Ozone Production and Its Sensitivity to NOx and VOCs during LISTOS 2018

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Long Island Sound Tropospheric Ozone Study Meeting

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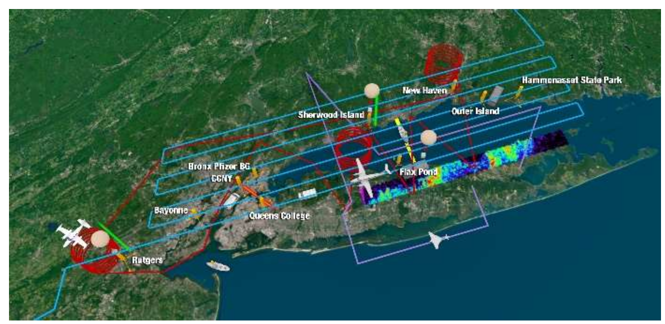
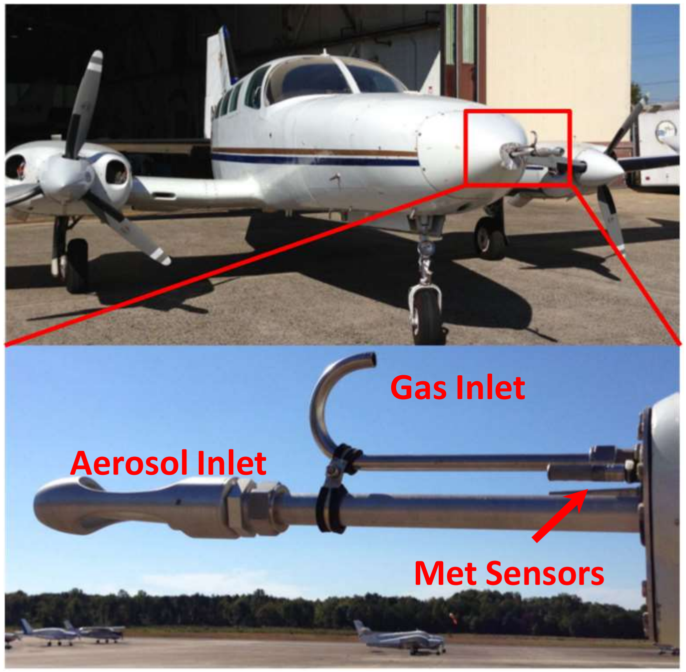
LISTOS

Long Island Sound Tropospheric Ozone Study



UMD Cessna 402B Research Aircraft



GPS Position (Lat, Long, Altitude)

Met (T, RH, P, wind speed/direction with a diferential GPS)

Trace gases:

O_3: UV Absorption, modified TECO
NO_2: Cavity Ring Down, Los Gatos
NO/NOy: Chemiluminescence, modified TECO
SO_2: Pulsed Fluorescence, modified TECO
$CH_4/CO_2/CO$: Cavity Ring Down, Picarro
HCHO: Laser Induced Fluorescence
VOCs: grab samples with GC-FID

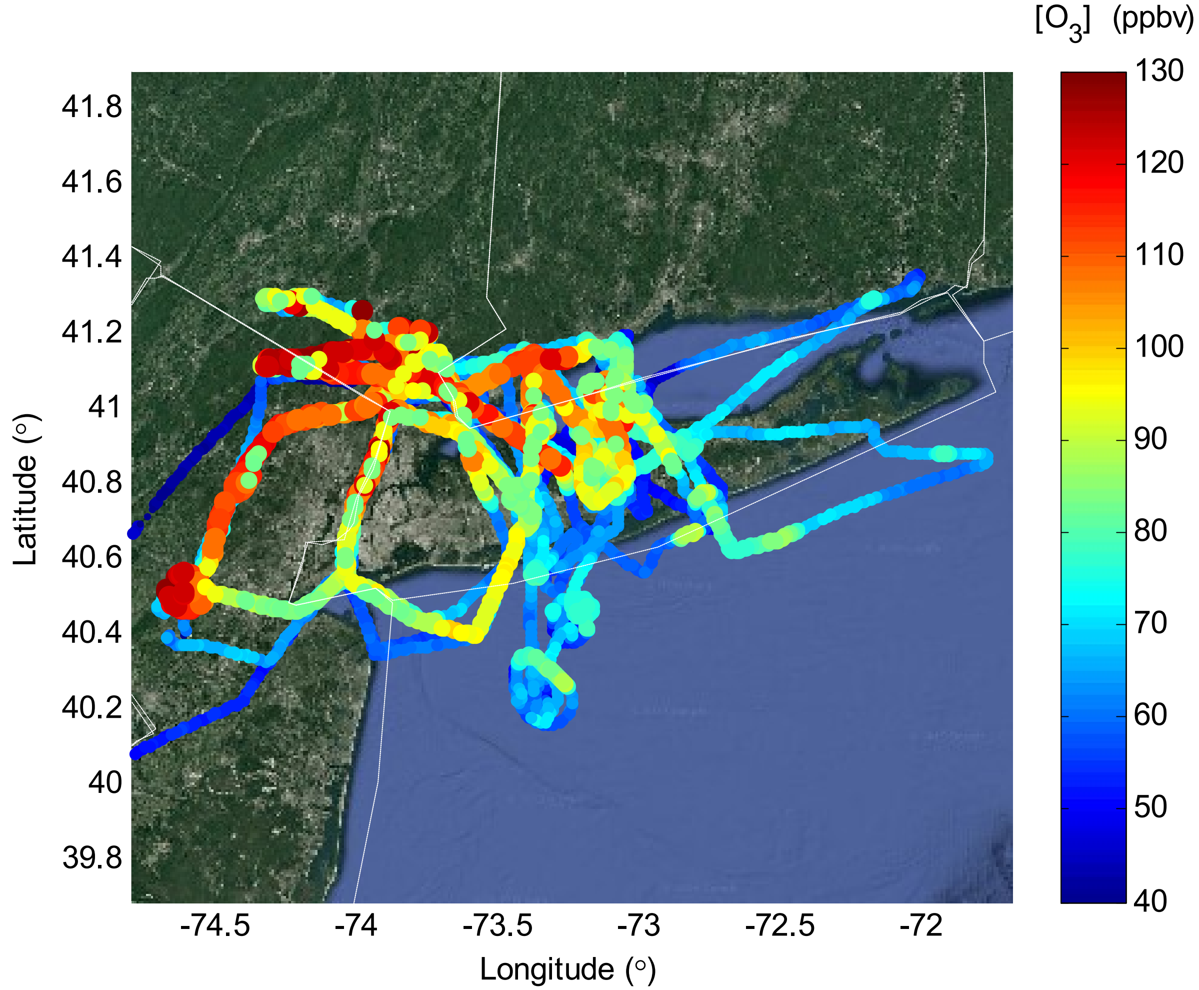
Aerosol Optical Properties:

Scattering: b_{scat} (@450, 550, 700 nm), Nephelometer
Absorption: b_{ap} (@565 nm), PSAP
Black Carbon: Aethalometer AE33

- 8 flights on 4 ozone days: July 1-2 & Aug. 15-16
- Data available at the NASA LISTOS archive:

https://www-air.larc.nasa.gov/cgi-bin/ArcView/listos

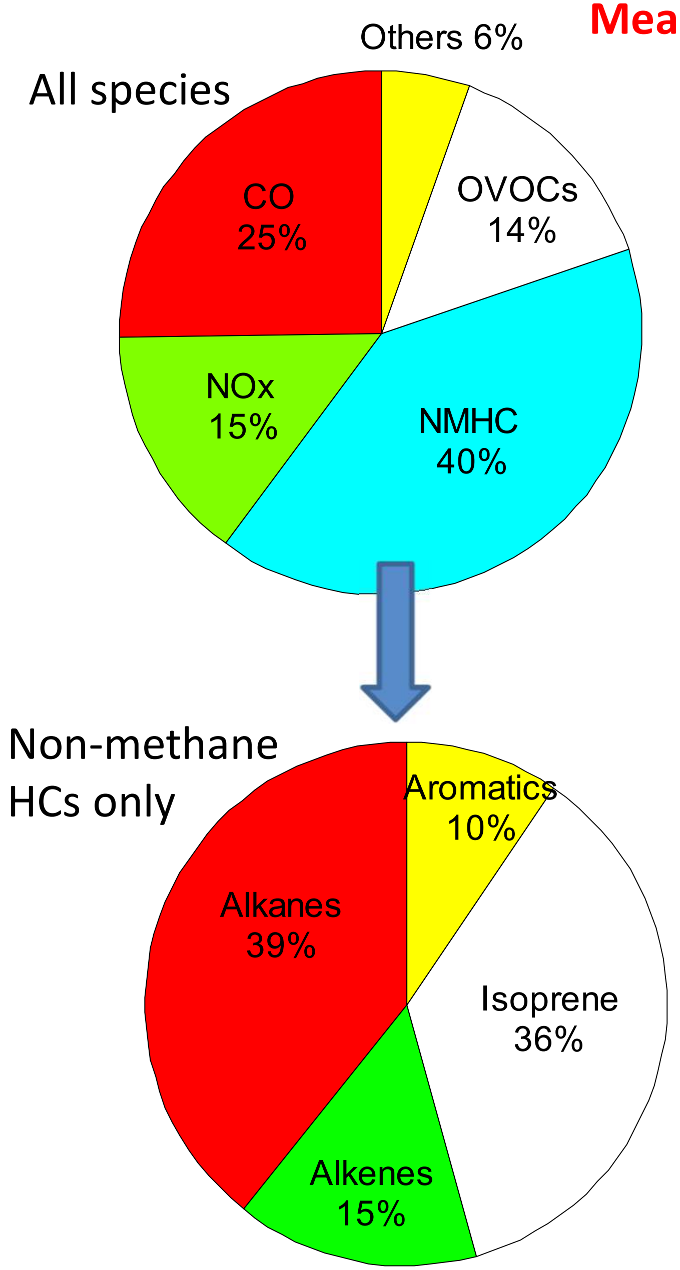
UMD Cessna flights during LISTOS 2018

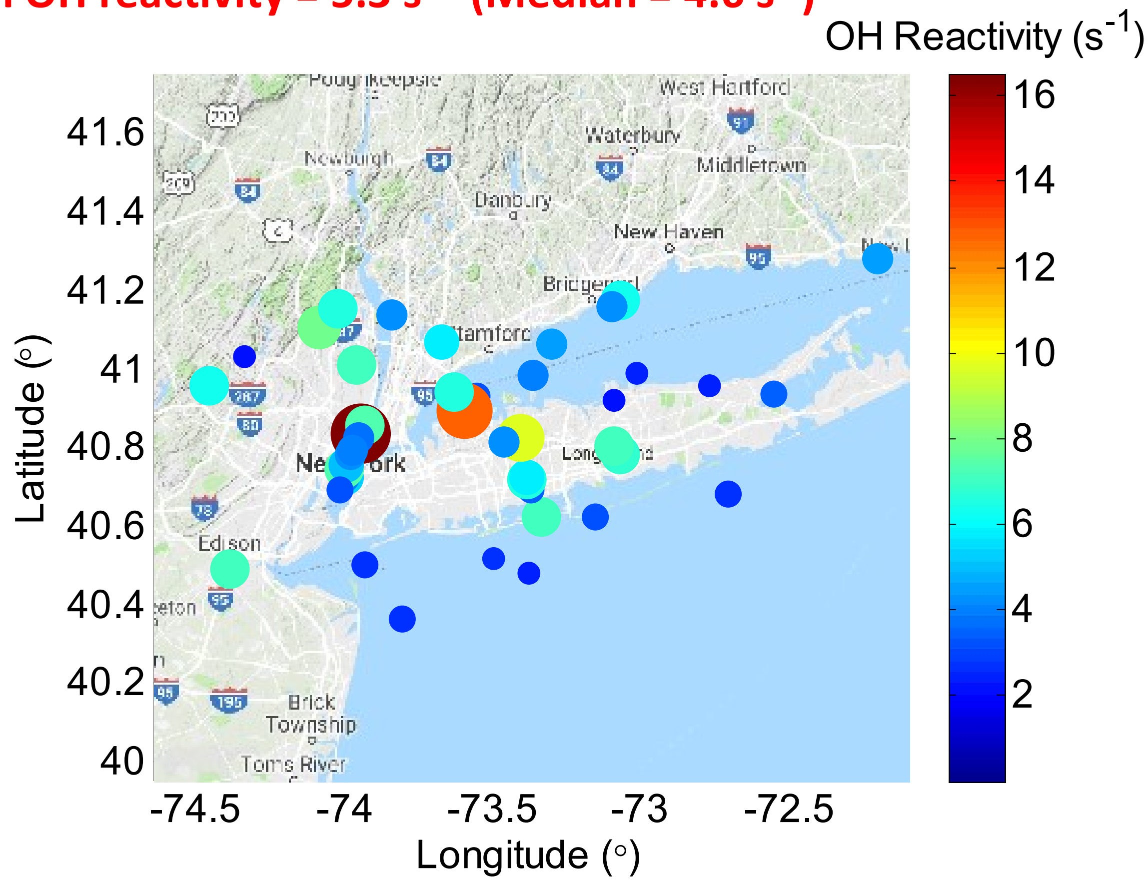


- Measurements of ozone and its precursors NOx and VOCs
- 1-minute average of ozone up to 130 ppb was observed in NYC/LIS.

OH Reactivity during LISTOS 2018

Mean OH reactivity = 5.3 s^{-1} (Median = 4.6 s^{-1})





- CO and NMHC contribute significantly to total OH reactivity
- Alkanes and isoprene are dominant non-methane hydrocarbons.

Box Model Simulations

- Mechanism: Regional Atmospheric Chemistry Mechanism, Version 2 (RACM2) (*Golliff et al., 2013*)
- Model constrained by measured chemical specie and meteorological parameters (T/P/RH/J values) along the flight tracks.
- Model output: OH, HO_2, RO_2 and other reactive intermediates.
- Modeled data points: 46 VOC samples during LISTOS 2018

We can use model results to calculate ozone production and its sensitivity to NOx and VOCs.

Photochemical Ozone Production, $P(O_3)$

$$HO_2 + NO \rightarrow OH\ NO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$NO_2 + hv \rightarrow NO + O_3$$

$$P(O_3) = k_{NO+HO2}\ [NO][HO_2] + \Sigma_i\ k_{NO+RO2i}\ [NO][RO_{2i}]$$

$$L(O_3) = k_{O1D+H2O}[O(^1D)][H_2O] + k_{HO2+O3}\ [O_3][HO_2]$$
$$+ k_{OH+O3}[O_3][OH] + k_{OH+NO2+M}\ [OH][NO_2][M]$$

Net photochemical $P(O_3)$: $P(O_3)_{net} = P(O_3) - L(O_3)$

$P(O_3)$ Sensitivity to NOx and VOC

$P(O_3)$ is a function of NOx and VOC reactivity as:

$$P(O_3) = KQ^{C1}[NO_x]^{C2}[VOC_R]^{C3}$$

and the sensitivity of ozone production can be determined by an indicator, **L_N/Q**:

$$\frac{dlnP(O_3)}{dln[NOx]} = \frac{1-1.5*L_N/Q}{1-0.5*L_N/Q} \quad \text{and} \quad \frac{dlnP(O_3)}{dln[VOCR]} = \frac{L_N/Q}{2-L\quad/Q}$$

where, L_N: Radical loss due to NOx;

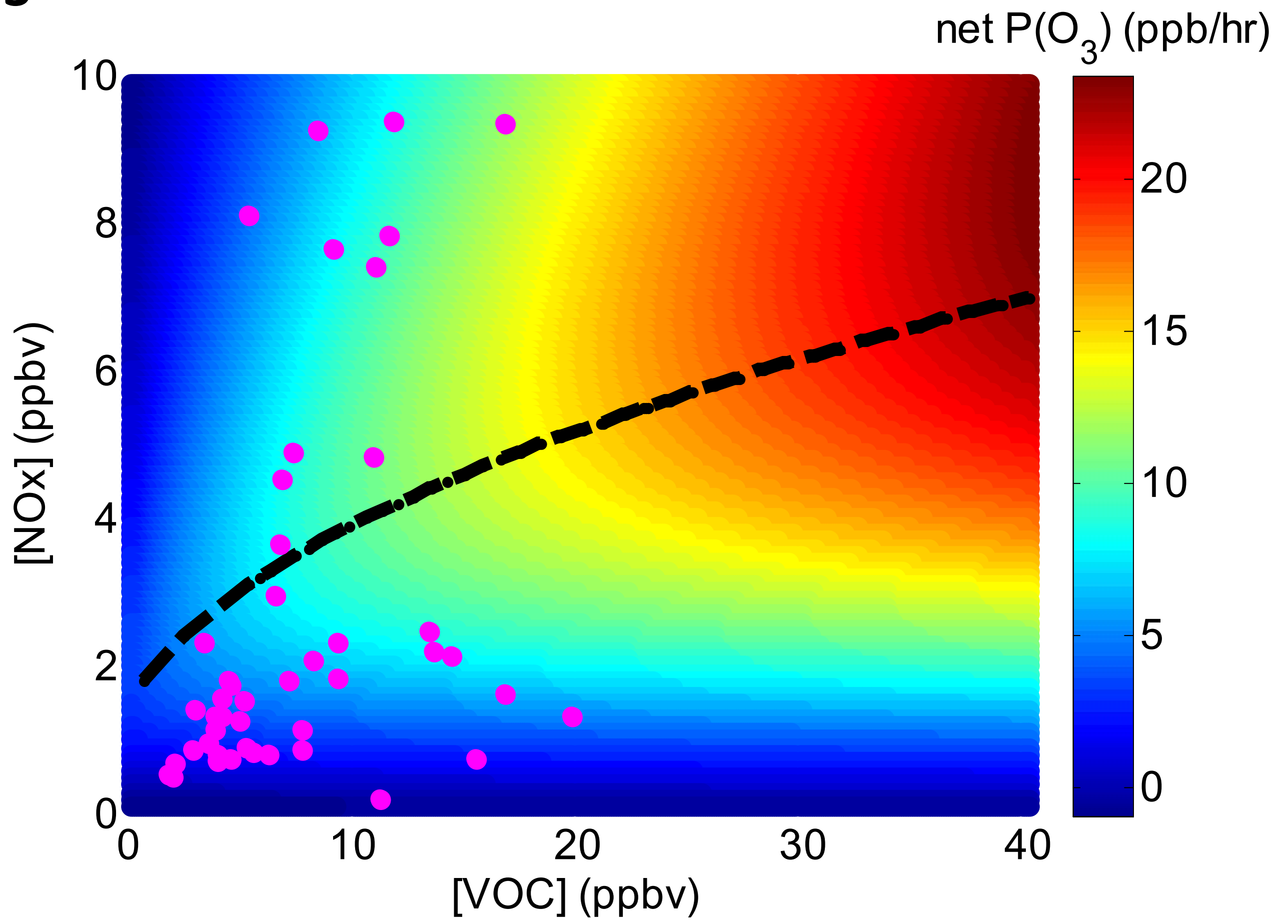
Q: Total primary radical production

$L_N/Q > 0.5$ ➔ $P(O_3)$ is VOC-sensitive

$L_N/Q < 0.5$ ➔ $P(O_3)$ NOx-sensitive

(Kleinman et al., 2001)

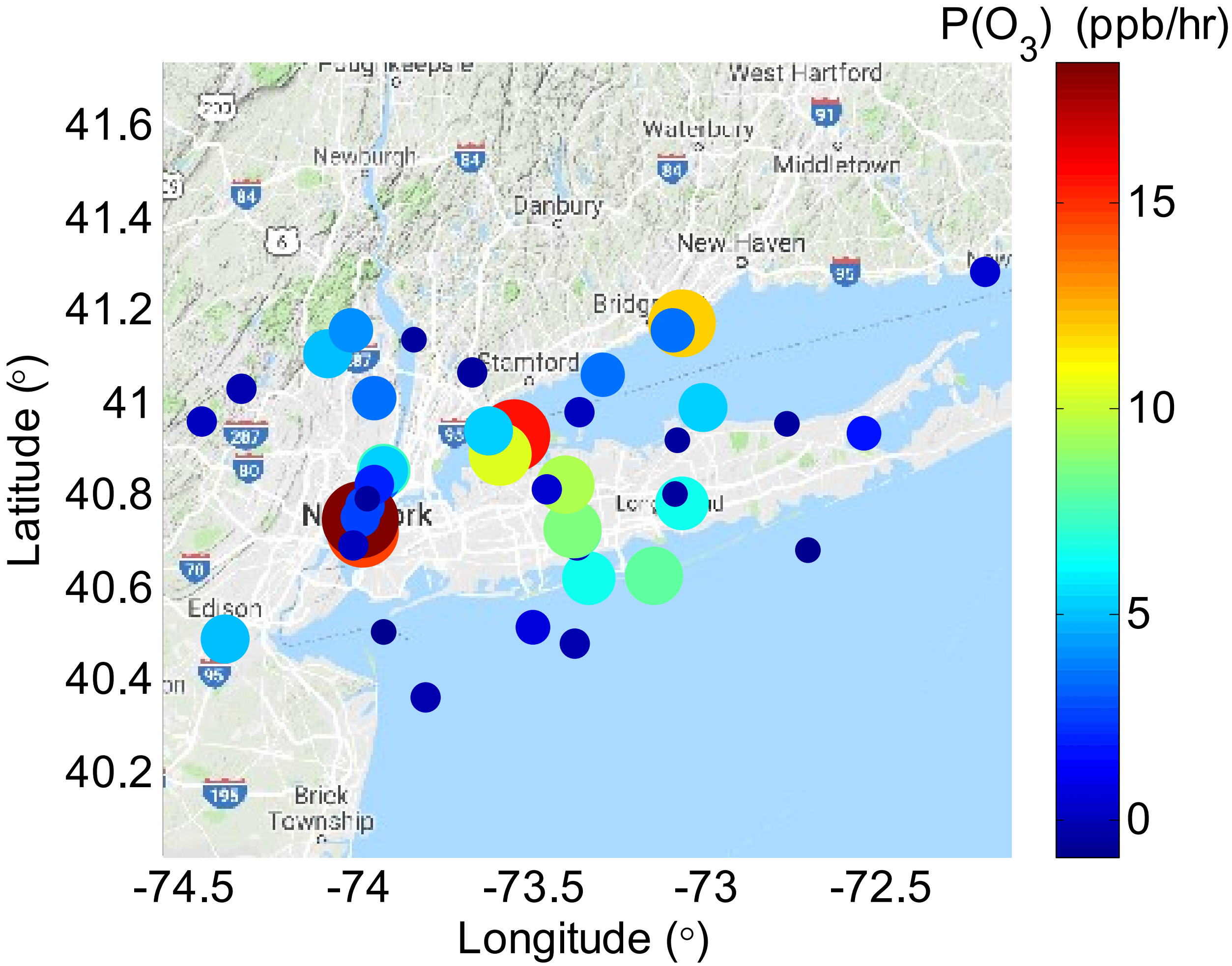
$P(O_3)$ Isopleth Diagram during LISTOS 2018



- Background: $P(O_3)$ as a function of NOx & VOCs based on mean met & chemical conditions
- Circles: data points with VOC measurements
- Most samples are NOx-sensitive with other samples to be VOC-sensitive
- Controlling both NOx and VOCs to reduce $P(O_3)$

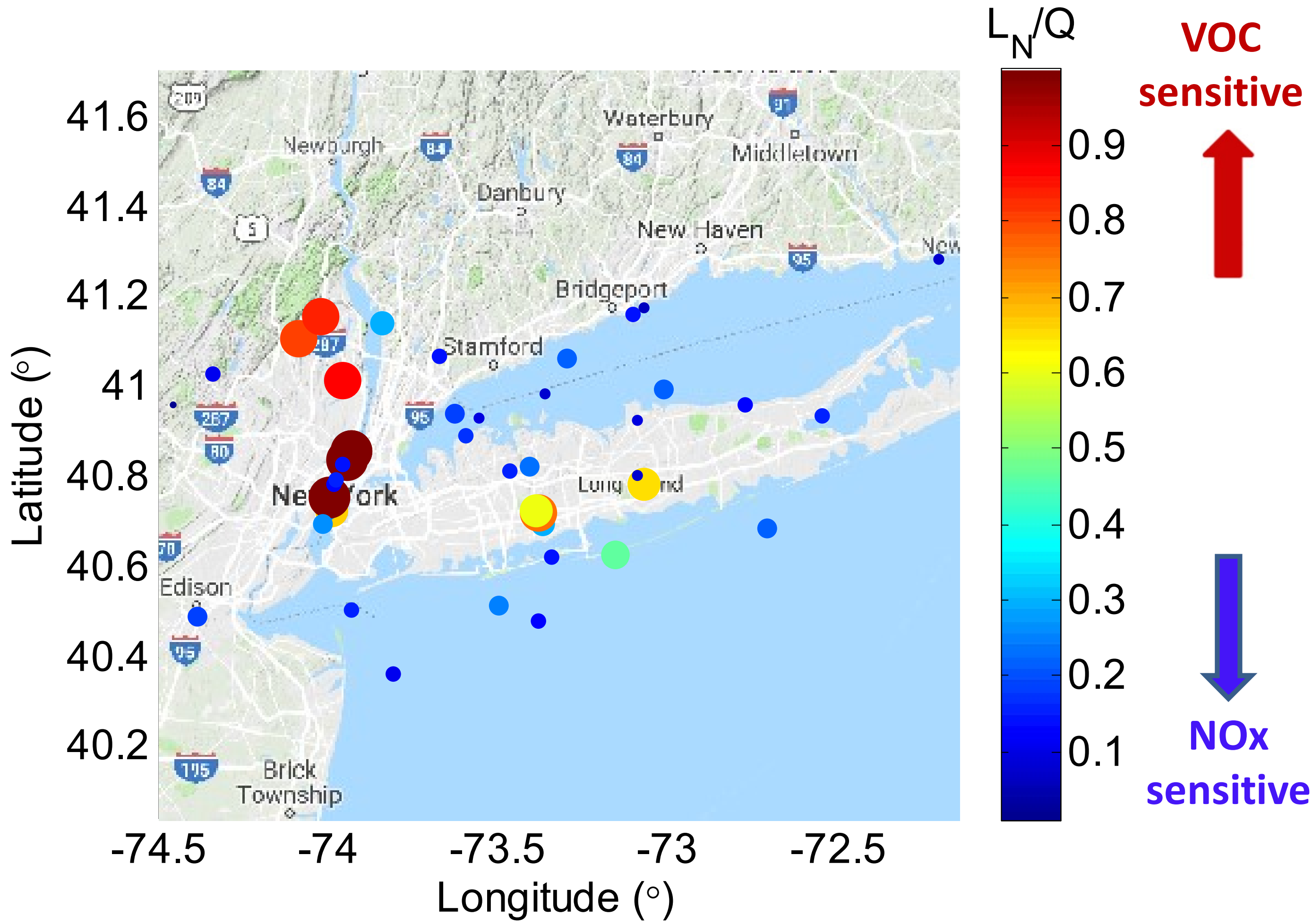
Net $P(O_3)$: Spatial Variation

Mean net $P(O_3)$ = 3.9 ppb/hr (Median = 3.0 ppb/hr)



- Each circle reprents the location where we collected VOC samples.
- In general higher $P(O_3)$ near emission source regions

P(O_3): Sensitivity to NOx and VOCs



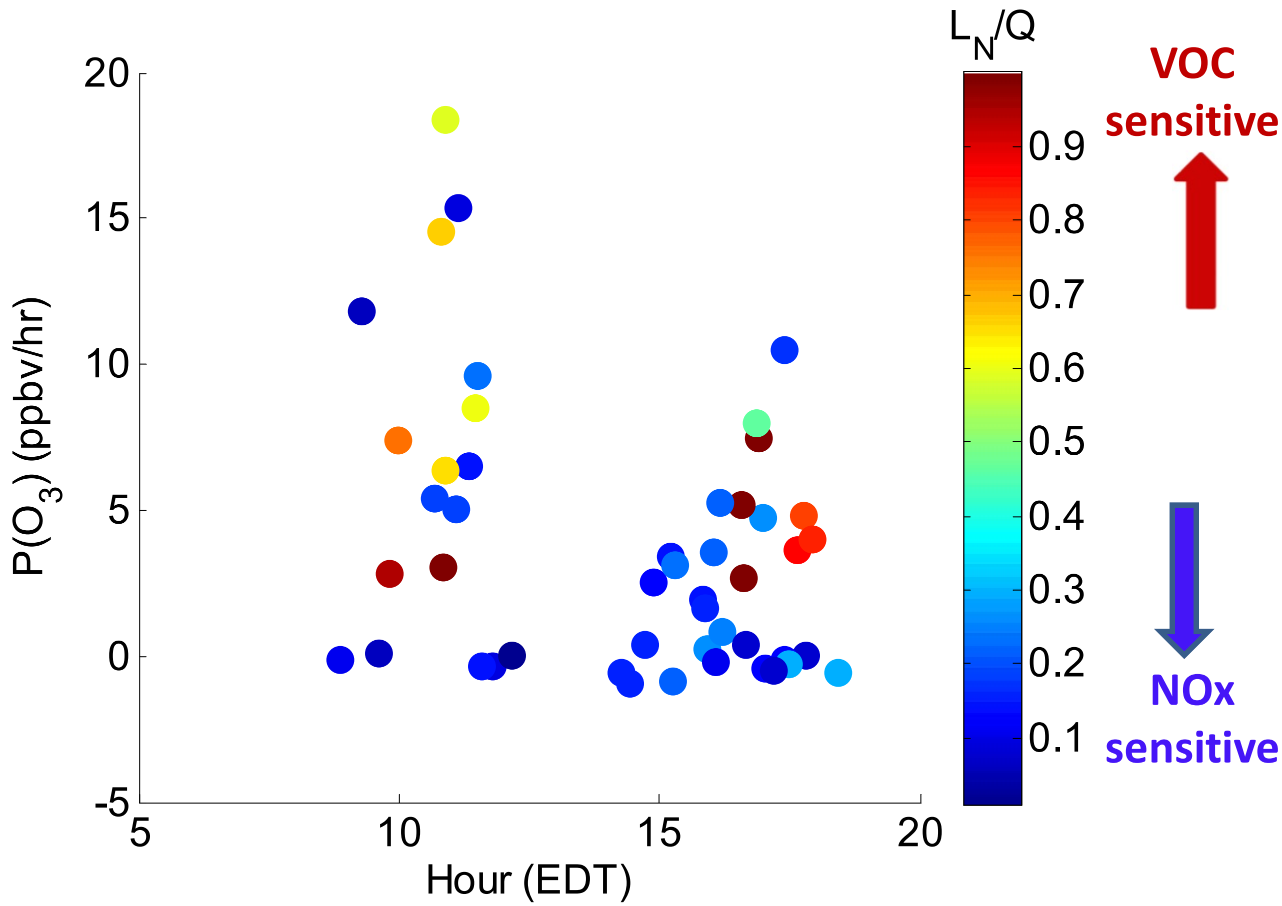
- In general VOC sensitive near emission sources
- NOx sensitive away from source regions.

Key Points

- Box modeling was conducted to study ozone production and its sensitivity to NOx and VOC using the aircraft data collected during LISTOS 2018 .
- In general ozone production, or $P(O_3)$ is VOC sensitive near emission sources and NOx sensitive away from source regions.
- Controlling both NOx and VOCs to reduce $P(O_3)$ in NYC/LIS:
  - Reducing VOCs can reduce $P(O_3)$ in emission source regions.
  - Reducing NOx can reduce $P(O_3)$ in areas away from the source regions.

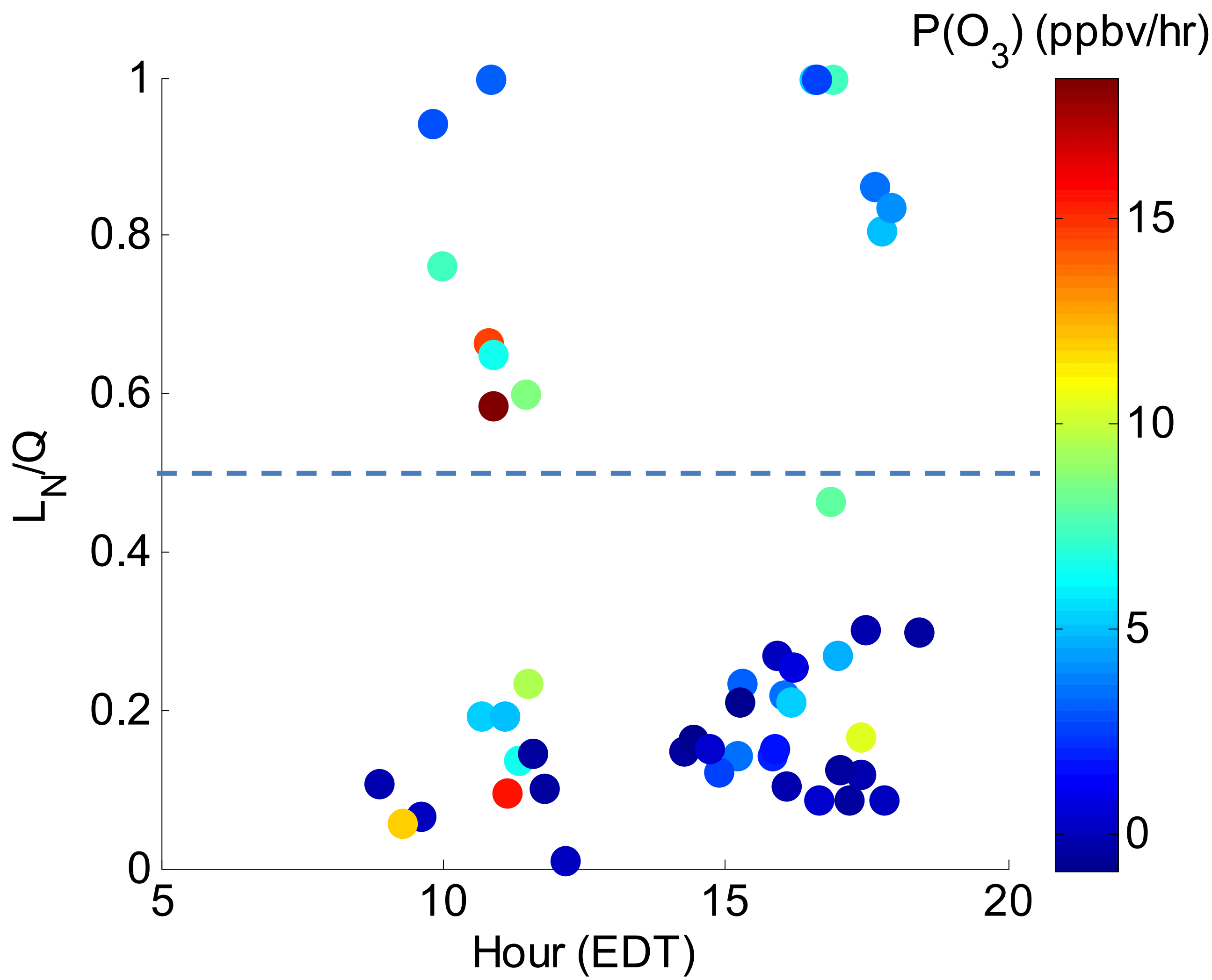
Backup slides

$P(O_3)$: Diurnal Variation

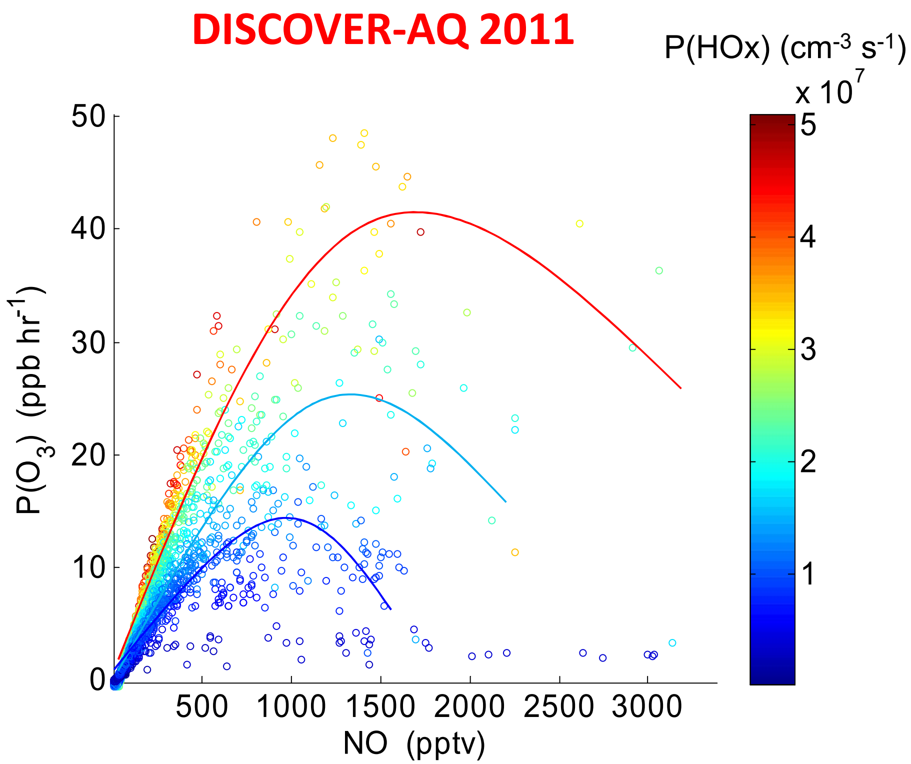


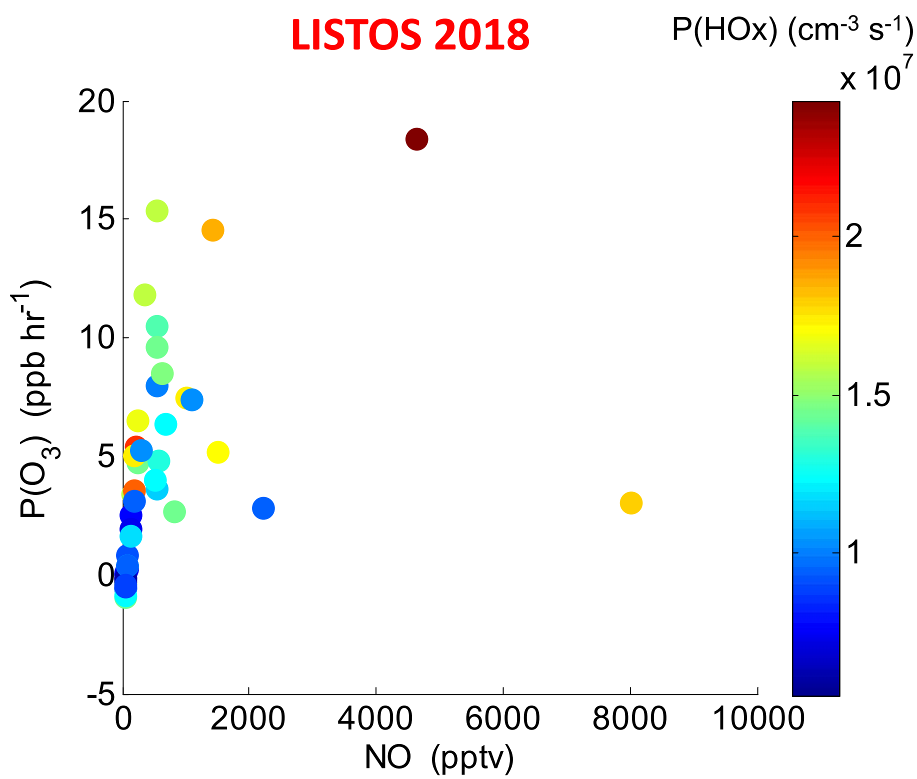
- High $P(O_3)$ in both NOx and VOC sensitive regimes.

$P(O_3)$: Sensitivity to NOx and VOCs



$P(O_3)$: NO Dependence





- NO dependence of $P(O_3)$ as we would expect:
  - Higher P(O3) at higher P(HOx) or photochemical reacitivity
  - Lower [NOx] turning point with less P(JHOx) or photochemical reactivity