Assessment of NOX & VOC in Urban Areas: Potential Implications for O_3 Planning

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Motivation

- Characterize the spatial and temporal variability in the relative mix of NO_X and VOCs (surrogate for O_3 formation regime) in U.S. urban areas using readily available data
- Can a photochemical model be used for this type of characterization, does it match limited observations?
- This type of evaluation also provides an assessment of how appropriately the modeling system may respond to changes in precursor emissions
  - If predicted VOC:NO_2 ratios don't match observed ratios, O_3 production regimes are likely not correctly characterized
- Is VOC/NO_X a useful indicator of the effectiveness of NO_X and VOC reductions? Is model response directionally consistent with what is expected with the VOC/NOX ratio?
- Is this type of evaluation limited to areas dominated by production, i.e., won't work on areas affected predominantly by transport?

Ozone Formation Regimes

VOC limited

- All urban centers (Milford et al, 1989; Milford et al, 1994)
- Los Angeles (Milford et al, 1989; Harley et al 1993)
- San Francisco (Steiner et al, 2006)
- Phoenix (Kleinman et al, 2005)
- New York City (Kleinman et al, 2000)

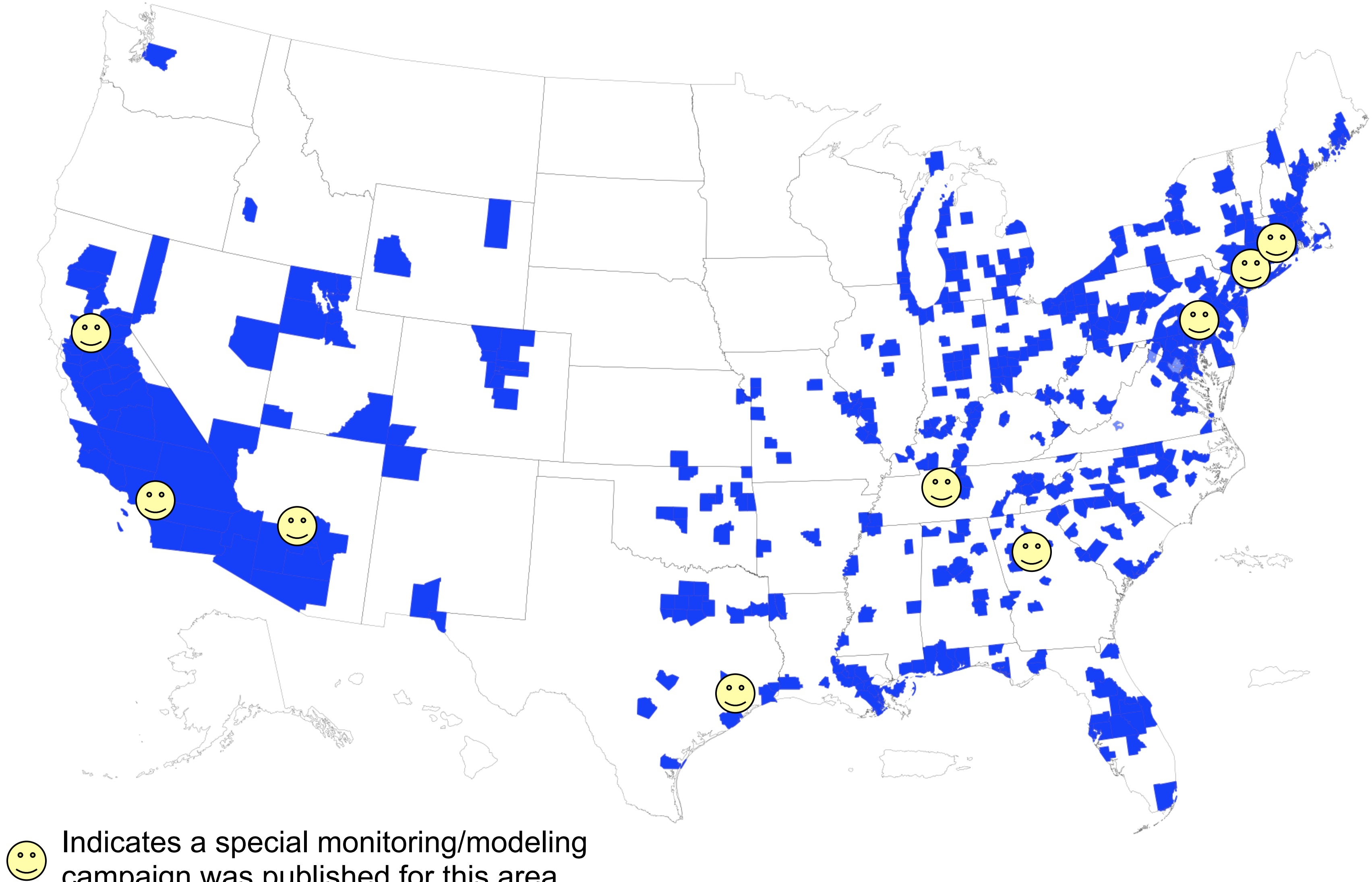
NO_X limited

- Rural/suburban areas (Milford et al, 1989; Milford et al, 1994)
- Atlanta (Sillman, 1995; Daum et al, 1996)
- Nashville (Kleinman et al, 2005)
- Northeast corridor downwind of NYC (Cardelino and Chameides, 1995; Sillman et al, 1995)

Both VOC and NO_X limited

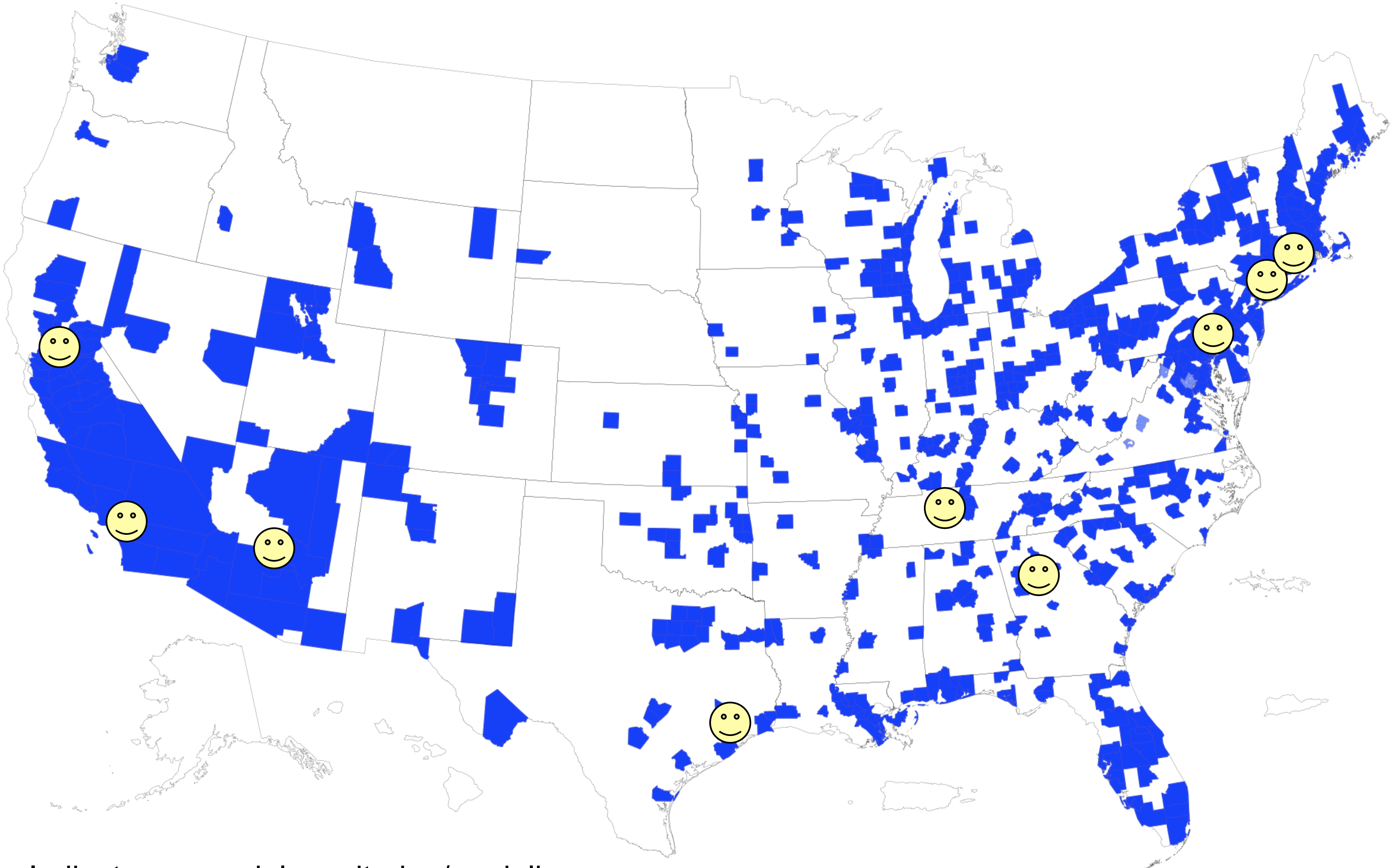
- Houston (Daum et al, 2004)
- Philadelphia (Kleinmen et al, 2005)

Counties with O_3 Design Value > 70 ppb



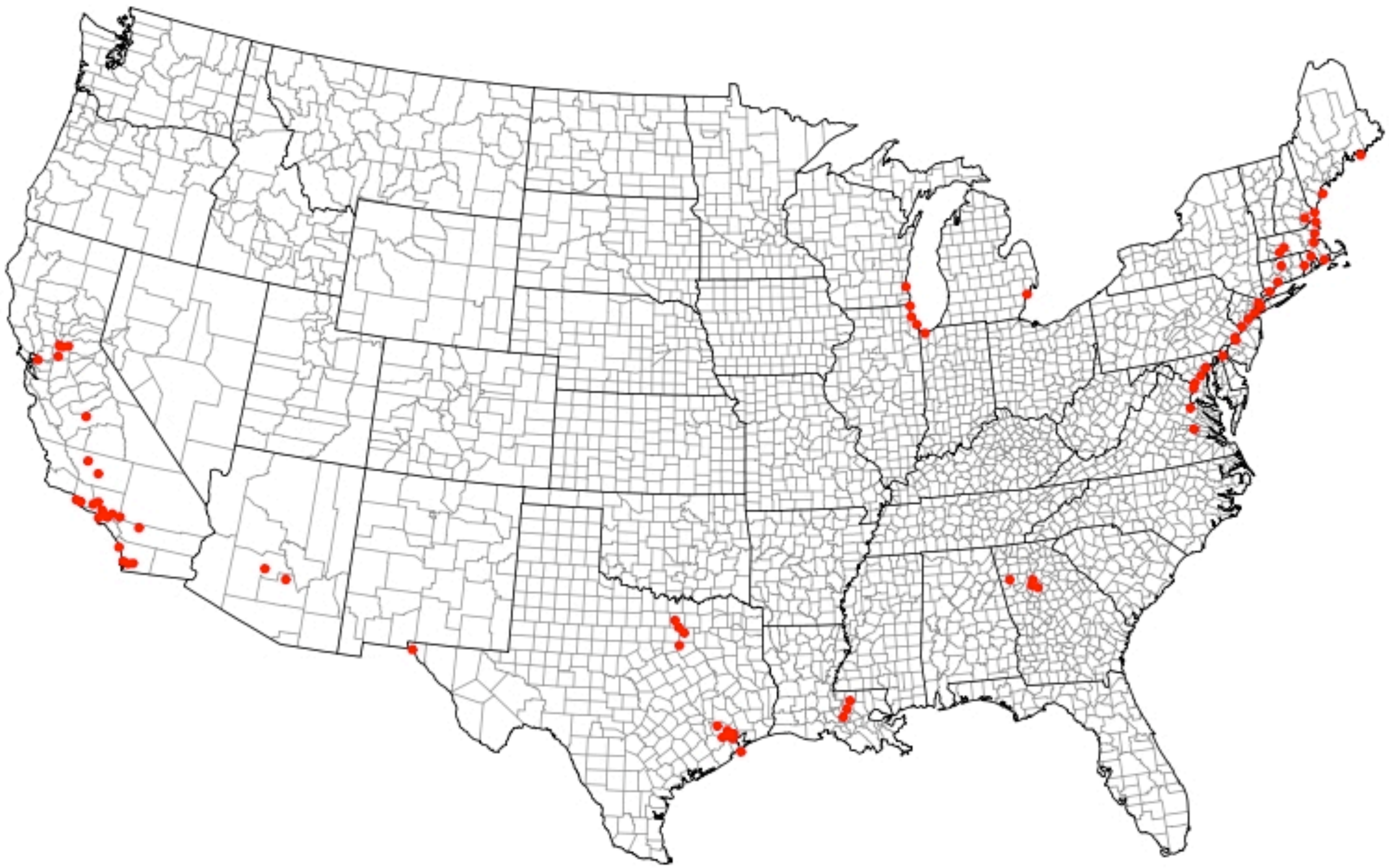
Indicates a special monitoring/modeling campaign was published for this area

Counties with O_3 Design Value > 65 ppb



Indicates a special monitoring/modeling campaign was published for this area

Colocated VOC and NO_X monitors in 2002

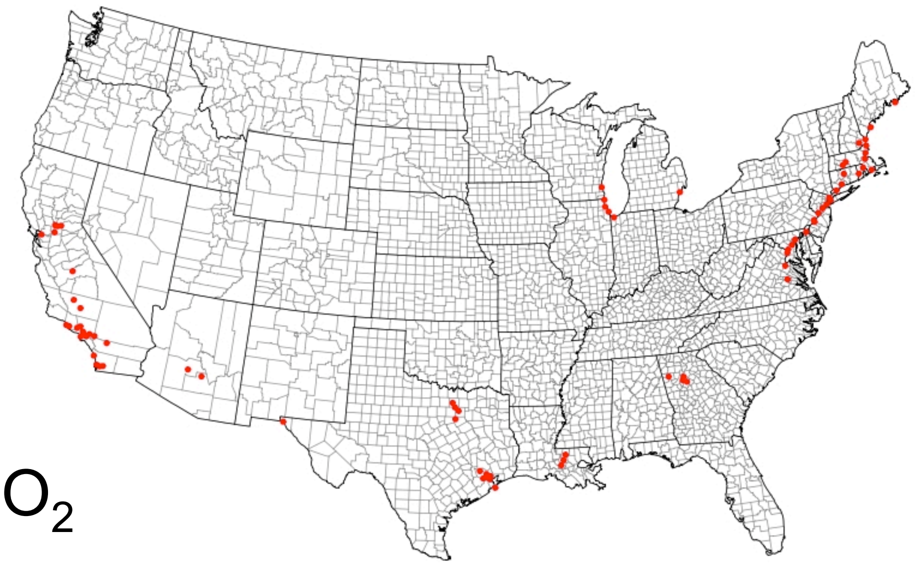


Methods: PAMS Observations

Ambient measurement data from the **P**hotochemical **A**ssessment **M**onitoring **S**tations (PAMS) network

Data obtained from EPA's TTN website (www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm)

PAMS sites operated during ozone season & located in urban areas



2002, 2005 PAMS species:
Total NMOC, isoprene, O_3, NO_2

Methods: Modeling System

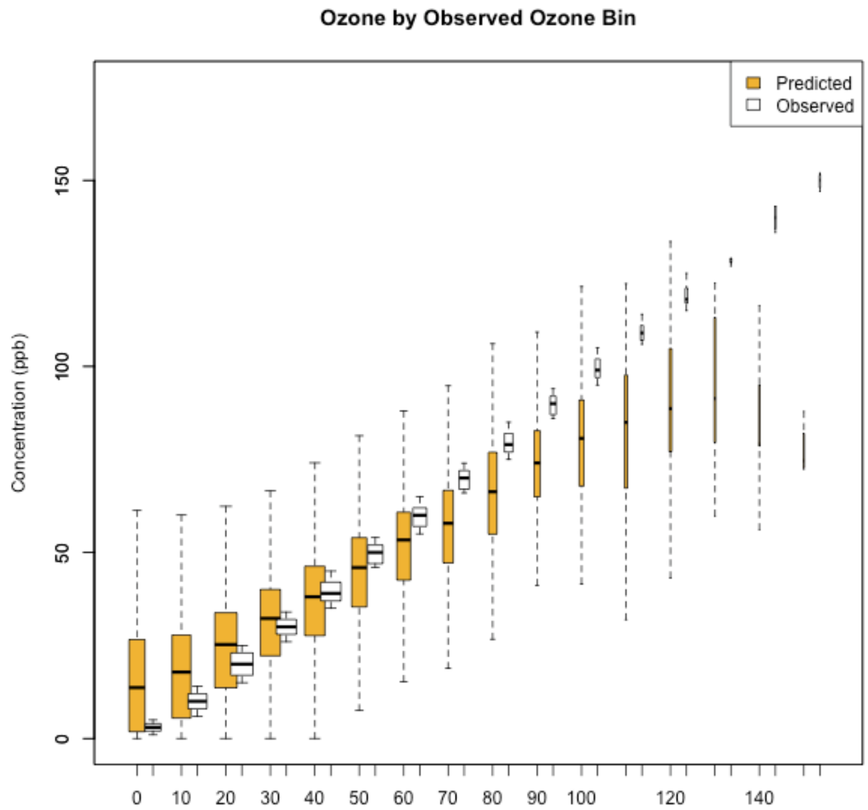
- CMAQ v4.6.1i and CMAQ v4.7
- CB-05 gas phase chemical mechanism
- Annual 2002 & 2005 simulations:
  - 12 km Eastern U.S.
  - 12 km Western U.S.
- Annual 2020 simulation:
  - 12 km Eastern U.S.
- 14 vertical layers (15 km top)
- Boundary conditions from a 36 km CONUS CMAQ simulation

Results

- Operational performance assessment for O_3, NO_2, TNMOC (TNMOC=VOC for this presentation)
- NO_2 measurement uncertainty at PAMS monitors
- Spatial and temporal assessment of VOC:NO_2 ratios
- Model estimated TNMOC:NO_2 in 2002 compared to 2020
- How does the model respond to NO_X and VOC reductions?

Focusing Evaluation on Elevated Ozone

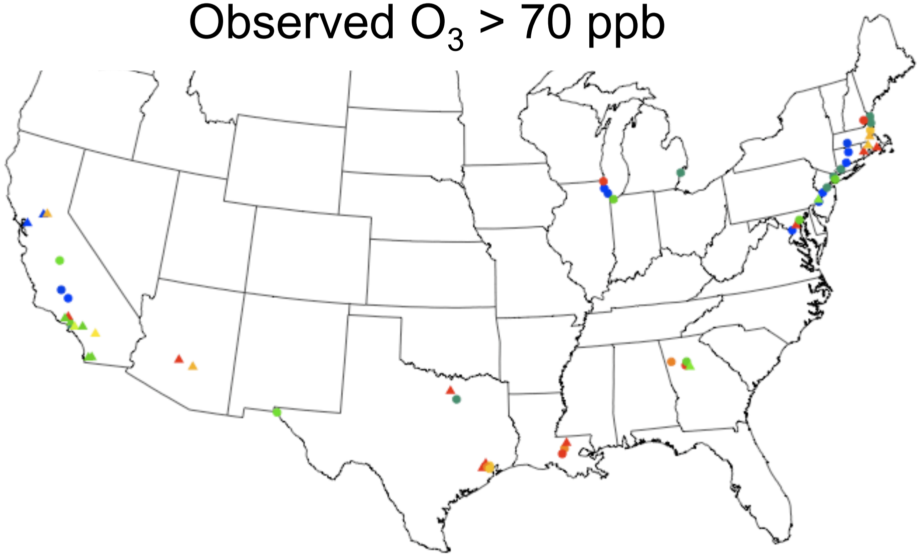
- Examine VOC/NO_2 ratio and other precursors when observed ozone is elevated
- Modeling system tends to underestimate peak ozone formation events
- Operational evaluation most important for these events to better understand why peaks are missed

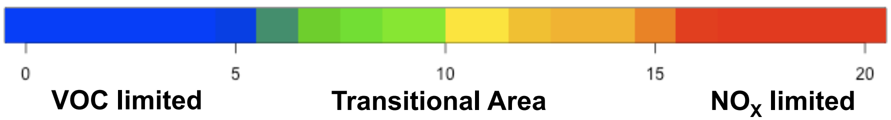


Obs. Ozone Concentration bin (ppb)

Observed 2002

Average TNMOC/NO_2* Ratio for
Observed O_3 > 70 ppb



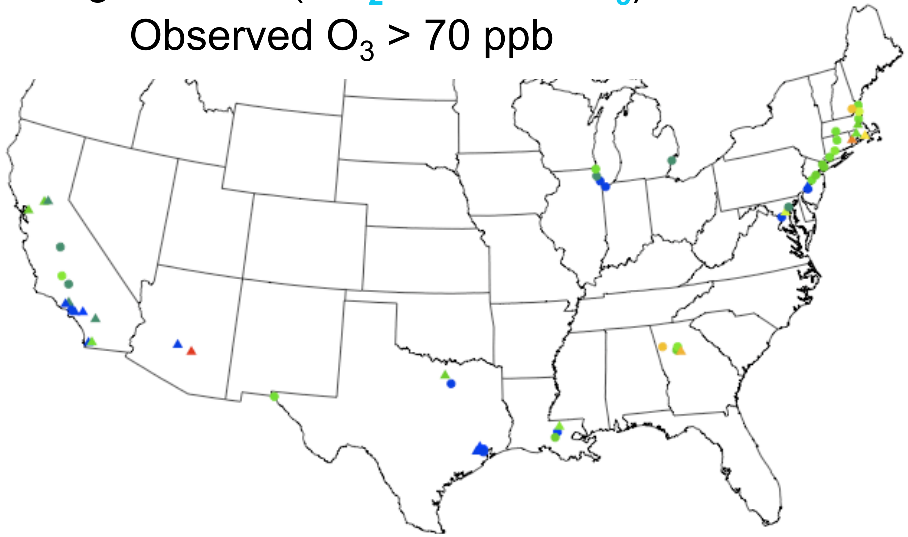


Circle indicates N >= 10

Triangle indicates N < 10

Model Predicted 2002

Avg TNMOC/(NO_2+PAN+HNO_3)
Observed O_3 > 70 ppb



Model Predicted 2002

Avg TNMOC/NO_2 Ratio for
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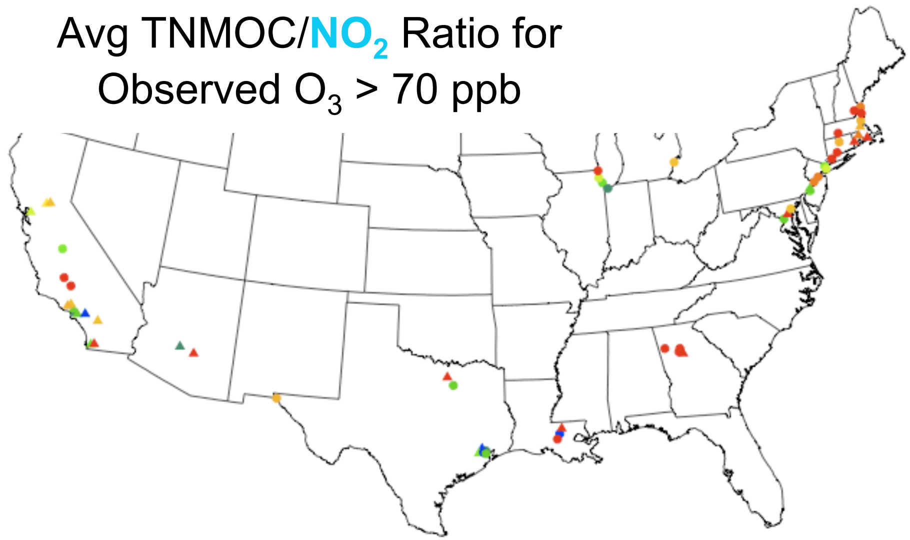
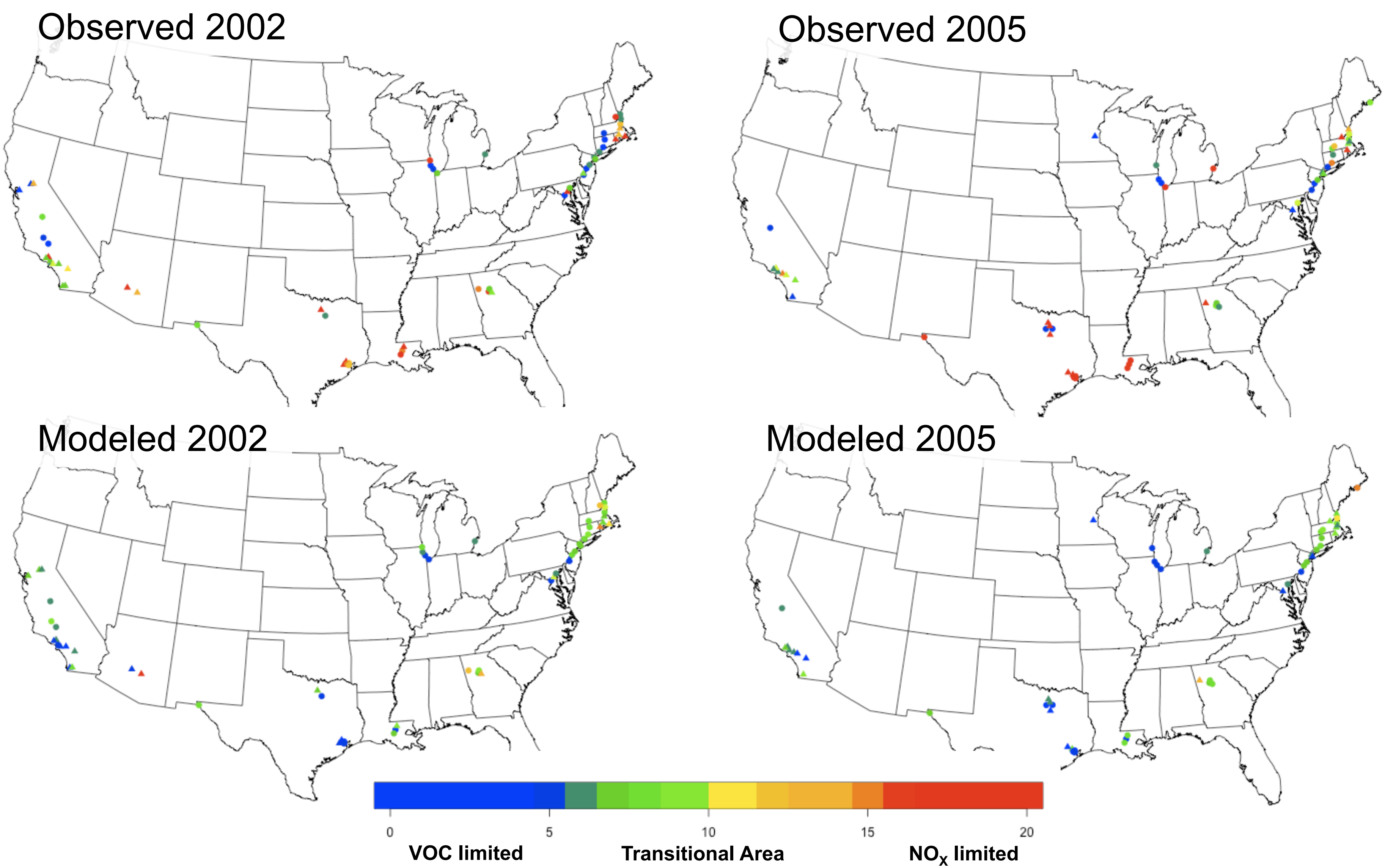
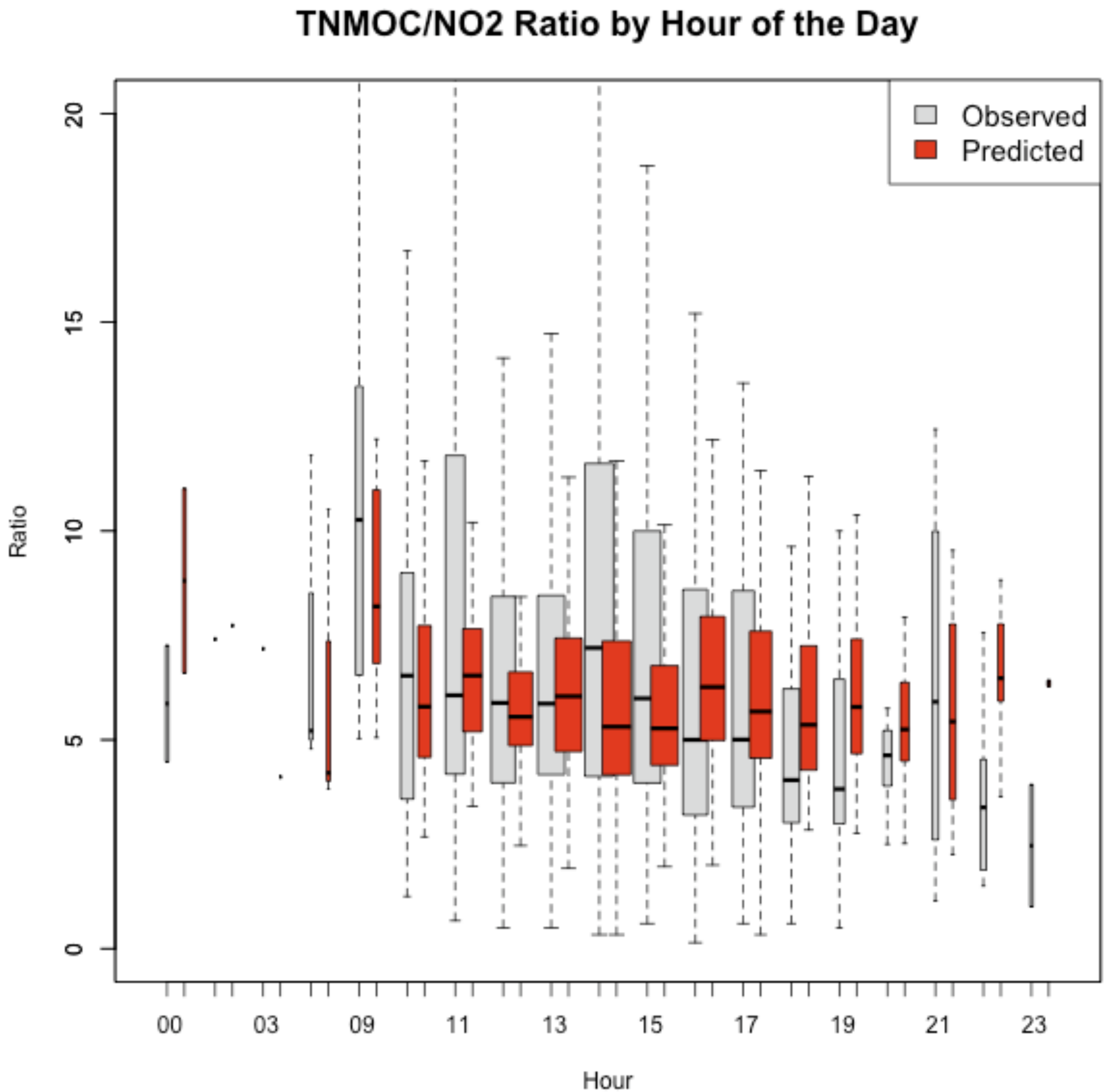


Average TNMOC/"NO_2" Ratio when Observed O_3 > 70 ppb



Model estimates and observations are shown paired in time but not space



Only shown are observations and model estimates where observed O_3 > 70 ppb

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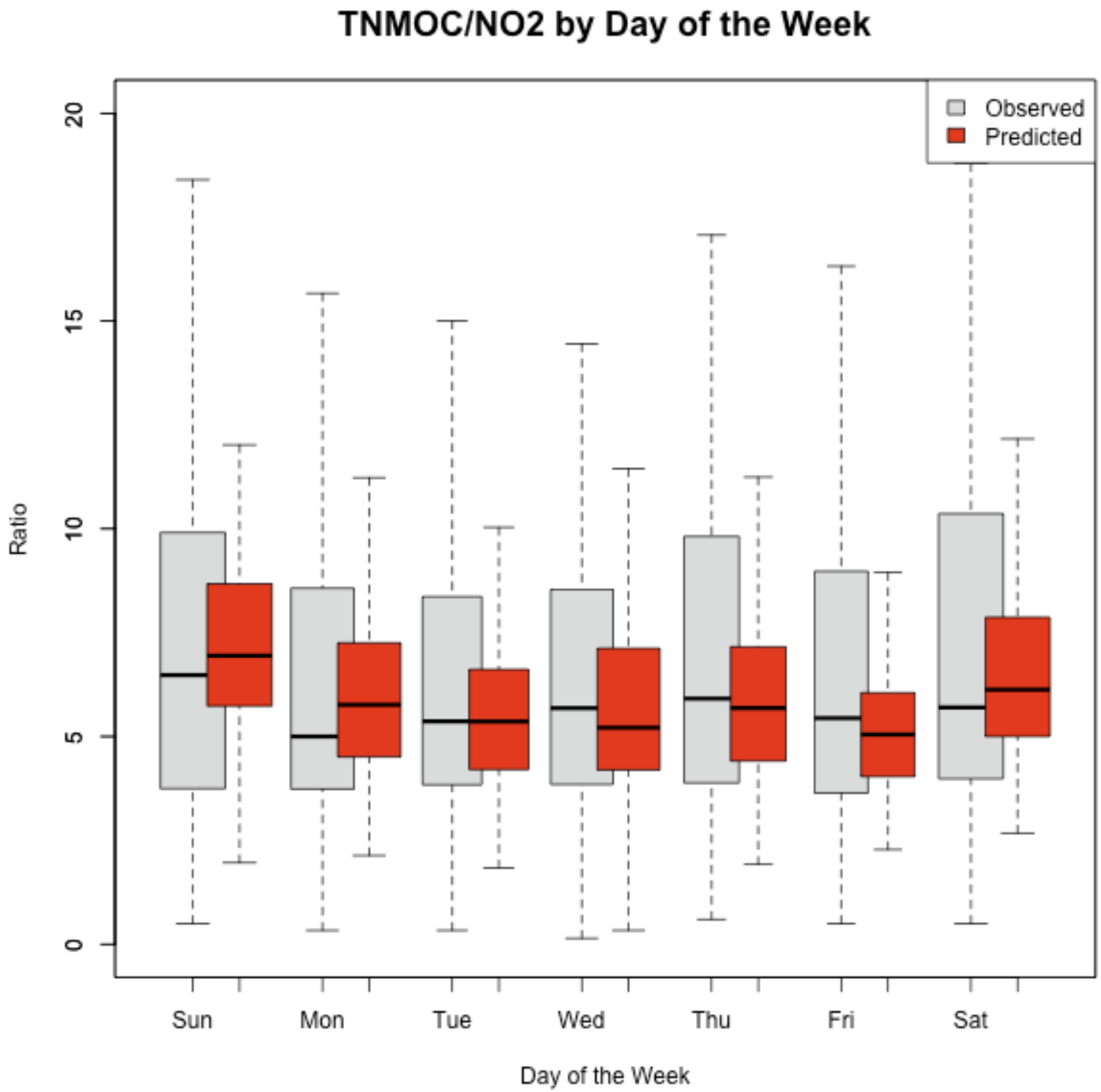

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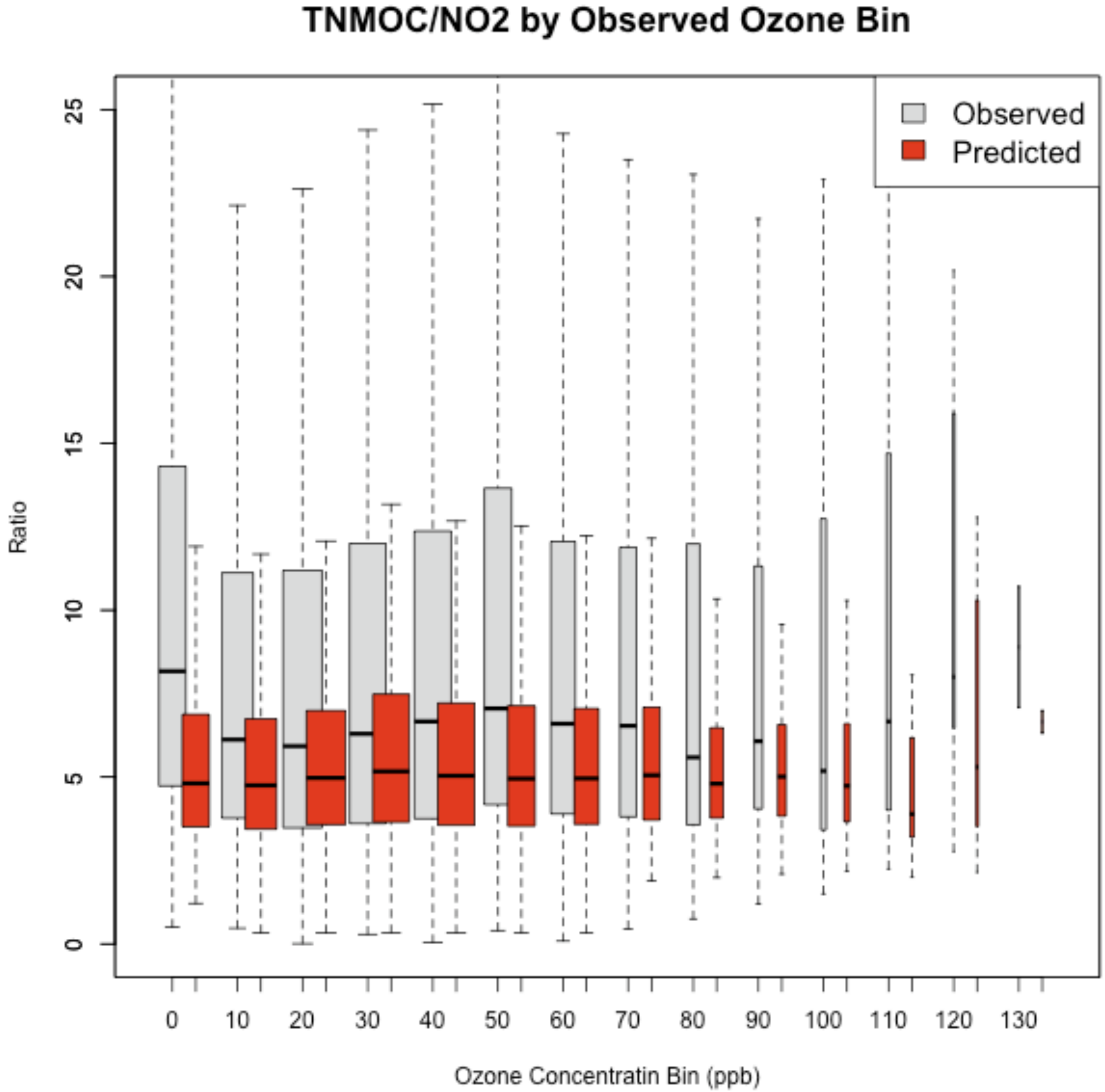
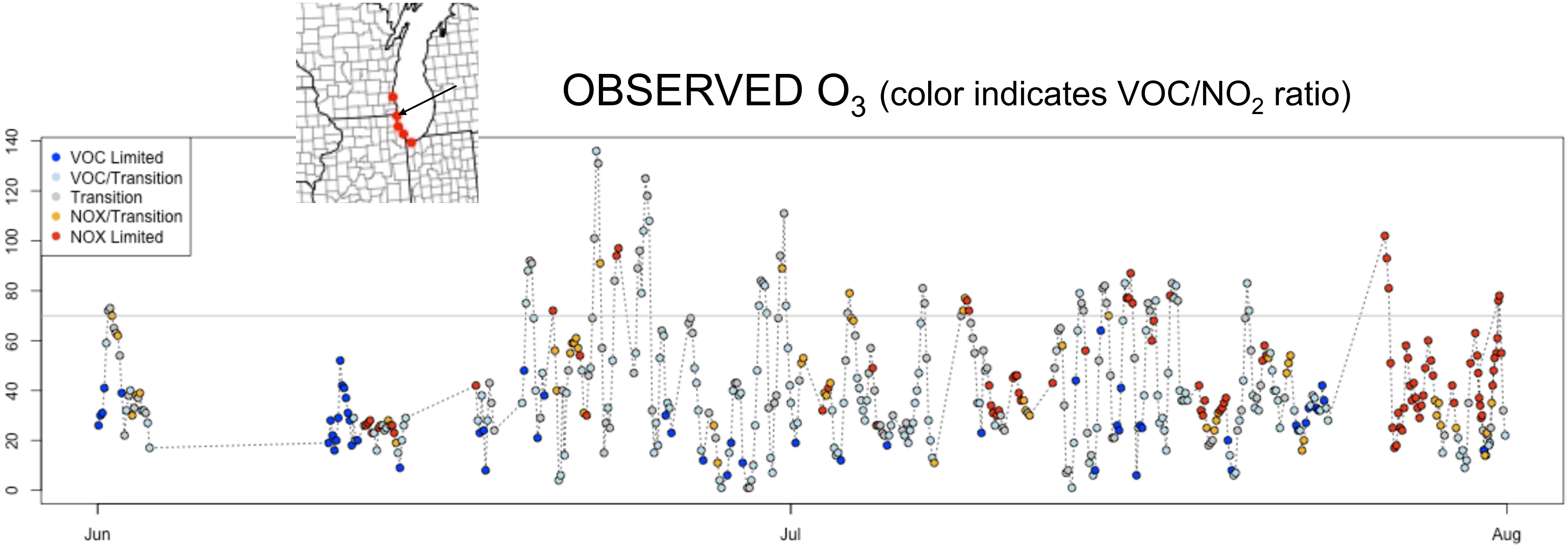
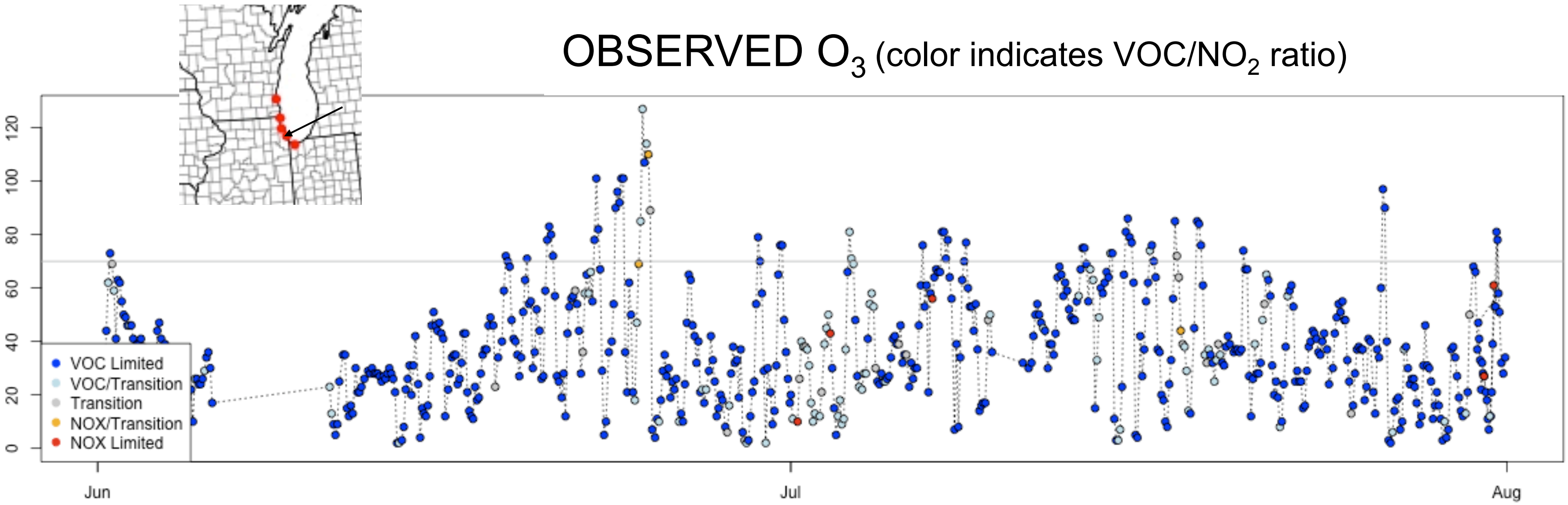


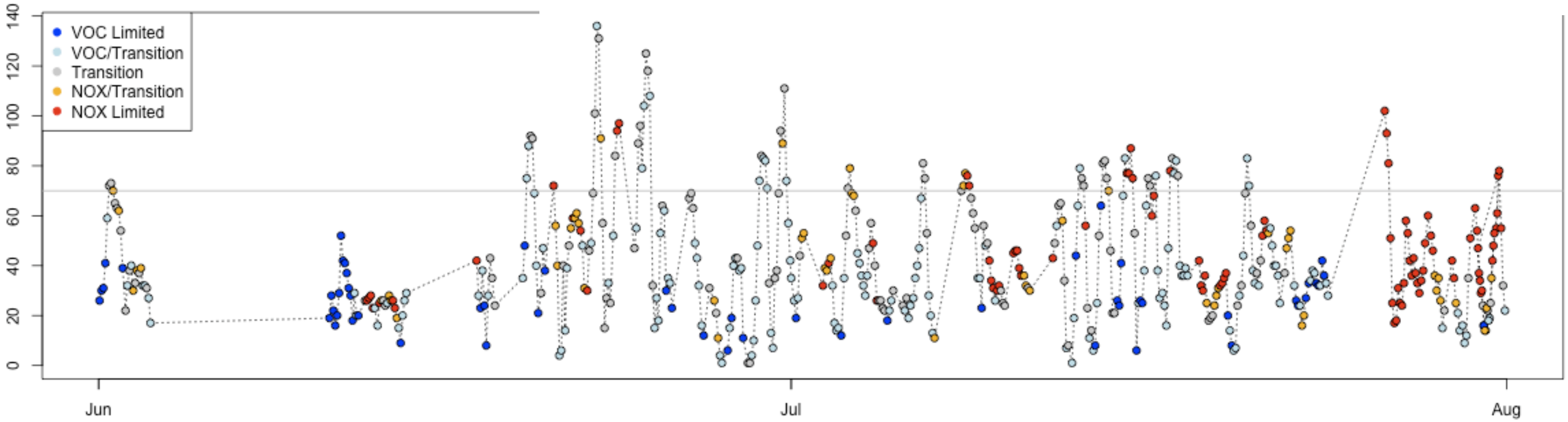
Time series at 2 Chicago area monitors



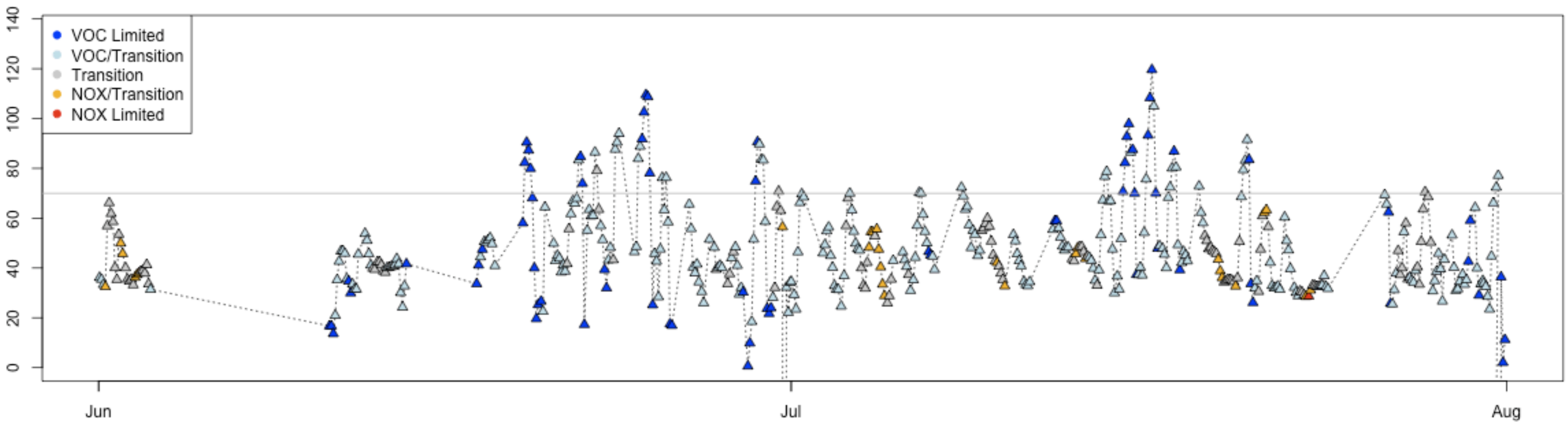


Timeseries: North Chicago 2002

OBSERVED O_3 (color indicates VOC/NO_2 ratio)

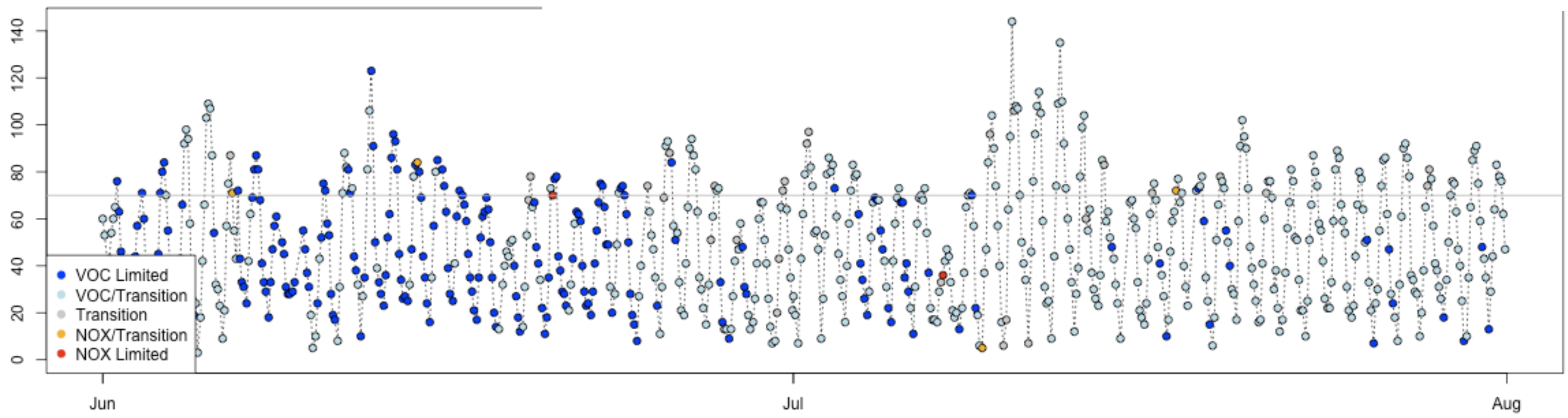


MODELED O_3 (color indicates VOC/NO_2 ratio)

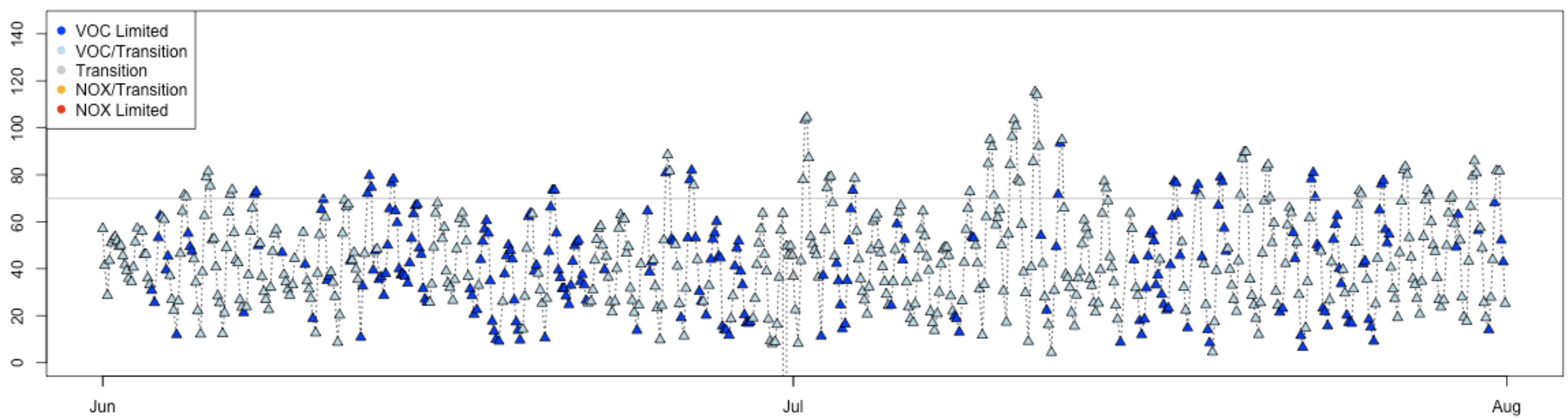


Timeseries: Los Angeles 2002

OBSERVED O_3 (color indicates VOC/NO2 ratio)



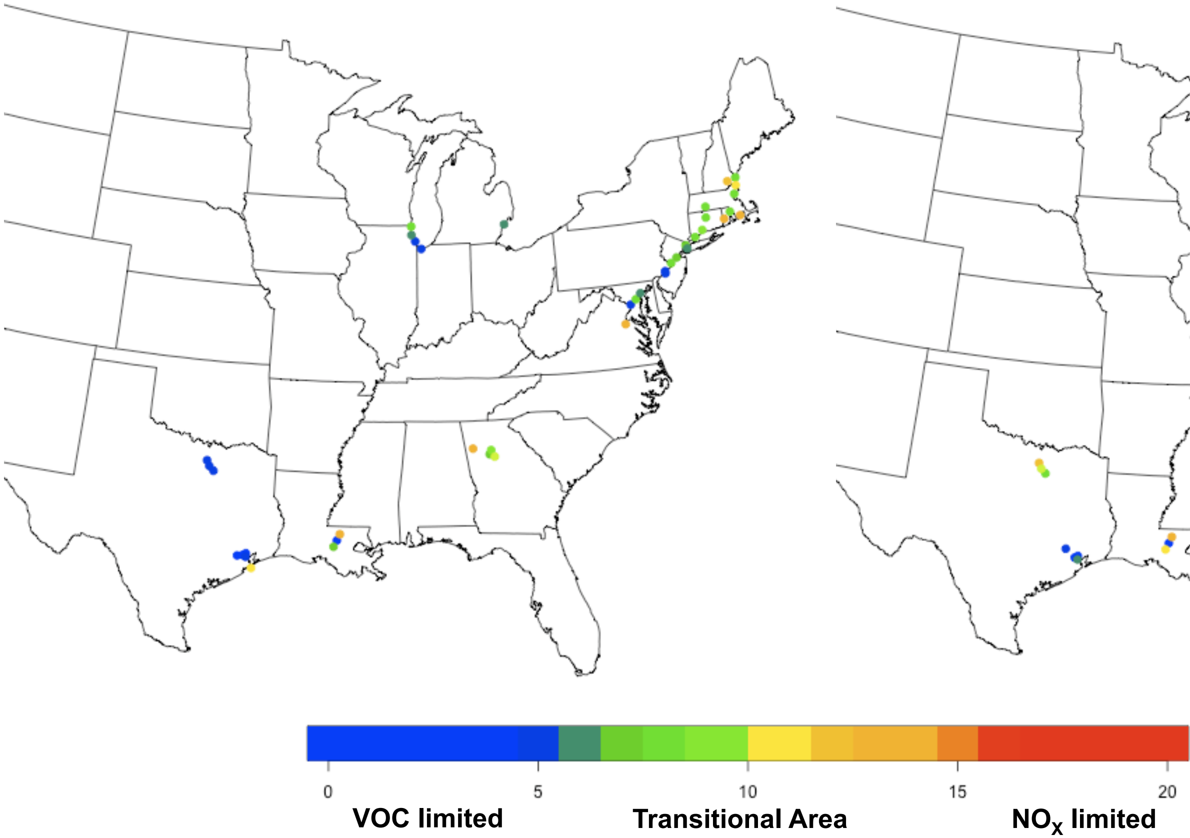
MODELED O_3 (color indicates VOC/NO2 ratio)



VOC/NOX Ratio Projected Estimates

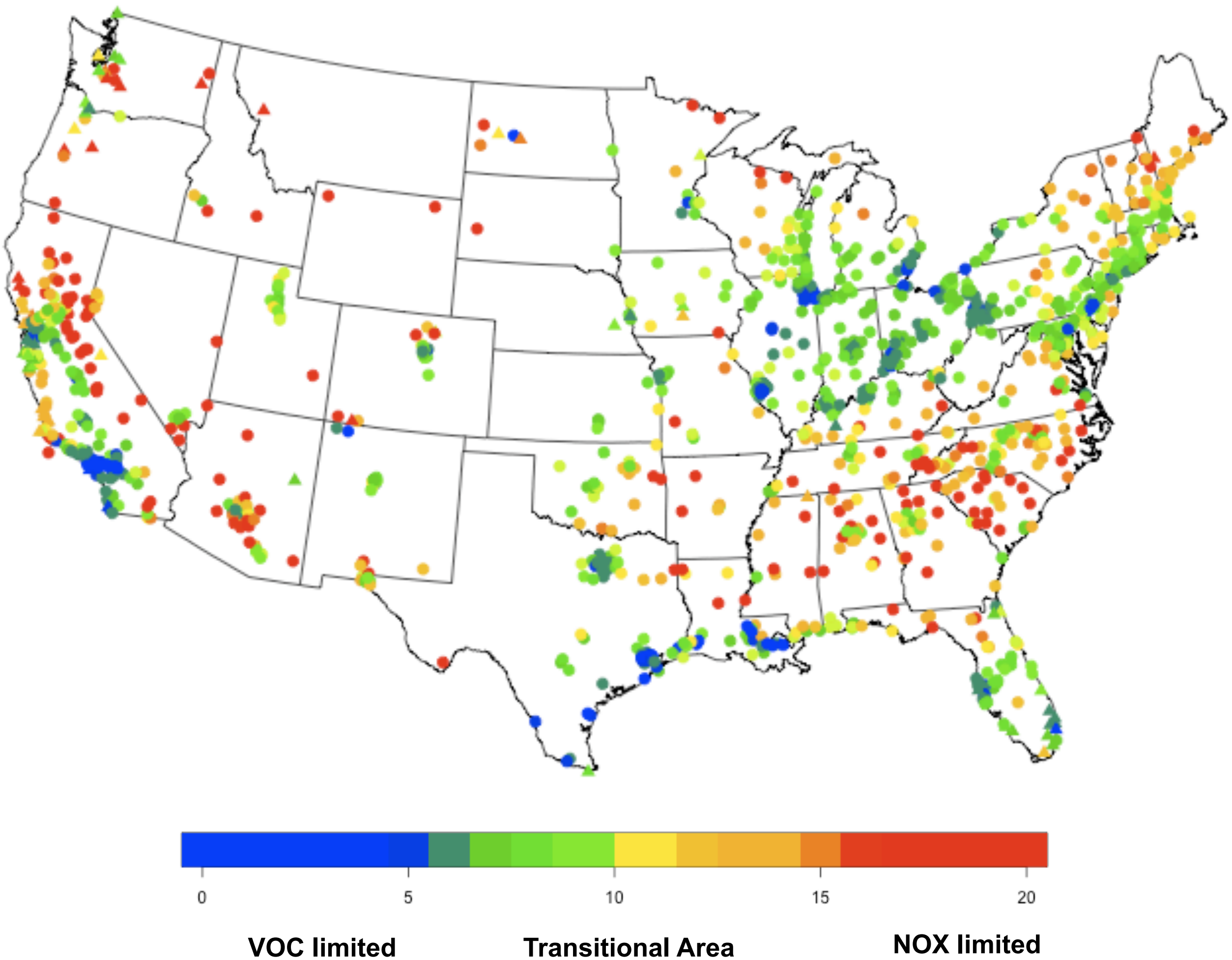
Average VOC/NO2 Ratio where observed O_3 in 2002 > 70 ppb

Model Predicted **2002** | Model Predicted **2020**



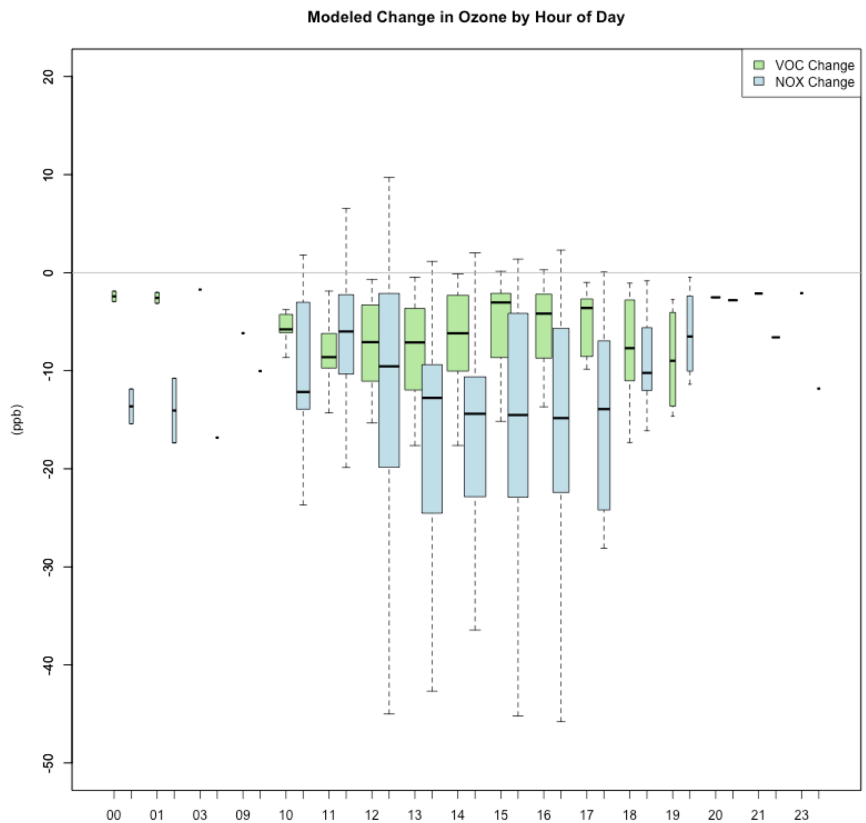
TNMOC/(NO2+PAN+HNO3) where Obs O_3 > 70

Modeled estimates at all ozone monitor locations

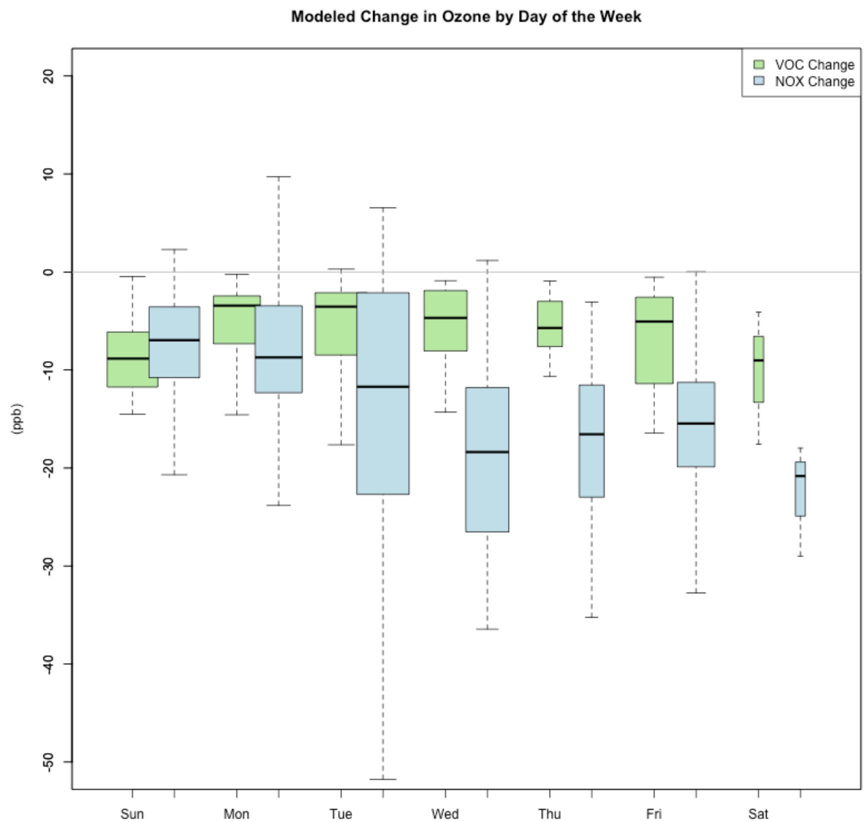


Modeled Change in Ozone

where predicted hourly ozone > 70 ppb



Hour of the Day (LST)

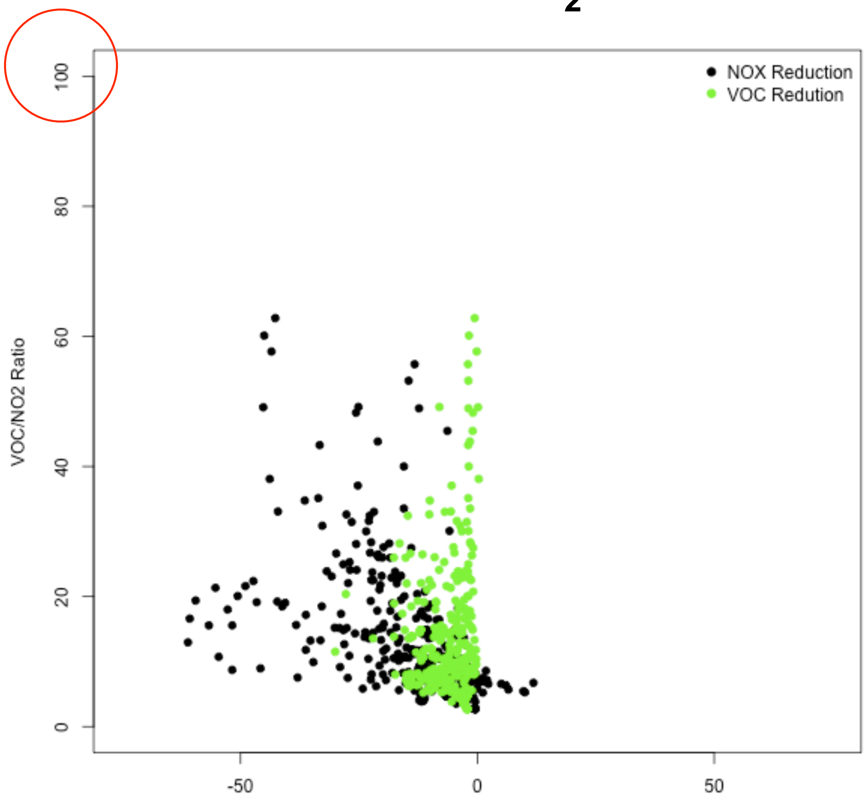


Day of the Week

Model Response

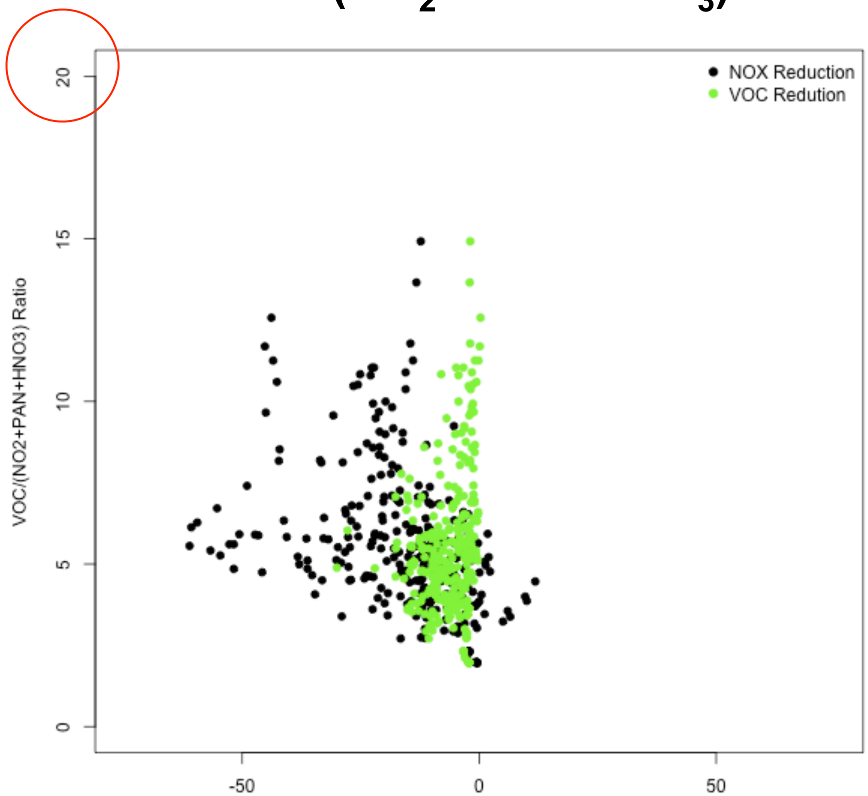
- Comparing the model predicted change in O_3 (X axis) to the model predicted VOC/ NO_X ratio (Y axis); where observed O_3 > 70 ppb

VOC/NO_2



Predicted Ozone Delta (ppb)

$VOC/(NO_2+PAN+HNO_3)$



Predicted Ozone Delta (ppb)

Important Findings

- Observed VOC:NO_2 ratios vary from urban area to urban area; within urban areas; and sometimes from hour to hour

- CMAQ-predicted and PAMS-observed VOC:NO_2 ratios agree well in some parts of the country but not all
  - This suggests CMAQ may not be accurately capturing O_3 production regimes.
  - Emissions inventories may need improvement in some areas

- Current PAMS NO_2 measures NO_2 plus other nitrogen species which may confound interpretation

- Modeling system predicts urban areas will be more NO_X limited in the future

- Model often responds to NO_X and VOC reductions regardless of model estimated VOC/NO_X ratio