Reply to review comments by anonymous referee #1 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 this 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.

General Comments:

1. Page 10117, lines 5-6 and Page 10120, lines 3-4: The authors state that thermodynamic equilibrium overestimates the portion of ammonium nitrate in coarse mode (and underestimates the fine mode). Nevertheless, later in the text (page 10118, lines 23-25) they say that equilibrium method neglects differences in the chemical driving forces of the specific aerosol size bins. This means that during equilibrium most of ammonium nitrate will condense in the fine mode, which has most of the surface area, resulting in an underprediction in the coarse mode (and overprediction of the fine mode). In fact, Capaldo et al. (2000) and other studies (i.e. Karydis et al., 2010; Karydis, Tsimpidi, et al., 2011) have reported an underprediction of nitrate in the coarse mode (and overprediction of fine mode), using the equilibrium method, and a significant increase on coarse nitrate after using the hybrid approach (and a decrease of the fine mode). With that said, I think it would be useful to identify the source of this discrepancy between these studies and the Feng and Penner (2007) study (and presumably the current study too), and include a discussion that explains why the use of hybrid approach decreases the ammonium nitrate in the coarse mode in contrast to the Capaldo et al. (2000) and Karydis et al. (2010; 2011) findings.

Reply: The statement that thermodynamic equilibrium overestimates the portion of ammonium nitrate in the coarse mode was based on the findings in Feng and Penner (2007). They reported the difference in the global average prediction of the fine and coarse mode nitrate aerosol along with nitric acid gas between the equilibrium method and the hybrid dynamic method (see Figure 13 in Feng and Penner, 2007).

It is difficult to know precisely why Capaldo et al. (2000) found different results without carrying out simulations similar to theirs (which is beyond our scope of work). Capaldo et al. (2000) were examining a completely different case, namely, a marine air parcel moving over land areas where nitrate was emitted starting at hour 13 (and only during the day). The calculation ended after 38 hours. NH_3 emissions were for 2 spikes for 10 minutes at hour 16 and 32. They also assume an initial size distribution with a coarse mode having large initial NO_3 concentrations (in bin 7) as well as a large fraction of NaCl (in all coarse bins). In contrast, Feng and Penner (2007) have a variety of cases represented in their global average and it is unclear how NH_3 alters the cases. The maximum in the coarse mode for the hybrid method is over the sub-Saharan region and Middle East (Figure 2 in Feng and Penner, 2007) while the fine mode is over the U.S., Europe, and Asia in the winter. Since the global and annual average in Feng and Penner (2007) does not correspond to the same case as that examined by Capaldo et al. (2000),

and since nitrate in aerosols may both form and evaporate, it is hardly surprising that results may differ.

Karydis et al. (2010, 2011) use the CAMx model over a 210km x 210 km with a 3 km x 3 km grid resolution over a domain that includes Mexico city and model results are presented for March. This model predicted changes in their domain average NO_3 for submicron and coarse mode aerosols that differed from the results of Feng and Penner (2007). Here differences might be due to the different concentrations regimes in the global average model (it's maximum values occur in places that may not correspond to those simulated in Karydis et al.) or perhaps to differences caused by the frequency of wet deposition (or perhaps its treatment) for nitrate and ammonium. Nitrate and ammonium in the global model has a lifetime that is primarily determined by wet deposition. In the MILAGRO campaign (modeled by Karydis et al., 2011), precipitation mainly occurred during the last week of the campaign (Fast et al., ACP, 2007).

While we agree it would be interesting to understand the differences between Feng and Penner's results and those of the above studies, we think it would distract from our main results and would require significant investment to explore, beyond the scope of our study. Hence we prefer not to add any of the above discussion to our paper.

2. Section 3.4: I believe that there are two important issues that are needed to be addressed in this section. 1/ How much the performance of the model improved, compared to the previous study (FP07), by the improvement of the sulfate aerosol dynamics? and 2/ why nitrate is so seriously overpredicted over North America? The latter is also discussed in FP07 study but since the main focus of the current paper is the ammonium nitrate, I think it would be helpful to include a short discussion here as well.

Reply: The discussion on the differences and similarities between the present study and the previous study was addressed in detail in Xu (2012). We will add the following discussion in the revised manuscript.

"Compared with 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). However, the modeled aerosol concentrations for sulfate, ammonium and nitrate were similar to the comparisons conducted in FP07 and A99, so will not be repeated here. We note that nitrate over North America is overpredicted in the model in comparison with measurements, possibly as a result of evaporation from the filter packs resulting in values that are biased low in the measurements (Adams et al., 1999; Pakkanen et al., 1999)."

Specific Comments:

1. Page 10116 line 14: I suggest to add a short explanation on how nitric acid contributes on indirect radiative forcing. For example, the statement can be

rewritten as: "almost all of which is due to condensation of nitric acid gas onto growing droplets (-0.08 W m-2)".
Reply: We will rephrase this as suggested by the referee (page 10116, line 14) in the revised manuscript.

2. Page 10117 lines 15-19: Please include a short comment on why this will be the case. I assume that after the reduction of SO2 emissions, the free NH3 in the atmosphere will be increased resulting in an increase of ammonium nitrate formation.
Reply: We will add the following sentence "Reduction of sulfate in aerosols results in an increase of NH_3 in the atmosphere, which allows a larger formation of ammonium nitrate." at the end of line 19, page 10117 in the revised manuscript.

3. Page 10119 lines 3: I would rephrase the statement to: "because it takes from several hours to up to a week to reach equilibrium". What is important here is that, at any case, it takes more than an hour (which is the time step of the model) to achieve equilibrium.
Reply: We will rephrase this as suggested by the referee (page 10119, line 3) in the revised manuscript.

4. Page 10122, first paragraph: How did you choose the prescribed background size distributions? Are they based on measurements? If so, please add the corresponding citations.
Reply: The prescribed background size distribution for non-sulfate aerosols follows that of previous studies which were based on measurements (Liu et al, 2005; Penner et al., 1998). We will add these references to the table and add the following statement in the revised manuscript.
"Note although the size distribution of OM/BC for pollution is adopted from an observation from a forest fire (Liu et al. (2005); Penner et al. (1998)), the median diameter of the mass distribution (i.e., 0.16 μm) is close to that measured (0.18 μm) in Schwarz et al. (2010)."

5. Page 10131, line 6: replace "though" with "through"
Reply: We will replace this in the revised manuscript.

6. Page 10133, lines 8-9: Please add references for the aerosol hygroscopicities (especially for organic mass and dust as they seem to be in the high end of the reported values in literature).
Reply: The values of aerosol hygroscopicities are taken from Ghan et al. (2001). We will add this reference in the revised manuscript. The organic value is somewhat higher than the average Kappa value reported in Jiminez et al. (2009) but seems reasonable for the more oxidized compounds that represent the organics in aerosols at longer time scales.

7. Page 10136, lines 16: Why for clear-sky conditions there is no heating over the biomass burning regions of central Africa?
Reply: The inclusion of absorbing aerosols (BC and/or OM) in biomass burning regions can cause heating when the aerosol is above a cloud or above a reflecting surface

(Haywood and Shine, 1995). In clear skies, aerosols would only heat if the surface albedo is large and the proportion of absorbing material is large enough. Although we use a refractive index for OM in biomass aerosols that represents the absorption seen in measurements (Kirchstetter et al., 2004), we do not find that this absorption leads to a positive forcing in clear sky regions. This result may depend on the specific surface albedo fields used here. We will add this short discussion in the revised manuscript.

8. Page 10138, lines 24: The CDN concentrations are predicted high over the southern remote oceans (more than 100 cm-3) and slightly low over the polluted regions (less than 500 cm-3). How are the predictions of the model compared to other published global CDN fields (i.e. Penner et al., 2006; Merikanto et al., 2010; Chen et al., 2010; Karydis, Kumar, et al., 2011)?

Reply: Differences between predicted CDN concentrations and observations can arise from many different aspects (e.g, predicted aerosol mass concentrations, different aerosol size distribution, the cloud droplet parameterization, the representation of the in-cloud updraft velocity, etc.) as examined in Chen and Penner (2005). The difference associated with the cloud droplet effective radius can range from 4% to 9% when switching from the Nenes and Seinfeld method (Nenes and Seinfeld, 2003) or the Chuang and Penner method (Chuang et al., 1997) to the parameterization in the base case (Abdul-Razzak and Ghan, 2002) while that associated with the representation of the in-cloud updraft velocity between the probability distribution function method and the TKE method is about 8% (Chen and Penner, 2005). Uncertainties in the cloud droplet number concentration are much larger than uncertainties in effective radius due to the one-third power relationship between CDN and the effective radius. The modeled CDN concentration in this study generally shares a similar spatial pattern as that predicted in some previous studies (e.g., Merikanto et al., 2010; Karydis et al., 2011). The predicted CDN concentrations are highest over polluted regions since the aerosol concentrations are greatest over these regions. The modeled CDN concentrations in this work, however, are slightly lower over the polluted regions (less than 500 cm-3) than that in some previous studies (e.g., Merikanto et al., 2010; Karydis et al., 2011), possibly because the calculated in-cloud updraft velocities in this study followed the method described in Wang and Penner (2010) which are less than 0.3 m/s over the land in contrast to the constant updraft velocity of 0.4 m/s and 0.3 m/s over the land adopted in Merikanto et al. (2010) and Karydis et al. (2011), respectively. We will add this discussion in the revised manuscript.

9. Page 10139, line 28: Why the additional HNO3 gas in the TN case results in a significant negative response of sulfate in Northern America?

Rely: As discussed in page 10139, line 5 to page 10140, line 12, the negative response of sulfate in Northern America is due to the dynamic competition for water vapor in the complex multi-component system, partially resulting from the positive response of fossil fuel and biomass burning aerosols to the additional HNO_3 gas (compare Figure 12 and Figure 13).

10. Page 10142, line 8: replace "frame work" with "framework"

Reply: We will replace this in the revised manuscript.

11. Page 10143, line 16: Add “at” before the “surface”

Reply: We will add 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.