AQ0647 UKEAP

2014

Annual Report

Prepared for Defra

And the Devolved Administrations

by

NERC Centre for Ecology & Hydrology

&

Ricardo Energy & Environment

Ricardo –Energy & Environment :

C Conolly, M Davies, M Davies, D Knight, K Vincent, A Sanocka, J Lingard, S Richie, B Donovan, A Collings and the UKEAP field team

CEH:

CF Braban, YS Tang, MM Twigg, MR Jones, I Simmons, M Coyle, J Kentisbeer, S Leeson, N van Dijk, E Nemitz, B Langford, WJ Bealey, D Leaver, J Poskitt, HT Carter, S Thacker, M Patel, PO Keenan, G Pereira, AJ Lawlor, A Warwick, P Farrand & MA Sutton

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Main authors: CF Braban, YS Tang, MM Twigg, J Kentisbeer	

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Contact:

Chris Conolly
Ricardo Energy & Environment
Gemini Building, Harwell, Didcot, OX11 0QR

t: 01235 753375

e: Christopher.Conolly@ricardo.com

Ricardo Energy & Environment is certificated to ISO9001 and ISO14001

Author:

Christopher Conolly, Justin Lingard, Keith Vincent

Approved By:

Christopher Conolly

Date:

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UK Eutrophying and Acidifying Atmospheric Pollutant (UKEAP)

Networks Annual Summary

Delivery of National and International Air Quality Evidence

The Defra rural air pollutant monitoring networks project, AQ0647, **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)** comprises the following measurement activities:

- **UK EMEP monitoring supersites** (Harwell and Auchencorth)
- **National Ammonia Monitoring Network** (NAMN)
- **Acid Gases and Aerosol Network** (AGA-Net)
- **Precipitation chemistry Network** (Precip-Net)
- **Rural NO$_2$ diffusion tube network** (NO$_2$-Net)

- The 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.
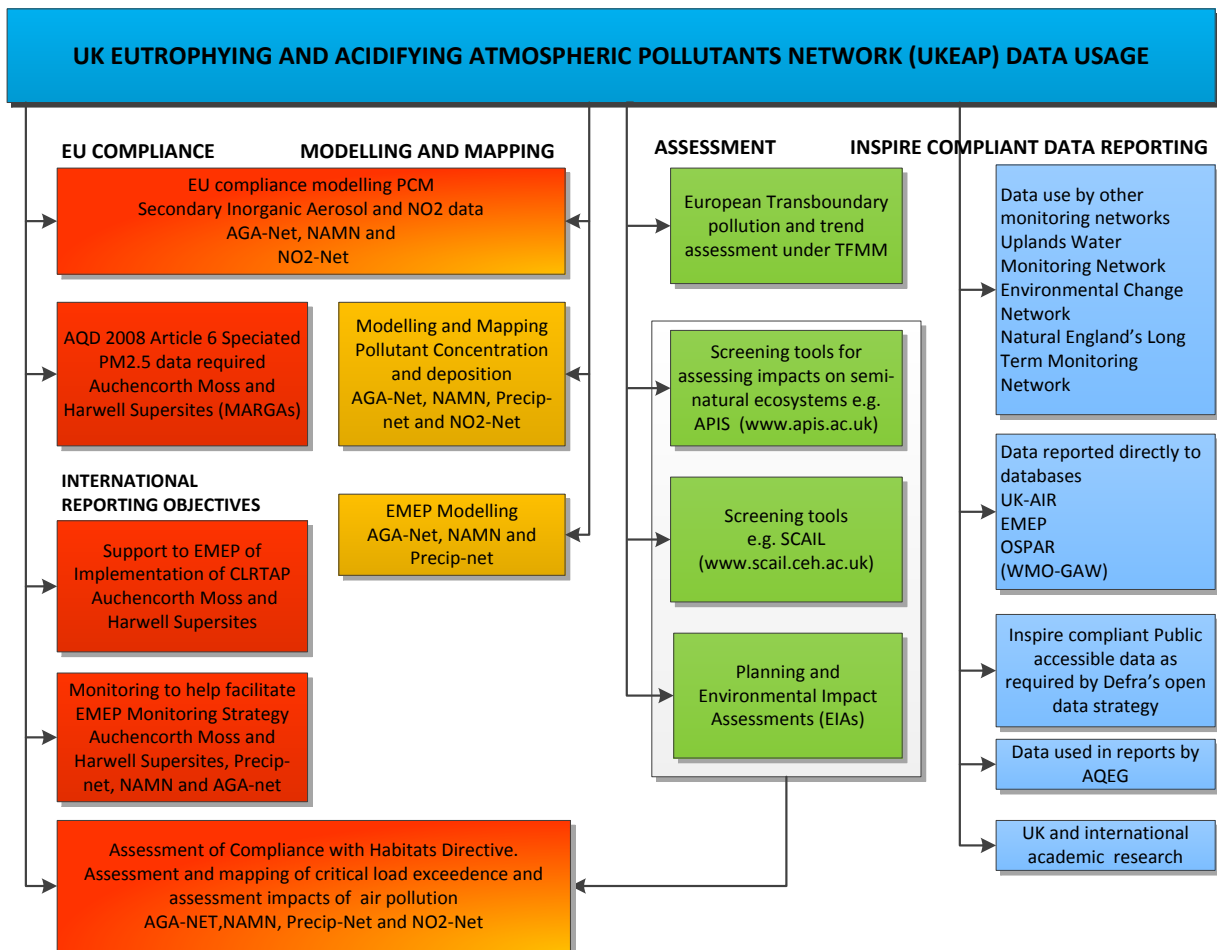
Measurement data for compliance assessment, policy development and other air quality assessments

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.

Defra AQ0650 Modelling Ambient Air Quality (MAAQ)

- Ambient concentratrions 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)](.).

Defra AQ0846 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.

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 depositon 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)](.)

Defra AQ0947 Support for National Air Pollution Control Strategies 2013-2015

- 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 Critcial 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 Harwell 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.

UKEAP 2014 Measurement Headlines

UK EMEP Supersites: Harwell and Auchencorth Moss

- Spring PM event clearly identified as ammonium nitrate rather than Saharan dust event.
- First major Icelandic volcanic eruption to impact the UK with a sulpur-rich plume in recent history chemically characterised.

Precipitation Network (Precip-Net)

- The highest ammonium, nitrate and non- seasalt sulphate concentrationsare in the regions of the country where coal continues to be used for electricity production.
- The 2014 Icelandic plume was visible across the UK in the Precip-Net data

NO_2-Net

- Nitrogen dioxide concentrations have continued to decrease at the more polluted rural locations. However, there is some evidence that nitrogen dioxide concentrations have increased slightly at the more remote locations.

Acid Gas and Aerosols Network (AGA-Net)

- In Spring 2003, an episode of elevated concentrations of ammonium nitrate was measured across the UK, impacting on annual mean concentrations for that year. The episode was subsequently attributed to a persistent high pressure system over the UK.
- In Autumn 2014, elevated concentrations of sulphur dioxide and nitric acid, as well as particulate sulphate, nitrate and ammonium occurred in September which is attributed to the Icleandic volcano plume observed over the UK.

National Ammonia Monitoring Network (NAMN)

- Whilst UK emissions of NH_3 declined by about 18% during the operation of NAMN, NH_3 concentrations from the overall dataset show no detectable trend over the same period.
- The 2014 NAMN results continue to illustrate the high spatial variability in NH_3 concentration and the seasonal variability of ammonia concentrations, reflecting the large regional variability in NH_3 emissions.

2014 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 exhaustive search of the literature and enagagement with stakeholders.

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- Curtis, C. J. Simpson, G. L. **Trends in bulk deposition of acidity in the UK, 1988–2007, assessed using additive models** Ecological Indicators, 37, Part B, 2014, 274–286,
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- Farr, G; Hall, J. 2014 **Atmospheric deposition at groundwater dependent wetlands: implications for effective catchment management and Water Framework Directive groundwater classification in England and Wales**. Nottingham, UK, British Geological Survey, 62pp. (OR/14/047) (Unpublished)
- Field, C. D.; Dise, N. B., Payne, R. J.; Britton, A.J.;. et al. **The Role of Nitrogen Deposition in Widespread Plant Community Change Across Semi-natural Habitats,** Ecosystems, 2014, 17 (5), 864-877
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- Malley C.S et al.. 2014. **The application of hierarchical cluster analysis and non-negative matrix factorization to European atmospheric monitoring site classification**. Atmos. Res. 138:30-40.
- Ots , R., Dore, A., Tang, Y.S., Braban, C. F., et al. **Modelling Past and Future Changes in Secondary Inorganic Aerosol Concentrations in the UK**, Air Pollution Modeling and its Application XXIII, Part of the series Springer Proceedings in Complexity pp 179-182, 2014
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- Rowe, E. C., Tipping, E., Posch, M., Oulehle, F., et al. **Predicting nitrogen and acidity effects on long-term dynamics of dissolved organic matter**, Env. Poll., 184, 2014, 271–282
- Schafers R.. 2014. Volatile organic compounds: ambient flux measurements. :76pp
- Schroder W., Pesch R., Schonrock S., Harmens H., 2014. **Mapping correlations between nitrogen concentrations in atmospheric deposition and mosses for natural landscapes in Europe**. Ecological Indicators. 36:563-571.
- Smith, S. W., Johnson, D., Quin, S.L.O, Munro, K., et al. **Combination of herbivore removal and nitrogen deposition increases upland carbon storage**, 21 (8), 2015,3036–3048
- Vieno, M.; Heal, M. R.; Hallsworth, S.; Famulari, D.; et al. **The role of long-range transport and domestic emissions in determining atmospheric secondary inorganic particle concentrations across the UK**, Atmos. Chem. and Phys. 14.16 (2014): 8435
- Werner, M., Kryza, M, Dore A.J., , **Differences in the Spatial Distribution and Chemical Composition of PM10 Between the UK and Poland,** Environmental Modeling & Assessment, June 2014, Volume 19, Issue 3, pp 179-192.

Contents

UKEAP Annual Report 2014

1. Introduction

The Defra rural air pollutant monitoring networks project, AQ0647, **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)** is operated jointly between Ricardo-AEA 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 2014.
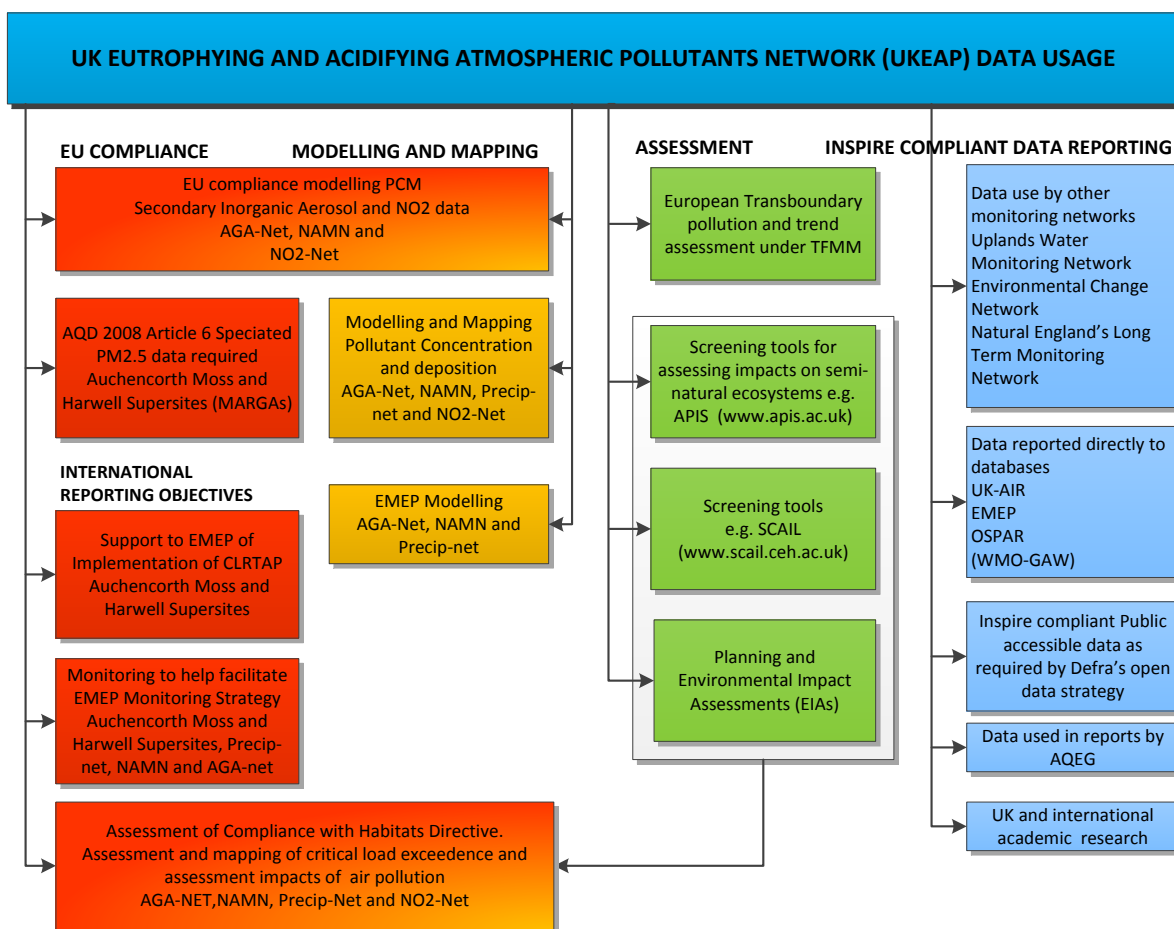

UK EUTROPHYING AND ACIDIFYING ATMOSPHERIC POLLUTANTS NETWORK (UKEAP) DATA USAGE

EU COMPLIANCE

EU compliance modelling PCM Secondary Inorganic Aerosol and NO2 data AGA-Net, NAMN and NO2-Net

AQD 2008 Article 6 Speciated PM2.5 data required Auchencorth Moss and Harwell Supersites (MARGAs)

INTERNATIONAL REPORTING OBJECTIVES

Support to EMEP of Implementation of CLRTAP Auchencorth Moss and Harwell Supersites

Monitoring to help facilitate EMEP Monitoring Strategy Auchencorth Moss and Harwell Supersites, Precip-net, NAMN and AGA-net

Assessment of Compliance with Habitats Directive. Assessment and mapping of critical load exceedence and assessment impacts of air pollution AGA-NET, NAMN, Precip-Net and NO2-Net

MODELLING AND MAPPING

Modelling and Mapping Pollutant Concentration and deposition AGA-Net, NAMN, Precip-net and NO2-Net

EMEP Modelling AGA-Net, NAMN and Precip-net

ASSESSMENT

European Transboundary pollution and trend assessment under TFMM

Screening tools for assessing impacts on semi-natural ecosystems e.g. APIS (www.apis.ac.uk)

Screening tools e.g. SCAIL (www.scail.ceh.ac.uk)

Planning and Environmental Impact Assessments (EIAs)

INSPIRE COMPLIANT DATA REPORTING

Data use by other monitoring networks Uplands Water Monitoring Network Environmental Change Network Natural England's Long Term Monitoring Network

Data reported directly to databases UK-AIR EMEP OSPAR (WMO-GAW)

Inspire compliant Public accessible data as required by Defra's open data strategy

Data used in reports by AQEG

UK and international academic research

Figure 1 Summary of UKEAP data use pathways

UKEAP is comprised of:

- **National Ammonia Monitoring Network** (NAMN)
- **Acid Gases and Aerosol Network** (AGA-Net)
- **Precipitation chemistry Network** (Precip-Net)
- **Rural NO2 diffusion tube network** (NO2-Net)
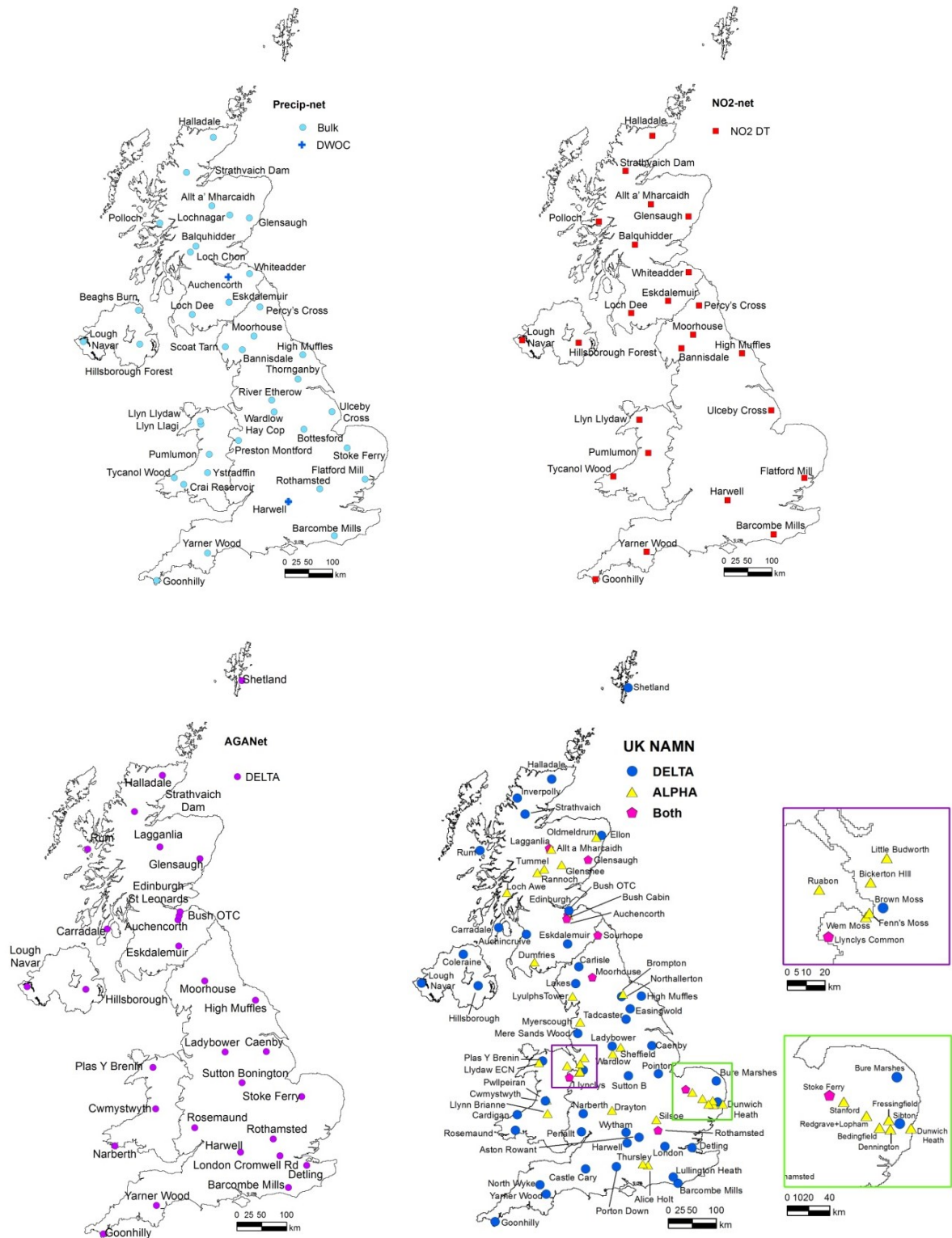- **UK EMEP Supersites** (Harwell and Auchencorth)

Figure 2 UK Eutrophying and Acidifying Atmospheric Pollutants rural networks

2. UKEAP Networks

2.1 Precipitation Network (Precip-Net)

The major ions precipitation network, Precip-Net, consists of 39 fortnightly bulk rain monitoring sites and 2 daily wet only (DWOC) collectors at which the chemical composition of precipitation is measured. The locations of the monitoring sites are shown in Figure 2. A sampler is shown in Figure 4.
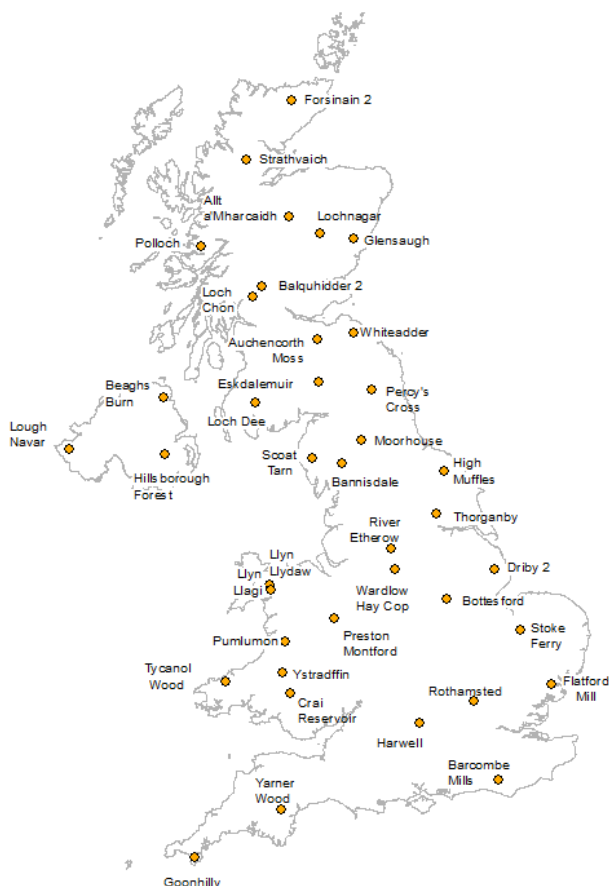

Figure 3 Precip-Net site map

Figure 4 Bulk rain sampler (Bannisdale)

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. Daily collection of precipitation samples using Daily Wet Only Precipitation Collectors (DWOC) are operated at the Auchencorth Moss and Harwell 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 acidity, non-seasalt sulphate, nitrate and ammonium are presented in Figure 5 for 2014. 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.
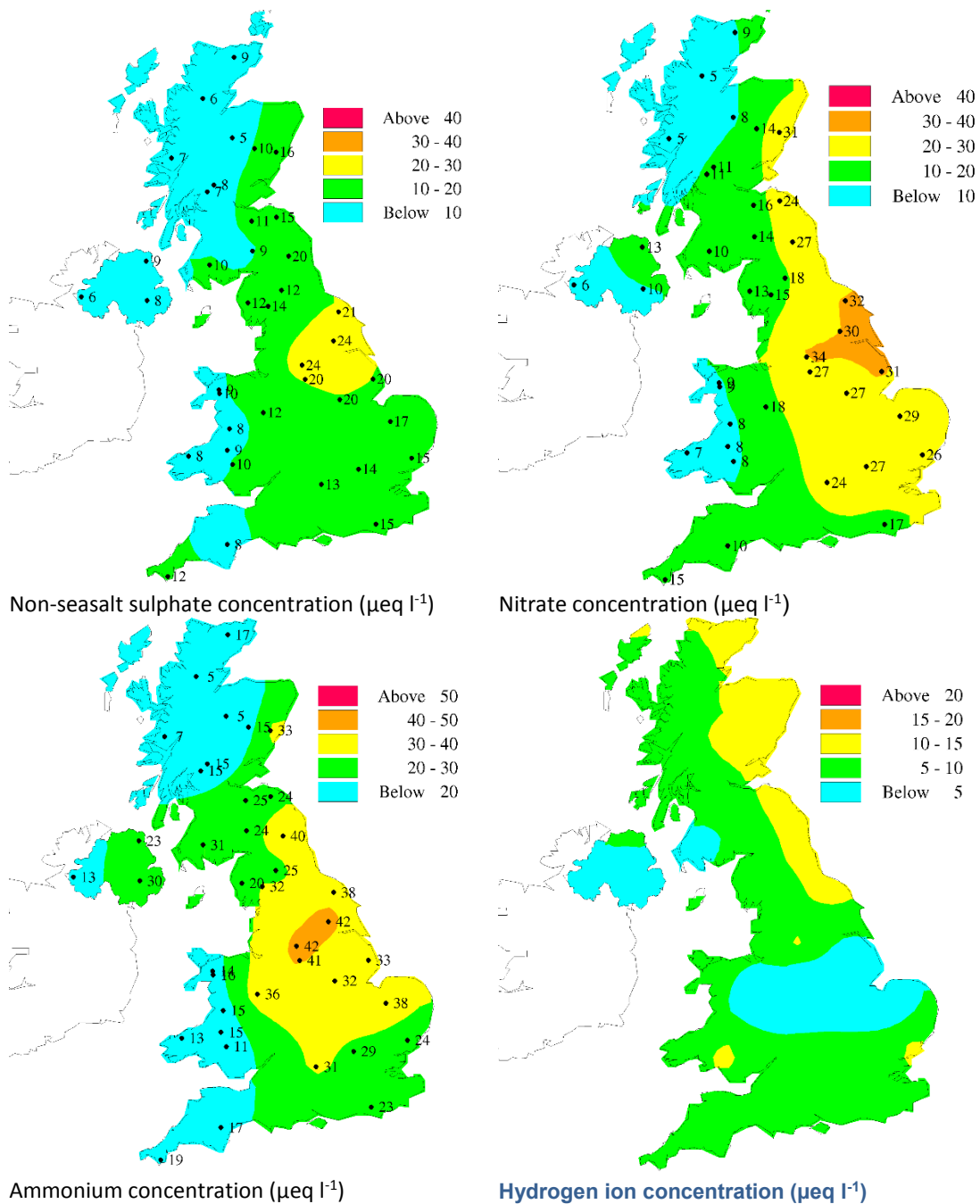
Non-seasalt sulphate concentration (μeq l^{-1})

Nitrate concentration (μeq l^{-1})

Ammonium concentration (μeq l^{-1})

Hydrogen ion concentration (μeq l^{-1})

Figure 5 Interpolated concentration maps for non-sea salt sulphate, nitrate, ammonium and hydrogen ion

(μeq l^{-1})

Since the monitoring network began in 1986 there has been significant decrease in sulphur dioxide and oxides of nitrogen emissions- though the rate of decrease for sulphur dioxide was greater than the decrease for oxides of nitrogen. For example, Figure 6 shows that sulphur dioxide emissions have decreased by about ninety percent whereas oxides of nitrogen have decreased by about sixty percent.
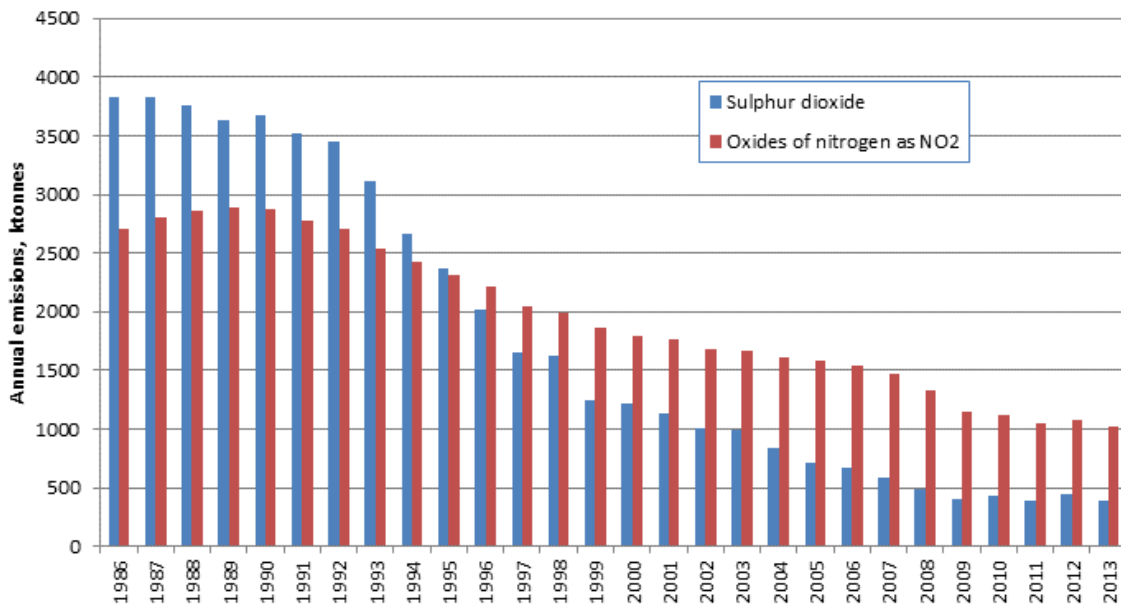
Figure 6 Sulphur dioxide and oxide of nitrogen emissions since 1986 Reference for emissions data. http://naei.defra.gov.uk/

In terms of trends in sulphur concentrations in rainwater there has been a steady decrease in non-sea salt sulphate at all monitoring stations. The rate of decrease has varied throughout the UK with the largest decreases occurring for monitoring stations located near to the large power stations in the Aire Valley and Trent Valley. This is illustrated in Figure 7 LHS which shows the average decrease in non-sea salt sulphate concentration (μeq l^{-1} year^{-1}) derived from a linear regression on annual mean concentrations for those stations currently operating in 2013 with at least 15 years of monitoring data. The largest decreases in annual concentration (about 2.7 μeq l^{-1} year^{-1}) are observed for stations such as Thorganby and Bottesford whereas the smallest decreases for stations in the west of the UK, for example, the annual decrease for at Lough Navar is 0.5 μeq l^{-1} year^{-1}.

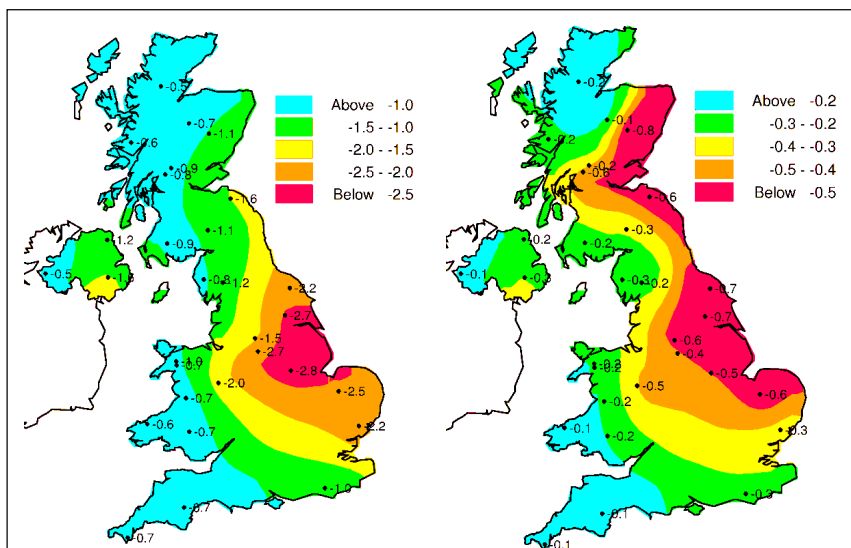**Figure 7 Annual change in non-seasalt sulphate and nitrate concentration (μeq l-1 year-1)**

The right hand map in Figure 7 shows the equivalent plot for nitrate concentrations. The map differs in that the class boundaries are five times smaller than the non-seasalt sulphate. In general at each sampling station the rate of decrease for nitrate is concentrations is much lower, typically three to five times, that for non-seasalt sulphate. Since about 2009 the non-seasalt sulphate and nitrate concentration at most monitoring station in Wales and Scotland (and Lough Navar in Northern Ireland) have reduced to levels that would have been regarded as regional background concentration (less than 8 µeq l[-1]) when the monitoring network began in 1986. Ammonium concentrations in rainwater have also tended to decrease but the picture is more complex due to the smaller percentage reductions in ammonia emissions, local geographic and temporal variability of ammonia emissions and concentrations, as well as dry deposition on funnels and sample storage uncertainties, the inter-annual variability is large and hence trend analysis more challenging to quantify.

Figure 8 and Figure 9 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.
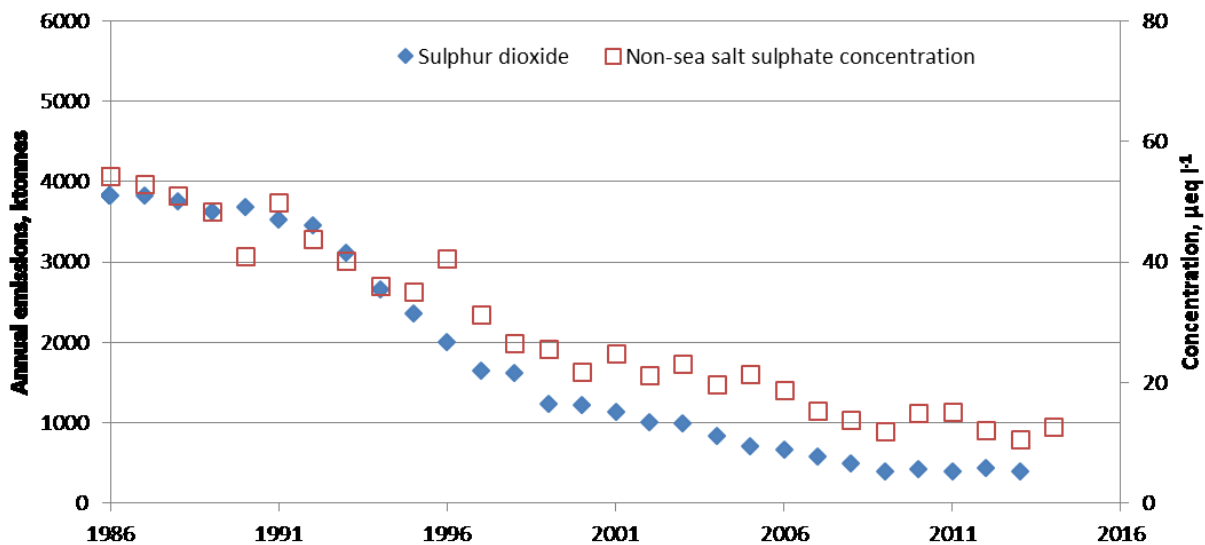

Figure 8 Sulphur dioxide emissions and sulphate concentrations in rainwater concentration
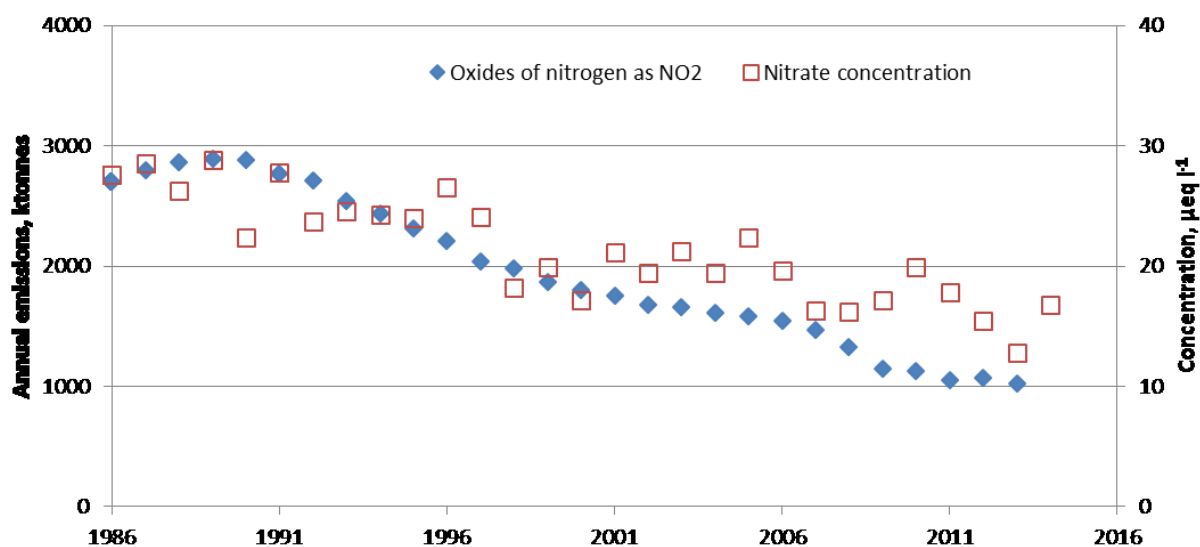
Figure 9 Oxide of nitrogen emissions and nitrate in rainwater concentration

2.2 NO₂-Net Network

The NO₂ network (NO₂-Net) consists of 24 sites (Figure 2) at which diffusion tubes, in triplicate, were exposed for 4-week exposure periods. The annual average NO₂ 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.

Table 1 2014 NO₂ concentration from the Diffusion Tubes in the NO₂-Net

Site Name	2014 concentration ($\mu g\ m^{-3}$)	Data capture	Site Name	2014 concentration ($\mu g\ m^{-3}$)	Data capture
Allt a'Mharcaidh	2.1	100%	Hillsborough Forest	7.1	100%
Balquhidder 2	3.1	100%	Llyn Llydaw	3.1	85%
Bannisdale	4.9	100%	Loch Dee	3.4	84%
Barcombe Mills	9.5	100%	Lough Navar	2.6	100%
Driby 2	10.2	100%	Moorhouse	5.1	100%
Eskdalemuir	3.6	92%	Percy's Cross	5.6	100%
Flatford Mill	10.5	100%	Polloch	1.6	100%
Forsinain 2	2.6	88%	Pumlumon	4.2	100%
Glensaugh	4.1	100%	Strathvaich	1.7	100%
Goonhilly	3.7	100%	Tycanol Wood	3.7	100%
Harwell	10.5	100%	Whiteadder	4.0	100%
High Muffles	6.9	100%	Yarner Wood	4.3	100%

The annual average NO₂ concentrations from 2010-2014 are shown in Figure 10 below that gives an indication of the differing levels at rural locations across the UK. Emissions of nitrogen oxides are generally

from combustion processes including transport. Although the emissions have decreased since 1990, no readily observable decline across the board is seen in the recent year's measurements shown in Figure 10. However, some sites with the higher concentrations do appear to show a slight decline over the 5 years shown e.g. Flatford Mill and Harwell. Figure 11 shows the longer term trends where estimated emisisons are plotted against selected sites in the network.
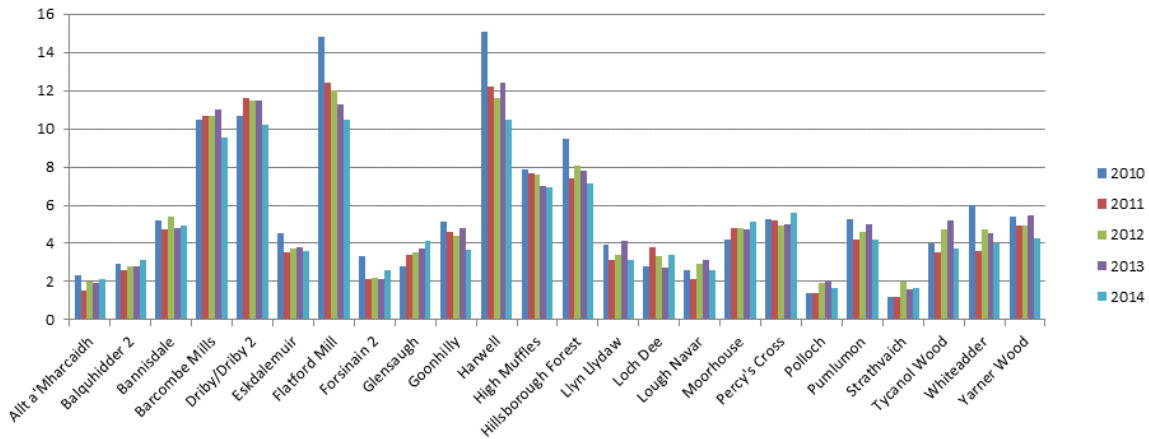

Figure 10 Annual mean NO$_2$ concentration (µg m^{-3}) at the NO$_2$-Net sites 2010-2014
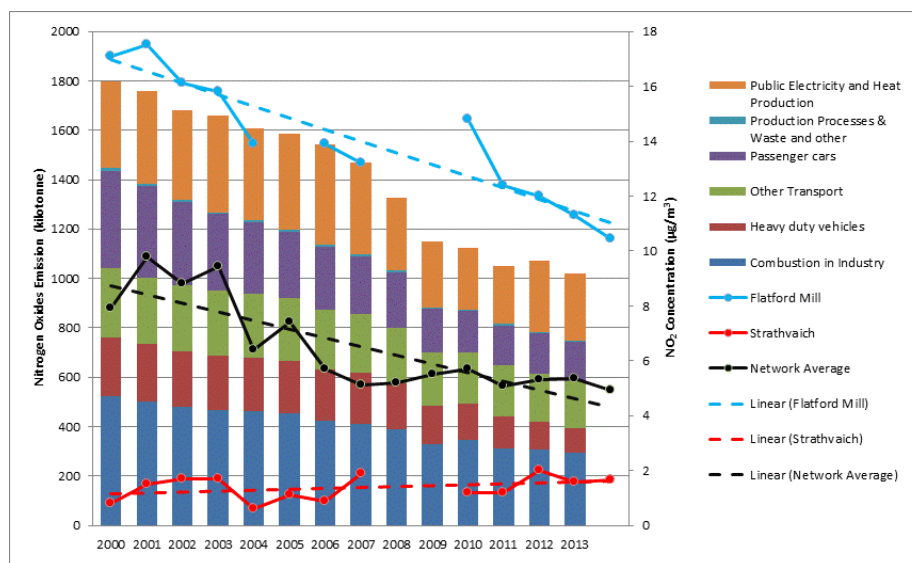

Figure 11 NAEI NOx Emission Estimates and monitored NO$_2$ Concentrations at two UKEAP sites

Figure 11 above displays the emissions estimated by the National Atmospheric Emissions Inventory (NAEI) plotted alongside selected NO$_2$-Net measurements. NO$_2$-Net average concentrations have been plotted (black) along with two other selected sites, providing a comparison between high concentration (Flatford Mill, blue) and low concentration rural site (Strathviach Dam, red). It can be seen from the figure that the estimated emissions from NAEI correlate with concentration reductions for the NO$_2$-Net average and for the more polluted site of Flatford Mill. The same cannot be said of the rural site of Strathviach Dam where little change is observed. This difference may be expected given the different source influencing the sites: Flatford Mill is a southern site closer to London and hence is more influenced by road transport and combustion sources, whereas the Strathviach 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 souces especially in more recent years when the reduction in estimated emissions has slowed slightly.

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, HCl) and aerosols (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, Ca^{2+}, Mg^{2+}) at 30 sites across the UK. Mean annual concentrations of trace gas and aerosols at individual sites in the network are compared in Figure 12 and Figure 13. It is noted that the DELTA methodology assessment once accepted will lead to a correction to the HNO_3 measurements to take into account NO_y positive interferences. These will be detailed in the next annual report and a peer review publication is in preparation. Therefore the HNO_3 concentrations should be taken as an upper value.
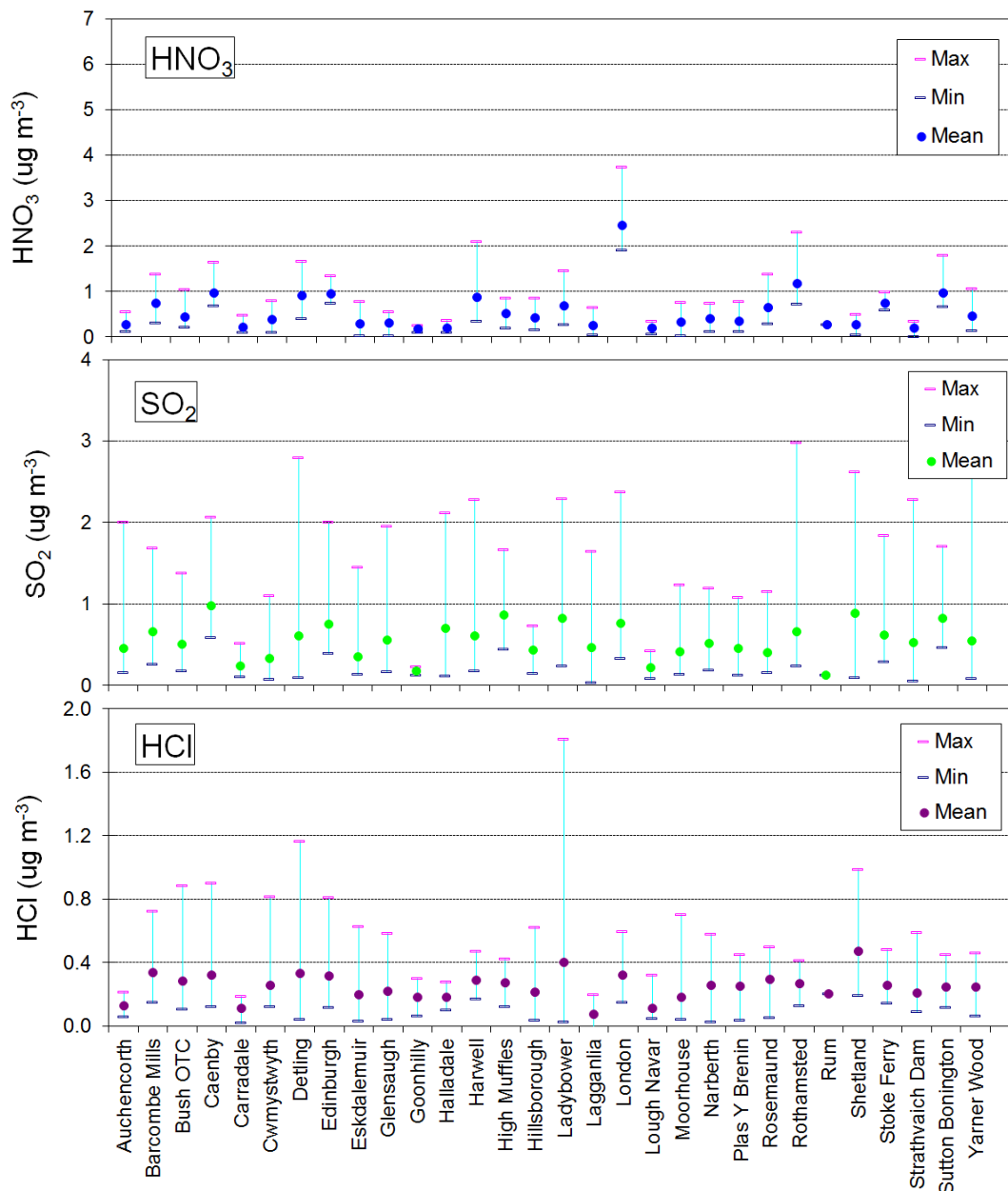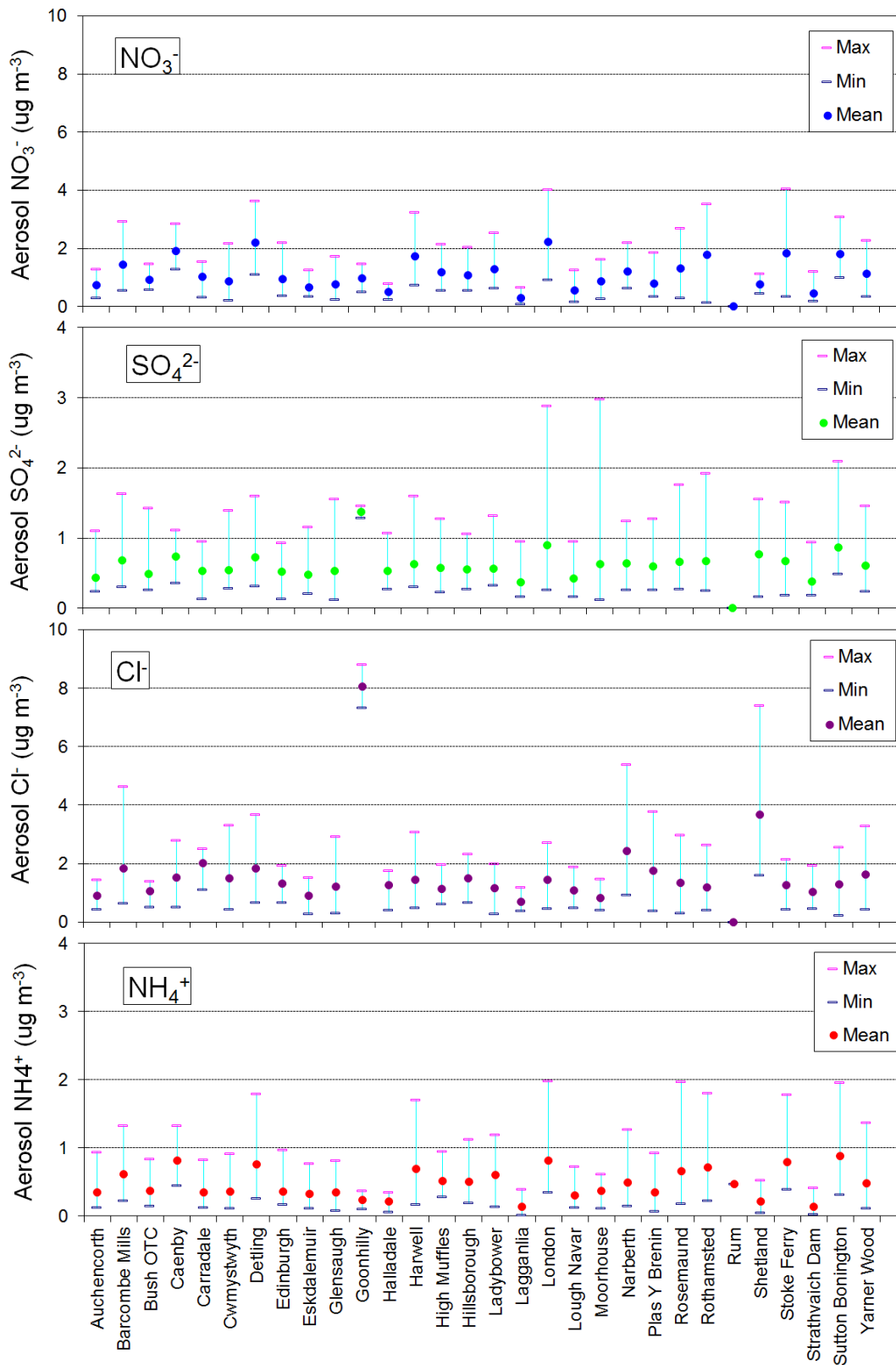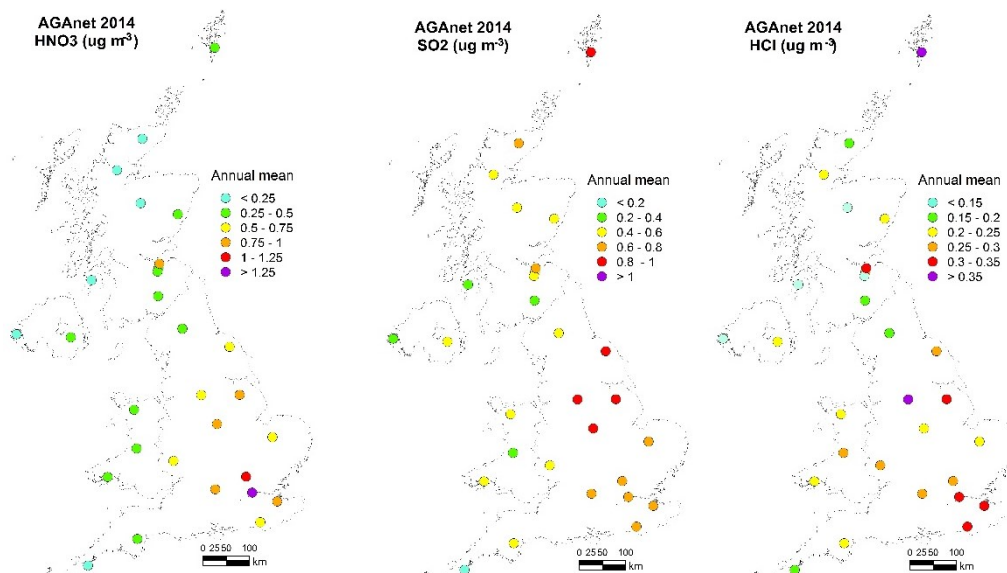

Figure 12: Mean monitored annual concentrations of gaseous HNO_3, SO_2, and HCl at individual sites in AGA-Net. Each data point represents the averaged concentrations of monthly measurements made at each site in 2014, whilst the bars show the minimum and maximum concentrations observed.

9

Figure 13: Mean monitored annual concentrations of particulate NO₃⁻, SO₄²⁻ , Cl⁻ and NH₄⁺ at individual sites in AGANet. Each data point represents the averaged concentrations of monthly measurements made at each site in 2014, whilst the bars show the minimum and maximum concentrations observed.

The main features of the spatial distribution in the pollutants measured in 2014 are shown in the annual maps (Figure 14, Figure 15, Figure 16). 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 30 sites the higher spatial variability in gaseous species can be seen; it should be noted that there will also be seasonal variations.

The largest HNO_3 concentrations were measured in southeast England (e.g. London; 2014 annual mean of = 2.8 µg HNO_3 m^{-3}, range = 1.9 – 3.6 µg HNO_3 m^{-3}), however this will also reflect larger interferences from NO_y in the HNO_3 measurement in the more polluted atmosphere in the southern half of the UK. The lowest HNO_3 concentrations were observed at remote locations away from sources and also where the influence of continental Europe was minimal (e.g. Lough Navar in Northern Ireland; 2013 annual mean = 0.33 µg HNO_3 m^{-3}, range = 0.06 – 0.84 µg HNO_3 m^{-3}). Atmospheric HNO_3 is expected to be more spatially variable than NO_3^- aerosol, but this is not clear from measurements from only 30 sites. The concentrations of base cations (Figure 16) vary greatly depending on the species. The concentration map for Na^+ is similar to that for Cl^-, showing the close coupling between the two species.

Figure 14 Annual mean monitored atmospheric reactive gas concentrations (HNO₃, SO₂, HCl) across the UK from averaged monthly measurements made in 2014. Note: S47 Rum = single measurement in January only (not mapped) and S103 Goonhilly = two measurement data in January and December only only
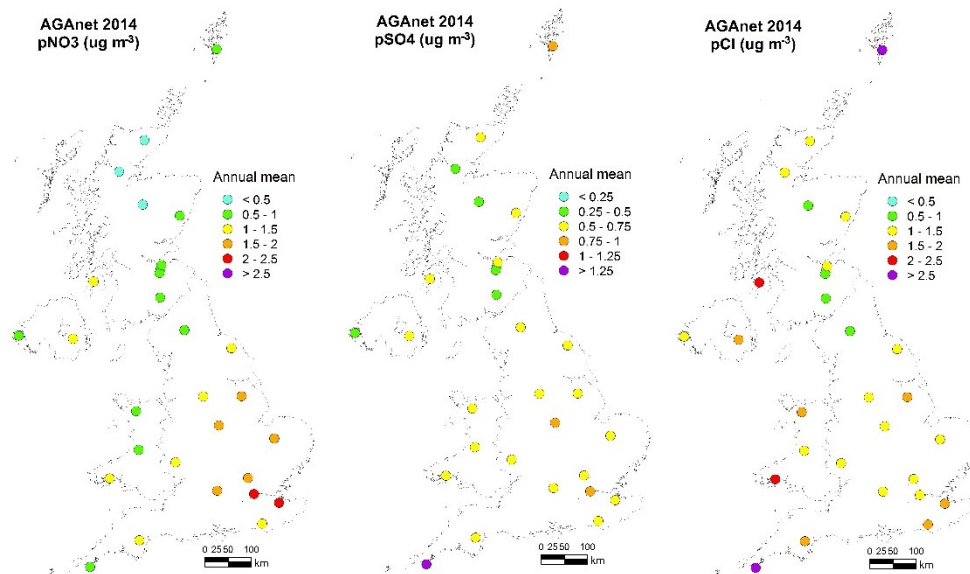
Figure 15: Annual mean monitored atmospheric aerosols (particulate NO$_3^-$, SO$_4^{2-}$, Cl$^-$) concentrations across the UK from averaged monthly measurements made in 2014. Note: S47 Rum site = no particulate data and S103 Goonhilly = two measurement data in January and December only.
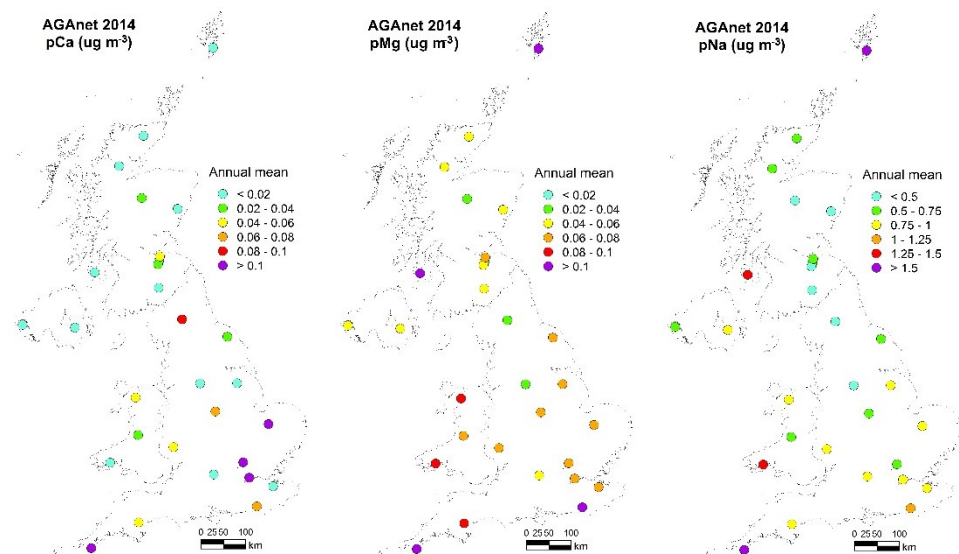
Figure 16: Annual mean monitored atmospheric base cation (Ca^{2+}, Mg^{2+} and Na$^+$) concentrations across the UK from the averaged monthly measurements made in 2014. Note: S47 Rum site = no particulate data and S103 Goonhilly = two measurement data in January and December only.

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$_3$ concentration is 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$_3^-$. However, aerosol NO$_3^-$ is in molar excess over SO$_4^{2-}$ and is even somewhat larger in terms of equivalents of H$^+$. Whilst there is no discernible relationship between particulate Cl$^-$ and NH$_4^+$, there is a near 1:1 relationship between Cl$^-$ and Na$^+$, consistent with a marine origin for these ions in the UK. The high correlations between the aerosol species also indicate the quality of the measurements, since uncertainty in the measurements on a monthly basis would propagate through to scatter in these plots.

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The long-term trends in gaseous HNO_3, SO_2, HCl and particulate NO_3^-, SO_4^{2-}, Cl^-, NH_4^+ (

Figure 17) are shown by plotting annual averages of measurement data from all sites, and also from the original 12 sites for the 15 year period from 2000 to 2014. Data from 1999 were excluded from analysis since the network only started in September 1999. Annual mean concentrations in HCl/Cl^- and NH_3 were higher for the 30 sites than the original 12 sites and this can be explained by 1) addition of new coastal sites, e.g. S103 Goonhilly and S19 Shetland with larger contribution from seasalt, and 2) addition of sites in intensive agricultural areas/high NH_3 emission areas, e.g. S102 Caenby and S44 Hillsborough. Higher HNO_3 concentrations is due to inclusion of 2 urban sites, S36 London and S60 Edinburgh. This therefore highlights very clearly the importance of site selections and maintaining site continuity for assessing long-term trends in data records.

Overall, the dataset shows no detectable trend in HNO_3, NO_3^-, HCl or Cl^-. Gaseous SO_2 concentration on the other hand continues to show a gradual downward trend, in line with UK SO_2 emission trends. The average concentration of SO_2 from AGA-Net decreased by a factor of 3 over the measurement period, from an annual mean of 1.9 μg SO_2 m^{-3} in 2000 to 0.58 μg SO_2 m^{-3} in 2014. The general decreasing trend in gaseous SO_2 concentrations is also accompanied by a smaller decline in particulate SO_4^{2-} concentrations over the same period.

Temporal trends can be seen to be strongly influenced by inter-annual variability and it is necessary to consider the trends in terms of local, regional and national drivers.

In Spring 2003, an episode of elevated concentrations of ammonium nitrate was measured across the UK, impacting on annual mean concentrations for that year. The episode was subsequently attributed to a persistent high pressure system over the UK from February to April resulting in a build-up of emissions from both transboundary and domestic sources (Vieno et al. 2014).

In Autumn 2014, elevated concentrations of SO_2 and HNO_3, as well as particulate SO_4^{2-}, NO_3^- and NH_4^+ occurred in September (Figure 18), coinciding with the Icelandic volcanic eruptions, with back-trajectories showing air mass moving across most of the UK at that time. By contrast, HCl (from local combustion sources such coal burning) and particulate Cl^- (mainly of marine origin) were not affected by the pollution event. Ammonia concentrations were also not affected from an analysis of NH_3 data from the same 30 AGA-Net sites.
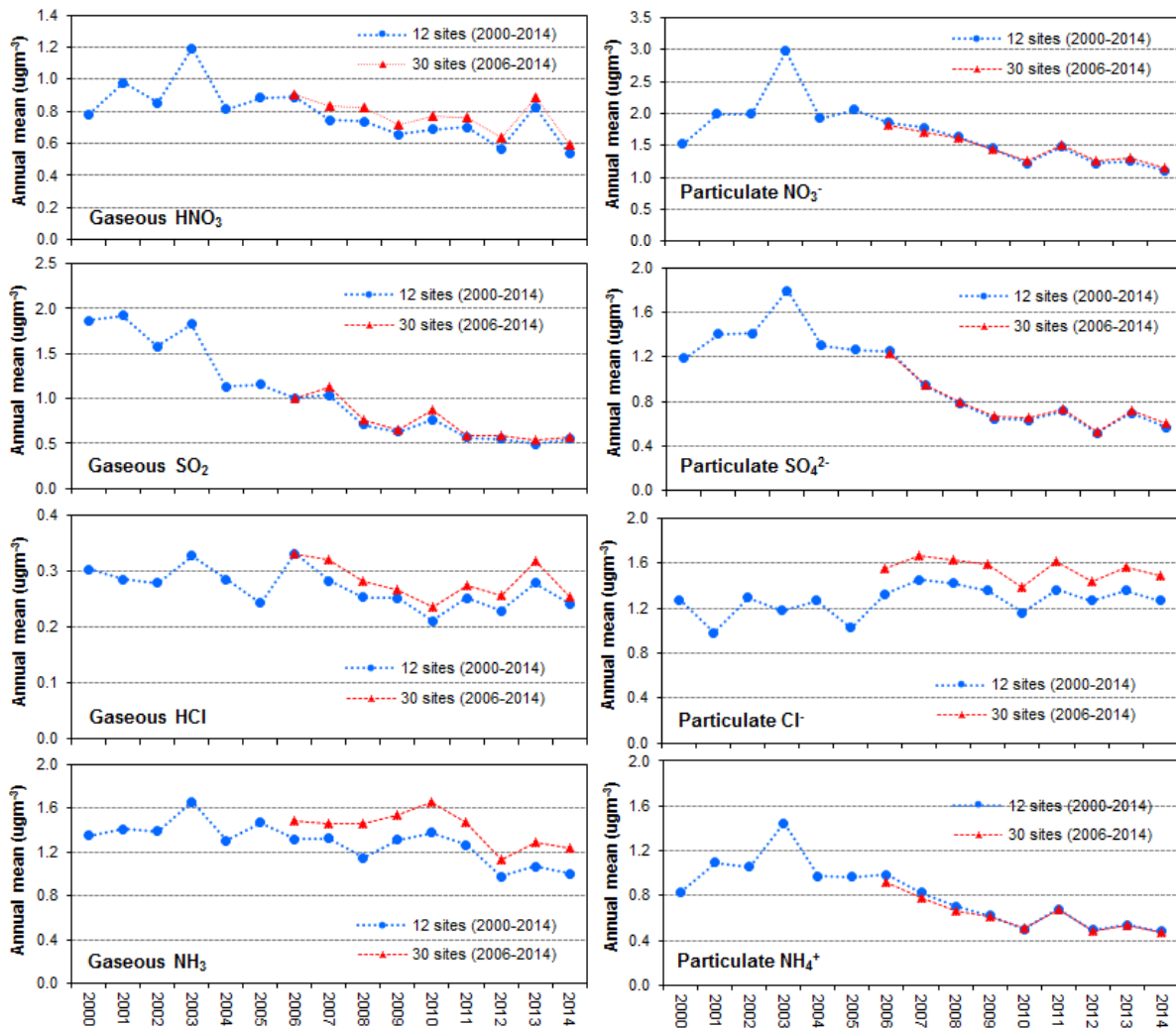
Figure 17: Long-term trend in annual mean concentrations of gases and aerosols monitored in the AGA-Net network. Each data point represents the averaged annual mean from all sites (increased from 12 to 30 sites since Jan 2006) and also the original l2 monitoring sites in the network. NAMN ammonia gas data forAGANet sites are also shown, for comparison.

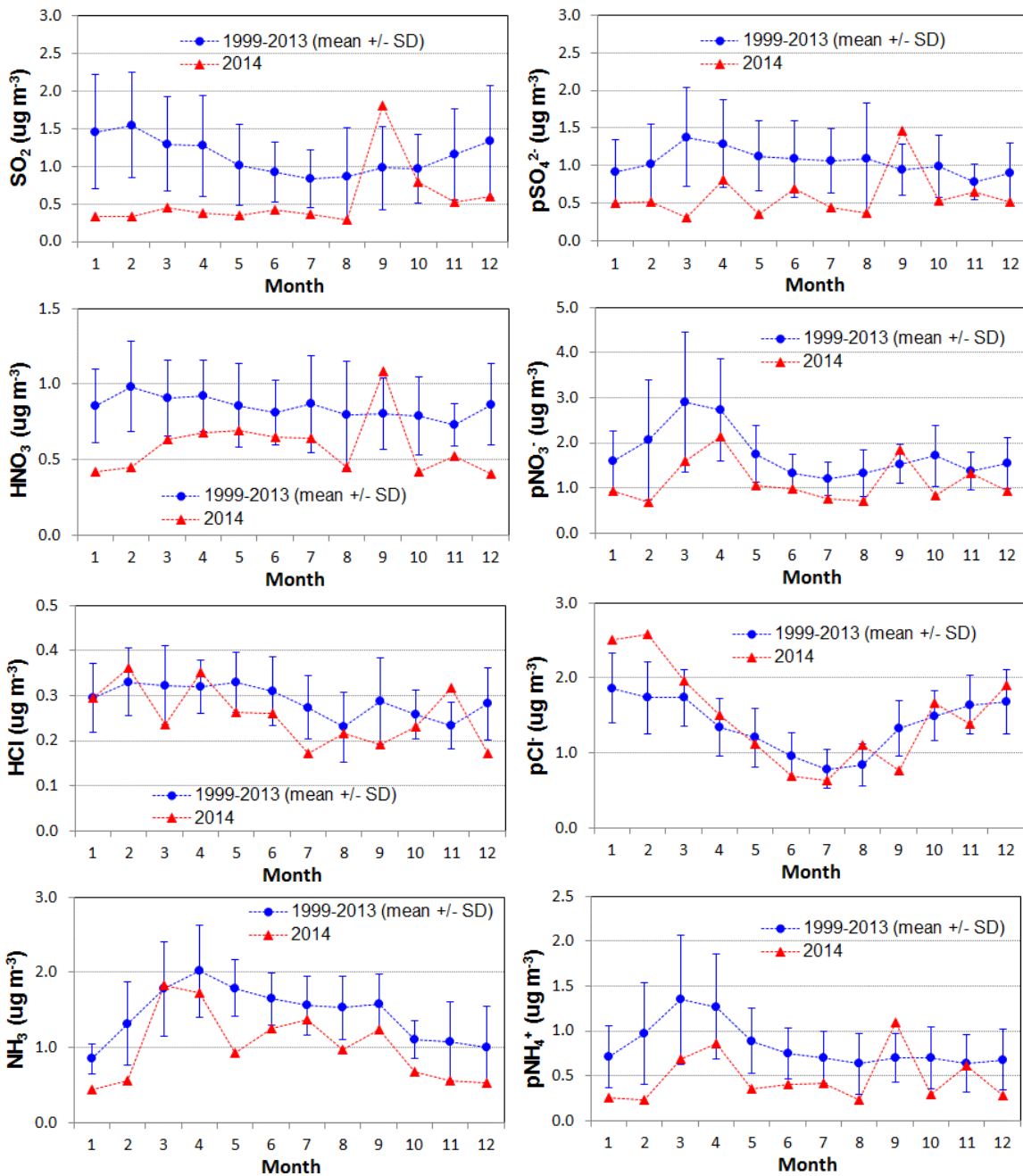**Figure 18: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (1999-2013: mean +/- SD) against year 2014. For all component (except NH₃, HCl and Cl⁻), large peaks in concentrations were observed in September which deviated from the recorded trends to date. NAMN NH₃ data are also shown for the same 30 AGANet sites to complete the picture.**

2.2 National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly speciated measurements of atmospheric NH_3 in 2014 was 85, summarised in Table 2. Particulate NH_4^+, a secondary product is spatially less variable and is monitored at a subset of 30 sites that are part of AGANet reported above. Data capture and the percentage of samples passing the main QC criteria in NAMN provide an indication of network performance and are summarised in the Appendix.

The average NH_3 concentrations observed at each of the sites in 2014 are shown in Figure 19, along with the range of monthly values. The graphs are all plotted on the same scale, to allow a direct comparison of ammonia concentrations between sites to be made. The 2014 NAMN results continue to illustrate the high spatial variability in NH_3 concentration and the seasonal variability of ammonia concentrations reflecting the large regional variability in NH_3 emissions.

Table 2 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2014

Site Type	Number
DELTA sites sampling gaseous NH_3	56
AGANet DELTA sites (sampling gaseous NH_3, HNO_3, SO_2, HCl & aerosol NH4+, NO_3^-, SO_4^2, Cl^-, Na^+, Ca^{2+}, Mg^{2+})	30
ALPHA sites sampling gaseous NH_3 only	48
Intercomparison sites with both DELTA & ALPHA	9
Total number of sites	85

NH_3 concentration data from NAMN over the period 1998 to 2014 is summarised in a box plot (Figure 20). 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 18% 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.
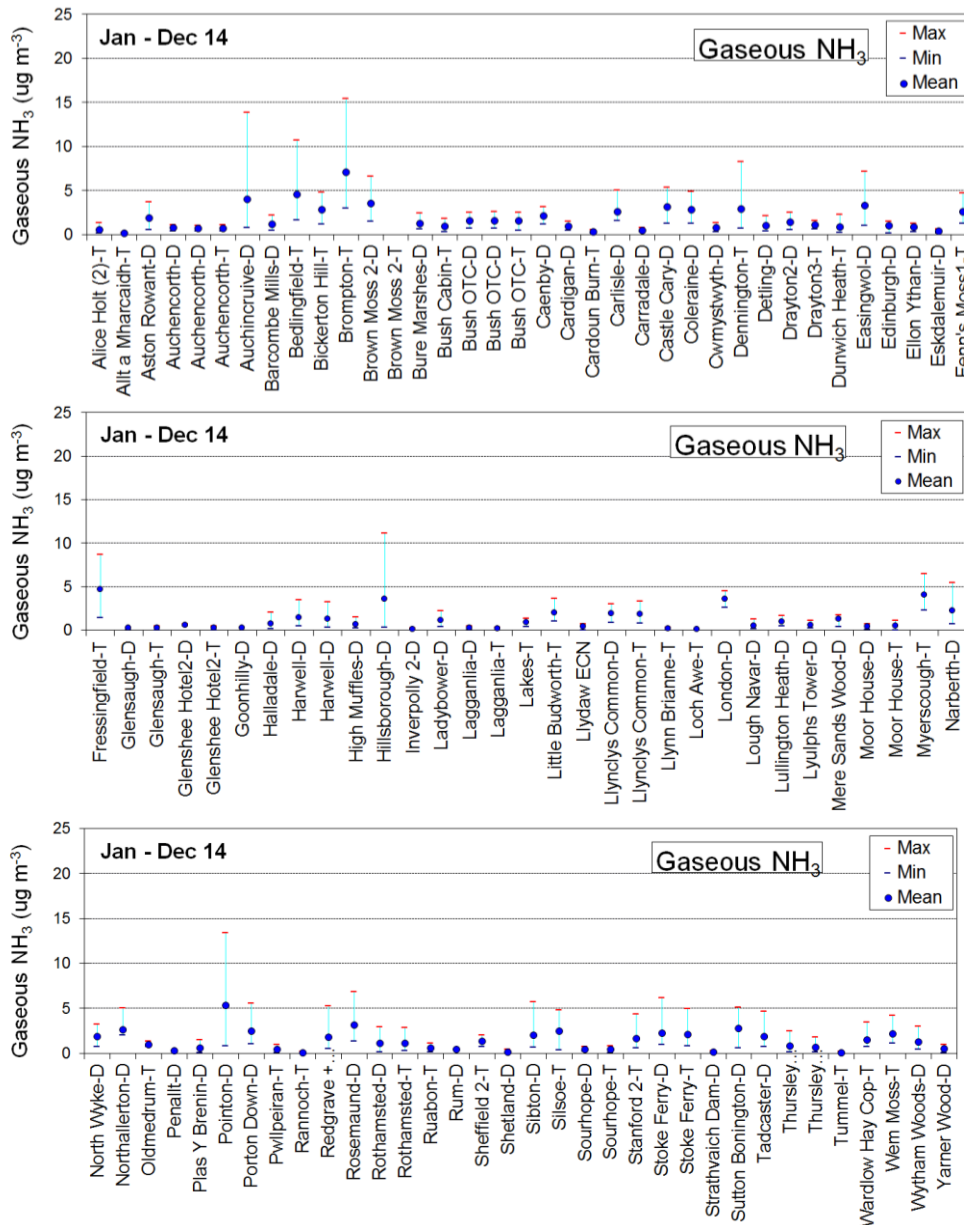
Figure 19: Annual mean monitored concentrations of gaseous NH₃ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2014, whilst the bars show the minimum and maximum concentrations observed.
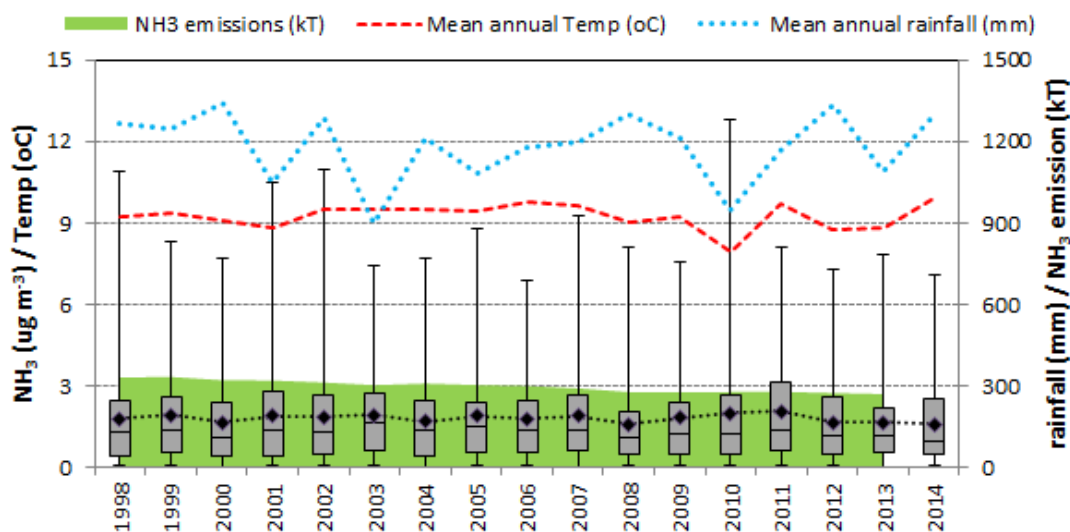
Figure 20: Changes in atmospheric NH₃ averaged over all sites in NAMN operational between 1998 and 2014 summarised in a box plot (sites with short runs excluded). The whiskers shows the absolute max and min and the diamonds is the mean annual concentration. Annual mean UK meteorological data (source http://www.metoffice.gov.uk/) are plotted ontop to illustrate the relationship between inter-annual variability in NH₃ concentrations with changing temperature and rainfall. UK annual NH₃ emissions (source http://naei.defra.gov.uk/) declined by 18 % over this period.

The DELTA sites are distributed widely across the UK to provide the regional patterns of NH_3 (and NH_4^+ at the 30 AGAnet sites), while complementary passive sampling with ALPHA samplers is used to assess meso-scale variability of NH_3 in source areas as a test of the NH_3 emission-dispersion modelling. National maps of both NH_3 and NH_4^+ (Figure 21) concentrations derived from the NAMN confirm the high spatial variability of NH_3 (0.07 – 7.1 µg NH_3 m⁻³), consistent with it being a primary pollutant emitted from ground-level sources.

For particulate NH_4^+, the annual mean concentrations ranged from the lowest of 0.13 (S41 Lagganlia) to highest of 0.88 (S40 Sutton Bonington) µg NH_4^+ m⁻³. Aerosol NH_4^+ shows a spatially smooth concentration field as expected for an secondary inorganic component. It also has a similar distribution to the sulphate and nitrate aerosol UK maps (Figures 13 and 14), as would be expected due to the formation of stable and semi-stable particle phase salts, e.g. ammonium sulphate and ammonium nitrate, respectively.
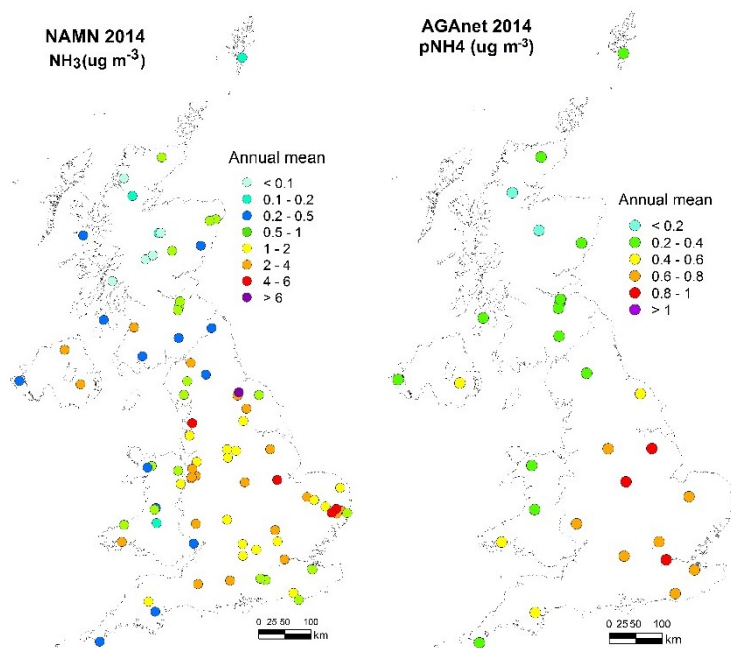
Figure 21: Spatial patterns of annual NH₃ and aerosol NH₄⁺ concentrations from monthly NAMN/AGAnet measurements. Since Sep 2009, ammonium is measured at the 30 AGANet sites only.

The regression between NH₃ 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 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 NH₃ dry deposition.

3. UK EMEP Supersites 2014 measurement overview

Harwell and Auchencorth Moss have operated as atmospheric observatories for long term measurements since the twentieth century and became EMEP Supersites in 2006. 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 2014 s are summarised in Table 3.

Both EMEP Supersites are rural sites. The sites provide the **required coverage**, of at least once station every 100,000 km^2, to determine the composition of PM$_{2.5}$ at rural background locations as required under [Annex IV](#) of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe. The chemical composition of PM$_{2.5}$ is determined for the following species:

- Elemental carbon (EC) and organic carbon (OC), from the UK Particle Concentrations and Numbers Monitoring Network.
- Inorganic species (K$^+$, Na$^+$, NH$_4^+$, Ca^{2+}, Mg^{2+}, Cl$^-$, NO$_3^-$, SO$_4^{2-}$), from the MARGA instrument.

The PM$_{2.5}$ time coverage at both EMEP Supersites exceeds the *minimum* time coverage (14%) specified in the Directive for indicative PM$_{2.5}$ measurements and in some cases meets the minimum threshold for fixed PM$_{2.5}$ measurements (90%). The high resolution data is sufficient to allow comparison with atmospheric models and back-trajectory source apportionment.

Auchencorth and Harwell 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 DefraThis report summarises the measurements made between January and December 2014. The statistics reported on UK-AIR are those reported to the Commissin 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): **Harwell 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$_4^{2-}$), **Harwell and Auchencorth Moss.**
- On line mercury measurements (Harwell: elemental mercury; Auchencorth Moss: elemental and speciated mercury).

Table 3 Pollutants measured at the UK EMEP Supersites during 2014

Pollutant	Ha[1]	Au[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-AEA**
$PM_{2.5}$ K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**	**CEH/Ricardo-AEA**
PM_{10} K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-} (MARGA)	**X**	**X**	**II**	**Hourly**	**UKEAP**	**CEH/Ricardo-AEA**
Elemental mercury	**X**	**X**	**I**	**Hourly**	**UKEAP**	**CEH/Ricardo-AEA**
Total gaseous mercury in air	**X**		**II**	**Hourly**	**UKEAP**	**CEH/Ricardo-AEA**
Meteorological parameters (WS, WD, T, RH, rainfall)	**X**	**X[2]**	**I**	**Hourly**	**UKEAP/CEH**	**CEH/Ricardo-AEA**
Precipitation chemistry	**X**	**X**	**I**	**Daily**	**UKEAP**	**CEH/Ricardo-AEA**
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-AEA
PAH in PM_{10}, air and rain	X	X	I	Monthly	PAH	NPL*
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	Rural metals	CEH
Mercury in precipitation	X	X		Monthly	Rural metals	CEH
Heavy metals in PM_{10}	X	X	II	Weekly	Rural 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]	

[1]Ha: Harwell; Au: Auchencorth Moss; [2]NERC CEH National capability funded * NPL: National Physical Laboratory, Teddington, Middlesex.

During 2014, in addition to the normal operations, the Auchencorth Moss supersite hosted other short-term experiments and measurements. Activities and outputs are summarised on the Auchencorth Moss website. In 2014 more than 17 research outputs (papers or presentations) have been identified.

Table 4 Summary of other atmospheric measurements at Auchencorth Moss Supersite in 2014

Measurements	Reason	Contact	Status of work
EMEP Intensive PM analysis	EMEP intensive study period	Christine Braban	Draft report submitted to Defra; EMEP report published: (Fagerli et al., 2014)
PTR measurements of isoprene	NERC Sandwich student biogenic VOCs study	Ben Langford	Placement report http://nora.nerc.ac.uk/505862/
Chamber flux measurement of N_2O and methane	EU FP7 research project (ECLAIRE)	Eiko Nemitz	In progress.

3.1 Auchencorth

There were no significant operational issues in 2014 with the MARGA. Table 5 show the 2014 annual mean and % data capture for the PM10, PM2.5, and trace gas species, respectively, measured by the Auchencorth Moss MARGA. The statistics presented are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2014 Auchencorth Moss MARGA measurements (major species and trace gases) are shown in Figure 22, Figure 23 and Figure 24.

Table 5 Annual summary of trace gas mass concentration from the Auchencorth EMEP Supersite, 2014.

Trace gas	Annual mean (μg m^{-3})	Data capture (%)
NH$_3$	1.17	84
HCl	0.18	83
HNO$_3$	0.13	84
HNO$_2$	0.13	84
SO$_2$	0.42	84
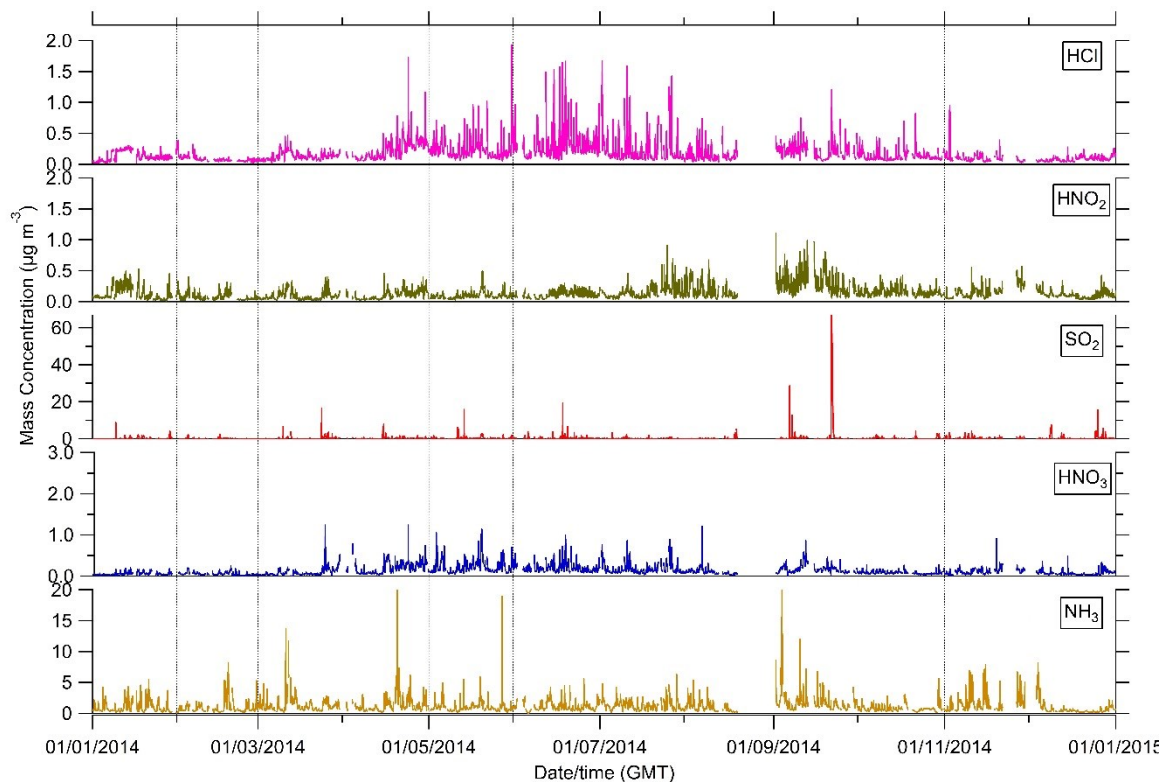
Figure 22 Ratified gas measurements from the MARGA instrument at Auchencorth Moss for 2014.

Table 6 Annual summary of the speciated PM₁₀ mass concentration from the Auchencorth EMEP Supersite, 2014

Ion (PM$_{10}$)	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	0.74	76
Na^+	0.57	79
K^+	0.04	79
Ca^{2+}	0.05	79
Mg^{2+}	0.07	79
Cl^-	1.07	80
NO_3^-	1.28	80
SO_4^{2-}	1.27	80
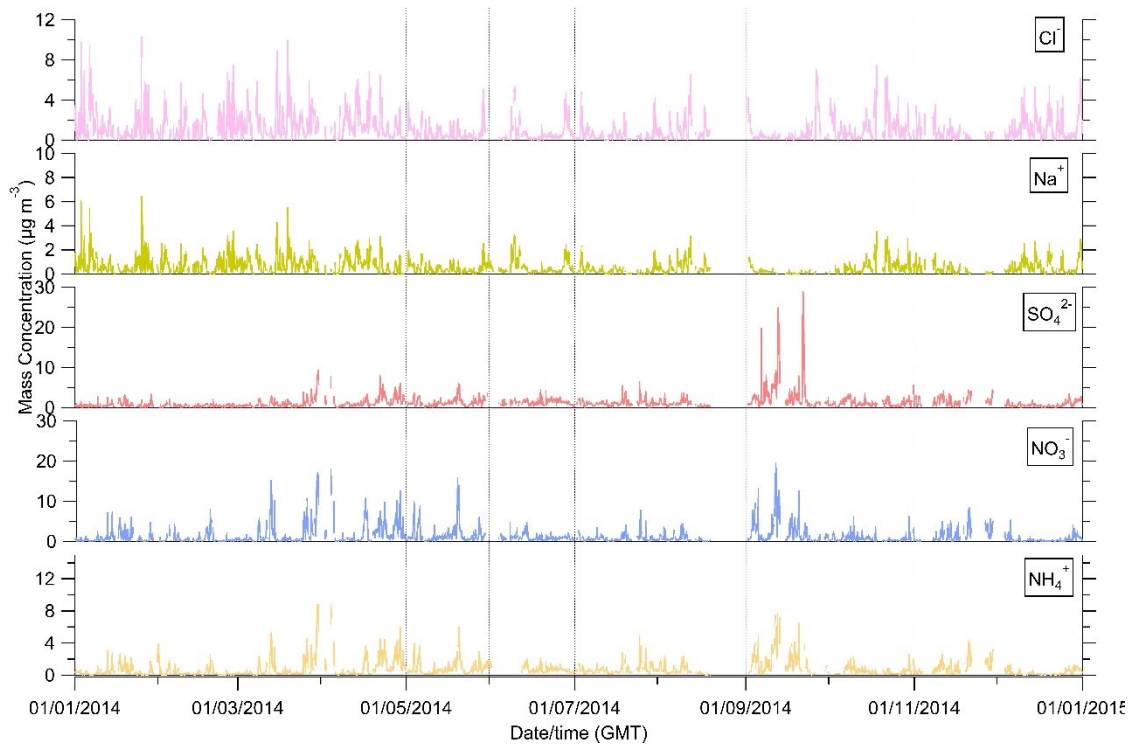
Figure 23 Ratified PM₁₀ measurements from the MARGA instrument at Auchencorth Moss for 2014.

Table 7 Annual summary of the speciated PM$_{2.5}$ mass concentration from the Auchencorth EMEP Supersite, 2014

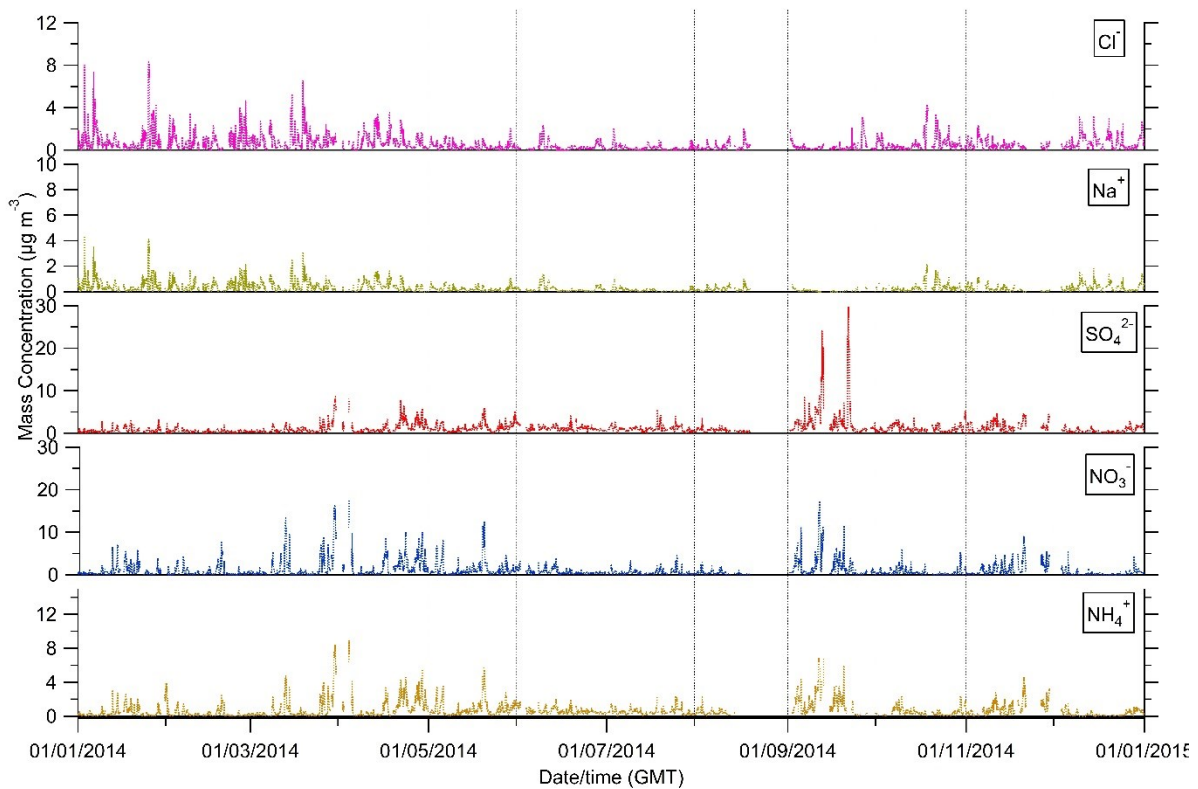| Ion (PM$_{2.5}$)	Annual mean (µg m^{-3})	Data capture (%)
NH$_4^+$	0.68	78
Na$^+$	0.30	79
K$^+$	0.02	79
Ca^{2+}	0.02	79
Mg^{2+}	0.07	79
Cl$^-$	0.58	83
NO$_3^-$	1.05	83
SO$_4^{2-}$	1.16	83

Figure 24 Ratified PM$_{2.5}$ measurements from the MARGA instrument at Auchencorth Moss for 2014.

Mercury measurements

There were no significant operational issues in 2014 with the gaseous elemental mercury measurement. The Tekran speciation unit required repair at the manufacturers leading to a lower data capture. Table 8 shows the 2014 annual mean and % data capture for the gaseous elemental mercury, particulate bound mercury and gaseous oxidized mercury respectively. The statistics presented are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2014 Auchencorth Moss measurements are shown in Figure 25.

Table 8 Auchencorth mercury measurements 2014 data statistics

	Annual mean	Data capture
Gaseous elemental mercury	1.3859 n.m^{-3}	90.95%
Particulate bound mercury (PM$_{2.5}$)	2.2821 pg.m^{-3}	26.31%
Gaseous oxidised mercury	0.8496 pg.m^{-3}	26.31%
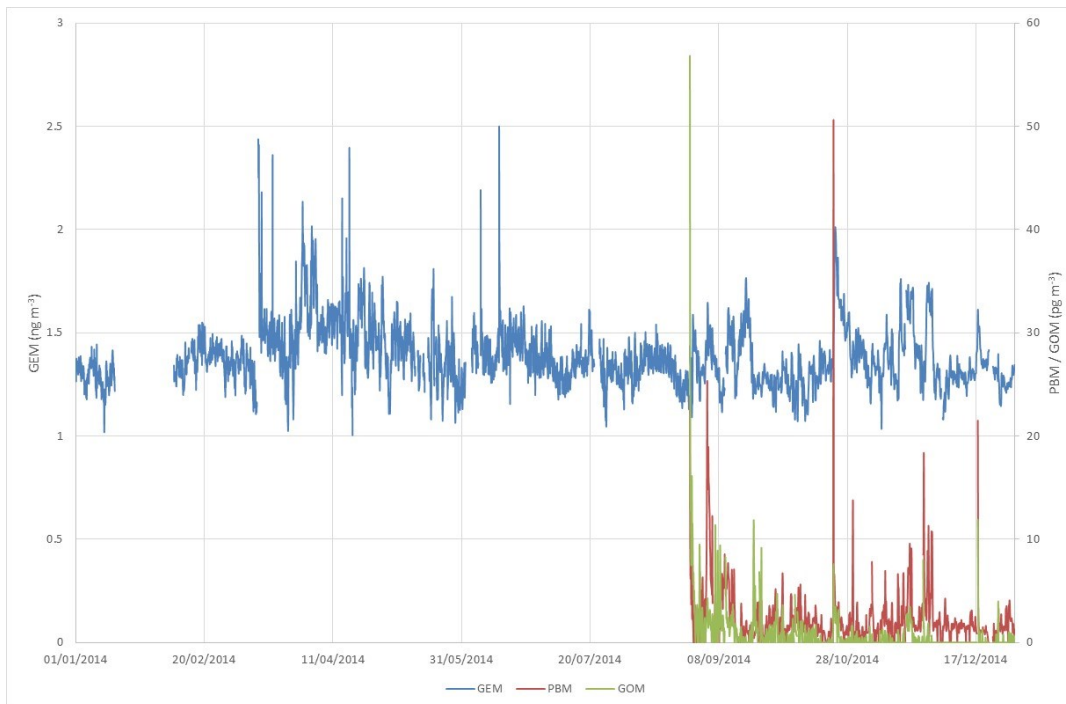
Figure 25 Auchencorth Moss 2014 gaseous elemental mercury (GEM), particulate bound mercury (PBM) and gaesous oxidised mercury (GOM).

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3.2 Harwell

Annual mean concentrations of trace gas and aerosol measuremet are summarised in Table 9, Table 10, Table 11, detailing the annual mean and % data capture for the PM_{10}, $PM_{2.5}$, and trace gas species, respectively, measured by the Harwell MARGA. Overall <10% of the measurement data was lost due to intermittent blockages and operational issues and there were no significant operational issues in 2014. The statistics presented are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2014 Harwell MARGA measurements (major species and trace gases) are shown in Figure 26, Figure 27, and Figure 28 below.

Table 9 Annual summary of trace gas mass concentration from the Harwell EMEP Supersite, 2014.

Trace gas	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_3	1.96	90
HCl	0.03	94
HNO_3	0.16	95
HNO_2	0.46	95
SO_2	0.24	94
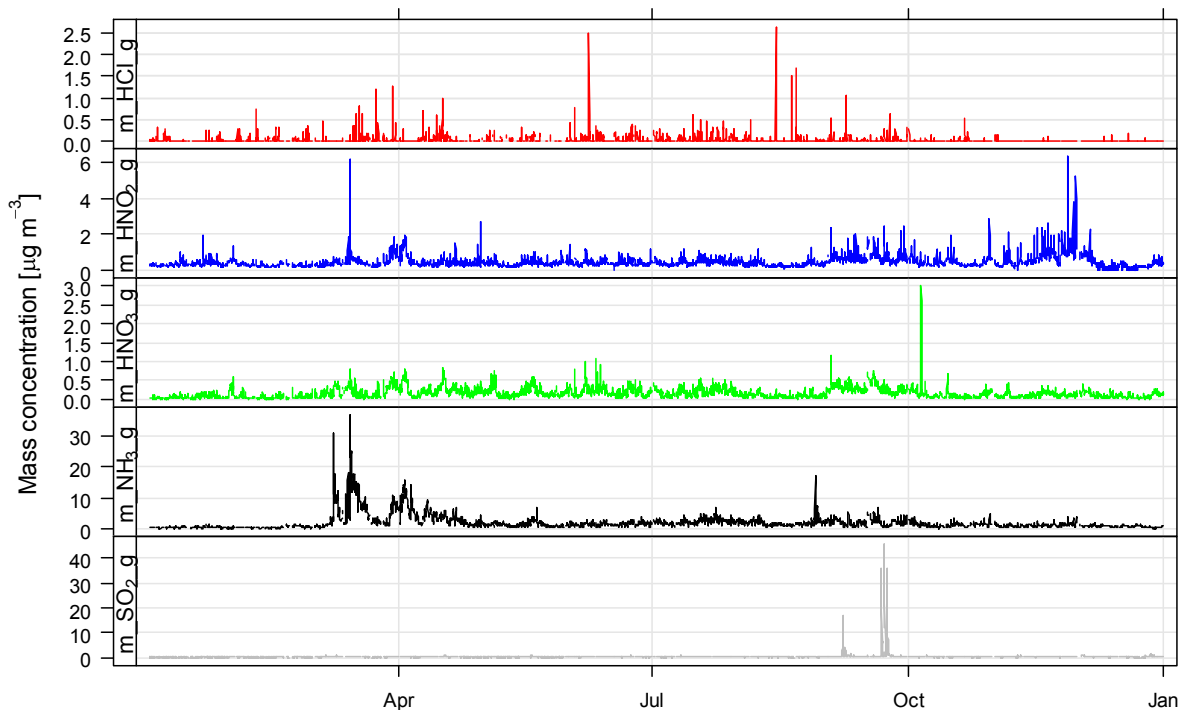
Figure 26 Time series plot of the trace gas (HCl, HNO_2, HNO_3, NH_3, SO_2) measurments from the Harwell MARGA, 2014.

Table 10 Annual summary of the speciated PM$_{10}$ mass concentration from the Harwell EMEP Supersite, 2014.

Ion (PM$_{10}$)	Annual mean (μg m^{-3})	Data capture (%)
NH$_4^+$	1.31	90
Na$^+$	0.71	90
K$^+$	0.06	89
Ca^{2+}	0.15	89
Mg^{2+}	0.12	90
Cl$^-$	1.05	90
NO$_3^-$	2.97	90
SO$_4^{2-}$	2.02	90
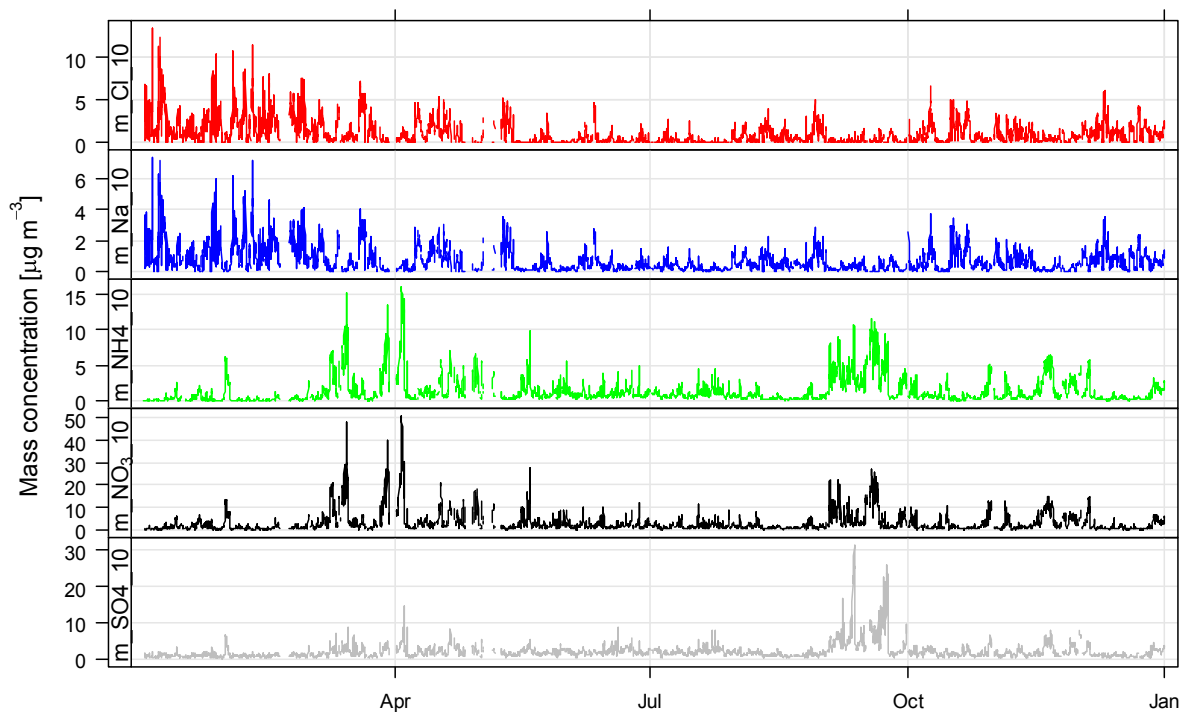
Figure 27 Time series plot of the major PM$_{10}$ species (Cl$^-$, Na$^+$, NH$_4^+$, NO$_3$-, and SO$_4^{2-}$) measurments from the Harwell MARGA, 2014. Base cation species (Ca^{2+}, Mg^{2+} and K$^+$) measurements not shown.

Table 11 Annual summary of the speciated PM$_{2.5}$ mass concentration from the Harwell EMEP Supersite, 2014.

Ion (PM$_{2.5}$)	Annual mean (µg m^{-3})	Data capture (%)
NH$_4^+$	1.25	94
Na$^+$	0.40	94
K$^+$	0.04	94
Ca^{2+}	0.05	94
Mg^{2+}	0.08	94
Cl$^-$	0.56	94
NO$_3^-$	2.62	94
SO$_4^{2-}$	1.87	94
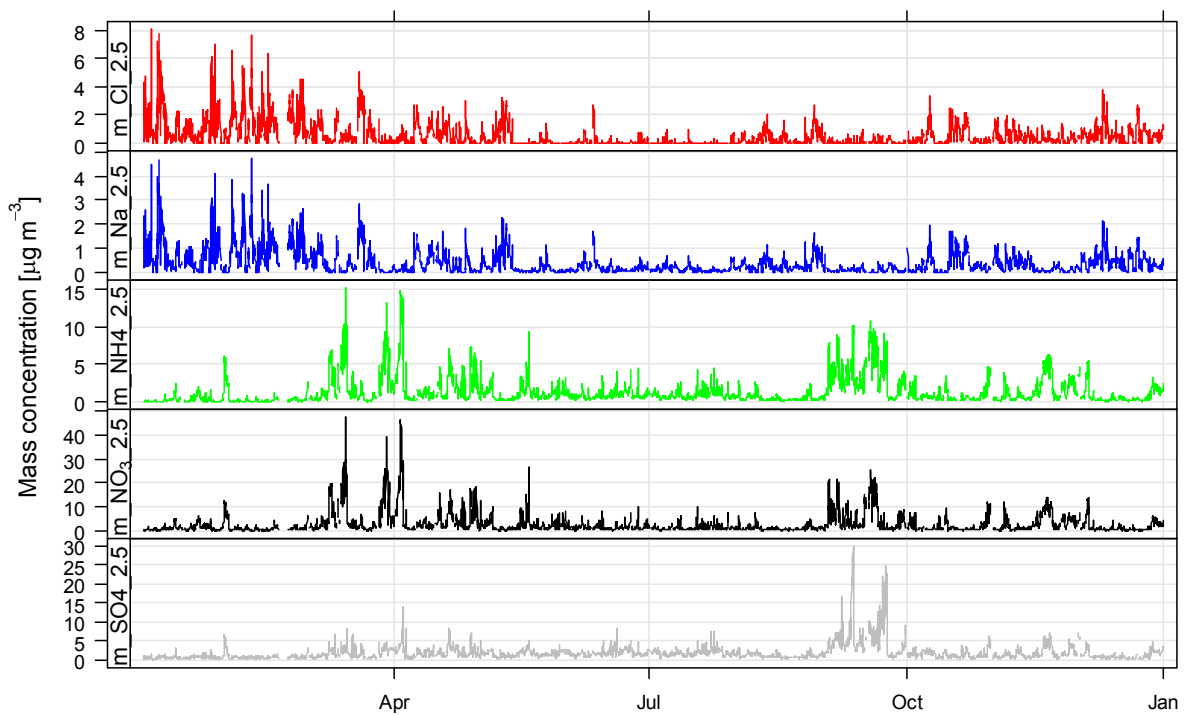
Figure 28 Time series plot of the major PM$_{2.5}$ species (Cl$^-$, Na$^+$, NH$_4^+$, NO3$^-$, and SO$_4^{2-}$) measurments from the Harwell MARGA, 2014. Base cation species (Ca^{2+}, Mg^{2+} and K$^+$) measurements not shown.

Typical meteorological parameters are measured at the Harwell EMEP Supersite. The 2014 annual means and data captures are summarised in Table 12. Data capture for the parameters measured was typically above 97% except for dewpoint which had a slightly lower data capture of 90%.

Table 12 2014 Summary of the Harwell EMEP Supersite meteorological observations

Meteorological parameter	Annual mean	Data capture (%)
Barometric pressure (mbar)	996	100%
Dewpoint (°C)	9	90%
Wind direction (°)	145	100%
Wind speed (m s-1)	3	100%
Relative humidity (%)	82	97%
Temperature (°C)	11	100%
Meteorological parameter	Total	Data capture (%)
Rainfall (mm)	856	100%

Mast measurements of the 10 m wind speed (U10) and directional frequency were performed at the Harwell EMEP Supersite during 2014. Figure 29 shows a plot of the directional frequency (in 10° sectors) for 2014. The Figure shows that the air masses arriving at the Harwell EMEP Supersite predominantly originated from the south and south-east and were therefore dominated by European air masses. The southerly and south-easterly winds were typically of the order of 2 to 5 m s^{-1}, which is consistent with the annual mean presented in Figure 29, and maximums of up to 13 m s^{-1}. Figure 30 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, east and north-west. One notable feature of the monthly summary plots was that in the winter month's (November, December, January) winds speeds were higher, with light south easterly winds dominant in the summer months (May, June, July).
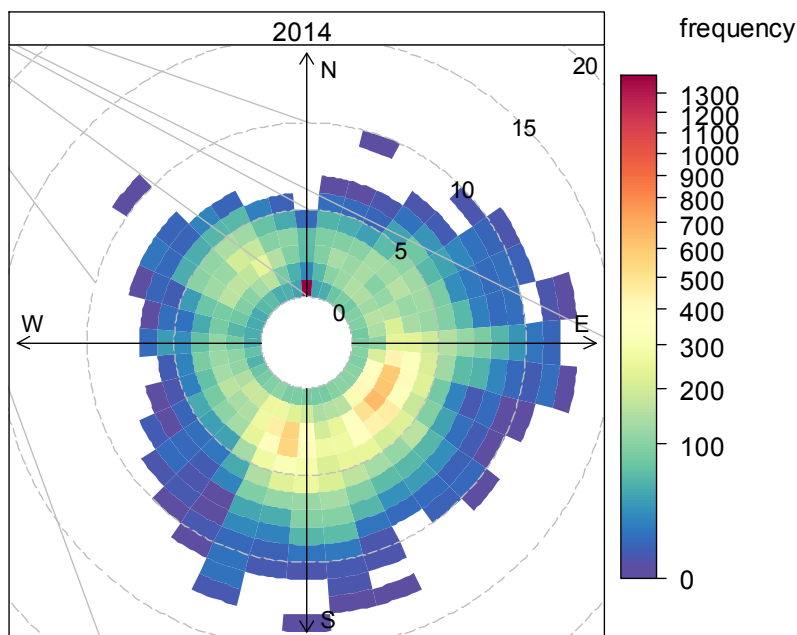
Figure 29 Wind speed (m s^{-1}) and directional frequency for the Harwell EMEP Supersite, 2014.
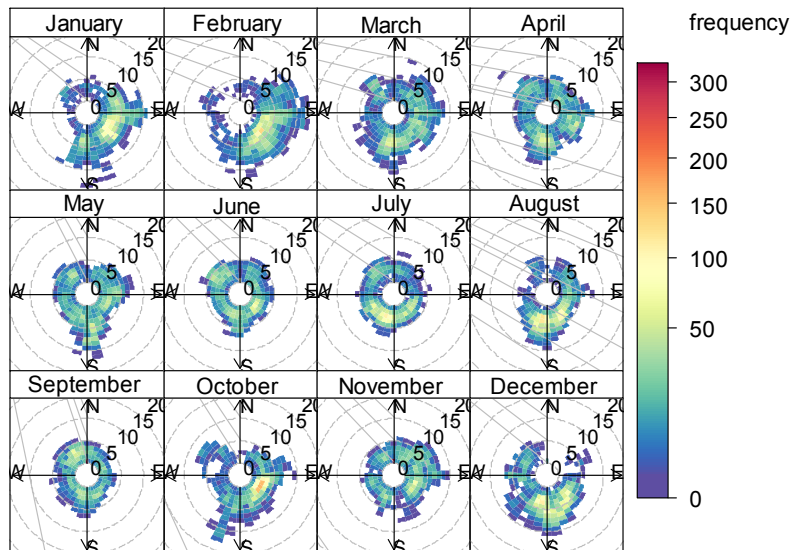
Figure 30 Monthly variations of hourly wind speed and directional frequency for the Harwell EMEP Supersite, 2014.

Mercury measurements

There were some operational issues in 2014 with the Tekran total gaseous mercury measurement. The Tekran speciation unit required repair by CEH at the CEH laboratories, leading to a lower data capture. Table 13 shows the 2014 annual mean and % data capture for the measurements. The statistics presented are based on the ratified measurements supplied to UK-AIR. The time series plot of the 2014 data is shown in Figure 31.

Table 13 Harwell mercury measurements 2014 data statistics

	Annual mean	Data capture
total gaseous mercury	1.4419 ng.m^{-3}	54.68%
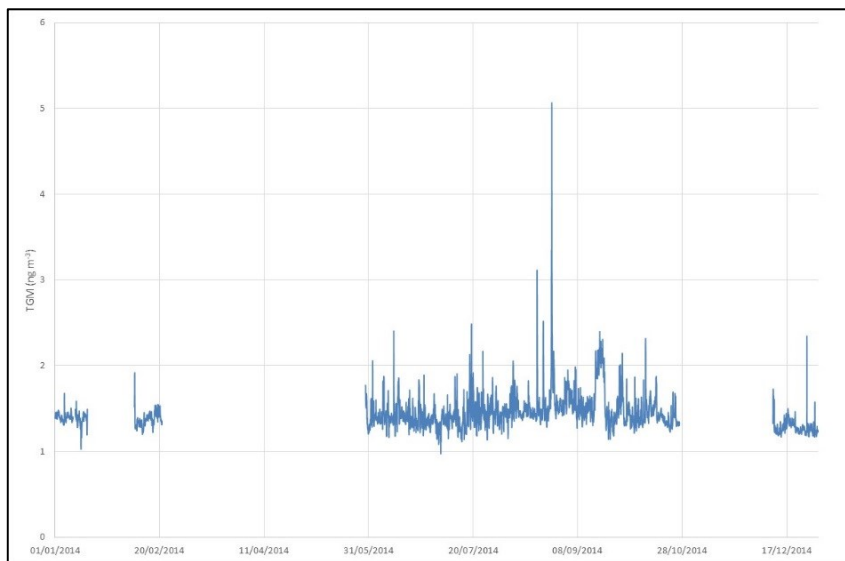
Figure 31 Harwell 2014 total gaseous mercury time series.

4. UKEAP Air Quality Case studies 2014

4.1 Spring 2014 Elevated levels of PM event:

Headline: Supersites observe detailed PM composition during air quality episodes

In March 2014, the media reported widely on a Saharan dust event which was resulting in a marked increase in PM in the UK (e.g. the BBC[1], the Guardian[2], and the Daily Mail[3]). The two UK supersites were able to give a fast response to the pollution event and identify that in fact the event was mainly driven by ammonium nitrate for most of the pollution period. A modelling study used the supersite measurements to verify that elevated PM were anthropogenic in origin and much was produced outside of the UK (Vieno *submitted*). The contribution of Saharan dust was demonstrated by a combination of modelling and measurements from the EMEP supersites to have been restricted to the latter part of the reported pollution event and only relevant to the south of the UK. Figure 32 is a demonstration of the supersite measurements vs modelling by EMEP4UK (Vieno *et al*. 2014) during the pollution event. The importance of having a fast online response looking at composition of PM, is clear as some chemical transport models did not apportion the composition correctly in their forecast, hence the details were not clear[2]. This has implications for policy in addressing PM events, where Saharan sand being 'natural' cannot be addressed by policy but NH_4NO_3 can, as the major sources are anthropogenic in nature.
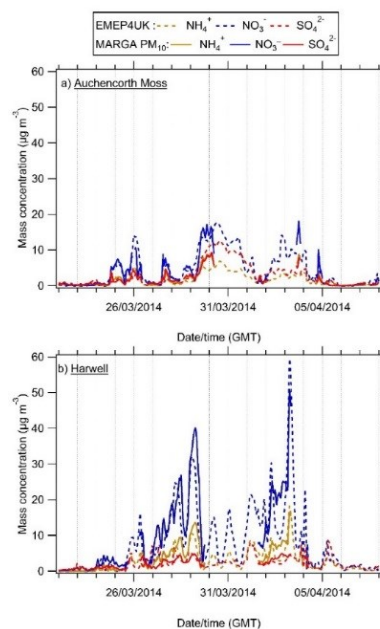
Figure 32 Hourly means calculated by the EMEP4UK model (dashed lines) and measured by the MARGA instruments (solid lines) at Auchencorth Moss (top) and Harwell (bottom) for the major secondary inorganic components of PM_{10}: NH_4^+ orange lines, NO_3^- blue lines and SO_4^{2-} red lines.

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[1] http://www.bbc.co.uk/news/uk-26844425
[2] http://www.theguardian.com/uk-news/2014/apr/01/london-smog-saharan-dust-storms-downing-street
[3] http://www.dailymail.co.uk/wires/ap/article-2594987/Sahara-desert-dust-brings-smog-Britain.html

4.2 Autumn 2014 Bárðarbunga volcanic plume observations:

Headline: UKEAP Supersites and Networks observe UK atmospheric perturbations

The recent eruption within the Bárðarbunga volcanic system in Iceland (August 2014- February 2015) was the largest Icelandic eruption in terms of erupted magma and gas volume since the 1783-1784 CE Laki event. Periodically the UK experienced episodes of elevated SO_2 as a direct result of volcanic activities. Observations from the EMEP supersites in the UK not only experienced elevated SO_2 but elevated sulfate too periodically during the period. The largest observed event was from the 21/09/14 to 23/09/14 Figure 33 where elevated PM surface concentrations, measured by the AURN network were observed. The MARGA instruments from the two EMEP supersites were able to explain the elevation to be due to sulfate PM found in the plume from Bárðarbunga.
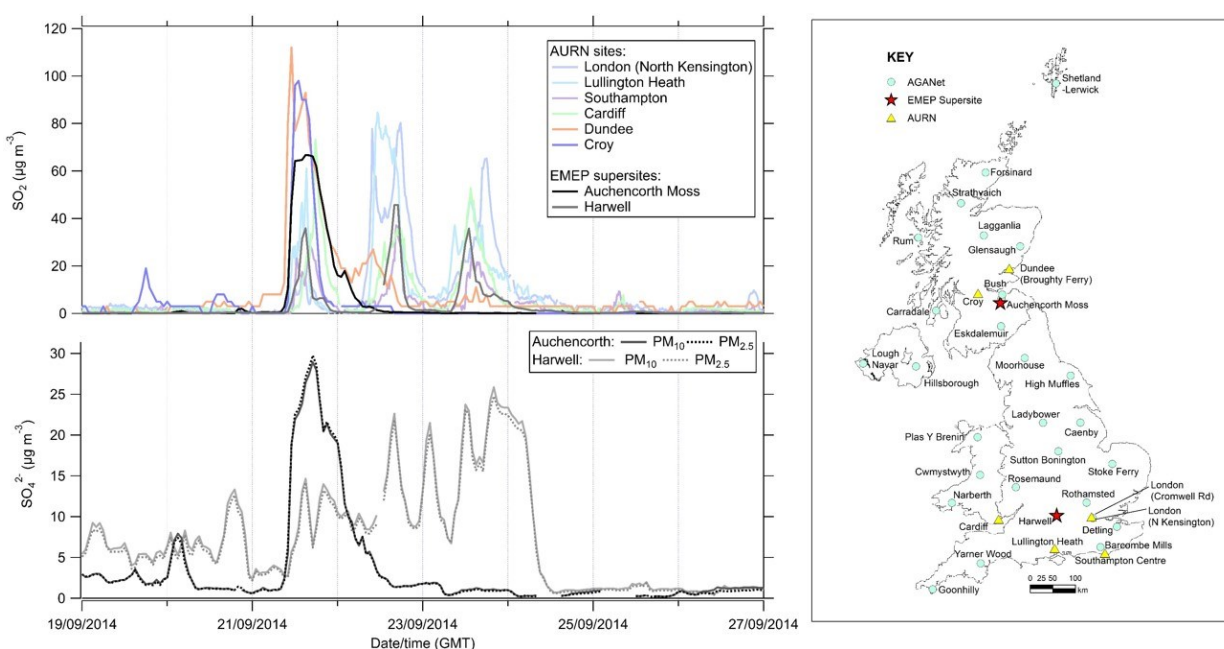
Figure 33 Time series of SO_2 hourly measurements made at 6 AURN sites in the UK and the two UK EMEP supersites measurements of SO_2 and $PM_{10/2.5}$ sulphate. B) Map of sites measuring SO_2 in the UK used in this study. (NOTE: SO_2 at Auchencorth Moss is underestimated between 11:00 and 22:00 (GMT) on the 21/09/14) taken from (Twigg et al. In prep.)

As well as high resolution measurements observing the Bárðarbunga event, the long term AGA-Net also observed elevated SO_2 for the last four months of 2014 at background sites in North Scotland. The observed concentrations of SO_2 were significantly high in North Scotland, as they were higher than when the AGA-Net was first established in 1999 (Figure 34). In parallel, the Precip-Net measurements also captured the wet deposition of sulphate across the country both in the fortnightly data and the daily wet-only measurements at the Supersites (Figure 35 and Figure 36). The detailed analysis of these datasets and the net input of sulphur to the UK ecosystems can be assessed with this data.

The volcanic eruption from Bárðarbunga was smaller than the Laki eruption, which was known to alter climate and impact on human health not only in Iceland but in the rest of Euorpe. Therefore the current datasets produced by the UKEAP network, both high resolution and low resolution, are unique as it is the first known record of the composition of both the gas phase and aerosol distal plume following a long term

Icelandic effusive eruption. This is important as it gives modellers an opportunity to understand the potential impact of future eruptions from Iceland which is currently high on the UK risk register held by the Cabinet Office.
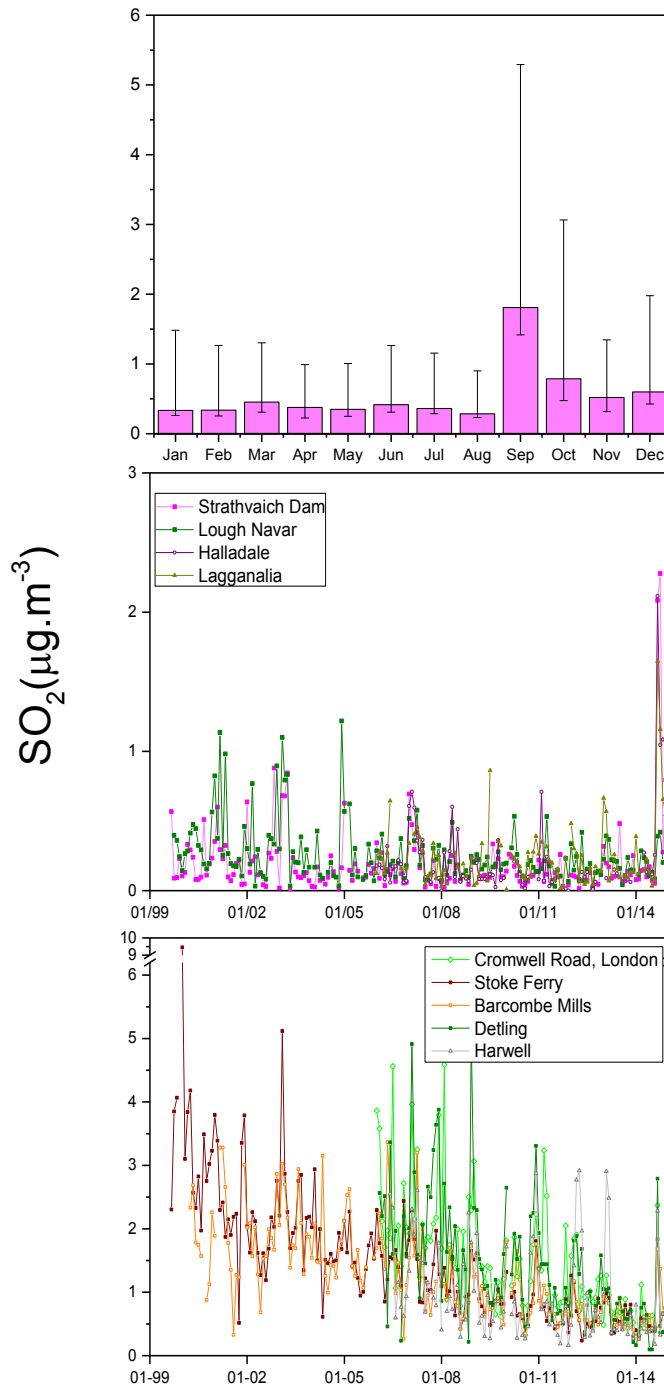
**Figure 34 UK AGA-Net monthly SO₂: Top panel: 2014 monthly network average SO₂ concentration (30 sites, whiskers maximum and minimum values); Middle Panel: 5 remote sites in the network; Bottom Panel: 5 sites in southern England (Taken from Twigg *et al in prep)*

33
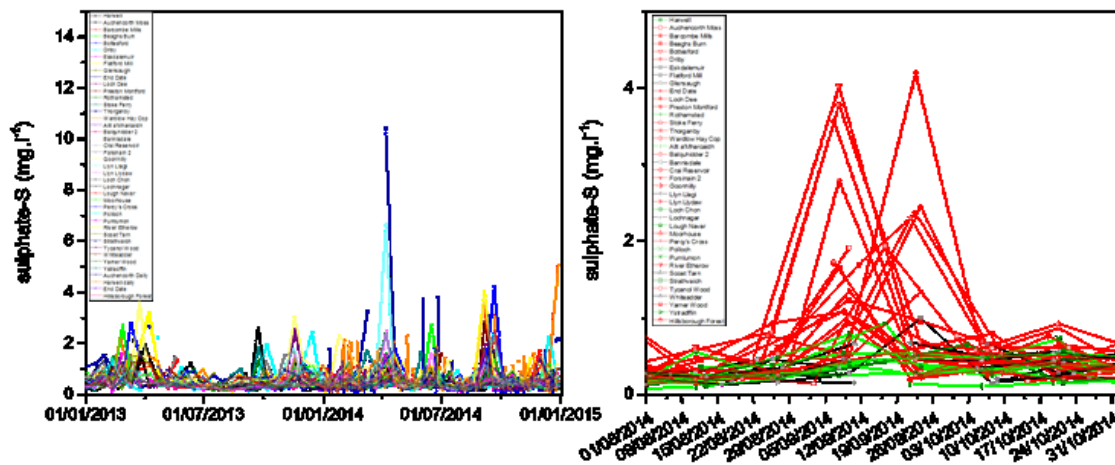
Figure 35 UK Precip-Net data: LHS: All data for 2013 and 2014; RHS: Data for all stations during September and October 2014; Red lines: sites with elevated sulphate during period; Green: sites with no clear elevation of sulphate and grey: sites with data missing; Note fortnightly data with data plotted using the start date of the measurement period.
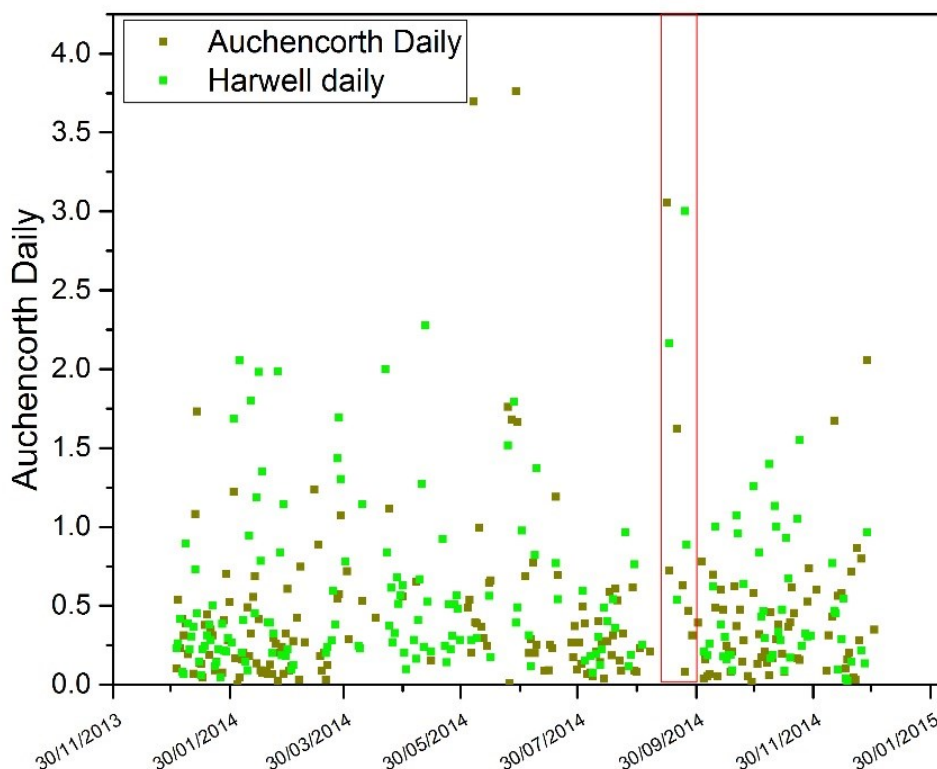
Figure 36 Daily wet only precipitation sulphate for 2013 and 2014 at Auchencorth Moss and Harwell. Red squre indicates period when volcano plume passed over the UK.

4.3 Precip-Net Network Size Evaluation

Headline: Impact of site reductions on uncertainty assessed
(summary of Smith et al. 2013 Defra submitted report)

The number of sites in the Precip-Net network were reduced iteratively by between 1 and 28 starting from the UKEAP Precip-Net site network of 38 sites as at end 2013. The request was specifically to explore the effect of site numbers on the estimated uncertainty, and therefore the chosen procedure was to randomly remove sites and use these reduced networks to recalculate the maps and estimate their uncertainties. For each level of site reduction, i.e. from 1 to 28 sites, there were 100 simulations of the possible new networks produced and interpolated maps generated for ammonium, nitrate, non-seasalt sulphate and total sulphate in rainfall. Both the uncertainty related to mapping deposition and the spatial changes in the maps produced for the UK from reduced numbers of sites were considered.

The change in national deposition estimates was assessed using histograms of the % uncertainty (expressed as twice the coefficient of variation (cv) calculated for each 5km square from the kriging outputs, where ±2*cv approximates to a 95% confidence interval). The histograms summarise data from all 100 simulations for the 11172 5km squares. Sets of histograms are shown in Figure 3 of Smith et al. 2013 for total sulphate, non-seasalt sulphate, ammonium and nitrate for reductions of 1, 5, 10, 20 and 28 sites (not reproduced here). The results were then summarised in Figure 4 in Smith et al. 2013 showing the change in the median percentage uncertainties for the UK from the sets of 100 simulations.

Table 1 gives an alternative presentation of these data. When the number of sites is reduced by 10, then the median percentage uncertainty increases by just over 10% for ammonium and nitrate but slightly less for the sulphate and non-seasalt sulphate. If there were only 5 sites removed, then the median percentage uncertainty would increase by only 3% to 5%. The total sulphate (i.e. including seasalt sulphate) is a less spatially variable map and is dominated by the seasalt component, which is the reason for the increases in uncertainty to be less than for the other ions.

The major spatial changes in the mean SO_4^{2-}, NO_3^- and NH_4^+ concentration across the UK are shown in Figure 37 (Figure 6 from Smith et al. 2013) for a number of chosen locations covering most of the map domain. Boxplots for each location for non-seasalt sulphate, ammonium and nitrate show the predicted values from the 100 simulations at each location, and represent the amount by which the map value changes at that location as site numbers are reduced. This is different from changes in the uncertainty related to producing the maps from the measured concentrations (as discussed above), and reflects the chance that we will still predict a similar concentration map from a smaller number of sites.

In the west and north of the UK, the effect of dropping sites has not just been to increase the uncertainty, but it is also likely to *increase* the estimated concentrations of non-seasalt sulphate, ammonium and nitrate at these locations. The opposite effect occurs down the east and south of the UK, where there is increasing uncertainty but a *decrease* in the estimated concentration at these locations, particularly clear for non-seasalt sulphate and nitrate and shown to a lesser extent for ammonium.

The outcome of this study was that reductions of the network size by more than 10 sites would substantially increase uncertainty estimates, particularly for ammonium and nitrate in rainfall where uncertainties of over ±100% uncertainties are not uncommon at a large number of mapped grid squares.

The risk was also identified that the mapped concentrations will alter at important locations, thus introducing discontinuities in trends of specific indicators purely as a result of network reorganisation, and this may be a particular issue for ammonium and nitrate. There was expected to be a noticeable loss of quality in estimated concentrations and deposition if any reduction of more than 10 sites were implemented.

Table 14 Increase in median % uncertainties from the 100 simulations for dropping 1 to 20 sites from the current networks for ammonium, nitrate, non-seasalt sulphate and total sulphate in rainfall.

No. of sites dropped	Increase in median % uncertainty			
	NO_3	NH_4	non-seasalt SO_4	SO_4
1	0	0	0	0
2	2	1	1	0
3	2	2	1	1
4	2	4	3	2
5	3	5	3	3
6	8	5	4	5
7	6	5	5	3
8	7	6	7	4
9	8	6	9	7
10	11	11	8	5
11	17	11	9	7
12	12	10	13	6
13	13	8	12	4
14	11	14	12	10
15	13	14	15	10
16	12	13	15	5
17	21	16	14	9
18	22	12	20	7
19	22	15	19	9
20	19	18	23	9
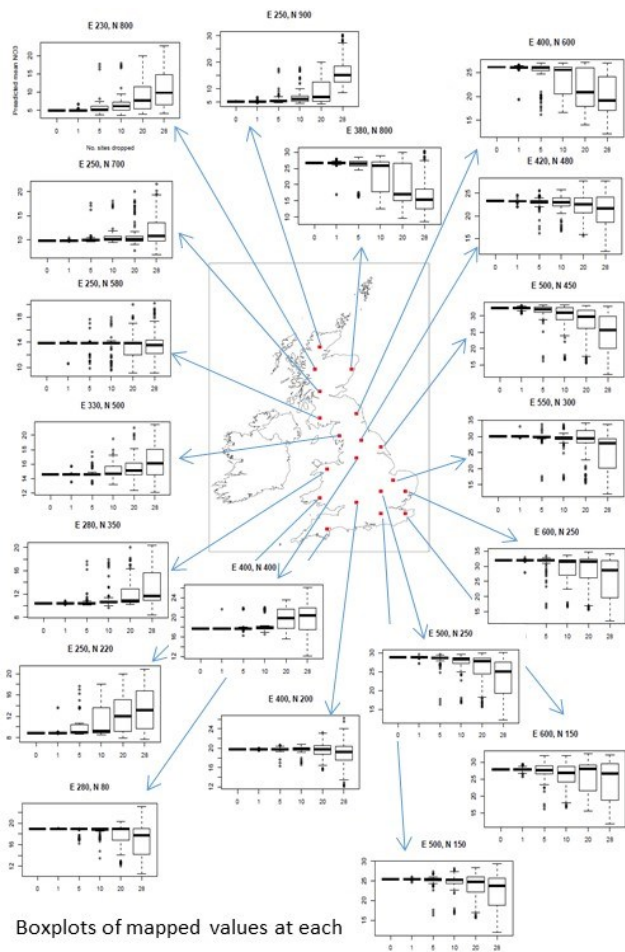
Boxplots of mapped values at each location against numbers of sites dropped (nitrate)
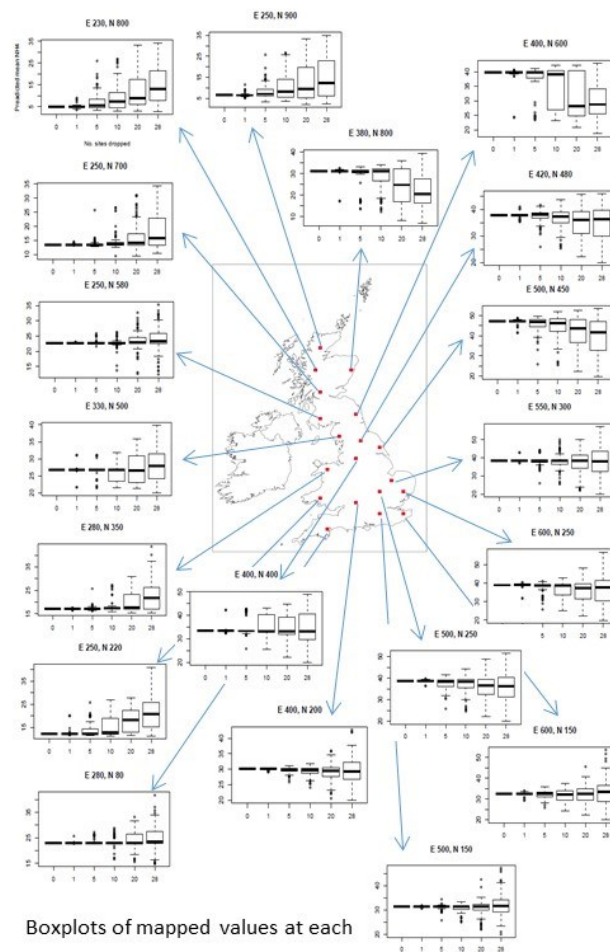
Boxplots of mapped values at each location against numbers of sites dropped (ammonium)
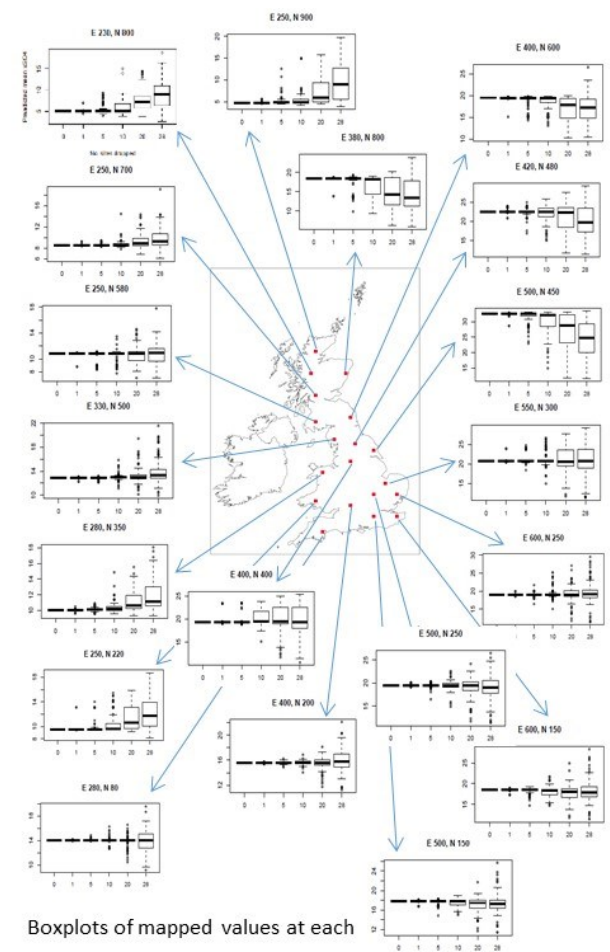
Boxplots of mapped values at each location against numbers of sites dropped (non-seasalt sulphate)

Figure 37 Changes in mapped concentrations at the chosen location (Figure 4) for non-seasalt sulphate, ammonium and nitrate in rainfall with reductions by 0, 1, 5, 10, 20 and 28 sites.

5. Acknowledgements

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Appendix 1: Guide to UKEAP data and Data usage

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

Harwell EMEP Supersite

Trace gas and aerosols (MARGA) Contact: Dr Justin Lingard, Ricardo-AEA

Lingard, J., 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*)

Hourly NO and NO$_2$ (ANNOX instrument): Contact: Mr Steve Telling, Ricardo-AEA

Telling, S., Lingard, J., Ritchie, S., Conolly, C. UK Eutrophying and Acidifying Atmospheric Pollutant project's ANNOX instrument, 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*)

Meteorological Data: Contact Dr Justin Lingard, Ricardo-AEA

Auchencorth Moss EMEP Supersite

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

Twigg, M.M., Leeson, S.R. Morrison, E., Tang, Y.S., van Dijk, N., 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**)

ANNOX: Contact: Mr John Kentisbeer, NERC Centre for Ecology and Hydrology

Kentisbeer, J., 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**)

Meteorological Data: Contact Dr Mhairi Coyle, NERC Centre for Ecology and Hydrology

Acid Gas and Aerosol Network

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

Tang, Y.S. , Poskitt, J., Nemitz, E., Bealey, W.J., Leaver, D., Beith, S., Thacker, S., Simmons, I., Letho, K., Wood, C., Pereira, G., Lawlor A.J., Sutton, M.A., Davies, M., Conolly, C., Donovan, B., 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, AGANet, 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

Tang, Y.S. , Poskitt, J., Nemitz, E., Bealey, W.J., Leaver, D., Simmons, I, Pereira, G., Sutton, M.A., Davies, M., Conolly, C., Donovan, B., 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, AGANet, 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-AEA

Conolly, C., Yardley, R., Collings, A., Davies, M., 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-AEA

Conolly, C., Yardley, R., Collings, A., Davies, M., 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 2013

Harwell operations

2013 is the fifth year of operation of the southernmost UK EMEP Supersite established at Harwell, Oxfordshire. The Harwell EMEP Supersite is operated by Ricardo-AEA and is a rural air quality monitoring site situated in a stand-alone building at the Meashill Plantation area of the Harwell International Business Centre at 51.57°N, 1.33°W (OS grid reference SU 467860) at an elevation of 126 m ASL, summarised on UK-AIR. There were no modifications to the site infrastructure in 2013.

Ricardo-AEA acted as Local Site Operator for the Harwell EMEP Supersite measurements for all measurements except those conducted by NPL (as shown in Table 3) and NERC CEH was LSO for Auchencorth Moss. During 2014 no health and safety incidents occurred at either site in relation to the operation of the EMEP Supersite.

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.

Harwell MARGA QC

The MARGA 2S is a research-grade instrument. Currently there is no proposed or accepted ISO, CEN or equivalent BS standard method for the determination of the concentration of anionic or cationic species in PM_{10} and $PM_{2.5}$. 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. The MARGA made continuous measurements of the chemical composition of PM_{10} and $PM_{2.5}$ throughout 2014. The percentage data capture for the twenty-one channels of measurements returned by the instrument were between 89-94%,

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 Harwell MARGA in 2014 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.

The quarterly results and % relative error of the nominal concentration are shown in

Table 15. The % relative errors ranged from 4-21% of the nominal concentration for Li$^+$ and Br$^-$.

Table 15 Analytical results of Li+ and Br- and the % relative error of the nominal concentration.

Quarter	Analysis method	Ion	Nominal concentration (Li: ppb, Br: mg L^{-1})	Laboratory analysis (Li: ppb, Br: mg L^{-1})	Relative error (%)
Q1	ICP-MS	Li$^+$	320000†	294000	8%
			320*	281	12%
Q2			320000†	282000	12%
			320*	276	14%
Q3			320000†	293000	8%
			320*	291	9%
Q4			320000†	283000	12%
			320*	264	18%
Q1	IC	Br$^-$	3680†	3830	4%
			3.68*	3.46	6%
Q2			3680†	2900	21%
			3.68*	3.43	7%
Q3			3680†	3600	2%
			3.68*	3.89	6%
Q4			3680†	3150	14%
			3.68*	2.99	19%

† stock solution, * working solution

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 16) 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 16 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 neccesary							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

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 31st EMEP Inter-comparison

The inter-comparison in 2013 was the 32nd time such an inter-comparison took place. The samples provided included synthetic rainwater samples and nitrogen dioxide in absorbing solution.

Table 17 below compares the expected and measured concentrations for different components of the rainwater samples. The agreement between the expected and measured for the laboratory used in the UKEAP network was considered satisfactory by EMEP for the majority of the measurements which is the highest rating for the EMEP quality norm. The results of the inter-comparison shows that the analytical laboratory used in the UKEAP network is performing very well particularly for Sulphate, Nitrate and pH with all of the measurements for these species being within less than 5% of the expected values.

Ricardo Energy & Environment uses the results from this inter-comparison to feedback to the laboratory performance and have recently met with the laboratory manager of the analytical laboratory to ensure that the overall excellent quality of the analysis is maintained.

Table 17 32nd EMEP Inter-comparison

Species	Sample code	Expected concentration µeq l⁻¹	Measured concentration µeq l⁻¹	Absolute Mean difference (%)
Sulphate	G1	0.59	0.572	-3%
	G2	1.716	1.651	-4%
	G3	0.912	0.867	-5%
	G4	1.883	1.814	-4%
Nitrate	G1	0.214	0.206	-4%
	G2	0.695	0.684	-2%
	G3	0.335	0.325	-3%
	G4	0.78	0.774	-1%
Ammonium	G1	0.134	0.146	9%
	G2	0.374	0.381	2%
	G3	0.187	0.204	9%
	G4	0.401	0.411	2%
Sodium	G1	0.147	<u>0.116</u>	-21%
	G2	0.562	0.537	-4%
	G3	0.293	0.271	-8%
	G4	0.623	0.607	-3%
Chloride	G1	0.116	0.102	-12%
	G2	0.425	0.403	-5%
	G3	0.232	0.21	-9%
	G4	0.463	0.443	-4%
Calcium	G1	0.089	<u>0.075</u>	-16%
	G2	0.23	0.213	-7%
	G3	0.115	0.1	-13%
	G4	0.255	0.235	-8%
Potassium	G1	0.102	0.098	-4%
	G2	0.407	0.401	-1%
	G3	0.17	0.165	-3%
	G4	0.509	0.505	-1%
pH *	G1	4.7	<u>4.59</u>	-2%
	G2	4.13	4.09	-1%
	G3	4.4	4.335	-1%
	G4	4.1	4.065	-1%

* pH as pH units

[1] EMEP quality norm given as Satisfactory, Questionable or Unsatisfactory

[2] Questionable results underlined all other results were satisfactory.

NO$_2$-Net

Results of the 32nd EMEP Inter-comparison

The inter-comparison in 2014 was the 32nd time such an inter-comparison took place. The results of the Nitrogen Dioxide absorbing solution are shown below in Table 18. The results of this intercomparison are excellent with between a 1.5% and 3% absolute difference which is easily within the criteria for satisfactory reported by EMEP which is the highest rating for the EMEP quality norm.

Table 18 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 (%)
C1	0.067	0.068*	1.5
C2	0.081	0.0824*	2.1
C3	0.135	0.137	3.0
C4	0.108	0.11	3.0

* Decimal place transcription error removed following identification after submission deadline

Comparison with co-located automatic sites

Four of the UKEAP NO$_2$ diffusion tube monitoring sites are co-located with automatic urban and rural monitoring network (AURN) sites these are Eskdalemuir, Harwell, High Muffles and Yarner Wood. The data from these sites have been plotted in Figure 38 and the dashed lines correspond to the automatic data from the co-located sites.
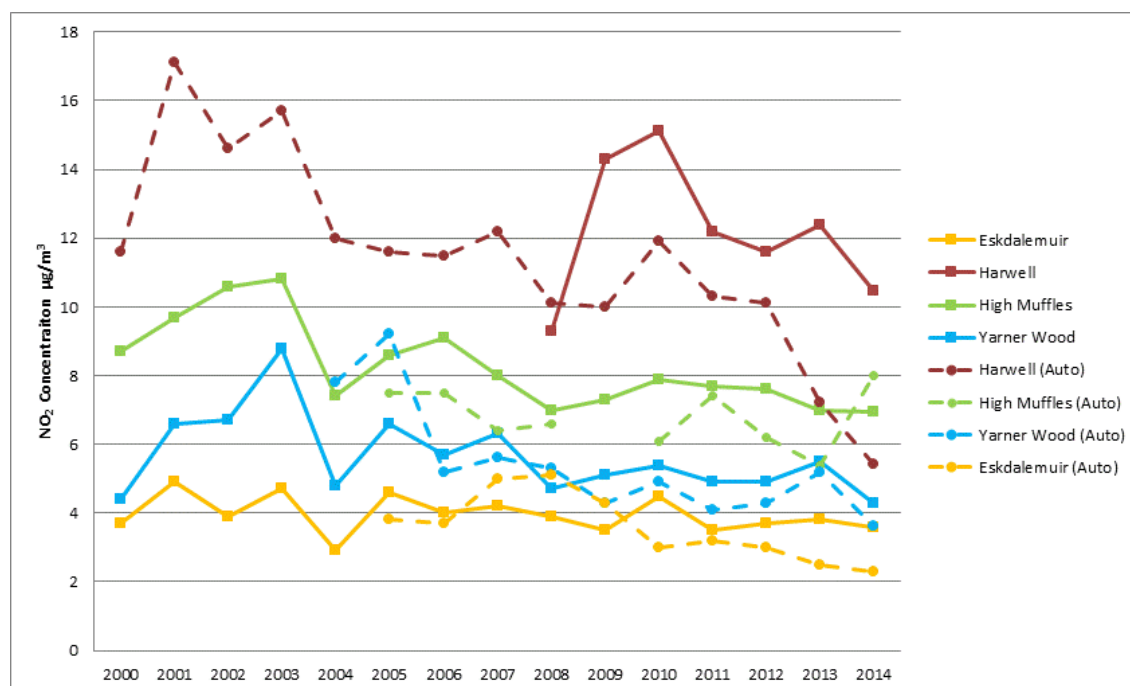
Figure 38 Comparison of measured concentrations of NO$_2$ by diffusion tube and automatic monitoring at collocated UKEAP sites * Not bias corrected

It is apparent from the comparison of the automatic and diffusion tube measurements that generally the NO$_2$ 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. 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 these often very remote locations provide a good cost effective approach to measurement.

AGANet

All DELTA systems are serviced annually. As part of this service the gas meter is calibrated and the system PAT tested.

The use of 2 glass denuders in series in the DELTA methodology (Sutton et al, 2001, Tang et al. 2009) allows the capture efficiency of every sample to be assessed, by comparing the amount of chemical species in both denuders. The collection efficiency correction (E) is applied to the measurement (Sutton et al. 2001). Where less than 75% of the total captured is recorded in the first denuder, data are flagged as being less certain. The monthly averaged denuder capture efficiency from the 30 AGANet sites for NH$_3$, HNO$_3$, SO$_2$ and HCl are shown in

Figure 39. The quality control using a double denuder system confirms that the capture efficiency in the denuders is adequate and that the correction factors are small (typically ~ 5 %).
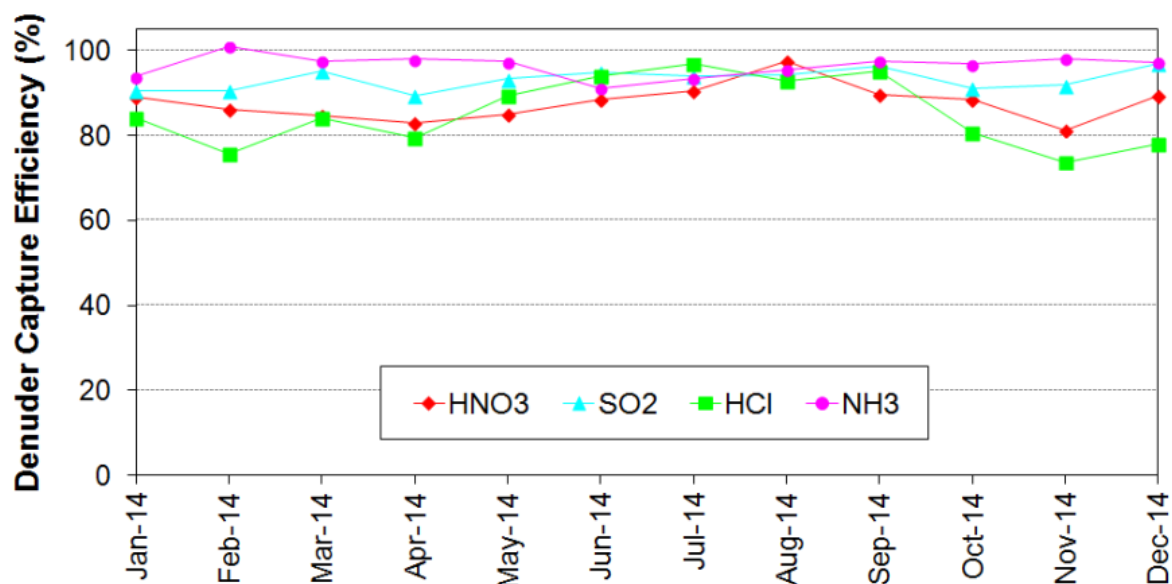

Figure 39: Monthly mean denuder capture efficiency (E) during 2014 for HNO$_3$, SO$_2$ and HCl from the 30 monitoring sites. E = amount in 1st denuder / (amounts captured in 1st + 2nd denuders)*100 %.

NAMN:

The percentage of samples passing the main QC criteria in NAMN provide an indication of network performance (Tang et al. 2003). During 2014, > 90% of data passed the QC thresholds. Parallel measurement by both DELTA and ALPHA methods are carried out at 9 intercomparison sites so the number of measurements in NAMN providing data for each month is 9 larger than the total number of sites in the network.
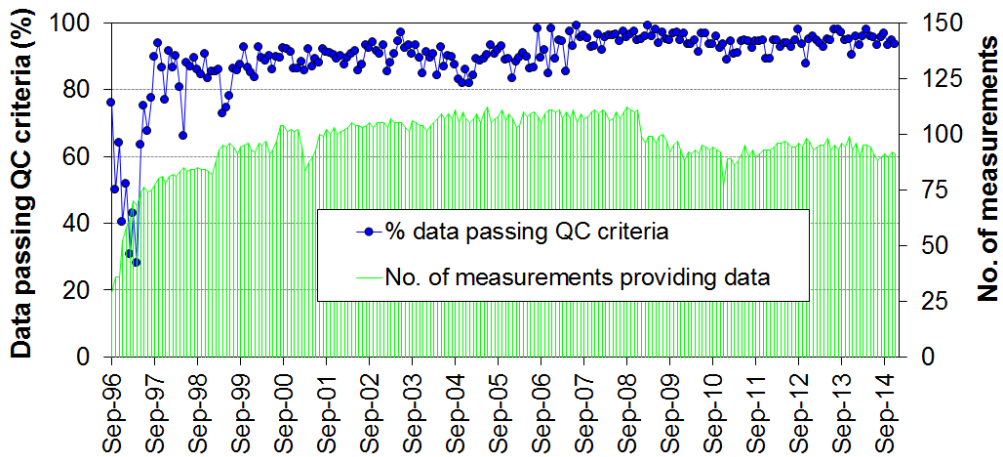
Figure 40: Assessing NAMN performance through monitoring total data capture, and % of data passing the QC thresholds (DELTA: capture of $NH_3 \geq 75$ % in the first of the 2 denuders, flow rate = > 0.22 L min^{-1}; DT/ALPHA: % CV for replicate samples < 30 % and < 15 % respectively).

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 41. 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.
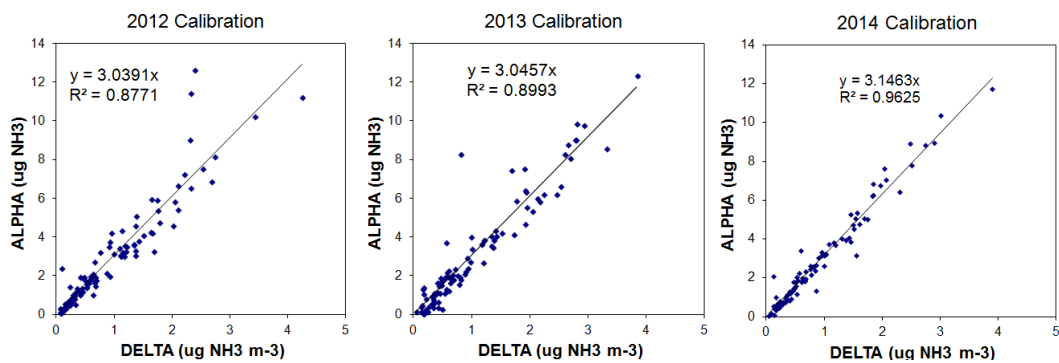
Figure 41: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers in years 2012, 2013 and 2014.