Ozone Production in New York State: Insight from Long Term Measurements

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Collaborators: NYS DEC operators, engineers, and scientists; ARA, Envair, and EPRI colleagues; Clarkson and URoch colleagues.

Statement of Problem

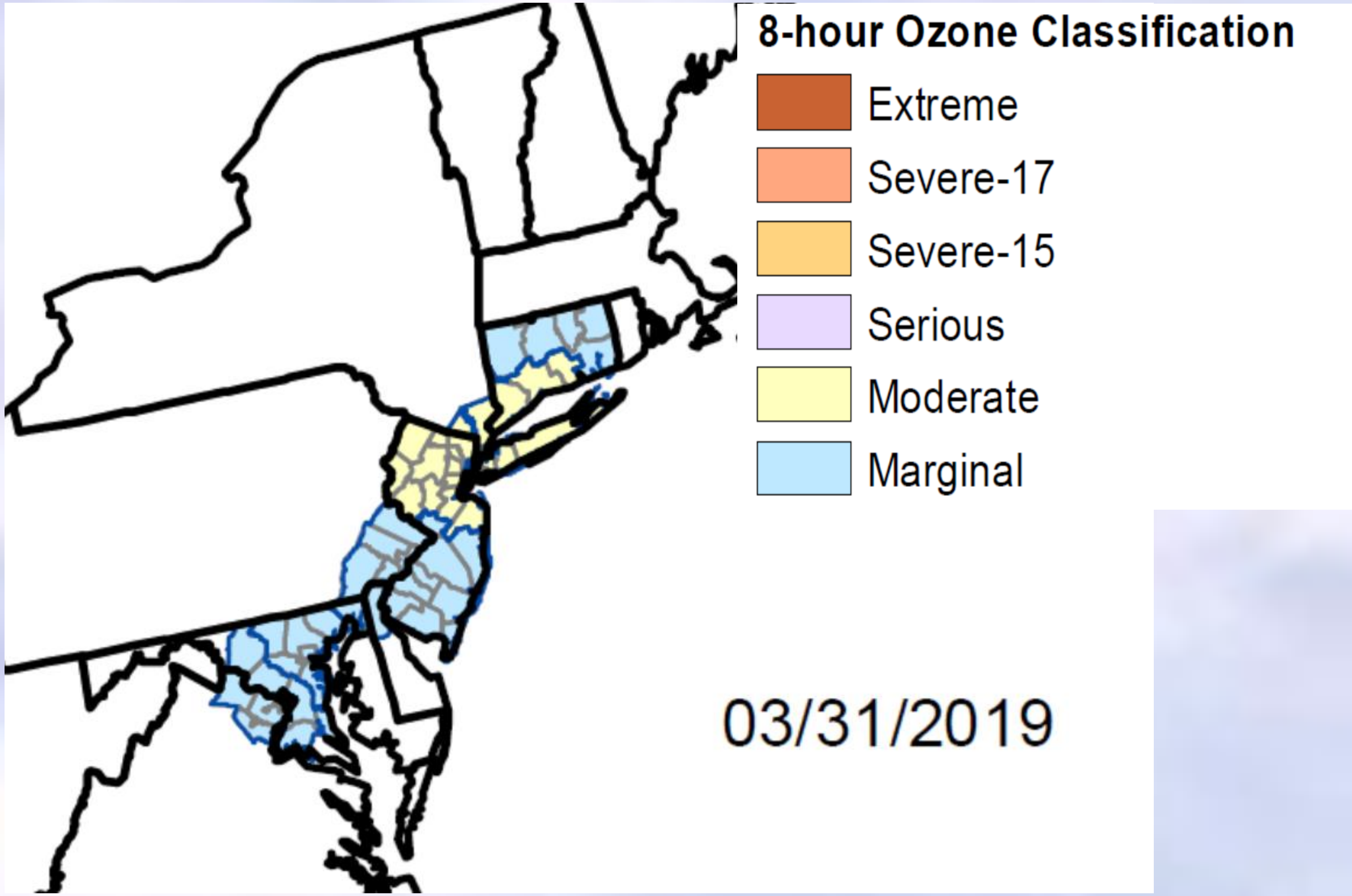
- US EPA sets the **Ozone** National Ambient Air Quality Standard (or **NAAQS**) – main purpose is protection of human health.

- **Ozone Nonattainment** – states with areas that fail to "meet the standard" must develop and execute a plan to reach attainment.

- This required air quality improvement invariably comes at a **significant cost** to states, businesses that emit pollutants, and citizens.

The Situation In New York State

- All of the New York City metro area (nine counties) are classified as moderate nonattainment.
- NYC Metro area has experienced from 4 to 19 ozone exceedances each year for the past 10 years (19 in 2018!).



Where does ozone come from?

- Ozone is a **secondary** pollutant – that is, it is **not** a directly emitted pollutant.
- Ozone is produced photochemically from **precursor gases** in combination with **sunlight**.
- It is ultimately transported downwind to less polluted areas.
- *The solution to pollution is dilution.*
- The problem remains for urban and near urban downwind areas – and needs to be addressed by lowering emissions of NOx and VOC precursor emissions.
- The **HOW** remains elusive!

Addressing the ozone exceedance problem

- We have known quite a bit about ozone formation chemistry for decades!
- **However**, there are complications and complex dependencies in the formation chemistry.
- The **Ozone Production Rate (OPR)** depends on the absolute NOx level, the NOx/VOC ratio, the type of VOC species, and more.
- As we move to lower NOx concentrations (a result of lower NOx emissions as just shown in previous presentations), the “complexities” come into play in greater measure.

Case in Point: Ozone Production Efficiency and Its Dependence on NOx Concentration

- We will restrict our consideration to regions and scenarios where there is net ozone production due to the levels of NOx and VOCs.

- This constraint is fully appropriate for regions that suffer “ozone pollution”, and specifically for all of New York State.

- The NOx-VOC sensitivity for the rural areas presented here, while different than the NYC metro area, points to where the NYC metro area may be headed in the future.

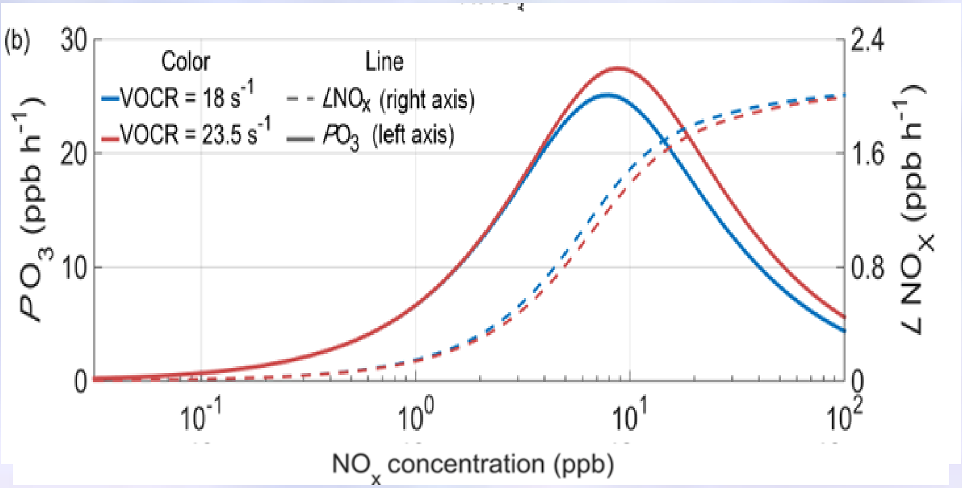
Factors that Drive Ozone Production

- In principle, these may be ways to "control" ozone.
- Sunlight (and warmth)
- Water vapor
- NOx ($NO+NO_2$) emissions – from power plants, combustion sources, motor vehicles, etc.
- Volatile Organic Carbon (VOC) emissions – industry, consumer products, trees and plants, etc.
- Ozone Production Efficiency

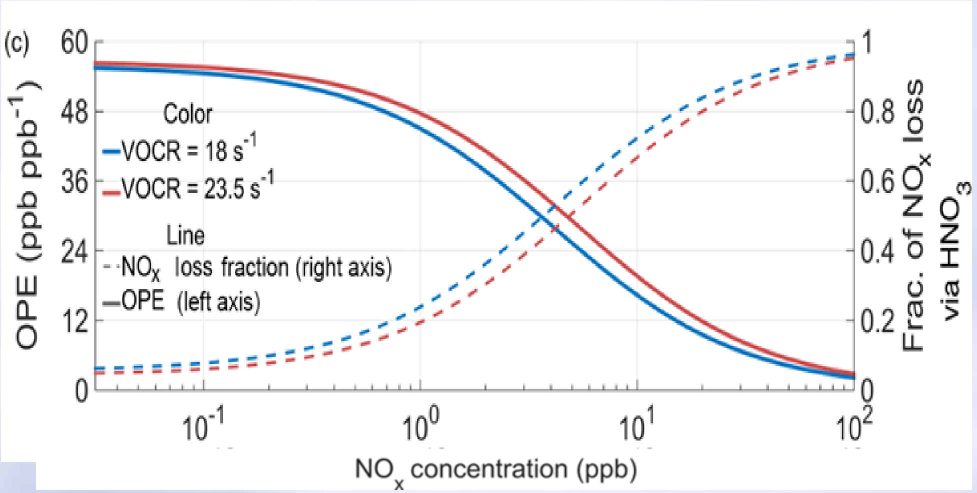
Ozone Production Rate (OPR) and Ozone Production Efficiency (OPE)

- Ozone Production Rate is directly calculated from concentrations of precursors (and environmental variables).
- Ozone Production Efficiency describes how many **ozone molecules** are produced for each **NOx molecule** in the system (the number of ozone molecules produced for each NOx removed from the system).
- Each of these measures (OPR and OPE) depend strongly on the NOx concentration in the system.

Ozone Production Rate



Ozone Production Efficiency



- Inverted "U" shape for OPR vs. [NOx]
- At low [NOx], low OPR since OPR ~ [NOx]
- At high [NOx], low OPR since OPE low
- At typical [VOC], OPR peaks ≈ 1-10 ppbv

Romer et al. ACP, 2018

Using Observations to Constrain OPE

- Recall that OPE is the number of ozone molecules produced for each NOx removed from the system.
- To make this quantitative, consider NOx (directly emitted precursor), NO_y (all forms of oxidized nitrogen), and $NO_z = NO_y – NO_x$ = oxidation products of NO_x precursors (also equals NO_x removed by oxidation).
- Empirically then
  - **$OPE = \Delta O_3/\Delta NO_z$**
- This is the slope of a linear regression line in a plot of O_3 (y-axis) versus NO_z (x-axis).
- The y-intercept of the plot gives a measure of the background O_3.

More about OPE

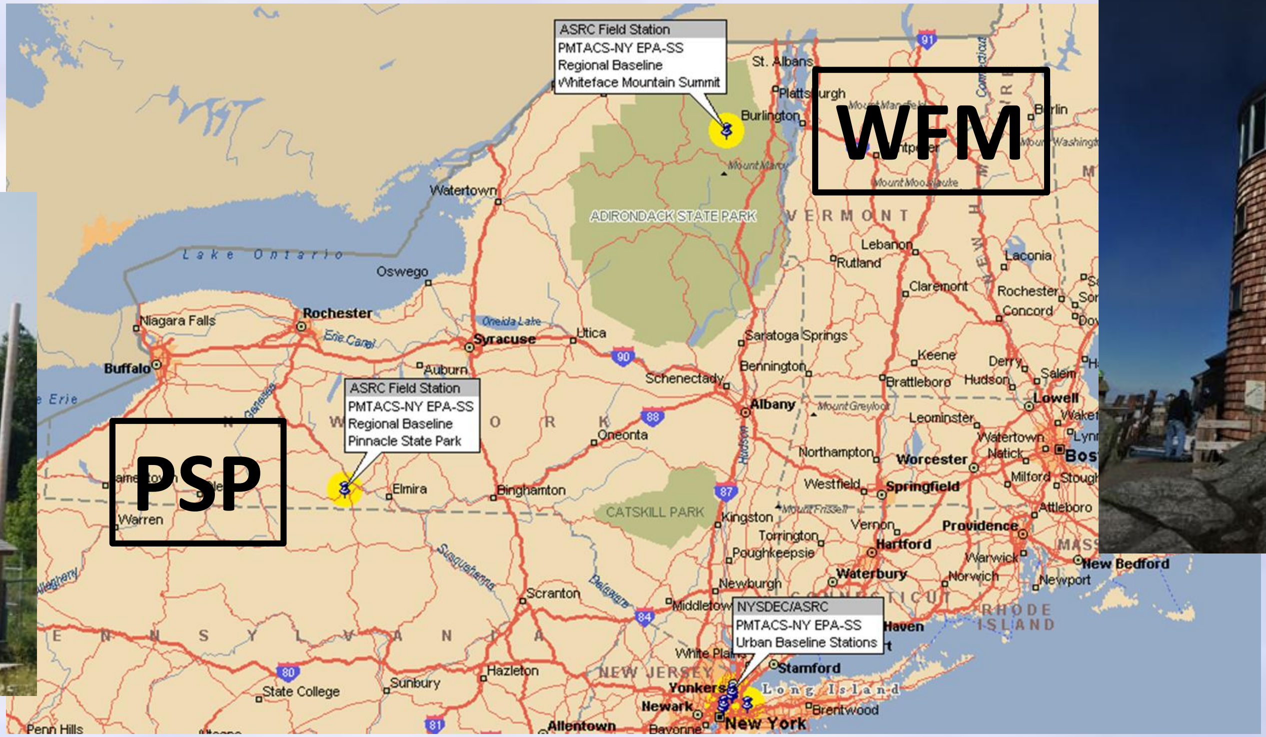
- Positive correlation between O_3 and NO_z → photochemical O_3 production occurs due to anthropogenic NO_x emissions.
- Knowing the OPE and its response to changes in [NO_x] is important in assessing effectiveness of O_3 control strategies based on [NO_x] reductions.
- The empirical OPE calculations are a powerful analytical tool, **but**
- One must be mindful of their limitations!

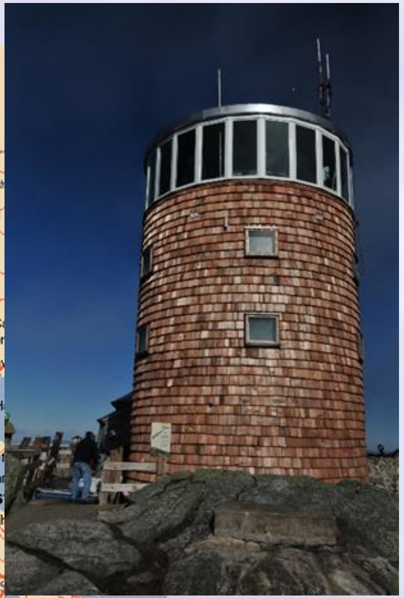
Specific Data Filters for OPE Analysis

- Choose only "photochemically active" periods – summertime (May – September) from 1100 to 1600 hours.
- Require ambient temperature greater than 20 °C.
- Require adequate solar insolation (greater than 500 W/m^2).
- Require positive correlation with $r^2 > 0.25$ for full summer regressions, and positive correlation with $r^2 > 0.40$ for daily regressions.
- Filter for outliers.
- At Whiteface Mountain summit, due to its complex meteorology, we also impose an atmospheric stability condition.

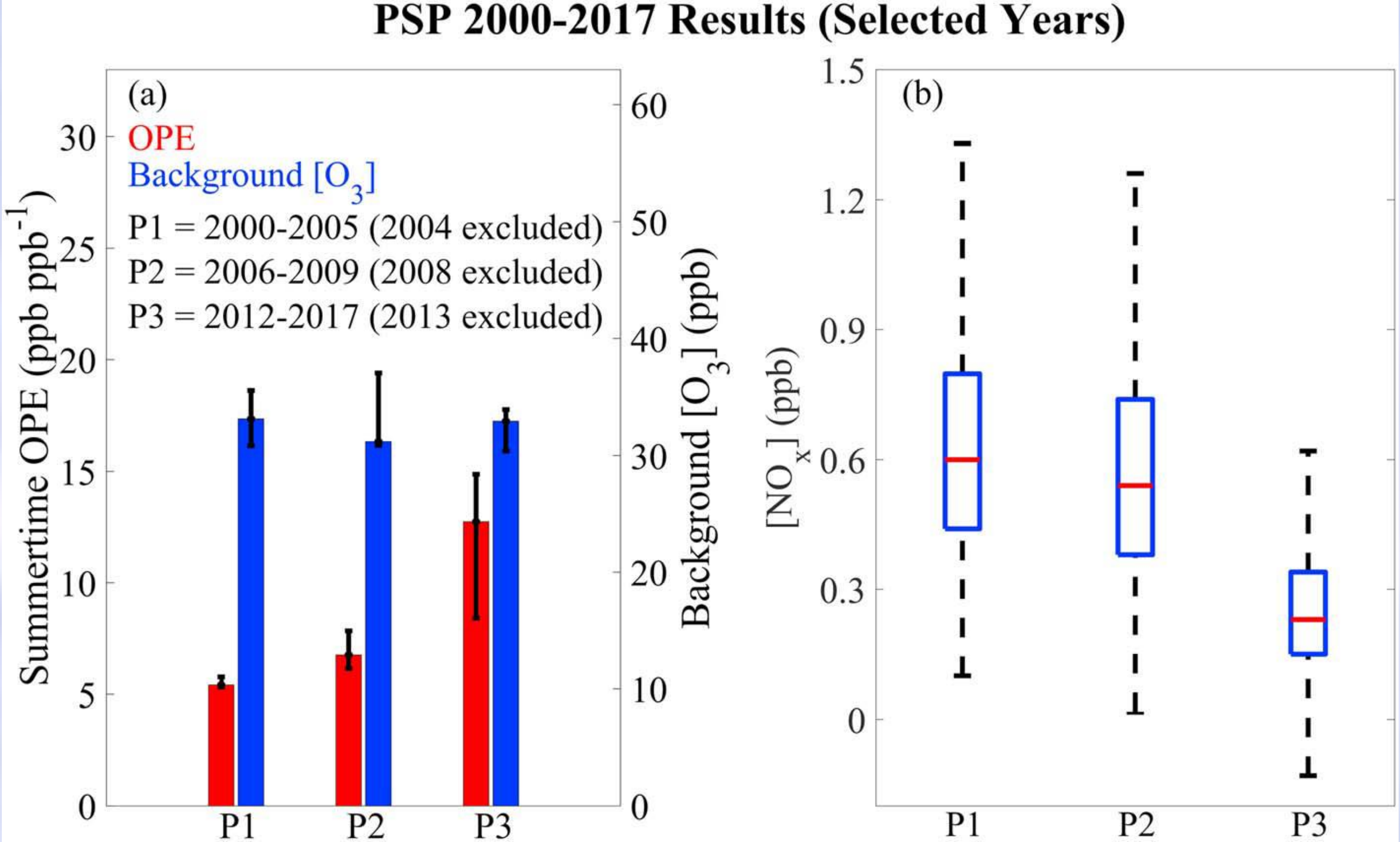
Data Sets

- Pinnacle State Park (Addison, NY) 2000- 2017: Parameters measured – O_3, NO_y, NO, and NO_2.
- Whiteface Mountain summit (Wilmington, NY) 2015-2017: Parameters measured – O_3, NO_y, NO, and NO_2.





PSP OPE, background O_3, and $[NO_x]$ levels



Ninneman et al., JGRD (2019)

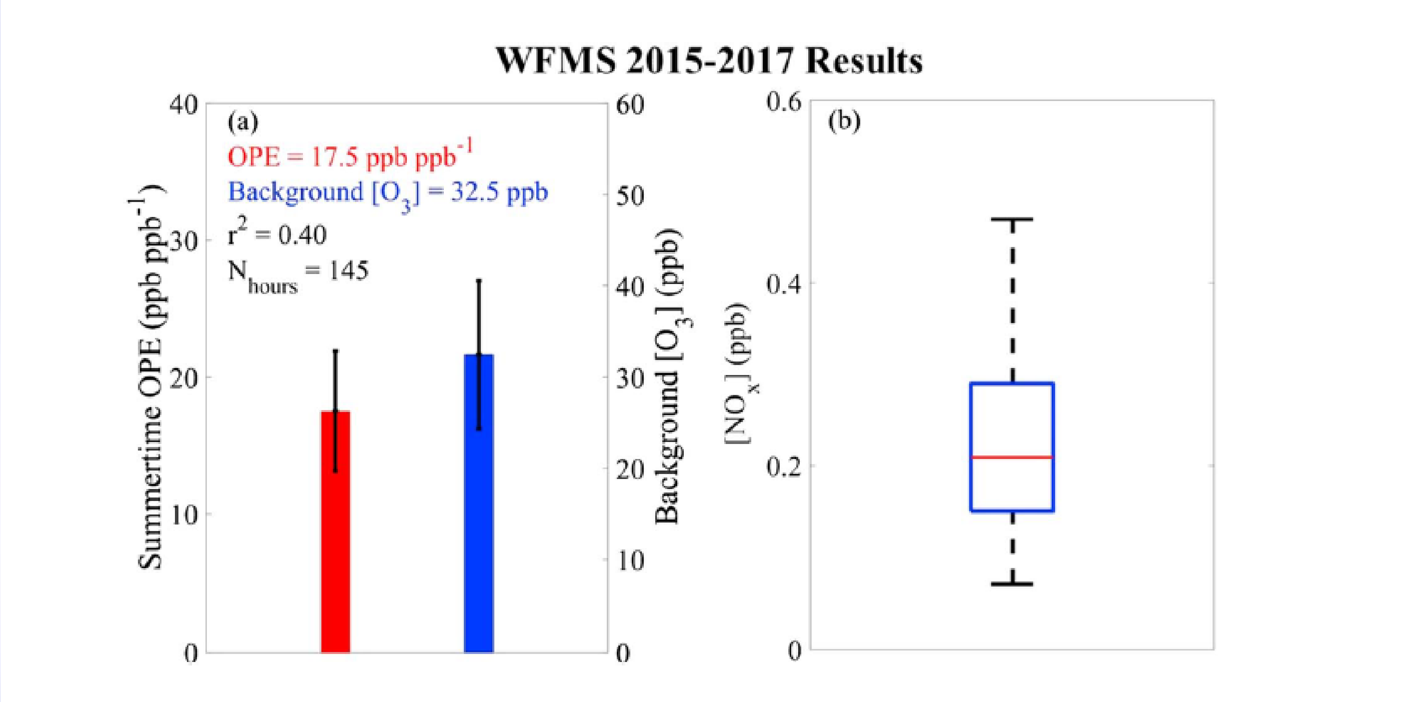
Results - PSP

- No change in background O_3.
- OPE increases more than a factor of two over the period, while at the same time
- The median and average $[NO_x]$ levels decrease by more than a factor of two

Table 3
OPE Results at PSP Over Three Selected Time Intervals: Statistics From Figure 3a

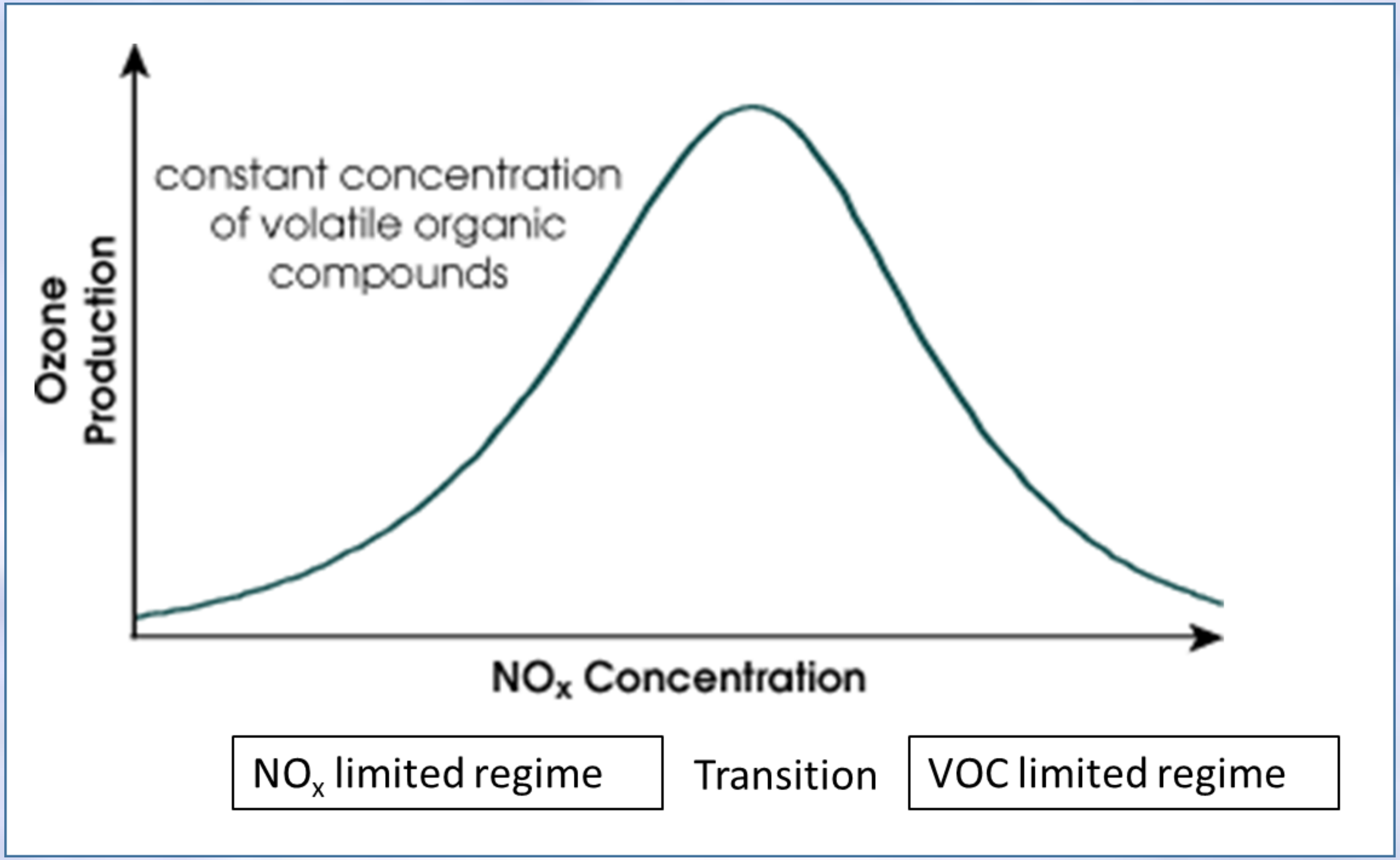
Time Period	Median Summertime OPE (ppb ppb^{-1})	Median Summertime Background [O_3] (ppb)	Median r^2	N_{hours}
2000–2005 (excluding 2004)	5.4	33.1	0.46	895
2006–2009 (excluding 2008)	6.8	31.2	0.57	671
2012–2017 (excluding 2013)	12.7	32.9	0.51	1479

What about Whiteface?



- [NO_x] is lower, and OPE is higher than PSP
- Consistent with our understanding of OPE and OPR dependence on [NO_x] levels.

Ozone Production and [NO_x]

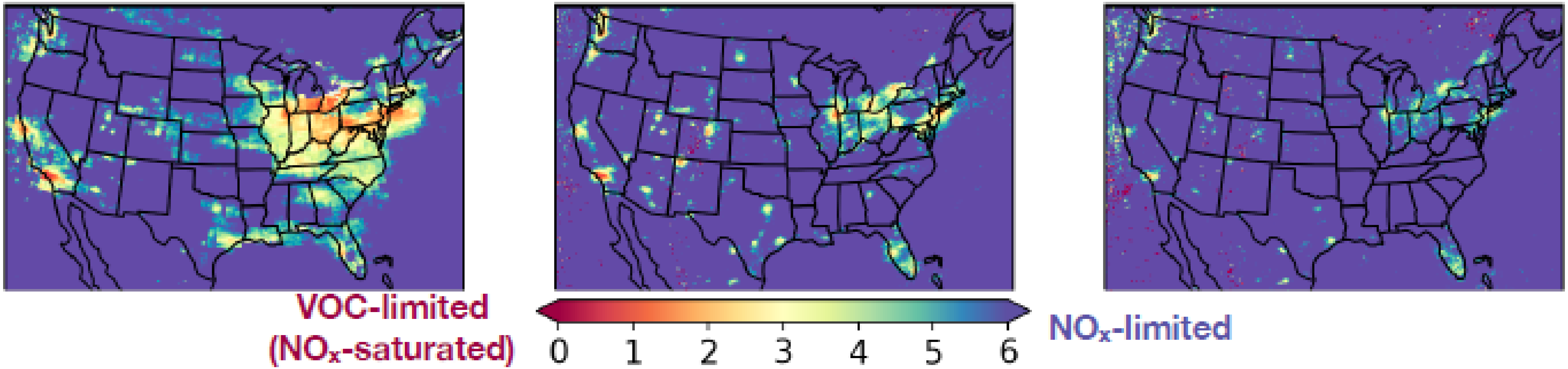


Ozone Production Regime or Sensitivity

- Understanding the ozone production regime (NO_x/VOC sensitivity) is critical to any attempt to address the ozone pollution issue!
- Reductions in [NO_x] due to regulations and increases in combustion efficiency have changed the sensitivity of many locations, including the NYC metro area.
- We can evaluate this "sensitivity" using space-based measurements of the HCHO/NO_2 column abundances (Jin et al., JRGD, 2017).
- Continued work by Fiore group explores this sensitivity further.

Increasing NO_x sensitivity over U.S.A as emissions decline

$HCHO/NO_2$ in 1997 (Warm) | $HCHO/NO_2$ in 2006 (Warm) | $HCHO/NO_2$ in 2016 (Warm)



1997	2006	2016
New York	New York	New York
Los Angeles	Los Angeles	Los Angeles
Chicago	Chicago	Chicago
Philadephia	Philadephia	Philadephia
Seattle	Seattle	Seattle
San Francisco	San Francisco	San Francisco
Phoenix	Phoenix	Phoenix
Denver	Denver	Denver
Houston	Houston	Houston
Atlanta	Atlanta	Atlanta

Jin et al., in prep

Conclusions (Take Home Points)

- NYC Metro area has an ozone pollution problem.
- While there have been decreases in [NO_x] across New York State, there have been simultaneous increases in OPE to (partially?) offset these changes.
- While the NYC Metro area may still be VOC-limited on average, it is moving toward the more complex “transition” regime.
- We are not out of the woods yet!

Thank you!

Outlier Filter for Daily OPE Estimates

- For Daily OPEs, at least four out of six hours must meet meteorological filters;
- Daily OPEs must have $r^2 > 0.4$;
- OPE estimates that were < 5th percentile of all daily OPEs, or > 95th percentile of all daily OPEs were considered outliers and omitted.

WFM Stability Analysis - Details

- The **Froude number (F_r)** can be defined as the ratio of the wind speed perpendicular to a mountain barrier to the static stability of the air mass at the base of the mountain.

- $F_r < 1$ represents atmospherically stable conditions;
- $F_r > 1$ represents atmospherically unstable conditions;

- **WFMS data were filtered for days with $F_r < 1$ at least 70% of the time.**