

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

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12

13 **Abstract**

14 Uncertain photolysis rates and emission inventory impair the accuracy of state-level ozone (O₃)
15 regulatory modeling. Past studies have separately used satellite-observed clouds to correct the
16 model-predicted photolysis rates, or satellite-constrained top-down NO_x emissions to identify
17 and reduce uncertainties in bottom-up NO_x emissions. However, the joint application of multiple
18 satellite-derived model inputs to improve O₃ State Implementation Plan (SIP) modeling has
19 rarely been explored. In this study, Geostationary Operational Environmental Satellite (GOES)
20 observations of clouds are applied to derive the photolysis rates, replacing those used in Texas
21 SIP modeling. This changes modeled O₃ concentrations by up to 80ppb and improves O₃
22 simulations by reducing modeled normalized mean bias (NMB) and normalized mean error
23 (NME) by up to 0.1. A sector-based discrete Kalman filter (DKF) inversion approach is
24 incorporated with the Comprehensive Air Quality Model with extensions (CAMx)-Decoupled

1 Direct Method (DDM) model to adjust Texas NO_x emissions using a high resolution Ozone
2 Monitoring Instrument (OMI) NO₂ product. The discrepancy between OMI and CAMx NO₂
3 vertical column densities (VCD) is further reduced by increasing modeled NO_x lifetime and
4 adding an artificial amount of NO₂ in the upper troposphere. The region-based DKF inversion
5 suggests increasing NO_x emissions by 10-50% in most regions, deteriorating the model
6 performance in predicting ground NO₂ and O₃, while the sector-based DKF inversion tends to
7 scale down area and non-road NO_x emissions by 50%, leading to a 2-5ppb decrease in ground
8 h O₃ predictions. Model performance in simulating ground NO₂ and O₃ are improved using
9 sector-based inversion constrained NO_x emissions, with 0.25 and 0.04 reductions in NMBs and
10 0.13 and 0.04 reductions in NMEs, respectively. Using both GOES-derived photolysis rates and
11 OMI-constrained NO_x emissions together reduces modeled NMB and NME by 0.05 and
12 increases the model correlation with ground measurement in O₃ simulations and makes O₃ more
13 sensitive to NO_x emissions in the O₃ non-attainment areas.

14 **1. Introduction**

15 Tropospheric O₃ is a secondary air pollutant formed via the reactions between nitrogen oxides
16 (NO_x = NO + NO₂) and volatile organic compounds (VOCs) with heat and sunlight (Seinfeld and
17 Pandis, 2006). Eastern Texas is one of the most populous areas in the United States and has been
18 suffering from O₃ pollution for decades due to large anthropogenic emission sources such as
19 motor vehicles, petrochemical facilities, and coal-burning power plants with unique
20 meteorological conditions of extended heat and humidity and intense solar radiation (Kleinman
21 et al., 2002; Ryerson et al., 2003; Daum et al., 2004; Rappenglück et al., 2008; Kim et al., 2011;
22 Zhou et al., 2014).

1 In eastern Texas, several regions require careful air quality planning for O₃ reductions.
2 First and foremost, the Houston-Galveston-Brazoria (HGB) region and the Dallas-Fort Worth
3 (DFW) region exceed the 2008 O₃ National Ambient Air Quality Standard (NAAQS) of 75 ppb
4 and thus are both classified by US Environmental Protection Agency (US EPA) as O₃ non-
5 attainment areas. Next, Beaumont-Port Arthur (BPA), Northeast Texas (NE Texas), and Austin
6 and San Antonio regions require attention for closely approaching that standard (Gonzales and
7 Williamson, 2011).

8 To comply with the O₃ NAAQS, the U.S. EPA requires the Texas Commission on
9 Environmental Quality (TCEQ) to identify regulatory strategies using photochemical air quality
10 models for attaining the O₃ standard in non-attainment areas. However, model uncertainties may
11 impair the accuracy of model performance and potentially misdirect emission control strategies
12 (Fine et al., 2003; Digar and Cohan, 2010; Simon et al., 2012). Recent studies show that
13 uncertain bottom-up emission inventories and modeled photolysis rates are two leading
14 uncertainties in O₃ modeling (Deguillaume et al., 2007; Digar et al., 2011) and can significantly
15 impact simulated O₃ concentrations and their sensitivities in Texas (Cohan et al., 2010; Xiao et
16 al., 2010). Hence, identifying and reducing these uncertainties are essential to ensuring the
17 reliability of regulatory decision making.

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

1 Community Multiscale Air Quality (CMAQ) model. Results showed large differences between
2 model-predicted and satellite-derived photolysis rates, leading to significant changes in modeled
3 O₃ concentrations. Guenther et al. (2012) found that the Weather Research and Forecasting
4 (WRF) and MM5 models, which are usually used to generate meteorological fields for CAMx or
5 CMAQ, underpredict cloud fractions, leading to more modeled solar radiation reaching the
6 ground and overestimations of modeled photolysis rates and sunlight-sensitive biogenic
7 emissions.

8 Studies using satellite NO₂ measurements to create top-down NO_x emissions for
9 atmospheric modeling have also shown promising results (Streets et al., 2013; Martin et al., 2003;
10 Müller and Stavrou, 2005; Jaeglé et al., 2005; Lin et al., 2010; Konovalov et al., 2006, 2008;
11 Napelenok et al., 2008; Kurokawa et al., 2009; Zhao and Wang, 2009; Chai et al., 2009;
12 Zyrichidou et al., 2015). Most recently, Tang et al. (2013) performed region-based DKF
13 inversions using OMI NO₂ data to adjust NO_x emission inventory used in Texas SIP modeling;
14 however, results showed that the region-based DKF inversions with National Aeronautics and
15 Space Administration (NASA) OMI NO₂ standard product, version 2, tended to scale up the NO_x
16 emission inventory by factors of 1.02 to 1.84 and deteriorated model performance as evaluated
17 by ground NO₂ and O₃ monitors.

18 A challenge of using satellite data for inverse modeling is that atmospheric models are
19 primarily evaluated based on ground-level data, and may not accurately simulate pollutants aloft.
20 Several studies (Hudman et al., 2007; Henderson et al., 2011; Allen et al., 2012; ENVIRON,
21 2013) have demonstrated that models tend to underestimate upper tropospheric NO₂ level even
22 after lightning and aviation NO_x sources are included. Though the reason is unclear,

1 underestimation could result from errors in the chemical mechanism in simulating NO_x sinks
2 (Mollner et al., 2010; Henderson et al., 2012, Lin et al., 2012, Stavrakou et al., 2013). Efforts to
3 eliminate low bias for upper tropospheric NO₂ simulations over Texas have been unsuccessful to
4 date (ENVIRON 2013). Another discrepancy often noted between models and satellite data is a
5 narrower spread between urban and rural NO₂ in satellite observations (Streets et al., 2013).
6 Recently developed high resolution OMI NO₂ retrievals increase the rural-urban spread, which
7 may decrease the difference between models and satellite observations.

8 In this work, first, GOES-derived photolysis rates are applied to the CAMx model, and
9 the influence on the modeled NO₂ and O₃ is investigated. Second, the model shortcomings of
10 underestimating upper tropospheric and rural NO₂ demonstrated in Tang et al. (2013) are further
11 addressed by comparing with aircraft measurements and reducing the reaction rate constant of
12 the reaction OH + NO₂ to increase modeled NO_x lifetime. Third, the sector-based DKF inversion
13 using the recently developed NASA high resolution OMI NO₂ product to Texas NO_x emissions
14 is explored and compared to the region-based DKF inversion. In addition, inverse modeling is
15 extended to adjust Texas VOC emissions via directly comparing modeled VOC concentrations
16 with ground observations (Supplement, Sect. 4).

17 **2. Methodology**

18 **2.1 CAMx modeling**

19 CAMx version 5.3 (ENVIRON, 2010) with the Carbon Bond version 2005 (CB-05) chemical
20 mechanism was used to simulate a SIP modeling episode developed by TCEQ for the HGB O₃
21 attainment demonstration (Fig. 1) from 13 August to 15 September 2006, coinciding with the
22 intensive measurement campaign TexAQS 2006. The meteorology fields were modeled by the

1 NCAR/Penn State (National Center for Atmospheric Research/Pennsylvania State University)
2 Mesoscale Model, Version 5, release 3.7.3 (MM5v.3.7.3) (Grell et al., 1994), and the boundary
3 conditions were taken from the Model for Ozone and Related Chemical Tracers (MOZART)
4 global model (ENVIRON, 2008). The base case emission inventory for HGB SIP modeling was
5 provided by TCEQ (TCEQ, 2010). Lightning and aviation NO_x emissions were added into the
6 base emission inventory. The lightning NO_x emission is developed based on the measured
7 National Lightning Detection Network (NLDN) data with intra-cloud flashes assumed to be three
8 times of cloud-to-ground flashes and 500 moles NO emissions per flash (Kaynak et al., 2008),
9 and the aviation NO_x emissions, obtained from the Emission Database for Global Atmospheric
10 Research (EDGAR), were placed at the model height of 9km. The soil NO_x emission was
11 doubled from its base value because the Yienger and Levy method (YL95) (Yienger and Levy,
12 1995) has been found to underpredict soil NO_x by around a factor of 2 over the United States
13 (Hudman et al., 2010). More details about the model inputs and configurations, the emission
14 inventory development, and evaluations of model meteorological inputs can be found in Tang et
15 al. (2013).

16 **2.2 GOES-derived photolysis rates**

17 The photolysis rate calculations in CAMx include two steps (ENVIRON, 2010). First, a
18 Tropospheric Ultraviolet and Visible (TUV) Radiation Model developed by the National Center
19 for Atmospheric Research (NCAR) is used to generate a multi-dimensional table of clear sky
20 photolysis rates (Madronich, 1987; NCAR, 2014) as inputs for the CAMx model as shown in Eq.
21 (1).

22 Clear sky photolysis rates (s⁻¹) are calculated as:

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

where $\sigma(\lambda)$ ($m^2/molecule$) is the absorption cross-section, λ is the wavelength (μm), $\phi(\lambda)$ is the quantum yield ($molecules/photon$), and $F(\lambda)$ is the actinic flux ($photons/m^2/s/\mu m$).

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):

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

Above the cloud, photolysis rates are modified as:

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

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.

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

13 **2.3 Emission regions and sectors for the inversion**

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

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

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

13 NO₂ sensitivities to NO_x emission in each emission sector used in the following sector-
14 based DKF inversions are calculated through DDM (Fig. 5). The biogenic, lightning, and non-
15 EGU point sources have their own spatial patterns that differ from the other emission sectors. For
16 example, the aviation source shows strong sensitivity centered from the DFW and HGB regions
17 and slowly spreading elsewhere. The sensitivities from the area, non-road and on-road sources
18 have similar spatial patterns concentrated in urban areas due to strong anthropogenic activities,
19 while the on-road source can be distinguished by the strong highway emissions. Previous studies
20 (Rodgers, 2000; Curci et al., 2010) indicated that the inversion results would be ill-conditioned
21 to estimate strongly overlapped sources. Therefore, in this study, the area and non-road sources
22 are grouped as a single sector in the DKF inversions.

1 **2.4 DKF Inversion**

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

5 The DKF inversion process (Prinn 2000), driven by the difference between the measured
6 NO₂ ($C_{NO_2}^{observed}$) and the modeled NO₂ ($C_{NO_2}^{predicted}$), seeks the optimal emission perturbation factors
7 ($\hat{\mathbf{X}}$) (a posteriori) by adjusting NO_x emissions in each designated emission region or sector
8 iteratively until each a priori emission perturbation factor (\mathbf{X}^-) converges within a prescribed
9 criterion, 0.01.

$$10 \quad \hat{\mathbf{x}}_{NO_x} = \mathbf{x}_{NO_x}^- + \mathbf{P}_{NO_x}^- \mathbf{S}^T (\mathbf{S} \mathbf{P}_{NO_x}^- \mathbf{S}^T + \mathbf{R}_{OMI})^{-1} (\mathbf{C}_{NO_2}^{observed} - \mathbf{C}_{NO_2}^{predicted} - \mathbf{S} \mathbf{x}_{NO_x}^-) \quad (5)$$

11 \mathbf{S} in Eq. (5), calculated via DDM in this study, is the first-order semi-normalized
12 sensitivity matrix of NO₂ concentrations to either region-based or sector-based NO_x emissions.
13 The uncertainty value in the measurement error covariance matrix (\mathbf{R}) for the OMI observed
14 NO₂ is set to 30% (Bucsela et al., 2013) for all diagonal elements. The uncertainties adopted
15 from Hanna et al. (2001) provide the values for each of the diagonal elements in the emission
16 error covariance matrix (\mathbf{P}). A value of 100% is assigned to each emission region, and to the area,
17 non-road, aviation, on-road, and biogenic emission sectors, but a value of 50% is assigned to the
18 non-EGU point emission sector. The uncertainty of lightning NO_x emissions was estimated in
19 recent studies, ranging from 30% (Martin et al., 2007) to 60% (Schumann and Huntrieser, 2007)
20 on a global scale; thus, the uncertainty value in the lightning sector is set to 50% here. The off-

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

3 **2.5 NO₂ observations**

4 **2.5.1 Satellite NO₂ observations**

5 The Dutch-Finnish OMI aboard the NASA Aura satellite measures daily NO₂ at around 13:40
6 local time (LT) with the highest spatial resolution of 13×24 km² at nadir viewpoint (Levelt et al.,
7 2006a, b; Boersma et al., 2007). Tang et al. (2013) used the NASA OMI standard, version 2.1
8 (Bucsela et al., 2013; Lamsal et al., 2014) NO₂ retrieval with an a priori profile generated from
9 the Global Modeling Initiative (GMI) model to conduct inverse modeling, and reported an
10 overestimation of NO₂ levels in rural areas. More recently, a high resolution OMI NO₂ retrieval
11 was developed based on the NASA standard product, version 2.1, but using an a priori NO₂
12 profile generated from nested GEOS-Chem simulations (0.5°×0.666°) with a 2005 emission
13 inventory. Because the emission inventory used in GEOS-Chem simulations includes lightning
14 and other elevated sources, it may better represent the upper tropospheric NO₂ in the retrieval;
15 hence, in this study, the high resolution NASA retrieval is chosen for the DKF inversions. In the
16 high resolution NASA product, only the OMI pixels with sizes less than 16×40km² (scan
17 position 10-50) in the clear-sky condition (cloud radiance fraction < 0.5) are selected in creating
18 the gridded data at 0.1°×0.1° resolution and then mapped to the 12km CAMx modeling domain.
19 Since applying OMI averaging kernels (Eskes and Boersma, 2003) may introduce more
20 uncertainties to the CAMx-derived NO₂ VCD in this case (Supplement, Sect. 1), the CAMx
21 modeled NO₂ are compared to the OMI NO₂ directly (Supplement, Sect. 1).

1 **2.5.2 Ground and P-3 aircraft NO₂ observations**

2 The CAMx simulated NO₂ is evaluated by both ground and aircraft measurements. The ground-
3 level NO₂ measurements data are taken from the U.S. EPA Air Quality System (AQS) NO₂
4 ground monitoring network (Fig. 1) (<http://www.epa.gov/ttn/airs/airsaqs/>). The correction factors
5 (Lamsal et al., 2008; Tang et al., 2013) are applied to the ground measured NO₂ before
6 comparing with the modeled results due to the measurement artifacts in the heated molybdenum
7 catalytic converter used by AQS NO₂ monitors.

8 The NOAA P-3 aircraft measurements

9 (<http://www.esrl.noaa.gov/csd/tropchem/2006TexAQS/>) are available on 31 August, 11
10 September, 13 September, and 15 September 2006 in our modeling period. The NO₂ was
11 measured by UV photolysis converter-chemiluminescence (Ryerson et al., 2000), and NO_y was
12 measured by Au converter-chemiluminescence (Ryerson et al., 1999) aboard the P-3 aircraft,
13 from ground to approximately 5km aloft and with a time resolution of 1-second; thus, hourly
14 averaged P-3 NO₂ and NO_y are calculated to compare with the modeled data at corresponding
15 time and grid cells.

16 **2.5.3 NASA DC-8 flight NO₂ observations**

17 The NO₂ measured by NASA DC-8 flights (<http://www-air.larc.nasa.gov/cgi-bin/arcstat>) during
18 the Intercontinental Chemical Transport Experiment-North America (INTEX-NA) field
19 campaign in 2004 (Singh et al., 2006) is used in this study to evaluate the modeled NO₂ vertical
20 profile, especially in the upper troposphere. The DC-8 flight NO₂ measurements were made on a
21 total of 18 days from 1 July to 14 August 2004, spanning from 7:00 to 20:00 CST with 1-second
22 resolution. The NO₂ was measured by the Thermal Dissociation-Laser Induced Fluorescence
23 (TD-LIF) instrument. TD-LIF measurements of NO₂ can be impacted by methyl peroxy nitrate

1 (CH₃O₂NO₂) and HO₂NO₂ in a temperature-dependent manner; thus, corrections based on the
2 method of Browne et al., (2011) are applied before comparing with the modeled profile. The
3 modeled NO₂ in grid cells within the 36km domain are used to match the measurement data in
4 space, and then all measurement data at each model layer are averaged over all measurement
5 time to compare with the monthly 12-h (7:00-20:00LT) averaged modeled data at the
6 corresponding layer. Although the measurements took place in 2004 and our modeling period is
7 in 2006, we assume the inter-annual variation is insignificant because the upper tropospheric
8 NO₂ is mainly contributed by natural sources and cross-tropopause transport.

9 **3. Results and Discussion**

10 **3.1 Impact of GOES-derived photolysis rates on modeled NO₂ and O₃**

11 The GOES-retrieved cloud fractions and broadband transmissivity as described in section 2.2 are
12 used to adjust the photolysis rates in CAMx. To investigate the impact from GOES-derived
13 photolysis rates, the differences of modeled ground-level NO₂ photolysis rate (J_{NO_2}), NO₂, and O₃
14 between CAMx modeling with and without the GOES-retrieved cloud fractions and
15 transmissivity are calculated.

16 Using GOES-observed clouds corrects the cloud underprediction issue in the current
17 meteorological models (Pour-Biazar et al., 2007; Guenther et al., 2012; ENVIRON 2012),
18 making J_{NO_2} decreases over most of the domain in this study. While on the average there is a
19 domain-wide reduction in J_{NO_2} , the impact on O₃ production is not uniform (Figs. 2 and 3),
20 mostly paired with the NO_x emission distributions. The general impact of using GOES
21 observations is that where the J_{NO_2} decreases, modeled NO₂ increases, and O₃ decreases (Figs. 2
22 and 3), indicating that slower photochemical activity inhibits O₃ formation and thus consumes

1 less NO₂, and vice versa. However, an exception occurs at places close to the Houston Ship
2 Channel, showing that although the J_{NO₂} decreases, modeled NO₂ still decreases (Fig. 3b) and O₃
3 slightly increases (Fig. 3c). This is probably caused by the availability of other pathways for
4 consuming NO_x in the VOC-rich environment, and the inhibition of NO regeneration due to
5 reduction in photochemical activity. The largest discrepancy of 80ppb in modeled O₃ occurs at
6 13:00 on 2 September 2006 over the DFW region during the modeling period. At that time,
7 GOES-based modeling showed up to 6 times higher J_{NO₂} (reaching approximately 36s⁻¹), and
8 10ppb lower NO₂ in this region (Fig. 2). However, the differences in modeled J_{NO₂}, NO₂, and O₃
9 are much more moderate on a monthly 8-h (10:00-18:00) averaged basis, reaching only up to 3s⁻¹
10 for J_{NO₂}, 0.6ppb for NO₂, and 3ppb for O₃, with largest discrepancies in the HGB region (Fig. 3).
11 For the changes in O₃ sensitivities, approximately 6% less J_{NO₂} on a domain-wide makes
12 modeled O₃ overall less sensitive to NO_x emissions (Fig. 3d) and more sensitive to VOC
13 emissions (Fig. 3e).

14 The modeled daily 8-h (10:00-18:00LT) NO₂ and O₃ using either satellite-derived or base
15 model photolysis rates are evaluated by AQS measured data for the entire modeling period. The
16 positive changes in spatiotemporal correlation (R²) and negative changes in NMB and NME
17 indicate that satellite-derived photolysis rates improved model performance (Fig. 4). For O₃
18 simulations (Fig. 4 right), the difference in R² increases 1% on average and reaches up to 7% on
19 26 August, while the differences in NMBs and NMEs decrease 1% on average and reach up to
20 10% on 11 September, suggesting the satellite-corrected photolysis rates improve the model
21 performance in simulating ground O₃. However, NMB and NME for NO₂ simulations (Fig. 4 left)
22 do not improve despite an increase in R², probably because other uncertainties in the model and
23 measurements may have a larger impact on NO₂ performance.

1 **3.2 Pseudodata test for the sector-based DKF inversion**

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

7 The pseudodata test for the sector-based DKF inversion is conducted on 10 modeling
8 days (13 August to 22 August), but the modeling results from the first 3 days are discarded to
9 eliminate the model initialization error. A 7-day (16 August to 22 August) averaged modeled
10 NO₂ VCD at 13:00-14:00LT with the base case NO_x emission inventory is treated as a pseudo-
11 observation, and the one using perturbed NO_x emissions in six emission sectors with known
12 perturbation factors ranging from 0.5 to 2.0 (Fig. 6) is used as a priori case. As described in
13 section 2.3, the area and non-road emission sources are considered as one sector (ARNR), and
14 EGU point source is excluded from the inversion. The emission uncertainties are set to 50% for
15 the non-EGU and lightning sectors and to 100% for the others. The measurement error for the
16 pseudo-observation is set to 30%.

17 The pseudodata test results (Fig. 6 top) show that the a posteriori modeled NO₂ closely
18 matches the base case modeled value, indicating the DKF inversion is capable of correcting the
19 perturbed NO_x emissions in each emission sector. The sensitivity analysis results (Fig. 6 bottom)
20 illustrate that the inversions are insensitive to both emission and observation error covariance
21 matrices for the pseudo-cases.

1 **3.3 A priori NO₂ VCD**

2 The a priori NO_x emission inventory used in this study is based on the TCEQ base case emission
3 inventory with added lightning and aviation and doubled soil NO_x emissions (Tang et al., 2013).
4 The reaction rate constant of the reaction NO₂ + OH in CB05 chemical mechanism is reduced by
5 25% based on Mollner et al. (2010); this tends to increase NO_x lifetime and transport to rural
6 regions.

7 To evaluate the extent to which the addition of lightning and aviation NO_x closes the
8 gap between observed and modeled NO₂ in the upper troposphere noticed by Napelenok et al.
9 (2008), the modeled NO₂ vertical profile is compared with INTEX-NA DC-8 measured NO₂
10 profiles from the ground to the free troposphere. The comparison (Fig. 7 left) shows that CAMx
11 with the a priori emission inventory strongly overestimates NO₂ near the ground, reasonably
12 agrees with DC-8 NO₂ measurements from 1km to 5km, slightly overestimates NO₂ from 6km to
13 9km, and slightly underestimates NO₂ from 10km to 15km. The modeled NO₂ profile is further
14 evaluated by the P-3 measured NO₂ from ground to 5km (Fig. 7 right), showing the same pattern
15 of the overestimated surface NO₂ and good agreement with aircraft observations from 1km-5km.
16 The injection of the aviation NO_x into a single model layer at altitude 6km to 9km rather than
17 more broadly distributed vertically probably causes the overestimation of modeled NO₂
18 compared to DC-8 at that altitude (ENVIRON, 2013). A low bias of modeled NO₂,
19 approximately 40ppt, exists in the upper troposphere, from 10km to 15km altitude, which is the
20 CAMx model top layer. Similar low bias of the modeled NO₂ in the upper troposphere compared
21 to the DC-8 measurement also has been found in Allen et al. (2012). Because the low bias in the
22 upper troposphere may arise from model uncertainties other than those associated with emissions
23 (Henderson et al., 2011; 2012), we follow the adjustment approach of Napelenok et al. (2008)

1 and add 40ppt NO₂ homogeneously to the top layer (10-15km) of the model results when
2 computing the CAMx NO₂ VCD.

3 Although the revised CB05 chemical mechanism and artificially added upper
4 tropospheric NO₂ increase modeled NO₂ VCD in the inversion region by an average of 13%
5 (Supplement, Sect. 2), CAMx modeled NO₂ VCD remain an average of 2×10^{14} molecules/cm²
6 less than OMI observations in rural regions (Fig. 8c).

7 **3.4 Top-down NO_x emissions constrained by DKF inversions**

8 The DKF inversions with OMI NO₂ are performed to constrain NO_x emissions in each
9 designated emission region and emission sector. To ensure sufficient spatial coverage, a monthly
10 averaged OMI NO₂ VCD (13 August to 15 September) is calculated and paired with the
11 corresponding modeled NO₂ VCD at satellite passing time (13:00-14:00LT). The DKF
12 inversions are then conducted with 2116 data points covering every grid cell in the inversion
13 region, and the hourly a priori NO_x emissions are adjusted iteratively until the inversion process
14 converges.

15 **3.4.1 Region-based DKF inversion**

16 The region-based DKF inversion is conducted to adjust the NO_x emissions in each inversion
17 region. The inversion results suggest to moderately adjust the a priori NO_x emissions in most
18 regions with scaling factors ranging from 0.97 to 1.49 (Table 2) and increases NO₂ VCD by 8%
19 toward OMI measurement over the inversion region (Fig. 8d). Because this inversion is based on
20 a new OMI-retrieved and an improved a priori NO₂ VCD, the required adjustments in each
21 inversion region are much lower compared to the results in Tang et al. (2013) with scaling
22 factors ranging from 0.56 to 1.98 and 30% increased NO₂ VCD.

1 The model performance is then evaluated by the ground and aircraft measurements. The
2 DKF inversion adjusts DFW NO_x emissions by only 3%, while it adds 49% to BPA emissions
3 and less than 15% to other urban regions. The NMB and NME of the a posteriori modeled NO₂
4 VCD decrease in every urban area and are reduced from -0.11 to -0.05 and from 0.17 to 0.16
5 overall compared to OMI. The spatial correlations between monthly averaged OMI and CAMx
6 NO₂ VCD (R²) are improved only in the BPA and Austin and San Antonio areas, but the overall
7 region-wide performance is improved (Table 3). The modeled NO₂ with a priori NO_x emissions
8 overpredicts ground-level NO₂ (Table 4); hence, the increase in NO_x emissions at most urban
9 places suggested by the inversion actually deteriorates the ground-level NO₂ simulations in all
10 urban areas except in the DFW region. The modeled NMB and NME of ground O₃ are reduced
11 in the HGB and BPA regions, but not in DFW, probably because the increased NO_x in the first
12 two regions titrates more ground O₃ at night and inhibits O₃ formation during the day, decreasing
13 the O₃ concentrations which are already overestimated in the a priori simulation (Table 6). No
14 improvements of model performance are found in simulating P-3 observed NO₂ and NO_y using
15 the inverted NO_x emissions.

16 Applying a single scaling factor to an entire inversion region may not well capture the
17 NO_x spatial distributions (Tang et al., 2013). Since DDM can also track the spatial relationship
18 between modeled NO₂ concentrations and NO_x emissions in each emission sector, a sector-based
19 DKF inversion can potentially serve as an alternative approach to constrain NO_x emissions in
20 order to have more heterogeneous adjustments in each inversion region.

1 **3.4.2 Sector-based DKF inversion**

2 The sector-based DKF inversion is first conducted on six NO_x emission sectors: area and
3 nonroad (ARNR), on-road, biogenic, aviation, lightning, and non-EGU points (Case I). The
4 scaling factors generated by the inversion ranges from 0.54 to 4.10, with the largest scale-down
5 in the ARNR sector and the largest scale-up in the aviation sector. The inversion reduces NO_x
6 emission in the biogenic sector by 30% from the a priori inventory which had doubled soil NO_x
7 from the base model. The inversion leaves on-road, lightning, and non-EGU points sectors nearly
8 unchanged, applying less than 4% adjustments (Table 2). The NO₂ VCD is increased by only 6%
9 toward OMI measurement over the inversion region in this case. Most of the increase in NO₂
10 VCD occurs in rural areas, and some declines occur in urban areas (Fig 8e).

11 The NO_x emission in each inversion region is recalculated after applying adjustments to
12 each emission sector, and model performance is evaluated by the ground and aircraft
13 measurements. The scaling factors in each region now are different and closer to 1 than those
14 generated by the region-based inversion, ranging from 0.86 in NE TX to 1.17 in DFW. The
15 modeled NMB and NME in simulating OMI NO₂ are all decreased in five urban areas. Within
16 the inversion region, the overall modeled NMB and NME are reduced from -0.11 to -0.04 and
17 from 0.17 to 0.14, respectively using inverted NO_x emissions (Table 3). The 50% cut in the
18 ARNR sector helps to improve the model performance in simulating ground-level NO₂ and O₃
19 which had been overestimated using a priori NO_x emissions. The inverted NO_x emissions
20 decrease modeled NMB and NME in all five urban areas and overall decrease NMB by 0.25 and
21 0.04, and NME by 0.13 and 0.04 in simulating ground-level NO₂ and O₃, respectively (Table 4
22 and Table 6). The model performance is also improved compared against P-3 measurements. For
23 NO₂, NMB is reduced from 0.09 to -0.02, and NME is reduced by 0.09. For NO_y, NMB is

1 reduced by 0.16 and NME is reduced by 0.11 (Table 5). The scaled-down ground NO_x emissions
2 lead to a 2-5 ppb lower modeled 8-h (10:00-18:00LT) ground O₃ and make O₃ formation
3 chemistry less sensitive to the VOC emissions, with reduction of 1-3ppb sensitivity coefficients
4 over the inversion region. The O₃ sensitivity to NO_x emissions also decreases by approximately
5 1-2ppb over most of the inversion region; however, the O₃ formation chemistry in the urban
6 cores of the DFW, HGB, and Austin and San Antonio regions shifts toward being more NO_x-
7 limited, leading to a 1-3 ppb increase of O₃ sensitivity to NO_x emissions (Fig. 9).

8 Although the inversion improves the model performance, the sensitivity analysis
9 (Supplement, Sect. 3) shows that the aviation and ARNR sectors are relatively responsive to the
10 emission uncertainty values and offset each other (Fig. S2), indicating the DKF inversion may
11 not be capable of fully distinguishing these two emission sectors. Therefore, the aviation source
12 is then merged with ARNR and the DKF inversion is re-conducted on five emission sectors: area,
13 nonroad, and aviation (ARNRAV), on-road, biogenic, lightning, and non-EGU points (Case II).
14 In case II, the inversion results are more stable and insensitive to the emission uncertainties in
15 each emission sector (Fig. S2). However, the inversion tends to scale up all three source
16 categories in the ARNRAV sector together by 50% to compensate for the rural NO₂ gap. The
17 inversion reduces on-road and biogenic NO_x emissions by 12% and 16%, respectively. The
18 adjustments for the lightning and non-EGU points sectors are still less than 4% (Table 2). On the
19 region basis, the inversion tends to increase NO_x emissions in all regions with increments
20 ranging from 1% in the Austin and San Antonio region to 18% in the NE TX region; it thus
21 increases the modeled NO₂ VCD by 7% on average. The inversed NO₂ VCD in this case is very
22 similar to that from the region-based inversion (Fig. 8f). The model performance of simulating
23 OMI NO₂ VCD is improved and similar to the results from case I (Table 3). However, unlike

1 case I, no improvements are found in simulating ground measured NO₂ and O₃ and P-3-
2 measured NO₂ and NO_y using the inverted NO_x emissions in case II (Table 4-6). Because the
3 ground NO_x emissions are increased in this case, the inversion impacts the O₃ simulations in the
4 opposite direction than in case I. The modeled 8-h ground O₃ increases by around 2ppb and
5 becomes more sensitive to both NO_x and VOC emissions over most of the inversion region;
6 however, the O₃ formation chemistry shifts toward being more VOC-limited in DFW and HGB
7 (Fig. 9).

8

9 **4. Conclusions**

10 Satellite-derived photolysis rates and NO_x emissions are both applied to a Texas SIP modeling
11 episode to investigate the capabilities of using satellite data to enhance state-level O₃ regulatory
12 modeling. Results show that the ground-level O₃ simulations are improved with reductions of
13 modeled NMB from 0.42 to 0.37 and modeled NME from 0.50 to 0.45 by using GOES-derived
14 photolysis rates and sector-based DKF (case I) with OMI NO₂ inverted NO_x emission inventory
15 (Table 6). The GOES-derived photolysis rates and OMI-constrained NO_x emissions decrease
16 monthly averaged 8-h O₃ concentrations by 2-5ppb over the entire inversion region and turn O₃
17 formation chemistry toward being less sensitive to NO_x and VOC emissions over most of
18 inversion areas, while being more NO_x sensitive in the two O₃ nonattainment areas, DFW and
19 HGB (Fig. 10).

20 Applying GOES-retrieved cloud coverage and transmissivity reduce the modeled
21 photolysis rates over most of the domain, leading to less photochemical activity and O₃
22 production and shifting O₃ formation chemistry toward being less sensitive to NO_x emissions,

1 except in the DFW region where modeled photolysis rates are increased by the GOES retrieval,
2 leading to impacts in the opposite direction. In comparing with the AQS ground measurements,
3 the GOES-derived photolysis rates improve the ground-level O₃ simulations but not the NO₂
4 simulations, indicating other model errors may dominate the accuracy of model performance in
5 simulating ground-level NO₂. The GOES-retrieved clouds applied here adjusted only the
6 modeled photolysis rates, while modeled clouds continued to drive the dynamics and aqueous
7 phase chemistry. This inconsistency in the placement of clouds is similar to the approach of a
8 previous study (Pour-Biazar et al., 2007). Thus, this work demonstrates a sensitivity study of
9 using satellite-derived photolysis rates on model performance rather than a full integration of
10 satellite-observed clouds into all aspects of the model. Future work could extend the use of
11 GOES-retrieved clouds to also correct model dynamics and aqueous phase chemistry and
12 investigate their impacts on NO_x and O₃ modeling.

13 The DKF inversion approach has been successfully incorporated with the CAMx-DDM
14 model and was conducted on both region-based and sector-based NO_x emissions. A controlled
15 pseudodata test conducted on the sector-based DKF inversion confirmed that it accurately
16 captures known perturbations in NO_x emission sectors. In addition to implementing lightning and
17 aviation NO_x emissions in the upper troposphere and doubling soil NO_x emissions from the
18 ground, the NO_x lifetime is increased by reducing 25% the reaction rate constant of the reaction
19 OH + NO₂. The upper tropospheric NO₂ underestimation is further eliminated by adding a 40ppt
20 homogenous NO₂ layer in the model top. On the other hand, the high resolution OMI retrieval
21 with a priori profile from the nested GEOS-Chem simulation further enhances NO₂ in urban
22 areas and reduces NO₂ in rural. However, the comparison still shows that the OMI has higher
23 NO₂ VCD than CAMx in rural areas, by around 2×10^{14} molecules/cm². It is not clear that the

1 discrepancy between OMI and CAMx in rural areas is caused by uncertainties in NO_x emission
2 inventory or errors in OMI retrieval and other model uncertainties. The OMI NO₂ retrieval can
3 be further improved by using the finer resolution terrain and albedo data (Russell et al., 2011)
4 and observed vertical profiles from aircraft spiral measurements in the recent DISCOVER-AQ
5 Houston measurement campaign (Crawford et al., 2014). The accuracy of CAMx modeled NO₂
6 VCD can benefit from further improving the modeled chemical and transport processes
7 (ENVIRON 2013), such as updating NO_x recycling process to increase NO_x lifetime, or adding
8 cross-tropopause transport processes to allow more stratospheric NO₂ penetrate to upper
9 troposphere. This may obtain better spatial distribution of modeled NO₂ rather than adding a
10 homogeneous layer at top to compensate the model deficiency.

11 The region-based DKF inversion still over scales NO_x emissions in urban areas to
12 compensate for the rural NO₂ differences because the NO₂ VCD gap in rural areas is not
13 eliminated, leading to 10-50% increase of NO_x emissions at most regions and worsening the
14 ground-level O₃ simulations; however, the scaling factors generated in this study are much more
15 moderate than those were found in Tang et al. (2013). The sector-based DKF inversion (case I)
16 takes the aviation source to compensate the NO₂ gap in rural area, probably because its relatively
17 spread-out emission pattern over rural area corresponds with the NO₂ discrepancy distributions,
18 leading to appropriate adjustments in the ground emissions and improving both ground-level
19 NO₂ and O₃ simulations; however, the aviation source is unrealistically adjusted by applying a
20 suggested factor of 4 to its base value, and the adjustments offset the area and nonroad sector
21 with varying emission uncertainties in the sensitivity analysis. Although merging the aviation
22 source into the area and nonroad emission sector makes the inversion (case II) more stable, the
23 large scaling factor for the aviation sector is now shared with area and nonroad emissions,

1 leading to area and nonroad NO_x emissions being scaled up by 50%. Thus, the model
2 performance in ground-level NO₂ and O₃ simulations is deteriorated and is even worse than the
3 results generated from the region-based inversion. The lightning NO_x emissions seem to be well
4 estimated and are adjusted little by the inversion. However, it may also indicate that the OMI
5 retrieved NO₂ is insensitive to the lightning source, most probably due to the NO_x partitioning
6 predominantly to NO in the upper troposphere and the clear-sky cloud screening criterion used in
7 the OMI data processing. The NO₂ discrepancy between OMI and CAMx drives the DKF
8 inversion and is assumed to be mostly contributed by the uncertainties in the NO_x emission
9 inventory. However, findings from this study indicate that if the uncertainty in the a priori NO_x
10 emissions is low, errors in the satellite retrieval and model itself cannot be neglected, making the
11 inversion less capable of reducing the uncertainties in the bottom-up NO_x emission inventory.

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

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

6 The direct scaling inversion (Supplement, Sect. 4) using PAMS measured VOCs
7 improves the model performance in simulating five chosen VOC species and indicates the TCEQ
8 VOC emission inventory used in HGB SIP modeling is now much better than the previous
9 reported emissions with values off by an order of magnitude. However, the inverted VOC
10 emissions have insignificant impact on the ground-level NO₂ and O₃ simulations, probably
11 because of the limited spatial coverage of the PAMS measurement sites and most VOC-saturated
12 conditions in the inversion region. Future work could explore the capabilities of using satellite-
13 observed formaldehyde data to constrain the Texas isoprene or even other anthropogenic VOC
14 emissions (Defour et al., 2009; Curci et al., 2010).

15 The statistical results show that although the modeled NMB and NME are reduced,
16 OMI-constrained NO_x emissions barely improve the spatiotemporal correlations (R^2) with
17 ground-measured NO₂ and O₃, indicating that either applying the scaling factors generated at the
18 OMI passing time is unable to reduce the emission uncertainty at each hour or the current OMI
19 resolution is insufficient to capture the spatial distributions of the NO_x emission pattern. The
20 future launch of NASA Tropospheric Emission: Monitoring of Pollution (TEMPO) geostationary
21 satellite (Streets et al., 2013) could help address these shortcomings by providing a temporal
22 resolution down to an hour and a spatial resolution down to 4km×4km measurement.

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8

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1 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 |

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

3

4 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 |

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1 Table 3. Evaluation of CAMx modeled NO₂ using OMI NO₂.

| 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 |

2 a. Compared to OMI observations in all inversion regions

3 b. Normalized mean bias: $\Sigma(\text{Mod-Obs})/\Sigma(\text{Obs})$

4 c. Normalized mean error: $\Sigma|(\text{Mod-Obs})|/\Sigma|(\text{Obs})|$

5

6 Table 4. Evaluation of CAMx modeled NO₂ using hourly AQS ground-measured NO₂.

| 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 |

7 a. Compared to all ground sites

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1 Table 5. Evaluation of CAMx modeled NO₂ using P-3 aircraft-measured NO₂ 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 |

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

3

4 Table 6. Evaluation of CAMx modeled O₃ using hourly AQS ground-measured O₃.

| 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 |

5 a. Compared to all ground sites

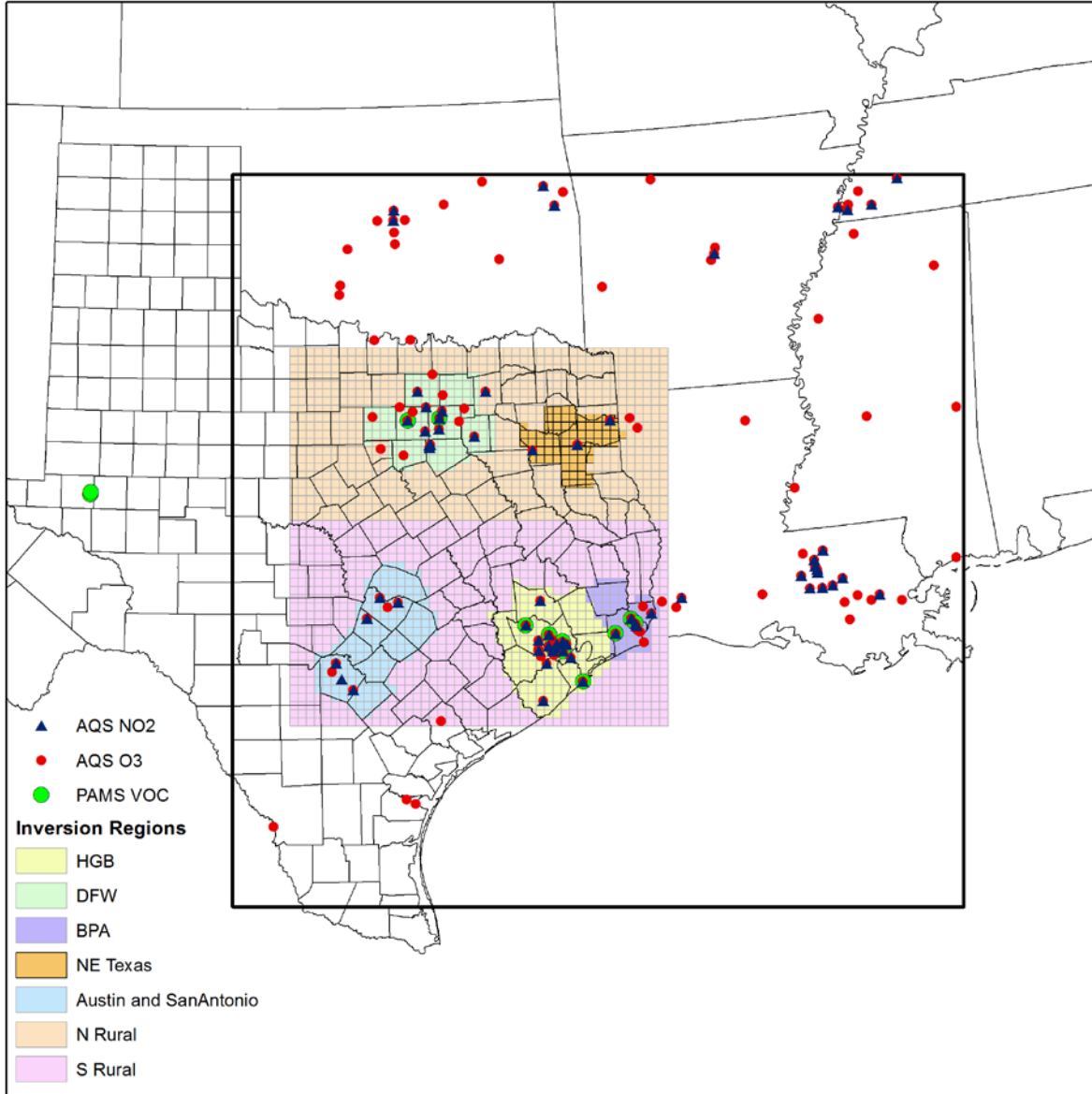
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3 Figure 1. Seven designated inversion regions in eastern Texas (shaded) within 12-km CAMx
4 modeling domain (black square) covered by ground NO₂ monitoring sites (blue triangles), VOC
5 monitoring sites (green circles), and O₃ monitoring sites (red circles).

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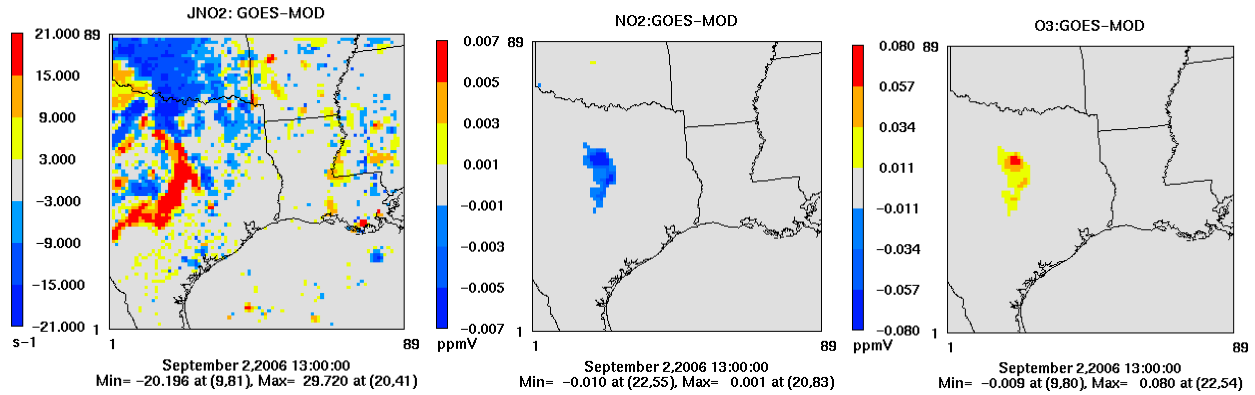


Figure 2. Differences between satellite-derived (GOES) and model predicted (MOD) J_{NO_2} (left) in simulating NO_2 (middle) and O_3 (right) at 13:00 on 2 September 2006.

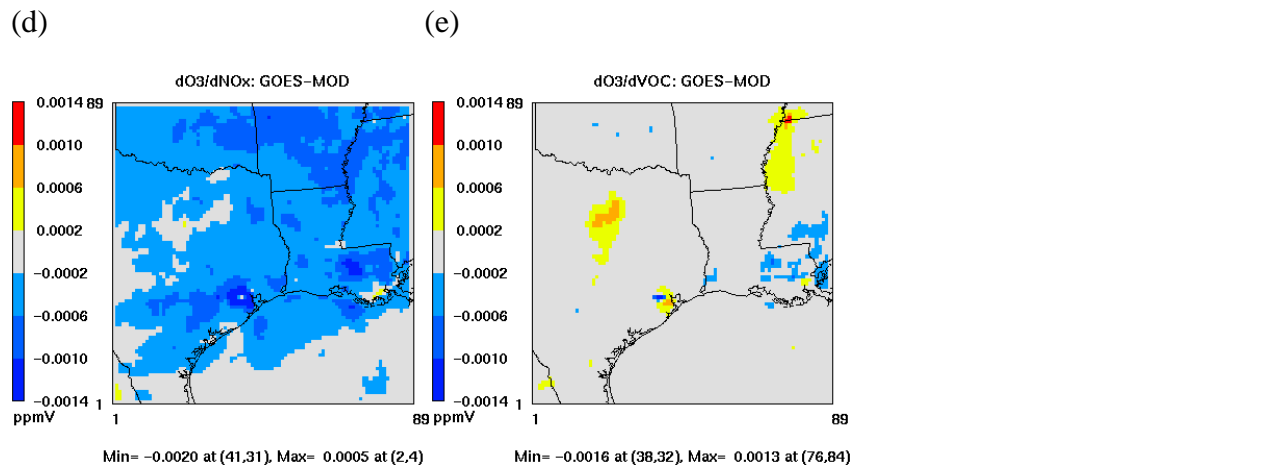
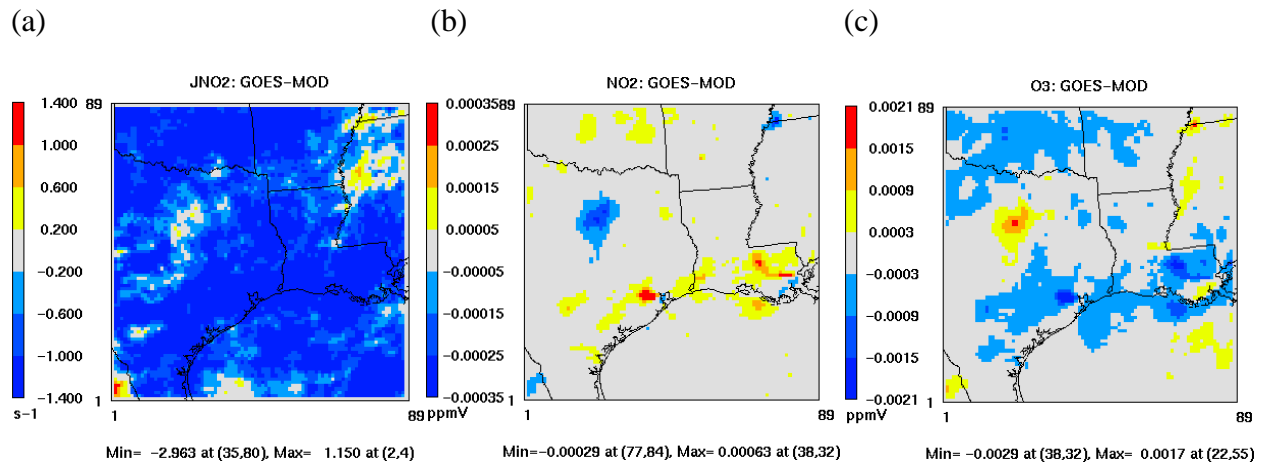
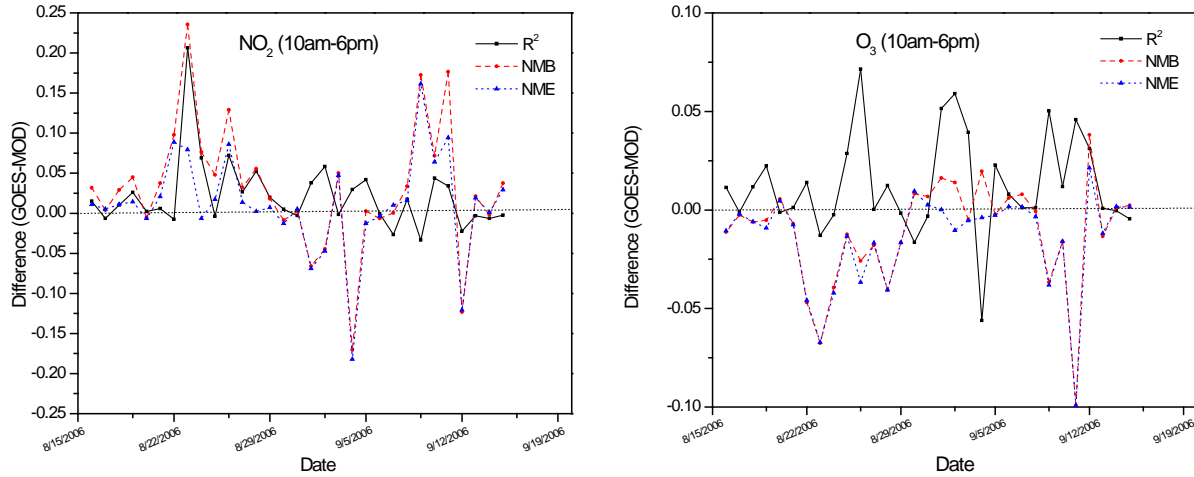


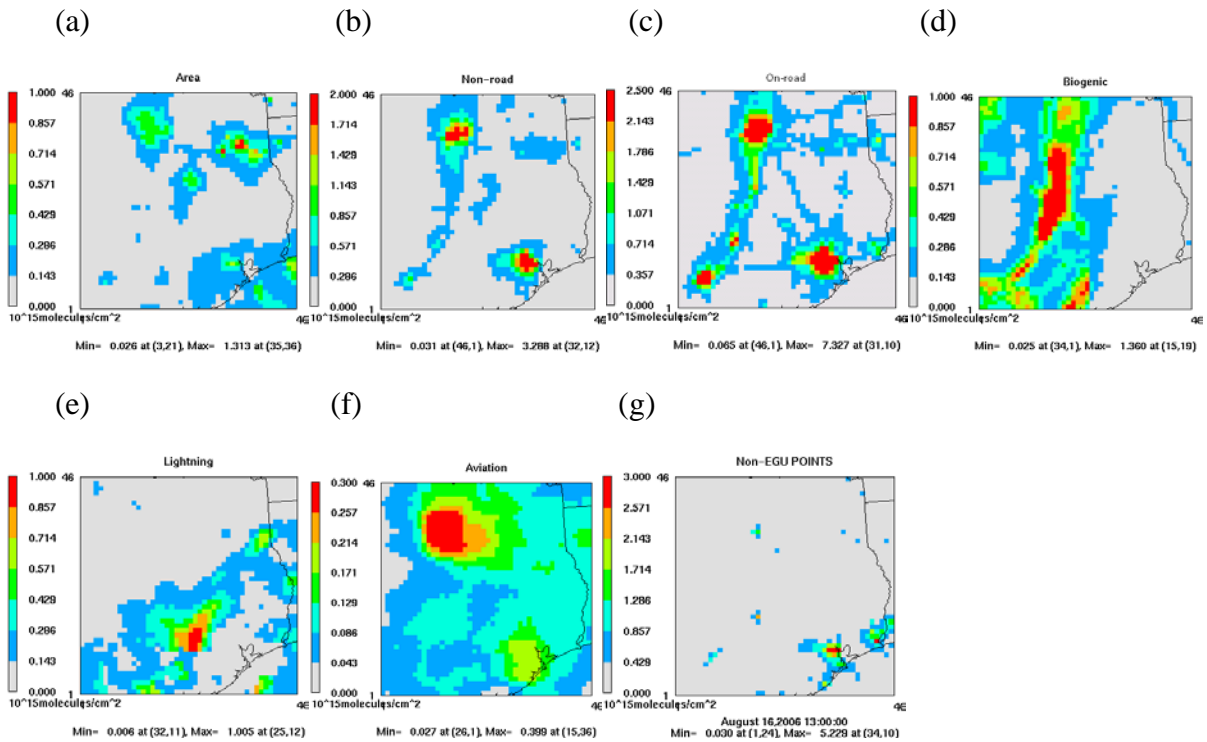
Figure 3. Monthly 8-h (10:00-18:00LT) averaged differences between satellite-derived (GOES) and model predicted (MOD) (a) JNO_2 in simulating (b) NO_2 , (c) O_3 , and O_3 sensitivities to (d) NO_x and (e) VOC.



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 2 Figure 4. Change in model performance (R^2 , NMB, and NME) in simulating daily 8 hours
 3 (10:00-18:00LT) NO_2 (left) and O_3 (right) caused by satellite-derived photolysis rates.

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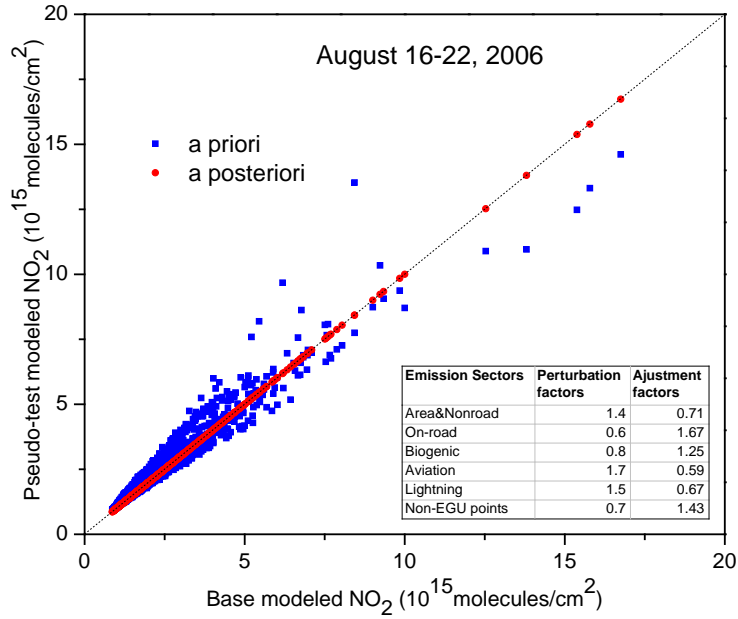


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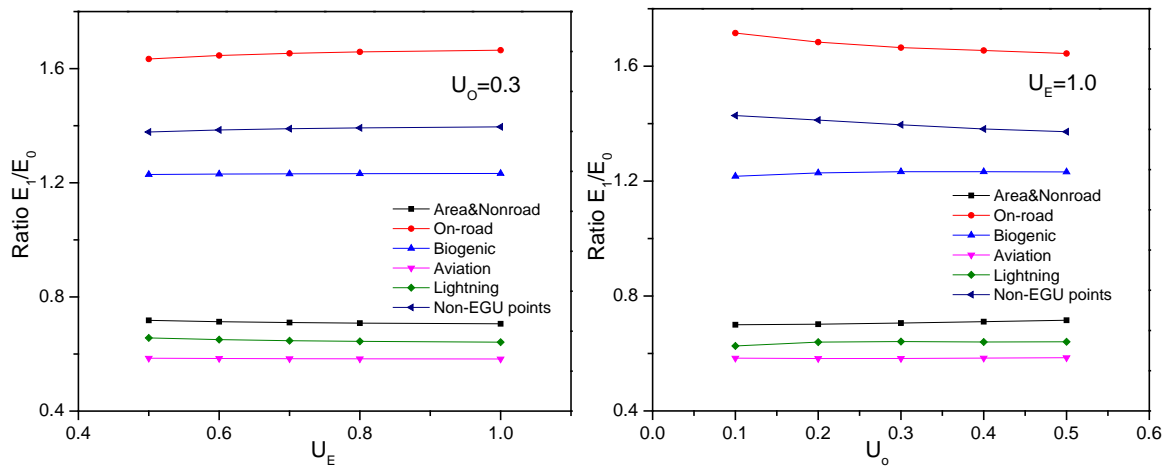
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9 Figure 5. Vertical column densities of NO_2 sensitivities to NO_x emissions of (a) area, (b) non-
 10 road, (c) on-road, (d) biogenic, (e) lightning, (f) aviation, and (g) non-EGU points source sectors.



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

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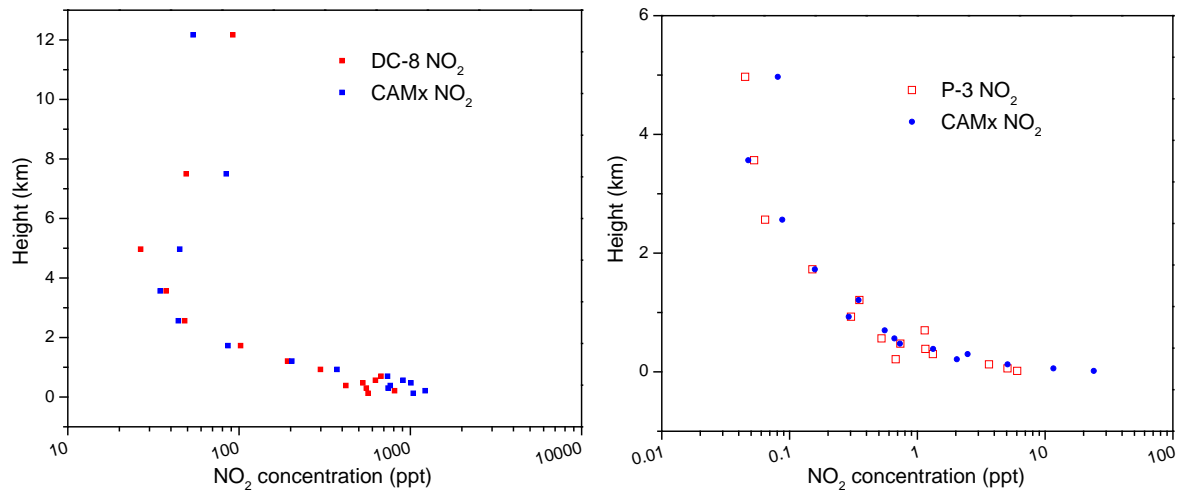
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3 Figure 7. Comparisons of modeled NO₂ vertical distributions with INTEX NASA DC-8 flight
4 (left) and TexAQS 2006 NOAA P-3 aircraft (right) measurements.

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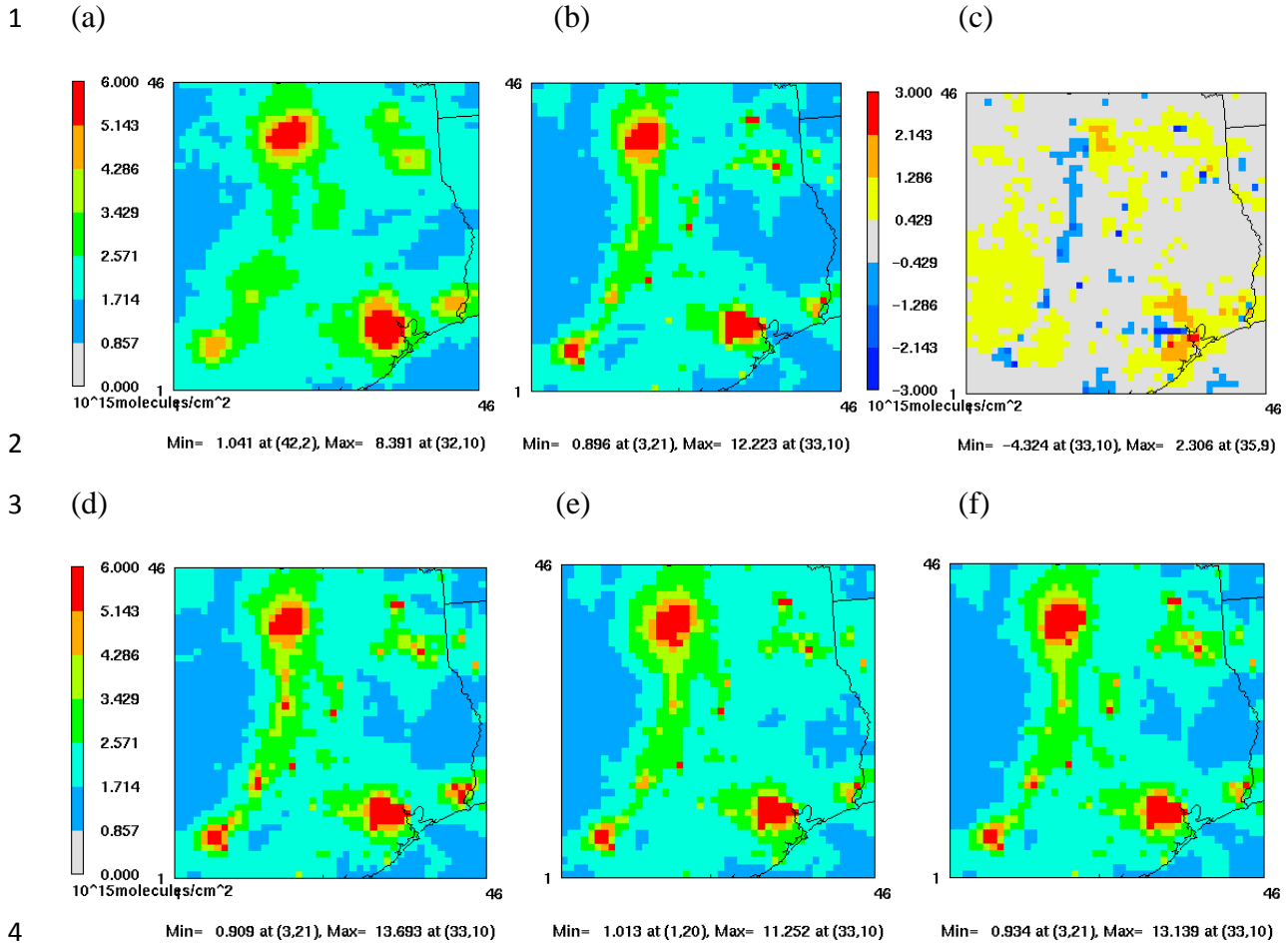
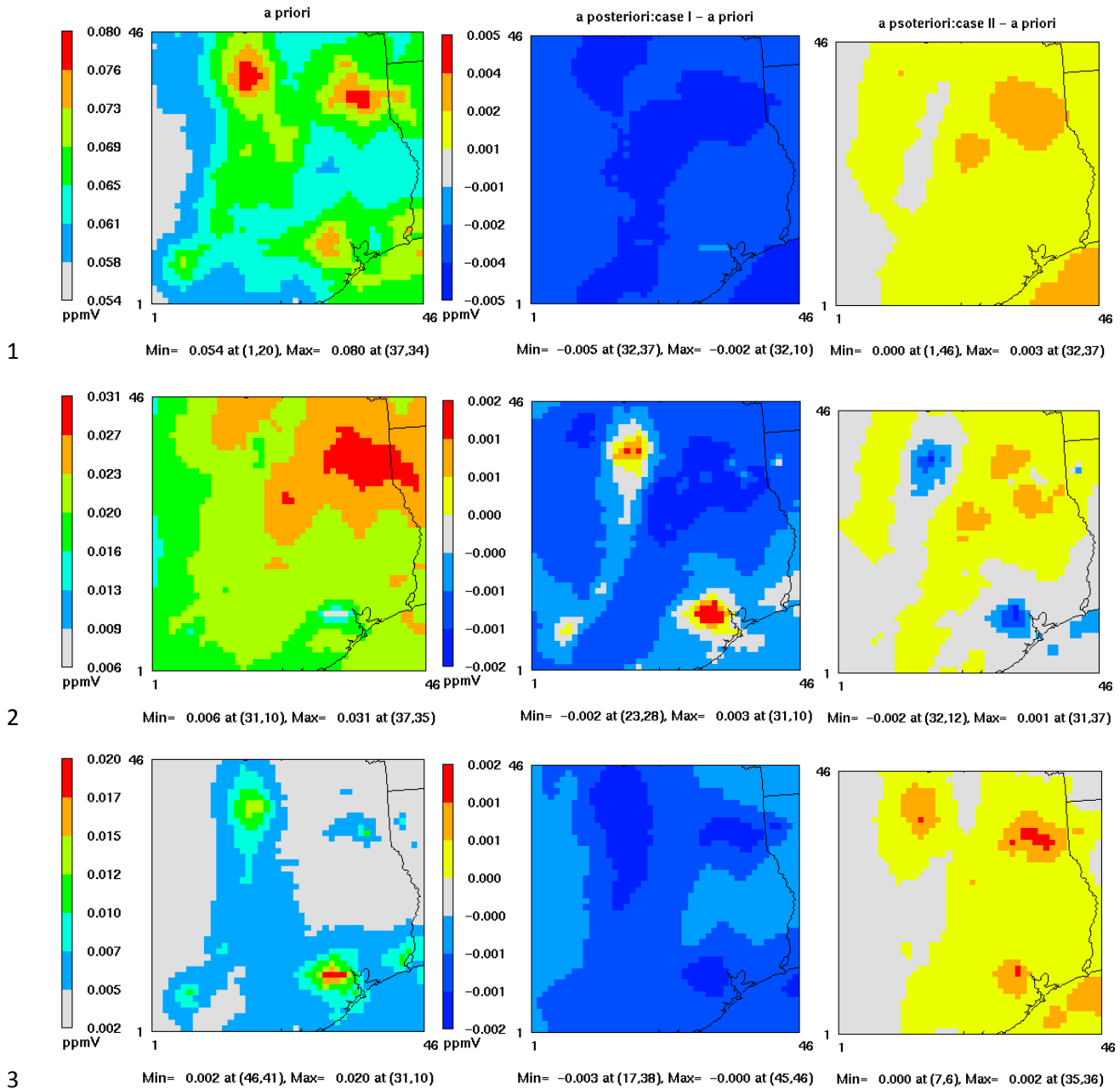


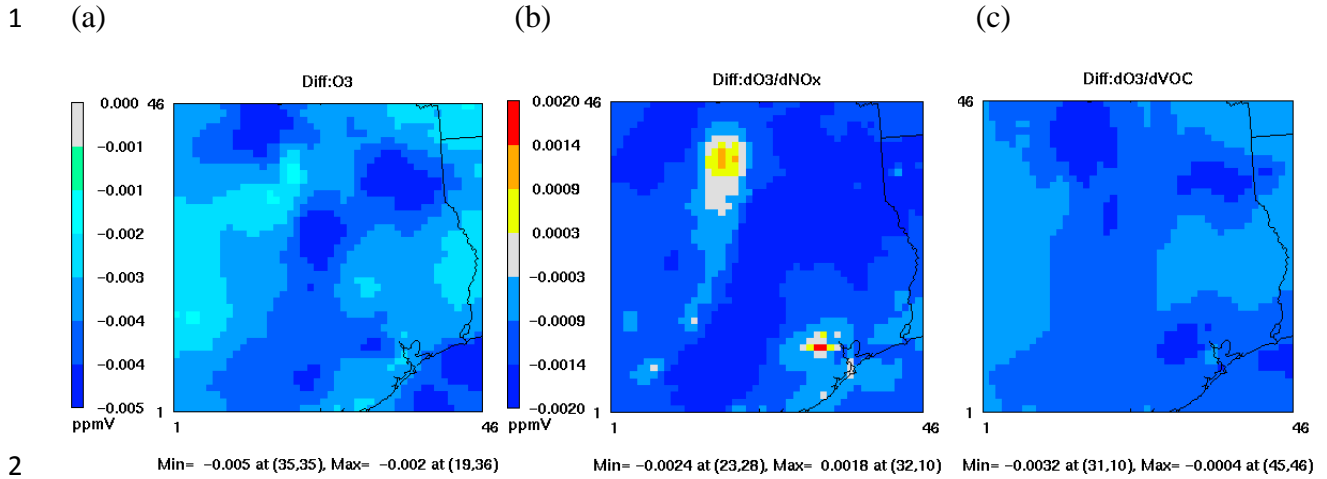
Figure 8. Monthly averaged (16 August to 15 September) tropospheric NO₂ VCD at 13:00-14:00LT from (a) OMI, (b) a priori simulation, (c) difference between OMI and a priori simulation, and simulations using a posteriori NO_x emissions generated by (d) region-based DKF inversion, and sector-based DKF inversion (e) case I and (f) case II.



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

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3 Figure 10. Monthly 8-h (10:00-18:00LT) averaged differences in modeled (a) ground O₃
 4 concentrations, (b) O₃ sensitivity to NO_x, and (c) O₃ sensitivity to VOC resulting from use of
 5 both satellite-derived photolysis rates and NO_x emissions in place of a priori data.