Changes in ozone chemical regime over the contiguous United States inferred by the inversion of NO_x and VOC emissions using satellite observation

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Ozone chemical regime in the U.S.

- During the last few decades, a number of nation-wide regulations have been implemented to reduce O_3 and its precursor concentrations. **The substantial reduction in O_3 precursor emissions may induce change in the O_3 chemical regime.**
- The identification of the O_3 chemical regime is essential to determining the effectiveness of O_3 control policies. Hence, numerous studies that have been undertaken to explain changes in the O_3 chemical regime have employed **the satellite-derived HCHO-to-NO_2 ratio (HCHO/NO_2) as an indicator for O_3-NO_x-VOC sensitivity** and numerical modeling (Choi et al., 2012; Duncan et al., 2010; Martin et al., 2004; Schroeder et al., 2017; Tonnesen and Dennis, 2000).

Ozone chemical regime in the U.S.

➢ However,

1) Recent studies have reported **the changes in satellite-observed NO_2 and HCHO columns do not reflect the trend in the U.S. NEI and near-surface air quality**.

   - NO_2: the relative contribution of the background sources of NOx in the troposphere (e.g., lightning and soils) has increased (Kang et al., 2019; Silvern et al., 2019)
   - HCHO: biogenic and biomass burning (open fire) emissions, primarily driven by the temperature, are generally dominant over the southeastern and western U.S., respectively, in summer months (Curci et al., 2010; Palmer et al., 2003; Zhu et al., 2017).

2) CTMs are useful for not only connecting the column and surface air quality but also identifying the response of O_3 to changes in the emissions of its precursors. **The uncertainty of emission inventories often causes significant bias** in the results of models when they are compared to observed values.

Object of this study

- We applied an analytical inverse modeling technique with the Ozone Monitoring Instrument (OMI) NO_2 and HCHO column retrievals and estimated top-down nitrogen oxide (NOx) and non-methane volatile organic compounds (NMVOCs) emissions over the contiguous U.S. (CONUS) in the summers of 2011, 2014, and 2017.

- **From adjusted emissions, we examined changes in the ozone chemical regime over the CONUS throughout the study period**.

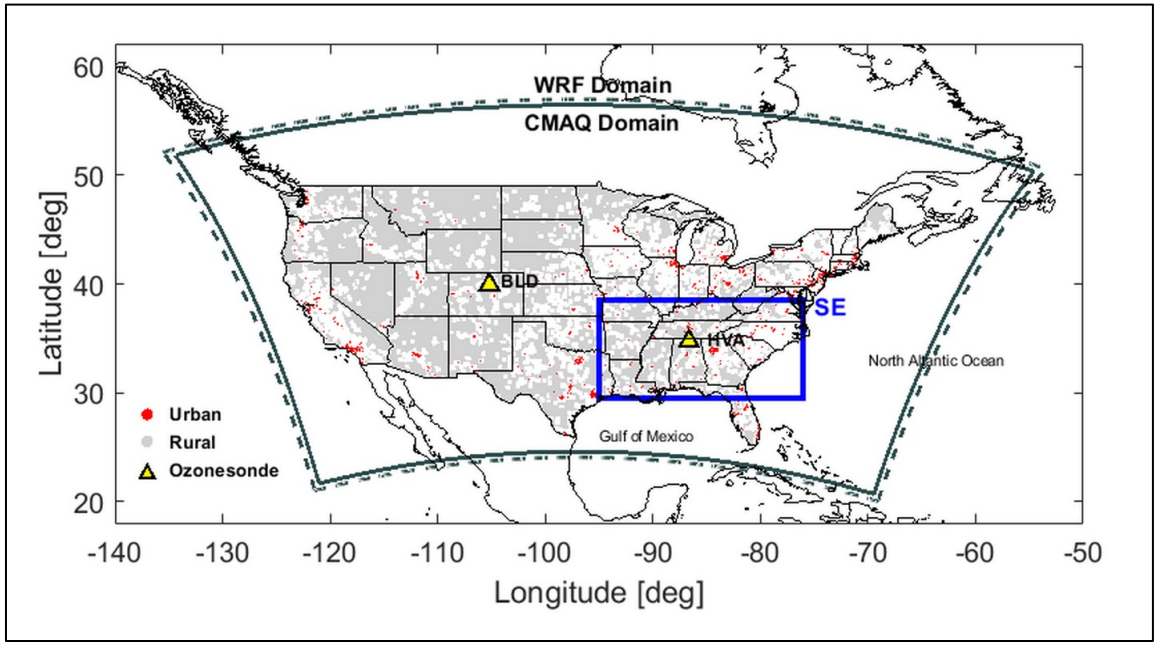


Figure 1. Map of the study domain and definition of urban (red) and rural (gray) regions over the CONUS. The yellow triangle symbols represent the location of ozonesonde stations (BLD: Boulder, HVA: Huntsville).

Modeling setup

- We used the CMAQ DDM-3D model version 5.2 (Cohan et al., 2005; Napelenok et al., 2006), developed and released by the EPA.
  - CB6r3 and AERO6 mechanism
  - WRF4.0 with the NARR
  - Emission data

Anthropogenic emission	U.S. EPA NEI 2011 v6.3, 2014 v7.1, and 2017
Biogenic emission	The Biogenic Emission Inventory System (BEIS) version 3.61
Lightning-induced emission	In-line lightning NO(LNO) production module with hourly flash rates from the National Lightning Detection Network (NLDN)
Biomass burning emission	The Fire Inventory from National Center for Atmospheric Research (FINN) version 1.5

Table 1. Model configurations.

WRF version 4.0	
Microphysics	Morrison double-moment scheme
Longwave and shortwave radiation	RRTMG scheme
Land surface	The Pleim-Xiu land surface model (Pleim and Xiu, 1995; Xiu and Pleim, 2001)
Surface layer	Pleim-Xiu surface layer (Pleim, 2006)
Planetary boundary layer	The ACM2 planetary boundary layer model (Pleim, 2007a, 2007b)
Cumulus parameterization	Kain-Fritsch (KF2) scheme with sub-grid cloud fraction interaction with radiation (Alapaty et al., 2012; Herwehe et al., 2014)
Four-dimensional data assimilation (FDDA)	· Indirect soil moisture and temperature nudging technique (Pleim and Gilliam, 2009; Pleim and Xiu, 2003) · A FDDA option every 6 hours above the PBL for the temperature, the water vapor mixing ratio, and wind components (magnitude of 10^{-5}) (Hogrefe et al., 2015)
Initial and boundary conditions for meteorology	National Centers for Environmental Prediction (NCEP) North American Reginal Reanalysis (NARR) data
CMAQ-DDM version 5.2	
Chemical mechanism	CB6 and AERO6
Horizontal advection	YAMO
Vertical advection	WRF omega formula
Horizontal diffusion	Multiscale
Vertical diffusion	ACM2
Initial and boundary conditions for chemistry	The CMAQ model version 5.3 with the in-line dust module covering the entire northern hemisphere in conjunction with scaling for gaseous species based on the comparison with satellite measurements

OMI NO_2 and HCHO column retrievals

- The OMI was launched in 2004 on the NASA Earth Observing System (EOS) Aura satellite, which is in a sun-synchronous polar orbit with a local equator crossing time of 13:45 ± 0:15.
- In this study, we use the tropospheric NO_2 and total HCHO columns from the OMI operational retrieval products (Level 2 and version 3) released by the NASA Goddard Earth Sciences Data and Information Service Center (GES DISC).
  - Filtered out unqualified pixels with a cloud fraction, a terrain reflectivity, a solar zenith angle, a data quality flag, a cross-track quality flag, etc.
  - Recalculated the air mass factor (AMF) and replaced the prior profile of OMI data with the profile of the CMAQ simulation of this study.

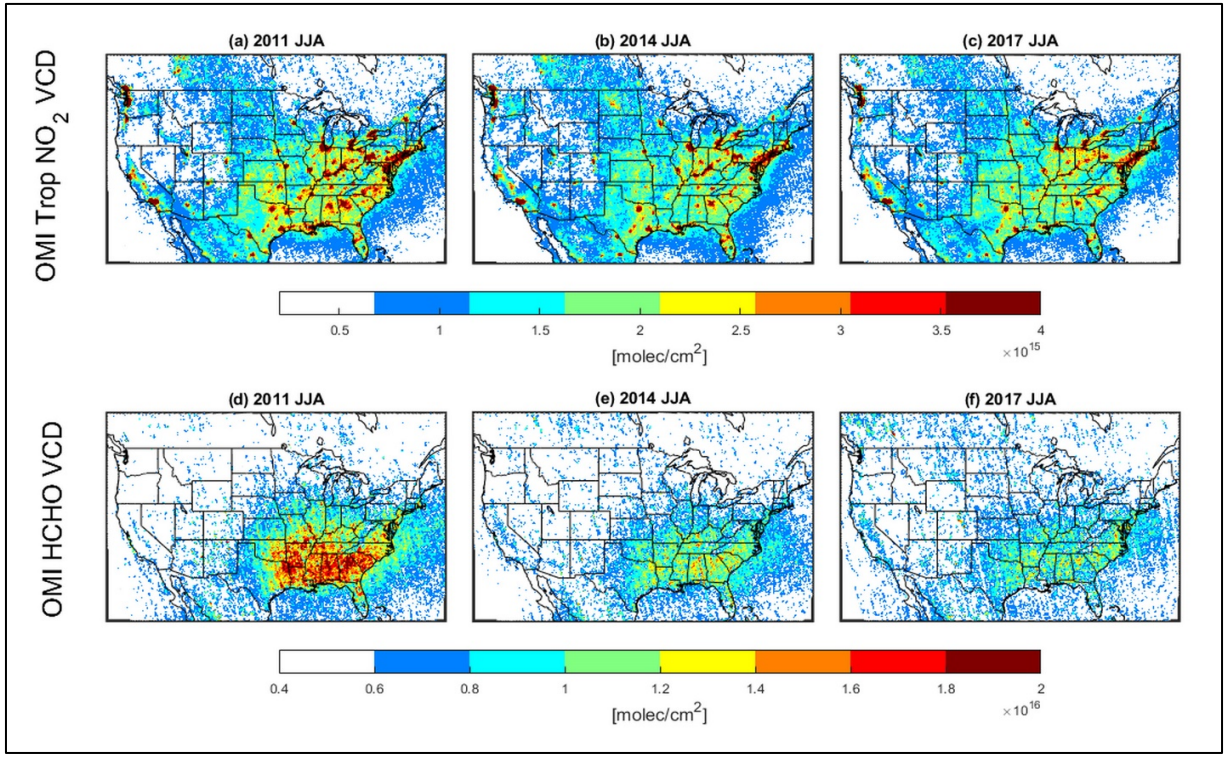
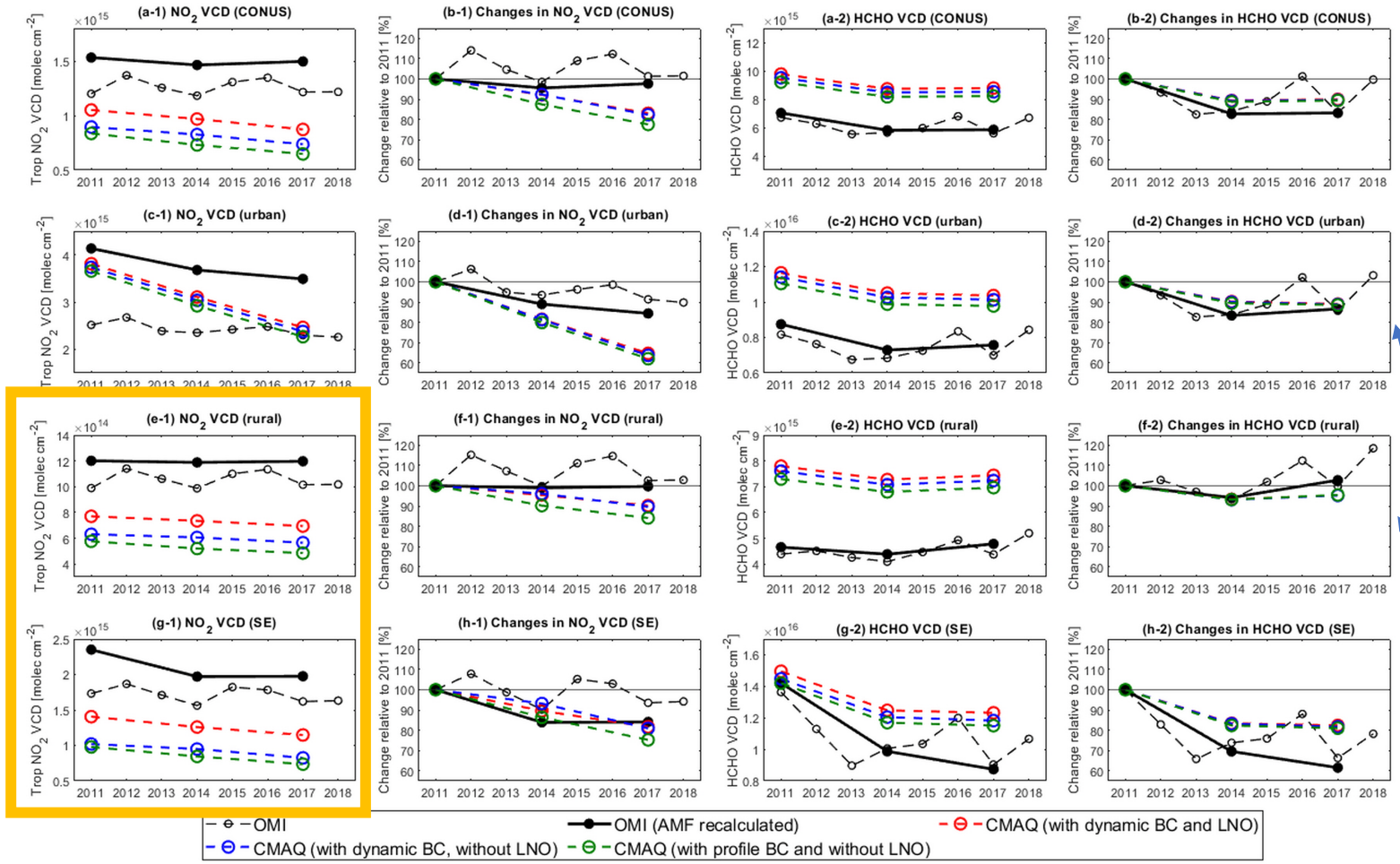


Figure 2. Spatial distribution of (a to c) the OMI tropospheric NO_2 vertical column density (VCD) and (d to f) the OMI HCHO VCD in the summers (June - August) of 2011, 2014, and 2017.

Changes in the NO_2 and HCHO Column Retrievals and the Contribution of Background Sources to the Upper Troposphere



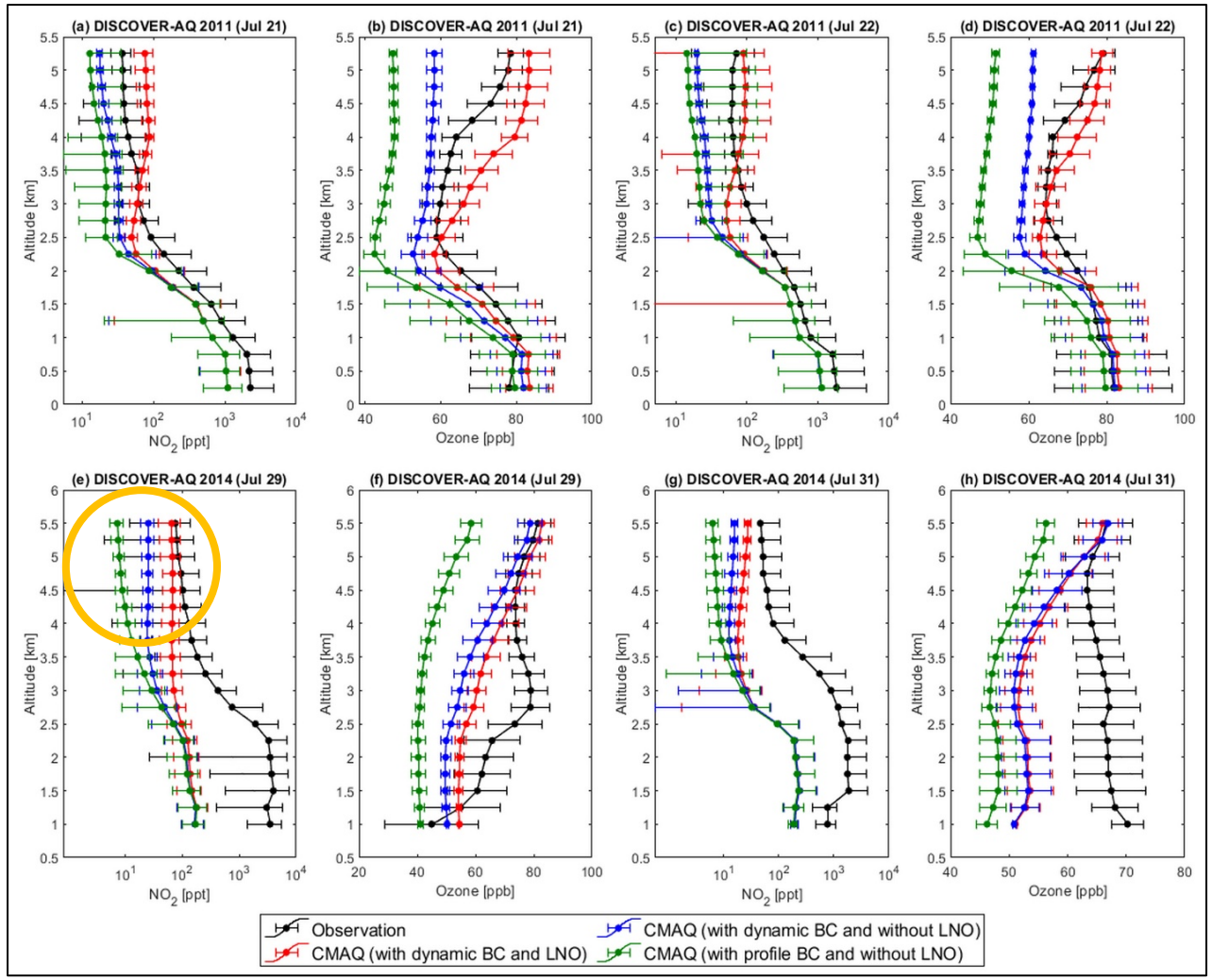
CMAQ background setup **(with prior emissions)**	
1	**With profile (static) boundary conditions (BC) and without lightning-induced emissions (LNO)**
2	**With dynamic BC and without LNO**
3	**With dynamic BC and with LNO**

- The CMAQ model with the in-line dust model covering the entire Northern Hemisphere (HCMAQ), providing dynamic chemical boundary conditions in a consistent physical configuration.
- we applied seasonal scaling with multiple satellite datasets (e.g., NASA OMI/Aura O_3, HCHO, NO_2, and MOPITT CO).

* SE area is excluded

Figure 3. Long-term trend in summertime averaged tropospheric (a-1 to h-1) NO_2 and (a-2 to h-2) HCHO columns observed by the OMI satellite (2011 – 2018) and simulated by the CMAQ model (2011, 2014 and 2017), and their relative changes in the CONUS and urban, rural, and southeastern U.S. regions.

The Contribution of Background Sources to the Upper Troposphere



- Comparison with NO_2 and O_3 concentrations measured by P-3B aircraft during the NASA DISCOVER-AQ 2011 and 2014 campaigns, which took place over the Baltimore/Washington D.C. metropolitan area and northern Colorado.
- The results show the need to account for background sources in the free troposphere, which would **prevent the misalignment of emission adjustments**.

CMAQ background setup **(with prior emissions)**	
1	**With profile (static) boundary conditions (BC) and without lightning-induced emissions (LNO)**
2	**With dynamic BC and without LNO**
3	**With dynamic BC and with LNO**

Figure 4. Comparisons of the vertical distribution of ozone and nitrogen dioxide (NO_2) concentrations measured during the DISCOVER-AQ (a to d) 2011 (July 21 and 22) and (e to h) 2014 (July 29 and 31) campaigns and modeled concentrations with prior emissions and three background setups. Error bars represent the standard deviation.

Top-down Estimation of NOx and NMVOC emission inventories

- Given the relatively short lifetime of NO_2 and HCHO, their satellite columns often correlate with NO_x and NMVOCs emissions and can be applied to estimations of top-down emission inventories.
- To constrain bottom-up emissions, we apply the Gauss-Newton method, an analytical inversion approach to finding solutions to problems that are not rigorously nonlinear, described in Rodgers (2000).
- This approach assumes no correlation between observations and emission errors, and the error covariances of observations and emissions with zero base Gaussian probability density functions.

$$J(x) = \frac{1}{2}\left(y - F(x)\right)^T S_o^{-1}\left(y - F(x)\right) + \frac{1}{2}(x - x_a)^T S_\epsilon^{-1}(x - x_a) \quad (1)$$

$$x_{i+1} = x_a + S_a K_i^T (K_i S_a K_i^T + S_\epsilon)^{-1}[y - F(x_i) + K_i(x_i - x_a)] \quad (2)$$

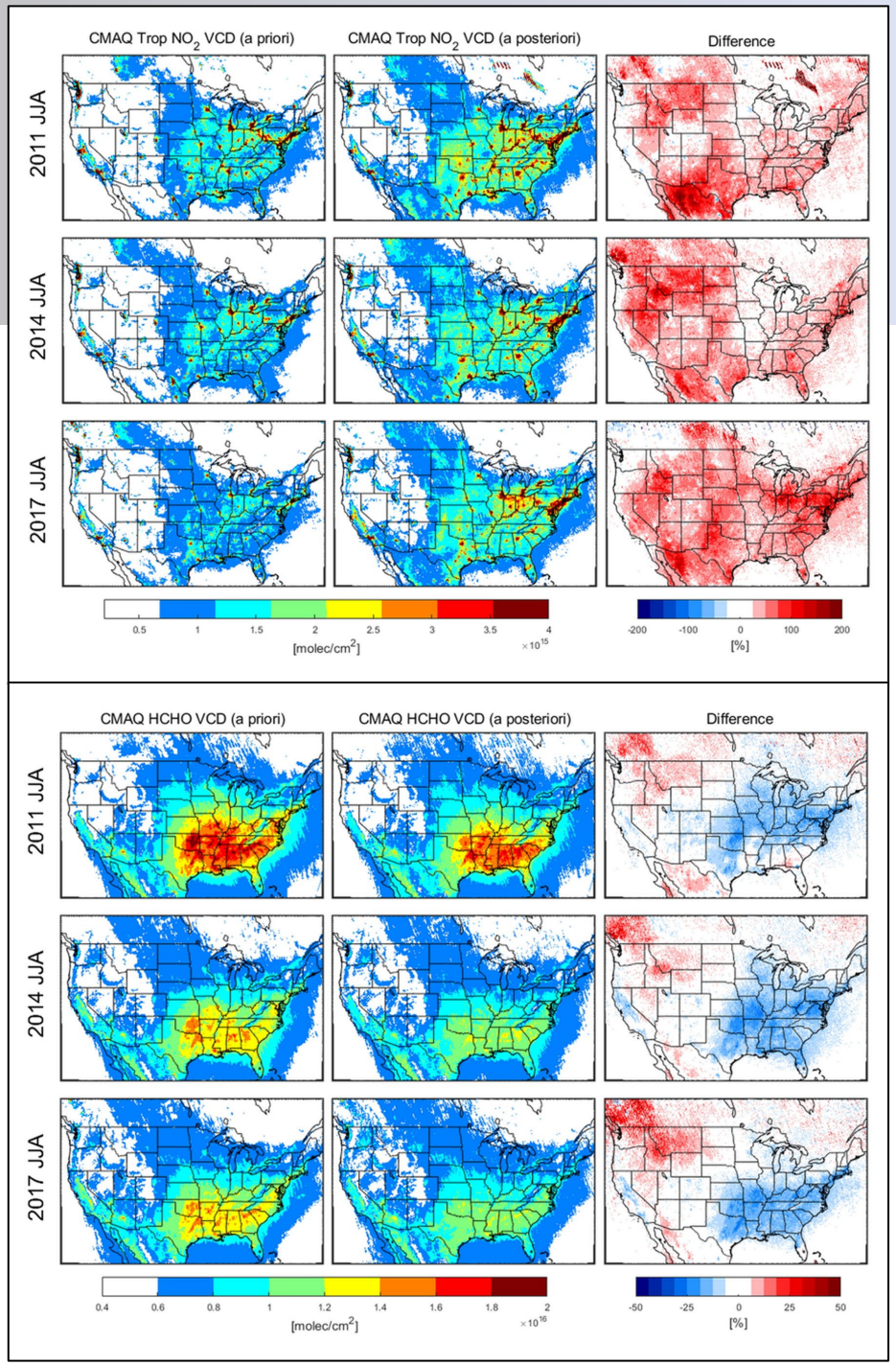
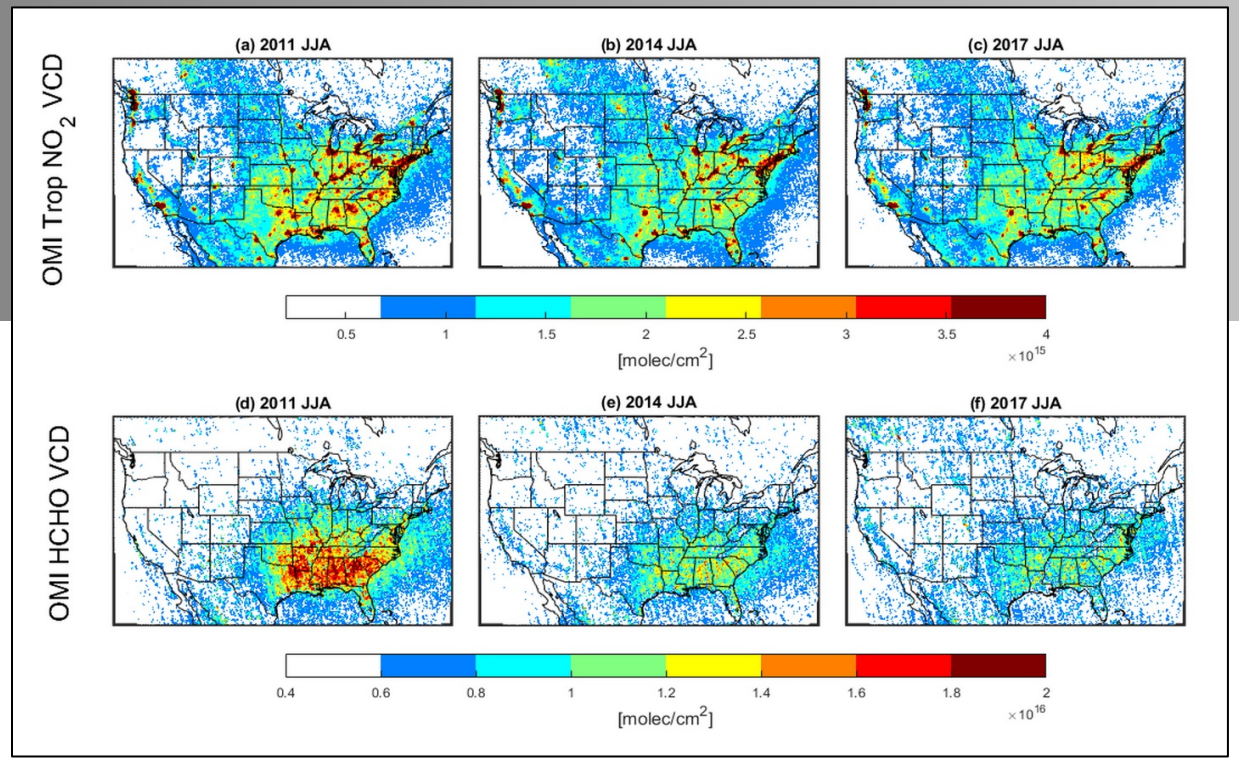
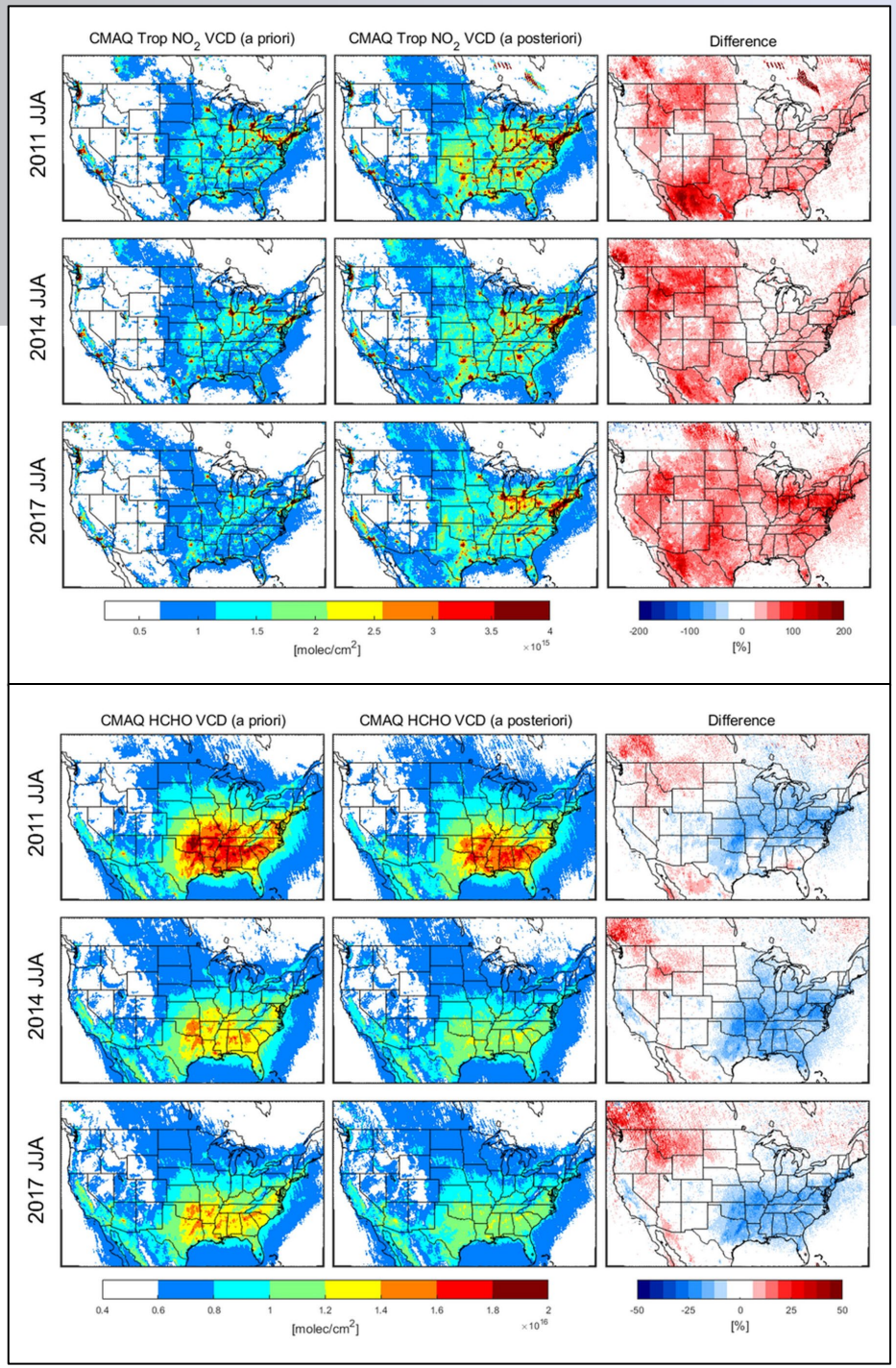


Figure 5. Spatial distribution of the modeled NO_2 and HCHO VCDs with prior and posteriori emissions, and their differences with respect to the modeled column density with priori emissions in the summers (June - August) of 2011, 2014, and 2017.





- Satellite-constrained NOx and NMVOC posterior emissions **significantly mitigate the discrepancy between satellite-observed and modeled columns**; nation-wide increases in tropospheric NO_2 column by 21.55 ± 28.76%, and the decrease in HCHO column over the southeastern US by -6.77 – -14.85%.
  - increased NOx emissions and NO_2 columns in Mexico and Canada
  - enhancement of the HCHO column over the northwestern U.S. with posterior emissions, possibly related to open fire events; the magnitude, however, was relatively small

Changes in the Ozone Chemical Regime over the CONUS

- To avoid the misclassification of the ozone chemical regime, we conducted an experiment to define threshold values by using the CMAQ model **with top-down estimated (posteriori) emission inventory**.

Difference between surface O3 concentration in the base CMAQ and emission reduction cases with respect to the modeled HCHO/NO2 ratio

Cumulative probability of NOx-limited and NOx-saturated conditions with respect to the modeled HCHO/NO2 ratio

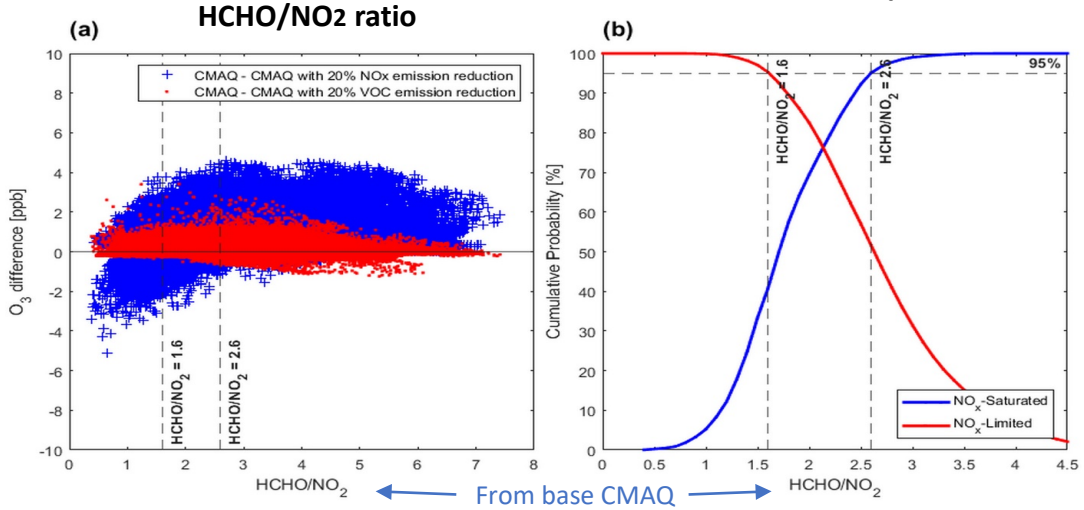


Figure 6. (a) Difference between the surface ozone concentrations of the baseline model output (with posterior emissions) and emission reduction cases in the summer of 2011; (b) the cumulative probability of NOx-limited and NOx-saturated conditions with respect to the ratio of the modeled column to the NO_2 column following Jin et al. (2017).

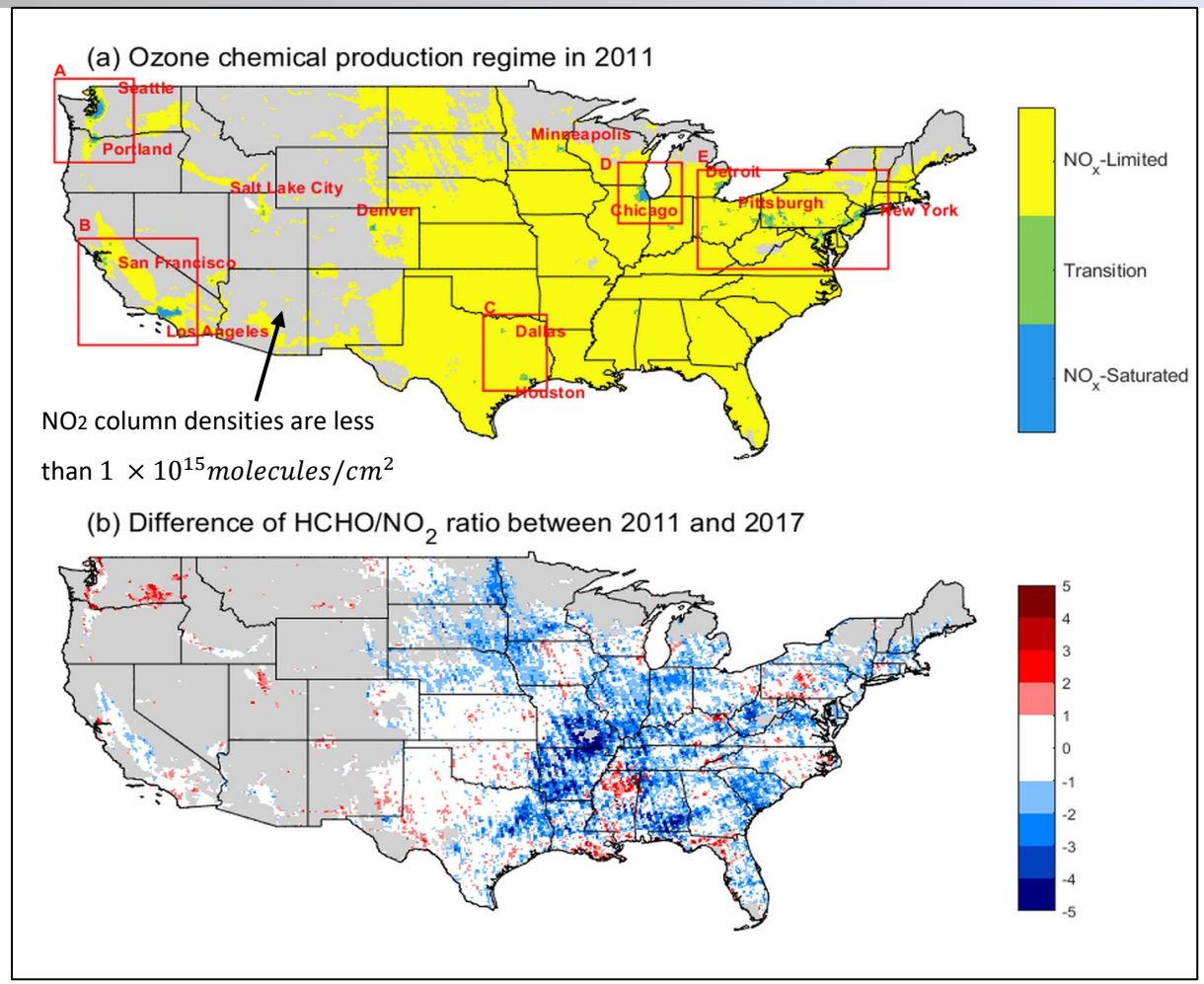
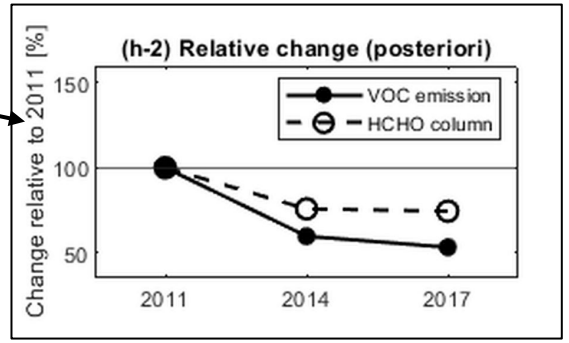
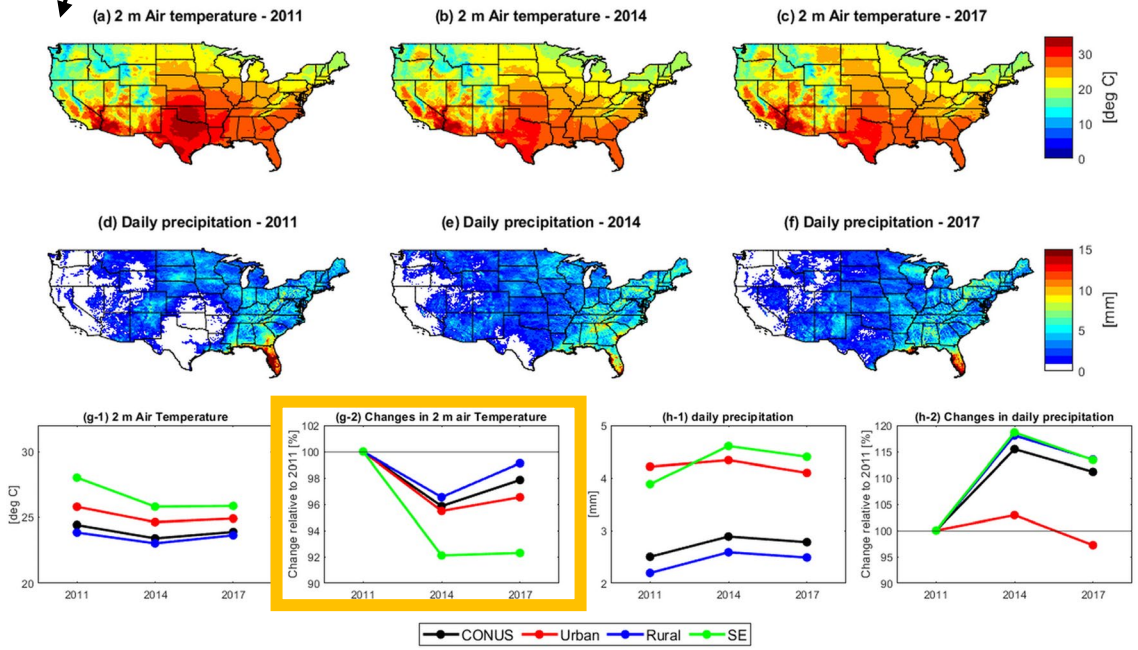


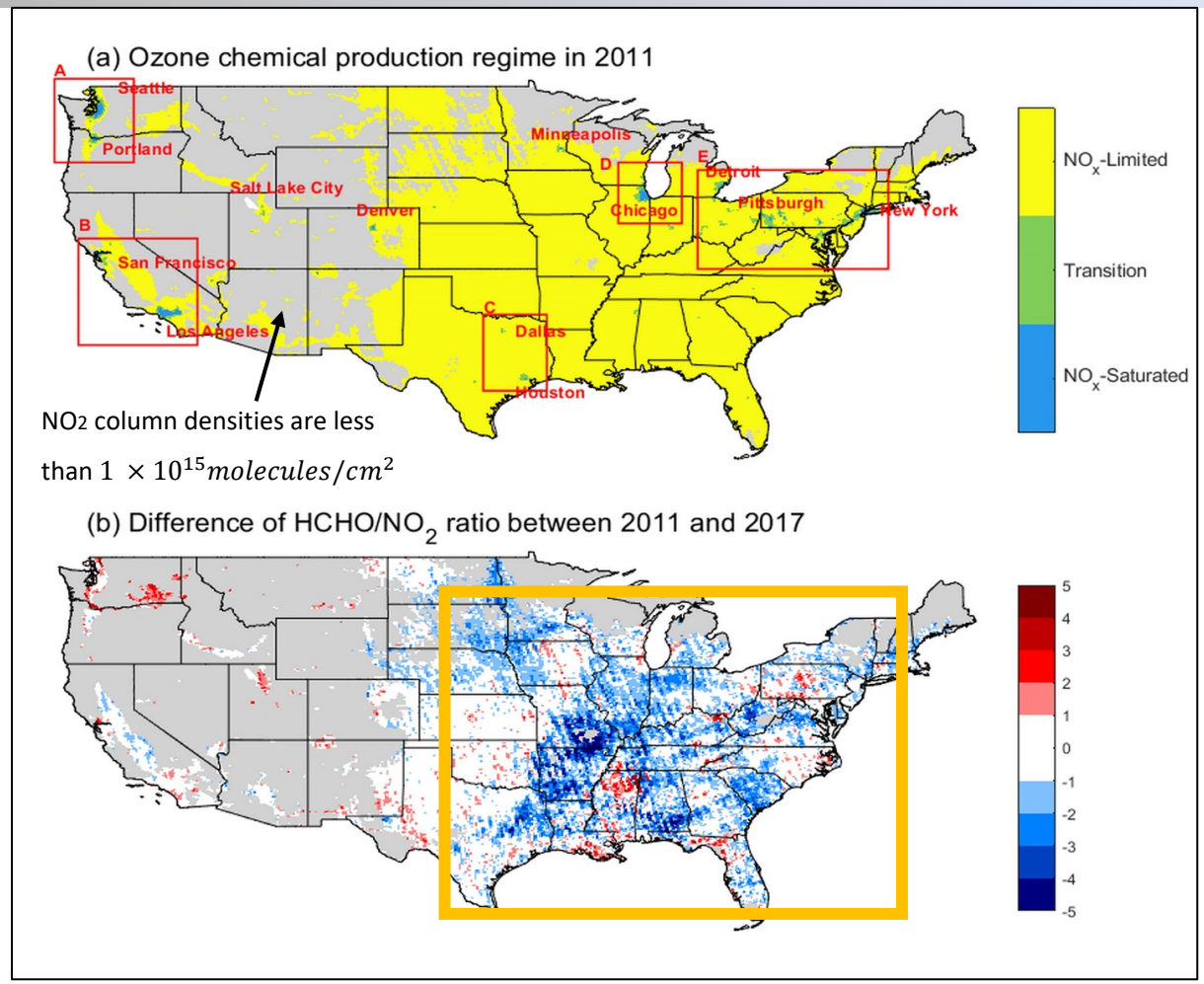
Figure 7. (a) Spatial distribution of the ozone chemical production regime over the CONUS for the year 2011. (b) The difference between the HCHO/NO2 ratios of 2011 and 2017.

Changes in the Ozone Chemical Regime over the CONUS

- **Relative changes in VOC emission and HCHO column (posteriori) over the southeastern (SE) U.S.**
- **Modeled 2 m air temperature and precipitation**







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Changes in the Ozone Chemical Regime over the CONUS

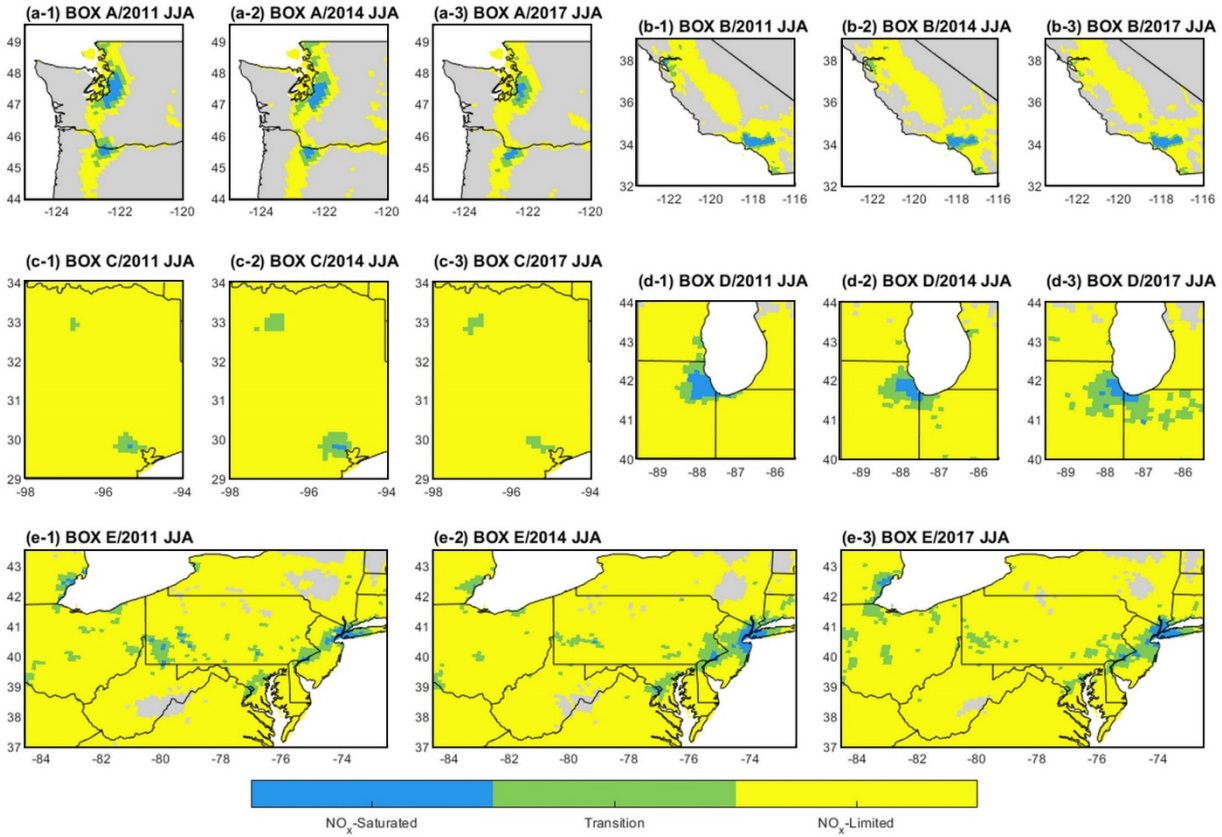

Figure 8. Changes in the ozone production regime over the 5 boxes.

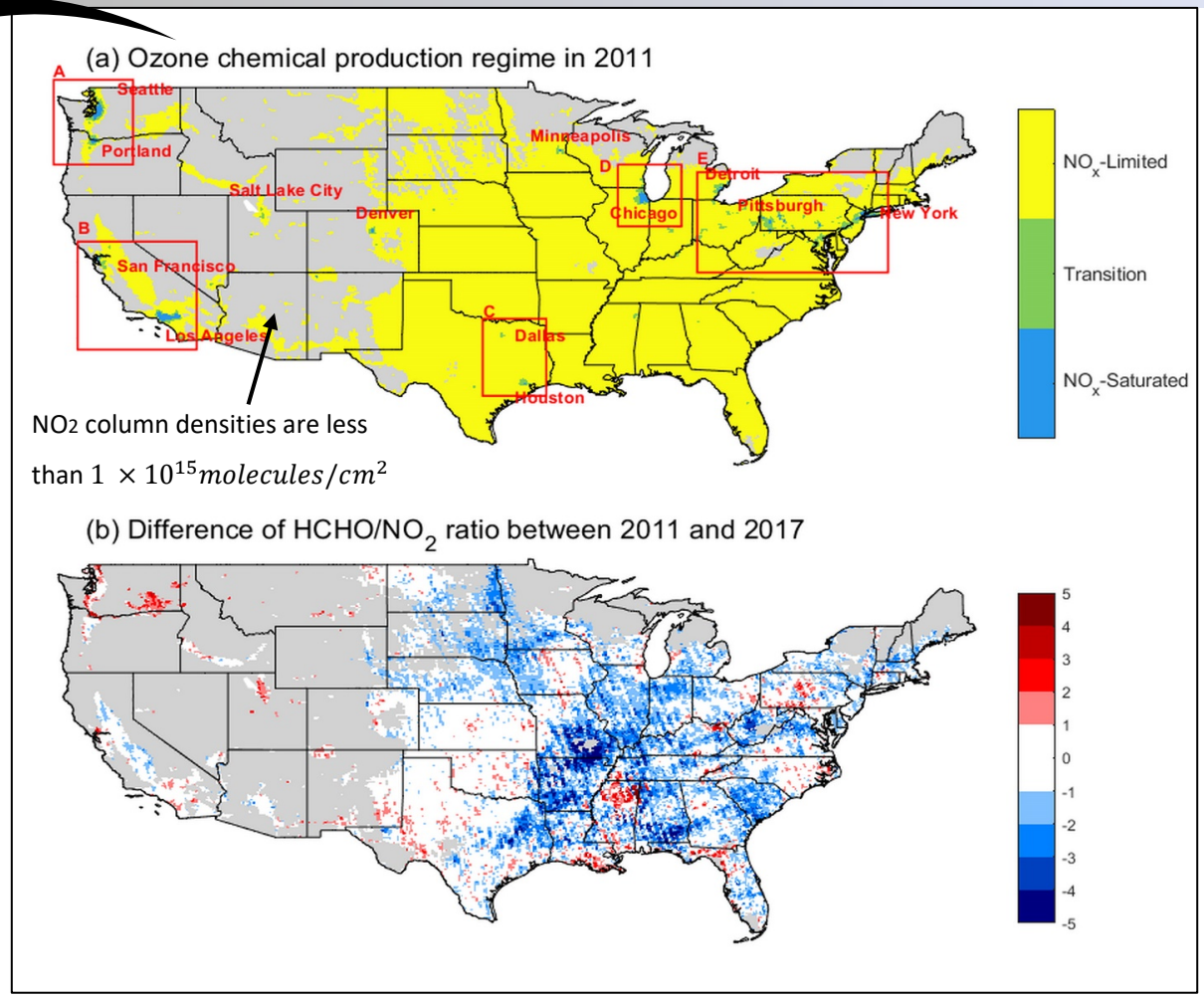

Figure 7. (a) Spatial distribution of the ozone chemical production regime over the CONUS for the year 2011. (b) The difference between the HCHO/NO2 ratios of 2011 and 2017.

Changes in the Ozone Chemical Regime over the CONUS

- Changes in the ozone chemical regime for 12 main cities over the CONUS

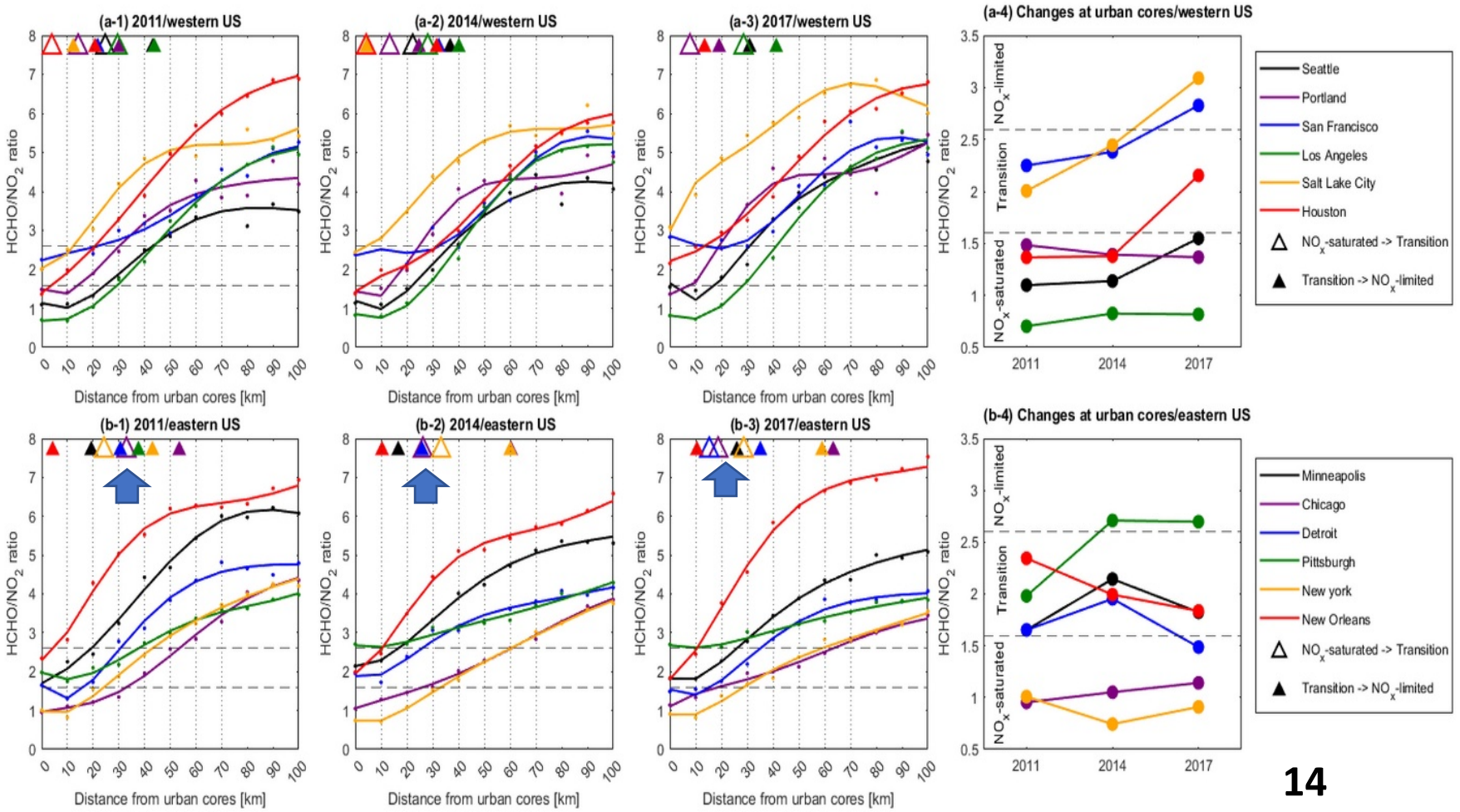

Figure 9. Changes in the HCHO/NO2 ratio according to the distance from urban cores and at urban cores for 12 main cities over (a-1 to a-4) the western U.S. (Seattle, Portland, San Francisco, Los Angeles, Salt Lake City, and Houston), and (b-1 to b-4) the eastern U.S. (Minneapolis, Chicago, Detroit, Pittsburgh, New York, and New Orleans).

Conclusion

- To investigate the changes in ozone chemical production regime over the continuous United States with accurate knowledge of concentrations of its precursors, we applied an inverse modeling technique with the OMI NO_2 and HCHO columns to estimate NO_x and NMVOC emissions in the summers of 2011, 2014, and 2017.
- Results showed **gradual spatial changes in the O_3 production regime near urban cores** during the study period, as well as **apparent shifts from NOx-saturated regime to transition regime (or transition regime to NOx-limited regime) over most of the major cities in the western U.S.** between 2014 and 2017.
- In contrast, rural areas in the southeastern United States, exhibited a decreased $HCHO/NO_2$ column ratio by -1.30 ± 1.71 **with a significant reduction in HCHO column primarily driven by meteorology, becoming sensitive to VOC emissions**.
- The results of this study show that incorporating satellite observation into numerical modeling could be helpful to implement appropriate emission control policies for O_3 air quality in time.

Thank you! ☺

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