$PM_{2.5}$ Suppression of Ozone Formation at High Mass Loading

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Statement of Problem

- It is quite common for ozone and $PM_{2.5}$ pollution episodes to co-occur during summer months and both pollutants create problems for regulators in areas subject to air quality problems.
- Understanding the relationship between these two pollutants on poor air quality days can help develop strategies for prevention and mitigation of these problems.
- We selected twelve major cities in the Eastern U.S. and analyzed the relationship between summertime maximum 8-hour average ozone (MDA8 O_3) and the daily average $PM_{2.5}$ (DA24 $PM_{2.5}$).

$PM_{2.5}$ Suppression of Ozone Formation

- At low $PM_{2.5}$ loading the relationship between O_3 and $PM_{2.5}$ is well described by a monotonic near linear increasing function.
- At very high PM concentrations (like those observed in China, India, Africa, and elsewhere) there is a leveling off or even decreasing dependence of O_3 on $PM_{2.5}$.
- This flat or declining relationship has been partly attributed to the scavenging of HO_2 and/or NO_3 by high concentrations of PM that inhibits the photochemical production of O_3; and/or reduced photolysis rates due to the radiation decrease caused by the high PM.

How to describe this suppression?

- Work from our group (Zhang et al., 2022) has used a non-linear polynomial function to describe the relationship between O_3 and $PM_{2.5}$ for NYC based on surface measurements. This relationship consists of:
  - A linear term reflecting the O_3/$PM_{2.5}$ co-occurrence;
  - A negative power function term reflecting the suppression of O_3 formation by $PM_{2.5}$; and
  - A constant term.

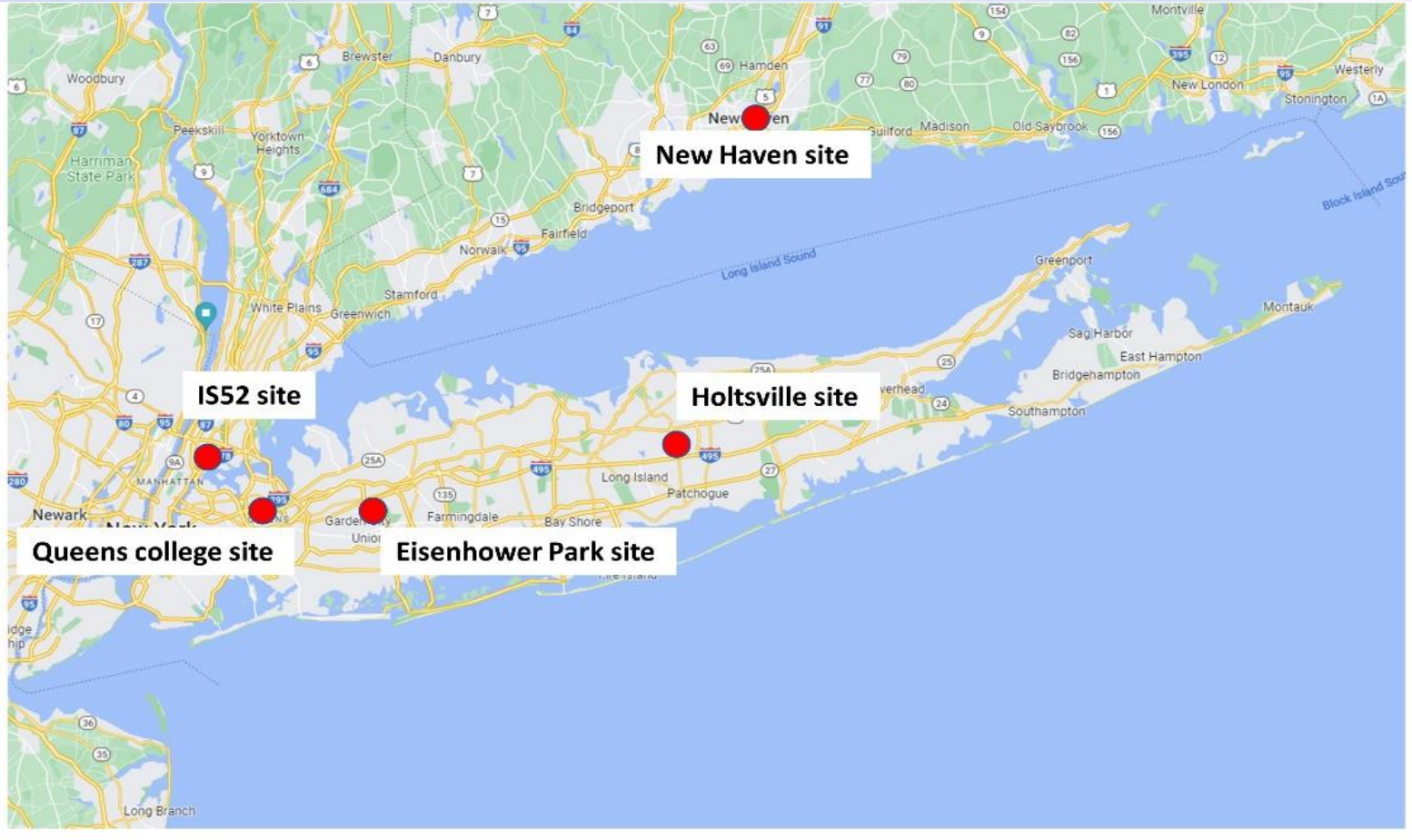
Non-linear fitting expression

- $O_3 = aPM_{2.5} - b(PM_{2.5})^{5/3} + c$
  - a is the slope of the linear part of the relationship
  - b is the power function coefficient, or the "suppression factor"
  - c is the constant term

Ozone sensitivity regime

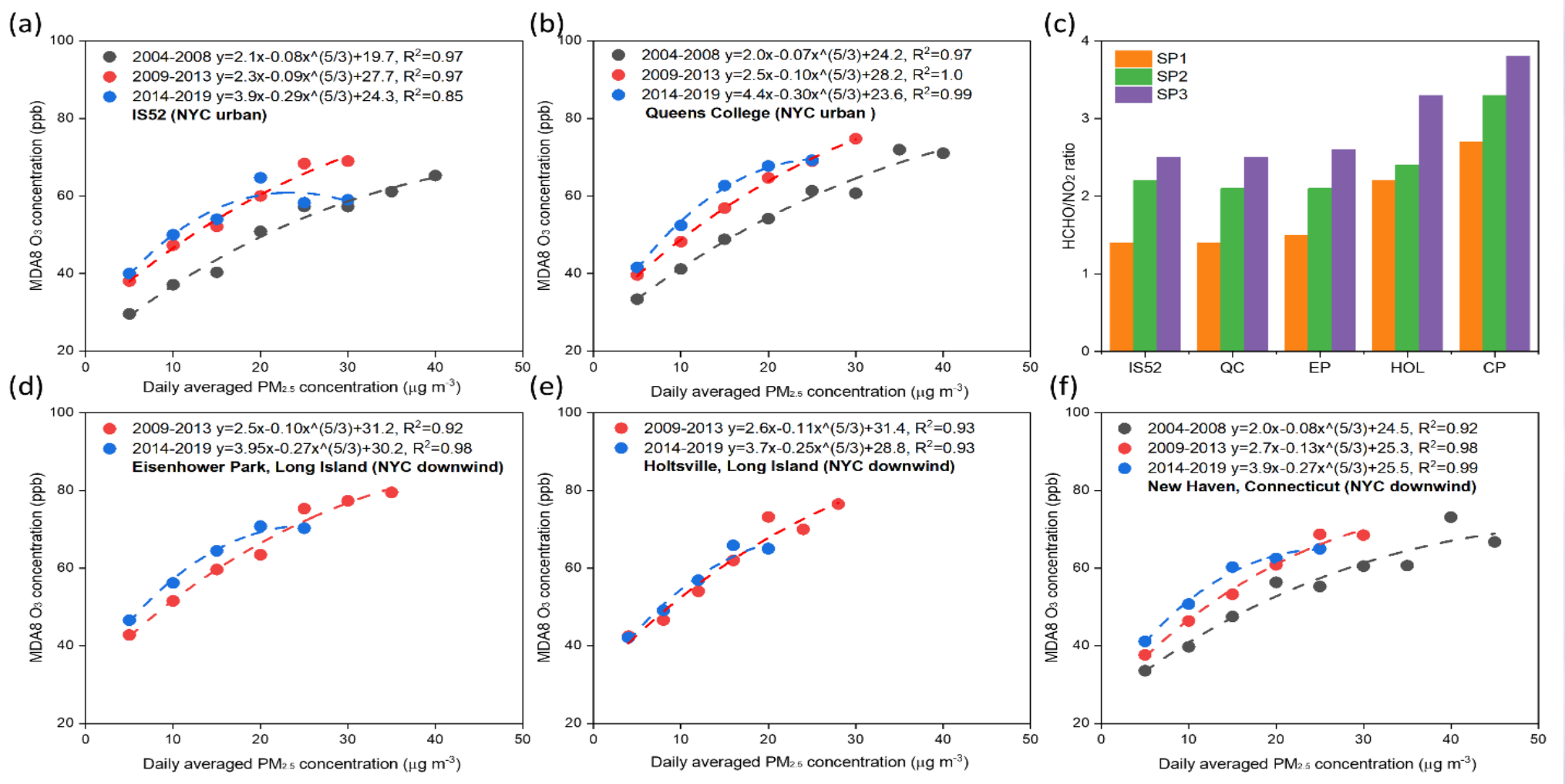
- Regions are often described as NO_x-limited or VOC-limited with respect to ozone production depending on which pollutant group is the limiting reagent.
- Large urban areas have historically been NO_x-limited due to large anthropogenic emissions of VOCs. Conversely, more rural regions have historically been VOC-limited.
- Reductions in VOC emissions have caused many urban areas (like NYC) to trend more toward VOC-limited (or into a transition zone between the two limiting cases).
- The $PM_{2.5}$ suppression factor can help indicate the ozone formation regime and can be compared the commonly used indicator from satellite column measurements of the HCHO to NO_2 ratio. (OMI and TROPOMI)

Data Analysis



Locations for the analysis of MDA8 O_3 and DA24 $PM_{2.5}$ data from 2004-2019

Plots and Fitted relationships for these sites



- Data has been binned
- Time evolution is Black to Red to Blue.

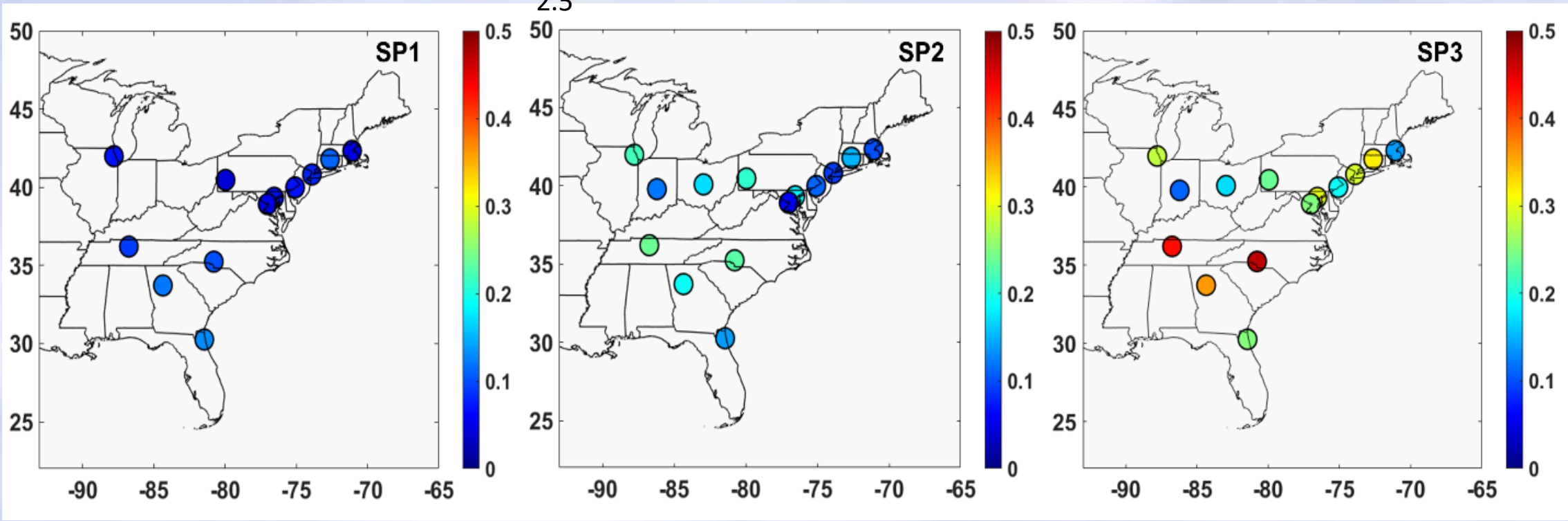
Evolution of $PM_{2.5}$ Suppression Factors

Time Period	IS52 (Bronx)	Queens College	EP, Long Island	Holtsville, LI	New Haven, CT
2004-2008	0.08	0.07	n/a	n/a	0.08
2009-2013	0.09	0.10	0.19	0.11	0.13
2014-2019	0.23	0.30	0.27	0.25	0.27

- The increase in $PM_{2.5}$ suppression factor over this time period is consistent with the increase in $HCHO/NO_2$ ratio, which is used to indicate the O_3-sensitivity regime.
- The increased $HCHO/NO_2$ ratio (and therefore the increased $PM_{2.5}$ suppression factor) represents a shift of the NYC area from the VOC-limited to the NO_x-limited regime.

Extend the analysis to 12 Major Eastern U.S. cities

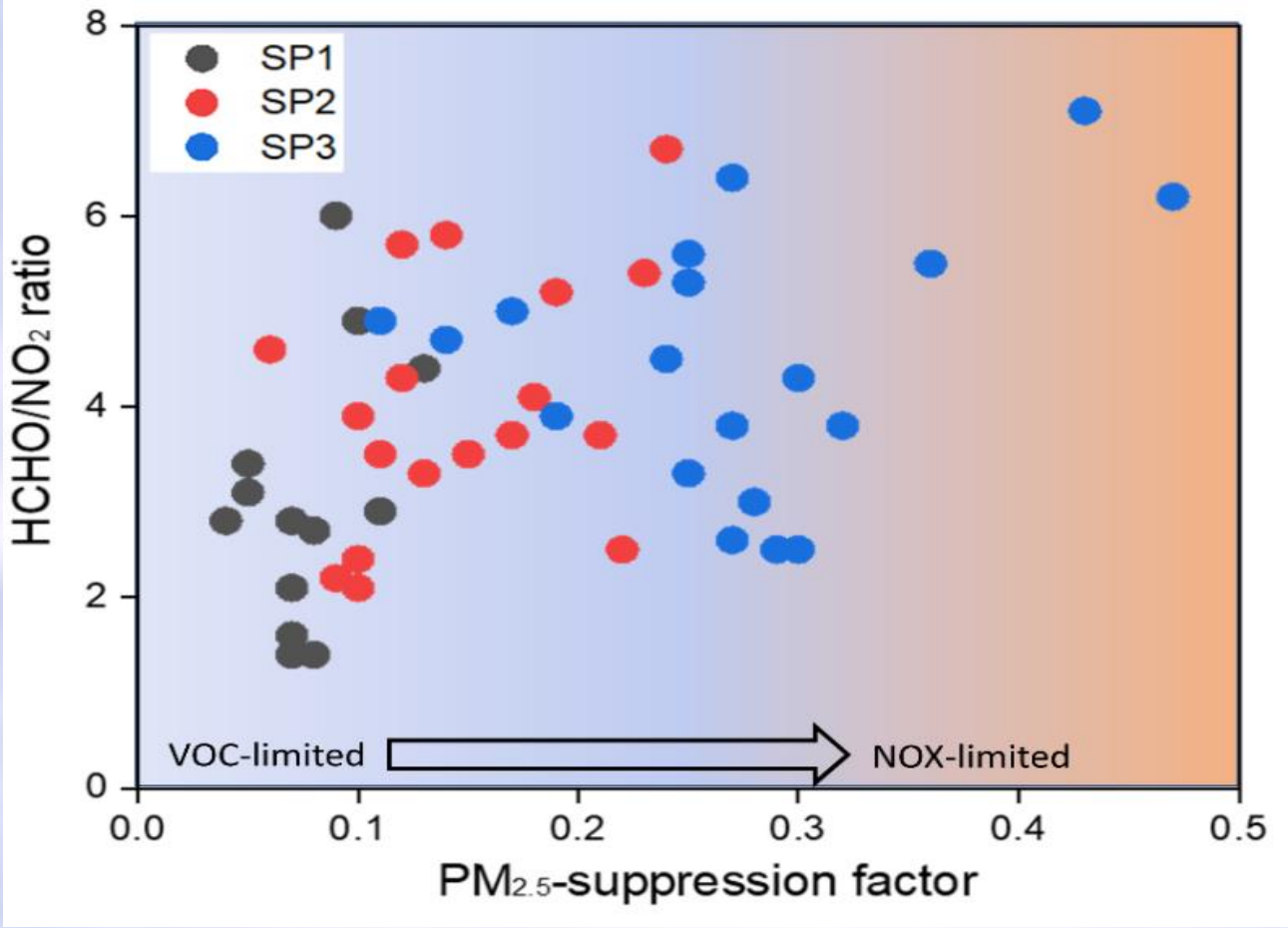
$PM_{2.5}$ SUPPRESSION FACTORS



2004-2008 2009-2013 2014-2019

- Clear trend toward increasing suppression factors across the domain

Combining satellite derived $HCHO/NO_2$ ratio and $PM_{2.5}$ Suppression Factors



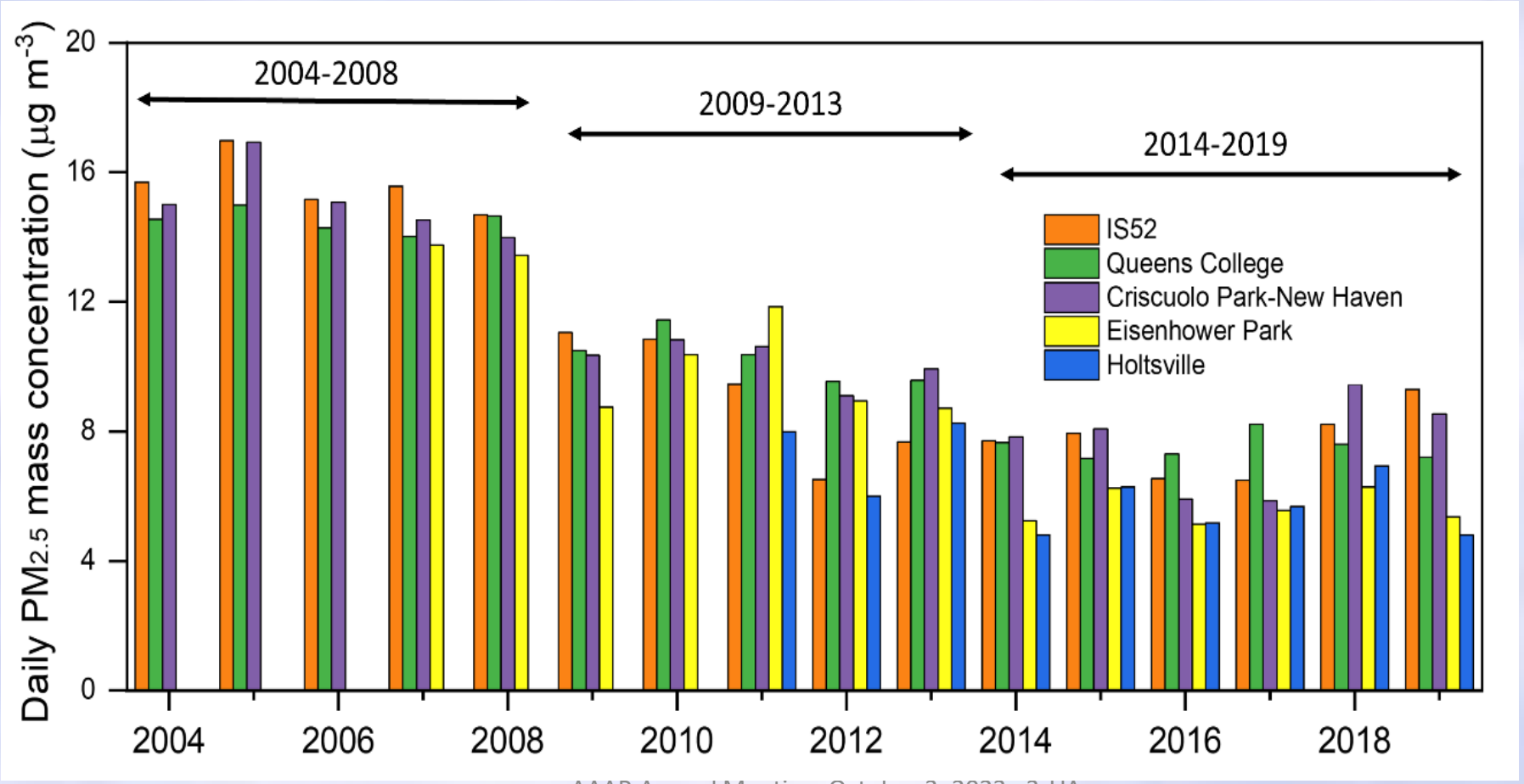
Conclusions (Take Home Points)

- The O_3 to $PM_{2.5}$ relationship at high PM has a non-linear rollover that is related to $PM_{2.5}$ suppression of ozone formation (maybe due the HO_2 uptake by aerosols?).
- The non-linear suppression factor has increased over time – possibly due to increasing organic carbon in the PM.
- This is consistent with the trend in the $HCHO/NO_2$ indicator ratio for ozone formation regime.
- This $PM_{2.5}$ suppression factor offers an alternative, but largely confirming measure of ozone formation regime.

Thank you!

Back Up Slides

- The time series of the annual summertime average DA24 $PM_{2.5}$ in NYC urban sites and downwind sites for each subperiod.



$HCHO/NO_2$ satellite derived ratios for cities used in the study.