Measurements of Trace Gases at the Manvel Croix and Galveston Sites during DISCOVER-AQ

Winston Luke[1], Paul Kelley[1,2], Xinrong Ren[1,2]

[1]NOAA Air Resources Laboratory

[2]Dept of Atmos. & Oceanic Sci., Univ. of Maryland

Outline

- Data collection during DISCOVER-AQ
- Data status
- Preliminary data analysis
  a) Trace gases measurements at two ground sites
  b) Comparisons of surface measurements with the NASA P-3B measurements
  c) Ozone production efficiency

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DISCOVER-AQ in Houston in September 2013

Site selection:

(1) Manvel Croix

- S of downtown Houston
- SSW of Ship Channel

(2) Galveston

- SSE of Texas City
- SE of downtown Houston and Ship Channel

Manvel Croix Site

NO_2 Analyzer based on Cavity Ring-Down Spectroscopy (CRDS)

The CRD NO_2 analyzer includes:
(1) An in-line internal air dryer to remove moisture in the sample air
(2) A metal oxide scrubber to provide a chemical zero.

Detection limit: ~30 pptv (1σ, 1 min)

TCEQ also conducted O_3, NO/NOx and Met measurements.

Manvel Croix Site

CRD NO_2 Analyzer Operation:

- Continuous measurement from Aug. 31 to Sept. 28, 2013
- Data were recorded at 1 Hz and are averaged to 10 s and 1min.
- Auto zero using scrubber every 30 min
- Daily zero/span using zero air and NO_2 calibration gas
- Full calibrations before/during/after the field deployment using both NO_2 cal gas and Gas Phase Titration (GPT)
- Weekly filter changes

Galveston Site

We deployed:

- 3-channel NO/NO_2/NOy system based on chemiluminescence with NO_2 based on blue light photolysis conversion;
- O_3 based on UV absorption photometry;
- SO_2 based on pulsed fluorescence.

TCEQ also has O_3, NO/NOx and Met measurements.

Galveston Site

Instrument operation:

- Continuous measurement from Aug. 31 to Sept. 28, 2013
- Data were recorded at 1 Hz and are averaged to 1min.
- Hourly zero check using zero air
- Zero/span twice a day using zero air and SO_2/NO and NO_2 calibration gases
- Full calibrations before/during/after the field deployment using cal gases and GPT.
- Weekly filter changes and NOy inlet rinse

Data Status

- All data collected at the two sites have been finalized.
- Final data with 1-min time resolution will be submitted to the NASA DISCOVER-AQ archive soon.

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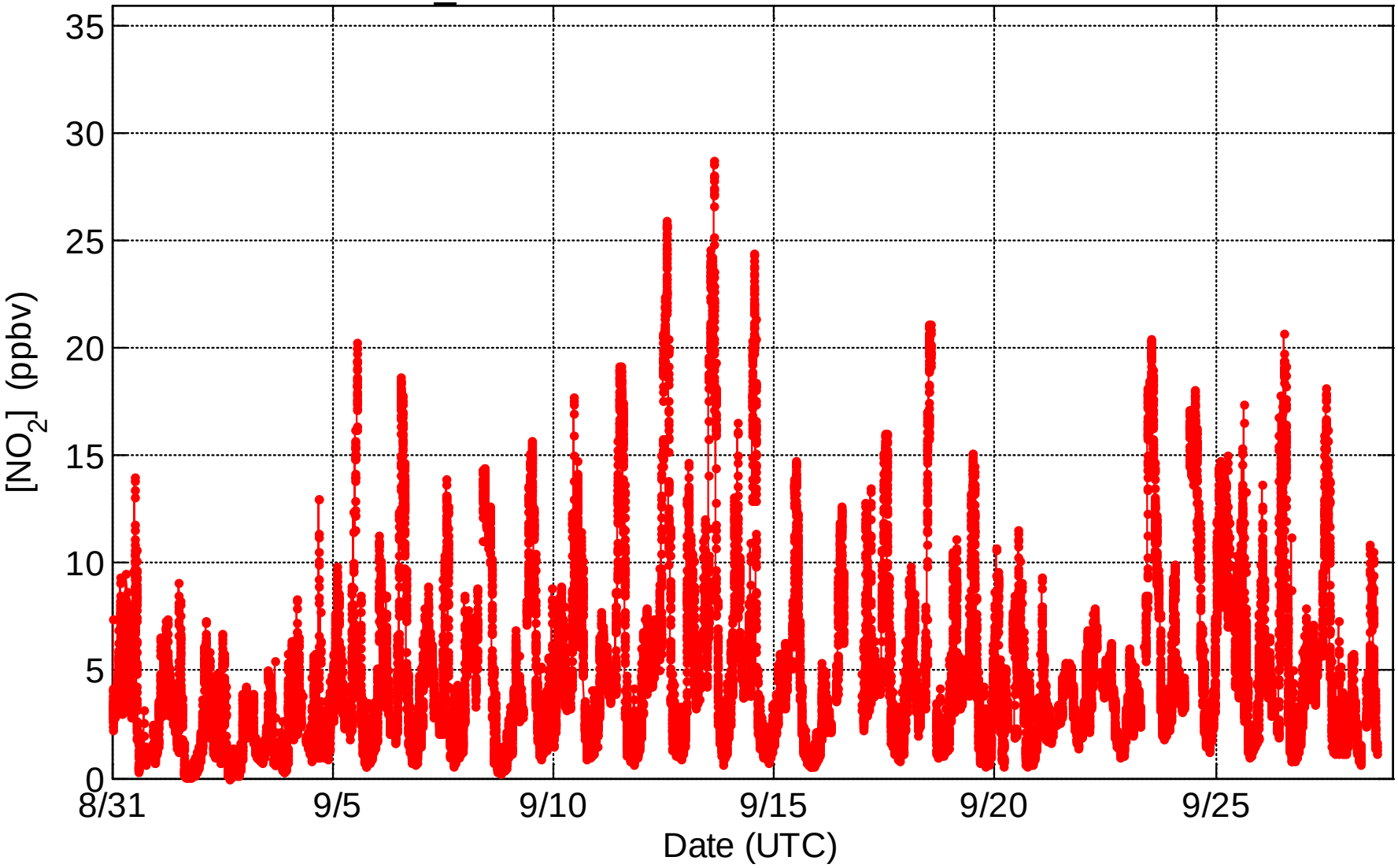
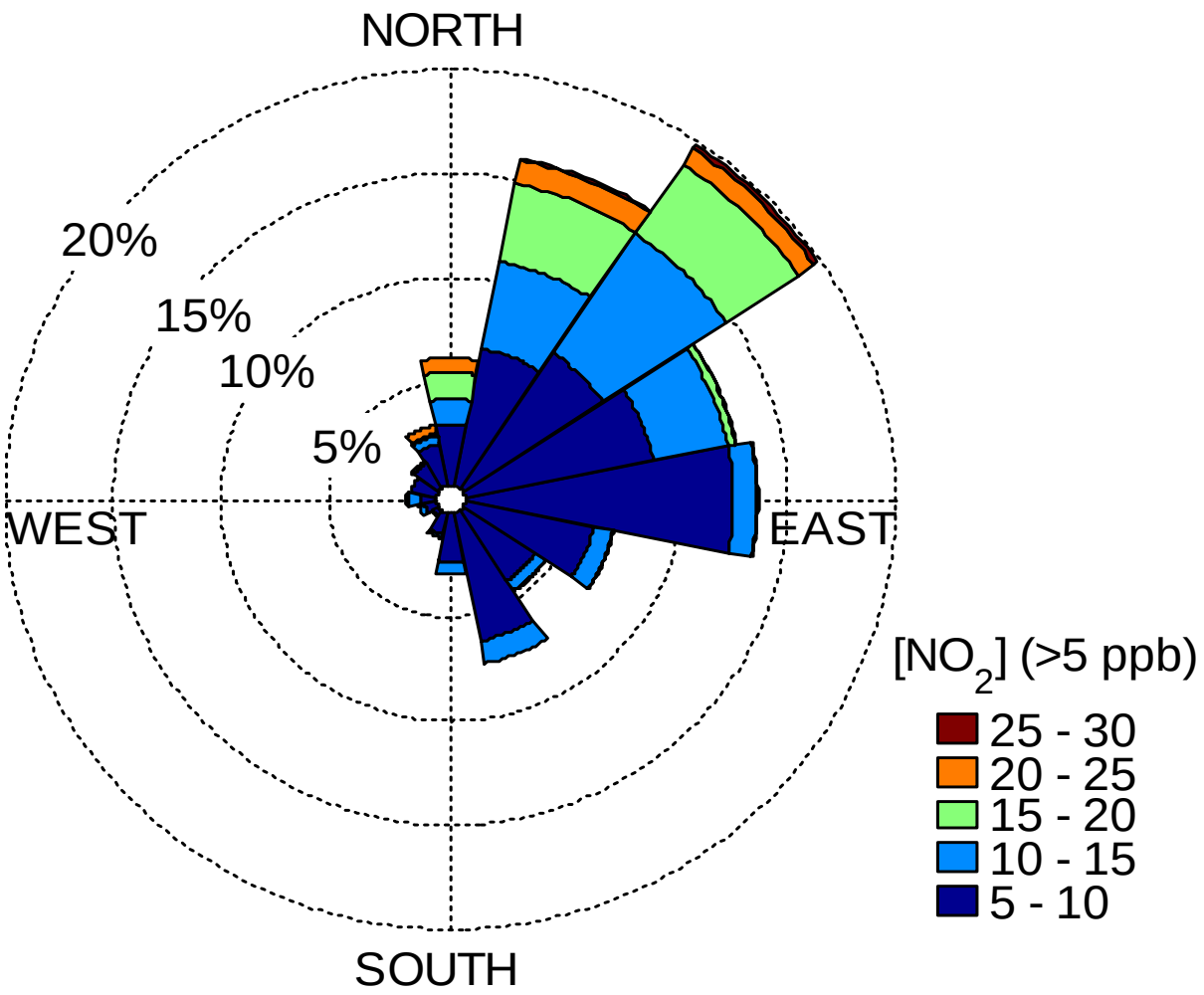
NO_2 at the Manvel Croix Site



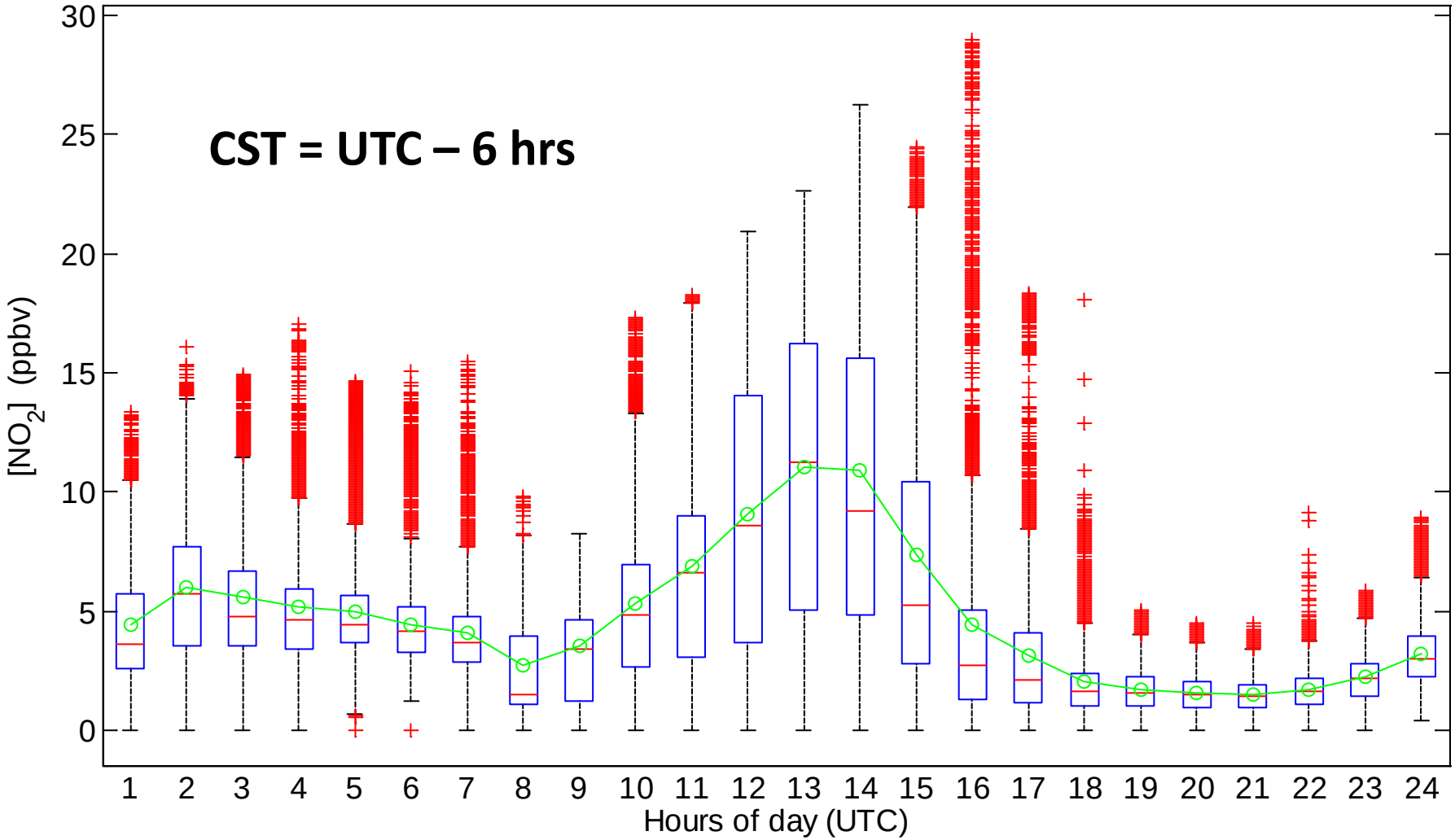
- Ranged from close to zero to 29 ppbv
- Typical day-to-day variations with peak during morning rush hour.

Elevated [NO_2] at the Manvel Croix Site



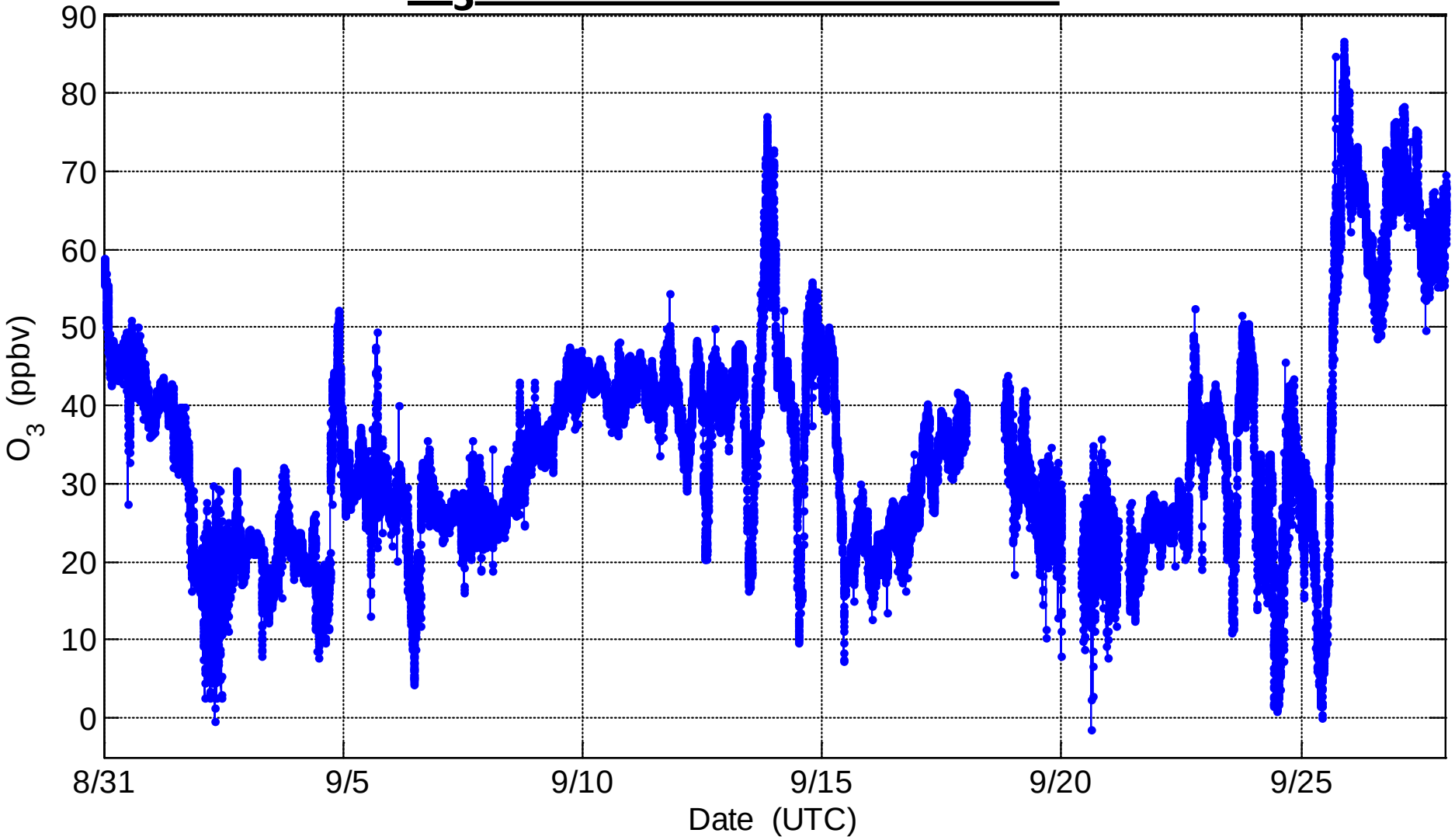
- The highest [NO_2] were observed in the winds from N & NE.
- Elevated [NO_2] were also observed in almost all directions, suggesting nearby local emissions.

Diurnal [NO_2] Variation at the Manvel Croix Site



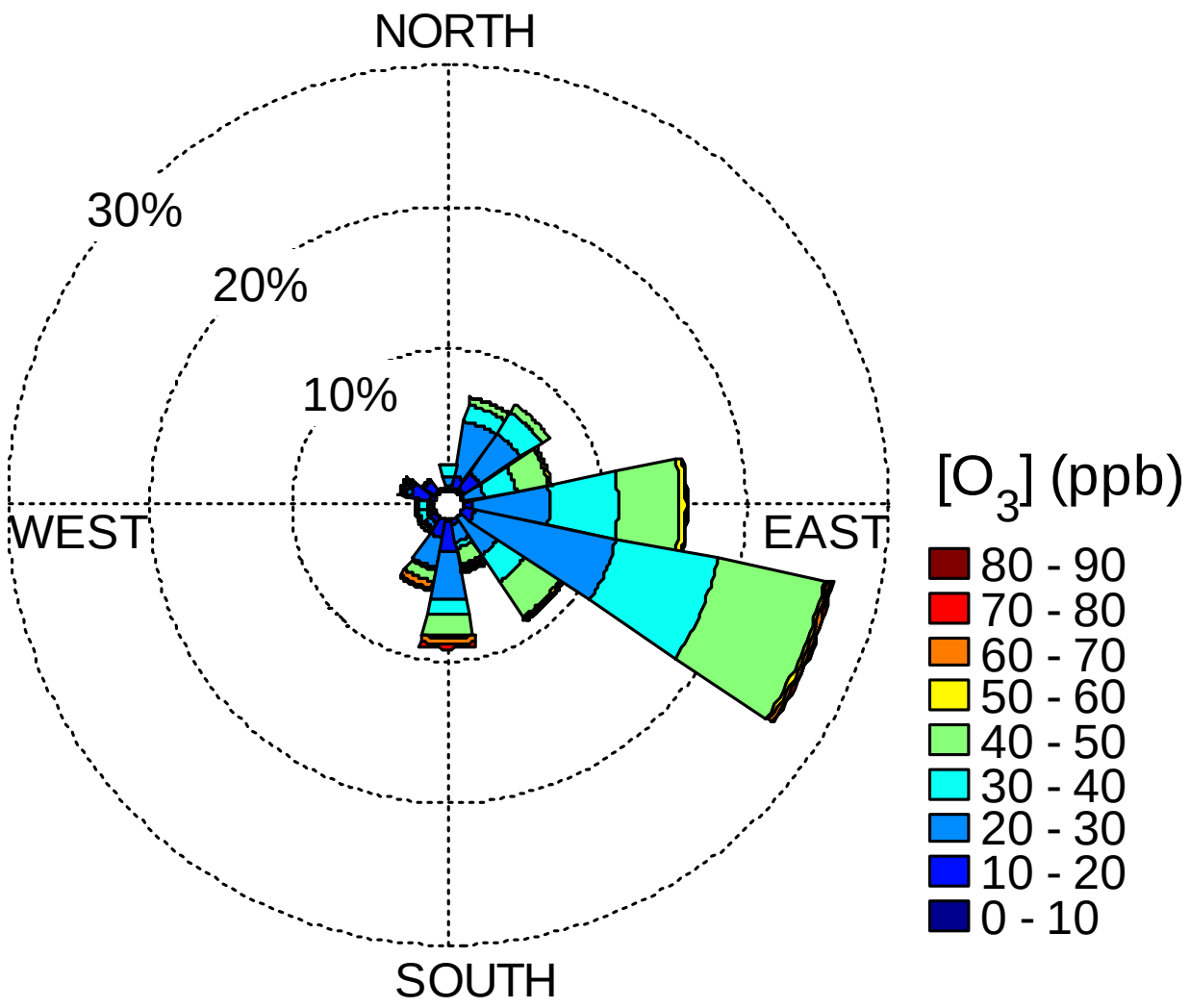
- Max. [NO_2] of 11 ppbv at ~13:00-14:00 UTC (7:00-8:00 CST).
- Min. [NO_2] of 1-2 ppbv between 19:00–21:00 UTC (13:00-15:00 CST)
- Slightly increasing in the late afternoon and early evening, mainly due to the afternoon rush hour traffic and lower boundary heights.

O_3 at the Galveston Site



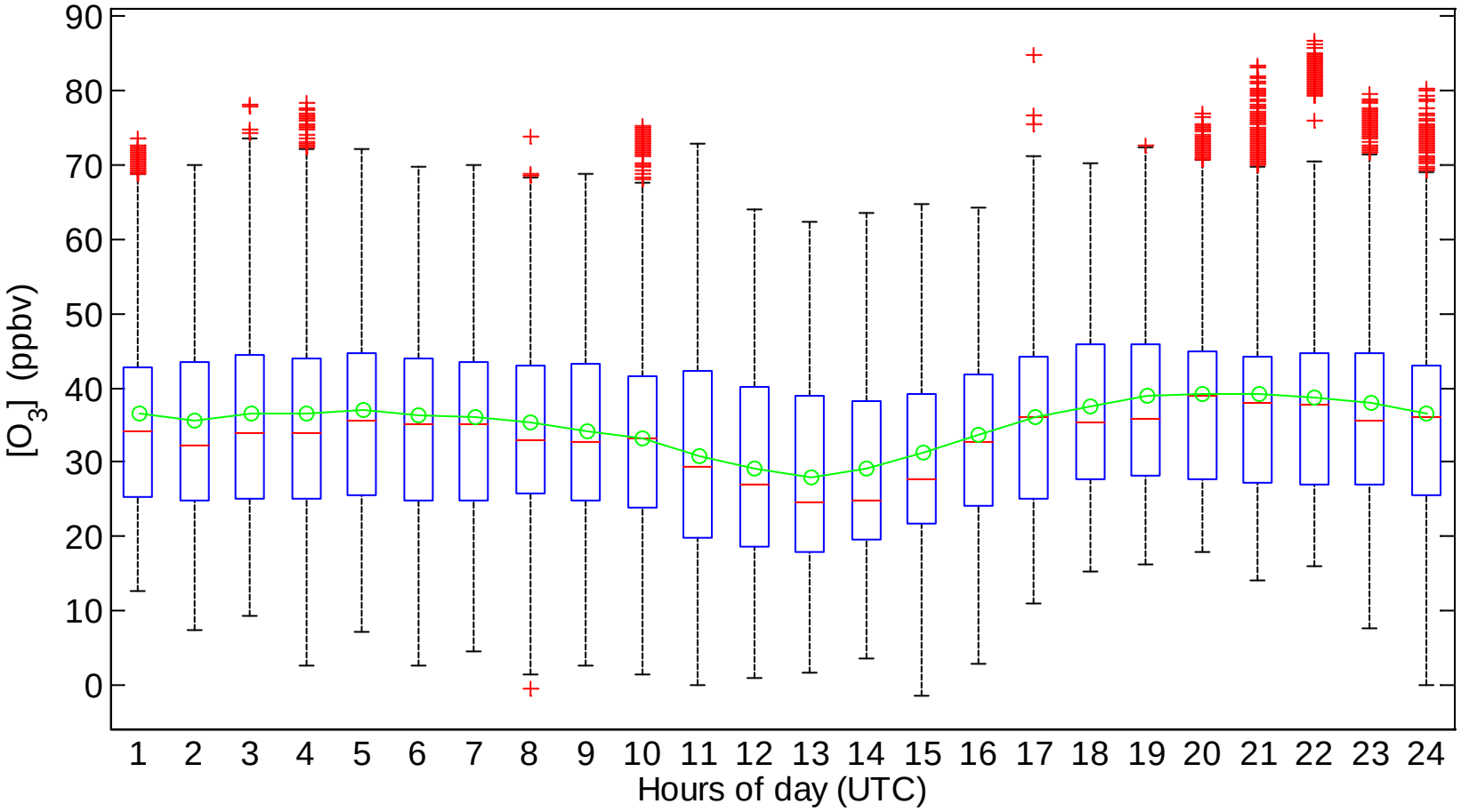
- A typical coastal site with influences from clean marine air masses, local emission sources, and pollution plumes
- Some of very low O_3 (close to zero) levels were due to titration by NO in early morning.

Wind dependence of $[O_3]$ at the Galveston Site



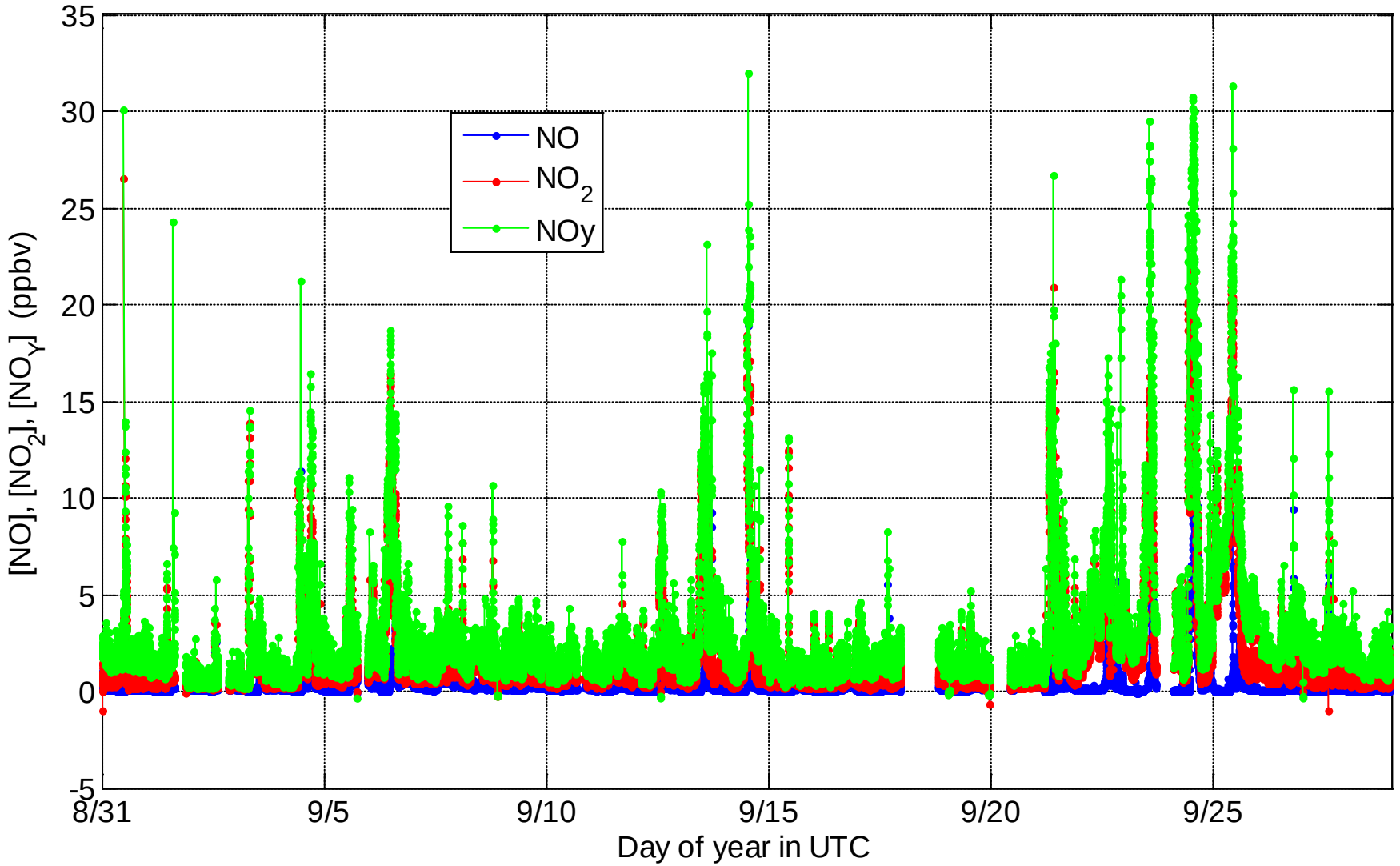
- Highest $[O_3]$ were observed in the winds from S & SE – recirculation?

Diurnal [O_3] Variation at the Galveston Site



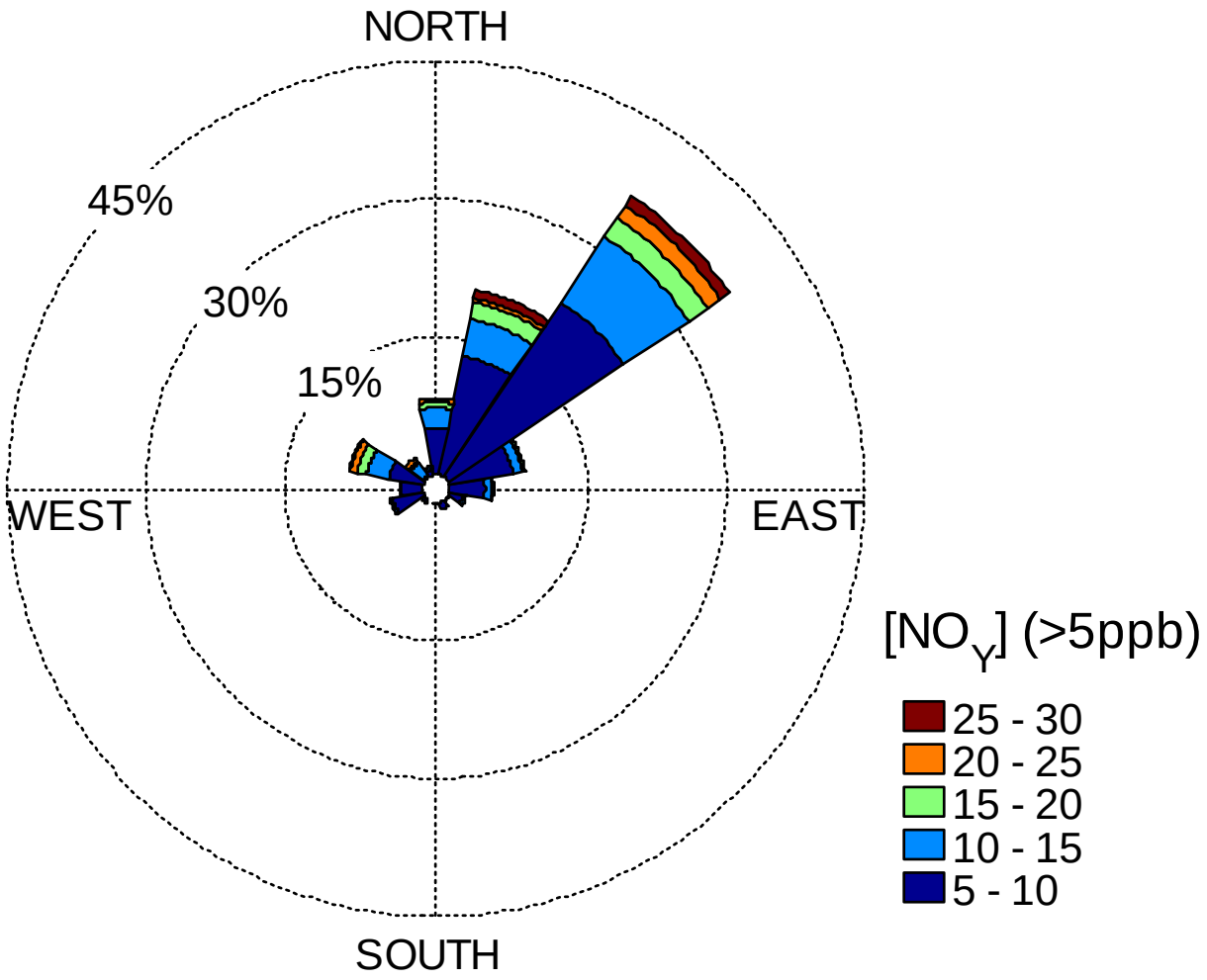
- Not much diurnal variation of [O_3] on average.
- Min. [O_3] of ~30 ppbv on average in the morning at 13:00 UTC (7:00 CST) due to high NOx levels during the morning rush hour.
- Nighttime [O_3] ~30 - 40 ppb with little variation.

$NO/NO_2/NO_Y$ at the Galveston Site



- Typical morning peaks during rush hour
- Max. 1-min averaged values : [NO]=19 ppb, $[NO_2]$=27 ppb and $[NO_Y]$=32 ppb

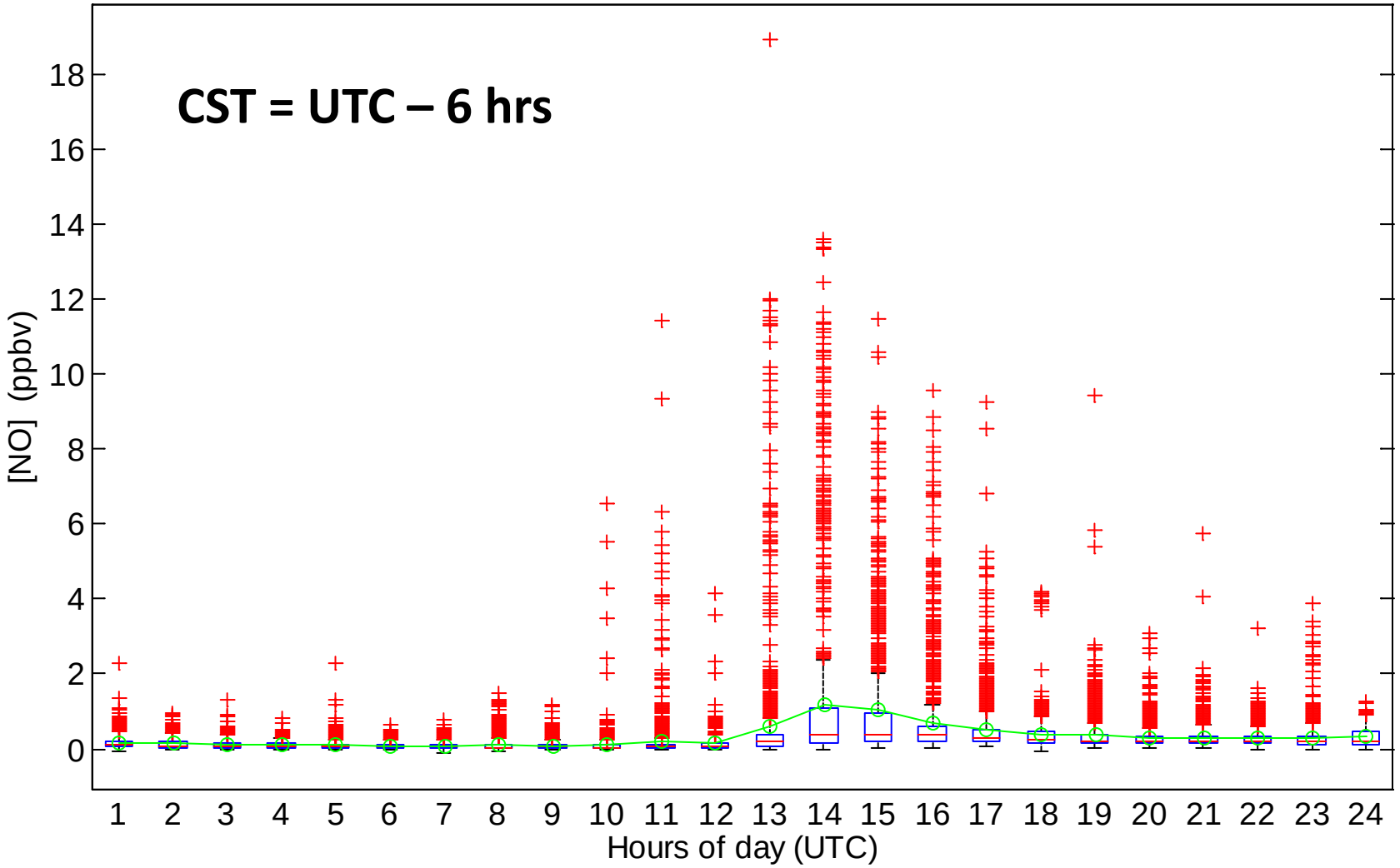
Wind dependence of [NO_Y] at the Galveston Site



- Highest [NO_Y] were observed in the winds from NNE

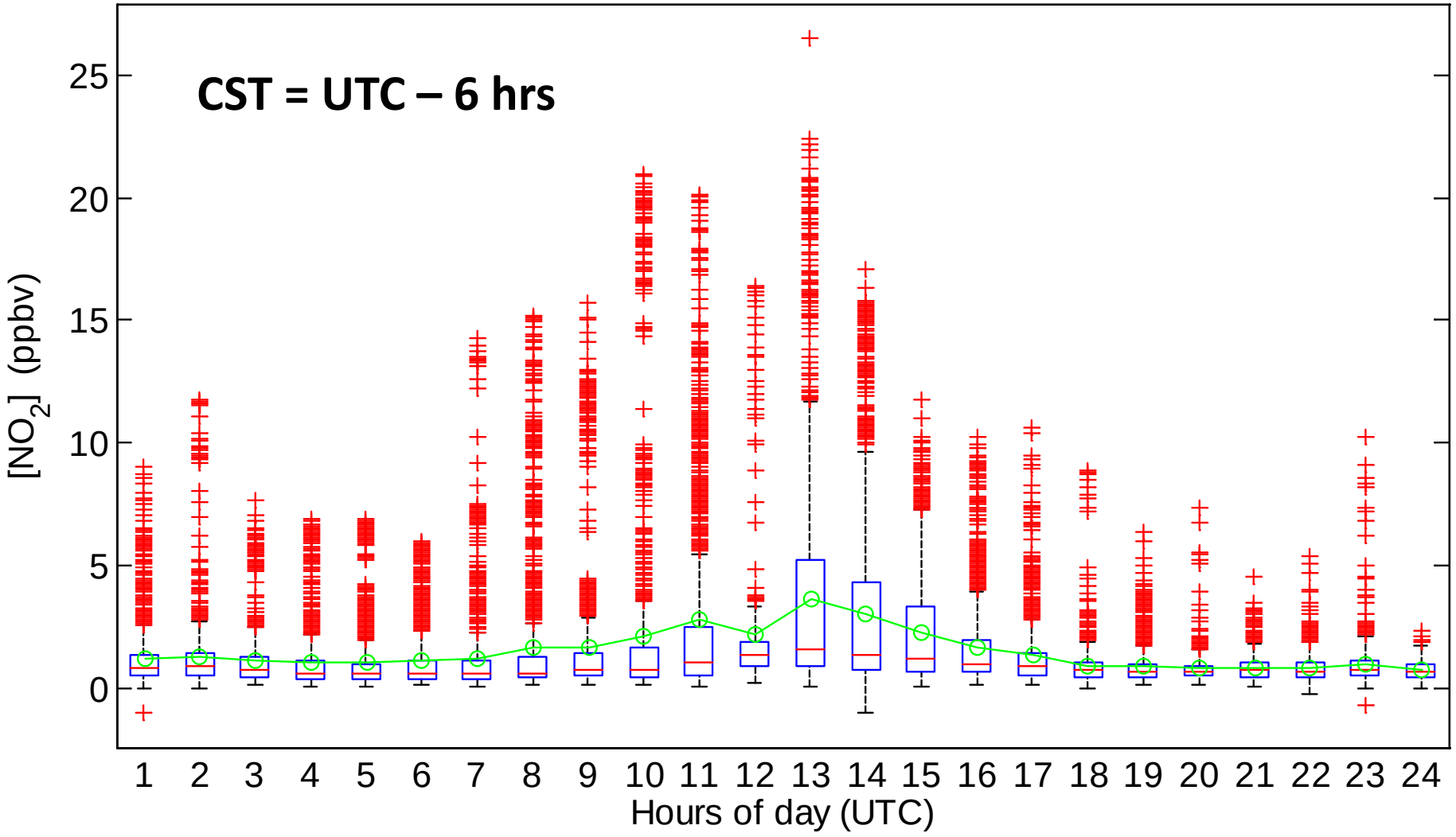
Influence of Galveston Port to the Galveston Site

Diurnal [NO] Variation at the Galveston Site



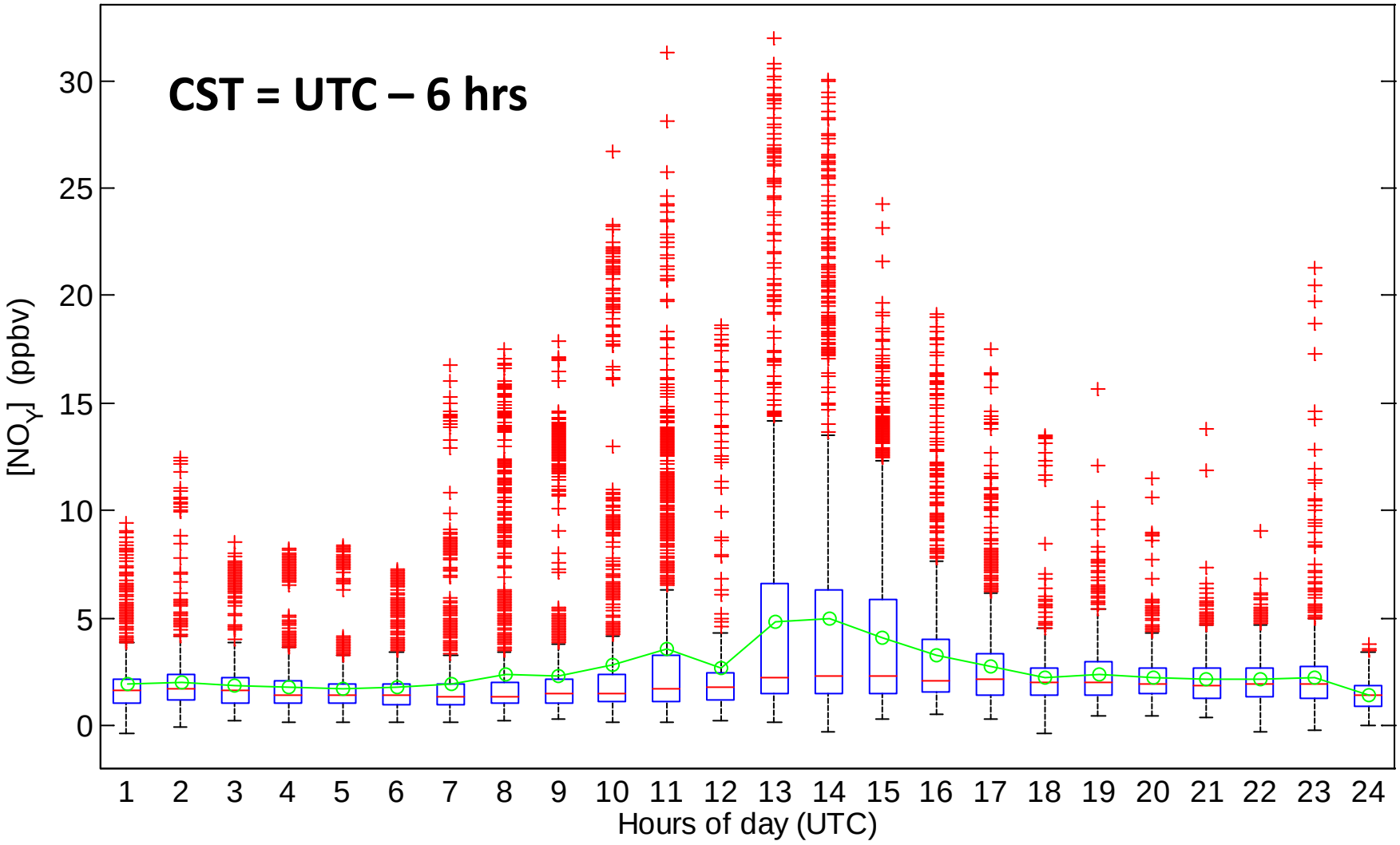
- Peak values in the morning and consistently low values at night.

Diurnal [NO_2] Variation at the Galveston Site



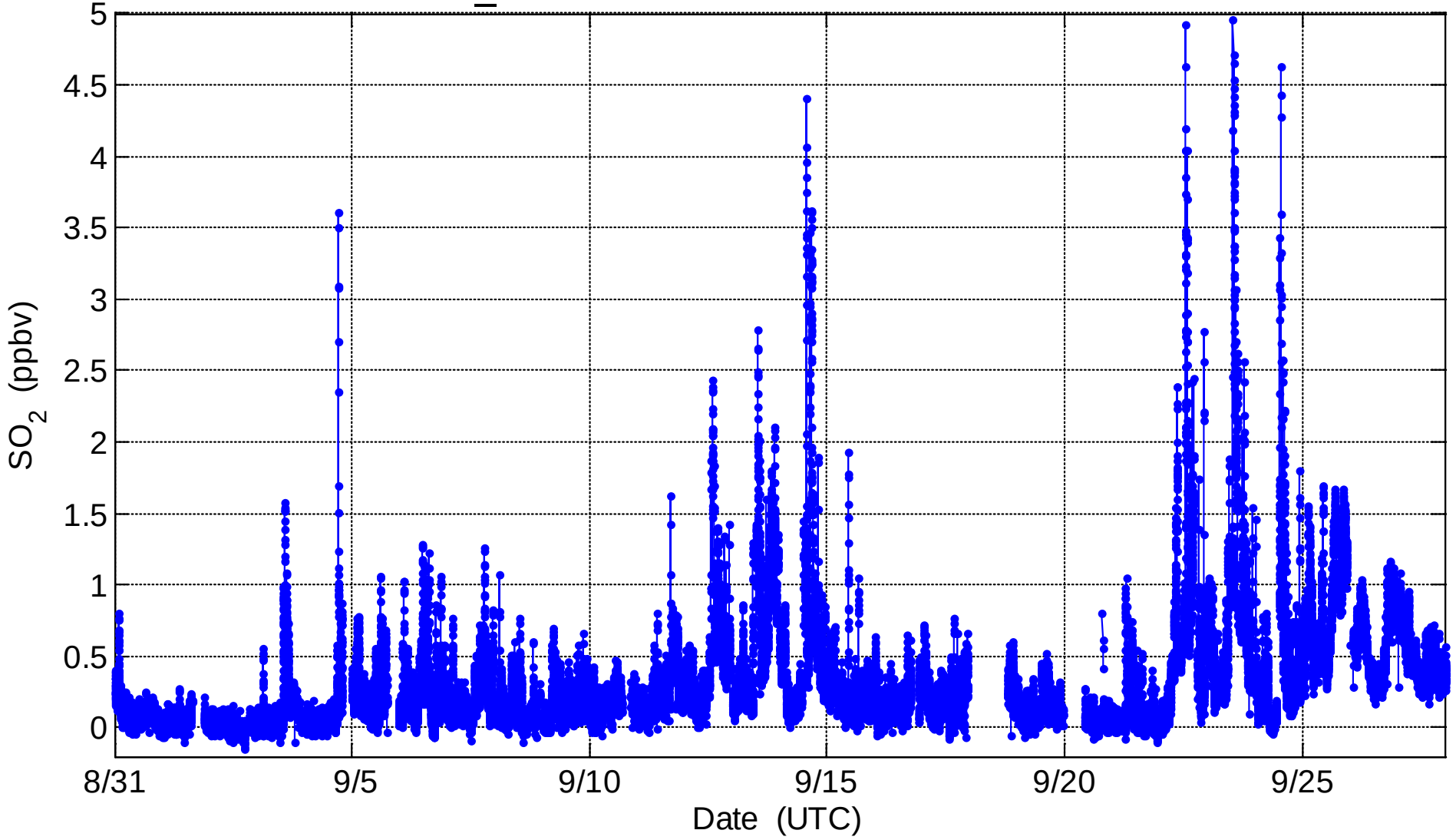
- Peak values in the morning and consistently low values at night.
- Different from the Manvel Croix site: no late afternoon/early evening increase.

Diurnal [NO_Y] Variation at the Galveston Site



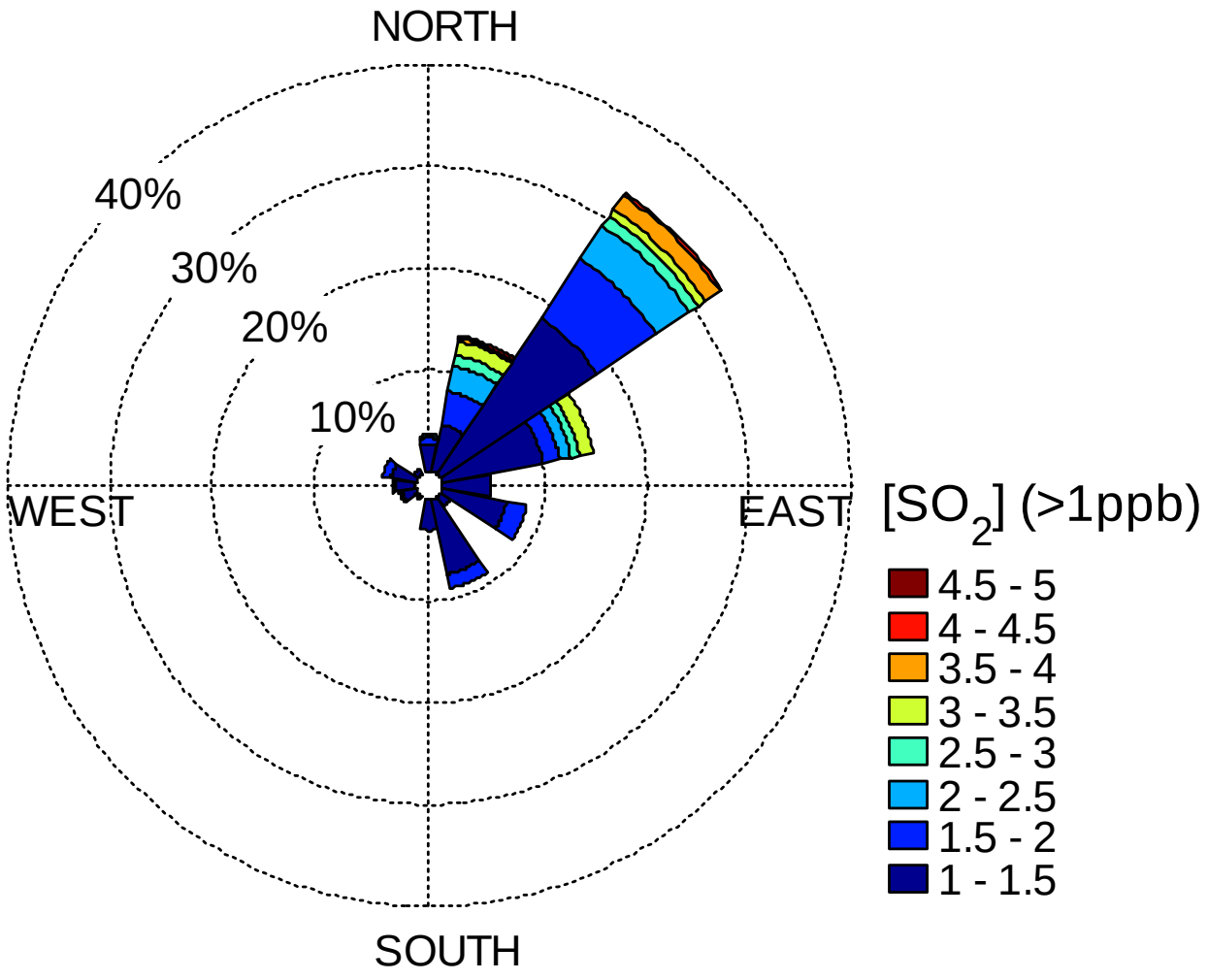
- Peak values in the morning and consistently low values at night.
- Nighttime [NO_Y] ~1.8-2.0 ppbv .

SO_2 at the Galveston Site



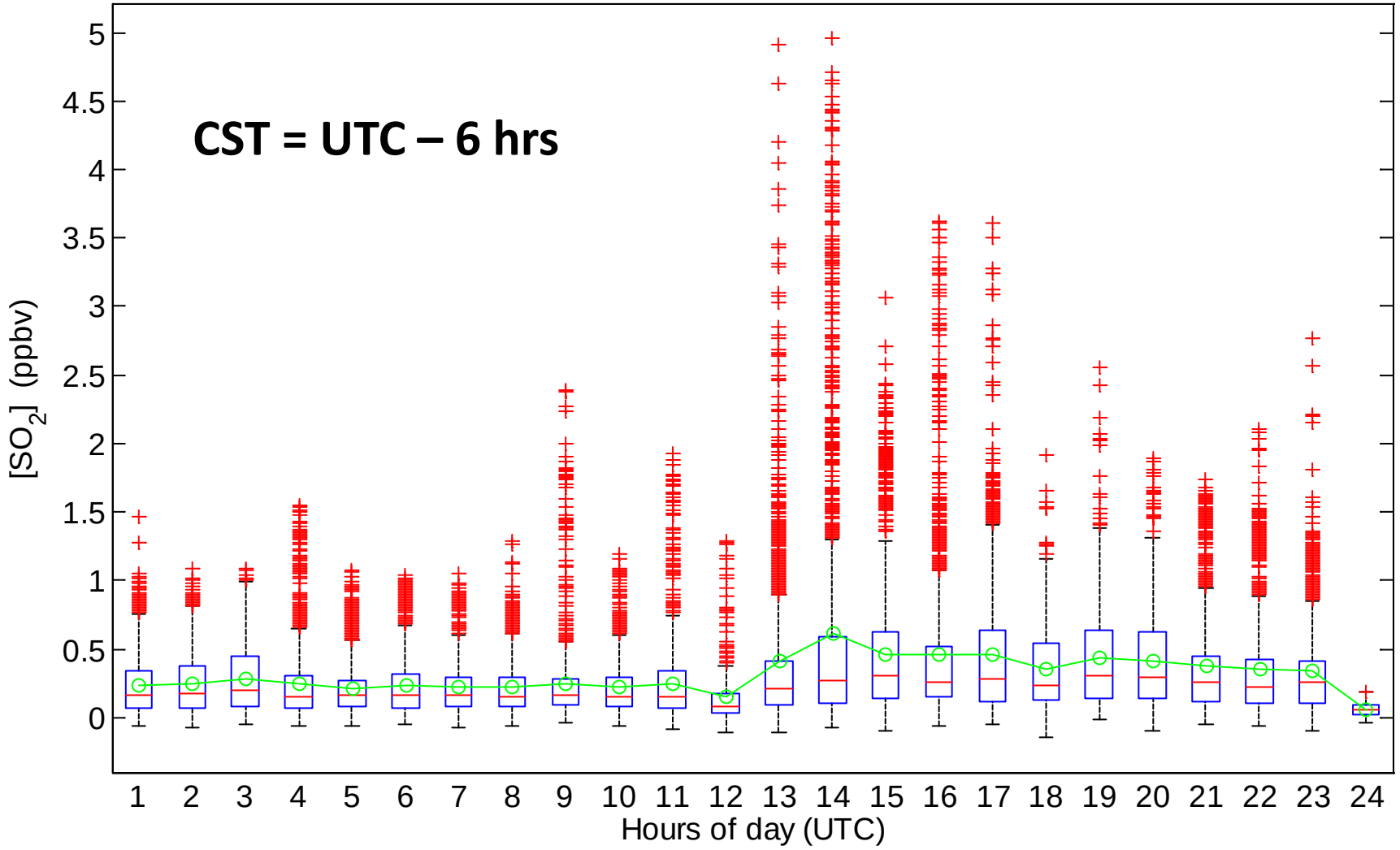
- Generally low [SO_2] due to emission controls established in recent years.
- Highest [SO_2]: ~4-5 ppbv (1 min).

Wind dependence of [SO_2] at the Galveston Site



- Highest SO_2 levels of 4-5 ppbv in winds from NNE – Influence of Galveston Port?

Diurnal [SO_2] Variation at the Galveston Site



- Daytime levels (0.4-0.6 ppbv) > nighttime levels (0.2-0.3 ppbv).

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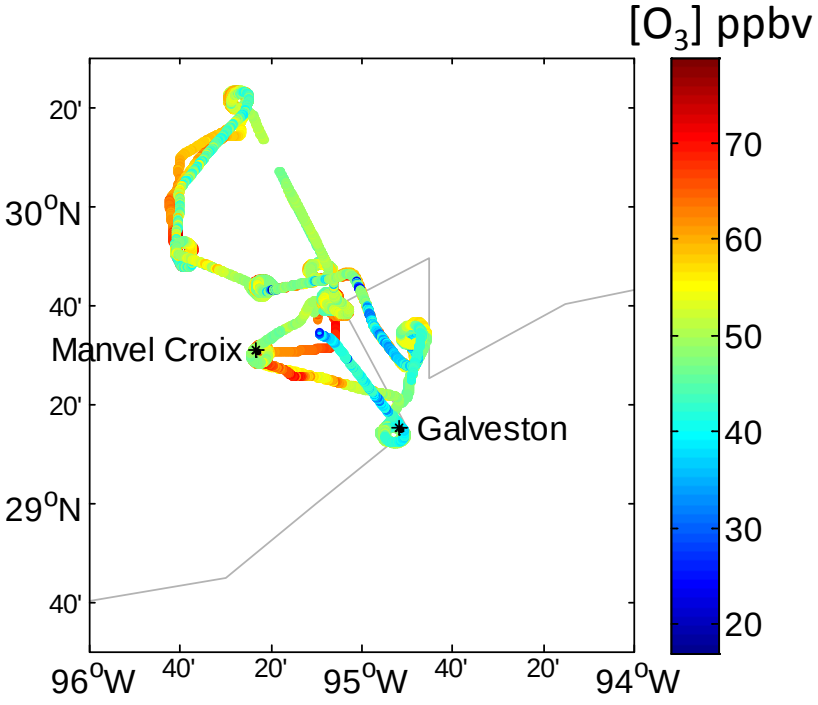
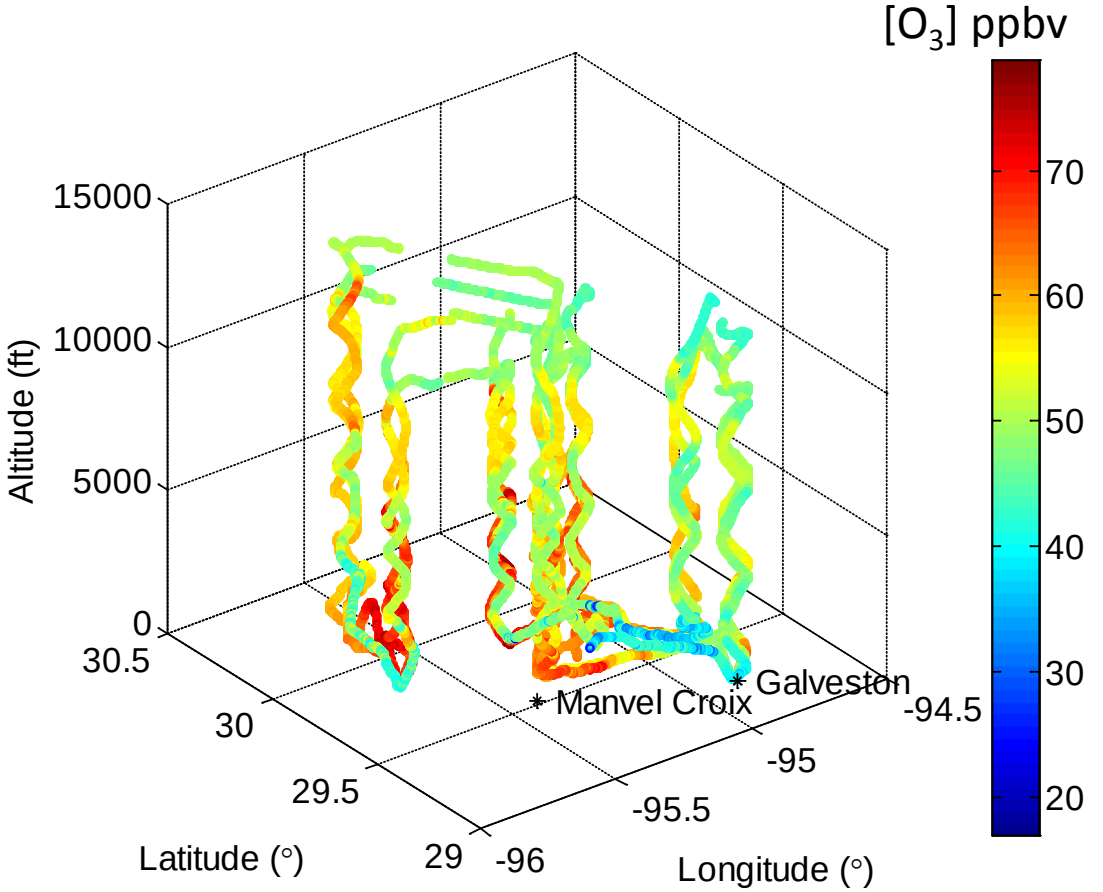
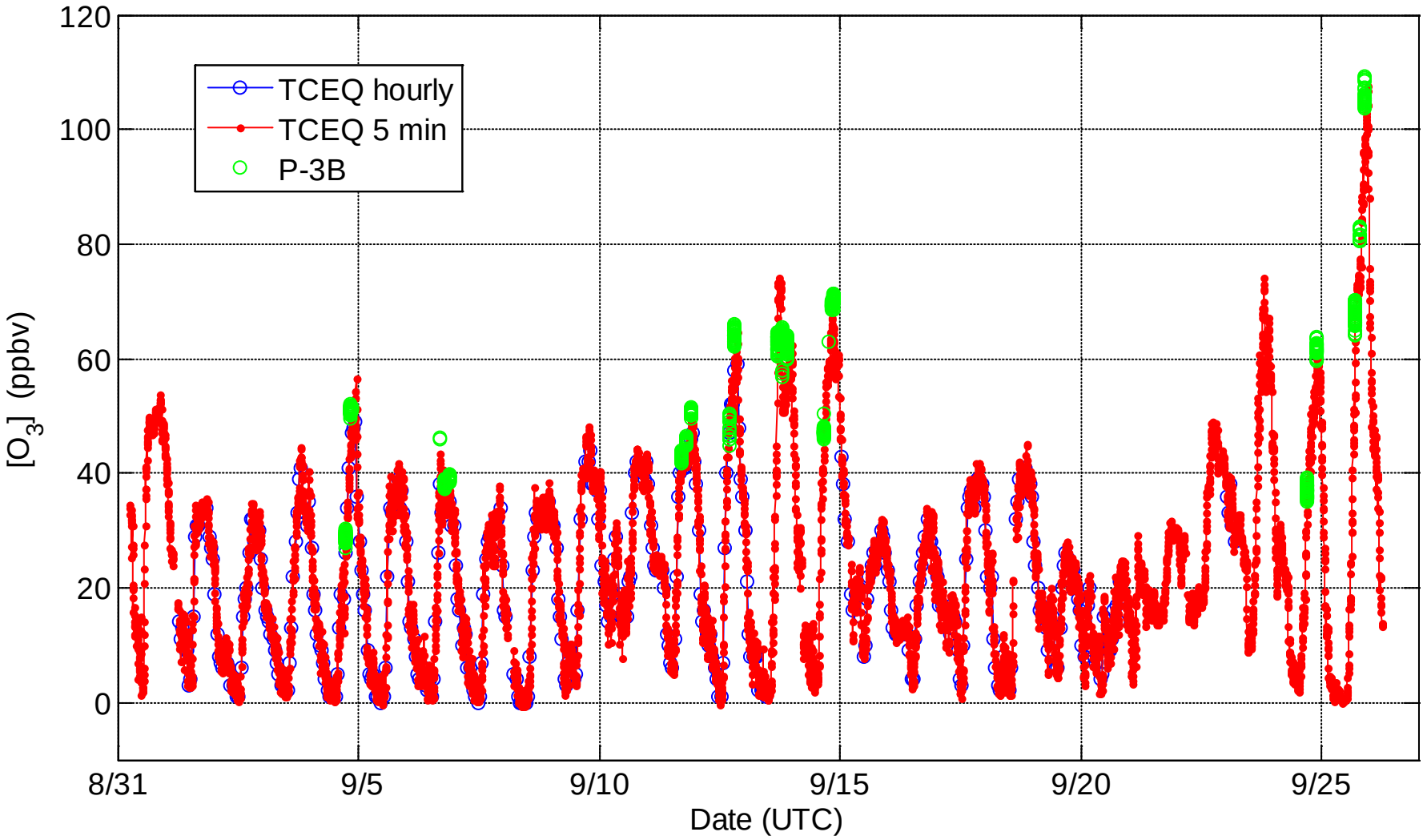
P-3B Ozone during Flight 09/13





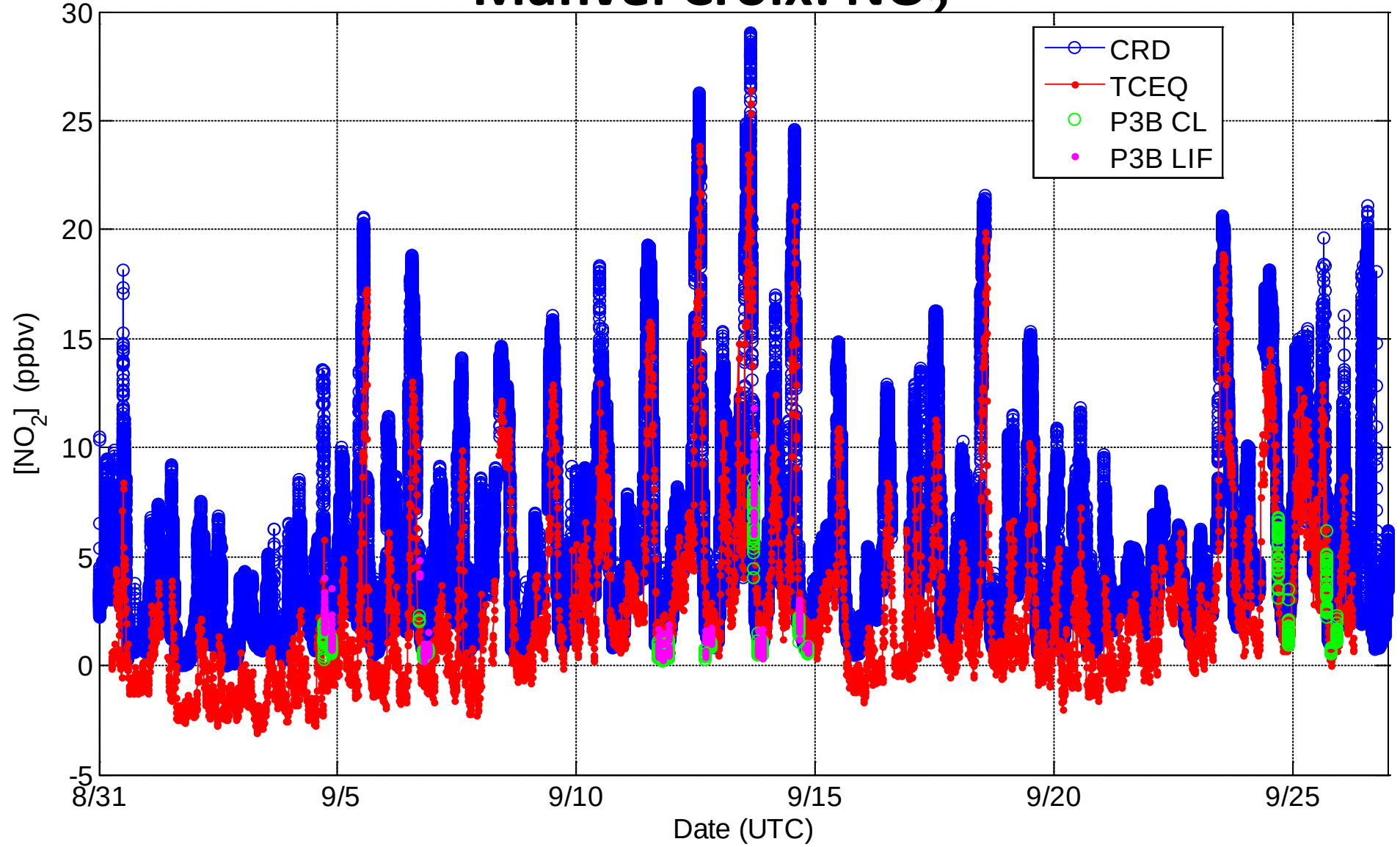
- Limit P-3B data for comparisons:
  - (1) below 1000 ft
  - (2) within +/-0.02˚ of the site longitude/latitude (~+/- 2 km)

Manvel Croix: O_3



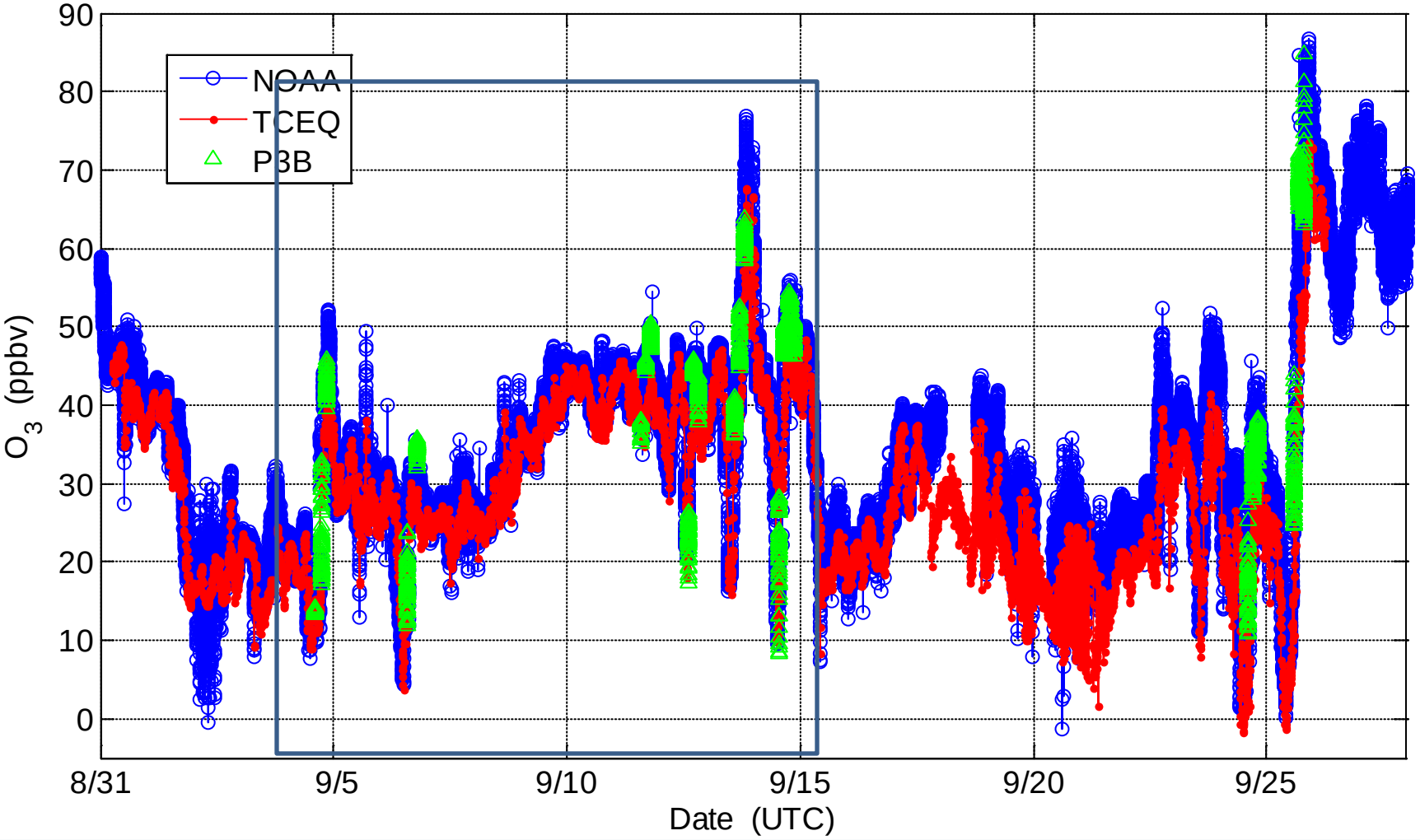
- P-3B [O_3] agrees well with the ground [O_3].

Manvel Croix: NO_2

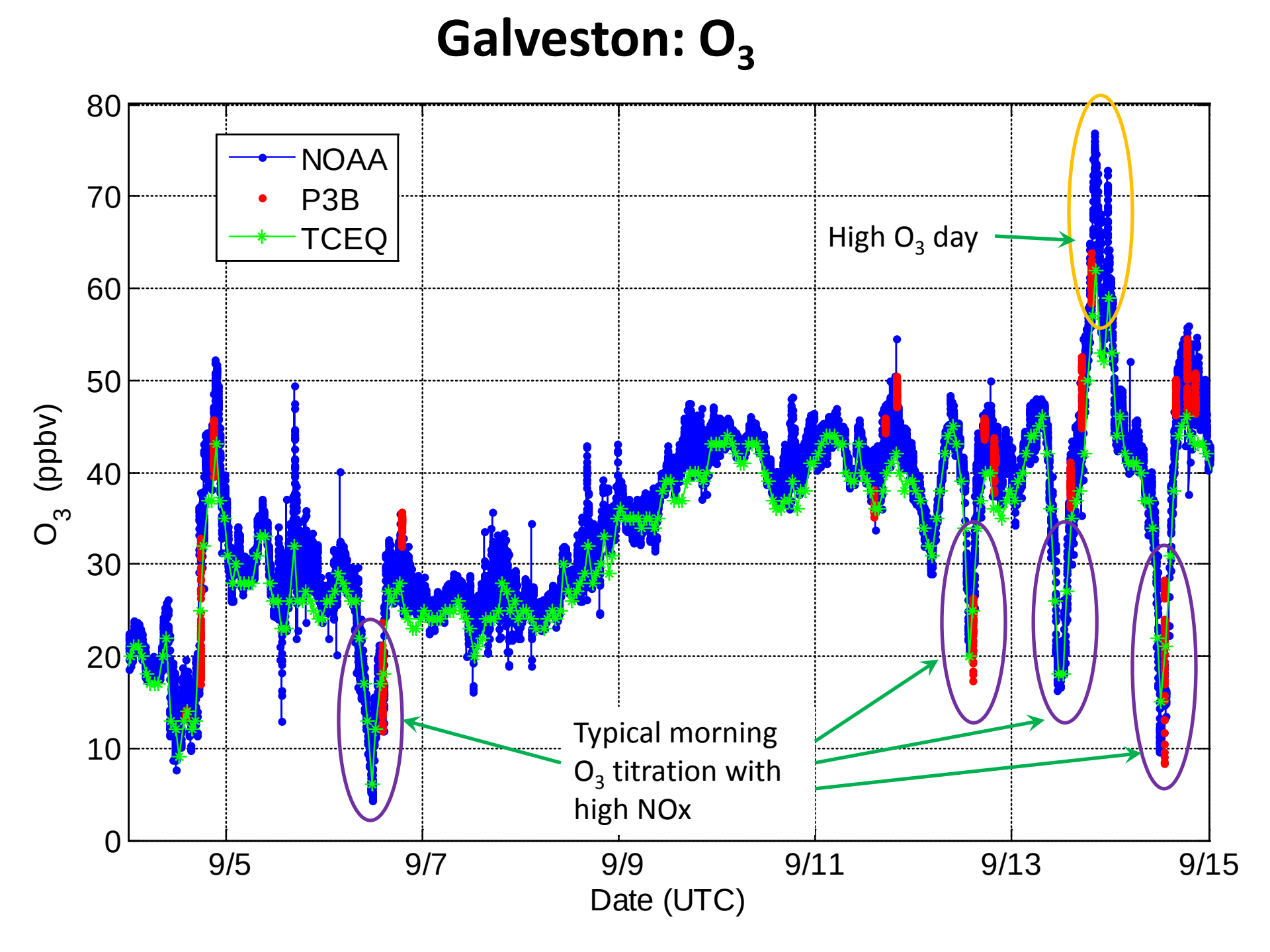


- General good agreement
- P-3B [NO_2] < surface [NO_2] ➔ strong vertical gradients?

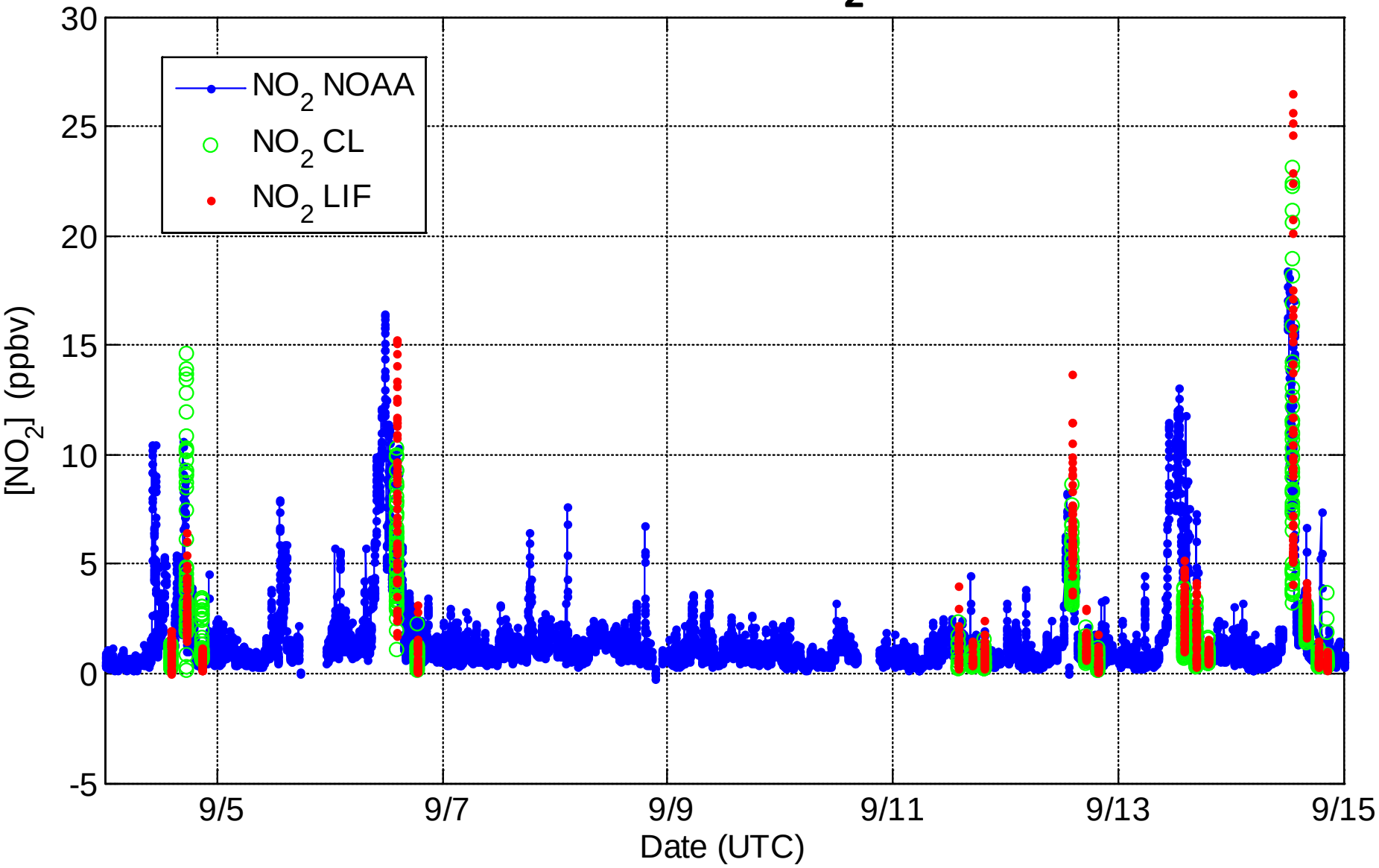
Galveston: O_3



- Good agreement between surface and P-3B: missed approaches
- Max. [O_3] on September 25: up to 86 ppbv at the surface & P-3B

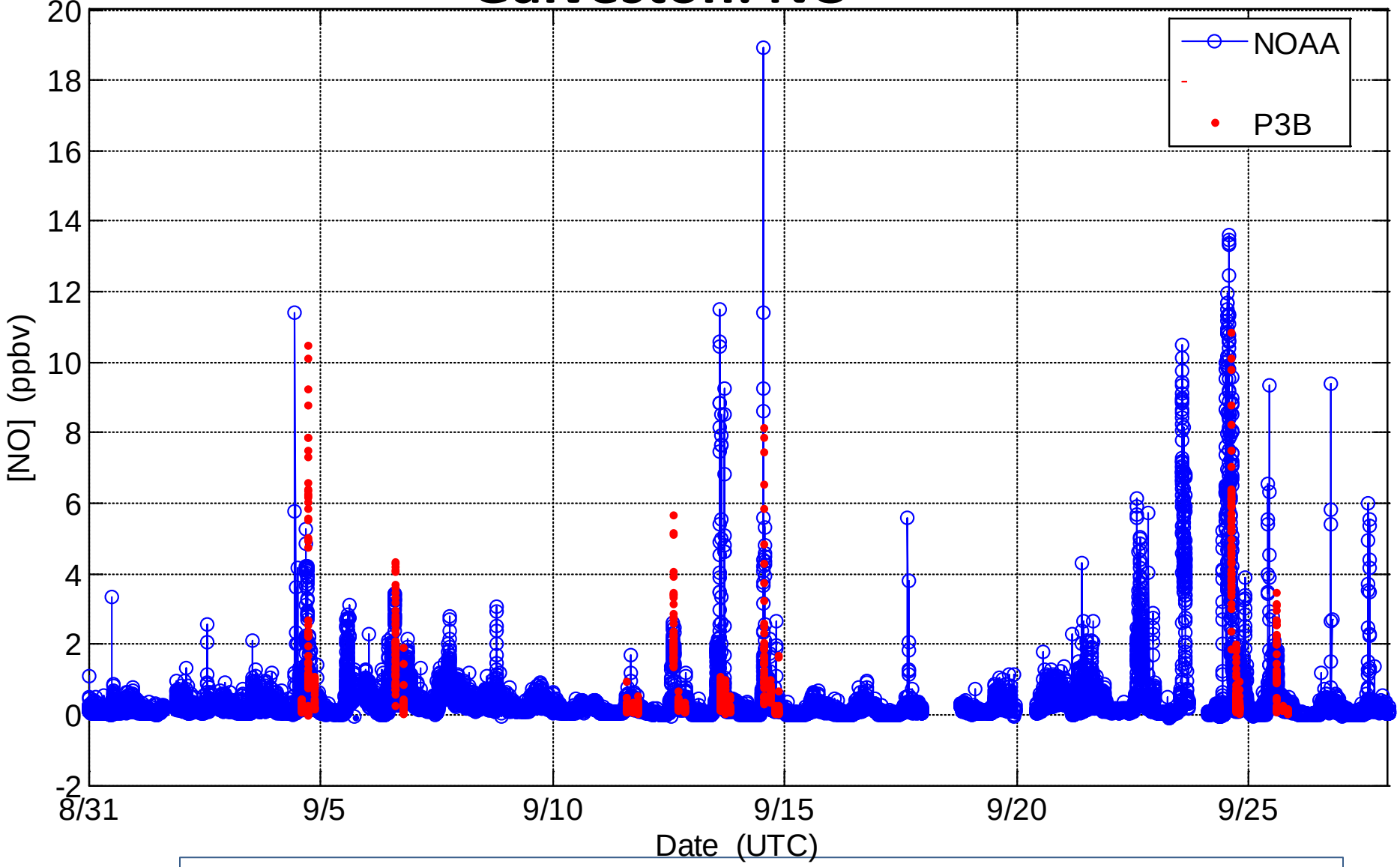

Galveston: O3
NOAA
P3B
TCEQ
High O3 day
Typical morning
O3 titration with
high NOx
O3 (ppbv)
Date (UTC)
0
10
20
30
40
50
60
70
80
9/5
9/7
9/9
9/11
9/13
9/15

Galveston: NO_2



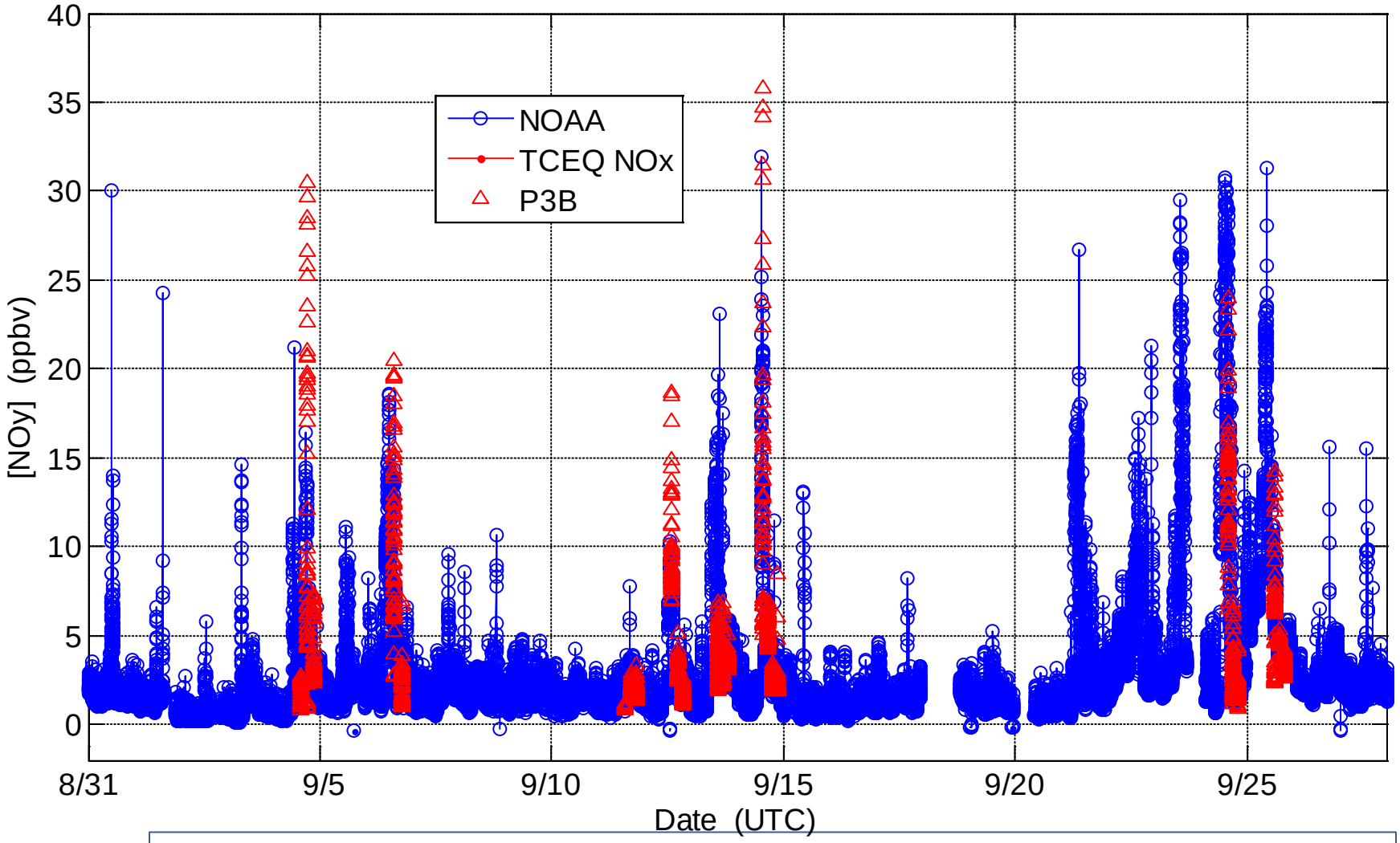
- P-3B [NO_2] agrees generally well with the ground [NO_2].

Galveston: NO



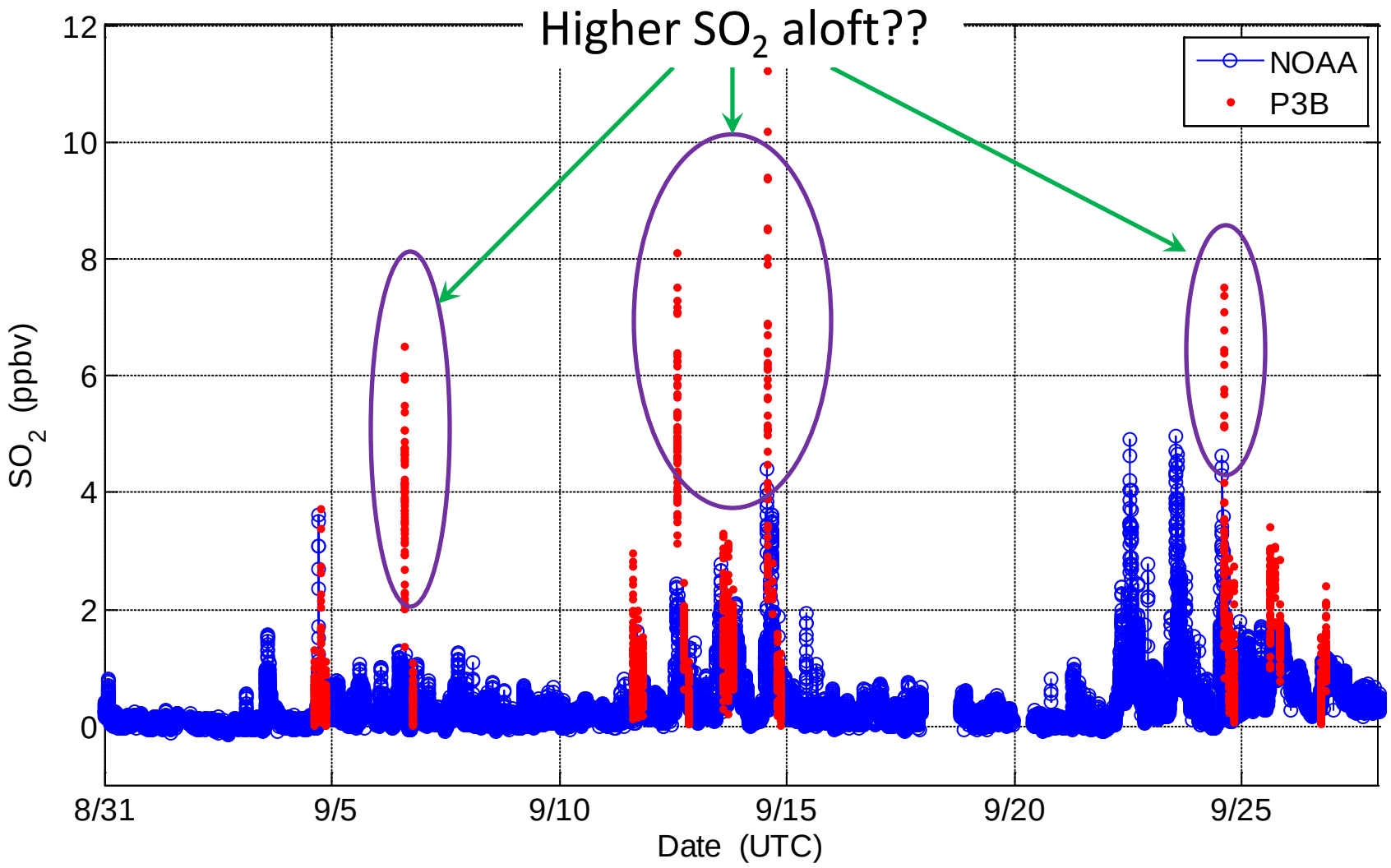
- P-3B [NO] agrees generally well with the ground [NO].
- P-3B variations: possible vertical/horizontal variations.

Galveston: NOy



- P-3B [NO_Y] agrees generally well with the ground [NO_Y].
- P-3B variations: possible vertical/horizontal variations.

Galveston: SO_2



- P-3B [SO_2] is generally higher than the ground [SO_2].
- Possible point-source emissions of SO2 from elevated stacks.

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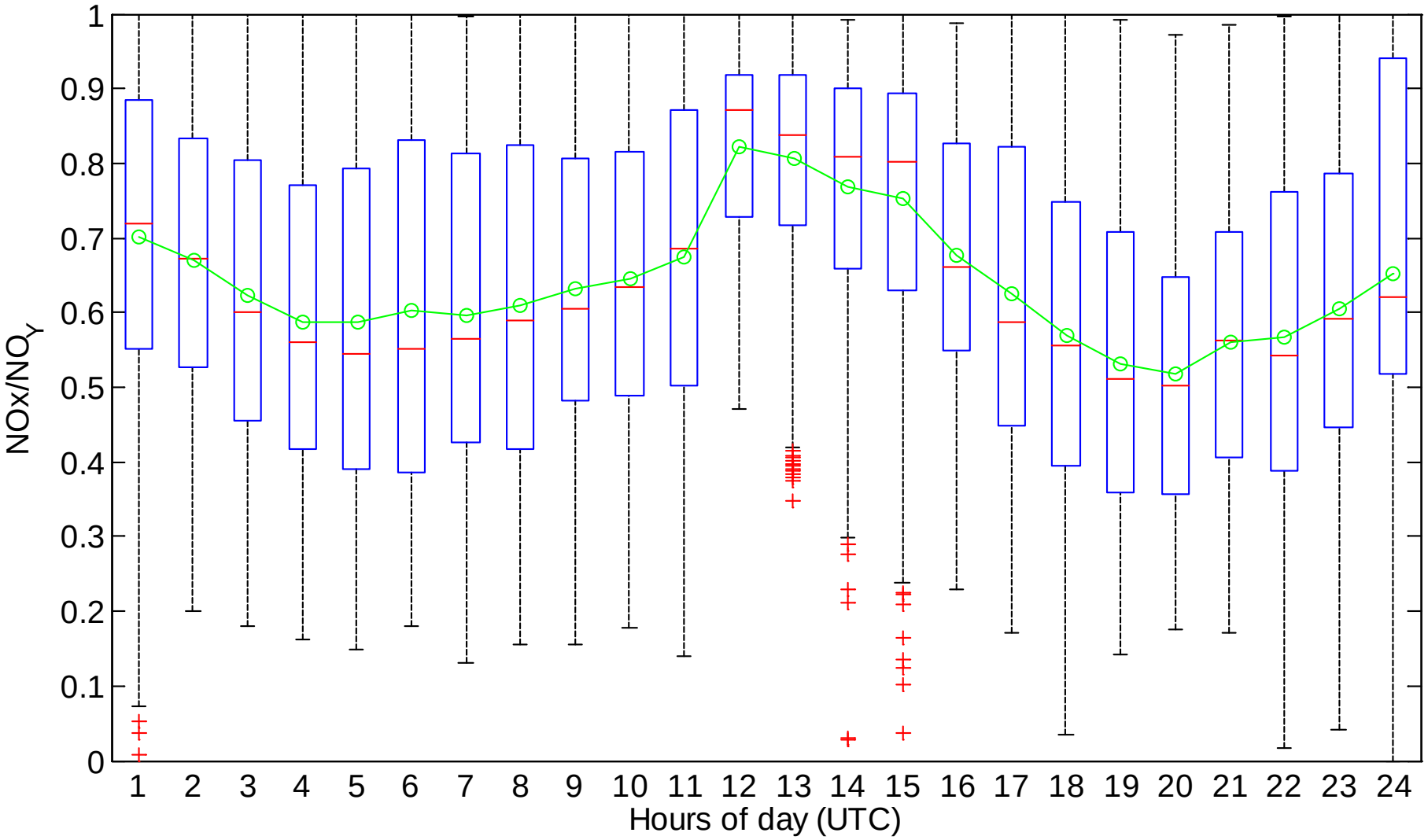
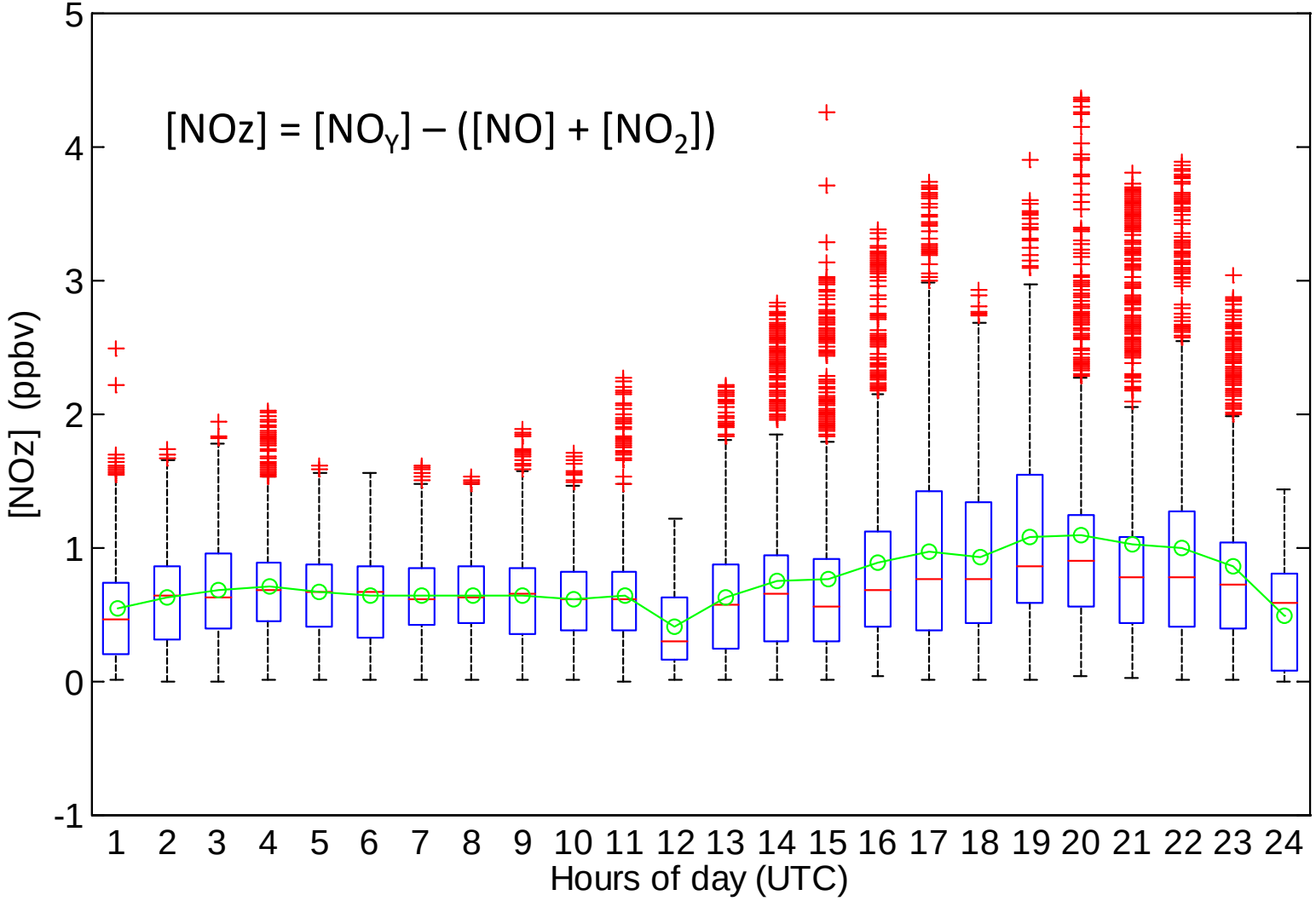
Galveston: NOx/NOy Ratios



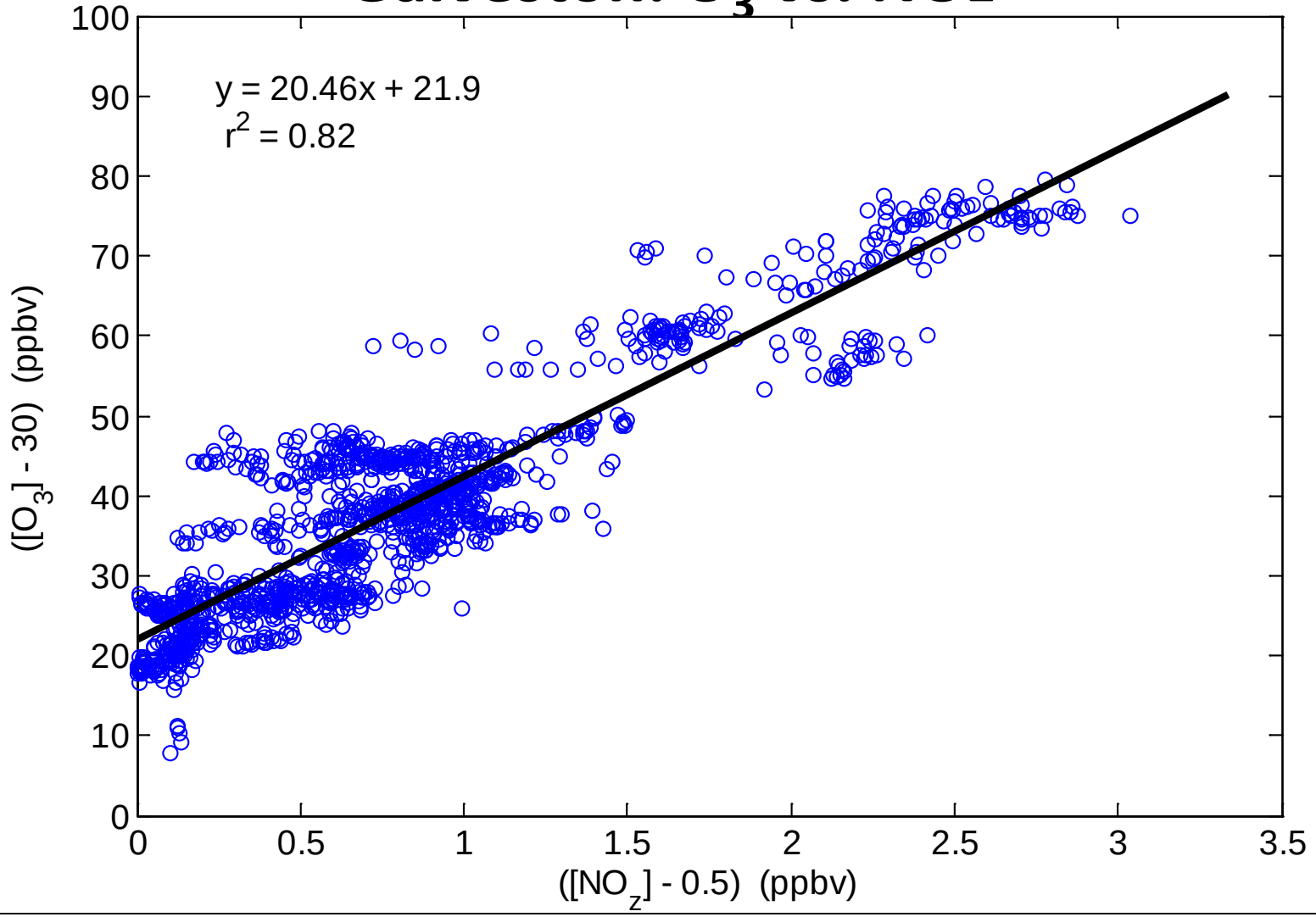
- Mean NOx/NOy = 0.64, with a peak (0.82) in the morning and a min. (0.52) in the afternoon ➔ Relatively “young” air mass

Galveston: NOz



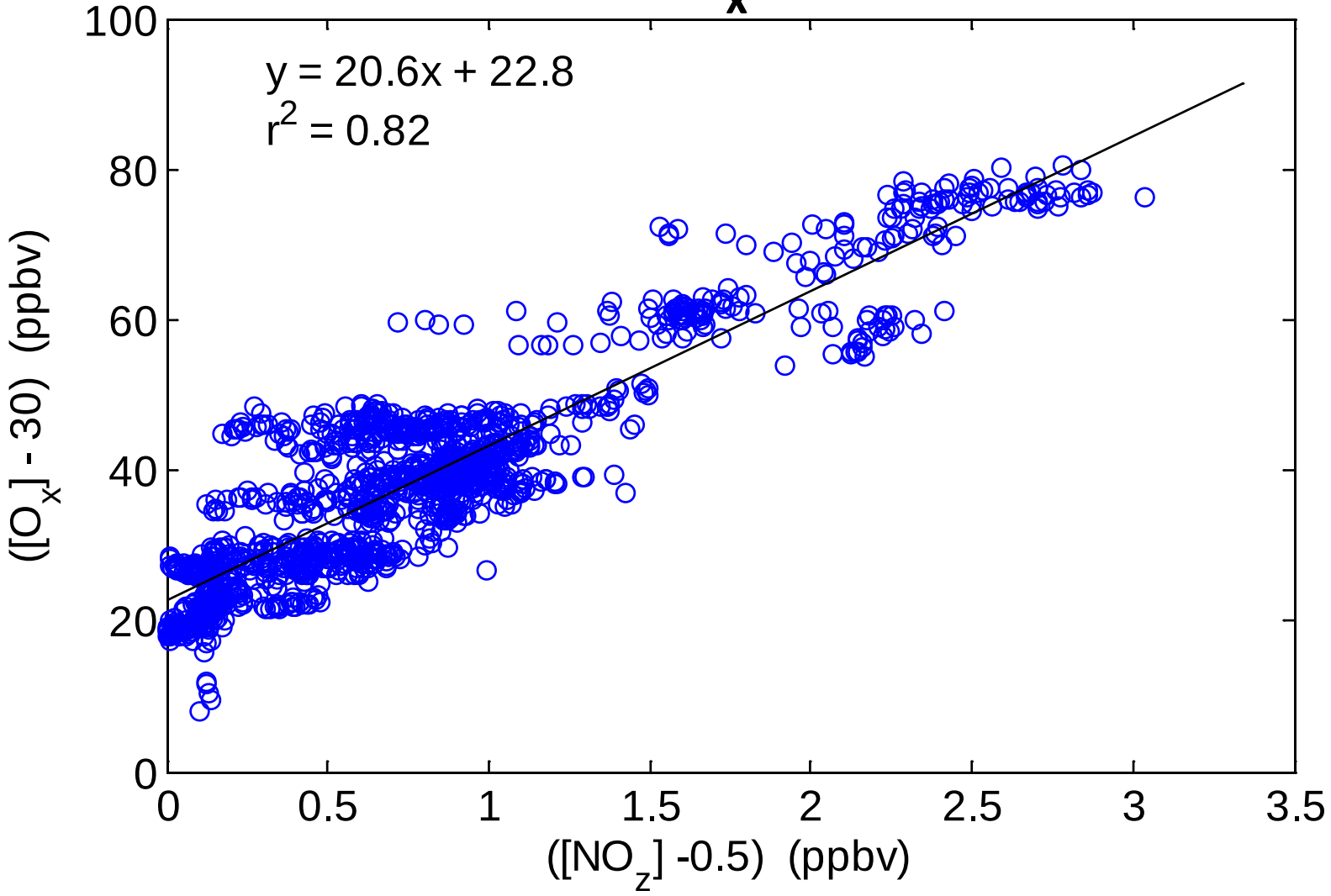
- Peak NOz (~1 ppb) in the afternoon ➔ photochemical sources.
- Nighttime NOz levels: relatively constant (~0.5-0.6 ppbv).

Galveston: O_3 vs. NOz



- During daytime: 9am-5pm (CST)
- About 20 ppb O_3 is created before 1 ppb NOx converted to NOy.
- During DAQ-Baltimore/Washington 2011, this number is ~8.

Galveston: O_x vs. NOz



- Specific for the mean transport times from the emission source regions to Galveston
- Assuming minimal depositional loss of NO_Y species such as HNO_3.

Summary

- A full month trace gas data collected at the Galveston and Manvel Croix sites during DISCOVER-AQ.
- NO_2 levels at Manvel Croix were influenced by plumes from downtown Houston and Ship Channel.
- Trace gases at Galveston: relatively low levels, but influenced by pollution plumes.
- Comparisons with the P-3B data: generally good agreement, but there are more variations in the P-3B data.
- Estimated ozone production efficiency of ~20 ppb O_3/ppb NOx: a factor of 2.5 larger than that during DISCOVER-AQ 2011.

On-going and Future Work

- Comparisons with the final P-3B and TCEQ data.
- Estimate of ozone production with available measurements to constrain HO_2+RO_2

$$P(O_3) = (k_1[HO_2] + k_2[RO_2])[NO]$$

$$= J_{NO2}[NO_2] - k_3[O_3][NO]$$

- Further analysis for the final report

Acknowledgements

- AQRP & TCEQ for $$ support
- Jim Thomas and Vince Torres for logistic support
- Dave Sullivan and Maria Stanzione for project management support
- The P-3B science team for use of the aircraft data
- Mark Estes for providing us the TCEQ data