

RESEARCH ARTICLE

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Key Points:

- Simulate effects of ammonia and fine PM formation on surface air quality
- Increasing livestock ammonia emissions reduces bias throughout California
- Surface PM peaks in winter in Central Valley with summer peak near LA

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An investigation of ammonia and inorganic particulate matter in California during the CalNex campaign

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Abstract Airborne observations from the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign in May and June 2010 are used to investigate the role of ammonia (NH₃) in fine particulate matter (PM_{2.5}) formation and surface air quality in California and test the key processes relevant to inorganic aerosol formation in the GEOS-Chem model. Concentrations of ammonia throughout California, sulfur dioxide (SO₂) in the Central Valley, and ammonium nitrate in the Los Angeles (LA) area are underestimated several-fold in the model. We find that model concentrations are relatively insensitive to uncertainties in gas-particle partitioning and deposition processes in the region. Conversely, increases to anthropogenic livestock ammonia emissions (by a factor of 5) and anthropogenic sulfur dioxide emissions in the Central Valley (by a factor of 3–10) and a reduction of anthropogenic NO_x emissions (by 30%) substantially reduce the bias in the simulation of gases (SO₂, NH₃, HNO₃) throughout California and PM_{2.5} near LA, although the exact magnitudes of emissions in the region remain uncertain. Using these modified emissions, we investigate year-round PM_{2.5} air quality in California. The model reproduces the wintertime maximum in surface ammonium nitrate concentrations in the Central Valley (regional mean concentrations are three times higher in December than in June), associated with lower planetary boundary layer heights and colder temperatures, and the wintertime minimum in the LA region (regional mean concentrations are two times higher in June than December) associated with ammonia limitation. Year round, we attribute at least 50% of the inorganic PM_{2.5} mass simulated throughout California to anthropogenic ammonia emissions.

1. Introduction

Atmospheric ammonia (NH₃) plays a key role in both the formation of fine particulate matter (PM_{2.5}) and in the biogeochemical cycling of nitrogen. Basic ammonia can act to neutralize the acidity of atmospheric acids, leading to the formation of inorganic aerosol (e.g., ammonium sulfate or ammonium nitrate). Understanding the formation of these aerosols is critical to addressing air quality issues, as exposure to particles has negative effects on human health [Pope *et al.*, 2009]. Aerosols can also impact climate, given their ability to adjust the energy budget of the planet through scattering and absorption of solar radiation and their role in cloud formation [IPCC, 2007]. Finally, the nitrogen contained in these aerosols can be transported and eventually deposited downwind, a particular concern for sensitive ecosystems [Beem *et al.*, 2010]. If nitrogen becomes oversaturated in the soil or aquatic ecosystems, environmental degradation through acidification and eutrophication may occur [Erisman *et al.*, 2007].

Prior to the development of industrial agriculture practices, the major sources of ammonia to the atmosphere included biomass burning, wild animals, and natural soils [Holland *et al.*, 1999]. Human population growth has increased the need for reliable food sources in the form of crops and livestock. The industrial production of ammonia as a fertilizer has increasingly supplied this need over the last century [Erisman *et al.*, 2008; Sutton *et al.*, 2008]. Thus, large agriculture operations now account for the majority of global ammonia emissions [Dentener and Crutzen, 1994]. These emission sources include fertilizers applied to plant crops and the waste

by-products of domesticated animals, particularly those raised in large feedlots. Other sources of ammonia include industrial manufacturing processes, the ocean, fossil fuel combustion, and automobile catalytic conversion [Bouwman *et al.*, 1997]. However, due largely to the challenges associated with in situ measurement of atmospheric ammonia [von Bobrotzki *et al.*, 2010] and local variations in emission control factors such as livestock diet and waste management and storage [Hristov *et al.*, 2011], uncertainties in these emissions and the subsequent transformations into the particle phase remain large.

Sulfur dioxide emitted into the atmosphere is oxidized to form sulfuric acid (H_2SO_4), which readily partitions to the aqueous phase, dissociating to produce sulfate (SO_4^{2-}). In the presence of atmospheric ammonia, a progression of salt formation occurs with increasing total ammonia levels: ammonium bisulfate to ammonium sulfate to fully neutralized ammonium sulfate. In higher relative humidity (RH) conditions and at lower total ammonia levels, the aerosol is more likely to stay in aqueous phase as a solution of component ions [Seinfeld and Pandis, 2006]. After all available sulfuric acid has been neutralized, the remaining ammonia can react with nitric acid (HNO_3) to form ammonium nitrate aerosol. Thus, ammonium nitrate formation generally occurs in areas of high ammonia and nitric acid and low sulfate concentrations. For ammonium nitrate, the gas and aerosol phases exist in equilibrium, dependent on temperature (T) and RH. Lower temperature and higher RH enhance partitioning to the aerosol phase. The phase of ammonium nitrate aerosol can vary between aqueous and solid as well, depending on the temperature, RH, and the history of RH (i.e., hysteresis of deliquescence). This thermodynamically coupled system, as well as the presence of additional species with displacement potential (e.g., NaCl, organic acids) in the same environment, complicates the formation and equilibrium of inorganic aerosol.

Much of California (CA) experiences high ambient concentrations of surface-level particulate matter. Both the Los Angeles (LA) Basin and the Central Valley are often in exceedance of the Environmental Protection Agency's (EPA) air quality standards for $\text{PM}_{2.5}$, which have been established to reduce the negative health effects caused by exposure to atmospheric particles. In particular, the 98th percentile of the 24 h $\text{PM}_{2.5}$ concentration in both regions exceeded the standard of $35 \mu\text{g m}^{-3}$ every year from 1999 to 2007 [Cox *et al.*, 2009]. The $\text{PM}_{2.5}$ in these areas of high human population and large agricultural production is largely composed of inorganic aerosol formed through acid-base neutralization, where urban centers are a source of ammonia and NO_x ($\text{NO} + \text{NO}_2$) from mobile sources, which mix with ammonia from fertilizer and animal waste in agriculturally productive areas. Ammonia emissions in California are some of the highest in the country [Goebeles *et al.*, 2003]. Sulfur dioxide is emitted from power generation and shipping near the coast. The topography of California also plays an important role in controlling $\text{PM}_{2.5}$ levels as the numerous valleys and mountain ranges allow for trapping and diversion of pollutants. Thus, it is particularly critical in California to understand inorganic $\text{PM}_{2.5}$ formation and the role of precursor emissions to achieve air quality compliance.

Observations made in the LA Basin show that inorganic $\text{PM}_{2.5}$ is formed from gas precursors in the urban core and that ammonia emissions from agriculture on the eastern side of the basin drive the conversion of nitric acid to nitrate downwind. Both emission of ammonia from volatilization and the transition of aerosol into the gas phase are more likely when temperatures are higher, such as due to daytime heating or during the summer months [Russell and Cass, 1986; Chow *et al.*, 1994; Neuman *et al.*, 2003; Nowak *et al.*, 2012]. Inorganic species are 50–60% of the $\text{PM}_{2.5}$ mass in the summer in the LA Basin and about 40% in the winter [Chow *et al.*, 1994; Hand *et al.*, 2012].

Although not as well studied, inorganic $\text{PM}_{2.5}$ formation in the Central Valley is becoming a larger concern as both human population and agriculture are currently growing at a rate higher than that in the LA Basin [Hall *et al.*, 2008]. The acidity of the region is determined by local sources, with complete neutralization of acids closer to high agricultural ammonia emissions sources [Jacob *et al.*, 1986; Chow *et al.*, 1996, 1998; Neuman *et al.*, 2003]. Clarisse *et al.* [2010] report summertime ammonia concentrations ranging from 10 to 20 ppb detected by the Infrared Atmospheric Sounding Interferometer (IASI) satellite instrument in the Central Valley. These ammonia concentrations are much larger than the 2 ppb observed outside the valley. Inorganic $\text{PM}_{2.5}$ makes up 25–35% of the total $\text{PM}_{2.5}$ here in the summer but 50% in the winter [Chow *et al.*, 1996; Hand *et al.*, 2012].

In this study, we use aircraft measurements made during the California Research at the Nexus of Air Quality and Climate Change (CalNex) campaign to investigate inorganic $\text{PM}_{2.5}$ formation and ammonia emissions in California as represented by the GEOS-Chem model. The CalNex observations are particularly valuable for investigating inorganic aerosol formation as both gas-phase precursors and speciated aerosol were measured in this campaign. This includes a rare characterization of vertically

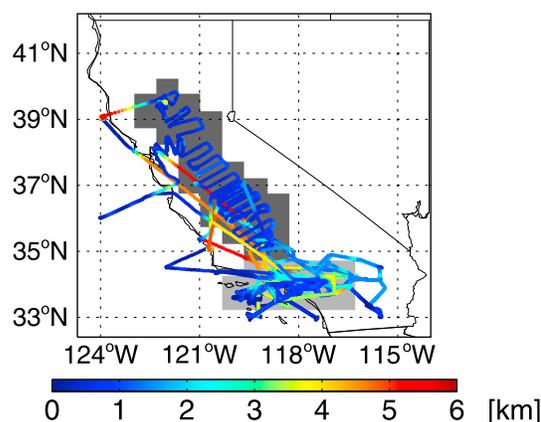


Figure 1. Location of 16 NOAA WP-3D flights during the CalNex field campaign (May–June 2010) used in this study, colored by aircraft altitude. Also shown are the two regions used in the analysis: Southern CA (shaded light gray) and the Central Valley (shaded dark gray).

distributed ammonia concentrations [Neuman *et al.*, 2003; Nowak *et al.*, 2012], which are challenging to measure in situ [von Bobrutski *et al.*, 2010] and are a critical element to fine PM formation in California.

2. CalNex Airborne Observations

The CalNex field study (www.esrl.noaa.gov/csd/projects/calnex/) took place during May and June 2010 in California and the nearby Pacific coastal waters [Ryerson *et al.*, 2013]. For this analysis, we use in situ observations from 16 NOAA WP-3D aircraft flights throughout California (flight tracks shown in Figure 1). Aircraft sampling was generally conducted below 6 km altitude, with much of the flight time dedicated to the lower troposphere. The majority of flight time (about 80%) also occurred during the day.

In this study, we use CalNex observations of both gas- and particle-phase inorganic species concentrations. Ammonia was measured by chemical ionization mass spectrometry (CIMS) [Nowak *et al.*, 2007, 2012] with an average uncertainty of $\pm(30\% + 0.2 \text{ ppb})$ (calibration uncertainty + measurement imprecision). This imprecision is determined from the variability in the periodic background measurements, which are interpolated for use in the calculation of the ambient concentration (total signal – background) at each measurement. Sulfur dioxide was measured by pulsed UV fluorescence [Ryerson *et al.*, 1998] with an uncertainty of $\pm(15\% + 0.5 \text{ ppb})$. Nitric acid was measured by CIMS [Neuman *et al.*, 2002] with an uncertainty of $\pm(15\% + 0.052 \text{ ppb})$. The sub-micron particle ions were measured by aerosol mass spectrometry (AMS) [Jayne *et al.*, 2000; Jimenez *et al.*, 2003; Bahreini *et al.*, 2009] with an average uncertainty of $\pm 30\%$. The aerosol concentrations are reported in $\mu\text{g sm}^{-3}$, where standard conditions are set to 1013.25 hPa and 0°C. The AMS nominally reports submicron aerosol mass concentrations [Liu *et al.*, 2007]; we note that this may represent an underestimate of fine aerosol mass when compared with the model simulation (see section 3). Gas-phase nitrogen oxides, NO and NO₂, were measured by ozone-induced chemiluminescence [Ryerson *et al.*, 2000; Pollack *et al.*, 2010] with an approximate uncertainty of $\pm 4\%$. The gas-phase species and meteorology parameters (T, RH) were reported at 1 s resolution and the particle ions at 10 s resolution. All observations are averaged to 1 min prior to analysis, and we retain only those minutes with valid measurements for all six of our key species (ammonia, nitric acid, sulfur dioxide, ammonium, nitrate, and sulfate). For comparison with the GEOS-Chem model, airborne CalNex observations are then gridded to the spatial and temporal resolution of the model (see section 3.1).

3. GEOS-Chem Model Simulation

3.1. General Description

The GEOS-Chem chemical transport model (www.geos-chem.org) is used to interpret the CalNex plane flight observations. GEOS-Chem is driven by assimilated meteorology from the NASA Global Modeling and Assimilation Office; here we use the GEOS-5 product. For this analysis, we perform a series of nested simulations of GEOS-Chem v9-01-01 over North America for 2010 at $0.5^\circ \times 0.667^\circ$ horizontal resolution with 47 vertical layers, typically seven layers within the lowest 1 km [Wang *et al.*, 2004; Chen *et al.*, 2009]. Boundary conditions are produced with the same version of the global model at $2^\circ \times 2.5^\circ$ horizontal resolution.

The sulfate-nitrate-ammonium aerosol system, coupled to gas-phase chemistry, is represented in GEOS-Chem [Park *et al.*, 2004]. Gas-aerosol phase partitioning of these species is described by the thermodynamic equilibrium model ISORROPIA II [Fountoukis and Nenes, 2007] and dependent on local temperature and RH conditions. The implementation of ISORROPIA II in GEOS-Chem assumes that the species exist on the upper, metastable branch of the hygroscopic hysteresis curve, a valid assumption in all regions where the RH regularly exceeds the deliquescence relative humidity [Pye *et al.*, 2009], see section 5.3 for further discussion. Gas and particle removal occurs via wet scavenging in convective and stratiform precipitation [Mari *et al.*, 2000;

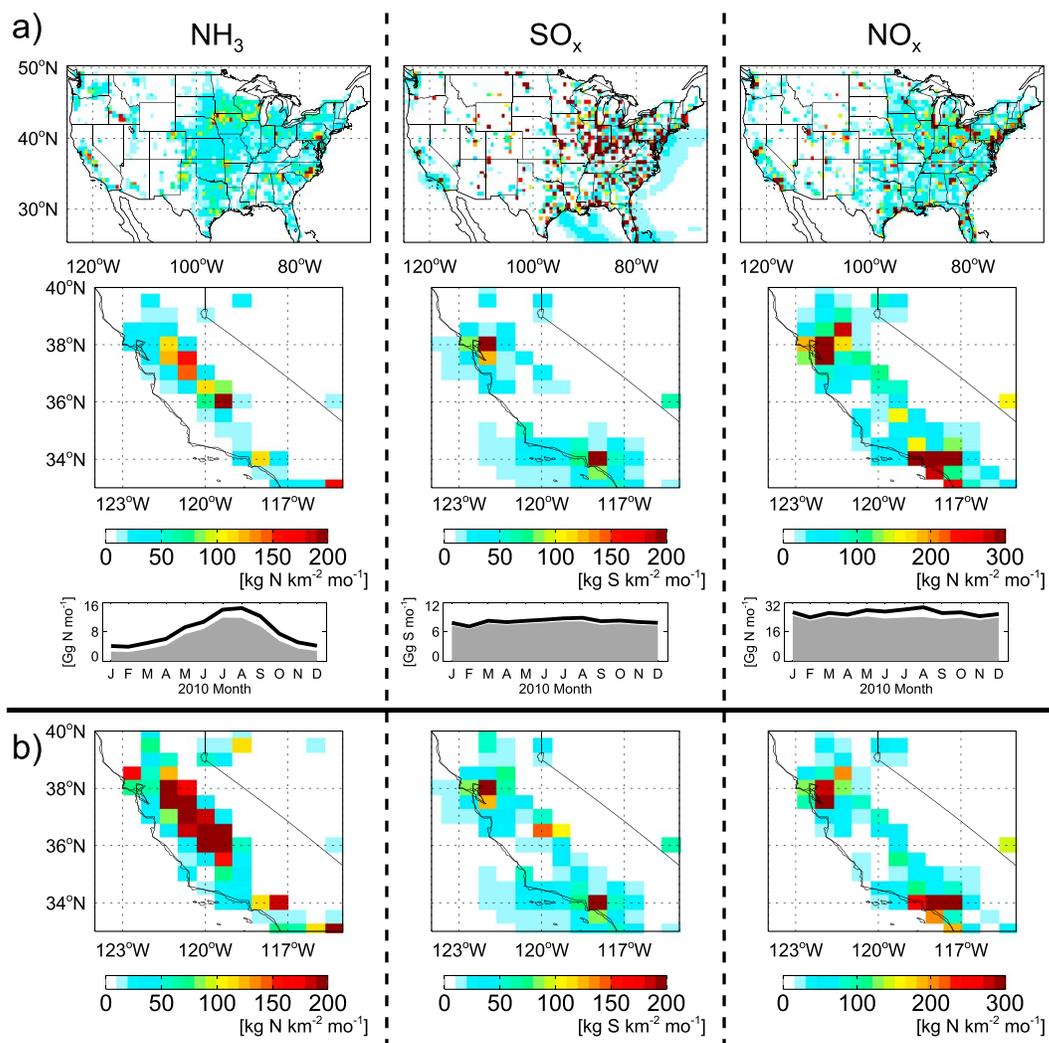


Figure 2. (a) May 2010 standard GEOS-Chem anthropogenic emission rate for ammonia, SO_x, and NO_x in the (top) United States and (middle) California. (bottom) Monthly total emission for each species over California in 2010: all sources (black line), anthropogenic sources only (shaded gray). SO_x emissions include ship sources over oceans. (b) May 2010 modified anthropogenic emission rate for ammonia, SO_x, and NO_x in California.

Liu *et al.*, 2001] as well as dry deposition based on surface layer resistances [Wesely, 1989]. These removal methods will be discussed in greater detail in section 5.2. We include a fix for unreasonably low nighttime GEOS-5 planetary boundary layer (PBL) heights as described by Heald *et al.* [2012].

3.2. Inorganic Emission Inventories

Over the United States, anthropogenic emissions in GEOS-Chem follow the Environmental Protection Agency's National Emissions Inventory for 2005 (EPA NEI-2005). The NEI-2005 used in GEOS-Chem is a compilation of several inventories as described by Kim *et al.* [2011]. Emissions rates in NEI-2005 are reported for an August weekday, and these rates are temporally scaled in GEOS-Chem for individual species. For SO_x (sulfur dioxide + sulfate) and NO_x, an annual scale factor based on emissions trends as well as monthly and weekday/weekend scaling based on NEI-1999 is applied (since such scaling factors are not available from NEI-2005). Only monthly scaling is applied to ammonia emissions [van Donkelaar *et al.*, 2008], where this scaling is uniform across the U.S. Figure 2a shows the GEOS-Chem NEI-2005 emissions of ammonia, SO_x, and NO_x for May 2010 over both the continental U.S. and zoomed in to California. Anthropogenic ammonia emissions (which include gasoline vehicles, livestock, agricultural fertilizer, and many smaller sources) are largest in agricultural areas, such as the Midwest, Great Plains, and the Central Valley of California. Additional ammonia emission hot spots occur over cities with high automobile usage, such as Los Angeles. Anthropogenic SO_x

emissions are associated with electricity production, industrial processes, and near-coastal shipping activities. Anthropogenic NO_x emissions are largely from mobile sources in urban areas and interstate corridors.

Figure 2a also shows the seasonality of ammonia, SO_x , and NO_x emissions from all sectors in California. Anthropogenic sources provide the largest portion for all three species. Only ammonia shows a strong seasonal variation, with a summer peak, representing the higher volatility corresponding to higher temperatures and increased agricultural activity. This seasonality is described by *Park et al.* [2004]. Total annual anthropogenic emissions over the domain in California shown for ammonia, SO_x , and NO_x are 75 Gg N yr^{-1} , 91 Gg S yr^{-1} , and 285 Gg N yr^{-1} , respectively.

Biofuel emissions, referring to burning of fuel for domestic use, such as heating and cooking by wood or coal, in GEOS-Chem generally follow the NEI-1999 inventory in the United States, which includes weekday and weekend emissions values. This is true for both SO_x and NO_x . Ammonia biofuel emissions, however, are from the 1990 Global Emissions Inventory Activity (GEIA) as described by *Bouwman et al.* [1997]. Biofuel has little variability throughout the year but does peak in the winter due to increased heating needs.

The Fire INventory from NCAR (FINN) [*Wiedinmyer et al.*, 2011] is used to describe the daily biomass burning emissions of particulate matter and reactive trace gases, including sulfur dioxide, NO_x , and ammonia, for 2010. In the U.S., emissions from biomass burning are the largest in the summer months, driven primarily from wildfires in the western states [*Wiedinmyer and Neff*, 2007]. For May 2010, biomass burning contributes 0.7% of ammonia emissions and 0.3% of NO_x emissions in California.

Natural ammonia emissions are also from the 1990 GEIA inventory and include emissions from natural ecosystems and the ocean. These natural emissions show a summertime peak similar to that of the anthropogenic sector and are the second largest category after anthropogenic sources, making up 13% of total ammonia emissions in California in May.

Lightning NO_x has been updated in GEOS-Chem v9-01-01 by *Murray et al.* [2012] to provide an improved parameterization through regional scaling. All other relevant emissions, such as soil NO_x , are described by *Pye et al.* [2009].

3.3. Previous GEOS-Chem Studies of Inorganic PM in the United States

A number of previous studies have evaluated the GEOS-Chem simulation of surface inorganic $\text{PM}_{2.5}$; we highlight here some recent relevant results. *Pye et al.* [2009] find that concentrations of inorganic aerosol are widely underpredicted over the entire United States, but they conclude that ammonia inventory errors are not the primary reason for these discrepancies and instead point to missing processes and low model horizontal resolution (horizontally $4^\circ \times 5^\circ$). *Zhang et al.* [2012], who also use the high-resolution nested version of GEOS-Chem used in this study, report little bias in NH_x (ammonia + ammonium) but significant positive biases for nitric acid, ammonium, and nitrate, which they suggest may be associated with excess production of nitric acid from N_2O_5 hydrolysis. Based on comparisons with IASI satellite observations, *Heald et al.* [2012] suggest that California ammonia emissions are underestimated in the GEOS-Chem model, which leads to underproduction of nitrate at the surface in this region. Elsewhere in the U.S., they find a high bias in nitrate in all seasons except spring, consistent with *Zhang et al.* [2012]. *Walker et al.* [2012] also report an underestimate of surface ammonium nitrate concentrations in California. They suggest that a doubling of ammonia emissions is required to simulate annual observed nitrate concentrations in southern California, while even a tenfold increase in the Central Valley does not make up for the low bias in nitrate in that region. They also suggest that a high bias in the GEOS-5 mixed layer depth may account for some of the low nitrate bias, as particles are allowed to disperse into a greater volume near the surface.

4. Model Simulation of CalNex Observations

For this analysis, we separate the CalNex observations into two regions: the LA Basin and surrounding area, referred to here as the "Southern CA" region, and both the Sacramento and San Joaquin Valleys, referred to collectively here as the "Central Valley" region (shown in Figure 1). The demarcation is 34.75°N latitude, with about 75% of the observations over the Southern CA region and about 25% over the Central Valley.

Measurements taken outside of these two primary regions (e.g., over the ocean, in the San Francisco Bay area) constitute about 15% of the number of total measurements from CalNex and are not included in our analysis. As shown by NEI-2005, the Southern CA region is dominated by NO_x and ammonia emissions from vehicles and industrial SO_x , especially within the Los Angeles core area. Ammonia emissions from agriculture

dominate the Central Valley region. High NO_x emissions are seen over urban areas in the Central Valley, and SO_x emissions are quite low here compared to Southern CA (Figure 2a).

Given that the CalNex aircraft does not uniformly sample a grid box and that it is not possible for a coarse Eulerian model, such as GEOS-Chem, to reproduce plumes as concentrations diffuse through a grid box [Rastigejev *et al.*, 2010], any of the isolated high-concentration plumes observed during CalNex can bias the comparison with model concentrations. Thus, all averaging done in these comparisons will use median value in a grid box or bin, rather than mean, as a test of model performance. Furthermore, plume-chasing aircraft sampling strategies can further bias the comparison between model and measurements. It is not clear to what degree this may impact our comparisons; we use regional averages throughout this study in an attempt to mitigate this effect.

The median concentrations of the six main species of interest (gases: ammonia, sulfur dioxide, nitric acid; and particle ions: ammonium, sulfate, nitrate) at all altitudes for both observations and the model are compared over the entire region in Figure 3. The model reproduces the general spatial distribution of these species, and particularly the transition from the Southern CA to Central Valley regions. However, the model substantially underestimates observed ammonia concentrations, by up to 24 ppb gridded median in the Central Valley, consistent with the underestimates reported by Heald *et al.* [2012] and Walker *et al.* [2012]. Sulfur dioxide in the model is noticeably low in the Central Valley as well, especially in the southern Central Valley. Model values for nitric acid and all three aerosol species are slightly underestimated in the southern Central Valley, and slightly overestimated on the northern end. Nitric acid, ammonium, and nitrate are slightly low in Southern CA. Heald *et al.* [2012] report a consistent low bias in simulated nitrate in southern California compared to surface observations in 2004 but little to no bias in mid-northern California. Except for ammonia, the median model biases for an individual grid box are less than 2 ppb (for the gas-phase species) or $2 \mu\text{g sm}^{-3}$ (for the particle-phase species). Uncertainties in the observations are proportional to the measured concentration. Typical uncertainties in this region are 3 ppb for 10 ppb measured ammonia, 0.15 ppb for 1 ppb measured sulfur dioxide, 0.3 ppb for 2 ppb measured nitric acid, and $0.3 \mu\text{g sm}^{-3}$ for $1 \mu\text{g sm}^{-3}$ measured particle ion species.

Figure 4 compares the median vertical profiles of the inorganic gas and particle species in the Southern CA and Central Valley regions. The standard deviation of the observations in each altitude bin is also shown to denote the high degree of observed variability. Some of the high variability and vertical structure reported aloft reflects the limited number of observations at these altitudes, particularly in the Central Valley where the aircraft mainly sampled below 3 km altitude. In general, both the observations and the simulation agree that species concentrations decrease with increasing altitude due to surface sources and the short lifetimes of these species. Exception to this occurs in the near-surface layer, where deposition can reduce concentrations. Median model near-surface ammonia is biased low by a factor of 5 in the Central Valley and a factor of 2.5 in Southern CA. The model simulation of ammonium and nitrate is correspondingly low in Southern CA, consistent with an underestimate in ammonia precursor emissions. However, the model overproduces ammonium nitrate concentrations in the Central Valley despite the very low simulated ammonia concentrations, suggesting both that ammonium nitrate formation is not ammonia limited in this region and that ammonium nitrate production is overestimated in the model. This is inconsistent with Walker *et al.* [2012] who find that 2009 surface nitrate concentrations are underestimated by the GEOS-Chem model throughout California; however, they apply different scaling factors to their emissions, and a direct comparison is not possible, as they do not provide emission totals for California. The model simulation in the Central Valley also suffers from an underestimate of sulfur dioxide levels by about a factor of 3 (below 2 km), with a simultaneous overestimate in near-surface sulfate. Although the nitric acid comparison is good in both regions, the simulated near-surface NO_x concentration, also shown in Figure 4, is biased high in Southern CA by 27% and low in the Central Valley by 52%.

The discrepancies between the CalNex observations and GEOS-Chem model simulation identified above could be due to several factors within the model. In the following section, we explore these factors, diagnose simulated sensitivities due to model uncertainties, and propose solutions to reconcile these differences.

5. Exploring the Sensitivities of the GEOS-Chem Simulation

5.1. Gas-to-Particle Partitioning

The ISORROPIA II thermodynamic equilibrium model in GEOS-Chem determines both the partitioning of ammonia into ammonium in order to neutralize sulfate and the partitioning of ammonium nitrate between

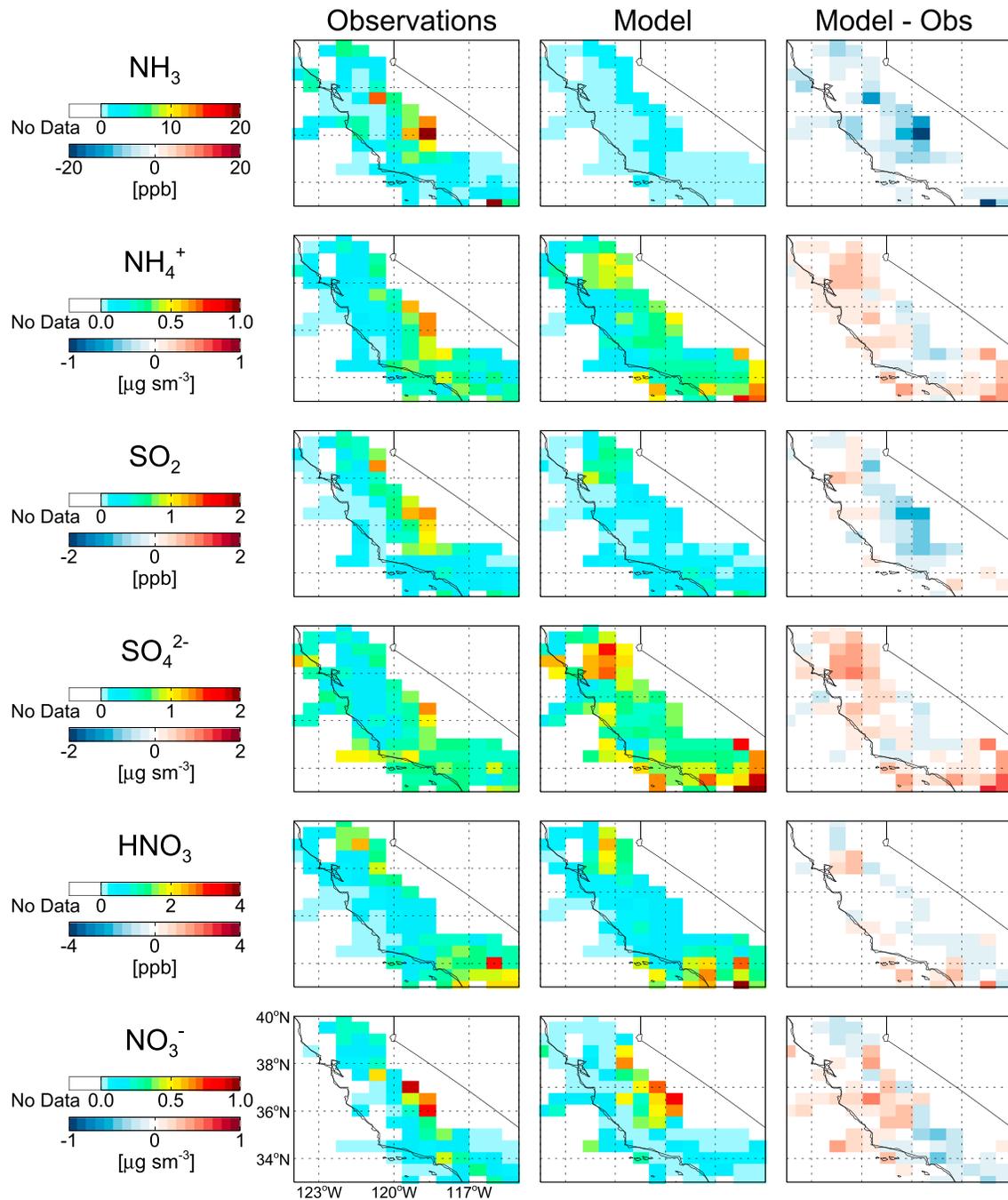


Figure 3. (left column) Median CalNex airborne observations and (middle column) median GEOS-Chem simulated concentrations along the flight paths averaged vertically over each grid box. (right column) Difference between observations and model. Color bars are saturated at respective values.

the particle and gas phases. In GEOS-Chem, these calculations are based on the model ambient temperature and RH and the model concentrations of total ammonia, sulfate, total nitrate, sodium, and chloride. The concentration of ions present in submicron dust can also be treated in ISORROPIA II, but this is not included in the GEOS-Chem implementation due to the challenges of characterizing the variability in dust composition. Given the assumption of metastable equilibrium enforced by the GEOS-Chem model, ammonium nitrate particles remain deliquesced in ISORROPIA II through the lowest ambient RH levels (see section 5.3 for further discussion).

Due to the sensitivity of ammonium nitrate equilibrium to temperature and RH, any bias in these parameters from the assimilated meteorology could affect the ammonium and nitrate equilibrium concentrations.

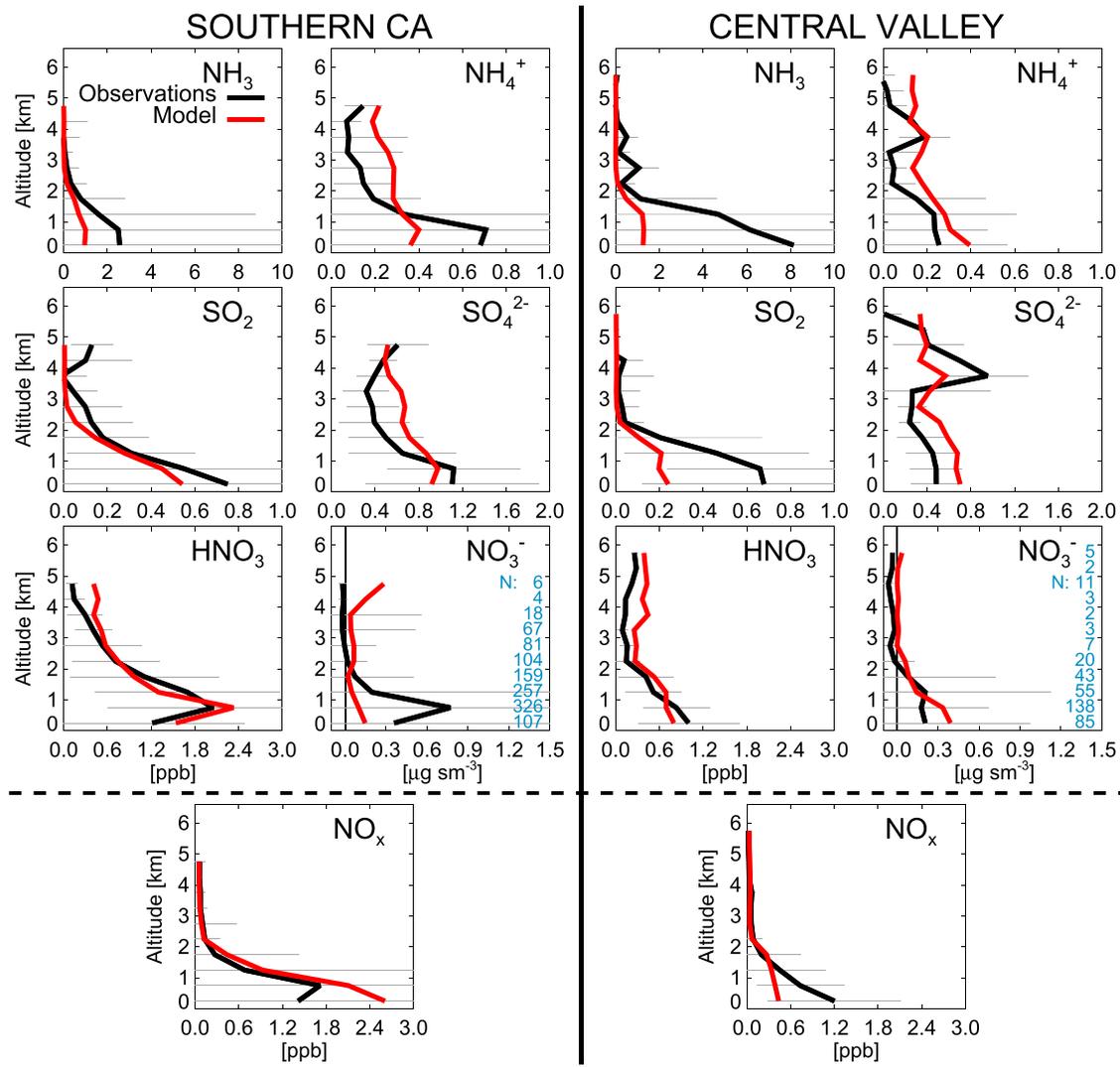


Figure 4. Vertical profiles of median CalNex plane flight observations (black) and median GEOS-Chem simulated concentration along those flight paths (red) averaged in 500 m altitude bins for the (top) six main gas precursors and particle ions and (bottom) NO_x as a precursor to nitric acid. The Southern CA region and Central Valley region are shown separately. The standard deviation of the observations in each altitude bin is shown in gray. The number of points in each bin is shown in blue.

Figure 5 compares the observed and model (assimilated) meteorology for both the Southern CA and Central Valley regions. The median model temperature profile is generally biased low by about 1°C in both regions, with a modest overestimate near the surface in the Southern CA region. However, the model and observations are highly correlated, with linear regression slopes close to 1. The RH comparison is somewhat more scattered, as expected given the challenges of both measuring and predicting RH. The median model bias in RH for individual observations ranges from about 5 to 10%, in both directions, but no mean bias is evident.

In order to determine the effects that these errors in meteorology (T, RH) could have on the simulated profiles, we perform a series of sensitivity simulations where the meteorological inputs into ISORROPIA II are varied. Given T and RH conditions experienced at the surface in California during this time of year, little sensitivity is expected; however, at the colder and drier condition aloft, errors in meteorology may more adversely affect the simulation. Thus, simulations are performed for $\pm 1^\circ\text{C}$ and $\pm 10\%$ RH from the original GEOS-5 values at all vertical levels. The impact of varying the temperature within the observed uncertainty on species concentration is very small with virtually no change in the median concentration profiles (maximum variation in a vertical bin for any species is $0.2 \mu\text{g sm}^{-3}$, not shown). The impact of varying RH is similarly small for all regions, except for nitrate concentrations aloft (maximum variation in a vertical bin of $0.5 \mu\text{g sm}^{-3}$ at 5 km), where

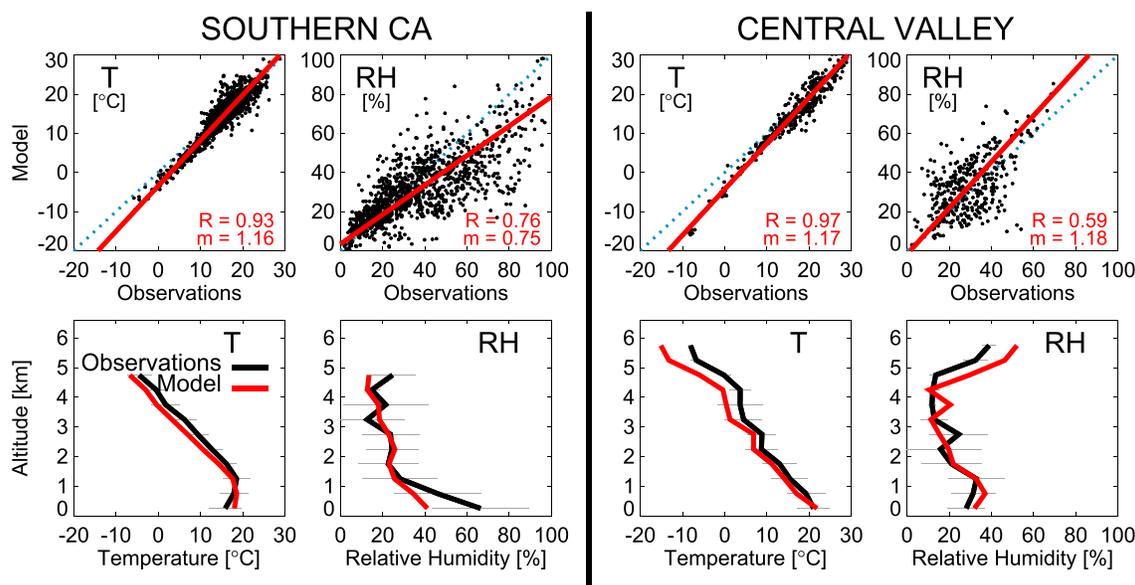


Figure 5. Comparison of CalNex plane flight observations and GEOS-Chem model meteorology along those flight paths for temperature (T) and relative humidity (RH). Southern CA region and Central Valley region are shown separately. (top) Scatterplots (orthogonal regression line in red, 1:1 line in broken blue, R is correlation coefficient, m is slope). (bottom) Median vertical profiles (as in Figure 4).

limited observations are available to evaluate the simulation. Thus, we conclude that the simulation of nitrate concentrations below 3 km is not sensitive (less than $0.2 \mu\text{g sm}^{-3}$ variation) to the estimated uncertainty in model RH for the region. Overall, we conclude that model bias in temperature and RH during CalNex does not significantly impact the gas-to-particle partitioning in the model and cannot account for model bias in the simulation.

Chloride ion (Cl^-) can impact the fine inorganic PM system discussed here in two ways. First is from the reaction of sea salt (NaCl) with nitric acid, which leads to the formation of sodium nitrate (NaNO_3) while releasing hydrochloric acid (HCl). In GEOS-Chem, only accumulation mode sea salt is included in the calculation of the gas-aerosol equilibrium state with ISORROPIA II. Second is through the neutralization reaction of hydrochloric acid with ammonia to form ammonium chloride (NH_4Cl). Hydrochloric acid for this reaction is typically emitted directly from urban sources [Kaneyasu *et al.*, 1999], which are not included in GEOS-Chem. We find that AMS-observed airborne chloride concentrations during CalNex were low (less than $1.2 \mu\text{g sm}^{-3}$ at all points) throughout the region studied. This chloride measured is typically in the form of ammonium chloride, rather than sea-salt chloride [Canagaratna *et al.*, 2007]. The model overpredicts the median chloride concentrations by a factor of 2, suggesting that, while the comparison is not exact, the missing hydrochloric acid sources in the model are not critical for predicting chloride levels. Sensitivity tests verify that reducing simulated chloride concentrations to observed levels (or less) does not significantly impact the equilibrium of ammonium nitrate formation in the model (less than $0.1 \mu\text{g sm}^{-3}$ mean concentration change near the surface). Therefore, there is little evidence that we are missing a substantial source of ammonium or nitrate in the form of sodium nitrate or ammonium chloride in our simulation of California.

ISORROPIA II represents only the equilibrium partitioning of fine particles; therefore, any possible sink of nitric acid onto coarse sea salt or dust is not represented here. However, the comparison of Figure 4 does not suggest that we are missing a large nitric acid sink in California, as simulated nitric acid values are within 20% of observations at all altitudes. While we have neglected the impact of organic acids and dust on nitrate formation in the GEOS-Chem simulation, we do not expect either to play a dominant role in the inorganic gas-particle system or the simulation biases described here as concentrations of these species are low during California summer [Fairlie *et al.*, 2010; Myriokefalitakis *et al.*, 2011].

5.2. Wet and Dry Deposition

Wet deposition processes allow for the removal of chemical species from the atmosphere as they are incorporated into precipitation. GEOS-Chem uses wet deposition schemes by Liu *et al.* [2001] for aerosols and Mari *et al.* [2000]

for gases to determine how much of a given species is removed. These schemes are driven primarily by the presence of convection and precipitation within the meteorological input parameters.

Over the California domain shown in Figure 1, the NH_x wet deposition flux makes up a much smaller fraction of total NH_x deposition than dry deposition ($0.8 \text{ Gg N month}^{-1}$ mean wet deposition compared to $2.2 \text{ Gg N month}^{-1}$ mean dry deposition for May and June 2010). The CalNex time period represents the driest season in California. Most of the precipitation occurs over the mountains to the east of the Central Valley. As this is largely driven by the regional meteorology, wet deposition of SO_x and total nitrate follows similar seasonal patterns.

We use monthly mean wet deposition measurements from the National Atmospheric Deposition Program National Trends Network (NADP/NTN) (nadp.sws.uiuc.edu/ntn) at nine sites in California in 2010 to test the simulated wet deposition in GEOS-Chem. The observations and model agree that wet deposition levels of all three ion species in May and June are low, both in absolute terms (Figure 6) and compared to other times of the year (not shown). The comparison of observed and simulated mean wet deposition fluxes in Figure 6 shows a slight model underestimate of wet deposition at sites east of the Central Valley, but these sites are outside of the domain of the aircraft measurements. Thus, wet removal does not control the budget of trace gases and particles over California in this season, and biases in the GEOS-Chem simulation cannot be attributed to this process.

GEOS-Chem uses the Wesely [1989] resistance parameterization for dry deposition. This scheme combines aerodynamic resistance, boundary layer resistance, and canopy surface resistance terms to calculate a deposition velocity. This deposition velocity is combined with the ambient species concentration to determine the dry deposition flux.

Dry deposition of gaseous ammonia dominates the simulated NH_x mass loss to deposition during May and June in California (63% of total NH_x deposition, 85% of NH_x dry deposition). Similarly for SO_x and total nitrate, the dry deposition of the gas species dominates that of the aerosol. Dry deposition of nitric acid clearly dominates the total nitrogen deposition throughout California in May and June, accounting for $6.9 \text{ Gg N month}^{-1}$ of the $11 \text{ Gg N month}^{-1}$ mean total nitrogen deposition (63%). This is consistent with U.S. nitrogen deposition budget reported by Zhang *et al.* [2012], where nitric acid dry deposition makes up the largest portion of total nitrogen deposition annually throughout the U.S. Simulated May 2010 dry deposition velocities over land in California range from 0.3 to 0.5 cm s^{-1} for ammonia and from 0.2 to 4.0 cm s^{-1} for nitric acid. These velocities are highly affected by land type and density of vegetation.

Average dry deposition velocity values from seven California sites in the EPA Clean Air Status and Trends Network (CASTNET) (www.epa.gov/castnet) are compared with GEOS-Chem for May and June 2010 in Figure 6. CASTNET does not report ammonia dry deposition velocities. It is critical to note that the dry deposition velocities from CASTNET are derived quantities from the Multilayer Model. Thus, the comparison with GEOS-Chem is in fact a comparison of two models. However, we use these comparisons to provide an estimate of potential bias in the GEOS-Chem simulation. Based on these few point sites for comparison, the model deposition velocity is biased high for sulfur dioxide and nitric acid and somewhat low for the aerosols.

We conduct a sensitivity simulation to test whether these potential biases in dry deposition velocity may contribute to the discrepancies between the simulation and the CalNex observations. In this simulation, sulfur dioxide and nitric acid dry deposition velocities are reduced by 50%, lowering the minimum sulfur dioxide velocity from 0.3 cm s^{-1} to 0.2 cm s^{-1} , and the aerosol dry deposition velocity is increased by 70%, all changed to match the CASTNET values. The impacts of this change on sulfur dioxide are small. The near-surface median sulfur dioxide concentration in Southern CA is increased by 0.04 ppb , nearly halving the bias in this region. A relatively insignificant increase of about 0.03 ppb is seen in the Central Valley. Nitric acid experiences a larger change in the near-surface concentration in both regions, with median increases of 0.37 ppb in Southern CA and 0.12 ppb in the Central Valley. This creates an overestimation in nitric acid in Southern CA and matches the CalNex observations in the Central Valley. The increase in nitric acid also enhances ammonium nitrate formation. The overall change is larger in the Central Valley however, where the ammonium nitrate increase in Southern CA is completely offset by increased aerosol deposition. Only a small decrease in concentration, less than $0.03 \text{ } \mu\text{g sm}^{-3}$ for all aerosol species, can be attributed to the change of the aerosol dry deposition velocity alone. While the improvement in surface sulfur dioxide concentration in Southern CA and nitric acid concentration in the Central Valley made by altering the dry deposition velocities

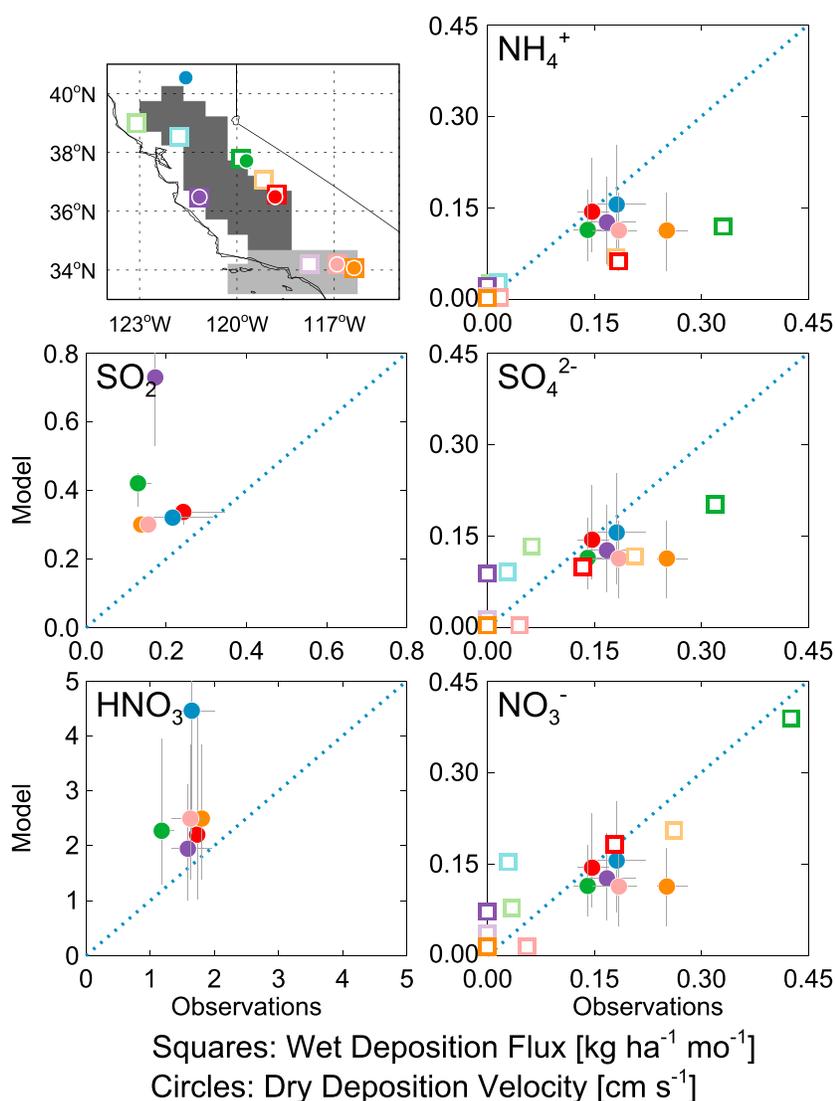


Figure 6. Scatterplots of mean May–June 2010 NADP/NTN and GEOS-Chem wet deposition flux at nine sites (squares) and CASTNET and GEOS-Chem dry deposition velocity at six sites (circles) in California. Site locations are shown in upper left; 1:1 line is shown in broken blue. Gray lines represent extent of minimum and maximum weekly observed and daily model velocity values. Ammonia dry deposition is not measured by CASTNET. Only wet deposition of ions is measured by NADP/NTN.

corrects much of the original discrepancy for those species seen in Figure 4, confidence in the derived CASTNET values is low, and thus, it is not clear that the bias in sulfur dioxide and nitric acid can be correctly attributed to errors in dry deposition velocity. We note that the dry deposition velocities of ammonia have not been evaluated against observations; although, a similar 50% decrease in simulated ammonia dry deposition velocity does not produce any significant changes to the species concentrations simulated for CalNex (nor do we see any significant change in concentrations under the extreme test of reducing ammonia dry deposition velocities by 90%). The modest sensitivity of the simulation to the assumed sulfur dioxide and nitric acid dry deposition velocities suggests that this could be a small source of bias in the model simulation.

5.3. Emissions

Given the changes in human and livestock populations in parts of California as well as changes in mitigation technology, the NEI-2005 used in GEOS-Chem may not adequately describe our study period in 2010. *Russell et al.* [2012] indicate that NO₂ concentrations have decreased by about 30% in cities across the U.S., including near LA, between 2005 and 2011 due to increased emission controls. This likely accounts for the model

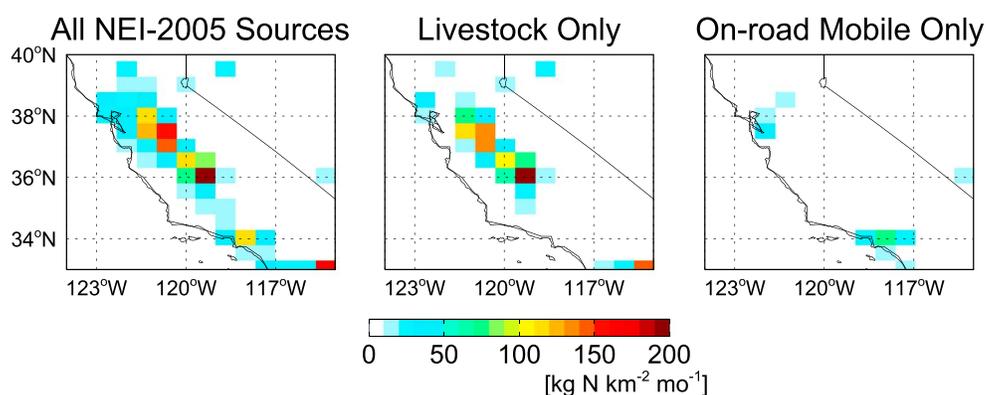


Figure 7. NEI-2005 ammonia emissions in GEOS-Chem for May 2010 over California: all sources, livestock only, and on-road mobile only.

overestimate of NO_x in the Southern CA region shown in Figure 4. As for ammonia, the total number of cattle, a key source of ammonia, in the San Joaquin Valley increased by 24% from 2002 to 2010 (United States Department of Agriculture California livestock inventory (www.nass.usda.gov/ca)), creating a large emissions underestimate. Applying ammonia emissions inventories correctly is also difficult given the variety of waste management and dietary factors which can affect the local emission levels at a given time.

We investigate the magnitude of adjustment to the NEI-2005 anthropogenic emissions which can reconcile our model simulation with the CalNex observations. Our initial comparisons showed that the model ammonia concentrations were low throughout California, but this difference is much greater in the Central Valley. Figure 7 disaggregates the NEI-2005 California ammonia emissions into two key source sectors: livestock and on-road mobile sources. This clearly delineates the livestock ammonia emission in the Central Valley region and the on-road mobile ammonia source in the Southern CA region, as well as in the vicinity of San Francisco. We investigate the impact of increasing the livestock ammonia emission by a factor of 5 over the entire inventory area in our modified simulation. In addition, using the same CalNex airborne measurements as in this study, Nowak *et al.* [2012] show that the NEI-2005 ammonia emissions are quite low for the eastern side of the LA Basin, where many dairy operations exist. They report a measured ammonia emission rate of $12\text{--}64 \text{ Gg yr}^{-1}$ from livestock in this eastern LA region, compared to the NEI-2005 rate of about 0.37 Gg yr^{-1} . We set the livestock ammonia emission rate in the single east LA model grid box consistent with the region discussed by Nowak *et al.* [2012] to 12 Gg yr^{-1} in our modified simulation. This is more than 30 times the original value rather than the 5 times increase imposed elsewhere. Although not yet available in gridded format, the NEI-2008 version 3 (www.epa.gov/ttnchie1/net/2008inventory.html) supports a large growth in livestock ammonia emissions in California, compared to NEI-2005: a doubling in the Central Valley and 17 times increase in Southern CA.

The model sulfur dioxide concentrations are underestimated in the Central Valley as well. This low bias is larger in the southern Central Valley region than in the north. In an effort to better represent observed concentrations, we increase the northern and southern Central Valley sulfur dioxide emission by 3 times and 10 times, respectively, in our modified simulation. This increases the Central Valley mean May 2010 SO_x emission rate from $3 \text{ kg S km}^{-2} \text{ month}^{-1}$ to $31 \text{ kg S km}^{-2} \text{ month}^{-1}$. This model underestimate of sulfur dioxide concentrations in the Central Valley may be related to upwind urban sources (e.g., from Fresno, Sacramento, Bay Area) or local sources of sulfur dioxide. However, we are unable to attribute this discrepancy based on the observations used here. This requires further exploration. The scaling factors selected are based solely on the observed bias in the baseline simulation (Figure 4). We also implement a 30% reduction in anthropogenic NO_x emission from the NEI-2005 values based on Russell *et al.* [2012]. The new May emission rates for anthropogenic ammonia, SO_x , and NO_x in the modified GEOS-Chem simulation are shown in Figure 2b. The annual anthropogenic emissions rates over the California domain shown are now 280 Gg N yr^{-1} , 118 Gg S yr^{-1} , and 209 Gg N yr^{-1} for ammonia, SO_x , and NO_x , respectively.

Vertical profiles comparing the results from the modified emissions simulation with the standard run are shown in Figure 8. In the Southern CA region, the low ammonia concentration bias is overcorrected by the increased emissions. The increase in emissions compensates for much of the bias in ammonia in the Central Valley; however,

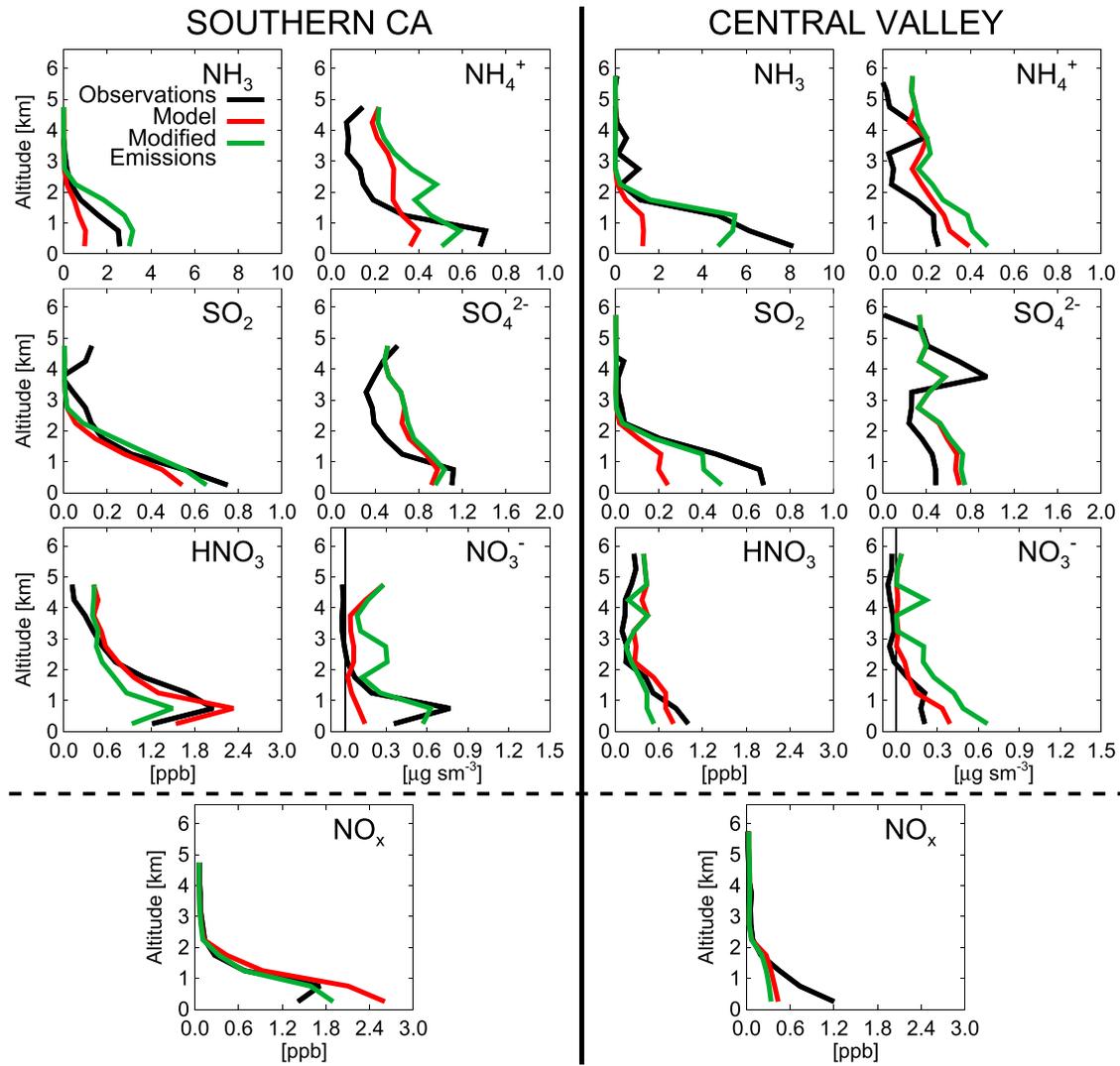


Figure 8. Same as Figure 4 but with vertical profiles resulting from the GEOS-Chem simulation with modified emissions added in green. The number of points per bin remains the same.

a pronounced near-surface underestimate remains. The low bias in sulfur dioxide concentrations is halved in the Central Valley and completely eliminated in Southern CA. Increased ammonia emissions in both regions act to neutralize more nitric acid, decreasing its concentration while promoting ammonium nitrate aerosol formation. The NO_x concentration comparison in Southern CA is much improved with lower NO_x emissions, while a low bias remains in the Central Valley. However, this drop in NO_x creates a modest low bias in nitric acid near the surface in both the Central Valley and Southern CA which is much larger than the nitric acid decrease caused by the ammonia increase alone. Excess dry deposition of nitric acid in the model (discussed in section 5.2) may also contribute to this underestimation. Inorganic aerosol concentrations increase in both regions due to increased availability of ammonia and sulfur dioxide. This substantially improves the simulation of inorganic $\text{PM}_{2.5}$ in Southern CA but worsens the already high-biased simulation of ammonium and sulfate in the Central Valley and produces an overestimate in nitrate (consistent with the U.S.-wide overestimate in nitrate concentrations reported by Heald *et al.* [2012]). We note here that these comparisons may also be influenced by the AMS size cutoffs which may underestimate the fine PM mass concentrations when compared to the model.

The results of these emissions modifications, in concert with the sensitivities explored in sections 5.1 and 5.2, suggest that uncertainties in the GEOS-Chem simulation of the inorganic gas-particle system are dominated by emissions. Accurate emission inventories are critical to the ability to effectively model reactive nitrogen and $\text{PM}_{2.5}$ formation in California. The emissions modifications we have made are the largest source of

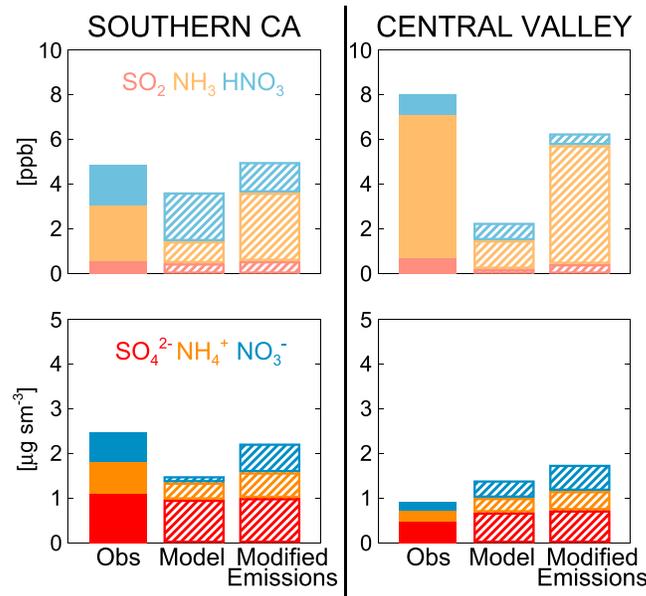


Figure 9. Median species concentrations below 1 km. Comparing (top) gases species with (bottom) aerosol species, Southern CA region with Central Valley region for three cases: CalNex airborne observations, standard GEOS-Chem simulation, and simulation with modified emissions.

concentration variation and the closest we have come to reducing initial errors among the factors examined in section 5. However, we note that we have applied uniform scaling factors to the NEI-2005, where emission trends likely differ considerably at the county level.

Figure 9 summarizes the near-surface air quality and inorganic PM_{2.5} composition for our two regions in California by comparing the CalNex airborne observations with the standard and modified emissions GEOS-Chem simulations. The CalNex observations show that, below 1 km, inorganic PM_{2.5} concentrations are about three times as high in Southern CA as in the Central Valley, with median concentrations of 2.47 and 0.91 µg sm⁻³, respectively. However, the relative speciation of inorganic fine PM is similar across California (sulfate contributes 50% and nitrate makes up about 25%, both by mass).

On a more local scale, both CalNex airborne observations and GEOS-Chem simulation (with updated emissions based on Nowak *et al.* [2012]) capture the formation of ammonium nitrate downwind of LA as the oxidized NO_x emitted from the city core reacts with large amounts of ammonia from farms to the east of LA. Observed near-surface inorganic PM_{2.5} in East LA is 24% higher than in LA (4.32 µg sm⁻³ compared to 3.48 µg sm⁻³) and is made up of 44% nitrate compared to 34% in LA. The modified simulation better captures the higher ammonium nitrate concentration in East LA, producing 3.57 µg sm⁻³ inorganic PM_{2.5} compared to 1.65 µg sm⁻³ in the standard simulation.

Increasing ammonia, sulfur dioxide, and decreasing NO_x emissions as described in the modified simulation decreases the overall regional biases seen in the initial comparison of the observations and standard GEOS-Chem (Figure 9). Comparison of gas species is improved or consistent with the initial comparisons in both regions. Aerosol concentrations in Southern CA are also greatly improved, especially for ammonium and nitrate. The largest remaining discrepancy is the simulated Central Valley inorganic particle concentrations, which are initially too high (by 51%) compared to the observations and are increased further with the modified emissions (now 89% overestimate). This occurs despite the continued underestimate of the gas-phase precursors in the same region of 23%. One possible cause of this particle mass overestimate could be the deliquescence assumptions applied in the model. Ammonium nitrate deliquescence exhibits a hysteresis, where the RH exposure history of the particle dictates whether the particle is deliquesced when exposed to RH between the crystallization and deliquescence RH. Given that a three-dimensional model cannot track this particle history, an assumption that the particle remains on the upper deliquesced branch (metastable) or lower crystallized branch (stable) must be applied. In the GEOS-Chem model, the default is the use of the metastable assumption, which is appropriate under higher RH conditions [Pye *et al.*, 2009]. However, under the dry summertime conditions in California, this assumption may be erroneous. In Figure 10, we examine this behavior by comparing the difference in the simulated nitrate concentrations predicted under the modified emissions scenario with the stable and metastable assumption along the CalNex flight tracks. Using a stable assumption, which allows for both solid and liquid aerosol, rather than only liquid as in the metastable assumption, generally reduces ammonium nitrate formation. This occurs throughout California, except in conditions when both nitric acid and ammonia concentrations are sufficiently high to exceed the equilibrium constant for the solid formation of ammonium nitrate, seen, for example, at the surface in LA. In terms of the median comparisons presented in Figures 8 and 9, the stable assumption eliminates about half of the ammonium nitrate overestimate in the Central Valley, but at the same time, it degrades the comparison with ammonium nitrate observations in Southern CA. This may represent a key

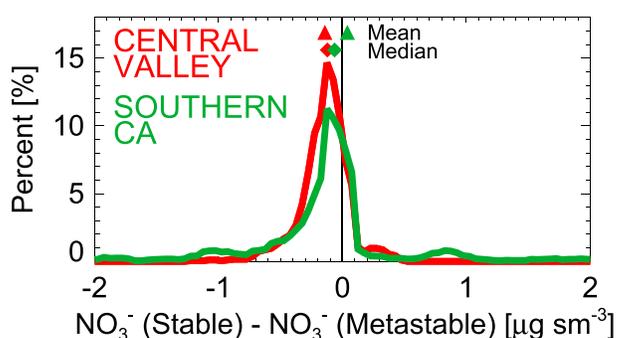


Figure 10. Histograms show the difference in simulated nitrate concentrations along the CalNex flight tracks over the Central Valley (red) and Southern CA (green) when applying the stable versus metastable assumption in the GEOS-Chem model. All simulations are shown with modified emissions scenario (described in section 5.3). Also displayed are the mean (triangle) and median (diamond) values for each distribution. All differences for the Central Valley are within the given range, while 4% of Southern CA differences are above $2 \mu\text{g sm}^{-3}$ and 1% are below $-2 \mu\text{g sm}^{-3}$.

uncertainty in the simulation of ammonium nitrate in relatively dry locations. However, we see from Figure 10 that in Southern CA, the median and the mean difference in concentrations due to this shift in ammonium nitrate formation regime are of opposite sign. Thus, the relative importance of this effect likely varies with location and evaluation metric. The true particle history is also likely a mixture of hydration and dehydration, suggesting that our metastable and stable simulations bracket the “true” ammonium nitrate formation conditions. Other possible causes of the overprediction of ammonium nitrate in the Central Valley include a missing loss mechanism, insufficient ventilation or poor representation of transport and export from the Central Valley due to insufficiently resolved terrain, or underestimation of the fine PM mass observed with AMS. Further investigation is required to improve the PM simulation in this challenging region.

Finally, ammonia emissions likely peak in the afternoon due to the influence of temperature on the volatility of ammonia and increased anthropogenic activity (farming practices, vehicle operation) during the day [Pinder *et al.*, 2006]. However, ammonia emissions in GEOS-Chem remain constant throughout the day, and this could be another limitation on the model’s ability to represent surface-level air quality. In Figure 11, we explore the sensitivity of the diurnal pattern of regional surface ammonia, ammonium, and nitrate concentrations to both the diurnal profile of ammonia emissions and the mixing depth for May–June 2010. By emitting ammonia in a daytime pulse and raising the overnight PBL height by 50 hPa (an arbitrary value chosen to test sensitivity), we see that the simulated diurnal pattern of surface concentrations of ammonia and ammonium nitrate are highly sensitive to these factors. The sensitivity to ammonium nitrate formation is higher in Southern CA, which is ammonia limited. Except for the increase in surface ammonia concentration in the Central Valley, midday concentrations appear unaffected, while the nighttime differences are on average a factor of 2. There is little impact on sulfate concentrations under both of these scenarios (not shown). This suggests that characterizing the diurnal trend in both emissions and mixing depth is critical to accurately simulating hourly fine PM exposure. We note that the model simulation of predominantly daytime airborne measurements during CalNex is virtually insensitive to these factors. Further investigation, with a large data set of hourly measurements in multiple seasons, is required to further investigate the processes controlling the diurnal variability of fine inorganic PM in California.

6. Application of Modified Emissions to Year-Round Surface Air Quality in California

6. Application of Modified Emissions to Year-Round Surface Air Quality in California

We use this same modified emissions simulation, based on the summertime CalNex period evaluation, to investigate the year-round inorganic $\text{PM}_{2.5}$ formation and surface-level concentrations in California. In Figure 12, observed and simulated surface inorganic $\text{PM}_{2.5}$ concentration and percent mass composition are compared at nine EPA Air Quality System (AQS) sites in California (six in Central Valley, three in Southern CA) (www.epa.gov/ttn/airs/airsaqs) for 2010. Ion species discussed here are collected on a nylon filter after $\text{PM}_{2.5}$ inlet, extracted and analyzed using ion chromatography. The model is sampled for valid observation days for the grid box containing each of the sites. The seasonality of the simulated concentrations generally compares well with the observations in both regions, supporting the validity of the emissions modifications year round and the model’s usefulness to address air quality issues throughout the year. The notable exception is the high bias in simulated nitrate in the Southern CA region through the summer and fall. However, the AQS sites in the Southern CA region are close to LA and represent near-source air masses rather than the regional averages shown elsewhere in this study, and therefore, reported concentrations are higher. Ammonium nitrate formation is highly sensitive to changes in NH_x and total nitrate under these conditions, so a slight

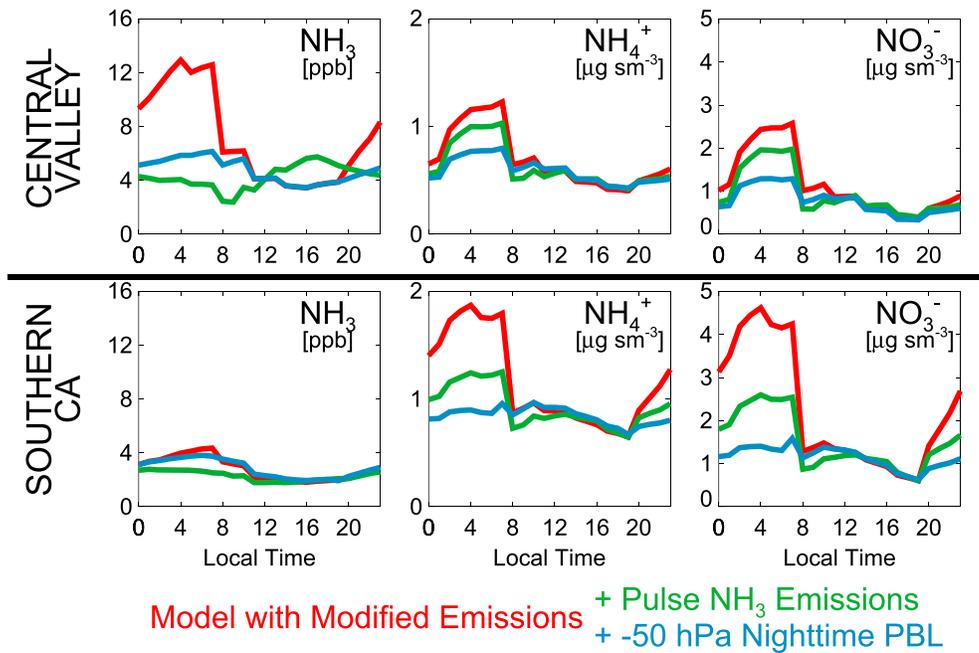


Figure 11. Hourly mean regional surface concentrations of (left column) ammonia, (middle column) ammonium, and (right column) nitrate for May–June 2010 simulated with GEOS-Chem: standard simulation with modified total emissions (red), afternoon pulse of ammonia emissions (green), and lifting of the overnight PBL by 50 hPa (blue). All simulations include the modified total emissions described in section 5.3.

high bias in either of these, perhaps due to overly rapid oxidation of NO_x to nitric acid, could cause an overprediction of the particle mass. The mean ammonium nitrate concentrations at the surface shown here are not sensitive to the stable/metastable assumption in the model, consistent with *Heald et al.* [2012]. This is the result of both somewhat higher RH conditions at the surface, and an averaging out of localized increases and decreases (refer to Figure 10). The only exception to this is in LA where concentrations of nitric acid and ammonia are

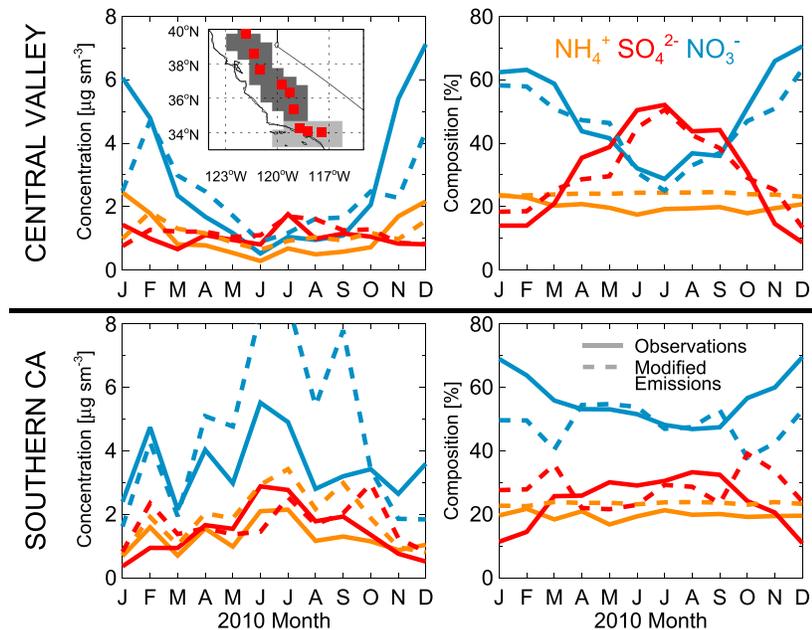


Figure 12. Mean monthly surface concentrations and percent of total particle species for 2010 in California. Comparing EPA Air Quality System (AQS) sites (solid line) and GEOS-Chem simulation with modified emissions (dashed line) in each of two regions. Simulated values are sampled for grid box corresponding to surface site and days with valid observed concentrations.

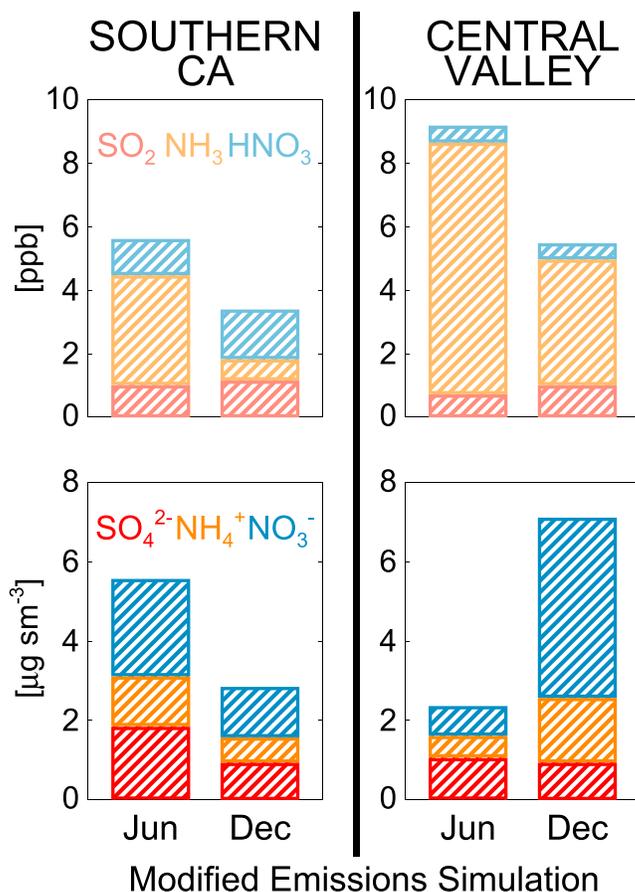


Figure 13. Regional mean simulated species concentrations at the surface for June and December 2010 for model with modified emissions. Comparing (top) gas species with (bottom) aerosol species. Southern CA region on left with Central Valley region on right.

consistently high enough to promote greater ammonium nitrate formation under stable conditions. However, this leads to a maximum regional mean increase in nitrate of about $0.5 \mu\text{g sm}^{-3}$ at the Southern CA sites and makes up at most about 25% of the difference between model and observations in Figure 12.

Figure 13 contrasts the mean regional simulated surface concentrations for both gas and aerosol species in the Southern CA and Central Valley regions in June and December. These results are insensitive to the stable/metastable assumption in the model. In the Central Valley, the mean regional simulated surface inorganic aerosol concentrations are three times higher in December ($7.07 \mu\text{g sm}^{-3}$) compared to June ($2.32 \mu\text{g sm}^{-3}$). This relative change is supported by the seasonal variation shown by the AQS observations. Despite wintertime ammonia emissions reductions, there remains abundant available ammonia in the atmosphere in the Central Valley. The nitrate fraction of inorganic PM in the Central Valley increases from 30% in June to 64% in December. A higher wintertime frequency of inversion events and a lower mean PBL height trap pollutants in the Central Valley region and contribute to these higher PM levels. The mean simulated PBL height in this region decreases from 1.7 km in June to 0.7 km in December. About 75% of the simulated increase in ammonium nitrate is due to effects of the lower wintertime PBL height, while the remainder is due to colder temperatures enhancing ammonium formation balanced with lower ammonia emissions. Given this high sensitivity, PBL height measurements could be useful to investigate whether the modest ammonium nitrate underestimate in the winter, shown in Figure 12, is a result of errors in meteorology and/or mixing. Frequent winter rain, cloud, and fog activity in the Central Valley can also accelerate the deposition of PM species during this time [Jacob *et al.*, 1986]. This removal counters the increase in sulfate production which occurs when more liquid water is available, leaving sulfate concentrations relatively constant throughout the year.

Conversely, in Southern CA, the simulated regional mean inorganic PM_{2.5} concentration is two times lower in December ($2.80 \mu\text{g sm}^{-3}$) than in June ($5.52 \mu\text{g sm}^{-3}$), while the relative composition of the inorganic PM_{2.5}

remains the same. The thermodynamic potential for ammonium nitrate formation and total nitrate levels is comparable in Southern CA and the Central Valley in the wintertime. However, unlike in the Central Valley, the Southern CA region is ammonia limited in the winter. While the relative wintertime decrease in ammonia emissions is similar in both regions, the absolute ammonia supply is considerably lower in Southern CA, restricting ammonium nitrate formation. This effect is larger than seasonal changes in temperature and PBL height, which are more moderate than in the Central Valley, and would otherwise increase the ammonium nitrate concentrations. Like in the Central Valley, the wintertime change in sulfate concentration is a balance between increased production and wet deposition. A series of widespread, gas- and particle-phase concentration measurements (with collocated profilers to help characterize mixing depth) are required to further investigate the relative role of emissions, meteorology, and mixing on surface PM air quality in California in different seasons.

By removing all anthropogenic ammonia emissions from our simulation with modified emissions, we estimate that about 40–60% of surface inorganic PM_{2.5} in California during the summer and up to 78% in the Central Valley region in the winter (56% in the Southern CA) are attributable to anthropogenic sources of ammonia. Ammonia that is not partitioned into aerosol or deposited near its emission region can be transported, given the proper meteorological conditions, and react or be deposited elsewhere. This excess ammonia often occurs due to the very large emission rates in certain areas, such as in the Central Valley. Future flight campaigns in these remote areas or the use of space-based remote sensing instruments could help evaluate the effects of increasing ammonia emissions on air quality and ecosystems downwind of the CalNex region.

7. Conclusions

We have evaluated the representation of the ammonia and inorganic aerosol system in the GEOS-Chem chemical transport model using aircraft observations from the CalNex campaign in May and June 2010. Initial comparisons of observations with the simulation show underprediction of ammonia and sulfur dioxide in two regions in California, near LA and the Central Valley. Median concentrations of ammonium, sulfate, and nitrate are underpredicted near LA as well but overpredicted in the Central Valley. NO_x is overpredicted in the region near LA.

Sensitivity analysis of several processes within the model indicates that underestimated/overestimated emissions are most likely to account for model biases. Increasing anthropogenic emissions of ammonia and sulfur dioxide enhance inorganic PM formation in both regions. A decrease in anthropogenic NO_x, as suggested by *Russell et al.* [2012], counters some of this formation. These modifications reduce the initial model bias in all species, except aerosols in the Central Valley. This suggests that the NEI-2005 does not adequately describe livestock ammonia and anthropogenic NO_x throughout California and anthropogenic sulfur dioxide sources in the Central Valley. This trend is consistent with the trends in emissions suggested by the NEI-2008. Furthermore, we find that ammonium nitrate concentrations simulated along the CalNex flight tracks may be sensitive to thermodynamic assumptions made in the model, but this sensitivity is negligible for mean surface concentrations (with the exception of LA).

We use this model with improved emissions to investigate surface inorganic fine PM, which contributes to poor air quality in California. The simulated concentrations confirm observations, where inorganic PM_{2.5} is highest in the Central Valley during the winter and highest in Southern CA during the summer. June PM_{2.5} concentrations are more than a factor of 2 higher near LA than in the Central Valley. This is reversed in December when ammonium nitrate formation is favored in the Central Valley. Central Valley inorganic PM_{2.5} concentrations are three times as high during this time than in June. Nitrate accounts for the largest portion of mass and seasonal variation in fine inorganic PM in both regions. Unlike in most of the U.S., inorganic PM_{2.5} in California is not dominated by sulfate, so ammonia emissions control could be an effective method to lower the inorganic PM_{2.5} concentration in the region. Our simulations suggest that more than half of the inorganic PM_{2.5} throughout California is produced as a result of anthropogenic ammonia emissions.

The remaining reservoir of ammonia in the Central Valley indicates that the formation of inorganic PM_{2.5} and its associated air quality degradation could dramatically increase should the concentration of atmospheric acids increase. This seems possible given current projections of southern Central Valley human population: about 20% increase over 2010 population by 2020 and 60% increase by 2040 [*State of California*, 2012]. However, advances in emissions technology and implementation may counteract some or all of the effects of population growth [*Steiner et al.*, 2006]. The balance of these trends will likely dictate future PM_{2.5} air quality in California.

Acknowledgments

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