Chemical Condition and Surface Ozone in Urban Cities of Texas During the Last Decade: Observational Evidence from OMI, CAMS, and Model Analysis

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Ozone and its precursors

- Ozone production
  - Nitrogen oxides (NO_x=NO+NO_2) and Volatile Organic Compounds (VOCs)
  - Complex non-linear photochemistry
  - Indicators:
    - Individual species or species ratios that can provide evidence on the ozone-NO_x-VOC relationship
  - HCHO/NO_2 ratio
    - NO_x-saturated, -mixed or –sensitive regimes

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Ozone monitoring

- The anthropogenic emissions of NOx declined by 48% between 1990 and 2013 (EPA, 2013)
- VOC emissions from anthropogenic sources declined by 38% between 1990 and 2013
- EPA (2010) has lowered the ozone standard from its 8-hour average (i.e. 75ppbv to 60-70 ppbv)

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Ozone monitoring

- Lefohn et al. (2010) using a period data of 1980-2008 and 1994-2008 found that most metropolitan and rural regions in the United States exhibited either a negative or zero trend resulting probably from a decline in ozone precursors.

- The low ozone concentrations have likely increased as NOx has decreased, resulting from a decline in the amount of ozone quenched through NOx titration.

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Research Objectives

- Trend of NO_2 (2005-2013)
- Trend of HCHO
- Seasonal pattern of ozone and its relationship to air masses
- Trend of ozone (maximum, annual, minimum)
- The relationship between the trends
- Model analysis (different emission inventories)

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Trend analysis

- Least Squares Harmonic Estimation (LS-HE)
  - $Obs = r_0 + r_1 t + \sum_{i=1}^{m} a_i cos 2\pi\omega_i (t - \varphi_i)$
  - Reduces the uncertainity by 5-15%

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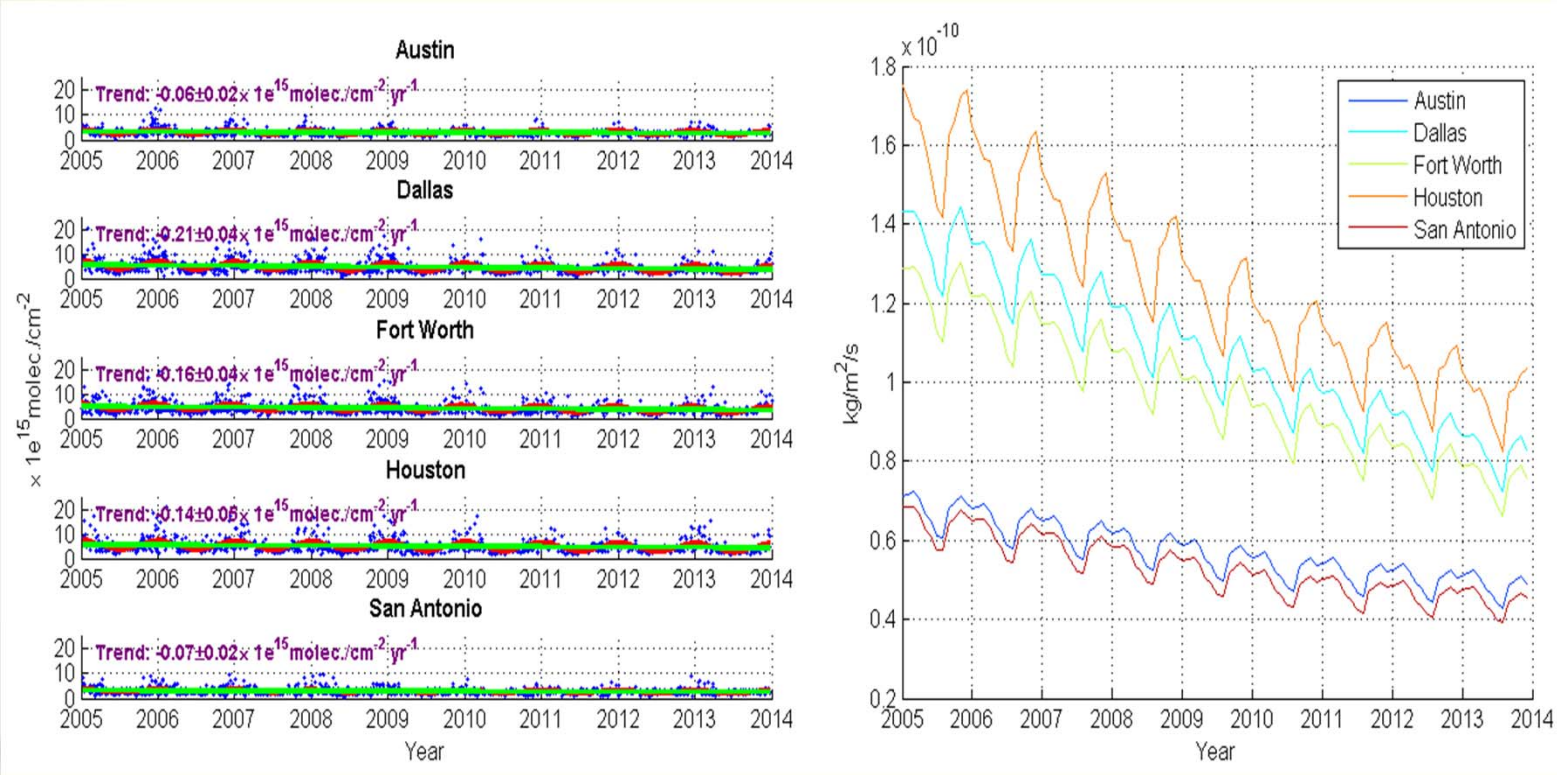
OMI NO_2

- OMI NO_2 daily observations ($0.25^o \times 0.25^o$, level 3) from NASA (noisy observations have been filtered out)



Left: OMI, Right (MACCity)

OMI NO_2

- OMI: Austin (-6%), Dallas (-21%), Fort Worth (-16%), Houston (-11%) and San Antonio (-7%)
- CAMS: Dallas (-40.1%), Fort Worth (-43.9%) and Houston (-34.6%)
- Except for San Antonio, which our results showed was 10% lower, which may be the result of different spatial resolutions and subsets

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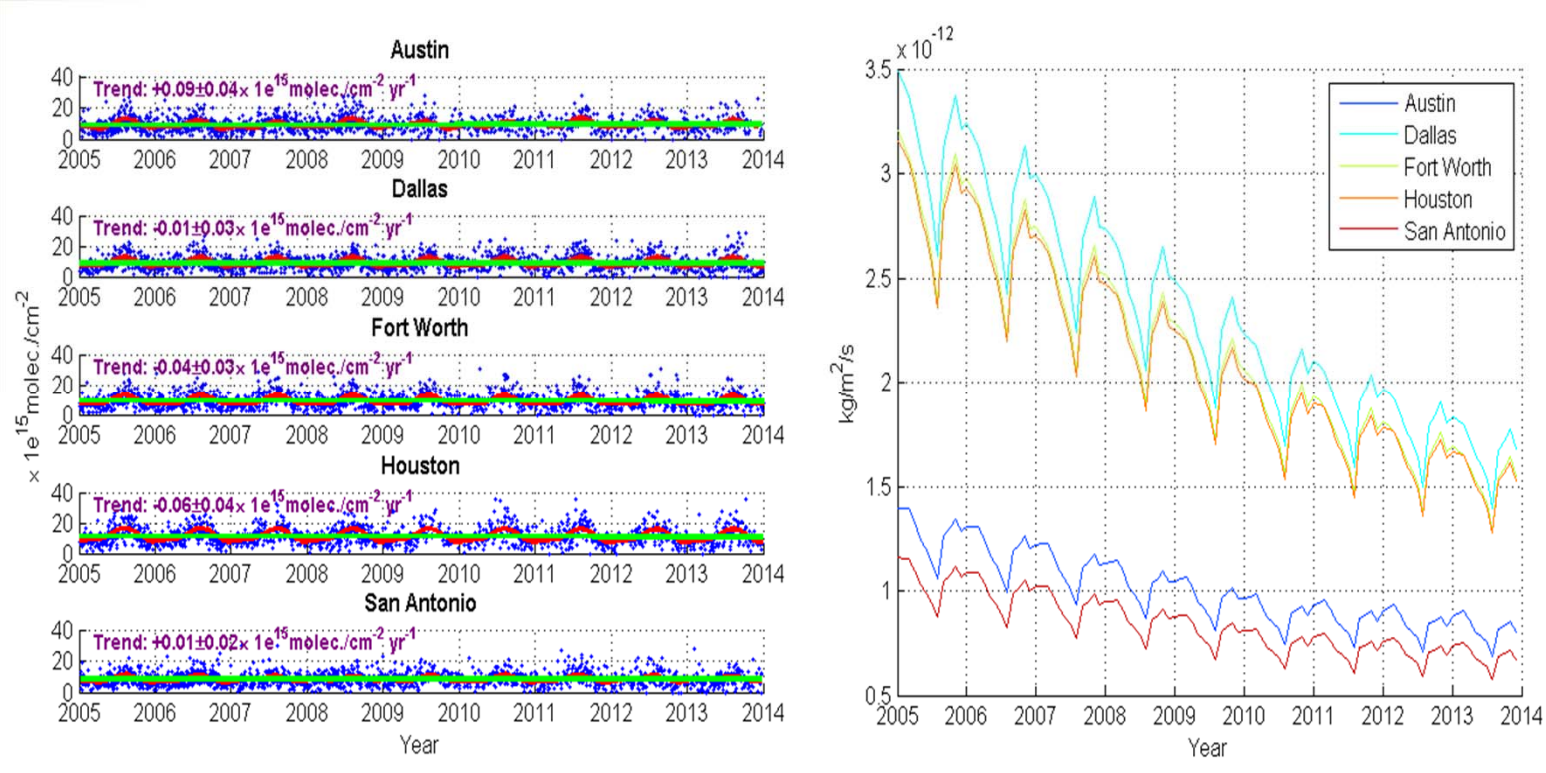
OMI HCHO

- SAO OMI HCHO (0.25°×0.25°) (filtering+ a first-order polynomial +0.34±0.01×10^{15}molec./cm^2 yr^{-1})



Left: OMI HCHO, Right:MACCity

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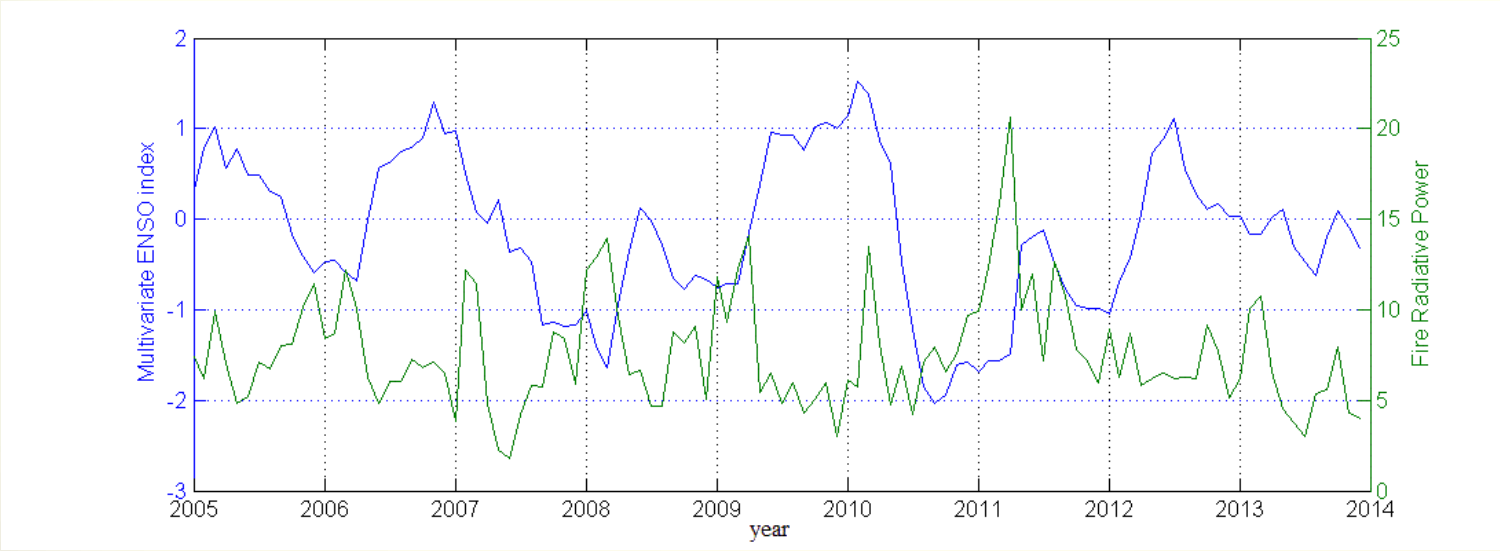
OMI HCHO

- Austin (+9%), Dallas (-1%), Fort Worth (-4%), Houston (-5%) and San Antonio (+1%)
- La Niña (warmer summers) periods of 2006, 2008-2009, and 2011 years



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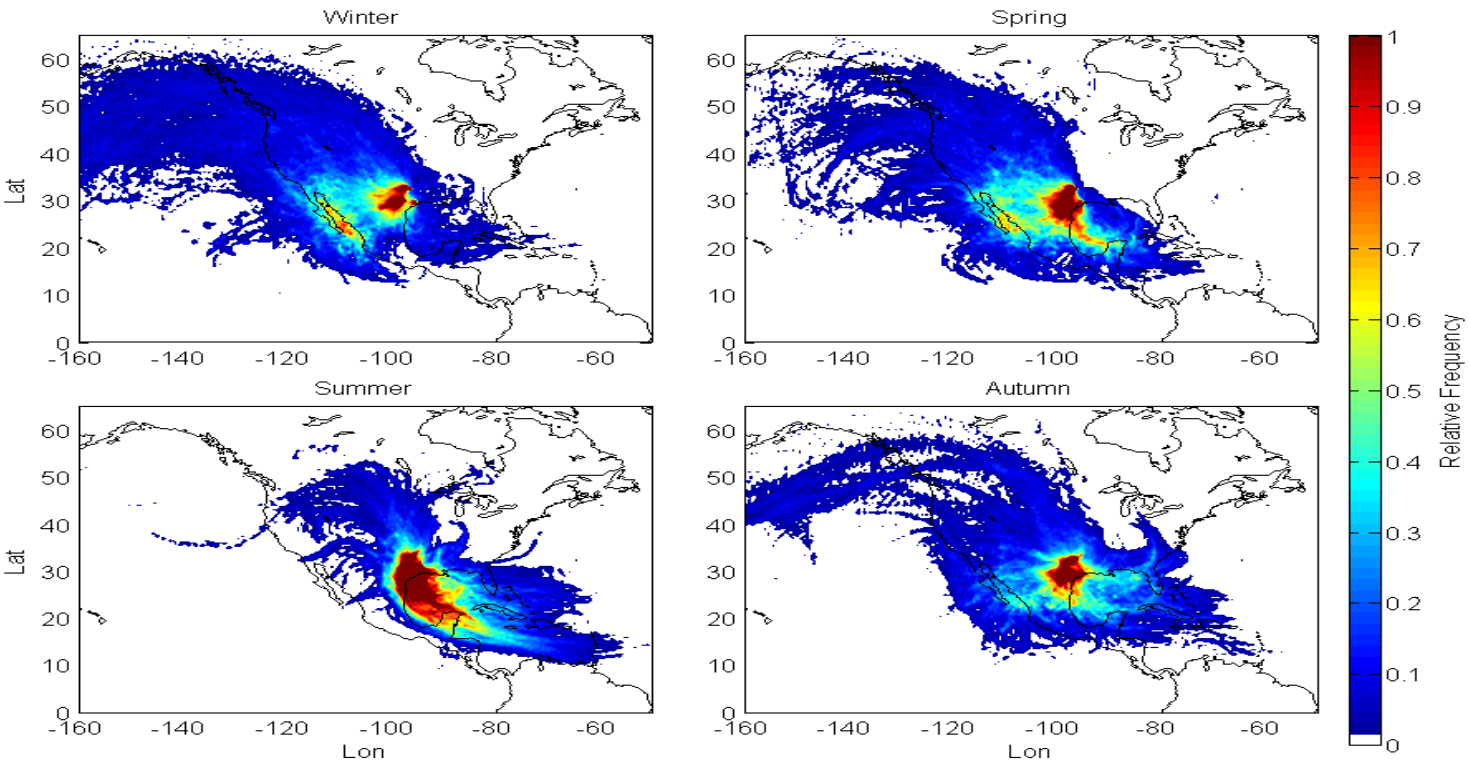
OMI HCHO/NO_2

- According to HCHO/NO_2, the most NO_x-saturated (Dallas) and NO_x-sensitive cities (Austin) were shown.
- The 2%, 7%, 6%, 5%, 3% of the selected days were NO_x-saturated (i.e., the NO_x-saturated regime to be the ratio <1) for Austin, Dallas, Fort Worth, Houston, and San Antonio
- All of the cities have gradually become more NO_x-sensitive because of higher downward trend of NO_2 than HCHO.
- The slope of this change was found for Austin (0.10±0.04 yr^{-1}), Dallas (0.08±0.03 yr^{-1}), Fort Worth (0.07±0.03 yr^{-1}), Houston (0.06±0.03 yr^{-1}), and San Antonio (0.08±0.03 yr^{-1})

Surface Ozone

	HCHO	NO_2	HCHO Graph	NO_2 Graph	Surface Ozone Graph
Austin	0.52	-0.80			
Dallas	0.90	-0.92			
Fort Worth	0.92	-0.85			
Houston	0.67	-0.79			
San Antonio	0.39	-0.73			



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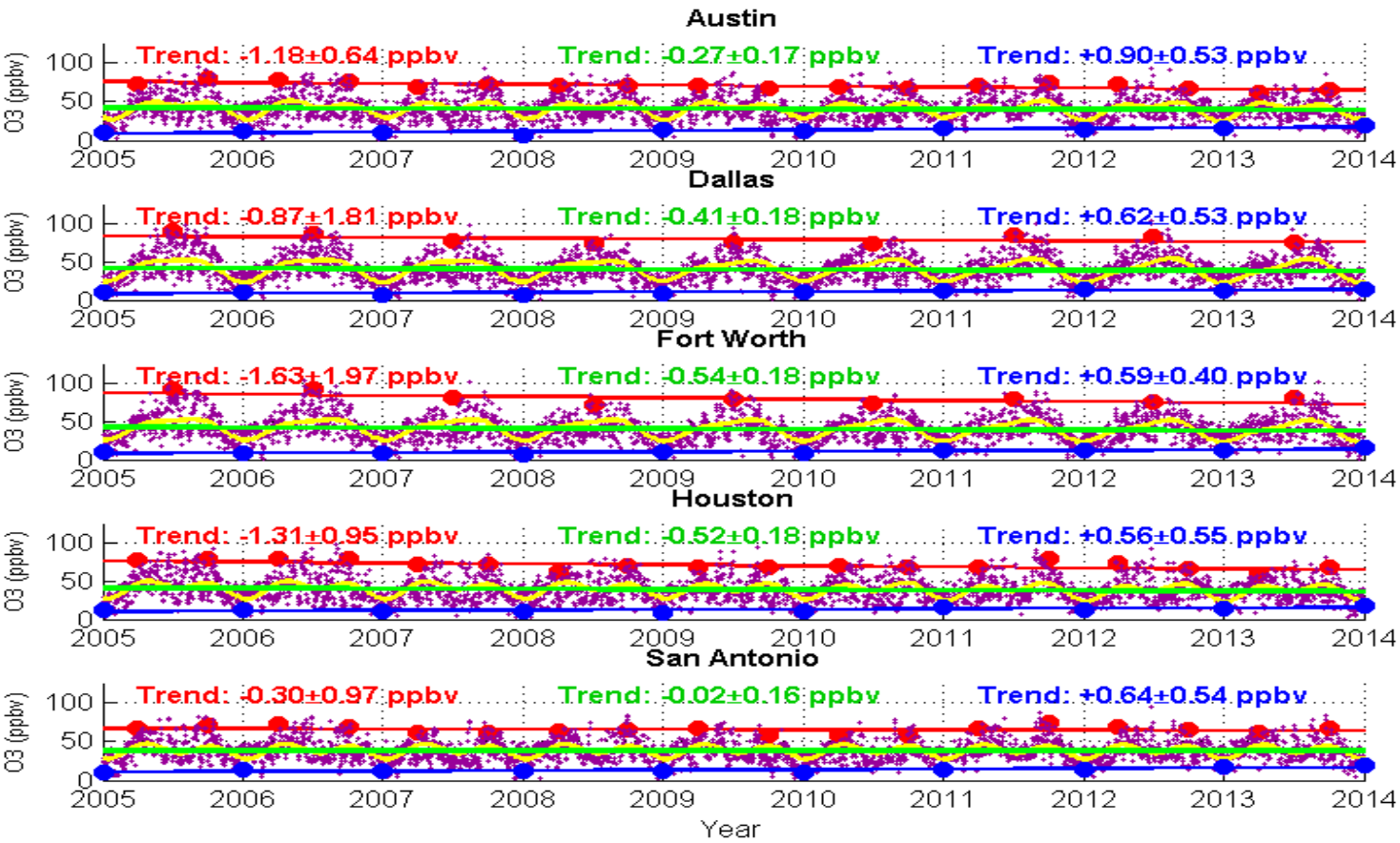

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Surface Ozone

- If observations after 2011 were excluded, all of the cities would show a reduction in ozone maxima resulting from a decline in NO_x emissions in an NO_x-sensitive regime, suggesting how crucial climatic variability and associated wildfires after the period were.
- All of the cities showed an upward minimum trend: Austin> Dallas>San Antonio>Fort Worth>Houston.
- Downward trends of 5%, 8%, 11%, 11%, and 1% were found with respect to the 2005 ozone mixing ratio.

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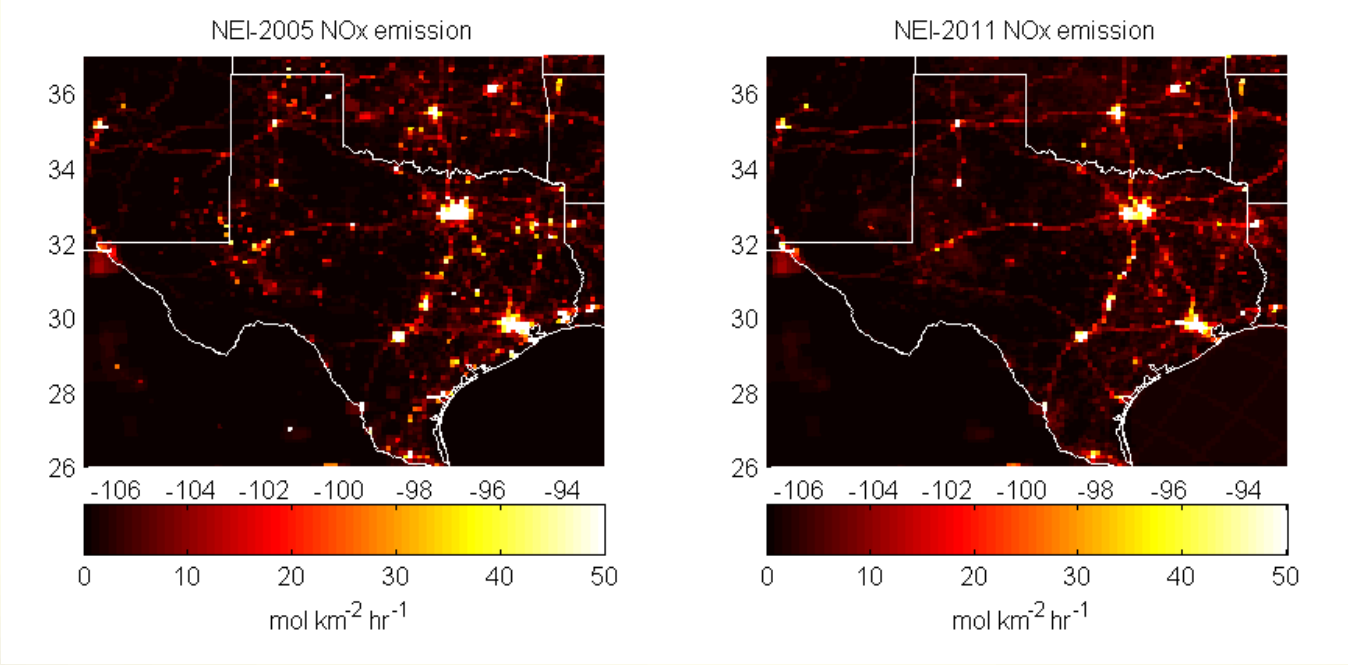
Model analysis (Sep. of 2013)

- EPA National Emission Inventory (NEI) 2005 and NEI2011
- NO_x emissions decreased by 19%, 20%, 16%, 50%, and 18% in Austin, Dallas, Fort Worth, Houston, and San Antonio.



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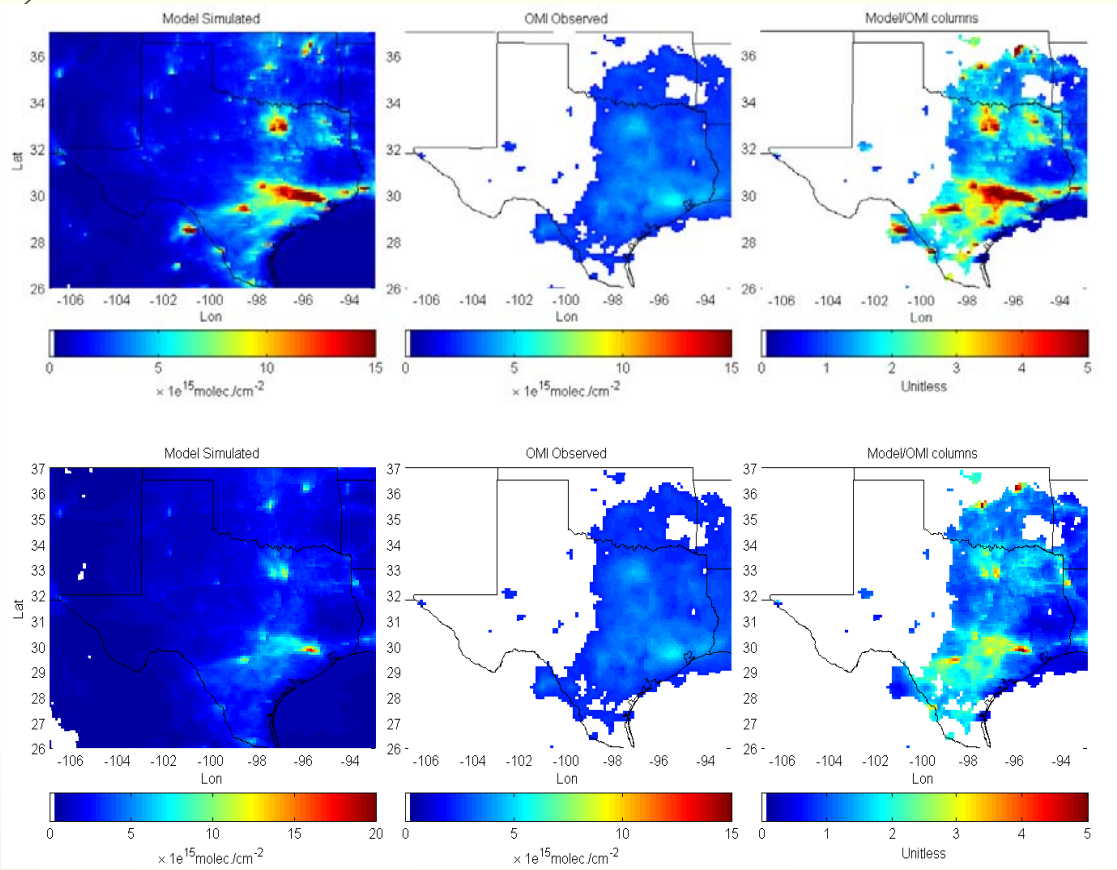
Model analysis (NO_2 column)

- OMI NO_2 versus WRF-Chem

NEI2005

NEI2011



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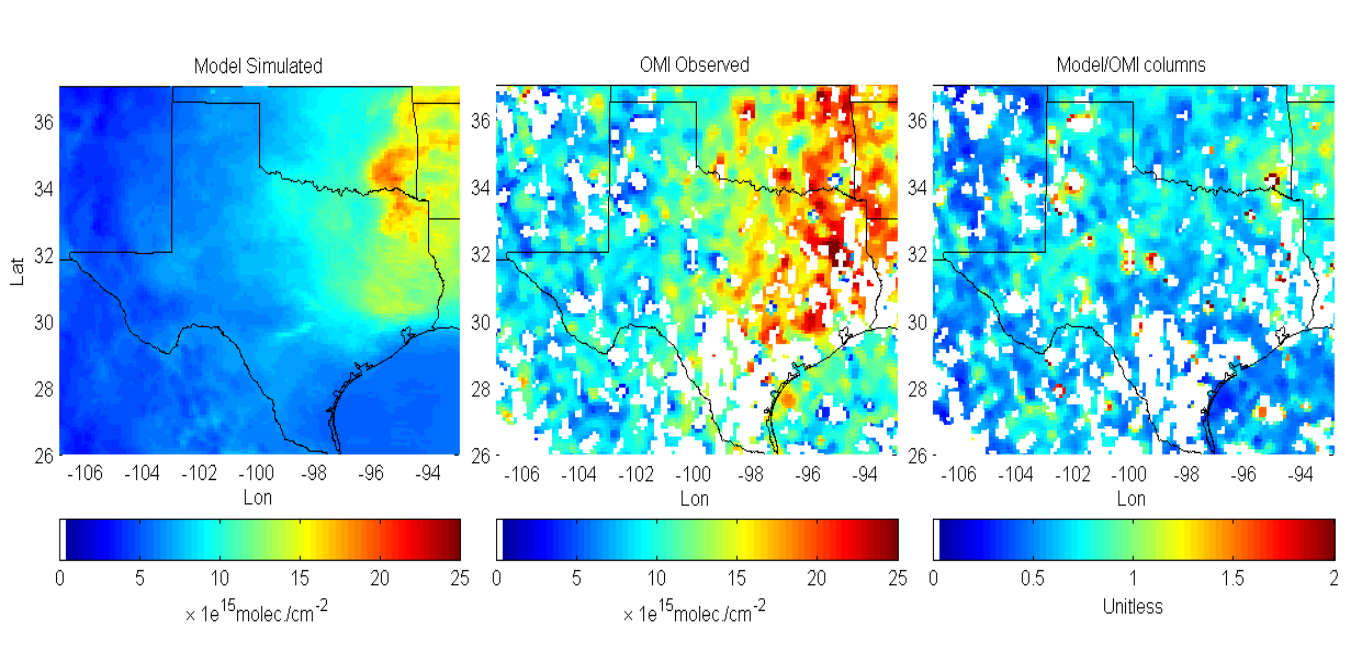
Model analysis (HCHO column)

- OMI HCHO versus WRF-Chem



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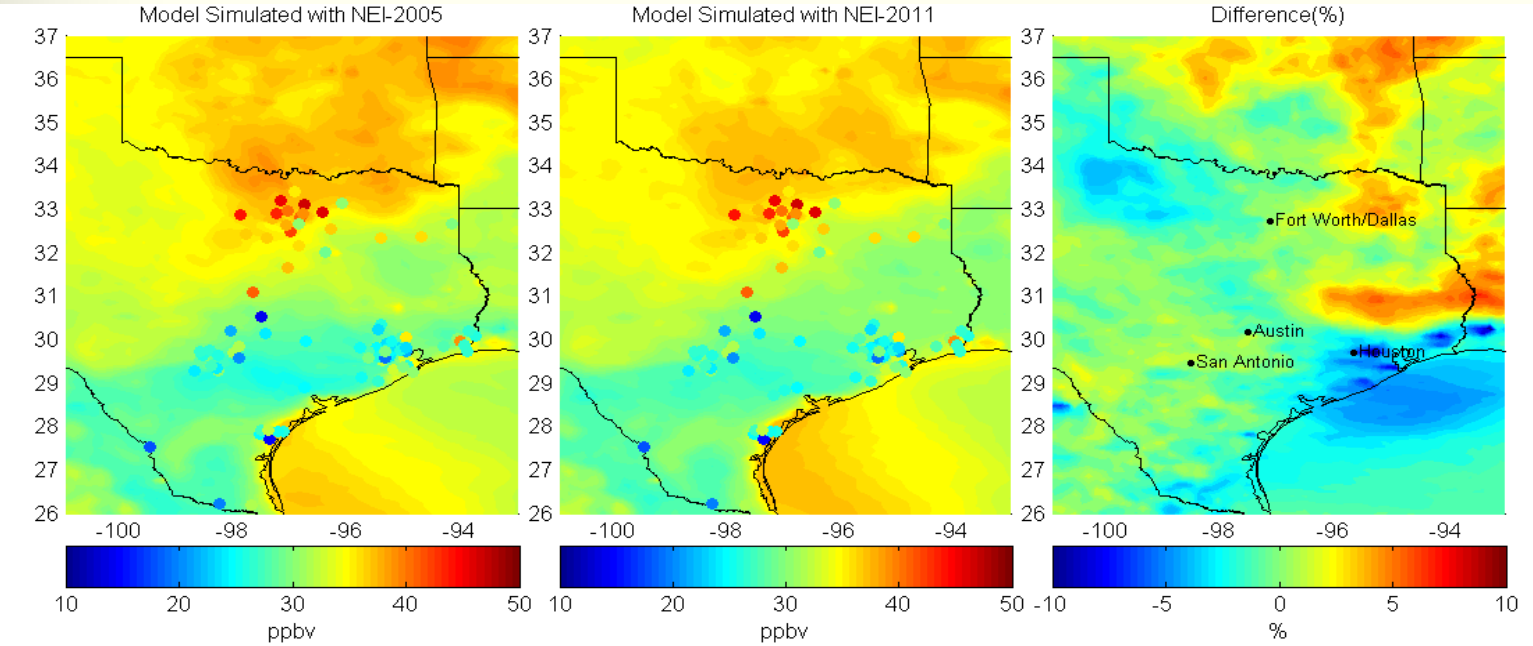
Model analysis (surface O_3)

- The reduction 3% in Dallas and 0.5% in Fort Worth.
- The increase by 0.7% in Austin, 0.8% in San Antonio, and 7% in Houston.
- The overestimation of NO_2 and the underestimation of HCHO might deplete available radicals in Austin, San Antonio, and Houston, leading to less production of ozone (indicating that model is problematic).



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- A declined in anthropogenic sources led to a statistically significant downward trend for NO_2.
- Only Austin showed a statistically significant increase (+9%) in annual trends of HCHO, resulting from climatic variability that was not cancelled out by the low decline in anthropogenic HCHO emissions.
- The differences between both trends gradually changed the chemical conditions of the Texas cities from NO_x-saturated/mixed to more NO_x-sensitive chemical conditions.

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- Climatic variability plays the major role in summertime surface ozone trends
- Decline in annual ozone

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- MTSE air masses strongly influenced the ozone pattern in July in the lower latitudes, and NO_x and PAN emissions from the eastern United States resulted in high ozone in the autumn.

- WRF-Chem in two different scenarios in September 2013:
- Reductions in ozone levels from the first to second scenarios in Dallas (3%) and Forth Worth (0.5%).

- But increases surface ozone in Austin (0.7%), San Antonio (0.8%), and Houston (7%).

- Partially resulting from the underestimation of VOC contributions from petrochemical facilities and biogenic the overestimation of NO_x in the NEI-2005 inventory that led to false low $HCHO/NO_2$ ratios.

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Thank you for your attention