Manuscript # ACP-2015-793

Responses to Reviewer #1

General Comments: This is a well written and, in general, clearly presented paper that seems to present a good case for the dominance of nitrates for aerosols concentrations in the upper troposphere and lower stratosphere over the Asian summer monsoon sector. I have made suggestions for minor revisions.

My primary criticism concerns the comparisons of observed and modeled concentrations of O_3 and HNO_3. The authors claim that observed concentrations are well represented by the model, but offer no context for that comparison. I think the authors should answer the question: Given the discrepancies between observed and modeled O_3 and HNO_3 – what are the uncertainties of modeled nitrate concentrations?

Sec. 4.2 and Fig. 8, which compares modeled concentrations to in situ surface observations, should be deleted. While it is interesting to see such comparisons, the sampling is poor, which, together with the mismatch of sampling time, makes the comparisons difficult to interpret.

Sec. 4.3 shows the comparison of vertical distributions of aerosol extinction from the model with SAGE observations. Comparisons of horizontal distributions in the UTLS should be performed as well.

Responses to general comments:
    We have addressed the major issues mentioned in the general comments:
    (1) We now give quantitative descriptions on the discrepancies between observed and simulated O_3 and HNO_3. We have added the following sentences for HNO_3 in the third paragraph of Section 3.1: "At 100 hPa, the observed HNO_3 mixing ratio averaged over the TP/SASM region (70−105°E, 10−40°N) is 301.3 pptv, which is lower than the simulated value of 349.1 pptv. The difference between the simulated and observed HNO_3 mixing ratio lies within the confidence range of ±500−1000 pptv of the MLS instruments (Livesey et al., 2011). Considering all the grid cells with MLS HNO_3 data available, the simulated seasonal mean HNO_3 concentrations show normalized mean bias (NMB) of +15.9% at 100 hPa over the TP/SASM region (70−105°E, 10−40°N) in summer of year 2005." We have added the following sentences for O_3 in the second paragraph of Section 3.2: "At 100 hPa, simulated and MLS observed O_3 mixing ratios averaged over the TP/SASM region (70−105°E, 10−40°N) are 190.6 and 145.1 ppbv, respectively. Compared to MLS observations, simulated O_3 concentrations at 100 hPa have a NMB of +31.4% over the TP/SASM region in summer of 2005." We have also

added a sentence in the second paragraph of the conclusion section: "At 100 hPa, simulated seasonal mean HNO_3 and O_3 mixing ratios show NMBs of +15.9% and +31.4%, respectively, over the TP/SASM region (70–105°E, 10–40°N) in summer of year 2005."

(2) We have performed several new sensitivity studies to examine the uncertainties with simulated nitrate concentrations in the UTLS. Anthropogenic emissions of NO_x, NH_3, and SO_2 are changed according to the NMBs of the simulated concentrations of sulfate and nitrate. These sensitivity studies all confirm that nitrate aerosol is a dominant aerosol species in the UTLS, which are presented in our new Section 7 of "Impacts of uncertainties in surface-layer aerosol concentrations on simulated nitrate in the UTLS".

(3) The comparisons of simulated surface-layer aerosol concentrations with observations in Section 4.2 are performed to evaluate the model's ability to simulate various aerosols. Considering yours and the other reviewer's suggestions on discussions of uncertainties associated with simulated nitrate in the UTLS, we have performed several sensitivity studies on the basis of the biases in simulated surface-layer aerosols (see our new Section 7). Thus, we prefer to retain Section 4.2 and Fig. 8 in the revised manuscript.

(4) It is difficult to compare the simulated horizontal distributions of aerosol extinction coefficient with SAGE II observations, because SAGE II data do not provide the information on horizontal distribution for a specific month. The SAGE II instrument vertically scans the limb of the atmosphere during spacecraft sunsets and sunrises (fifteen sunsets and fifteen sunrises each day). The 57 degrees inclined orbit of the ERBS spacecraft evenly distributes the SAGE II measurements every 24 degrees of longitude along a slowly shifting latitude circle. (http://www.nasa.gov/centers/langley/news/factsheets/SAGE.html). For the anticyclone region of (20–120°E, 10–40°N), the measurements are available at about 28 sites and each site has only one profile during the month of July in 2005. Therefore, we average the profiles observed over the region of our interest during the month of July in 2005 to compare monthly vertical distribution of aerosol extinction in our manuscript.

Our point-to-point responses to the reviewer's comments are listed below.

Specific Comments:

1. Page 32050, Lines 9-10: Mention that $PM_{2.5}$ is the sum of the previous aerosols listed.
Response:
We have clarified here that $PM_{2.5}$ is the sum of sulfate, nitrate, ammonium, black carbon, and organic carbon aerosols.

2. Page 32050, Line 12: It would be better to state that nitrate is of secondary importance near the surface. There are other aerosols that have as large (or

nearly as large) concentrations; stating that nitrate has the second largest concentration without acknowledging that other aerosols are as important is not a fair assessment.

Response:

We have revised the sentence as "Nitrate aerosol is simulated to be of secondary importance near the surface but the most dominant aerosol species in the UTLS over the studied region."

3. p. 32050, l. 22: Change 'time to 'times'

Response:

Changed.

4. p. 32050, l. 22: Change 'which influence' to 'influencing'

Response:

Changed.

5. p. 32051, l. 16,17: Remove 'M.' from 'M. Park'

Response:

Because there are two references of Park et al. (2004) in the manuscript, 'M.' was added to one of them by the journal's Production Office.

6. p. 32053, l. 1: Remove '(> 75%)'

Response:

Removed.

7. p. 32056, l. 17-18: Seasonal cycles if SO_2, OC and BC are very weak.

Response:

Yes, the seasonal cycles of SO_2, OC, and BC are week. We have deleted the sentence of "Emissions of SO_2, OC and BC are the highest during wintertime as a result of the winter heating."

8. p. 32057, Fig. 3a: Why are concentrations high (the highest of any region) over south equatorial Africa?

Response:

As discussed in Liao et al. (2003), high concentrations of HNO_3 over south equatorial Africa result from high biomass burning emissions in that region in summer of every year. We have clarified in the text that "Concentrations of HNO_3 exceed 1 ppbv over the industrialized areas such as Europe, North America, central and eastern Asia, and over biomass burning regions in the tropics, in agreement with the distributions and magnitudes reported in Liao et al. (2003)."

9. p. 32058, Fig. 4: There are factor of 2 (and greater) discrepancies between model and observations – how does this uncertainty translate into an

uncertainty in nitrate aerosol?

Response:

We have added in the third paragraph of Section 3.1 the quantitative description on the discrepancies between observed and simulated HNO_3: "Considering all the grid cells with MLS HNO_3 data available, the simulated seasonal mean HNO_3 concentrations show normalized mean bias (NMB) of +15.9% at 100 hPa over the TP/SASM region in summer of year 2005."

The uncertainties in HNO_3 and nitrate are associated with the uncertainties in anthropogenic emissions of chemical species such as NO_x, NH_3, and SO_2. We have performed several sensitivity studies to examine the uncertainties of simulated nitrate concentrations, as we present in our new Section 7 "Impacts of uncertainties in surface-layer aerosol concentrations on simulated nitrate in the UTLS".

10. p. 32060, l. 25: Concentrations of ammonium and organic carbon are just as (or nearly as) large as nitrate – though technically accurate, it is misleading to state that nitrate is the second largest without acknowledging that other aerosols are just as important.

Response:

We have revised the description as "NO_3^- is simulated to be of secondary importance at the surface over the region of our interest."

11. p. 32062, l. 8: Change '8b-j' to '8b-f'

Response:

Changed.

12. p. 32064, Table 2: Certain values in Table 2 do not make sense and indicate that the calculations of concentration are not performed consistently among constituents. This is most obvious for values of concentrations averaged over TP/SASM that are smaller than the corresponding values for the individual TP and SASM. If the concentrations are calculated in a consistent manner then the values for TP/SASM have to lie between the values for TP and those for SASM. Please check these the accuracy of the calculations or, if the calculations are not consistent by design, please explain why.

Response:

Thanks for pointing this out. We have recalculated the concentrations in a consistent manner and the new results are displayed in Table 2.

13. p. 32065, l. 16-17: Explain why you are not using winds used in GEOS-CHEM.

Response:

The assimilated GEOS-5 meteorological fields used to drive the GEOS-Chem simulation do not have vertical winds

(http://wiki.seas.harvard.edu/geos-chem/index.php/List_of_GEOS-5_met_fields), so we use the ECMWF reanalysis wind fields to do the analysis. This is now explained in the text.

14. p. 32066, Sec. 6.2: Explain why you are not able to use GEOS-CHEM chemistry to determine precisely what the mechanisms for nitrate formation are.

Response:

The chemical mechanism for nitrate formation in the GEOS-Chem model was described in R. J. Park et al. (2004), which is comprehensive and has been used extensively in previous studies to simulate nitrate aerosol (R. J. Park et al., 2004; Pye et al., 2009; Zhang et al., 2010; Zhu et al., 2012; Jiang et al., 2013; Lou et al., 2014). The same chemistry mechanism was also used to examine the global distributions and concentrations of nitrate aerosol in Liao et al. (2004) and Liao and Seinfeld (2005). Nitrate forms from the partitioning of HNO_3 between gas and aerosol phases. Major reactions for the production and loss of HNO_3 were listed in Liao and Seinfeld (2005) (see Table R1 below). Therefore the formation of gas-phase HNO_3 and the partitioning of HNO_3 between gas and aerosol phases are the two major chemical processes that influence nitrate concentrations. We have evaluated the ability of the GEOS-Chem model to simulate gas-phase HNO_3 in Section 3.1 (by comparisons of our model results with MLS observations and concentrations from previous modeling studies), so we quantify in Section 6.2 the nitrate formation from gas-to aerosol conversion of HNO_3 based on the ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes, 2007) in the GEOS-Chem model. We have added these explanations in Sections 6.1 and 6.2.

Table R1. Annual mean HNO_3 budget for present-day and year 2100 simulations (taken from Liao and Seinfeld, 2005)

	Present-Day		Year 2100	
	Baseline	NOHET	Baseline	NOHET
Chemical Productions, Tg yr^{-1}	153.5	154.5	464.0	457.3
(R1) $NO_2 + OH + M \rightarrow HNO_3 + M$	36.5%	55.5%	36.8%	61.8%
(R2) $NO_3 + CH_2O \rightarrow HNO_3 + prod.$	1.1%	3.8%	2.2%	8.9%
(R3) $ALD2 + NO_3 \rightarrow HNO_3 + prod.$	0.8%	3.2%	1.8%	6.6%
(R4) $RIO2 + NO \rightarrow HNO_3 + prod.$	9.3%	9.1%	3.9%	3.7%
(R5) $RIO1 + NO \rightarrow HNO_3 + prod.$	0.8%	0.7%	0.4%	0.3%
(R6) $IAO2 + NO \rightarrow 0.08HNO_3 + prod.$	0.3%	0.3%	0.1%	0.1%
(R7) $VRO2 + NO \rightarrow HNO_3 + prod.$	0.9%	0.9%	0.4%	0.4%
(R8) $MRO2 + NO \rightarrow HNO_3 + prod.$	0.6%	0.6%	0.3%	0.2%
(R9) $MVN2 + NO \rightarrow 0.1HNO_3 + prod.$	0.0%	0.1%	0.0%	0.1%
(R10) $INO2 + NO \rightarrow 0.85HNO_3 + prod.$	4.7%	5.8%	2.6%	3.6%
(R11) $ALK4 + NO_3 \rightarrow HNO_3 + prod.$	0.0%	0.4%	0.1%	0.5%
(R12) $RCHO + NO_3 \rightarrow HNO_3 + prod.$	0.1%	0.4%	0.2%	0.7%
(R13) $MEK + NO_3 \rightarrow HNO_3 + prod.$	1.1%	3.3%	0.8%	2.9%
(R14) $INO2 + MO2 \rightarrow 0.425HNO_3 + prod.$	0.6%	0.8%	0.2%	0.3%
(R15) $GLYX + NO_3 \rightarrow HNO_3 + prod.$	0.0%	0.0%	0.0%	0.0%
(R16) $MGLY + NO_3 \rightarrow HNO_3 + prod.$	0.2%	0.8%	0.3%	1.5%
(R17) $MACR + NO_3 \rightarrow HNO_3 + prod.$	0.3%	0.7%	0.2%	0.8%
(R18) $C_2H_6 + NO_3 \rightarrow HNO_3 + prod.$	0.0%	0.0%	0.1%	0.2%
(R19) $INO2 + MCO3 \rightarrow 0.85HNO_3 + prod.$	2.2%	2.8%	1.0%	1.1%
(R20) $DMS + NO_3 \rightarrow HNO_3 + prod.$	7.4%	10.8%	4.1%	6.3%
(R21) $NO_2 + (aerosols) \rightarrow 0.5HNO_3 + prod.$	6.2%	0.0%	8.2%	0.0%
(R22) $NO_3 + (aerosols) \rightarrow HNO_3 + prod.$	0.3%	0.0%	0.4%	0.0%
(R23) $N_2O_5 + (aerosols) \rightarrow 2HNO_3$	26.5%	0.0%	35.8%	0.0%
Total loss, Tg yr^{-1}	153.5	154.5	464.0	457.3
Chem. loss, Tg yr^{-1}	10.7	20.0	24.9	44.6
(R24) $HNO_3 + OH \rightarrow prod.$	34.6%	37.0%	32.9%	36.8%
(R25) $HNO_3 + hv \rightarrow prod.$	65.4%	63.0%	67.1%	63.2%
Dust uptake, Tg yr^{-1}	37.1	0	73.0	0
Loss to nitrate,^{b} Tg yr^{-1}	36.9 (105.3−68.4)	46.0 (123.5−77.5)	168.7 (394.4−225.7)	176.1 (470.7−294.6)
Dry deposition, Tg yr^{-1}	27.3	35.6	80.1	97.2
Wet deposition, Tg yr^{-1}	41.5	52.9	117.3	139.4
Burden, Tg	1.30	1.78	2.16	2.98

^{a}The numbers for reactions (R1)−(R25) are contributions to chemical production or loss from each reaction. Please see http://www-as.harvard.edu/chemistry/trop/geos/doc/chem_mech/geoschem_mech.pdf for the formula of the species in these reactions and for the rate constants.
^{b}The first number in the parentheses is the loss of gas-phase HNO_3 to nitrate formation, and the second number shows the release of gas-phase HNO_3 from nitrate, which are determined by aerosol thermodynamics.

15. p. 32066, l. 17: Change 'in consistent' to 'consistent'.
Response:
     Changed.

16. p. 32066, l. 21-22: Delete the sentence 'Besides being . . .'. It is not clear that cold temperatures near the tropopause have a casual influence on upwelling there nor is it important to your study for that to be the case.
Response:
     Deleted as suggested.

17. p. 32067, l. 19: Change 'scarcely' to 'are not' or change 'particles in the UTLS of the TP/SASM scarcely composed of coarse and aspherical particles such as NAT' to 'coarse and aspherical particles such as NAT are scarce in the UTLS of the TP/SASM'.
Response:
     Thanks for the suggestion. We have changed "particles in the UTLS of the TP/SASM scarcely composed of coarse and aspherical particles such as NAT" to "coarse and aspherical particles such as NAT are scarce in the UTLS of the TP/SASM".

18. p. 32067, l. 23: Delete 'by simulation'.
Response:
     Deleted.

19. p. 32067, l. 26: Change 'capability in simulating' to 'ability to simulate'.

Response:
    Changed.

20. p. 32068, l. 1: Regarding 'agree well'. You need to put the model-observations comparisons into the context of nitrate formation in order to say they agree well. That is, you need to determine what the uncertainties of nitrate concentrations are given the uncertainties of O_3 and HNO_3 concentrations (as determined by the model-observation discrepancies).
Response:
    We now give quantitative descriptions on the discrepancies between observed and simulated O_3 and HNO_3: "At 100 hPa, simulated seasonal mean HNO_3 and O_3 mixing ratios show NMBs of +15.9% and +31.4%, respectively, over the TP/SASM region (70–105°E, 10–40°N) in summer of year 2005". The discussions on uncertainties in simulated nitrate concentrations are presented in our new Section 7.

21. p. 32068, l. 8: Regarding 'second largest'. See above comment for p. 32060, l. 25.
Response:
    We have revised the description as "Nitrate aerosol is simulated to be of secondary importance near the surface over the region of our interest."

22. p. 32068, l. 17: Instead of 'the GEOS-CHEM model reproduces well', state how well it reproduces (e.g., with 10% or whatever) observed values.
Response:
    We have added one quantitative sentence here: "The discrepancies between the simulated and observed aerosol extinction coefficient are within 8% in the UTLS (averaged over 14–16 km)."

23. p. 32068, l. 29: Change 'convections' to 'convection'.
Response:
    Changed.

References:
Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+–Ca^{2+}–Mg^{2+}–NH_4^+–Na^+–SO_4^{2-}–NO_3^-–Cl^-–H_2O aerosols, Atmos. Chem. Phys., 7, 4639–4659, 2007.
Jiang, H., Liao, H., Pye, H., Wu, S., Mickley, L. J., Seinfeld, J. H., and Zhang, X.: Projected effect of 2000–2050 changes in climate and emissions on aerosol levels in China and associated transboundary transport, Atmos. Chem. Phys., 13, 7937–7960, 2013.
Liao, H., Adams, P. J., Chung, S. H., Seinfeld, J. H., Mickley, L. J., and Jacob,

D. J.: Interactions between tropospheric chemistry and aerosols in a unified general circulation model, J. Geophys. Res., 108, 4001, doi:10.1029/2001JD001260, 2003.

Liao, H., Seinfeld, J. H., Adams, P. J., and Mickley L. J.: Global radiative forcing of coupled tropospheric ozone and aerosols in a unified general circulation model, J. Geophys. Res., 109, D16207, doi:10.1029/2003JD004456, 2004.

Liao, H., and Seinfeld, J. H.: Global impacts of gas-phase chemistry-aerosol interactions on direct radiative forcing by anthropogenic aerosols and ozone, J. Geophys. Res., 110, D18208, doi:10.1029/2005JD005907, 2005.

Livesey, N. J., Read, W. G., Wagner, P. A., Froidevaux, L., Lambert, A., Manney, G. L., Pumphrey, H. C., Santee, M. L., Schwartz, M. J., Wang, S., Cofield, R. E., Cuddy, D. T., Fuller, R. A., Jarnot, R. F., Jiang, J. H., and Knosp, B. W.: Version 3.3 Level 2 data quality and description document, JPL D-33509, 2011.

Lou, S., Liao, H., and Zhu, B.: Impacts of aerosols on surface-layer ozone concentrations in China through heterogeneous reactions and changes in photolysis rates, Atmos. Environ., 85, 123-138, doi:10.1016/j.atmosenv.2013.12.004, 2014.

Park, M., Randel, W. J., Kinnison, D. E., Garcia, R. R., and Choi, W.: Seasonal variation of methane, water vapor, and nitrogen oxides near the tropopause: Satellite observations and model simulations, J. Geophys. Res., 109, D03302, doi:10.1029/2003JD003706, 2004.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, J. Geophys. Res., 109, D15204, doi:10.1029/2003JD004473, 2004.

Pye, H., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K., and Seinfeld, J.: Effect of changes in climate and emissions on future sulfate–nitrate–ammonium aerosol levels in the United States, J. Geophys. Res., 114, D01205, doi:10.1029/2008JD010701, 2009.

Zhang, L., Liao, H., and Li, J.: Impacts of Asian summer monsoon on seasonal and interannual variations of aerosols over eastern China, J. Geophys. Res., 115, D00K05, doi:10.1029/2009JD012299, 2010.

Zhu, J., Liao, H., and Li, J.: Increases in aerosol concentrations over eastern China due to the decadal-scale weakening of the East Asian summer monsoon, Geophys. Res. Lett., 39, L09809, doi:10.1029/2012GL051428, 2012.