Analysis of Ozone Formation Sensitivity in Houston Using the Data Collected during DISCOVER-AQ

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Motivation

- To investigate the spatial and temporal variations of ozone production and its sensitivity to NO_x and VOCs.
- To provide scientific information for policy-makers to develop a non-uniform emission reduction strategy for O_3 pollution control.

DISCOVER-AQ provided great data sets to look into this!

Box Model Simulations

- Mechanism:
  CB05: Carbon Bond Chemical Mechanism
  (Yarwood et al., Report to US EPA, 2005)
  -- 51 chemical species and 156 reactions
  -- Updated chemistry for higher aldehydes, internal olefins, organic peroxides, and methylperoxy radical

- Model input: the P-3B observations (1-min merge file):
  -- Inorganic species: O_3, NO, NO_2, CO, SO_2,
  -- VOC species: HCHO, PTR-TOF (isoprene, terpenes, and aromatics), and CMAQ-calculated alkanes/alkenes
  -- J values: calculated with the TUV model and scaled to measured $J(NO_2)$
  -- Meteorological parameters: T, P, and RH

- Model output
  steady state OH, HO_2, RO_2 and other intermediates

- Modeling period: nine P-3B flights

Alkanes/Alkenes Input for the Box Model

CMAQ-calculated alkanes and alkenes (not measured on the P-3B) were used to constrain the box model, including:

PAR: Paraffin carbon bond (C-C)

ETHA: Ethane

ETH: Ethene

OLE: Terminal olefin carbon bond (R-C=C)

IOLE: Internal olefin carbon bond (R-C=C-R)

Toluene-scaled alkanes and alkenes based on SHARP on Moody Tower:

[PAR] = 73.6 x [Toluene]

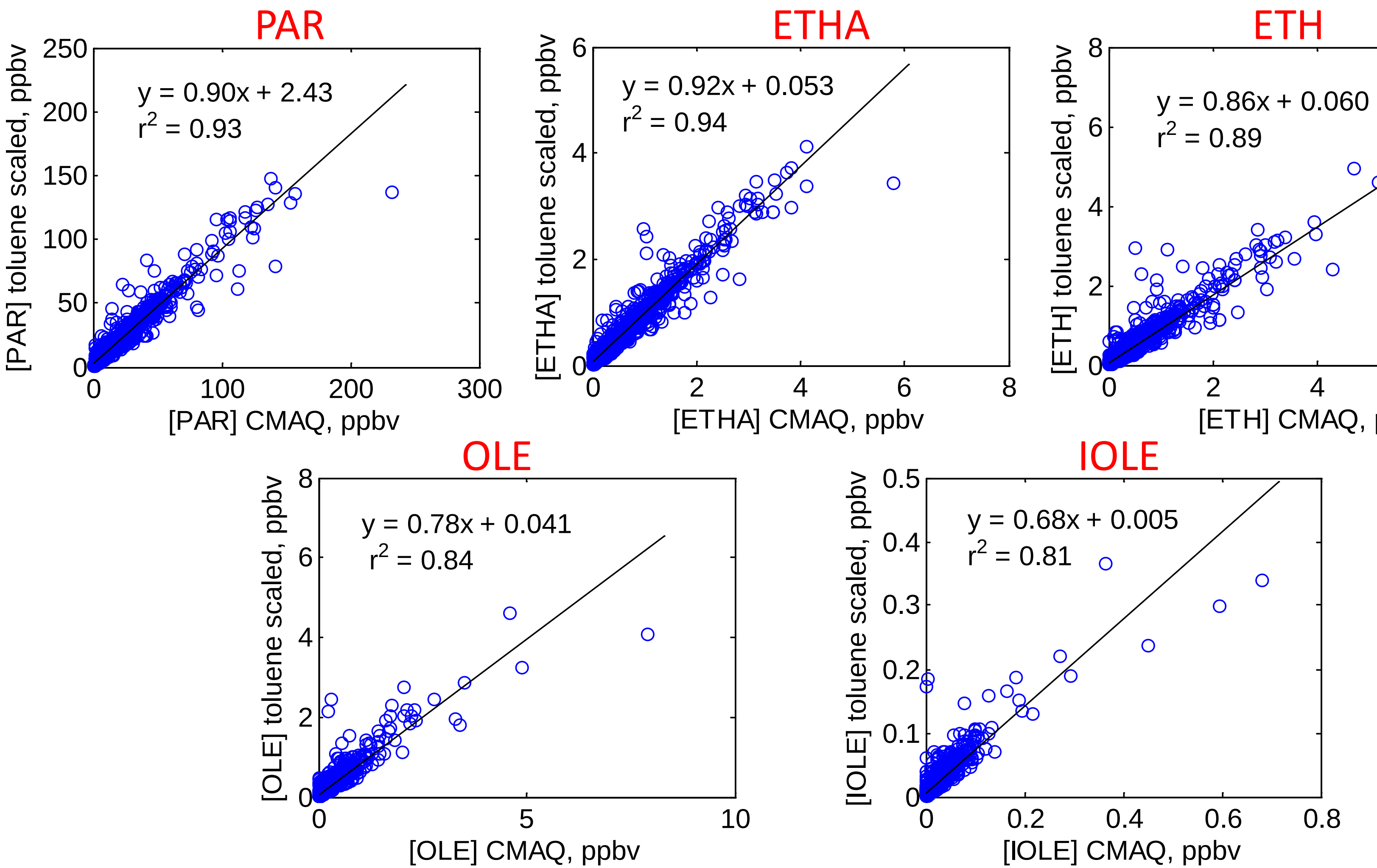
[ETHA] = 9.28 x [Toluene]

[ETH] = 2.34 x [Toluene]

[OLE] = 1.84 x [Toluene]

[IOLE] = 0.218 x [Toluene]

Alkanes/Alkenes Input for the Box Model



- Good agreement between CMAQ-calculated and toluene-scaled VOCs
- We will conduct sensitivity analysis to assess the uncertainty.

Photochemical $P(O_3)$ Calculation

NO_x-O_3 photo-stationary state

(1) $NO_2 + h\nu \rightarrow NO + O(^3P)$

(2) $O(^3P) + O_2 \rightarrow O_3$

(3) $O_3 + NO \rightarrow NO_2 + O_2$

No net O_3 is produced.

(4) $HO_2 + NO \rightarrow NO_2 + OH$

(5) $RO_2 + NO \rightarrow \alpha\, NO_2 + RO$

Net O_3 is produced.

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

α_i: NO_2 yield in RO_{2i}+ NO

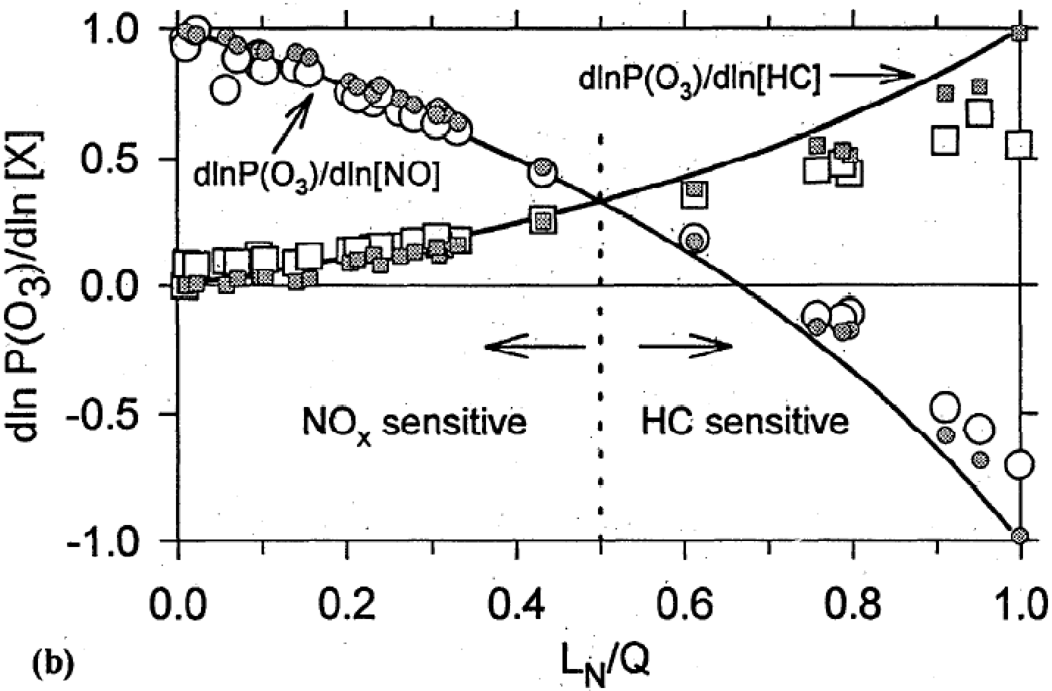
$$L(O_3) = k_{OH+NO2+M}\,[OH][NO_2][M] + k_{O1D+H2O}[O(^1D)][H_2O]$$
$$+\, k_{HO2+O3}\,[O_3][HO_2] + k_{OH+O3}[O_3][OH] + \Sigma\, k_{O3+VOCi}\,[O_3][VOC_i]$$

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

$P(O_3)$ Sensitivity to NO_x and VOCs

- L_N: Radical loss due to NOx
- Q: Total primary radical production
- L_N/Q: the fraction of radical loss due to NOx
- $L_N/Q > 0.5$: VOC-sensitive
- $L_N/Q < 0.5$: NOx-sensitive

(Kleinman, Atmos. Environ., 2005)

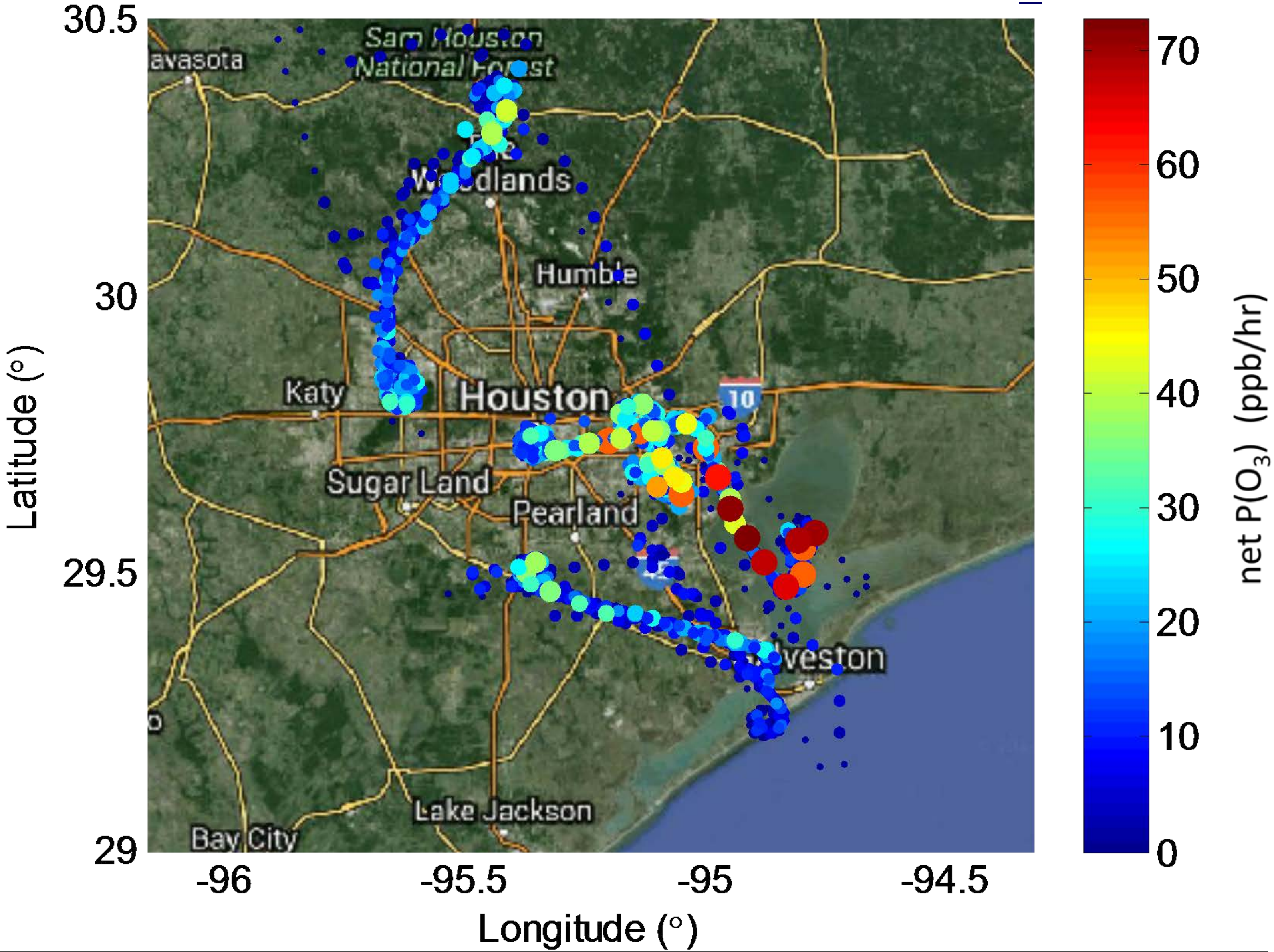


$$P(O_3) = KQ^{C1}[NO_x]^{C2}(VOC_R)^{C3}$$

$$\frac{d\ln P(O_3)}{d\ln [NO_x]} = \frac{(1 - 3/2\, L_N/Q)}{(1 - 1/2\, L_N/Q)},$$

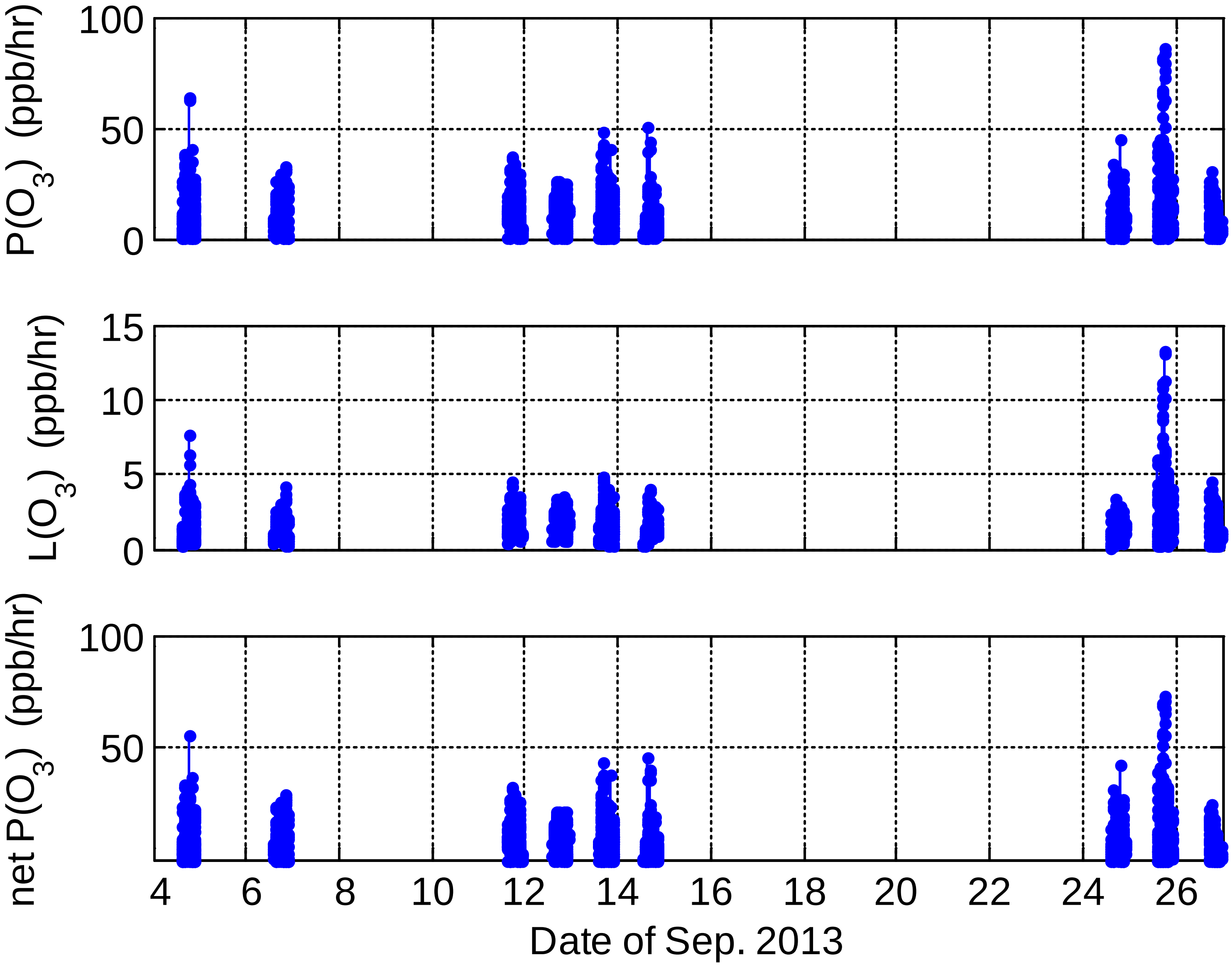
$$\frac{d\ln P(O_3)}{d\ln (VOC_R)} = \frac{1/2\, L_N/Q}{(1 - 1/2\, L_N/Q)}$$

Spatial variations of net $P(O_3)$



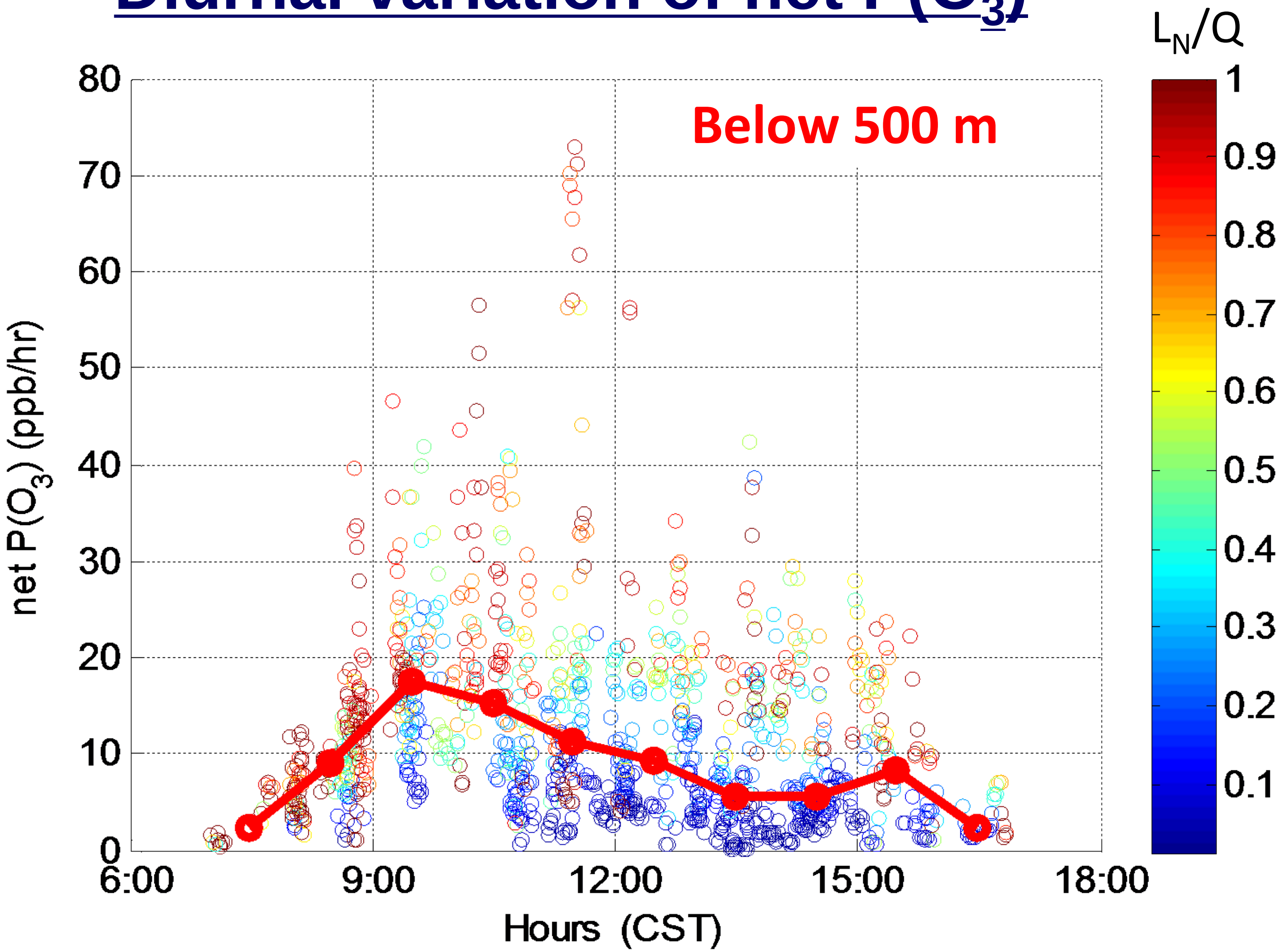
- $P(O_3)$ hot spots: Houston Ship Channel and its downwind over Galveston Bay

Time series of $P(O_3)$, $L(O_3)$, and net $P(O_3)$



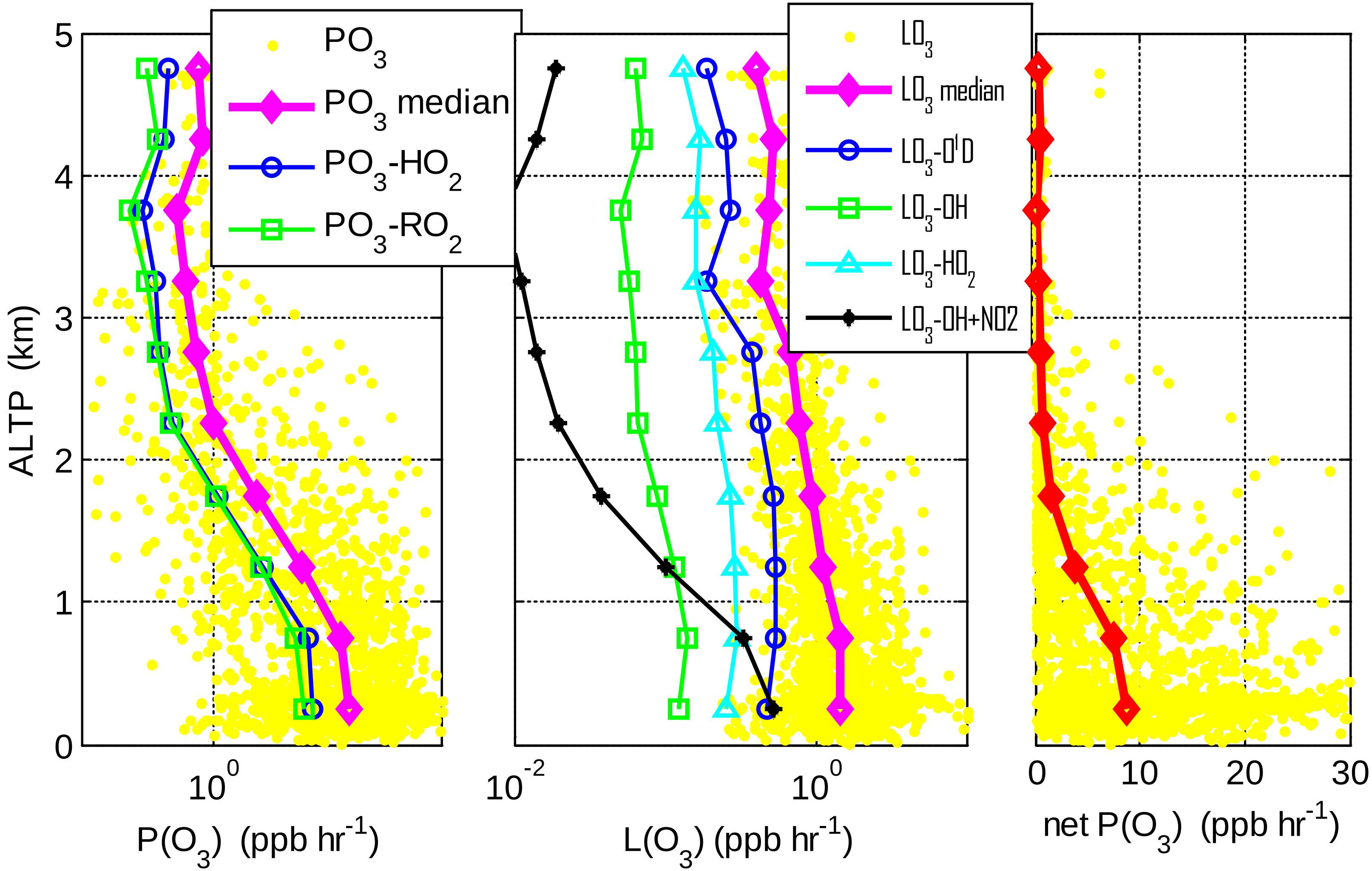
Note: the highest $P(O_3)$ on Sep. 25

Diurnal variation of net P(O_3)



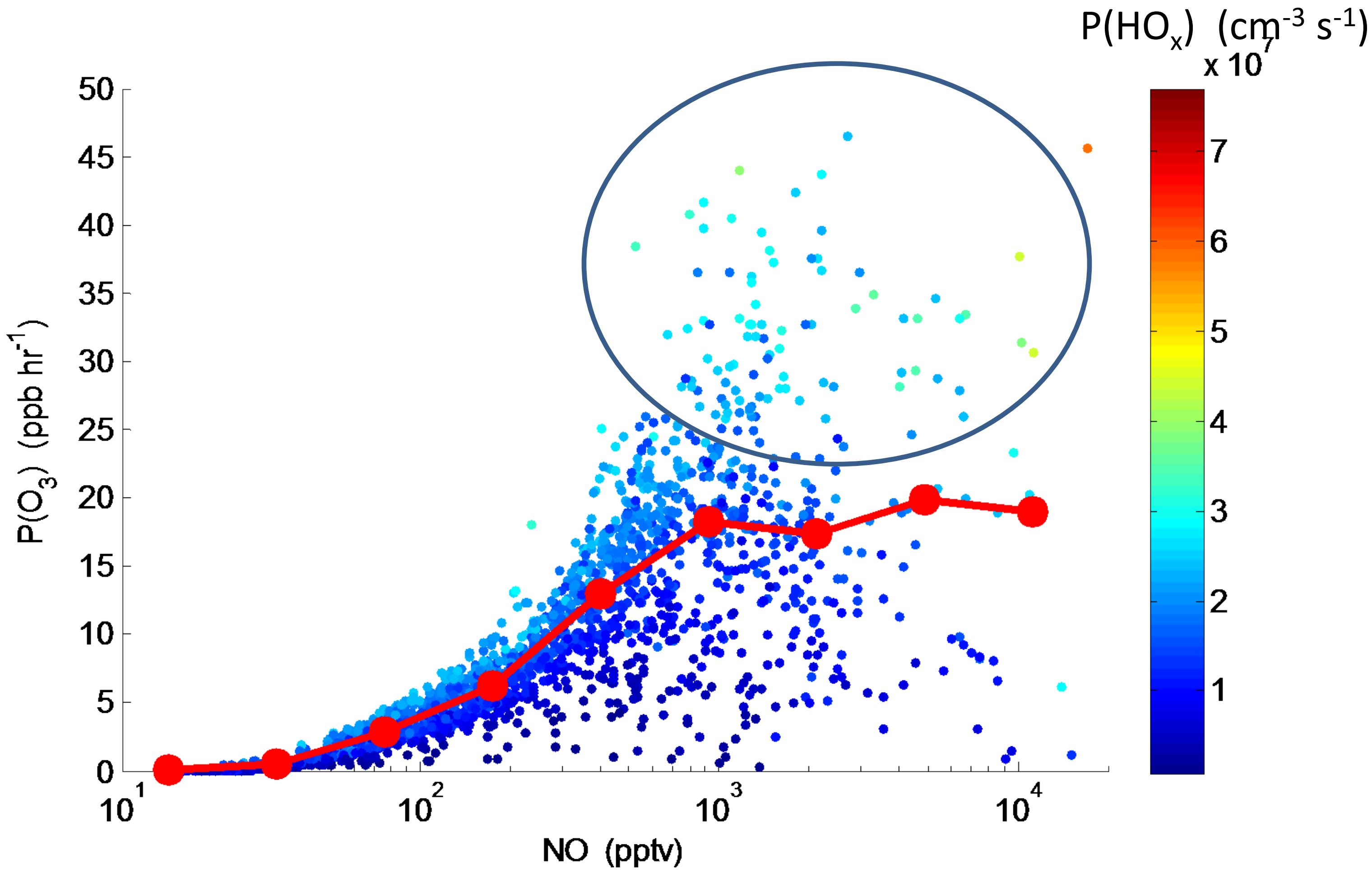
- High P(O_3) mainly with $L_N/Q > 0.5$ (i.e., VOC sensitive)
- A broad peak in the morning, with significant P(O_3) in the afternoon

Vertical profiles of P(O_3), L(O_3), and net P(O_3)



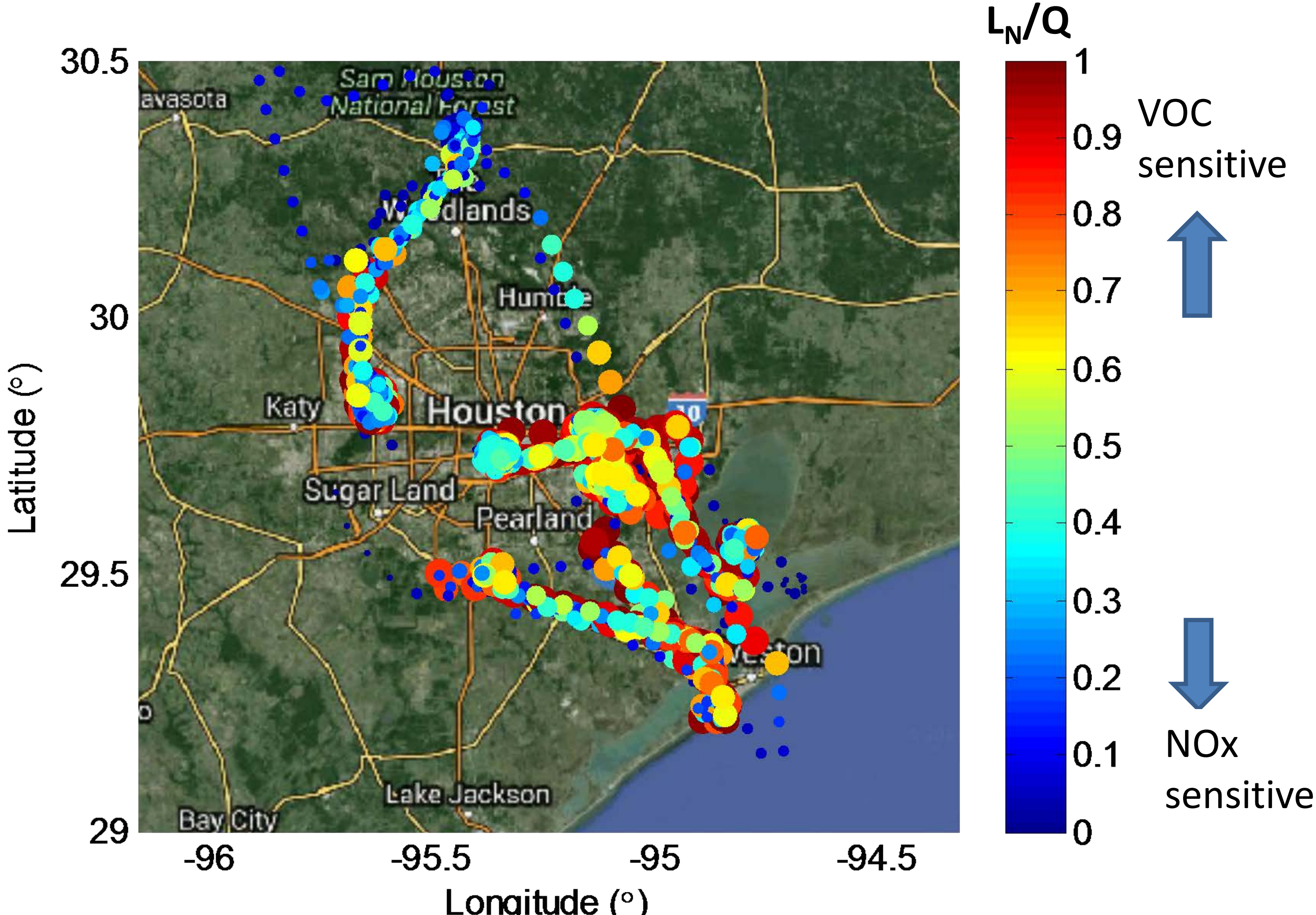
- P(O_3): RO_2+ NO makes about the same O_3 as HO_2+NO in the model.
- L(O_3): O_3 photolysis followed by O(^{1}D)+H_2O is a dominant photochemical ozone loss .
- Net P(O_3): maximum near the surface

Dependence of $P(O_3)$ on NO and $P(HO_x)$



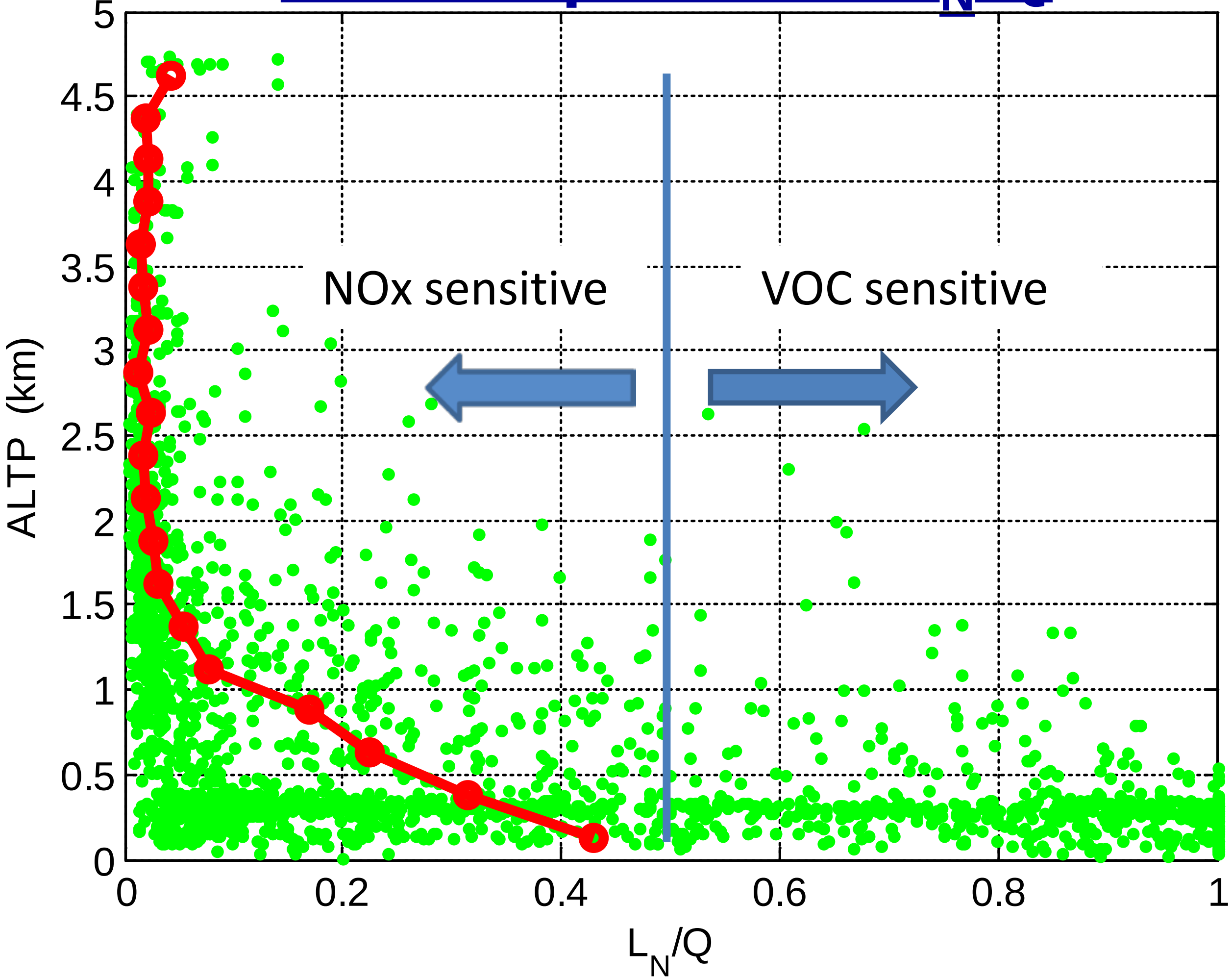
- [NO] < ~1 ppbv: $P(O_3)$ increases as [NO] increases
- [NO] > ~1ppbv: $P(O_3)$ levels off as [NO] further increases
- Higher P(HOx) ➔ higher $P(O_3)$

P(O_3) sensitivity to NOx and VOCs



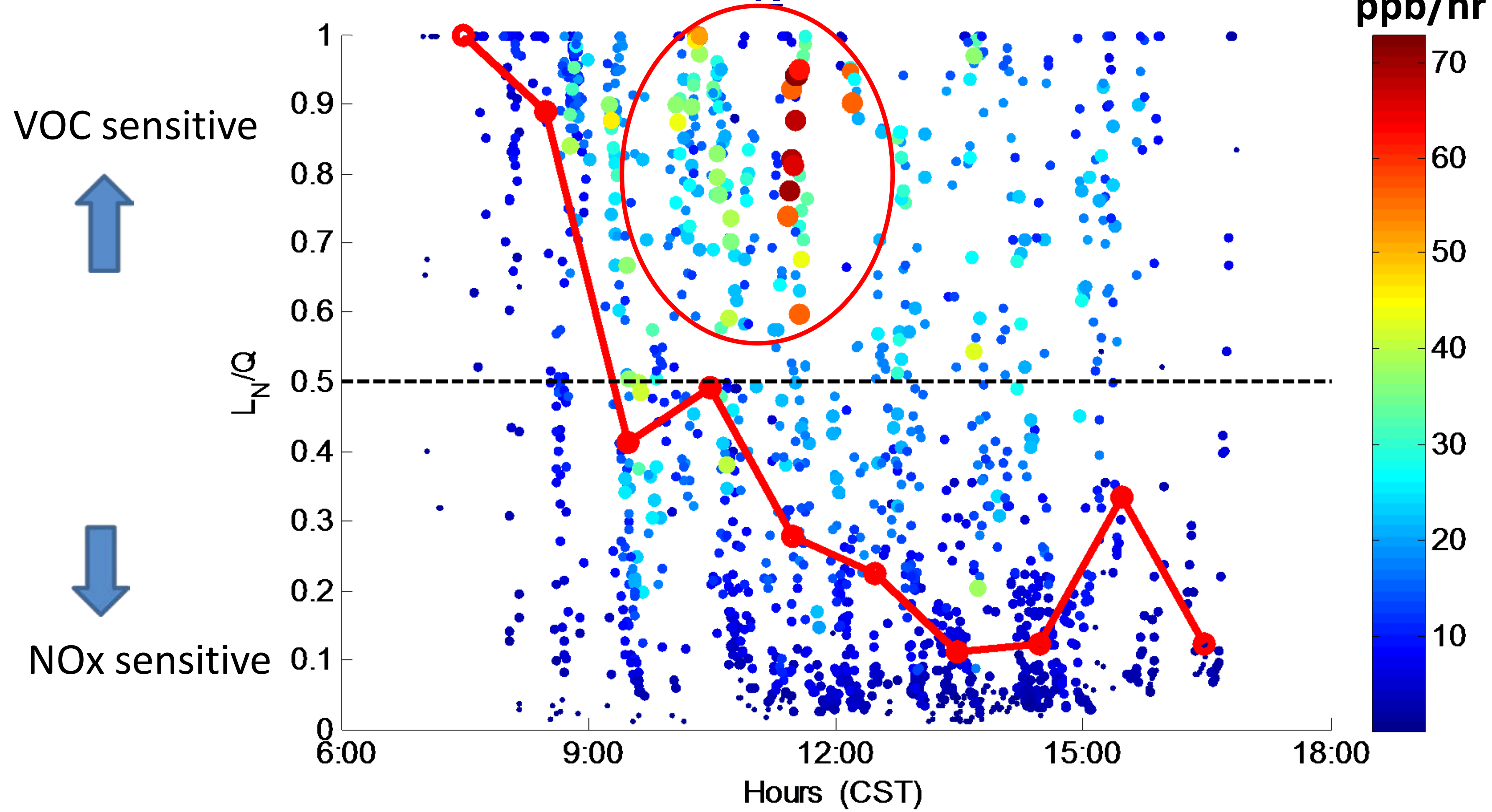
• P(O_3) tends to be more VOC sensitive in the urban center and Ship Channel.

Vertical profile of L_N/Q



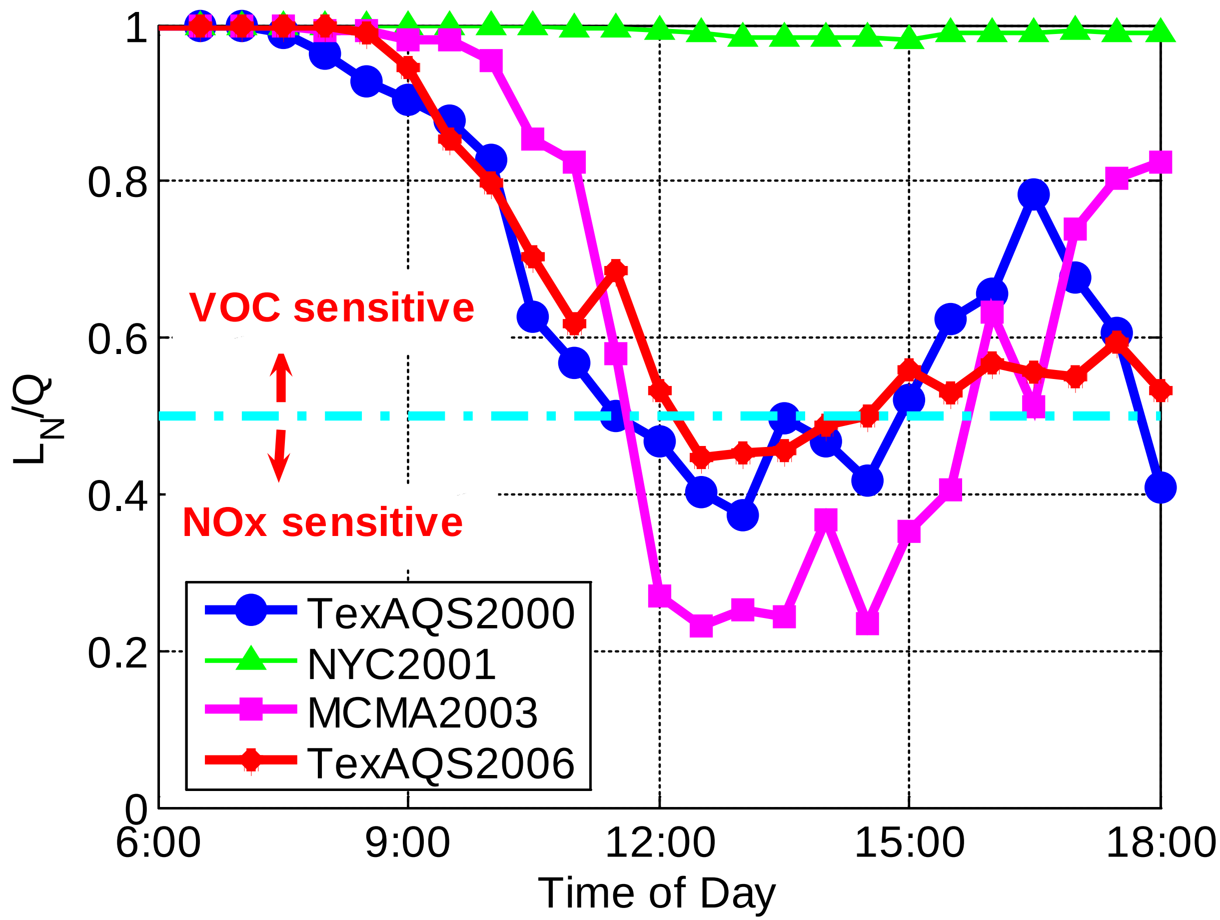
- Above ~500 m, $P(O_3)$ is NOx sensitive in general.
- Below ~500 m, either NOx or VOC sensitive

Diurnal Variation of L_N/Q below 1000 m



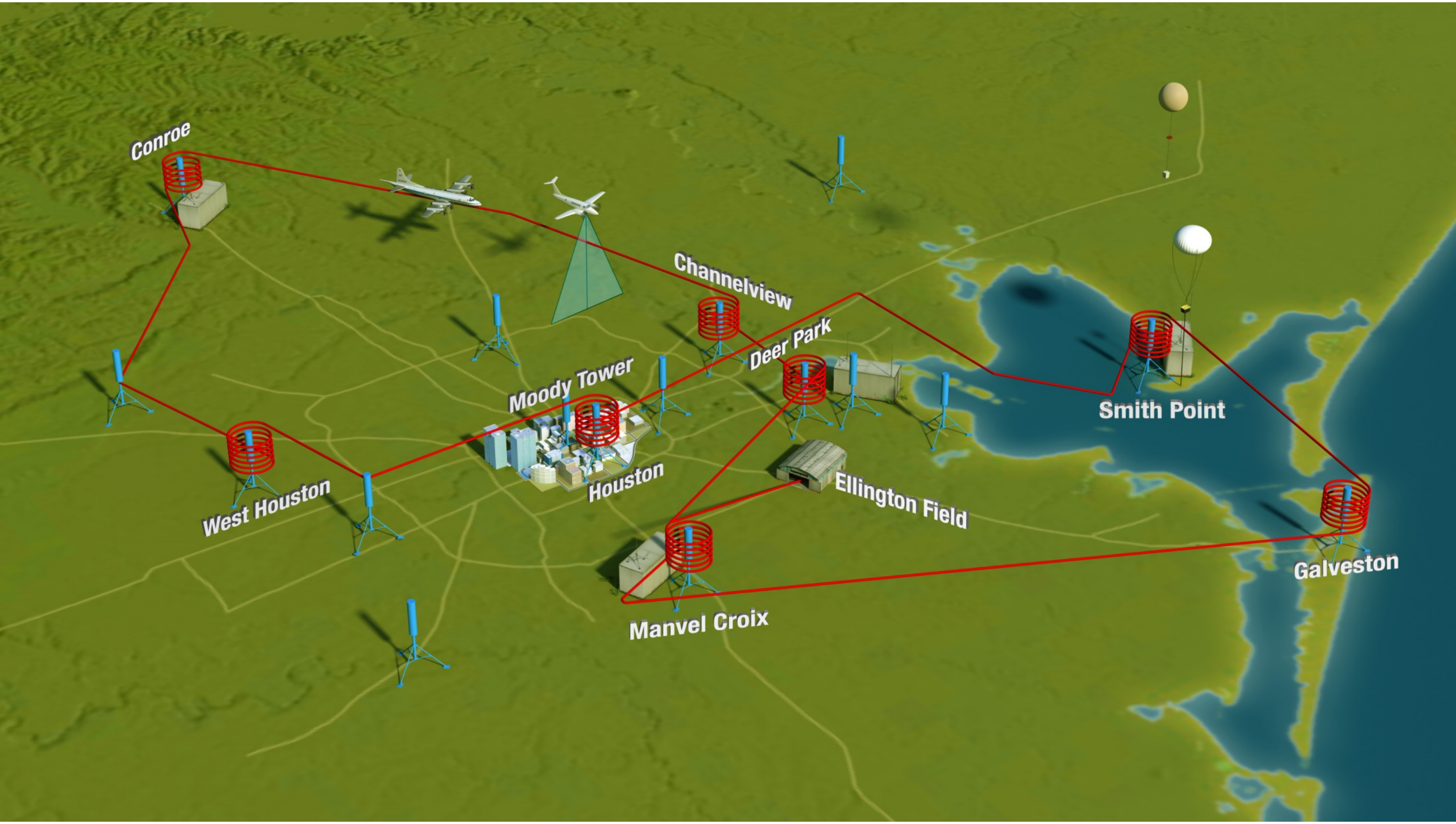
- $P(O_3)$ towards more VOC sensitive in the early morning and then towards more NOx sensitive later the day.
- High $P(O_3)$ in the morning with VOC sensitive
- There are spots/times with VOC sensitive in the afternoon.

Sensitivity of $P(O_3)$ in Some Ground-based Studies

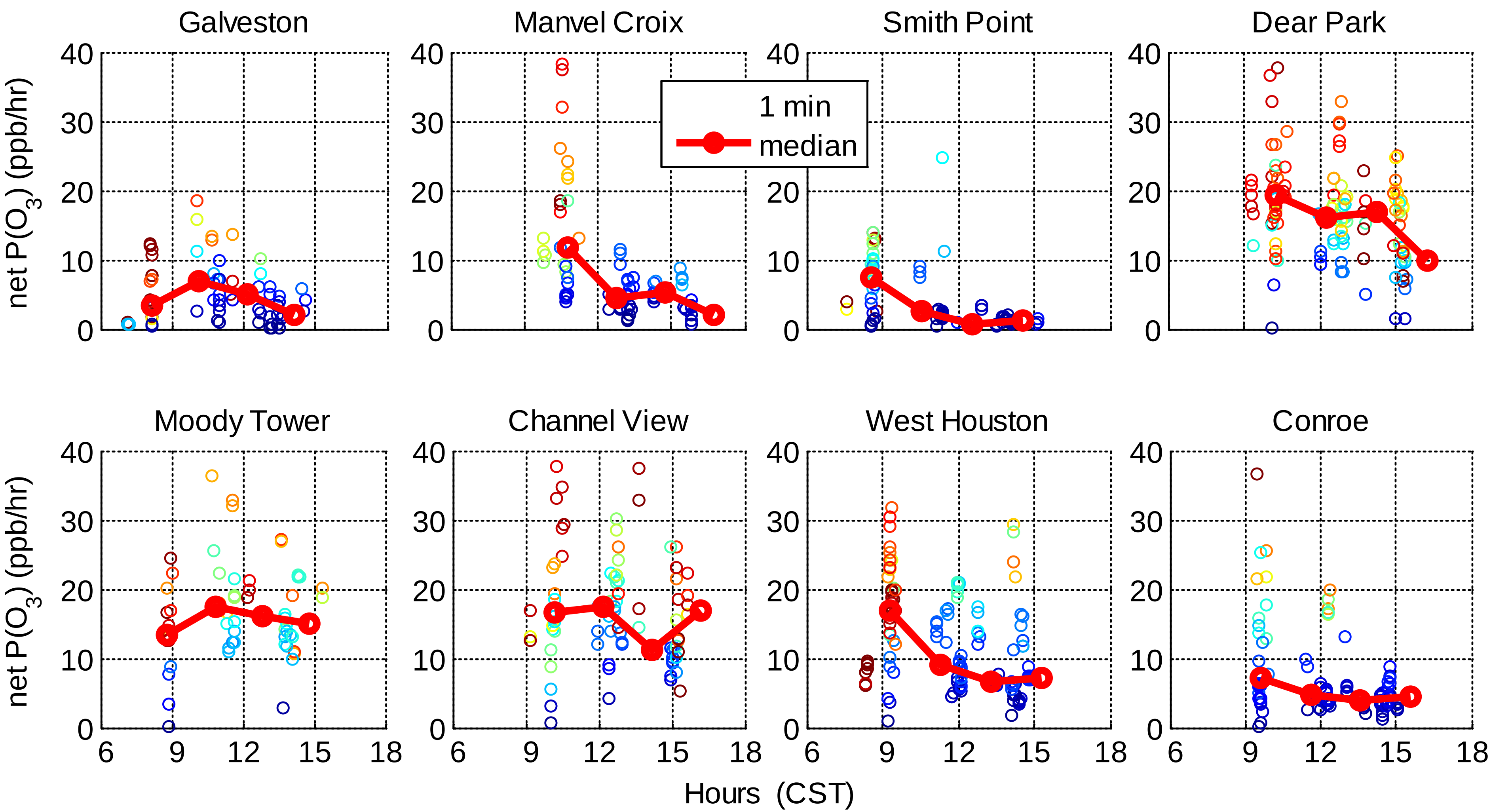


- Similar trends in airborne and ground-based studies in Houston, except in the afternoon.
- Houston and Mexico City are similar, both having large VOC levels.
- $P(O_3)$ in New York City (NYC) was exclusively VOC sensitive.

P(O_3) and Its Sensitivity at Spiral Locations

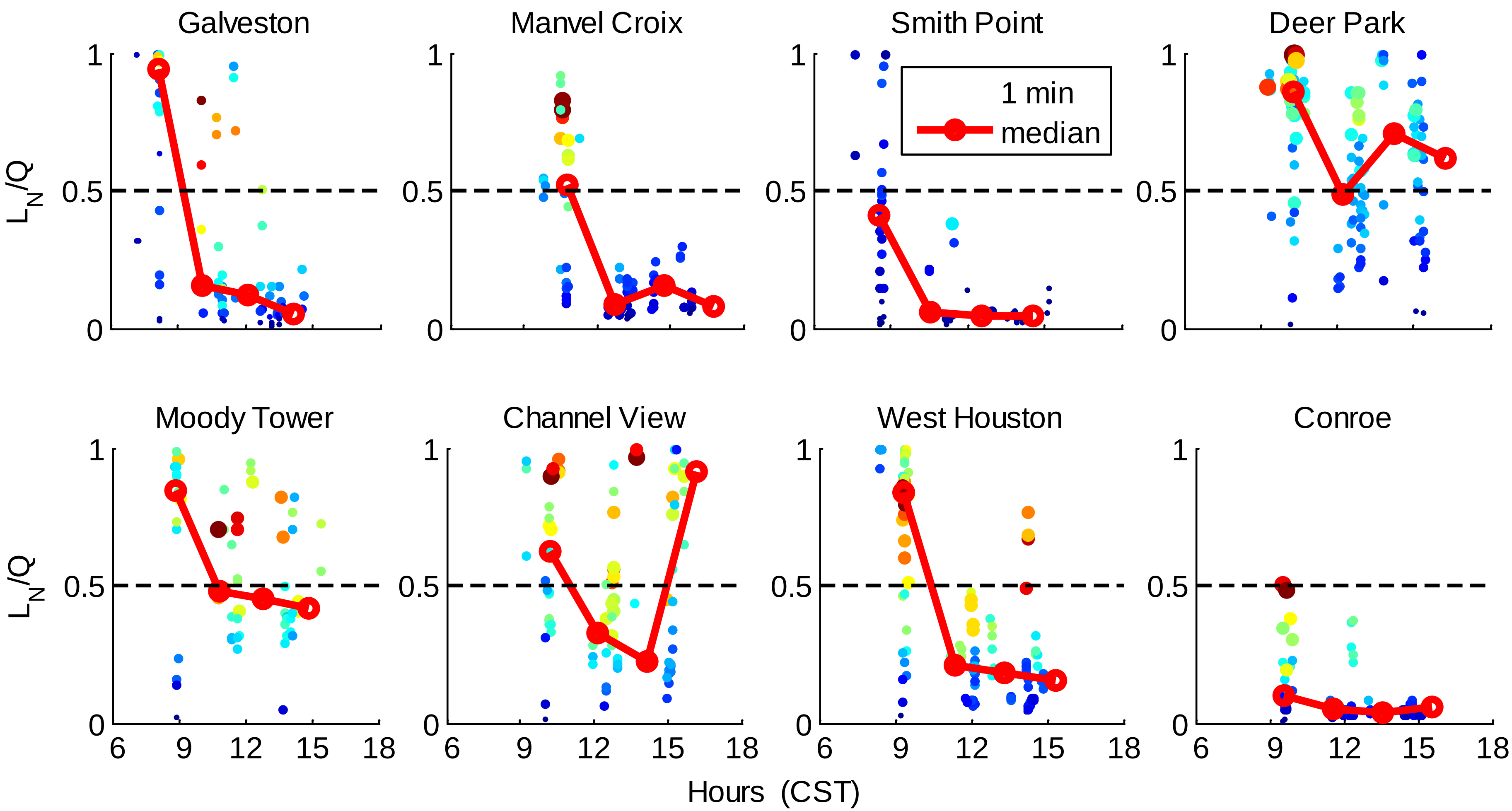


Net P(O_3) at 8 Spiral Sites below 1000 m



- Deer Park, Moody Tower and Channel View: P(O_3) > 10 ppb hr^{-1} on average
- Galveston, Smith Point, and Conroe: P(O_3) < 10 ppb hr^{-1} on average

L_N/Q at 8 Spiral Sites below 1000 m



- At Dear Park: $P(O_3)$ is mostly VOC sensitive for the entire day.
- At Moody Tower and Channel View: $P(O_3)$ is VOC sensitive or in the transit regime.
- At Smith Point and Conroe: $P(O_3)$ is mostly NOx sensitive for the entire day.

Summary

$P(O_3)$ in Houston:

- Averages below 500 m: 20-30 ppb/hr in the morning
  5-10 ppb/hr in the afternoon
- Increases as [NO] increases up to 1 ppbv and then levels off.
- Hot spots in Houston Ship Channel and Galveston Bay

$P(O_3)$ sensitivity : temporally & spatially variable

- Tends to be more VOC sensitive in the morning with high $P(O_3)$—control of VOC is a way to effectively control O_3 .
- Generally NOx sensitive in the afternoon with spatial variations

On-going work

- CMAQ process analysis on $P(O_3)$ and comparison with box model
- Investigate ozone production efficiency at different locations at different times of day
- Sensitivity analysis of the use of CMAQ-calculated alkanes and alkenes to constrain the box model
- Compare modeled $P(O_3)$ with measured $P(O_3)$ at the Moody Tower site

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