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 HNO3 and NO3- vs NOx 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 NOx 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 m-3).
m-3) and HCl (from 0.31 to 0.20 µg HCl m-3) over the same period (Figure 13a). Particulate SO42-, NO3- and NH4+ 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 NH3, NH4+ 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 NOx, SO2, HCl and NH3 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. µg HNO3 m-3 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 HNO3, SO2, HCl and particulate NO3-, SO42-, 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 AGANet sites for the 10 year period from 2006 to 2015 (Figure 15, Table 4). NH3 and NH4+ 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 HNO3 and NO3- vs NOx emissions. The overall downward trends in HNO3 and NO3- are seen to be broadly consistent with the ~49 % fall in estimated NOx 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 NOx 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 HNO3 and NO3- annual data show
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 NOx 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 NOx 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 NOx, through reaction with OH. or heterogeneous conversion of N2O5, it provides an important measure of the fraction of NOx emissions that is oxidised and signals any long-term changes in the atmospheric processing timescales of NOx 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 NOx 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 NOx emissions lends support to a linear response in HNO3 concentrations to reductions in NOx emissions.

3.8.2 Trends in SO2 and SO42- vs SO2 emissions. Unlike NOx, 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 NOx 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
atmosphere with larger decline in SO2 than NOx.

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.

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,
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 \(\mu g\) SO2 m\(^{-3}\), \(n = 12\)) approaching that of the other acid gases HNO3 (0.21 \(\mu g\) HNO3 m\(^{-3}\), \(n = 12\)) and HCl (0.20 \(\mu g\) 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 \(\mu g\) NH3 m\(^{-3}\) (\(n = 12\)) in 2015. The changes in measured concentrations of SO2, HNO3, HCl and NH3 are consistent with the estimated decrease in emissions of SO2, NOx, 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 SO\(\Delta\)n2 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 leave 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
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.

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$_2$SO$_4$ (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$_2$SO$_4$ to form ammonium sulphate compounds (NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$), with any excess NH$_3$ then available to react with HNO$_3$ and HCl to form NH$_4$NO$_3$ and NH$_4$Cl that are volatile. Analysis of the different particulate components in sect. 3.5 showed that the ammonium aerosols are mainly made up of (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$.

With the large reduction in SO$_2$, more NH$_3$ is available to react with HNO$_3$ to form NH$_4$NO$_3$ and concentrations of NH$_4^+$ and NO$_3^-$ are now observed to be in molar excess over SO$_4^{2-}$, providing evidence of a change in the particulate phase from (NH$_4$)$_2$SO$_4$ to NH$_4$NO$_3$ (Figure 18b). A change to an NH$_4$NO$_3$ rich atmosphere and the potential for NH$_4$NO$_3$ to release NH$_3$ and HNO$_3$ in warm weather, together with the surfeit of NH$_3$ also means that a larger fraction of the reduced and oxidised N is remaining in the gas phase as NH$_3$ and HNO$_3$. An increased partitioning to the gas phase may account for the larger decrease in particulate NH$_4^+$ (MK $-62\%$ between 2000-2015, $n = 12$) and NO$_3^-$ (MK $-52\%$ between 2000-2015, $n = 12$) than NH$_3$ (MK $-30\%$ between 2000-2015, $n = 12$) and HNO$_3$ (MK $-45\%$ between 2000-2015, $n = 12$) (Table 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.

Currently, the critical loads of acidity (sulphur and nitrogen) are exceeded by 44 % of the area of sensitive habitats in the UK (based on mean deposition data for 2012-2014), whereas the figure for exceedance of eutrophication (nutrient nitrogen) is even larger, at 62 % (based on deposition data for 2012 – 2014) (Hall & Smith, 2016). Air quality policies have been very successful in abating SO$_2$ emissions ($-80\%$: 2000 – 2015) and moderately successful with NO$_x$ emissions ($-58\%$: 2000 – 2015), with both on course to meet the emission reduction targets set out under the 2012 Gothenburg protocol and 2016 NECD. NH$_3$ 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 NH$_3$ 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 NH$_3$ emissions from agriculture.

Based on the current emission trends and evidence from AGANet and NAMN long-term measurements, atmospheric N deposition from oxidised N (NO$_x$, HNO$_3$ and NO$_3^-$) and from reduced N (NH$_3$, NH$_4^+$) are likely to continue to exceed critical loads of N deposition over large areas of sensitive habitats, with implications for UK’s commitment to maintain or restore natural habitats (e.g. Natura 2000 sites; Hallsworth et al., 2010) to a favourable conservation status under the EU Habitats Directive (Council Directive 92/43/EEC). The changes are also relevant for human health effects assessments, since NH$_4$NO$_3$ and (NH$_4$)$_2$SO$_4$ 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$_4$)$_2$SO$_4$ to NH$_4$NO$_3$, coupled to import of NH$_4$NO$_3$ 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.

2) The discussion of the trends of NH$_3$ and HNO$_3$ are sometimes a bit difficult to follow as the change in aerosol composition and loading over the time frame of the measure-
ments impacts the gas phase concentrations. Consider discussing these trends as total nitrate (gaseous HNO\textsubscript{3} + aerosol NO\textsubscript{3}) and NH\textsubscript{x} (gaseous NH\textsubscript{3} + aerosol NH\textsubscript{4}).

Author Response: Interactions and partitioning between the gas phase (SO\textsubscript{2}, HNO\textsubscript{3}, NH\textsubscript{3}) and aerosol phase (SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{3}-, NH\textsubscript{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\textsubscript{3} + aerosol NO\textsubscript{3}-) and total inorganic NH\textsubscript{x} (TIA, sum of gaseous NH\textsubscript{3} + aerosol NH\textsubscript{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\textsubscript{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 HNO\textsubscript{3} and NH\textsubscript{3}.

Author Response: Text revised in abstract.

2) Abstract Page 2 lines 5-6: “. . . indications that the atmospheric lifetime of HNO\textsubscript{3} and NH\textsubscript{3} 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 NO\textsubscript{3} and NH\textsubscript{3} due to changes in SO\textsubscript{2}. This likely decreases the atmospheric lifetime of total nitrate and reduced nitrogen compounds as NH\textsubscript{3} and HNO\textsubscript{3} typically dry deposit faster than aerosol NO\textsubscript{3} and NH\textsubscript{4}.

Author Response: See also response to Reviewer 1 (comment 32). Text revised in abstract: “Since 1999, AGANet has shown substantial decrease in SO\textsubscript{2} concentrations relative to HNO\textsubscript{3} and NH\textsubscript{3}, accompanied by large reductions also in the aerosol components, with evidence of a shift in the particulate phase from (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} to NH\textsubscript{4}NO\textsubscript{3}. The potential for NH\textsubscript{4}NO\textsubscript{3} to act as a reservoir for NH\textsubscript{3} and HNO\textsubscript{3}, together with the surfeit of NH\textsubscript{3} means that a larger fraction of the nitrogen is remaining in the gas phase, maintaining higher concentrations of NH\textsubscript{3} and HNO\textsubscript{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: 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 (Na\textsubscript{2}CO\textsubscript{3}) is an effective sorbent
for acid gases, allowing simultaneous collection of HNO3, SO2 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 (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 2\(\text{Cl}\)+SO42-, as NH3 is neutralised by HNO3 and H2SO4 to form NH4NO3 and (NH4)2SO4, respectively (Connelly 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+ (\(\mu\)eq): (2\(\times\)SO42- + NO3-) (\(\mu\)eq) Expect 1:1 as NH3 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.

R Stence 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 \(\mu\)g m-3 cf mean ADS = 2.18 \(\mu\)g m-3) and 4 % for HCl (mean DELTA = 0.40 \(\mu\)g m-3 cf mean ADS = 0.41 \(\mu\)g m-3).” Linear regression (R2) is provided in table 2. Regression plots (DELTA v ADS) were provided in Supple-
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 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, 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 vary, depending on the emission source types in the vicinity of the measurement site, see Tang et al. 2018). For-

formation 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 increases 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 limits 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 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 in-
crease 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 concentra-
tions (ca. 35 nmol 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

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 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 in-
crease 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 life-
time. 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 cli-
mate (paragraph 5 and 6)” “At the same time, reduction in emissions of the precur-
ror 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 affin-
ity 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 com-
ounds (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 partic-
ulate 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 concentra-
tion of the gas-phase HNO3 and NH3 may therefore be maintained in the atmosphere
than expected on the basis of the emissions trends in NOx 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.”
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).