

Response to Reviews

ACPD article "Simulation of nitrate, sulfate, and ammonium aerosols over the United States"

We thank the referees for very helpful comments. The manuscript has been revised to address these comments. After publication of Heald et al. (2012), we have removed the analysis of IASI satellite ammonia data to avoid duplication with that paper, which presents a similar analysis of IASI satellite data to that in the ACPD version of this paper. Our revised manuscript now contains a full analysis of TES data (suggested by referee 1). In this way, Heald et al. (2012) and the present study can be viewed as complementary. We note a change in authorship from the ACPD version that reflects the removal of the IASI data and addition of S. Philip and R.V. Martin related to implementation of GEOS-Chem boundary layer processes. Referee comments are noted below in black and our responses are in blue.

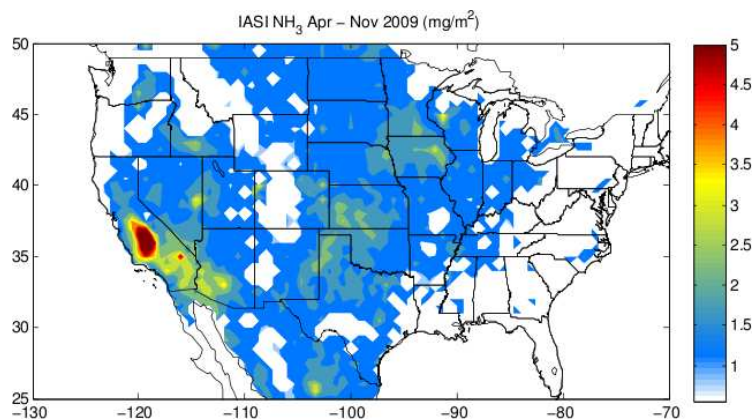
Response to Referee #1

The submitted manuscript titled, Simulation of nitrate, sulfate, and ammonium aerosols over the United States, is concise and very well written. There is still significant uncertainty in the model-simulated concentrations of nitrate, sulfate, and ammonium aerosols over the United States (and even more so globally). Surface and satellite observations of NH₃ provide valuable information on the performance of the chemical transport models, especially over California. There are many advantages of utilizing the recently available satellite NH₃ observations, but due to the nature of the infrared retrievals they can be challenging to evaluate. There are many advantages of utilizing the recently available satellite NH₃ observations, but due to the nature of the infrared retrievals further details and explanations are needed. This research is very relevant, but it does not appear to be as consistent with recent similar analysis in as simple of a way as currently presented for this CA case study and will need to be addressed (see comments below).

Main Comments:

1. There are a couple IASI data oddities that would benefit from further explanation:
 - a) There are two peaks in WA that are greater than any values in the Midwest. The one on the right might be plausible its over a farming valley. The one on the left is not its over the North Cascade National Park. Not sure what could be emitting NH₃ in this region.

These peaks were an artifact of the interpolation: two high measurements affected the April-November 2009 average shown in the figure because there were very few IASI measurements over this area. A corrected version is shown below, in which a grid cell was set as missing if there were not at least 2 measurements per month, for at least 5 months of the Apr-Nov 2009 period.



b) IASI doesn't appear to pick up the hotspot in North Carolina, which according to EPA has the highest density of hog farms of any county in the country, and thus high NH_3 .

It is likely that IASI lacks sensitivity to surface concentrations there, probably related to thermal contrast.

2. NH_3 lifetime:

a) According to Seinfeld and Pandis, NH_3 lifetime is as long as 10 days (page 38), although most people would estimate its lifetime to be much shorter, as short as a few hours. Regardless, Turner et al. (2012) showed that columns of NH_3 in GEOS-Chem can be influenced by NH_3 emissions several grid cells away. Thus, directly relating model vs. IASI NH_3 concentrations is challenging so please provide justification.

The challenges noted by Turner et al. (2012) are related to the use of inverse methods to estimate emissions from satellite measurements:

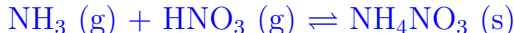
“A common method of estimating emissions of shortlived species is to average a set of satellite measurements over a particular location and derive top-down constraints on surface emissions using a mass balance approach... In this method, atmospheric transport is assumed to be negligible as the short chemical lifetime of the species translates to a smearing length scale less than the width of the model grid-cell...”

In our study, we are not using inverse methods to estimate ammonia emissions from the satellite data, but rather we are comparing satellite measured ammonia concentrations to the ammonia concentrations predicted by the GEOS-Chem model (in which the emissions are prescribed from the bottom up using EPA National Emissions Inventory and other emissions data). In a given grid cell, ammonia concentrations predicted by GEOS-Chem will be influenced by ammonia emissions from other grid cells, through atmospheric transport; the same also is true for the ammonia concentrations measured by satellite, which are also

influenced by emissions from other locations through atmospheric transport. Thus, the comparison of model-predicted concentrations with satellite-measured concentrations is justified.

3. IASA and TES indicate that NH_3 concentrations are also underestimated throughout much of the country. However, in the Midwest / east, nitrate is overestimated. So there appears to be a conflict here as I don't think this CA case study presented is as consistent with the Lye et al., 2012, Heald et al., 2012, and Zhang et al., 2012 in as simple way as is presented here. Not that I am doubting that the CA NH_3 emissions are underestimated all signs (recent studies) do point in that direction. Its just there may be more happening to explain nitrate nation wide.

Nitrate aerosol (solid or aqueous) exists in thermodynamic equilibrium with NH_3 (g) and HNO_3 (g):



The concentration of nitrate aerosol depends on the concentrations of NH_3 and HNO_3 , as well as the temperature and relative humidity (with the thermodynamic equilibrium favoring the aerosol phase in colder and more humid conditions). Depending on relative abundances of NH_3 and HNO_3 , nitrate aerosol formation can be either ammonia-limited or nitric acid-limited. In our study, as well as in Heald et al., 2012 and Zhang et al., 2012 (we were unable to determine which publication Lye et al., 2012, the referee was referring to), nitrate is over-predicted in the Midwest / East, even though IASI and TES data indicate that ammonia concentrations are under-predicted over the US. These results indicate that even with this under-prediction of ammonia there is still sufficient simulated ammonia in the Midwest / East that the modeled nitrate aerosol formation in this area is nitric acid-limited rather than ammonia-limited. Heald et al. found that when they reduced HNO_3 concentrations to 75% of their simulated values, the positive nitrate bias over the Midwest / East was corrected, a result which confirms that the simulated nitrate aerosol formation over this region is HNO_3 -limited rather than NH_3 -limited. Thus, the under-prediction of ammonia in the midwestern and eastern states does not conflict with the over-prediction of nitrate in this area, since simulated nitrate aerosol formation is HNO_3 -limited in this area, and our results are consistent with Zhang et al. and Heald et al. We have added additional explanation to our revised manuscript to clarify these points.

In California, the conditions are somewhat different than in the Midwest / East. IASI and TES data indicate that ammonia concentrations are underestimated in California, as they are in the rest of the country. However, our model results indicate that, in contrast to the midwestern and eastern states, the simulated nitrate formation is ammonia-limited rather than nitric acid-limited over much of California. Thus the under-prediction of ammonia in GEOS-Chem does account for much of the negative bias in nitrate over many areas of California. In our revised manuscript, we have explored this in more detail, to determine

which areas of California are ammonia-limited and the extent to which an increase in ammonia emissions is required to correct the negative nitrate bias in these areas.

For example, if NH_3 is increased by 300% in CA, that leads to more NH_4NO_3 , which then downwind will exacerbate overestimates of nitrate in other parts of the country.

Ammonium nitrate aerosol is washed out of the atmosphere very effectively by deposition processes; its lifetime is short enough that an increase in predicted NH_4NO_3 in California will not affect predicted downwind concentrations in the Midwest because it would be removed from the atmosphere by deposition long before making it as far as the Midwest or other areas farther east.

4. Observational errors.

a) It would be helpful if the authors please provide typical estimated observational errors.

Estimates of measurement precision for surface aerosol observations have been added to the manuscript.

5. In regards to the satellite observations in Section 4.2.

a) Please provide the reader with more details on the exact IASI inverse retrieval methodology used in this study and its characteristics (i.e. apriori, sensitivity, assumptions, and estimated errors, etc.).

Since IASI data are no longer being used in the present study, these details are no longer relevant. However, these details do now pertain to the TES retrievals, and all the necessary details relevant for the TES retrievals are given in the manuscript.

b) Several limitations in the utilization of the satellite observations are mentioned (i.e. reliable satellite averaging kernels were not available. . . ., . . . ammonia columns are not available during the winter months due to insufficient ammonia sensitivity. . . . Could the IASI observations with great spatial coverage not be supplemented with satellite observations from the Aura TES, which operationally produces reliable averaging kernels, error estimates, and better sensitivity (but less dense spatial coverage), to provide greater insight over the U.S?

The revised manuscript now includes satellite data from TES.

c) It should be noted in the manuscript (maybe just an additional sentence or so with a references) that a more robust and quantitative assessment of GEOS-Chem emissions using satellite observations would be obtained through more detailed inverse modeling using the satellite observational operator (averaging kernel, apriori, errors).

We have noted this in the revised manuscript.

d) Page 19, lines:19-23. In order to include these lines more supporting evidence needs to be presented for the statement about the vertical sensitivity from IASI from 0-2km being uniform. Even though the temperature contrast and elevated amounts of NH₃ over California can significantly improve the vertical sensitivity of the infrared retrievals, it is still generally not the case that the vertical sensitivity is uniform. For example, routine observational Aura TES NH₃ retrievals (which typically has greater sensitivity) over California show a non-linear vertical sensitivity (see attached Fig 1. of a typical TES averaging kernel over CA). I don't think this will change the resulting qualitative scientific conclusions based on the IASI observations in the manuscript as California is a region with the greatest infrared satellite vertical sensitivity in the boundary layer. Therefore, I would suggest just changing lines 19-23 to something along the lines that the linear assumption is made, and that it is realized that the sensitivity in the boundary layer changes from profile-to-profile and not in general equally sensitive in the bottom 0-2 km (provide a reference), but that in the California region the satellite observations do in general have good boundary layer sensitivity.

In the revised manuscript (that no longer includes IASI data), we have used TES ammonia data and have applied the TES satellite operator (a priori and averaging kernels) to the GEOS-Chem model predictions for comparison, so no assumptions need to be made about vertical sensitivity of the satellite measurements.

6. Sensitivity sampling errors between GEOS-CHEM and IASI.

a) This is an active area of research and it is not expected or the goal of this manuscript to address this, but it should be noted in the manuscript that some differences in the IASI GEOS-Chem comparisons could be due to the different sampling and sensitivity. For example, IASI has a much smaller 15 km footprint...

Inherent in our comparison is a mismatch in scales, since the TES footprint is approximately 5 x 8 km (Shephard, 2011), compared with the GEOS-Chem grid box size of approximately 56 x 60 km in California. However, since the predominant sources of ammonia in California are agricultural sources emitting over extended areas, we expect that sub-grid scale variations will be relatively small. We have noted this in the manuscript.

...and is mostly sensitive to elevated NH_3 values, which could skew mean values compared with the model.

In our revised analysis, we have compared individual TES measurements with predicted concentrations at each corresponding hour and grid box in GEOS-Chem, rather than comparing monthly or annual means, so this is no longer an issue.

Response to Referee #2

Walker et al. aimed to explain model biases of nitrate aerosol concentrations over the US (underestimates in California, and overestimates in the East and Midwest) using the GEOS-Chem chemical transport model. They examined the uncertainties in ammonia emissions by comparing with satellite measurements, and also tested the nighttime nitric acid formation by heterogeneous N_2O_5 hydrolysis. They showed reducing the N_2O_5 uptake coefficient did not explain the nitrate overestimates in the East and Midwest, while the underestimates in California is likely due to underestimates of ammonia emissions. The study is well conducted and well fits the scope of ACP. A similar study was conducted independently at the same time by Heald et al. (ACPD 2012; cited in the manuscript). Heald et al. (ACPD 2012) focused on explaining the model nitrate overestimate in the East and Midwest, and this study focused on the underestimate of nitrate aerosol in California.

My main comment on the manuscript is whether it can achieve a more quantitative conclusion. The manuscript conclude that the underestimate of nitrate aerosol concentrations in California is likely due to underestimate of ammonia emissions. It does not answer how much increase in California ammonia emissions is needed to reproduce the measured nitrate concentrations, and whether the increase is consistent with constraints from satellite measurements. I suggest add some discussions on it and also discuss other possible factors that might contribute to the model bias.

We have expanded the sensitivity analysis and extended our discussion to address these comments. An approximate doubling of ammonia emissions is needed to reproduce observed nitrate concentrations in southern California and in other ammonia sensitive areas of California. This result is qualitatively consistent with TES satellite measurements, which indicate that predicted ammonia concentrations in California are biased low by 79%, although this is over a limited number of relatively sparse measurements, so more detailed conclusions regarding seasonal or annual emissions are not called for. However, even a tenfold increase in ammonia emissions yields predicted nitrate concentrations that are still biased low in the central valley of California. It is concluded that the under-prediction of nitrate aerosol in the central valley of California is likely a result of under-prediction of both ammonia and nitric acid in this region.

I have a few more comments listed below:
Specific comments:

1. Page 19501, Introduction: I do not think that the Introduction section provides enough background knowledge for this study. More sentences on our current understanding of aerosol simulation (capability and uncertainty), and understanding of precursors emissions in particular ammonia emissions over the US would help readers to understand the context better.

In view of literature already in this area, we do not feel that additional background discussion is necessary.

2. Page 19503, Line 17: This paragraph and Fig. 2 shall cite Evans and Jacob (GRL 2005) that describes the parameterization of N₂O₅ hydrolysis in GEOS-Chem. Evans, M. J. and Jacob, D. J.: Impact of new laboratory studies of N₂O₅ hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, *Geophys. Res. Lett.*, 32, L09813, 2005.

The citation has been added to the paragraph and figure caption.

3. Page 19504, Line 12-14: Does GEOS-Chem only simulate fine particulate matter of sulfate, ammonium and nitrate? Please check Pye et al. (JGR 2009) (first paragraph of section 2.3) that "ISORROPIA II is implemented in GEOS-Chem to compute gas- aerosol equilibrium partitioning of nitric acid and ammonia. Particles in this study are not size-resolved; however, they can be generally assumed to represent PM_{2.5} since formation of sulfate-nitrate-ammonium on coarse mode sea salt and dust is excluded." Pye, H. O. T., et al.: Effect of changes in climate and emissions on future sulfate- nitrate-ammonium aerosol levels in the United States, *J. Geophys. Res.*, 114, D01205, 2009.

GEOS-Chem includes the formation of inorganic aerosols on coarse mode sea salt; however, after examining the model predictions over the region of interest in our study (the continental US), we found that these concentrations comprise a negligible fraction of predicted inorganic aerosols. GEOS-Chem does not include the formation of inorganic aerosols on coarse mode dust. Therefore we can assume that the inorganic aerosols predicted in the simulations are fine mode, and we have revised the analysis to compare with PM_{2.5} observations, rather than PM₁₀, in the CARB data.

4. Page 19505, Line 11-12: Model sulfate aerosol concentrations are biased low by 34

The value of the bias in predicted sulfate concentrations has been added to this paragraph in the revised manuscript.

5. Page 19505, Line 25-27: Can you discuss other possible factors that may contribute to the nitrate overestimates in the East and Midwest in the model?

Heald et al. (2012) investigated other possible factors that might contribute to the nitrate overestimates in the East and Midwest, including: uncertainties in daytime formation of HNO_3 due to uncertainties in emissions of NO_x , concentrations of OH, or the rate of NO_2 oxidation by OH, and uncertainties in the dry deposition removal rates of nitric acid. They found that none of these uncertainties could fully account for the reduction in HNO_3 required to correct the nitrate bias. Over-prediction of nitrate in the Midwest and eastern states remains to be explained. A summary of their findings has been added to the revised manuscript for completeness.

6. Page 19506, Line 2: Does Table 3 show the biases in the annual concentrations or the averaged normalized mean biases in the monthly concentrations? The comment also applies to the title of Table 3.

This table showed the biases in the annual concentrations at each specific site, based on the monthly predictions and observations at each site. We have removed this table from the revised manuscript and have included the relevant values within the text, with additional clarification of the calculation method for these biases.

7. Page 19506, Line 22-25: Can you explain the statement "either the thermodynamic partitioning between the gas and aerosol phases or the removal of atmospheric HNO_3 is the limiting factor"? In the following discussion, you also attributed the limiting factor to the availability of ammonia.

Nitrate aerosol is formed in thermodynamic equilibrium with gas-phase ammonia and nitric acid. The thermodynamic partitioning between the gas phase and aerosol phase nitrate is determined by the relative abundances of ammonia and nitric acid (as well as by the temperature and relative humidity, which affect the equilibrium constant). Thus, the thermodynamic partitioning of nitrate to the aerosol phase can be limited by availability of nitric acid or the availability of ammonia. If ammonia concentrations are low compared with the available nitric acid, then in thermodynamic equilibrium much of the HNO_3 will remain in the gas phase rather than the aerosol phase. If HNO_3 concentrations are low compared with the available ammonia (for example, if the gas phase HNO_3 has been removed too vigorously by modeled deposition) then this could also limit the nitrate aerosol formation. This discussion in the revised manuscript has been edited to expand and clarify on these points. See also the response to item 3 from Referee 1 for more details.

Fig. 9 also shows there is a large fraction of gas-phase ammonia at both California sites. Is it inconsistent with the conclusion of limited availability of ammonia?

The annual average total ammonia (gas phase ammonia plus aerosol ammonium, expressed as NH_3) concentrations at the three sites shown in Figure 9 are similar: $2.3 \mu\text{g}/\text{m}^3$ at Fresno, $1.8 \mu\text{g}/\text{m}^3$ at Riverside, and $2.4 \mu\text{g}/\text{m}^3$ at Bondville. Because atmospheric conditions are warmer and drier at the California sites compared to the Bondville site, the thermodynamic equilibrium favors gas phase HNO_3 and NH_3 more at the California sites compared to Bondville, as can be seen by the larger fraction of total ammonia and total nitrate in the aerosol phase at Bondville. In the relatively warm and dry conditions at the California sites, higher concentrations of HNO_3 and NH_3 can exist in the gas phase, with relatively small fractions forming aerosols. In order to have aerosol phase ammonium and nitrate in California at similar concentrations as those predicted at Bondville, the gas phase ammonia and/or nitric acid concentrations would need to be considerably higher than those shown in Figure 9. Thus the large fraction of gas phase ammonia at the California sites does not contradict the conclusion of limited availability of ammonia. However, in further analysis shown in our revised manuscript, we determined that ammonia limitation drives the under-prediction of nitrate in many, but not all areas of California. Riverside is a location of ammonia-limited predicted nitrate aerosol, while the under-prediction of nitrate aerosol at Fresno is likely a result of under-prediction of both ammonia and nitric acid at this location.

Would the model underestimate of ammonium aerosol be in part caused by the underestimate of sulfate?

Ammonium aerosol exists primarily in the forms of ammonium sulfate and ammonium nitrate, so an underestimate of sulfate can lead to an underestimate of ammonium aerosol. However, in California, sulfate concentrations are generally much lower than nitrate concentrations, and the negative bias in predicted nitrate is much larger than the bias in predicted sulfate, so the under-prediction in ammonium aerosol is largely driven by the under-prediction of nitrate.

8. Page 19508, Section 4.2: The comparison with IASI measurements of ammonia column seems not consistent with Heald et al. (ACPD 2012) that I think follows the appropriate way to compare with satellite measurements. In their manuscript (Fig. 4) they applied the IASI retrieval averaging kernel and a priori to the GEOS-Chem simulation and showed significant changes in the model results. Their Fig. 4 showed that GEOS-Chem ammonia column concentrations were much higher than IASI before applying the averaging kernel and a priori over the US Midwest. That reflects either IASI a priori profiles are very different from GEOS-Chem profiles or the averaging kernel is not uniform vertically. This is not consistent with Fig. 11 in this manuscript that directly comparing the GEOS-Chem model results with IASI measurements. Please check.

The revised manuscript no longer includes IASI data, so this comment is no longer relevant. For the convenience of the reader, however, we address the referee’s question, as follows.

The IASI dataset provided to us for this study was an updated version of the dataset used by Heald et al. (2012). In the IASI dataset used by Heald et al. (2012), ammonia retrievals were calculated from all IASI observations, whereas the updated IASI dataset in our original ACPD manuscript used a conditional retrieval based on sufficiently large ammonia signal. Consequently, the IASI dataset in our original study included fewer retrievals, and only those with a sufficiently large signal, so the IASI averages shown in the prior Figure 11 are much higher than those shown in Figure 4 of Heald et al. (2012); this difference is large enough that our GEOS-Chem predicted ammonia columns were lower than the IASI columns, in contrast to Figure 4 of Heald et al., in which the GEOS-Chem predicted columns (before applying the satellite operator) were higher than the IASI columns.

9. Page 19525, Fig 10: It is not clear to me that in Fig. 10 plotting the hourly time series is very helpful. What drives the variability in the hourly nitrate time series? Does the ammonia emissions in the model have a hourly resolution? Would it be more helpful if reducing the resolution to daily and over-plotting the measurements for comparison?

The ammonia emissions in the model vary seasonally using scaling factors (Park et al., 2004), but they do not vary on shorter time scales such as hourly. NO_x emissions in the model vary seasonally using scaling factors based on the EPA VISTAS emissions inventory, and also hourly with diurnal scaling factors derived from the EDGAR emissions inventory (http://wiki.seas.harvard.edu/geos-chem/index.php/Scale_factors_for_anthropogenic_emissions). The variability in the hourly nitrate time series is driven by variability in NO_x precursor emissions as well as variability in meteorological conditions (temperature and relative humidity), which affect the thermodynamic partitioning between gas phase HNO_3 and aerosol nitrate.

We agree that reducing the time resolution and over-plotting the measurements for comparison is helpful, and have revised the figure accordingly. The revised figure shows monthly measured and predicted nitrate concentrations over a full year.

10. Page 19517: In the legend of Fig. 2, the red dashed line should be "Sulfate, $T > 282\text{K}$ ".

We have verified from Figure 11 of Hallquist et al. (2003), which is the basis for the temperature dependence parameterization in Table 1 of Evans and Jacob (2005), that the labels for the sulfate curves in our Figure 2 are correct as shown. The uptake efficiency as a function of relative humidity is the same for all temperatures up to 282 K, and decreases with temperature above 282 K, as shown in the example red dashed line for 293 K, which is below the blue dashed line for 282 K. Please note that there appears to be a typo in the first line of Table 1 of Evans and Jacob (2005), which should read $\gamma = \alpha \times 10^{-\beta}$, rather than

$\gamma = \alpha \times 10^\beta$. We confirmed this from Figure 11 of Hallquist et al. (2003), as well as from the text in Evans and Jacob (2005), which describes the uptake coefficient as decreasing with increasing temperature. We also confirmed that our figure is consistent with the GEOS-Chem code (function N2O5 in calcrate.F).

Reference: Hallquist, M., D. J. Stewart, S. K. Stephenson, and R. A. Cox (2003), Hydrolysis of N_2O_5 on sub-micron sulfate aerosol, *Phys. Chem. Chem. Phys.*, 5(16), 3453-3463.

11. Page 19522: Fig. 7 is not clear to read. I suggest make the symbols thicker or add lines over the symbols, and also make the labels of x- and y-axis larger.

The figure has been modified as suggested.

12. In the captions of Fig 6, 7, 8, and 9, please state the comparison year 2009.

The captions have been modified as suggested.