

Interactive comment on “Acid gases and aerosol measurements in the UK (1999–2015): regional distributions and trends” by Y. Sim Tang et al.

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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

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been revised and expanded to include a more thorough discussion of trends under new sub-headings. 3.8.1 Trends in HNO₃ and NO₃⁻ vs NO_x emissions 3.8.2 Trends in SO₂ and SO₄²⁻ vs SO₂ emissions 3.8.3 Trends in HCl and Cl⁻ vs HCl emissions 3.8.4 Trends in NH₃ and NH₄⁻ vs NH₃ 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.

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 shown in Figure 13a and Figure 13b, respectively. Annually averaged data from the original 12 sites for the period 2000 – 2015 (1999 data excluded since AGANet started in September 1999) and from the full network (30 sites) for the period 2006 – 2015 are plotted alongside each other for comparison. From 2006 – 2015, the decreasing trends for all gas and aerosol components from the expanded 30 sites are seen to be similar to those from the original 12 sites. The annual mean concentrations in gas and aerosol components derived from the expanded 30 sites (2006 – 2015), or from the original 12 sites over the same period are also in general comparable (Table 3). The exceptions are Na⁺ and Cl⁻ that have higher mean concentrations from the 30 sites than the original 12 sites, due to the addition of two coastal sites (Shetland and Rum), with larger contribution from sea salt. Larger HNO₃ concentrations are due to two urban sites, London and Edinburgh (higher NO_x emissions from vehicular traffic). The addition of three sites in high NH₃ emission (agricultural) areas (Rosemaund in England, Narberth in Wales and Hillsborough in Northern Ireland) also elevated measured annual mean NH₃ 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.

In the gas phase, SO₂ decreased 7-fold from an annual mean concentration of 1.9 μg SO₂ m⁻³ in 2000 to 0.25 μg SO₂ m⁻³ in 2015 (n = 12), compared with more modest reductions in HNO₃ (from 0.35 to 0.21 μg HNO₃ m⁻³), NH₃ (from 1.4 to 1.0 μg NH₃

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m-3) and HCl (from 0.31 to 0.20 $\mu\text{g HCl m}^{-3}$) 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.

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, 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. Annual trends (e.g. $\mu\text{g HNO}_3 \text{ m}^{-3} \text{ y}^{-1}$) and changes in measured concentrations over time (% median change) estimated from MK tests are summarised in Figure 15 and Table 4.

Since there was a change in the number of sites during the operation of the AGANet, statistical trend analyses for HNO_3 , SO_2 , HCl and particulate NO_3^- , SO_4^{2-} , Cl^- were performed on annually averaged mean concentrations from two time series: the original 12 AGANet sites for the 16 year period from 2000 to 2015, and the expanded 30

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AGANet sites for the 10 year period from 2006 to 2015 (Figure 15, Table 4). 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 (Figure 15, Table 4) 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.

The long-term trends in the gas and aerosol components, based on both LR and MK statistical analysis of monthly mean measurement data, are also shown for comparison in Figure S4 (mean monthly data of 12 sites for period 2000-2015) and Figure S5 (mean monthly data of 12 sites for period 2006-2015). Results of the trend analysis on monthly data (Tables S4, S5) were similar to trend analysis results of the annual data (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. Changes in the different gas and aerosol concentrations in relation to emission trends, and their interactions in a changing chemical climate are discussed further in the next sections.

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 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

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substantial inter-annual variability 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 HNO₃ and NO₃⁻ 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 HNO₃ and NO₃⁻ much closer to the relative trend line in NO_x emissions. In the later period between 2006 and 2015, the relative trend lines in HNO₃ and NO₃⁻ 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.

The reductions in annual HNO₃ concentrations are statistically significant for both periods (Figure 15; Table 4). The MK % median change in annual mean HNO₃ 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 HNO₃ is accompanied by a larger decrease in particulate NO₃⁻ (2000 - 2015: MK = -52 % (n = 12), 2006 – 2015: MK = -43 % (n = 30)) (Table 4). Since HNO₃ is one of the major oxidation products of NO_x, through reaction with OH. or heterogeneous conversion of N₂O₅, it provides an important measure of the fraction of NO_x emissions that is oxidised and signals any long-term changes in the atmospheric processing timescales of NO_x over the UK. NO₂ is measured at 24 rural sites across the UK in the UKEAP NO₂-net (Conolly et al., 2016), with 11 sites co-located with the AGANet. A comparison of the network averaged NO₂ concentrations with NO_x emissions by Conolly et al (2016) showed matching decreasing trends between 2000 and 2015, with annual mean NO₂ concentrations falling 2-fold to 4 μg NO₂ m⁻³ in 2015. Despite the uncertainty in corrected HNO₃ data (see section 3.3), the encouraging agreement between trends in HNO₃ and NO₂ concentrations and NO_x emissions lends support to a linear response in HNO₃ concentrations to reductions in NO_x emissions.

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3.8.2 Trends in SO₂ and SO₄²⁻ vs SO₂ emissions. Unlike NO_x, there has been a more substantial decline in SO₂, both in emissions and measured concentrations (Figure 14, Table 5). Between 2000 and 2009, SO₂ emissions fell substantially by 66 % from 1286 to 432 kt SO₂. The reduction reflects mitigation measures introduced in 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 the trends in NO_x emission, the decreasing trend in SO₂ emissions plateaued between 2009 and 2012 and then decreased again by a further 45% between 2012 and 2015 following the closure of a number of coal-fired power stations, as well as conversion of some coal-fired stations to burn biomass.

Over the same period, the network annual mean concentration decreased from 1.9 μg SO₂ m⁻³ in 2000 to 0.25 μg SO₂ m⁻³ in 2015 (mean of 12 sites), continuing the long-term decline in SO₂ concentrations observed at the background Eskdalemuir site (Sect. 3.5) and across the UK (ROTAP 2012). The relative trends in SO₂ 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 SO₄²⁻ however, there is an apparent “gap” between emissions and concentrations in the trend normalised against the year 2000. Like NO₃⁻, re-analysis of the same annual data normalised against 2001 instead of 2000 takes the relative trend line for SO₄²⁻ closer to the trend lines in both SO₂ 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 SO₂ concentrations of -81 % (2000 – 2015, n = 12) , and -60 % (2006 – 2015, n = 30) (Figure 15; Table 4) are consistent with the substantial reduction of -80 % and -64 % in SO₂ emissions across the two overlapping periods, respectively (Table 5). The decrease in SO₂ is also twice as large as HNO₃ over the same period (Table 5), illustrating the greater success in mitigating sulphur than nitrogen and the increasing dominance of N components in the

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atmosphere with larger decline in SO₂ than NO_x.

At the same time, the reduction in SO₂ emission and measured concentration is accompanied by a smaller negative trend in particulate SO₄²⁻ (2000-2015: -69 % MK; 2006-2015: -54 % MK) (Figure 15; Table 4), with concentrations falling 3-fold from an annual mean of 1.2 µg SO₄²⁻ m⁻³ in 2000 to 0.42 µg SO₄²⁻ m⁻³ in 2015. The smaller decrease in particulate SO₄²⁻ compared with SO₂, is similar to that observed at Eskdalemuir (Sect. 3.1.3). A similar picture is also seen in Europe, where atmospheric concentrations of gas phase SO₂ decreased by about 92 % compared with a smaller reduction of 65 % in particulate SO₄²⁻ in response to sulphur emissions abatement over the 1990-2012 period in the EMEP region (EMEP 2016).

Sea salt SO₄²⁻ (SS_SO₄) aerosol, as discussed in section 3.5, makes up a significant fraction of the total SO₄²⁻. It is possible that the smaller reduction in particulate SO₄²⁻, compared with SO₂, may be explained by an underlying increase in the relative proportion of SS_SO₄ to total SO₄²⁻. To assess the contribution of SS_SO₄ to the observed trends in total SO₄²⁻, SS_SO₄ concentrations (estimated according to the empirical equation described in Sect. 3.5) and NSS_SO₄⁻ (= total SO₄²⁻ - SS_SO₄) are compared with the long-term trends in total SO₄²⁻ in Figure 16. 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 SO₄²⁻. 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 16). 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 SO₄²⁻ 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; Table 5) showed decrease in concentrations of -78 % (2000-2015) and -62% (2006-2015), similar to that observed in SO₂ (-81 %: 2000–2015 and -60 %: 2006 – 2015), indicating a closer relationship between NSS_SO₄ and SO₂ than between total SO₄²⁻ and SO₂.

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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. 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 (Figure 14).

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⁻ and Na⁺ (Sect. 3.8.2, Figure 16) provides evidence of a constant background in seasalt in the UK atmosphere.

3.8.4 Trends in NH₃ and NH₄⁺ vs NH₃ emissions. In comparison to the acid gases,

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there is a more modest decrease of –10 % in NH₃ emissions, from 254 kt NH₃ in 2000 to 231 kt NH₃ in 2015 (NAEI, 2018). This is smaller than the larger 30 % decrease seen in the annually averaged NH₃ concentrations at the 12 AGANet sites (2000-2015: –30 % MK) (Figure 14, Figure 15, Table 4) over the same period (Table 5). A recent assessment by Tang et al. (2018) showed that NH₃ trends are highly dependent on site selection and categorisation of sites in the analysis. A more comprehensive analysis of a larger number of sites shows smaller reductions over time, whereas a significant decreasing trend in NH₃ concentrations was observed in the grouped analysis of sites in areas classed as dominated by pig and poultry emissions, against an upward (non-significant) trend for sites in cattle-dominated areas. Therefore there is a large degree of uncertainty in interpreting the trends in NH₃ concentrations from a subset of just 12 sites, since NH₃ emissions are dominated by agricultural emissions (> 80%) that vary hugely on a local to regional scale across the UK.

At the same time, there is a larger decrease in particulate NH₄⁺ concentrations (–62 % MK), contrasting with the smaller decrease in NH₃ concentrations (–30 % MK) over the period 2010–2015 (Table 4), with the NH₃:NH₄⁺ ratio increasing with time (Figure 17). This provides evidence for a shift in partitioning from the particulate phase NH₄⁺ to the gaseous phase NH₃ in the UK data, discussed in Tang et al. (2018). The change in partitioning from particulate NH₄⁺ to gaseous NH₃ is also occurring in other parts of Europe, where decreases in NH₃ concentrations have been smaller than emission trends would suggest, due to large decreases in SO₂ emissions (Bleeker et al., 2009; Horvath et al., 2009).

3.8.5 Changes in UK chemical climate. Atmospheric SO₂ 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 SO₂ m⁻³, n = 12) approaching that of the other acid gases HNO₃ (0.21 µg HNO₃ m⁻³, n = 12) and HCl (0.20 µg HCl m⁻³, n = 12). NH₃ measured at the same time at the AGANet sites also decreased, but to a smaller extent, to a mean concentration of 1.0 µg NH₃ m⁻³ (n = 12) in 2015. The

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changes in measured concentrations of SO₂, HNO₃, HCl and NH₃ are consistent with the estimated decrease in emissions of SO₂, NO_x, HCl and NH₃ since 2000. SO₂ is therefore no longer the dominant acid gas, with HNO₃ and HCl together contributing a larger fraction of the total acidity in the UK atmosphere.

Past studies have shown that the increasing ratio of NH₃ to SO₂ in the atmosphere leads to enhanced dry deposition of SO₂, accelerating the decrease in atmospheric SO₂ concentrations than would be achieved by emissions reduction alone (Fowler et al., 2001, 2009; ROTAP 2012). The dry deposition of SO₂ and NH₃, by uptake of the gases in a liquid film on leaf surfaces, is known to be enhanced when both gases are present in a process termed “co-deposition” (Fowler et al., 2001). Where ambient NH₃ concentrations exceed that of SO₂, there is enough NH₃ to neutralize acidity in the liquid film and oxidise deposited SO₂, and maintain large rates of deposition of SO₂. 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 NH₃/combined acidity (sum of SO₂, HNO₃ and HCl) molar ratio, rather than based on SO₂ alone (Fowler et al., 2009).

To look at the UK situation, an analysis of the molar ratios of NH₃ to acid gases is presented in Figure 18a. The molar ratio of NH₃ to acid gases (sum of SO₂, HNO₃ and HCl) increased with time, from 1.9 in 2000 to 4.7 in 2015, confirming that NH₃ is increasingly in molar excess over atmospheric acidity. The ratio of annual mean molar concentrations of NH₃ (80 nmol m⁻³) to SO₂ (29 nmol m⁻³) was 2.7 in 2000, which increased in 2015 to 15 (annual mean concentrations of NH₃ = 58 nmol m⁻³ cf. SO₂ = 4 nmol m⁻³). Molar concentrations of HNO₃ (4 nmol m⁻³) and HCl (6 nmol m⁻³) were comparable to SO₂ in 2015, highlighting the increasing importance of HNO₃ and HCl in contributing to atmospheric acidity. A larger decrease in SO₂ (–81 %) than particulate sulphate (–69%) in the AGANet data (Table 4) would appear at first to suggest that the large NH₃:SO₂ ratio is contributing to a more rapid decrease in SO₂ concentrations. However, when the seasalt fraction of SO₄²⁻ is removed from

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the sulphate trend, the decrease in NSS_SO4 (–78%) is similar to SO₂ (–81%) which would suggest that maximum deposition rates for SO₂ may have been reached with the smaller SO₂ concentrations since 2000.

At the same time, reduction in emissions of the precursor gases have also led to a lower formation of particulate phase NH₄⁺, NO₃⁻ and SO₄²⁻ in the atmosphere and changes in atmospheric composition. Since the affinity of H₂SO₄ (oxidation product of SO₂) for NH₃ is much larger than that of HNO₃ and HCl, available NH₃ is first taken up by H₂SO₄ to form ammonium sulphate compounds (NH₄HSO₄ and (NH₄)₂SO₄), with any excess NH₃ then available to react with HNO₃ and HCl to form NH₄NO₃ and NH₄Cl that are volatile. Analysis of the different particulate components in sect. 3.5 showed that the ammonium aerosols are mainly made up of (NH₄)₂SO₄ and NH₄NO₃. With the large reduction in SO₂, more NH₃ is available to react with HNO₃ to form NH₄NO₃ and concentrations of NH₄⁺ and NO₃⁻ are now observed to be in molar excess over SO₄²⁻, providing evidence of a change in the particulate phase from (NH₄)₂SO₄ to NH₄NO₃ (Figure 18b). A change to an NH₄NO₃ rich atmosphere and the potential for NH₄NO₃ to release NH₃ and HNO₃ in warm weather, together with the surfeit of NH₃ also means that a larger fraction of the reduced and oxidised N is remaining in the gas phase as NH₃ and HNO₃. An increased partitioning to the gas phase may account for the larger decrease in particulate NH₄⁺ (MK –62% between 2000-2015, n = 12) and NO₃⁻ (MK –52% between 2000-2015, n = 12) than NH₃ (MK –30% between 2000-2015, n = 12) and HNO₃ (MK –45 % between 2000-2015, n = 12) (Table 5) and the increase in gas to aerosol ratios (NH₃:NH₄⁺ and HNO₃:NO₃⁻) over the 16 year period (Figure 17). A higher concentration of the gas-phase HNO₃ and NH₃ may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in NO_x and NH₃. Given the larger deposition velocities of NH₃ and HNO₃ compared to aerosols, more of the NH₃ and HNO₃ emitted will have the potential to deposit more locally with a smaller footprint within the UK.

Currently, the critical loads of acidity (sulphur and nitrogen) are exceeded by 44 % of

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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 SO₂ emissions (–80 %: 2000 – 2015) and moderately successful with NO_x emissions (–58 %: 2000 – 2015), with both on course to meet the emission reduction targets set out under the 2012 Gothenburg protocol and 2016 NECD. NH₃ emissions however has decreased by only 10 % over the same period, with an increasing trend since 2013 and it is likely that abatement measures may be required to meet emission reduction targets. In recognising the need to tackle the increasing NH₃ emissions, 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 NH₃ emissions from agriculture.

Based on the current emission trends and evidence from AGANet and NAMN long-term measurements, atmospheric N deposition from oxidised N (NO_x, HNO₃ and NO₃⁻) and from reduced N (NH₃, NH₄⁺) 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). The changes are also relevant for human health effects assessments, since NH₄NO₃ and (NH₄)₂SO₄ 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 (NH₄)₂SO₄ to NH₄NO₃, coupled to import of NH₄NO₃ from long-range transport (driven by emissions of NH₃ 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, SO₂ and NH₃ are higher.

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 measure-

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ments impacts the gas phase concentrations. Consider discussing these trends as total nitrate (gaseous HNO₃ + aerosol NO₃) and NH_x (gaseous NH₃ + aerosol NH₄).

Author Response: Interactions and partitioning between the gas phase (SO₂, HNO₃, NH₃) and aerosol phase (SO₄²⁻, NO₃⁻, NH₄⁺) 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 HNO₃ + aerosol NO₃⁻) and total inorganic NH_x (TIA, sum of gaseous NH₃ + aerosol NH₄⁺) 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 HNO₃ 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

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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 SO₂ concentrations relative to HNO₃ and NH₃, accompanied by large reductions also in the aerosol components, with evidence of a shift in the particulate phase from (NH₄)₂SO₄ to NH₄NO₃. The potential for NH₄NO₃ to act as a reservoir for NH₃ and HNO₃, together with the surfeit of NH₃ means that a larger fraction of the nitrogen is remaining in the gas phase, maintaining higher concentrations of NH₃ and HNO₃ 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: Replicated information deleted.

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 to: "Sodium carbonate (Na₂CO₃) is an effective sorbent

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for acid gases, allowing simultaneous collection of HNO₃, SO₂ and HCl on denuders (e.g. Fern 1986). Since the measurement of aerosol Na⁺ is also of key interest in AGANet however, a potassium carbonate (K₂CO₃) coating is used instead to eliminate the possibilities of Na⁺ contamination from Na₂CO₃. Glycerol is added to the K₂CO₃ 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 NH₄⁺ and the sum of NO₃⁻ and 2iSO₄²⁻, as NH₃ is neutralised by HNO₃ and H₂SO₄ to form NH₄NO₃ and (NH₄)₂SO₄, 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 HNO₃, SO₂ 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 NH₄⁺ (μeq): (2*SO₄²⁻ + NO₃⁻) (μeq) Expect 1:1 as NH₃

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neutralised by HNO₃ and SO₂ (H₂SO₄) to form NH₄NO₃ and (NH₄)₂SO₄ 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 outliers?

Author Response: 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 SO₂ (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 (R²) is provided in table 2. Regression plots (DELTA v ADS) were provided in Supple-

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mentary 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 may 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 μm @ 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 NH_x 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, SO₂ concentrations are highest in winter (January and February) and lowest in summer (June – August). The peak in SO₄²⁻ concentrations however occur in March every year, where peaks in concentrations of NH₃ and NH₄⁺ from measurements made at the same time from the same sites are also observed (please note that the seasonal cycle of ammonia varies, depending on the emission source types in the vicinity of the measurement site, see Tang et al. 2018). For

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mation of SO₄²⁻ is largely governed by the availability of SO₂ and NH₃ to form the stable (NH₄)₂SO₄, and the spring peak may be attributed to enhanced formation of (NH₄)₂SO₄, since peaks in concentrations of NH₃ and NH₄⁺ also occur in spring. Import of particulate (NH₄)₂SO₄ from long-range transboundary transport also enhances the springtime concentration. In summer, sunny, warmer conditions increase photochemical oxidation of SO₂ to H₂SO₄ and subsequent formation of sulphate aerosols leading to higher aerosol SO₄²⁻ concentrations in summer than in winter.

Revised/expanded text in “section 3.6 Seasonal variation in acid gases and aerosols (paragraph 5) “SO₂, by contrast, are highest in the winter, with concentrations exceeding summer values on average by a factor of 2 (Figure 8). Increased emissions of SO₂ 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 SO₂ with NH₃ to form (NH₄)₂SO₄ is effectively irreversible (Bower et al., 1997), the ratio of the concentrations of SO₂ and SO₄²⁻ (Figure 9) is largely governed by the availability of SO₂ and NH₃ to form (NH₄)₂SO₄. The temporal profile of SO₄²⁻ has a peak in concentrations in spring, although not as pronounced as the NO₃⁻ peak (Figure 8). The spring peak may be attributed to enhanced formation of (NH₄)₂SO₄, since peaks in concentrations of NH₃ and NH₄⁺ also occur in spring (Figure 8) and from the import of particulates from long-range transboundary transport. Unlike SO₂, aerosol SO₄²⁻ concentrations are higher in summer than in winter, due to increased photochemical oxidation of SO₂ to H₂SO₄ and subsequent formation of sulphate aerosols in sunnier and warmer conditions (Mihalopoulos et al., 2007). In winter, lower SO₂ oxidation rates limit H₂SO₄ formation and therefore also the formation of (NH₄)₂SO₄.”

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 rock salt (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

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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 not measured here. More context is needed.

Author Response: OK, thanks. Sentence has been deleted. Changes in NH₃ 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

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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 NH₄⁺, NO₃⁻ and SO₄²⁻ in the atmosphere and changes in atmospheric composition. Since the affinity of H₂SO₄ (oxidation product of SO₂) for NH₃ is much larger than that of HNO₃ and HCl, available NH₃ is first taken up by H₂SO₄ to form ammonium sulphate compounds (NH₄HSO₄ and (NH₄)₂SO₄), with any excess NH₃ then available to react with HNO₃ and HCl to form NH₄NO₃ and NH₄Cl that are volatile. Analysis of the different particulate components in sect. 3.5 showed that the ammonium aerosols are mainly made up of (NH₄)₂SO₄ and NH₄NO₃. With the large reduction in SO₂, more NH₃ is available to react with HNO₃ to form NH₄NO₃ and concentrations of NH₄⁺ and NO₃⁻ are now observed to be in molar excess over SO₄²⁻, providing evidence of a change in the particulate phase from (NH₄)₂SO₄ to NH₄NO₃ (Figure 18b). A change to an NH₄NO₃ rich atmosphere and the potential for NH₄NO₃ to release NH₃ and HNO₃ in warm weather, together with the surfeit of NH₃ also means that a larger fraction of the reduced and oxidised N is remaining in the gas phase as NH₃ and HNO₃. An increased partitioning to the gas phase may account for the larger decrease in particulate NH₄⁺ (MK -62% between 2000-2015, n = 12) and NO₃⁻ (MK -52% between 2000-2015, n = 12) than NH₃ (MK -30% between 2000-2015, n = 12) and HNO₃ (MK -45 % between 2000-2015, n = 12) (Table 5) and the increase in gas to aerosol ratios (NH₃:NH₄⁺ and HNO₃:NO₃⁻) over the 16 year period (Figure 17). A higher concentration of the gas-phase HNO₃ and NH₃ may therefore be maintained in the atmosphere than expected on the basis of the emissions trends in NO_x and NH₃. Given the larger deposition velocities of NH₃ and HNO₃ compared to aerosols, more of the NH₃ and HNO₃ emitted will have the potential to deposit more locally with a smaller footprint within the UK. "

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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).

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