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Persistent sensitivity of Asian aerosol to emissions of nitrogen oxides

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[1] We use a chemical transport model and its adjoint to examine the sensitivity of secondary inorganic aerosol formation to emissions of precursor trace gases from Asia. Sensitivity simulations indicate that secondary inorganic aerosol mass concentrations are most sensitive to ammonia (NH_3) emissions in winter and to sulfur dioxide (SO_2) emissions during the rest of the year. However, in the annual mean, the perturbations on Asian population-weighted ground-level secondary inorganic aerosol concentrations of 34% due to changing nitrogen oxide (NO_x) emissions are comparable to those from changing either SO_2 (41%) or NH_3 (25%) emissions. The persistent sensitivity to NO_x arises from the regional abundance of NH_3 over Asia that promotes ammonium nitrate formation. IASI satellite observations corroborate the NH_3 abundance. Projected emissions for 2020 indicate continued sensitivity to NO_x emissions. We encourage more attention to NO_x controls in addition to SO_2 and NH_3 controls to reduce ground-level East Asian aerosol.
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1. Introduction

[2] Atmospheric aerosols have major implications for human health, visibility, and climate. Aerosol concentrations in parts of South and East Asia are the highest in the world with annual mean $PM_{2.5}$ concentrations that exceed 50 $\mu g\,m^{-3}$ over broad areas [van *Donkelaar et al.*, 2010]. Such high aerosol concentrations could reduce life expectancy by several years [*Lim et al.*, 2012]. A large fraction of the aerosol mass in Asia is composed of secondary inorganic ions as sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) [*Huang et al.*, 2012a, 2012b]. Emission control strategies are complicated by complex chemical feedbacks that affect the relation of secondary inorganic mass with precursor emissions of SO_2, NH_3, and NO_x [*Pinder et al.*, 2007; Wang *et al.*, 2011, 2012].

[3] Satellite remote sensing reveals intense concentrations over Asia of NO_2 [*Richter et al.*, 2005], SO_2 [*Lee et al.*, 2009], and NH_3 [*Clarisse et al.*, 2009]. Oxidation of SO_2 yields sulfuric acid (H_2SO_4) which has a low vapor pressure such that it exists primarily in the condensed phase. The sulfuric acid can be neutralized by NH_3 to form ammonium bisulfate (NH_4HSO_4) or ammonium sulfate ($(NH_4)_2SO_4$). The nitric acid (HNO_3) formed from NO_x oxidation tends to partition into the aerosol phase as ammonium nitrate (NH_4NO_3) if there is free NH_3 that has not reacted with sulfuric acid, and condenses most readily when temperatures are low and relative humidity is high. China has set SO_2 emission control as a high priority in its air quality management strategy with the intention of reducing inorganic aerosol levels (Ministry of Environment Protection in China (MEP), 2009, http://english.mep.gov.cn/standards_reports/soe/soe2009/) [*Wang et al.*, 2012a, 2012b]. *Zhang et al.* [2012] report that the SO_2 growth rate slowed down in 2005 and that Chinese emissions start to decrease after 2006. However, *Lin et al.* [2010] suggest that these controls are insufficient to reduce aerosol concentrations. Emissions continue to increase for SO_2 from India and for NO_x for broad regions of South and East Asia [*Prasad et al.*, 2011; *Wang et al.*, 2012a, 2012b]. The trend in NH_3 emissions is uncertain but likely has a steady or increasing trend [*Zheng et al.*, 2012].

[4] Here we examine the sensitivity of ground-level secondary inorganic aerosol to precursor emissions. We simulate the spatial variation of secondary inorganic aerosol (sulfate-nitrate-ammonium) mass concentration and its sensitivity to precursor (i.e., NO_x, SO_2, and NH_3) emissions from South and East Asia using the GEOS-Chem nested forward model and population-weighted GEOS-Chem adjoint model simulations. Simulated NH_3 concentrations are evaluated against IASI satellite observations. Projected emissions for 2020 are used to assess long-term sensitivities.

2. Model Description

[5] We use the GEOS-Chem chemical transport model (version 09-01-02; www.geos-chem.org) to calculate the sensitivity of secondary inorganic aerosols to precursor emissions. The GEOS-Chem model is driven by assimilated meteorological data from the Goddard Earth Observation System (GEOS-5) of the NASA Global Modeling and Assimilation Office (GMAO) for the year 2006 with a temporal resolution of 6 h (3 h for surface variables and mixing depths). The nested version of GEOS-Chem for Asia

All Supporting Information may be found in the online version of this article.

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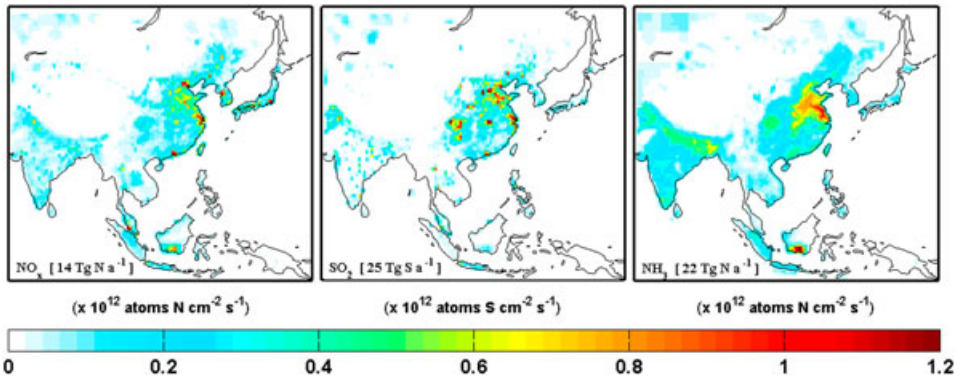

Figure 1. Spatial distribution of emissions of inorganic aerosol precursors (NO_x, SO_2, and NH_3) over the Asian region for the year 2006. Inset values indicate the total emission rate over the domain.

(70°E–150°E, 11°S–55°N) uses the native resolution of GEOS-5 meteorological fields at 0.5° × 0.67° [*Chen et al.*, 2009]. The lowest model layer thickness is ~130 m. A global simulation at 2° × 2.5° spatial resolution is used to provide the boundary conditions every 3 h for the nested domain. GEOS-Chem includes a fully coupled treatment of tropospheric ozone-NO_x-VOC-aerosol chemistry [*Park et al.*, 2004]. Gas-aerosol phase partitioning of the sulfate-nitrate-ammonium-water system is calculated using the ISORROPIA II thermodynamic equilibrium model that includes the effects of temperature and relative humidity [*Fountoukis and Nenes*, 2007]. We use monthly anthropogenic emissions of NO_x and SO_2 from *Zhang et al.* [2009]. NH_3 emissions are from *Streets et al.* [2003], with a reduction of 30% as recommended by *Huang et al.* [2012a, 2012b] for Asia, and seasonality as implemented

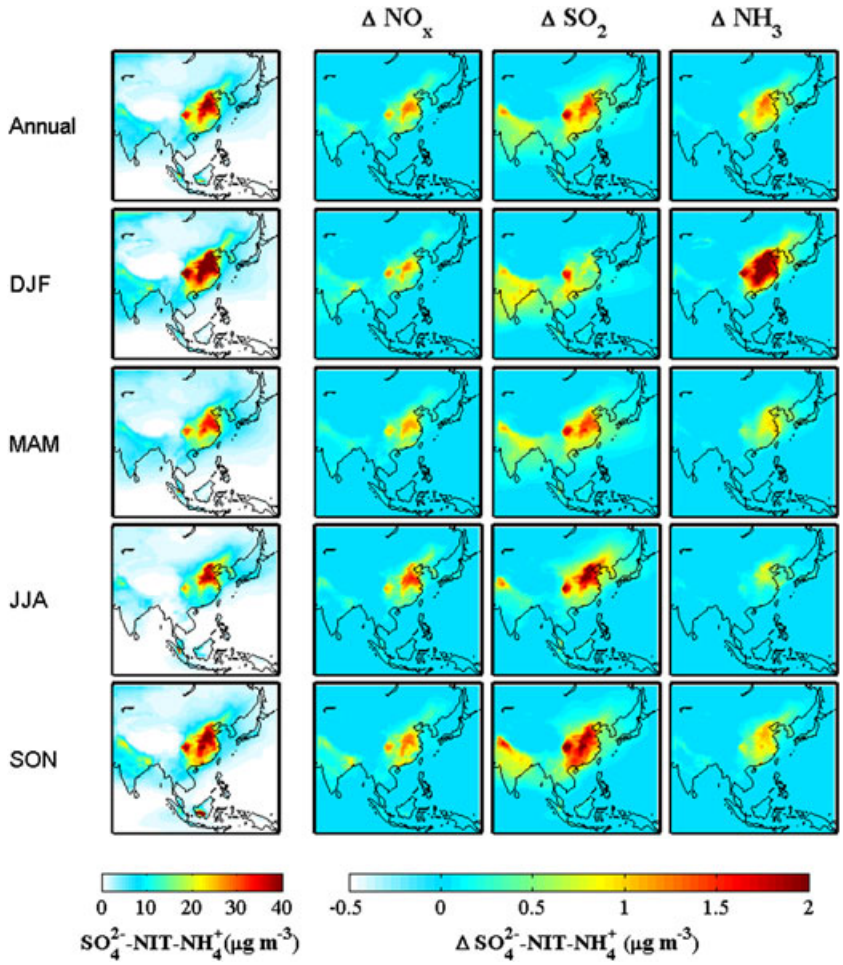

Figure 2. Spatial distribution of secondary inorganic aerosol mass concentrations over Asia. The columns on the right show absolute difference in secondary inorganic aerosol mass concentration due to 10% increase in NO_x, SO_2, and NH_3 anthropogenic emissions.

by *Fisher et al.* [2011]. Errors in the model representation of too shallow nighttime mixing depths and overproduction of HNO_3 are corrected following *Heald et al.* [2012] and *Walker et al.* [2012]. The GEOS-Chem secondary inorganic aerosol simulation has been evaluated extensively with measurements over East Asia [e.g., *Lin et al.*, 2010; *Zhang et al.*, 2010; *Jeong et al.*, 2011; *Wang et al.*, 2012a, 2012b].

[6] Figure 1 shows the spatial distribution of total (natural and anthropogenic) NO_x, SO_2, and NH_3 emissions for South and East Asia. Populated regions of East China exhibit substantial collocated NO_x, SO_2, and NH_3 enhancements associated with power generation, vehicles, and agriculture. North India has pronounced NH_3 sources but weaker NO_x and SO_2 sources. The total NH_3 source (9.5×10^{35} atoms N a^{-1}) is comparable to the sum of SO_2 (4.7×10^{35} atoms S a^{-1}) and NO_x (5.9×10^{35} atoms N a^{-1}). Indeed, retrievals from the IASI [*Clarisse et al.*, 2009] (Figure A1) and TES [*Shephard et al.*, 2011] satellite instruments indicate substantial concentrations of gas-phase NH_3 over both East China and North India. This gas-phase NH_3 implies a reservoir that is able to promote aerosol formation if additional sulfuric acid or nitric acid becomes available. We more quantitatively examine the implications of this excess NH_3 in section 3.

[7] In addition, we use the GEOS-Chem adjoint model [*Henze et al.*, 2007] with updates to v8-02-01 at a resolution of $2° \times 2.5°$. The adjoint model provides an efficient means for analyzing the sensitivity of model outputs to changes in model inputs. *Henze et al.* [2009] demonstrated the applicability of the GEOS-Chem adjoint to inorganic $PM_{2.5}$ control strategies. Here the gradient of a cost function (population-weighted secondary inorganic aerosols; Supporting Information) is evaluated with respect to the model input parameters (i.e., emission estimates). For each adjoint run, concentrations from a GEOS-Chem forward simulation are computed and stored first, and are later used during the backward integration of the adjoint. The use of the adjoint allows us to quantify the sensitivity of the population-weighted secondary inorganic aerosols to emissions within specific GEOS-Chem grid cells. Population weighting is chosen for relevance to health implications. The population data are from the Socioeconomic Data and Applications Center Gridded Population of the World v3 [*Balk et al.*, 2010].

3. Sensitivity of Fine Particulate Matter to Emissions

[8] We perform four different simulations of the nested forward model, including one standard and three sensitivity simulations with 10% increases to the anthropogenic emissions of NO_x, SO_2, and NH_3, respectively. The model is spun up for 1 month to minimize influence of the initial conditions. The left column of Figure 2 shows the spatial distribution of annual and seasonal mean secondary inorganic aerosol mass concentrations for the standard simulation. Annual mean concentrations reflect the distribution of precursor emissions with maximum values over East China. Secondary inorganic aerosol mass concentrations are highest in winter (DJF) and lowest in summer (JJA) over both regions, associated with increased nitrate aerosol concentration at low temperatures and high SO_2 and NO_x emissions in winter. The left column of Figure 3 contains the speciation of this secondary inorganic aerosol. *Yang et al.* [2011] used a three-channel speciation sampler equipped with nylon filter and denuder for accurate measurement of NO_3^- and

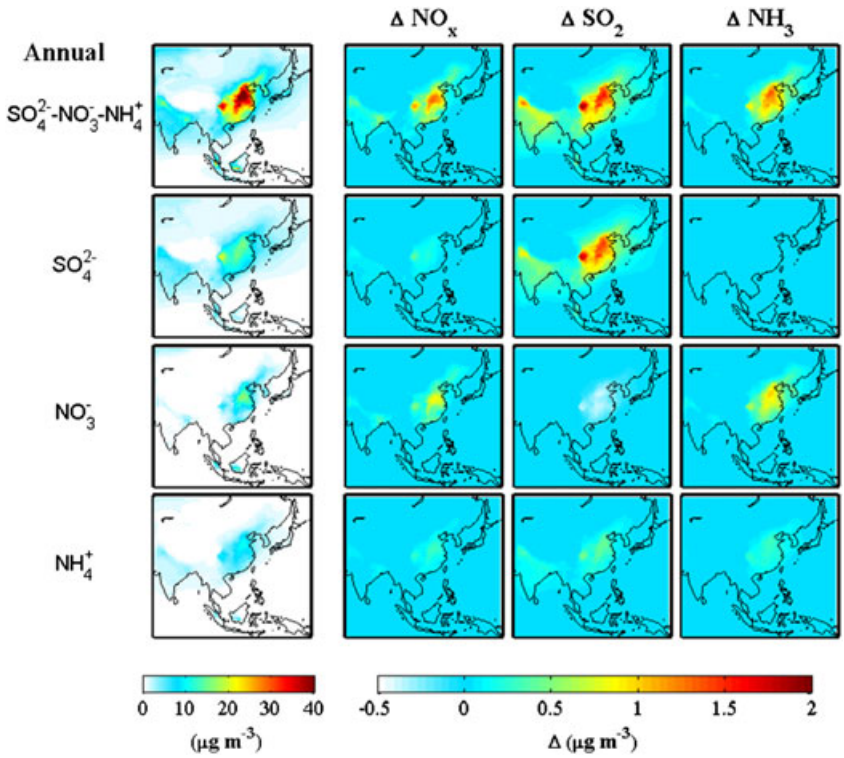

Figure 3. The left column indicates the spatial distribution of annual mass concentration of secondary inorganic aerosol, sulfate, nitrate, and ammonium for 2006. The remaining columns indicate the sensitivity of each component to a 10% increase in precursor emissions (NO_x, SO_2, or NH_3).

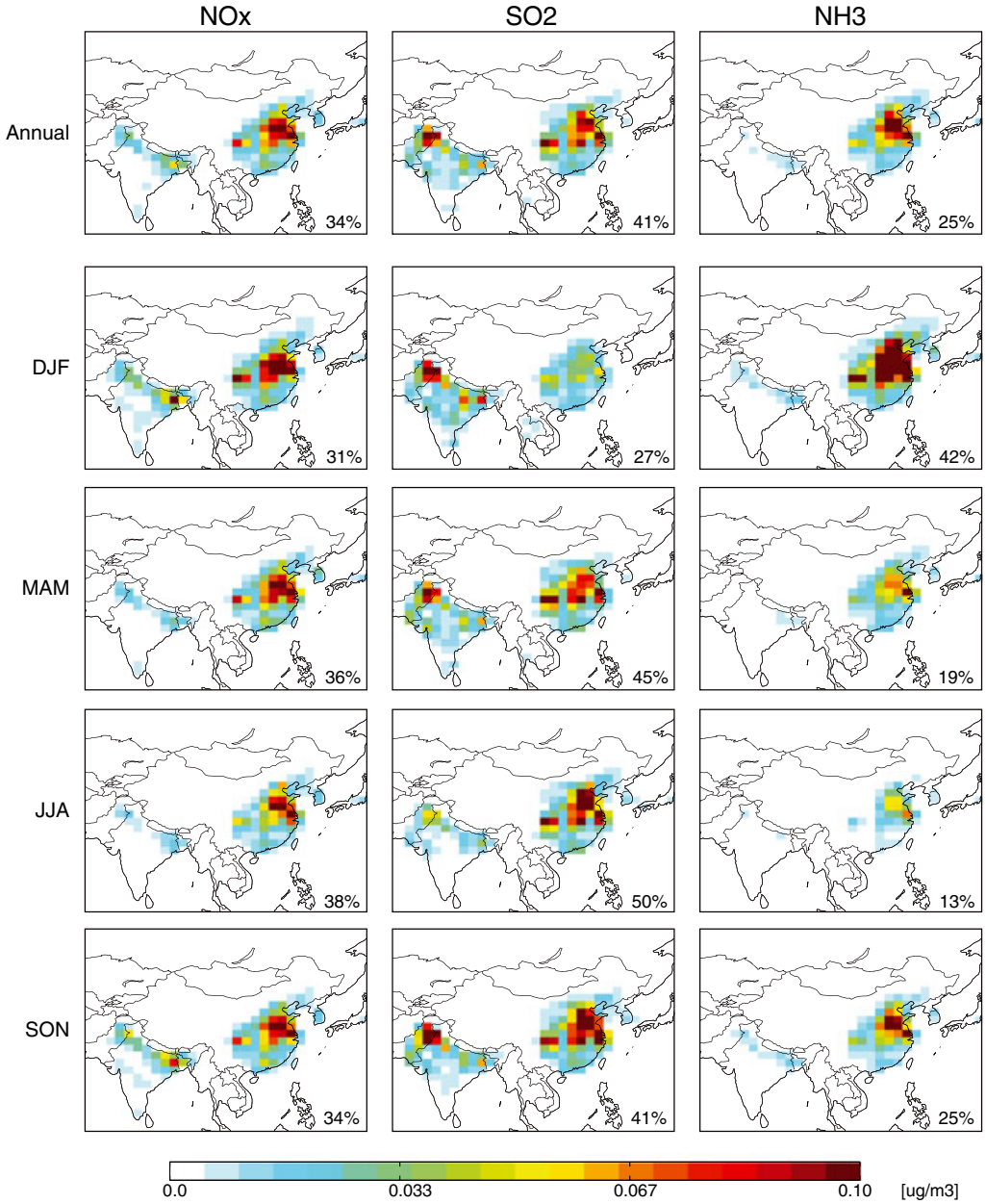

Figure 4. Adjoint model sensitivities of the domain wide population-weighted secondary inorganic aerosol surface concentration with respect to NO_x, SO_2, and NH_3 emissions. The percentages listed on each plot represent the effect of the specific emission investigated in the plot as compared to the total effect of all emissions in a particular season, or annually.

found a NO_3^-/SO_4^{2-} ratio of 0.64 ± 0.57 in Beijing (40.32°N, 116.32°E) and 0.21 ± 0.16 in Chongqing (29.56°N, 106.53°E) for 2006. This is consistent with the values of 0.77 and 0.32 in our simulation for the same locations and time period.

[9] The remaining columns of Figure 2 show the absolute difference in sulfate-nitrate-ammonium mass concentrations due to 10% increases in NO_x, SO_2, and NH_3 emissions. As expected, secondary inorganic aerosol is most sensitive to SO_2 emissions during most of the year [*Wang et al.*, 2012a, 2012b]. In winter, secondary inorganic aerosol is most sensitive to NH_3 emissions [*Wang et al.*, 2011; *Wang et al.*, 2012a, 2012b]. However, secondary inorganic aerosol remains sensitive to NO_x emissions in all seasons. In the annual mean, secondary inorganic aerosol is nearly as sensitive to NO_x emissions as to SO_2 emissions. The persistent sensitivity to NO_x arises from the availability of excess NH_3 as calculated from the molar ratio of $(NH_3 + NH_4^+)/2 \times SO_4^{2-}$. *Wang et al.* [2011] similarly found that excess NH_3 is available to promote ammonium nitrate formation if NO_x emissions increase in the North China Plain and Yangtze River Delta. The sensitivity to NO_x is weakest in winter when ammonium nitrate formation is more often NH_3 limited on certain days.

[10] Figure 3 shows the effect on each inorganic ion of changing emission sources. Over China, increasing SO_2 emissions increases SO_4^{2-} at the expense of NO_3^- and increasing NH_3 efficiently increases NO_3^-. Increasing NO_x emissions increases NO_3^- over China and to a lesser extent over India. Increasing NO_x emissions also slightly increases SO_4^{2-} by increasing regional oxidant concentrations.

[11] Figure 4 further quantifies the population-weighted sensitivities using the adjoint model simulation. The population-weighted sensitivities show the amount by which the population-weighted $PM_{2.5}$ concentrations would change per fractional change in emissions at each location. The sensitivities are consistent with forward model sensitivity simulations. We find that annual mean population-weighted secondary inorganic aerosol over the entire domain is notably sensitive to NO_x emissions (34%) compared to SO_2 (41%) and NH_3 (25%) emissions. While the relative sensitivity of inorganic aerosol over China to NO_x is similar (33%) to that over India (32%), the absolute impact of NO_x on inorganic aerosol over China is much greater (Figures A2 and A3), reflecting a combination of low temperatures over China that favor condensed phase ammonium nitrate, and comparatively less NO_x over India leading to low nitrate formation. The high degree of neutralization of aerosol over India prevents additional SO_2 from displacing NO_3^- as shown in Figure 3.

[12] The sensitivity of inorganic aerosol to NO_x emissions depends on the NH_3 source. NH_3 emissions are considerably more uncertain than emissions of SO_2 or NO_x [*Streets et al.*, 2003]. Figure A1 compares the modeled GEOS-Chem NH_3 column with IASI satellite retrievals [*Clarisse et al.*, 2009]. As described in *Heald et al.* [2012], these retrievals have low degrees of freedom for signal that makes model evaluation challenging. Nonetheless, after accounting for the influence of the retrieval a priori NH_3 profile, these retrievals provide evidence that the GEOS-Chem NH_3 emissions used here are unlikely to be overestimated, except perhaps for North China in summer. Over South Asia and to a lesser extent over East Asia, NH_3 retrieved from the TES satellite instrument tends to be higher than simulated with a different GEOS-Chem simulation that had higher, yet aseasonal, NH_3 Asian emissions [*Shephard et al.*, 2011]. *Meng et al.* [2011] indicate that there is a large urban NH_3 source in Beijing that may be underestimated. Thus, the sensitivity of inorganic aerosol to NO_x emissions could be even larger than found here.

[13] We repeat the forward model sensitivity simulations with the projected emissions for 2020 using Intergovernmental Panel on Climate Change representative concentration pathways (RCPs) averaged over all four RCPs [*Moss et al.*, 2010]. The projected emissions of NO_x increase by 39% for India and by 29% for China. SO_2 emissions increase by 15% for China and 48% for India. NH_3 emissions increase by 25% for India and remain within 19% for China. The relative sensitivity of secondary inorganic aerosol to precursors persists to within 1% for the 2020 emission scenario. The increase in SO_2 emissions in the RCP inventory is unlikely, because China's recent control measures have reduced national SO_2 emissions by 11% between 2005 and 2010 [*Zhang et al.*, 2012] and additional 8% reduction target has been set up for 2010–2015 (http://zfs.mep.gov.cn/fg/gwyw/201109/t20110907_217069.htm). Stronger controls on SO_2 emissions [e.g., *Wang et al.*, 2012a, 2012b] would further increase the relevance of NO_x emissions.

4. Conclusions

[14] In summary, NO_x emissions are, and could continue to be, a major contributor to secondary inorganic aerosol over East Asia. In addition to ongoing efforts to reduce SO_2 emissions for East Asia, concurrent decreases in NO_x and NH_3 (especially in winter) emissions are needed to reduce aerosol concentrations.

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