UKEAP 2019 Annual Report

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And the Devolved Administrations

By

NERC Centre for Ecology & Hydrology

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Ricardo Energy & Environment

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1. Summary

1.1 Overview

The Defra rural air pollutant monitoring networks project, (2017-2020: ECM48524), UK **Eutrophying and Acidifying Atmospheric Pollutants (UKEAP)** comprises the following measurement activities:

- UK EMEP monitoring supersites (Chilbolton and Auchencorth)
- National Ammonia Monitoring Network (NAMN)
- Acid Gases and Aerosol Network
- Precipitation chemistry Network (Precip-Net)
- Rural NO₂ diffusion tube network (NO₂-Net)
- The air quality measurements of Natural England's Long Term Monitoring Network are embedded in NAMN and Precip-Net
- The UKEAP network data underpins UK rural air quality modelling and mapping.

(AGA-Net)

- The diagram below highlights the most significant data applications in the UK and internationally (Figure 1).
- The UKEAP network is operated by the UK Centre for Ecology and Hydrology and Ricardo Energy and Environment.
- Measurements would not be possible without the dedicated support of Local Site Operators across the UK throught the year



Figure 1. Summary of the data applications of the UKEAP datasets prior to the UKs EU exit. (*Note: It is assumed that EU reporting objectives will continue and be transposed into UK law.*)

1.2 Evidence and Policy Use of UKEAP Measurement data

Measurement data from the UKEAP networks are in place to support compliance assessment, assess exceedance of critical levels and loads, as well as inform policy development. A summary of on-going activities is presented below:

Modelling Ambient Air Quality (MAAQ)

- Ambient concentrations of sulphate, nitrate and ammonium measured within the AGA-Net and NAMN networks are used to produce maps of the secondary inorganic aerosol components of PM_{2.5} and PM₁₀.
- The Rural NO₂-Net is used to produce the rural background NO_x concentration field in the Pollutant Climate Mapping compliance modelling process.

Further details of how these measurements are used in compliance assessment modelling can be found on http://uk-air.defra.gov.uk (<u>here)</u>.

Mapping and Modelling of Critical Loads and Levels

Concentration Based Estimated Deposition (CBED):

- UKEAP Precip-Net, AGA-Net, NAMN and NO₂-Net data used to produce annual concentration & surface deposition maps of nitrogen and sulphur pollutants, separating wet and dry components.
- Long term trends and impact assessment.

Further details of this work may be found on http://www.cldm.ceh.ac.uk/uk-national-focal-centre (here).

Fine Resolution Atmospheric Multi-pollutant Exchange (FRAME)

• NAMN data used with the model for calculating ammonia concentrations in the UK at 5 km and 1 km resolution and assessing critical level exceedance.

Further details of this work may be found on http://www.pollutantdeposition.ceh.ac.uk/frame (<u>here</u>)

UK Critical Loads and Levels mapping:

Maps from CBED and FRAME are used to assess:

- Impacts on UK ecosystems from sulphur and nitrogen.
- UK trends in ecosystems exceeding critical loads <u>headline indicator (B5a)</u> for Defra, JNCC and the Devolved Administrations.
- CBED calcium and base cation deposition used to derive UK acidity critical loads.
- UK critical loads submitted to the UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP) Working group for abatement strategy development.

Further details of this work may be found on http://www.cldm.ceh.ac.uk/ (here)

Support for National Air Pollution Control Strategies

 Source-receptor data is calculated with FRAME to input to the UK Integrated Assessment Model and used to support national policy on strategies for control of air pollution, as well as for source attribution of Surphur and Nitrogen deposition in APIS. See <u>here</u> for further details

Air Pollution Information System (APIS) (SEPA, JNCC, EA, NE, NRW, NIEA and SNH)

- Resource for UK agencies, local authorities, SMEs and the public for information on air pollution related to ecosystem effects; uses UKEAP, CBED and Critical Loads maps.
- Searchable site relevant critical loads and source attribution.
- Assessment by habitat, ecosystem or species and literature database.

Habitats Directive assessments (JNCC and others)

- Assessments based on critical loads exceedance for habitats which are sensitive to nitrogen
- Assessment of pressures and threats from air pollution as part of the conservation status assessments for Annex I habitats for the Article 17.
- Assessments used to inform judgements of conservation status.

Article 6 and <u>Annex IV</u> of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe

The Air Quality Directive requires the speciation of $PM_{2.5}$ at rural background locations with a spatial coverage of 1 station per 100,000 km². This sampling is coordinated with the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) through the two supersites at Chilbolton and Auchencorth Moss.

National Emission Ceiling Directive Article 9

The NECD Article 9 requires the submission of site based monitoring of air pollution impacts on ecosystems. UKEAP data from NAMN, AGANet, Precip-Net and NO2-Net sites which are co-located with Defra, Natural England, Forest Research and other UKRI National Capabilityecosystem long-term monitoring networks are provided for the UK data collation and submission.

Direct public provision of air quality data

All the UKEAP data is managed through a centralised database and is available for download through the <u>UK-AIR</u> web site. Data are also submitted to the <u>OSPAR</u> and <u>EMEP</u> databases. UKEAP Team members at Ricardo and UKCEH are available to give information on the measurements when requested.

1.3 Publications

Reports and research papers published in 2019 and 2020 using UKEAP site air quality data, maps derived from UKEAP data or science supported at UKEAP sites

Aas, W. and Bohlin-Nizzetto, P. (no date) 'Heavy metals and POP measurements, 2017', p. 172.

Agbotui, P. Y. (2019) Characterisation of flow regimes of the East Yorkshire Chalk Aquifer. University of Leeds.

- Akritidis, D. et al. (2020) 'A complex aerosol transport event over Europe during the 2017 Storm Ophelia in CAMS forecast systems: analysis and evaluation', Atmospheric Chemistry and Physics Discussions, pp. 1–31.
- Aleksankina, K. et al. (2019) 'Advanced methods for uncertainty assessment and global sensitivity analysis of an Eulerian atmospheric chemistry transport model', Atmospheric Chemistry and Physics, 19(5), pp. 2881–2898.
- AQEG, (2020), Estimation of changes in air pollution emissions, concentrations and exposure during the COVID-19 outbreak in the UK.Rapid evidence review –June2020.https://uk-

air.defra.gov.uk/assets/documents/reports/cat09/2007010844_Estimation_of_Changes_in_Air_Pollution_During_ COVID-19_outbreak_in_the_UK.pdf

- Archibald, A. T. et al. (2020) 'Description and evaluation of the UKCA stratosphere–troposphere chemistry scheme (StratTrop vn 1.0) implemented in UKESM1', Geosci. Model Dev., 13(3), pp. 1223–1266. doi: 10.5194/gmd-13-1223-2020.
- Barthel, S., Tegen, I. and Wolke, R. (2019) 'Do new sea spray aerosol source functions improve the results of a regional aerosol model?', Atmospheric Environment, 198, pp. 265–278.
- Billett, M. F., Garnett, M. H. and Leith, F. I. (2020) 'An assessment of chamber 14C methodologies for sampling aquatic CO2 evasion', Ecohydrology, 13(2), p. e2191.
- Boichu, M. et al. (2019) 'Large-scale particulate air pollution and chemical fingerprint of volcanic sulfate aerosols from the 2014-2015 Holuhraun flood lava eruption of Bárðarbunga volcano (Iceland)'.
- Braban, C. F. et al. (2020) 'Ammonia in a time of COVID-19. A submission of evidence to Defra/AQEG'.
- Brown, R. J. et al. (2020) 'Consistency and uncertainty of UK measurements of mercury in precipitation', Chemosphere, p. 127330.
- 'Characterisation of ambient Total Gaseous Mercury concentrations over the South African Highveld' (2019) Atmospheric Pollution Research, 10(1), pp. 12–23. doi: 10.1016/j.apr.2018.06.001.
- Chiwa, M. et al. (2018) 'Long-term interactive effects of N addition with P and K availability on N status of Sphagnum', Environmental Pollution, 237, pp. 468–472.
- Chiwa, M. et al. (2019) 'P and K additions enhance canopy N retention and accelerate the associated leaching', Biogeochemistry, 142(3), pp. 413–423.
- Clifton, O. E. et al. (2020) 'Dry Deposition of Ozone Over Land: Processes, Measurement, and Modeling', Reviews of Geophysics, 58(1), p. e2019RG000670. doi: 10.1029/2019RG000670.
- Coyle, M. et al. (2019) 'Meteorological measurements at Auchencorth Moss from 1995 to 2016', Geoscience Data Journal, 6(1), pp. 16–29.
- Dacre, H. F., Mortimer, A. H. and Neal, L. S. (2020) 'How have surface NO2 concentrations changed as a result of the UK's COVID-19 travel restrictions?', Environmental Research Letters. Available at: http://iopscience.iop.org/10.1088/1748-9326/abb6a2.
- Dean, J. F. et al. (2019) 'The Potential Hidden Age of Dissolved Organic Carbon Exported by Peatland Streams', Journal of Geophysical Research: Biogeosciences, 124(2), pp. 328–341. doi: 10.1029/2018JG004650.
- Diaz, F. M. et al. (2020) 'Ozone Trends in the United Kingdom over the Last 30 Years', Atmosphere, 11(5), p. 534.
- Dore, A. et al. (2019) 'Modelling the Concentration of Ammonia and Exceedance', Air Pollution Modeling and its Application XXVI, p. 59.
- Dubache, G. et al. (2019) 'Modeling ammonia volatilization following urea application to winter cereal fields in the United Kingdom by a revised biogeochemical model', Science of The Total Environment, 660, pp. 1403–1418.
- Emetere, M. E. and Akinlabi, E. T. (2020) 'Modeling Big Data and Further Analysis', in Introduction to Environmental Data Analysis and Modeling. Springer, pp. 79–155.

- Farr, G. et al. (2019) 'Atmospheric deposition at groundwater dependent wetlands phase 2: nutrient source apportionment case studies from England and Wales'.
- Finch, D. P. and Palmer, P. I. (2020) 'Increasing ambient surface ozone levels over the UK accompanied by fewer extreme events', Atmospheric Environment, p. 117627.
- Flechard, C. R. (no date) 'Supplement of Carbon–nitrogen interactions in European forests and semi-natural veg-etation–Part 1: Fluxes and budgets of carbon, nitrogen and greenhouse gases from ecosystem monitoring and modelling'.
- Forde, E. et al. (2019) 'Characterisation and source identification of biofluorescent aerosol emissions over winter and summer periods in the United Kingdom', Atmospheric Chemistry and Physics, 19(3), pp. 1665–1684. doi: 10.5194/acp-19-1665-2019.
- Gambaro, N. (2020) Sentinels of environmental impact: using principal component analysis to improve the detection of shale gas contamination in England. Department of Earth Sciences, Durham University.
- Goddard, Sharon L. et al. (2019) 'Concentration trends of metals in ambient air in the UK: a review', Environmental Monitoring and Assessment, 191(11), p. 683.
- Goddard, S. L. et al. (2019) 'Determination of antimony and barium in UK air quality samples as indicators of non-exhaust traffic emissions', Environmental monitoring and assessment, 191(11), p. 641.
- Hambley, G. et al. (2019) 'Net ecosystem exchange from two formerly afforested peatlands undergoing restoration in the Flow Country of northern Scotland', Mires and Peat, (23), pp. 1–14. doi: 10.19189/MaP.2018.DW.346.
- Hei-Laan Yeung, K. et al. (2020) 'From sink to source: long-term (2002-2019) trends and anomalies in net ecosystem exchange of CO2 from a Scottish temperate peatland.', in EGU General Assembly Conference Abstracts, p. 5967.
- Hjellbrekke, A.-G. (2020) 'Data report 2018. Particulate matter, carbonaceous and inorganic compounds.', EMEP/CCC-Report.
- Hjellbrekke, A.-G. (no date) 'Particulate matter, carbonaceous and inorganic compounds', p. 150.
- Hjellbrekke, A.-G. and Solberg, S. (2019) 'Ozone measurements 2017', EMEP/CCC-Report.
- Insausti, M. et al. (2020) 'Advances in sensing ammonia from agricultural sources', Science of The Total Environment, 706, p. 135124.
- Jafar, H. A. and Harrison, R. M. (2020) 'Spatial and temporal trends in carbonaceous aerosols in the United Kingdom', Atmospheric Pollution Research.
- Kelly, M. P. C. (2019) 'Effects of drain blocking and nitrogen deposition on greenhouse gas emissions from peatlands'.
- Khan, M. A. H. et al. (2019) 'Investigating the behaviour of the CRI-MECH gas-phase chemistry scheme on a regional scale for different seasons using the WRF-Chem model', Atmospheric Research, 229, pp. 145–156.
- Kiheri, H. et al. (2020) 'Fungal colonization patterns and enzymatic activities of peatland ericaceous plants following long-term nutrient addition', Soil Biology and Biochemistry, p. 107833.
- Levy, P. et al. (2019) 'Response of a peat bog vegetation community to long-term experimental addition of nitrogen', Journal of Ecology, 107(3), pp. 1167–1186.
- Lewis, A., Carslaw, D. and Moller, S. J. (2020) 'Non-methane Volatile Organic Compounds in the UK'.
- Lewis, A., Moller, S. J. and Carslaw, D. (2019) 'Non-Exhaust Emissions from Road Traffic'.
- Lin, M. et al. (2019) 'Sensitivity of ozone dry deposition to ecosystem-atmosphere interactions: A critical appraisal of observations and simulations', Global Biogeochemical Cycles, 33(10), pp. 1264–1288.
- Liu, L. et al. (2020) 'Global estimates of dry ammonia deposition inferred from space-measurements', Science of the Total Environment, p. 139189.
- Manninen, S. et al. (2016) 'Nitrogen deposition does not enhance Sphagnum decomposition', Science of the Total Environment, 571, pp. 314–322.
- Martin, N. A. et al. (2019) 'Validation of ammonia diffusive and pumped samplers in a controlled atmosphere test facility using traceable Primary Standard Gas Mixtures', Atmospheric Environment, 199, pp. 453–462.
- Menut, L. et al. (2020) 'Impact of lockdown measures to combat Covid-19 on air quality over western Europe', Science of the Total Environment, 741, p. 140426.
- Mircea, M. et al. (2019) 'EURODELTA III exercise: An evaluation of air quality models' capacity to reproduce the carbonaceous aerosol', Atmospheric Environment: X, 2, p. 100018.
- Mitchell, E. J. S. et al. (2019) 'A Review of the Impact of Domestic Combustion on UK Air Quality'.

Nair, A. A. and Yu, F. (2020) 'Quantification of atmospheric ammonia concentrations: A review of its measurement and modeling'.

- Ni, Y. (no date) 'Climate change mitigation potential of lignocellulosic succinic acid: assessing feedstock supply and integrated land use options in a UK Wheat-Miscanthus bio-succinic acid-based bioplastics production system'.
- Pan, Y. et al. (2020) Revisiting the concentration observations and source apportionment of atmospheric ammonia. Springer.
- Rennie, S. et al. (2020) 'The UK Environmental Change Network datasets–integrated and co-located data for long-term environmental research (1993–2015)', Earth System Science Data, 12(1), pp. 87–107.
- Rowe, E. et al. (no date) 'Trends Report 2020: Trends in critical load and critical level exceedances in the UK'.
- Savi, F. et al. (2020) 'Neural network analysis to evaluate ozone damage to vegetation under different climatic conditions', Frontiers in Forests and Global Change, 3, p. 42.
- Solberg, S. et al. (2020) 'VOC measurements 2018', EMEP/CCC-Report.
- Stacey, B., Harrison, R. M. and Pope, F. (2020) 'Evaluation of ultrafine particle concentrations and size distributions at London Heathrow Airport', Atmospheric Environment, 222, p. 117148. doi: 10.1016/j.atmosenv.2019.117148.
- Stow, D. et al. (2019) 'Illumination geometry and flying height influence surface reflectance and NDVI derived from multispectral UAS imagery', Drones, 3(3), p. 55.
- Swenson, M. M. et al. (2019) 'Carbon balance of a restored and cutover raised bog: implications for restoration and comparison to global trends.', Biogeosciences, 16(3).
- Tang, Y. S., Tanna, B., et al. (2019) 'Fenn's, Whixall, Bettisfield, Wem & Cadney Mosses. Atmospheric ammonia monitoring data report for period: Jul 2018–Dec 2018'.
- Tang, Y. S., Hernandez, C. M., et al. (2019) 'Report on the UK NECD Network to monitor the impacts of air pollution on ecosystems. UK Monitoring sites-revised submission'.
- Tang, Y. S. et al. (2020) 'Pan-European rural atmospheric monitoring network shows dominance of NH\$_\mathbf3\$ gas and NH\$_\mathbf4\$NO\$_\mathbf3\$ aerosol in inorganic pollution load', Atmospheric Chemistry and Physics Discussions, 2020, pp. 1–61. doi: 10.5194/acp-2020-275.
- Tao, Y. and Murphy, J. G. (2019) 'The sensitivity of PM2. 5 acidity to meteorological parameters and chemical composition changes: 10-year records from six Canadian monitoring sites.', Atmospheric Chemistry & Physics, 19(14).
- Vohra, K. et al. (2020) 'Long-term trends in air quality in major cities in the UK and India: A view from space', Atmospheric Chemistry and Physics Discussions, pp. 1–45.
- Walker, H. L. et al. (2019) 'Changing supersites: assessing the impact of the southern UK EMEP supersite relocation on measured atmospheric composition', Environmental Research Communications, 1(4), p. 041001.
- Walker, H. L. et al. (2020) 'Use of filter radiometer measurements to derive local photolysis rates and for future monitoring network application', Atmospheric Measurement Techniques Discussions, 2020, pp. 1–32. doi: 10.5194/amt-2020-219.
- Wyche, K. P., Nichols, M., et al. (2020) 'Changes in Ambient Air Quality and Atmospheric Composition and Reactivity in the South East of the UK as a Result of the COVID-19 Lockdown', Science of The Total Environment, p. 142526.
- Wyche, K. P., Cordell, R. L., et al. (2020) 'The spatio-temporal evolution of black carbon in the North-West European "air pollution hotspot", Atmospheric Environment, p. 117874.
- Xu, J. et al. (2020) 'Increased dissolved organic carbon concentrations in peat-fed UK water supplies under future climate and sulfate deposition scenarios', Water Resources Research, 56(1), p. e2019WR025592.
- Yang, M. et al. (2020) 'Temporal and spatial trends in aerosols near the English Channel An air quality success story?', Atmospheric Environment: X, 6, p. 100074. doi: 10.1016/j.aeaoa.2020.100074.
- Kακαβάς, Σ. (2019) Estimation of dust emissions and their effects on atmospheric pollution over Europe. Thesis. Available at: http://nemertes.library.upatras.gr/jspui//handle/10889/12831 (Accessed: 5 July 2020).

UKEAP data is freely available to download from UK-AIR and EMEP databases. Appendix 1 suggests citations formats for users. Data use is not tracked on the databases; the list collated above represents an non-exhaustive search of the literature.

2. Introduction

The Defra, Environment Agency and Devolved Administrations rural air pollutant monitoring networks project, **UK Eutrophying and Acidifying Atmospheric Pollutants (UKEAP),** is operated jointly between Ricardo Energy & Environment and the UK NERC Centre for Ecology and Hydrology (UKCEH).

UKEAP measurements are undertaken to allow improvements in understanding of the chemical composition, deposition and removal processes and to allow validation of atmospheric transport models. This report summarises operation and monitoring data for 2019.

UKEAP is comprised of:

- National Ammonia Monitoring Network (NAMN 74 sites)
- Acid Gases and Aerosol Network (AGA-Net 27 sites)
- **Precipitation chemistry Network** (Precip-Net 41 sites)
- Rural NO₂ diffusion tube network (NO₂-Net 24 sites)
- UK EMEP Supersites (Chilbolton Observatory and Auchencorth Moss)

The geographical distribution of the NAMN and AGANet networks are shown in Figure 2 and Figure 3 respectively, Precip-Net and NO₂-Net in Figure 4. Natural England **Long Term Monitoring Network** air quality measuremewnts are embedded in UKEAP networks Precip-Net and NO₂-Net.



Figure 2 UK National Ammonia Monitoring Network (NAMN)



Figure 3 UK Acid Gases and Aerosol Network (AGANet)



Figure 4 UK Precipitation chemistry (Precip-Net) and NO₂ diffusion tube (NO₂-Net) Network

2. UKEAP Networks Reports

2.1 Precipitation Network (Precip-Net)

Precip-Net operated without major change in 2019. Samples continued to be collected 41 fortnightly bulk rain monitoring sites and 2 daily wet only (DWOC) collectors in operation throughout the year.

Bulk precipitation samples are collected using bulk deposition collectors (Figure 5 Bulk rain sampler (Bannisdale)) at fortnightly intervals, details of which can be found in previous reports. Precip-Net sites are located across the UK (Figure 4) and consists of both new Natural England Long Term Monitoring Network (LTMN) sites and those which were part of the original 1985-2016 network prior to the 2016 network review (Figure 6 and Figure 7 Precip-Net monitoring network respectively).

Unratified quarterly monitoring data are made available publically quarterly and the annual ratified data made available through the <u>UK-AIR website</u>. Measurement data is supported by site specific information such as site location, co-location of other air quality networks and site metadata (e.g. altitude and location photos).

Two daily collection of precipitation sampler using Daily Wet Only Collectors (DWOC) are operated at two sites: Auchencorth Moss and Chilbolton sites which deliver to UK contribution to the Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP).

Local Sites Operators (LSOs) are used to undertake the site operation including replacing rain collection bottles, cleaning funnels, replacing debris filters and making observations at the site. LSOs also ensure the return of the collected rain samples. Quality assurance and laboratory intercomparison results from 2019 are summarised in the Appendices of this report.



Figure 5 Bulk rain sampler (Bannisdale)



Figure 6 LTMN sites forming part of the Precip-Net monitoring network (eight sites)



Figure 7 Precip-Net monitoring network

The spatial pattern of ammonia, nitrate and acidity and non-seasalt sulphate are shown in Figure 8. The spatial pattern has low concentrations of pollutants in the western seaboard and north west of Scotland. As expected concentrations of nitrate and ammonium is significantly higher than sulphate.

Figure 9 summarises the National Emissions Inventory (NAEI) estimated annual emission of precursor gases since the inception of the Precip-Net network in 1986. All of the emission estimates have decreased though the rate of decrease for sulphur dioxide was greater than that for oxides of nitrogen and ammonium. Sulphur dioxide emissions have decreased by about ninety six percent, oxides of nitrogen emissions have decreased by more than 71 % and ammonia emissions have decreased by about 14 %. Figure 9 also presents projected emissions for the respective gases from the National Emissions Inventory (NAEI).

As in previous years the concentration of pollutants in rain are generally in line with the variability of emissions (Figure 9 and Figure 10-12), however the interannual variability means that a direct correlation with annual changes is not observable in the simple timeline plots and detail statistical analysis with both meterology and emissions would be needed for causal changes to be identified, particularly in the case of NO_3^- in rain given small changes in annual emissions. For most sites non-ses salt sulphate is generally less than 10 μ eq.l⁻¹, nitrate and ammonium concentrations are on average approximately 20 μ eq.l⁻¹.

Figures 13-15 summarise the long term time series trends in non-sea salt sulphate, nitrate and ammonium at Precip-Net sites across the UK. The figures illustrated the large spatial variability of trends and the different patterns of change.

Non-sea salt sulphate is decreasing across most Precip-Net sites, however at a few sites, the rate of decrease has slowed in the past 5 years (e.g. Eskdalemuir, Beagh's Burnand Loch Dee) whereas others are still continuing a similar rate of decrease (e.g. Yarner Wood, Goonhilly, River Etherow). From an atmospheric chemistry perspective, "natural" non-sea salt sulphate would be driven by volcanic emissions globally and non-anthropogenic biomass burning.

Nitrate in precipitation is decreasing at most Precip-Net sites on an internannual basis with the rate of decrease slowed in the past 5 years (in line with emissions rate decrease). For some cleaner sites, there is an interannual veraibility as large as the magnitude of the concentration (e.g. Ystraffdin and Hillsborough Forest amongst several) therefore care needs to be taken in interpreting the changes in concentration overtime.

For ammonium in precipitation, although a trendline has been fitted, there is a significant level of noise in the interannual data over the decadal timescale, likely due to the strong impact of meteorology on ammonia emissions and atmospheric processing prior to wet deposition.



Figure 8 Interpolated concentration maps for non-sea salt sulphate, nitrate, ammonium and hydrogen ion (µeq I⁻

¹)



Figure 9 Sulphur dioxide, oxides of nitrogen and ammonia emissions since 1986



Figure 10 Sulphur dioxide emissions and sulphate concentrations in rainwater



Figure 12 Ammonia emissions and ammonium concentrations in rainwater



Figure 13 Non-sea salt sulphate concentrations measured at sites with the Precip-Net since 1986



Figure 14 Nitrate concentrations measured at sites with the Precip-Net network since 1986



Figure 15 Ammomium concentrations measured at sites with the Precip-Net network since 1986

2.2 NO₂-Net Network

The NO₂ network (NO₂-Net) consists of 24 sites at which diffusion tubes, in triplicate, were exposed for approximately 4-week exposure periods. The annual average NO₂ measured at each site, together with data capture, are shown in Table 1. Diffusion tubes consist of a polypropylene tube (7.1 cm in length), on one end of which is a low-density polyethylene cap. Two stainless steel grids impregnated with the absorbent chemical are mounted within this cap. In this case, the absorbent is a solution of triethanolamine and acetone.

The mean data capture of the diffusion tubes for all of the site in 2019 was 94% with 19 of the 24 sites achieving > 90% and 17 sites achieving 100% data capture. There were various reasons for the lower data capture at Balquidder 2 and Llyn Llydaw such as local site operator availability and extended tube exposure.

Site Name	Raw 2019 concentratio n (µg m ⁻³)	2019 concentratio n Bias Corrected (0.828) ¹	Data capture	Site Name	Raw 2019 concentratio n (µg m ⁻³)	2019 concentratio n Bias Corrected (0.828) ¹	Data capture
Allt a'Mharcaidh	1.25	1.03	100%	Llyn Llydaw	2.35	1.95	47%
Balquhidder 2	1.93	1.60	62%	Loch Dee	2.54	2.10	100%
Bannisdale	3.46	2.87	100%	Lough Navar	2.40	1.99	100%
Chilbolton Observatory	9.22	8.44	100%	Lullington Heath	9.65	7.99	100%
Driby 2	8.89	7.36	100%	Moorhouse	3.29	2.72	100%
Eskdalemuir	2.42	1.99	100%	Percy's Cross	3.67	3.04	100%
Flatford Mill	9.78	8.10	92%	Polloch	1.22	1.01	100%
Forsinard RSPB	1.47	1.22	100%	Pumlumon	2.79	2.31	100%
Glensaugh	2.54	2.10	100%	Strathvaich	1.20	1.00	76%
Goonhilly	3.67	3.04	85%	Tycanol Wood	3.53	2.92	100%
High Muffles	5.42	5.08	100%	Whiteadder	3.37	2.79	87%
Hillsborough Forest	6.82	5.64	100%	Yarner Wood	3.82	3.83	100%

Table 1	2019 NO ₂	concentration	from the	Diffusion	Tubes in	the NO ₂ -Net

¹ All sites bias adjusted by 0.828 with the exception of Chilbolton, Eskdalemuir, High Muffles and Yarner Wood which were corrected using co-located samplers, See appendix for details.

Figure 16 shows the trend in emissions of NO_x and NO_2 concentrations measured by the diffusion tubes in the network as a network average, very rural site (Strathvaich) and less rural site (Flatford Mill). It is apparent that the estimated emissions of NO_x in the UK as a whole show a reduction over the period shown and there is also a reduction in the average concentrations of all of the active NO_2 -

Net site over the period. More information relating to emissions in the UK can be found on the National Atmospheric Emissions Inventory (NAEI) <u>website</u>.

NO₂ are associated with transport or industrial processes involving combustion, therefore there are smaller influences in concentrations at rural locations. The difference between the less rural site of Flatford Mill site which has an urban influence being about 50 miles from London and between Colchester and Ipswich and the more rural Strathvaich site located in the north of Scotland can also be seen in the plot. The trend in concentrations at the Strathvaich site does not appear to show any observable reduction in NO₂ concentration whereas the Flatford Mill sites shows a similar rate of reduction to that of the NAEI estimated.



Figure 16 Long term trends where estimated emissions are plotted against selected sites in the network

The annual average uncorrected NO_2 concentrations from 2010-2019 (Figure 17) indicates the differing NO_2 concentrations at rural locations across the UK. Most of the sites show some reduction between 2010 and 2019 but the larger decreases being seen at the sites that are closer to the sources of NO_x .



Figure 17 Annual mean NO₂ concentration (µg m-3) at the NO₂-Net sites 2010-2019

2.3 National Ammonia Monitoring Network (NAMN)

The number of National Ammonia Monitoring Network (NAMN) sites providing monthly measurements of atmospheric NH₃ in 2019 was 71, summarised in Figure 2. The LTMN site at North Derwent Valley/Thorganby was not operational and removed from the network. The 2019 annual NAMN results are summarised by the average and range of annual NH₃ concentrations observed at each site in Figure 18. There is high spatial variability in NH₃ concentrations across the UK and significant seasonal variability. This reflects the large heterogeneity of NH₃ sources in the rural countryside and variability in levels of NH₃ emissions (see <u>Tang et. 2018</u> for a more detailed discussion). During 2019 average data capture across NAMN was 76.9%. (QC criteria summarised in the Appendix of this report).

Site Type	Number
DELTA sites sampling gaseous NH ₃	29
AGANET DELTA sites (sampling gaseous NH₃, HNO₃, SO₂, HCl & aerosol NH₄⁺, NO₃⁻, SO₄², Cl⁻, Na⁺, Ca²⁺, Mg²⁺)	27
ALPHA sites sampling gaseous NH ₃ only	51
Intercomparison sites with both DELTA & ALPHA	9
Total number of sites	71

Table 2 Summary of National Ammonia Monitoring Network (NAMN) monitoring site types during 2019

2019 annual mean concentrations of ammonia across all NAMN sites are shown in Figure 18. Annual average concentrations range between <0.1 μ g.m⁻³ at the cleaner background sites (e.g. Inverpolly and and Strathvaich Dam) to just under 10 μ g.m⁻³ at the highest concentration sites (Brompton A). As a network average (Figure 19) the ammonia concentration was within variability from the previous two years. The spatial variability for both ammonia and ammonium (NH₄⁺) (Figure 20), the lowest concentrations can be seen in the west of Scotland with most sites being in the range of 0.5-5 μ g.m⁻³ across the UK.



Figure 18 Annual mean concentrations of gaseous NH₃ in the NAMN. Each data point represents the averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations observed (A = ALPHA sampler; D=DELTA)



Figure 19: Changes in atmospheric NH₃ averaged over all sites in NAMN operational between 1998 and 2019 summarised in a box plot. The whiskers show the absolute max and min and the diamond is the mean annual concentration. Annual mean UK meteorological data (source http://www.metoffice.gov.uk/) are plotted on top to illustrate the relationship between inter-annual variability in NH₃ concentrations with changing temperature and rainfall.



Figure 20: Spatial patterns of annual NH₃ and aerosol NH₄⁺ concentrations from monthly NAMN/AGANET measurements. Since February 2017, ammonium is measured at the 27 AGANET sites only.

2.4 Acid Gas and Aerosol Network (AGANET)

The UK Acid Gas and Aerosol Network (AGANET) provides monthly speciated measurements of atmospheric reactive gases (HNO₃, SO₂) and aerosols (NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺, Na⁺, Ca²⁺, Mg²⁺) at 27 sites across the UK. The spatial distributions of acid gases and aerosol ions, which are primarily anthropogenic in origin, in particular HNO₃/NO₃⁻ and SO₂/SO₄²⁻, have the highest concentrations in the south and east of the UK. Atmospheric gases including SO₂ and HNO₃ are somewhat more spatially variable than aerosol species, reflecting the longer atmospheric residence time of the latter. Although on the UK scale with only 27 sites the higher spatial variability in gaseous species can be seen.



Figure 21: Mean monitored annual concentrations of gaseous HNO₃ and SO₂ at individual sites in AGANET. Each data point represents averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations observed. Data for gaseous NH₃ measured under NAMN is also shown for comparison.



Figure 22: Mean monitored annual concentrations of particulate NO₃⁻, SO₄²⁻, Cl⁻ and NH₄⁺ at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations observed.



Figure 23 Mean monitored annual concentrations of particulate Mg, Ca and Na at individual sites in AGANET. Each data point represents the averaged concentrations of monthly measurements made at each site in 2019, whilst the bars show the minimum and maximum concentrations



Figure 24 Annual mean monitored atmospheric reactive gas concentrations (HNO₃ and SO₂ from AGANET and NH₃ from NAMN) across the UK from annual averaged monthly measurements made in 2019.



Figure 25: Annual mean monitored atmospheric aerosols (particulate NO₃⁻, SO₄²⁻, and Cl⁻ from AGANET and NH₄⁺ from NAMN) concentrations across the UK from averaged monthly measurements made in 2019.



Figure 26: Annual mean monitored atmospheric base cation (Ca²⁺, Mg²⁺ and Na⁺) concentrations across the UK from the averaged monthly measurements made in 2019.



Figure 27: Long-term trend in annual mean concentrations of gases and aerosols monitored in AGANET. Each data point represents the time-weighted averaged annual mean from all sites (2006 – 2016 = 30 sites; from 2017 = 27 sites) and also the original I2 monitoring sites in the network. Since 2016, HCl is no longer measured in the new DELTA sampling train configuration. NAMN NH₃ data for AGANET sites are also shown, for comparison.



Figure 28: Temporal trends in reactive gas and aerosol concentrations across the UK, comparing the mean seasonal profile (2000-2019: mean +/- SD of 27 AGANET sites) against year 2019.

3. UK EMEP Supersites 2019 measurement overview

There are two UK EMEP supersites, Auchencorth Moss has operated as an atmospheric observatory for long term measurements since 1995 and became EMEP Supersite in 2006, whereas Chilbolton completed its first year of measurements in 2016, following a relocation from Harwell (2006-2015) due to decommissioning of the site. EMEP – the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe operates under the <u>UNECE</u> <u>Convention on Long Range Transboundary Air Pollutants</u>). Measurements made at the supersites in 2018 are summarised in Table 3.

Both EMEP Supersites are rural sites. The sites provide the **required coverage**, of at least once station every 100,000 km², to determine the composition of PM_{2.5} at rural background locations as required under <u>Annex IV</u> of Directive 2008/50/EC on Ambient Air Quality and Cleaner Air For Europe. The chemical composition of PM_{2.5} is determined for the following species:

- Elemental carbon (EC) and organic carbon (OC), from the UK Particle Concentrations and Numbers Monitoring Network.
- Inorganic species (K⁺, Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻), from the MARGA instrument.

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

Auchencorth and Chilbolton are part of all major UK air quality measurement networks including Defra's Automated Urban and Rural Network (<u>AURN</u>), the UK-wide network providing evidence for the UK for compliance with the <u>EU Ambient Air Directives</u> and the <u>Gothenberg Protocol</u> of automatic air quality monitoring stations measuring oxides of nitrogen (NO_X), nitrogen dioxide (NO₂), sulphur dioxide (SO₂), ozone (O₃), carbon monoxide (CO) and atmospheric particulate matter (PM₁₀ and PM_{2.5}).

Non-automatic measurements of (rural) heavy metal concentrations in PM₁₀ and precipitation; particulate-phase base cations, anions and trace gases; polycyclic aromatic hydrocarbons (PAHs) in PM₁₀, air and precipitation were also made at the site. Automated real-time measurements of total particle number and soot (also termed "Black Carbon") were made at the site as part of the UK Particle Concentrations and Numbers Monitoring Network.

UK Particle Concentrations and Numbers Monitoring Network also provided a daily assessment of the contribution of Organic Carbon (OC), Elemental Carbon (EC), and Total Carbon (TC), to the airborne ambient PM₁₀ and PM_{2.5} mass concentration at the site. All the above air pollutant measurement activities were funded by Defra. This report summarises the measurements made between January and December 2019. The statistics reported on UK-AIR are those reported to the Commission to demonstrate compliance with the air quality Directives.

Measurements funded under this project and described here are specifically:

- Meteorological observations (barometric pressure, dewpoint, wind speed & direction, relative humidity, temperature, (total) rainfall): Chilbolton reported here, Auchencorth available on request and archived on CEDA
- Trace gas (HCl, HONO, HNO₃, NH₃, SO₂) and PM₁₀ and PM_{2.5} aerosol concentrations (K⁺, Na⁺, NH₄⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, SO₄²⁻), Chilbolton and Auchencorth Moss.
- On line mercury measurements (Chilbolton: elemental mercury; Auchencorth Moss: elemental and speciated mercury).

					-	
Pollutant	CHO1	AUC ¹	EMEP Level	Averaging period	Monitoring network (Ha/Au)	Contract holder
SO ₂ , HCl, HNO ₃ , HONO, NH ₃ (MARGA)	х	х	П	Hourly	UKEAP	CEH/Ricardo E&E
PM _{2.5} K ⁺ , Na ⁺ , NH ₄ ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ (MARGA)	х	Х	П	Hourly	UKEAP	CEH/Ricardo E&E
PM ₁₀ K ⁺ , Na ⁺ , NH ₄ ⁺ , Ca ²⁺ , Mg ²⁺ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ (MARGA)	Х	х	П	Hourly	UKEAP	CEH/Ricardo E&E
Elemental mercury		х	Ш	Hourly	UKEAP	CEH/Ricardo E&E
Total Particulate mercury		х	Ш	Hourly	UKEAP	CEH/Ricardo E&E
Total gaseous mercury (TGM) in air	Х	х	П	Hourly	UKEAP	CEH/Ricardo E&E
Meteorological parameters	Х	X ²	I.	Hourly	UKEAP/CEH	CEH/Ricardo E&E
(WS, WD, T, RH, rainfall)						
Precipitation chemistry	Х	Х	I	Daily	UKEAP	CEH/Ricardo E&E
NO and NO ₂ (thermal converter)	Х	х	I.	Hourly	AURN	Bureau Veritas
Sulphur dioxide	Х		I.	Hourly	AURN	Bureau Veritas
Ozone	Х	х	I.	Hourly	AURN/CEH	Bureau Veritas
Particulate matter PM _{2.5} , PM ₁₀	х	х	I	Hourly	AURN	Bureau Veritas
VOCs in air	х		II	Hourly	Automated HC Network	Ricardo E&E
PAH in PM10, air and rain	Х	х	I	Monthly	РАН	NPL*/Ricardo E&E
Black carbon	Х	х	Ш	Hourly	Particle numbers/CEH	NPL
Particle counts (>7 nm)	Х	X ²	Ш	Hourly	Particle numbers/CEH	NPL
Particle size distribution	Х	X ²	Ш	Hourly	Particle numbers	NPL
PM_{10} carbon-content (elemental carbon, EC, organic carbon, OC, total carbon, TC)	Х	Х	Ш	Weekly	Particle numbers	Bureau Veritas
DELTA sampler (particulate-phase ions: Ca ²⁺ , Mg ²⁺ , Na ⁺ , Cl ⁻ , NH ₄ ²⁺ , NO ₃ ⁻ , SO ₄ ²⁻)	х	х	I	Monthly	UKEAP	СЕН
Trace gases (HCI, HNO ₃ , NH ₃ , and SO ₂)	Х	х	I.	Monthly	UKEAP	CEH
Heavy metals in precipitation	х	х	I	Monthly	Heavy Metals	NPL
Mercury in precipitation	Х	х		Monthly	Heavy Metals	NPL
Heavy metals in PM ₁₀	х	х	П	Weekly	Heavy Metals	CEH
Persistent Organic Pollutants (POPs) in air	х	Х	I	Monthly	TOMPS	University of Lancaster
CO ₂ measurements		Х	Ш	Hourly	ICOS	CEH
Trace gas fluxes (O ₃ ,)		Х	Ш	Hourly	NERC NC ²	CEH
NO and NO $_2$ (photolytic)		x	I	Hourly	NERC NC ²	CEH National Capability funded

Table 3 Pollutants measured at the UK EMEP Supersites during 2019

¹CHO: Chilbolton; AUC: Auchencorth Moss; ²NERC CEH National capability funded * NPL: National Physical Laboratory, Teddington, Middlesex.

In 2019-20 more than 50 research outputs (papers or presentations) have been identified using data from Auchencorth Moss and Chilbolton and are summarised at the beginning of this report. It is noted that Auchencorth Moss is an integrated climate, air quality and ecosystem research infrastructure and Chilbolton is also a <u>national facitility for remote sensing</u> as well as air quality monitoring.

High resolution trace gas and aerosol composition measurements (MARGA instrument)

The annual summary of speciated PM_{10} and $PM_{2.5}$ and trace gases concentrations are presented in Table 4 and the following Figures. The MARGA instrument at both the Auchencorth Moss and Chilbolton sites were upgraded during 2018. The low data capture in January 2019 at the Auchencorth Moss site was due to a faulty valve resulting in contamination of the internal standard and invalidating all data.

At the Chilbolton site, the average data capture for 2019 for all pollutants was 65.1% however for PM_{10} pollutants average data capture is 70.5% for $PM_{2.5}$ pollutants is 50.5% and for gas pollutants is 78.4%. The difference in data capture between PM_{10} and $PM_{2.5}$ is caused by the SJAC heater starting to fail in April and it was replaced in July.

	C	hilbolton	Aucheno	corth Moss
lon (PM₁₀)	Annual mean (μg m³)	Data capture (%)	Annual mean (µg m⁻³)	Data capture (%)
NH_4^+	1.38	72	0.55	80
Na⁺	0.89	72	0.46	78
K⁺	0.09	71	0.04	79
Ca ²⁺	0.33	70	0.05	80
Mg ²⁺	0.19	70	0.06	80
Cl ⁻	1.54	71	0.83	81
NO ₃ -	3.56	73	1.19	81
SO42-	1.43	73	0.76	81
lon (PM _{2.5})	Annual mean (µg m⁻³)	Data capture (%)	Annual mean (µg m⁻³)	Data capture (%)
NH4 ⁺	1.27	49	0.49	83
Na⁺	0.46	51	0.27	83
K⁺	0.07	50	0.03	83
Ca ²⁺	0.1	50	0.03	82
Mg ²⁺	0.12	49	0.03	83
Cl	0.81	51	0.47	83
NO ₃ -	3.06	52	0.98	83
SO42-	1.17	52	0.65	83
Trace Gases	Annual mean (μg m ⁻³)	Data capture (%)	Annual mean (µg m ⁻³)	Data capture (%)
NH ₃	4.81	78	1.31	86
HCI	0.03	77	0.13	86
HNO ₃	0.13	79	0.11	86
HONO	0.42	79	0.08	86
SO ₂	0.08	79	0.08	86

Table 4 Summary of the ratified speciated PM10 and PM2.5 and trace gases of annual mean concentrations and data capture for Auchencorth Moss and Chilbolton



Figure 29 Ratified PM₁₀ speciated measurements by the MARGA at the Chilbolton supersite



Figure 30 Ratified PM_{2.5} speciated measurements by the MARGA at the Chilbolton supersite



Figure 31 Ratified PM_{10} speciated measurements by the MARGA at the Auchencorth Moss supersite



Figure 32 Ratified PM_{2.5} speciated measurements by the MARGA at the Auchencorth Moss supersite



Figure 33 Ratified trace gas measurements by the MARGA at the Auchencorth Moss supersite



Figure 34 Ratified trace gas measurements by the MARGA at the Chilbolton supersite

Mercury Measurements

The annual means and data capture for the 2019 ratified mercury measurements are shown below in Table 5. Time series plots of the 2019 Auchencorth Moss measurements are shown in Figure 35 At the beginning of the year the system suffered with unstable flow issues. This led to contamination issues later in the year and the rejection of some of the speciated data.

The mercury data from Chilbolton is shown in the time series in Figure 36. The instrument has suffered with an unstable baseline fault which is intermittent & led to much of the years data being removed.

	Annual Mean	Data capture
Auchencorth Moss		
Gaseous Elemental Hg (GEM) ng m ⁻³	1.32	55.48%
Gaseous Oxidised Hg (GOM) pg m ⁻³	0.85	36.46%
Particulate Bound Hg (PM2.5) pg m ⁻³	1.88	38.58%
Chilbolton		
Total Gaseous Hg (TGM) ng m ⁻³	1.53	24.77%

Table 5 Ratified mercury measurements









4. Acknowledgements

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

Appendix 1: Guide to UKEAP data and Data usage

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

Chilbolton EMEP Supersite

Trace gas and aerosols (MARGA) Contact: Mr Chris Conolly, Ricardo Energy & Environment

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

Mercury measurements: Contact: Ms Sarah Leeson, NERC Centre for Ecology and Hydrology

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

Meteorological Data: Contact Mr Chris Conolly Ricardo Energy & Environment

Auchencorth Moss EMEP Supersite

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

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

Mercury: Contact: Ms Sarah Leeson, NERC Centre for Ecology and Hydrology

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

Acid Gas and Aerosol Network

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

Stephens, A.C.M, Tang, Y.S., Leaver, D., Martin, C., Beith, S., Thacker, S., Simmons, I., Pereira, G., Tanna, B., Patel, M., Lawlor A.J., Sutton, M.A., Braban C.F., UK Eutrophying and Acidifying Atmospheric Pollutant project's Acid Gas and Aerosol Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, AGA-Net, http://uk-air.defra.gov.uk/networks/network-info?view=ukeap), Date received: (*insert date of data receipt*)

National Ammonia Monitoring Network

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

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

Precipitation Network

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo Energy & Environment

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

NO₂-Network

Contact: Mr Christopher Conolly and Dr Keith Vincent, Ricardo Energy & Environment

Conolly, C., Collings, A., Knight, D., Vincent, K., Donovan, B., UK Eutrophying and Acidifying Atmospheric Pollutant project's rural NO₂-Network (Data funded by Defra and the Devolved Administrations and published under the Open Government Licence v3.0, NO₂-Net, http://uk-air.defra.gov.uk/networks/network-info?view=ukeap), Date received: (*insert date of data receipt*)

Appendix 2: QC summary for 2019

A. Chilbolton and Auchencorth operations

The Chilbolton EMEP Supersite is operated by Ricardo summarised on UK-AIR. There were no modifications to the site infrastructure in 2016. Ricardo acted as Local Site Operator for the Chilbolton EMEP Supersite measurements for all measurements except those conducted by NPL.

The Auchencorth Moss EMEP Supersite is operated by NERC CEH, summarised on UK-AIR. CEH is LSO for all measurements at Auchencorth Moss. No instruments were changed during 2019

During 2019 no health and safety incidents occurred at either site in relation to the operation of the EMEP Supersites.

B. MARGA

Operational details

Measurements of particulate-phase cations and anions in PM_{10} and $PM_{2.5}$: sulphate (SO_4^{2-}), nitrate (NO_3^{-}), sodium ion (Na^+), potassium ion (K^+), ammonium ion (NH_4^+), chloride ion (Cl^-), calcium ion (Ca^{2+}), and magnesium ion (Mg^{2+}) were provided by an automated continuous-flow denuder and steam-jet aerosol sampler (MARGA 2S, <u>Metrohm-Applicon Ltd.</u>). The MARGA uses an automated continuous-flow, wet-rotating denuder (WRD) coupled to a steam-jet aerosol collector (SJAC) sampler. It provides hourly measurements of the water-soluble species (listed above) in PM_{10} and $PM_{2.5}$. It also provides a measure of the concentration of water-soluble trace acid gases (HCl, HONO, HNO₃, NH_3 , and SO_2) in the sampled air. The MARGA 2S consists of two units or "boxes", both identical; one for the sampling and entrainment of the PM_{10} particulate and gas-phase species, the other for $PM_{2.5}$. A third, detector box houses the syringe pump module analytical components, including the IC columns, and the process control interfaces, including the PC.

The MARGA 2S samples the ambient air through a PM_{10} size-selective inlet head at a nominal flow rate of 2 m³ hr⁻¹ (1 m³ 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 realtime, 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 PM₁₀ and PM_{2.5} sampling boxes.

The MARGA 2S is a research-grade instrument. The MARGA is designed to be operational 24 hours a day, 365 days a year, but as the analyser is a research instrument it has some reliability issues.

Measurements gaps occur throughout the year due to scheduled maintenance and servicing activities, such as replacement of the anion and cation columns, replacement of in-line filters for the steam jet aerosol collector (SJAC), and wet rotating denuder (WRD), pump maintenance, system zeros, and system cleaning. Routine maintenance of the MARGA was undertaken each week, and more frequently if required, i. e. when an error or problem was identified. System maintenance was carried out in-line with the manufacturer's guidance. The instrument status was monitored on an on-going basis. Key system parameters, peak retention times, and chromatograms were checked daily and adjusted accordingly. System blanks were carried out once a month. As well as being used to identify any potential contamination in the system, the results from the system blanks were used in determining the limit of detection, for certain species, during the ratification of the measurements. The calibration of the mass flow controllers are undertaken each month to ensure a sample flowrate of 1 m³ 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 PM₁₀ 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. At Auchencorth Moss the solutions are: stock solution: Li^+ 28 mg/L and Br⁻ 325 mg/L, working solution: Li^+ 70 ppb Br⁻ 800 ppb. The Chilbolton instrument's working solution was made-up periodically by diluting) 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) of Br⁻.

Sub-samples of the internal standard used at both sites were analysed by CEH Lancaster to ensure that both the stock and working solutions contained the correct, within $\pm 20\%$, 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.

QC

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 \pm 20% of the nominal concentration.

A regular maintenance scheme is in place on the MARGA instrument (Table 6) includes monthly calibration of the 2 mass flow controllers in the instrument, to ensure the correct flow rate through a steam jet aerosol collector (SJAC), which has been designed to operate at $1 \text{ m}^3/\text{hr}$. The frequency of calibration is increased if the positions of annular denuders in the system are altered. As part of the MARGAs ongoing QC a monthly blank. As well as being used to identify any potential contamination in the system, it was used in the calculation of a detection limit for certain species which is used in the ratifying process.

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

1x change cation IC column if necessary						х			

1 x change cation pre-concentration							x		
column if necessary									
1 x change anion pre-concentration						х			
column if necessary									
(*)	-		D			a af la la alv <u>a</u> a	1 £:1+ a var a ! a		h

Table 6 Maintenance Schedule - MARGA 2S (separate air pump/white WRD heads) at Auchencorth Moss

(*) 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

3. Precip-Net: EMEP Inter-comparison

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 sixty analytical laboratories in Europe, and to other internationally recognised analytical laboratories. The inter-comparison exercise is required as part of the EMEP monitoring programme – such a fundamental check on analytical performance is essential if response to emission reductions can be observed consistently throughout Europe.

Results of the 37th EMEP Inter-comparison

The inter-comparison in 2019 was the 37th time such an inter-comparison took place. The samples provided included nitrogen dioxide in absorbing solution (Table 16) and synthetic rainwater samples (Table 17).

Nitrogen dioxide absorbing solution

The inter-comparison in 2019 was the 37th time such an inter-comparison took place. The results of the Nitrogen Dioxide absorbing solution are shown below in Table 16. The results of this intercomparison are excellent with absolute mean difference all less than 1 %. They are within the criteria for satisfactory reported by EMEP which is the highest rating for the EMEP quality norm. The analytical laboratory has been made aware of the performance to they are aware their performance meets expectations.

Table 7 Comparison of Expected and Measured Concentrations of Nitrogen Dioxide in Absorbing Solution

Sampe code	Expected concentration µg NO ₂ -N/ml	Measured concentration µg NO ₂ -N/ml	Difference (%)	EMEP quality norm
C1	0.29	0.288	-0.7%	S
C2	0.271	0.272	0.4%	S
C3	0.1	0.1	0.0%	S
C4	0.092	0.092	0.0%	S

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

Synthetic Rainwater Samples:

The performance of Ricardo's chosen laboratory (SOCOTEC UK Limited) has decreased slightly since the 36th intercomparison. The results of the intercomparison and the expected results are shown in Table 17. The 2019 intercomparison has four questionable results and three unsatisfactory.

The analytical laboratory has been made aware of the analytical performance and the results that have been obtain from the intercomparison. They are currently investigating the poor pH data along with errors identified with the results for sulphate and ammonium.

Species	Sample Expected Measured		Difference (%)	EMEP Quality	
openeo	code	concentration	concentration		Norm
		mg l ⁻¹	mg l ⁻¹		
	G1	0.209	0.187	-10.5%	Q
SO4-2	G2	0.22	0.194	-11.8%	Q
504	G3	0.419	0.380	-9.3%	S
	G4	0.422	0.383	-9.2%	S
	G1	0.08	0.062	-22.5%	Q
NH .+	G2	0.16	0.139	-13.1%	S
11114	G3	0.401	0.370	-7.7%	S
	G4	0.454	0.415	-8.6%	S
	G1	0.149	0.150	0.7%	S
NO3 ⁻	G2	0.267	0.268	0.4%	S
INU3	G3	0.547	0.561	2.6%	S
	G4	0.635	0.648	2.0%	S
	G1	0.268	0.248	-7.5%	S
Not	G2	0.39	0.363	-6.9%	S
ina.	G3	0.891	0.826	-7.3%	S
	G4	1.06	0.984	-7.2%	S
	G1	0.083	0.082	-1.2%	S
N4~ ²⁺	G2	0.062	0.068	9.7%	S
IVIB-	G3	0.206	0.179	-13.1%	S
	G4	0.175	0.154	-12.0%	S
	G1	0.347	0.314	-9.5%	S
	G2	0.502	0.456	-9.2%	S
CI-	G3	1.24	1.120	-9.7%	S
	G4	1.47	1.340	-8.8%	S
	G1	0.115	0.123	7.0%	S
C = 2+	G2	0.153	0.145	-5.2%	S
Car	G3	0.153	0.151	-1.3%	S
	G4	0.204	0.187	-8.3%	S
	G1	0.119	0.110	-7.6%	S
1/+	G2	0.187	0.163	-12.8%	S
K'	G3	0.255	0.223	-12.5%	S
	G4	0.323	0.278	-13.9%	S
	G1	5.49	5.360	-2.4%	Q
*الم	G2	5.48	5.790	5.7%	U
рн	G3	5.45	5.720	5.0%	U
	G4	5.43	6.120	12.7%	U
	G1	5.96	5.960	0.0%	S
Cond	G2	7.8	7.270	-6.8%	S
Cond	3	14.47	13.950	-3.6%	S
	4	16.4	15.960	-2.7%	S

Table 8 37th EMEP Inter-comparison

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

4. NO₂-Net

Establishment of a correction factor for nitrogen dioxide concentrations measured in the Rural NO2 Network (UKEAP).

Diffusion tubes have been co-located alongside automatic analysers (chemiluminescence) within the Rural Nitrogen Dioxide Network since 2003. Each year we have observed that the nitrogen dioxide measured by diffusion tubes tend to be higher than measured by automatic analysers. Reasons for the overread are complex and may include wind effects (which shortens the diffusion path) and/or in tube conversion of NO_x to NO₂ or laboratory analytical performance.

In order to extrapolate bias to a wider network <u>technical guidance</u> provided to local authorities TG(16) recommends, either:

- Use results from the national bias adjustment spreadsheet
- Use a locally obtained bias adjustment factor, in this case the diffusion tubes co-located with the AURN automatic analysers.

Nitrogen dioxide concentrations are measured within the Rural NO₂ Network to provide an estimate of the rural background concentration field. This work is carried out by Pollution Climate Mapping team as required for compliance modelling against Limit Values.

The objective of this study is review the bias adjustment factors in both the national bias adjustment spread and the co-located samplers in the NO₂-Net Network and then recommend which adjustment factors should be applied.

National Bias Adjustor Spreadsheet

Socotec (formerly ESG and HSL) have analysed the diffusion tubes since the inception of the Rural NO₂ Network. They have also acted as diffusion tube analyst for more than fifty local authorities involved in local air quality management since 2000 and hence appear in the National Bias Adjustor Spreadsheet. Figure 37 shows comparison of nitrogen dioxide measured by diffusion tube and diffusion tube since 2000 at sites where Socotec analysis diffusion tubes. This includes three hundred and seventy-eight co-located pairs for a range of sampling site classifications (majority are roadside, 61 %). The diffusion tube over reads in the vast majority (97 %) of cases.

Locally derived adjustment factors: co-location of UKEAP diffusion tubes within AURN.

Triplicate diffusion tubes have been located at Eskdalemuir and Yarner Wood since 2006, at Harwell since 2007 (site closed at end of 2015 but replaced by Chilbolton) and at High Muffles since 2012. At each of these sites the diffusion tubes were co-located with an automatic analyser.

A comparison of the nitrogen dioxide concentrations measured by diffusion tube and automatic analyser is presented in Table 9 Annual mean nitrogen dioxide concentrations (μ g m-3) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis). As was seen for the co-located samples in the national spreadsheet, concentrations measured by diffusion tube are higher than measured by the automatic analyser.

Figure 38 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each presents the data for those occasions where data capture was greater than 75 %. The smallest concentrations are measured at Eskdalemuir and the largest at Chilbolton.



Figure 37 A comparison of annual mean nitrogen dioxide concentrations measured by diffusion tube and automatic analyser

	Chilbolton	Observatory	Eskda	alemuir	Har	Harwell		l High Muffles		Yarner Wood	
	DT	СМ	DT ^b	СМ	DT	СМ	DT ^b	СМ	DT ^b	CM	
2003			4.7			15.7(87)	10.8	14.4(18)	8.8	10.7(29)	
2004			2.9	5.7(6)		12.0(96)	7.4	9.0(70)	4.8	7.8(99)	
2005			4.6	3.8(93)		11.6(91)	8.6	7.5(89)	6.6	9.2(82)	
2006			4.0	3.7(89)		11.5(93)	9.1	7.5(88)	5.7	5.2(88)	
2007			4.2	5.0(78)		12.2(91)	8.0	6.4(98)	6.3	5.6(91)	
2008			а	5.1(93)	а	10.1(98)	а	6.6(98)	а	5.3(82)	
2009			а	4.3(94)	а	10.0(98)	а	7.5(56)	а	4.3(87)	
2010			4.5(100)	3.0(98)	15.1(100)	11.9(97)	7.9(95)	6.1(92)	5.4(100)	4.9(98)	
2011			3.5(100)	3.2(92)	12.2(100)	10.3(97)	7.7(100)	7.4(95)	4.9(100)	4.1(85)	
2012			3.7(100)	3.0(99)	11.6(100)	10.1(97)	7.6(100)	6.2(97)	4.9(100)	4.3(97)	
2013			3.8(92)	2.5(97)	12.4(100)	12.5(50)	7.0(100)	5.4(96)	5.5(99)	5.2(85)	
2014			3.6(92)	2.3(99)	10.5(100)	8.0(97)	6.9(100)	5.4(89)	4.3(100)	3.6(92)	
2015			3.2(100)	2.2(98)	9.0(100)	7.7(97)	6.2(100)	5.3(92)	3.9(100)	3.9(99)	
2016	11.7(96)	14.3(88)	2.9(100)	2.0(97)			5.8(100)	5.4(91)	4.6(100)	4.5(93)	
2017	10.1(100)	11.2(97)	2.4(100)	2.0(93)			5.6(100)	5.1(79)	3.6(100)	3.2(89)	
2018	9.9(100)	9.5(99)	2.3(100)	1.9(97)			5.1(100)	4.9(95)	4.0(83)	4.3(98)	
2019	9.2(100)	8.9(87)	2.4(100)	1.9(97)	#N/A	#N/A	5.4(100)	4.9(99)	3.8(100)	3.8(98)	

Table 9 Annual mean nitrogen dioxide concentrations (µg m⁻³) measured by diffusion tube and automatic analysers (Data capture is provided in parenthesis)

Notes: ^a Data were downloaded from Archive database. The database does not yet contain the annual mean concentrations as measured by diffusion tube for 2008 and 2009; ^b Data captures were not calculated for diffusion tubes concentrations archived before 2010. Diffusion tubes were sampling in triplicate at Yarner Wood and Eskdalemuir since 2006; at Harwell since 2007 (replaced by Chilbolton 2016); at High Muffles since 2012. These are shaded.



Figure 38 A comparison of nitrogen dioxide concentrations measured by automatic analysers and diffusion tube at each

Recommendation for bias correct factors

TG16 recommends that each local authority should, if they been involved in a co-location study, present both the local and national bias adjustment bias spreadsheet and justify which value should be used in the final bias adjustment. Here we would recommend using the values derived each year from the Rural NO₂ Network. This is because:

- the 'quality' of the measurement made by automatic analyser in the Rural NO₂ Network will always be to a "reference" standard;
- the measurement environment will be always rural background whereas the national study will comprise a range of environments most of which will be roadside or urban background;
- Samples are dispatched, handled and exposed in a consistent way;
- As the results from the AURN and Rural NO₂ Network will be available before the end of May each year, they will be available in time for the PCM modelling.

Calculation of average bias factor for the four co-located NO₂ sampling sites (Chilbolton, Eskdalemuir, Yarner Wood and High Muffles)

Following the guidance provided in TG16 we have calculated monthly mean NO₂ concentrations for the automatic analysers corresponding to the periods the diffusion tubes were exposed. We have also updated the calculation spreadsheet[1] to allow for time weighting the mean concentrations and bias adjustment factors. As we have four co-located sampling sites we will need to follow the advice provided in Paragraph 7.193[2] to combine the respective bias B factors.

The individual bias B factors were calculated as follows: The average of the three values is calculated to be 20.72 % giving a bias adjustment factor of 0.828[3]. We would recommend multiplying each of the remaining diffusion tubes in the Rural NO₂ Network by this factor.[1] See <u>https://laqm.defra.gov.uk/bias-adjustment-factors/local-bias.html</u> and Figure 7.1 of TG(16) The text from Paragraph 7.193 is: Two bias factors are output, A and B, and in this example they are 0.78 and 28% respectively. The Bias factor A is the local bias correction factor. If there is more than one local collocation study, then the A factors should not be averaged. Instead, a reasonable approximation can be derived by averaging the B values. For example, if there were 2 studies of 22% and 28%, then the average would be 25%. This is then expressed as a factor, e.g. 25% is 0.25. Next add 1 to this value, e.g. 0.25 + 1.00 = 1.25. Finally, take the inverse to give the bias adjustment factor, e.g. 1/1.25 = 0.80. Calculated as (1 / (bias average+1))

Table	10 NO2	Bias	factors	for	2019

	Eskdalemuir	Yarner Wood	High Muffles	Chilbolton
Bias factor, B	47%	8%	15%	13%

AGA-Net and NAMN Performance and Data capture

All DELTA systems are serviced annually. As part of this service the gas meter is calibrated and the system PAT tested. Figure 39 below contains the average percentage data capture across all sites for each chemical of interest. Average data capture was 61.4 % for AGANet and 76.9% for NAMN.



Figure 39 2019 NAMN and AGANet Percentage data capture by chemical component

ALPHA DELTA intercomparison

NAMN measurements continue 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 do not deviate significantly with time. The annual regression used to calibrate the ALPHA sampler is shown in Figure 41. The annual calibration functions of ALPHA samplers show good consistency between years. This can be seen in the historical ALPHA uptake rates plotted in Figure 40.



Figure 40 Historical UKEAP uptake rate for ALPHA samplers.



Figure 41 Historical UKEAP uptake rate for ALPHA samplers.