Manuscript # ACP-2015-793
Responses to Referee #2: Report #1

The authors have made an effort to address the questions raised by the reviewers. The model sensitivity tests as performed by the authors should be helpful for further understanding the sources and formation mechanisms of nitrate aerosols in the UTLS over the TP/SASM region. The authors' responses are generally fine, but additional issues arising need to be addressed further. Below are my specific comments and suggestions.

It is interesting to see that compared to surface NO3-, nitrate aerosols in the UTLS over the TP/SASM region are not so sensitive to a 50% reduction of anthropogenic NOx emissions in Asia. What could one learn from this result with regards to the sources and formation mechanism of nitrate aerosols (and their gas precursors) in the UTLS over the TP/SASM region? Specifically, does it mean that anthropogenic NOx emissions in Asia (including South and Southeast Asia) do not have large impacts on nitrate aerosols in the UTLS over the TP/SASM region? The authors may want to give a short discussion on the implications of this sensitivity result, instead of merely arguing that nitrate is more important than sulfate for the UTLS aerosol layer even under a situation of 50% NOx emission reduction. The authors are suggested to use a different title for Sect. 7, .e.g. "Sensitivities of simulated nitrate in the UTLS to anthropogenic NOx, NH3 and SO2 emissions in Asia".

Response:

Thanks for the suggestions. We have made the following changes in the text:

(1) We have added discussions on why nitrate aerosol in the UTLS over the TP/SASM region is not sensitive to a 50% reduction of anthropogenic NO_x emissions in Asia: "As shown in Table 3, for the surface layer, simulated nitrate concentration over the TP/SASM region decreases by 46.8% with a 50% reduction in anthropogenic NO_x emissions in Asia, and it decreases by 22.3% when anthropogenic NH_3 emissions are reduced by the same percentage, indicating that surface-layer nitrate aerosol is more sensitive to anthropogenic emissions of NO_x than to those of NH_3. Relative to the baseline simulation, simulated nitrate concentrations at 200 hPa and 100 hPa decrease, respectively, by 49.0% and 17.7% with a 50% reduction in NH_3 emissions, whereas only by 2.1% and 1.3% with a 50% reduction in NO_x emissions. Over the studied region, the role of NH_3 in the sulfate-nitrate-ammonium aerosol system can be quantified by the gas ratio of $\mathrm{GR} = \frac{\text{free ammonia}}{\text{total nitrate}} = \frac{\mathrm{TA}-2\times\mathrm{TS}}{\mathrm{TN}}$ (Ansari and Pandis, 1998), where $\mathrm{TA} = \mathrm{NH_3} + \mathrm{NH_4^+}$, $\mathrm{TS} = \mathrm{SO_4^{2-}}$, and $\mathrm{TN} = \mathrm{HNO_3} + \mathrm{NO_3^-}$. Over the TP/SASM region, GR is generally positive both at the surface and in the UTLS, especially over 20–40°N where deep convection exits (Fig. 11), indicating that S(VI) is in from of sulfate and free ammonia is available to react with nitrate (Seinfeld and Pandis 2006). However, GR is generally less than 1.0 above 400 hPa in summer over the TP/SASM region, which indicates nitrate concentrations are most sensitive to changes in NH_3 and explains the small sensitivity of nitrate aerosol to NO_x emissions in the UTLS."

(2) We have changed the title of Sec. 7 to "Sensitivities of simulated nitrate in the UTLS to anthropogenic NO_x, NH_3, and SO_2 emissions in Asia".

PM2.5 is an important parameter usually used for air quality study, and it might not have to be used to describe the aerosols in the UTLS. Was PM2.5 simulated as a tracer in GEOS-Chem or it was calculated just by summing simulated SO4=, NO3-, NH4+, BC and OC? Mineral dust and sea salt aerosols, which were simulated and used for the calculation of extinction coefficient in this study, should also be taken into account for PM2.5. Otherwise, more clear definition/descriptions should be given in the text. In the abstract (Line37-38), for example, it might be written as "defined as the sum of sulfate, nitrate, ammonium, black carbon, and organic carbon aerosols in this study". In Fig. 7, the sub-panels for PM2.5 can be omitted, and instead the distributions of mineral dust and sea salt aerosols might be displayed.

Response:

We have revised the abstract to describe clearly that "$PM_{2.5}$ is defined as the sum of sulfate, nitrate, ammonium, black carbon, and organic carbon aerosols in this study".

We agree that the consideration of sea salt and mineral dust aerosols may influence our calculated contribution of nitrate to total aerosol mass. We have done the calculation (see Figure A below) and added the following quantitative discussions at the end of Section 5: "Considering the large uncertainties in simulated sea salt (Jaeglé et al., 2011) and mineral dust (Fairlie et al., 2007) aerosols, we tend to be focused on anthropogenic aerosol species (SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC) in this work. In our model, concentrations of sea salt (or mineral dust) are simulated to be 1.0–1.7 ng m^{-3} (or 5.0–7.0 ng m^{-3}) over the studied region in the summer of 2005, which contribute less than 1.2% (or 5.0%) to total aerosol mass at 100 hPa. Therefore the consideration of sea salt and mineral dust can slightly reduce C_{NIT} values, but C_{NIT} values at 100 hPa are still as high as 45-65% over the TP/SASM region in summer."

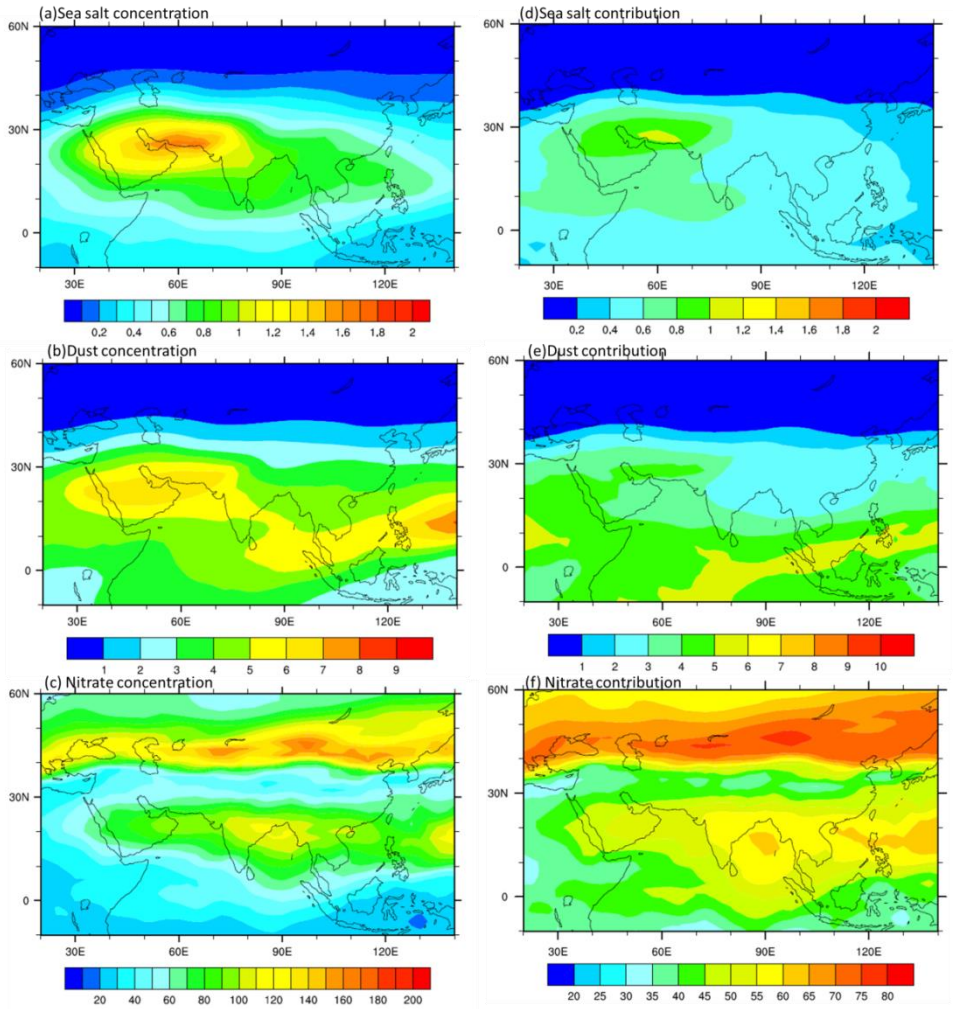

Figure A. Simulated seasonal mean concentrations (ng m^{-3}) of (a) sea salt (sum of mass over two size bins of 0.1–0.5, 0.5–8 μm), (b) mineral dust (sum of mass over four size bins of 0.1–1.0, 1.0–1.8, 1.8–3.0, 3.0–6.0 μm), and (c) nitrate for summer (June-August) of year 2005. (c)–(f) show, respectively, the seasonal mean contributions (%) of sea salt, mineral dust, and nitrate to total aerosol mass (sum of sulfate, nitrate, ammonium, OC, BC, sea salt, and mineral dust) at 100 hPa.

The physical, chemical and dynamical processes related to the formation of the UTLS aerosol layer are complex and need further investigations in future studies. Therefore, I would suggest that a more detailed description of the aerosol module used in this study be given for the convenience of comparisons of future work with this study. How many size bins or modes of the aerosols were adopted in the GEOS-Chem used in this study? What ionic aerosols were considered in the ISORROPIA II used in this study, NH4+/SO4=/NO3-, or NH4+/Na+/K+/Ca2+/Ma2+/SO4=/NO3-/Cl-/CO3=, or others? Were the aerosols treated as internal, or external mixed, or both (the same question as in my first round review)? One can see from Table 3 that OC and BC concentrations are constant for different simulations, indicating that they are external mixed.

Response:

Thanks for the suggestions. In the GEOS-Chem model, anthropogenic

aerosols are treated as bulk mass concentrations (particles of SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC are not size-resolved). These anthropogenic aerosol species are usually summed to represent $PM_{2.5}$ in previous studies on aerosols in the United States and in China (Liu et al., 2004; Zhang et al., 2010; Tai et al., 2012; Jiang et al, 2013; Lou et al., 2014). Anthropogenic aerosols are treated as bulk mass concentrations (particles of SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC are not size-resolved). Sea Salt mass is simulated for two size bins (0.1–0.5 and 0.5–8 μm) and mineral dust is simulated for four size bins (0.1–1.0, 1.0–1.8, 1.8–3.0, and 3.0–6.0 μm). In the version of the GEOS-Chem model used in this work, irons considered in ISOROPIA II include $H^+/Na^+/NH_4^+/Cl^-/SO_4^{2-}/HSO_4^-/NO_3^-/OH^-$. Aerosol species are treated as an external mixture in the calculation of aerosol optical properties. We have revised the description of GEOS-Chem model (Sec. 2.1) to include the above information.

With respect to the formation mechanisms for SO4= and NO3- in the UTLS (Line 547-553), simple comparison of the changes in the gas-phase oxidation of SO2 and the gas-particle equilibria of NO3- with temperature (altitude) might not be sufficient to explain the difference in their vertical distributions. Note that the reaction of NO2 (not NO as written in Line 546) with OH also changes with temperature, the same as for the reaction of SO2 with OH. Was H2SO4 simulated in the GEOS-Chem? If so, comparisons of both the formation and nucleation rates of H2SO4 and HNO3 might be helpful. It seems that the gas-phase oxidation of SO2 was not addressed in the work of X.Y. Zhang et al. (2012), not mentioned to the change of its reaction rate with temperature. Therefore, this work should not be cited here (Ling 550).

Response:

We agree with the reviewer. Nearly all the chemical reactions are influenced by changes in temperature. Dawson et al. (2007) examined the sensitivities of sulfate and nitrate concentrations to temperature by using the Particulate Matter Comprehensive Air Quality Model with extensions (PMCAMx). The sensitivity test was performed by fixing all meteorological parameters but perturbing temperature. Their sensitivity simulations showed that the increases in temperature led to increases in sulfate concentrations and decreases in nitrate concentrations. Compared to nitrate, sulfate concentrations showed smaller sensitivity to temperature changes (Dawson et al., 2007); as temperature increased, nitrate concentrations decreased by 19% K^{-1} and 17% K^{-1} in January and July respectively, while sulfate concentration increased by 0.12% K^{-1} and 1.3% K^{-1} in January and July, respectively. We have clarified this in the second paragraph of Sec. 6.1.

H_2SO_4 is simulated in the GEOS-Chem (Park et al., 2004).

Thanks for pointing out the mistake with the reference of X.Y. Zhang et al. (2012). We have deleted it.

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Responses to Referee #3: Report #2

The paper "Summertime nitrate aerosol in the upper troposphere and lower stratosphere over the Tibetan Plateau and the South Asian summer monsoon region" by Gu et al. describes results from global model simulations of aerosol chemical composition over the Tibetan plateau.
However, the title is misleading as not only UTLS but also surface concentrations are analyzed and compared with observations, which are a substantial contribution to the total manuscript.

Generally, the paper is reasonably well written and provides a basic evaluation of the aerosol chemical composition with a focus on aerosol nitrate over the Tibetan plateau. However, the applied horizontal resolution of the global model,

i.e. 2° by 2.5° is quite coarse for a focus on a specific region, such that no detailed information on the regional distribution over the TP can be addressed properly.

Overall, the paper can be published after addressing the major (and minor) points below.

Responses to general comments:

(1) Although we are focused on aerosols in the UTLS, we have to show and evaluate aerosol concentrations at the surface, because previous studies have shown that chemical species in the UTLS over the TP/SASM region are influenced by their concentrations at the surface (convection associated with the SASM is a vital pathway to transport chemical species from the lower troposphere into the stratosphere) (Chen et al., 2006; Randel and Park, 2006; Randel et al., 2010; Bian et al., 2011). Observational and modeling studies have shown that persistent maxima of atmospheric constituents (H_2O, CO, CH_4, HCN, etc.) exist in the UTLS above the TP/SASM region because of the deep convection during boreal summer (Gettelman et al., 2004; Li et al., 2005; Randel and Park, 2006; M. Park et al., 2004, 2007, 2008, 2009, Randel et al., 2010).

(2) We use the version of the GEOS-Chem model with 2°×2.5° resolution because of the following reasons:

a. The models with a 2°×2.5° horizontal resolution have been shown to have the ability to address the distributions of atmospheric constituents in the UTLS over the TP/SASM region in previous modeling studies. Li et al. (2005) used the GEOS-Chem model with a horizontal resolution of 2°×2.5° to examine the transport of South Asian pollutants to the upper troposphere during 25 August – 6 September, 2004, and showed that the horizontal distribution of CO at 150 hPa agreed well with the MOPITT and MLS observations. Fadnavis et al. (2013) used the ECHAM5-HAMMOZ model with a horizontal resolution of 2.8°×2.8° to study the transport of aerosols into the UTLS over the TP/SASM during the Asian summer monsoon season of 2003, and showed that the vertical distribution of aerosol extinction was in agreement with that obtained from HALOE and SAGE II measurements.

b. We agree with the reviewer that it's better to use a higher resolution model to address the regional distribution over the TP/SASM region. The nested version of the GEOS-Chem has a higher resolution of 0.5°x0.666°, but the region with nested grids covers only 70–150°E, which cannot cover the whole anticyclone region studied in the manuscript.

c. We have compared the horizontal distribution of nitrate simulated with a 2°x2.5° resolution with that simulated with a 0.5°x0.666° resolution by using the GEOS-Chem model (See Figure B below). Over the nested domain (including China, India, and the Tibetan Plateau), the distribution and magnitude of nitrate with these two horizontal resolutions agree fairly well.

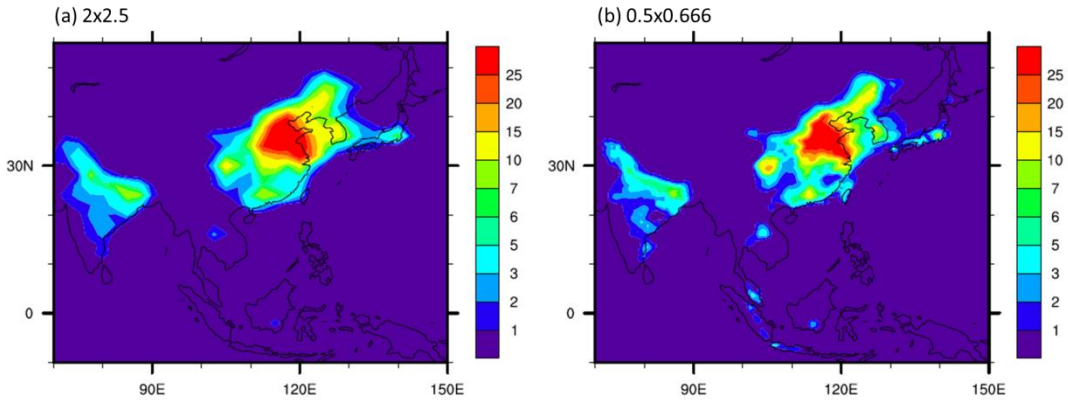

Figure B. The horizontal distribution of surface-layer nitrate aerosol concentration (μg m^{-3}) in July of 2005 simulated from the GEOS-Chem model with horizontal resolutions of (a) 2°x2.5° and (b) 0.5°x0.666°.

Overall, the paper can be published after addressing the major (and minor) points below:

There are three major points in the current manuscript, which inhibit publication in the current form. These are:

1) The effect of nitrate aerosols is difficult to address from a simulation with and without nitrate as the chemical regime of the aerosol thermodynamic partitioning depend strongly on the availability of nitrate. Consequently, a completely different aerosol composition is derived, and from this a modified aerosol microphysical processing results as well as properties of the size distribution with implications for aerosol extinction. Consequently, this whole part should better be addressed by conclusions drawn from the experiments with a modified emission strength (+- 20%), as this will not completely alter the chemical regime of the thermodynamics. The comparison with SAGE data for extinction suffers from the same problem. However, total extinction is reasonably well matched. A key question is whether the model is able to represent the stratospheric aerosol layer (originating mostly from COS oxidation and to a minor extent also anthropogenic SO2), as this will contribute to a major extent to the aerosol layer in the UTLS.

Response:

(1) Our description on numerical experiment may not be clear enough, which leads to a misunderstanding by the reviewer. There are five experiments discussed in the manuscript: one is our baseline simulation, and the other four are sensitivity experiments as presented in Sec. 7. All the simulations are conducted with full chemistry including all the gas-phase species and aerosols in the GEOS-Chem. When we show vertical distributions of aerosol extinction coefficients “with nitrate” (or “without nitrate”) in Fig. 9(b), we mean that we account for (or do not account for) the contribution of nitrate aerosol in our calculation of aerosol extinction. To avoid confusion, we have revised our description on Figure 9 in Sec. 4.3: “The vertical distributions of aerosol extinction coefficients “with nitrate” and “without nitrate” are both from the baseline run with full chemistry. The vertical distribution of aerosol extinction coefficient “with nitrate” (or “without nitrate”) indicates that the contribution of

nitrate aerosol to aerosol extinction is (or is not) accounted for."

(2) We agree with the reviewer that the oxidation of COS contributes to the concentrations of sulfate aerosol in the stratosphere. Currently, COS is not considered in the standard version of the GEOS-Chem model. However, the absence of COS in our simulations should not compromise our major conclusions for the following reasons:

a. Early studies considered that the oxidation of COS is the major source of the background stratospheric sulfate during non-volcanic period (Crutzen, 1976; Maroulis et al., 1977). However, studies during the past two decades had different opinions (Hoffman et al., 1991; Chin and Davis, 1995; Weisenstein et al., 1997; Thomason et al., 1997; Kjellström, 1998; Sturges et al., 2001). Based on numerical simulations, the stratospheric production of SO_2 from COS oxidation was estimated to be 0.01–0.05 Tg S yr^{-1} (Crutzen and Schmailzl, 1983; Chin and Davis, 1995; Weisenstein et al., 1997; Kjellström, 1998), which was 3–5 times smaller than the amount (0.043–0.17 Tg S yr^{-1}) needed to sustain the stratospheric sulfate (Chin and Davis, 1995). Besides, Sturges et al. (2001) found that the changes in COS concentrations were relatively small compared to the increases in sulfate concentrations in the stratosphere in the 20th century, indicating that COS might not be the main source of the increases in stratospheric sulfate. Based on the observations in Laramie, Wyoming, Hoffman et al. (1991) suggested that the high-altitude aircraft emissions might account for 65% of the sulfur sources in the stratosphere. By using a three-dimensional general circulation model ECHAM, Kjellström (1998) suggested that SO_2 transported from the troposphere was the most important for sulfate in the stratosphere below 20 km while COS oxidation was the most important source for sulfate above 25 km. Although COS is not considered in our work, the emissions of volcanoes and aircrafts (Table 1) as well as the detailed simulations of SO_2 (R. J. Park et al., 2004) are all included in our model.

b. The UTLS over the TP/SASM region has been reported to be largely influenced by anthropogenic emissions, since the deep convection associated with the SASM is a vital pathway to transport air mass from the lower troposphere into the stratosphere (Chen et al., 2006; Randel and Park, 2006; Randel et al., 2010; Bian et al., 2011). The global COS source is estimated to be 0.4–0.9 Tg S yr^{-1} (Chin and Davis, 1995; Seinfeld and Pandis, 2006; Brühl et al., 2012), which is much lower than the anthropogenic emissions of SO_2 (Table 1).

c. COS in the stratosphere leads to the formation of SO_2 via photolysis and oxidation reactions. As a result, COS mixing ratio decreases rapidly with altitude, from about 500 pptv at the tropopause to less than 10 pptv at about 30 km altitude (Chin and Davis, 1995). About 2/3 of the stratospheric COS oxidation takes place at altitudes above 25 km (Kjellström, 1998; Brühl et al., 2012). Kjellström (1998), indicating that COS played a minor role in sulfate formation at altitudes below 20 km. Since we are focused on aerosols in the UTLS, COS is expected to play a small role in sulfate concentration here.

2) The other key problem is the comparison with satellite data with a coarse vertical resolution. As HNO3 (as well as ozone) has an increasing gradient from the troposphere to the stratosphere, the detection from the satellite could

easily be influenced by the upper part of the sampling layers which might be dominated by the stratospheric air masses. This is e.g. obvious from the Figures 4 and 5, which are clearly influenced by the differences in tropospheric and stratospheric air masses at the given altitude. However, also in Fig. 7 there is only a very reduced impact of surface emissions or lifting patterns along the TP or the SASM visible, but the distribution looks basically as influenced by the tropopause distinguishing tropospheric and stratospheric air masses (comparable to a plot of potential vorticity).

Response:

Indeed there are large uncertainties with satellite data. As described in Sect. 3 of our manuscript, the MLS datasets provide HNO_3 and O_3 mixing ratios at vertical resolutions of 3–4 km and 2.5-3 km, respectively, in the UTLS region. The uncertainties of the MLS HNO_3 and O_3 datasets in the UTLS are about ±0.5-1 ppbv and 0.02-0.04 ppmv, respectively (Livesey et al., 2011). However, the UTLS datasets of MLS have been considered to be valuable and been used in previous studies to evaluate model results (Jin et al., 2009; Feng et al., 2011; Miyazaki et al., 2012; Brakebusch et al., 2013; Liu et al., 2013).

Concentrations of chemical species are determined by emissions, chemical production, chemical removal, transport, and deposition. Observational and modeling studies have shown that persistent maxima of CO, NO_x, CH_4, C_2H_6, OC, and BC exist in the UTLS over the TP/SASM region (Kar et al., 2004; Li et al., 2005; M. Park et al., 2004, 2008; Fadnavis et al., 2013), which are closely associated with the transport of air mass by deep convection during the Asian summer monsoon season (Chen et al., 2006; Randel and Park, 2006; Randel et al., 2010; Bian et al., 2011). In addition to the important role of transport, we are emphasizing in our work the role of chemical production during the vertical transport (Sect. 6), such as the gas-to-aerosol conversion of HNO_3 (the high relative humidity and low temperature associated with the deep convection over the TP/SASM region are favorable for nitrate formation).

3) The authors claim that vertical transport of nitrate (as it is the second most abundant aerosol compound in near surface air) is responsible for enhanced values in the UT. This cannot be true, as the vertical transport cannot change the ratios of sulphate to nitrate by transport alone; the transport algorithms usually transport all compounds in the same way.

Precipitation scavenging of aerosol species is controlled by their size and the hygroscopic properties of nitrate aerosols are so close to those of sulphate particles such that also cloud activation cannot play a role in altering the ratios of nitrate to sulphate either. Both gaseous HNO3 and H2SO4 are so soluble that in case of precipitation events, the concentrations would be equally reduced to almost zero. SO2 which is slightly less soluble might have a larger chance of reaching the UT without a complete scavenging, but as seen from previous studies UTLS sulphate mostly originates from COS and other long lived species.

Consequently, convective transport of nitrate has to be ruled out almost completely to lead to the enhanced nitrate concentrations, even though the authors attribute a substantial fraction to this process (see e.g. Fig.13). STE might offer an alternative pathway of HNO3 entering the UT from above, but

most likely the HNO3 is formed in situ by NOx chemistry or by the release of NOy from long lived, hardly soluble compounds such as PAN. However, chemical in situ production is missing completely in Fig.13 and the corresponding discussion.

Response:

We agree with the reviewer that the vertical transport alone cannot change the ratios of sulfate to nitrate. The change in the ratio of sulfate to nitrate during vertical transport is explained by that the chemical mechanisms for SO_4^{2-} and NO_3^- have different sensitivity to meteorological conditions (Sect. 6). During the vertical transport, temperature decreases, which reduces the gas-phase oxidation of SO_2 (Yao et al., 2002; Seinfeld and Pandis 2006) but promotes the formation of NO_3^- by shifting gas-particle equilibria (Dawson et al., 2007; Liao et al., 2009).

The wet deposition of both gas-phase species and aerosols are accounted for in the GEOS-Chem model. The aerosol wet deposition scheme has been implemented in the GEOS-Chem model following Liu et al. (2001). It accounts for scavenging in convective updrafts, rainout and washout from convective anvils and large-scale precipitation, and allows for return of chemical species to the atmosphere following evaporation. For the scavenging of aerosols, SO_4^{2-}, NO_3^-, NH_4^+, and hydrophilic OC and hydrophilic BC aerosols are assumed to be fully soluble. The model also includes soluble gases on the basis of their effective Henry's law partitioning in warm clouds, and surface coating or cocondensation of ice crystals in cold clouds (R. J. Park et al., 2004). As mentioned by the reviewer, precipitation scavenging of nitrate is close to that of sulfate, which should not be a factor to change ratio of sulfate to nitrate during vertical transport. Therefore again we conclude that the change in the ratio of sulfate to nitrate during vertical transport is explained by that the chemical mechanisms for SO_4^{2-} and NO_3^- have different sensitivity to temperature and relative humidity.

The STE, the formations of HNO_3 by NO_x chemistry, and the release of NO_y from long lived, hardly soluble compounds such as PAN are all considered in the GEOS-Chem. 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 (Liu et al., 2004; R. J. Park et al., 2004; Pye et al., 2009; Zhang et al., 2010; Tai et al., 2012; Jiang et al, 2013; Lou et al., 2014; Eastham, 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 HNO3 based on the ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes, 2007) in the GEOS-Chem model.

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.

Other points:

a) The comparison with ozone soundings does not really provide a good agreement (except for the general shape). Tropospheric O3 is substantially deviating (factor of 2) from the observations which on the given scale. Therefore, it is misleading that the agreement is good, at least not below 12 km altitude.

Response:

Compared to O_3 in the UTLS, O_3 in the lower troposphere is more sensitive to anthropogenic activities (Bian et al., 2012); various local emissions can result in the discrepancies between the observed and simulated O_3 mixing ratios in the lower troposphere. Besides, the mismatch of the sampling year may also contribute to the discrepancies between the observations and model results. We have clarified this in Sec. 3.2:"The comparisons with multi-year observations show that the model can reproduce the vertical distributions of O_3 above 12 km in Kunming and Lhasa."

b) The authors do not discuss whether the S(VI) is in from of sulphate or bisulphate (both close the surface and in the UT) and how the ammonium is distributed between S(VI) and nitrate.

Are other cations available (K+, Mg+, Ca2+)? What are their concentrations in the model simulations?

Response:

Whether S(VI) is in the form of sulphate or bisulphate is decided by the thermodynamics of the H_2SO_4–HNO_3–NH_3 aerosol system. The sulfate aerosols can be partly or totally neutralized by NH_3 and form ammonium sulfate or ammonium bisulfate depending on NH_3 concentrations. If excess NH_3 is available beyond that required for sulfate neutralization to ammonium sulfate, nitrate aerosol can form; otherwise, and except for cloudy conditions, HNO_3 remains in the gas phase (Seinfeld and Pandis, 2006). The H_2SO_4–HNO_3–NH_3 aerosol system is simulated by ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes, 2007) in the GEOS-Chem model (R. J. Park et al., 2004).

Figure C displays the latitude-altitude cross section of GR averaged over 70–105°E during June–August of year 2005. The positive GR ($\mathrm{TA} > 2\mathrm{TS}$) values indicate that sulfate aerosol can be totally neutralized by NH_3, and S(VI) is in the form of sulfate. The negative GR ($\mathrm{TA} < 2\mathrm{TS}$) values indicate that there is insufficient NH_3 to neutralize the available sulfate, and sulfate may exist as bisulfate (Seinfeld and Pandis, 2006). Over the TP/SASM region, GR is generally positive both at the surface and in the UTLS, especially over 20–40°N where deep convection exits (Fig. 11), indicating that S(VI) is in from of sulfate and free ammonia is available to react with nitrate. We have added these discussions in Sec. 7.

The formation of nitrate on mineral dust aerosol is not considered in the publicly released versions of the GEOS-Chem model, so K^+, Mg^{2+}, and Ca^{2+} are not available in the model.

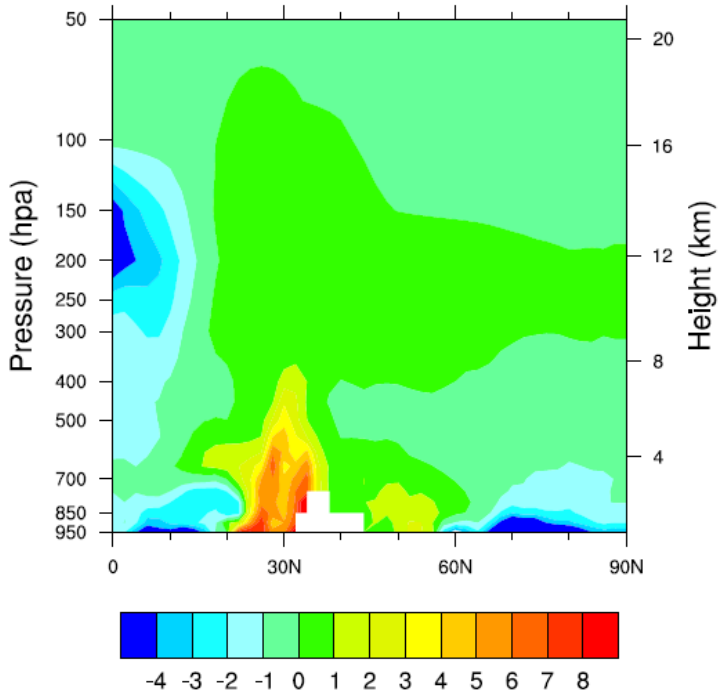

Figure C. The latitude-altitude cross section of GR averaged over 70–105°E during June–August of the year 2005. $\mathrm{GR} = \frac{\text{free ammonia}}{\text{total nitrate}} = \frac{\mathrm{TA}-2\times\mathrm{TS}}{\mathrm{TN}}$ (Ansari and Pandis, 1998), where $\mathrm{TA} = \mathrm{NH_3} + \mathrm{NH_4^+}$, $\mathrm{TS} = \mathrm{SO_4^{2-}}$, and $\mathrm{TN} = \mathrm{HNO_3} + \mathrm{NO_3^-}$.

c) Is there a reasonable correlation between enhanced nitrate and low

temperature together with high RH? The patterns of the two meteorological quantities are very smoothed out, such that this correlation (even though generally valid from a thermodynamically viewpoint) is not necessarily driving enhanced nitrate concentrations.

Response:

We agree with the reviewer that it's better to calculate the correlation coefficient between the enhanced nitrate and low temperature or high RH. However, large sample size is needed to obtain a stable correlation since the reliability of the correlation decreases with the sample size (http://www.r-bloggers.com/at-what-sample-size-do-correlations-stabilize/). To determine the effects of temperature and RH on summertime nitrate concentrations, at least decadal simulation is needed. For one-year simulation as described in the manuscript, it is difficult to quantify the effects of meteorological variables on nitrate concentrations by correlation coefficients or regression analysis.

Actually, the responses of nitrate concentrations to temperature and humidity have been analyzed by Dawson et al. (2007) using the Particulate Matter Comprehensive Air Quality Model with extensions (PMCAMx). The sensitivity test was performed by fixing all meteorological parameters but perturbing temperature or humidity in the simulation. Their sensitivity simulations showed that the increases in temperature led to increases in sulfate concentrations and decreases in nitrate concentrations. Compared to nitrate, sulfate concentrations showed smaller sensitivity to temperature changes (Dawson et al., 2007); as temperature increased, nitrate concentrations decreased by 19% K^{-1} and 17% K^{-1} in January and July respectively, while sulfate concentration increased by 0.12% K^{-1} and 1.3% K^{-1} in January and July, respectively. We have clarified this in the second paragraph of Sec. 6.1.

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Responses to Editor

Comments to the Author:

Dear authors,

After the first revision your manuscript has been improved significantly. However, there is still a large room for further improvement, in particular, the scientific quality of this study should further enhanced, as required by the referees. Please study the referee's comments carefully and address the issues raised. In addition, I have three minor technical comments:

Line 204: "...hydrophilic OC and BC aerosols are assumed ...". Did you assume BC is 100% hydrophilic? If not, how did you treat this issue?

Line 339: "BD" = "Brewer-Dobson"? There seems no previous definition. It is not suggested to use this abbreviation.

Line 1426: change "datasets" to "data

Sincerely,

Xiaobin Xu

Response:

We have addressed the issues suggested by the editor.

(1) Both BC and OC consist of hydrophilic and hydrophobic fractions in the model. It is assumed that 80% of BC and 50% of OC emitted from all primary sources are hydrophobic (Cooke et al., 1999; Chin et al., 2002; Chung and Seinfeld, 2002), which become hydrophilic with an e-folding time of 1.2 days following Cooke et al. (1999) and Chin et al. (2002). All secondary OC is assumed to be hydrophilic. Hydrophilic fractions of both BC and OC aerosols are assumed to be fully soluble.

(2) We have deleted the abbreviation of BD in the manuscript.

(3) Changed “datasets” to “data”..

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Summertime nitrate aerosol in the upper troposphere and lower stratosphere over the Tibetan Plateau and the South Asian summer monsoon region

Yixuan Gu[a,b], Hong Liao[c,*], and Jianchun Bian[d]

[a]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China.

[b]University of Chinese Academy of Sciences, Beijing, China

[c]School of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, China

[d]Key Laboratory of Middle Atmosphere and Global Environment Observation (LAGEO), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China.

*Corresponding author address:

Prof. Hong Liao

School of Environmental Science and Engineering

Nanjing University of Information Science & Technology

Nanjing 210044, China

E-mail: hongliao@nuist.edu.cn

Abstract

We use the global three-dimensional Goddard Earth Observing System chemical transport model (GEOS-Chem) to examine the contribution of nitrate aerosol to aerosol concentrations in the upper troposphere and lower stratosphere (UTLS) over the Tibetan Plateau and the South Asian summer monsoon (TP/SASM) region during summertime of year 2005. Simulated surface-layer aerosol concentrations are compared with ground-based observations, and simulated aerosols in the UTLS are evaluated by using the Stratospheric Aerosol and Gas Experiment II satellite data. Simulations show elevated aerosol concentrations of sulfate, nitrate, ammonium, black carbon, organic carbon, and $PM_{2.5}$ (particles with diameter equal or less than 2.5 μm, defined as the sum of sulfate, nitrate, ammonium, black carbon, and organic carbon aerosols in this study) in the UTLS over the TP/SASM region throughout the summer. 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. Averaged over summertime and over the TP/SASM region, C_{NIT} (the ratio of nitrate concentration to $PM_{2.5}$ concentration) values are 5–35% at the surface, 25–50% at 200 hPa, and could exceed 60% at 100 hPa. The mechanisms for the accumulation of nitrate in the UTLS over the TP/SASM region include vertical transport and the gas-to-aerosol conversion of HNO_3 to form nitrate. The high relative humidity and low temperature associated with the deep convection over the TP/SASM region are favorable for the gas-to-aerosol conversion of HNO_3.

1 Introduction

Aerosols in the upper troposphere and lower stratosphere (UTLS) have much longer residence times than those in the lower troposphere, influencing atmospheric chemistry and the Earth's climate with large spatial and temporal coverage (Rasch et al., 2008). Aerosols in the UTLS influence the concentrations of chemical species via changes in photolysis rates and heterogeneous reactions (Pitari et al., 2014). For example, heterogeneous reactions on sulfate aerosol can perturb the chemical partitioning in the lower stratosphere, leading to significant O_3 depletion through enhanced chlorine, bromine, and odd-hydrogen catalytic cycle (Zhao et al., 1997; Considine et al., 2001; Talukdar et al., 2012; Tang et al., 2014; Pitari et al., 2014). Aerosols in the UTLS also influence climate by altering properties of cirrus clouds via homogeneous or heterogeneous ice nucleation (Li et al., 2005; Liu et al., 2009; Yin et al., 2012; Fadnavis et al., 2013). Injection of aerosols into the UTLS has been reported to induce complex responses in circulation, temperature, and water vapor (Liu et al., 2009; Wu et al., 2011; Su et al., 2011; Fadnavis et al., 2013).

Aerosols over the Tibetan Plateau (TP) and the Asian summer monsoon region are especially important. The TP is surrounded by countries with large anthropogenic emissions (Li et al., 2005; Lau et al., 2006). Aerosols from India, Southeast Asia, and southern China can be transported to the TP by prevailing winds in the premonsoon and monsoon seasons (Lawrence and Lelieveld, 2010; Xia et al., 2011). Observational and modeling studies have shown that persistent maxima of atmospheric constituents, such as water vapor (Gettelman et al., 2004; Randel and Park, 2006; Park et al., 2007), CO (Kar et

al., 2004; Li et al., 2005; Park et al., 2007, 2008, 2009), CH_4 (M. Park et al., 2004; Xiong et al., 2009), NO_x (M. Park et al., 2004), HCN (Park et al., 2008; Randel et al., 2010), C_2H_6 and C_2H_2 (Park et al., 2008), exist in the UTLS above the TP and the South Asian summer monsoon (SASM) region because of the deep convection during boreal summer. Satellite observations suggested that the convection associated with the SASM is a vital pathway to transport air mass from the lower troposphere into the stratosphere (Chen et al., 2006; Randel and Park, 2006; Randel et al., 2010; Bian et al., 2011a). The heating associated with the persistent deep convection during summertime leads to the formation of the Tibetan anticyclone in the UTLS, which acts to isolate air within the anticyclone and traps the uplifted pollutants at that altitude (Park et al., 2007; Vernier et al., 2011; Bourgeois et al., 2012; Fadnavis et al., 2013; He et al., 2014). The stratosphere-troposphere exchange (STE) over the TP contributes largely to the global STE (Chen et al., 2006).

Previous studies have reported that aerosols exist in the UTLS over the TP/SASM region. Kim et al. (2003) carried out optical measurements with a ground-based lidar in Lhasa from August to October of 1999, and found an enhancement in aerosol concentration near the local tropopause with scattering ratio (SR, the ratio of aerosol plus molecular backscatter to molecular backscatter alone) of 1.1–1.2. Tobo et al. (2007) reported an enhancement of sub-micron aerosols (effective radius r = 0.15–0.6 μm) near the summertime tropopause (about 130 to 70 hPa), on the basis of in situ balloon measurements from an Optical Particle Counter at the same location in August of 1999. Vernier et al. (2009) examined satellite measurements from the Cloud-Aerosol Lidar with Orthogonal Polarization (CALIOP) onboard

Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) and reported the presence of small depolarizing particles with high SR values (about 1.20 at 532 nm) at 16–17 km altitude over South Asia in July and August of 2007 and 2008. Bourgeois et al. (2012) found that an aerosol layer existed at 16–18 km altitude over the Asian continent and Indian Ocean (20°S–30°N, 5–105°E) on the basis of the CALIOP observations. Recently, He et al. (2014) examined the vertical profiles of aerosol extinction coefficients measured with a Micro Pulse Lidar at Naqu, a meteorological station located in the central part of the TP, and also showed a maximum in aerosol extinction coefficient (~2.10^{-3} km^{-1}) in the UTLS (18–19 km) during the summer of 2011.

A number of previous studies have attempted to understand the chemical composition of aerosols in the UTLS. Froyd et al. (2009) measured aerosol composition with the National Oceanic and Atmospheric Administration (NOAA) single-particle mass spectrometer aboard the National Aeronautics and Space Administration (NASA) WB-57 high altitude aircraft platform, and reported that particles in the tropical tropopause layer were rich in nitrogen. Vernier et al. (2011) suggested that aerosol layer at the tropopause of Asia could be sulfur and/or organics, considering that Asian pollutants consisted of black carbon, organic carbon, SO_2, and NO_x (Park et al., 2009; Randel et al., 2010). Weigel et al. (2011) analyzed the volatility of aerosols obtained from in situ airborne measurements and reported that about 75–90 % of the particles in the tropical tropopause layer were volatile, but this study did not give any detailed analyses of chemical composition of aerosols. Bourgeois et al. (2012) showed, by using the ECHAM5.5-HAM2 model, that sulfate, water, and OC contributed, respectively, 53%, 29%, and 11% to aerosol extinction in the vicinity of the

tropical tropopause layer. The ECHAM5.5-HAM2 model used by Bourgeois et al. (2012) simulated all major aerosol species in the atmosphere except for nitrate.

Few previous studies have examined nitrate aerosol in the UTLS, although nitrate is expected to be important for the following reasons. First, emissions of precursors of nitrate, such as NO_x and NH_3, are high over India, Southeast Asia, and China (Streets et al., 2003; Datta et al., 2012; Huang et al., 2012). Second, simulated nitrate concentrations are high over those regions (Liao and Seinfeld, 2005; Mu and Liao, 2014; Lou et al., 2014). Third, measured concentrations of nitrate are comparable to or larger than those of sulfate at rural and urban sites in the SASM region. Shrestha et al. (2000) carried out measurements of aerosols at Phortse, Nepal, during September 1996–November 1997, and showed that the average concentration of nitrate during the monsoon season (June-September) was 0.34 μg m^{-3}, higher than that of sulfate (0.17 μg m^{-3}). Decesari et al. (2010) reported, on the basis of measurements at the Nepal Climate Observatory-Pyramid from 2006 to 2008, that the concentrations of nitrate and sulfate were 0.37 μg m^{-3} and 0.50 μg m^{-3}, respectively, during the monsoon season. Chatterjee et al. (2010) measured aerosols at a high altitude station in northeastern Himalayas during January-December 2005. They found that the average concentrations of fine-mode nitrate and sulfate were 3.31±2.25 μg m^{-3} and 3.80±2.9 μg m^{-3}, respectively. At Lahore, an urban site in Pakistan, the observed daytime nitrate concentration of 21.8 μg m^{-3} was also higher than sulfate concentration of 12.6 μg m^{-3} (Lodhi et al., 2009), as the observations were averaged over November 2005 to March 2006. Fourth, the low temperatures in the UTLS would favor

nitrate formation (Seinfeld and Pandis, 2006). Therefore, it is of interest to take nitrate aerosol into consideration when we examine aerosols in the UTLS.

In this work we simulate nitrate aerosol and its contribution to aerosol concentrations in the UTLS over the TP (70–105°E, 25–40°N) and the SASM region (70–105°E, 10–25°N) by using the global chemical transport model GEOS-Chem driven by the assimilated meteorological fields. These regions of interest are shown in Fig. 1. Simulated surface-layer aerosol concentrations are compared with ground-based observations, and simulated aerosols in the UTLS are evaluated by using the Stratospheric Aerosol and Gas Experiment II (SAGE II) satellite data. Section 2 is a brief description of the GEOS-Chem model and numerical experiment. Section 3 presents the simulation and evaluation of distributions and concentrations of HNO_3 and O_3 to show model's capability in simulating the NO_x-O_3-HNO_3 cycle over the studied regions. Section 4 shows simulated aerosols and Section 5 presents the simulated contribution of nitrate to aerosol concentrations in the UTLS over the TP and the SASM region. Section 6 discusses the mechanisms for high concentrations of nitrate in the UTLS. Section 7 discusses the impacts of uncertainties in surface-layer aerosol concentrations on simulated nitrate in the UTLS.

2 Model description and numerical experiment

2.1 GEOS-Chem model

We simulate gas-phase species and aerosols using the global chemical transport model GEOS-Chem (version 9-01-03, http://acmg.seas.harvard.edu/geos/index.html) driven by the GEOS-5 assimilated meteorological fields from the Goddard Earth Observing System of

174 the NASA Global Modeling and Assimilation Office. The version of the model
175 used here has a horizontal resolution of 2° latitude by 2.5° longitude and 47
176 vertical layers extending from the surface to 0.01 hPa. Over the TP and the
177 SASM region, the model has about 34 layers in the troposphere and 12 layers
178 in the stratosphere.

179 The GEOS-Chem model has a fully coupled treatment of tropospheric
180 NO_x-CO-hydrocarbon-aerosol chemistry and aerosols including sulfate (SO_4^{2-}),
181 nitrate (NO_3^-), ammonium (NH_4^+), organic carbon (OC), black carbon (BC) (R. J.
182 Park et al., 2003; 2004; Pye et al., 2009), mineral dust (Fairlie et al., 2007), and
183 sea salt (Alexander et al., 2005; Jaeglé et al., 2011). Anthropogenic aerosols
184 are treated as bulk mass concentrations (particles of SO_4^{2-}, NO_3^-, NH_4^+, BC,
185 and OC are not size-resolved). Sea Salt mass is simulated for two size bins
186 (0.1–0.5 and 0.5–8 μm) and mineral dust is simulated for four size bins
187 (0.1–1.0, 1.0–1.8, 1.8–3.0, and 3.0–6.0 μm). Both BC and OC consist of
188 hydrophilic and hydrophobic fractions in the model. It is assumed that 80% of
189 BC and 50% of OC emitted from all primary sources are hydrophobic (Cooke
190 et al., 1999; Chin et al., 2002; Chung and Seinfeld, 2002), which become
191 hydrophilic with an e-folding time of 1.2 days following Cooke et al. (1999) and
192 Chin et al. (2002). All secondary OC is assumed to be hydrophilic. Hydrophilic
193 fractions of both BC and OC aerosols are assumed to be fully soluble.

194 The gas-aerosol partitioning of nitric acid and ammonium is calculated
195 using the ISORROPIA II thermodynamic equilibrium module (Fountoukis and
196 Nenes, 2007). In the version of the GEOS-Chem model used in this work, irons
197 considered in ISOROPIA II include $H^+/Na^+/NH_4^+/Cl^-/SO_4^{2-}/HSO_4^-/NO_3^-/OH^-$. The
198 two-way coupling between aerosols and gas phase chemistry provides

consistent chemical fields for aerosol simulation and aerosol mass for heterogeneous processes and calculations of gas-phase photolysis rates. Heterogeneous reactions include hydrolysis of N_2O_5 (Evans and Jacob, 2005), irreversible absorption of NO_3 and NO_2 on wet aerosols (Jacob, 2000), and the uptake of HO_2 by aerosols (Liao and Seinfeld, 2005; Thornton et al., 2008). Aerosol species are treated as an external mixture in the calculation of aerosol optical properties.

With respect to chemistry in the stratosphere, stratospheric O_3 concentrations are calculated using the linearized parameterization scheme (McLinden et al., 2000). The monthly mean production rates and loss frequencies of other stratospheric species (including long-lived species such as CFCs and N_2O) use those from NASA Global Modeling Initiative (GMI) Combo simulations (Duncan et al., 2007; Considine et al., 2008; Murray et al., 2012).

Convective transport in GEOS-Chem mimics that in the parent GEOS general circulation model (GCM) (Hack, 1994; Zhang and McFarlane, 1995), which accounts for updraft, downdraft, and entrainment mass fluxes for deep and shallow convection (Wu et al., 2007). The aerosol wet deposition scheme in the GEOS-Chem follows that of Liu et al. (2001). For the scavenging of aerosols, SO_4^{2-}, NO_3^-, NH_4^+, and hydrophilic OC and hydrophilic BC aerosols are assumed to be fully soluble. Dry deposition follows the standard resistance-in-series model of Wesely (1989).

Global emissions of aerosols and their precursors in the GEOS-Chem follow R. J. Park et al. (2003, 2004), with anthropogenic emissions of NO_x, CO, SO_2, and non-methane volatile organic compounds (NMVOC) in Asia

224 overwritten by David Streets' 2006 emission inventory
225 (http://mic.greenresource.cn/intex-b2006). Emissions of NH_3 in Asia are taken
226 from Streets et al. (2003). Since NH_3 emissions in China showed large
227 uncertainties in previous studies (Streets et al., 2003; Kim et al., 2006; Y.
228 Zhang et al., 2010; Huang et al., 2011, 2012), we use the most recent estimate
229 of NH_3 emissions in China by Huang et al. (2012), which is 9.8 Tg yr^{-1}, instead
230 of 13.5 Tg yr^{-1} from Streets et al. (2003). Table 1 summarizes the annual
231 emissions of NO_x, SO_2, NH_3, OC, and BC in Asia domain (60–155°E,
232 10–55°N).

233 Natural NO_x emissions from lightning are calculated using the scheme
234 described by Sauvage et al. (2007) and Murray et al. (2012), and those from
235 soil are simulated following Wang et al. (1998). Natural NH_3 emissions from
236 soil, vegetation, and the oceans are taken from the Global Emissions Inventory
237 Activity inventory (Bouwman et al., 1997). Biomass burning emissions are from
238 the monthly Global Fire Emissions Database (GFED v3) driven by satellite
239 observations of fire activity (van der Werf et al., 2010). Biogenic VOC (volatile
240 organic compounds) emissions are calculated from the Model of Emissions of
241 Gases and Aerosols from Nature (Guenther et al., 2006).

242 The monthly variations of emissions of SO_2 and NO_x follow Wang et al.
243 (2013) and those of BC and OC follow Lou et al. (2014). The monthly scaling
244 factors for NH_3 emissions follow the global inventory compiled by Marcel
245 Meinders and Lex Bouwman (Fisher et al., 2011). Monthly variations of
246 emissions (anthropogenic plus natural emissions) of NO_x SO_2, NH_3, OC, and
247 BC over Asia are displayed in Fig. 2. The emissions of NH_3 are the highest in
248 June as a result of the agriculture practice and high temperatures (Wang et al.,

2013).

2.2 Numerical experiment

To examine the contribution of nitrate to aerosol concentrations in the UTLS over the TP/SASM region, we simulate aerosol concentrations by using the emissions of and meteorological fields of year 2005. Year 2005 is chosen so that we can use the observational datasets for this year from SAGE II and MLS, as described in Sects. 3 and 4. Following Rasch et al. (2008), we perform a 10-year spin-up run to generate the initial conditions (to allow the stratospheric species to reach quasi-steady state conditions). We would consider that the tropospheric simulation can be representative of year 2005 but stratosphere simulation should represent a multi-year average, because the production rates and loss frequencies in the stratosphere are the averages over years of 2004–2010 (http://wiki.seas.harvard.edu/geos-chem/index.php/ Stratospheric_ chemistry).

3 Simulated concentrations of HNO_3 and O_3 and model evaluation

Nitrate aerosol forms when nitric acid (HNO_3) reacts with alkaline gases (for example, ammonia) in the atmosphere (Seinfeld and Pandis, 2006). HNO_3, as the important precursor of nitrate, is the major oxidation product of nitrogen oxides (NO_x = NO+NO_2) (Seinfeld and Pandis, 2006). To show the model's capability in simulating the NO_x-O_3-HNO_3 cycle over the studied regions, we present and evaluate the simulated HNO_3 and O_3 in this section.

Simulated mixing ratios of HNO_3 and O_3 in the UTLS are evaluated by using datasets from the limb viewing satellite instrument of Microwave Limb Sounder (MLS, version 3.3, level 2,

ftp://acdisc.gsfc.nasa.gov/data/s4pa///Aura_MLS_Level2/). The MLS datasets provide valuable information on atmospheric compositions in the UTLS (Waters et al., 2006). For HNO_3, the MLS provides datasets for 215 to 1.5 hPa, with a vertical resolution of 3–4 km and a horizontal resolution of 400–500 km. Since further evaluations are needed for datasets at altitudes with pressures higher than 215 hPa (Livesey et al., 2011), we use only datasets for pressures lower than that. For O_3, the MLS provides datasets for 261 to 0.02 hPa, with a vertical resolution of 2.5–3 km and a horizontal resolution of 300–400 km in the UTLS (Santee et al., 2007; Livesey et al., 2011). The uncertainties of the MLS HNO_3 and O_3 datasets in the UTLS are about ±0.5–1 ppbv and 0.02–0.04 ppmv, respectively (Livesey et al., 2011).

3.1 HNO_3

Figure 3(a) shows the simulated global distribution of HNO_3 concentrations averaged over June-August of 2005. 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). Over South Asia, simulated HNO_3 concentrations are high (0.3–1 ppbv) in the northern Indian subcontinent, because the emissions of NO_x and NH_3 are high in this region (Streets et al., 2003; Zhang et al., 2009; Datta et al., 2012).

Figures 4(a)-4(b) show the simulated HNO_3 concentrations in the UTLS averaged over June-August of 2005. Since the tropopause is located at 70–150 hPa (12–15 km) over the TP/SASM region (Li et al., 2005; Bian et al., 2011b; Fadnavis et al., 2014), we choose the vertical layers of 200 hPa and 100 hPa to represent the UTLS. At both 200 hPa and 100 hPa, the highest

299 HNO_3 concentrations are simulated to occur in the high latitude regions in the
300 Northern Hemisphere (NH) (Fig. 4(a) and Fig. 4(b)). Simulated HNO_3
301 concentrations at 100 hPa are low over the region of 40–100°E and 10–30°N,
302 which is part of the anticyclone region defined in Fig. 1. Figure 4(c) shows the
303 latitude-altitude cross section of simulated seasonal mean HNO_3 mixing ratios
304 averaged over 70–105°E. In boreal summer, the highest HNO_3 mixing ratios
305 are simulated to occur at 30 hPa over the Polar Regions in both hemispheres.
306 Over high latitudes, HNO_3 concentrations in the Southern Hemisphere (SH)
307 are simulated to be higher than those in the NH.

308 To evaluate the simulated HNO_3, Figures 4(d)-4(f) show HNO_3
309 concentrations in the UTLS from MLS that are averaged over June-August of
310 2005. At 200 and 100 hPa altitudes, the observed HNO_3 mixing ratios are high
311 in the high latitudes in the NH, which are captured by the GEOS-Chem model.
312 The observed HNO_3 at 100 hPa exhibits low values of less than 400 pptv over
313 30–100°E and 10–30°N in the Asian monsoon anticyclone region (Fig. 4(e)). At
314 100 hPa, the observed HNO_3 mixing ratio averaged over the TP/SASM region
315 (70–105°E, 10–40°N) is 301.3 pptv, which is lower than the simulated value of
316 349.1 pptv. The difference between the simulated and observed HNO_3 mixing
317 ratio lies within the confidence range of ±500–1000 pptv of the MLS
318 instruments (Livesey et al., 2011). Considering all the grid cells with MLS
319 HNO_3 data available, the simulated seasonal mean HNO_3 concentrations show
320 normalized mean bias (NMB) of +15.9% at 100 hPa over the TP/SASM region
321 in summer of year 2005. The observed pattern of the HNO_3 vertical distribution
322 (Fig. 4(f)) is also captured by the GEOS-Chem model (Fig. 4(c)). The
323 distributions of HNO_3 in the UTLS are associated with the Brewer-Dobson

circulation proposed by Brewer (1949) and Dobson (1956), traveling upwards across the tropopause to the stratosphere at the equator and downwards to the troposphere near the Polar region.

3.2 O_3

Figure 3(b) shows the global distribution of simulated summertime surface-layer O_3 concentrations. Simulated O_3 concentrations are in a range of 40–70 ppbv over Europe, North America, China, and the biomass burning region of South Africa. Our model results agree closely with the simulated distributions and magnitudes reported in Mickley et al. (1999), Collins et al., (2000), Liao et al. (2003), Wu et al., (2008), Zeng et al. (2008), and Fadnavis et al. (2014). Fadnavis et al. (2014) also presented aircraft measurements over India in September of 2010 during the Cloud Aerosol Interaction and Precipitation Enhancement Experiment (CAIPEEX). Our simulated O_3 concentrations of 30–40 ppbv over India agree with the CAIPEEX measurements.

Figures 5(a)-5(b) show the simulated O_3 concentrations in the UTLS averaged over June-August of 2005. The distributions of O_3 concentrations in the UTLS are similar to those of HNO_3, with elevated values in the high latitudes of the NH. Relatively low O_3 mixing ratios of less than 200 ppbv are simulated at 100 hPa over 10–30°N, 20–110°E, within the anticyclone region defined in Fig. 1. Our simulated distributions and magnitudes of O_3 agree with those reported in Bian et al. (2011b), which examined the summertime distributions of O_3 in the UTLS during 2005–2009 by using the MLS version 2.2 level 2 products (Livesey et al., 2008). Because the background O_3 concentrations are generally high in the UTLS and the stratosphere, the low O_3

concentrations in the UTLS over the TP/SASM region are caused by the deep convection that transports O_3-poor air upward (Fu et al., 2006; Randel and Park, 2006; Park et al., 2007; Bian et al., 2011b). Figure 5(c) displays the latitude-altitude cross section of seasonal mean O_3 mixing ratios averaged over 70–105°E. As a result of the Brewer-Dobson circulation, O_3 concentrations in the UTLS are lower over the tropics than in the Polar Regions, even though the maximum O_3 concentrations are located around 10 hPa over the tropics (Brewer, 1949). Our simulated O_3 concentrations in the UTLS agree well with the measurements from MLS (Fig. 5(d)-5(f)). 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. Our simulated global STE of O_3 is 420 Tg yr^{-1}, which is within the range reported in previous studies (475±120 Tg yr^{-1} in McLinden et al. (2000), 420 Tg yr^{-1} in Škerlak et al. (2014), 556±154 Tg yr^{-1} in Stevenson et al. (2006), and 550±140 Tg yr^{-1} in Solomon et al. (2007)).

In addition to the comparisons against MLS products, the simulated O_3 profiles are compared with balloon-borne sonde measurements in Fig. 6. The measurements were carried out at Kunming (KM, 102.7°E, 25.0°N) in August of 2009 and 2012, and at Lhasa (LH, 91.1°E, 29.7°N) in August of 2010 and 2013. The uncertainties of the observed O_3 mixing ratios were estimated to be within 5–10% (Bian et al. 2012). The comparisons with multi-year observations show that the model can reproduce the vertical distributions of O_3 above 12 km in Kunming and Lhasa. At 100 hPa, the simulated monthly mean O_3 mixing

ratio in KM is 112.6 ppbv, and the observed value is 124.2 ppbv in 2009 and 113.5 ppbv in 2012. In LH, the simulated monthly O_3 mixing ratio at 100 hPa is 152.6 ppbv, and the observed O_3 mixing ratio at that altitude is 142.4 ppbv in 2010 and 167.9 ppbv in 2013. The magnitudes of O_3 mixing ratios from these balloon-borne sonde measurements support those from MLS; O_3 mixing ratios in the UTLS are less than 200 ppbv over the TP/SASM region.

4 Simulated aerosols and model evaluation

4.1 Simulated aerosols

Figure 7 (a) shows the simulated surface-layer concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC, BC, and $PM_{2.5}$ (the sum of the mass of SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC aerosols) averaged over June-August of year 2005. As expected, simulated aerosol concentrations are high over polluted regions such as India and eastern China as a result of the high anthropogenic emissions of aerosol precursors and aerosols (Streets et al., 2003; Huang et al., 2012). Over the TP/SASM region (70–105°E, 10–40°N), the average concentrations of SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC are 1.70, 0.94, 0.85, 0.30, and 0.94 μg m^{-3}, respectively. NO_3^- is simulated to be of secondary importance at the surface over the region of our interest. The simulated distributions and magnitudes of these aerosol species are similar to those reported in Wang et al. (2013) and Mu and Liao (2014).

Figures 7(b) and 7(c) also show the simulated concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC, BC, and $PM_{2.5}$ in the UTLS. Elevated concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC, BC and $PM_{2.5}$ are simulated over the TP and Plateau south slope at 200 hPa altitude, and extend from eastern Mediterranean to western

China at 100 hPa. The simulated enhanced concentrations of SO_4^{2-}, OC, and BC at 100 hPa over the anticyclone region (20–120°E, 10–40°N) agree with previous observational and modeling studies (Lelieveld et al., 2001; Li et al., 2005; Fadnavis et al., 2013). Li et al. (2005) reported elevated CO concentrations in the upper troposphere over the TP, on the basis of both MLS measurements and the GEOS-Chem simulation for September 2004. Fadnavis et al. (2013) also simulated maximum concentrations of SO_4^{2-}, OC, BC, and mineral dust aerosols in the UTLS during the Asian summer monsoon season owing to convective uplifting of the boundary layer pollutants. With NO_3^- aerosol accounted for in our simulation, NO_3^- is simulated to be the most dominant aerosol species in the UTLS over the TP/SASM region, followed by SO_4^{2-}, NH_4^+, OC, and BC. At 100 hPa, the averaged concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC, and BC over the TP/SASM region (70–105°E, 10–40°N) region are 0.026, 0.069, 0.014, 0.011, and 0.002 μg m^{-3}, respectively.

4.2 Comparisons of simulated aerosol concentrations with in-situ observations

The simulated aerosol concentrations in East Asia in the GEOS-Chem model have been evaluated in previous studies (L. Zhang et al., 2010; Fu et al., 2012; Jeong and Park, 2013; Jiang et al., 2013; Wang et al., 2013; Lou et al., 2014). Here we are focused on the evaluation of aerosols in the South Asian monsoon region. For lack of publicly accessible in situ measurements of summertime aerosols in South Asia monsoon area, we compiled monthly or seasonal mean measured concentrations of each aerosol species based on measurements reported in the literature (see Table S1 in the Supplementary Material). These measurements were carried out over years of 1992–2010.

The locations of sites with measurements available are shown in Fig. 8(a). Most sites are located in the upwind directions of the TP, with pollutants that can be transported to the UTLS during the South Asian summer monsoon season. The observed PM_{10} concentrations listed in Table S1 are multiplied by 0.6 to convert to $PM_{2.5}$ for model evaluation, following the suggestions in Zhang et al. (2002) and Chatterjee et al. (2010).

Figures 8(b)–8(f) show the scatterplots of simulated versus observed seasonal mean aerosol concentrations. Compared with measurements, simulated SO_4^{2-}, NO_3^-, NH_4^+, OC and BC have NMBs of –17.0%, +38.8%, +42.0%, –69.7% and –41.0%, respectively, as the concentrations of all seasons are considered. The correlations between model results and observations have *R* values of 0.49–0.85 for all aerosol species, indicating that the model is capable of capturing the spatial distributions and seasonal variations of each aerosol species in the South Asian monsoon region despite the biases in concentrations. If we consider simulated and measured concentrations for JJA alone, the simulated concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC and BC exhibit seasonal NMBs of –14.7%, +51.5%, +74.9%, –57.2% and –32.2%, respectively, and the values of *R* are in the range of 0.24–0.85. Note that the measurements of NO_3^- and NH_4^+ are quite limited in terms of the number of samples, and the discrepancies between model results and measurements may also arise from the mismatch of the model year 2005 with the years of 1992–2010 with observations available.

4.3 Comparisons of simulated aerosol extinction coefficients with SAGE II datasets

Satellite datasets from the Stratospheric Aerosol and Gas Experiment II

449 (SAGE II, https://eosweb.larc.nasa.gov/project/sage2/sage2_v620_table) are
450 used to evaluate the simulated aerosol extinction in the UTLS. The SAGE II
451 instrument was launched in October 1984 aboard the Earth Radiation Budget
452 Satellite (ERBS) and terminated on 8 September 2005 (McCormick et al. 1987;
453 Chu et al. 1989). The datasets used here are aerosol extinction coefficients at
454 525 nm from the version 6.20 SAGE retrievals, covering from 0.5 to 40 km with
455 a vertical resolution of 0.5 km. Many validation studies have been conducted
456 on the SAGE II aerosol data (Russell and McCormick, 1989; Oberbeck et al.,
457 1989; Wang et al., 1989), which indicated that extinction coefficients have
458 uncertainties of 20–30%. The extinction coefficients of aerosols in the
459 GEOS-Chem model are calculated using aerosol mass concentration,
460 extinction efficiency, effective radius, particle mass density, and the assumed
461 aerosol size distribution (Drury et al., 2010). The hygroscopic growth of each
462 aerosol species with relative humidity is accounted for, using the hygroscopic
463 growth factors listed in Martin et al. (2003).

464 Figure 9(a) presents the simulated monthly mean distribution of aerosol
465 extinction coefficients at 100 hPa for July of 2005. At 100 hPa, the simulated
466 aerosol extinction coefficients are relatively high over the anticyclone region,
467 where anthropogenic aerosol species (Fig. 7) and natural aerosols such as
468 mineral dust and sea salt contribute to aerosol extinction coefficients in
469 summer. Note that the contributions of sulfate, nitrate, ammonium, OC, sea
470 salt, and mineral dust are all considered when we calculate aerosol extinction
471 coefficients. Aerosol extinction coefficients are simulated to be $1.2–2\times10^{-3}$
472 km^{-1} at 100 hPa over the Asian continent and Indian Ocean (20°S–30°N,
473 30°–105°E). These values agree closely with aerosol extinction coefficients

474 measured at Naqu during August of 2011 for the same altitude, the maximum
475 of which was 2.4×10^{-3} km^{-1} (He et al., 2014). Vernier et al. (2011) also
476 identified this Asian aerosol layer with high SR at 100 hPa by observations of
477 CALIPSO for JJA of 2006–2008.

478 Figure 9(b) displays the monthly mean vertical profiles of aerosol extinction
479 coefficients averaged over the Asian monsoon anticyclone region (20–120°E
480 10–40°N) (Fig. 1) for July of 2005. The SAGE II datasets are available for July
481 only in 2005. The profiles from SAGE II and the GEOS-Chem simulation are all
482 shown. The vertical distributions of aerosol extinction coefficients “with nitrate”
483 and “without nitrate” are both from the baseline run with full chemistry. The
484 vertical distribution of aerosol extinction coefficient “with nitrate” (or “without
485 nitrate”) indicates that the contribution of nitrate aerosol to aerosol extinction is
486 (or is not) accounted for. Accounting for all aerosol species, the GEOS-Chem
487 model reproduces well the aerosol extinction coefficients above 10 km, but the
488 discrepancies are rather large in altitudes less than 10 km. Note that the
489 uncertainties in satellite datasets increase as the altitude decreases
490 (Vanhellemont et al., 2008；Kulkarni and Ramachandran, 2015), and the
491 missing data in the lower troposphere along the satellite trajectories over the
492 region of our interest also contribute to the discrepancies

493 Comparisons of profiles of aerosol extinction coefficients with and without
494 nitrate aerosol indicate that the profiles show small differences in altitudes less
495 than 6 km but large discrepancies from 6 km to the tropopause. With nitrate
496 aerosol accounted for, the simulated aerosol extinction coefficients agree
497 closely with SAGE II datasets in the UTLS (averaged over 14–16 km, the
498 simulated value is 8.6×10^{-4} km^{-1} while the observed value is 8.0×10^{-4} km^{-1}).

499 Without nitrate aerosol, the simulated aerosol extinction coefficient at 14–16
500 km altitude is 1.5×10^{-4} km^{-1}, which underestimates the aerosol extinction
501 coefficient by 82.6% compared to that calculated with all the aerosol species.
502 These comparisons of extinction coefficients with and without nitrate aerosol
503 suggest that nitrate aerosol plays an important role in aerosol extinction in the
504 UTLS over the region of our interest.
505
506 **5 Contribution of nitrate to aerosol concentrations in the UTLS**
507 Since nitrate aerosol is simulated to be the most abundant aerosol species in
508 the UTLS over the TP/SASM region, we analyze the contribution of nitrate to
509 $PM_{2.5}$ concentration (C_{NIT}=nitrate concentration/$PM_{2.5}$ concentration) in this
510 section. Figure 10 shows the simulated seasonal mean distributions of C_{NIT} for
511 June-August of year 2005. At the surface layer (Fig. 10(a)), simulated high C_{NIT}
512 values are located over the areas with high nitrate concentrations (India and
513 eastern China) as well as the oceans where NO_3^- also forms on sea salt and
514 mineral dust particles (Arimoto et al., 1996; Nakamura et al., 2005; George and
515 Nair, 2008). Over the TP/SASM region, the C_{NIT} values in JJA are 5–35% at the
516 surface, 25–50% at 200 hPa (Fig. 10(b)), and could exceed 60% at 100 hPa
517 (Fig. 10(c)). The latitude-altitude cross section of C_{NIT} (Fig. 10(d)) shows that
518 C_{NIT} over 20–40°N increases with altitude and reaches maximum values
519 around the extratropical tropopause.
520 Table 2 lists the mean concentrations of SO_4^{2-}, NO_3^-, NH_4^+, BC and OC, and
521 their contributions to $PM_{2.5}$ during summertime of 2005 over the TP/SASM, TP,
522 and SASM regions. Over the TP/SASM region, SO_4^{2-}, NO_3^-, NH_4^+, BC and OC
523 are simulated to contribute 35.9%, 19.8%, 18.1%, 6.4%, and 19.8%,

524 respectively, to $PM_{2.5}$ mass concentration at the surface layer. The
525 contributions increase significantly in the UTLS. The largest C_{NIT} is simulated
526 in the SASM region at 100 hPa, where NO_3^- accounts for 60.5% of $PM_{2.5}$ mass
527 concentration. The high C_{NIT} values indicate that NO_3^- plays an important role
528 in the aerosol layer in the UTLS over the TP/SASM region.
529 Considering the large uncertainties in simulated sea salt (Jaeglé et al.,
530 2011) and mineral dust (Fairlie et al., 2007) aerosols, we tend to be focused on
531 anthropogenic aerosol species (SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC) in this work. In
532 our model, concentrations of sea salt (or mineral dust) are simulated to be
533 1.0–1.7 ng m^{-3} (or 5.0–7.0 ng m^{-3}) over the studied region in the summer of
534 2005, which contribute less than 1.2% (or 5.0%) to total aerosol mass at 100
535 hPa. Therefore the consideration of sea salt and mineral dust can slightly
536 reduce C_{NIT} values, but C_{NIT} values at 100 hPa are still as high as 45-65% over
537 the TP/SASM region in summer.
538
539 **6 Mechanisms for high nitrate concentrations in the UTLS**
540 **6.1 Upward transport of nitrate from the lower troposphere**
541 The intense convective transport of chemical species into the UTLS over the
542 TP/SASM region during summertime has been widely discussed in previous
543 studies (Randel et al., 2010; Bian et al., 2011a; Fadnavis et al., 2013, 2014;
544 Qie et al., 2014; He et al., 2014). Since nitrate aerosol is simulated to be of
545 secondary abundant aerosol species in the surface layer over the TP/SASM
546 region (Fig. 7), the vertical mass transport through the deep convection in this
547 region contributes to the accumulation of NO_3^- in the UTLS. Figure 11 shows
548 the latitude-altitude cross sections of simulated concentrations of SO_4^{2-} and

549 NO_3^- averaged over 70–105°E in June-August of 2005, together with the
550 wind vectors obtained from the European Centre for Medium-Range Weather
551 Forecasts (ECMWF) ERA-Interim Reanalysis data. Note that the assimilated
552 GEOS-5 meteorological fields do not have vertical winds
553 (http://wiki.seas.harvard.edu/geos-chem/index.php/List_of_GEOS-5_met_field
554 s), so we use the ECMWF reanalysis wind fields to do the analysis here. High
555 values of aerosol concentrations are found on the south slope of the
556 Himalayas, where the deep convection exists. Although both SO_4^{2-} and NO_3^-
557 are transported upward to the extratropical tropopause, the details of the
558 vertical distributions are different. At altitudes higher than 8 km, the
559 concentrations of NO_3^- do not decrease with altitude as quickly as those of
560 SO_4^{2-}, and the concentrations of NO_3^- over 10–40°N are higher than those of
561 SO_4^{2-}.

562 The chemical mechanisms for the formation of SO_4^{2-}, NO_3^-, and NH_4^+
563 aerosols in the GEOS-Chem model were described in R. J. Park et al. (2004),
564 which are comprehensive and have been used extensively in previous studies
565 to simulate these three aerosol species (R. J. Park et al., 2004; Pye et al.,
566 2009; L. Zhang et al., 2010; Zhu et al., 2012; Jiang et al., 2013; Lou et al.,
567 2014). Sulfate aerosol forms from gas-phase oxidation of SO_2 by OH and from
568 in-cloud oxidation of SO_2 by O_3 and H_2O_2. Nitrate forms from the partitioning of
569 HNO_3 between gas and aerosol phases, which is calculated by the
570 ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes,
571 2007) in the GEOS-Chem model. Major reactions for the production and loss
572 of HNO_3 were listed in Liao and Seinfeld (2005). HNO_3 is produced by the
573 reaction of NO_2 with OH during daytime and by hydrolysis of N_2O_5 on aerosol

surfaces at night. The chemical mechanisms for SO_4^{2-} and NO_3^- have different sensitivity to meteorological conditions. During the vertical transport, temperature decreases, which reduces the gas-phase oxidation of SO_2 (Yao et al., 2002; Seinfeld and Pandis 2006) but promotes the formation of NO_3^- by shifting gas-particle equilibria (Dawson et al., 2007; Liao et al., 2009). Dawson et al. (2007) examined the sensitivities of sulfate and nitrate concentrations to temperature by using the Particulate Matter Comprehensive Air Quality Model with extensions (PMCAMx). The sensitivity test was performed by fixing all meteorological parameters but perturbing temperature. Their sensitivity simulations showed that the increases in temperature led to increases in sulfate concentrations and decreases in nitrate concentrations. Compared to nitrate, sulfate concentrations showed smaller sensitivity to temperature changes (Dawson et al., 2007); as temperature increased, nitrate concentrations decreased by 19% K^{-1} and 17% K^{-1} in January and July respectively, while sulfate concentration increased by 0.12% K^{-1} and 1.3% K^{-1} in January and July, respectively. Therefore the different chemical mechanisms for SO_4^{2-} and NO_3^- formation contribute to the differences in their vertical distributions.

6.2 The gas-to-aerosol conversion of HNO_3 to form nitrate

As mentioned above, 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 NO_3^- 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 here NO_3^- formation from

gas-to-aerosol conversion of HNO_3 based on the ISORROPIA II thermodynamic equilibrium module (Fountoukis and Nenes, 2007). The gas-to-aerosol conversion of HNO_3 to form NO_3^- is very sensitive to relative humidity (RH) and temperature (Fountoukis and Nenes 2007; Dawson et al., 2007). Low temperature and high RH are favorable for NO_3^- formation. Figure 12 shows the seasonal mean horizontal distributions of RH and temperature at 100 hPa and the latitude-altitude cross sections of these two parameters averaged over 70–105°E. RH exhibits high values in the TP/SASM region, which are consistent with the high H_2O mixing ratios in this area reported in Gettelman et al. (2004), M. Park et al. (2004), and Fu et al. (2006). At 100 hPa, the locations with high RH of exceeding 45% correspond well with those with high C_{NIT} values (Fig. 10(c)). The latitude-altitude cross section of RH (Fig. 12(c)) shows that RH has high values over the places with intense upward transport (Fig. 11). For temperature, as Fig. 12(b) and 12(d) show, summertime temperatures are cold (190–200 K) at 100 hPa in the TP/SASM region, consistent with the distribution and magnitude reported for August, 2011, in He et al. (2014) on the basis of the NCEP Reanalysis data. The low temperatures over the TP/SASM region are associated with the adiabatic expansion of ascending air mass of the deep convections (Yanai et al., 1992; Park et al., 2007; He et al., 2014).

Because of the favorable conditions of RH and temperature, the gas-to-aerosol conversion of HNO_3 to form nitrate can occur during the upward transport and in the UTLS. Figure 13 shows the mass budget for nitrate aerosol within the selected box of (70–105°E, 10–40°N, 8–16 km) to see the role of nitrate formation over the TP/SASM region. The horizontal mass fluxes

have a net negative value of 0.10 Tg season^{-1}, reducing nitrate aerosol in the selected box. The vertical transport and the gas-to-aerosol conversion of HNO_3 increase nitrate mass in the selected box, with values of 0.09 Tg season^{-1} and 0.11 Tg season^{-1}, respectively, indicating that the gas-to-aerosol conversion plays an important role in the enhancement of nitrate in the UTLS over the TP/SASM region. Although relatively high RH exists near the tropopause of the TP/SASM region, the air near the tropopause is still dryer compared to that in the lower altitudes. Model results show that the gas-to-aerosol partition of HNO_3 decreases with altitude over 8–16 km, indicating that the gas to aerosol conversion contributes to nitrate accumulation in the UTLS mainly during the process of upward transport.

Previous studies have also reported that nitric acid trihydrates (NAT, HNO_3•$(H_2O)_3$) could form in the polar and tropical stratosphere at low temperatures through two mechanisms: (1) the homogeneous nucleation out of supercooled ternary solutions, and (2) the heterogeneous formation on ice particles (Hofmann et al., 1989; Carslaw et al., 1998; Voigt et al., 2000; Popp et al., 2006; Kirner et al., 2011). A typical NAT condensation temperature is approximate 193 K (Kirner et al., 2011). As shown in Fig. 12, the temperatures around 100 hPa over the TP/SASM region are in the range of 190–200 K, which are low enough to produce some NAT particles. However, balloon-borne measurements of depolarization ratio and backscattering ratio of aerosols at Lhasa during August-October of 1999 by Kim et al. (2003) and Tobo et al. (2007) suggested that coarse and aspherical particles such as NAT are scarce in the UTLS of the TP/SASM.

7 Sensitivities of simulated nitrate in the UTLS to anthropogenic NO_x, NH_3, and SO_2 emissions in Asia

Since simulated SO_4^{2-}, NO_3^- and NH_4^+ concentrations have, respectively, NMBs of –17.0%, +38.8%, and +42.0% on an annual mean basis and of –14.7%, +51.5%, and +74.9% in summer (Section 4.2), we perform four sensitivity simulations to examine the impacts of uncertainties in surface-layer aerosol concentrations on simulated nitrate in the UTLS. In the first three cases, anthropogenic emissions of NO_x, NH_3, and SO_2 in Asia are changed by –50%, –50%, and +20%, respectively, relative to those in our standard simulation. In the last case, anthropogenic emissions of all these three species are changed simultaneously, with NO_x reduced by 50%, NH_3 reduced by 50%, and SO_2 increased by 20% in Asia relative to the standard case. The purpose of these sensitivity studies is to reduce NMBs of simulated surface-layer concentrations of SO_4^{2-}, NO_3^- and NH_4^+ and see whether NO_3^- is still the most dominant aerosol species in the UTLS. Model results from these sensitivity studies for summer of 2005 are presented in Table 3.

As anthropogenic emissions of SO_2 in Asia are increased by 20%, the NMB of simulated surface-layer SO_4^{2-} concentrations is –4.4%, which is an improvement compared to the NMB of –14.7% in the standard simulation. However, the increases in SO_2 emissions lead to larger NMBs of surface-layer NO_3^- and NH_4^+ because of the increased formation of ammonium sulfate or ammonium bisulfate. The percentage contributions of SO_4^{2-} to total aerosol mass in the UTLS increase slightly by 2.7% at 200 hPa and by 1.6% at 100 hPa, and nitrate in the UTLS also shows small sensitivity to the change in SO_2 emissions.

With anthropogenic emissions of NO_x in Asia reduced by 50%, the NMB of simulated surface-layer NO_3^- concentrations changes from +51.5% in the standard simulation to −11.7% in this sensitivity run. The contribution of each of SO_4^{2-}, NO_3^- and NH_4^+ aerosols to total aerosol mass in the UTLS is not sensitive to this reduction in NO_x emissions at the surface; the percentage contribution obtained from this sensitivity run is very close to the value obtained in the standard simulation (Table 3). Similarly, in the sensitivity study with NH_3 emissions reduced by 50% in Asia, simulated surface-layer concentrations of NO_3^- and NH_4^+ are improved in terms of the values of NMBs, but the improvement in simulated aerosol concentrations at the surface-layer does not influence our conclusion of high nitrate aerosol concentration in the UTLS.

As shown in Table 3, for the surface layer, simulated nitrate concentration over the TP/SASM region decreases by 46.8% with a 50% reduction in anthropogenic NO_x emissions in Asia, and it decreases by 22.3% when anthropogenic NH_3 emissions are reduced by the same percentage, indicating that surface-layer nitrate aerosol is more sensitive to anthropogenic emissions of NO_x than to those of NH_3. Relative to the baseline simulation, simulated nitrate concentrations at 200 hPa and 100 hPa decrease, respectively, by 49.0% and 17.7% with a 50% reduction in NH_3 emissions, whereas only by 2.1% and 1.3% with a 50% reduction in NO_x emissions. Over the studied region, the role of NH_3 in the sulfate-nitrate-ammonium aerosol system can be quantified by the gas ratio of $\mathrm{GR} = \frac{\text{free ammonia}}{\text{total nitrate}} = \frac{\mathrm{TA}-2\times\mathrm{TS}}{\mathrm{TN}}$ (Ansari and Pandis, 1998), where $\mathrm{TA} = \mathrm{NH_3} + \mathrm{NH_4^+}$, $\mathrm{TS} = \mathrm{SO_4^{2-}}$, and $\mathrm{TN} = \mathrm{HNO_3} + \mathrm{NO_3^-}$. Over the TP/SASM region, GR is generally positive both at the surface and in the UTLS, especially

699 over 20–40°N where deep convection exits (Fig. 11), indicating that S(VI) is in
700 from of sulfate and free ammonia is available to react with nitrate (Seinfeld and
701 Pandis 2006). However, GR is generally less than 1.0 above 400 hPa in
702 summer over the TP/SASM region, which indicates nitrate concentrations are
703 most sensitive to changes in NH_3 and explains the small sensitivity of nitrate
704 aerosol to NO_x emissions in the UTLS.

705 In the sensitivity study with emissions of NO_x, NH_3, and SO_2 in Asia
706 changed simultaneously, simulated surface-layer concentrations of SO_4^{2-}, NO_3^-
707 and NH_4^+ have NMBs of –8.3%, –27.0% and +55.4%, respectively, which are
708 all improved compared to those in the standard simulation. Even though nitrate
709 aerosol is now underestimated at the surface, it still accounts for 53.3% of the
710 $PM_{2.5}$ concentration at 100 hPa over the TP/SASM region in summer.

711 It should be noted that the concentrations of OC and BC are also
712 underestimated, with NMBs of –57.2% and –32.2%, respectively, in summer
713 (Section 4.2). We have done a simple calculation with the concentrations of
714 OC and BC in the UTLS multiplied by 2.3 and 1.5, respectively, and nitrate is
715 still the most dominant aerosol species in summertime in the UTLS over the
716 TP/SASM region (not shown in Table 3). Therefore the uncertainties in surface
717 aerosol concentrations do not compromise the conclusion of this study.

718

719 **8 Conclusions**

720 In this work we simulate nitrate aerosol and its contribution to aerosol
721 concentrations in the UTLS over the TP/SASM region (70–105°E, 10–40°N)
722 for summertime of year 2005, using the global chemical transport model
723 GEOS-Chem driven by the assimilated meteorological fields.

Simulated HNO_3 and O_3 are evaluated to show the model's ability to simulate the NOx-O_3-HNO_3 cycle over the studied region. In the UTLS, both the horizontal and vertical distributions of simulated HNO_3 and O_3 agree well with the MLS observations. 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, and the model biases lie within the confidence range of the MLS instruments. Both simulated and observed O_3 concentrations show relatively low values of less than 200 ppbv at 100 hPa over the TP/SASM region.

Averaged over the TP/SASM region, the surface-layer concentrations of SO_4^{2-}, NO_3^-, NH_4^+, BC, and OC are simulated to be 1.70, 0.94, 0.85, 0.30, and 0.94 μg m^{-3}, respectively. Nitrate aerosol is simulated to be of secondary importance near the surface over the region of our interest. Comparisons of simulated aerosol concentrations with ground-based observations show that simulated summertime concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC and BC have NMB of –14.7%, +51.5%, +74.9%, –57.2% and –32.2%, respectively. Note that the measurements of NO_3^- and NH_4^+ are quite limited in terms of the number of samples.

Model results show elevated concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC, BC and $PM_{2.5}$ in the UTLS over the TP/SASM region throughout the summer. NO_3^- is simulated to be the most dominant aerosol species in the UTLS of the TP/SASM region. Accounting for NO_3^- aerosol, the GEOS-Chem model reproduces well the magnitude of aerosol extinctions above 10 km, as model results are compared with the SAGE II measurements. The discrepancies between the simulated and observed aerosol extinction coefficient are within 8%

in the UTLS (averaged over 14–16 km). Simulated vertical profiles of aerosol extinction coefficients with and without nitrate aerosol show large discrepancies from 6 km to tropopause, indicating the important role of nitrate in aerosol layer in the UTLS over the TP/SASM region.

The contribution of NO_3^- to aerosols in the TP/SASM region is quantified by C_{NIT} (the ratio of nitrate concentration to $PM_{2.5}$ concentration). Over the TP/SASM region, the C_{NIT} values in summer are 5–35% at the surface, 25–50% at 200 hPa, and could exceed 60% at 100 hPa. The mechanisms for the accumulation of nitrate in the UTLS over the TP/SASM region include vertical transport and the gas-to-aerosol conversion of HNO_3 to form nitrate. Such gas-to-aerosol conversion occurs during the upward transport and in the UTLS. The high relative humidity and low temperature associated with the deep convection over the TP/SASM region are favorable for nitrate formation.

Results from the present study indicate that nitrate is an important aerosol species in the UTLS over the ASM/TP region. Considering the scarce measurements of nitrate in the UTLS and the model uncertainties, more observational and modeling studies are needed to further explore the aerosol composition in the Asian tropopause aerosol layer. Further simulations of nitrate aerosol in the UTLS also need to account for NAT formation at low temperatures (Kirner et al., 2011) and the roles of natural aerosols, including the transport of mineral dust and sea salt to the UTLS as well as nitrate formation on these natural particles (Ma et al., 2003).

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Table 1. Summary of Annual Emissions of Aerosols and Aerosol Precursors in Asia (60°E-155°E, 10°N-55°N)

Species	Global	Asia
NO_x (Tg N yr^{-1})		
Aircraft	0.5	0.08
Anthropogenic	28.6	9.96
Biomass burning	4.7	0.27
Fertilizer	0.7	0.31
Lightning	5.9	0.87
Soil	5.9	0.96
Total	46.3	12.45
SO_2 (Tg S yr^{-1})		
Aircraft	0.1	0.01
Anthropogenic	52.6	23.46
Biomass burning	1.2	0.07
Volcanoes	4.4	1.04
No_eruption	8.9	1.78
Ship	7.4	0.94
Total	74.6	27.30
NH_3 (Tg N yr^{-1})		
Anthropogenic	34.9	17.83
Natural	14.2	2.01
Biomass burning	3.5	0.21
Biofuel	1.6	0.71
Total	54.2	20.76
OC (Tg C yr^{-1})		
Anthropogenic	3.1	1.42
Biomass burning	18.7	1.10
Biofuel	6.3	3.28
Biogenic	9.7	1.22
Total	37.8	7.02
BC (Tg C yr^{-1})		
Anthropogenic	3.0	1.43
Biomass burning	2.2	0.12
Biofuel	1.6	0.86
Total	6.8	2.41

Table 2. Simulated seasonal mean concentrations of aerosols and their contributions to $PM_{2.5}$ (in percentages in parentheses) during summertime (June-August) of 2005 for the TP/SASM, TP, and SASM regions. The unit is μg m^{-3} for concentrations at the surface, and 10^{-2} μg m^{-3} for concentrations at 200 hPa and 100 hPa.

	$PM_{2.5}$	SO_4^{2-}	NO_3^-	NH_4^+	OC	BC
			TP/SASM			
Surface	4.73	1.70(35.9%)	0.94(19.8%)	0.85(18.1%)	0.94(19.8%)	0.30(6.4%)
200 hPa	16.19	3.27(20.2%)	7.57(46.8%)	2.67(16.5%)	2.22(13.7%)	0.44(2.7%)
100 hPa	12.14	2.60(21.4%)	6.90(56.8%)	1.43(11.8%)	1.05(8.6%)	0.16(1.3%)
			TP			
Surface	5.44	2.12(39.0%)	1.05(19.3%)	1.08(19.9%)	0.88(16.1%)	0.31(5.7%)
200 hPa	19.80	4.16(21.0%)	9.43(47.6%)	3.25(16.4%)	2.49(12.6%)	0.47(2.4%)
100 hPa	10.58	2.60(24.6%)	5.51(52.0%)	1.35(12.7%)	0.99(9.4%)	0.14(1.3%)
			SASM			
Surface	4.02	1.28(31.8%)	0.83(20.5%)	0.63(15.6%)	1.00(24.8%)	0.29(7.2%)
200 hPa	12.57	2.38(18.9%)	5.72(45.5%)	2.10(16.7%)	1.95(15.5%)	0.41(3.3%)
100 hPa	13.71	2.60(19.0%)	8.30(60.5%)	1.52(11.1%)	1.11(8.1%)	0.18(1.3%)

Table 3. Sensitivity simulations to examine the impacts of uncertainties in surface-layer aerosol concentrations on simulated NO_3^- in the UTLS. "Conc" and "Ctri" denote, respectively, simulated seasonal mean concentrations of SO_4^{2-}, NO_3^-, NH_4^+, OC, BC and their contributions to $PM_{2.5}$ (in percentages) during summertime (June-August) of 2005. The mass concentrations are averaged over the TP/SASM region, with unit of μg m^{-3} at the surface layer and of 10^{-2} μg m^{-3} at 200 hPa and 100 hPa. Also shown are the NMBs, as the simulated surface-layer concentrations are compared with measurements described in Section 4.2.

Species	Baseline Case			SO_2 (+20%)			NO_x (-50%)			NH_3 (-50%)			All Change		
	Conc.	Ctri.	NMB	Conc.	Ctri.	NMB	Conc.	Ctri.	NMB	Conc.	Ctri.	NMB	Conc.	Ctri.	NMB
Surface															
SO_4^{2-}	1.70	35.9%	–14.7%	1.92	38.1%	–4.4%	1.58	39.5%	–18.1%	1.70	38.1%	–14.7%	1.78	43.2%	–8.3%
NO_3^-	0.94	19.8%	+51.5%	0.94	18.7%	+53.5%	0.50	12.5%	–11.7%	0.73	16.4%	+24.1%	0.39	9.5%	–27.0%
NH_4^+	0.85	18.1%	+74.9%	0.94	18.6%	+93.8%	0.68	17.1%	+44.1%	0.78	17.6%	+64.6%	0.71	17.3%	+55.4%
OC	0.94	19.8%	–57.2%	0.94	18.6%	–57.2%	0.94	23.4%	–57.2%	0.94	21.0%	–57.2%	0.94	22.7%	–57.2%
BC	0.30	6.4%	–32.2%	0.30	6.0%	–32.2%	0.30	7.5%	–32.2%	0.30	6.8%	–32.2%	0.30	7.3%	–32.2%
200 hPa															
SO_4^{2-}	3.27	20.2%		3.67	22.9%		3.31	20.6%		3.29	29.1%		3.74	33.7%	
NO_3^-	7.57	46.8%		7.05	43.9%		7.41	46.0%		3.86	34.2%		3.19	28.7%	
NH_4^+	2.67	16.5%		2.67	16.6%		2.71	16.8%		1.49	13.2%		1.50	13.5%	
OC	2.22	13.7%		2.22	13.8%		2.22	13.8%		2.22	19.7%		2.22	20.0%	
BC	0.44	2.7%		0.44	2.7%		0.44	2.7%		0.44	3.9%		0.44	4.0%	
100 hPa															
SO_4^{2-}	2.60	21.4%		2.80	23.0%		2.66	21.9%		2.60	25.2%		2.87	27.2%	
NO_3^-	6.90	56.8%		6.72	55.3%		6.81	56.1%		5.68	55.0%		5.62	53.3%	
NH_4^+	1.43	11.8%		1.43	11.7%		1.45	12.0%		0.84	8.1%		0.84	8.0%	
OC	1.05	8.6%		1.05	8.6%		1.05	8.7%		1.05	10.2%		1.05	10.0%	
BC	0.16	1.3%		0.16	1.3%		0.16	1.3%		0.16	1.6%		0.16	1.5%	

Figure Captions

Figure. 1. Regions examined in this study: the Tibetan Plateau region (TP, 70–105°E, 25–40°N), the SASM region (SASM, 70–105°E, 10–25°N), and the anticyclone region of (20–120°E, 10–40°N).

Figure. 2. Monthly variations in emissions of NO_x (Tg N month^{-1}), SO_2 (Tg S month^{-1}), NH_3 (Tg N month^{-1}), OC (Tg C month^{-1}), and BC (Tg C month^{-1}) over Asia. Values shown are the total emissions (anthropogenic plus natural emissions listed in Table 1).

Figure. 3. Simulated global distributions of surface-layer HNO_3 (pptv) and O_3 (ppbv) averaged over June-August, 2005.

Figure. 4. Comparisons of simulated HNO_3 concentrations (pptv) with observations (pptv) from MLS. (a) and (b) are simulated concentrations at 200 hPa and 100 hPa, respectively. (c) is the latitude-altitude cross section of simulated HNO_3 concentrations averaged over 70–105°E. (d)-(f) are the same as (a)-(c), except that (d)-(f) are observations from MLS. The white areas in (d) and (f) have no datasets available from MLS. All the datasets are averaged over June-August of 2005.

Figure. 5. Comparisons of simulated O_3 concentrations (ppbv) with observations (ppbv) from MLS. (a) and (b) are simulated concentrations at 200 hPa and 100 hPa, respectively. (c) is the latitude-altitude cross section of simulated O_3 concentrations averaged over 70–105°E. (d)-(f) are the same as (a)-(c), except that (d)-(f) are observations from MLS. All the datasets are averaged over June-August of 2005.

Figure. 6. The simulated and observed vertical profiles of monthly mean O_3 mixing ratios at (a) Kunming and (b) Lhasa in August. The model results are from the simulation of year 2005. The observations in Kunming were conducted during August 7–13 (11 profiles of O_3 collected) in 2009 and during August 12–31 in 2012 (daily observations). The observations in Lhasa were conducted during August 22–28 in 2010 (12 profiles of O_3 collected) and during August 4–26 in 2013 (daily observations).

Figure. 7. Simulated seasonal mean concentrations (μg m^{-3}) of sulfate, nitrate, ammonium, organic carbon, black carbon, and $PM_{2.5}$ at (a) the surface layer, (b) 200 hPa, and (c) 100 hPa, during summer (June-August) of year 2005. Note that color bars are different for concentrations at the surface, 200 hPa, and 100 hPa.

Figure. 8. (a) Locations with measured aerosol concentrations from previous studies. Also shown are surface winds during summertime. (b)–(f) show the comparisons of simulated seasonal mean concentrations of sulfate, nitrate, ammonium, OC, and BC with measured values, respectively. Also shown in (b)–(f) are the 1:1 line (dashed), linear fit (solid line and equation), correlation coefficient between simulated and measured concentrations (R), and

normalized mean bias (NMB) (defined as NMB=$\frac{\sum_{i=1}^{n}(P_i-O_i)}{\sum_{i=1}^{n}O_i}$ ×100%, where P_i and O_i are predicted and observed concentrations at station *i* for each aerosol species).

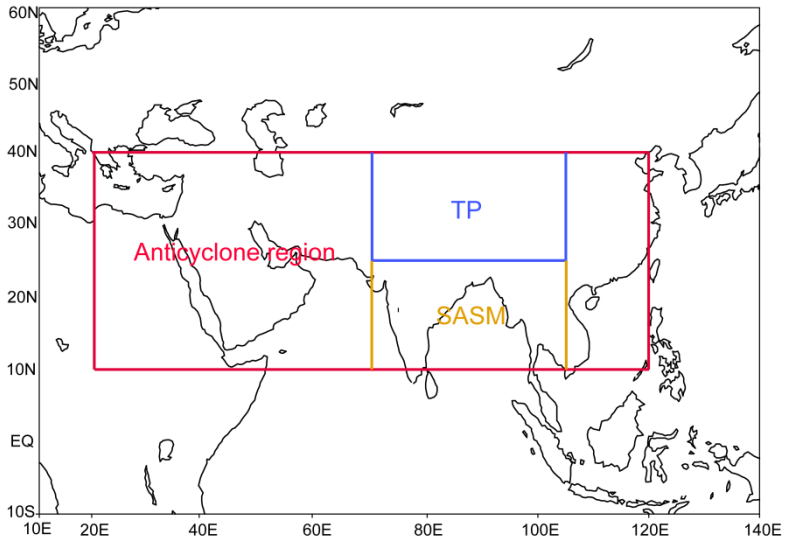
Figure. 9. (a) Monthly mean distribution of aerosol extinction coefficients (km^{-1}) at 100 hPa for July of 2005. (b) Monthly mean vertical distributions of aerosol extinction coefficients (at 525 nm for SAGE II and 550 nm for GEOS-Chem) (km^{-1}) averaged over the Asian monsoon anticyclone region (20–120°E, 10–40°N) for July of 2005. The horizontal dashed line represents the tropopause averaged over the Asian monsoon anticyclone region simulated by the GEOS-Chem model.

Figure. 10. Simulated contributions of nitrate to $PM_{2.5}$ (C_{NIT}= [NIT]/ [$PM_{2.5}$] ×100%) averaged over summer (June-August) of year 2005 at (a) surface-layer, (b) 200 hPa, and (c) 100 hPa. (d) The latitude-altitude cross section of simulated C_{NIT} (%) averaged over 70–105°E.

Figure. 11. Latitude-altitude cross sections of simulated concentrations (color shades, μg m^{-3}) of SO_4^{2-} and NO_3^- averaged over 70–105°E in June-August of 2005, together with the wind vectors obtained from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim Reanalysis data. The black line is the tropopause simulated by the GEOS-Chem model.

Figure. 12. (a)-(b) Distributions of RH (%) and temperature (K) at 100 hPa. (c)-(d) The latitude-altitude cross sections of RH (%) and temperature (K) averaged over 70–105°E. RH and temperature are from the GEOS5 assimilated meteorological fields, and all the values are the averages over June-August of year 2005.

Figure. 13. Mass budget for nitrate aerosol within the selected box of (70–105°E, 10–40°N, 8–16 km). E/W transport indicates net mass flux through the east and west lateral boundaries, N/S transport indicates net mass flux through the north and south lateral boundaries, and upward transport is the net mass flux through the top and bottom sides of the box. The mass flux is positive if it increases nitrate mass within the box. Unit of fluxes is Tg $season^{-1}$. All the values are the averages over June-August of 2005.



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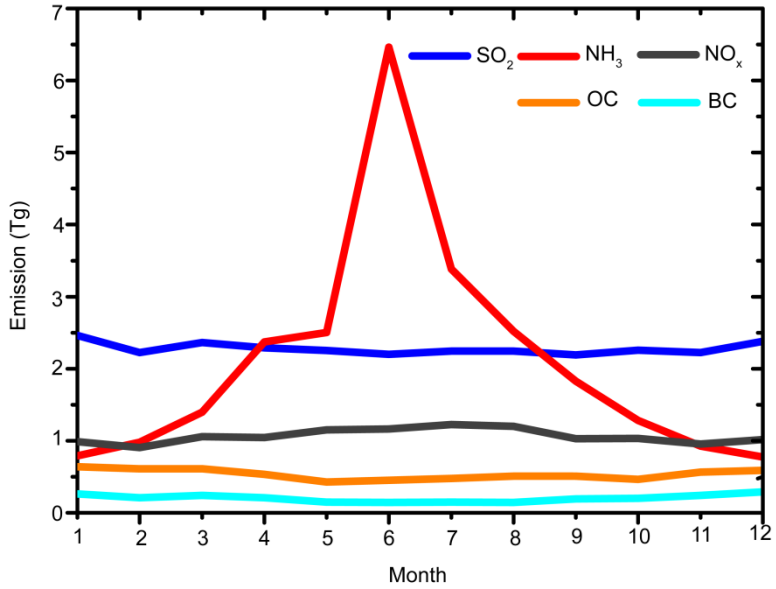

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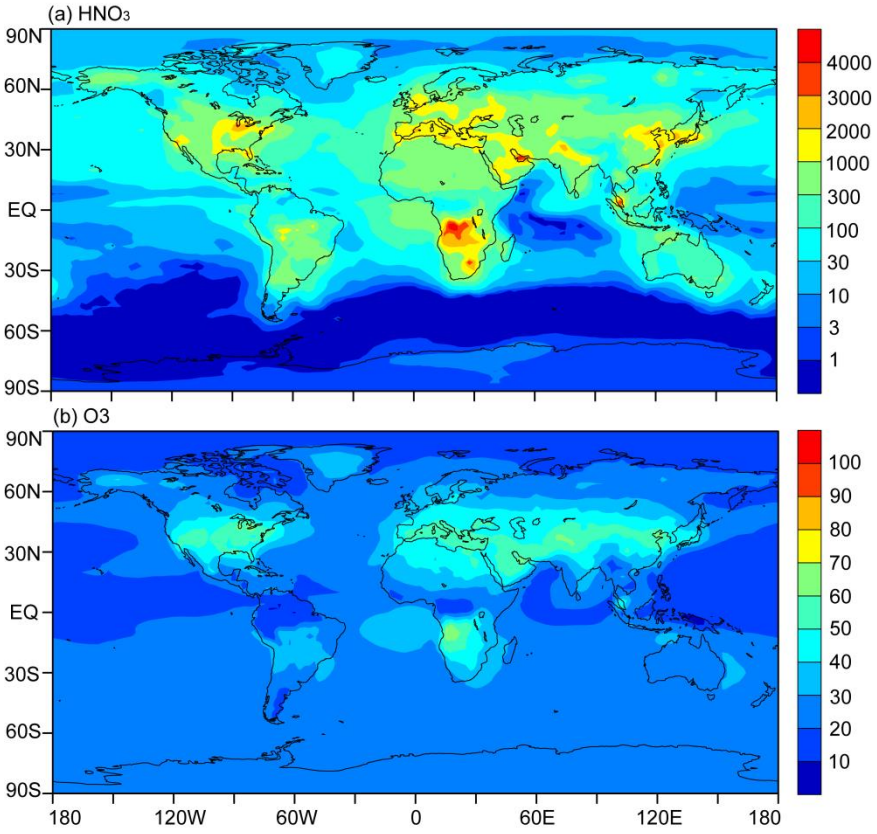

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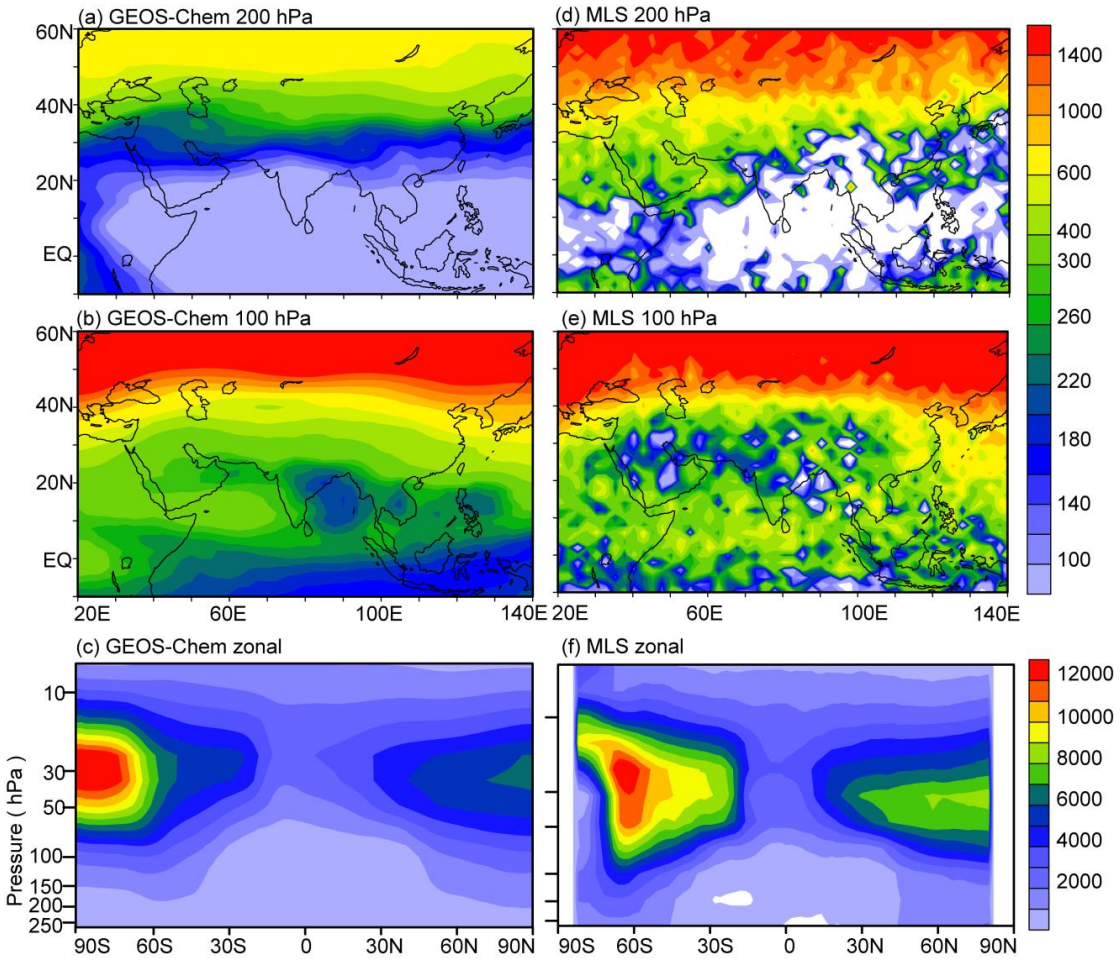

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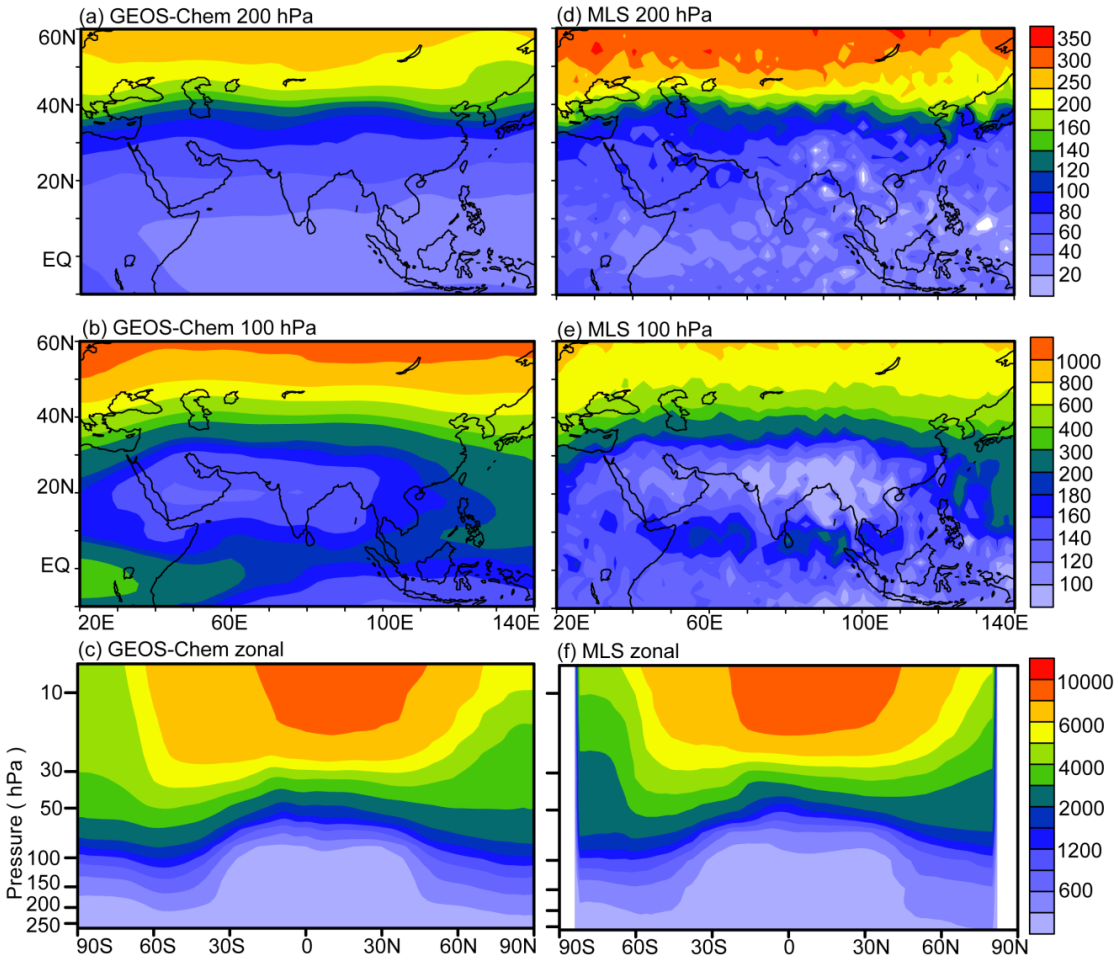

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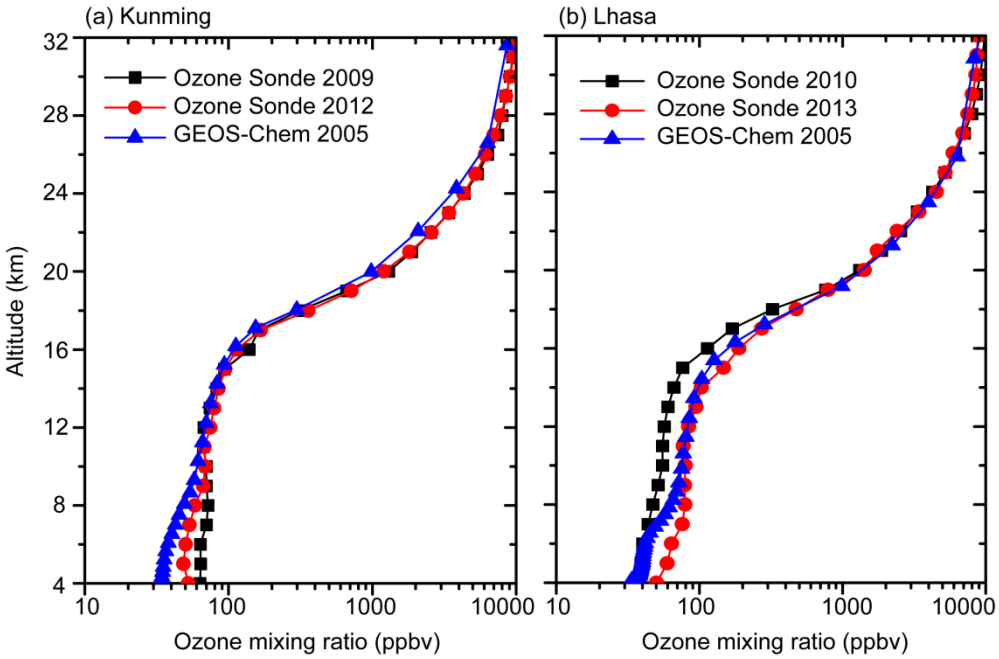

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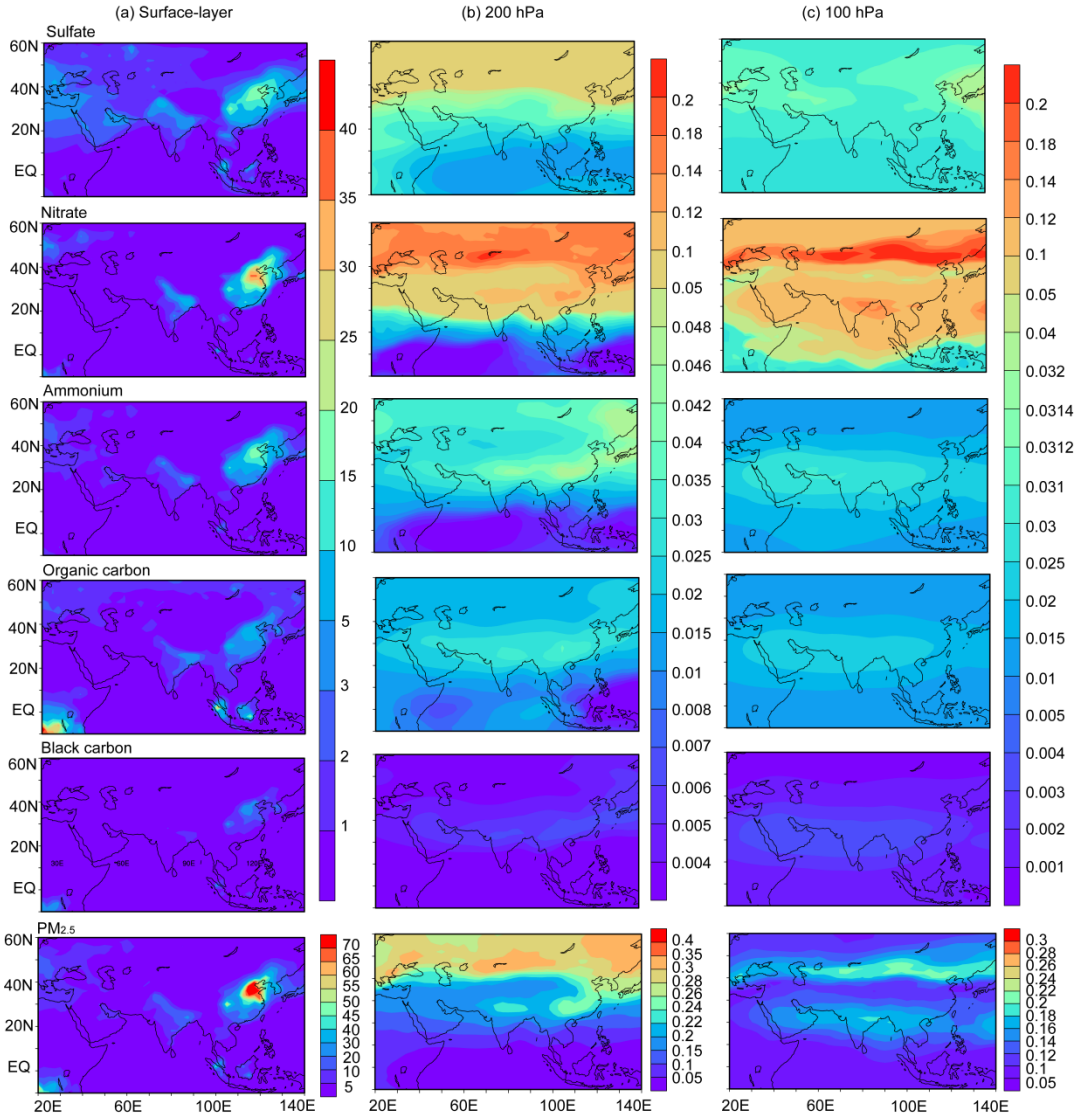

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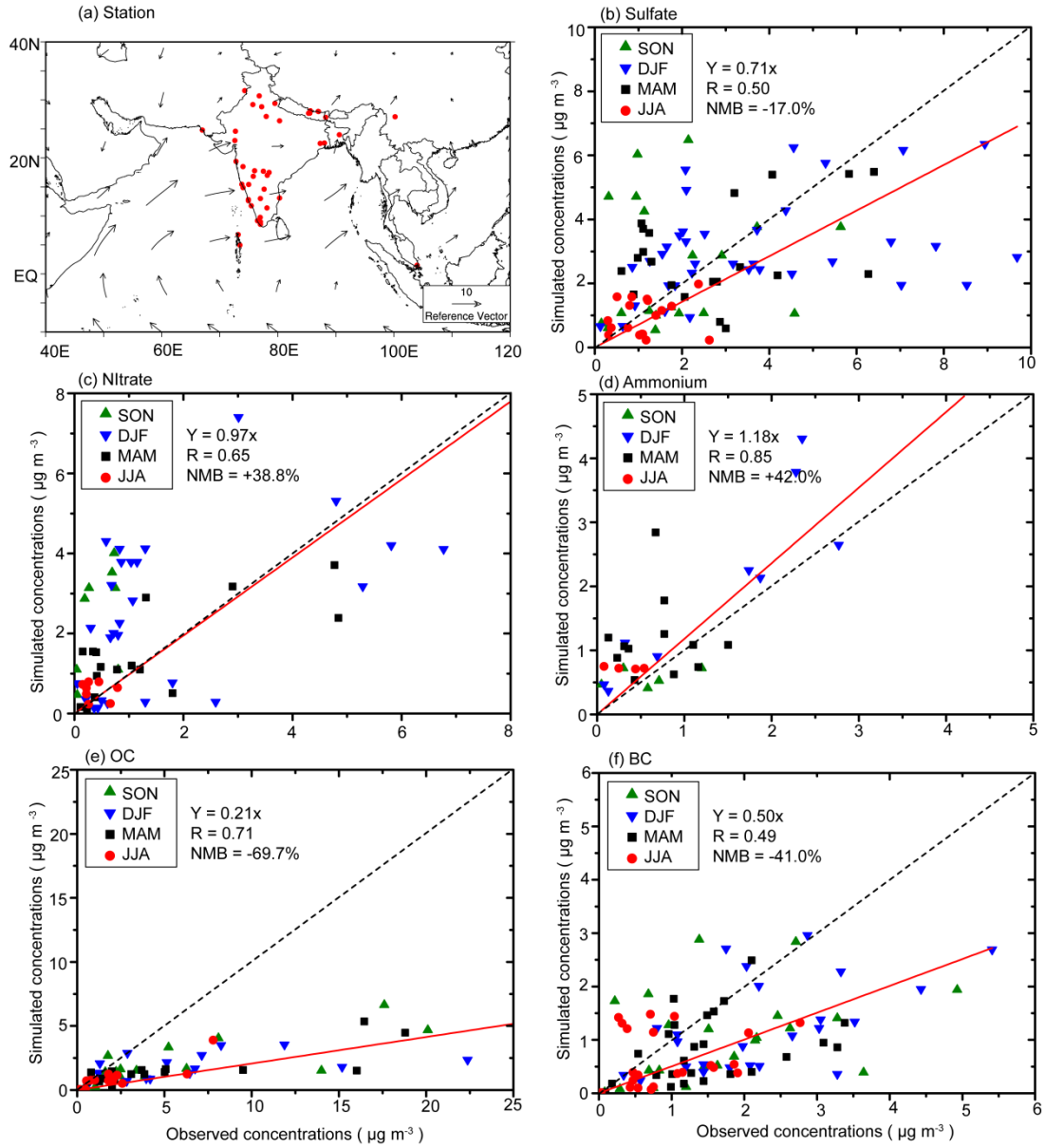

Figure. 8. (a) Locations with measured aerosol concentrations from previous studies. Also shown are surface winds during summertime. (b)–(f) show the comparisons of simulated seasonal mean concentrations of sulfate, nitrate, ammonium, OC, and BC with measured values, respectively. Also shown in (b)–(f) are the 1:1 line (dashed), linear fit (solid line and equation), correlation coefficient between simulated and measured concentrations (R), and normalized mean bias (NMB) (defined as NMB=$\frac{\sum_{i=1}^{n}(P_i-O_i)}{\sum_{i=1}^{n}O_i}$ ×100%, where P_i and O_i are predicted and observed concentrations at station *i* for each aerosol species).

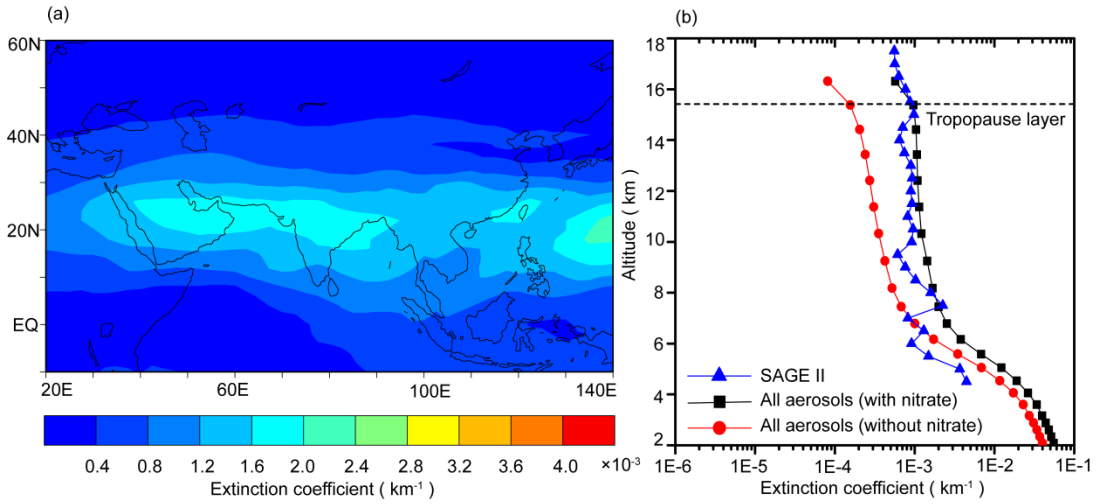

Figure. 9. (a) Monthly mean distribution of aerosol extinction coefficients (km^{-1}) at 100 hPa for July of 2005. (b) Monthly mean vertical distributions of aerosol extinction coefficients (at 525 nm for SAGE II and 550 nm for GEOS-Chem) (km^{-1}) averaged over the Asian monsoon anticyclone region (20–120°E, 10–40°N) for July of 2005. The horizontal dashed line represents the tropopause averaged over the Asian monsoon anticyclone region simulated by the GEOS-Chem model.

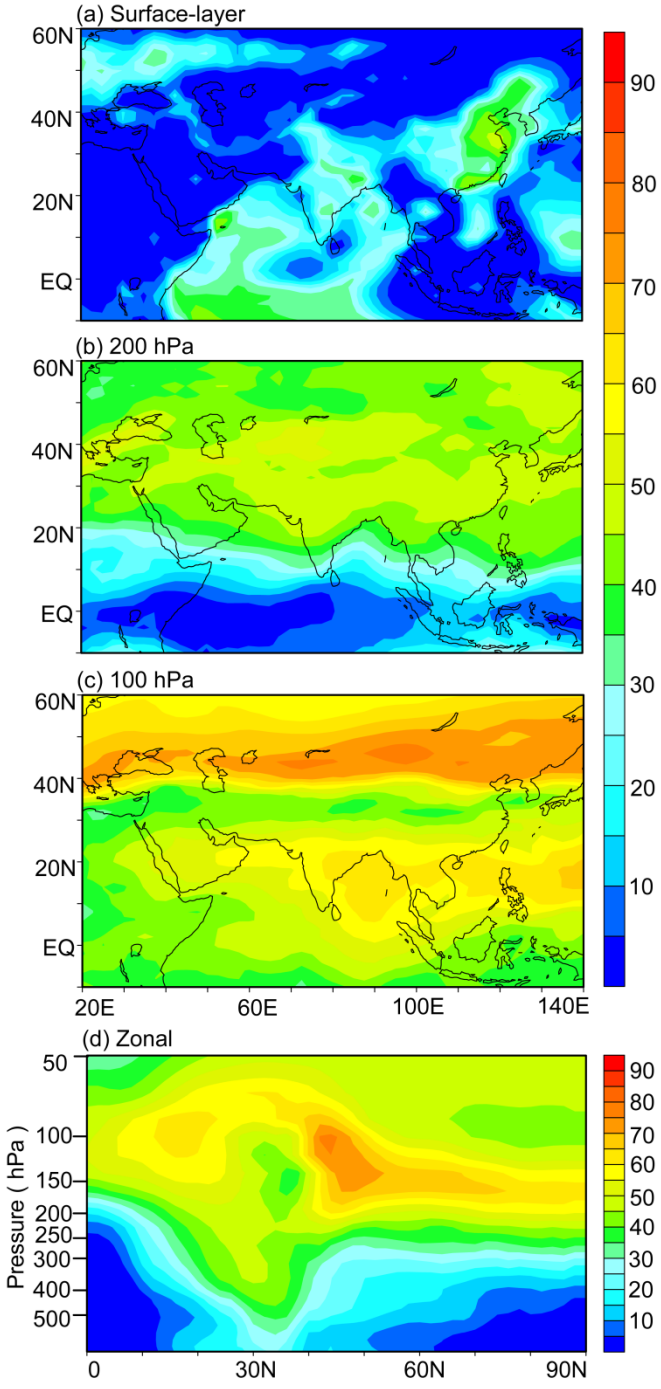

Figure. 10. Simulated contributions of nitrate to $PM_{2.5}$ (C_{NIT}= [NIT]/ [$PM_{2.5}$] ×100%) averaged over summer (June-August) of year 2005 at (a) surface-layer, (b) 200 hPa, and (c) 100 hPa. (d) The latitude-altitude cross section of simulated C_{NIT} (%) averaged over 70–105°E.

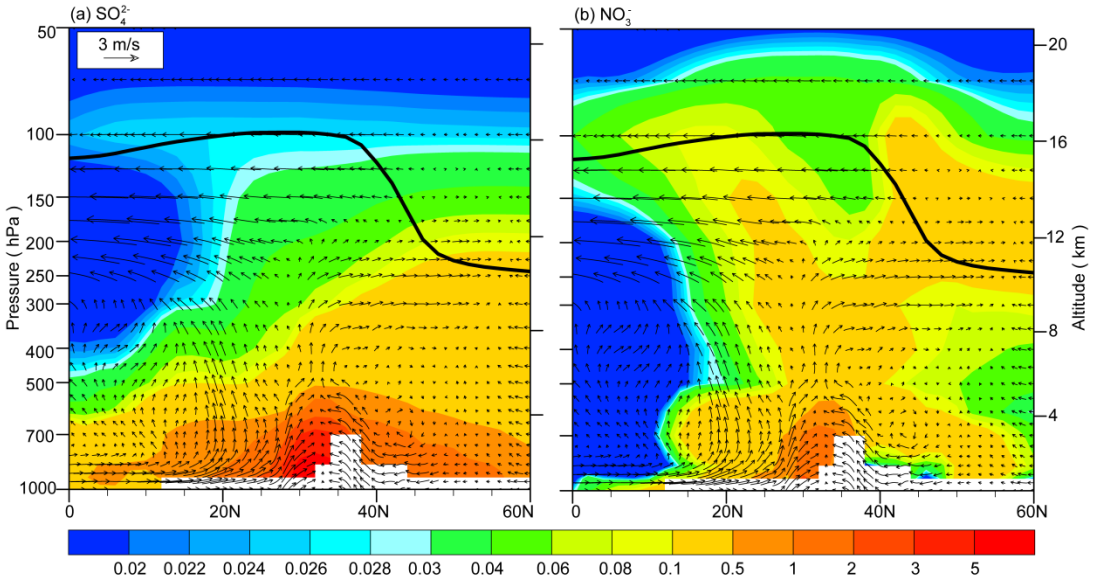

Figure. 11. Latitude-altitude cross sections of simulated concentrations (color shades, μg m^{-3}) of SO_4^{2-} and NO_3^- averaged over 70–105°E in June-August of 2005, together with the wind vectors obtained from the European Centre for Medium-Range Weather Forecasts (ECMWF) ERA-Interim Reanalysis data. The black line is the tropopause simulated by the GEOS-Chem model.

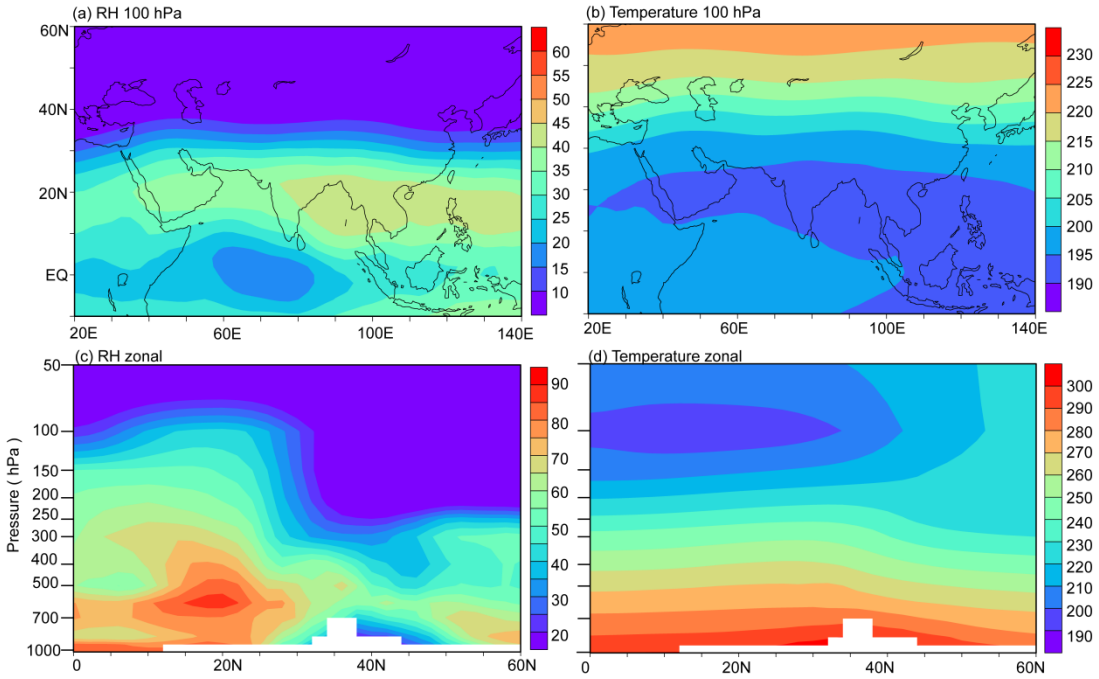

Figure. 12. (a)-(b) Distributions of RH (%) and temperature (K) at 100 hPa. (c)-(d) The latitude-altitude cross sections of RH (%) and temperature (K) averaged over 70–105°E. RH and temperature are from the GEOS5 assimilated meteorological fields, and all the values are the averages over June-August of year 2005.

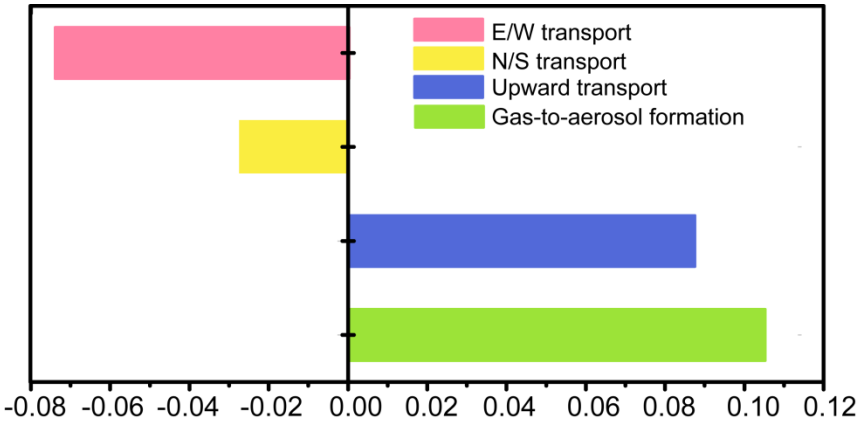

Figure. 13. Mass budget for nitrate aerosol within the selected box of (70–105°E, 10–40°N, 8–16 km). E/W transport indicates net mass flux through the east and west lateral boundaries, N/S transport indicates net mass flux through the north and south lateral boundaries, and upward transport is the net mass flux through the top and bottom sides of the box. The mass flux is positive if it increases nitrate mass within the box. Unit of fluxes is Tg season^{-1}. All the values are the averages over June-August of 2005.