

Atmospheric ammonia and particulate inorganic nitrogen over the United States

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Abstract

We use in situ observations from the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network, the Midwest Ammonia Monitoring Project, 11 surface site campaigns as well as Infrared Atmospheric Sounding Interferometer (IASI) satellite measurements with the GEOS-Chem model to investigate inorganic aerosol loading and atmospheric ammonia concentrations over the United States. IASI observations suggest that current ammonia emissions are underestimated in California and in the springtime in the Midwest. In California this underestimate likely drives the underestimate in nitrate formation in the GEOS-Chem model. However in the remaining continental United States we find that the nitrate simulation is biased high (normalized mean bias ≥ 1.0) year-round, except in

Spring (due to the underestimate in ammonia in this season). None of the uncertainties in precursor emissions, the uptake efficiency of N_2O_5 on aerosols, OH concentrations, the reaction rate for the formation of nitric acid, or the dry deposition velocity of nitric acid are able to explain this. We find that reducing nitric acid concentrations to 75% of their simulated values corrects the bias in nitrate (as well as ammonium) in the U.S. However the mechanism for this potential reduction is unclear and may be a combination of errors in chemistry, deposition and sub-grid near-surface gradients. This “updated” simulation reproduces PM and ammonia loading and captures the strong seasonal and spatial gradients in gas-particle partitioning across the United States. We estimate that nitrogen makes up 15-35% of inorganic fine PM mass over the U.S., and that this fraction is likely to increase in the coming decade, both with decreases in sulfur emissions and increases in ammonia emissions.

1 Introduction

Ammonia (NH_3) is the most abundant form of gas-phase reduced nitrogen in the atmosphere and contributes to both the formation of particulate matter (PM) and the deposition of reactive nitrogen to the environment. Particulate matter in the atmosphere degrades air quality and visibility and can modify the radiative balance of the Earth both directly and indirectly through the formation of cloud droplets. Human morbidity has been shown to increase linearly with PM concentrations (Dockery et al., 1993; Pope et al., 2009), suggesting that while air quality standards are set to protect human health, there are no “safe” levels of PM. Typically over half of the fine PM in the United States is made up of inorganic aerosol (defined here as the sum of: sulfate, nitrate and ammonium) (NARSTO, 2004). These aerosols are formed in the atmosphere from gas-phase precursors (sulfur dioxide, nitrogen oxides and ammonia), which are largely emitted from anthropogenic activity, including agriculture. The formation of these aerosols is thermodynamically linked, with ammonium nitrate formation generally taking place only when sulfate has been fully neutralized. Ammonia sources have increased through the 20th century with industrial fertilizer production (Erisman et al., 2008), provoking concerns regarding excess nitrogen deposition to sensitive ecosystems (Beem et al., 2010). Recent trends in wet deposition and air quality indicate that the relative role of reduced vs oxidized nitrogen is changing (Pinder et al., 2011). Thus ammonia and particulate nitrogen play important roles in both air quality and ecosystem health.

Model studies suggest that the reduction of SO₂ emissions in the U.S. may shift aerosol composition towards nitrate formation (eg. (Pye et al., 2009)) and that ammonia emissions control could play an increasing role in achieving compliance with air quality standards (Pinder et al., 2008;Pinder et al., 2007). While such predictions are predicated on accurate model descriptions of both ammonia and the complete inorganic gas-particle system, there have been few observational constraints available to verify the fidelity of these models. This is largely the result of the challenges of measuring ammonia, a sticky, semi-volatile compound with ambient concentrations that vary over several orders of magnitude (von Bobruzki et al., 2010). Model simulations have been widely validated against surface network observations of inorganic aerosol concentrations and wet deposition (eg. (Park et al., 2004;Adams et al., 1999;Bessagnet et al., 2004)). Observations of gas-phase precursors alongside aerosol concentrations are more rare. Efforts have been made to optimize inorganic aerosol precursor emissions based on observed particle concentrations (Henze et al., 2009), however errors in PM formation and loss may cloud the links between precursor emissions and ambient particle concentrations. Recently, infrared satellite instruments have demonstrated the capability to measure ammonia from space (Beer et al., 2008;Clarisse et al., 2009). The spatial and continuous global coverage of such observations provides critical complementarity to specific field campaign observations. However, the sensitivity of these infrared sounders can be limited, particularly as atmospheric ammonia is largely present in the boundary layer, where thermal contrast can be low. Our goal here is to apply a series of unique satellite and surface inorganic measurements to investigate both atmospheric ammonia and particle phase nitrogen in the United States.

Thermodynamic models have been developed to describe the partitioning of semi-volatile species. Several studies have confirmed that the assumption of equilibrium partitioning is valid for ambient aerosol (eg (Ellis et al., 2011;Nowak et al., 2010;Nowak et al., 2006)). Thus 3-D model simulation errors are not likely to result from errors in the description of thermodynamic partitioning but rather from (1) errors in precursor emission estimates (2) errors in formation of sulfate or nitric acid (3) biases in temperature and humidity leading to biased gas-particle partitioning or (4) errors in gas and particle deposition. Here we investigate the skill of the GEOS-Chem global model in reproducing regional ammonia loadings and inorganic concentrations and partitioning. We note that the study of Walker et al, (2012), completed at the same time as this work, addresses some of the same issues, particularly in California, and reports similar results to those presented here. Our objective is

to identify obvious biases in the key processes outlined above and to suggest what kind of field measurements could be particularly valuable. Routine measurement of ammonia will be added in the coming years to select sites in the IMPROVE network in the United States, providing additional constraints on inorganic gas-particle partitioning. These future observations and those discussed herein can contribute to an improved understanding of the complete inorganic system. This will be critical to the accurate interpretation of new satellite observations of ammonia and resulting estimates of the role of nitrogen in PM formation, climate, and ecosystem health.

2 Measurement Description

2.1 IMPROVE network aerosol measurements and the Midwest Ammonia Monitoring Project

The Interagency Monitoring of PROtected Visual Environments (IMPROVE) network of stations was established in 1987 to monitor visibility in national parks and other protected environments in the United States (Malm et al., 1994). Surface concentrations of fine particle ($PM_{2.5}$) sulfate, nitrate, organic carbon and elemental carbon are measured as 24-hour averages every third day. The ammonium ion is not routinely measured in the IMPROVE network. Nitrate (and sulfate) are collected on a Nylasorb substrate after passing through a carbonate denuder tube, minimizing both nitrate volatilization and gas-phase contamination (Malm et al., 2004). We show here comparisons at 238 sites operating in 2004 in the continental United States.

We also examine measurements from the Midwest Ammonia Monitoring Project (MWNH₃), a field intensive at 10 sites (9 co-located at IMPROVE sites) from November 2003 through October 2005 (Blanchard and Tanenbaum, 2005; Sweet et al., 2005). We show only measurements from 2004. Measurements of fine particle sulfate, nitrate, ammonium as well as gas-phase ammonia, nitric acid and sulfuric acid were collected every 6th day by the Illinois State Water Survey. The measurement system consisted of two denuders, one to collect HNO₃ and SO₂ and the second to collect NH₃, followed by a Teflon and Nylon filter to collect the particles. Measured sulfate & nitrate agreed well with co-located IMPROVE measurements (Blanchard and Tanenbaum, 2005).

2.2 In situ measurements

Several field experiments were designed and conducted to investigate the chemical composition of PM_{2.5} aerosol and the concentrations of trace gases (HNO₃, NH₃ and SO₂) at monitoring locations for the IMPROVE program from the late 1990's through 2010 (Figure 1). Daily 24-hr measurements were made in a variety of seasons during 1999, 2002, 2003 and 2004. Study sites included Big Bend National Park (July – October, 1999), Yosemite National Park (July – September, 2002), Bondville, Illinois (February 2003), San Geronio Wilderness Area, California (April and July 2003), Grand Canyon National Park, Arizona (May 2003), Brigantine National Wildlife Refuge, New Jersey (November 2003), and Great Smoky Mountains National Park, Tennessee (July/August 2004). Aerosol composition measured at these sites has previously been reported (Yu et al., 2005b; Lee et al., 2004; Lee et al., 2008a; Yu et al., 2006). In addition, a series of year-long intensive measurements were made in Rocky Mountain National Park (Nov 2008-Oct 2009, daily), Boulder, WY (Dec 2006-December 2010, 3&4-day average), and Brush and Loveland, CO (Dec 2008-Nov 2009, weekly average).

A URG (University Research Glassware) cyclone/annular denuder/filter pack system was used for PM_{2.5} and trace gas (HNO₃, NH₃ and SO₂) sampling. Ambient air is drawn into the URG sampler through a cyclone (D₅₀=2.5 µm, 10 LPM), and through two denuders in series for collection of the gaseous species of interest. Na₂CO₃ (or NaCl for Big Bend NP and Boulder, WY) coated the first denuder for collection of gaseous HNO₃ and SO₂ and the second denuder was coated with phosphorus acid (or citric acid for Big Bend NP) to collect gaseous NH₃. SO₂ concentrations are not measured at Big Bend NP and in Boulder, WY. The air stream continued through either a nylon filter (Nylasorb, 1.0 µm pore size, Pall Corporation) and a backup phosphorus acid-coated denuder or a 3-stage filter pack with a Teflon filter (Teflo, 2.0 µm pore size, Pall Corporation), a nylon filter (Nylasorb, 1.0 µm pore size, Pall Corporation) and a backup citric acid-coated cellulose filter (or quartz filter). Sampling at the ammonia-rich Brush, CO site was performed with a lower flow rate (3 LPM) and with an extra ammonia denuder before the filter to ensure that ammonia collection capacity was not exceeded. Analysis of PM_{2.5} filter and denuder extracts focused on the main PM_{2.5} ionic species (SO₄²⁻, NO₃⁻, NH₄⁺), and trace gases (HNO₃, NH₃ and SO₂). Sampling and analysis details are described in detail elsewhere (Yu et al., 2005b; Lee et al., 2004; Lee et al., 2008b). Species detection limits were typically 20-70 ngm⁻³ while measurement precisions

were typically in the range of 3-9% (RSD) for individual samples, but are correspondingly smaller for the monthly or seasonal means shown here. Accuracy checks on key components of the measurement (sample volume, extract volume, and ion concentration) typically reveal biases of a few percent, with a range from approximately 1-10%. PM_{2.5} ion concentrations measured with the URG compare well ($R^2 > 0.9$ and mean biases less than 10% across the US) with online measurements, as discussed by Lee et al. (2008b).

2.3 Infrared Atmospheric Sounding Interferometer (IASI)

The Infrared Atmospheric Sounding Interferometer (IASI) was launched aboard the MetOp-A platform in October 2006. This nadir sounder provides global measurements of a suite of atmospheric trace gases, including ammonia (Clerbaux, 2009). The instrument footprint (12 km x 12 km) is combined with extensive cross-track scanning (2200 km) to provide detailed global daily coverage. Measurements from sun-synchronous polar orbit are made twice daily at 9:30 and 21:30 local time.

Ammonia retrievals are based on an absorption feature $\sim 950 \text{ cm}^{-1}$. Initial global retrievals reported by *Clarisse et al.* (2009) were based on a brightness temperature scaling approach, but here retrievals apply formal optimal estimation methods (Rodgers, 2000) to retrieve the profile of ammonia($\hat{\mathbf{x}}$):

$$\hat{\mathbf{x}} = \mathbf{x}_a + \mathbf{A}(\mathbf{x} - \mathbf{x}_a) + \epsilon \quad (1)$$

where \mathbf{x} is the true profile, \mathbf{x}_a is the a priori constraint, which is a constant global moderately polluted mean profile from the TM5 model, and ϵ is the spectral measurement error. The averaging kernels (\mathbf{A}) describe the vertical sensitivity of the instrument and depend on the thermal contrast and vertical distribution of ammonia. IASI NH₃ measurements are generally most sensitive at 1-2 km altitude, where concentrations are highest and thermal contrast sufficient for detection. Thermal contrast is also highest during daytime, and therefore only daytime retrievals are used here. Retrieved ammonia is shown here as an integrated column concentration given the low vertical sensitivity.

The retrievals are performed in near real time using the fast radiative transfer model FORLI (Hurtmans et al., 2012). Note that with the constraints applied to allow for global retrievals, the averaging kernels and degrees of freedom (DOF) are unrealistically small for this research

product (typically < 0.3 over the continental United States), especially in comparison to the initial work of Clarisse et al.(2010) over the San Joaquin Valley. This does not impact the quality of the retrievals; however, low DOFs imply larger reliance on the a priori when attempting to compare the IASI retrievals with other measurements or models. This is discussed further in Section 4.2.

3 Model Description

We compare here measurements of the inorganic gas-particle system with the GEOS-Chem global model of atmospheric chemistry (www.geos-chem.org). We employ v9-01-01 of the model driven by GEOS-5 assimilated meteorology from the NASA Global Modeling and Assimilation Office (GMAO). We conduct a series of coupled oxidant-aerosol nested grid simulations ($0.5^{\circ} \times 0.67^{\circ}$ horizontal resolution) (Chen et al., 2009) over North America for three years (2004, 2009 and 2010) and show results over the continental United States. Boundary conditions are from global simulations performed at $2^{\circ} \times 2.5^{\circ}$ horizontal resolution for the same years.

The GEOS-Chem oxidant-aerosol simulation includes $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-NH}_3$ aerosol thermodynamics coupled to an ozone- NO_x -hydrocarbon-aerosol chemical mechanism (Park et al., 2004). Partitioning of total ammonia and nitric acid between the gas and particle phases is calculated using the ISORROPIA II thermodynamic equilibrium model (Fountoukis and Nenes, 2007) as implemented in GEOS-Chem by Pye *et al.* (2009). The gas-particle equilibrium considers sodium and chloride from accumulation mode sea salt as well as sulfate, nitrate and ammonium. Formation of inorganic aerosol on coarse mode dust and sea salt is excluded, thus estimated aerosol concentrations represent $\text{PM}_{2.5}$ concentrations. In this implementation of ISORROPIA the inorganic aerosol are assumed to be metastable on the upper branch of the hygroscopicity hysteresis curve. The metastable assumption likely holds near the surface where relative humidities exceed the deliquescence relative humidity on a daily basis, but may not be appropriate in the free troposphere (Wang et al., 2008).

Anthropogenic emissions of aerosol precursors over the US are specified according to the US EPA National Emission Inventory for 2005 (NEI05, with seasonality as in Park et al. (2004)), with biofuel emissions from the US EPA National Emission Inventory for 1999 (NEI99) and year-specific biomass burning from the GFED2 inventory (van der Werf et al., 2006).

1 Anthropogenic emissions are scaled to the model year following national energy use statistics
2 as described by van Donkelaar et al. (2008). Natural and agricultural ammonia emissions in
3 GEOS-Chem follow the global inventory of *Bouwman et al.* (1997) with seasonal variation as
4 described by *Park et al.* (2004). Natural emissions of DMS, NO_x from lightning and soils, and
5 sea salt depend on meteorology and are computed online in the model (see description in Pye
6 et al. (2009)). Emission totals for ammonia, NO_x and SO_x over the United States for 2004 are
7 given in Table 1.

8 Wet deposition of soluble aerosols and gases follows the scheme of *Liu et al.* (2001) including
9 contributions from scavenging in convective updrafts, rainout, and washout. Dry deposition
10 follows a standard resistance-in-series model (Wesely, 1989) and is discussed further in
11 Section 4.3.

12 The GEOS-5 meteorology fields used here suffer from an artificially low planetary boundary
13 layer (PBL) height at nighttime which can produce large biases in simulated nighttime surface
14 concentrations (and thus 24-hr or monthly means). We implement a correction to the standard
15 v9.01.01 version of GEOS-Chem by restricting the PBL height from dropping below a
16 minimum mechanical mixing depth, defined as a function of local friction velocity (Lin and
17 McElroy, 2010;Koracin and Berkowicz, 1988). This restriction brings PBL heights in line
18 with values measured at the ARM-Southern Great Plains site (not shown). This also
19 eliminates an erroneously large increase in nitrate concentrations at night.

20 Previous studies using GEOS-Chem and the MARS-A thermodynamic scheme have shown
21 large biases (up to a factor of two) in simulated nitrate over the United States (Park et al.,
22 2004;Henze et al., 2009). Recent evaluation of the inorganic aerosol simulation using
23 ISORROPIA also shows large biases in nitrate, which is overestimated by GEOS-Chem in the
24 Eastern U.S. and underestimated in the Western US (Pye et al., 2009). Zhang et al. (2012),
25 using a similar model configuration to our work (but using the MARS-A scheme), show that
26 both nitric acid and ammonium nitrate concentrations are overestimated in the model when
27 sulfate is unbiased, particularly in wintertime. They suggest that this is the result of excessive
28 HNO₃ formation via N₂O₅ hydrolysis. In addition, they show that ammonia measurements in
29 the upper Midwest support an increase in springtime emissions compared to the standard
30 seasonality applied in GEOS-Chem based on Park et al. (2004).

31 We build on this work by bringing new measurements of both ammonia (satellite) and gas-
32 particle partitioning (*in situ*) to bear on the inorganic system. We evaluate daily mean

concentrations simulated for 2004 with the URG observations from 1999, 2002, 2003 and 2004 described in Section 2. Thus interannual variability in meteorology may degrade the comparison, particularly the ability to reproduce daily variability. The same 2004 simulation is compared to monthly mean measurements across the IMPROVE network and the Midwest Ammonia Monitoring Project. Monthly mean measurements from 2009 in Wyoming and Colorado are compared to the 2009 simulation. For comparison with IASI measurements we match simulated ammonia profiles with the location and time of each retrieval and then apply the IASI averaging kernel and a priori ammonia profile as in equation 1, and integrate over the vertical column. The paired comparisons are then re-gridded to the GEOS-Chem horizontal resolution.

4 Results

4.1 Initial fine PM evaluation

The over 200 IMPROVE stations reporting surface $PM_{2.5}$ composition in 2004 provide dense coverage of the United States and a good basis for model evaluation. Figure 2 shows that the model reproduces the spatial and seasonal distribution of observed sulfate in 2004, with a small positive bias in the Northeast in the summer/fall (responsible for the normalized mean bias of 0.30 in the Fall; $NMB = \sum_i M_i - O_i / \sum_i O_i$, where O_i =observed values and M_i =model values) and a small underestimate in the Southeast in summertime. However regression slopes between observed and simulated means are close to unity, with the exception of the Northeast in the fall, and thus these errors do not substantially degrade the model simulation of PM.

Figure 3 shows the same comparison for nitrate. The model captures the large scale patterns and seasonality, with two obvious, significant biases. Nitrate concentrations are underestimated in California, possibly due to an underestimate of ammonia or nitrogen oxide emissions in the region. The model underestimate of nitrate in the southwest may also be associated with the failure to represent coarse mode nitrate on dust, the tail of which Lee et al. (2008a) show can be included in $PM_{2.5}$ measurements. Nitrate concentrations are overestimated in the rest of the United States year-round. This is consistent with the overestimate reported in other studies using both GEOS-Chem and other models (Pye et al., 2009; Henze et al., 2009; Zhang et al., 2012; Yu et al., 2005a; Walker et al., 2012). Note that regression lines and NMB statistics are shown separately for the Eastern and Western U.S. to

demonstrate these differences. In the Eastern United States normalized mean biases are close to or greater than 1.0 in all seasons, except spring. Similar biases are seen with respect to CASTNet network observations of both nitrate and ammonium (not shown here, but reported by Zhang et al. (2012)). However CASTNet measurements do not provide a good quantitative test of the fine PM simulation given that measurements may include contamination from coarse mode nitrate (no size-selective sampling) which can be significant (Lee et al., 2008a), and CASTNet ammonium nitrate measurements are more susceptible to re-volatilization errors from the Teflon filters used (Ames and Malm, 2001).

Potential causes for the nitrate overestimate seen in Figure 3 include (1) overestimated precursor emissions of either ammonia or nitrogen oxides (2) excess nitric acid formation (3) an underestimate in nitrate (or nitric acid) deposition (4) a cold or wet bias in the model that favors excess ammonium nitrate formation or (5) the absence of HNO_3 reactions with coarse mode PM. We explore the bias in simulated nitrate in the following sections.

4.2 Investigating ammonia emissions

Extensive evaluation in the U.S. against aircraft and satellite observations effectively precludes errors in NO_x emissions as the source of the observed nitrate bias (Lamsal et al., 2011; Zhang et al., 2012; Martin et al., 2006). However, ammonia emissions are poorly constrained.

Figure 4 compares seasonal gridded mean ammonia concentrations observed by the IASI instrument with the GEOS-Chem simulation from May 2009 through April 2010. Only gridboxes with at least 4 observations during a season are shown in order to avoid drawing conclusions from limited, variable measurements. We first show the number of retrievals averaged in each gridbox, to demonstrate both the extensive cross-track coverage of IASI, and the seasonal variability in the number of successful retrievals of ammonia. This is most likely due to cloud coverage, particularly in the fall and winter. We also see in Figure 4 the high degree of reliance on the a priori in the retrieval. This is particularly evident when comparing the native GEOS-Chem simulation with the “retrieved” simulation where the IASI ammonia averaging kernel and a priori are applied as in equation 1. Both the IASI and GEOS-Chem retrieved values rarely drop below the a priori column concentration ($\sim 0.3 \times 10^{16}$ molecules cm^{-2}) and seasonality is reduced, consistent with the reported characteristics of the ammonia retrievals for the Tropospheric Emission Spectrometer (TES) (Shephard et al., 2011).

Furthermore, all the features of the GEOS-Chem ammonia distribution are considerably damped by application of the averaging kernel.

IASI ammonia concentrations peak in the springtime in the Midwest, in contrast with simulated concentrations which peak in the summertime. However, comparison of the native and retrieved GEOS-Chem fields suggest that that IASI sensitivity in the Midwest may be lower in the summer than the springtime, which may contribute to this apparent difference. The distribution of simulated ammonia agrees reasonably well in the region in summertime, but the comparison suggests that springtime ammonia emissions are far too low in GEOS-Chem. This is consistent with Zhang et al. (2012) who find that comparisons with the MWNH₃ observations support a broadening of the NH₃ emission peak from summer into spring and fall, with more than a doubling of March and April emissions. Total U.S. ammonia emissions increase by 18% (see Table 1). Some previous studies also support a springtime peak in ammonia emissions in the United States (Pinder et al., 2006; Gilliland et al., 2006); however, optimized ammonia emissions from Henze et al. (2009) peak in the summertime. These differences in part confirm the challenge of constraining ammonia emissions from wet deposition or aerosol measurements as done in the preceding studies. The increase in springtime ammonia concentrations resulting from applying the Zhang et al. (2012) seasonality in GEOS-Chem is washed out when the IASI averaging kernels are applied and does not close the gap with the IASI observations. In fact, an extremely large and likely unrealistic increase in ammonia concentrations (in excess of a factor of 5) would be required to reconcile the GEOS-Chem simulation with the IASI measurements over the Midwest. As discussed in Section 2.3 this is due to the artificially low IASI degrees of freedom for signal and that the averaging kernels do not accurately represent the balance between a priori and detected information in the retrieval. Thus, for this study, the IASI retrievals are only used qualitatively. In light of this, we conclude that IASI measurements support the springtime enhancement of ammonia emissions suggested by Zhang et al., (2012) and include this increase in the comparisons that follow (referred to as “New NH₃ Seasonality”). Wells et al. (2012) find a similar springtime underestimate of methanol in the GEOS-Chem simulation compared to the IASI methanol retrievals, which they attribute to an underestimate of biogenic emissions from new leaves in mid-latitude ecosystems. Ammonia emissions from vegetation are negligible (Guenther et al., 2012), thus enhanced springtime emissions are far more likely associated with agricultural practices, for example earlier fertilizer application in

1 the Midwest, or seasonal changes in cattle feed availability as associated emissions (Hristov et
2 al., 2011).

3 Figure 4 also indicates that ammonia emissions in California and particularly in the San
4 Joaquin Valley (SJV) are underestimated in GEOS-Chem. This mainly rural and agricultural
5 region features some of the largest ammonia emissions in the country (Goebes et al.,
6 2003;Makar et al., 2009), and regularly reports some of the highest PM loading in the United
7 States (Chow et al., 1996;Watson et al., 2000), leading to frequent violations of the National
8 Ambient Air Quality Standards. Clarisse et al. (2010) previously estimated that mean
9 summertime surface ammonia concentrations in the SJV regionally exceed 15 ppb. Figure 4
10 shows that California is well-observed by IASI, with the exception of the wintertime, and
11 while the spatial and seasonal patterns of enhanced ammonia are captured by GEOS-Chem,
12 IASI concentrations are significantly underestimated from spring through fall. Retrieval
13 characteristics preclude a quantitative estimate of the associated emissions gap (see previous
14 discussion); however, an underestimate in ammonia in the region is consistent with the
15 ammonium nitrate formation underestimate implied by the nitrate underestimate in the region
16 (Figure 3), as also suggested by Walker et al. (2012). Nowak et al. (2012) report an
17 underestimate of dairy emissions in the South Coast Air Basin in the NEI-05 emission
18 inventory which could contribute to the underestimate in California.

19 Figure 5 presents a further evaluation of simulated ammonia, which illustrates some of the
20 challenges associated with local comparisons and strong regional gradients. We compare
21 simulated and measured ammonia at four field sites located in some proximity (within 700
22 km, Figure 1). The model (with “New NH₃ Seasonality” emissions as discussed above)
23 reproduces ammonia well at the rural site in Wyoming which is removed from local sources.
24 The Colorado sites represent a strong west to east gradient from the very clean Rocky
25 Mountain National Park to Brush, CO which is east and often down-wind of one of the largest
26 inventory of cattle in the United States (Weld County). Observed monthly mean ammonia
27 concentrations increase more than 20-fold across this gradient, while model concentrations at
28 most double. While the underestimation of ammonia emissions associated with these
29 agricultural operations has a limited impact on ammonium nitrate formation in the model
30 (limited by the nitric acid supply), it implies potentially large underestimates of simulated
31 regional nitrogen deposition.

The qualitative information provided by the IASI instrument suggests that the ammonia emissions biases may be responsible for two aspects of the GEOS-Chem nitrate simulation shown in Figure 3: (1) The underestimate of nitrate in California is associated, at least in part, with an underestimate in ammonia emissions in the region. (2) A springtime underestimate of ammonia emissions in the Midwest masks some of the bias in nitrate present year-round in the simulation. Increasing the ammonia emissions in springtime as suggested by Zhang et al. (2012) increases the nitrate bias seen in Figure 3 (slope increases from 1.04 to 1.77 – see increase in annual mean nitrate concentrations in Figure 6). Thus, while further validation of ammonia emission inventories is clearly called for, there is no evidence to suggest that the excess nitrate levels in GEOS-Chem are associated with biases in emissions.

4.3 Further exploration of the nitrate bias

Alternate explanations for the nitrate bias in the GEOS-Chem model include errors in nitric acid formation or deposition. Surface nitric acid concentrations are challenging to evaluate as a result of the strong vertical gradient associated with surface uptake. Zhang et al. (2012) make an attempt to account for this by adjusting the lowest model gridbox center (70 m) simulated concentrations to the 10m CASTNet measurement altitude using an aerodynamic resistance correction. They report an 18% annual average high bias in the model following this correction, which they attribute to an overestimation of nitric acid formation via N_2O_5 hydrolysis on ammonium nitrate aerosols. However this is unlikely given that McIntyre and Evans (2010) show that the sensitivity of the NO_x budget to a decrease in the uptake coefficient of N_2O_5 is less than 10% given the current values of the uptake coefficient assumed in GEOS-Chem. This is confirmed in Figure 6 which shows that nitrate concentrations decrease by less than 10% when the uptake coefficient of N_2O_5 is reduced by an order of magnitude in the model.

Nitric acid formation could also be promoted by an excessively oxidizing environment. However, nitrate concentrations are found to be relatively insensitive to modest changes in OH. A reduction in simulated OH levels by 25% does not impact simulated nitrate levels (within 5% of baseline concentrations), as a reduction in nitric acid formation is somewhat compensated by an increase in lifetime. Similarly, ~15% overestimation of the reaction rate of NO_2 oxidation by OH suggested by recent studies (Mollner et al., 2010; Henderson et al.,

2012), does not significantly impact nitrate concentrations at the surface over the United States (within 5% of baseline GEOS-Chem simulated concentrations).

An additional sink of nitric acid, not considered in the GEOS-Chem simulation here, is the uptake of nitric acid on coarse mode dust or sea salt (eg. (Goodman et al., 2000; Abbatt and Waschewsky, 1998)). Neglecting this effect could lead to a high bias in surface nitric acid, particularly in the southwest near dust sources, and in coastal regions influenced by coarse mode sea salt. However, Fairlie et al. (2010) show that including the uptake of nitric acid on dust in the GEOS-Chem simulation does not eliminate the nitric acid bias in dusty outflow from Asia. Thus, while this effect may contribute locally to the model overestimate of nitric acid and fine particulate nitrate, it is unlikely that this can explain the fine nitrate surface bias through most of the eastern US.

Ammonium nitrate formation is favored in cold and humid conditions. GEOS-Chem uses assimilated meteorology and thus temperature and relative humidity are unlikely to be subject to large systematic biases. Meteorological parameters are not reported for the IMPROVE sites shown here, but were made during the field intensives described in Section 2.2. A general comparison of 2004 simulated values with the temperature and relative humidity detected at these sites in various years does not reveal any consistent biases. It is therefore highly unlikely that a strong, consistent, year-round, cold and/or wet bias exists in the model and could be the cause of excess ammonium nitrate formation. Such a bias would also imply a corresponding underestimate in nitric acid, which is inconsistent with our simulations and the results of Zhang et al. (2012). We also verify that surface concentrations of ammonium nitrate are insensitive to the metastable assumption employed in our implementation of ISORROPIA II (see Section 3).

Errors in deposition of either particle or gas-phase nitrate could contribute to a biased simulation of nitrate. Zhang et al. (2012) show that annual mean wet deposition of nitrate in GEOS-Chem is biased slightly high but within 10% of measurements from the National Atmospheric Deposition Program (NADP) over the continental United States. Dry deposition of aerosols is size-dependent in the model and any bias in this process would manifest itself in simulated sulfate as well as nitrate. As the sulfate simulation is relatively unbiased and dry deposition of particles makes a minor contribution to total nitrogen deposition (Zhang et al., 2012) we rule this out as a dominant factor in the simulated nitrate overestimate. However, the dry deposition velocity of nitric acid over various land types is considerably larger and not

1 well constrained. Derived estimates from CASTNet sites across the United States vary from
2 0.8 to 3.3 cm s^{-1} (Clarke et al., 1997). Schwede et al. (2011) show that the choice of
3 deposition models can result in deposition velocities that differ by a factor of 2 to 3, and that
4 CASTNet estimates of nitric acid deposition velocities are consistently lower than comparable
5 estimates derived using the CAPMoN network model. Annual mean simulated dry deposition
6 velocities over the continental United States in GEOS-Chem vary from 0.2 to 3.9 cm s^{-1} , a
7 similar range to values reported by CASTNet. Given the poor constraints on this value, we
8 test the sensitivity of simulated nitrate to the deposition velocity for nitric acid by doubling
9 this value year-round. Figure 6 shows that particulate nitrate concentrations decrease by less
10 than 10%, and therefore that uncertainties in deposition velocities cannot reconcile the GEOS-
11 Chem simulation with the nitrate observations at the IMPROVE sites. Alvarado et al. (2010)
12 previously showed that nitric acid concentrations measured during the ARCTAS campaign
13 were overestimated by over a factor of two in GEOS-Chem and invoke insufficient
14 precipitation scavenging in the Arctic. A good simulation of the wet removal of aerosols over
15 the continental United States (Fisher et al., 2011) in concert with the high solubility of nitric
16 acid makes this an unlikely source of the bias here; however, uncertainties in precipitation
17 distribution and frequency are large and we cannot rule out an underestimate of wet
18 scavenging as a contributing factor in the nitrate bias.

19 Figure 6 shows that when nitric acid concentrations are artificially decreased to 75% of their
20 values at each timestep (as an input to the thermodynamic gas-particle partitioning only),
21 annual mean U.S. surface nitrate concentrations can decrease by up to 2 $\mu\text{g m}^{-3}$. This decrease
22 brings the nitrate simulation into near agreement with the IMPROVE measurements (Figure
23 7), with the exception of California, where the existing bias is exacerbated (see Section 4.1).
24 Nitrate concentrations remain somewhat high in the Northeast (NMB=0.42 for the Eastern
25 US), particularly in winter when ammonium nitrate formation is favored. However, overall,
26 model performance is substantially improved by this forced reduction in nitric acid with NMB
27 values in the Eastern U.S. considerably lower (all below 0.50) than baseline values shown in
28 Figure 3. Figure 8 shows how this decreased nitric acid brings the model into agreement with
29 the ammonia, nitrate and ammonium observations from the Midwest Ammonia Monitoring
30 Project in 2004. A reduction of nitric acid reduces ammonium nitrate formation and
31 conversely forces more ammonia into the gas-phase, particularly in the fall and winter.
32 Ammonium nitrate concentrations may still be overestimated in the simulation, consistent

1 with the Figure 6 comparison with IMPROVE sites, but overall model bias is drastically
2 reduced.

3 Figure 9 shows that this “updated” simulation with reduced nitric acid also compares well
4 with the year-round nitrate observations in Wyoming and Colorado. Nitrate at the Loveland
5 and Brush sites is underestimated in the wintertime with the “updated” simulation, however
6 Figure 5 suggests that this is associated with an underestimated wintertime supply of
7 ammonia. Year-round cattle operations in the region likely maintain ammonia emissions in
8 cooler seasons above the summertime-peaking seasonality currently applied to all
9 anthropogenic ammonia emissions in the NEI-05 inventory. This calls for a dis-aggregation of
10 ammonia emissions and an investigation of the seasonality of emissions in various sectors.

11 While we can identify no single process or uncertainty that could result in the current
12 overestimation of surface nitrate concentrations in the GEOS-Chem simulation, it is clear that
13 a simple year-round reduction of nitric acid can improve model performance drastically. A
14 number of processes may potentially contribute to this. First, while we have tested the impact
15 of oxidant loading and N_2O_5 hydrolysis, there may be other unrecognized chemical pathways
16 for NO_y cycling which may reduce nitric acid formation. Second, an underestimate of
17 deposition of nitric acid could contribute to this bias, however as shown above, this cannot
18 explain the entire model bias. Third, uptake of HNO_3 on coarse PM (not treated here) may
19 reduce both nitric acid and nitrate concentrations, particularly in the dusty southwest. Fourth,
20 the vertical sub-grid gradient of nitric acid at the surface may induce a similar gradient in
21 ammonium nitrate formation which has not been accounted for here. Sievering et al.(2001)
22 find that the vertical gradient in nitrate is weaker than for HNO_3 , suggesting that
23 thermodynamic equilibrium may not be maintained through the surface layer. de Brugh et al.
24 (2012) suggest that not accounting for this effect can mute the simulated diurnal cycle. They
25 recommend artificially increasing the altitude of the meteorological input parameters in coarse
26 resolution models to correct for this effect; however, they show that this correction is only
27 valid in unstable conditions. It is unclear how this would impact the comparison of daily mean
28 surface concentrations. Additional time-resolved gas-particle vertical profile measurements
29 through the boundary layer are required to investigate this phenomenon further and develop
30 an appropriate global correction for coarse resolution models such as GEOS-Chem. We note
31 that no effort was made to optimize our artificial nitric acid reduction seasonally, and the
32 uncertainties outlined above may play a role in different seasons, as well as different regions.

4.4 Application of “updated” simulation

Figure 10 compares this “updated” (HNO_3 reduced to 75%) simulation with the daily observations of inorganic PM from the seven focus sites (Section 2.2) as an independent check on the comparisons discussed in Section 4.3. The timeseries also illustrates the regional and temporal variability of inorganic PM across the United States. Sites are ordered roughly west to east. Note that measurements do not correspond to the 2004 year of the simulation for six of the seven sites, and thus meteorological variability can degrade these comparisons. The “updated” model simulation reproduces the character of inorganic PM across the US both in magnitude and variability. Concentrations are highest in the East and contributions from nitrate are largest in the fall/winter and in the western US. Elevated PM concentrations are episodic and generally persist for 2-3 days.

The seasonal mean simulated gas fraction for the three inorganic classes (SO_x , NH_x and total nitrate) are compared to these same observations in Figure 11. These patterns illustrate the complex gas-particle partitioning regimes across the United States. This figure particularly illustrates the spatial variability in gas-particle partitioning and the necessity of using high-resolution simulations to resolve this behavior and usefully compare with in situ measurements. We see that sulfate formation is most efficient in the summertime due to higher oxidant loadings and that the short lifetime of SO_2 results in gas fraction hot spots near local sources. GEOS-Chem captures this seasonal SO_x partitioning across the United States, with the exception of the remote Brigantine, NJ site, which itself may experience predominantly processed emissions as sulfate, but which is located in a gridbox with fresh emissions.

Figure 11 shows that much of the ammonia in the eastern U.S. neutralizes acidity in the region to form ammonium salts, and thus the N(-III) gas fraction is low. Important source regions in both California and the Midwest produce excess ammonia which locally remains predominantly in the gas-phase, particularly in the summertime. The model reproduces the observed N(-III) partitioning with the exception of the Big Bend site near the Texas-Mexico border. Observed concentrations of ammonia are very low at this site ($< 0.4 \mu\text{g m}^{-3}$), and are overestimated by the model by at least a factor of two (likely due to an underestimate in sulfate, Figure 10). Given the low PM concentrations at the site, this significantly degrades the gas fraction comparison.

Much of the nitric acid in the Eastern U.S. participates in ammonium nitrate formation given the up-wind source of ammonia from the Midwest. Conversely, much of the Western U.S. is limited by the ammonia supply. This East-West gradient in the N(V) gas fraction is reproduced by the model, with the exception of the San Geronio site in California in springtime, where both complex terrain unresolved by the model, and the ammonia underestimate discussed in Section 4.2 and seen in Figure 4 likely play a role. We note that using surface measurements to evaluate the simulation of total nitrate partitioning presumes that any near-surface gradient is consistent between nitric acid and nitrate.

Figure 12 quantifies the nitrogen contribution to inorganic PM mass. In particular we see that in wintertime nitrogen makes up over a third of inorganic PM mass in the Northern United States. In all seasons at least 15% of continental inorganic PM mass is nitrogen, and this fraction will almost certainly grow as drastic further reductions in sulfur emissions expected in the United States (van Vuuren et al., 2011) are likely to outpace the recent decline in NO_x emissions (Pinder et al., 2011). Furthermore, organic nitrogen may contribute significant additional nitrogen mass to total fine PM (Fry et al., 2009; Rollins et al., 2009).

5 Conclusions

Model simulations of inorganic PM are typically evaluated by network measurements of sulfate and nitrate concentrations or wet deposition. Comparison of a 2004 GEOS-Chem simulation with observations of sulfate and nitrate at IMPROVE sites reveals the following features: (1) a good simulation of sulfate concentrations year-round with a modest high bias in the Northeast in the Fall and a modest underestimate in the Southeast in the summer; (2) an underestimate of nitrate concentrations year-round in California and (3) a large positive bias in nitrate year-round across the rest of the United States, likely associated with an overestimate in nitric acid concentrations previously reported by Zhang et al. (2012). IASI observations confirm that ammonia concentrations are underestimated in California and are likely the source of the nitrate underestimate in this region. A recent, independent study by Walker et al. (2012) reaches the same conclusion. A spatially diverse set of full year observations is required in the region to further characterize the emission discrepancies. Comparison with IASI also suggests that ammonia concentrations are underestimated in the springtime with current assumed emission seasonality, however increasing emissions in this region only exacerbates the nitrate bias.

1 We explore the sensitivity of simulated nitrate to a number of uncertain model parameters
2 related both to chemistry and deposition but are unable to identify the cause of the model
3 overestimate. We do find that decreasing nitric acid concentrations uniformly to 75% of
4 simulated values brings the model into close agreement with the IMPROVE nitrate
5 measurements, as well as the ammonium and nitrate measured during the Midwest Ammonia
6 Monitoring Project and the year-round nitrate measured at a suite of sites in Wyoming and
7 Colorado. Further investigation into the role of sub-grid near-surface processes and the nitric
8 acid budget are required to resolve this. In particular, tower-based measurements of the
9 boundary layer vertical profile and fluxes could provide critical insight into this question.
10 Further investigation of the importance of coarse mode nitrate as a control on nitric acid
11 concentrations and fine particle nitrate throughout the US is also required.

12 We demonstrate the challenges of reproducing strong ammonia gradients near source regions.
13 However we also show that the impact of underestimating ammonia near these sources on PM
14 formation is limited, at least in the near-field. The fate of this excess ammonia and the
15 prevalence of these underrepresented “hot spot” emissions in the United States requires
16 further investigation in order to accurately characterize local deposition and ecosystem
17 response. Furthermore, our full year comparisons for sites in Wyoming and Colorado suggest
18 that fertilizer and livestock ammonia emissions may exhibit quite different seasonality with
19 implications for ammonium nitrate formation in wintertime.

20 This study uses a suite of in situ and satellite measurements, in particular focusing on
21 ammonia, to evaluate our understanding of the inorganic gas-particle system. While we
22 provide examples of model skill, the complexity of this system remains a challenge to capture
23 with full fidelity. For example, inclusion of bi-directional treatment of ammonia fluxes may
24 improve day-to-day variability in the model and the simulation of downwind concentrations
25 (Cooter et al., 2010). Additional co-located measurements of both gas and particle phase
26 inorganics are required to further constrain models and refine schemes that can be applied to
27 accurately characterize both PM formation and nitrogen deposition in the United States.

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13

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8

9

1 Table 1. Continental U.S. emissions for 2004. Ammonia emissions with “new
2 seasonality” shown in brackets (see Section 4.2)

Species	Emission
Ammonia (NH₃)	2.8 (3.3) TgNyr⁻¹
Anthropogenic	2.0 (2.5)
Biofuel	0.2
Biomass Burning	0.002
Natural	0.6
Sulfur Oxides (SO_x)	6.8 TgSyr⁻¹
Anthropogenic	6.7
Biofuel	0.001
Aircraft	0.01
Biomass Burning	0.09
Volcanic	0.02
Nitrogen Oxides (NO_x)	6.8 TgNyr⁻¹
Anthropogenic	5.5
Biofuel	0.01
Aircraft	0.2
Fertilizer	0.09
Biomass Burning	0.03
Lightning	0.7
Soil	0.4

3

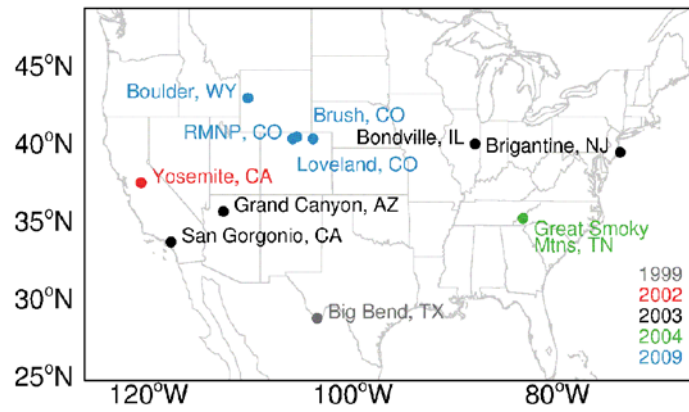


Figure 1: Surface measurement site locations, colored by year of measurement.

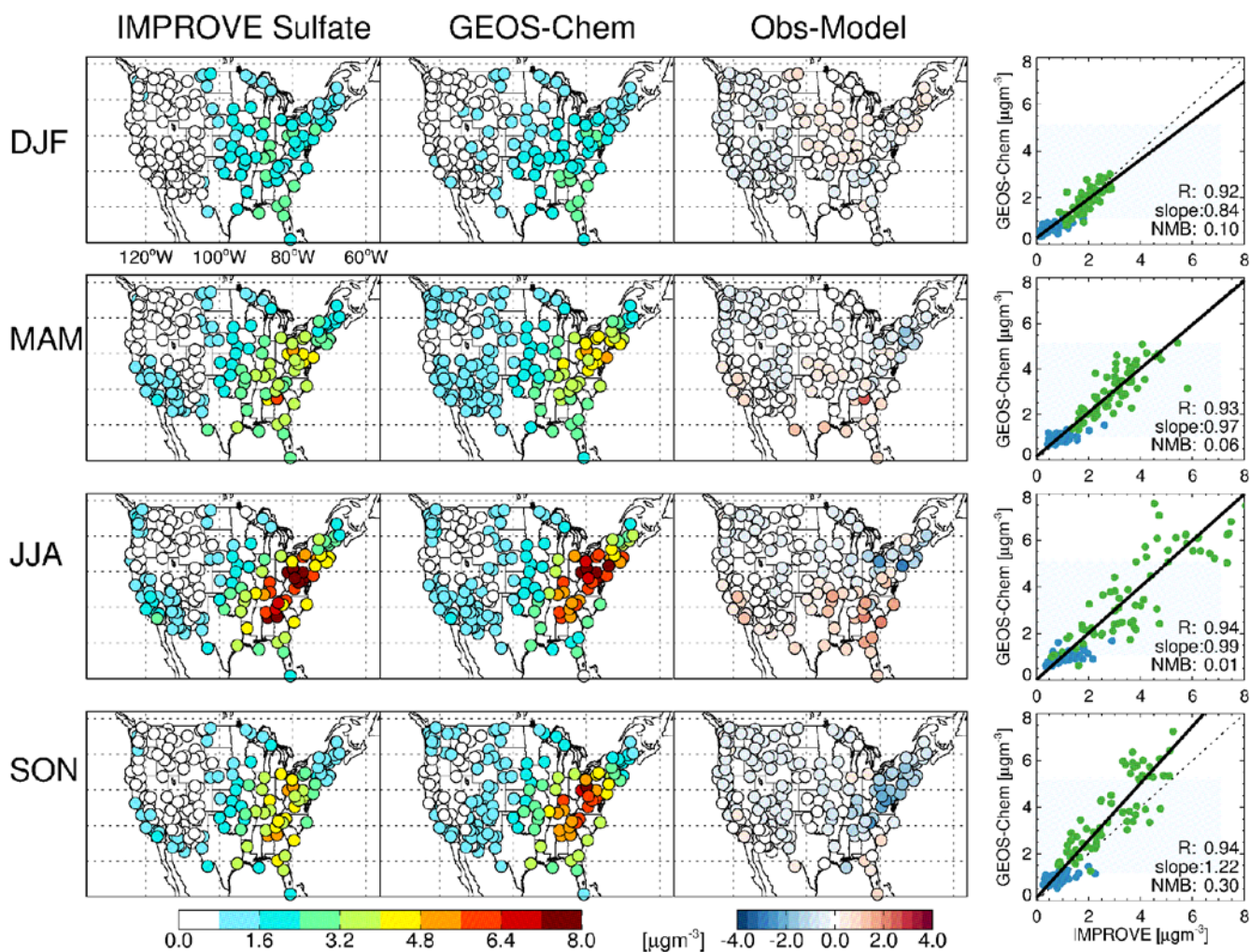


Figure 2: Sulfate mean seasonal surface concentrations measured, simulated with GEOS-Chem (baseline simulation), and the difference at IMPROVE sites in 2004. Scatterplot of seasonal means also shown with reduced-major-axis regression fit (solid black line). Correlation coefficient (R), slope and normalized mean bias (NMB) shown in inset. Sites located west of 100°W shown in blue, sites east of this longitude shown in green (longitude labels given in top panel for reference).

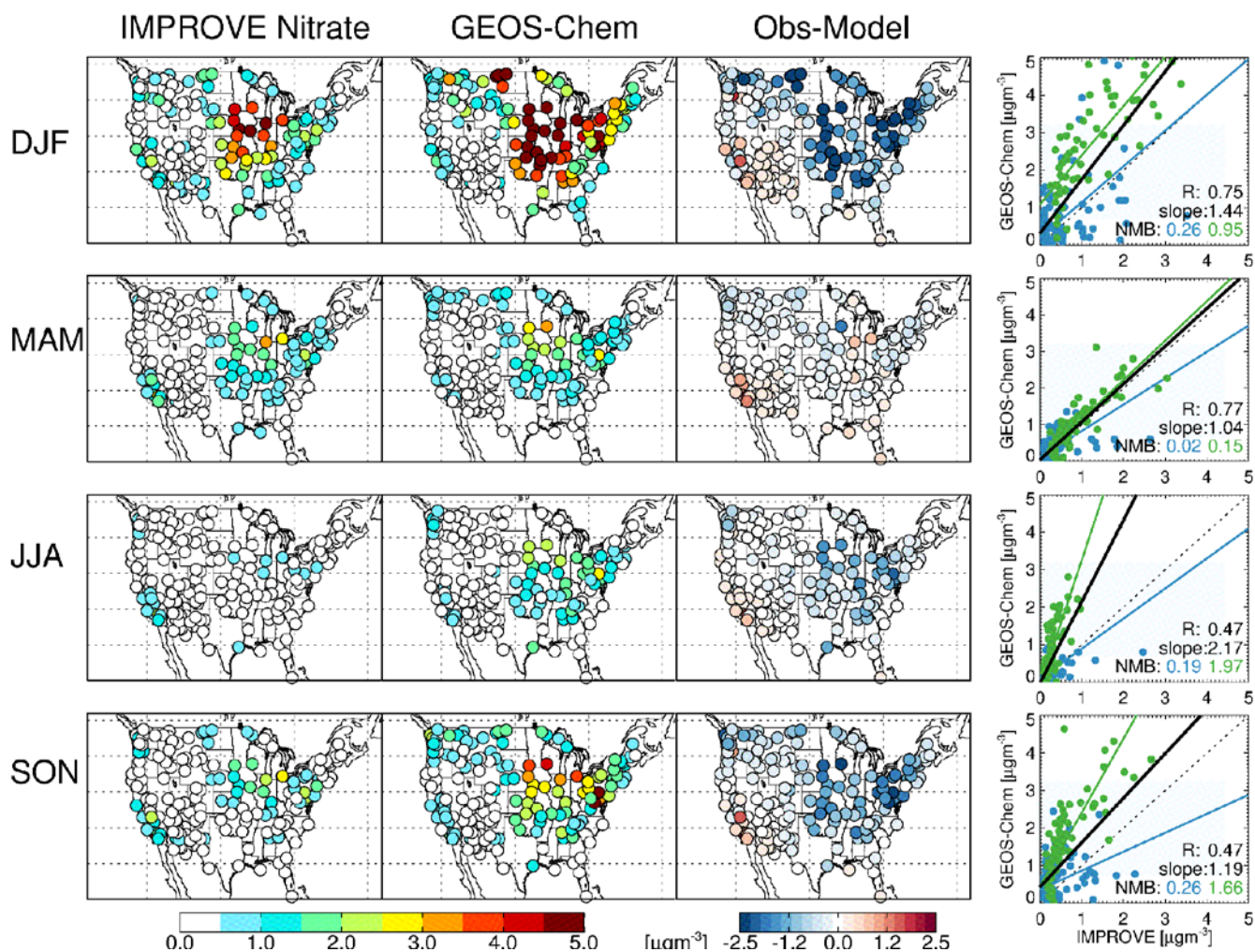
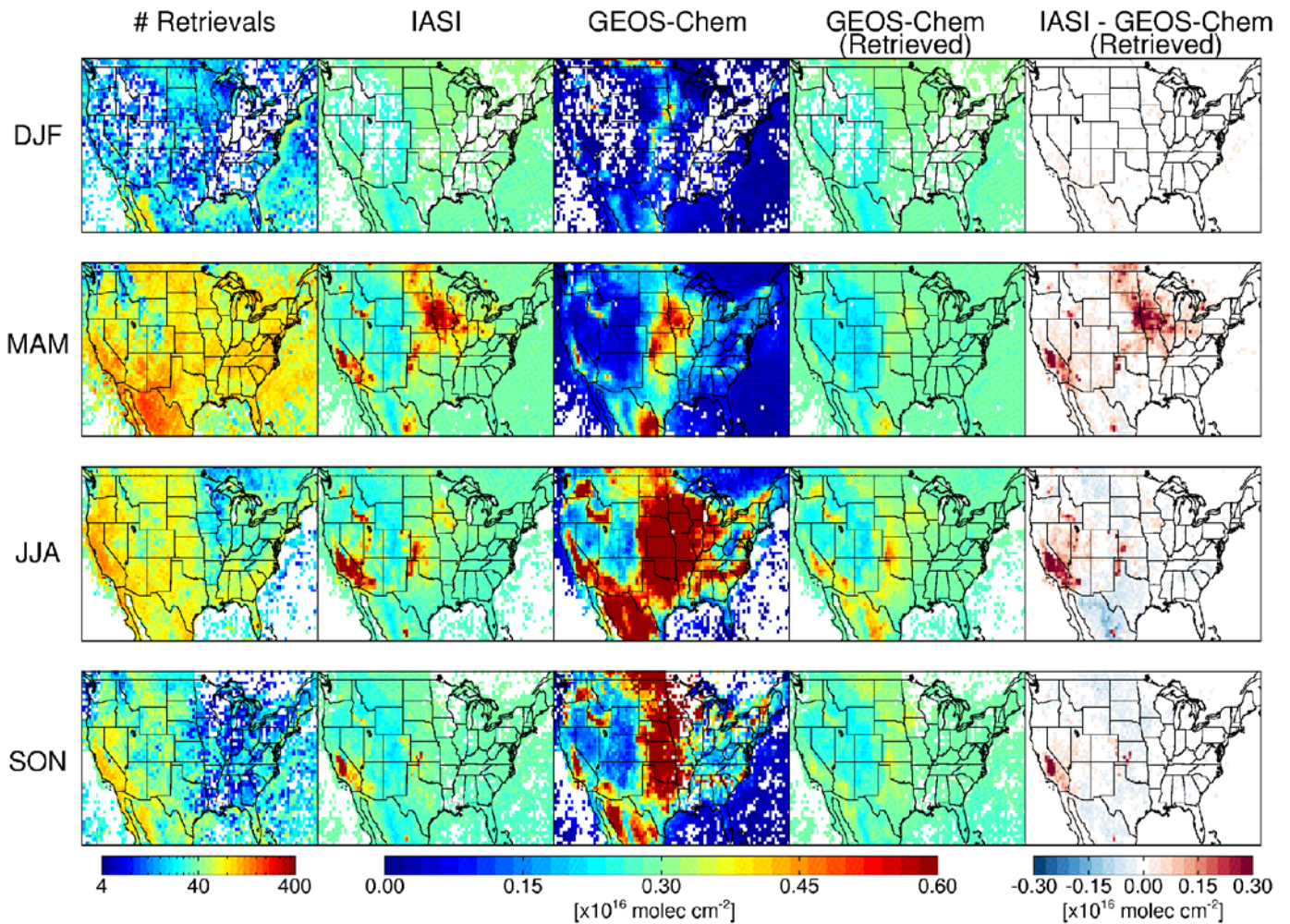
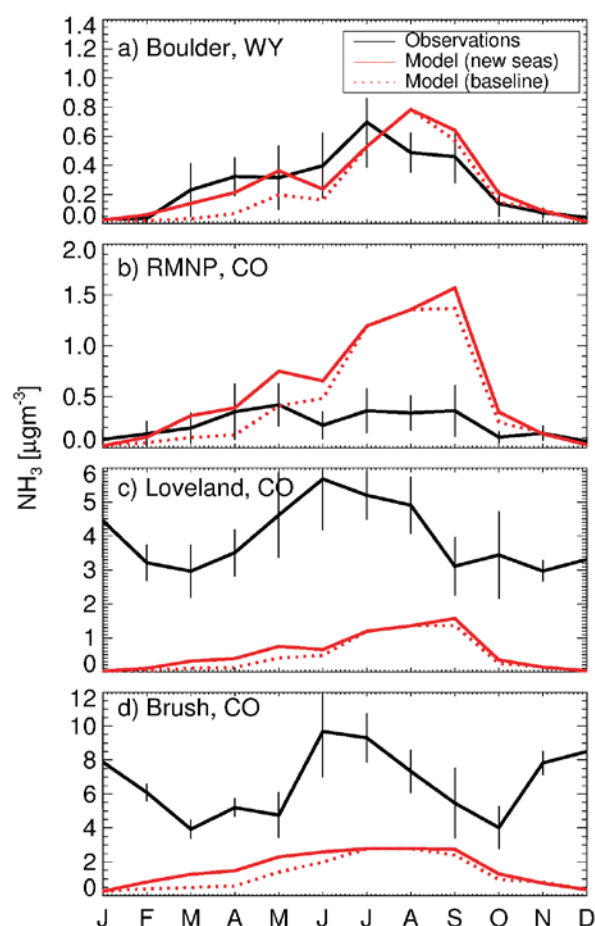


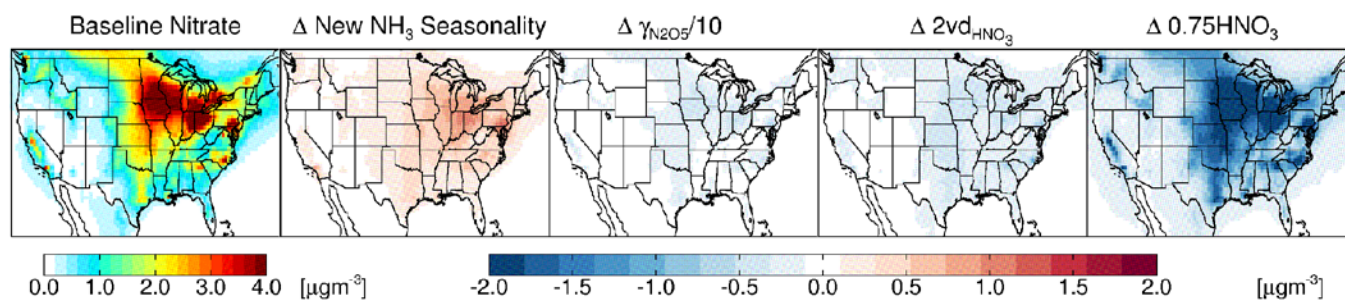
Figure 3: Nitrate mean seasonal surface concentrations measured, simulated with GEOS-Chem (baseline simulation), and the difference at IMPROVE sites in 2004. Scatterplot of seasonal means also shown with reduced-major-axis regression fit (solid black line). Sites located west of 100°W shown in blue, sites east of this longitude shown in green, with reduced-major-axis regression fits for each shown separately as solid lines. Correlation coefficient (R), slope and normalized mean bias (NMB) for east and west region shown in inset.



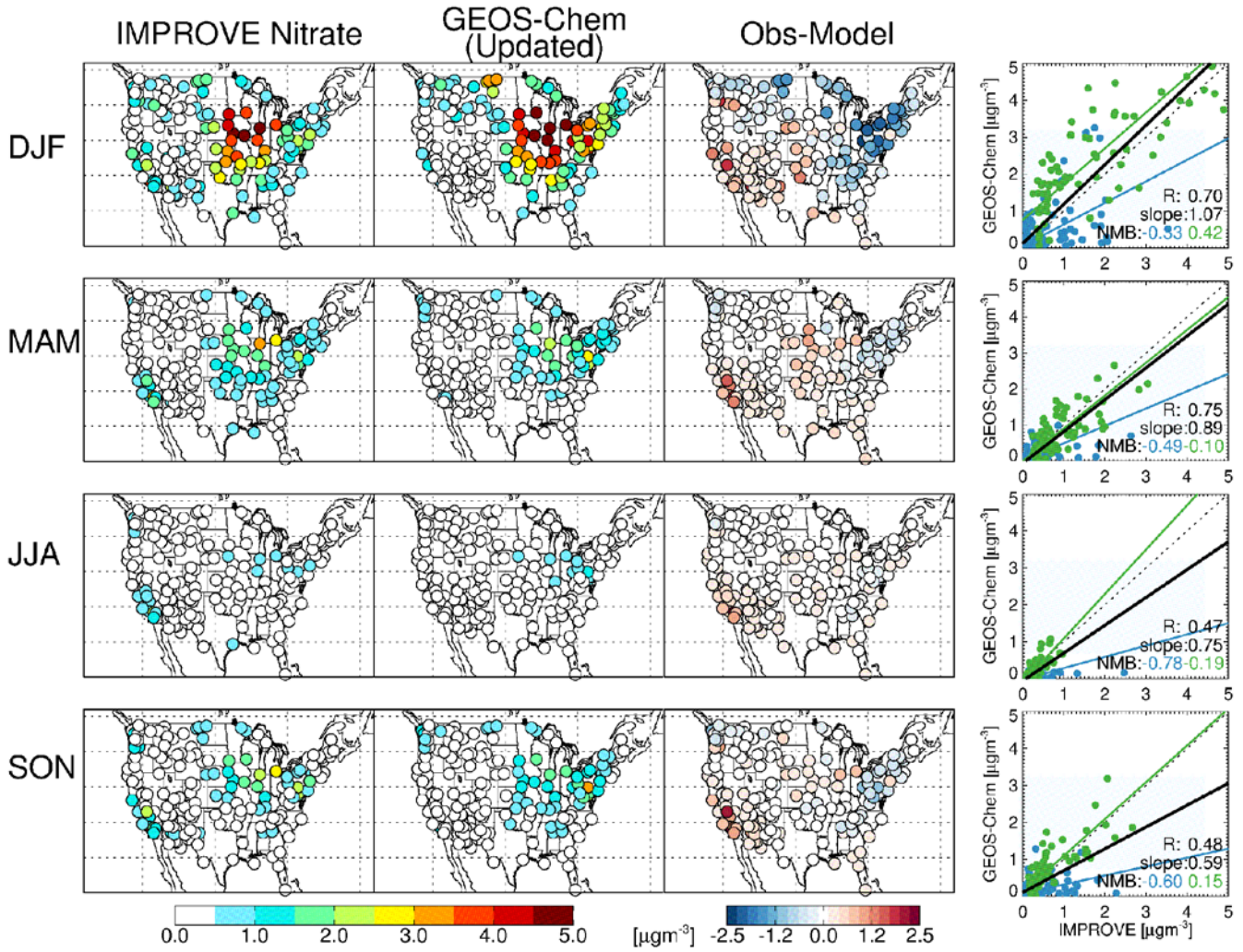
1
2 Figure 4: Comparison of atmospheric ammonia column concentrations observed by IASI and
3 simulated with the baseline GEOS-Chem model over the United States from May 2009
4 through April 2010. The IASI retrieval averaging kernel and a priori have been applied to the
5 GEOS-Chem simulation as in equation 1 (4th column) for quantitative comparison with the
6 satellite observations. Gridded model and observations only shown in gridboxes with 4 or
7 more retrievals per season. Color scales are saturated at respective values.



1
2 Figure 5: Timeseries of year-long monthly mean ammonia concentrations measured (black)
3 and simulated (red) in 2009 at 4 sites (from west to east): a) Boulder, WY, b) Rocky
4 Mountain National Park, CO, c) Loveland, CO and d) Brush, CO. Both the baseline
5 simulation (dotted) and simulation with updated ammonia emissions seasonality (solid) are
6 shown. Standard deviations of the individual observations averaged for each month are shown
7 as error bars.
8

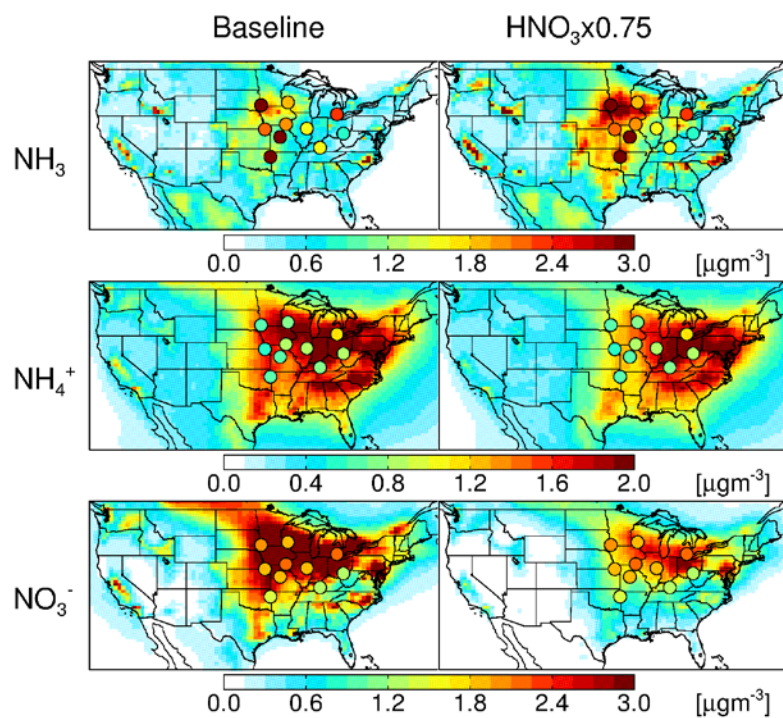


2 Figure 6: Annual mean simulated surface nitrate (left) and the difference from this baseline
 3 (labeled as Δ) for four sensitivity simulations. The four sensitivity simulations are as follows
 4 from left to right: (1) The increase in springtime ammonia emissions, (2) the decrease in the
 5 uptake coefficient of N_2O_5 by a factor of 10, (3) a doubling of the dry deposition velocity for
 6 nitric acid and (4) a reduction of nitric acid concentrations to 75% of baseline values.

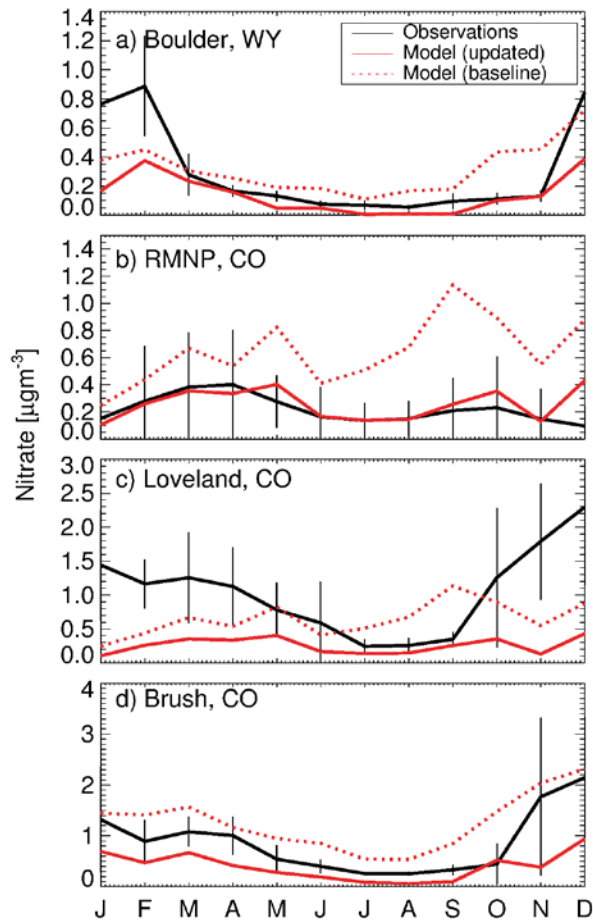


1 Figure 7: Nitrate mean seasonal surface concentrations measured, simulated with GEOS-
2 Chem (updated simulation where HNO_3 is reduced to 75% of baseline concentrations), and
3 the difference at IMPROVE sites in 2004. Scatterplot of seasonal means also shown with
4 reduced-major-axis regression fit (solid black line). Sites located west of 100°W shown in
5 blue, sites east of this longitude shown in green, with reduced-major-axis regression fits for
6 each shown separately as solid lines. Correlation coefficient (R), slope and normalized mean
7 bias (NMB) for east and west region shown in inset. Compare to Figure 3.

8

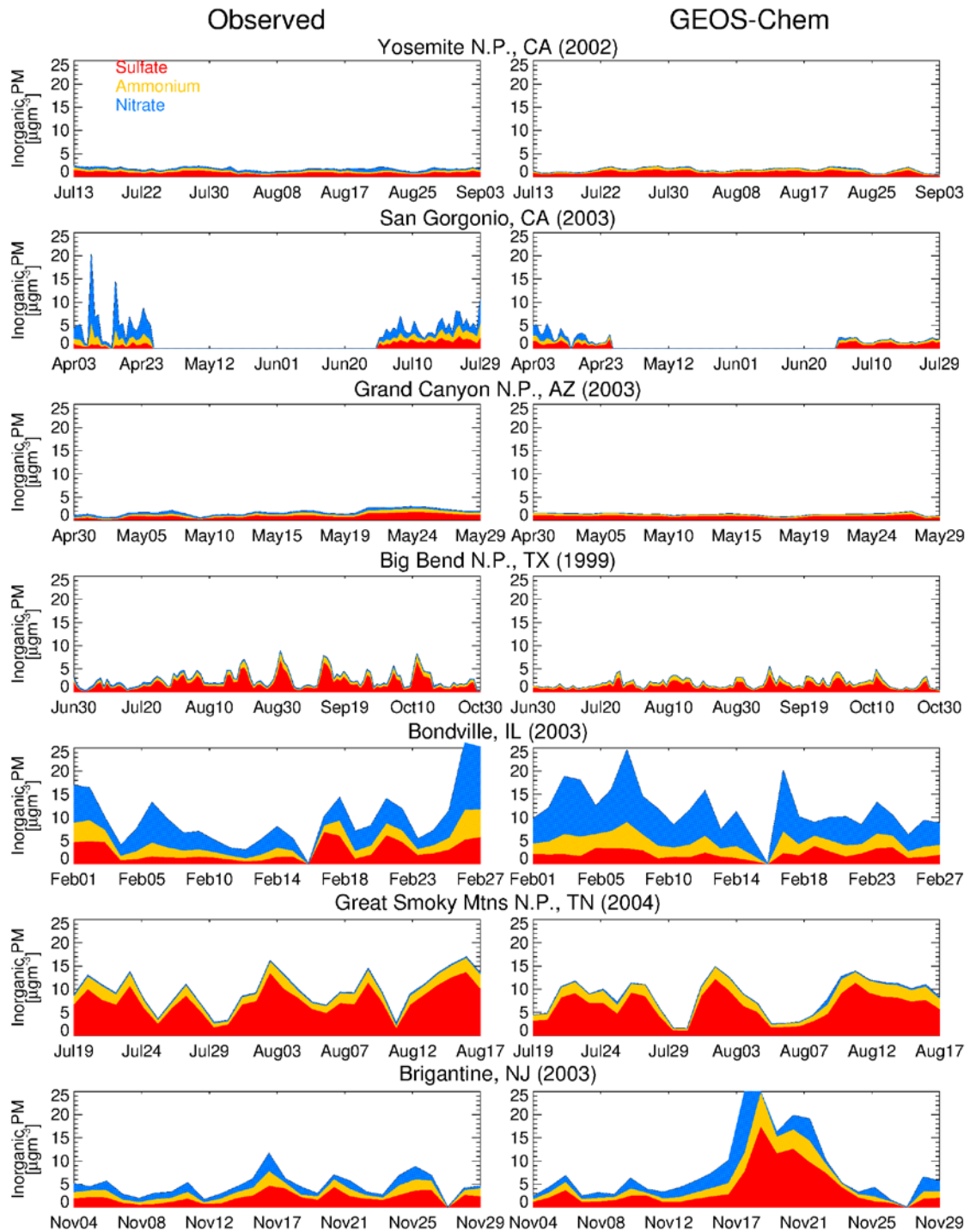


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2 Figure 8: Annual mean concentrations of ammonia and speciated fine ammonium nitrate
3 during the Midwest Ammonia Monitoring Project in 2004. GEOS-Chem means (left=baseline
4 simulation, right=updated simulation) are shown with observed means overlaid.
5



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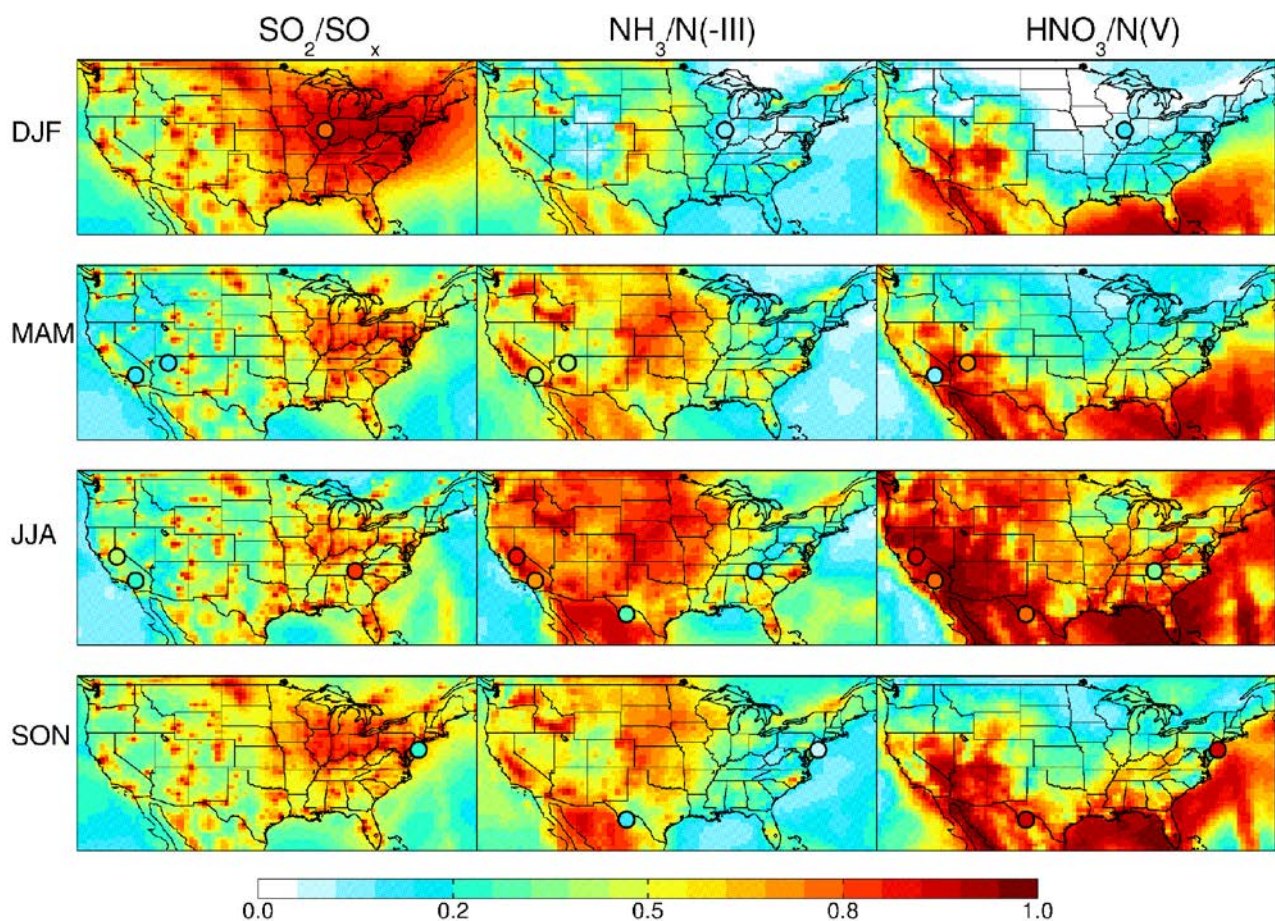
2 Figure 9: Timeseries of year-long monthly mean fine nitrate concentrations measured (black)
 3 and simulated (red) in 2009 at 4 sites (from west to east): a) Boulder, WY, b) Rocky
 4 Mountain National Park, CO, c) Loveland, CO and d) Brush, CO (solid). Standard deviation
 5 of the individual observations averaged for each month shown as error bars.
 6



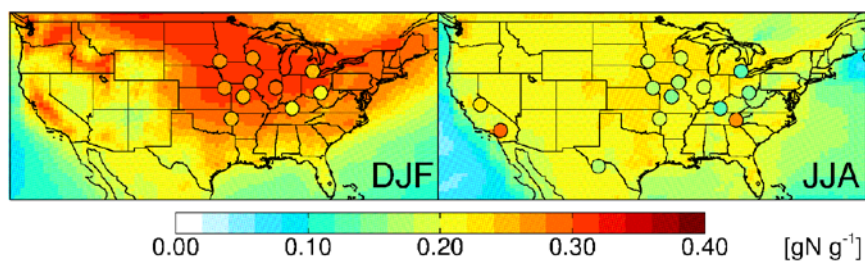
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2 Figure 10: Timeseries of daily mean aerosol concentrations observed (left) and simulated
 3 (right) at the 7 focus sites. GEOS-Chem simulation is for 2004, years of measurements shown
 4 with site names.

5



1
2 Figure 11: Seasonal mean surface gas fractions simulated with GEOS-Chem for 2004. Mean
3 observations (from 1999, 2002, 2003 and 2004) overlaid on corresponding season. SO_2
4 concentrations were not measured at the Big Bend National Park site (Section 2.2).
5



1
2 Figure 12: Fraction of nitrogen in winter (left) and summer (right) mean surface inorganic PM
3 mass simulated with GEOS-Chem for 2004. Mean observations both from focus sites (from
4 1999, 2002, 2003 and 2004) and 2004 MWNH3 campaign overlaid on corresponding season.