UKEAP
2018
Annual Report

Prepared for the Environment Agency

&

Defra

And the Devolved Administrations

By

NERC Centre for Ecology & Hydrology

&

Ricardo Energy & Environment

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NERC CEH REPORT SUMMARY

NERC CEH Client: Environment Agency	
Client Project number: ECM48524	CEH Project number: NEC05967
Project Title: UK Eutrophying and Acidifying Atmospheric Pollutants	
Start date: 01/02/2017	Completion date: 31/07/2020
Client Project Officer: Mr Matt Brazier/Mr Rob Jones/Ms Jo Scully	
CEH Project Officer: Dr C F Braban	
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RICARDO ENERGY & ENVIRONMENT REPORT SUMMARY

Customer:

Environment Agency

Customer reference:

ECM48524

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Contents

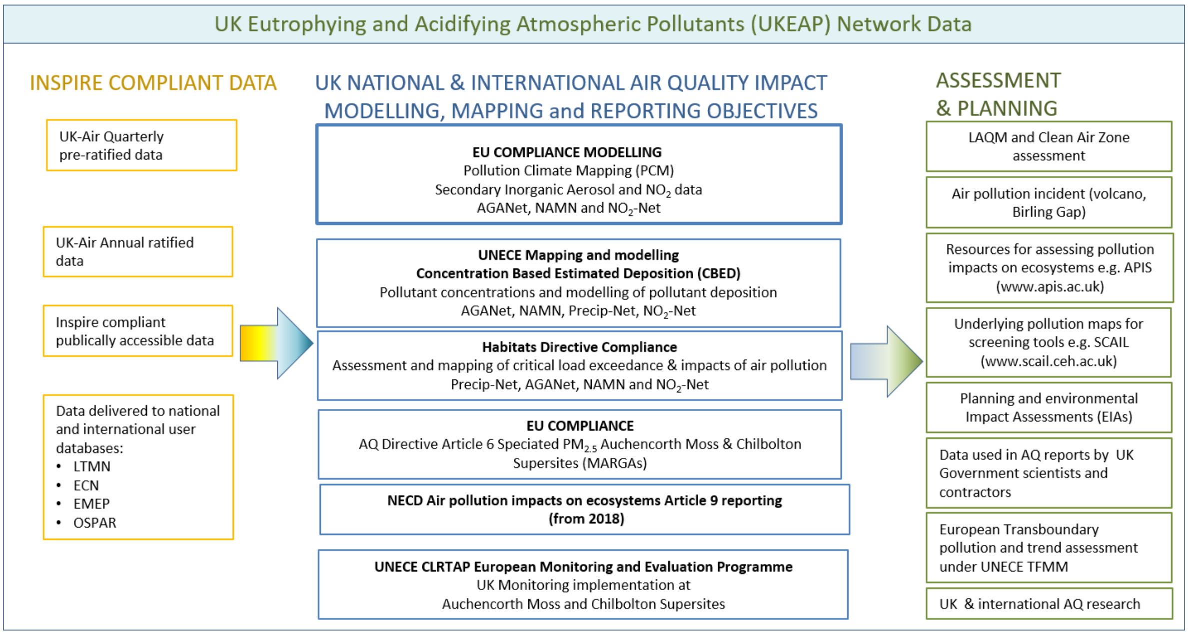
1. Summary

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_2 diffusion tube network** (NO_2-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.
- The UKEAP network is operated by the 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 throughout the year



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 $PM_{2.5}$ and PM_{10}.
- The Rural NO_2-Net is used to produce the rural background NOx concentration field in air quality PCM compliance modelling.

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, AGA-Net, NAMN and NO_2-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.apis.ac.uk (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 S and N 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 $PM_{2.5}$ at rural background locations with a spatial coverage of 1 station per 100,000 km^2. 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 NO2-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. Staff are available to give information on the measurements when requested.

1.3 Publications

Reports and research papers published in 2018 and early 2019 using UKEAP data, maps derived from UKEAP data or science supported at UKEAP sites

1. Lee JA, Caporn SJM, Carroll J, Foot JP, Johnson D, Potter L, et al. 22. Effects of ozone and atmospheric nitrogen deposition on bryophytes. Bryology for the Twenty-first Century. 2018;
2. Eze S, Palmer SM, Chapman PJ. Negative effects of climate change on upland grassland productivity and carbon fluxes are not attenuated by nitrogen status. Sci Total Environ. 2018 Oct 1;637-638:398–407.
3. Noble A, O'Reilly J, Glaves DJ, Crowle A, Palmer SM, Holden J. Impacts of prescribed burning on Sphagnum mosses in a long-term peatland field experiment. PLoS One. 2018 Nov 1;13(11):e0206320.
4. Imamura N, Iwai N, Tanaka N, Ohte N. A Comparison between Wet-only and Bulk Deposition at Two Forest Sites in Japan. Asian Journal of Atmospheric Environment (AJAE). 2018;12(1).
5. Hood C, MacKenzie I, Stocker J, Johnson K, Carruthers D, Vieno M, et al. Air quality simulations for London using a coupled regional-to-local modelling system. Atmos Chem Phys. 2018;18(15):11221–11245.
6. Tang YS, Tanna B, Keenan PO, Stephens ACM. Fenn's, Whixall, Bettisfield, Wem & Cadney Mosses. Atmospheric ammonia monitoring data report for period: Jul 2018–Dec 2018. 2019;
7. Bottrell S, Hipkins EV, Lane JM, Zegos RA, Banks D, Frengstad BS. Carbon-13 in groundwater from English and Norwegian crystalline rock aquifers: a tool for deducing the origin of alkalinity? Sustain Water Resour Manag. 2019 Mar;5(1):267–287.
8. Pescott OL, Jitlal M, Beckmann B, Roy DB, Walker KJ, Dore A, et al. The use of National Plant Monitoring Scheme data for making inferences concerning air pollution impacts. 2018;
9. Ni Y, Mwabonje ON, Richter GM, Qi A, Yeung K, Patel M, et al. Assessing availability and greenhouse gas emissions of lignocellulosic biomass feedstock supply – case study for a catchment in England. Biofuels, Bioprod Bioref. 2019 May;13(3):568–581.
10. Aleksankina K, Reis S, Vieno M, Heal MR. Advanced methods for uncertainty assessment and global sensitivity analysis of a Eulerian atmospheric chemistry transport model. Atmos Chem Phys Discuss. 2018 Jul 26;1–30.
11. Stow D, Nichol CJ, Wade T, Assmann JJ, Simpson G, Helfter C. Illumination geometry and flying height influence surface reflectance and NDVI derived from multispectral UAS imagery. Drones. 2019;3(3):55.
12. Walker HL, Heal MR, Braban CF, Ritchie S, Conolly C, Sanocka A, et al. Changing supersites: assessing the impact of the southern UK EMEP supersite relocation on measured atmospheric composition. Environmental Research Communications. 2019;1(4):041001.
13. Tang YS, Braban CF, Dragosits U, Simmons I, Leaver D, van Dijk N, et al. Acid gases and aerosol measurements in the UK (1999–2015): regional distributions and trends. Atmos. Chem. Phys., 18, 16293–16324, 2018.
14. Ramsay R, Di Marco CF, Heal MR, Twigg MM, Cowan N, Jones MR, et al. Surface–atmosphere exchange of inorganic water-soluble gases and associated ions in bulk aerosol above agricultural grassland pre- and postfertilisation. Atmos Chem Phys. 2018 Nov 30;18(23):16953–16978.
15. Braban CF, de Bree F, Crunaire S, Fröhlich M, Fromage-Mariette A, Goelen E, et al. Literature review on the performance of diffusive samplers for the measurement of ammonia in ambient air and emissions to air. 2018;
16. Hjellbrekke A-G, Solberg S. Ozone measurements 2017. EMEP/CCC-Report. 2019;
17. Hjellbrekke A-G. Data report. Particulate matter, carbonaceous and inorganic compounds. EMEP/CCC-Report. 2018;
18. Hobeichi S. Supplement of Derived Optimal Linear Combination Evapotranspiration (DOLCE): a global gridded synthesis ET estimate. 2018;
19. Baldocchi D, Chu H, Reichstein M. Inter-annual variability of net and gross ecosystem carbon fluxes: A review. Agric For Meteorol. 2017 Jun;249:520–533.
20. Aas W, Bohlin-Nizzetto P. Heavy metals and POP measurements, 2016. NILU; 2018.
21. Pimpin L, Retat L, Fecht D, De Preux Gallone LB, Sassi F, Gulliver J, et al. Estimation of costs to the NHS and social care due to the health impacts of air pollution. 2018;
22. Cinnirella S, D'Amore F, Bencardino M, Sprovieri F, De Simone F, Hedgecock IM, et al. GOS4M: THE GEO FLAGSHIP TO SUPPORT THE MINAMATA CONVENTION ON MERCURY. 2018. p. 89.

23. Aleksankina K. Application of global methods for sensitivity analysis and uncertainty assessment of atmospheric chemistry transport models. 2019;
24. Schrader F. Challenges and perspectives in modelling biosphere-atmosphere exchange of ammonia. 2019;
25. Barthel S, Tegen I, Wolke R. Do new sea spray aerosol source functions improve the results of a regional aerosol model? Atmos Environ. 2018 Oct;198:265–278.

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 NERC Centre for Ecology and Hydrology (CEH).

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 2018.

UKEAP is comprised of:

- **National Ammonia Monitoring Network** (NAMN – 72 sites)
- **Acid Gases and Aerosol Network** (AGA-Net – 27 sites)
- **Precipitation chemistry Network** (Precip-Net – 41 sites)
- **Rural NO_2 diffusion tube network** (NO_2-Net – 24 sites)
- **UK EMEP Supersites** (Chilbolton and Auchencorth)

The geographical distribution of the NAMN and AGANet networks are shown in Figure 1 and Figure 2 respectively, Precip-Net and NO_2-Net in Figure 3. Natural England **Long Term Monitoring Network** air quality measurements are embedded in UKEAP networks Precip-Net and NO_2-Net.

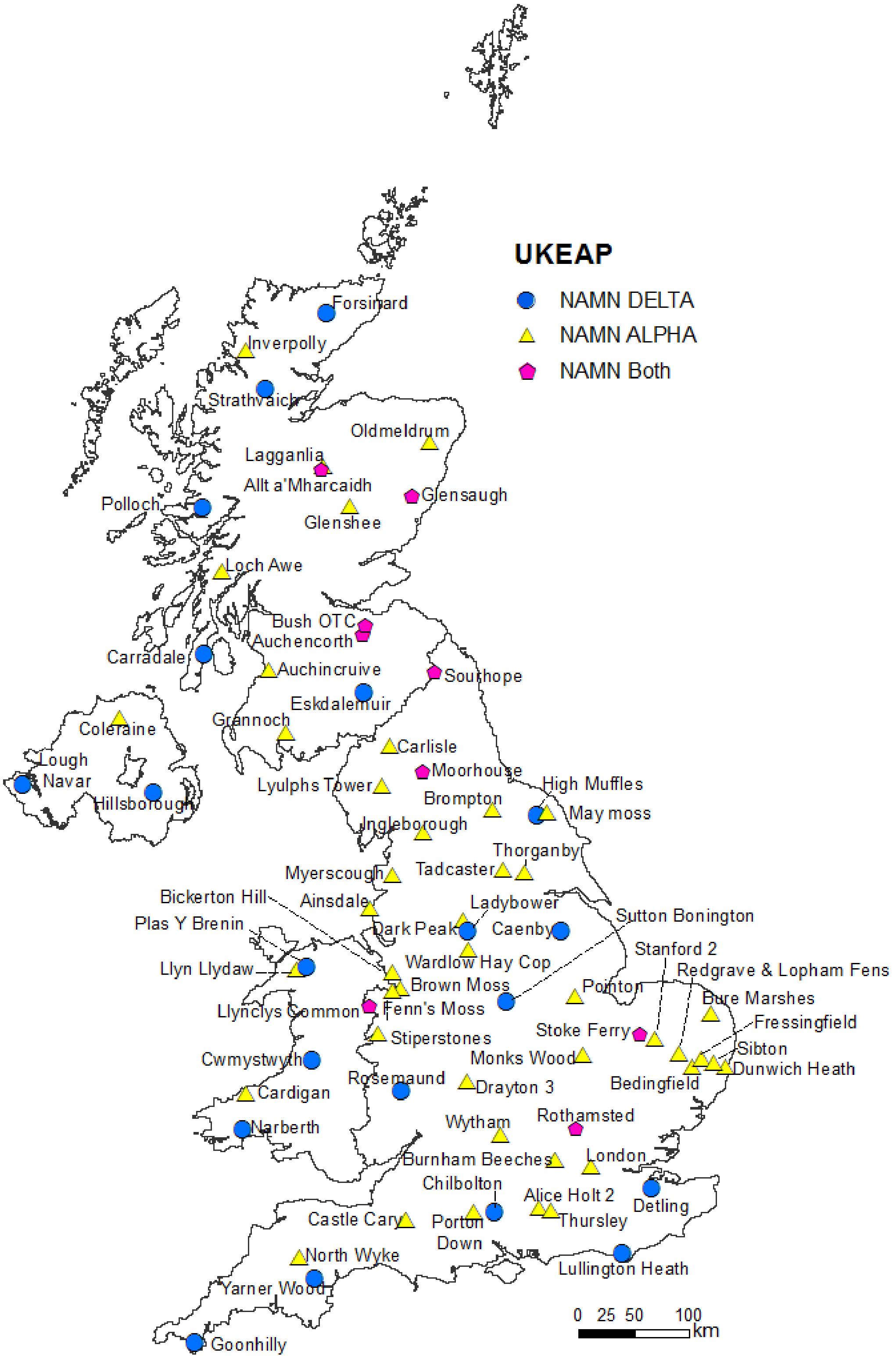


Figure 1 UK National Ammonia Monitoring Network

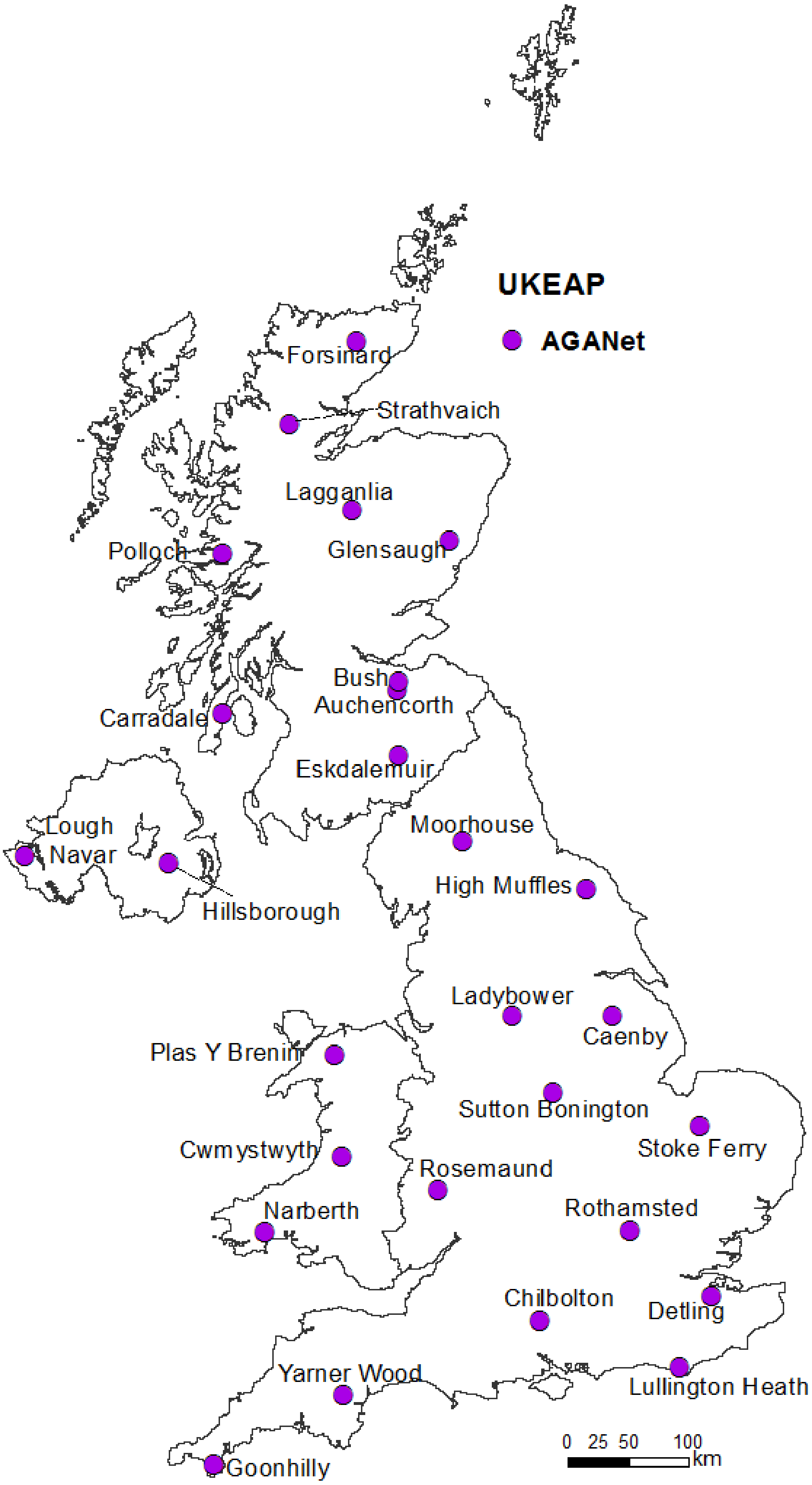


Figure 2 Acid Gases and Aerosol Network

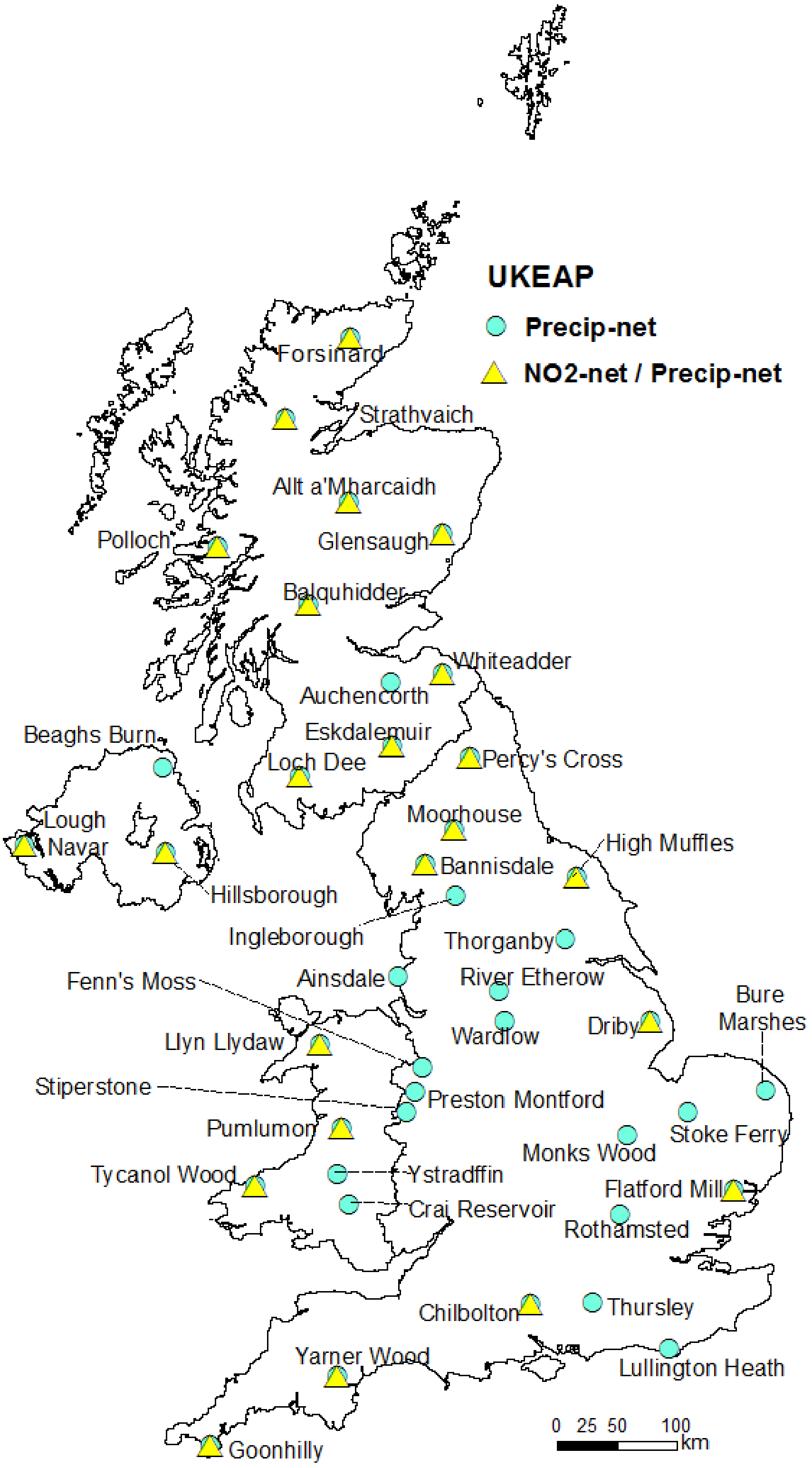


Figure 3 Precipitation and NO_2 diffusion tube chemistry Network

2. UKEAP Networks Reports

2.1 Precipitation Network (Precip-Net)

Precip-Net operated without major change in 2018. Samples continued to be collected 41 fortnightly bulk rain monitoring sites and 2 daily wet only (DWOC) collectors in operation throughout the year. One minor site relocation occurred at Crai Reservoir was moved to a nearby location on 24th October 2018 (called Crai Reservoir 2) due to a local site operator (LSO) change.

Bulk precipitation samples are collected using bulk deposition collectors (Figure 4) 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 1985-2016 network prior to the 2016 network review (Figure 5 and Figure 6 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).

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 2018 are summarised in the Appendices of this report.

Figure 4 Bulk rain sampler (Bannisdale)

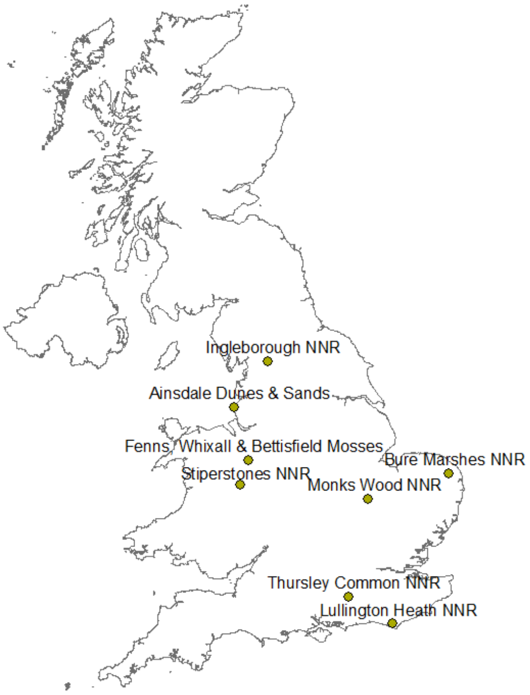


Figure 5 LTMN sites forming part of the Precip-Net monitoring network (eight sites)

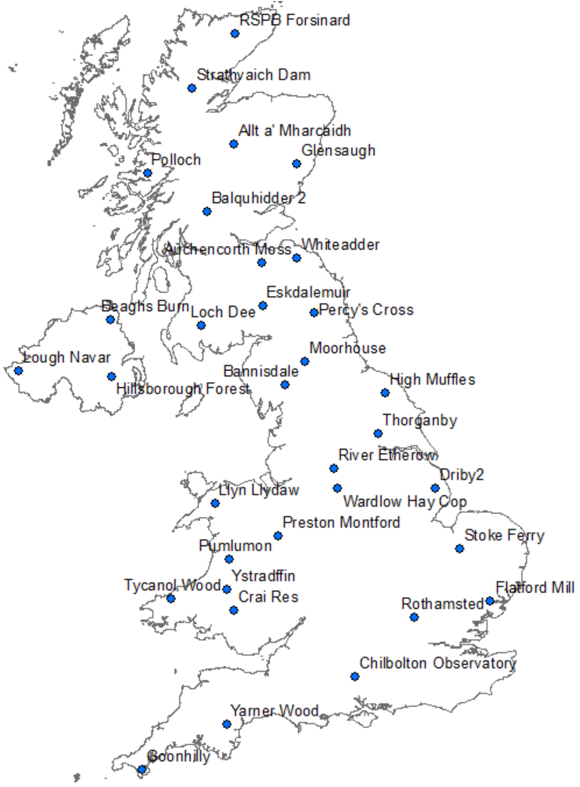
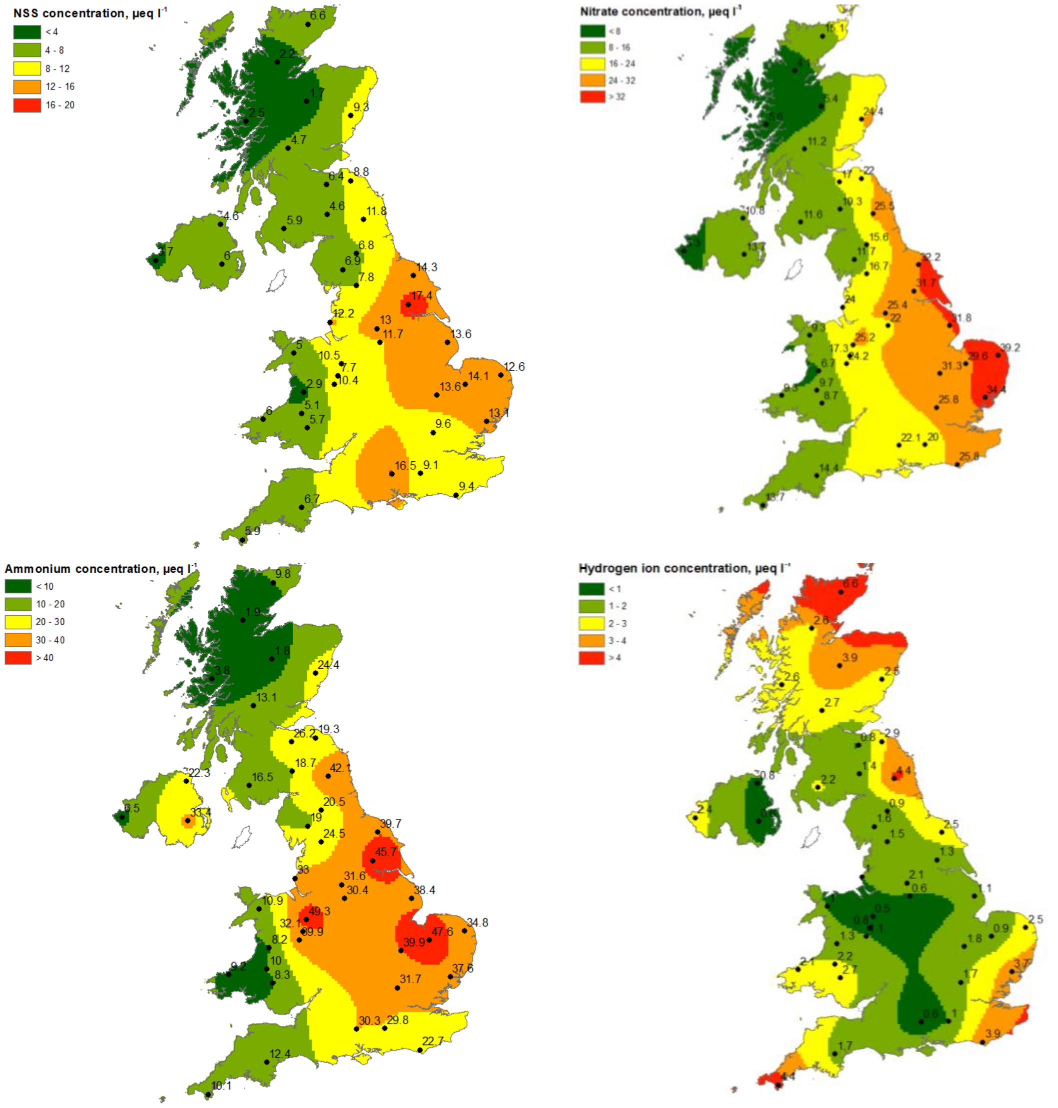


Figure 6 Precip-Net monitoring network (originating pre-2016)



NSS concentration, μeq l^{-1}

Nitrate concentration, μeq l^{-1}

Ammonium concentration, μeq l^{-1}

Hydrogen ion concentration, μeq l^{-1}

Figure 7 Interpolated concentration maps for non-sea salt sulphate, nitrate, ammonium and hydrogen ion (μeq l^{-1})

The spatial patterns of the annual mean precipitation-weighted concentration of non-seasalt sulphate, nitrate, ammonium and hydrogen are presented in Figure 7 for 2018. The maps show that: the non-sea salt sulphate and nitrate concentrations tend to be highest on the eastern seaboard where the rainwater volume is smallest. Ammonium concentrations are highest in the areas of the UK where intensive livestock activity is highest. There is no clear pattern in the hydrogen ion concentration.

Figure 8 summarises the reported emissions of all the precursor gases since the inception of the Precip-Net sites. It is noted that all precursor gas emissions have decreased though the rate of decrease for sulphur dioxide was greater than that for oxides of nitrogen and ammonium. SO_2 emissions have decreased by about ninety percent, oxides of nitrogen emissions have decreased by nearly 70% and ammonia emissions have decreased by about 12%. Figure 8 also presents projected emissions for the respective gases from the National Emissions Inventory (NAEI).

Figure 9, Figure 10 and Figure 11 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 Figures 12-14 for non-sea salt sulphate, nitrate and ammonium, respectively).

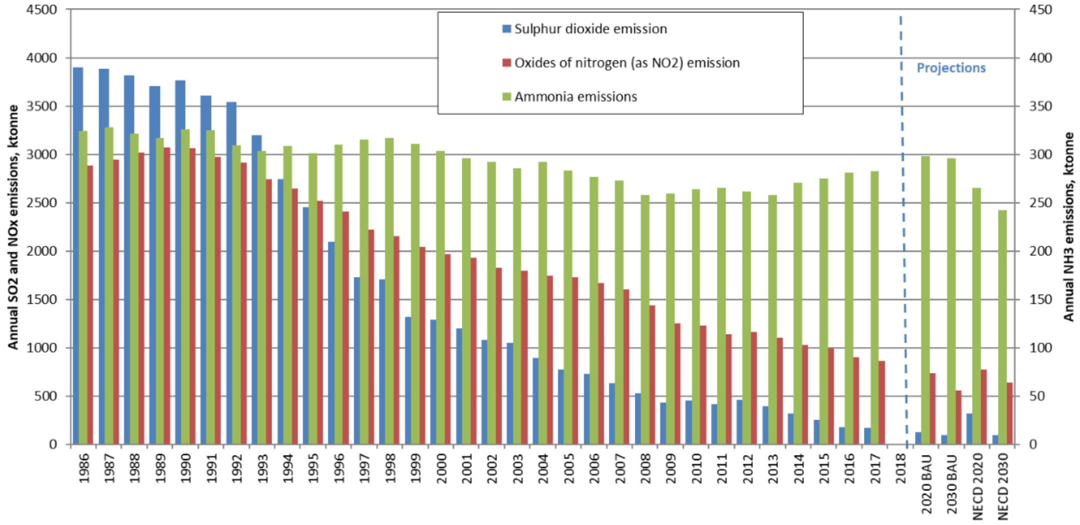


Figure 8 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986

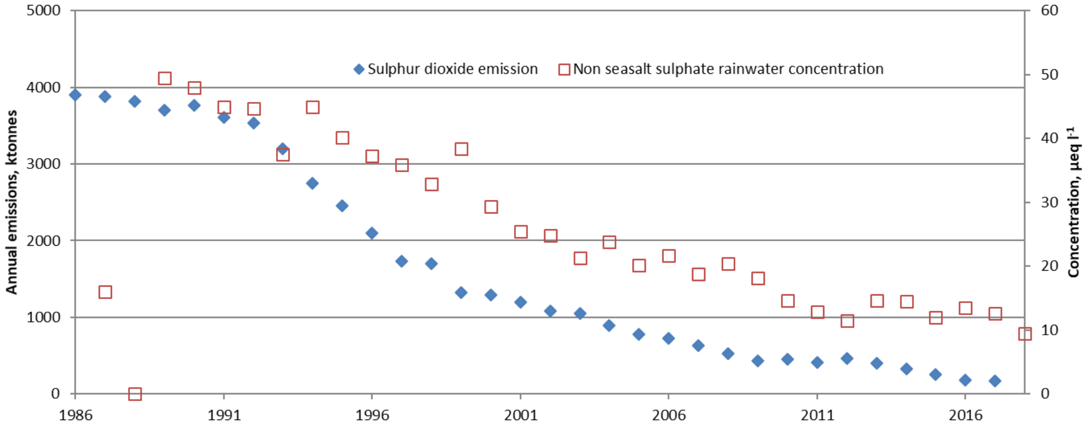


Figure 9 Sulphur dioxide emissions and sulphate concentrations in rainwater

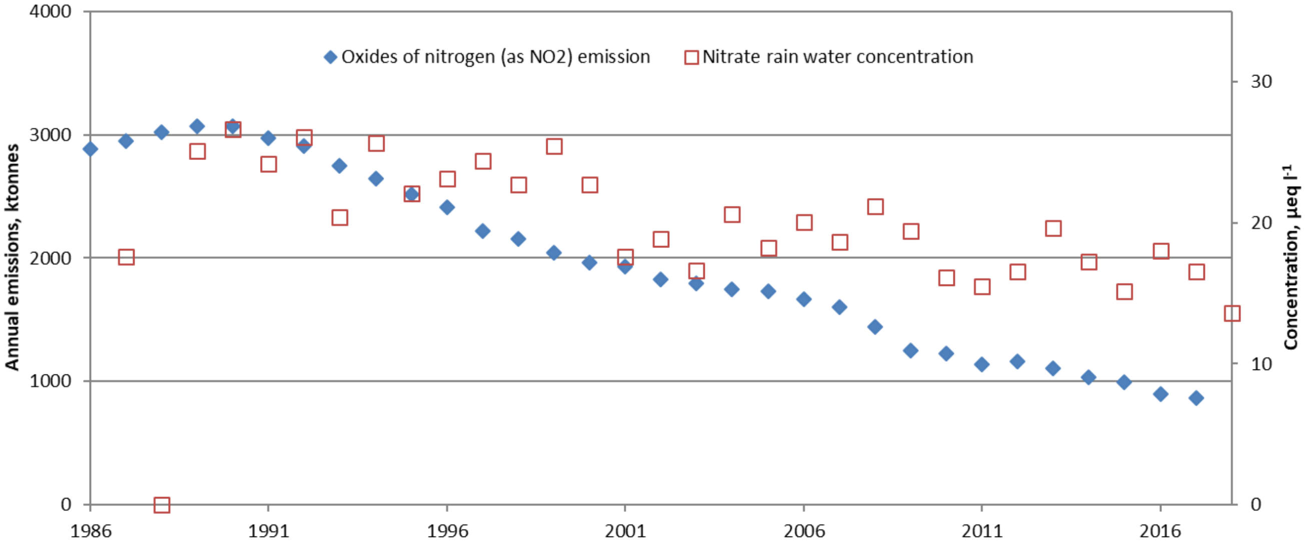


Figure 10 Oxides of nitrogen emissions and nitrate concentrations in rainwater

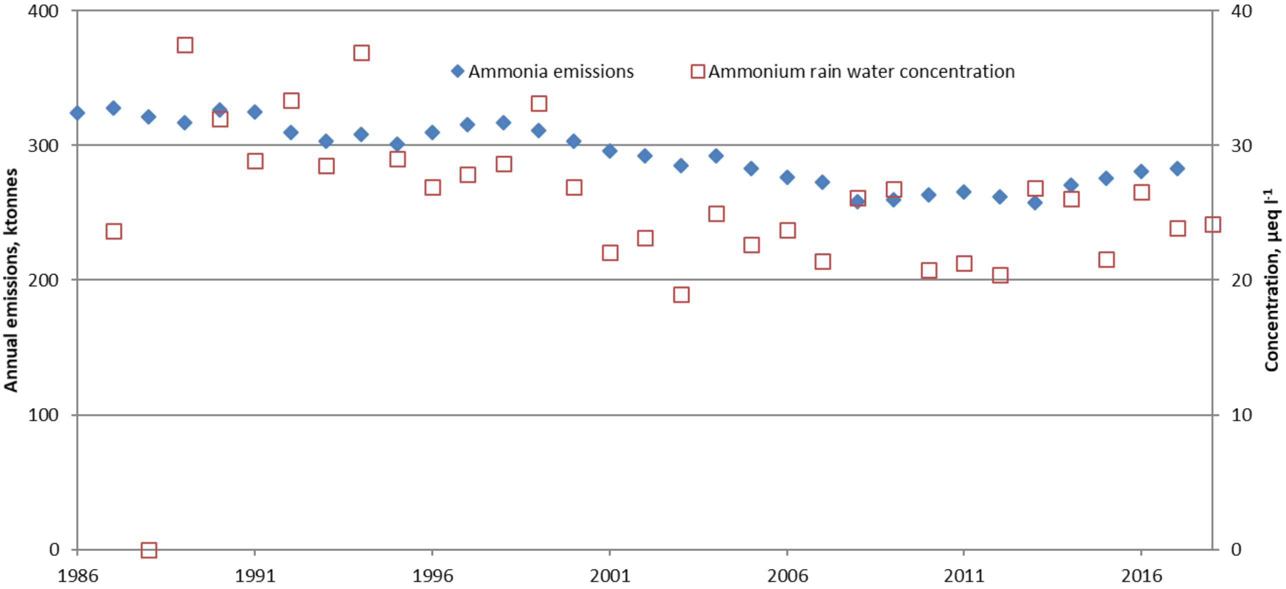


Figure 11 Ammonia emissions and ammonium concentrations in rainwater

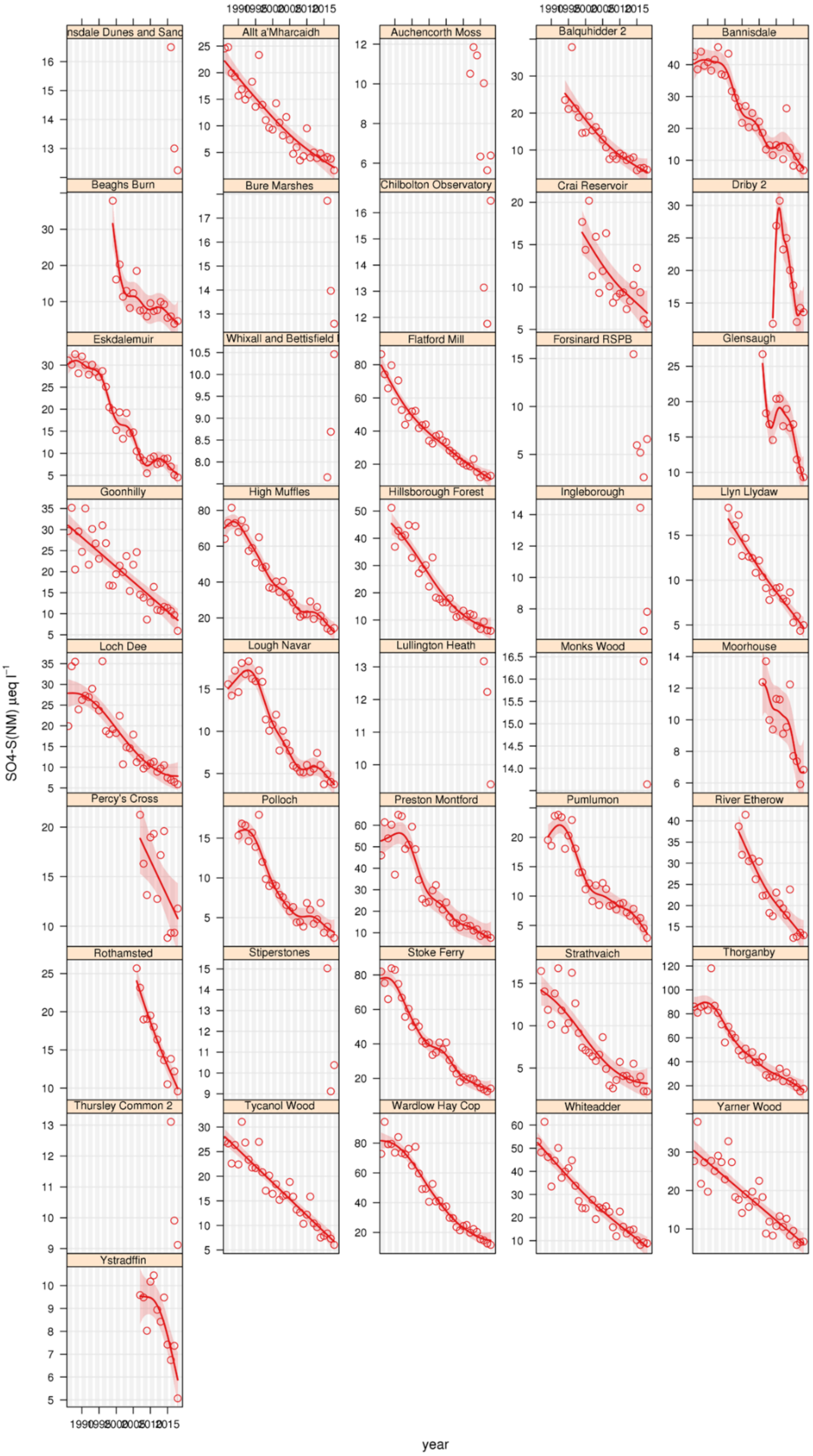


Figure 12 Non sea salt sulphate concentrations measured at sites with the Precip-Net since 1986

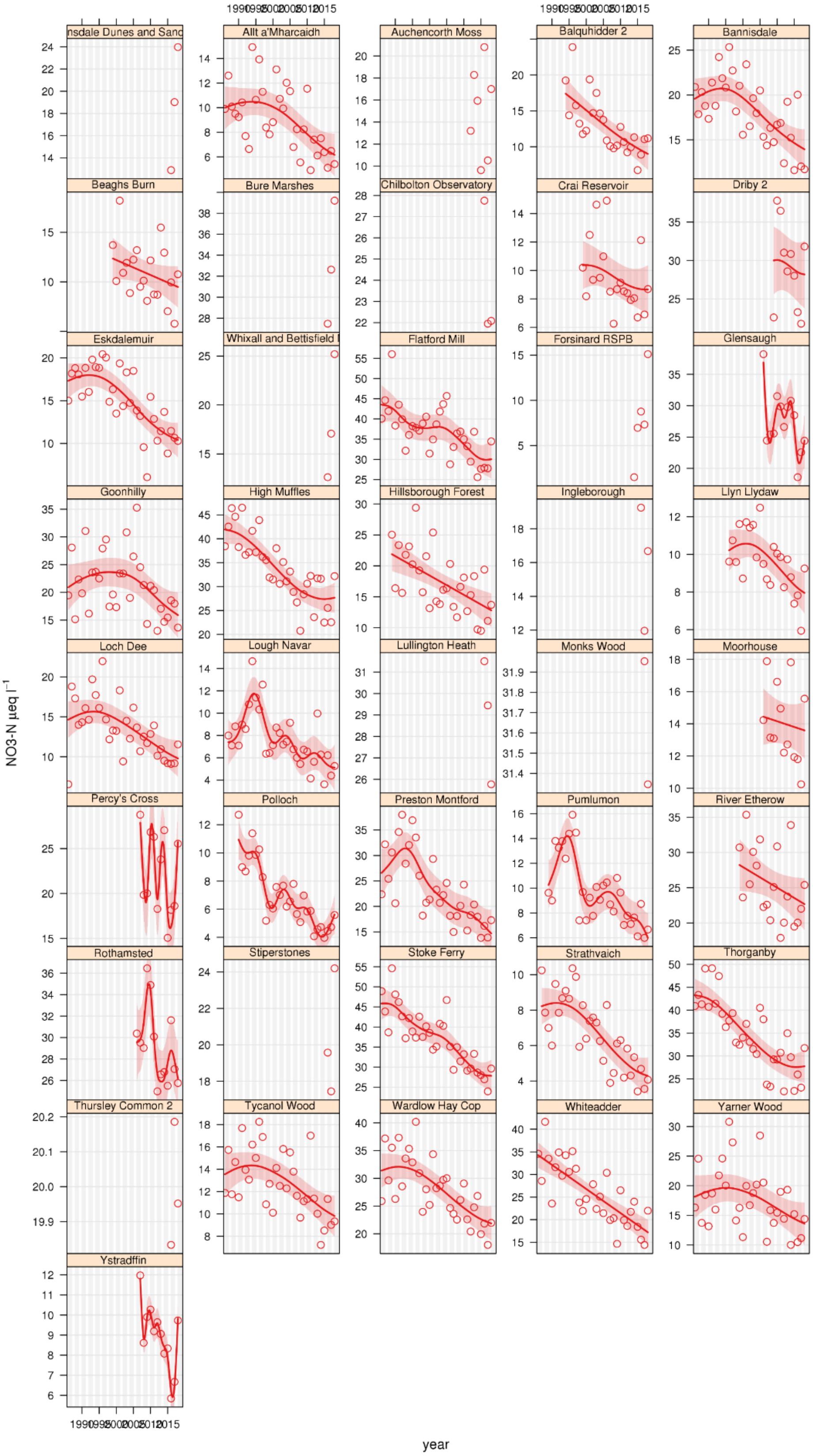


Figure 13 Nitrate concentrations measured at sites with the Precip-Net network since 1986

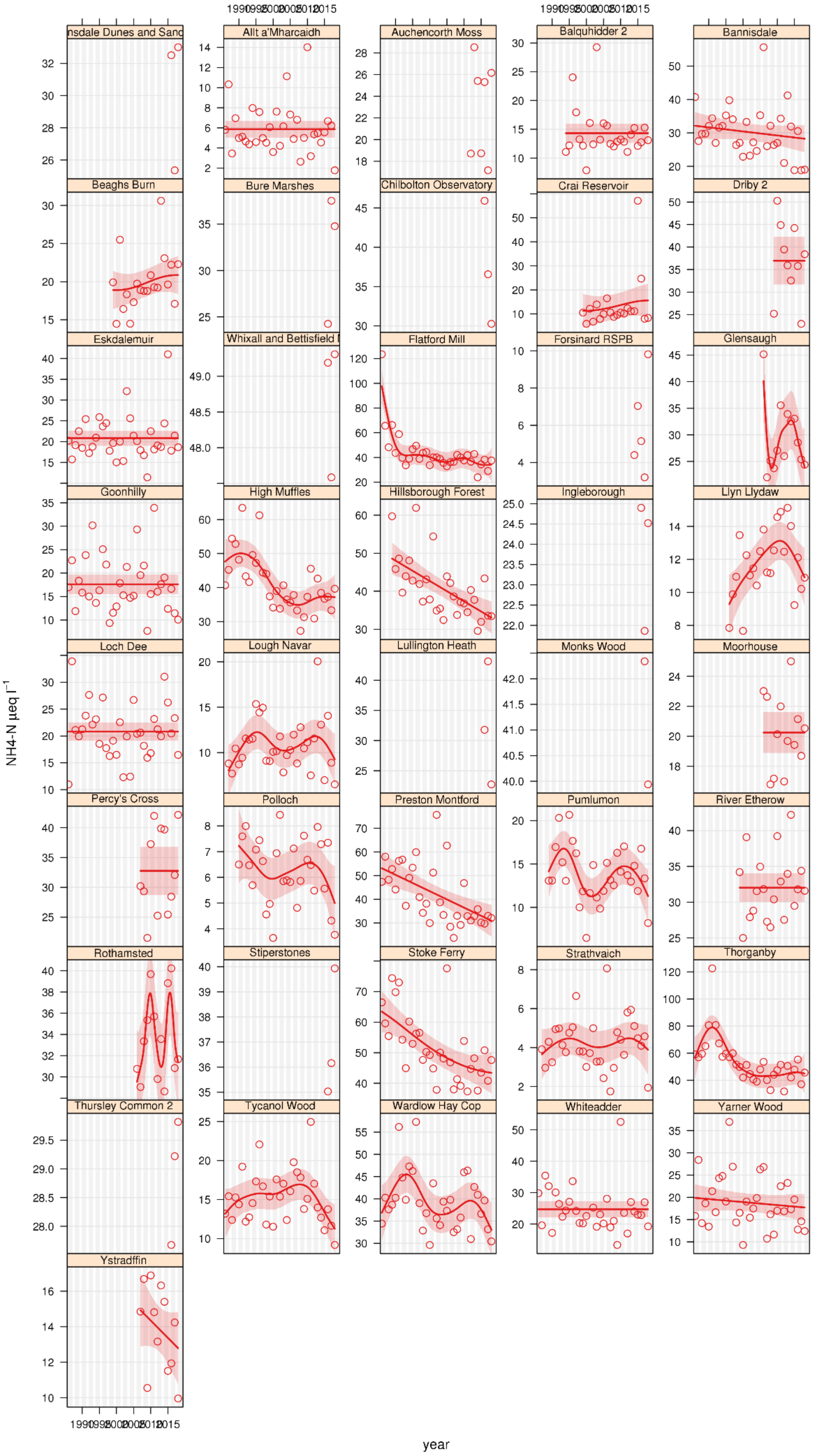


Figure 14 Ammonium concentrations measured at sites with the Precip-Net network since 1986

2.2 NO_2-Net Network

The NO_2 network (NO_2-Net) consists of 24 sites at which diffusion tubes, in triplicate, were exposed for approximately 4-week exposure periods. The annual average NO_2 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 2018 was 96% with 21 of the 24 sites achieving > 90% and 19 sites achieving 100% data capture. There were various reasons for the lower data capture at Llyn Llydaw, Whiteadder and Yarner Wood such as local site operator availability and extended tube exposure.

Table 1 2018 NO_2 concentration from the Diffusion Tubes in the NO_2-Net

Site Name	Raw 2018 concentration ($\mu g\ m^{-3}$)	2018 concentration Bias Corrected (0.897)[1]	Data capture	Site Name	Raw 2018 concentration ($\mu g\ m^{-3}$)	2018 concentration Bias Corrected (0.897)	Data capture
Allt a'Mharcaidh	1.43	1.28	100%	Llyn Llydaw	2.78	2.49	85%
Balquhidder 2	2.33	2.09	100%	Loch Dee	2.53	2.27	100%
Bannisdale	4.15	3.72	100%	Lough Navar	2.06	1.85	100%
Chilbolton Observatory	9.85	9.74	100%	Lullington Heath	10.56	9.47	100%
Driby 2	8.60	7.71	100%	Moorhouse	3.96	3.55	92%
Eskdalemuir	2.33	1.91	100%	Percy's Cross	4.25	3.81	100%
Flatford Mill	9.08	8.15	100%	Polloch	1.25	1.12	100%
Forsinard RSPB	1.48	1.33	100%	Pumlumon	3.55	3.18	100%
Glensaugh	3.33	2.99	100%	Strathvaich	0.95	0.85	92%
Goonhilly	3.89	3.49	100%	Tycanol Wood	3.45	3.09	100%
High Muffles	5.15	5.21	100%	Whiteadder	3.07	2.76	62%
Hillsborough Forest	6.76	6.06	100%	Yarner Wood	4.04	3.87	83%

[1] All sites bias adjusted by 0.896 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_x and NO_2 concentrations measured by the diffusion tubes in the network as a network average, very rural site (Strathvaich) and less rural site (Flatford

Mill). It is apparent that the estimated emissions of NO_x in the UK as a whole show a reduction over the period shown and there is also a reduction in the average concentrations of all of the active NO_2-Net site over the period. More information relating to emissions in the UK can be found on the National Atmospheric Emissions Inventory (NAEI) website.

NO_2 are associated with transport or industrial processes involving combustion, therefore there are smaller influences in concentrations at rural locations. The difference between the less rural site of Flatford Mill site which has an urban influence being about 50 miles from London and between Colchester and Ipswich and the more rural Strathvaich site located in the north of Scotland can also be seen in the plot. The trend in concentrations at the Strathvaich site does not appear to show any observable reduction in NO_2 concentration whereas the Flatford Mill sites shows a similar rate of reduction to that of the NAEI estimated.

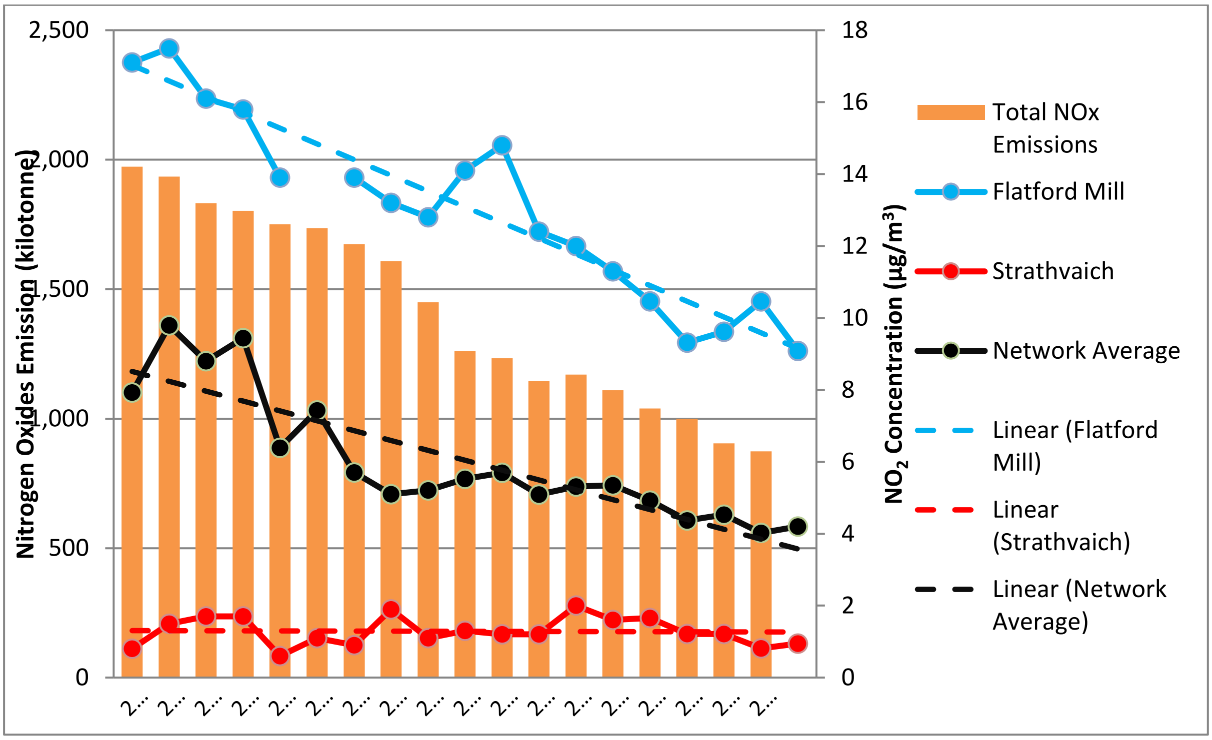


Figure 15 Long term trends where estimated emissions are plotted against selected sites in the network

The annual average uncorrected NO_2 concentrations from 2010-2018 (Figure 16) indicates the differing NO_2 concentrations at rural locations across the UK. Most of the sites show some reduction between 2010 and 2018 but the larger decreases being seen at the sites that are closer to the sources of NO_x.

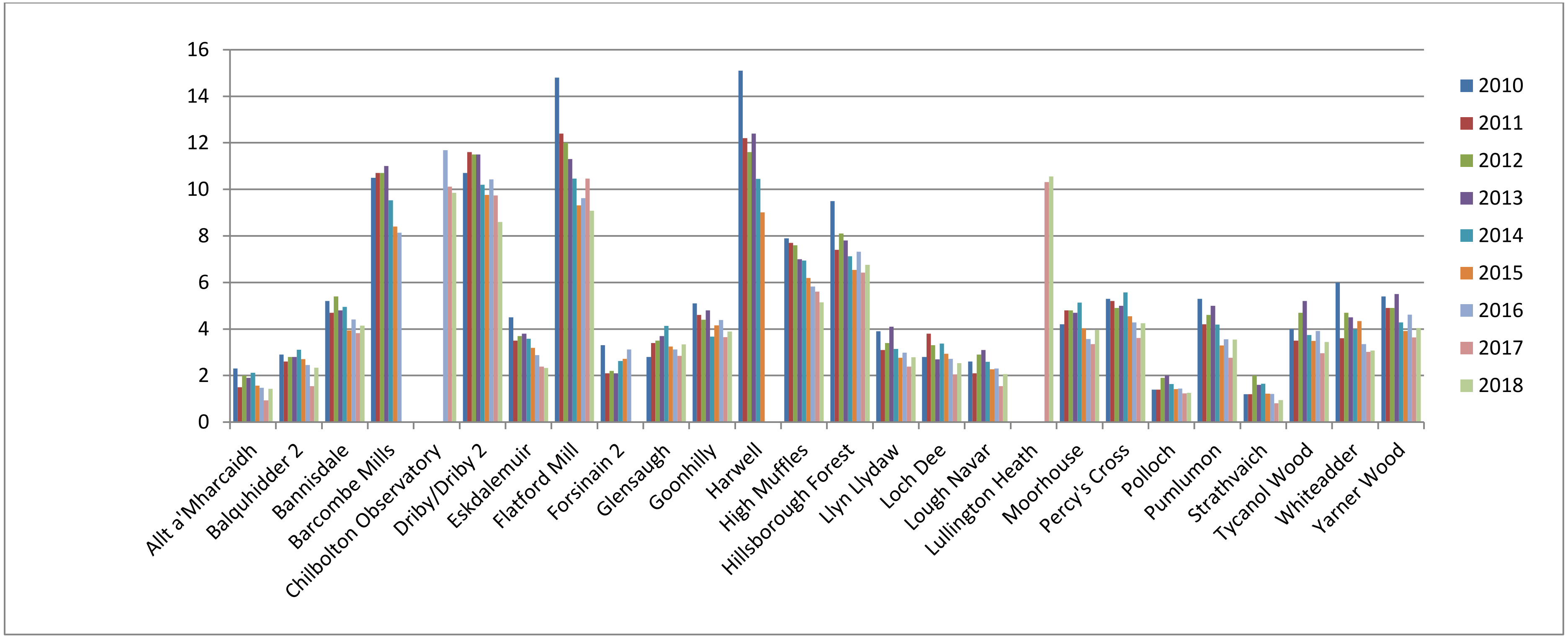


Figure 16 Annual mean NO_2 concentration (µg m-3) at the NO_2-Net sites 2010-2018

2.3 National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly measurements of atmospheric NH_3 in 2018 was 72, summarised in Figure 1. The 2018 annual NAMN results are summarised by the average and range of annual NH_3 concentrations observed at each site in Figure 17. There is high spatial variability in NH_3 concentrations across the UK and significant seasonal variability. This reflects the large heterogeneity of NH_3 sources in the rural countryside and variability in levels of NH_3 emissions (see Tang et. 2018 for a more detailed discussion). During 2018 average data capture across NAMN was 83%. (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_3	29
AGANET DELTA sites (sampling gaseous NH_3, HNO_3, SO_2, HCl & aerosol NH_4^+, NO_3^-, SO_4^2, Cl^-, Na^+, Ca^{2+}, Mg^{2+})	27
ALPHA sites sampling gaseous NH_3 only	52
Intercomparison sites with both DELTA & ALPHA	9
Total number of sites	72

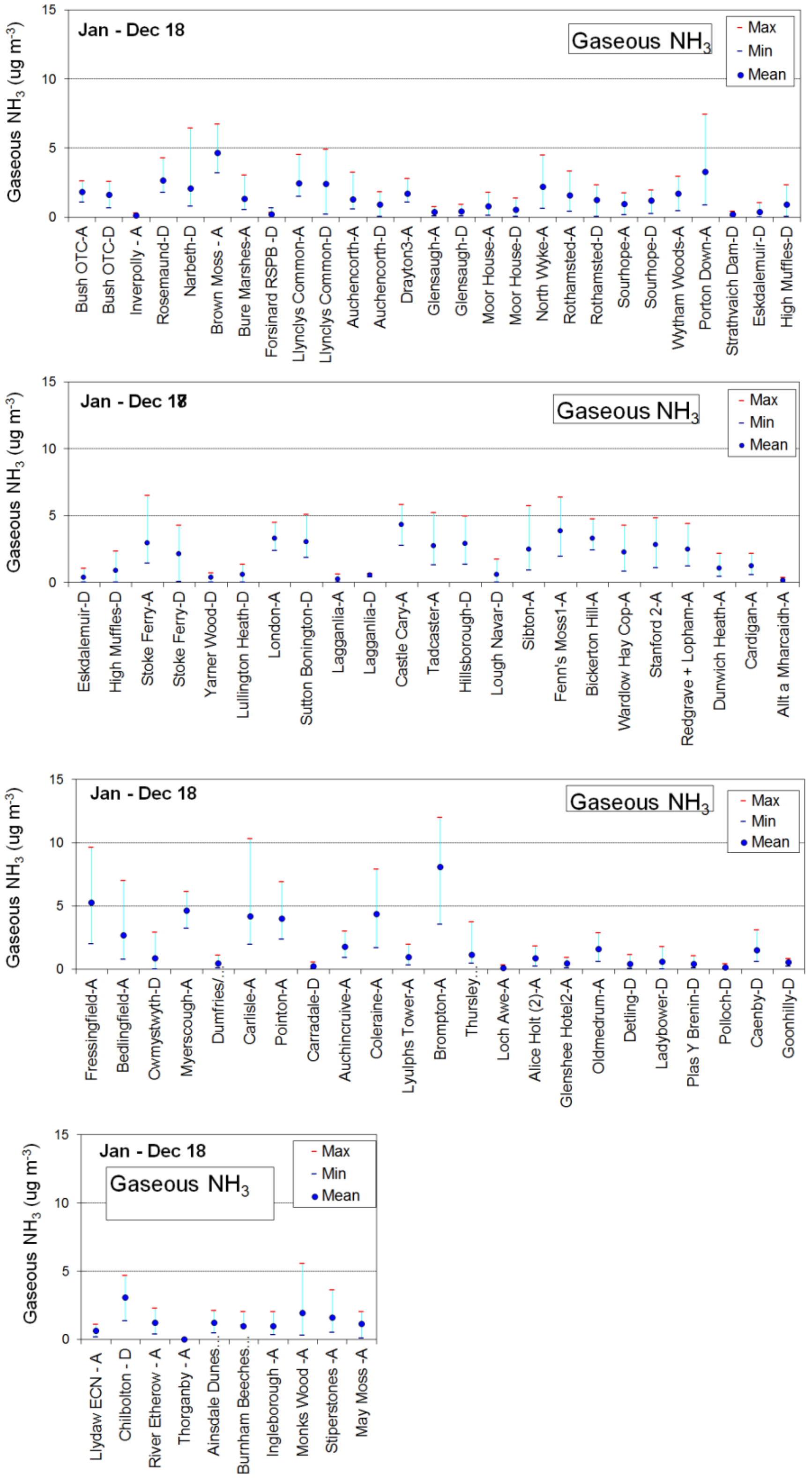


Figure 17 Annual mean concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2018, whilst the bars show the minimum and maximum concentrations observed (A = ALPHA sampler; D=DELTA)

NH_3 concentrations over the period 1998 to 2018 are summarised in a box plot (Figure 18). Data from 1996 and 1997 were excluded from analysis since this was the start-up phase of the network with incomplete annual data. The whiskers show the absolute max and min and the diamonds is the mean annual concentration of all sites. Changes in the number of sites and locations of sites occurred over the course of the network. Whilst UK emissions of NH_3 declined by about 11% over this period (Figure 8), NH_3 concentrations from the overall dataset show no detectable trend over the same period. The interquartile ranges and the spread of the data are variable from year to year and trends are not discernible, masked by spatial and temporal variability in concentrations. Met Office mean annual UK temperature and rainfall data are plotted on the same graph to show the influence of temperature and rainfall on inter-annual variability in NH_3 concentrations.

National maps of both NH_3 and NH_4^+ (Figure 19) concentrations derived from the NAMN confirm the high spatial variability of the annual average concentration of NH_3 (0.08 – 8.43 µg m^{-3}), consistent with it being a primary pollutant emitted from ground-level sources. The 29 NAMN DELTA sites are distributed widely across the UK to provide the regional patterns of NH_3 (and NH_4^+ at the 27 AGANET sites). For particulate NH_4^+, the annual mean concentrations ranged from the lowest of 0.12 (S41 Lagganlia) to highest of 1.40 (S33 Stoke Ferry) µg NH_4^+ m^{-3}. Aerosol NH_4^+ shows a spatially smooth concentration field as expected for a secondary inorganic component. It also has a similar distribution to the sulphate and nitrate aerosol UK maps (Figure 21), as would be expected due to the formation of stable and semi-stable particle phase salts, e.g. ammonium sulphate and ammonium nitrate, respectively.

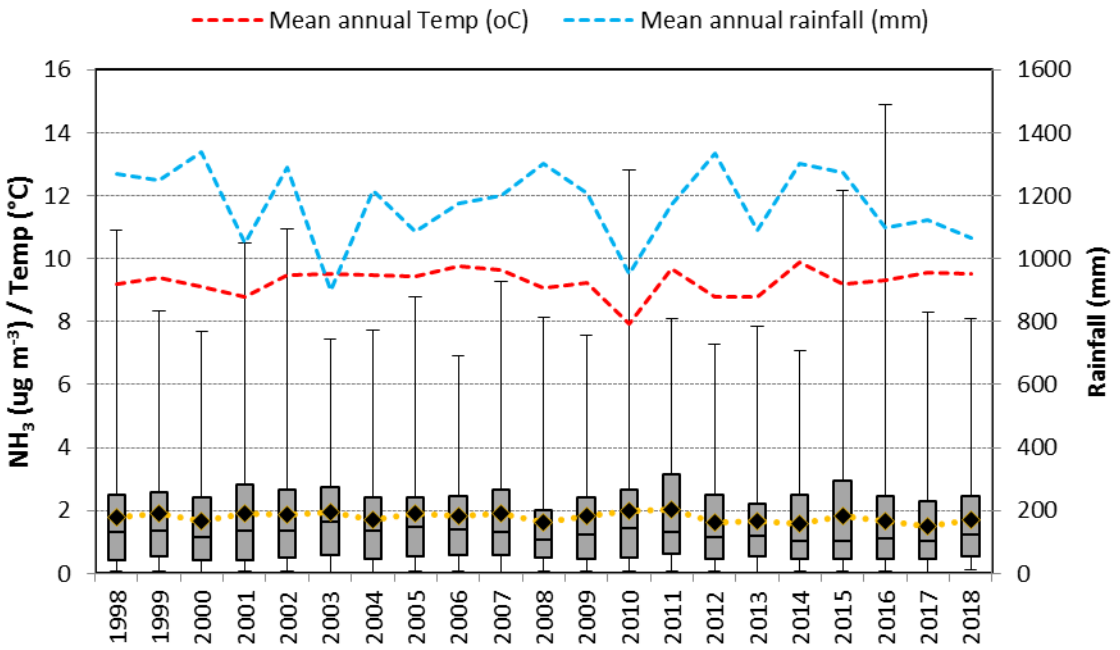


Figure 18: Changes in atmospheric NH_3 averaged over all sites in NAMN operational between 1998 and 2018 summarised in a box plot. The whiskers shows the absolute max and min and the diamond is the mean annual concentration. Annual mean UK meteorological data (source http://www.metoffice.gov.uk/) are plotted on top to illustrate the relationship between inter-annual variability in NH_3 concentrations with changing temperature and rainfall.

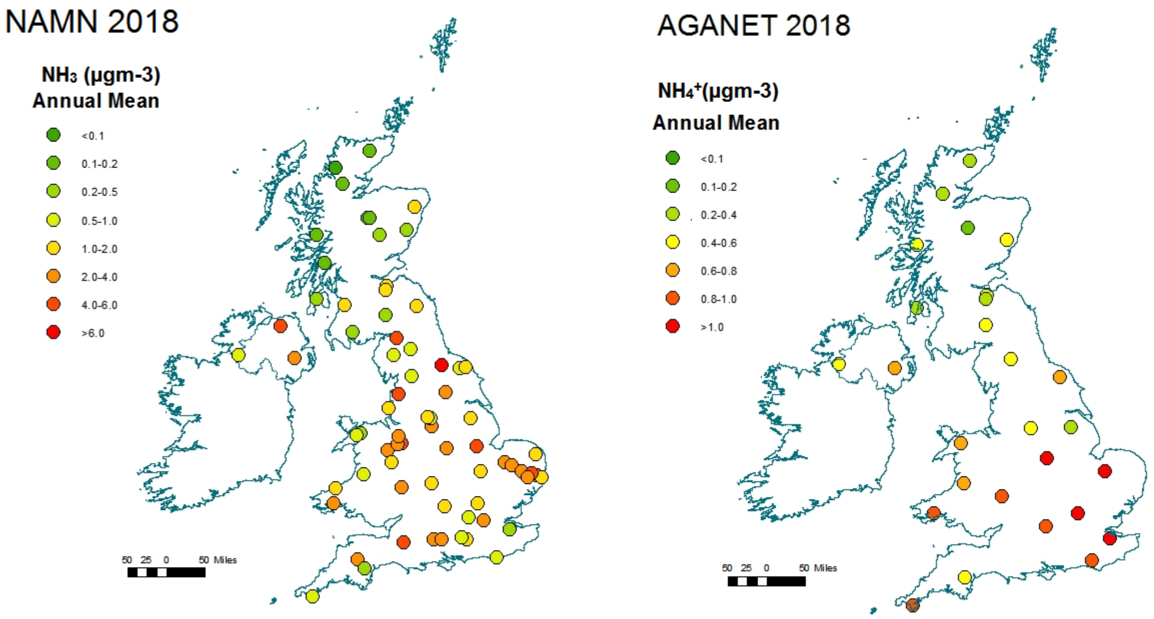


Figure 19: Spatial patterns of annual NH_3 and aerosol NH_4^+ concentrations from monthly NAMN/AGANET measurements. Since February 2018, ammonium is measured at the 27 AGANET sites only.

2.4 Acid Gas and Aerosol Network (AGANET)

The UK Acid Gas and Aerosol Network (AGANET) provides monthly speciated measurements of atmospheric reactive gases (HNO_3, SO_2) and aerosols (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, Ca^{2+}, Mg^{2+}) at 27 sites across the UK. The spatial distributions of acid gases and aerosol ions, which are primarily anthropogenic in origin, in particular HNO_3/NO_3^- and $SO_2/SO_4^{2-,}$ have the highest concentrations in the south and east of the UK. Atmospheric gases including SO_2 and 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.

Mean 2018 annual concentrations of trace gas and aerosols at individual sites in the network are compared in Figure 20, Figure 21 and Figure 22. The comparison of the gas phase concentrations shows that there is more NH_3 than either SO_2 or HNO_3 at these sites (on a molar basis), while HNO_3 concentrations are comparable to SO_2.

For the aerosol components, the ion balance of the particulate matter through acidic (NO_3^-, SO_4^{2-}) and basic (NH_4^+) aerosol components shows strong correlation (se Tang et al 2018b). Reduced nitrogen (NH_4^+) is in molar excess over SO_4^{2-} and NO_3^- (i.e. the acidic components are less that the basic) and NO_3^- is in molar excess over SO_4^{2-}. There is a near 1:1 relationship between Cl^- and Na^+, consistent with a primarily marine origin for these ions in the UK. The long-term trends in gaseous HNO_3, SO_2 and particulate NO_3^-, SO_4^{2-}, Cl^-, NH_4^+ (Figure 26) are shown by plotting annual averages of measurement data from all sites, and also from the original 12 sites for the 16 year period from 2000 to 2018.

Overall, the dataset shows no detectable trend in Cl^-. Gaseous SO_2 concentration continues to show a gradual downward trend, in line with UK SO_2 emission trends. The general decreasing trend in gaseous SO_2 concentrations is also accompanied by a decline in particulate SO_4^{2-} concentrations. There is a general downward trend in HNO_3 accompanied by a slight downward trend in NO_3^-.

In years 2016-2018 there is an increase in the network average particulate NO_3^-, SO_4^{2-} and NH_4^+ concentrations, primarily due to improved chemical capture resulting from a method change implemented from the beginning of 2016. However it can be seen that there is also significantly interannual variability. The average magnitude of the step changes across sites and a full assessment of whether a back-correction of historic data is in progress within the uncertainties given by the variability of PM across the UK spatially and temporally. For details of the method change see Tang et al. (2016).

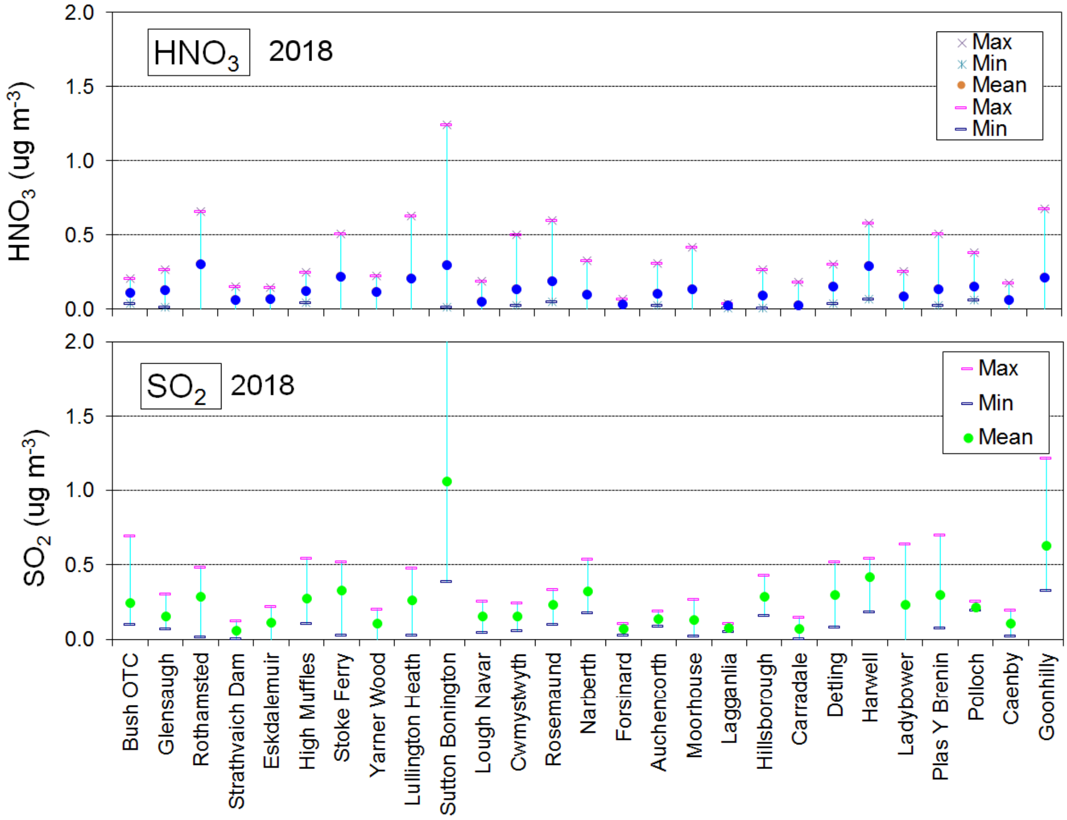


Figure 20: Mean monitored annual concentrations of gaseous HNO_3 and SO_2 at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2018, whilst the bars show the minimum and maximum concentrations observed. Data for gaseous NH_3 measured under NAMN is also shown for comparison.

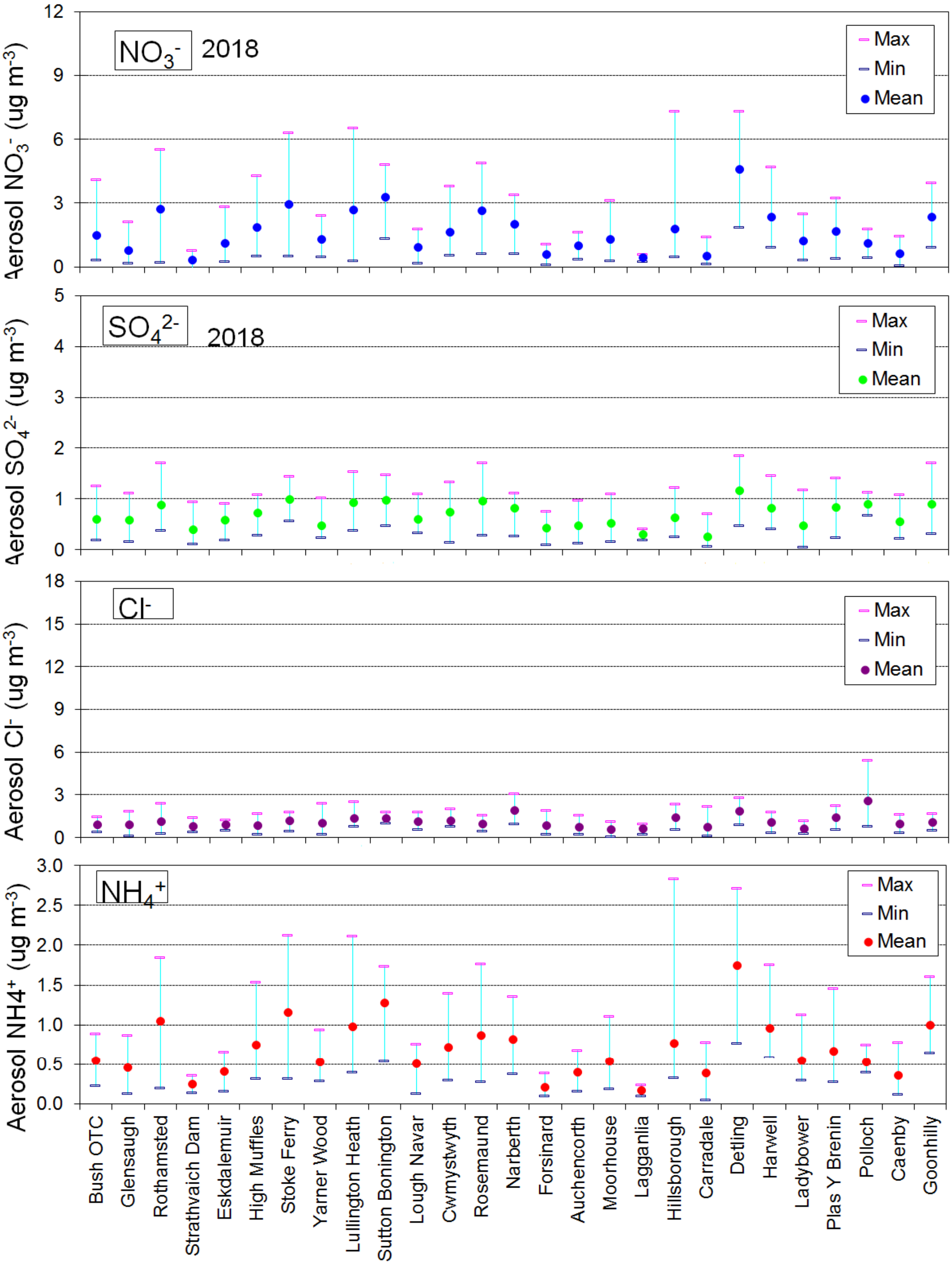


Figure 21: Mean monitored annual concentrations of particulate NO$_3^-$, SO$_4^{2-}$, Cl$^-$ and NH$_4^+$ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2018, whilst the bars show the minimum and maximum concentrations observed.

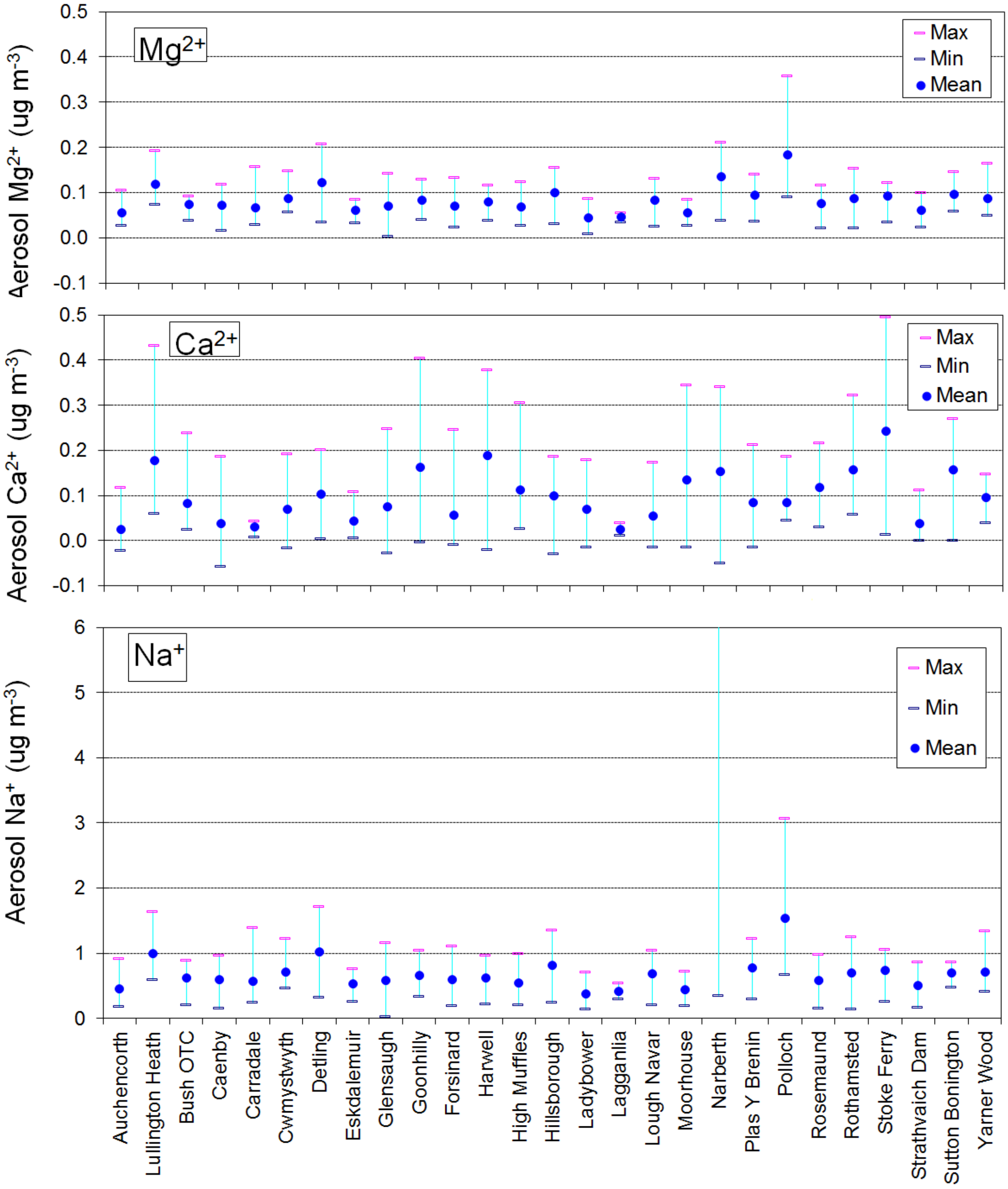


Figure 22 Mean monitored annual concentrations of particulate Mg, Ca and Na at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2018, whilst the bars show the minimum and maximum concentrations

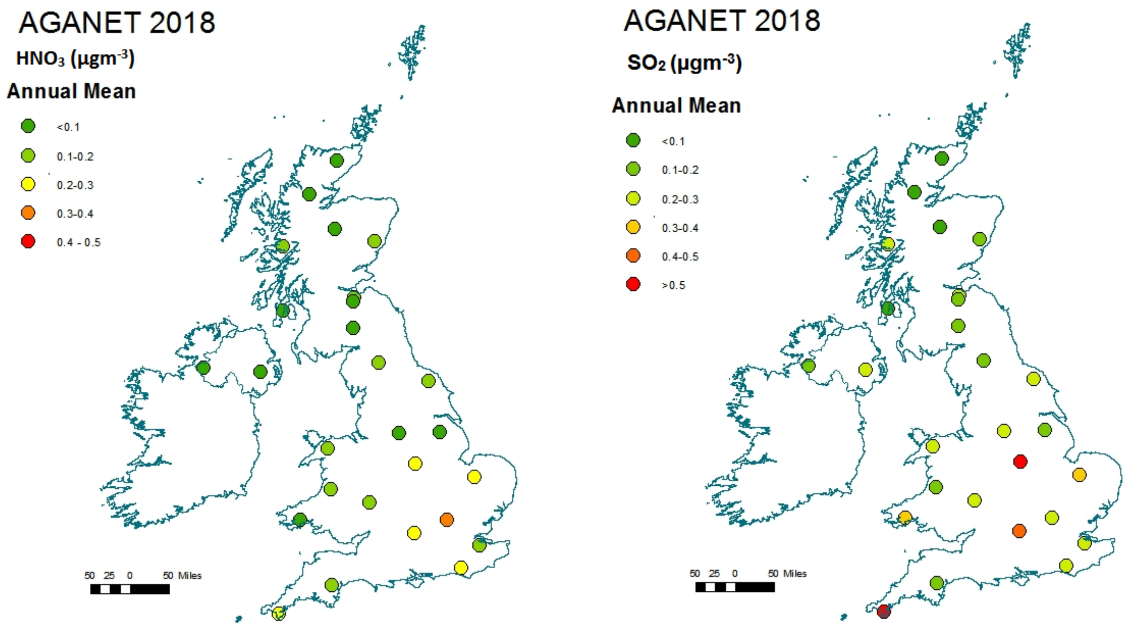


Figure 23 Annual mean monitored atmospheric reactive gas concentrations (HNO_3 and SO_2 from AGANET and NH_3 from NAMN) across the UK from annual averaged monthly measurements made in 2018.

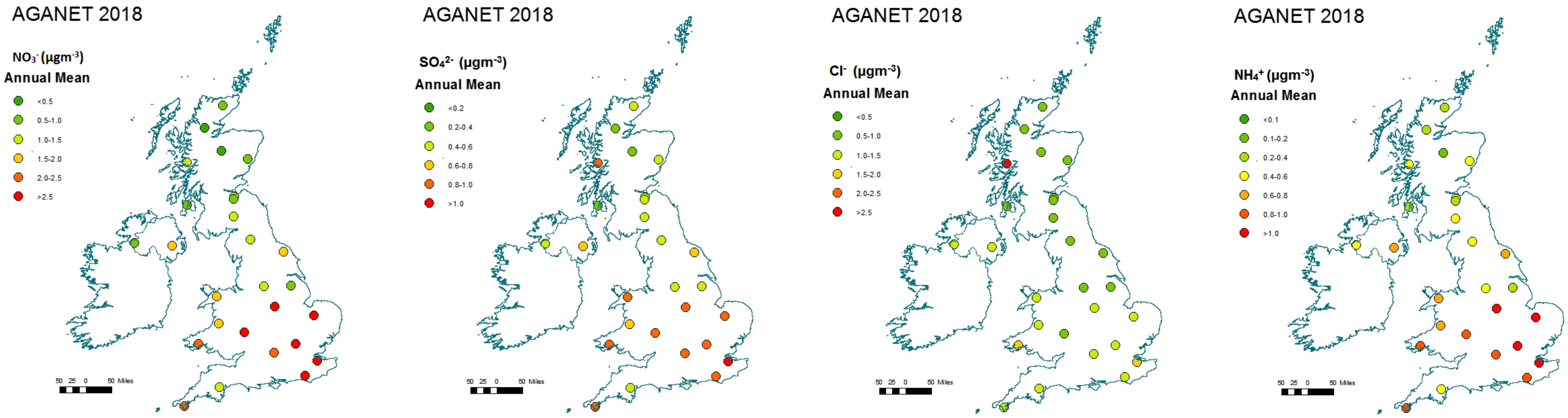


Figure 24: Annual mean monitored atmospheric aerosols (particulate NO_3^-, SO_4^{2-}, and Cl^- from AGANET and NH_4^+ from NAMN) concentrations across the UK from averaged monthly measurements made in 2018.

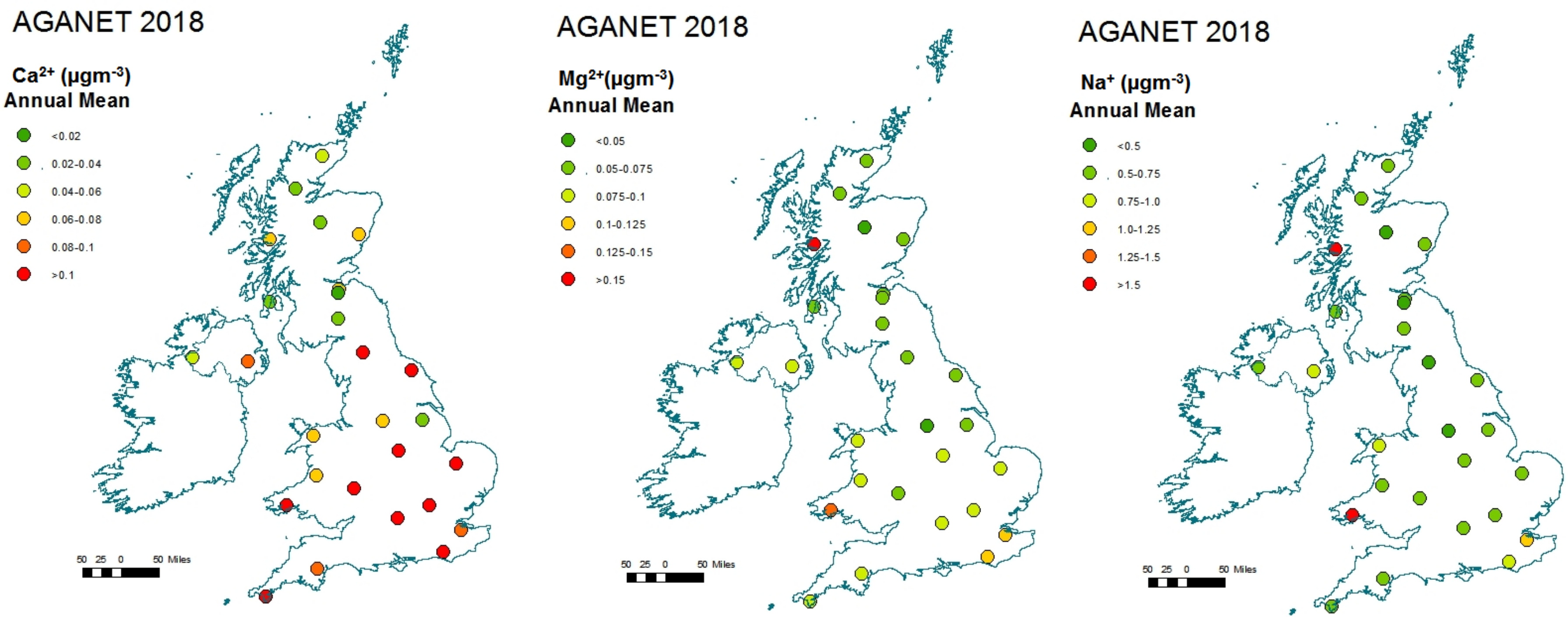


Figure 25: Annual mean monitored atmospheric base cation (Ca^{2+}, Mg^{2+} and Na^{+}) concentrations across the UK from the averaged monthly measurements made in 2018.

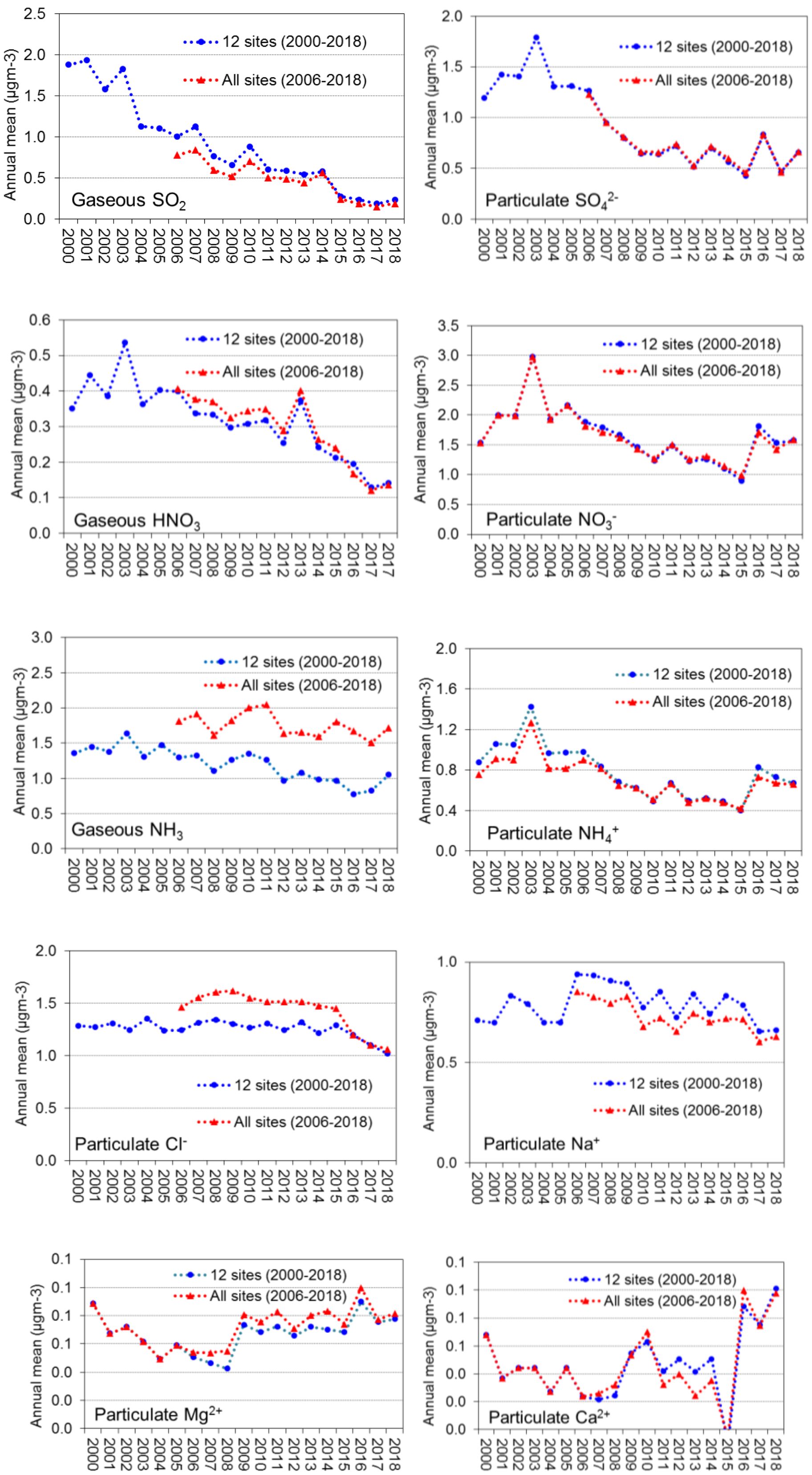


Figure 26: Long-term trend in annual mean concentrations of gases and aerosols monitored in AGANET. Each data point represents the time-weighted averaged annual mean from all sites (2006 – 2016 = 30 sites; from 2018 = 27 sites) and also the original l2 monitoring sites in the network. Since 2016, HCl is no longer measured in the new DELTA sampling train configuration. NAMN NH_3 data for AGANET sites are also shown, for comparison.

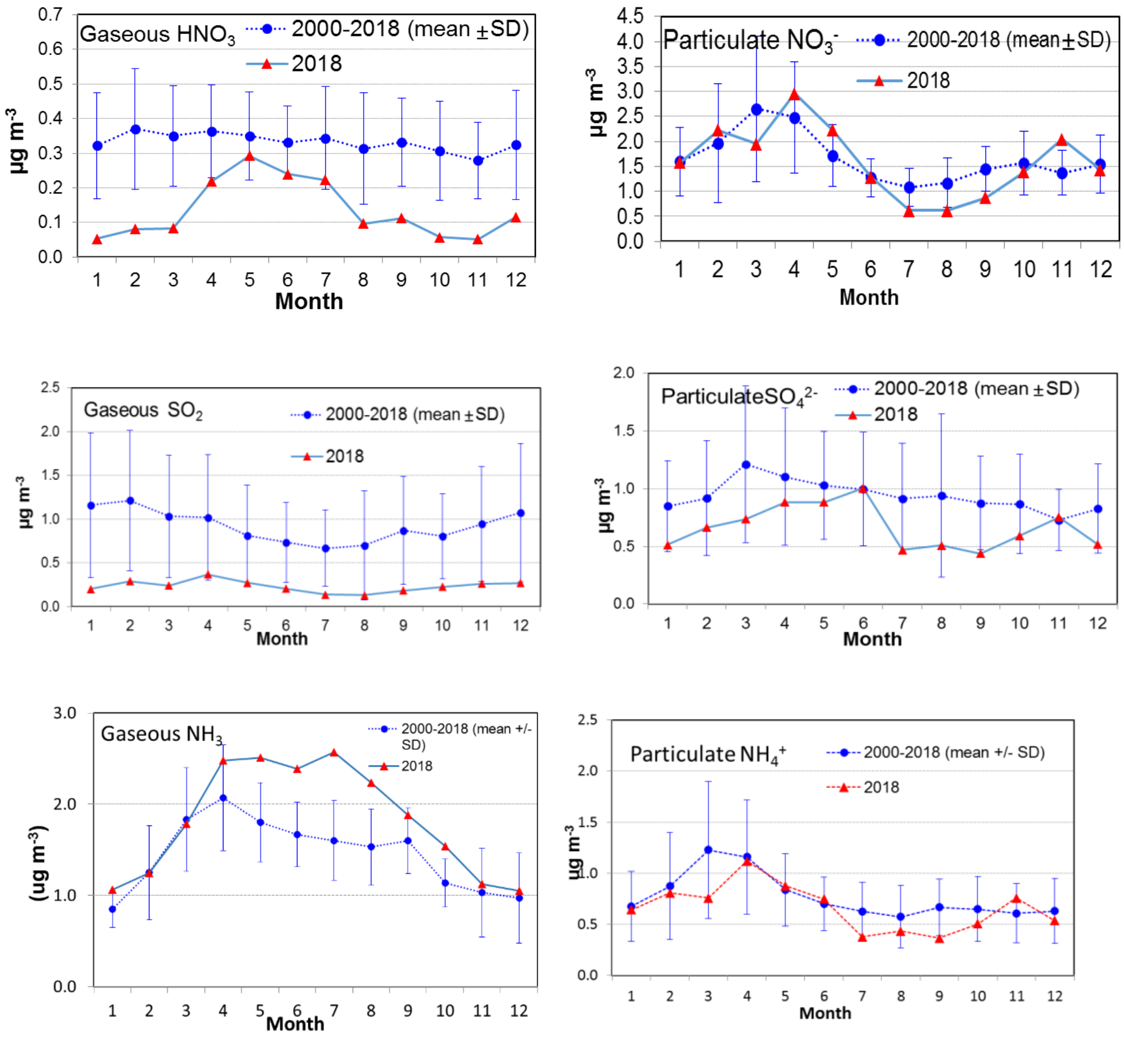


Figure 27: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (2000-2018: mean +/- SD of 27 AGANET sites) against year 2018.

3. UK EMEP Supersites 2018 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^2, to determine the composition of $PM_{2.5}$ 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 $PM_{2.5}$ is determined for the following species:

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

The $PM_{2.5}$ time coverage at both EMEP Supersites exceeds the *minimum* time coverage (14%) specified in the Directive for indicative $PM_{2.5}$ 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 Gothenburg Protocol of automatic air quality monitoring stations measuring oxides of nitrogen (NO_X), nitrogen dioxide (NO_2), sulphur dioxide (SO_2), ozone (O_3), carbon monoxide (CO) and atmospheric particulate matter (PM_{10} and $PM_{2.5}$).

Non-automatic measurements of (rural) heavy metal concentrations in PM_{10} and precipitation; particulate-phase base cations, anions and trace gases; polycyclic aromatic hydrocarbons (PAHs) in PM_{10}, 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_{10} and $PM_{2.5}$ 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 2016. 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_3, NH_3, SO_2) and PM_{10} and $PM_{2.5}$ aerosol concentrations (K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}), **Chilbolton and Auchencorth Moss.**
- On line mercury measurements (Chilbolton: elemental mercury; Auchencorth Moss: elemental and speciated mercury).

Table 3 Pollutants measured at the UK EMEP Supersites during 2018

Pollutant	**CHO[1]**	**AUC[1]**	**EMEP Level**	**Averaging period**	**Monitoring network (Ha/Au)**	**Contract holder**
SO_2, HCl, HNO_3, HONO, NH_3 (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**	**CEH/Ricardo E&E**
$PM_{2.5}$ K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**	**CEH/Ricardo E&E**
PM_{10} K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} (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*[2]**	**I**	**Hourly**	**UKEAP/CEH**	**CEH/Ricardo E&E**
Precipitation chemistry	**X**	**X**	**I**	**Daily**	**UKEAP**	**CEH/Ricardo E&E**
NO and NO_2 (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 $PM_{2.5}$, PM_{10}	X	X	I	Hourly	AURN	Bureau Veritas
VOCs in air	X		II	Hourly	Automated HC Network	Ricardo E&E
PAH in PM_{10}, 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[2]	II	Hourly	Particle numbers/CEH	NPL
Particle size distribution	X	X[2]	II	Hourly	Particle numbers	NPL
PM_{10} carbon-content (elemental carbon, EC, organic carbon, OC, total carbon, TC)	X	X	II	Weekly	Particle numbers	Bureau Veritas?
DELTA sampler (particulate-phase ions: Ca^{2+}, Mg^{2+}, Na^+, Cl^-, NH_4^{2+}, NO_3^-, SO_4^{2-})	**X**	**X**	**I**	**Monthly**	**UKEAP**	**CEH**
Trace gases (HCl, HNO_3, NH_3, and SO_2)	**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_{10}	X	X	II	Weekly	Heavy Metals	CEH
Persistent Organic Pollutants (POPs) in air	X	X	I	Monthly	TOMPS	University of Lancaster
CO_2 measurements		X	III	Hourly	ICOS	CEH
Trace gas fluxes (O_3,)		X	III	Hourly	NERC NC[2]	CEH
NO and NO_2 (photolytic)		x	I	Hourly	NERC NC[2]	CEH National Capability funded

[1]CHO: Chilbolton; AUC: Auchencorth Moss; [2]NERC CEH National capability funded * NPL: National Physical Laboratory, Teddington, Middlesex.

In 2018 more than 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_{10} and $PM_{2.5}$ and trace gases concentrations are presented in Table 4 and following Figures. The MARGA instrument at both the Auchencorth Moss and Chilbolton sites were upgraded during 2018. The low data capture at the start of 2018 at the Auchencorth Moss site was due the replacement of the instrument. Excluding January and February 2018, where there was down time due to instrument replacement and cations were excluded due to the incorrect set-up of the instrument, it was found data capture for March to December 2018 was on average 86 %.

At the Chilbolton site, the average data capture for 2018 for all pollutants was 72.3% however this excludes the cations (K, Mg and Ca) that were affected by an inherent ion chromatography issue with the new instrument installed in March 2018, which was causing instability in the cation baseline, and other technical issues summarised in the Appendix of this report. Including the cations affected by the baseline instability the data capture was 76.3% for the gaseous pollutants, 47.9% is for PM10 pollutants and 47.8% for PM2.5 pollutants.

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_{10})	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_4^+	1.32	71	0.50	72
Na^+	0.88	71	0.45	72
K^+	0.07	10	0.04	72
Ca^{2+}	0.66	8	0.04	73
Mg^{2+}	0.71	10	0.05	73
Cl^-	1.57	70	0.86	78
NO_3^-	3.26	71	0.98	78
SO_4^{2-}	1.58	71	0.72	78
Ion ($PM_{2.5}$)	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_4^+	1.39	65	0.46	73
Na^+	0.39	73	0.26	73
K^+	0.05	10	0.03	74
Ca^{2+}	0.33	8	0.02	74
Mg^{2+}	0.37	10	0.03	74
Cl^-	0.70	72	0.46	80
NO_3^-	2.73	73	0.81	80
SO_4^{2-}	1.39	73	0.64	80
Trace Gases	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**	**Annual mean ($\mu g\ m^{-3}$)**	**Data capture (%)**
NH_3	5.46	77	1.55	76
HCl	0.07	76	0.14	82
HNO_3	0.21	76	0.09	82
HONO	0.49	76	0.10	82
SO_2	0.13	76	0.08	82

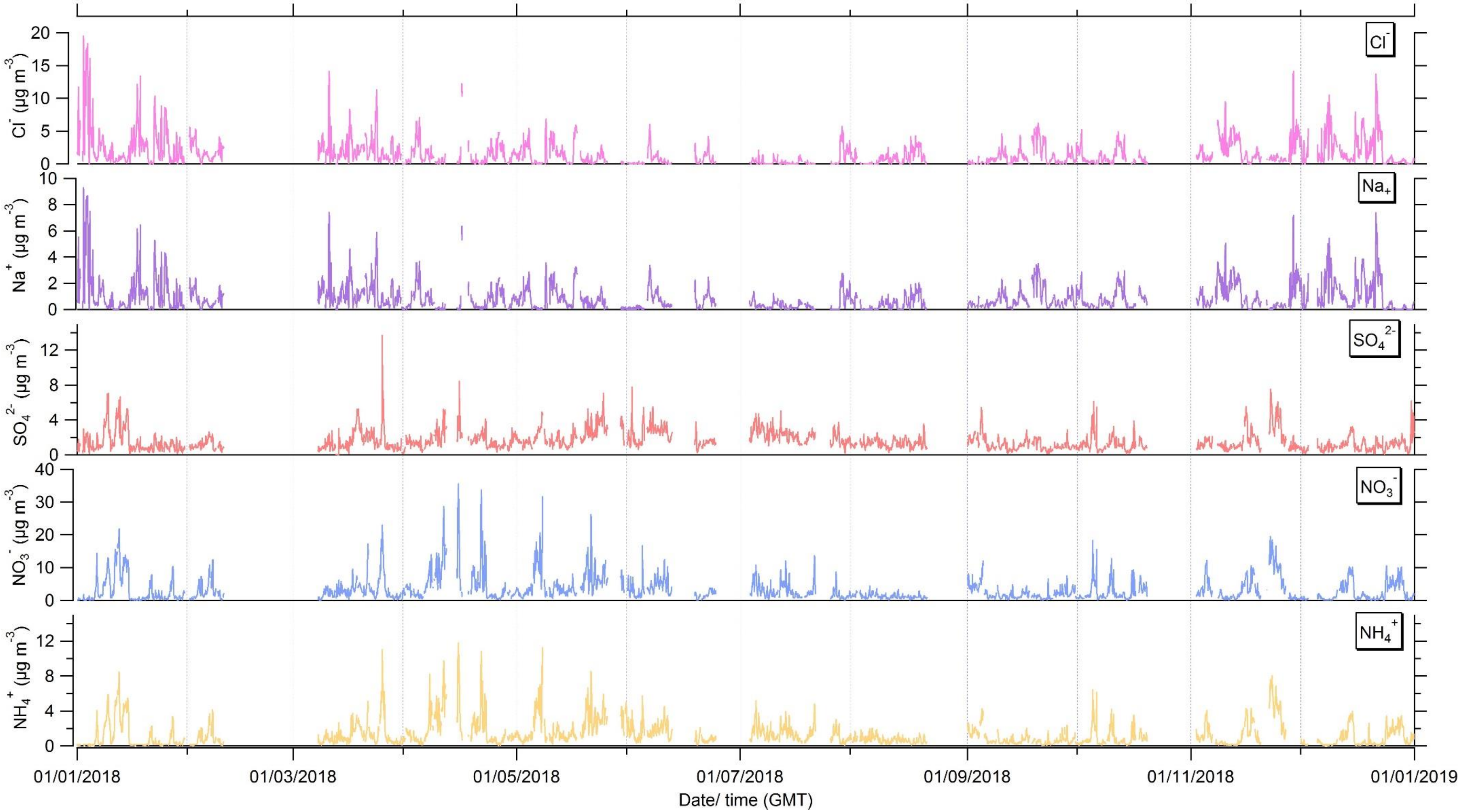


Figure 28 Ratified PM10 speciated measurements by the MARGA at the Chilbolton supersite

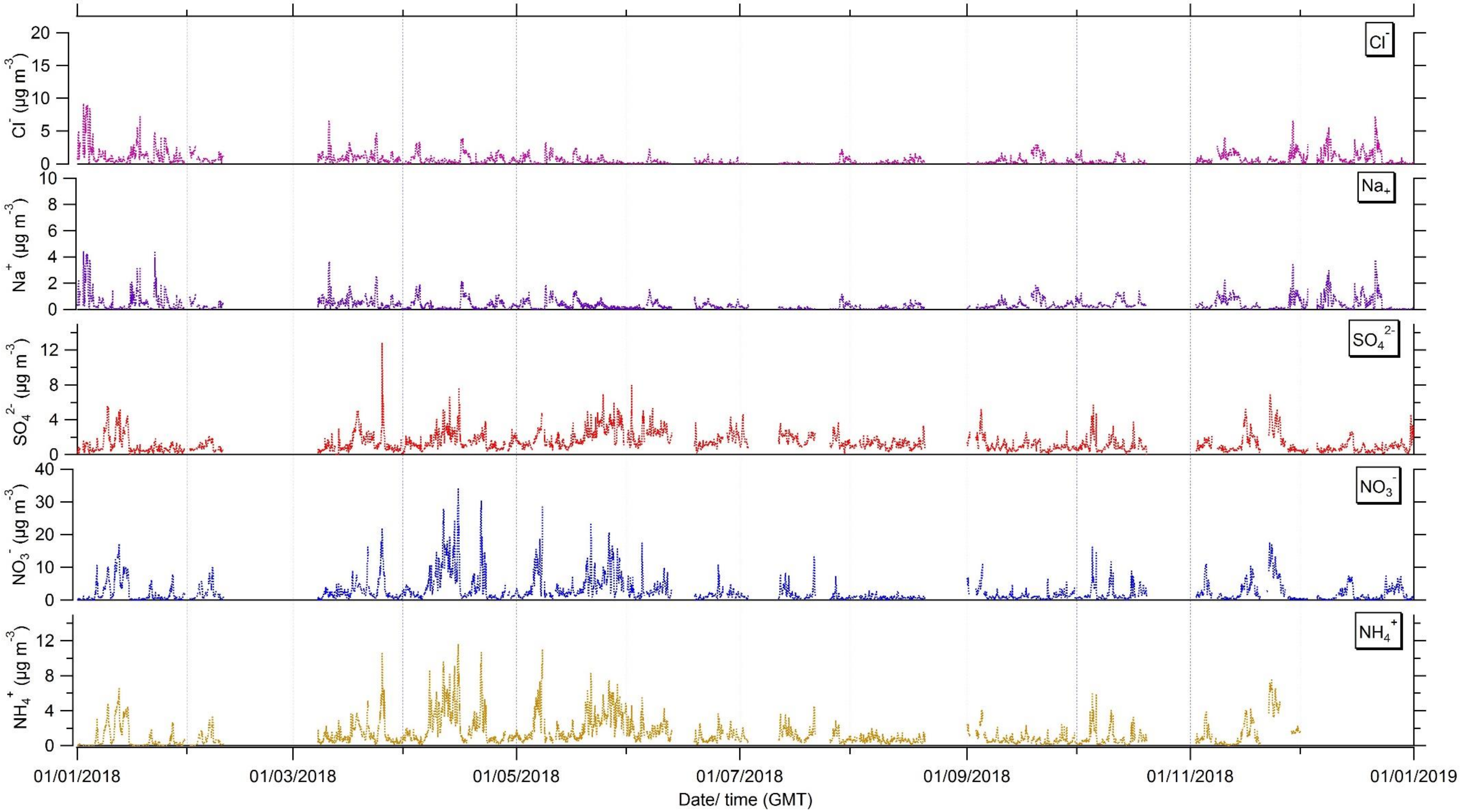


Figure 29 Ratified PM2.5 speciated measurements by the MARGA at the Chilbolton supersite

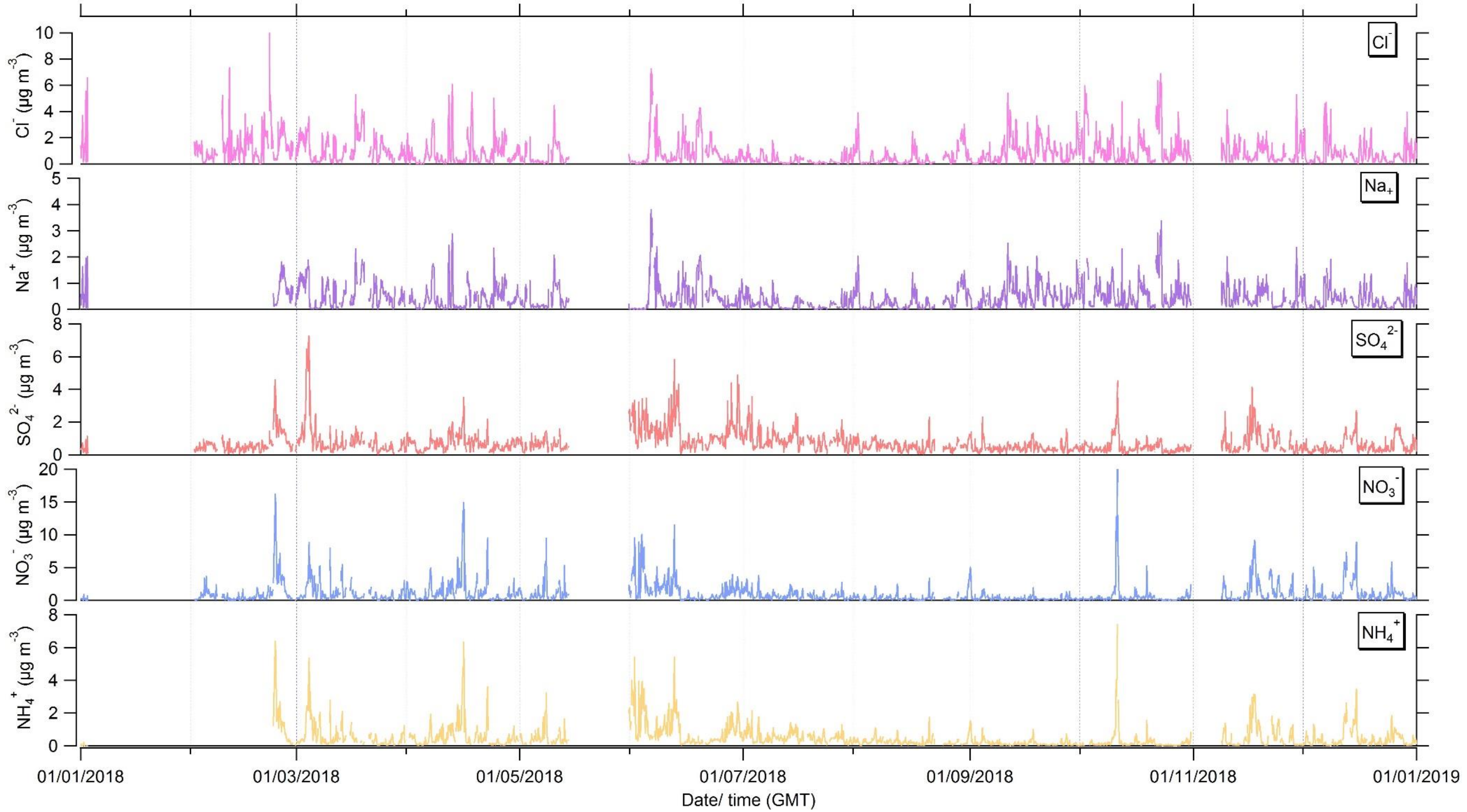


Figure 30 Ratified PM10 speciated measurements by the MARGA at the Auchencorth Moss supersite

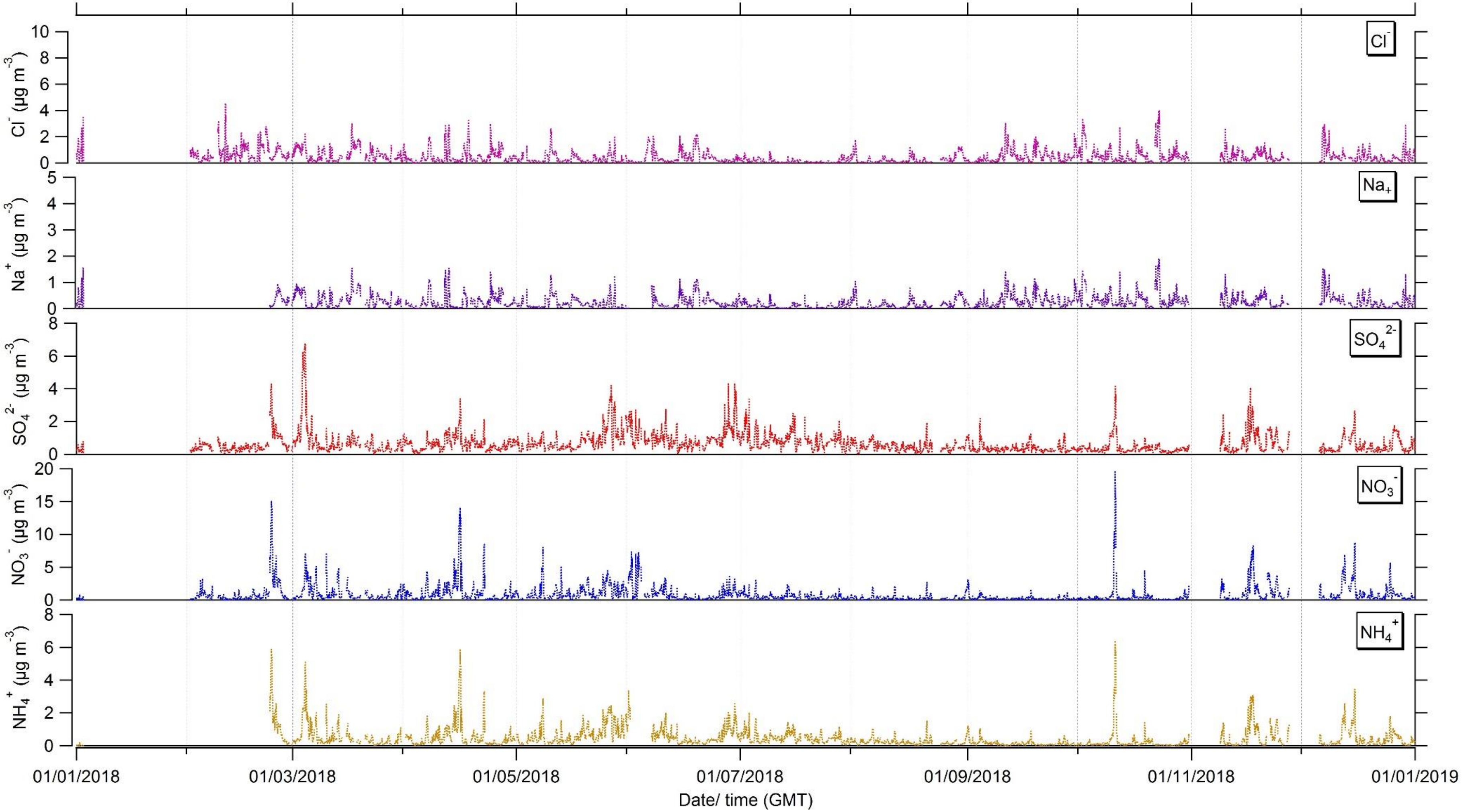


Figure 31 Ratified PM2.5 speciated measurements by the MARGA at the Auchencorth Moss supersite

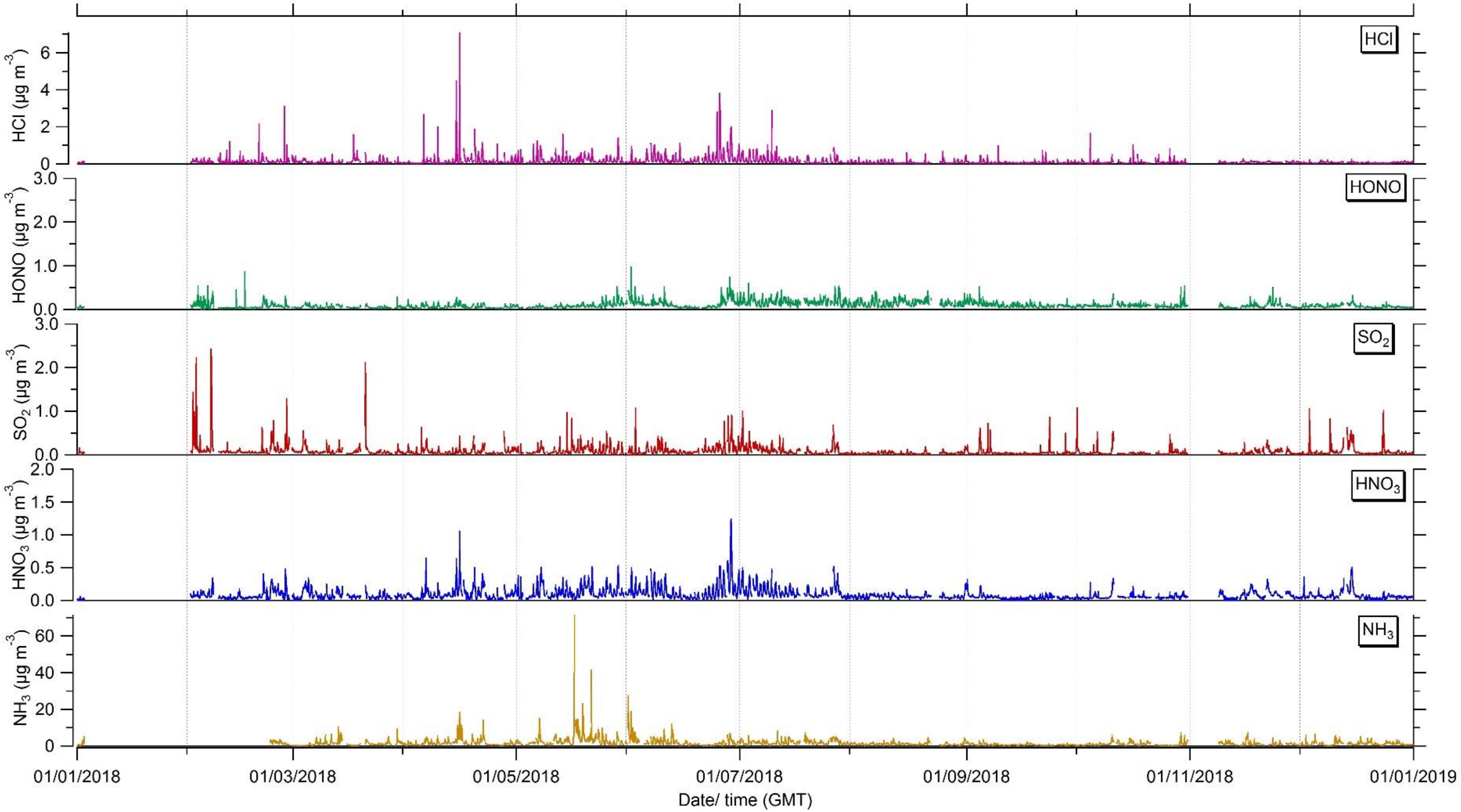


Figure 32 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite

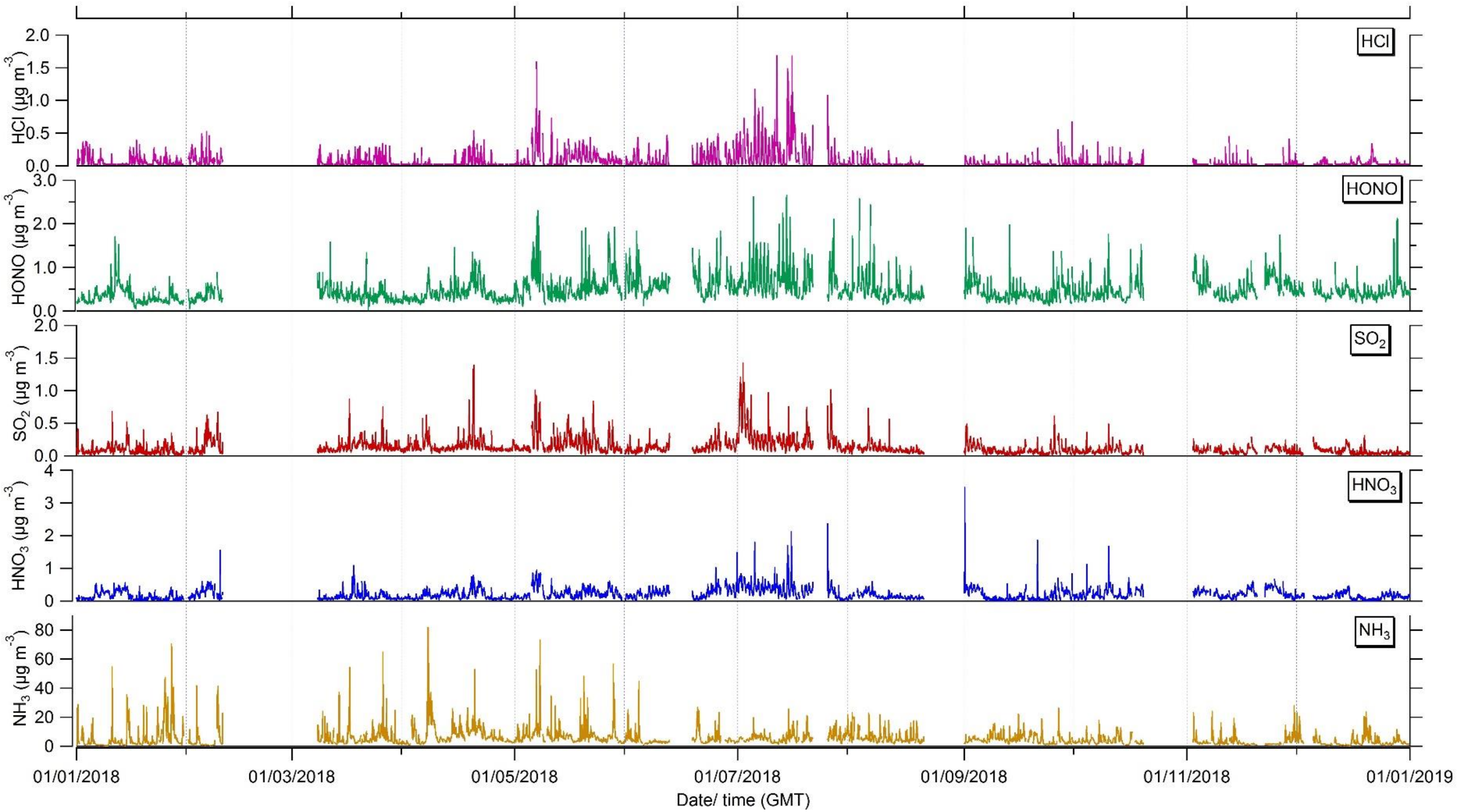


Figure 33 Ratified trace gas measurements by the MARGA at the Chilbolton supersite

Mercury Measurements

The annual means and data capture for the 2018 ratified mercury measurements are shown below in Table 5. Time series plots of the 2018 Auchencorth Moss measurements are shown in Figure 32 In the speciation sampling part of the system there was a major contamination issue which has led to the low data capture for particulate bound mercury (PBM) and gaseous oxidized mercury (GOM) species. Gaseous elemental mercury (GEM) was still sampled during this period as the analyser was working and does not require the speciation sampling unit to be operational.

The mercury data from Chilbolton is shown in the time series in Figure 35. For the period February to April the analyser had issues with its internal pump. This meant 2 months of data was lost due to the sample volume fluctuating. Later in the year this problem returned but the pump wasn't the source of the problem. The analyser was sent back to Canada for inspection and repair at Tekran. It was found it have an electrical fault on the motherboard which was replaced. It was returned to site and back sampling at the beginning of December 2018.

Table 5 Ratified mercury measurements

	Annual mean	**Data capture**
Auchencorth Moss		
Elemental mercury (GEM) ngm^{-3}	1.40	85.95%
Reactive mercury (GOM) pgm^{-3}	1.14	25.97%
Particulate mercury (PBM) pgm-3	3.27	26.03%
Chilbolton		
Total gaseous mercury (TGM) ngm^{-3}	1.48	24.34%

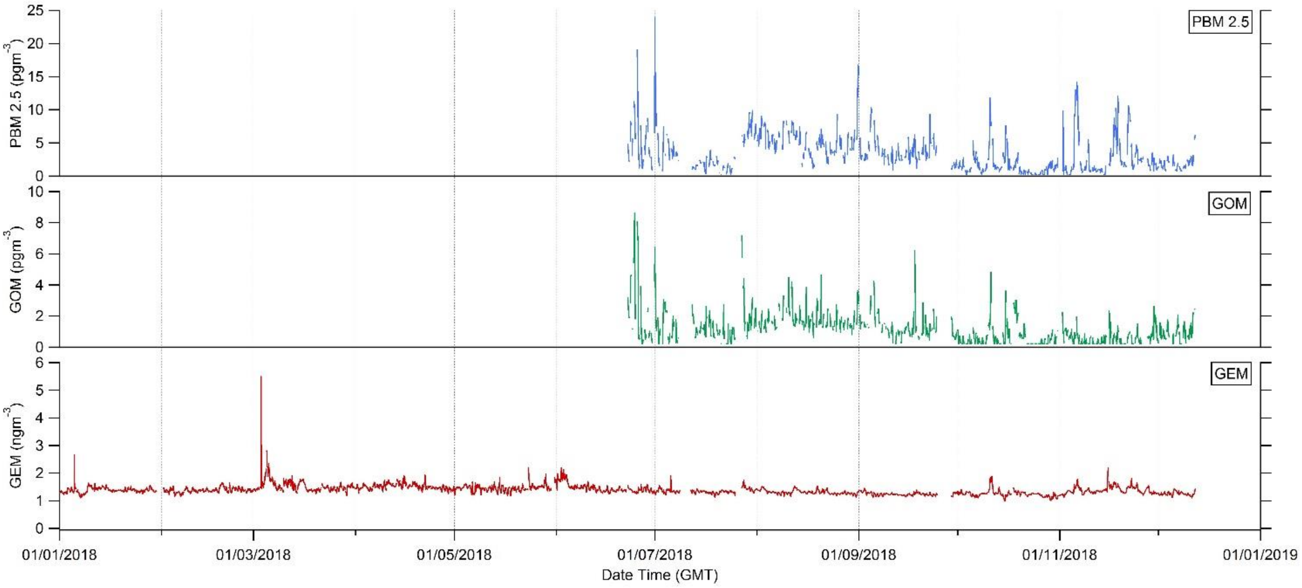


Figure 34 Ratified mercury measurements by the Tekran at the Auchencorth Moss supersite

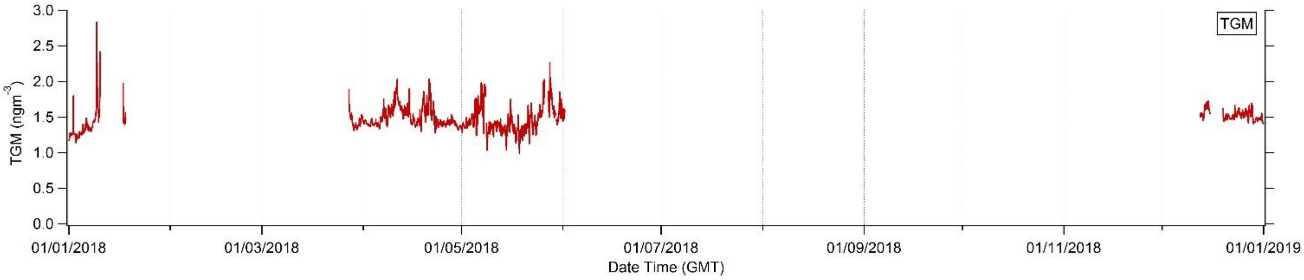


Figure 35 Ratified mercury measurements by the Tekran at Chilbolton Observatory

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

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***)

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

Leeson, S.R.J., 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**)

Meteorological Data: Contact Mr Chris Conolly Ricardo Energy & Environment

Auchencorth Moss EMEP Supersite

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

Twigg, M.M., Leeson, S.R., Simmons, I, Kentisbeer, J., 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**)

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

Leeson, S.R. J., Simmons, I, Jones, M.R., Harvey, D. UK Eutrophying and Acidifying Atmospheric Pollutant project's ANNOX 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**)

Acid Gas and Aerosol Network

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

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

Precipitation Network

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

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

NO_2-Network

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

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

Appendix 2: QC summary for 2018

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. During 2018 the MARGA and DWOCs, installed in 2006, were upgraded to new models.

During 2018 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 m^3 hr^{-1} (1 m^3 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°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 $m^3 hr^{-1}$. 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 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: Li^+ 28 mg/L and Br^- 325 mg/L, working solution: Li^+ 70 ppb Br^- 800 ppb. The Chilbolton instrument's working solution was made-up periodically by diluting) a high concentration stock solution of LiBr. The nominal concentration of Li^+ in the stock and work solutions were 320000 ppb and 320 ppb, respectively, and 3680 mg L^{-1} and 3.68 mg L^{-1} (1 mg L^{-1} = 1 ppm) of Br^-.

Sub-samples of the internal standard used at both sites were analysed by CEH Lancaster to ensure that both the stock and working solutions contained the correct, within ±20%, concentrations of Li^+ and Br^- when compared to the nominal concentrations. Spot samples of the stock and working solution were sent once a quarter via mail-out and analysed retrospectively. The Li^+ and Br^- concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC), respectively.

As part of the data ratification process, MARGA measurements were rejected if the measured concentrations of Li^+ and Br^-, in the internal standard, deviated by more than ± 20% of the nominal concentration.

A regular maintenance scheme is in place on the MARGA instrument (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^3/hr. The frequency of calibration is increased if the positions of annular denuders in the system are altered. As part of the MARGAs ongoing QC a monthly blank. As well as being used to identify any potential contamination in the system, it was used in the calculation of a detection limit for certain species which is used in the ratifying process.

In 2019, the Auchencorth Moss MARGA measurements had downtime at the beginning of the year due to instrument changeover.

In 2018, the new Chilbolton MARGA had a number of instrument issues, leading to a reduced data capture, these included:

- anion pump failure (February)
- Removal of old MARGA instrument (February)
- Suppressor failure (June)
- SJAC heater failure and replacement (June/July)
- MARGA PC replaced to attempt to eliminate clock stall error (August)
- Anion pump seal failure and pump seal replacements October/November

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_{10} 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% H2O2)	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 (H3PO4)		x							
2x empty waste container 30 Litre and add approximately 30 grams of $NaHCO_3$	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_2O_2 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 30 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 36th EMEP Inter-comparison

The inter-comparison in 2018 was the 36th time such an inter-comparison took place. The samples provided included nitrogen dioxide in absorbing solution (Table 16) and synthetic rainwater samples (Table 17). The results can be found on the NILU website.

Nitrogen Absorbing Solutions:

The inter-comparison in 2018 was the 36th 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 and improved from 2017 with between a 1.0% and 2.4% absolute difference which is 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 µg NO_2-N/ml	Measured concentration µg NO_2-N/ml	Mean Difference (%)	EMEP Assessment
C1	0.127	0.124	-2.4%	S
C2	0.166	0.163	-1.8%	S
C3	0.372	0.367	-1.3%	S
C4	0.297	0.294	-1.0%	S

Synthetic Rainwater Samples:

The performance of Ricardo's chosen laboratory (SOCOTEC UK Limited previously known as Environmental Scientifics Group Ltd) is reviewed through involvement in EMEP intercomparison in addition to other performance schemes that Socotec are involved in. The results of the 36th intercomparison produced three questionable and one unsatisfactory result. These questionable results were for a single SO_4^{2-} result, two K^+ results. The only unsatisfactory result related to a single conductivity result. The analytical laboratory has been made aware of the analytical performance and the results that have been obtain from the intercomparison.

Table 8 36th EMEP Inter-comparison

Species	**Sample code**	**Expected concentration µeq l^{-1}**	**Measured concentration µeq l^{-1}**	**Mean difference (%)**	**Assessment [1]**
SO4-2	G1	0.251	0.224	-10.76%	Q
	G2	0.366	0.332	-9.29%	S
	G3	0.527	0.49	-7.02%	S
	G4	0.463	0.428	-7.56%	S
NH_4^+	G1	0.107	0.1	-6.54%	S
	G2	0.134	0.127	-5.22%	S
	G3	0.481	0.486	1.04%	S
	G4	0.561	0.563	0.36%	S
NO_3^-	G1	0.165	0.166	0.61%	S
	G2	0.26	0.261	0.38%	S
	G3	0.577	0.58	0.52%	S
	G4	0.67	0.673	0.45%	S
Na^+	G1	0.286	0.274	-4.20%	S
	G2	0.408	0.395	-3.19%	S
	G3	0.769	0.738	-4.03%	S
	G4	1.019	0.994	-2.45%	S
Mg^{2+}	G1	0.072	0.075	4.17%	S
	G2	0.103	0.099	-3.88%	S
	G3	0.186	0.173	-6.99%	S
	G4	0.155	0.144	-7.10%	S
Cl-	G1	0.386	0.382	-1.04%	S
	G2	0.463	0.462	-0.22%	S
	G3	1.16	1.14	-1.72%	S
	G4	1.54	1.51	-1.95%	S
Ca^{2+}	G1	0.128	0.119	-7.03%	S
	G2	0.153	0.142	-7.19%	S
	G3	0.192	0.181	-5.73%	S
	G4	0.217	0.188	-13.36%	S
K^+	G1	0.102	0.083	-18.63%	Q
	G2	0.17	0.142	-16.47%	Q
	G3	0.238	0.203	-14.71%	S
	G4	0.272	0.234	-13.97%	S
pH*	G1	5.29	5.21	-1.51%	S
	G2	5.14	5.08	-1.17%	S
	G3	5.1	5.06	-0.78%	S
	G4	5.17	5.1	-1.35%	S
Cond	G1	7.005	11.12	58.74%	U
	G2	9.7	10.54	8.66%	S
	G3	16.9	17.55	3.85%	S
	G4	18.37	19.87	8.17%	S

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

4. NO_2-Net

Establishment of a correction factor for nitrogen dioxide concentrations measured in the Rural NO2 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_x to NO_2 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_2 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_2-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_2 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 36 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.

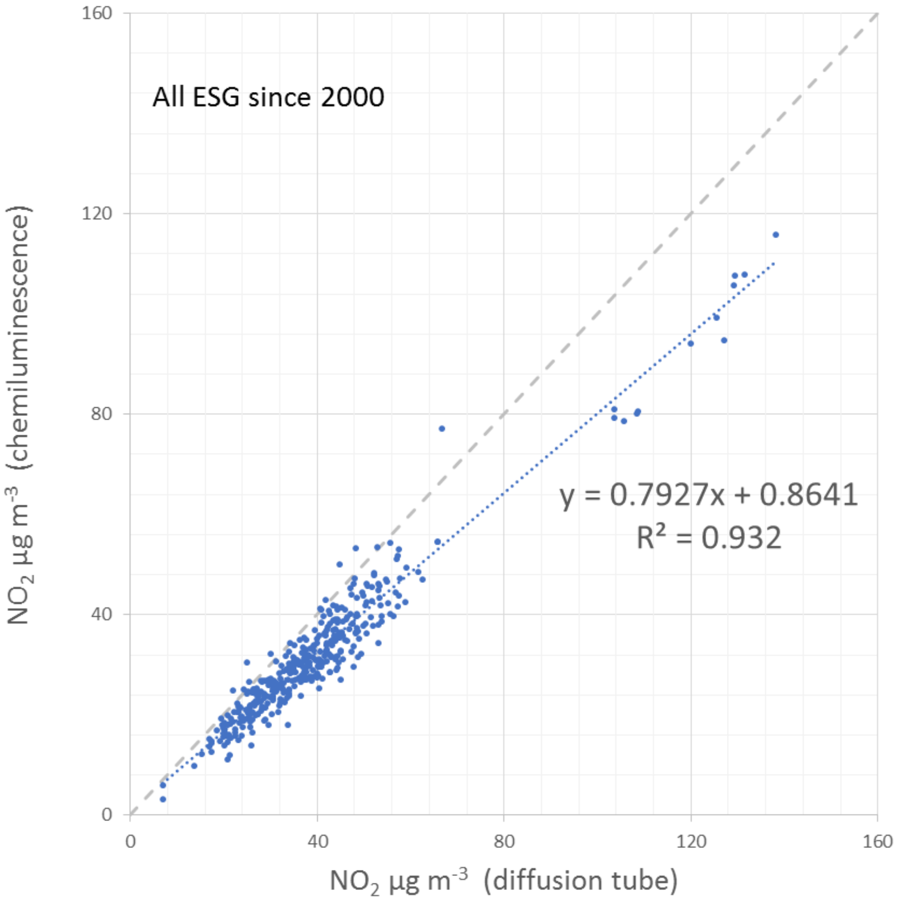


Figure 36 A comparison of annual mean nitrogen dioxide concentrations measured by diffusion tube and automatic analyser

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 9. 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 37 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 9 Annual mean nitrogen dioxide concentrations ($\mu g\ m^{-3}$) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis)

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

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

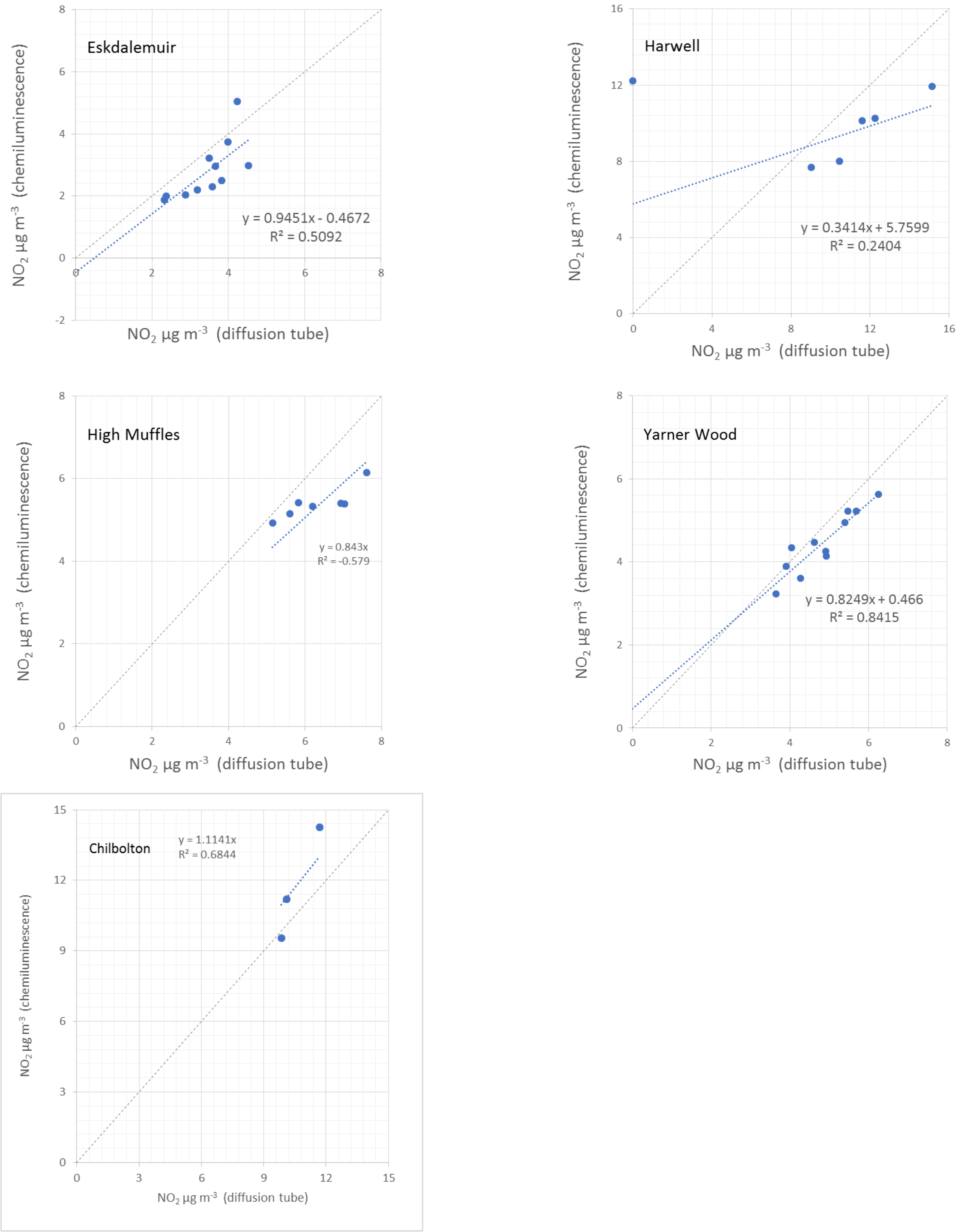


Figure 37 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each

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_2 Network. This is because:

- the 'quality' of the measurement made by automatic analyser in the Rural NO_2 Network will always be to a "reference" standard;
- the measurement environment will be always rural background whereas the national study will comprise a range of environments most of which will be roadside or urban background;
- Samples are dispatched, handled and exposed in a consistent way;
- As the results from the AURN and Rural NO_2 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_2 sampling sites (Chilbolton, Eskdalemuir, Yarner Wood and High Muffles)

Following the guidance provided in TG16 we have calculated monthly mean NO_2 concentrations for the automatic analysers corresponding to the periods the diffusion tubes were exposed. We have also updated the calculation spreadsheet[1] 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[2] 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	28%	6%	5%	7%

The average of the three values is calculated to be 11.51 % giving a bias adjustment factor of 0.897[3].

We would recommend multiplying each of the remaining diffusion tubes in the Rural NO_2 Network by this factor. However it should be noted that at Chilbolton the samplers are measuring different environment- they are at least 50 m apart and the inlet for the automatic analyse is 6 m above ground level whereas the diffusion tube is 1 m above ground level, whilst the site has been used in the assessment the user of data should be aware of this.

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

[2] 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.

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

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 38 below contains the average percentage data capture across all sites for each chemical of interest. Average data capture was 78% for AGANet and 84% for NAMN.

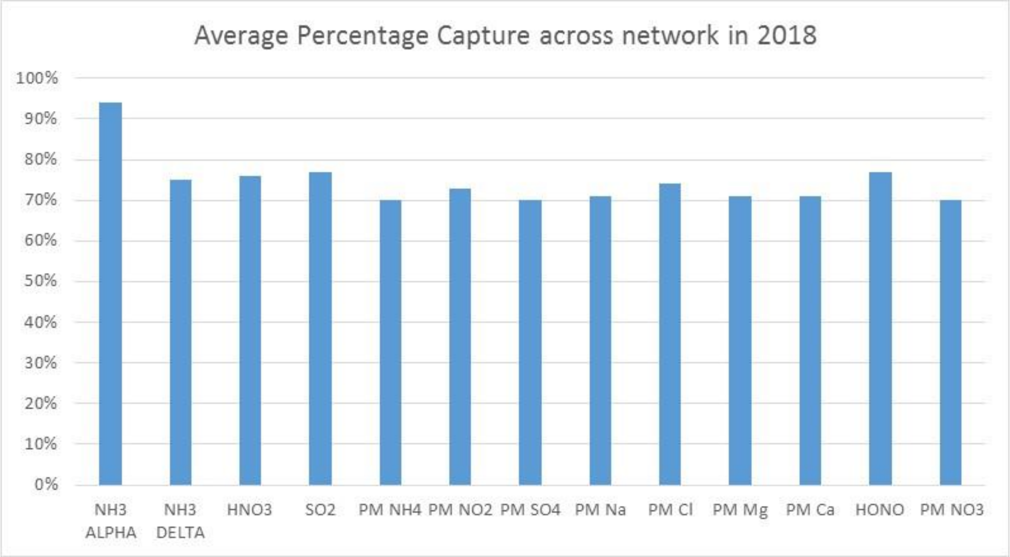

Figure 38 2018 NAMN and AGANet Percentage data capture by chemical component

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 39. The annual calibration functions of ALPHA samplers show good consistency between years.

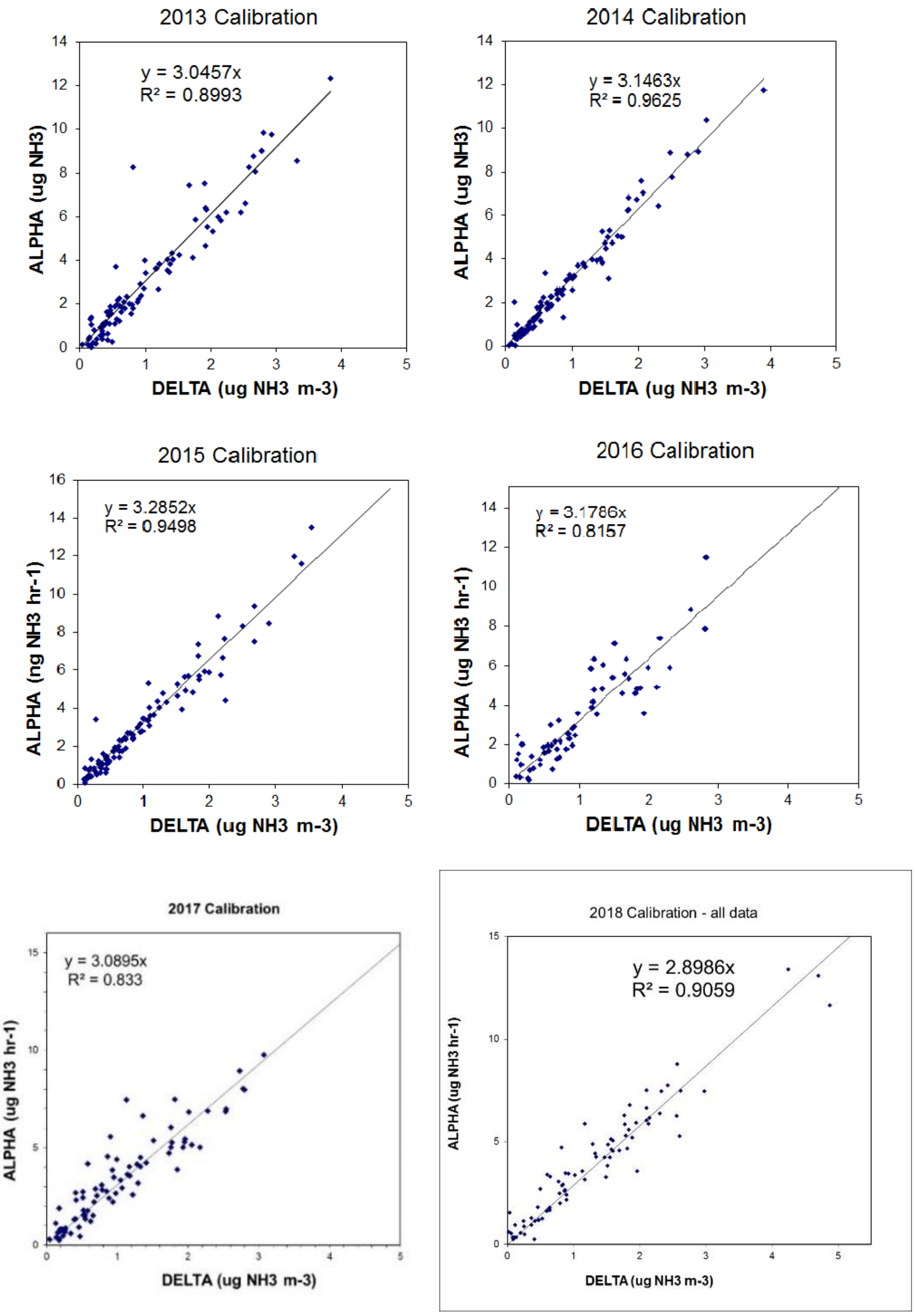

Figure 39: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers 2013- 2018.