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

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Abstract

Atmospheric concentrations of inorganic gases and aerosols (nitrate, sulfate, and ammonium) are simulated for 2009 over the United States using the chemical transport model GEOS-Chem. This work is motivated, in part, by the inability of previous modeling studies to reproduce observed high nitrate aerosol concentrations in California. Nitrate aerosol concentrations over most of the US are over-predicted relative to Inter-agency Monitoring of Protected Visual Environments (IMPROVE) and Clean Air Status and Trends Network (CASTNET) data. In California, on the other hand, nitrate and ammonium are under-predicted as compared to California Air Resources Board (CARB) measurements. Over-prediction of nitrate in the East and Midwest is consistent with results of recent studies, which have suggested that nighttime nitric acid formation by heterogeneous hydrolysis of N_2O_5 is over-predicted with current values of the N_2O_5 uptake coefficient, γ , onto aerosols. Accordingly, the value of γ is reduced here by a factor of 10. Despite this, predicted nitrate levels in the US Midwest remain higher than those measured and over-prediction of nitrate in this region remains to be explained. Data from the Infrared Atmospheric Sounding Interferometer (IASI) onboard the MetOp-A satellite indicate the presence of a strong ammonia maximum in central and southern California that is not present in the simulations, which are based on the EPA National Emissions Inventory (NEI) NH_3 emission inventory. In order to predict ammonia columns similar to the satellite measurements in the San Joaquin Valley, CA and Riverside, CA, the current ammonia emission inventory in California would need to be increased substantially. Based on the sensitivity of ammonium nitrate formation to the availability of ammonia, the present results suggest that under-prediction of ammonia emissions is likely the main cause for the under-prediction of nitrate aerosol in California.

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1 Introduction

Nitrate (NO_3^-), sulfate (SO_4^{2-}) and ammonium (NH_4^+) are major constituents of atmospheric aerosols. These species are formed primarily from chemical reactions in the atmosphere involving the gas-phase precursors, nitrogen oxides (NO_x), sulfur dioxide (SO_2) and ammonia (NH_3). In this work, we use the global chemical transport model GEOS-Chem to simulate nitrate, sulfate and ammonium aerosols over the United States and we compare model predictions with measurement data to assess model performance. This work is motivated, in part, by previous studies (Pye et al., 2009; Bauer et al., 2007; Myhre et al., 2006) that indicated that observed high nitrate levels in California have not been simulated adequately by global chemical transport models. In a recent GEOS-Chem simulation over the US, Zhang et al. (2012) found that although predictions of the gas-phase precursor NO_x agreed well with satellite measurements, predicted HNO_3 and nitrate aerosol had strong positive biases throughout most of the country.

We note the study of Heald et al. (2012), completed at the same time as this work, which addresses some of the same issues and reports similar results as those presented here. That two independent pieces of work arrive at essentially the same conclusions gives added weight to the results of both studies.

2 GEOS-Chem model

Atmospheric concentrations of aerosols and gas-phase species are simulated using the chemical transport model GEOS-Chem, version 9-01-02 (<http://acmg.seas.harvard.edu/geos/>). A nested version of the model (Chen et al., 2009) is used, on a $1/2^\circ$ (longitude) by $2/3^\circ$ (latitude) horizontal grid over North America (Fig. 1), with 47 vertical levels, nested within a global parent grid at $2^\circ \times 2.5^\circ$ horizontal resolution. The calendar year 2009 is simulated, with a spin-up period of one year. The model is driven by Goddard Earth Observing System (GEOS-5) assimilated meteorological fields from

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NASA's Global Modeling and Assimilation Office (GMAO). Meteorological data include winds, temperature, humidity, cloud fraction, precipitation and other fields at a 6-h temporal resolution, as well as mixed layer depth and surface properties at a 3-h temporal resolution.

Data from the EPA National Emissions Inventory (NEI) 2005 on emissions of NO_x , SO_2 , NH_3 , CO and volatile organic compounds (VOCs) were scaled to the simulation period according to trends in the EPA Acid Rain Program (<http://camddataandmaps.epa.gov/gdm/>) and the NEI Air Pollutant Emissions Trends Data (<http://www.epa.gov/ttn/chief/trends/>). Additional NO_x and SO_2 emission sources include aircraft, biofuel, and biomass burning, as well as emissions of NO_x from lightning, soil and fertilizer, and sulfur emissions from ships, volcanoes and oceans (Park et al., 2004). Natural emission sources of ammonia include soil, vegetation and oceans, as described by Bouwman et al. (1997).

The model includes a detailed ozone- NO_x -VOC gas-phase chemical mechanism involving approximately 80 species and 300 chemical reactions (Bey et al., 2001). Sulfate formation pathways include gas-phase oxidation of SO_2 by OH and aqueous-phase oxidation of SO_2 by ozone and hydrogen peroxide. Gas-phase sulfur chemistry also includes oxidation of dimethyl sulfide (DMS) by OH to form SO_2 and methanesulfonic acid, and oxidation of DMS by NO_3 to form SO_2 (Park et al., 2004). The partitioning between gas-phase and aerosol-phase nitrate, sulfate and ammonium is computed using ISORROPIA II (Fountoukis and Nenes, 2007), a thermodynamic equilibrium model for the K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosol system, implemented within GEOS-Chem.

Removal of nitrate, sulfate, ammonium and related gas-phase species through wet deposition and dry deposition is simulated. The wet deposition scheme includes scavenging of aerosols and soluble gases in wet convective updrafts, in-cloud scavenging by cloud droplets or ice crystals, and below-cloud scavenging by precipitation (Liu et al., 2001). Dry deposition is simulated with a resistance in series scheme (Weseley, 1989),

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with surface resistances for sulfate, nitrate and ammonium aerosols as described by Zhang et al. (2001).

Zhang et al. (2012) suggest that nitrate concentrations may be over-predicted owing to an overestimate of nighttime nitric acid formation through heterogeneous N_2O_5 hydrolysis, $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$, as N_2O_5 concentrations build up due to the gas phase reaction of NO_2 with NO_3 . The rate of HNO_3 production by this reaction is expressed as $2k[\text{N}_2\text{O}_5]$, where $k = \gamma v_{\text{N}_2\text{O}_5} A_{\text{Aerosol}}/4$ and $v_{\text{N}_2\text{O}_5}$ is the mean molecular speed of N_2O_5 , A_{Aerosol} is the aerosol surface area per unit volume, and γ is the uptake coefficient, which describes the probability that an N_2O_5 molecule impacting an aerosol particle will undergo the irreversible heterogeneous hydrolysis reaction (Seinfeld and Pandis, 2006).

Macintyre and Evans (2010) list the range of published values for γ as 10^{-4} to > 0.1 . They note that recent laboratory studies indicate lower values than previously considered, and suggest that the tropospheric value is likely in the range of 0.001 to 0.02. In a sensitivity analysis with GEOS-Chem, they find that within this range of values, the production of HNO_3 in the model is highly sensitive to the selected value of γ .

Figure 2 shows the values of γ used in the standard version of GEOS-Chem, for the various types of aerosols on which heterogeneous N_2O_5 hydrolysis is simulated. The uptake coefficient on sulfate aerosol is determined in GEOS-Chem as a function of temperature and relative humidity. For temperatures of 282 K and below, γ at a given RH is assumed to be independent of temperature; for temperatures above 282 K, γ at a given RH decreases with increasing temperature. It is evident in Fig. 2 that the value of γ is above 0.02 for organic carbon and sea salt aerosol, and well above 0.02 for sulfate aerosol at higher humidities, exceeding 0.1 at lower temperatures and high RH. Based on the recommendations of Macintyre and Evans (2010), the values of γ in GEOS-Chem likely lead to an overestimate of nighttime HNO_3 formation, with a corresponding overestimate of nitrate aerosol production. Following the approach of Zhang et al. (2012), we have reduced γ by a factor of 10 in the present GEOS-Chem simulations,

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in order to simulate nighttime nitric acid formation using an uptake coefficient more consistent with Macintyre and Evans (2010).

3 Surface-level atmospheric data

GEOS-Chem simulations are compared to measured aerosol concentrations for 2009 from three data sources: the Interagency Monitoring of Protected Visual Environments (IMPROVE, <http://views.cira.colostate.edu/web/DataWizard/>), the Clean Air Status and Trends Network (CASTNET, <http://views.cira.colostate.edu/web/DataWizard/>) and the California Air Resources Board (CARB, <http://www.arb.ca.gov/aqmis2/aqmis2.php>). Table 1 summarizes the sampling frequency and measured species in each dataset. Locations of the measurement sites are shown in Fig. 1.

The CARB dataset includes sulfate and nitrate concentrations measured by both PM_{10} and $\text{PM}_{2.5}$ samplers. Since the GEOS-Chem aerosol predictions are not size resolved (total particulate matter, TPM), the larger particulate size fraction is preferred for comparison with model predictions. However, the CARB PM_{10} nitrate measurements are affected by a negative sampling artifact due to volatilization of nitrate from the Teflon filters used in the PM_{10} samplers, whereas the CARB $\text{PM}_{2.5}$ samplers are equipped with reactive substrates to collect species volatilized from the inert filters, thereby minimizing volatilization losses. Since reported $\text{PM}_{2.5}$ nitrate concentrations frequently exceed the PM_{10} concentrations in the CARB measurements, $\text{PM}_{2.5}$ nitrate was selected as the most representative CARB dataset for comparison with model predictions. Sulfate PM_{10} measurements are not affected by volatilization losses; thus, the CARB PM_{10} sulfate was used for comparison with predicted sulfate.

4 Results

Figure 3 shows the predicted seasonal average concentrations of nitrate, sulfate and ammonium aerosol at the surface level. Predicted annual concentrations are compared

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with measurements over the entire US in Fig. 4 and over California in Fig. 5. Scatter plots of predicted versus measured annual concentrations are shown in Fig. 6. The normalized mean biases (NMB) of predicted seasonal and annual concentrations are summarized in Table 2, where $NMB = (\sum(P_i - O_i) / \sum O_i) \times 100\%$, where P_i is the predicted and O_i the observed seasonal average concentration, and the summation is over all measurement sites.

Predicted sulfate concentrations are in reasonable agreement with IMPROVE and CASTNET measurements (Fig. 6). Compared with the California CARB measurements, sulfate concentrations are under-predicted; however this is over a rather narrow range of measured concentrations. There is substantial over-prediction, by factors of approximately 3.5 and 2, respectively, in the predicted nitrate and ammonium aerosol concentrations relative to the IMPROVE and CASTNET measured values (Fig. 6). The bias in nitrate predictions in the eastern and midwestern states has a significant seasonal variation, with the highest overprediction in the summer (Table 2). On the other hand, in California, there is a substantial under-prediction of nitrate and ammonium concentrations.

Over-prediction of nitrate in the eastern and midwestern states in this study is consistent with results found by Zhang et al. (2012), who suggest that GEOS-Chem may over-predict nitrate concentrations owing to an overestimate of nighttime nitric acid formation through heterogeneous N_2O_5 hydrolysis. However, the reduction of the N_2O_5 uptake coefficient, γ , by a factor of 10 in the current simulation did not reduce substantially the nitrate bias compared with another identical simulation (results not shown) using the standard GEOS-Chem values for γ : the NMB in predicted annual nitrate is +296% (Table 2) when γ is reduced by a factor of 10, compared with an NMB of +321% when the standard γ values are used. These results suggest that an overestimate of heterogeneous N_2O_5 hydrolysis does not fully account for the nitrate bias and over-prediction of nitrate in the US Midwest remains to be explained.

Figure 7 shows predicted and measured inorganic aerosol concentrations at Bondville, IL, in the region of highest predicted nitrate concentrations in the Midwest,

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and at Fresno, CA and Riverside, CA. Table 3 summarizes the normalized mean biases of the predicted monthly concentrations at these three sites, relative to each available measurement dataset. At the California sites, predicted nitrate concentrations are below measured concentrations throughout most of the year, with substantial under-prediction particularly in the winter, whereas the predicted nitrate concentrations at Bondville exceed the measured concentrations throughout the year. At all three sites, predicted sulfate concentrations agree reasonably well with measured concentrations in magnitude and in the pattern of seasonal variation over the course of the year. At Fresno, predicted ammonium concentrations agree well with measurements except in the winter when predictions are very low compared to measured concentrations. Predicted ammonium concentrations are well below measured concentrations at Riverside throughout the year, and are above measured concentrations at Bondville throughout the year.

4.1 Nitrate under-prediction in California

Given the findings discussed in the previous section, it is unlikely that the under-prediction of nitrate in California is the result of an underestimate of HNO_3 production. Indeed, predicted HNO_3 concentrations in California are among the highest in the country (Fig. 8).

Figure 9 shows the partitioning between aerosol and gas-phase nitrate and ammonium predicted concentrations at the Bondville, Fresno, and Riverside sites. At both California sites, a large fraction of the predicted total inorganic nitrate is in the form of gas-phase nitric acid. Thus, availability of total inorganic nitrate does not appear to be the limiting factor in the production of nitrate aerosol in California; either the thermodynamic partitioning between the gas and aerosol phases or the removal of atmospheric HNO_3 is the limiting factor.

The formation of nitrate aerosol is dependent on the thermodynamic equilibrium between gas-phase ammonia and nitric acid with solid or aqueous ammonium nitrate. As noted previously, there is a substantial under-prediction of ammonium aerosol in

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California, indicating that availability of ammonia may be a factor in the low nitrate predictions.

We conducted a sensitivity analysis with GEOS-Chem, simulating the month of January 2009 with anthropogenic emissions of ammonia increased by a factor of two and by a factor of ten. Analysis of predicted hourly nitrate concentrations at Fresno and Riverside indicates significant sensitivity to ammonia availability, particularly at Riverside (Fig. 10). In the simulation with ammonia emissions doubled, the January 2009 monthly mean predicted nitrate concentrations are 1.33 and 2.04 times the standard model predictions at Fresno and Riverside, respectively. In the simulation with ammonia emissions increased tenfold, the January 2009 monthly mean predicted nitrate concentrations are 1.88 and 7.61 times the standard model predictions at Fresno and Riverside, respectively.

The large uncertainties in the ammonia emissions inventory and seasonal scaling factors used in GEOS-Chem could potentially result in a substantial underestimate of ammonia emissions and concentrations, along with a corresponding underestimate of nitrate aerosol if the conditions are ammonia-limited. In their study of aircraft data from the CalNex 2010 experiment, Nowak et al. (2012) found that ammonia emissions from dairy facilities in Southern California have a significant effect on nitrate aerosol formation, shifting the NH_4NO_3 equilibrium towards the particle phase and resulting in higher nitrate aerosol concentrations downwind of the dairy facilities. They also compared the CalNex aircraft data to NEI 2005 and CARB-ARCTAS 08 (Huang et al., 2010) emissions inventories of ammonia in the South Coast Air Basin and found that both emissions inventories underestimate ammonia emissions relative to emissions estimates derived from the aircraft data. In the NEI 2005 inventory, ammonia emissions from automobiles and dairy facilities in this region are 38 and 1 metric tonnes per day, respectively, compared to 56 and 11 tonnes per day, respectively, in the CARB-ARCTAS 08 inventory. Both these estimates are much lower than the emissions estimates derived by Nowak et al. (2012) from CalNex, of 38 to 86 tonnes per day from automobiles and 33 to 176 tonnes per day from dairy facilities.

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4.2 Satellite measurements of ammonia

To investigate the extent to which ammonia emissions in GEOS-Chem might be underestimated, predictions are compared to satellite measurements of ammonia from the Infrared Atmospheric Sounding Interferometer (IASI) (Clerbaux et al., 2009). IASI is a Fourier transform spectrometer onboard the MetOp-A satellite, which provides global coverage twice a day, with overpass times of 9:30 and 21:30 mean local solar time. The spectrometer measures infrared radiation, and NH_3 concentrations are retrieved using inverse methods (Clarisse et al., 2009, 2010). Vertical columns of ammonia over the US are available for the morning overpasses for the period 1 April to 30 November 2009, which overlaps with the GEOS-Chem simulation period. Ammonia columns are not available in the winter months due to insufficient ammonia sensitivity in the satellite measurements during these months.

To compare GEOS-Chem predictions with IASI satellite measurements, the GEOS-Chem predicted ammonia concentrations are integrated vertically over the model pressure levels to obtain vertical column concentrations. In this integration, all vertical levels in the model are weighted equally, because reliable satellite averaging kernels were not available, so the comparison with the satellite columns is approximate. However, a qualitative comparison of the columns is useful to investigate the predictions in California compared to the rest of the US. And in California in particular, where we perform a more detailed comparison, the satellite averaging kernels do not vary greatly and have fairly uniform sensitivity between 0 and 2 km (Clarisse et al., 2010), where the majority of the atmospheric ammonia is located; thus the error associated with an equal vertical weighting is not expected to be important.

Figure 11 shows predicted April–November average ammonia columns from GEOS-Chem and the April–November averages of the 9:30 a.m. measured concentrations from IASI. For this comparison, the satellite data were gridded onto the GEOS-Chem grid by averaging all the satellite measurements within a grid box each month to obtain monthly averages on the GEOS-Chem grid, and then averaging these monthly gridded

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measurements to obtain an April–November average. A large maximum in ammonia is evident in Central and Southern California in the satellite measurements, with concentrations exceeding those for the rest of the US. This strong NH_3 maximum is not present in the GEOS-Chem predictions: the predicted maximum in Central California is not significantly higher in magnitude, for example, than that in the Midwest. The satellite-model comparison indicates a large underestimate of ammonia concentrations in California. Figure 12 compares the monthly averages of the predicted 9:00–10:00 a.m. ammonia columns from GEOS-Chem with the monthly averages of the 9:30 a.m. ammonia columns measured by IASI in the San Joaquin Valley (SJV), between Fresno and Bakersfield, and at Riverside. Both sites show a large underprediction of ammonia columns throughout the year, as compared to the satellite measurements. Comparison of monthly columns at other sites in the SJV, such as Fresno and Sacramento, yields similar results. In order to obtain ammonia columns similar to the satellite measurements at SJV and Riverside, the ammonia emissions in GEOS-Chem would need to be increased by approximately 300 % and 320 %, respectively.

Based on the sensitivity of ammonium nitrate formation to the availability of ammonia, the present results, which are consistent with those of Nowak et al. (2012) and Heald et al. (2012), suggest that under-prediction of ammonia emissions is likely the main cause for the under-prediction of nitrate aerosol in California.

5 Conclusions

Atmospheric chemical transport models (ACTMs) provide a powerful means to evaluate the extent to which predicted atmospheric gas and particle concentrations based on an assumed emission inventory agree with those actually observed. Prediction of aerosol levels over the US is a subject of intense interest, owing to efforts to achieve compliance with air quality standards and to assess the extent to which air quality is affected by long-range transport beyond the US border. Previous ACTM simulations of aerosol levels have exhibited mixed success in terms of agreement between predicted

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and observed concentrations. When predictions and observations do not agree, assessing the cause of the discrepancy may not be entirely straightforward, as both the emission inventory and representation of atmospheric processes may be implicated. The present study addresses the prediction of aerosol nitrate, sulfate, and ammonium levels over the US for 2009. Lack of agreement between observed and predicted levels can be traced to both emission inventory inaccuracies as well as model representation of nighttime nitric acid formation. The GEOS-Chem model employed here is the most widely used ACTM worldwide. The present study, and others like it, is valuable in pinpointing sources of model-measurement discrepancy and thereby lead to improvements in treatment of atmospheric processes and emission estimates.

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Table 1. Measurement datasets.

Dataset	Site locations	Sampling frequency	Species measured
IMPROVE	Remote/rural areas	24-h samples every 3rd day	Fine particulate (< 2.5 μm) sulfate and nitrate
CASTNET	Remote/rural areas	7-day samples	Total particulate (not size selective) sulfate, nitrate and ammonium, SO_2 (g), HNO_3 (g)
CARB	Mostly urban	24-h samples every 6 days	Fine particulate (< 2.5 μm) sulfate, nitrate, and ammonium; PM_{10} sulfate and nitrate

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Table 2. Normalized mean bias (%) of predicted seasonal concentrations relative to measurements (IMPROVE, CASTNET, CARB).

Season	USA excluding California			California		
	Sulfate	Nitrate	Ammonium	Sulfate	Nitrate	Ammonium
DJF	+0.5	+237	+105	-25	-57	-56
MAM	+16	+178	+80	-42	-37	-19
JJA	+28	+535	+91	-24	-11	-24
SON	+33	+479	+161	-43	-43	-26
Annual	+20	+ 296	+107	-34	-43	-26

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Table 3. Normalized mean bias (%) of monthly mean predicted concentrations at selected sites.

Aerosol species	Dataset	Fresno, CA	Riverside, CA	Bondville, IL
Nitrate	IMPROVE	-71	N/A	+143
	CARB (PM ₁₀)	-51	-64	N/A
	CARB (PM _{2.5})	-73	-67	N/A
	CASTNET	N/A	N/A	+120
Sulfate	IMPROVE	-25	N/A	+17
	CARB (PM ₁₀)	-27	-54	N/A
	CARB (PM _{2.5})	-19	-35	N/A
	CASTNET	N/A	N/A	+0.1
Ammonium	IMPROVE	N/A	N/A	N/A
	CARB (PM ₁₀)	N/A	N/A	N/A
	CARB (PM _{2.5})	-59	-59	N/A
	CASTNET	N/A	N/A	+67

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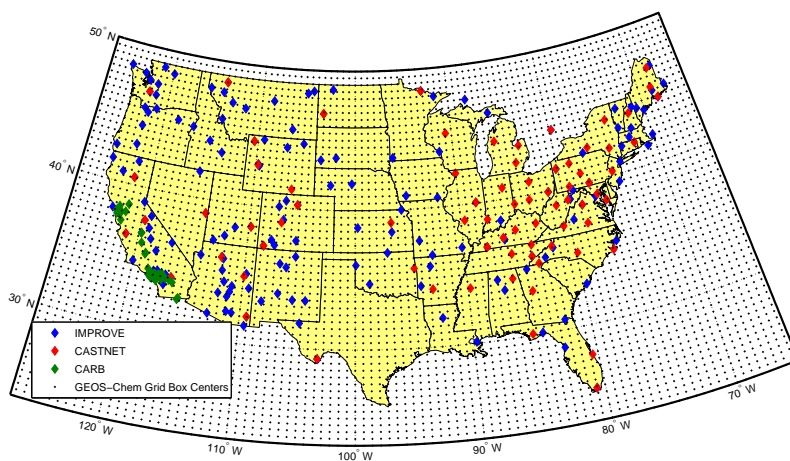


Fig. 1. Locations of IMPROVE, CASTNET, and CARB measurement sites, and GEOS-Chem grid box centers over the US.

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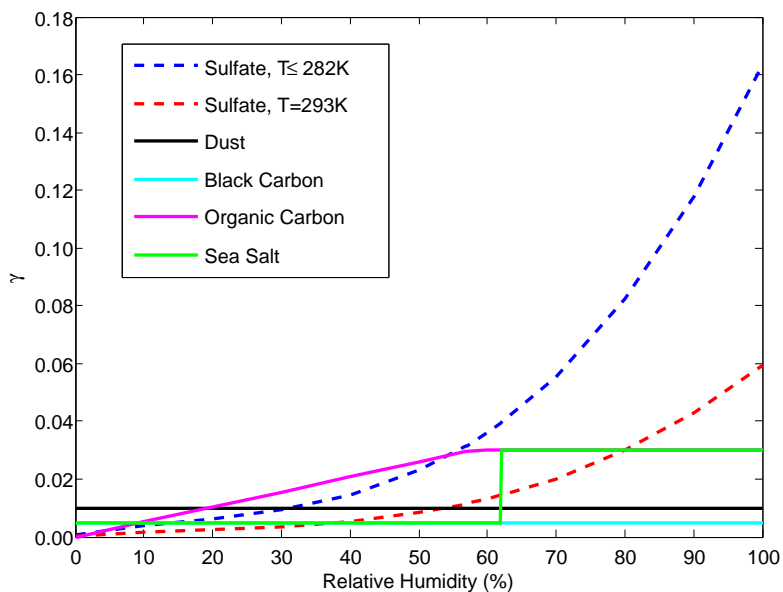


Fig. 2. Values of the N_2O_5 hydrolysis uptake coefficient γ in GEOS-Chem.

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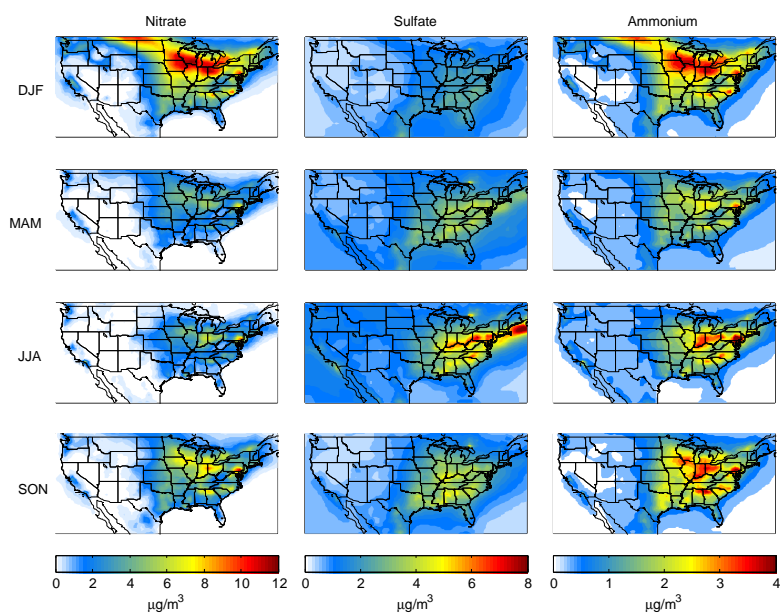


Fig. 3. Predicted concentrations of nitrate, sulfate and ammonium aerosol for 2009 December-January-February (DJF), March-April-May (MAM), June-July-August (JJA) and September-October-November (SON).

19518

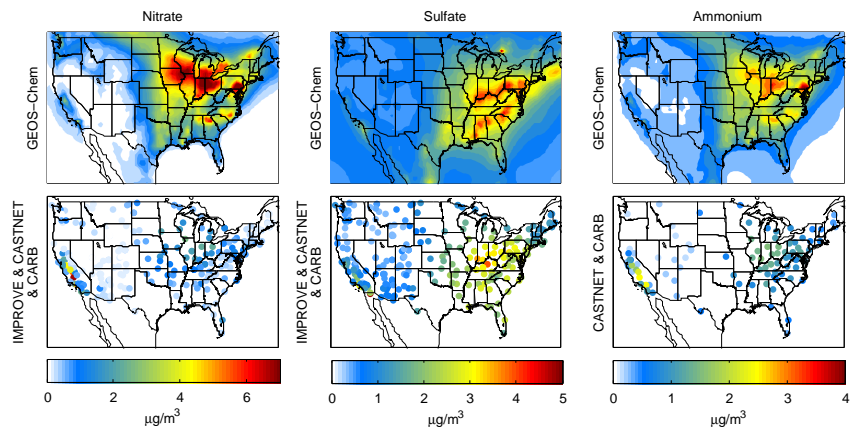


Fig. 4. Predicted 2009 annual mean concentrations compared with measured concentrations.

19519

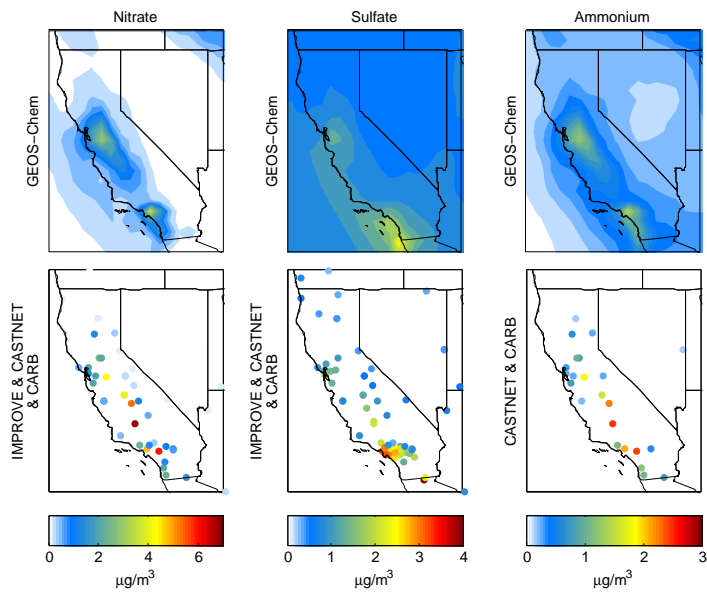


Fig. 5. Same as Fig. 4, but in detail for California.

19520

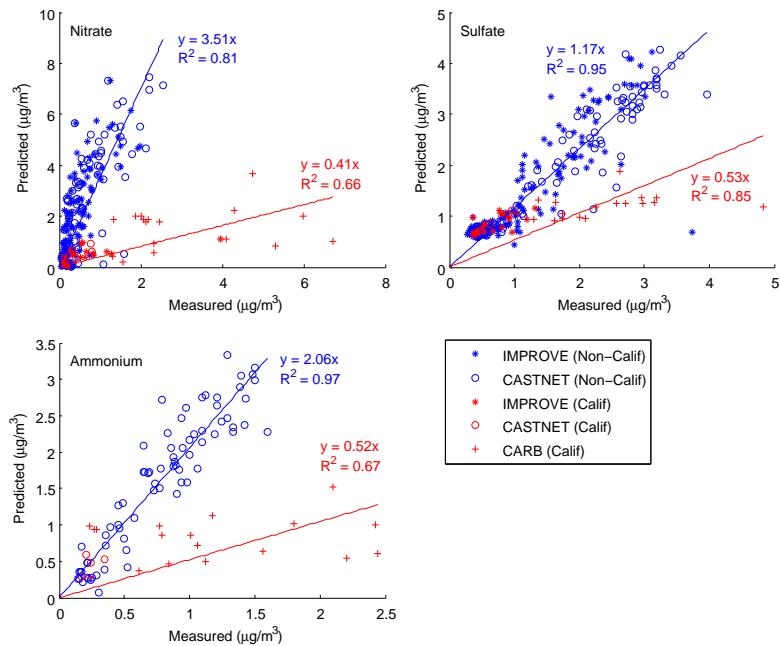


Fig. 6. Predicted versus measured annual mean concentrations. Each data point corresponds to an observed concentration at a measurement site along with the predicted concentration in the GEOS-Chem grid box containing the measurement site. Measured concentrations are IMPROVE ($\text{PM}_{2.5}$), CASTNET (TPM), and CARB ($\text{PM}_{2.5}$ for nitrate and ammonium, PM_{10} for sulfate). Red regression lines are for California sites only. Blue regression lines are for all sites excluding California. Coefficients of determination, R^2 , calculated for regression through the origin (Montgomery et al., 2006).

19521

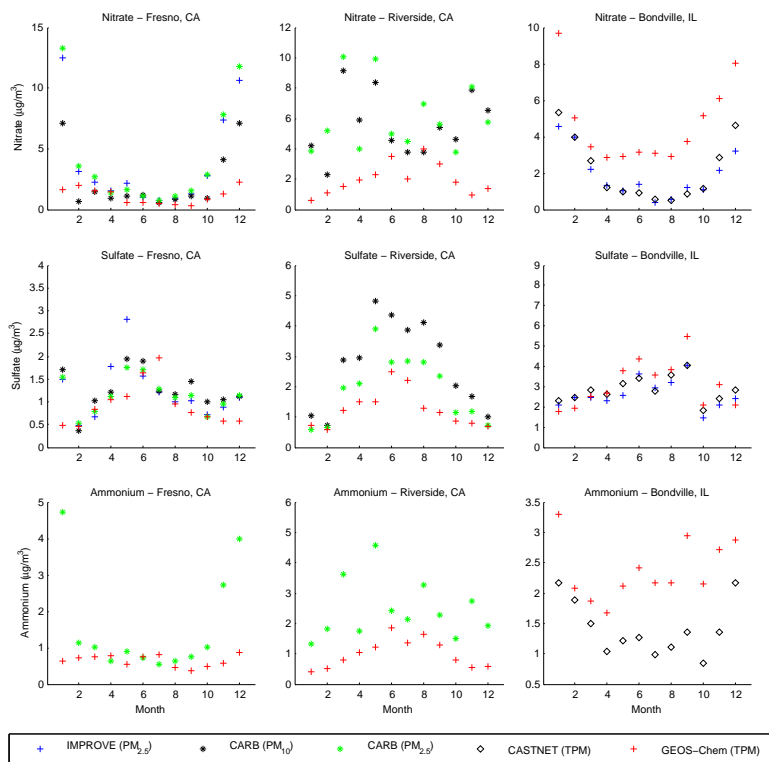


Fig. 7. Monthly mean predicted and measured aerosol nitrate, sulfate and ammonium concentrations at selected sites.

19522

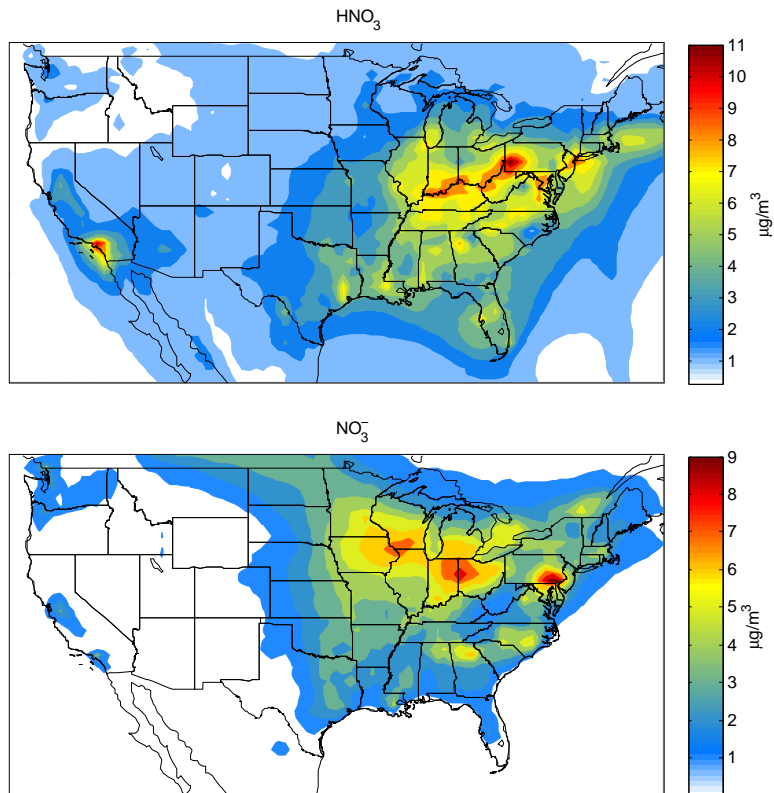


Fig. 8. Predicted annual mean concentrations of HNO₃ (upper panel) and nitrate aerosol (lower panel).

19523

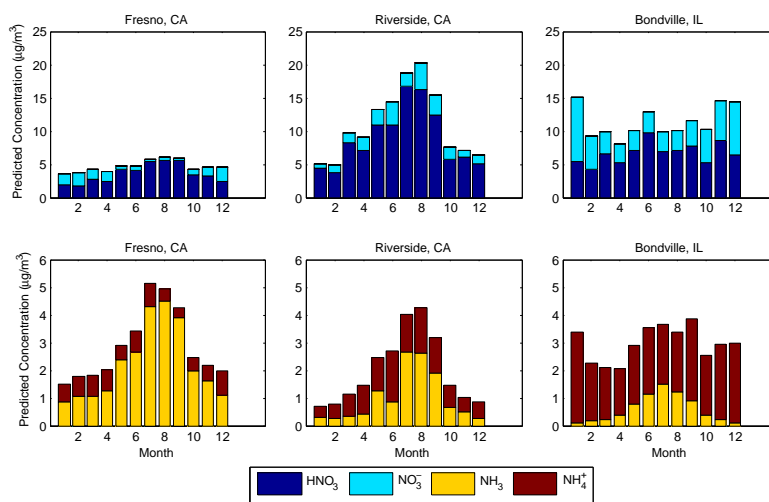


Fig. 9. Predicted monthly mean concentrations of gas-phase nitric acid, nitrate aerosol, gas-phase ammonia, and ammonium aerosol at selected sites.

19524

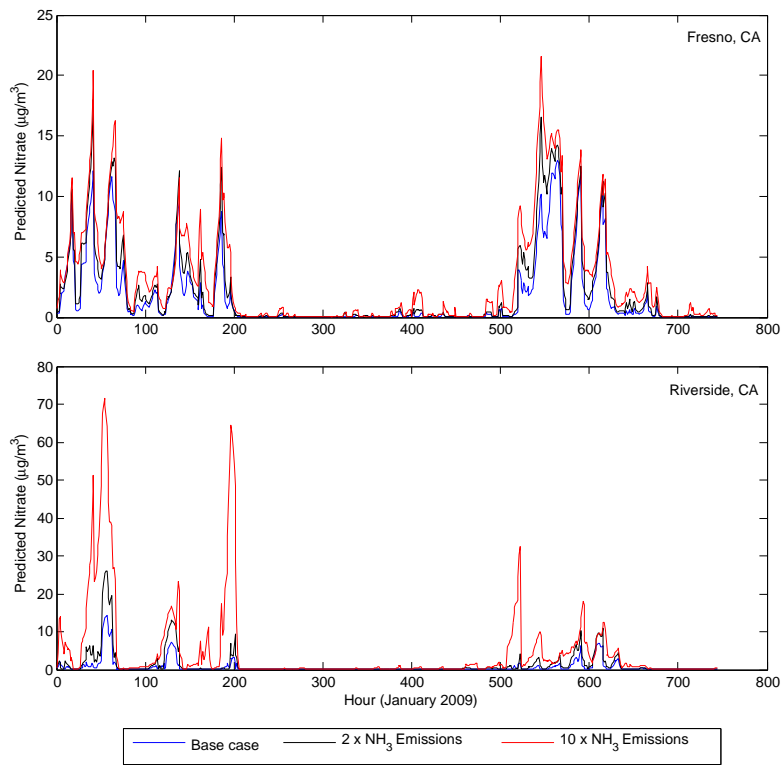


Fig. 10. Predicted hourly nitrate concentrations in ammonia sensitivity analysis.

19525

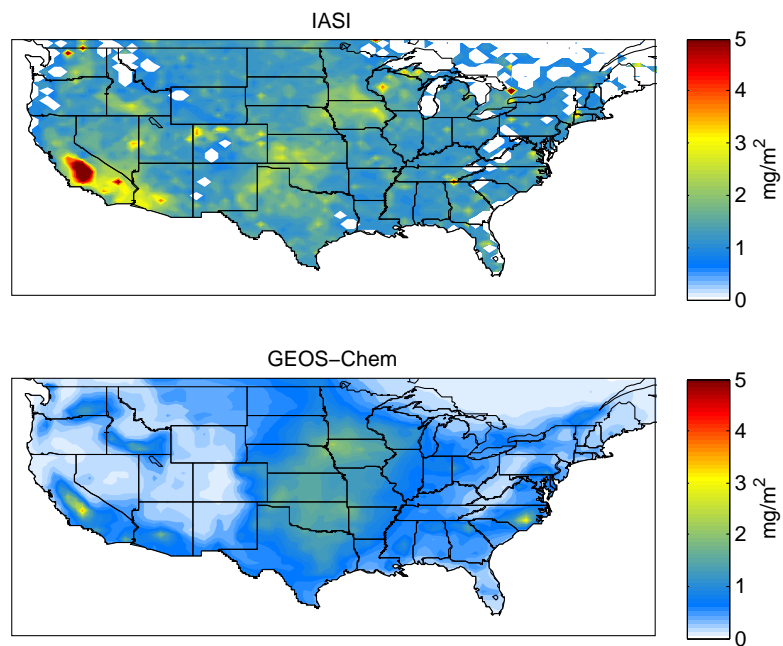


Fig. 11. Satellite-measured (IASI) and predicted April–November 2009 mean ammonia columns.

19526

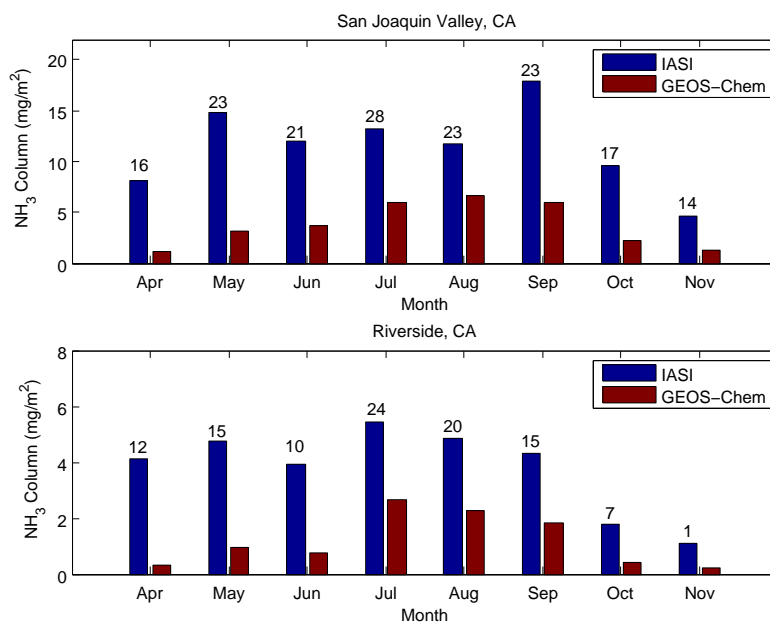


Fig. 12. Satellite-measured (IASI) and predicted monthly mean ammonia columns for April–November 2009 at a grid cell centered at 119.3°W, 36.0°N in the San Joaquin Valley, CA and at a grid cell centered at 117.3°W, 34.0°N in Riverside, CA. The number of IASI measurement days each month is indicated above each IASI monthly value.