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Comment

Interactive comment on “The influence of gas-particle partitioning and surface-atmosphere exchange on ammonia during BAQS-Met” by R. A. Ellis et al.

Anonymous Referee #2

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General Impression

The paper by Ellis et al. provides an in-depth interpretation of the behaviour of ammonia at the BAQS-Met supersite at Harrow, by comparing high resolution time-series of measured NH_3 and aerosol NH_4^+ with model predictions for the site. The subject of the paper is interesting, but some of the conclusions are poorly supported by the measurement evidence and I believe that, once further measurements are drawn into the analysis, conclusions will change significantly. Thus, taking on board the comments raised below, the authors should revise their interpretation of the measurements. Abstract and conclusions sections will need to be revised accordingly.

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Major Scientific Comments

Morning peak in ammonia

The authors rule out that desorption of ammonia from plant surfaces is responsible for the rise in NH_3 in the morning. They argue that air temperature rises at a later time in the day, which would take time to increase surface temperatures. However, in fact it is the rise in the surface temperature (by inception of solar radiation) that drives the increase in temperature in the morning. Thus leaf surface layers can evaporate as soon as they are illuminated by the sun, while the air temperature increases more slowly. Desorption of NH_3 has been observed following high humidity periods, even if no visible dew formation took place. Microscopic leaf water layers which form at RH well below 100% can store significant amounts of NH_3 (e.g. Flechard et al., 1999; in your reference list). Thus I do not think it can be ruled out that desorption of NH_3 from surfaces into a boundary layer that is still shallow contributes to the rise of NH_3 in the morning, at least initially.

Role of nitrate partitioning.

One principal concern about the manuscript is that ignores the interaction of NH_3 with HNO_3 to form NH_4NO_3 , although nitrate should be available from the AIM-IC. Nitric acid would be helpful for the interpretation, but I understand that the AIM-IC inlet was not suitable to measure this compound. Because the NH_3 - HNO_3 - NH_4NO_3 equilibrium is highly dynamic it is likely that HNO_3 has a strong influence on NH_3 concentrations in the gas phase, especially since the measurements indicate the presence of significant excess free NH_3 during the entire period. This would imply that the aerosol was probably neutralised during the period. However, the current paper does not provide any information on (a) whether the aerosol was neutralised or acidic and (b) what the importance was of ammonium nitrate compared with the ammonium sulphates. A plot comparing modelled and measured concentrations of NH_3 , NH_4^+ , NO_3^- and SO_4^{2-} would be helpful to form a fuller picture of the interactions. A comparison of the acidity

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of the measured and modelled aerosol would equally be very helpful. I suspect that the offline run of ISORROPIA predicts an acidity that is much closer to the measurements than predicted by AURAMS?

For a neutralised aerosol, NH_3 uptake onto the aerosol should not be governed by the aerosol sulphate loading, but by the in-situ production of sulphuric acid (are SO_2 data available to estimate H_2SO_4 concentrations?) and by HNO_3 concentrations. Under these conditions, large $\text{SO}_4=$ concentrations per se do not provide a large condensation sink for NH_3 . The NH_3 needs to be neutralised somehow. Thus, the decrease of NH_3 during the day could be associated with an increase in HNO_3 , which ties up more NH_3 into the aerosol phase. This process appears to be a more likely explanation for the diurnal cycles observed than the neutralisation of advected $\text{SO}_4=$ aerosol.

The current Fig. 9 is only partially informative because the entity shows in the x-axis ($\text{SO}_4=$) is effectively part of the denominator of the entity shown on the y-axis, making it circular. Nevertheless, if the NH_3 concentration is governed by the NH_3 - HNO_3 - NH_4NO_3 equilibrium, the NH_3 concentration may show a dependence on the $\text{SO}_4=$ / NO_3^- ratio, because NH_3 vapour pressures above mixed NO_3^- / $\text{SO}_4=$ aerosols are reduced compared with pure NO_3^- aerosol. This would also be consistent with Fig. 9. It may be interesting to use the offline version of ISORROPIA to predict the HNO_3 concentration based on the measured values and compare this with HNO_3 diurnal cycles in the literature.

If the modelled aerosol is often acid, whereas the measured aerosol was not (as Fig. 8 suggests), this would probably suggest that NH_3 emissions upwind of the measurement site are underestimated or (less likely) that the time-scale for neutralisation (NH_3 uptake onto the aerosol) is overestimated. This underestimation in NH_3 emissions may reflect missing plant emissions (from plant canopy compensation points), but it could equally reflect underestimated agricultural emissions.

Similarly, it would be interesting to investigate under what conditions, the model predict

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higher gas fractions than the measurements. These could be conditions, under which the NH_4^+ is dominated by NH_4NO_3 and the model does not predict sufficient NH_3 and HNO_3 for NH_4NO_3 production. This could indicate that HNO_3 formation from NO_x is underestimated during these conditions.

The analysis of the different operators affecting the NH_3 concentration at the site is interesting, but since the model does not predict the acidity of the aerosol correctly, I don't believe the results bear any relationship to reality. The model should be adjusted to get the results correct first, before this analysis is undertaken.

Compensation point modelling.

The temperature dependent compensation point, based on a constant value of gamma, is clearly the more correct approach to modelling bi-directional transport. If this does not solve the model/measurement discrepancy it is not the (only) missing process. Foliar compensation points will always act to raise day-time concentrations, because during night temperatures are lower and stomata are closed. It is unclear from the description, what parameterisations were used for simulating atmospheric (R_a , R_b), stomatal and cuticular exchange resistances.

Changes that would increase night-time concentrations include use of lower boundary layer height and larger attribution of the NH_3 emissions to the night in the diurnal emissions cycle.

In general, the single-point offline approach taken by the authors assumes that concentrations are in full equilibrium with each other (as predicted by ISORROPIA) and in equilibrium with the surface (as predicted by the bi-directional exchange model). In reality, both processes interact with each other as pointed out earlier in the manuscript with reference to the work of Wolff et al. (2010).

Minor Scientific Comments

Abstract. The authors should add a sentence on the conclusions drawn from the im-

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plementation of a bi-directional NH_3 flux parameterisation into the model.

P21897, l. 10ff: Some valuable plant communities only survive because of N limitation, because at higher N inputs they would be out-competed by nitrophilic plant communities. Thus, the statement that NH_3 is beneficial to N limited ecosystems needs to be qualified.

P21898, l. 18ff: Wolff et al. (2010) were not the first to study the interactions between surface/atmosphere exchange and gas-particle partitioning. More pivotal papers include Brost et al. (1988), Kramm & Dlugi (1994), Harrison et al. (1989).

P21898, l.26 ff. It may be worth including references to some other simultaneous $\text{NH}_3/\text{NH}_4^+$ measurements (e.g. Nemitz et al., 2004; Trebs et al., 2004; Schaap et al., 2010).

P21901, l.4. Has the effect of the heated inlet on $\text{NH}_3/\text{NH}_4^+$ phase partitioning been characterised? The heating could volatilise some NH_4NO_3 , which is obviously important in the context of the present analysis.

P12901, l. 15. The manuscript describes the fast response of the QC-TILDAS in some detail, but only 5 minute values are used for the analysis. Thus detection limit & precision for 5 minutes are more relevant here than for 1 s.

Section 2. Please provide information on length of sampling inlets for QC-TILDAS and AIM-IC as well as inlet height.

P21904, l. 9ff. Good correlation between NH_3 and other compounds does not necessarily prove common sources, but could just reflect a common control through boundary-layer dynamics.

Figure 2. The freely available OpenAir software provides a nice means to display exactly these kinds of relationships (www.openair-project.org).

P21905, l.17ff. The statement that deposition rates to water should be lower than to

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vegetation is counterintuitive because deposition rates of NH_3 to vegetation are often dominated by deposition to microscopic water layers on plant surfaces and increase as these water layers get thicker at high relative humidity. However, vertical mixing and therefore transport is less efficient above smooth surfaces such as water bodies.

P21906, l. 10. Do the authors have any information on soil wetness? Very wet soil conditions suppress NH_3 evaporation because the liquid pools can store a lot of NH_4^+ , reducing the likelihood for NH_3 volatilisation. Only in otherwise very dry conditions would I expect precipitation to enhance denitrification to an extent that it overrules this effect. You could also refer to Nemitz et al. (2000) and McCalley and Sparks (2008), both of whom demonstrated NH_3 increases with humidity/precipitation, from leaf litter and desert soil, respectively. However, have the authors investigated alternative explanations for the increase in NH_3 after rainfall, such as changes in air mass associated with frontal activity?

P21906, l. 1ff. Is the spike removal really justifiable? The aerosol measurement may also have included spikes, but these could not be resolved. Similarly, the model provides a grid-cell average, which also includes areas near sources.

P21908, l. 9f. I do not agree with the statement that if total NH_x is considered, the effect of phase partitioning is removed. Due to the difference in the deposition rate of NH_3 and NH_4^+ , the phase partitioning dictates the atmospheric lifetime and thus concentration of total NH_x .

Fig. 5. It would be good to see the results of the ISORROPIA offline run also.

Fig. 6. It is unclear to me whether the operator allocation is for the local grid cell only or for a larger area within the model.

Technical Corrections

Numerous spaces are missing throughout the manuscript as already noted by the editorial team.

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Numerous occurrences of ‘...’ before citations, which do not appear to make sense.

Introduce a space between values and their units throughout (e.g. “3 L/min” rather than “3L/min”)

P21901, I.25, change ‘outfitted’ to ‘fitted’?

P21904, I. 28, ‘stated’ instead of ‘states’?

P21905, I. 24. ‘... expected to be the highest ...’

P21911, I. 23. ‘dependant’ should be ‘dependent’.

Caption Fig. 8. Suggestion for alternative wording: “While the measured frequency distribution of the gas fraction is clustered in the middle of the histogram, the model is largely bi-modal, often attaining extreme values.”

Literature

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