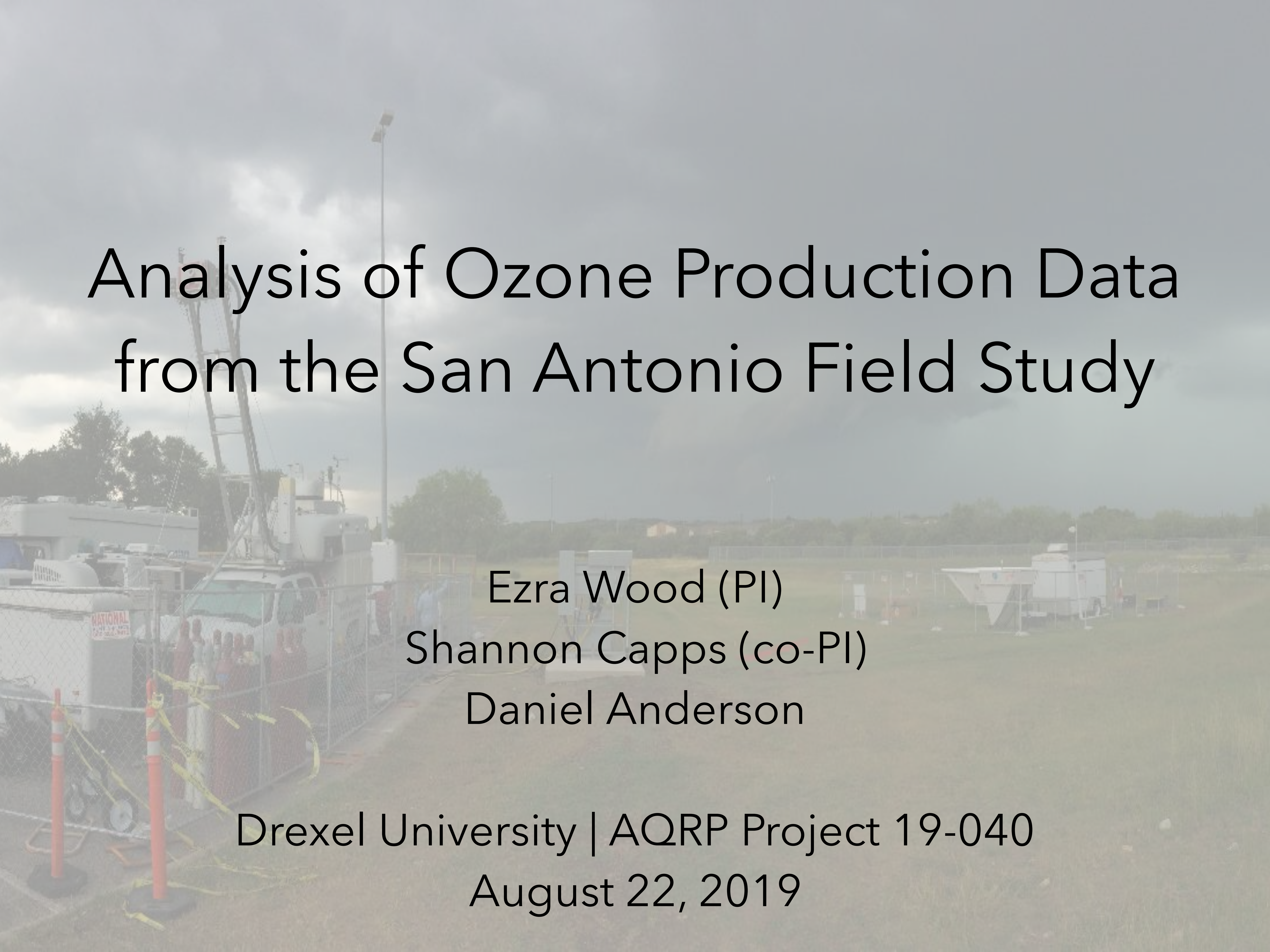

Analysis of Ozone Production Data from the San Antonio Field Study

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Shannon Capps (co-PI)
Daniel Anderson

Drexel University | AQRP Project 19-040

August 22, 2019

Acknowledgements

- Financial support from Texas AQRP through TCEQ under Project 19-040
- Baylor University: Rebecca Sheesley, Sascha Usenko, and Sujan Shrestha
- University of Houston: Jimmy Flynn
- Rice University: Rob Griffin
- Aerodyne: Scott Herndon, Tara Yacovitch, Rob Roscioli, Berk Knighton, Brian Lerner, Conner Daube, Ed Fortner, Jordan Krechmer, Paola Massoli
- Kirk Baker, U.S. EPA OAQPS for CMAQ modeling platform
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San Antonio Field Study (SAFS)

SAFS: characterize ozone formation in the greater San Antonio area

Project 19-040: quantify roles of ozone precursors on formation, evaluate chemical mechanism representations, and assess impacts of ozone precursor sources

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SAFS: characterize ozone formation in the greater San Antonio area

Project 19-040: quantify roles of ozone precursors on formation, evaluate chemical mechanism representations, and assess impacts of ozone precursor sources

Sites with peroxy radical measurements:

- University of Texas San Antonio (UTSA)
- Floresville
- Lake Corpus Christi (Corpus)

Additional site:

- Traveler's World

SAFS Measurements

Species	Instrument/Technique	AML	BU/UH/RU
NO	Thermo 42-i TL chemiluminescence	✔	✔
NO_2	AQD with photolytic converter		✔
CO	Cavity Ring Down Spectroscopy		✔
Isoprene, HCHO, CH_3CHO, Acetone, Benzene, Monoterpenes, Toluene	PTR-MS Ionicon	✔	✔
NO_2, CH_4, C_2H_6, CO, H_2O_2	QC-TILDAS	✔	✔
O_3	UV Absorption	✔	✔
C_2H_4, C_3H_6, cis-2-Butene, trans-2-Butene, 1-Pentene	Whole Air Sampling		✔
Various SVOCs / acids	Iodide CIMS	✔	
RO_2+HO_2 (XO_2)	Drexel ECHAMP	✔	
Speciated aerosols	Aerosol mass spectrometer	✔	✔

Aerodyne Mobile Lab (AML) measurements were taken at three sites. Baylor U. / U. of Houston / Rice U. (BU/UH/RU) Measurements were taken at Traveler's World.

Science Questions & Project Tasks

1. What is the dependence of ozone formation in the greater San Antonio area on concentrations of NOx, VOCs, and “ROx” radical precursors? Where is ozone formation “NOx-limited” or “VOC-limited”?

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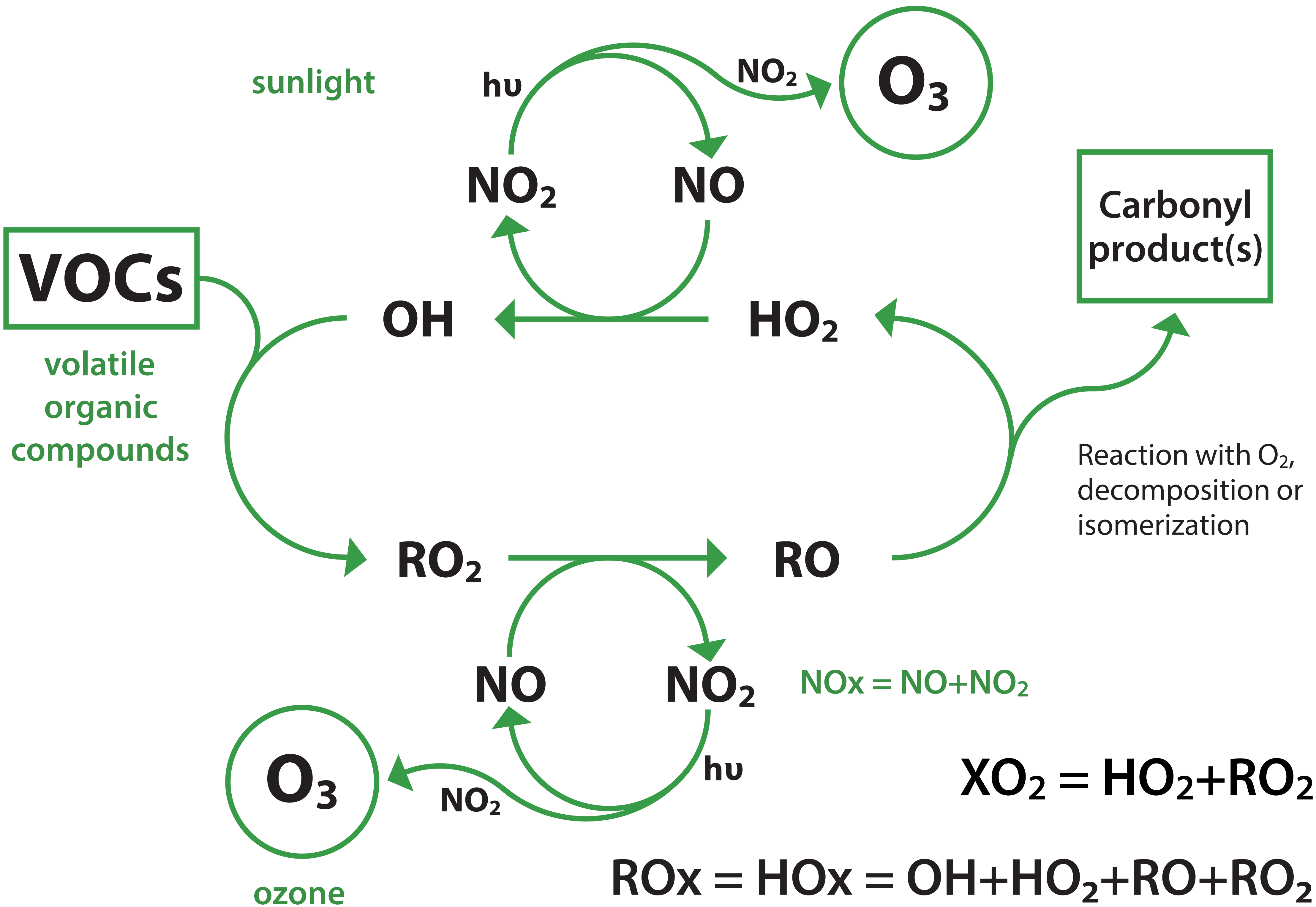
Quantify the dependence of the ozone production rate on the concentrations of NOx, VOCs, and other measurements at the three SAFS sites where peroxy radical concentrations were measured.

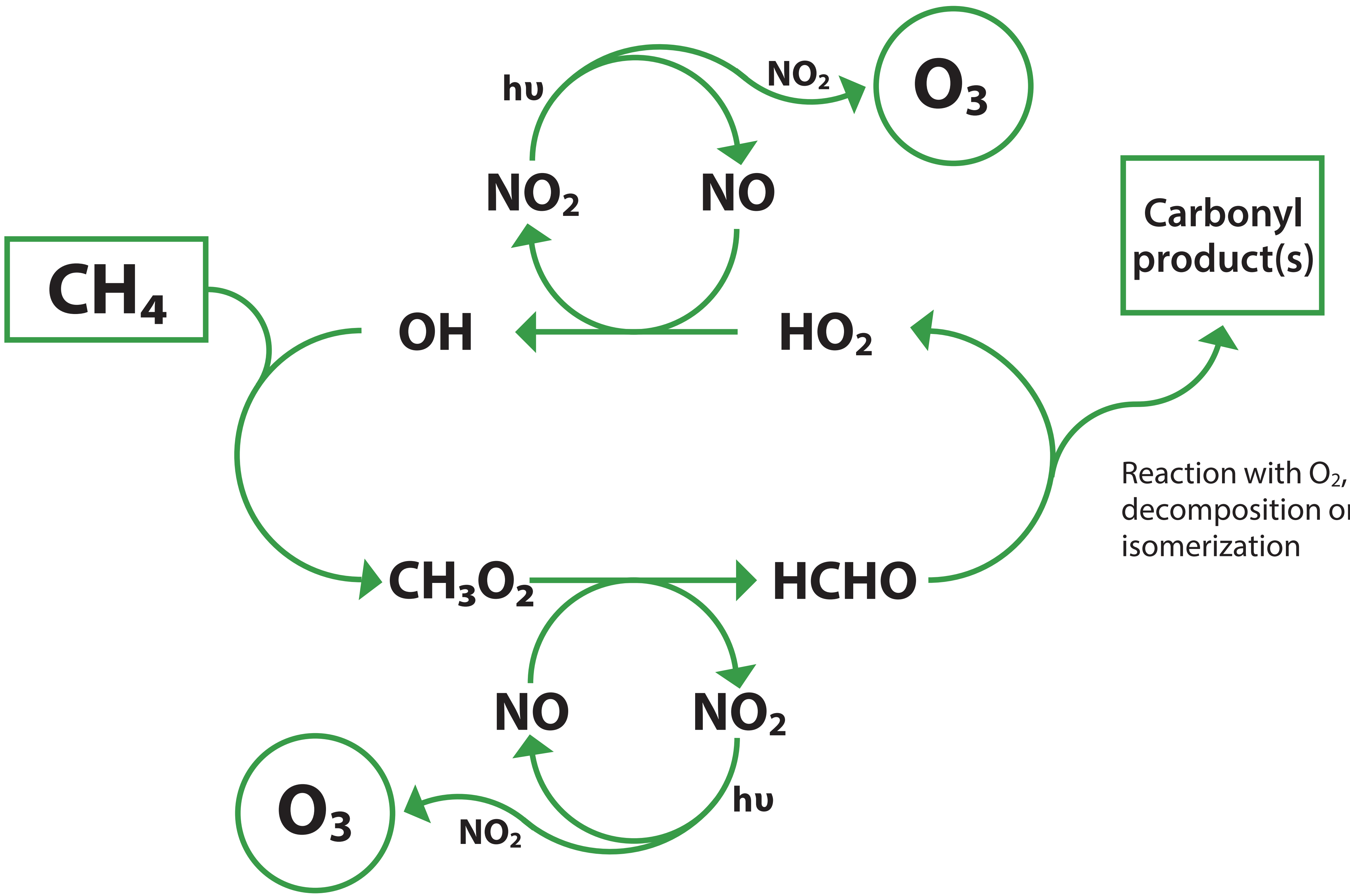
Constituents of Ozone Formation



modified from WHO, 2008

Example: Ozone Production Rate

$$P(O_3) = k_{HO_2+NO}[HO_2][NO] + \sum k_{CH_3O_2+NO}[CH_3O_2][NO]$$

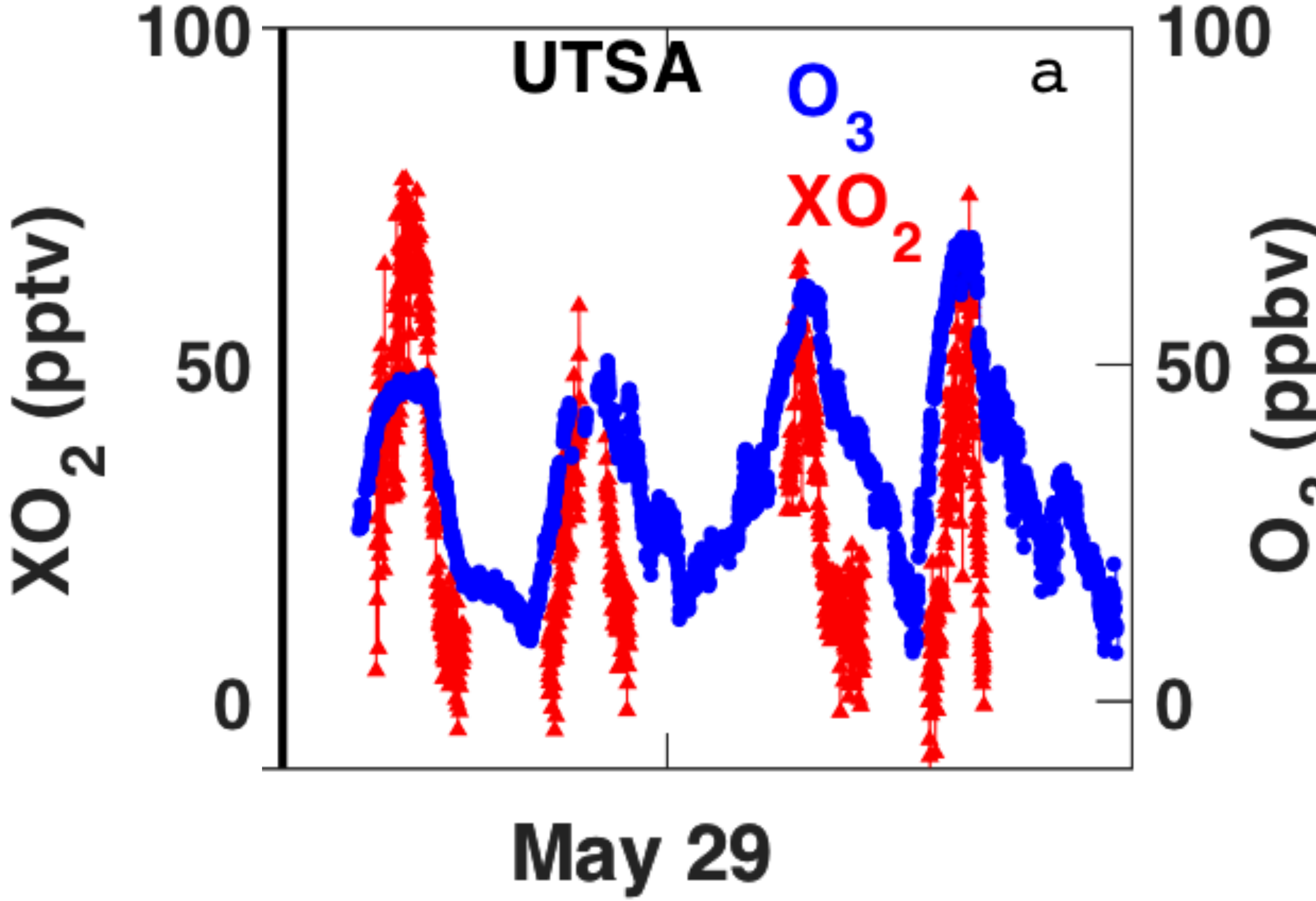


modified from WHO, 2008

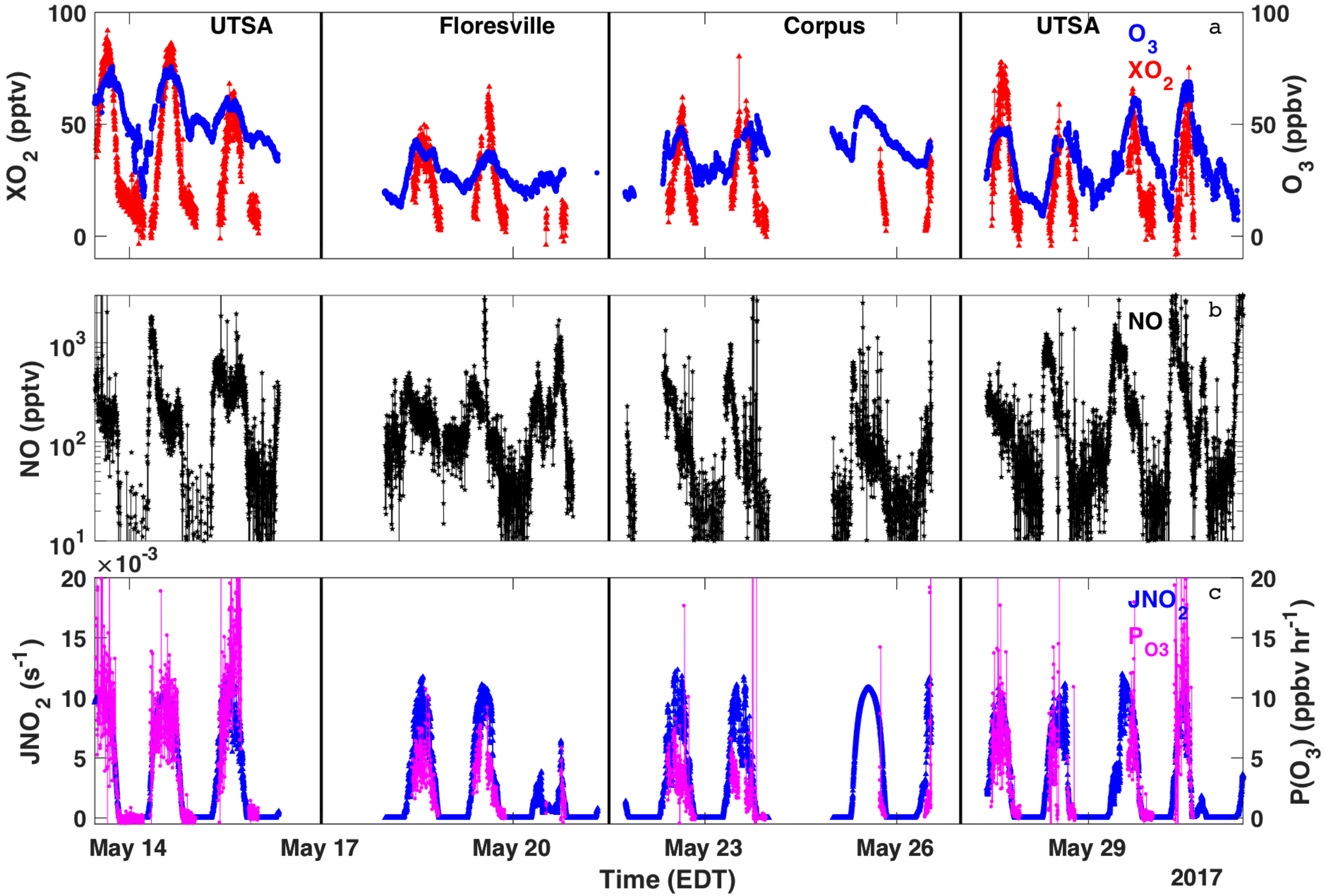
SAFS Measurements

15-minute averaging for all measurements

Observations at each site occurred in sequence



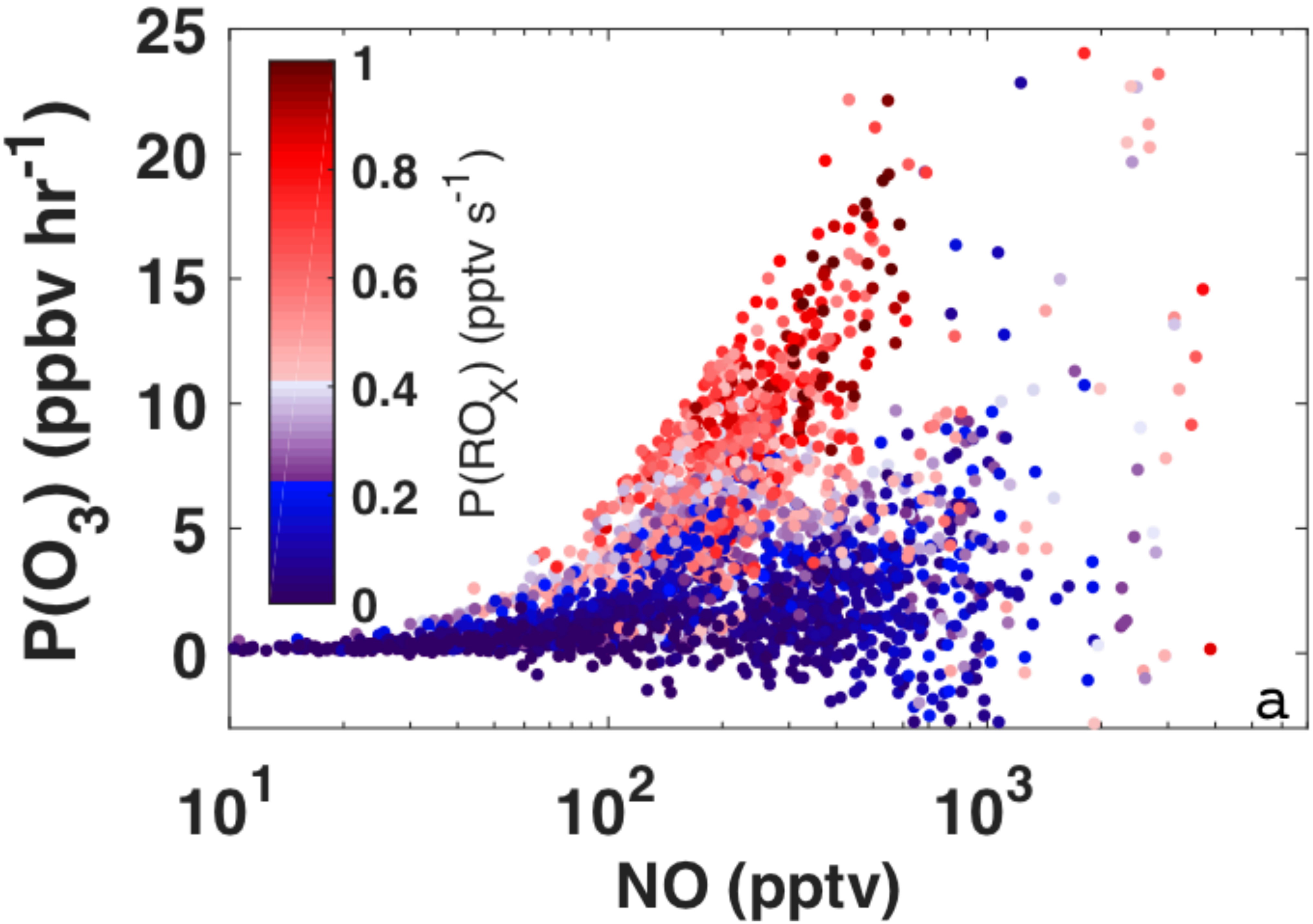
SAFS Measurements



Ozone Formation Dependence on NO

Daytime (7:00 - 20:00) observations from UTSA, Floresville, and Corpus sites.

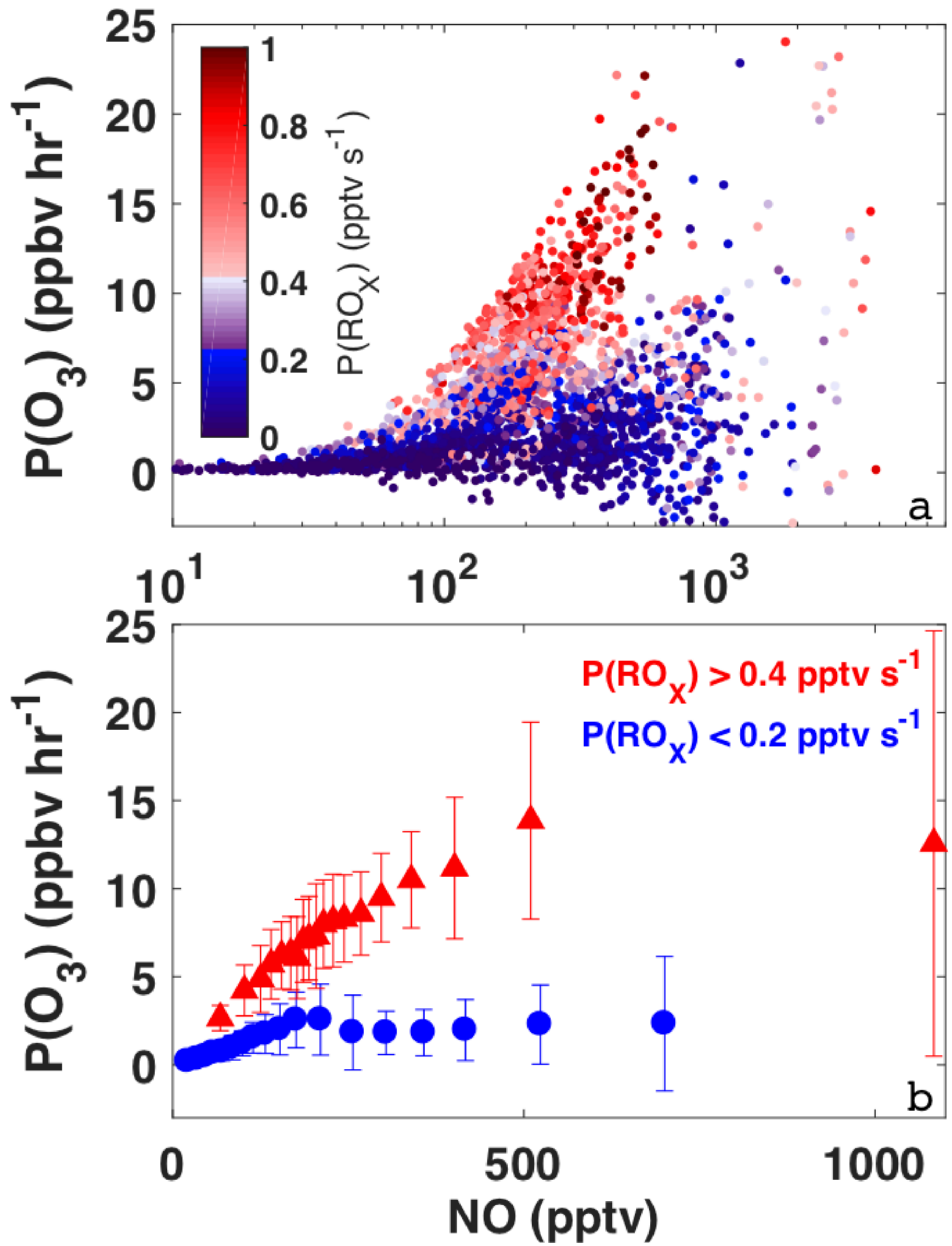
$P(O_3)$ was typically less than 15 ppb/hr.



Ozone Formation Dependence on NO

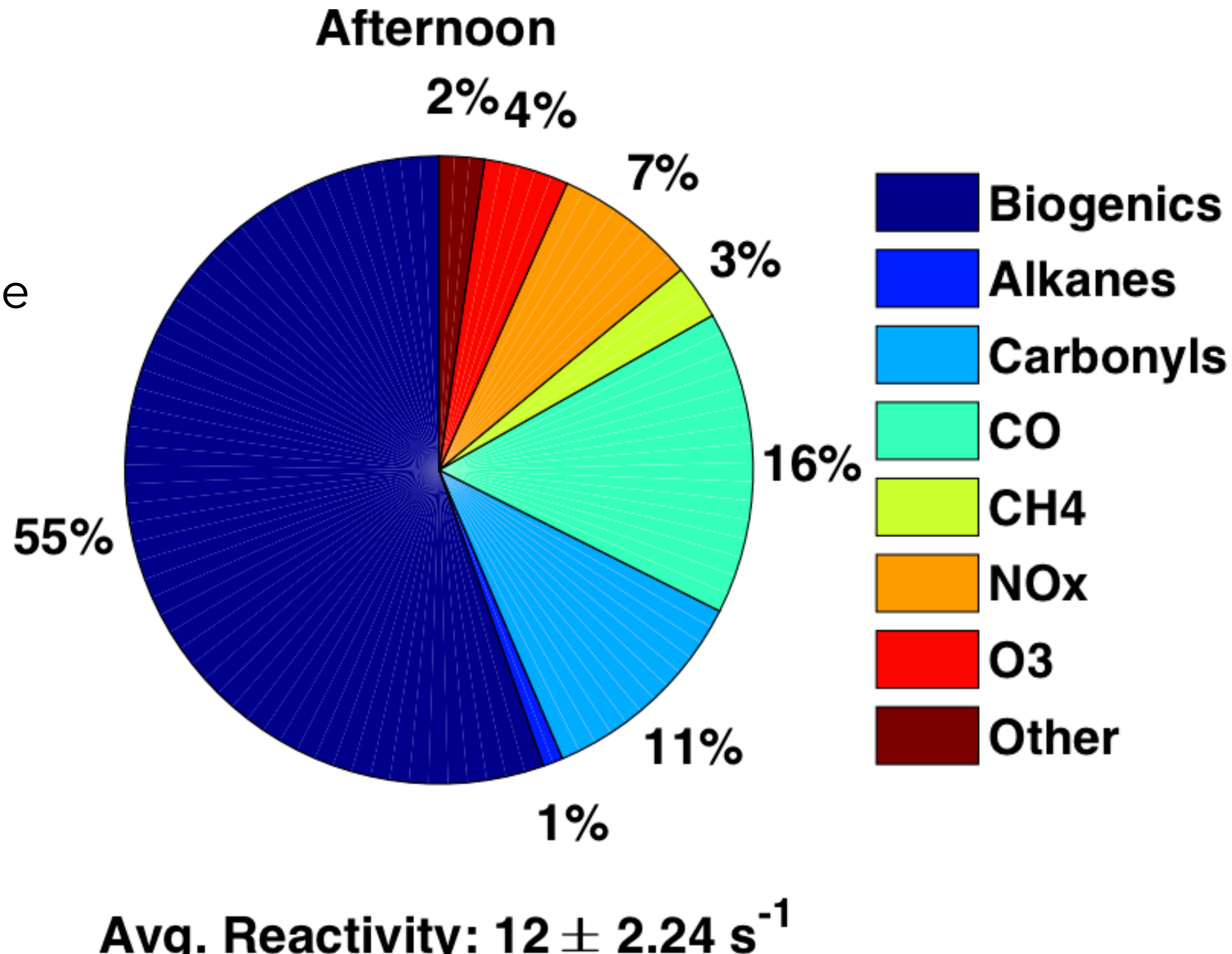
Higher P(ROx) values are associated with higher $P(O_3)$ for a given NO mixing ratio.

The turnover value for low P(ROx) is closer to 200 ppt NO whereas it is greater than 500 ppt for higher P(ROx).



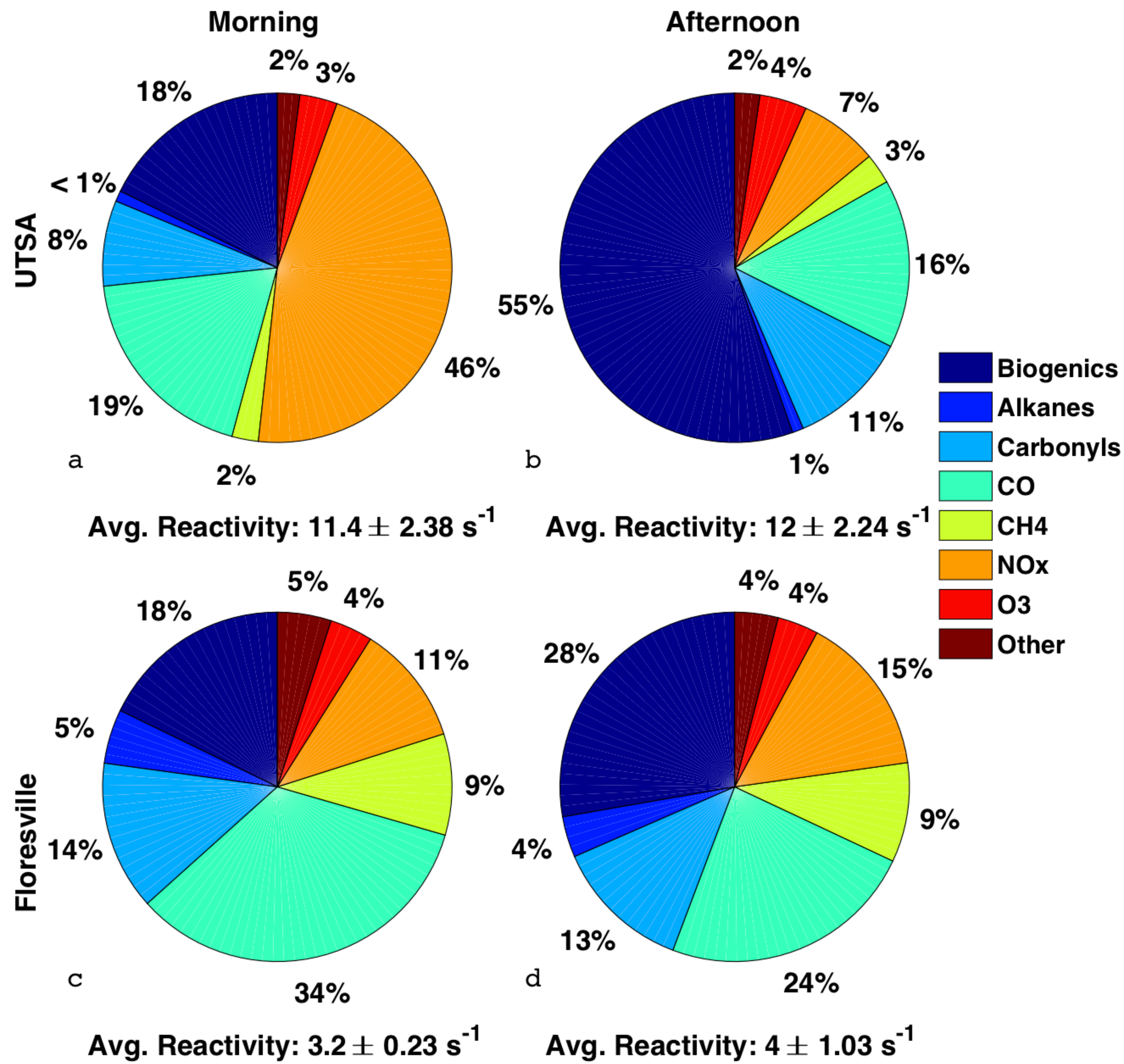
OH Reactivity at UTSA

NOx-limited conditions at this surface site suggest that VOC controls are not the most effective approach to reducing ozone.



OH Reactivity at UTSA & Floresville

Of the VOCs, biogenics contribute a large portion of the OH reactivity most of the time.



Science Questions & Project Tasks

2. Do current chemical mechanisms used in zero-dimensional (0-D) models correctly predict radical concentrations?

Science Questions & Project Tasks

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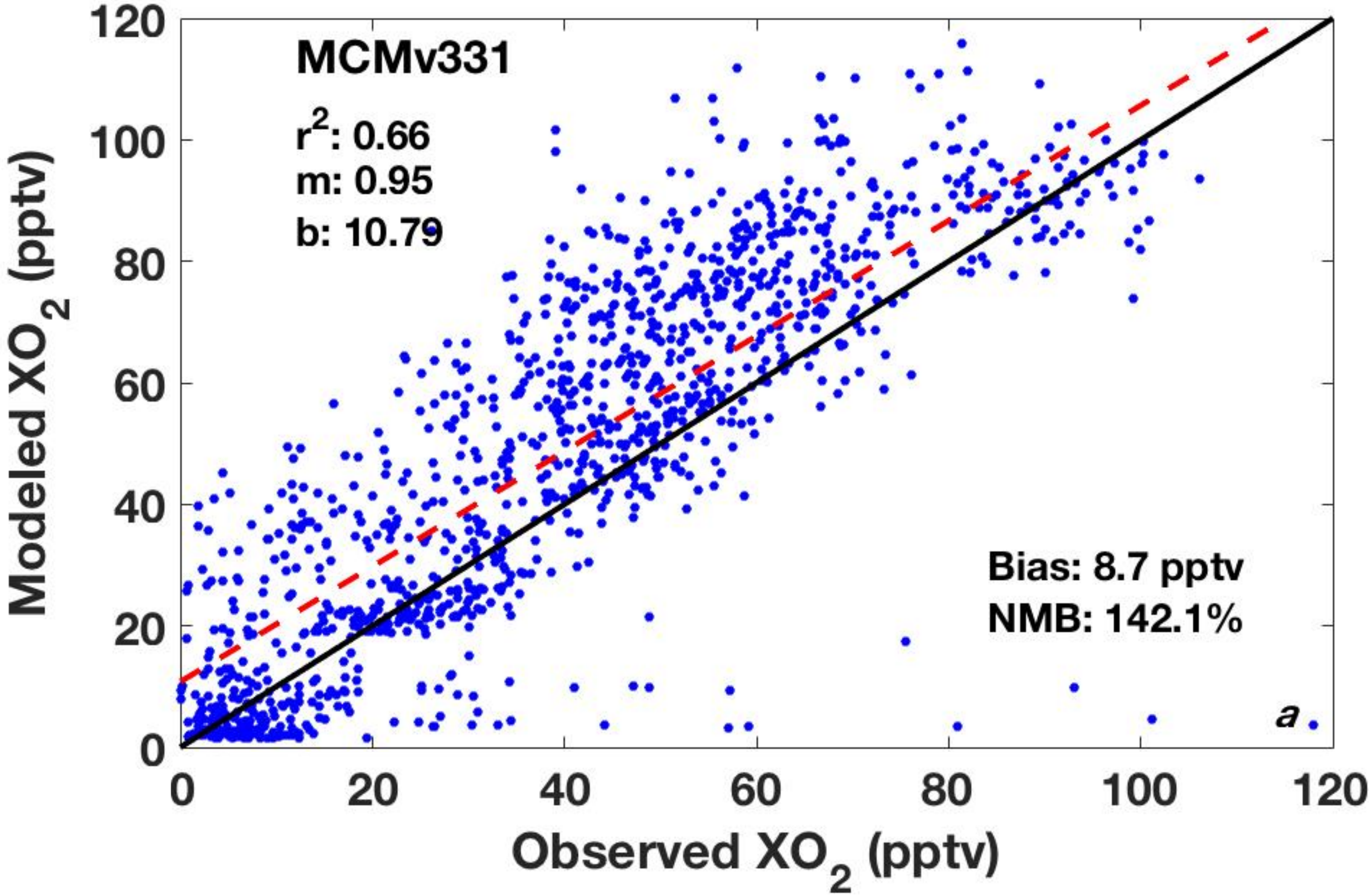
Conduct 0-D photochemical modeling constrained by the SAFS datasets with several model chemical mechanisms for four SAFS measurement sites, spanning a large range of NOx values.

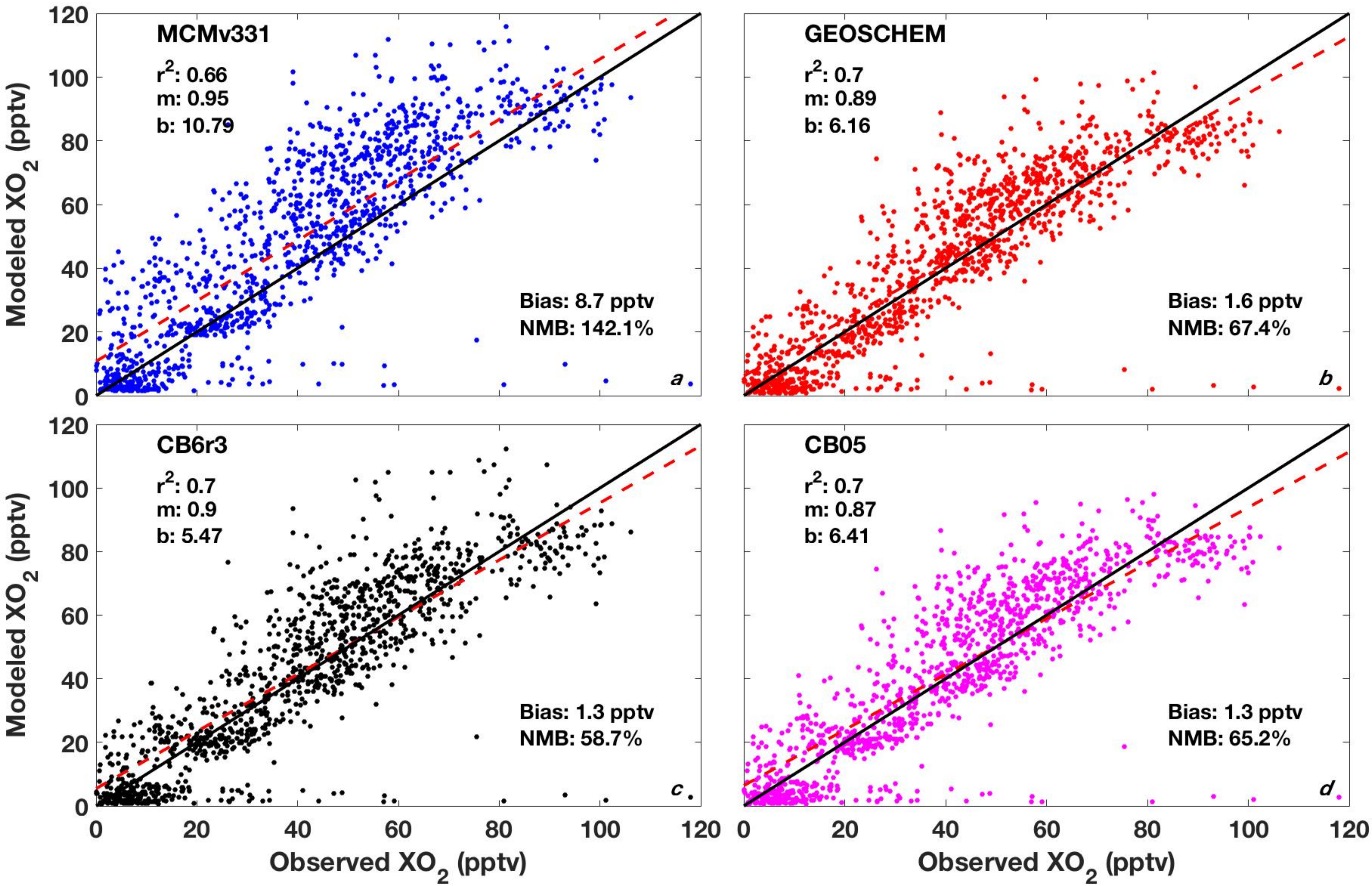
Chemical Mechanism Evaluation

Total peroxy radical = $XO_2 = HO_2 + RO_2$

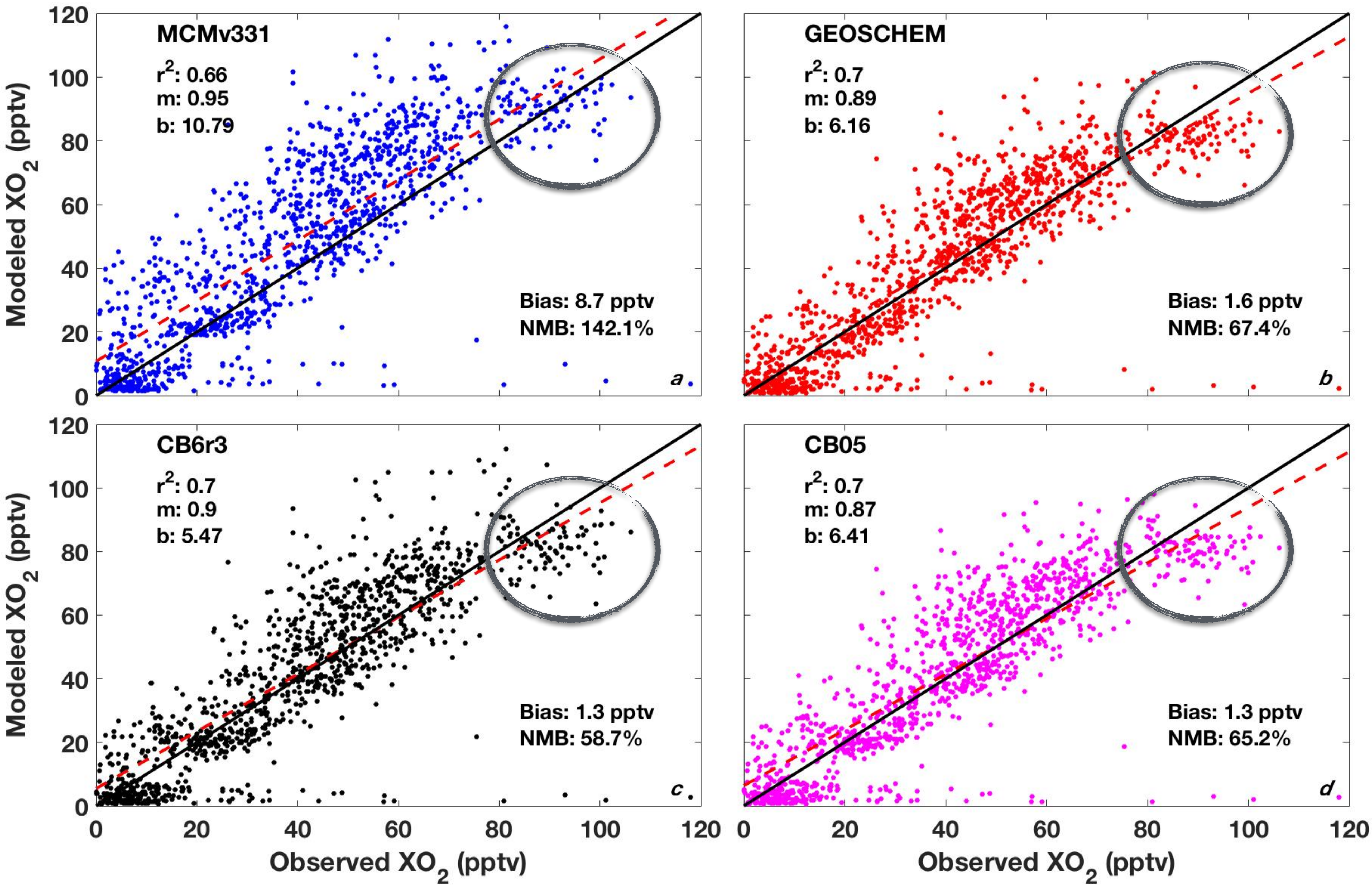
Modeling in the Framework for 0-D Atmospheric Modeling (F0AM) with the Master Chemical Mechanism compared reasonably with the observed values above 20 pptv at UTSA & Floresville.



Chemical Mechanism Evaluation



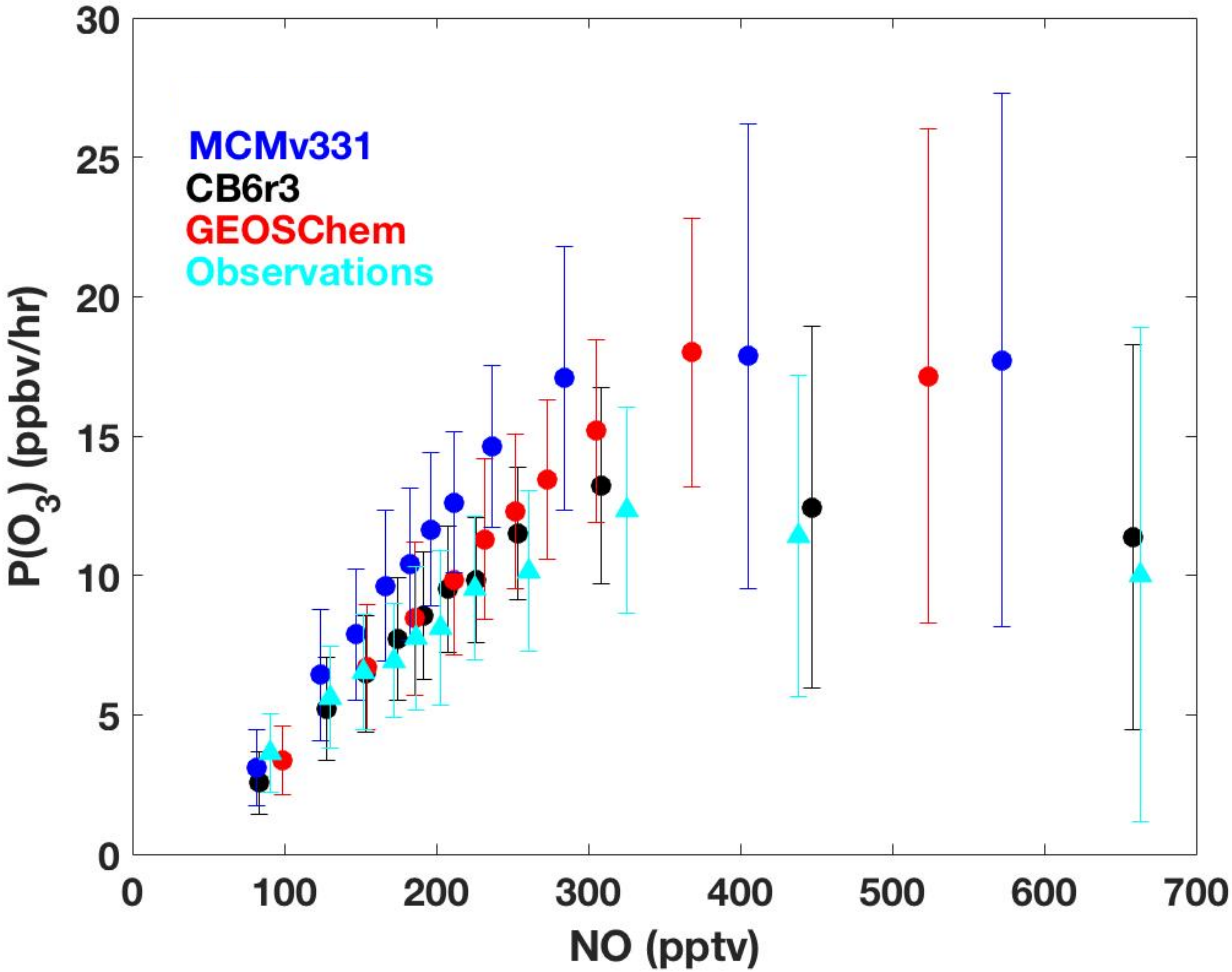
Chemical Mechanism Evaluation



Responsiveness of Modeled $P(O_3)$

Each mechanism captures the appropriate trend at UTSA.

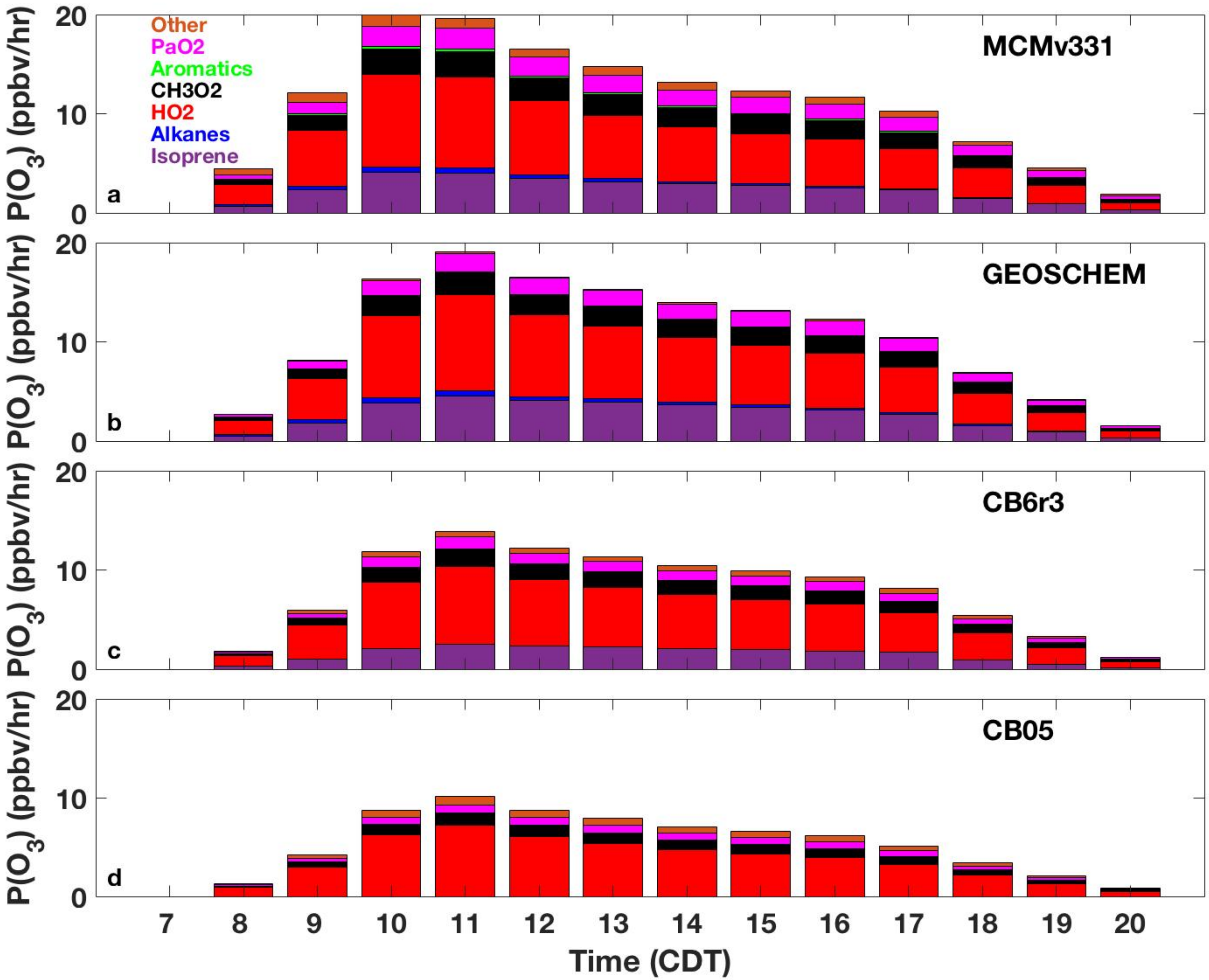
CB6r3 excels in representing the decrease observed above 330 ppt NO.



Diurnal $P(O_3)$ Contributions at UTSA

XO_2 constituents contribute to $P(O_3)$ differently throughout the day.

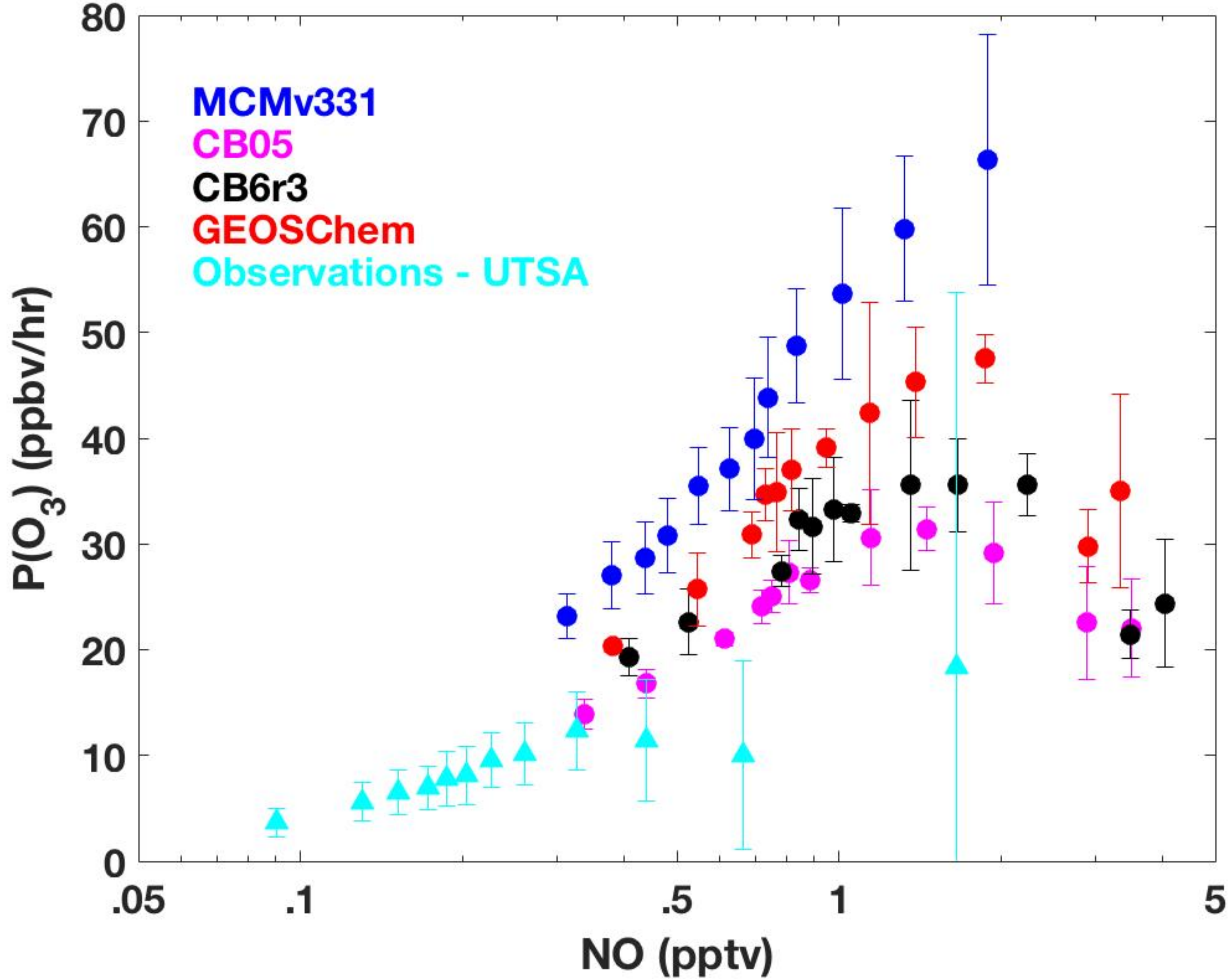
GEOS-Chem is most similar to MCM. CB6r3 has greater isoprene contributions than CB-05.



Model Responsiveness at Traveler's World

More VOC-limited behavior seems apparent at this downwind site at the surface.

MCM did not represent the turnover at 1.8 ppb as did the other mechanisms.



Science Questions & Project Tasks

3. What are the relative contributions of different emission sources to ozone concentrations in San Antonio?

Science Questions & Project Tasks

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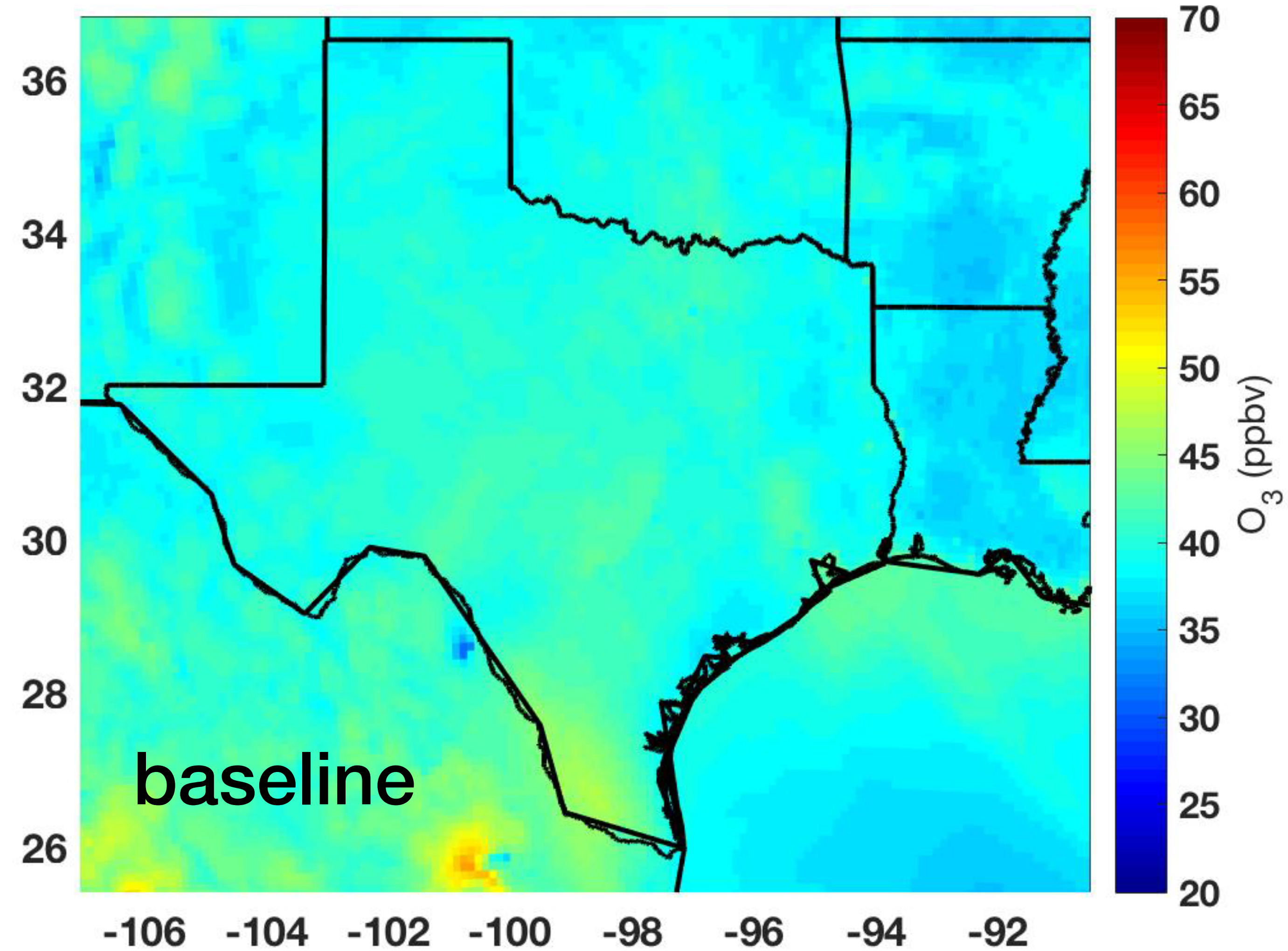
Apportion ozone concentrations to location-specific emission sources using 3-D air quality modeling with the instrumented Community Multiscale Air Quality model (CMAQ).

CMAQ Modeling

- *Meteorology:* Weather Research and Forecasting model
- *Emissions:* 2017 National Emissions Inventory, BEIS v.3.6.1
- *Resolution:* 12-km x 12-km horizontal, 35 layers
- *Chemistry:* CB6r3, aqueous chemistry in aero6
- *Aerosols:* thermodynamics, semivolatile primary organics
- *Domain:* continental US
- *Time:* May 2017



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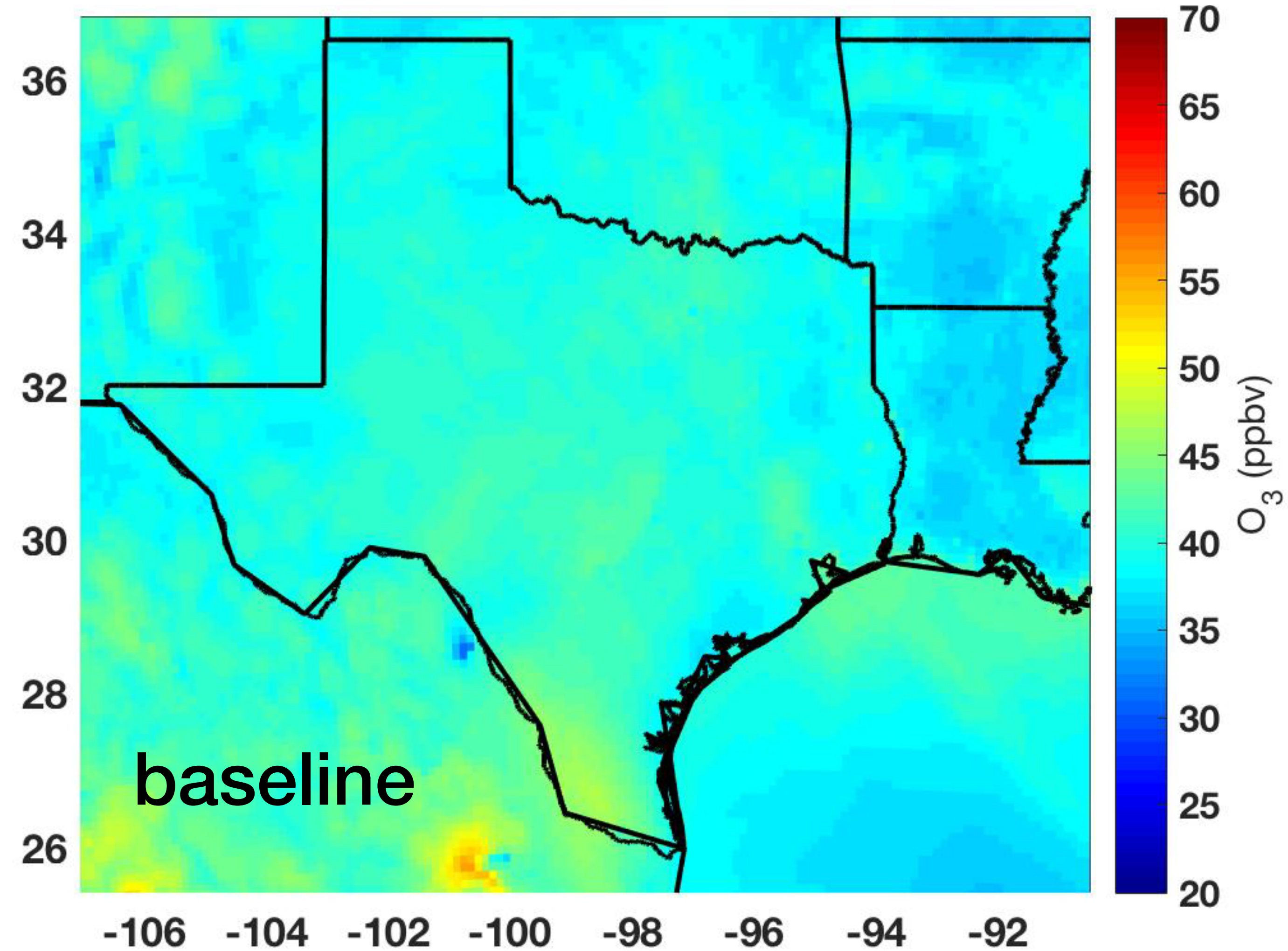
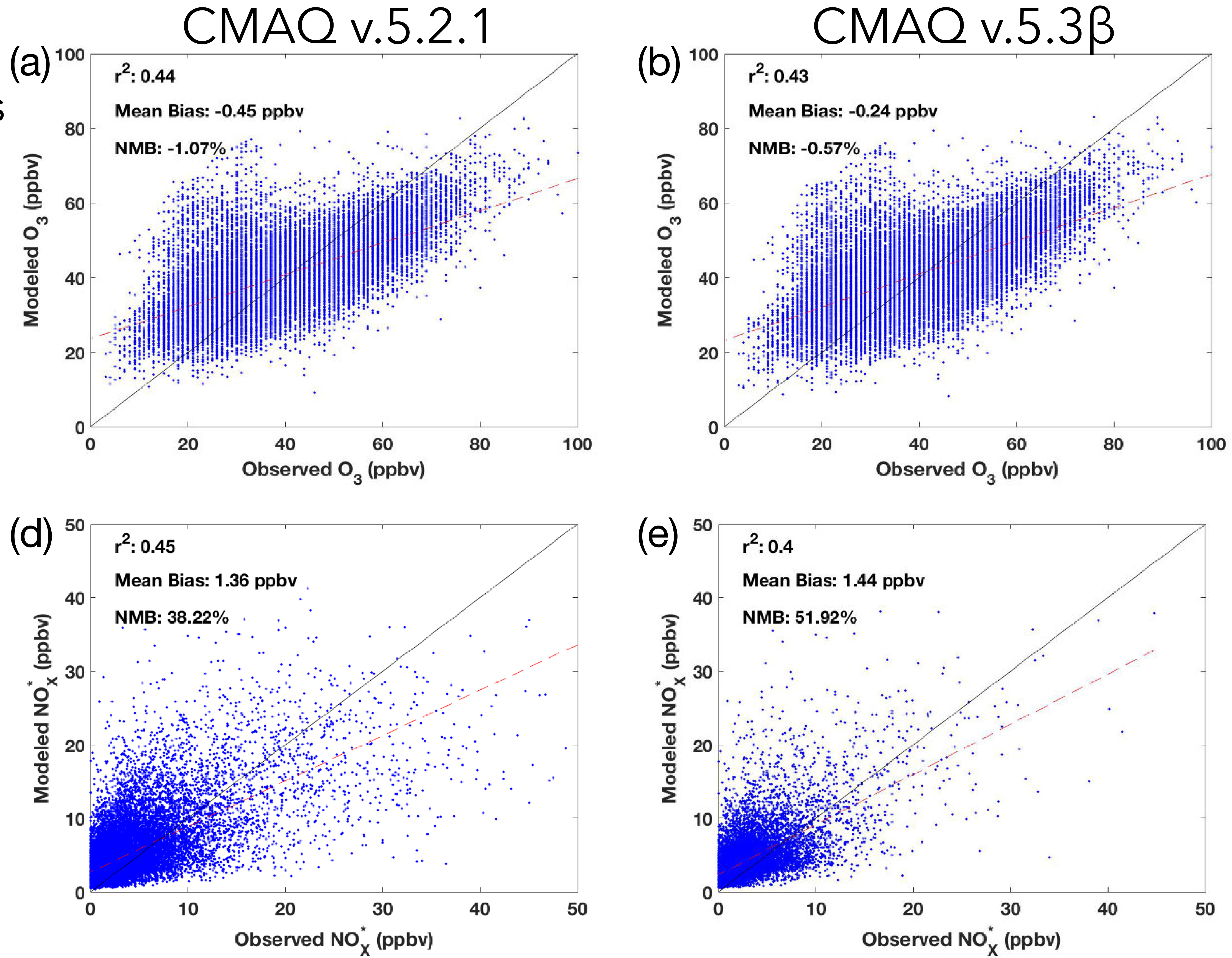
Model configurations

- CMAQ v.5.2.1
- CMAQ v.5.3β
- CMAQ v.5.3β with 30% area NOx emissions reduction (30NOx)



Evaluation of O_3 and NOx*

O_3 sites are all AQS sites in Texas while NOx* exclude roadside monitors.

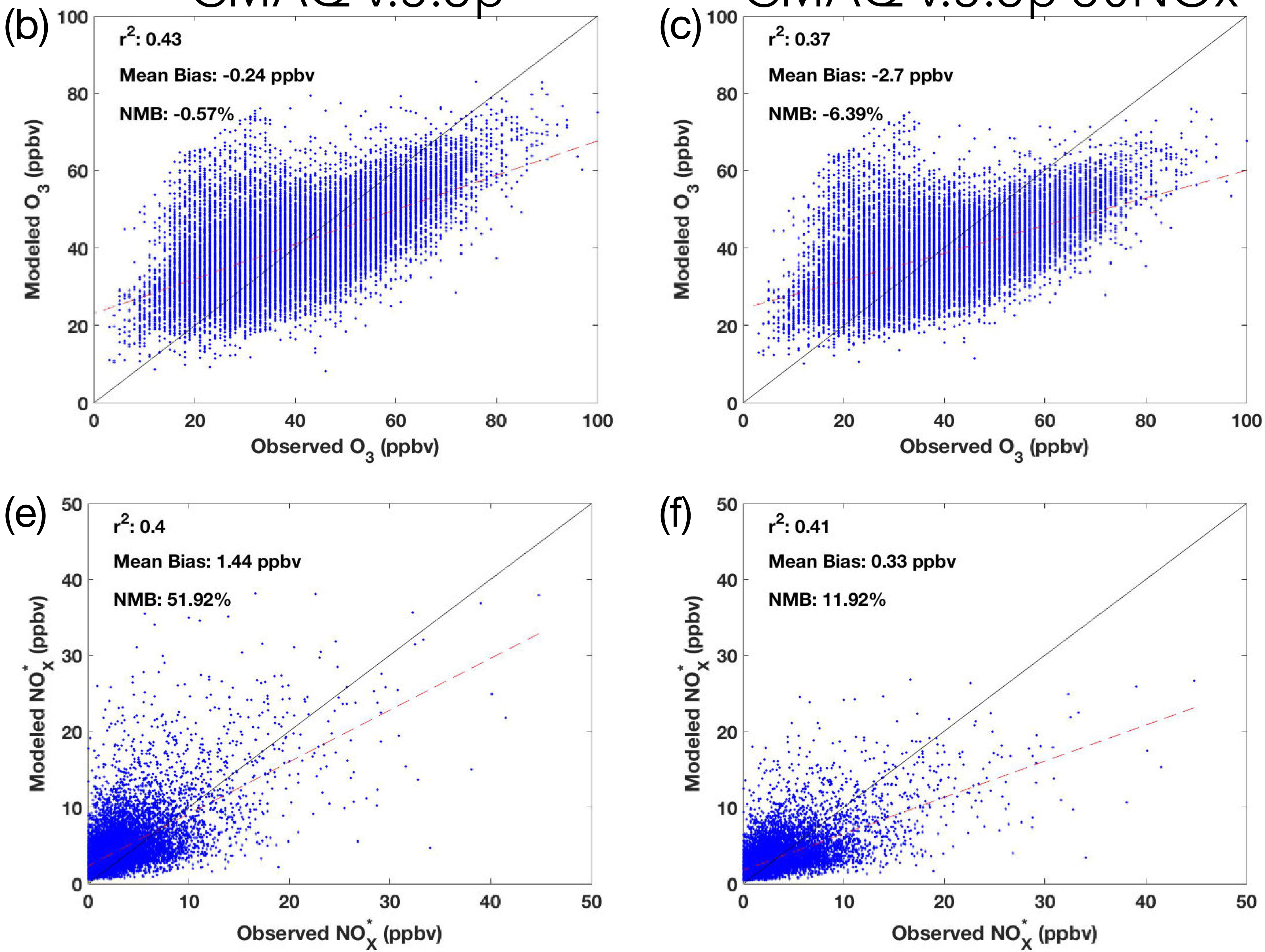


Observed NOx* is compared to modeled NO, NO_2, and organic nitrates.

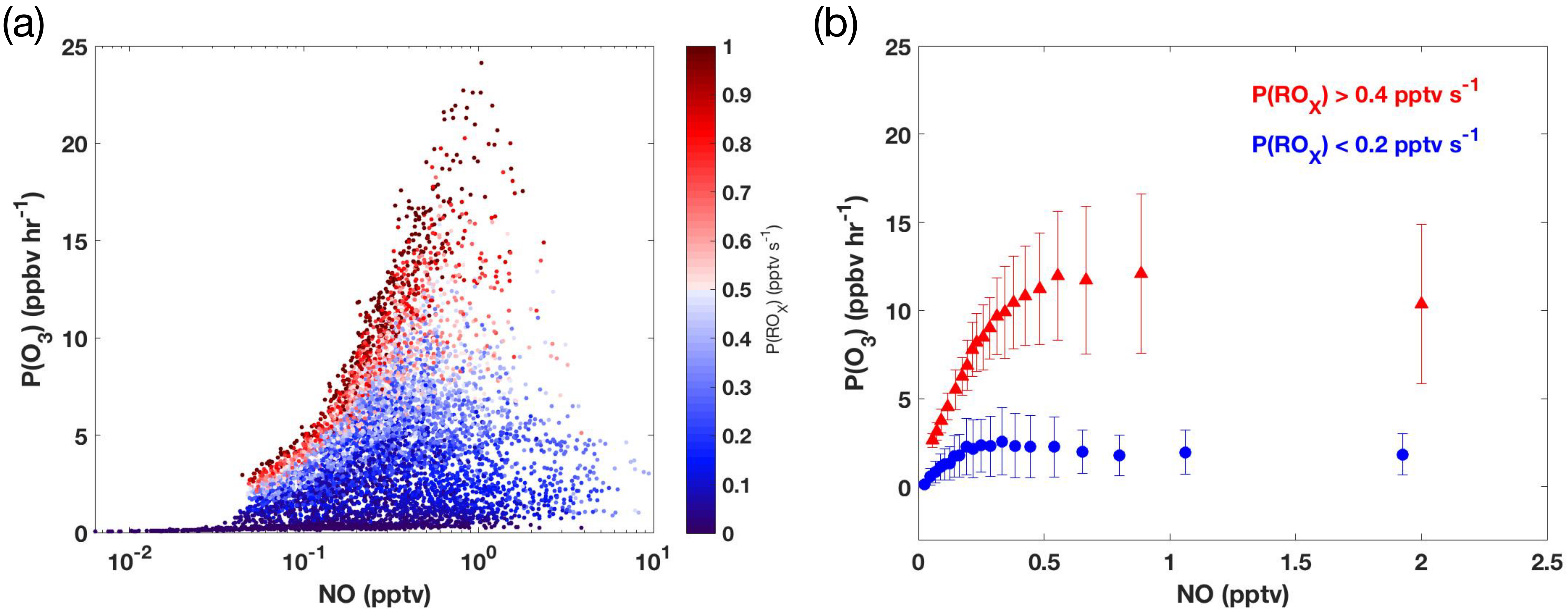
Evaluation of O_3 and NOx*

CMAQ v.5.3β

CMAQ v.5.3β 30NOx



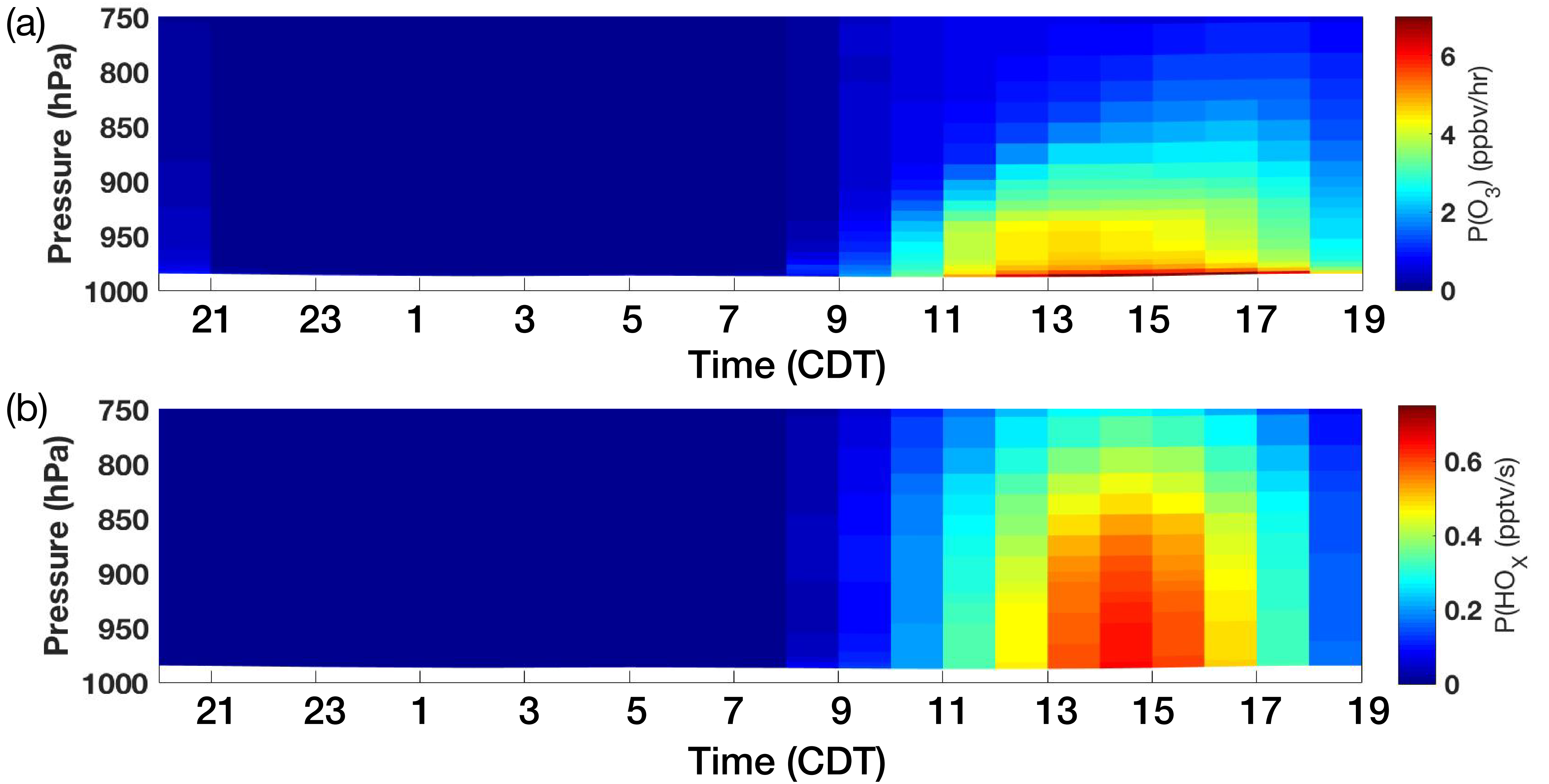
Representativeness of $P(O_3)$



Hourly average $P(O_3)$ in San Antonio compared to NO mixing ratios during 07:00-20:00 for the 30NOx case.

The turnover point for the low P(ROx) is slightly higher than observed while the decline in $P(O_3)$ is greater than few observations suggest.

Vertical Distribution of Modeled Production



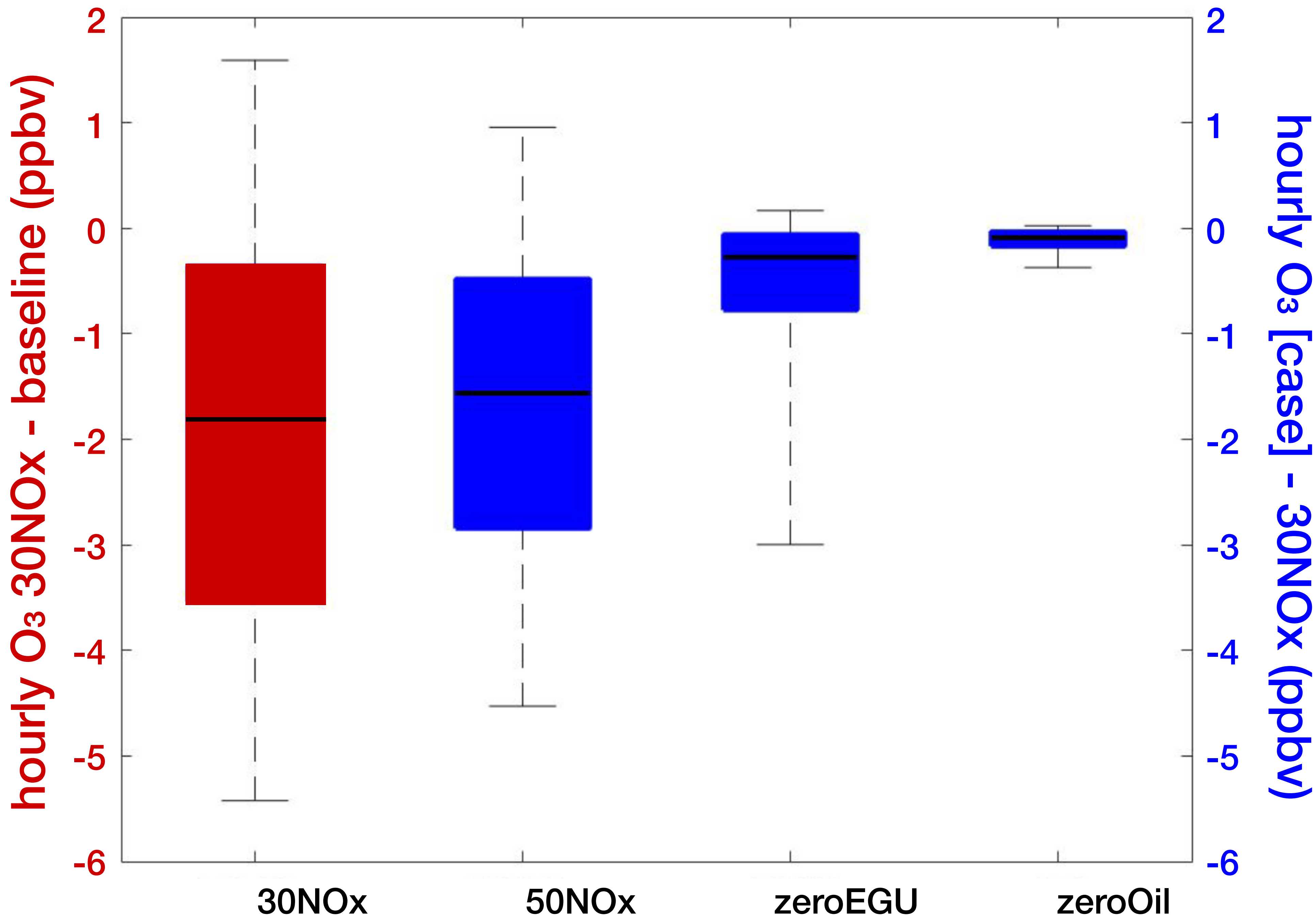
Vertical distributions of P(O3) from CMAQ suggest that surface measurements provide an indication of the highest value in the column at a given time.

Source Influence Assessment

Name	Species	Region	Source	Reduction
30NOx	NO, NO_2	Domain	area sources	30%
50NOx	NO, NO_2	Domain	area sources	50%
zeroEGU	all | NO, NO_2	Texas except San Antonio	EGU point sources | area sources	100% | 30%
zeroOil	all | NO, NO_2	Texas except San Antonio	oil & gas point sources | area sources	100% | 30%

A new feature implemented in CMAQ v.5.3 allows scaling of select emissions by species with spatial masks. Ben Murphy (EPA) provided early access. The feature was tested for accuracy before these sensitivity analyses were performed.

Source Influence Assessment



Hourly average O_3 differences in San Antonio between cases during 07:00-20:00 show most significant influences on ozone from area NOx sources of those tested.

Takeaways

- *quantify roles of ozone precursors on formation:* mainly observed NOx-limited regimes at the surface

- *evaluate chemical mechanism representations:* reasonable representation of ozone productivity responses to NO and P(ROx) compared to observations

- *assess impacts of ozone precursor sources:* regional modeling suggests area NOx influences ozone formation most substantially

Future Work

- CMAQ v.5.3 will have an Integrated Source Apportionment Model when it is released. Application of this instrumented model would allow spatially specific assessment of source impacts on San Antonio ozone.

- Assessment of the vertical distribution of $P(O_3)$, especially with plumes from biomass burning passing over a city, would enhance understanding of how surface-based measurements inform ozone production.

Acknowledgements

- Financial support from Texas AQRP under Project 19-040
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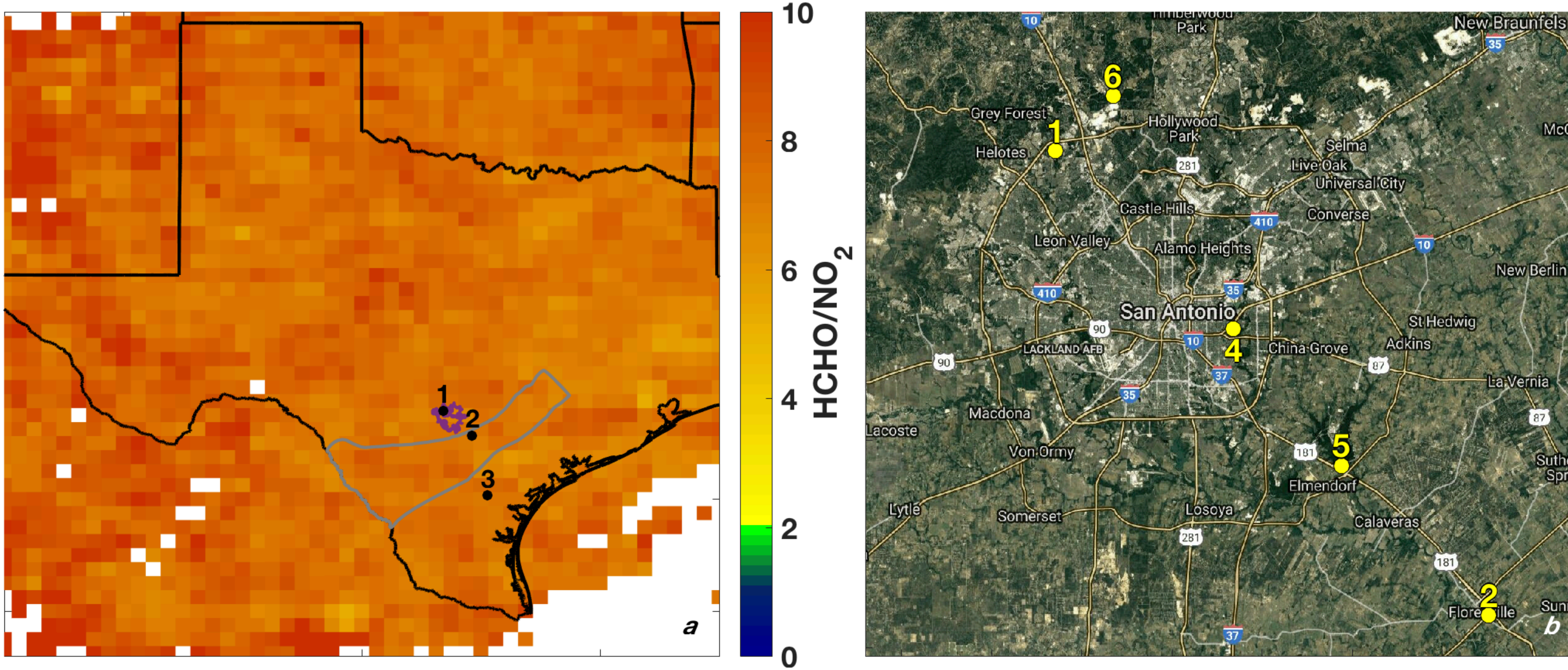
- Kirk Baker, U.S. EPA OAQPS for CMAQ modeling platform
- Ben Murphy, U.S. EPA ORD for early access to CMAQ v. 5.3 with emissions scaling

Additional Slides

Satellite-based HCHO:NO_2 Ratio

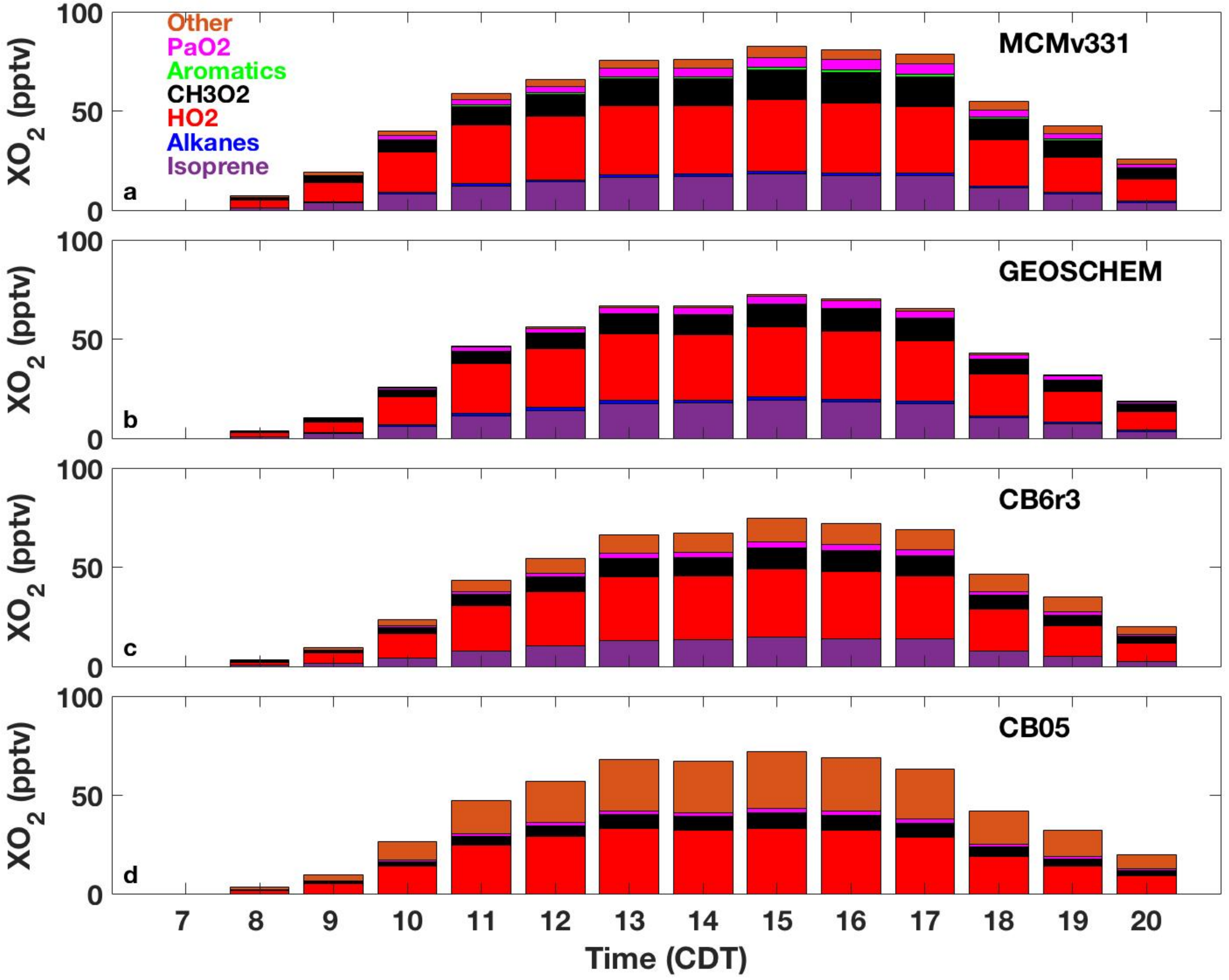


May - July 2017 temporal average HCHO:NO_2 suggests VOC-limited regime (>2).

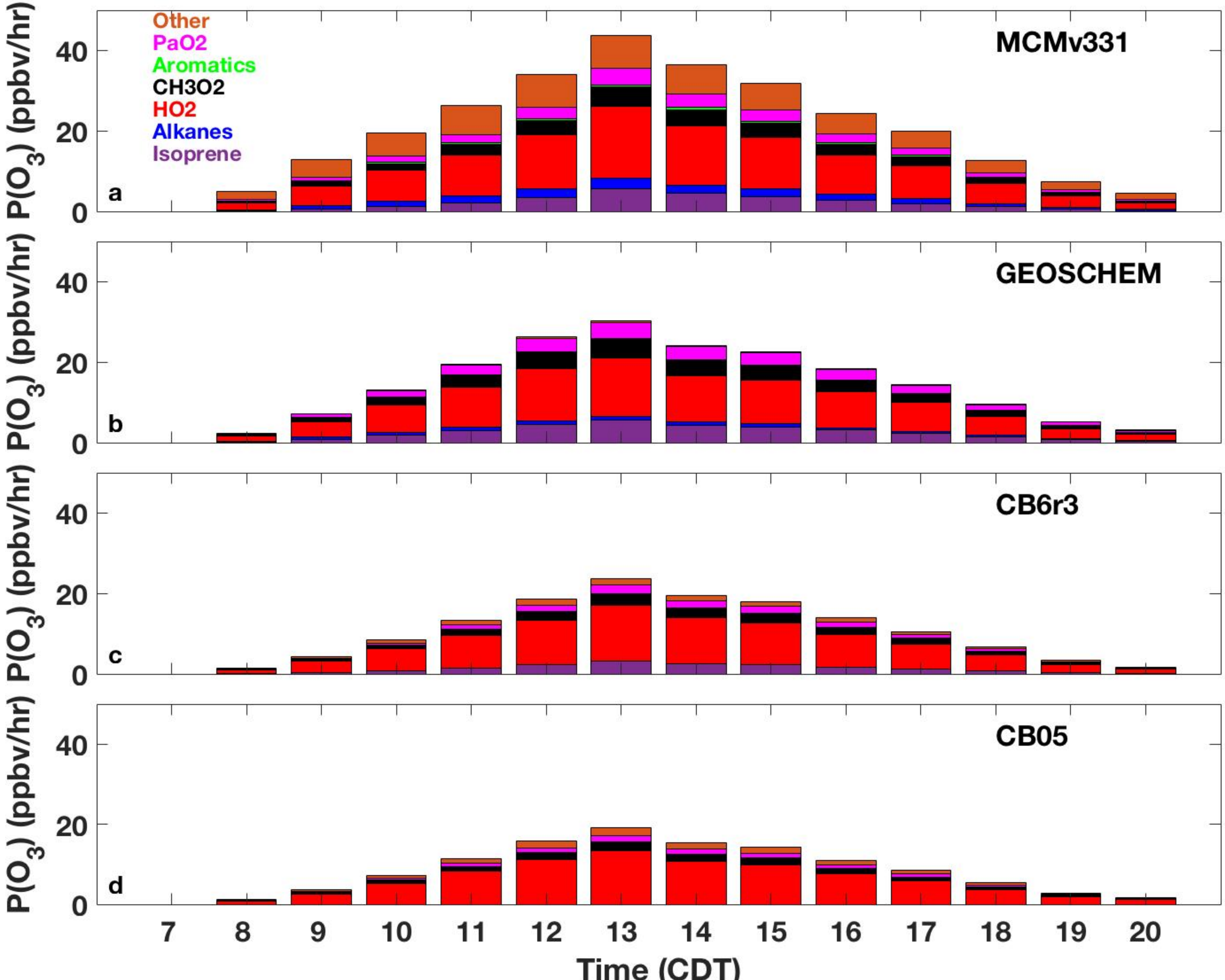
Mean Diurnal XO_2 Constituents

MCM & GEOS-Chem had similar constituents.

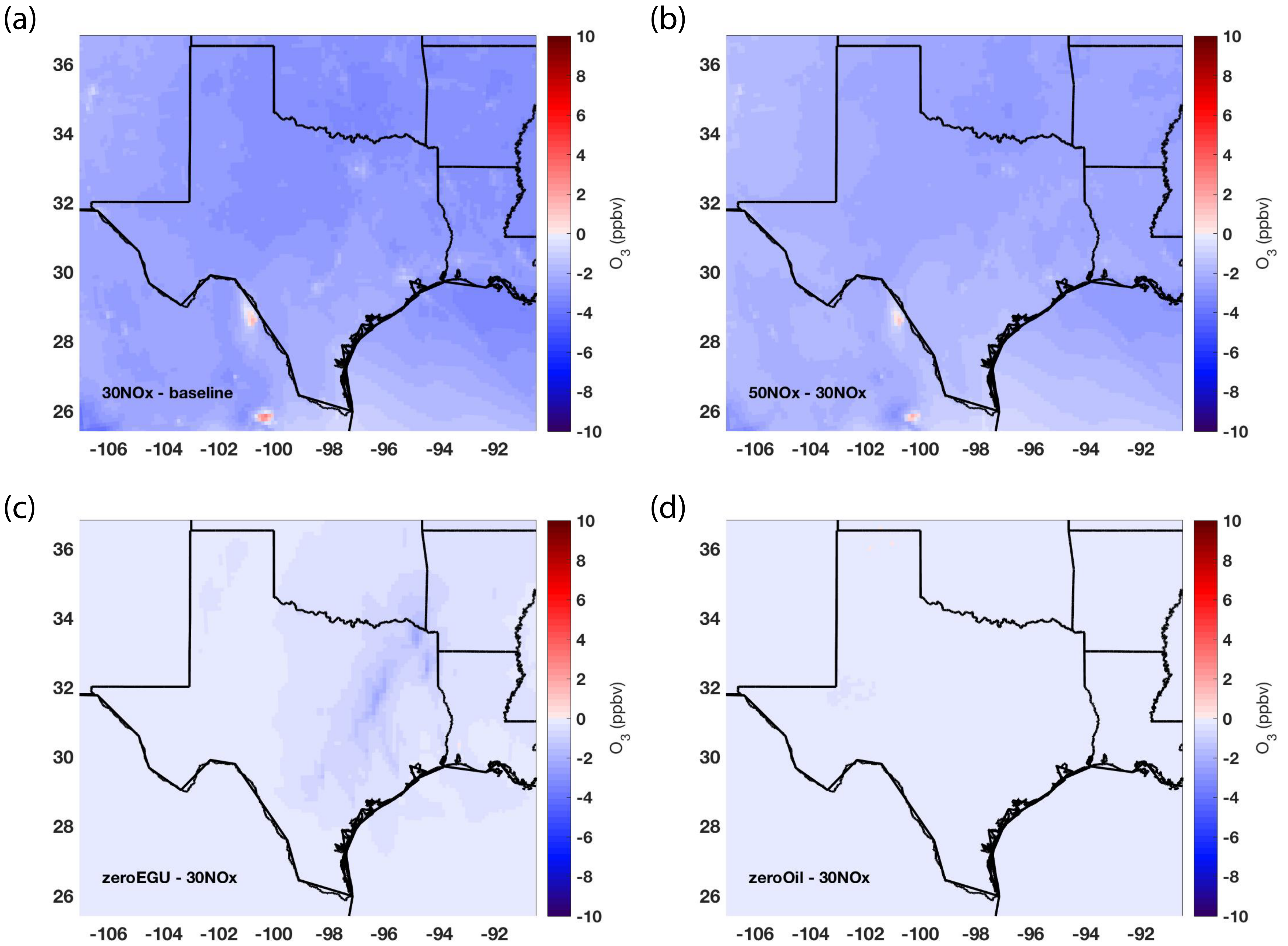
Although CB-05 and CB6r3 agree in total, the constituents differ significantly as expected.



Diurnal $P(O_3)$ Contributions at TW



Source Influence Assessment



Ozone Formation Dependence on NO

For lower P(ROx) values, the VOC reactivity impacts the responsiveness of $P(O_3)$ to NO. With very low reactivity, no impact of NO mixing ratios is evident while a turnover point is more obvious with mid-range VOC reactivities.