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

# adjoint model

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# 4 Abstract.

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Ammonia  $(NH_3)$  is an important contributer to air pollution, and it also has significant impacts on climate change and environmental health. How-6 ever, there are many uncertainties in ammonia emissions inventories, from 7 the total amount of emissions to the seasonal and diurnal variability, which 8 hinder the use of air quality models to address these issues. In this paper, 9 we constrain ammonia emissions in the U.S. by assimilating observations from 10 the TES remote sensing instrument with the GEOS-Chem model and its ad-11 joint. This inversion framework is first validated using simulated observations. 12 We then proceed to assimilate TES observations for April, July and Octo-13 ber of 2006 through 2009. We evaluate the inverse modeling results by com-14 paring the observationally constrained model simulations to independent sur-15 face measurements of  $NH_3$ ,  $NH_x$  ( $NH_4^+ + NH_3$ ) wet deposition, and  $SO_4^{2-}$ 16 and  $NO_3^-$  aerosol. Modeled  $NH_3$  concentrations have a decreased bias in April 17 and October compared to surface observations after assimilation and an in-18 creased correlation in each month. Modeled  $NH_x$  wet deposition after assim-19 ilation has a decreased normalized mean bias (NMB) in April and an increased 20 NMB in July and October compared to the wet  $NH_x$  observations, although 21 the correlation and linear regression coefficients are closer to unity in each 22 month. Modeled  $SO_4^{2-}$  and  $NO_3^{-}$  aerosols concentrations do not change sig-23 nificantly and persistent  $NO_3^-$  overestimation is noted, consistent with pre-24 vious studies. Overall, assimilation of NH<sub>3</sub> remote sensing data to constrain 25 NH<sub>3</sub> emissions improves the model simulation in several aspects, yet addi-26

- $_{\rm 27}$   $\,$  tional work on assessing wet deposition, nitric acid formation, and bi-directional
- <sup>28</sup> fluxes will be necessary to enhance model performance across the full range
- <sup>29</sup> of gas and aerosol evaluations.

### 1. Introduction

Emissions of ammonia  $(NH_3)$  from anthropogenic sources pose several environmental 30 concerns. Ammonia affects air quality and climate through its role in the mass, composi-31 tion and physical properties of tropospheric aerosol. Ammonium nitrate and ammonium 32 sulfate make up a substantial fraction of atmospheric fine particulate matter  $(PM_{2.5})$ , 33 exposured to which has been statistically associated with inhibited lung development, 34 cardiovascular diseases and premature mortality [Pope et al., 2002; Schwartz et al., 2002; 35 *Reiss et al.*, 2007]. These fine particulates  $(PM_{2.5})$  also contribute to haze that impacts 36 visibility. Further, when deposited in excess, reactive nitrogen, including ammonia, can 37 cause detrimental nutrient imbalances to sensitive ecosystems [Rodhe et al., 2002; Rabal-38 ais, 2002]. 39

Despite the recognized importance of  $NH_3$  emissions in the U.S. [Aneja et al., 2008], 40 knowledge of their magnitude is severely limited; NH<sub>3</sub> emissions are primarily from agri-41 cultural sources whose strengths are poorly understood. Uncertainty in NH<sub>3</sub> undermines 42 the efforts to understand historical and present levels of PM<sub>2.5</sub> [Yu et al., 2005; Nowak 43 et al., 2006; Zhang et al., 2008; Wu et al., 2008; Stephen and Aneja, 2008; Beusen et al., 44 2008; Simon et al., 2008; Henze et al., 2009] and hinders estimates of the response of 45  $PM_{2.5}$  to control measures because of the key role that  $NH_3$  plays in governing the bal-46 ance of inorganic fine particulate species [Dennis et al., 2008]. On a larger scale, rates in 47 NH<sub>3</sub> emissions are a critical source of uncertainty in global budgets of the atmospheric 48 transport and deposition of reactive nitrogen [Sutton et al., 2007; Galloway et al., 2008; 49 Schlesinger, 2009]. 50

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These are several reasons for the persistence of uncertainties in  $NH_3$  inventories. Char-51 acterizing NH<sub>3</sub> sources from the bottom up requires spatially and temporally resolved 52 data such as farming practices and intensity. These data are rarely available nationally 53 as direct measurements of  $NH_3$  emissions at such scales are prohibitive owing to cost. 54 Therefore, people have turned to top-down approaches to provide additional constraints 55 on  $NH_3$  emissions. While direct observations of gas-phase  $NH_3$  do exist in select loca-56 tions, observations of other chemically related species are much more prevalent. Further, 57 that  $NH_3$  can rapidly partition to form aerosol ammonium  $(NH_4^+)$  can limit the utility of 58 gas-phase surface observations alone. 59

Consequently, owing to the paucity of direct observations of  $NH_3$  and the difficulty of 60 constraining the  $NH_x$  (=  $NH_3 + NH_4^+$ ) system, measurements of species that are regulated 61 by the amount of available  $NH_3$  have been looked to for constraints on estimates of 62  $NH_3$  emissions. The current National Emissions Inventory (NEI) for  $NH_3$  is coarsely 63 constrained by top-down estimates from the inverse modeling studies of *Gilliland et al.* 64 [2003, 2006]. Measurements of wet deposited  $NH_x$  were used as constraints, because wet 65  $NH_x$  estimates depend less on model sensitivity to aerosol partitioning. A drawback to 66 this approach is the sensitivity to estimated precipitation and scavenging, aspects which 67 are difficult to model accurately and hinder the inversion during some seasons. Taking 68 an alternative approach, Henze et al. [2009] used measurements of  $SO_4^{2-}$  and  $NO_3^{-}$  from 69 the IMPROVE network to constrain the amount of NH<sub>3</sub> partitioned into the aerosol 70 phase as  $NH_4^+$  (which is strongly coupled to  $SO_4^{2-}$  and  $NO_3^-$ ). In this way, aerosol-phase 71 observations were used to constrain NH<sub>3</sub> concentrations and, hence, NH<sub>3</sub> emissions. This 72

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<sup>73</sup> approach, however, is susceptible to model bias in HNO<sub>3</sub>, which may be significant [*Zhang* <sup>74</sup> *et al.*, 2012].

Despite these recent efforts, comparisons between inverse modeling results to the recent 75 bottom-up  $NH_3$  inventory of *Pinder et al.* [2006] show that considerable discrepancies 76 remain in the spatial and seasonal distribution of  $NH_3$  emissions throughout the U.S. 77 *Henze et al.*, 2009; at odds are estimates of the relative magnitude of spring vs summer 78 emissions. A limiting factor in reconciling these differences is infrequent and sparse in situ 79 observations, even for the aerosol-phase measurements, and a shortage of direct constraints 80 on gas-phase  $NH_3$ . Without understanding the  $NH_x$  system as a whole, and without tools 81 to link observations of these species over the continent to emissions, studies of  $\rm NH_3$  or  $\rm NH_4^+$ 82 alone may suffer in terms of utility for constraining emissions inventories at a national 83 scale [Pinder et al., 2008]. 84

The detection of boundary layer ammonia from space [Beer et al., 2008; Clarisse et al., 85 2009, 2010; Shephard et al., 2011 provides a new and unprecedented opportunity for 86 reducing persistent uncertainties in our understanding of the distribution and impacts of 87 atmospheric ammonia. Initial comparisons to global model NH<sub>3</sub> distributions indicate that 88  $NH_3$  sources may be widely underestimated [*Clarisse et al.*, 2009; *Shephard et al.*, 2011]. 89 *Pinder et al.* [2011] have recently verified the utility of such measurements for tracking 90 observed spatial and temporal trends in surface level  $NH_3$  concentrations. Therefore, 91 we consider here how inverse modeling with assimilation of satellite observations of  $NH_3$ 92 can be used to further provide rigorous constraints on  $NH_3$  sources. Section 2 describes 93 the models and inverse methodology used in this study. We then present details of the 94 remote sensing observations (Section 3), followed by inverse modeling tests using simulated 95

<sup>96</sup> observations (Section 4), and real observations (Section 5). Finally, we evaluate the <sup>97</sup> modeled results by comparing them to independent data sets which are not used during <sup>98</sup> the inversion (Section 6) and present our conclusions (Section 7).

# 2. Methods

## 2.1. GEOS-Chem

GEOS-Chem is a chemical transport model driven using assimilated meteorology from 99 the Goddard Earth Observing System (GEOS) of the NASA Global Modeling and As-100 similation Office [Bey et al., 2001]. GEOS-Chem includes an online secondary inorganic 101 aerosol simulation introduced and described in full by Park et al. [2004]. Model estimates 102 of inorganic PM<sub>2.5</sub> have been compared to surface measurements [Park et al., 2004, 2006; 103 Liao et al., 2007; Henze et al., 2009; Pye et al., 2009] and measurements from aircraft 104 campaigns [*Heald et al.*, 2005, 2006];  $NH_3$  emissions are frequently indicated to be a likely 105 cause of discrepancies. 106

#### 2.2. GEOS-Chem adjoint model

The adjoint of the GEOS-Chem model was developed specifically for inverse modeling of 107 precursors of inorganic PM<sub>2.5</sub> with explicit inclusion of gas-phase chemistry, heterogeneous 108 chemistry, and treatment of the thermodynamic couplings of the sulfate - ammonium -109 nitrate - water aerosol system [Henze et al., 2007, 2009]. As the only adjoint model to ex-110 plicitly represent this system, it is uniquely capable of exploiting speciated measurements 111 of both gaseous and particulate components in novel ways. The accuracy of the adjoint 112 model calculations is verified through extensive comparisons of adjoint to finite difference 113 sensitivities. In order to maximize points of comparison between these two approaches, 114

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 not feasible, as it would require separate forward model calculations for each parameter). Fig. 1 shows the results of a week-long test of the sensitivity of aerosol nitrate to NH<sub>3</sub> emissions, demonstrating the accuracy of the adjoint.

# 2.3. Inverse modeling

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Data assimilation techniques provide a framework for combining observations and mod-120 els to form an optimal estimation of the state of a system, which in this case is the chemical 121 makeup of the troposphere. To start with, a range of models are typically constructed 122 using control variables,  $\sigma$ , to adjust elements of the vector of model parameters, p, via 123 application as scaling factors,  $p = p_a e^{\sigma}$ , where  $\mathbf{p}_a$  is the prior parameter estimate. The 124 approach we consider iteratively employs the adjoint of an air quality model in a method 125 referred to as 4D-Var [Sandu et al., 2005], used here for inverse modeling of emissions. The 126 advantage of this method is that numerous ( $\mathcal{O}(10^5)$ ) model parameters can be optimized 127 simultaneously while still retaining the constraints of the full forward model physics and 128 chemistry. This approach to inverse modeling seeks  $\sigma$  that minimizes the cost function, 129  $\mathcal{J}$ , given by 130

$$\mathcal{J} = \frac{1}{2} \sum_{\mathbf{c} \in \Omega} (H\mathbf{c} - (\mathbf{c}_{obs} - \mathbf{b}))^T \mathbf{S}_{obs}^{-1} (H\mathbf{c} - (\mathbf{c}_{obs} - \mathbf{b})) + \frac{1}{2} \gamma (\boldsymbol{\sigma} - \boldsymbol{\sigma}_a)^T \mathbf{S}_a^{-1} (\boldsymbol{\sigma} - \boldsymbol{\sigma}_a)$$
(1)

<sup>131</sup> where *H* is the observation operator,  $\gamma$  is the regularization parameter,  $\sigma_a$  is the prior <sup>132</sup> estimate of the control variables,  $\mathbf{S}_a$  and  $\mathbf{S}_{obs}$  are error covariance estimates of the control <sup>133</sup> variables and observations respectively, and  $\Omega$  is the domain over which observations,  $\mathbf{c}_{obs}$ ,

and model predictions are available, **b** is a bias correction explained in section 5. Overall, 134 the cost function is a specific model response, the minimum value of which balances 135 the objectives of improving model performance while ensuring the model itself remains 136 within a reasonable range (as dictated by  $\mathbf{S}_a^{-1}$ ) of the initial model. Gradients of the cost 137 function with respect to the parameter scaling factors calculated with the adjoint model, 138  $abla \sigma \mathcal{J}$ , are supplied to an optimization routine (the quasi-Newton L-BFGS-B optimization 139 routine Byrd et al. [1995]; Zhu et al. [1994]), and the minimum of the cost function is 140 sought iteratively. At each iteration, improved estimates of the model parameters are 141 implemented and the forward model solution is recalculated. 142

#### 3. Observations

## 3.1. Remotely sensed $NH_3$ observations from TES

The high spectral resolution and good signal-to-noise ratio of the TES instrument [Shep-143 hard et al., 2008 have enabled the first detection of tropospheric ammonia from space, 144 first demonstrated over Southern California and China [Beer et al., 2008]. TES is an 145 infrared Fourier transform spectrometer with spectral resolution of  $0.06 \text{ cm}^{-1}$  aboard the 146 NASA Aura satellite, launched July 15, 2004 [Schoeberl et al., 2006]. TES global survey 147 observations repeat with a 16-day cycle and have a nadir footprint of 5 km  $\times$  8 km; for 148 example, that is about  $\sim 180$  daytime scenes a month over North America after cloud 149 screening (optical depths < 1.0) and applying the TES retrieval quality control flags. 150

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

$$H\mathbf{c} = \mathbf{c}_a + \mathbf{A}(\mathbf{M}\mathbf{c} - \mathbf{c}_a) \tag{2}$$

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where  $\mathbf{c}$  is the model estimated NH<sub>3</sub> profile,  $\mathbf{M}$  is a matrix that maps these values to 151 the retrieval units and vertical levels, A is the averaging kernel, and  $\mathbf{c}_a$  is the a priori 152  $NH_3$  profile used for the retrieval [Shephard et al., 2011]. By comparing TES  $NH_3$  pro-153 files to mapped model estimates,  $H\mathbf{c}$ , rather than the native model NH<sub>3</sub> profile,  $\mathbf{c}$ , the 154 contribution of error in  $\mathbf{c}_a$  to the measurement error,  $\mathbf{S}_{obs}$ , is minimized [Rodgers, 2000]. 155 For the sake of 2D visualization, the Representative Volume Mixing Ratio (RVMR) 156 metric [Payne et al., 2009; Shephard et al., 2011] is used in this study to provide a means 157 of comparing TES profiles to model estimates in a manner that accounts for heterogeneity 158 in the instrument's sensitivity to  $NH_3$ . 159

## 3.2. Surface measurements

In this study, model estimates are evaluated using surface observations of ammonia, 160 sulfate, nitrate, ammonium and wet deposited  $NH_x$  from several monitoring networks 161 throughout the U.S.. Surface  $NH_3$  observations are from the National Atmospheric Depo-162 sition Program (NADP) Ammonia Monitoring Network (AMoN), which is comprised of 163 triplicate passive ammonia monitoring samplers located at 21 sites across the U.S. with a 164 two-week long observation cycle. The locations of these 21 monitoring stations are shown 165 in Fig. 2. Observation of each site is compared with modeled concentrations during the 166 year November 2007 through June 2010. 167

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 weekly long observation cycles. <sup>172</sup> Model estimates of sulfate and nitrate aerosols are compared to observations from the <sup>173</sup> Interagency Monitoring of Protected Visual Environments (IMPROVE) network for the <sup>174</sup> year 2008 [*Malm et al.*, 2004]. The IMPROVE network collects PM<sub>2.5</sub> particles on Teflon, <sup>175</sup> nylon, and quartz filters using a modular, cyclone-based sampler with critical orifice flow <sup>176</sup> control. Sulfate and nitrate aerosols are collected on nylon filters, which are sampled over <sup>177</sup> 24 h every third day.

## 4. Pseudo inversions

We first assess the capabilities and limitations of the GEOS-Chem inverse modeling 178 setup in idealized control conditions by designing inverse problems with known solutions. 179 Pseudo-observations are generated through application of the TES  $NH_3$  retrieval algorithm 180 to a simulated atmosphere from GEOS-Chem. The emissions used during this simulation 181 are designated as the true emissions. Sampling times, locations and error estimates reflect 182 those of actual TES observations. For these tests, 87 pseudo TES observations are used 183 from July 14 through 19, 2005, along roughly a dozen global survey transects crossing the 184 midwestern U.S.. 185

To test the inverse model,  $NH_3$  emissions parameters were initialized to values different 186 from the true emissions. In the first test, initial model emissions are half of the true 187 value. Fig. 3(a) shows these values in black along with linear line slope m and  $r^2$ . After 188 optimization, the recovered emissions are unbiased and have a visible variance around the 189 true emissions of  $\sim 30\%$ , as shown in blue in Fig. 3(a). In a second test using the same 190 pseudo observations, the model emissions were initially biased high by a factor of 1.8 (Fig. 191 3(b)). The emissions recovered after optimization have a 20% high bias and again a 30% 192 variance about the true values. While the variance of the recovered emissions is similar 193

<sup>194</sup> in both tests, the assimilation starting with emissions that are initially too high is less <sup>195</sup> successful.

To further investigate the reasons for this asymmetry and the variance of the optimized 196 emissions, additional tests are performed to separate the possible impacts of inversion 197 error, retrieval bias and measurement error. In each of the following tests, the true emis-198 sions are used to initialize the inversion. The first test uses the same pseudo observations 199 as previously generated. This test again results in a high bias. As the same model state is 200 used to generate the pseudo observations as was used to initialize the inversion, this bias 201 can be attributed to a high bias in the retrieval itself. Retrieval bias, as explained further 202 in Shephard et al. [2011], is owing to the fact that the retrieval always selects a moderate 203 or polluted profile as an initial guess in order to avoid the null space of the radiative 204 transfer operator. As the optimal estimation algorithm iterates towards a solution, the 205 process may halt when values reach TES's detection threshold, resulting in a high bias. 206 To test this, the retrieval algorithm is modified to use only a moderate profile as an initial 207 guess. Pseudo observations generated using these profiles lead to slightly less high bias 208 in the inversion, at the cost of increased variance, see Fig. 4(b). As the magnitude of the 209 final bias in tests (a) and (b) are similar to those in the pseudo inversions, it seems that 210 the retrieval bias explains the bias exhibited in the pseudo inversions, and thus the inverse 211 model itself is not appreciably intrinsically biased. To isolate the impact of measurement 212 noise, the model profiles from the true model are applied with the same size error as 213 the measurement error, and then assimilated. These profiles, unlike the previous tests, 214 correspond directly to the true model and are not retreived profiles from the retrieval pro-215 cess. The impact of this measurement noise is only a slight adjustment in the emissions. 216

Thus, the variance exhibited in the pseudo inversions is intrinsic to the inversion process 217 itself, and would occur even if observations were perfect. This happens because there are 218 variations in emissions that lie in the null space of the forward model. In other words, 219 having some emissions too high and some emissions too low can result in indistinguishable 220 (to TES) distributions of  $NH_3$ . Overall, the pseudo observation tests lead us to conclude 221 that (1) measurement noise alone will not lead to unstable inversions (2) emissions that 222 are underestimated can likely be recovered (3) emissions that are overestimated will be 223 decreased, though this is countered by bias in the retrievals leading to overestimate of 224 emissions in conditions where the model emissions are initially too high and (4) that many 225 more iterations and observations would be necessary to reduce the variance of the emis-226 sions estimates from the truth, which will be as best  $\sim 30\%$ . While substantial, this is a 227 significant improvement over initial errors of  $\sim 100\%$ . 228

#### 5. TES assimilation

We next proceed to constrain U.S.  $NH_3$  sources using real observations. TES observations throughout 2006 - 2009 are compared to model estimates from a 2008 GEOS-Chem chemical transport model in a global  $2^{\circ} \times 2.5^{\circ}$  simulation. Four years of observations are necessary to provide sufficient spatial data coverage. Inter-annual comparisons of AMoN  $NH_3$  data indicate no substantial trends in this time period.

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 X - 14

<sup>239</sup> Of Freedom For Signal (DOFS) greater than 0.1, or DOFS may less than 0.1 but with <sup>240</sup> high (absolute value greater than 7 K) thermal contrast. We use the retrievals from <sup>241</sup> daytime only, since retrievals from the night time do not capture the diurnal variability <sup>242</sup> of the surface NH<sub>3</sub> concentrations. The TES retrievals are corrected by subtracting mean <sup>243</sup> biases. These biases are generated from the discrepancy between TES retrievals and true <sup>244</sup> profiles [*Shephard et al.*, 2011], and the mean biases are calculated as three types according <sup>245</sup> to the types of the a priori profiles (see Supplementary Figure 1).

<sup>246</sup> A key aspect of inverse modeling is regularization through inclusion of the penalty, or <sup>247</sup> background, term in the cost function. To define  $\mathbf{S}_a$ , uncertainties of ammonia in the emis-<sup>248</sup> sions inventories are assumed to be 100% of the maximum emissions of ammonia across <sup>249</sup> the globe. Uncertainties of SO<sub>2</sub> and NO<sub>x</sub> are 20% and 50% of the maximum emission of <sup>250</sup> corresponding sources across the globe. We also assume the errors are uncorrelated. Us-<sup>251</sup> ing an L-curve [*Hansen*, 1998] (see Supplementary Figure 2), we select the regularization <sup>252</sup> parameter ( $\gamma$ ) to be 124 for April, 100 for July, and 50 for October.

TES NH<sub>3</sub> observations are assimilated using the GEOS-Chem adjoint-based inversion. 253 The total initial and optimized ammonia emissions are shown in Fig. 5. The initial model 254 estimates of  $NH_3$  profiles are predominately lower than the observations. The optimized 255 emissions generally increase over the entire U.S.. There are large increases in southern 256 California in all three months. Other large increases are located in the central U.S., as 257 well as Mexico and Cuba. We do not have much information about  $NH_3$  in Mexico and 258 Cuba due to lack of measurement records there, but large (e.g. 15 ppb)  $NH_3$  RVMR values 259 are observed in April whereas the corresponding GEOS-Chem model estimates using the 260

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.

The RVMR represents a TES sensitivity weighted boundary layer averaged value with 263 the influence of a priori reduced as much as possible [Shephard et al., 2011]. We calculate 264 RVMR only for good retrievals which have high SNR and high thermal contrast. The 265 RVMR is also calculated for the model in those locations which have valid TES retrievals. 266 Fig. 6 shows the comparison of  $NH_3$  RVMR from TES and GEOS-Chem model before 267 and after the assimilation. It has  $500 \sim 700$  RVMR values in each month including values 268 from 4 years. The slope of the linear regression line increases in each month. However, the 269 modeled NH<sub>3</sub> RVMRs at low values change only slightly after the optimization in all three 270 months. We note however that these differences in RVMR do not reflect observation bias 271 or uncertainty, which contribute to the cost function. In order to show the locations which 272 have significant changes in RVMR, we consider spatial plots of the difference between the 273 TES and GEOS-Chem RVMR before and after the assimilation for each month (Fig. 7). 274 Initially, the model RVMRs are generally less than the TES RVMRs, as indicated by the 275 red points in the map. After the optimization, model RVMRs increase in many places. 276 Some of them are larger than the TES RVMRs, as indicated by the blue points in the 277 map and the overall model bias relative to TES is reduced. The discrepancies of TES 278 RVMRs and model RVMRs change from positive to negative in Southern California and 279 Central U.S. in all three months, consistent with the spatial plots showing large increases 280 of ammonia emissions in these locations (Fig. 5). 281

We next assess the sensitivity of these results to the assumed a priori emissions errors,  $\mathbf{S}_{a}$ . Table 1 shows the effects of varying a prior errors on the total optimized emissions of different species. We assume  $S_a(NH_3)$  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, see Table 1. However, absolute changes in total emissions of SO<sub>2</sub> and NO<sub>x</sub> increase slightly as their uncertainties increase relative to those of NH<sub>3</sub>, while changes in NH<sub>3</sub> total emissions decrease as uncertainty of NH<sub>3</sub> decreases.

## 6. Evaluation

In the next section, we compare model estimates using the optimized emissions to independent data sets not used during the inversion.

## 6.1. AMoN

We first consider a comparison of the posterior model results to AMoN NH<sub>3</sub> observations 292 (Fig. 8). Initially, the model broadly underestimates AMoN values. After optimization, 293 the NH<sub>3</sub> concentrations increase in each month. The  $R^2$  increases by 22.4% in April, 294 28.9% in July and 27.2% in October. The slope increases by 353.3% in April, 96.1% in 295 July and 77.1% in October. However, while the root mean square error (RMSE) decreases 296 by 13% in April and 9.5% in October, it increases by 77.6% in July. The normalized mean 297 bias (NMB) after the optimization decreases from -0.678 to -0.069 in April, increases from 298 -0.045 and -0.138 to 0.659 and 0.166 in July and October, respectively. Overall, the model 299 does a better job of capturing the range and variability of NH<sub>3</sub> at AMoN sites in April 300 and October, while in July, the model estimates are consistently biased high. 301

TES has a detection limit of about 1 ppb, and a positive bias of about 0.5 ppb [*Shephard et al.*, 2011]. We can see model values that are below 1 ppb do not change significantly

before and after the optimization in all three months (Fig. 8). The bias shown in Fig. 8 304 for July is much higher than 0.5 ppb. One possible reason may be the sampling bias of the 305 TES retrievals. This can be assessed by analyzing  $NH_3$  simulations from high resolution 306  $(12 \text{ km} \times 12 \text{ km})$  Community Multi-scale Air Quality (CMAQ) model simulations. Sur-307 face level  $NH_3$  concentrations throughout the U.S. are compared to concentrations from 308 locations corresponding to successful TES retrievals. The mean surface  $NH_3$  concentra-309 tion of CMAQ at locations which have successful TES retrievals is about 30% larger than 310 the mean value of that for the whole U.S.. This comparison is facilitated by the fact that 311 the TES footprint (5 km  $\times$  8 km) and CMAQ grid cells are similar in size. As shown in 312 Fig. 8, changes in large concentrations drive the optimization. A lack of TES observations 313 constraining low values may allow for initial model values that already overestimate low 314  $NH_3$  concentrations to become even higher in the optimized model. In future work, re-315 sampling the TES retrievals may be one way to decrease the sampling bias. Increasing the 316 model resolution may also improve our ability to model localized peak NH<sub>3</sub> concentrations 317 measured by TES and to match observations from AMoN. 318

## 6.2. 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.

Fig. 9 shows the comparison of modeled wet deposition with the NTN observations. 327 Generally, the inversion increases the wet deposition during all three months. Also corre-328 lation  $(R^2)$  improves in each month. The square of correlation coefficient  $(R^2)$  increases by 329 30.6% in April, 393.9% in July and 27.9% in October. In July, optimized values increase 330 a lot; the slope of the linear regression line increases from 0.162 to 0.65, but in April 331 and October changes in  $NH_x$  wet deposition were not as significant as in July. Compar-332 isons between GEOS-Chem and NTN observations are also shown in *Zhang et al.* [2012]. 333 They compare the  $NH_3$  wet deposition from GEOS-Chem at the  $0.5^{\circ} \times 0.67^{\circ}$  resolution 334 with NTN observations from 2006. No significant annual biases and little seasonal bias 335 are found in the comparison. Differences between this study and the present work are 336 the model resolution and the number of months per season included in the comparisons 337 (one vs three). We will investigate using additional months and higher resolution inverse 338 models as these become available. 339

## 6.3. IMPROVE

For an additional evaluation, we also compare the assimilated results with aerosol observations from IMPROVE in 2008. Fig. 10 shows that model optimization slightly decreases the sulfate concentrations and increases the nitrate concentrations, which facilitates increases in NH<sub>3</sub> concentrations to match TES observations. Still, the changes are small, and the sulfate concentration from the model has a reasonable correlation with the IM-PROVE observation before and after optimization in each month. Note that the outlier point 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 347 observation to the local volcano source. For nitrate, optimization does not help the com-348 parison with the observations, which are initially too high. As modeled NH<sub>3</sub> increases to 349 improve agreement with TES, leading to more nitrate formation, the model nitrate bias 350 becomes even higher compared to IMPROVE. One hypothesis is that  $HNO_3$  formation 351 from  $N_2O_5$  hydrolysis is too high in the model [Zhang et al., 2012]. In contrast Henze 352 et al. [2009] uses sulfate and nitrate to constrain the NH<sub>3</sub> emissions, which implies NH<sub>3</sub> 353 sources are too high. Thus, to achieve closure relative to all data sets, it is evident that 354 assessment of model error beyond NH<sub>3</sub> sources, in terms of scavenging efficiencies and 355  $HNO_3$  production, is required. 356

## 7. Conclusions

Here we have considered the potential for space-based observations of NH<sub>3</sub> to constrain 357 monthly average emissions factors. Initial tests using pseudo-observations show that un-358 der ideal conditions (i.e., a perfect model) using two-weeks worth of TES data, 70% of 359 the variance of the emissions can be constrained in terms of total magnitude. We then 360 proceed to assimilate TES observations for multiple years. Here we present a range of 361 constrained inventories and show their output relative to independent data sets. Gener-362 ally, model optimization increases  $NH_3$  concentrations and  $NH_x$  wet deposition; nitrate 363 and sulfate concentrations are not largely impacted. Overall, the model does a better job 364 of capturing the range and variability of NH<sub>3</sub> at AMoN sites in April and October, while 365 in July, the model estimates are consistently biased high. Compared to the wet depo-366 sition observations of NTN, optimization decreases the normalized mean bias (NMB) in 367

April, enhances the NMB in July and October, but overall leads to increased correlation of modeled and observed values.

Overall, we conclude that inverse modeling with satellite information indeed helps con-370 strain the ammonia emissions, particularly in strong source regions; additional observa-371 tions or higher resolution inverse models may be necessary to constrain low values. The 372 findings indicate that initial  $NH_3$  emissions inventory are broadly underestimated in sev-373 eral areas throughout the U.S.. This is at odds with previous inverse constraints based 374 on nitrate aerosol alone [Henze et al., 2009]. However, these results are consistent with 375 more recent works regarding levels in the U.S. and globally [Clarisse et al., 2009; Zhang 376 et al., 2012. The absolute extent of the emissions underestimation is still in question, as 377 the precise accuracy of the satellite observations is difficult to specify. A greater fraction 378 of peak values are included in the assimilation owing to satellite detection limits, lead-379 ing to a sampling bias, which may cause the model to overestimate the emissions after 380 optimization. Future work will consider bi-directional flux since it may explain some of 381 these results. Also, we will look at additional observations from intensive field campaigns. 382 Resampling TES retrievals will also included in our future work in order to decrease the 383 sampling bias. 384

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Figure 1. Validation of adjoint model sensitivities via comparison to finite difference (FD) results for week-long simulations. Solid lines are 1:1, dashed are regressions with given  $r^2$  and slope m.



Figure 2. Monitoring sites locations of AMoN (Ammonia Monitoring Network)



Figure 3. To test the inverse model,  $NH_3$  emissions parameters were initialized to values different than the true emissions. (a) initial starts from half of true; (b) initial starts from 1.8 times of true.

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Figure 4. Tests for the possible impacts of inversion error, retrieval bias and measurement error. (a) retrieval algorithm was using a polluted profile as an initial guess; (b) retrieval algorithm was modified to use a moderate a polluted profile as the initial guess; (c) model profiles from the true model were applied error of the same size as the measurement error.



Figure 5. NH<sub>3</sub> emissions from GEOS-Chem before and after the assimilation in U.S.



Figure 6. Comparison of  $NH_3$  Representative volume Mixing Ratio (RVMR) from TES and GEOS-Chem before and after the assimilation in U.S.



Figure 7. Difference of  $NH_3$  Representative volume Mixing Ratio (RVMR) between TES and GEOS-Chem before and after the assimilation in U.S.



Figure 8. Comparison of GEOS-Chem  $NH_3$  concentrations with observations from AMoN sites before and after the assimilation. 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 dash lines are 1:1.



Figure 9. Comparison of GEOS-Chem  $NH_x$  wet deposition with observations from NTN(NADP) sites before and after the assimilation.

Table 1. The effects of uncertainty error on the emissions of different species. Total emissions changes in U.S. for  $NH_3$ ,  $NO_x$ , and  $SO_2$  after different uncertainty errors applied to the parameters.  $S_a$  is error covariance estimates of parameters.  $E^0$  is the initial emissions.

Month	Uncertainties, $\mathbf{S}_a/MAX(E^0)$	Total emissions changes
	$SO_2 NO_x NH_3$	$\Delta SO_2 \ \Delta NO_x \ \Delta NH_3$
April	$20\% \ 50\% \ 100\%$	-11.9% -14.69% 112.99%
	$50\% \ 50\% \ 50\%$	-11.58% -15.39% 99.95%
July	$20\% \ 50\% \ 100\%$	-8.35% -4.24% 54.80%
	$50\% \ 50\% \ 50\%$	-10.23% -4.58% 53.26%
October	$20\% \ 50\% \ 100\%$	-3.56% -1.99% 36.07%
	$50\% \ 50\% \ 50\%$	-3.64% -2.41% 35.16%



Figure 10. Comparison of GEOS-Chem  $SO_4f$  and  $NO_3f$  concentrations with observations from IMPROVE sites before and after the assimilation.



**Supplementary Figure 1.** The average discrepancy between TES retrievals and true profiles [*Shephard et al.*, 2011]. The mean biases are calculated as three types according to the types of the a priori profiles. Red represents polluted type. green represents moderate polluted type and blue represents unpolluted type.



Supplementary Figure 2. The L-curve plot for selecting the regularization parameter  $(\gamma)$  in July. We select  $\gamma$  to be 100 for July.

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