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Constraining Ammonia in Air Quality Models with Remote Sensing Observations and Inverse Modeling

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Constraining Ammonia in Air Quality Models with Remote Sensing Observations and Inverse Modeling

by

Liye Zhu

B.S., University of Science and Technology of China, 2009

A thesis submitted to the

Faculty of the Graduate School of the

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Constraining Ammonia in Air Quality Models with Remote Sensing Observations and Inverse Modeling
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has been approved for the Department of Mechanical Engineering

Prof. Daven K. Henze

Prof. Michael Hannigan

The final copy of this thesis has been examined by the signatories, and we find that both the content and the form meet acceptable presentation standards of scholarly work in the above mentioned discipline.
Zhu, Liye (Ph.D., Mechanical Engineering)

Constraining Ammonia in Air Quality Models with Remote Sensing Observations and Inverse Modeling

Thesis directed by Prof. Daven K. Henze

Ammonia is an important species in the atmosphere as it contributes to air pollution, climate change and environmental health. Ammonia emissions are known to be primarily from agricultural sources, however there is persistent uncertainty in the magnitudes and seasonal trends of these sources, as ammonia has not traditionally been routinely monitored. The first detection of boundary layer ammonia from space by the NASA Tropospheric Emissions Spectrometer (TES) satellite has provided an exciting new means of reducing this uncertainty. In this thesis, I explore how forward and inverse modeling can be used with satellite observations to constrain ammonia emissions. Model simulations are used to build and validate the TES ammonia retrieval product. TES retrievals are then used to characterize global ammonia distributions and model estimates. Correlations between ammonia and carbon monoxide, observed simultaneously by TES, provide additional insight into observed and modeled ammonia from biomass burning. Next, through inverse modeling, I show that ammonia emissions are broadly underestimated throughout the U.S., particularly in the West. Optimized model simulations capture the range and variability of in-situ observation in April and October, while estimates in July are biased high. To understand these adjustments, several aspects of the retrieval are considered, such as spatial and temporal sampling biases. These investigations lead to revisions of fundamental aspects of how ammonia emissions are modeled, such as the diurnal variability of livestock ammonia emissions. While this improves comparison to hourly in situ measurements in the SE U.S., ammonia concentrations decrease throughout the globe, up to 17 ppb in India and Southeastern China. Lastly, the bi-directional air-surface exchange of ammonia is implemented for the first time in a global model and its adjoint. Ammonia bi-directional exchange generally increases ammonia gross emissions (10.9%) and surface concentrations (up to 3.9 ppb)
throughout the globe in July, except in India and Southeastern China. It decreases ammonia gross emissions in the Northern Hemisphere (e.g., 42.5% in April in China) and increases ammonia in the Southern Hemisphere in April and October. While bi-directional exchange is fundamentally a better representation of ammonia emissions from fertilizers, emissions from primary sources are still likely underestimated.
Dedication

To my little girl, Emily Qi.
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Chapter 1

Introduction

1.1 Motivation and objectives

Nitrogen is an essential element for sustaining life. Nitrogen is converted between its various chemical forms through the nitrogen cycle, which is an important part of every ecosystem. However, natural nitrogen equilibrium has shifted dramatically in recent decades due to human activities. The nitrogen in ammonia ($\text{NH}_3$) is an important component of the nitrogen cycle, responsible for a significant fraction of long-range transport (100’s of km) of reactive nitrogen [Galloway et al., 2008]. Global emissions of $\text{NH}_3$ have already increased by a factor of 2 to 5 since pre-industrial times [Lamarque et al., 2011] and are projected to continue to rise over the next 100 years [Ciais, 2013]. Excessive deposition of $\text{NH}_3$ causes eutrophication in surface water and soil acidification [e.g., Carfrae et al., 2004; Paerl et al., 2002] and can further cause nutrient imbalances in sensitive ecosystems [Liu et al., 2013]. Current levels of reactive nitrogen deposition exceed those deemed critical for the protection of biodiversity in many regions of the U.S. [Ellis et al., 2013] and globally [Dentener et al., 2006].

In addition to being deposited to surface-level ecosystems, atmospheric $\text{NH}_3$ readily reacts with sulfurous acid and nitric acid to form ammonium sulfate and ammonium nitrate. These aerosols constitute about 50% of fine particulate matter (PM$_{2.5}$) over land, which harms human health [Schwartz et al., 2002; Reiss et al., 2007; Pope et al., 2002, 2009; Crouse et al., 2012]. Exposure to 10 $\mu$g/m$^3$ enhancements in PM$_{2.5}$ concentrations are associated with $\sim$4%, 6%, and 8% increases in the risk of all-cause, cardiopulmonary, and lung cancer mortality, respectively [Pope et al., 2002].
Ammonium sulfate and ammonium nitrate aerosol also have significant effects on global climate change by enhancing the scattering of incoming solar radiation [Adams et al., 2001], which induces a direct radiative forcing of 0.2 - 0.5 W/m$^2$ since pre-industrial times and a potentially even larger indirect radiative forcing through cloud feedbacks [Myhre, 2013]. Ammonium in particular can alter these forcings through its impact on the phase of the aerosol particles [Martin et al., 2004; Abbatt et al., 2006].

Despite the importance of NH$_3$, there are large uncertainties in the magnitude, temporal and spatial distributions of NH$_3$ emissions. While controlling NH$_3$ emissions has been recognized as an efficient and cost effective means of mitigating nitrogen deposition, PM$_{2.5}$ concentrations, and aerosol radiative forcing [Pinder et al., 2007; Henze et al., 2009; Paulot et al., 2013], these uncertainties undermine efforts [e.g., Koo et al., 2012] to develop mitigation strategies targeting NH$_3$ emissions, which are primarily from agricultural sources whose strengths are difficult to characterize (and politically difficult to regulate). There are also limitations in top-down emission constraints from inverse modeling [Gilliland et al., 2003, 2006; Henze et al., 2009; Paulot et al., 2014], such as uncertainties in NH$_3$ / NH$_4^+$ partitioning and model precipitation biases. Thus, the first detection of boundary layer ammonia from space by the NASA Tropospheric Emissions Spectrometer (TES) satellite [Beer et al., 2008; Shephard et al., 2011] has provided an exciting new means of furthering our understanding of ammonia sources and distributions.

Measurements of NH$_3$ from the TES instrument have been demonstrated to be well correlated with the in situ observations both spatially and seasonally [Pinder et al., 2011]. A primary objective of my thesis is thus to characterize the spatial and seasonal distribution of NH$_3$ with TES observations and explore how TES observations can be used in inverse modeling to better constrain NH$_3$ emissions. The correlation between NH$_3$ and carbon monoxide (CO), which are observed simultaneously by TES, provides an additional means of understanding NH$_3$ sources and distribution. Previous studies have exploited tracer correlations to inform emissions inversions, such as using observed CO$_2$:CO correlations to aid CO$_2$ flux estimates [Sutharalingam et al., 2004]. However, the correlations between CO and NH$_3$ have not yet been investigated.
In addition to adjusting NH$_3$ emissions according to the assimilation of TES remote sensing observations, I also investigate fundamentally improving the ability of air quality models to simulate NH$_3$. Differences in model biases between weekly average in situ measurements and twice-a-day TES retrievals (1:30 at day and night) lead to investigating model treatment of NH$_3$ diurnal variation [Zhu et al., 2013]. The constant diurnal NH$_3$ emissions employed in most models is found to lead to high biases at night in comparison to hourly observations in the Southeastern U.S. Revising the model treatment of the diurnal variability of livestock ammonia emissions can impact the diurnal variation of NH$_3$ without changing total NH$_3$ emissions [Bash et al., in prep].

Another issue in many air quality models (e.g., GEOS-Chem, Community Multiscale Air-Quality (CMAQ)) is the representation of the air-surface exchange of NH$_3$, which is always treated as being unidirectional. However, NH$_3$ air-surface exchange fluxes are observed to be bi-directional. Ignoring this bi-directional process in the model may cause biases in estimating NH$_3$ concentrations, emissions, and deposition. Several recent studies have begun to model resistance-based bi-directional exchange wherein the NH$_3$ flux direction is determined by comparing the ambient NH$_3$ concentration to the NH$_3$ in-canopy compensation point [Sutton et al., 1998; Nemitz et al., 2001; Cooter et al., 2010; Bash et al., 2010, 2013; Pleim et al., 2013; Zhang et al., 2010; Wichink Kruit et al., 2012]. Using the GEOS-Chem global chemical transport model, we have the chance to evaluate NH$_3$ bi-directional exchange on global scales for the first time. In this thesis, I implement bi-directional exchange of NH$_3$ in the GEOS-Chem model and explore the impacts on model estimation of NH$_3$ concentration, emission, and deposition.

Updates to fundamental model processes have implications for interpretation of top-down constraints on NH$_3$ sources. Bi-directional exchange will largely extend NH$_3$ lifetime in the atmosphere through the processes of deposition and re-emission [Sutton et al., 2007], and we would like to know how this will impact NH$_3$ inversions. Ultimately, we would like to include bi-directional exchange within NH$_3$ inverse modeling. As a first step, I develop the adjoint of bi-directional exchange in GEOS-Chem in this thesis. Through the adjoint method, I am able to assess source contributions to model estimates in particular response regions [e.g., Lee et al., 2014]. The adjoint
of the bi-directional exchange model also provides a useful method for quantifying the sensitivities of GEOS-Chem simulations with respect to important parameters of the bi-directional model, such as soil pH and fertilizer application rate, which are themselves uncertain.

1.2 Thesis organization

This thesis consists of work by the author published or in preparation for submission and contributions by the author extracted from co-authored works in various stages of publication. In Chapter 2, I introduce the TES NH$_3$ retrieval strategy and how model simulations are used to build and validate the TES retrievals. I also present the spatial and seasonal variability of NH$_3$ from TES observations globally and in twelve distinct regions and compare them to the GEOS-Chem estimates. This work contributed to the paper by Shephard et al. [2011]. In Chapter 3, I explore how inverse modeling with assimilation of TES remote sensing observations of NH$_3$ can be used to provide further constraints on NH$_3$ emissions [Zhu et al., 2013]. In Chapter 4, I present new treatment of NH$_3$ deposition, fertilizer emissions, and livestock emissions in the GEOS-Chem global chemical transport model and evaluate the performance of updating these fundamental physical processes through comparison to in situ observations [Zhu et al., in prep]. In Chapter 5, I investigate the correlations between NH$_3$ and CO in the boundary layer from TES observations and explore the potential of better characterizing NH$_3$ spatial and seasonal distribution with well-studied observations of CO [Luo et al., submitted]. Work in progress regarding the potential of future geostationary satellite observations to constrain process-level NH$_3$ emissions models is included in Appendix A.
Chapter 2

The spatial and seasonal variability of global ammonia observations from TES ¹

2.1 Introduction

Ammonia (NH₃) contributes to many environmental problems. When excess ammonia deposits to surface water it can cause soil acidification and eutrophication [e.g., Carfrae et al., 2004; Paerl et al., 2002]. NH₃ can also react with sulfuric acid and nitric acid to form ammonium sulfate and ammonium nitrate. These aerosol species constitute about 50% of fine particulate matter (PM₂.₅) over land, which has significant impacts on human health [Reiss et al., 2007; Crouse et al., 2012]. They also have impacts on climate through scattering of solar radiation and by affecting cloud formation [Abbatt et al., 2006; Myhre, 2013]. Thus, understanding the spatial and seasonal variability of NH₃ emissions as well as the magnitude of NH₃ emissions is very important for a wide range of environmental concerns.

Despite their recognized importance, NH₃ emissions contain large uncertainties in their magnitude, trends and spatial and temporal distribution [Galloway et al., 2008]. These large uncertainties in the NH₃ emission inventories are mainly due to sparse and infrequent in-situ observations. There are also limitations in top-down emission constraints from inverse modeling [Gilliland et al., 2003, 2006; Henze et al., 2009; Paulot et al., 2014], such as uncertainties in NH₃ / NH₄⁺ partition and model precipitation biases.

Satellite remote sensing observations present new opportunities for constraining our understanding of the sources and distributions of NH₃. NH₃ boundary layer observations from the Tro-

¹ The results of this Chapter have been published in Shephard et al. [2011].
pospheric Emissions Spectrometer (TES) were first reported by Beer et al. [2008], which presented preliminary TES NH$_3$ retrievals over Southern California and China. The Infrared Atmospheric Sounder Interferometer (IASI) instrument, which is similar to TES, also retrieves NH$_3$ with a better spatial coverage but higher detection limit [Clarisse et al., 2009]. TES has a higher spectral resolution (0.06 cm$^{-1}$) than that of other scanning satellites such as IASI and AIRS (0.5 cm$^{-1}$ - 1 cm$^{-1}$), and is thus a more precise measurement. TES is in a sun-synchronous orbit with a local overpass time of 1:30 in both daytime and nighttime. The overpass time in daytime provides an advantage for TES measurements since higher thermal contrast increases the TES sensitivity to NH$_3$ in the boundary layer. The footprint of TES is 5 km $\times$ 8 km. Therefore, TES measurements provide a unique potential for global information on NH$_3$ distributions as well as the magnitude of NH$_3$ sources.

Interpretation of satellite data is, however, not a straightforward endeavor, as the TES retrieval product is itself the result of an inverse modeling problem that blends the observed spectral measurement signal with prior information regarding NH$_3$ distributions. For this retrieval algorithm, an initial guess of the vertical distribution of the NH$_3$ volume mixing ratio (VMR), i.e., an a priori profile, is required. However, the NH$_3$ VMR vertical distribution is not known from any available measurements. Thus, we must first derive the a priori profile for retrievals based on model simulations. In this Chapter, we will introduce the TES NH$_3$ retrieval strategy (Section 2.3), and how the retrieval approach has been characterized (Sections 2.4 and 2.4.1) and validated (Section 2.4.3). We then evaluate TES NH$_3$ retrievals by comparing them to the results from GEOS-Chem simulations (Section 2.4.4) and analyze the spatial and seasonal variability of NH$_3$ from TES remote sensing observations globally and in twelve distinct regions (Section 2.4.5).

2.2 GEOS-Chem model

GEOS-Chem is a chemical transport model driven by assimilated meteorology from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO). The NH$_3$ emissions from anthropogenic and natural sources are based on the 1990 GEIA
inventory [Bouwman et al., 1997], with regional emission inventories replaced by Park et al. [2004] in the U.S., Streets et al. [2003] for Asia, and EMEP [Vestreng and Klein, 2002] for Europe. Biomass burning emissions are from Duncan et al. [2003], and biofuel emissions are from Yevich and Logan [2003]. The total annual NH$_3$ emission in the U.S. is scaled to match the top-down constraints in Gilliland et al. [2003], and monthly variability is scaled based on Adams et al. [1999].

### 2.3 TES retrieval strategy

The TES retrieval algorithm itself is an inverse model that minimizes the difference between the observed spectral radiance and estimates from a radiative transfer model. TES retrievals are estimated such that they are consistent with the probability distribution of the a priori information and the observed spectra [Bowman et al., 2006]. The resulting retrievals can be described by the following linearized formula [Rodgers, 2000],

$$\hat{x} = x_a + A(x - x_a) + Gn + GK_b(b - b_a),$$  \hspace{1cm} (2.1)

where $\hat{x}$ is the retrieval state, $x$ is the “true” state, and $x_a$ is the a priori state. $A$ is the averaging kernel, which is the sensitivity of the retrieval to the true state. $G$ is the gain matrix, which maps the measurement space to retrieval space. $n$ is the spectral radiance noise. $b$ is the true state of the related parameters, such as concentrations of interfering gases, and $b_a$ is their corresponding a priori values. $K_b = \partial L/\partial b$, where $L$ is the forward model radiance. Further description of the TES retrieval strategy is included in Shephard et al. [2011]. Here we consider more details of the NH$_3$ a priori profiles.

The NH$_3$ a priori profiles ($x_a$) for TES retrievals are derived from GEOS-Chem model simulations. The simulations are performed on a $2^\circ \times 2.5^\circ$ horizontal resolution for 2005. Figure 2.1 shows the global distribution of monthly average NH$_3$ volume mixing ratios (VMR) at surface level. The NH$_3$ VMR values vary across a wide range (less than 1 ppb to more than 10 ppb). Based on these simulations, we derive three types of NH$_3$ a priori profiles: polluted, moderately polluted, and unpolluted (Figure 2.2). The “polluted” a priori profile is the average of all profiles with NH$_3$
VMR larger than 5 ppbv at the surface. The “moderately polluted” a priori profile is the average of all profiles with surface NH$_3$ VMR between 1 ppbv to 5 ppbv as well as profiles with surface NH$_3$ VMR less than 1 ppbv but NH$_3$ VMR greater than 1 ppbv between the surface and 500 hPa. This type of TES NH$_3$ a priori represents conditions where NH$_3$ from a local source is less than the amount imported aloft from an upwind region. The “unpolluted” a priori profile is the average of all profiles with NH$_3$ VMR less than 1 ppbv between the surface and 800 hPa.

2.4 Results

2.4.1 TES detection limit

The standard TES retrieval products are temperature, water vapor, ozone, methane, and carbon monoxide. However, TES is able to detect NH$_3$ if the signal in the NH$_3$ spectral region (962.06 cm$^{-1}$ - 968.18 cm$^{-1}$) is greater than the noise, i.e., the Signal to Noise Ratio (SNR) is larger than 1. Thus, we group all profiles into two parts: SNR≥1 and SNR<1. The maximum NH$_3$ VMR values in profiles with SNR ≥1 are mainly larger than 1 ppbv, which indicate that the minimal requirement of TES detectability is for a profile with maximum NH$_3$ VMR values greater than 1 ppbv. Thus, TES is better at detecting NH$_3$ polluted profiles, and it is poorer at detecting NH$_3$ unpolluted profiles with peak values less than 1 ppbv. A full description of the determination of this detection limit is in Shephard et al. [2011].

2.4.2 Comparison methodology

At several points in this work we compare model NH$_3$ profiles to those from TES. In order to properly account for the influence of the a priori information within the TES retrieval, such comparisons are made by applying the TES observational operator, $H$, to the model NH$_3$ profiles as

$$H(x_{est}) = x_a + A(Mx_{est} - x_a),$$

(2.2)
Figure 2.1: GEOS-Chem monthly mean surface NH$_3$ mixing ratios (ppbv).
Figure 2.2: Three sets of atmospheric NH$_3$ monthly mean profiles (gray) from GEOS-Chem 2005 global model simulations. The mean profile for each set is shown in black. These three mean NH$_3$ profiles constitute the TES NH$_3$ retrieval a priori profiles.
where $x_{est}$ is the GEOS-Chem modeled NH$_3$ profile, $x_a$ is the a priori profile used for the retrieval, $A$ is the averaging kernel, and $M$ is a vertical interpolation matrix that maps $x_{est}$ from model space to retrieval space. The mapped model estimated profile will equal $x_a$ when there is little measurement information contained within the TES retrieval, as the averaging kernel will have very small values.

To evaluate spatial patterns in TES NH$_3$ profiles (or corresponding model values), it is useful to generate 2-D visualizations of TES observations. However, there is no single value from such profiles that well represents the boundary layer NH$_3$ VMR while accounting for the fact that the sensitivity of TES retrievals to NH$_3$ concentrations varies across the troposphere and that this sensitivity is unique for each retrieval (as described by each retrieval’s averaging kernel). The retrieved NH$_3$ VMR values at individual vertical levels are highly dependent upon the sensitivity of TES retrieval at this level. Thus, more than one level of TES retrieval information should be included in order to better represent the NH$_3$ VMR at boundary layer. To address this, Beer et al. [2008] introduced the concept of an averaging kernel weighted molar fraction (AKWMF), which is the weighted average of the scaled profile with the averaging kernel as the weighting function. A similar approach is also described in Payne et al. [2009], wherein the authors develop a representative tropospheric volume mixing ratio (RTVMR) for TES methane retrievals. It maps the retrieved profile to four points (surface, peak sensitivity, tropopause, top of atmosphere), and the value near the peak sensitivity of methane averaging kernel will be selected as the RTVMR. Shephard et al. [2011] developed a Representative Volume Mixing Ratio (RVMR) metric for TES NH$_3$ retrievals, which is a TES sensitivity weighted mean NH$_3$ across the boundary layer. We are able to achieve similar RVMR values over a similar altitude range with very different a priori profiles [Shephard et al., 2011]. Thus, RVMR provides a compact robust, plotable representation of the TES profile retrieval information.
Figure 2.3: Simulated retrieval results: retrieved profiles (left); retrieved - true profiles (middle), where the solid red line is mean difference, dashed red line is standard deviation, and the black line is the reference zero line; sum of the rows of the averaging kernel (right). Colors indicate type of true profile: polluted (red), moderate (green), unpolluted (blue).
2.4.3 TES retrieval accuracy

We evaluate the accuracy of the TES retrieval algorithm by performing TES retrievals on simulated atmospheric NH$_3$ distributions for which the true NH$_3$ profiles are thus known. We start by sampling 361 NH$_3$ profiles from GEOS-Chem simulations during July, 2005, over the central U.S. at the times and locations of the Aura overpass. We then apply the radiative transfer model and the expected TES retrieval noise to generate a set of TES pseudo observations. GEOS-Chem simulations are then re-generated with NH$_3$ emissions doubled; profiles from these simulations are used for the initial guess within the TES retrieval algorithm applied to the pseudo spectral observations. The true model profiles are compared to the resulting TES retrieval products by applying the TES observational operator (Equation 2.2) to the model profiles. Figure 2.3 shows the TES retrievals (left) and the differences between the retrieved and true profiles (middle). The averaged NH$_3$ retrieval is 0.7 ppbv at 825 hPa. The bias is 0.05 ppbv, which is very small relative to the mean retrieval value. The sum of the rows of the averaging kernel (right plot of Figure 2.3) indicates that the retrieval sensitivities usually peak between 700 to 900 hPa, and that the Degrees Of Freedom (DOFs, the trace of the averaging kernel) are always less than one.

2.4.4 Comparison of global ammonia satellite observations with GEOS-Chem model simulations

In this section, we will explore the spatial and seasonal variability of TES NH$_3$ retrievals compared to model estimates. Figure 2.4 shows the spatial distribution of RVMRs of TES NH$_3$ retrievals between 60°S and 60°N in January, April, July, and October of 2006 - 2009. Only retrievals with DOF greater than 0.5 are included. The retrievals over water and at higher latitudes are excluded for computational expediency. There are significant large average TES NH$_3$ RVMRs in the Indus and Ganges river valleys of Northern India in all four months, which is due to agriculture activities in all seasons of the year. High RVMR values also appear in Eastern South America in October and North Central Africa in January due to biomass burning. The large RVMR values in
Figure 2.4: TES RVMR averaged over $2^\circ \times 2.5^\circ$ boxes. The white grid boxes over land are regions without a valid TES RVMR. In this study we do not analyze observations over the ocean.
Midwest of America in July are due to agriculture activities.

In order to compare the simulated GEOS-Chem NH$_3$ to the TES retrieval, we calculate GEOS-Chem RVMR by applying the TES observational operator ($H$) using Equation 2.2 and RVMR weighting function to the GEOS-Chem simulated NH$_3$ profile from 2008. The averaging kernel and a priori profiles needed for calculating the GEOS-Chem RVMR are from the same TES retrievals shown in Figure 2.4. Figure 2.5 shows the spatial distribution of averaged NH$_3$ RVMR from GEOS-Chem between 60°S and 60°N. Figure 2.6 shows similar plots as Figure 2.4 and Figure 2.5 but for the difference of RVMR between TES and GEOS-Chem. The magnitude of the GEOS-Chem RVMR is predominately less than TES RVMR, which means the modeled NH$_3$ is less than the TES observations over the altitude range with high TES sensitivity. This is possibly due to the low biases in the model emission inventory. Since NH$_3$ VMR is highly influenced by local emission sources, the reason for GEOS-Chem RVMR underestimates could be a spatial sampling bias which is caused by the NH$_3$ spatial variability in the 2°× 2.5° model grid cell. It could also be that the TES retrieval places too much NH$_3$ in the higher vertical levels at which TES is sensitive to NH$_3$, while in fact NH$_3$ is higher at the surface in the model (although this seem unlikely here, as GEOS-Chem is used for the a priori profile). Another possible reason for the low bias is sampling bias owing to the lack of sensitivity for TES observations below 1 ppbv. Thus, TES observations could have positive biases beyond those identified in Section 2.4.3. The underestimates of GEOS-Chem RVMR in broad source regions, such as SE Asia, Central Africa, and Midwest U.S., may be due to underestimates in model emissions inventories. The underestimates in places with localized sources may be due to TES spatial sampling bias.

2.4.5 Spatial and seasonal variability of ammonia observations and model in regional scale

While there are clear discrepancies in the modeled versus observed RVMR values, here we consider the extent to which model simulations match observed seasonal trends, about which there is considerable uncertainly [e.g., Henze et al., 2009]. We select twelve large regions (Figure 2.7)
Figure 2.5: GEOS-Chem with TES observational operator and RVMR applied for $2^\circ \times 2.5^\circ$ averages.
Figure 2.6: Difference (TES - GEOS-Chem) RVMR plots for the 2° × 2.5° averages.
to investigate the seasonal variability of NH$_3$ TES observations and model estimates throughout
the globe. Figure 2.8 shows the bar plots of TES RVMR in Figure 2.4 averaged for each region.
Note that only the observations with RVMR $\geq 0.4$ and DOF $\geq 0.5$ are included. The number
of observations and maximum values are shown on the top of each plot. Plots of corresponding
GEOS-Chem RVMR are shown in Figure 2.9. Since the model underestimates the NH$_3$ RVMR,
the magnitudes of the plots in these two figures are not consistent.

We find similar seasonal trends in both TES observations and GEOS-Chem model estimates
in the Central U.S. (Figure 2.8 (d) and Figure 2.9 (d)), with peak values both occurring in summer.
The peak in summer is possibly due to higher temperatures that increase the emissions from animal
waste and fertilizers. The same factor may also cause the peak value that occurs in summer in
South America (Figure 2.8 (i) and Figure 2.9 (i)) and Australia (Figure 2.8 (l) and Figure 2.9
(l)) in both observations and model. However, the seasonality of RVMR in the observations and
model are not consistent in many regions. For example, TES RVMR peaks in summer, while GC
RVMR peaks in Spring in Southeast China (Figure 2.8 (f) and Figure 2.9 (f)) and Southwest Asia
(Figure 2.8 (g) and Figure 2.9 (g)). This indicates that revising the seasonal variability of emissions
inventories used in the GEOS-Chem model for the Asia region is necessary. North Central Africa
(Figure 2.8 (h) and Figure 2.9 (h)), where biomass burning is the primary source, has the seasonal
pattern that RVMR decreases from winter to summer. In Australia (Figure 2.8 (l) and Figure 2.9
(l)), the TES observation peaks in summer, which is the burning season, while the GEOS-Chem
model peaks in October. Similar patterns are also evident in South Africa. Seasonality in Eastern
Russia and Northern China shows less variability in the TES observations than in GEOS-Chem.
Most values of the GEOS-Chem RVMRs are very small in January and October, which may be due
to a lack of information in model emissions inventories in this region. Other possible reasons for
the different seasonal patterns between TES observations and GEOS-Chem include the influence of
temperature on the canopy compensation point in the soil and vegetation. The NH$_3$ concentration
in the atmosphere could be impacted by emissions from soil and vegetation via dynamic fluxes
of NH$_3$ that balance emission with deposition [e.g., Cooter et al., 2010]. Not considering this
Figure 2.7: Delimitation regions of interest that are grouped together for regional analysis.
The TES results from Europe (Fig. 15b and Fig. 16b) are harder to interpret and will need further detailed evaluation. GEOS-Chem predicts a strong maximum in July, while TES shows little seasonal variability. In contrast to other regions, the TES pattern over Europe may reflect a distribution of emissions more strongly influenced by sources with less seasonal variability, such as automobile sources (Perrino et al., 2002; Whitehead et al., 2007). Southern Canada also shows a maximum in October, which needs further investigation and again may be due to sampling or some strong sources have less seasonal dependence.

4 Summary/conclusions

We have presented a detailed description of the TES NH$_3$ retrieval strategy including the a priori selection algorithm and the spectral microwindows selected to reduce systematic errors from interfering species. A transformation matrix was also developed to map the retrieval level VMRs to a subset of RVMR value(s) that better represent the information provided by the satellite by reducing the influence of the a priori. This RVMR is particularly useful for applications involving simple single level maps of species with a limited amount of information, which can contain a significant amount of a priori information at any given retrieval level. The SNR sensitivity study estimated the TES level of detectability for NH$_3$ to be a profile with a peak concentration of 1 ppbv, or equivalently an RVMR of 0.4 ppbv, provided there is significant

Figure 2.8: TES NH$_3$ averages in Figure 2.5 for each region in Figure 2.7 for the 4 yr period spanning 2006 - 2009. The boxes are the 25 and 75 percentile, the line in the box is the median, the diamond is the mean, whiskers are the 10 and 90 percentile and the circles are the outlier values outside the whiskers.
Figure 2.9: GEOS-Chem NH$_3$ averages in Figure 2.5 for each region in Figure 2.7 for the 4 yr period spanning 2006 - 2009. The boxes are the 25 and 75 percentile, the line in the box is the median, the diamond is the mean, whiskers are the 10 and 90 percentile and the circles are the outlier values outside the whiskers.
biogeochemical process in the model may cause biases in estimating the NH$_3$ concentrations in the atmosphere, which will need to be explored in future work.

2.5 Conclusions

In this study, we introduce the TES NH$_3$ retrieval strategy as well as the a priori selection algorithm. We also determined the limit of TES detectability, which is for profiles with maximum NH$_3$ VMR values no less than 1 ppbv. We use the newly developed transformation matrix [Shephard et al., 2011] to map the NH$_3$ VMR to a point value RVMR which is a boundary layer sensitivity weighted average with a priori information reduced as much as possible; this best represents the information observed from TES satellite in 2-D. Corresponding RVMR values in the GEOS-Chem model are also calculated by applying the TES observational operator and RVMR weighting function. The comparisons of RVMRs from TES observations from 2006 - 2009 and GEOS-Chem model simulations from 2008 show important similarities and differences. In general, TES observations are larger than the GEOS-Chem situation results throughout the globe. The broad underestimates are possibly due to underestimates of emissions in the model. The underestimates in areas with localized sources may be due to the sampling bias from NH$_3$ spatial variability in the 2°×2.5° model grid cell. Comparisons of the seasonality of the TES RVMRs and the corresponding GEOS-Chem RVMRs in different regions suggest that there are greater uncertainties in our understanding of agricultural sources rather than in biomass burning sources. Areas for additional studies thus include validation with in-situ observations [Pinder et al., 2011], improving NH$_3$ emissions, investigating TES sampling biases, and comparing NH$_3$:CO ratios to evaluate the performance of simulating anthropogenic versus biogenic sources.
Chapter 3

Constraining U.S. ammonia emissions using TES remote sensing observations and the GEOS-Chem adjoint model

3.1 Abstract

Ammonia (NH$_3$) has significant impacts on biodiversity, eutrophication and acidification. Widespread uncertainty in the magnitude and seasonality of NH$_3$ emissions hinders efforts to address these issues. In this work, we constrain U.S. NH$_3$ sources using observations from the TES satellite instrument with the GEOS-Chem model and its adjoint. The inversion framework is first validated using simulated observations. We then assimilate TES observations for April, July and October of 2006 through 2009. The adjoint-based inversion allows emissions to be adjusted heterogeneously; they are found to increase in California throughout the year, increase in different regions of the West depending upon season, and exhibit smaller increases and occasional decreases in the Eastern U.S. Evaluations of the inversion using independent surface measurements show reduced model underestimates of surface NH$_3$ and wet deposited NH$_x$ in April and October; however, the constrained simulation in July leads to overestimates of these quantities, while TES observations are still under predicted. Modeled sulfate and nitrate aerosols concentrations do not change significantly and persistent nitrate overestimation is noted, consistent with previous studies. Overall, while satellite-based constraints on NH$_3$ emissions improve model simulations in several aspects, additional assessment at higher horizontal resolution of spatial sampling bias, nitric acid formation, and diurnal variability and bi-directionality of NH$_3$ sources may be necessary to enhance year-round

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1 This Chapter has been published in Zhu et al. [2013].
3.2 Introduction

Emissions of ammonia (NH$_3$) from anthropogenic sources pose several environmental concerns. Ammonia affects air quality and climate through its role in the mass, composition and physical properties of tropospheric aerosol. Ammonium nitrate and ammonium sulfate make up a substantial fraction of atmospheric fine particulate matter (PM$_{2.5}$), exposure to which has been statistically associated with inhibited lung development, cardiovascular diseases and premature mortality [Pope et al., 2002; Schwartz et al., 2002; Reiss et al., 2007]. These fine particulates (PM$_{2.5}$) also contribute to haze and thus impact visibility. Further, when deposited in excess, reactive nitrogen, including ammonia, can cause detrimental nutrient imbalances to sensitive ecosystems [Rodhe et al., 2002; Rabalais, 2002].

Despite the recognized importance of NH$_3$ emissions in the U.S. [Aneja et al., 2008], knowledge of their magnitude is severely limited; NH$_3$ emissions are primarily from agricultural sources whose strengths are difficult to characterize. Uncertainty in NH$_3$ undermines the efforts to understand historical and present levels of PM$_{2.5}$ [Yu et al., 2005; Nowak et al., 2006; Zhang et al., 2008; Wu et al., 2008; Stephen and Aneja, 2008; Beusen et al., 2008; Simon et al., 2008; Henze et al., 2009] and hinders estimates of the response of PM$_{2.5}$ to control measures because of the key role that NH$_3$ plays in governing the balance of inorganic fine particulate species [Dennis et al., 2008]. Model estimates of inorganic PM$_{2.5}$ have been compared to surface measurements [Park et al., 2004, 2006; Liao et al., 2007; Henze et al., 2009; Pye et al., 2009; Heald et al., 2012] and measurements from aircraft campaigns [Heald et al., 2005, 2006]; NH$_3$ emissions are frequently indicated to be a likely cause of discrepancies. On a larger scale, NH$_3$ emissions rates are a critical source of uncertainty in global budgets of the atmospheric transport and deposition of reactive nitrogen [Sutton et al., 2007; Galloway et al., 2008; Schlesinger, 2009].

These are several reasons for the persistence of uncertainties in NH$_3$ inventories. Characterizing NH$_3$ sources from the bottom up requires spatially and temporally resolved data such as detailed
farming practices and intensity. These data are rarely available nationally as direct measurements of NH$_3$ emissions at such scales are prohibitive owing to cost. Therefore, top-down approaches have become an attractive option for providing additional constraints. While direct observations of gas-phase NH$_3$ do exist in select locations, observations of other chemically related species are much more prevalent. Furthermore, NH$_3$ can rapidly partition to form aerosol ammonium (NH$_4^+$) which can limit the utility of gas-phase observations alone.

Consequently, owing to the paucity of direct observations of NH$_3$ and the difficulty of constraining the NH$_x$ (= NH$_3$ + NH$_4^+$) system, measurements of species that are regulated by the amount of available NH$_3$ have been looked to for constraints on estimates of NH$_3$ emissions. The current National Emissions Inventory (NEI) for NH$_3$ is coarsely constrained by top-down estimates from the inverse modeling studies of Gilliland et al. [2003, 2006]. Measurements of wet deposited NH$_x$ were used as constraints, because wet deposited NH$_x$ estimates depend less than NH$_3$ on model sensitivity to aerosol partitioning. A drawback to this approach is the sensitivity to the precipitation fields in the meteorological reanalysis data driving the chemical transport model and to the parameterization of NH$_x$ wet scavenging, both of which are aspects that are difficult to model accurately and hinder the inversion during some seasons. Taking an alternate approach, Henze et al. [2009] used surface measurements of SO$_4^{2-}$ and NO$_3^-$ from the IMPROVE network to constrain the amount of NH$_3$ partitioned into the aerosol phase as NH$_4^+$ (which is strongly coupled to SO$_4^{2-}$ and NO$_3^-$). In this way, aerosol-phase observations were used to constrain NH$_3$ concentrations and, hence, NH$_3$ emissions. This approach, however, is sensitive to model bias in HNO$_3$, which may be significant [Zhang et al., 2012; Heald et al., 2012].

Despite these recent efforts, comparisons of inverse modeling results to the bottom-up NH$_3$ inventory of Pinder et al. [2006] show that considerable disagreements remain in the spatial and seasonal distribution of NH$_3$ emissions throughout the U.S. [Henze et al., 2009]; at odds are estimates of the relative magnitude of spring vs summer emissions. A limiting factor in reconciling these differences is infrequent and sparse in situ observations, even for the aerosol-phase measurements, and a shortage of direct constraints on gas-phase NH$_3$. Without understanding the NH$_x$ system
as a whole, and without tools to link observations of these species over the continent to emissions, studies of NH$_3$ or NH$_4^+$ alone may suffer in terms of utility for constraining emissions inventories at a national scale [Pinder et al., 2006].

The detection of boundary layer ammonia from space [Beer et al., 2008; Clarisse et al., 2009, 2010; Shephard et al., 2011] provides a new and unprecedented opportunity for reducing persistent uncertainties in our understanding of the distribution and impacts of atmospheric ammonia. Initial comparisons to global model NH$_3$ distributions indicate that NH$_3$ sources may be widely underestimated [Clarisse et al., 2009; Shephard et al., 2011]. Pinder et al. [2011] have verified the utility of such measurements for tracking observed spatial and temporal trends in surface level NH$_3$ concentrations. Subsequent studies indicate underestimates of NH$_3$ sources exist in California and throughout the U.S. in the spring [Nowak et al., 2012; Walker et al., 2012; Heald et al., 2012]. Therefore, we consider here how inverse modeling with assimilation of satellite observations of NH$_3$ can be used to further provide constraints on NH$_3$ sources. Section 3.3 describes the models and inverse methodology used in this study. We then present details of the remote sensing observations (Section 3.4), followed by inverse modeling tests using simulated observations (Section 3.5) and real observations (Section 3.6). Finally, we evaluate the model results by comparing them to independent data sets omitted from the inversion (Section 3.7) and present our conclusions (Section 3.8).

### 3.3 Methods

#### 3.3.1 GEOS-Chem

GEOS-Chem is a chemical transport model driven with assimilated meteorology from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office [Bey et al., 2001]. The tropospheric oxidant chemistry simulation in GEOS-Chem includes a detailed ozone-NO$_x$-hydrocarbon chemical mechanism of 80 species and over 300 reactions [Bey et al., 2001]. GEOS-Chem includes an online secondary inorganic aerosol simulation introduced
and described in full by Park et al. [2004]. Global anthropogenic sources and natural sources of NH$_3$ are from the 1990 GEIA inventory [Bouwman et al., 1997]. Over the U.S., anthropogenic NH$_3$ emissions are taken from the 2005 U.S. National Emissions Inventory (NEI), with seasonality as described in Park et al. [2004], and the CAC inventory for Canada [van Donkelaar et al., 2008]. Biomass burning emissions are from van der Werf et al. [2006], and biofuel emissions are from Yevich and Logan [2003]. The total U.S. and global NH$_3$ emissions both before and after the optimization are shown in Table 3.1.

### Table 3.1: Total U.S. and global NH$_3$ emissions before and after optimization.

<table>
<thead>
<tr>
<th>Simulation</th>
<th>U.S. (Gg/month)</th>
<th>Global (Tg/month)</th>
</tr>
</thead>
<tbody>
<tr>
<td>April</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>234</td>
<td>5.67</td>
</tr>
<tr>
<td>Optimized</td>
<td>424</td>
<td>6.03</td>
</tr>
<tr>
<td>July</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>509</td>
<td>6.37</td>
</tr>
<tr>
<td>Optimized</td>
<td>799</td>
<td>6.76</td>
</tr>
<tr>
<td>October</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial</td>
<td>272</td>
<td>5.69</td>
</tr>
<tr>
<td>Optimized</td>
<td>362</td>
<td>5.80</td>
</tr>
</tbody>
</table>

### 3.3.2 GEOS-Chem adjoint model

The adjoint model is an efficient tool for calculating the gradient of a scalar model response function with respect to all model parameters simultaneously. The adjoint of the GEOS-Chem model was developed specifically for inverse modeling of precursors of inorganic PM$_{2.5}$ with explicit inclusion of gas-phase chemistry, heterogeneous chemistry, and treatment of the thermodynamic couplings of the sulfate - ammonium - nitrate - water aerosol system [Henze et al., 2007, 2009]. As the only adjoint model to explicitly represent this system, it is uniquely capable of assimilating speciated measurements of both gaseous and particulate components using the 4D-Var method [Sandu et al., 2005]. The accuracy of the adjoint model calculations is verified through extensive comparisons of adjoint to finite difference sensitivities. In order to maximize points of compari-
Figure 3.1: Validation of adjoint model sensitivities via comparison to finite difference (FD) results for week-long simulations. Shown here are the sensitivities of surface level NH$_3$ concentrations with respect to NH$_3$ emissions in an ensemble of column model simulations. Solid lines are 1:1, dashed are regressions with given $R^2$ and slope $m$.

son between these two approaches, we consider both ensembles of 1-D models (i.e., no horizontal transport) as well as spot tests of the full 3-D adjoint model (testing the full adjoint model for each parameter is prohibitively time consuming, as it would require separate forward model calculations for each of the approximately $10^5$ parameters). Figure 3.1 shows the results of a week-long test of the sensitivity of surface level NH$_3$ concentrations in each model column to NH$_3$ emissions in that column. Sensitivities calculated using the adjoint model are compared with sensitivities calculated using finite differences. All points lie along or near the 1:1 line, demonstrating the accuracy of the adjoint model. Further validation of the adjoint model can be found in previous papers [Henze et al., 2007, 2009, 2012].

3.3.3 Inverse modeling

Data assimilation techniques provide a framework for combining observations and models to form an optimal estimation of the state of a system, which in this case is the chemical makeup of the troposphere. To start with, a range of parameters are constructed using control variables, $\sigma$, to adjust elements of the vector of model parameters, $\mathbf{p}$, via application as scaling factors, $p = p_a e^{\sigma}$, where $p_a$ is the prior parameter estimate. The approach we consider iteratively employs
the adjoint of an air quality model in a method referred to as 4D-Var, used here for inverse modeling of emissions. The advantage of this method is that numerous ($O(10^5)$) model parameters can be optimized simultaneously while still retaining the constraints of the full forward model physics and chemistry. This approach to inverse modeling seeks $\sigma$ that minimizes the cost function, $J$, given by

$$J = \frac{1}{2} \sum_{c \in \Omega} (Hc - (c_{\text{obs}} - b))^T S_{\text{obs}}^{-1} (Hc - (c_{\text{obs}} - b))$$

$$+ \frac{1}{2} \gamma (\sigma - \sigma_a)^T S_a^{-1} (\sigma - \sigma_a)$$

(3.1)

where $H$ is the observation operator, $\gamma$ is the regularization parameter, $\sigma_a$ is the prior estimate of the control variables, $S_a$ and $S_{\text{obs}}$ are error covariance estimates of the control variables and observations respectively, $\Omega$ is the domain over which observations, $c_{\text{obs}}$, and model predictions are available, and $b$ is a bias correction explained in Section 3.6. Overall, the cost function is a specific model response functional, the minimum value of which balances the objectives of improving model performance while ensuring the model itself remains within a reasonable range (as dictated by $S_a^{-1}$) of the initial model. Gradients of the cost function with respect to the scaling factors calculated with the adjoint model, $\nabla \sigma J$, are supplied to an optimization routine (the quasi-Newton L-BFGS-B optimization routine [Byrd et al., 1995; Zhu et al., 1994]), and the minimum of the cost function is sought iteratively. At each iteration, improved estimates of the model parameters are updated and the forward model solution is recalculated.

3.4 Observations

3.4.1 Remotely sensed NH$_3$ observations from TES

The high spectral resolution and good signal-to-noise ratio of the TES instrument [Shephard et al., 2008] enabled the first detection of tropospheric ammonia from space, with measurements over Southern California and China [Beer et al., 2008]. TES is an infrared Fourier transform spectrometer with spectral resolution of 0.06 cm$^{-1}$ aboard the NASA Aura satellite, launched
July 15, 2004, with a local overpass time of 13:30 and 1:30 [Schoeberl et al., 2006]. TES global survey observations repeat with a 16-day cycle and have a nadir footprint of 5 km × 8 km; for example, that leads to about ∼180 daytime retrievals a month over North America after cloud screening (optical depths < 1.0) and applying the TES retrieval quality control flags.

Comparison of model estimates to satellite observations is done via application of the following formula for the TES observational operator, $H$,

$$ Hc = c_a + A(Mc - c_a) $$  \hspace{1cm} (3.2)

where $c$ is the model estimated NH$_3$ profile, $M$ is a matrix that maps these values to the retrieval units and vertical levels, $A$ is the averaging kernel, and $c_a$ is the a priori NH$_3$ profile used for the retrieval [Shephard et al., 2011]. By comparing TES NH$_3$ profiles to mapped model estimates, $Hc$, rather than the native model NH$_3$ profile, $c$, the contribution of error in $c_a$ to the measurement error, $S_{\text{obs}}$, is minimized [Rodgers, 2000].

For the sake of 2D visualization, the Representative Volume Mixing Ratio (RVMR) metric [Payne et al., 2009; Shephard et al., 2011] is used to provide a means of comparing TES profiles to model estimates in a manner that accounts for heterogeneity in the instrument’s sensitivity to NH$_3$. RVMR is the average volume mixing ratio within the boundary layer, weighted by a function derived from the retrieval’s averaging kernel. This represents a TES sensitivity weighted boundary layer averaged value with the influence of a priori reduced as much as possible [Shephard et al., 2011]. We calculate RVMR only for retrievals that have signal-to-noise greater than one and high thermal contrast. The RVMR is also calculated for the model in those locations which have valid TES retrievals.

### 3.4.2 Surface measurements

In this study, model estimates are evaluated using surface observations of NH$_3$, sulfate, nitrate, ammonium and wet deposited NH$_x$ from several monitoring networks throughout the U.S. Surface NH$_3$ observations are from the National Atmospheric Deposition Program (NADP) Am-
monia Monitoring Network (AMoN), which is comprised of triplicate passive ammonia monitoring samplers located at 21 sites across the U.S. with a two-week long sample accumulation [Puchalski et al., 2011]. All two-week long observations in each month are averaged to give monthly concentration. The locations of these 21 monitoring stations are shown in Figure 3.2. Observations from each site are compared with modeled concentrations during the November 2007 through June 2010 period.

Hourly surface NH$_3$ observations in July of 2008 are from the SouthEastern Aerosol Research and Characterization (SEARCH) network [Hansen et al., 2003], which has monitoring stations throughout the Southeast U.S. Different sample frequencies (e.g., daily, 3-day, 6-day, 1-min, 5-min, hourly) are available at different monitoring station. 5-min long observations are available in three stations, Oak Grove, MS, Jefferson Street, GA, and Yorkville, GA. The hourly NH$_3$ concentration used here is the average of all 5-min long observations of these three stations in each hour.

Wet deposition observations are taken from the NADP National Trends Network (NTN) (http://nadp.sws.uiuc.edu/NADP), which are predominantly located away from urban areas and point sources of pollution. NTN has more than 200 sites with week-long sample accumulation.

Model estimates of sulfate and nitrate aerosol are compared to observations from the Interagency Monitoring of Protected Visual Environments (IMPROVE) network for the year 2008 [Malm et al., 2004]. The IMPROVE network collects PM$_{2.5}$ particles on Teflon, nylon, and quartz.
filters using a modular, cyclone-based sampler with critical orifice flow control. Sulfate and nitrate aerosols are collected on nylon filters, which are sampled over 24 h every third day.

3.5 Inversions with pseudo data

We first assess the capabilities and limitations of the GEOS-Chem inverse modeling setup in idealized control conditions by designing inverse problems with known solutions. A common framework for testing inverse modeling is the so called twin experiment in which model simulations are used to generate pseudo observations [Talagrand and P. Courtier, 2008]. In our setup, pseudo observations are generated through application of the TES NH$_3$ retrieval algorithm [Shephard et al., 2011] to a simulated atmosphere from GEOS-Chem (i.e., radiative transfer calculations are performed to generate pseudo spectra with nominal TES instrument noise, and pseudo NH$_3$ retrievals produced from these). The standard model emissions used during this simulation are designated as the true emissions. Sampling times, locations and error estimates reflect those of actual TES observations, although retrieval bias ($b$) is not included in these tests. For these tests, 87 pseudo TES observations are used from July 14 through 19, 2005, along roughly a dozen global survey transects crossing the midwestern U.S.

To test the inverse model, NH$_3$ emissions parameters were initialized to values different from the true emissions. In the first test, initial model emissions are half of the true value. Figure 3.3(a) shows these values in black along with linear line slope $m$ and $R^2$. After optimization, the recovered emissions are unbiased and have a visible variance around the true emissions of $\sim$30%, as shown in blue in Figure 3.3(a). In a second test using the same pseudo observations, the model emissions were initially biased high by a factor of 1.8 (Figure 3.3(b)). The emissions recovered after optimization have a 20% high bias and again a 30% variance about the true values. While the variance of the recovered emissions is similar in both tests, the inversion starting with emissions that are initially too high is less successful.

To further investigate the reasons for this asymmetry and the variance of the optimized emissions, additional tests are performed to separate the possible impacts of inversion error, retrieval
Figure 3.3: Emissions before (initial) and after (optimized) inversions using TES pseudo observations. To test the inverse model, NH$_3$ emissions were initialized to values different than the true emissions. (a) The initial emissions are half of the true values. (b) The initial emissions are 1.8 times the true values. The black points are the total initial emissions in each grid cell, and the blue points are the optimized emissions (both in kg/box).
bias and measurement error. In each of the following tests, the true emissions are used to initialize the inversion. The first test uses the same pseudo observations as previously generated. This test again results in a high bias. As the same model state is used to generate the pseudo observations as was used to intialize the inversion, this bias can be attributed to a high bias in the retrieval itself. Retrieval bias, as explained further in Shephard et al. [2011], is owing to the fact that the retrieval always selects a moderate or polluted profile as an initial guess in order to avoid the null space of the radiative transfer operator. As the optimal estimation algorithm iterates towards a solution, the process may halt when values reach TES’s detection threshold, resulting in a high bias. To test this, the retrieval algorithm is modified to use only a moderate profile as an initial guess. Pseudo observations generated using these profiles lead to slightly less high bias in the inversion, at the cost of increased variance, see Figure 3.4(b). As the magnitude of the final bias in tests whose results shown in (a) and (b) are similar to those in the pseudo inversions, it seems that the retrieval bias explains the bias exhibited in the pseudo inversions, and thus the entire process of inverting for NH$_3$ emissions is not appreciably intrinsically biased. To isolate the impact of measurement noise, the model profiles from the true model are ascribed realistic measurement error and then assimilated. These profiles, unlike the previous tests, correspond directly to the true model and are not retrieved profiles from the retrieval process. The impact of this measurement noise is only a slight adjustment in the emissions. Thus, the variance exhibited in the pseudo inversions is intrinsic to the inversion process itself, and would occur even if observations were perfect. This happens because there are variations in emissions that lie in the null space of the forward model. In other words, having some emissions too high and some emissions too low can result in indistinguishable (to TES) distributions of NH$_3$. Overall, the pseudo observation tests lead us to conclude that (1) measurement noise alone will not lead to unstable inversions (2) emissions that are underestimated can likely be recovered (3) emissions that are overestimated will be decreased, though this is countered by bias in the retrievals leading to overestimate of emissions in conditions where the model emissions are intially too high and (4) that many more iterations and observations would be necessary to reduce the variance of the emissions estimates from the truth, which will be at best $\sim$30%. While this variance is
substantial, this is a significant improvement over initial errors of $\sim 100\%$. Contrast between points (2) and (3) is likely owing to the larger magnitude of the bias for retrievals with larger values (see Supplementary Figure 7.1).

### 3.6 TES assimilation

We next proceed to constrain U.S. NH$_3$ sources using real observations. TES observations are compared to model estimates from a 2008 GEOS-Chem global $2^\circ \times 2.5^\circ$ simulation, using Eq. (3.2) to assimilate individual observations. The lifetime of NH$_3$ is short compared to the residence time of an airmass in one grid cell of our model. As single retrievals may reflect strong sub-grid gradients in NH$_3$ concentration, we consider satellite observations during four years, 2006 - 2009, to provide enhanced spatial data coverage for comparison with the 2008 model simulations. Inter-annual comparisons of monthly AMoN NH$_3$ data indicate no substantial trends in this time period (See Supplementary Figure 7.3).

Thousands of TES retrievals are available for the assimilation, but not all of the TES retrievals are usable. The satellite can not always detect NH$_3$ for several reasons, such as the presence of clouds, low NH$_3$ concentrations (low signal to the noise ratio), and poor thermal contrast between the earth and atmosphere. Thus, quality and diagnostic flags are defined to classify and filter the retrievals, keeping only those that have Degree Of Freedom For Signal (DOFS) greater than 0.1, or DOFS less than 0.1 but with high (absolute value greater than 7 K) thermal contrast. We use the retrievals from daytime only as the retrievals at night are currently being further validated.

The TES retrievals are corrected by subtracting mean biases. These biases are generated from the discrepancy between TES retrievals and true profiles [Shephard et al., 2011], and the mean biases are calculated according to the type of the a priori profile (see Supplementary Figure 7.1). There is separate bias associated with each of the three types of a priori profiles used in the retrieval algorithm. For example, we apply the “unpolluted” bias correction to all observations in which the unpolluted a priori model profile was used in the retrieval algorithm.

A key aspect of inverse modeling is regularization through inclusion of the penalty, or back-
Figure 3.4: Tests for the possible impacts of inversion error, retrieval bias and measurement error: (a) retrieval algorithm with a polluted profile as an initial guess; (b) modified retrieval algorithm with a moderate profile as the initial guess; (c) model profiles from the true model were ascribed error of the same size as the measurement error. The black points are the total initial emissions in each grid cell, and the blue points are the optimized emissions (both in kg/box).
Figure 3.5: The average of TES retrieval profiles used in the assimilation (solid red line). The average model NH$_3$ profiles before (blue dot line) and after (blue dash line) the assimilation. The TES observation operator is applied to the model profiles.

ground, term in the cost function, specified through the prior error covariance matrix, $S_a$, and a regularization parameter, $\gamma$. In the absence of rigorous statistical information on the error covariances of the emissions, we assume the errors are uncorrelated and use an L-curve selection criteria [Hansen, 1998] (see Supplementary Figure 7.2) to regularize our solution. Still, the relative error for each species are specified as follows. Given the large discrepancies previously noted for NH$_3$ sources [Henze et al., 2009], uncertainties of NH$_3$ are taken to be 100% of the maximum NH$_3$ emissions across the globe. Based on work by other researchers, we assume that the uncertainties in SO$_2$ [Lee et al., 2011] and NO$_x$ (e.g., [Russell et al., 2012]), are smaller, conservatively 20% and 50% of the maximum (the impact of these assumed values is assessed in Section 3.6, Table 3.2). With these values, we select the regularization parameter ($\gamma$) to be 124 for April, 100 for July, and 50 for October.

TES NH$_3$ observations are assimilated using the GEOS-Chem adjoint-based inversion. The domain-wide average model NH$_3$ profiles before and after the inversion are shown along with the average TES profile in Figure 3.5. The model NH$_3$ profiles are predominately lower than the TES observations in the prior simulation and have shifted towards the TES profile in the optimized
simulation. This leads to reductions of the cost function of 66%, 42%, and 57%, for April, July, and October, respectively. The optimization is considered to have converged when consecutive iterations decrease the cost function by less than 2%. An example of the minimization is provided in Supplementary Figure 7.4. While we recognize that further iterations are possible, for practical purposes (each iteration requiring ~10 hours to compute), this was deemed a sufficient convergence criteria. Limited tests indicate that additional iterations did not drastically alter the results.

The total initial and optimized ammonia emissions are shown in Figure 3.6. The optimized emissions generally increase over the U.S., with adjustments that are seasonally and spatially heterogeneous. There are large increases in southern California in all three months. Other large increases are located in the central and western U.S., as well as parts of Mexico and Cuba. We do not have much information about NH$_3$ in Mexico and Cuba due to lack of ground-based measurement records there, but large (e.g. 15 ppb) NH$_3$ RVMR values are observed in April whereas the corresponding GEOS-Chem model estimates using the initial emissions are very small (e.g., 1.37 ppb). As a result of the inversion, emissions are increased in such areas by up to a factor of 9. Changes to emissions in the East are generally much smaller; emissions in the Altantic regional are generally unchanged in April and October, while they are higher in the North East in July, and even slightly lower in a few locations in the South.

Figure 3.7 shows the comparison of NH$_3$ RVMR from TES and GEOS-Chem before and after the assimilation. There are between 500 and 700 RVMR values in each month including values from 4 years. A linear fit of the model values to the observations is performed in each month, before and after optimization. The slope of this line increases in each month which indicates that most of the RVMR values from GEOS-Chem increase after the optimization. However, the modeled NH$_3$ RVMRs at low values change only slightly after the optimization in all three months. We note however that these differences in RVMR do not reflect observation bias or uncertainty, which contribute to the cost function. In order to show the locations which have significant changes in RVMR, we consider spatial plots of the difference between the TES and GEOS-Chem RVMR before and after the assimilation for each month (Figure 3.8). Initially, the model RVMRs are generally less
Figure 3.6: NH$_3$ emissions from GEOS-Chem before and after the assimilation.
than the TES RVMRs, as indicated by the blue points in the map. After the optimization, model RVMRs increase in many places. Some of the model RVMRs are larger than the TES RVMRs, as indicated by the red points in the map and the overall model bias relative to TES is reduced. The discrepancies between TES RVMRs and model RVMRs change from negative to positive in Southern California and Central U.S. in all three months, consistent with the spatial plots showing large increases of ammonia emissions in these locations (Figure 3.6).

We also assess the sensitivity of these results to the assumed a priori emissions errors, $S_a$. Table 3.2 shows the effects of varying a priori errors on the total optimized emissions of different species. We assume the error for NH$_3$, $S_a^{1/2}$($NH_3$), to be 50% of the maximum a priori emission for all species. Generally, the results of the inversion are not very different in terms of total emission changes for each species from the base case inversion. However, absolute changes in total emissions of SO$_2$ and NO$_x$ increase slightly as their uncertainties increase relative to those of NH$_3$, while changes in NH$_3$ total emissions decrease as uncertainty of NH$_3$ decreases. Differences between the emissions in Table 3.2 compared to Table 3.1 stem from the use of an earlier version of the model and TES dataset for performing the sensitivity calculations in Table 3.2; the overall findings are likely still applicable.

Table 3.2: The effects of a priori error emissions ($S_a$) on the optimized emissions of different species. Total emissions changes in the U.S. for NH$_3$, NO$_x$, and SO$_2$ when using different values for the diagonal of $S_a^{1/2}$ in the optimization. $E^0$ is the initial emissions.

<table>
<thead>
<tr>
<th>Month</th>
<th>Uncertainties, $S_a^{1/2}/max(E^0)$</th>
<th>Total emissions changes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SO$_2$</td>
<td>NO$_x$</td>
</tr>
<tr>
<td>April</td>
<td>20%</td>
<td>50%</td>
</tr>
<tr>
<td></td>
<td>50%</td>
<td>50%</td>
</tr>
<tr>
<td>July</td>
<td>20%</td>
<td>50%</td>
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<tr>
<td></td>
<td>50%</td>
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<tr>
<td>October</td>
<td>20%</td>
<td>50%</td>
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</tr>
</tbody>
</table>
Figure 3.7: Comparison of NH$_3$ Representative volume Mixing Ratio (RVMR) from TES and GEOS-Chem before and after the assimilation.
Figure 3.8: Difference of NH$_3$ Representative volume Mixing Ratio (RVMR) between TES and GEOS-Chem before and after the assimilation. The left column shows GEOS-Chem initial RVMR - TES RVMR; the right column shows GEOS-Chem optimized RVMR - TES RVMR.
3.7 Posterior model evaluation against independent data

In the following sections we compare output from model simulations using the optimized emissions to independent data sets not used during the inversion. This serves as an important assessment of the robustness of the inverse model solution. Even when the inverse model has converged to a solution in which the model prediction error is minimized and the emissions are consistent with the a priori error assumptions, the validity of the emissions constraints beyond this particular model framework is not guaranteed. The basic 4D-Var approach does not account for bias in the forward chemical transport model, which may significantly impact the top-down emissions constraints. Evaluating against independent data sets is thus critical.

3.7.1 AMoN and SEARCH

We first consider a comparison of the posterior model results to AMoN NH₃ observations (Figure 3.9). Initially, the model broadly underestimates AMoN values. After optimization, the NH₃ concentrations increase in each month. The $R^2$ increases by 22.4% in April, 28.9% in July and 27.2% in October. The slope increases by 353.3% in April, 96.1% in July and 77.1% in October. However, while the root mean square error (RMSE) decreases by 13% in April and 9.5% in October, it increases by 77.6% in July. The normalized mean bias (NMB) after the optimization decreases from -0.678 to -0.069 in April, and increases from -0.045 and -0.138 to 0.659 and 0.166 in July and October, respectively. Overall, the model does a better job of capturing the range and variability of NH₃ at AMoN sites in April and October, while in July, the model estimates are biased high.

TES has a detection limit of about 1 ppb, and a positive bias of about 0.5 ppb [Shephard et al., 2011]. Model values that are below 1 ppb do not change significantly after the optimization in all three months (Figure 3.9). The bias shown in Figure 3.9 for July is much higher than 0.5 ppb. One possible reason may be sampling bias due to the TES level-of-detectability, and spatial sampling differences between the TES footprint and the model grid. This is assessed by analyzing NH₃ simulations from high resolution (12 km × 12 km) Community Multi-scale Air
Figure 3.9: Comparison of GEOS-Chem NH$_3$ concentrations with observations from AMoN sites before and after the assimilation. The square of the correlation coefficient ($R^2$), root mean square error (RMSE), and normalized mean bias (NMB) are shown. Black solid lines are regressions. Grey dashed lines are 1:1.
Quality (CMAQ) model simulations. Surface level NH$_3$ concentrations throughout the U.S. are compared to concentrations from locations corresponding to successful TES retrievals. The mean surface NH$_3$ concentration of CMAQ at locations which have successful TES retrievals is about 30% larger than the mean value of that for the whole U.S. This comparison is facilitated by the fact that the TES footprint (5 km $\times$ 8 km) and CMAQ grid cells are similar in size. As shown in Figure 3.9, changes in large concentrations drive the optimization. A lack of TES observations constraining low values may allow for initial model values that already overestimate low NH$_3$ concentrations to become even higher in the optimized model, because high TES values, many of which are larger than the initial model estimate, will dominate the cost function. In future work, resampling the TES retrievals may be one way to decrease the sampling bias. Increasing the model resolution may also improve our ability to model localized peak NH$_3$ concentrations measured by TES and to match observations from AMoN.

Lastly, Jeong et al. [2013] also compared observations from TES and in situ NH$_3$ measurements to model simulations, noting similar cases where in situ measurements were lower than the model (CMAQ) simulations, but the TES observations were higher. It was suggested that treatment of the diurnal variability of summertime NH$_3$ emissions from livestock may play a role in this discrepancy. Comparison of GEOS-Chem hourly NH$_3$ concentrations to data from the SEARCH network in July paints a similar picture (see Figure 3.10): the constant hourly NH$_3$ emissions in GEOS-Chem lead to NH$_3$ concentrations that are overestimated at night, and thus also in the monthly average when compared to AMoN. Following Jeong et al. [2013], we perform a sensitivity calculation wherein NH$_3$ emissions from livestock are increased by 90% during the day and reduced by 90% at night. The impact is to decrease the monthly average surface concentrations by several ppb, while increasing daytime boundary layer NH$_3$ concentrations enough to reduce the cost function by 25%. In addition, Jeong et al. [2013] also showed that bi-directional exchange of NH$_3$ in July lead to increased and decreased emissions in different regions (10% overall increase), yet NH$_3$ concentrations increased everywhere. This is in contrast to April and October, where emissions and concentrations decreased. Physical mechanisms have thus been identified by which mid-day
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model profiles of NH$_3$ may be increased without large increases in emissions. Further consideration of mechanistic, process-based treatment of NH$_3$ sources in global models is therefore warranted.

### 3.7.2 NTN

As an additional check of the broad NH$_x$ budget, we consider the NH$_x$ wet deposition as recorded by NTN (NADP) sites. To make this comparison, we consider that simulated precipitation is a critical driver in the performance of the GEOS-Chem simulated wet deposition estimates, as biases in the model estimated precipitation can lead to biases in the GEOS-Chem model estimates. We therefore adjust the modeled wet deposition diagnostic to account for differences in the modeled and observed precipitation by linearly scaling the model estimated wet deposition by the ratio of the observed to estimated precipitation.

Figure 3.11 shows the comparison of modeled wet deposition with the NTN observations. Generally, the inversion increases wet deposition during all three months. Also, the square of the correlation coefficient ($R^2$) improves in each month: 11.4% in April, 14.1% in July and 10.3% in October. In April and October, optimized values compare better with the NTN observations. In contrast, the slope of the linear regression line increases from 1.08 to 1.59 in July. This is consistent with the high bias of the inversion relative to the AMoN surface observations of NH$_3$ in July. Comparisons between GEOS-Chem and NTN observations are also shown in Zhang et al. [2012]. They compare the NH$_3$ wet deposition from GEOS-Chem at the 0.5° × 0.67° resolution with NTN observations from 2006. Differences between this study and the present work are the model resolution, data filtering, the number of months per season included in the comparisons (one versus three) and the emission inventories (Zhang et al. [2012] adjust domain-wide seasonality using in situ observations to minimize seasonal bias).

### 3.7.3 IMPROVE

For an additional evaluation, we also compare the assimilated results with aerosol observations from IMPROVE in 2008. Figure 3.12 shows that model optimization slightly decreases the
Figure 3.10: Comparison of initial (un-optimized) GEOS-Chem hourly NH$_3$ concentrations with observations from SEARCH (blue) sites in July. The red color represents the hourly NH$_3$ concentrations with the standard constant hourly NH$_3$ emissions in GEOS-Chem. The black color represents the hourly NH$_3$ concentrations with NH$_3$ livestock emissions increased by 90% during the day and reduced by 90% at night.
Figure 3.11: Comparison of GEOS-Chem NH$_x$ wet deposition with observations from NTN (NADP) sites before (blue) and after (red) the assimilation.
sulfate concentrations and increases the nitrate concentrations, which facilitates increases in NH$_3$ concentrations to match TES observations. Still, the changes are small, and the sulfate concentration from the model has a reasonable correlation with the IMPROVE observation before and after optimization in each month. Note that the outlier in October that has a large observed value but a nearly zero model value is located in Hawaii. The model does not represent this high value owing to the proximity of the observation to the local volcano source.

Optimized NH$_3$ emissions do not help the comparison of simulated nitrate to IMPROVE observations, which initially are over predicted. The balance of sulfate and nitrate from IMPROVE sites alone implies that NH$_3$ sources are too high [Henze et al., 2009]. However, model NH$_3$ in the present work increases in order to improve agreement with TES NH$_3$, leading to more nitrate formation, and the nitrate bias becomes even higher compared to IMPROVE. It is thus a challenge to resolve the underestimates of boundary layer NH$_3$ with the overestimates of nitrate. HNO$_3$ formation in the model is perhaps excessive [Zhang et al., 2012], and overly shallow night time boundary layers may contribute to enhanced nitrate [Heald et al., 2012]. We perform additional sensitivity studies, reducing the heterogeneous uptake coefficient for N$_2$O$_5$ hydrolysis by an order of magnitude and adjusting the boundary layer height following Heald et al. [2012]. While such changes do impact the nitrate simulation, the nitrate high bias persists, and the comparison of the base model NH$_3$ to the AMoN and TES observations was not notably affected. Enforcing a diurnal variation in NH$_3$ livestock emissions decreased average surface nitrate concentrations by up to a $\mu$g/m$^3$, as the GEOS-Chem overestimates of night time NH$_3$ likely contributed to excessive partitioning of HNO$_3$ at night. Thus, to achieve closure relative to all data sets, it is evident that assessment of model error beyond NH$_3$ sources, in terms of scavenging efficiencies, deposition, diurnal variability, and further investigation of HNO$_3$ production is required.

### 3.8 Conclusions

Here we have considered the potential for space-based observations of NH$_3$ to constrain monthly average emissions. Initial tests using pseudo-observations show that under ideal condi-
Figure 3.12: Comparison of GEOS-Chem SO$_4$ and NO$_3$ concentrations with observations from IMPROVE sites before and after the assimilation.
tions (i.e., a perfect model) using two-weeks worth of TES data, 70% of the variance of the emissions can be constrained in terms of total magnitude. We then proceed to assimilate TES observations in April, July and October for multiple years. We present a range of constrained prediction results and evaluate them with independent data sets. Generally, model optimization increases NH$_3$ concentrations and NH$_x$ wet deposition. Overall, the model does a better job of capturing the range and variability of NH$_3$ at AMoN sites in April and October, while in July, the model estimates are consistently biased high. Compared to the wet deposition observations of NTN, optimization decreases the normalized mean bias (NMB) in April, enhances the NMB in July and October, but overall leads to increased correlation of modeled and observed values. Modeled SO$_4^{2-}$ aerosol concentrations slightly decrease and NO$_3^-$ aerosols concentrations increase, which increases the bias compared to the IMPROVE observations.

Overall, remote sensing constraints indicate that the initial NH$_3$ emissions inventory appears to be broadly underestimated in several areas throughout the U.S., particularly in the West. This is consistent with recent works regarding NH$_3$ levels in California throughout the year [Walker et al., 2012] and the U.S. in the spring [Heald et al., 2012], as well as in situ measurements in April and October. Still, the absolute extent of the emissions underestimation in these seasons is still in question, as the precise accuracy of the satellite observations is difficult to specify, model resolution is not matched to the satellite resolution, and model processes could have error contributing to uncertainty in the inversion. A greater fraction of peak values are included in the assimilation owing to satellite detection limits, leading to a sampling bias that may cause the inverse model to overestimate emissions in July, as indicated by high biases in the optimized model simulations of surface-level NH$_3$ concentrations and NH$_x$ deposition. Future work will apply a newly developed higher resolution (e.g., 0.5° × 0.67°) version of the inverse model to further address this issue.

Additional sensitivity studies, comparisons to hourly observations from SEARCH, and the recent regional modeling work of Jeong et al. [2013], indicate that diurnal variability of livestock emissions and bi-directional flux from fertilizer sources may play important roles in resolving discrepancies between average surface level concentrations and mid-day profiles of NH$_3$, and may
also impact the high bias of nitrate in GEOS-Chem [Heald et al., 2012]. Further assessment of mechanistic, process-based treatment of NH$_3$ sources in global models is thus needed. Additional measurements, either from expanded in situ monitoring networks or geostationary remote sensing instruments, would greatly serve this need.
Chapter 4

Global evaluation of ammonia bi-directional exchange

4.1 Abstract

Bi-directional air-surface exchange of ammonia (NH$_3$) has been neglected in many air quality models. In this study, we implement the bi-directional exchange of NH$_3$ in the GEOS-Chem global chemical transport model. We also introduce an updated diurnal variability scheme for NH$_3$ livestock emissions and evaluate the recently developed MASAGE_NH$_3$ bottom up inventory. While updated diurnal variability improves comparison of modeled-to-hourly in situ measurements in the Southeastern U.S., NH$_3$ concentrations decrease throughout the globe, up to 17 ppb in India and Southeastern China, with corresponding decreases in aerosol nitrate by up to 7 $\mu$g/m$^3$. The ammonium (NH$_4^+$) soil pool in the bi-directional exchange model largely extends the NH$_3$ lifetime in the atmosphere. Including bi-directional exchange generally increases NH$_3$ gross emissions (7.1%) and surface concentrations (up to 3.9 ppb) throughout the globe in July, except in India and Southeastern China. In April and October, it decreases NH$_3$ gross emissions in the Northern Hemisphere (e.g., 43.6% in April in China) and increases NH$_3$ gross emissions in the Southern Hemisphere. Bi-directional exchange does not largely impact NH$_4^+$ wet deposition overall. While bi-directional exchange is fundamentally a better representation of NH$_3$ emissions from fertilizers, emissions from primary sources are still underestimated and thus significant model biases remain when compared to in situ measurements in the U.S. The adjoint of bi-directional exchange has also been developed for the GEOS-Chem model and is used to investigate the sensitivity of NH$_3$

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1 This Chapter will be published in Zhu et al. [in prep].
concentrations with respect to soil pH and fertilizer application rate. This study thus lays the
groundwork for future inverse modeling studies to more directly constrain these physical processes
rather than tuning bulk uni-directional NH$_3$ emissions.

4.2 Introduction

Ammonia (NH$_3$) is an important precursor of particulate matter (PM$_{2.5}$) that harms human
health [Reiss et al., 2007; Pope et al., 2009; Crouse et al., 2012] and impacts climate through aerosol
and short-lived greenhouse gas concentrations [Langridge et al., 2012]. Global emissions of NH$_3$
have increased by a factor of 2 to 5 since pre-industrial times, and they are projected to continue to
rise over the next 100 years [Lamarque et al., 2011; Ciais, 2013]. NH$_3$ is an important component
of the nitrogen cycle and accounts for a significant fraction of long-range transport (100’s of km)
of reactive nitrogen [Galloway et al., 2008]. Excessive deposition of NH$_3$ already threatens many
sensitive ecosystems [Liu et al., 2013].

Uncertainties in estimates of NH$_3$ emissions are significant. Surface-level NH$_3$ measurements
have been limited in spatial and temporal coverage, leading to large discrepancies in emissions
estimates [Pinder et al., 2006]. Additional information from remote sensing observations has been
used to gain a better understanding of NH$_3$ distributions [Clarisse et al., 2009; Shephard et al.,
2011; Pinder et al., 2011; Van Damme et al., 2014]. These observations have also been used as
inverse modeling constraints on NH$_3$ emissions [Zhu et al., 2013]. While this approach leads to
improved results regarding the comparison of air quality model estimates to independent surface
observations in the U.S. [Zhu et al., 2013], several limitations of this approach were identified. First,
model biases in NH$_x$ wet deposition were not reduced. Emission constraints from remote sensing
measurements available only once per day were very sensitive to the model’s diurnal variation of
NH$_3$ sources. Also, the remote sensing observations used in Zhu et al. [2013] are sparsely distributed,
leading to a quantifiable sampling bias. Other inverse modeling studies of NH$_3$ emissions have been
performed using in situ observations, such as aerosol SO$_{4}^{2+}$ and NO$_3^-$ [Henze et al., 2009], aircraft
observations of NH$_3$ [Schiferl et al., 2014] or wet deposition of NH$_4^+$ [Paulot et al., 2014]. However,
these approaches still have disadvantages as they are limited to the small spatiotemporal coverage of available aircraft measurements, or are sensitive to large model biases in HNO$_3$ [Heald et al., 2012; Zhang et al., 2012] or precipitation Paulot et al. [2014].

The modest success of previous inverse modeling studies suggests that updates to the dynamic and physical processes governing NH$_3$ are needed in addition to improvements in emissions estimates. Nighttime NH$_3$ concentrations are consistently overestimated in many air quality models (e.g., GEOS-Chem, CMAQ). This may contribute to an overestimate of monthly averaged NH$_3$ concentration following the assimilation of Tropospheric Emission Spectrometer (TES) observations [Zhu et al., 2013]. The treatment of diurnal variability of livestock NH$_3$ emissions is suggested to be part of the reason for such biases, which is explored further in Appendix A.

Another area in which many air quality models are currently deficient is in treatment of the air-surface exchange of NH$_3$. Rigorous treatment of the bi-directional flux of NH$_3$ can substantially impact NH$_3$ deposition, emission, re-emission and atmospheric lifetime [Sutton et al., 2007]. Re-emission of NH$_3$ from soils can be a significant part of NH$_3$ sources in some regions. However, this bi-directional exchange mechanism is neglected by many air quality models (e.g., GEOS-Chem). Several recent studies have begun to include resistance-based bi-directional exchange wherein the NH$_3$ flux direction is determined by comparing the ambient NH$_3$ concentration to the NH$_3$ in-canopy compensation point. Sutton et al. [1998] and Nemitz et al. [2001] began with the air-canopy exchange model and extended the model by including air-soil exchange, but with no soil resistance. Cooter et al. [2010] and Bash et al. [2010] developed and extended the model to include a soil capacitance which assumes that NH$_3$ and NH$_4^+$ exist in equilibrium in the soil. Bi-directional exchange of NH$_3$ coupled in a regional air-quality model (Community Multiscale Air-Quality (CMAQ)) is evaluated in Bash et al. [2013] and Pleim et al. [2013].

Based on these previous studies, investigating the diurnal patterns of NH$_3$ emissions and bi-directional air-surface exchange is critical for reducing uncertainties in the GEOS-Chem model, which may in turn afford better top-down constraints NH$_3$ source distributions and temporal and seasonal variations. In this paper, we apply a new diurnal distribution pattern to NH$_3$ livestock
emissions in GEOS-Chem, which is developed based on observations of emissions in the Concentrated Animal Feeding Operation (CAFO) dominated areas in North Carolina [Bash et al., in prep]. We then implement bi-directional exchange of NH$_3$ in a global chemical transport model – GEOS-Chem – following Pleim et al. [2013], and compare the model to in situ observations. As a first step towards including bi-directional exchange in NH$_3$ inverse modeling, we also develop the adjoint of bi-directional exchange in GEOS-Chem; this also provides a useful method for quantifying the sensitivities of GEOS-Chem simulations with respect to important parameters in the bi-directional model, such as soil pH and fertilizer application rate, which are themselves uncertain.

Section 4.3 describes the model we use in this study. Section 4.4 introduces the in situ observation networks we use for evaluation. The impacts of implementing the new diurnal variation pattern of NH$_3$ emissions are presented in section 4.5. The details of developing bi-directional exchange and its adjoint in GEOS-Chem are described in section 4.6, followed by the evaluations and adjoint sensitivity analysis in section 4.7. We present our conclusions in section 4.8.

4.3 Methods

4.3.1 GEOS-Chem

GEOS-Chem is a chemical transport model driven with assimilated meteorology from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office [Bey et al., 2001]. We use the nested grid of the model (horizontal resolution 1/2° × 2/3°) over the U.S. and 2° × 2.5° horizontal resolution for the rest of the world. The year 2008 is simulated with a spin-up period of 3 months. The tropospheric oxidant chemistry simulation in GEOS-Chem includes a detailed ozone-NO$_x$-hydrocarbon-aerosol chemical mechanism [Bey et al., 2001] coupled with a sulfate-nitrate-ammonia aerosol thermodynamics module described in Park et al. [2004]. The wet deposition scheme of soluble aerosols and gases is described in Liu et al. [2001]. The dry deposition of aerosols and gases scheme is based on a resistance-in-series model [Wesely, 1989], updated here to include bi-directional exchange (see Section 4.6).
Global anthropogenic and natural sources of NH$_3$ are from the GEIA inventory 1990 [Bouwman et al., 1997]. The anthropogenic emissions are updated by the following regional inventories: the 2005 U.S. EPA National Emissions Inventory (NEI) for U.S., the Criteria Air Contaminants (CAC) inventory for Canada [van Donkelaar et al., 2008], the inventory of Streets et al. [2006] for Asia, and the Co-operative Program for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) inventory for Europe [Vestreng and Klein, 2002]. Monthly biomass burning emissions are from van der Werf et al. [2010], and biofuel emissions are from Yevich and Logan [2003].

4.3.2 GEOS-Chem adjoint model

An adjoint model is an efficient tool for investigating the sensitivity of model estimates with respect to all model parameters simultaneously. This approach has been applied in recent decades in chemical transport models for source analysis of atmospheric tracers [Fisher and Lary, 1995; Elbern et al., 1997] and for constraining emissions of tropospheric chemical species [Elbern et al., 2000]. Adjoint models have also been used in air quality model sensitivity studies [e.g., Martien and Harley, 2006]. The adjoint of GEOS-Chem is fully described and validated in Henze et al. [2007]. It has been used for data assimilation using in situ observations [e.g., Henze et al., 2009; Paulot et al., 2014] and remote sensing observations [e.g., Kopacz et al., 2010; Zhu et al., 2013; Xu et al., 2013]. In this paper, we use the adjoint model to investigate the sensitivity of modeled NH$_3$ with bi-directional exchange and a new diurnal distribution of NH$_3$ livestock emissions with respect to soil pH and fertilizer application rate.

4.4 Observations

4.4.1 Surface measurements

We use surface observations of NH$_3$ and wet deposited NH$_4^+$ from several networks to evaluate model estimates. The SouthEastern Aerosol Research and Characterization (SEARCH) network
contains monitoring stations throughout the Southeast U.S. The SEARCH network provides different sampling frequencies, such as daily, 3-day, 6-day, 1-min, 5-min and hourly, at different sites. Three monitoring stations (Oak Grove, MS, Jefferson Street, GA, and Yorkville, GA) provide 5-min long surface NH$_3$ observations. We average the 5-min long observations of these three sites and convert them to be hourly average NH$_3$ concentration in July 2008.

The Ammonia Monitoring Network (AMoN) of National Atmospheric Deposition Program (NADP) contains 21 sites across the U.S. with two-week long sample accumulation [Puchalski et al., 2011]. We average the two-week long observations from November 2007 through June 2010 to monthly NH$_3$ concentrations. The Interagency Monitoring of Protected Visual Environments (IMPROVE) network [Malm et al., 2004] consists of more than 200 sites in the continental U.S. which collect PM$_{2.5}$ particles over 24 hours every third day. We use monthly average sulfate and nitrate aerosols concentrations.

We use wet NH$_4^+$ deposition observations from several monitoring networks around the world. The NADP National Trends Network (NTN) (http://nadp.sws.uiuc.edu/NTN) contains more than 200 sites in U.S. which are predominately located in rural areas. It provides wet deposition observations of ammonium with week-long sample accumulation. The Canadian Air and Precipitation Monitoring Network (CAPMoN) (http://www.on.ec.gc.ca/natchem) contains about 26 sites which are predominately located in Central and Eastern Canada with 24-hour integrated sample times. The European Monitoring and Evaluation Program (EMEP) (http://www.nilu.no/projects/ccc/emepdata.html) contains about 70 sites which are predominately located away from local emission sources. It has daily, weekly, and bi-weekly observations of ammonium available in different sites. The Acid Deposition Monitoring Network in East Asia (EANET) (http://www.eanet.asia/product) contains 54 sites (21 urban, 13 rural, and 20 remote sites) with monthly observations of wet deposition of ammonium. We convert the daily/weekly/bi-weekly observations to monthly average NH$_4^+$ concentration in 2008.
4.5 Diurnal variability of ammonia livestock emission

4.5.1 Development of new diurnal distribution scheme

Simulated NH$_3$ surface concentrations in GEOS-Chem are significantly overestimated at nighttime compared to hourly observations from the SEARCH network [Zhu et al., 2013]. The standard NH$_3$ emissions in GEOS-Chem are evenly distributed throughout the 24 hours of each day of the month, as indicated by the blue line in Figure 4.1. That the simulated NH$_3$ emissions do not have any diurnal variation is a likely explanation for this discrepancy with hourly observation. Thus, a new diurnal distribution scheme for NH$_3$ livestock emissions has been developed in CMAQ [Bash et al., in prep]. Here we implement this algorithm in GEOS-Chem. The hourly NH$_3$ livestock emission, $E_h(t)$, is calculated from the monthly total emission, $E_m$, as

$$E_h(t) = E_m N_{met}(t),$$

where $N_{met}(t)$ is the hourly fraction of the NH$_3$ livestock emission during the month. This depends on the aerodynamic resistance, $R_a$ [s$^{-1}$m], and surface temperature, $T$ [K],

$$N_{met}(t) = \frac{H(t)/R_a(t)}{\sum_{t=1}^{n}(H(t)/R_a(t))},$$

where $n$ is the number of hours in a month, $t$ is the time during the month, from 1 to $n$, and $H(t)$ is the Henry’s equilibrium, calculated following Nemitz et al. [2000],

$$H(t) = \frac{161500}{T}e^{-\frac{10380}{T}}.$$

More details of the development of this diurnal variability scheme can be found in Bash et al. [in prep].

4.5.2 Global distribution

We replace the standard GEOS-Chem livestock emissions, which are evenly distributed for each hour of the day (static), with this new diurnal variability of livestock emissions that peaks in the middle of the day (dynamic) (Figure 4.1). This also introduces daily variability of livestock
Figure 4.1: Monthly averaged diurnal variation fractions of livestock emissions of year 2008 over the U.S. Blue line is the standard GEOS-Chem. Dark green, red and black lines are the newly developed diurnal pattern of NH$_3$ livestock emissions in April, July and October, respectively.
emissions into the simulation, which is not considered in the standard GEOS-Chem model. As the standard GEOS-Chem anthropogenic emissions do not distinguish the livestock emissions sector, we calculate the absolute NH$_3$ livestock emissions based on the fractions of livestock emissions in anthropogenic emissions in the 2008 NEI.

Significant improvements are found when we compare surface NH$_3$ concentrations to SEARCH observations after implementing the dynamic diurnal emissions. The dynamic case decreases the surface NH$_3$ concentration relative to the static case by several ppb at night and increases concentrations slightly (up to 1 ppb) in the day. This reduces the model mean bias by up to 2.9 ppb at night. Additional analysis of the impact of livestock emissions diurnal variability in nested GEOS-Chem simulations over the U.S. is included in Appendix A.

To apply the dynamic emissions scheme globally, we implement a new global NH$_3$ anthropogenic emissions inventory Magnitude And Seasonality of AGricultural Emissions model (MASAGE_NH$_3$, Paulot et al. [2014]), which contains sector-specific emissions for different agriculture sources, such as livestock emissions (the standard GEOS-Chem NH$_3$ emissions do not clearly distinguish this sector). Figure 4.2 shows the global distribution of surface NH$_3$ concentrations from the GEOS-Chem static and dynamic cases in April, July, and October of 2008. The third column shows the difference between the dynamic and the static cases. In general, the dynamic case decreases the monthly NH$_3$ surface concentration throughout the world with significant changes in Southeast China and India in all three months, which can be up to 17.1 ppb in China in October and 12.1 ppb in India in April. There are also large decreases in the Eastern U.S. (up to 3.3 ppb) and southeastern of South America.

The modeled Representative Volume Mixing Ratio (RVMR) [Shephard et al., 2011] underestimates the observed RVMR from TES in the U.S. and most places of the globe [Shephard et al., 2011; Zhu et al., 2013]. In this study, we also compare the modeled RVMR from static and dynamic cases to the TES RVMR. We calculate modeled RVMR at the same time and locations of TES retrievals during 2006 through 2009. We average the RVMRs at the 2° × 2.5° grid resolution for each month (April, July, and October). The static RVMR underestimates the TES RVMR
throughout the globe in all three months except in India and Southeastern China in April. With
the new diurnal variability scheme (dynamic case), the modeled RVMR increases in many places
(e.g., Eastern China, Northern India, South America) and decreases in the Middle U.S. and North-
ern Europe. The differences between the dynamic and static RVMR are from -1.5 ppb to 1.6 ppb.
These changes generally reduce differences between modeled and observed RVMR, while the dif-
ferences are enhanced in a few locations, such as Northern India in April. However, the magnitude of
these changes are small compared to the differences (from -11.4 ppb to 3 ppb) between the static
RVMR and TES RVMR. We are able to detect more obvious changes between the static and dy-
namic cases when focusing on a livestock source region (California) and a hotter day, during which
the dynamic RVMR increases 3.4 ppb [Henze et al., in prep.].

High biases of surface nitrate aerosol concentrations in GEOS-Chem are found in the U.S.
[e.g., Heald et al., 2012; Walker et al., 2012]. Here we consider the impact of dynamic NH$_3$
livestock emissions on surface nitrate concentration in the U.S., as well as globally. Figure 4.3 pres-
tents the global distribution of surface nitrate concentration from the GEOS-Chem static and dynamic
cases in April, July, and October of 2008. The dynamic case decreases the nitrate concentration
significantly in Eastern China in all three months, which can be as large as 7 µg/m$^3$ in October.
There are also large decreases in the Eastern U.S. which can be up to 2.7 µg/m$^3$ in July. In October,
there are large decreases in the dynamic case in comparison to static case in Northern India (up
to 3.9 µg/m$^3$) and Europe (up to 2.4 µg/m$^3$ in Poland).

Investigating the impacts of dynamic NH$_3$ livestock emissions on nitrogen deposition is also of
interest. In Figure 4.4, we show the global distribution of total nitrogen deposition (wet deposition
of NH$_3$, ammonium, HNO$_3$ and nitrate, and dry deposition of NH$_3$, ammonium, NO$_2$, PAN, N$_2$O$_5$,
HNO$_3$ and nitrate) from GEOS-Chem static and dynamic cases in April, July, and October of
2008. The dynamic case decreases nitrogen deposition in most places in the world, yet increases it
in several locations. The largest decrease of nitrogen deposition occurs in Northern India in April
by up to 3.6 kg N/ha/month. The total amount of nitrogen deposition in India decreases by 8.6%
in April. Decreases in nitrogen deposition in the dynamic case occur in Southeastern China in all
Figure 4.2: Spatial distribution of GEOS-Chem simulated NH$_3$ concentration at surface level in static, dynamic cases and their differences. Monthly averages are shown for April, July and October of 2008.
Figure 4.3: Spatial distribution of GEOS-Chem simulated nitrate concentration at surface level in static, dynamic cases and their differences. Monthly averages are shown for April, July and October of 2008.
Figure 4.4: Spatial distribution of GEOS-Chem simulated total N deposition in static, dynamic cases and their differences. Monthly averages are shown for April, July and October of 2008.
three months, with the total amount of nitrogen deposition in China decreasing by 4.7% in April, 2.8% in July, 3.1% in October. The new diurnal variability scheme has more NH₃ from livestock emissions emitted in the daytime, when the boundary layer is thicker than nighttime. Typically, this lowers deposition largely at night. However, it may also be conducive to more export of NH₃ in the atmosphere during the day. Thus, slight increases of nitrogen in the dynamic cases occur downwind of regions with large NH₃ sources in the base cases, such as increases in southeastern Russia owing to enhanced NH₃ export from Eastern China.

### 4.6 Bi-directional exchange of NH₃

#### 4.6.1 Bi-directional flux calculation

The dry deposition scheme in the standard GEOS-Chem model is based on the resistance in series formulation of Wesely [1989], which only considers the unidirectional flux of NH₃ from the air to the surface. However, the air-surface exchange is known to actually be bi-directional. In this paper, we update the dry deposition of NH₃ to combine NH₃ dry deposition from the atmosphere and emission from vegetation. A simplified schematic of the updated air-surface exchange process of NH₃ is shown in Figure 4.5. More details of this bi-directional scheme can be found in Cooter et al. [2010] and Pleim et al. [2013]. The total air-surface exchange flux, $F_t$, is calculated as a
function of the gradient between the ambient NH$_3$ concentration in the first (surface) layer of the model and the canopy compensation point [Bash et al., 2013; Pleim et al., 2013],

$$F_t = \frac{C_c - C_a}{R_a + 0.5R_{inc}},$$

(4.4)

where $C_a$ is the ambient NH$_3$ concentration of the first atmospheric layer of the model, $C_c$ is the canopy compensation point (which is set at one half of the in-canopy resistance, since NH$_3$ can come from either air or soil to the canopy, thus, splitting $R_{inc}$ symmetrically is appropriate), $R_a$ is the aerodynamic resistance, and $R_{inc}$ is the in-canopy aerodynamic resistance. $C_a > C_c$ will result in deposition from air to surface, and $C_a < C_c$ will result in emission from surface to air. $C_c$ is calculated as [Bash et al., 2013],

$$C_c = \frac{C_a}{R_a + 0.5R_{inc}} + \frac{C_{st}}{R_b + R_{st}} + \frac{C_g}{0.5R_{inc} + R_{bg} + R_{soil}},$$

(4.5)

where $R_b$, $R_{bg}$, $R_{st}$, $R_{soil}$ and $R_w$ are the resistances at the quasi-laminar boundary layer of leaf surface, the quasi-laminar boundary layer of ground surface, the leaf stomatal, soil and cuticle respectively. $R_a$, $R_b$, $R_{bg}$, $R_{st}$ and $R_w$ are already defined and used in the standard GEOS-Chem deposition scheme. Here we define and calculate $R_{soil}$ and $R_{inc}$ following Pleim et al. [2013]. $C_{st}$ and $C_g$ are the NH$_3$ concentrations in the leaf stomata and soil pores respectively. They are calculated as functions of temperature and NH$_3$ emission potential ($\Gamma_{st,g}$, dimensionless) in the leaf stomata and soil [Nemitz et al., 2000].

$$\Gamma = \frac{[\text{NH}_4^+]}{[\text{H}^+]}.$$  

(4.6)

$\Gamma_{st}$ is calculated as a function of land cover type, and the values of different land cover types are based on Zhang et al. [2010]. $\Gamma_g$ is calculated as a function of soil pH and NH$_4^+$ concentration in the soil, $[\text{NH}_4^+]_{soil}$. Soil pH data is taken from ISRIC - World Soil Information with a 0.5° × 0.5° global resolution (http://www.isric.org/data/data-download). We model the $[\text{NH}_4^+]_{soil}$ as an ammonium pool in the soil, which is a function of fertilizer application rate, deposition, nitrification, soil moisture, and emission in bi-directional exchange. The calculation of $[\text{NH}_4^+]_{soil}$ is described in the next section.
To compare the deposition (downward) flux and emission (upward) flux of the bi-directional case to the base case, we define diagnostic variables for gross deposition flux $F_{dep}$ and emission flux $F_{emis}$ as follows [Bash et al., 2013; Jeong et al., 2013],

$$F_{dep} = \frac{C_c - C_a}{R_a + 0.5R_{inc}} \bigg|_{C_{at}=0,C_y=0},$$  

$$F_{emis} = \frac{C_c}{R_a + 0.5R_{inc}} \bigg|_{C_a=0},$$  

(4.7)

(4.8)

where $F_{dep}$ is calculated under the assumption that there is no NH$_3$ emission potential from the soil and canopy, and $F_{emis}$ is calculated under the assumption that there is no NH$_3$ in the atmosphere. Thus, $F_{dep} + F_{emis} = F_t$.

### 4.6.2 Soil ammonium pool

Here we introduce a NH$_4^+$ pool to track the NH$_3$ and NH$_4^+$ in the atmosphere and in the soil. The inputs to the ammonium pool in the soil are NH$_x$ (NH$_3$ and NH$_4^+$) deposition from the atmosphere, NH$_3$ emission from the soil, and N fertilizer application rate. The annual N fertilizer application rates are from Potter et al. [2010], which has chemical fertilizer (global total 70 Tg N yr$^{-1}$) with a 0.5$^\circ \times$ 0.5$^\circ$ resolution for the year 2000. We assume that all forms of N fertilizers will convert to NH$_4^+$ rapidly after fertilizer application. This dataset is also used to develop the global soil nitric oxide emissions in GEOS-Chem in Hudman et al. [2012]. We use the same treatment of annual total fertilization as Hudman et al. [2012] to derive daily fertilizer application rates by applying 75% of the annual total fertilization amount around the first day of the growing season (green-up day), distributed with a Guassian distribution one month after. The other 25% is evenly distributed over the remaining time before the end of the growing season (brown-down day). The determination of green-up and brown-down days is based on the growing season dates derived from the MODIS Land Cover Dynamics product (MCD 12Q2) using the MODIS enhanced vegetation index (EVI) [Hudman et al., 2012].

Using the fertilizer inputs described above, in addition to inputs from deposition and outputs
from emission, the time dependent soil \( \text{NH}_4^+ \) pool [mol L\(^{-1}\)] is calculated as

\[
[\text{NH}_4^+]_{\text{soil}} = \frac{[\text{NH}_x]_{\text{dep}}}{d_s \theta N_A} + \frac{[\text{N}]_{\text{fert}}}{d_s \theta M_N} - \frac{[NH_3]_{\text{bidiemit}}}{d_s \theta N_A},
\]

(4.9)

where \( [\text{NH}_x]_{\text{dep}} \) [molec cm\(^{-2}\)] is deposition from wet and dry deposition of \( \text{NH}_3 \) and \( \text{NH}_4^+ \), \( [\text{N}]_{\text{fert}} \) [N g m\(^{-2}\)] is the \( \text{NH}_4^+ \) from fertilizer, \( [NH_3]_{\text{bidiemit}} \) [molec cm\(^{-2}\)] is the gross \( \text{NH}_4^+ \) emitting from the soil due to bi-directional exchange, \( M_N \) is the molar mass of nitrogen, \( d_s \) is the depth of the soil layer, taken to be 0.02 m, \( \theta \) is the soil wetness [m\(^3\) m\(^{-3}\)], and \( N_A \) is Avogadro’s number. We then solve the mass balance equation for \( [\text{NH}_x]_{\text{dep}} \) and \( [\text{N}]_{\text{fert}} \),

\[
\frac{d[\text{NH}_x]_{\text{dep}}}{dt} = S_{\text{dep}} - \frac{[\text{NH}_x]_{\text{dep}}}{\tau} - L_{\text{dep}},
\]

(4.10)

\[
\frac{d[\text{N}]_{\text{fert}}}{dt} = S_{\text{fert}} - \frac{[\text{N}]_{\text{fert}}}{\tau},
\]

(4.11)

where \( \tau \) is the decay time owing to nitrification rate of \( \text{NH}_4^+ \) in soil. We assume \( \tau \) is 15 days, since almost all \( \text{NH}_4^+ \) will convert to \( \text{NO}_3^- \) within that timespan [Matson et al., 1998]. \( S_{\text{dep}} \) is the deposition rate, \( S_{\text{fert}} \) is the fertilizer application rate, and \( L_{\text{dep}} \) is the deposition loss rate. We use the same assumption as Hudman et al. [2012] that only 60% of this deposited \( \text{NH}_x \) will enter the soil, while the rest of the \( \text{NH}_x \) deposition will runoff into waterways. Here we do not consider the production of \( \text{NH}_4^+ \) from \( \text{NO}_3^- \) in the nitrogen cycle from mineralization nor immobilization. The time scale of these processes can be years, which is much larger than the time scale of the \( \text{NH}_4^+ \) simulations considered here; Cooter et al. [2010] also found these processes were not needed to accurately simulate \( \text{NH}_3 \) over managed lands on similar time scales.

### 4.6.3 Adjoint of bi-directional exchange

To investigate the sensitivity of modeled \( \text{NH}_3 \) concentrations to the parameters in the bi-directional exchange model, and to facilitate future inverse modeling, we develop the adjoint of our updated \( \text{NH}_3 \) flux scheme. Here we consider two key parameters, soil pH and fertilizer application rate, since their values are highly approximate.
The adjoint sensitivity is defined as

\[ \lambda_\sigma = \frac{\partial J(NH_3)}{\partial \sigma}, \]  

(4.12)

where \( J(NH_3) \) is the total mass of ammonia at surface level in each grid box during 1 week. The unit of \( J(NH_3) \) is kg/box. \( \sigma \) in this study is defined as the soil pH scaling factor \( (\sigma_{pH}) \) or fertilizer application rate scaling factor \( (\sigma_{fert\_rate}) \). \( \sigma_{pH} \) is defined as \( \frac{pH}{pH^0} \) and \( \sigma_{fert\_rate} \) is defined as \( \frac{fert\_rate}{fert\_rate^0} \). \( pH^0 \) and \( fert\_rate^0 \) are the initial estimate of soil pH from ISRIC and fertilizer application rates from Potter et al. [2010]. \( \lambda_\sigma \) is the sensitivity of \( J(NH_3) \) with respect to the bi-directional exchange model parameters \( \sigma \).

4.6.4 Validating the adjoint of bi-directional exchange

We validate the accuracy of the adjoint model by comparing the sensitivity of NH\(_3\) surface concentrations with respect to soil pH and fertilizer application rate calculated using the adjoint model with sensitivities calculated using the finite differences method. In order to make such comparisons efficiently throughout the model domain, horizontal transport is turned off for these tests [e.g., Henze et al., 2007]. Figure 4.6 shows the comparison of sensitivities calculated by adjoint and finite difference. The cost function is evaluated once at the end of a one week simulation. The slope of a linear regression and square of correlation coefficient, R\(^2\), are both close to unity, demonstrating the accuracy of adjoint of the bi-directional model.

4.7 Results and Discussion

For the U.S. region, we use nested horizontal resolution \((1/2 \degree \times 2/3 \degree)\) simulations with the standard set of GEOS-Chem emission inventories. For the global simulation, we introduce a new bottom up emission inventory for NH\(_3\) agriculture sources, MASAGE_NH3 [Paulot et al., 2014]. The full description of the differences between the GESO-Chem standard NH\(_3\) emission inventories and MASAGE_NH3 is in Paulot et al. [2014]. We perform global simulation at a horizontal resolution of \(2 \degree \times 2.5 \degree\). All simulations include the dynamic treatment of the diurnal variability of livestock
Figure 4.6: The adjoint sensitivity of NH$_3$ surface level concentration with respect to soil pH (left) and fertilizer application rate (right) compared to finite difference gradients. The cost function is evaluated once at the end of a one week simulation which excludes horizontal transport.
emissions described in section 4.5.

4.7.1 U.S.

We run the GEOS-Chem model for April, July, and October of 2008 with the updated diurnal variation of NH$_3$ livestock emissions and the bi-directional exchange mechanism. Figure 4.7 shows the NH$_3$ total gross emissions from GEOS-Chem with (BIDI) and without (BASE) the bi-directional air-surface exchange. The total gross emissions of BIDI case are the sum of primary emissions and upward fluxes from soil and vegetation. Bi-directional exchange generally increases gross emissions in most parts of the U.S. in July (up to 0.43 Gg/month) and decreases gross emissions throughout the U.S. in October (up to 0.29 Gg/month). Significant decreases occur in the Great Plains region in both April and October with a magnitude of up to 0.23 Gg/month in April and 0.29 Gg/month in October. Bi-directional exchange does not much alter the total modeled emissions in the U.S. in July (increase by 5.9%) and October (decrease by 13.9%), but does lead to a decrease of 23.3% in April. With the ammonium soil pool, the model can preserve ammonia/ammonium in the soil rather than emitting it directly after fertilizer application. This is the main reason that gross emissions decrease in the Great Plains in April and October. In July, there is not as much fertilizer applied as in April. However, the bi-directional exchange between the air and surface can induce NH$_3$ to be re-emitted from the ammonium soil pool which reserve ammonium from previous deposition and fertilizer application.

The spatial distributions of surface NH$_3$ concentrations in GEOS-Chem are shown in Figure 4.8. In general, bi-directional exchange decreases monthly NH$_3$ surface concentrations in April (up to 1.8 ppb) and October (up to 2.1 ppb), and increases it in July (up to 2.8 ppb) throughout the U.S. There are peak decreases in NH$_3$ surface concentrations in the Great Plains in both April and October and increases in California in July. These changes of surface NH$_3$ concentration are consistent with the pattern of changes to NH$_3$ emissions in Figure 4.7.

**Evaluation with NH$_3$** We evaluate the GEOS-Chem simulation with bi-directional ex-
Figure 4.7: Spatial distribution of ammonia total emissions from GEOS-Chem with (BIDI) and without (BASE) bi-directional exchange and their differences in April, July and October of 2008. The total emissions in the BIDI case are the sum of upward fluxes from soil and vegetation from the bi-directional exchange and emissions from all other sources except fertilizers.

Figure 4.8: Spatial distribution of ammonia concentration at surface level of GEOS-Chem with (BIDI) and without (BASE) bi-directional exchange and their differences in April, July and October of 2008.
change by comparing the model values to in situ observations from AMoN. Figure 4.9 shows the comparison of GEOS-Chem surface NH$_3$ concentrations in the BASE and BIDI cases with AMoN observations. Bi-directional exchange decreases the normalized mean bias (NMB) from -0.227 to -0.165 in July, and increases the NMB from -0.701 and -0.197 to -0.829 and 0.283 in April and October, respectively. The root mean square error (RMSE) decreases by 18.3% in July, and increases by 16.7% in April and 19.2% in October. R$^2$ values increase by 20.6% in July, and decrease by 37.6% in April and 49.1% in October. The slope slightly increases by 0.5% in July, and decreases by 53.5% and 37.5% in April and October, respectively. The changes in slopes can also be seen in Figure 4.8 as bi-directional exchange decreases the NH$_3$ monthly average concentration at AMoN sites in April and October while it increases the NH$_3$ monthly average concentrations in July. Modeled surface NH$_3$ concentrations are significantly lower than the AMoN observations in April and October by a factor of 2 - 5, which is not unreasonable given likely underestimates in primary emissions [Zhu et al., 2013; Nowak et al., 2012; Schiferl et al., 2014]. Such large underestimation is not corrected by applying the NH$_3$ bi-directional exchange to the model. Other improvements in the model besides bi-directional exchange, such as updating primary NH$_3$ emissions, are also required for better estimating NH$_3$ surface concentrations.

**Evaluation with aerosol nitrate** We also compare the simulated nitrate aerosol concentrations to the aerosol observations from IMPROVE. Figure 4.10 shows the simulated monthly average nitrate aerosol surface concentration from the GEOS-Chem BASE and BIDI cases in comparison to IMPROVE observations in 2008. GEOS-Chem overestimates nitrate in the BASE case in all three months. The overestimates in BASE cases can be 5 times larger in October. Bi-directional exchange generally decreases the nitrate concentrations in April, which makes the slope of the regression line decrease by 45.4%. However there are still large overestimates (~ a factor of 2 on average) in the Northeast U.S. and large underestimates (up to 1.7 µg m$^{-3}$) in South California in the BIDI case in April. Bi-directional exchange slightly increases (less than 0.5 µg m$^{-3}$) nitrate in July and decreases (less than 0.4 µg m$^{-3}$) nitrate in October, which does not significantly impact
Figure 4.9: Comparison of GEOS-Chem simulated NH$_3$ concentration at surface level in BASE and BIDI cases with AMoN observations in April, July, and October of 2008. $R^2$ is the square of the correlation coefficient. Solid lines are regressions. Gray dashed lines are 1:1.
the comparison of modeled nitrate with IMPROVE observations.

Overestimation of nitrate in GEOS-Chem is a long recognized problem [Park et al., 2004; Liao et al., 2007; Henze et al., 2009; Heald et al., 2012; Walker et al., 2012; Zhu et al., 2013]. Heald et al. [2012] recommend that reducing the nitric acid to 75% would bring the magnitude of nitrate aerosol concentration into agreement with the IMPROVE observations. In our study, based on the comparison of BASE modeled nitrate concentration and IMPROVE observation, we perform sensitivity studies by reducing the nitric acid to 50% in July and to 20% in October at each timestep in the GEOS-Chem model for both BASE and BIDI cases. Modeled nitrate concentrations reduce dramatically with this adjustment in July and October, but overestimates still exist in many places in the Eastern U.S. We also compare the modeled NH$_3$ surface concentrations in the sensitivity simulations with adjusted nitric acid concentrations to the AMoN observations, since reducing the nitric acid in the model may cause NH$_3$ to partition more to the gas phase, which could bring modeled NH$_3$ concentrations into better agreement with AMoN observations. However, no significant impacts are found in NH$_3$ concentrations at AMoN site locations with these nitric acid adjustments, consistent with earlier assessments that the model’s nitrate formation is NH$_3$ limited throughout much of the U.S. [Park et al., 2004]. Overall, overestimation of model nitrate by a factor of 3 to 5 appears to be a model deficiency beyond the issue of NH$_3$ bi-directional exchange.

Comparison to inverse modeling  Inverse modeling estimates of uni-directional NH$_3$ emissions using TES observations lead to overestimates of ammonia concentration in comparison to surface observations from AMoN in July [Zhu et al., 2013], and emissions estimates in July are much higher than other top-down or bottom up studies [Paulot et al., 2014]. It is thus of interest to evaluate whether bi-directional exchange of NH$_3$ would reduce this high bias. Although repeating the inverse modeling with TES NH$_3$ observations and bi-directional exchange is beyond the scope of this work, we can use the optimized emissions from Zhu et al. [2013] as the basis upon which bi-directional exchange is applied. Figure 4.11 shows the modeled NH$_3$ monthly average surface concentrations in comparison to the AMoN observations. The left column of Figure 4.11 is
Figure 4.10: Comparison of GEOS-Chem simulated nitrate aerosol concentration at surface level in BASE and BIDI cases with IMPROVE observations in April, July, and October of 2008. R is the correlation coefficient.
Figure 4.11: Left column: comparison of GEOS-Chem optimized NH$_3$ concentration at surface level from Zhu et al. [2013] with AMoN observations. Right column: comparison of GEOS-Chem simulated NH$_3$ concentration at surface level in BIDI case using optimized NH$_3$ emissions from Zhu et al. [2013] with AMoN observations. $R^2$ is the square of the correlation coefficient. Gray dashed lines are 1:1.
from the optimized NH\textsubscript{3} estimates from Zhu et al. [2013]. In the right column, the modeled NH\textsubscript{3} monthly average concentrations are from GEOS-Chem with NH\textsubscript{3} bi-directional exchange using the optimized emissions from Zhu et al. [2013]. The model with bi-directional exchange decreases the high bias in July: the NMB decreases by 80.4%; the RMSE decreases by 56.7%. The $R^2$ value increases by 43.3%. However, the model with bi-directional exchange now underestimates the NH\textsubscript{3} monthly average concentrations in April and October. The RMSE increases by 4.1% in April and 28.8% in October. The impacts of NH\textsubscript{3} concentration with respect to emissions in the model with bi-directional exchange are nonlinear. Using the optimized NH\textsubscript{3} emissions inventories from the TES NH\textsubscript{3} assimilation with the BASE model does not guarantee a better estimation of NH\textsubscript{3} surface concentrations with the BIDI model. Therefore, full coupling of inverse modeling with TES NH\textsubscript{3} observations and bi-directional exchange is necessary. Also, investigating the sensitivities of bi-directional model results to the NH\textsubscript{3} emissions, as well as other critical parameters, is important for improving the NH\textsubscript{3} concentration estimation.

### 4.7.2 Global modeling results

While bi-directional exchange of NH\textsubscript{3} has previously been implemented in regional models [e.g., Bash et al., 2013; Zhang et al., 2010; Wichink Kruit et al., 2012], with the GEOS-Chem model we have the chance to evaluate NH\textsubscript{3} bi-directional exchange on global scales for the first time. The global distribution of NH\textsubscript{3} gross emissions in both BASE and BIDI cases, as well as their differences, are shown in Figure 4.12. Generally, bi-directional exchange decreases NH\textsubscript{3} emissions in the Northern Hemisphere, and increases NH\textsubscript{3} gross emissions in the Southern Hemisphere in April and October. Total NH\textsubscript{3} emissions in the Northern Hemisphere decrease by 22.6% in April and 7.8% in October. In July, bi-directional exchange increases NH\textsubscript{3} emissions in most places (7.1% globally), except China and India. Significant decreases in NH\textsubscript{3} emissions in the BIDI case occur in Southeastern China and Northern India in all three months. The magnitudes of the decreases can be up to 18.4 Gg/month in China and 16.5 Gg/month in India in July. Total NH\textsubscript{3} emissions in China decrease by 43.6% in April, 31.4% in July, and 24.7% in October. Total NH\textsubscript{3} emissions
in India decrease by 28.8% in April, 22.8% in July, and 7.2% in October. There are also large decreases of total NH$_3$ emissions in the US, Mexico and Europe in April of up to 6.5 Gg/month.

The changes of NH$_3$ gross emissions between BASE and BIDI cases can be seen more directly from the comparison of fertilizers emissions in the BASE case with those in the BIDI case. In Figure 4.13, we show the global distribution of NH$_3$ fertilizer emissions in the BASE and BIDI cases. In BIDI case, the fertilizer emissions are the upward fluxes from soil and vegetation from bi-directional exchange. The third column is the NH$_3$ emissions from all other sources except fertilizers in April, July, and October of 2008. In the BASE case, fertilizers emissions have peak values in Eastern China and Middle East Asia and much smaller values elsewhere. Fertilizers emissions in the BIDI case increase in many places where there are no or near zero values in the BASE case. In the BIDI case, the fertilizer emissions distribution is much more homogeneous. As we described in Section 4.7.1, fertilizer emissions are lower in the BIDI case under cool spring and fall time conditions due to the temperature effects on NH$_3$ emissions and storage in the soil ammonium pool. The deposition and re-emission processes in bi-directional exchange model thus extend the effect of NH$_3$ emissions from fertilizers. There are obvious trends that fertilizer emissions in the Northern Hemisphere are larger than those in the Southern Hemisphere in spring and summer, and fertilizer emissions in the Southern Hemisphere are larger than those in the Northern Hemisphere in fall. The global amount of NH$_3$ fertilizer emissions is 27.8% of total emissions from all sources in the BASE case and 12.8% in the BIDI case in April.

Figure 4.14 shows the global distribution of NH$_3$ monthly surface concentrations in the BASE and BIDI cases and their differences in April, July and October. In general, bi-directional exchange increases NH$_3$ concentrations throughout the world in July by up to 3.9 ppb. It decreases NH$_3$ concentrations in the Northern Hemisphere (up to 27.6 ppb) and increases NH$_3$ concentrations in the Southern Hemisphere (up to 4.2 ppb) in April and October. Significant decreases of NH$_3$ concentrations occur in China in all three months with up to 20.6 ppb in April, 12.8 ppb in July, and 15.7 ppb in October. Paulot et al. [2014] indicated the MASAGE NH$_3$ emissions, which we use in this study, were higher than the bottom-up NH$_3$ emissions from Huang et al. [2012] in China in
Figure 4.12: Global distribution of ammonia gross emissions from GEOS-Chem with (BIDI) and without (BASE) bi-directional exchange and their differences in April, July and October of 2008. The total emissions in the BIDI case are the sum of upward fluxes from soil and vegetation from the bi-directional exchange and emissions from all other sources except fertilizers.
Figure 4.13: Global distribution of original ammonia fertilizer emissions in BASE case (BASE fertilizer), upward flux from soil and vegetation in BIDI case (BIDI fertilizer), and ammonia emissions from all other sources except fertilizers (All others) in April, July and October of 2008.
April and July, and similar to the emissions from Streets et al. [2003] in April, July, and October. Overestimation of NH$_3$ surface concentrations in GEOS-Chem in China are found in Wang et al. [2013] when using NH$_3$ emissions from Streets et al. [2003], leading to an overestimation of nitrate aerosol concentrations in China. Observations from IASI have discrepancies over China with NH$_3$ concentrations in GEOS-Chem [Kharol et al., 2013; Clarisse et al., 2009] that may in part be improved by the impacts of bi-directional exchange. However, observations from TES show NH$_3$ concentrations in GEOS-Chem (with NH$_3$ emissions from Streets et al. [2003]) are underestimated in many places of the globe including China [Shephard et al., 2011]. We must note that the lower NH$_3$ concentrations presented here are daily averages, while IASI and TES data are for a particular hour of the day. The changes in the emissions profile may reduce the model underestimate against the satellite observations while decreasing the mean NH$_3$ concentrations.

4.7.3 Wet deposition evaluation (Global and U.S.)

We compare the model NH$_4^+$ wet deposition to in situ observations in several regions of the world using NTN for the continental U.S., CAPMoN for Canada, EMEP for Europe, and EANET for East Asia, see Figure 4.15. For the model NH$_4^+$ wet deposition, we also include the model NH$_3$ wet deposition since NH$_4^+$ wet deposition from in situ observations includes precipitated NH$_3$. Since there are biases in the modeled precipitation, we scale the model wet deposition by multiplying the modeled deposition by the ratio of the observed to modeled precipitation, $Flux_{model} \times \left(\frac{P_{obs}}{P_{model}}\right)^{0.6}$, following the correction method in Paulot et al. [2014]. We only include observations that have $0.25 < \frac{P_{obs}}{P_{sim}} < 4$ to limit the effect of this correction [Paulot et al., 2014], and we also exclude observations which are beyond three times the standard deviation of observed NH$_4^+$ wet deposition to avoid outliers.

In general, the GEOS-Chem model underestimates NH$_4^+$ wet deposition throughout the world in the BASE case. Large increases in NH$_4^+$ wet deposition in the BIDI cases are found in the U.S., Canada, and Europe in July (up to 6.31 kg/ha/yr). The slopes of the regression line when compared to observations increase by 37.9% in US, 54.9% in Canada, and 17.7% in Europe in the BIDI cases.
Figure 4.14: Global distribution of ammonia concentration at surface level of GEOS-Chem with (BIDI) and without (BASE) bi-directional exchange and their differences in April, July and October of 2008.

Figure 4.15: Comparisons of GEOS-Chem modeled NH$_4^+$ wet deposition in BASE (blue) and BIDI (red) cases with in situ observations in U.S. (1st column), Canada (2nd column), Europe (3rd column), and East Asia (4th column) in April (1st row), July (2nd row), and October (3rd row) of 2008. The y-axis represent the model values, and the x-axis represent observations from NTN (for US), CAPMoN (for Canada), EMEP (for Europe), EANET (for East Asia). $R^2$ is the square of the correlation coefficient.
in July, all becoming closer to unity. However, the bi-directional exchange increases the RMSE by 64.3% in the U.S., 37.2% in Canada, and 36.0% in Europe.

Bi-directional exchange does not impact the $\text{NH}_4^+$ wet deposition much in April and October. It decreases $\text{NH}_4^+$ wet deposition slightly (up to 3.77 kg/ha/yr in Europe) at most of the observation locations in the U.S., Canada, and Europe in April. The slopes decrease by 14.3% in the U.S., 6.8% in Canada, and 12.3% in Europe. Bi-directional exchange decreases the NMB by 46.4% in the U.S., 37.6% in Europe in April, but increases the NMB by 28.3% in Canada, and 11.6% in East Asia. In October, bi-directional exchange increases $\text{NH}_4^+$ wet deposition slightly at most of the observation locations (up to 3.85 kg/ha/yr). The changes in RMSE between BASE and BIDI cases are small, less than 10%.

The overall differences of $\text{NH}_4^+$ wet deposition between the BASE and BIDI cases are generally small (from -4.95 kg/ha/yr to 6.31 kg/ha/yr), even when the differences in NH$_3$ emissions are substantial. For example, total NH$_3$ emissions decrease by 43.6% in China in April with bi-directional exchange, but changes in $\text{NH}_4^+$ wet deposition are not very large (from -4.95 kg/ha/yr to 2.52 kg/ha/yr). While implementing NH$_3$ bi-directional exchange leads to improvements in some regions and seasons, it does not uniformly reduce error in model estimation of $\text{NH}_4^+$ wet deposition.

4.7.4 Adjoint sensitivity analysis

**Global adjoint sensitivities** In section 4.6.3, we demonstrated the accuracy of the sensitivities calculated using the adjoint of the GEOS-Chem bi-directional model. In this section, we present the adjoint sensitivities of NH$_3$ surface concentrations with respect to the important parameters in the bi-directional model. Figure 4.16 shows the adjoint sensitivities of NH$_3$ surface concentration with respect to the scaling factors for the soil pH (left) and for the fertilizer application rate (right) in April, July, and October, 2008. The sensitivities with respect to both parameters are always positive throughout the globe. Sensitivities of NH$_3$ to fertilizer application rate are positive as excess fertilizer application will increase the NH$_3$ soil emission potential. Sensi-
tivities of NH$_3$ to soil pH are also positive as low H$^+$ concentrations in soil (high soil pH) increases dissociation of NH$_4^+$ to NH$_3$, thereby increasing the potential for volatilization of NH$_3$.

The relationship between NH$_3$ concentration and soil pH is stronger during the growing season since more ammonium is in the soil pool. Slight changes in pH may have large impacts on the amount of NH$_3$ emitted from soil and further induce large differences in NH$_3$ surface concentrations. As we can see in the left column of Figure 4.16, the sensitivities of NH$_3$ surface concentrations with respect to soil pH scaling factors are larger in the Northern Hemisphere than those in the Southern Hemisphere in April and July, and less in the Northern Hemisphere than those in the Southern Hemisphere in October, since the growing seasons are in April in the Northern Hemisphere and in October in the Southern Hemisphere. Large sensitivities in July in the Northern Hemisphere are due to ammonium in the soil pool accumulated from CAFO emissions via deposition. However, some caution is warranted in interpreting the seasonality of these sensitivities, as our model does not include any seasonal variations in soil pH. Seasonal variability of soil pH is driven by fertilizer rate, timing of fertilizer application, root and bacterial activity, soil moisture, organic matter, and salt levels [Murdock and Call, 2006]. Soil pH is observed to be highest at or near mid-winter and lowest at late summer [Slattery and Ronnfeldt, 1992]. Variation of soil pH can be more than one unit from spring to fall [Angima, 2010], thus the uncertainty in the constant annual soil pH used here could be about 20% owing to neglecting seasonality.

The relationship between NH$_3$ concentration and fertilizer application rate is also seasonally dependent. The seasonal trends of sensitivities of NH$_3$ to fertilizer application rate are similar to sensitivities of NH$_3$ to soil pH. Larger sensitivities appear in places with lower fertilizer application rates than those with plenty of fertilizer. For example, the largest fertilizer application rates appear in Southeast China, Northwest Europe and Northern India in April, and sensitivities are nearly zero in each of these locations. That the magnitude of the fertilizer application rates itself is an important factor in determining the sensitivities of NH$_3$ concentration to the fertilizer application rate is indicative of the nonlinear relationship introduced by treatment of bi-directional exchange.

Through investigating the sensitivities of NH$_3$ surface concentration to the soil pH and the
Figure 4.16: The adjoint sensitivities of NH$_3$ surface level concentration with respect to soil pH scaling factor (left) and fertilizer application rate scaling factor (right) in April, July, and October of 2008. Note that sensitivities in the left and right columns have different scales.
fertilizer application rate, we know that NH$_3$ surface concentrations are very sensitive to these parameters in many places of globe. We also find that NH$_3$ surface concentrations are more sensitive to soil pH than fertilizer application rate in general. In addition to the adjoint sensitivity analysis of NH$_3$ concentrations to the soil pH and the fertilizer application rate, it is also interesting to know the ranking of sensitivities of NH$_3$ concentrations with respect to other parameters, such as NH$_3$ concentrations at compensation points ($C_c$, $C_{st}$, $C_g$), NH$_3$ emission potentials ($\Gamma_g$, $\Gamma_{st}$), and resistances ($R_a$, $R_{inc}$, $R_{soil}$, $R_g$, $R_{st}$, $R_{bg}$, $R_w$). Knowledge of the sensitivity of NH$_3$ concentrations with respect to these parameters may help improve the model estimation of the spatial and temporal distributions as well as the magnitudes of NH$_3$ concentrations.

**Comparison to in situ NH$_3$ with adjusted BIDI parameters** Based on the adjoint sensitivity analysis we have shown above and forward sensitivity analysis for all the parameters mentioned above (results not shown), we know that soil pH is one of the most critical parameters in the GEOS-Chem bi-directional exchange model. It is interesting to explore to what extent biases in the modeled NH$_3$ concentrations may be explained by uncertainties in the parameters of the bi-directional model, rather than e.g., revising livestock NH$_3$ emissions. To test this, we increase the soil pH value by a factor of 1.1, since uncertainties of seasonal soil pH are about 20%. As expected, the NH$_3$ surface concentrations generally increase over the globe (e.g., up to 3.4 ppb in April). Large increases occur in places with large sensitivities to soil pH (Figure 4.16, upper right). NH$_3$ concentrations are underestimated in the model in comparison to the AMoN observations in the U.S. They are also underestimated in many parts of globe in comparison to TES observations [Shephard et al., 2011]. With this adjustment to soil pH, the discrepancy between TES observations and the model in upper levels of the boundary layer may potentially be reduced in regions where GEOS-Chem NH$_3$ is underestimated before the growing seasons and overestimated after the growing seasons. Slight increases in NH$_3$ surface concentrations are found throughout the U.S. as NH$_3$ is not very sensitive to soil pH in the U.S. (see Figure 4.16). Thus, this adjustment does not improve the comparison to AMoN observations in the U.S.
Figure 4.17: Comparison of NH$_3$ surface concentrations from GEOS-Chem with bi-directional exchange to AMoN observations. The livestock emissions in the model are increased by a factor of 6 in April, and 3 in October.
In this study, we did not consider the adjustment of soil pH in agricultural areas by the farmers who limit the soil pH in a certain range to improve crop yield [Haynes and Naidu, 1998]. However, no significant changes in the modeled surface NH$_3$ concentrations occur with bi-directional exchange when we limit the soil pH in the agricultural areas between 5.5 and 6.5 (generally less than 1 ppb over the globe, up to 3.4 ppb in India), since sensitivities are not very strong in the agricultural areas (see left column of Figure 4.16).

Small differences between bi-directional and unidirectional fluxes in the U.S. are also indicated in Dennis et al. [2013], wherein sensitivity tests were performed varying the soil emission potential ($\Gamma_g$, a parameter which includes both soil pH and fertilizer application rate) in CMAQ. It was found that the impact on total N deposition at continental scales was generally small ($\leq$ 5%), with very few ($\leq$ 10%) grid cells having differences up to 20%.

From Zhu et al. [2013], we know that the underestimation of NH$_3$ emissions in the unidirectional model can be as much as a factor of 9 in the U.S. We also notice that NH$_3$ may not change much when fertilizer emissions increase a lot in regions such as Midwest U.S. and Northern Australia (see Figure 4.13 and Figure 4.14). Thus, low emissions from other sources, such as livestock, may be a big part of the reason for underestimating NH$_3$ concentrations in the bi-directional exchange model. To better understand this, we also test increasing NH$_3$ livestock emissions by a factor of 8 in April and 3 in October as NH$_3$ concentrations are generally underestimated by around 8 and 3 times (Figure 4.9) compare to AMoN observations in April and October, respectively. These adjustments bring the NH$_3$ concentrations into a much better agreement with the magnitude of AMoN observations, see Figure 4.17. However, uniformly increasing the livestock emissions does not well represent the NH$_3$ spatial distribution with the AMoN observations (correlations of model and observation are very low). Overall, treatment of bi-directional exchange can improve our understanding of NH$_3$ emissions from fertilizers, but this alone may not improve estimation of NH$_3$ concentrations, NH$_4^+$ wet depositions, and nitrate aerosol concentrations. Additional work including bi-directional exchange in NH$_3$ inverse modeling is needed, as large underestimates in NH$_3$ primary sources exist in the model and simply applying the scheme to optimized emissions from
inverse modeling can not well capture the spatial variability of NH$_3$ concentrations that are the responses of both bi-directional exchange processes and emissions.

**Spot sensitivity analysis**  Here we investigate to what extent bi-directional exchange increases the NH$_3$ lifetime, which is a critical issue for controlling nitrogen deposition and PM$_{2.5}$ formation. Through the adjoint method, we are able to assess source contributions to model estimates in particular response regions [e.g., Lee et al., 2014]. In Figure 4.18, we show the adjoint sensitivity of NH$_3$ surface concentration at a single location [88°W, 40°N] with respect to the NH$_3$ anthropogenic emissions at all grid cells in April, 2008. In the BASE case (left panel), the NH$_3$ surface concentration is most sensitive to the emissions from the same grid cell, and is less sensitive to the emissions from surrounding grid cells. With the bi-directional exchange (right panel), the NH$_3$ concentration is sensitive to the emissions from a much wider range, which extends all the way to Canada. Some of the sensitivities are very strong even though they are a long distance away from the location of the NH$_3$ concentration under consideration. The deposition and re-emission processes in the bi-directional exchange extends the spatial range of influence of NH$_3$ emissions and, in effect, the NH$_3$ lifetime. Thus, modeled NH$_3$ concentrations in Illinois can be impacted by the emissions from Kansas or even from Canada.
4.8 Conclusions

In this study, we have considered a more detailed, process-level treatment of NH$_3$ sources in a global chemical transport model (GEOS-Chem) and evaluated the model behavior in terms of biases in estimated NH$_3$, nitrate, and NH$_4^+$ wet deposition, and the factors driving these processes in the model. First, we update the diurnal variability of NH$_3$ livestock emissions. In general, by implementing this diurnal variability scheme, the global NH$_3$ concentrations, nitrate aerosol concentrations, and nitrogen deposition all decrease. The largest decreases always occur in Southeastern China and Northern India. More NH$_3$ from livestock emitted in the daytime largely decreases the NH$_3$ surface concentrations in the night and increases concentrations during the day, which is more conducive to export of NH$_3$.

We have also developed bi-directional exchange of NH$_3$ and its adjoint in the GEOS-Chem model. Bi-directional exchange generally increases NH$_3$ gross emissions in most parts of the U.S. and most places around the globe in July, except China and India. These are mainly due to the NH$_3$ re-emissions from the ammonium soil pool that accumulates ammonium from previous months. Bi-directional exchange generally decreases NH$_3$ gross emissions in the U.S. in April and October. On a global scale, bi-directional exchange decreases NH$_3$ gross emissions in the Northern Hemisphere in April and October, and increases NH$_3$ gross emissions in the Southern Hemisphere. During the growing seasons, the ammonium soil pool preserves ammonia/ammonium in the soil rather than emitting it directly after fertilizer application.

Bi-directional exchange increases monthly NH$_3$ surface concentrations throughout the world in July, which improves comparison to the AMoN observations in the U.S. It decreases NH$_3$ surface concentrations in the Northern Hemisphere and increases NH$_3$ concentrations in the Southern Hemisphere in April and October. Bi-directional exchange does not have a large impact on model biases in nitrate aerosol, which are likely owing to overestimated nitric acid concentration [Heald et al., 2012]. However, with the deposition and re-emission of NH$_3$ inherent in bi-directional exchange, NH$_3$ can be impacted by sources from a much greater distance, which is a critical issue
when considering strategies for controlling nitrogen deposition and PM$_{2.5}$ formation.

Bi-directional exchange largely increases NH$_4^+$ wet deposition in the U.S., Canada, and Europe in July, but slightly decreases NH$_4^+$ wet deposition in April and has little impact in October. The overall differences of NH$_4^+$ wet deposition between the BASE and BIDI cases are generally small, even when the differences in NH$_3$ fertilizer emissions are large. While observations of wet deposition have been used to constrain NH$_3$ sources in previous works [Gilliland et al., 2003, 2006; Zhang et al., 2012; Paulot et al., 2014], this dataset does not appear sufficient to provide constraints on model treatment of bi-directional exchange.

Using the adjoint of bi-directional exchange, we investigate the spatial and seasonal dependency of NH$_3$ surface concentrations in the GEOS-Chem model on the soil pH and fertilizer application rate, which are themselves uncertain. Soil pH is known to be seasonally variable. Updating the soil pH with seasonal variability would impact the results of bi-directional exchange across wide regions of globe. However, updating the soil pH with seasonal variability does not seem sufficient to improve comparison with in situ observations in the U.S., as primary sources are likely underestimated by a factor of 3 or more. Further, uniformly increasing the emissions from primary sources degrades the spatial variability of simulated NH$_3$.

Overall, bi-directional exchange largely extends the lifetime of NH$_3$ in the atmosphere via deposition and re-emission processes. This model provides a better fundamental description of NH$_3$ emissions from fertilizers. However, implementing bi-directional exchange does not uniformly improve estimation of NH$_3$ concentrations, NH$_4^+$ wet deposition, and nitrate aerosol concentrations. Domain-wide adjustments to soil pH or livestock emissions do not improve the model comparison to the full suite of measurements from different platforms, locations and seasons considered here. Thus, incorporating bi-directional exchange in an inverse model is required in future work to correct the low biases in NH$_3$ primary sources without over adjusting these sources to account for model error from neglecting bi-directional exchange processes.
Chapter 5

Global distributions and correlations of ammonia and carbon monoxide in model simulations and satellite observations

5.1 Introduction

Ammonia (NH$_3$) is important as it contributes to many environment issues such as soil acidification and water eutrophication. It also harms human health as a component of fine particulate matter (PM$_{2.5}$) [e.g., Crouse et al., 2012]. Carbon monoxide (CO) is also an important species that impacts the environment both directly and indirectly [Raub et al., 2000; White et al., 1989]. CO can be oxidized to form carbon dioxide (CO$_2$), which is an important greenhouse gas. CO is also a precursor of ozone under high NO$_x$ conditions. The lifetime of CO is weeks to months; it thus can have intercontinental-scale impacts through long-range transport [Liang et al., 2004; Yashiro et al., 2009]. In contrast, NH$_3$ has a short lifetime (hours to days). However, NH$_3$ can react with nitric acid and sulfuric acid to form ammonium aerosols which itself can transport longer distances (100 ∼ 1000 km). CO emissions are mainly from incomplete combustion of various fuels (e.g., wood, coal, oil), while NH$_3$ emissions are primarily from agriculture activities (e.g., animal waste, fertilizer application).

As CO and NH$_3$ both play an important role in atmospheric chemistry and climate change, many studies have investigated sources and distributions of CO and NH$_3$ with models and in-situ observations in different regions [e.g., Hooghiemstra et al., 2011; Skjøth et al., 2011]. However, there are large uncertainties in both CO and NH$_3$ bottom-up emission inventories [Zhao et al.,

\footnote{The results of this Chapter will be published in Luo et al. [submitted].}
Satellite observations of CO [e.g., Edwards et al.; Luo et al., 2007] and NH$_3$ [Clarisse et al., 2009; Shephard et al., 2011; Van Damme et al., 2014] are valuable for gaining a better knowledge of the distributions of each. The Tropospheric Emission Spectrometer (TES) instrument aboard the Aura satellite is the first satellite instrument to provide measurements of multiple gas-phase species (e.g., CO, NH$_3$, ozone, methane) simultaneously in the lower troposphere. High spectral resolution (0.06 cm$^{-1}$), stability [Connor et al., 2011], and low detection limit ($\sim$1 ppbv) [Shephard et al., 2011] allow TES to be able to measure NH$_3$, which is primarily located near the surface. TES is mainly sensitive to NH$_3$ in the range 700 - 900 hPa with the degree of freedom (DOF) for signal typically less than one [Shephard et al., 2011]. TES NH$_3$ retrievals have been evaluated in Pinder et al. [2011], wherein the spatial and seasonal variability of TES NH$_3$ retrievals were shown to be well correlated with in-situ observations in North Carolina. TES is also sensitive to CO across the lower-mid troposphere. The DOF of TES CO retrievals is 0.5 to 1.5 in the tropics and mid-latitudes [Luo et al., 2007]. TES CO has been validated through aircraft measurements and observations from Measurements of Pollution in the Troposphere (MOPITT) satellite [Luo et al., 2007; Lopez et al., 2008; Ho et al., 2009].

Investigating the correlation between CO and NH$_3$ is very helpful for understanding NH$_3$ emissions with better known CO emissions in biomass burning regions. Similar methods have been used to constrain CO$_2$ emissions using observed CO$_2$:CO correlations from aircraft campaigns [Suntharalingam et al., 2004]. However, as of yet the correlations between CO and NH$_3$ have not been exploited. In this study, we present the global distribution of CO and NH$_3$ from both TES observations and GEOS-Chem simulations of 2007 (Section 5.4.1, Section 5.4.2). We then investigate the NH$_3$:CO correlations in both GEOS-Chem and TES (Section 5.4.3, Section 5.4.4). Finally, we present our conclusions in Section 5.5.
5.2 TES data and the GEOS-Chem Model

5.2.1 TES Data

The TES CO and NH$_3$ retrievals used in this study are from the version V005 data products (http://avdc.gsfc.nasa.gov/index.php?site=635564035&id=10), which includes both Global Survey (consisting of 16 orbits every other day) and Special Observation (carried out on the Global Survey “off” days) modes. We use data from the entire year of 2007 and group them into four seasons: winter (Dec., Jan., Feb.), spring (Mar., Apr., May), summer (Jun., Jul., Aug.), fall (Sep., Oct., Nov.).

5.2.2 GEOS-Chem simulations

GEOS-Chem is a 3D global chemical transport model driven by assimilated meteorology from the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and Assimilation Office (GMAO). The simulations used in this study are from 2007, and they are based on GEOS-Chem version v8-02-01 with 2° × 2.5° horizontal resolution. The global anthropogenic sources and natural sources of NH$_3$ are based on the 1990 GEIA inventory [Bouwman et al., 1997]. The seasonality of emissions over the U.S. is updated by Park et al. [2004]. The emission inventory used in Canada is from the Criteria Air Contaminants (CAC) [van Donkelaar et al., 2008]. The inventory of Streets et al. [2006] is used for Asia. The Co-operative Program for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) inventory is used for Europe. Biofuel emissions of NH$_3$ are from Yevich and Logan [2003]. The global CO anthropogenic emissions are based on the Emissions Database for Global Atmospheric Research (EDGAR) inventory [Olivier and Berdowski, 2001], updated by the following regional emission inventories: The US Environmental Protection Agency National Emission Inventory for 2005 in North America, the CAC inventory for Canada (http://www.ec.gc.ca/pdb/cac/cac_home_e.cfm), the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study Emissions Inventory for Mexico [Kuhns et al., 2003], and the EMEP inventory for Europe [Vestreng and Klein, 2002].
The monthly biomass burning emissions of CO and NH$_3$ are from the GFED2 inventory \cite{van_der_Werf_2006}. The daily average profiles of NH$_3$ and CO are simulated both with and without biomass burning emissions.

### 5.3 Comparison methodology

To investigate the spatial distribution of NH$_3$ and CO and to avoid profile-to-profile comparisons, we use the Representative Volume Mixing Ratio (RVMR) of NH$_3$ and CO to generate spatial plots. The NH$_3$ RVMR is developed and fully described in \cite{Shephard_2011} and has been used in \cite{Zhu_2013} for 2D comparisons of TES observations and GEOS-Chem model simulations. The RVMR is a TES sensitivity weighted boundary layer averaged value with the influence of the a priori reduced as much as possible. It is calculated by applying the TES observational operator \cite{Shephard_2011} and RVMR transformation matrix. Since TES is sensitive to CO at a wide range of vertical levels, usually including the level at which TES is most sensitive to NH$_3$, we map the CO profiles to the corresponding pressure levels of NH$_3$ profiles and apply the same RVMR weighting matrix of corresponding NH$_3$ RVMR to obtain CO RVMR. This mapping approach is also used in \cite{Wells_2013} for comparison of CHOOH and CO.

### 5.4 Results

#### 5.4.1 Global distribution of CO from TES and GEOS-Chem

We show the global distribution of CO RVMR from both TES observations in Figure 5.1 and GEOS-Chem simulations in Figure 5.2. In general, the magnitude of CO RVMR from GEOS-Chem is less than that from TES, which may be due to underestimates of CO emissions in GEOS-Chem or vertical transport errors in the model, which estimates less CO in the upper troposphere than is observed by TES \cite[e.g.,][]{Kopacz_2010, Jiang_2013}. However, the seasonalities of CO RVMR from TES and GEOS-Chem are similar: CO RVMR is higher in the Northern Hemisphere than in the Southern Hemisphere in DJF and MAM (first row of Figure 5.1 and Figure 5.2); CO
Figure 5.1: Global averages of TES CO RVMR for four seasons in 2007. Data are averaged over 2° latitude by 4° longitude bins.
Figure 5.2: Global averages of GEOS-Chem CO RVMR for four seasons in 2007. Data are averaged over 2° latitude by 4° longitude bins.
RVMR is higher in the Southern Hemisphere in JJA and SON (second row of Figure 5.1 and Figure 5.2). There are large biomass burning sources in winter and spring which cause more CO emissions. The long lifetime of CO in cold seasons (weeks - months) also makes CO accumulate in the atmosphere and leads to the high CO RVMR during winter and spring. High CO RVMR in Southeastern China and India persists in all seasons due to heavy CO emissions from industry, traffic, and agricultural activities associated with large population densities [Beusen et al., 2008; Meng et al., 2011]. Observations from MODIS satellite also indicate there are fire events every year over Southeastern Asia in spring [Justice et al., 2002], as well as in Central Africa and South America.

5.4.2 Global distribution of NH$_3$ from TES and GEOS-Chem

Figure 5.3 and Figure 5.4 show the spatial distribution of NH$_3$ RVMR from TES observations and GEOS-Chem simulations in 2007. The NH$_3$ RVMR from GEOS-Chem is generally lower than TES NH$_3$ RVMR, which is consistent with previous studies [Shephard et al., 2011; Zhu et al., 2013]. The NH$_3$ RVMR shows larger spatial variability in TES observations than in GEOS-Chem simulations. The underestimates in GEOS-Chem are due to the low NH$_3$ emissions in GEOS-Chem, which can be 9 times lower than the observations in the U.S. [Zhu et al., 2013]. Also, the sampling bias from the spatial variability of NH$_3$ within the $2^\circ \times 4^\circ$ grid cells may contribute to these underestimates. Another reason for these underestimates may be differences in the NH$_3$ vertical distribution between the model and observations, with model values low at the levels at which TES is sensitive to NH$_3$. TES NH$_3$ RVMR shows spatial variabilities in all seasons of 2007. Peak values persist in Northern India in all seasons due to intense year-round agriculture activities. The “hot” spots in South America in spring (SON), North Central Africa in winter (DJF) are due to the biomass burning sources and fires. Other localized hot spots are due to the sparse and localized NH$_3$ sources.
Figure 5.3: Global averages of TES NH$_3$ RVMR for four seasons in 2007. Data are averaged over 2° latitude by 4° longitude bins.
Figure 5.4: Global averages of GEOS-Chem NH$_3$ RVMR for four seasons in 2007. Data are averaged over 2° latitude by 4° longitude bins.
### 5.4.3 \textbf{NH₃:CO correlations in GEOS-Chem}

In order to investigate NH₃:CO correlations more efficiently, we select six regions of the globe where both NH₃ and CO have high RVMRs: Mid-US, South America, North-Central Africa, South-Central Africa, South-Central Asia, and North-Central China (Figure 5.5). These regions include biomass burning dominated areas such as NC Africa, SC Africa, and S America, and areas with combined sources from agriculture and industrials activities (SC Asia, NC China, and Mid-US).

Strong correlations between CO and NH₃ are observed during a fire event in Duke Forest, North Carolina, during June 8 - 18, 2008. The time series comparison of NH₃ and CO concentrations from in-situ near-surface measurements is presented in Luo et al. [submitted]. NH₃ and CO have a very strong correlation under the fire events condition. Here we want to investigate the impacts of biomass burning emissions on the NH₃:CO correlations globally. Figure 5.6 shows the differences of CO RVMR from GEOS-Chem simulations with all emissions sources and from those without biomass burning sources in 2007. We select three regions to investigate NH₃:CO correlations in the model based on the “hot” areas in Figure 5.6 and their corresponding seasons: North-Central Africa (DJF), South-Central Africa (JJA), and South America (SON). The scatter plots of NH₃:CO correlations are shown in Figure 5.7. In these biomass burning dominated regions, NH₃ and CO show very strong correlations; the correlation coefficient, $r$, is from 0.65 to 0.8. The ratios of NH₃:CO are all equal to 0.01 in these three cases.

As expected, NH₃:CO correlations are high in the biomass burning dominated regions and seasons as biomass burning emissions of NH₃ and CO are well correlated in the GFED inventory that drives the model simulations. However, it is interesting to investigate NH₃:CO correlations in regions and seasons with a large amount of emissions other than biomass burning sources. With this motivation, we select a region in South-Central Asia, which has a large amount of emissions from agricultural and industrial sources. We compare the NH₃ RVMR with CO RVMR from the GEOS-Chem model with no biomass burning source in South-Central Asia during four seasons (Figure 5.8). The NH₃:CO ratios range from 0.02 to 0.08. The correlations are weaker (0.35 - 0.6)
Figure 5.5: Data from the six regions shown in the boxes are selected to examine the correlations between NH$_3$ and CO from TES and GEOS-Chem.
Figure 5.6: Similar figures as Figure 5.2, but for the differences of CO RVMR in GEOS-Chem between the simulations with all emissions sources (Figure 5.2) and simulations without biomass burning sources.

Figure 5.7: NH$_3$:CO RVMR correlations in South America of SON, 2007, South-Central Africa of JJA, 2007, and North-Central Africa of DJF, 2007. The RVMR values of NH$_3$ and CO are the differences of RVMR from GEOS-Chem with all emissions sources and without biomass burning source.
Figure 5.8: NH$_3$:CO RVMR correlations in South-Central Asia for four seasons of 2007. The RVMR values of NH$_3$ and CO are from GEOS-Chem without biomass burning.
than those shown in Figure 5.7.

5.4.4 NH$_3$:CO correlations in TES observations

In this section, we investigate the NH$_3$:CO correlations from TES observations and compare them to those in GEOS-Chem described in the previous section. We first consider NH$_3$:CO correlations from TES and GEOS-Chem in the regions and seasons dominated by biomass burning, and compare them to those with little biomass burning. Thus, we select South America in spring (SON) and fall (MAM), and North-Central Africa in winter (DJF) and summer (JJA). In the biomass burning dominated regions and seasons (first column of Figure 5.9), NH$_3$ RVMR and CO RVMR show strong correlations with $r$ values from 0.52 to 0.64 in TES observations and from 0.73 to 0.74 in GEOS-Chem simulations. There are frequent fire events in South America in spring (SON) which enhance emissions of both NH$_3$ and CO. The NH$_3$:CO ratios in TES and GEOS-Chem are similar. However, the NH$_3$:CO correlations in the regions and seasons with little biomass burning emissions are not detectable in both TES observations and GEOS-Chem simulations (second column of Figure 5.9). CO RVMR is low in South America in fall (MAM) as no obvious fire event occurred in this region during fall of 2007, while the moderate NH$_3$ RVMR is due to agricultural activities. There is little biomass burning emissions in North-Central Africa in summer (JJA), which indicates low RVMR values for both NH$_3$ and CO. Although RVMR values from TES observations are higher than those from GEOS-Chem for both NH$_3$ and CO, the NH$_3$:CO correlations are still very weak.

Some of the regions have strong emissions but more complicated emission sources, such as South-Central Asia and North-Central China. It is also interesting to investigate the NH$_3$:CO correlations in these regions. Thus, we select South-Central Asia as an example, since the emissions in this region are strong and come from different types of sources, such as agriculture, industry, and biomass burning. The NH$_3$:CO RVMR correlations from both TES and GEOS-Chem in South-Central Asia for four seasons of 2007 are shown in Figure 5.10. NH$_3$:CO is well correlated in winter (DJF) with $r = 0.61$ in both TES and GEOS-Chem, which is due to the strong biomass
Figure 5.9: $\text{NH}_3$:CO RVMR correlations from TES (red) and GEOS-Chem (blue) in South America in spring (SON) and fall (MAM) of 2007 (first column), and North-Central Africa in winter (DJF) and summer (JJA) (second column) of 2007.
Figure 5.10: NH$_3$:CO RVMR correlations from TES (red) and GEOS-Chem (blue) in South-Central Asia for four seasons of 2007.
burning emissions. In summer, CO RVMR values are smaller than other seasons, which is due to the reaction with enhanced OH in the atmosphere. Meanwhile, the large NH$_3$ RVMR values are due to enhanced emissions from manure waste. The NH$_3$:CO correlations are thus weaker in spring than in winter as NH$_3$ and CO are from different sources. The large NH$_3$ RVMR values are mainly due to the enhanced emissions from fertilizer application, while CO may be from the fire events. Similar trends also occurred in fall of 2007, but with smaller magnitudes of both NH$_3$ and CO RVMR. In all four seasons, the NH$_3$:CO ratios in TES are higher (0.04 - 0.12) than the ratios in GEOS-Chem (0.02 - 0.08). This may be due to the high bias in the TES NH$_3$ retrieval [Shephard et al., 2011] or low emissions in GEOS-Chem emission inventory [Zhu et al., 2013].

5.5 Conclusions

The TES observations of NH$_3$ and CO from throughout the globe provide us the capability of comparing these two species at the same time and same location. Biomass burning emissions of NH$_3$ and CO are well correlated in the GFED inventory that drives the GEOS-Chem simulation (correlation equals 1 overall). Despite different processes affecting these species (e.g., chemical reaction, removal) in the model and differences in the TES measurement sensitivities for each (i.e., NH$_3$ versus CO averaging kernels), the RVMR values of NH$_3$ and CO still have good correlations (up to 0.82) in biomass burning dominated region. Similarities in the correlations between the observations and model indicate that the spatial and temporal timescales of these processes are well represented, even if source strengths are not. This provides evidence that differences between modeled and observed NH$_3$ distributions [e.g., Shephard et al., 2011; Zhu et al., 2013] are not likely owing to model deficiencies in NH$_3$ removal processes.

In this section, we present the NH$_3$ and CO RVMR global distributions from TES observations and GEOS-Chem simulations for all seasons of 2007. Similar seasonal variations of global CO RVMR are found in both TES and GEOS-Chem. However, TES CO RVMR is generally larger than GEOS-Chem CO RVMR. Similar trends are also evident in NH$_3$ RVMR, and TES NH$_3$ RVMR is much larger than GEOS-Chem RVMR on global scales. TES NH$_3$ RVMRs show larger spatial
variations than GEOS-Chem. Analysis of the NH$_3$:CO ratio shows strong positive correlations between these species in biomass burning dominated regions and seasons (e.g., South America in spring) in both TES and GEOS-Chem and weaker correlations in regions and seasons (e.g., South-Central Asia) with a large amount of emissions from multiple sources (e.g. agricultural, industry, and traffic).

The NH$_3$:CO ratios are usually within the range of 0.01 to 0.08 in GEOS-Chem and 0.01 to 0.12 in TES. NH$_3$:CO ratios in TES are slightly higher than the ratios in GEOS-Chem in regions and seasons dominated by biomass burning as NH$_3$ emissions are underestimated in GEOS-Chem and/or TES NH$_3$ retrievals have a positive bias. However, the global distribution patterns and NH$_3$:CO correlations trends in TES and GEOS-Chem are in good agreement, which indicates the capability of TES observations to capture the correlations between NH$_3$ and CO sources. The TES observed NH$_3$:CO ratios are much larger than the modeled NH$_3$:CO ratios in the regions with multiple emissions sources, indicating that the model largely underestimates NH$_3$ emissions from non biomass burning sources. Thus, analyzing relationships between NH$_3$ RVMR and CO RVMR in TES observations is a useful method of understanding the NH$_3$ and CO global distributions and their correlations.
Chapter 6

Summary and conclusions

In this thesis, I explore constraining ammonia emissions using forward and inverse modeling, as well as satellite observations of ammonia. In Chapter 2, I show how model simulations are used to derive the a priori profiles of TES retrievals and to validate the TES retrievals. It is determined that the limitation of the TES detectability is for profiles that have maximum NH$_3$ VMR values no less than 1 ppb. Next, I show how TES observations can be used to characterize NH$_3$ sources and distributions. The NH$_3$ VMR profile is mapped to a point value RVMR for 2D visualization. GEOS-Chem RVMR is calculated with the TES observation operator and the RVMR weighting function of the corresponding TES retrieval. From comparisons throughout the globe during 2006 - 2009, TES RVMR is generally larger than the GEOS-Chem RVMR. Such broad underestimates are suspected to be due to the underestimation of NH$_3$ emissions in GEOS-Chem. The resolution of the model is $2^\circ \times 2.5^\circ$, which is not comparable to TES retrieval footprint ($5\text{ km} \times 8\text{ km}$). The sampling bias from NH$_3$ spatial variability within model grid cells could be the reason for the model underestimate in areas with localized sources. Comparisons of the seasonality of TES RVMR and model RVMR in the twelve select regions suggest that there are greater uncertainties in our understanding of agricultural sources rather than in biomass burning sources.

After analyzing the NH$_3$ observations from TES in Chapter 2 [Shephard et al., 2011] and validating the TES observations in Pinder et al. [2011], the next step is to explore how to improve model estimates of NH$_3$ sources using knowledge from TES observations. In Chapter 3, I show how TES observations of NH$_3$ can be used in inverse modeling. The inverse modeling is first
tested with pseudo TES observations, which are generated by applying the TES retrieval algorithm to simulated profiles. It is found that 70% of the variance of the emissions can be constrained under these idealized conditions (i.e., no model error). I then assimilate real TES observations in April, July, and October for multiple years. The posterior results indicate that ammonia emission inventories are broadly underestimated throughout the U.S., particularly in the West. The posterior model simulation generally increases ammonia over the U.S. and captures the range and variability of in situ observations (AMoN) in April and October, while in July, estimates are biased high. To understand these adjustments, we consider several aspects of the retrieval. The sampling bias, which is due to the TES detection limit, may in part lead to the overestimated emissions in July as a greater fraction of peak values are included in the assimilation. Other factors, such as errors in physical processes in the model, could also contribute to the uncertainty in the inversion.

Therefore, in Chapter 4, I focus on revising fundamental aspects of how ammonia emissions are modeled, such as diurnal variability of NH$_3$ emissions and bi-directional air-surface exchange of NH$_3$. TES observes NH$_3$ twice a day at 1:30 am and pm. Discrepancies between the model and TES observations at these two hours depend on not only the total emissions magnitude, but also the diurnal variation of NH$_3$ emissions. I thus revise the diurnal variation pattern for NH$_3$ livestock emissions in GEOS-Chem, which were previously constant throughout the month, with a new scheme that peaks in the mid-day. The new diurnal variability scheme improves the estimation of NH$_3$ surface concentration in comparison to hourly in situ measurements in the Southeastern U.S. by decreasing NH$_3$ at night (up to 2.9 ppb) and increasing NH$_3$ during the day (up to 1 ppb). Increased livestock emissions during the daytime are more conducive to the export of NH$_3$ from the surface level. Globally, NH$_3$ concentrations decrease overall by up to 17 ppb in India and Southeastern China, with corresponding decreases in aerosol nitrate by up to 7 µg/m$^3$.

Next, I show details of how to implement bi-directional exchange in GEOS-Chem and evaluate the impacts on NH$_3$, nitrate aerosol, and wet deposition of NH$_4^+$ in the U.S. and globally. The GEOS-Chem model with bi-directional exchange generally increases NH$_3$ gross emissions (10.9%) and surface concentrations (up to 3.9 ppb) throughout the globe in July, except in India and
Southeastern China. These increases are mainly due to re-emissions of NH$_3$ from the ammonium soil pool that accumulates during previous months. Bi-directional exchange decreases NH$_3$ gross emissions (up to 20.3%) and surface concentrations (up to 27.5 ppb) in the Northern Hemisphere in April and October, and increases NH$_3$ gross emissions and surface concentrations (up to 4.2 ppb) in the Southern Hemisphere. These decreases are mainly due to NH$_3$ that remains in the ammonium soil pool rather than being emitted directly after fertilizer application during the growing season. Bi-directional exchange does not impact NH$_4^+$ wet deposition much overall, even when the differences in NH$_3$ fertilizer emissions are large.

As a first step towards including bi-directional exchange within NH$_3$ inverse modeling, I develop the adjoint of this process in GEOS-Chem. Using the adjoint method, I show that bi-directional exchange enhances the source footprint of NH$_3$ by several hundred kilometers. I also show that the sensitivity of NH$_3$ concentrations to soil pH is seasonally dependent, and it is stronger during the growing seasons than other seasons. The sensitivity of NH$_3$ concentrations to fertilizer application rate is also seasonally dependent, the seasonal trend of which is similar to the sensitivity of NH$_3$ concentrations to soil pH. Since seasonal variation of soil pH has not been included in this study, I test the impact of increasing the soil pH by 10% (seasonal variability is $\sim$20%). As expected, the NH$_3$ surface concentrations generally increase over the globe (by up to 3.4 ppb in April). However, no significant improvement is found when compared to AMoN observations in the U.S. with this adjustment, since sensitivities are small over the U.S. and large underestimates exist in livestock emissions. To test this, I also test how the model responds to increasing livestock emissions by a factor of 6 in April and 3 in October. The modeled NH$_3$ concentrations with this adjustment largely increase, and are in a better agreement with the magnitude of AMoN observations, however the correlations are much worse. Thus, uniformly increasing the livestock emissions in the model does not reduce uncertainties in spatial variation of NH$_3$, which again emphasizes the necessity of including bi-directional exchange within inverse modeling as future work. It is shown in Appendix A that constraints provided by potential future geostationary satellite observation would be very beneficial towards constraining such fundamental aspects of NH$_3$ emissions processes.
In Chapter 5, I introduce an additional method for understanding NH$_3$ sources and distributions using correlations between NH$_3$ and CO. As introduced in Chapter 2 and Chapter 3, the NH$_3$ VMR profile can be mapped to a point value RVMR. In this Chapter, we also map the CO VMR profile to a point value CO RVMR at the pressure level of the corresponding NH$_3$ RVMR. The global NH$_3$ RVMR and CO RVMR from GEOS-Chem are compared with those from TES observations for four seasons of 2007. The seasonal trends of global CO RVMR from TES and GEOS-Chem are similar. However, TES CO RVMR is generally larger than GEOS-Chem CO RVMR. TES NH$_3$ RVMR is much larger than GEOS-Chem CO RVMR, which is most likely due to underestimation of NH$_3$ emissions as demonstrated in the previous chapters. NH$_3$ RVMR from TES has larger spatial variations than GEOS-Chem. We also compare the correlations between NH$_3$ RVMR and CO RVMR from GEOS-Chem with the correlations from TES in six different regions. NH$_3$ and CO have strong correlations in both TES and GEOS-Chem in biomass burning dominated regions and seasons, such as South America in Spring. In these regions, the NH$_3$:CO ratios in TES are slightly higher than the ratios in GEOS-Chem since NH$_3$ emissions are underestimated in GEOS-Chem and/or TES NH$_3$ retrievals have a positive bias. However, given that the emissions of NH$_3$ and CO from biomass burning sources in the model are perfectly correlated, yet the lifetimes of these species are several orders of magnitude different, the consistency between the NH$_3$:CO correlations in the biomass burning regions between the model and TES indicate that the model does not likely contain any major deficiencies in removal processes for these species. In other regions and seasons with multiple large emissions sources, the NH$_3$:CO ratios are much larger than the ratios in GEOS-Chem, which again indicates that NH$_3$ emissions from non biomass burning sources are largely underestimated in the model.
Chapter 7

Supplementary figures
Figure 7.1: The average discrepancy between TES retrievals and true profiles [Shephard et al., 2011]. The mean biases are calculated according to the type of the a priori profile used in the retrieval.

Figure 7.2: The L-curve plot used for selecting the regularization parameter ($\gamma$) in July. $J_{\text{parameter}} = \frac{1}{2} \sum_{c \in \Omega} (H_c - (c_{\text{obs}} - b))^T S_{\text{obs}}^{-1} (H_c - (c_{\text{obs}} - b)).$ $J_{\text{prediction}} = \frac{1}{2} (\sigma - \sigma_a)^T S_a^{-1} (\sigma - \sigma_a).$ We select $\gamma$ to be 100 in this case.
Figure 7.3: Comparison of variations in monthly average NH$_3$ concentrations from AMoN observation during the year 2007-2010 versus year 2008.

Figure 7.4: The normalized cost function reduction in July at each accepted iteration of the optimizing process. The cost function reduces more than 40% when converged.


Kuhns, H., M. Green, and V. Etyemezian (2003), Big bend regional aerosol and visibility observational (BRAVO) study emissions inventory, report prepared for bravo steering committee, desert research institute, las vegas, nevada.


Appendix A

Geostationary observations of NH$_3$

A.1 Introduction

Remote sensing observations of NH$_3$ are currently or soon to be available from TES, IASI, CrIS, and AIRS instruments, all of which are onboard satellites in low-earth, sun-synchronous orbits. These measurements thus each provide two observations daily (e.g., at 1:30 am and 1:30 pm for TES). The spatial coverage is either sparse (TES global survey measurements return to the same location every 16 days, with several hundred km separating each footprint) or the instrument detection limit is not low enough to characterize many of the smaller NH$_3$ signatures (e.g., the detection limit for the IASI NH$_3$ product is likely 3 - 5 ppb [Clarisse et al., 2010]). Such measurements may be insufficient to characterize fundamental aspects of the NH$_3$ emissions process, such as the dependence of NH$_3$ bi-directional exchange on the surface emissions potential, or the diurnal variability of NH$_3$ emissions from livestock operations. Worse, the lack of spatially and temporally comprehensive and accurate data coverage can lead to biases in inverse modeling studies [e.g., Zhu et al., 2013].

The GEO-CAPE mission, recommended under the NASA decadal survey [National Research Council, 2007], would provide geostationary measurements of tropospheric constituents relevant to air quality and climate for the first time over North America. Specific missions characteristics are described in Fishman et al. [2012]. The high spatial and temporal resolution of GEO-CAPE offers new possibilities for constraining emissions that are not achievable with low-earth-orbit (LEO) platforms. GEO-CAPE, with significantly higher spatial resolution than any available LEO obser-
vations, could allow nearby pollution sources to be separated and observed individually, e.g., roads, farms, or point sources in densely populated regions. Current bottom-up inventories typically give annual or monthly average emissions estimates; emissions estimates at finer temporal scales (daily or hourly) are highly uncertain due to limited information about the temporal variations in source activity. GEO-CAPE provides critical tests for the temporal behavior of existing inventories and could improve mechanistic models that predict emissions when direct observations are not available. GEO-CAPE could also allow development of high space and time resolution emission fields that enable detailed evaluation of other components of a chemical-transport model (CTM), e.g. chemical mechanisms or boundary layer fluid dynamics.

As part of GEO-CAPE, the TEMPO (Tropospheric Emissions: Monitoring of Pollution, https://directory.eoportal.org/web/eoportal/satellite-missions/t/tempo) mission has been selected for funding, with launch slated for 2019. This instrument will measure in the UV and visible range. This will allow hourly observations at 4 km resolution primarily of NO$_2$ and ozone, in addition to some constraints on aerosols. As the spectral range is limited to the UV and visible frequency, TEMPO will not measure the absorption of species such as CO, CH$_4$, nor NH$_3$. For these, the GEO-CAPE science team supports a second mission, now referred to as GCIRI, which would complement TEMPO with measurements in the IR range necessary to detect these species.

In this work we explore the potential of a GCIRI geostationary measurement of NH$_3$ to fundamentally improve our understanding of NH$_3$ sources at a mechanistic level. This will allow us to make improvements to air quality models that outlast the lifetime of the instrument itself (a uniquely different goal from, e.g., forecasting, wherein the aim is purely to use existing data to improve a forecast, without making fundamental revisions to the model itself). Specifically, we hope to improve the representation of NH$_3$, ammonium and nitrate aerosol, and deposition of reactive nitrogen. In Section A.2 we introduce our method of using model simulations and radiative transfer calculations to evaluate the extent to which GCIRI versus existing data from LEO instruments (e.g., TES) have the potential to constrain process-level uncertainties in NH$_3$ models. Results from GEOS-Chem model simulations are provided in Section A.3. Radiative
transfer calculations based upon these model simulations, performed by collaborators Dr. Karen Cady-Pereira and Dr. Mark Shepard, are still in progress. For completeness, we do however show results of their radiative transfer calculations applied to simulations from CMAQ performed by collaborator Dr. Jesse Bash. We then finish with a brief set of conclusions based upon the initial GEOS-Chem modeling results and the completed CMAQ results.

A.2 Approach

The general approach used for characterizing the potential value of GCIRI observations is as follows. We perform several sets of simulations, using different mechanistic models of NH₃ emissions, using multiple chemical transport models. We use GEOS-Chem nested simulations at the 0.5° × 0.667° resolution (described in Section 4.3) as well as CMAQ 12×12 km² simulations [Bash et al., in prep]. Pseudo observations are then generated from these simulated NH₃ distributions using both geostationary (GEO) and sun-synchronous (LEO) sampling strategies. The measurement characteristics of GCIRI follow that of a TES-like instrument, whose measurement capabilities are described in Section 2.1, with the same measurement error and a priori profiles, just with the spatial and temporal frequencies greatly enhanced – i.e., hourly measurements every 4 km. We then analyze how differences in NH₃ source characterizations are reflected in these two different data sets. My role has been in running the GEOS-Chem simulations and performing analysis of the GEOS-Chem model simulated fields. These results are then passed along to collaborators Dr. Cady-Pereira and Dr. Shepard who perform the radiative transfer calculations to create the GEO and LEO pseudo observations from the model NH₃ fields.

The first question we aim to address is whether or not geostationary observations would provide constraints on the diurnal variability of NH₃ emissions from livestock. In Chapter 4 we showed that this can have significant impacts on NH₃ and nitrate concentrations throughout the globe. Here we investigate this question in more detail with higher resolution simulations over the U.S. A concern raised in Zhu et al. [2013] is that inverse modeling of NH₃ sources may be biased high owing to assimilation of observations at only a single time per day. It is known that the
diurnal variability of NH$_3$ sources strongly affects surface-level concentrations near such sources. What has not been shown is whether or not the impact of this mechanism is significant enough to cause detectable changes in the NH$_3$ vertical profile seen by satellites, i.e., changes occurring at altitudes in the 900 - 700 hPa range.

A.3 Results

A.3.1 Surface-level model responses to diurnal variability

We first consider the impact of the diurnal variability of livestock NH$_3$ emissions on purely modeled NH$_3$ concentrations, focusing specifically on values over the U.S. using higher resolution simulations than were presented previously. The new diurnal variability scheme for NH$_3$ livestock emissions described in Chapter 4 is run in nested simulations over North America for July, 2008. We also perform simulations using the standard livestock emissions (constant monthly values), aka the static case. Plots of the spatial distribution over the U.S. in July of 2006 of NH$_3$, nitrate, and nitrogen deposition, are shown in Figures A.1, A.2, and A.3. The impacts on monthly mean NH$_3$ concentrations can be significant, up to 50%. Concentrations are reduced as less NH$_3$ is emitted into shallow boundary layers during the night using the dynamic scheme; instead, emissions peak during the day, when dynamic export away from the surface is more efficient and the increased boundary layer height (relative to nighttime) decreases the NH$_3$ concentration. There are corresponding reductions in aerosol nitrate. For both NH$_3$ and nitrate, some of the largest decreases are in spatially isolated regions, such as the San Joaquin Valley for NH$_3$, or the New Jersey area for nitrate. These changes are much weaker in the global $2^\circ \times 2.5^\circ$ simulations shown in Figures 4.2 and 4.3; thus, it seems likely that the impacts of the dynamic diurnal variability scheme may be particularly important for higher-resolution nested models. The impacts on nitrogen deposition however are fairly small, impacting total reactive nitrogen less than 10%, as oxidized nitrogen dominates reactive nitrogen deposition in much of the country [e.g., Ellis et al., 2013].
Figure A.1: Average surface-level NH$_3$ over the U.S. during July, 2006, from GEOS-Chem high-resolution ($0.5^\circ \times 0.667^\circ$) simulations.

Figure A.2: Average surface nitrate over the U.S. during July, 2006, from GEOS-Chem high-resolution ($0.5^\circ \times 0.667^\circ$) simulations.

Figure A.3: Total nitrogen deposition in the U.S. during July, 2006, from GEOS-Chem high-resolution ($0.5^\circ \times 0.667^\circ$) simulations.
A.3.2 LEO detection of diurnal variability

We first consider the impact of the diurnal variability on profiles corresponding to times and locations of existing NH$_3$ measurements from TES global survey transects. We consider the impacts on both the native model NH$_3$ profiles (i.e., without the application of the satellite instrument’s observational operator), and those after the application of the observation operator. To begin with, we consider profiles corresponding to locations of TES NH$_3$ global survey during July of 2006 - 2009 over the U.S. with DOF $>$0.5. This amounts to 566 and 72 profiles during the day and night. The differences between the dynamic versus static simulations in native model profiles (black), as well as the profile as visible to TES (blue), are not remarkably different in the day or night. While there are some noticeable differences in the nighttime surface-level model concentrations, which are only half as large in the dynamic case, these are not reflected in the pseudo TES observations, which are not universally sensitive to surface-level concentrations. We next consider restricting our analysis to regions more likely affected by the different livestock emissions schemes. Figure A.5 shows a similar comparison, this time restricted to locations over California wherein the emissions are dominated ($>$75%) by livestock. However, again we see that the detectable differences from a LEO sampling scheme such as TES are not highly sensitive to the NH$_3$ diurnal variability. It is thus (a) unlikely that these measurements alone would be sufficient to increase our fundamental understanding of NH$_3$ diurnal variability and (b) the use of static monthly emissions (i.e., the lack of diurnal variability) in the inverse modeling over the US of Zhu et al. [2013] did not likely have a significant impact on the inversion results. Further analysis is required to determine whether or not the lack of diurnal variability in the model impacted comparisons of the model versus TES in Shephard et al. [2011] in other locations of the world where the impacts of diurnal variability are greater than the U.S. (see Figure 4.3).
US, day, n=566

US, night, n=72

Figure A.4: Averaged profile of NH$_3$ VMR over the U.S. at locations with good TES retrieval DOF > 0.5 and for daytime and night time in July, 2006 – 2009.
Figure A.5: Averaged profile of NH$_3$ VMR over the California with livestock emissions larger than 75% and at locations with good TES retrieval DOF>0.5 for daytime and night time in July, 2006 – 2009.
A.3.3 GEO detection of diurnal variability

In the next section, we consider the impacts of the static vs dynamic emissions from livestock on NH$_3$ profiles sampled at the geo-stationary spatial and temporal frequency. While for simplicity we only consider measurements being available once every 3 hours, in practice it is possible they would be available every hour (the frequency of observations required to address science questions such as uncertainties in diurnal variability is an active GGIRI design consideration being explored). Based on results from the previous section, we restrict our analysis to locations in California dominated (>75%) by livestock emissions. We also further restrict our analysis to July 22nd, which was a particularly hot day, as differences between the static and dynamic simulations are amplified by higher temperatures. In this sense, we are likely exploring the best case scenario for detecting differences in diurnal emissions schemes from space. The results are shown in Figure A.6, with the static simulations shown in blue and the dynamic simulations in red. There are eight panels corresponding to profiles from eight different hours of the day, indicated by the number at the top of each panel. The differences between the dynamic versus static simulations is clearly more pronounced when looking across these numerous intervals and higher density of sites. During the day, we see the surface level concentrations in the dynamic case are slightly higher than the static case, with the opposite occurring at night. These differences are noticeable well above 800 hPa, which means that there is a good chance that such differences in the NH$_3$ profiles would be detectable from a GCIRI instrument with TES-like spectral resolution and instrument noise.

The next step of this analysis will be to analyze the retrievable portion of the NH$_3$ profiles shown in Fig. A.6., i.e., the variations after applying the observation operator to these profiles. This work is still in progress. We can, however, consider results from similar experiments performed using simulations from the CMAQ model, run at the 12 km scale using the same statics versus dynamic emissions schemes. These are shown in Figure A.7. The top panel shows the difference between the CMAQ model surface concentrations from the dynamic case minus the static case in locations in California with dominant livestock emissions on July 22, 2006. The trends and magnitudes of the
Figure A.6: Average profile of NH$_3$ VMR over the California with livestock emissions larger than 75% from the Static (blue) and Dynamic (Red) simulations for July 22, 2006.
differences are similar to those from the GEOS-Chem simulations. In the second row of Figure A.7, the differences in CMAQ RVMR values are shown, and in the third row the differences in RVMRs detectable from the GCIRI instrument (aka Geo-TES) are shown. The latter shows that the GCIRI instrument is likely to detect significantly lower NH$_3$ concentrations at night, with a mean difference of 2 ppb at 4 am, and slight increases during the day, with a mean difference of up to 0.5 ppb in the mid-afternoon. Also shown in this figure is the pressure level of the peak instrument sensitivity that contributes to the RVMR, the DOFs, and the thermal contrast (TCON). Despite the smaller thermal contrast at night, the differences in NH$_3$ concentrations between the static and dynamic cases are still detectable.

### A.4 Conclusions

Model simulations and radiative transfer calculations are used to assess the value of GEO versus LEO remote sensing observations for constraining fundamental processes (the diurnal variability of livestock sources) within a NH$_3$ emissions model. It is found that over the U.S., the differences between a constant monthly NH$_3$ emissions and one in which the livestock emissions respond dynamically to local environmental conditions on an hourly basis is not detectable in the national-scale average NH$_3$ profiles by LEO instruments (e.g., TES). Some small differences are notable over select locations, such as restricting analysis to a few grid boxes in California where the satellite retrieval DOFs were high (>0.5) and the local emissions were dominated by livestock sources (>75%), yet the differences were still less than a fraction of a ppb. In contrast, GEOS-Chem simulations in California for a warm day show significant differences at hourly timescales in the simulated NH$_3$ profiles. Further, simulated geostationary observations generated from higher resolution CMAQ simulations similarly show large (up to 2.5 ppb) signals in the difference between day and nighttime concentrations. This provides promising evidence that geostationary observations could be used to constrain diurnal variability in NH$_3$ sources, even when instrument sensitivities peak above the surface level. While there is not an indication that the impact of diurnal variability was significant enough to bias the inverse modeling estimates of Zhu et al. [2013] over the U.S., previous
Figure A.7: Results of CMAQ model simulations using dynamic - static diurnal emissions. The top row shows differences in model surface concentrations. The second row shows the model RVMR corresponding to pseudo geostationary observations that are shown in the third row. The bottom three rows show the retrieval peak sensitivity pressure level, DOFs, and thermal contrast (TCON).
comparisons [Shephard et al., 2011] in other parts of the world (such as China) of a static model to TES observations may have had model estimates biased low owing to the diurnal variability of the emissions, rather than underestimated emissions magnitude.