Response to Reviewer #1

The authors would like to thank Reviewer 1 for the thoughtful comments and constructive suggestions about investigating further into the main uncertainties in the inversion process and adjusting the constraints on the inversion.

The discrepancies between the base model and satellite retrieved NO_2 columns arise primarily because of the lower modeled than observed NO_2 in rural areas. As noted in the review by Streets et al. (2013), wider spreads between urban and rural NO_2 in models than in satellite observations have been reported in other studies. We note in Section 3.3 our methods of alleviating such discrepancies by adjusting the $OH+NO_2$ reaction rate and correcting CAMx's low bias for upper tropospheric NO_2 based on the findings of earlier studies. However, additional model shortcomings likely remain (ENVIRON, 2013). In addition, while the NASA OMI NO_2 product, version 2.1, used in this study is the latest available retrieval, it does have some errors that vary spatially and temporally (Lamsal et al., 2014) and retrieval algorithms continue to be refined. It is beyond the scope of this study to fully diagnose or correct all the causes of uncertainties and discrepancies, and to quantify the possible errors in the retrieval processes over our modeling domain.

We have analyzed the influence on the region-based inversion caused by each of the adjustments we made either to the OMI retrieval product or the CAMx a priori simulations (Table R1). It shows that, in this case, missing emission sources (lightning, aviation and soil NO_x emissions) had the largest effect on the inversion results, especially in rural areas. Using the updated OMI product (with higher resolution) had the second largest effect on the inversion results. Since the new OMI NO_2 narrowed the urban-rural spread, the adjustments over most urban areas and rural areas decrease. The adjustments made in the CAMx model such as decreasing the $OH+NO_2$ reaction rate and adding an artificial NO_2 layer in the upper troposphere had smaller effects on the inversion results compared to the other changes (Table R1).

The seven inversion regions, five urban regions encompassed by two large rural regions, were carefully designed using sensitivity simulations to ensure NO_x emissions in each inversion region is mostly responsible for its NO_2 concentrations (Tang et al., 2013). In addition, the five urban regions were chosen to correspond to the urban ozone control regions that are relevant for regulatory attainment and emission control efforts in Texas SIP. The number of source categories is limited by the categorization of emissions in the TCEQ emission inventory. Visual inspection and pseudo-data testing of the categorized emissions were conducted to ensure that the source categories had sufficiently distinct spatial patterns to enable the Kalman filter to distinguish among the sources.

Table R1. Scaling factors for NO_x emissions in each region under alternate inversion cases.

Region-based inversion					
Emission region	Scaling factor (unitless)				
	Missing emission sources[a]	W/ additional emission sources[b]	Using updated OMI product[c]	Decreasing $OH+NO_2$ rate[d]	Adding a 40ppt layer[e]
HGB	1.31	1.03	1.21	1.18	1.11
DFW	1.32	1.14	1.04	0.98	0.97
BPA	1.90	1.75	1.70	1.72	1.49
NE Texas	1.40	0.56	1.12	1.20	1.10
Austin and San Antonio	1.90	1.70	1.21	1.24	1.15
N rural	2.88	1.98	1.45	1.48	1.24
S rural	3.84	1.72	1.25	1.15	0.98

a. Inversion conducted based on OMI v.2.1 and a priori simulation using base case NO_x emissions; adopted from Tang et al. (2013).
b. Inversion conducted based on OMI v.2.1 and a priori simulation using base case with added lightning and aviation and doubled soil NO_x emissions; adopted from Tang et al. (2013).
c. Inversion conducted based on updated OMI v.2.1 (using an a priori NO_2 profile generated from nested GEOS-Chem simulations with a 2005 emission inventory) and a priori simulation with NO_x emissions from b.
d. Inversion conducted based on updated OMI v.2.1 and a priori simulation with NO_x emissions from b and decreased $OH+NO_2$ reaction rate.
e. Inversion conducted based on updated OMI v.2.1 and a priori simulation from d with an added 40ppt layer in the upper troposphere.

Following are our responses to each of the reviewer's general and specific comments (shown in italics):

General comments:

1. *Both region-based and sector-based NOx emission adjustments were made in the paper, but only "sector-based" approach is mentioned in the abstract.*

A sentence "The region-based DKF inversion suggests increasing NO_x emissions in most regions, deteriorating the model performance in predicting ground-level NO_2 and O_3" was added to the abstract.

2. *In the Introduction section, more references should be added when discussing "studies using satellite NO2 measurements to create top-down NOx emissions for atmospheric modeling".*

References to Martin et al., (2003); Müller and Stavrakou, (2005); Jaeglé et al., (2005); Lin et al., (2010); Konovalov et al., (2006, 2008); Napelenok et al., (2008); Kurokawa et al., (2009); Zhao and Wang, (2009); Chai et al., (2009); and Zyrichidou et al., (2015) were added to the Introduction and Reference sections.

Specific comments:

1. *Please check equation 5 (last term).*

The last term is correct, because we need to consider the difference between prediction and observation at each iteration. The term "Sx" reflects adjustments after each iteration.

2. *Page 24491, line 23, "while it adds 50% ...": Should it be 49% ?*

We have changed the number to 49% in the sentence.

3. *Page 24493, line 16, "0.09 reduction in both modeled NMB ...": Is it 0.09 reduction in NMB? Table 5 shows that it is from 0.09 to -0.02.*

We have changed the sentence to "The model performance is also improved compared against P-3 measurements. For NO_2, NMB is reduced from 0.09 to -0.02, and NME is reduced by 0.09. For NO_y, NMB is reduced by 0.16 and NME is reduced by 0.11 (Table 5)."

4. *Table 3: Are the "overall" evaluation statistics based on the data from all regions listed above them? Then, the "overall" numbers do not seem to be right. The values should fall between the minimums and the maximums of the separate regions. For instance, in the last column, the NMEs are all above or equal to 0.30, but the overall NME is shown as 0.16.*

We double checked the numbers, and they are correct. The "overall" statistics are calculated based on data from all inversion regions, including two large rural regions that encompass the five urban regions presented in the tables. The OMI observations cover each grid cell, and thus the two large rural regions influence the overall statistics in Table 3. For Tables 4 and 6, there are few observation sites outside the five urban regions, making the overall values more similar to the urban values.

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Response to Reviewer #2

The authors would like to thank Reviewer 2 for the thoughtful comments and description of this paper as well written and as interesting to the regional air quality community.

Following are our responses to each of the reviewer's general and specific comments (shown in italics):

General comments:

1. *My concern with using GOES cloud fractions to adjust photolysis rates in the model is that it introduces an inconsistency with the modeled dynamics. Changing the cloud fraction directly affects the heat flux and therefore stability and the height of the boundary layer, both important drivers of ground level O3. I understand that it may take considerable effort to fully include satellite-observed cloud fractions in the chemistry and meteorological models. However, I think the authors should at least include a broader discussion of this topic and frame this analysis as a sensitivity study.*

We agree with the reviewer on this point. The model dynamic and aqueous phase chemistry haven't been adjusted by the GOES cloud fractions, and thus are inconsistent with the GOES-based photolysis rates. This work represents a sensitivity study of the impact of satellite-based photolysis rates but not a complete assimilation of satellite-based clouds. We have more fully discussed this limitation in the conclusion (page 24495, lines 13-15) by the sentences:

"The GOES-retrieved clouds applied here adjusted only the modeled photolysis rates, while modeled clouds continued to drive the dynamics and aqueous phase chemistry. This

inconsistency in the placement of clouds is similar to the approach of a previous study (Pour-Biazar et al., 2007). Thus, this work demonstrates a sensitivity study of using satellite-derived photolysis rates on model performance rather than a full integration of satellite-observed clouds into all aspects of the model. Future work could extend the use of GOES-retrieved clouds to also correct model dynamics and aqueous phase chemistry and investigate their impacts on NO_x and O_3 modeling."

2. *The last sentence of the introduction states that the manuscript will also present inverse modeling of VOC emissions, but there is no mention of this in the methodology. Some results of VOC inversions are presented in the Conclusions and the reader is directed to supplementary information. If this analysis is to be presented as one of the main aims of the manuscript, I think that the methodology and results should appear earlier in the manuscript.*

The reason we studied VOC is that we want to see if the uncertainties in VOC emissions will significantly affect our NO_x inversion results. Since this is not the main aim of this paper and the findings are not significant, we have moved the description of VOC emissions part in the introduction section (page 24480, lines 7-20) into the supplementary material. We keep the last sentence regarding the VOC work in the introduction section (page 22481, lines 1-2) and point it directly to the supplement.

3. *The last sentence of the 2.5.1 states that the "the OMI averaging kernels are not applied here." I think this is misleading because it implies that the vertical sensitivity of the retrieval and dependence on the a-priori profile are ignored. This is in fact not the case, as is shown in the supplement, and I would urge the authors to reword this.*

We have changed the sentence in page 24486, lines 12-14 to "Since applying OMI averaging kernels (Eskes and Boersma, 2003) may introduce more uncertainties to the CAMx-derived NO_2 VCD in this case (Supplement, Sect. 1), the CAMx modeled NO_2 are compared to the OMI NO_2 directly." to avoid any confusion.

Specific comments:

1. *Page 24478 Line 13: The term 'ozone design values' is not common outside of U.S. air quality policy circles. Thus a typical reader may not understand the implications of ozone design values above the NAAQS standard. It might be good here to give a brief definition of the term, or phrase this in a different way.*

We have removed the term "ozone design value" and rephrased the sentence in page 24478, lines 11-17 to "First and foremost, the Houston-Galveston-Brazoria (HGB) region and the Dallas-Fort Worth (DFW) region exceed the 2008 O_3 National Ambient Air Quality Standard (NAAQS) of 75 ppb and thus are both classified by US Environmental Protection Agency (US EPA) as O_3 non-attainment areas. Next, Beaumont-Port Arthur (BPA), Northeast Texas (NE Texas), and Austin and San Antonio regions require attention for closely approaching that standard (Gonzales and Williamson, 2011)."

2. *I think it's misleading to say that GOES measures cloud fraction. The 12 km cloud fraction is derived from the fraction of GOES subpixels that are deemed cloudy. This should at least be made more clear.*

We agree with reviewer on this point. The cloud fraction in the 12km model grid was integrated from GOES sub-pixels. The terms we use in our paper are "GOES-retrieved clouds" and "GOES-derived photolysis rates". We have changed the sentence in page 24483, lines 11-12 to "In this study, hourly GOES observations with integrated 12km cloud properties from sub-pixels have been used." to avoid any confusion.

References

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Gonzales, M. and Williamson, W.: Updates on the National Ambient Air Quality Standards and the State Implementation Plans for Texas, presented in TCEQ Trade Fair, Austin, TX, 4 May, 2011.

Pour-Biazar, A., McNider, R. T., Roselle, S. J., Suggs, R., Jedlovec, G., Byun, D. W., Kim, S., Lin, C. J., Ho, T. C., Haines, S., Dornblaser, B., and Cameron, R.: Correcting photolysis rates on the basis of satellite observed clouds. J. Geophys. Res., 112, D10302, doi: 10.1029/2006JD007422, 2007.

List of changes in the revised manuscript:

1. A sentence "The region-based DKF inversion suggests increasing NO_x emissions in most regions, deteriorating the model performance in predicting ground-level NO_2 and O_3" was added to the abstract.
2. References to Martin et al., (2003); Müller and Stavrakou, (2005); Jaeglé et al., (2005); Lin et al., (2010); Konovalov et al., (2006, 2008); Napelenok et al., (2008); Kurokawa et al., (2009); Zhao and Wang, (2009); Chai et al., (2009); and Zyrichidou et al., (2015) were added to the Introduction (page 24479, line 15) and Reference sections.
3. The number of "50%" in Page 24491, line 23 was revised to "49%".
4. The sentence in page 24493, lines 15-17 was revised to "The model performance is also improved compared against P-3 measurements. For NO_2, NMB is reduced from 0.09 to -0.02, and NME is reduced by 0.09. For NO_y, NMB is reduced by 0.16 and NME is reduced by 0.11 (Table 5)."
5. The sentences "The GOES-retrieved clouds applied here adjusted only the modeled photolysis rates, while modeled clouds continued to drive the dynamics and aqueous phase chemistry. This inconsistency in the placement of clouds is similar to the approach of a previous study (Pour-Biazar et al., 2007). Thus, this work demonstrates a sensitivity study of using satellite-derived photolysis rates on model performance rather than a full integration of satellite-observed clouds into all aspects of the model. Future work could extend the use of GOES-retrieved clouds to also correct model dynamics and aqueous phase chemistry and investigate their impacts on NO_x and O_3 modeling." were added to Conclusion (page 24495, line 14).

6. The description of VOC emissions part in the introduction section (page 24480, lines 7-20) was moved to the supplement.
7. The sentence in page 24486, lines 12-14 was revised to “Since applying OMI averaging kernels (Eskes and Boersma, 2003) may introduce more uncertainties to the CAMx-derived NO_2 VCD in this case (Supplement, Sect. 1), the CAMx modeled NO_2 are compared to the OMI NO_2 directly.”
8. The sentences in page 24478, lines 11-17 were rephrased to “First and foremost, the Houston-Galveston-Brazoria (HGB) region and the Dallas-Fort Worth (DFW) region exceed the 2008 O_3 National Ambient Air Quality Standard (NAAQS) of 75 ppb and thus are both classified by US Environmental Protection Agency (US EPA) as O_3 non-attainment areas. Next, Beaumont-Port Arthur (BPA), Northeast Texas (NE Texas), and Austin and San Antonio regions require attention for closely approaching that standard (Gonzales and Williamson, 2011).”
9. The sentence in page 24483, lines 11-12 was revised to “In this study, hourly GOES observations with integrated 12km cloud properties from sub-pixels have been used.”

Influence of satellite-derived photolysis rates and NO_x emissions on Texas ozone modeling

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Abstract

Uncertain photolysis rates and emission inventory impair the accuracy of state-level ozone (O_3) regulatory modeling. Past studies have separately used satellite-observed clouds to correct the model-predicted photolysis rates, or satellite-constrained top-down NO_x emissions to identify and reduce uncertainties in bottom-up NO_x emissions. However, the joint application of multiple satellite-derived model inputs to improve O_3 State Implementation Plan (SIP) modeling has rarely been explored. In this study, Geostationary Operational Environmental Satellite (GOES) observations of clouds are applied to derive the photolysis rates, replacing those used in Texas SIP modeling. This changes modeled O_3 concentrations by up to 80ppb and improves O_3 simulations by reducing modeled normalized mean bias (NMB) and normalized mean error (NME) by up to 0.1. A sector-based discrete Kalman filter (DKF) inversion approach is incorporated with the Comprehensive Air Quality Model with extensions (CAMx)-Decoupled

Direct Method (DDM) model to adjust Texas NO_x emissions using a high resolution Ozone Monitoring Instrument (OMI) NO_2 product. The discrepancy between OMI and CAMx NO_2 vertical column densities (VCDs) is further reduced by increasing modeled NO_x lifetime and adding an artificial amount of NO_2 in the upper troposphere. The region-based DKF inversion suggests increasing NO_x emissions by 10-50% in most regions, deteriorating the model performance in predicting ground NO_2 and O_3, while the sector-based DKF inversion tends to scale down area and non-road NO_x emissions by 50%, leading to a 2-5ppb decrease in ground 8-h O_3 predictions. Model performance in simulating ground NO_2 and O_3 are improved using sector-based inversion constrained NO_x emissions, with 0.25 and 0.04 reductions in NMBs and 0.13 and 0.04 reductions in NMEs, respectively. Using both GOES-derived photolysis rates and OMI-constrained NO_x emissions together reduces modeled NMB and NME by 0.05 and increases the model correlation with ground measurement in O_3 simulations and makes O_3 more sensitive to NO_x emissions in the O_3 non-attainment areas.

1. Introduction

Tropospheric O_3 is a secondary air pollutant formed via the reactions between nitrogen oxides (NO_x = NO + NO_2) and volatile organic compounds (VOCs) with heat and sunlight (Seinfeld and Pandis, 2006). Eastern Texas is one of the most populous areas in the United States and has been suffering from O_3 pollution for decades due to large anthropogenic emission sources such as motor vehicles, petrochemical facilities, and coal-burning power plants with unique meteorological conditions of extended heat and humidity and intense solar radiation (Kleinman et al., 2002; Ryerson et al., 2003; Daum et al., 2004; Rappenglück et al., 2008; Kim et al., 2011; Zhou et al., 2014).

In eastern Texas, several regions require careful air quality planning for O_3 reductions. First and foremost, the Houston-Galveston-Brazoria (HGB) region and the Dallas-Fort Worth (DFW) region exceed the 2008 O_3 National Ambient Air Quality Standard (NAAQS) of 75 ppb and thus are both classified by US Environmental Protection Agency (US EPA) as O_3 non-attainment areas. Next, Beaumont-Port Arthur (BPA), Northeast Texas (NE Texas), and Austin and San Antonio regions require attention for closely approaching that standard (Gonzales and Williamson, 2011).

To comply with the O_3 NAAQS, the U.S. EPA requires the Texas Commission on Environmental Quality (TCEQ) to identify regulatory strategies using photochemical air quality models for attaining the O_3 standard in non-attainment areas. However, model uncertainties may impair the accuracy of model performance and potentially misdirect emission control strategies (Fine et al., 2003; Digar and Cohan, 2010; Simon et al., 2012). Recent studies show that uncertain bottom-up emission inventories and modeled photolysis rates are two leading uncertainties in O_3 modeling (Deguilaume et al., 2007; Digar et al., 2011) and can significantly impact simulated O_3 concentrations and their sensitivities in Texas (Cohan et al., 2010; Xiao et al., 2010). Hence, identifying and reducing these uncertainties are essential to ensuring the reliability of regulatory decision making.

Direct measurements of emissions and photolysis rates are spatially limited and impractical to perform covering the entire modeling domain. However, satellite-based measurements provide a valuable opportunity to observe some atmospheric parameters and air pollutants from space and generate a rich measurement dataset with great spatial coverage. Pour-Biazar et al. (2007) used the GOES-based cloud information to reproduce photolysis rates in the

Community Multiscale Air Quality (CMAQ) model. Results showed large differences between model-predicted and satellite-derived photolysis rates, leading to significant changes in modeled O_3 concentrations. Guenther et al. (2012) found that the Weather Research and Forecasting (WRF) and MM5 models, which are usually used to generate meteorological fields for CAMx or CMAQ, underpredict cloud fractions, leading to more modeled solar radiation reaching the ground and overestimations of modeled photolysis rates and sunlight-sensitive biogenic emissions.

Studies using satellite NO_2 measurements to create top-down NO_x emissions for atmospheric modeling have also shown promising results (Streets et al., 2013; Martin et al., 2003; Müller and Stavrakou, 2005; Jaeglé et al., 2005; Lin et al., 2010; Konovalov et al., 2006, 2008; Napelenok et al., 2008; Kurokawa et al., 2009; Zhao and Wang, 2009; Chai et al., 2009; Zyrichidou et al., 2015). Most recently, Tang et al. (2013) performed region-based DKF inversions using OMI NO_2 data to adjust NO_x emission inventory used in Texas SIP modeling; however, results showed that the region-based DKF inversions with National Aeronautics and Space Administration (NASA) OMI NO_2 standard product, version 2, tended to scale up the NO_x emission inventory by factors of 1.02 to 1.84 and deteriorated model performance as evaluated by ground NO_2 and O_3 monitors.

A challenge of using satellite data for inverse modeling is that atmospheric models are primarily evaluated based on ground-level data, and may not accurately simulate pollutants aloft. Several studies (Hudman et al., 2007; Henderson et al., 2011; Allen et al., 2012; ENVIRON, 2013) have demonstrated that models tend to underestimate upper tropospheric NO_2 level even after lightning and aviation NO_x sources are included. Though the reason is unclear,

underestimation could result from errors in the chemical mechanism in simulating NO_x sinks (Mollner et al., 2010; Henderson et al., 2012, Lin et al., 2012, Stavrakou et al., 2013). Efforts to eliminate low bias for upper tropospheric NO_2 simulations over Texas have been unsuccessful to date (ENVIRON 2013). Another discrepancy often noted between models and satellite data is a narrower spread between urban and rural NO_2 in satellite observations (Streets et al., 2013). Recently developed high resolution OMI NO_2 retrievals increase the rural-urban spread, which may decrease the difference between models and satellite observations.

In this work, first, GOES-derived photolysis rates are applied to the CAMx model, and the influence on the modeled NO_2 and O_3 is investigated. Second, the model shortcomings of underestimating upper tropospheric and rural NO_2 demonstrated in Tang et al. (2013) are further addressed by comparing with aircraft measurements and reducing the reaction rate constant of the reaction OH + NO_2 to increase modeled NO_x lifetime. Third, the sector-based DKF inversion using the recently developed NASA high resolution OMI NO_2 product to Texas NO_x emissions is explored and compared to the region-based DKF inversion. In addition, inverse modeling is extended to adjust Texas VOC emissions via directly comparing modeled VOC concentrations with ground observations (Supplement, Sect. 4).

2. Methodology

2.1 CAMx modeling

CAMx version 5.3 (ENVIRON, 2010) with the Carbon Bond version 2005 (CB-05) chemical mechanism was used to simulate a SIP modeling episode developed by TCEQ for the HGB O_3 attainment demonstration (Fig. 1) from 13 August to 15 September 2006, coinciding with the intensive measurement campaign TexAQS 2006. The meteorology fields were modeled by the

NCAR/Penn State (National Center for Atmospheric Research/Pennsylvania State University) Mesoscale Model, Version 5, release 3.7.3 (MM5v.3.7.3) (Grell et al., 1994), and the boundary conditions were taken from the Model for Ozone and Related Chemical Tracers (MOZART) global model (ENVIRON, 2008). The base case emission inventory for HGB SIP modeling was provided by TCEQ (TCEQ, 2010). Lightning and aviation NO_x emissions were added into the base emission inventory. The lightning NO_x emission is developed based on the measured National Lightning Detection Network (NLDN) data with intra-cloud flashes assumed to be three times of cloud-to-ground flashes and 500 moles NO emissions per flash (Kaynak et al., 2008), and the aviation NO_x emissions, obtained from the Emission Database for Global Atmospheric Research (EDGAR), were placed at the model height of 9km. The soil NO_x emission was doubled from its base value because the Yienger and Levy method (YL95) (Yienger and Levy, 1995) has been found to underpredict soil NO_x by around a factor of 2 over the United States (Hudman et al., 2010). More details about the model inputs and configurations, the emission inventory development, and evaluations of model meteorological inputs can be found in Tang et al. (2013).

2.2 GOES-derived photolysis rates

The photolysis rate calculations in CAMx include two steps (ENVIRON, 2010). First, a Tropospheric Ultraviolet and Visible (TUV) Radiation Model developed by the National Center for Atmospheric Research (NCAR) is used to generate a multi-dimensional table of clear sky photolysis rates (Madronich, 1987; NCAR, 2014) as inputs for the CAMx model as shown in Eq. (1).

Clear sky photolysis rates (s^{-1}) are calculated as:

$$J = \int_{\lambda_1}^{\lambda_2} \sigma(\lambda)\varphi(\lambda)F(\lambda)d\lambda \quad (1)$$

where σ(λ) (*m^2/molecule*) is the absorption cross-section, λ is the wavelength (*μm)*, φ(λ) is the quantum yield (*molecules/photon*), and *F(λ)* is the actinic flux (*photons/m^2/s/μm*).

Second, the tabular clear sky photolysis rates are interpolated into each grid cell in the modeling domain and adjusted based on cloud information generated by the meteorology model in standard operational procedure, as shown in Eqs. (2) and (3). Below the cloud, photolysis rates are adjusted as (Chang et al., 1987):

$$J_{below} = J_{clear}\left[1 + f_c(1.6\ tr_c \cos(\theta) - 1)\right] \quad (2)$$

Above the cloud, photolysis rates are modified as:

$$J_{above} = J_{clear}\left[1 + f_c \cos(\theta)(1 - tr_c)\right] \quad (3)$$

where f_c is the cloud fraction for a grid cell, tr_c is cloud transmissivity at each model grid layer, and θ is the solar zenith angle.

In CAMx, tr_c is calculated using Eq. (4) (Stephens, 1978),

$$tr_c = \frac{5 - e^{-\tau_c}}{4 + 3\tau_c(1 - \beta)} \quad (4)$$

where τ_c is the cloud optical depth simulated in the model and β is the scattering phase-function asymmetry factor assumed to be 0.86 (Chang et al., 1987). The f_c in each grid cell is predicted by the MM5 model.

GOES-observed cloud properties recover f_c and broadband tr_c, which can be used directly in Eqs. (2) and (3) to adjust photolysis rates below and above the clouds, bypassing the need for estimating those values in the model. Within the cloud, the photolysis rates are adjusted via the interpolation of calculated values between satellite-retrieved cloud top and model-estimated cloud base. GOES is capable of measuring cloud properties with spatial resolution down to 1-km and temporal resolution down to an hour or less (Haines et al., 2004), ensuring the sufficient spatial and temporal data coverage for the modeling episode. In this study, hourly GOES observations with integrated 12km cloud properties from sub-pixels have been used. However, due to the satellite data availability, satellite-retrieved f_c and broadband tr_c may not be available in the early morning and late afternoon. In such cases, the f_c and tr_c generated by standard operational procedures in CAMx will be used. More details regarding satellite retrievals of f_c and tr_c can be found at Pour-Biazar, et al. 2007.

2.3 Emission regions and sectors for the inversion

As in Tang et al. (2013), an inversion region inside the 12km model domain is designed for both region-based and sector-based DKF inversions, including five urban areas HGB, DFW, BPA, NE Texas, and Austin and San Antonio, surrounded by a north rural area (N rural) and a south rural area (S rural) (Fig. 1).

Six separate NO_x emission sectors, area, non-road mobile, on-road mobile, biogenic, electric generating units (EGU) and non-EGU point sources are provided by TCEQ. Lightning and aviation NO_x emission sectors were developed in Tang et al. (2013) and added into base emission inventory as independent elevated sources (Table 1). Area sources, including small-scale industry and residential sources such as oil and gas production, gas stations and restaurants,

contribute 10% of total emissions in the entire inversion region and 25% in NE Texas in the base inventory. Non-road sources, including construction equipment, locomotives and commercial marine, contribute 14% overall. Mobile source emissions by on-road vehicles contribute 27% of total NO_x emissions and dominate in the cities such as HGB and DFW. The biogenic NO_x source is from soil emissions, which contribute 16% of total NO_x emissions but dominate in remote regions. Lightning and aviation sources contribute 8% and 6% to the total emission, respectively. Non-EGU point sources such as refineries, big boilers and flares, contribute 40% of NO_x emissions in BPA and 21% in HGB, the two regions with most of the petrochemical industries. EGU point emissions are from major power plants with the hourly NO_x emissions measured by continuous emissions monitoring (CEM) systems, which are considered the most accurate NO_x emission source in the bottom-up emission inventory. Thus, in this study, EGU NO_x emissions are assumed to be correct and are not adjusted by DKF inversions.

NO_2 sensitivities to NO_x emission in each emission sector used in the following sector-based DKF inversions are calculated through DDM (Fig. 5). The biogenic, lightning, and non-EGU point sources have their own spatial patterns that differ from the other emission sectors. For example, the aviation source shows strong sensitivity centered from the DFW and HGB regions and slowly spreading elsewhere. The sensitivities from the area, non-road and on-road sources have similar spatial patterns concentrated in urban areas due to strong anthropogenic activities, while the on-road source can be distinguished by the strong highway emissions. Previous studies (Rodgers, 2000; Curci et al., 2010) indicated that the inversion results would be ill-conditioned to estimate strongly overlapped sources. Therefore, in this study, the area and non-road sources are grouped as a single sector in the DKF inversions.

2.4 DKF Inversion

Two DKF inversion approaches, region-based and sector-based, are applied in this study to create top-down NO_x emissions for Texas. The procedure of incorporating DKF method into the CAMx-DDM model was described in detail in Tang et al. (2013).

The DKF inversion process (Prinn 2000), driven by the difference between the measured NO_2 ($\mathbf{C}_{NO_2}^{observed}$) and the modeled NO_2 ($\mathbf{C}_{NO_2}^{predicted}$), seeks the optimal emission perturbation factors ($\hat{\mathbf{x}}$) (a posteriori) by adjusting NO_x emissions in each designated emission region or sector iteratively until each a priori emission perturbation factor ($\mathbf{x}^-$) converges within a prescribed criterion, 0.01.

$$\hat{\mathbf{x}}_{NO_x} = \mathbf{x}^-_{NO_x} + \mathbf{P}^-_{NO_x}\mathbf{S}^T(\mathbf{S}\,\mathbf{P}^-_{NO_x}\mathbf{S}^T + \mathbf{R}_{OMI})^{-1}(\mathbf{C}^{observed}_{NO_2} - \mathbf{C}^{predicted}_{NO_2} - \mathbf{S}\,\mathbf{x}^-_{NO_x}) \quad (5)$$

S in Eq. (5), calculated via DDM in this study, is the first-order semi-normalized sensitivity matrix of NO_2 concentrations to either region-based or sector-based NO_x emissions. The uncertainty value in the measurement error covariance matrix (**R**) for the OMI observed NO_2 is set to 30% (Bucsela et al., 2013) for all diagonal elements. The uncertainties adopted from Hanna et al. (2001) provide the values for each of the diagonal elements in the emission error covariance matrix (**P**). A value of 100% is assigned to each emission region, and to the area, non-road, aviation, on-road, and biogenic emission sectors, but a value of 50% is assigned to the non-EGU point emission sector. The uncertainty of lightning NO_x emissions was estimated in recent studies, ranging from 30% (Martin et al., 2007) to 60% (Schumann and Huntrieser, 2007) on a global scale; thus, the uncertainty value in the lightning sector is set to 50% here. The off-

diagonal elements in **P** are set to zero since each emission component is assumed to be independent.

2.5 NO_2 observations

2.5.1 Satellite NO_2 observations

The Dutch-Finnish OMI aboard the NASA Aura satellite measures daily NO_2 at around 13:40 local time (LT) with the highest spatial resolution of 13×24 km^2 at nadir viewpoint (Levelt et al., 2006a, b; Boersma et al., 2007). Tang et al. (2013) used the NASA OMI standard, version 2.1 (Bucsela et al., 2013; Lamsal et al., 2014) NO_2 retrieval with an a priori profile generated from the Global Modeling Initiative (GMI) model to conduct inverse modeling, and reported an overestimation of NO_2 levels in rural areas. More recently, a high resolution OMI NO_2 retrieval was developed based on the NASA standard product, version 2.1, but using an a priori NO_2 profile generated from nested GEOS-Chem simulations (0.5°×0.666°) with a 2005 emission inventory. Because the emission inventory used in GEOS-Chem simulations includes lightning and other elevated sources, it may better represent the upper tropospheric NO_2 in the retrieval; hence, in this study, the high resolution NASA retrieval is chosen for the DKF inversions. In the high resolution NASA product, only the OMI pixels with sizes less than 16×40km^2 (scan position 10-50) in the clear-sky condition (cloud radiance fraction < 0.5) are selected in creating the gridded data at 0.1°×0.1° resolution and then mapped to the 12km CAMx modeling domain. Since applying OMI averaging kernels (Eskes and Boersma, 2003) may introduce more uncertainties to the CAMx-derived NO_2 VCDs in this case (Supplement, Sect. 1), the CAMx modeled NO_2 are compared to the OMI NO_2 directly (Supplement, Sect. 1).

2.5.2 Ground and P-3 aircraft NO_2 observations

The CAMx simulated NO_2 is evaluated by both ground and aircraft measurements. The ground-level NO_2 measurements data are taken from the U.S. EPA Air Quality System (AQS) NO_2 ground monitoring network (Fig. 1) (http://www.epa.gov/ttn/airs/airsaqs/). The correction factors (Lamsal et al., 2008; Tang et al., 2013) are applied to the ground measured NO_2 before comparing with the modeled results due to the measurement artifacts in the heated molybdenum catalytic converter used by AQS NO_2 monitors.

The NOAA P-3 aircraft measurements (http://www.esrl.noaa.gov/csd/tropchem/2006TexAQS/) are available on 31 August, 11 September, 13 September, and 15 September 2006 in our modeling period. The NO_2 was measured by UV photolysis converter-chemiluminescence (Ryerson et al., 2000), and NO_y was measured by Au converter-chemiluminescence (Ryerson et al., 1999) aboard the P-3 aircraft, from ground to approximately 5km aloft and with a time resolution of 1-second; thus, hourly averaged P-3 NO_2 and NO_y are calculated to compare with the modeled data at corresponding time and grid cells.

2.5.3 NASA DC-8 flight NO_2 observations

The NO_2 measured by NASA DC-8 flights (http://www-air.larc.nasa.gov/cgi-bin/arcstat) during the Intercontinental Chemical Transport Experiment-North America (INTEX-NA) field campaign in 2004 (Singh et al., 2006) is used in this study to evaluate the modeled NO_2 vertical profile, especially in the upper troposphere. The DC-8 flight NO_2 measurements were made on a total of 18 days from 1 July to 14 August 2004, spanning from 7:00 to 20:00 CST with 1-second resolution. The NO_2 was measured by the Thermal Dissociation-Laser Induced Fluorescence (TD-LIF) instrument. TD-LIF measurements of NO_2 can be impacted by methyl peroxy nitrate

($CH_3O_2NO_2$) and HO_2NO_2 in a temperature-dependent manner; thus, corrections based on the method of Browne et al., (2011) are applied before comparing with the modeled profile. The modeled NO_2 in grid cells within the 36km domain are used to match the measurement data in space, and then all measurement data at each model layer are averaged over all measurement time to compare with the monthly 12-h (7:00-20:00LT) averaged modeled data at the corresponding layer. Although the measurements took place in 2004 and our modeling period is in 2006, we assume the inter-annual variation is insignificant because the upper tropospheric NO_2 is mainly contributed by natural sources and cross-tropopause transport.

3. Results and Discussion

3.1 Impact of GOES-derived photolysis rates on modeled NO_2 and O_3

The GOES-retrieved cloud fractions and broadband transmissivity as described in section 2.2 are used to adjust the photolysis rates in CAMx. To investigate the impact from GOES-derived photolysis rates, the differences of modeled ground-level NO_2 photolysis rate (J_{NO2}), NO_2, and O_3 between CAMx modeling with and without the GOES-retrieved cloud fractions and transmissivity are calculated.

Using GOES-observed clouds corrects the cloud underprediction issue in the current meteorological models (Pour-Biazar et al., 2007; Guenther et al., 2012; ENVIRON 2012), making J_{NO2} decreases over most of the domain in this study. While on the average there is a domain-wide reduction in J_{NO2}, the impact on O_3 production is not uniform (Figs. 2 and 3), mostly paired with the NO_x emission distributions. The general impact of using GOES observations is that where the J_{NO2} decreases, modeled NO_2 increases, and O_3 decreases (Figs. 2 and 3), indicating that slower photochemical activity inhibits O_3 formation and thus consumes

less NO_2, and vice versa. However, an exception occurs at places close to the Houston Ship Channel, showing that although the J_{NO2} decreases, modeled NO_2 still decreases (Fig. 3b) and O_3 slightly increases (Fig. 3c). This is probably caused by the availability of other pathways for consuming NO_x in the VOC-rich environment, and the inhibition of NO regeneration due to reduction in photochemical activity. The largest discrepancy of 80ppb in modeled O_3 occurs at 13:00 on 2 September 2006 over the DFW region during the modeling period. At that time, GOES-based modeling showed up to 6 times higher J_{NO2} (reaching approximately $36s^{-1}$), and 10ppb lower NO_2 in this region (Fig. 2). However, the differences in modeled J_{NO2}, NO_2, and O_3 are much more moderate on a monthly 8-h (10:00-18:00) averaged basis, reaching only up to $3s^{-1}$ for J_{NO2}, 0.6ppb for NO_2, and 3ppb for O_3, with largest discrepancies in the HGB region (Fig. 3). For the changes in O_3 sensitivities, approximately 6% less J_{NO2} on a domain-wide makes modeled O_3 overall less sensitive to NO_x emissions (Fig. 3d) and more sensitive to VOC emissions (Fig. 3e).

The modeled daily 8-h (10:00-18:00LT) NO_2 and O_3 using either satellite-derived or base model photolysis rates are evaluated by AQS measured data for the entire modeling period. The positive changes in spatiotemporal correlation (R^2) and negative changes in NMB and NME indicate that satellite-derived photolysis rates improved model performance (Fig. 4). For O_3 simulations (Fig. 4 right), the difference in R^2 increases 1% on average and reaches up to 7% on 26 August, while the differences in NMBs and NMEs decrease 1% on average and reach up to 10% on 11 September, suggesting the satellite-corrected photolysis rates improve the model performance in simulating ground O_3. However, NMB and NME for NO_2 simulations (Fig. 4 left) do not improve despite an increase in R^2, probably because other uncertainties in the model and measurements may have a larger impact on NO_2 performance.

3.2 Pseudodata test for the sector-based DKF inversion

A controlled pseudodata test was performed in Tang et al. (2013) to test the applicability of the DKF inversion to adjust the NO_x emission in each inversion region with the CAMx-DDM model. This showed that the DKF method adjusted the perturbed NO_x emission in each region accurately back to its base case. In this study, a similar controlled pseudodata test is conducted to test the applicability of the sector-based DKF inversion with CAMx-DDM.

The pseudodata test for the sector-based DKF inversion is conducted on 10 modeling days (13 August to 22 August), but the modeling results from the first 3 days are discarded to eliminate the model initialization error. A 7-day (16 August to 22 August) averaged modeled NO_2 VCDs at 13:00-14:00LT with the base case NO_x emission inventory is treated as a pseudo-observation, and the one using perturbed NO_x emissions in six emission sectors with known perturbation factors ranging from 0.5 to 2.0 (Fig. 6) is used as a priori case. As described in section 2.3, the area and non-road emission sources are considered as one sector (ARNR), and EGU point source is excluded from the inversion. The emission uncertainties are set to 50% for the non-EGU and lightning sectors and to 100% for the others. The measurement error for the pseudo-observation is set to 30%.

The pseudodata test results (Fig. 6 top) show that the a posteriori modeled NO_2 closely matches the base case modeled value, indicating the DKF inversion is capable of correcting the perturbed NO_x emissions in each emission sector. The sensitivity analysis results (Fig. 6 bottom) illustrate that the inversions are insensitive to both emission and observation error covariance matrices for the pseudo-cases.

3.3 A priori NO_2 VCDs

The a priori NO_x emission inventory used in this study is based on the TCEQ base case emission inventory with added lightning and aviation and doubled soil NO_x emissions (Tang et al., 2013). The reaction rate constant of the reaction NO_2 + OH in CB05 chemical mechanism is reduced by 25% based on Mollner et al. (2010); this tends to increase NO_x lifetime and transport to rural regions.

To evaluate the extent to which the addition of lightning and aviation NO_x closes the gap between observed and modeled NO_2 in the upper troposphere noticed by Napelenok et al. (2008), the modeled NO_2 vertical profile is compared with INTEX-NA DC-8 measured NO_2 profiles from the ground to the free troposphere. The comparison (Fig. 7 left) shows that CAMx with the a priori emission inventory strongly overestimates NO_2 near the ground, reasonably agrees with DC-8 NO_2 measurements from 1km to 5km, slightly overestimates NO_2 from 6km to 9km, and slightly underestimates NO_2 from 10km to 15km. The modeled NO_2 profile is further evaluated by the P-3 measured NO_2 from ground to 5km (Fig. 7 right), showing the same pattern of the overestimated surface NO_2 and good agreement with aircraft observations from 1km-5km. The injection of the aviation NO_x into a single model layer at altitude 6km to 9km rather than more broadly distributed vertically probably causes the overestimation of modeled NO_2 compared to DC-8 at that altitude (ENVIRON, 2013). A low bias of modeled NO_2, approximately 40ppt, exists in the upper troposphere, from 10km to 15km altitude, which is the CAMx model top layer. Similar low bias of the modeled NO_2 in the upper troposphere compared to the DC-8 measurement also has been found in Allen et al. (2012). Because the low bias in the upper troposphere may arise from model uncertainties other than those associated with emissions (Henderson et al., 2011; 2012), we follow the adjustment approach of Napelenok et al. (2008)

and add 40ppt NO_2 homogeneously to the top layer (10-15km) of the model results when computing the CAMx NO_2 VCDs.

Although the revised CB05 chemical mechanism and artificially added upper tropospheric NO_2 increase modeled NO_2 VCDs in the inversion region by an average of 13% (Supplement, Sect. 2), CAMx modeled NO_2 VCDs remain an average of 2×10^{14} molecules/cm^2 less than OMI observations in rural regions (Fig. 8c).

3.4 Top-down NO_x emissions constrained by DKF inversions

The DKF inversions with OMI NO_2 are performed to constrain NO_x emissions in each designated emission region and emission sector. To ensure sufficient spatial coverage, a monthly averaged OMI NO_2 VCD (13 August to 15 September) is calculated and paired with the corresponding modeled NO_2 VCD at satellite passing time (13:00-14:00LT). The DKF inversions are then conducted with 2116 data points covering every grid cell in the inversion region, and the hourly a priori NO_x emissions are adjusted iteratively until the inversion process converges.

3.4.1 Region-based DKF inversion

The region-based DKF inversion is conducted to adjust the NO_x emissions in each inversion region. The inversion results suggest to moderately adjust the a priori NO_x emissions in most regions with scaling factors ranging from 0.97 to 1.49 (Table 2) and increases NO_2 VCDs by 8% toward OMI measurement over the inversion region (Fig. 8d). Because this inversion is based on a new OMI-retrieved and an improved a priori NO_2 VCDs, the required adjustments in each inversion region are much lower compared to the results in Tang et al. (2013) with scaling factors ranging from 0.56 to 1.98 and 30% increased NO_2 VCDs.

The model performance is then evaluated by the ground and aircraft measurements. The DKF inversion adjusts DFW NO_x emissions by only 3%, while it adds 49% to BPA emissions and less than 15% to other urban regions. The NMB and NME of the a posteriori modeled NO_2 VCDs decrease in every urban area and are reduced from -0.11 to -0.05 and from 0.17 to 0.16 overall compared to OMI. The spatial correlations between monthly averaged OMI and CAMx NO_2 VCDs (R^2) are improved only in the BPA and Austin and San Antonio areas, but the overall region-wide performance is improved (Table 3). The modeled NO_2 with a priori NO_x emissions overpredicts ground-level NO_2 (Table 4); hence, the increase in NO_x emissions at most urban places suggested by the inversion actually deteriorates the ground-level NO_2 simulations in all urban areas except in the DFW region. The modeled NMB and NME of ground O_3 are reduced in the HGB and BPA regions, but not in DFW, probably because the increased NO_x in the first two regions titrates more ground O_3 at night and inhibits O_3 formation during the day, decreasing the O_3 concentrations which are already overestimated in the a priori simulation (Table 6). No improvements of model performance are found in simulating P-3 observed NO_2 and NO_y using the inverted NO_x emissions.

Applying a single scaling factor to an entire inversion region may not well capture the NO_x spatial distributions (Tang et al., 2013). Since DDM can also track the spatial relationship between modeled NO_2 concentrations and NO_x emissions in each emission sector, a sector-based DKF inversion can potentially serve as an alternative approach to constrain NO_x emissions in order to have more heterogeneous adjustments in each inversion region.

3.4.2 Sector-based DKF inversion

The sector-based DKF inversion is first conducted on six NO_x emission sectors: area and nonroad (ARNR), on-road, biogenic, aviation, lightning, and non-EGU points (Case I). The scaling factors generated by the inversion ranges from 0.54 to 4.10, with the largest scale-down in the ARNR sector and the largest scale-up in the aviation sector. The inversion reduces NO_x emission in the biogenic sector by 30% from the a priori inventory which had doubled soil NO_x from the base model. The inversion leaves on-road, lightning, and non-EGU points sectors nearly unchanged, applying less than 4% adjustments (Table 2). The NO_2 VCD is increased by only 6% toward OMI measurement over the inversion region in this case. Most of the increase in NO_2 VCDs occurs in rural areas, and some declines occur in urban areas (Fig 8e).

The NO_x emission in each inversion region is recalculated after applying adjustments to each emission sector, and model performance is evaluated by the ground and aircraft measurements. The scaling factors in each region now are different and closer to 1 than those generated by the region-based inversion, ranging from 0.86 in NE TX to 1.17 in DFW. The modeled NMB and NME in simulating OMI NO_2 are all decreased in five urban areas. Within the inversion region, the overall modeled NMB and NME are reduced from -0.11 to -0.04 and from 0.17 to 0.14, respectively using inverted NO_x emissions (Table 3). The 50% cut in the ARNR sector helps to improve the model performance in simulating ground-level NO_2 and O_3 which had been overestimated using a priori NO_x emissions. The inverted NO_x emissions decrease modeled NMB and NME in all five urban areas and overall decrease NMB by 0.25 and 0.04, and NME by 0.13 and 0.04 in simulating ground-level NO_2 and O_3, respectively (Table 4 and Table 6). The model performance is also improved compared against P-3 measurements. For NO_2, NMB is reduced from 0.09 to -0.02, and NME is reduced by 0.09. For NO_y, NMB is

reduced by 0.16 and NME is reduced by 0.11 (Table 5). The scaled-down ground NO_x emissions lead to a 2-5 ppb lower modeled 8-h (10:00-18:00LT) ground O_3 and make O_3 formation chemistry less sensitive to the VOC emissions, with reduction of 1-3ppb sensitivity coefficients over the inversion region. The O_3 sensitivity to NO_x emissions also decreases by approximately 1-2ppb over most of the inversion region; however, the O_3 formation chemistry in the urban cores of the DFW, HGB, and Austin and San Antonio regions shifts toward being more NO_x-limited, leading to a 1-3 ppb increase of O_3 sensitivity to NO_x emissions (Fig. 9).

Although the inversion improves the model performance, the sensitivity analysis (Supplement, Sect. 3) shows that the aviation and ARNR sectors are relatively responsive to the emission uncertainty values and offset each other (Fig. S2), indicating the DKF inversion may not be capable of fully distinguishing these two emission sectors. Therefore, the aviation source is then merged with ARNR and the DKF inversion is re-conducted on five emission sectors: area, nonroad, and aviation (ARNRAV), on-road, biogenic, lightning, and non-EGU points (Case II). In case II, the inversion results are more stable and insensitive to the emission uncertainties in each emission sector (Fig. S2). However, the inversion tends to scale up all three source categories in the ARNRAV sector together by 50% to compensate for the rural NO_2 gap. The inversion reduces on-road and biogenic NO_x emissions by 12% and 16%, respectively. The adjustments for the lightning and non-EGU points sectors are still less than 4% (Table 2). On the region basis, the inversion tends to increase NO_x emissions in all regions with increments ranging from 1% in the Austin and San Antonio region to 18% in the NE TX region; it thus increases the modeled NO_2 VCDs by 7% on average. The inversed NO_2 VCD in this case is very similar to that from the region-based inversion (Fig. 8f). The model performance of simulating OMI NO_2 VCDs is improved and similar to the results from case I (Table 3). However, unlike

case I, no improvements are found in simulating ground measured NO_2 and O_3 and P-3-measured NO_2 and NO_y using the inverted NO_x emissions in case II (Table 4-6). Because the ground NO_x emissions are increased in this case, the inversion impacts the O_3 simulations in the opposite direction than in case I. The modeled 8-h ground O_3 increases by around 2ppb and becomes more sensitive to both NO_x and VOC emissions over most of the inversion region; however, the O_3 formation chemistry shifts toward being more VOC-limited in DFW and HGB (Fig. 9).

4. Conclusions

Satellite-derived photolysis rates and NO_x emissions are both applied to a Texas SIP modeling episode to investigate the capabilities of using satellite data to enhance state-level O_3 regulatory modeling. Results show that the ground-level O_3 simulations are improved with reductions of modeled NMB from 0.42 to 0.37 and modeled NME from 0.50 to 0.45 by using GOES-derived photolysis rates and sector-based DKF (case I) with OMI NO_2 inverted NO_x emission inventory (Table 6). The GOES-derived photolysis rates and OMI-constrained NO_x emissions decrease monthly averaged 8-h O_3 concentrations by 2-5ppb over the entire inversion region and turn O_3 formation chemistry toward being less sensitive to NO_x and VOC emissions over most of inversion areas, while being more NO_x sensitive in the two O_3 nonattainment areas, DFW and HGB (Fig. 10).

Applying GOES-retrieved cloud coverage and transmissivity reduce the modeled photolysis rates over most of the domain, leading to less photochemical activity and O_3 production and shifting O_3 formation chemistry toward being less sensitive to NO_x emissions,

except in the DFW region where modeled photolysis rates are increased by the GOES retrieval, leading to impacts in the opposite direction. In comparing with the AQS ground measurements, the GOES-derived photolysis rates improve the ground-level O_3 simulations but not the NO_2 simulations, indicating other model errors may dominate the accuracy of model performance in simulating ground-level NO_2. The GOES-retrieved clouds applied here adjusted only the modeled photolysis rates, while modeled clouds continued to drive the dynamics and aqueous phase chemistry. This inconsistency in the placement of clouds is similar to the approach of a previous study (Pour-Biazar et al., 2007). Thus, this work demonstrates a sensitivity study of using satellite-derived photolysis rates on model performance rather than a full integration of satellite-observed clouds into all aspects of the model. Future work could extend the use of GOES-retrieved clouds to also correct model dynamics and aqueous phase chemistry and investigate their impacts on NO_x and O_3 modeling.

The DKF inversion approach has been successfully incorporated with the CAMx-DDM model and was conducted on both region-based and sector-based NO_x emissions. A controlled pseudodata test conducted on the sector-based DKF inversion confirmed that it accurately captures known perturbations in NO_x emission sectors. In addition to implementing lightning and aviation NO_x emissions in the upper troposphere and doubling soil NO_x emissions from the ground, the NO_x lifetime is increased by reducing 25% the reaction rate constant of the reaction $OH + NO_2$. The upper tropospheric NO_2 underestimation is further eliminated by adding a 40ppt homogenous NO_2 layer in the model top. On the other hand, the high resolution OMI retrieval with a priori profile from the nested GEOS-Chem simulation further enhances NO_2 in urban areas and reduces NO_2 in rural. However, the comparison still shows that the OMI has higher NO_2 VCDs than CAMx in rural areas, by around 2×10^{14} molecules/cm^2. It is not clear that the

discrepancy between OMI and CAMx in rural areas is caused by uncertainties in NO_x emission inventory or errors in OMI retrieval and other model uncertainties. The OMI NO_2 retrieval can be further improved by using the finer resolution terrain and albedo data (Russell et al., 2011) and observed vertical profiles from aircraft spiral measurements in the recent DISCOVER-AQ Houston measurement campaign (Crawford et al., 2014). The accuracy of CAMx modeled NO_2 VCDs can benefit from further improving the modeled chemical and transport processes (ENVIRON 2013), such as updating NO_x recycling process to increase NO_x lifetime, or adding cross-tropopause transport processes to allow more stratospheric NO_2 penetrate to upper troposphere. This may obtain better spatial distribution of modeled NO_2 rather than adding a homogeneous layer at top to compensate the model deficiency.

The region-based DKF inversion still over scales NO_x emissions in urban areas to compensate for the rural NO_2 differences because the NO_2 VCDs gap in rural areas is not eliminated, leading to 10-50% increase of NO_x emissions at most regions and worsening the ground-level O_3 simulations; however, the scaling factors generated in this study are much more moderate than those were found in Tang et al. (2013). The sector-based DKF inversion (case I) takes the aviation source to compensate the NO_2 gap in rural area, probably because its relatively spread-out emission pattern over rural area corresponds with the NO_2 discrepancy distributions, leading to appropriate adjustments in the ground emissions and improving both ground-level NO_2 and O_3 simulations; however, the aviation source is unrealistically adjusted by applying a suggested factor of 4 to its base value, and the adjustments offset the area and nonroad sector with varying emission uncertainties in the sensitivity analysis. Although merging the aviation source into the area and nonroad emission sector makes the inversion (case II) more stable, the large scaling factor for the aviation sector is now shared with area and nonroad emissions,

leading to area and nonroad NO_x emissions being scaled up by 50%. Thus, the model performance in ground-level NO_2 and O_3 simulations is deteriorated and is even worse than the results generated from the region-based inversion. The lightning NO_x emissions seem to be well estimated and are adjusted little by the inversion. However, it may also indicate that the OMI retrieved NO_2 is insensitive to the lightning source, most probably due to the NO_x partitioning predominantly to NO in the upper troposphere and the clear-sky cloud screening criterion used in the OMI data processing. The NO_2 discrepancy between OMI and CAMx drives the DKF inversion and is assumed to be mostly contributed by the uncertainties in the NO_x emission inventory. However, findings from this study indicate that if the uncertainty in the a priori NO_x emissions is low, errors in the satellite retrieval and model itself cannot be neglected, making the inversion less capable of reducing the uncertainties in the bottom-up NO_x emission inventory.

The region-based DKF inversion applies a single scaling factor to each inversion region, and assumes the a priori emission pattern in each inversion region is correct, causing deterioration of the model performance in this case. While the sector-based DKF inversion applies a single scaling factor to each emission sector, that leads to more heterogeneous adjustments in each inversion region and relatively better modeling results than those from the region-based inversion. However, the sector-based inversion assumes the spatial distribution of NO_x emissions in each sector is accurately estimated in the bottom-up NO_x emission inventory, which is also a simplification. For example, TCEQ recently developed a single-day aviation emission inventory using the Advanced Emission Model (AEM3) for the new Rider 8 modeling domain, which has more accurate flight profile and distributes emissions more broadly in the vertical direction, leading to the spatial pattern of NO_x emissions somewhat different than that obtained from EDGAR (ENVIRON 2013). In addition, the newly developed Berkeley-Dalhousie

Soil NO_x Parameterization (BDSNP) scheme (Hudman et al., 2012) recently was implemented into the CMAQ model to estimate soil NO_x emissions, showing large spatial and temporal differences compared to those estimated by the YL95 scheme over eastern Texas. All these changes described above in the a priori NO_x emission inventory may have significant impact on the sector-based inversion results.

The direct scaling inversion (Supplement, Sect. 4) using PAMS measured VOCs improves the model performance in simulating five chosen VOC species and indicates the TCEQ VOC emission inventory used in HGB SIP modeling is now much better than the previous reported emissions with values off by an order of magnitude. However, the inverted VOC emissions have insignificant impact on the ground-level NO_2 and O_3 simulations, probably because of the limited spatial coverage of the PAMS measurement sites and most VOC-saturated conditions in the inversion region. Future work could explore the capabilities of using satellite-observed formaldehyde data to constrain the Texas isoprene or even other anthropogenic VOC emissions (Defour et al., 2009; Curci et al., 2010).

The statistical results show that although the modeled NMB and NME are reduced, OMI-constrained NO_x emissions barely improve the spatiotemporal correlations (R^2) with ground-measured NO_2 and O_3, indicating that either applying the scaling factors generated at the OMI passing time is unable to reduce the emission uncertainty at each hour or the current OMI resolution is insufficient to capture the spatial distributions of the NO_x emission pattern. The future launch of NASA Tropospheric Emission: Monitoring of Pollution (TEMPO) geostationary satellite (Streets et al., 2013) could help address these shortcomings by providing a temporal resolution down to an hour and a spatial resolution down to 4km×4km measurement.

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Table 1. NO_x emission rates for seven sectors in seven inversion regions (tons/day).

Source Region	Area	On-road	Non-road	Biogenic	Aviation	Lightning	Non-EGU points	EGU	Total
HGB	28 (6%)	159 (36%)	71 (16%)	10 (2%)	28 (6%)	21 (5%)	92 (21%)	29 (7%)	438
DFW	35 (8%)	152 (37%)	77 (19%)	60 (14%)	44 (11%)	23 (6%)	19 (5%)	6 (1%)	416
BPA	8 (8%)	24 (24%)	7 (7%)	2 (2%)	3 (3%)	8 (8%)	40 (40%)	8 (8%)	101
NE Texas	43 (25%)	34 (20%)	28 (16%)	2 (1%)	3 (2%)	14 (8%)	9 (5%)	41 (24%)	174
Austin and San Antonio	9 (3%)	113 (37%)	37 (12%)	72 (24%)	12 (4%)	5 (2%)	21 (7%)	34 (11%)	303
N Rural	82 (11%)	161 (21%)	103 (13%)	142 (19%)	51 (7%)	94 (12%)	39 (5%)	91 (12%)	763
S Rural	85 (13%)	123 (18%)	79 (12%)	176 (26%)	30 (4%)	61 (9%)	61 (9%)	57 (8%)	672
Total	290 (10%)	766 (27%)	402 (14%)	464 (16%)	171 (6%)	226 (8%)	281 (10%)	266 (9%)	2866

Note: percentage indicates the apportionment of each emission sector to the regional total.

Table 2. Scaling factors of region-based and sector-based inversions.

Region-based inversion		Sector-based inversion I		Sector-based inversion II	
Emission region	Scaling factor (unitless)	Emission sector	Scaling factor (unitless)	Emission sector	Scaling factor (unitless)
HGB	1.11	Area	0.54	Area	1.49
DFW	0.97	Non-road	0.54	Non-road	1.49
BPA	1.49	On-road	1.03	On-road	0.88
NE Texas	1.10	Biogenic	0.71	Biogenic	0.84
Austin and San Antonio	1.15	Aviation	4.10	Aviation	1.49
N rural	1.24	Lightning	0.98	Lightning	1.03
S rural	0.98	Non-EGU points	0.96	Non-EGU points	0.96

Table 3. Evaluation of CAMx modeled NO_2 using OMI NO_2.

Inversion region	Priori			Posteriori: region-based inversion			Posteriori: sector-based inversion I			Posteriori: sector-based inversion II		
	R^2	NMB[b]	NME[c]	R^2	NMB	NME	R^2	NMB	NME	R^2	NMB	NME
HGB	0.57	-0.25	0.36	0.57	-0.17	0.35	0.57	-0.21	0.32	0.57	-0.18	0.34
DFW	0.74	-0.21	0.29	0.72	-0.21	0.28	0.70	-0.12	0.25	0.75	-0.13	0.30
BPA	0.40	-0.46	0.47	0.45	-0.33	0.43	0.37	-0.42	0.43	0.39	-0.43	0.44
NE Texas	0.24	-0.40	0.44	0.24	-0.36	0.43	0.21	-0.39	0.43	0.25	-0.31	0.42
Austin and San Antonio	0.45	-0.25	0.35	0.47	-0.18	0.35	0.43	-0.23	0.33	0.44	-0.23	0.34
Overall[a]	0.74	-0.11	0.17	0.75	-0.05	0.16	0.75	-0.04	0.14	0.75	-0.04	0.16

a. Compared to OMI observations in all inversion regions
b. Normalized mean bias: $\Sigma(Mod-Obs)/\Sigma(Obs)$
c. Normalized mean error: $\Sigma|(Mod-Obs)|/\Sigma|(Obs)|$

Table 4. Evaluation of CAMx modeled NO_2 using hourly AQS ground-measured NO_2.

Inversion region	Priori			Posteriori: region-based inversion			Posteriori: sector-based inversion I			Posteriori: sector-based inversion II		
	R^2	NMB	NME	R^2	NMB	NME	R^2	NMB	NME	R^2	NMB	NME
HGB	0.51	0.46	0.67	0.51	0.61	0.77	0.50	0.26	0.56	0.51	0.59	0.76
DFW	0.49	0.43	0.66	0.49	0.40	0.65	0.48	0.14	0.53	0.50	0.55	0.74
BPA	0.45	0.92	1.02	0.45	1.74	1.77	0.45	0.72	0.86	0.45	0.99	1.08
NE Texas	0.70	0.86	0.93	0.70	1.07	1.12	0.70	0.33	0.52	0.70	1.36	1.40
Austin and San Antonio	0.46	0.60	0.87	0.47	0.80	1.01	0.48	0.37	0.73	0.47	0.58	0.86
Overall[a]	0.51	0.51	0.72	0.48	0.67	0.85	0.50	0.26	0.59	0.51	0.63	0.81

a. Compared to all ground sites

Table 5. Evaluation of CAMx modeled NO_2 using P-3 aircraft-measured NO_2 and NO_y.

Statistical parameters	NO_2[a]				NO_y[a]			
	Priori	Posteriori: region-based inversion	Posteriori: sector-based inversion I	Posteriori: sector-based inversion II	Priori	Posteriori: region-based inversion	Posteriori: sector-based inversion I	Posteriori: sector-based inversion II
R^2	0.22	0.23	0.24	0.21	0.34	0.35	0.35	0.34
NMB	0.09	0.15	-0.02	0.17	0.70	0.76	0.54	0.79
NME	0.99	1.03	0.90	1.06	0.98	1.03	0.87	1.04

a. Comparison available for only four days (August 31, September 11, September 13, and September 15, 2006).

Table 6. Evaluation of CAMx modeled O_3 using hourly AQS ground-measured O_3.

Source region	Priori			Posteriori: region-based inversion			Posteriori: sector-based inversion I			Posteriori: sector-based inversion II			Sector-I inversed NO_x emissions & GOES photolysis		
	R^2	NMB	NME	R^2	NMB	NME	R^2	NMB	NME	R^2	NMB	NME	R^2	NMB	NME
HGB	0.46	0.68	0.75	0.47	0.67	0.74	0.46	0.65	0.72	0.45	0.70	0.76	0.54	0.62	0.69
DFW	0.64	0.21	0.32	0.64	0.23	0.33	0.64	0.18	0.29	0.64	0.21	0.33	0.66	0.18	0.28
BPA	0.47	0.66	0.70	0.47	0.59	0.66	0.49	0.60	0.64	0.45	0.69	0.73	0.52	0.59	0.63
NE Texas	0.49	0.36	0.43	0.49	0.38	0.44	0.50	0.32	0.40	0.48	0.37	0.45	0.55	0.30	0.38
Austin and San Antonio	0.52	0.40	0.46	0.52	0.40	0.46	0.52	0.35	0.43	0.52	0.42	0.48	0.57	0.34	0.41
Overall[a]	0.50	0.42	0.50	0.51	0.42	0.50	0.50	0.38	0.46	0.49	0.43	0.51	0.55	0.37	0.45

a. Compared to all ground sites

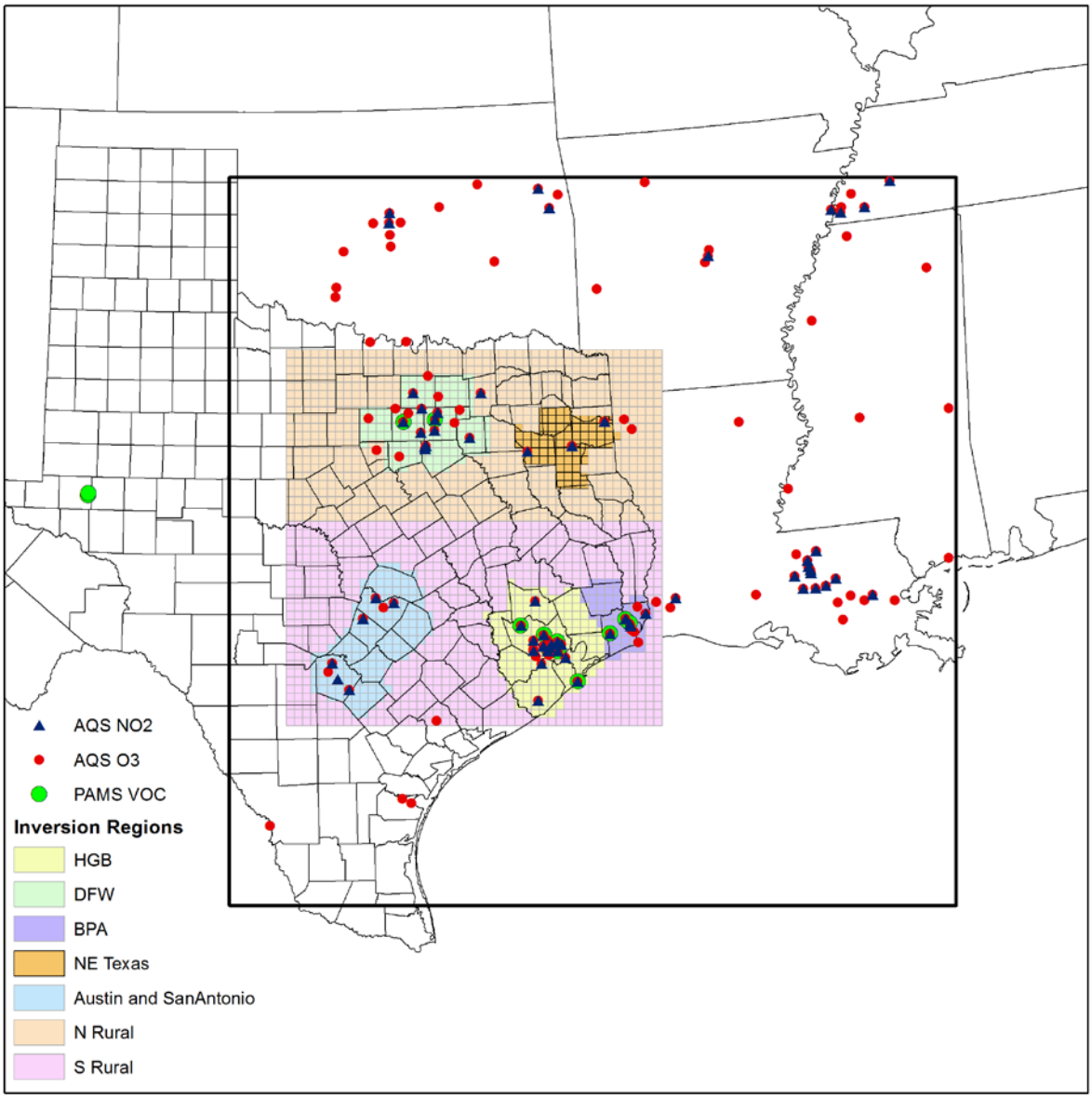


Figure 1. Seven designated inversion regions in eastern Texas (shaded) within 12-km CAMx modeling domain (black square) covered by ground NO_2 monitoring sites (blue triangles), VOC monitoring sites (green circles), and O_3 monitoring sites (red circles).

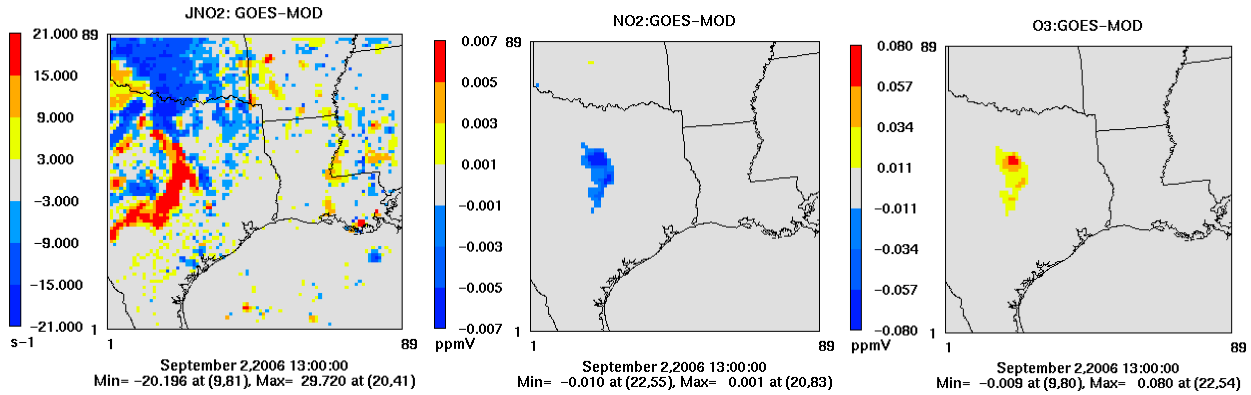
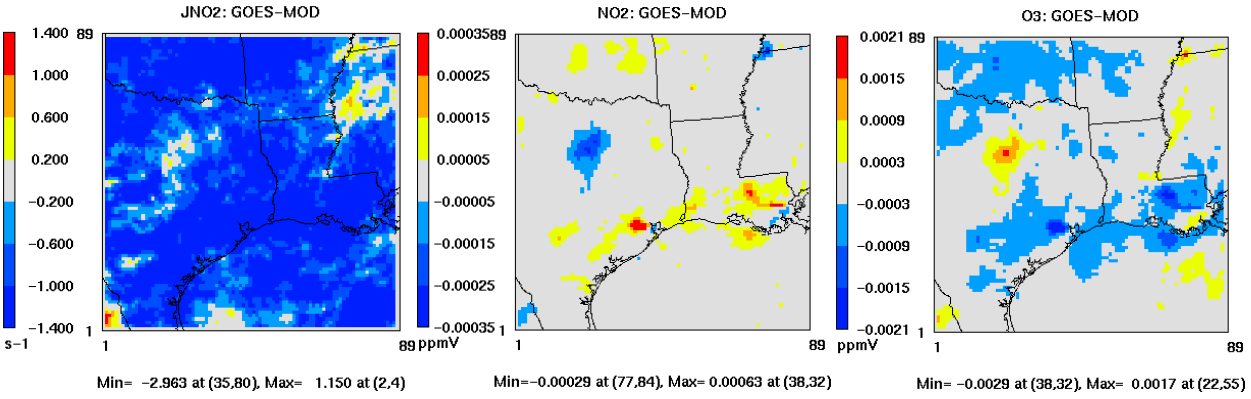


Figure 2. Differences between satellite-derived (GOES) and model predicted (MOD) J_{NO2} (left) in simulating NO_2 (middle) and O_3 (right) at 13:00 on 2 September 2006.

(a) (b) (c)



(d) (e)

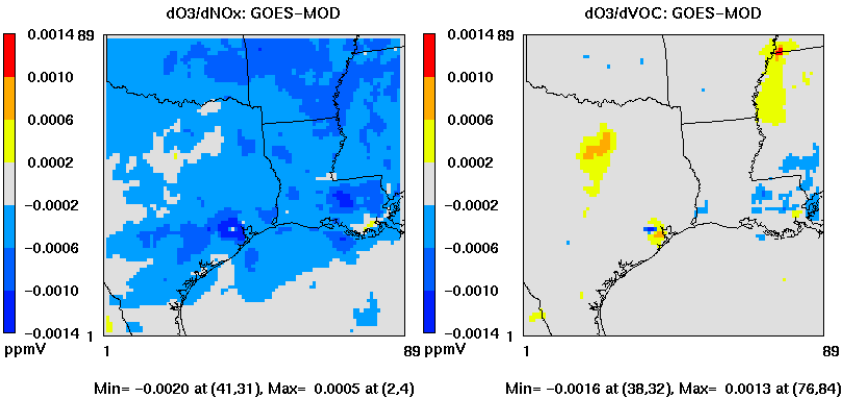


Figure 3. Monthly 8-h (10:00-18:00LT) averaged differences between satellite-derived (GOES) and model predicted (MOD) (a) JNO_2 in simulating (b) NO_2, (c) O_3, and O_3 sensitivities to (d) NO_x and (e) VOC.

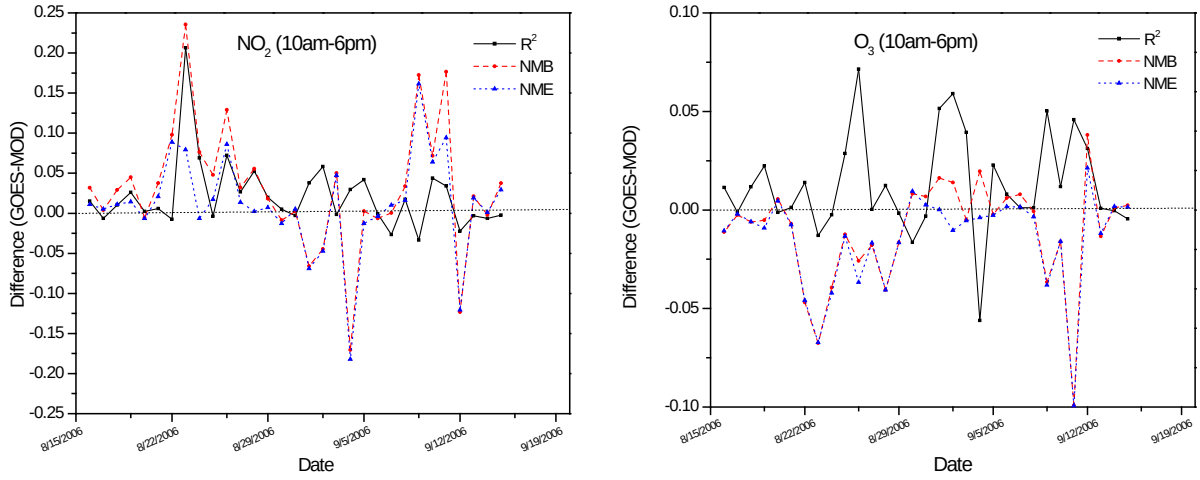
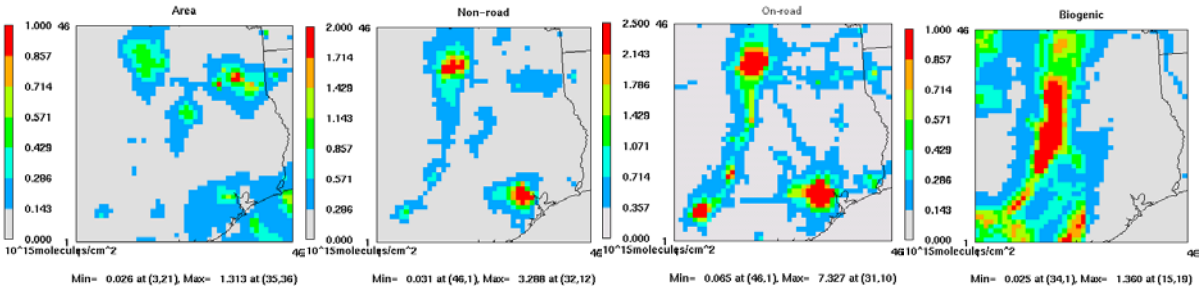


Figure 4. Change in model performance (R^2, NMB, and NME) in simulating daily 8 hours (10:00-18:00LT) NO_2 (left) and O_3 (right) caused by satellite-derived photolysis rates.

(a) (b) (c) (d)



(e) (f) (g)

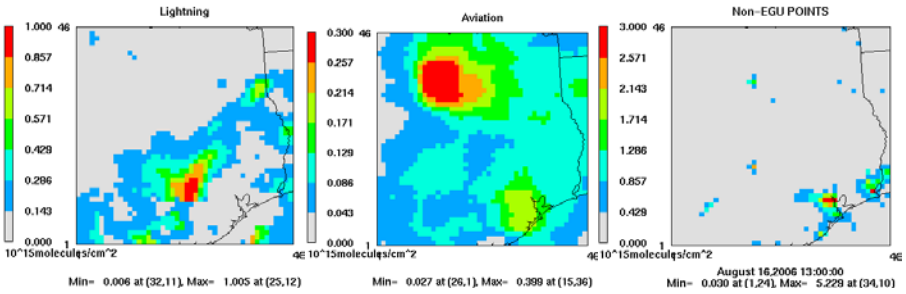


Figure 5. Vertical column densities of NO_2 sensitivities to NO_x emissions of (a) area, (b) non-road, (c) on-road, (d) biogenic, (e) lightning, (f) aviation, and (g) non-EGU points source sectors.

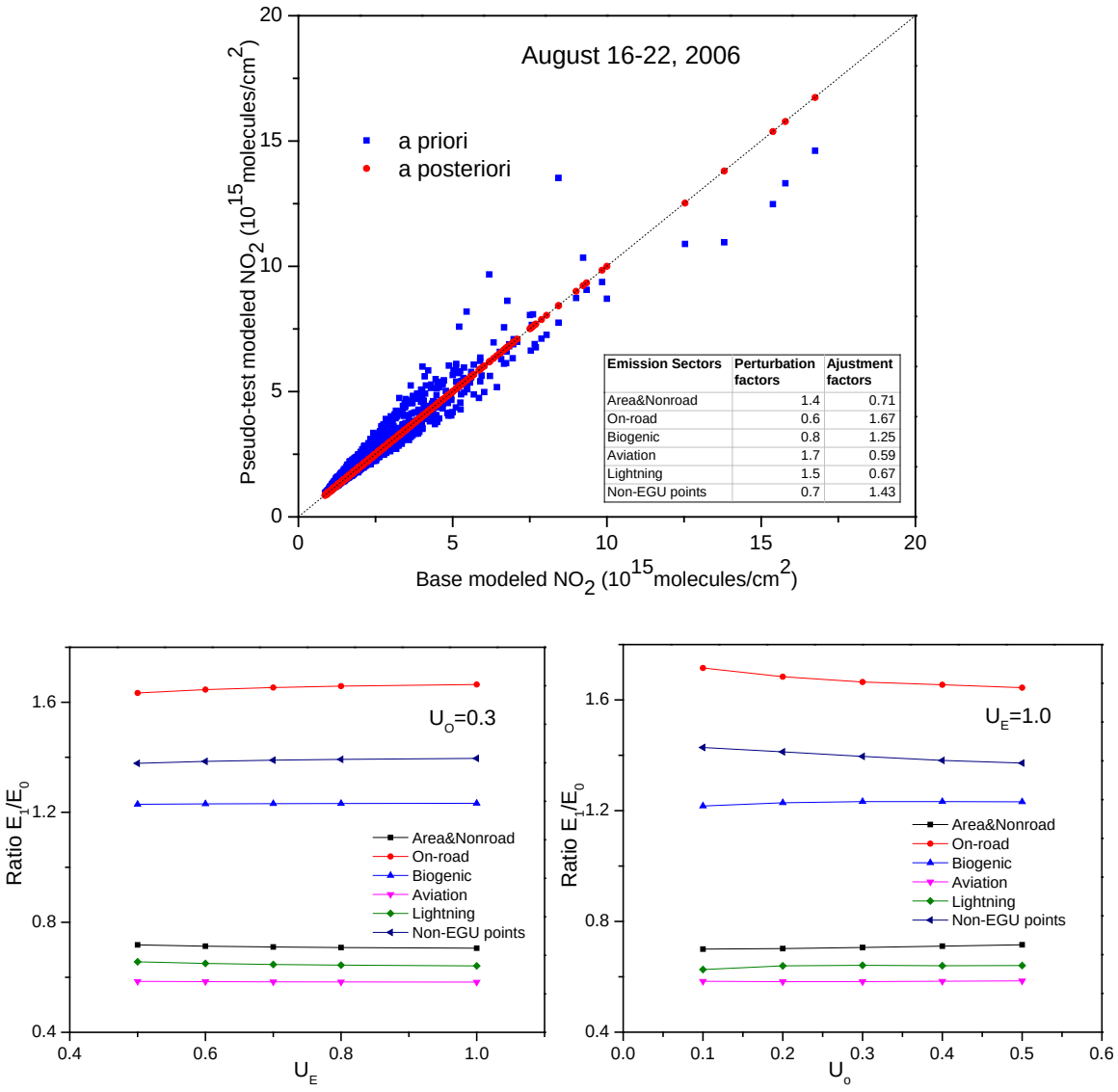


Figure 6. Pseudodata analysis for the sector-based DKF inversion (top), and its sensitivities to varied uncertainties in emissions (U_E) (bottom left) with 30% uncertainty in observation (U_O) and in observations (bottom right) with 100% uncertainty in emissions.

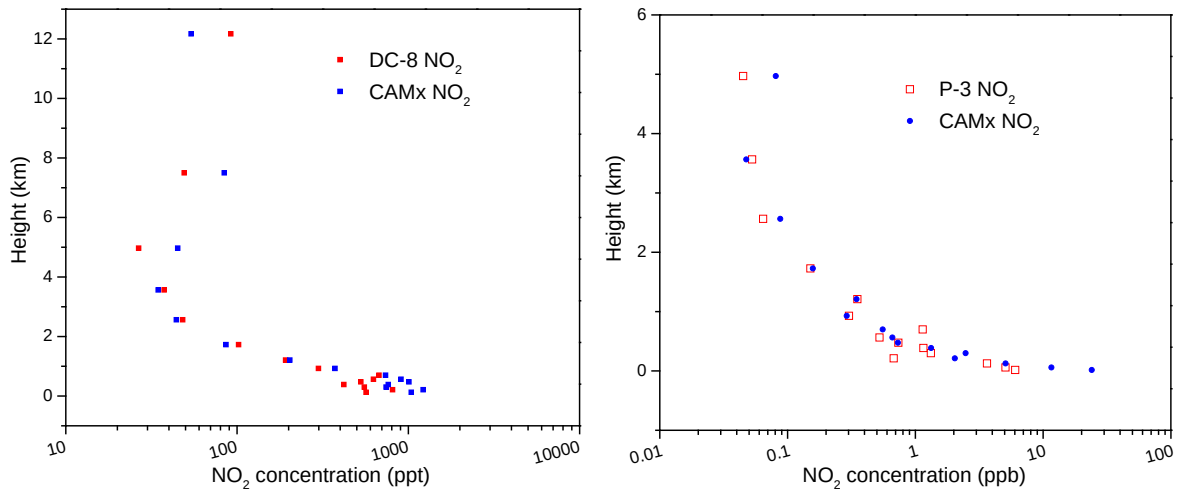


Figure 7. Comparisons of modeled NO_2 vertical distributions with INTEX NASA DC-8 flight (left) and TexAQS 2006 NOAA P-3 aircraft (right) measurements.

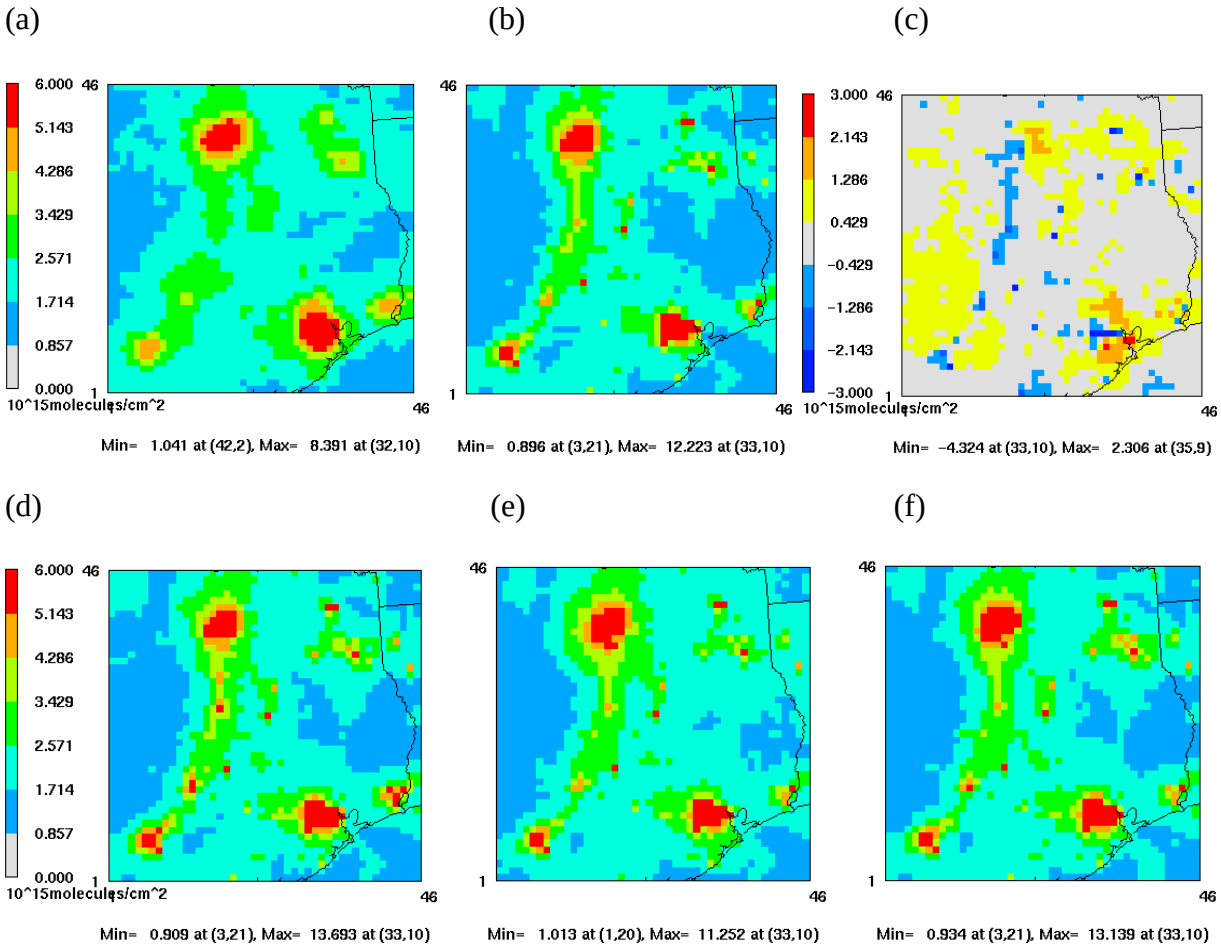


Figure 8. Monthly averaged (16 August to 15 September) tropospheric NO_2 VCDs at 13:00-14:00LT from (a) OMI, (b) a priori simulation, (c) difference between OMI and a priori simulation, and simulations using a posteriori NO_x emissions generated by (d) region-based DKF inversion, and sector-based DKF inversion (e) case I and (f) case II.

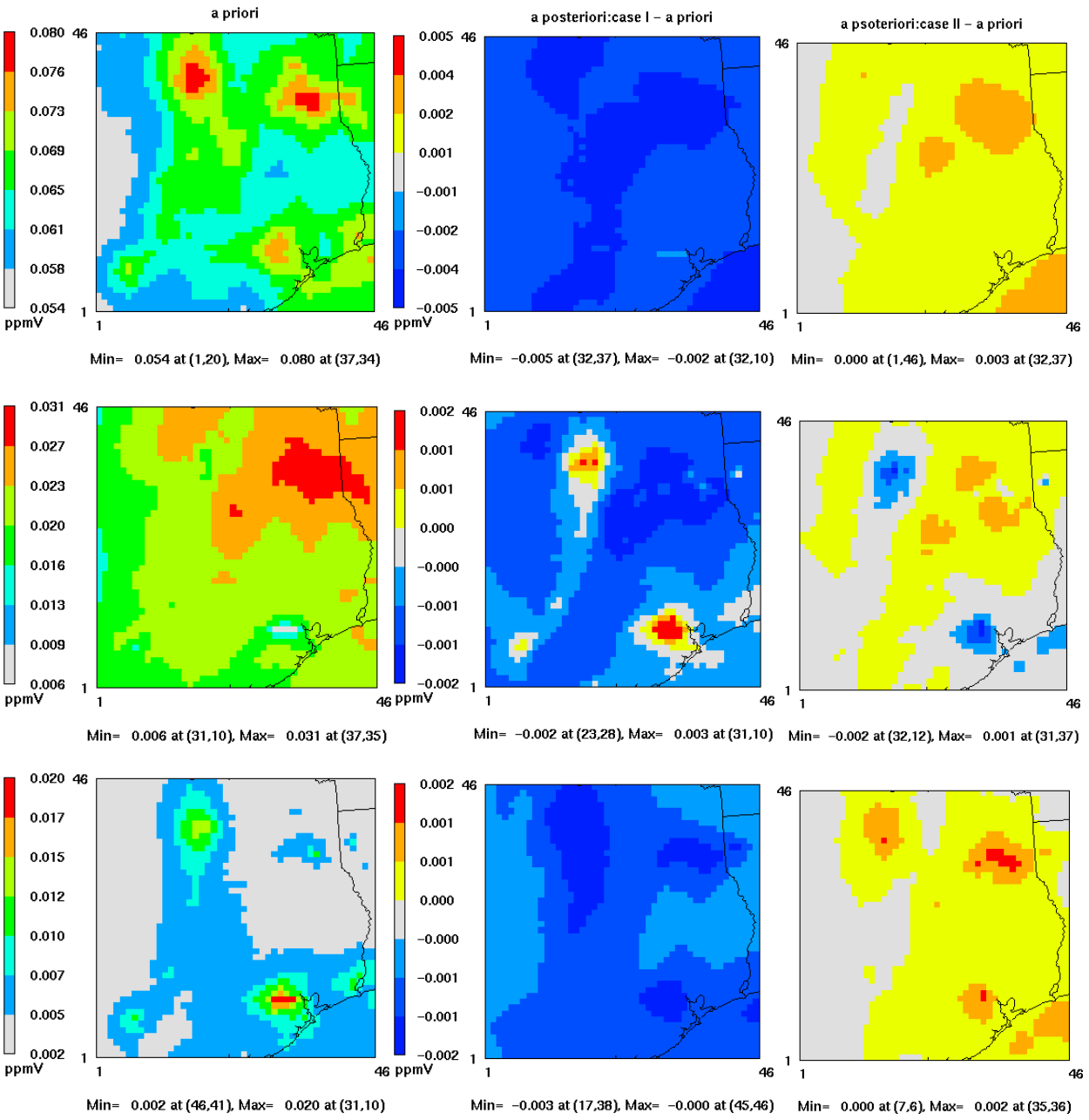


Figure 9. Monthly 8-h (10:00-18:00LT) averaged ground O_3 concentrations (top), O_3 sensitivity to NO_x (middle), and O_3 sensitivity to VOC (bottom) for the a priori case (left), and differences between a posteriori and a priori for the sector-based DKF inversions case I (middle) and case II (right).

(a) (b) (c)

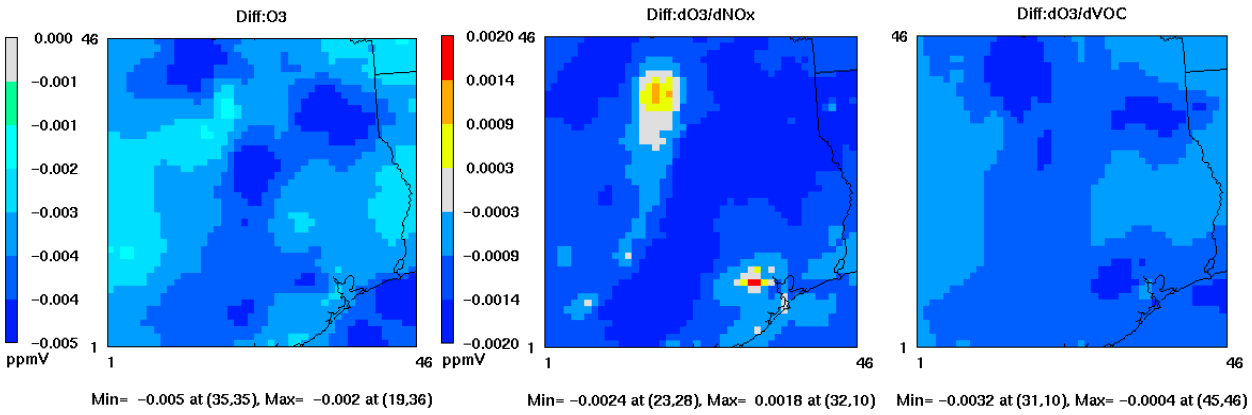


Figure 10. Monthly 8-h (10:00-18:00LT) averaged differences in modeled (a) ground O_3 concentrations, (b) O_3 sensitivity to NO_x, and (c) O_3 sensitivity to VOC resulting from use of both satellite-derived photolysis rates and NO_x emissions in place of a priori data.

Supplement

1. CAMx modeled profile-based OMI retrieval

The OMI-retrieved tropospheric NO_2 vertical column density (VCD) used in this study is calculated via Eq. (S1) (Bucsela et al., 2013),

$$V_{c(GEOSChem)} = \frac{S_{c(OMI)}}{AMF_{GEOSChem}} \quad \text{(S1)}$$

where $S_{c(OMI)}$ is the OMI tropospheric NO_2 slant column density, *AMF* stands for the air mass factor which is computed based on a priori GEOS-Chem modeled profile and scattering weights (*SW*) calculated by the TOMRAD model (Bucsela et al., 2013), and $V_{c(GEOSChem)}$ is the GEOS-Chem modeled profile-based OMI tropospheric NO_2 VCD. A satellite NO_2 retrieval error analysis study (Boersma et al., 2004) shows that the estimated a priori profile from global models may contribute approximately 10% uncertainty to the AMF calculations and propagate that uncertainty to the retrieved NO_2 VCD. Therefore, when OMI VCD is compared to any modeled VCD, OMI averaging kernels (*AK*s) (Eskes and Boersma, 2003), calculated in Eq. (S2), are recommended to be applied to the modeled VCD via Eq. (S3), in order to remove the influence from the a priori profile used in the OMI retrievals.

$$AK_i = \frac{SW_i}{AMF_{GEOSChem}} \quad \text{(S2)}$$

$$\begin{aligned} C_{NO_2}^{predicted} &= \sum(AK_i \times CAMx_{vci}) = \sum(\frac{SW_i}{AMF_{GEOSChem}} \times CAMx_{vci}) = \frac{\sum(SW_i \times CAMx_{vci})}{AMF_{GEOSChem}} \\ &= CAMx_{vctot} \times \frac{\sum(SW_i \times CAMx_{vci}) / CAMx_{vctot}}{AMF_{GEOSChem}} \end{aligned} \quad \text{(S3)}$$

In Eq. (S3), $CAMx_{vci}$ represents the CAMx modeled NO_2 VCD at each model layer (i), and $CAMx_{vctot}$ is the CAMx modeled total tropospheric VCD. The AMF which contains the a priori GEOS-Chem modeled profile is now merged with the CAMx modeled VCD.

The way of removing the a priori GEOS-Chem modeled profile via applying AKs is carried out by generating the CAMx modeled profile-based AMF_{CAMx} as shown in Eq. (S4),

$$AMF_{CAMx} = \Sigma(SW_i \times \frac{CAMx_{vci}}{CAMx_{vctot}}) = \frac{\Sigma(SW_i \times CAMx_{vci})}{CAMx_{vctot}} \quad \text{(S4)}$$

using AMF_{CAMx} to replace $AMF_{GEOSChem}$ in Eq. (S1) and then creating a CAMx modeled profile-based OMI tropospheric NO_2 VCD ($V_{c(CAMx)}$). However, this procedure can only be realized in the inversion process by comparing the AKs applied CAMx VCD ($C_{NO_2}^{predicted}$) and original OMI retrieved VCD ($V_{c(GEOSChem)}$).

The numerator in Eq. (S3) can be replaced by the AMF_{CAMx} generated in Eq. (S4) to form Eq. (S5).

$$C_{NO_2}^{predicted} = CAMx_{vctot} \times \frac{AMF_{CAMx}}{AMF_{GEOSChem}} \quad \text{(S5)}$$

When applying $C_{NO_2}^{predicted}$ to the direct scaling method (Martin et al., 2003; Tang et al., 2013) in Eq. (S6),

$$E_t = E_b \times \frac{V_{c(GEOSChem)}}{C_{NO_2}^{predicted}} = E_b \times \frac{\frac{S_{c(OMI)}}{AMF_{GEOSChem}}}{CAMx_{vctot} \times \frac{AMF_{CAMx}}{AMF_{GEOSChem}}} = E_b \times \frac{\frac{S_{c(OMI)}}{AMF_{CAMx}}}{CAMx_{vctot}} = E_b \times \frac{V_{c(CAMx)}}{CAMx_{vctot}} \quad \text{(S6)}$$

the $AMF_{GEOSChem}$ is canceled out, and $V_{c(CAMx)}$ is formed through AMF_{CAMx} to compare with the CAMx modeled VCD directly.

When applying OMI AKs to the CAMx modeled NO_2 and its sensitivity VCD in the DKF method (Tang et al., 2013) as shown in Eq. (S7),

$$\hat{\mathbf{x}}_{\mathrm{NO_x}} = \mathbf{x}^{-}_{\mathrm{NO_x}} + \mathbf{P}^{-}_{\mathrm{NO_x}} \times \left(\frac{AMF_{CAMx}}{AMF_{GEOSChem}}\right)\mathbf{S}^{\mathbf{T}}_{vc} \times \left(\left(\frac{AMF_{CAMx}}{AMF_{GEOSChem}}\right)^2 \mathbf{S}_{vc}\mathbf{P}^{-}_{\mathrm{NO_x}}\mathbf{S}^{\mathbf{T}}_{vc} + \left(\frac{S_{c(OMI)}}{AMF_{GEOSChem}}\varepsilon_{OMI}\right)^2\right)^{-1} \times \left(\left(\frac{S_{c(OMI)}}{AMF_{GEOSChem}}\right) - \left(CAMx_{vctot} \times \frac{AMF_{CAMx}}{AMF_{GEOSChem}}\right) - \left(\frac{AMF_{CAMx}}{AMF_{GEOSChem}}\right)\mathbf{S}_{vc}\mathbf{x}^{-}_{\mathrm{NO_x}}\right) \quad \text{(S7)}$$

where ε_{OMI} is the OMI measurement uncertainty, Eq. (S8) derived

$$\hat{\mathbf{x}}_{\mathrm{NO_x}} = \mathbf{x}^{-}_{\mathrm{NO_x}} + \mathbf{P}^{-}_{\mathrm{NO_x}} \times \mathbf{S}^{\mathbf{T}}_{vc} \times \left(\mathbf{S}_{vc}\mathbf{P}^{-}_{\mathrm{NO_x}}\mathbf{S}^{\mathbf{T}}_{vc} + \left(\frac{S_{c(OMI)}}{AMF_{CAMx}}\varepsilon_{OMI}\right)^2\right)^{-1} \times \left(\frac{AMF_{GEOSChem}}{AMF_{CAMx}}\right) \times \left(\frac{S_{c(OMI)}}{AMF_{GEOSChem}} - \left(CAMx_{vctot} \times \frac{AMF_{CAMx}}{AMF_{GEOSChem}}\right) - \left(\frac{AMF_{CAMx}}{AMF_{GEOSChem}}\right)\mathbf{S}_{vc}\mathbf{x}^{-}_{\mathrm{NO_x}}\right) \quad \text{(S8)}$$

and further transformed to Eq. (S9),

$$\hat{\mathbf{x}}_{\mathrm{NO_x}} = \mathbf{x}^{-}_{\mathrm{NO_x}} + \mathbf{P}^{-}_{\mathrm{NO_x}} \times \mathbf{S}^{\mathbf{T}}_{vc} \times \left(\mathbf{S}_{vc}\mathbf{P}^{-}_{\mathrm{NO_x}}\mathbf{S}^{\mathbf{T}}_{vc} + \left(V_{c(CAMx)}\varepsilon_{OMI}\right)^2\right)^{-1} \times \left(V_{c(CAMx)} - CAMx_{vctot} - \mathbf{S}_{vc}\mathbf{x}^{-}_{\mathrm{NO_x}}\right) \quad \text{(S9)}$$

where all $AMF_{GEOSChem}$ are removed, and the original $V_{c(GEOSChem)}$ becomes $V_{c(CAMx)}$.

There is an alternative way to create $V_{c(CAMx)}$ instead of applying OMI AKs, which is to use the CAMx modeled profile directly in the OMI retrieval process. In this case, the error of interpolating AKs values into the CAMx layer can be avoided, and the CAMx profile-based OMI retrieval can be calculated directly and viewed. In this study, we have created a CAMx profile-based OMI product that uses a CAMx profile in the retrieval process for the AMF calculation

and planned to use this new OMI retrieval product at the beginning for the inversion study. However, we find that the CAMx profile-based OMI overestimates NO_2 VCD by approximately 30% compared to the original OMI retrieval using a GEOS-Chem profile (Fig. S1, right). We further compare the monthly averaged 13:00-14:00LT CAMx NO_2 profile to the GEOS-Chem NO_2 profile over the 12km domain (Fig. S1 left) and find that the CAMx profile shows much higher amounts of NO_2 in the boundary layer but lower amounts of NO_2 in the upper troposphere. This may reduce the AMF values (Eq. S4) because instrument sensitivity related SW is much higher in the upper troposphere than in the boundary layer and thus increases the total retrieval quantity. Unfortunately, there are no corresponding measurement data available to validate the CAMx and GEOS-Chem profiles in Fig. (S1), but similar bias has been found in the CAMx modeled NO_2 profile compared to the DC-8 and P-3 aircraft NO_2 measurements (Fig. 8). Using the CAMx profile here may introduce more errors to the OMI retrieval and inversions; hence, we do not recommend to either apply AK to the CAMx modeled VCD or to use the CAMx profile-based OMI in this study unless the CAMx profile is validated.

2. Impact of increased NO_x lifetime and artificial layer on modeled NO_2 VCDs

The NASA OMI high resolution product used in this study shows reduced NO_2 in rural areas, while enhanced NO_2 in urban, compared to the NASA standard retrieval, version 2 (Tang et al., 2013); however, it still shows more smeared-out pattern than the CAMx modeled NO_2 VCDs (Fig. S3a). The CAMx simulations with the a priori NO_x emission inventory created in Tang et al. (2013) shows larger NO_2 VCDs in the cities, while lower NO_2 VCDs in the rural places than OMI (Fig. S3b). Reducing the reaction rate constant of the reaction OH + NO_2 by 25% in the CB05 chemical mechanism increases the NO_x lifetime, makes more NO_x transport to rural, and enhances around 3% NO_2 VCDs on average in the inversion region, but the impact is small (Fig.

S3c). Implementing 40ppt NO_2 homogeneously into the model top layer adds about 1.6×10^{14} molecules.cm^{-1} NO_2 densities to each model grid and increases approximately 8% NO_2 VCDs in the inversion region, further alleviating the NO_2 gap between OMI and CAMx in rural areas (Fig. S3d).

3. Sensitivity of DKF inversion to error covariance matrices

The sensitivities of the DKF inversion-generated scaling factors to the uncertainties in the emission and observation error covariance matrices are tested for both region-based and sector-based DKF inversions to evaluate the robustness of the inversion results (Fig. S2). The OMI observation uncertainties are fixed to 30% in the sensitivity tests for the emission error covariance matrix, while the emission uncertainties are varied from 50% to 100% (Fig. S2 left). In contrast, the OMI observation uncertainties are varied from 10% to 50% in the sensitivity tests for the observation error covariance matrix, while the emission uncertainties in each sector are fixed to 100% (Fig. S2 right). In the region-based inversion, the emission uncertainties have insignificant impact on the inversion results. The inversion seems to be relatively responsive to the lower observation uncertainties, but results become more stable when the uncertainties are over 30% (Fig. S2 top). In the sector-based inversion, the scaling factors decrease when uncertainties in the observations increase, but the inversion results are less sensitive to the emission uncertainties. However, an exception occurs in the sector-based DKF inversion case I, where the adjustments in the aviation sector are relatively more sensitive to the emission uncertainty, ranging from 3.9 to 4.6 when emission uncertainty increases from 50% to 100%. It seems to offset against area and nonroad sector which the scaling factors reduce from 0.6 to 0.5 (Fig. S2 middle). However, the inversion becomes insensitive to the emission uncertainties in the sector-based DKF inversion case II when merging aviation into the area and nonroad sector (Fig.

S2 bottom), indicating the DKF inversion in case II is more stable and less responsive to the uncertainty matrices than that in case I.

4. Top-down VOC emissions

An accurate VOC emission inventory is also important for Texas O_3 modeling and NO_x inversion studies. The HGB and BPA regions in eastern Texas feature highly reactive VOC (HRVOC) emissions from petrochemical activities (Kleinman et al., 2002; Murphy and Allen, 2005; Nam et al., 2006; Webster et al., 2007; Vizuete et al., 2008). However, large uncertainties were found in the Texas VOC emission inventory during two intensive measurement campaigns, Texas Air Quality Study (TexAQS) 2000 and 2006, that reported HRVOC emissions were underestimated up to an order of magnitude (Ryerson et al., 2003; Wert et al., 2003; Jiang and Fast, 2004; Gilman et al., 2009; de Gouw et al., 2009; Parrish et al., 2009; Washenfelder et al., 2010). Byun et al. (2007) directly multiplied Texas HRVOC inventory values by factors of 3 to 12, and Kim et al. (2011) reconstructed HRVOC emissions in the 2005 National Emission Inventory using Solar Occultation Flux measurements, with both showing improved O_3 simulations over the Houston area.

In this study, five VOC species, ethylene (ETH), ethane (ETHA), isoprene (ISOP), toluene (TOL), and xylene (XYL) are chosen to conduct the inversion because of their explicit model outputs and sufficient measurement data. ETH, ISOP, TOL, and XYL are defined as highly reactive VOC (HRVOC) by TCEQ for regulatory purposes, due to their high reactivity with OH and propensity for contributing to rapid O_3 formation (Thomas et al., 2008). Although ETHA is not a HRVOC, the high concentrations in urban environments make it also play very important role in forming O_3 (Katzenstein et al., 2003; Buzcu and Fraser, 2006).

4.1 Base case VOC emission inventory

The base case VOC emission inventory for the HGB SIP modeling from 13 August to 15 September 2006 was developed by TCEQ (Table S1). The non-EGU point source VOC emissions were from the State of Texas Air Reporting System (STARS) database, a special inventory containing reported hourly VOC emissions from 15 August to 15 September targeting a specific list of non-EGU points and from Tank Landing Loss surveys of hourly landing loss VOC emissions. The EGU point source VOC emissions were from the EPA Acid Rain database (ARD) with the emissions calculated based on VOC:NO_x ratios. The VOC emissions from motor vehicle were generated by the Motor Vehicle Emission Simulator 2010a (MOVES2010a) model for the on-road vehicles and the Texas NONROAD (TexN) model for the off-road vehicles. The VOC emissions from the other non-road and area sources were from the Texas Air Emissions Repository (TexAER) database (TCEQ 2010). The Global Biosphere Emissions and Interactions System model, version 3.1 (GloBEIS3.1) was used for developing biogenic VOC emissions (Yarwood et al., 1999). Four HRVOC species emissions, ethylene, propylene, 1,3-butadiene, and butenes were further corrected using the Potential Source Contribution Function (PSCF) technique with Automatic Gas Chromatographs (Auto-GC) measured data in the HGB area (TCEQ 2010).

For the five chosen VOC species, ETH and ISOP emissions are mostly contributed by the biogenic source around 60% and 99%, respectively, while TOL and XYL are entirely anthropogenic, originating mostly from area emissions. Area sources also dominate emissions of ETHA, which does not appear in the on-road mobile source. EGUs emissions are minor contributors to all five VOC species (Table S1).

4.2 VOC observations

The U.S. EPA Photochemical Assessment Monitoring Stations (PAMS) VOC measurement data (http://www.epa.gov/ttn/airs/airsaqs/) are used here to adjust emissions for the five chosen VOC species. All five VOC species were measured by the gas chromatographs-flame ionization detector (GC-FID) with 1-hr resolution for the entire modeling period from 13 August to 15 September 2006 in the unit of ppmC (U.S. EPA 1998). Measurements are available only for a total of 11 PAMS monitoring sites in the inversion region: 2 in DFW, 3 in BPA and 6 in HGB (Fig 1). The measurement data are first converted into the unit of ppb for each VOC species, and then averaged monthly over all monitoring sites in each region and compared to the corresponding modeled data.

The NOAA P-3 aircraft measured VOC data (http://www.esrl.noaa.gov/csd/tropchem/2006TexAQS/) are further used for evaluating the model performance in simulating aloft VOCs. Only four chosen VOC species, ETH, ISOP, TOL, and XYL are measured by P-3. ETH is measured using Laser Photoacoustic Spectroscopy (LPAS) with 20s resolution (de Gouw et al., 2009), and ISOP, TOL, and XYL are measured using Proton Transfer Reaction Mass Spectrometer (PTRMS) with 15s resolution (de Gouw et al., 2003). The P-3 measured ISOP, TOL, and XYL are available on 4 days (31 August, 11 September, 13 September, and 15 September 2006), while measured ETH is only available on 3 days (31 August, 13 September, and 15 September 2006) during our modeling period. The P-3 measured VOC data are averaged hourly and compared with the hourly modeled data at corresponding grid cells.

4.3 Results

Since all modeled ETH, ETHA, ISOP, TOL, and XYL are from the primary emissions, a direct scaling (DS) inversion method that adjusts VOC emissions based on the ratios between modeled VOC and PAMS measured VOC is applied here. The inversion is conducted on a regional basis, which means the scaling factor calculated from the measurement data in one region only applies to adjust the emissions in that region. Therefore, due to the availability of observations, the five chosen VOC species emissions are adjusted in only three regions, DFW, HGB, and BPA.

The scaling factors generated from the inversions vary significantly in different regions (Table S2) and show that the HRVOC emissions in the 2006 TCEQ emission inventory for HGB SIP modeling are much better than the reported uncertainty of an order of magnitude (Ryerson et al., 2003; Parrish et al., 2009) but still much higher than the uncertainty in NO_x emissions. The ETHA emissions require the largest adjustments in all three regions with scaling factors ranging from 3.14 to 4.63. The inversion scales down ETH emissions in the HGB and DFW regions by only 10%, but in BPA, it requires a scaling factor of 3.33. The mostly biogenic source contributed ISOP emission only requires 4% scale-up adjustment in HGB, but relatively larger scale-down adjustments ranging from 30-50% in DFW and BPA. The anthropogenic source contributed TOL emissions require scale-up adjustments in all three regions by scaling factors ranging from 1.32 to 2.22. The XYL emissions are well estimated in the base case emission inventory for the HGB region, but require scale-down by approximately 70% in DFW and scale-up around 50% in BPA.

The temporal variations of the five VOC species (Fig.S4) show that the discrepancies between observed VOCs and the a priori modeled VOCs are significantly reduced by using the a posteriori emissions. The inverted ETHA emission improves modeled $R^2$and reduces modeled

NMB and NME by 0.5 and 0.1, respectively (Table S3). The inversed ETH shows increased R^2 and 0.13 reduced NMB, but no improvement in the modeled NME against ground measurement (Table S3); however, it shows 0.4 reductions in both modeled NMB and NME against P-3 measured data (Table S4). The inverted ISOP emissions reduce approximately 20% NMB and NME in ground ISOP simulation (Table S3), but no improvements are found compared against aircraft measurement (Table S4). The modeled NMB in the inversed TOL is reduced by approximately 0.4 (Table S3) compared against PAMS and 0.13 compared against P-3 (Table S4), while the modeled NME has not been improved. The inversed XYL shows increased R^2 and around 0.2 reduced modeled NMB and NME compared to ground measurement (Table S3) and 0.02 reduced modeled NMB and NME compared to aircraft measurement (Table S4). However, no improvements are found in the model performance of simulating ground-level NO_2 (Table S5), and there is a slight decreasing, around 0.01, of modeled NMB and NME in ground-level O_3 simulations using the inverted VOC emissions (Table S6).

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Table S1. Emission rates of five VOC species for six emission sectors in the inversion region (tons/day).

VOCs	Area	On-road	Non-road	Biogenic	Non-EGU points	EGU points	Total
ETH	19.2 (11.5%)	14.9 (8.9%)	11.1 (6.6%)	104.8 (62.6%)	17.2 (10.3%)	0.1 (0.06%)	167.3
ETHA	232.4 (82.3%)	0 (0%)	5 (1.8%)	22.5 (8.0%)	20.4 (7.2%)	2.1 (0.7%)	282.4
ISOP	0.4 (0.002%)	0.8 (0.005%)	0.5 (0.003%)	15835.8 (99.9%)	0.2 (0.001%)	0 (0%)	15837.9
TOL	53.3 (48.9%)	24.5 (22.5%)	25.1 (23.1%)	0 (0%)	5.3 (4.9%)	0.7 (0.6%)	108.9
XYL	116.7 (58.3%)	38.2 (19.1%)	39.7 (19.8%)	0 (0%)	3.3 (1.6%)	2.2 (1.1%)	200.1

Note: percentage indicates the apportionment of each emission sector to the regional total.

Table S2. Direct scaling factors for VOC species in three inversion regions.

Source Region	A priori (tons/day)					Direct Scaling factors relative to a priori (unitless)				
	ETHA	ETH	ISOP	TOL	XYL	ETHA	ETH	ISOP	TOL	XYL
HGB	52.7	26.4	635.5	23.9	42.1	3.45	0.92	1.04	1.71	0.98
DFW	14.3	11.5	780.5	20.6	45.1	4.63	0.90	0.71	1.32	0.33
BPA	27.6	7.1	282.2	5.7	6.9	3.14	3.33	0.50	2.22	1.47

Table S3. Evaluation of CAMx modeled VOCs using hourly PAMS-measured VOCs.

Source Region	Priori					Posteriori				
	ETHA	ETH	ISOP	TOL	XYL	ETHA	ETH	ISOP	TOL	XYL
R^2	0.12	0.05	0.04	0.09	0.07	0.13	0.10	0.04	0.09	0.12
NMB	-0.71	-0.20	0.32	-0.41	0.24	-0.22	-0.07	0.05	-0.03	0.01
NME	0.73	0.80	1.04	0.63	0.90	0.61	0.81	0.86	0.69	0.69

Table S4. Evaluation of CAMx modeled VOCs using P-3 aircraft-measured VOCs[a].

Source Region	Priori				Posteriori			
	ETH[b]	ISOP	TOL	XYL[c]	ETH	ISOP	TOL	XYL
NMB	-0.63	-0.81	-0.60	-0.53	-0.59	-0.81	-0.47	-0.51
NME	0.84	1.05	0.72	0.80	0.80	1.05	0.72	0.78

a. Comparison available for four days (31 August, 11 September, 13 September, and 15 September 2006).
b. Comparison only available for three days (31 August, 13 September, and 15 September 2006).
c. Compared with measured C-8 aromatics

Table S5. Evaluation of CAMx modeled NO_2 using hourly AQS ground-measured NO_2.

Source Region	Priori			Posteriori		
	R^2	NMB	NME	R^2	NMB	NME
HGB	0.51	0.46	0.67	0.51	0.46	0.67
DFW	0.49	0.43	0.66	0.49	0.43	0.66
BPA	0.45	0.92	1.02	0.45	0.92	1.02
Overall	0.51	0.51	0.72	0.51	0.51	0.73

Table S6. Evaluation of CAMx modeled O_3 using hourly AQS ground-measured O_3.

Source Region	Priori			Posteriori		
	R^2	NMB	NME	R^2	NMB	NME
HGB	0.46	0.68	0.75	0.46	0.68	0.75
DFW	0.64	0.21	0.32	0.64	0.20	0.31
BPA	0.47	0.66	0.70	0.46	0.65	0.69
Overall	0.50	0.42	0.50	0.50	0.41	0.49

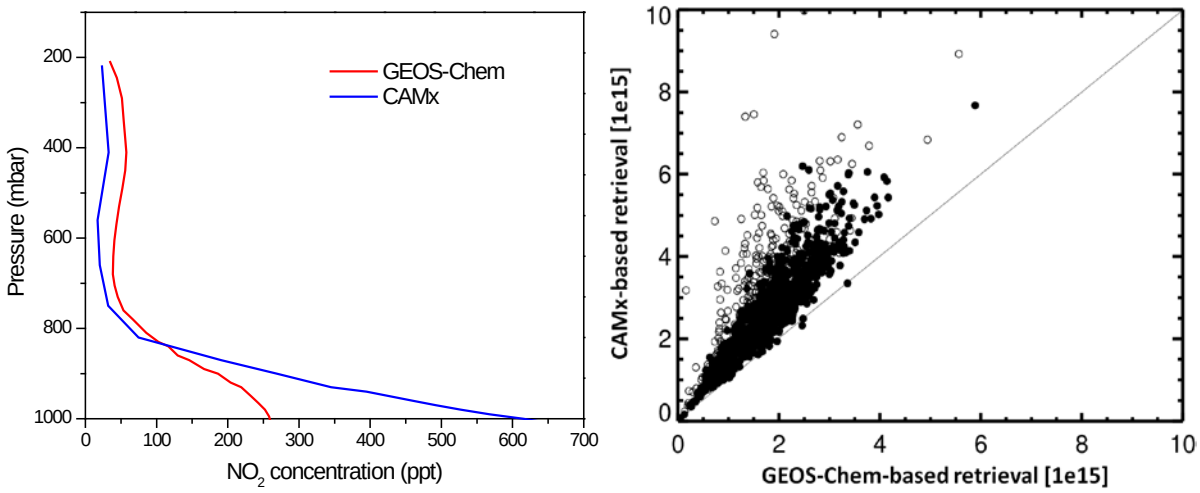

Figure S1. Comparisons between GEOS-Chem and CAMx modeled NO_2 vertical profiles (left) and corresponded OMI retrievals (right). Filled circles represent observations under clear sky condition (cloud fraction <0.5), and open circles are all observations.

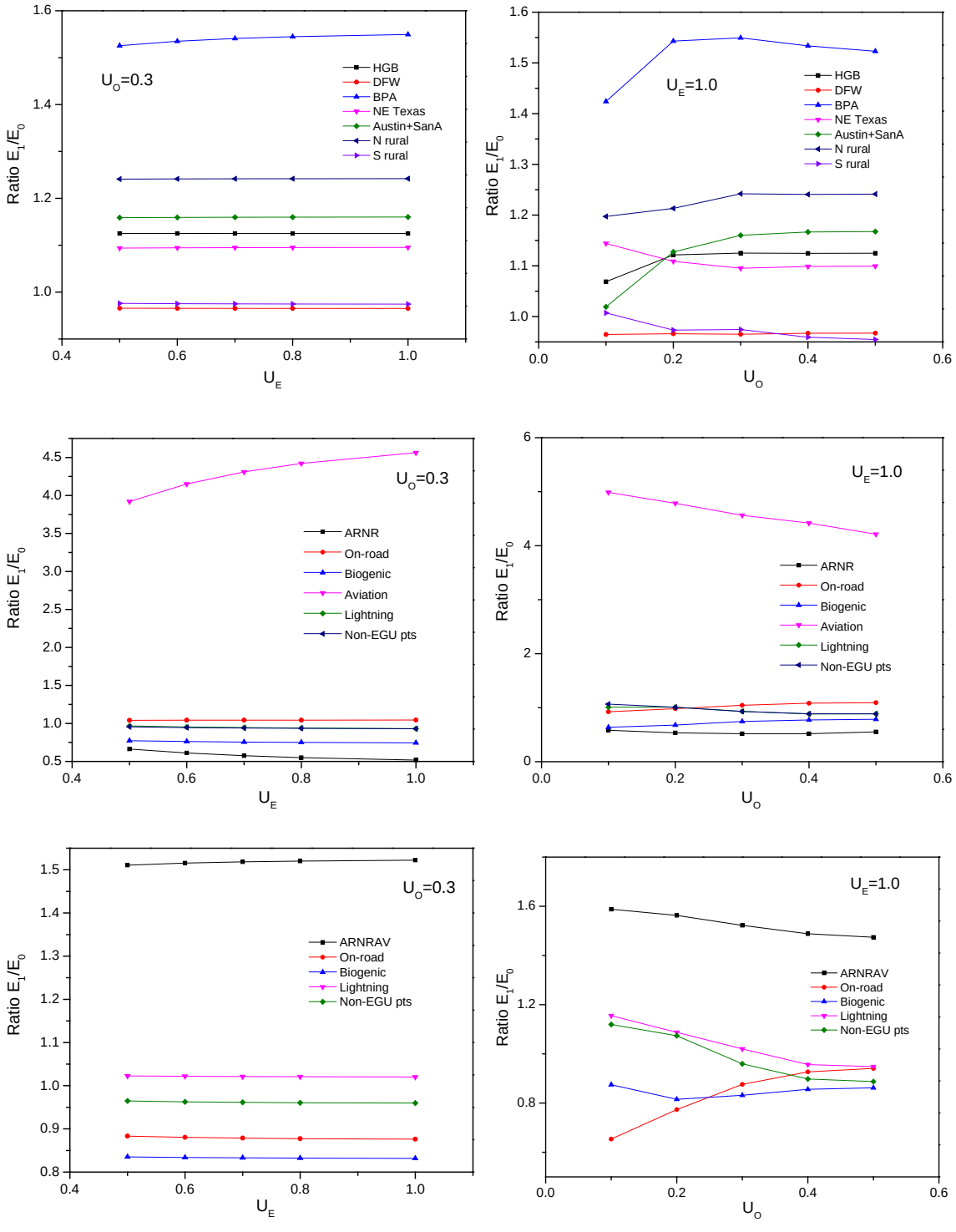

Figure S2. Sensitivities of the DKF inversions to the uncertainties in emissions (left) and in OMI observations (right) in region-based inversion (top), sector-based inversion case I (middle), and sector-based inversion case II (bottom).

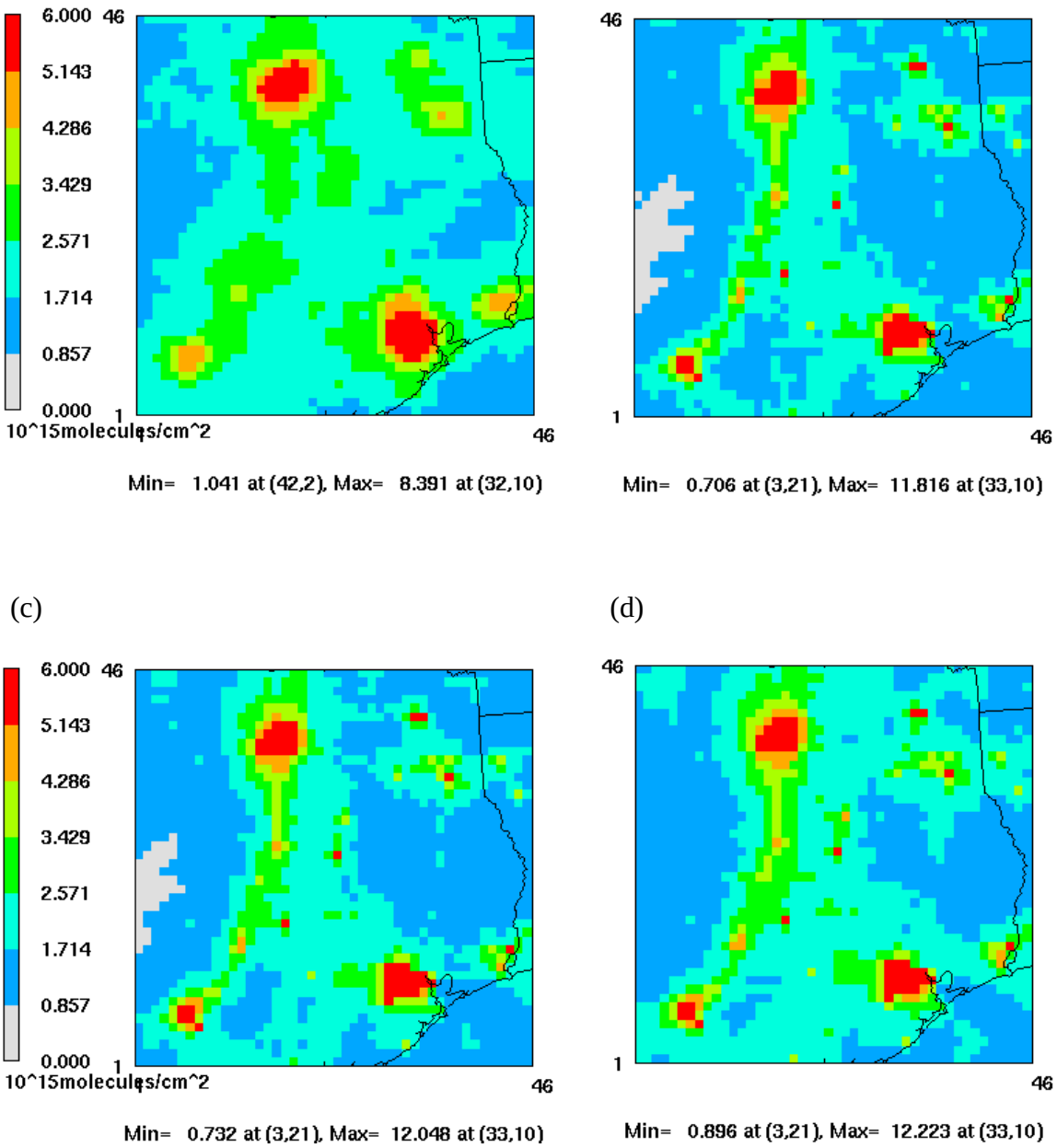

Figure S3. Monthly averaged (16 August to 15 September) tropospheric NO_2 VCDs at 13:00-14:00LT from (a) OMI, (b) simulations using NO_x emissions from Tang et al., (2013), (c) simulations with the lower rate constant of the reaction $OH+NO_2$ from (b), and (d) simulations with added 40ppt NO_2 layer from (c).

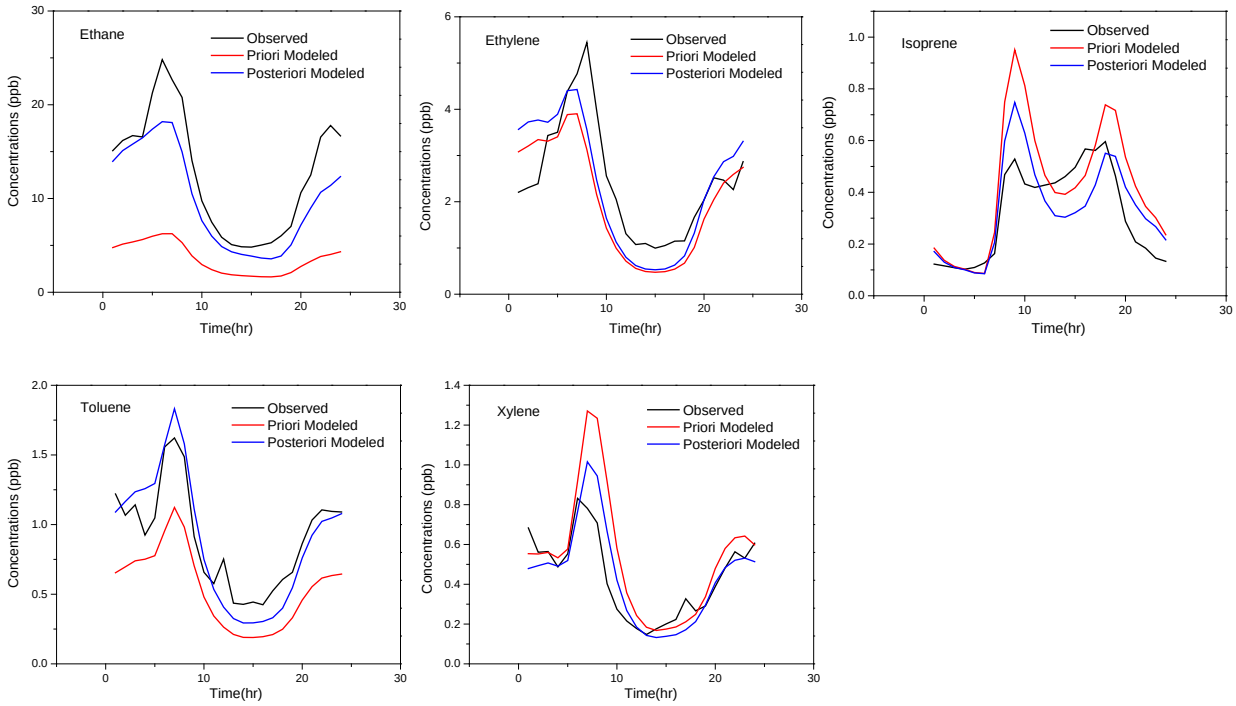

Figure S4. Comparisons of monthly averaged daily variation between observed (black) and modeled VOC species using the a priori (red) and the a posteriori (blue) VOC emission inventory over all monitoring sites.