

# UKEAP 2020 Annual Report

Prepared for the Environment Agency

&

Defra

And the Devolved Administrations

By

UK Centre for Ecology & Hydrology

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Ricardo Energy & Environment

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## UKCEH REPORT SUMMARY

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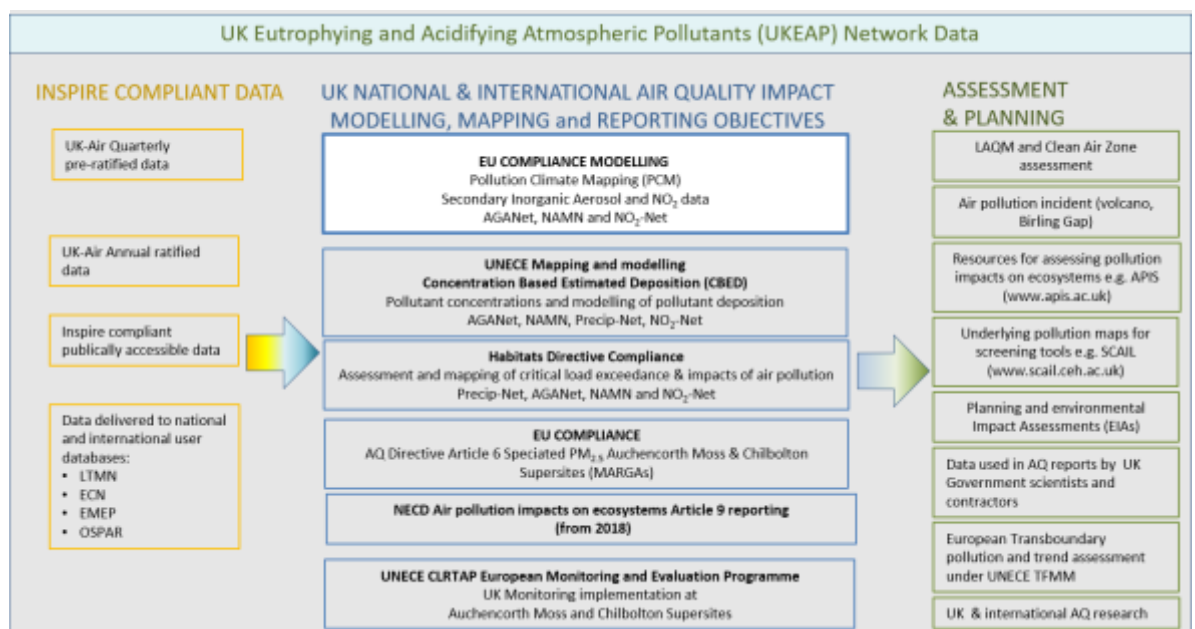
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# 1. Summary

## 1.1 Overview

The Defra rural air pollutant monitoring networks project, (2017-2021: 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** (AGANet)
  - **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 (Figure 1) highlights the most significant data applications in the UK and internationally. It is assumed that the EU reporting objectives will continue and be transposed into UK law following EU exit.
  - The UKEAP network is operated by the UK Centre for Ecology & 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 UK's EU exit. (Note: It is assumed that the 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 AGANet 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

#### **CBED:**

- UKEAP Precip-Net, AGANet, 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 UK 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 2020 using UKEAP site air quality data, maps derived from UKEAP data or science supported at UKEAP sites*

- Akritidis, D. et al. (2020) 'A complex aerosol transport event over Europe during the 2017 Storm Ophelia in CAMS forecast systems: analysis and evaluation', *Atmospheric Chemistry and Physics Discussions*, pp. 1–31.
- AQEG, (2020), Estimation of changes in air pollution emissions, concentrations and exposure during the COVID-19 outbreak in the UK. Rapid evidence review – June 2020. [https://uk-air.defra.gov.uk/assets/documents/reports/cat09/2007010844\\_Estimation\\_of\\_Changes\\_in\\_Air\\_Pollution\\_During\\_COVID-19\\_outbreak\\_in\\_the\\_UK.pdf](https://uk-air.defra.gov.uk/assets/documents/reports/cat09/2007010844_Estimation_of_Changes_in_Air_Pollution_During_COVID-19_outbreak_in_the_UK.pdf)
- Archibald, A. T. et al. (2020) 'Description and evaluation of the UKCA stratosphere–troposphere chemistry scheme (StratTrop v1.0) implemented in UKESM1', *Geosci. Model Dev.*, 13(3), pp. 1223–1266. doi: 10.5194/gmd-13-1223-2020.
- Billett, M. F., Garnett, M. H. and Leith, F. I. (2020) 'An assessment of chamber 14C methodologies for sampling aquatic CO<sub>2</sub> evasion', *Ecohydrology*, 13(2), p. e2191.
- Braban, C. F. et al. (2020) 'Ammonia in a time of COVID-19. A submission of evidence to Defra/AQEG'.
- Brown, R. J. et al. (2020) 'Consistency and uncertainty of UK measurements of mercury in precipitation', *Chemosphere*, p. 127330.
- Clifton, O. E. et al. (2020) 'Dry Deposition of Ozone Over Land: Processes, Measurement, and Modeling', *Reviews of Geophysics*, 58(1), p. e2019RG000670. doi: 10.1029/2019RG000670.
- Dacre, H. F., Mortimer, A. H. and Neal, L. S. (2020) 'How have surface NO<sub>2</sub> concentrations changed as a result of the UK's COVID-19 travel restrictions?', *Environmental Research Letters*. Available at: <http://iopscience.iop.org/10.1088/1748-9326/abb6a2>.
- Diaz, F. M. et al. (2020) 'Ozone Trends in the United Kingdom over the Last 30 Years', *Atmosphere*, 11(5), p. 534.
- Emetere, M. E. and Akinlabi, E. T. (2020) 'Modeling Big Data and Further Analysis', in *Introduction to Environmental Data Analysis and Modeling*. Springer, pp. 79–155.
- Finch, D. P. and Palmer, P. I. (2020) 'Increasing ambient surface ozone levels over the UK accompanied by fewer extreme events', *Atmospheric Environment*, p. 117627.
- Gambaro, N. (2020) Sentinels of environmental impact: using principal component analysis to improve the detection of shale gas contamination in England. Department of Earth Sciences, Durham University.
- Hei-Laun Yeung, K. et al. (2020) 'From sink to source: long-term (2002–2019) trends and anomalies in net ecosystem exchange of CO<sub>2</sub> from a Scottish temperate peatland.', in *EGU General Assembly Conference Abstracts*, p. 5967.
- Hjellbrekke, A.-G. (2020) 'Data report 2018. Particulate matter, carbonaceous and inorganic compounds.', EMEP/CCC-Report.
- Hjellbrekke, A.-G. and Solberg, S. (2019) 'Ozone measurements 2017', EMEP/CCC-Report.
- Insausti, M. et al. (2020) 'Advances in sensing ammonia from agricultural sources', *Science of The Total Environment*, 706, p. 135124.
- Jafar, H. A. and Harrison, R. M. (2020) 'Spatial and temporal trends in carbonaceous aerosols in the United Kingdom', *Atmospheric Pollution Research*.
- Kiheri, H. et al. (2020) 'Fungal colonization patterns and enzymatic activities of peatland ericaceous plants following long-term nutrient addition', *Soil Biology and Biochemistry*, p. 107833.
- Lewis, A., Carslaw, D. and Moller, S. J. (2020) 'Non-methane Volatile Organic Compounds in the UK'.
- Liu, L. et al. (2020) 'Global estimates of dry ammonia deposition inferred from space-measurements', *Science of the Total Environment*, p. 139189.
- Menut, L. et al. (2020) 'Impact of lockdown measures to combat Covid-19 on air quality over western Europe', *Science of the Total Environment*, 741, p. 140426.
- Nair, A. A. and Yu, F. (2020) 'Quantification of atmospheric ammonia concentrations: A review of its measurement and modeling'.
- Pan, Y. et al. (2020) Revisiting the concentration observations and source apportionment of atmospheric ammonia. Springer.

- Rennie, S. et al. (2020) 'The UK Environmental Change Network datasets—integrated and co-located data for long-term environmental research (1993–2015)', *Earth System Science Data*, 12(1), pp. 87–107
- Savi, F. et al. (2020) 'Neural network analysis to evaluate ozone damage to vegetation under different climatic conditions', *Frontiers in Forests and Global Change*, 3, p. 42.
- Solberg, S. et al. (2020) 'VOC measurements 2018', EMEP/CCC-Report.
- Stacey, B., Harrison, R. M. and Pope, F. (2020) 'Evaluation of ultrafine particle concentrations and size distributions at London Heathrow Airport', *Atmospheric Environment*, 222, p. 117148. doi: 10.1016/j.atmosenv.2019.117148.
- Tang, Y. S. et al. (2020) 'Pan-European rural atmospheric monitoring network shows dominance of NH<sub>3</sub> gas and NH<sub>4</sub><sup>+</sup> aerosol in inorganic pollution load', *Atmospheric Chemistry and Physics Discussions*, 2020, pp. 1–61. doi: 10.5194/acp-2020-275.
- Tao, Y. and Murphy, J. G. (2019) 'The sensitivity of PM<sub>2.5</sub> acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites.', *Atmospheric Chemistry & Physics*, 19(14).
- Vohra, K. et al. (2020) 'Long-term trends in air quality in major cities in the UK and India: A view from space', *Atmospheric Chemistry and Physics Discussions*, pp. 1–45.
- Walker, H. L. et al. (2020) 'Use of filter radiometer measurements to derive local photolysis rates and for future monitoring network application', *Atmospheric Measurement Techniques Discussions*, 2020, pp. 1–32. doi: 10.5194/amt-2020-219.
- Wyche, K. P., Nichols, M., et al. (2020) 'Changes in Ambient Air Quality and Atmospheric Composition and Reactivity in the South East of the UK as a Result of the COVID-19 Lockdown', *Science of The Total Environment*, p. 142526.
- Wyche, K. P., Cordell, R. L., et al. (2020) 'The spatio-temporal evolution of black carbon in the North-West European "air pollution hotspot"', *Atmospheric Environment*, p. 117874.
- Xu, J. et al. (2020) 'Increased dissolved organic carbon concentrations in peat-fed UK water supplies under future climate and sulfate deposition scenarios', *Water Resources Research*, 56(1), p. e2019WR025592.
- Yang, M. et al. (2020) 'Temporal and spatial trends in aerosols near the English Channel – An air quality success story?', *Atmospheric Environment: X*, 6, p. 100074. doi: 10.1016/j.aeaoa.2020.100074.

**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 an 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 2020.

**UKEAP is comprised of:**

- **National Ammonia Monitoring Network** (NAMN – 70 sites)
- **Acid Gases and Aerosol Network** (AGANet – 26 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 within UKEAP networks maps for Precip-Net and NO<sub>2</sub>-Net.

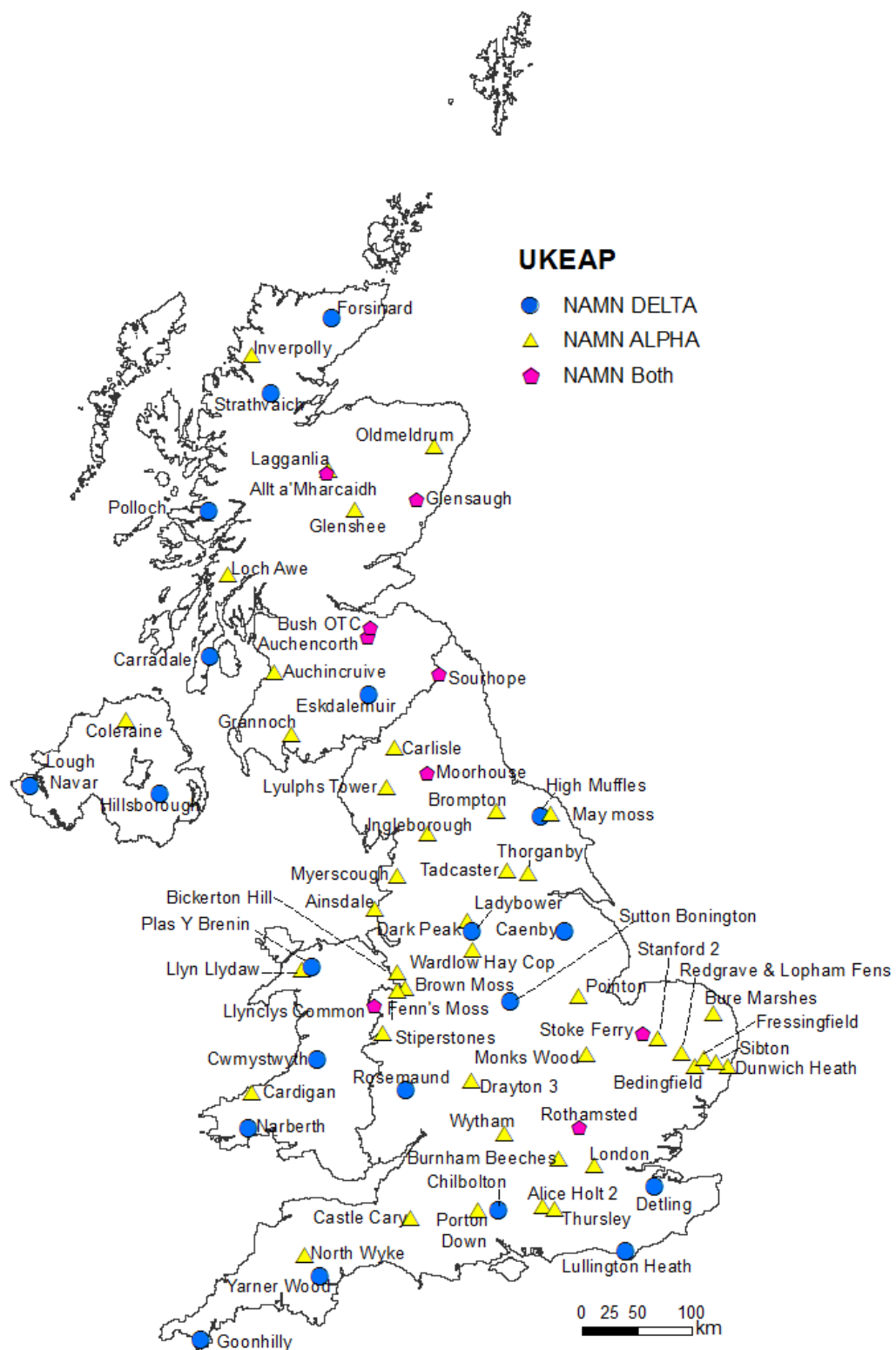
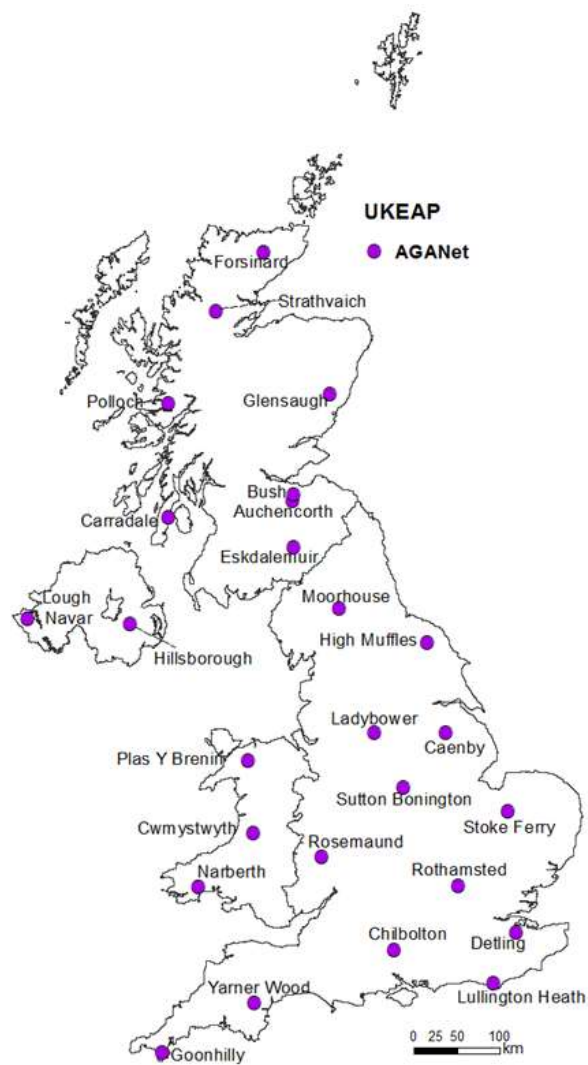


Figure 2 UK National Ammonia Monitoring Network (NAMN)



**Figure 3 UK Acid Gases and Aerosol Network (AGANet)**

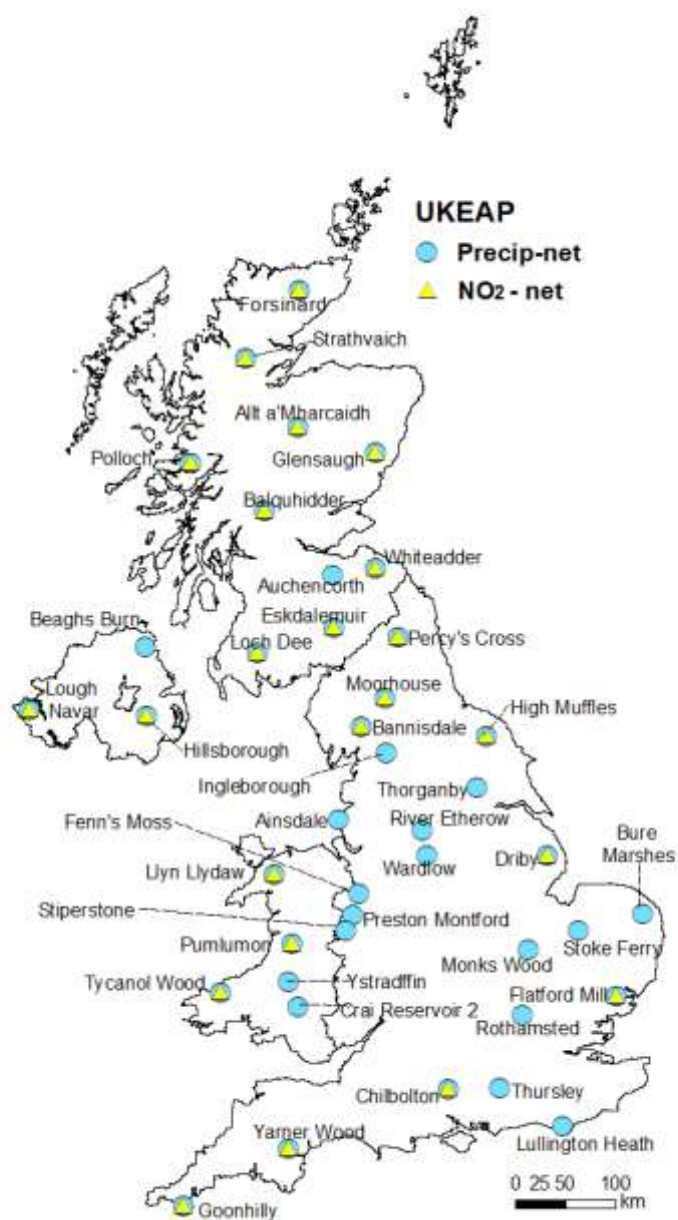


Figure 4 UK Precipitation chemistry (Precip-Net) and NO<sub>2</sub> diffusion tube (NO<sub>2</sub>-Net) Network

### 3. UKEAP Networks Reports

#### 3.1 Precipitation Network (Precip-Net)

Precip-Net operated without major change in 2020. 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) at fortnightly intervals, details of which can be found in previous reports. Precip-Net sites are located across the UK (Figure 3) and consists of both new Natural England Long Term Monitoring Network (LTMN) sites and those which were part of the original 1986-2016 network prior to the 2016 network review (Figure 6 and Figure 7 respectively). Unratified quarterly monitoring data are made available publicly 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).

In addition to the Precip-Net bulk sampler network, 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 2020 are summarised in the Appendices of this report.



**Figure 5 Bulk rain sampler (Bannisdale)**

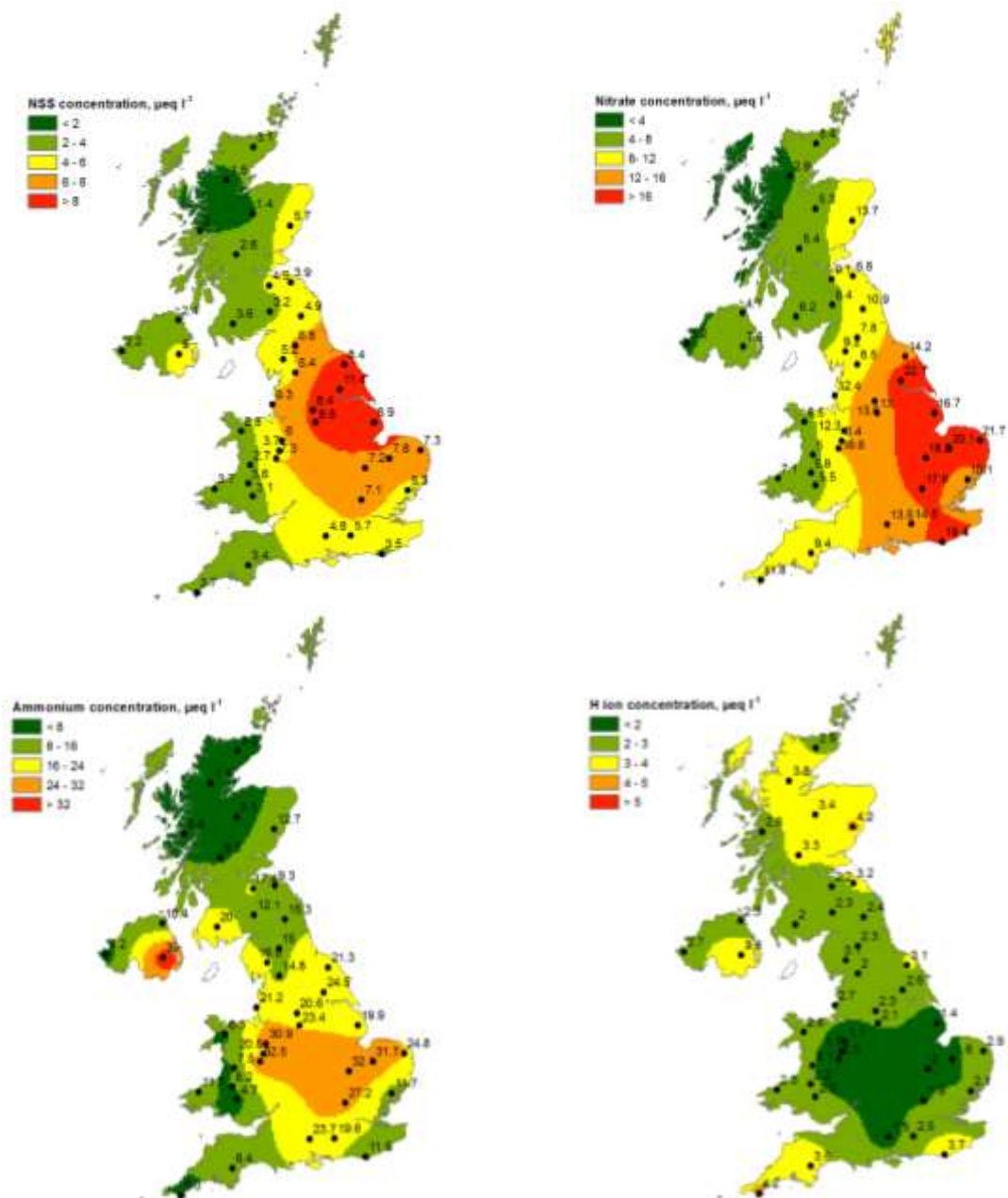


Figure 6 LTMN sites forming part of the Precip-Net monitoring network (eight sites)



Figure 7 Precip-Net monitoring network

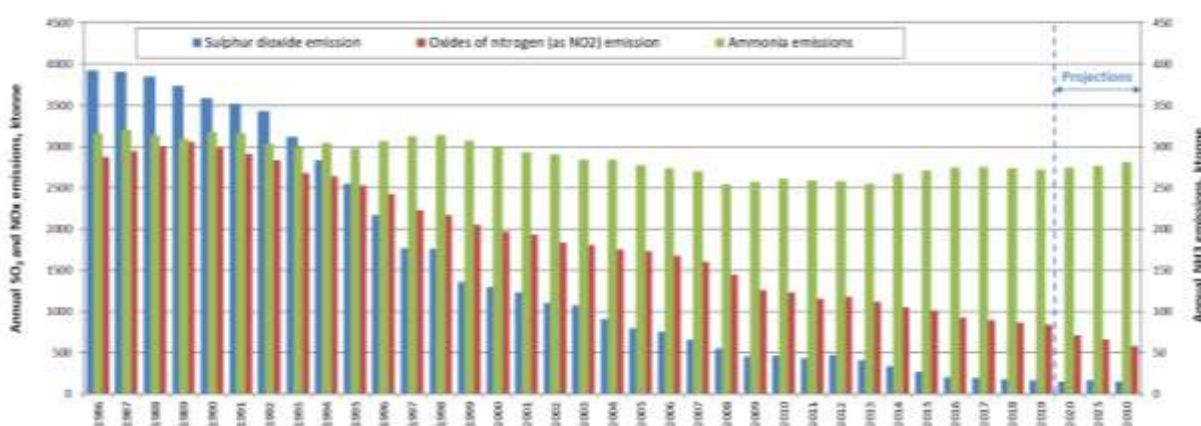
The spatial patterns of the annual mean precipitation-weighted concentration of non-seasalt sulphate, nitrate, ammonium and hydrogen are presented in Figure 8 for 2020. The maps show that: the non-seasalt sulphate and nitrate concentrations tend to be highest on the eastern seaboard where the rainwater 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 8** Interpolated concentration maps for non-sea salt sulphate, nitrate, ammonium and hydrogen ion ( $\mu\text{eq l}^{-1}$ ) The spatial patterns of the annual mean precipitation-weighted



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 70 % and ammonia emissions have decreased by about 13 %. Figure 9 also presents projected emissions for the respective gases from the National Emissions Inventory (NAEI)<sup>1</sup>.



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

Figure 10, Figure 11 and Figure 12 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. Significant geographical variations can be seen clearly by comparing individual sites in Figure 13 to Figure 16 for non-sea salt sulphate, nitrate and ammonium, respectively.

The impact of Covid-19 on transport and consequently on NO<sub>x</sub> emissions has been well documented (AQEG)<sup>2</sup> with significant reductions in NO<sub>x</sub> from transport emissions during the first national lock down. From 2019 to 2020, NO<sub>x</sub> emissions from road transport are projected to decrease by about 28%. Extrapolating whether such reductions lead directly to the observed changes in the network mean concentrations from 2019 to 2020 may be speculative but the network average nitrate concentrations decreased from 0.21 mg l<sup>-1</sup> (14.6 µeq l<sup>-1</sup>) in 2019 to 0.15 mg l<sup>-1</sup> (10.5 µeq l<sup>-1</sup>) in 2020, a decrease of 29 %. At the national scale, total NO<sub>x</sub> emissions are projected to decrease by about 16 % from 2019 to 2020 so a step change down in nitrate concentration in rainwater might be expected.

<sup>1</sup> The emissions for 2020, 2025 and 2030 shown in Figure 8 are NECD Annex iv projections. They were obtained from the workbook: *annex\_iv\_projections\_reporting\_template\_2021\_GB\_v1.0.xls* (available from <https://naei.beis.gov.uk/data/>).

<sup>2</sup> Air Quality Expert Group, Estimation of changes in air pollution emissions, concentrations and exposure during the COVID-19 outbreak in the UK, June 2020. Available from [https://uk-air.defra.gov.uk/assets/documents/reports/cat09/2007010844\\_Estimation\\_of\\_Changes\\_in\\_Air\\_Pollution\\_During\\_COVID-19\\_outbreak\\_in\\_the\\_UK.pdf](https://uk-air.defra.gov.uk/assets/documents/reports/cat09/2007010844_Estimation_of_Changes_in_Air_Pollution_During_COVID-19_outbreak_in_the_UK.pdf)



A similar percentage decrease (29 %) was observed for non-sea salt sulphate which showed decreases from  $0.11 \text{ mg l}^{-1}$  ( $7 \text{ } \mu\text{eq l}^{-1}$ ) to  $0.08 \text{ mg l}^{-1}$  ( $5 \text{ } \mu\text{eq l}^{-1}$ ). The total sulphur dioxide emissions were projected to decrease by about 10 %.

By contrast, the national ammonia emission is projected to increase very slightly from 2019 to 2020 (271.9 kt to 274.4 kt) but the network average ammonium concentration in rainwater decreased from  $0.26 \text{ mg l}^{-1}$  ( $18.3 \text{ } \mu\text{eq l}^{-1}$ ) to  $0.22 \text{ mg l}^{-1}$  ( $16.0 \text{ } \mu\text{eq l}^{-1}$ ) - a decrease of 13 %.

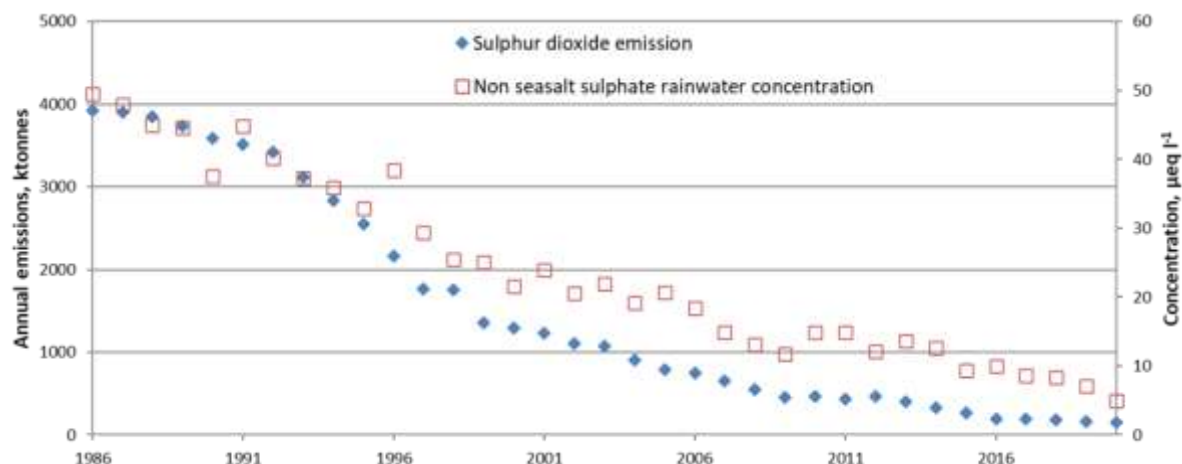


Figure 10 UK Sulphur dioxide emissions and site average sulphate concentrations in rainwater

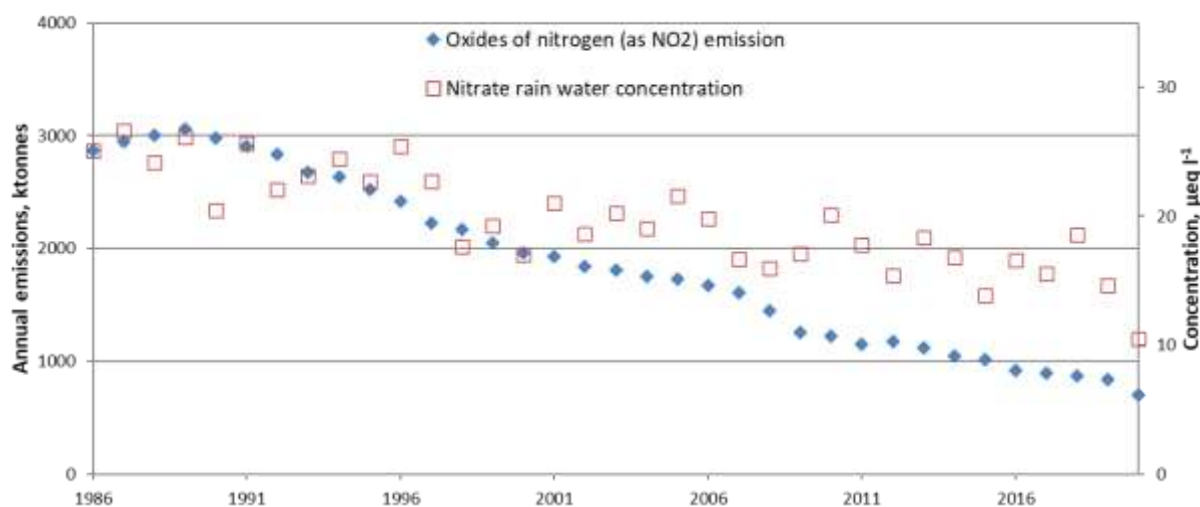


Figure 11 UK Oxides of nitrogen emissions and site average nitrate concentrations in rainwater

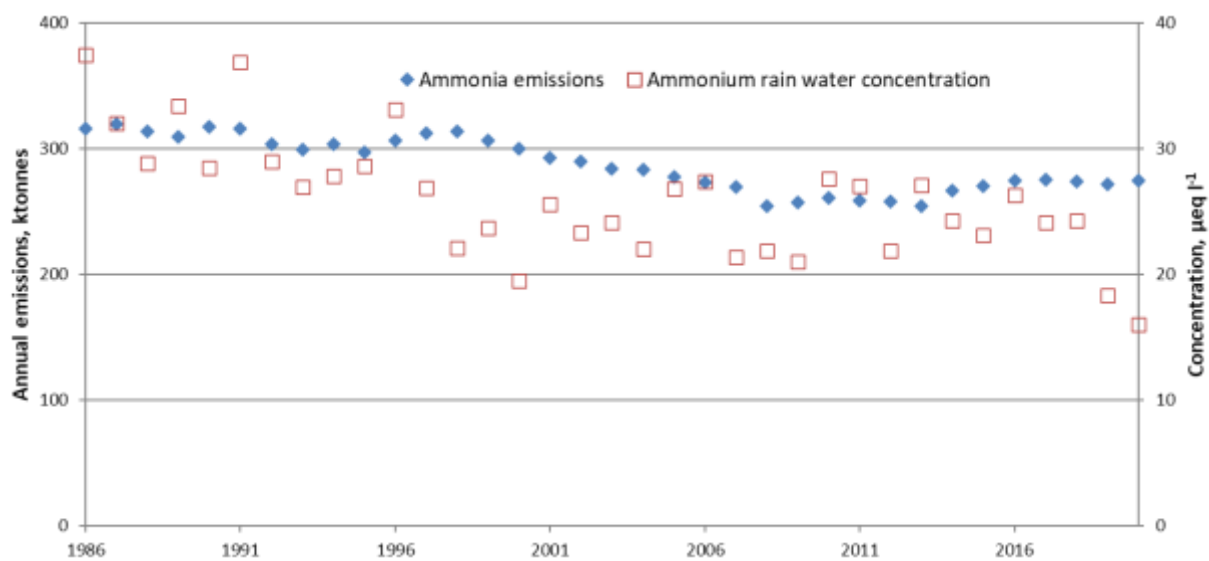


Figure 12 UK Ammonia emissions and site average ammonium concentrations in rainwater

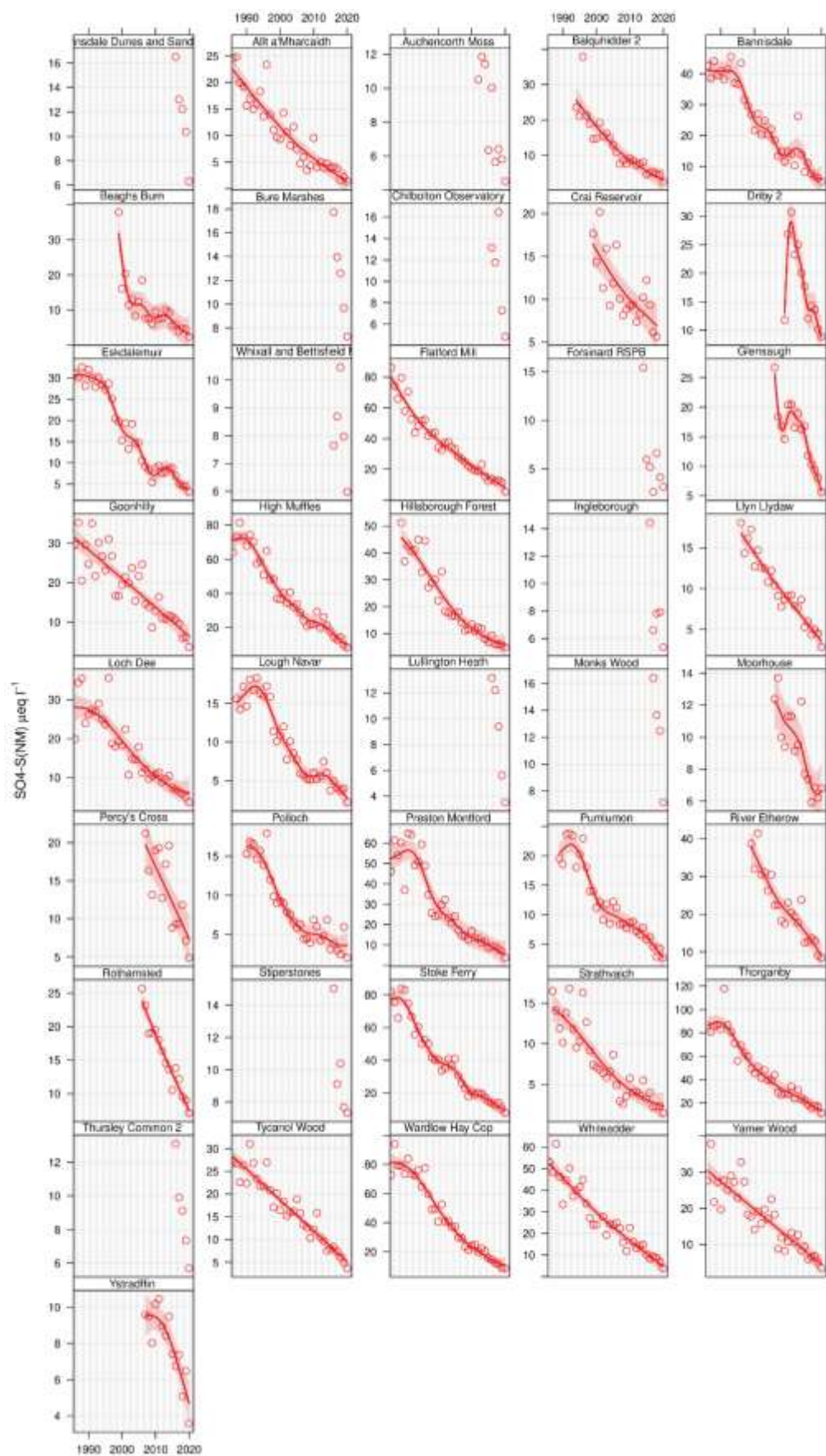


Figure 13 Non sea salt sulphate concentrations measured at sites with the Precip-Net since 1986

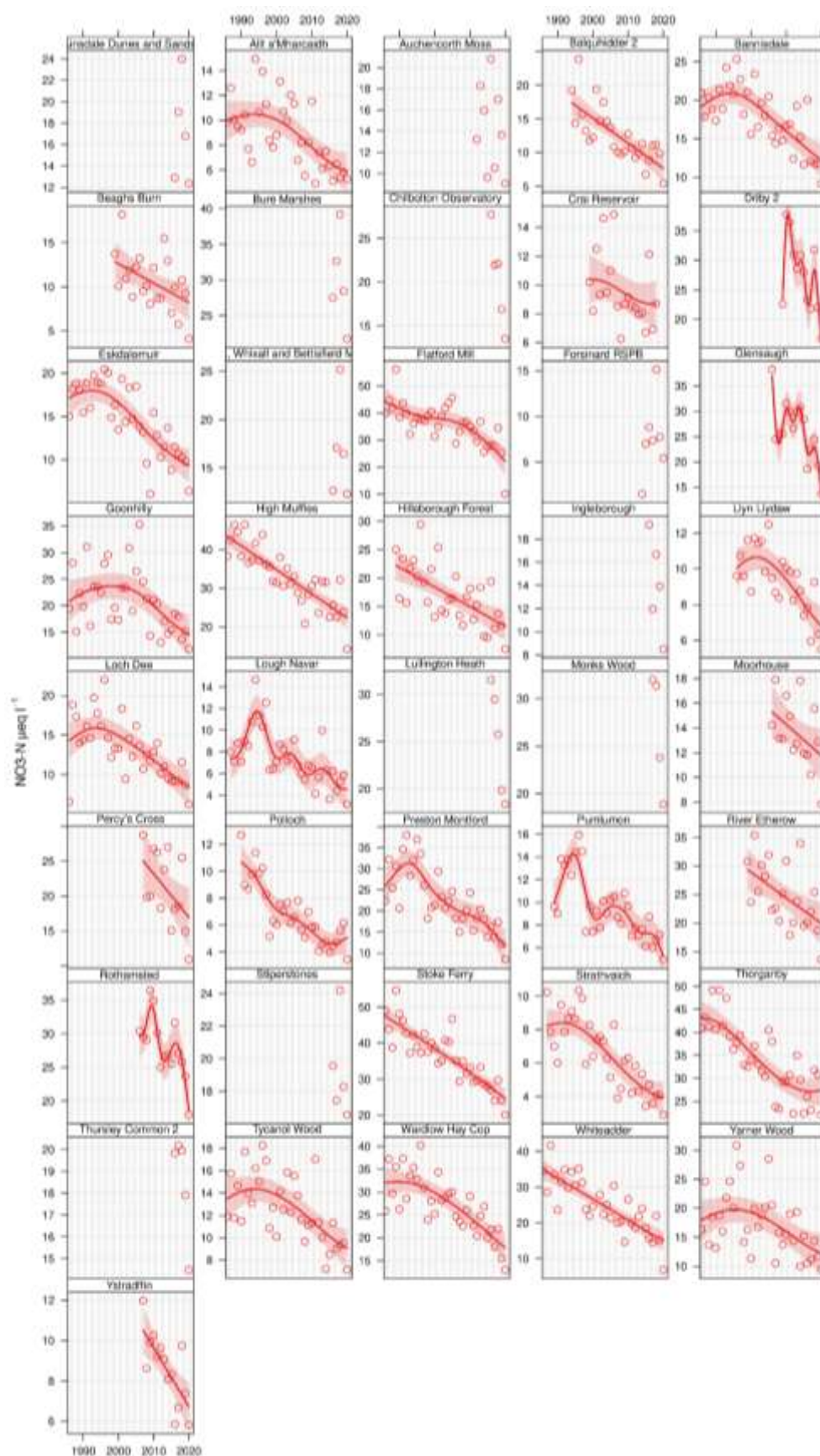


Figure 14 Nitrate concentrations measured at sites with the Precip-Net network since 1986



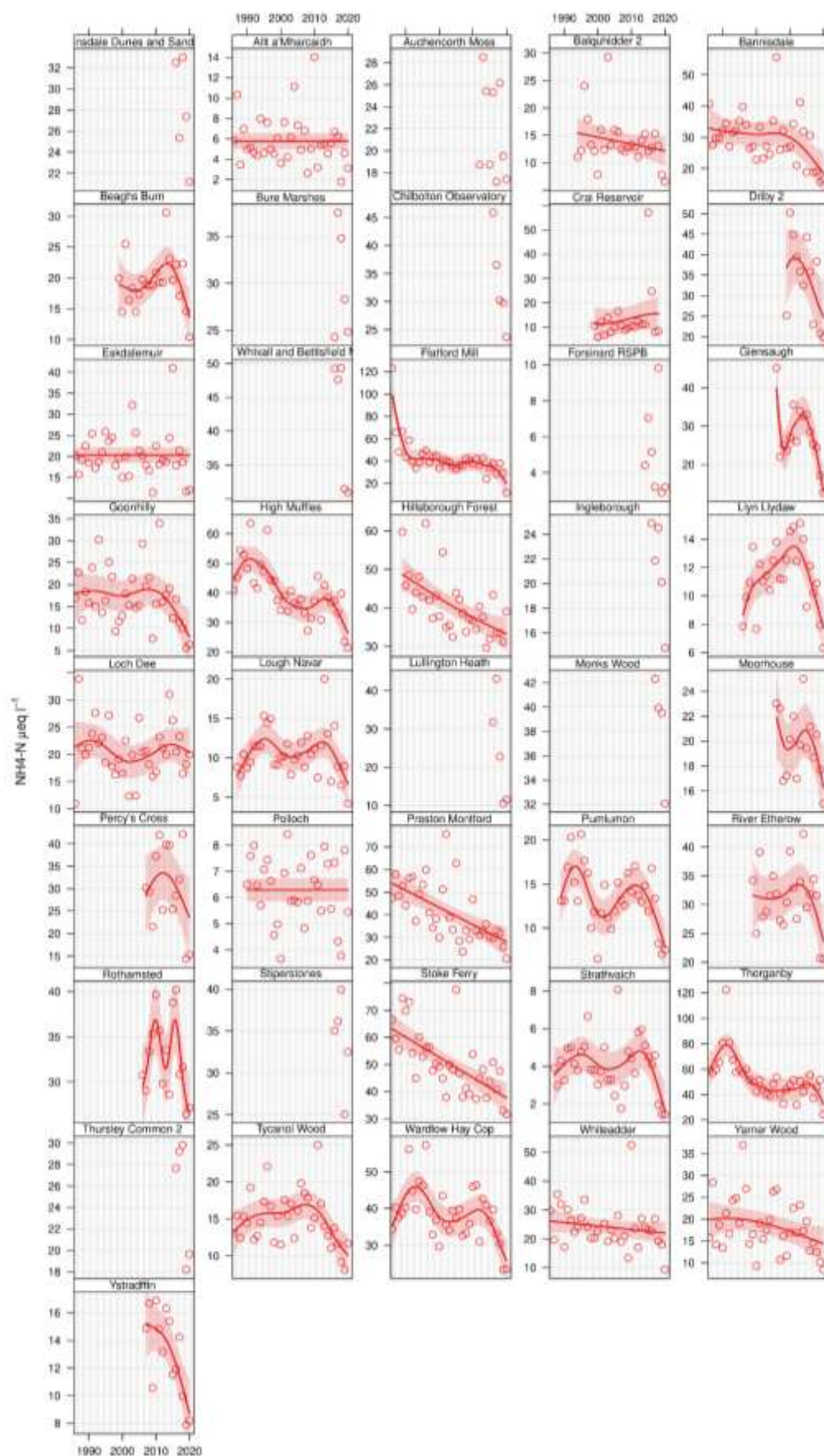


Figure 15 Ammonium concentrations measured at sites with the Precip-Net network since 1986

## 3.2 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. 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 annual average NO<sub>2</sub> measured at each site, together with data capture, are shown in Table 1.

The mean data capture of the diffusion tubes for all of the site in 2020 was 94% with 18 of the 24 sites achieving > 90% and 16 sites achieving 100% data capture. There were various reasons for the lower data capture at Flatford Mill, Llyn Llydaw, Loch Dee, Lullington Heath, Moorhouse and Pumlumon, such as local site operator availability due to the impact of Covid 19 and extended tube exposure leading to data rejection.

**Table 1 2020 NO<sub>2</sub> concentration from the Diffusion Tubes in the NO<sub>2</sub>-Net**

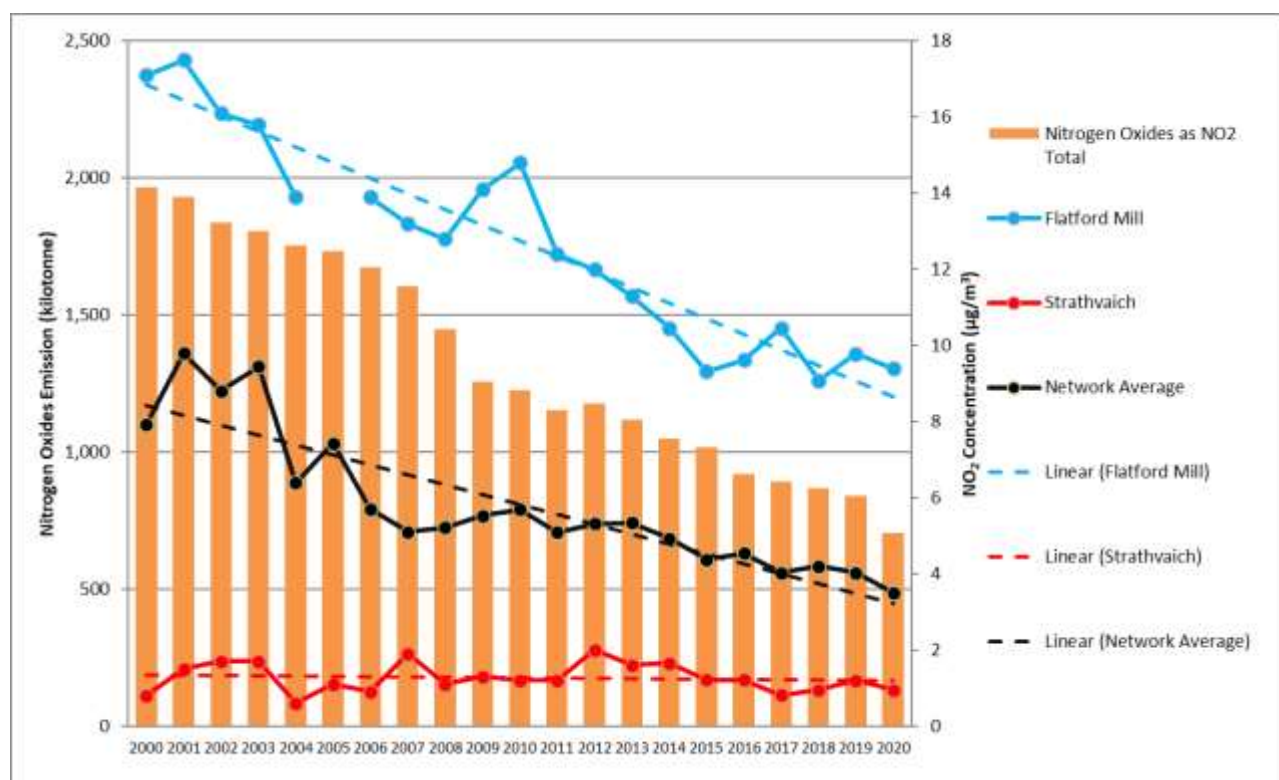
Site Name	Raw 2020 concentration (µg m <sup>-3</sup> )	2020 concentration Bias Corrected (0.811) <sup>1</sup>	Data capture	Site Name	Raw 2020 concentration (µg m <sup>-3</sup> )	2020 concentration Bias Corrected (0.811) <sup>1</sup>	Data capture
Allt a'Mharcaidh	0.75	0.61	100%	Llyn Llydaw	1.88	1.53	86%
Balquhiddier 2	1.86	1.50	98%	Loch Dee	1.93	1.57	68%
Bannisdale	2.64	2.14	93%	Lough Navar	1.88	1.53	100%
Chilbolton Observatory	8.46	6.59	100%	Lullington Heath	8.29	6.72	77%
Driby 2	8.78	7.12	100%	Moorhouse	2.39	1.94	87%
Eskdalemuir	2.05	1.73	100%	Percy's Cross	3.10	2.51	100%
Flatford Mill	9.40	7.62	51%	Polloch	0.96	0.78	100%
Forsinard RSPB	1.38	1.12	100%	Pumlumon	2.17	1.76	85%
Glensaugh	2.49	2.02	100%	Strathvaich	0.95	0.77	100%
Goonhilly	3.72	3.01	100%	Tycanol Wood	2.57	2.08	100%
High Muffles	4.38	3.96	100%	Whiteadder	2.75	2.23	100%
Hillsborough Forest	5.98	4.85	100%	Yarner Wood	3.25	2.88	100%

<sup>1</sup> All sites bias adjusted by 0.811 with the exception of Chilbolton, Eskdalemuir, High Muffles and Yarner Wood which were corrected using co-located samplers, See appendix for details.

Figure 15 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](#)<sup>3</sup>.

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 2010-2020 (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 2020 but the larger decreases being seen at the sites that are closer to the sources of NO<sub>x</sub>. The site at Goonhilly on the Lizard Peninsular, in the far southwest of England, shows relatively stable concentrations.

<sup>3</sup> The emissions for 2020 are projections and were obtained from the workbook: *annex\_iv\_projections\_reporting\_template\_2021\_GB\_v1.0.xls* (available from <https://naei.beis.gov.uk/data/>).

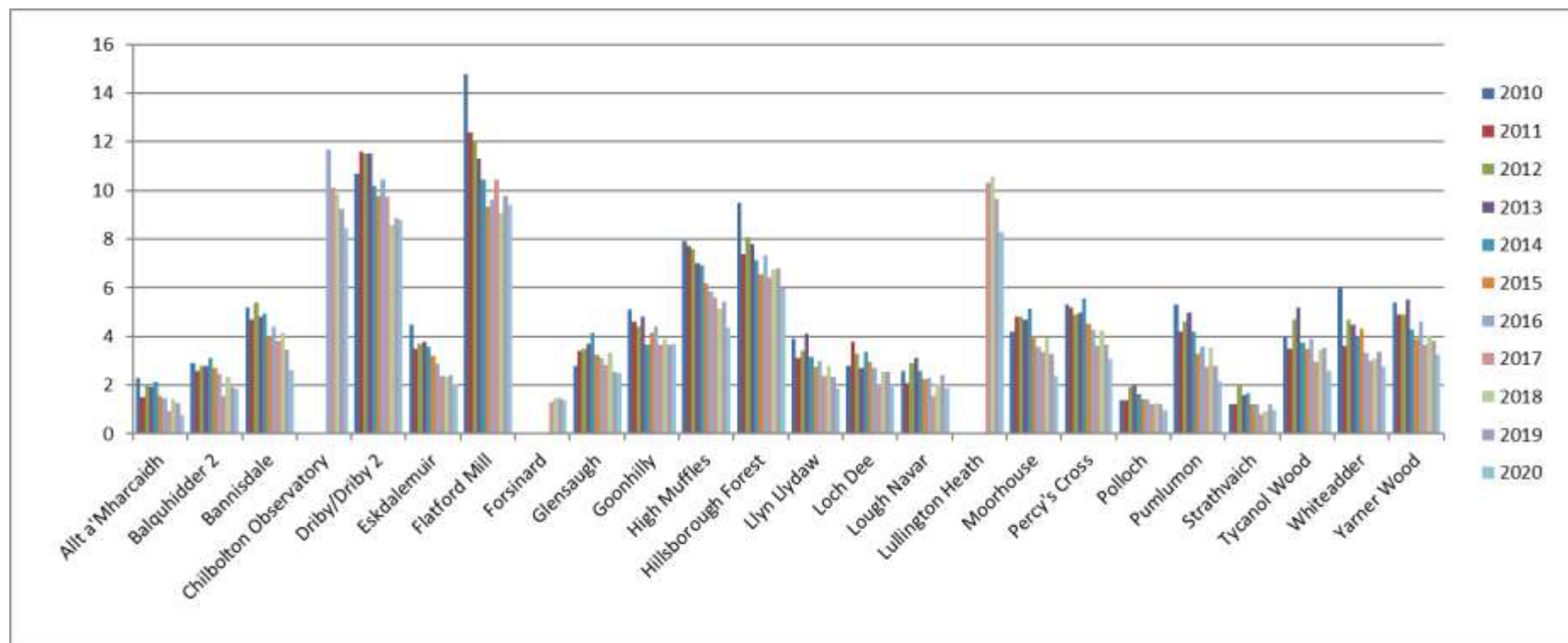


Figure 17 Annual mean NO<sub>2</sub> concentration (µg m<sup>-3</sup>) at the NO<sub>2</sub>-Net sites 2010-2020



### 3.3 National Ammonia Monitoring Network (NAMN)

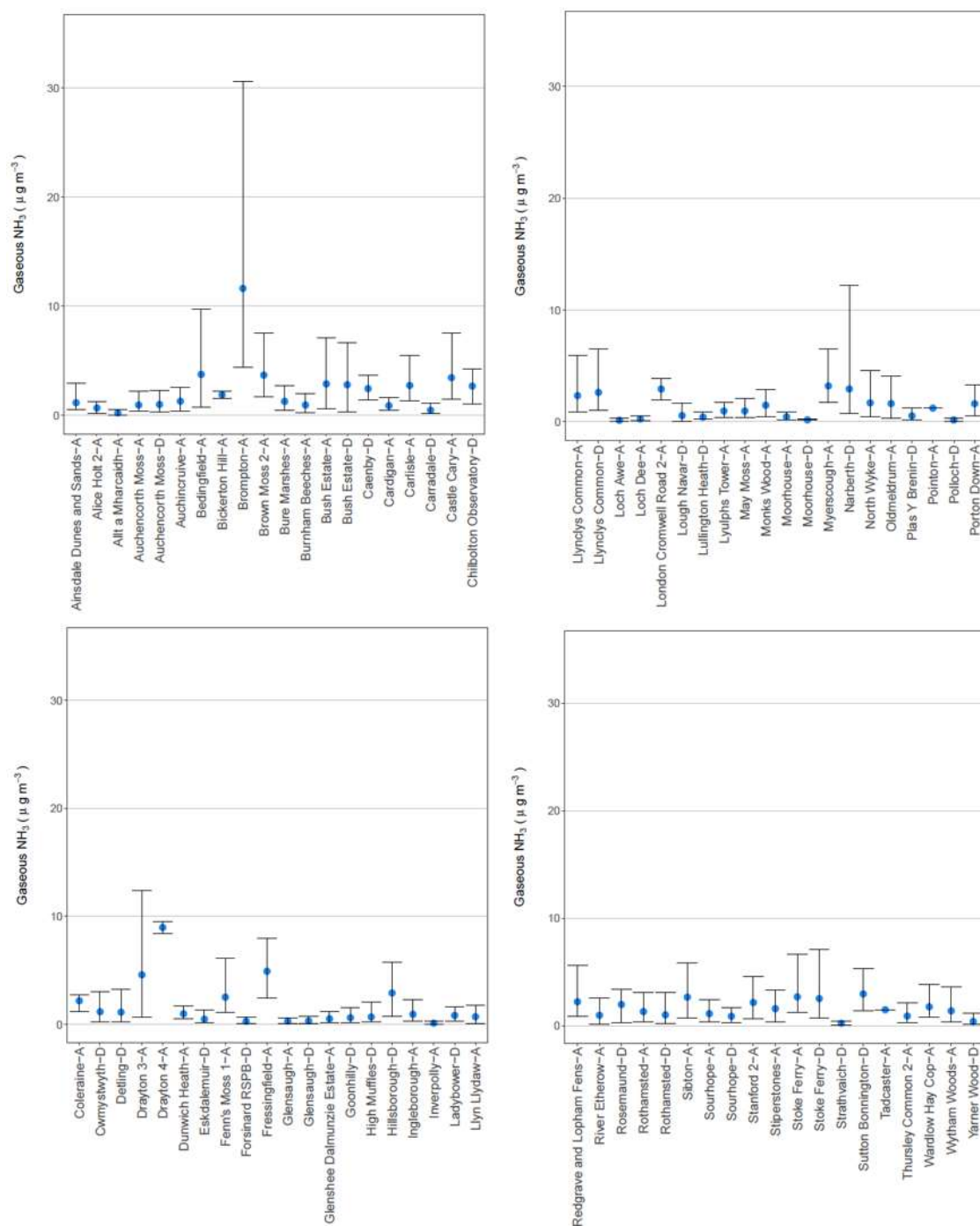
The number of National Ammonia Monitoring Network (NAMN) sites providing monthly measurements of atmospheric  $\text{NH}_3$  in 2020 was 70, summarised in Table 2. The 2020 annual NAMN results are summarised by the average and range of annual  $\text{NH}_3$  concentrations observed at each site in Figure 18. There is high spatial variability in  $\text{NH}_3$  concentrations across the UK and significant seasonal variability. During 2020 average data capture across NAMN was 80%. (QC criteria summarised in the Appendix of this report). The data loss was primarily driven by issues from the COVID-19 pandemic, however the network maintained operations through out. Concentration ranges are similar to previous years which was to be expected given that agriculture operations continued throughout the year.

Historical changes in the annual average  $\text{NH}_3$  concentrations can be seen in Figure 19 with corresponding annual meteorological data also displayed. There is no observable decrease of the NAMN average concentration range and the maxima concentrations are at a similar level to those previously observed.

The spatial variability of the annual average concentrations of  $\text{NH}_3$  and  $\text{NH}_4^+$  across the UK network are presented in Figure 20. For  $\text{NH}_3$ , lower concentrations (shown in green) are primarily located in the north west of costland and some southern coastal sites. Similarly  $\text{NH}_4^+$  concentrations are lowest in N England and Scotland, and highest on the Eastern side of England over the past decade.

**Table 2: Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2020**

Site Type	Number
DELTA sites sampling gaseous $\text{NH}_3$	28
AGANET DELTA sites (sampling gaseous $\text{NH}_3$ , $\text{HNO}_3$ , $\text{SO}_2$ , $\text{HCl}$ & aerosol $\text{NH}_4^+$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{Cl}^-$ , $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ )	26
ALPHA sites sampling gaseous $\text{NH}_3$ only	51
Intercomparison sites with both DELTA & ALPHA	8
Total number of sites	70



**Figure 18: Annual mean concentrations of gaseous  $\text{NH}_3$  in the NAMN. Each data point represents the annually averaged concentrations of monthly measurements made at each site in 2020, whilst the bars show the minimum and maximum concentrations observed (A = ALPHA sampler; D=DELTA)**

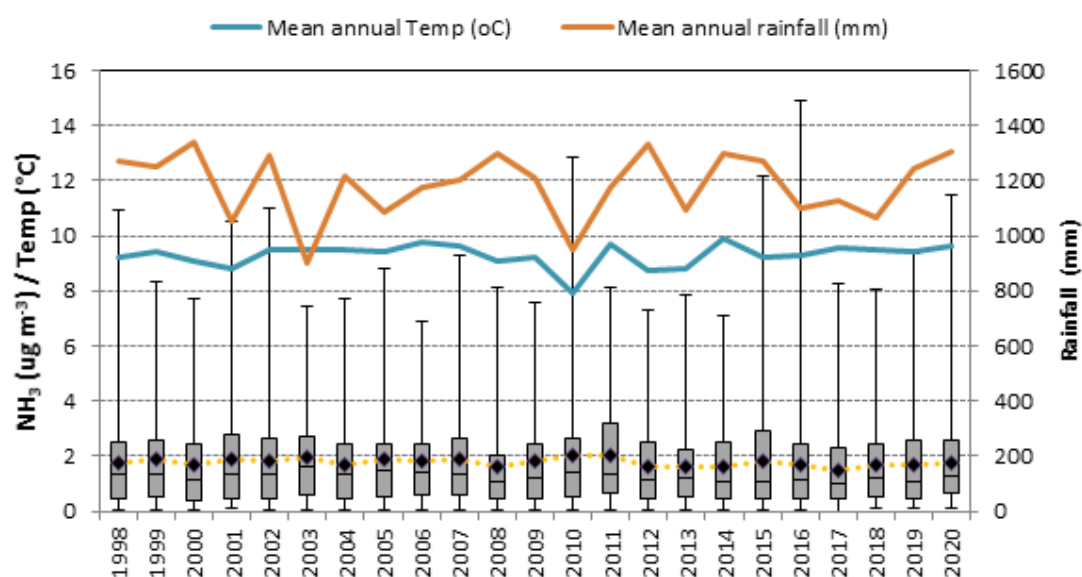


Figure 19: Changes in atmospheric  $\text{NH}_3$  averaged over all sites in NAMN operational between 1998 and 2020 summarised in a box plot. The whiskers show the absolute max and min and the diamond is the mean annual concentration. Annual mean UK meteorological data (source: <https://www.metoffice.gov.uk/research/climate/maps-and-data/summaries/index>) are plotted on top to illustrate the relationship between inter-annual variability in  $\text{NH}_3$  concentrations with changing temperature and rainfall.

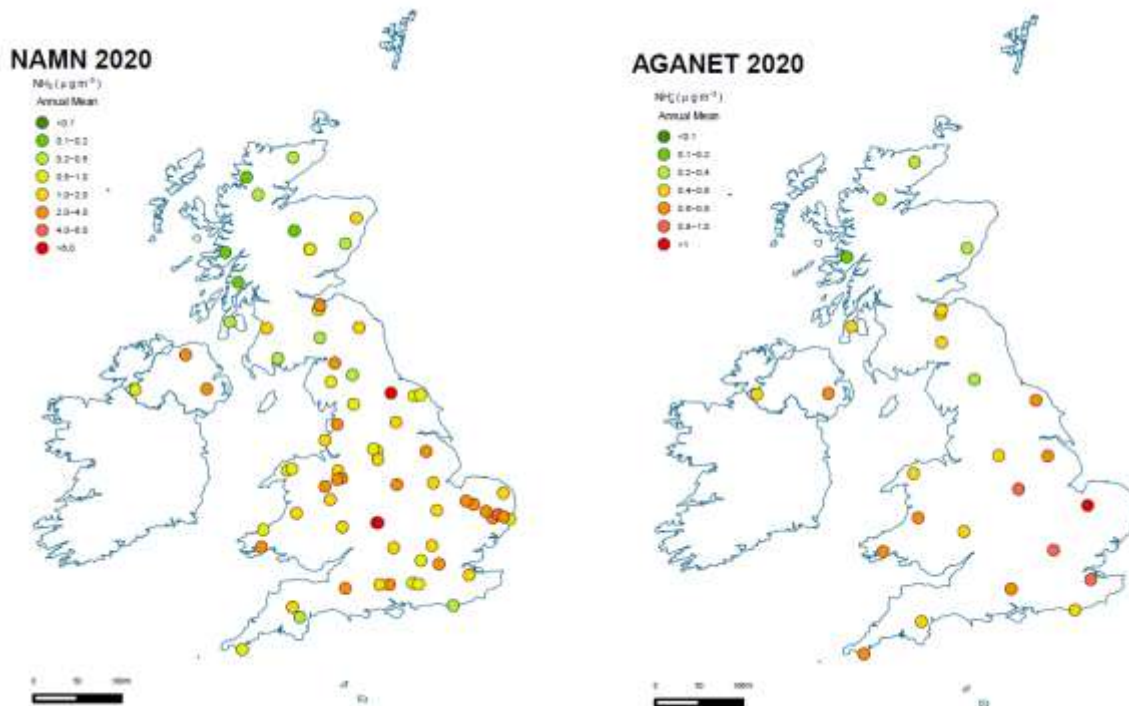


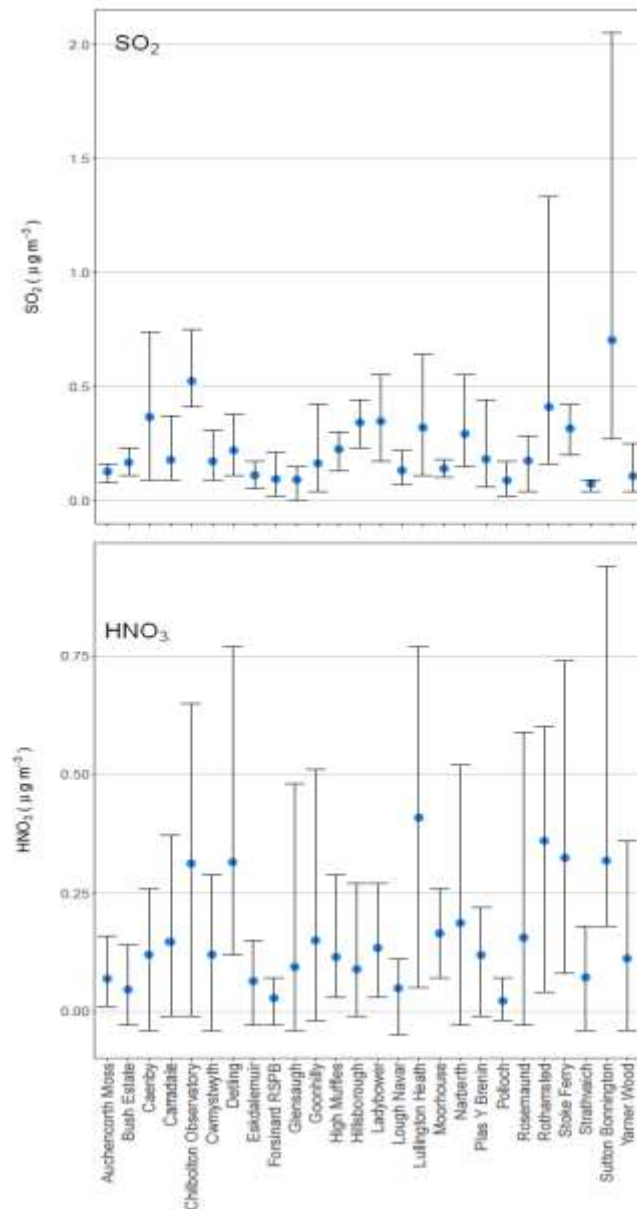
Figure 20: Spatial patterns of annual  $\text{NH}_3$  and aerosol  $\text{NH}_4^+$  concentrations from monthly NAMN/AGANet measurements. Since February 2017, ammonium is measured at the 27 AGANet sites only.

### 3.4 Acid Gas and Aerosol Network (AGANet)

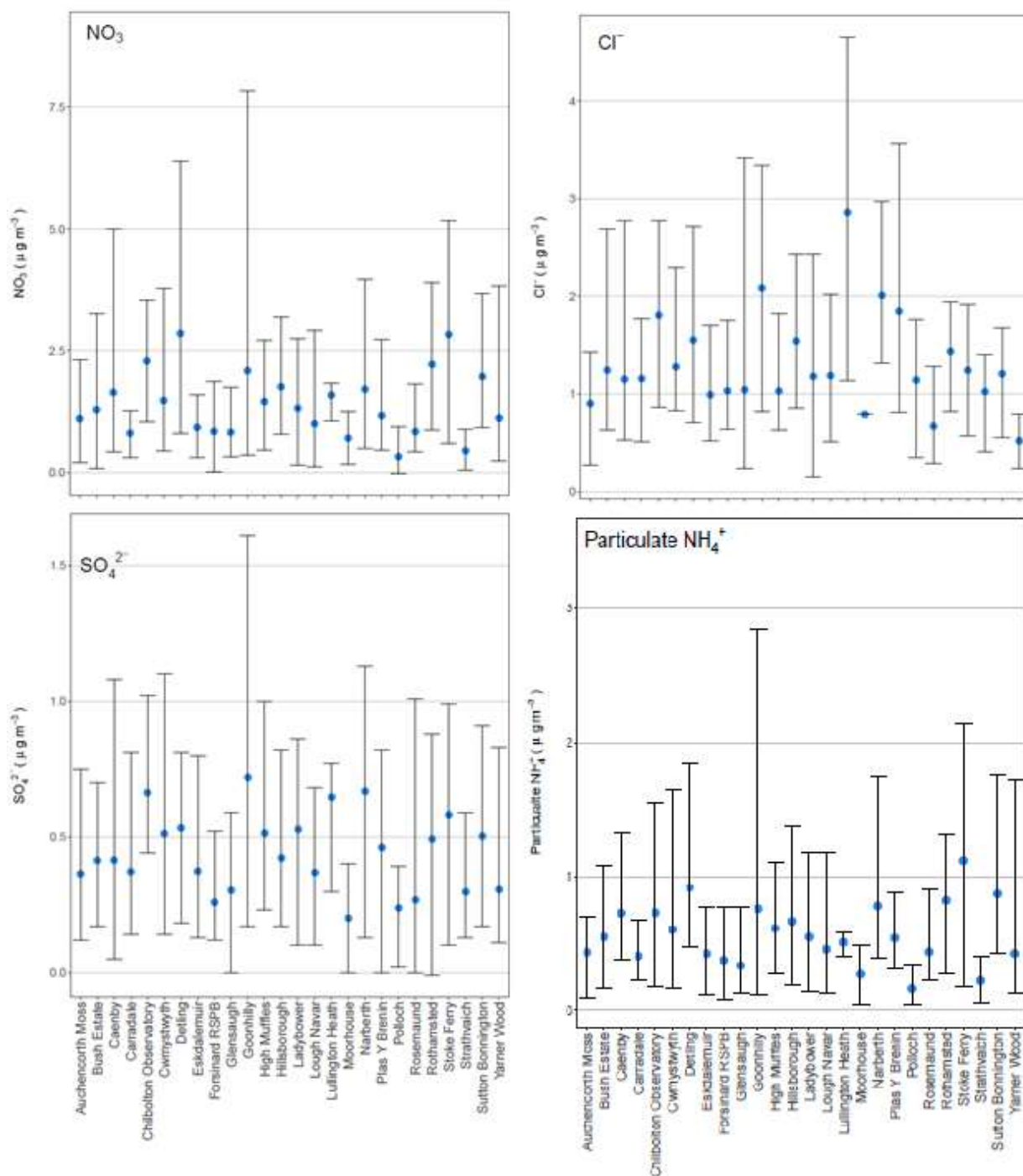
The UK Acid Gas and Aerosol Network (AGANet) provides monthly speciated measurements of atmospheric reactive gases ( $\text{HNO}_3$ ,  $\text{SO}_2$ ) and aerosols ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) at 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.

Figure 21 summarises the  $\text{SO}_2$  and  $\text{HNO}_3$  annual average and maximum and minimum concentrations across AGANet. Concentrations of both pollutants are both  $<1\mu\text{g.m}^{-3}$  across all sites, with the exception of Sutton Bonnington and Rothamsted for  $\text{SO}_2$ . Figure 24 shows the maps of annual average concentrations and it can be seen that the  $\text{HNO}_3$  concentrations are significantly higher in the south east quarter of the UK, with the lowest concentration in the north of the UK (Scotland and Northern Ireland sites). A similar pattern is seen for  $\text{SO}_2$  where as for  $\text{NH}_3$  the concentrations are higher up into southern Scotland and in N Ireland reflecting the wider geographical extent of agricultural activity. Figure 22 and Figure 23 report the annual average and maximum and minimum concentrations for the particulate chemical components. The  $\text{NH}_4$ ,  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations are not highly variable between sites that is due to the secondary formation mechanism of the salts. However, the spatial increase in SE quarter of the UK similar to the gases can still be seen for  $\text{NO}_3^-$  where as  $\text{SO}_4^{2-}$  has slight enhancement in coastal areas of England (Figure 25). There is a slightly wider variability of Na and Cl concentrations reflecting the primary source of NaCl being sea salt and the coastal sites e.g. Lullington Heath and Goonhilly (Figure 25 and Figure 26). The base cations  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  are present at low concentrations however are slightly higher across England and Wales. However interannual and spatial variability is high with these very low concentrations.

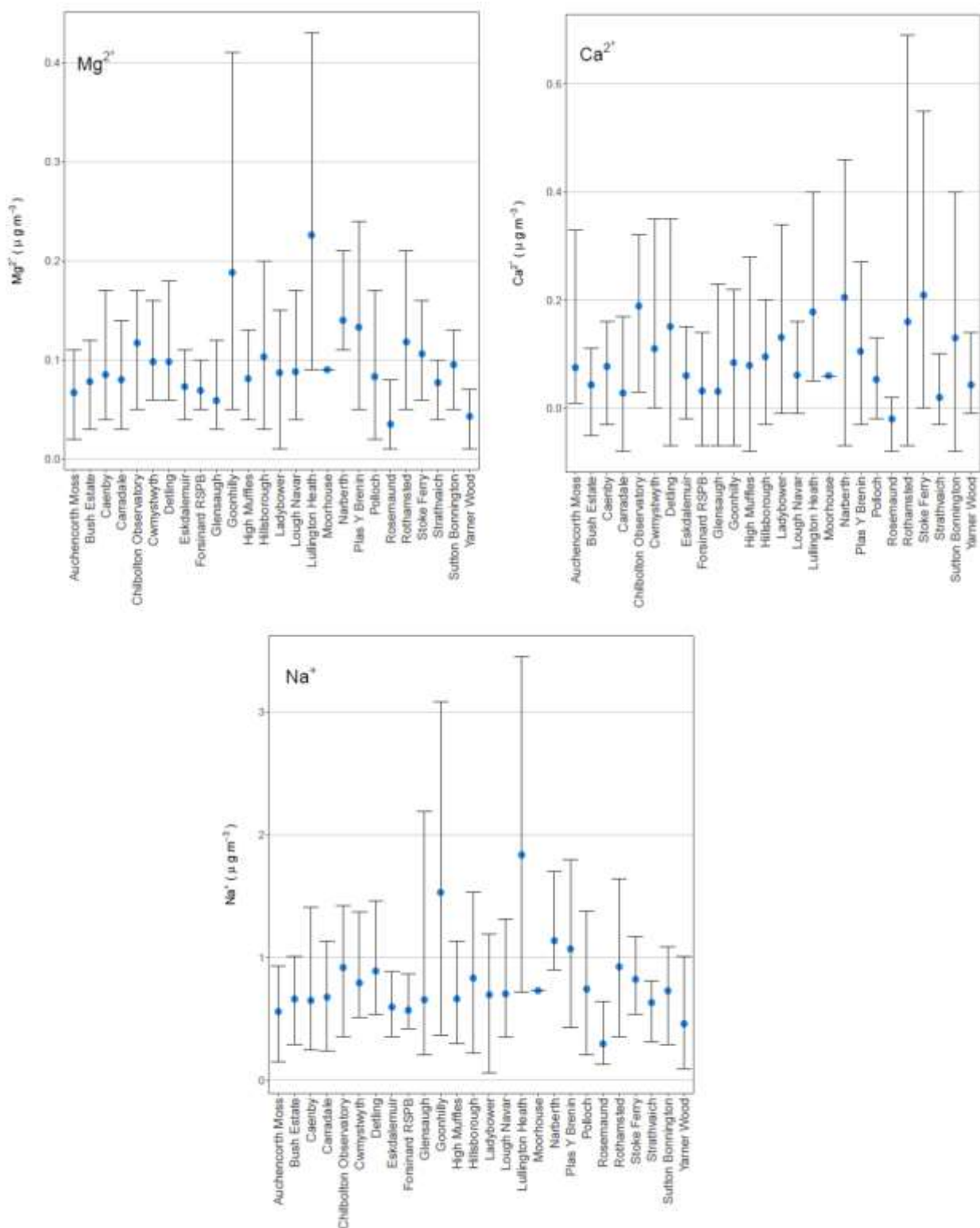
The long-term network average concentration trends are shown in Figure 27 for AGANet gas and aerosol chemical components.  $\text{HNO}_3$ ,  $\text{SO}_2$  and  $\text{NH}_3$  concentrations have been relatively constant over the past 4 years.  $\text{NH}_3$  has been within variability constant for the past two decade whereas  $\text{SO}_2$  and  $\text{HNO}_3$  had decrease over this time period. Particulate  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$  had a clear step change increase in 2016 with the method change increasing quantitative capture of the components (detailed in previous reports), however since this change a similar interannual variability is qualitatively observed with concentrations relatively stable within  $\pm 0.5\mu\text{g.m}^{-3}$  in the past 5 years for all components. Figure 28 summarises the annual seasonal cycle of AGANet and NAMN measurements, comparing the 2020 data to the mean seasonal profile. It can be seen that the  $\text{NH}_3$ ,  $\text{NH}_4^+$ ,  $\text{SO}_2$  and  $\text{SO}_4^{2-}$  follow a similar seasonal concentration cycle to the long term profile. However it is noted that the  $\text{NH}_3$  concentrations are at or above the +1SD of the long term average, particularly in the Mar-May months, indicating 2020 had a significantly high  $\text{NH}_3$  concentration across the UK in 2020.



**Figure 21: Mean monitored annual concentrations of gaseous HNO<sub>3</sub> and SO<sub>2</sub> at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2020, whilst the bars show the minimum and maximum concentrations observed**



**Figure 22: Mean monitored annual concentrations of particulate NO<sub>3</sub><sup>-</sup>, 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 2020, whilst the bars show the minimum and maximum concentrations observed**



**Figure 23: Mean monitored annual concentrations of particulate  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Na^+$  at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2020, whilst the bars show the minimum and maximum concentrations**



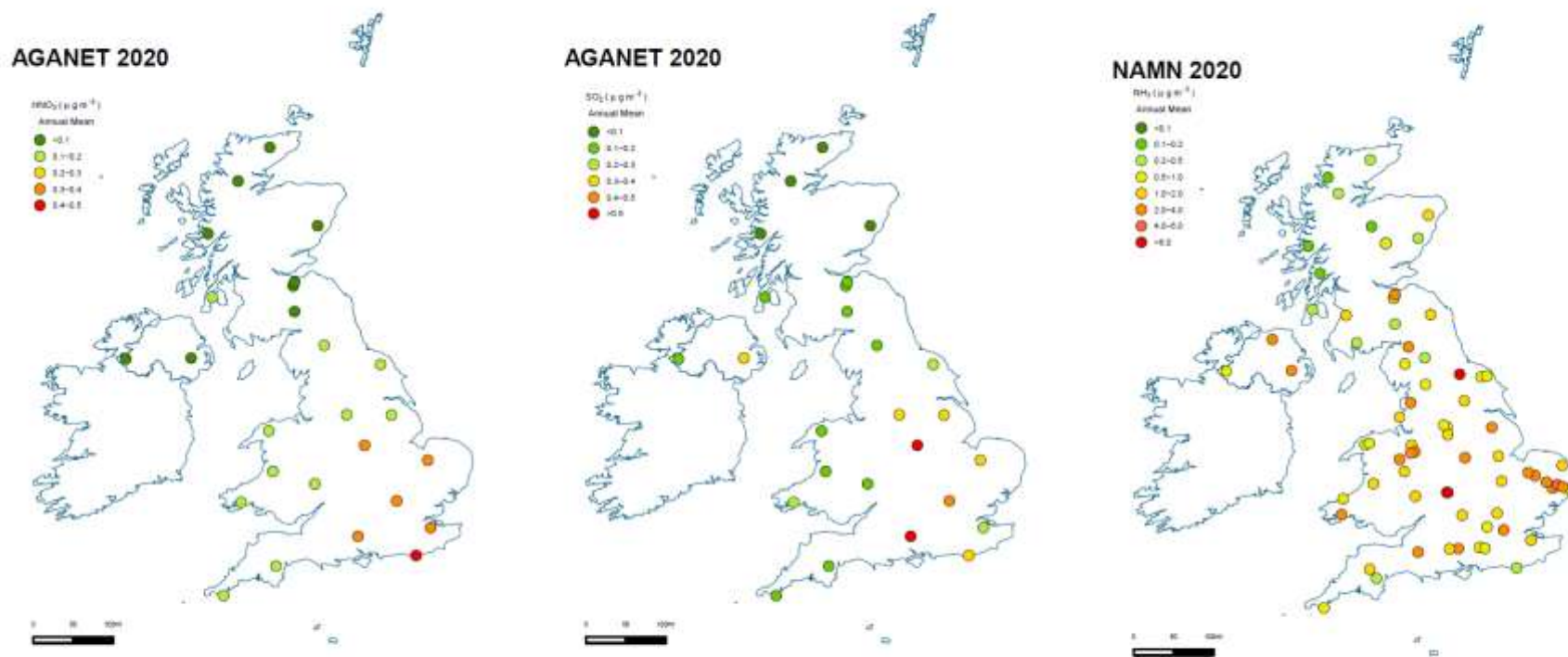


Figure 24: Annual mean monitored atmospheric reactive gas concentrations ( $\text{HNO}_3$  and  $\text{SO}_2$  from AGANET and  $\text{NH}_3$  from NAMN) across the UK from annual averaged monthly measurements made in 2020.

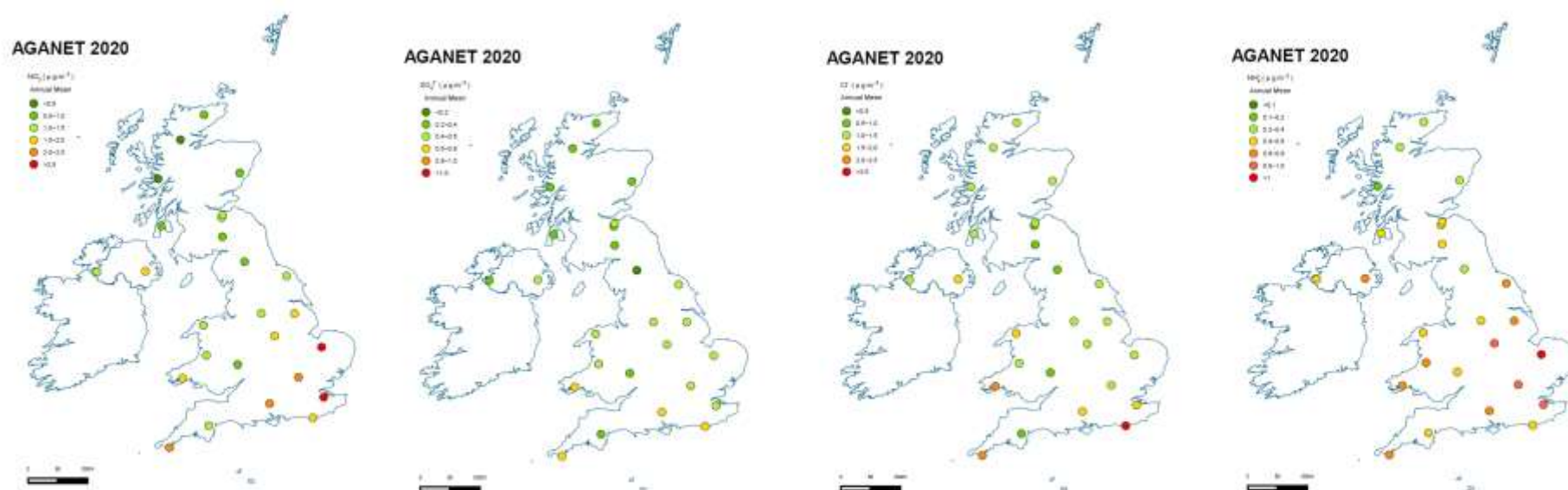


Figure 25: Annual mean monitored atmospheric aerosols (particulate  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{Cl}^-$  from AGANET and  $\text{NH}_4^+$  from NAMN) concentrations across the UK from averaged monthly measurements made in 2020.

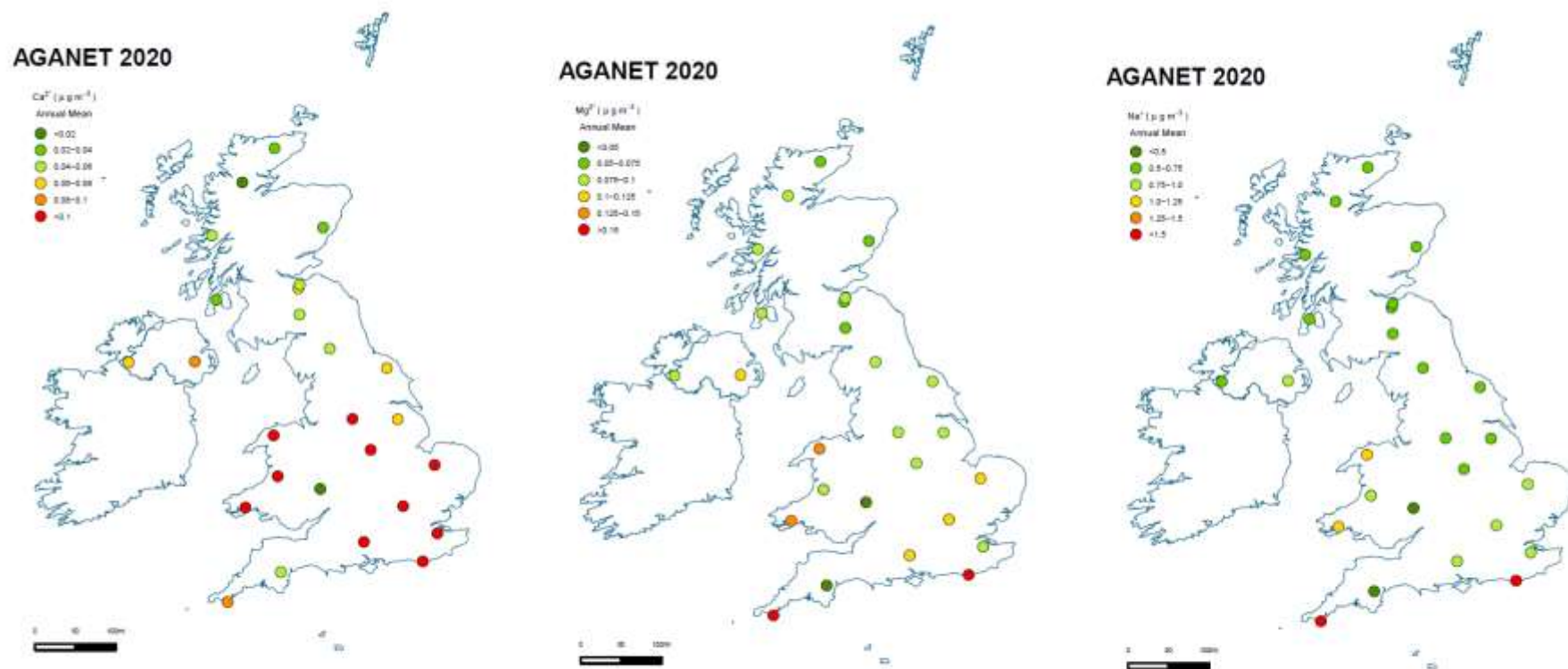
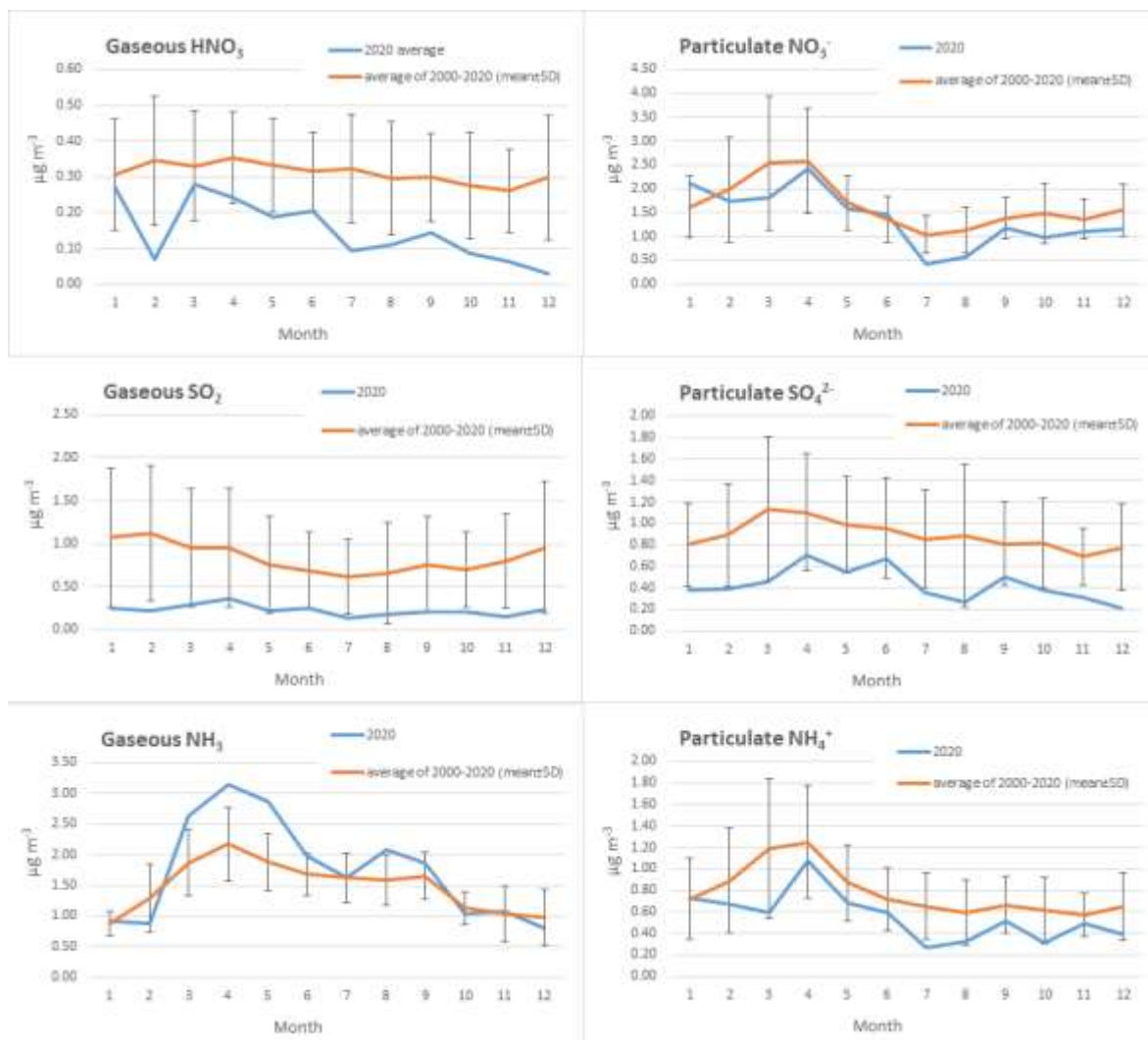


Figure 26: Annual mean monitored atmospheric base cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^{+}$ ) concentrations across the UK from the averaged monthly measurements made in 2020.



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 12 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 (2000-2020: mean  $\pm$  SD of 27 AGANET sites) against year 2020.**



### 3.5 UK EMEP Supersites 2020 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 was required under Annex IV of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe, which is assumed to be transposed into UK law. 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, assumed to have been transposed to UK law following EU exit, 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 2020. 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 2020**

Pollutant	CHO <sup>1</sup>	AUC <sup>1</sup>	EMEP Level	Averaging period	Monitoring network (CHO/AUC)	Contract holder
SO <sub>2</sub> , HCl, HNO <sub>3</sub> , HONO, NH <sub>3</sub> (MARGA)	X	X	II	Hourly	UKEAP	UKCEH/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	UKCEH/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	UKCEH/Ricardo E&E
Elemental mercury		X	III	Hourly	UKEAP	UKCEH/Ricardo E&E
Total Particulate mercury		X	III	Hourly	UKEAP	UKCEH/Ricardo E&E
Total gaseous mercury (TGM) in air	X	X	II	Hourly	UKEAP	UKCEH/Ricardo E&E
Meteorological parameters (WS, WD, T, RH, rainfall)	X	X <sup>2</sup>	I	Hourly	UKEAP/UKCEH	UKCEH/Ricardo E&E
Precipitation chemistry	X	X	I	Daily	UKEAP	UKCEH/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/UKCEH	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	Ricardo E&E
Black carbon	X	X	II	Hourly	Particle numbers	NPL
Particle counts (>7 nm)	X	X <sup>2</sup>	II	Hourly	Particle numbers/UKCEH	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	NPL
<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	UKCEH
<b>Trace gases (HCl, HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub>)</b>	X	X	I	Monthly	UKEAP	UKCEH
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	UKCEH
Persistent Organic Pollutants (POPs) in air	X	X	I	Monthly	TOMPS	University of Lancaster
CO <sub>2</sub> measurements		X	III	Hourly	ICOS	UKCEH
Trace gas fluxes (O <sub>3</sub> ,)		X	III	Hourly	NERC NC <sup>2</sup>	UKCEH
NO and NO <sub>2</sub> (photolytic)		x	I	Hourly	NERC NC <sup>2</sup>	UKCEH

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

In 2020 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 infrastructures 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 following Figures. At Auchencorth Moss there was low data capture in July 2020 due to a faulty valve for the internal standard which was replaced.

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

- In January, the degasser pump failed and a new one was installed on the 11<sup>th</sup> March 2020.
- The cation pump failed on the 11<sup>th</sup> September 2020 and a new one was fitted on the 7<sup>th</sup> October 2020.
- In November, the SJAC heater blocked and a new was installed in February 2021.
- Part supply and an engineer support was affected by Covid-19 and EU exit.

**Table 4 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 <sub>10</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>	1.047	52.84	0.348	79.24
Na <sup>+</sup>	0.635	52.24	0.468	79.24
K <sup>+</sup>	0.047	52.31	0.026	79.24
Ca <sup>2+</sup>	0.441	47.02	0.034	79.08
Mg <sup>2+</sup>	0.247	46.90	0.056	79.24
Cl <sup>-</sup>	1.371	52.35	0.877	78.19
NO <sub>3</sub> <sup>-</sup>	3.013	52.53	0.735	78.19
SO <sub>4</sub> <sup>2-</sup>	1.370	51.06	0.557	78.19
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>	0.984	51.92	0.311	80.77
Na <sup>+</sup>	0.300	52.23	0.283	80.82
K <sup>+</sup>	0.037	52.28	0.018	80.82
Ca <sup>2+</sup>	0.073	46.93	0.017	80.66
Mg <sup>2+</sup>	0.118	51.37	0.032	80.82
Cl <sup>-</sup>	0.702	51.70	0.520	79.75
NO <sub>3</sub> <sup>-</sup>	2.404	52.21	0.608	79.75
SO <sub>4</sub> <sup>2-</sup>	1.137	50.71	0.474	79.75
Trace Gases	Annual mean (µg m <sup>-3</sup> )	Data capture (%)	Annual mean (µg m <sup>-3</sup> )	Data capture (%)
NH <sub>3</sub>	4.930	55.08	1.204	85.09
HCl	0.028	55.70	0.093	84.06
HNO <sub>3</sub>	0.141	55.28	0.063	84.06
HONO	0.467	55.18	0.063	84.06
SO <sub>2</sub>	0.093	53.71	0.047	79.32



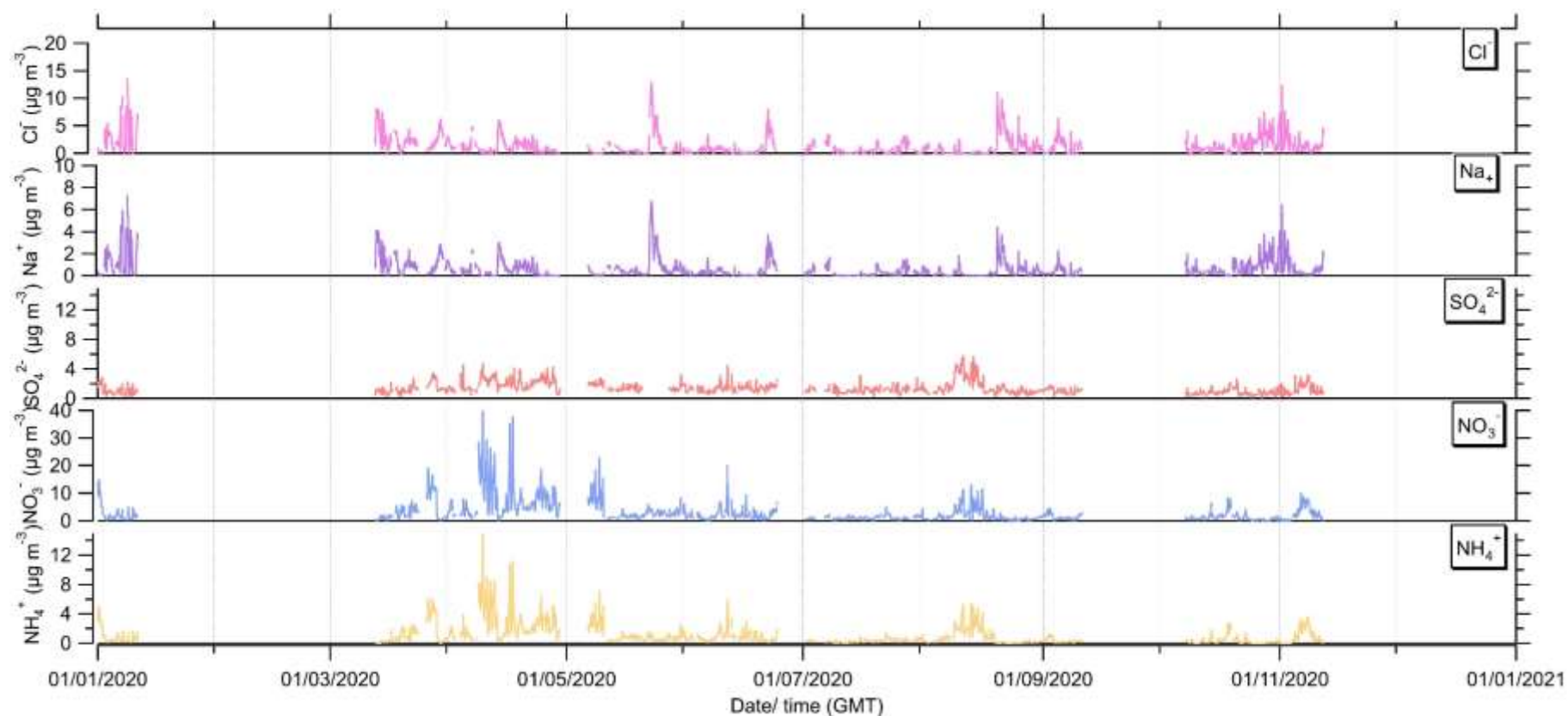


Figure 29 Ratified PM<sub>10</sub> speciated measurements by the MARGA at the Chilbolton supersite

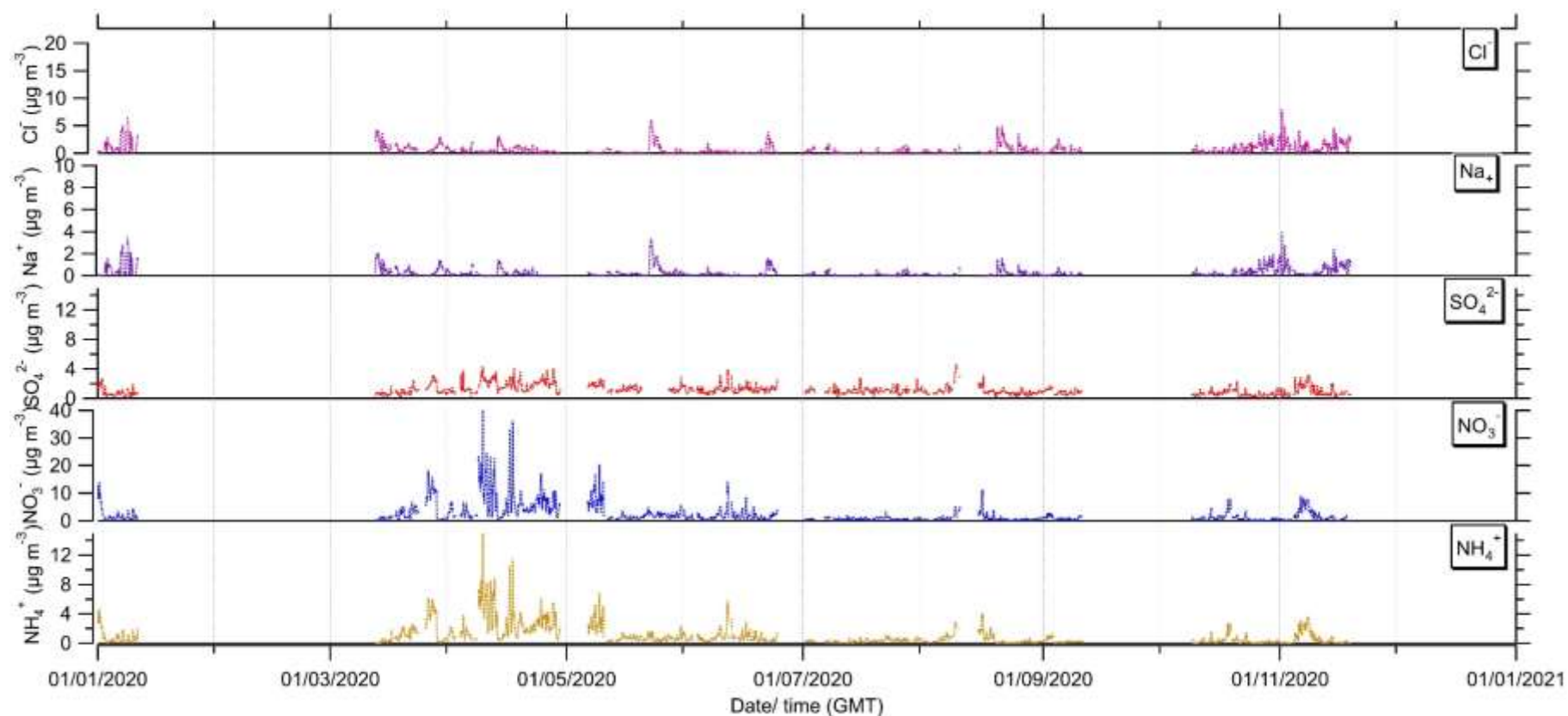


Figure 30 Ratified PM<sub>2.5</sub> speciated measurements by the MARGA at the Chilbolton supersite

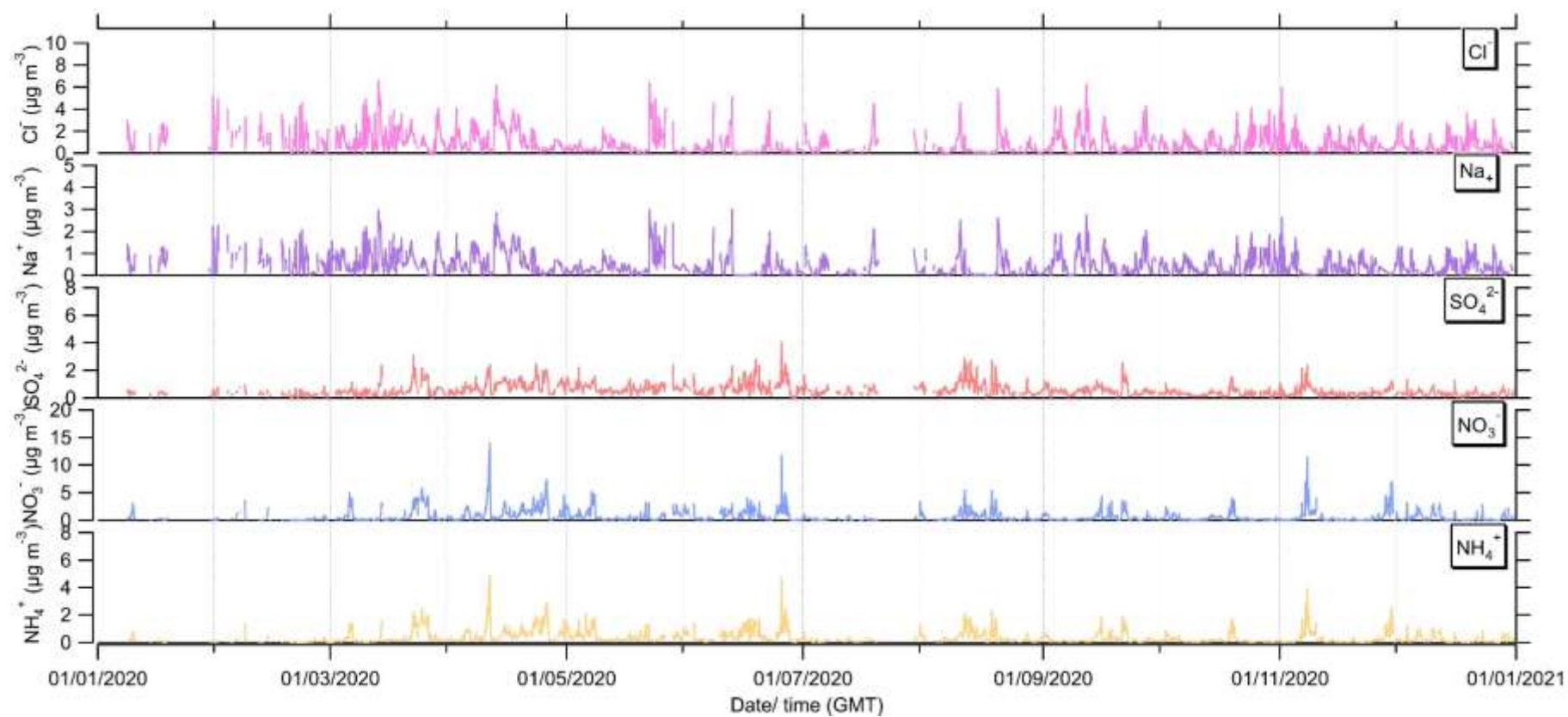


Figure 31 Ratified PM<sub>10</sub> speciated measurements by the MARGA at the Auchencorth Moss supersite

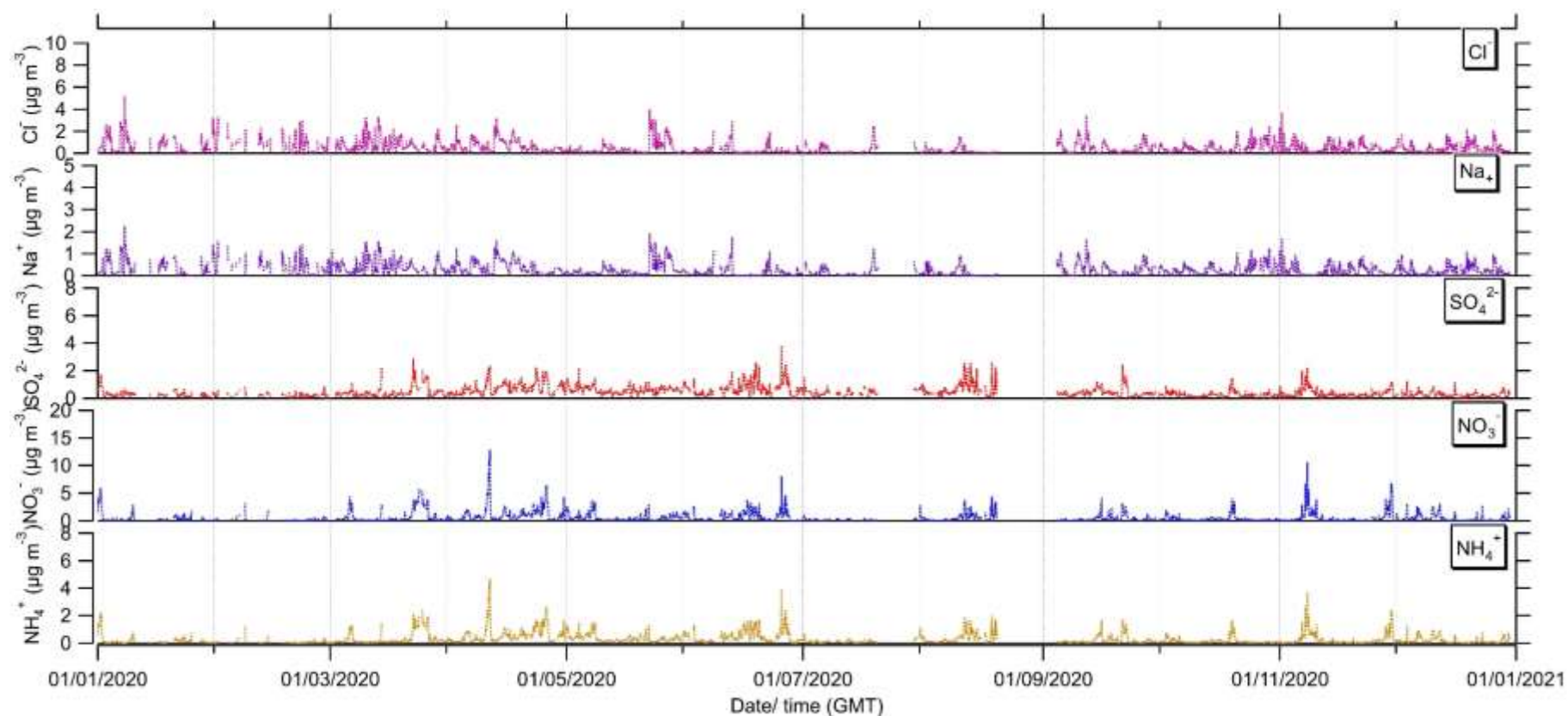


Figure 32 Ratified PM<sub>2.5</sub> speciated measurements by the MARGA at the Auchencorth Moss supersite

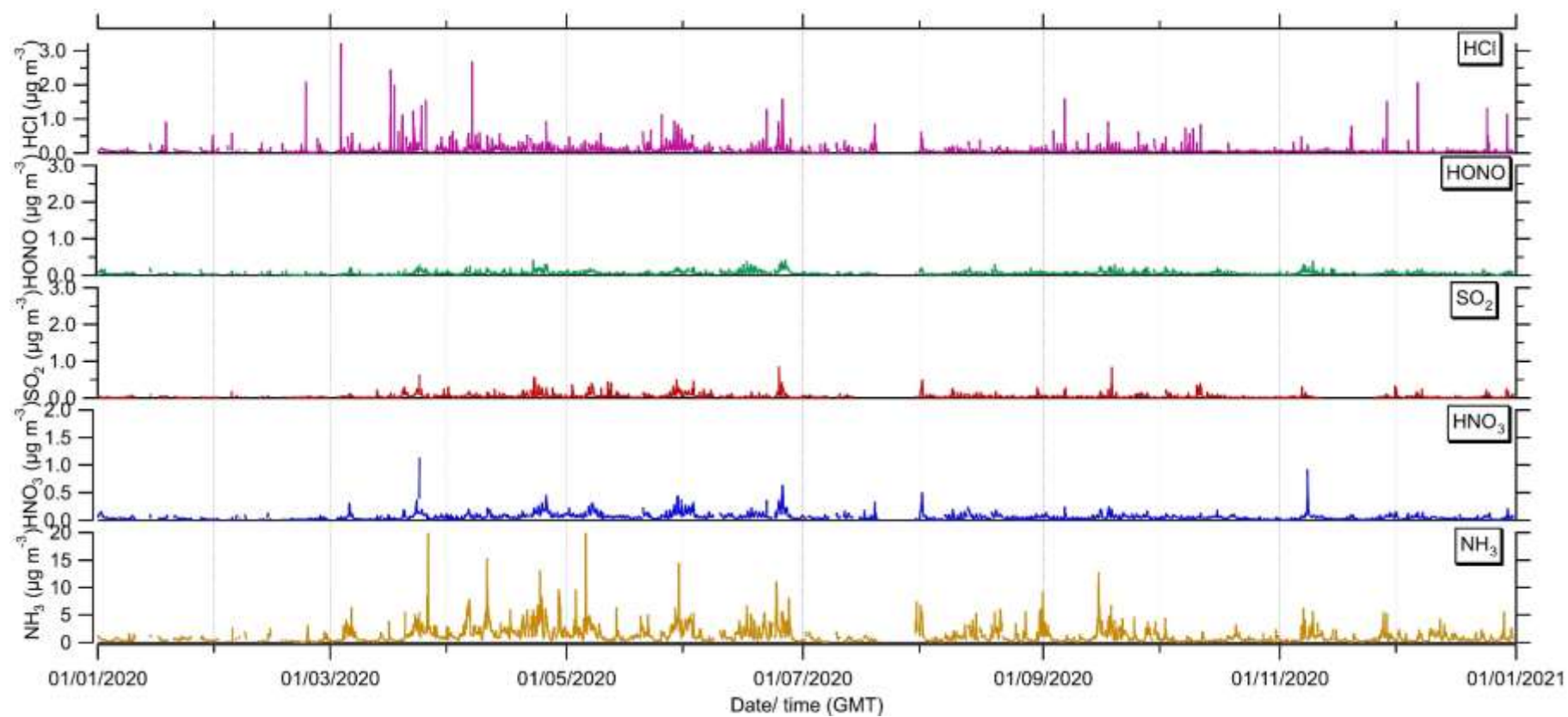


Figure 33 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite

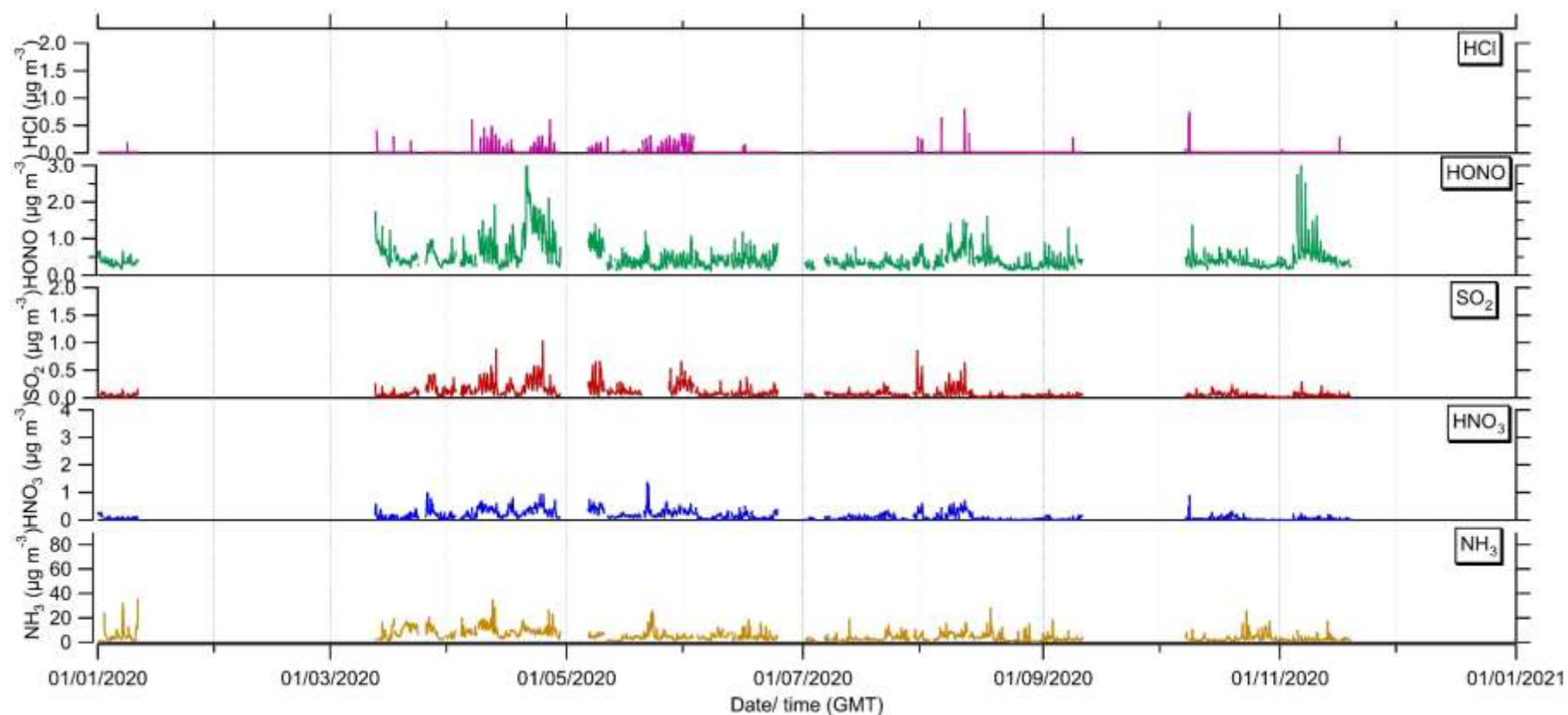


Figure 34 Ratified trace gas measurements by the MARGA at the Chilbolton supersite



## Mercury Measurements

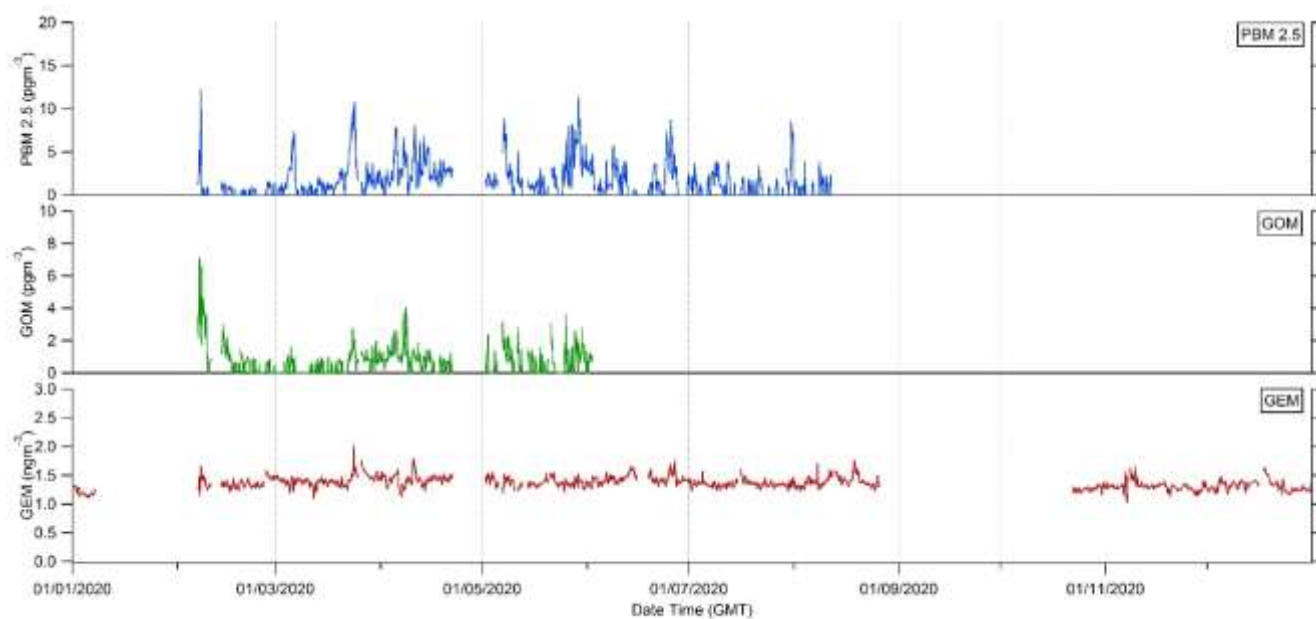
The annual means and data capture for the 2020 ratified mercury measurements are shown below in Table 5. Time series plots of the 2020 Auchencorth Moss measurements are shown in Figure 35. At the beginning of the year the system suffered with unstable flow issues. This led to contamination issues later in the year and the rejection of some of the speciated data. This was because the unit at its end of life. It was replaced in 2021.

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. The instrument was removed in January 2020 from Chilbolton to undergo repairs.

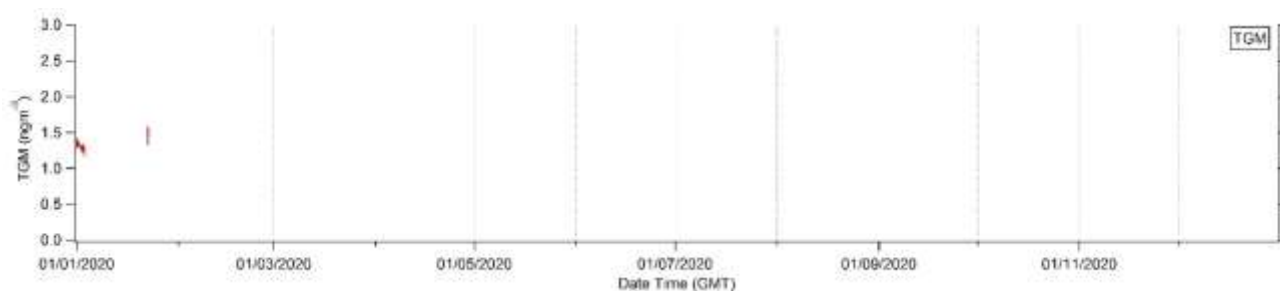
**Table 5 Ratified mercury measurements**

	<b>Annual Mean</b>	<b>Data Capture (%)</b>
<b>Auchencorth Moss</b>		
Gaseous Elemental Hg (GEM) ng m <sup>-3</sup>	1.362	66.08
Gaseous Oxidised Hg (GOM) pg m <sup>-3</sup>	0.800	41.99
Particulate bound Hg (PM <sub>2.5</sub> ) pg m <sup>-3</sup>	1.720	25.03
<b>Chilbolton</b>		
Total Gaseous Hg (TGM) ng m <sup>-3</sup>	1.332	0.75





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



**Figure 36 Ratified mercury measurements by the Tekran at Chilbolton Observatory**

## 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

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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=uheap>, Data downloaded/received (*insert date of data receipt*))

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**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=uheap>, 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, 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=uheap>, Data downloaded/received (*insert date of data receipt*))

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**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=uheap>, Data downloaded/received (*insert date of data receipt*))

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## Acid Gas and Aerosol Network (AGANet)

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**Contact:** *Dr Christine Braban 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. UKEAP (UK Eutrophying and Acidifying Atmospheric Pollutants) 2020 dataset: Acid Gas and Aerosol Network (AGANet). April 2021, <https://uk-air.defra.gov.uk/data/>

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## National Ammonia Monitoring Network (NAMN)

**Contact:** *Dr Christine Braban 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. UKEAP (UK Eutrophying and Acidifying Atmospheric Pollutants) 2020 dataset: National Ammonia Monitoring Network (NAMN). April 2021, <https://uk-air.defra.gov.uk/data/>

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## Precipitation Network (Precip-Net)

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

## Appendix 2: QC summary for 2020

### 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 2020. 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 2020.

During 2020 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  $PM_{10}$  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 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  $PM_{10}$  and  $PM_{2.5}$ . It also provides a measure of the concentration of water-soluble trace acid gases (HCl, HONO,  $HNO_3$ ,  $NH_3$ , and  $SO_2$ ) in the sampled air. The MARGA 2S consists of two units or “boxes”, both identical; one for the sampling and entrainment of the  $PM_{10}$  particulate and gas-phase species, the other for  $PM_{2.5}$ . 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  $PM_{10}$  size-selective inlet head at a nominal flow rate of  $2\text{ m}^3\text{ hr}^{-1}$  ( $1\text{ m}^3\text{ hr}^{-1}$  per box). The  $PM_{2.5}$  fraction is separated from the sampled  $PM_{10}$  by means of a cyclone separator fitted at the inlet to the  $PM_{2.5}$  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  $120^\circ\text{C}$ ) 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  $PM_{10}$  and  $PM_{2.5}$  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 Chilton 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  $\text{Li}^+$  and  $\text{Br}^-$ , 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  $1 \text{ m}^3/\text{hr}$ . 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	

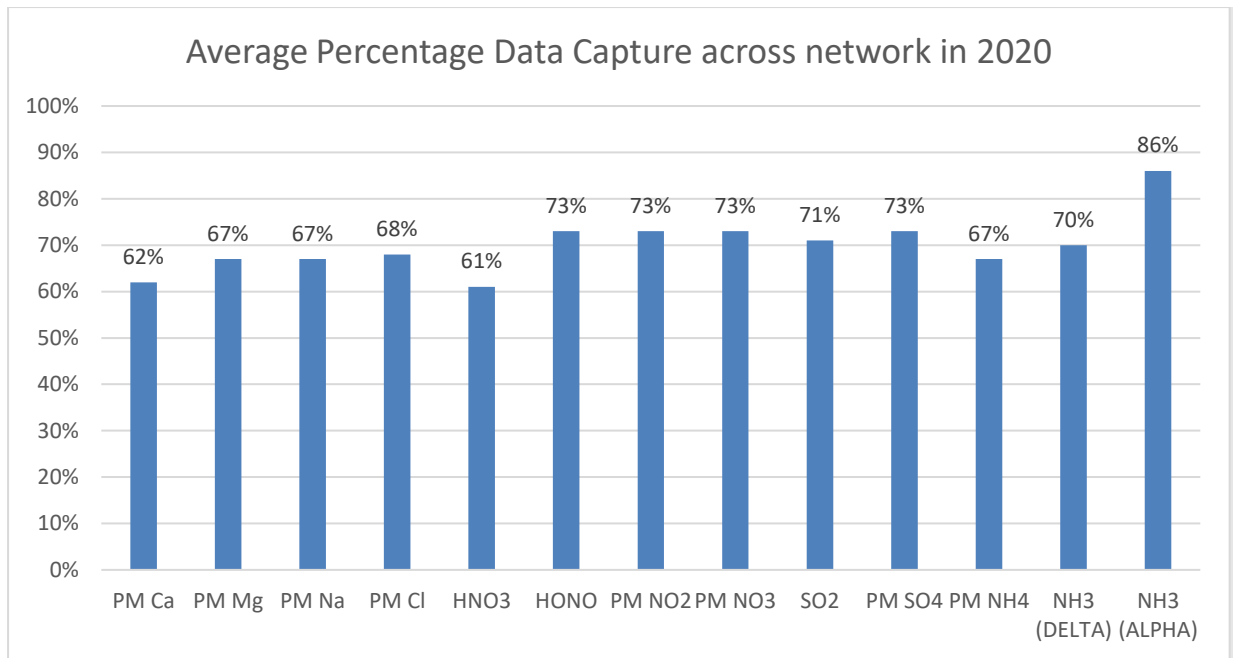
2x clean SJAC in 1% H <sub>2</sub> O <sub>2</sub> for 10 minute in an ultrasonic bath **							x		
2x clean WRD **							x		
clean or change all Teflon tubing 1/16" boxes**								x	
2x change guard column: 1 anion, 1 cation (+filters if dirty)			x						
1x change anion IC column if necessary ****				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

## 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 37 below contains the average percentage data capture across all sites for each chemical of interest. Average data capture was 69 % for AGANet and 80% for NAMN.





**Figure 37: 2020 NAMN and AGANet percentage data capture by chemical component**

### COVID-19 Impacts

16% of data capture losses on AGANET and NAMN in 2020 were directly or indirectly related to the COVID-19 pandemic. Examples of reasons for data losses included:

- Inability of local site operators to make changes
- Samplers lost in post as receiving offices were closed due to the national lockdowns
- Inability or delays to unscheduled engineer visits due to access permissions or lockdown prohibiting travel
- Saturation of samplers exposed for extended periods
- Delays in receiving parts for repairs as suppliers faced delays

### 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 uptake rate is shown in Figure 38. 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 39.

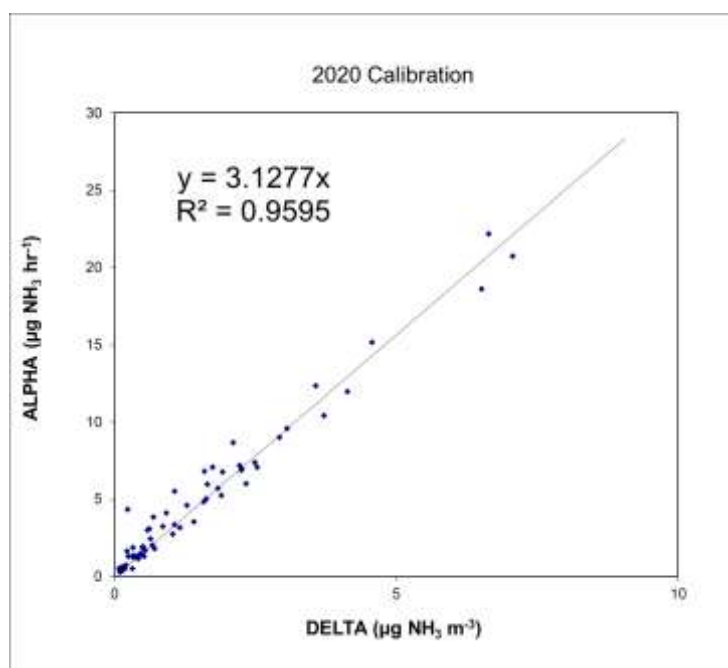


Figure 38: 2020 UK ALPHA® uptake rate calibration

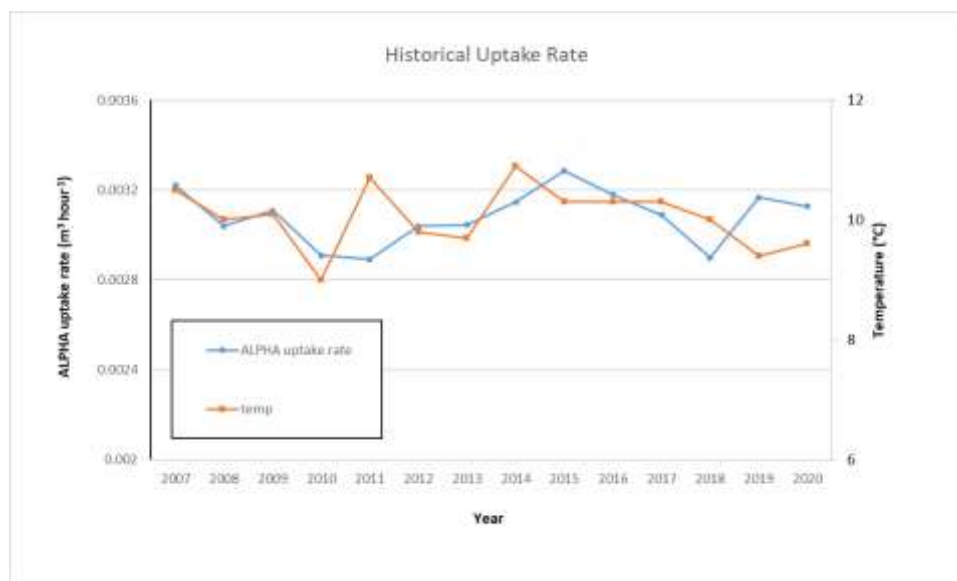


Figure 39: Historical UKEAP uptake rate for ALPHA samplers and UK annual average temperature (source: <https://www.metoffice.gov.uk/research/climate/maps-and-data/summaries/index>)

## Appendix 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 38<sup>th</sup> EMEP Inter-comparison

The inter-comparison in 2020 was the 38<sup>th</sup> time such an inter-comparison took place. The samples provided included nitrogen dioxide in absorbing solution (Table 7) and synthetic rainwater samples (Table 8).

### Nitrogen dioxide absorbing solution

The inter-comparison in 2020 was the 38<sup>th</sup> time such an inter-comparison took place. The results of the nitrogen dioxide absorbing solution are shown below in Table 7. The results of this intercomparison are excellent with absolute mean difference all  $\leq 5$  %. They are within the criteria for satisfactory reported by EMEP which is the highest rating for the EMEP quality norm. The analytical laboratory has been made aware of the performance to they are aware their performance meets expectations.

**Table 7 Comparison of Expected and Measured Concentrations of Nitrogen Dioxide in Absorbing Solution**

Sample code	Expected concentration $\mu\text{g NO}_2\text{-N/ml}$	Measured concentration $\mu\text{g NO}_2\text{-N/ml}$	Difference (%)	EMEP quality norm
C1	0.057	0.06	-5.00	S
C2	0.063	0.066	-4.55	S
C3	0.102	0.104	-1.92	S
C4	0.108	0.11	-1.82	S

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

### Synthetic Rainwater Samples

The results of the intercomparison and the expected results are shown in Table 8. The 2019 intercomparison produced four questionable results and three unsatisfactory results, the 2020 intercomparison has eight questionable results and eight unsatisfactory results.

The species with unsatisfactory results included:

- Ammonium: G1
- Magnesium: G1, G2, G3 and G4
- Calcium: G3 and G4
- pH: G1

The species with questionable results included:

- Potassium: G1, G2, G3 and G4
- Sodium : G1 and G2
- Calcium: G1
- pH: G2.

**Table 8 38<sup>th</sup> EMEP Inter-comparison**

Species	Sample code	Expected concentration mg	Measured concentration mg	Difference (%)	EMEP Quality Norm
SO <sub>4</sub> <sup>2-</sup>	G1	0.18	0.165	-8.3	S
	G2	0.205	0.187	-8.8	S
	G3	0.617	0.563	-8.8	S
	G4	0.499	0.456	-8.6	S
NH <sub>4</sub> <sup>+</sup>	G1	0.06	0.037	-38.3	U
	G2	0.172	0.153	-11.0	S
	G3	0.296	0.27	-8.8	S
	G4	0.344	0.311	-9.6	S
NO <sub>3</sub> <sup>-</sup>	G1	0.204	0.2	-2.0	S
	G2	0.336	0.331	-1.5	S
	G3	0.489	0.477	-2.5	S
	G4	0.587	0.577	-1.7	S
Na <sup>+</sup>	G1	0.254	0.202	-20.5	Q
	G2	0.326	0.266	-18.4	Q
	G3	0.848	0.776	-8.5	S
	G4	1.1	1.01	-8.2	S
Mg <sup>2+</sup>	G1	0.072	0.051	-29.2	U
	G2	0.083	0.057	-31.3	U
	G3	0.258	0.19	-26.4	U
	G4	0.206	0.147	-28.6	U
Cl <sup>-</sup>	G1	0.27	0.254	-5.9	S
	G2	0.386	0.361	-6.5	S
	G3	1.16	1.1	-5.2	S
	G4	1.54	1.47	-4.5	S
Ca <sup>2+</sup>	G1	0.089	0.075	-15.7	Q
	G2	0.102	0.087	-14.7	S
	G3	0.319	0.219	-31.3	U
	G4	0.255	0.173	-32.2	U
K <sup>+</sup>	G1	0.272	0.214	-21.3	Q
	G2	0.325	0.272	-16.3	Q
	G3	0.374	0.307	-17.9	Q
	G4	0.509	0.432	-15.1	Q
pH*	G1	5.49	5.14	-6.4	U
	G2	5.49	5.35	-2.6	Q
	G3	5.44	5.4	-0.7	S
	G4	5.44	5.47	0.6	S
Cond	G1	5.96	5.85	-1.8	S
	G2	7.9	7.58	-4.1	S
	G3	15.66	15.13	-3.4	S
	G4	17.15	16.83	-1.9	S

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

The analytical laboratory was made aware of the analytical performance and an improvement plan discussed. Many parts of the improvement plan have already put in place and more will follow in 2022. The improvements are summarised below:

#### **pH probe**

- Replaced previous pH probe with one that is more suited to low concentration samples.
- Allow pH probe to stabilise in a second aliquot sample before reading is taken
- Change the matrix of the standards to match the samples as closely as possible.
- The change in method is outside current scope so will require revalidating and resubmitting for accreditation. This is due to commence in January 2022 and is expected to be completed in around 2-3 months for submission to UKAS.

#### **Instrument**

All columns on the cation instrument were changed at the beginning of September 2021. Since then, an improvement of the analysis has been monitored on both the recording of system suitability checks (SSC) and monitoring of the low level cation MQC.

#### **New Instrument**

The analysts have approval for the purchase of a new dual system instrument that is able to analyse anions & cations. The analyst are due to meet instrument manufacturer in early 2022 to discuss all options on the instrument including optimisation to reduce our detection limit.

#### **39<sup>th</sup> EMEP intercomparison**

Samples for the 39<sup>th</sup> EMEP intercomparison have been analysed and submitted to NILU. The ion balances are better than those obtained for the 38<sup>th</sup> intercomparison. This is an early indication that the performance will be better. The 'expected' results are due in the Spring 2022.

#### **Comparison of EMEP samples with range of concentrations measured in UK**

As part of the review of the suitability of the analytical methods for analysing trace ion concentrations in rainwater, a review was undertaken to compare the range of concentrations provided in the 38<sup>th</sup> EMEP intercomparison with the range of concentrations measured in the network. To do this, the 25<sup>th</sup> (Q1), 50<sup>th</sup> (Q2) and 75<sup>th</sup> (Q3) percentiles were calculated for all ions in 2020 as well as all years back to 1986.

Table 9 compares the measured quartiles for measured components of rainwater for 2020 and the range of concentrations (minimum and maximum values) for intercomparison samples (G1, G2, G3 and G4). The calcium, magnesium, ammonium and sulphate interquartile ranges are shown to be very similar to the range of concentrations measured in the EMEP samples. The nitrate and potassium concentrations measured in the UK are somewhat lower than the EMEP samples. The chloride concentrations measured in the UK are over a wider range than the EMEP samples.

The data in the table shows that the EMEP samples are suitable as quality control checks on rainwater samples in the UK.

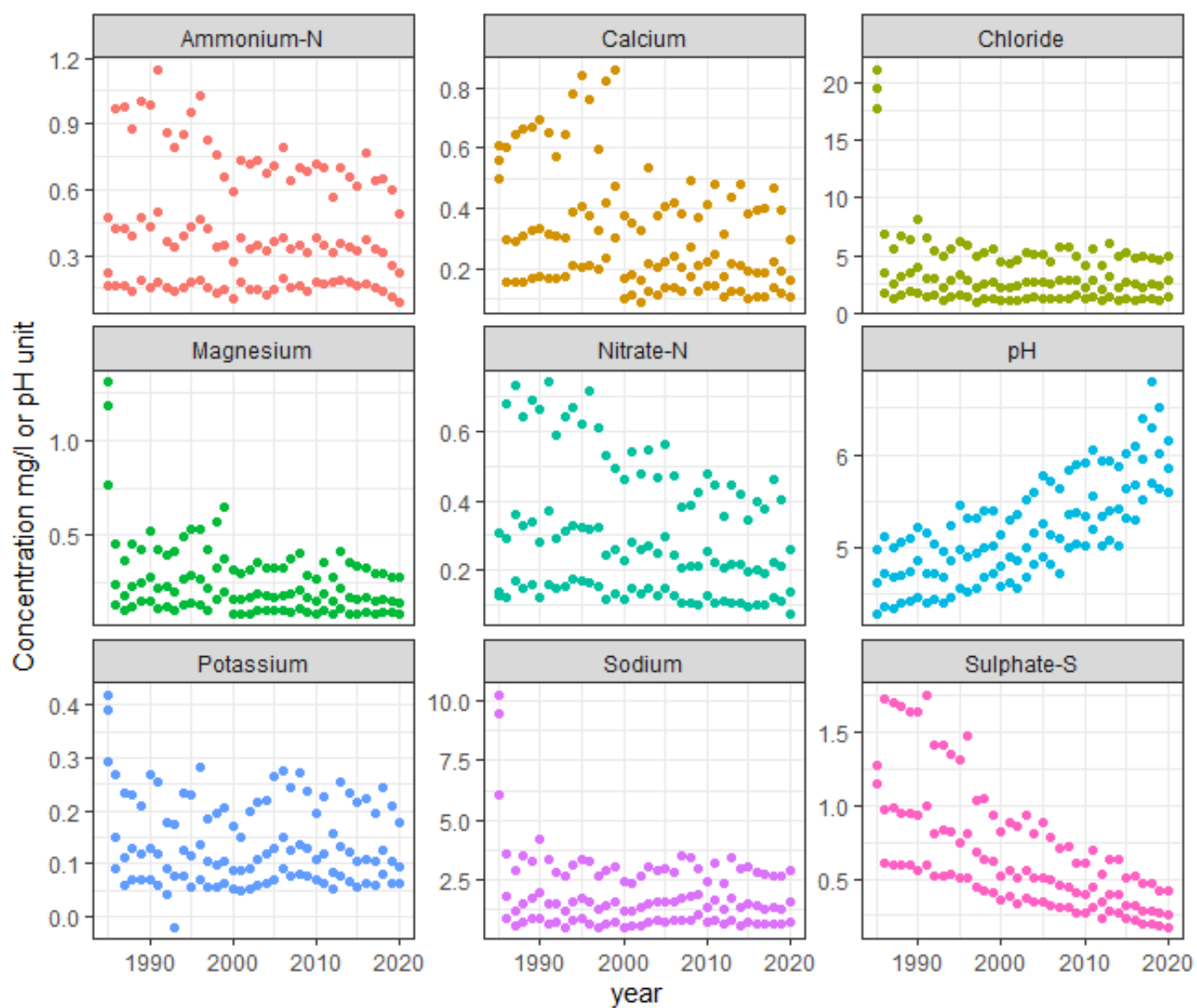
Figure 40 shows how the quartiles have changed since 1986. Clear decreases in sulphate, nitrate and ammonium are observed. There seems to have been a step down in concentration for the first quartile for ammonium from 2017 onwards (ammonium trends were discussed in Section 2.1). An increase in pH values is also observed. This is important as samples with a pH greater than 6 are not submitted for reanalysis. These samples we collect at sites will have bicarbonate component which is not currently analysed and hence not included in the ion balance. In 2020 about 35 % of the samples had a pH above 6. The analysts have been asked to investigate measuring bicarbonate concentrations.

**Table 9 A comparison of the measured quartiles for components of rainwater and the range of concentrations (minimum and maximum values) for intercomparison samples (G1, G2, G3 and G4)**

Species measured	Quartiles for components of UK rainwater samples in 2020			Range of G1, G2, G3 and G4 samples for 38 <sup>th</sup> Intercomparison		Comment
	25%	50%	75%	Min	Max	
Calcium	0.108	0.161	0.295	0.089	0.319	EMEP similar to interquartile range
Chloride	1.350	2.790	4.985	0.270	1.540	EMEP range wider than UK
Potassium	0.064	0.096	0.177	0.272	0.509	EMEP higher than UK values
Magnesium	0.080	0.143	0.279	0.072	0.258	EMEP similar to interquartile range
Sodium	0.770	1.565	2.870	0.254	1.100	EMEP range smaller than UK
Ammonium-N	0.089	0.218	0.494	0.060	0.344	EMEP similar to interquartile range
Nitrate-N	0.074	0.140	0.261	0.204	0.587	EMEP higher than UK values
pH	5.602	5.850	6.150	5.440	5.490	UK interquartile range wider than EMEP range
Sulphate-S	0.172	0.251	0.416	0.180	0.617	EMEP similar to interquartile range



**Figure 40 Trends in 25<sup>th</sup>, 50<sup>th</sup> and 75<sup>th</sup> percentile for measured rainwater components measured for all samples at all sites since 1986.**



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

### Bias 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 over-read 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 41 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.

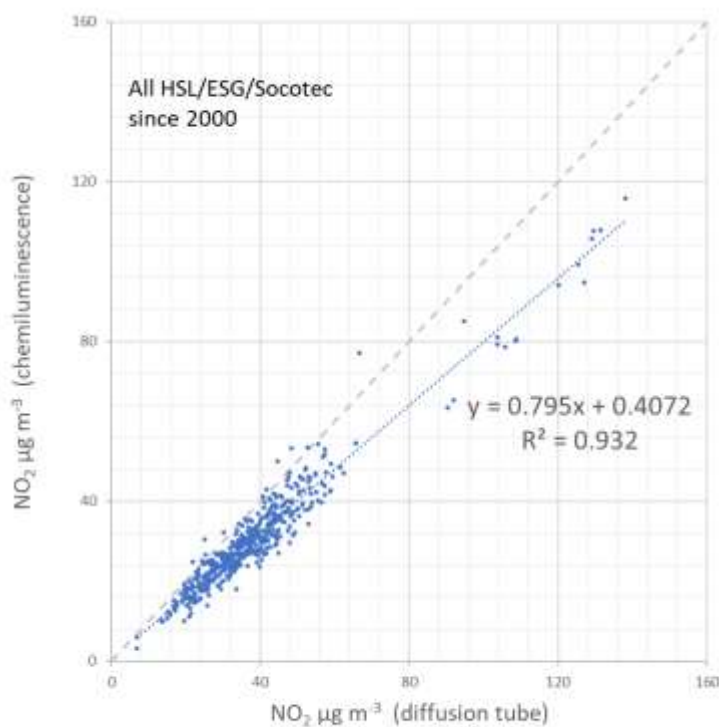


Figure 41 A comparison of annual mean nitrogen dioxide concentrations measured by diffusion tube and automatic analyser

#### 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 42 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.

**Table 10 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)			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)	3.8(93)	3.3(100)	2.8(96)

**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.

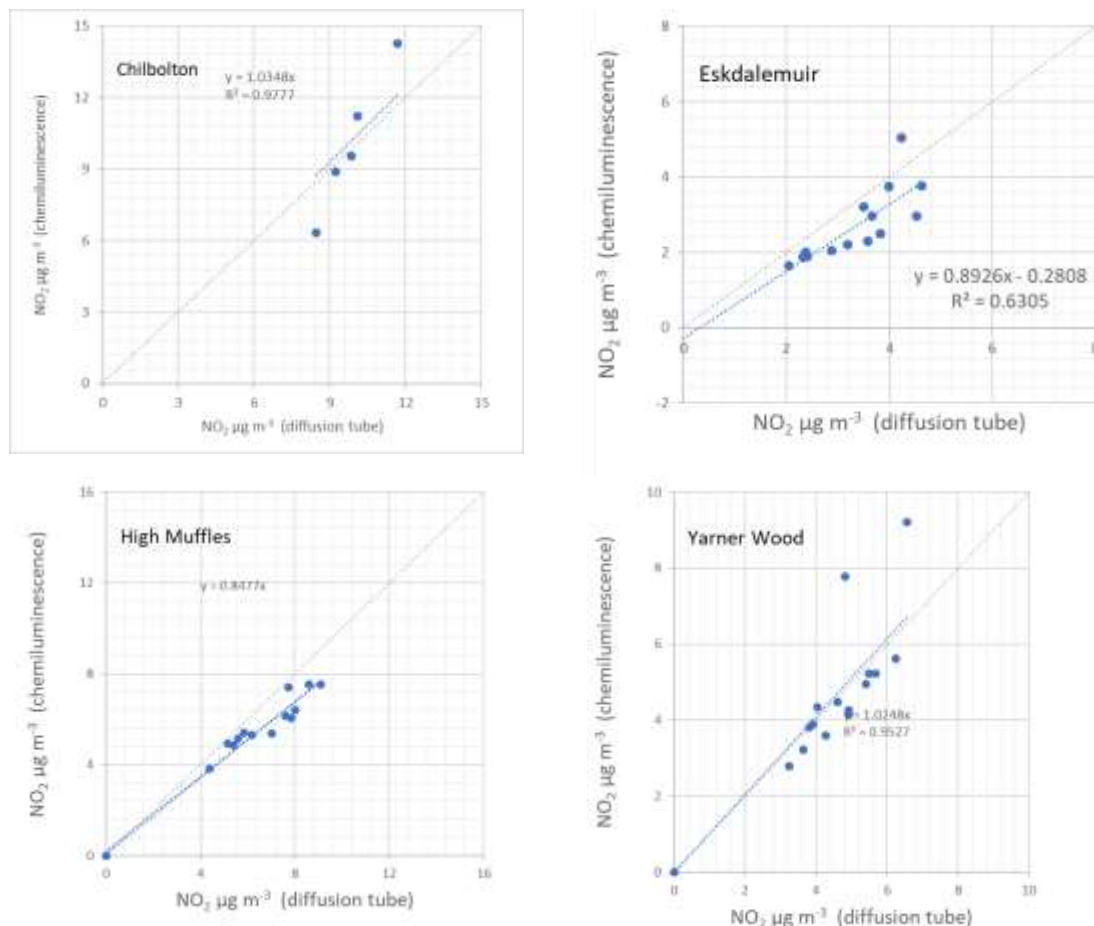


Figure 42 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each

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  $\text{NO}_2$  Network measurements. This is because:

- the 'quality' of the measurement made by automatic analyser in the Rural  $\text{NO}_2$  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 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>4</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>5</sup> to combine the respective bias B factors.

The individual bias B factors were calculated as follows:

	Eskdalemuir	Yarner Wood	High Muffles	Chilbolton
Bias factor, B	27%	16%	15%	35%

The average of the four values is calculated to be 23.24 % giving a bias adjustment factor of 0.811<sup>6</sup>.

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<sup>4</sup> See <https://aqm.defra.gov.uk/bias-adjustment-factors/local-bias.html> and Figure 7.1 of TG(16)

<sup>5</sup> 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.

<sup>6</sup> Calculated as (1 / (bias average+1))