

Reply to review comments by anonymous referee #3 on “Global simulations of nitrate and ammonium aerosols and their radiative effects” by L. Xu and J. E. Penner

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We appreciate the comments of the reviewer, which have allowed us to improve the manuscript and clarify ambiguities. We address each comment below. The reviewer’s comments are in bold followed by our response.

(1) In section 2.2, it says the equilibrium model is applied in size bin 1 for 5 aerosol types “consecutively”: does it mean that the thermodynamic equilibrium is not solved simultaneously between gas phase and five aerosol types (with the same size cuts)? If so, does the order of solving equilibrium make any difference in calculated concentrations of nitrate and ammonium?

Reply: We conducted a sensitivity test with respect to the order of solving equilibrium and found that “Changing the reaction order that is used for dust and sea salt changes the nitrate and ammonium concentration by less than 10% for high concentrations of both dust and sea salt.” as stated in page 10126, lines 12-14. Note that sulfate (i.e. pure sulfate, sulfate associated with fossil fuel OM/BC and sulfate associated with biomass burning OM/BC) is first neutralized by ammonia and then nitric acid is allowed to react with ammonia and the other aerosol types (page 10126, lines 11-12). To minimize the influence of this assumed sequence, we stated that “In order to eliminate the differences induced by this assumed sequence, we switched the order of the reactions by solving the reaction with dust first at odd time steps and with sea salt first at even time steps” on page 10126, lines 12-14.

(2) Also in section 2.2, the assumption of externally mixed pre-existing aerosols needs reference. Are there any improvements in the predictions of nitrate and ammonium concentrations by assuming external aerosol mixtures and adding nucleation of sulfate aerosols in the present study? as they significantly increases the computation cost.

Reply: One reason for making an assumption of external aerosol mixtures was to be consistent with the treatment of aerosols in other processes (e.g., emission, transport, deposition, etc) in the global transport model. The computational efficiency is one aspect that definitely needs to be improved in the future, since the method requires about a factor of two more computer time than the FP07 method. We will add the following discussion:

“We allow internal mixing of the primary species formed in polluted regions (i.e. sulfate, nitrate, ammonium) but assume external mixing of dust and sea salt (which are normally from different source regions). This treatment differs from that in FP07, who treated all aerosols as internally mixed when predicting nitrate and ammonium aerosols. While we thought this might make an important difference, the results from this model were similar to those of Feng and Penner (2007).”

We will also add the following discussion in the revised manuscript.

“Compared to the previous study (FP07), this work predicts a burden of nitrate and

ammonium that is 10% and 4% lower, respectively, than that in FP07. Our study has higher total sources and sinks, and, therefore, shorter lifetimes by 25% and 18% for aerosol nitrate and ammonium. These differences are caused by the different treatments for the interaction between nitric acid and ammonia and pre-existing aerosols as well as different deposition schemes (since our scheme assumes external mixtures and FP07 do not).”

(3) In section 4, in the calculation of AOD, are the calculated nitrate and ammonium concentrations being re-distributed following the non-sulfate aerosol size distributions? Why? This is not consistent with the global transport model results of size-resolved aerosol concentrations. If internal mixing is assumed, why is the constitute composition described as “coated” in Table 2. What time-averaged aerosol concentrations does the radiative transfer model use? And what relative humidity data is used to estimate aerosol wet size? Which year of AERONET data is used in comparison? The global model is driven by the meteorology for year 1997 and most of the aerosol emissions are representative for the 1990s. Observations used in model evaluation should be comparable with these model simulations.

Reply: We calculated the AOD in an off-line model after saving the concentrations of nitrate and ammonium associated with the 11 aerosol populations given in Table 2 (i.e., ammonium/nitrate associated with fine mode ($D < 1.25 \mu\text{m}$) pure sulfate, FF OM/BC, BB OM/BC as well as those associated with dust and sea salt for bins 1/2/3/4). However, in the calculation of AOD, we need a much finer size resolution in order to calculate forcing accurately. Therefore, we distributed nitrate and ammonium concentrations associated with each aerosol type or size category following the assumed surface area for each non-sulfate aerosol size distribution. This treatment is consistent with that in our global chemical transport model. Regarding the comment on internal mixing, it is our understanding that “coated” aerosol is part of an internally mixed aerosol (as opposed to externally mixed), but we can change this to “associated” in Table 2 to avoid confusion. Since we actually use volume-averaged refractive indices for internally mixed aerosols together with Mie theory in our estimates of radiative forcing and since a strict definition of “coating” would require a core-shell treatment, it is better to use “associated”. In the present study, we used monthly averaged aerosol concentrations in the radiative transfer model. Sensitivity tests using daily and hourly aerosol concentrations were examined in Xu (2012) and the results were within 5% for the direct effect and 10% for the indirect effect. We will add this to the revised paper. The relative humidity data used the 4-hourly meteorology field that was used to drive the off-line radiation transfer model described in Wang and Penner (2009). AERONET data was provided by S. Kinne from Max Planck Institute who used all available level 2 data from 1996 to 2010.

(4) In section 5.2, how good is the treatment of nitrate acid in cloud droplet activation used here, i.e., compared with parcel model calculations?

Reply: Chen (2006) compared this treatment for nitric acid in conjunction with the parameterization of aerosols activated as cloud droplets (Abdul-Razzak and Ghan, 2002) with the simulated cloud droplets formed in a parcel model. Results show that the substitution method used here can generally capture the increase of cloud droplets due to the condensation of nitric acid gas. The difference in the prediction of cloud droplets

between the substitution method and the parcel model was within 20%. We will add this to the revised paper.

(5) In the Summary, the statement of “nitrate and ammonium is generally more hygroscopic than sulfate” is incorrect.

Reply: According to the kappa values given in Petters and Kreidenweis (2007), ammonium nitrate is more hygroscopic than ammonium sulfate. We will modify this sentence to “ammonium nitrate is more hygroscopic than ammonium sulfate in terms of the kappa parameter (Petters and Kreidenweis, 2007)”.

Other comments: 1) Introduction is a little bit long. Consider to shorten the discussions about the different treatments of gas-aerosol partitioning, as the focus of this paper is not about introducing a new method, but applying the hybrid method in aerosol and radiative forcing estimates.

Reply: Thanks for suggestion. We will shorten the discussion about different treatments of gas-aerosol partitioning in the section of the introduction in the revised manuscript.

2) The authors may consider to shorten some of the discussions in section 3, since they are largely similar to those in previous studies, or move them to the supplement.

Reply: Thanks for suggestion. In fact, to our knowledge, no previous study has ever shown the effects of nitrate and ammonium formation on five types of pre-existing aerosols as presented in this study. The inclusion of this discussion and figures in the main text provides useful information for readers with a general interest. However, we will strive to shorten this section and emphasize the differences in our study and previous studies.

3) On page 10117, line 3, change “have” to “has”

Reply: We will change this in the revised manuscript.

4) On page 10119, line 20, what “equilibrium”? please clarify.

Reply: We changed “equilibrium” to “thermodynamic equilibrium”

5) On page 10136, line 27, change “earth” to “Earth”

Reply: We will change this in the revised manuscript.

Reference:

Xu, L.: Global simulation of nitrate and ammonium aerosols and their radiative effects and comparison of satellite-based and modeled aerosol indirect forcing, Ph.D. thesis, Department of Atmospheric, Oceanic and Space Sciences, University of Michigan, Ann Arbor, 306 pp., 2012.