

## ***Interactive comment on “Drivers for spatial, temporal and long-term trends in atmospheric ammonia and ammonium in the UK” by Yuk S. Tang et al.***

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RESPONSE TO REVIEWERS L. Horváth (Referee)

The authors thank Prof. Horváth 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 “Emission sources According to the MS (Fig. 10b) the share of fertilizers is 16.2% together with

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'other animals'. This is a simplification, these two sources have to split, since it takes 4-5 times higher contribution than that of sheep. So I miss displaying fertilizers from some figures (7, 10, 16)."

Author Response: There is one NAMN site only classed as dominated by emissions from the "fertiliser" emission source sector (see section 3.1 describing the classification of each NAMN sites according to one of seven specific dominant emission source sectors). At this site, NH<sub>3</sub> is measured but not NH<sub>4</sub><sup>+</sup> (see Supp. Fig. 2a). Temporal and trend analysis have therefore not been carried out for the "fertilisers" source sector. The focus of Fig. 10b is on three specific dominant emission source sectors (Cattle, Pigs & Poultry, Sheep), compared with other emissions.

Since the "fertiliser" category is not considered in the paper (due to too few sites), "other animals + fertilisers" in the pi-chart have been grouped together for simplicity. "Fertiliser" category has not been considered separately in Figs 7 and 16 for the same reason.

UK annual ammonia emissions data are downloaded from <http://naei.defra.gov.uk/data/>: Other animals (horses) = 1.39 % and fertilisers = 14.86 %. Sum of "other animals + fertiliser" = 16.2 % (Fig. 10b).

"Long-term trend analysis Ammonia emission in UK decreased substantially during the examined period while concentration remained at same level as it have been observed in other countries in Europe. Authors mentioned, it is the effect of sulphur dioxide emission and concentration decrease. It is true, but I miss a more detailed explanation of this mechanism. Fowler et al., 2001 (Water Air Soil Poll, Focus 1, 39-48) pointed out firstly the importance of co-deposition of ammonia and sulphur dioxide. I.e. there is a direct proportion between the SO<sub>2</sub> concentration and the dry deposition velocity of NH<sub>3</sub> onto natural surfaces that strongly influences the ammonia level in the atmosphere.

Author Response: See response to Comment 2 (p9).

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“Seasonal trend analysis Source strength of ammonia – of course – strongly depends on temperature, so seasonal trend of  $\text{NH}_x$  is mainly determined by this factor. But, as to the ammonia/ammonium transformation it is partly an equilibrium process due to the  $\text{NH}_3 + \text{HNO}_3 : \text{NH}_4\text{NO}_3$  reaction as it mentioned in the first paragraph of 3.5.6. The dissociation constant of ammonium nitrate depends on temperature, relative humidity and particle size (Mozurkewich, Atmos Envir 27A:261-270, 1993). At low relative air humidity (r.h. <60-70) ammonium nitrate does not exist in air at all. This phenomenon may strongly effect on seasonal variation of  $\text{NH}_3$  and  $\text{NH}_4^+$  concentrations as a consequence of difference of summer/winter humidity even if part of ammonium is associated with hydrogen sulphate or sulphate ions. Authors should also describe this mechanism in the interpretation of  $\text{NH}_x$  seasonal trend. A sulphate/nitrate ratio in aerosol phase in different seasons would give a good qualitative picture. In Fig. 18a we can observe nitrate dominance against the sulphate (2:1 in case of ammonium nitrate-ammonium hydrogen sulphate regime) that underlines the importance of ammonium nitrate in controlling the ammonium/ammonia ratio. Spring maxima for particle ammonium has observed and explained by the effect of non-domestic (continental) sources (after Vieno et al., 2014). But, the reason of that did not mentioned. How is the possible mechanism responsible for high continental ammonium (or ammonia) concentrations and transport from the continent in spring?”

Author Response: Section 3.3, paragraph 5 has been expanded to include explanation of the equilibrium between gas and aqueous aerosol phase as drivers in the seasonal variations of particulate  $\text{NH}_4^+$ .

“For particulate  $\text{NH}_4^+$ , as expected for a secondary pollutant, concentrations are more decoupled from the dominant  $\text{NH}_3$  source sectors in the vicinity of a site. Although the formation of particulate  $\text{NH}_4^+$  primarily depends on the occurrence of  $\text{NH}_3$  in the atmosphere, synoptic meteorology and long range transboundary transport from continental Europe are important drivers influencing the seasonal variations of  $\text{NH}_4^+$  across the UK, due to its’ longer lifetime. The seasonal trends in particulate  $\text{NH}_4^+$  are seen

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to be broadly similar for the four different emission source sectors (Figure 7b), with the magnitude of the  $\text{NH}_4^+$  concentrations reflecting  $\text{NH}_3$  concentrations at a regional level. In the atmosphere, particulate  $\text{NH}_4^+$  are primarily in the form of  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$ , formed when the acid gases  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  in the atmosphere are neutralised by  $\text{NH}_3$  (Putaud et al., 2010).  $\text{NH}_3$  preferentially neutralizes  $\text{H}_2\text{SO}_4$  due to its low saturation vapour pressure (forming  $\text{NH}_4\text{HSO}_4$  followed by  $(\text{NH}_4)_2\text{SO}_4$ ), while  $\text{NH}_4\text{NO}_3$  is formed when abundant  $\text{NH}_3$  is available. In contrast to  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  is a semi-volatile component (Stelson & Seinfeld, 1982). Long-term data from the UK Acid Gas and Aerosol Network (AGANet, Conolly et al., 2016) shows a change in the particulate phase of  $\text{NH}_4^+$  from  $(\text{NH}_4)_2\text{SO}_4$  to  $\text{NH}_4\text{NO}_3$ , with particulate nitrate concentrations exceeding that of particulate sulphate approximately three-fold (on a molar basis) (Fig. 18a). This suggests that the thermodynamic equilibrium between the gas phase  $\text{NH}_3$  and  $\text{HNO}_3$  and the aerosol phase  $\text{NH}_4\text{NO}_3$  will have a much greater effect on the seasonal concentrations of  $\text{NH}_4^+$  than  $(\text{NH}_4)_2\text{SO}_4$ . The formation and dissociation of  $\text{NH}_4\text{NO}_3$  depend strongly on ambient temperature and humidity (Stelson and Seinfeld, 1982). Warm, dry weather in summer promotes dissociation, decreasing particulate phase  $\text{NH}_4\text{NO}_3$  relative to gas phase  $\text{NH}_3$  and  $\text{HNO}_3$ . During the winter months, low temperature and high humidity favour the formation of  $\text{NH}_4\text{NO}_3$  from the gas phase  $\text{NH}_3$  and  $\text{HNO}_3$ . By contrast, the spring peak in  $\text{NH}_4^+$  concentrations may be attributed to photochemical processes (elevated ozone) leading to enhanced formation of  $\text{HNO}_3$  during this period (Pope et al., 2016) and also to import of particulate  $\text{NO}_3^-$  through long-range transboundary transport, e.g. from continental Europe, as discussed in Vieno et al. (2014). Nevertheless, it is notable that the winter minima for  $\text{NH}_4^+$  aerosol concentrations at sheep and background sites are more pronounced than that for pig, poultry and cattle dominated sites. This may be a result of a combination of smaller  $\text{NH}_3$  emissions in winter in these areas (as indicated by Figure 7a) and differences in long-range transport to the more remote areas in winter conditions.” References added:

Pope, R.J., Butt, E.W., Chipperfield, M.P., Doherty, R.M., Fenech, S., Schmidt,  
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A., Arnold, S.R and Savage, N.H. The impact of synoptic weather on UK surface ozone and implications for premature mortality. *Environmental Research Letters*. 11, doi:10.1088/1748-9326/11/12/124004, 2016.

Putaud, J.P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrus, J., Flenjtje, H., Fuzzi, S., Gehrig, R., Hansson, H.C. and Harrison, R.M. A European aerosol phenomenology–3: Physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmospheric Environment*, 44(10), 1308-1320, doi:10.1016/j.atmosenv.2009.12.011, 2010.

Stelson, A. W., and Seinfeld, J. H.: Relative humidity and temperature dependence of the ammonium nitrate dissociation constant, *Atmospheric Environment*, 16, 983-992, doi: 10.1016/0004-6981(82)90184-6, 1982.

“Sampling networking. Because the short lifetime of ammonia it is difficult to find a “representative” measurement site for comparison with modelled concentrations on a 5\_5 km grid. Authors mention a reason of the discrepancy between modelled concentration for the whole UK and concentration for the grids involving one or more measurement sites. This happens in the low and high concentrations regimes (<0.5 and >3.0  $\mu\text{g}/\text{m}^3$ ) in different directions (over- or underestimation), as it also appears clearly in Figure 5. Authors describe some reasons of that (page 9 lines 39-41 though page 10 lines 1-2), mentioning that samplings were influenced by nearby emission sources. In this case some sites are not representative for the given 5\_5 km grid. It is illustrated by the relationship between modelled and measured concentrations in the lower range (selected for the range of between the range of 0 and 4.5  $\mu\text{g}/\text{m}^3$ ) where the relationship is stronger. Further analysis is needed how FRAME model correlated with measured  $\text{NH}_3$  concentrations in the work of Dore et al. 2015. Is there any discrepancy between modelled and measured concentrations in low and high ranges? How the model was validated? At sites with low concentrations samplings were performed in a clearing of forests. Question is: do model predict concentrations for layer above the canopy or for the ground level, where effect of deposition of the nearby forest is substantial? It would

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be the source of another bias between the modelled and measured ammonia concentrations. Other possible source of bias could be derived by the difference between the monthly sampling applied in the NAMN network and the sampling/measurement method for the validation of model. Are there any inter-comparison among the methods described in this manuscript and other methods based on daily or shorter time basis? In any case, taking into account that the modelled and measured concentrations agree well in middle range and in the average for the whole UK, the network seems to be suitable to establish trends for ammonia/ammonium concentrations.”

Re: “Further analysis is needed how FRAME model correlated with measured NH<sub>3</sub> concentrations in the work of Dore et al. 2015. Is there any discrepancy between modelled and measured concentrations in low and high ranges? How the model was validated?”

Author Response: Validation of the atmospheric transport model FRAME (Fine Resolution AMmonia Exchange) in estimating atmospheric concentrations and deposition rates of gaseous NH<sub>3</sub> and particulate NH<sub>4</sub><sup>+</sup> have previously been made by comparison with measurements from the UK NAMN (Dore et al., 2007) and by comparison with other models (Dore et al., 2015). When compared with other atmospheric chemistry transport models, FRAME was found to correlate well with measured NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations from NAMN (Dore et al., 2015). The comparison of NAMN NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> measurements with modelled NH<sub>3</sub> concentrations from the FRAME model in the paper is made for an example year of 2012 in the paper, This updates an earlier inter-comparison assessment carried out by Dore et al. (2007) for the year 2002, and demonstrates that the FRAME model is performing well in describing the spatial distribution of both NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup>.

The FRAME model uses a database of NH<sub>3</sub> emissions with a 5×5 km grid-square resolution as input. In the present comparison of the FRAME model estimates (based on 2012 UK AENEID NH<sub>3</sub> emission data) with the NAMN measurement results for 2012 (Figure 5), the network annual mean concentrations for each site is compared

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against the model estimate for the 5-km grid square in which it occurs, and the point is classified according to the estimated dominant source sector of the grid square. Both the model outputs and the measurement agree that background and sheep sites are characterised by small NH<sub>3</sub> concentrations (< 1 µg NH<sub>3</sub> m<sup>-3</sup> annual mean), while agricultural areas, particularly areas with intensive pig and poultry areas, are associated with large NH<sub>3</sub> concentrations (up to 8 µg NH<sub>3</sub> m<sup>-3</sup> annual mean). Overall, the comparison suggests a fairly good fit with regard to both the magnitude and spatial variability of NH<sub>3</sub> concentrations at a national scale, with an R<sup>2</sup> value of 0.6 (Figure 7). The results of the network thus broadly support the predictions of the FRAME model, lending support to the AENEID model outputs. There are however, systematic differences in the comparison of FRAME and the measurements, depending on the air concentration and dominant source. Figure 5 shows that concentrations are overestimated by FRAME in areas dominated by cattle, pig and poultry, compared with the measurement data, while the results agree well in sheep and non-agricultural areas. Possible reasons for the overestimation of cattle, pig and poultry farming by FRAME compared to the measurements may be due to the following:

a) spatial location of the sampling site relative to the distribution of sources. Ammonia exhibits large sub-grid spatial variability (Dragosits et al. 2002), with the result that single site measurements may not reflect the concentrations across the 5 km grid squares. For example, at many of the sites where the model overestimates concentrations, the measurements are in fact made in nature reserves, which would on average be more distant from sources than assumed in the FRAME 5 km average estimates, thereby underestimating concentrations. This effect is particularly important in areas with high local variability in ammonia emissions, such as intensive agricultural areas. This illustrates the importance of having a large number of sites for comparison,

b) accuracy of the emissions data that are critical to the performance of the model. For example accuracy of emission factors for different livestock classes affecting the model estimates, or

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c) that dispersion in the model is slightly underestimated. Clearly further work is required to address these questions.

Dore, A. J., Vieno, M., Tang, Y. S., Dragosits, U., Dosio, A., Weston, K. J., & Sutton, M. A. (2007). Modelling the atmospheric transport and deposition of sulphur and nitrogen over the United Kingdom and assessment of the influence of SO<sub>2</sub> emissions from international shipping. *Atmospheric Environment*, 41(11), 2355-2367.

Dore, A. J., Carslaw, D. C., Braban, C., Cain, M., Chemel, C., Conolly, C. & Lawrence, S. (2015). Evaluation of the performance of different atmospheric chemical transport models and inter-comparison of nitrogen and sulphur deposition estimates for the UK. *Atmospheric Environment*, 119, 131-143.

Re: “At sites with low concentrations samplings were performed in a clearing of forests. Question is: do model predict concentrations for layer above the canopy or for the ground level, where effect of deposition of the nearby forest is substantial? It would be the source of another bias between the modelled and measured ammonia concentrations.”

Author Response: FRAME is a Lagrangian model that incorporates horizontal and vertical gradients of NH<sub>3</sub> and calculates vertical concentration profiles with diffusion through 33 layers of varying depth. The modelled concentrations output is from the 1-2 m layer, used to compare with NAMN measurements that are made at approx. 1.5 m above ground.

Additional text has been added to Section 2.1, paragraph 1, after the first sentence to provide further information on siting of sites to provide representative measurements:

“The network covers a wide distribution of monitoring sites with measurements in both agricultural and semi-natural areas. Monitoring locations are sited away from point sources (> 150 m) such as farm buildings, which avoids overestimating NH<sub>3</sub> concentrations compared with the grid square, since the aim is to provide meso-scale and

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regional patterns. In addition, where sampling is carried out in woodland areas, it is made in clearings.”

Re: “Other possible source of bias could be derived by the difference between the monthly sampling applied in the NAMN network and the sampling/measurement method for the validation of model. Are there any inter-comparison among the methods described in this manuscript and other methods based on daily or shorter time basis?”

Author Response: Comparison between model and measurement discussed in this paper is based on annual concentrations. Annual mean concentrations from NAMN are derived from the mean of monthly measured concentrations.

Inter-comparison among the methods described in this manuscript; ALPHA vs Daily Annular Denuder Method – see section 2.2.2, last paragraph: In the USA (Puchalski et al., 2011), the ALPHA samplers performed well against a reference annular denuder method with a median relative percent difference of  $-2.4\%$ . The ALPHA and DELTA methods described in this manuscript have also been compared with other methods with shorter time resolution and performed well. Some examples and references are given below.

Comparison with different methods with daily timescales: DELTA vs Daily Annular Denuder method – see Tang et al., 2009 Tang, Y. S., Simmons, I., van Dijk, N., Di Marco, C., Nemitz, E., Dammggen, U., Gilke, K., Djuricic, V., Vidic, S., Gliha, Z., Borovecki, D., Mitosinkova, M., Hanssen, J. E., Uggerud, T. H., Sanz, M. J., Sanz, P., Chorda, J. V., Flechard, C. R., Fauvel, Y., Ferm, M., Perrino, C., and Sutton, M. A.: European scale application of atmospheric reactive nitrogen measurements in a low-cost approach to infer dry deposition fluxes, *Agriculture Ecosystems & Environment*, 133, 183-195, doi.org/10.1016/j.agee.2009.04.027, 2009.

DELTA vs Daily Filter Pack (EMEP method) – (Tang et al., 2017 unpublished data, paper in prep) Response Figure 1 (attached) shows the comparison of total inorganic

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ammonium, TIA (sum of  $\text{NH}_3$  +  $\text{NH}_4^+$ ) concentrations at the Eskdalemuir monitoring station (EMEP station code = GB0002R; UK-AIR ID = UKA00130) measured under the EMEP program with concentrations of the corresponding gas and aerosol from the UK National Ammonia Monitoring Network (NAMN,  $\text{NH}_3$  and  $\text{NH}_4^+$ ). EMEP values (data downloaded from <http://ebas.nilu.no/>) are means of daily measurements for TIA by the EMEP filter pack method, matched to the NAMN sampling periods (monthly). Filter pack measurements at Eskdalemuir terminated in December 2000.

Comparison with different methods with shorter timescales: DELTA and ALPHA vs AMOR at Zegfeld (ID 633; Dutch National Air Quality Monitoring Network, LML): An intercomparison of  $\text{NH}_3$  measurements by the RIVM AMOR system (hourly) and the CEH DELTA sampling system (monthly) have been carried out at the Zegweld site in the Netherlands since July 2003. Since September 2012, CEH ALPHA measurements have also been included. To compare results, monthly mean concentrations were derived from the average of hourly AMOR data for the corresponding DELTA and ALPHA monthly sampling periods. The long-term comparison with the AMOR at Zegfeld, NL, has been added to the Supplementary Material. The following text is added to the Manuscript in Section 2.2.4 and the Graph is Supp. Figure S6)

“An intercomparison of  $\text{NH}_3$  measurements by the RIVM AMOR system (hourly, Wyers et al., 1993;) and the DELTA sampling system (monthly) have been carried out at the Zegweld site (ID 633) in the Dutch National Air Quality Monitoring Network (van Zanten et al., 2017) since July 2003. Since September 2012, ALPHA measurements have also been included. To compare results, monthly mean concentrations were derived from the average of hourly AMOR data for the corresponding DELTA and ALPHA monthly sampling periods with good agreement (supp. Figure S6).” .”

âĀĀ Re: “Methods The sampling and analytical methods need more detailed descriptions. Detection limit precision, sensitivity if any should be mentioned for all sampling and analytical procedures (where appropriate).”

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Author Response: Detailed descriptions of the DELTA and ALPHA methodologies are available from the references provided in the paper (Sutton et al., 2001a, 2001c and Tang et al., 2001a). We feel that sufficient analytical details have already been provided in section 2.2.1. DELTA methods and section 2.2.2. Passive Methods. Some additional text describing sample analysis and LODs has been added at end of Section 2.2.3,

Chemical analysis:

“The extracted samples were analysed for  $\text{NH}_4^+$  against a series of  $\text{NH}_4^+$  standards and quality controls. Parallel analysis of laboratory and field blank (unexposed) samples were used to determine the amounts of  $\text{NH}_4^+$  derived from  $\text{NH}_3$  and  $\text{NH}_4^+$  in the atmosphere during transport and storage. The limit of detection (LOD) calculation of the ALPHA and DELTA methodologies are determined as three times the standard deviations of the laboratory blanks. For the DELTA method, the LODs were  $0.01 \mu\text{g m}^{-3}$  for gaseous  $\text{NH}_3$  and  $0.02 \mu\text{g m}^{-3}$  for particulate  $\text{NH}_4^+$ . For the ALPHA method, the LOD was determined as  $0.03 \mu\text{g m}^{-3}$ ”

Re: “Interpretations Manuscript has too many figures and tables. I suggest to reduce them. For example Fig 11 relationships among rainfall amount, temperature and ammonia emission can hardly be seen. Moreover this kind of relations have still demonstrated by Fig. 9. Also, for figures 12 and 13. One of them is unnecessary. It should be decided what is the more representative interpretation statistically, the trend of yearly or monthly data. I believe the latter. Do not repeat information both by figures and in tables. Statistical parameters are displayed in figures and also in tables (e.g. figures 13, 14, 15 and corresponding tables). Also there are redundancies with figures 17a and 18a.”

Author Response: The authors feel that there is justification for the number of graphs presented as each has a particular purpose. We have explained this for each graph below, though we have agreed that Figure 17a was redundant as similar data was also shown in Figure 18a.

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Re: “Figure 11” Author Response: Figure 9 demonstrates the relationships between monitored monthly mean NH<sub>3</sub> concentrations with locally available monthly temperature and rainfall data at an example site. Figure 11 on the other hand provides an important comparison on a national level the annual mean NH<sub>3</sub> concentrations of all NAMN sites with UK annual mean temperature and rainfall. We strongly suggest to retain this graph, since it shows the strong inter- and intra-annual variability in the parameters considered. The annually averaged data of all sites masks considerable spatial and seasonal variability in NH<sub>3</sub> concentrations. Drivers contributing to this variability include the influence of climate on emissions, variations in management practice for a particular emission source, and influence of local emission sources and chemical interactions with other chemical species on NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations that are discussed in the paper. Re: “Figures 12 and 13 - one of them is unnecessary. It should be decided what is the more representative interpretation statistically, the trend of yearly or monthly data. I believe the latter” Author Response: The authors feel that both annual and seasonal variability are of equal interest. Since ammonia is strongly seasonally variable, it is important to demonstrate this graphically. In addition, the monthly data allows the seasonality to be accounted for in the seasonal Mann-Kendall test, which takes into account the 12 month seasonality and tests whether there is a trend not due to seasonality. Re: “Statistical parameters are displayed in figures and also in tables (e.g. figures 13, 14, 15 and corresponding tables).” Author Response: The data has been shown graphically and in table form in order for data transparency and so that readers may use the parameterisations if they wish. Re: “Also there are redundancies with figures 17a and 18a.” Author Response: Agree, Figure 17a deleted.

Re: “Conclusion Too long and overlaps with discussions. It has to cut insisting only on the most important findings.”

Author Response: We feel that the conclusions are not too long and are not particularly discursive. Therefore we would prefer to leave them as they are.

2) Specific comments: “Page 2: First paragraph: Authors should describe the

mechanism, how SO<sub>2</sub> reduction influences the concentration and deposition of ammonia; here or/and in line 31, in 3.5.6.,line 15 on page 17. Namely the decreased efficiency of co-deposition of SO<sub>2</sub> and NH<sub>3</sub> onto surfaces.”

Author Response: the following text has been added section 3.5.6, after paragraph 2:

“Dry deposition of SO<sub>2</sub> and NH<sub>3</sub> are enhanced in the presence of both gases, an interaction referred to as “co-deposition” (Fowler et al., 2001). The acid-base neutralization by each of the gases provides an efficient sink for dry deposition on leaf surfaces and deposition enhancement for each gas depends on the relative air concentrations of NH<sub>3</sub> and SO<sub>2</sub>. For SO<sub>2</sub>, the dry deposition process has been shown to be strongly influenced by ambient concentrations of NH<sub>3</sub> because the surface resistance is regulated mainly by uptake in moisture on foliar surfaces, which, in turn, is strongly influenced by the presence of NH<sub>3</sub>. The large reduction in SO<sub>2</sub> emissions and ambient concentrations, compared with the relative stagnation in NH<sub>3</sub> emissions and concentrations over the same period has meant that the SO<sub>2</sub>/NH<sub>3</sub> ratio has decreased dramatically. This has led to a systematic decrease in canopy resistance to uptake of SO<sub>2</sub> on surfaces, increasing dry deposition of SO<sub>2</sub> in the UK (ROTAP 2012). The underlying cause of the decrease in surface resistance is that the ambient NH<sub>3</sub> is sufficient to neutralize acidity from the solution and oxidation of deposited SO<sub>2</sub>, maintaining large rates of deposition.”

“Line 13: SO<sub>2</sub> and NO<sub>x</sub> are not acids, but acid anhydrides (as to SO<sub>2</sub> and NO<sub>2</sub>).”

Author Response: text changed from “acids” to “acid gases”

“Line 13: emitted “mainly” from combustion processes. (Do not forget natural sources esp. on global scale).”

Author Response: text added “and from natural sources”

“Line 14: Primary product of neutralization is the NH<sub>4</sub>HSO<sub>4</sub> followed by forming (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> only in case when ammonia is available in quantity enough.”

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Author Response: text added. See Author response 1c. on page 2.

“Line 16: do not forget the role of PM in cloud/for formation as condensation nuclei.”

Author Response: We have modified the sentence . . . . “The effects of PM on atmospheric visibility, radiative scattering, cloud formation (and resultant climate effects). . .”

“Page 4: “Lines 17-18: The sentence “the network has a good representation in the middle air concentration classes of 3-4  $\mu\text{g m}^{-3}$ ” does not agree with Fig. 1c where measured concentration in the range of 3-4.5  $\mu\text{g m}^{-3}$  is doubled. I would state instead “the network has a good representation in the middle air concentration classes of 0.5-3  $\mu\text{g m}^{-3}$ ”, so it is true. Otherwise it would make questionable the statement in lines 24-25, but this correlation should be justified also by figures.”

Author Response: We changed the sentence to:

“..the network has a good representation in the middle air concentration classes of 0.5 – 1.5  $\mu\text{g m}^{-3}$  (33 % of NAMN sites, compared with 29 % of all FRAME 5 km x 5 km grid squares) and 1.5 - 3  $\mu\text{g m}^{-3}$  (32 % of NAMN sites, compared with 39 % of all FRAME 5 km x 5 km grid squares), but with . . . . (Figure 1c).

“Page 5: line 18: clarify the filter pack. I suppose the first filter is a Teflon one to capture particles.” Author Response: The filter is cellulose impregnated with citric acid. The word “cellulose” has been added to the sentence. There is no second filter.

“Page 7: lines 12-13: was the two instruments inter-calibrated?” Author Response: Yes the passive diffusion tube and ALPHA method are calibrated against the active sampling DELTA method on a monthly basis as discussed in Section 2.2.2 paragraph 3.

“Page 18, lines 4-5: the formation of ammonia takes place by the same procedure with the same kinetic parameters, so cannot be “slower” rather less effective.” Author Response: The authors agree and think this was a typo. We have revised the text changing “slower” to “lower”

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“Fig. 4 is not demonstrative to me, e.g. the relation between discrete measurement points and emission map is hardly seen. An iso-line picture for ammonia instead of discrete figures would show better the situation, but the comparison of emission with concentration in this way has not much sense, because the effect of transport and transformation processes.”

Re: “An iso-line picture for ammonia instead of discrete figures would show better the situation”

Author Response: Interpolated concentration maps have not been used since the interpolation of the discrete measurement points (e.g. using bilinear interpolation) will give the reader a false sense of the spatial variability of air concentrations from the limited number of measurement locations. The number of sites required to replicate the spatial resolution of the emissions map (5 km x 5 km grid resolution) will be impossibly high. The measured annual concentrations have therefore been shown as coloured dots on the map to show the observed spatial variability across the UK. Interpolated concentration maps can be produced from the discrete measurement points and added in Supplementary Materials, if required.

Re: “but the comparison of emission with concentration in this way has not much sense, because the effect of transport and transformation processes”

Author Response: The authors acknowledge that concentrations are affected by effect of transport and transformation processes, but at the same time, concentrations are also largely driven by emissions. The large variability in NH<sub>3</sub> emissions across the UK is reflected by both modelled (FRAME) and observed spatial variability in NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> concentrations, with largest concentrations in the largest emission source areas and lowest in background areas. The comparison of the measured concentrations (shown as discrete point data) with the emissions maps support this in Figure 4.

The FRAME model uses as input annual ammonia emissions data from the UK National Atmospheric Emissions Inventory (<http://naei.defra.gov.uk/>) and incorporates the

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main atmospheric processes (emission, diffusion, chemistry and deposition) to calculate annual NH<sub>3</sub> concentration fields in the UK at a 5 km x 5 km grid resolution. The spatial variability estimated by the FRAME model mirrors the variability in emissions across the country, with largest concentrations in the largest emission source areas.

“Figures involving temperature relating ammonia concentration: not mentioned but I believe they are air temperatures. But, emission of ammonia rather depends on soil surface temperature since decomposition of manure happens in the upper layer of soil. I know, soil temperature strongly correlates with air temperature but it has to be mentioned.”

Author Response: We confirm that the temperatures used are air temperatures, which are more available across the domain than soil temperatures. As Prof. Horvath points out, the soil and air temperatures do correlate.

“Figure 16b: mean NH<sub>3</sub> of what? Square bracket suggests it is molar concentration, but mass concentration was used all over the MS. Better to name “NH<sub>3</sub> concentration” on the axis and avoid bracket.”

Author Response: The authors agree and have adjusted the graph axis label and the figure caption.

“How concentrations in Fig. 16b were calculated? Did authors split the ammonia concentration among the number of animals, taking into account the variation of the latter? How other sources were taken into account? Others than cows, pigs, poultry takes 1/3 of total emission. What does it mean “Total” in Fig.16. I suppose this is the total of cows, pigs, and poultry only rather than total emission from all of sources. Otherwise the blue line on Fig 16b should be uniform with pink one on 17a. Explain please in the legend. On the other hand concentrations does not directly relate to emission to compare.”

Author Response: The authors apologise, we omitted a description of Figure 16 in the

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text. This has now been added to Section 3.5.4 paragraph 3 as follows:

“In Figure 16, the relative changes in UK emissions between 1998 and 2014 are compared with relative changes in mean measured NH<sub>3</sub> concentrations for all NAMN sites, and for grouped sites classified as dominated by cattle, pigs & poultry, and sheep.”

Fig. 18a: nanomoles per what? Cubic meter?

Author Response: Nanomoles per cubic metre. Axis on graph corrected. 3) Technical comments “Figures: use unambiguous and uniform in legends of vertical axes. E.g. concentration or emission of something (dimension in bracket).”

Author Response: Most graphs are systematically labelled but we have adjusted Figure 18 to put the percentage in brackets.

“Fig. 7, 8: Split the two figures (a and b), vertical axis of “b” is too close to “a””

Author response: Thank you for spotting this. We have adjusted the a and b so they are separated more widely.

“Use greek mü instead u for micro in all figures”

Author Response: Yes, we have checked and updated all figures. Figures 8a, 8b corrected Supp. Figure 1a, 1b corrected

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Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-259>, 2017.

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