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UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)

B. Annual Report 2009

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Index

1. Introduction.....	1
2. UKEAP Review 2009 (adapted from Review Report to Defra).....	2
2.1 UKEAP Review Report Summary.....	2
2.1.1 Context of UKEAP measurements within UK Measurements.....	2
2.1.2 Key points of the review.....	2
2.1.3 PrecipNet.....	2
2.1.4 AGANet.....	3
2.1.5 PS-Net.....	3
2.1.6 NO ₂ -Net.....	3
2.1.7 UK NAMN.....	3
2.1.8 Option recommendations:.....	4
2.2 Changes to UKEAP post-Review.....	4
3. UKEAP structure and operation 2009.....	4
3.1 Overview.....	4
3.2 Quality Assurance.....	4
3.2 Precip-Net.....	5
3.3 PS-Net.....	6
3.4 NO ₂ -Net.....	6
3.5 AGA-Net.....	6
3.6 NAMN.....	7
3.7 Data Dissemination and Communications.....	7
3.7.1 Data archiving and submission.....	8
3.7.2 LSO/User Group Meeting 2009.....	9
4. UKEAP Measurements 2008.....	9
4.1 Precip-Net.....	9
4.1.1 Fortnightly bulk rain sampling.....	9
4.1.2 Daily Bulk and Daily wet only rain sampling.....	13
4.2 PS-Net.....	15
4.3 NO ₂ -Net.....	15
4.4 AGANet.....	18
4.5 NAMN.....	20
5. References.....	24
6. Links.....	24
7. Acknowledgements.....	24

1. Introduction

This is the first annual report prepared for the Defra UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP). Within this report there is a summary and complete record of the measurements made in 2008 under the previous contracts (Acid Deposition Monitoring Network, ADMN, and National Ammonia Monitoring Network, NAMN). The new UKEAP project combines the ADMN and NAMN into a combined set of networks which are operated by CEH Edinburgh and AEA Technology. 2009, the first year of UKEAP, has been a very busy year logistically. In the first six months the operation and scientific underpinning of the UKEAP measurements was the subject of a full Review which has shaped the component monitoring networks to be fit for current and future purpose. In addition CEH and AEA undertook training and operational logistical challenges in order to share the servicing of the UKEAP field sites.

This report is structured as follows:

UKEAP Review 2009 gives an overview of the outcome of the Review commissioned by Defra to assess the current best practice for acidifying and eutrophying pollutant monitoring.

UKEAP structure and operation in 2009 describes the monitoring networks and the sampling techniques employed, together with the changes made to the network in 2008 and 2009, and also changes which will be made in 2010 as a result of the UKEAP review.

2008 Results section consists of the data collected by the UKEAP monitoring sites in 2008 (under the previous contract) and presents concentration maps for species measured, together with the trends where available. Note that the details of all site measurements for 2008 and the historic trends are presented where appropriate in Annual Reports Part C: 2008 Data reports.

2. UKEAP Review 2009 (adapted from Review Report to Defra)

2.1 UKEAP Review Report Summary

The UKEAP Review document was commissioned by Defra to help assess the current status of, and future needs for monitoring of acidifying and eutrophying pollutants in the United Kingdom. As part of this review Defra wished to identify potential cost savings and efficiencies. All CEH and AEA staff and members of the Review Panel worked to produce the UKEAP Review Background document and the Review Panel Review Report Summary document. Below is the summary from the later document which summarises the key points and recommendations of the Review.

2.1.1 Context of UKEAP measurements within UK Measurements

Measurements of pollutant concentrations in air and rain within the UKEAP allow maps of pollutant exposure and pollutant budgets to be calculated. This is a key element in estimating risks to ecosystems and evaluating the impact of policy measures in reducing such risks. The measurements also help validate modelling studies and support many of the other measurements made within Defra and other Agency supported monitoring in the UK, for example at ECN sites and heavy metal monitoring sites. Of these other networks only the ECN is likely to undergo a substantial revision in the near future with the transformation to the ECBN. The coordination of UKEAP sites with the changing ECBN could not be considered in detail at this stage, but there is continuing liaison between the two projects which may be expected to increase in the future.

2.1.2 Key points of the review

Overall the current UKEAP measurement suite captures most of the important species relevant to the objectives of the project, specifically concentrations in precipitation and ambient concentrations of the most important aerosol and gas phase species. All the species measured are still considered to be relevant to meeting the UKEAP project aims. Other species considered for measurement are organic carbon, organic nitrogen and halogen acids in addition to chlorine (F, Br, I). It is considered that the organic nitrogen (organic-N) component is a key measurement which is not being made, but a methodology for routine monitoring of organic-N is not yet available. Developing such a methodology should be given high priority. Monitoring of organic carbon and non-chlorine halogen acids are not considered important to the objectives of the UKEAP network.

A decision with respect to the future organisation of data archiving and public access needed to be confirmed in consultation with Defra. The status quo is that the archiving is carried out using the Air Quality Archive for Precip-Net and NO₂-Net data and UK Pollutant Deposition for AGA-Net and NAMN data.

2.1.3 PrecipNet

The measurement of wet deposition in the UK is a key national network and continues to be very important. Dry deposition to bulk collectors is a significant sampling artefact and is not quantifiable. It is believed to be site specific and largest for ammonium. However wet-only methods require power and more infrastructure. A move towards this

technology may improve the UKEAP dataset in the long term, but the net benefits of wet-only sampling for the network have yet to be demonstrated. Precip-Net fortnightly has a sufficient number of sites for UK mapping and modelling. It is strongly recommended that the sampling frequency of the Precip-Net fortnightly bulk measurements remains the same or increases due to the effect of bird-strike on data capture. Sites where bird strike is identified as an issue should be examined and improved bird protection installed where necessary.

Precip-Net daily bulk measurement is a long running time series at Eskdalemuir. The fortnightly and daily sampling at Eskdalemuir give good agreement.

Daily Wet-only (EMEP) at Auchencorth and Harwell is part of the requirements for Level II site status therefore should be continued

2.1.4 AGANet

The measurements of acid gases and aerosol components are important contributions to the UK monitoring networks. Measurements of HNO₃ have allowed the importance of HNO₃-N dry deposition in the UK N budget and its spatial distribution to be assessed for the first time. Monthly measurements are optimal for 1) assessment of temporal patterns, annual means and long-term trends, 2) pollutant mapping, 3) verification of annually averaged concentrations generated with atmospheric transport models (FRAME, EMEP4UK) and 4) modelling annual deposition budgets (e.g. CBED).

Measurements of HNO₃ and NO₃ using the DELTA methodology may be subject to artefacts due to other NO_y species (e.g. conversion of NO₂⁻ to NO₃⁻); however in most rural cases this is expected to be causing a relatively small effect.

2.1.5 PS-Net

PS-Net consists of 5 sites making daily measurements of particulate sulphate. It does not measure the other components of aerosol. The daily measurements may be important to some epidemiology studies and also allow directional source apportionment. In the past few years, poor equipment reliability has led to low data capture. The method is not a reference method. Therefore, if this measurement continues, changing the technique used in the network is recommended.

The purpose of the network, in addition to the AGANet network, has not been demonstrated. There is a strong division of opinion within the project partners as to the need and relevance of PS-Net measurements.

2.1.6 NO₂-Net

NO₂-Net four weekly sampling is in line with the AURN sampling therefore it is not recommended to change the frequency. NO₂-Net measurements are used to provide measured UK NO₂ fields in conjunction with the AURN measurements.

2.1.7 UK NAMN

The core measurement of reduced N as NH₃ and NH₄⁺ (= NH_x) are provided by the UK NAMN, in support of acid gases and aerosols monitored in the AGANet. Inputs of NH_x are the dominant driver of ecological effects of deposited N, and the importance of NH_x

will increase relative to oxidised N, as NO_x emissions decrease further. Monthly measurements are optimal for the reasons listed under AGANet. Spatial variability for NH₃ in particular is difficult to capture; the high density of sites allow the UK to derive a good assessment of spatial patterns and source sector analysis. Changing DELTA-NH₃ only sites to ALPHA sites would lead to a small savings per annum and reducing the number of DELTA sites providing NH₄⁺ measurements (additional to NH₃) from 35 to 30 sites would lead to minor savings.

2.1.8 Option recommendations:

Option 1 Research Study Recommendations.

- a. Development of Organic-N methodology for implementation in UKEAP
- b. Characterisation of sampling uncertainty in measurement of HNO₃ and NO₃
- In DELTA methodology.

2.2 Changes to UKEAP post-Review

Specific changes recommended were:

- PS-Net daily sulphate measurements stopped
- Daily bulk rain chemistry measurements at Eskdalemuir stopped
- Decreasing the number of ammonium measurement sites from 35 to 30 to match the AGANET
- Decreasing the number of ammonia intercomparison sites from 12 to 9
- Closure of 5 ammonia measurements sites which had historically been set up for spatial variation assessment and other reasons.
- Addition of 2 NO₂ sites in South/Central England.
- Option for DELTA system assessment and improvement adopted.

It was agreed by Defra that the recommendations by the UKEAP review Panel were to be adopted and that the option to study the DELTA system methodology would be funded. By the end of 2009 most of these changes have been implemented with the exception of the final decision on use of ECN NO₂ sites for NO₂ measurements.

3. UKEAP structure and operation 2009

3.1 Overview

UKEAP and its component networks were brought together under the same contract in January 2009. The component networks all have a long history of monitoring the acidifying and eutrophying atmospheric pollutants in the UK. The methodologies of each of the measurements made in the component networks are summarised in Table 1 and have been reported in detail in the AQ0616 contract proposal and previous contract reports which are held on the Air Quality Archive and the UK Pollutant deposition websites (see Section 6 for links to on-line databases). Note that previously these details were included within this annual report, however for brevity the reader is referred to previous contract reports as the methodologies have not changed within the year of this report.

3.2 Quality Assurance

Quality Assurance is maintained through the careful implementation of established sampling protocols, and monitoring of laboratory performance through internal audit and participation in external inter-comparisons, for example the EMEP and WMO-GAW inter-

comparison schemes for analytical laboratories. During the UKEAP Review and the first year of the joint contract improvements to high level QC, specifically interannual assessment of data capture statistics, has been added to the established protocols.

Analytical analyses have taken part in annual international intercomparisons. The WMO-GAW 40th Laboratory inter-comparison summary results are available from <http://gasac-america.org/> and the EMEP 26th Laboratory inter-comparison results are available from the EMEP website - EMEP/CCC-Report 6/2009.

Table 1: Summary of UKEAP component networks

	Species	Frequency	Sites	Sampler	Analytical Techniques
PrecipNet <i>Fortnightly</i>	Ionic composition of rain	Fortnightly	38	Rain-catcher	Ion chromatography ICP-OES pH Conductivity
<i>Daily Wet only</i> EMEP <i>Supersites</i>	Ionic composition of rain	Daily	1(2)*	DWOC Sampler	Ion chromatography ICP-OES pH Conductivity
NO2-Net	NO _{2(g)}	4-weekly	24	Diffusion tubes	Colorimetry
PSNet	Sulphate	Daily	5	Stopped	
AGANet	Gas phase: HNO ₃ , SO ₂ , HCl (NH ₃) Particulate: NO ₃ ⁻ , SO ₄ ²⁻ , Cl ⁻ , Na ⁺ , Ca ²⁺ , Mg ²⁺ , (NH ₄ ⁺)	Monthly	30	DELTA samplers	IC ICP-OES Selective Conductivity (AMPHIA)
NAMN	NH _{3(g)} NH ₄ ⁺ (p)	Monthly	85 30	DELTA and ALPHA samplers	Selected ion Conductivity (AMPHIA)

* 2 sites from 03/09

3.2 Precip-Net

Fortnightly precipitation samples are collected at 38 sites using bulk collectors based on the design of Hall (1986). Operation of the Precip-Net has gone smoothly in 2009, and sites which were identified with a historical problem with bird strike have received specific attention during the site servicing carried out in 2009. The data captured of 2009 with respect to the data record will be assess in the first quarter of 2009 and in 2010 the effects of sampler bird-deterrent changes (see Figure 1 below) will be assessed.

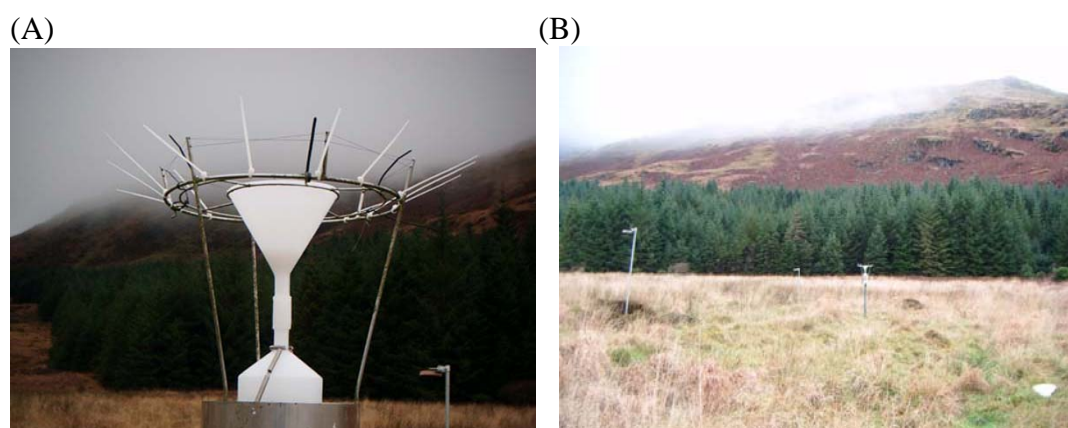


Figure 1: Loch Dee bulk sampling site. (A) Cable tie "ring-fence" on funnel cage to deter birds from perching, and (B) 2 x decoy posts set up in vicinity of bulk sampler.

Daily precipitation composition measurements were made at Eskdalemuir with a bulk collector until June 2009 (when it was stopped as per Defra instruction). The results for the first half of 2009 will be submitted in the 2010 Annual reports with a short summary of the data record for closure purposes.

Daily wet-only collector (DWOC) measurements have been made at Auchencorth Moss EMEP Supersite since 2006 and in March 2009 the second DWOC was commissioned at Harwell the other UK EMEP Supersite. During 2009 both samplers worked reliably and the data for the first three-quarters of 2009 is currently undergoing QC. A revised Protocol for sample handling and QC has been developed for 2010 to improve the efficiency of data reporting in order to fulfil quarterly reporting.

3.3 PS-Net

Daily sulphate concentrations continue to be measured at five sites until June 2009 at which point they were stopped on the recommendation of the UKEAP Review Panel and defra. Measurements in the Particle Counting and Speciation Network (<http://www.npl.co.uk/environmental-measurement/products-and-services/particle-counting-and-speciation-network>) will become the primary source of data for daily particulate sulphate (and other components) measurements at 2 urban sites and Harwell. In addition particulate phase sulphate is monitored on a monthly average basis as part of the UKEAP AGANet measurements. The results for the first half of 2009 will be submitted in the 2010 Annual reports with a short summary of the data record for closure purposes.

The sampling instruments (6-port bubblers) which are Defra capital equipment have been decommissioned and re-housed as appropriate in consultation with Defra.

3.4 NO₂-Net

Nitrogen dioxide concentrations are measured using passive diffusion tubes. Diffusion tubes are exposed singly at 21 locations and in triplicate at three locations. Care is taken to ensure identical exposure conditions for triplicate tubes. NO₂-Net has operated smoothly in 2009.

Currently the possibility of adding 2 extra sites into the NO₂ rural background measurements is being investigated with the possibility of using existing Environmental Change Network (ECN, see section 6) sites. This will be finalised within the first quarter of 2010.

3.5 AGA-Net

AGA-Net was previously termed the Nitric Acid network under the Acid Deposition Monitoring Network contract. AGA-Net consists of 30 sites which measure the composition of gas phase and particulate phase inorganic species. The methodology is the DENuder for Long-Term Atmospheric sampling (DELTA) for monthly measurements of nitric acid, nitrate and associated acids and aerosols. AGA-Net has operated smoothly during 2009 with site servicing including renewing one of the wind/solar powered DELTA systems at Glensaugh.

In 2010 UKEAP will be implementing a programme of testing with a view to improving the DELTA methodology to take into account the recent work of Robert Gehrig et al., and

that of CEH and NitroEurope (see Section 6) co-workers with a view to improving the DELTA system in concert with other DELTA and mini-denuder system users.

The primary issues with DELTA measurements are:

- a) Collection of particulate on the connecting tube before the filters
- b) Carry over of nitrate onto ammonium filter
- c) Potential NO₂ and other NO_y species artefacts on denuder and filters (UKEAP SID3 original Option 4).

Specific tests on the current DELTA systems need to be carried out to quantify the magnitude of the issues a - c and to test the next generation of DELTA systems for future incorporation into AGA-Net. The work plan should lead to a clearer understanding of the low cost DELTA system and how to improve the accuracy of its operation in the long term. Results from this option could allow a recommendation for changeover of AGA-Net in 2012 to an improved methodology.

3.6 NAMN

Given the high spatial variability of NH₃, the strategy for NAMN is to sample at a large number of sites to map the UK NH₃ concentration field, using low-frequency sampling. To address the issue of how representative sites are of the area, assessment of sub-grid variability at selected locations have previously been made in some cases (see previous contract reports). There were 89 sites in NAMN in 2008/9. Post the UKEAP review; this number will be reduced to 83. The types of site are summarised in Table 2.

Table 2. NAMN Sites pre and post UKEAP Review 2009 (valid from January 2010).

Number of sites	89	83
DELTA sites	58	54
DELTA NH ₃ only	23	24
DELTA (NH ₃ + NH ₄ ⁺)	35	30
(DELTA AGANet)	(30)	(30)
ALPHA sites	43	38
DELTA-ALPHA parallel sites	12	9

NAMN operation has been relatively smooth and the transfer of sample analysis from CEH Edinburgh to CEH Lancaster went well. CEH Edinburgh UKEAP personnel continue to support the Lancaster staff as part of the general operation of the network.

3.7 Data Dissemination and Communications

The UK network also forms part of the wider network of the European Monitoring and Evaluation Programme (EMEP). Results from this network are used to underpin the modelling studies that form the basis of negotiation of UNECE Protocols, which control the transboundary transport of acidifying pollutants. It is envisaged that all UKEAP data will be made available to EMEP as soon as possible. Metadata and data formatting for the NAMN and AGANet databases is currently underway and should be completed such that 2009 data can be submitted to EMEP in the next contract year.

Datasets produced by the UKEAP provide information on the current state of the environment with respect to acidification and eutrophication. The individual measurements are used in a number of projects supported by Defra and the Devolved Administrations:

- **Acid Deposition Processes/ Pollutant Deposition Processes** (current contractor: CEH Edinburgh): The measurements made in the UKEAP component networks form the basis to the Concentration Based Estimates of Deposition (CBED) maps produced by CEH Edinburgh. These, and site-specific deposition rates, are used to validate the performance of long range chemical transport models.
- **Pollution Climate Mapping** (current contractor: AEA): The measurements of sulphur dioxide, nitrogen dioxide and particulate sulphate made in the Acid Deposition Monitoring Network provide input to the modelling approaches developed by AEA, to meet the reporting requirements under the first Air Quality Daughter Directive.
- **Freshwater Critical Load Exceedences** (current contractor: ENSIS). A number of the sites in the Acid Deposition Monitoring Network are located in sensitive catchments and freshwater systems. The measurements made in the sampling programme therefore provide a direct measure of the atmospheric input and can be compared with critical loads of such systems.
- **Dynamic Modelling** (current contractor: CEH Bangor): A number of Acid Deposition Monitoring sites are located in sensitive catchments and freshwater systems. The measurements made in the sampling programme therefore provide a direct measure of the atmospheric input, and are used in dynamic models used to assess the impact of acid and nitrogen deposition on freshwater and terrestrial habitats.
- **FRAME modelling:** (current contractor: CEH Edinburgh)

The measurements made in these networks have been, and continue to be, key inputs into the expert reviews of our understanding of acid deposition, provided formerly by the Review Group on Acid Rain and more recently by the Review of Transboundary Air Pollution (RoTAP, see Section 6). In addition, wet deposition and particulate sulphate measurements have long been key inputs to the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP). Rainfall composition, daily particulate sulphate and gas/particle ratio measurements made within the Acid Deposition Monitoring Network are submitted to EMEP as part of the UK's Acidification and Eutrophication requirements under the new EMEP Monitoring Strategy.

3.7.1 Data archiving and submission

The following data was sent to CCC, NILU:

- Particulate sulphate concentrations measured at Eskdalemuir, Lough Navar, Yarner Wood High Muffles, Strathvaich Dam for 2008;
- Daily rainwater composition data collected at Eskdalemuir for 2008;
- Fortnightly rainwater composition data collected at Eskdalemuir, Lough Navar, Yarner Wood High Muffles, Strathvaich Dam for 2008.

The ratified DWOC data from Auchencorth Moss for 2008 was sent to the CEH EMEP database in December 2009. It is planned by the end of 2010 all UKEAP data will be submitted to EMEP.

Precip-Net, PS-Net and NO₂-Net data are publicly archived in the Air Quality Archive database (Section 6 links) and the AGANet and NAMN data on the UK Pollutant Deposition database.

3.7.2 LSO/User Group Meeting 2009

The first UKEAP user and local site operators meeting was held on 6th November 2009, hosted at CEH Edinburgh. The meeting was attended by 13 site operators, representing a total of 18 sites in the UKEAP network, as well as representatives from AEA, CEH and Defra, and a number of users/stakeholders. A summary report will be available in 2010 on the UKEAP website.

4. UKEAP Measurements 2008

4.1 *Precip-Net*

Rainwater is collected using bulk rainwater collectors based on the design of Hall (1986). Solar heating is minimised by enclosing the bottle in a polished steel canister painted black inside. On average the UK in 2008 had above average rainfall, particularly in the summer months with respect to the Met Office 1971-2000 average.

4.1.1 Fortnightly bulk rain sampling

The measurements of precipitation composition made using the bulk collectors are presented in the UKEAP Data Report (Precip-Net) and are summarised in Table 3. It should be noted that the tables in the Data Report contain all the analytical results obtained, including those samples affected by contamination by bird strike. A phosphate concentration > 0.1 mg P l⁻¹ (or >1.0 µeq l⁻¹) was taken as evidence of contamination. Although all these samples have been included in the tables, they were not included in the calculation of annual mean precipitation-weighted ion concentrations.

In Figures 2-5, the annual average UK concentration map is shown for the H⁺, non-sea salt sulphate, nitrate and ammonium ions with the equivalent map for the Year 2000 shown where available on the same scale. Table 4 summarises the trends in the major ions (hydrogen, sulphate, nitrate and ammonium) for the period of measurement at each site. The majority of sites continue to have a significant downward trend in hydrogen and sulphate concentration. In case of nitrate there is a more mixed picture with no overall trend at 38% of the sites, with a decrease at the remainder. All but 2 sites show no significant decreasing or increasing trend in ammonium concentrations.

Table 3: Summary of Precip-Net site annual average ion concentrations and total rainfall

	SO4	NO3	NH4	Na	Mg	Ca	Cl	K	PO4	nss	H+	rainfall
Yarner Wood	25.2	15.9	16.3	109.6	24.5	13	118.7	3.3	0.6	12	12.3	1164.4
Goonhilly	50.9	20.8	21.5	306.7	66.3	23.5	328.6	7	0.7	14	13.6	836.6
Barcombe Mills	49.9	22.5	23.5	154.7	38.2	39.8	175.3	31.5	3	31.3	3	518.2
Harwell	23.9	25.4	28.9	42.4	10.7	17.7	45.3	2.3	1.1	18.8	6.9	722.4
Rothamsted	24.4	28.9	33.3	45.6	11.2	14.7	48.2	2.3	0.7	18.9	7.5	658.7
Crai reservoir	19.1	6	8.6	89.8	19.5	10.1	96.9	2.5	1.2	8.3	7.1	2111.7
Flatford Mill	32.6	36.5	42.1	64.9	16	20.1	70.9	4.2	1.5	24.7	10.2	519.1
Tycanol Wood	30.1	9.7	18.3	140	30.3	15.1	152.6	3.9	1.4	13.2	8.7	1875
Ystradffin	20.8	8.6	16.8	94.1	19	9.6	101.9	3	1.1	9.4	6.5	1688.7
Pumlumon	18.2	8.1	12.5	80.3	17.3	8.4	87.1	2.1	1.2	8.5	6.1	2537.9
Stoke Ferry	29.8	35	41.3	59.1	14.7	20.4	64.3	2.7	1.3	22.7	10.6	731.6
Preston Montford	21.6	18.2	33	58.2	12.4	12.2	63.5	4.3	1.3	14.5	4.4	561.3
Bottesford	28.7	28.2	35.9	38.8	11.1	21.8	42.2	3.3	1.1	24.1	6.1	547.4
Llynllagi	25.4	10.1	13.7	131.7	27.1	13.6	143.1	3.4	1.1	9.6	6.2	2929.6
Llyn Llydaw	17.5	8.4	11.2	80.4	16.7	9.6	85.6	2.2	0.7	7.8	6.5	2388.8
Ulceby Cross	40	33.8	60.3	96.3	23.2	252.6	107	20	1.8	28.4	9.2	449.7
Wardlow Hay Cop	32.7	22.5	33.1	75.7	17.2	26	82.2	3	0.9	23.5	2	955.2
Driby	58.7	27.3	55.5	187.1	40	24.7	204.4	4.7	0.5	36.2	3.5	44.1
River Etherow	25.1	20.4	26.5	55.3	12.8	12.5	58.3	2.1	0.9	18.4	9.2	1102.1
Thorganby	33.3	23.2	32.7	54.3	14.4	20.6	59.1	4.2	1.1	26.8	6.7	540.6
High Muffles	29.3	20.7	27.2	73.3	17.9	17.2	79.8	5.6	0.9	20.5	7.1	862.5
Bannisdale	32.5	17.2	34.4	139	29.3	18.9	151.7	4.3	2	15.7	4.7	2366.1
Scot Tarn	24.8	11.9	18.9	116	24.3	10.9	126.5	3.2	0.6	10.8	7	2815.8
Hillsborough Forest	21.3	11.7	33.8	84.4	16.1	9.4	92.4	2.7	1	11.1	2.1	822
Lough Navar	28.2	5.5	12.6	191.3	40.6	17.6	209.8	5.3	1.4	6.1	3.7	1487.5
Moorhouse	17.1	13.3	17.1	58.4	12.6	9.3	62.3	1.9	0.7	10.1	6.8	1554.2
Loch Dee	21.2	12.7	18.4	94.1	19.4	8	102.3	2.5	0.5	9.9	7.1	1717.4
Baegh's Burn	27.5	10.7	20.2	159	33.3	13	172.2	4.4	0.9	9	4.6	1315.2
Percy's Cross	27.9	20.9	31.6	87.6	19.4	17	95.4	3.4	1.3	17.3	6.7	816.1
Eskdalemuir	17.5	9.6	17.4	73.6	15.5	9.7	79.1	2.4	1.2	8.6	6.6	1471.3
White Adder	24.8	21.2	22.1	71.6	17.1	13.5	75.6	2.6	1.4	16.1	12.5	563.5
Loch Chon	22	6.1	7.8	141.5	29.5	10.8	155.4	3.3	0.8	4.9	6.7	1670.5
Balquhidder	19.7	10.1	12.7	91	20.2	10.1	99.8	2.6	0.7	8.7	7.2	1832.1
Polloch	29.9	5.1	6.1	210.3	45.1	15.2	230.8	4.7	0.8	5.5	6.9	1785
Loch Nagar	18.3	16.8	20.2	37.7	9.3	10.3	38.5	1.7	1	13.8	11.5	754.6
Glensaugh	27.3	25.2	25	90.1	20.1	11.2	95.6	2.7	0.9	16.4	17.1	862.4
Allt a' Mharcaidh	14.4	5.4	2.6	91.6	18.9	8.4	99.2	2.4	0.6	3.9	8.6	679
Strathvaich Dam	23.9	4.5	3	178.4	37.9	12.1	194.7	4	0.8	3.5	7.5	1281.6
Network average	27.3	16.8	23.6	104.1	22.9	21.3	113.1	4.5	1.1	14.8	7.4	1251.1

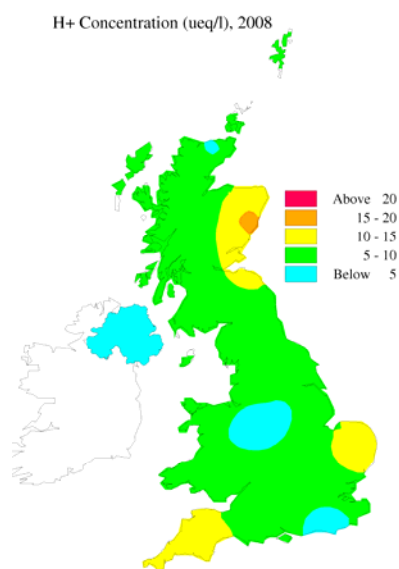


Figure 2: Hydrogen ion concentrations in precipitation: UK map for 2008.

NSS Concentration (ueq/l), 2008

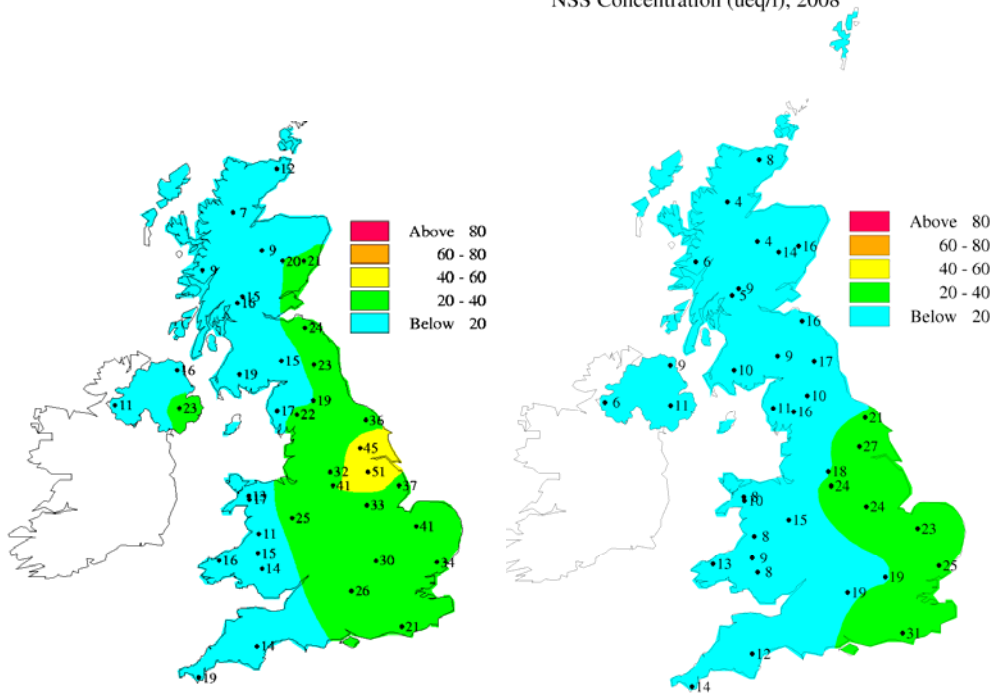


Figure 3: Non-sea salt sulphate concentrations in precipitation: UK maps for 2000 (LHS) and 2008 (RHS).

NO3 Concentration (ueq/l), 2008

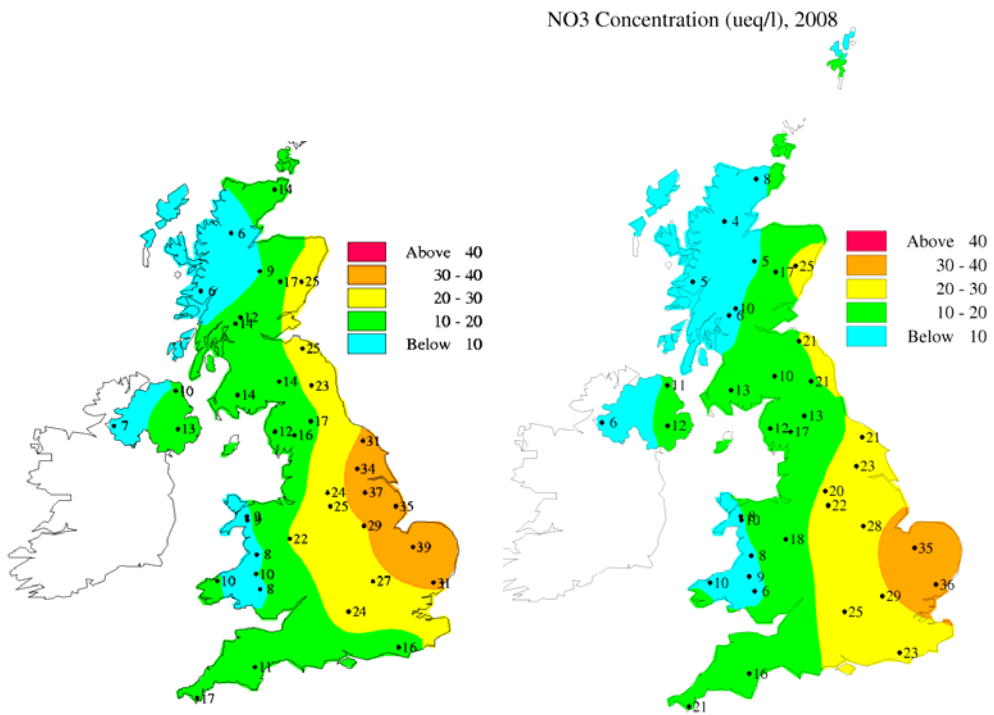


Figure 4: Nitrate concentrations in precipitation: UK maps for 2000 (LHS) and 2008 (RHS).

NH4 Concentration (ueq/l), 2008

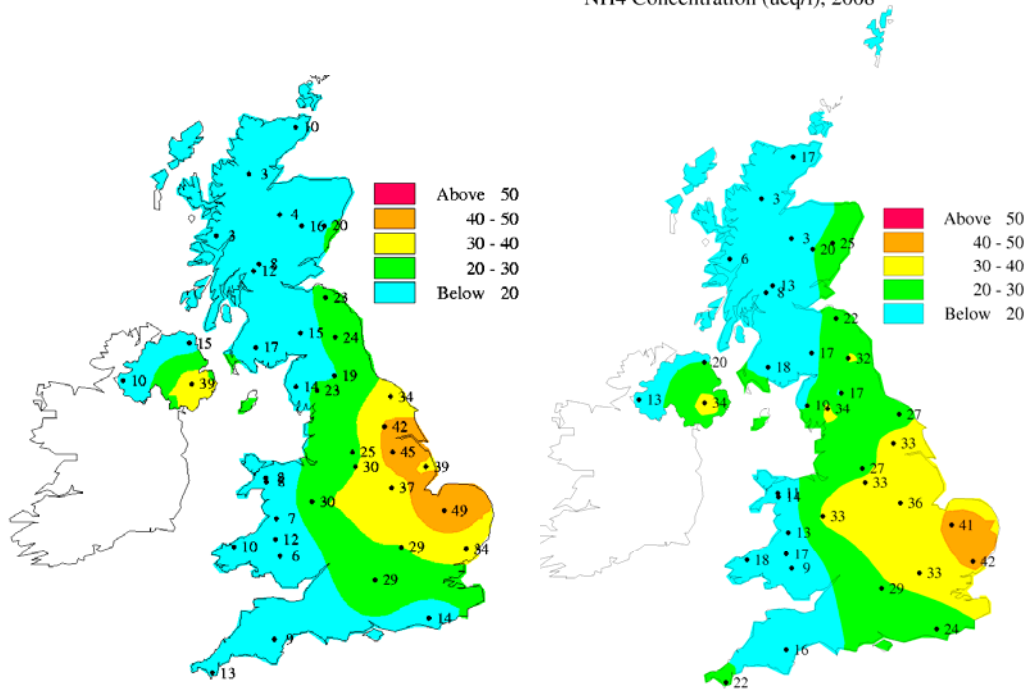


Figure 5: Ammonium concentrations in precipitation: UK maps for 2000 (LHS) and 2008 (RHS).

Table 4. Summary of trends in major ion concentrations (Precipitation-weighted values) at Precip-Net sites.

Note: details of the relative significance of individual f trends are specified in the UKEAP Data Report

	H ion	NSS sulphate	Nitrate	Ammonium
Yarner Wood	No trend	Decrease	No trend	No trend
Goonhilly	No trend	Decrease	No trend	No trend
Barcombe Mills	Decrease	Decrease	Decrease	Decrease
Harwell				
Rothamsted				
Crai reserrior				
Flatford Mill	Decrease	Decrease	Decrease	Decrease
Tycanol Wood	Decrease	Decrease	No trend	No trend
Ystradfin				
Pumlumon	Decrease	Decrease	Decrease	No trend
Stoke Ferry	Decrease	Decrease	Decrease	Decrease
Preston Montford	Decrease	Decrease	Decrease	No trend
Bottesford	Decrease	Decrease	Decrease	Decrease
Llynllagi	Decrease	Decrease	No trend	No trend
Llyn Llydaw	Decrease	Decrease	Decrease	Decrease
Ulceby Cross				
Wardlow Hay Cop	Decrease	Decrease	Decrease	Decrease
Driby	Decrease	Decrease	Decrease	Decrease
River Etherow	Decrease	Decrease	No trend	No trend
Thorganby	Decrease	Decrease	Decrease	Decrease
High Muffles	Decrease	Decrease	Decrease	Decrease
Bannisdale	Decrease	Decrease	No trend	No trend
Scot Tarn	Decrease	Decrease	No trend	No trend
Hillsborough Forest	Decrease	Decrease	Decrease	Decrease
Lough Navar	Decrease	Decrease	No trend	No trend
Moorhouse				
Loch Dee	Decrease	Decrease	Decrease	No trend
Baegh's Burn	No trend	Decrease	No trend	No trend
Percy's Cross				
Eskdalemuir	Decrease	Decrease	Decrease	Increase
White Adder	Decrease	Decrease	Decrease	No trend
Loch Chon	Decrease	Decrease	Decrease	No trend
Balquihidder	Decrease	Decrease	No trend	No trend
Polloch	Decrease	Decrease	Decrease	No trend
Loch Nagar				
Glensaugh				
Allt a'Mharcaidh	Decrease	Decrease	No trend	No trend
Strathvaich Dam	Decrease	Decrease	Decrease	no trend

4.1.2 Daily Bulk and Daily wet only rain sampling

The results for the Daily bulk rain composition measurements at Eskdalemuir and the daily wet-only rain composition are summarised in the Precip-Net Data report. In Figure 6 the monthly rainfall at Auchencorth Moss is summarised, with 1004 mm of rainfall being recorded in total, which is slightly less than the average rainfall recorded by the PrecipNet of 1250 mm. The results mirror the overall trend for most of the UK with higher than average rainfall over the summer months and in the autumn.

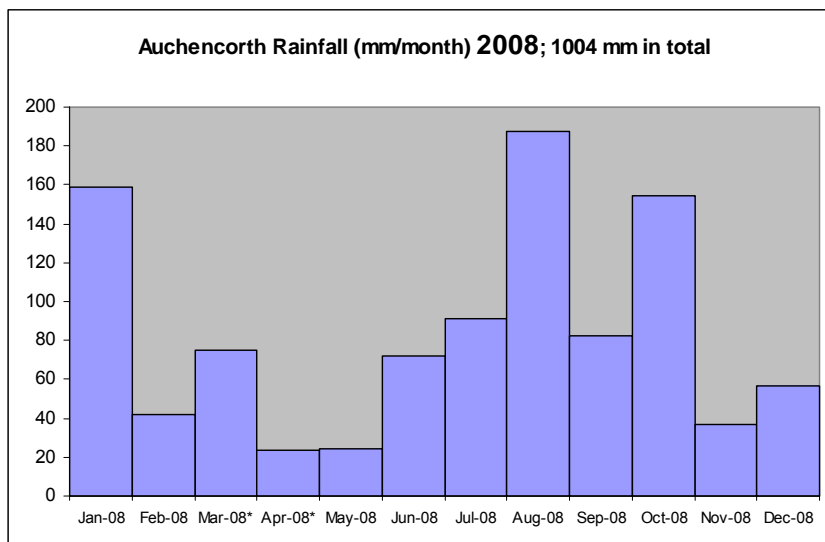


Figure 6: Monthly average rainfall at Auchencorth Moss

The chemistry data from the bulk and wet-only (DWOC) are submitted to EMEP annually. The concentrations of the major ions throughout the year are shown in Figure 7 A and B. Note the sampler was not operational from mid-February to April leading to the gap in the data. A summary of the sea salt/non-sea salt fraction is shown in Figure 8. The data shows that the source of sulphate in the precipitation varies between marine and anthropogenic with usually a mixture of both being present. The dataset being obtained now at Auchencorth and Harwell will be available for further analyses in future.

(A)

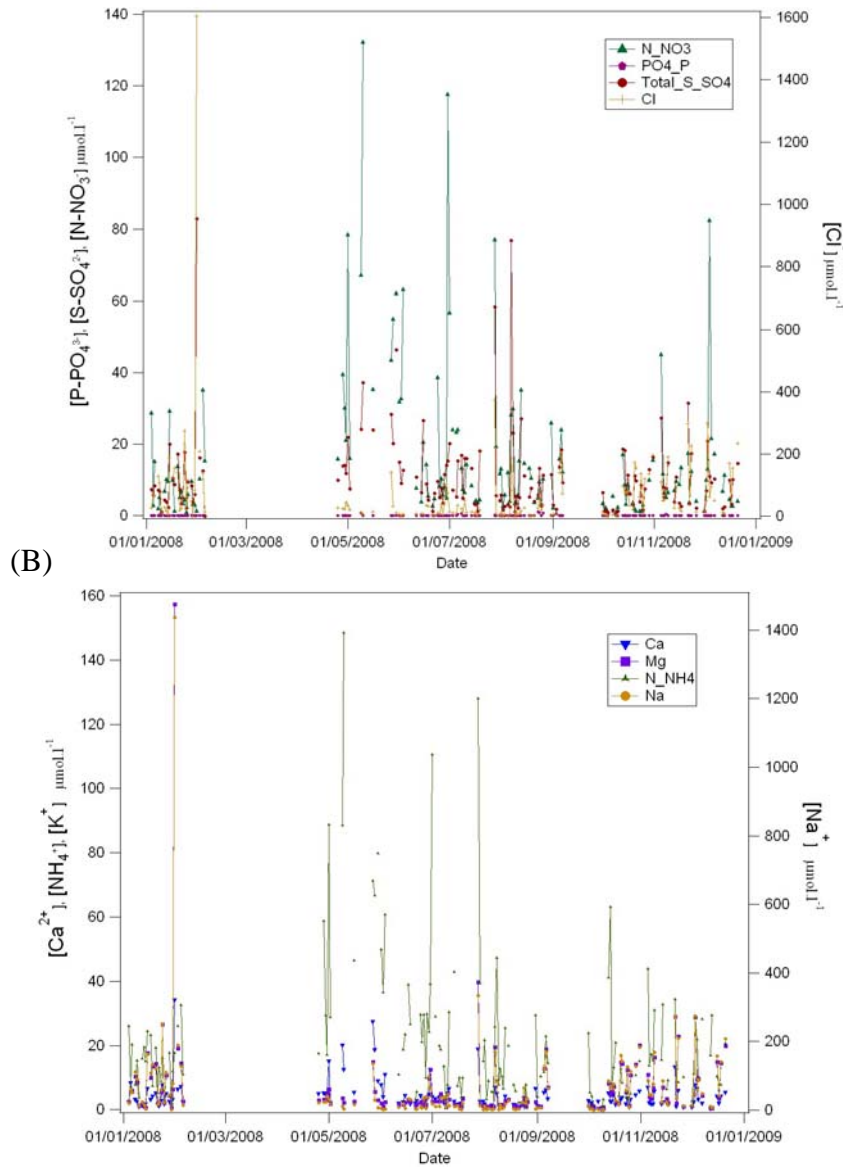


Figure 7 Auchencorth Moss Daily Wet-only Precipitation chemistry measurements: A: Anions; B: Cations.

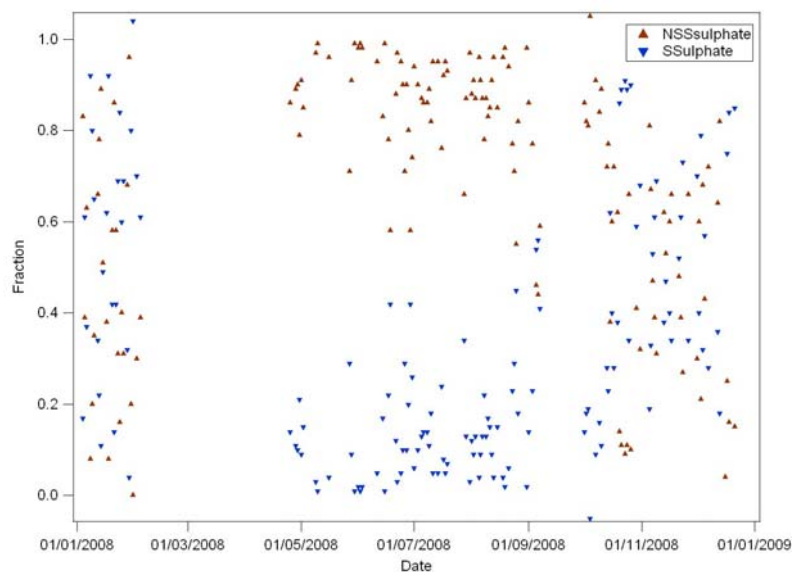


Figure 8: Fraction of sea salt sulphate and non-sea salt sulphate in Precipitation at Auchencorth Moss in 2008.

4.2 PS-Net

The annual data for the five PS-Net sites for 2008 is summarised in Table 5. The threshold data capture for reporting annual mean values is 75% and only Eskdalemuir reached that threshold in 2008. The interannual trend is summarised in Figure 9. For the single 2008 data point for Eskdalemuir, the concentration continued the downward trend observed since the measurements made in 1986.

Table 5 Monthly average daily particulate sulphate (as S) concentrations for 2008

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Annual mean	SD	% Data capture
Lough Navar	0.26	0.54	0.28	0.30	0.57	0.29	-	0.22	0.28	0.18	0.25	0.47	0.28	0.10	50
Eskdalemuir	0.18	0.34	0.18	0.41	0.67	0.33	0.41	0.29	0.42	0.21	0.21	0.28	0.34	0.15	83
High Muffles	0.28	0.20	0.31	0.30	-	-	0.52	0.45	0.58	0.25	0.32	0.38	0.43	0.13	42
Yarner Wood	0.45	0.59	0.33	0.30	0.82	0.49	0.48	-	1.02	0.19	0.43	0.55	0.57	0.24	50
Barcombe Mills	0.22	0.75	0.74	0.30	1.01	0.93	0.67	0.45	0.63	0.52	0.71	0.77	0.68	0.18	58

Units: $\mu\text{g SO}_4\text{-S.m}^{-3}$. Numbers in grey indicated that 75% data capture threshold was not achieved

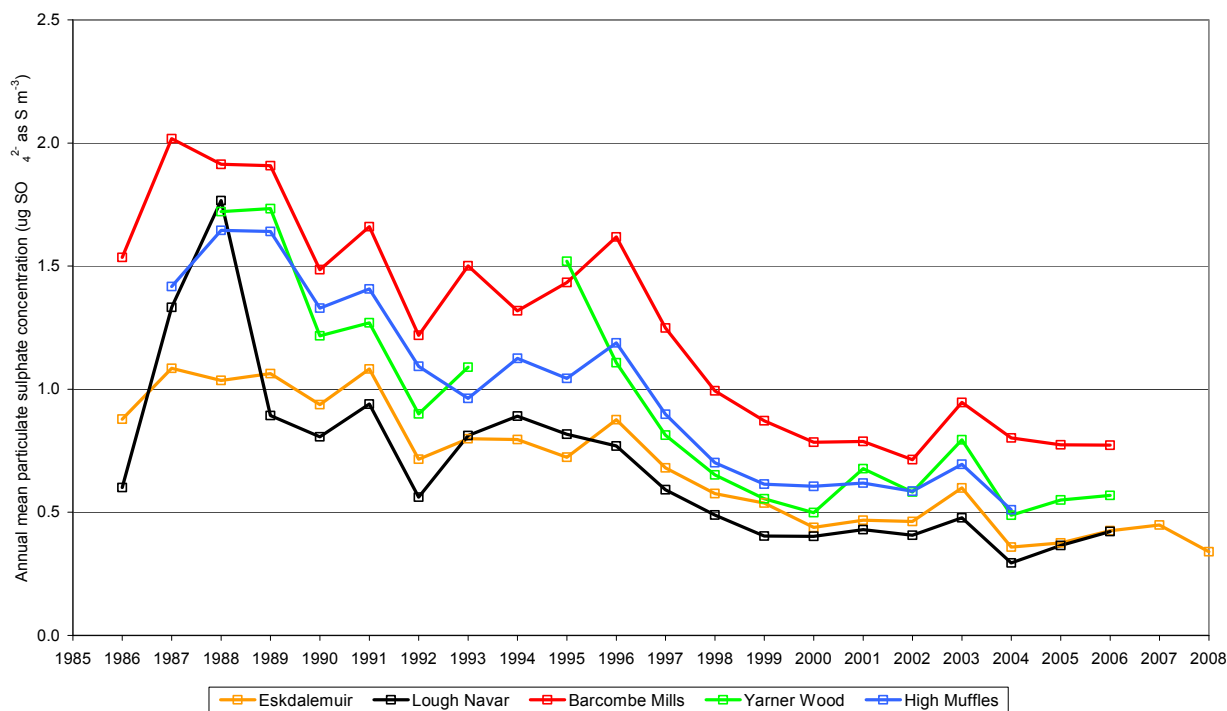


Figure 9: Annual mean concentrations of particulate sulphate at the daily sites, from 1986 to 2008 ($\mu\text{g SO}_4\text{-S. m}^{-3}$)

4.3 NO₂-Net

Diffusion tube measurements have been used to produce a map of the UK rural nitrogen dioxide concentrations for 2008, as shown in Figure 10 and the historical trend for 8 sites are shown in Figure 11. UK total emissions of nitrogen oxides have decreased since 1990 with the switch from coal to gas for power generation and the introduction of catalytic converters on petrol-engine vehicles. Given the relatively poor precision of the diffusion tube method at low concentrations, the fall in nitrogen dioxide concentrations is most clearly observed at the relatively high concentration sites such as High Muffles and

Barcombe Mills, although lower concentration sites such as Yarnier Wood, Strathvaich Dam Eskdalemuir also show evidence of a decline. Nitrogen dioxide concentrations in 2008 were in line with those measured during 2007 however slightly lower at most inland sites. .

The highest concentrations in 2008 were observed in the south east of England with an annual mean concentration of 12.4 ppb measured at Flatford Mill. In the main, this reflects the proximity to the sampling sites of roads and other aspects of urbanisation. The UK rural background map shows little difference in the spatial patterns between 2000 and 2008 and some evidence of a decrease in nitrogen dioxide concentrations across the UK.

Historically, these UK maps, based on diffusion tube measurements, defined the rural nitrogen dioxide concentration field, upon which urban contributions were superimposed. With the introduction of automatic analysers, mainly in England, a hybrid approach is now adopted in the mapping work (Kent *et al.*, 2006). The preparation of the urban-enhanced maps is undertaken under another contract (*Pollution Climate Mapping*). These measurements have been provided to the Pollution Climate Mapping project team.

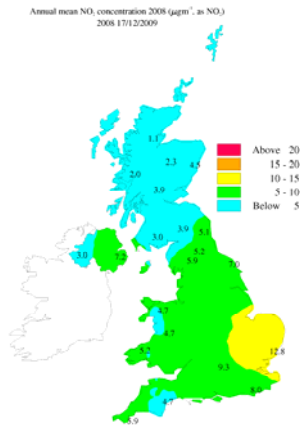


Figure 10: Annual Mean rural NO₂ concentration map 2008

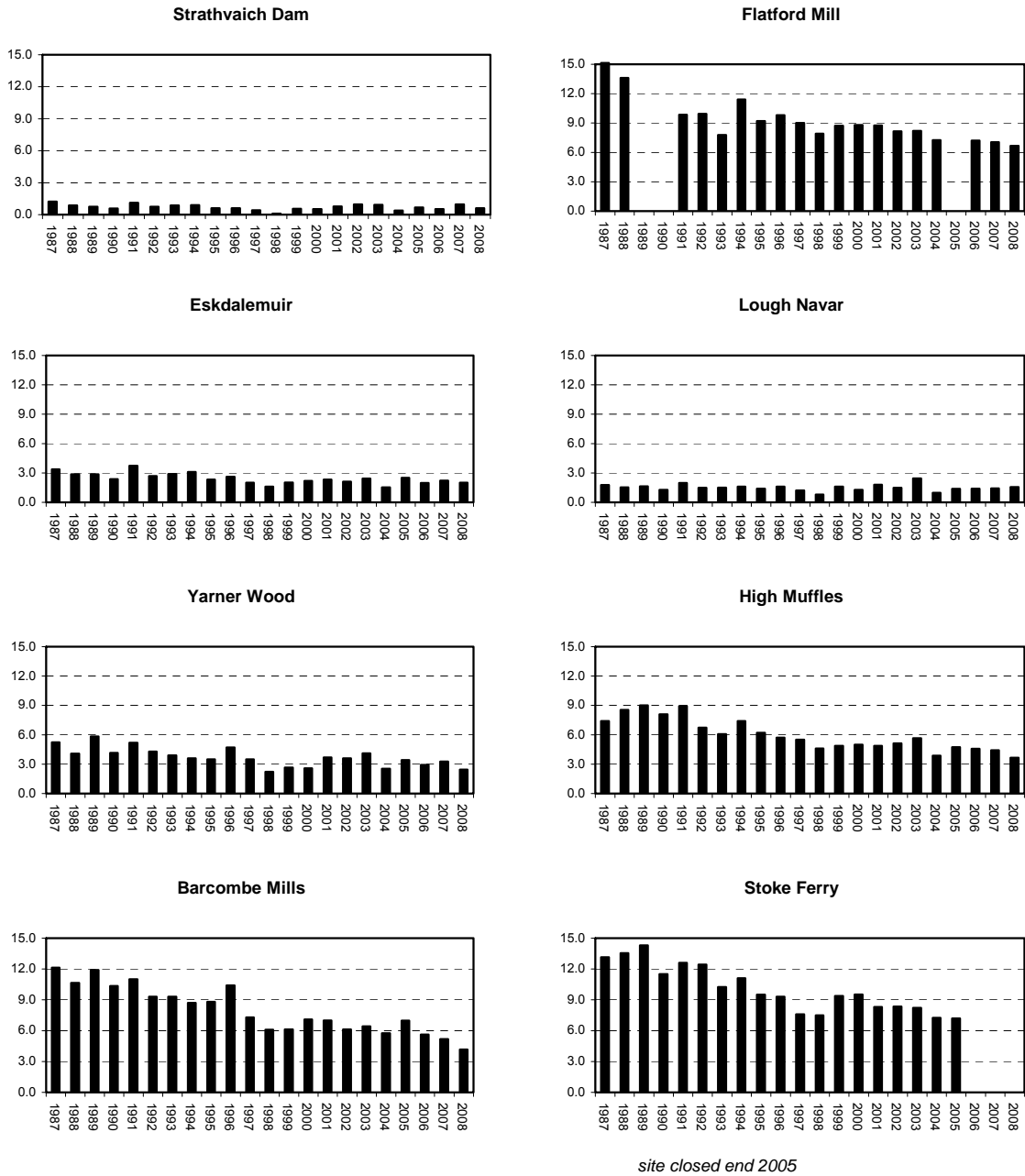


Figure 11: Historical Trends of NO₂ annual average concentrations.

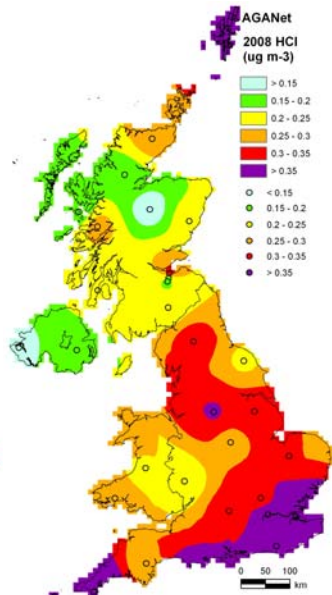
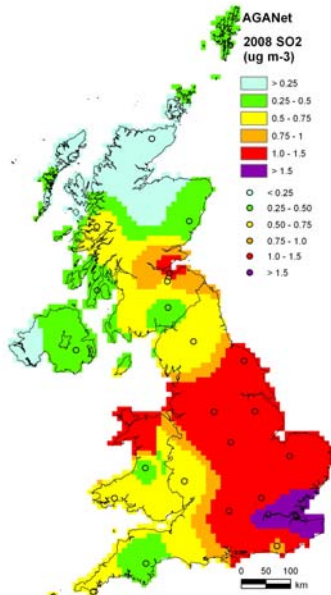
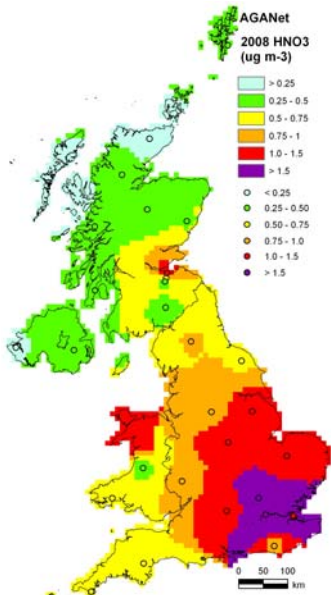
4.4 AGANet

Interpolated concentration fields for 2008 across the UK from the 30 monitoring sites are shown in Figure 12 A-I. A bilinear interpolation procedure was used to provide the mean concentration field at a grid resolution of 10 km x 10 km. The spatial distributions of acid gases and aerosol ions, which are primarily due to anthropogenic activity, in particular $\text{HNO}_3/\text{NO}_3^-$ and $\text{SO}_2/\text{SO}_4^{2-}$, 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. However on the UK scale with 30 sites the higher spatial variability in gaseous species can be seen however it is noted that there will also be seasons.

The largest annual mean SO_2 concentrations derived from the DELTA measurements occurred at London Cromwell Road, Detling and Edinburgh, with annual mean concentrations of greater than $1.3 \mu\text{g SO}_2 \text{ m}^{-3}$. It noted that these concentrations are somewhat lower than the annual averages for 2007. SO_2 concentrations generally decreased towards the west and north of the UK, with the lowest concentrations of $< 0.5 \mu\text{g SO}_2 \text{ m}^{-3}$ in northern Scotland. SO_2 is 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 the largest in the coastal regions; however it is interesting to note that inland concentrations of HCl are relatively more elevated than that of particulate phase chloride. This reflects the dual contributions of anthropogenic and marine sources, with both primary and secondary emission of HCl . The concentration of base cations varies greatly depending on the species. The concentration map for Na^+ is similar to Cl^- , showing the close coupling between the two species.

A summary of the annual average concentrations of each species at all the AGANet sites are shown in Table 6 with basic statistics. There is a wide range of concentrations for most species across the UK, with the highest concentrations of S-species and oxidised nitrogen species occurring in the urban centres and sites in the SE England

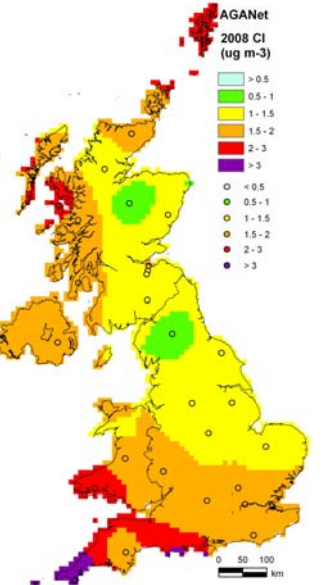
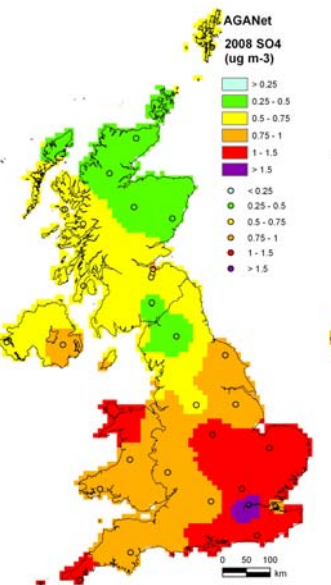
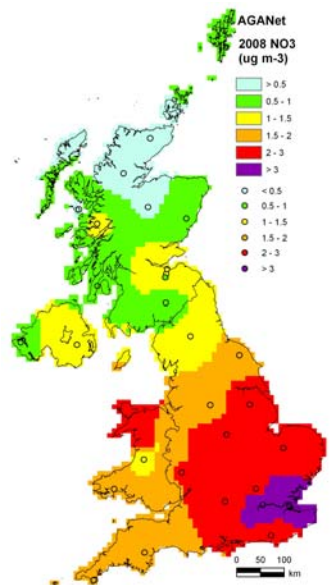
Monthly values from AGANet have provided an improved spatial concentration field across the UK. The main features of the spatial distribution in the pollutants measured are shown in the annual maps. In general, there is a reasonable correlation between the concentrations of the different pollutants at the 30 monthly monitoring sites, and for some species there are very high spatial correlations. In the case of the gases, this can be attributed to the regional distribution of sources being similar, meanwhile for the aerosol the chemistry must obviously balance between the major cations and anions. . The 2007 ADMN reports summarised the trends and spatial distributions. These patterns have not significantly changed in 2008. With a longer time series of measurements becoming available with time, a more detailed analysis of the spatial patterns and trends will be carried out in 2010. It is noted that as most measurements have been made over a time period of the order of 10 years, temporal trends are most likely to be strongly influenced by inter-annual variability, so it will be necessary to consider the trends in terms of local, regional and national drivers.



A

B

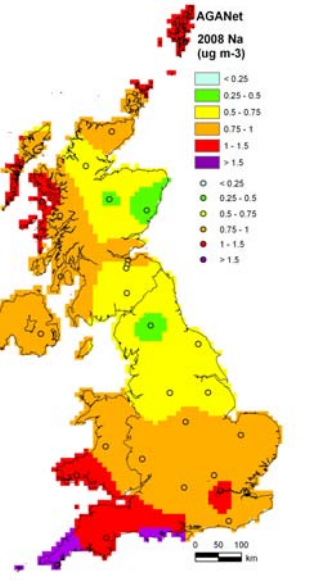
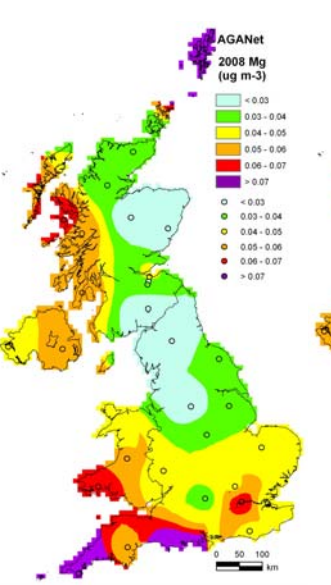
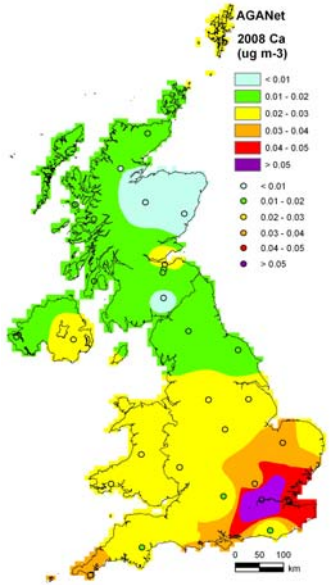
C



D

E

F



G

H

I

Figure 12: Annual concentration maps in the UK AGANet from averaged monthly measurements made in 2008. Maps produced by bilinear interpolation, 10 km x 10 km grid resolution; A: HNO₃; B:SO₂; C: HCl; D: NO₃⁻; E:SO₄²⁻; F:Cl⁻; G: Ca²⁺; H: Mg²⁺; I: Na⁺

Table 6: Annual Averages and statistics for AGANet Sites

	NH3	HNO3	SO2	HCl	NH4	NO3	SO4	Cl	Ca	Mg	Na
Bush OTC	0.97	0.52	0.84	0.2	0.42	1.01	0.5	0.86	0.01	0.02	0.6
Bush OTC	1.18	0.56	0.94	0.2	0.48	1.09	0.59	1.11	0.02	0.03	0.69
Rosemaund	3.97	0.82	0.52	0.22	0.86	2.01	0.92	1.56	0.02	0.04	0.81
Narberth	3.11	0.66	0.7	0.28	0.73	1.66	0.91	2.4	0.02	0.07	1.3
Halladale	0.93	0.24	0.21	0.27	0.21	0.5	0.41	1.59	0.01	0.04	0.85
Auchencorth	0.75	0.4	0.59	0.18	0.42	0.97	0.56	1.16	0.02	0.03	0.64
Shetland	0.15	0.27	0.44	0.34	0.19	0.66	0.66	3.33	0.04	0.13	1.61
Glensaugh	0.26	0.54	0.35	0.22	0.27	0.67	0.35	1.01	0	0.01	0.51
Moorhouse	0.46	0.76	0.6	0.33	0.5	1.05	0.47	0.88	0.02	0.02	0.47
Rothamsted	1.13	1.49	1.09	0.32	1.06	2.66	1.08	1.52	0.03	0.05	0.91
Strathvaich Dam	0.11	0.26	0.1	0.18	0.27	0.39	0.38	1.35	0.01	0.03	0.7
Eskdalemuir	0.39	0.42	0.34	0.23	0.41	0.86	0.48	1.09	0.01	0.02	0.63
High Muffles	0.83	0.74	1.08	0.25	0.71	1.73	0.8	1.22	0.02	0.04	0.68
Stoke Ferry	2.1	1.07	1.02	0.3	1.2	2.73	1.07	1.32	0.03	0.04	0.75
Yarner Wood	0.48	0.7	0.46	0.28	0.71	1.59	0.87	1.66	0.02	0.06	1.07
London	3.7	3.84	1.86	0.37	1.43	4.15	1.96	1.7	0.11	0.07	1.06
Sutton Bonnington	3.91	1.19	1.18	0.28	1.03	2.39	1.04	1.47	0.02	0.04	0.8
Laganlia	0.39	0.28	0.15	0.13	0.22	0.46	0.5	0.83	0	0.02	0.49
Hillsborough Forest	5.19	0.41	0.39	0.19	0.73	1.47	0.77	1.81	0.02	0.06	0.93
Lough Navar	0.6	0.27	0.18	0.14	0.42	0.92	0.58	1.51	0.02	0.04	0.77
Rum	0.47	0.15	0.17	0.16	0.22	0.48	0.56	2.03	0.02	0.07	1.13
Edinburgh	1.19	1.41	1.35	0.34	0.51	1.54	0.82	1.59	0.03	0.05	0.98
Cywystwyth	1.77	0.46	0.44	0.23	0.64	1.35	0.78	1.87	0.02	0.06	0.95
Carradale	0.47	0.42	0.42	0.22	0.32	0.65	0.6	1.75	0.01	0.06	0.98
Barcombe Mills	1.28	0.95	0.99	0.37	1.07	2.47	1.16	1.73	0.02	0.05	1
Detling	1.35	1.5	1.79	0.53	1.07	3.15	0.99	1.81	0.04	0.05	1.03
Harwell	1.33	1.15	1.02	0.32	0.9	2.18	0.86	1.52	0.02	0.04	0.79
Ladybower	0.74	0.9	1.25	0.35	0.78	1.7	0.73	1.24	0.02	0.02	0.61
Plas y Brenin	0.37	0.44	0.64	0.27	0.5	1.08	0.74	1.65	0.01	0.05	0.96
Caenby	3.97	1.15	1.35	0.33	0.94	2.47	0.91	1.42	0.02	0.04	0.73
Maximum	5.19	3.84	1.86	0.53	1.43	4.15	1.96	3.33	0.11	0.13	1.61
Minimum	0.11	0.15	0.1	0.13	0.19	0.39	0.35	0.83	0	0.01	0.47
Statistical mean	1.45	0.80	0.75	0.27	0.64	1.53	0.77	1.53	0.02	0.05	0.85
SD	1.39	0.70	0.48	0.08	0.34	0.92	0.32	0.49	0.02	0.02	0.25

4.5 NAMN

The complete NAMN data set is summarised by site in the UKEAP Annual Data Report. NAMN measurements continued to be made with a mixture of active DELTA systems and passive ALPHA samplers. To ensure that bias is not introduced in the sampling and to maintain the validity of long-term trends, the calibration is analysed on an annual basis as a check that the passive samplers in relation to the DELTA does not deviate significantly with time. The annual regression used to calibrate the diffusion tube and ALPHA sampler and data is shown in Figure 13. Note that the gradient of 3.238 for 2008 compares with 3.2405 in 2007 (<1% variation). The annual calibration functions of both the diffusion tubes and ALPHA samplers show both high precision and constancy between years (see previous

reports archived on UK Pollutant Deposition (Section 6). This is very important, as it lends support for the detection of temporal trends in ammonia concentrations. 96% of NAMN data passed the QC acceptance criteria, which is up from 94% in 2007.

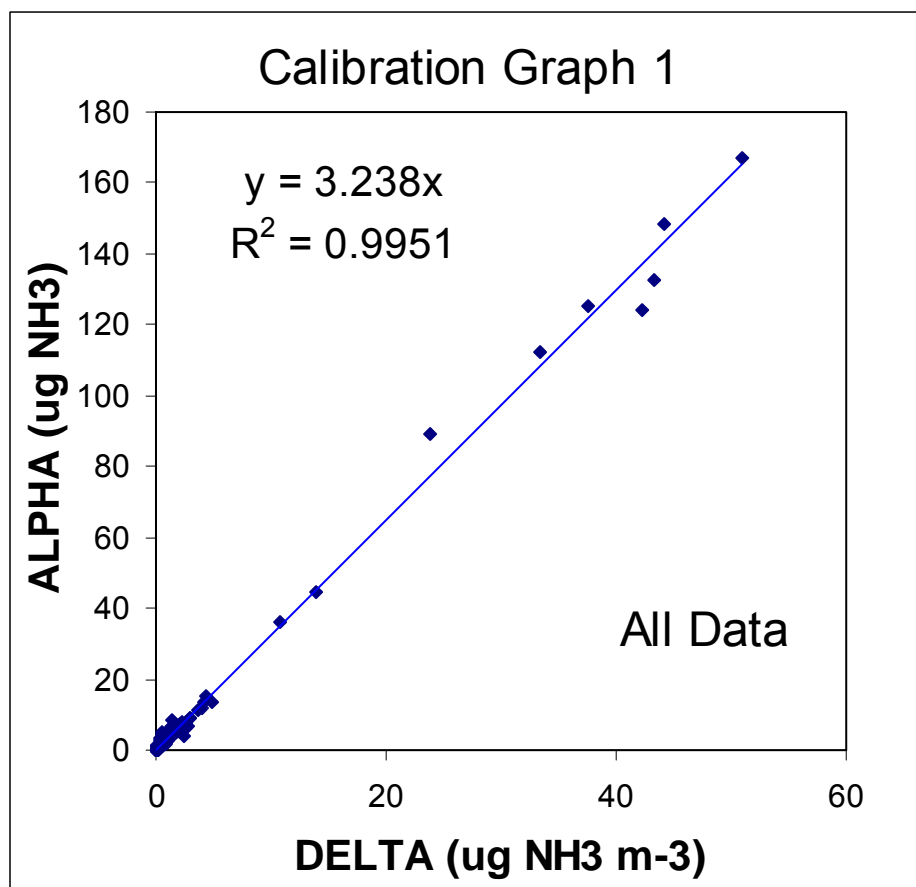


Figure 13: Regression of ALPHA vs DELTA used to derive an effective uptake rate for the ALPHA samplers. Data shown are the period Feb-08 – Jan09.

Annual average concentration maps in the UK NAMN from averaged monthly measurements made in 2008 are shown in Figure 14. Maps are produced by bilinear interpolation at 10 km x 10 km grid resolution. National maps of both gaseous NH_3 and aerosol NH_4^+ concentrations are derived from the NAMN. It is noted that NAMN interpolated maps are for indicative purposes only. The FRAME model derives ammonia concentrations, using the National Atmospheric Emissions Inventory (NAEI) to initialise sources, model ammonia dispersion and the NAMN data for calibration, is the recommended UK ammonia concentration maps.

The 2008 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. The trends of ammonia emissions from the different sectors and across the country have been reported in previous NAMN annual reports (Section 6 links). Further studies of the trends will be the subject of a specific study in 2010 as part of a review of the first 10 years of the National Ammonia Monitoring Network and an appraisal of the method for identifying the primary source sector categorisation. Over the past decade, there has been a twenty per cent decrease in ammonia emissions documented in the NAEI. This decrease is very variable when emissions are considered by sector. Initial studies show that the decrease in emissions

are reflected in some of the NAMN results however a more detailed study will be required in order to assess the statistical significance of this.

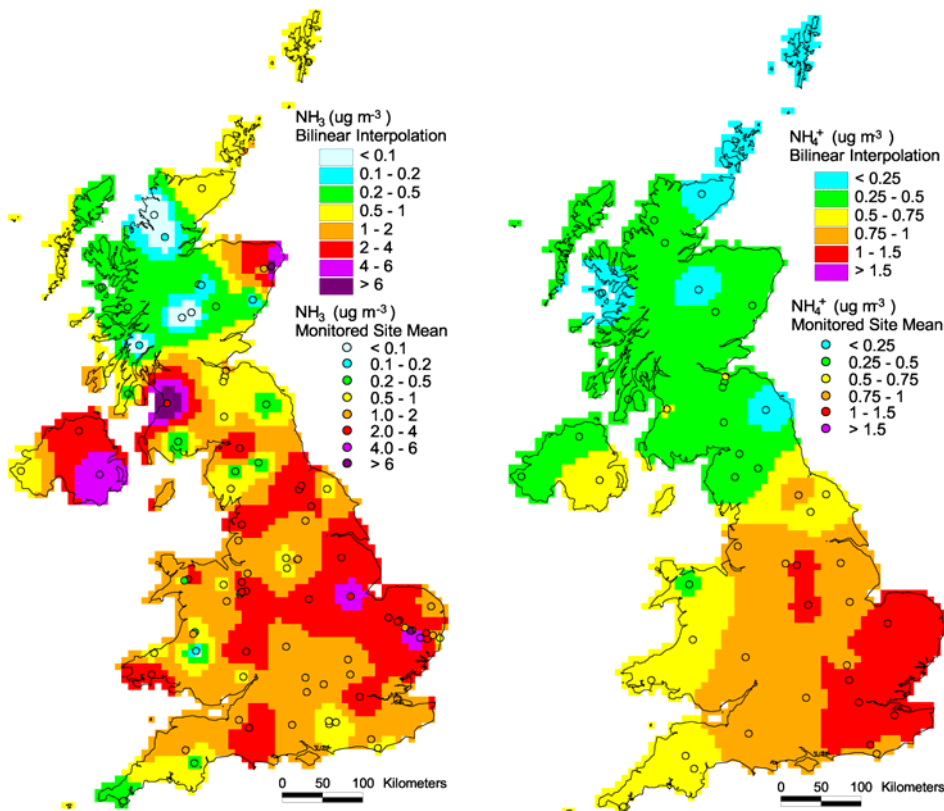


Figure 14: Annual concentration maps in the UK NAMN from averaged monthly measurements made in 2008. Maps are produced by bilinear interpolation at 10 km x 10 km grid resolution

The concentrations at all the NAMN sites are summarised in Figure 15. The largest NH_3 concentrations occurred at sites that are in regions with high ammonia emissions, e.g. Hinderclay Fen in East Anglia (pig & poultry emissions); 2008 annual mean of = $8.68 \mu\text{g NH}_3 \text{ m}^{-3}$, range = $4.2 - 19.9 \mu\text{g NH}_3 \text{ m}^{-3}$. The smallest NH_3 concentrations were observed at remote sites locations usually to the north and west of the UK, that are located in less populated areas, and with few ammonia emission sources, e.g. S3 Inverpolly, S30 Strathvaich Dam in Northern Scotland. The exception to this are where there is intensive agricultural installations, e.g. in South West Scotland.

For particulate NH_4^+ , the annual mean concentrations ranged from 0.19 to $1.43 \mu\text{g NH}_4^+ \text{ m}^{-3}$. Aerosol NH_4^+ shows a spatially smooth concentration field as expected for an aerosol component and as can be seen in Figure 12 has a similar distribution to the sulphate and nitrate aerosol UK maps as would be expected due to the formation of stable and semi-stable particle phase salts, e.g. ammonium sulphate and ammonium nitrate respectively.

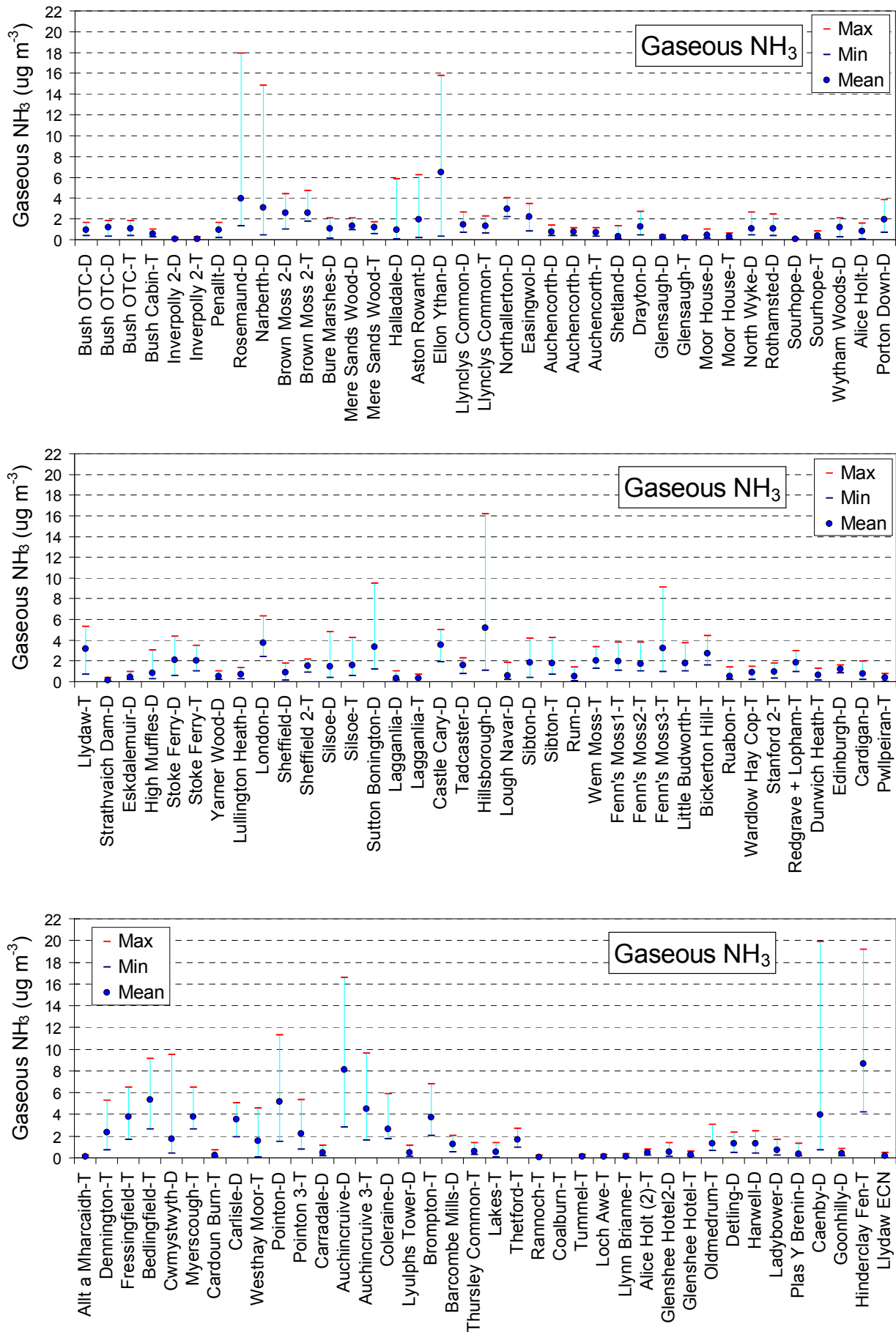


Figure 15: Summary of 2008 annual mean, maximum and minimum ammonia concentrations measured at NAMN sites.

5. References

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6. Links

Air Quality Archive www.airquality.co.uk

UK Pollutant Deposition <http://www.uk-pollutantdeposition.ceh.ac.uk>

Review of Transboundary Air Pollution <http://www.rotap.ceh.ac.uk/>

FRAME (Fine Resolution Atmospheric Multi-pollutant Exchange) model:
<http://www.uk-pollutantdeposition.ceh.ac.uk/frame>

7. Acknowledgements

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