

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.

L. Horváth (Referee)

horvath.l@met.hu

Received and published: 8 May 2017

MS is a good presentation of decrease of the ammonia emission in UK and the subsequent result of that measure. I believe it fits to the scope of ACP and merits to publish after revision. I suggest the following changes and improvements.

1) General observations

a) Emission sources According to the MS (Fig. 10b) the share of fertilizers is 16.2% together with “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).

C1

b) 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 SO₂ concentration and the dry deposition velocity of NH₃ onto natural surfaces that strongly influences the ammonia level in the atmosphere.

c) Seasonal trend analysis Source strength of ammonia – of course – strongly depends on temperature, so seasonal trend of NH_x is mainly determined by this factor. But, as to the ammonia/ammonium transformation it is partly an equilibrium process due to the NH₃ + HNO₃ ↔ NH₄NO₃ 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 NH₃ and NH₄⁺ 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 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?

C2

d) 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 NH₃ 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 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.

e) 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).

C3

f) 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.

g) Conclusion Too long and overlaps with discussions. It has to cut insisting only on the most important findings.

2) Specific comments:

Page 2:

First paragraph: Authors should describe the mechanism, how SO₂ 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 SO₂ and NH₃ onto surfaces.

Line 13: SO₂ and NO_x are not acids, but acid anhydrides (as to SO₂ and NO₂).

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

Line 14: Primary product of neutralization is the NH₄HSO₄ followed by forming (NH₄)₂SO₄ only in case when ammonia is available in quantity enough.

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

Page 4:

Lines 17-18: The sentence “the network has a good representation in the middle air

C4

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.

Page 5: line 18: clarify the filter pack. I suppose the first filter is a Teflon one to capture particles.

Page 7: lines 12-13: was the two instruments inter-calibrated?

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.

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.

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.

Figure 16b: mean NH_3 of what? Square bracket suggests it is molar concentration, but mass concentration was used all over the MS. Better to name " NH_3 concentration" on the axis and avoid bracket. 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.

C5

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.

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

3) Technical comments

Figures: use unambiguous and uniform in legends of vertical axes. E.g. concentration or emission of something (dimension in bracket).

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

Use greek mü instead u for micro in all figures

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

C6