UKEAP

2016

Annual Report

Prepared for the Environment Agency

&

Defra

And the Devolved Administrations

By

NERC Centre for Ecology & Hydrology

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Ricardo Energy & Environment

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NERC CEH REPORT SUMMARY

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1. Summary

1.1 Delivery of National and International Air Quality Evidence

The Defra rural air pollutant monitoring networks project, (2012-2017:AQ0647; 2017: 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
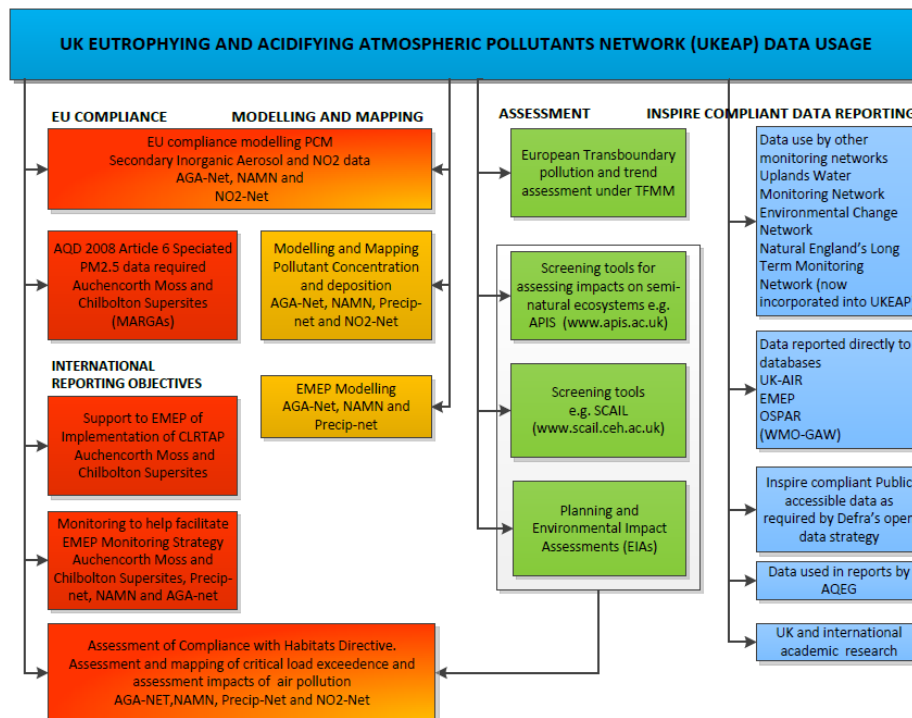
1.2 Summary of UKEAP Headlines 2016

Key points from 2016:

- UKEAP data and site information are currently available at https://uk-air.defra.gov.uk/data/

- All ratified 2016 network data were provided to UK-Air and EMEP databases and were publically available from July 2017.

EMEP Supersite Operations

- In January 2016 the Chilbolton EMEP supersite opened and commenced measurements following the closure of Harwell in 2015. This site now has both the surface *in-situ* air quality measurements and the remote sensing capabilities under NERC/STFC (now both within UKRI)

- In 2016 data from the Defra and EA networks operating at Auchencorth Moss were used in >20 government reports and research papers assessing air quality and its impacts both in the UK and internationally.

Precip-Net Operations

- The Precip-Net sites mostly operated smoothly in 2016. Chemical analysis quality assurance checks led to a review of ammonium data with the contract laboratory; issue now resolved.

- As reported in previous years the sulphate and nitrate continue to have a decreasing trend though there are indications sulphate levels are plateauing. Ammonium in precipitation continues not to decline, highlighting the static emissions NH_3 over the past decade.

NO_2-Net Operations

- NO_2-Net operated smoothly in 2016. The new site at Chilbolton has high concentrations of NO_2 for background rural UK, but levels are similar to the Harwell site.

- The data will be used by the Pollution Climate Mapping to build the background concentration map for the UK

AGA-Net and NAMN Operations

- AGA-Net and NAMN operated smoothly over 2016.

- The AGA-Net method change proposed by Tang et al. in 2016 was implemented across the network in January 2016. This will provide a more accurate HNO_3 concentration measurement and more quanitative PM composition measurements.

- Back corrected data for all HNO_3 pre-2015 was submitted to UK-Air in December 2015. It is anticipated that the assessment in changes in PM will require detailed checking before any data correction issued, however as background PM is low it is anticipated the increase in concentrations will not affect UK total PM assessments significantly

1.3 Measurement data for compliance assessment, policy development and other air quality assessments

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.

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.

1.4 2016-17 reports and publications using UKEAP or derived UKEAP data

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 below represents an non-exhaustive search of the literature and engagement with stakeholders.

Alastuey, A., X. Querol, et al. (2016). "Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013." Atmos. Chem. Phys. 16(10): 6107-612

Aslan-Sungur, G., X. Lee, et al. (2016). "Large interannual variability in net ecosystem carbon dioxide exchange of a disturbed temperate peatland." Science of The Total Environment 554(Supplement C): 192-202.

Aulinger, A., V. Matthias, et al. (2016). "The impact of shipping emissions on air pollution in the greater North Sea region - Part 1: Current emissions and concentrations." Atmospheric Chemistry and Physics 16(2): 739-758.

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

Brown, R. J. C., D. M. Butterfield, et al. (2016). "Wavelength dependent light absorption as a cost effective, real-time surrogate for ambient concentrations of polycyclic aromatic hydrocarbons." Atmospheric Environment 127(Supplement C): 125-132.

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

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Malley, Christopher S.; Cape, J. Neil; Jones, Matthew R.; Leeson, Sarah R.; Coyle, Mhairi; Braban, Christine F.; Heal, Mathew R.; Twigg, Marsailidh M.. 2016 Regional and hemispheric influences on measured spring peroxyacetyl nitrate (PAN) mixing ratios at the Auchencorth UK EMEP supersite. Atmospheric Research, 174-175. 135-141. 10.1016/j.atmosres.2016.02.013

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Redington, A. L., C. S. Witham, et al. (2016). "Source apportionment of speciated PM10 in the United Kingdom in 2008: Episodes and annual averages." Atmospheric Environment 145(Supplement C): 251-263.

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Sozanska-Stanton, M., P. D. Carey, et al. (2016). "Balancing conservation and climate change – a methodology using existing data demonstrated for twelve UK priority habitats." Journal for Nature conservation 30(Supplement C): 76-89.

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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 2016.

UKEAP is comprised of:

- **National Ammonia Monitoring Network** (NAMN – 84 sites)

- **Acid Gases and Aerosol Network** (AGA-Net – 30 sites)

- **Precipitation chemistry Network** (Precip-Net – 39 sites)

- **Rural NO$_2$ diffusion tube network** (NO$_2$-Net – 24 sites)

- **UK EMEP Supersites** (Chilbolton and Auchencorth)

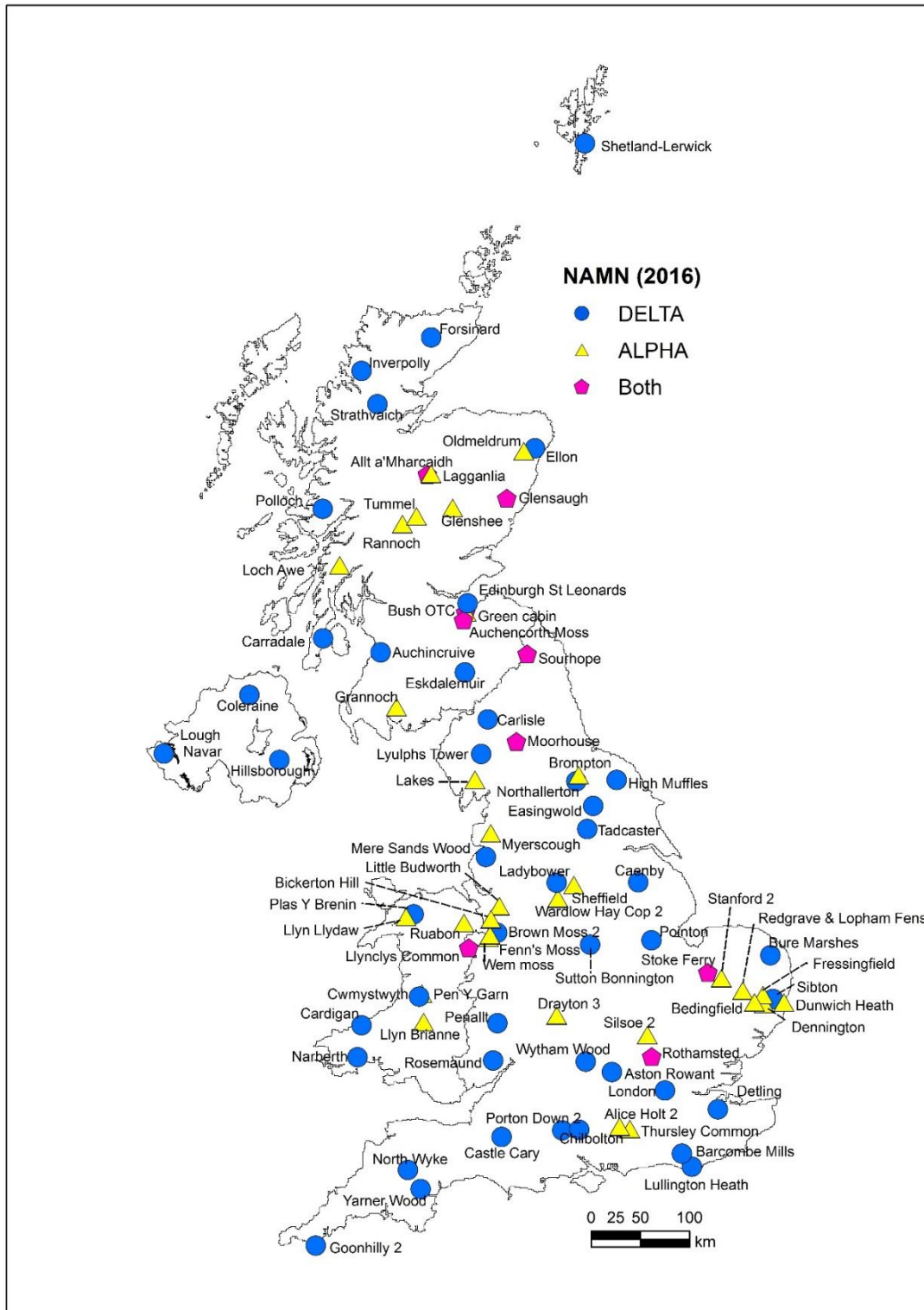- **The air quality measurements of the Natural England Long Term Monitoring Network**
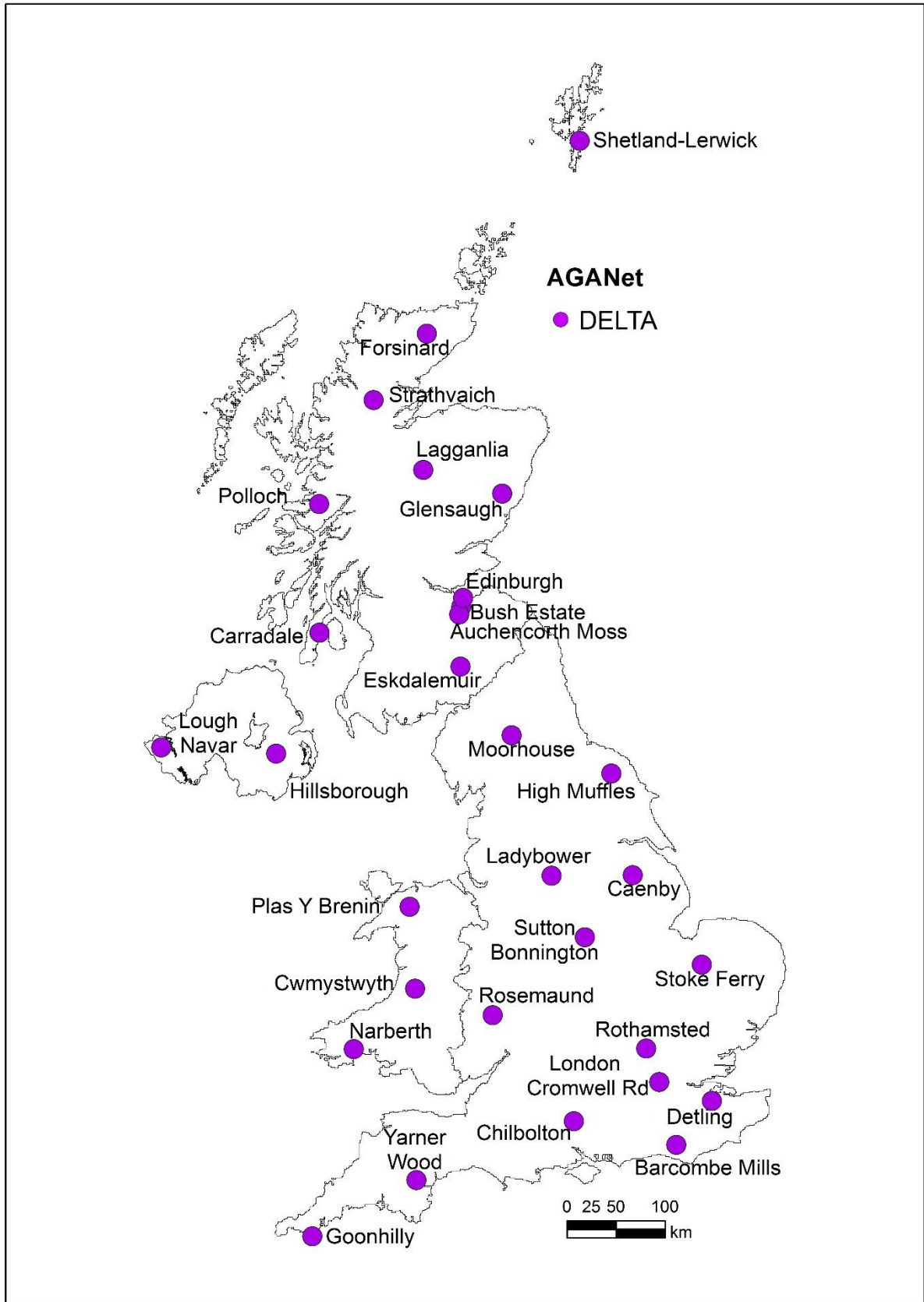
Figure 1 UK National Ammonia Monitoring Network
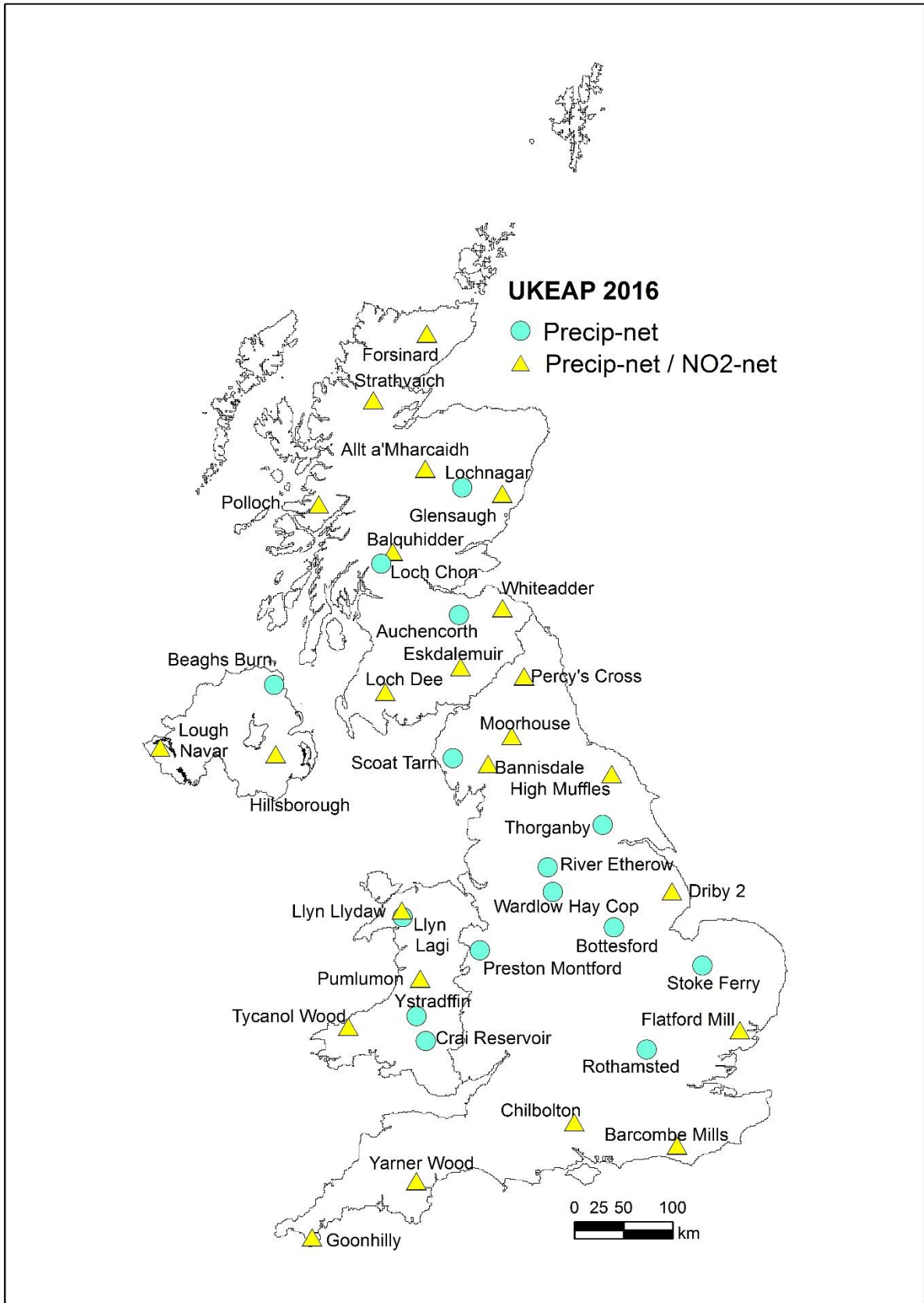
Figure 2 Acid Gases and Aerosol Network

UKEAP 2016
- ○ Precip-net
- △ Precip-net / NO2-net

Forsinard
Strathvaich
Allt a'Mharcaidh
Lochnagar
Glensaugh
Polloch
Balquhidder
Loch Chon
Whiteadder
Auchencorth
Eskdalemuir
Beaghs Burn
Percy's Cross
Loch Dee
Moorhouse
Lough Navar
Scoat Tarn
Bannisdale
High Muffles
Hillsborough
Thorganby
River Etherow
Driby 2
Llyn Llydaw
Wardlow Hay Cop
Llyn Lagi
Bottesford
Preston Montford
Pumlumon
Stoke Ferry
Ystradffin
Tycanol Wood
Flatford Mill
Crai Reservoir
Rothamsted
Chilbolton
Barcombe Mills
Yarner Wood
Goonhilly

0 25 50   100
km

Figure 3 Precipitation chemistry Network

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2. UKEAP Networks

2.1 Precipitation Network (Precip-Net)

Precip-Net has operated since the mid-1980s and has had several step changes in site density across the UK in that time period. Following consultation between Defra, the DAs and network operators network changes were implemented during 2016, leading to significant changes to the Precip-Net monitoring network - seven sites were closed due to network assessments, and eight sites were added. The new sites are part of the Natural England Long Term Monitoring Network (LTMN) and joined the network in late 2016. Also as discussed in last year's report the Supersite at Harwell was relocated to Chilbolton Observatory.

Table 1 summarises the sites starting in 2016 and the UK-AIR website for each site which provides further information about the site and access to the rainwater composition data.

Table 2 summarises the 2016 closing sites including the the last sample date. The sites at Barcombe Mills, Bottesford and Harwell were closed as required by changes in land use. The other closures were Upland Waters Monitoring Programme sites.

Table 1 Precip-Net monitoring stations starting since 2016

LTMN Site	Sampling start date	More details about site available from
Ainsdale Dunes & Sands	14/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00635
Bure Marshes NNR	02/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00641
Fenns, Whixall & Bettisfield Mosses	04/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00642
Ingleborough NNR	01/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00637
Lullington Heath NNR	01/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00152
Monks Wood NNR	04/01/2017	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00639
Stiperstones NNR	15/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00640
Thursley Common NNR	01/11/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00588
Relocated EMEP Supersite		
Chilbolton Observatory	15/01/2016	https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00614

Table 2 Precip-Net sites closed in 2016

Site	Sampling status or site closure date
Barcombe Mills	04/10/2016
Bottesford	12/10/2016
Harwell	06/01/2016
Llyn Llagi	17/10/2016
Loch Chon	05/10/2016
Lochnagar	20/09/2016
Scoat Tarn	08/10/2016

The major ions in wet deposition (rain or snow) are measured in the Precipitation Network, Precip-Net. Up until late 2016 there were 39 sites in the network and from 2017 the network consists of 41 fortnightly bulk rain monitoring sites.

In addition at the EMEP Supersites, Auchencorth Moss and Chilbolton there are daily wet only (DWOC) collectors at which the chemical composition of precipitation is measured. The locations of the monitoring sites are shown in Figure 4. A bulk sampler is shown in Figure 5.
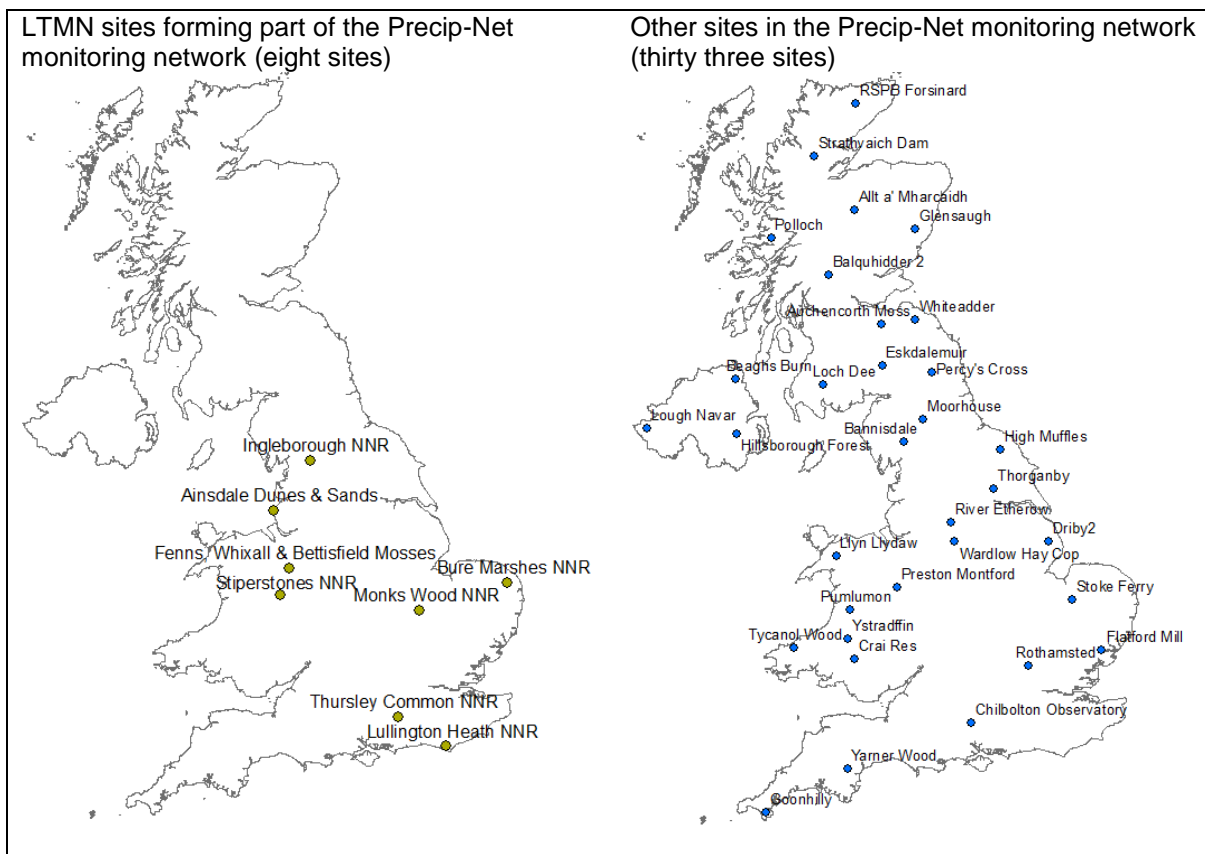

Figure 4 Precip-Net LTMN sites (LHS) and existing sites (RHS)

Figure 5 Example bulk rain sampler (Bannisdale)

Precipitation samples are 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. Daily collection of precipitation samples, using Daily Wet Only Precipitation Collectors (DWOCs), is undertaken at the Auchencorth Moss and Chilbolton sites, to meet part of the EMEP commitments by the UK. DWOC sampling of precipitation is minimally affected by dry deposition than bulk samplers. At all Precip-Net sites, Local Sites Operators (LSOs) undertake the site operation including replacing rain collection bottles, cleaning funnels, replacing debris filters and making observations at the site. LSOs also ensure the timely return of the collected rain samples which is much appreciated.

During 2016 there was an analysis issue identified through performance in the annual EMEP intercomparison and other performance tests. The issue was with ammonium analysis and as a result the analytical laboratory voluntarily suspended their UKAS accreditation. The issue was traced to poor performance at low levels (less than 1.1mg/l) and a second calibration was introduced which allowed UKAS accreditation to be re-established. The issue occurred for analysis between November 2015-April 2017. The laboratory have estimated the uncertainty for the ammonium analysis during and after this time as 24.2% and 16%, respectively. Whilst there may be some increased uncertainty in the reported ammonium concentration data prior to the improvements it is not considered sufficient to invalidate the data.

The spatial patterns of the annual mean precipitation-weighted concentration of acidity, non-seasalt sulphate, nitrate and ammonium are presented in Figure 7 for 2016. 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.

Data from thirty-three UKEAP sites operating throughout 2016 were used to create the concentration maps shown in Figure 6. This process is used to identify any individual anomalous measurements. The measured concentrations at the individual LTMN sites and sites closed within 2016 are also presented on the map (with the exception of Harwell).
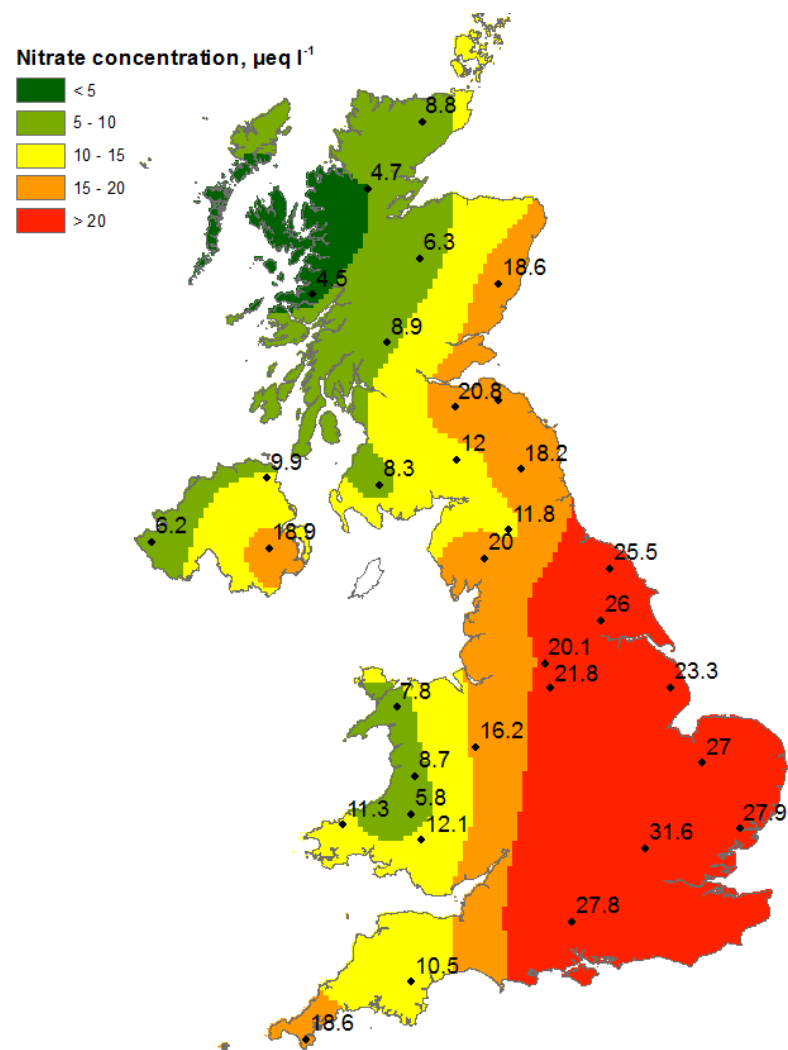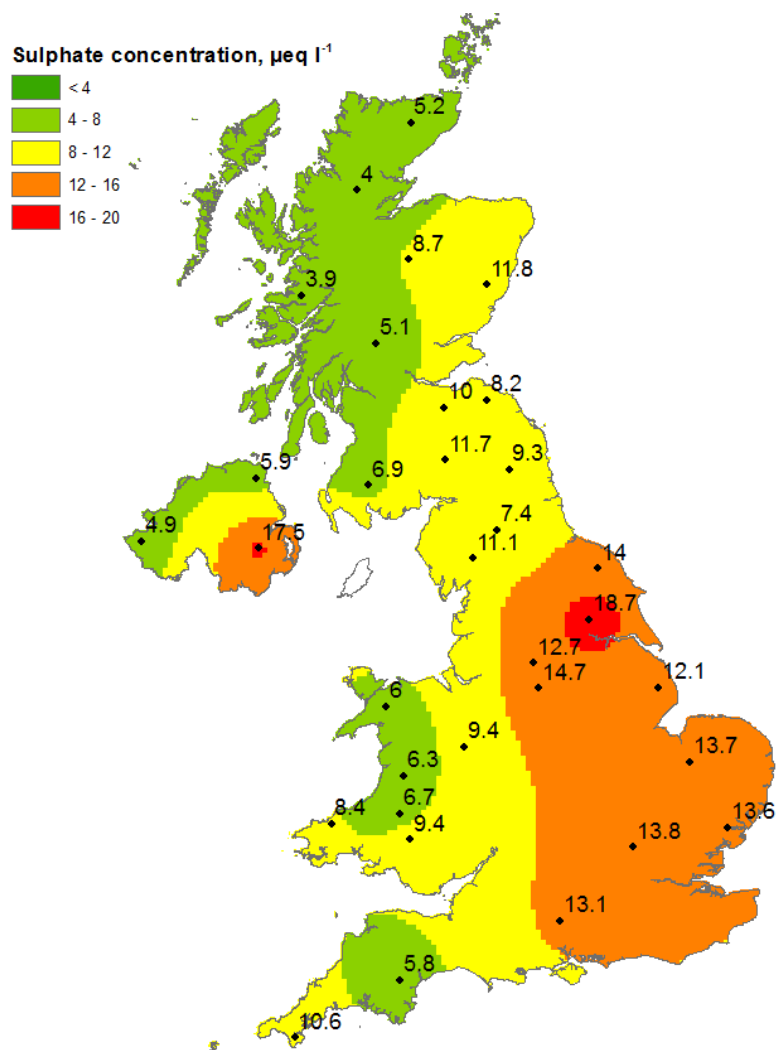
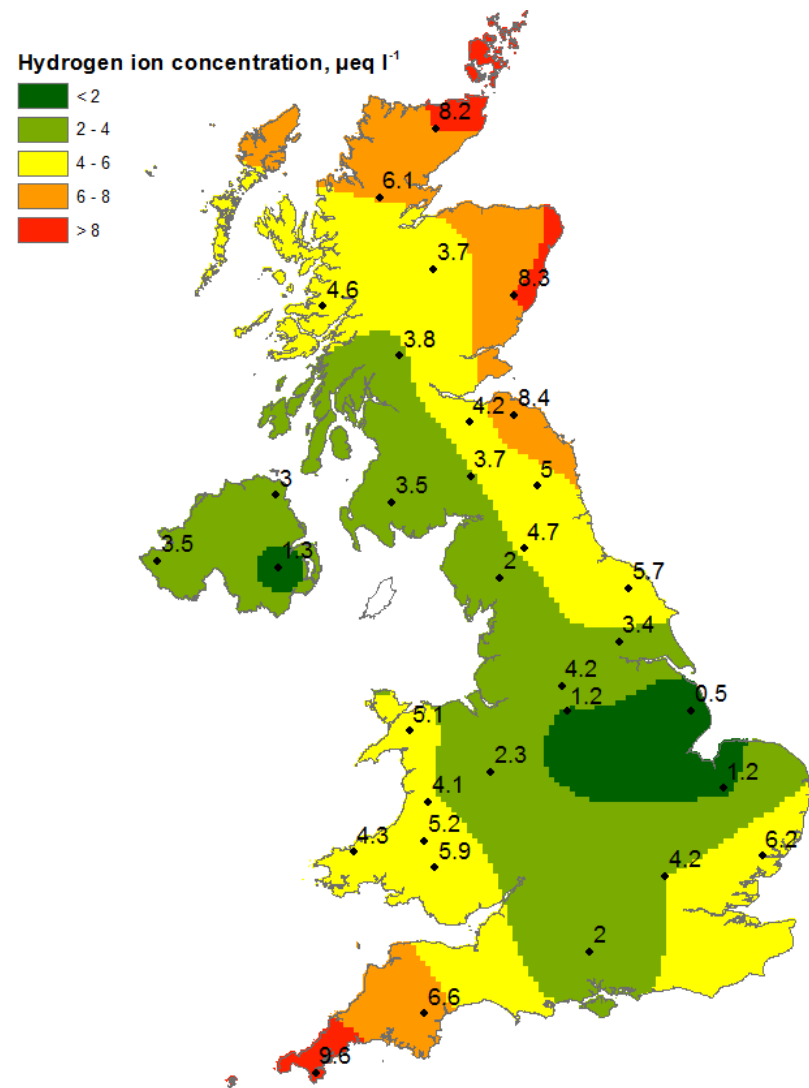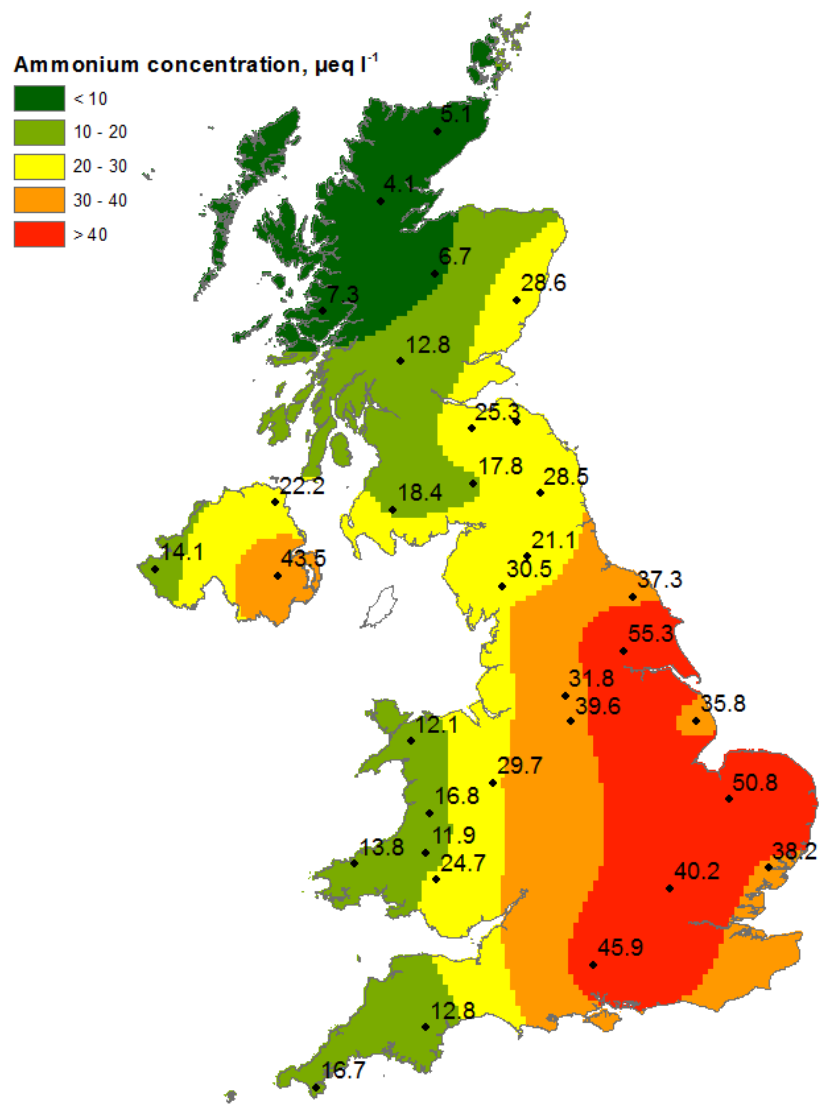**Figure 6. Interpolated concentration maps for non-sea salt sulphate and nitrate ion (µeq l-1)**

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Figure 7. Interpolated concentration maps for ammonium and hydrogen ion (μeq l-1)

Since 1986 there has been significant decrease in sulphur dioxide and oxides of nitrogen emissions. The rate of decrease for sulphur dioxide was greater than the decrease for oxides of nitrogen. For example, Figure 8 shows that sulphur dioxide emissions have decreased by about ninety percent whereas oxides of nitrogen have decreased by about sixty percent.
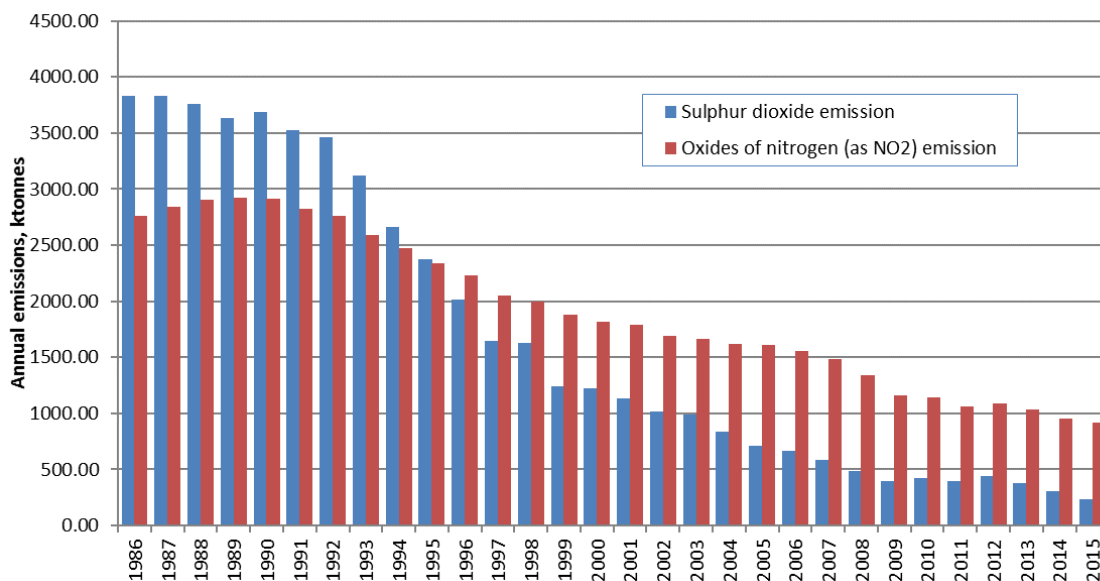

Figure 8 Sulphur dioxide and oxide of nitrogen emissions since 1986 Reference for emissions data. http://naei.defra.gov.uk

Figure 9 and Figure 10 compare the total sulphur dioxide and estimated oxide of nitrogen emissions for the UK with the Precip-Net average non-seasalt sulphate and nitrate concentrations, respectively. The rate of decrease in nitrate concentration can be seen to be smaller than that for sulphate. The inter-annual variability for nitrate is larger than that for sulphate reflecting the more complex chemistry for nitrate compared to sulphate chemistry.
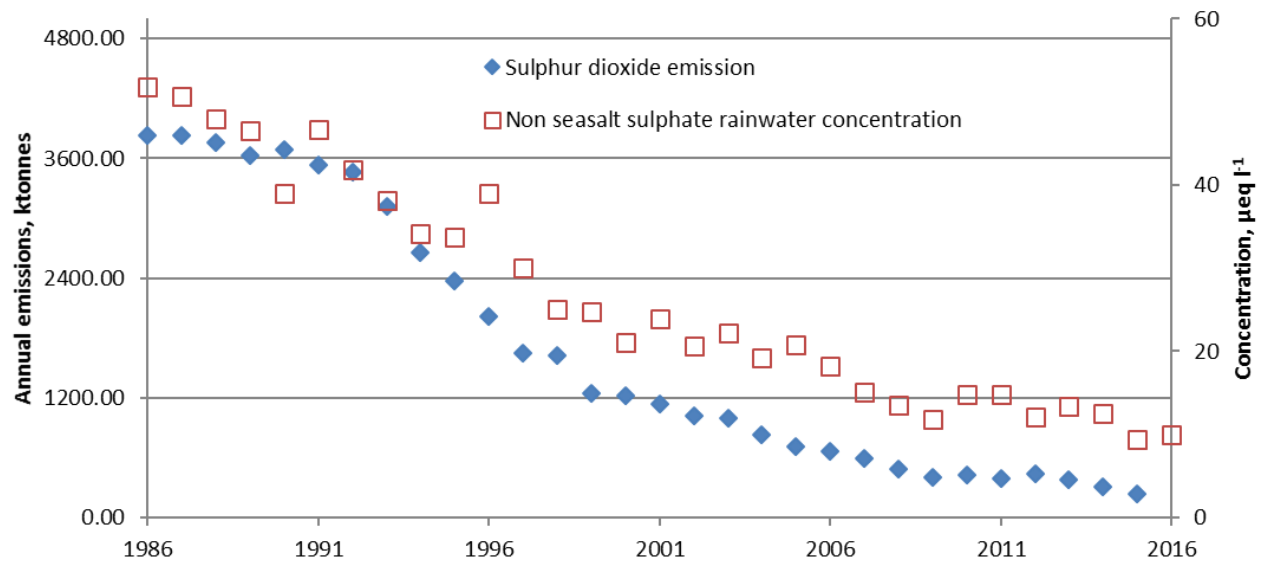
Figure 9 Sulphur dioxide emissions and sulphate concentrations in rainwater concentration
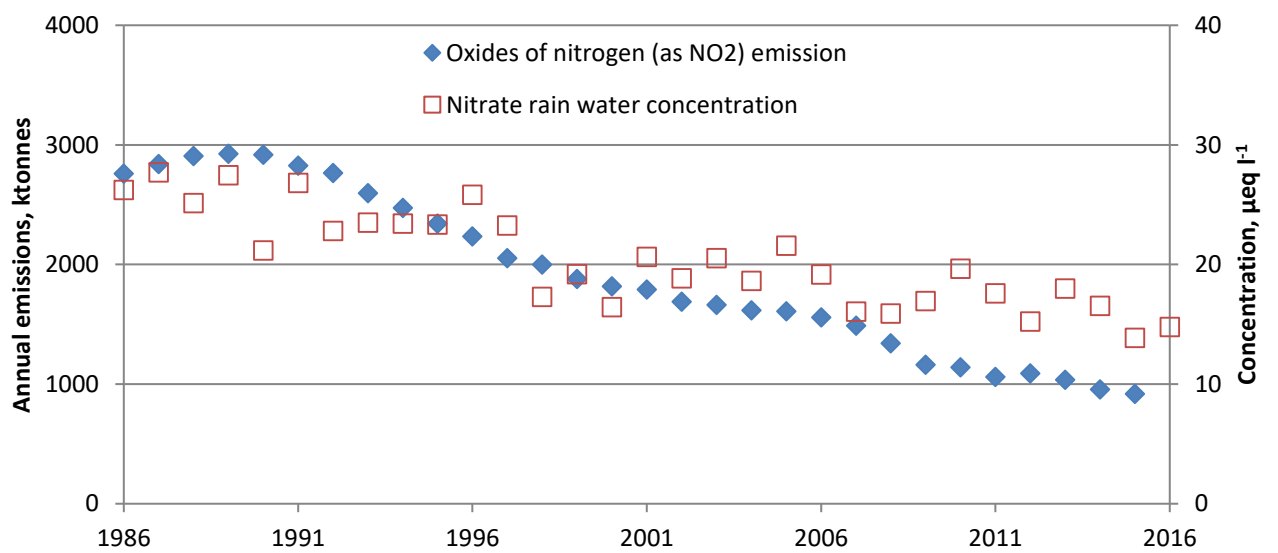

Figure 10 Oxide of nitrogen emissions and nitrate in rainwater concentration

2.2 NO$_2$-Net Network

The NO$_2$ network (NO$_2$-Net) consists of 24 sites (Table 3) at which diffusion tubes, in triplicate, were exposed for 4-week exposure periods. The annual average NO$_2$ measured at each site, together with data capture, are shown in Table 3. 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.

Table 3 2016 NO$_2$ concentration from the Diffusion Tubes in the NO$_2$-Net

Site Name	2016 concentration (µg m^{-3})	Data capture	Site Name	2016 concentration (µg m^{-3})	Data capture
Allt a'Mharcaidh	1.5	96.1%	Hillsborough Forest	7.3	100%
Balquhidder 2	2.4	100%	Llyn Llydaw	3.0	100%
Bannisdale	4.4	100%	Loch Dee	2.7	85.2%
Barcombe Mills	8.1	75.8%	Lough Navar	2.3	100%
Chilbolton Observatory	11.7	96.0%	Moorhouse	3.6	100%
Driby 2	10.4	100%	Percy's Cross	4.23	99.9%
Eskdalemuir	2.9	100%	Polloch	1.4	96.1%
Flatford Mill	9.6	100%	Pumlumon	3.6	100%
Forsinard RSPB	2.4	100%	Strathvaich	1.2	97.0%
Glensaugh	3.1	100%	Tycanol Wood	3.9	100%
Goonhilly	4.4	100%	Whiteadder	3.3	100%
High Muffles	5.8	100%	Yarner Wood	4.6	100%

The mean data capture of the diffusion tubes for all of the site in 2016 was 97.75% with 22 of the 24 sites achieving >90% and 17 sites achieving 100% data capture. The sites with lowest data captures during 2016 were Barcombe Mills and Loch Dee. Barcombe Mill ceased operation in early October 2016 due to the land owners no longer able to operate the site.

The NO$_2$ measurements in the area were restarted in 2017 at the Lullington Heath UKEAP site. In the case of Loch Dee, the site operator was not always able to attend site and therefore an alternative local site operator has been identified and data capture should improve in 2017.

The annual average NO$_2$ concentrations from 2010-2016 are shown in Figure 11 giving an indication of the differing levels at rural locations across the UK. Emissions of nitrogen oxides are generally from combustion processes including the transport sector.

Although the emissions have decreased since 1990, no readily observable decline across the board is seen in the recent years' measurements shown in Figure 11. Some of the sites with higher concentrations do appear to show a slight decline over the 6 years shown e.g. Flatford Mill, Harwell, High Muffles and Hillsborough Forest.
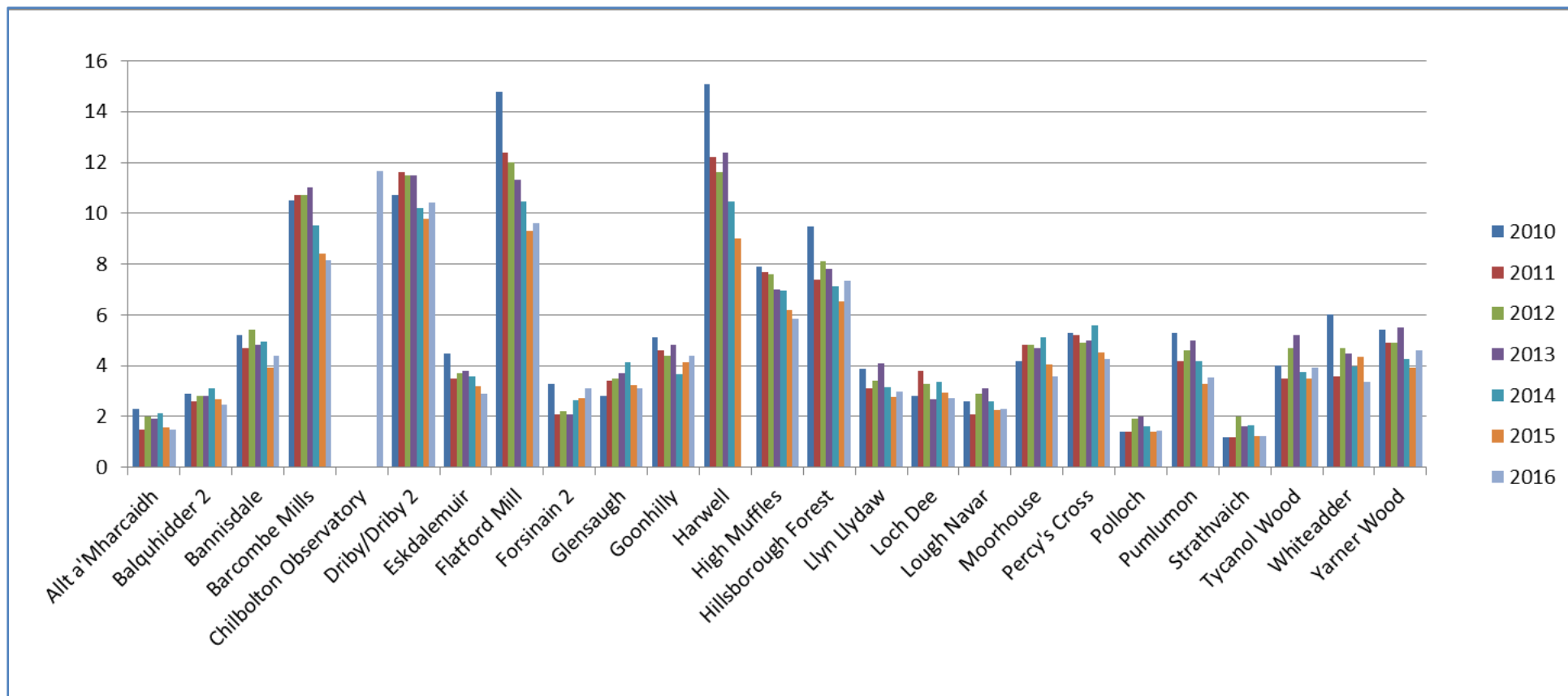
Figure 11 Annual mean NO$_2$ concentration (µg m^{-3}) at the NO$_2$-Net sites 2010-2016
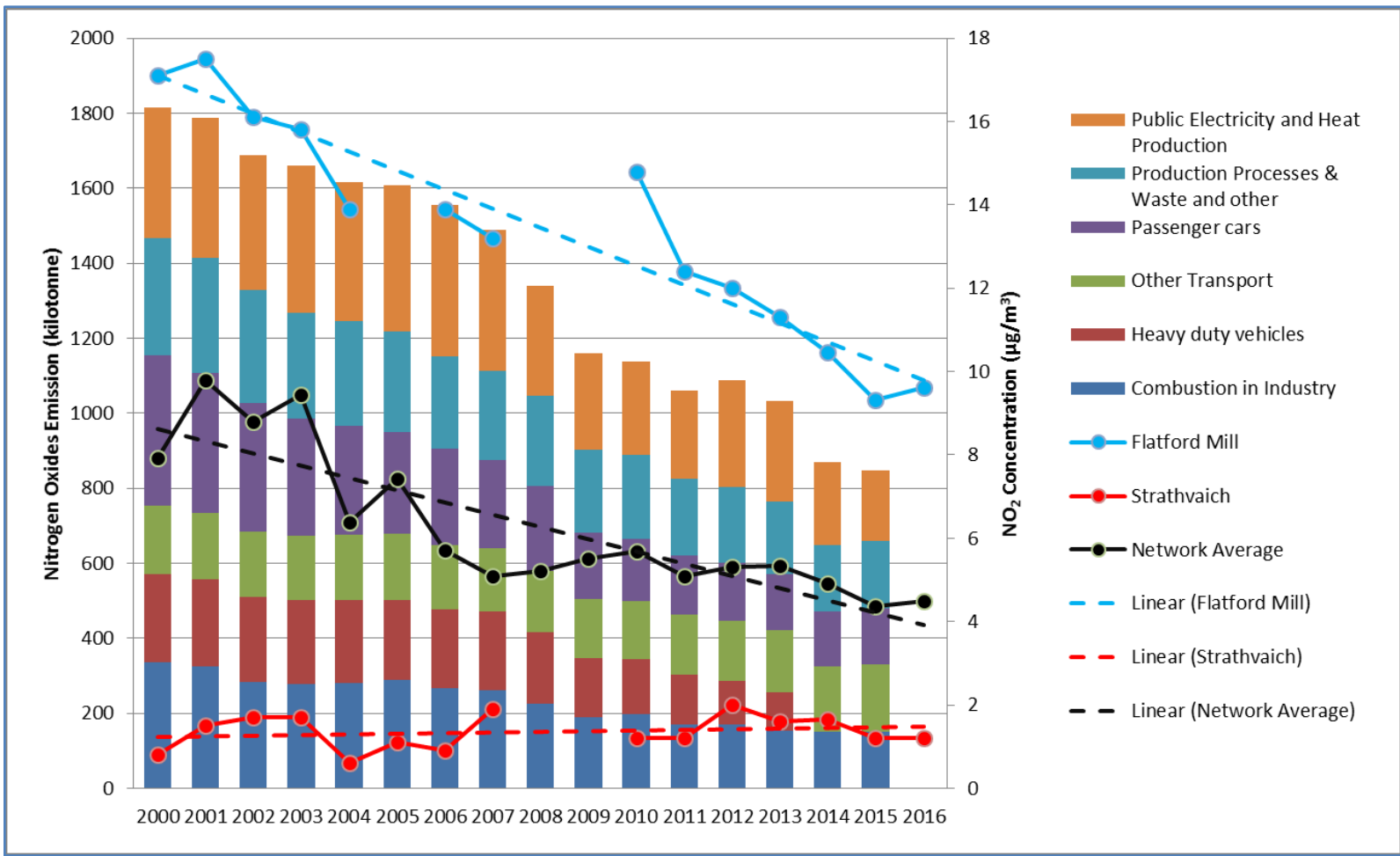
Figure 12 NAEI NOx Emission Estimates and monitored NO$_2$ Concentrations at two UKEAP sites

Figure 12 shows the emissions estimated by the National Atmospheric Emissions Inventory (NAEI) plotted alongside selected NO_2-Net measurements. The average concentrations of all the sites in the NO_2-Net have been plotted (black) along with two other selected sites, providing a comparison between high concentration (Flatford Mill, blue) and low concentration rural site (Strathvaich Dam, red). It is apparent that estimated emissions from NAEI correlate with concentration reductions for the NO_2-Net average and for the more polluted site of Flatford Mill. However in contrast, there is significantly less of a trend at the rural site of Strathvaich Dam with little apparent change in ambient concentration.

These differences in trends at the two sites are likely to be due to the different sources that are likely to be influencing the sites: Flatford Mill is a southern site closer to London and as such will be more influenced by road transport and combustion sources, whereas the Strathvaich Dam site is a remote rural location in North Scotland with minimal influence from any local sources so would not be affected by the reductions in the urban sources especially in more recent years when the reduction in estimated emissions has slowed slightly.

 The indications from the network are that background concentrations of NO_2 at most remote rural location sites are not changing significantly and at 13 sites, the concentration was slightly increased in 2016 compared to 2015.

2.2 National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly measurements of atmospheric NH_3 in 2016 was 84, summarised in Table 4. Particulate ammonium (NH_4^+), formed as a secondary product from the primary NH_3 emissions, is spatially less variable and was measured at the 30 AGA-Net sites which are a nested sub-set of NAMN. (AGA-Net results are discussed in section 2.3). It is noted that NAMN changes were implemented at the end of 2016 and the new network configuration comprises 72 sites in total, following closure of 20 sites at the end of 2016 and opening of 9 Long Term Monitoring Network Sites. The number of NH_4 measurement sites was reduced from 30 to 27 with the closure of the urban (Edinburgh St Leonards) and London Cromwell Road converting from an DELTA AGA-Net site to an ALPHA NH_3 site. A detailed report of the changes will be presented in the 2017 Annual Report however the changes agreed are shown in Figure 13 .

The 2016 results from NAMN are summarised by the average and range of annual NH_3 concentrations observed at each site in Figure 14. The graphs are all plotted on the same scale, to allow a direct comparison of NH_3 concentrations between sites. The 2016 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 2016 average data capture across all sites was 86%. (QC criteria summarised in the Appendix of this report).

Table 4 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2016

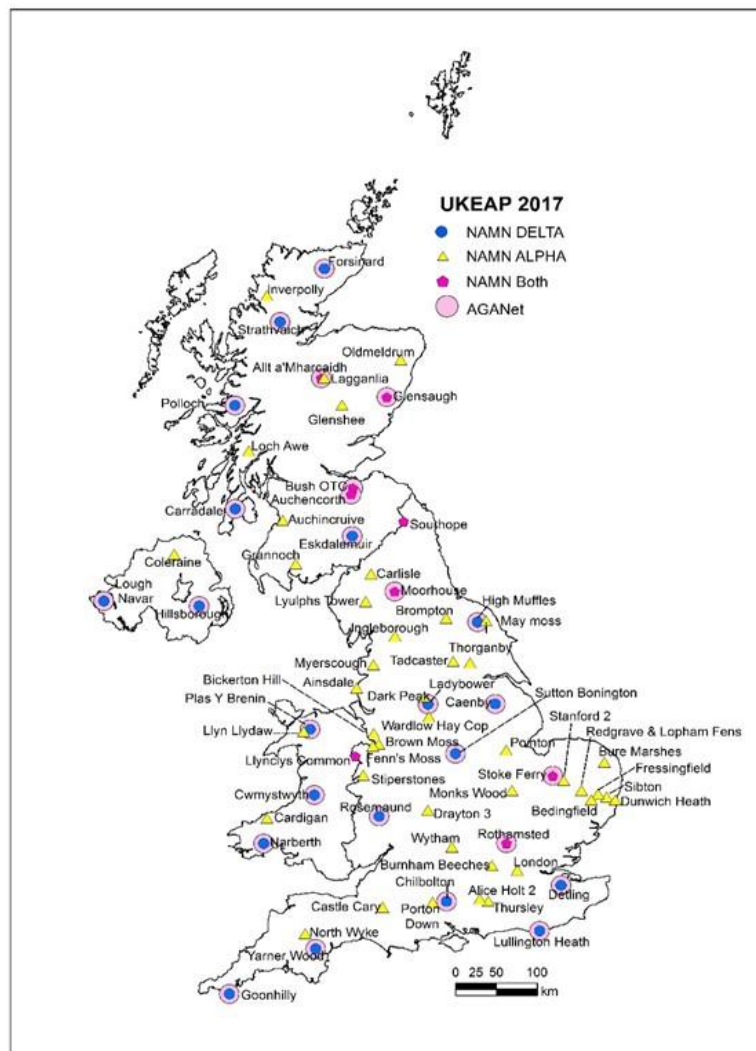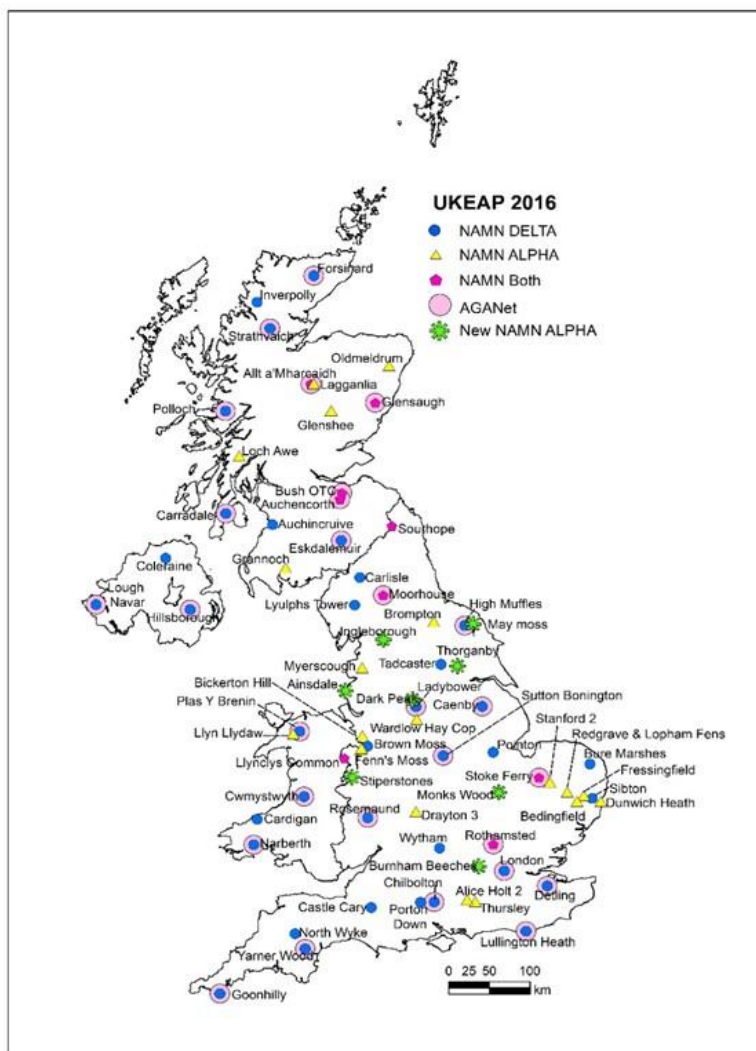| Site Type	Number
DELTA sites sampling gaseous NH_3	54
AGA-Net DELTA sites (sampling gaseous NH_3, HNO_3, SO_2, HCl & aerosol NH_4^+, NO_3^-, SO_4^2, Cl^-, Na^+, Ca^{2+}, Mg^{2+})	30
ALPHA sites sampling gaseous NH_3 only	40
Intercomparison sites with both DELTA & ALPHA	9
Total number of sites	84

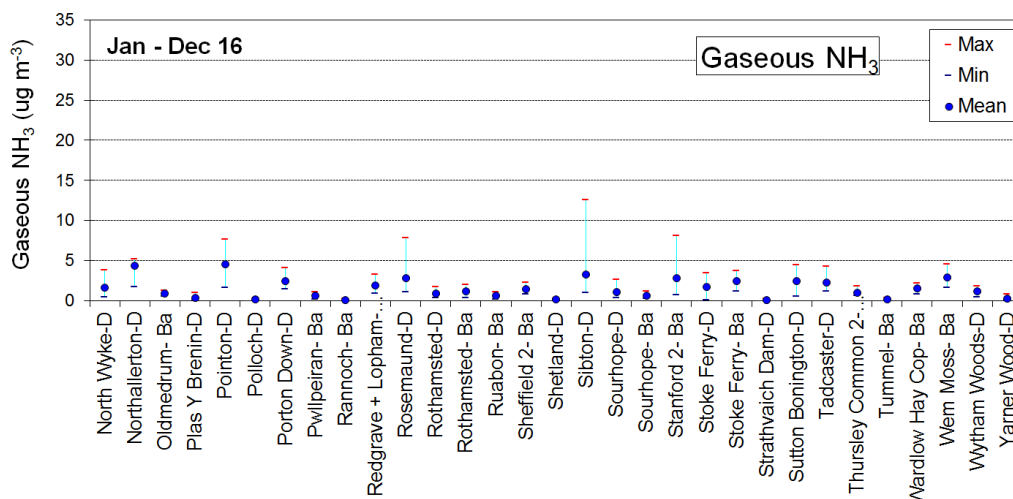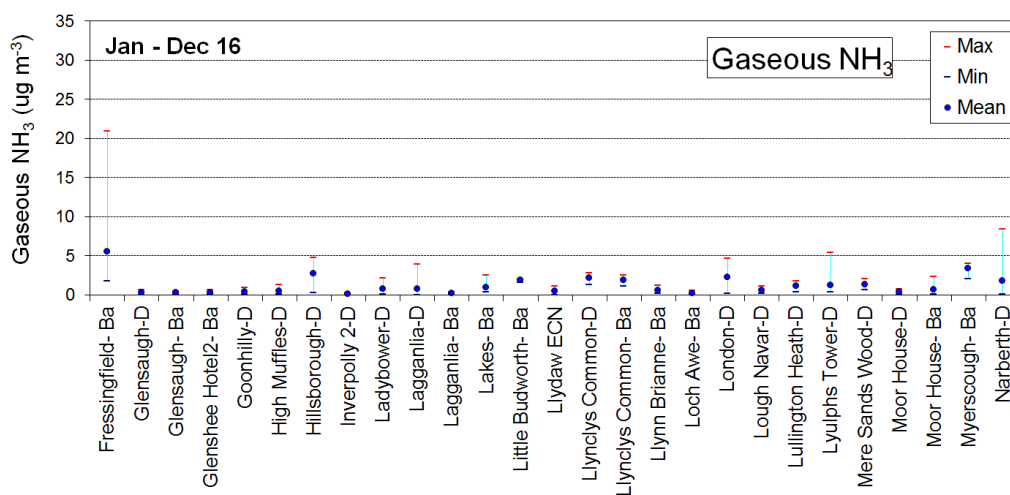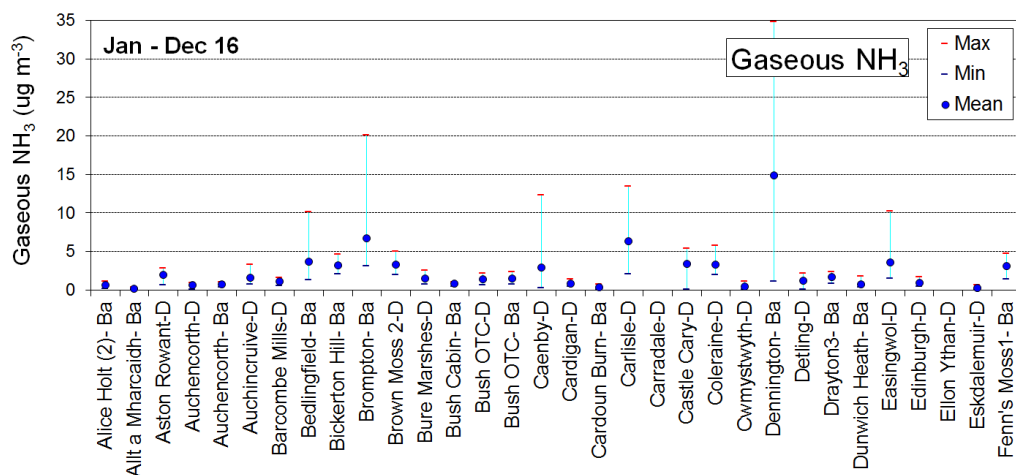**Figure 13 2016 and 2017 UKEAP ammonia monitoring sites**

27

Figure 14: Annual mean concentrations of gaseous NH₃ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2016, whilst the bars show the minimum and maximum concentrations observed (Ba = ALPHA sampler; D= DELTA sampler type).

NH$_3$ concentrations over the period 1998 to 2016 are summarised in a box plot (Figure 15). 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. To avoid bias in the analysis, sites which did not operate over the 17 year period were also excluded. This left 60 sites in 1998, 67 sites in 1999 and 75 sites from 2000 onwards.

Whilst UK emissions of NH$_3$ declined by about 29% during the operation of NAMN, 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. The mean annual UK temperature and rainfall data (source http://www.metoffice.gov.uk/) are plotted on the same graph to show the influence of temperature and rainfall on inter-annual variability in NH$_3$ concentrations. A detailed analysis of NAMN has recently been published by Tang et al. to Atmospheric Chemistry and Physics (Tang *et al.*, 2017).
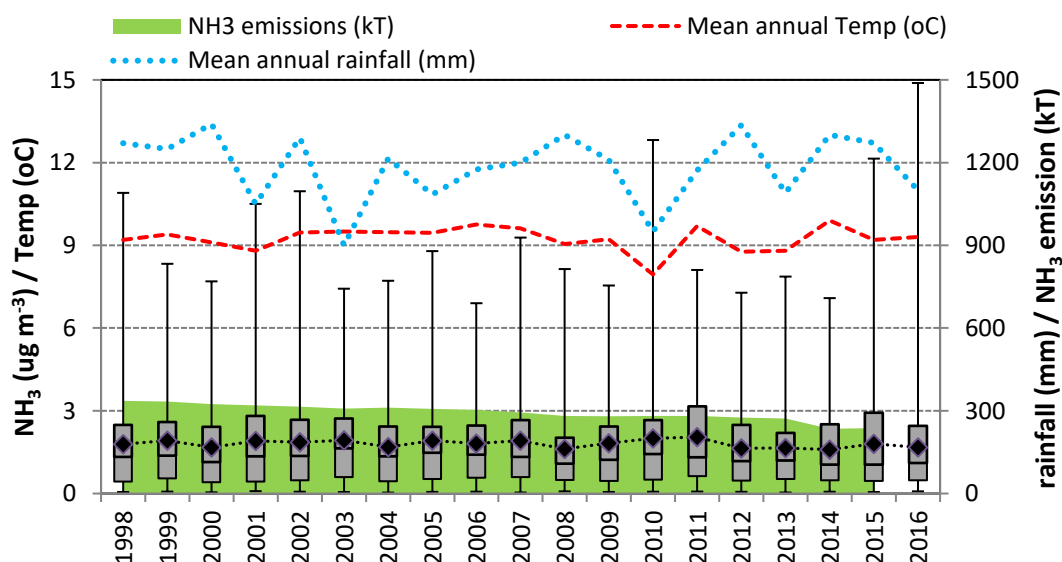

Figure 15: Changes in atmospheric NH$_3$ averaged over all sites in NAMN operational between 1998 and 2016 summarised in a box plot (sites with short runs excluded). The whiskers shows the absolute max and min and the diamond is the mean annual concentration. Annual mean UK meteorological data (source 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. UK annual NH$_3$ emissions (source http://naei.defra.gov.uk/) declined by 29% over the period 1998 - 2016.

National maps of both NH$_3$ and NH$_4^+$ (Figure 16) concentrations derived from the NAMN confirm the high spatial variability of the annual average concentration of NH$_3$ (0.08 – 14.89 µg m^{-3}), consistent with it being a primary pollutant emitted from ground-level sources. The 30 AGA-Net DELTA sites are distributed widely across the UK to provide the regional patterns of NH$_3$ (and NH$_4^+$ at the 30 AGA-Net sites). For particulate NH$_4^+$, the annual mean concentrations ranged from the lowest of 0.20 (S19 Shetland) to highest of 1.31 (S103 Caenby) 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 20), as would be expected due to the formation

of stable and semi-stable particle phase salts, e.g. ammonium sulphate and ammonium nitrate, respectively.
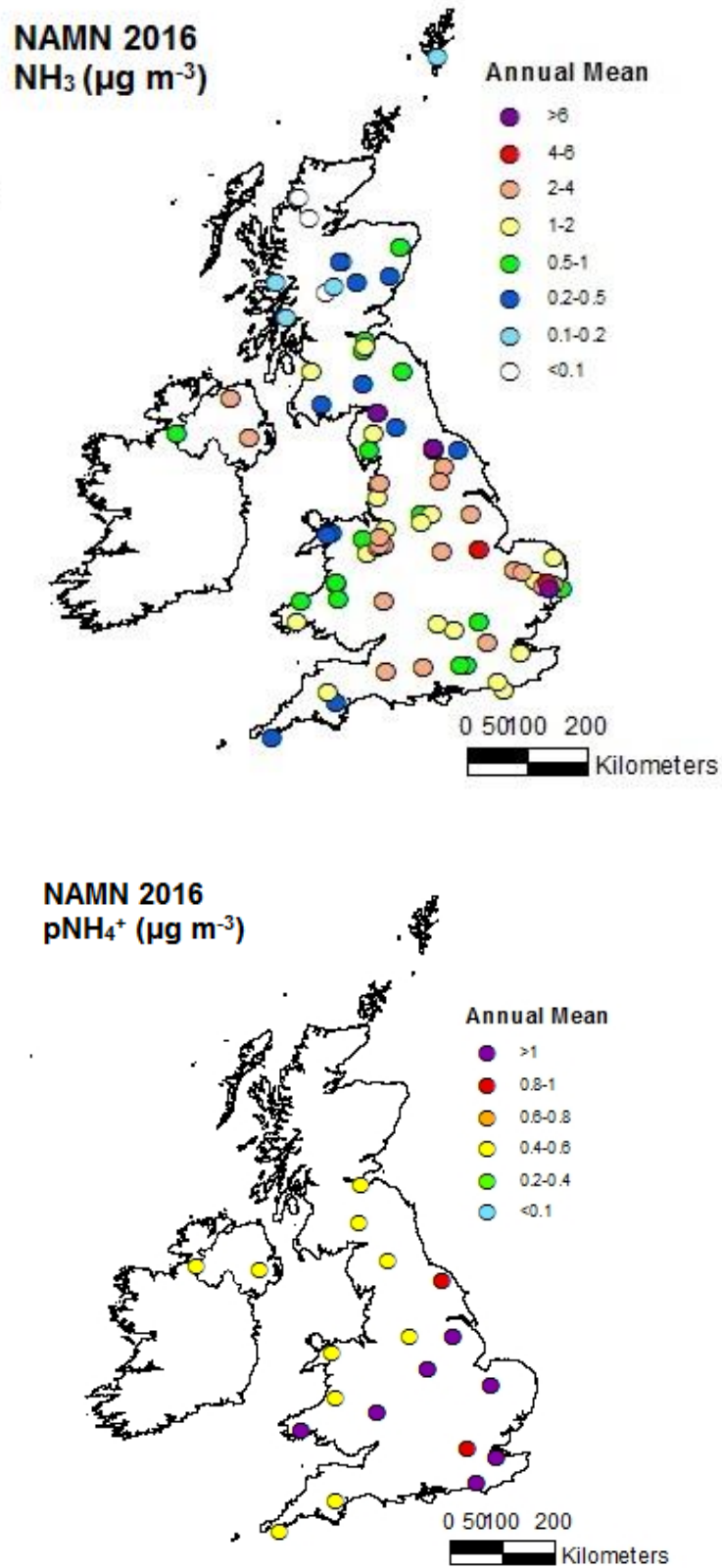

Figure 16: Spatial patterns of annual NH$_3$ and aerosol NH$_4^+$ concentrations from monthly NAMN/AGA-Net measurements. Since Sep 2009, ammonium is measured at the 30 AGA-Net sites only.

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.

2.3 Acid Gas and Aerosol Network (AGA-Net)

The UK Acid Gas and Aerosol Network (AGA-Net) 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 30 sites across the UK. A major change of sampler configuration was implemented in the network in 2016 following recommendations in a report for Defra (Tang et al. 2016, summarised in the UKEAP 2015 annual report) where the operation and sampling capability of the DELTA samplers was assessed. Following Tang et al. (2016) AGA-Net reduced the chemicals measured, removing HCl as a target chemical due to using more chemically specific NaCl coated denuders for measurement of HNO_3. In addition the filter pack sampler was reconfigured to have a more quantitative capture of particulate matter (PM_4). The impact on the annual average concentrations of the PM chemical components are discussed below.

Mean 2016 annual concentrations of trace gas and aerosols at individual sites in the network are compared in Figure 17 and Figure 18. The main features of the spatial distribution in the pollutants measured in 2016 are shown in the annual maps (Figure 19, Figure 20, Figure 21). 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 30 sites the higher spatial variability in gaseous species can be seen.
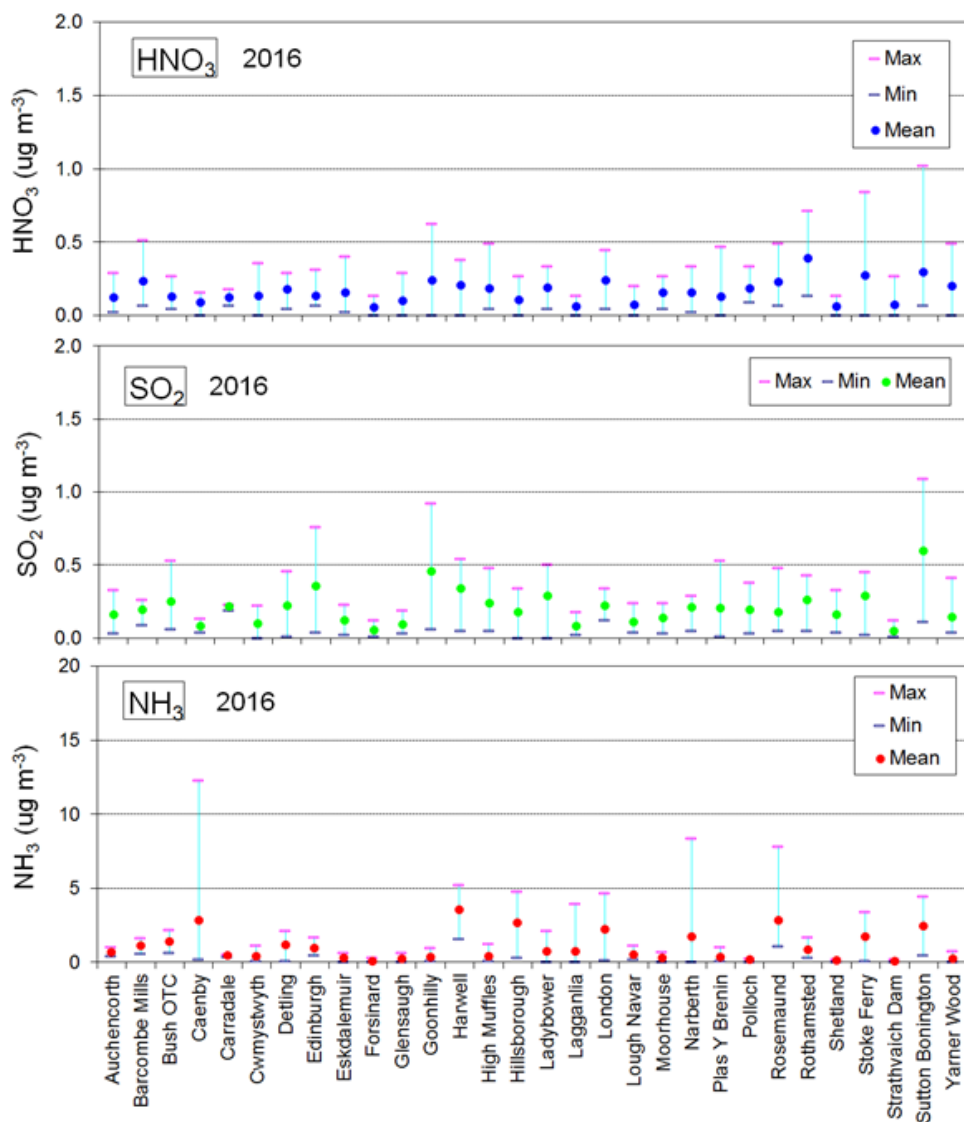
Figure 17: Mean monitored annual concentrations of gaseous HNO₃ and SO₂ at individual sites in AGA-Net. Each data point represents averaged concentrations of monthly measurements made at each site in 2016, whilst the bars show the minimum and maximum concentrations observed. Data for gaseous NH₃ measured under NAMN is also shown for comparison.
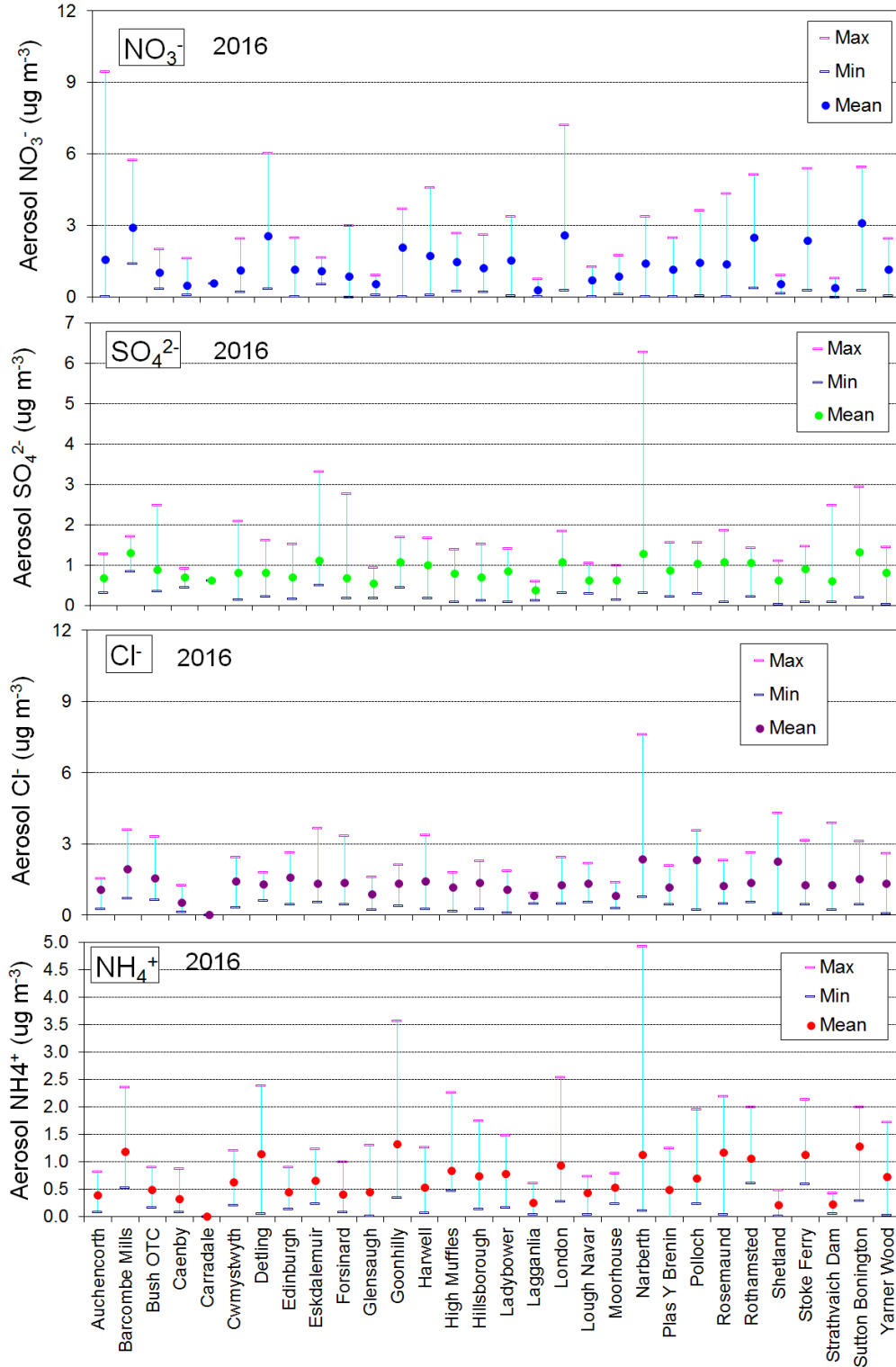
Figure 18: Mean monitored annual concentrations of particulate NO$_3^-$, SO$_4^{2-}$, Cl$^-$ and NH$_4^+$ at individual sites in AGA-Net. Each data point represents the averaged concentrations of monthly measurements made at each site in 2016, whilst the bars show the minimum and maximum concentrations observed.
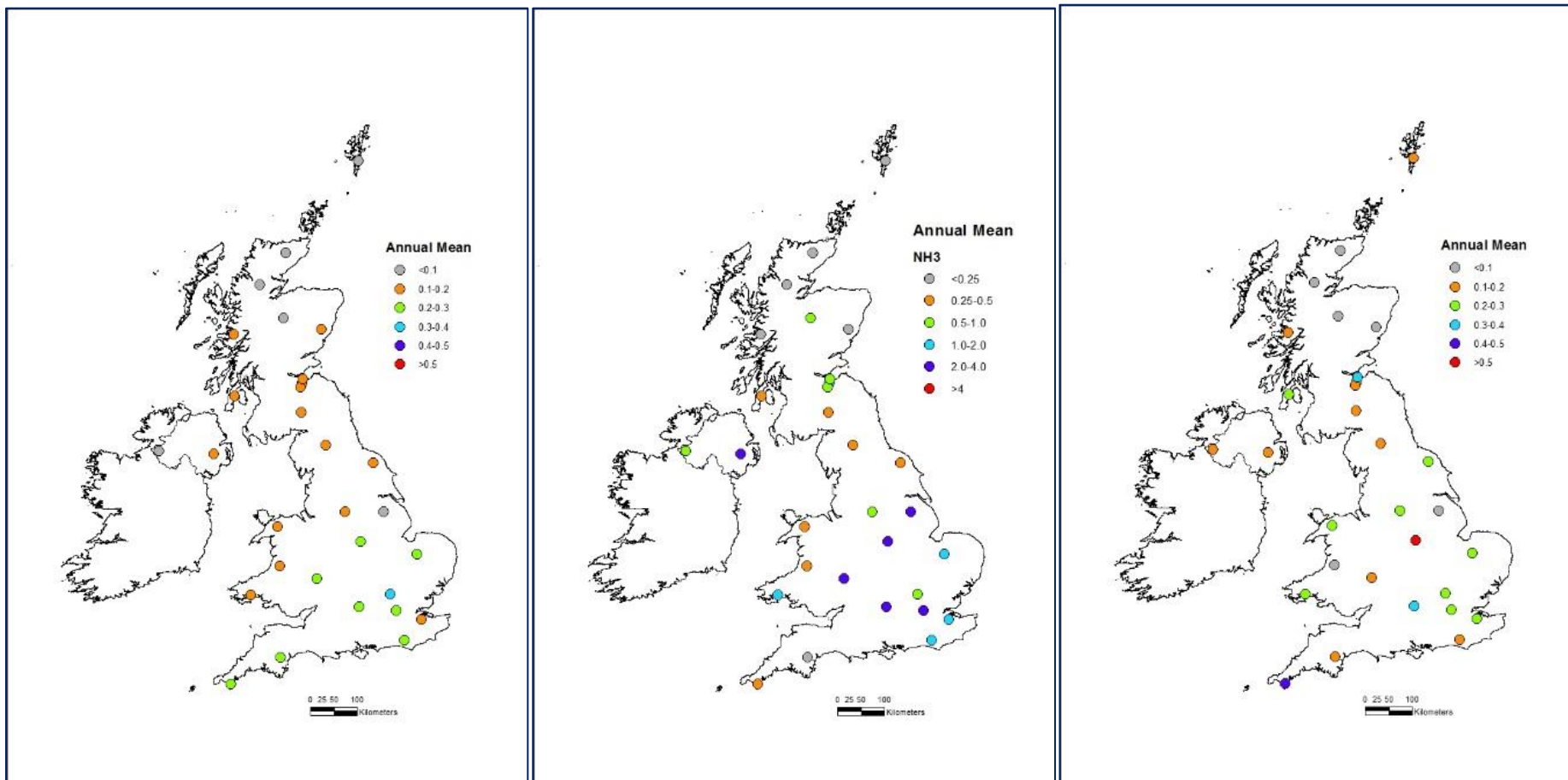
Figure 19 Annual mean monitored atmospheric reactive gas concentrations (HNO$_3$ (LHS)and SO$_2$ (RHS) from AGA-Net and NH$_3$ from NAMN (middle)) across the UK from annual averaged monthly measurements made in 2016.
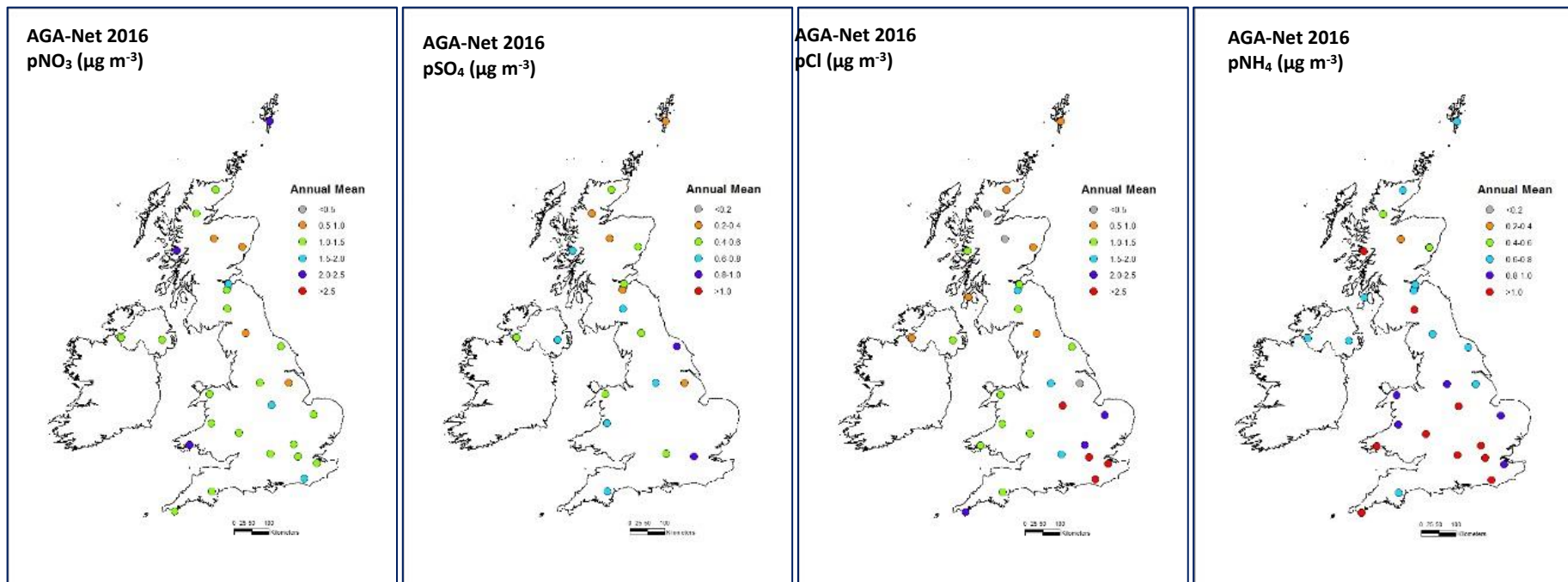
Figure 20: Annual mean monitored atmospheric aerosols (particulate NO₃⁻, SO₄²⁻, and Cl⁻ from AGA-Net and NH₄⁺ from NAMN) concentrations across the UK from averaged monthly measurements made in 2016.
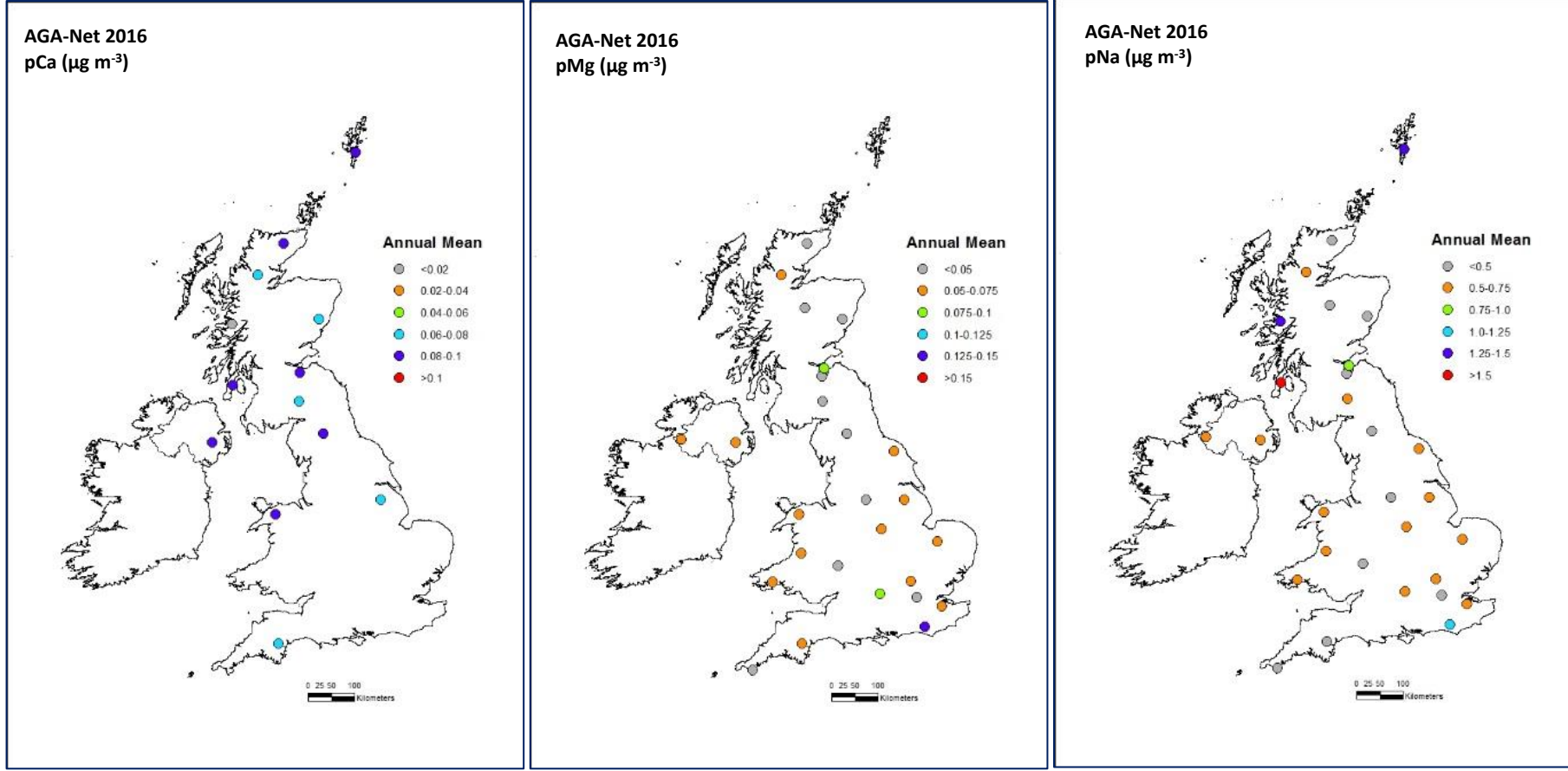
Figure 21: Annual mean monitored atmospheric base cation (Ca²⁺, Mg²⁺ and Na⁺) concentrations across the UK from the averaged monthly measurements made in 2016.

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. There is now a more specific HNO_3 measurement for which a back correction has been applied in the dataset on UK-AIR (see Tang et al. 2016 for details), this is clearly seen in Figures 21 and 22, where the *uncorrected* historic HNO_3 is plotted for reference. The decrease in HNO_3 absolute concentrations however has the caveat that other gaseous oxidised nitrogen pollutants were contributing to the artefact-added HNO_3 measured pre-2016, therefore it is noted that the net effect of gas phase oxidised-nitrogen pollution deposition is uncertain.

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 22) 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, (see above). 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).
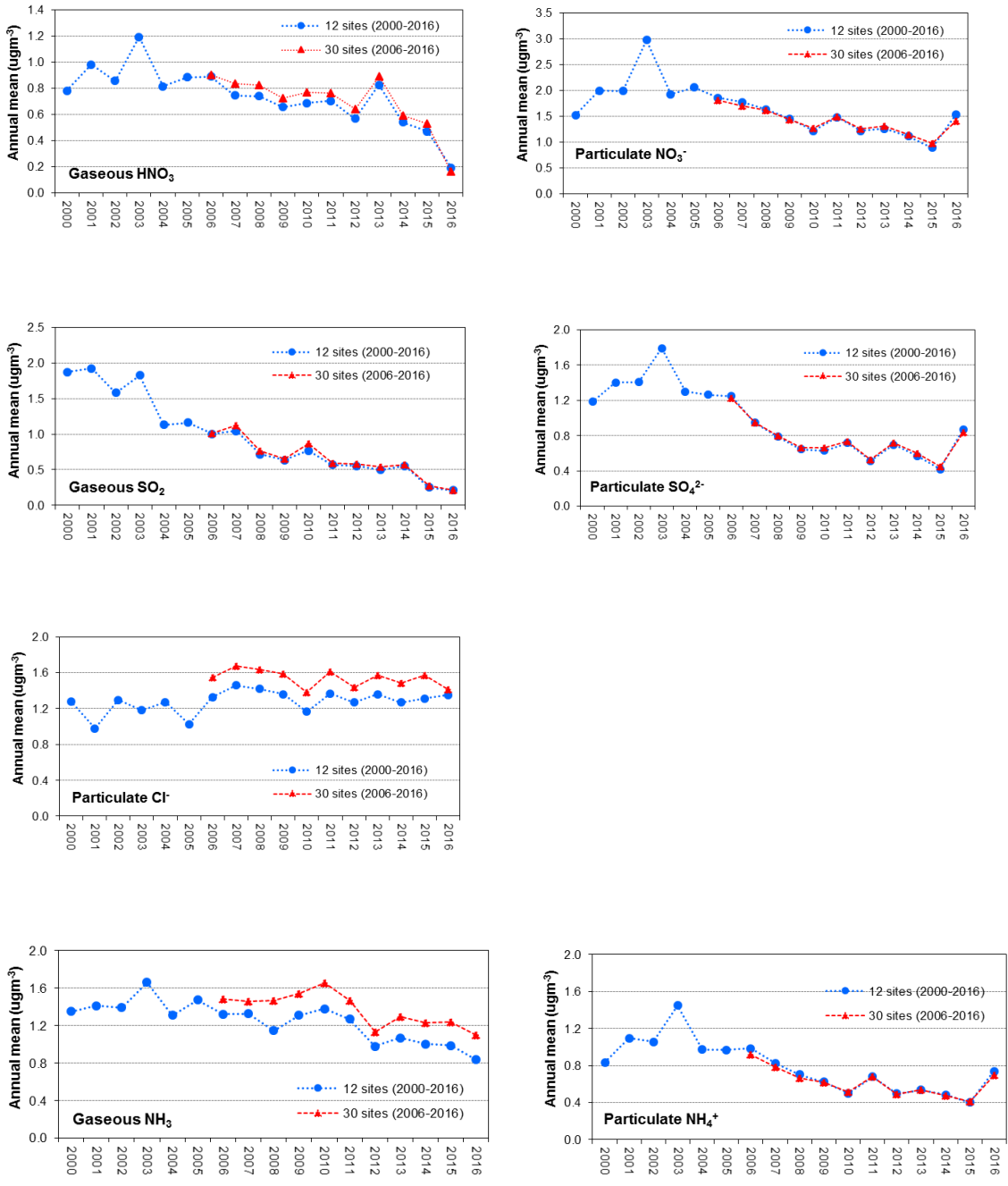
Figure 22: Long-term trend in annual mean concentrations of gases and aerosols monitored in AGA-Net. Each data point represents the averaged annual mean from all sites (increased from 12 to 30 sites since Jan 2006) and also the original l2 monitoring sites in the network. NAMN NH₃ data for AGA-Net sites are also shown, for comparison.
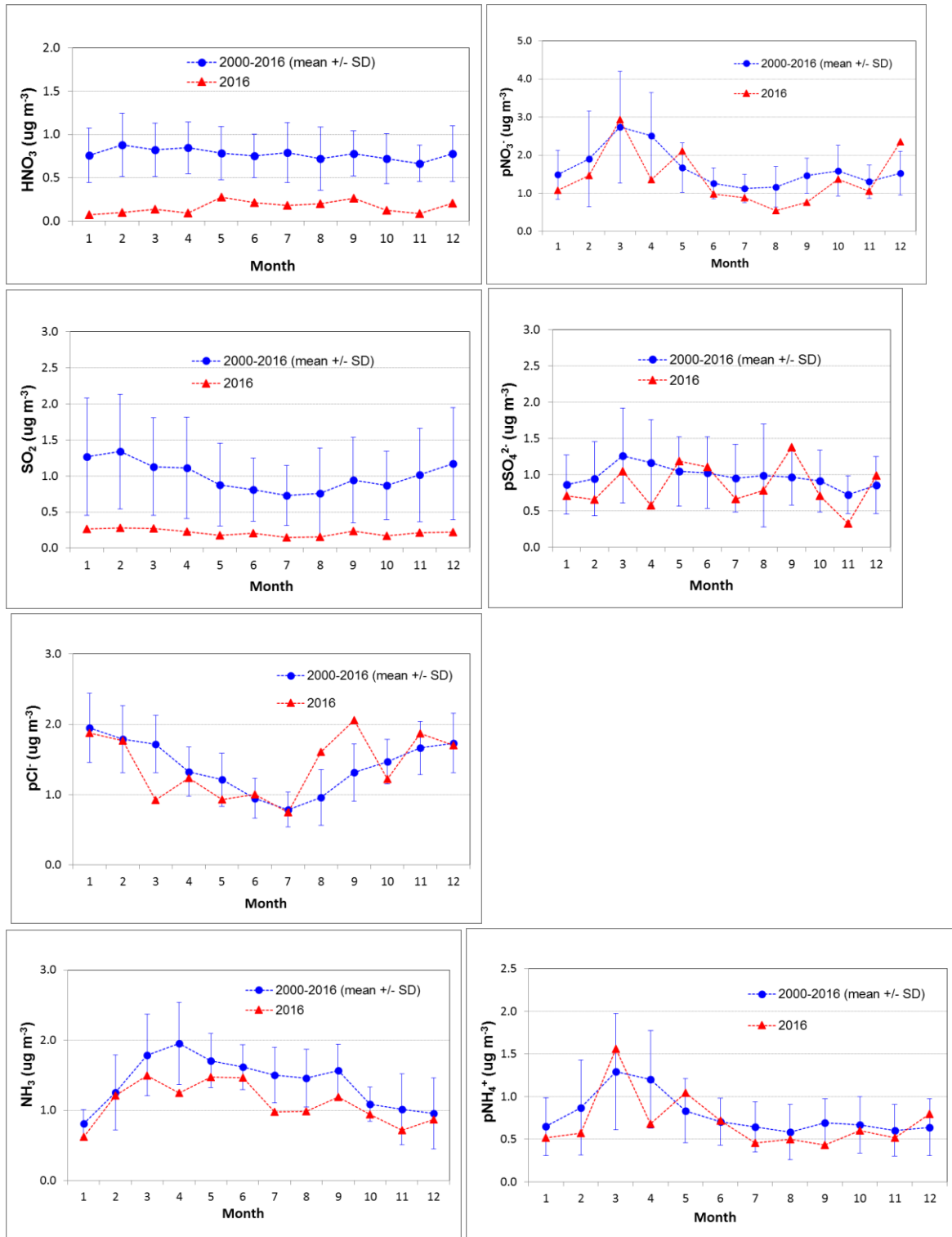
Figure 23: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (2000-2016: mean +/- SD of 30 AGA-Net sites) against year 2016.

3. UK EMEP Supersites 2016 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 2016 are summarised in Table 5.

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 Gothenberg 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.**
- 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 5   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 2016 more than 20 research outputs (papers or presentations) have been identified using data from Auchencorth Moss (see p. vii)

3.1   Auchencorth

MARGA summary

The annual summary of trace gas mass concentration from the Auchencorth EMEP Supersite for 2016 is shown in Table 6 and in Figure 24. 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 66% for trace gases and in the range 54-65% for particulate mass components. The data capture was low than in the previous two years due to failure in the IC unit which led to nearly 2 months downtime whilst waiting for a replacement. New instruments are on order for 2018.

Table 6 Annual summary of trace gas mass concentration measurements at Auchencorth Moss

Trace gas	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_3	1.23	66
HCl	0.13	66
HNO_3	0.10	66
HNO_2	0.13	66
SO_2	0.17	66

Figure 24 Ratified gas measurements from the MARGA instrument at Auchencorth Moss for 2016.

Table 7 Annual summary of the speciated PM$_{10}$ mass concentration from the Auchencorth EMEP Supersite, 2016

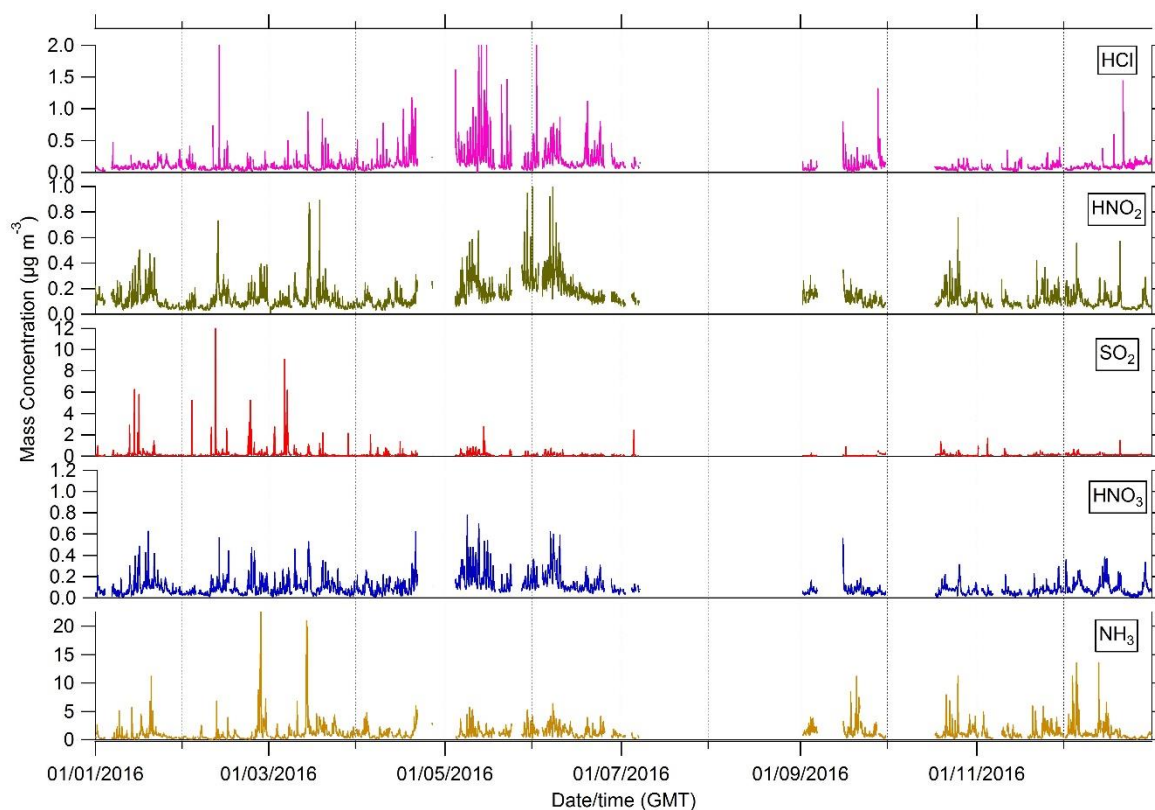| Ion (PM$_{10}$)	Annual mean (µg m^{-3})	Data capture (%)
NH$_4^+$	0.62	59
Na$^+$	0.58	55
K$^+$	0.05	58
Ca^{2+}	0.05	59
Mg^{2+}	0.06	58
Cl$^-$	1.11	58
NO$_3^-$	1.36	63
SO$_4^{2-}$	0.88	63
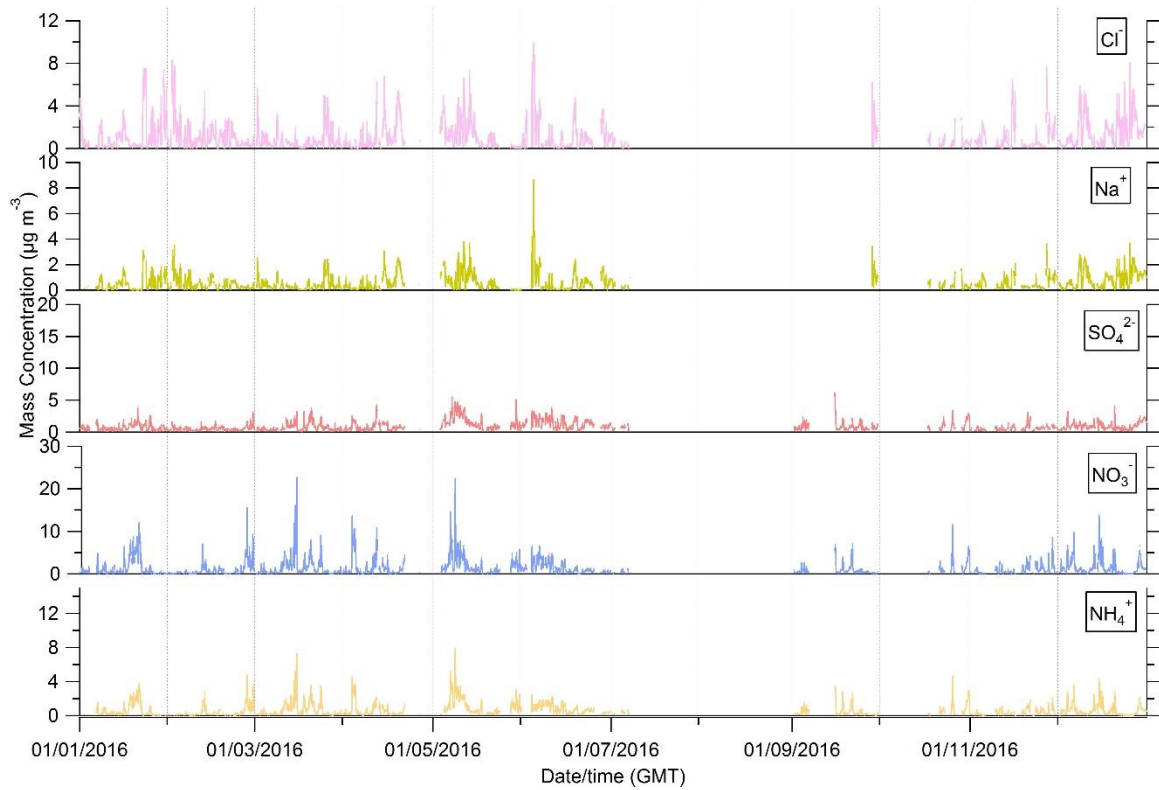
Figure 25 Ratified PM$_{10}$ measurements from the MARGA instrument at Auchencorth Moss for 2016.

Table 8 Annual summary of the speciated PM2.5 mass concentration from the Auchencorth EMEP Supersite, 2016

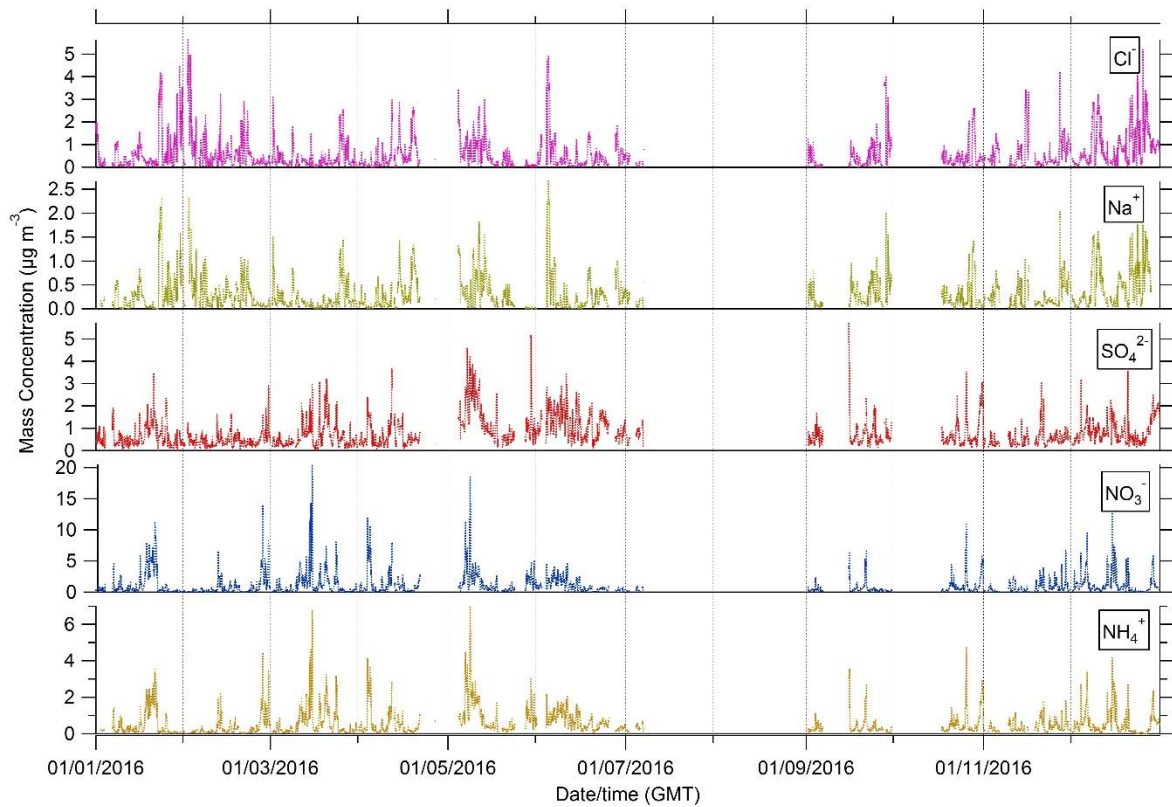| Ion (PM$_{2.5}$)	Annual mean (µg m^{-3})	Data capture (%)
NH$_4^+$	0.56	63
Na$^+$	0.31	62
K$^+$	0.03	63
Ca^{2+}	0.02	61
Mg^{2+}	0.03	63
Cl$^-$	0.59	66
NO$_3^-$	1.11	66
SO$_4^{2-}$	0.77	66

Figure 26 Ratified PM$_{2.5}$ measurements from the MARGA instrument at Auchencorth Moss for 2016

Mercury Measurements

The Auchencorth mercury measurements data capture for 2016 are shown in the Table 9 below. The statistics presented are based on the ratified measurements supplied to UK-Air. Time series plots of the 2016 Auchencorth Moss measurements are shown in Figure 27. There were several operational issues with the instruments during 2016 which has led to low data capture and quality throughut the year. The most significant was during September, when the lamp stabilization circuit board in the 2537A instrument ceased operating normally leaving the analyser inoperative. Unfortunately this ceased all Gaseous elemental Mercury (GEM), particulate bound mercury (PBM) and gaseous oxidized mercury (GOM) measurements on site for the remainder of the year. Provision of a new 2537X analyser in early 2017 should vastly improve operations.

Table 9: Auchencorth Moss mercury measurements 2016 statistics

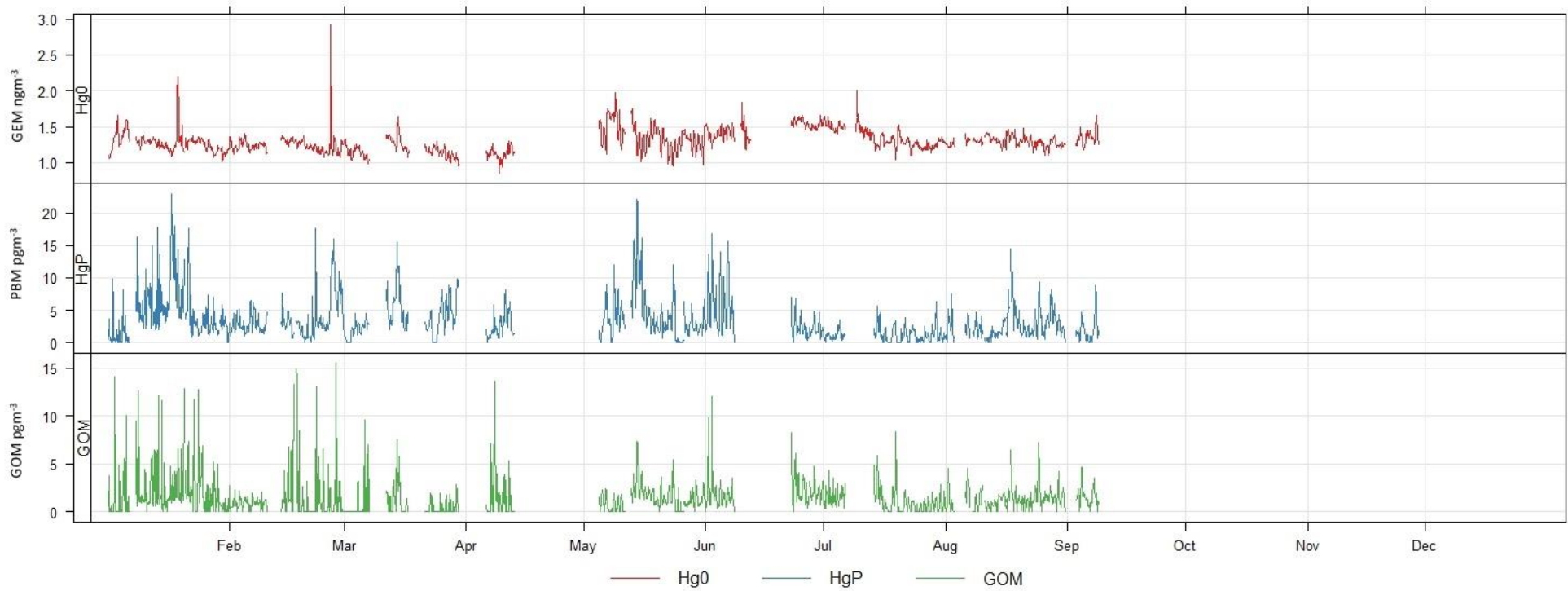|	Annual Mean	Data Capture
Gaseous Elemental Mercury (GEM)	1.30 ngm^{-3}	48.8%
Particulate Bound Mercury (PBM, PM$_{2.5}$)	3.34 pgm^{-3}	45.8%
Gaseous Oxidised Mercury (GOM)	1.48 pgm^{-3}	45.8%

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Figure 27: Speciated Mercury Measurements at Auchencorth Moss, 2016

3.2 Chilbolton

The Harwell site and its predecessors has been operating as a monitoring site in some capacity since June 1976. In December 2015, it was decided that the site should be relocated to the Chilbolton Science and Technology Facilities Council (STFC) site in Hampshire. The site was relocated due to redevelopment at the Harwell site and could not be used as representative of a rural location in the south east of England.

Annual mean concentrations of trace gas and aerosol measurement are summarised in Tables 10-12 detailing the annual mean and % data capture for the PM_{10}, $PM_{2.5}$, and trace gas species, respectively, measured by the Chilbolton MARGA. Overall <42% of the measurement data was lost due to intermittent blockages and operational issues, the latter of which was a significant problem in 2016. Specific issues were the MARGA relocation to Chilbolton in January 2016. On 8th February Applicon serviced instrument after relocation. In July MARGA was offline due to degasser failure. The new part was fitted on 17th August.

The annual summary statistics presented in Tables 11-13 are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2016 Chilbolton MARGA measurements (major species and trace gases) are shown in Figure 28, Figure 29, and Figure 30 below.

Table 10 Annual summary of trace gas mass concentration from the Chilbolton EMEP Supersite, 2016.

Trace gas	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_3	5.89	54
HCl	0.08	58
HNO_3	0.16	57
HNO_2	0.49	58
SO_2	0.16	58

Table 11 Annual summary of the speciated PM10 mass concentration from the Chilbolton EMEP Supersite, 2016.

Ion (PM_{10})	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	1.35	51
Na^+	0.66	51
K^+	0.11	51
Ca^{2+}	0.23	51
Mg^{2+}	0.14	51
Cl^-	1.04	54
NO_3^-	3.5	54
SO_4^{2-}	1.55	54

Table 12 Annual summary of the speciated PM2.5 mass concentration from the Chilbolton EMEP Supersite, 2016.

Ion ($PM_{2.5}$)	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	1.28	54
Na^+	0.3	53
K^+	0.09	54
Ca^{2+}	0.07	54
Mg^{2+}	0.08	54
Cl^-	0.47	58
NO_3^-	2.98	58
SO_4^{2-}	1.43	58
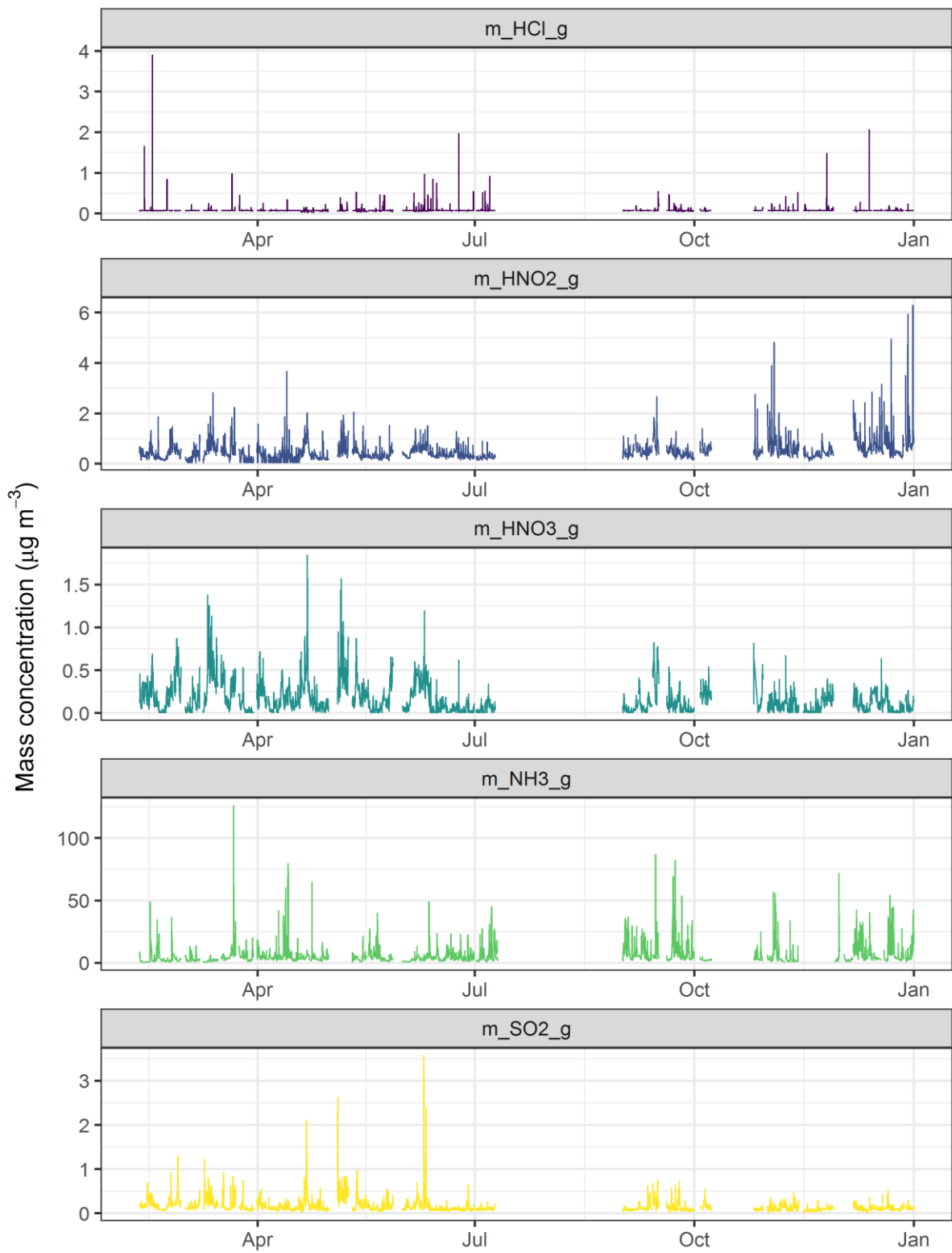
Figure 28 Time series plot of the trace gas (HCl, HNO2, HNO3, NH3, and SO2) measurements from the Chilbolton MARGA, 2016.
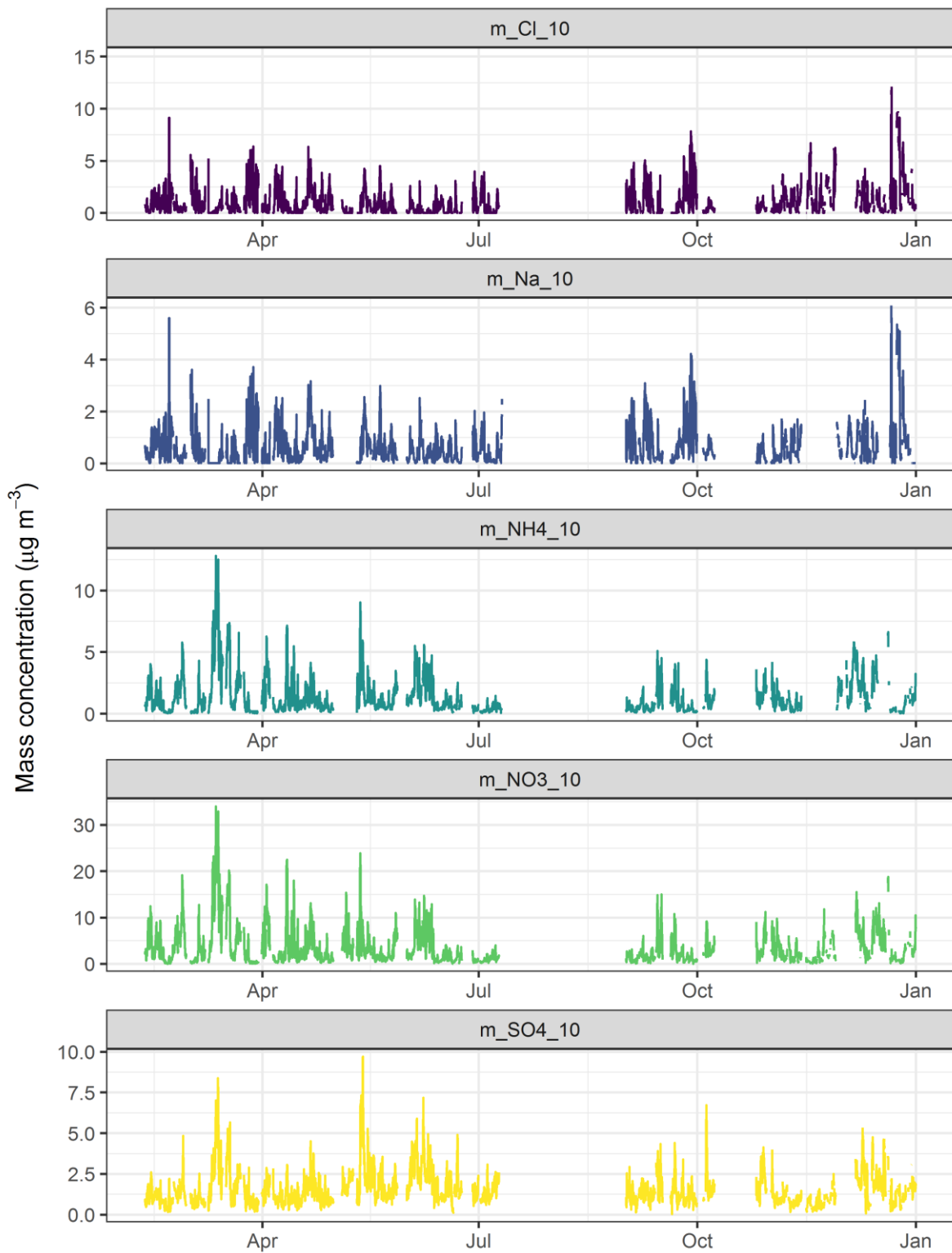
Figure 29 Time series plot of the major PM10 species (Cl⁻, Na⁺, NH₄⁺, NO₃⁻, and SO₄²⁻) measurements from the Chilbolton MARGA, 2016. Base cation species (Ca²⁺, Mg2⁺ and K⁺) measurements not shown.

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Figure 30 Time series plot of the major PM$_{2.5}$ species (Cl$^-$, Na$^+$, NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$) measurements from the Chilbolton MARGA, 2016. Base cation species (Ca^{2+}, Mg2$^+$ and K$^+$) measurements not shown.

Typical meteorological parameters are measured at the Chilbolton EMEP Supersite. The 2016 annual means and data captures are summarised in Table 13. Data capture for the parameters measured was typically above 97%.
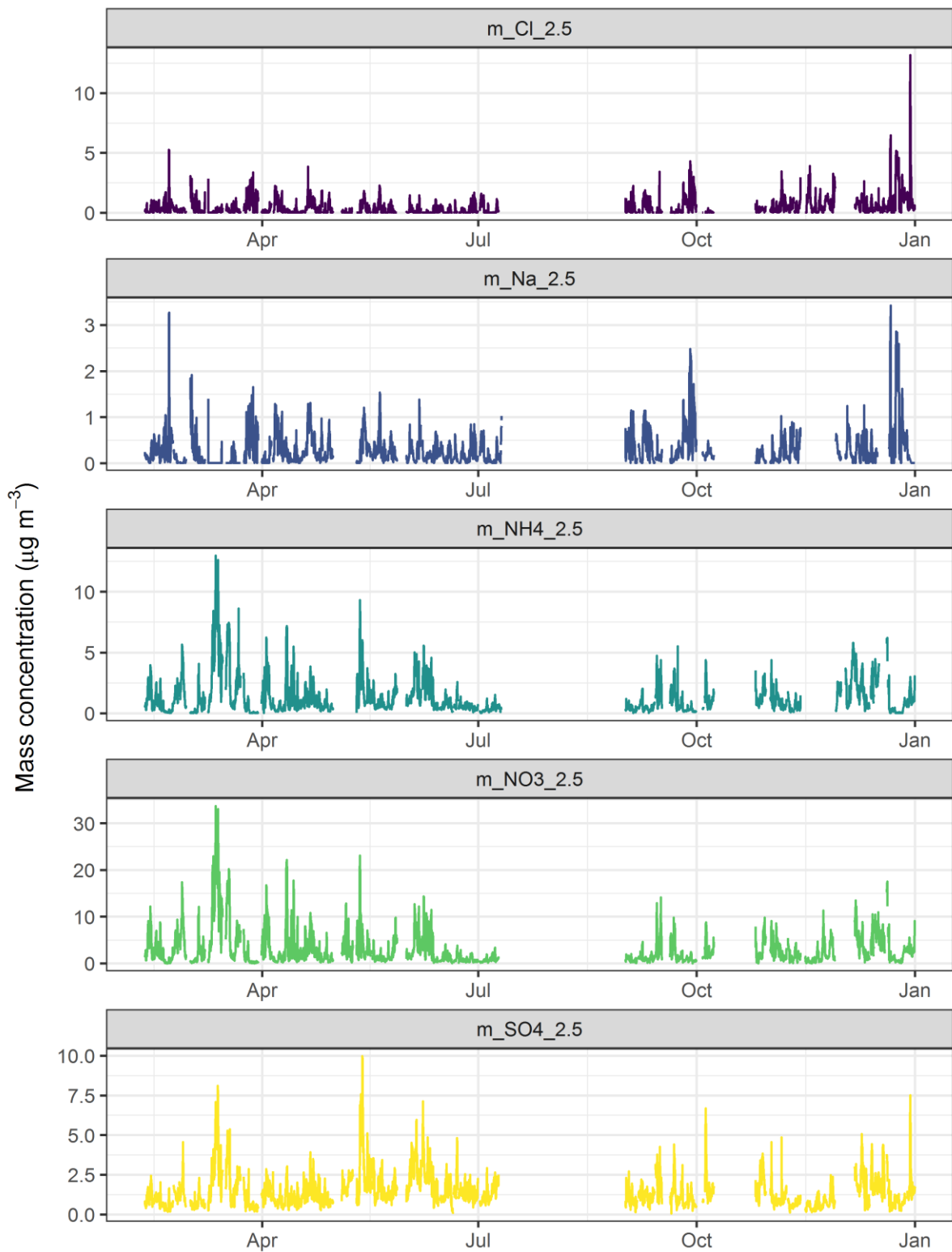
Table 13 2016 Summary of the Chilbolton EMEP Supersite meteorological observations

Meteorological parameter	Annual mean	Data capture (%)
Barometric pressure (mbar)	1007.1	97.9%
Dewpoint (°C)	8	97.9%
Wind direction (°)	185.3	97.9%
Wind speed (m s-1)	3.7	97.9%
Relative humidity (%)	83.1	97.9%
Temperature (°C)	10.4	97.9%
Meteorological parameter	Total	Data capture (%)
Rainfall (mm)	768.1	97.8%

Meteoritical measurements Chilbolton EMEP Supersite during 2016. Figure 31 shows a plot of the directional frequency (in 10° sectors) for 2016. The Figure shows that the air masses arriving at the Chilbolton EMEP Supersite predominantly originated from the south 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 31, and maximums of up to 16 m s^{-1}. Figure 32 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 north-west. One notable feature of the monthly summary plots was that in the winter month's (December, January, February) wind speeds were higher, with light south easterly winds dominant in the summer months (May, June, July).
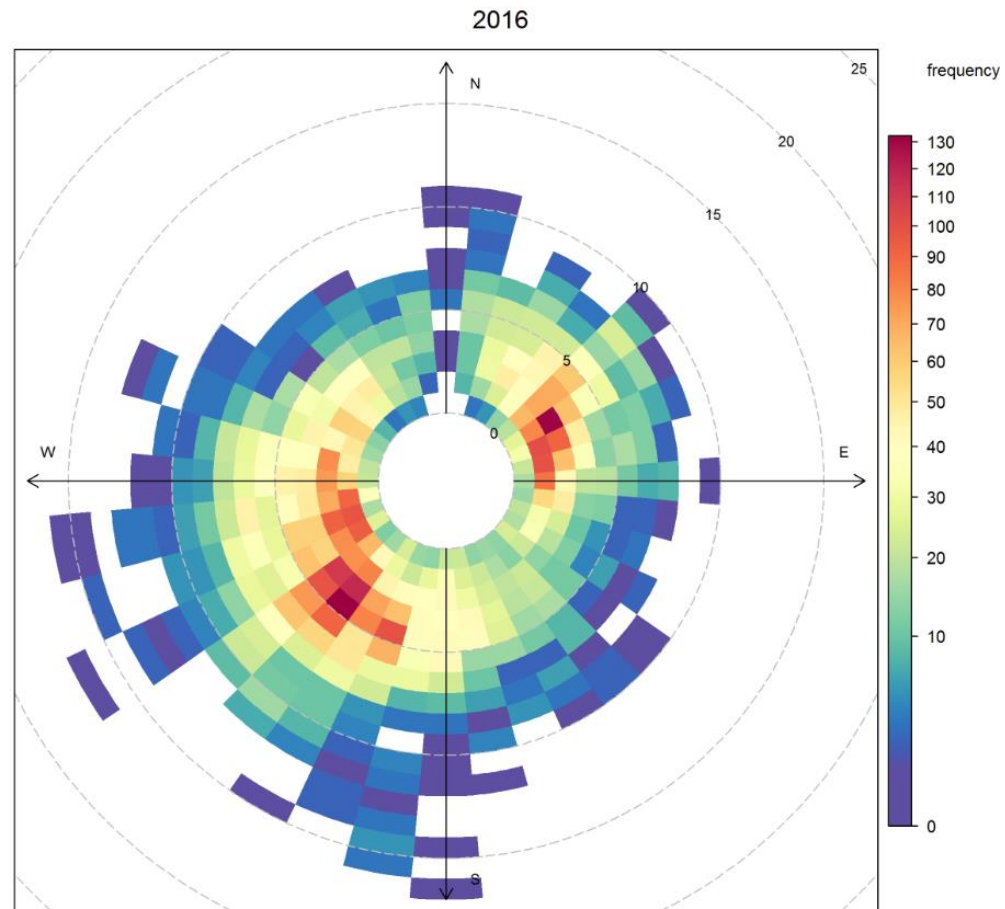
Figure 31 Wind speed (m s^{-1}) and directional frequency for the Chilbolton EMEP Supersite, 2016.
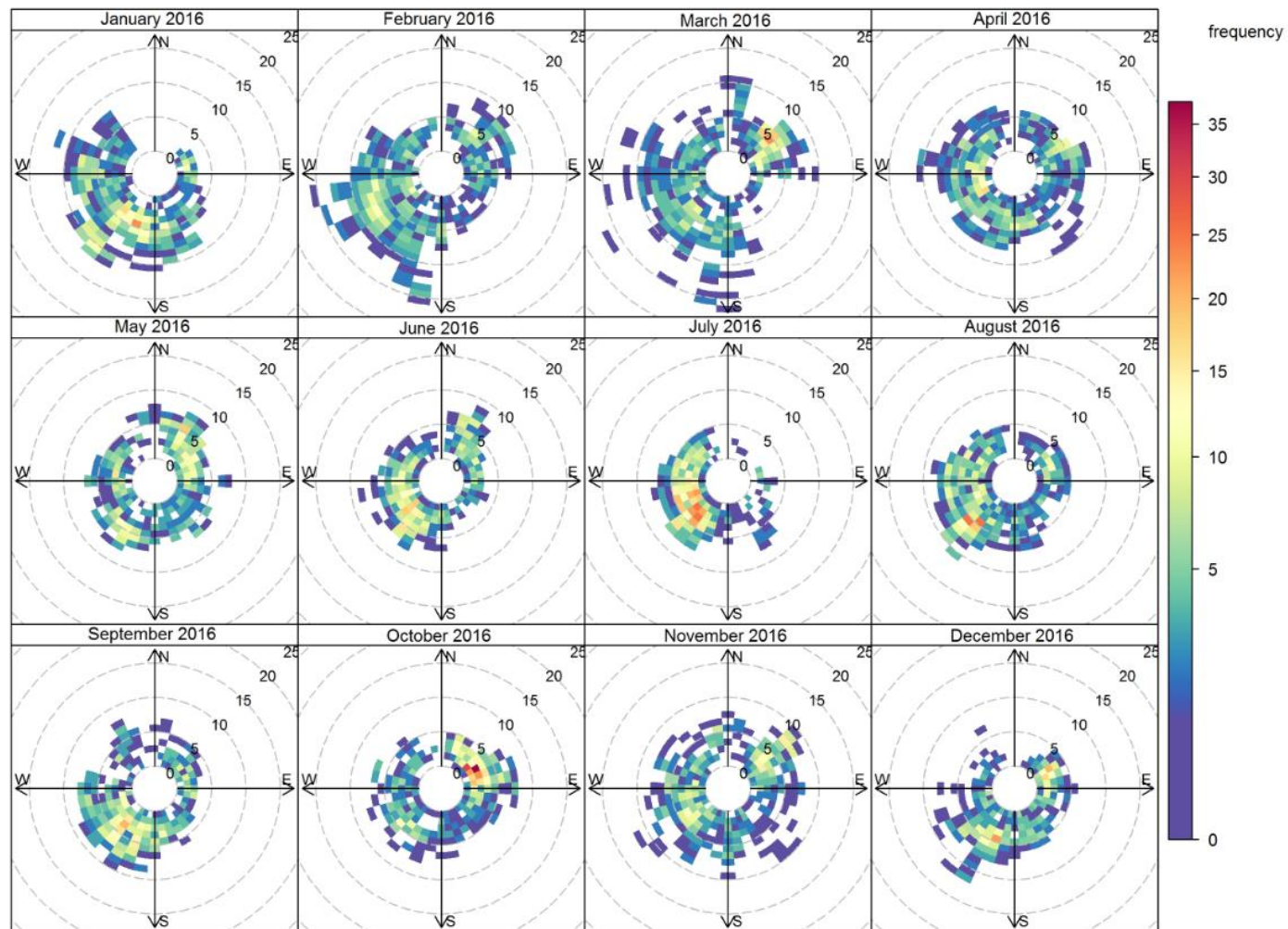
Figure 32 Monthly variations of hourly wind speed and directional frequency for the Chilbolton EMEP Supersite, 2016.

Mercury measurements

The Chilbolton mercury measurements data capture for 2016 are shown in the Table 5 below. There were a few operational issues with the instruments during 2016 which has led to some gaps in data capture, but a vast improvement on that for 2015. Data collection at the Chilbolton site did not commence until February, when the instrument and setup were commissioned. During August and September, various operational issues due to lamp stability and data capture prevented data collection. Provision of a new 2537X analyser in early 2017 should vastly improve operations. The statistics presented are based on the ratified measurements supplied to UK-Air. Time series plot of the 2016 Chilbolton measurements are shown in Figure 6.

Table 14: Chilbolton Mercury measurements 2016 statistics

	Annual Mean	Data Capture
Total Gaseous Mercury (TGM)	1.57 ngm^{-3}	73.5%
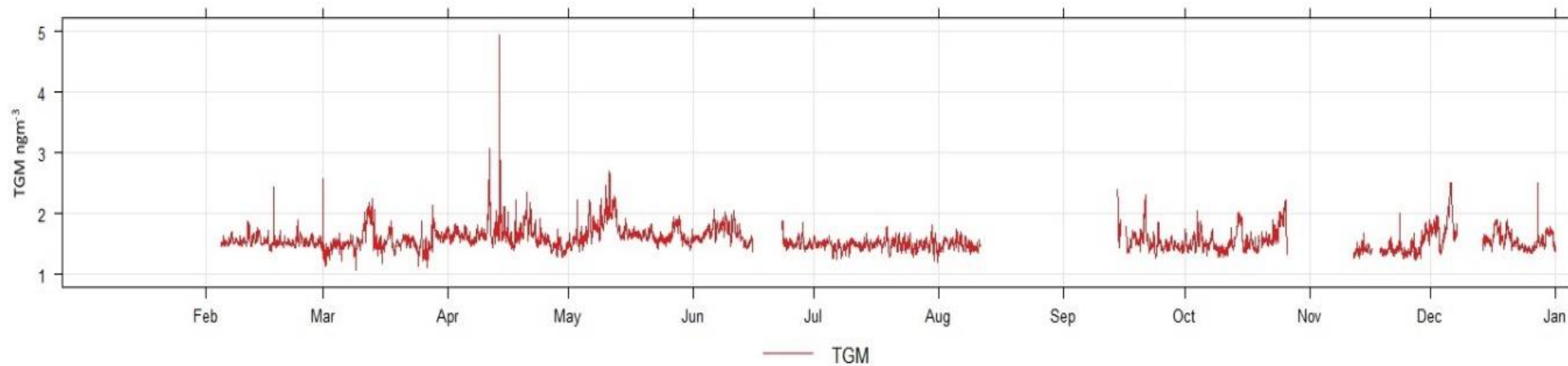
Figure 33: Total Gaseous Mercury Measurements at Chilbolton, 2016

Acknowledgements

5. References

Tang, Y.S., Braban, C.F., Dragosits, U., Dore, A.J., Simmons, I., van Dijk, N., Poskitt, J., Dos Santos Pereira, G., Keenan, P.O., Conolly, C., Vincent, K., Smith, R.I., Heal, M.R. & Sutton, M.A. (2017) Drivers for spatial, temporal and long-term trends in atmospheric ammonia and ammonium in the UK. *Atmos. Chem. Phys. Discuss.*, **2017**, 1-39.

Tang, Y.S.; Cape, J.N.; Braban, C.F.; Twigg, M.M.; Poskitt, J.; Jones, M.R.; Rowland, P.; Bentley, P.; Hockenhull, K.; Woods, C.; Leaver, D.; Simmons, I.; van Dijk, N.; Nemitz, E.; Sutton, M.A.. 2015 Development of a new model DELTA sampler and assessment of potential sampling artefacts in the UKEAP AGA-Net DELTA system: summary and technical report. London, Defra. (CEH Project no. C04544, C04845)

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., 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., 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., 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 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 2016

Chilbolton operations

2016 is the first year of operation of the southernmost UK EMEP Supersite established at Chilbolton, Hampshire. 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. NERC CEH was LSO for Auchencorth Moss. During 2016 no health and safety incidents occurred at either site in relation to the operation of the EMEP Supersites.

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.

MARGA 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 were lost 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 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. The instrument's working solution was made-up periodically by diluting (1000-fold) 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), respectively, 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 15) 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 15 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

Precip-Net: 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 34th EMEP Inter-comparison

The inter-comparison in 2016 was the 34th time such an inter-comparison took place. The samples provided included synthetic rainwater samples and nitrogen dioxide in absorbing solution.

The performance of Ricardo's chosen laboratory (Environmental Scientifics Group Ltd) has been made aware of the analytical performance and the results that have been obtain from the intercomparison and are currently improving their analysis with particular reference to ammonium (NH_4^+) which were unsatisfactory. The way in which this intercomparison helped to highlight a potential issue with analysis shows the importance of intercomparisons to ensure quality is maintained and where issues are identified methods are improved to ensure the quality of the data.

Table 16 34th EMEP Inter-comparison

Species	Sample code	Expected concentration µeq l⁻¹	Measured concentration µeq l⁻¹	Mean difference (%)	Assessment [1]
SO4-2	G1	1.035	0.927	12%	Q
	G2	0.695	0.618	12%	Q
	G3	1.784	1.603	11%	Q
	G4	1.648	1.498	10%	Q
NH$_4^+$	G1	0.234	0.16	46%	U
	G2	0.293	0.214	37%	U
	G3	0.399	0.321	24%	Q
	G4	0.545	0.481	13%	S
NO$_3^-$	G1	0.41	0.364	13%	Q
	G2	0.445	0.398	12%	Q
	G3	0.812	0.729	11%	Q
	G4	0.905	0.821	10%	Q
Na$^+$	G1	0.414	0.365	13%	S
	G2	0.399	0.343	16%	Q
	G3	0.833	0.78	7%	S
	G4	0.638	0.608	5%	S
Mg^{2+}	G1	0.113	0.124	-9%	S
	G2	0.081	0.083	-2%	S
	G3	0.099	0.103	-4%	S
	G4	0.17	0.186	-9%	S
Cl-	G1	0.232	0.232	0%	S
	G2	0.313	0.309	1%	S
	G3	0.554	0.54	3%	S
	G4	0.389	0.386	1%	S
Ca^{2+}	G1	0.121	0.153	-21%	Q
	G2	0.083	0.102	-19%	Q
	G3	0.196	0.23	-15%	S
	G4	0.185	0.23	-20%	Q
K$^+$	G1	0.197	0.204	-3%	S
	G2	0.26	0.272	-4%	S
	G3	0.388	0.407	-5%	S
	G4	0.322	0.34	-5%	S
pH*	G1	4.36	4.4	-1%	S
	G2	4.54	4.57	-1%	S
	G3	4.05	4.1	-1%	S
	G4	4.12	4.18	-1%	S
Cond	G1	22.6	24	-6%	S
	G2	18.1	18.1	0%	S
	G3	44.7	45.1	-1%	S
	G4	41.4	41.7	-1%	S

* pH as pH units

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

NO₂-Net

Results of the 34th EMEP Inter-comparison

The inter-comparison in 2016 was the 34th time such an inter-comparison took place. The results of the Nitrogen Dioxide absorbing solution are shown below in Table 17. The results of this intercomparison are excellent with between a 4.8% and 8.2% absolute difference which whilst is not as impressive as in 2015 it 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 in case they wish to review procedures.

Table 17 Comparison of Expected and Measured Concentrations of Nitrogen Dioxide in Absorbing Solution

Sample code	Expected concentration µg NO₂-N/ml	Measured concentration µg NO₂-N/ml	Absolute Mean difference (%)	EMEP Assessment
C1	0.139	0.146	4.8%	S
C2	0.125	0.132	5.3%	S
C3	0.055	0.059	6.8%	S
C4	0.067	0.073	8.2%	S

Comparison with co-located automatic sites

During 2016 there were four UKEAP NO₂ diffusion tube monitoring sites are co-located with automatic urban and rural monitoring network (AURN) sites these were the newly established Chilbolton Observatory, Eskdalemuir, High Muffles and Yarner Wood. Prior to the Chilbolton Observatory site being established the Harwell site has collocated diffusion tubes and automatic monitoring. The data from these sites, including both Harwell and Chilbolton Observatory have been plotted

Figure 34 and the dashed lines correspond to the automatic data from the co-located sites.
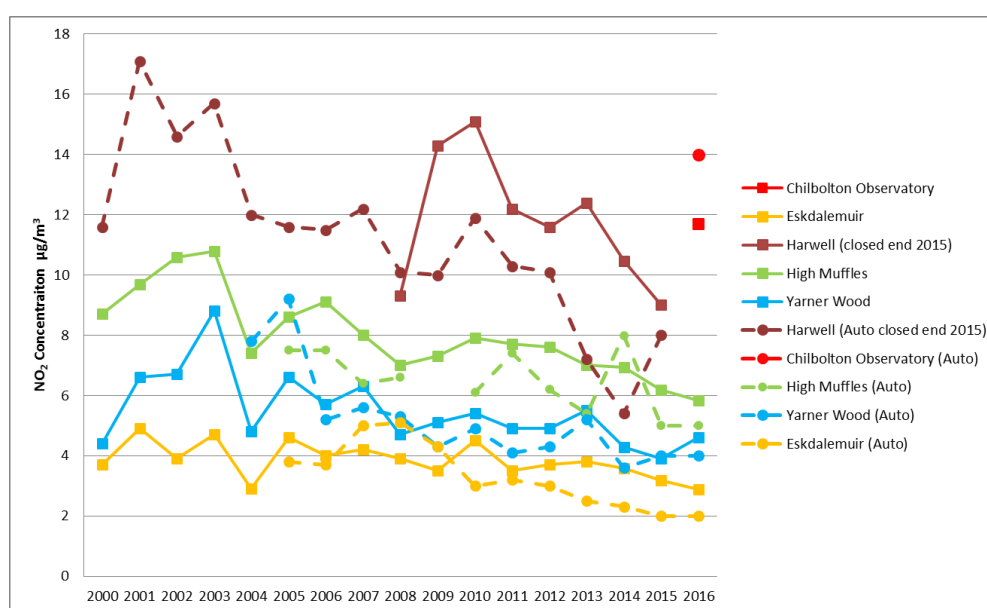
It is apparent from the comparison of the automatic and diffusion tube measurements that generally the NO₂ diffusion tubes appear to over-read when compared to the automatic sites and that the over-read appears more pronounced at the sites with higher concentrations with the exception of the newly established Chilbolton Observatory site which appears to under-read. Diffusion tube measurements are less accurate than automatic measurements however are of lower cost in terms of purchase and operation. The diffusion tube measurements do show relatively good agreement with the automatic sites which gives some confidence in the measurements for the other rural sites with diffusion tube measurements. The use of diffusion tubes in the UKEAP NO₂-net network provide a good cost effective approach to measurement and are particularly useful at very remote locations where power for automatic equipment would need to be established.

AGA-Net

All DELTA systems are serviced annually. As part of this service the gas meter is calibrated and the system PAT tested. Figure 35 below contains the average percentage data capture across all sites for each chemical of interest. All capture rates are greater than 75%. Issues with data capture have arisen in the AGA-Net due to:

1. Flow rates are insufficient as pumps reach the end of their life and need to be replaced. Sites with pumps showing early signs of failure have been highlighted and are due to be changed in the 2017 site service visits.
2. LSO availability – Many LSO are volunteers or are changing samples as part of agreements with other organisations. Many organisations are facing cutbacks in the current economic climate making reliable site operators harder to source.
3. Failure of mains power. Issues have been raised to those responsible for the power provision. Unfortunately at sites with issues, wind/solar systems are unlikely to generate sufficient power so are not an alternative option.
4. Sample loss due to damage – Some samples damaged in transit, improvements have been made to packing to reduce sample loss.
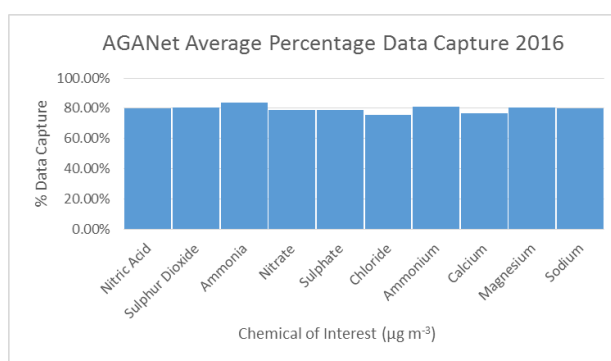

Figure 35: Average percentage data capture for 2016

NAMN

The percentage data capture in NAMN provides an indication of network performance .During 2016 average data capture across all sites was 86%. Where issues have arisen with data capture the main issues have been the same as for AGA-Net.

Parallel measurement by both DELTA and ALPHA methods are carried out at 9 intercomparison sites therefore there are 9 more measurements reported than the total number of sites in the network.

ALPHA DELTA intercomparison

NAMN measurements continue to be made with a mixture of active DELTA systems (Sutton et al. 2001) and passive ALPHA samplers (Tang et al. 2001). 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 36. The annual calibration functions of ALPHA samplers show good consistency between years. This is very important, as it lends support for the detection of temporal trends in ammonia concentrations.
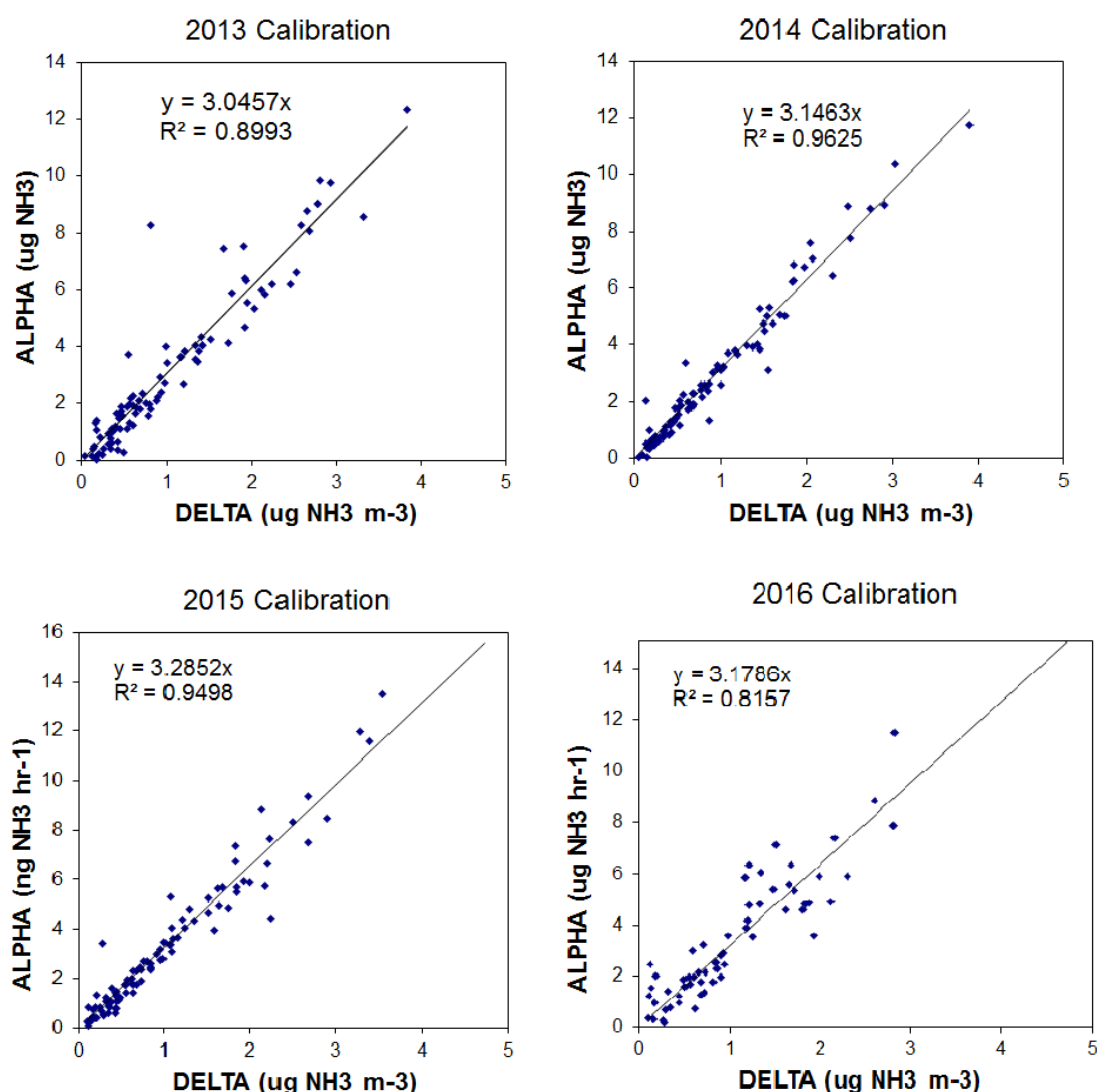

Figure 36: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers in years 2013, 2014, 2015 and 2016.