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And the Devolved Administrations

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NERC Centre for Ecology & Hydrology

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Ricardo Energy & Environment

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UK Eutrophying and Acidifying Atmospheric Pollutant (UKEAP) Annual Executive Summary

The UK Eutrophying and Acidifying Atmospheric Pollutant (UKEAP) project monitors the composition of precipitation, atmospheric gases and aerosol across the UK. This Executive Summary highlights the operation and activities carried out within UKEAP during 2015.

Key points from 2015:

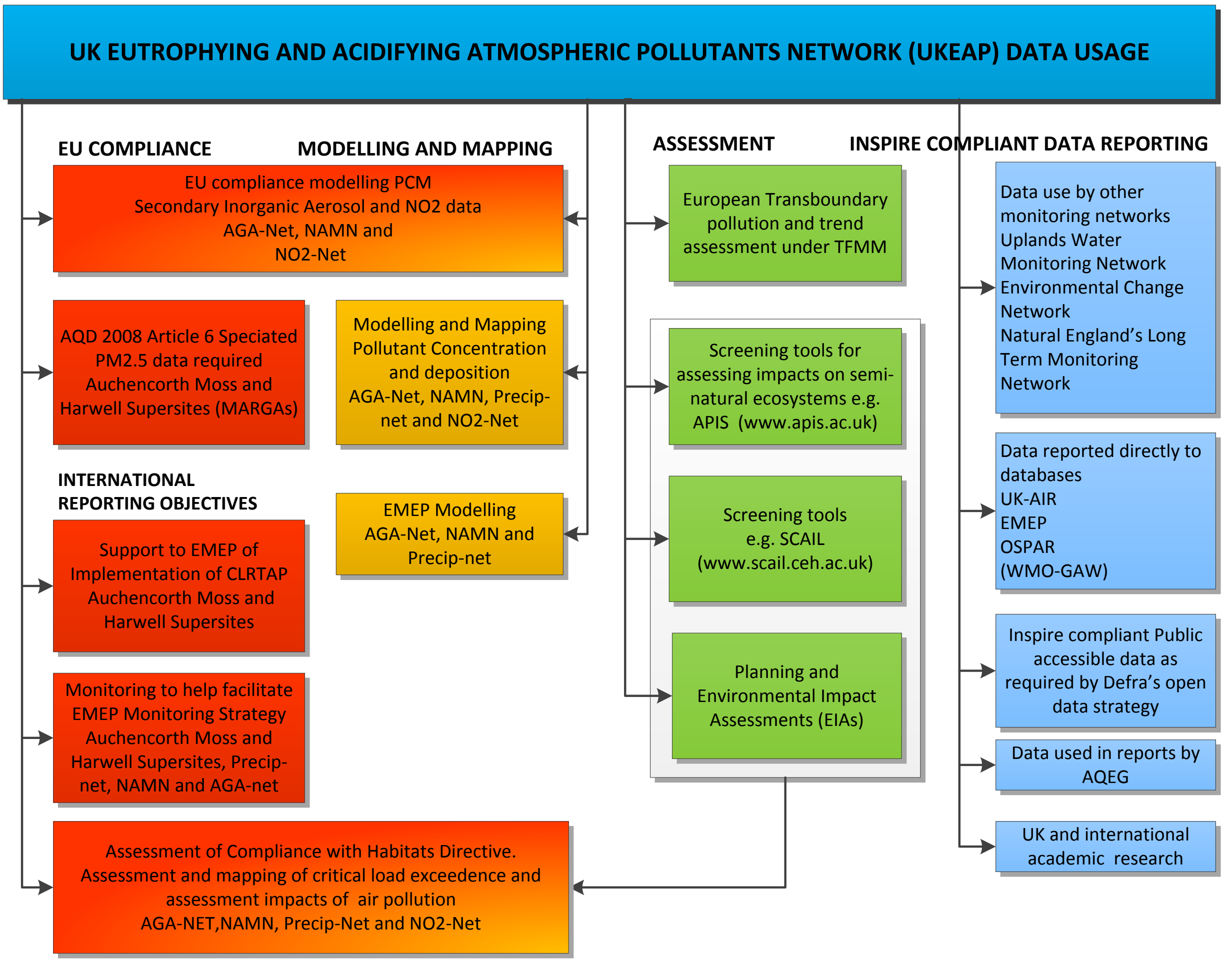
1. UKEAP consists of 4 component networks and the Auchencorth Moss and Harwell Supersites:
    a. Precipitation Network (Precip-net)
    b. Rural NO_2 monitoring network (NO_2-Net)
    c. Acid gas and aerosol network (AGA-Net)
    d. National Ammonia Monitoring Network (NAMN)
    e. EMEP Supersites
2. UKEAP data and information are currently available on UK-Air and Supersite data was submitted to EMEP.
3. High temporal resolution air quality 2015 data from the UK EMEP Supersites, Auchencorth and Harwell are available to analyse background air quality and pollution events
4. 2015 was the final year of operation of the southern UK EMEP Supersite at Harwell. Instrumentation were moved and re-commissioned at Chilbolton in 2016.
5. Precip-Net operated smoothly in 2012, with long term trends in sulphate decline continuing.
6. NO_2-Net data capture of the diffusion tubes in 2015 was 99% with 20 of the 24 sites achieving 100% data capture.
7. NAMN: During 2015 >90% of data passed the QC thresholds and the network operated smoothly.
8. AGANet DELTA II systems were successfully operated for the first full calendar year in 2015 after the network upgrade in 2014.
9. Fluoride in vegetation analytical intercomparison was completed.
10. UKEAP data in 2015 supported Euroepan, UK national, regional and local pollutant impact mapping and modelling for air qualiy impact assessment and more than 25 reports and peer-review publications have used the data.

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 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).

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 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)

Defra AQ0947 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 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.

2015-16 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 a non-exhaustive search of the literature and engagement with stakeholders.

- Cape, J.N.; Smith, R.I.; Leaver, D.. 2015 Missing data in spatiotemporal datasets: the UK rainfall chemistry network. Geoscience Data Journal, 2 (1). 25-30. 10.1002/gdj3.24
- Cape, J.N.; Smith, R.I.; Fowler, D.; Beswick, K.; Choularton, T.. 2015 Long-term trends in rain and cloud chemistry in a region of complex topography. Atmospheric Research, 153. 335-347. 10.1016/j.atmosres.2014.09.003
- Derwent, R. G., J. I. R. Dernie, et al. (2014). "Twenty years of continuous high time resolution volatile organic compound monitoring in the United Kingdom from 1993 to 2012." Atmospheric Environment 99: 239-247.
- Dragosits, U.; Carnell, E.J.; Misselbrook, T.H.; Stevens, C.; Jones, L.; Rowe, E.; Hall, J.R.; Dise, N.; Dore, A.J.; Tomlinson, S.J.; Sheppard, L.J.; O'Shea, L.; Reis, S.; Bealey, W.; Braban, C.F.; Smyntek, P.; Sutton, M.A.. 2015 Identification of potential “Remedies” for Air Pollution (nitrogen) Impacts on Designated Sites (RAPIDS). London, Defra, 58pp. (CEH Project no. C05034, Defra Project AQ0834)
- Fagerli H., Aas W., Mareckova K.. 2015. Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components. EMEP Status Report 1/2015.
- Fowler D., Steadman C.E., Stevenson D., Coyle M., Rees R.M., Skiba U.M., Sutton M.A., Cape J.N., Dore A.J., Vieno M. et al.. 2015. Effects of global change during the 21st century on the nitrogen cycle. Atmospheric Chemistry and Physics. 15(24):13849-13893.
- Hall, Jane; Curtis, Chris; Dore, Tony; Smith, Ron. 2015 Methods for the calculation of critical loads and their exceedances in the UK. Bangor, UK, NERC/Centre for Ecology & Hydrology, 108pp. (CEH Project no. C04913)
- Hall, Jane; Smith, Ron. 2015 Trends in critical load exceedances in the UK. Bangor, UK, NERC/Centre for Ecology & Hydrology, 23pp. (CEH Project no. C04913)
- Hoerger C.C, Werner A., Plass-Duelmer C., Reimann S., Eckart E., Steinbrecher R., Aalto J., Arduini J., Bonnaire N., Cape J.N et al.. 2015. ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO-GAW and EMEP observation networks. Atmospheric Measurement Techniques. 8:2715-2736
- Kentisbeer J., Leeson S.R, Clark T., Malcolm H.M, Cape J.N. 2015. Influences on and patterns in total gaseous mercury (TGM) at Harwell, England. Envionmental Science Processes & Impacts. 17(586):586-595.
- Kentisbeer J., Leeson S., Clark T., Twigg M., Jones M., Malcolm H., Braban C.F., Cape J.N.. 2015. Tracing the mercury in the UK atmosphere – peaks and sources. 12th International Conference on Mercury as a Global Pollutant (ICMGP 2015).
- Khan, M. A. H., W. C. Morris, et al. (2015). "Estimation of Daytime NO3 Radical Levels in the UK Urban Atmosphere Using the Steady State Approximation Method." Advances in Meteorology.
- Malley C.S., Braban C.F., Dumitrean P., Cape J.N., Heal M.R.. 2015. The impact of speciated VOCs on regional ozone increment derived from measurements at the UK EMEP supersites between 1999 and 2012. Atmospheric Chemistry and Physics. 15(14):8361-8380.
- Malley C.S, Heal M.R, Mills G., Braban C.F. 2015. Trends and drivers of ozone human health and vegetation impact metrics from UK EMEP supersite measurements (1990–2013). Atmospheric Chemistry and Physics. 15(8):4025-4042.
- Masiol, M. and R. M. Harrison (2015). "Quantification of air quality impacts of London Heathrow Airport (UK) from 2005 to 2012." Atmospheric Environment 116: 308-319.
- Metzger C., Jansson P.E, Lohila A., Aurela M., Eickenscheidt T., Belelli-Marchesini L., Dinsmore K., Drewer J., van Huissteden J., Drosler M.. 2015. CO2 fluxes and ecosystem dynamics at five European treeless peatlands – merging data and process oriented modelling. Biogeosciences. 12(1):125-146.
- Monteith, Don; Henrys, Peter; Banin, Lindsay; Smith, Ron; Morecroft, Mike; Scott, Tony; Andrews, Chris; Beaumont, Deborah; Benham, Sue; Bowmaker, Victoria; Corbett, Stuart; Dick, Jan; Dodd, Bev; Dodd, Nicki; McKenna, Colm; McMillan, Simon; Pallett, Denise; Pereira, M. Gloria; Poskitt, Jan; Rennie, Sue; Rose, Rob; Schafer, Stefanie; Sherrin, Lorna; Tang, Sim; Turner, Alex; Watson, Helen. 2016 Trends and variability in weather and atmospheric deposition at UK Environmental Change Network sites (1993–2012) [in special issue: Assessing ecosystem resilience through long term ecosystem research: observations from the first twenty years of the UK Environmental Change Network] Ecological Indicators, 68. 21-35. 10.1016/j.ecolind.2016.01.061
- Oulehle, F., Jiri, K., Tomas, C., Vladimir, C., Iva, H., Jakub, H., Pavel, K., Zora, L., Tomas, N., Petr, S., Miroslav, T., and Christopher, E. D.: Predicting sulphur and nitrogen deposition using a simple statistical method, Atmospheric Environment, 140, 456-468, 2016.

- Sier, Andrew; Monteith, Don. 2016 The UK Environmental Change Network after twenty years of integrated ecosystem assessment: key findings and future perspectives [in special issue: Assessing ecosystem resilience through long term ecosystem research: observations from the first twenty years of the UK Environmental Change Network] Ecological Indicators, 68. 1-12. 10.1016/j.ecolind.2016.02.008
- Steinle S., Reis S., Sabel C.E, Semple S., Twigg M.M, Braban C.F, Leeson S.R, Heal M.R, Harrison D., Lin C. et al.. 2015. Personal exposure monitoring of PM2.5 in indoor and outdoor microenvironments. Science of The Total Environment. 508:383-394.
- Sutton MA, Howard CM, Nemitz E, Arneth A, Simpson D, Mills G, de Vries W, Winiwarter W, Amann M, Alonso R et al.. 2015. ECLAIRE: Effects of Climate Change on Air Pollution Impacts and Response Strategies for European Ecosystems. Project final report.
- 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. et al.. 2015. Development of a new model DELTA sampler and assessment of potential sampling artefacts in the UKEAP AGANet DELTA system: summary and technical report.
- Twigg M.M., Aruffo E., Kentisbeer J., Malley C., Leeson S., Jones M.R., Nemitz E., Di Carlo P., Braban C.. 2015. Deriving a speciated atmospheric nitrogen budget at Auchencorth Moss, a background site in south east Scotland. EGU 2015.
- Twigg M.M., Leeson S.R., Ilyinskaya E., Loughlin S., Braban C.. 2015. Evidence of change in UK atmospheric composition as a result of Icelandic volcanic emissions in 2014. EGU 2015.
- Vieno, M.; Heal, M.R.; Williams, M.L.; Carnell, E.J.; Nemitz, E.; Stedman, J.R.; Reis, S.. 2016 The sensitivities of emissions reductions for the mitigation of UK PM2.5. Atmospheric Chemistry and Physics, 16 (1). 265-276. 10.5194/acp-16-265-2016
- Vieno, M.; Heal, M.R.; Twigg, M.M.; MacKenzie, I.A.; Braban, C.F.; Lingard, J.J.N.; Ritchie, S.; Beck, R.C.; Moring, A.; Ots, R.; Di Marco, C.F.; Nemitz, E.; Sutton, M.A.; Reis, S.. 2016 The UK particulate matter air pollution episode of March–April 2014: more than Saharan dust. Environmental Research Letters, 11 (4), 044004. 12, pp. 10.1088/1748-9326/11/4/044004
- Witham, Claire ; Aspinall, Willy; Braban, Christine; Hall, Jane; Loughlin, Sue; Schmidt, Anja; Vieno, Massimo; Bealey, Bill; Hort, Matthew; Ilyinskaya, Evgenia; Kentisbeer, John; Roberts, Elin; Rowe, Ed. 2015 UK hazards from a large Icelandic effusive eruption. Effusive Eruption Modelling Project final report. Exeter, Met Office, 226pp.

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UKEAP Annual Report 2015

1. Introduction

The **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network** 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 2015.

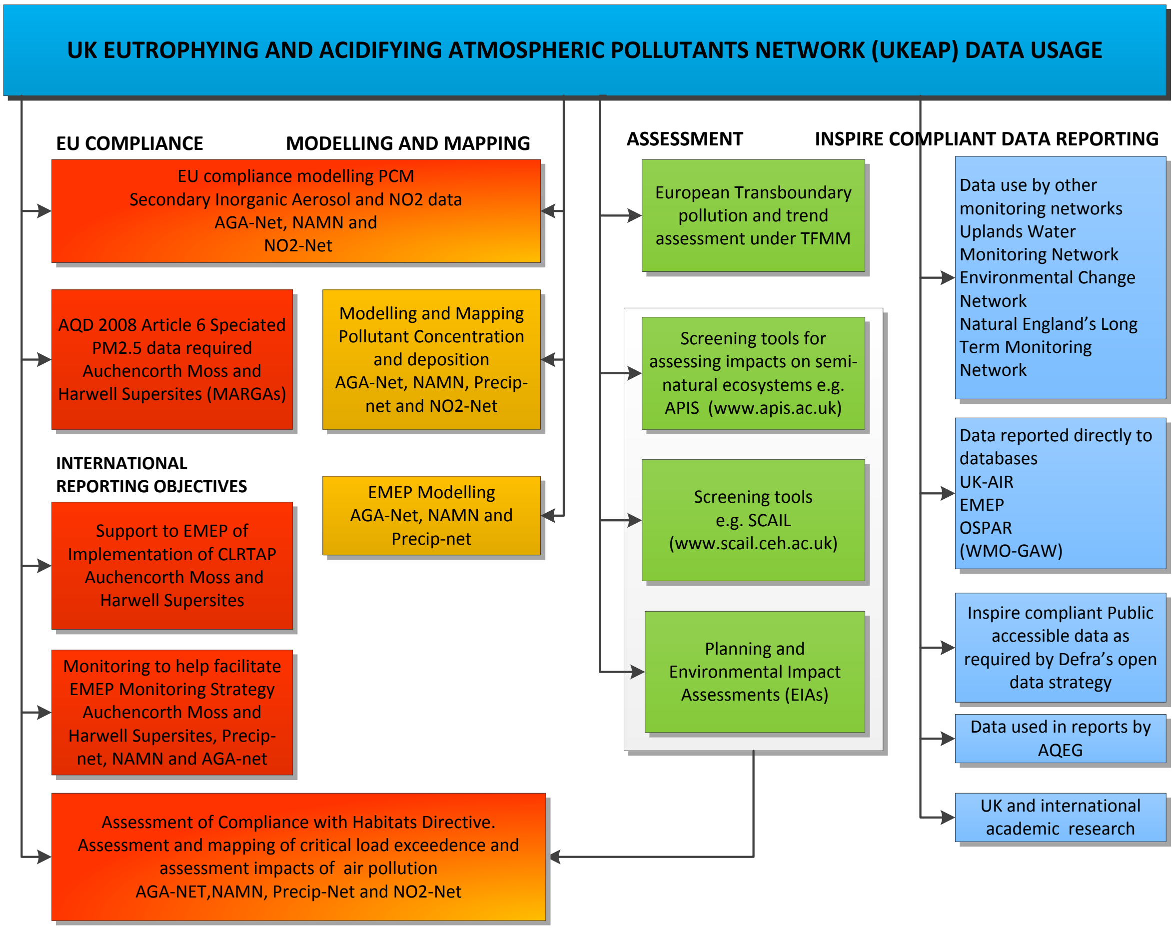


Figure 1 Summary of UKEAP data use pathways

In 2015 the UKEAP network comprised of the:

- **National Ammonia Monitoring Network** (NAMN – 84 sites)
- **Acid Gases and Aerosol Network** (AGANet – 30 sites)
- **Precipitation chemistry Network** (Precip-Net – 39 sites)
- **Rural NO_2 diffusion tube network** (NO_2-Net – 24 sites)
- **UK EMEP Supersites** (Harwell and Auchencorth)

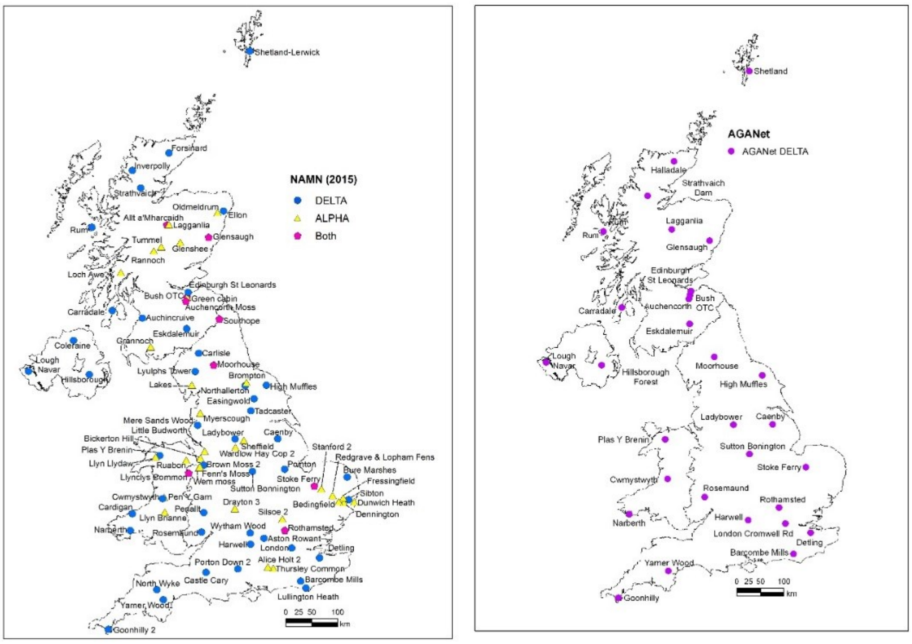


Figure 2 UK Eutrophying and Acidifying Atmospheric Pollutants rural networks part 1

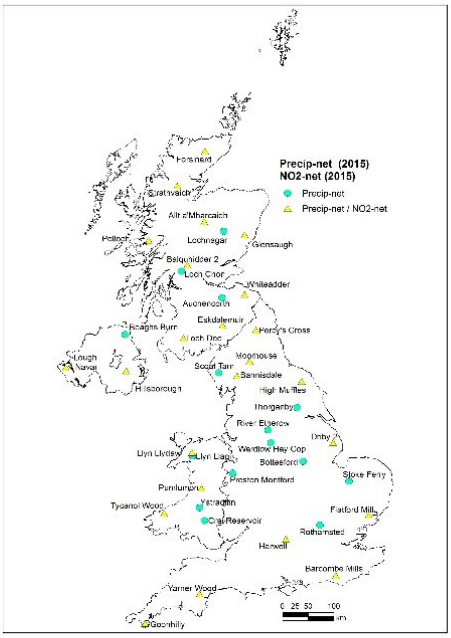


Figure 2 UK Eutrophying and Acidifying Atmospheric Pollutants rural networks part 2

2. UKEAP Networks

2.1 Precipitation Network (Precip-Net)

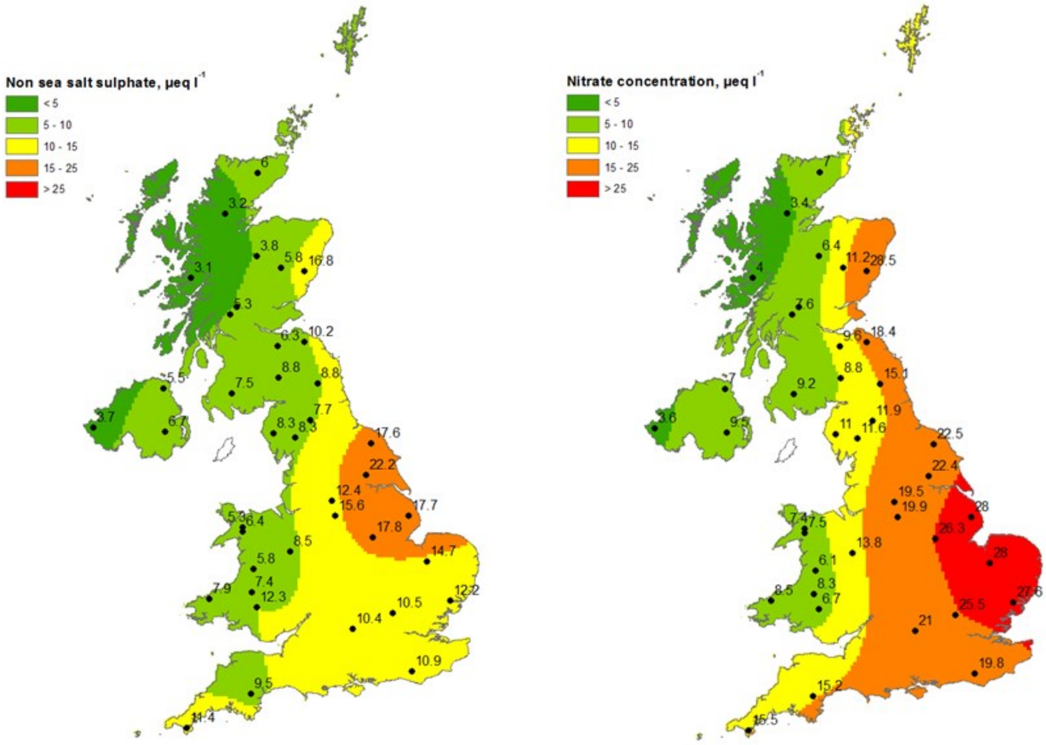
The major ions precipitation network, Precip-Net, consists of 39 fortnightly bulk rain monitoring sites and 2 daily wet only (DWOC) collectors at which the chemical composition of precipitation is measured. The locations of the monitoring sites are shown in Figure 3. A sampler is shown in Figure 4.

Figure 3 Precip-Net site map

Figure 4 Bulk rain sampler (Bannisdale)

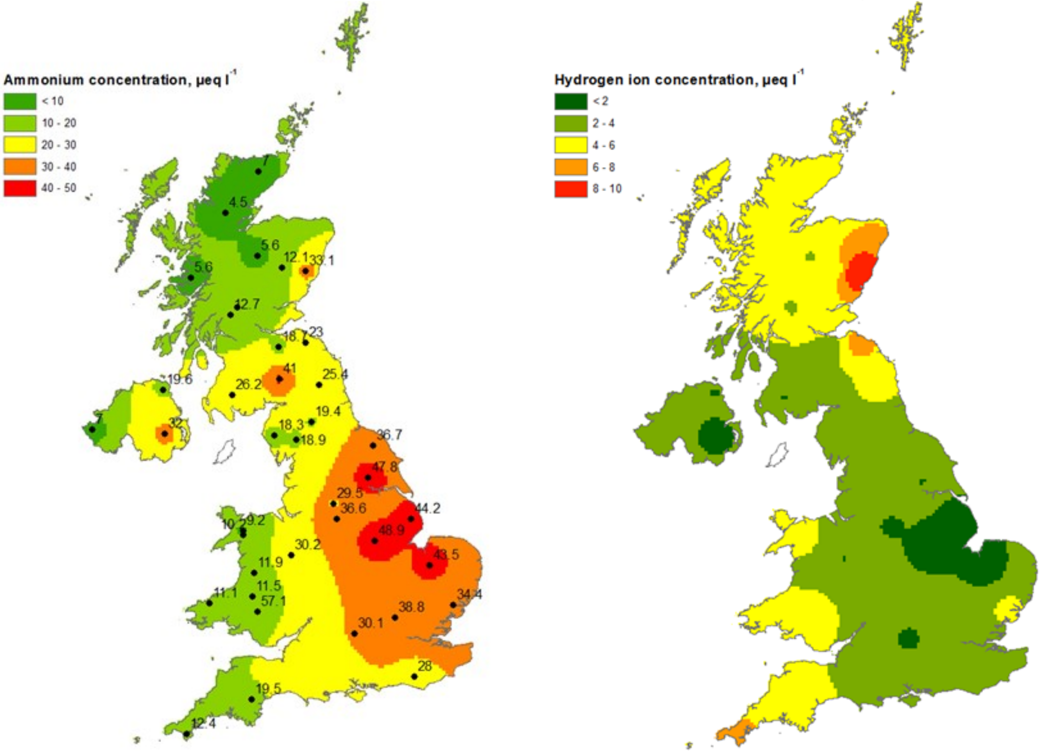
Precipitation samples were collected using a sampler design that has been used in the UK network since the inception of the Acid Deposition Monitoring Network in 1986, details of which can be found in previous reports. Daily collection of precipitation samples using Daily Wet Only Precipitation Collectors (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 2015. 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.

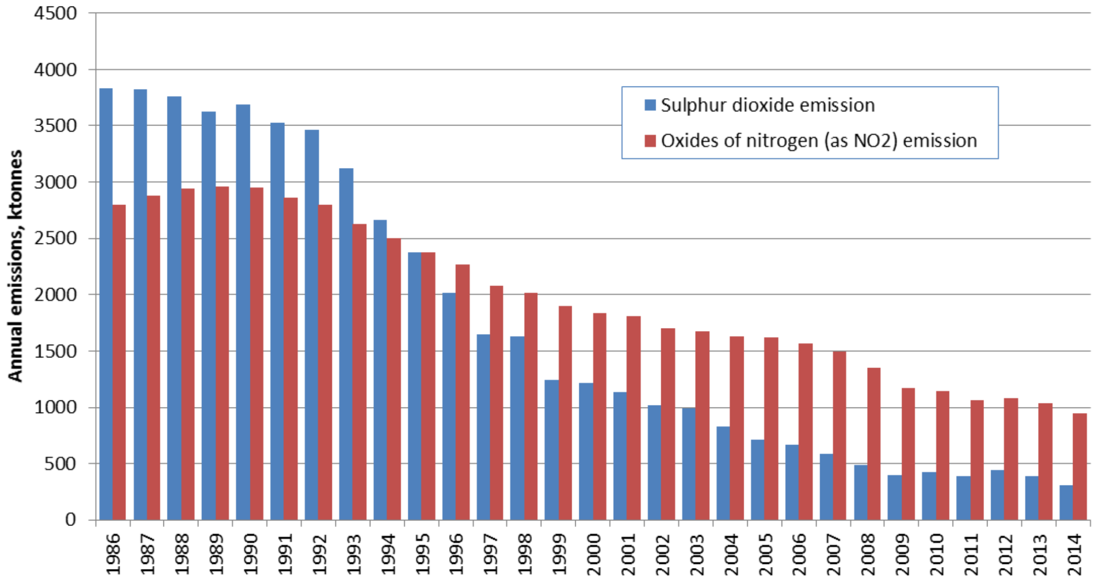


Figure 6 Sulphur dioxide and oxide of nitrogen emissions since 1986 Reference for emissions data. http://naei.defra.gov.uk/

Figure 7 and Figure 8 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.

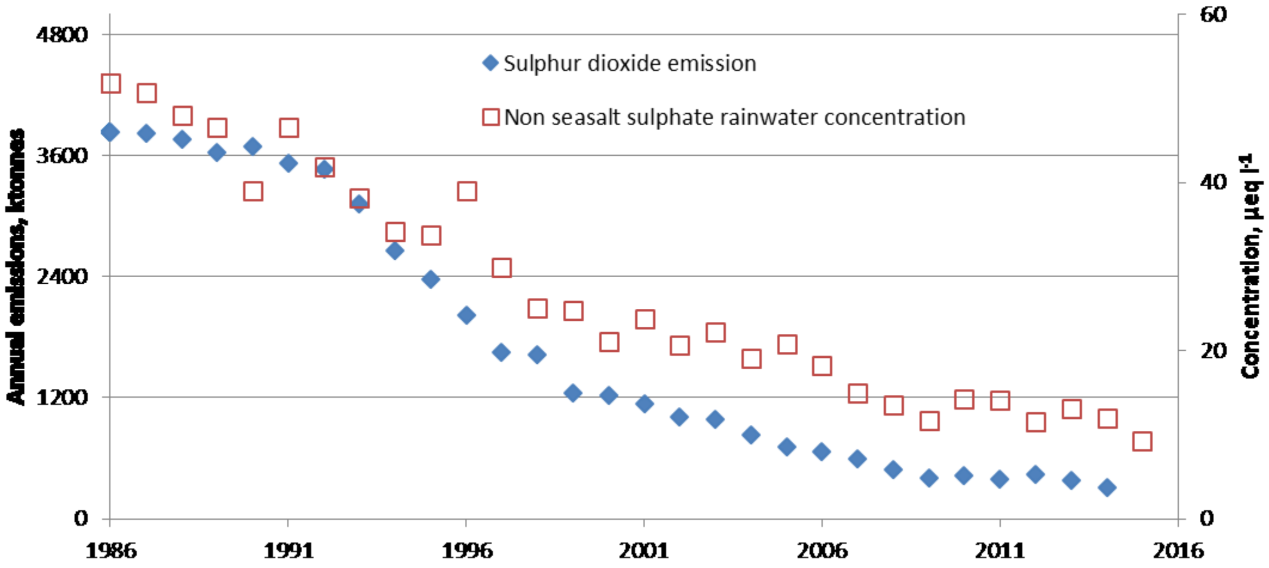


Figure 7 Sulphur dioxide emissions and sulphate concentrations in rainwater concentration

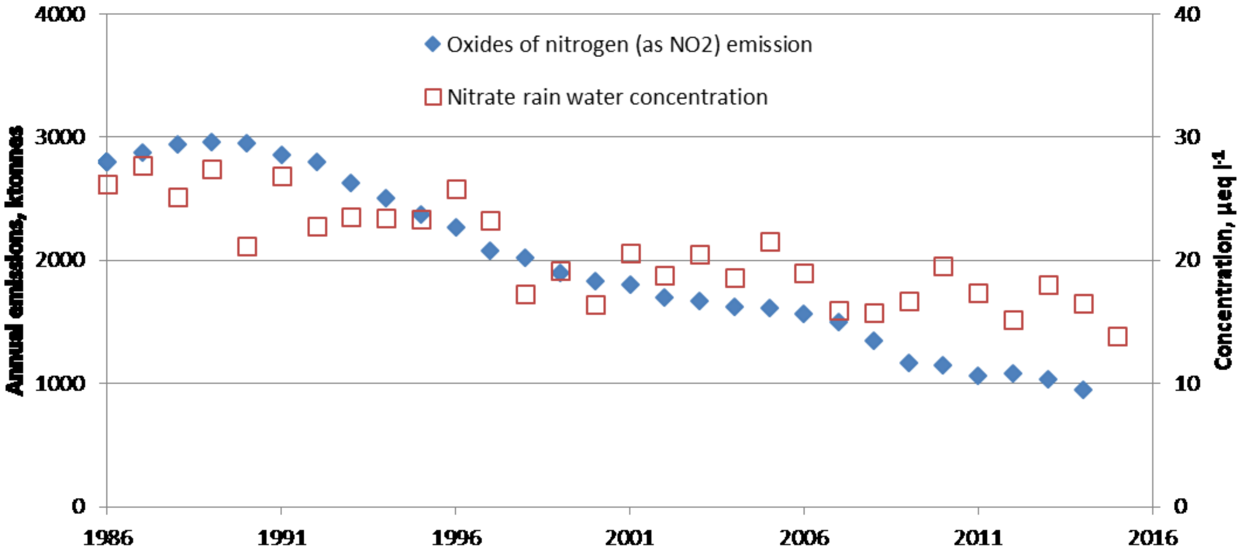


Figure 8 Oxide of nitrogen emissions and nitrate in rainwater concentration

2.2 NO_2-Net Network

The NO_2 network (NO_2-Net) consists of 24 sites (Figure 2) 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 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 2015 NO_2 concentration from the Diffusion Tubes in the NO_2-Net

Site Name	2015 concentration ($\mu g\ m^{-3}$)	Data capture	Site Name	2015 concentration ($\mu g\ m^{-3}$)	Data capture
Allt a'Mharcaidh	1.6	100%	Hillsborough Forest	6.5	100%
Balquhidder 2	2.7	100%	Llyn Llydaw	2.8	98.1%
Bannisdale	3.9	100%	Loch Dee	2.9	100%
Barcombe Mills	8.4	100%	Lough Navar	2.3	100%
Driby 2	9.8	100%	Moorhouse	4.0	100%
Eskdalemuir	3.2	100%	Percy's Cross	4.5	100%
Flatford Mill	9.3	100%	Polloch	1.4	100%
Forsinain 2	2.7	97.6%	Pumlumon	3.3	100%
Glensaugh	3.3	100%	Strathvaich	1.2	100%
Goonhilly	4.2	84.1%	Tycanol Wood	3.5	100%
Harwell	9.0	100%	Whiteadder	4.3	91.5%
High Muffles	6.2	100%	Yarner Wood	3.9	100%

The data capture of the diffusion tubes in 2015 was 99% with 20 of the 24 sites achieving 100% data capture.

The annual average NO_2 concentrations from 2010-2015 are shown in Figure 9 that gives 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 year's measurements shown in Figure 9.

Some of the sites with higher concentrations do appear to show a slight decline over the 5 years shown e.g. Flatford Mill, Hillsborough Forest and Harwell. Figure 10 shows the longer term trends where estimated emissions are plotted against selected sites in the network.

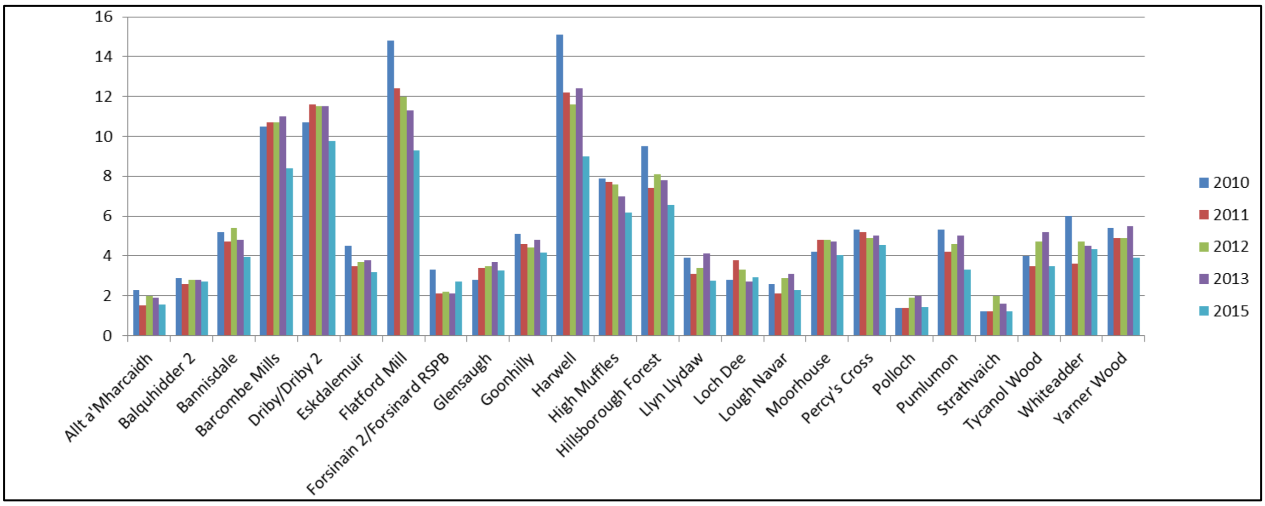


Figure 9 Annual mean NO_2 concentration (µg m^{-3}) at the NO_2-Net sites 2010-2015

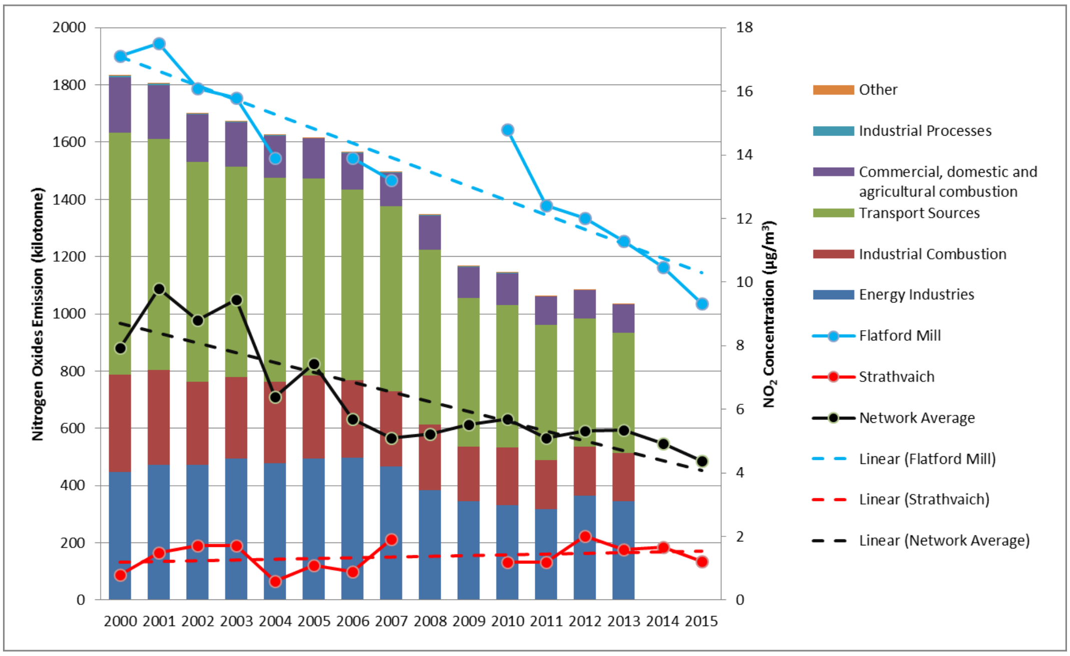


Figure 10 NAEI NOx Emission Estimates and monitored NO_2 Concentrations at two UKEAP sites

Figure 10 above displays 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 (Strathviach 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.

There doesn’t appear to be a trend at the rural site of Strathviach Dam where little change is observed. This difference in trends at the two sites is 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.

2.3 Acid Gas and Aerosol Network (AGANet)

The UK Acid Gas and Aerosol Network (AGANet) provides monthly speciated measurements of atmospheric reactive gases (HNO_3, SO_2, HCl) and aerosols (NO_3^-, SO_4^{2-}, Cl^-, NH_4^+, Na^+, Ca^{2+}, Mg^{2+}) at 30 sites across the UK. Mean 2015 annual concentrations of trace gas and aerosols at individual sites in the network are compared in Figure 11 and Figure 12.

The main features of the spatial distribution in the pollutants measured in 2015 are shown in the annual maps (Figure 13, Figure 14, Figure 15). 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 HNO_3 data presented here for 2015 have been adjusted by a correction factor of *0.45. This is to correct for co-collection of oxidised reactive Nitrogen species such as HONO on the carbonate coated denuders, as detailed in the report by Tang et al. 2015 (see reports list above). The largest HNO_3 concentrations were measured in southeast England (e.g. London; 2015 annual mean of = 1.1 µg HNO_3 m^{-3}, range = 0.93 – 1.4 µg HNO_3 m^{-3}).

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; 2015 annual mean = 0.09 µg HNO_3 m^{-3}, range = 0.03 – 0.15 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 15) 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.

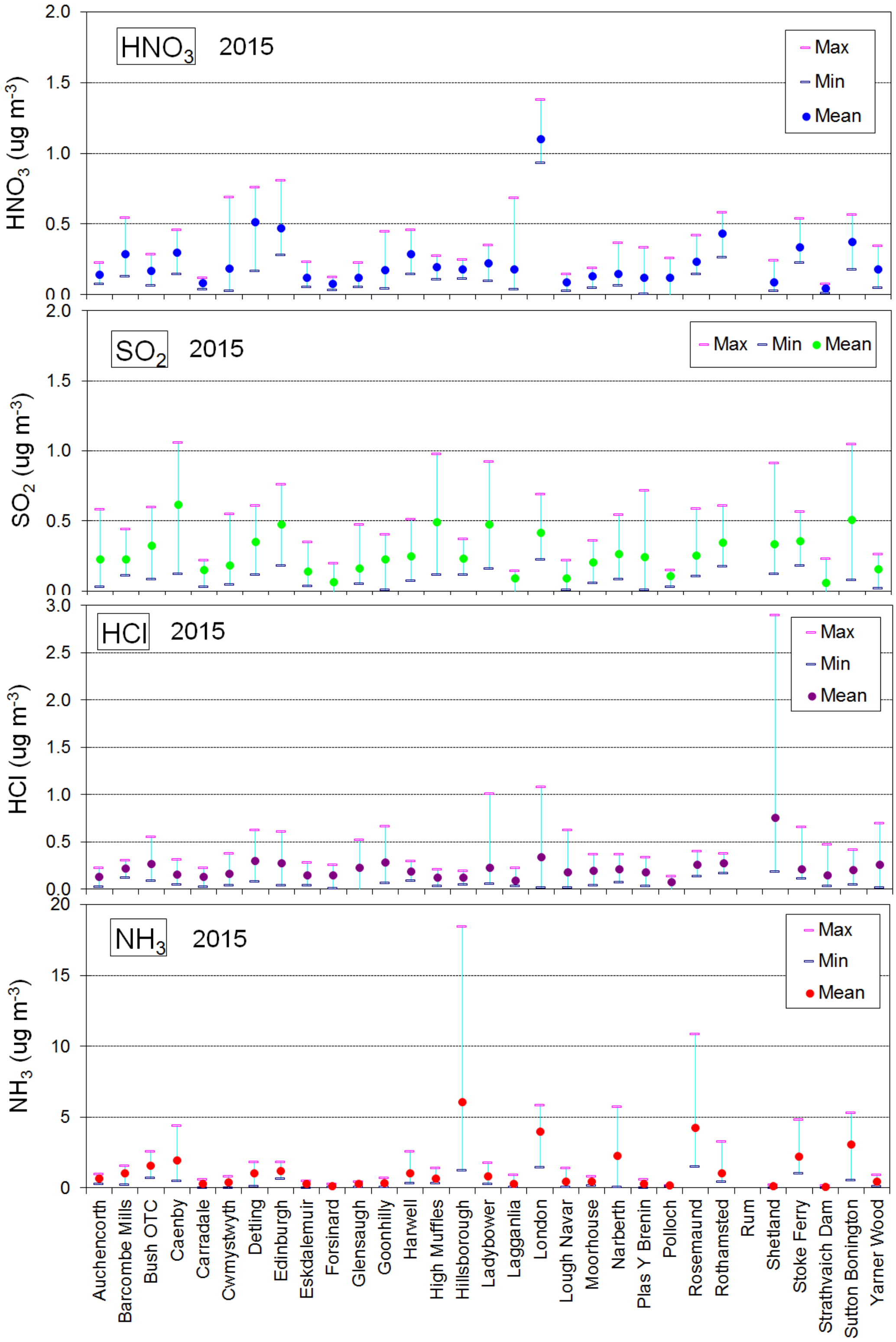


Figure 11: Mean monitored annual concentrations of gaseous HNO_3, SO_2, and HCl at individual sites in AGANet. Each data point represents averaged concentrations of monthly measurements made at each site in 2015, whilst the bars show the minimum and maximum concentrations observed. The HNO_3 data presented here for 2015 have been adjusted by a correction factor of 0.45. Data for gaseous NH_3 measured under NAMN is also shown for comparison.

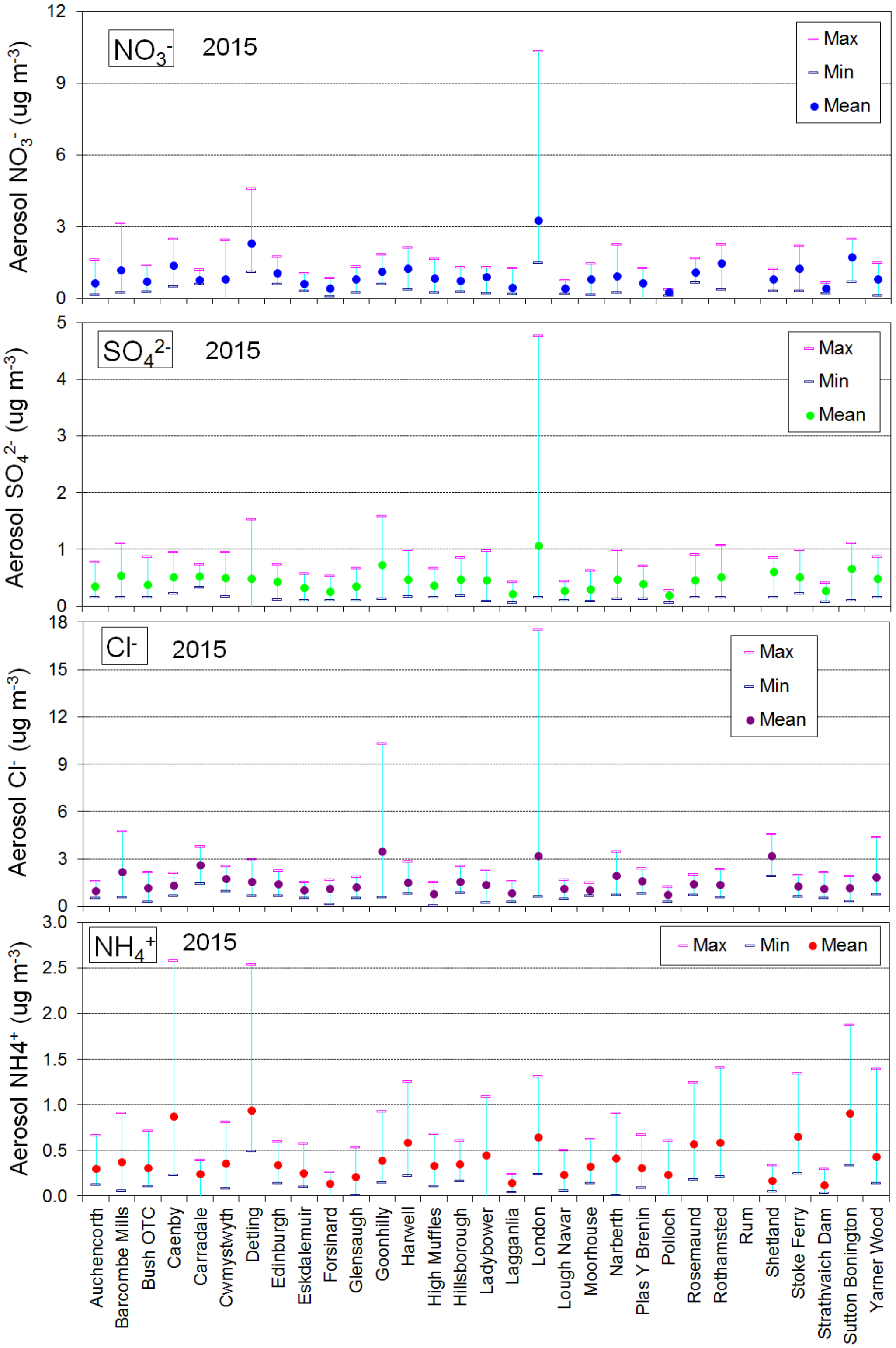


Figure 12: Mean monitored annual concentrations of particulate NO_3^-, SO_4^{2-} , Cl^- and NH_4^+ at individual sites in AGANet. Each data point represents the averaged concentrations of monthly measurements made at each site in 2015, whilst the bars show the minimum and maximum concentrations observed.

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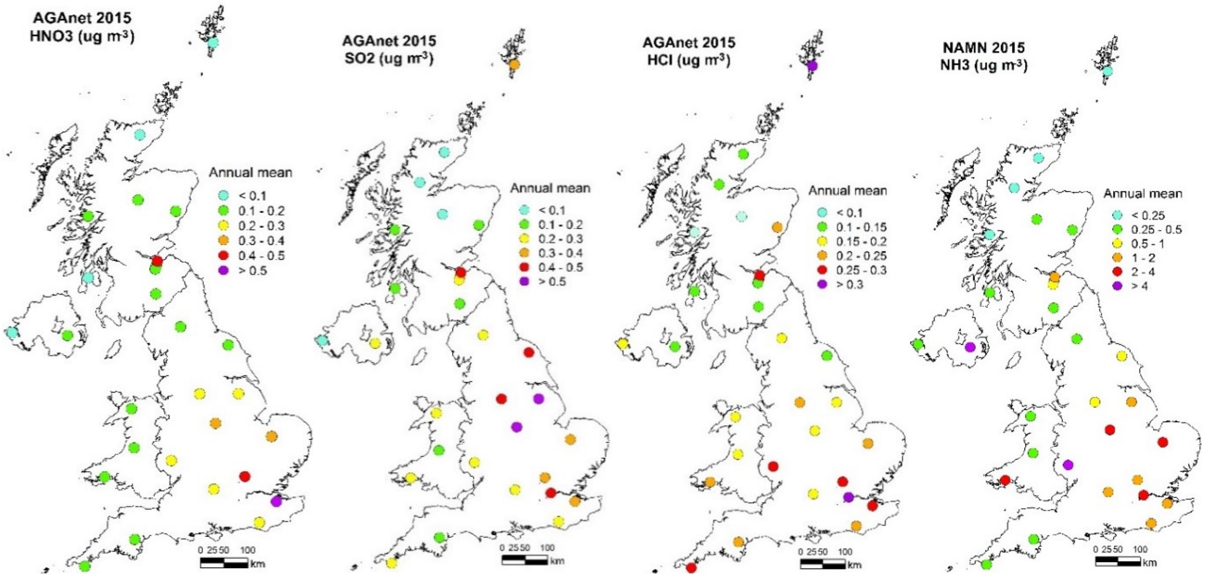

Figure 13 Annual mean monitored atmospheric reactive gas concentrations (HNO_3, SO_2, HCl from AGANet and NH_3 from NAMN) across the UK from annual averaged monthly measurements made in 2015. Note: S47 Rum = no data. S103 Goonhilly = two measurement data in January and December only. S101 Polloch (replaced S47 Rum in Oct 2015) = 3 months only (Oct-Dec15).

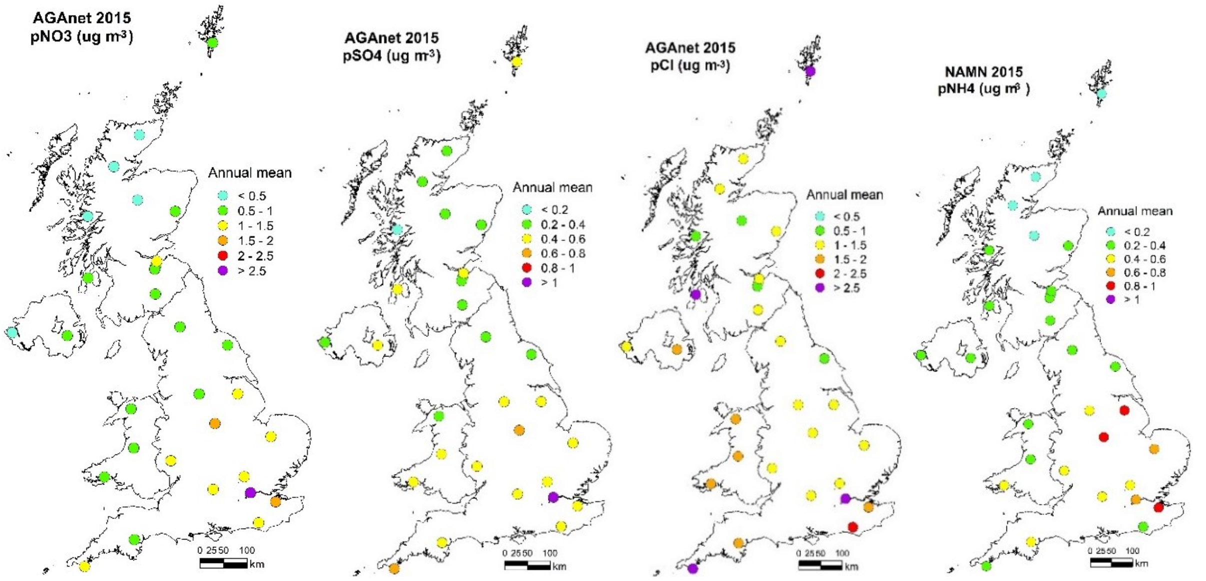

Figure 14: Annual mean monitored atmospheric aerosols (particulate NO_3^-, SO_4^{2-}, Cl^- from AGANet and NH_4^+ from NAMN) concentrations across the UK from averaged monthly measurements made in 2015. Note: S47 Rum site = no data. S103 Goonhilly = two measurement data in January and December only. S101 Polloch (replaced S47 Rum in Oct 2015) = 3 months only (Oct-Dec15).

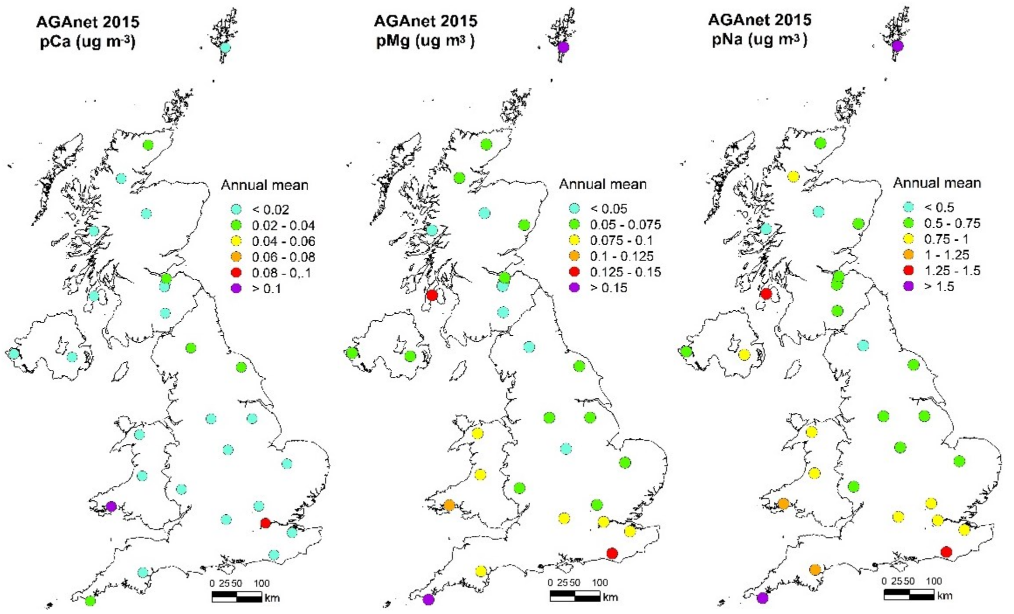

Figure 15: Annual mean monitored atmospheric base cation (Ca^{2+}, Mg^{2+} and Na^{+}) concentrations across the UK from the averaged monthly measurements made in 2015. Note: S47 Rum site = no data. S103 Goonhilly = two measurement data in January and December only. S101 Polloch (replaced S47 Rum in Oct 2015) = 3 months only (Oct-Dec15).

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-}.

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.

The long-term trends in gaseous HNO_3, SO_2, HCl and particulate NO_3^-, SO_4^{2-}, Cl^-, NH_4^+ (Figure 16) 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 2015. 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. Larger 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 0.27 µg SO_2 m^{-3} in 2015.

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, from an annual mean of 1.2 µg SO_4^{2-} m^{-3} in 2000 to 0.45 µg SO_4^{2-} m^{-3} in 2015.

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. For example, 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).

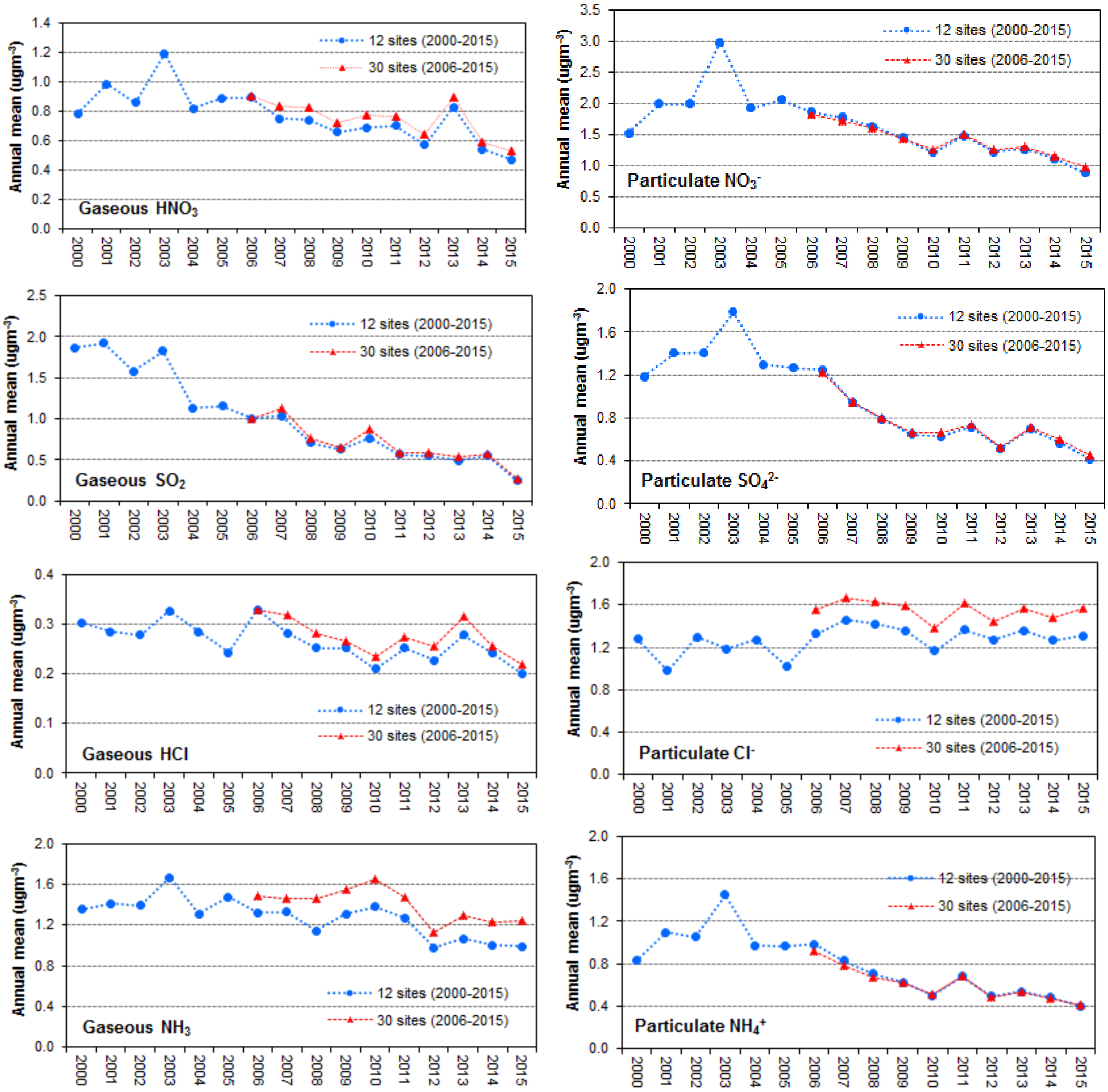

Figure 16: Long-term trend in annual mean concentrations of gases and aerosols monitored in AGANet. Each data point represents the averaged annual mean from all sites (increased from 12 to 30 sites since Jan 2006) and also the original l2 monitoring sites in the network. NAMN NH$_3$ data for AGANet sites are also shown, for comparison.

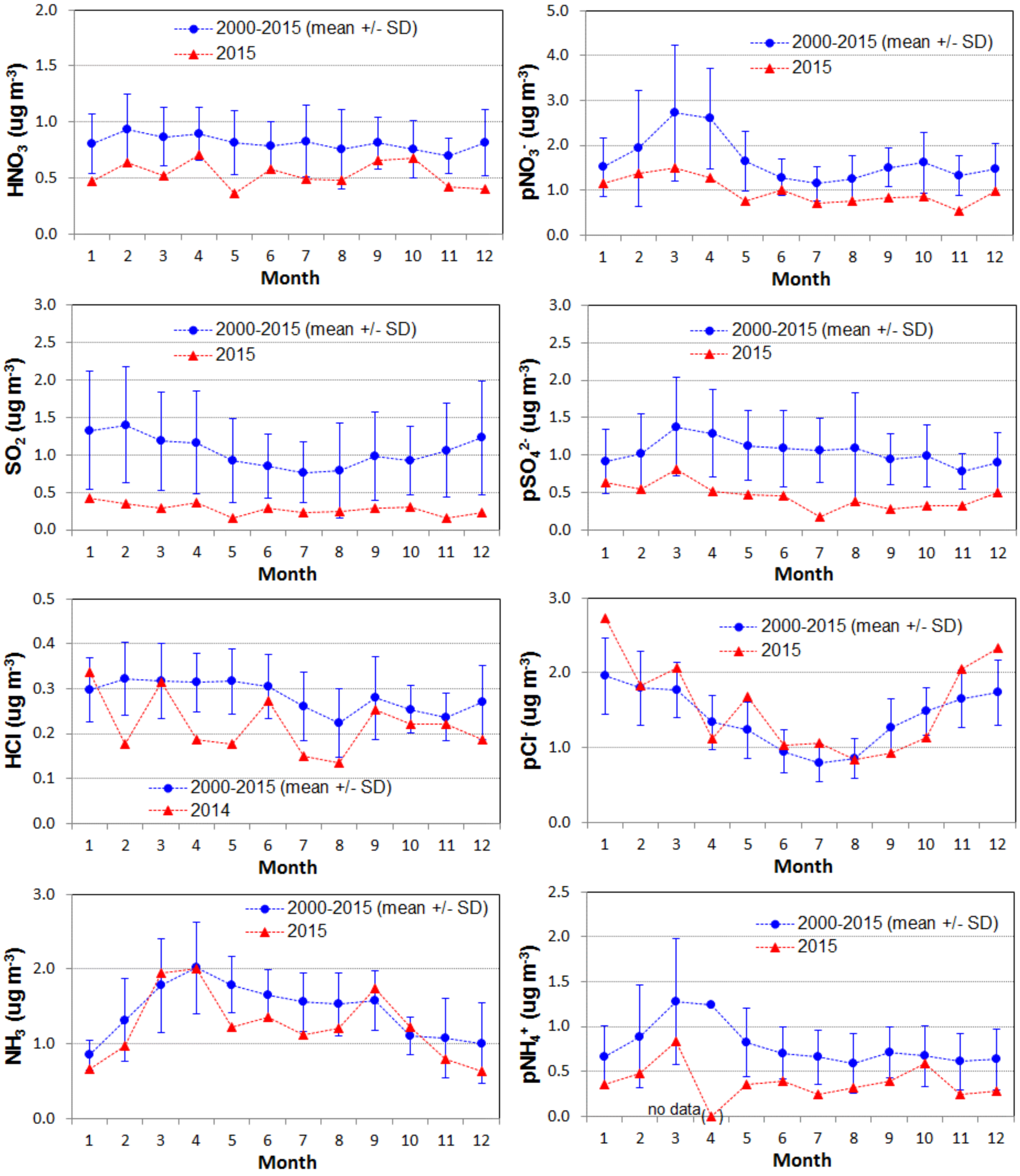

Figure 17: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (2000-2015: mean +/- SD of 30 AGANet sites) against year 2015.

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 2015 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 2015 are shown in Figure 18, 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 2015 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.

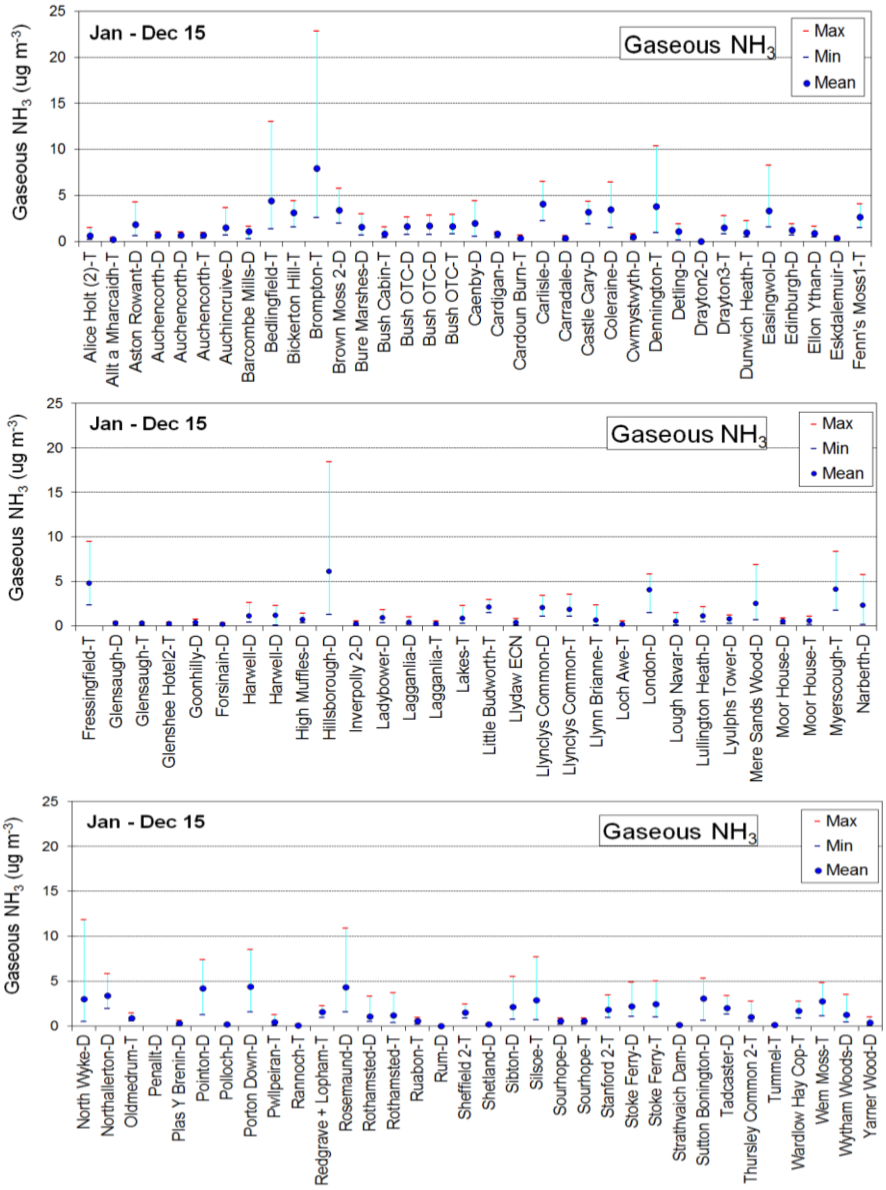

Figure 18: Annual mean monitored concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2015, whilst the bars show the minimum and maximum concentrations observed.

Table 2 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2015

Site Type	Number
DELTA sites sampling gaseous NH_3	53
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	40
Intercomparison sites with both DELTA & ALPHA	9
Total number of sites	84

NH_3 concentration data from NAMN over the period 1998 to 2015 is summarised in a box plot (Figure 19). 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 16% 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.

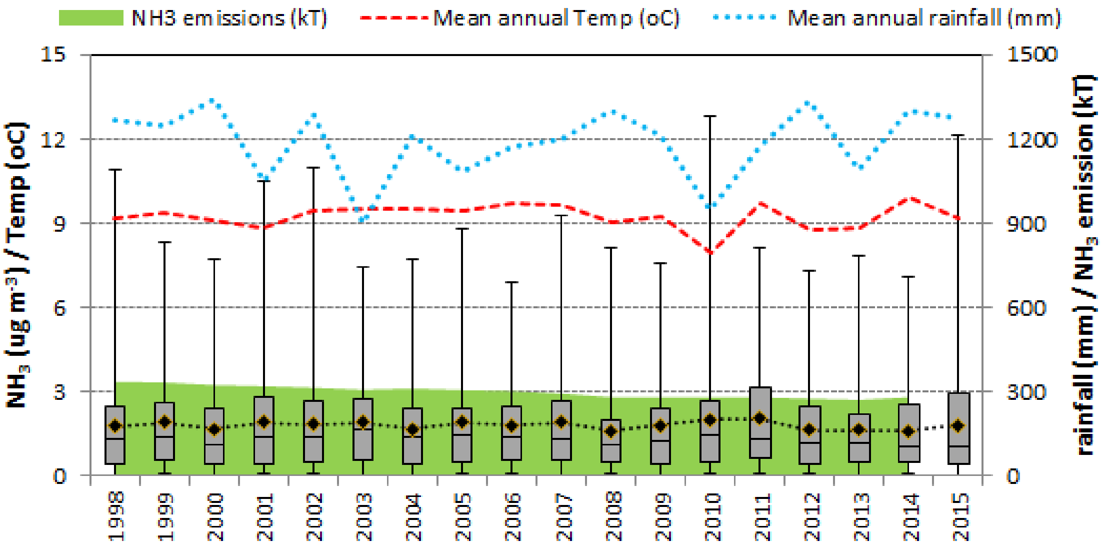

Figure 19: Changes in atmospheric NH_3 averaged over all sites in NAMN operational between 1998 and 2015 summarised in a box plot (sites with short runs excluded). The whiskers shows the absolute max and min and the diamonds is the mean annual concentration. Annual mean UK meteorological data (source http://www.metoffice.gov.uk/) are plotted 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 16 % over the period 1998 - 2014.

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 mesa-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 20) concentrations derived from the NAMN confirm the high spatial variability of NH_3 (0.06 – 7.9 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 0.12 (S41 Lagganlia) to highest of 0.93 (S40 Sutton Bonnington) 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 (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.

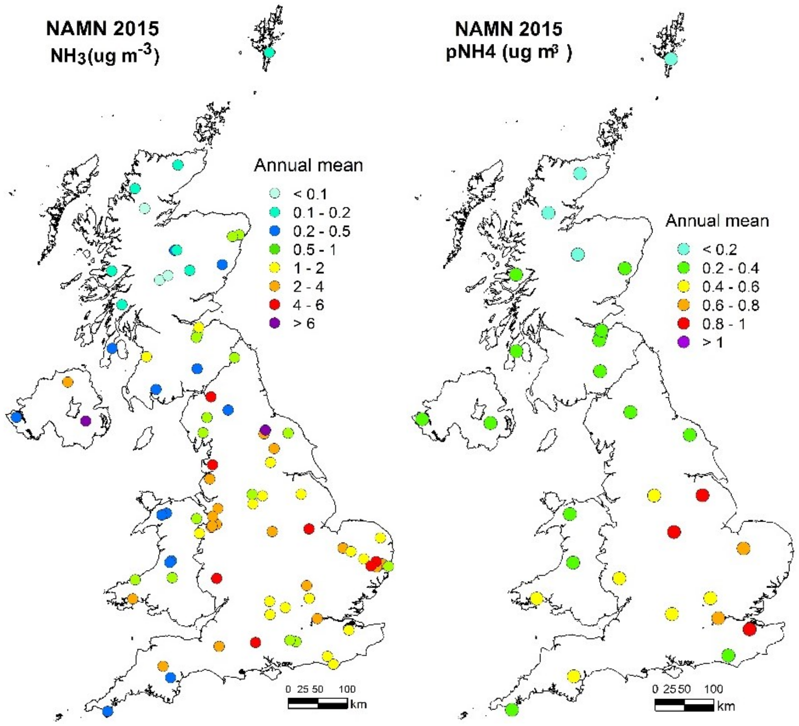

Figure 20: Spatial patterns of annual NH_3 and aerosol NH_4^+ concentrations from monthly NAMN/AGAnet measurements. Since Sep 2009, ammonium is measured at the 30 AGANet sites only.

The 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 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.

3. UK EMEP Supersites 2015 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 2015 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 Defra. This report summarises the measurements made between January and December 2015. 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): **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 2015

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 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*
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 (CEH)
Mercury in precipitation	X	X		Monthly	Heavy Metals	NPL (CEH)
Heavy metals in PM_{10}	X	X	II	Weekly	Heavy Metals	NPL (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]Ha: Harwell; Au: Auchencorth Moss; [2]NERC CEH National capability funded * NPL: National Physical Laboratory, Teddington, Middlesex. Changed to Ricardo 2016.

During 2015, 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 2015 more than 16 research outputs (papers or presentations) have been identified.

Table 4 Summary of other air quality measurements at Auchencorth Moss Supersite in 2015

Measurements	***Reason***	***Contact***	***Status of work***
ACTRIS II N intensive	Understanding N speciation in the atmosphere	Christine Braban	Poster presentation at EGU 2015 and project report
PTR measurements of isoprene	NERC Sandwich student biogenic VOCs study (continuation of 2014 measurements)	Ben Langford	Paper in preparation
Chamber flux measurement of N_2O and methane	EU FP7 research project (ECLAIRE) continuation of 2014 work	Eiko Nemitz	Measurements complete and report written.

3.1 Auchencorth

Overall data capture for 2015 was 65% for the trace gases and between 53 and 66% for the particulate mass components. This is a decrease in data capture compared to 2014 and was in particular due to two significant downtimes 1) Failure of cation IC motor which had to be sent to manufacturer for repair (16/04/15 – 06/05/16) 2) an electrical fault which required an engineer from the Netherlands to repair system, (19/08/15 - 23/10/15).

Tables 5-7 show the 2015 annual mean and % data capture for the PM_{10}, $PM_{2.5}$ 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 2015 Auchencorth Moss MARGA measurements (major species and trace gases) are shown in Figure 21, Figure 22 and Figure 23.

Table 5 Annual summary of trace gas mass concentration from the Auchencorth EMEP Supersite, 2015.

Trace gas	Annual mean (µg m^{-3})	Data capture (%)
NH_3	0.93	65
HCl	0.13	65
HNO_3	0.09	66
HNO_2	0.14	65
SO_2	0.18	65

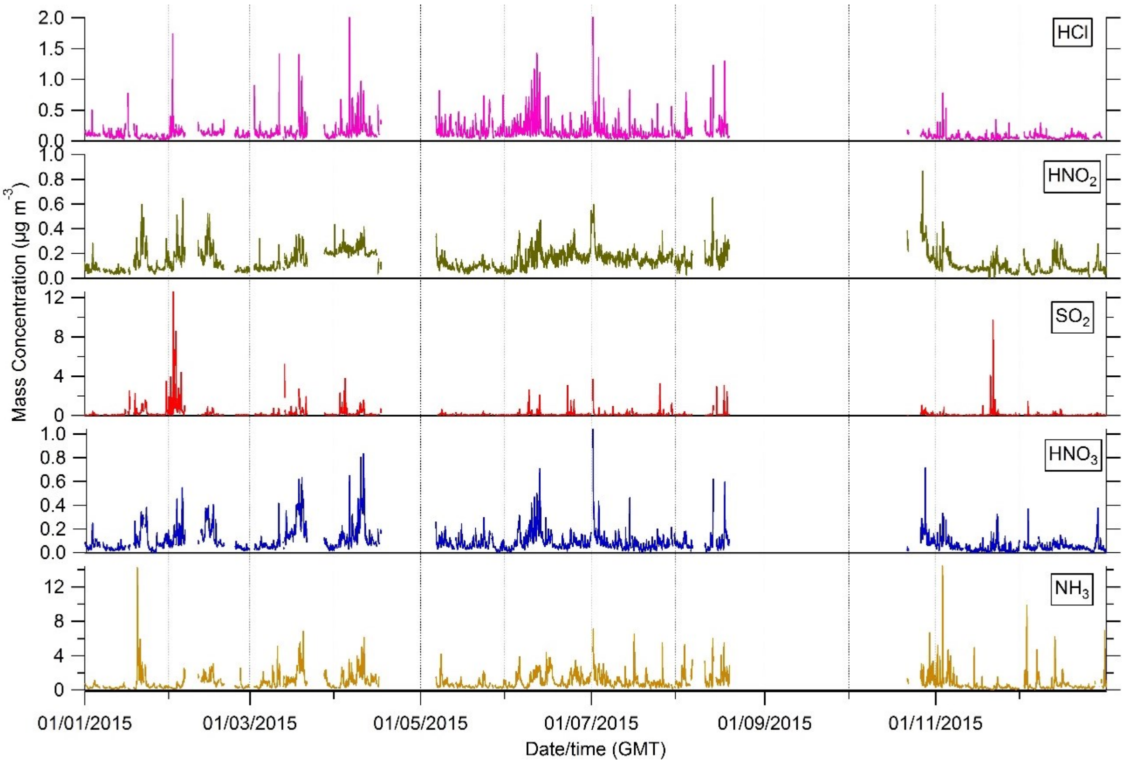

Figure 21 Ratified gas measurements from the MARGA instrument at Auchencorth Moss for 2015.

Table 6 Annual summary of the speciated PM_{10} mass concentration from the Auchencorth EMEP Supersite, 2015

Ion (PM_{10})	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	0.56	55
Na^+	0.60	56
K^+	0.04	56
Ca^{2+}	0.04	56
Mg^{2+}	0.07	56
Cl^-	1.19	65
NO_3^-	0.90	66
SO_4^{2-}	0.90	65

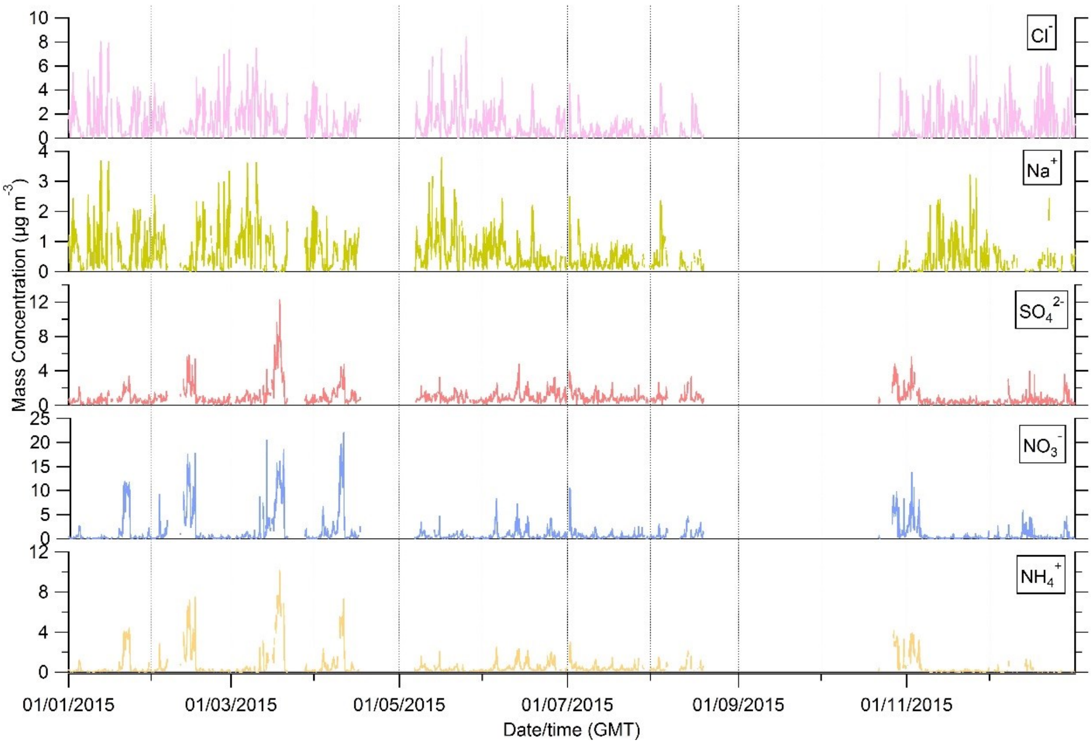

Figure 22 Ratified PM_{10} measurements from the MARGA instrument at Auchencorth Moss for 2015.

Table 7 Annual summary of the speciated PM2.5 mass concentration from the Auchencorth EMEP Supersite, 2015

Ion ($PM_{2.5}$)	Annual mean ($\mu g\ m^{-3}$)	Data capture (%)
NH_4^+	0.46	53
Na^+	0.33	53
K^+	0.02	53
Ca^{2+}	0.02	53
Mg^{2+}	0.04	53
Cl^-	0.63	61
NO_3^-	0.90	62
SO_4^{2-}	0.72	62

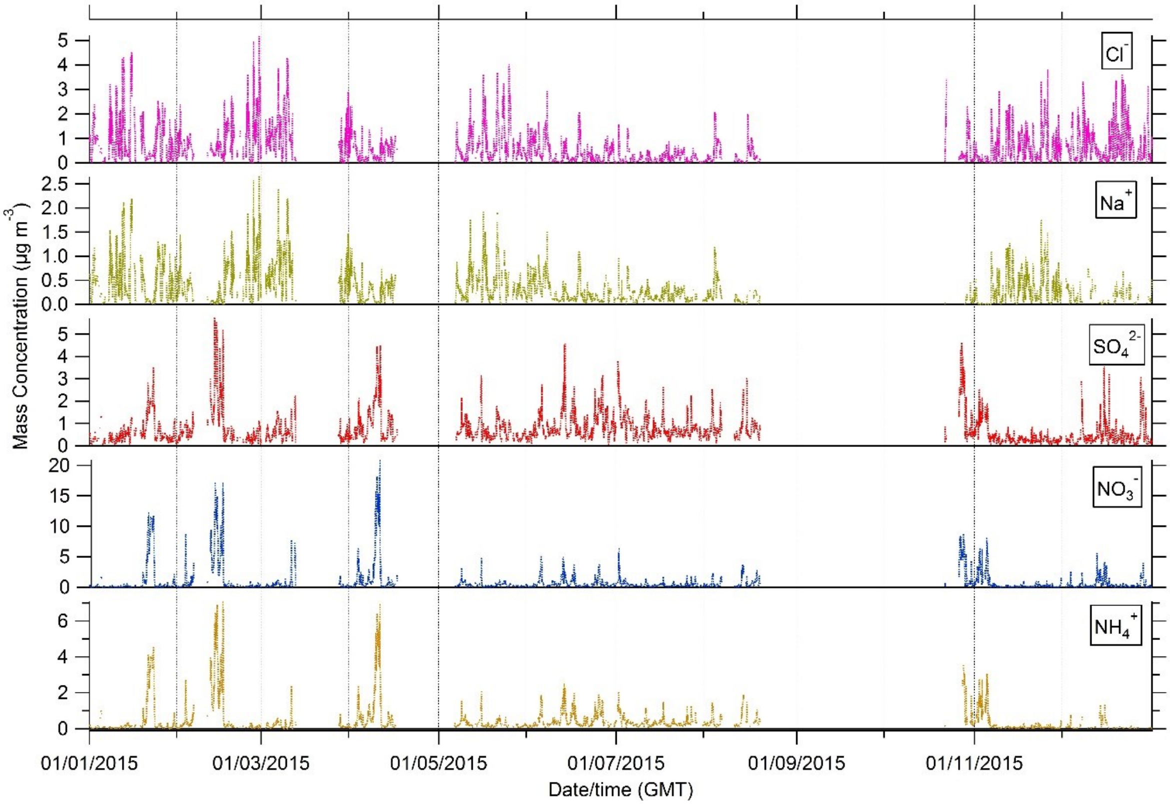

Figure 23 Ratified $PM_{2.5}$ measurements from the MARGA instrument at Auchencorth Moss for 2015.

The Auchencorth mercury measurements data capture was 56% for gaseous elemental mercury and 36% for the particulate bound and gaseous oxidized mercury. There were significant operational issues in 2015 with the gaseous elemental mercury measurement, which has a knock-on effect for the particulate bound and gaseous oxidized species. The Tekran 2537 analyser had prolonged stability issues at the start of the year, leading to a lower data capture. Table 8 shows the 2015 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 2015 Auchencorth Moss measurements are shown in Figure 24.

Table 8 Auchencorth mercury measurements 2015 data statistics

	Annual mean	Data capture
Gaseous elemental mercury	1.3093 n.m^{-3}	56.46%
Particulate bound mercury ($PM_{2.5}$)	2.8323 pg.m^{-3}	36.79%
Gaseous oxidised mercury	1.0557 pg.m^{-3}	36.69%

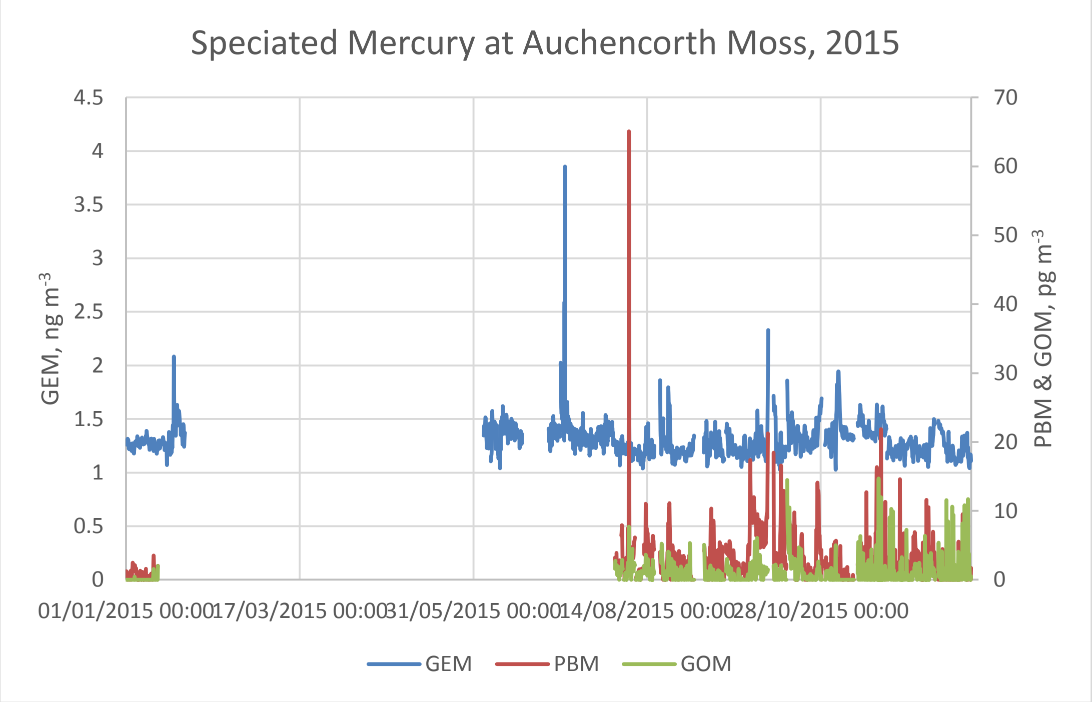

Figure 24 Auchencorth Moss 2015 gaseous elemental mercury (GEM), particulate bound mercury (PBM) and gaseous oxidised mercury (GOM).

3.2 Harwell

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 related due to redevelopment at the Harwell site and may not be considered 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 9-11 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 less than 33% of the measurement data was lost due to intermittent blockages and operational issues and there were significant operational issues in 2015. The main operational issue start on 2nd of September and lasted until the 10th November. The downtime was initially thought to be due to failure of cation pump however following its replacement and system restart it was found that the fault was also caused by a corroded cation detector. The cation detector was replaced and instrument was then put back to measurement mode.

The statistics presented are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2015 Harwell MARGA measurements (major species and trace gases) are shown in Figure 25, Figure 26, and Figure 27 below.

Table 9 Annual summary of trace gas mass concentration from the Harwell EMEP Supersite, 2015.

Trace gas	Annual mean (µg m^{-3})	Data capture (%)
NH_3	2.05	70
HCl	0.06	70
HNO_3	0.15	70
HNO_2	2.25	70
SO_2	1.31	70

Table 10 Annual summary of the speciated PM10 mass concentration from the Harwell EMEP Supersite, 2015.

Ion (PM_{10})	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	1.01	68
Na^+	0.98	68
K^+	0.09	68
Ca^{2+}	0.12	66
Mg^{2+}	0.13	68
Cl^-	1.41	68
NO_3^-	2.66	68
SO_4^{2-}	1.48	68

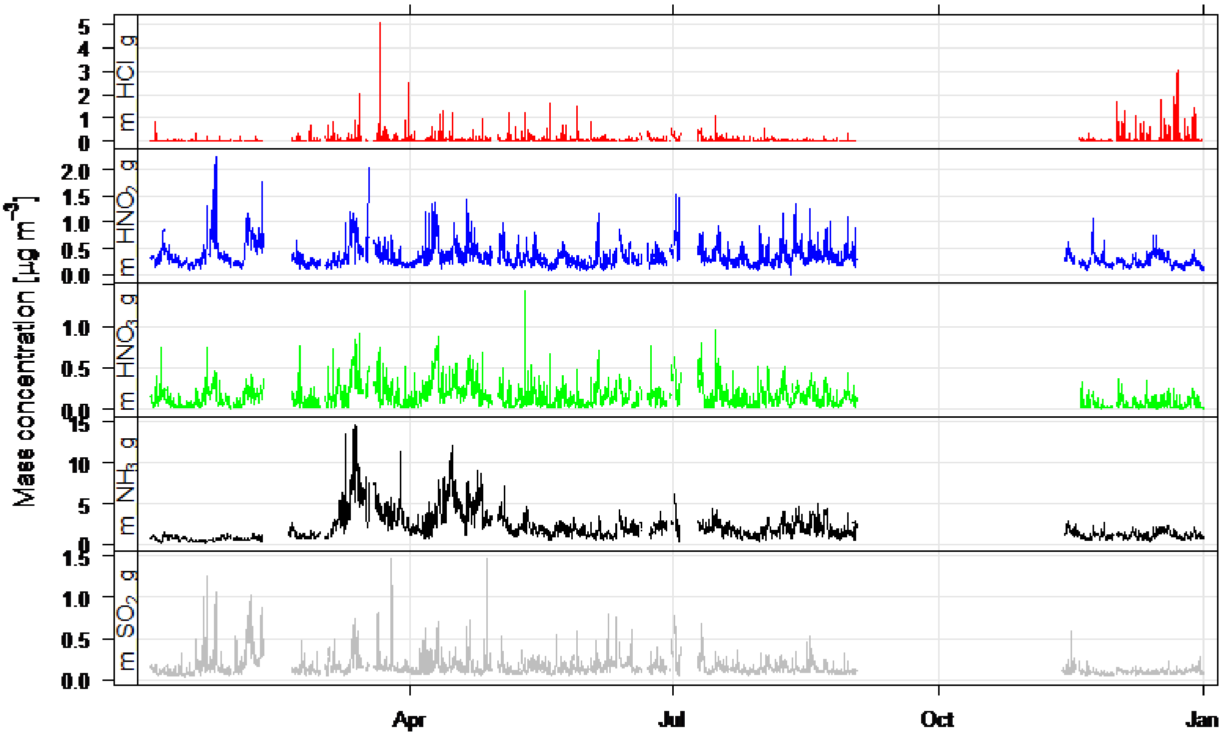

Figure 25 Time series plot of the trace gas (HCl, HNO$_2$, HNO$_3$, NH$_3$, SO$_2$) measurements from the Harwell MARGA, 2015.

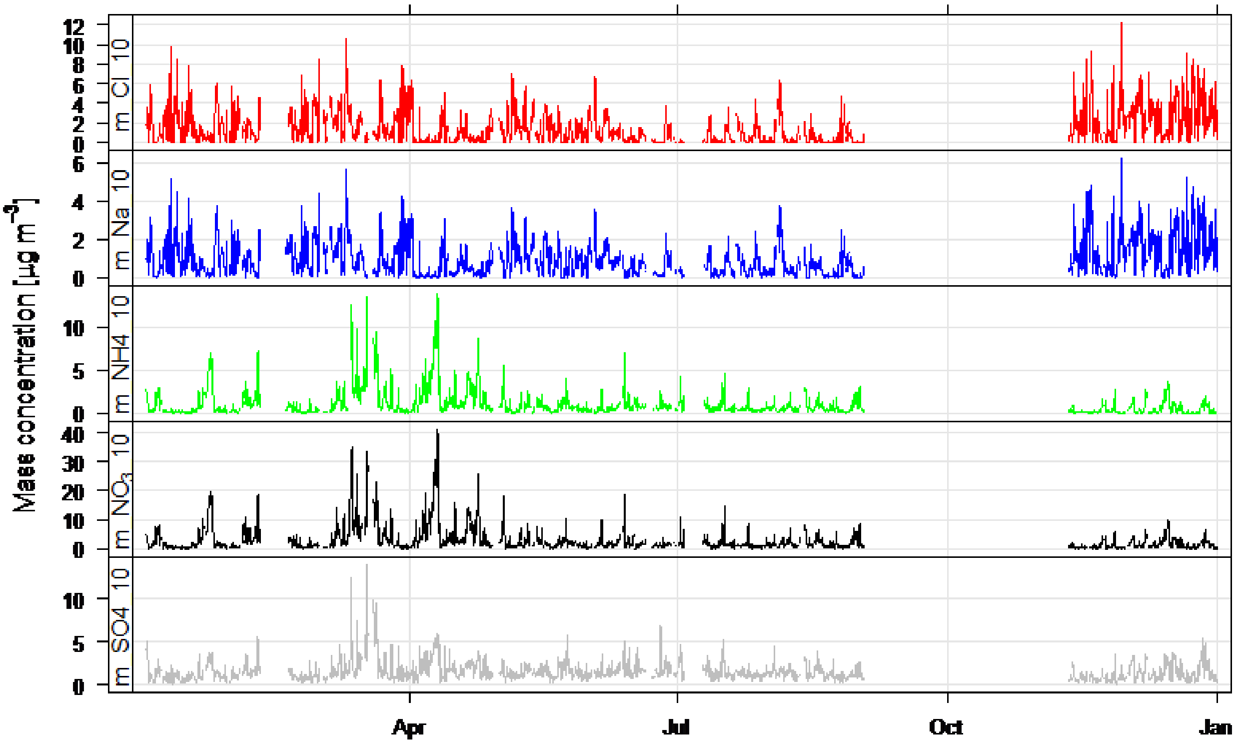

Figure 26 Time series plot of the major PM10 species (Cl-, Na+, NH4+, NO3-, and SO42-) measurements from the Harwell MARGA, 2015. Base cation species (Ca2+, Mg2+ and K+) measurements not shown.

Table 11 Annual summary of the speciated PM2.5 mass concentration from the Harwell EMEP Supersite, 2015.

Ion ($PM_{2.5}$)	Annual mean (μg m^{-3})	Data capture (%)
NH_4^+	1.25	67
Na^+	0.56	69
K^+	0.06	69
Ca^{2+}	0.04	69
Mg^{2+}	0.08	69
Cl^-	0.80	69
NO_3^-	2.26	69
SO_4^{2-}	1.32	69

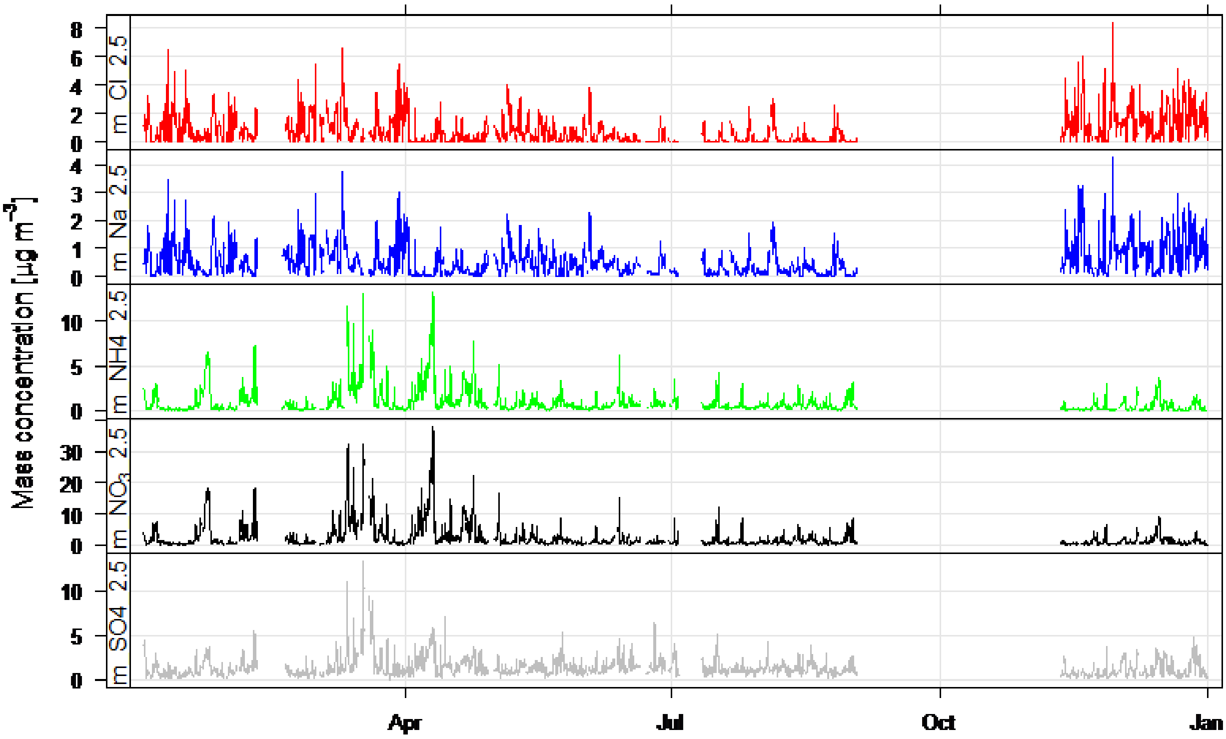

Figure 27 Time series plot of the major PM2.5 species (Cl-, Na+, NH4+, NO3-, and SO42-) measurements from the Harwell MARGA, 2015. Base cation species (Ca2+, Mg2+ and K+) measurements not shown.

Typical meteorological parameters are measured at the Harwell EMEP Supersite. The 2015 annual means and data captures are summarised in Table 12. Data capture for the parameters measured was typically above 97% except for dew point which had a slightly lower data capture of 90%.

Table 12 2015 Summary of the Harwell EMEP Supersite meteorological observations

Meteorological parameter	**Annual mean**	**Data capture (%)**
Barometric pressure (mbar)	1001	100%
Dew point (°C)	8	78%
Wind direction (°)	158	100%
Wind speed (m s-1)	3	100%
Relative humidity (%)	80	90%
Temperature (°C)	10	100%
Meteorological parameter	Total	Data capture (%)
Rainfall (mm)	571.8	90%

Mast measurements of the 10 m wind speed (U10) and directional frequency were performed at the Harwell EMEP Supersite during 2015. Figure 28 shows a plot of the directional frequency (in 10° sectors) for 2015. 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 28, and maximums of up to 13 m s^{-1}. Figure 29 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).

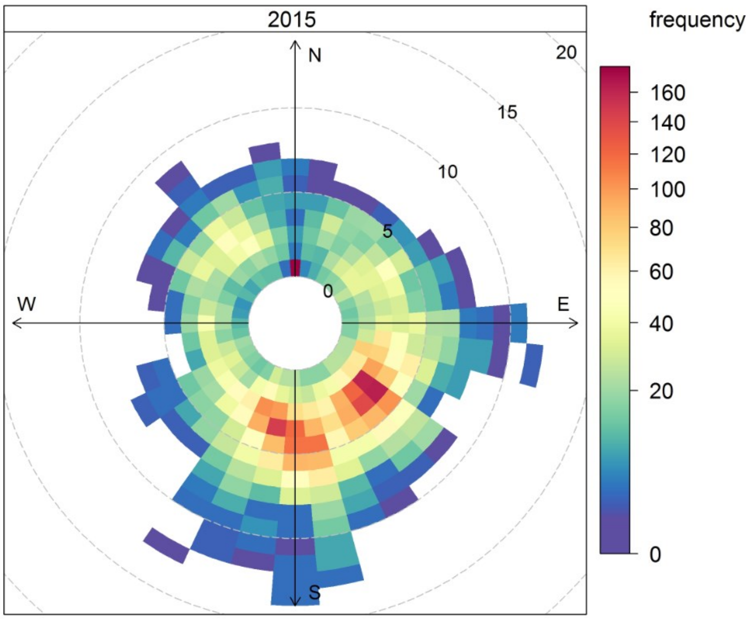

Figure 28 Wind speed (m s^{-1}) and directional frequency for the Harwell EMEP Supersite, 2015.

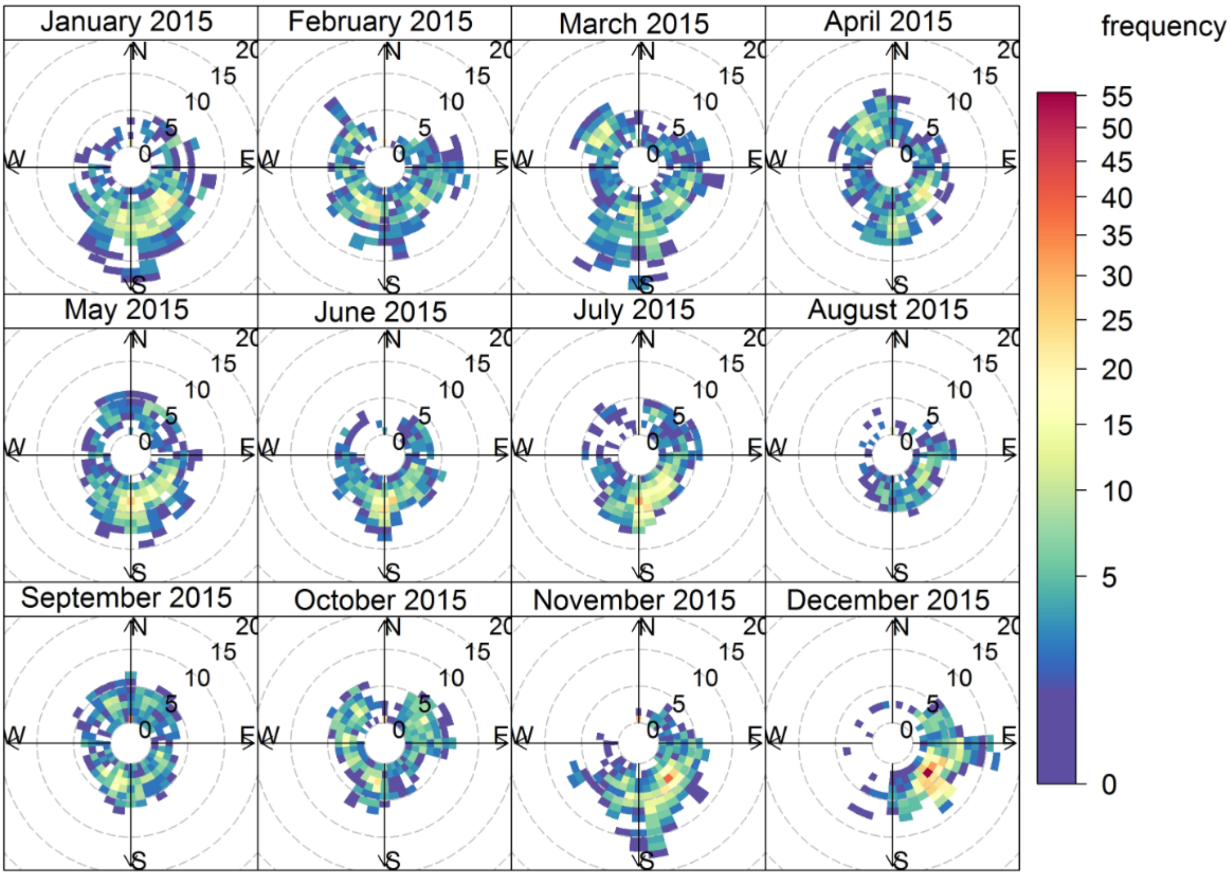

Figure 29 Monthly variations of hourly wind speed and directional frequency for the Harwell EMEP Supersite, 2015.

Mercury measurements

There were some operational issues in 2015 with the Tekran total gaseous mercury measurement. The Tekran analyser unit required repair by CEH at the CEH laboratories, leading to a lower data capture. Table 13 shows the 2015 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 2015 data is shown in Figure 30.

Table 13 Harwell mercury measurements 2015 data statistics

	Annual mean	Data capture
total gaseous mercury	1.8898 ng.m^{-3}	31.31%

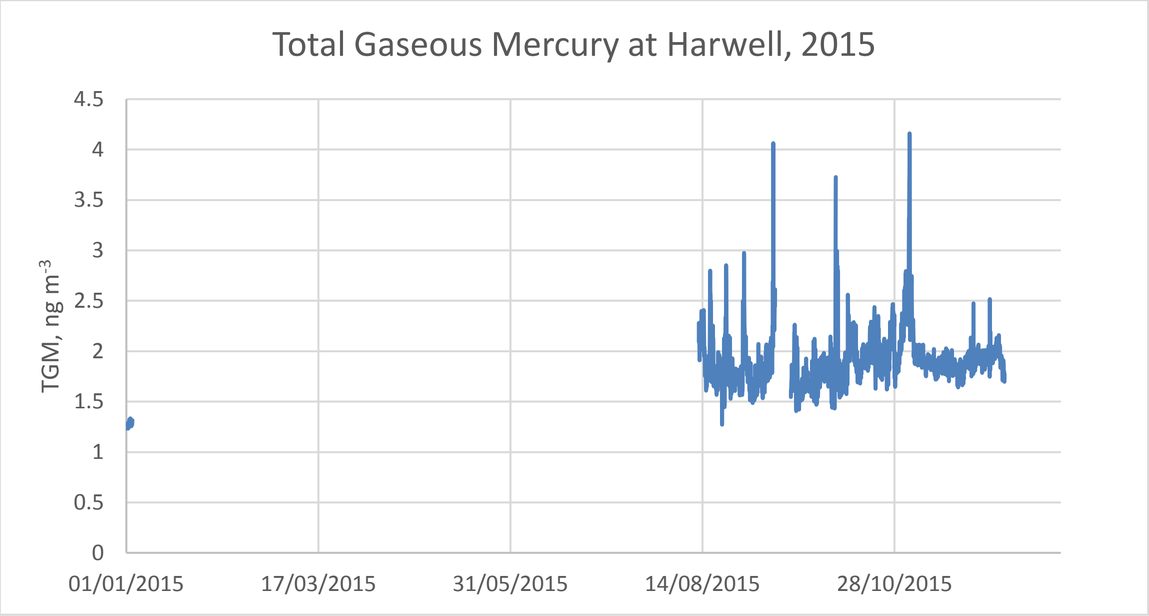

Figure 30 Harwell 2015 total gaseous mercury time series.

3. UKEAP Air Quality Case studies 2015

4.1 Fluoride in UK rain: Supersite Data

Headlines:

- Fluoride deposition occurs at low levels at UK Supersites.
- UK background established.
- On-going measurements allow background trends to be monitored and future assessment of volcano plume deposition to be quantified.

Acidic precipitation was a significant problem in Western Europe during the twentieth century with the acidity being anthropogenically driven. It continues to be an issue in many parts of the world with oxidised sulphur and nitrogen pollution dominating the inorganic components of precipitation. Both the acidity and the input of nutrients into ecosystems through dry and wet deposition are recognised as threats to ecosystems (Cape et al., 2003). Fluoride emission sources into the environment include brick kilns, aluminium and zinc smelters e.g. recent literature examples (Bhat et al., 2015; Talovskaya et al., 2015), the car wash industry (Genuino et al., 2012) and long term degradation of fluoride containing- hydrocarbons. Natural sources of hydrogen fluoride (HF) include volcanoes, both through passive degassing and eruptive emissions (Bellomo et al., 2007).

Fluoride was not routinely measured in UK precipitation before the 2010 Icelandic volcano eruption and during both the Ejyafjallajokul and Grimsvotn volcanic eruptions in 2010 and 2011 it was identified that there was only sparse data on the background variation of fluoride in UK precipitation therefore it was not possible to clearly identify any volcanic signal in rain samples taken during an eruption period. The absence of baseline data meant that background levels and variation due to the presence of either natural or anthropogenic sources were unknown.

From January 2012 fluoride in daily precipitation has been analysed along with the standard suite of inorganic ions and cations at the two European Monitoring and Evaluation Programme (EMEP) UK Supersites. Auchencorth Moss is in southern Scotland and it rains ~50-60% days per year and ~1000 mm per annum, whereas Harwell in south-central England has precipitation 40-50% of the days in a year and ~800 mm rain. The first three years of DWOC fluoride data from Harwell and Auchencorth has been summarised and an initial assessment of the origins of the observed fluoride attempted.

The daily wet only precipitation collectors (NSA 181/S Eigenbrodt, Germany) operated at Harwell and Auchencorth catch only the wet precipitation. This is in contrast to bulk samplers, which collect both the wet deposition and the dry deposits (e.g. dust). The precipitation collector is equipped with a cover lid opened only during deposition. When opening the cover the funnel lid rises, turns to the side and sets down so the lid is not in the scatter field. The collected precipitation flows from the funnel down a pipe into a collecting bottle. When precipitation has ceased and after evaporation of the sensor surface the funnel lid closes automatically. The adjustable, controlled heating of the funnel reduces the possibility of freezing precipitation in the funnel. There is a controlled heating inside the sample room installed to keep the sample from freezing.

At Harwell and Auchencorth between 2012 and 2014, there were 135 and 107 days when F^- concentrations were above the LOD. Fluoride deposition over the period 2012-2104 was in the range 3- 7.5 $mg.m^{-2}$ and was similar at both sites. Intermittent periods of elevated fluoride were observed and back trajectory analysis indicates that the higher concentrations are observed in air masses which have spent more time over land rather than the air masses which have a predominantly marine history (cluster analysis available in full report).

Overall it is an economic addition to the DWOC samplers' analytes and provides robust long term measurements against which to assess impacts of any future volcanic plume deposition. It also allows there to be a long term up to date method which can be applied to the wider bulk network should that be required in an event-driven responsive mode.

Table 14 Summary statistics for 3 years measurements of fluoride at Auchencorth and Harwell, UK

				Concentration *($mg.l^{-1}$ unless otherwise stated)*				**Deposition** *($mg.m^{-2}$)*		
	Year	N	% days	Vol weighted Mean [F^-]	SD	[F^-] ($\mu eq.l^{-1}$)	Max	Mean	SD	Annual Total
Auchencorth	2012	226	62	0.007	0.041	0.351	0.277	0.032	0.041	7.132
	2013	178	49	0.007	0.092	0.351	1.193	0.027	0.140	4.806
	2014	204	56	0.004	0.027	0.234	0.383	0.019	0.032	3.784
Harwell	2012	162	44	0.010	0.053	0.504	0.577	0.047	0.093	7.587
	2013	146	40	0.004	0.009	0.182	0.086	0.013	0.051	1.955
	2014	183	50	0.004	0.006	0.206	0.072	0.016	0.022	2.932

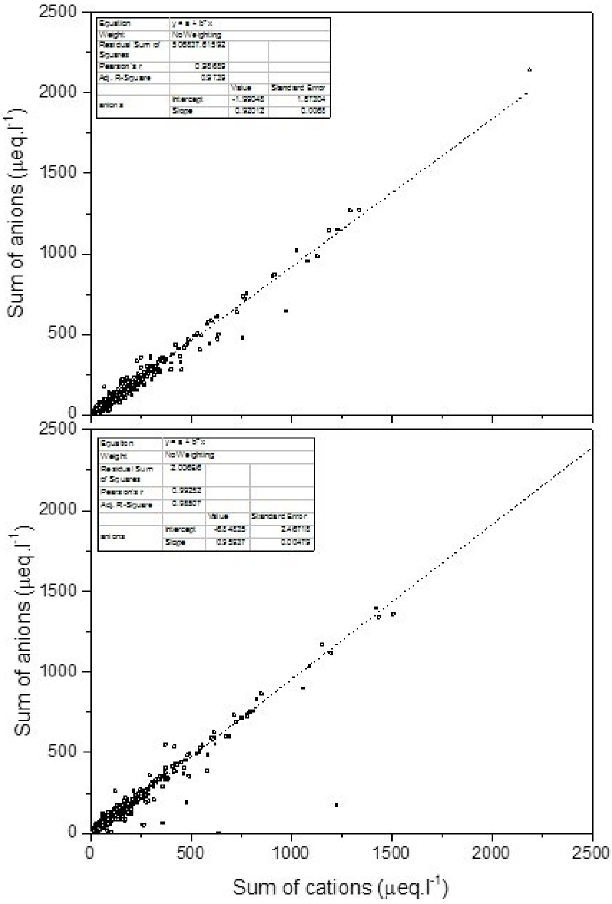

Figure 31: Ion balance for 2012-2014 DWOC precipitation. Upper panel: Harwell; Lower panel: Auchencorth. Dotted line represents unweighted liner regression

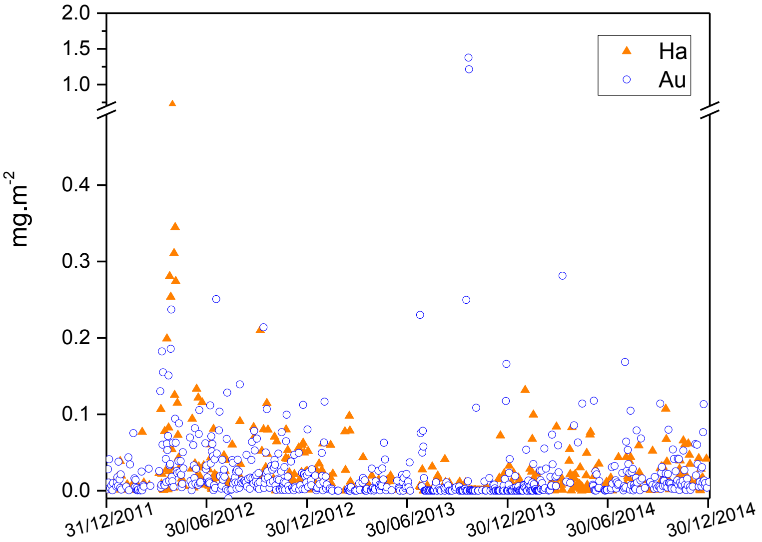

Figure 32 Daily fluoride deposition in precipitation for 2012-2014.Harwell (orange triangle); Auchencorth Moss (blue circle)

4.2 UKEAP Fluoride Intercomparison Summary

(Full report submitted to Defra, Prof Alan Davison lead author)

NERC Centre for Ecology and Hydrology and Prof Alan Davison have coordinated a laboratory intercomparison of fluoride measurements in vegetation and other substrates. The requirement was to assess capabilities and standards in the UK for such work which would be required in the event of a fluoride deposition event, such as is possible subsequent to an Icelandic volcano eruption. UK Environment Agencies and Universities were contacted for participation in the intercomparison. This exercise identified that there is very limited capability in this area and with these methodologies in the UK with only NERC CEH and SEPA having capability for this type of analysis. Several overseas laboratories also took part in the exercise.
Plant and mineral samples were sourced from areas with known fluoride emission sources (e.g. near aluminium smelters). In collaboration with the NMI Laboratory, Iceland, all samples were analysed for fluoride content. Ten samples were selected to be used in the intercomparison, covering a range of fluoride concentrations and different sample matrices. These selected samples were sent “blind” to the participating laboratories.

Results from the analyses together with details of the methodology used by individual laboratories were returned to Prof Davison. Overall, results indicated a sufficiently good level of agreement between laboratories compared to previous fluoride in vegetation studies with most results with z<2 from the ensemble mean (Figure 33). The study has clearly shown that an acid extraction method is suitable for monitoring fluoride deposition onto vegetation and other matrices. Within the results there is still variability which is inherent in the method and matrices involved. This indicates that on-going quality control both within laboratories and between laboratories, is important to maintain standards and confidence in results. The results from the seven laboratories (out of nine) which have reported results are summarised in Figure 1 and the z score for each measurement summarised in Table 2. Due to the relatively small sample population, no outliers were removed. All measurements, with the exception of 2 have a z score of 2 or less. Note, individual ratings should be used cautiously as the system is relative to a consensus mean and the data collection may not be normally distributed.

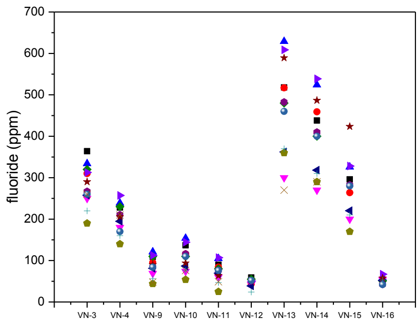

Figure 33 Fluoride concentrations for 10 intercomparison samples. All data using all methods are shown.

Outcomes

1. Fluoride analysis methods are needed when regulators and policy makers need to assess fluoride in the environment after a natural or anthropogenic event where fluoride is likely to have been emitted into the environment and deposited on vegetation (crops or semi-natural vegetation) or other surfaces.
2. This study has facilitated an updating of methods used in the UK and overseas

4.3 DEnuder for Long-Term Atmospheric sampling (DELTA) sampler tests

Headline: AGANet DELTA sampler study published in 2015 is summarised.

Report available at: https://uk-air.defra.gov.uk/library/reports?report_id=861

- The **DE**nuder for **L**ong-**T**erm **A**tmospheric sampling (DELTA) system is a sampler developed for low-cost measurements of: acid gases: hydrochloric acid, sulphur dioxide, nitric acid and nitrous acid (HCl, SO_2, HNO_3, HONO respectively) on two potassium carbonate (K_2CO_3)-glycerol coated denuders; ammonia (NH_3) on two citric acid denuders; inorganic anions & cations (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, Ca^{2+}) on a K_2CO_3-glycerol impregnated filter; ammonium (NH_4^+) on a citric acid impregnated filter
- The DELTA sampler is currently deployed in the Acid Gas and Aerosol Network (AGANet) across the UK at 30 sites for the purpose of measuring the UK-scale distribution of concentrations and the long-term trends.
- DELTA samplers were developed for ammonia sampling and then extended to other components. Tests in Defra project AC0103 have shown that the DELTAs sample the $PM_{4.5}$ fraction.
- Concerns were discussed regarding potential artefacts from NO_y species (NO_2, HONO, N_2O_5, PANs, $ClNO_2$ and other oxidised nitrogen species) collected on the K_2CO_3-glycerol denuders and biases in the methodology; therefore a series of test were initiated, prior to the DELTA sampler upgrade.
- Specifically these covered the following: specificity of the HNO_3 measurement, loss of particulate to connecting tube in sampling train, performance of the filter pack configuration and further tests were carried out by NERC CEH to assess alternative coatings for the denuders

Key conclusions

Specificity of the HNO_3 measurement:

- The K_2CO_3-glycerol coated denuders have significant interferences in the HNO_3 measurement from other oxidised nitrogen species except NO_2. The interference dominating measured concentrations in the urban DELTA system
- Results from parallel sampling (NaCl denuders vs K_2CO_3-glycerol denuder) showed the following average ratios: urban NaCl: K_2CO_3-glycerol denuder ratio = 0.21 (London Cromwell Road), non-urban sites = 0.44±0.15 (4 sites)
- There are many unknowns for the interfering chemical species, including ambient concentration variation, deposition velocities and possible bi-directionalities in fluxes
- K_2CO_3-glycerol denuders are quantitative for SO_2 and HCl gas measurements
- NaCl and KF denuders were tested; NaCl is the most specific for HNO_3 but is not quantitative for SO_2 and HCl measurements are not possible. KF coating gave similar results as K_2CO_3-glycerol.
- Two NaCl denuders followed by a K_2CO_3-glycerol denuder captures $HN0_3$ quantitatively on the NaCl and other reactive-nitrate forming species on the K_2CO_3-glycerol, however this configuration is not suitable to measure HCl.

Loss of particulate to sampler connecting tube in sampling train:

- NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+} aerosol losses to LDPE connecting tube in sampling train are relatively small, on average being < 7% of the total aerosol ion concentration.
- Ca^{2+} measurements had a high uncertainty due to variability in LDPE blanks & low concentrations
- The new DELTA II design is linear, eliminating the use of the LDPE connecting tube.

Performance of the filter pack configuration:

- To test the particulate capture, all ions were analysed on both the K_2CO_3-glycerol and acidic filters plus a PTFE filter was introduced between the two filters to measure breakthrough from the first filter.
- Analysis of the K_2CO_3-glycerol coated filters showed negligible amounts of NH_4^+ are retained.
- A sampling efficiency for the accumulation mode of about 71% for SO_4^{2-} and fine NO_3^- and of about 89% for NH_4^+ was measured, with close to quantitative measurement of Na^+, Cl^- and Mg^{2+} on the K_2CO_3-glycerol filter
- The 2µm porosity PTFE membrane quantitatively captures the SO_4^{2-} and NO_3^- PM components therefore this approach is suitable with an acid coated filter after the Teflon to capture NH_4

Future sampling recommendations

HNO_3/gas phase oxidised nitrogen measurement

Four possible options were examined: Continuation with the current configuration, change to a three stage denuder train: (NaCl –NaCl – K_2CO_3-glycerol), continue with the current configuration but add a parallel (NaCl or K_2CO_3-glycerol) denuder at selected sites, assess alternative methods *e.g.* shift to on-line high resolution instrumentation.

The second option (option B in the report) was recommended as the most cost-effect future sampling method. However HCl measurements will be discontinued with this option. NaCl denuders provided the best available quantitative measure of HNO_3 from the results found in the parallel experiments. Adding the final K_2CO_3-glycerol denuder allows quantitative measurement of SO_2, a key measurement of the DELTA samplers in AGANet and the “total nitrate” measurement to be maintained.

Connecting tube:

- No issue was found with the LDPE connecting tubing, apart from Ca.
- The new DELTA II is in a linear configuration, eliminating the use of the LDPE connecting tube.

Filter pack configuration It is proposed to change to a three-stage filter pack: PTFE-nylon-acid coated, which is the same configuration as used by the US EPA.

Implications for historic data

HNO_3/gas phase oxidised nitrogen measurement: Discussions between the experimental team and pollutant deposition modellers were undertaken as to how to adjust for the over-reporting of HNO_3 concentrations. It was recommended that a correction factor of 0.45 be applied to the historic HNO_3 measurements. The range of ratios was 0.44±0.15 (±2SD), i.e. 0.29-0.59, therefore it is reasonably likely that the value lies between 0.4 and 0.5. Therefore a correction factor of 0.45 should be applied. Historic measurements of SO_2 and HCl from K_2CO_3-glycerol coated denuders do not need correction.

The sulphate and nitrate datasets should be historically corrected. However it is primarily important to correct appropriately. It is recommended that an assessment of the best method and any further specific tests for concentration effects be carried out before a historic data correction is applied. The dataset from the parallel measurements can be used to provide an interim correction.

Acknowledgements

NERC CEH and Ricardo Energy & Environment gratefully appreciate the help and support of all the UKEAP Local Site Operators who change the samples and return them to the laboratories every month of every year!

The leadership of the late Professor Alan Davison was much appreciated in undertaking the fluoride intercomparison and the work will be written up for peer review for him. His death is a great loss to the fluoride science in the UK.

5. References

Fagerli, H., Schulz, M., Gauss, M., Tsyro, S., Jonson, J.E., Bebedictow, A., Simpson, D., Valdebenito, A., Griesfeller, J., Semeena, V.S., Wind, P., Olivie, D., Aas, W., Hjellebrekke, A.-G., Solberg, S., Torseth, K., Espen Yttri, K., Mareckova, K., Alastuey, A., Hamburger, T., Posch, M. & Tuovinen, J.P. (2014) Transboundary particulate matter, photo-oxidants, acidifying and eutrophying components, . In: *EMEP Status Report 2014, Joint MSC-W & CCC & CEIP Report* Meteorlogisk Institut, Norway.

Fournier N, Pais VA, Sutton MA, Weston KJ, Dragosits U, Tang YS & Aherne J (2002) Parallelisation and application of a multi-layer atmospheric transport model to quantify dispersion and deposition of ammonia over the British Isles. *Environmental Pollution*, 116, 95-107.

Sutton MA, Tang YS, Miners B & Fowler D (2001) A new diffusion denuder system for long-term, regional monitoring of atmospheric ammonia and ammonium. Water, Air and Soil Pollution: Focus, 1, Part 5/6, 145-156.

Tang YS, Simmons I ,van Dijk N, Di Marco C, Nemitz E, Dämmgen U, Gilke K, Djuricic V, Vidic S, Gliha Z, Borovecki D, Mitosinkova M, Hanssen JE, Uggerud TH, Sanz MJ, Sanz P, Chorda JV, Flechard CR, Fauvel Y, Ferm M, Perrino C & Sutton MA (2009) European scale application of atmospheric reactive nitrogen measurements in a low-cost approach to infer dry deposition fluxes. Agriculture, Ecosystems and Environment: NitroEurope Special issue. (133), 183-195.

Tang YS. & Sutton MA (2003) Quality management in the UK National Ammonia Monitoring Network. In: Proceedings of the International Conference "QA/QC in the field of Emission and Air Quality Measurements" 21 – 23 May 2003, Prague (CZ).

Twigg, MM; S.R. Leeson, Y.S. Tang, E. Ilyinskaya, S. Loughlin, R.I. Smith, J. Poskitt, S. Ritchie, J. Lingard, D. Green, A. Richter, M. Vieno, B. Langford, E. Nemitz and C.F. Braban (in prep.). Impact of the 2014-2015 Bárðarbunga volcano (Holuhraun) eruption on the UK atmosphere.

Vieno, M.; Heal, M.R.;Twigg, M. M; MacKenzie, I.A; Braban, C.F; Lingard, J; Ritchie, S.; Beck, R.; Moring, A.; Ots, R.; Di Marco; C. Nemitz, E.; and Reis, S. (submitted to Environmental Research Letters October 2015.) The UK particulate matter air pollution episode of March-April 2014: more than Saharan dust

Vieno, M.; Heal, M.R.; Hallsworth, S.; Famulari, D.; Doherty, R.M.; Dore, A.J.; Tang, Y.S.; Braban, C.F.; Leaver, D.; Sutton, M.A.; Reis, S.. 2014 The role of long-range transport and domestic emissions in determining atmospheric secondary inorganic particle concentrations across the UK. *Atmospheric Chemistry and Physics*, 14 (16). 8435-8447. 10.5194/acp-14-8435-2014

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: Mr Chris Conolly, Ricardo-AEA

Lingard, J., Ritchie, S., Sanocka, A., 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., 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-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**)

Mercury and NOx measurements: 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 2015

Harwell operations

2015 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 2015 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. 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. The MARGA made continuous measurements of the chemical composition of PM_{10} and $PM_{2.5}$ throughout 2015.

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 2015 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† 320*	294000 281	8% 12%
Q2			320000† 320*	282000 276	12% 14%
Q3			320000† 320*	293000 291	8% 9%
Q4			320000† 320*	283000 264	12% 18%
Q1	IC	Br^-	3680† 3.68*	3830 3.46	4% 6%
Q2			3680† 3.68*	2900 3.43	21% 7%
Q3			3680† 3.68*	3600 3.89	2% 6%
Q4			3680† 3.68*	3150 2.99	14% 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_2O_2 for 10 minute in an ultrasonic bath **							x		
2x clean WRD **							x		
clean or change all Teflon tubing 1/16" boxes**								x	
2x change guard column: 1 anion, 1 cation (+filters if dirty)			x						
1x change anion IC column if necessary ****				x		x			
1x change cation IC column if necessary ****						x			
1 x change cation pre-concentration column if necessary							x		
1 x change anion pre-concentration column if necessary						x			

(*) preventive replacement frequency based on local experience. Prevent filter blockage. Indicators of blocked filters: significant phosphate peak around 6 min; (**) Frequency depends on location of instrument, clean when visibly dirty; (***) Frequency depends on location of instrument, exchange when blocked/ together with 1/16" tubing. Exchange at least every 2 years (wear); (***) Frequency depends on local conditions (quality of solutions; for anion column: concentration of peroxide); (*****) Pump tubing including connectors

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 33rd EMEP Inter-comparison

The inter-comparison in 2015 was the 33rd time such an inter-comparison took place. The samples provided included synthetic rainwater samples and nitrogen dioxide in absorbing solution.

In 2015 the samples were submitted to the analysts however they were analysed using a different standard operating protocol (SOP) for some of the cation analysis leading to the calibration for these ions being incorrect. This was caused by the analyst forcing the calibration through zero for some of these non-standard UKEAP samples. As a result of this the laboratory did not compare well in the EMEP intercomparison for some cations. UKEAP samples collected within the network were not affected by the calibration error. It is not possible to rerun the samples to assess the performance with the same samples however the measured concentrations can be recalculated using the correct calibration. All results are shown below. After the recalculation following the recalibration the performance of the laboratory was improved with all but three samples being satisfactory which is the highest rating for the EMEP intercomparison.

Ricardo’s chosen laboratory (Environmental Scientifics Group Ltd) is always made aware of the performance in the intercomparison and the analysts are aware of how the calibrations should be undertaken in any future intercomparisons.

Table 17 33rd EMEP Inter-comparison

Species	Sample code	Expected concentration μeq l^{-1}	Measured concentration μeq l^{-1}	Recalculated Measured concentration μeq l^{-1}	Mean difference (%)	Recalculated Mean difference (%)	Assessment (using recalculated concentrations)
SO_4^{2-}	G1	0.666	0.685		2.9%		S
	G2	0.535	0.539		0.7%		S
	G3	1.474	1.54		4.5%		S
	G4	1.319	1.359		3.0%		S
NO_3^-	G1	0.357	0.361		1.1%		S
	G2	0.379	0.381		0.5%		S
	G3	0.607	0.633		4.3%		S
	G4	0.707	0.721		2.0%		S
Cl^-	G1	0.193	0.177		-8.3%		S
	G2	0.27	0.251		-7.0%		S
	G3	0.386	0.375		-2.8%		S
	G4	0.347	0.336		-3.2%		S
Na^+	G1	0.304	0.316		3.9%		S
	G2	0.283	0.281		-0.7%		S
	G3	0.608	0.611		0.5%		S
	G4	0.548	0.543		-0.9%		S
NH_4^+	G1	0.187	0.233	0.1862	24.6%	-0.4%	S
	G2	0.241	0.299	0.2534	24.1%	5.1%	S
	G3	0.267	0.328	0.3087	22.8%	15.6%	Q
	G4	0.401	0.5	0.4504	24.7%	12.3%	S
Mg_2^+	G1	0.103	0.075	0.1023	-27.2%	-0.7%	S
	G2	0.093	0.064	0.0928	-31.2%	-0.2%	S
	G3	0.175	0.135	0.1656	-22.9%	-5.4%	S
	G4	0.155	0.119	0.1455	-23.2%	-6.1%	S
Ca_2^+	G1	0.128	0.096	0.1174	-25.0%	-8.3%	S
	G2	0.115	0.138	0.1057	20.0%	-8.1%	S
	G3	0.217	0.168	0.1857	-22.6%	-14.4%	S
	G4	0.192	0.15	0.1603	-21.9%	-16.5%	Q
K^+	G1	0.17	0.131	0.1538	-22.9%	-9.5%	S
	G2	0.204	0.155	0.1772	-24.0%	-13.1%	S
	G3	0.34	0.293	0.3044	-13.8%	-10.5%	S
	G4	0.306	0.246	0.2715	-19.6%	-11.3%	S
pH	G1	4.57	4.6		0.7%		S
	G2	4.7	4.73		0.6%		S
	G3	4.18	4.22		1.0%		S
	G4	4.22	4.26		0.9%		S
Cond	G1	17.7	15.2		-14.1%		S
	G2	15.2	12.7		-16.4%		Q
	G3	39.3	38.2		-2.8%		S
	G4	37	35.6		-3.8%		S

* pH as pH units

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

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

NO_2-Net

Results of the 33rd EMEP Inter-comparison

The inter-comparison in 2015 was the 33rd 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 0.0% and 3.06% 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 (%)	EMEP Assessment
C1	0.057	0.057	0.00%	S
C2	0.043	0.042	2.38%	S
C3	0.101	0.098	3.06%	S
C4	0.131	0.128	2.34%	S

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 34 and the dashed lines correspond to the automatic data from the co-located sites.

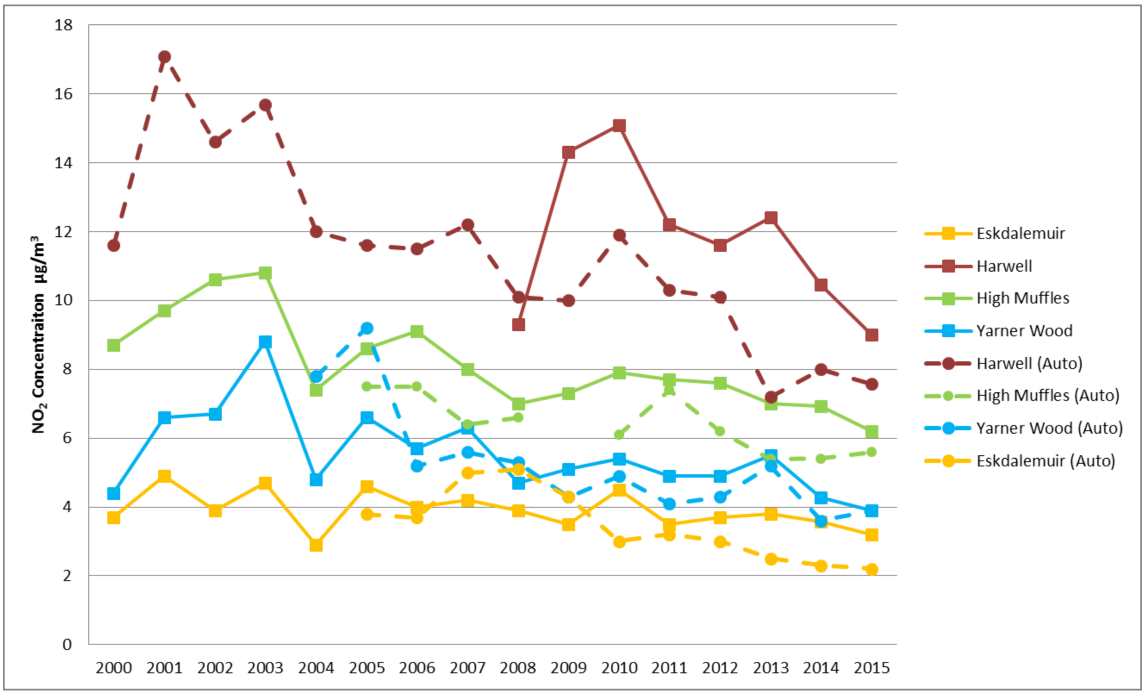

Figure 34 Comparison of measured concentrations of NO_2 by diffusion tube and automatic monitoring at collocated UKEAP sites * Not bias corrected

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. 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 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 35. 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 %).

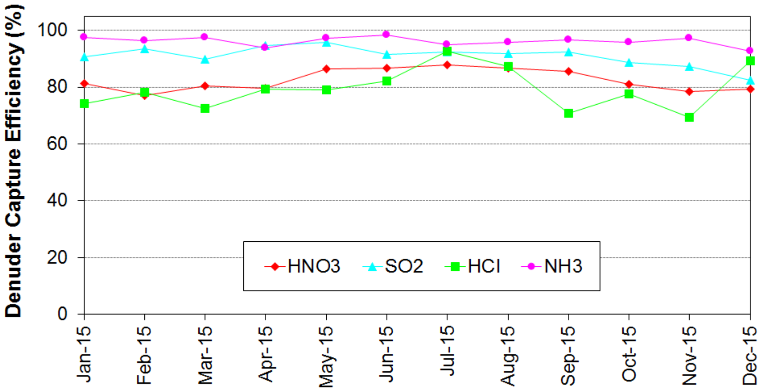

Figure 35: Monthly mean denuder capture efficiency (E) during 2015 for HNO_3, SO_2 and HCl from the 30 monitoring sites. E = amount in 1st denuder / (amounts captured in 1st + 2nd denuders)*100 %.

NAMN:

The percentage of samples passing the main QC criteria in NAMN provide an indication of network performance (Tang et al. 2003). During 2015, > 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.

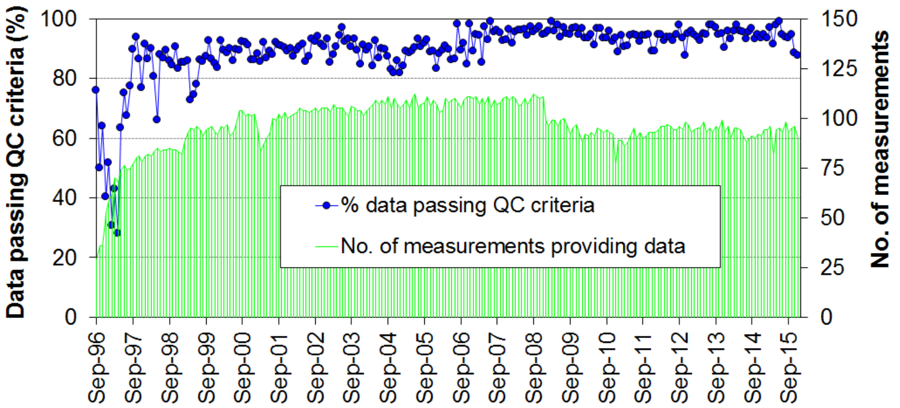

Figure 36: Assessing NAMN performance through monitoring total data capture, and % of data passing the QC thresholds (DELTA: capture of $NH_3 \geq 75$ % in the first of the 2 denuders, flow rate = > 0.22 L min^{-1}; DT/ALPHA: % CV for replicate samples < 30 % and < 15 % respectively).

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 37. 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.

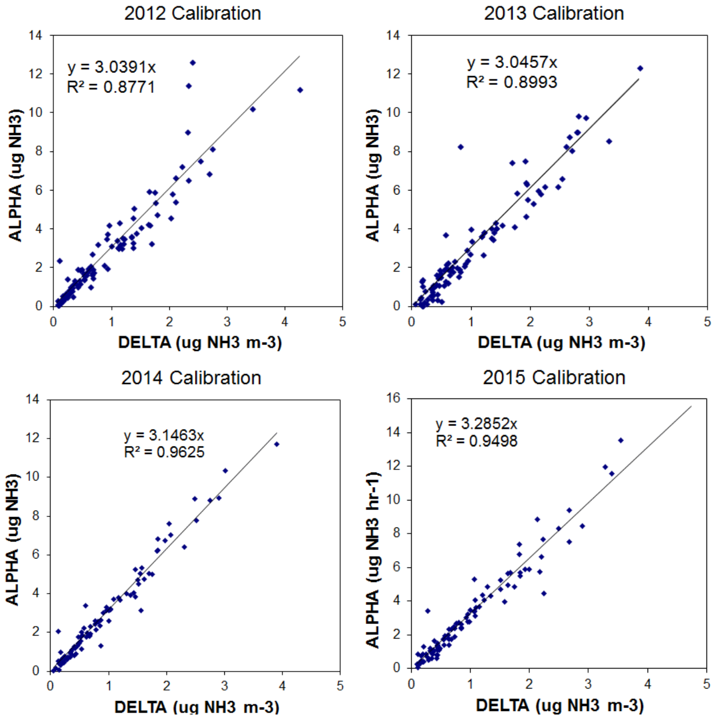

Figure 37: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers in years 2012, 2013, 2014 and 2015.