Changes in Ozone Production Chemistry across the U.S. between 2007 and 2016: An Integrated Modeling Assessment

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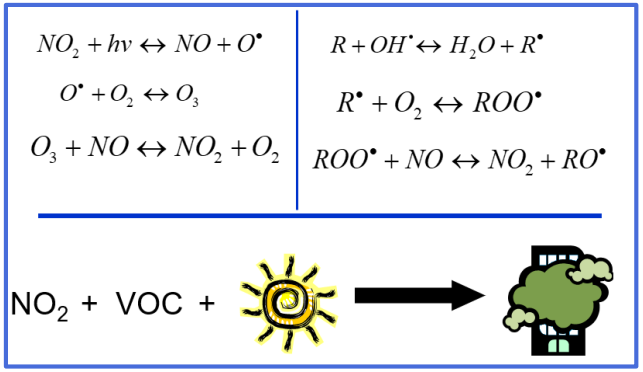
Ozone Production Chemistry

- **VOC limited**
  - Ozone ↓ with ↓ VOC
  - Ozone ↑ with ↓ NOx
  - Occurs at *high* NOx/VOC ratios
  - Most common:
    - Near large NOx emissions: roadways; stack plumes etc
    - At times with ***less*** photochemical activity: winter, cloudy days etc

- **NOx limited**
  - Ozone ↓ with ↓ NOx
  - Ozone insensitive to changes in VOC
  - Occurs at *low* NOx/VOC ratios
  - Most common
    - Rural areas; downwind of urban core
    - Near high biogenic VOC emissions
    - At times with ***more*** photochemical activity: summer, sunny days etc



Evolution of Ozone Control Strategies in the US

- 1980s-1990s
  - Many major ozone nonattainment areas were VOC-limited or transitional (NRC,1991; Russell and Dennis, 200)
  - CAA and SIP regulations focused on NOx and VOC emissions controls
- 2000s
  - More areas were transitional or NOx-limited (Jin et al., 2017; 2020)
  - Some major nonattainment areas remained VOC-limited (Jin et al., 2017; 2020)
  - Major federal regulations focused on regional/national NOx emissions controls
    - NOx SIP call to address interstate transport in the East fully implemented by 2004
    - Tier 2 vehicle emissions standards fully implemented by 2009
- 2010s
  - Additional federal regulations aimed at regional/national NOx emissions reductions
    - Cross-state Air Pollution Rule (CSAPR)
    - Tier 3 vehicle emissions standards

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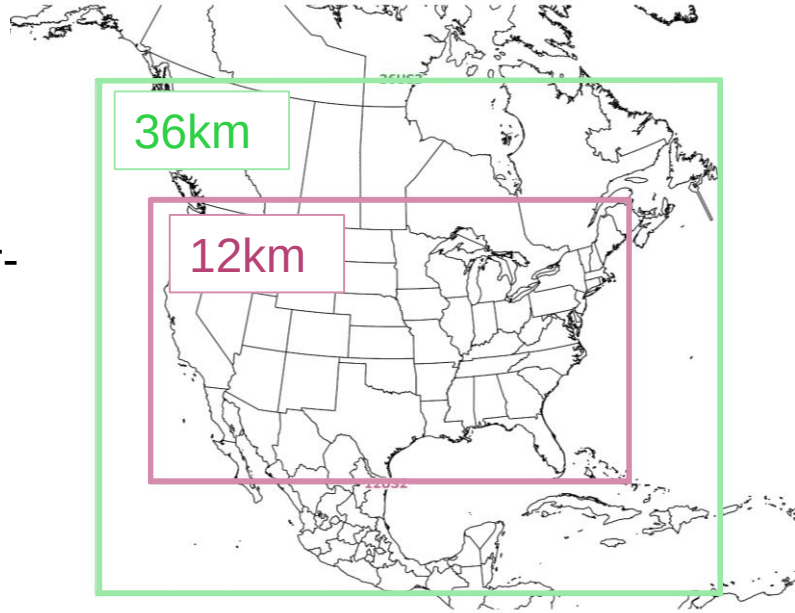
Where are we now?

Tools to Examine O3 Chemical Sensitivity in 2007 and 2016

- Ambient data
  - AQS O3 measurements from 49 nonattainment areas (2015 NAAQS) across the US for 2007 and 2016

- Photochemical modeling
  - Full-year 2007 and 2016 simulations
  - CAMx v6.5 photochemical model with higher-order decoupled direct method (HDDM)
    - gridded hourly O3 concentrations
    - gridded hourly O3 sensitivity to US anthropogenic NOx and VOC emissions
  - One-way nested 36 km and 12 km grid resolution domains
  - Meteorology from WRF v3.8
  - Boundary conditions obtained from hemispheric-CMAQ



Types of Analyses

- **Day-of-week analysis:** First build confidence in model's ability to simulate O3 change as a result of emissions (and meteorological) changes using:
  - Ambient MDA8 ozone data in 2007 and 2016
  - Modeled MDA8 ozone data in 2007 and 2016

  - Can the model capture observed day-of-week ozone patterns?
  - Can the model capture changes in observed day-of-week ozone patterns between 2007 and 2016?

- **Model-based sensitivity analysis:** Then use model capabilities to isolate impact of emissions alone
  - HDDM capability provides gridded nonlinear MDA8 ozone response to US anthropogenic NOx and VOC emissions changes

Day-of-Week Methods

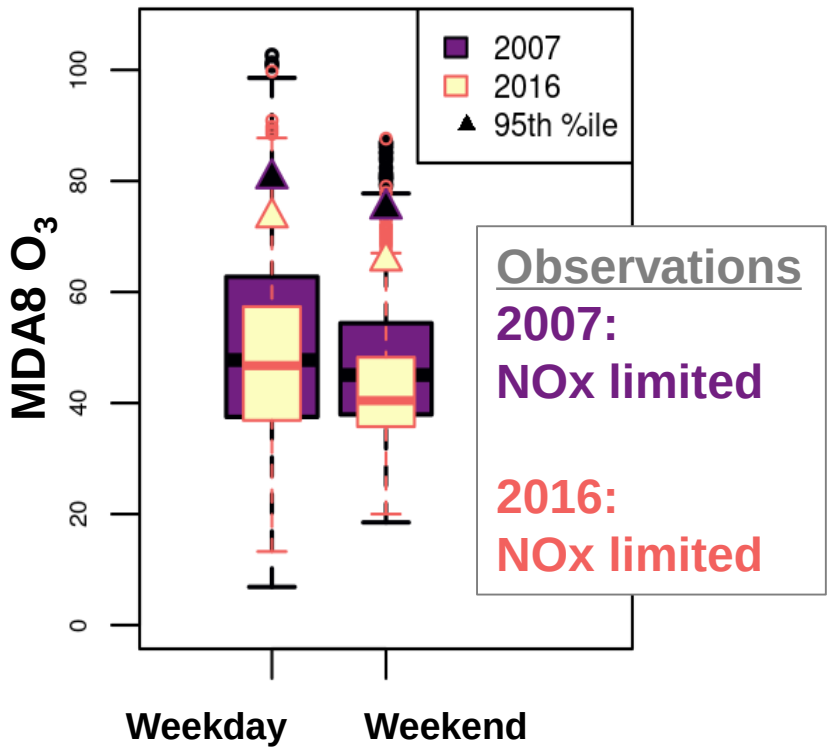
- Since the 1970s researchers have noted day-of-week differences in ozone and postulated this effect resulted from weekly emissions cycles

- Marr and Harley (2002) showed differential traffic patterns in California by day-of-week could provide insight into ozone formation regime
  - LD gasoline activity decreased by ~10% on weekends (VOC + NOx)
  - HD diesel activity decreased by 70-80% on weekends (NOx-only)
  - VOC remained steady while NOx decreased on weekends

- In concept, all else being equal (i.e. no systematic day-of-week meteorological differences)
  - Higher O3 on weekends indicates VOC-limited conditions
    - (Ozone ↑ with ↓ NOx)
  - Lower O3 on weekends indicates NOx-limited conditions
    - (Ozone ↓ with ↓ NOx)

Day-of-Week Analysis (May-Sep): New York City Example

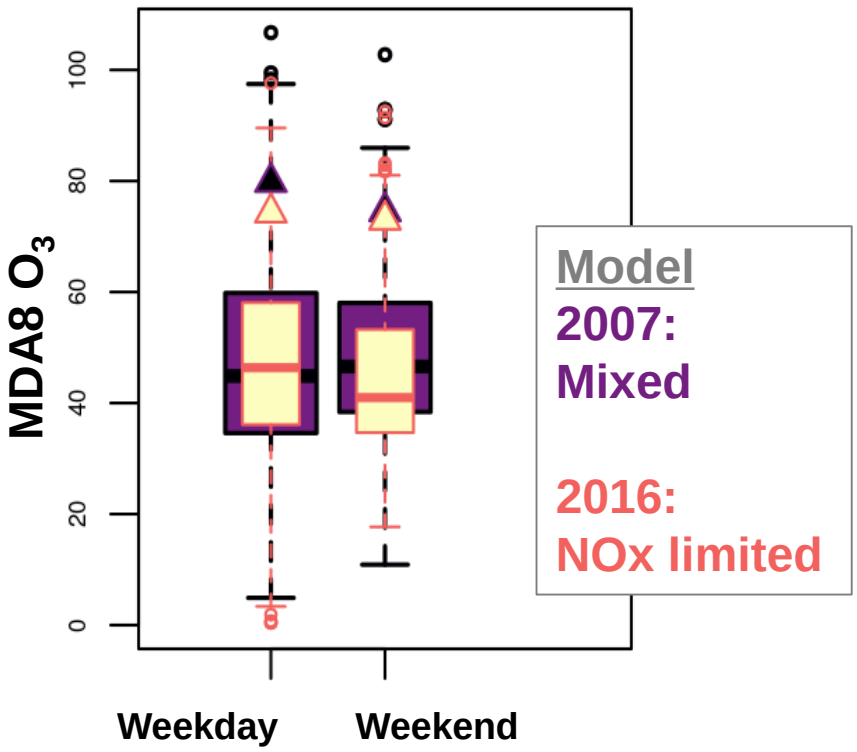
Observed WE-WD change in MDA8 O3



Observations
2007:
NOx limited

2016:
NOx limited

Modeled WE-WD change in MDA8 O3



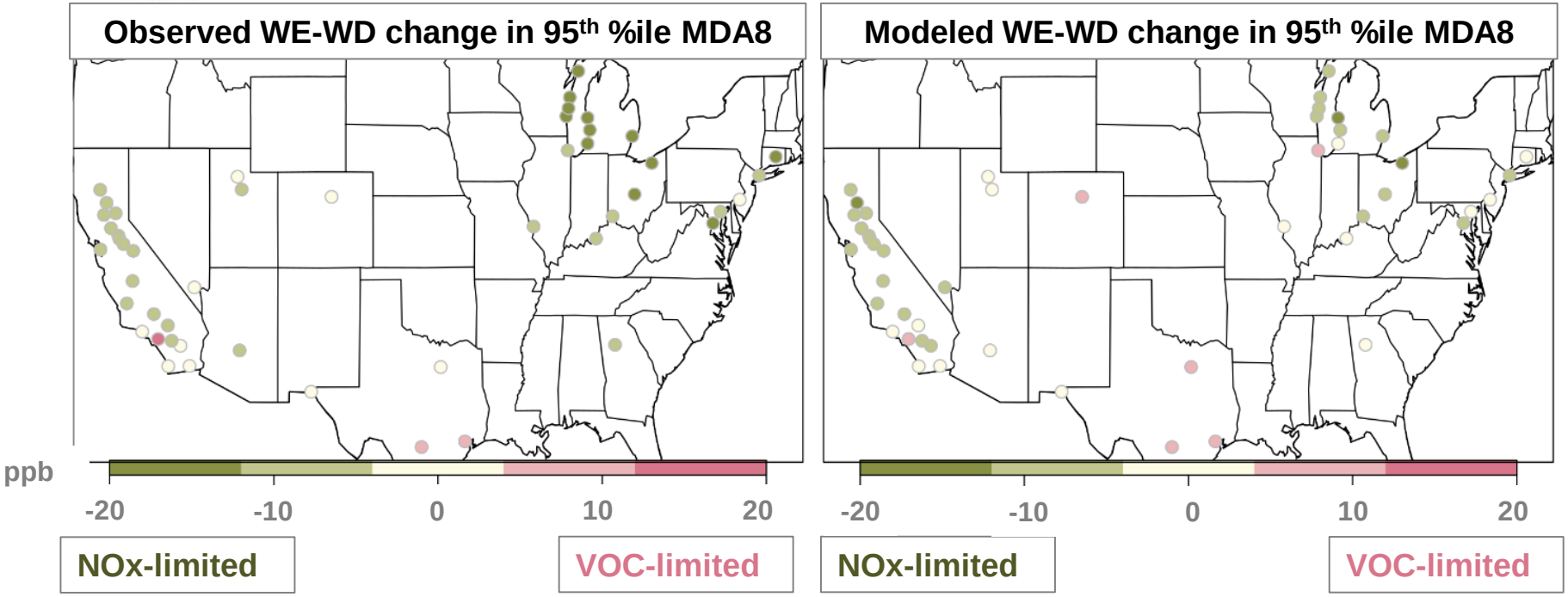
Model
2007:
Mixed

2016:
NOx limited

Conducted t-test of MDA8 O3 distributions on Weekends vs Weekdays

- **NOx-limited:** P-val < 0.05 & Weekend O_3 < Weekday O_3
- **VOC-limited:** P-val < 0.05 & Weekend O_3 > Weekday O_3
- **Mixed:** P-val > 0.05

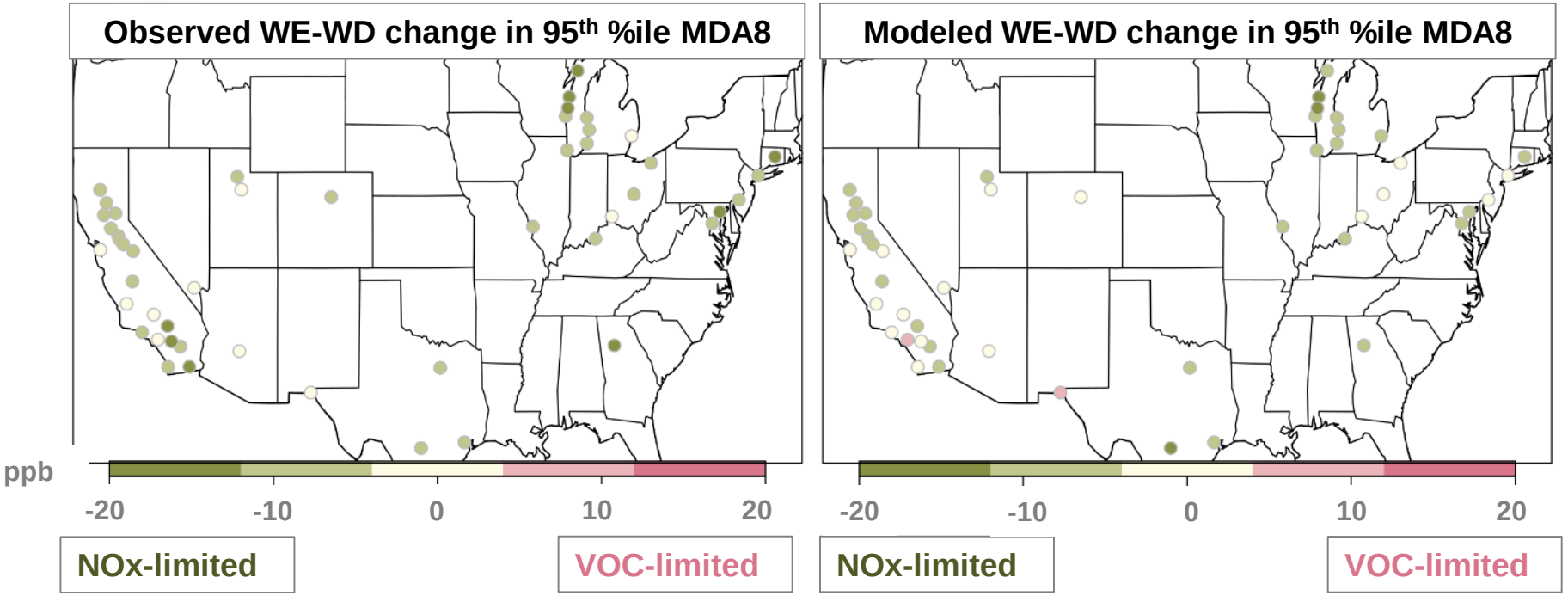
Day-of-Week Analysis: US Nonattainment Areas (2007)



- Modeled chemical regime based on DOW differences match monitor-based characterizations in 33 out of 49 nonattainment areas in 2007

- Both observations and model suggest that only a small number of nonattainment areas were VOC limited in 2007
  - Observations: 7 out of 49
  - Model: 11 out of 49

Day-of-Week Analysis: US Nonattainment Areas (2016)



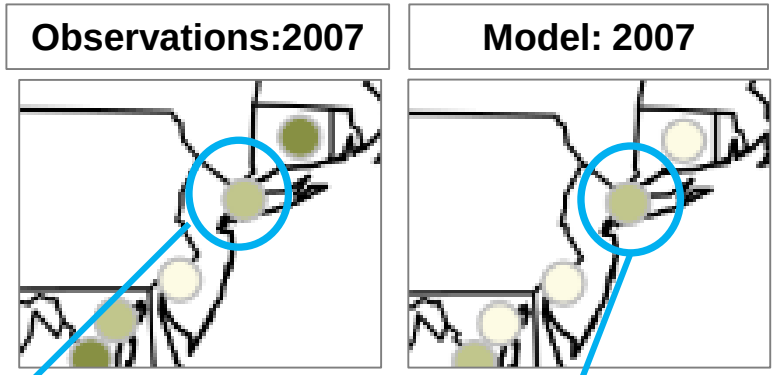
- Modeled chemical regime based on DOW differences match monitor-based characterizations in 42 out of 49 nonattainment areas in 2016

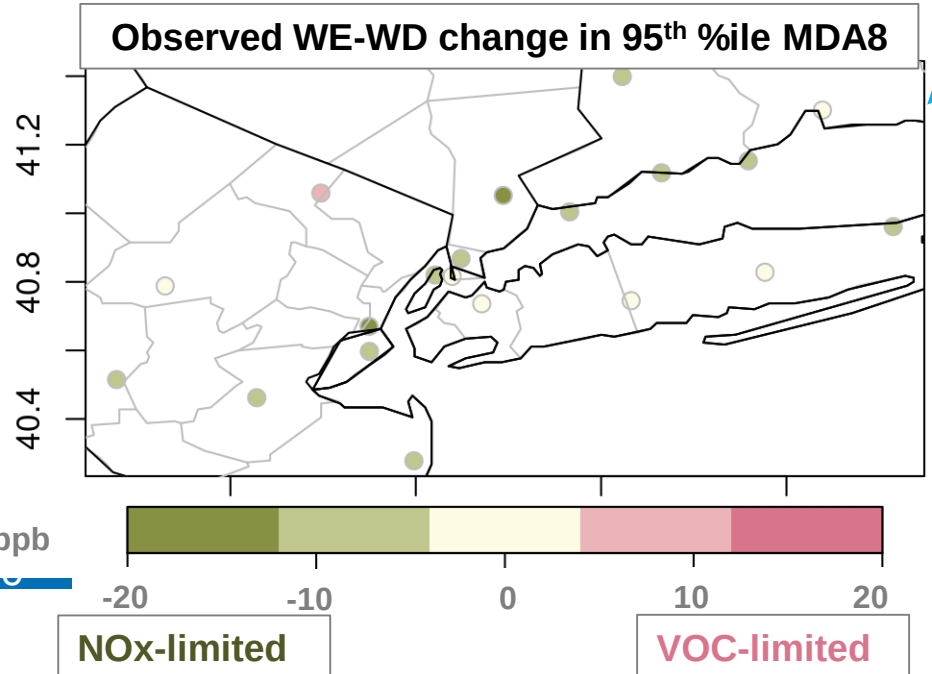
- Both observations suggest that the number of VOC-limited nonattainment areas decreased between 2007 and 2016
  - Observations: 7 (2007) → 1 (2016) (San Francisco)
  - Model: 11 (2007) → 4 (2016) (Dona Ana, LA, San Diego, San Francisco)

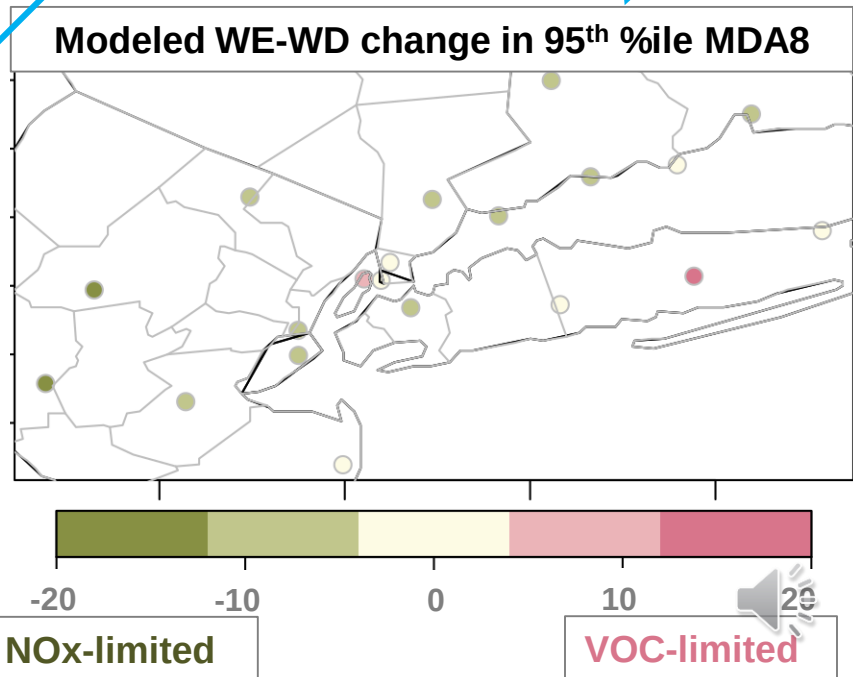
One Category for an Entire Area Does Not Tell the Whole Story

- While the NY nonattainment area appears NOx-limited when looking across all monitors, some locations within the area are transitional or VOC-limited

- The Model still appears to reasonably capture observed day-of-week patterns within the area







Limitations of Day-of-Week Analysis

1) Monitors are not ubiquitous and therefore cannot provide full information

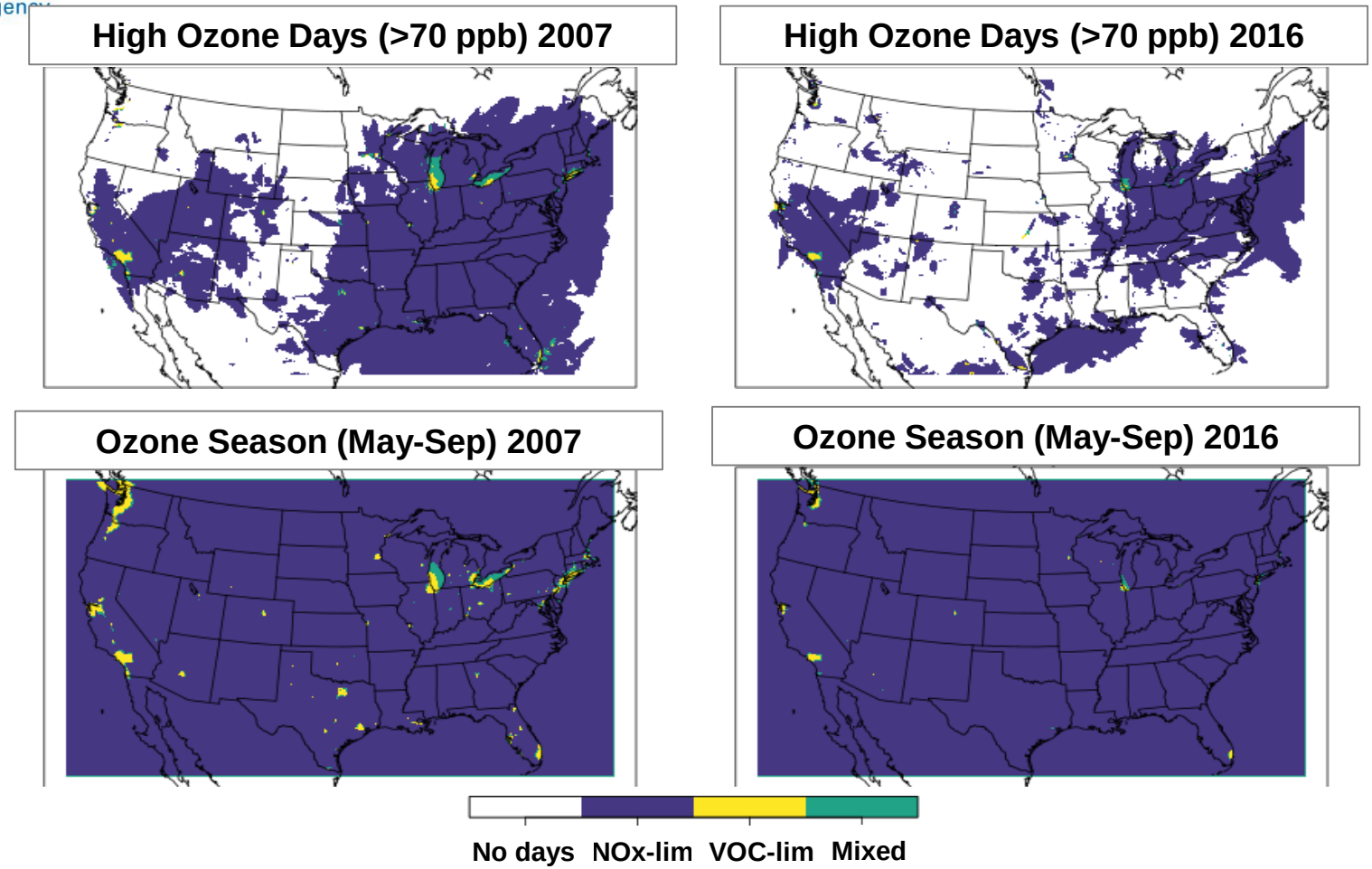
2) Weekly cycles cannot definitively separate impacts from meteorology versus emissions
   - With single year analyses there are a limited number of May-September days.
   - By chance, meteorology may be more conducive to ozone formation on average across weekends or weekdays

- Modeling is the only method that can truly isolate the impacts of emissions alone

- HDDM sensitivity modeling allows for evaluation of all times and locations and examination of ozone response to theoretical NOx versus VOC emissions changes

National Ozone Production Chemistry

United States Environmental Protection Agency



- Compared to 2007, fewer locations with days > 70 in 2016
- Most locations move to NOx-limited by 2016; on high O3 days only Los Angeles and Chicago still showing mixed or VOC-limited behavior on average

Conclusions

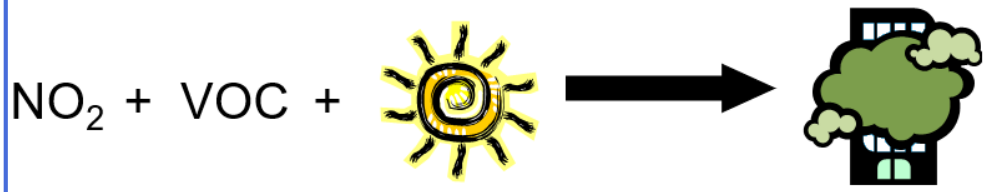
- Day-of-week analysis builds confidence in model's ability to simulate O3 changes in response to variable emissions and meteorology
  - Weekly patterns with a single year
  - Changes in weekly patterns between years
- Ambient and modeling data both show that US has become more NOx-limited between 2007 and 2016
- Model-based sensitivity analysis predicts only a few remaining cities any VOC-limited locations in 2016
  - New York urban core
  - Chicago
  - Minneapolis
  - San Francisco
  - Los Angeles

United States Environmental Protection Agency

Disclaimer: *The views expressed in this presentation are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.*

$$NO_2 + h\nu \leftrightarrow NO + O^{\bullet}$$
$$O^{\bullet} + O_2 \leftrightarrow O_3$$
$$O_3 + NO \leftrightarrow NO_2 + O_2$$

$$R + OH^{\bullet} \leftrightarrow H_2O + R^{\bullet}$$
$$R^{\bullet} + O_2 \leftrightarrow ROO^{\bullet}$$
$$ROO^{\bullet} + NO \leftrightarrow NO_2 + RO^{\bullet}$$



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Extra Slides

Additional example cities for DOW analysis:

Denver and Dallas

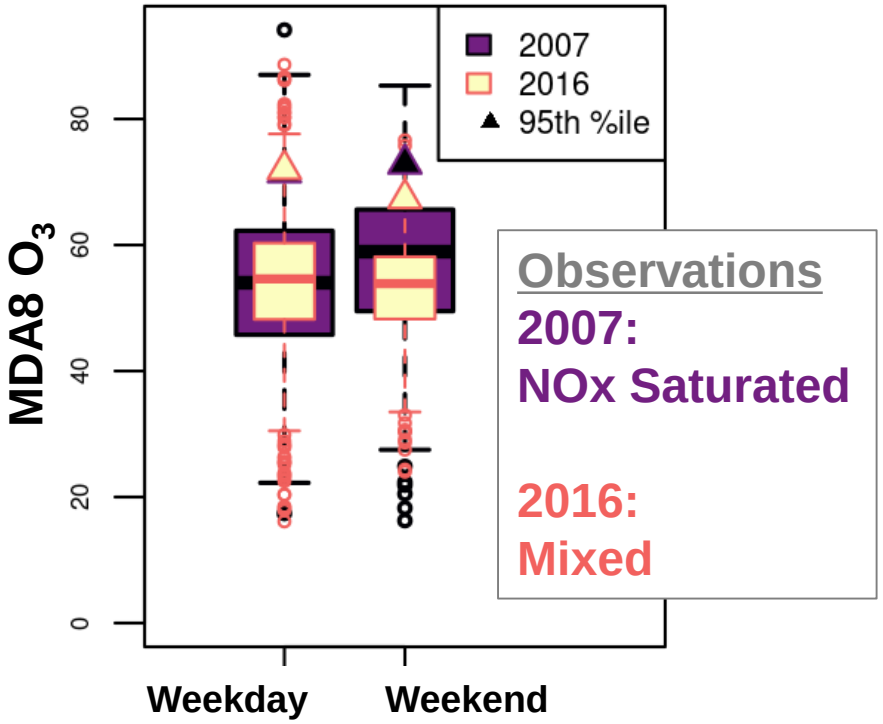
EPA
United States
Environmental Protection
Agency

Denver

Day-of-Week Analysis: Denver Example

United States Environmental Protection Agency

Observed WE-WD change in MDA8 O3



Observations
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NOx Saturated

2016:
Mixed

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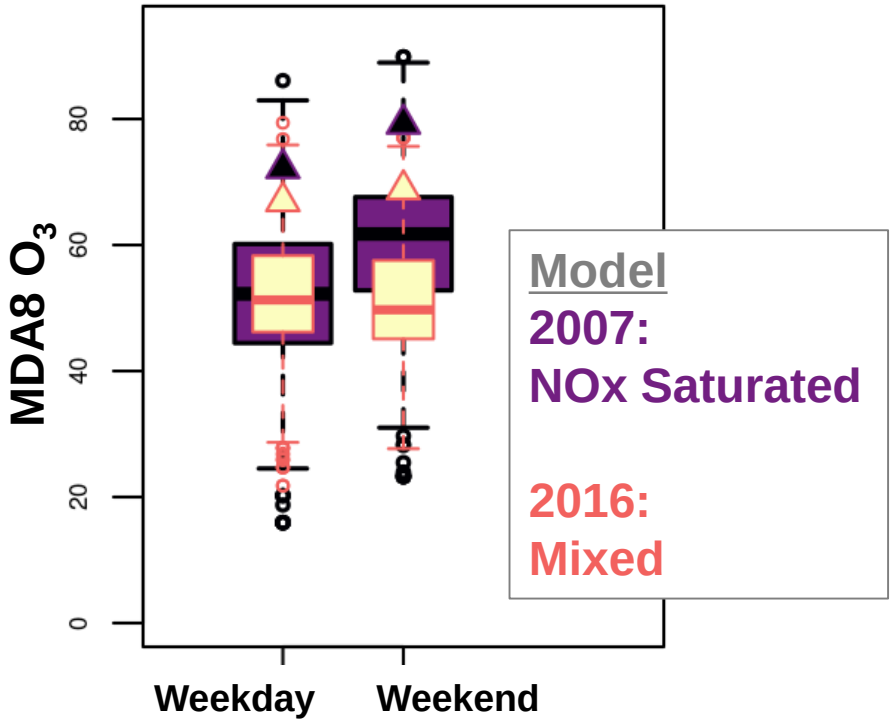

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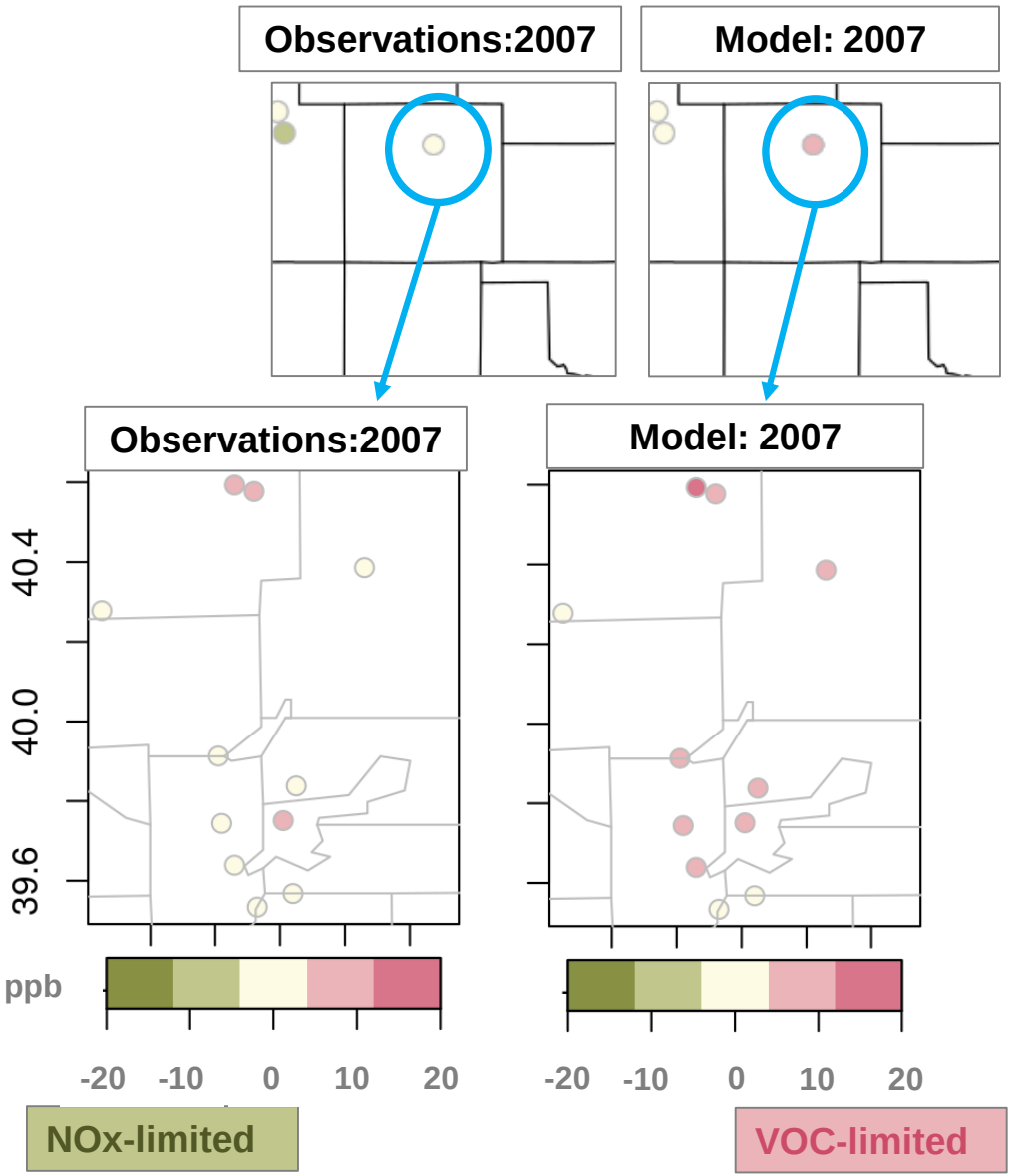
One Category for an Entire Area Does Not Tell the Whole Story

- While the day-of-week based on observations in the Denver nonattainment area show a transitional regime when looking across all monitors, some locations within the area are VOC-limited
- The model-based day-of-week analysis also shows some transitional and some VOC-limited monitors but tends more towards VOC-limited than the observations



EPA
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Environmental Protection
Agency

Dallas

Day-of-Week Analysis: Denver Example

United States Environmental Protection Agency

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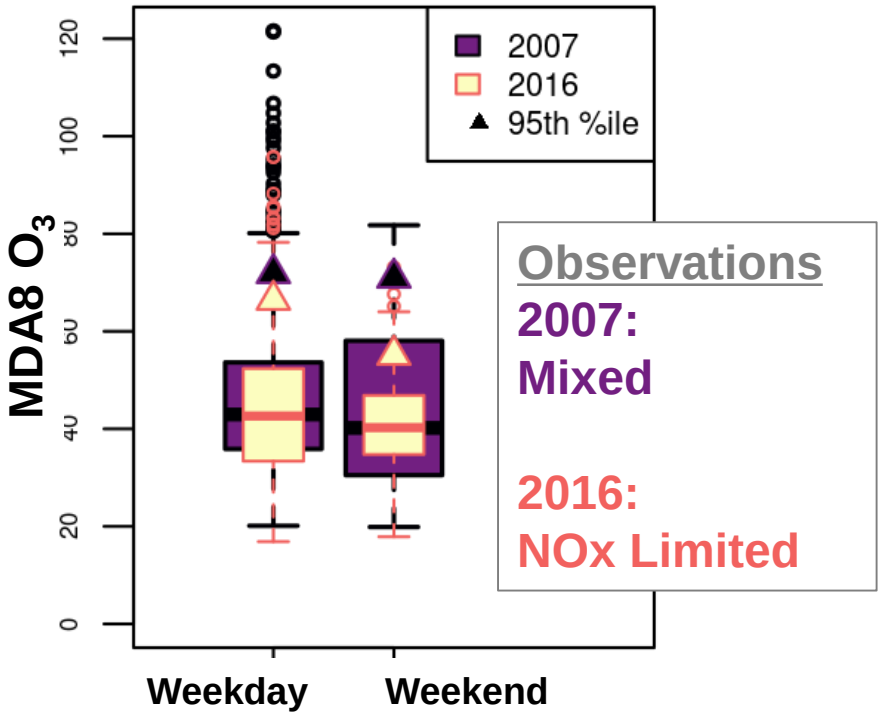

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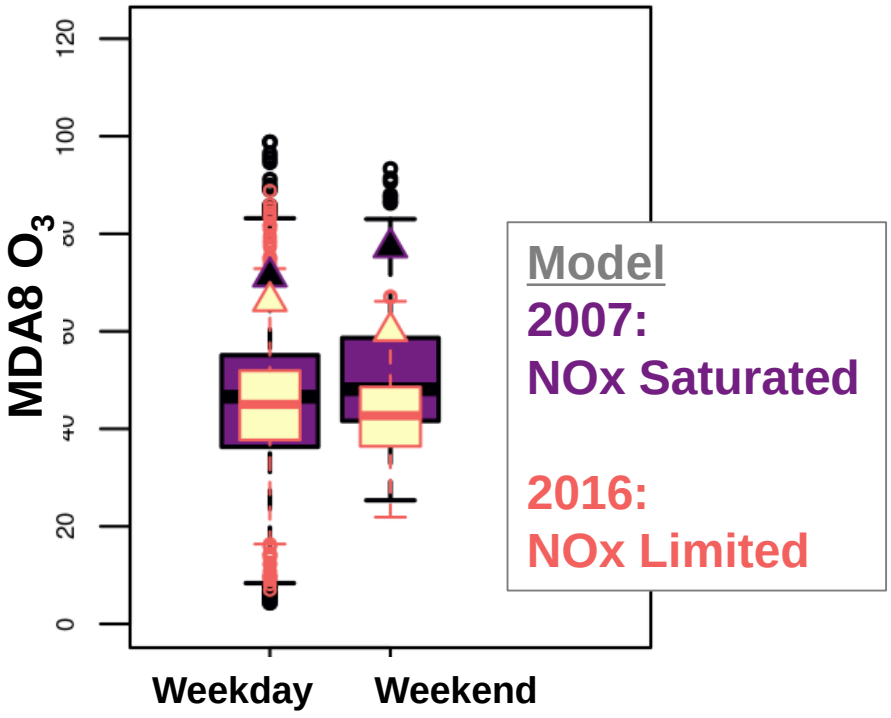

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One Category for an Entire Area Does Not Tell the Whole Story

- While the day-of-week based on observations in the Dallas nonattainment area show a transitional regime when looking across all monitors, some locations within the area are NOx-limited or VOC-limited
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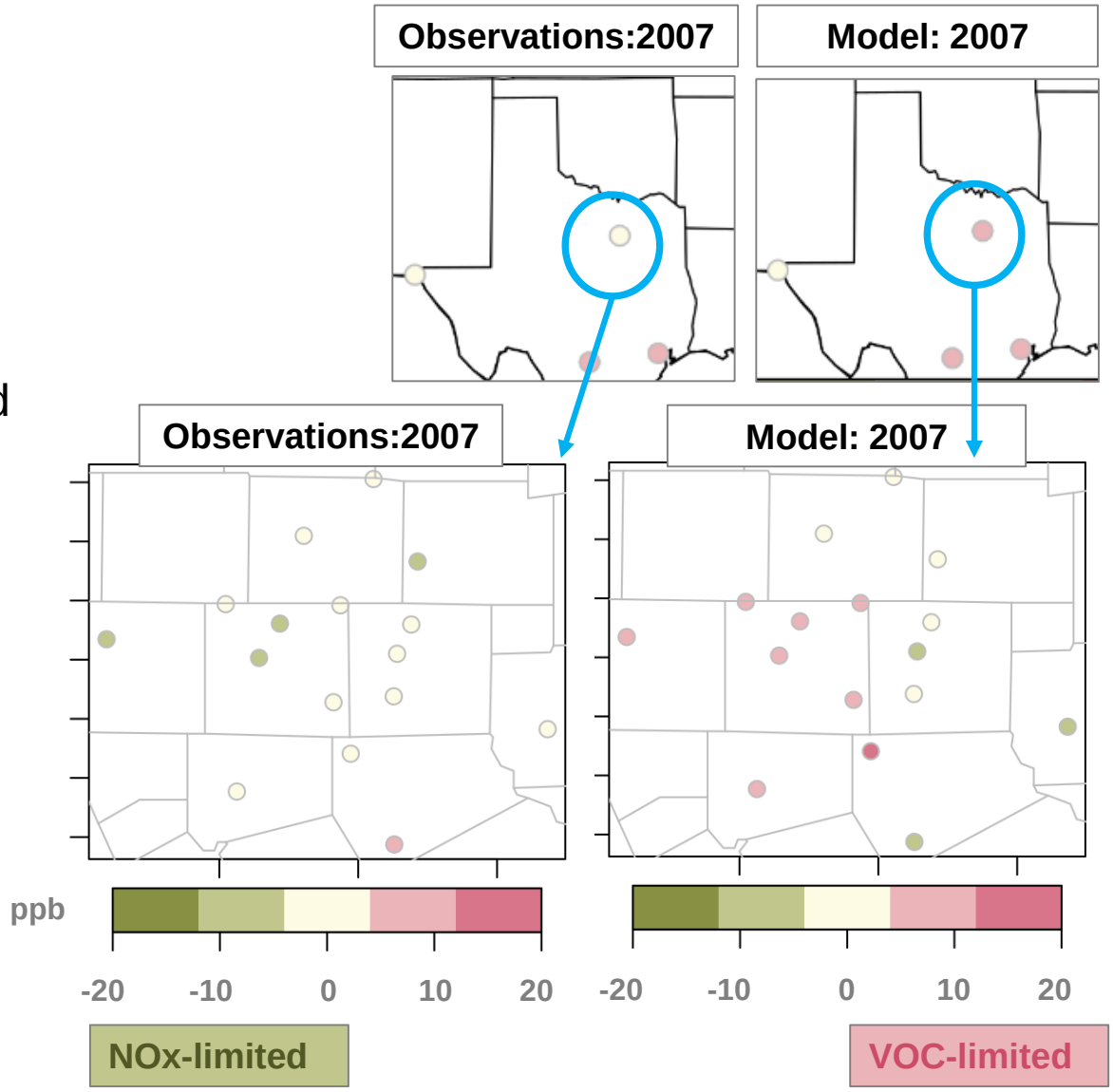
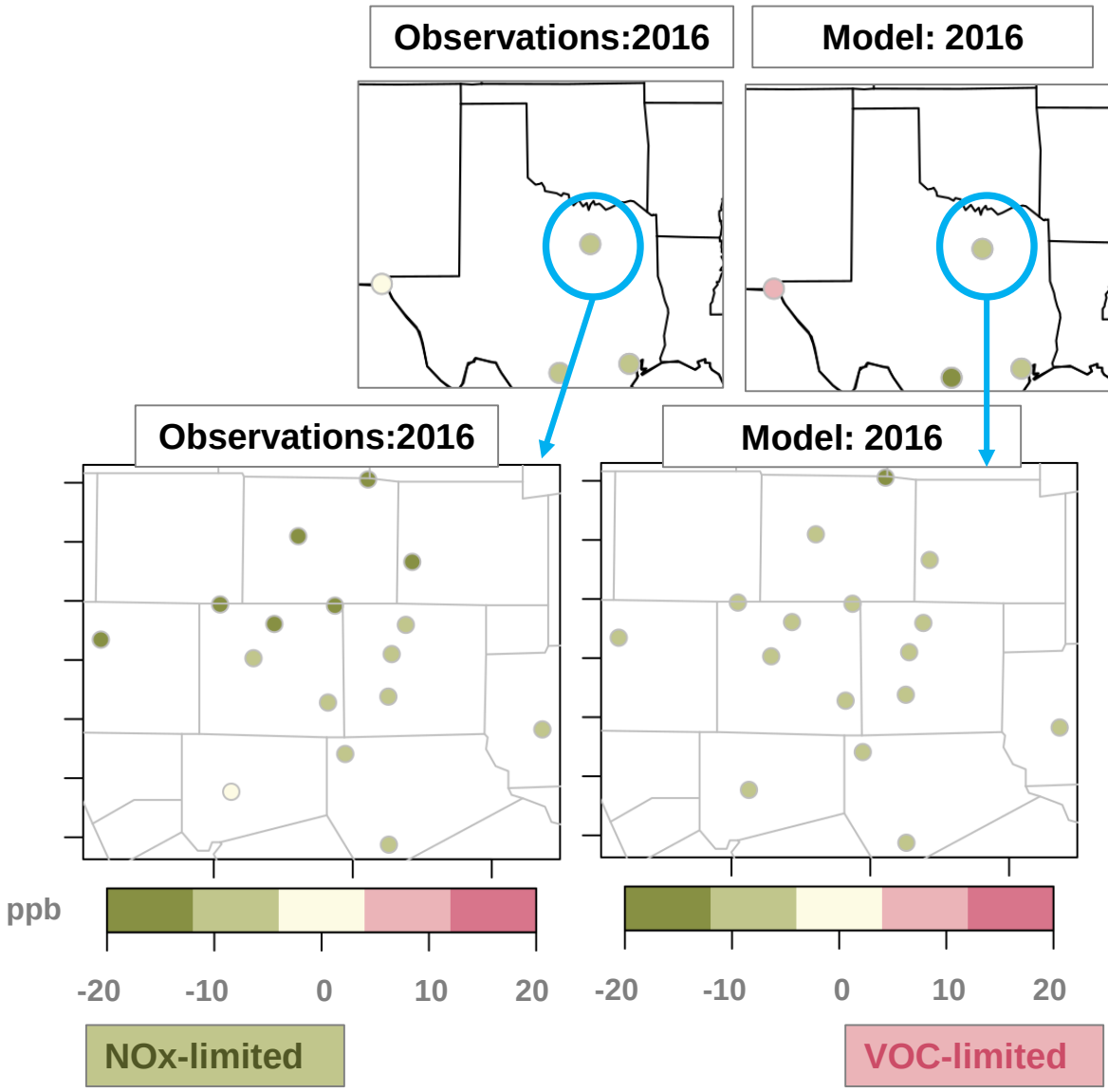


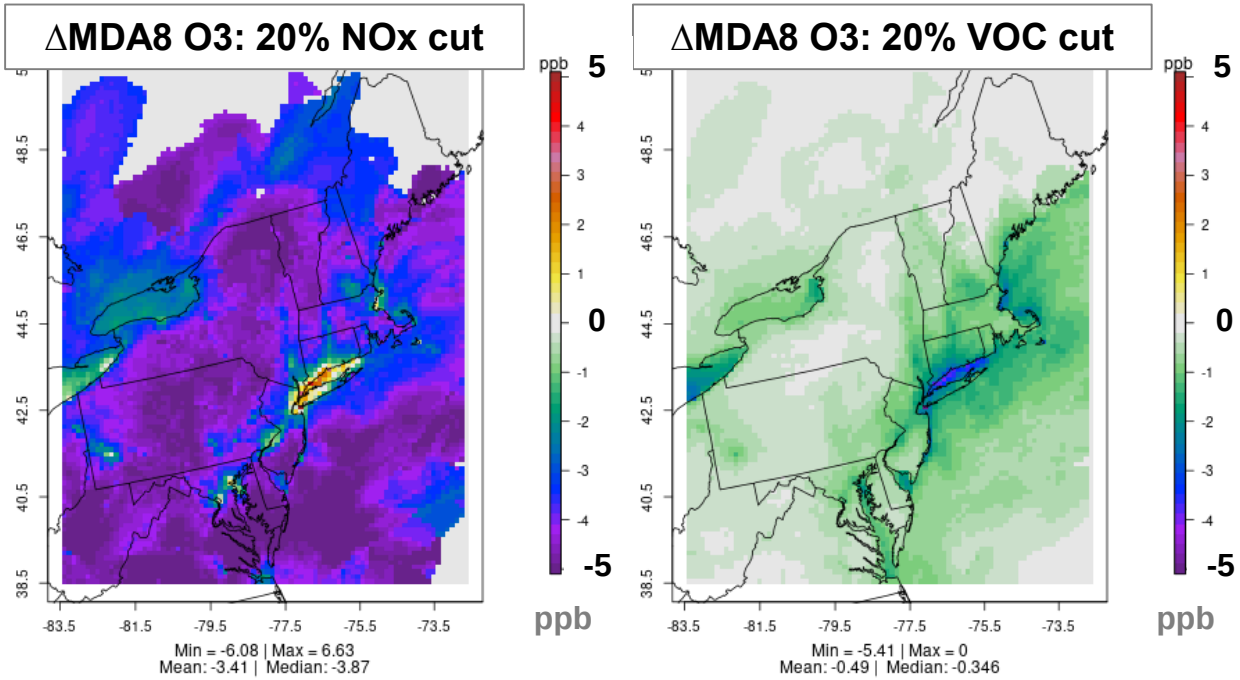
One Category for an Entire Area Does Not Tell the Whole Story

- By 2016 both model and observed day-of-week analysis suggests NOx-limited conditions in Dallas
- Observations suggest that some monitors remain transitional while the model suggestions more consistent NOx-limited conditions across monitors



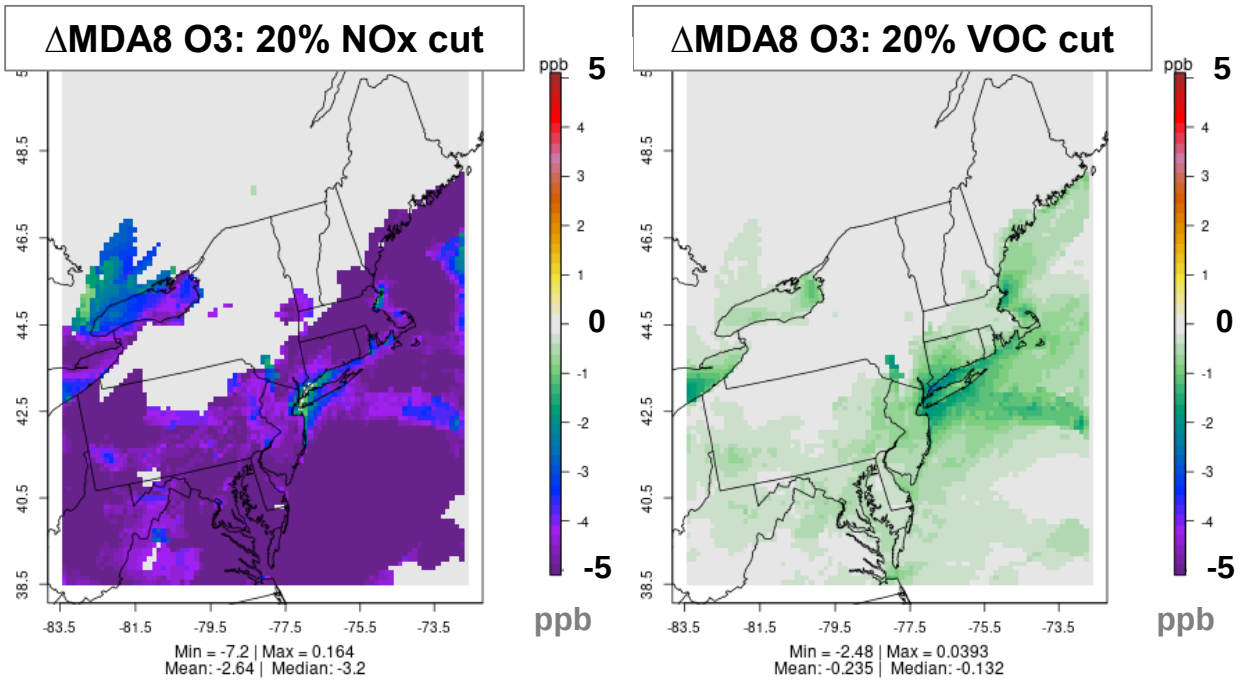
2007: Days > 70 ppb

- Larger reductions evident on “high” O_3 days than on all days
- O_3 increases (orange/red) evident with NOx cuts in: NYC, Boston, Philadelphia, Baltimore/DC
- O_3 decreases from NOx larger than O_3 decreases from VOC in the rest of the domain



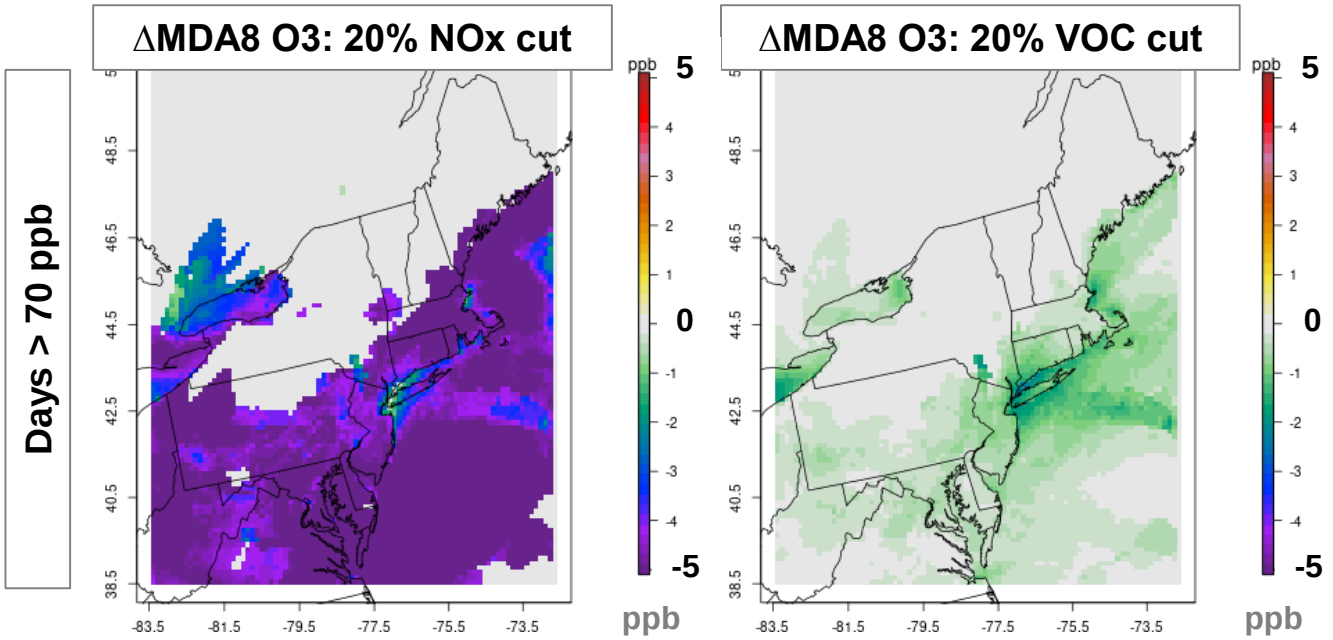
2016: Days > 70 ppb

- Compared to 2007, fewer locations with days > 70
- On high days, O_3 increases no longer evident in: Boston, Philadelphia, Baltimore/DC
- With exception of small NYC urban core area, entire domain NOx-limited on high O3 days

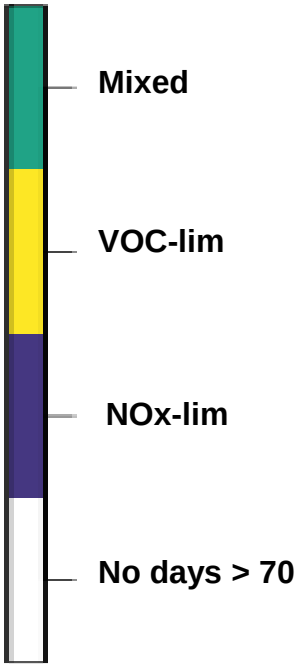


Characterizing NOx-limited and VOC-limited Regimes on Days > 70 ppb

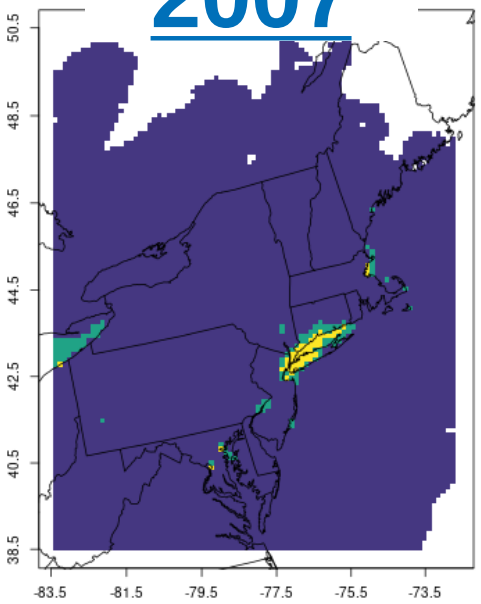
United States Environmental Protection Agency



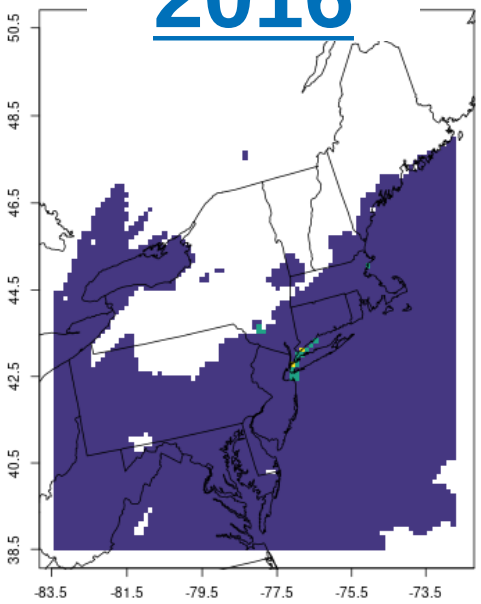
- **NOx-limited:**
  - ΔMDA8 O_3 with a 20% NOx cut < 0 **AND**
  - |ΔMDA8 O_3: 20% NOx cut| > |ΔMDA8 O_3: 20% VOC cut|
- **VOC-limited:**
  - ΔMDA8 O_3 with a 20% NOx cut > 0
- **Mixed:**
  - ΔMDA8 O_3 with a 20% NOx cut < 0 **AND**
  - |ΔMDA8 O_3: 20% NOx cut| < |ΔMDA8 O_3: 20% VOC cut|



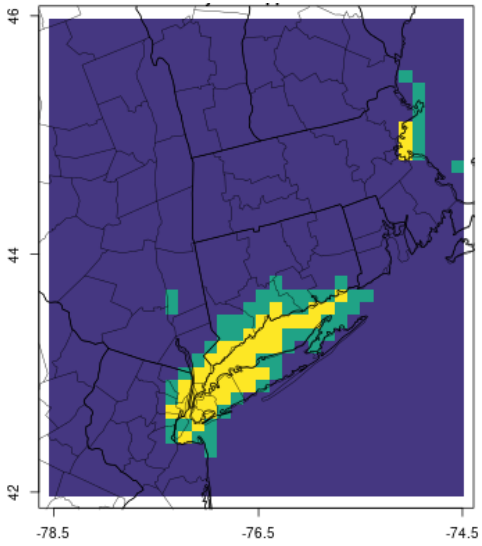
2007

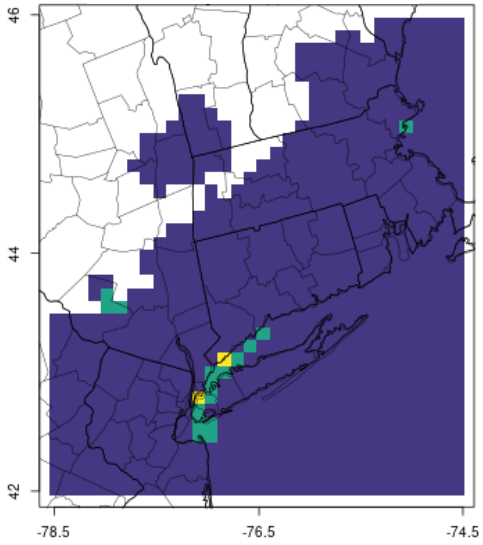


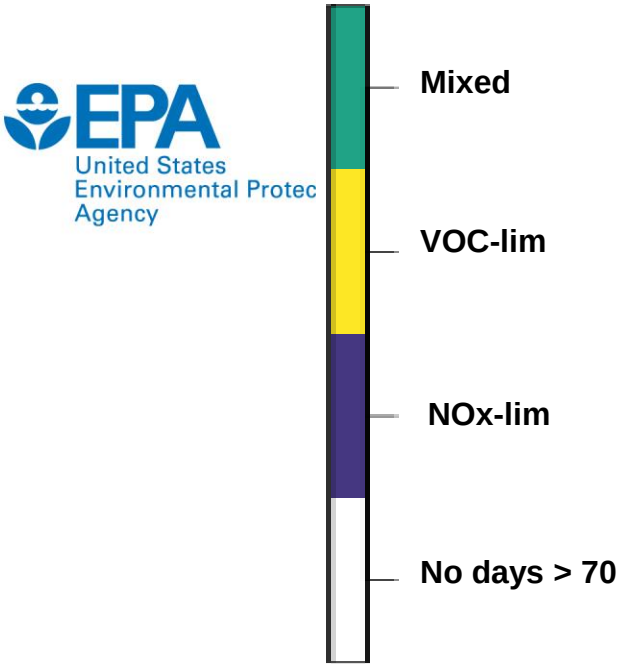
2016



- 2007: multiple urban areas in the Northeastern US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the Northeastern US
  - The extend of VOC-limited locations in NYC has shrunk to the urban core







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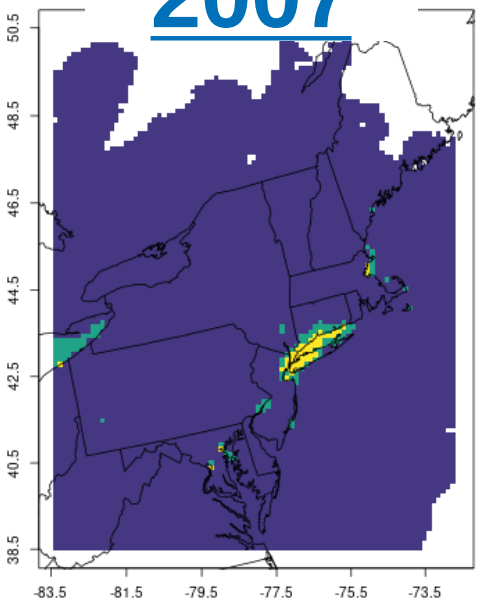

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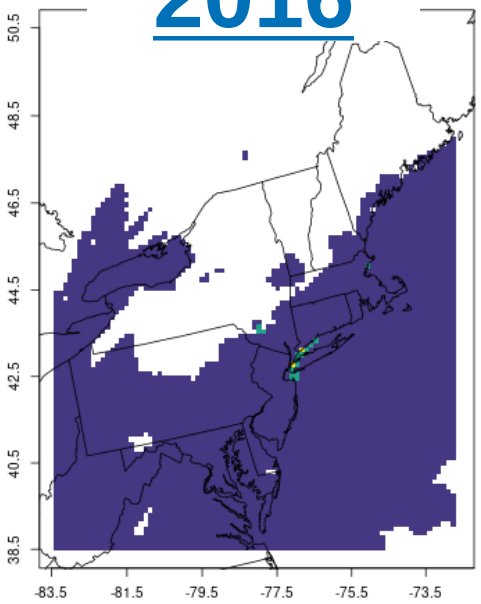
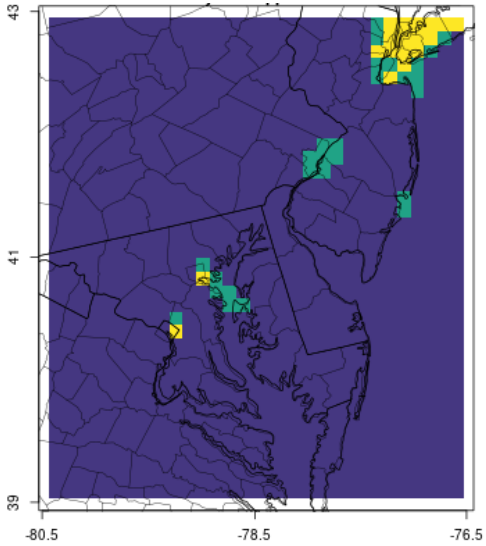
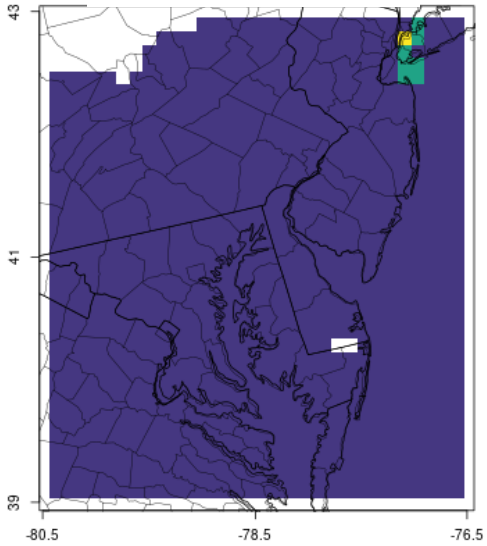


- 2007: multiple urban areas in the Northeastern US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the Northeastern US
  - Baltimore, DC, and Philadelphia predicted to be NOx-limited





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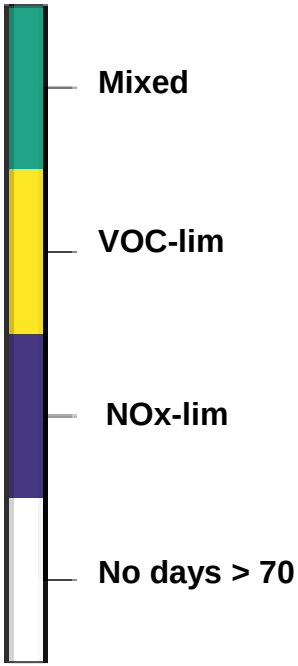

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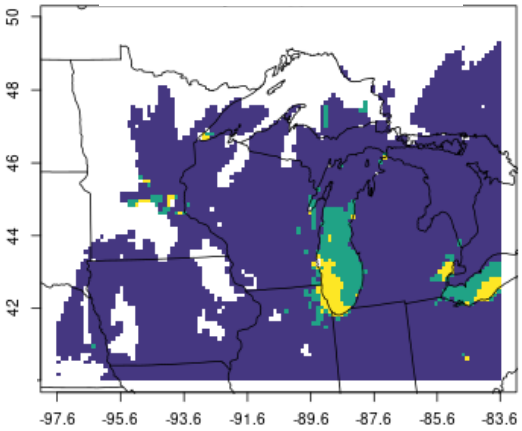
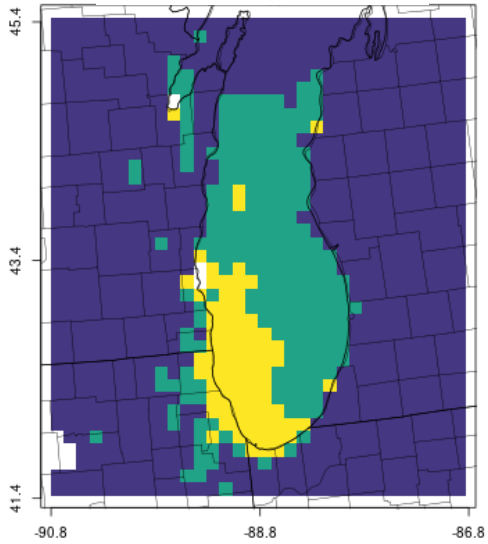
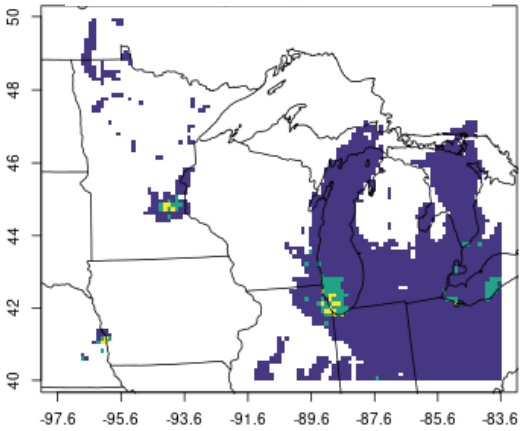
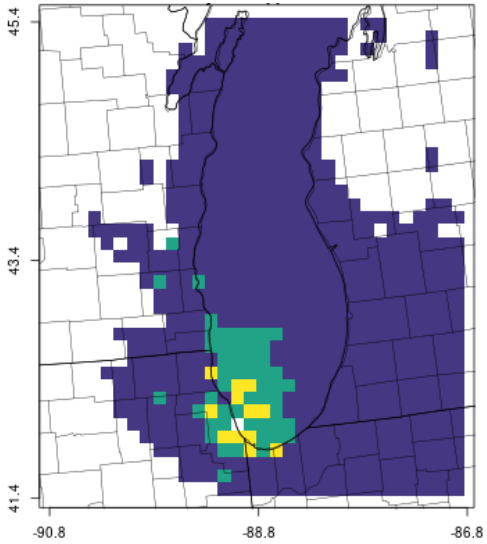


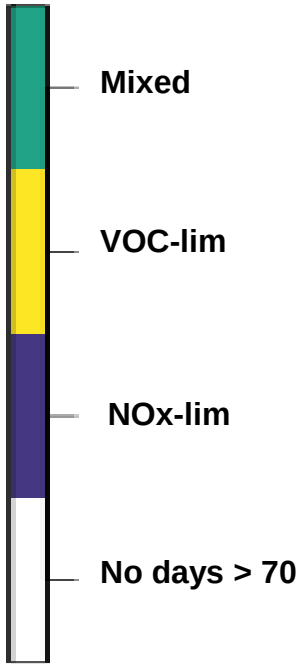


2016



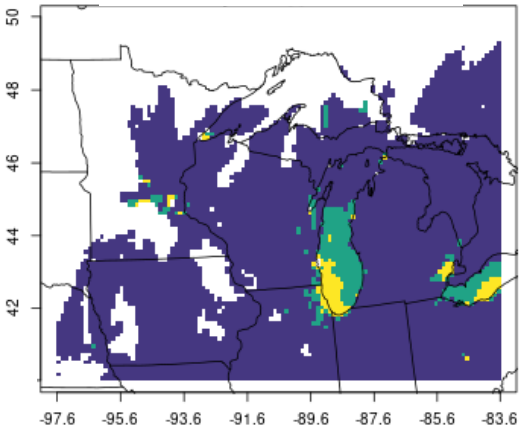


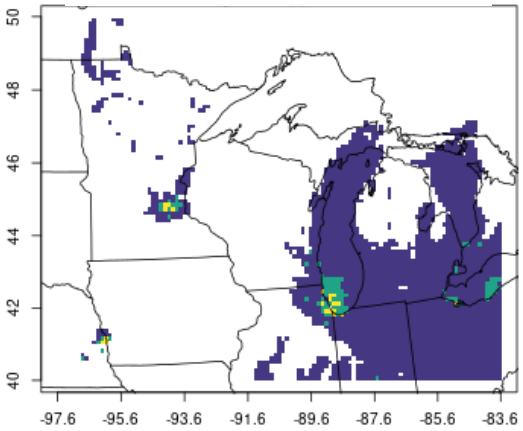
- 2007: multiple urban areas in the Midwest US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the Midwest
  - The extend of VOC-limited locations in Chicago has shrunk to the urban core



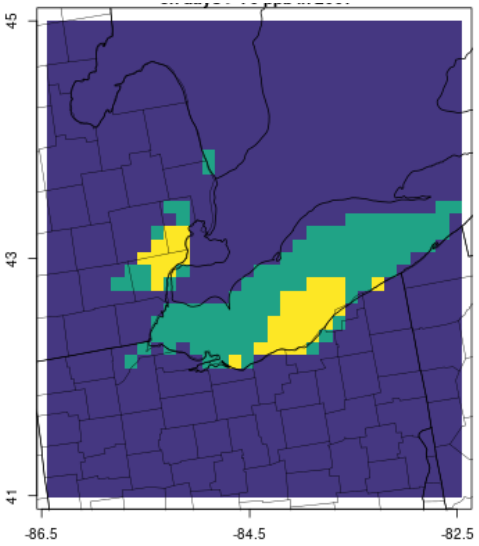
2007

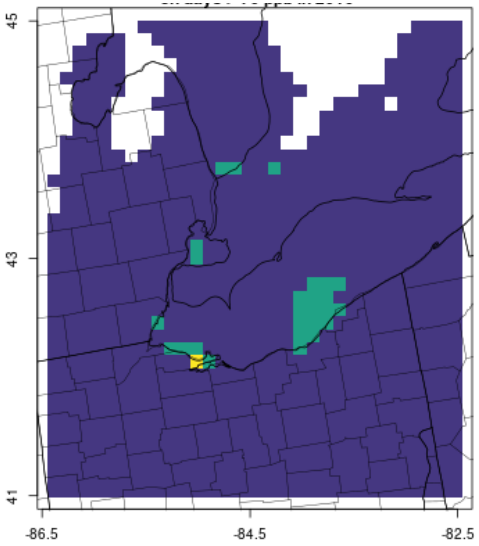
2016

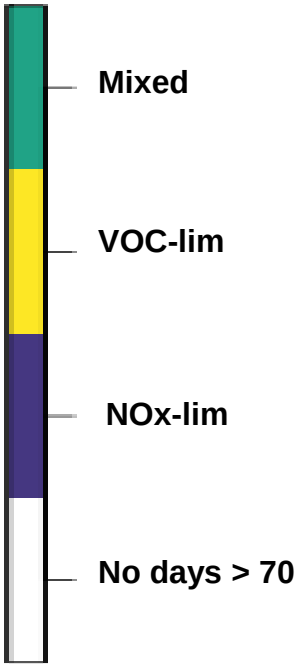




- 2007: multiple urban areas in the Midwest US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the Midwest
  - Detroit and Cleveland predicted to be mostly NOx-limited

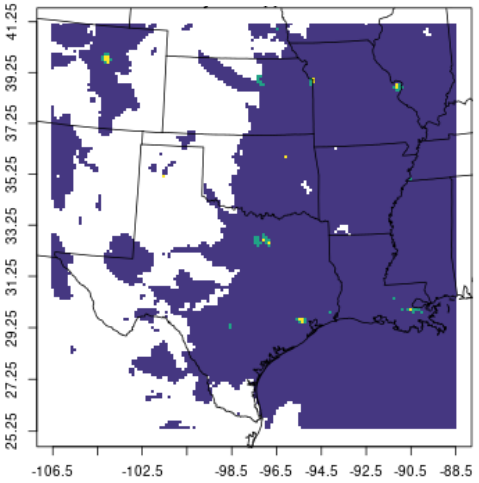


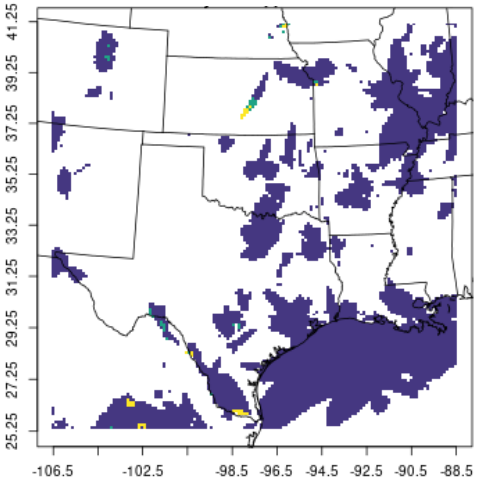




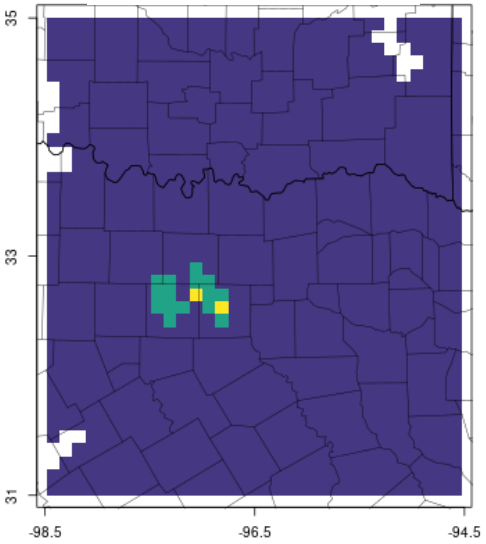
2007

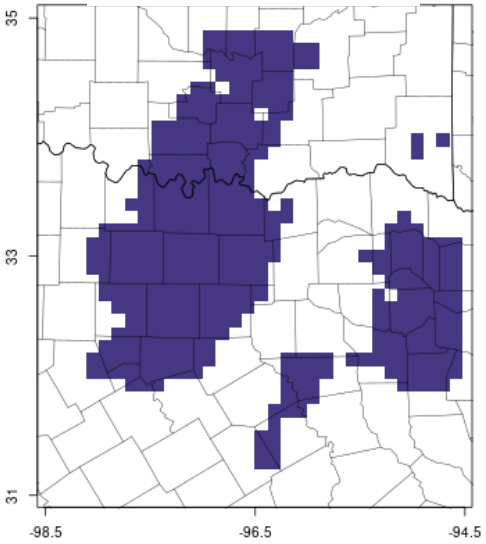
2016

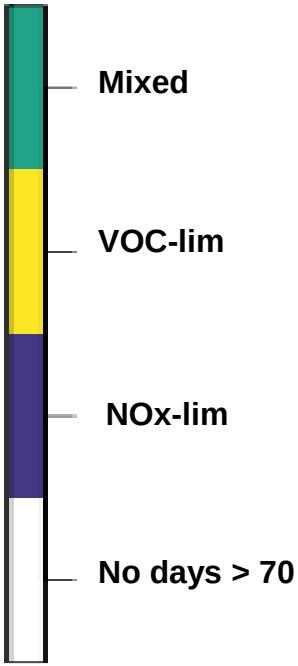




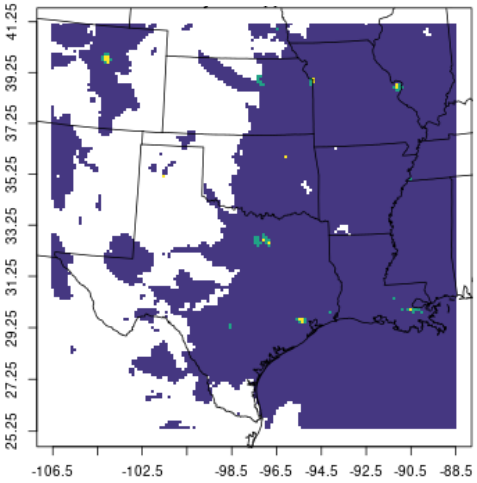
- 2007: multiple urban areas in the Southern US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the South
  - Dallas predicted to be NOx-limited

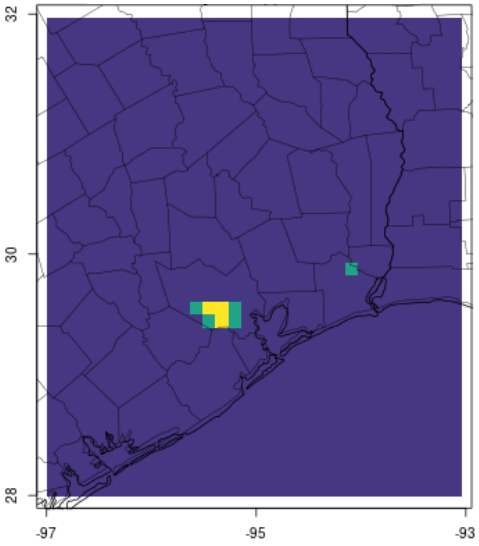




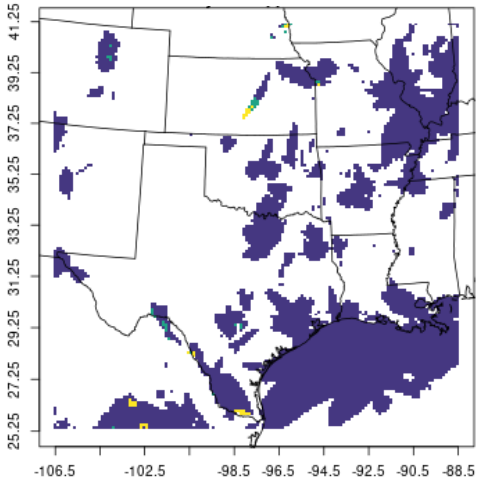


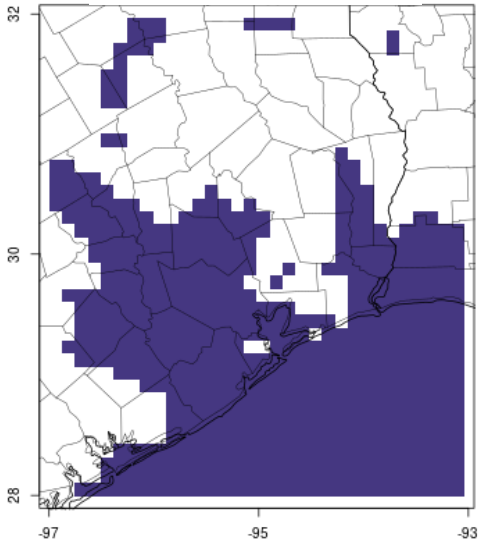
2007



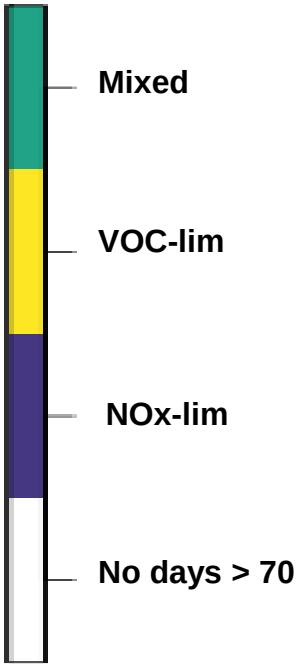


2016



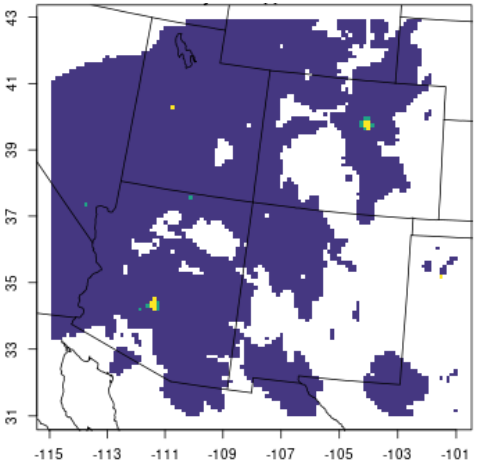


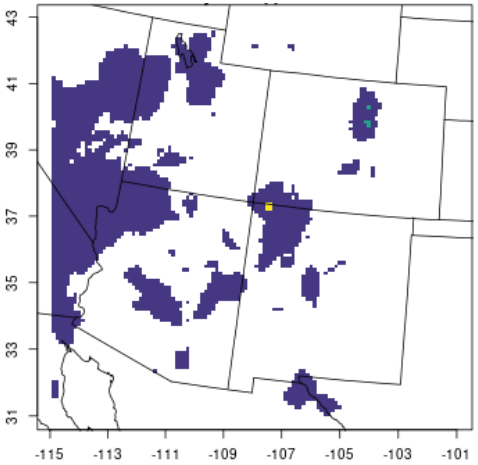
- 2007: multiple urban areas in the Southern US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the South
  - Houston predicted to be NOx-limited

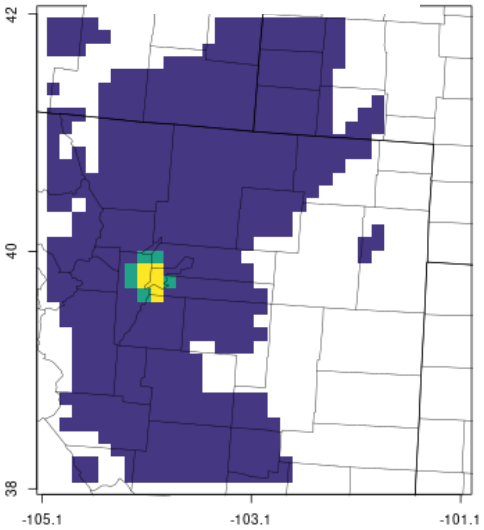


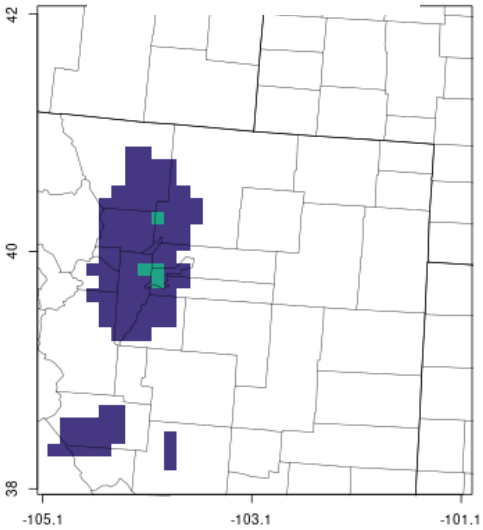
2007

2016

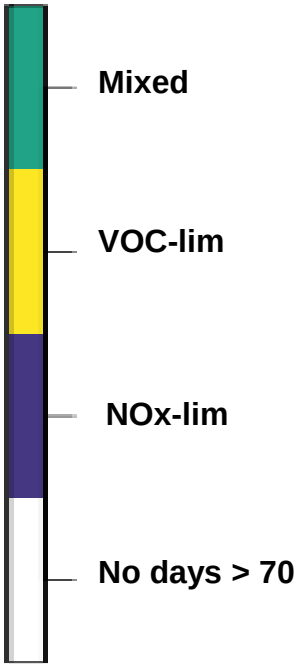




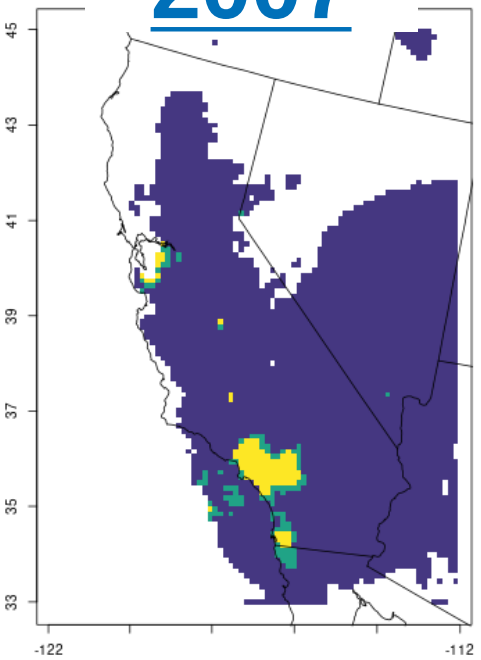


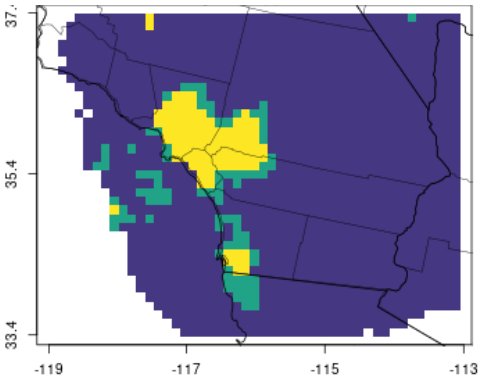


- 2007: multiple urban areas in the Southwestern US predicted to be VOC-limited
- 2016: few VOC-limited areas remain in the Southwest
  - Denver predicted to be mostly NOx-limited

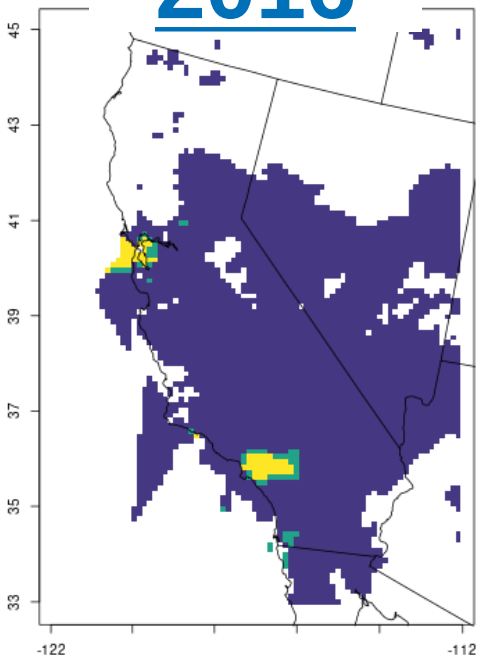


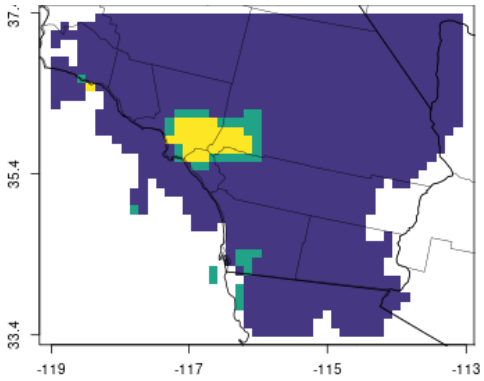
2007





2016





- 2007: multiple urban areas in the Western US predicted to be VOC-limited
- 2016: Spatial extend of VOC-limited areas has shrunk
  - VOC-limited locations in Los Angeles cover a small area closer to the city center