Review of acp-2019-703

“Aerosol dynamics and gas-particle conversion in dry deposition of inorganic reactive nitrogen in a temperate forest”

General Impression.

The paper presents a 1-dimensional model of coupled phase-partitioning and multi-layer canopy to study the process of NH_4NO_3 aerosol evaporation and water uptake on surface atmosphere exchange fluxes of reactive nitrogen compounds. A number of studies have observed remarkably high apparent deposition rates of ammonium and nitrate aerosol which have been linked to aerosol evaporation processes, but few studies have attempted to model the process and thereby quantify the overall effect on N deposition. This paper presents a detailed model for this purpose and applies to reproduce concentration gradients measured above a Japanese forest. Whilst the model is detailed, the measurements are comparably basic and poorly time-resolved which limits their value in really testing the model. Nevertheless, the paper presents a useful first application of the model and makes a valuable contribution to the literature on the subject. I recommend its publication once a few concerns have been addressed as detailed below. Importantly, the description of the model and its application is very brief and important detail is missing. In addition, the authors could exploit their results a little more comprehensively.

My suspicion is that this would result in a sufficient amount of new, additional text to necessitate a re-review of the manuscript.

Major concern

1. My major concern relates to the use of long-term average concentrations. Please make the time resolution of the filter pack measurements more explicit. It suggests in Line 147 that integration times were 9 hrs (day-time) and 15 hrs (night-time), whilst line 284 talks about weekly measurements. In either case I do not understand why they were used as spot measurements in the interpolation (Figs. 1 and 4). Should the model not be initialised with the same concentration for those time-intervals? Otherwise the average of the interpolated time-series does not match the measured average. Similarly, the length of the intervals of the dots in Figure 4 do not suggest that the measurements were continuous.
   Line 251 and Figure 6. I would be very surprised if the conditions for NH_4NO_3 condensation were met in this forest. Normally, these conditions are found over strong sources of NH_3 (e.g. Nemitz et al., 2009). If I understand the manuscript correctly, the authors are using long-term average concentration measurements with long-term average meteorology. In general, the vapour pressures of NH_3 and HNO_3 are dependent on temperature and humidity in a highly non-linear relationship. This means, if long-term average concentrations are paired with long-term averages in temperature and humidity, it is unlikely that the comparison of measured concentrations with the thermodynamic equilibrium concentrations evaluated with the ISORROPIA2 model can correctly assess whether there is potential for NH_4NO_3 evaporation of condensation. With the long-term integrated samples this problem cannot be fully resolved and as a result the entire manuscript needs to be

reformulated to some degree that full agreement between modelled and measured conditions cannot be expected. The application to this measurement dataset can only be considered a first test of the model, rather than a conclusive assessment of its capability. This problem needs to be discussed and, potentially, a sensitivity analysis could explore the uncertainty introduced by the averaging. In addition, the concentrations used for initialisation are subject to measurement uncertainty that may further limit the model / measurement comparison.

2. Overall, I am missing results and discussion on the effect of gpc (and also the equilibration with water content) on the exchange with the vegetation, in addition to the effect on the fluxes above the canopy. Only if this effect is shown to be significant, would there a need to incorporate this additional complexity into deposition schemes. To assess the importance, I would encourage the authors to quantify, from their results, the effect on the actual ecosystem flux of the various forms of N, total reactive N and also the effective bulk deposition velocity of the aerosol at the surface (V_{ds}), which changes because particle size changes. Presumably, this change in V_{ds} is the reason for gpc changing also the in-canopy gradient of SO_4^{2-} (Fig. 5) although it does not take part in the gpc process itself. The implications should be discussed.
3. Related to this, the discussion of Figure 9 is very cryptic and only accessible to those already very familiar with the subject. It is closely linked to the observations of apparent bi-directional size-segregated fluxes (e.g. Nemitz and Sutton, 2004; Ryder, 2010) and this link should be made.

Additional scientific comments and needs for clarification:

Abstract. It would be helpful to be more quantitative and also to include a statement on the effect on the NH3 flux as well as the total reactive N flux. By what fraction does the change in phase partitioning change the net N flux?

Line 65. Please clarify if the model also predicts the relative humidity profile which is important in controlling the phase partitioning. Related to this, Figure 3 should convey better whether the measured (in-canopy) profiles in the meteorological parameters are correctly reproduced by the model, i.e. the emphasis should be on the vertical change rather than the time-series.

Lines 100ff. I do not understand the approach taken for calculating c_d. The text reads as if this is chosen to match the atmospheric concentration at each canopy layer. Surely, in this case F_{gd} becomes zero if the canopy layer air concentration matches the gas phase concentration in equilibrium with the G_d of the leaf water layer, and r_d ceases to have any effect. It is exactly the departure from equilibrium that drives the flux. Instead, G_d is controlled by the previous accumulated deposition onto the leaf cuticle and the size of the water pool. How is the water pool size calculated in the model? Related to this, I am not convinced the use of an r_d that is linked to acid/NH_3 ratio and a leaf water emission potential are internally consistent. Parameterisations of the cuticular resistance as a function of this ratio have been developed and applied within the framework of a zero leaf water emission potential (e.g. Nemitz, 2015; Fowler et al., 2009) meant to account for the effect of a non-zero leaf water concentration. By additionally introducing a non-zero G_d value, this effect is accounted for twice.

Line 113. I realise that the authors are here only summarising the principles of a paper that is described in more detail elsewhere. Nevertheless, it would help to cite the approach taken to estimate the aerosol capture efficiency. Similarly, the origin of Eq. (4) needs to be mentioned.

Line 130. In addition to the ISORROPIA2 thermodynamic module, does the model treat any gas-phase chemistry? This may be important as an additional source for HNO3. If not, the authors should discuss the implications somewhere.

Line 198. It is not clear how the leaf water content was prescribed. This should affect the overall RH profile throughout the canopy and thus the results should be quite sensitive to this parameter?

Line 203. The meaning of f_{io} is not clearly introduced. I understand it to be the ratio of inorganic to total aerosol mass. If so, it is constrained by the observations (in contradiction to what is stated in the manuscript) by the comparison of total inorganic aerosol mass (from the filter-pack measurements) to total aerosol mass (approximated via the ELPI+ aerosol volume). What is not constraint is its size dependence.

Section 3.2. I am missing more explanation as to how the measurements were used to drive the model and provide initial or boundary conditions. In fact the content of this section does not match its title. Did you use concentrations at a single height (if so, which one?) or several heights? How often was the model re-initialised with the measurements. Was it allowed to run to steady-state conditions or was it continuously perturbed by the measurements? Was a spin-up time used? Maybe, the input could be illustrated by adding the constraining concentrations as a top panel to Figure 4. In addition, it is numerically problematic to use the same aerosol composition across all sizes as the Kelvin effect then causes evaporation from the smallest particles and condensation on the larger ones. This would drive some of the changes in the diameters (Fig. 7), which would then not represent a response to vertical gradients but reflect inadequate initial conditions. How was this problem dealt with? In this context (and in general) I would encourage the authors to study and refer the work of Ryder (2010) who also developed a similar model and applied it to existing datasets of exchange.

Line 210. Values of c_g and c_s as high as 300 ppb and 2000 ppb are completely unrealistic and inconsistent with the paper of Massad et al. (2010). They also ignore the temperature dependence of Eq. (3). Do the authors mean G_g = 300 and G_s = 2000 (no units!)? G_g is mentioned for the first time here and needs to be introduced much earlier on. Again, this calls for introducing the model in more detail than is currently done.

Section 5.1 and Line 349ff. Figure 4 suggests to me that the extrapolation of concentration into the canopy led to better agreement in the run that did NOT include gpc, whilst the text talks about an improvement. Please clarify. In general, to assess model performance, it would be much more illustrative to rearrange Figure 5 so that the three lines (Obs, no gpc, gpc) can be compared on a single plot for each compound. In addition, it would be interesting to compare a plot of how fluxes changes with height.

Line 326. I am not convinced the authors' argument here is correct. I would expect, to the first order, HNO_3 and NH_3 to be driven off the aerosol in stoichiometric ratios and thus the flux divergence for both compounds (and their aerosol counterparts) should be similar in absolute (molar) terms, independent of the deposition rate of the individual compounds. However, Fig. 5 shows normalised (i.e. relative) concentration changes and here the authors are correct with their second explanation: the relative effect on NH_4^+ is smaller than on NO_3^- because it partly represents non-volatile sulfates.

Technical corrections:

Title. The word “in” does not read right in my mind. How about “The effect of aerosol dynamics and gas-particle conversion on dry deposition …”

Line 88. “fluxes with stomata … and with leaf water surfaces …”

Eqs. (1), (2), (3), (5). Please make sure the text introduces all symbols used in the equations. Many symbols (e.g. R, a, G_s) are not introduced.

Eq. (3) would benefit from a reference.

Eq. (5). Is the meaning of a here the same as in Eqs. (1) and (2)? If not, please use a different symbol.

Eq. (5) and (6) and associated text. It would help here to make any dependence on particle diameter explicit, e.g. by writing $E_p(D_p)$.

Line 130. “… transfer is driven by the difference …”

Line 173. It is not clear to me what the word “latter” refers to. Please rephrase.

Line 190. It would be useful to state the total number of layers of the model.

Line 214. The acronym “gpc” is not introduced. Presumably it stands for gas-particle conversion? I wonder whether “thermodynamic gas-particle partitioning” would be a better concept to use throughout?

Figure 6. Please clarify in the figure caption the height for which this flux is provided as the flux is height dependent. In addition, it may be illustrative to display the actual exchange with the ecosystem under both model scenarios.

All figures: horizontal zero lines on all figures would help interpret these more easily. The font size of some labels and legends should be increased for better readability.

Line 322. This should read “2004” rather than “2004a” here, I believe.

References:

Nemitz, E., Dorsey, J. R., Flynn, M. J., Gallagher, M. W., Hensen, A., Erisman, J.-W., Owen, S. M., Dämmgen, U., and Sutton, M. A.: Aerosol fluxes and particle growth above managed grassland, Biogeosciences, 6, 1627–1645, https://doi.org/10.5194/bg-6-1627-2009, 2009.

Ryder, J., 2010. Emission, deposition and chemical conversion of atmospheric trace substances in and above vegetation canopies. PhD Thesis, University of Manchester, UK. Available from the University or via https://nora.nerc.ac.uk