UKEAP

2017

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	
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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 NO₂ diffusion tube network** (NO₂-Net)

- The air quality measurements of Natural Englnad''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 throught the year
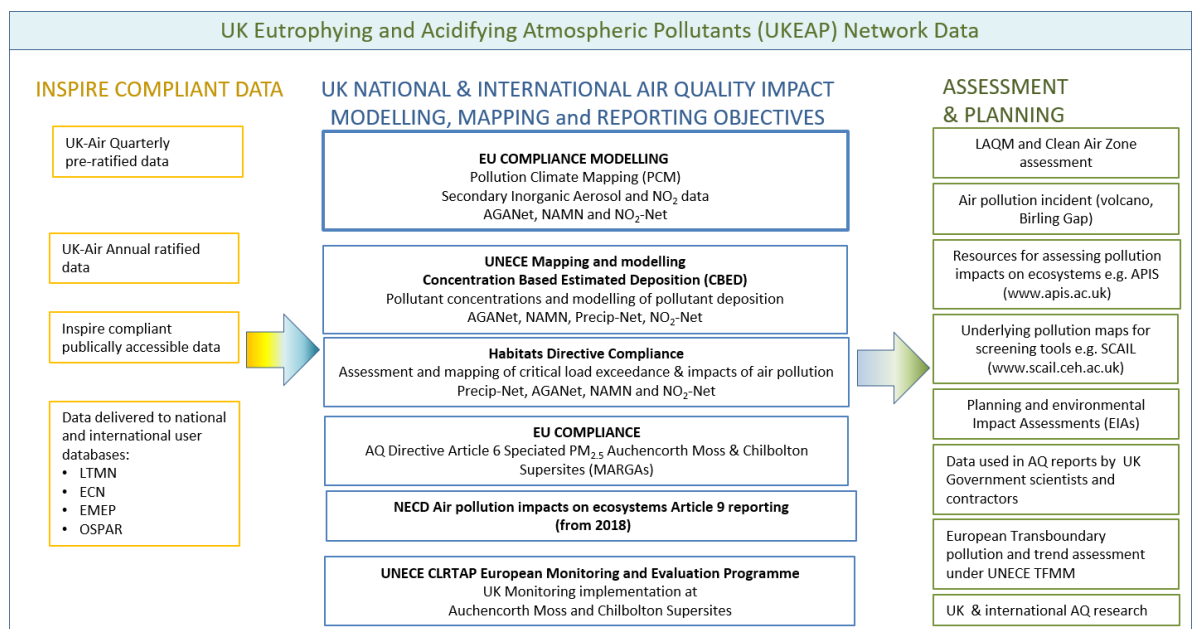
1.2 Evidence and Policy Use of UKEAP Measurement data

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 (Defra project AQ0947), 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.

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 2017 and early 2018 using UKEAP data, maps derived from UKEAP data or science supported at UKEAP sites

Aas, W. and P.B. Nizzetto, Heavy metals and POP measurements, 2015. EMEP/CCC-Report, 2017.

Aksoyoglu, S., et al., Secondary inorganic aerosols in Europe: sources and the significant influence of biogenic VOC emissions, especially on ammonium nitrate. Atmospheric Chemistry and Physics, 2017. 17(12): p. 7757.

Aleksankina, K., et al., Advanced methods for uncertainty assessment and global sensitivity analysis of a Eulerian atmospheric chemistry transport model. Atmospheric Chemistry and Physics Discussions, 2018.

Baldocchi, D., H. Chu, and M. Reichstein, Inter-annual variability of net and gross ecosystem carbon fluxes: A review. Agricultural and Forest Meteorology, 2017.

Bleeker, A., Ph. D thesis, Quantification of nitrogen deposition and its uncertainty with respect to critical load exceedances. 2018.

Braban, C.F., et al., Literature review on the performance of diffusive samplers for the measurement of ammonia in ambient air and emissions to air. 2018.

Britton, A.J., et al., Pollution and climate change drive long-term change in Scottish wetland vegetation composition. Biological Conservation, 2017. 210(Part A): p. 72-79.

Butterfield, D.M. and P. Quincey, An Investigation into the Effects of Off-Shore Shipping Emissions on Coastal Black Carbon Concentrations. Aerosol and Air Quality Research, 2017. 17(1): p. 218-229.

Cinnirella, S., et al. Gos4m: the geo flagship to support the Minamata Convention on mercury. In conference proceedings of the cnr-institute of atmospheric pollution research. 2018.

Derwent, R.G., et al., Origins and trends in ethane and propane in the United Kingdom from 1993 to 2012. Atmospheric Environment, 2017. 156(Supplement C): p. 15-23.

El-Madany, T.S., K. Niklasch, and O. Klemm, Stomatal and Non-Stomatal Turbulent Deposition Flux of Ozone to a Managed Peatland. Atmosphere, 2017. 8(9): p. 175.

Field, C.D., et al., Long-term nitrogen deposition increases heathland carbon sequestration. Science of The Total Environment, 2017. 592(Supplement C): p. 426-435.

Gencarelli, C.N., et al., Sensitivity model study of regional mercury dispersion in the atmosphere. Atmospheric Chemistry and Physics, 2017. 17(1): p. 627-643.

Goeminne, C.P., et al., The impact of acute air pollution fluctuations on bronchiectasis pulmonary exacerbation. A case-crossover analysis. European Respiratory Journal, 2018: p. 1702557.

Griffiths, N.A., et al., Temporal and spatial variation in peatland carbon cycling and implications for interpreting responses of an ecosystem-scale warming experiment. Soil Science Society of America Journal, 2017.

Hellsten, S., et al., Uncertainties and implications of applying aggregated data for spatial modelling of atmospheric ammonia emissions. Environmental Pollution, 2018. 240: p. 412-421.

Hyland, J., The health and socioeconomic impact of traffic-related air pollution in Scotland, 2017, University of St Andrews.

Jones, L., et al., Can on-site management mitigate nitrogen deposition impacts in non-wooded habitats? Biological Conservation, 2017. 212(Part B): p. 464-475.

Jones, S.K., et al., The nitrogen, carbon and greenhouse gas budget of a grazed, cut and fertilised temperate grassland. Biogeosciences, 2017. 14(8): p. 2060-2088.

Kalisa, E., et al., Temperature and air pollution relationship during heatwaves in Birmingham, UK. Sustainable Cities and Society, 2018.

Karlsson, P.E., et al., Past, present and future concentrations of ground-level ozone and potential impacts on ecosystems and human health in northern Europe. Science of the Total Environment, 2017. 576: p. 22-35.

Kelleghan, D.B., et al., Mapping ammonia risk on sensitive habitats in Ireland. Science of the Total Environment, 2019. 649: p. 1580-1589.

Kentisbeer, J., S. Leeson, and S. Ritchie, How has the relocation of a monitoring site changed our understanding of UK rural atmospheric mercury? Poster, International Mercury Conference, 2017.

Lin, C., et al., Spatiotemporal evaluation of EMEP4UK-WRF v4.3 atmospheric chemistry transport simulations of health-related metrics for NO_2, O_3, PM_{10}, and $PM_{2.5}$ for 2001–2010. Geosci. Model Dev., 2017. 10(4): p. 1767-1787.

Malley, C., et al., Analysis of the distributions of hourly NO_2 concentrations contributing to annual average NO_2 concentrations across the European monitoring network between 2000 and 2014. Atmospheric Chemistry and Physics, 2018: p. 3563-3587.

Mitchell, R.J., et al., Decline in atmospheric sulphur deposition and changes in climate are the major drivers of long-term change in grassland plant communities in Scotland. Environmental Pollution, 2018. 235: p. 956-964.

Munir, S., Analysing temporal trends in the ratios of $PM_{2.5}/PM_{10}$ in the UK. Aerosol and Air Quality Research, 2017. 17(1): p. 34-48.

Pescott, O.L., et al., The use of National Plant Monitoring Scheme data for making inferences concerning air pollution impacts, in National Plant Monitoring Scheme, 2018.

Pickard, A.E., et al., Temporal changes in photoreactivity of dissolved organic carbon and implications for aquatic carbon fluxes from peatlands. Biogeosciences, 2017. 14(7): p. 1793-1809.

Ratcliffe, J., et al., Contemporary carbon fluxes do not reflect the long-term carbon balance for an Atlantic blanket bog. The Holocene, 2018. 28(1): p. 140-149.

Singh, V., et al., Trends of atmospheric black carbon concentration over United Kingdom. Atmospheric Environment, 2018. 178: p. 148-157.

Smedley, P.L., et al., Stream-water geochemical atlas of the Clyde Basin. Nottingham, UK, British Geological Survey, 168pp. (OR/16/015), 2017.

Solberg, S., A. Claude, and S. Reimann, VOC measurements 2014-2015. EMEP/CCC-Report, 2017.

Song, Y., D. Han, and M.A. Rico-Ramirez, High temporal resolution rainfall rate estimation from rain gauge measurements. Journal of Hydroinformatics, 2017. 19(6): p. 930-941.

Stieger, B., et al., Measurements of PM_{10} ions and trace gases with the online system MARGA at the research station Melpitz in Germany–A five-year study. Journal of Atmospheric Chemistry, 2018. 75(1): p. 33-70.

Tang, Y.S., et al., Drivers for spatial, temporal and long-term trends in atmospheric ammonia and ammonium in the UK. Atmos. Chem. Phys. Discuss., 2017. 2017: p. 1-39.

Vivanco, M.G., et al., Modeled deposition of nitrogen and sulfur in Europe estimated by 14 air quality model systems: evaluation, effects of changes in emissions and implications for habitat protection. Atmospheric Chemistry and Physics, 2018. 18(14): p. 10199-10218.

Welden, N., P. Wolseley, and M. Ashmore, Citizen science identifies the effects of nitrogen deposition, climate and tree species on epiphytic lichens across the UK. Environmental Pollution, 2018. 232: p. 80-89.

Woodall, G., et al., Interpreting Mobile and Handheld Air Sensor Readings in Relation to Air Quality Standards and Health Effect Reference Values: Tackling the Challenges. Atmosphere, 2017. 8(10): p. 182.

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 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 2017.

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)

Air quality measurements of the Natural England **Long Term Monitoring Network** are embedded in
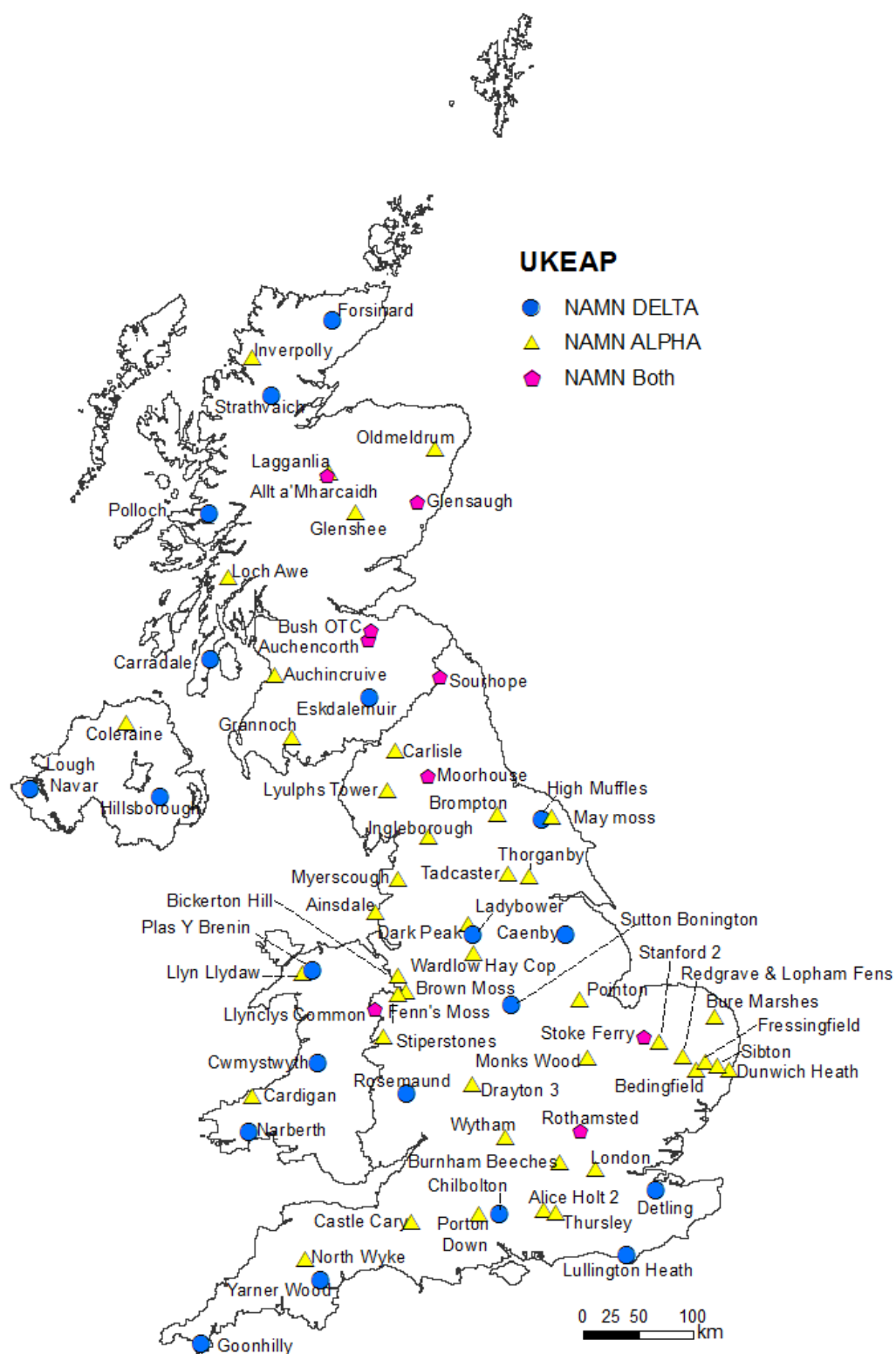
NAMN and Precip-Net
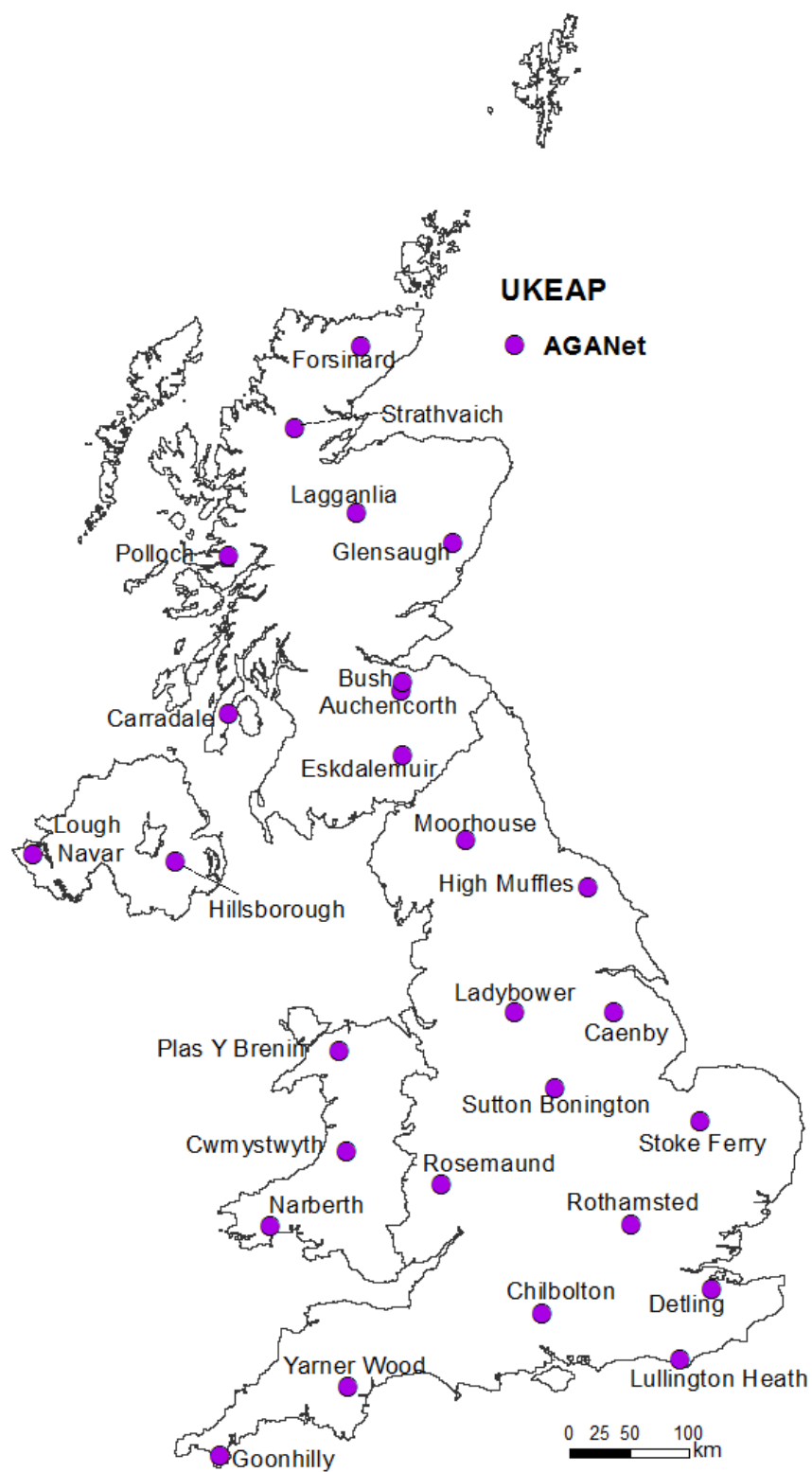
Figure 1 UK National Ammonia Monitoring Network
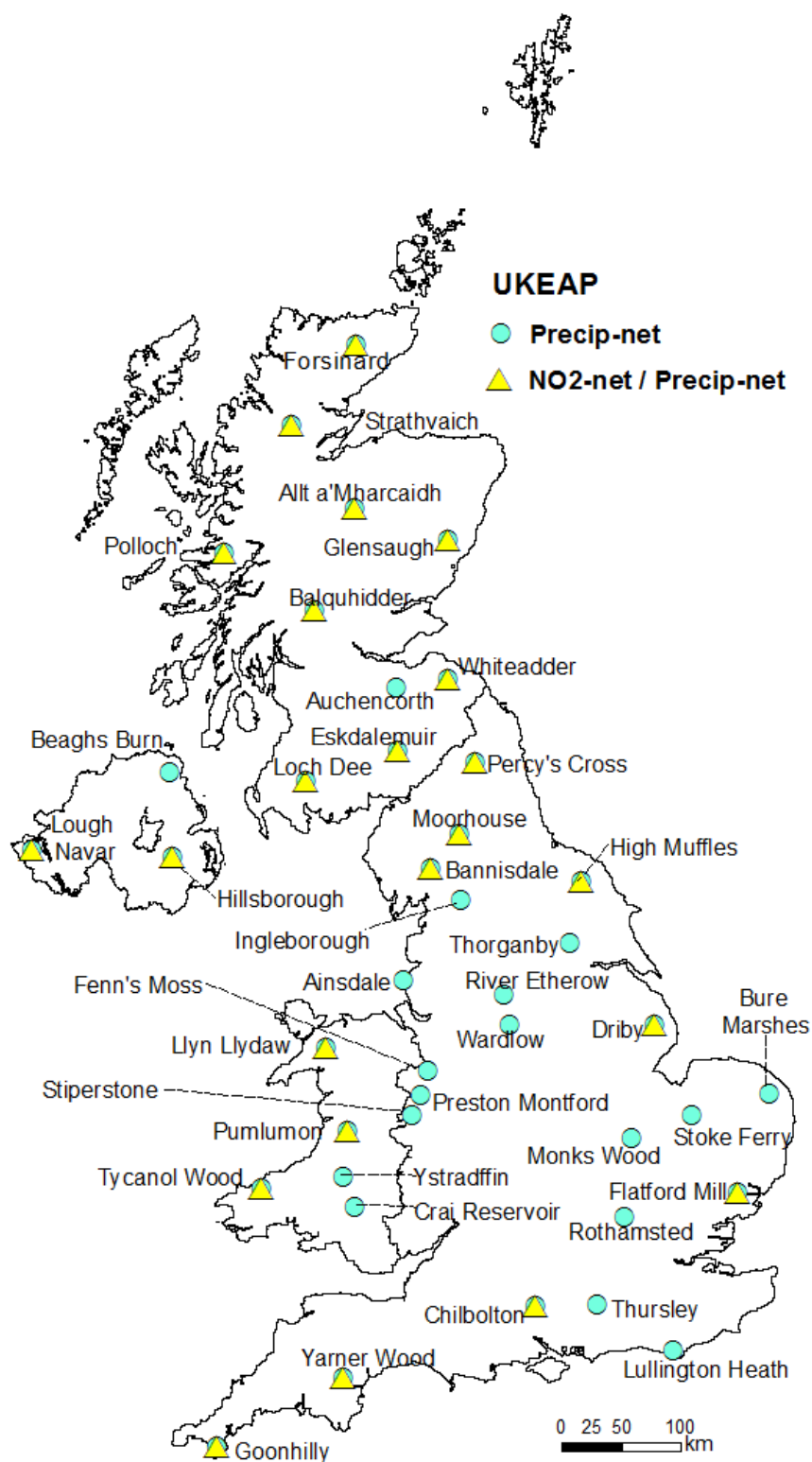
Figure 2 Acid Gases and Aerosol Network

Figure 3 Precipitation and NO$_2$ diffusion tube chemistry Network

2. UKEAP Networks Reports

2.1 Precipitation Network (Precip-Net)[1]

During 2017 there were no significant changes to the network with all 41 fortnightly bulk rain monitoring sites and 2 daily wet only (DWOC) collectors in operation throughout the year. Bulk precipitation samples were collected using a sampler design that has been used in the UK network since the inception of the Acid deposition monitoring network in 1986, details of which can be found in previous reports and is pictured in Figure 4. The locations of the Precip-Net sites are shown in Figure 3. Those sites which are part of Natural England's Long term Monitoring Network and integrated with the existing Precip-Net network are highlighted in Figure 5.

Monitoring data were provided to the Data Dissemination Unit quarterly and made available through the UK-AIR website[2]. Further information, such as site location, altitude and photos are also available[3].

Daily collection of precipitation samples using Daily Wet Only Precipitation Collectors (DWOC) are operated at the Auchencorth Moss and Chilbolton sites that meet part of the EMEP commitments by the UK. 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. The spatial patterns of the annual mean precipitation-weighted concentration of non-seasalt sulphate, nitrate, ammonium and hydrogen are presented in Figure 7 for 2017. 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 4 Bulk rain sampler (Bannisdale)

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[1] https://uk-air.defra.gov.uk/interactive-map?network=precipnet

[2] https://uk-air.defra.gov.uk/data/data_selector_service?q=1043421#mid

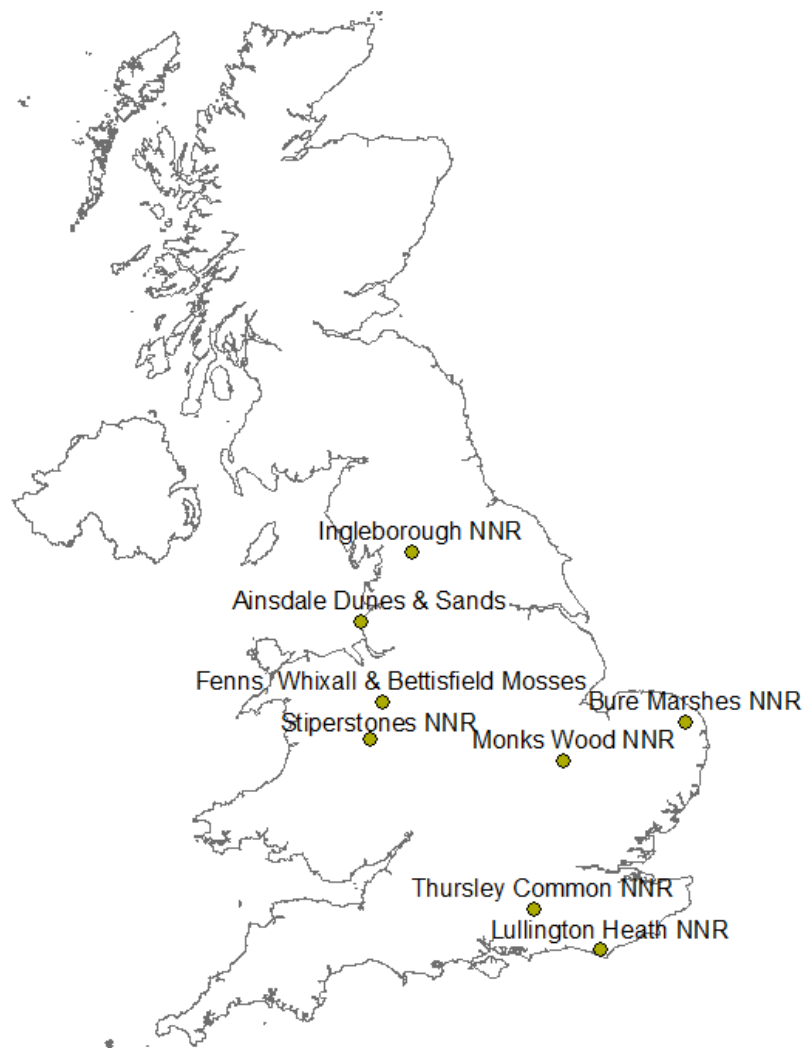[3] https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00635

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

Figure 6 Other sites in the Precip-Net monitoring network (thirty three sites)
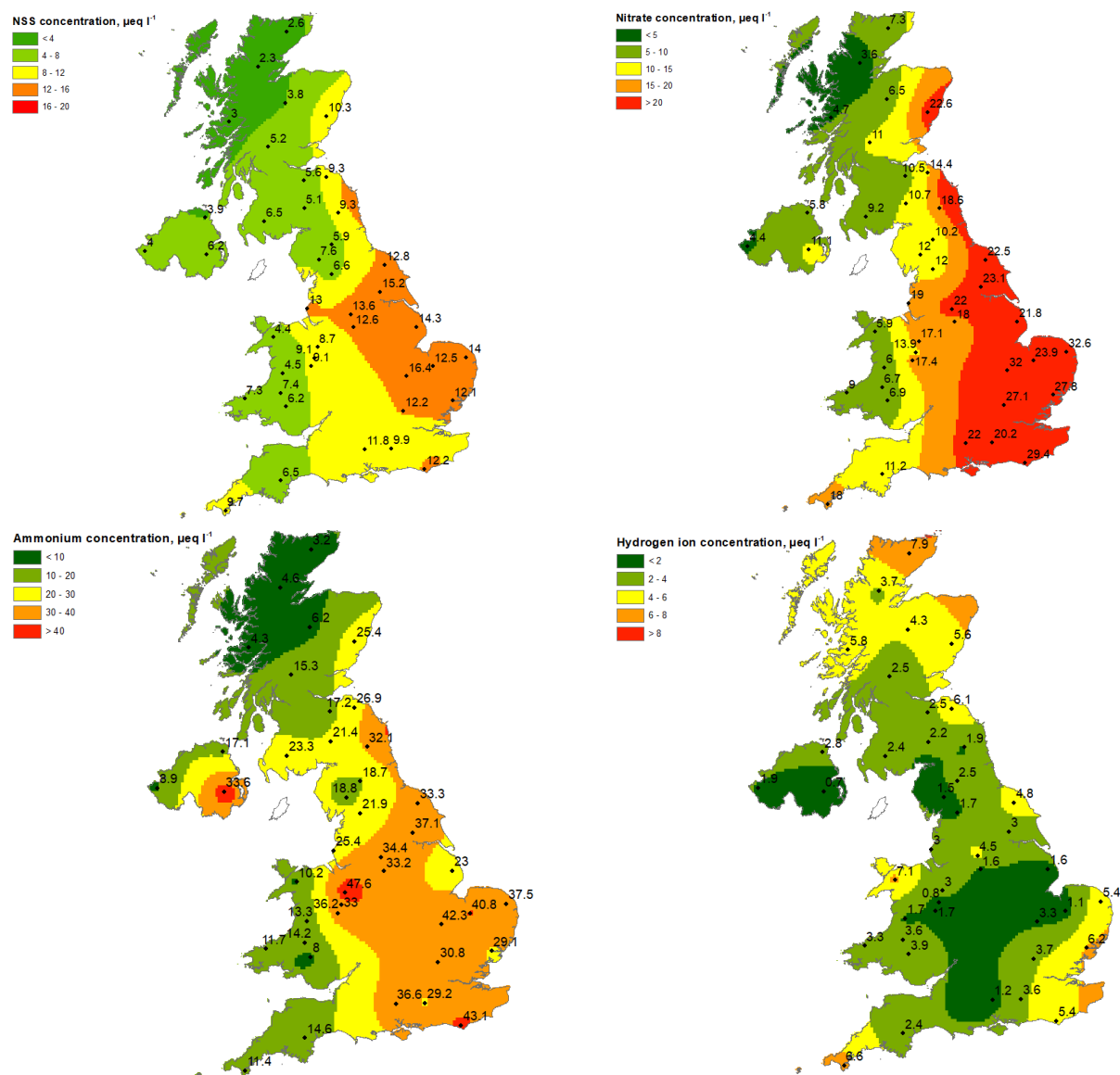
Figure 7 Interpolated concentration maps for non-sea salt
sulphate, nitrate, ammonium and hydrogen ion (µeq l^{-1})

Since the monitoring network began in 1986 emissions of all the precursor gases have decreased though the rate of decrease for sulphur dioxide was greater than that for oxides of nitrogen and ammonium. For example, Figure 8 shows that sulphur dioxide emissions have decreased by about ninety percent, oxides of nitrogen emissions have decreased by nearly 70% and ammonia emisssions have decreased by about 12%.

Figure 8 also presents projected emissions[4] for the respective gases from the National Emissions Inventory (NAEI). According to current projections for 2020 and 2030 ammonia emissions are not expected to decrease due to an increase in agricultural production. On the basis of these projections it appear unlikely that the UK will meet the National Emissions Ceiling Directive (NECD) targets for ammonia which by 2020 and 2030 are projected to be 12 % and 22 % above the NECD targets set to protect ecosystems. For sulphur dioxide and oxides of nitrogen emissions, the NECD target is expected to be met for 2020 but not for 2030.

Figure 9, Figure 10 and Figure 11 compare the total sulphur dioxide, oxides of nitrogen and ammomium emissions for the UK with the network average concentrations for non-seasalt sulphate, nitrate and ammonium, respectively. At this highly aggregated scale the rate of decrease in nitrate and ammonium concentration are smaller than that for sulphate. The aggregated analysis does not the significant geographical variations which are shown clearly by individual site trends. (see Figure 12Figures 12-14) for non sea salt sulphate, nitrate and ammonium, respectively).

Clear downward trends are found for sulphate and nitrate. Trends in ammonium concentrations are generally less clear. At locations where the ammonium concentration was greater than 50 µeq l^{-1} in the 1980s (for example, Bottesford. Flatford Mill, Preston Montford, Stoke Ferry and Hillsborough Forest) the decrease in concentration was at least 10 µeq l^{-1} over the thirty year period . At the other sites the inter year variability was large. At many of these locations there is no discernable decrease in ammonium concentration in water. Such observations may be expected given the relatively constant emissions for ammonia shown in Figure 8.

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[4] https://consult.defra.gov.uk/environmental-quality/clean-air-strategy-consultation/user_uploads/clean-air-strategy-2018-consultation.pdf
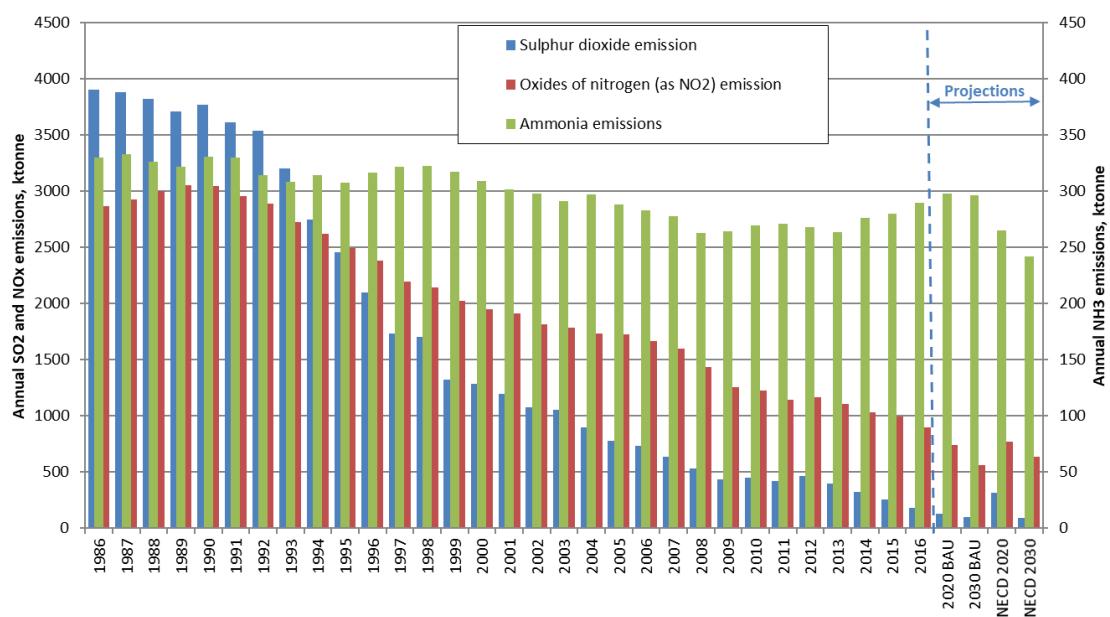
Figure 8 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986[5]
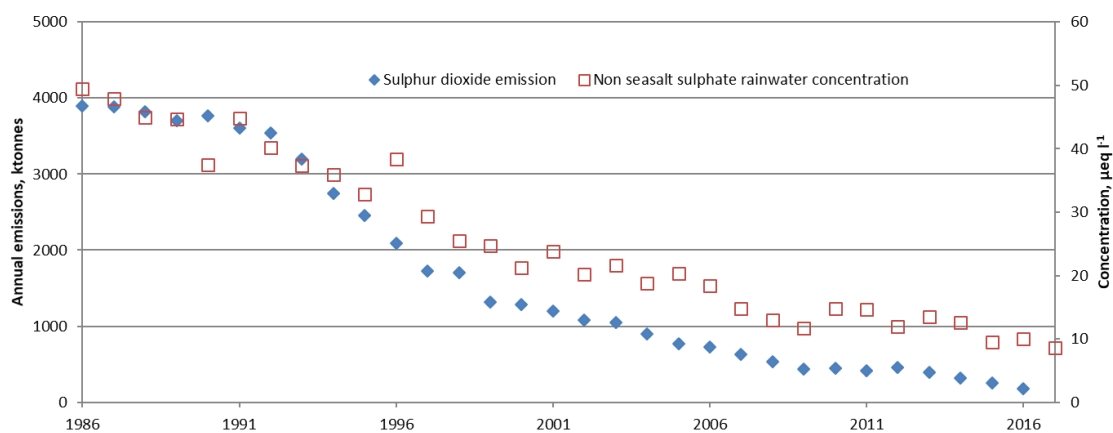
Figure 9 Sulphur dioxide emissions and sulphate concentrations in rainwater

[5] Reference for emissions data. http://naei.defra.gov.uk/
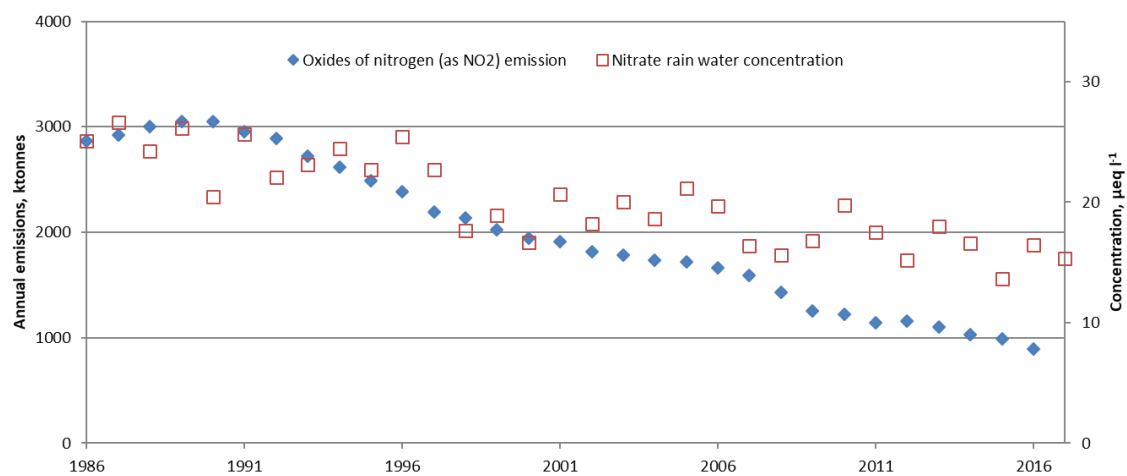
Figure 10 Oxides of nitrogen emissions and nitrate concentrations in rainwater
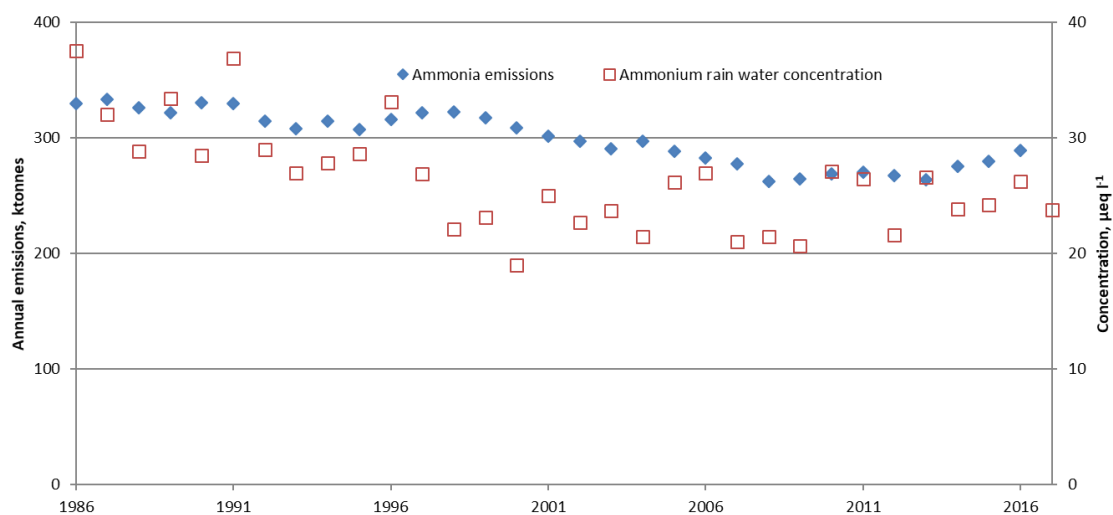
Figure 11 Ammonia emissions and ammonium concentrations in rainwater

16
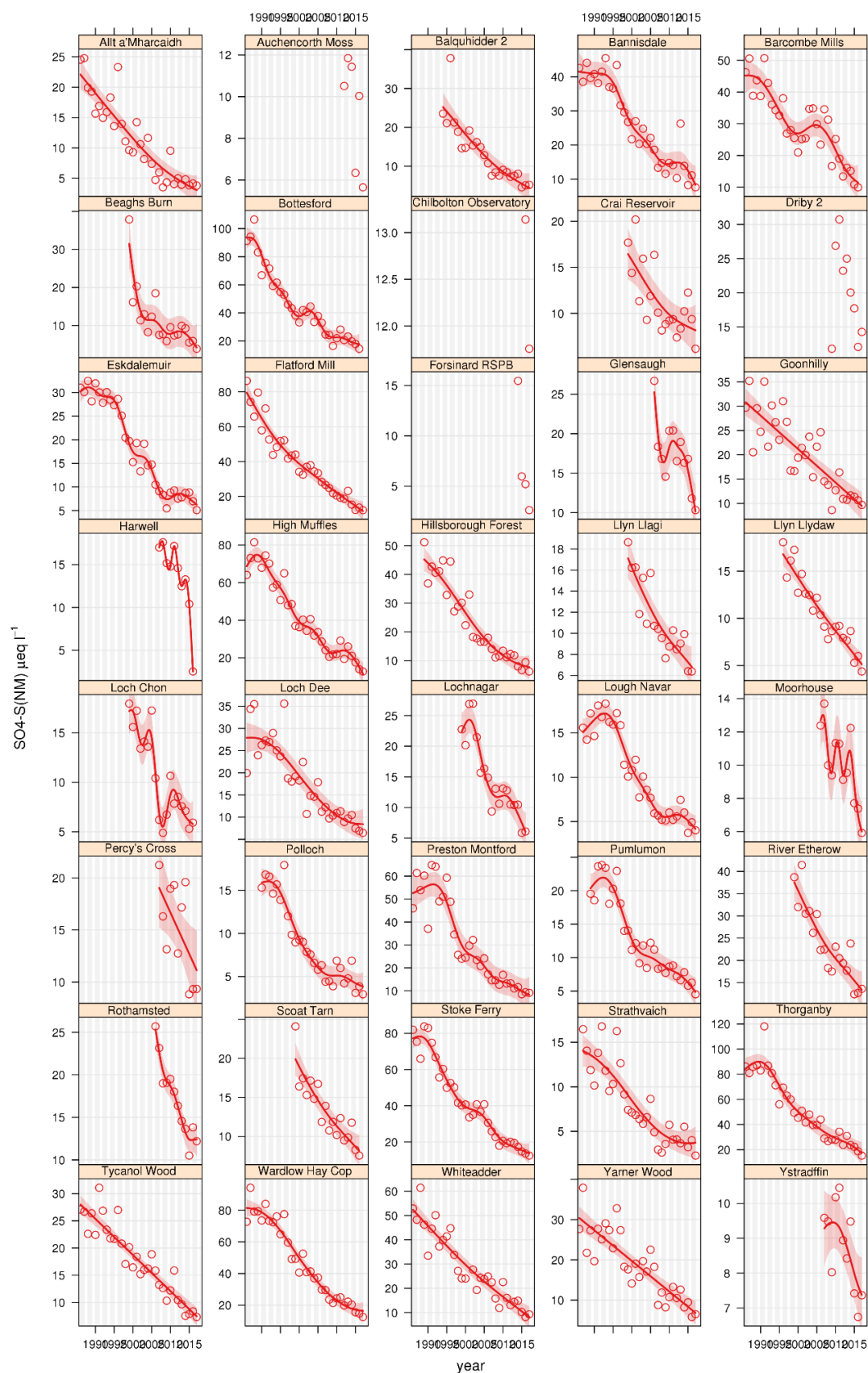
Figure 12 Non sea salt sulphate concentrations measured at sites with the Precip-Net since 1986
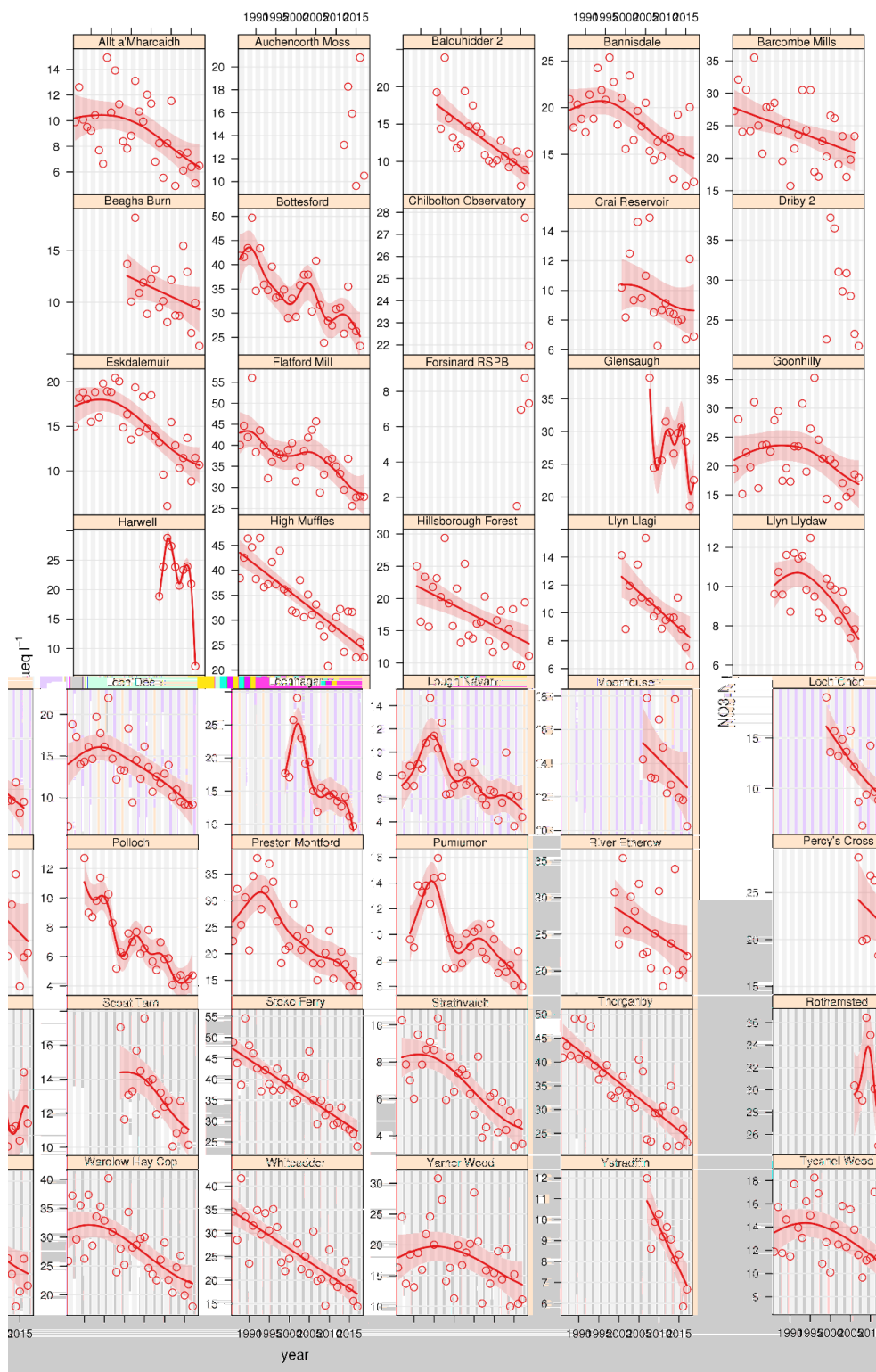
Figure 13 Nitrate concentrations measured at sites with the Precip-Net network since 1986
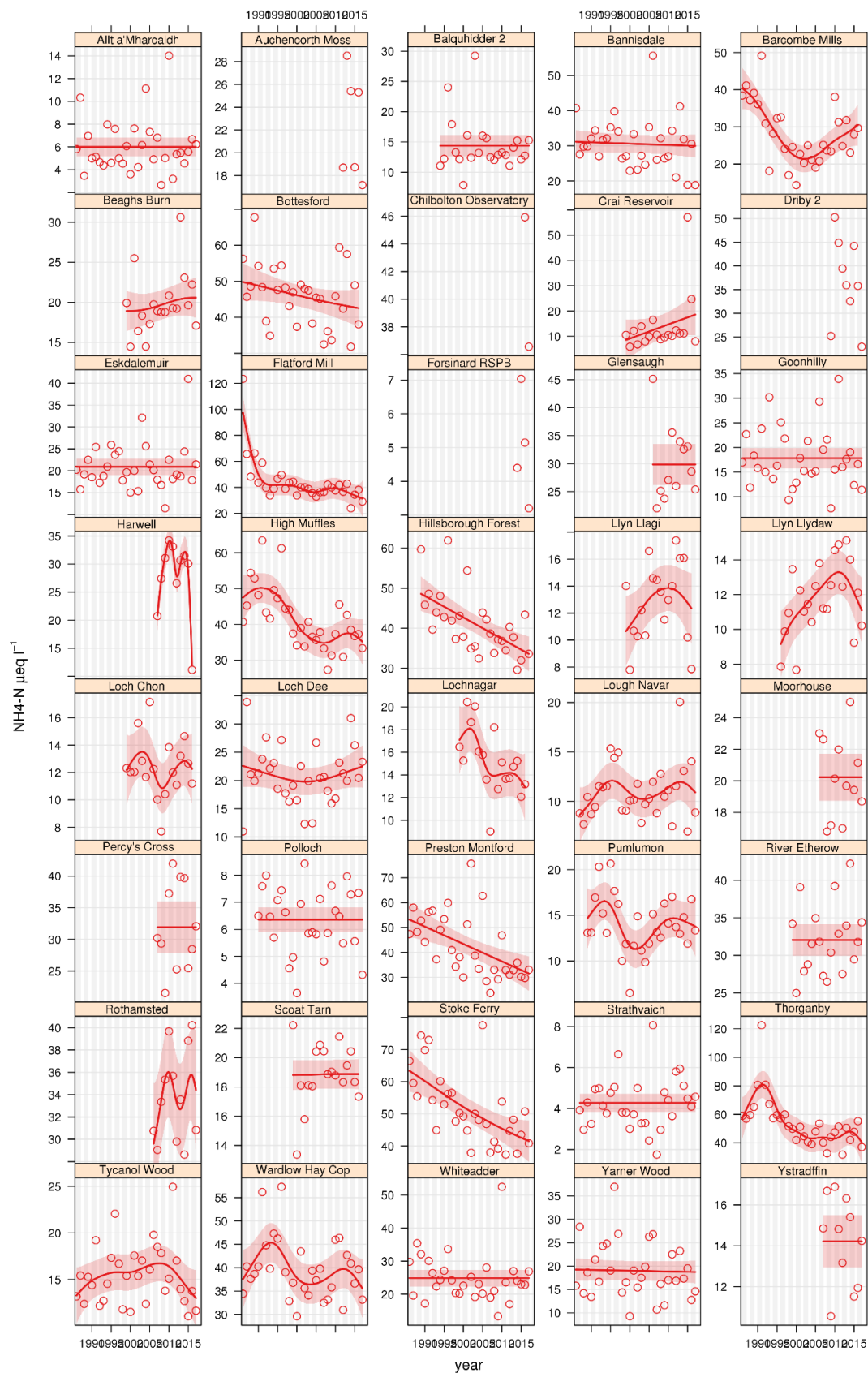
Figure 14 Ammomium concentrations measured at sites with the Precip-Net network since 1986

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 2017 was 97% with 22 of the 24 sites achieving > 90% and 19 sites achieving 100% data capture. The poor data capture at Llyn Llydaw was caused by the diffusion tubes being exposed or extended periods what could not be used to calculate the annual mean. The 82% data capture at Lullington Heath was due to the site not starting until early March 2017

Table 1 2017 NO$_2$ concentration from the Diffusion Tubes in the NO$_2$-Net

Site Name	Raw 2017 concentration (µg m^{-3})	2017 concentration Bias Corrected (0.828)[1]	Data capture	Site Name	Raw 2017 concentration (µg m^{-3})	2017 concentration Bias Corrected (0.828)	Data capture
Allt a'Mharcaidh	0.93	0.77	100%	Llyn Llydaw	2.39	1.98	60%
Balquhidder 2	1.55	1.28	92%	Loch Dee	2.05	1.70	100%
Bannisdale	3.82	3.16	96%	Lough Navar	1.55	1.28	100%
Chilbolton Observatory	10.11	8.37	100%	Lullington Heath	10.31	8.54	82%
Driby 2	9.74	8.06	100%	Moorhouse	3.35	2.78	100%
Eskdalemuir	2.38	2.06	100%	Percy's Cross	3.62	2.99	100%
Flatford Mill	10.46	8.66	93%	Polloch	1.24	1.02	100%
Forsinard RSPB	1.30	1.08	100%	Pumlumon	2.76	2.29	100%
Glensaugh	2.84	2.35	100%	Strathvaich	0.81	0.67	100%
Goonhilly	3.65	3.02	100%	Tycanol Wood	2.96	2.45	100%
High Muffles	5.60	4.96	100%	Whiteadder	3.02	2.50	100%
Hillsborough Forest	6.42	5.32	100%	Yarner Wood	3.64	3.24	100%

[1] All sites bias adjusted by 0.828 with the exception of Eskdalemuir, High Muffles and Yarner Wood which were corrected using co-located samplers, Appendix for details. [2] Chilbolton has co-located sampling but due to inlet height differences and unusual comparison with automatic data a factor of 0.828 was used.

The annual average uncorrected NO_2 concentrations from 2010-2017 are shown in Figure 16 that gives an indication of the differing levels at rural locations across the UK. Most of the sites show some reduction between 2010 and 2017 but the larger decreases being seen at the sites that could be considered as less rural such as Harwell (now closed) and Flatford Mill. This may be anticipated as these will be closer to the sources of NO_2 and hence changes in the emissions would have more influence on measured concentrations.

Figure 15 shows the trend in emissions of NO_x and NO_2 concentrations measured by the diffusion tubes in the network. It is apparent from the above plot 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 during each years however the rate of decline in concentration is slightly less than the rate of reduction in concentrations.

This might be expected as emissions of NO_2 are associated with transport or industrial processes involving combustion so would have less influence 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.
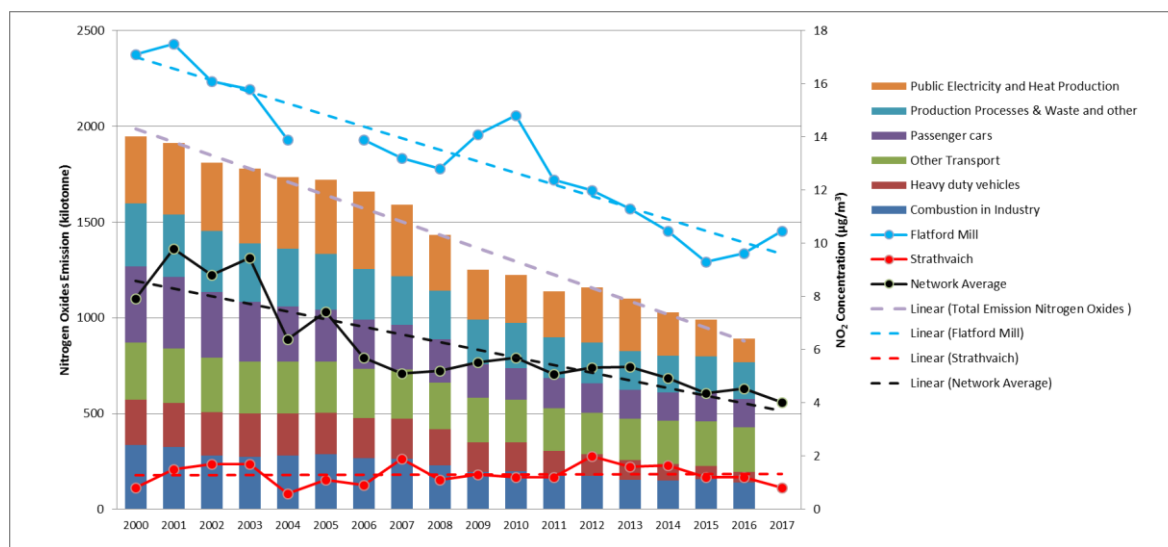

Figure 15 Long term trends where estimated emissions are plotted against selected sites in the network
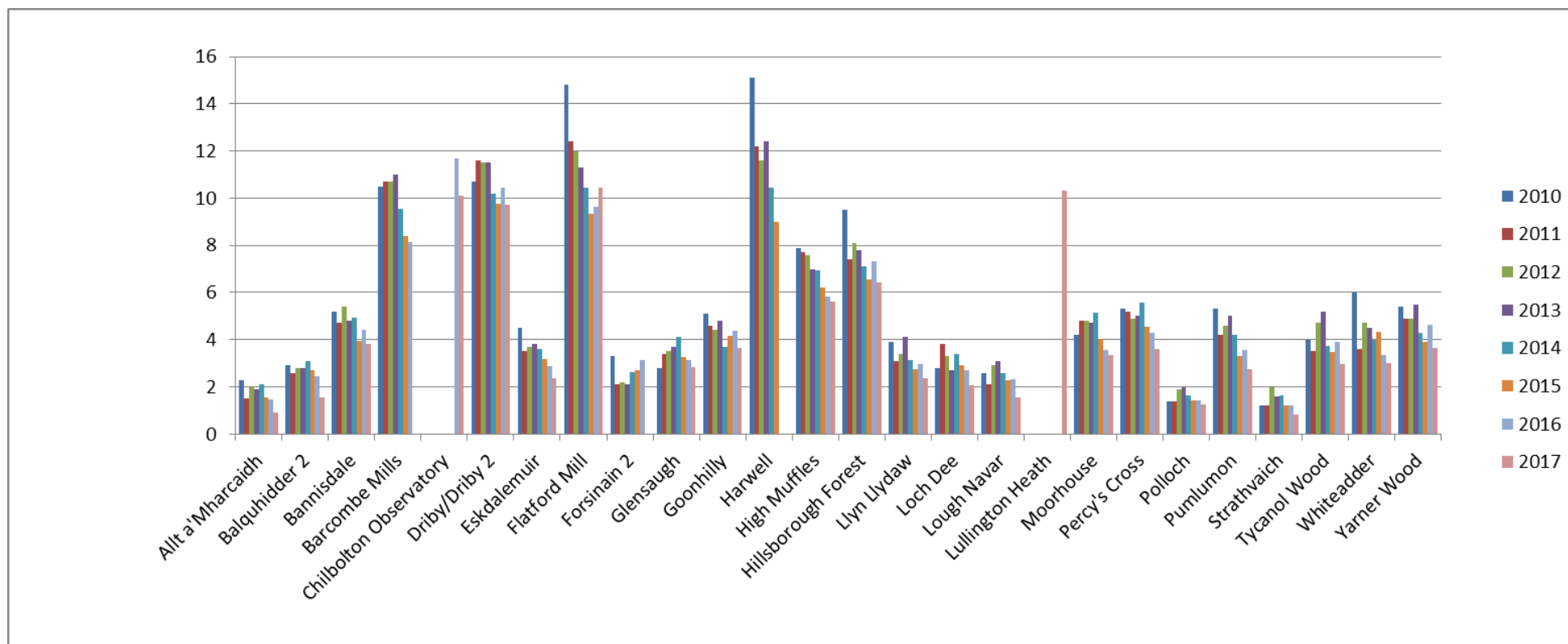
Figure 16 Annual mean NO$_2$ concentration (µg m-3) at the NO$_2$-Net sites 2010-2017

2.3 National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly measurements of atmospheric NH_3 in 2017 was 72, summarised in Table 2. Several changes to NAMN were implemented at the beginning of 2017: 15 sites which measured NH_3 with a powered DELTA air sampler were converted to passive ALPHA samplers (see Table 3). In addition, Lullington Heath site was converted to an AGANET DELTA site, replacing the AGANet site which had been at Barcombe Mills which closed in 2016. The conversions were undertaken at the beginning of February 2017, coordinating with the regular sampler change to minimise network disruption. Figure 1 summarises all the sites operating in NAMN in 2017 measuring ammonia gas and Figure 2 shows the Acid Gas and Aerosol network (AGANet), where in addition, particulate ammonium (NH_4^+), formed as a secondary product from the primary NH_3 emissions, is measuremened. AGANET results are discussed in section 2.3.

The 2017 annual NAMN results are summarised by the average and range of annual NH_3 concentrations observed at each site in Figure 17Table 3. The graphs are all plotted on the same scale, to allow a direct comparison of NH_3 concentrations between sites. The 2017 NAMN results continue to illustrate the high spatial variability in NH_3 concentration and the seasonal variability of NH_3 concentrations reflecting the large regional variability in NH_3 emissions. During 2017 average data capture across all sites was 83%. (QC criteria summarised in the Appendix of this report). This data capture is expected to improve going forward with all network changes now complete.

Table 2 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2017 (post site conversion)

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

Table 3 Summary of DELTA to ALPHA site conversions in 2017

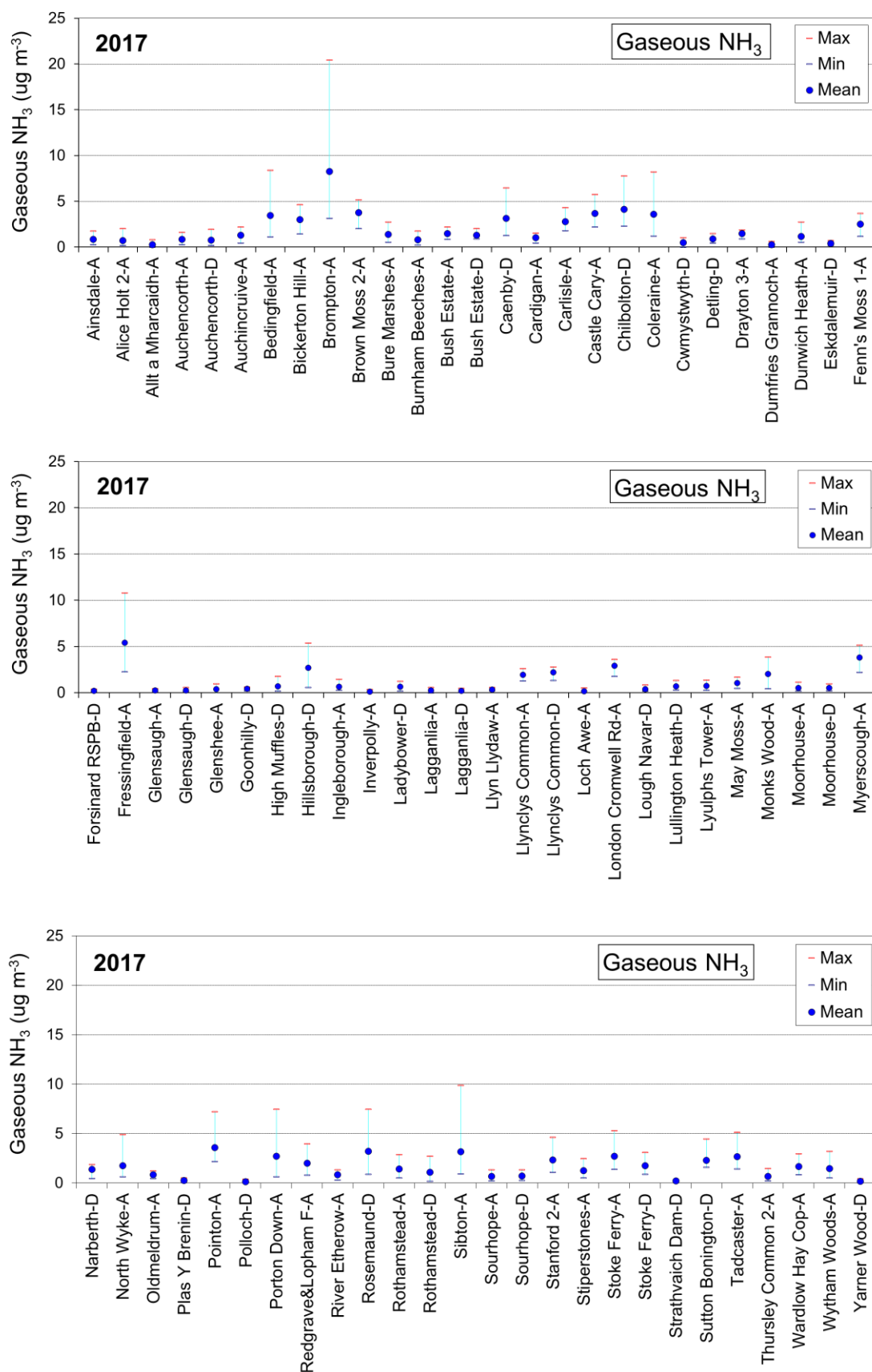| Site Name	Network site Number
Auchincruive	78C
Brown Moss 2	9B
Cardigan	63
Carlisle	74
Castle Cary	42
Coleraine	79
Inverpolly	3B
London Cromwell Road 2	36C
Lyulphs Tower	80
North Wyke	23
Pointon	76
Porton Down	28
Sibton	46
Tadcaster	43
Wytham Woods	26

Figure 17 Annual mean concentrations of gaseous NH3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2017, whilst the bars show the minimum and maximum concentrations observed (A = ALPHA sampler; D=DELTA)

NH₃ concentrations over the period 1998 to 2017 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 NH₃ declined by about 11% during the operation of NAMN, NH₃ 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 NH₃ concentrations. A detailed analysis of NAMN has recently been published by Tang et al. in Atmospheric Chemistry and Physics (Tang et al. 2017)
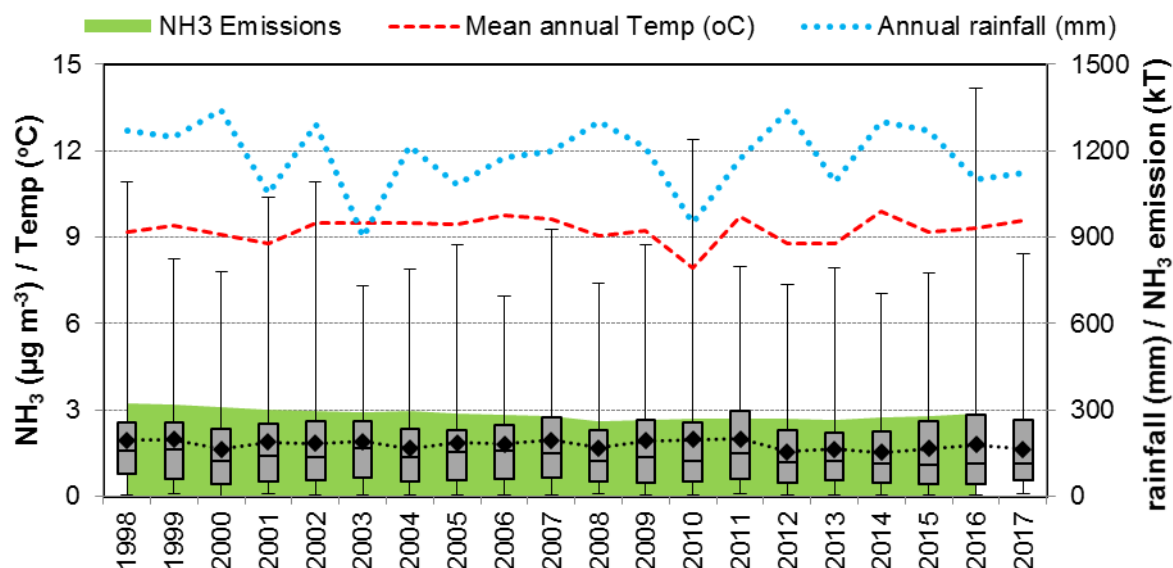
Figure 18: Changes in atmospheric NH₃ averaged over all sites in NAMN operational between 1998 and 2017 summarised in a box plot. The whiskers shows the absolute max and min and the diamond is the mean annual concentration. Annual mean UK meteorological data (source http://www.metoffice.gov.uk/) are plotted on top to illustrate the relationship between inter-annual variability in NH₃ concentrations with changing temperature and rainfall. UK annual NH₃ emissions (source http://naei.beis.gov.uk/data/) declined by 11 % over the period 1998 - 2016.

National maps of both NH₃ and NH₄⁺ (Figure 19) concentrations derived from the NAMN confirm the high spatial variability of the annual average concentration of NH₃ (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 NH₃ (and NH₄⁺ at the 27 AGANET sites). For particulate NH₄⁺, the annual mean concentrations ranged from the lowest of 0.12 (S41 Lagganlia) to highest of 1.40 (S33 Stoke Ferry) µg NH₄⁺ m⁻³. Aerosol NH₄⁺ 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 24), as would be expected due to the formation of stable and semi-stable particle phase salts, e.g. ammonium sulphate and ammonium nitrate, respectively.

The NAMN data is used in annual mapping exercises including regression between NH$_3$ measurements from NAMN and the FRAME model (Fournier 2002) is used to scale the FRAME estimates to the network. This approach is considered to provide the best estimate of the UK NH$_3$ concentration field overall and the transformed FRAME estimates are then applied as input to the CBED (Concentration Based Estimates of Deposition) inferential model of Smith et al. (2000) (NEGTAP 2001) to map and estimate UK budgets of NH$_3$ dry deposition as applied in the Defra Mapping and Modelling of Critical Loads and Levels contract.
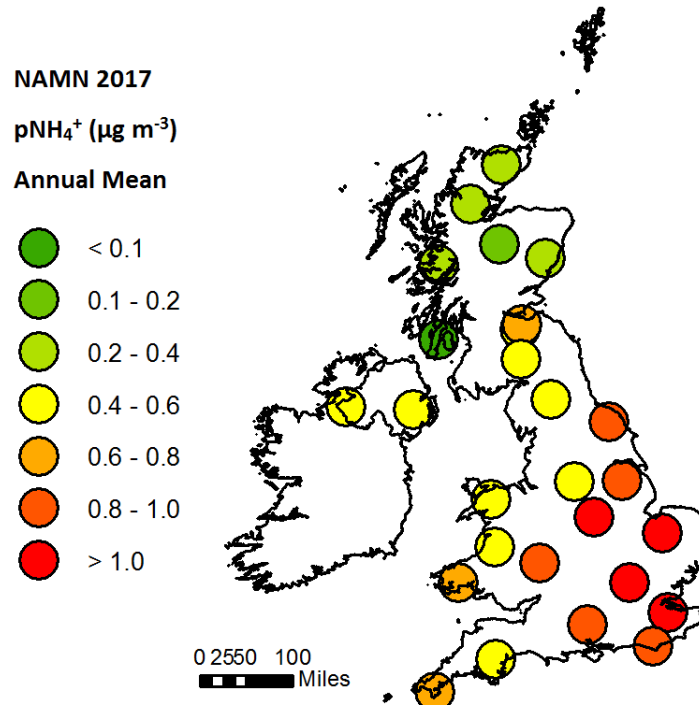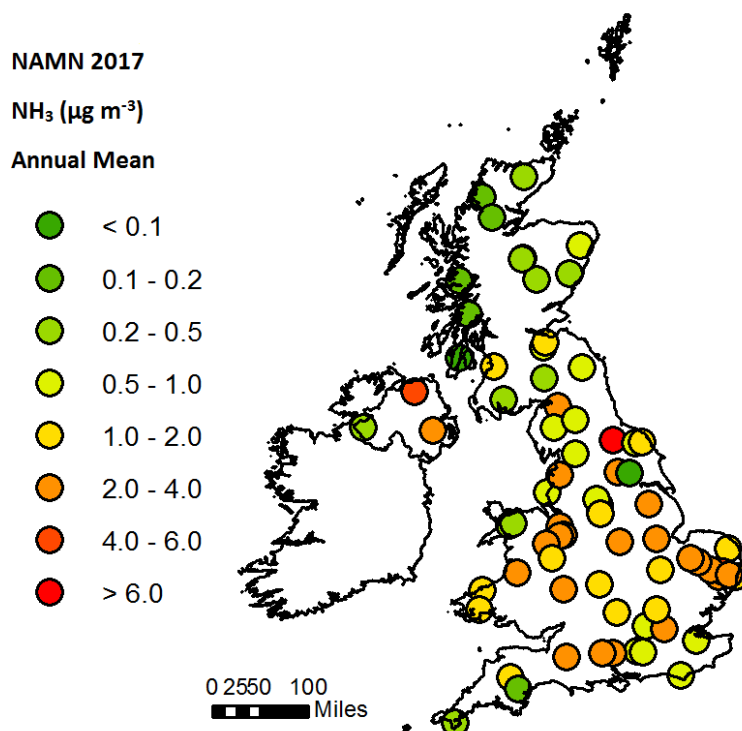
Figure 19: Spatial patterns of annual NH₃ and aerosol NH₄⁺ concentrations from monthly NAMN/AGANET measurements.
Since February 2017, ammonium is measured at the 27 AGANET sites only.

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 2017 annual concentrations of trace gas and aerosols at individual sites in the network are compared in Figure 20, and Figure 21 and Figure 22 respectively. 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 close coupling between acidic (NO_3^-, SO_4^{2-}) and basic (NH_4^+) aerosol components is demonstrated by the high correlations. As with the gases, 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) However, aerosol 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 2016. Data from 1999 were excluded from analysis since the network only started in September 1999.

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 2016 there is an increase in the network average particulate NO_3^-, SO_4^{2-} and NH_4^+ concentrations by approximately 50, 100 and 100% respectively. This is 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 of the same order of magnitude. Further data will be needed to confirm the magnitude of the step changes across sites and a full assessment of whether a back-correction of historic data is possible given the variability of PM across the UK spatially and temporally. For details of the method change see Tang et al. (2016).
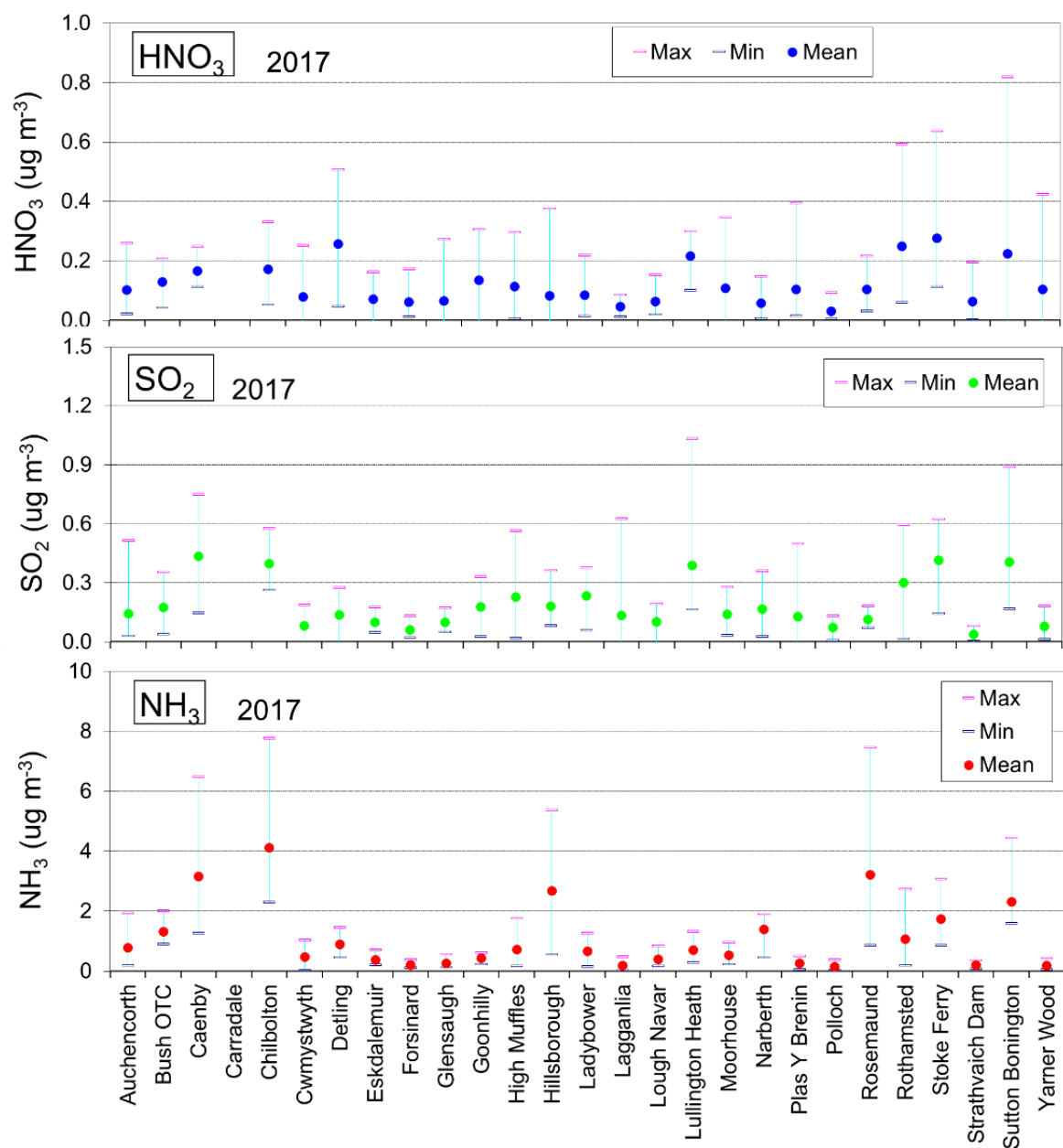
Figure 20: Mean monitored annual concentrations of gaseous HNO_3 and SO_2 at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2017, whilst the bars show the minimum and maximum concentrations observed. Data for gaseous NH_3 measured under NAMN is also shown for comparison. Note: Carradale site non-operational in 2017 (no power).
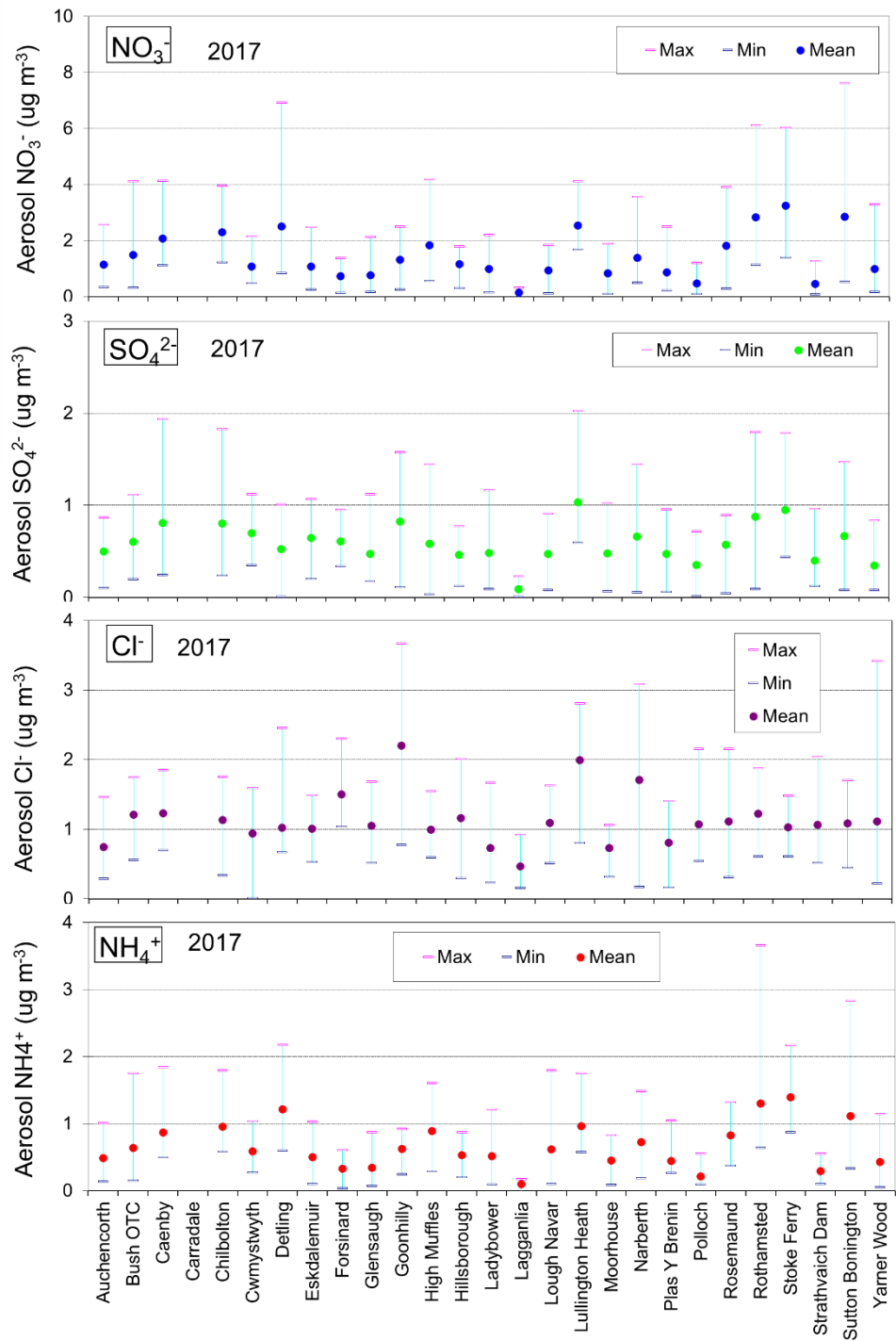
Figure 21: Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-}, Cl^- and NH_4^+ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2017, whilst the bars show the minimum and maximum concentrations observed. Note: Carradale site non-operational in 2017 (no power).
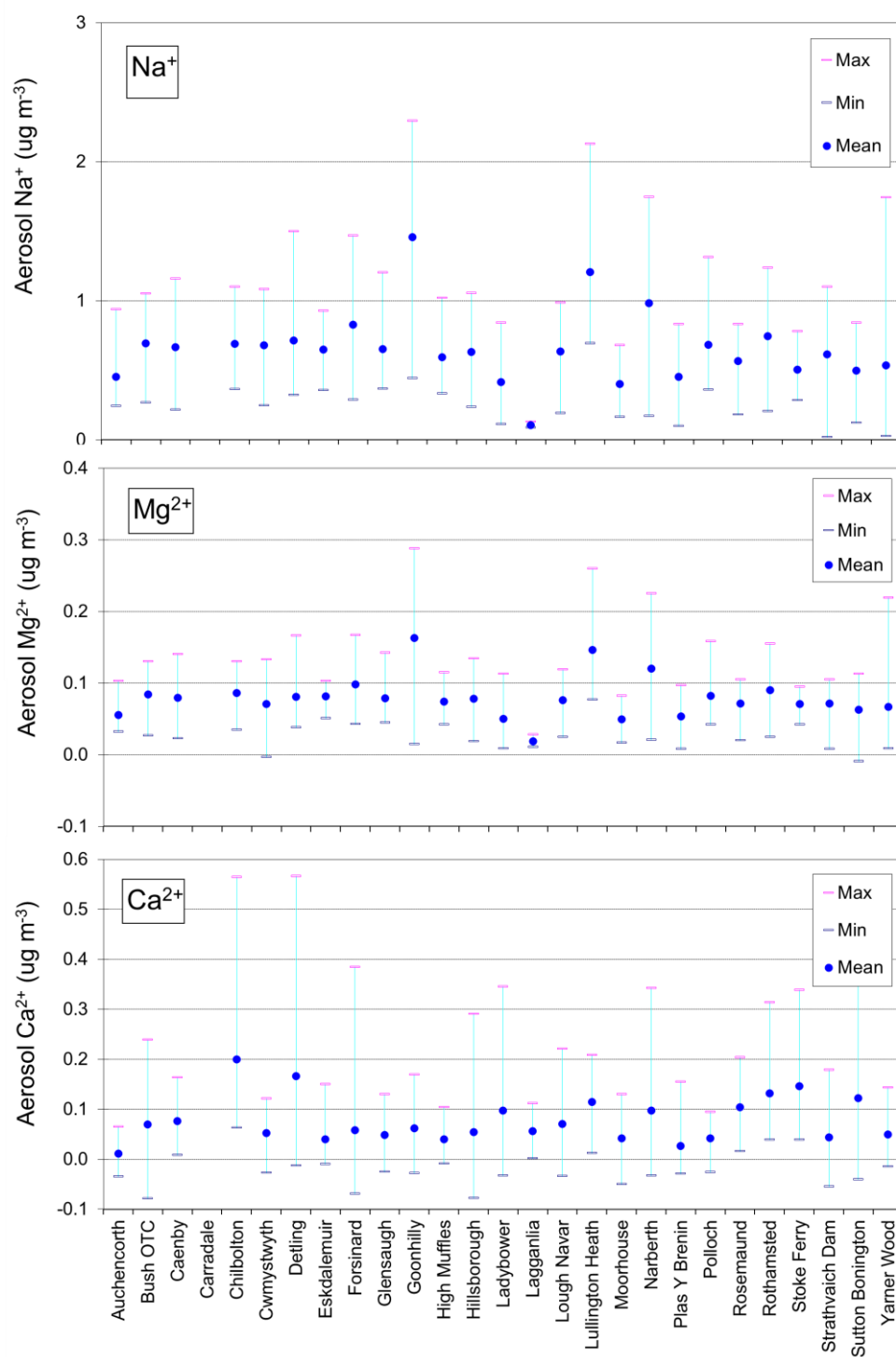
Figure 22 Mean monitored annual concentrations of particulate Mg, Ca and Na at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2017, whilst the bars show the minimum and maximum concentrations
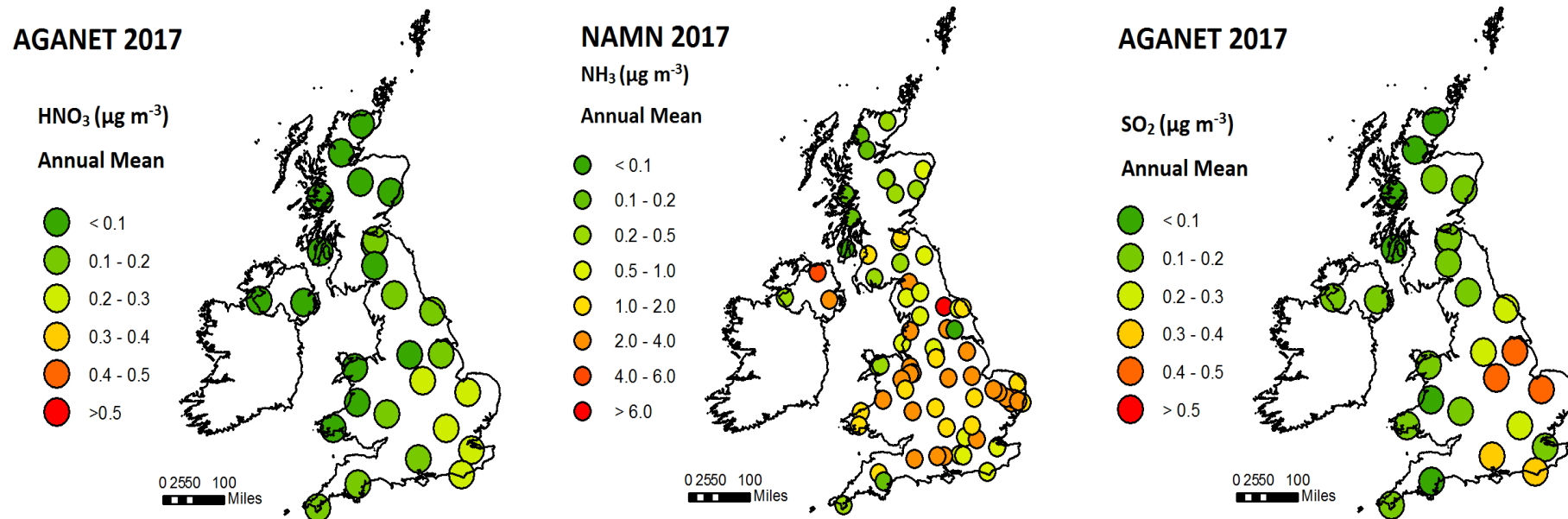
Figure 23 Annual mean monitored atmospheric reactive gas concentrations (HNO_3 and SO_2 from AGANET and NH_3 from NAMN) across the UK from annual averaged monthly measurements made in 2017.
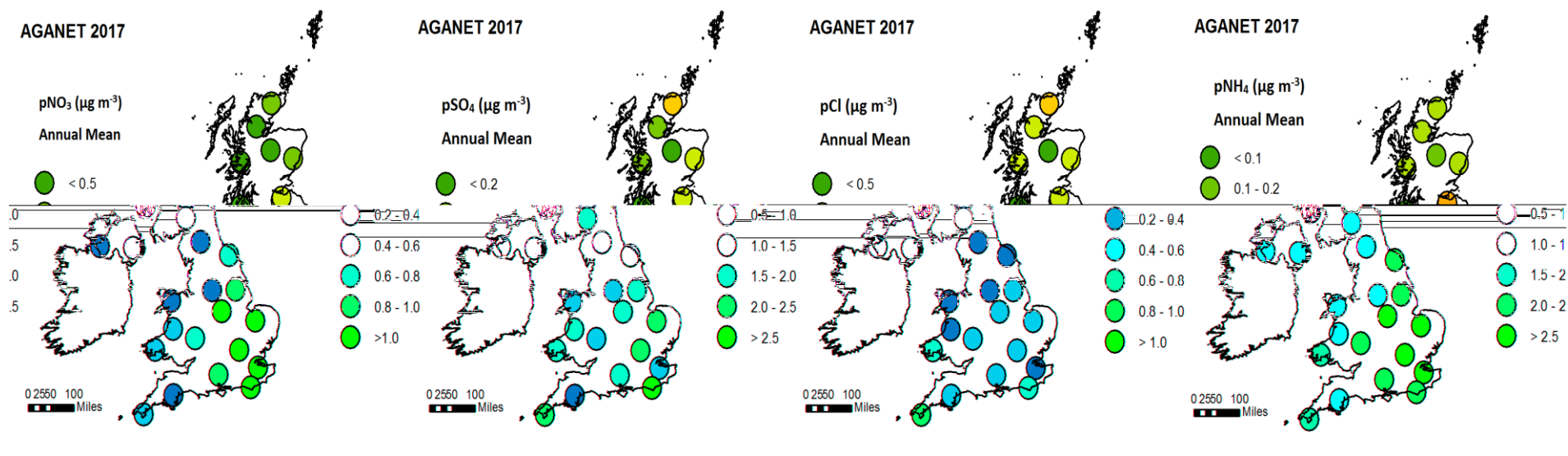
Figure 24: Annual mean monitored atmospheric aerosols (particulate NO_3^-, SO_4^{2-}, and Cl^- from AGANET and NH_4^+ from NAMN) concentrations across the UK from averaged monthly measurements made in 2017.
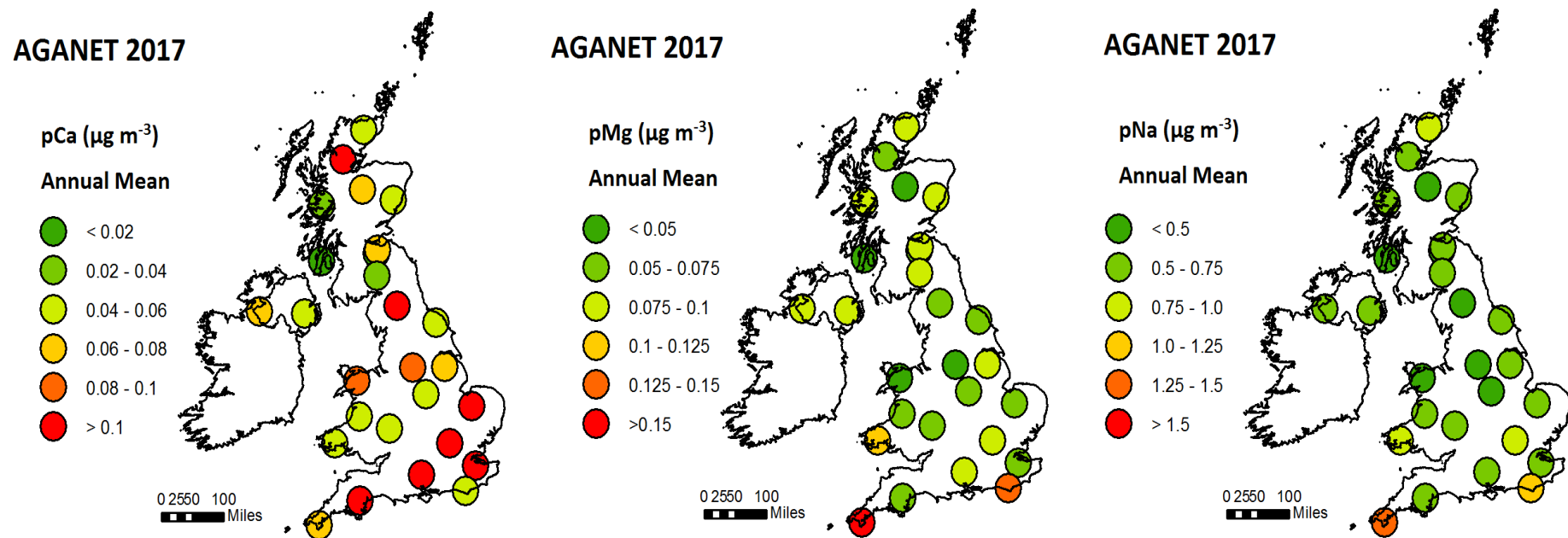
Figure 25: Annual mean monitored atmospheric base cation (Ca^{2+}, Mg^{2+} and Na$^+$) concentrations across the UK from the averaged monthly measurements made in 2017.
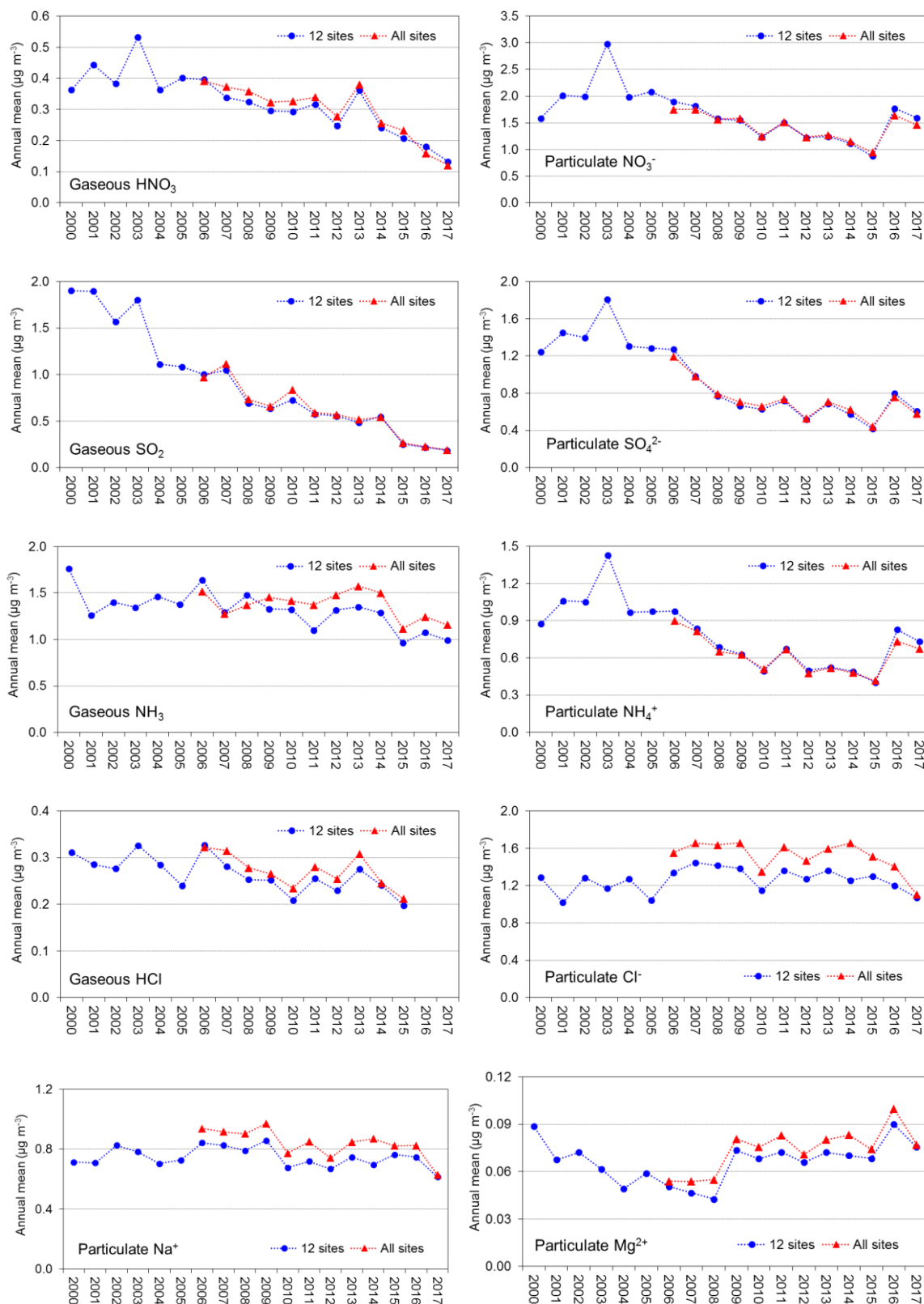
Figure 26: Long-term trend in annual mean concentrations of gases and aerosols monitored in AGANET. Each data point represents the time-weighted averaged annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites) and also the original l2 monitoring sites in the network. Since 2016, HCl is no longer measured in the new DELTA sampling train configuration. NAMN NH$_3$ data for AGANET sites are also shown, for comparison.
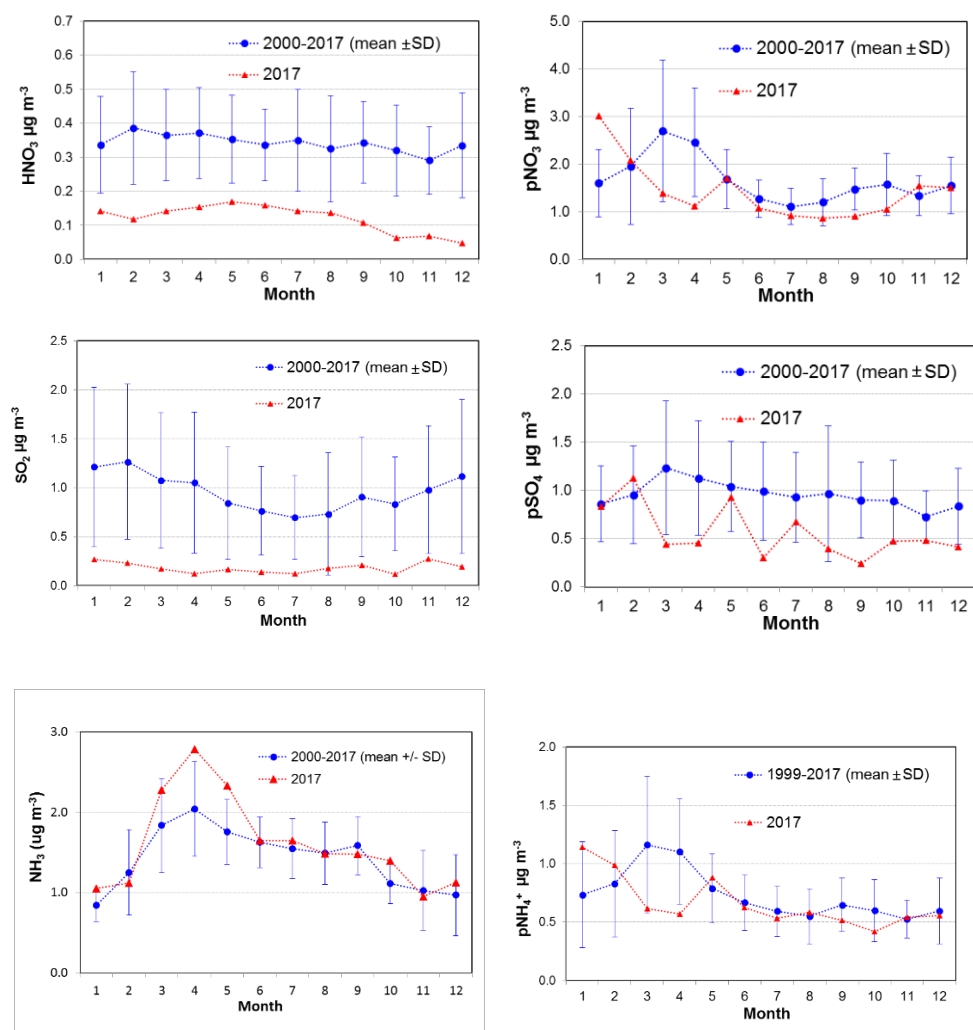
Figure 27: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (2000-2017: mean +/- SD of 27 AGANET sites) against year 2017.

3. UK EMEP Supersites 2017 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 <u>UNECE Convention on Long Range Transboundary Air Pollutants</u>). Measurements made at the supersites in 2016 are summarised in Table 4.

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 <u>Annex IV</u> 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 (<u>AURN</u>), the UK-wide network providing evidence for the UK for compliance with the <u>EU Ambient Air Directives</u> and the <u>Gothenberg Protocol</u> 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 4   Pollutants measured at the UK EMEP Supersites during 2016

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**	**X**	**I**	**Hourly**	**UKEAP**	**CEH/Ricardo E&E**
Total gaseous mercury in air	**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	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
Particulate matter $PM_{2.5}$, PM_{10}	X	X	I	Daily	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	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		II	Daily	Particle numbers	NPL
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
Trace gas fluxes (O_3, NOx, SO_2)		X	III		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 2017 more than 20 research outputs (papers or presentations) have been identified using data from Auchencorth Moss.

3.1 Auchencorth

MARGA summary

The annual summary of trace gas mass concentration from the Auchencorth EMEP Supersite for 2017 is shown in Table 5 and in Figure 28. The particulate matter (PM_{10} and $PM_{2.5}$) summary is in Table 7-8 and Figures 22-23 respectively. Overall data capture at Auchencorth Moss was 74% for trace gases and in the range 52-74% for particulate mass components. The data capture was low due to failure in the cation IC unit which led to downtime. A new instrument was installed in 2018.

Table 5 Annual summary of trace gas mass concentration measurements at Auchencorth Moss for 2017

Trace gas	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_3	1.32	71
HCl	0.13	75
HNO_3	0.10	74
HNO_2	0.10	74
SO_2	0.11	74

Table 6 Annual summary of the speciated PM_{10} mass concentration from the Auchencorth EMEP Supersite, 2017

Ion (PM_{10})	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	0.56	52
Na^+	0.58	54
K^+	0.05	54
Ca^{2+}	0.02	54
Mg^{2+}	0.05	54
Cl^-	1.14	72
NO_3^-	1.20	72
SO_4^{2-}	0.87	72

Table 7 Annual summary of the speciated PM2.5 mass concentration from the Auchencorth EMEP Supersite, 2017

Ion ($PM_{2.5}$)	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	0.54	52
Na^+	0.34	52
K^+	0.03	53
Ca^{2+}	0.01	55
Mg^{2+}	0.02	55
Cl^-	0.62	74
NO_3^-	1.00	74
SO_4^{2-}	0.77	74
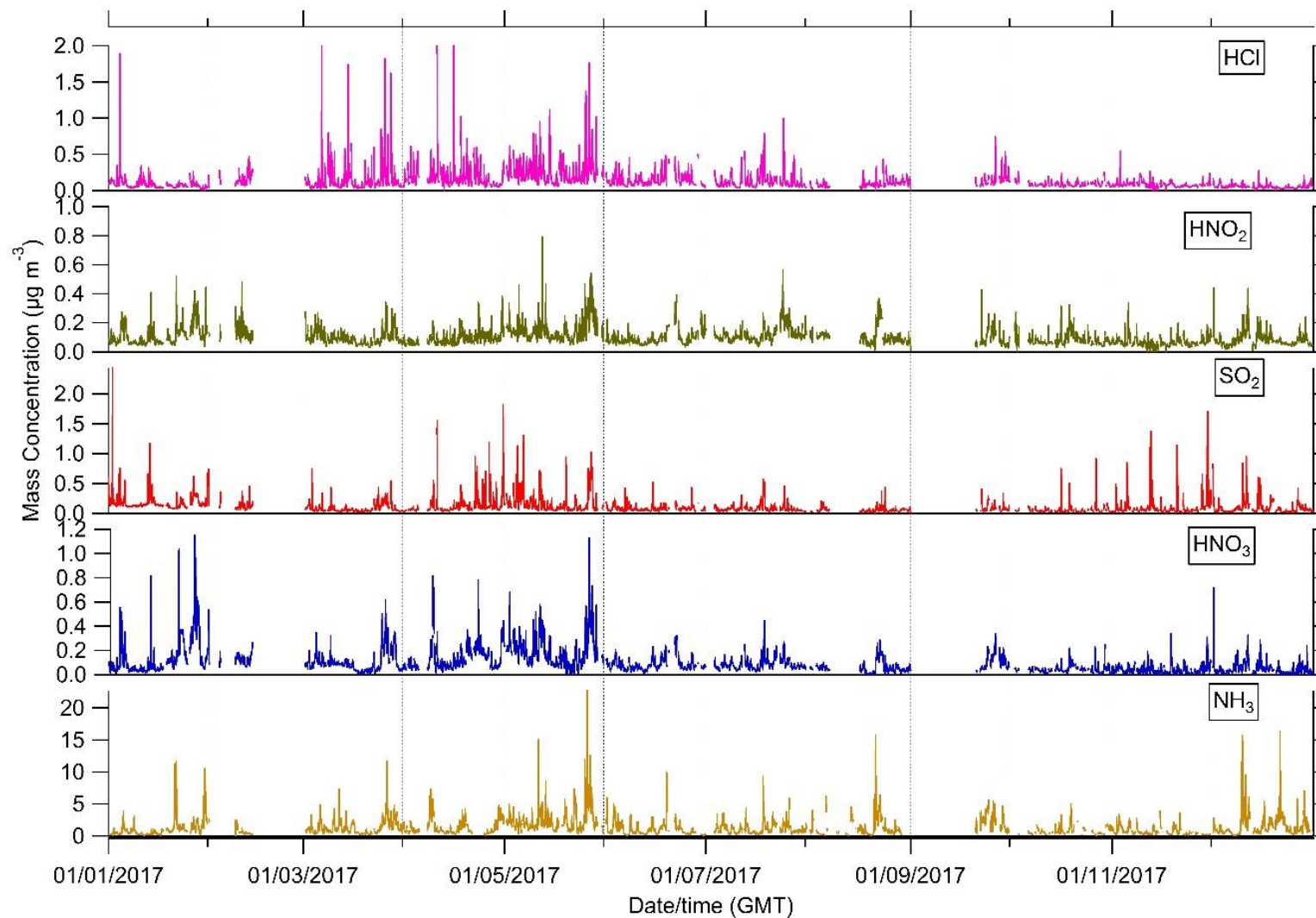
Figure 28 Ratified gas measurements from the MARGA instrument at Auchencorth Moss for 2017
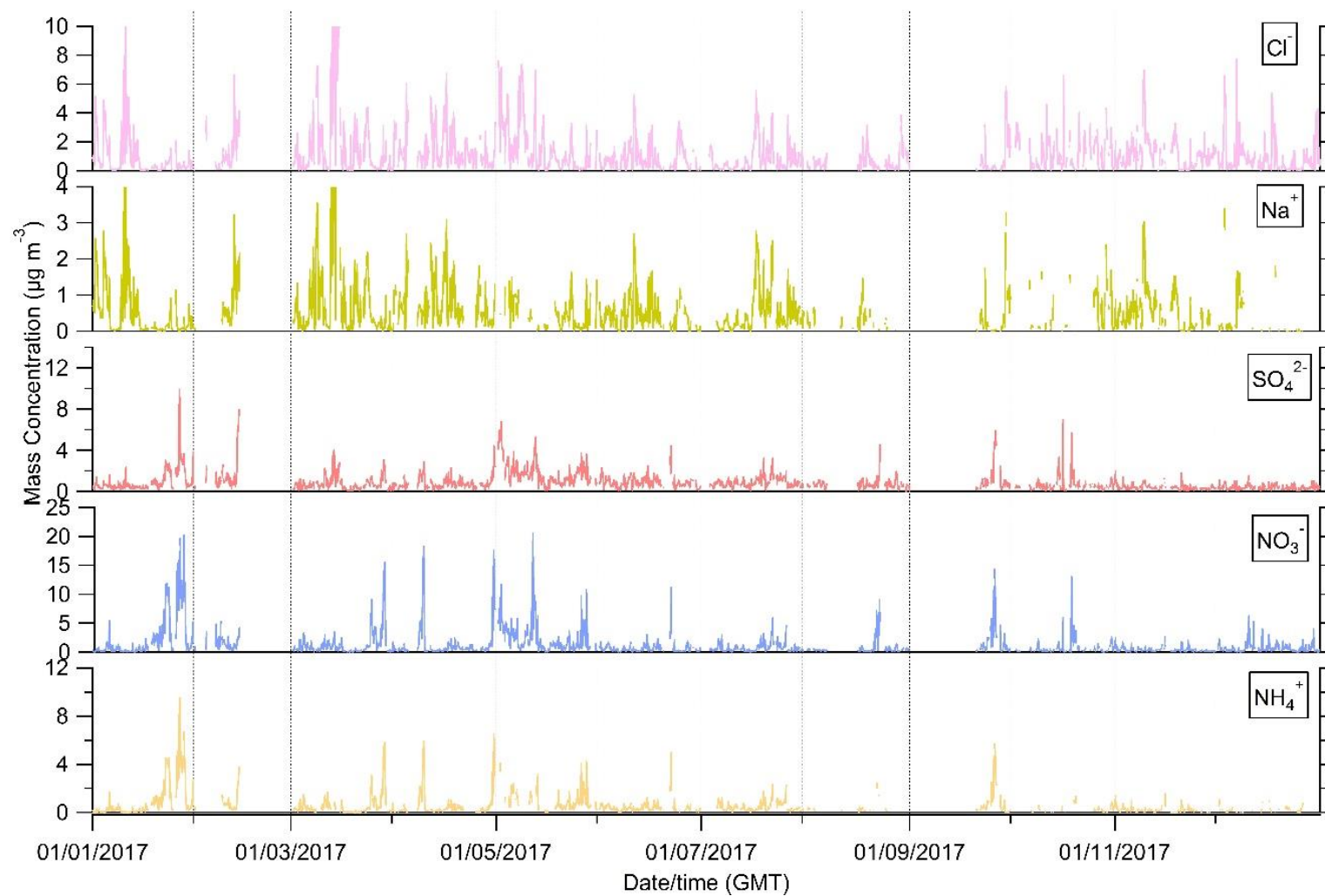
Figure 29 Ratified PM$_{10}$ measurements from the MARGA instrument at Auchencorth Moss for 2017.
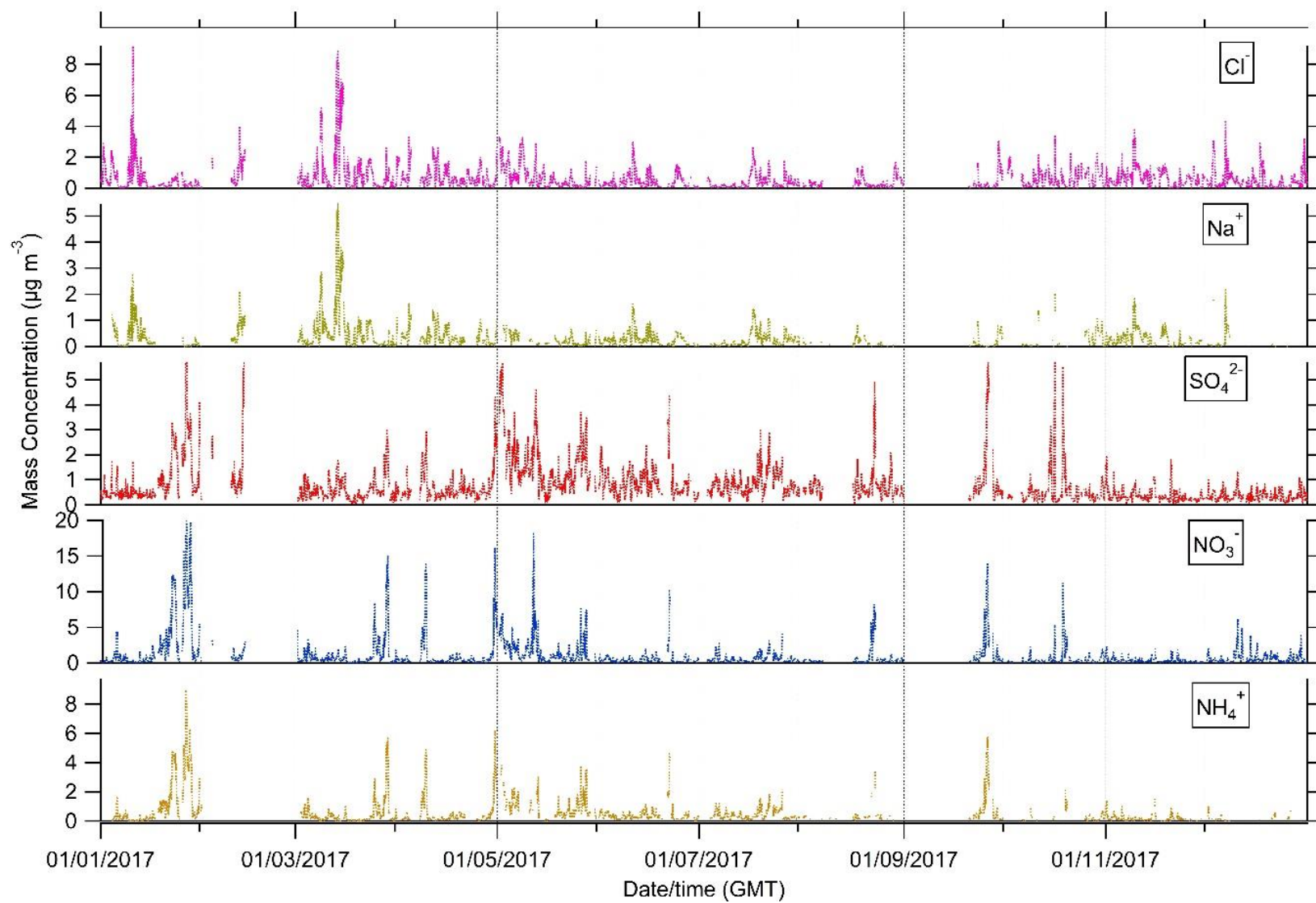
Figure 30 Ratified PM$_{2.5}$ measurements from the MARGA instrument at Auchencorth Moss for 2017

Mercury Measurements

The Auchencorth mercury measurements data capture for 2017 are shown in the Table 8. The statistics presented are based on the ratified measurements supplied to UK-Air. Time series plots of the 2017 Auchencorth Moss measurements are shown in Figure 31.

From the beginning of the year until April when the new analyser was installed there is no data capture due to the lamp stabilization circuit board in the 2537A instrument failing, leaving the analyser inoperative. 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 new anaylser was working and does not require the speciation sampling unit.

Table 8: Auchencorth Moss mercury measurements 2017 statistics

	Annual Mean	Data Capture
Gaseous Elemental Mercury (GEM)	1.37 ngm^{-3}	61.95 %
Particulate Bound Mercury (PBM, PM$_{2.5}$)	3.10 pgm^{-3}	4.52 %
Gaseous Oxidised Mercury (GOM)	1.39 pgm^{-3}	4.44 %
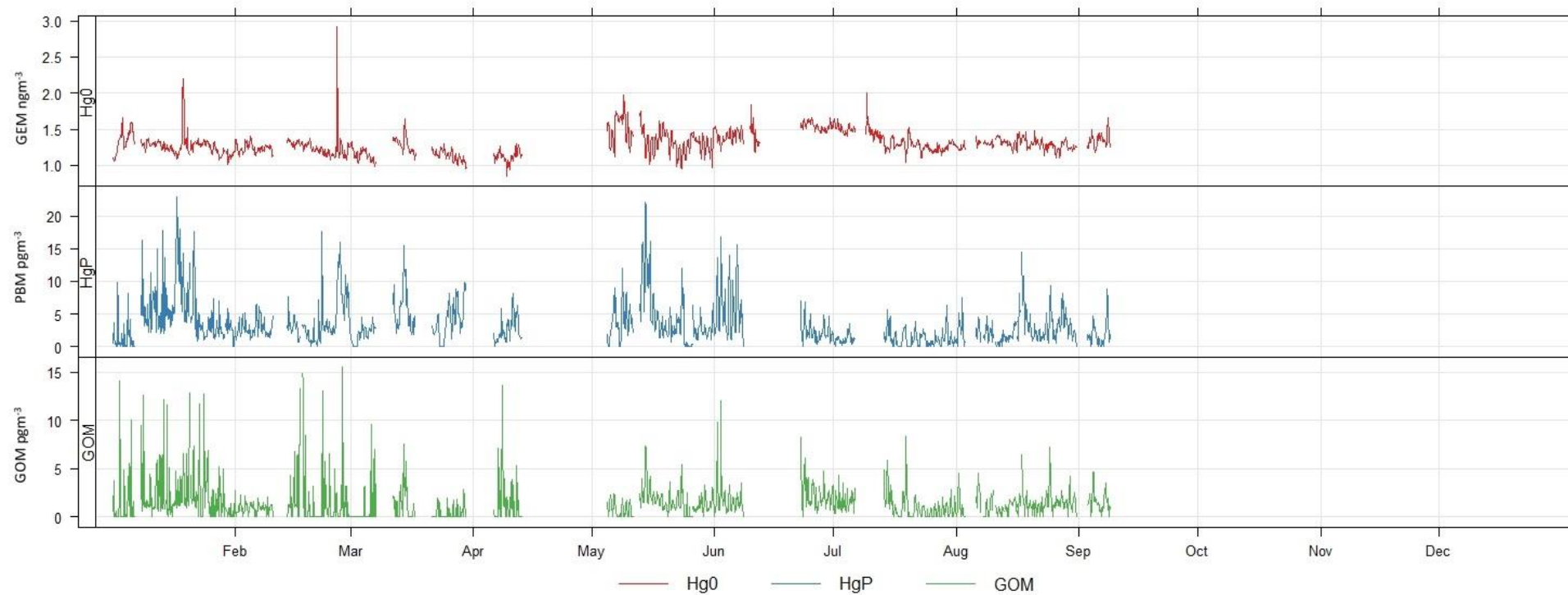
Figure 31: Speciated Mercury Measurements at Auchencorth Moss, 2017

3.2 Chilbolton

The Chilbolton site was commissioned in early 2016 after a decision was made to cease the Harwell monitoring site which has been operating as a monitoring site in some capacity since June 1976. The site was relocated due to redevelopment at the Harwell site and may not have be considered as representative of a rural location in the south east of England. The MARGA that was operating at Harwell was relocated to the Chilbolton Science and Technology Facilities Council (STFC) site in Hampshire.

Annual mean concentrations of trace gas and aerosol measurement are summarised in Tables 9-11 detailing the annual mean and % data capture for the PM_{10}, $PM_{2.5}$, and trace gas species, respectively, measured by the Chilbolton MARGA. On average less than 26% of the measurement data was lost due to intermittent blockages in the equipment sampling lines and operational issues in 2017. The main operational issue starts 4th July and was resolved by the 9th August which was related to a software issue within the instrument that required intervention from the manufacturer.

The statistics presented are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2017 Chilbolton MARGA measurements (major species and trace gases) are shown in Figure 32, Figure 33, and Figure 34 below.

Table 9 Annual summary of trace gas mass concentration from the Chilbolton EMEP Supersite, 2017.

Trace gas	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_3	2.51	82
HCl	0.06	79
HNO_3	0.17	79
HNO_2	0.45	79
SO_2	0.13	78

Table 10 Annual summary of the speciated PM10 mass concentration from the Chilbolton EMEP Supersite, 2017.

Ion (PM_{10})	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	0.91	80
Na^+	0.73	69
K^+	0.14	36
Ca^{2+}	0.52	80
Mg^{2+}	0.35	80
Cl^-	1.06	77
NO_3^-	1.77	78
SO_4^{2-}	1.41	76

Table 11 Annual summary of the speciated PM2.5 mass concentration from the Chilbolton EMEP Supersite, 2017.

Ion ($PM_{2.5}$)	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	0.84	81
Na^+	0.36	63
K^+	0.13	24
Ca^{2+}	0.14	81
Mg^{2+}	0.20	81
Cl^-	0.58	77
NO_3^-	1.50	78
SO_4^{2-}	1.22	77
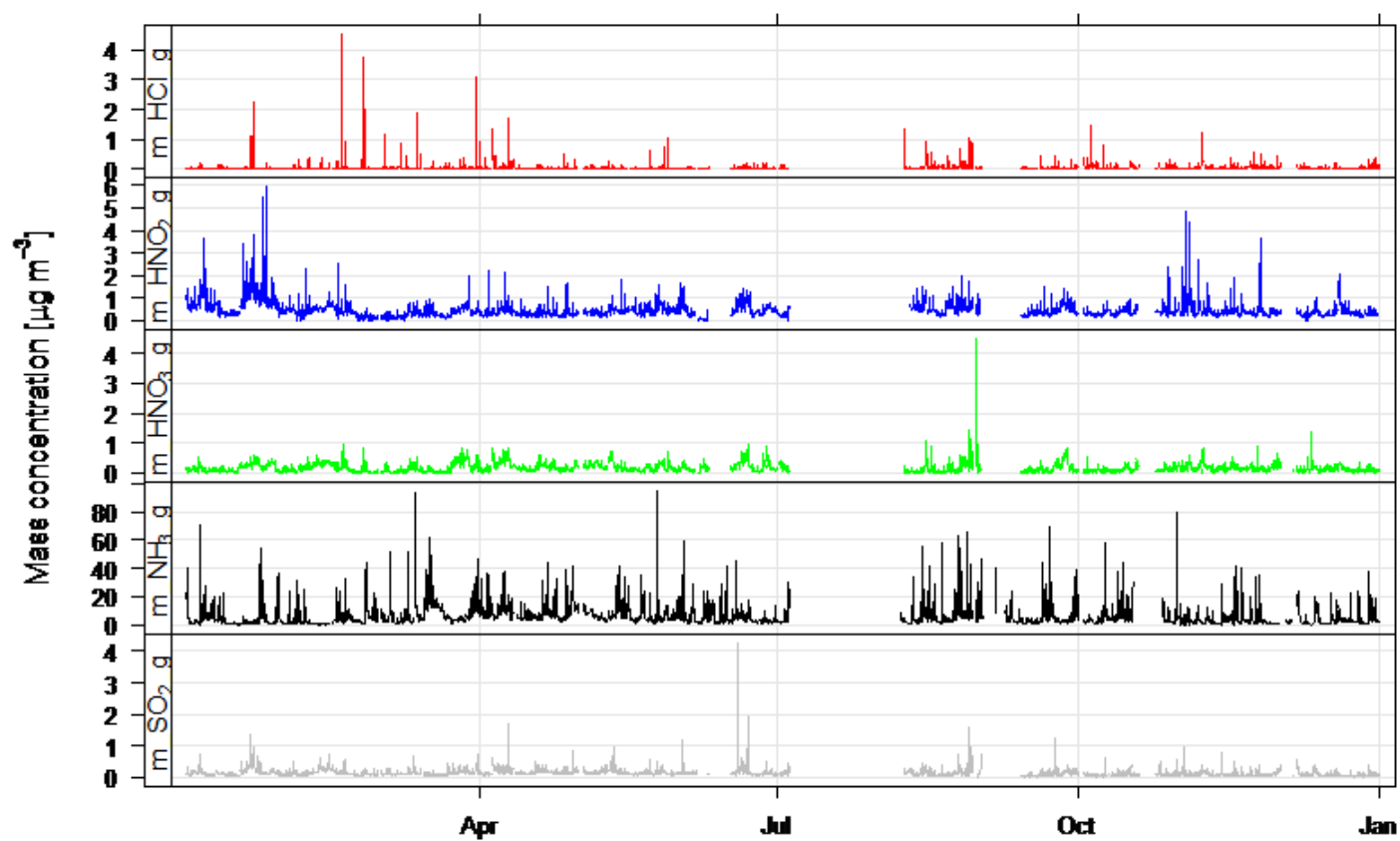
Figure 32 Time series plot of the trace gas (HCl, HNO₂, HNO₃, NH₃, SO₂) measurements from the Chilbolton MARGA, 2017.

Figure 33 Time series plot of the major PM10 species (Cl$^-$, Na$^+$, NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$) measurements from the Chilbolton MARGA, 2017. Base cation species (Ca^{2+}, Mg^{2+} and K$^+$)measurements not shown.
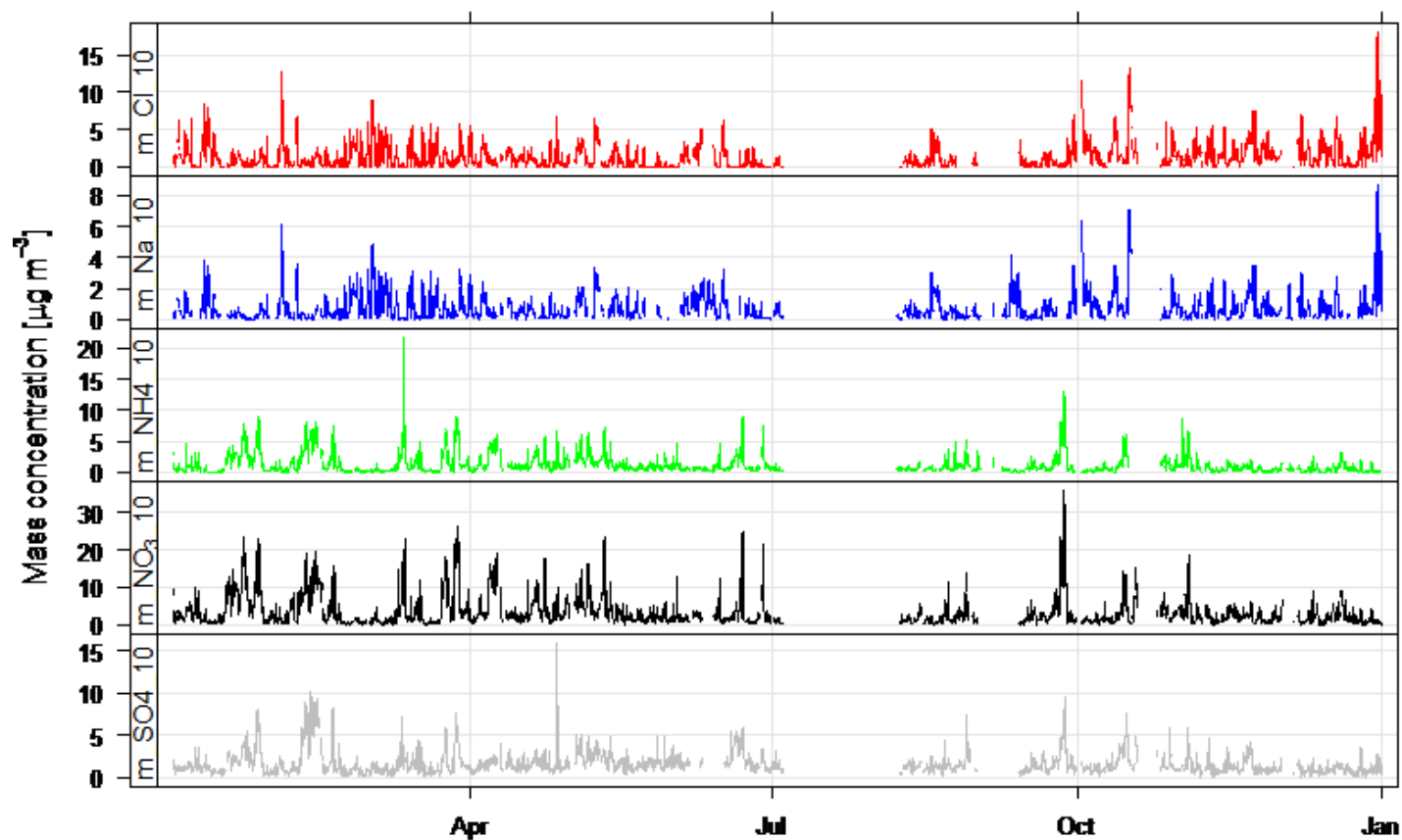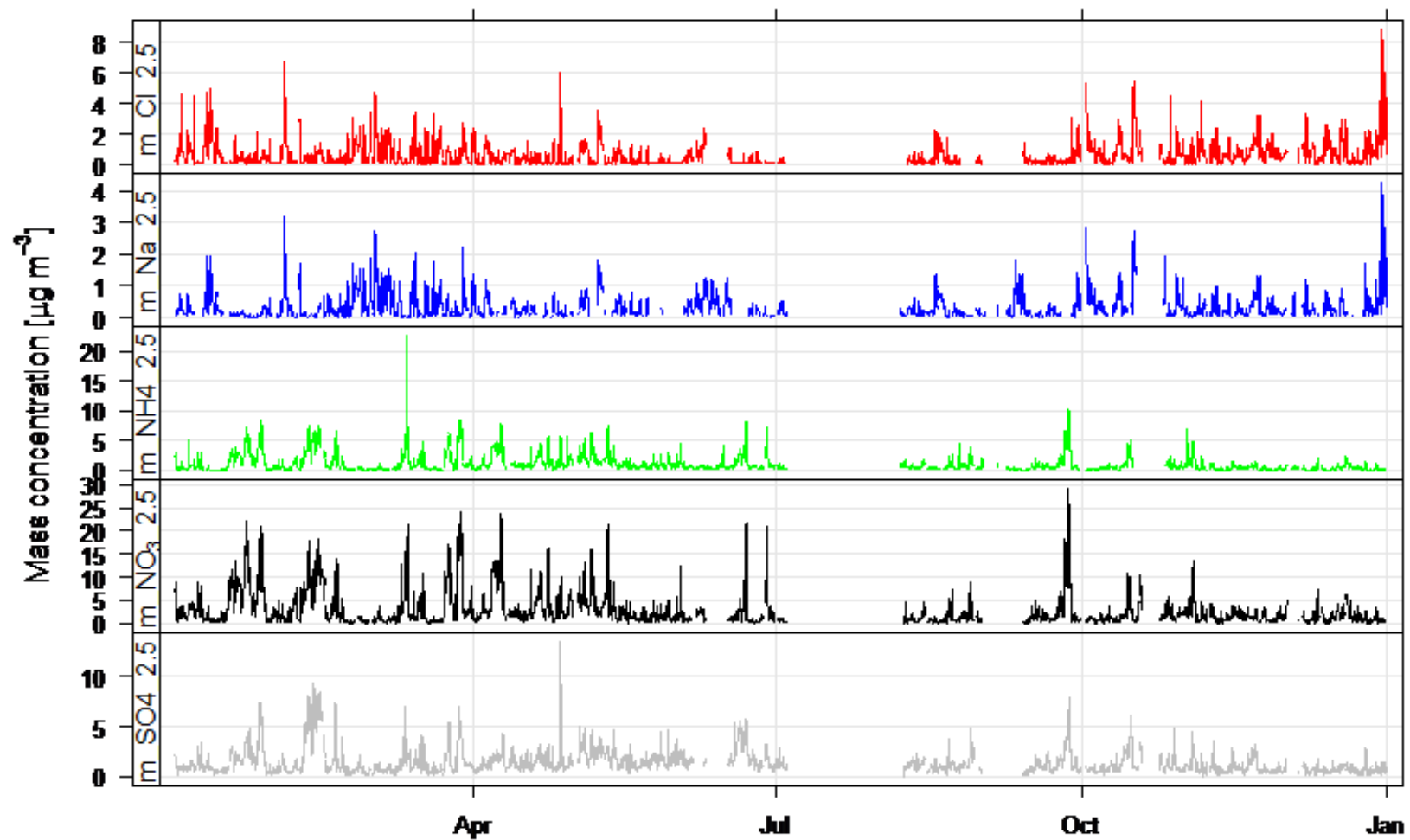
Figure 34 Time series plot of the major PM2.5 species (Cl⁻, Na⁺, NH₄⁺, NO3-, and SO₄²⁻) measurements from the Chilbolton MARGA, 2017. Base cation species (Ca²⁺, Mg²⁺ and K⁺) measurements not shown.

Typical meteorological parameters are measured at the Chilbolton EMEP Supersite. The 2017 annual means and data captures are summarised in Table 12. Data capture for the parameters measured was 100%.

Table 12 2017 Summary of the Chilbolton EMEP Supersite meteorological observations

Meteorological parameter	Annual mean	Data capture (%)
Barometric pressure (mbar)	1008.1	100%
Dewpoint (°C)	7.6	100%
Wind direction (°)	206.5	100%
Wind speed (m s-1)	3.8	100%
Relative humidity (%)	83.5	100%
Temperature (°C)	10.7	100%
Meteorological parameter	Total	Data capture (%)
Rainfall (mm)	701.7	100%

Meteoritical measurements Chilbolton EMEP Supersite during 2017. Figure 35 shows a plot of the directional frequency (in 10° sectors) for 2017. The Figure shows that the air masses arriving at the Chilbolton EMEP Supersite predominantly originated from the west and south-west and were therefore dominated by European air masses.

The southerly and south-westerly winds were typically of the order of 2 to 5 m s^{-1}, which is consistent with the annual mean presented in Figure 35, and maximums of up to 16 m s^{-1}. Figure 36 shows the same observations disaggregated by calendar month in order to highlight monthly and seasonal trends. The monthly summary plots show that high wind speeds were associated with winds originating from the south, west and south-west. One notable feature of the monthly summary plots was that in the winter month's (December, January, February) winds speeds were higher, with light south easterly winds dominant in the summer months (May, June, July).
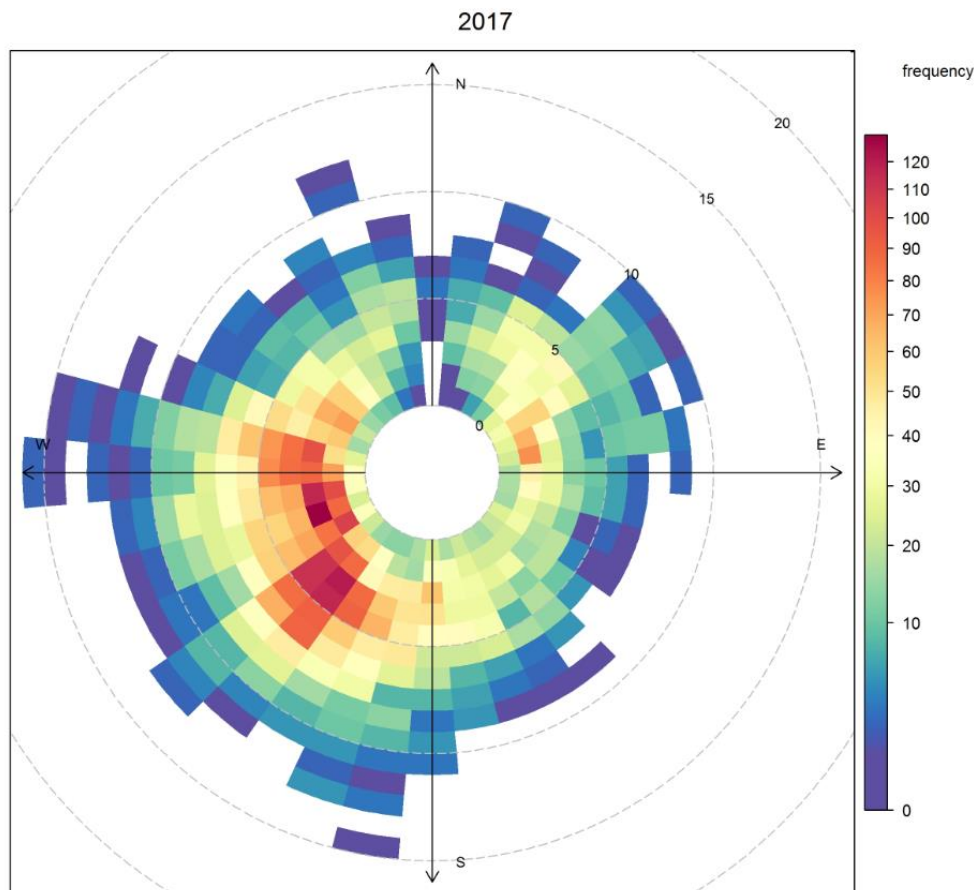
Figure 35 Wind speed (m s^{-1}) and directional frequency for the Chilbolton EMEP Supersite, 2017.
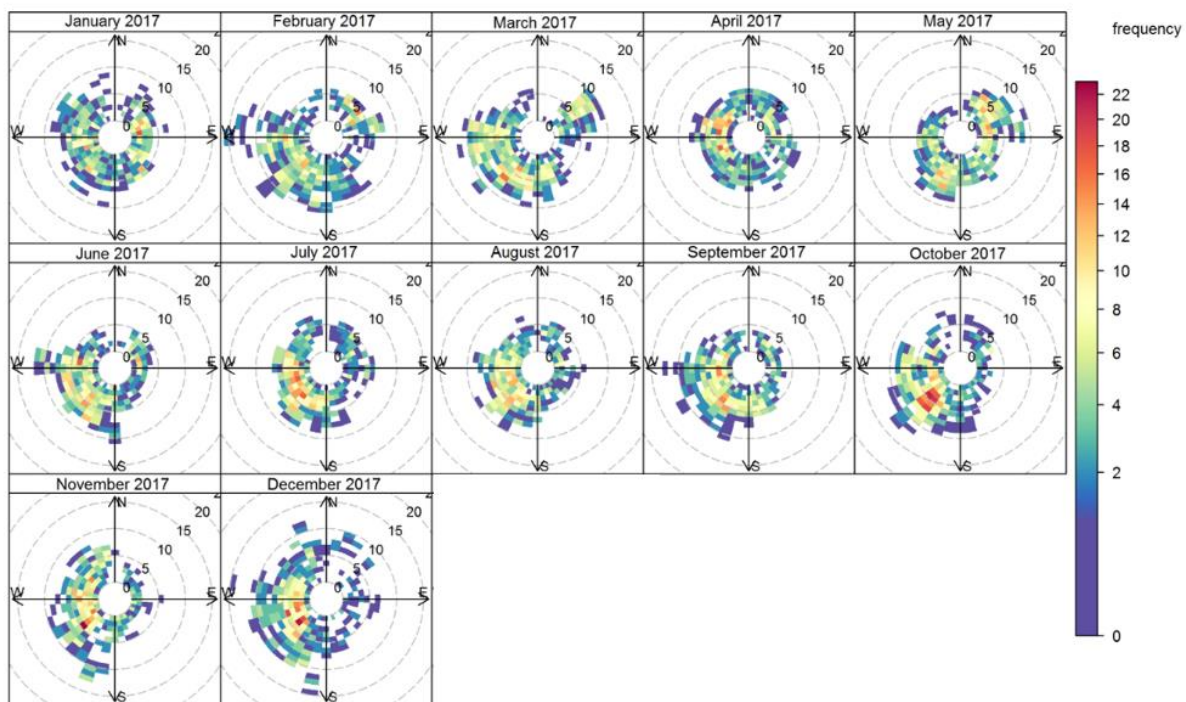
Figure 36 Monthly variations of hourly wind speed and directional frequency for the Chilbolton EMEP Supersite, 2017

Mercury measurments

The Chilbolton mercury measurements data capture for 2017 are shown in Table 13. The statistics presented are based on the ratified measurements supplied to UK-Air. Time series plots of the 2017 Chilbolton measurements are shown in Figure 37. A new analyser was installed in April 2017. From mid-November to the end of the year the instrument had flow issues. As a result the data collected in this period has been made invalid as the sample volumes were incorrect.

	Annual Mean	Data Capture
Total Gaseous Mercury (TGM)	1.41 ngm^{-3}	70.3 %

.

Table 13 Mercury measurement statistics, Chilbolton 2017
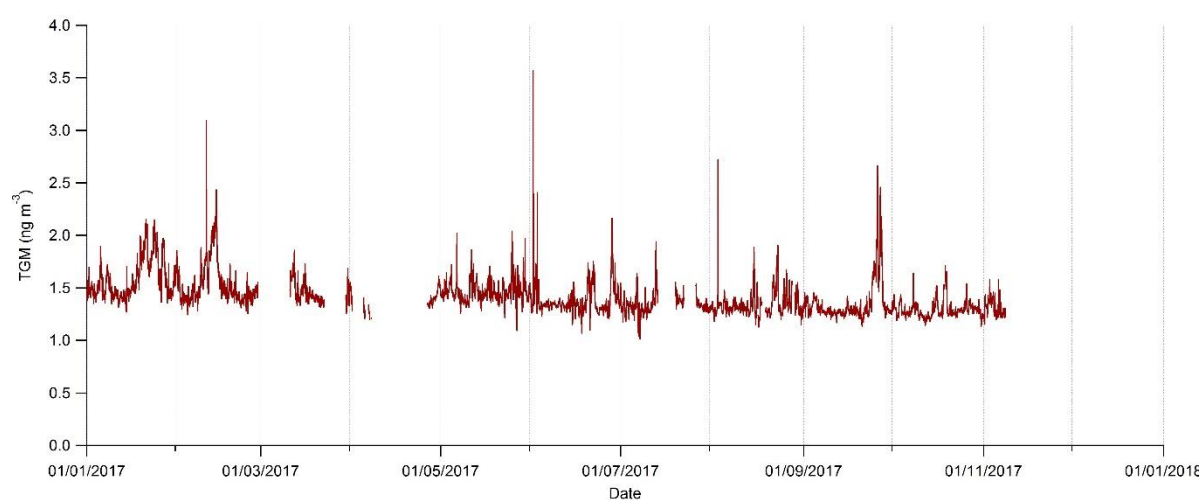
Figure 37 Total Mercury Measurements at Chilbolton, 2017

3.3 Harwell-Chilbolton relocation: Initial assessments

In 2017-2018 a PhD student associated with the CEH co-funding of the UKEAP network contract has been investigating changes in pollutant concentrations measured by the UK air quality networks following the relocation of instrumentation from Harwell to Chilbolton at the beginning of 2016. In particular the high resolution measurements of SO_2, NH_3, NO_x and ozone in the gas phase, and the PM measurements are being analysed. Results from the SO_2 and NH_3 are presented below.

Using the MARGA hourly data, there is no clear step change in SO_2 concentrations (Figure 38) following relocation. SO2 concentrations are generally < 1-2 $\mu g.m^{-3}$ at both locations with occasional peaks which are attributed to transient plumes, the largest of which is the 2014 volcano plumes which have been reported previously.

There is a clear step change in NH_3 concentrations. This is confirmed both with the original data and with data following meteorological effects being statisticaly smoothed out using a Deweather function (Carslaw et al. 2015)(Figure 39). The step change increase is probably due to local sources of NH3 from the nearby farms in the south west direction - this is highlighted in the polar plot (Figure 40). Further studies on the changes between sites are continuing.
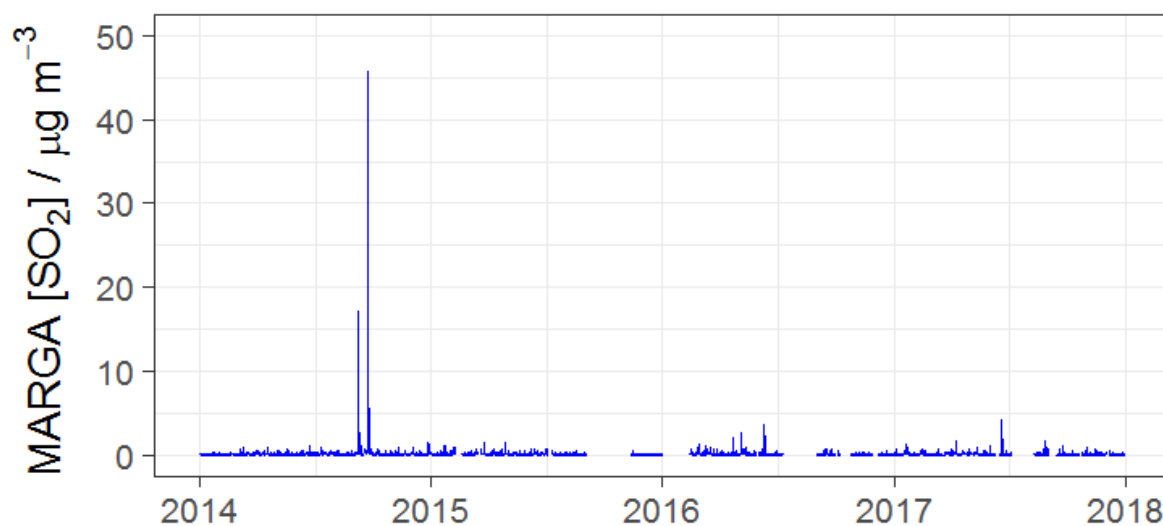
Figure 38 Time series of SO2 from the MARGA instrument. Measurements were made on-site at Harwell from 1st January 2014 until 31st December 2015, before resuming at Chilbolton on 11th January 2016 until 31st December 2017.
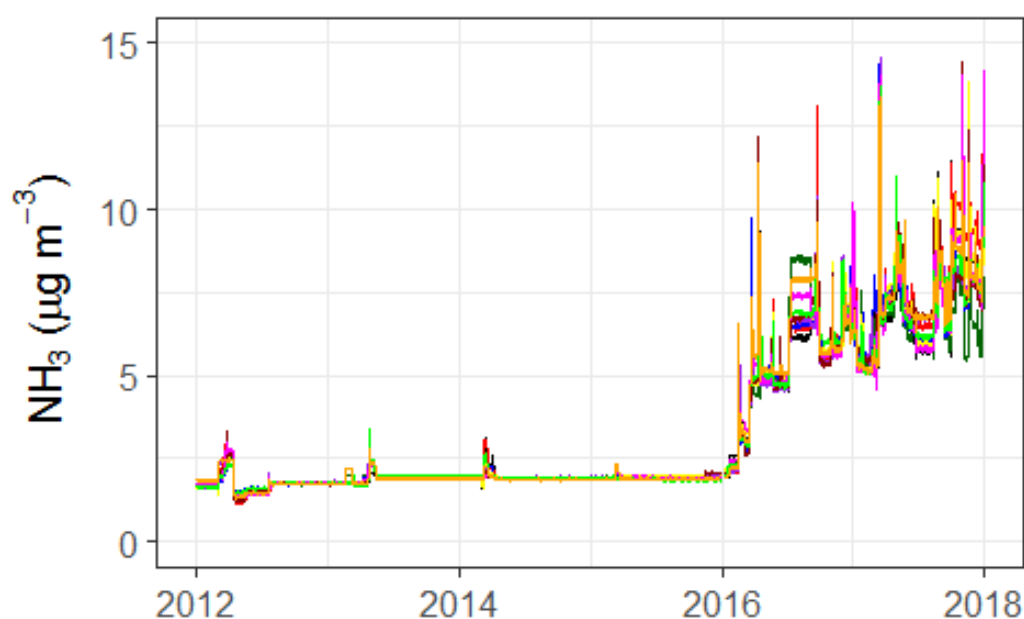
Figure 39 Modelled pollutant concentrations using the deweather function (Carslaw, 2015), smoothed by plotting daily average for NH_3. Measurements were made on-site at Harwell from 1st January 2014 until 31st December 2015, before resuming at Chilbolton on 11th January 2016 until 31st December 2017.
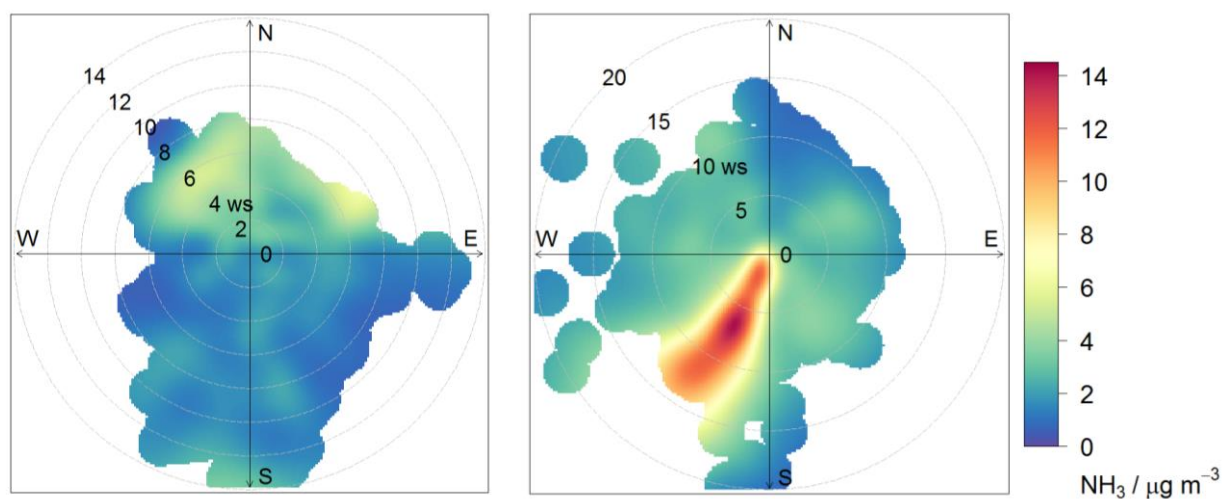
Figure 40 Polar plots of NH_3 as a function of wind speed and direction at Harwell 2015 (left) and Chilbolton 2016-2017 (right). Harwell shows lower concentrations for all wind directions and speeds with slightly elevated concentrations from the north (~ 4 µg m^{-3}). However the polar plot for Chilbolton provides evidence of a local major source, showing largest concentrations for winds (0-15 m s^{-1}) from the south-west

4. Acknowledgements

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: Mr John Kentisbeer, NERC Centre for Ecology and Hydrology

Kentisbeer, J., Ritchie, S., Leeson, S.R. 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: Mr John Kentisbeer, NERC Centre for Ecology and Hydrology

Kentisbeer, J., Simmons, I, Jones, M.R., Harvey, D., Leeson, S.R. 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., Poskitt, J., Nemitz, E., 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. , Poskitt, J., Nemitz, E., 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 2017

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 2016 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. There is a proposed CEN standard method being discussed in 2016 for the determination of the concentration of anionic or cationic species in PM_{10} and $PM_{2.5}$, however it is at proposal stage. 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 at least three times a week, namely on Mondays, Wednesdays and Fridays, 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 flowrate through each box was 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 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 in the Chilbolton MARGA in 2016 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 14) 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.

Table 14 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$_2$O$_2$ 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 35th EMEP Inter-comparison

The inter-comparison in 2017 was the 35th time such an inter-comparison took place. The samples provided included nitrogen dioxide in absorbing solution (Table 16) and synthetic rainwater samples (Table 17).

Nitrogen Absorbing Solutions:
The inter-comparison in 2017 was the 35th time such an inter-comparison took place. The results of the Nitrogen Dioxide absorbing solution are shown below in Table 15 The results of this intercomparison are excellent with between a 1.2% and 4.0% 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 15 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	Absolute Mean difference (%)	EMEP Assessment
C1	0.092	0.089	3.3%	S
C2	0.099	0.095	4.0%	S
C3	0.163	0.159	2.5%	S
C4	0.17	0.168	1.2%	S

Synthetic Rainwater Samples:
The performance of Ricardo's chosen laboratory (SOCOTEC UK Limited previously known as Environmental Scientifics Group Ltd) has improved since the 34th intercomparison. The results of the intercomparison and the expected results are shown in Table 16. The 2017 intercomparison produced five questionable results and one unsatisfactory result. The analytical laboratory has been made aware of the analytical performance and the results that have been obtain from the intercomparison. They have investigated the poor pH data along with smaller errors identified with the results for calcium and potassium and have improved processes.

The issues identified in the previous intercomparison in 2016 (34th intercomparison) relating to the analysis of ammonium (NH_4^+) appear to have been resolved with all of the results being satisfactory and within 3% of the expected values.

Table 16 35th EMEP Inter-comparison

Species	Sample code	Expected concentration μeq l⁻¹	Measured concentration μeq l⁻¹	Mean difference (%)	Assessment [1]
SO_4^{-2}	G1	1.319	1.30	-1.7%	S
	G2	0.856	0.84	-2.0%	S
	G3	2.08	2.06	-1.2%	S
	G4	2.2	2.16	-1.8%	S
NH_4^+	G1	0.241	0.23	-3.0%	S
	G2	0.16	0.16	-1.5%	S
	G3	0.401	0.39	-2.9%	S
	G4	0.535	0.52	-2.2%	S
NO_3^-	G1	0.546	0.55	0.4%	S
	G2	0.364	0.37	0.6%	S
	G3	0.911	0.93	2.0%	S
	G4	0.942	0.96	1.5%	S
Na^+	G1	0.548	0.51	-7.5%	S
	G2	0.365	0.33	-10.5%	S
	G3	0.913	0.88	-3.9%	S
	G4	0.73	0.71	-3.1%	S
Mg^{2+}	G1	0.155	0.14	-11.1%	S
	G2	0.093	0.08	-14.1%	S
	G3	0.206	0.19	-9.9%	S
	G4	0.206	0.19	-9.5%	S
Cl^-	G1	0.347	0.32	-6.9%	S
	G2	0.232	0.21	-8.7%	S
	G3	0.579	0.56	-4.0%	S
	G4	0.463	0.44	-5.1%	S
Ca^{2+}	G1	0.192	0.17	-11.5%	S
	G2	0.115	0.10	-16.4%	Q
	G3	0.255	0.22	-13.6%	S
	G4	0.255	0.22	-13.5%	S
K^+	G1	0.306	0.26	-16.1%	Q
	G2	0.204	0.16	-20.7%	Q
	G3	0.509	0.45	-11.8%	S
	G4	0.407	0.35	-13.3%	S
pH*	G1	4.22	4.43	0.21	U
	G2	4.4	4.52	0.12	Q
	G3	4	4.13	0.13	Q
	G4	4	4.07	0.07	S
Cond	G1	35.3	35.4	0.3%	S
	G2	23.4	23	-1.7%	S
	G3	57.9	57.9	0.0%	S
	G4	57.9	61.6	6.4%	S

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

4. NO₂-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 overread 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)[6] recommends, either:

- Use results from the national bias adjustment spreadsheet[7];
- 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 Rural NO2 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 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.

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[6] https://laqm.defra.gov.uk/technical-guidance/

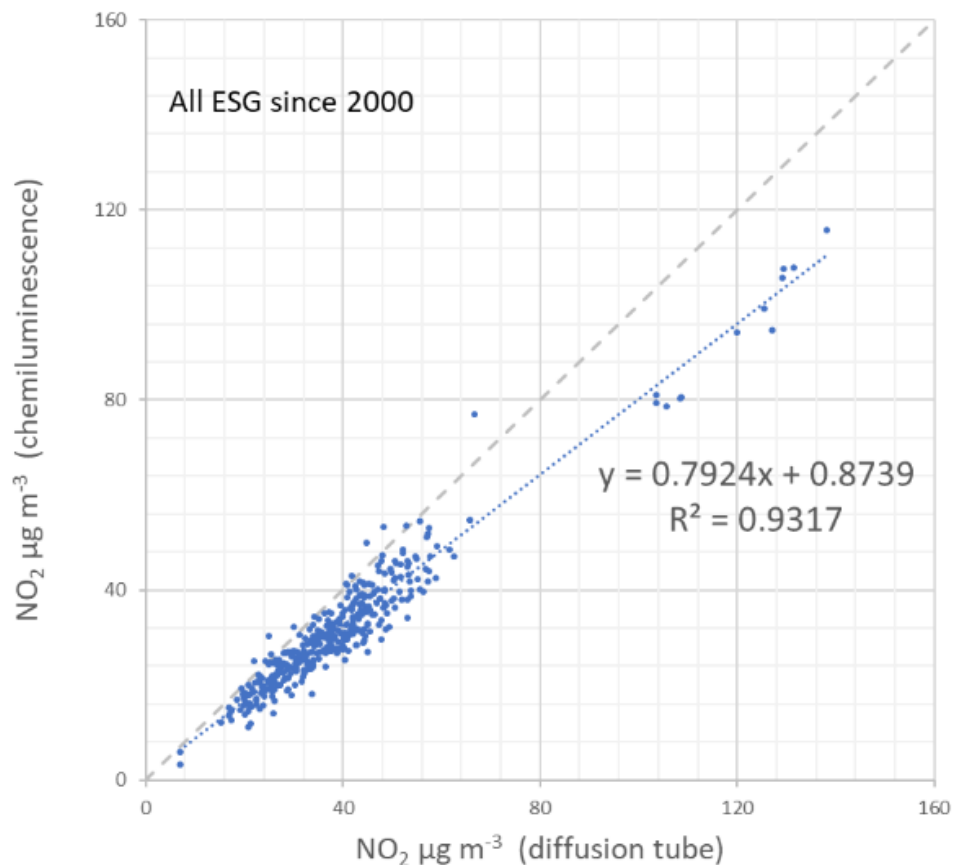[7] https://laqm.defra.gov.uk/bias-adjustment-factors/national-bias.html

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 17. 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. While there are only two years of data collected so far, the behaviour of the concentrations at Chilbolton appears anomalous – the concentration measured by the automatic analyser are higher than measured by the diffusion tubes. This may result from the fact that 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.

Table 17 Annual mean nitrogen dioxide concentrations (µg m^{-3}) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis)

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

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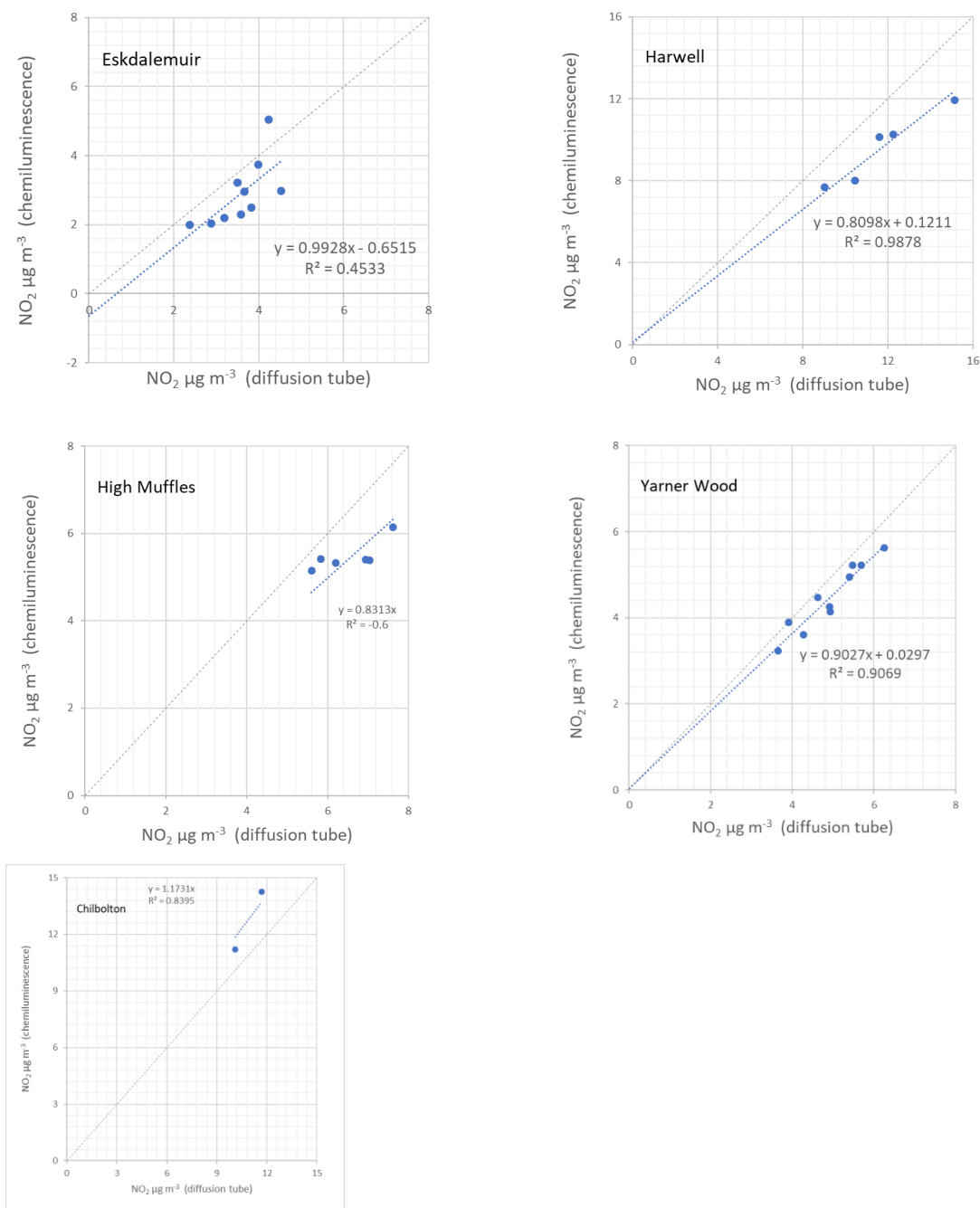
Figure 42 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each

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 three co-located NO$_2$ sampling sites (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[8] to allow for time weighting the mean concentrations and bias adjustment factors. As we have three co-located sampling sites we will need to follow the advice provided in Paragraph 7.193[9] to combine the respective bias B factors.

The individual bias B factors were calculated as follows:

	Eskdalemuir	Yarner Wood	High Muffles
Bias factor, B	29%	19%	15%

The average of the three values is calculated to be 20.74 % giving a bias adjustment factor of 0.828[10].

We would recommend multiplying each of the remaining diffusion tubes in the Rural NO$_2$ Network by this factor.

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[8] See https://laqm.defra.gov.uk/bias-adjustment-factors/local-bias.html   and Figure 7.1 of TG(16)
[9] 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.
[10] Calculated as (1 / (1+0.2074))

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 43 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.
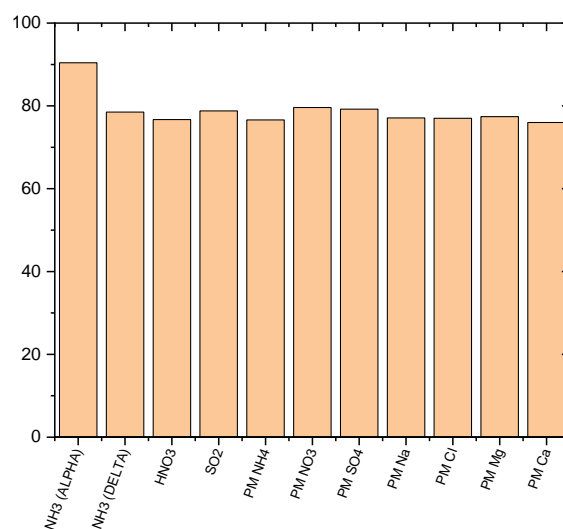

Figure 43 2017 NAMN and AGANet Percentage data capture by chemical component

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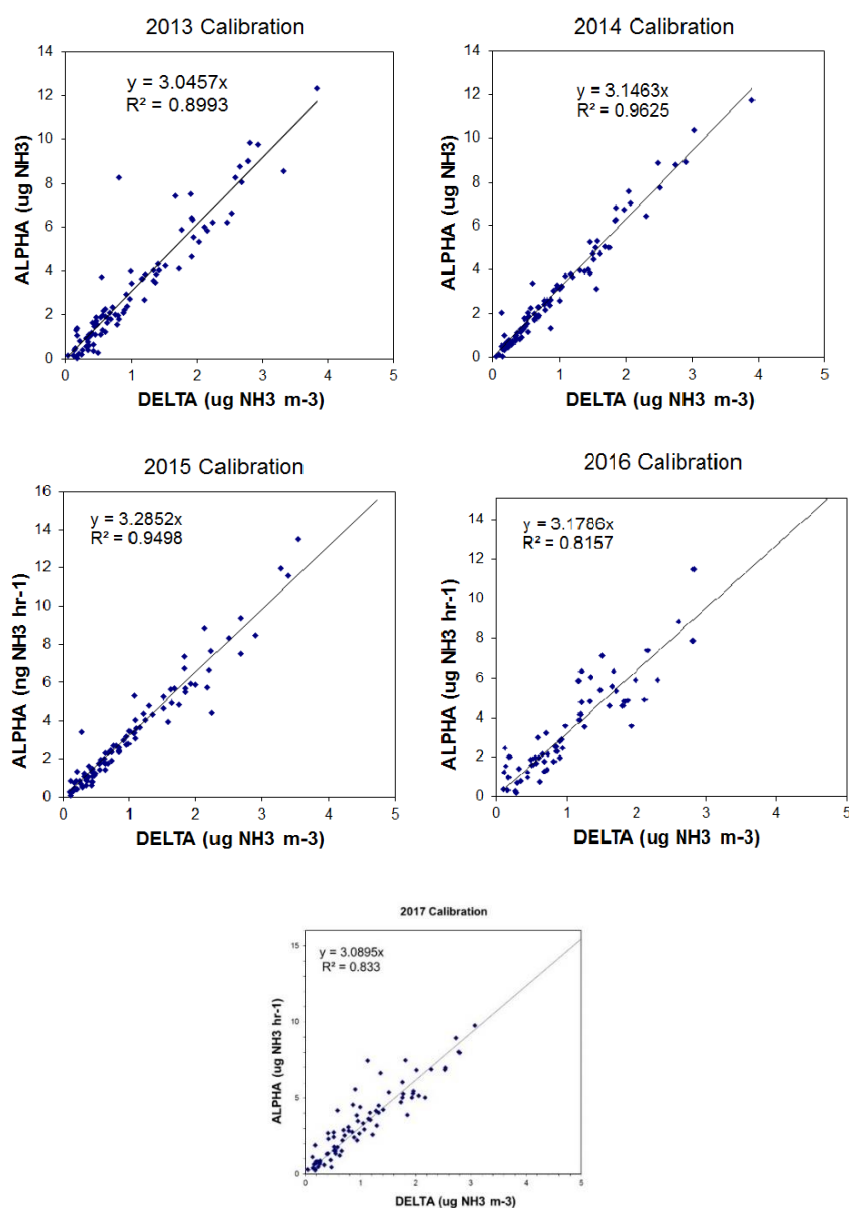

Figure 44: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers in years 2013-2016 and 2017.