Interactive comment on Atmos. Chem. Phys. Discuss., doi.org/10.5194/acp-2018-489, 2018

## RESPONSE TO REVIEWER 1

### C.R. Flechard (Referee)

The authors thank Dr. Flechard for his constructive comments and for taking the time to look at all the details described in the manuscript. We have carefully considered all comments. Please refer to the specific responses.

### *1) General observations*

*The mean weakness in the quality of the dataset is likely the large uncertainty in HNO3 caused by interferences by other NOy compounds on potassium carbonate coated denuders. This is mentioned in the methods but not referred to later on in the discussion in relation to trends in measured HNO3 and reported NOx emissions. With a flat and constant correction factor of 0.45 for HNO3 measured from K2CO3 coated denuders (meaning that 55% of the raw concentration is substracted to provide a corrected number), one can wonder whether the apparent decrease in HNO3 since 2000 is significant, or if the slope of the apparent decrease has any meaning. With large changes in NOx emissions and in the general pollution climate of the UK over the last 20 years, and therefore with possibly large changes in the ratios of HNO3 to the interfering NOy gases (NO2, HONO, PAN, etc), it is risky to assume a constant 0.45 correction factor for the whole period, and also across the whole country, given the large differences in pollution profiles between the sites of the network*

### Author Response:

Additional text has been added under new heading "Section 3.3: Uncertainties in $HNO_3$ determination" to address the reviewer's comments.

See below:

"$HNO_3$ data were corrected for sampling artefacts in the measurements with an empirical correction factor of 0.45 (see section 2.6). Interferences in $HNO_3$ 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 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 $HNO_3$ in the UK (e.g. Kitto & Harrison 1992, Connolly et al. 2016). Interference from $NO_2$ 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, Benner et. al. 1991, 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 et al. (2009) on the AGANet $K_2CO_3$/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 $HNO_3$" signal from the carbonate coated denuders will be dependent on the relative concentrations of $HNO_3$ 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 AGANet TIN with EMEP filter pack TIN data (slope = 0.835, $R^2$ = 0.95) at Eskdalemuir (see section 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 $K_2CO_3$/glycerol coated denuder to collect $SO_2$. At three sites (Auchencorth, Bush OTC and Stoke Ferry), parallel measurements of the old configuration (two $K_2CO_3$/glycerol coated denuders) and new configuration (two NaCl coated denuders + $K_2CO_3$/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 $K_2CO_3$ denuder are assumed to come from other oxidised nitrogen species and are not reported. Comparing the sum of nitrate concentrations from the new (2xNaCl + 1x$K_2CO_3$) with the old (2x$K_2CO_3$) 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 2x$K_2CO_3$ 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 NaCl and $K_2CO_3$ coated denuders. Initial analysis of 2016 data (unpublished data) showed that the mean ratio of nitrate on NaCl:$K_2CO_3$ 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 in the DELTA method and the effects of a method change in the AGANet forms the subject for a next paper. "

Additional text also added to revised/expanded text in Section 3.6 Seasonal variation in acid gases and aerosols (paragraph 2):

"$HNO_3$ 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 due 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 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 $^{\cdot}OH$ radicals for reaction with $NO_2$ to form $HNO_3$), masking the true extent in the seasonal profile."**

*2) Specific Comments*
*p6, l4, '...sampling rate of 0.2-0.4 l/min...' Please mention at this stage, or just below in the paragraph describing the aerosol collection system, what the particle size cut-off is for the DELTA sampler (mentioned later on p10, l3). It is important to know what the size spectrum of collected aerosols is, and that some (coarse) particles are not sampled, eg dust, large marine aerosols.*

## Author Response:

The text below was inserted at the end of the paragraph 3 (section 2.2 Extended DELTA methodology for sampling acid gases and aerosol in AGANet).

"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 < $PM_{4.5}$."

*3) p7, l6-7, change of analytical labs from Harwell to CEH Lancaster in 2009: was there a transitional period of overlapping parallel measurements by the two labs, to make sure no bias was introduced in the long term time series by the change of laboratory?*

**Author Response:**

There was no transitional period of overlapping measurements, but measurements of replicated samples were compared between the two labs to ensure that there was no bias in chemical analysis prior to the lab. switch. CEH Lancaster laboratory is UKAS accredited, with experience of DELTA measurements prior to taking over the network measurements from Harwell lab.

*4) p7, l26, '...flagging up occurrences of poorly coated denuders and/or sampling issues...'*

*Another possibility is that concentrations are so large that the first denuder saturates and thus much is collected by the second denuder. This can happen for NH3 at agricultural sites after fertilisation; it is much less likely for acid gases due to lower concentrations, unless perhaps at some polluted urban stations?*

**Author Response:**

At high concentrations, saturation of the first denuder can indeed lead to lower gas capture efficiencies (breakthrough and capture on second denuder). The monitoring network sites are however located away from sources to monitor ambient concentrations. In 2015, the mean capture efficiencies for $NH_3$, $HNO_3$, $SO_2$ and HCl were 96%, 83%, 91% and 79 %, respectively.

*5) p8, l15, the term 'bias' is used in relation to the 0.45 correction factor for HNO3, in the title of 2.6 and also other parts of the text. This is perhaps misleading as a bias suggests an offset, while the multiplicative correction applied acts on the span. Further, in the Tang et al 2015 report, the authors write that '... It is recommended that a correction factor of 0.45 be applied to the historic HNO3 measurements. The range of ratios was 0.44±0.15 (±2SD), i.e. 0.29-0.59, therefore it is reasonably likely that the value lies between 0.4 and 0.5. Therefore a correction factor of 0.45 should be applied...' It is quite clear that the percentage of non-HNO3 NOy compounds that is measured after extracting K2CO3-coated denuders depends on the relative abundances of these gases compared with HNO3, as well as their collection efficiencies on K2CO3 and their oxidation/reaction rate following adsorption. I would expect large seasonal changes, and large spatial/geographical variations, in these concentrations and the associated chemical processes, as reflected in the observed 0.29-0.59 range.*
*Applying the same correction factor at all sites of the network, that range from remote to coastal to rural to sub-urban and urban, does not seem to be adequate. This is hinted at in the Eskdalemuir example of Fig. 3, where applying the large 0.45 multiplier makes the DELTA TIN values diverge from the EMEP filter pack measurements, ie at this rural background site the need for such a large correction is not warranted.*
*The correction factor should account for the differences in pollution climates between sites, and also for changes over the 20-year period. Could an empirical correction be derived from chemical transport modelling (eg EMEP4UK), whereby the ratios of modelled HNO3 to NO2, HONO, PAN, etc, are used to construct a geographically- and temporally-varying index to drive the correction function? The HNO3 data reported in Tang et al (2015) for NaCl vs K2CO3 coating, with measurements made in contrasted situations (rural, urban, remote, see Table 1 in that report), may be used for calibrating such a function.*

**Author Response:**

The tile of section 2.6 has been changed to "$HNO_3$ measurement artefacts and correction"

Regarding the empirical correction of the $HNO_3$ data, please see author response to general comments on pages 1 - 2.

*6) p8-11, section 2.7 Performance of the DELTA method: strictly speaking, this section describes measurement results from intercomaprison experiments or even long term datasets (Bush, Eskdalemuir) does not belong in Methods, and should be moved to the beginning of Section 3- Results*

**Author Response:**

Section 2.7 Performance of the DELTA method was included in the method section to separate this component from the main focus of presenting AGANet data in the results and discussion section.

But agree:

Moved to beginning of section 3 – Results and Discussion.

3.1 Performance of DELTA method

3.1.1 Comparison with daily annular denuder measurements

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

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

*7) p10, l12: Ca++ and Mg++ concentrations were near detection limits because they are mostly in the coarse fraction, with particle sizes near or above the DELTA cut-off. How much of the NaCl is similarly not collected by the DELTA system? Also, in relation to the DELTA v. ADS intercomparison, the loss of NO3, Na and Cl on the surface of the cyclone is put forward as an explanation for the lower ADS aerosols concentrations (compared with DELTA) (p10, l10), but why in that case is SO4= 23% larger in the ADS?*

**Author Response:**

NaCl is the main constituent of seasalt aerosol and size of seasalt aerosols ranges widely from ~0.05 to 10 µm in diameter, with their particle sizes also varying with humidity. The DELTA cut-off is estimated to be around 4.5 µm, so the DELTA will sample NaCl aerosols in the $PM_{4.5}$ particle size region. $Na^+$ measured on the DELTA are above detection limits, with concentrations ranging between 0.4 to 1.8 ug Na $m^{-3}$ (annual mean in 2015). In the DELTA v ADS intercomparison of base cation measurements, the slope for Na was 3.0 ($R^2$ = 0.24) and for Mg, the slope was 2.4 ($R^2$ = 0.24), but a lot of scatter for $Ca^{2+}$ as both ADS and DELTA $Ca^{2+}$ data were at or below LOD. The DELTA therefore captures $Mg^{2+}$ and $Na^+$ well, but not $Ca^{2+}$, which is what we find in the AGANet data.

The slope for $SO_4^{2-}$ in DELTA v ADS intercomparison is 0.69 ($R^2$ = 0.89). The smaller $SO_4^{2-}$ signal on the DELTA may be due to incomplete capture of fine mode sulphate on the DELTA base coated cellulose filters. In the DELTA assessment report by Tang et al. (2015), up to 30 % of the total acid sulphate was measured on a 2µm porosity PTFE membrane placed behind the $K_2CO_3$ coated filter to capture break-through. Since 2016, an additional PTFE membrane is added in front of the carbonate and acid coated cellulose filters.

A 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 previosuly shown close agreement between the two methods, providing confidence in $SO_2$ and $SO_4^{2-}$ measurements by the DELTA. Sulphur measurements provided by the DELTA replaced filter pack measurements in 1999.

Further work is ongoing to understand, assess and correct the bias in $SO_4^{2-}$ measurements in historic data. Since the DELTA method was unchanged for the assessment period in this paper, the bias in $SO_4^{2-}$ should not influence the interpretation of long-term trends in the data.

8) p13, l2: the highest HCl concentrations are in the SE and SW of England, but also in the Midlands

**Author Response:**

Thank you. For an international audience, they may not know where the Midlands is. I propose to use “central England” instead of “Midlands”,

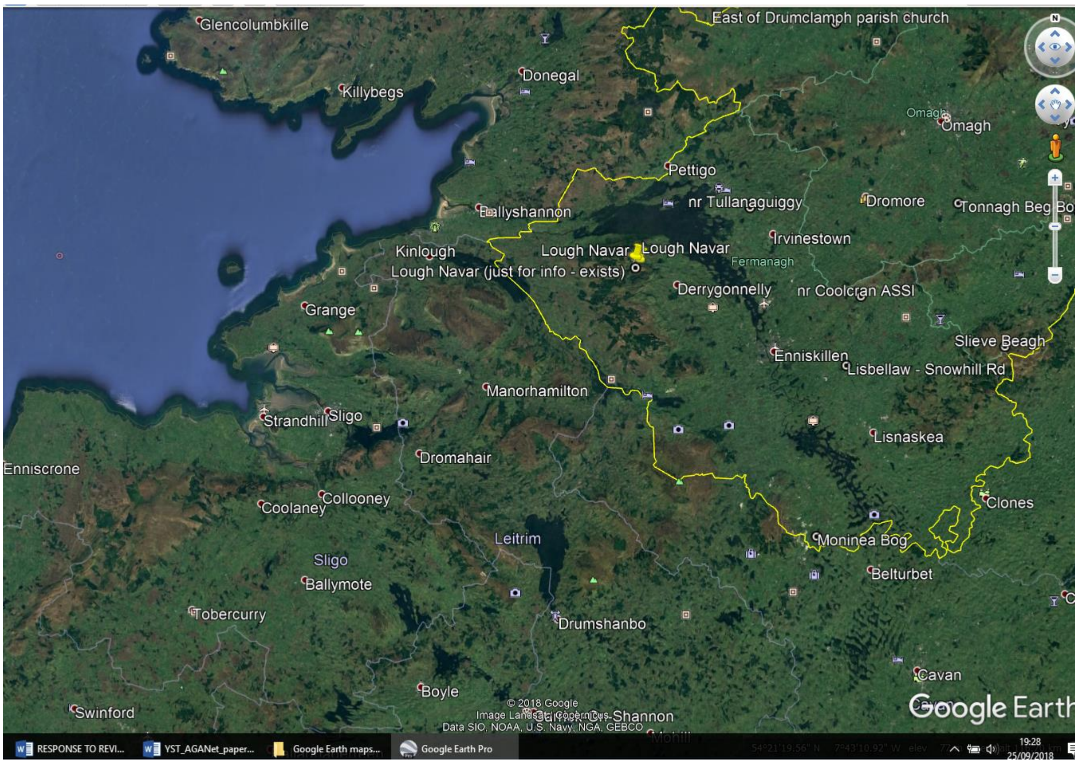
Revised text below:

“HCl in the atmosphere are mostly emitted from coal combustion and the highest concentrations of HCl are in the source areas in SE and SW of England, and also in central England (north of the Ratcliffe-on-Soar power station)…,…”

9) p13, l5: '...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...' Lough Navar is very near the coast (10km) and yet NaCl concentrations are very low (similar to concentrations in the Midlands), compared with all other western sites in the network (Fig. 5); what could be the reason?

**Author Response:**

The Lough Navar site is actually approx. 40 km inland, close to the border between Northern Ireland and Republic of Ireland, within a forested area. The UK maps in the manuscript are all shown without Republic of Ireland, which may have given a false impression of Lough Navar being closer to the sea than it is in reality. Given its location inland, and the prevailing wind direction coming from the SW, it is far from the influence of seasalts.



*10) p13, l5: For Cl- and Na+, '...largest concentrations at coastal sites in the south (Barcombe Mills) and west (Yarner Wood)...'; actually the highest concentrations are at Goonhilly at the SW tip of Cornwall.*

**Author Response:**

Thank you for spotting that.

Barcombe Mills and Yarner Woods are two of the original 12 sites that were established in 1999 in AGANet. As coastal sites, $Na^+$ and $Cl^-$ were always highest at these two sites up to the point when the new Goonhilly site in Cornwall was added as part of the network expansion in 2006. $Na^+$ and $Cl^-$ are indeed higher at Goonhilly than Barcombe Mills and Yarner woods.

Text has been corrected accordingly.

"The spatial distributions of $Cl^-$ and $Na^+$ were similar, with largest concentrations at the coastal sites Goonhilly in SW England and Lerwick-Shetland in the Shetland Isles,…."

*11) p13, l9-10, '...There is however no clear spatial pattern for Ca2+, with concentrations that are mostly at or below LOD...' For both Ca and Mg, which are mostly in the coarse fraction, it may be argued that the DELTA system does not allow a realistic assessment of the total concentration, because a large share of coarse particles are not collected.*
Please comment.

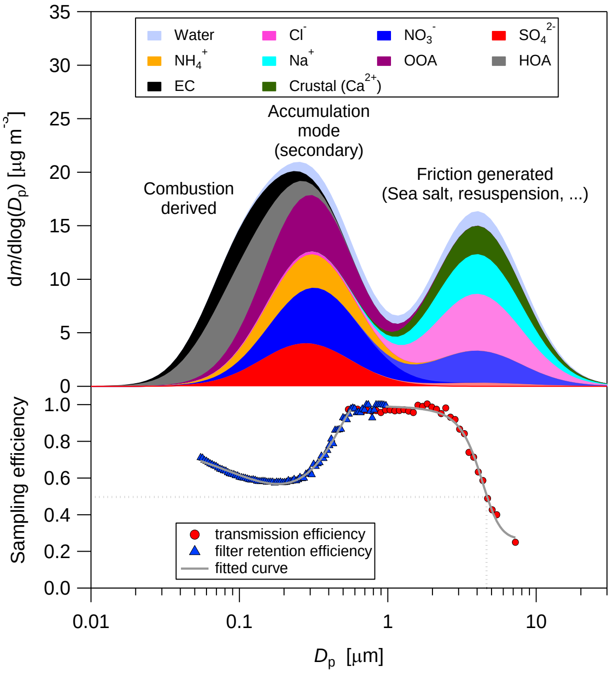
## Author Response:

Ca, Na and Mg are mainly in the 1 – 10 µm fraction in ambient aerosol. The size cut-off for the DELTA is around 4.5 µm, which means it will sample base cations in the $PM_{4.5}$ fraction.

In the DELTA ($PM_{4.5}$) v ADS ($PM_{2.5}$) intercomparison of base cation measurements (see response to comment 7 earlier), the slope for Na was 3.0 ($R^2 = 0.24$) and for Mg, the slope was 2.4 ($R^2 = 0.24$), but no relationship was established for Ca2+ as both ADS and DELTA $Ca^{2+}$ data were at or below LOD.

This suggests that the DELTA captures $Mg^{2+}$ and $Na^+$ in the $PM_{4.5}$ fraction reasonably well. At all AGANet sites, Na and Mg measurements are above LOD, whereas $Ca^{2+}$ are mostly at or below LOD. Aerosol filter blanks for $Ca^{2+}$ are also much more variable than Na or Mg. $Ca^{2+}$ is particularly problematic in chemical analysis as adsorption losses readily occur due to electrostatic interaction between $Ca^{2+}$ and surfaces, especially plastic. To this end, aerosol sample extracts are acidified to minimise adsorption of $Ca^{2+}$ to surfaces.

Sampling of $Ca^{2+}$ is also likewise problematic as $Ca^{2+}$ can potentially stick to inlets and surfaces. Tests conducted to assess adsorption losses of components to the connecting 6-mm diameter LDPE tube in the DELTA sampling train showed that measured concentrations of $Ca^{2+}$ were within the noise of the LDPE tube blanks (i.e. clean LDPE tubes extracted with deionised water), adding to the uncertainty in $Ca^{2+}$ measurements (see also response to next reviewer comment 12).



Retention and transmission efficiency of the DELTA sampling train as used in the AGANET network

*12) Further, our own tests with DELTA systems at INRA indicated very substantial losses for Mg and Ca in all the non-filter parts of the sampling train (particularly the 6-mm diameter LDPE elbow connecting the 2nd acid denuder to the first NH3 denuder, Fig.S1), which are therefore not measured on the filter. We analysed the loss fraction LDPE / (LDPE + den + filter) for all compounds; for NH4+ and NO3- this was less than 5%; for Cl- and Na+ this was 5-10%; for SO4= and Mg2+ this was 10-15%; while for Ca2+ this was 30-40%. Beyond the question of coarse aerosols that were not sampled at all (did not enter the sampling train), there is the question of those coarse aerosols that 'did not make it' to the filter pack. Did the authors carry out similar tests, and could the results be shown in the supplement? It may be that the new straight design for the DELTA sampling train allowed a reduction of these losses?*
Please comment.

**Author Response:**
Potential loss of particulate components to the connecting tube 6-mm diameter LDPE in the DELTA sampling train (Fig.S1) was investigated and reported in the DELTA assessment report by Tang et al. (2015).
Our test results (extracted from Tang et al., 2015) are similar to the INRA findings outlined above:

- $NO_3^-$: loss to LDPE tube is negligible (2.4 ± 0.8 % (mean ± SD) across all sites for all available data).
- $NO_2^-$, $SO_4^{2-}$ and $Cl^-$: losses to LDPE are small (< 6%).
- Base cations $Na^+$ and $Mg^{2+}$: losses to LDPE are slightly higher (<7%).
- Base cations $Ca^{2+}$: there is a large degree of uncertainty in the calcium assessment, due to 1) variability of $Ca^{2+}$ in the blank LDPE tube extracts and 2) very low $Ca^{2+}$ on LDPE tubes from sites, that were similar to blank values and close to the detection limit (LOD = 0.05 mg/L $Ca^{2+}$).

Since January 2016, the new DELTA sample train configuration is linear, eliminating the use of the LDPE connecting tube.

*13) P15, l1: This section 3.4 is mostly about sub-annual (seasonal) variations, so could be re-named 'Seasonal variations in acid gases and aerosols', as opposed to long term trends of Sections 3.5-3.6*

**Author Response:**
OK. Agree. Renamed
"3.6 Seasonal variation in acid gases and aerosols"

*14) p15, l9-10: '...In spring, the peak in HNO3 and NO3...' Fig.7 does not actually show any spring peak for HNO3; the late winter (Feb-Mar) concentrations are only marginally higher (but not significantly different accoring to the error bars) than the rest of the year? The opening sentence of the paragraph should read '...maximum in late winter and early spring...'*

**Author Response:**
Thank you. Text revised in "Section 3.6 Seasonal variation in acid gases and aerosols"

See below:
"$HNO_3$ 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). $HNO_3$ has a weak seasonal cycle with slightly higher concentrations in late winter and early spring that may be due 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 $\cdot OH$ radicals for reaction with $NO_2$ to form $HNO_3$), masking the true extent in the seasonal profile."

*15) p15, l22, '...this contributes to the winter minimum in NH4NO3...' : the minimum NO3- actually occurs in July?*

**Author Response:**

Thank you. Text revised in "Section 3.6 Seasonal variation in acid gases and aerosols"

See below:

"Warm, dry conditions in summer promotes dissociation, increasing gas-phase $HNO_3$ relative to particulate-phase $NH_4NO_3$, limiting peak $NO_3^-$ aerosol concentrations (Figure 8). This process accounts for the minima in $NO_3^-$ concentrations (Figure 7) and the highest ratio of $HNO_3$ to $NO_3^-$ seen in July (Figure 8). Cooler conditions in the spring than early autumn sees a larger fraction of the volatile $NH_4NO_3$ remaining in the aerosol phase. The peak in $NO_3^-$ concentrations and the low $HNO_3$:$NO_3^-$ ratio in spring-time (Figure 8) is thus a combination of larger $NO_3^-$ from reaction between higher concentrations of the precursor gases $HNO_3$ and $NH_3$, and partitioning to the aerosol phase. 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 $NH_4NO_3$ from the gas-phase $HNO_3$ and $NH_3$. Since $NH_3$ concentrations are lowest in winter however, with less $NH_3$ available for reaction, $NH_4NO_3$ concentrations are correspondingly smaller in winter than in spring or autumn."

*16) p16, l9-13: how far should seasonal cycles for Mg and especially Ca be discussed, given the low collection efficiency (and thus high uncertainty) of filter data (see my comment above on aerosol size cut-off and losses in sampling train for these large aerosols)?*

**Author Response:**

The discussion of the seasonal cycles on $Mg^{2+}$ and $Ca^{2+}$ are based on what the measurement shows. $Mg^{2+}$ measurements were above LOD, with similar trends (spatial and seasonal) to $Na^+$, so a discussion on seasonal cycle for Mg is warranted. In the case of $Ca^{2+}$, uncertainties in interpretation of the $Ca^{2+}$ data is discussed.

*17) p17 and beyond, general comment on sections 3.5-3.6: a linear regression is fitted to all datasets from 1999 through 2015, but looking closely at the 15-yr time series for the 12 sites (eg Fig. 12-13), for HNO3, NO3-, SO4=, NH4+, NH3, it appears that concentrations were rather stable (with some interannual variability but no trend) in the period 2000-2007, and then only started declining after 2007. The only exception is SO2 with a continuous decline all the way. Fitting a linear trend is helpful to quantify an multi-annual rate of decrease (which is what you do), but is not an accurate representation of the time course of concentrations. Can you think of any plausible explanation for a change of course around the year 2007: change or implementation of pollution control policies? Decadal change in weather patterns? It might be useful to show (in the supplement)a summary of weather patterns for all sites of the network, the 15-yr time course of temperature, rainfall, wind speed etc.*

**Author Response:**

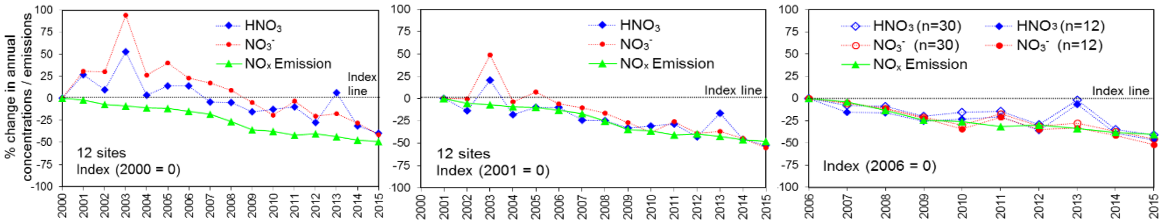
"Section 3.8 Assessment of trends in relation to UK emissions" has been revised and expanded to include a more thorough discussion of trends under new sub-headings.

3.8.1 Trends in $HNO_3$ and $NO_3^-$ *vs* $NO_x$ emissions
3.8.2 Trends in $SO_2$ and $SO_4^{2-}$ *vs* $SO_2$ emissions
3.8.3 Trends in HCl and $Cl^-$ *vs* HCl emissions
3.8.4 Trends in $NH_3$ and $NH_4^-$ *vs* $NH_3$ emissions
3.8.5 Changes in UK chemical climate

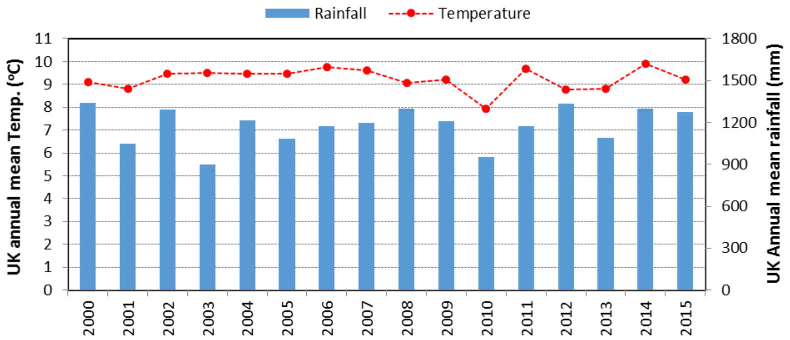
Revised/expanded text:

"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 emission 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 (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 inter-annual variability and in particular are dominated by the large 2003 peak in concentrations (see sect. 0). Variability in the annual data thus highlights the sensitivity of the trend 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 line 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 $NO_3^-$ using mean data from 12 or 30 sites were not significantly different and emissions and concentrations trends followed each other closely.“



Regarding the reviewers comment on the possibility of change in weather patterns to explain the apparent biphasic trend, the UK annual average temperature and rainfall (https://www.metoffice.gov.uk/climate/uk/summaries) show no overall trend in the 16 years of climate data between 1998 and 2015. 2010 was however an unusual year, with a lower than average mean annual temperature of 7.9 °C due to an exceptional cold winter, with Dec 2010 recorded as the coldest for over 100 years (cf. 9.2 °C average for 2000 to 2015) and lower than average rainfall of 950 mm (cf. 1180 mm average for 2000 to 2015). Graph of UK annual mean temperature and rainfall has been added to supplementary materials.



*In terms of implementation of pollution control policies that could explain the change in course of the pollutant trend concentrations*:

In 2007, the designation of Nitrate Vulnerable Zones (NVZs) in the UK was introduced to strengthen the range of measures in the Nitrates Action Programme under the Nitrates Directive (91/676/EEC). NVZs are areas designated as being at risk from agricultural nitrate pollution and farms within NVZs must comply with the rules laid down on use of nitrogen fertiliser and storage of organic manure. Adoption of NAP by farms will also likely reduce emissions of $NH_3$. $NH_3$ data from the 12 sites in AGANet were stable from 2000-2010 and decreased between 2010 and 2012 with concentrations again stabilising after 2012.

It could be surmised that there was more $NH_3$ before 2007 to react with the acid gases and form / maintain higher concentrations of aerosols. But it has also to be borne in mind that the period between 2000 and 2007 was subject to a pollutant episode in 2003 and the data, as you also pointed out, is extremely variable. The apparent change in course of pollutant concentrations in $NO_3^-$ and $SO_4^{2-}$ is more likely due to influences of import from long range transboundary pollutant transport and meteorology.

*18) p18, l6: '...The long-term time series in annually averaged concentrations of the gas and aerosol components are shown in Figure 12a and Figure 12b...': would it be possible to show, alongside the measured DELTA time series, the modelled NO/NO2 time series (from a CTM, eg EMEP4UK) for the same sites? In a way this would account for both NOx emission changes as well as climatic variability over the period.*

**Author Response:**
Dr Massimo Vieno (CEH) is currently working on a paper comparing EMEP4UK with measurement data from NAMN and AGANet.

$NO_2$ concentrations is however measured at rural sites across the UK in the UKEAP NO2-net ($NO_2$ diffusion tube network), some of which are co-located with the AGANet. The network average in annual mean $NO_2$ concentrations showed a downward trend, decreasing from ~8 µg $NO_2$ $m^{-3}$ in 2000 to ~ 4 µg $NO_2$ $m^{-3}$ in 2015 (Conolly et al. 2016).

In terms of climatic variability from the UK, there is no apparent trend in the UK rainfall and temperature data (see earlier response to comment 17).

Additional text added in section 3.8.1 Trends in $HNO_3$ and $NO_3^-$ *vs* $NO_x$ emissions, end of last paragraph.

A comparison of the network averaged $NO_2$ concentrations with $NO_x$ emissions by Conolly et al (2016) showed matching decreasing trends between 2000 and 2015, with annual mean $NO_2$ concentrations falling 2-fold to 4 µg $NO_2$ $m^{-3}$ in 2015 (Conolly et al. 2016). Although there is uncertainty in the corrected $HNO_3$ data (see section3.3), the encouraging agreement between $HNO_3$, $NO_2$ concentrations and $NO_x$ emissions lends support to a linear response in $HNO_3$ concentrations to reductions in $NO_x$ emissions.

*19) p18, l12 '...The exceptions are Na+ and Cl- that have higher mean concentrations...' : Na+ is not shown in Fig.12.*

**Author Response:**
Mean concentration of $Na^+$ from 12 and 30 sites are compared in Table 4.
Table 4 inserted at the end of the sentence:
"The exceptions are $Na^+$ and $Cl^-$ that have higher mean concentrations from the 30 sites than the original 12 sites (Table 4)."

*20) Figures 13, 14: use only one type of regression to simplify the figures (LR and MK give almost identical results)*

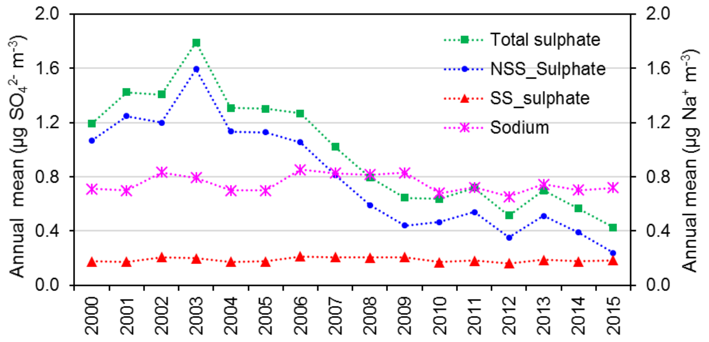
**Author Response:**
Figures 13 and 14 have been amalgamated into one single figure, with LR analyses taken out and moved to supplementary materials.

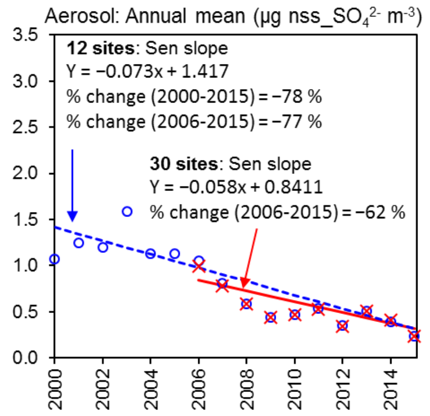
*21) p20, l24-25 '...the reduction in SO2 emission and measured concentration is accompanied by a smaller negative trend in particulate SO4=...', and l27, '...The smaller decrease in particulate SO4= compared with its gaseous precursor, SO2, is similar to that observed at Eskdalemuir...'. Question: Is the smaller reduction rate in SO4= (compared with SO2) a reflection of the fact that increasingly in the UK, total sulphate includes a larger and larger fraction of marine sulphate, such that the decrease in anthropogenic SO4= (resulting from SO2 abatement) has a increasingly small effect on total sulphate?*
*Is it possible to re-calculate the SO4= trend separately for coastal and inland (eg Midland/London) sites?*

## Author Response:

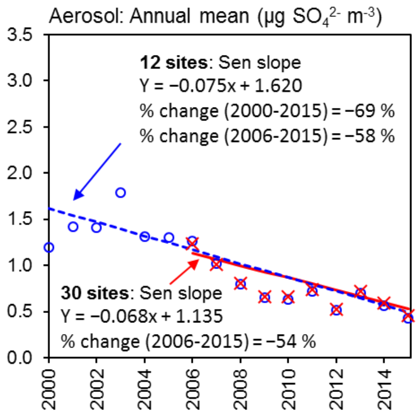
Additional text added in "section 3.8.2 Trends in $SO_2$ and $SO_4^{2-}$ vs $SO_2$ emissions" to discuss sea salt $SO_4^{2-}$ (SS_SO4) – see below:

"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 to the empirical equation 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 trend in the long-term annual mean SS_SO4 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 either, 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 (Tables 4 and 5) showed decrease in concentrations of –78 % (2000-2015) 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 $SO_2$."





NSS_SO4



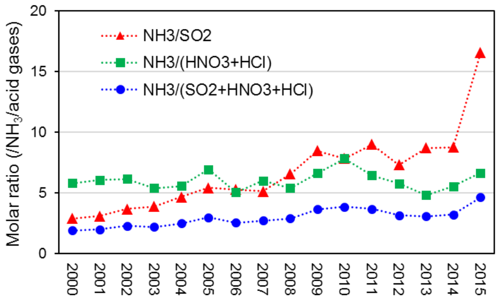
Total SO4

*22) p21, l5-22: The argument about the NH3/SO2 ratio impacting the dry deposition velocities of SO2 and NH3 was developed in the 1980s and early 1990s, when SO2 concentrations were still very large in W. Europe. It is no longer sufficient to consider the NH3/SO2 ratio alone, since SO2 no longer massively dominates the acid load in W. European atmospheres. Instead, the ratio NH3/(2*SO2 + HNO3 + HCl) should be computed to analyse long terme trends, as shown in Fowler et al. (Atmospheric Environment 43 (2009) 5193–5267, see Fig. 4.5). It is the combined effects of all acids and NH3 that determines the pH of cosystem/vegetation surfaces and hence their sink strength for water-soluble pollutants.*

**Author Response:**

Additional analysis of the change in molar ratios of $NH_3$ to acid gases and molar ratios of $NH_4^+$ to $NO_3^-$ and $SO_4^{2-}$ with time has been carried out – new figure added in manuscript: 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.

1)



Long-term changes in the molar ratio of $NH_3$ to acid gases ($SO_2$, $HNO_3$ and HCl) between 2000 and 2015 from measurements made at 12 sites in AGANet.

Revised/expanded text added, replacing text on *p21, l5-22*

"3.8.5 Changes in UK chemical climate"

"Past studies have shown that the increasing ratio of $NH_3$ to $SO_2$ in the atmosphere leads to enhanced 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, is 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 (Fowler et al., 2009).

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 molar concentrations of $NH_3$ (80 nmol m$^{-3}$) to $SO_2$ (29 nmol m$^{-3}$) was 2.7 in 2000, which increased in 2015 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, the decrease in NSS_SO4 (−78%) is similar to $SO_2$ (−81%) which would suggest that maximum deposition rates for $SO_2$ may have been reached with the smaller $SO_2$ concentrations since 2000."

*23) p21, l30: '...The increase in ratio of HNO3:NO3- is similar to changes in upward trend in gas-aerosol partitioning between NH3 and NH4+ over time...': what do you call similar? For HNO3/NO3-, the ratio increases by _20%, while for NH3/NH4+, the ratio increases by 100% (according to Fig. 18) ?*

**Author Response:**

Apologies for the ambiguity in the sentence. I simply meant that both sets of data ($HNO_3$:$NO_3^-$ and $NH_3$:$NH_4^+$) show an upward trend.

Text revised/expanded in section 3.8.5. Changes in UK chemical climate, paragraph 5.

"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 $HNO_3$. 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 5) and the increase in gas to aerosol ratios ($NH_3$:$NH_4^+$ and $HNO_3$:$NO_3^-$) over the 16 year period (Figure 17). A higher concentration of the gas-phase $HNO_3$ and $NH_3$ may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in $NO_x$ and $NH_3$. 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. "

*24) p22, l11-12, '...a change in the particulate phase from (NH4)2SO4 to NH4NO3. This change is expected to increase residence times of NH3 and HNO3 in the atmosphere...'I am not convinced the shift from ammonium sulphate to ammonium nitrate should increase the residence time, since NH3 and HNO3 will deposit faster (higher deposition velocities) than either aerosol form?*

**Author Response:**

See revised/expanded text in "section 3.6. Seasonal variation in acid gases and aerosols"

Specifically:

"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**Error! Reference source not found.**). $NH_3$, the main neutralising gas in the atmosphere that reacts with $HNO_3$ to form $NH_4NO_3$, 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 9). 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 $NH_4NO_3$, 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 $NH_4NO_3$, when the concentration product $[NH_3].[HNO_3]$ exceeds equilibrium values, with $NH_4NO_3$ serving as a potential reservoir for the gases. **Since $NH_4NO_3$ 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."

*25) p22, l12 '...expected to increase residence times of NH3 and HNO3 in the atmosphere...' and p22, l15 '...NH3 and NOx emitted will deposit more locally with a smaller footprint...': these two statements appear to contradict each other?*

**Author Response:**

See response to comment 23 above and response to comment 26 after this.

*26) p22, l12: perhaps another way to analyse this trend is to calculate the (changing) linear regression slopes of NO3- vs NH4+ and SO4= vs NH4+, for each year of the 2000-2015 period (as in Fig. 6b), and examine how the two slopes change over time, as an indicator of the fraction of the total NH4+ that neutralizes NO3- and SOA= and its trend over time.*

**Author Response:**

New 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.

Text revised/expanded in section 3.8.5. Changes in UK chemical climate (paragraph 3)
Specifically:
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.

*27) p24, l14 '...Higher concentrations of the NH3 and HNO3 in the atmosphere will deposit more locally...' But then, NH3 and HNO3 concentrations are actually decreasing; they are not higher than before?*

**Author Response:**

Text revised/expanded in section 3.8.5. Changes in UK chemical climate (paragraph 5)
"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 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 their gaseous precursors ($NH_3$: MK −30% between 2000-2015, n=12 and $HNO_3$: MK −45 % between 2000-2015, n=12) (Table 5) and the increase in ratios of $NH_3$:$NH_4^+$ and $HNO_3$:$NO_3^-$ over the 16 year period (Figure 15). **A higher concentration of the gas-phase nitrogen species ($HNO_3$ and $NH_3$) may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in $NO_x$ and $NH_3$.** Given the larger deposition velocity of $NH_3$ and $HNO_3$ compared to particulate $NH_4^+$ and $NO_3^-$, more of the $NH_3$ and $HNO_3$ emitted will have the potential to deposit more locally with a smaller footprint within the UK."

*28) Technical Corrections*
*Units: different units are used. They should either be harmonized, or else each figure should state explicitly what the unit is, especially for the difference between element (N,S) based or molecule (HNO3, SO2) based. For example, mean HNO3 at the Bush site is reported as 0.55 µg m-3 in Fig.2 (average of 0.54 and 0.56 for samplers A and B), while the color code on the concentration map (Fig. 5) indicates a concentration in the range 0.15-0.25, from which I infer that Fig.2 is µg HN03 m-3, while Fig.5 is µg N m-3 ? Similarly, p12, l16, is the Cromwell site HNO3 concentration 1.3 µg HNO3 m-3, or 1.3 µg HNO3-N m-3? From Figure 5 I expect it is the latter (N, not HNO3 as written in the text). Further below, are the SO2 concentrations at Sutton Bonington given as µg SO2 m-3, or in fact µg SO2-S m-3 ? Given that the map in Fig. 5 gives numbers in µg N or µS per m3, it would be good to use the same units. Thus I would recommend to check carefully throughout the text in this paragraph and in the whole paper and make the necessary text changes to eliminate the ambiguity in units.*

**Author Response:**
Thank you – checked and corrected.

*29) p4, l26-27, delete '...that is also deployed at some CASTnet sites (Rumsey and Walker, 2016).' (already mentioned same page, l14)*
**Author Response:**
OK – deleted.

*30) p4, l32, suggest change 'temporal' to 'seasonal'*
**Author Response:**
OK. Changed 'temporal' to 'seasonal'

*31) p5, l9-12: this mostly repeats what was said in the introduction p4, l20-25*
**Author Response:**
OK – sentence below deleted.

~~"Since 2009, the AGANet, together with the NAMN (monthly $NH_3$ and $NH_4^+$), Precip-net (2-weekly wet deposition measurements) and $NO_2$-net (4-weekly $NO_2$ concentrations) were unified under the UKEAP network to provide long-term measurements of eutrophying and acidifying atmospheric pollutants (Conolly et al., 2016)."~~

*32) p7, l20, please provide the equation for the calculation of the denuder capture efficiency*
**Author Response:**
Calculation of denuder capture efficiency is described in "section 4 Calculation of air concentrations"
"The denuder capture efficiency for each of the gas is calculated by comparing the concentrations of the individual gases in the denuder pairs"

Equation is now also provided:

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

*33) p35: Figure 2 contains scatter plots and a statistical summary table for the Bush DELTA intercomparison (parallel sampling). It would be good to adapt the same or similar style of display for the other intercomparisons (scatter plots + stats table). Thus for the comparison with ADS (2.7.2), take Fig. S2 out of the supplement and stack it above the statistics given in Table 2. Similarly for the intercomparisons of DELTA vs EMEP TIA/TIN (add statistical table), as is already also done for DELTA vs Bubble/FP Eskdalemuir (Fig 4).*

**Author Response:**

Thank you for suggestions:
Fig S2 and Table 2 combined into Figure 2
Figure 3 (DELTA vs EMEP TIA/TIN), summary stats table added.

There are now however quite a large number of figures.

*34) p11, sections 2.8 and 3.6: throughout the time series trend analysis, both linear regressions and non-parametric MK tests are used, but as far as I can see, there is essentially no difference between the slopes for any of the pollutant time series. To improve readability and reduce unnecessary redundant information, I would suggest to stick to just one of the methods; it would suffice to say in the methods that both regressions were used and no significant differences were found, and thus henceforth only one regression is displayed.*

**Author Response:**
Thank you for the suggestion.
Figures 13 and 14: graphs with both linear regression and MK analyses moved to supplementary materials. Replaced by a single Figure 14 showing results of MK analysis only for both time series.

Tables 5 and 6: summary tables comparing LR and MK moved to supplementary section. Replaced by a single Table 4 showing results of MK analysis only for both time series.

Additional text included at end of <section 2.8 Time series trend analyses
"…but 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 (Figures S7, S8 and Tables S4 - S6). "

*35) p12, l22, '...A peak MONTHLY concentration of...'*
**Author Response:**
Thank you – corrected

*36) p12,l28, '...expected to be more SPATIALLY homogeneous...'*
**Author Response:**
Thank you – corrected

*37) p15, l19 '...in summer promotes AEROSOL dissociation...'*
**Author Response:**
Thank you – corrected

*38) p17, l12 change to '...are available SINCE 1989...'*
**Author Response:**
Thank you – corrected

*39) p18, l31, '...To QUANTIFY changes...'*

**Author Response:**

Thank you – corrected
(paragraph moved to section 2.7 Time series trend analyses)

*40) p18, l32, the unit for the annual trend is µg HNO3-N m-3 y-1*

**Author Response:**

The unit is for annual trend is µg $HNO_3$ $m^{-3}$ $y^{-1}$
Units used in trend analysis are on a molecule basis

*41) p19, l3: '...The LR % annual trends for each time series...' Delete 'annual', since the % reduction are not expressed per year, but over the whole period ? Note that if the concentration reduction were a constant percentage every year, say -10% per year, then the overall time course over 15 years would not look linear, but exponential: if yr1=100, then yr2=90, yr3=81, yr4=72.9, yr5=65.6, ...yr15=20.6*

**Author Response:**

Thank you - text corrected:

"The LR and MK % change in annual mean concentrations for the two time series are estimated from the slope and intercept…."

*42) p19, l6: same as above, delte 'annual'*

**Author Response:**

Thank you - equation corrected:

$$\% \text{ change} = 100 \,.\, \frac{[Yi - Yo)}{Yo}$$

*43) p21, l17-18 '...The dry deposition... IS known to be enhanced...'*

**Author Response:**

Thank you - corrected

*44) p23, l9, delete 'from coal combustion'*

**Author Response:**

Thank you - deleted

*45) p24, l1, '... modest reductionS in HNO3...' (plural)*

**Author Response:**

Thank you - corrected

*46) p24, l12, '...smaller THAN emission trends...'*

**Author Response:**

Thank you – corrected

*47) All figures: when the units displayed on axes or legends are given in µg m-3, please specify whether this is on an element basis (NH3-N, HNO3-N, SO2-S) or molecule basis (NH3, HNO3, SO2)*

**Author Response:**

Figure 10a, Y-axis changed to Oxidised N (µg N $m^{-3}$)
Figure 10b, Y-axis changed to Reduced N (µg N $m^{-3}$)
Figure 11, Y-axes changed to $SO_2$ (µg S $m^{-3}$) and $SO_4^{2-}$ (µg S $m^{-3}$)
To show more clearly that the units are on an element basis ($NH_3$-N, $HNO_3$-N, $SO_2$-S, etc.)

All other figures are on a molecule basis ($NH_3$, $HNO_3$, $SO_2$, etc)– axis and legends should be correct.

*48) Figure 8: "...Average annual cycles in the ratios of gas:aerosol component concentrations (µg m-3)...' The unit for the ratio is not µg m-3, it must be dimensionless, or mol mol-1?*

**Author Response:**

The Y axis label on the graphs are dimensionless.
In the figure caption, (µg $m^{-3}$) is the unit of gas and aerosol concentrations that are compared. As this is causing confusion, the caption in Figure 8 (now Figure 9, because Suppl. Figure S2 added as Figure 2) has been revised to:

"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 $m^{-3}$) are from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) measured at the same time. Each data point in the graphs represents the mean ± SD of monthly measurements of 12 sites operational in the network over the period 2000 to 2015.

*49) Figures 13-14: keep only one of the two trend lines (LR or MK); and delete Fig.14 but add the n=30 datapoints to Fig. 13 as a different symbol shape or color*

**Author Response:**

Figures 13 – 14 replaced with a single figure as suggested by reviewer above.

*50) Figure 18: the left-hand side panels show the same data as Figs. 13-14 and should therefore not be repeated here.*

**Author Response:**

The left hand panels provides a direct comparison of the concentrations and trends of each of the gas and aerosol pairs ($HNO_3$/ $NO_3^-$, $SO_2$/$SO_4^{2-}$ etc.).
The author agrees with the reviewer that the left hand panels shows the same data as Figures 13 and 14 and they have been removed.

Interactive comment on Atmos. Chem. Phys. Discuss., doi.org/10.5194/acp-2018-489, 2018

## RESPONSE TO REVIEWER 2

**Anonymous (Referee)**

The authors thank reviewer 2 for his constructive comments and for taking the time to look at all the details described in the manuscript. We have carefully considered all comments. Please refer to the specific responses.

### General comments

1. *Currently the manuscript is primarily focused on documenting trends and events and with a smaller focus on the changes in atmospheric composition and pollutant fate due to changes in emissions. This manuscript would benefit from a bit more focus. I suggest focusing more on the trends and how they relate to emission changes and less on specific events captured in the data.*

**Author Response:**

Section 3.8 Assessment of trends in relation to UK emissions" has been revised and expanded to include a more thorough discussion of trends under new sub-headings.

3.8.1 Trends in $HNO_3$ and $NO_3^-$ *vs* $NO_x$ emissions
3.8.2 Trends in $SO_2$ and $SO_4^{2-}$ *vs* $SO_2$ emissions
3.8.3 Trends in HCl and $Cl^-$ *vs* HCl emissions
3.8.4 Trends in $NH_3$ and $NH_4^-$ *vs* $NH_3$ emissions
3.8.5 Changes in UK chemical climate

Discussion on specific events captured in the data have not been revised/truncated as they are important for interpreting anomalies in the trends.

2. *The discussion of the trends of NH3 and HNO3 are sometimes a bit difficult to follow as the change in aerosol composition and loading over the time frame of the measurements impacts the gas phase concentrations. Consider discussing these trends as total nitrate (gaseous HNO3 + aerosol NO3) and NHx (gaseous NH3 + aerosol NH4).*

**Author Response:**

Interactions and partitioning between the gas phase ($SO_2$, $HNO_3$, $NH_3$) and aerosol phase ($SO_4^{2-}$, $NO_3^-$, $NH_4^+$) are important drivers for concentrations and trends in the respective components. Discussion of the gas phase and particulate phase atmospheric components for oxidised and reduced nitrogen, rather than total inorganic nitrate (TIN, sum of gaseous $HNO_3$ + aerosol $NO_3^-$) and total inorganic NHx (TIA, sum of gaseous $NH_3$ + aerosol $NH_4^+$) allows a clearer understanding of the processes occurring in the atmosphere, which drive trends and environmental effects. TIN and TIA is only considered in the manuscript for comparing DELTA with EMEP filter pack measurements at Eskdalemuir.

The expanded "Section 3.8 Assessment of trends in relation to UK emissions" (see response to your comment 1 above) should hopefully provide a clearer discussion on the change in gas and aerosol composition and their interactions in a changing chemical climate.

3. *There are lots of small sections in this manuscript, some consisting of single sentences. Consider combining them into more general sections. Specifically, 2.3.1-2 and 2.5-6.*

**Author Response:**

Following your suggestion:
"*2.3.1 Base coated denuders and filters" and "2.3.1 Acid coated denuders and filters"* combined into a single section "2.3.1 Chemically coated denuders and filters"

*"2.5 Data Quality Control" and "2.6 Bias correction applied to $HNO_3$ data"* have not been combined as they cover different aspects.

4. *Many sentences leading paragraphs are structured as "For {atmospheric constituent},. . .". This is a bit formulaic and the authors may want to revise these sentences.*
**Author Response:**
Thank you. We have gone through and revised where appropriate.

**Specific comments**
1. *Abstract: I find the final two sentences of the abstract to be the most compelling. There is a lot of detail, primarily on page 1, that would be better suited for the results section. Consider summarizing the text on the spatial and temporal trends and better connecting them to the changes in atmospheric HNO3 and NH3.*
**Author Response:**
Text revised in abstract.

2. Abstract Page 2 lines 5-6: ". . . indications that the atmospheric lifetime of HNO3 and NH3 has increased . . .". This does not seem correct to me. The lifetime of these gases has not increased but rather the phase/composition of these species have. There are now more gaseous and less aerosol bound NO3 and NH3 due to changes in SO2. This likely decreases the atmospheric lifetime of total nitrate and reduced nitrogen compounds as NH3 and HNO3 typically dry deposit faster than aerosol NO3 and NH4.

**Author Response:**
See also response to Reviewer 1 (comment 32).

Text revised in abstract:

"Since 1999, AGANet has shown substantial decrease in $SO_2$ concentrations relative to $HNO_3$ and $NH_3$, accompanied by large reductions also in the aerosol components, with evidence of a shift in the particulate phase from $(NH_4)_2SO_4$ to $NH_4NO_3$. The potential for $NH_4NO_3$ to act as a reservoir for $NH_3$ and $HNO_3$, together with the surfeit of $NH_3$ means that a larger fraction of the nitrogen is remaining in the gas phase, maintaining higher concentrations of $NH_3$ and $HNO_3$ in the UK. …"

3. Page 4 lines 17-29: This paragraph contains similar information as the previous paragraph. Consider combining it with the previous paragraph
**Author Response:**
See below (replicated information deleted):
Page 4 lines 17-29: "testing, but the high costs and resources required for these measurements make them unsuitable for the assessment of long-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 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) ~~that is also deployed at some CASTnet sites (Rumsey and Walker, 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. "

Page 5, lines 9 – 12 deleted (repeat of what has already been written on Page 4 lines 17-29)
~~"Since 2009, the AGANet, together with the NAMN (monthly $NH_3$ and $NH_4^+$), Precip-net (2-weekly wet deposition measurements) and $NO_2$-net (4-weekly $NO_2$ concentrations) were unified under the UKEAP network to provide long-term measurements of eutrophying and acidifying atmospheric pollutants (Conolly et al., 2016)."~~

4. Page 6 lines 21-22: This is an awkward introductory sentence for this paragraph. Consider revising or adding an introductory paragraph that introduces the importance of the denuder base coating.

**Author Response:**
Revised text
Page 6 lines 21-22: "For the base coating, $K_2CO_3$ is used instead of $Na_2CO_3$ (Ferm et al., 1986) to sample acid gases so that the system can also measure aerosol $Na^+$ concentrations. Glycerol increases adhesion, stabilizes the base coating (Ferm, 1986; Finn et al., 2001)……"

Revised to:
"Sodium carbonate ($Na_2CO_3$) is an effective sorbent for acid gases, allowing simultaneous collection of $HNO_3$, $SO_2$ and HCl on denuders (e.g. Ferm 1986). Since the measurement of aerosol $Na^+$ is also of key interest in AGANet however, a potassium carbonate ($K_2CO_3$) coating is used instead to eliminate the possibilities of $Na^+$ contamination from $Na_2CO_3$. Glycerol is added to the $K_2CO_3$ coating, as it increases adhesion…….,"

5. Sections 2.5: Are data that failed the quality checks removed from the analysis?
**Author Response:**
Sections 2.5 Data Quality Control
"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."

Data failing the above quality check are not automatically removed from analysis.

Air flow rates:
The air pumps used are relatively stable, at 0.2 – 0.4 l $min^{-1}$. If a low air flow rate is due to temporary loss of power and/or air pump issue, the data is accepted provided that the flow rate does not drop below 25% of the normal range. The data is flagged as valid (EMEP data flag), but has higher uncertainty. If low air flow rate is due to a leak or obstruction (e.g. kinking of tubing), the data is rejected.

Denuder capture efficiency:
Two denuders in series are used for every sample to check capture efficiency for reactive gas: two carbonate denuders for capture of $HNO_3$, $SO_2$ and HCl and two acid coated denuders for capture of NH3. Samples with < 75% of the total gas captured in the first of the two denuders are accepted but are flagged as valid (EMEP data flag) but has higher uncertainty.

Ion balance checks:
**Ratio of $NH_4^+$ (µeq): ($2*SO_4^{2-}$ + $NO_3^-$) (µeq)**
Expect 1:1 as $NH_3$ neutralised by $HNO_3$ and $SO_2$ ($H_2SO_4$) to form $NH_4NO_3$ and $(NH_4)_2SO_4$
Acceptable range = 0.2 to 3.
Ion balance checks are carried out at site level and in collated file (with regression plots for outliers)
Data are rejected if the ratio is outside the range.

**Ratio of Na (µeq):Cl (µeq).**
Expect 1:1 as Na and Cl aerosols derived mainly from sea salt.
Acceptable range 0.2 to 3.
Ion balance checks are carried out at site level and in collated file (with regression plots for outliers)
Data are rejected if the ratio is outside the range.

6. Section 2.5 iv) What is the criteria to determine anomalies and outlies?

**Author Response:**

Sections 2.5 Data Quality Control

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

This is a screening process carried out for a small number of runs where there was clearly a sampling malfunction. This exclusion includes events such as vandalized or damaged samples, water ingress or equipment/analytical problems (e.g. mix-up between carbonate and acid coated filters).

7. Section 2.6 Line 22: Does the empirical factor used for HNO3 bias correction exhibit any dependence on season, temperature or solar radiation? If the bias is due to oxidants, then I would expect a dependence in the bias on seasonal and environmental parameters.

**Author Response:**

See response to reviewer 1 (comment 1, pages 1 – 2).

8. Page 9 lines 28-29: The mean difference between the measurements are given here but what is the scatter between the measurements and the median difference. A correlation coefficient would provide some information about the scatter and a median difference would indicate how normal the distribution is and if the bias is being driven by high values in one of the measurement techniques.

**Author Response:**

*Page 9 lines 28-29: "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* $m^{-3}$*)."*

Linear regression ($R^2$) is provided in table 2.

Regression plots (DELTA v ADS) were provided in Supplementary materials (Figure S2) – since there were already a lot of figures and tables in the paper.

Supplement Figure S2 and Table 2 has been combined into a single Figure 2 – see response to review 1 (comment 32, page 16).

9. Page 9 line 32: Difference in the instrumentation flow rates and/or inlets could result in the instruments measuring different sized aerosols and my influence the differences in SO4.

**Author Response:**

Page 10 line 3: "A particle size cut-off of around 4.5 µm was estimated for the DELTA air inlet) (Tang et al., 2015)".

Page 10 lines 6 to 7: "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"

ADS size cut-off (cyclone) = 2.5 um @ flow rate of 10 LPM. Note that the cyclone is in front of the aerosol filters, and not at the inlet, as in the case for the URG ADS (http://www.urgcorp.com/index.php/systems/manual-sampling-systems/annular-denuder-system)

10. Page 16 lines 1-2: The peaks in NHx and SO4 in the spring may just be coincidental. The spring time could also be a time in which the aqueous formation pathway of SO4 is at its maximum or the SO2 emissions from heating or transportation may be larger. In the US, the SO4 concentrations typically peak in the summer while the NH3 concentrations peak in the spring.

**Author Response:**
In the UK, $SO_2$ concentrations are highest in winter (January and February) and lowest in summer (June – August). The peak in $SO_4^{2-}$ concentrations however occur in March every year, where peaks in concentrations of $NH_3$ and $NH_4^+$ from measurements made at the same time from the same sites are also observed (please note that the seasonal cycle of ammonia vary, depending on the emission source types in the vicinity of the measurement site, see Tang et al. 2018).
Formation of $SO_4^{2-}$ is largely governed by the availability of $SO_2$ and $NH_3$ to form the stable $(NH_4)_2SO_4$, and the spring peak 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. Import of particulate $(NH_4)_2SO_4$ from long-range transboundary transport also enhances the springtime concentration. In summer, sunny, warmer conditions increases photochemical oxidation of $SO_2$ to $H_2SO_4$ and subsequent formation of sulphate aerosols leading to higher aerosol $SO_4^{2-}$ concentrations in summer than in winter.

Revised/expanded text in "section 3.6 Seasonal variation in acid gases and aerosols (paragraph 5)
"$SO_2$, by contrast, are highest in the winter, with concentrations exceeding summer values on average by a factor of 2 (Figure 8). Increased 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). The spring peak 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 $(NH_4)_2SO_4$."

11. Page 16 Line 5: "Na+ and Cl-" have highest concentrations during winter . . .' Is salt used for the treatment of road surfaces in the Winter in the UK?
**Author Response:**
Yes, indeed rocksalt (NaCl) is used to treat road surfaces in the winter in the UK. About 2 million tonnes are used every year, with most of it going on motorways, trunk roads and main roads.

Aerial salt spray has been shown to increase the concentrations of particulate NaCl in the immediate vicinity of treated road surfaces. For example, a study by Palmer et al. (2004) found that the concentrations of particulate NaCl at the road edge (2m) was 25 - 70% higher than at 10 m away from the road edge, with concentrations at 10 m approaching background NaCl concentrations (*ca*. 35 nmoles $m^{-3}$ from UK AGANet).

Aerial salt spray from treatment of road surfaces in winter is however unlikely to contribute to an increase at regional / national level in the UK. Sources of seasalt aerosol (NaCl) in UK has been shown by high time-resolution measurements (MARGA) in the UK to originate from air masses coming into the UK with the predominant south-westerly winds (seasalt aerosol generated off the atlantic) (pers. comm.).

AGANet sites are all located away from roads, and should not be affected by local seasalt from gritting.

Reference:
Palmer S.C.F, Cape J.N, Truscott A-M, Black H.I.J, Tang Y.S, Swaine, Van Dijk N, Smart S.M, Sutton M.A, Fowler D, Biodiversity in roadside verges: CEH Final Report to SEERAD. 108 pages. 2004.

12. Page 20 line 18: Significant has a specific statistical meaning. I think “larger” would be a more appropriate.
**Author Response:**
Thank you. “significant” replaced with “substantial”

13. Page 21 line 5: “. . . SO2 towards it being dominated by NH3, . . .” This appears to be a bit binary. There are lots of constituents in the air, many of which were note measured here. More context is needed.
**Author Response:**
OK, thanks.
Sentence has been deleted.
Changes in $NH_3$ relative to other acid gases are discussed in section 3.8.5 Changes in UK chemical climate.

14. Page 22 line 12: “expected to increase residence times of NH3 and HNO3 in the atmosphere” If we are in an NH3 limited environment, I can see how this would increase HN4NO3 and how that could increase the atmospheric lifetime of HNO3 as it is partitioned to NO3 aerosols. However, I do not see how this increases the NH3 lifetime. NH3 will preferentially partition with SO4, which is more thermodynamically stable than NH4NO3, this should decrease the lifetime of NH3 if anything as the NH4NO3 will evaporate where the (NH4)2SO4 aerosol would not.

**Author Response:**
See revised/expanded text in “3.8.5 Changes in UK chemical climate (paragraph 5 and 6)”

“At the same time, reduction in emissions of the precursor gases have also led to a lower formation of particulate phase $NH_4^+$, $NO_3^-$ and $SO_4^{2-}$ in the atmosphere and changes in atmospheric composition. Since the affinity of $H_2SO_4$ (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 $H_2SO_4$ to form ammonium sulphate compounds ($NH_4HSO_4$ and $(NH_4)_2SO_4$), with any excess $NH_3$ then available to react with $HNO_3$ and HCl to form $NH_4NO_3$ and $NH_4Cl$ that are volatile. Analysis of the different particulate components in sect. 3.5**Error! Reference source not found.** showed that the ammonium aerosols are mainly made up of (NH4)2SO4 and $NH_4NO_3$. With the large reduction in $SO_2$, more $NH_3$ is available to react with $HNO_3$ to form $NH_4NO_3$ 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 $(NH_4)_2SO_4$ to $NH_4NO_3$ (Figure 18b).

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 $HNO_3$. 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 5) and the increase in gas to aerosol ratios ($NH_3$:$NH_4^+$ and $HNO_3$:$NO_3^-$) over the 16 year period (Figure 17). A higher concentration of the gas-phase $HNO_3$ and $NH_3$ may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in $NO_x$ and $NH_3$. 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. “

15. Figure 8: I am happy to see a measure of scatter on these plots as the SD. However, a 5% and 95% CI would be more informative as it would give the reader an idea about the distribution of the data.

**Author Response:**
The 4 graphs in Figure 8 have been replotted showing the 95% CI (T test).

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

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**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 ranges in site-annual mean concentrations (nmol m$^{-3}$) in 2015 for the gases were:  $HNO_3$: 0.7-17; HCl: 2.4-21; $SO_2$: 0.9-10, while those for aerosol were: $NO_3^-$: 6.3-53; $Cl^-$: 22-89; $SO_4^{2-}$: 2.2-11; $Na^+$: 20-74; $Ca^{2+}$: <lod-2.6; $Mg^{2+}$: 1.3-6.8.~~ 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~~. For~~ HCl are~~,~~ highest ~~concentrations are~~ in the southeast, ~~and~~ 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). ~~The spatial distributions of~~ $Na^+$ and $Cl^-$ are spatially correlated~~were similar~~, with largest concentrations at coastal sites~~ in the south and west and at Shetland~~, reflecting a contribution from sea salt ~~(NaCl) since a near 1:1 relationship was also observed in their concentrations~~. Temporally, peak concentrations in $HNO_3$ ~~and $NO_3^-$~~ occurred in late winter and early spring ~~and early summer, due~~attributed to photochemical processes~~ and transboundary pollutant transport~~. ~~The spring peak in~~ $NO_3^-$ and $SO_4^{2-}$ have a spring maxima that~~concentrations~~ 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, ~~accompanied by~~ large reductions and changes ~~also~~ in the aerosol components~~, with concentrations of $NO_3^-$ and $NH_4^+$ in molar excess over $SO_4^{2-}$. At the same time, a positive trend in $HNO_3$:$NO_3^-$ and $NH_3$:$NH_4^+$ ratios, contrasting with a negative trend in $SO_2$:$SO_4^{2-}$ ratio~~ provides evidence of a shift~~change~~ in the particulate phase from $(NH_4)_2SO_4$ to $NH_4NO_3$~~, with indications that atmospheric lifetime of $HNO_3$ and $NH_3$ has increased~~. 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 (~~Defra, 2017;~~ NAEI, 201~~7~~8). 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 (~~Defra 2017~~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) 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 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, 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.

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). 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 (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). ~~In the UK, the MARGA approach is deployed for continuous hourly measurements at just two sites (Twigg et al., 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-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 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)~~ that is also deployed at some CASTnet sites (Rumsey and Walker, 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., 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. ~~Since 2009, the AGANet, together with the NAMN (monthly $NH_3$ and $NH_4^+$), Precip-net (2-weekly wet deposition measurements) and $NO_2$-net (4-weekly $NO_2$ concentrations) were unified under the UKEAP network to provide long-term measurements of eutrophying and acidifying atmospheric pollutants (Conolly et al., 2016).~~

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~~Figure 1~~, Table 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 ~~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 < $PM_{4.5}$.

~~For the base coating, $K_2CO_3$ is used instead of $Na_2CO_3$ (Ferm et al., 1986) to sample acid gases so that the system can also measure aerosol $Na^+$ concentrations.~~ $Na_2CO_3$ 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~~s~~ adhesion, stabilize~~s~~ the base coating (Ferm, 1986; Finn et al., 2001)~~,~~ and ~~is reported~~ 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.

## ~~Analytical methodology~~

## 2.3 Chemical analysis

### ~~2.3.1 Base coated denuders and filters~~

$K_2CO_3$/glycerol~~Base~~-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 ~~A~~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 ~~T~~tables S1 and S2, respectively.

### ~~2.3.2 Acid coated denuders and filters~~

~~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).~~

## 2.4 Calculation of air concentrations

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

$$\chi a = \frac{Q}{V} \qquad (1)$$

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 ($\chi_{a\ (corrected)}$) according to equation ~~2~~3 (see Sutton et al., 2001b, Tang et al., 2018):

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

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

(~~2~~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.

~~**Bias correction applied to**~~

### 2.6 $HNO_3$ measurement artefact and correction~~data~~

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~~bias~~ 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.

### ~~2.71.1 Performance of the DELTA method~~

#### ~~2.7.11.1.1 Measurement reproducibility~~

~~Replicated DELTA measurements are made at 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 < ± 3 % for all components and ± 6 % for HCl).~~

~~<INSERT Figure 2 HERE>~~

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#### ~~2.7.21.1.1 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 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 $min^{-1}$. For comparison against the monthly DELTA measurements, daily ADS values were averaged to the corresponding monthly periods, with results summarised in Table 2 and Figure S2.~~

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~~For $HNO_3$, the DELTA (mean = 1.56 µg $m^{-3}$, *n* = 11) was on average 23 % higher than the ADS (mean = 1.31 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 bias adjustment factor described in Sect. 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 m$^{-3}$), compared with a significantly higher concentration (mean = 0.41 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 (see graph in supp. Figure S2). 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.~~

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~~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$^{-3}$) (Table 2). $NO_3^-$ 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). For $SO_4^{2-}$, some will be coarse mode sea salt $SO_4^{2-}$ (see section 3.3). A particle size cut-off of 4–5 µm was estimated for the DELTA air inlet) (Tang et al., 2015), which would suggest that 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, which confirms 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.~~

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### ~~2.7.31.1.1 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). For assessment of oxidised and reduced nitrogen species, the daily EMEP filter pack method are implemented at 39 sites across Europe (Colette et al., 2016; Tørseth et al.,~~

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

~~**<INSERT Figure 3 HERE>**~~

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~~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 3 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 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).~~

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### ~~2.7.4~~1.1.1 ~~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 4). 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 4). 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-~~

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~~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 4 HERE>~~

### ~~2.8~~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

~~**Measurement reproducibility**~~

This section presents the performance of the DELTA measurements, including a comparison with other air sampling methods and networks. Replicated sampling with the DELTA me~~asurements~~thod were~~are~~ also made to assess measurement reproducibility and this is shown for example for ~~at~~ the Bush OTC site in Scotland (UKA00128). A comparison of the parallel measurements (Figure 2~~Figure 2~~) showed good reproducibility in the method, with close agreement for all components (e.g. mean difference of < ± 3 % for all components and ± 6 % for HCl).

**<INSERT ~~Figure 2~~ Figure 2 HERE>**

### 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 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~~For~~ compar~~ison~~e against the monthly DELTA measurements, daily ADS values were averaged to the corresponding monthly periods, with results summarised in ~~Table 2 and Figure S2~~ Figure 3.

**<INSERT ~~Table 2~~ Figure 3 HERE>**

In the measurement of gases, ~~For~~ $HNO_3$~~,~~ determination on ~~the~~ 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 ~~bias adjustment~~ factor described in ~~S~~sect~~.~~ion 2.6~~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 (~~see graph in supp. Figure S2~~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

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(DELTA = 2.10 *vs* ADS = 2.74 µg $SO_4^{2-}$ $m^{-3}$) (~~Table 2~~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 ~~. For~~ some of the $SO_4^{2-}$ ~~, some~~ will be coarse mode sea salt $SO_4^{2-}$ (see section ~~3.3~~ 3.5). A particle size cut-off of 4~~–~~.5 µm was estimated for the DELTA air inlet) (Tang et al., 2015), so~~which would suggest that~~ 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, ~~which~~ confirm~~s~~ing 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 ~~For~~ daily filter pack method continues to be implemented at 39 sites across Europe for assessment of oxidised and reduced nitrogen species~~, the daily EMEP filter pack method are implemented at 39 sites across Europe (Colette et al., 2016; Tørseth et al., 2012)~~, 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~~Figure 3~~ 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~~Figure 3~~ 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, $R^2$

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= 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~~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~~Figure 4~~). 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~~Figure 4~~). 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~~

### ~~3.1~~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 (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

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(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).

### 3.3 Uncertainties in $HNO_3$ determination

$HNO_3$ data were corrected for sampling artefacts in the DELTA method with an empirical correction factor of 0.45 (see Sect. 2.6). Interferences in $HNO_3$ 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 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 $HNO_3$ 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 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 $HNO_3$” signal from the carbonate coated denuders will also be dependent on the relative concentrations of $HNO_3$ 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 $K_2CO_3$/glycerol coated denuder to collect $SO_2$. At three sites (Auchencorth, Bush OTC and Stoke Ferry), parallel measurements of the old configuration (two $K_2CO_3$/glycerol coated denuders) and new configuration (two NaCl coated denuders + $K_2CO_3$/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 $K_2CO_3$ denuder are assumed to come from other oxidised nitrogen species and are not reported. Comparing the sum of nitrate concentrations from the new (2xNaCl + 1x$K_2CO_3$) with the old (2x$K_2CO_3$) 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 2x$K_2CO_3$ 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 $K_2CO_3$ coated denuders. Initial analysis of 2016 data (unpublished data) showed that the mean ratio of nitrate on NaCl:$K_2CO_3$ 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.

### ~~3.2~~3.4 Spatial patterns in relation to pollutant sources and transport

In Figure 6, ~~T~~the spatial patterns for each of the gas and aerosol components measured are shown in the annual maps for the example year 2013 ~~(Figure 5)~~. 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.

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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~~higher~~ 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~~Figure 5~~ HERE>**

~~For~~ HCl are mostly emitted from coal combustion and ~~,~~ the highest concentrations are in the source areas in the southeast and southwest~~ of England~~, and also in central England (north of Ratcliffe-on-Soar power station). There is also a ~~that may be attributed to dual contribution from anthropogenic (coal combustion) and~~ marine source~~s~~ for HCl formed by the ~~(~~reaction of sea salt with $HNO_3$ and $H_2SO_4$ ~~to form HCl)~~ (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 ~~in the south (Barcombe Mills) and west (Yarner Wood)~~ Goonhilly in southwest England and ~~at~~ 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). ~~For~~ $Mg^{2+}$~~,~~ 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 $m^{-3}$)~~, but the spatial distribution is similar to $Na^+$ and $Cl^-$ and suggests that it may be in the form of $MgCl_2$~~. There is however no clear spatial pattern for $Ca^{2+}$, but since ~~with~~ concentrations ~~that~~ 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~~Figure 5~~), due to the close coupling between species from the formation of particle phase $(NH_4)_2SO_4$ and $NH_4NO_3$ (see next section).

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### ~~3.3~~3.5 Correlations between gas and aerosol species

Correlations plots between the gas and aerosol phases of the different components are shown~~ummarised~~ in Figure 7, with ~~Figure 6~~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, ~~For $HNO_3$ and $SO_2$,~~ the~~re~~ significant ~~is a stronger~~ 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) ~~which~~ may be related ~~due~~ 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 6~~ Figure 7 HERE>**

**<INSERT Table 2 HERE>**

In~~For~~ 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 6~~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×$SO_4^{2-}$) 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 ~~3~~4 and ~~4~~5, respectively (Keene et al., 1986; O'Dowd and de Leeuw, 2007).

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[nss_SO4] = [$SO_4^{2-}$] - (0.25 x [$Na^+$]) (~~3~~4)

[nss_Cl] = [$Cl^-$] - (1.80 x [$Na^+$]) (~~4~~5)

Applying Equation ~~3~~4 to the $SO_4^{2-}$ data in~~ Figure 6~~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_$SO_4$ *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)~~Figure 6)~~. 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 $NH_4^+$.

~~For $Cl^-$ (mean = 1.3 µg m$^{-3}$, *n* = 188), e~~Estimated nss_Cl concentrations according to Equation 4 was however~~ere~~ 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.

### ~~3.4~~3.6 Seasonal variation ~~Temporal trends~~ 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~~Figure 7~~. Clear differences are observed in these seasonal cycles, influenced by local to regional emissions, climate, meteorology and photochemical processes.

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~~The seasonal cycle for $HNO_3$ and $NO_3^-$ has a maximum in spring (Figure 7).~~ $HNO_3$ 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). ~~In spring, the peak in $HNO_3$ and $NO_3^-$ concentrations~~ A weak seasonal cycle is observed in $HNO_3$, with slightly higher concentrations in late winter and early spring that may be attributed ~~are due~~ to ~~i)~~ photochemical processes with elevated ozone in spring (AQEG 2009) leading to formation of $HNO_3$ during this period (Pope et al., 2016)~~, and ii) long-range transboundary pollution from Europe, leading to regional enhancement across the UK (Vieno et al., 2014, 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

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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 $^{\cdot}OH$ radicals for reaction with $NO_2$ to form $HNO_3$), masking the true extent in the seasonal profile.

~~The ratio of the concentrations of $HNO_3$ and $NO_3^-$ can also be seen to fluctuate throughout the year; largest in July and smallest in spring (Figure 8) which may be explained as follows.~~ 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 $NH_4NO_3$, 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 ~~An~~ equilibrium that exists between gaseous $HNO_3$, $NH_3$ and particulate $NH_4NO_3$, the latter of which is appreciably volatile at ambient temperatures (Stelson and Seinfeld, 1982). ~~The atmospheric residence times and therefore concentrations of $HNO_3$ and $NH_3$ are strongly dependent on their partitioning between the gas and aerosol phase.~~ 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 $NH_4NO_3$ aerosol, when the concentration product [$NH_3$].[$HNO_3$] exceeds equilibrium values. Since $NH_4NO_3$ 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 $NH_4NO_3$ ~~(Figure 8)~~. 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 $NH_4NO_3$ 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 $NH_4NO_3$ 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, $NH_4NO_3$ concentrations are correspondingly smaller in winter than in spring or autumn.~~this contributes to the winter minimum in $NH_4NO_3$. The low $HNO_3$:$NO_3^-$ ratio in spring-time on the other hand is a result of higher $NO_3^-$, from higher concentrations of the precursor gases $HNO_3$ and $NH_3$, and 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).~~

**<INSERT ~~Figure 8~~ Figure 9 HERE>**

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~~For~~ $SO_2$, by contrast, are ~~the temporal profile shows~~ highest ~~concentrations~~ in the winter, with concentrations exceeding summer values on average by a factor of 2 (~~Figure 7~~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 8~~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 7~~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~~Figure 7~~) 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 7~~Figure **8**). While sea-salt 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 9~~ 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 9~~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 9~~Figure 10). Meteorological back trajectory analysis

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of the period showed air masses coming across the UK from Europe, and the pollution episode was attributed to the formation and transport of $NH_4NO_3$ 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 $NH_4NO_3$ (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 $NH_4NO_3$, 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.

### ~~3.5~~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 ~~going back to~~since 1989 (Sect.~~ 2.7.3~~3.1.2). In~~ Figure 10~~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 ~~889~~928 to ~~280~~302 kt $NO_2$-N) (~~defra, 2017~~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 1~~0~~3 % reduction in $NH_3$ emissions (from 26~~8~~5 to 2~~4~~31 kt $NH_3$-N) (~~defra, 2017~~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.

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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. ~~2.7.4~~3.1.3) with AGANet $SO_2$ and $SO_4^{2-}$ data (Sep-99 to Dec-15) (~~Figure 11~~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 25~~3~~70 to 12~~0~~6 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.

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### ~~3.6~~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~~shown~~ in Figure 13~~Figure 12~~a and Figure 13~~Figure 12~~b, respectively. Since there was a change in the number of sites during the operation of the AGANet, ~~A~~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~~Table 4~~). 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~~Figure 12~~ HERE>**

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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 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 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.

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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 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 ~~Since there was a change in the number of sites during the operation of the AGANet, statistical trend analyses~~ are compared in Figure 15 and summarised in Table 4 for ~~$HNO_3$, $SO_2$, HCl and particulate $NO_3^-$, $SO_4^{2-}$, $Cl^-$ were performed on annually averaged mean concentrations from~~ 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 2006 to 2015. ~~$NH_3$ and $NH_4^+$ concentrations from the NAMN that were measured at the same time at the AGANet sites were also included for comparison and to aid interpretation of the acid gas and aerosol data.~~ 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.

~~Results of the Linear Regression (LR) and Mann-Kendall (MK) tests (Section 2.8) are summarised in Figure 13 and Table 5 for the original 12 sites (2000 – 2015), and in Figure 14 and Table 6 for the expanded 30 sites (2006 – 2015).~~ To quantify~~assess~~ changes in measured concentrations over time, annual trends (e.g. μg HNO$_3$ m$^{-3}$ ~~-1~~ y$^{-1}$) are~~were~~ estimated from the regression results of the ~~LR and~~ 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 ~~The LR % annual trends for each time series are estimated from the LR's slope and intercept, while the MK~~ % ~~median~~ median change)~~annual trends~~ in the time series are estimated from the MK Sen's slope and intercept (~~e~~Equation ~~5~~6). MK annual trends and % median change are summarised in Figure 15 and Table 4.

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% median~~annual~~ change $= 100\,.\,\frac{[Yi-Yo)}{Yo}$ ~~[~~(~~5~~6~~]~~)

where (*y*$_0$) and (*y*$_\mathrm{i}$) = 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 ~~The long-term trends~~ in the gas and aerosol components~~, based on statistical analysis of monthly mean measurement data,~~ are also shown for comparison in Supp. Figure S~~4~~3 (mean monthly data of 12 sites for period 2000-2015) and Figure S~~5~~4 (mean monthly data of 12 sites for period 2006-2015). MK annual trends and % median change, based on ~~Results of the trend analysis on~~the monthly data (Supp. Tables S~~4~~7, S~~5~~8) were similar to the ~~were similar to trend analysis results of the~~ annual test results~~data~~ (~~Table 5; Table 6~~Table 4). While not discussed further here, since assessment of long-term trends in this paper focusses 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 ~~Figure 13~~ HERE>**
**<INSERT Table 4~~Table 5~~ HERE>**
~~**<INSERT Figure 14 HERE>**~~
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~~Measured concentrations of $HNO_3$ and particulate $NO_3^-$ from the AGANet show a clear significant decreasing trend, although less substantial than for $SO_2$ and $SO_4^{2-}$ (Figure 12). Between 2000 and 2015, $HNO_3$ decreased by 45 % (MK, LR = −42 %), compared with a 2-fold higher reduction of 81% (MK, LR = −84 %) in $SO_2$ concentrations (Table 5). The decrease in $HNO_3$ between 2006 and 2015 from the expanded 30 sites network (−36 % MK, −30 % LR) is similarly half that of $SO_2$ (−60 % MK / LR) over the same period (Table 6). The decrease in $HNO_3$ is accompanied by a slightly larger decrease in particulate $NO_3^-$ (2000-2015: MK = −52 %, LR = −51 %, 2006–2015: MK = −43 %, LR = −39 %) (Table 7). By contrast, the decline in particulate $SO_4^{2-}$ (2000-2015: MK = −69 %, LR = −70 %, 2006–2015: MK = −54 %, LR = −53 %) is smaller than its precursor $SO_2$ and larger than the decrease in $NO_3^-$ (Table 7).~~

~~The formation of both $NO_3^-$ and $SO_4^{2-}$ requires $NH_4^+$ as a counter-ion, which decreased by 62 % (MK, −64 % LR) over the period 2000 – 2015 (Table 5) and by 49 % (MK, −48 % LR) between 2006 and 2015 (Table 6). The decrease in $NH_4^+$ is 2-fold higher than the decline in its precursor $NH_3$ gas (2000-2015 = −30 % MK / LR, 2006-2015 = −18 % MK / −21% LR), and intermediate between that of $NO_3^-$ and $SO_4^{2-}$ (Table 7). For HCl and Cl-, there is a decreasing trend in HCl (2000-2015: MK = −28 %, LR = −26 %, 2006–2015: MK = −24 %, LR = −21 %), but overall there is no detectable trend in particulate $Cl^-$ (Table 5, Table 6).~~

~~**<INSERT Table 7 HERE>**~~
~~**<INSERT Figure 15 HERE>**~~

### 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 (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 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 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. ~~Large decreasing trends in estimated emissions for NO$_x$, and in particular for SO$_2$ continued since monitoring in AGANet began in 1999. NO$_x$ emissions decreased by 58 % between 2000 and 2015, followed closely by a similar reduction in measured HNO$_3$ ( 45 % MK / 42 % LR) and NO$_3^-$ concentrations ( 52 % MK / 51 % LR) over the same period (Figure 15a; Table 7). Results from the trend analysis of 30 AGANet sites between 2006 and 2015 (HNO$_3$ = 36 % MK / -30 % LR, NO$_3^-$ = 43 % MK / 39 % LR) are also consistent with the 41 % decline in NO$_x$ emissions over this period, in agreement with the emissions inventory (Figure 15b; Table 7).~~ Since $HNO_3$~~,~~ is one of the major oxidation products ~~as a secondary product~~ 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 ~~within the country~~ and signals any long-term changes in the atmospheric processing timescales of $NO_x$ over the country. ~~Since the decreasing trends in estimated NO$_x$ emissions and measured HNO$_3$ are similar, there appears to have been no change in the oxidation and processing of NO$_x$ in the atmosphere.~~ $NO_2$ 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>>**

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

Unlike $NO_x$, ~~For $SO_2$,~~ there has been a more significant decline in $SO_2$, both in emissions and measured concentrations during this period (Figure 14~~Figure 16~~). 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, ~~T~~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~~3.5~~) 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.

From the MK trend analysis, the decrease in annual mean $SO_2$ concentrations of –81 % ~~(MK, LR = –84 %) between (~~2000–2015, *n* = 12) ~~(Table 5)~~, and –60 % ~~(MK and LR) between (~~2006 – 2015, *n* = 30) ~~-~~(Figure 15, Table 4~~Table 6~~) are consistent with the substantial reduction of –80 % and –64 % in $SO_2$ emissions over the two overlapping periods, respectively (~~Figure 16; Table 7~~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~~/ –70 % LR~~; 2006-2015: –54 % MK~~/ –53 % LR~~) (~~Table 5; Table 7~~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. ~~3.5~~3.1.3). A similar picture is also seen in Europe, where 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.

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 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) 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 $SO_2$.

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### 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 $NH_3$ and $NH_4^{+-}$ vs $NH_3$ emissions

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~~By contrast,~~ 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 ~~a~~ smaller than the ~~30 %~~ decrease ~~is~~ seen in the annually averaged $NH_3$ concentrations at the 12 AGANet sites (2000-2015: –30 % MK~~/LR~~) ~~(Figure 13; Table 5). This decrease is larger than the decrease in $NH_3$ emissions of 10 %~~ over the same period (Figure 14, Figure 15, Table 5~~Table 7~~). 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~~a~~ more comprehensive analysis of a larger number of sites shows smaller reductions over time, whereas~~. By contrast,~~ 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 ~~against~~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.

~~What the $NH_3$ data from the 12 sites does show, however, is that there is a shift from air being dominated by $SO_2$ towards it being dominated by $NH_3$,~~

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).

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### 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$_2$, NOx, 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.

~~with a rapidly changing chemical climate in terms of relative concentrations of NH$_3$ and SO$_2$. 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 (Figure 18). By 2015, this ratio had increased to 15 (annual mean concentrations of NH$_3$ = 58 nmol m$^{-3}$ and SO$_2$ = 4 nmol m$^{-3}$) (Figure 18). At the same time, there is a larger decrease in NH$_4^+$ concentrations (−62 % MK / −64 % LR), contrasting with a smaller decrease in NH$_3$ concentrations over the period 2010–2015 (−30 % MK / LR) (Table 7), with the NH$_3$:NH$_4^+$ ratio increasing with time (Figure 18). 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).~~

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Past ~~S~~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$_2$.~~ Supporting evidence for enhanced deposition of SO$_2$ in a NH$_3$-rich atmosphere is provided by the AGANet data that shows a more rapid decline in SO$_2$ concentrations than SO$_4^{2-}$, and the negative trend in the ratio of SO$_2$:SO$_4^{2-}$.~~ 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).

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~~with a rapidly changing chemical climate in terms of relative concentrations of NH$_3$ and SO$_2$.~~ 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 ~~(Figure 18)~~. By 2015, this ratio had increased to 15 (annual mean concentrations of $NH_3$ = 58 nmol $m^{-3}$ *cf*~~and~~ $SO_2$ = 4 nmol $m^{-3}$)~~ (Figure 18). ~~. 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.

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~~At the same time, there is a larger decrease in $NH_4^+$ concentrations (−62 % MK / −64 % LR), contrasting with a smaller decrease in $NH_3$ concentrations over the period 2010–2015 (−30 % MK / LR) (Table 7), with the $NH_3$:$NH_4^+$ ratio increasing with time (Figure 18). 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).~~

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 $H_2SO_4$ (oxidation product of $SO_2$) for $NH_3$ is much larger than that of $HNO_3$ and HCl, available $NH_3$ is first taken up by $H_2SO_4$ to form ammonium sulphate compounds ($NH_4HSO_4$ and $(NH_4)_2SO_4$), with any excess $NH_3$ then available to react with $HNO_3$ and HCl to form $NH_4NO_3$ and $NH_4Cl$. Analysis of the different particulate components in section 3.5 showed that the ammonium aerosols are mainly made up of $(NH4)2SO4$ and $NH_4NO_3$. With the large reduction in $SO_2$, more $NH_3$ is available to react with $HNO_3$ to form $NH_4NO_3$ 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 $(NH_4)_2SO_4$ to $NH_4NO_3$ (Figure 18b).

~~The increase in ratio of $HNO_3$:$NO_3^-$ is similar to changes in upward trend in gas-aerosol partitioning between $NH_3$ and $NH_4^+$ over time (Figure 18). The negative trend in ratio of $SO_2$:$SO_4^{2-}$, contrasting with the positive trend in ratio of $HNO_3$:$NO_3^-$ (Figure 18) lends further support that reduction in $SO_2$ emissions is contributing to a more rapid decrease in particulate $(NH_4)_2SO_4$ concentrations, as more $NH_3$ becomes available to react with $HNO_3$ to form the $NH_4NO_3$, A change to an $NH_4NO_3$ rich atmosphere may account for the smaller negative trend in particulate $NO_3^-$ observed here.~~

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 $HNO_3$. 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.

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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 %: ~~between~~ 2000 – 2015) and moderately successful with $NO_x$ emissions (–58 %: ~~between~~ 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 ~~There remains however little political will to reduce emissions of~~ $NH_3$~~.~~ is reflected in the smaller reduction in $NH_3$ emissions (–9 %: 2000 – 2015), with emissions increasing, rather than decreasing since 2013 and ~~Since estimated emissions of $NH_3$ decreased by only 10 % over the same period,~~ 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.

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~~At the same time, results from the AGANet show a change in the particulate phase from $(NH_4)_2SO_4$ to $NH_4NO_3$. This change is expected to increase residence times of $NH_3$ and $HNO_3$ in the atmosphere, as the semi-volatile $NH_4NO_3$ will volatilise in warm weather to release $HNO_3$ and $NH_3$. A higher concentration of the gas-phase nitrogen species ($HNO_3$ and $NH_3$) may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in $NO_x$ and $NH_3$. More of the $NH_3$ and $NO_x$ emitted will deposit more locally with a smaller footprint within the UK.~~

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 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 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 $NH_4^+$ 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 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 from Europe, and smallest in western Scotland and Northern Ireland. HCl concentrations are also largest in the southeast, ~~and~~ southwest and central ~~of~~ 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) ~~from coal combustion~~. 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~~$HNO_3$ and $NO_3^-$ have a maximum during late spring and early summer, due to photochemical production processes and from long-range transboundary pollutant transport. $SO_4^{2-}$ concentrations also have a peak in spring time, coinciding with the peak in concentrations of $NH_3$ and $NH_4^+$, and is therefore likely to be attributed to formation of $(NH_4)_2SO_4$ 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 ~~and calcium are both~~is a crustal elements, but which is~~are~~ 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 $MgCl_2$.~~ For $Ca^{2+}$, the winter maxima is much less pronounced and its seasonal variability is likely to be influenced by both crustal dust and sea salt.~~

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. ~~For $SO_2$, a~~A significant decreas~~ing trend in annual mean $SO_2$ concentrations~~ of –81 % (MK~~, LR = –84 %~~) in annual mean concentrations of $SO_2$ between~~from~~ 2000 and~~–~~ 2015 was in agreement with the estimated –80 % reduction in $SO_2$ emissions~~ reductions~~, but larger than the accompanying decline in particulate $SO_4^{2-}$ (–69 % MK~~/ –70 % LR~~). A more modest reduction in $HNO_3$ (–45 % MK~~/ –42 % LR~~) and particulate $NO_3^-$ (–52 % MK~~/ –51 % LR~~) are consistent with the estimated 58 % decline in $NO_x$ emissions over this same period.~~ At the same time, $NH_3$ measurements made under NAMN shows a shift from air being dominated by $SO_2$ towards it being dominated by $NH_3$. For~~The decrease in particulate $NH_4^+$~~, the decrease in concentrations~~ (–62 % MK~~/ –64 % LR~~) 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 ~~10~~9 %. However, it should be noted that $NH_3$ trends are highly dependent on site selection~~ and a~~according to an earlier assessment made on a more comprehensive dataset from the UK NAMN.~~ more comprehensive analysis of a larger number of sites shows smaller reductions over time.~~

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~~. At the same time, a change in the particulate phase from $(NH_4)_2SO_4$ to $NH_4NO_3$ would contribute to slowing down the negative~~

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~~trend in particulate $NO_3^-$ observed here~~. 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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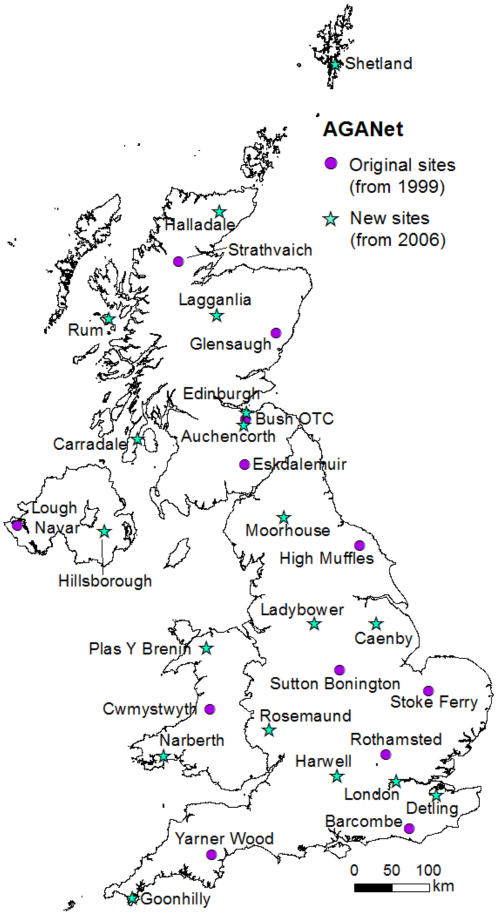
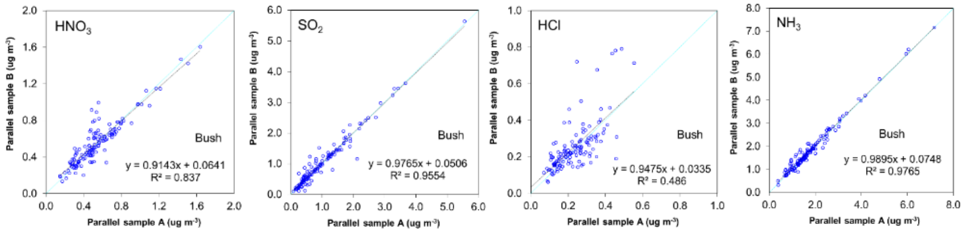
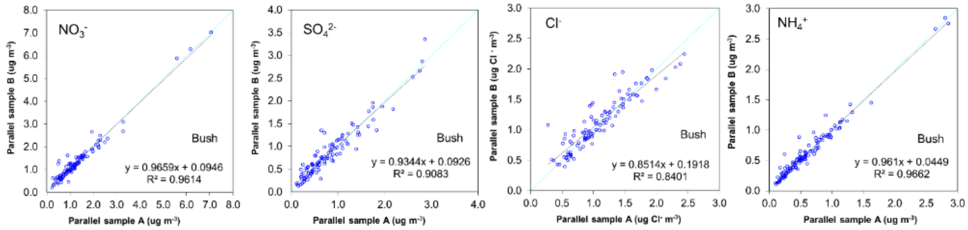


**Figure 1:** Site map of the UK Acid Gases and Aerosol Network (AGANet). The AGANet was established in September 1999 with 12 sites and expanded to 30 sites from January 2006 to improve national coverage. These sites also provide measurements of $NH_3$ and $NH_4^+$ for the UK National Ammonia Monitoring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

(a) Gases ($HNO_3$, $SO_2$, HCl, $NH_3$)



(b) Particulate ($NO_3^-$, $SO_4^{2-}$, $Cl^-$, $NH_4^+$)



(c) Summary of regression analysis

| | Gases | | | | Particulates | | | |
|---|---|---|---|---|---|---|---|---|
| | $HNO_3$ | $SO_2$ | HCl | $NH_3$ | $NO_3^-$ | $SO_4^{2-}$ | $Cl^-$ | $NH_4^+$ |
| $R^2$ | 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:**~~

**Figure 2:** Comparisons of parallel measurement of monthly (a) atmospheric reactive gases ($HNO_3$, $SO_2$, HCl and $NH_3$) and (b) particulate ($NO_3^-$, $SO_4^{2-}$, $Cl^-$ and $NH_4^+$) 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.

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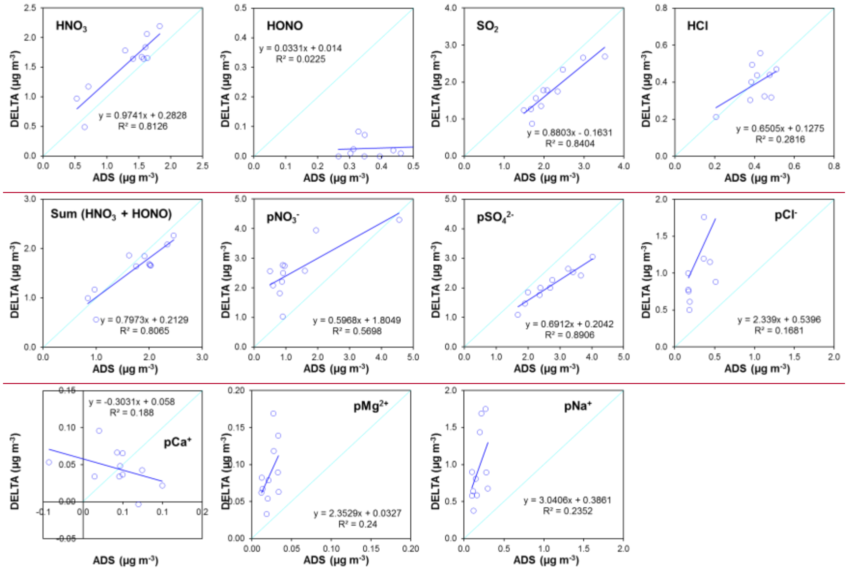

| | **Gases** | | | | | **Particulates** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | **HNO$_3$** | **(HNO3+HONO)** | **HONO** | **SO$_2$** | **HCl** | **NO$_3^-$** | **SO$_4^{2-}$** | **Cl$^-$** | **Na$^+$** | **Ca$^{2+}$** | **Mg$^{2+}$** |
| Linear regression: $R^2$ | 0.813*** | 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 |

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 HNO$_3$, HONO, sum (HNO$_3$+HONO), SO$_2$, HCl and aerosol NO$_3^-$, SO$_4^{2-}$, Cl$^-$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$ 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 corresponding DELTA sampling periods (monthly). HNO$_3$ values shown for DELTA and ADS are as calculated from the amount of NO$_3^-$ 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

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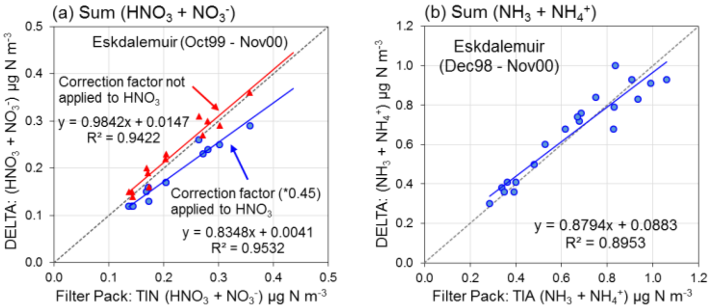

| | DELTA TIN | EMEP TIN | DELTA TIN (corrected HNO$_3$) | EMEP TIN | DELTA TIA | EMEP TIA |
|---|---|---|---|---|---|---|
| Linear regression: $R^2$ | 0.942*** | | 0.953*** | | 0.895*** | |
| slope | 0.984$^{ns}$ | | 0.835* | | 0.879$^{ns}$ | |
| intercept | 0.015$^{ns}$ | | 0.004$^{ns}$ | | 0.088$^{ns}$ | |
| 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 ($p > 0.05$)

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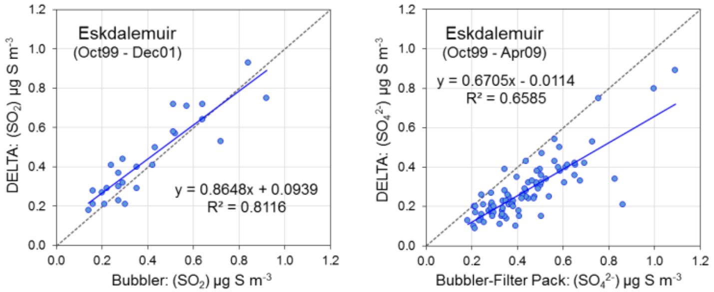
~~**Figure 3:**~~

**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 4:**~~

**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.

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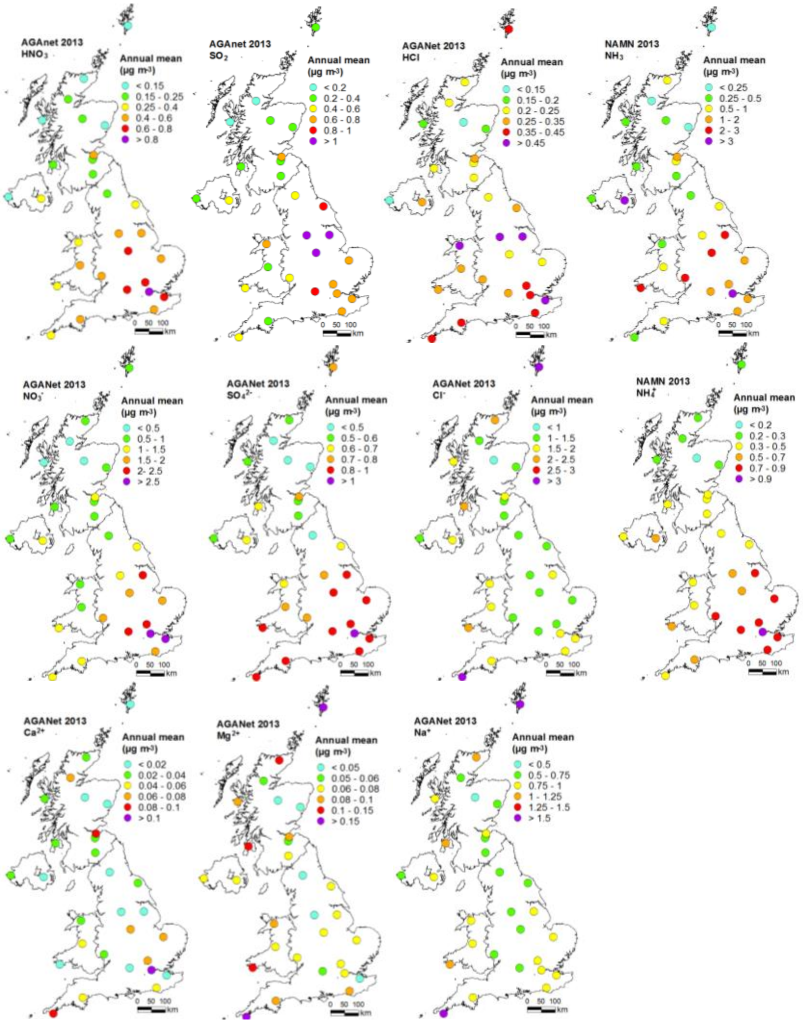
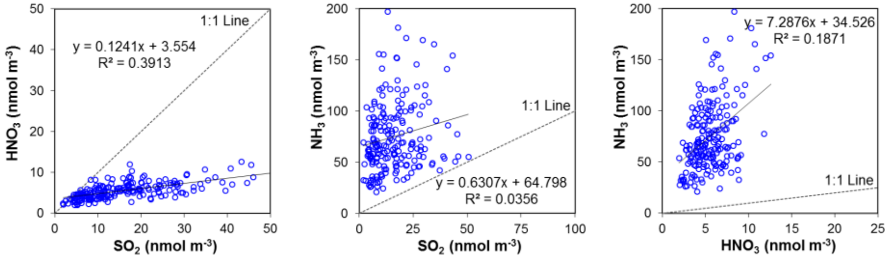
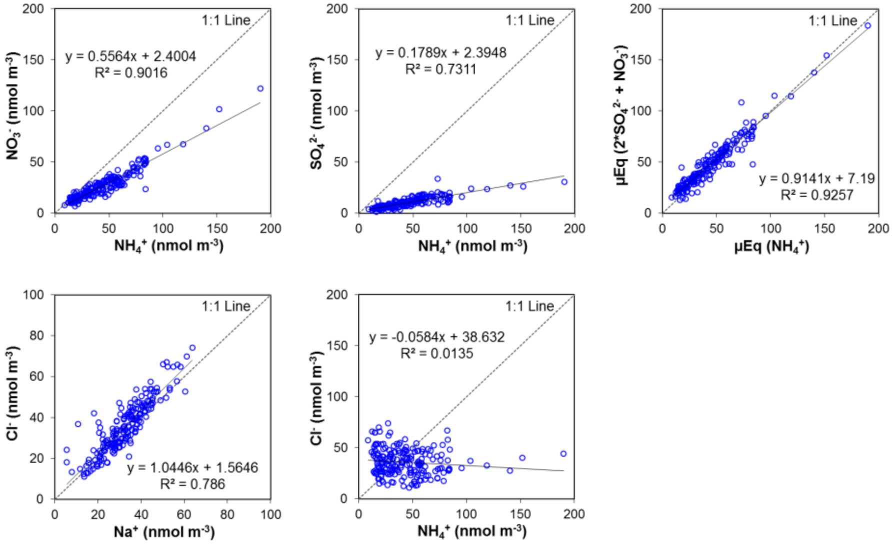


~~**Figure 5:**~~
**Figure 6:** Annual mean monitored acid gas (HNO$_3$, SO$_2$, HCl) and aerosol (NO$_3^-$, SO$_4^{2-}$, Cl$^-$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$) concentrations from the UK Acid Gas and Aerosol Monitoring Network (AGANet) across the UK from annual averaged monthly measurements made in 2013. NH$_3$ and NH$_4^+$ measured at the same time from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also shown alongside for comparison.

**(a) Gaseous components**

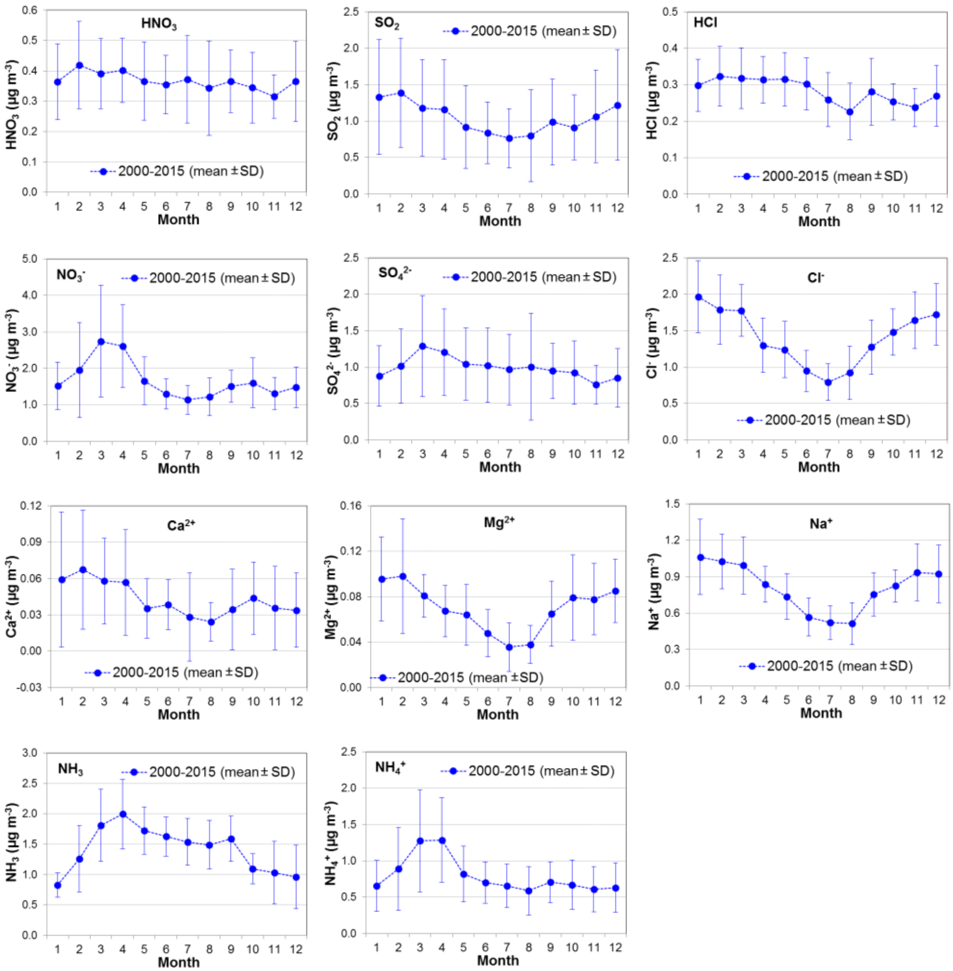


**(b) Particulate components**



~~Figure 6:~~

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.



~~Figure 7:~~ **Figure** 8: Average annual cycles for $HNO_3$, $SO_2$, **HCl and aerosol $NO_3^-$, $SO_4^{2-}$, $Cl^-$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$ from the UK Acid Gases and Aerosol Monitoring Network (AGANet). The $NH_3$ and $NH_4^+$ 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.**

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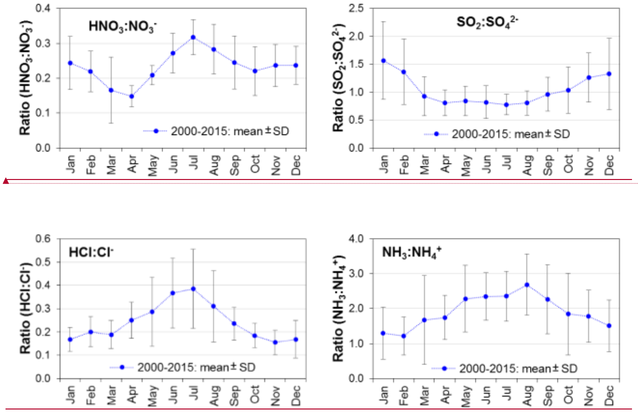

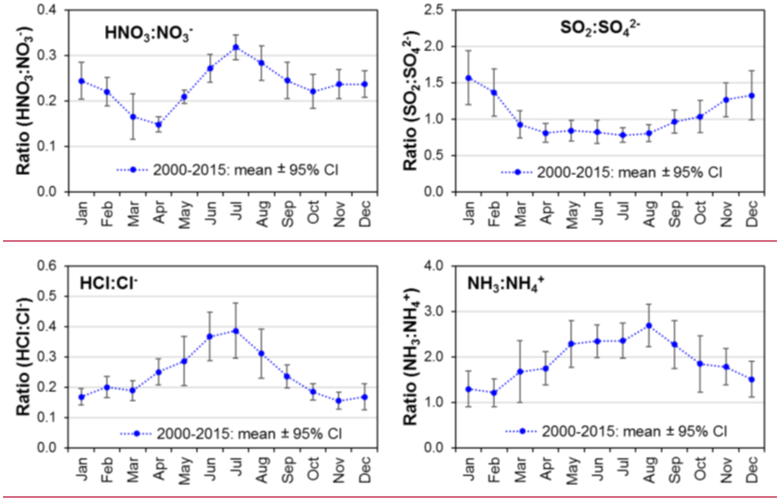

~~Figure 8:~~

**Figure 9:** Average annual cycles in the ratios of gas:aerosol component concentrations ~~(µg m-3)~~. 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~~concentrations~~ (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)~~SD~~ of monthly measurements of 12 sites operational in the network over the period 2000 to 2015.

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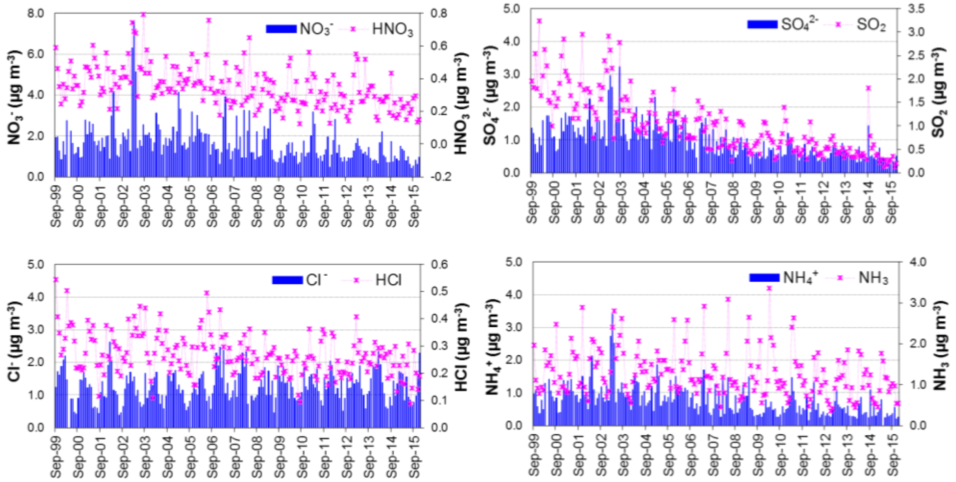

~~Figure 9:~~

**Figure 10:** Monthly mean concentrations in gaseous $HNO_3$, $SO_2$, HCl and aerosol $NO_3^-$, $SO_4^{2-}$, $Cl^-$ from the UK Acid Gases and Aerosol Monitoring Network (AGANet). Monthly mean concentrations of $NH_3$ and $NH_4^+$ 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.

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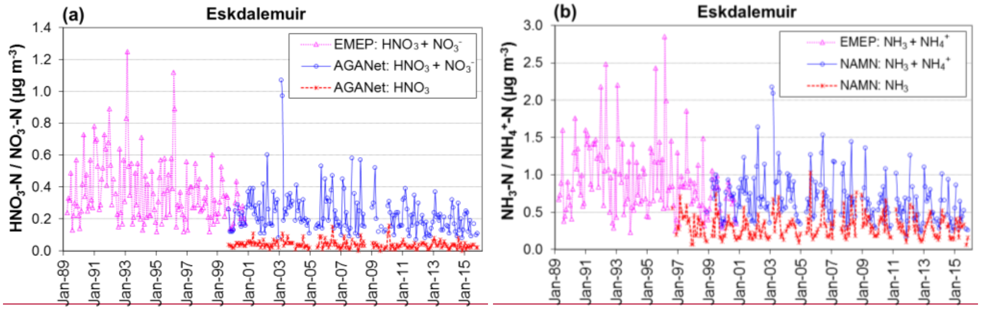

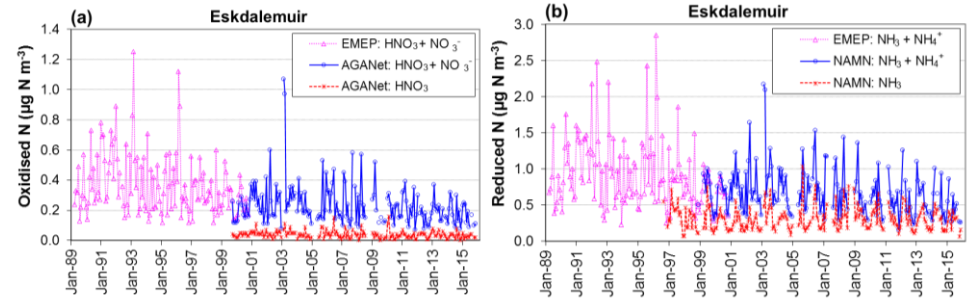

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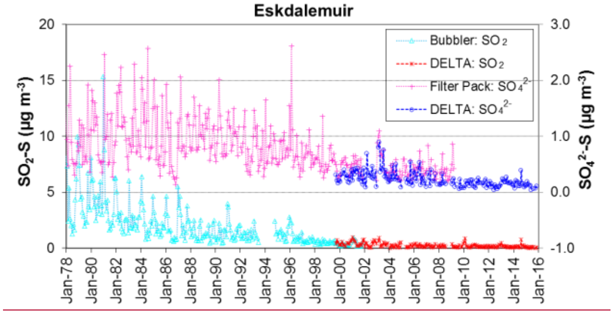
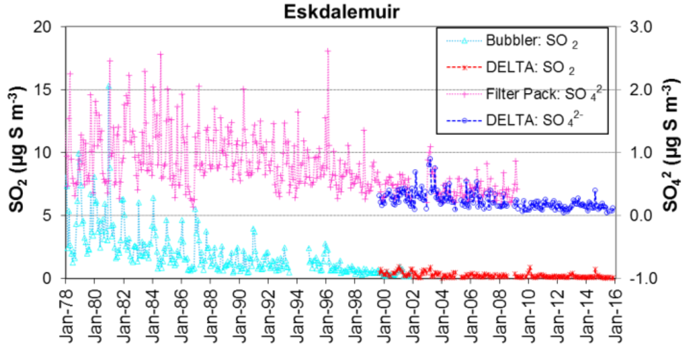
~~Figure 10:~~

**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~~2.6~~).





~~Figure 11:~~

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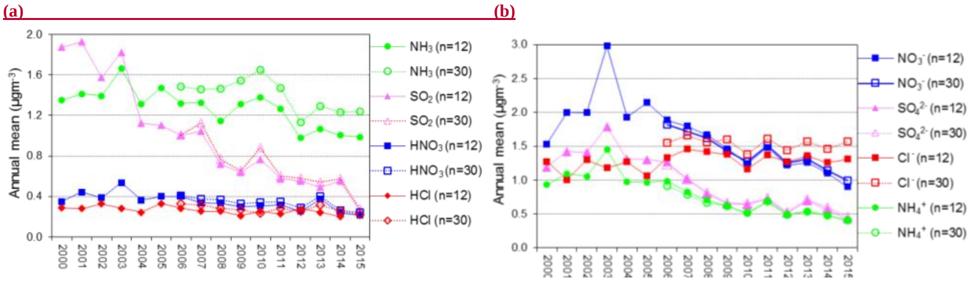
**Figure 12:** Long-term time series of SO$_2$ (Dec-77 – Jul-93) and SO$_4^{2-}$ (Dec-77 – Dec-01) concentrations measured in the UK Acid Deposition Monitoring Network (ADMN) (Hayman et al., 2007) and the AGANet DELTA measurements (Oct-99 – Dec-15) at the Eskdalemuir monitoring station (EMEP station 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 12:~~

**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.

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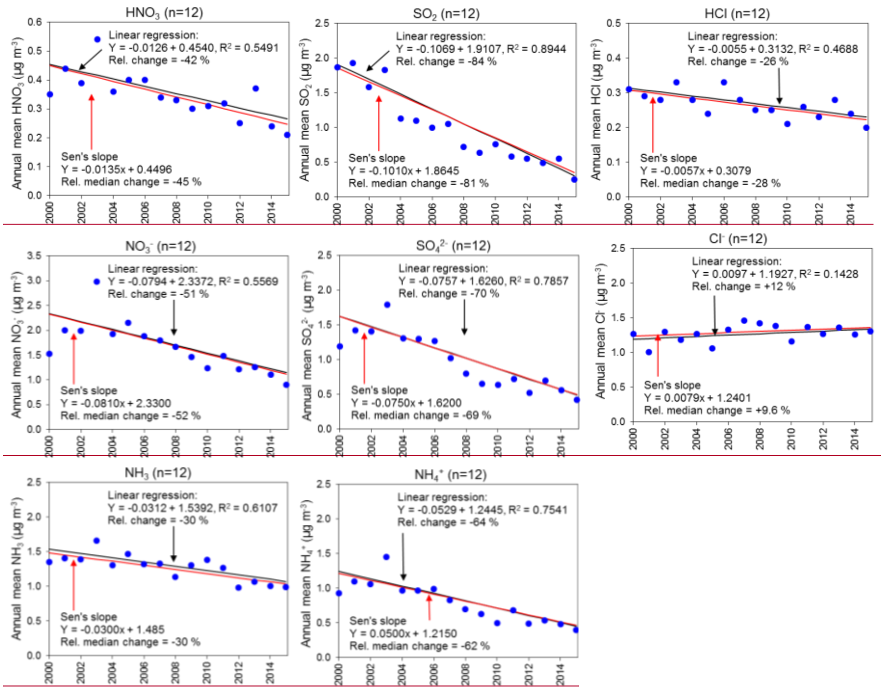
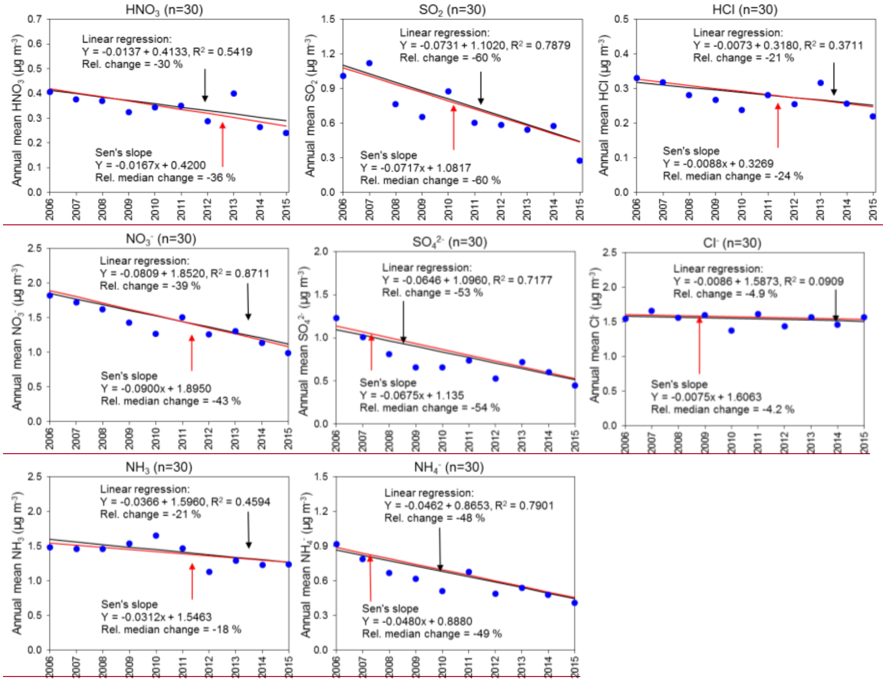
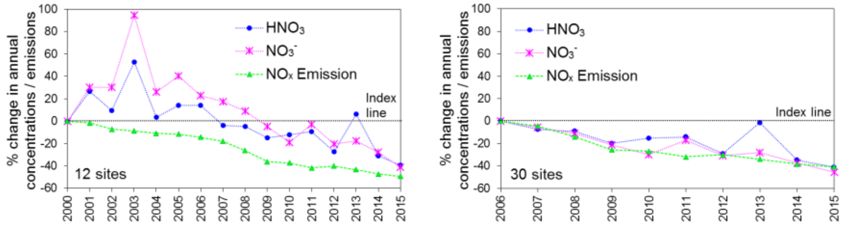


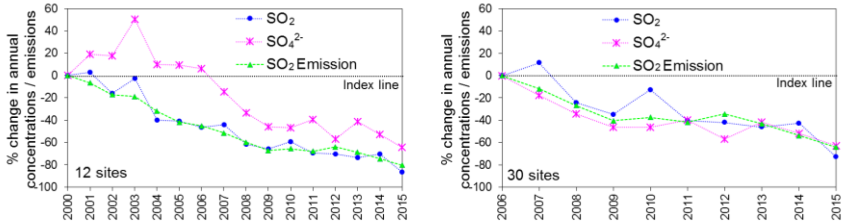
**~~Figure 13:~~** ~~Time series trend analysis by non-parametric Mann-Kendall Sen slope and by parametric linear regression on annually averaged gas and aerosol concentration data from the UK Acid Gases and Aerosol Monitoring Network (AGANet) of 12 sites that were operational over the period 2000 to 2015. NH$_3$ and NH$_4^+$ concentrations measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison.~~



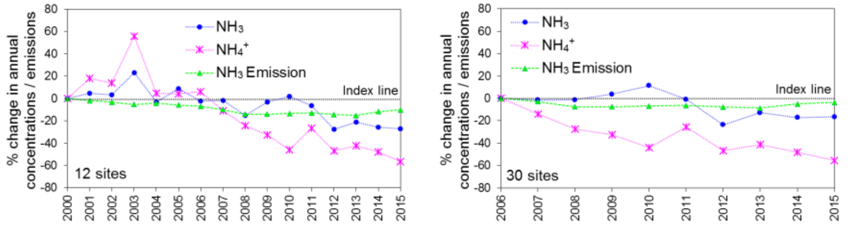
~~**Figure 14:** Time series trend analysis by non-parametric Mann-Kendall Sen slope and by parametric linear regression on annually averaged gas and aerosol concentration data from the UK Acid Gases and Aerosol Monitoring Network (AGANet) of 30 sites that were operational over the period 2006 to 2015. 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 15:** Relative trends in UK $NO_x$ emissions (Defra 2017) and in annually averaged $HNO_3$ and particulate $NO_3^-$ concentrations for (a) the original 12 AGANet sites for the 16 year period from 2000 to 2015, and (b) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015.~~



~~**Figure 16:** Relative trends in UK $SO_2$ emissions (Defra 2017) and in annually averaged $SO_2$ and particulate $SO_4^{2-}$ concentrations for (a) the original 12 AGANet sites for the 16 year period from 2000 to 2015 and (b) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015.~~



~~**Figure 17:** Relative trends in UK $NH_3$ emissions (Defra 2017) and in annually averaged $NH_3$ and particulate $NH_4^+$ concentrations from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) for (a) the original 12 AGANet sites for the 16 year period from 2000 to 2015 and (b) the expanded 30 AGANet sites for the 10 year period from 2006 to 2015.~~

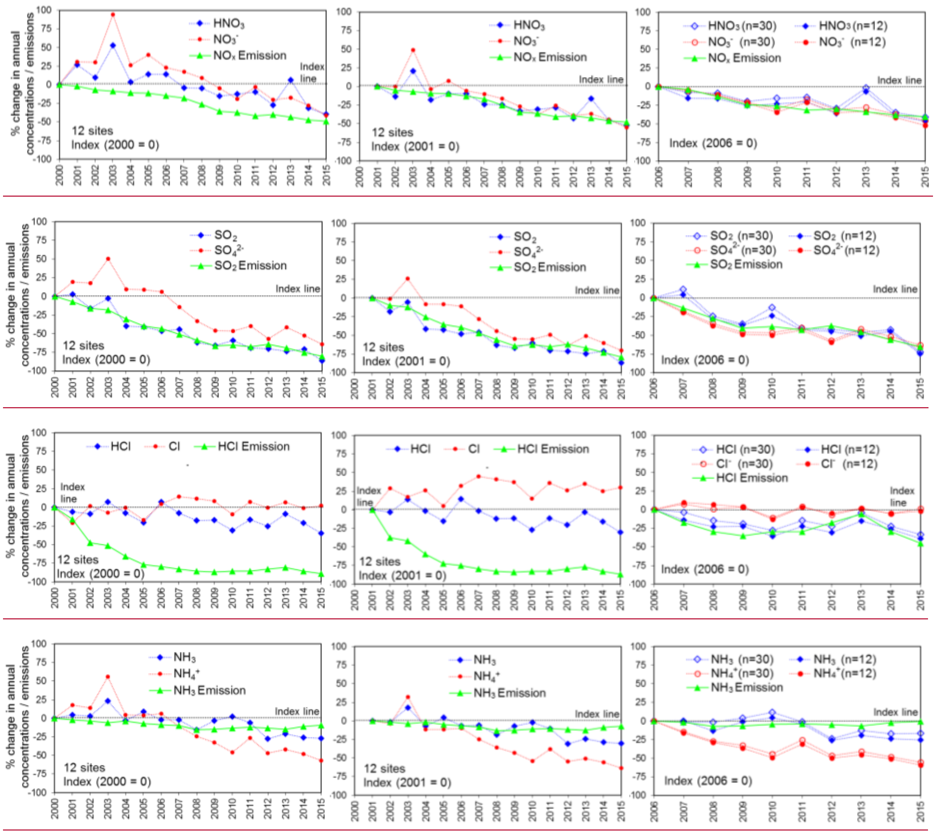


**Figure 14:** Relative trends in UK emissions (NAEI 2018) and in annually averaged gas and particulate concentrations from the UK AGANet and UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) for (left) original 12 sites for the 16 year period from 2000 to 2015, and (right) expanded 30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

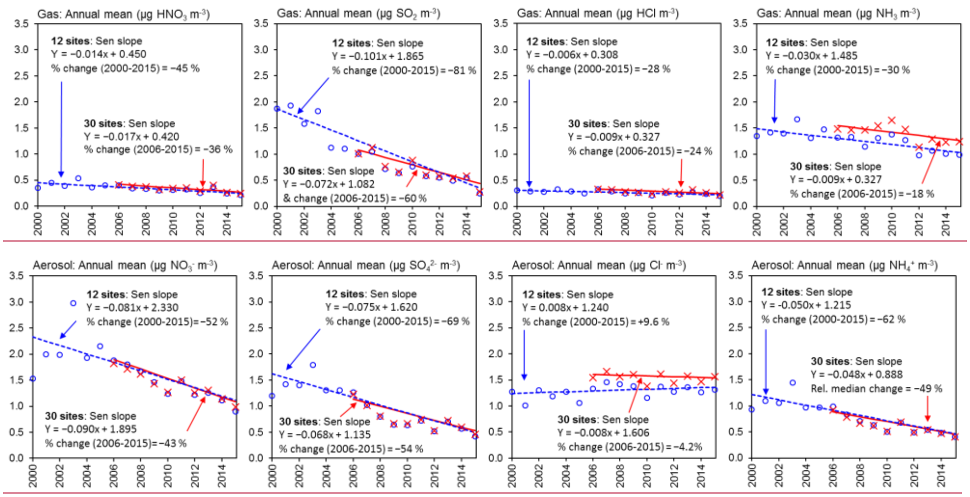


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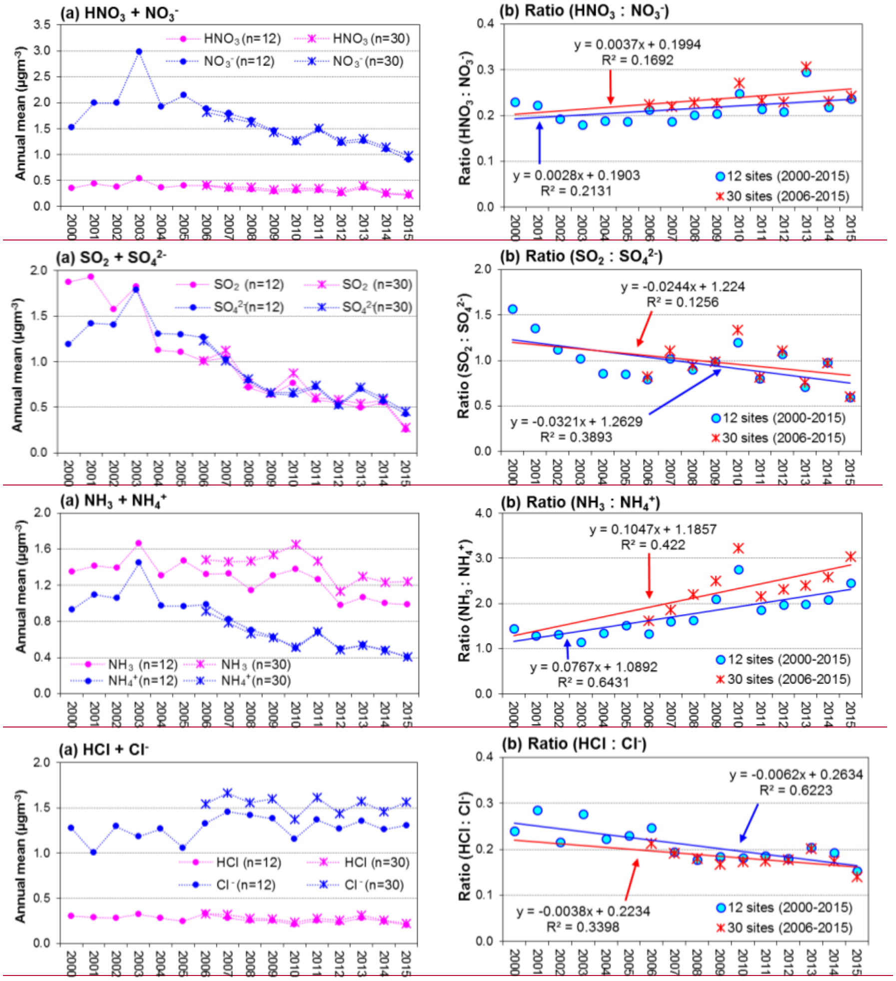
**Figure 15:** Time series trend analysis by non-parametric Mann-Kendall Sen slope on annually averaged gas and aerosol concentration data from the UK Acid Gases and Aerosol Monitoring Network (AGANet) of (i) 12 sites with complete time series over the period 2000 to 2015 and (ii) expanded 30 sites with 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 18:** (a) Long-term trends in annual mean concentrations of acid gas and aerosol ($HNO_3$ / $NO_3^-$ and $SO_2$ / $SO_4^{2-}$) from the UK Acid Gases and Aerosol Network (AGANet) and in reduced nitrogen ($NH_3$ / $NH_4^+$) from the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) measured at the same time for comparison. Data are the annually averaged concentrations of 12 sites with complete time series from 2000 to 2015, and 30 sites with complete time series from 2006 to 2015. (b) Long-term trends in the gas:aerosol ratio, from the data in figure (a), indicating differences in direction of trends in this ratio with time.~~

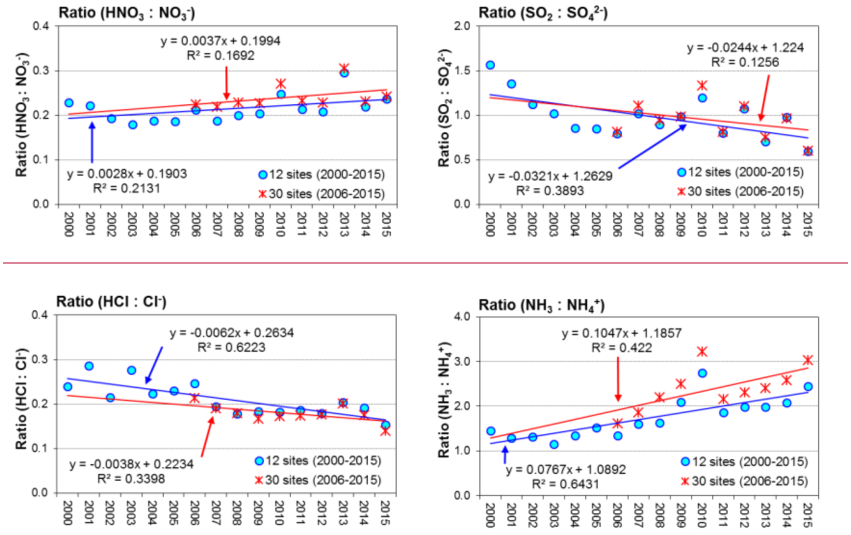


**Figure 16:** Long-term trends in the gas:aerosol ratio, from a comparison of the annual mean concentrations of 12 sites with complete time series from 2000 to 2015, and 30 sites with complete time series from 2006 to 2015, showing indicative differences in direction of trends in this ratio with time.

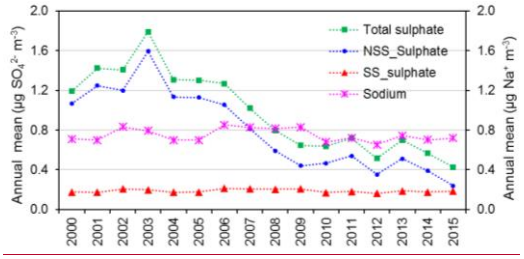


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**Figure 17**: Comparison of long-term trends in annual mean concentrations of total sulphate (as determined from the amount of sulphate collected on the AGANet aerosol filter), NSS_sulphate (estimated from the empirical relationship: [NSS_SO4] = [$SO_4^{2-}$] - (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.

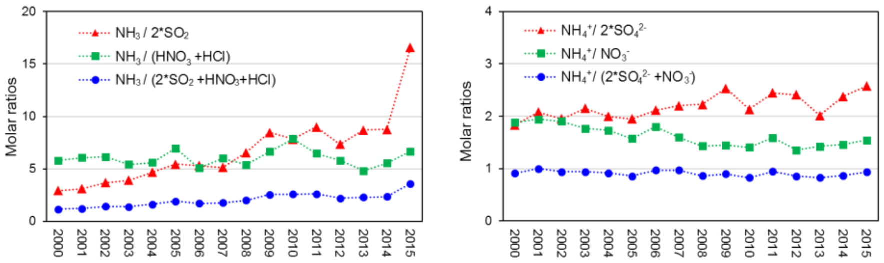

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**Figure 18**: Long-term changes between 2000 and 2015 in (a) molar ratio of $NH_3$ to acid gases ($SO_2$, $HNO_3$ and HCl) and (b) molar ratio of particulate $NH_4^+$ to acid aerosols ($SO_4^{2-}$ and $NO_3^-$) from measurements made at 12 sites in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

**~~Table 3:~~**

**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 4:~~

**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 5:** Summary of Mann-Kendall (MK) and Linear Regression (LR) time series trend analysis on annually averaged gas and aerosol concentrations from the UK Acid Gases and Aerosol Monitoring Network (AGANet) for the 12 sites that were operational over the period 2000 to 2015. $NH_3$ and $NH_4^+$ concentrations measured at the same time in the UK National Ammonia Monitoring Network (NAMN, Tang et al., 2018) are also included for comparison. For the MK tests, the 95% confidence interval (CI) for the median trend and relative change are also estimated.~~

| ~~2000 - 2015 (12 sites: annual data)~~ | ~~Mann-Kendall (MK)~~ | | ~~Linear Regression (LR)~~ | | |
|---|---|---|---|---|---|
| | ~~[a]Median annual trend & [95% CI] (µg $y^{-1}$)~~ | ~~[b]Relative median change 2000-2015 & [95% CI] (%)~~ | ~~[c]Annual Trend (µg $NH_3$ $y^{-1}$)~~ | ~~[d]Relative change 2000-2015 [%]~~ | ~~$R^2$~~ |
| ~~$HNO_3$~~ | ~~-0.0135<br>[-0.0067, -0.0180]~~ | ~~-45** [-26, -55]~~ | ~~-0.0126~~ | ~~-42**~~ | ~~0.549~~ |
| ~~$SO_2$~~ | ~~-0.1010<br>[-0.0729, -0.1250]~~ | ~~-81*** [-72, -91]~~ | ~~-0.1069~~ | ~~-84***~~ | ~~0.894~~ |
| ~~HCl~~ | ~~-0.0057<br>[-0.0020, -0.0100]~~ | ~~-28*** [-11, -42]~~ | ~~-0.0055~~ | ~~-26**~~ | ~~0.469~~ |
| ~~$NH_3$~~ | ~~-0.0300<br>[-0.0125, -0.0433]~~ | ~~-30** [-13, -39]~~ | ~~-0.0312~~ | ~~-30***~~ | ~~0.611~~ |
| ~~$NO_3^-$~~ | ~~-0.0810<br>[-0.0520, -0.1125]~~ | ~~-52** [-37, -63]~~ | ~~-0.0794~~ | ~~-51***~~ | ~~0.557~~ |
| ~~$SO_4^{2-}$~~ | ~~-0.0750<br>[-0.0450, -0.-0988]~~ | ~~-69** [-52, -82]~~ | ~~-0.0757~~ | ~~-70***~~ | ~~0.786~~ |
| ~~$Cl^-$~~ | ~~0.0079<br>[-0088, 0.0236]~~ | ~~9.6$^{ns}$ [-9.5, 33]~~ | ~~0.0097~~ | ~~+12$^{ns}$~~ | ~~0.143~~ |
| ~~$NH_4^+$~~ | ~~-0.0500<br>[-0.0375, -0.0675]~~ | ~~-62** [-51, -74]~~ | ~~-0.0529~~ | ~~-64***~~ | ~~0.754~~ |

~~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 = µg $y^{-1}$)~~

~~[b]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*[($yi$-$y_0$) /$y_0$])~~

~~[c]Annual trend = fitted slope of linear regression (unit = µg $NH_3$ $y^{-1}$)~~

~~[d]Relative 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 slope and intercept (=100*[($yi$-$y_0$) /$y_0$])~~

~~**Table 6:** Summary of Mann-Kendall (MK) and Linear Regression (LR) time series trend analysis on annually averaged gas and aerosol concentrations from the UK Acid Gases and Aerosol Monitoring Network (AGANet) for the 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. For the MK tests, the 95% confidence interval (CI) for the median trend and relative change are also estimated.~~

| ~~2006 - 2015 (30 sites: annual data)~~ | ~~Mann-Kendall (MK)~~ | | ~~Linear Regression (LR)~~ | | |
|---|---|---|---|---|---|
| | ~~[a]Median annual trend & [95% CI] (µg $NH_3$ $y^{-1}$)~~ | ~~[b]Relative median change 2000-2015 & [95% CI] (%)~~ | ~~[c]Annual Trend (µg $NH_3$ $y^{-1}$)~~ | ~~[d]Relative change 2000-2015 [%]~~ | ~~$R^2$~~ |
| ~~$HNO_3$~~ | ~~-0.0167<br>[-0.0075, -0.0200]~~ | ~~-36* [-18, -41]~~ | ~~-0.0137~~ | ~~-30*~~ | ~~0.542~~ |
| ~~$SO_2$~~ | ~~-0.0717<br>[-0.0300, -0.0108]~~ | ~~-60*** [-33, -73]~~ | ~~-0.0731~~ | ~~-60***~~ | ~~0.788~~ |
| ~~HCl~~ | ~~-0.0088<br>[0.0000, -0.0200]~~ | ~~-24* [0.0, -47]~~ | ~~-0.0073~~ | ~~-21$^{ns}$~~ | ~~0.371~~ |
| ~~$NH_3$~~ | ~~-0.0312<br>[0.0033, -0.0625]~~ | ~~-18$^{ns}$ [+2.0, -31]~~ | ~~-0.0366~~ | ~~-21*~~ | ~~0.459~~ |
| ~~$NO_3^-$~~ | ~~-0.0900<br>[-0.0580, -0.1300]~~ | ~~-43*** [-30, -56]~~ | ~~-0.0809~~ | ~~-39***~~ | ~~0.871~~ |
| ~~$SO_4^{2-}$~~ | ~~-0.0675<br>[-0.0233, -0.1167]~~ | ~~-54** [-25, -78]~~ | ~~-0.0646~~ | ~~-53***~~ | ~~0.718~~ |
| ~~$Cl^-$~~ | ~~-0.0075<br>[+0.0167, -0.0300]~~ | ~~-4.2$^{ns}$ [+12, -16]~~ | ~~-0.0086~~ | ~~-4.9$^{ns}$~~ | ~~0.091~~ |
| ~~$NH_4^+$~~ | ~~-0.0480<br>[0.0267, -0.0700]~~ | ~~-49** [-33, -64]~~ | ~~-0.0462~~ | ~~-48***~~ | ~~0.790~~ |

~~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 = µg $y^{-1}$)~~

~~[b]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*[($yi$-$y_0$) /$y_0$])~~

~~[c]Annual trend = fitted slope of linear regression (unit = µg $NH_3$ $y^{-1}$)~~

~~[d]Relative 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 slope and intercept (=100*[($yi$-$y_0$) /$y_0$])~~

**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 (µg m$^{-3}$) | Mann-Kendall (MK): 12 sites (2000 - 2015) | | Mann-Kendall (MK): 30 sites (2006 – 2015) | |
|---|---|---|---|---|
| | $^a$Median annual trend & [95% CI] (µg y$^{-1}$) | $^b$Relative median change & [95% CI] (%) | $^a$Median annual trend & [95% CI] (µg y$^{-1}$) | $^b$Relative median change & [95% CI] (%) |
| $HNO_3$ | -0.0135**<br>[-0.0067, -0.0180] | -45** [-26, -55] | -0.0167*<br>[-0.0075, -0.0200] | -36* [-18, -41] |
| $SO_2$ | -0.1010***<br>[-0.0729, -0.1255] | -81*** [-72, -91] | -0.0717**<br>[-0.0300, -0.0108] | -60** [-33, -73] |
| HCl | -0.0057**<br>[-0.0020, -0.0100] | -28** [-11, -42] | -0.0088*<br>[0.0000, -0.0200] | -24* [0.0, -47] |
| $NH_3$ | -0.0300**<br>[-0.0125, -0.0433] | -30*** [-13, -39] | -0.0312$^{ns}$<br>[0.0033, -0.0625] | -18$^{ns}$ [+2.0, -31] |
| $NO_3^-$ | -0.0810***<br>[-0.0520, -0.1125] | -52*** [-37, -63] | -0.0900**<br>[-0.0580, -0.1300] | -43** [-30, -56] |
| $SO_4^{2-}$ | -0.0750***<br>[-0.0450, -0.-0988] | -69*** [-52, -82] | -0.0675**<br>[-0.0233, -0.1167] | -54** [-25, -78] |
| $NSS\_SO_4^{2-}$ | -0.0733***<br>[-0.0500, -0.-1012] | -78*** [-64, -92] | -0.0575**<br>[-0.0167, -0.1033] | -62** [-25, -86] |
| $Cl^-$ | 0.0079$^{ns}$<br>[-0088, 0.0236] | 9.6$^{ns}$ [-9.5, 33] | -0.0075$^{ns}$<br>[+0.0167, -0.0300] | -4.2$^{ns}$ [+10, -16] |
| $NH_4^+$ | -0.0500***<br>[-0.0375, -0.0675] | -62*** [-51, -74] | -0.0480**<br>[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 = µg 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*[($yi$-$y_0$) /$y_0$])

~~**Table 7:**~~ **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 ($=100*[(yi-y_0)/y_0]$)

~~[b] Relative 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 slope and intercept ($=100*[(yi-y_0)/y_0]$)~~

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