Acid gases and aerosol measurements in the UK (1999-2015): regional distributions and trends

Y. Sim Tang[1], Christine F. Braban[1], Ulrike Dragosits[1], Ivan Simmons[1], David Leaver[1], Netty van Dijk[1], Janet Poskitt[2], Sarah Thacker[2], Manisha Patel[2], Heather Carter[2], M. Glória Pereira[2], Patrick O. Keenan[2], Alan Lawlor[2], Christopher Conolly[3], Keith Vincent[3], Mathew R. Heal[4] & Mark A. Sutton[1]

[1]CEH, Bush Estate, Penicuik, Midlothian EH26 0QB
[2]CEH, Lancaster Environment Centre, Bailrigg, Lancaster LA1 4AP
[3]Ricardo Energy & Environment, Gemini Building, Fermi Avenue, Harwell, Oxon, OX11 0QR
[4]School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ

Correspondence to: Y. Sim Tang (yst@ceh.ac.uk)

Abstract. The UK Acid Gases and Aerosol Monitoring Network (AGANet) was established in 1999 (12 sites, increased to 30 sites from 2006), to provide long-term national monitoring of acid gases (HNO_3, SO_2, HCl) and aerosol components (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}). An extension of a low-cost denuder-filter pack system (DELTA) that is used to measure NH_3 and NH_4^+ in the UK National Ammonia Monitoring Network (NAMN) provides additional monthly speciated measurements for the AGANet. A comparison of the monthly DELTA measurement with averaged daily results from an annular denuder system showed close agreement, while the sum of HNO_3 and NO_3^- and the sum of NH_3 and NH_4^+ from the DELTA are also consistent with previous filter pack determination of total inorganic nitrogen and total inorganic ammonium, respectively. With the exception of SO_2 and SO_4^{2-}, the AGANet provides for the first time the UK concentration fields and seasonal cycles for each of the other measured species. The largest concentrations of HNO_3, SO_2, and aerosol NO_3^- and SO_4^{2-} are found in south and east England and smallest in western Scotland and Northern Ireland, whereas HCl are highest in the southeast, southwest and central England, that may be attributed to dual contribution from anthropogenic (coal combustion) and marine sources (reaction of sea salt with acid gases to form HCl). Na^+ and Cl^- are spatially correlated, with largest concentrations at coastal sites, reflecting a contribution from sea salt. Temporally, peak concentrations in HNO_3 occurred in late winter and early spring attributed to photochemical processes. NO_3^- and SO_4^{2-} have a spring maxima that coincides with the peak in concentrations of NH_3 and NH_4^+, and are therefore likely attributable to formation of NH_4NO_3 and $(NH_4)_2SO_4$ from reaction with higher concentrations of NH_3 in spring. By contrast, peak concentrations of SO_2, Na^+ and Cl^- during winter are consistent with combustion sources for SO_2 and marine sources in winter for sea salt aerosol. Key pollutant events were captured by the AGANet. In 2003, a spring episode with elevated concentrations of HNO_3 and NO_3^- was driven by meteorology and transboundary transport of NH_4NO_3 from Europe. A second, but smaller episode occurred in September 2014, with elevated concentrations of SO_2, HNO_3, SO_4^{2-}, NO_3^- and NH_4^+ that was shown to be from the Icelandic Holuhraun volcanic eruptions. Since 1999, AGANet has shown substantial decrease in SO_2 concentrations relative to HNO_3 and NH_3, consistent with estimated decline in UK emissions. At the same time, large reductions and changes in the aerosol components provides

evidence of a shift in the particulate phase from $(NH_4)_2SO_4$ to NH_4NO_3. The potential for NH_4NO_3 to release NH_3 and HNO_3 in warm weather, together with the surfeit of NH_3 also means that a larger fraction of the reduced and oxidised N is remaining in the gas phase as NH_3 and HNO_3 as indicated by the increasing trend in ratios of $NH_3:NH_4^+$ and $HNO_3:NO_3^-$ over the 16 year period. Due to different removal rates of the component species by wet and dry deposition, this change is expected to affect spatial patterns of pollutant deposition with consequences for sensitive habitats with exceedance of critical loads of acidity and eutrophication. The changes are also relevant for human health effects assessment, particularly in urban areas as NH_4NO_3 constitutes a significant fraction of fine particulate matter (< 2.5 µm) that are linked to increased mortality from respiratory and cardiopulmonary diseases.

1   Introduction

Monitoring the atmospheric concentrations of acid gases and their aerosol reaction products is important for assessing their effects on human health, ecosystems, long-range transboundary transport and global radiative balance. Concentration data are necessary for quantifying long-term trends and spatial patterns, understanding gas-aerosol phase interactions, and estimating the contributions of different pollutants to dry deposition fluxes (ROTAP, 2012; AQEG, 2013a; Colette et al., 2016), as well as to provide data for testing the performance of atmospheric models (e.g. Chemel et al., 2010; Vieno et al. 2014, 2016). Acid gases in the atmosphere include sulphur dioxide (SO_2), nitrogen oxides (NO_x), nitric acid (HNO_3), hydrochloric acid (HCl) and nitrous acid ($HONO$). Secondary inorganic aerosols (SIA) include sulphate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-) and nitrite (NO_2^-) that are formed from reactions of SO_2 and NO_x (and HNO_3, a secondary product of NO_x) with ammonia (NH_3) in the atmosphere. These aerosols make an important contribution to concentrations of particulate matter (PM) in the UK (15 to 50 % of the mass of atmospheric PM) and constitute a significant fraction of fine particles that are less than 2.5 µm in diameter ($PM_{2.5}$) implicated in harming human health (AQEG, 2012; 2013b). In addition, base cations in aerosol are also of interest to estimate the extent to which acidity is neutralized and to estimate the contribution of marine influences (ROTAP, 2012; Werner et al., 2011).

Anthropogenic emissions of SO_2, NO_x, HCl and NH_3 in the UK declined by 81, 51, 87 and 13 %, respectively, over the period 1999 to 2015 (NAEI, 2018). Despite the success in mitigating SO_2 emissions however, sulphur still remains a pollutant of national importance, because reduction in sulphur deposition in remote sensitive areas have been more modest than close to major sources (ROTAP, 2012). HCl was also recently identified as another important acidifying pollutant for sensitive habitats (Evans et al., 2014). Emissions of HCl (from coal burning in power stations) have however declined to very low levels (from 74 kt in 1999 to 9 kt in 2015), although it could still pose a threat to habitats close to sources. For NO_x, the more modest decrease in emissions reflects difficulties in their abatement, while for NH_3, the decrease to date is largely a result of changes in animal numbers (NAEI, 2018).

With the decline in SO_2 emissions and deposition, the large number of reactive nitrogen compounds in the atmosphere are assuming greater importance owing to the complexities of the global N cycle and associated challenges in their abatement. These include the gas phase components NH_3, with over 80% estimated from agricultural emissions (EEA, 2017) and nitrogen oxides (NO, NO_2) from combustion, the secondary gas phase reaction products HNO_3, HONO and PAN (peroxyacetyl nitrate)

5   and particulate phase components (($NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3) formed by the reaction between NH_3 and acid gases. (AQEG, 2012). Ammonia and the N-containing aerosols are known to cause nitrogen enrichment and eutrophication, as well as contributing to acidification processes (Sutton et al., 2011). Oxidised nitrogen species (NO_x) are precursors to ground-level O_3 formation, while the production of acids (HNO_3, HONO) and PAN in the atmosphere affects air quality and is damaging both to human health and to vegetation (Cowling et al., 1998, Bobbink et al., 2010).

In Europe, air pollution policies regarding acidification and nitrogen eutrophication apply the "critical loads approach" (Bull, 1995; Gregor et al., 2001), which requires that atmospheric deposition inputs be mapped at an appropriate scale for the assessment of effects. In parallel, the "critical levels" of concentrations addresses the direct impacts of concentrations of nitrogen components in the atmosphere (Bull, 1991; Gregor et al., 2001; Cape et al., 2009). Quantifying the dry deposition of

15   reactive nitrogen compounds is a major challenge and a key source of uncertainty for effects assessment (Dentener et al., 2006; Flechard et al., 2011; Schrader et al., 2018; Sutton et al., 2007). While deposition may be estimated using atmospheric transport and chemistry models (e.g. Dore et al., 2015; Flechard et al., 2011; Smith et al., 2000), air concentration data at sufficient spatial resolution are needed, both to assess the atmospheric models and provide input data for estimating deposition using inferential models.

In light of policies to reduce atmospheric emissions, e.g. the amended 2012 Gothenburg Protocol (UNECE, 2018) and the revised National Emissions Ceilings Directive (NECD, EU Directive 2016/2284) (EU, 2016), it is important to assess long-term trends in the measured pollutants, since this provides the only independent means to assess the effectiveness of any abatement policies. Both these international agreements set emissions reduction commitments for SO_2, NO_x and NH_3, of 59,

25   42, and 6 %, respectively, by 2020 (with 2005 as base year) and includes $PM_{2.5}$ for the very first time. Under the 2016 NECD, further reduction commitments of 79 % (SO_2), 63 % (NO_x) and 19 % (NH_3) are also set for the EU 28 countries from 2030. Since emissions of these gases comes from different sources, emissions controls require very different strategies, making it important to monitor and assess the the relative concentrations and deposition of nitrogen and sulphur components.

30   The spatial and temporal patterns of gases and particulate phases of these pollutants differ substantially. Although it is widely acknowledged that speciation between reactive gas and aerosol measurement is critical, there are few national long-term monitoring programmes dedicated to measuring separately their concentrations and dry depositions at high spatial resolution (Torseth et al., 2012). Across Europe, the European Monitoring and Evaluation Programme (EMEP, 2014) continues to recommend using a daily filter pack sampling method to measure oxidised nitrogen (total inorganic nitrate, TIN) and reduced

nitrogen (total inorganic ammonia, TIA) (Torseth et al., 2012; Colette et al., 2016). The filter pack method is generally considered as robust for measuring SO_2 and SO_4^{2-} concentrations (EMEP, 2014; Hayman et al., 2006; Sickles et al., 1999). However, many papers have shown that there are potential artefacts in filter-pack sampling for HNO_3 and HCl, due to interactions with NH_3 and the volatility of NH_4NO_3 and NH_4Cl aerosol (Pio, 1992; Sickles et al., 1999; Cheng et al., 2012).

5 Results from EMEP filter pack measurements are therefore reported as TIN and TIA, due to phase uncertainties in the method (Torseth et al., 2012). This has been complemented by daily measurements of HNO_3 and NO_3^- using annular denuders (Allegrini et al., 1987; EMEP, 2014) that are made at a restricted number of sites because of the resources required. In North America, filter pack sampling is also used in weekly measurements of sulphur and nitrogen species in the CASTnet (Clean Air Status Trends Network) national monitoring network of 95 sites across USA, Canada and Alaska

10 (https://www.epa.gov/castnet). At a small number of CASTnet sites, hourly measurements of water-soluble gases and aerosols are made with the Monitor for AeRosols and GAses in ambient air (MARGA) system (Rumsey and Walker, 2016).

High time-resolution measurements of gases and aerosols are useful at selected locations for detailed analysis and model testing, but the high costs and resources required for these measurements make them unsuitable for the assessment of long-

15 term trends at many sites, particularly where spatial patterns are required. To achieve this, a larger number of sites operated at lower time-resolution is needed. In the UK, the Eutrophying and Acidifying Atmospheric Pollutants (UKEAP) network provides long-term measurements for the UK rural atmospheric concentrations and deposition of air pollutants that contribute to acidification and eutrophication processes (Conolly et al., 2016). UKEAP comprises of two EMEP supersites and four component networks: precipitation network (Precip-net), NO_2 diffusion tube network (NO_2-net), National Ammonia

20 Monitoring Network (NAMN) and the Acid Gases and Aerosol Network (AGANet). At the two EMEP supersites (Auchencorth and Harwell – relocated to Chilbolton in 2016), semi-continuous hourly speciated measurements of reactive gases and aerosols are made with the MARGA system (Twigg et al., 2016). These measurements are contributing to the validation and improvement of atmospheric models, such as FRAME (Dore et al., 2015) and EMEP4UK (Vieno et al., 2014, 2016) that are used to develop and provide the evidence base for air quality policies, both nationally and internationally.

The long-term dataset of monthly speciated measurements from the AGANet (1999 – 2015) are analysed in this paper to provide a comprehensive assessment of the spatial, temporal and long-term trends in atmospheric concentrations of the acid gases HNO_3, SO_2, HCl and related aerosol components NO_3^-, SO_4^{2-} and Cl^- (and also base cations Na^+, Ca^{2+} and Mg^{2+}) across the UK, together with an assessment of the DELTA denuder-filter pack sampling method (Sutton et al., 2001b; Tang et al.,

30 2009) as compared with other sampling techniques. To aid interpretation of the relative changes and trends in the acid gases and aerosols, NH_3 and particulate NH_4^+ data from the NAMN (Tang et al., 2018) are included, since atmospheric NH_3 is a major interacting precursor gas in neutralisation reactions with the acid gases.

2 Methods

2.1 Acid Gases and Aerosol monitoring Network (AGANet)

The UK Acid Gases and Aerosol Network (AGANet), known previously as the nitric acid monitoring network, was started in September 1999 under the Acid Deposition Monitoring Network (ADMN, Hayman et al., 2007) to deliver for the very first time, long-term monthly speciated measurement data on gaseous HNO_3 and particulate NO_3^- across the UK. Other acid gases (SO_2, HCl) and aerosols (SO_4^{2-}, Cl^-, plus base cations Na^+, Ca^{2+}, Mg^{2+}) are also measured and reported.

AGANet and NAMN are closely integrated, with AGANet established at a subset of NAMN sites to provide additional speciated measurements of the acid gases and aerosol components. To improve on national coverage, the number of sites in AGANet was increased in 2006 from 12 to 30 (Figure 1, Table 1). At the same time, the Rural Sulphur Dioxide Monitoring Program ceased, replaced by SO_2 and SO_4^{2-} measurements made under the expanded AGANet (Hayman et al., 2007). A broad spatial coverage of the UK is provided by the AGANet sites, with a focus on sites providing parallel information on other air pollutants (e.g., co-location with the Automatic Urban and Rural Network that provides compliance monitoring against the Ambient Air Quality Directives (https://uk-air.defra.gov.uk/networks/) and ecosystem assessments (e.g. Environmental Change Network, http://www.ecn.ac.uk/) (Monteith et al., 2016).

\<INSERT Figure 1 HERE\>
\<INSERT Table 1 HERE\>

2.2 Extended DELTA methodology for sampling acid gases and aerosol in AGANet

A low-cost manual denuder-filter pack method, DELTA (DEnuder for Long-Term Air sampling) implemented in the NAMN for measurement of NH_3 gas and aerosol NH_4^+ (Sutton et al., 2001a,b; Tang et al., 2018) is extended to provide additional simultaneous monthly time-integrated average concentrations of acid gases (HNO_3, SO_2, HCl) and particulate phase NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+} and Mg^{2+} for the AGANet (Conolly et al., 2016; Tang et al., 2015).

The DELTA method used in AGANet has also been applied in an extensive European-scale network of 58 sites to deliver 4 years of atmospheric concentrations and deposition data for reactive trace gas and aerosols from 2006 to 2009 (Tang et al., 2009; Flechard et al., 2011). Detailed descriptions of the DELTA method are provided by Sutton et al. (2001b) and by Tang et al. (2009, 2015). In brief, a small air pump is used to provide low sampling rates of 0.2–0.4 L min^{-1}, and air volumes are measured by a high-sensitivity diaphragm gas meter. By sampling air slowly, the method is optimised for monthly measurements, with sufficient sensitivity to resolve low concentrations at clean background sites (e.g. LOD = 0.05 μg m^{-3} for HNO_3 for monthly sampling; see Supplement Tables S1, S2). In addition, the power requirement is very small, and low voltage versions (using 6 V and 12 V micro-air pumps) of the system powered by wind-solar energy operate at some remote sites.

An extended denuder-filter pack sampling train is used to provide speciated sampling of reactive gases and aerosols (Supplement Figure S1) (Tang et al., 2009, 2015). A Teflon inlet (2.8 cm long) at the front end ensures development of a laminar air stream (Table S3), followed by a first pair of K_2CO_3 and glycerol coated denuders to collect HNO_3, SO_2 and HCl, a second pair of citric acid coated denuders to collect NH_3 and a 2-stage filter pack at the end to collect aerosol components. Stage 1 of the filter pack is a cellulose filter impregnated with K_2CO_3 and glycerol to collect NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}, with evolved aerosol NH_4^+ from this filter collected on the stage 2 citric acid impregnated filter. The separation of gases and aerosol is achieved by higher diffusivities of reactive gases to the denuder walls where they react with the chemical coating and are retained, whereas aerosol components pass through and are retained by post-denuder filters (Ferm, 1979). In this approach, potential artefacts caused by phase interactions associated with filter packs and bubblers are avoided (e.g. Sickles et al., 1999). A particle size cut-off of around 4.5 µm was estimated for the DELTA air inlet (Tang et al., 2015). The DELTA will therefore also sample fine mode aerosols in the $PM_{2.5}$ fraction, as well as some of the coarse mode aerosols < $PM_{4.5}$.

Na_2CO_3 is reported to be an effective sorbent for acid gases, allowing simultaneous collection of HNO_3, SO_2 and HCl on denuders (e.g. Ferm 1986), but since the measurement of aerosol Na^+ is also of key interest in AGANet, a K_2CO_3 coating is used instead to eliminate possible Na^+ contamination from Na_2CO_3. Glycerol is added to increase adhesion, stabilize the base coating (Ferm, 1986; Finn et al., 2001) and to minimise potential oxidation of nitrite that is also collected on the denuder to nitrate in the presence of atmospheric oxidants such as ozone (Allegrini et al., 1987; Perrino et al., 1990). The lengths of denuders (borosilicate glass tubes 10 cm and 15 cm long to capture > 95 % of NH_3 and acid gases, respectively) in the sampling train was calculated according to the procedures described by Sutton et al. (2001b), based on the calculations derived by Gormley and Kennedy (1948) and Ferm (1979) (see Supp. Table S3). All sites were set up as "outdoor" systems sampling directly from the atmosphere, avoiding potential adsorption losses (in particular HNO_3, which is highly surface active) and artefacts in air inlet lines. The sampling train is installed inside a simple watertight housing (Supp. Figure S1), which is mounted on a steel post in the desired location. A low density polyethylene funnel (89 mm aperture) is placed at the inlet as a rain shelter, and sampling height is approx. 1.5 m.

2.3   Chemical analysis

K_2CO_3/glycerol-coated denuders and aerosol filters are extracted into 5 mL of deionised H_2O for analysis. Anions (NO_3^-, SO_4^{2-} and Cl^-) in the denuder and filter extracts are analysed by Ion Chromatography (IC). Base cations Na^+, Mg^{2+} and Ca^{2+} from the filter extracts were analysed by IC between 1999 – Jun 2008 and by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES/ICP-AES) from Jul 2008. Citric acid coated denuders and filter papers are also extracted into

deionised H_20 (3 mL and 4 mL, respectively), with analysis of NH_4^+ performed on a high sensitivity ammonia flow injection analysis system, as described in Tang et al. (2018).

Up to June 2009, analyses were carried out at Harwell Laboratory (Hayman et al., 2007) and from July 2009 at CEH Lancaster (Conolly et al. 2016). The limit of detection (LOD) for the DELTA method for the different components are calculated by analysing a series of laboratory blanks. The mean and standard deviation of the results are calculated and the LOD is calculated as three times the standard deviation divided by 15 m^3, the typical volume of air sampled over a month by the DELTA system. Details of changes in laboratory, analytical methods and LODs for the gases and aerosols are summarised in supplementary tables S1 and S2, respectively.

2.4   Calculation of air concentrations

The air concentration (χ_a) of a gas or aerosol is calculated according to equation 1 (see Sutton et al., 2001b, Tang et al., 2018):

$$\chi a = \frac{Q}{V} \tag{1}$$

where Q = amount of a gas or aerosol collected on a denuder or aerosol filter, and

V = volume of air sampled (from gas meter, typically 15 m^3 in a month)

The denuder capture efficiency for each of the gas is calculated by comparing the concentrations of the individual gases in the denuder pairs (Equation 2) and are applied in an infinite series correction on the raw data to provide corrected air concentrations ($\chi_{a \text{ (corrected)}}$) according to equation 3 (see Sutton et al., 2001b, Tang et al., 2018):

$$\text{Denuder capture efficiency (\% CE)} = 100 \text{ x } \frac{\text{Denuder 1}}{(\text{Denuder 1} + \text{Denuder 2})} \tag{2}$$

$$\chi_a \text{ (corrected)} = \chi_a \text{ (Denuder 1)} \times \frac{1}{1 - \chi_a \left[\frac{\chi_a (\text{Denuder 2})}{\chi_a (\text{Denuder 1})} \right]} \tag{3}$$

Sutton et al. (2001b) and Tang et al. (2003) have shown that this procedure provides an important quality control, flagging up occurrences of poorly coated denuders and/or sampling issues. With denuder capture efficiency better than 90 %, the correction represents < 1 % of the corrected air concentration of the gas. Below 60 %, the correction is large (> 50 %) and is not applied, and the air concentration is then calculated as the sum of concentrations of the denuder pair. The amount of correction for gas not captured that is added to the corrected gas concentration, is subtracted from the estimated aerosol concentrations of matching anions and cations (see Tang et al., 2018).

2.5 Data Quality Control

The following data quality checks are applied to the network data, as part of the network quality management system (Tang and Sutton, 2003; Conolly et al., 2016):

    i)   Air flow rate ($0.2 – 0.4$ L min^{-1}): where this is below the expected range for a sampling period, the data is flagged as valid but failing the QC standard.

    ii)   Denuder capture efficiency: where this is less than 75% for a sample, the data is flagged as valid but less certain.

    iii)   Ion balance checks: close agreement expected between NH_4^+ and the sum of NO_3^- and $2\times SO_4^{2-}$, as NH_3 is neutralised by HNO_3 and H_2SO_4 to form NH_4NO_3 and $(NH_4)_2SO_4$, respectively (Conolly et al., 2016), and for Na^+ and Cl^-, as these are marine (sea salt) in origin.

    iv)   Screening the whole dataset for sampling anomalies and outliers, e.g. due to contamination or other issues.

2.6 HNO₃ measurement artefact and correction

Tang et al. (2009, 2015) have identified that HNO_3 concentrations (NO_3^- on denuders assumed to be from HNO_3) may be overestimated on carbonate coated denuders, due to partial co-collection of other oxidized nitrogen components such as nitrous acid (HONO). In the case of HONO, this collects on the denuder carbonate coating as nitrite (NO_2^-), but oxidizes to nitrate (NO_3^-) in the presence of oxidants such as ozone (Bytnerowicz et al., 2005) which can result in a positive interference in HNO_3 determination (Tang et al., 2009, 2015). Other oxidised nitrogen species present in the atmosphere such as peroxyacetyl nitrate (PAN) and nitrogen oxides (NO_x) can also potentially contribute to a further small interference (Allegrini et al., 1987; Bai et al., 2003). Based on the tests of Tang et al. (2015), raw HNO_3 data are corrected with an empirical factor of 0.45 which is estimated to be uncertain by ± 30 %. Apart from where stated, all HNO_3 data reported in this study have the 0.45 correction factor applied.

2.7 Time series trend analyses

Statistical trend analyses using both parametric linear regression (LR) and non-parametric Mann-Kendall (MK) (Gilbert, 1987; Chatfield, 2016) tests were performed on annually averaged data from AGANet, and on a subset of annually averaged data from NAMN made at the same AGANet sites. The datasets are considered sufficiently long-term (>10 years) and produced by a consistent method for effective statistical trend analyses. Both the LR and MK approaches are widely adopted for trend analyses in long-term atmospheric data (e.g. Meals et al., 2011; Colette, 2016; Jones and Harrison, 2011; Marchetto et al., 2013; Hayman et al., 2007; Conolly et al., 2016), and were used in a recent trend assessment of atmospheric NH_3 and NH_4^+ data (1998 – 2014) from the NAMN (Tang et al., 2018). As described in Tang et al. (2018), LR tests were performed using R, and MK tests used the R 'Kendall' package (McLeod, 2015), with estimation of the MK Sen's slope (fitted median slope of a

linear regression joining all pairs of observations) and confidence interval of the fitted trend using the R 'Trend' package (Pohlert, 2016). Results from both tests provides an indication of uncertainty associated with the choice of approach. Since there was no difference between either tests, MK results only are presented and discussed in the paper. A comparison of trend analyses from both approaches is however provided in supplementary materials (Supp. Figures S6 and S7 and Tables S4 - S6).

3   Results and Discussion

3.1   Performance of the DELTA method

This section presents the performance of the DELTA measurements, including a comparison with other air sampling methods and networks. Replicated sampling with the DELTA method were also made to assess measurement reproducibility and this

10   is shown for example for the Bush OTC site in Scotland (UKA00128). A comparison of the parallel measurements (Figure 2) showed good reproducibility in the method, with close agreement for all components (e.g. mean difference of $< \pm 3$ % for all components and ± 6 % for HCl).

<INSERT Figure 2 HERE>

15   ### 3.1.1   Comparison with daily annular denuder measurements

An assessment of the DELTA method for NH_3 has previously been reported by Sutton et al. (2001b). Following the extension to additionally sample acid gases and aerosols, the modified system was compared with independent daily measurements from an annular denuder system (ADS). The ADS (ChemspecTM model 2500 air sampling system, R&P Co. Inc.) was operated at Barcombe Mills in southern England (UKA00069) alongside the AGANet DELTA monthly measurements for a period of 18

20   months. Due to significant instrument and local site issues resulting in low data capture with the ADS, only 11 months of data were available for intercomparison. The sampling train used in the ADS consisted of 2 K_2CO_3/glycerol-coated annular denuders (same coating as AGANet DELTA), 2 citric acid-coated annular denuders; a cyclone with 2.5 µm cut-off, followed by a 2-stage filter pack containing a 2 µm PALL Zefluor teflon membrane (collection NO_3^-, SO_4^{2-}, Cl^-, Na^+, Mg^{2+}, Ca^{2+}) and a 1 µm PALL Nylasorb nylon membrane (collection of evolved NO_3^-), with a sampling rate of 10 L min^{-1}. To compare against

25   the monthly DELTA measurements, daily ADS values were averaged to the corresponding monthly periods, with results summarised in Figure 3.

<INSERT Figure 3 HERE>

30   In the measurement of gases, HNO_3 determination on DELTA (mean = 1.56 HNO_3 µg m^{-3}, $n = 11$) was on average 23 % higher than the ADS (mean = 1.31 HNO_3 µg m^{-3}, $n = 11$). Since both methods used the same carbonate coating on the denuders to

sample acid gases, the HNO_3 data here have not been corrected with the empirical factor described in section 2.6. Nitrous acid (HONO) was found to be close to or below limit of detections for most of the DELTA measurements (mean = of 0.03 µg HONO m^{-3}), compared with a significantly higher concentration (mean = 0.41 HONO µg m^{-3}) from the ADS. Since the sampling period of the ADS is daily, any HONO collected as nitrite on the ADS is likely to remain as nitrite and not oxidised to nitrate. The very low HONO (nitrite on the denuders assumed to be from HONO) concentrations from the DELTA supports the hypothesis of the retention of HONO that is subsequently oxidised to nitrate, resulting in an artefact in HNO_3 determination (Possanzini et al., 1983; Allegrini et al., 1987; Tang et al., 2015). Further corroboration is provided by the improved agreement between both methods (line of fit closer to the 1:1 line) when comparing the sum of HNO_3 and HONO (Figure 3). Agreement between the DELTA and ADS was within 19 % for SO_2 (mean DELTA = 1.75 µg m^{-3} *cf* mean ADS = 2.18 µg m^{-3}) and 4 % for HCl (mean DELTA = 0.40 µg m^{-3} *cf* mean ADS = 0.41 µg m^{-3}). Given the limited data available, it is not clear why SO_2 measured on the ADS is higher than the DELTA, since there was good agreement for HCl.

For the particle-phase components, NO_3^- measured by the DELTA method (mean = 2.59 µg NO_3^- m^{-3}) was on average 2-fold higher than the ADS method (mean = 1.32 µg NO_3^- m^{-3}), whereas SO_4^{2-} by the DELTA method was on average 23 % lower (DELTA = 2.10 *vs* ADS = 2.74 µg SO_4^{2-} m^{-3}) (Figure 3). NO_3^- and SO_4^{2-} are both present as fine mode (< 1 µm) NH_4NO_3 and $(NH_4)_2SO_4$ (Putaud et al., 2010). Some NO_3^- can also be present in the coarse mode (> 2.5 µm), likely as calcium nitrate ($Ca(NO_3)_2$) from a reaction between gas-phase HNO_3 (or its precursors) and soil dust particles (Putaud et al., 2010), while some of the SO_4^{2-} will be coarse mode sea salt SO_4^{2-} (see section 3.5). A particle size cut-off of 4.5 µm was estimated for the DELTA air inlet) (Tang et al., 2015), so the DELTA will also sample a small amount of coarse mode aerosols. An ion balance check of the ratio of µeq NH_4^+ to sum µeq ($NO_3^- + SO_4^{2-}$) yielded a near unity value, confirming that NO_3^- and SO_4^{2-} collected by the DELTA aerosol filter are mainly fine mode NH_4NO_3 and $(NH_4)_2SO_4$. In comparison, the ADS has a 2.5 µm cyclone in front of the aerosol filters to collect aerosols < 2.5 µm on the aerosol filters. NH_4^+ was unfortunately not analysed in these tests, which would have allowed a similar ion balance check. Na^+ and Cl^- concentrations on the DELTA were also on average 331% and 444 % higher than on the ADS and the ion balance check of the ratio of Na^+:Cl^- was unity for both methods. In the absence of analytical errors, loss of NO_3^-, Na^+ and Cl^- on the surface of the cyclone, coupled to a small fraction of the aerosols > 2.5 µm that is collected (but not analysed) in the cyclone, could partly account for the observed lower concentrations of the aerosol components. Since Ca^{2+} and Mg^{2+} concentrations by both methods were at or below detection limits, comparisons of these are not meaningful and have not been made.

3.1.2   Comparisons with filter pack measurements: HNO_3/NO_3^- and NH_3/NH_4^+

The EMEP network (www.emep.int) measures atmospheric concentrations and depositions of a wide range of pollutants at rural background sites across Europe (Aas, 2014; Tørseth et al., 2012). A daily filter pack method continues to be implemented at 39 sites across Europe for assessment of oxidised and reduced nitrogen species, with results reported as Total Inorganic

Nitrate (TIN: $HNO_3 + NO_3^-$) and Total Inorganic Ammonia (TIA: $NH_3 + NH_4^+$) (Colette et al., 2016; Torseth et al., 2012), as these are considered more reliable than reporting for the gas and aerosol components separately.

<INSERT Figure 4 HERE>

At the UK Eskdalemuir site (EMEP station code GB0002R; UKAIR ID UKA00130), a Scottish rural background site on the border between Scotland and England, daily filter pack measurements of TIN and TIA were made as part of the EMEP network from 1989 to 2000 (EMEP, 2017a). Following installation of the DELTA system in September 1999, both methods were operated in parallel for 14 months at Eskdalemuir, allowing a comparison to be made of TIN and TIA from both systems. Comparison results are shown in Figure 4 of parallel data from the AGANet (sum of HNO_3 and NO_3^-) and NAMN (sum of NH_3 and NH_4^+), demonstrating close agreement between the two independent measurements. The EMEP values shown are daily measurements of TIN and TIA averaged to corresponding monthly means for comparison with the DELTA data. For TIN, the regression between EMEP TIN and AGANet (sum of uncorrected $HNO_3 + NO_3^-$) is close to unity (slope = 0.984, R^2 = 0.94), which provided independent verification and support of the DELTA HNO_3 measurements at the start of the network. After applying a bias adjustment factor of 0.45 to the HNO_3 data (see Sect. 2.6), the AGANet values (sum of corrected HNO_3 + NO_3^-) are smaller than the EMEP TIN (slope = 0.835, R^2 = 0.95). It is possible however, that the filter pack method may also be subject to similar artefacts in HNO_3 determination due to co-collection of other oxidised nitrogen species (Tang et al., 2015).

3.1.3   Comparisons with bubbler and filter pack measurements: SO_2 and SO_4^{2-}

Independent measurements of SO_2 and SO_4^{2-} with a daily bubbler and filter pack method, respectively, are also available for comparison with the DELTA method at the Eskdalemuir site. Daily SO_2 data with a bubbler method (Hayman, 2005) from Dec-77 to Dec-01 and daily SO_4^{2-} data with an EMEP filter pack method from Dec-77 to Apr-09 (Hayman, 2006) were downloaded from the EMEP website (EMEP, 2017b). A close agreement is found between the bubbler and DELTA method for SO_2 (slope = 0.86, R^2 = 0.82), while there is more scatter between the filter pack and DELTA method for SO_4^{2-} (slope = 0.67, R^2 = 0.66) (Figure 5). Concentrations of SO_2 for the 26 month overlap period were comparable (mean of bubbler method = 0.40 µg S m^{-3} *cf* mean of DELTA method = 0.44 µg S m^{-3}), whereas the filter pack SO_4^{2-} concentration (mean = 0.44 µg S m^{-3}, n = 87) is larger than the corresponding monthly DELTA measurement (mean = 0.28 µg S m^{-3}, n = 87) (Figure 5). An earlier detailed assessment of the DELTA system against filter pack with a focus on SO_2 and SO_4^{2-} in 1999 by Hayman et al. (2006) had shown close agreement between the methods. It is therefore unclear why the DELTA gives a reading lower than the filter pack SO_4^{2-} at Eskdalemuir in this assessment, since the dataset was a continuation of the original inter-comparison. Possible explanations include uncertainties associated with limit of detection of the daily filter pack method at the very low concentrations encountered at this site, or the sampling of coarser particles by this method (due to high flow rate and open-

face sampling) with higher concentrations of sea salt sulphate. The DELTA methodology was unchanged for the duration of the AGANet dataset (1999 - 2015) in this manuscript, which allows a consistent assessment of overall trends in the SO_4^{2-} data.

\<INSERT Figure 5 HERE\>

3.2   AGANet data

Annual data from the AGANet (and also from the NAMN) are submitted to the Department for Environment, Food & Rural Affairs (Defra) UK-AIR database (https://uk-air.defra.gov.uk/), in a format consistent with other UK Authority air quality networks and relevant reporting requirements. Every concentration value is labelled with a validity flag and an EMEP flag

10   (see http://www.nilu.no/projects/ccc/flags/index.html). Ratified calendar year data are published from around June the year following collection. Currently, work is also in progress for the data to be made available from the EMEP database (http://ebas.nilu.no/). All data used in this paper (up to 2015), except where specified, are accessed from the UK-AIR website (Tang et al. 2017a, b).

15 **3.3   Uncertainties in HNO₃ determination**

HNO₃ data were corrected for sampling artefacts in the DELTA method with an empirical correction factor of 0.45 (see Sect. 2.6). Interferences in HNO₃ determination arise through the simultaneous collection of reactive oxidized nitrogen species on the K_2CO_3 coating that forms nitrate ions in the aqueous extracts of exposed denuders. Potential interfering species include HONO, NO_2, N_2O_5 and PAN, as well as other inorganic and organic nitrogen species. HONO is most likely to contribute to

20   the interference, since it is collected effectively on a carbonate coating and concentrations of HONO have been reported to be comparable to, and in some places exceed HNO₃ in the UK (e.g. Kitto & Harrison 1992; Connolly et al., 2016). Interference from NO_2 on the other hand should be small, since the reactivity of a carbonate coating surface towards NO_2 is low (Allegrini et al., 1987), with capture of NO_2 on carbonate ranging from 0.5 to 5 % (Allegrini et al., 1987; Fitz 2002) and their concentrations are also small at rural AGANet sites (< 10 µg NO_2 m^{-3}; Conolly et al., 2016). Tests by Steinle (2009) on the

25   DELTA K_2CO_3/glycerol coated denuders also confirmed low capture (*ca* 3 %) of NO_2.

The correction factor was derived from two years of field intercomparison measurements at five sites across a range of pollutant concentrations across the UK, from a clean rural background site in Southern Scotland (Auchencorth) to a polluted urban site (London Cromwell road) in Southern England (Tang et al., 2015). It is recognised that the correction factor to derive the "real

30   HNO₃" signal from the carbonate coated denuders will also be dependent on the relative concentrations of HNO₃ to interfering species present in the atmosphere and likely to be both site and season specific. The 2 years of data indeed show this variability between sites and between seasons. Given the complexities of atmospheric chemistry of the large family of oxidised nitrogen

species, further work is clearly needed to understand what the carbonate denuders is measuring, before an improved correction algorithm for the HNO$_3$ data can be developed with any confidence.

The empirical 0.45 HNO$_3$ is therefore at present a best estimate across a range of pollutant concentrations and seasons encountered in the UK, based on available test data from 5 sites. At the cleanest rural sites (e.g. Eskdalemuir), where a much smaller HONO and NO$_2$ interference of the DELTA HNO$_3$ signal is expected, the HNO$_3$ concentrations may be under-estimated after correction. This may partly explain the slope deviating from unity in the comparison of corrected DELTA TIN with EMEP filter pack TIN data (slope = 0.835, R^2 = 0.95) at Eskdalemuir (see Sect. 3.1.2). Conversely, at more polluted sites such as London that are affected by a larger interference from HONO and NO$_2$, the HNO$_3$ determination may be over-estimated after correction. Apart from two urban sites (London and Edinburgh), all other sites in the AGANet are rural, located away from traffic, and the 0.45 correction factor should be more representative.

Since January 2016, the DELTA denuder sample train configuration in AGANet was changed to two NaCl coated denuders (selective for HNO$_3$, e.g. Allegrini et al., 1987), with a third K$_2$CO$_3$/glycerol coated denuder to collect SO$_2$. At three sites (Auchencorth, Bush OTC and Stoke Ferry), parallel measurements of the old configuration (two K$_2$CO$_3$/glycerol coated denuders) and new configuration (two NaCl coated denuders + K$_2$CO$_3$/glycerol coated denuder) were conducted over 12 months in 2016. In the new configuration, nitrate measured on the NaCl denuders are reported as HNO$_3$, whereas nitrate on the K$_2$CO$_3$ denuder are assumed to come from other oxidised nitrogen species and are not reported. Comparing the sum of nitrate concentrations from the new (2xNaCl + 1xK$_2$CO$_3$) with the old (2xK$_2$CO$_3$) configurations indicated matching capture of total nitrate by the two parallel systems (new/old nitrate ratio = 0.95). A comparison of nitrate concentrations on the 2xNaCl denuders only (new configuration) with the 2xK$_2$CO$_3$ denuders (old configuration) yielded an average ratio of 0.42, lending further support to the 0.45 empirical factor. Additionally, the new sample train configuration is providing an extensive dataset which will allow the magnitude of HNO$_3$ interference at each site to be quantified, by comparing the amount of nitrate measured on the 2xNaCl and K$_2$CO$_3$ coated denuders. Initial analysis of 2016 data (unpublished data) showed that the mean ratio of nitrate on NaCl:K$_2$CO$_3$ of all sites was 0.44, ranging from 0.31 (Bush OTC) to 0.59 (Moorhouse). Seasonally, the average monthly ratio (taken as the mean across all sites for each month) was lowest in winter (0.25 in December and 0.27 in January) and highest between May to June (0.59, 0.56 and 0.57). It may therefore be possible to derive an improved correction algorithm that is both site and season specific, and work is ongoing to make this assessment. A detailed assessment of sampling artefacts and uncertainties in the DELTA method and the effects of a method change in the AGANet forms the subject of a next paper that is currently in preparation.

3.4 Spatial patterns in relation to pollutant sources and transport

In Figure 6, the spatial patterns for each of the gas and aerosol components measured are shown in the annual maps for the example year 2013. A gradient in the concentrations of acid gases HNO_3 and SO_2, and related aerosols NO_3^- and SO_4^{2-} can be seen across the UK, highest in the south and east (combustion/vehicular sources and long-range transboundary pollutant transport from Europe) and lowest in the north and west of the UK (fewer sources, furthest from influence of Europe). The ranges in site-annual mean concentrations (μg molecule m^{-3}) in 2013 for the gases were: HNO_3: 0.12 – 1.2; HCl: 0.15 - 0.52; SO_2: 0.10 – 1.08, while those for aerosol were: NO_3^-: 0.33 – 3.1; Cl^-: 0.54 – 3.3; SO_4^{2-}: 0.35 – 1.2; Na^+: 0.35 – 1.8; Ca^{2+}: <lod - 0.11; Mg^{2+}: 0.03 – 0.19.

The largest HNO_3 concentrations were measured at the London Cromwell site (2013 site annual mean = 1.3 μg HNO_3 m^{-3} *cf* 2013 mean of 30 sites = 0.40 μg HNO_3 m^{-3}). London and Edinburgh are the only two urban sites in the AGANet, with the other 28 sites all in rural environments. HNO_3 concentrations in Edinburgh, the capital of Scotland with a population that is 18 times smaller than London (0.5 million *vs* 8.8 million), is about 2 times lower than London, but larger than the national average (2013 annual mean = 0.58 μg HNO_3 m^{-3}). For SO_2, the highest concentrations were recorded at Sutton Bonington due to close proximity to the 2000 MW capacity coal-fired Ratcliffe-on-Soar power station (2 km North). A peak monthly concentration of 10.9 μg SO_2 m^{-3} was recorded in May 2000 at this site, with an annual mean concentrations of 5.9 μg SO_2 m^{-3} for that year that was also 3 times higher than the national average (mean of 12 sites = 1.9 SO_2 m^{-3} *cf*. mean of 11 sites (excl. Sutton Bonington = 1.5 SO_2 m^{-3}). At remote sites further away from sources, concentrations of HNO_3 and SO_2 are smaller, e.g. Lough Navar in Northern Ireland (2013 annual mean: 0.15 μg HNO_3 m^{-3} and 0.21 μg SO_2 m^{-3}) and Strathvaich Dam in northwest Scotland (2013 annual mean = 0.17 μg HNO_3 m^{-3} and 0.18 μg SO_2 m^{-3}). NO_3^- and SO_4^{2-} as secondary aerosols have longer residence times in the atmosphere and are expected to be more spatially homogeneous than their precursor gases. The spatial distribution in concentrations of particulate NO_3^- (0.33 – 3.1 μg m^{-3}) and SO_4^{2-} (0.35 – 1.2 μg m^{-3}) are however similar to that of HNO_3 (0.12 – 1.3 μg m^{-3}) and SO_2 (0.10 – 1.1 μg m^{-3}), with no clear differences in the main regional patterns from only 30 sites.

<INSERT Figure 6 HERE>

HCl are mostly emitted from coal combustion and the highest concentrations are in the source areas in the southeast and southwest, and also in central England (north of Ratcliffe-on-Soar power station). There is also a marine source for HCl formed by the reaction of sea salt with HNO_3 and H_2SO_4 (Roth and Okada 1998; Ianniello et al., 2011) that may contribute to additional enhancement of local to regional HCl concentrations. The spatial distributions of Cl^- and Na^+ were similar, with largest concentrations at the coastal sites Goonhilly in southwest England and Lerwick Shetland in the Shetland Isles, highlighting the importance of marine sources to the sea salt (NaCl) aerosol. Further away from the coast and influence of marine aerosol,

the smallest concentrations of Cl^- and Na^+ are measured in the west of the country (Lough Navar in Northern Ireland and Cwmystwyth in mid-Wales) and most of Scotland (with the exception of Shetland). Mg^{2+} is also seen to show a similar spatial distribution to Na^+ and Cl^-, which suggests that it may be in the form of $MgCl_2$, although the range of concentrations at sites are small (0.03 – 0.19 µg m^{-3}). There is however no clear spatial pattern for Ca^{2+}, but since concentrations are mostly at or below LOD, any assessment of this component is highly uncertain.

In the case of NH_3, the extensive spatial heterogeneity seen is related to large variation in emission sources at ground level across the UK (Tang et al., 2018). Aerosol NH_4^+, as expected for a secondary component, show a less variable concentration field. The spatial distribution of NH_4^+ is similar to SO_4^{2-} and NO_3^- over the UK (Figure 6), due to the close coupling between species from the formation of particle phase $(NH_4)_2SO_4$ and NH_4NO_3 (see next section).

3.5   Correlations between gas and aerosol species

Correlations plots between the gas and aerosol phases of the different components are shown in Figure 7, with a summary of the regression results provided in Table 2. The comparison of gas phase concentrations show that gaseous NH_3 is poorly correlated with either SO_2 or HNO_3, as might be expected since the emission sources of these pollutants are different. In the case of the acid gases however, the significant correlations between HNO_3:SO_2 ($R^2 = 0.35$), HNO_3:HCl ($R^2 = 0.25$) and SO_2:HCl ($R^2 = 0.21$) may be related to similarity in the regional distribution of their emissions. These comparisons show that there is on average 5 times more NH_3 than SO_2 and 13 times more NH_3 than HNO_3 at the AGANet sites (on a molar basis), and that SO_2 concentration is nearly 3 times larger than HNO_3 (on a molar basis).

<INSERT Figure 7 HERE>

<INSERT Table 2 HERE>

In the aerosol components, there is very high correlation between NO_3^-, SO_4^{2-} and NH_4^+, and between Na^+ and Cl^-, but no discernible relationship between NH_4^+ and Cl^- (Figure 7). The near 1:1 relationship in the scatter plot of the sum of NO_3^- and SO_4^{2-} (µeq m^{-3}) *versus* NH_4^+ (µeq m^{-3}) (slope = 0.91, $R^2 = 0.93$), in the absence of any correlation between NH_4^+ and Cl^-, suggests that H_2SO_4 and HNO_3 in the atmosphere are fully neutralised by NH_3 to form $(NH_4)_2SO_4$, NH_4HSO_4 and NH_4NO_3 (Aneja et al. 2001). For Cl^-, the high correlation with Na^+ (slope = 1.04, $R^2 = 0.8$) lends support that the Cl^- measured in the DELTA are derived mainly from sea salt (NaCl). Similar to the relative concentrations of gases, NH_4^+ concentrations (on a molar basis) are larger than SO_4^{2-} and NO_3^-, but NO_3^- is in molar excess over SO_4^{2-}. The correlations between NH_4^+ and sum ($NO_3^- + 2 \times SO_4^{2-}$) and for Na^+ and Cl^- forms the basis of ion balance checks in data quality assessment, as discussed in section 2.5 and shows that robust data are obtained .

Sea salt aerosol, derived from sea spray has essentially the same composition as seawater (Keene et al., 1986). The marine aerosol comprises two distinct aerosol types: (1) primary sea salt aerosol produced by the mechanical disruption of the ocean surface and (2) secondary aerosol, primarily in the form of non-sea salt (nss) sulphate and organic species, formed by gas-to-particle conversion processes such as binary homogeneous nucleation, heterogeneous nucleation and condensation (O'Dowd and Leeuw, 2007). It has been shown that the ratio of the mass concentrations of SO_4^{2-} and Cl^- to the reference Na^+ species in seawater may be used to estimate mass concentrations of non-sea salt SO_4^{2-} (nss_SO4) and non-sea salt Cl^- (nss_Cl) in aerosol, according to equations 4 and 5, respectively (Keene et al., 1986; O'Dowd and de Leeuw, 2007).

$[nss\_SO4] = [SO_4^{2-}] - (0.25 \times [Na^+])$ (4)

$[nss\_Cl] = [Cl^-] - (1.80 \times [Na^+])$ (5)

Applying Equation 4 to the SO_4^{2-} data in Figure 7, nss_SO4 is estimated to comprise on average 25 % (range = 3 – 83 %, n = 187) of the measured total SO_4^{2-} aerosol. Regression of nss_SO4 vs NH_4^+ (slope = 0.18, intercept = 0.47, R^2 = 0.71) (Supp. Figure S3) was not significantly different from the regression of total SO_4^{2-} vs NH_4^+ (slope = 0.18, intercept = 2.4, R^2 = 0.73) (Figure 7). Sources of nss_SO4 are (i) biological oxidation of dimethylsulphide and (ii) oxidation of SO_2 (O'Dowd and de Leeuw, 2007). This analysis demonstrates that sea salt SO_4^{2-} aerosol makes up a significant and variable fraction of the total SO_4^{2-} measured, consistent with observations of the contribution by sea salt SO_4^{2-} to the total SO_4^{2-} in precipitation in the UK (ROTAP 2012). The improved intercept from the nss_SO4 regression (Supp. Figure S3) suggests that nss_SO4 are mainly associated with NH_4^+.

Estimated nss_Cl concentrations according to Equation 4 was however negligible (mean = –0.09 µg m^{-3}, n = 188), compared to the total Cl^- (mean = 1.3 µg m^{-3}, n = 188). Studies have shown that part of the chloride of sea salt can be substituted by SO_4^{2-} and NO_3^- through a reaction with H_2SO_4 and HNO_3, known as the Cl^- deficit (Ayers et al., 1999). The close coupling between Cl^- and Na^+ (near 1:1 relationship) presented here suggests that the measured Cl^- in the aerosol are mostly sea salt in origin, with no evidence of depletion of Cl^- from sea salt aerosols.

3.6   Seasonal variation in acid gases and aerosols

The average seasonal cycles for all gas and aerosol components derived from the mean of monthly data of all sites for the period 2000 to 2015 are compared in Figure 8. Clear differences are observed in these seasonal cycles, influenced by local to regional emissions, climate, meteorology and photochemical processes.

<INSERT Figure 8 HERE>

HNO$_3$ is a secondary product of NO$_x$, but NO$_x$ emissions are dominated by vehicular sources which are not expected to show large seasonal variations. Seasonal changes in chemistry and meteorology are therefore more likely to be a source of the observed variations in HNO$_3$ and NO$_3^-$ (Figure 8). A weak seasonal cycle is observed in HNO$_3$, with slightly higher concentrations in late winter and early spring that may be attributed to photochemical processes with elevated ozone in spring (AQEG 2009) leading to formation of HNO$_3$ during this period (Pope et al., 2016).As discussed in section 3.3, a constant correction factor was applied to all HNO$_3$ data, which does not take into account seasonal dependency. The concentrations in HNO$_3$ may therefore be over-estimated in winter (less HNO$_3$ formed from photochemical processes) and under-estimated in summer (larger HNO$_3$ concentrations due to increased ·OH radicals for reaction with NO$_2$ to form HNO$_3$), masking the true extent in the seasonal profile.

In contrast, the seasonal cycle for particulate NO$_3^-$ is more distinct with a large peak in concentrations that occur every spring, together with a second smaller peak in autumn (Figure 8). NH$_3$, the main neutralising gas in the atmosphere that reacts with HNO$_3$ to form NH$_4$NO$_3$, has a correspondingly large peak in concentration in spring, a second smaller peak in autumn, but with elevated concentrations in summer and lowest in winter (Figure 8). Although particulate NO$_3^-$ formation is dependent upon the availability of NH$_3$ for reaction with HNO$_3$, its' concentration is also governed by the equilibrium that exists between gaseous HNO$_3$, NH$_3$ and particulate NH$_4$NO$_3$, the latter of which is appreciably volatile at ambient temperatures (Stelson and Seinfeld, 1982). Partitioning between the gas and aerosol phase is therefore also a key driver for their atmospheric residence times and concentrations. HNO$_3$ and NH$_3$ that are not removed by deposition may react together in the atmosphere to form NH$_4$NO$_3$ aerosol, when the concentration product [NH$_3$].[HNO$_3$] exceeds equilibrium values. Since NH$_4$NO$_3$ is semi-volatile, any that is not dry or wet deposited can potentially dissociate to release NH$_3$ and HNO$_3$, effectively increasing their residence times in the atmosphere. The formation and dissociation in turn are strongly influenced by ambient temperature and humidity.

Warm, dry conditions in summer promotes dissociation, increasing gas-phase HNO$_3$ relative to particulate-phase NH$_4$NO$_3$. This process accounts for the minima in NO$_3^-$ concentrations (Figure 8) and the highest ratio of HNO$_3$ to NO$_3^-$ seen in July (Figure 9). Cooler conditions in the spring and autumn sees a larger fraction of the volatile NH$_4$NO$_3$ remaining in the aerosol phase. The largest peak in NO$_3^-$ concentrations (Figure 8) and the lowest HNO$_3$:NO$_3^-$ ratio in spring-time (Figure 9) is thus a combination of increased NO$_3^-$ formation from reaction between higher concentrations of the precursor gases HNO$_3$ and NH$_3$, and increased partitioning to the aerosol phase in cooler, more humid climate. Import from long-range transboundary transport of particulate NO$_3^-$, e.g. from continental Europe into the UK, as discussed in Vieno et al. (2014, 2016) adds to the elevated NO$_3^-$ concentrations. In winter, low temperature and high humidity also shifts the equilibrium to formation of NH$_4$NO$_3$ from the gas-phase HNO$_3$ and NH$_3$. Since NH$_3$ concentrations are also lowest in winter, with less NH$_3$ available for reaction, NH$_4$NO$_3$ concentrations are correspondingly smaller in winter than in spring or autumn.

<INSERT Figure 9 HERE>

SO_2, by contrast, are highest in the winter, with concentrations exceeding summer values on average by a factor of 2 (Figure 8). Higher emissions of SO_2 from combustion processes (heating) during the winter months, coupled to stable atmospheric conditions resulting in build-up of concentrations at ground level contributes to the winter maximum. Since the reaction of SO_2 with NH_3 to form $(NH_4)_2SO_4$ is effectively irreversible (Bower et al., 1997), the ratio of the concentrations of SO_2 and SO_4^{2-} (Figure 9) is largely governed by the availability of SO_2 and NH_3 to form $(NH_4)_2SO_4$. The temporal profile of SO_4^{2-} has a peak in concentrations in spring, although not as pronounced as the NO_3^- peak (Figure 8). This may be attributed to enhanced formation of $(NH_4)_2SO_4$, since peaks in concentrations of NH_3 and NH_4^+ also occur in spring (Figure 8) and from the import of particulates from long-range transboundary transport. Unlike SO_2, aerosol SO_4^{2-} concentrations are higher in summer than in winter, due to increased photochemical oxidation of SO_2 to H_2SO_4 and subsequent formation of sulphate aerosols in sunnier and warmer conditions (Mihalopoulos et al., 2007). In winter, lower SO_2 oxidation rates limits H_2SO_4 formation and therefore also the formation of $(NH_4)_2SO_4$.

Na^+ and Cl^- also have highest concentrations during winter, highlighting the importance of marine sources (more stormy weather) in winter for sea salt aerosol. The seasonal trends in Mg^{2+} is similar to Na^+, with maxima during winter and minima in summer (Figure **8**). While seasalt aerosols comprise mainly of NaCl, other chemical ions are also common in seawater, such as K^+, Mg^{2+}, Ca^{2+} and SO_4^{2-} (Keene et al., 1986). Some of the sea salt aerosol may therefore be in the form of $MgCl_2$. Magnesium is however also a crustal element, and so it is not as good as sodium as a tracer for sea salt. Similarly, calcium is also a rock-derived element and its presence in the atmosphere is thought to come from chemical weathering of carbonate minerals (Schmitt & Stille, 2005). The seasonal cycle of Ca^{2+} is similar to, but less pronounced than Na^+ and Mg^{2+}. Measured concentrations of Ca^{2+} were mostly at or below the method LOD which makes interpretation uncertain, but the higher concentrations of Ca^{2+} in the winter months is likely to be both crustal dust and sea salt in origin.

<INSERT Figure 10 HERE>

Large inter- and intra-annual variability are also observed in the long-term mean monthly concentrations of gas and aerosol components, as illustrated in Figure 10. In 2003, elevated concentrations of HNO_3 and NO_3^- (and also NH_4^+) were observed between February to April that were more pronounced than the normal peak in concentrations that occur in Spring. The large spike in concentrations was of a sufficient magnitude to elevate the annual mean concentrations for 2003 of HNO_3 (0.54 µg m^{-3} cf 0.39 and 0.36 µg m^{-3} for 2002 and 2004, respectively), particulate NO_3^- (2.98 µg m^{-3} cf 1.99 and 1.93 µg m^{-3} for 2002 and 2004, respectively) and NH_4^+ (1.45 µg m^{-3} cf 1.06 and 0.97 µg m^{-3} for 2002 and 2004, respectively). In comparison, a much smaller spike in elevated SO_4^{2-} concentrations resulted in a slight increase in annual average SO_4^{2-} (1.79 µg m^{-3} cf 1.41 and 1.31 µg m^{-3} for 2002 and 2004, respectively) (Figure 10). Meteorological back trajectory analysis of the period showed air masses coming across the UK from Europe, and the pollution episode was attributed to the formation and transport of

NH$_4$NO$_3$ from Europe, since other gases (SO$_2$, HCl and NH$_3$) and particulate Cl$^-$ were not affected (Vieno et al., 2014). At the same time, stable atmospheric conditions due to a persistent high pressure system over the UK led to an accumulation of pollutant concentrations from both local and import sources. A similar pollution episode, but of shorter duration occurred in Spring 2014. At the time, the observed elevated PM was blamed on a Saharan dust plume, but which in fact was then shown to be from long-range transport of NH$_4$NO$_3$ (Vieno et al., 2016). Although the 2014 episode was not sufficiently large to be captured in the monthly AGANet data, it reaffirms the substantial contribution of long-range transport into the UK of NH$_4$NO$_3$, with precursor gas emissions from outside of the UK presenting a major driver (Vieno et al., 2016).

A second, but smaller pollutant episode that was captured by the AGANet occurred in September 2014, with elevated concentrations of SO$_2$, HNO$_3$, SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ that came from the Icelandic Holuhraun volcanic eruptions (Twigg et al., 2016). The elevated SO$_2$ concentration in September 2014 led to a modest increase in annual concentrations in SO$_2$ for 2014 (0.58 µg m^{-3}, *cf* annual mean = 0.54 and 0.27 µg m^{-3} for 2013 and 2015, respectively). For the other components (HNO$_3$, particulate SO$_4^2$, NO$_3^-$ and NH$_4^+$), the spikes in concentrations were smaller than for SO$_2$ and did not noticeably elevate their annual mean concentrations for that year. These pollution events together illustrate very clearly how short pollutant episodes can have a major influence on the measured annual concentrations in the UK, and that changes in meteorological conditions, coupled with long-range transboundary import can have a large effect on the UK concentration field.

3.7   Long-term trends at Eskdalemuir

At the Eskdalemuir rural background site, EMEP filter pack data in TIN (sum of HNO$_3$ and NO$_3^-$) and TIA (sum of NH$_3$ and NH$_4^+$) are available since 1989 (Sect.3.1.2). In Figure 11, the EMEP filter pack TIN and TIA time series (Apr-89 to Dec-00) is extended with AGANet (HNO$_3$ and NO$_3^-$) and NAMN (NH$_3$ and NH$_4^+$) DELTA data (Sep-99 to Dec-15), with an overalpping period of 14 months. The combined time series shows that the annual concentrations of TIN has halved in 26 years between 1990 to 2015, from 0.36 to 0.16 µg N m^{-3}, compared with a 3-fold reduction in NO$_x$ emissions (from 928 to 302 kt NO$_2$-N) (NAEI, 2018) over the same period. For TIA, the 52 % decrease between 1990 to 2015 (from 0.93 to 0.45 µg N m^{-3}) is larger than the corresponding 13 % reduction in NH$_3$ emissions (from 265 to 231 kt NH$_3$-N) (NAEI, 2018). Speciated NH$_3$ and NH$_4^+$ data from NAMN over the period 2000 – 2015 shows that the decrease in TIA is mainly driven by NH$_4^+$, which decreased by 59 % between 2000 (annual mean = 0.62 µg NH$_4^+$ m^{-3}) and 2015 (annual mean = 0.25 µg NH$_4^+$ m^{-3}), compared with no change in NH$_3$ (annual mean 0.32 µg NH$_3$ m^{-3} in 2000, unchanged in 2015). This is consistent with findings by Tang et al. (2018) that contrary to the reported decrease in UK NH$_3$ emissions, NH$_3$ concentrations at background sites (defined by 5 km grid average NH$_3$ emissions <1 kg N ha^{-1} y^{-1}) are showing an indicative increasing trend, while at the same time, a large downward trend in particulate NH$_4^+$ is observed. Together, the AGAnet and NAMN are thus providing an important long-term dataset that distinguishes between the gas and aerosol phase, allowing gas:aerosol phase interactions to be explored.

<INSERT Figure 11 HERE>

An extended time series illustrating the continued decline in SO_2 and SO_4^{2-} has also been constructed by combining historic SO_2 and SO_4^{2-} measurement data at the Eskdalemuir site going back to December 1977 (see Sect. 3.1.3) with AGANet SO_2 and SO_4^{2-} data (Sep-99 to Dec-15) (Figure 12). A substantial decline in SO_2 is observed, falling by 98 % from 4.5 µg S m^{-3} in 1978 to 0.07 µg S m^{-3} in 2015, in good agreement with similarly large reduction in UK SO_2 emissions over the same period of 95 % (from 2570 to 126 kt SO_2-S) (NAEI, 2018). The decrease in SO_4^{2-} is of a smaller magnitude, declining by 88 % from an annual mean concentration of 0.89 µg S m^{-3} in 1978 to 0.11 µg S m^{-3} in 2015, highlighting the non-linearity in relationship between the atmospheric gas and aerosol phase of sulphur at this background site.

<INSERT Figure 12 HERE>

3.8 Assessment of trends in relation to UK emissions

The long-term time series in annually averaged concentrations of the gas and aerosol components are compared in Figure 13a and Figure 13b, respectively. Since there was a change in the number of sites during the operation of the AGANet, annually averaged data from the original 12 sites for the period 2000 – 2015 (1999 data excluded since AGANet started in September 1999) and from the full network (30 sites) for the period 2006 – 2015 are plotted alongside each other for comparison. From 2006 – 2015, the decreasing trends for all gas and aerosol components from the expanded 30 sites are seen to be similar to those from the original 12 sites. The annual mean concentrations in gas and aerosol components derived from the expanded 30 sites (2006 – 2015) or from the original 12 sites over the same period are also in general comparable (Table 3). The exceptions are Na$^+$ and Cl$^-$ that have higher mean concentrations from the 30 sites than the original 12 sites (Table 3), due to the addition of two coastal sites (Shetland and Rum), with larger contribution from sea salt. Larger HNO_3 concentrations are due to two urban sites, London and Edinburgh (higher NO_x emissions from vehicular traffic). The addition of three sites in high NH_3 emission (agricultural) areas (Rosemaund in England, Narberth in Wales and Hillsborough in Northern Ireland) also elevated measured annual mean NH_3 concentrations. The comparisons here thus illustrates very clearly the need to consider the effect of site changes in a national network and the importance of maintaining consistency and site continuity for assessing long-term trends.

<INSERT Figure 13 HERE>

<INSERT Table 3 HERE>

In the gas phase, SO_2 decreased 7-fold from an annual mean concentration of 1.9 µg SO_2 m^{-3} in 2000 to 0.25 µg SO_2 m^{-3} in 2015 (*n* = 12), compared with more modest reductions in HNO_3 (from 0.35 to 0.21 µg HNO_3 m^{-3}), NH_3 (from 1.4 to 1.0 µg

NH_3 m^{-3}) and HCl (from 0.31 to 0.20 µg HCl m^{-3}) over the same period (Figure 13a). Particulate SO_4^{2-}, NO_3^- and NH_4^+ also decreased in concentrations with time, but unlike their gas phase precursors, the trends of these aerosol components track each other closely, differing only in the magnitude of concentrations (Figure 13b), illustrating very clearly the close coupling between these components. On the other hand, the absence of a trend in the particulate Cl$^-$ is likely to reflect the sea salt origin

5   of Cl$^-$ which is not expected to vary over time.

Important changes in the chemical climate is captured by the parallel monitoring of acid gases and aerosols in AGANet and of NH_3, NH_4^+ in NAMN. It is clear from the long-term data that there is substantial intra- (Figure 10) and inter-annual variability in the annual mean concentrations of both the gas and aerosol phases (Figure 13), in particular the spike in concentrations in

10   2003 (see Sect. 3.6) that buckles the trend. An interpretation of the direct relationship between emissions and concentrations in the atmosphere is therefore not straight forward, as the concentrations are also influenced by other factors such as variations in meteorological conditions and long-range transboundary import into the UK.

<INSERT Figure 14 HERE>

In Figure 14, the relative trends in UK NO_x, SO_2, HCl and NH_3 emissions (NAEI, 2018) are compared with the annually averaged gas and particulate concentrations measured in the AGANet and NAMN for (i) original 12 sites for the 16 year period from 2000 to 2015, (ii) original 12 sites for the 15 year period from 2001 to 2015 (because annual mean concentrations in 2000 for all components were smaller than in 2001 – 2006), and (iii) expanded 30 sites and also original 12 sites for the 10 year

20   period from 2006 to 2015. All data were normalised to zero for the start years in each of the comparison.

The long-term trends in HNO_3, SO_2, HCl and particulate NO_3^-, SO_4^{2-}, Cl$^-$, based on MK statistical trend analysis (Sect. 2.7) of annual mean measurement data are compared in Figure 15 and summarised in Table 4 for the two time series: i) the original 12 AGANet sites for the 16 year period from 2000 to 2015, and ii) the expanded 30 AGANet sites for the 10 year period from

25   2006 to 2015. This approach avoids introducing bias as a result of changes in the sites and ensures site continuity for the long-term trend assessment. NH_3 and NH_4^+ concentrations from the NAMN that were measured at the same time at the AGANet sites were included for comparison and to aid interpretation of the acid gas and aerosol data.

To quantify changes in measured concentrations over time, annual trends (e.g. µg HNO_3 m^{-3} y^{-1}) are estimated from the

30   regression results of the MK tests. This is considered to provide a more reliable estimate of trend than comparing measured annual concentrations at the beginning and end of the time series, which is subject to bias due to substantial variability in annual concentrations between years (Tang et al., 2018). Changes in measured concentrations over time (MK % median change) in the time series are estimated from the MK Sen's slope and intercept (Equation 6). MK annual trends and % median change are summarised in Figure 15 and Table 4.

$$\% \text{ median change } = 100 \cdot \frac{[Yi - Yo)}{Yo} \qquad (6)$$

where   (y_0) and (y_i) = estimated annual mean concentrations at the start and end of the selected time period, estimated from
the slope and intercept of the LR or MK tests.

Statistical trend analysis of monthly mean measurement data in the gas and aerosol components are also shown for comparison
in Supp. Figure S3 (mean monthly data of 12 sites for period 2000-2015) and Figure S4 (mean monthly data of 12 sites for
period 2006-2015). MK annual trends and % median change, based on the monthly data (Supp. Tables S7, S8) were similar to
the annual test results (Table 4). While not discussed further here, since assessment of long-term trends in this paper focusses

10   on trends in annual mean concentrations for comparison with trends in estimated annual emissions, the monthly plots serves
to illustrate the large intra-annual variability of concentrations in gases and aerosols.

<INSERT Figure 15 HERE>
<INSERT Table 4 HERE>

15   **3.8.1   Trends in HNO$_3$ and NO$_3^-$ *vs* NO$_x$ emissions**

The overall downward trends in HNO$_3$ and NO$_3^-$ are seen to be broadly consistent with the −49 % fall in estimated NO$_x$
emissions (NAEI, 2018) over the 16 year period between 2000 and 2015 (Figure 14). Reductions in combustion (power stations
and industrial) and vehicular sources (fitting of catalytic converters), coupled to tighter regulations are major contributory
factors to the decrease in UK NO$_x$ emissions. The rate of reduction however stagnated in the period 2009 and 2012

20   (improvement in emissions abatement offset by proportionate increase from diesel combustion and increase in vehicle
numbers), followed by a 16 % decrease between 2012 and 2015 due to the closure of a number of coal-fired power stations.

It is notable that the first 6 years (2000-2006) of HNO$_3$ and NO$_3^-$ annual data show substantial variability between years and
in particular is dominated by the large 2003 peak in concentrations (see Sect. 3.6). This highlights the sensitivity of the trend

25   assessment to the selection of a reference start for the time series, since the annual mean concentrations of both HNO$_3$ and
NO$_3^-$ in 2000 are in fact smaller than concentrations in the following 6 years. Re-analysis of the same annual data normalised
against 2001 instead of 2000 takes the relative trend lines for HNO$_3$ and NO$_3^-$ much closer to the relative trend line in NO$_x$
emissions. In the later period between 2006 and 2015, the relative trend lines in HNO$_3$ and NO$_3^-$ derived from the mean of
either 12 or 30 sites were not significantly different, and the relative trend lines in emission and concentrations followed each

30   other closely (Figure 14).

Results of MK tests showed that the reductions in annual HNO_3 concentrations are statistically significant for both time series (Figure 15; Table 4). The MK % median change in annual mean HNO_3 was -45 % (2000 – 2015, $n = 12$) and -36 % (2006 – 2015, $n = 30$), consistent with the -49 % and -40 % fall in estimated NO_x emissions over the corresponding periods (Table 5). The decrease in HNO_3 is accompanied by a larger decrease in particulate NO_3^- (2000 - 2015: MK = -52 % ($n = 12$), 2006 – 2015: MK = -43 % ($n = 30$)) (Table 4) and an indicative small increasing trend is observed in the ratio of HNO_3 to NO_3^- with time (Figure 16), hinting at an increased partitioning to the gas phase. Since HNO_3 is one of the major oxidation products of NO_x, through reaction with $OH^.$ or heterogeneous conversion of N_2O_5, it provides an important measure of the fraction of NO_x emissions that is oxidised and signals any long-term changes in the atmospheric processing timescales of NO_x over the country. NO_2 is measured at 24 rural sites across the UK in the UKEAP NO_2-net, with 11 sites co-located with the AGANet (Conolly et al., 2016). The long-term time series in the data also showed a matching decreasing trend in network averaged NO_2 concentrations with NO_x emissions between 2000 and 2015, with annual mean NO_2 concentrations across the network falling 2-fold to 4 µg NO_2 m^{-3} in 2015 (Conolly et al., 2016). Despite the uncertainty in corrected HNO_3 data (Sect. 3.3), the encouraging agreement between trends in HNO_3 and NO_2 concentrations and NO_x emissions lends support to a linear response in HNO_3 concentrations to reductions in NO_x emissions.

\<INSERT Figure 16 HERE\>

\<INSERT Table 5 HERE\>\>

3.8.2 Trends in SO_2 and SO_4^{2-} vs SO_2 emissions

Unlike NO_x, there has been a more significant decline in SO_2, both in emissions and measured concentrations during this period (Figure 14). Between 2000 and 2009, SO_2 emissions fell substantially by 66 % from 1286 to 432 kt SO_2. The reduction reflects mitigation measures introduced since the 1980s (fitting of flue gas desulphurisation to coal fired power stations) to control S pollution, reductions in energy production and manufacturing and the switch from coal to gas at the same time. Similar to trends in NO_x emission, the decreasing trend in SO_2 emissions plateaued between 2009 and 2012 and then decreased again by a further 45% between 2012 and 2015 following the closure of a number of coal-fired power stations, as well as conversion of some coal-fired stations to burn biomass.

Over the same period, the network annual mean concentration decreased from 1.9 µg SO_2 m^{-3} in 2000 to 0.25 µg SO_2 m^{-3} in 2015 (mean of 12 sites), continuing the long-term decline in SO_2 concentrations observed at the background Eskdalemuir site (Sect. 3.1.3) and across the UK (ROTAP 2012). The relative trends in SO_2 emissions and concentrations tracked each other closely for all the time periods considered and it is clear that these decreases are highly correlated (Figure 14). In the case of particulate SO_4^{2-} however, there is an apparent "gap" between emissions and concentrations in the trend normalised against the year 2000. Like NO_3^-, re-analysis of the same annual data normalised against 2001 instead of 2000 takes the relative trend

line for SO_4^{2-} closer to the trend lines in both SO_2 emissions and concentrations (Figure 14), thus again highlighting the potential bias in the use of a measured value at a specific time point in trend assessments when there is substantial inter-annual variability in the data.

5 From the MK trend analysis, the decrease in annual mean SO_2 concentrations of –81 % (2000–2015, $n = 12$), and –60 % (2006 – 2015, $n = 30$) (Figure 15, Table 4) are consistent with the substantial reduction of –80 % and –64 % in SO_2 emissions over the two overlapping periods, respectively (Table 5). The decrease in both emissions and concentrations SO_2 is also almost twice as large as HNO_3 (Table 5), illustrating the greater success in mitigating sulphur than nitrogen and the increasing dominance of N components in the atmosphere compared with S, with larger decline in SO_2 than NO_x.

At the same time, the reduction in SO_2 emission and measured concentration is accompanied by a smaller negative trend in particulate SO_4^{2-} (2000-2015: –69 % MK; 2006-2015: –54 % MK) (Table 5), with concentrations falling 3-fold from an annual mean of 1.2 µg SO_4^{2-} m^{-3} in 2000 to 0.42 µg SO_4^{2-} m^{-3} in 2015. The smaller decrease in particulate SO_4^{2-} compared with its gaseous precursor, SO_2, is similar to that observed at Eskdalemuir (Sect. 3.1.3). A similar picture is also seen in Europe, where

15 atmospheric concentrations of gas phase SO_2 decreased by about 92 % compared with a smaller reduction of 65 % in particulate SO_4^{2-} in response to sulphur emissions abatement over the 1990-2012 period in the EMEP region (EMEP 2016). The ratio of SO_2:SO_4^{2-} is also seen to show a decreasing trend over time (Figure 16), with the largest change occurring between 2000 and 2006 that matches the period of largest decline in SO_2 emissions.

20 Sea salt SO_4^{2-} (ss_SO4) aerosol, as discussed in section 3.5, makes up a significant fraction of the total SO_4^{2-}. It is possible that the smaller reduction in particulate SO_4^{2-}, compared with SO_2, may be explained by an underlying increase in the relative proportion of ss_SO4 to total SO_4^{2-}. To assess the contribution of ss_SO4 to the observed trends in total SO_4^{2-}, ss_SO4 concentrations (estimated according Equation 4 described in Sect. 3.5) and nss_SO4$^-$ (= total SO_4^{2-} – ss_SO4) are compared with the long-term trends in total SO_4^{2-} in Figure 17. Overall, there is no apparent trend in the long-term annual mean ss_SO4

25 data, with concentrations in range of 0.16 to 0.21 µg SO_4^{2-}. Since ss_SO4 is derived from an empirical relationship with Na^+ (Sect. 3.5), the long-term trend data for Na^+ is also included in the analysis (Figure 17). Similar to ss_SO4, there is no overall trend in the Na^+ data, with small inter-annual variability and annual mean concentrations in the range of 0.65 – 0.85 µg Na^+ m^{-3}. ss_SO4 made up just 10% of the total SO_4^{2-} in 2000, but by 2015, this had increased to just over 50% due to the decrease in nss_SO4 over that time. MK analysis of the nss_SO4 (Table 4) showed decrease in concentrations of –78 % (2000-2015)

30 and –62% (2006-2015), similar to that observed in SO_2 (–81 %: 2000 –2015 and –60 %: 2006 – 2015), indicating a closer relationship between nss_SO4 and SO_2 than between total SO_4^{2-} and SO_2.

<INSERT Figure 17 HERE>

3.8.3   Trends in HCl and Cl⁻ vs HCl emissions

HCl emissions in the UK also decreased substantially by 89 % between 2000 and 2015, from 82 kt to 9 kt in 2015 (NAEI 2018), contrasting with a smaller, but non-significant decreasing trend in HCl concentrations (Figure 14, Figure 15, Table 5). The annual mean monitored concentrations in HCl over this period decreased from 0.30 µg HCl m^{-3} in 2000 to 0.19 µg HCl m^{-3} in 2015. Most of the reduction in HCl emissions occurred before 2006 (−79%, from 82kt in 2000 to 17kt in 2006), with emissions plateauing since 2006 (NAEI, 2018) (Figure 14). A corresponding decrease is not seen in the HCl measurement data, where concentrations remained fairly stable at between 0.31 µg m^{-3} HCl in 2000 to 0.33 µg m^{-3} HCl in 2006. Since 2006 however, the relative change in HCl emissions is closely tracked by changes in concentrations of both the annual mean data from the original 12 sites and from the expanded 30 sites in the AGANet, with the small peak in HCl emissions in 2013 also captured in the annual mean data. This part of the time series therefore clearly shows a direct relationship between emissions and concentrations.

So why is the most significant fall in HCl emissions between 2000 and 2006 not captured by the network? HCl are mainly released as point sources. Coal burning, particularly from coal-fired power stations, is responsible for the majority of UK emissions: 92 % in 1990 and 76 % in 2015 and reductions in HCl emissions in the UK inventory is largely as a result of declining coal use and the installation of emissions abatement measures at coal-fired power stations (implemented since 1993) aimed at reducing S that also coincidentally reduced HCl emissions. It may be that a network of only 12 sites in the early periods failed to capture peak emissions and changes in source areas. While there is an indicative, but non-significant decreasing trend in HCl (2000-2015: MK = –28 %, 2006–2015: MK = –24 %), no detectable trend in particulate Cl⁻ can be seen (Table 4). Since Cl⁻ is mainly associated with Na⁺ (seasalt) in the AGANet measurements (Sect. 3.5), the absence of a trend in Cl⁻ (Figure 15) and Na⁺ (Sect. 3.8.2, Figure 17) provides evidence of a constant background in seasalt in the UK atmosphere.

3.8.4   Trends in NH₃ and NH₄⁺⁻ vs NH₃ emissions

In comparison to the acid gases, there is a more modest decrease of −9 % in NH$_3$ emissions, from 254 kt NH$_3$ in 2000 to 231 kt NH$_3$ in 2015 (NAEI, 2018). This is smaller than the decrease seen in the annually averaged NH$_3$ concentrations at the 12 AGANet sites (2000-2015: –30 % MK) over the same period (Figure 14, Figure 15, Table 5). A recent assessment by Tang et al. (2018) showed that NH$_3$ trends are highly dependent on site selection and categorisation of sites in the analysis. A more comprehensive analysis of a larger number of sites shows smaller reductions over time, whereas a significant decreasing trend in NH$_3$ concentrations was observed in the grouped analysis of sites in areas classed as dominated by pig and poultry emissions, contrasting with an upward (non-significant) trend for sites in cattle-dominated areas. Therefore there is a large degree of

uncertainty in interpreting the trends in NH_3 concentrations from a subset of just 12 sites, since NH_3 emissions are dominated by agricultural emissions (> 80%) that vary hugely on a local to regional scale across the UK.

At the same time, there is a larger decrease in particulate NH_4^+ concentrations (–62 % MK), contrasting with the smaller decrease in NH_3 concentrations over the period 2010–2015 (–30 % MK) (Table 4), with the NH_3:NH_4^+ ratio also increasing with time (Figure 16). This provides evidence for a shift in partitioning from the particulate phase NH_4^+ to the gaseous phase NH_3 in the UK data, discussed in Tang et al. (2018). The change in partitioning from particulate NH_4^+ to gaseous NH_3 is also occurring in other parts of Europe, where decreases in NH_3 concentrations have been smaller than emission trends would suggest, due to large decreases in SO_2 emissions (Bleeker et al., 2009; Horvath et al., 2009).

3.8.5   Changes in UK chemical climate

Atmospheric SO_2 concentrations in the UK has declined to very low levels over the 16 years of measurements in AGANet, with annual mean concentrations in 2015 (0.25 µg SO_2 m^{-3}, $n = 12$) approaching that of the other acid gases HNO_3 (0.21 µg HNO_3 m^{-3}, $n = 12$) and HCl (0.20 µg HCl m^{-3}, $n = 12$). NH_3 measured at the same time at the AGANet sites also decreased, but to a smaller extent, to a mean concentration of 1.0 µg NH_3 m^{-3} ($n = 12$) in 2015. The changes in measured concentrations of SO_2, HNO_3, HCl and NH_3 are consistent with the estimated decrease in emissions of SO_2, NO_x, HCl and NH_3 since 2000. SO_2 is therefore no longer the dominant acid gas, with HNO_3 and HCl together contributing a larger fraction of the total acidity in the UK atmosphere.

Past studies have shown that the increasing ratio of NH_3 to SO_2 in the atmosphere leads to increased dry deposition of SO_2, accelerating the decrease in atmospheric SO_2 concentrations than would be achieved by emissions reduction alone (Fowler et al., 2001, 2009; ROTAP 2012). The dry deposition of SO_2 and NH_3, by uptake of the gases in a liquid film on leave surfaces, are known to be enhanced when both gases are present in a process termed "co-deposition" (Fowler et al., 2001). Where ambient NH_3 concentrations exceed that of SO_2, there is enough NH_3 to neutralize acidity in the liquid film and oxidise deposited SO_2, and maintain large rates of deposition of SO_2. With changes in the relative concentrations of acid gases in the UK and across Europe however, the deposition rates will increasingly be controlled by the NH_3/combined acidity (sum of SO_2, HNO_3 and HCl) molar ratio, rather than based on SO_2 alone (Fowler et al., 2009).

<INSERT Figure 18 HERE>

To look at the UK situation, an analysis of the molar ratios of NH_3 to acid gases is presented in Figure 18a. The molar ratio of NH_3 to acid gases (sum of SO_2, HNO_3 and HCl) increased with time, from 1.9 in 2000 to 4.7 in 2015, confirming that NH_3 is increasingly in molar excess over atmospheric acidity. The ratio of annual mean concentrations of NH_3 (80 nmol m^{-3}) to SO_2

(29 nmol m^{-3}) was 2.7 in 2000. By 2015, this ratio had increased to 15 (annual mean concentrations of NH$_3$ = 58 nmol m^{-3} *cf* SO$_2$ = 4 nmol m^{-3}). Molar concentrations of HNO$_3$ (4 nmol m^{-3}) and HCl (6 nmol m^{-3}) were comparable to SO$_2$ in 2015, highlighting the increasing importance of HNO$_3$ and HCl in contributing to atmospheric acidity. A larger decrease in SO$_2$ (−81 %) than particulate sulphate (−69 %) in the AGANet data (Table 4) would appear at first to suggest that the large NH$_3$:SO$_2$ ratio is contributing to a more rapid decrease in SO$_2$ concentrations. However, when the seasalt fraction of SO$_4^{2-}$ is removed from the sulphate trend (Sect. 3.8.2), the decrease in NSS_SO4 (−78%) is similar to SO$_2$ (−81%) (Table 4). Since the decreasing trend in the ratio of SO$_2$ to SO$_4^{2-}$ also appeared to stabilise after 2006 (Sect. 3.8.2), this would suggest that maximum deposition rates for SO$_2$ may have been reached with the smaller SO$_2$ concentrations since 2006.

The substantial decrease in UK SO$_2$ emissions and concentrations, while UK NO$_x$ emissions and concentrations remain relatively high in comparison, set against a much smaller decrease in NH$_3$ emissions and concentrations since 2000 is leading to changes in the respective particulate SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ concentrations. Since the affinity of H$_2$SO$_4$ (oxidation product of SO$_2$) for NH$_3$ is much larger than that of HNO3 and HCl, available NH$_3$ is first taken up by H$_2$SO$_4$ to form ammonium sulphate compounds (NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$), with any excess NH$_3$ then available to react with HNO$_3$ and HCl to form NH$_4$NO$_3$ and NH$_4$Cl. Analysis of the different particulate components in section 3.5 showed that the ammonium aerosols are mainly made up of (NH4)2SO4 and NH$_4$NO$_3$. With the large reduction in SO$_2$, more NH$_3$ is available to react with HNO$_3$ to form NH$_4$NO$_3$ and concentrations of NH$_4^+$ and NO$_3^-$ are now observed to be in molar excess over SO$_4^{2-}$, providing evidence of a change in the particulate phase from (NH$_4$)$_2$SO$_4$ to NH$_4$NO$_3$ (Figure 18b).

A change to an NH$_4$NO$_3$ rich atmosphere and the potential for NH$_4$NO$_3$ to release NH$_3$ and HNO$_3$ in warm weather, together with the surfeit of NH$_3$ also means that a larger fraction of the reduced and oxidised N is remaining in the gas phase as NH$_3$ and HNO$_3$. An increased partitioning to the gas phase may account for the larger decrease in particulate NH$_4^+$ (MK −62% between 2000-2015, n = 12) and NO$_3^-$ (MK −52% between 2000-2015, n = 12) than NH$_3$ (MK −30% between 2000-2015, n = 12) and HNO$_3$ (MK −45 % between 2000-2015, n = 12) (Table 4) and the increase in gas to aerosol ratios (NH$_3$:NH$_4^+$ and HNO$_3$:NO$_3^-$) over the 16 year period (Figure 16). A higher concentration of the gas-phase NH$_3$ and HNO$_3$ may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in NH$_3$ and NO$_x$. Given the larger deposition velocities of NH$_3$ and HNO$_3$ compared to aerosols, more of the NH$_3$ and HNO$_3$ emitted will have the potential to deposit more locally with a smaller footprint within the UK.

Currently, the critical loads of acidity (sulphur and nitrogen) are exceeded by 44 % of the area of sensitive habitats in the UK (based on mean deposition data for 2012-2014), whereas the figure for exceedance of eutrophication (nutrient nitrogen) is even larger, at 62 % (based on deposition data for 2012 – 2014) (Hall & Smith, 2016). Air quality policies have been very successful in abating SO$_2$ emissions (–80 %: 2000 – 2015) and moderately successful with NO$_x$ emissions (–58 %: 2000 – 2015), with both on course to meet the emission reduction targets set out under the 2012 Gothenburg protocol and 2016 NECD. Difficulties

in abating NH_3 is reflected in the smaller reduction in NH_3 emissions (–9 %: 2000 – 2015), with emissions increasing, rather than decreasing since 2013 and it is likely that abatement measures may be required to meet emission reduction targets. In recognising the need to tackle the ammonia problem, the Code of Good Agricultural Practice (COGAP) was published under the UK government's Clean Air Strategy (launched in July 2018) as a step towards reducing NH_3 emissions from agriculture.

Based on the current emission trends and evidence from AGANet and NAMN long-term measurements, atmospheric N deposition from oxidised N (NO_x, HNO_3 and NO_3^-) and from reduced N (NH_3, NH_4^+) are likely to continue to exceed critical loads of N deposition over large areas of sensitive habitats, with implications for UK's commitment to maintain or restore natural habitats (e.g. Natura 2000 sites; Hallsworth et al., 2010) to a favourable conservation status under the EU Habitats

10 Directive (Council Directive 92/43/EEC) and ecosystem monitoring under Article 9 and Annex V of Directive 2016/2284 (NECD). The changes are also relevant for human health effects assessments, since NH_4NO_3 and $(NH_4)_2SO_4$ are mainly in the fine mode and constitute a significant fraction of $PM_{2.5}$ that are associated with acute and chronic human health problems. The change in partitioning from $(NH_4)_2SO_4$ to NH_4NO_3, coupled to import of NH_4NO_3 from long-range transport (driven by emissions of NH_3 and NO_x from outside the UK) poses policy challenges in protection of human health from effects of air

15 pollution, particularly in urban areas where concentrations of the $PM_{2.5}$ precursor gases NO_x, SO_2 and NH_3 are higher.

4   Conclusions

The UK Acid Gases and Aerosol network (AGANet) is delivering, uniquely, a comprehensive UK long-term dataset of speciated acid gases (HNO_3, SO_2, HCl) and aerosol components (NO_3^-, SO_4^{2-}, Cl^-, Na^+, Ca^{2+}, Mg^{2+}) and also of NH_3 and NH_4^+

20 measured within the National Ammonia Monitoring Network (NAMN). Speciated measurements are made with an established low-cost DELTA denuder-filter pack methodology, allowing assessment of atmospheric chemical composition and gas-aerosol phase interactions. Other manual denuder-filter implementations designed for high time-resolution measurements are useful at selected locations for detailed analysis and model testing, but they are resource intensive and expensive. The DELTA monthly measurements on the other hand are cost-efficient for estimating annual mean concentrations, providing sufficient

25 resolution for analysis of temporal trends and which can be operated at a large number of sites in the network to provide long-term trends and temporal/spatial patterns.

Large regional patterns in concentrations are observed, with the largest concentrations of HNO_3, SO_2, and aerosol NO_3^- and SO_4^{2-} in south and east England, attributed to anthropogenic (combustion, vehicular) and long-range transboundary sources

30 from Europe, and smallest in western Scotland and Northern Ireland. HCl concentrations are also largest in the southeast, southwest and central England, attributed to dual contribution from anthropogenic (coal combustion) and marine sources

(reaction of sea salt with HNO_3 and H_2SO_4 to form HCl). For Cl^-, this has a similar spatial distribution as Na^+, with highest concentrations of at coastal sites, reflecting their origin from marine sources (sea salt).

Distinctive temporal trends are established for the different components, with the seasonal variability influenced by local to regional emissions, climate, meteorology and photochemistry. A weak seasonal cycle is observed in HNO_3, with slightly higher concentrations in late winter and early spring, due to formation from photochemical production processes. Particulate NO_3^- and SO_4^{2-} have highest concentrations in spring, coinciding with the peak in concentrations of NH_3 and NH_4^+, and are therefore likely to be attributed to formation of NH_4NO_3 and $(NH_4)_2SO_4$ from reaction with a surplus of higher concentrations of NH_3 at that time of year. Conversely, peak concentrations of SO_2, Na^+ and Cl^- occur during winter, likely from combustion processes (heating) for SO_2 and marine sources in winter (more stormy weather) for sea salt generation. Magnesium is a crustal elements, but which is also present in sea salt aerosols. The seasonal trend in Mg^{2+} is similar to Na^+, with maxima during winter and minima in summer; therefore some of the sea salt aerosol may be in the form of $MgCl_2$.

Enhancement of local to regional concentrations of reactive gases and aerosols in the UK from long-range transboundary transport of pollutants into the UK is highlighted by two pollution events, captured in the long-term AGANet monthly measurements. In 2003, a spring episode with elevated concentrations of HNO_3 and NO_3^- was driven by meteorology, with easterly winds transporting NH_4NO_3 formed in Europe into the UK and a high pressure system over the UK (Feb-April) that led to a build-up of NH_4NO_3 and HNO_3 concentrations from both local and transboundary sources. A second, but smaller episode of elevated concentrations of SO_2 and HNO_3, as well as of particulate SO_4^2, NO_3^- and NH_4^+, in September 2014 was shown to be from transport of pollutant plume from the Icelandic Holuhraun volcanic eruptions at that time.

After more than 16 years of operation, the AGANet is also capturing important long-term changes in the concentrations and partitioning between gas and aerosol of the N and S components in the atmosphere. A significant decrease of –81 % (MK) in annual mean concentrations of SO_2 between 2000 and 2015 was in agreement with the estimated –80 % reduction in SO_2 emissions, but larger than the accompanying decline in particulate SO_4^{2-} (–69 % MK). A more modest reduction in HNO_3 (–45 % MK) and particulate NO_3^- (–52 % MK) are consistent with the estimated 58 % decline in NO_x emissions over this same period. The decrease in particulate NH_4^+ (–62 % MK) is larger than the precursor gas NH_3 (2000 – 2015 = –30 % MK / LR) and larger than the estimated decline in estimated NH_3 emissions of 9 %. However, it should be noted that NH_3 trends are highly dependent on site selection according to an earlier assessment made on a more comprehensive dataset from the UK NAMN.

The substantial decrease in UK SO_2 emissions and concentrations, while UK NO_x emissions and concentrations (HNO_3) remain relatively high in comparison, set against a much smaller decrease in NH_3 emissions and concentrations since 2000 is leaving more NH_3 available to react with HNO_3 to form the semi-volatile particulate NH_4NO_3. Particulate NH_4^+ and NO_3^- are now in

molar excess over SO_4^{2-}, providing evidence of a shift in the particulate phase from $(NH_4)_2SO_4$ to NH_4NO_3. A change to an NH_4NO_3 rich atmosphere and the potential for NH_4NO_3 to release NH_3 and HNO_3 in warm weather, together with the surfeit of NH_3 also means that a larger fraction of the reduced and oxidised N is remaining in the gas phase as NH_3 and HNO_3. The change in partitioning from particulate NH_4^+ to gaseous NH_3 is also occurring in other parts of Europe, where decreases in NH_3 concentrations have been smaller then emission trends would suggest, due to successful mitigation in SO_2 emissions. Higher concentrations of the NH_3 and HNO_3 in the atmosphere will deposit more locally, exacerbating the effects of local N deposition loads over large areas of sensitive habitats, with implications for UK's commitment to maintain or restore natural habitats (e.g. Natura 2000 sites) to a favourable conservation status under the EU Habitats Directive (Council Directive 92/43/EEC). The changes are also important in terms of human effects assessment since NH_4NO_3 constitute a significant fraction of $PM_{2.5}$ that are implicated in acute and chronic human health effects and linked to increased mortality from respiratory and cardiopulmonary diseases.

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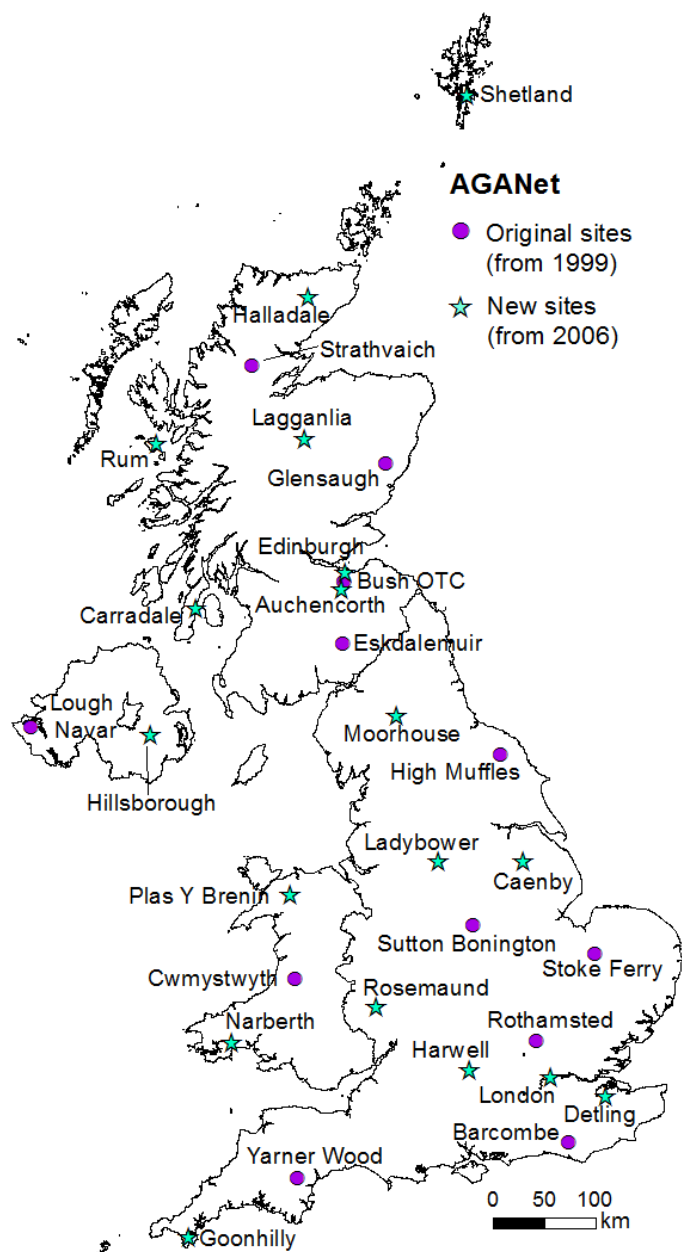
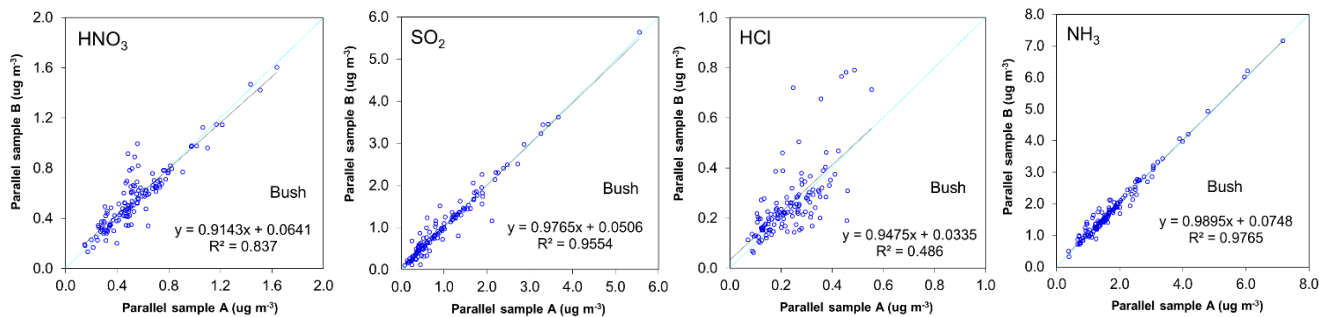
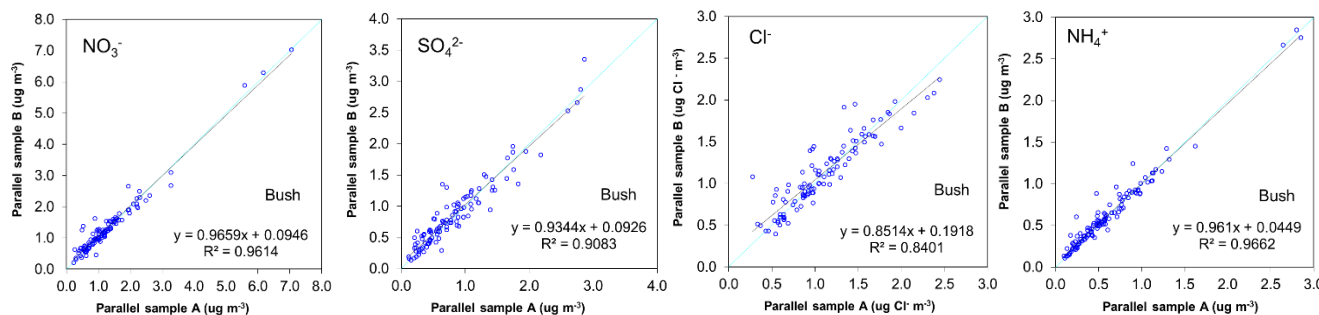
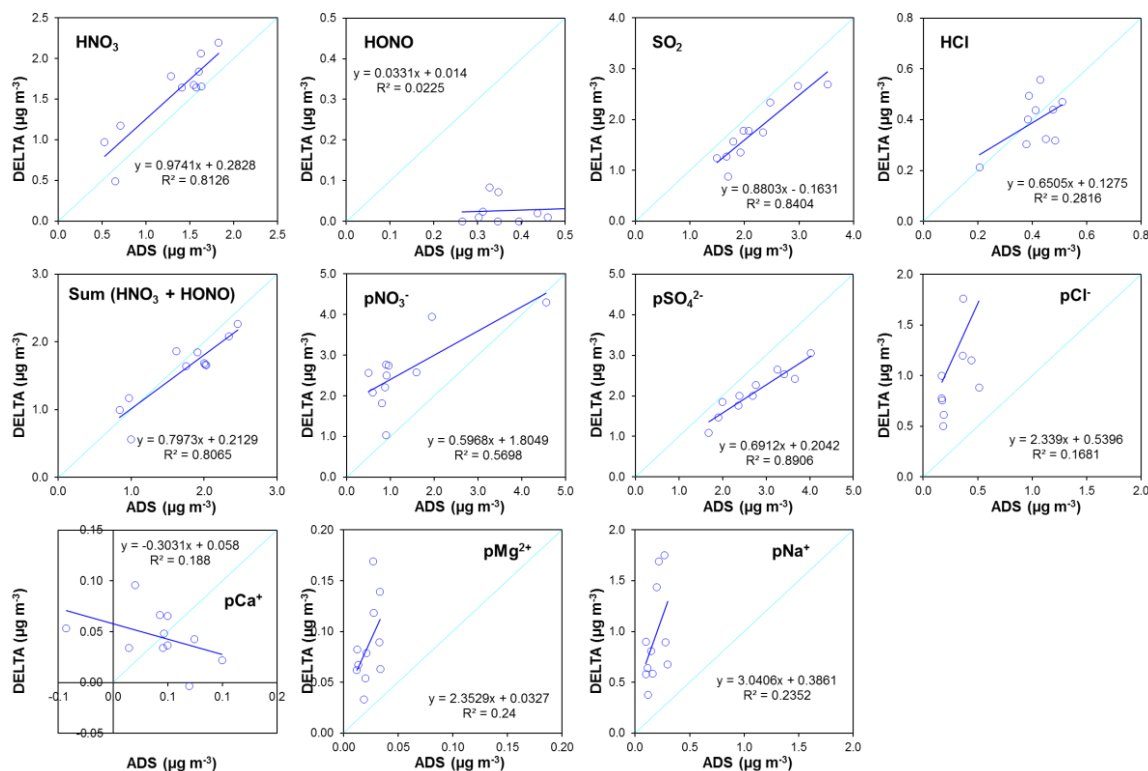


Figure 1: Site map of the UK Acid Gases and Aerosol Network (AGANet). The AGANet was established in September 1999 with 12 sites and expanded to 30 sites from January 2006 to improve national coverage. These sites also provide measurements of NH_3 and NH_4^+ for the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018).

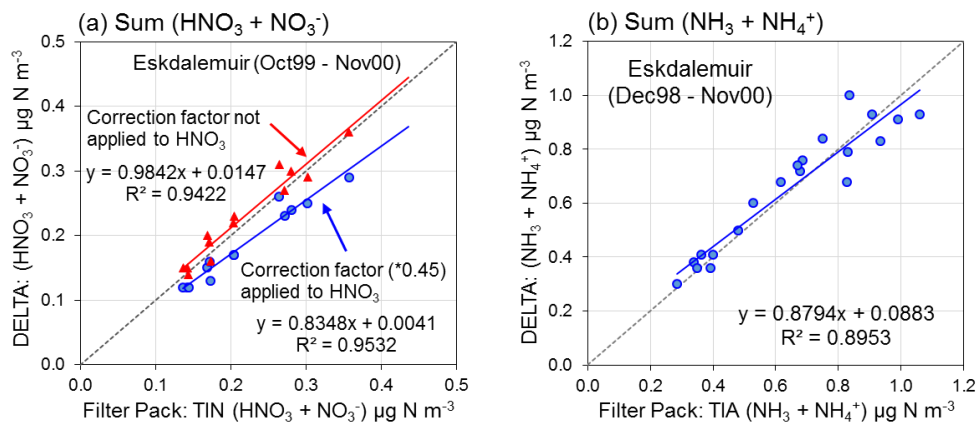
(a) Gases (HNO₃, SO₂, HCl, NH₃)

(b) Particulate (NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺)

(c) Summary of regression analysis

	Gases				Particulates			
	HNO₃	SO₂	HCl	NH₃	NO₃⁻	SO₄²⁻	Cl⁻	NH₄⁺
R^2	0.837***	0.955***	0.486***	0.976***	0.961***	0.908***	0.840***	0.966***
slope	0.914*	0.976^{ns}	0.947^{ns}	0.989^{ns}	0.966 ^{ns}	0.934*	0.851***	0.961*
intercept	0.064**	0.051*	0.033^{ns}	0.075**	0.095**	0.093**	0.192***	0.045***
No. observations (n)	130	130	128	140	108	108	104	119
mean A (µg m⁻³)	0.54	1.02	0.23	1.75	1.29	0.84	1.09	0.61
mean B (µg m⁻³)	0.56	1.05	0.25	1.80	1.34	0.87	1.12	0.63

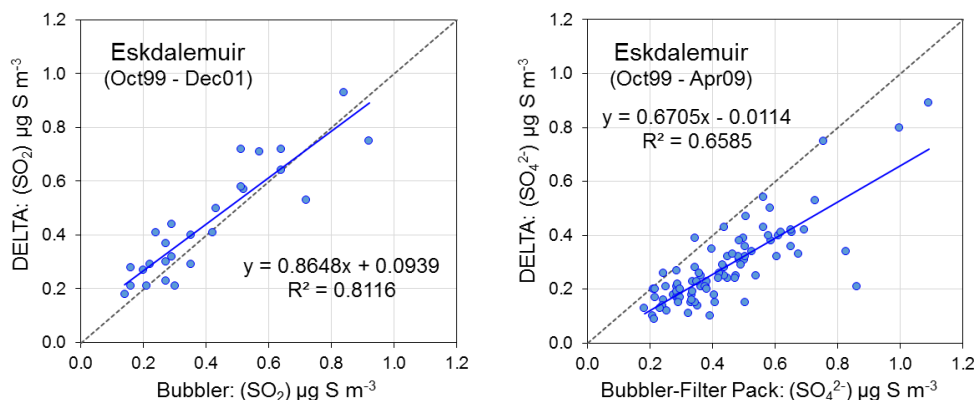
Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. ns = not significant ($p > 0.05$)

Figure 2: Comparisons of parallel measurement of monthly (a) atmospheric reactive gases (HNO₃, SO₂, HCl and NH₃) and (b) particulate (NO₃⁻, SO₄²⁻, Cl⁻ and NH₄⁺) concentrations from duplicate DELTA sampling at the UK Acid Gas and Aerosol Monitoring Network (AGANet) and National Ammonia Monitoring Network (NAMN) site Bush OTC (UKA00128) in Southern Scotland for the period 1999 to2015. (c) A summary of the regression analyses. Each point represents a comparison between the paired monthly DELTA measurements.

	Gases					Particulates					
	HNO₃	(HNO3+HONO)	HONO	SO₂	HCl	NO₃⁻	SO₄²⁻	Cl⁻	Na⁺	Ca²⁺	Mg²⁺
Linear regression: R^2	0.813***	0.806***	0.022^{ns}	0.840***	0.282^{ns}	0.570**	0.891***	0.168^{ns}	0.813***	0.188^{ns}	0.24^{ns}
slope	0.974^{ns}	0.797^{ns}	0.033***	0.880^{ns}	0.650^{ns}	0.570*	0.691**	2.339^{ns}	0.974^{ns}	-0.303	2.353
intercept	0.283^{ns}		0.014^{ns}	-0.163^{ns}	0.127^{ns}	1.809***	0.204^{ns}	0.540^{ns}	0.283^{ns}	0.058***	0.033^{ns}
Observations: n	11	11	11	11	10	11	11	11	11	11	11
mean DELTA (µg m⁻³)	1.56	1.58	0.03	1.75	0.40	2.59	2.10	1.24	1.56	0.05	0.09
mean ADS (µg m⁻³)	1.31	1.72	0.41	2.18	0.41	1.32	2.74	0.30	1.31	0.04	0.02

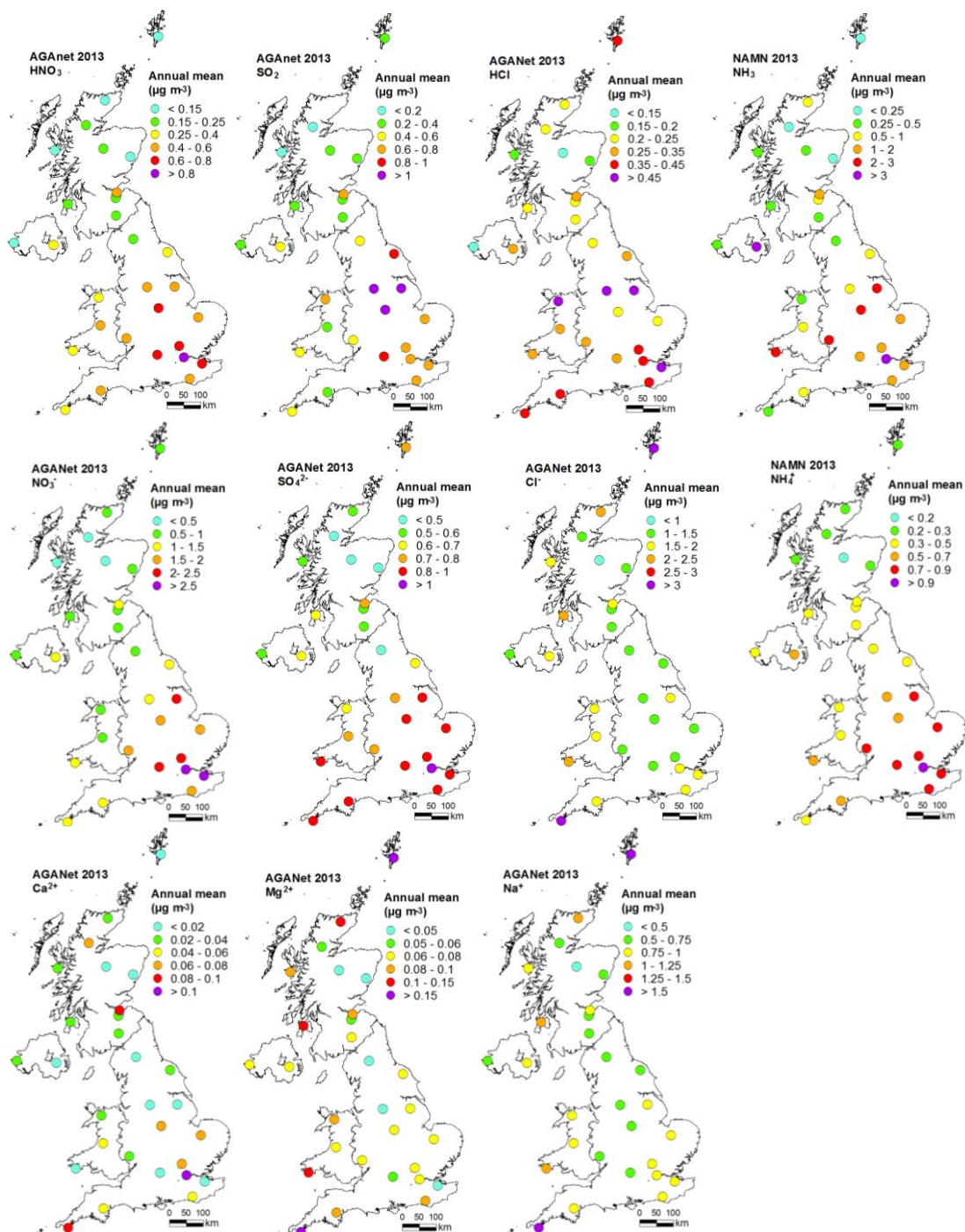
5   Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. ns = not significant ($p > 0.05$)

Figure 3: Comparison of HNO₃, HONO, sum (HNO3+HONO), SO₂, HCl and aerosol NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, Ca²⁺, Mg²⁺ concentrations by the Acid Gases and Aerosol Network (AGANet) DELTA method with available measurements from the co-located ChemSpec Daily Annular Denuder system (ADS) at Barcombe Mills (UKA00069). Mean concentrations were derived from the average of daily ADS data for the
10   corresponding DELTA sampling periods (monthly). HNO₃ values shown for DELTA and ADS are as calculated from the amount of NO₃⁻ collected on the denuders and have not been adjusted by a bias correction factor (see Sect. 0). A summary of the regression analyses is provided in the table below the graphs

	DELTA TIN	EMEP TIN	DELTA TIN (corrected HNO$_3$)	EMEP TIN	DELTA TIA	EMEP TIA
Linear regression: R^2	0.942***		0.953***		0.895***	
slope	0.984^{ns}		0.835*		0.879^{ns}	
intercept	0.015^{ns}		0.004^{ns}		0.088^{ns}	
mean (μg N m^{-3})	0.23	0.22	0.19	0.22	0.58	0.54
No. of observations (n)	13	13	13	13	13	13

Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. ns = not significant ($p > 0.05$)

Figure 4: Comparison of (a) total inorganic nitrate, TIN (sum of HNO$_3$ + NO$_3^-$) and (b) total inorganic ammonium, TIA (sum of NH$_3$ +
NH$_4^+$) concentrations at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130) measured under
the EMEP program with concentrations of the corresponding gas and aerosol from the UK Acid Gases and Aerosol (AGANet, HNO$_3$ and
NO$_3^-$) and UK National Ammonia Monitoring Network (NAMN, NH$_3$ and NH$_4^+$). EMEP values (data downloaded from http://ebas.nilu.no/)
are means of daily measurements for TIN and TIA by the EMEP filter pack method, matched to the AGANet and NAMN sampling periods
(monthly). Filter pack measurements at Eskdalemuir terminated in December 2000. A summary of the regression analyses is provided in the
table below the graphs.

	AGANet DELTA: SO$_2$	Bubbler: SO$_2$	AGANet DELTA: SO$_4^{2-}$	Filter Pack: SO$_4^{2-}$
Linear regression: R^2	0.812***		0.658***	
slope	0.865^{ns}		0.670***	
intercept	0.094*		0.011^{ns}	
mean (µg S m^{-3})	0.44	0.40	0.28	0.44
No. of observations (n)	26	26	87	87

Significance level (slope different from 1, intercept = 0): * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. ns = not significant ($p > 0.05$)

Figure 5: Comparison of gaseous SO$_2$ and particulate SO$_4^{2-}$ concentrations at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130) measured under the Acid Deposition Monitoring Program (ADMN, Hayman et al., 2007) with the corresponding gas and aerosol from the UK Acid Gases and Aerosol network (AGANet). ADMN values (data downloaded from http://ebas.nilu.no/) are means of daily measurements for SO$_2$ by the bubbler method and SO$_4^{2-}$ by the EMEP filter pack method (Hayman et al., 2007), matched to the AGANet sampling periods (monthly). Bubbler and filter pack measurements at Eskdalemuir terminated in December 2001 and Apr 2009, respectively. A summary of the regression analyses is provided in the table below the graphs.

5   **Figure 6:** Annual mean monitored acid gas (HNO₃, SO₂, HCl) and aerosol (NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, Ca²⁺, Mg²⁺) concentrations from the UK Acid Gas and Aerosol Monitoring Network (AGANet) across the UK from annual averaged monthly measurements made in 2013. NH₃ and NH₄⁺ measured at the same time from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown alongside for comparison.

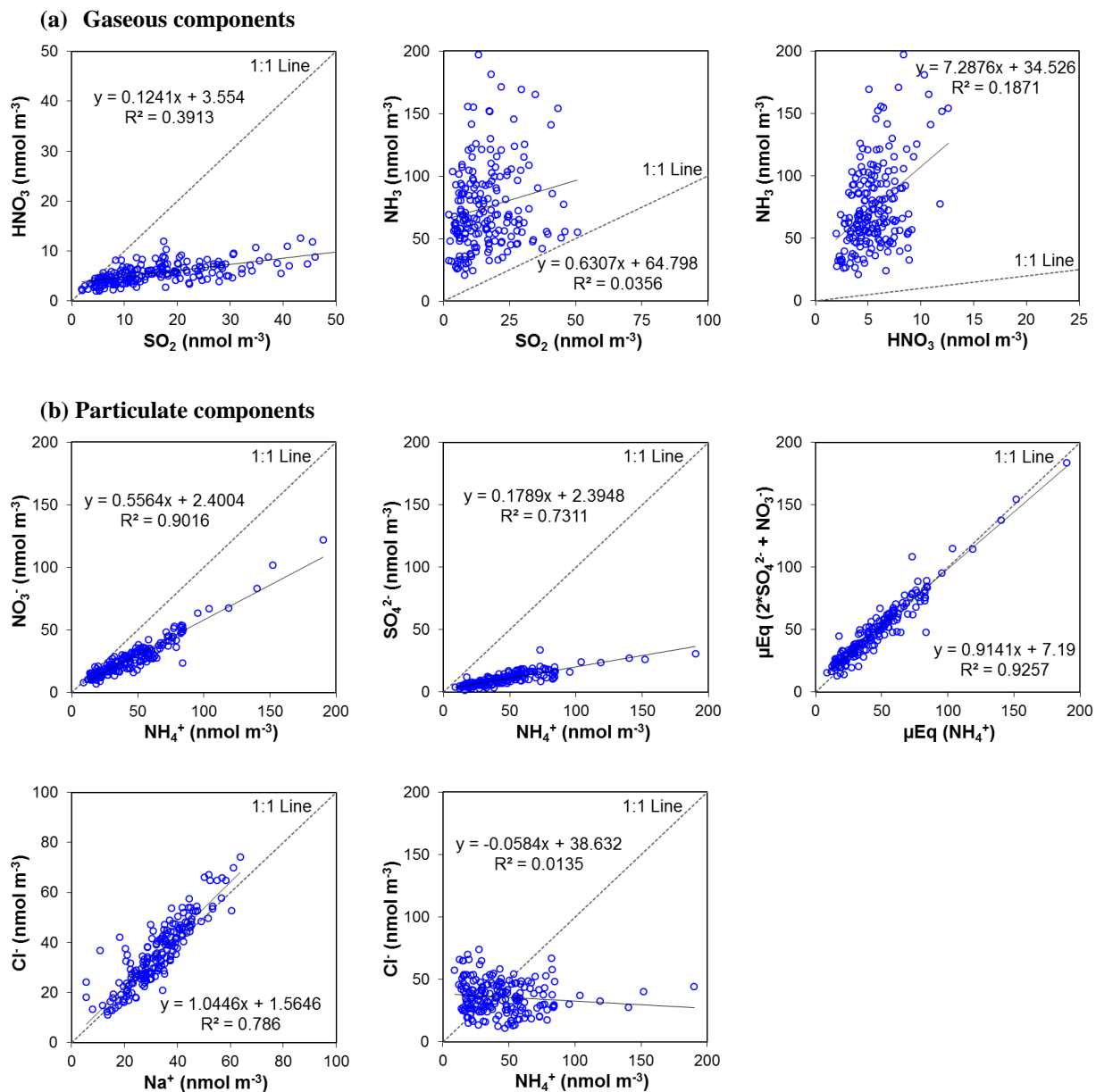
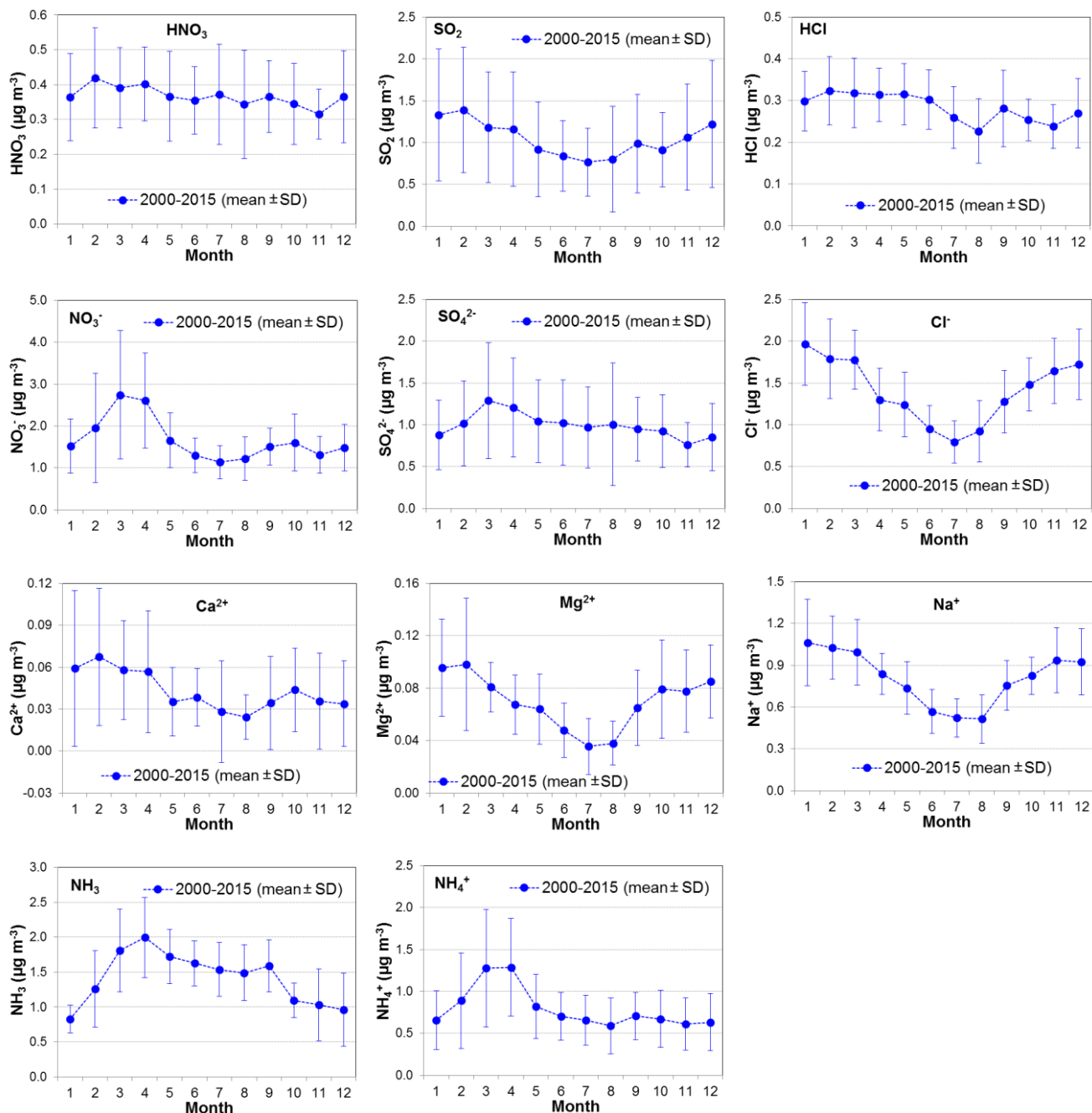



Figure 7: Scatter plots between concentrations of (a) gaseous species HNO_3, SO_2 and NH_3, and (b) particulate species NO_3^-, SO_4^{2-}, NH_4^+, Cl^- and Na^+ from mean monthly measurements (1999-2015) from the 12 sites in the UK Acid Gas and Aerosol Monitoring Network (AGANet) that were operational over the whole period. NH_3 and NH_4^+ data are from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) made at the same time. Each data point represents a single monthly DELTA measurement.

5 **Figure** 8: Average annual cycles for HNO₃, SO₂, **HCl and aerosol NO₃⁻, SO₄²⁻, Cl⁻, Na⁺, Ca²⁺ and Mg²⁺ from the UK Acid Gases and Aerosol Monitoring Network (AGANet). The NH₃ and NH₄⁺ concentrations measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown for comparison. Each data point in the graphs represents the mean ± SD of monthly measurements of all sites in the network.**

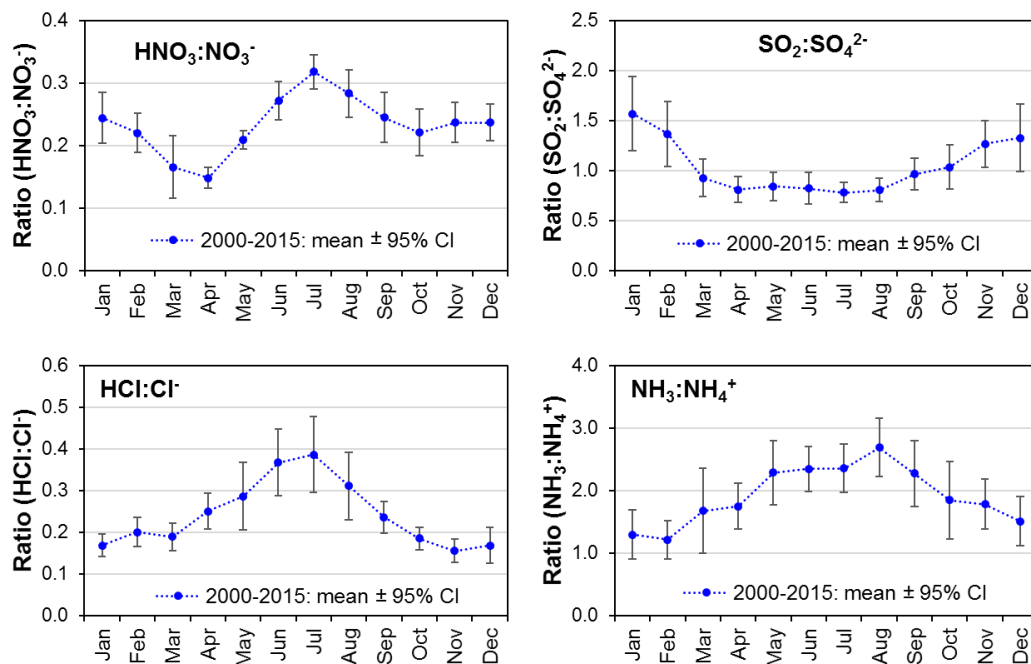
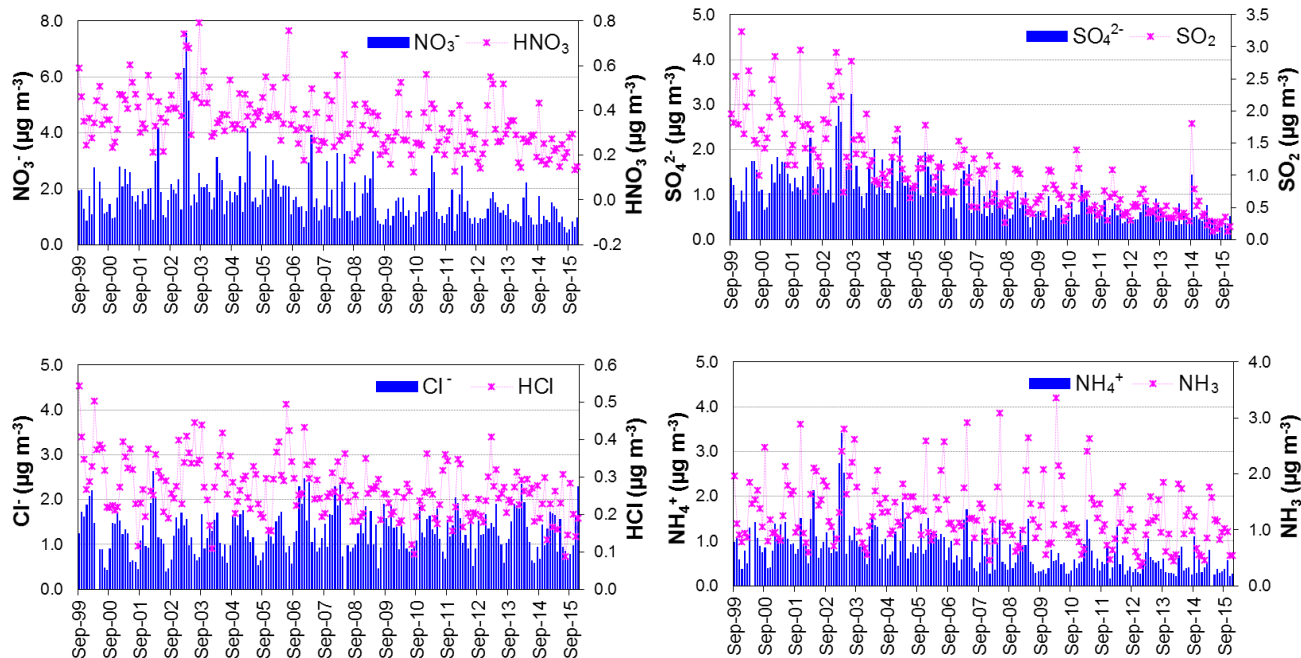



Figure 9: Average annual cycles in the ratios of gas:aerosol component concentrations. HNO_3, SO_2, HCl and aerosol NO_3^-, SO_4^{2-}, Cl^- data (annual mean, µg m-3) are from the UK Acid Gases and Aerosol Monitoring Network (AGANet). NH_3 and NH_4^+ data (annual mean, µg m-3) that are measured at the same time for the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown for comparison. Each data point in the graphs represents the mean ± 95% confidence interval (CI) of monthly measurements of 12 sites operational in the network over the period 2000 to 2015.

5 **Figure 10:** Monthly mean concentrations in gaseous HNO₃, SO₂, HCl and aerosol NO₃⁻, SO₄²⁻, Cl⁻ from the UK Acid Gases and Aerosol Monitoring Network (AGANet). Monthly mean concentrations of NH₃ and NH₄⁺ that were measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown for comparison. Each data point in the graphs represents the mean of monthly measurements of 12 sites operational in the network over the period Sep 1999 to December 2015. The same plots for the full 30 site network from 2006 - 2015 are shown in Supp. Figure S6.

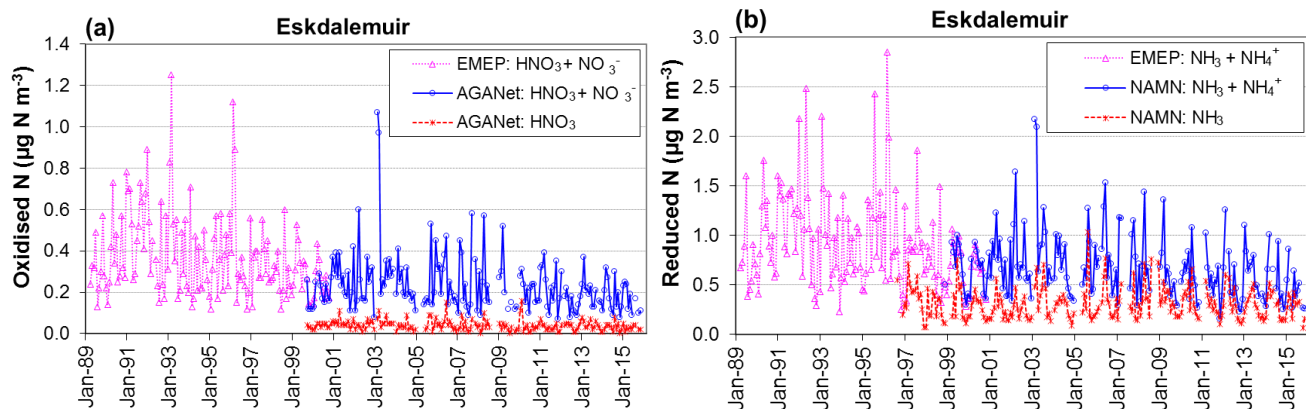
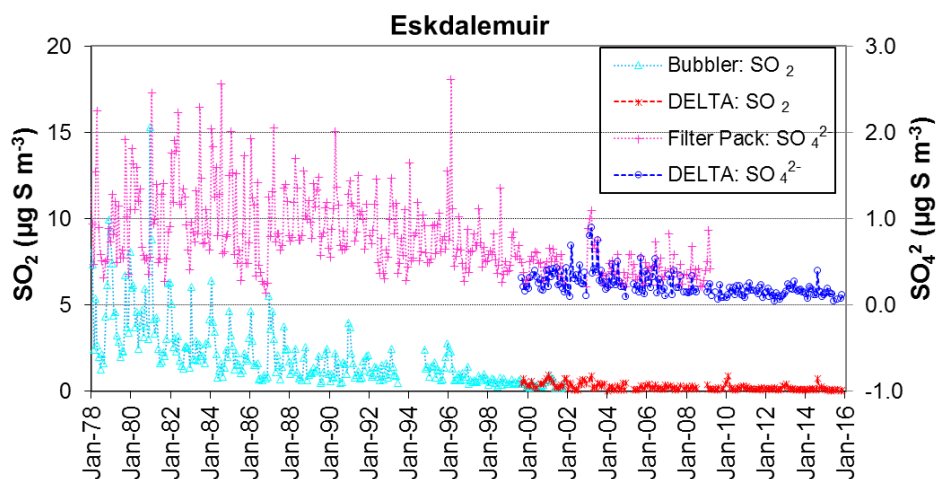



Figure 11: Long-term time series of (a) oxidised nitrogen (HNO_3 and NO_3^-) and (b) reduced nitrogen (NH_3 and NH_4^+) concentrations at Eskdalemuir (EMEP station code = GB0002R; UK-AIR ID = UKA00130). EMEP values (data downloaded from http://ebas.nilu.no/) are monthly means of daily measurements for total inorganic nitrogen, TIN (sum of HNO_3 and NO_3^-) and total inorganic nitrogen, TIA (sum of NH_3 and NH_4^+) by the EMEP filter pack method (Apr-89 – Nov-00), matched to the AGANet and NAMN sampling periods (monthly) where the measurements overlap. The AGANet and NAMN data are for gaseous HNO_3 and NH_3 and for the sum of (HNO_3 + NO_3^-) and sum of (NH_3 + NH_4^+), respectively, by the DELTA method. The AGANet HNO_3 values shown here includes the bias correction (Section 0).

5 **Figure 12:** Long-term time series of SO_2 (Dec-77 – Jul-93) and SO_4^{2-} (Dec-77 – Dec-01) concentrations measured in the UK Acid Deposition Monitoring Network (ADMN) (Hayman et al., 2007) and the AGANet DELTA measurements (Oct-99 – Dec-15) at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130). ADMN values (data downloaded from http://ebas.nilu.no/) are monthly means of daily measurements for SO_2 and SO_4^{2-} by a daily bubbler and filter pack method, respectively, matched to the AGANet sampling periods (monthly) where the measurements overlap.

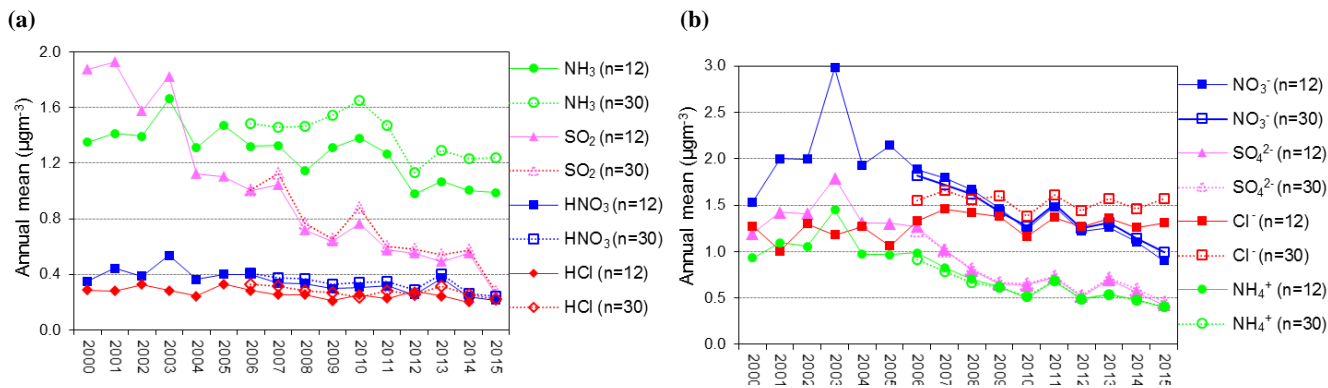



Figure 13: Long-term trends in (a) acid gases and (b) aerosol concentrations (μg molecule m^{-3}) from the UK Acid Gases and Aerosol Network (AGANet). Each data point represents the annually averaged measurements from either the original 12 AGANet sites for the 16-year period from 2000 to 2015 or the expanded 30 AGANet sites for the 10-year period from 2006 to 2015. NH$_3$ and particulate NH$_4^+$ measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison.

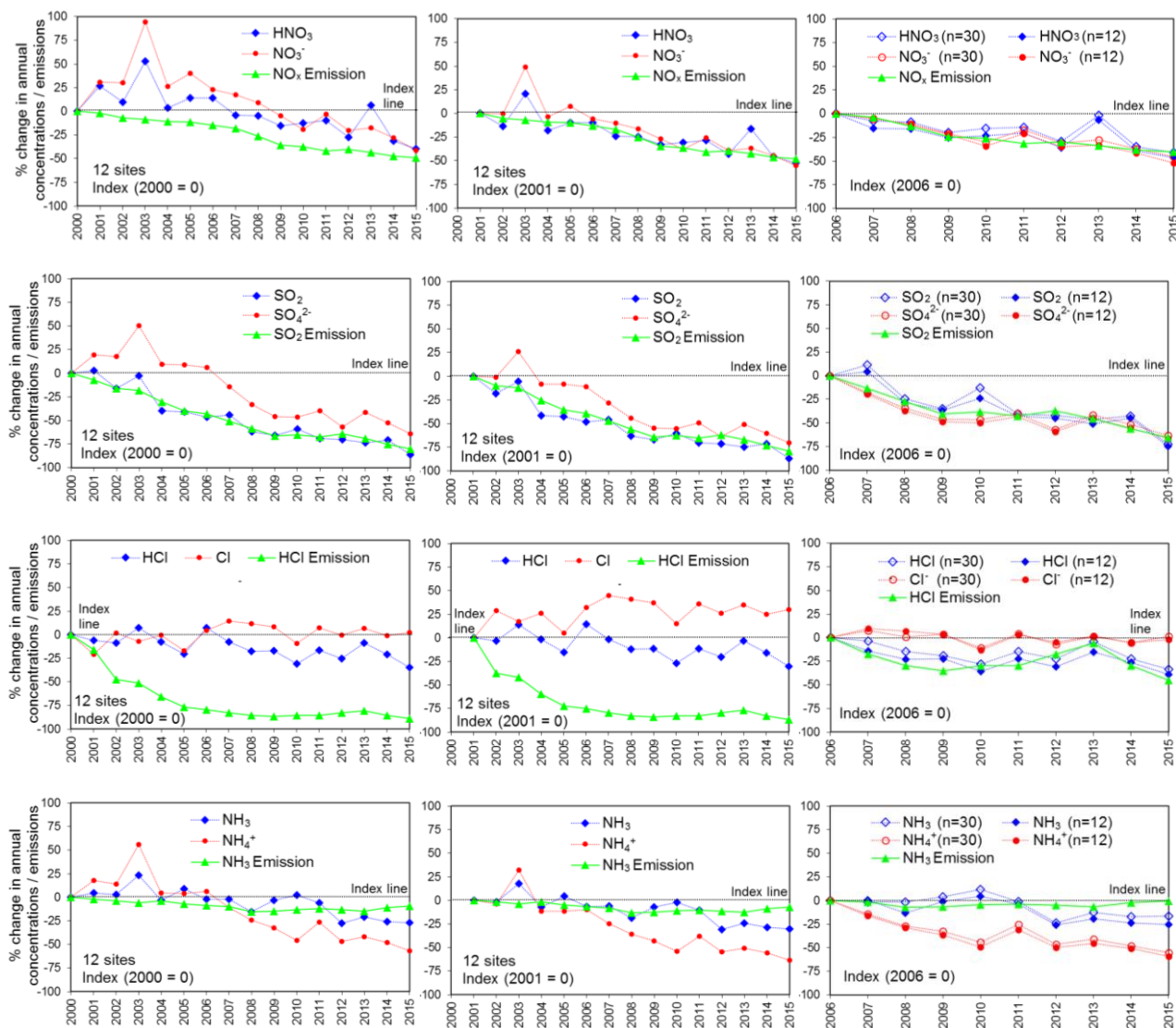



Figure 14: Relative trends in UK emissions (NAEI 2018) and in annually averaged gas and particulate concentrations from the UK AGANet and UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) for (left) original 12 sites for the 16 year period from 2000 to 2015, and (right) expanded 30 sites compared with the original 12 sites for the 10 year period from 2006 to 2015.

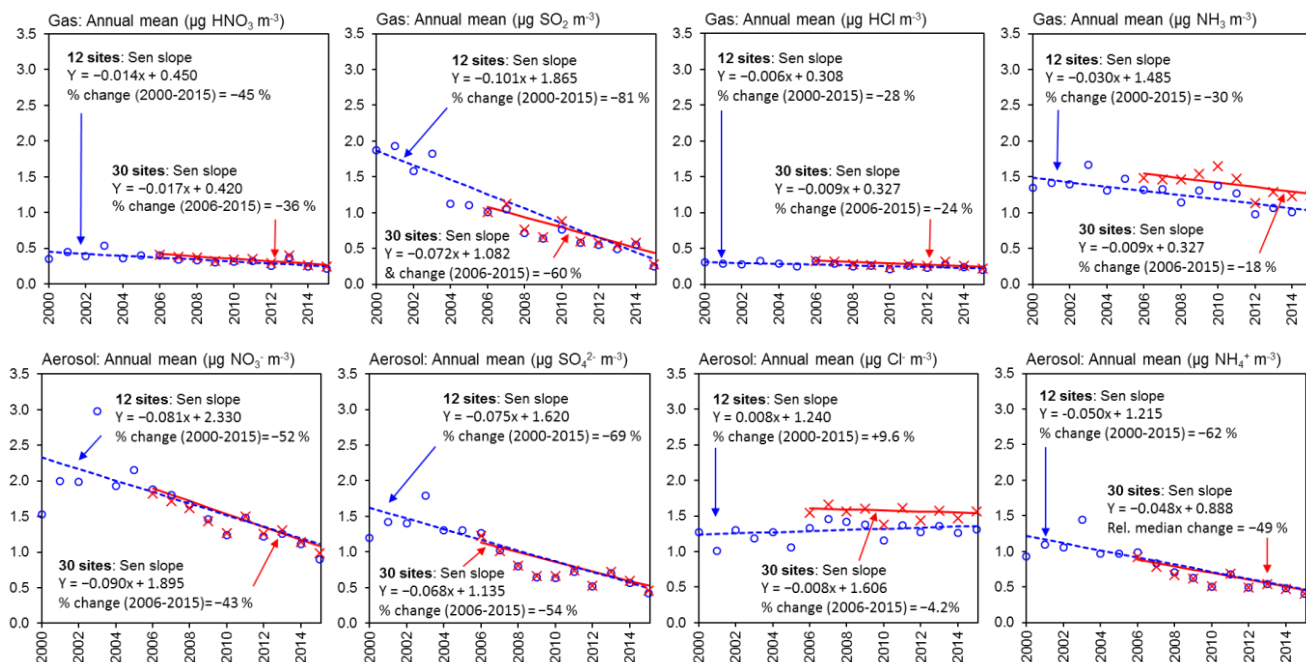



Figure 15: Time series trend analysis by non-parametric Mann-Kendall Sen slope on annually averaged gas and aerosol concentration data from the UK Acid Gases and Aerosol Monitoring Network (AGANet) of (i) 12 sites with complete time series over the period 2000 to 2015 and (ii) expanded 30 sites with complete times series over the period 2006-2015. NH_3 and NH_4^+ concentrations data measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al.,2018) are also included for comparison.

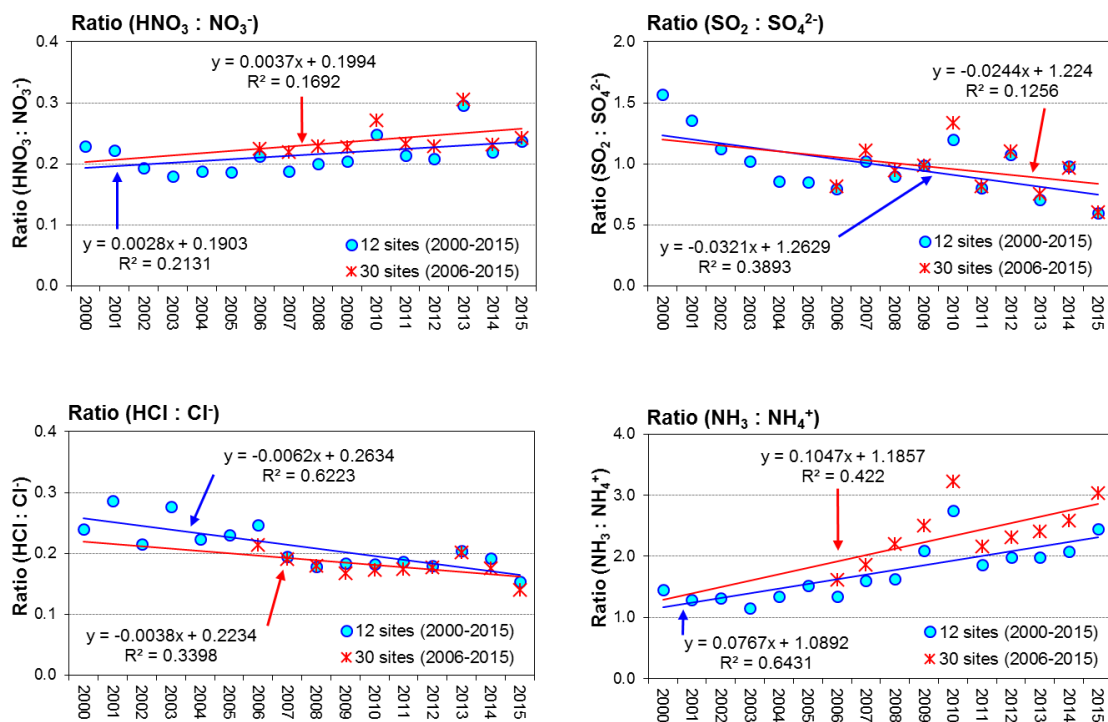
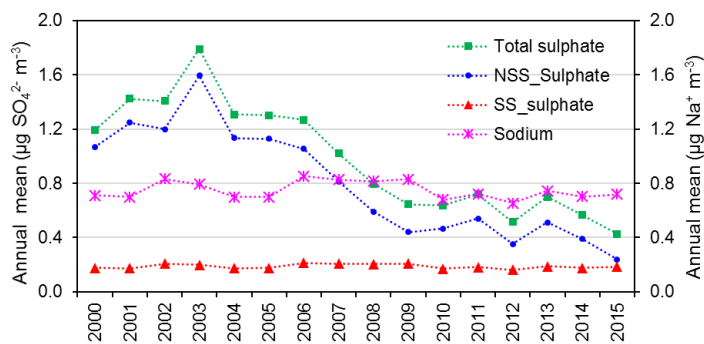



Figure 16: Long-term trends in the gas:aerosol ratio, from a comparison of the annual mean concentrations of 12 sites with complete time series from 2000 to 2015, and 30 sites with complete time series from 2006 to 2015, showing indicative differences in direction of trends in this ratio with time.

5   **Figure 17**: Comparison of long-term trends in annual mean concentrations of total sulphate (as determined from the amount of sulphate collected on the AGANet aerosol filter), NSS_sulphate (estimated from the empirical relationship: [NSS_SO4] = [SO4^{2-}] - (0.25 x [Na$^+$]), SS_sulphate (Total – NSS) and sodium. Each data point represents the annually averaged mean concentration of 12 sites for the 16 year period from 2000 to 2015.

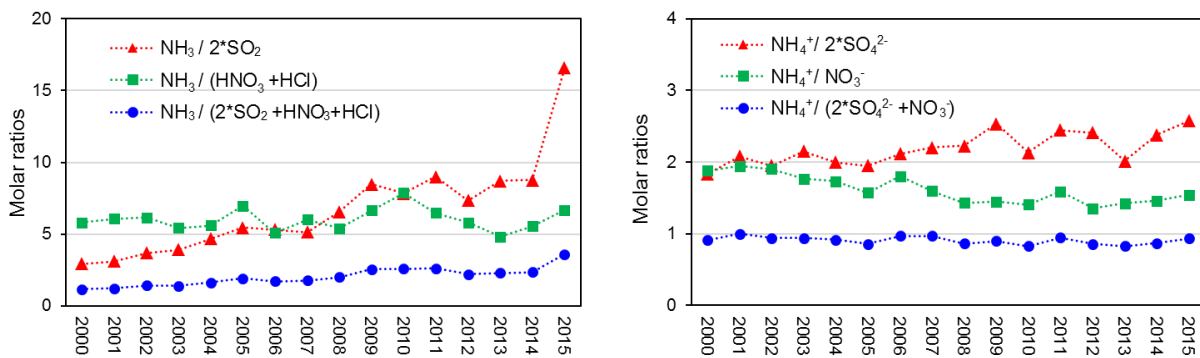



Figure 18: Long-term changes between 2000 and 2015 in (a) molar ratio of NH_3 to acid gases (SO_2, HNO_3 and HCl) and (b) molar ratio of particulate NH_4^+ to acid aerosols (SO_4^{2-} and NO_3^-) from measurements made at 12 sites in AGANet.

Table 1: List of sites in the UK Acid Gas and Aerosol Network (AGANet) with details of locations, start dates and UK-AIR ID (https://uk-air.defra.gov.uk/networks/network-info?view=aganet).

Site Name	UK-AIR ID	Latitude	Longitude	Start
Barcombe Mills	UKA00069	50.9191	0.0486	Apr '00
Bush OTC	UKA00128	55.8623	-3.2058	Sep '99
Cwmystwyth	UKA00325	52.3524	-3.8053	Sep '99
Eskdalemuir	UKA00130	55.3153	-3.2061	Sep '99
Glensaugh	UKA00348	56.9072	-2.5594	Sep '99
High Muffles	UKA00169	54.3349	-0.8086	Sep '99
Lough Navar	UKA00166	54.4395	-7.9003	Oct '99
Rothamsted	UKA00275	51.8065	-0.3604	Sep '99
Stoke Ferry	UKA00317	52.5599	0.5061	Sep '99
Strathvaich	UKA00162	57.7345	-4.7766	Sep '99
Sutton Bonington	UKA00312	52.8366	-1.2512	Sep '99
Yarner Wood	UKA00168	50.5976	-3.7165	Sep '99
New sites added from January 2006				
Auchencorth Moss	UKA00451	55.7922	-3.2429	Jan '06
Caenby	UKA00492	53.3979	-0.5074	Feb '06
Carradale	UKA00389	55.5825	-5.4962	Jan '06
Detling	UKA00481	51.3079	0.5827	Feb '06
Edinburgh St Leonards	UKA00454	55.9456	-3.1822	Jan '06
Goonhilly	UKA00056	50.0506	-5.1815	Jan '06
Halladale	UKA00314	58.4124	-3.8758	Jan '06
Harwell	UKA00047	51.5711	-1.3253	May '06
Hillsborough	UKA00293	54.4525	-6.0833	Jan '06
Ladybower	UKA00171	53.4034	-1.7520	Feb '06
Lagganlia	UKA00290	57.1110	-3.8921	Jan '06
Lerwick	UKA00486	60.1392	-1.1853	Jan '06
London Cromwell Road 2	UKA00370	51.4955	-0.1787	Jan '06
Moorhouse	UKA00357	54.6901	-2.3769	Jan '06
Narberth	UKA00323	51.7818	-4.6915	Mar '06
Plas Y Brenin	UKA00493	53.1018	-3.9179	May '06
Rosemaund	UKA00491	52.1214	-2.6363	Jan '06
Rum	UKA00276	57.0100	-6.2718	Feb '06

Table 2: Correlation coefficients (R^2) for different species across the 30 measurement sites.

	HNO_3	HCl	SO_2	NO_3^-	Cl^-	SO_4^{2-}	NH_4^+	Na^+
HNO_3	1.00	0.25***	0.39***	0.45***	0.07***	0.54***	0.49***	0.02*
HCl	-	1.00	0.21***	0.14***	0.01^{ns}	0.24***	0.19***	0.04**
SO_2	-	-	1.00	0.30***	0.00^{ns}	0.47***	0.37***	0.01^{ns}
NO_3^-	-	-	-	1.00	0.00^{ns}	0.61***	0.90***	0.02^{ns}
Cl^-	-	-	-	-	1.00	0.04**	0.01^{ns}	0.79***
SO_4^{2-}	-	-	-	-	-	1.00	0.73***	0.00^{ns}
NH_4^+	-	-	-	-	-	-	1.00	0.00^{ns}
Na^+	-	-	-	-	-	-	-	1.00

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$. ns = not significant ($p > 0.05$)

Table 3: Comparison of mean concentrations from the original 12 Acid gases and Aerosol Network (AGANet) sites *vs* the expanded 30 AGANet sites for the different gas and aerosol components. NH_3 and NH_4^+ measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. Each data point are the mean ± SD of annual mean concentrations over the period 2006 to 2015.

	Mean concentration (2006 – 2015), µg m^{-3}										
	HNO_3	SO_2	HCl	NO_3^-	SO_4^{2-}	Cl^-	Na^+	Ca^{2+}	Mg^{2+}	NH_3	NH_4^+
12 sites (mean±SD)	0.31± *0.06*	0.66 ± *0.24*	0.25 ± *0.04*	1.40 ± *0.31*	0.73 ± *0.25*	1.33 ± *0.09*	0.75 ± *0.07*	0.04 ± *0.03*	0.06 ± *0.01*	1.18 ± *0.16*	0.62 ± *0.18*
30 sites (mean±SD)	0.34 ± *0.06*	0.70 ± *0.25*	0.28 ± *0.04*	1.41 ± *0.26*	0.74 ± *0.23*	1.54 ± *0.09*	0.84 ± *0.08*	0.04 ± *0.02*	0.07 ± *0.01*	1.40 ± *0.16*	0.61 ± *0.16*

Table 4: Summary of Mann-Kendall (MK) time series trend analysis on annually averaged gas and aerosol concentrations from the UK Acid Gases and Aerosol Monitoring Network (AGANet) for i) 12 sites that were operational over the period 2000 to 2015 and ii) 30 sites that were operational over the period 2006 to 2015. NH_3 and NH_4^+ concentrations data measured at the same time from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. The 95% confidence interval (CI) for the median trend and relative median change (%) are also estimated.

Annual mean data ($\mu g\ m^{-3}$)	Mann-Kendall (MK): 12 sites (2000 - 2015)		Mann-Kendall (MK): 30 sites (2006 – 2015)	
	[a]Median annual trend & [95% CI] ($\mu g\ y^{-1}$)	[b]Relative median change & [95% CI] (%)	[a]Median annual trend & [95% CI] ($\mu g\ y^{-1}$)	[b]Relative median change & [95% CI] (%)
HNO_3	-0.0135** [-0.0067, -0.0180]	-45** [-26, -55]	-0.0167* [-0.0075, -0.0200]	-36* [-18, -41]
SO_2	-0.1010*** [-0.0729, -0.1255]	-81*** [-72, -91]	-0.0717** [-0.0300, -0.0108]	-60** [-33, -73]
HCl	-0.0057** [-0.0020, -0.0100]	-28** [-11, -42]	-0.0088* [0.0000, -0.0200]	-24* [0.0, -47]
NH_3	-0.0300** [-0.0125, -0.0433]	-30*** [-13, -39]	-0.0312[ns] [0.0033, -0.0625]	-18[ns] [+2.0, -31]
NO_3^-	-0.0810*** [-0.0520, -0.1125]	-52*** [-37, -63]	-0.0900** [-0.0580, -0.1300]	-43** [-30, -56]
SO_4^{2-}	-0.0750*** [-0.0450, -0.-0988]	-69*** [-52, -82]	-0.0675** [-0.0233, -0.1167]	-54** [-25, -78]
$NSS\_SO_4^{2-}$	-0.0733*** [-0.0500, -0.-1012]	-78*** [-64, -92]	-0.0575** [-0.0167, -0.1033]	-62** [-25, -86]
Cl^-	0.0079[ns] [-0088, 0.0236]	9.6[ns] [-9.5, 33]	-0.0075[ns] [+0.0167, -0.0300]	-4.2[ns] [+10, -16]
NH_4^+	-0.0500*** [-0.0375, -0.0675]	-62*** [-51, -74]	-0.0480** [0.0267, -0.0700]	-49** [-33, -64]

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, [ns] non-significant ($p > 0.05$)

[a]Median annual trend = fitted Sen's slope of Mann-Kendall linear trend (unit = $\mu g\ y^{-1}$)

[b]Relative median change estimated from the annual concentration at the start (y_0) and at the end (y_i) of time series computed from the Sen's slope and intercept ($=100*[(y_i-y_0)\ /y_0]$)

Table 5: Comparison of % change in estimated UK NO_x, SO_2 and NH_3 emissions reported by the National Atmospheric Emission Inventory (NAEI) (data from http://naei.defra.gov.uk/) with % change between 2000-2015 (12 sites with complete time series) and between 2006-2015 (30 sites with complete time series) in annually averaged HNO_3 / NO_3^- and SO_2 / SO_4^{2-} concentrations from the UK Acid Gas and Aerosol Monitoring Network (AGANet), and annually averaged NH_3 / NH_4^+ concentrations from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018).

Components	2000 – 2015 (12 sites)		2006 – 2015 (30 sites)	
	UK emissions[b] % change	MK Sen Slope % relative median change[a]	UK emissions[c] % change	MK Sen slope % relative median change[a]
Gas HNO_3	-49 (NO_x)	-45**	-40 (NO_x)	-36*
Particulate NO_3^-		-52***		-43**
Gas SO_2	-80 (SO_2)	-81***	-65 (SO_2)	-60***
Particulate SO_4^{2-}		-69***		-54**
NSS_ SO_4^{2-}		-78***		-62**
Gas HCl	-87 (HCl)	-28[ns]	-45 (HCl)	-24[ns]
Particulate Cl^-		+10[ns]		-4[ns]
Gas NH_3	-9 (NH_3)	-30***	-0.7 (NH_3)	-18[ns]
Particulate NH_4^+		-62***		-49**

Significance level: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$, [ns] non-significant ($p > 0.05$)

[a]Relative median change calculated based on the estimated annual concentration at the start (y_0) and at the end (y_i) of time series computed from the Sen's slope and intercept (=100*[(y_i-y_0) /y_0])

[b]UK emissions data from NAEI (http://naei.beis.gov.uk/data/, accessed 17/09/18)