

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

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Response to Referee 2:

Morning peak in ammonia The authors rule out that desorption of ammonia from plant surfaces is responsible for the rise in NH₃ 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 NH₃ has been observed following

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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.

The reviewer raises a valuable point and we have altered the manuscript accordingly: “It is possible that the temperature of the soil increases slightly earlier than the temperature of the atmosphere at 2 m (the height of our RH/T probe), but we have no measurements of the soil temperature. While the rate of increase of NH_3 in the morning was not substantially higher following nights with formation of dew, Flechard et al., (1999) states that significant amounts of ammonia can be stored in leaf water layers formed at relative humidities below 100%. Without measurements of surface wetness and surface temperature, we cannot conclusively confirm or rule out volatilization from the surface.”

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

Figure 4 has been updated to include the mole equivalents of NH_3 , NH_4^+ , SO_4^{2-} and NO_3^- and shows that the aerosol was neutralized except for some afternoons with very high sulfate loadings. The model predicted significant amounts of acidic aerosol, throughout the study, which often led to predictions of zero ammonia. and (b) what the importance was of ammonium nitrate compared with the ammonium sulphates. A plot

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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 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?

The updated Figure 4 also demonstrates that nitrate was an insignificant constituent of the aerosol. This is consistent with the analysis of Markovic et al. (2010) who used AMS data from the same site and saw that nitrate was only important in the early morning hours. AURAMS predictions of nitrate also peaked in the morning and were of similar magnitude to the observations. Markovic et al. (2010) also includes model-measurement comparisons and offline ISORROPIA runs which show aerosol acidity much closer to measurements. In the mid-afternoon when we saw the largest discrepancies between the model and measurements the formation of ammonium nitrate was not important.

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 SO_4^{2-} 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 SO_4^{2-} aerosol.

The data shows that the formation of ammonium nitrate is not favoured in the afternoon and while we do not have measurements of HNO_3 it is unlikely that it is acting as a condensation sink of ammonia. As discussed above, in some instances of high sulfate mass loadings the aerosol was acidic and net uptake of ammonia would be expected. On days with neutralized aerosol, as the reviewer points out, the net uptake rate of ammonia is governed by the production rate of H_2SO_4 . We estimated this using

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observed midday SO₂ of 2 ppb, assuming 5x10⁶ OH, and obtained a production rate of 0.04 ppb h⁻¹. Since two equivalents of ammonia are required to neutralize, this works out to 0.08 ppb h⁻¹ or 0.056 μg m⁻³ h⁻¹ loss of NH₃. This calculation is a lower limit as it does not account for heterogeneous production of H₂SO₄. The calculated production rate is significant compared to the rate of surface exchange (0.3 μg m⁻³ h⁻¹) calculated by the model for afternoon conditions. This implies that even in cases with neutral aerosol, a strong condensation sink in the atmosphere still exists and if this term was included in the model it would have an impact on the surface fluxes. This explanation has been added to the manuscript.

The current Fig. 9 is only partially informative because the entity shows in the x-axis (SO₄⁼) is effectively part of the denominator of the entity shown on the y-axis, making it circular. Nevertheless, if the NH₃ concentration is governed by the NH₃-HNO₃-NH₄NO₃ equilibrium, the NH₃ concentration may show a dependence on the SO₄⁼/NO₃⁻ ratio, because NH₃ vapour pressures above mixed NO₃⁻/SO₄⁼ aerosols are reduced compared with pure NO₃⁻ aerosol. This would also be consistent with Fig. 9. It may be interesting to use the offline version of ISORROPIA to predict the HNO₃ concentration based on the measured values and compare this with HNO₃ diurnal cycles in the literature.

We plotted the NH₃ concentration (and gas fraction) versus the SO₄²⁻/NO₃⁻ ratio as the reviewer suggested but the graphs did not provide any additional information. As in our discussion above, the observed ammonia concentrations were not governed by the NH₃-HNO₃-NH₄NO₃ equilibrium in the afternoon. Because there is such little nitrate in the aerosol, observations do not provide a useful constraint to predict HNO₃ concentrations from ISORROPIA.

If the modelled aerosol is often acid, whereas the measured aerosol was not (as Fig. 8 suggests), this would probably suggest that NH₃ emissions upwind of the measurement site are underestimated or (less likely) that the time-scale for neutralisation (NH₃ uptake onto the aerosol) is overestimated. This underestimation in NH₃ emissions may

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reflect missing plant emissions (from plant canopy compensation points), but it could equally reflect underestimated agricultural emissions.

The reviewer is correct that if the emissions in upwind adjacent grid squares were higher, the predicted aerosol would not be as acidic. However, scaling up agricultural emissions would result in uniformly higher NH_x , which would reduce the number of zero gas fraction points but not the high gas fraction population. Therefore this explanation does not appear to resolve the model-measurement discrepancy.

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

Figure 9 shows that the high gas fractions occur when the SO_4^{2-} is low. There is no dependence of the gas fraction on nitrate.

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.

The mass tracking operators were investigated in an attempt to discern the extent to which processes in the model govern ammonia concentrations at our site. We did not intend to use the model to explain real world behaviour because, as the reviewer points out, the model results do not match observations. We have clarified this in the manuscript.

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

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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.

With our temperature dependent compensation point approach, we also used ISORROPIA to iteratively partition the NH_3 in the same manner as with the constant value compensation point. We did not use a resistance based parameterization in our approach. This has been clarified in the text. While a foliar compensation point may also be relevant, the reviewer suggests it would raise daytime concentrations whereas our simple model approach is already biased high during the day.

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.

Reducing the boundary layer height or changing the diurnal cycle of NH_3 emissions are ways of changing the ammonia concentrations in the model without invoking the bi-directional flux. However these methods would not improve the discrepancy in the gas fraction distribution. If bi-directional flux is indeed occurring then a change in boundary layer height will have no impact assuming that concentrations quickly converge to the compensation point.

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).

This is what we were referring to in the statement “Thus atmospheric gas phase ammonia is simultaneously participating in two equilibria, one with atmospheric particulate ammonium, and one with a pool of ammonium at the surface. If the condensation sink

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increases (e.g. by an increase in aerosol sulfate), the atmosphere is depleted of ammonia, potentially lowering the ambient mixing ratios below the compensation point, and triggering emissions from the plants and soil.”

Abstract. The authors should add a sentence on the conclusions drawn from the implementation of a bi-directional NH₃ flux parameterisation into the model.

Added “A simple representation of an offline bi-directional flux parameterization using ISORROPIA was successful at reducing the population of zero gas fraction points, but not higher gas fraction points.”

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 NH₃ is beneficial to N limited ecosystems needs to be qualified.

Changed statement to “Deposition of NH₃ and NH₄⁺ to the Earth’s surface can fertilize nitrogen-limited ecosystems, and have detrimental effects such as eutrophication, soil acidification, and biodiversity loss in sensitive ecosystems”

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). Included suggested references.

P21898, l.26 ff. It may be worth including references to some other simultaneous NH₃/NH₄⁺ measurements (e.g. Nemitz et al., 2004; Trebs et al., 2004; Schaap et al., 2010) Included suggested references.

P21901, l.4. Has the effect of the heated inlet on NH₃/NH₄⁺ phase partitioning been characterised? The heating could volatilise some NH₄NO, which is obviously important in the context of the present analysis.

The heated inlet has not been tested for volatilization but theoretical calculations indi-

cate that the temperature is not high enough and the residence time through the inlet is too short (due to a high flow of 9 L min⁻¹) to volatilize NH₄NO₃ before the virtual impactor.

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.

Data is averaged to 5 minutes to produce a clearer picture of trends in the time series in Figure 1. When averaging to 5 minutes our detection limit is 42 ppt with a precision of 14 ppt. We have included these numbers in the revised manuscript.

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

The QC-TILDAS and AIM-IC inlets were co-located at a height of 3 m above the ground. We have added: “During BAQS-Met, the inlet was mounted on top of the measurement trailer, at a height of 3 m above the ground, and connected to the QC-TILDAS via a 2.5 m long, 3/8 inch PFA sample tube.” Information on the QC-TILDAS inlet was further clarified “Following the campaign, it was determined that the sampling inlet (1/2 inch OD Teflon-coated aluminum tube (URG, North Carolina) breaching a 4 inch diameter PVC pipe) was not appropriate for the quantitative sampling of gases, especially soluble ones such as HNO₃ and NH₃, so only the PM_{2.5} measurements are used in this analysis. Based on comparisons with the AMS instrument at our site, it does not appear that there were losses of particles due to electrostatic effects in the inlet.”

P21904, l. 9ff. Good correlation between NH₃ and other compounds does not necessarily prove common sources, but could just reflect a common control through boundary-layer dynamics.

We are referring to correlation between species on very fast time scales (seconds to minutes) which is faster than the change in boundary layer height.

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

We believe the relationships are conveyed well by the graphs in their current format.

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

Clarified statement to “On the other hand, the deposition velocity of surface reactive gases such as ammonia is lower over water than over land due to less vigorous vertical mixing over water, possibly extending the lifetime of ammonia against deposition”

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?

Unfortunately we do not have measurements of soil wetness. From a regional analysis which identified changes in air mass at the site, there were no air mass changes during those times. Of the 4 instances of NH_3 increase after rainfall, the local wind direction changed on 2 occasions, but this was characterized by very low wind speeds, indicating stagnant air and not a major frontal shift. We have included this information in the revised manuscript.

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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.

The spatial allocation for emissions in the model is not appropriate to resolve emissions from individual vehicles, so the removal of spikes is required in this case. It is true that the hourly measurement from the AIM-IC may have included spikes in aerosol ammonium, but it is not clear whether the short duration spikes would be in equilibrium with NH_3 and thus have an impact on the ammonia concentrations. Most of our analysis is based on diurnal cycles and there is no statistical difference between diurnal plots of ammonia with spikes and without spikes. Also the spikes occurred mostly at night, while our analysis is concentrated on daytime concentrations.

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 .

We agree with the reviewer and have clarified statement to: “At equilibrium, a decrease in NH_3 would result in an increase in NH_4^+ , and a plot of NH_x would be constant assuming no additional sources or sinks. Thus, the effect of gas-particle partitioning is removed in plots of NH_x , and the diurnal variability is thus only controlled by transport and vertical exchange.”

Fig. 5. It would be good to see the results of the ISORROPIA offline run also. Figure 5 has been updated to include the ISORROPIA run.

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.

The allocation is for the local grid cell over Harrow at 2.5 km resolution. This has been added to the manuscript.

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Technical Corrections Numerous spaces are missing throughout the manuscript as already noted by the editorial team. Numerous occurrences of ‘. . .’ before citations, which do not appear to make sense. Both errors were introduced in the processing of the manuscript and will be corrected in the final draft.

Introduce a space between values and their units throughout (e.g. “3 L/min” rather than “3L/min”) Done. P21901, l.25, change ‘outfitted’ to ‘fitted’? Done. P21904, l. 28, ‘stated’ instead of ‘states’? Done. P21905, l. 24. ‘. . . expected to be the highest . . .’ Done. P21911, l. 23. ‘dependant’ should be ‘dependent’. Done.

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.” Changed wording as suggested.

Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/10/C11209/2010/acpd-10-C11209-2010-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 21895, 2010.

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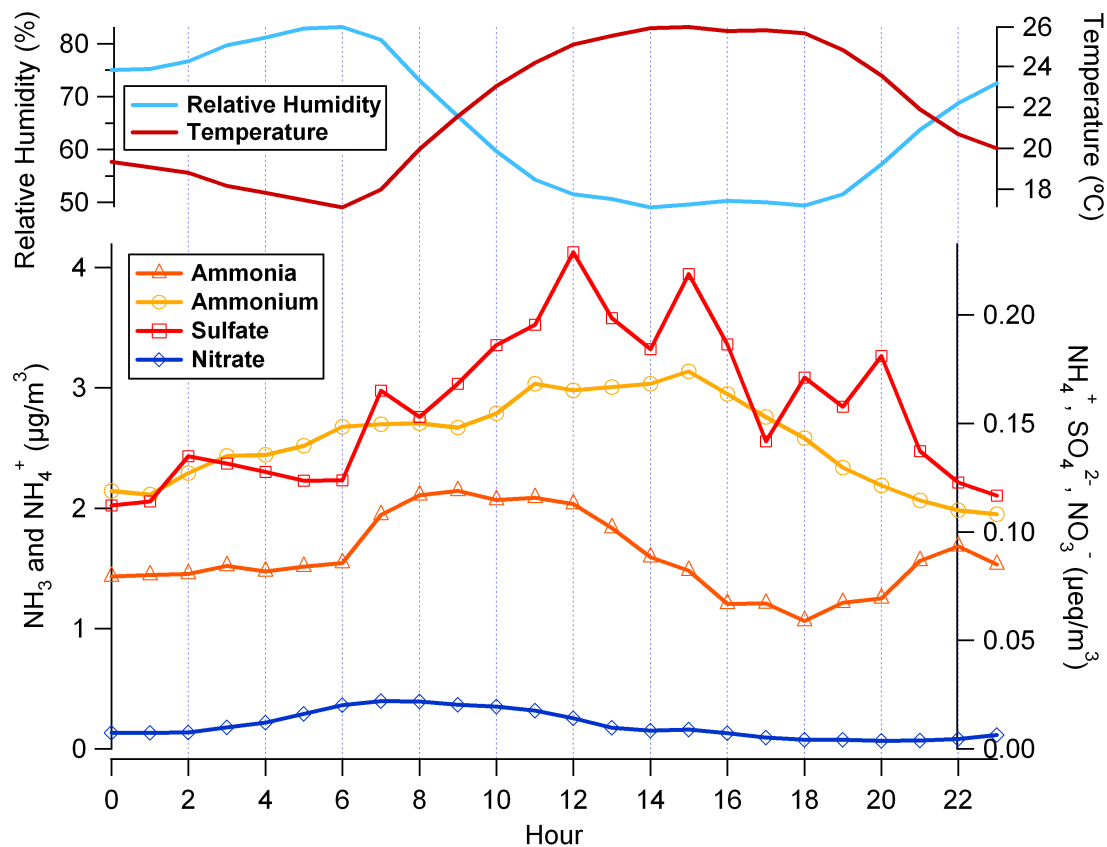


Fig. 1. Updated Figure 4

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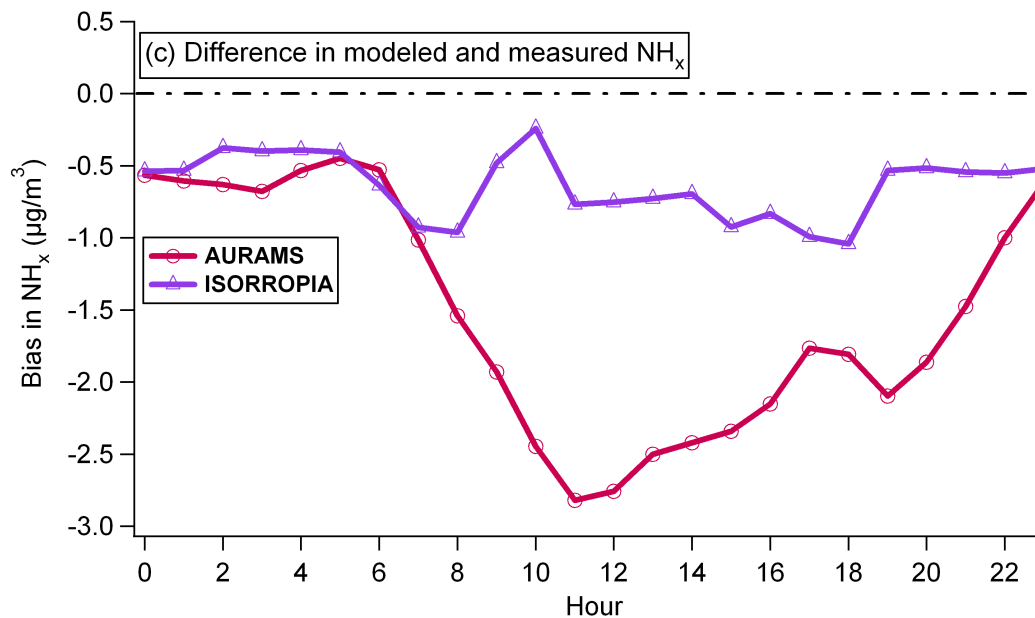
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Fig. 2. Updated Figure 5(c)

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