**Atmospheric
Chemistry
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Discussions**

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

R. A. Ellis et al.

rellis@chem.utoronto.ca

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Response to Referee 1:

Can the authors rule out any measurement uncertainty or bias that may explain the discrepancies? It is noted that no discussion is provided in this paper on the uncertainty or quantitative accuracy of the measurement data.

Readers are directed to the QC-TILDAS characterization paper (Ellis et al., 2010) for detailed information on the instrument figures of merit. Uncertainty in our measurements may arise from uncertainties in the calibration source (NH_3 permeation tube), stability of the permeation oven, the measurement of the temperature and pressure in

the optical cell and the spectroscopic data given in the HITRAN database. Of all these, the biggest source of uncertainty should be the output of the permeation tube source, which can be determined offline using an ion chromatograph to better than 10%. The instrument has been compared to 10 other measurements techniques (von Bobrutzki et al., 2010) and does not exhibit any discernible bias. The biggest discrepancy between the model and measurements is in the gas fraction distribution, and a systematic measurement bias would not resolve this disagreement. 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.

Is it possible that there is a significant component of ammonium associated with the coarse particle mode, which could influence observed gas phase NH3 levels and hence the measured gas fraction.

While we do not have measurements of ammonium content for particle sizes larger than PM2.5, we do not anticipate a significant amount of ammonium in coarse mode aerosol. Size-resolved particle composition measurements in Southern Ontario described in VandenBoer et al., (2010) and Zhang et al., (2008) show negligible contributions of ammonium in particles larger than 2.5 microns. Additionally, AURAMS predicts 3 orders of magnitude less NH4+ in the coarse mode than in PM2.5.

Could it not be argued that based on Fig 9, which compares the ammonia gas fraction versus sulfate, that the measurements and model discrepancy is systemic and that the authors should not just focus on the discrepancies at either sulfate concentration extreme (which is the basis for the bi-directional flux from/to plants as a function of gas ammonia concentrations). One could argue that the model overall does a poor job and thus is likely lacking in many respects. It is noted that even when a bi-directional flux is included (though it may be a crude representation), the improvements were marginal.

Figure 9 shows that the model underestimates gas fraction at high sufate, and over-

estimates it at low sulfate, so there is not a systematic discrepancy, but rather one that appears to depend on the chemical composition of the atmosphere. Thus while there could be several reasons for the discrepancy between measurements and model (emissions too low, deposition too high, incorrect representation of gas-particle partitioning, advection), we believe that the full implementation of a bi-directional flux parameterization will be most successful at reducing the discrepancy. Our uncoupled representation of bi-directional flux was successful at significantly reducing the very low gas fraction population in the model distribution but further improvement may need a more sophisticated treatment.

As a side question, why do plants attempt to keep gas phase ammonium in a certain concentration range? Could the proposed missing source realistically provide the amount of missing ammonia needed to bring models in agreement with observation during high sulfate conditions?

The physiological control of gas phase ammonia exchange between plants and the atmosphere is based on Henry's Law and dissociation equilibrium between the aqueous phase ammonia and ammonium in the soil water or plant apoplast or cuticles. As long as a sufficient pool of ammonium exists at the surface, this flux can be maintained. Detailed information is given in the references offered in the manuscript.

Pg, 21901 line 10, give the calculated cut size of the inertial separator used to remove particle interferences. The NH_3 inlet configuration is also not clear; does the complete inlet only consist of a 10cm quartz tube, or are there additional sections. How high was the inlet located above ground level and how was it located relative to activities around the site?

Added the theoretical cut size of particles larger than 300 nm. The whole inlet is made of quartz, 10 cm in length, with three 2.5 cm long protrusions on one side for attachment of zero, cal and sample lines. A 3 m PFA sample line connected the quartz inlet and the instrument optical cell. For more information on inlet configuration please

see Ellis et al., (2010). Added, "During BAQS-Met, the inlet was mounted on top of the measurement trailer, at a height of 2.5 m above the ground, and connected to the QC-TILDAS via a 3 m long, 3/8 inch PFA sample tube."

Pg 21902, clarify the sentence: $\frac{1}{2}$" OD Teflon-coated aluminum tube breaching a 4" diameter PVC pipe. Also, I assume this was the same inlet used for particles. Include an estimate of particle sampling looses (or lack of them). Are there issues sampling particles through a teflon-coated tube due to electrostatic effects. No information is provided on the AIM accuracy (eg, was it compared to filters etc), measurement LODs or uncertainties.

The Teflon-coated aluminum tube is distributed by University Research Glassware and is designed for the sampling of fine particulate with minimal losses. We have added: "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." Detection limits are provided in the manuscript. We have provided more quantitative information on accuracy: "An off-line calibration of the AIM-IC was performed in-field by directly injecting multiple ion standards into each IC, providing accuracy of better than 15 %."

Pg 21904, line 9, clarify what is meant by exact overlap, what time scales were associated with the miss-match? Line 26, give distance to road.

When spikes of ammonia occurred (mainly at night) spikes in other species did not occur at the same time, but either before or after separated by several minutes. Added distance to road, approximately 40 m.

Pg 21905, lines 4 and 5, but was there a direct correlation between the field work and measured NH3, this is implied but not explicitly stated. Line 24, missing "be" (to be expected?).

Unfortunately the field work was not logged and we cannot discern whether this activity had any effect on the ammonia concentrations. We simply offer this as a possible

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contribution to variability in local ammonia emissions. Added "be".

Pg 21908, regarding the discussion of variability between 10:00 to 15:00, numbers are needed to justify the statement that partitioning contributed to NH3 decrease during this time (line 15). In Fig 5a, it appears that there is a 10% decrease in NHx, is this significant relative to the decrease in NH3?

Added "During the hours of 10:00 – 15:00, ammonia decreased by 30% while only a 10% decrease was observed in NHx"

Pg 21910 line 18-20, what about changes in BL height and variability in the vertical concentration profile of NHx as a process that influences NHx concentrations in each model grid cell.

To clarify, we are reporting the model results in the lowest grid cell which extends from the surface to 6.89 m. The depth of the mixed layer may affect the predicted NHx levels if the PBL height predicted by the weather forecast model is too high, resulting in more significant vertical diffusion from the lowest grid cell, making the concentrations too low. However, by the same argument, all of the other pollutants should be too low in concentration as well (e.g. NOx, CO should be low in the model output). This was not observed, and in fact the model was biased high for NOx and CO (Makar et al., 2010). So the model and observations for other species do not support the idea that NHx underestimates are due only to PBL height overestimates - the other species are not being affected the same way.

Pg 21911 and 21912 regarding the discussion of bi-directional flux of NH3 involving ambient NH3 concentrations and plant apoplastic fluid. The argument is that plants attempt to keep some form of equilibrium between apoplastic fluid and ambient NH3 levels and that this explains the discrepancy between the model and observations. Is it reasonable to assume that the plants can adjust that quickly and with sufficient emissions to account for the large differences observed?

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As discussed in these references (Farquhar et al., 1980; Sutton et al., 1993; Sutton et al., 1995; Asman et al., 1998; Nemitz et al., 2001) given in the manuscript, the equilibrium is established based on the Henry's Law constant and acid dissociation and is thus a temperature dependent function of the ratio of NH_4^+/H^+ in solution. The timescale on which this equilibrium can be achieved should depend on the timescales of vertical mixing in the atmosphere, which in the lowest grid of the model should be on the order of minutes.

In the Conclusions definitive statements are made but were not completely proven in the body of the paper. Eg, Pg 21913 line 5, I don't believe that spikes at night were proven to be from cars, I thought it was only speculated. Other statements should be considered and qualified if need be.

We have restated our conclusions to take into account the comments of both reviewers.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/10/C11203/2010/acpd-10-C11203-2010-supplement.pdf

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