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Annual Report

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And the Devolved Administrations

by

NERC Centre for Ecology & Hydrology and Ricardo-AEA

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NERC CEH REPORT SUMMARY

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Executive Summary

Overview

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

UKEAP data is submitted to UK-AIR, OSPAR and EMEP databases and are publically available

Publications and output using UKEAP data in 2013

Data directly provided to Defra project and modelling work including:

- Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME) model
- Mapping for UK pollutant maps and deposition fields (CBED)
- Derived products are used to undertake the UK critical loads and levels mapping
- Defra's MAAQ used for national compliance assessment.

Reports and papers:

Mckenzie, R.: Fluxes of nitrogen in a semi-natural ecosystem, Ph.D. Thesis, University of Manchester, http://ethos.bl.uk/OrderDetails.do?uin=uk.bl.ethos.576906 (Auchencorth Moss Supersite).

Oxley et al.: Modelling future impacts of air pollution using the multi-scale UK Integrated Assessment Model (UKIAM), Environment International, Volume 61, November 2013, Pages 17-35 DOI: 10.1016/j.envint.2013.09.009 (AGANet).

Redington and Derwent: Modelling secondary organic aerosol in the United Kingdom. Atmospheric Environment, 2013. 64: p. 349-357.

Sutton et al.: Towards a climate-dependent paradigm of ammonia emission and deposition [in special issue: The global nitrogen cycle in the twenty-first century] Philosophical Transactions of the Royal Society (B), 368 (1621). 2013368 2013016620130166.13, 10.1098/rstb.2013.0166 (AGANet).

Vogt et al.: Heterogeneity of atmospheric ammonia at the landscape scale and consequences for environmental impact assessment. Environmental Pollution, 179, 120-131 (NAMN).

Vogt et al.: Estimation of nitrogen budgets for contrasting catchments at the landscape scale. Biogeosciences, 10 (1). 119-133. 10.5194/bg-10-119-2013 (NAMN, Auchencorth Supersite).

Talks and posters:

Langford et al.: 2013 Initial EMEP intensive results from 2012 and 2013 experiments Auchencorth and Harwell. [Speech] In: *14th Annual meeting of EMEP Task Force on Measurements and Modelling (TFMM), Zagreb, Croatia, 6-8 May 2013*.

Tang et al.: 2013 UK Eutrophying and Acidifying Atmospheric Pollutants Monitoring networks UKEAP. [Speech] In: *14th Annual meeting of EMEP Task Force on Measurements and Modelling (TFMM), Zagreb, Croatia, 6-8 May 2013*.

Kentisbeer et al.: 2013 Mercury at the UK EMEP supersite Auchencorth Moss: Trends, patterns and sources. [Keynote] In: 11th International Conference on Mercury as a Global Pollutant, Edinburgh, Scotland, 28 July - 2 August 2013.

Kentisbeer et al.: Total gaseous mercury monitoring at Harwell, UK – trends, patterns and a source analysis. [Poster] In: 11th International Conference on Mercury as a Global Pollutant, Edinburgh, Scotland, 28 July - 2 August 2013.

UKEAP data is freely available to download from UK-AIR and EMEP databases but data use is not tracked. See Appendix 1 for suggested citations relating to the use of specific UKEAP datasets. It would be very much appreciated if the UKEAP project team are acknowledged when data is published as part of other work.

Measurement Headlines

UK EMEP Supersites: Harwell and Auchencorth Moss

- *Data capture > 80% for hourly gas, $PM_{2.5}$ and PM_{10} composition measurements*
  - ➢ Trace gases and aerosol measurements were made throughout 2013. The best operational performance were achieved in 2013, since the MARGAs were commissioned. At Harwell, average data capture exceeded 85% (except for Ca^{2+} and Mg^{2+}) and Auchencorth Moss exceeded 80%.
- *Changes in SO_2 concentrations observed due to closures of coal/oil fired power stations:*
  - ➢ The Harwell 2013 annual mean SO_2 concentration was 1.6 µg m^{-3}. Decreased concentrations are observed after Didcot 'A' closed in 22nd March 2013. Similarly SO_2 decreases were observed at Auchencorth after Cockenzie power station (East Lothian) was decommissioned with a change in annual average from 0.21-0.43 µg m^{-3} (2007 to 2012) to 0.14 µg m^{-3} in 2013.
- *Major storms and air quality events observed and characterised:*
  - ➢ The PM event in March 2013 was observable at both sites and the PM and gas composition were made available rapidly for Defra.
  - ➢ December 2013 to January 2014 showed dominant sea salt PM driven by several Atlantic storms bringing pristine air masses to the site.
- *NO and NO_2 measurements with the ANNOX instrument have low data capture:*
  - ➢ 2013 data capture was 30-31% &40% at Harwell & Auchencorth Moss respectively.

Precipitation Network (Precip-Net)

- Precip-Net has completed the 28th year of monitoring
- The rate of decrease in sulphur concentration has been shown to vary throughout the UK- with the largest decrease seen in the power producing areas of the country.
- Nitrate concentrations have decreased at a significantly lower rate than sulphate.

NO_2-Net

- Since 2000, the network annual average NO_2 concentration measured by diffusion tube has decreased in line with national emission totals of oxides of nitrogen (as NO_2).
- Data capture for the network in 2013 was >90% & concentrations ranged from <2-12 µg m^{-3}

Acid Gas and Aerosols Network (AGA-Net)

- Monthly atmospheric composition measurements of PM_4 and trace gases with the DELTA systems achieved >75% data capture at 28 out of 30 sites.
- Intercomparison between new and current design DELTAs was completed and report submitted to Defra (currently under revision).

National Ammonia Monitoring Network (NAMN)

- During 2013 >90% of data passed the QC thresholds.
- Annual average ammonia concentrations range between 0.04-7.9 µg m^{-3}.
- Whilst UK emissions of NH_3 declined by about 17% during the operation of NAMN (http://naei.defra.gov.uk/), NH_3 concentrations from the overall dataset show no detectable trend over the 16 year period. The hypothesised reasons for this include the changing background SO_2 concentrations, climate variation and the short atmospheric lifetime and deposition effects of ammonia.

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UKEAP Annual Report, 2013

1. Introduction

The Defra rural air pollutant monitoring networks project, AQ0647, **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)** is operated jointly between Ricardo-AEA and the NERC Centre for Ecology and Hydrology and comprises the following component measurement activities:

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

and the UK rural pollutants monitoring networks (site maps in Figure 1).

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

This report summarises operation and monitoring data for 2013. 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. The UK contribution to the EMEP monitoring strategy is two Level II 'Supersites', one in the north at Auchencorth Moss, Midlothian, and one in the south, at Harwell, Oxfordshire. Both EMEP Supersites form part of Defra's Automated Urban and Rural Network (AURN), a UK-wide network 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 $PM_{2.5}$). Together both sites provide the coverage of at least one station per 100,000 km^2, as required under Annex IV of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe to determine the composition of $PM_{2.5}$ at rural background locations. 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 Monitor for AeRosols and Gases in ambient Air (MARGA) instrument.

The 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%). Non-automatic measurements of (rural) heavy metal concentrations in PM_{10} and precipitation; particulate-phase base cations, anions and trace gases; and 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, Elemental Carbon, 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.

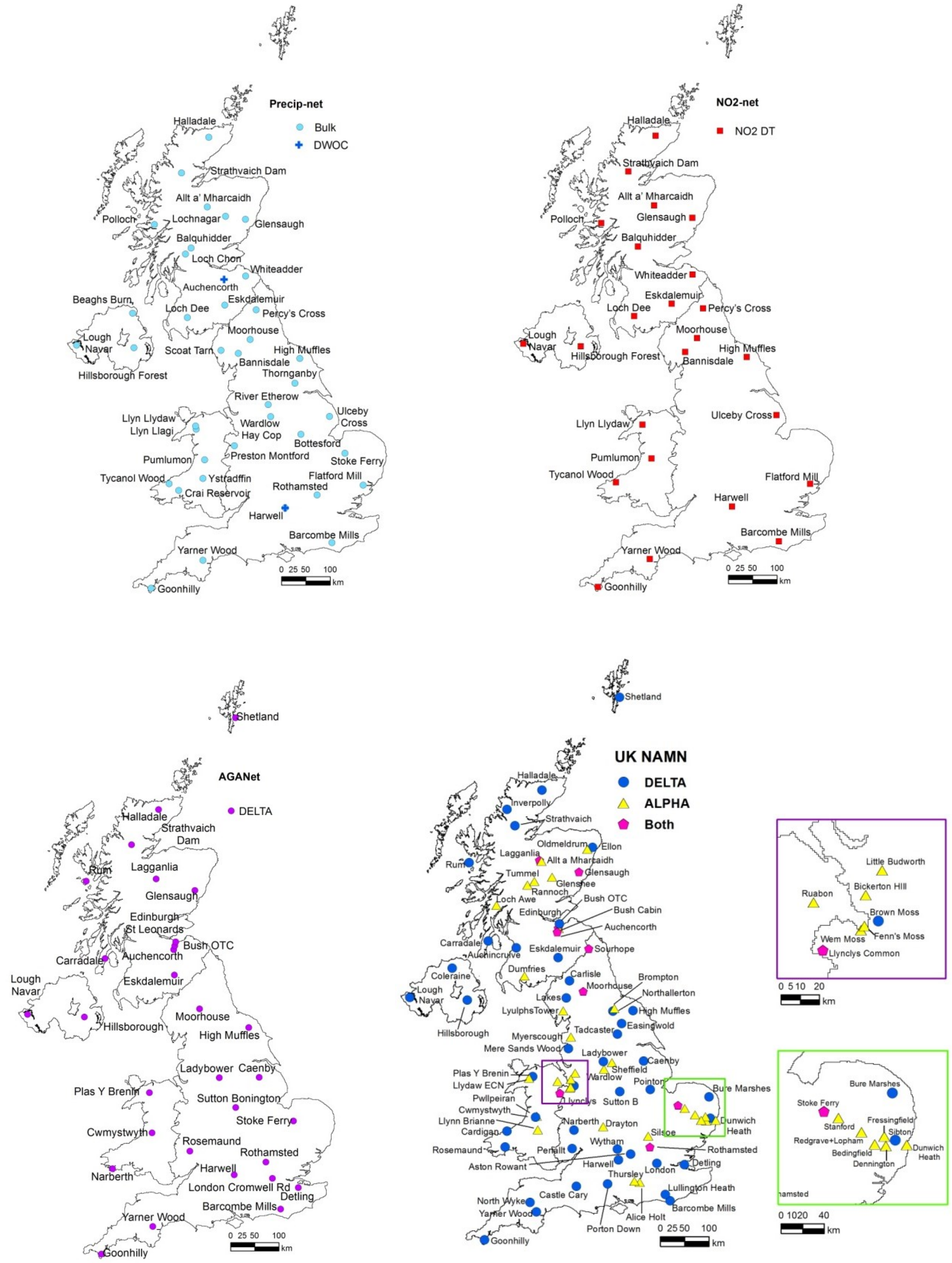

Figure 1 UK Eutrophying and Acidifying Atmospheric Pollutants rural networks

The rural networks which form part of the UKEAP network for assessing long-term atmospheric concentrations of inorganic acidifying and eutrophying pollutants are shown in Figure 1 and comprise:

1. the Precipitation Network (Precip-Net) measuring rain composition at 39 sites.
2. National Ammonia Monitoring Network (NAMN), measuring ammonia concentrations at 85 sites.
3. the Acid Gas and Aerosol Network (AGANet), measuring acid gas concentrations and inorganic aerosol composition at 30 sites.
4. the NO2-Net network, measuring indicative NO_2 concentrations at 24 sites.

UKEAP measurements are undertaken to improve understanding of chemical deposition and removal processes and to allow validation of long range transport models. Data use is summarised in Figure 2.

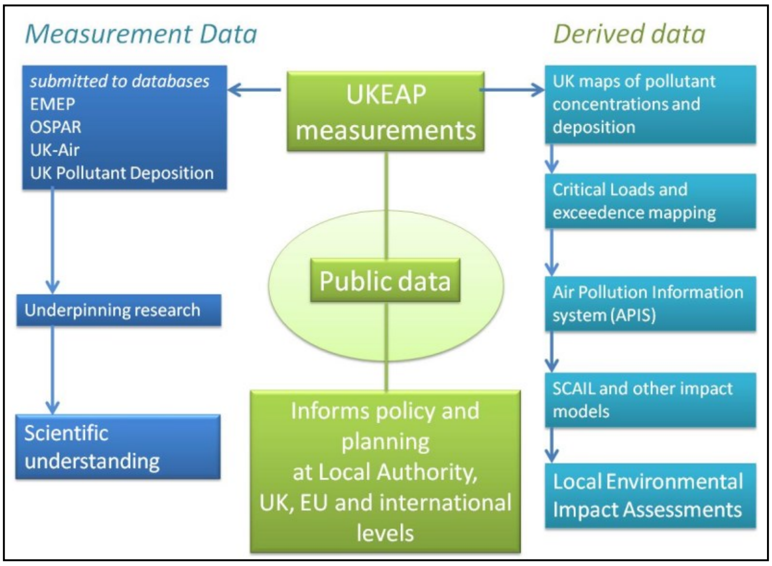

Figure 2 Summary of UKEAP data pathways

All data is reported annually to UK-AIR, Defra's Air Information Resource website, and most data is submitted to the EMEP database. Data is also provided to the Defra UK pollutant deposition mapping projects and to any individual or organisation with interest in the data.

Relevant websites:

- http://uk-air.defra.gov.uk
- http://pollutantdeposition.defra.gov.uk/networks
- http://www.ceh.ac.uk/sci_programmes/ukeap-project.html
- http://gaw.empa.ch/gawsis/reports.asp?StationID=2076203029

UKEAP measurements contribute to greater scientific understanding of pollutant transport and deposition processes and enable model validation, which may be applied in international negotiations (such as the Gothenburg Protocol) to reduce emissions and pollution effects. Measurements from the UKEAP Network have substantially aided the development of UK based long-range transport models, such as FRAME, MAAQ, CMAQ, HARM, MetUM and TRACK and have been involved in the Defra model intercomparison exercise.

2. UK EMEP Supersites

The pollutants measured at the Harwell and Auchencorth Moss EMEP Supersite in 2013, and the networks to which they belong, are summarised in Table 1. Ricardo-AEA acted as Local Site Operator (LSO) for the Harwell EMEP Supersite measurements for all measurements except those conducted by NPL (as shown in Table 1). NERC CEH was LSO for Auchencorth Moss. During 2013 no health and safety incidents occurred at either site in relation to the operation of the EMEP Supersites.

This report summarises the measurements made between January and December 2013. 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 include:

- Meteorological observations (barometric pressure, dewpoint, wind speed & direction, relative humidity, temperature, (total) rainfall) (**Harwell reported here; Auchencorth measurements made by NERC CEH, available on request)).**
- Trace gas (HCl, HONO, HNO_3, NH3, 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).**
- Speciated NO_X measurements were made using a photolysis-based, ANNOX instrument **(Harwell and Auchencorth Moss)**

Table 1 Pollutants measured at the UK EMEP Supersites during 2013

Pollutant	Ha[1]	Au[1]	EMEP Level	Averaging period	Monitoring network (Ha/Au)	Contract holder
Oxides of nitrogen (thermal converter)	X	X	I	Hourly	AURN	Bureau Veritas
Oxides of nitrogen (ANNOX, photolytic converter)	**X**	**X**	**I**	**Hourly**	**UKEAP**	**Ricardo-AEA**
Sulphur dioxide	X	X	I	Hourly	AURN	Bureau Veritas
Ozone	X	X	I	Hourly	AURN/CEH	Bureau Veritas
Particulate matter $PM_{2.5}$, PM_{10}	X	X	I	Hourly	AURN	Bureau Veritas
Particulate matter $PM_{2.5}$, PM_{10}	X	X	I	Daily	AURN	Bureau Veritas
VOCs in air	X		II	Hourly	Automated HC Network	Ricardo-AEA
MARGA (acid & alkali gases, water-soluble components of PM_{10} and $PM_{2.5}$)	**X**	**X**	**II**	**Hourly**	**UKEAP**	**Ricardo-AEA**
Meteorological parameters (WS, WD, T, RH, rainfall)	**X**	**X**	**I**	**Hourly**	**UKEAP/CEH**	**Ricardo-AEA**
Precipitation chemistry	**X**	**X**	**I**	**Daily**	**UKEAP**	**Ricardo-AEA**
PAH in PM_{10}, air and rain	X	X	I	Monthly	PAH	NPL*
Black carbon	X	X	II	Hourly	Particle numbers/CEH	NPL
Particle counts (>7 nm)	X	X	II	Hourly	Particle numbers/CEH	NPL
Particle size distribution	X	X		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**
DELTA sampler (Trace gases: HCl, HNO_3, NH_3, and SO_2)	**X**	**X**	**I**	**Monthly**	**UKEAP**	**CEH**
Heavy metals in precipitation	X	X	I	Monthly	Rural metals	CEH
Mercury in precipitation	X	X		Monthly	Rural metals	CEH
Heavy metals in PM_{10}	X	X	II	Weekly	Rural metals	CEH
Elemental mercury	X	X	I	Hourly	Rural metals	CEH
Total gaseous mercury in air	X	X	II	Hourly	Rural metals	CEH
Persistent Organic Pollutants (POPs) in air	X	X	I	Monthly	TOMPS	University of Lancaster
Trace gas fluxes (O_3, NOx, SO_2)		X	III		Acid Deposition Processes	CEH

[1]Ha: Harwell; Au: Auchencorth Moss* NPL: National Physical Laboratory, Teddington, Middlesex.

2.1 Harwell Operational Update

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

2.2 Auchencorth Operational Update

During 2013, in addition to the normal operations, the Auchencorth Moss supersite was host to other short term experiments and measurements, some of which were relevant to atmospheric composition, summarised in Table 2. The EMEP intensive analyses of mineral dust composition were published in the 2014 EMEP status report (Fagerli *et al.*, 2014)

Table 2 Summary of other atmospheric measurements at Auchencorth Moss Supersite in 2013

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

2.3 Meteorological measurements

2.3.1 Harwell

Typical meteorological parameters are measured at the Harwell EMEP Supersite. The 2013 annual means and data capture rates are summarised in Table 3. Data capture for the parameters measured was typically above 95% except for dewpoint which had a slightly lower data capture of 82%.

Table 3 2013 Summary of the Harwell EMEP Supersite meteorological observations

Meteorological parameter	**Annual mean**	**Data capture (%)**
Barometric pressure (mbar)	999	99
Dewpoint (°C)	7.4	82
Wind direction (°)	169	99
Wind speed (m s^{-1})	3.1	99
Relative humidity (%)	81	97
Temperature (°C)	9.6	99
Rainfall (mm)	631	99

Mast measurements of the 10 m wind speed (U_{10}) and directional frequency were performed at the Harwell EMEP Supersite during 2013. Figure 3 shows a plot of the directional frequency (in 10° sectors) for 2013. 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 Table 3, and maximums of up to 13 m s^{-1}. Figure 4 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).

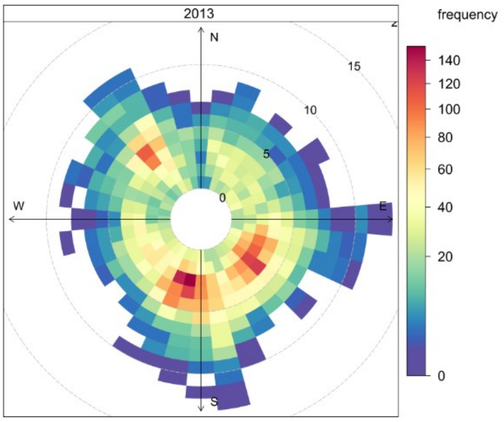

Figure 3 Wind speed (m s^{-1}) and directional frequency for the Harwell EMEP Supersite, 2013.

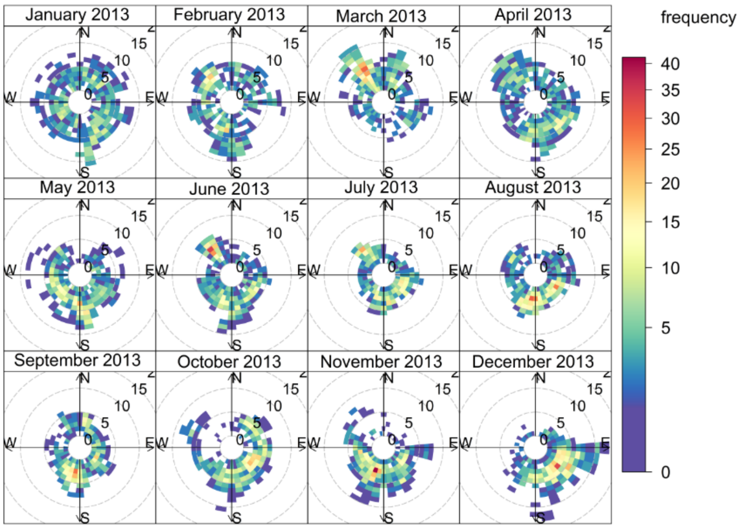

Figure 4 Monthly variations of hourly wind speed and directional frequency for the Harwell EMEP Supersite, 2013

2.3.2 Auchencorth

The 2013 meteorological measurements are summarised in Table 4. These measurements were not made under the Defra UKEAP contract, but are available on request.

Table 4 Annual summary of basic meteorological parameters from the Auchencorth EMEP Supersite, 2013

Instrument	Annual mean	% Data Capture
Wind speed, Direction	4.1 m s-1 / 175.5°	94.7% / 94.5%
Air temperature	7.6°C	100%
Relative Humidity	85.3%	100%
Barometric Pressure	98.1 kPa	100%
Surface Wetness	50 %	98.8%

Precipitation (30-min)	844 mm	100%

2.4 Trace gas and aerosol concentrations (MARGA 2S)

Measurements of particulate-phase cations and anions in PM_{10} and $PM_{2.5}$, sulphate (SO_4^{2-}), nitrate (NO_3^-), sodium (Na^+), potassium (K^+), ammonium (NH_4^+), chloride (Cl^-), calcium (Ca^{2+}), and magnesium (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) for PM_{10} and $PM_{2.5}$ fractions. 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 identical units or “boxes” for the sampling and entrainment of particulate and gas phase species; one for PM_{10} and 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.

2.4.1 Harwell

Tables 5-7 show the 2013 annual mean and % data capture for the PM_{10}, $PM_{2.5}$, and trace gas species, respectively, measured by the Harwell MARGA. The statistics presented are based on the ratified measurements supplied to UK-AIR. Time series plots of the 2013 Harwell MARGA measurements (major species and trace gases) are shown in Figure 5, Figure 6 and Figure 7. Fewer operational issues were noted in 2013 than in 2012 for the Harwell MARGA instrument. Measurements were lost due to intermittent blockages and operational issues, despite on-going weekly maintenance and periodic checks. There was only one major operational issue in 2013: a blockage in one of electronic switches above the PM_{10} syringe block was first detected on 12th July 2013. This problem persisted until 5th August 2013. Measurements were also lost due to diagnostic tests conducted on the instrument during this time. Table 5 and 6 show that the 2013 Mg^{2+} data capture was the lowest of any particulate-phase species. This was due to non-acceptance of the Mg^{2+}, PM_{10} and $PM_{2.5}$ measurements from 01/04 – 23/04 as during this period, the ratio Mg^{2+}: Na^+ was greater than 0.12, the weight ratio in seawater (Mouri *et al.*, 1993). This was believed to be due to contamination of the cation sample loop, possibly by the adsorption of Mg-bearing material onto the internal surface of the loop.

The MARGA PM_{10} measurements were compared with filter measurements of PM_{10} analysed by Particle-induced X-ray Emission (PIXE) made during the EMEP Intensive from 11th January 2013 to 6th February 2013. This comparison showed that the ratio of Mg^{2+} to Na^{+} from the MARGA to be around 0.2 whilst that from the PIXE analysis was closer to 0.14. This was indicative of over-reading of the Mg^{2+} mass concentration by the MARGA during this time.

2.4.2 Auchencorth

The MARGA instrument has been operational since 2006. During 2013 the MARGA instrument data capture continued to improve following the instrument upgrade of 2011 and overall for the 21 atmospheric components measured data capture exceeded 80% (Tables 8 to 10). Further training was provided to personnel in the operation of the MARGA system, as well as the associated data analysis improving the efficiency of the instrument operation. Developments in QC and QA are summarised in Appendix 2. Annual average concentrations and data capture statistics for all the species are summarised in Tables 8 to10.

Only two months had data capture below75%. March 2013 (average data capture 74%) had intermittent faults, including syringe valve failure, and October 2013 (average data capture 65%) had a SJAC supply pump tubing issue, which led to downtime of 9 days. As can be seen in Figure 8, Figure 9 and Figure 10 and the gas phase concentrations and PM mass observed at Auchencorth Moss are low but with high levels of variability over the year, with air masses either dominated by sea salt or by anthropogenic emissions for example agricultural or long range transport.

In the gas phase, the annual average for NH_3 in 2013 was similar to that of previous years, however the maximum concentration of NH_3 was 19.98 $\mu g\ m^{-3}$, which is somewhat lower than the preceding six years (2007 to 2012) with the exception of 2011. The annual average concentration of HNO_3 of 0.10 $\mu g\ m^{-3}$ was similar to previous years. SO_2 was 0.14 $\mu g\ m^{-3}$, significantly lower than that of previous years which were between 0.21 and 0.43 $\mu g\ m^{-3}$ for the years 2007 to 2012. It is thought that this is a direct consequence of the closure on the 15th March 2013 of Cockenzie Power Station which lies approximately 25 km NE of Auchencorth Moss. This was the only major source of SO_2 close to the site and would explain the drop in annual average of SO_2 at Auchencorth Moss.

In the aerosol phase, PM_{10} NH_4^+ annual averages are similar to that of 2007 to 2012 (0.61-0.89 $\mu g\ m^{-3}$). PM_{10} NO_3^- annual average is within the range of that of previous years reported by the MARGA where annual averages have ranged from 0.98 to 1.54 $\mu g\ m^{-3}$ (2007 to 2012). The maximum concentration of PM_{10} NO_3^- of 24.6 $\mu g\ m^{-3}$ occurred on 5 March 2013, coinciding with the maximum concentration of the $PM_{2.5}$ NO_3^- . Further details of this event, are discussed below in the case study. No significant change in the annual average SO_4^{2-} concentrations were observed. Though as discussed above the closure of Cockenzie Power Station had a significant effect on the SO_2, the plume was not sufficiently aged to contribute significantly to the SO_4^{2-} levels measured at Auchencorth Moss.

Table 5 Annual summary of the speciated PM_{10} mass concentration from the Harwell EMEP Supersite, 2013.

Ion (PM_{10})	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	1.57	87
Na^+	0.82	85
K^+	0.08	88
Ca^{2+}	0.34	86
Mg^{2+}	0.14	59
Cl^-	1.18	87
NO_3^-	3.68	87
SO_4^{2-}	2.06	85

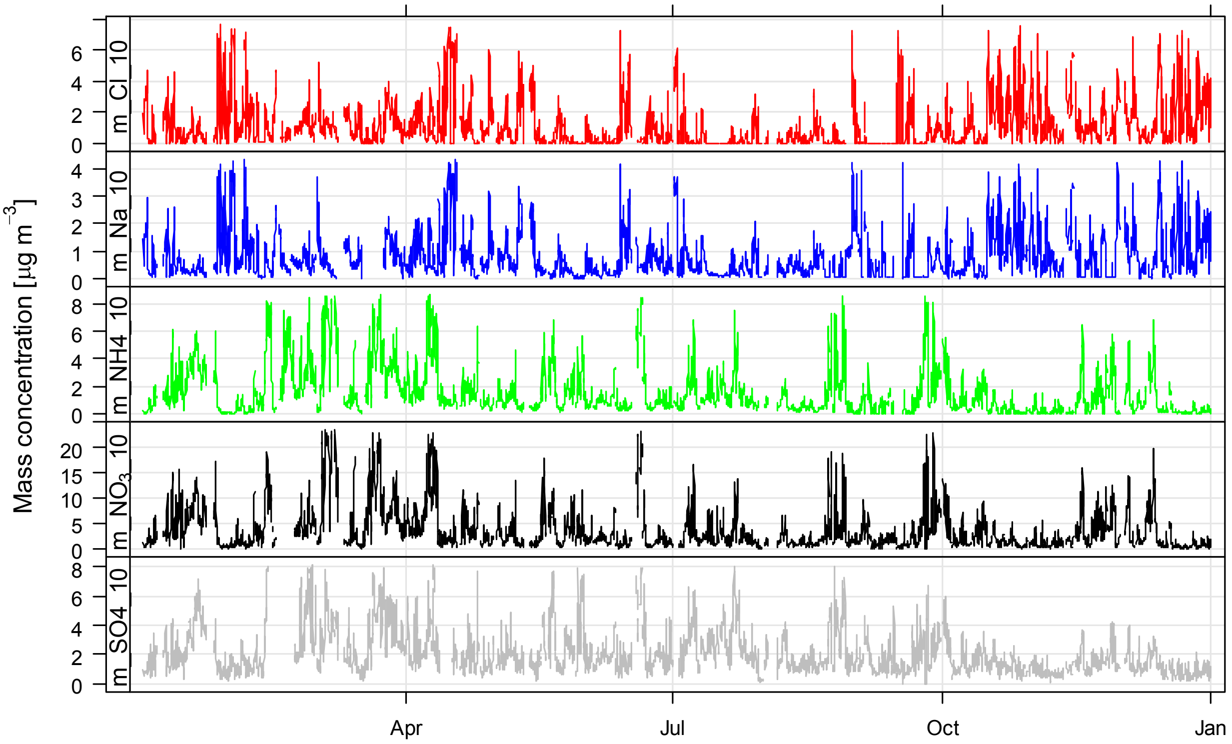

Figure 5 Time series plot of the major PM_{10} species (Cl^-, Na^+, NH_4^+, NO3-, and SO_4^{2-}) measurements from the Harwell MARGA, 2013. Minor species (Ca^{2+}, Mg^{2+} and K^+) measurements not shown.

Table 6 Annual summary of the speciated $PM_{2.5}$ mass concentration from the Harwell EMEP Supersite, 2013.

Ion ($PM_{2.5}$)	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	1.55	89
Na^+	0.47	87
K^+	0.05	89
Ca^{2+}	0.15	70
Mg^{2+}	0.08	62
Cl^-	0.59	89
NO_3^-	3.29	89
SO_4^{2-}	1.97	86

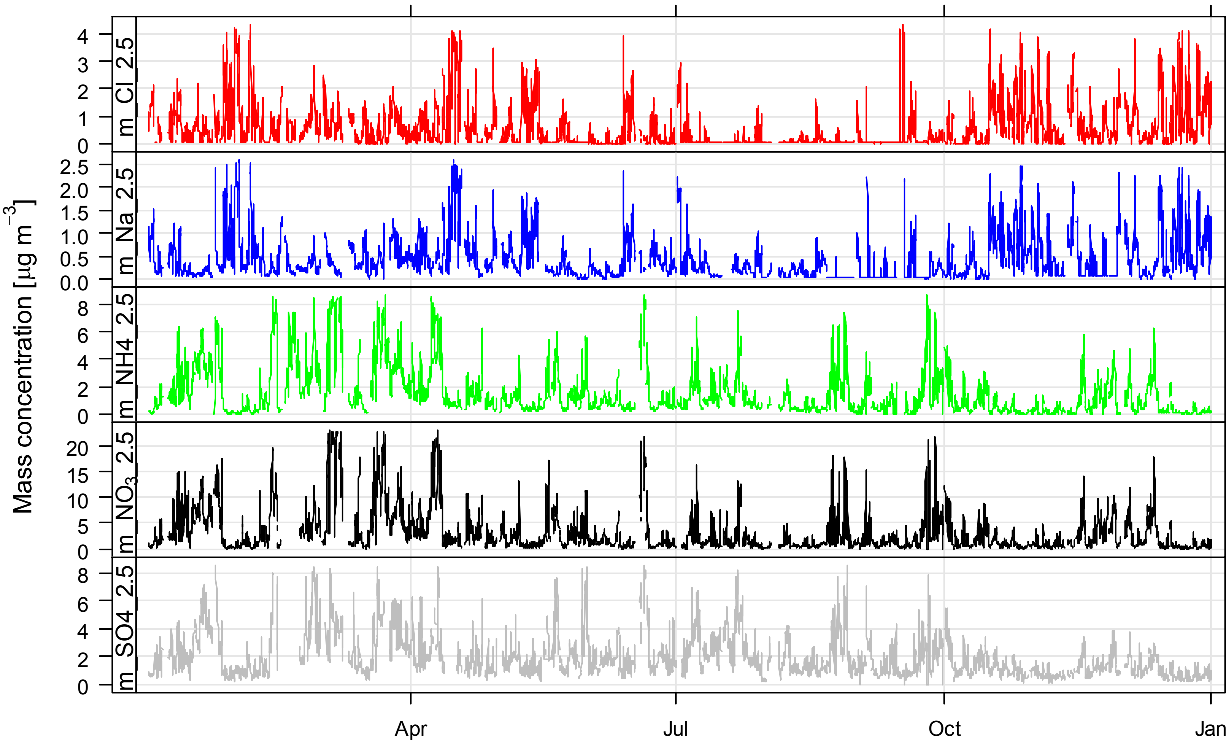

Figure 6 Time series plot of the major $PM_{2.5}$ species (Cl^-, Na^+, NH_4^+, NO3-, and SO_4^{2-}) measurements from the Harwell MARGA, 2013. Minor species (Ca^{2+}, Mg^{2+} and K^+) measurements not shown.

Table 7 Annual summary of trace gas mass concentration from the Harwell EMEP Supersite, 2013.

Trace gas	Annual mean (µg m^{-3})	Data capture (%)
NH_3	1.87	89
HCl	0.07	88
HNO_3	0.22	89
HNO_2	0.54	90
SO_2	0.46	88

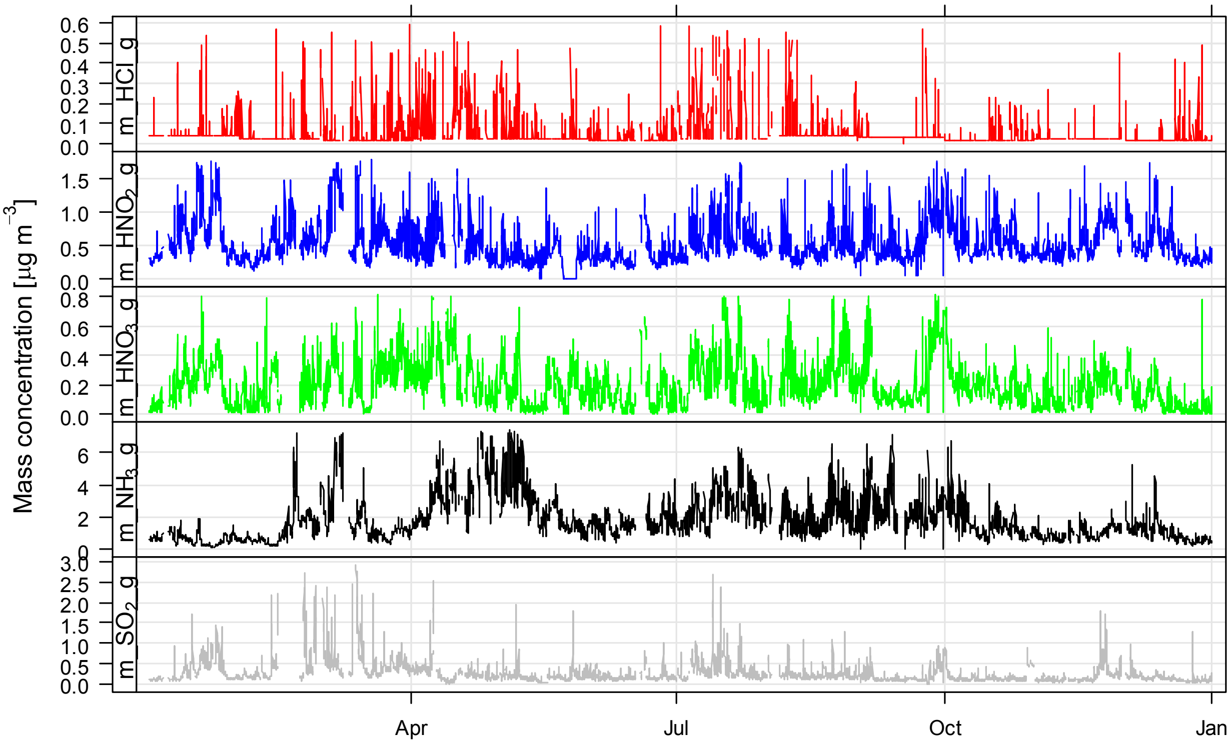

Figure 7 Time series plot of the trace gas (HCl, HNO_2, HNO_3, NH_3, and SO_2) measurements from the Harwell MARGA, 2013.

Table 8 Annual summary of trace gas mass concentration from the Auchencorth EMEP Supersite, 2013.

Trace gas	Annual mean (µg m^{-3})	Data capture (%)
NH_3	1.19	84
HCl	0.12	85
HNO_3	0.10	83
HNO_2	0.18	85
SO_2	0.14	83

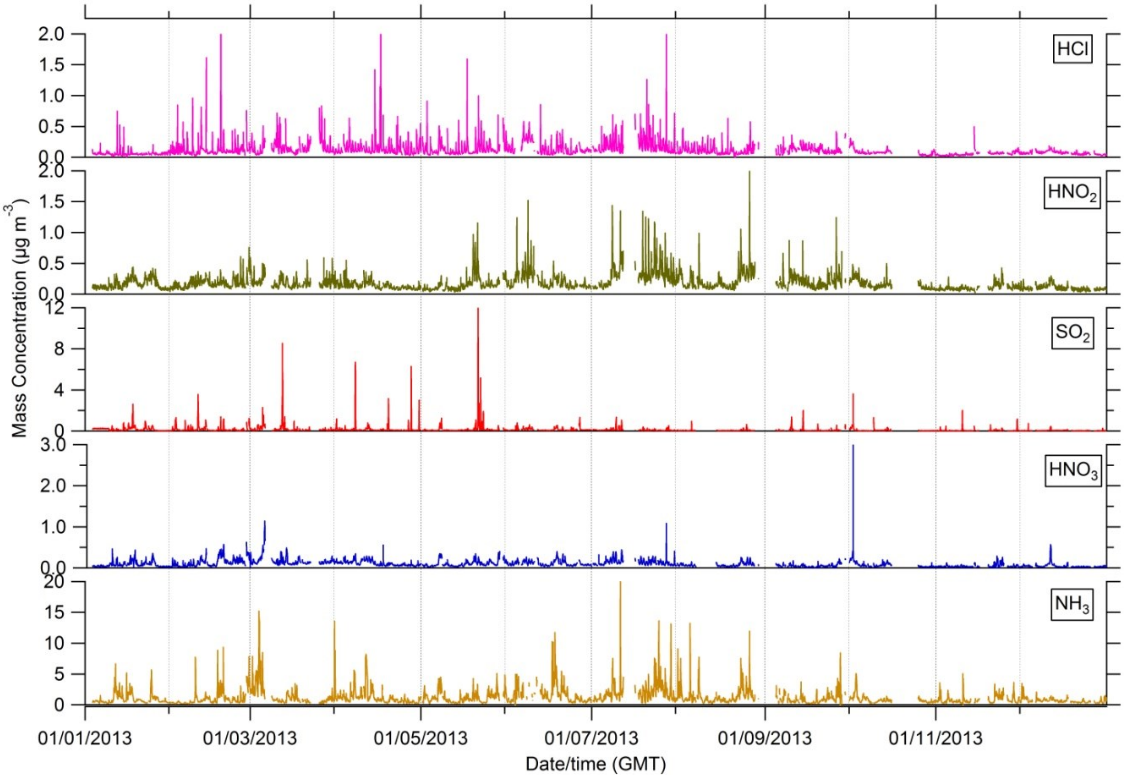

Figure 8 Ratified gas measurements from the MARGA instrument at Auchencorth Moss for 2013.

Table 9 Annual summary of the speciated PM_{10} mass concentration from the Auchencorth EMEP Supersite, 2013

Ion (PM_{10})	**Annual mean (µg m^{-3})**	**Data capture (%)**
NH_4^+	0.74	83
Na^+	0.73	79
K^+	0.07	86
Ca^{2+}	0.06	82
Mg^{2+}	0.08	86
Cl^-	1.15	83
NO_3^-	1.28	83
SO_4^{2-}	1.16	83

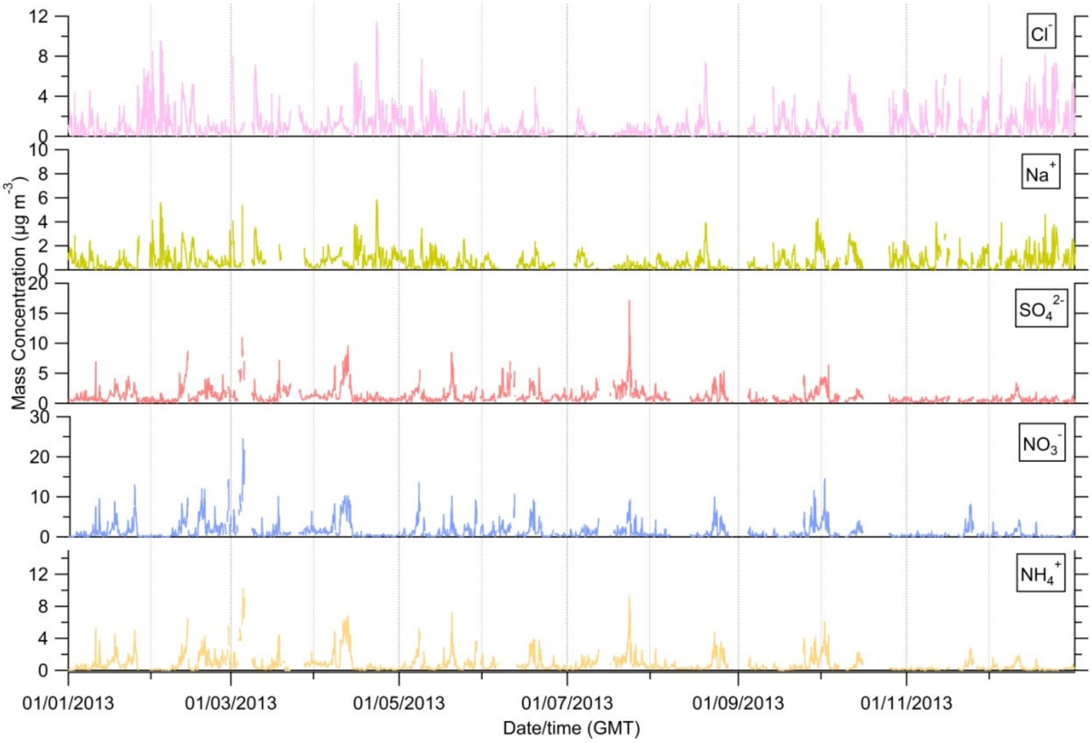

Figure 9 Ratified PM_{10} measurements from the MARGA instrument at Auchencorth Moss for 2013.

Table 10 Annual summary of the speciated $PM_{2.5}$ mass concentration from the Auchencorth EMEP Supersite, 2013

Ion ($PM_{2.5}$)	Annual mean (µg m^{-3})	Data capture (%)
NH_4^+	0.65	80
Na^+	0.45	80
K^+	0.04	81
Ca^{2+}	0.05	83
Mg^{2+}	0.05	83
Cl^-	0.66	85
NO_3^-	1.08	84
SO_4^{2-}	1.05	84

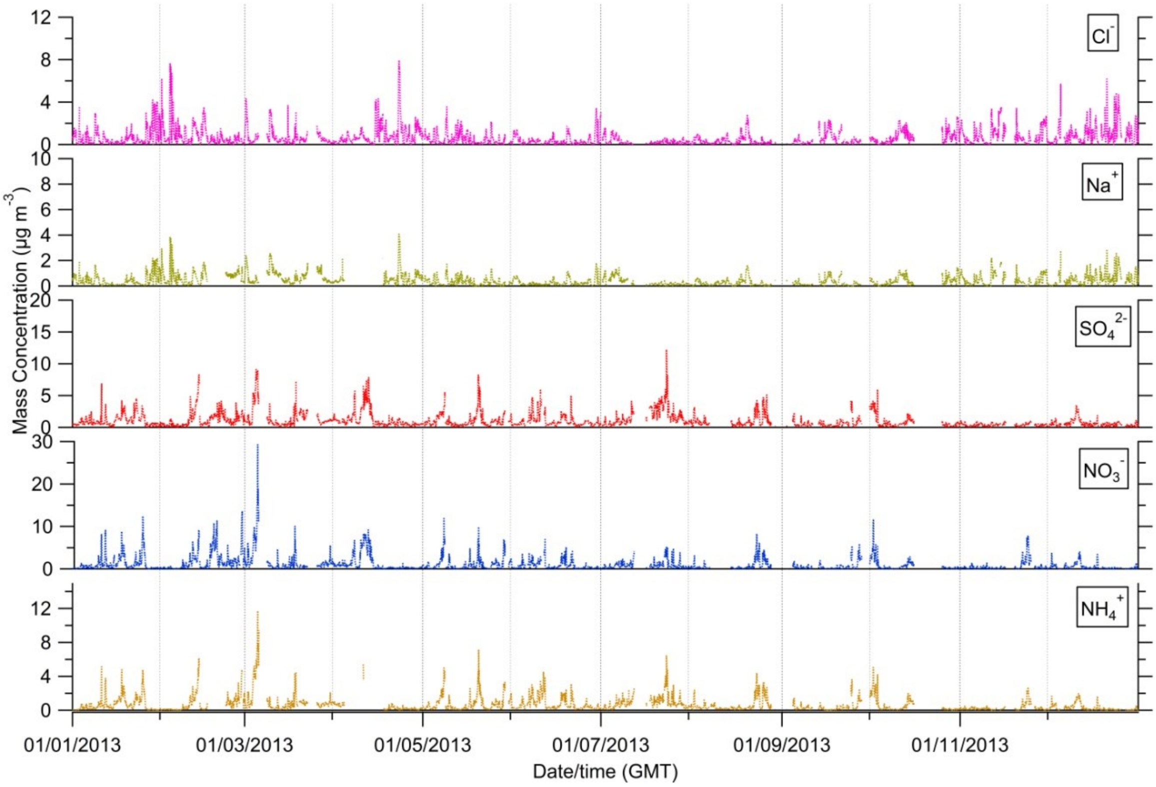

Figure 10 Ratified $PM_{2.5}$ measurements from the MARGA instrument at Auchencorth Moss for 2013.

2.5 ANNOX measurements

The ANNOX instrument is a high sensitivity chemiluminescent NO_X analyser composed of a PLC 860 photolytic converter and CLD 88p measurement system and uses UV photolysis, rather than molybdenum catalyst, to convert NO_2 to NO prior to analysis, as specified by the EMEP protocol. It is therefore NO_2 specific and does not respond to other oxidised nitrogen species such as PANs and HNO_3. These compounds act as positive artefacts when using a thermal convertor and thereby erroneously enhance the measurements of ambient NO_2.

The results for both Harwell and Auchencorth Moss for 2013 are shown in Table 11. This is the third year that NO, NO_2, and NO_X measurements were made at the Harwell EMEP Supersite using an ANNOX NO_X analyser. A number of operational issues were encountered with both ANNOX instruments during 2013 resulting in annual data captures below 50%. For Harwell two major faults occurred: 1) a fault with the sample manifold occurred between 13th May and 30th October 2013, and 2) Suppressed NO_2 concentrations measured between 30th October and 31st December 2013. Following the inlet manifold repair, concentrations of NO_2 reported by the ANNOX were much lower than expected and do not correspond with the co-located AURN measurements. The reason for this was never determined. All calibration measurements were reviewed and no clear reason for the suppressed response was found. The Auchencorth Moss ANNOx system was off-line several times during 2013 due to instrument failure and being sent off site for repair. The main down period was between February and August, There were additional down periods in September – October due to a faulty switching valve, and also in December. During the periods of normal operation, levels of NO and NO_2 measured by the ANNOx were low with an annual mean concentrations of 0.15 ppb and 2.49 ppb for NO and NO_2 respectively. It is noted that for significant proportion of time when the instrument is running the concentrations are below the instrument detection limit. The annual means are summarised but it is noted that the data capture for both species was below 50% and therefore not useful as representative annual mean for 2013.

Table 11 Annual summary of the ANNOX measurements made at the Harwell and Auchencorth EMEP Supersites, 2013.

		NO_2	**NO**	**NO_X**
Harwell	Average (µg m^{-3})	15.5	2.2	17.7
	Data capture (%)	30	31	30
Auchencorth	Average (µg m^{-3})	3.1	0.19	3.3
	Data capture (%)	35.4	43.6	40

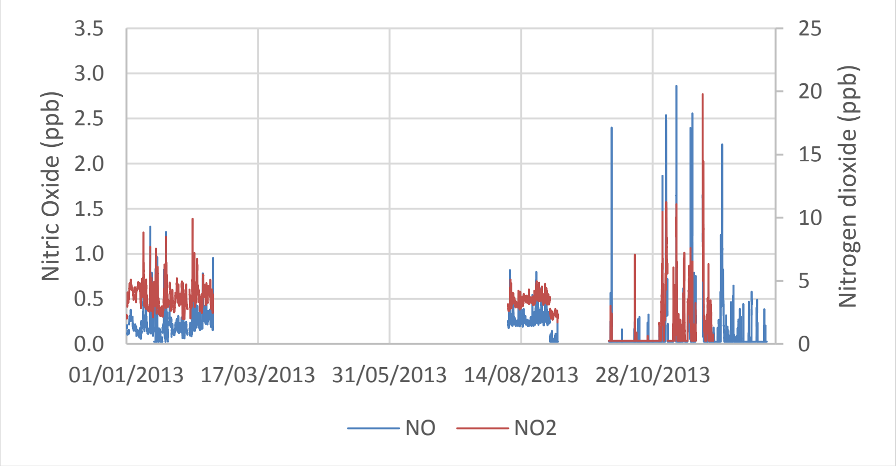

Figure 11 2013 Data for NO and NO_2 concentrations at Auchencorth Moss

2.6 2013 Case studies

2.6.1 SO_2 concentrations and changes due to local source closure at Harwell

SO_2 is emitted when sulphur-containing fuels are combusted. It is a pollutant which contributes to acid deposition which in turn can lead to potential changes in soil and water quality and adverse effects on aquatic and terrestrial ecosystems. SO_2 emission also contributes to formation of secondary particulate matter in the atmosphere. European SO_2 emissions have decreased by 66% between 1990 and 2005, and UK emissions have decreased in line with this trend. This reduction has been achieved through a range of measures such as limiting emissions from large point sources, including industrial plant and power stations, and road transport.

On the 22nd March 2013 the 2,000 MW dual-fired (coal and oil) 'A' station at Didcot power station closed. The operator of Didcot 'A' power station opted-out of the Large Combustion Plant Directive as a decision was made not to install Flue Gas Desulphurisation equipment which would have allowed continued generation beyond this date. This meant that it was only permitted to run for up to 20,000 hours after 1st January 2008 and could not operate past 31st December 2015 at the latest.

While typical SO_2 concentrations at the Harwell EMEP Supersite are typically a few µg m^{-3}; the 2013 annual mean SO_2 concentration at the site was 1.6 µg m^{-3}. Prior to the closure of the Didcot 'A' power station, concentrations of SO_2 exceeded 100 µg m^{-3} on occasion and were measured at the Harwell EMEP Supersite. Figure 12 shows good agreement in the corresponding SO_2 measurements from the AURN API instrument and the MARGA in the weeks preceding the closure Didcot 'A' power station, but also illustrates the detection limit issues the API instrument can have at <5 µg m^{-3}.

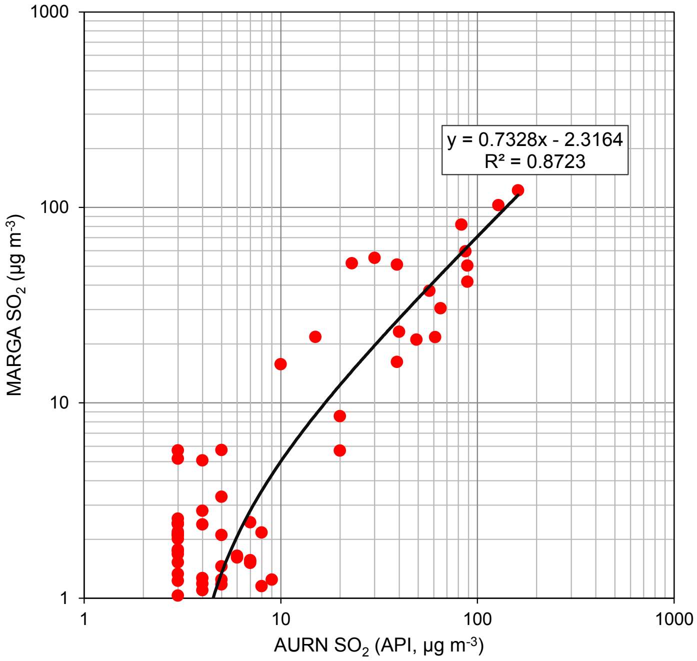

Figure 12 AURN and Marga SO_2 measurements during the weeks preceding the closure Didcot 'A' power station in March 2013.

2.6.2 Natural sea salt PM events at Harwell

The weather in the UK throughout December 2013 and into the early part of January 2014 was characterised by a storm surge which brought with it high winds, heavy rainfall and extensive flooding to many parts of the UK[1]. These prevailing metrological conditions were reflected in the PM_{10} composition and the meteorological observations made at the Harwell EMEP Supersite.

The influence of the storms on PM_{10} composition be seen in Figure 13 on and after 14th December. Prior to the 14th, PM_{10} mass concentrations were high, almost reaching 50 µg m^{-3}. At this time, the PM was dominated by secondary species: ammonium nitrate and sulphate, with only a small contribution from sea salt (Na^+ and Cl^-). Particulate-phase (PM_{10}) mass concentrations of ammonium (NH_4^+), sulphate (SO_4^2) and nitrate (NO_3^-) at this time were 7, 3 and 20 µg m^{-3} respectively. These measurements were indicative of chemically aged aerosol. The first dip in the PM_{10} mass concentration was seen around the 7th December. This was coincident with the first winter storm; a low pressure centre that crossed northern Scotland on the 5th. This brought strong winds and heavy rain to much of the UK.

Severe gales and heavy rain affected Scotland again on 14th and 15th December. During this time PM_{10} mass concentrations measured at the Harwell EMEP Supersite fell. The onset of precipitation can be seen in the rainfall panel of Figure 14. The PM_{10} mass concentration subsided, as did the barometric pressure, and the contribution of secondary species to the PM_{10} mass. From the 14th December onwards, until 12th January 2014, the PM_{10} mass concentrations were below 20 µg m^{-3} and principally composed of sea salt (Na^+ and Cl^-) entrained within the air mass of the storm surge. During this period, chloride (Cl^-) mass concentrations peaked at 15 µg m^{-3} and sodium (Na^+) at 8 µg m^{-3}, though typical concentrations were a third to half of these values.

After the 14th December the barometric pressure dropped to a low of 960 mbar as a further deep Atlantic low pressure system passed over the site during Christmas. The rainfall peaked on Christmas Eve, with 30 mm of rain falling, followed by a further heavy down-pour on Christmas day. The barometric pressure rose until the New Year, dipped down again in the first couple of days of the year and waivered around 980 mbar, until a heavy down pour of 50 mm of rain on the 7th January 2014. The barometric pressure rose after this time until the 12th January when the first secondary aerosol of the year was briefly measured at the site. Throughout December 2013 and January 2014 the Cl^- to Na^+ ratio was 1.74, compared to 1.80 for sea salt, and the Mg^{2+} to Na^+ ratio was 0.16, compared to 0.12 for sea salt.

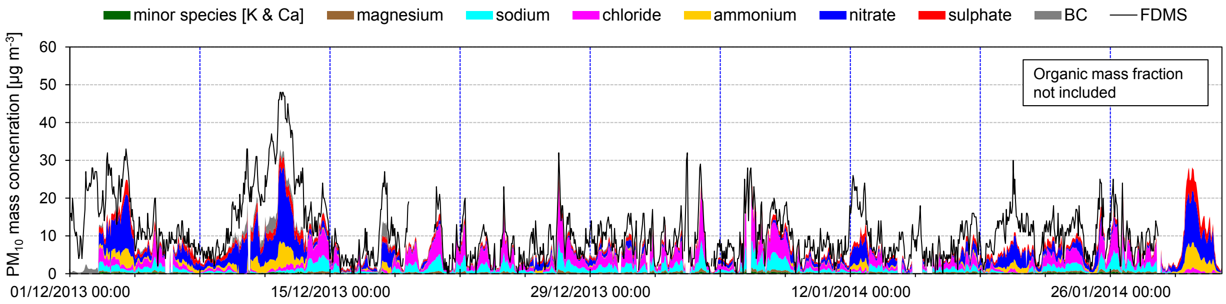

Figure 13 Summary of the PM10 composition measured at the Harwell EMEP Supersite in December 2013 and January 2014

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[1] 2013 weather summaries – December (accessed 24/09/2014), http://www.metoffice.gov.uk/climate/uk/summaries/2013/december.

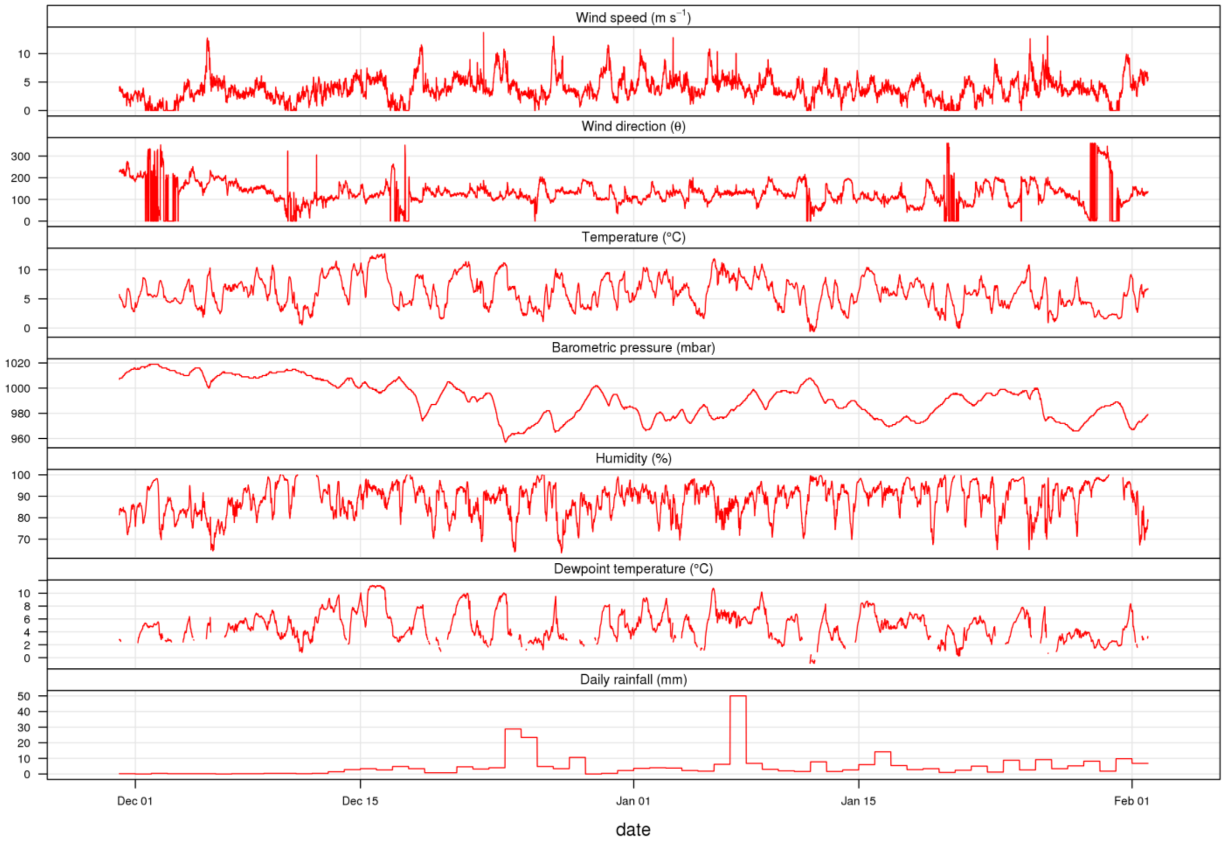

Figure 14 Summary of the Harwell EMEP Supersite meteorological observations in December 2013 and January 2014

2.6.3 UK secondary inorganic pollution event as observed at Auchencorth Moss

NH_4^+ and NO_3^- aerosols, reported by the MARGA instrument are often associated with anthropogenic emissions. During 2013, the maximum concentrations recorded of these two species were 12.17µg m^{-3} $PM_{2.5}$ NH_4^+ and 29.27 µg m^{-3} $PM_{2.5}$ NO_3 (Figure 15), which is high compared to the annual average. Both are believed to be attributed to similar air masses, though the observed peaks in concentrations were staggered by 18 hours with NO_3^- peaking on the 5th March 2013 at 11:00 and NH_4^+ peaking on the 6 May 2013 at 05:00. The air masses observed on the 5th and 6th March 2013 travelled down the North Sea, through tip of mainland Europe and back up through the UK to Auchencorth Moss (Figure 6, produced using Open Air (Carslaw & Ropkins, 2012; Ropkins & Carslaw, 2012)).

These observations coupled with the back-trajectories support previous analyses which attribute UK NH_4^+ and NO_3^- during PM events to be a combination of domestic and European emissions, (e.g., Vieno *et al.,* 2014 and references therein). Vieno et al. estimated on average 20-60% of observed NO_3^- concentrations are result of imported European emissions whilst the rest was derived from domestic emissions, all of which is driven by the meteorology. As expected, meteorology is a strong driver of atmospheric composition at Auchencorth Moss, for example in Atlantic Ocean air masses e.g. on 1 March 2013, the $PM_{2.5}$ Na^+ and Cl^- fraction dominates the total aerosol mass, compared to NH_4^+ and NO_3^- (Figure 5 and 6).

During the pollution event on the 5 to 6 April increases in other pollutant species are potentially observable, for example an increase was also observed for gaseous elemental mercury on the 5 March 2013 (Figure 17), with a maximum of 2.48 ng m^{-3} compared to the annual average in 2013 of 1.33 ng m^{-3} (standard deviation = 0.34 ng m^{-3}). The TEOM-FDMS systems, part of the AURN network, also showed an increase in the total $PM_{2.5}$ mass (Figure 15). It was, however, not until the 7 March 2013 at 16:00, that the total $PM_{2.5}$ peaked with a mass of 61 µg m^{-3} compared to the annual average of 4.4 µgm^{-3} (data downloaded from UK-Air). This was the maximum $PM_{2.5}$ mass concentration reported in 2013. There was no data available from the MARGA on the 7th March 2013 due to inlet filter contamination.

Though this was the largest PM_{10} and $PM_{2.5}$ pollution event during 2013 at Auchencorth Moss, it did not exceed the 24 hour mean limit value of 50 µg m^{-3} of PM_{10}, (as set out in the European Air Quality Framework Directive (Directive 2008/50/EC)), with a 24 hour mean maximum of 45.5µg m^{-3} PM_{10}. At the same time other areas of the UK experienced higher concentrations, for example on the 5th March 2013 London Marylebone Road reported a maximum hourly value of 121 µg m^{-3} PM_{10}. As a result Defra released a statement warning the public of the risks to those with health conditions (https://www.gov.uk/government/news/air-pollution-advice-to-the-public) in the UK.

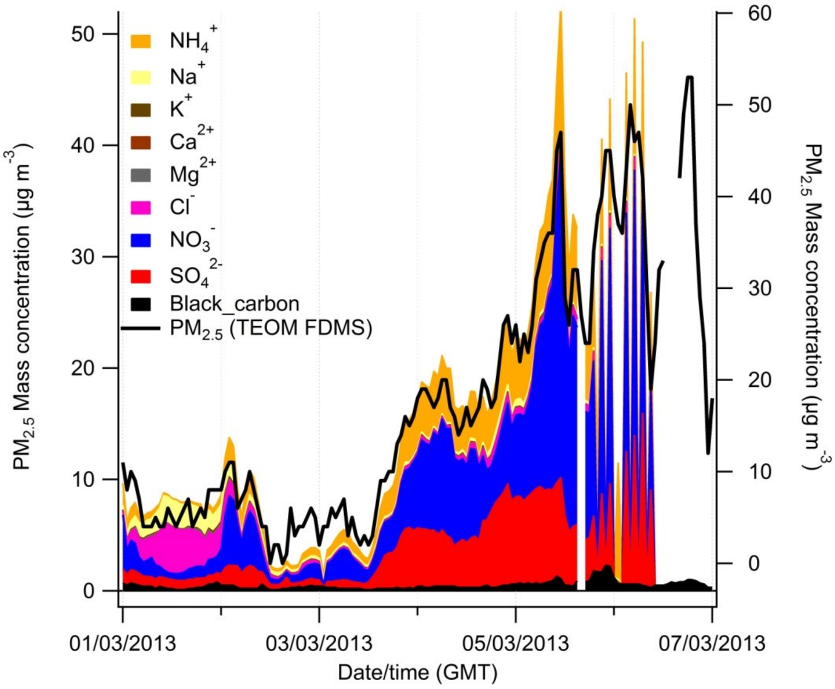

Figure 15 Ratified $PM_{2.5}$ measurements for 1 to 6 March 2013 at Auchencorth Moss. Individual species are measured by the MARGA instrument, with exception black carbon (cut-off unknown) which was downloaded from UK-Air website on the 18th September 2014. The $PM_{2.5}$ total mass was measured by the TEOM FDMS, part of the AURN network. Data was downloaded from the UK-Air website on the 18th September 2014.

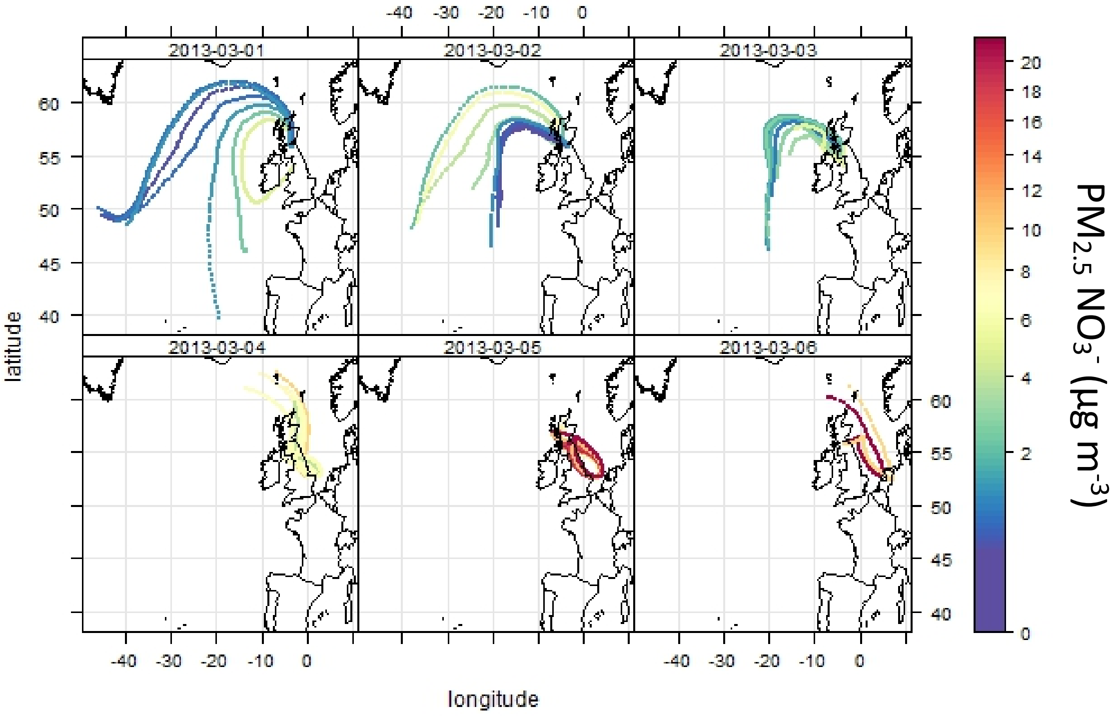

Figure 16 96 hour back trajectories, run at 6 hour intervals for Auchencorth Moss coloured according to the concentration of $PM_{2.5}$ NO_3^- (plot produced using openair, Carslaw and Ropkins (2012)).

Figure 17 Gaseous Elemental Mercury measurements for the 1st to 6th March 2013 at Auchencorth Moss.

3. Precipitation Network (Precip-Net)

The major ions precipitation network, Precip-Net, consists of 39 fortnightly bulk rain monitoring sites and two daily wet only collectors (DWOC) at which the chemical composition of precipitation is measured. The locations of the monitoring sites are shown in Figure 1. 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 the DWOC was operated at the Auchencorth Moss and Harwell sites that meet part of the UK's EMEP commitments. LSOs are responsible for 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 18 for 2013. The maps show that non-sea salt sulphate and nitrate concentrations tend to be highest on the eastern seaboard where the rainwater volume is smallest. Ammonium concentrations are highest in the areas of the UK where intensive livestock activity is highest. There is no clear pattern in the hydrogen ion concentration.

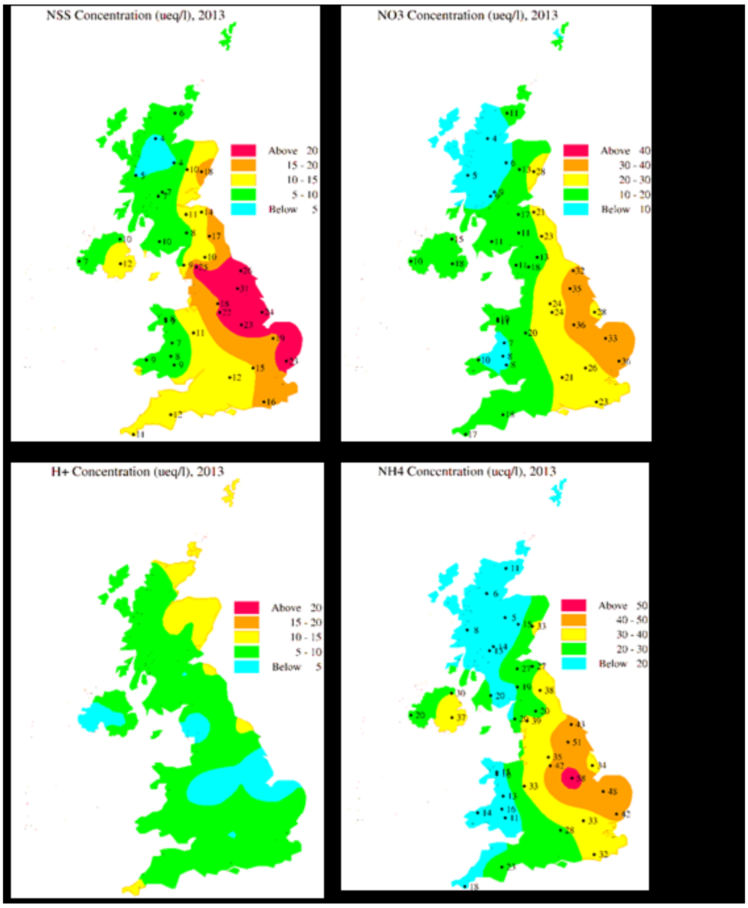

Figure 18 2013 spatial patterns of annual mean precipitation-weighted concentration of acidity, non-seasalt, sulphate, nitrate and ammonium

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 19 shows that sulphur dioxide emissions have decreased by about ninety percent whereas oxides of nitrogen have decreased by about sixty percent.

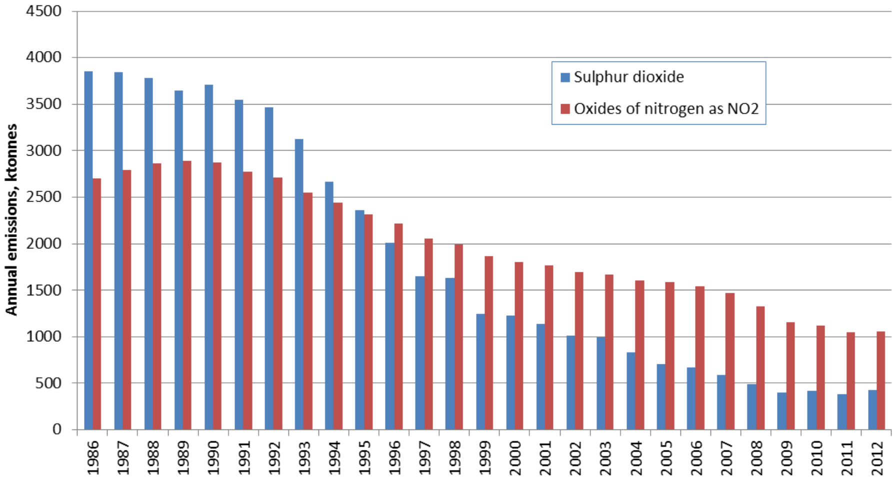

Figure 19 Sulphur dioxide and oxide of nitrogen emissions since 1986

In terms of trends in sulphur concentrations in rainwater there has been a steady decrease in non-sea salt sulphate at all monitoring stations. The rate of decrease has varied throughout the United Kingdom with the largest decreases occurring for monitoring stations located near to the large power stations in the Aire Valley and Trent Valley. This is illustrated in Figure 20 LHS which shows the average decrease in non-sea salt sulphate concentration (µeq l^{-1} $year^{-1}$) derived from a linear regression on annual mean concentrations for those stations currently operating in 2013 with at least 15 years of monitoring data. The largest decreases in annual concentration (about 2.7 µeq l^{-1} $year^{-1}$) are observed for stations such as Thorganby and Bottesford whereas the smallest decreases are observed for stations in the west of the United Kingdom, for example, the annual decrease for at Lough Navar is 0.5 µeq l^{-1} $year^{-1}$.

The right hand map in Figure 20 shows the equivalent plot for nitrate concentrations. The map differs in that the class boundaries are five times smaller than the non-sea salt sulphate. In general at each sampling station the rate of decrease for nitrate concentration is much lower, typically three to five times lower, than that for non-sea salt sulphate. Since about 2009 the non-sea salt sulphate and nitrate concentration at most monitoring stations in Wales and Scotland (and Lough Navar in Northern Ireland) have reduced to levels that would have been regarded as regional background concentration (say less than 8 µeq l^{-1}) when the monitoring network began in 1986. Ammonium concentrations in rainwater have also tended to decrease but the picture is more complex due to the smaller percentage reductions in ammonia emissions, local geographic and temporal variability of ammonia emissions and concentrations, as well as dry deposition on funnels and sample storage uncertainties. The inter-annual variability is also large and hence trend analysis more challenging to quantify.

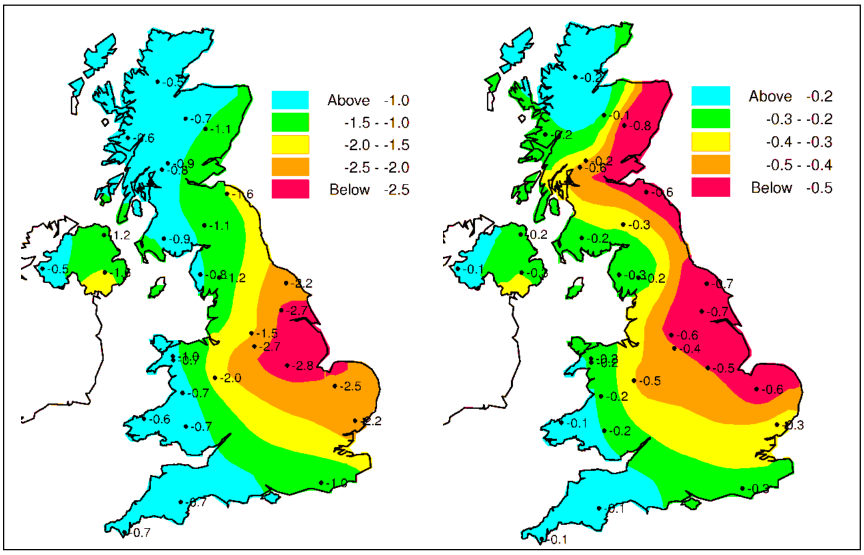

Figure 20 Annual change in non-sea salt sulphate and nitrate concentration (μeq l^{-1} $year^{-1}$)

Figure 21 and Figure 22 compare the total sulphur dioxide and estimated oxide of nitrogen emissions for the UK with the Precip-Net average non-sea salt 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..

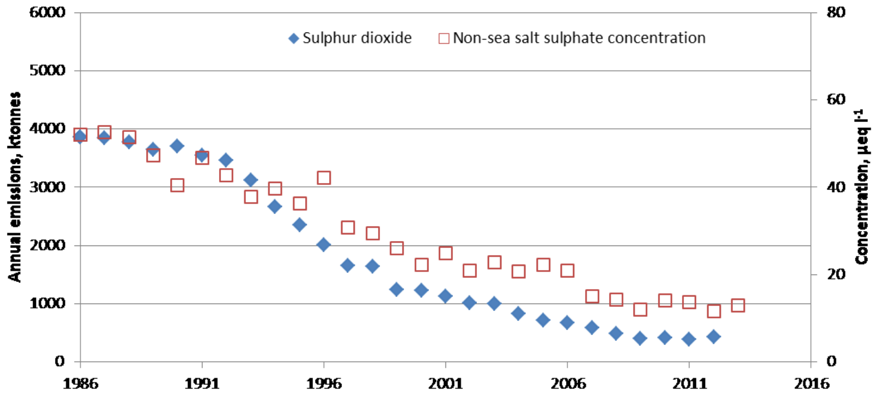

Figure 21 A comparison of total sulphur dioxide emission with annual network average non-sea salt sulphate concentration

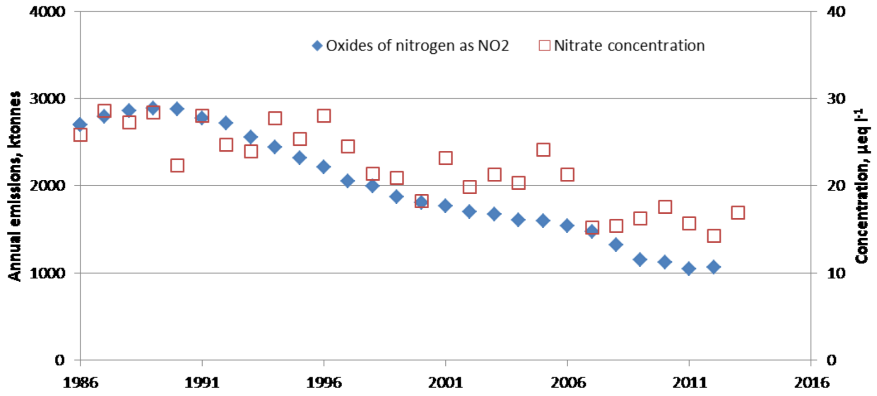

Figure 22 A comparison of total oxides of nitrogen (as NO_2) emission with annual network average nitrate concentration

4. NO_2-Net Network

The NO_2 network (NO_2-Net) consists of 24 sites (Figure 1) at which diffusion tubes, in triplicate, were exposed for four-weekly exposure periods. The annual average NO_2 measured at each site, together with data capture, are shown in Table 12. Diffusion tubes consist of a polypropylene tube (7.1 cm in length), on one end of which is a low density polyethylene cap. Two stainless steel grids impregnated with the absorbent chemical are mounted within this cap. In this case, the absorbent is a solution of triethanolamine and acetone. The annual average concentrations from 2010-2013 are shown in Figure 23. At most sites the annual average concentration has remained more or less constant over this four year period.

Table 12 NO_2 concentration from the Diffusion Tubes in the NO_2-Net network, 2013

Site Name	Concentration (µg m^{-3})	Data capture	Site Name	Concentration (µg m^{-3})	Data capture
Allt a'Mharcaidh	1.9	100%	Hillsborough Forest	7.8	100%
Balquhidder 2	2.8	100%	Llyn Llydaw	4.1	100%
Bannisdale	4.8	100%	Loch Dee	2.7	65%
Barcombe Mills	11.0	100%	Lough Navar	3.1	100%
Driby 2	11.5	100%	Moorhouse	4.7	100%
Eskdalemuir	3.8	92%	Percy's Cross	5.0	100%
Flatford Mill	11.3	100%	Polloch	2.0	100%
Forsinain 2	2.1	92%	Pumlumon	5.0	100%
Glensaugh	3.7	100%	Strathvaich	1.6	100%
Goonhilly	4.8	100%	Tycanol Wood	5.2	100%
Harwell	12.4	100%	Whiteadder	4.5	100%
High Muffles	7.0	100%	Yarner Wood	5.5	99%

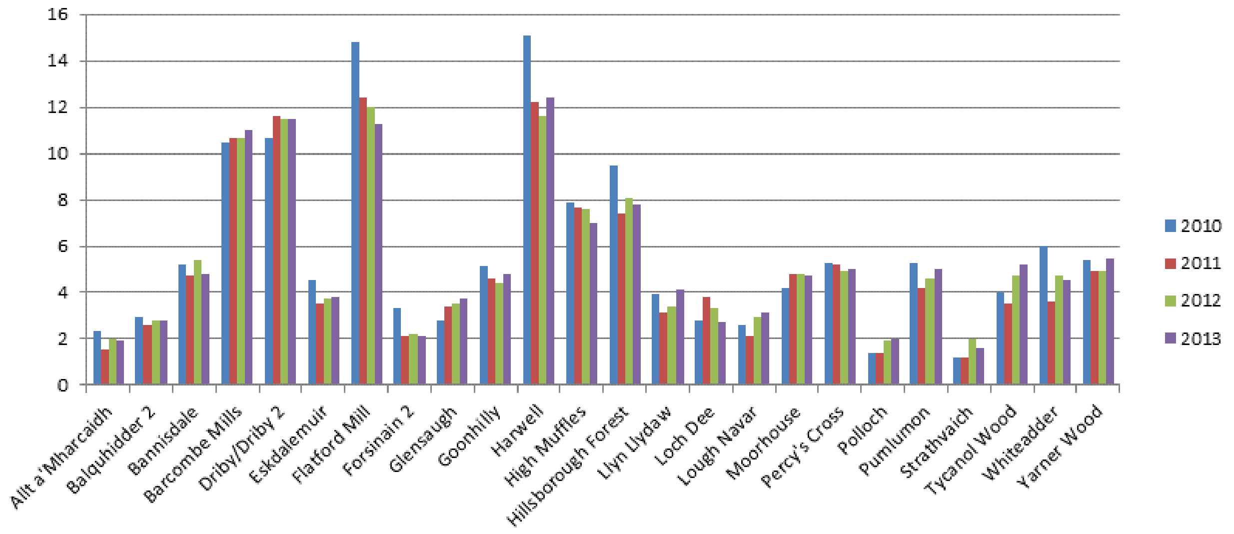

Figure 23 Annual average NO_2 concentration (µg m^{-3}) at the NO2-Net sites 2010-2013

Figure 24 displays the oxides of nitrogen (as NO_2) emissions since 2000 estimated by the National Atmospheric Emissions Inventory (NAEI) plotted alongside NO_2-Net network measurements. The network average of annual average concentrations for all sites has been plotted (black) along with two other selected sites: Flatford Mill (a relatively high concentration location, blue line) and Strathvaich Dam (a low concentration site, red line). Comparison of the network annual average concentration for all years since 2000 with emissions of oxides of nitrogen (as NO_2) from all sources shows that the average NO_2 concentration has decreased more or less in line with emissions.

The same rate of decrease can be seen for Flatford Mill. However a comparable decrease is not observed at Strathviach Dam where little change is observed. The differences are thought to be due to the different source influences on the sites: Flatford Mill is a southern site closer to London and hence is more influenced by road transport and combustion sources whereas the Strathvaich Dam site is a very rural location in Scotland with minimal influence from any local sources. Figure 24 shows the longer term trends: estimated emissions are plotted against selected sites in the network.

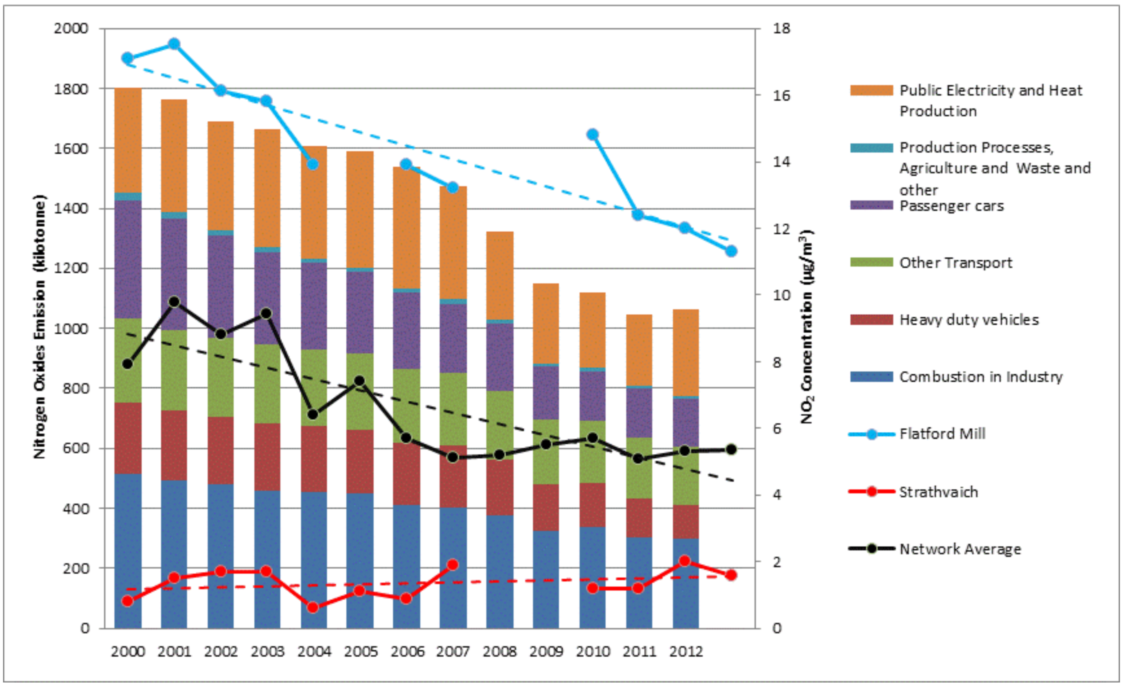

Figure 24 NAEI NOx Emission Estimates and NO2 Concentrations at two UKEAP sites

5. 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. Monitored mean annual concentrations at individual sites in the network are summarised in Figure 25 and the spatial distribution of the concentration measured in 2013 are shown in Figure 26 and Figure 27. The largest HNO_3 concentrations were measured in southeast England (e.g. London; 2013 annual mean of = 2.8 µg HNO_3 m^{-3}, range = 1.9 - 3.6 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; 2013 annual mean = 0.33 µg HNO_3 m^{-3}, range = 0.06-0.84 µg HNO_3 m^{-3}).

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 (accross 30 sites), the higher spatial variability in gaseous species can be seen, however it should be noted that there will also be seasonal variations. 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. It is noted that the interference due to HONO and other NO_y species are likely to lead to these numbers being revised in 2014, with a significant component of denuder measured nitrate being due directly to HNO_3 (approximately 45%) and the remainder due to other NO_y species reacting to form nitrate on the denuder (draft report submitted to Defra, November 2013).

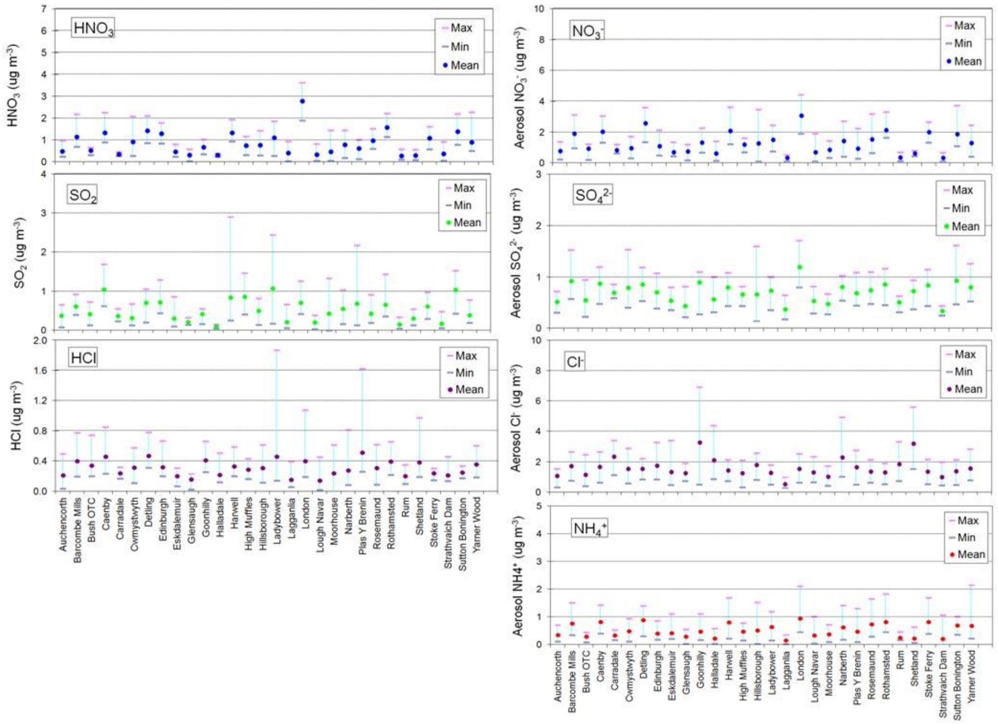

Figure 25: AGANet mean monitored annual concentrations of gaseous HNO_3, SO_2, HCl and NH_3 and particulate NO_3^-, SO_4^{2-}. Cl^- and NH_4^+. Each data point represents the annual averaged concentrations of monthly measurements made at each site in 2013, whilst the bars show the minimum and maximum concentrations observed.

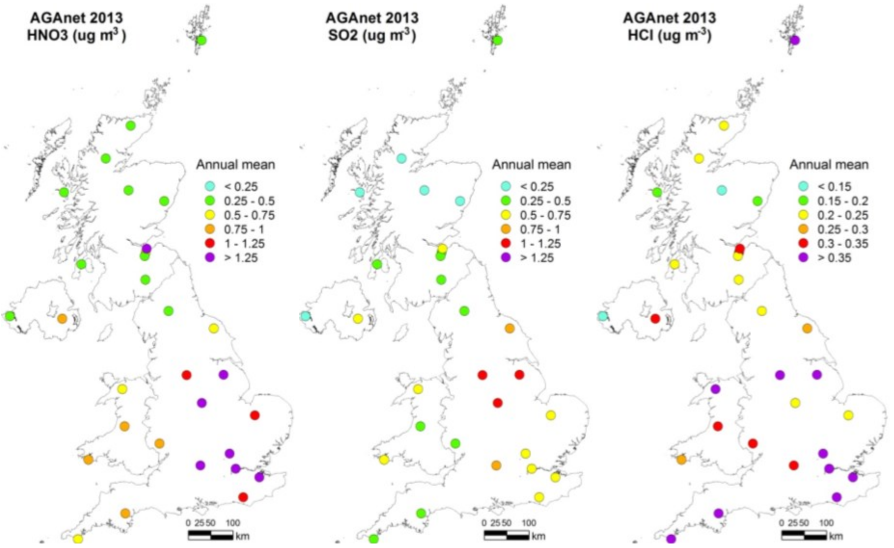

Figure 26: Annual mean monitored atmospheric reactive gas concentrations (HNO_3, SO_2, HCl) across the UK from averaged monthly measurements made in 2013.

For SO_2, the largest concentrations were measured at Ladybower (annual mean of 1.1 µg SO_2 m^{-3}) in the Peak district national park and neighbouring sites Sutton Bonington to the South and Caenby to the East (annual mean of 1.0 µg SO_2 m^{-3}). At these sites, the large annual mean concentration was due to high SO_2 concentrations from January to March, coinciding with a period of very cold weather. The 2000 MW capacity coal fired Ratcliffe-on-Soar power station is 2km North of Sutton Bonington. SO_2 concentrations generally decreased towards the west and north of the UK, with the lowest concentrations of <0.5 µg SO_2 m^{-3} in northern Scotland and at Lough Navar in the West of Northern Ireland . SO_2 is also seen to be more spatially variable than SO_4^{2-} aerosol, reflecting the long atmospheric residence time of the latter.

HCl and Cl^- concentrations are largest in the south-east and south-west of England (Barcombe Mills, YarnerWood) and lowest in the west of the country (Lough Navar, Eskdalemuir and Cwmystwyth) and most of Scotland (with the exception of Shetland) (Figure 26, Figure 27). The distribution may reflect the dual contribution to atmospheric Cl^- of anthropogenic and marine sources. The highest HCl concentrations in the south may be derived from emission or reaction of sea-salt with HNO_3 to produce HCl. In contrast, the higher CL^- concentration in the south-west probably reflects a marine contribution to the aerosol. The concentrations of base cations vary greatly depending on the species. The concentration map for Na^+ is similar to that for Cl^-, illustrating the close coupling between the two species.

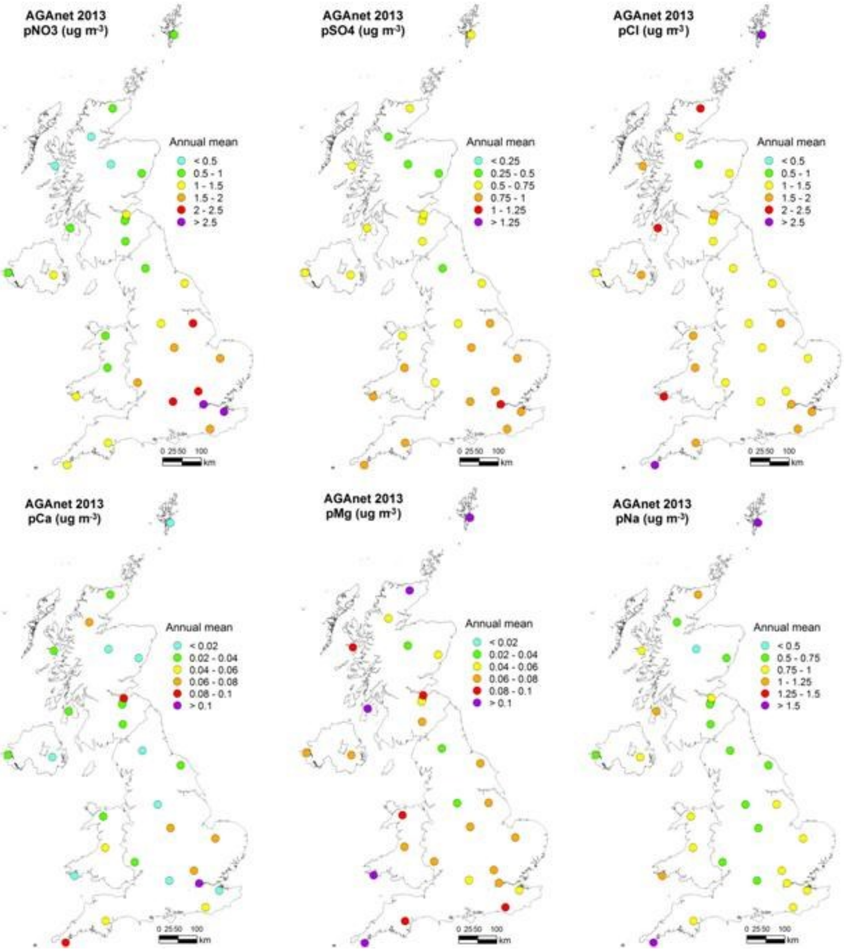

Figure 27: 2013 annual average monitored atmospheric aerosols (particulate NO_3^-, SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+} and Na^+) concentrations across the UK

The long-term trends in gaseous HNO_3, SO_2, HCl (Figure 28) and particulate NO_3^-, SO_4^{2-}, Cl^-, NH_4^+ (Figure 29) are shown by plotting monthly averages of measurement data from all sites, and also from the 12 original sites for the period 1999-2013. Temporal trends can be seen to be strongly influenced by inter-annual variability and it is necessary to consider the trends in terms of local, regional and national drivers.

In spring 2003, an episode of elevated concentrations of ammonium nitrate was measured across the UK, impacting on annual mean concentrations for that year (also discussed in Section 3). 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).

Overall, the dataset shows no detectable trend in gaseous HNO_3 or particulate NO_3^-. Gaseous SO_2 concentration on the other hand continues to show a gradual downward trend, in agreement with UK SO_2 emission trends. The average concentration of SO_2 from AGANet 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 0.5 µg SO_2 m^{-3} in 2013. The decrease in gaseous SO_2 concentrations is also accompanied by a smaller decline in particulate SO_4^{2-} concentrations.

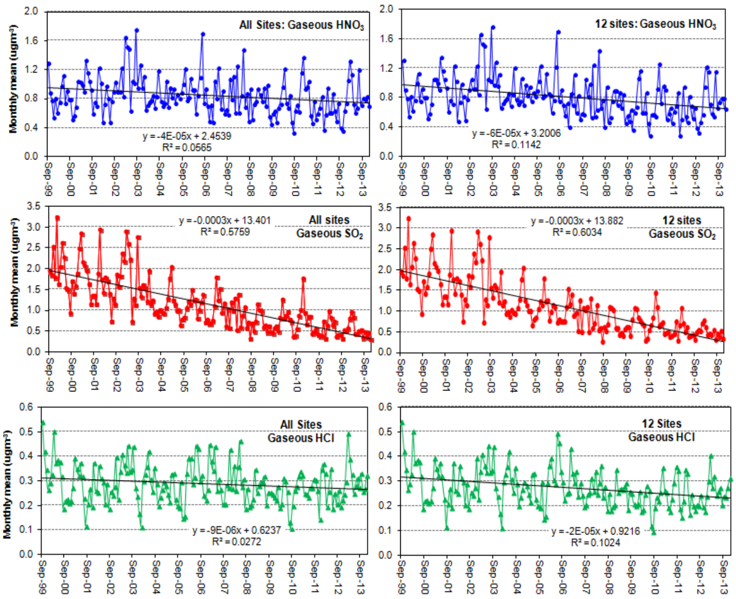

Figure 28: Long-term trend in gaseous HNO_3, SO_2, HCl concentrations. Each data point represents the averaged monthly measurements from all sites (increased from 12 to 30 sites since Jan 2006) and also the original l2 monitoring sites in the network.

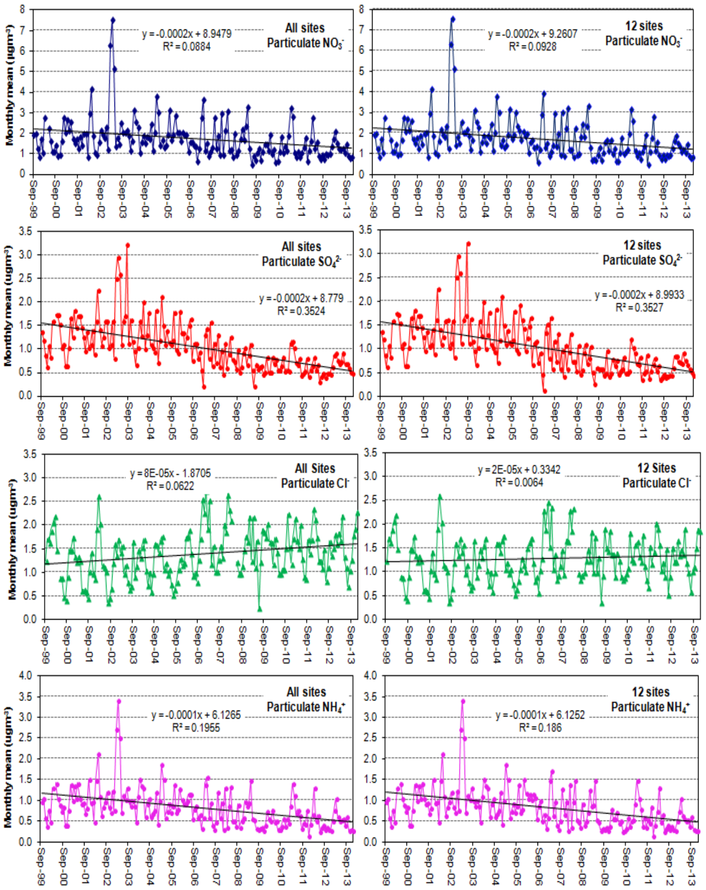

Figure 29 Long-term trend in particulate NO_3^-, SO_4^{2-}, Cl^- and NH_4^+ concentrations (each data point represents the averaged monthly measurements from all sites (increased from 12 to 30 sites since Jan 2006) and also the original 12 monitoring sites in the network

Scatter plots of the concentrations of gas and aerosol phases of the different components show that there are significant spatial correlations between the concentrations of the different pollutants at the 30 monthly monitoring sites (Figure 30). In the case of the gases, this can be attributed to the regional distribution of sources being similar, whereas for the aerosol, the chemistry must obviously balance between the major cations and anions. 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 degree of correlation observed. As with the gases, reduced nitrogen (NH_4^+) is in molar excess over SO_4^{2-} and NO_3^-. However, aerosol NO_3^- is in molar excess over SO_4^{2-} and is even somewhat larger in terms of equivalents of H^+. Whilst there is no discernible relationship between particulate Cl^- and NH_4^+, there is a near 1:1 relationship between Cl^- and Na^+, consistent with a marine origin for these ions in the UK.

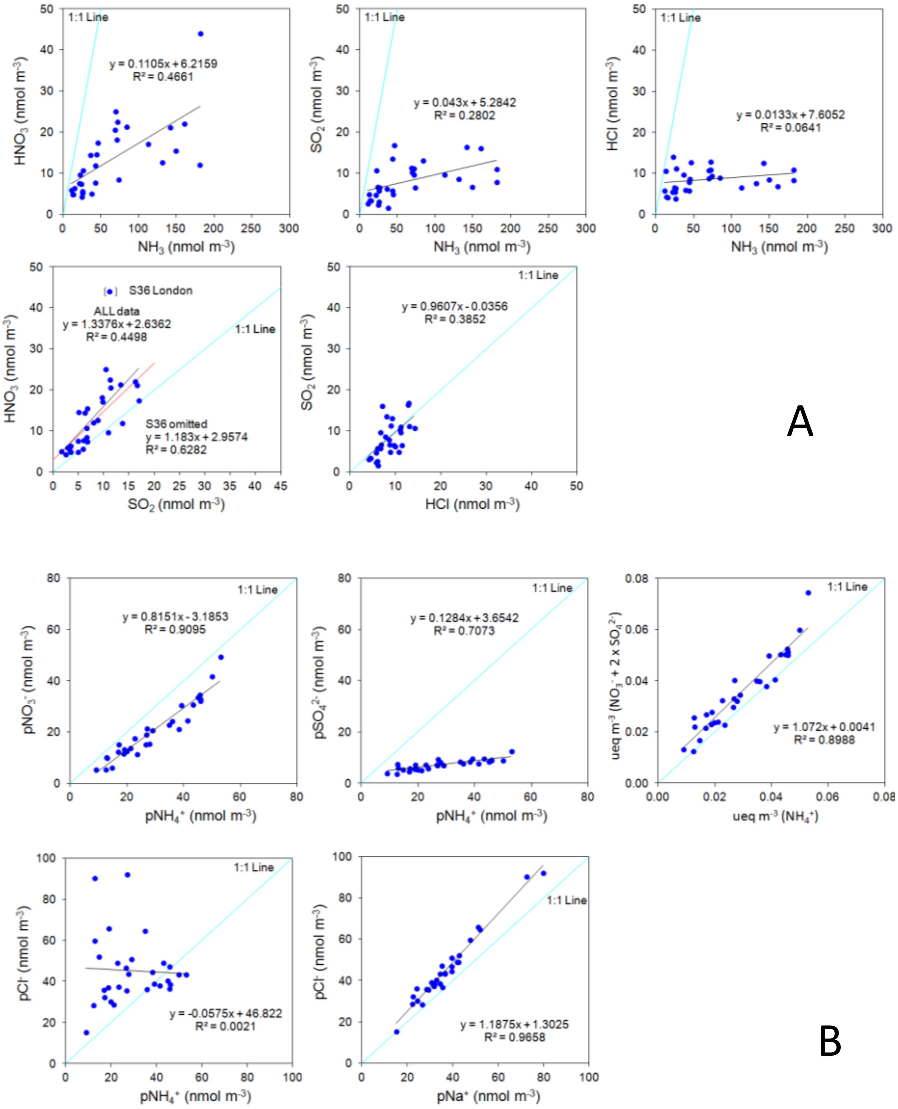

Figure 30: Scatter plots showing the relationships between concentrations of A: HNO_3, SO_2, NH_3, B: NO_3^-, SO_4^{2-}, NH_4^+, Cl^-, and Na^+ from the monthly measurements in 2013 at all 30 sites.

6. National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly speciated measurements of atmospheric NH_3 in 2013 was 85, summarised in Table 13. 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 in Section 6 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 Appendix 2. The average NH_3 concentrations observed at each of the sites in 2013 are shown Figure 31, 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 2013 NAMN results continue to illustrate the high spatial variability in NH_3 concentration and the seasonal variability of ammonia concentrations reflecting the large regional variability in NH_3 emissions.

Table 13 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2013

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

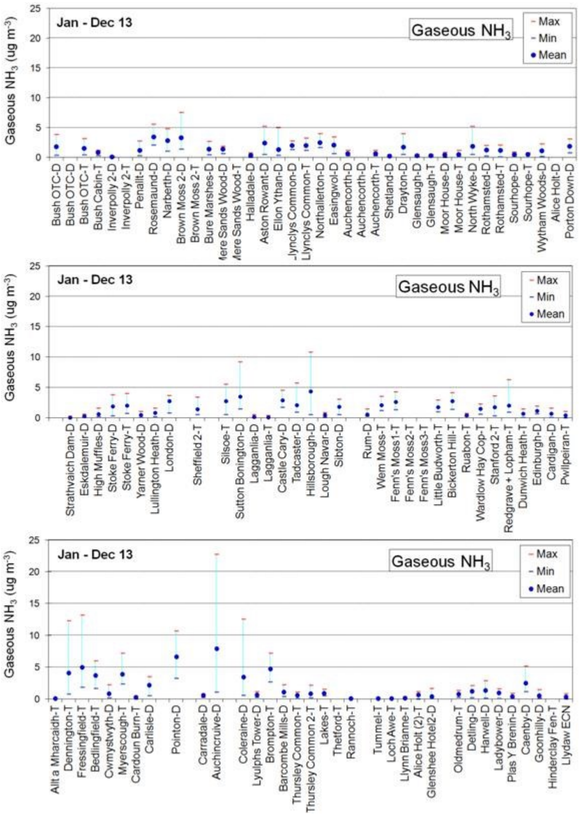

Figure 31 Annual mean monitored concentrations of gaseous NH_3 in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2013, whilst the bars show the minimum and maximum concentrations observed.

The DELTA sites are distributed widely across the UK to provide the regional patterns of NH_3 (and NH_4^+ at the 30 AGANet sites), while complementary passive sampling with ALPHA samplers is used to assess meso-scale variability of NH_3 in source areas as a test of the NH_3 emission-dispersion modelling. National maps of both NH_3 and NH_4^+ concentrations derived from the NAMN confirm the high spatial variability of NH_3 (0.04 – 7.9 μg 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 (Lagganlia) at 0.12 μg m^{-3} to highest (S36C London) at 0.95 μg m^{-3}. Aerosol NH_4^+ shows a spatially smooth concentration field as expected for an aerosol component. It also has a similar distribution to the sulphate and nitrate aerosol UK maps (Figures 27), as would be expected due to the formation of stable and semi-stable particle phase salts, e.g. ammonium sulphate and ammonium nitrate, respectively.

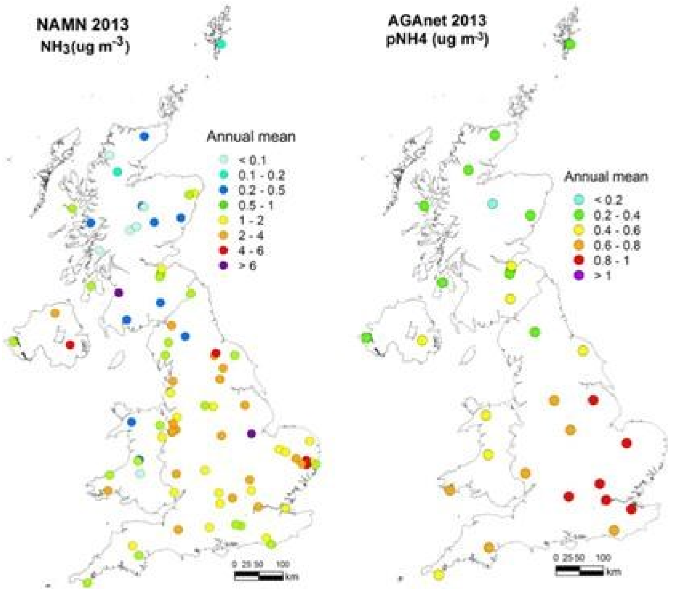

Figure 16: Spatial patterns of annual NH_3 and aerosol NH_4^+ concentrations from monthly NAMN/AGAnet measurements in 2013. Since Sep 2009, ammonium is measured at the 30 AGANet sites only

The annual NH_3 concentration data from the whole NAMN over the period 1998 to 2013 has been summarised, shown here in a box plot (Figure 32). 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 maximum and minimum concentrations and the diamonds represent the mean annual concentration for 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 16 year period were also excluded. After this adjustment, 60 sites remained in 1998, 67 sites in 1999 and 75 sites from 2000 onwards. Whilst UK emissions of NH_3 declined by about 17% during the operation of NAMN (http://naei.defra.gov.uk/), NH_3 concentrations from the overall dataset show no detectable trend over the 16 year 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.

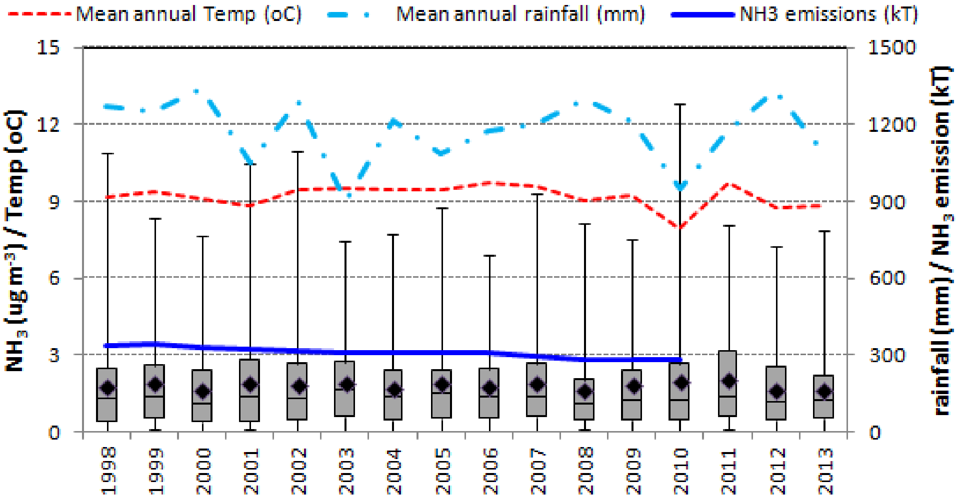

Figure 32: Changes in atmospheric NH_3 averaged over all sites in NAMN operational between 1998 and 2013 (sites with short runs excluded). Annual mean UK meteorological data (source http://www.metoffice.gov.uk/) are also plotted to illustrate the relationship between inter-annual variability in NH_3 concentrations with changing temperature and rainfall.

7. References

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Acknowledgements

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Appendices

Appendix 1: Guide to UKEAP data and Data usage

A1.1 Links to all networks with measurements at supersites on UKAir:

Auchencorth Moss:
http://uk-air.defra.gov.uk/interactive-map?ll=55.792160,-3.242900

Harwell:
http://uk-air.defra.gov.uk/interactive-map?ll=51.571078,-1.325283

A1.2 Contact and data citation guidance for 2013 data

Please contact Ricardo-AEA or NERC Centre for Ecology and Hydrology for authorship of multiyear datasets.

Harwell EMEP Supersite

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

Lingard, J., Ritchie, S., Conolly, C. UK Eutrophying and Acidifying Atmospheric Pollutant project's Monitoring instrument for AeRosols and reactive Gases (MARGA), Harwell Supersite(Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (***insert date of data receipt***)

Hourly NO and NO_2 (ANNOX instrument): Contact: Mr Steve Telling, Ricardo-AEA

Telling, S., Lingard, J., Ritchie, S., Conolly, C. UK Eutrophying and Acidifying Atmospheric Pollutant project's ANNOX instrument, Harwell Supersite (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (***insert date of data receipt***)

Meteorological Data: Contact Dr Justin Lingard, Ricardo-AEA

Auchencorth Moss EMEP Supersite

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

Twigg, M.M., Leeson, S.R. Morrison, E., Tang, Y.S., van Dijk, N., Braban, C.F., UK Eutrophying and Acidifying Atmospheric Pollutant project's Monitoring instrument for AeRosols and reactive Gases (MARGA), Auchencorth Supersite(Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (**insert date of data receipt**)

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

Kentisbeer, J., Leeson, S.R. UK Eutrophying and Acidifying Atmospheric Pollutant project's ANNOX instrument, Auchencorth Supersite(Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, UK EMEP Supersite, http://uk-air.defra.gov.uk/networks/network-?view=ukeap, Data downloaded/received (**insert date of data receipt**)

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

Acid Gas and Aerosol Network

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

Tang, Y.S. , Poskitt, J., Nemitz, E., Bealey, W.J., Leaver, D., Beith, S., Thacker, S., Simmons, I., Letho, K., Wood, C., Pereira, G., Sutton, M.A., Davies, M., Conolly, C., Donovan, B., Braban C.F., UK Eutrophying and Acidifying Atmospheric Pollutant project's Acid Gas and Aerosol Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, AGANet, http://uk-air.defra.gov.uk/networks/network-info?view=ukeap), Date received: (***insert date of data receipt***)

National Ammonia Monitoring Network

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

Tang, Y.S. , Poskitt, J., Nemitz, E., Bealey, W.J., Leaver, D., Simmons, I, Pereira, G., Sutton, M.A., Davies, M., Conolly, C., Donovan, B., Braban C.F., UK Eutrophying and Acidifying Atmospheric Pollutant project's National Ammonia Monitoring Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, AGANet, http://uk-air.defra.gov.uk/networks/network-info?view=ukeap), Date received: (***insert date of data receipt***)

Precipitation Network

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo-AEA

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

NO_2-Network

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo-AEA

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

Appendix 2: QC summary for 2013

A2.1 Harwell

MARGA QC

The MARGA 2S is a research-grade instrument. Currently there is no proposed or accepted ISO, CEN or equivalent BS standard method for the determination of the concentration of anionic or cationic species in PM_{10} and $PM_{2.5}$. The MARGA is designed to be operational 24 hours a day, 365 days a year, but as the analyser is a research instrument it has some reliability issues. The MARGA made continuous measurements of the chemical composition of PM_{10} and $PM_{2.5}$ throughout 2013. The percentage data capture for the twenty-one channels of measurements returned by the instrument were between 59-90%, as shown in Table 5, Table 6, and Table 7.

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, and wet rotating denuder, 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, though no blank was run in November 2013. 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 assessed 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 2013 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 14. The % relative errors ranged from 0-19% of the nominal concentration for both Li^+ and Br^-, but were generally higher for Li^+.

Table 14 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*	286000 295	11% 8%
Q2			320000† 320*	271617 275	15% 14%
Q3			320000† 320*	258041 277	19% 14%
Q4			320000† 320*	291000 270	9% 16%
Q1	IC	Br^-	3680† 3.68*	4130 3.94	12% 7%
Q2			3680† 3.68*	3662 3.23	0% 12%
Q3			3680† 3.68*	3812 4.20	4% 14%
Q4			3680† 3.68*	3690 3.36	0% 9%

† 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.

A2.6 Auchencorth Moss

MARGA QC

The MARGA instrument relies on an internal standard (LiBr) to quantify species which is prepared by the LSO. As part of the quality control process, regular sub samples were taken and sent to a UKAS accredited laboratory for analysis to confirm the concentrations (Table 15). Below are the results from the samples analysed in 2013. Due to the low values in Li^+ during the first half of 2013, a new LiBr stock solution was prepared in July 2013 from which the internal standard working solution was prepared. This explains the improvement in the Li^+ and Br^- concentrations in Table 15. Measurements by the MARGA are rejected where deviation from known concentrations exceeds ± 20%.

Table 15 Analytical results of Li+ and Br- and the % of the theoretical concentration.

Sample	Li^+ (µg l^{-1})	% Li^+ *c.f.* theoretical concentration	Br^- (µg l^{-1})	% Br^- *c.f.* theoretical concentration
January 2013	63.6	91	708	87
March 2013	61.8	88	724	89
April 2013	58.5	84	741	91
June 2013	57.3	82	796	98
July 2013	58.9	84	809	100
August 2013	65	93	766	94
September 2013	65.3	93	756	93
November 2013	66.7	95	765	94
December 2013	66.9	96	771	95

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, 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 MARGA ongoing QC, a monthly blank was introduced into the routine maintenance of the instrument in March 2013. As well as being used to identify any potential contamination in the system, it was used in the calculation of a detection limit for certain species which is used in the ratifying process.

Table 16 Maintenance Schedule - MARGA 2S (separate air pump/white WRD heads) at Auchencorth Moss

change every:	**1**	**2**	**1**	**2**	**3**	**4**	**6**	**1**	**2**
component	**week**	**week**	**month**	**month**	**month**	**month**	**month**	**year**	**Years**
Clean cyclone and PM$_{10}$ head			x						
Replace air tubing					X	x			
Carry out a blank			x						
Take a subsample of internal standard for analysis					x				
2x absorbance liquid 20 Litre (with 1ml 30-35% H2O2)	x								
2x eluent (anion and cation, both 8 Litre)	x								
Internal standard LiBr 4 (or 5) Litre				x					
suppressor liquid 5 Litre 0.35M phosphoric acid (H3PO4)		x							
2x empty waste container 30 Litre and add approximately 30 grams of NaHCO$_3$	x								
2x sample filters behind SJAC		x							
2x sample filters behind WRD			x						
2x aspiration filters anion/cation			x						
2x inline eluent filter behind pump before pulsation dampener			x						
2x inline liquid filter behind suppressor pump			x						
2x suppressor pump tubing								x	
4x WRD seals located inside WRD heads								X	
4x WRD seals on outer tubing located against WRD heads								x	
2x IC pump seals								x	
2x IC pump check inlet valves								x	
2x IC pump check outlet valves								x	
2x membrane of gas sampling vacuum pump								x	
2x clean SJAC in 1% H$_2$O$_2$ for 10 minute in an ultrasonic bath **							x		
2x clean WRD **							x		
clean or change all Teflon tubing 1/16" boxes**								x	
2x change guard column: 1 anion, 1 cation (+filters if dirty)			x						
1x change anion IC column if necessary ****				x		x			
1x change cation IC column if necessary ****						x			
1 x change cation pre-concentration column if neccesary							x		
1 x change anion pre-concentration column if necessary						x			

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

A2.3 Precip-Net

EMEP Inter-comparison

An important data quality assessment is organised annually by the EMEP Chemical Co-ordinating Centre (CCC) at the Norwegian Institute for Air Research (NILU). Each year, samples are sent to over 30 analytical laboratories in Europe, and to other internationally recognised analytical laboratories. The inter-comparison exercise is required as part of the EMEP monitoring programme and represents a fundamental check on analytical performance that is essential if response to emission reductions is to be observed consistently throughout Europe.

Results of the 31st EMEP Inter-comparison

The inter-comparison in 2013 was the 31st time such an inter-comparison took place. The samples provided included synthetic rainwater samples and nitrogen dioxide in absorbing solution.

Table 17 below compares the expected and measured concentrations for different components of the rainwater samples. The agreement between the expected and measured data for the laboratory used in the UKEAP network was considered satisfactory by EMEP which is the highest rating for the EMEP quality norm. The results of the inter-comparison shows that the analytical laboratory used in the UKEAP network is performing exceptionally well particularly for sulphate, nitrate, magnesium, sodium and pH with all of the measurements for these species being within less than 3% of the expected values.

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

Table 17 EMEP Inter-comparison

Species	Sample code	Expected concentration µeq l^{-1}	Measured concentration µeq l^{-1}	Absolute Mean difference (%)
Sulphate	G1	0.673	0.658	2%
	G2	0.776	0.7545	3%
	G3	1.319	1.278	3%
	G4	1.474	1.436	3%
Nitrate	G1	0.274	0.2805	-2%
	G2	0.396	0.3995	-1%
	G3	0.529	0.536	-1%
	G4	0.612	0.623	-2%
Ammonium	G1	0.16	0.1735	-8%
	G2	0.214	0.2315	-8%
	G3	0.267	0.284	-6%
	G4	0.348	0.3735	-7%
Magnesium	G1	0.124	0.1245	0%
	G2	0.114	0.1155	-1%
	G3	0.155	0.1545	0%
	G4	0.175	0.1775	-1%
Sodium	G1	0.208	0.2135	-3%
	G2	0.329	0.3305	0%
	G3	0.476	0.4695	1%
	G4	0.465	0.464	0%
Chloride	G1	0.154	0.139	10%
	G2	0.232	0.216	7%
	G3	0.347	0.334	4%
	G4	0.386	0.377	2%
Calcium	G1	0.102	0.0915	10%
	G2	0.115	0.1015	12%
	G3	0.192	0.168	13%
	G4	0.217	0.199	8%
Potassium	G1	0.136	0.129	5%
	G2	0.204	0.1985	3%
	G3	0.306	0.285	7%
	G4	0.374	0.358	4%
pH *	G1	4.57	4.54	1%
	G2	4.48	4.44	1%
	G3	4.22	4.175	1%
	G4	4.18	4.09	2%

* pH as pH units

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

A2.4 NO_2-Net

Results of the 31st EMEP Inter-comparison

The inter-comparison in 2013 was the 31st time such an inter-comparison took place. The results of the nitrogen dioxide absorbing solution are shown below in Table 18. The results of this intercomparison are excellent, with between a 1 and 3% absolute difference, which is easily within the criteria for satisfactory results reported by EMEP which is the highest rating for the EMEP quality norm.

Table 18 Comparison of Expected and Measured Concentrations of Nitrogen Dioxide in Absorbing Solution

Sample code	Expected concentration µg NO_2-N/ml	Measured concentration µg NO_2-N/ml	Absolute Mean difference (%)
C1	0.077	0.076	-1%
C2	0.047	0.044	-1%
C3	0.100	0.103	-2%
C4	0.107	0.107	-3%

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

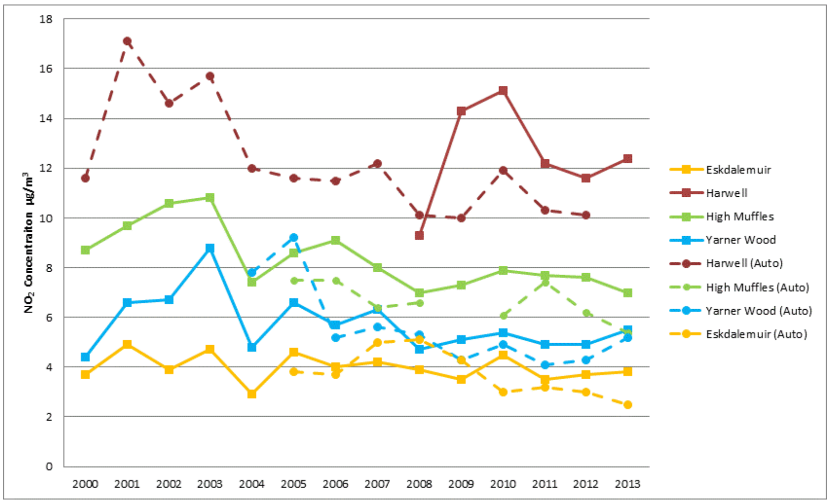

Figure 33 Comparison of measured concentrations of NO_2 by diffusion tube and automatic monitoring at collocated UKEAP sites * Not bias corrected

It is apparent from the comparison of the automatic and diffusion tube measurements that generally the NO_2 diffusion tubes appear to over-read when compared to the automatic sites and that the over-read appears more pronounced at the sites with higher concentrations. The diffusion tube measurements do show relatively good agreement with the automatic sites which gives some confidence in other rural site diffusion tube measurements. The use of diffusion tubes in these often very remote locations provide a cost effective approach to measurement.

A2.5 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 samples 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 34. 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 %).

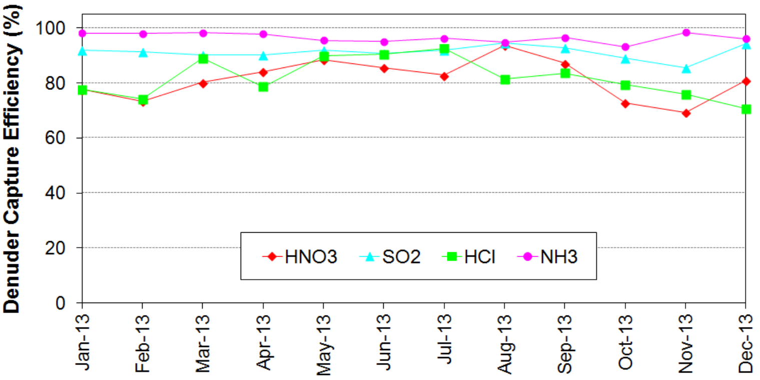

Figure 34: Monthly mean denuder capture efficiency (E) during 2013 for HNO_3, SO_2 and HCl from the 30 monitoring sites. E = amount in 1st denuder / (amounts captured in 1st + 2nd denuders)*100 %.

A2.6 NAMN

QC criteria

The measurements in NAMN are triplicate exposures, plus at 9 sites currently, the DELTA and ALPHA samplers are run in parallel. During 2013, over 90% of data passed the QC thresholds.

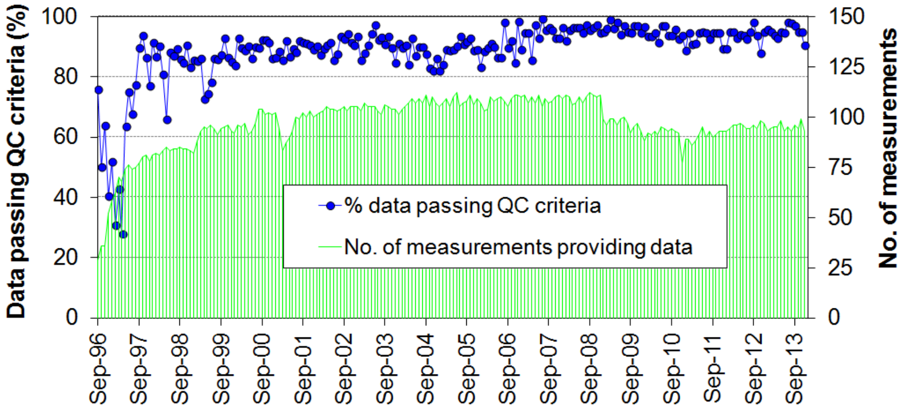

Figure 35: Assessing NAMN performance through monitoring total data capture, and % of data passing the QC thresholds (DELTA: capture of $NH_3 \geq 75$ % in the first of the 2 denuders, flow rate = > 0.22 L min^{-1}; DT/ALPHA: % CV for replicate samples < 30 % and < 15 % respectively).

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 do not deviate significantly in relation to the DELTA samplers with time. The annual regression used to calibrate the ALPHA sampler is shown in Figure 36. The annual calibration functions of ALPHA samplers show good consistency between years (slope of 3.046 *cf* slope of 3.039 in 2012).

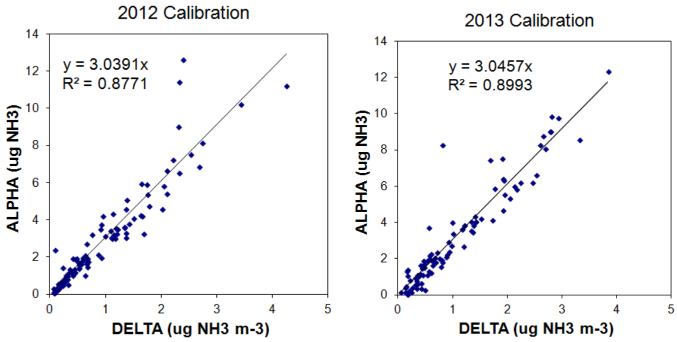

Figure 36: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers in years 2012 and 2013.