**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Gas-particle interactions above a Dutch heathland:III. Modelling the influence of the NH_3-HNO_3-NH_4NO_3 equilibrium on size-segregated particle fluxes" *by* E. Nemitz and M. A. Sutton

E. Nemitz and M. A. Sutton

Many thanks to the anonymous referee for their encouraging feedback. The referee develops some interesting general thoughts on how this work could be taken forward. As the referee will appreciate, some of these steps would require additional measurements or new targeted studies and, although we can comment on the potential benefits of such studies, we cannot anticipate the results.

Specific comments

1. As NH_3 and NH_4NO_3 are converted into each other, the flux of total ammonium (TA = NH_3 + NH_4NO_3) remains conserved. The same holds for total nitrate (TN = HNO_3

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+ NH_4NO_3). Hence, flux divergence of NH_3 is of the same magnitude, but opposite sign than that of bulk NH_4NO_3. This is a pure mass conservation argument and as such independent of the aerosol size distribution. Since the flux of NH_3 (independent of its sign) tends to be larger than the flux of NH_4NO_3, the flux divergence has a larger relative effect on the net NH_4NO_3 flux than on the net NH_3 flux. If the flux divergence reaches −100% of the flux, flux divergence results. It is true, however, that the flux divergence will affect different size ranges to different degree. This also depends on the shape of the size distribution.

2. Yes we feel "bi-directional" is a good word to use in this context.

3. While MS Word got confused in printing this equation, it turns out fine in the LaTex style of Atmos. Chem. Phys. Discuss.

4. β_i is clearly defined as the "accommodation factor" in the line following Eq. (4).

5. We agree that several of these simplifications may be violated under extreme conditions. We have down-tuned this statement to read: "f) For the size-range under consideration, the effects of coagulation (estimated from Seinfeld and Pandis, 1997) and hygroscopic growth associated with relative humidity (h) gradients are generally assumed to be negligible compared with growth caused by condensation of NH_3 and HNO_3, although there may be situations where h gradients have a significant effect."

6. Thanks for pointing out these mistakes in the original manuscript. They have already been resolved at the type setting stage.

7. Many thanks to the referee for these encouraging words. We are glad the referee appreciates the complexity of our modelling approach; Fig. 10 should probably indeed be regarded a good result, given the number of input parameters and simplifying assumptions.

8. The referee voices an interesting thought when he suggests the data may be used to identify the equilibrium height. We do not think that the time-scales can be used

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to identify the equilibrium height. Instead, we had originally tried to extrapolate the gradients of HNO_3, NH_3, T and h to find the height at which equilibrium is attained in an iterative numerical process. This worked for some periods, but other have no or even several solution. As explained in the text, we opted for comparing measured (K_m) and equilibrium (K_e) concentration products at different heights (average measurement height of 1 m, virtual surface, z_0, and an arbitrary height of 50 m (Nemitz, 1998). There was remarkable agreement between (K_m) and (K_e) at this notional height of 50 m for much of the time. A limitation for both approaches is the fact that the extrapolation assumes that flux divergence is negligible. Also, in a constantly changing atmosphere and landscape, actual equilibrium may not exist at any height.

9. We agree that the presence of NH_4NO_3 on plant surfaces may in fact be the main cause of the non-zero R_c for HNO_3. This has been clarified in the text: "This indicates that the significant canopy uptake resistance (R_c) observed for HNO_3 is a real feature of the exchange process, quite possibly caused by the evaporation of NH_4NO_3 from leaf surfaces." This study has made good progress in explaining the bi-directional nature of the aerosol fluxes. However, the accurate relative attribution of the reduced HNO_3 deposition between NH_4NO_3 evaporation above the canopy, inside the canopy and from leaf surfaces remains a major challenge as all these processes are governed by the same equilibria and their controls through h and T.

10. Although equilibrium may not be attained at any height (see comment 8 above), it is most likely to be attained at high heights with little influence of surface / atmosphere exchange and emissions. Hence, measurements at such a high height may provide a measurement of K_e for the measurement conditions, and this would include the effect of particle chemical compositionon K_e which is particularly difficult to predict theoreti-cally. By contrast, we are not proposing to include this height in the calculation of fluxes by the aerodynamic gradient method. The referee correctly points out that this would result in problems with fetch and advection errors. We have clarified the purpose of the measurements at a higher height in the manuscript.

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11. We fully agree, a next step would be to test the model in other conditions such as conditions of NH_4NO_3 formation following strong NH_3 emission. Unfortunately, the model requires a very extensive suite of measurements and it is not easy (or cheap) to obtain suitable measurements.

12. The referee raises a very important question. This paper addresses the influence of gas-particle-interactions on the measurement of surface / atmosphere exchange fluxes, with particular emphasis on size-segregated particle fluxes. In addition, the chemical conversion changes local N budgets. For example, if NH_3 emission, usually controlled by compensation points, is associated with formation of NH_4NO_3, this lowers the surface concentration of NH_3, stimulating further NH_3, while some of the emitted NH_3 would be deposited locally as particles. Conversely, at Elspeet slowly depositing NH_4NO_3 volatilized near the surface to form the rapidly depositing gaseous counter-parts, and this enhanced the effective deposition rate of both total nitrate and total ammonium. The overall effect depends on the relative magnitudes of the concentra-tions, and a separate study and paper would be needed to quantify and discuss these effects properly.

13. Ideally, we would, with time, develop eddy-covariance (or relaxed eddy accumula-tion) systems for size-segregated NH_4NO_3, NH_3 and HNO_3, which would allow us to measure fluxes at several heights and derive vertical flux divergence directly. Some progress has recently been made in in this area, but the availability of such instru-mentation to measure fluxes accurately enough to detect differences of often < 10% is still a long way off. We have added this additional suggestion to Section 5.3: "In this study surface / atmosphere exchange fluxes of the chemical species were derived from measurements of concentration gradients. For a full and independent validation of the model predictions, it would be necessary to measure the fluxes of the individual chem-ical species (NH_3, HNO_3 and size-segregated NH_4NO_3) at several heights to quantify the vertical flux divergence directly. Eddy-covariance and (relaxed) eddy accumulation approaches needed for these measurements have only just begun to be extended to

these reactive compounds and it is unlikely that they will become sufficiently accurate to derive flux gradients of often < 10% in the near future."

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 1567, 2004.

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