	Hourly	UKEAP	CEH/Ricardo E&E
PM <sub>10</sub> K <sup>+</sup> , Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup> , Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> (MARGA)	X	X	II	Hourly	UKEAP	CEH/Ricardo E&E
Elemental mercury		X	III	Hourly	UKEAP	CEH/Ricardo E&E
Total Particulate mercury		X	III	Hourly	UKEAP	CEH/Ricardo E&E
Total gaseous mercury (TGM) in air	X	X	II	Hourly	UKEAP	CEH/Ricardo E&E
Meteorological parameters (WS, WD, T, RH, rainfall)	X	X <sup>2</sup>	I	Hourly	UKEAP/CEH	CEH/Ricardo E&E
Precipitation chemistry	X	X	I	Daily	UKEAP	CEH/Ricardo E&E
NO and NO <sub>2</sub> (thermal converter)	X	X	I	Hourly	AURN	Bureau Veritas
Sulphur dioxide	X		I	Hourly	AURN	Bureau Veritas
Ozone	X	X	I	Hourly	AURN/CEH	Bureau Veritas
Particulate matter PM <sub>2.5</sub> , PM <sub>10</sub>	X	X	I	Hourly	AURN	Bureau Veritas
VOCs in air	X		II	Hourly	Automated HC Network	Ricardo E&E
PAH in PM <sub>10</sub> , air and rain	X	X	I	Monthly	PAH	NPL*/Ricardo E&E
Black carbon	X	X	II	Hourly	Particle numbers/CEH	NPL
Particle counts (>7 nm)	X	X <sup>2</sup>	II	Hourly	Particle numbers/CEH	NPL
Particle size distribution	X	X <sup>2</sup>	II	Hourly	Particle numbers	NPL
PM <sub>10</sub> carbon-content (elemental carbon, EC, organic carbon, OC, total carbon, TC)	X	X	II	Weekly	Particle numbers	Bureau Veritas
<b>DELTA sampler (particulate-phase ions: Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>)</b>	X	X	I	Monthly	UKEAP	CEH
<b>Trace gases (HCl, HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub>)</b>	X	X	I	Monthly	UKEAP	CEH
Heavy metals in precipitation	X	X	I	Monthly	Heavy Metals	NPL
Mercury in precipitation	X	X		Monthly	Heavy Metals	NPL
Heavy metals in PM <sub>10</sub>	X	X	II	Weekly	Heavy Metals	CEH
Persistent Organic Pollutants (POPs) in air	X	X	I	Monthly	TOMPS	University of Lancaster
CO <sub>2</sub> measurements		X	III	Hourly	ICOS	CEH
Trace gas fluxes (O <sub>3</sub> ,)		X	III	Hourly	NERC NC <sup>2</sup>	CEH
NO and NO <sub>2</sub> (photolytic)		x	I	Hourly	NERC NC <sup>2</sup>	CEH National Capability funded

<sup>1</sup>CHO: Chilbolton; AUC: Auchencorth Moss; <sup>2</sup>NERC CEH National capability funded \* NPL: National Physical Laboratory, Teddington, Middlesex.

In 2019-20 more than 50 research outputs (papers or presentations) have been identified using data from Auchencorth Moss and Chilbolton and are summarised at the beginning of this report. It is noted that Auchencorth Moss is an integrated climate, air quality and ecosystem research infrastructure and Chilbolton is also a [national facility for remote sensing](#) as well as air quality monitoring.

## High resolution trace gas and aerosol composition measurements (MARGA instrument)

The annual summary of speciated PM<sub>10</sub> and PM<sub>2.5</sub> and trace gases concentrations are presented in Table 4 and the following Figures. The MARGA instrument at both the Auchencorth Moss and Chilbolton sites were upgraded during 2018. The low data capture in January 2019 at the Auchencorth Moss site was due to a faulty valve resulting in contamination of the internal standard and invalidating all data.

At the Chilbolton site, the average data capture for 2019 for all pollutants was 65.1% however for PM<sub>10</sub> pollutants average data capture is 70.5% for PM<sub>2.5</sub> pollutants is 50.5% and for gas pollutants is 78.4%. The difference in data capture between PM<sub>10</sub> and PM<sub>2.5</sub> is caused by the SJAC heater starting to fail in April and it was replaced in July.

Table 4 Summary of the ratified speciated PM<sub>10</sub> and PM<sub>2.5</sub> and trace gases of annual mean concentrations and data capture for Auchencorth Moss and Chilbolton

Ion (PM <sub>10</sub> )	Chilbolton		Auchencorth Moss	
	Annual mean (µg m <sup>-3</sup> )	Data capture (%)	Annual mean (µg m <sup>-3</sup> )	Data capture (%)
NH <sub>4</sub> <sup>+</sup>	1.38	72	0.55	80
Na <sup>+</sup>	0.89	72	0.46	78
K <sup>+</sup>	0.09	71	0.04	79
Ca <sup>2+</sup>	0.33	70	0.05	80
Mg <sup>2+</sup>	0.19	70	0.06	80
Cl <sup>-</sup>	1.54	71	0.83	81
NO <sub>3</sub> <sup>-</sup>	3.56	73	1.19	81
SO <sub>4</sub> <sup>2-</sup>	1.43	73	0.76	81
Ion (PM <sub>2.5</sub> )	Annual mean (µg m <sup>-3</sup> )	Data capture (%)	Annual mean (µg m <sup>-3</sup> )	Data capture (%)
NH <sub>4</sub> <sup>+</sup>	1.27	49	0.49	83
Na <sup>+</sup>	0.46	51	0.27	83
K <sup>+</sup>	0.07	50	0.03	83
Ca <sup>2+</sup>	0.1	50	0.03	82
Mg <sup>2+</sup>	0.12	49	0.03	83
Cl <sup>-</sup>	0.81	51	0.47	83
NO <sub>3</sub> <sup>-</sup>	3.06	52	0.98	83
SO <sub>4</sub> <sup>2-</sup>	1.17	52	0.65	83
Trace Gases	Annual mean (µg m <sup>-3</sup> )	Data capture (%)	Annual mean (µg m <sup>-3</sup> )	Data capture (%)
NH <sub>3</sub>	4.81	78	1.31	86
HCl	0.03	77	0.13	86
HNO <sub>3</sub>	0.13	79	0.11	86
HONO	0.42	79	0.08	86
SO <sub>2</sub>	0.08	79	0.08	86



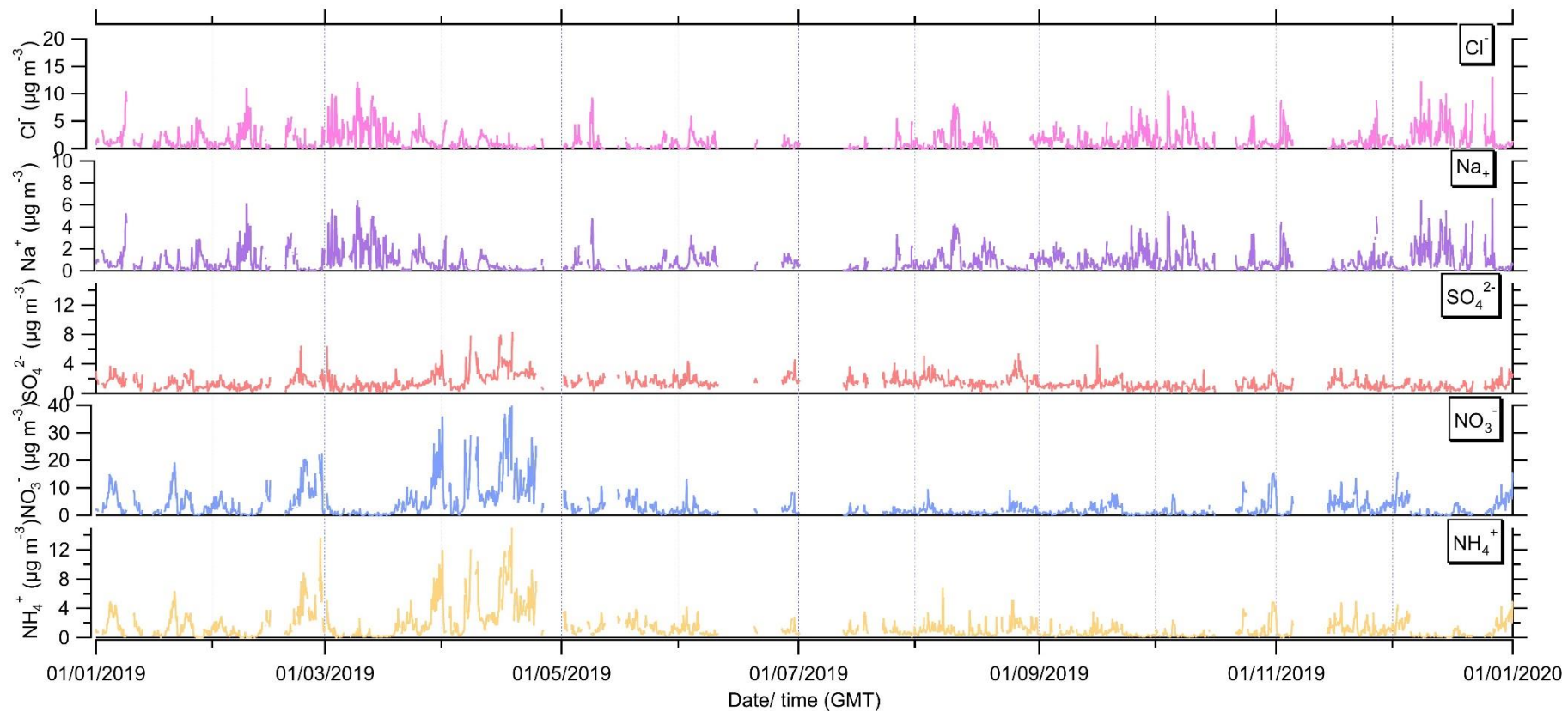


Figure 29 Ratified PM<sub>10</sub> speciated measurements by the MARGA at the Chilbolton supersite

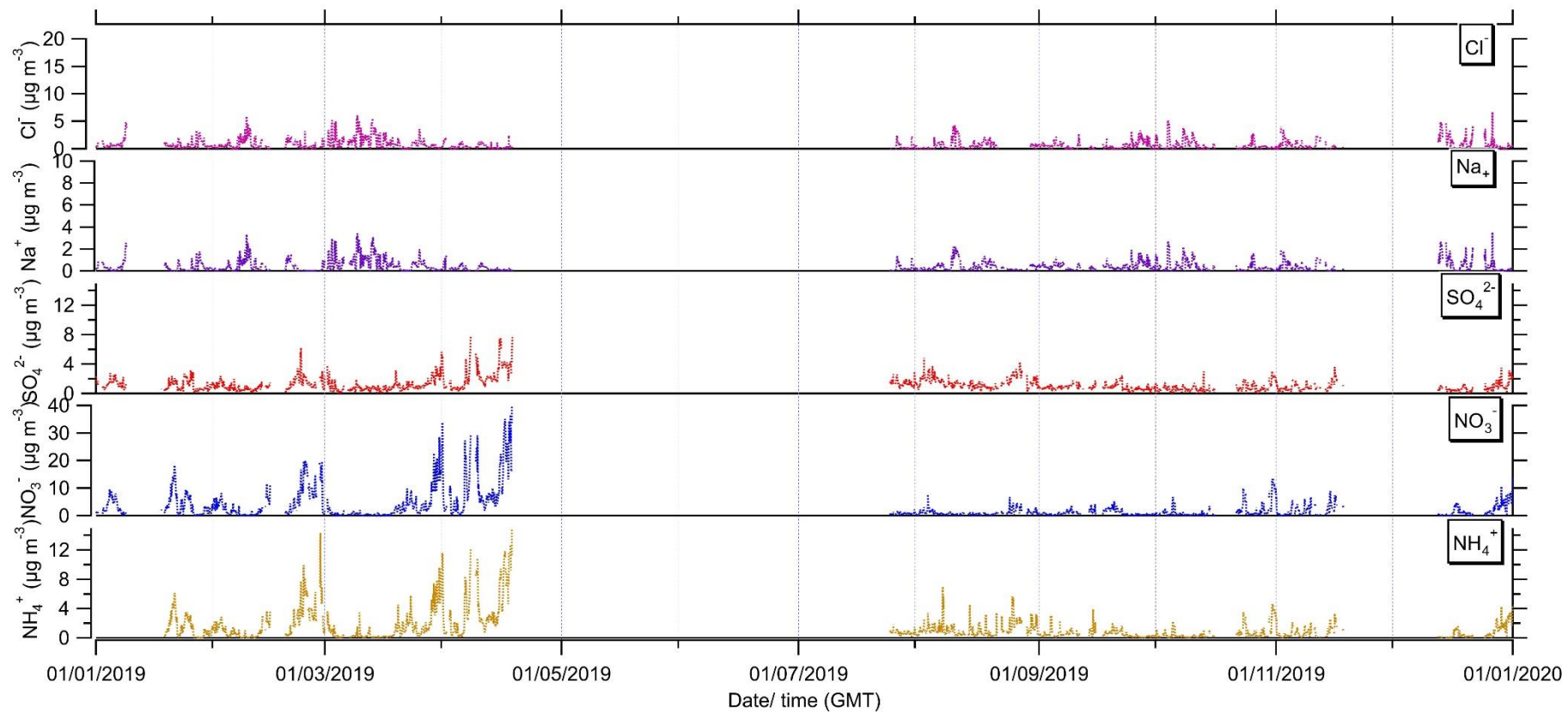


Figure 30 Ratified PM<sub>2.5</sub> speciated measurements by the MARGA at the Chilbolton supersite

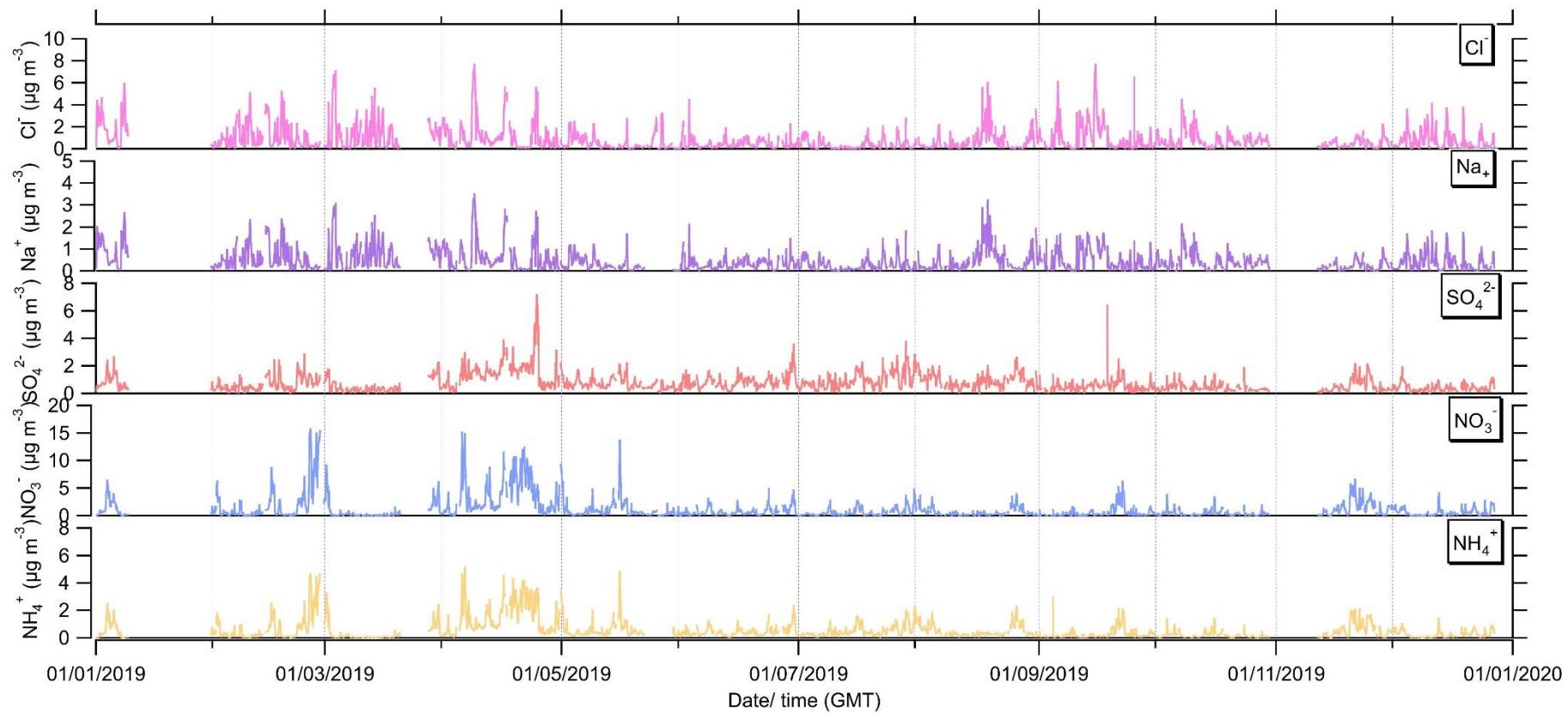


Figure 31 Ratified PM<sub>10</sub> speciated measurements by the MARGA at the Auchencorth Moss supersite

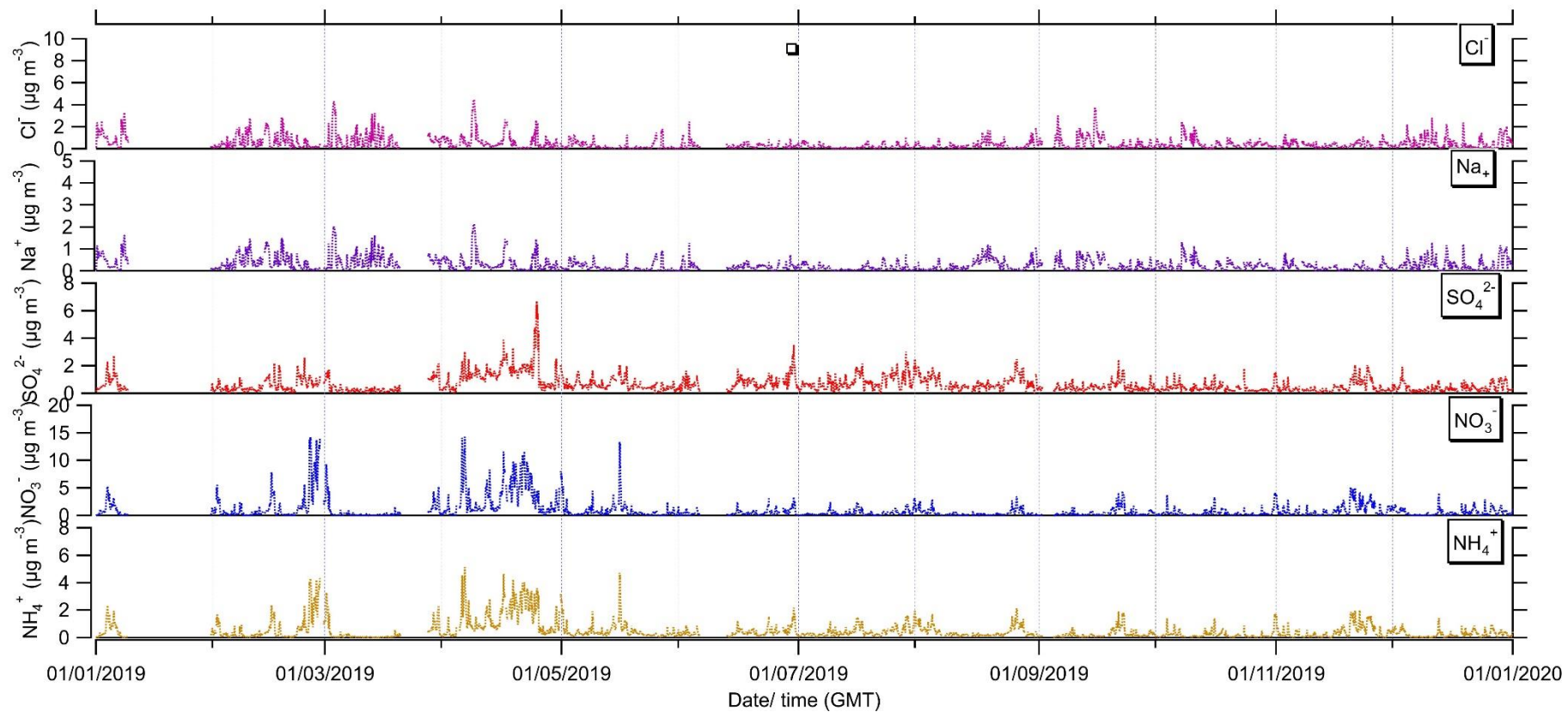


Figure 32 Ratified PM<sub>2.5</sub> speciated measurements by the MARGA at the Auchencorth Moss supersite

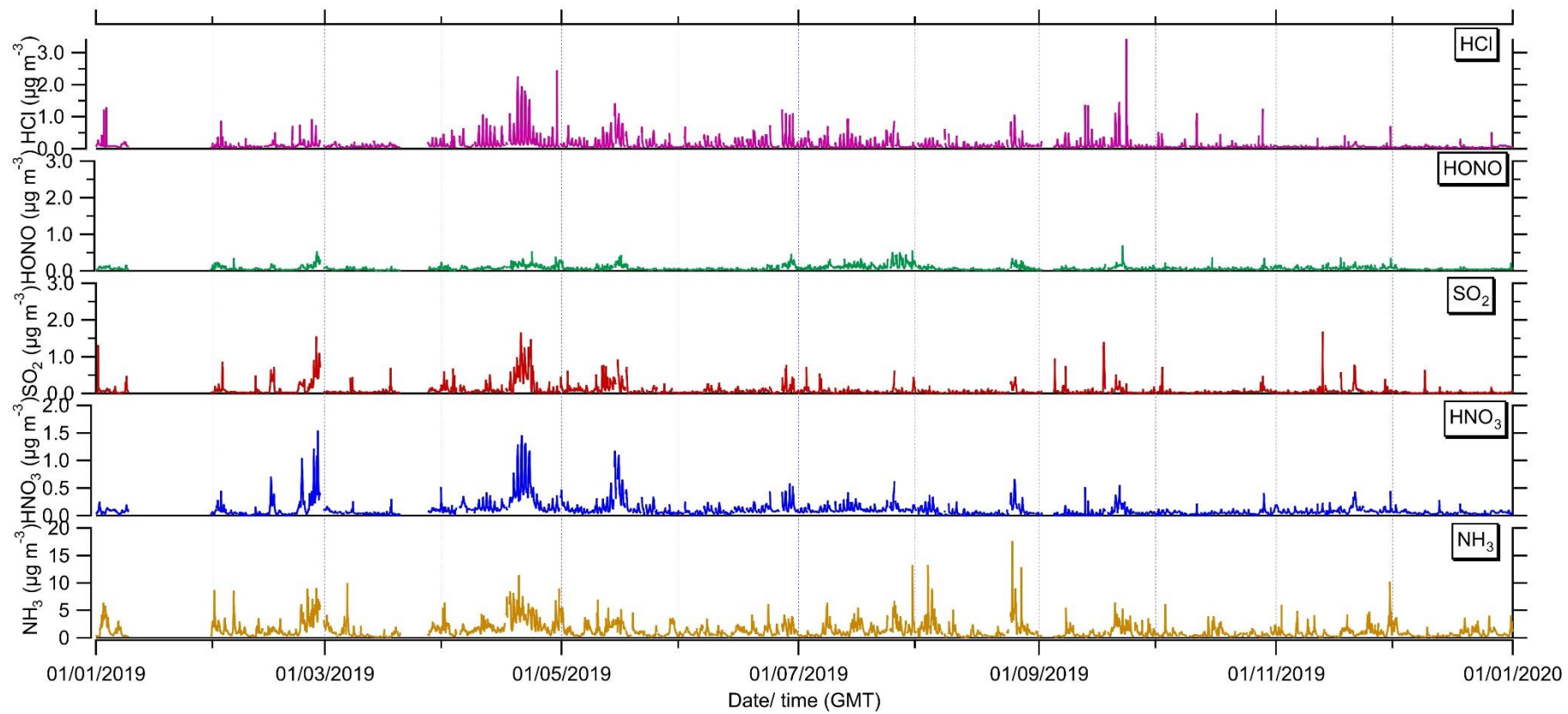


Figure 33 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite



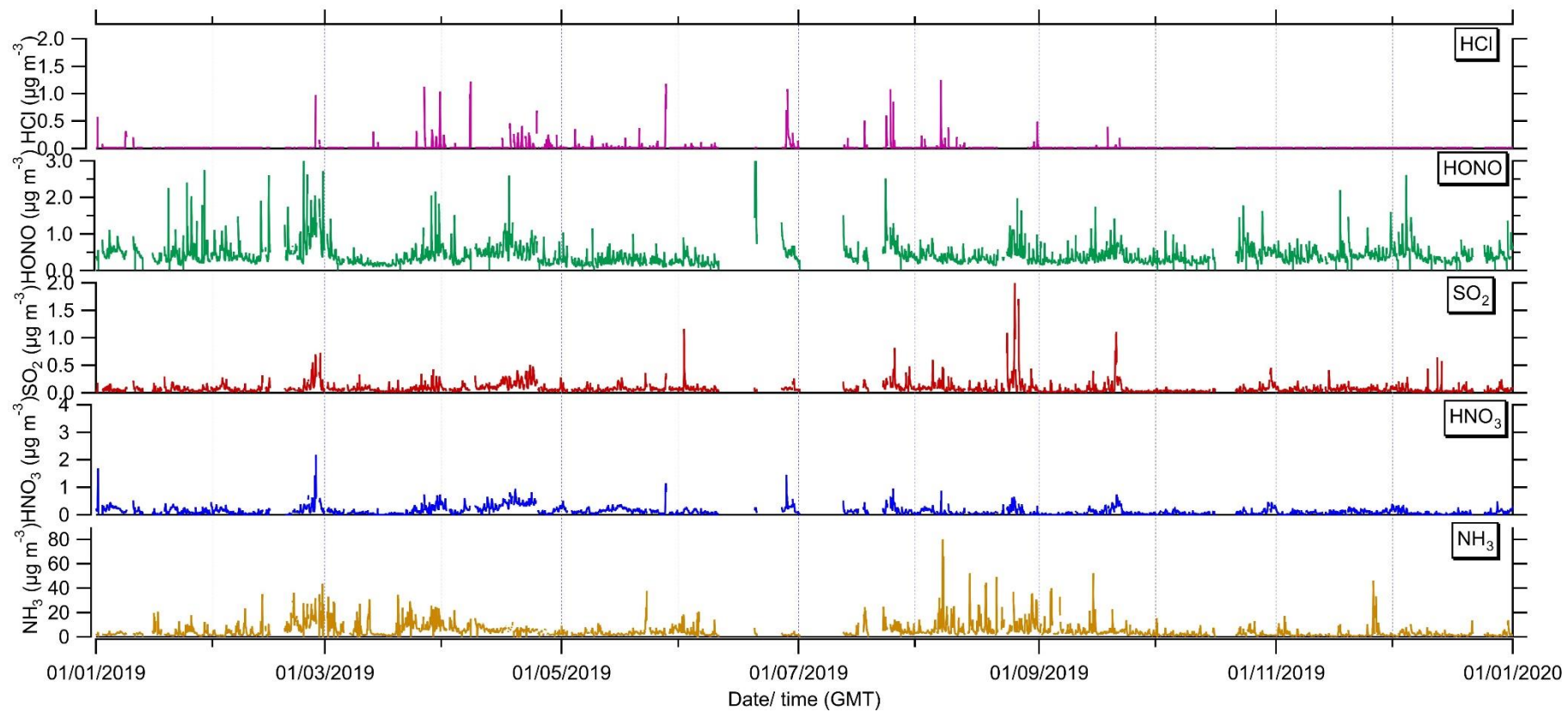


Figure 34 Ratified trace gas measurements by the MARGA at the Chilbolton supersite

## Mercury Measurements

The annual means and data capture for the 2019 ratified mercury measurements are shown below in Table 5. Time series plots of the 2019 Auchencorth Moss measurements are shown in Figure 35. At the beginning of the year the system suffered with unstable flow issues. This led to contamination issues later in the year and the rejection of some of the speciated data.

The mercury data from Chilbolton is shown in the time series in Figure 36. The instrument has suffered with an unstable baseline fault which is intermittent & led to much of the years data being removed.

Table 5 Ratified mercury measurements

	Annual Mean	Data capture
<b>Auchencorth Moss</b>		
Gaseous Elemental Hg (GEM) ng m <sup>-3</sup>	1.32	55.48%
Gaseous Oxidised Hg (GOM) pg m <sup>-3</sup>	0.85	36.46%
Particulate Bound Hg (PM2.5) pg m <sup>-3</sup>	1.88	38.58%
<b>Chilbolton</b>		
Total Gaseous Hg (TGM) ng m <sup>-3</sup>	1.53	24.77%

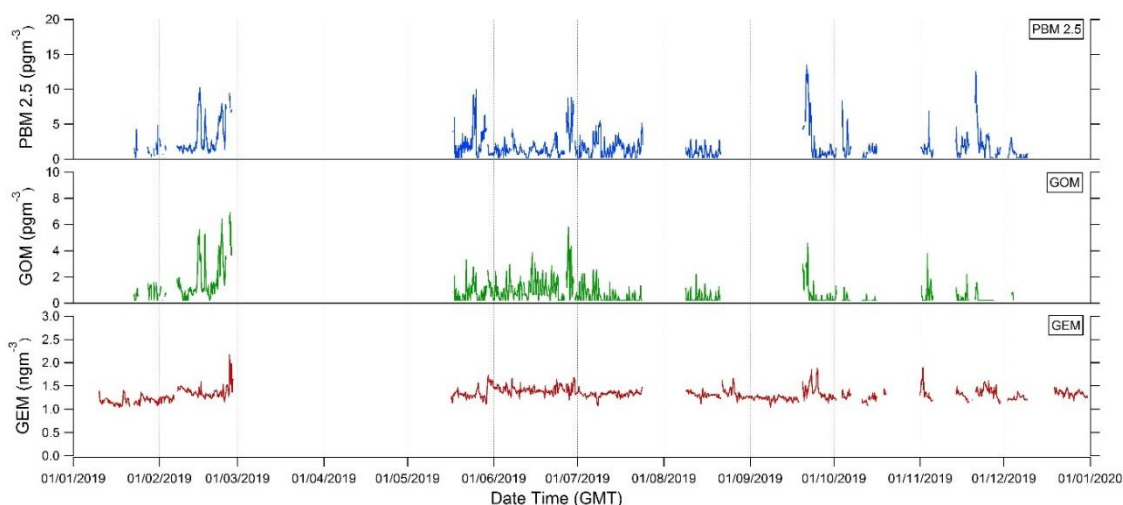


Figure 35 Ratified mercury measurements by the Tekran at the Auchencorth Moss supersite

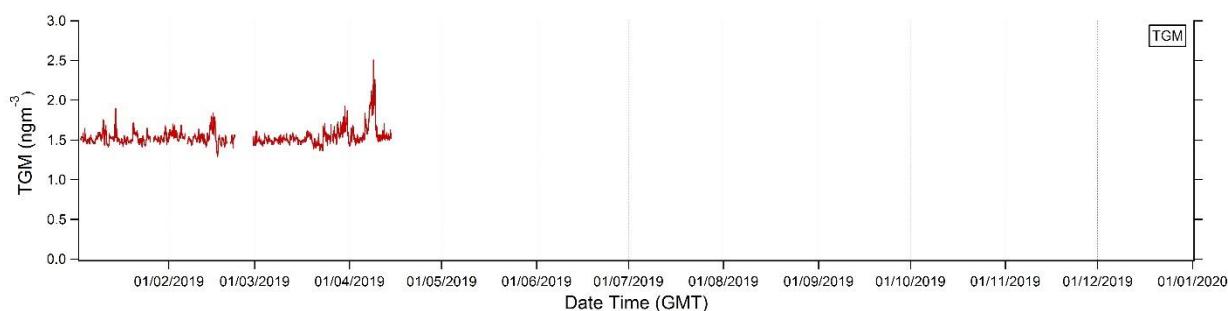


Figure 36 Ratified mercury measurements by the Tekran at Chilbolton Observatory

## **4. Acknowledgements**

Defra, the Devolved Administrations and the Environment Agency, NERC CEH and Ricardo Energy & Environment gratefully appreciate the help and support of all the UKEAP Local Site Operators who change the samples and return them to the laboratories every month of every year!



## Appendix 1: Guide to UKEAP data and Data usage

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

### Chilbolton EMEP Supersite

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***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 (*insert date of data receipt*))

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***Mercury measurements: Contact: Ms Sarah Leeson, NERC 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 (*insert date of data receipt*))

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**Meteorological Data: Contact Mr Chris Conolly Ricardo Energy & Environment**

### Auchencorth Moss EMEP Supersite

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***MARGA: Contact: Dr Marsailidh Twigg, NERC 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 (*insert date of data receipt*))

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***Mercury: Contact: Ms Sarah Leeson, NERC 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 (*insert date of data receipt*))

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## Acid Gas and Aerosol Network

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**Contact: Dr Christine Braban and Ms Sim Tang, NERC Centre for Ecology and Hydrology**

Stephens, A.C.M, Tang, Y.S., Leaver, D., Martin, C., Beith, S., Thacker, S., Simmons, I., Pereira, G., Tanna, B., Patel, M., Lawlor A.J., Sutton, M.A., Braban C.F., UK Eutrophying and Acidifying Atmospheric Pollutant project's Acid Gas and Aerosol Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, AGA-Net, <http://uk-air.defra.gov.uk/networks/network-info?view=ukeep>), Date received: (*insert date of data receipt*)

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## National Ammonia Monitoring Network

**Contact: Dr Christine Braban and Ms Sim Tang, NERC Centre for Ecology and Hydrology**

Stephens, A.C.M, Tang, Y.S., Bealey, W.J., Leaver, D., Beith, S., Thacker, S., Simmons, I., Pereira, G., Tanna, B., Patel, M., Lawlor A.J., Sutton, M.A., Braban C.F., UK Eutrophying and Acidifying Atmospheric Pollutant project's National Ammonia Monitoring Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, AGA-Net, <http://uk-air.defra.gov.uk/networks/network-info?view=ukeep>), Date received: (*insert date of data receipt*)

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## Precipitation Network

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**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=ukeep>), Date received: (*insert date of data receipt*)

## NO<sub>2</sub>-Network

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**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<sub>2</sub>-Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, NO<sub>2</sub>-Net, <http://uk-air.defra.gov.uk/networks/network-info?view=ukeep>), Date received: (*insert date of data receipt*)

## Appendix 2: QC summary for 2019

### A. Chilbolton and Auchencorth operations

The Chilbolton EMEP Supersite is operated by Ricardo summarised on UK-AIR. There were no modifications to the site infrastructure in 2016. Ricardo acted as Local Site Operator for the Chilbolton EMEP Supersite measurements for all measurements except those conducted by NPL.

The Auchencorth Moss EMEP Supersite is operated by NERC CEH, summarised on UK-AIR. CEH is LSO for all measurements at Auchencorth Moss. No instruments were changed during 2019

During 2019 no health and safety incidents occurred at either site in relation to the operation of the EMEP Supersites.

### B. MARGA

#### Operational details

Measurements of particulate-phase cations and anions in PM<sub>10</sub> and PM<sub>2.5</sub>: sulphate (SO<sub>4</sub><sup>2-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), sodium ion (Na<sup>+</sup>), potassium ion (K<sup>+</sup>), ammonium ion (NH<sub>4</sub><sup>+</sup>), chloride ion (Cl<sup>-</sup>), calcium ion (Ca<sup>2+</sup>), and magnesium ion (Mg<sup>2+</sup>) were provided by an automated continuous-flow denuder and steam-jet aerosol sampler (MARGA 2S, [Metrohm-Applicon Ltd.](#)). The MARGA uses an automated continuous-flow, wet-rotating denuder (WRD) coupled to a steam-jet aerosol collector (SJAC) sampler. It provides hourly measurements of the water-soluble species (listed above) in PM<sub>10</sub> and PM<sub>2.5</sub>. It also provides a measure of the concentration of water-soluble trace acid gases (HCl, HONO, HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub>) in the sampled air. The MARGA 2S consists of two units or “boxes”, both identical; one for the sampling and entrainment of the PM<sub>10</sub> particulate and gas-phase species, the other for PM<sub>2.5</sub>. A third, detector box houses the syringe pump module analytical components, including the IC columns, and the process control interfaces, including the PC.

The MARGA 2S samples the ambient air through a PM<sub>10</sub> size-selective inlet head at a nominal flow rate of 2 m<sup>3</sup> hr<sup>-1</sup> (1 m<sup>3</sup> hr<sup>-1</sup> per box). The PM<sub>2.5</sub> fraction is separated from the sampled PM<sub>10</sub> by means of a cyclone separator fitted at the inlet to the PM<sub>2.5</sub> WRD. 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 inertial separation in a cyclone. The solutions of dissolved gases and aerosol species are analysed on-line, and in near real-time, by ion chromatography. Parallel IC systems are used for the detection of the cationic and anionic species.

An internal standard of lithium bromide (LiBr) is used for on-going calibration purposes. Before anion and cation IC analysis, the WRD sample and the internal standard are degassed and mixed. The liquid streams from the WRD and SJAC are collected separately into the syringe pump module which is located in the detector box. The syringe pump module consists of two sets of two pairs of syringes (four pairs in total). Two sets of syringes are required to enable tandem analysis and sampling: whilst the solutions in one set of syringes are transported in-turn to the anion and cation columns for analysis the next set are filled with solution from the WRD and SJAC from the PM<sub>10</sub> and PM<sub>2.5</sub> sampling boxes.

## QC

The MARGA 2S is a research-grade instrument. The MARGA is designed to be operational 24 hours a day, 365 days a year, but as the analyser is a research instrument it has some reliability issues.

Measurements gaps occur throughout the year due to scheduled maintenance and servicing activities, such as replacement of the anion and cation columns, replacement of in-line filters for the steam jet aerosol collector (SJAC), and wet rotating denuder (WRD), pump maintenance, system zeros, and system cleaning. Routine maintenance of the MARGA was undertaken each week, and more frequently if required, i. e. when an error or problem was identified. System maintenance was carried out in-line with the manufacturer's guidance. The instrument status was monitored on an on-going basis. Key system parameters, peak retention times, and chromatograms were checked daily and adjusted accordingly. System blanks were carried out once a month. As well as being used to identify any potential contamination in the system, the results from the system blanks were used in determining the limit of detection, for certain species, during the ratification of the measurements. The calibration of the mass flow controllers are undertaken each month to ensure a sample flowrate of  $1 \text{ m}^3 \text{ hr}^{-1}$ . This was essential two-fold: (1) to ensure the correct flow rate through a steam jet aerosol collector (SJAC), and (2) to ensure the correct cut-off ( $d_{50\%}$ ) of the  $\text{PM}_{10}$  sample head. This process helped identify problems with the mass flow controllers and the sample pumps.

### Internal standard

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:  $\text{Li}^+$  28 mg/L and  $\text{Br}^-$  325 mg/L, working solution:  $\text{Li}^+$  70 ppb  $\text{Br}^-$  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  $\text{Li}^+$  in the stock and work solutions were 320000 ppb and 320 ppb, respectively, and  $3680 \text{ mg L}^{-1}$  and  $3.68 \text{ mg L}^{-1}$  ( $1 \text{ mg L}^{-1} = 1 \text{ ppm}$ ) of  $\text{Br}^-$ .

Sub-samples of the internal standard used at both sites were analysed by CEH Lancaster to ensure that both the stock and working solutions contained the correct, within  $\pm 20\%$ , concentrations of  $\text{Li}^+$  and  $\text{Br}^-$  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  $\text{Li}^+$  and  $\text{Br}^-$  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<sup>+</sup> and Br<sup>-</sup>, in the internal standard, deviated by more than  $\pm 20\%$  of the nominal concentration.

A regular maintenance scheme is in place on the MARGA instrument (Table 6) 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<sup>3</sup>/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.

Table 6 Maintenance Schedule - MARGA 2S (separate air pump/white WRD heads) at Auchencorth Moss

change every:	1	2	1	2	3	4	6	1	2
component	week	week	month	month	month	month	month	year	Years
Clean cyclone and PM <sub>10</sub> head			x						
Replace air tubing					X	x			
Carry out a blank			x						
Take a subsample of internal standard for analysis					x				
2x absorbance liquid 20 Litre (with 1ml 30-35% H <sub>2</sub> O <sub>2</sub> )	x								
2x eluent (anion and cation, both 8 Litre)	x								
Internal standard LiBr 4 (or 5) Litre				x					
suppressor liquid 5 Litre 0.35M phosphoric acid (H <sub>3</sub> PO <sub>4</sub> )		x							
2x empty waste container 30 Litre and add approximately 30 grams of NaHCO <sub>3</sub>	x								
2x sample filters behind SJAC		x							
2x sample filters behind WRD			x						
2x aspiration filters anion/cation			x						
2x inline eluent filter behind pump before pulsation dampener			x						
2x inline liquid filter behind suppressor pump			x						
2x suppressor pump tubing								x	
4x WRD seals located inside WRD heads								X	
4x WRD seals on outer tubing located against WRD heads								x	
2x IC pump seals								x	
2x IC pump check inlet valves								x	
2x IC pump check outlet valves								x	
2x membrane of gas sampling vacuum pump								x	
2x clean SJAC in 1% H <sub>2</sub> O <sub>2</sub> for 10 minute in an ultrasonic bath **							x		
2x clean WRD **							x		
clean or change all Teflon tubing 1/16" boxes**								x	
2x change guard column: 1 anion, 1 cation (+filters if dirty)			x						
1x change anion IC column if necessary ****				x		x			
1x change cation IC column if necessary ****						x			
1 x change cation pre-concentration column if necessary							x		
1 x change anion pre-concentration column if necessary						x			

(\*) preventive replacement frequency based on local experience. Prevent filter blockage. Indicators of blocked filters: significant phosphate peak around 6 min; (\*\*) Frequency depends on location of instrument, clean when visibly dirty; (\*\*\*) Frequency depends on location of instrument, exchange when blocked/ together with 1/16" tubing. Exchange at least every 2 years (wear); (\*\*\*\*) Frequency depends on local conditions (quality of solutions; for anion column: concentration of peroxide); (\*\*\*\*\*) Pump tubing including connectors

### 3. 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 37<sup>th</sup> EMEP Inter-comparison

The inter-comparison in 2019 was the 37<sup>th</sup> time such an inter-comparison took place. The samples provided included nitrogen dioxide in absorbing solution (Table 16) and synthetic rainwater samples (Table 17).

#### Nitrogen dioxide absorbing solution

The inter-comparison in 2019 was the 37<sup>th</sup> time such an inter-comparison took place. The results of the Nitrogen Dioxide absorbing solution are shown below in Table 16. The results of this intercomparison are excellent with absolute mean difference all less than 1 %. 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 7 Comparison of Expected and Measured Concentrations of Nitrogen Dioxide in Absorbing Solution

Sampe code	Expected concentration µg NO <sub>2</sub> -N/ml	Measured concentration µg NO <sub>2</sub> -N/ml	Difference (%)	EMEP quality norm
C1	0.29	0.288	-0.7%	S
C2	0.271	0.272	0.4%	S
C3	0.1	0.1	0.0%	S
C4	0.092	0.092	0.0%	S

<sup>1</sup> EMEP quality norm given as Satisfactory (S), Questionable (Q) or Unsatisfactory (U)

#### Synthetic Rainwater Samples:

The performance of Ricardo's chosen laboratory (SOCOTEC UK Limited) has decreased slightly since the 36<sup>th</sup> intercomparison. The results of the intercomparison and the expected results are shown in Table 17. The 2019 intercomparison has four questionable results and three unsatisfactory.

The analytical laboratory has been made aware of the analytical performance and the results that have been obtain from the intercomparison. They are currently investigating the poor pH data along with errors identified with the results for sulphate and ammonium.

Table 8 37th EMEP Inter-comparison

Species	Sample code	Expected concentration mg l <sup>-1</sup>	Measured concentration mg l <sup>-1</sup>	Difference (%)	EMEP Quality Norm
SO <sub>4</sub> <sup>2-</sup>	G1	0.209	0.187	-10.5%	Q
	G2	0.22	0.194	-11.8%	Q
	G3	0.419	0.380	-9.3%	S
	G4	0.422	0.383	-9.2%	S
NH <sub>4</sub> <sup>+</sup>	G1	0.08	0.062	-22.5%	Q
	G2	0.16	0.139	-13.1%	S
	G3	0.401	0.370	-7.7%	S
	G4	0.454	0.415	-8.6%	S
NO <sub>3</sub> <sup>-</sup>	G1	0.149	0.150	0.7%	S
	G2	0.267	0.268	0.4%	S
	G3	0.547	0.561	2.6%	S
	G4	0.635	0.648	2.0%	S
Na <sup>+</sup>	G1	0.268	0.248	-7.5%	S
	G2	0.39	0.363	-6.9%	S
	G3	0.891	0.826	-7.3%	S
	G4	1.06	0.984	-7.2%	S
Mg <sup>2+</sup>	G1	0.083	0.082	-1.2%	S
	G2	0.062	0.068	9.7%	S
	G3	0.206	0.179	-13.1%	S
	G4	0.175	0.154	-12.0%	S
Cl <sup>-</sup>	G1	0.347	0.314	-9.5%	S
	G2	0.502	0.456	-9.2%	S
	G3	1.24	1.120	-9.7%	S
	G4	1.47	1.340	-8.8%	S
Ca <sup>2+</sup>	G1	0.115	0.123	7.0%	S
	G2	0.153	0.145	-5.2%	S
	G3	0.153	0.151	-1.3%	S
	G4	0.204	0.187	-8.3%	S
K <sup>+</sup>	G1	0.119	0.110	-7.6%	S
	G2	0.187	0.163	-12.8%	S
	G3	0.255	0.223	-12.5%	S
	G4	0.323	0.278	-13.9%	S
pH*	G1	5.49	5.360	-2.4%	Q
	G2	5.48	5.790	5.7%	U
	G3	5.45	5.720	5.0%	U
	G4	5.43	6.120	12.7%	U
Cond	G1	5.96	5.960	0.0%	S
	G2	7.8	7.270	-6.8%	S
	3	14.47	13.950	-3.6%	S
	4	16.4	15.960	-2.7%	S

pH as pH units \* EMEP quality norm given as Satisfactory (S), Questionable (Q) or Unsatisfactory (U)



#### 4. NO<sub>2</sub>-Net

##### **Establishment of a correction factor for nitrogen dioxide concentrations measured in the Rural NO<sub>2</sub> Network (UKEAP).**

Diffusion tubes have been co-located alongside automatic analysers (chemiluminescence) within the Rural Nitrogen Dioxide Network since 2003. Each year we have observed that the nitrogen dioxide measured by diffusion tubes tend to be higher than measured by automatic analysers. Reasons for the overread are complex and may include wind effects (which shortens the diffusion path) and/or in tube conversion of NO<sub>x</sub> to NO<sub>2</sub> or laboratory analytical performance.

In order to extrapolate bias to a wider network [technical guidance](#) provided to local authorities TG(16) recommends, either:

- Use results from the [national bias adjustment spreadsheet](#)
- Use a locally obtained bias adjustment factor, in this case the diffusion tubes co-located with the AURN automatic analysers.

Nitrogen dioxide concentrations are measured within the Rural NO<sub>2</sub> Network to provide an estimate of the rural background concentration field. This work is carried out by Pollution Climate Mapping team as required for compliance modelling against Limit Values.

The objective of this study is review the bias adjustment factors in both the national bias adjustment spread and the co-located samplers in the NO<sub>2</sub>-Net Network and then recommend which adjustment factors should be applied.

##### **National Bias Adjustor Spreadsheet**

Socotec (formerly ESG and HSL) have analysed the diffusion tubes since the inception of the Rural NO<sub>2</sub> Network. They have also acted as diffusion tube analyst for more than fifty local authorities involved in local air quality management since 2000 and hence appear in the National Bias Adjustor Spreadsheet. Figure 37 shows comparison of nitrogen dioxide measured by diffusion tube and diffusion tube since 2000 at sites where Socotec analysis diffusion tubes. This includes three hundred and seventy-eight co-located pairs for a range of sampling site classifications (majority are roadside, 61 %). The diffusion tube over reads in the vast majority (97 %) of cases.

##### **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 9](#) Annual mean nitrogen dioxide concentrations (µg m<sup>-3</sup>) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis). 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 38 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each presents the data for those occasions where data capture was greater than 75 %. The smallest concentrations are measured at Eskdalemuir and the largest at Chilbolton.

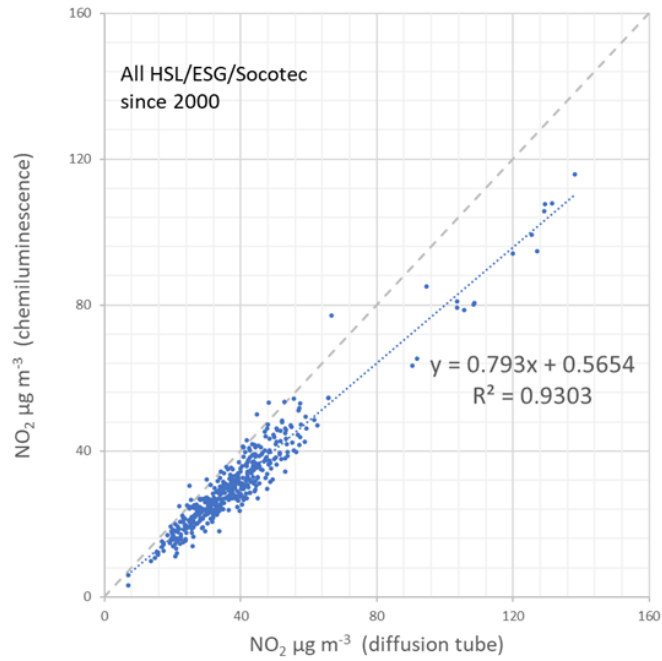


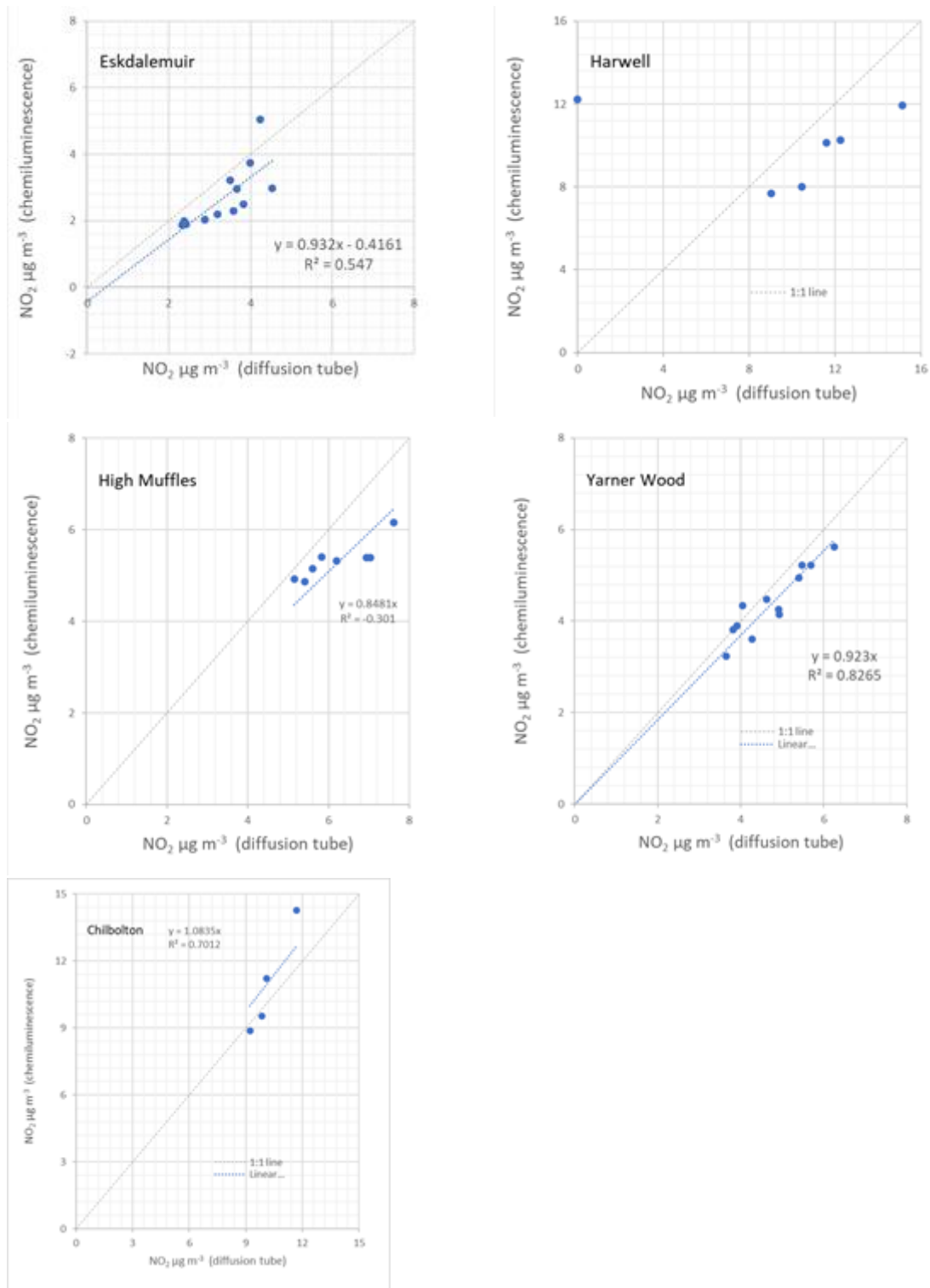
Figure 37 A comparison of annual mean nitrogen dioxide concentrations measured by diffusion tube and automatic analyser

Table 9 Annual mean nitrogen dioxide concentrations ( $\mu\text{g m}^{-3}$ ) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis)

	Chilbolton Observatory		Eskdalemuir		Harwell		High Muffles		Yarner Wood	
	DT	CM	DT <sup>b</sup>	CM	DT	CM	DT <sup>b</sup>	CM	DT <sup>b</sup>	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			<sup>a</sup>	5.1(93)	<sup>a</sup>	10.1(98)	<sup>a</sup>	6.6(98)	<sup>a</sup>	5.3(82)
2009			<sup>a</sup>	4.3(94)	<sup>a</sup>	10.0(98)	<sup>a</sup>	7.5(56)	<sup>a</sup>	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)	#N/A	#N/A	5.4(100)	4.9(99)	3.8(100)	3.8(98)

**Notes:** <sup>a</sup> 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; <sup>b</sup> 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 38 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each



## Recommendation for bias correct factors

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. Here we would recommend using the values derived each year from the Rural NO<sub>2</sub> Network. This is because:

- the ‘quality’ of the measurement made by automatic analyser in the Rural NO<sub>2</sub> 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;
- As the results from the AURN and Rural NO<sub>2</sub> Network will be available before the end of May each year, they will be available in time for the PCM modelling.

## Calculation of average bias factor for the four co-located NO<sub>2</sub> sampling sites (Chilbolton, Eskdalemuir, Yarner Wood and High Muffles)

Following the guidance provided in TG16 we have calculated monthly mean NO<sub>2</sub> concentrations for the automatic analysers corresponding to the periods the diffusion tubes were exposed. We have also updated the calculation spreadsheet<sup>[1]</sup> to allow for time weighting the mean concentrations and bias adjustment factors. As we have four co-located sampling sites we will need to follow the advice provided in Paragraph 7.193<sup>[2]</sup> to combine the respective bias B factors.

The individual bias B factors were calculated as follows: The average of the three values is calculated to be 20.72 % giving a bias adjustment factor of 0.828<sup>[3]</sup>. We would recommend multiplying each of the remaining diffusion tubes in the Rural NO<sub>2</sub> Network by this factor.<sup>[1]</sup> See <https://laqm.defra.gov.uk/bias-adjustment-factors/local-bias.html> and Figure 7.1 of TG(16) The text from Paragraph 7.193 is: 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. Calculated as (1 / (bias average+1))

Table 10 NO<sub>2</sub> Bias factors for 2019

	Eskdalemuir	Yarner Wood	High Muffles	Chilbolton
Bias factor, B	47%	8%	15%	13%

### AGA-Net and NAMN Performance and Data capture

All DELTA systems are serviced annually. As part of this service the gas meter is calibrated and the system PAT tested. Figure 39 below contains the average percentage data capture across all sites for each chemical of interest. Average data capture was 61.4 % for AGANet and 76.9% for NAMN.

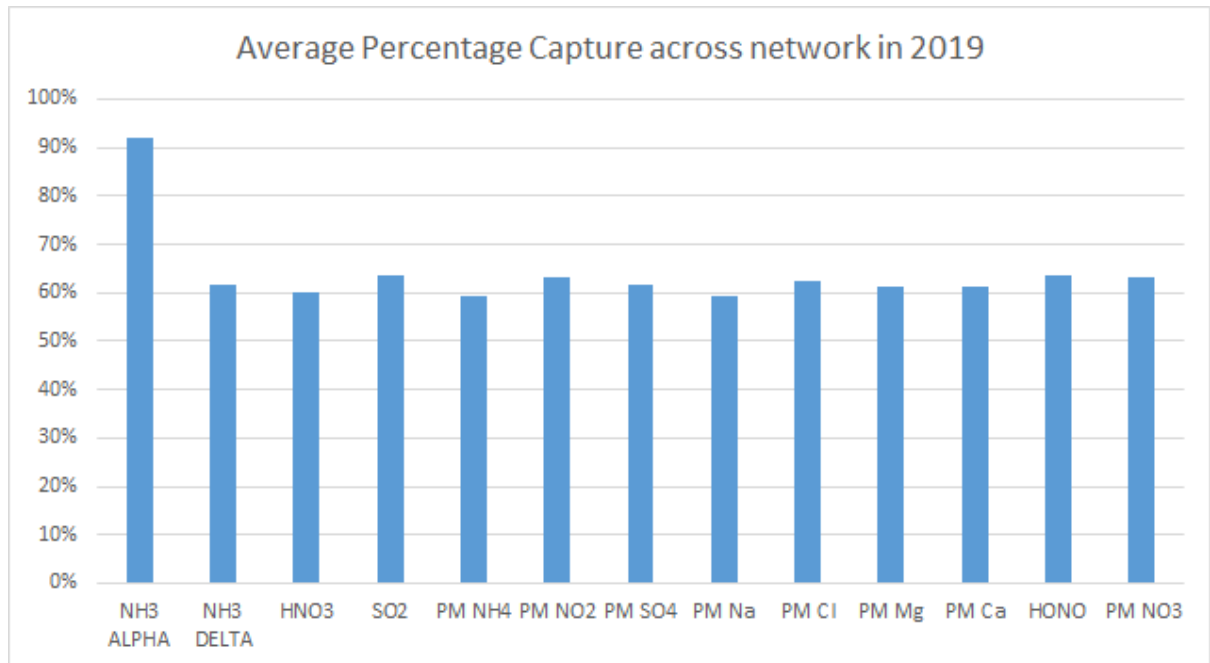


Figure 39 2019 NAMN and AGANet Percentage data capture by chemical component

### ALPHA DELTA intercomparison

NAMN measurements continue to be made with a mixture of active DELTA systems and passive ALPHA samplers. To ensure that bias is not introduced in the sampling and to maintain the validity of long-term trends, the calibration is analysed on an annual basis as a check that the passive samplers in relation to the DELTA do not deviate significantly with time. The annual regression used to calibrate the ALPHA sampler is shown in Figure 41. The annual calibration functions of ALPHA samplers show good consistency between years. This can be seen in the historical ALPHA uptake rates plotted in Figure 40.

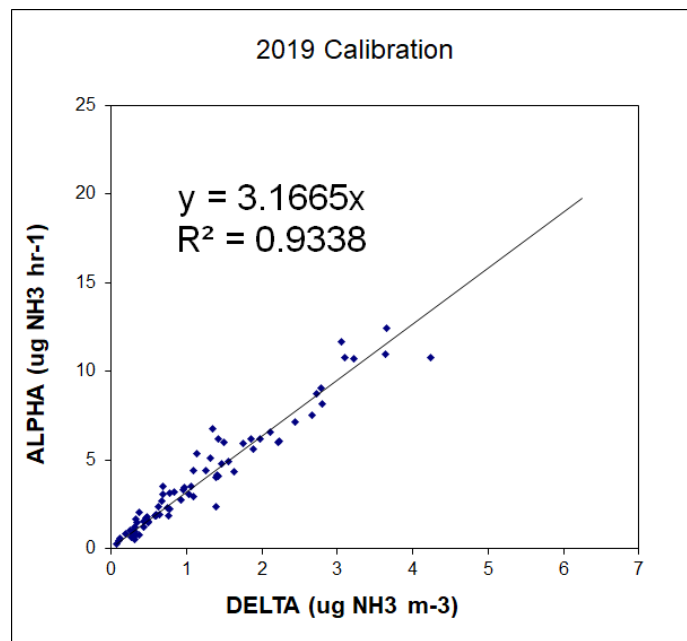


Figure 40 Historical UKEAP uptake rate for ALPHA samplers.

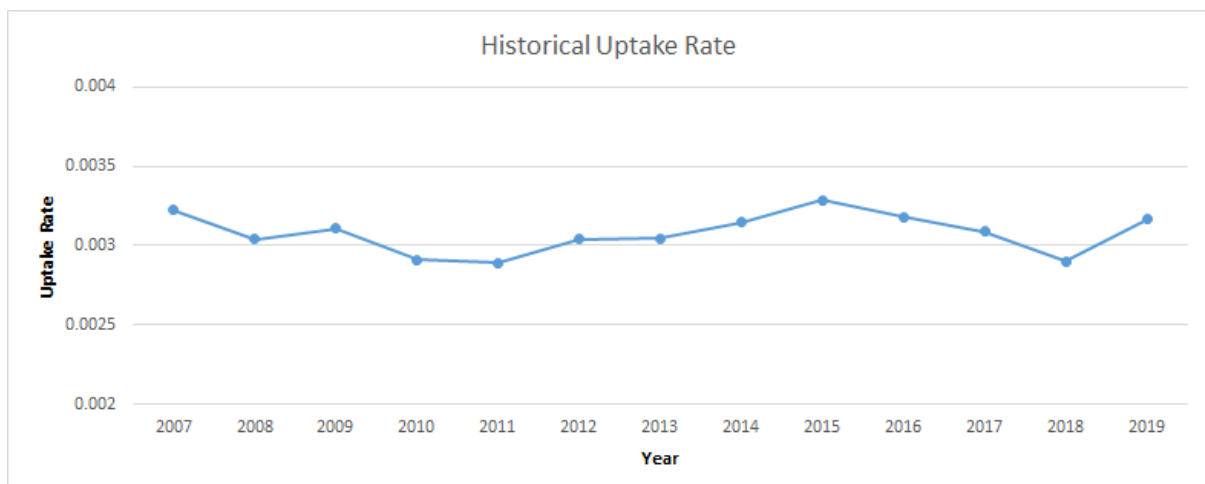


Figure 41 Historical UKEAP uptake rate for ALPHA samplers.