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Atmospheric Chemistry and Physics Discussions

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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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

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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 HNO3 determination" to address the reviewer's comments. See below: "HNO3 data were corrected for sampling artefacts in the measurements with an empirical correction factor of 0.45 (see section 2.6). Interferences in HNO3 determination arise through the simultaneous collection of reactive oxidized nitrogen species on the K2CO3 coating that forms nitrate ions in the aqueous extracts of exposed denuders. Potential interfering species include HONO, NO2, N2O5 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 HNO3 in the UK (e.g. Kitto & Harrison 1992, Connolly et al. 2016). Interference from NO2 should be small, since the reactivity of a carbonate coating surface towards NO2 is low (Allegrini et al., 1987), with capture of NO2 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 NO2 m-3; Conolly et al., 2016). Tests by Steinle et al. (2009) on the AGANet K2CO3/glycerol coated denuders also confirmed low capture (ca 3 %) of NO2. 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

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(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 HNO3” signal from the carbonate coated denuders will be dependent on the relative concentrations of HNO3 to interfering species present in the atmosphere and likely to be both site and season specific. The 2 years of data indeed show this variability between sites and between seasons. Given the complexities of atmospheric chemistry of the large family of oxidised nitrogen species, further work is clearly needed to understand what the carbonate denuders is measuring, before an improved correction algorithm for the HNO3 data can be developed with any confidence. The empirical 0.45 HNO3 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 NO2 interference of the DELTA HNO3 signal is expected, the HNO3 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, R2 = 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 NO2, the HNO3 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 HNO3, e.g. Allegrini et al., 1987), with a third K2CO3/glycerol coated denuder to collect SO2. At three sites (Auchencorth, Bush OTC and Stoke Ferry), parallel measurements of the old configuration (two K2CO3/glycerol coated denuders) and new configuration (two NaCl coated denuders + K2CO3/glycerol coated denuder) were conducted over 12 months in 2016. In the new configuration, nitrate measured on the NaCl denuders are reported as HNO3, whereas nitrate on the K2CO3 denuder are assumed to come from other oxidised nitrogen species and are not reported. Comparing the sum of nitrate concentrations from the new (2xNaCl + 1xK2CO3) with the old

(2xK2CO3) 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 2xK2CO3 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 HNO3 interference at each site to be quantified, by comparing the amount of nitrate measured on the NaCl and K2CO3 coated denuders. Initial analysis of 2016 data (unpublished data) showed that the mean ratio of nitrate on NaCl:K2CO3 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): “HNO3 is a secondary product of NOx, but NOx 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 HNO3 and NO3- (Figure 8). A weak seasonal cycle is observed in HNO3, 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 HNO3 during this period (Pope et al., 2016). As discussed in section 3.3, a constant correction factor was applied to all HNO3 data, which does not take into account seasonal dependency. The concentrations in HNO3 may therefore be over-estimated in winter (less HNO3 formed from photochemical processes) and under-estimated in summer (larger HNO3 concentrations due to increased .OH radicals for reaction with NO2 to form HNO3), 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 PM2.5 fraction, as well as some of the coarse mode aerosols < PM4.5."

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 NH3, HNO3, SO2 and

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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 “HNO3 measurement artefacts and correction”

Regarding the empirical correction of the HNO3 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: HNO3/NO3- and NH3/NH4+ 3.1.3 Comparisons with bubbler and filter pack measurements: SO2 and SO42-

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 $\sim$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 PM4.5 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 (R2 = 0.24) and for Mg, the slope was 2.4

(R2 = 0.24), but a lot of scatter for Ca2+ as both ADS and DELTA Ca2+ data were at or below LOD. The DELTA therefore captures Mg2+ and Na+ well, but not Ca2+, which is what we find in the AGANet data.

The slope for SO42- in DELTA v ADS intercomparison is 0.69 (R2 = 0.89). The smaller SO42- 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 K2CO3 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 SO2 and SO42- in 1999 by Hayman et al. (2006) had previosuly shown close agreement between the two methods, providing confidence in SO2 and SO42- 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 SO42- measurements in historic data. Since the DELTA method was unchanged for the assessment period in this paper, the bias in SO42- 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)…,…”

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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 PM4.5 fraction.

In the DELTA (PM4.5) v ADS (PM2.5) intercomparison of base cation measurements (see response to comment 7 earlier), the slope for Na was 3.0 (R2 = 0.24) and for Mg, the slope was 2.4 (R2 = 0.24), but no relationship was established for Ca2+ as both ADS and DELTA Ca2+ data were at or below LOD.

This suggests that the DELTA captures Mg2+ and Na+ in the PM4.5 fraction reasonably well. At all AGANet sites, Na and Mg measurements are above LOD, whereas Ca2+ are mostly at or below LOD. Aerosol filter blanks for Ca2+ are also much more variable than Na or Mg. Ca2+ is particularly problematic in chemical analysis as adsorption losses readily occur due to electrostatic interaction between Ca2+ and surfaces, especially plastic. To this end, aerosol sample extracts are acidified to minimise adsorption of Ca2+ to surfaces.

Sampling of Ca2+ is also likewise problematic as Ca2+ 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 Ca2+ were within the noise of the LDPE tube blanks (i.e. clean LDPE tubes extracted with deionised water), adding to the uncertainty in Ca2+ measurements (see also response to next reviewer comment 12).

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

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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: NO3-: loss to LDPE tube is negligible (2.4 ± 0.8 % (mean ± SD) across all sites for all available data). NO2-, SO42- and Cl-: losses to LDPE are small (< 6%). Base cations Na+ and Mg2+: losses to LDPE are slightly higher (<7%). Base cations Ca2+: there is a large degree of uncertainty in the calcium assessment, due to 1) variability of Ca2+ in the blank LDPE tube extracts and 2) very low Ca2+ on LDPE tubes from sites, that were similar to blank values and close to the detection limit (LOD = 0.05 mg/L Ca2+). 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: "HNO3 is a secondary product of NOx, but NOx 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 HNO3 and NO3- (Figure 8). HNO3 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 HNO3 during this period (Pope et al., 2016). As discussed in section 3.3, a constant correction factor was applied to all HNO3 data, which does not take into account seasonal dependency. The concentrations in HNO3 may therefore be over-estimated in winter (less HNO3 formed from photochemical processes) and under-estimated in summer (larger HNO3 concentrations due to increased .OH radicals for reaction with NO2 to form HNO3), 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 HNO3 relative to particulate-phase NH4NO3, limiting peak NO3- aerosol concentrations (Figure 8). This process accounts for the minima in NO3- concentrations (Figure 7) and the highest ratio of HNO3 to NO3- seen in July (Figure 8). Cooler conditions in the spring than early autumn sees a larger fraction of the volatile NH4NO3 remaining in the aerosol phase. The peak in NO3- concentrations and the low HNO3:NO3- ratio in spring-time (Figure 8) is thus a combination of larger NO3- from reaction between higher concentrations of the precursor gases HNO3 and NH3, and partitioning to the aerosol phase. Import from long-range transboundary transport of particulate NO3- e.g. from continental Europe into the UK, as discussed in Vieno et al. (2014, 2016) adds to the elevated NO3- concentrations. In winter, low temperature and high humidity also shifts the equilibrium to formation of NH4NO3 from the gas-

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phase HNO3 and NH3. Since NH3 concentrations are lowest in winter however, with less NH3 available for reaction, NH4NO3 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 Mg2+ and Ca2+ are based on what the measurement shows. Mg2+ 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 Ca2+, uncertainties in interpretation of the Ca2+ 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 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

Revised/expanded text: “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 13). 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 are dominated by the large 2003 peak in concentrations (see sect. 3.6). 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 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 line 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- 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 ïĆřC due to an exceptional cold winter, with Dec 2010 recorded as the coldest for over 100 years (cf. 9.2 ïĆřC 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 NH3. NH3 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 NH3 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 NOÂň3- and SO42- 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.

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

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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 HNO3 and NO3- vs NOx emissions, end of last paragraph. 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 (Conolly et al. 2016). Although there is uncertainty in the corrected HNO3 data (see section3.3), the encouraging agreement between HNO3, NO2 concentrations and NOx emissions lends support to a linear response in HNO3 concentrations to reductions in NOx 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 an-

thropogenic 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 SO2 and SO42- vs SO2 emissions” to discuss sea salt SO42- (SS_SO4) – see below: “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 (Tables 4 and 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.”

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 NH3 to acid gases and molar ratios of NH4+ to NO3- and SO42- 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 NH3 to acid gases (SO2, HNO3 and HCl) and (b) molar ratio of particulate NH4+ to acid aerosols (SO42- and NO3-) 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 NH3 to SOÂň2 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 (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 = 58 neq. m-3) was 2.7 in 2000, which increased in 2015 to 15 (annual mean concentrations of NH3 = 58 nmol

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m-3 cf. SO_2 = 4 nmol m-3 = 8 neq. 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 HNO_3:NO_3^- is similar to changes in upward trend in gas-aerosol partitioning between NH_3 and NH_4^+ over time...': what do you call similar? For HNO_3/NO_3^-, the ratio increases by _20%, while for NH_3/NH_4^+, 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 NOx 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 NO3- is more distinct with a large peak in concentrations that occur every spring, together with a second smaller peak in autumn (Figure 8). NH3, the main neutralising gas in the atmosphere that reacts with HNO3 to form NH4NO3, 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 NO3- formation is dependent upon the availability of NH3 for reaction with HNO3, its’ concentration is also governed by the equilibrium that exists between gaseous HNO3, NH3 and particulate NH4NO3, 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. HNO3 and NH3 that are not removed by deposition may react together in the atmosphere to form NH4NO3, when the concentration product [NH3].[HNO3] exceeds equilibrium values, with NH4NO3 serving as a potential reservoir for the gases. Since NH4NO3 is semi-volatile, any that is not dry or wet deposited can potentially dissociate to release NH3 and HNO3, 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.

âĂČ 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 NH3 to acid gases (SO2, HNO3 and HCl) and (b) molar ratio of particulate NH4+ to acid aerosols (SO42- and NO3-) 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 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 SO2 (−81%) which would suggest that maximum deposition rates for SO2 may have been reached with the smaller SO2 concentrations since 2000.”

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 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. The 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 their gaseous precursors (NH3: MK -30% between 2000-2015, n=12 and HNO3: MK -45 % between 2000-2015, n=12) (Table 5) and the increase in ratios of NH3:NH4+ and HNO3:NO3- over the 16 year period (Figure 15). A higher concentration of the gas-phase nitrogen species (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 velocity of NH3 and HNO3 compared to particulate NH4+ and NO3-, more of the NH3 and HNO3 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 NH3 and NH4+), Precip-net (2-weekly wet deposition measurements) and NO2-net (4-weekly NO2 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: Denuder capture efficiency (% CE) =100 x (Denuder 1)/((Denuder 1+ Denuder 2)) âĂČ 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 HNO3 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: % change =100 . ([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 – cor-

rected

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 SO2 (μg S m-3) and SO42- (μg S m-3) To show more clearly that the units are on an element basis (NH3-N, HNO3-N, SO2-S, etc.)

All other figures are on a molecule basis (NH3, HNO3, SO2, 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. HNO3, SO2, HCl and aerosol NO3-, SO42-, Cl- data (annual mean, μg m-3) are from the UK Acid Gases and Aerosol Monitoring Network (AGANet). NH3 and NH4+ 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 (HNO3/ NO3-, SO2/SO42- 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., https://doi.org/10.5194/acp-2018-489, 2018.