Can column formaldehyde observations inform air quality monitoring strategies for ozone and related photochemical oxidants?

K. R. Travis[1], L. M. Judd[1], J. H. Crawford[1], Gao Chen[1], James Szykman[2], Andrew Whitehill[2], Luke Valin[2], Elena Spinei[3], Scott Janz[4], Caroline Nowlan[5], Hyeong-Ahn Kwon[5], Alan Fried[6], James Walega[6]

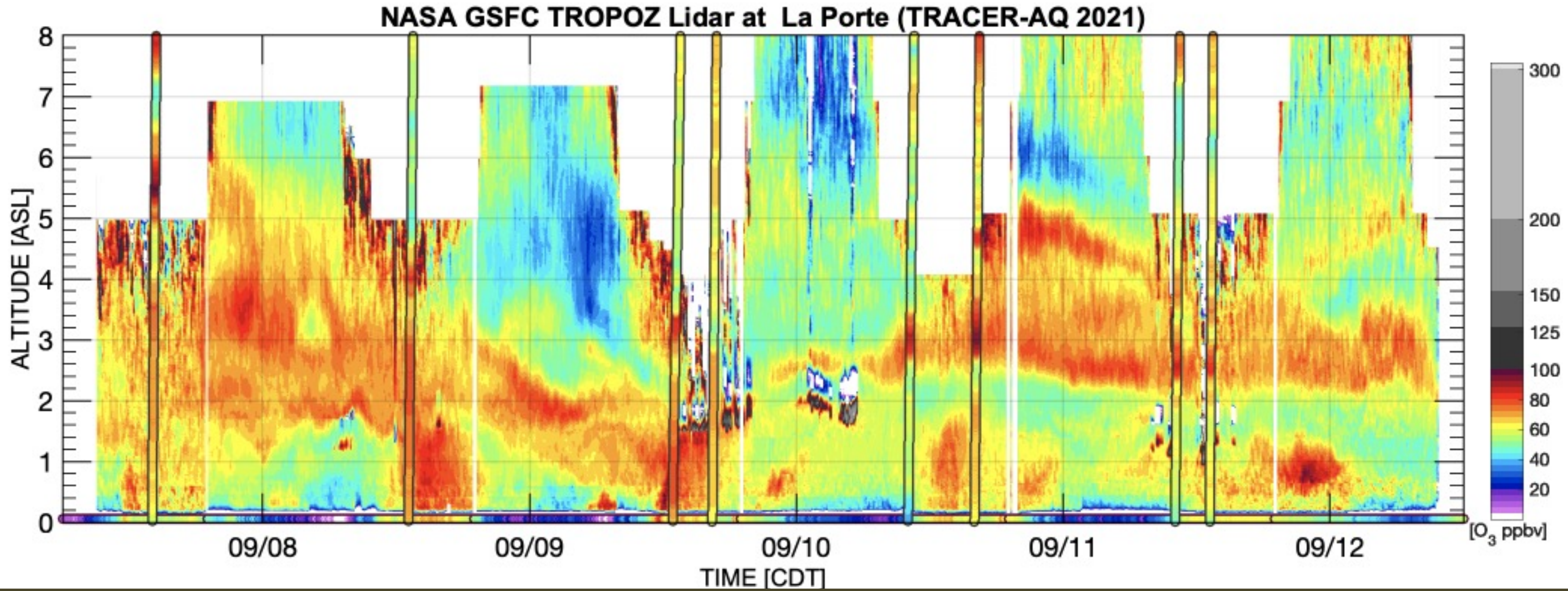
[1]NASA LaRC, [2]EPA, [3]Virginia Tech, [4]NASA Goddard, [5]Harvard CFA, [6]INSTAAR

This work was recently accepted in JGR-Atmospheres.

Motivation:

1) Observing surface ozone from space is hindered a combination of poor retrieval sensitivity and the largest signal being uncoupled from the surface (e.g., stratosphere/free troposphere)

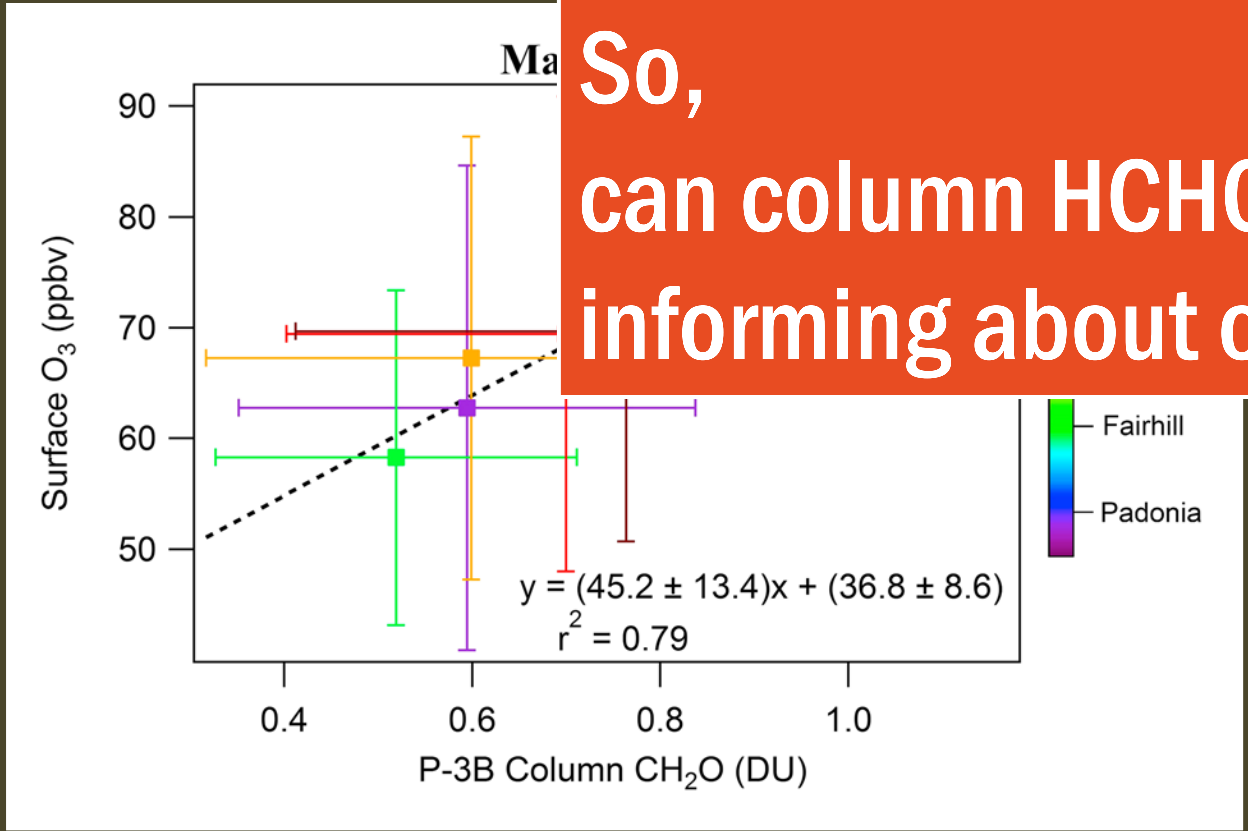
Tropospheric Ozone Curtain during an ozone event in Houston September 2021

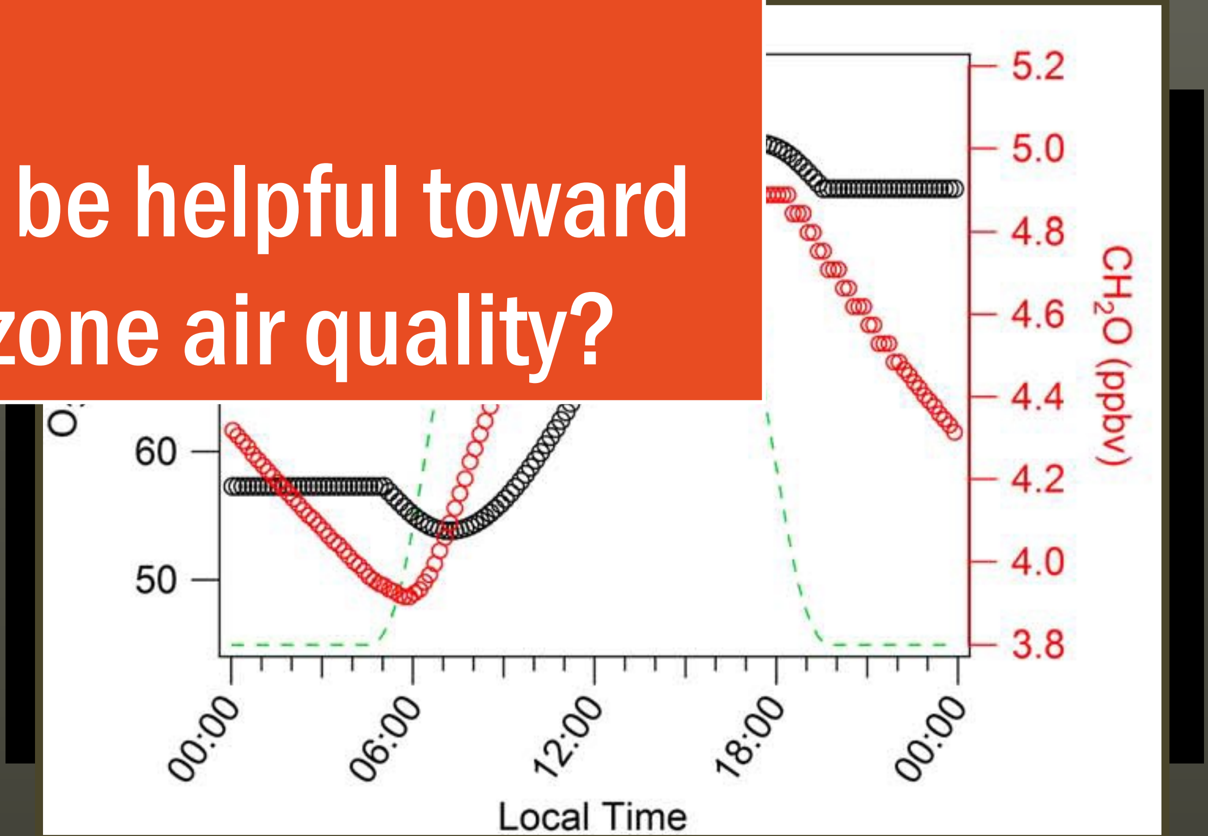


Motivation:

2) Evidence of column HCHO correlation with surface ozone during DISCOVER-AQ

(Schroeder et al. (2016): doi:10.1002/2016JD025419)





So,
can column HCHO be helpful toward informing about ozone air quality?

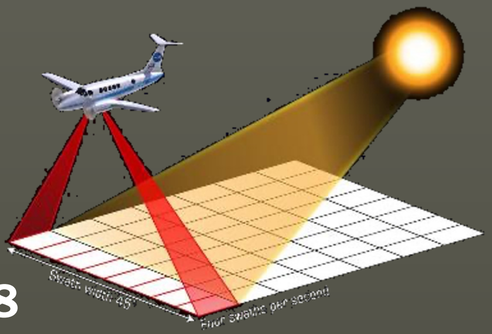
Follow on datasets:

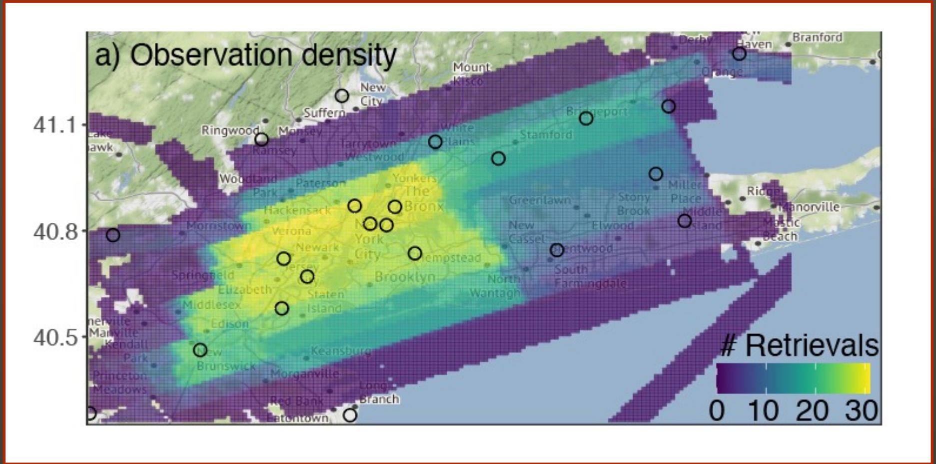
LISTOS 2018:

Long Island Sound Tropospheric Ozone Study

Ozone: US EPA Hourly Data in 2018

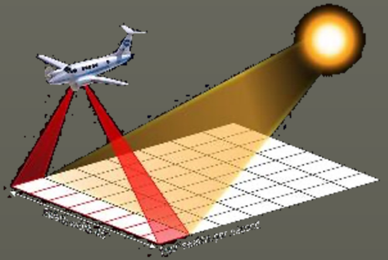
ΩHCHO : GCAS or GeoTASO 1km columns collected over 13 days from June-September 2018 (Janz et al. 2019; Judd et al. 2020)



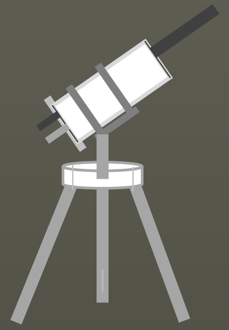


KORUS-AQ 2016:

Korea-United States Air Quality study

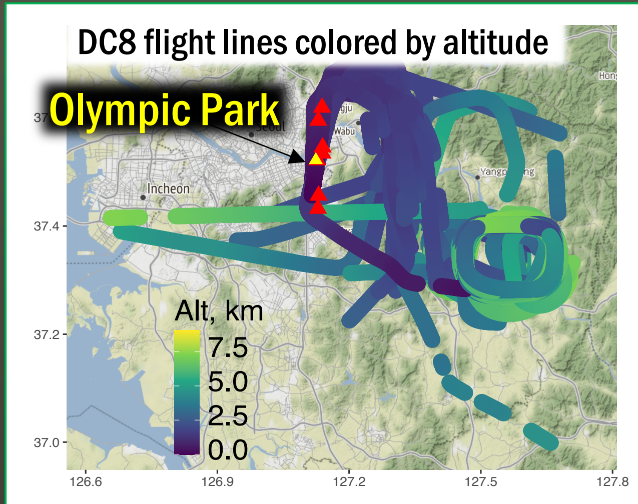


Ozone and NO_2: AirKorea 5 minute data

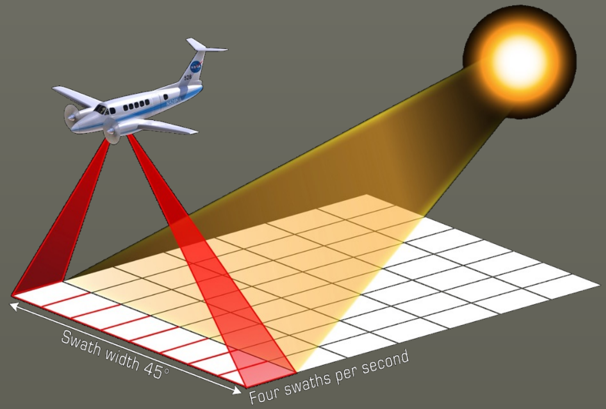


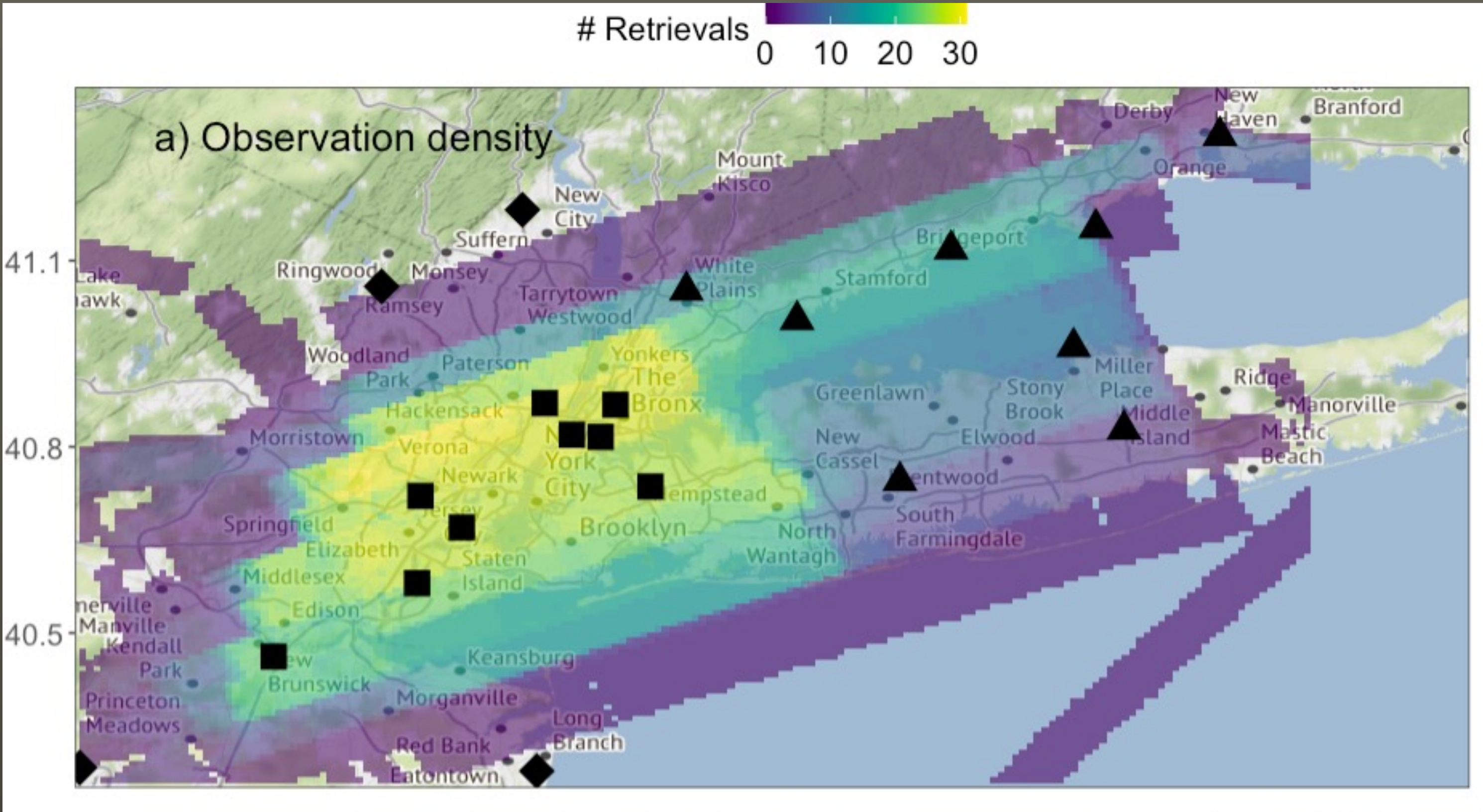
ΩHCHO:

- 32 integrated in situ HCHO profiles from DC8 descents over Olympic Park
- GeoTASO
  - 17 days
  - 24 overpasses during 17 days
  - Kwon et al. 2021
- Pandora Spectrometer
  - Over 5000 coincidences
  - Delrin interference corrected: Spinei et al., 2021



LISTOS provided repeated mapping of ΩHCHO of the NYC region with GCAS/GeoTASO airborne spectrometers

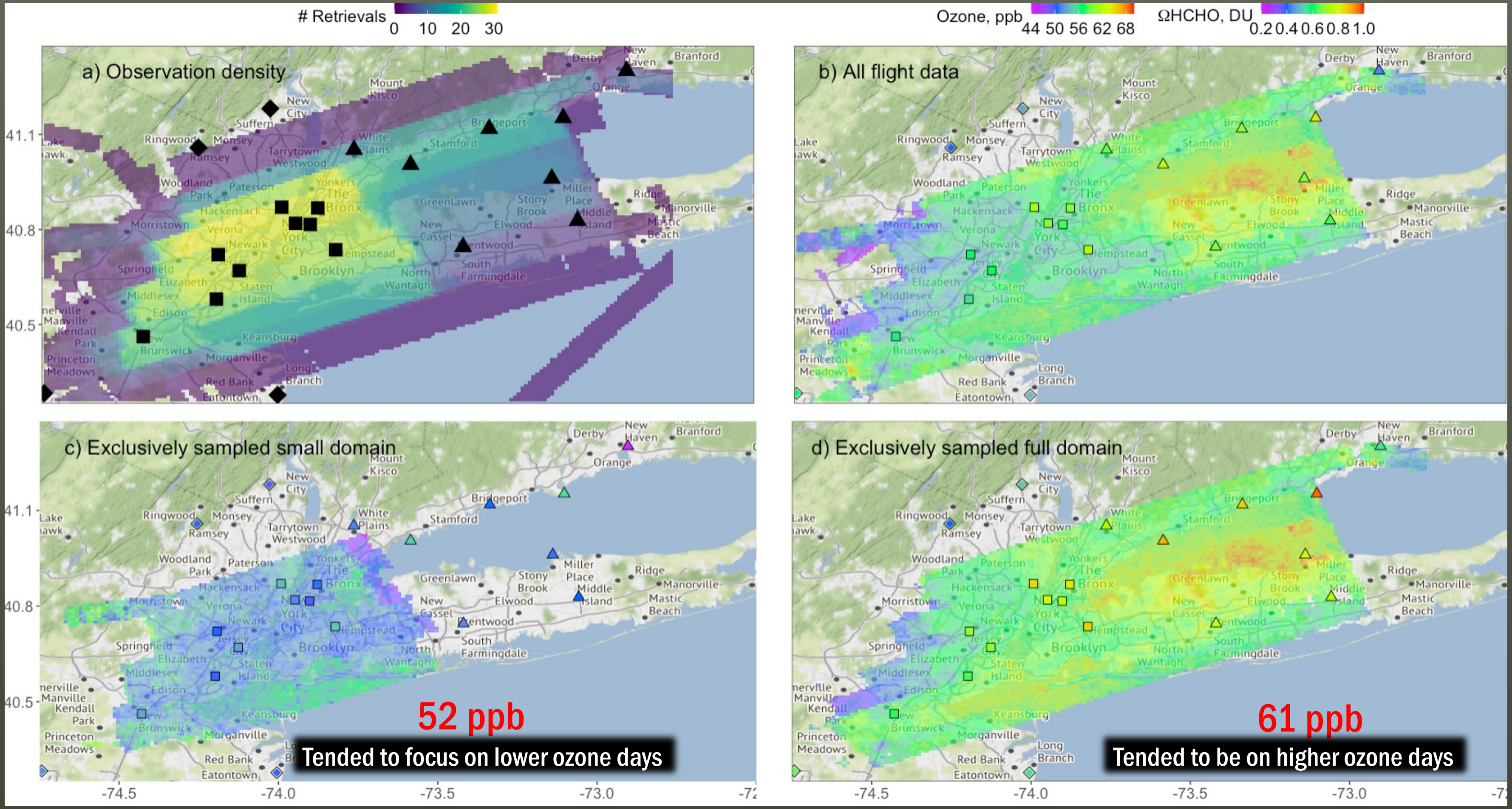




■▲◆ State and local monitoring sites (SLAMS) for ozone

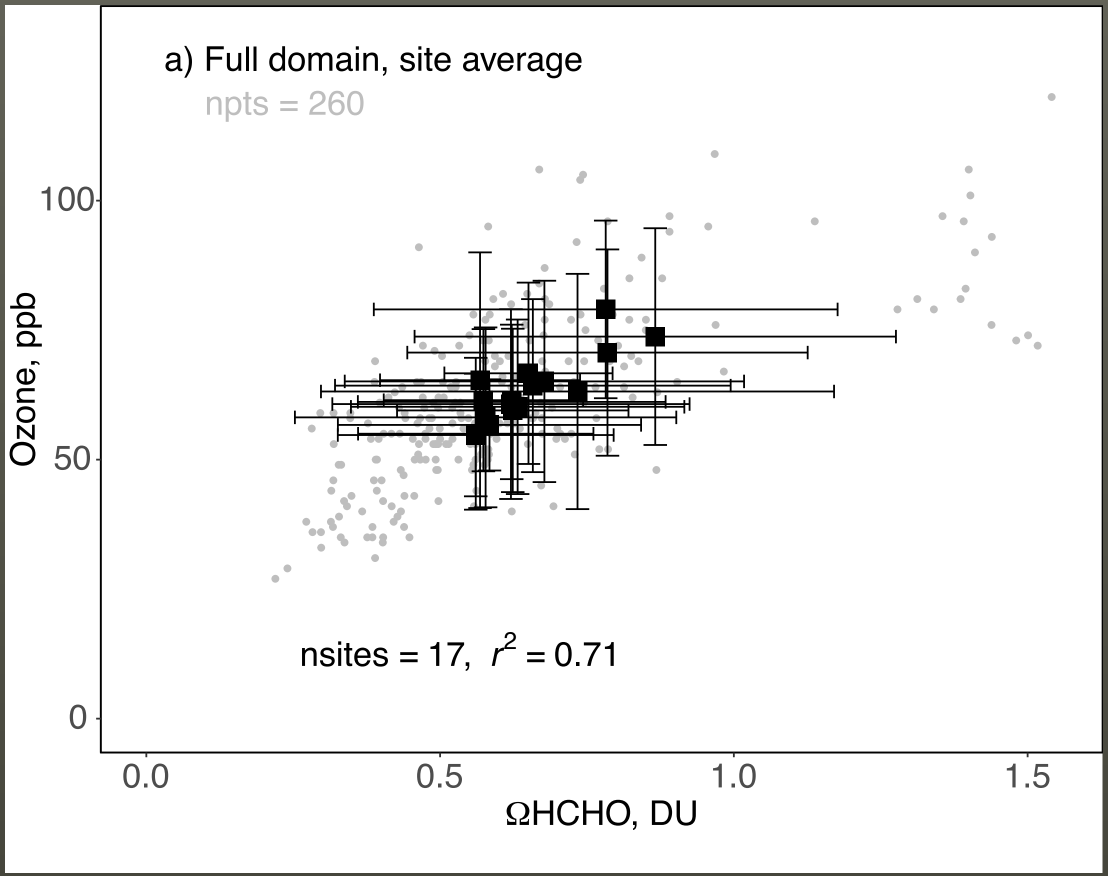
- All flight data
  - 13 flight days/26 flights (37 raster maps) for the entire study region.
- Exclusively sampled full domain
  - 10 flight days/18 flights (21 raster maps) for the entire study region.
- Exclusively sampled small domain
  - 5 flight days/8 flights (16 raster maps) for the New York City area.
- Small domain
  - 13 flight days/26 flights (37 raster maps) for the subset of data over the New York City area.

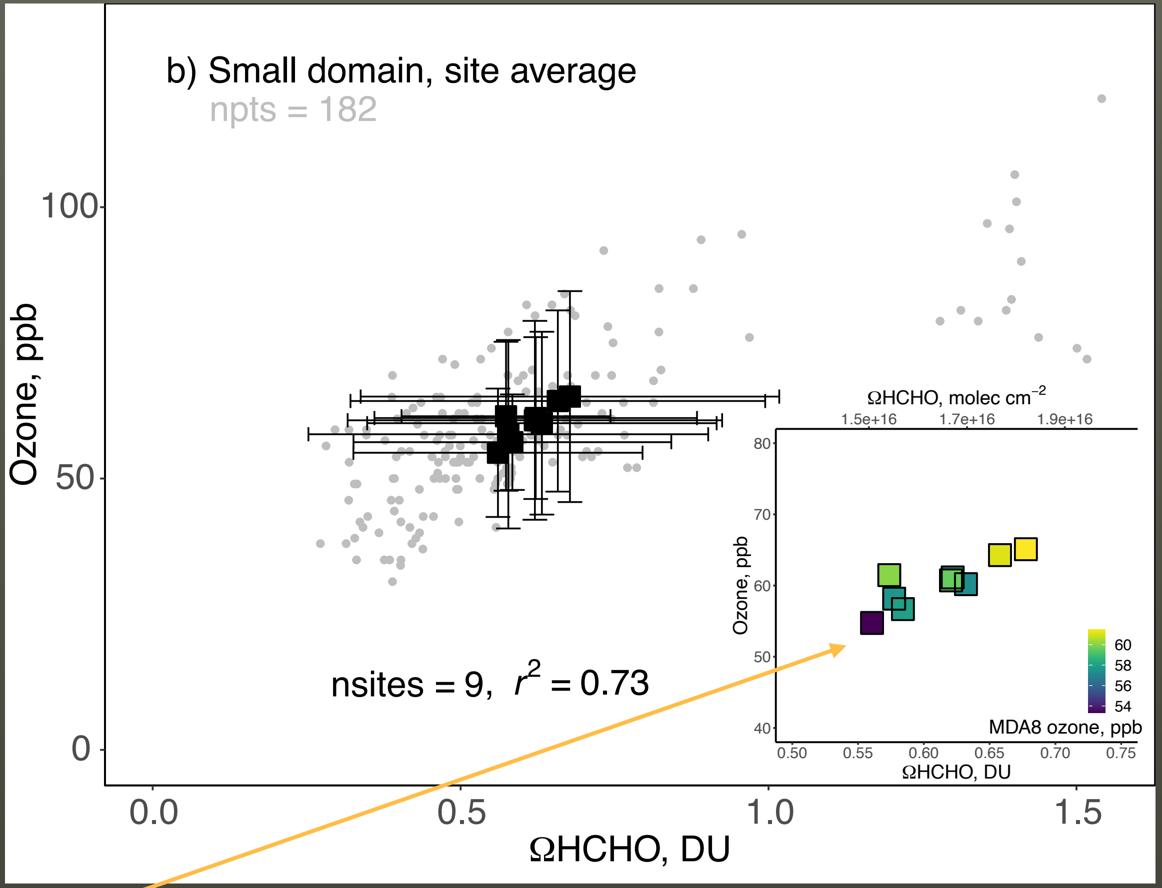
Clear ΩHCHO-ozone relationship between airborne spectrometers and ozone monitors



→ However inconsistent mapping resulted in different average ozone maps

Strong spatial correlation between ΩHCHO and surface ozone

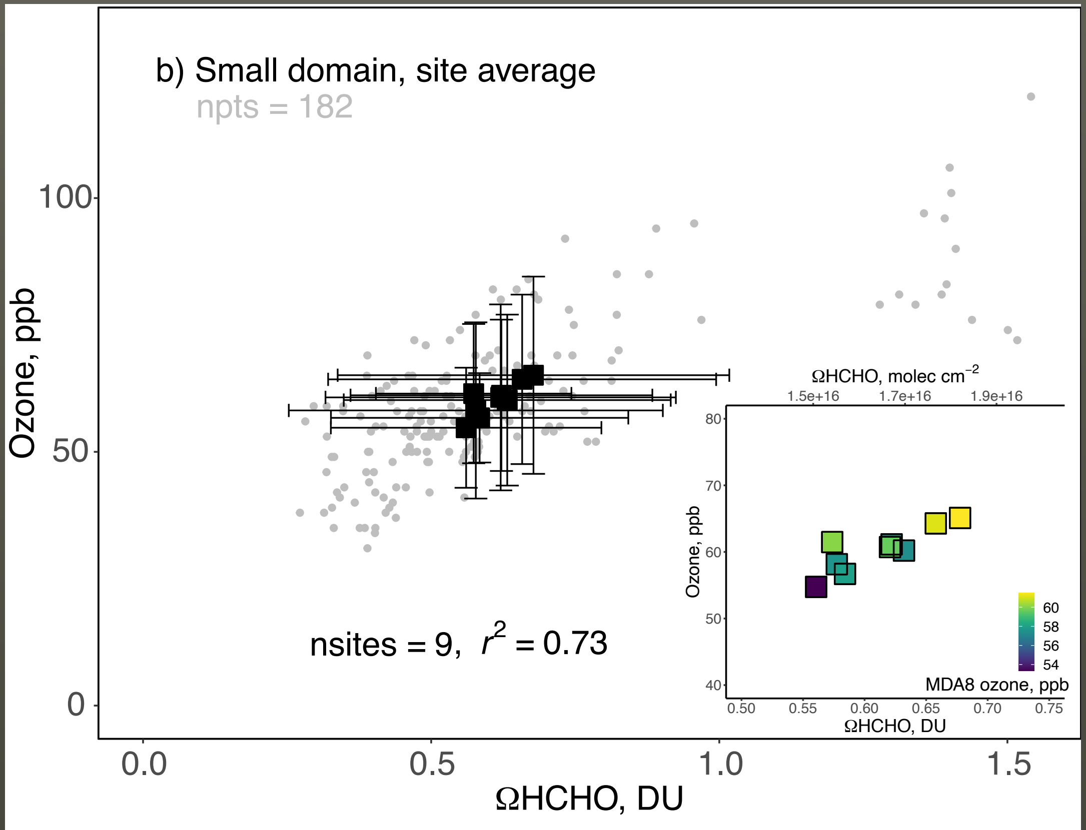




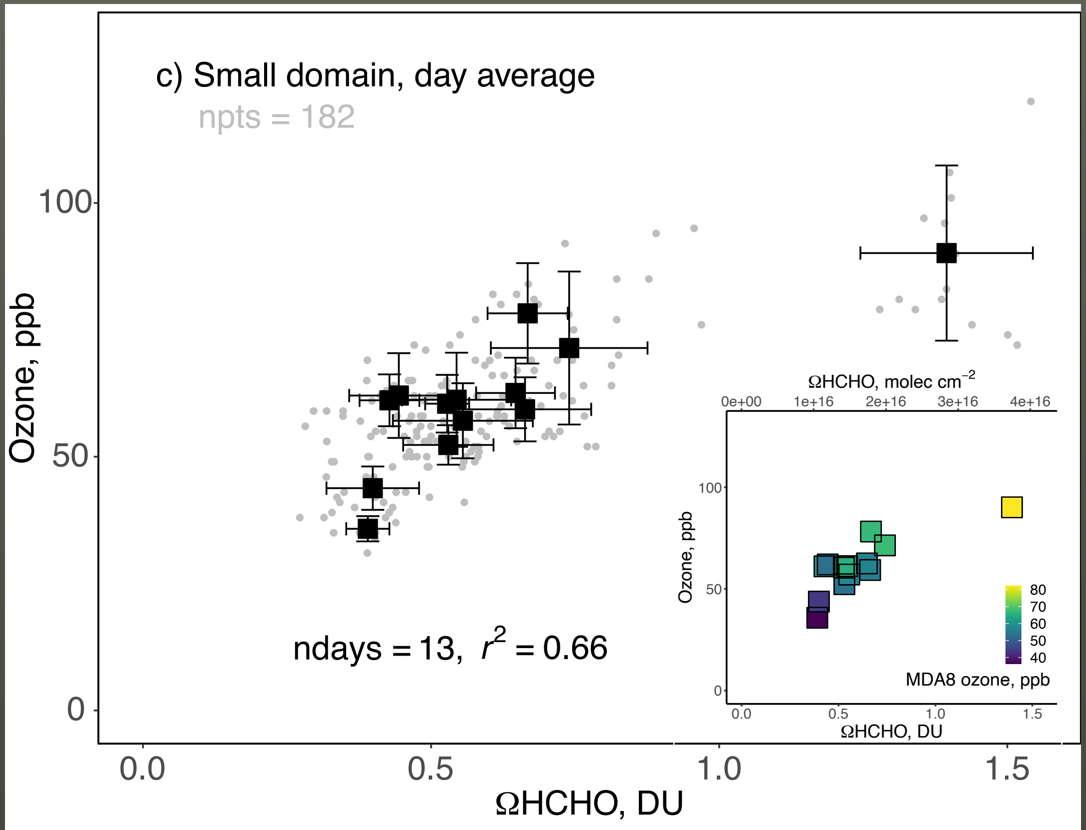
- The consistently sampled sites show a strong spatial pattern that correlates with MDA8. Additional sampling would be needed to improve confidence in the spatial pattern of the full domain (i.e. west of NYC).

Larger variability in the temporal (daily) than spatial average

Site Average



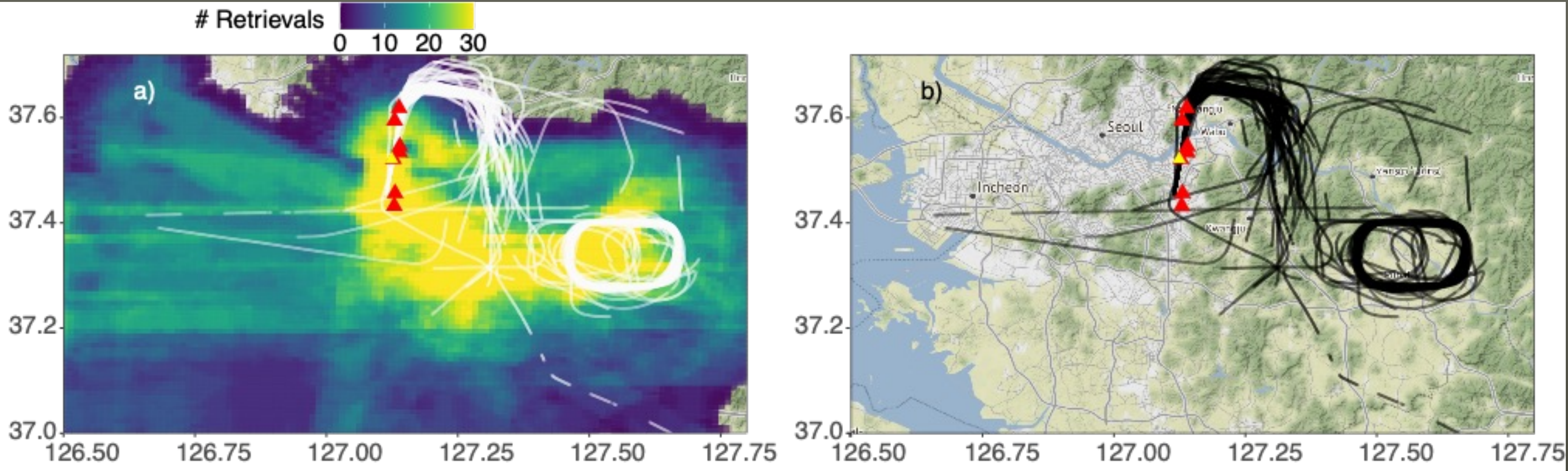
Day Average

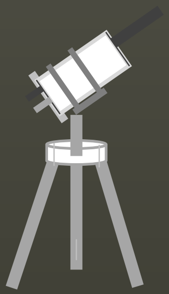


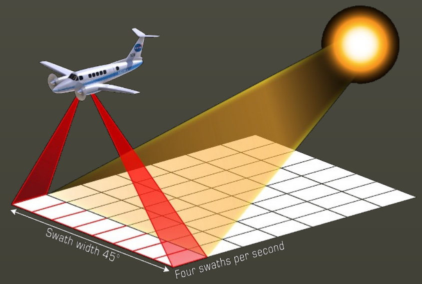
- All 9 sites in the small domain exhibit a significant temporal relationship (r^2=0.40 to 0.77).
- Domain responds coherently to day-to-day changes in photochemical production of ozone & HCHO.

KORUS-AQ provides the opportunity to compare 3 ΩHCHO perspectives:

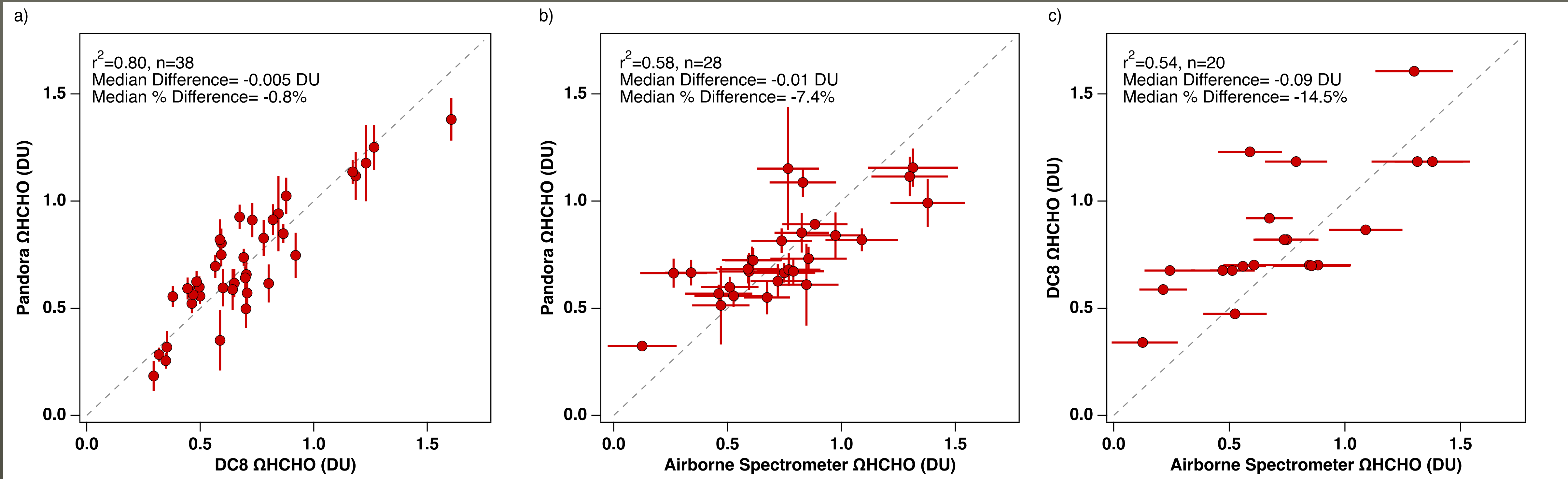
Delrin-corrected Pandora, airborne spectrometer, and in situ aircraft





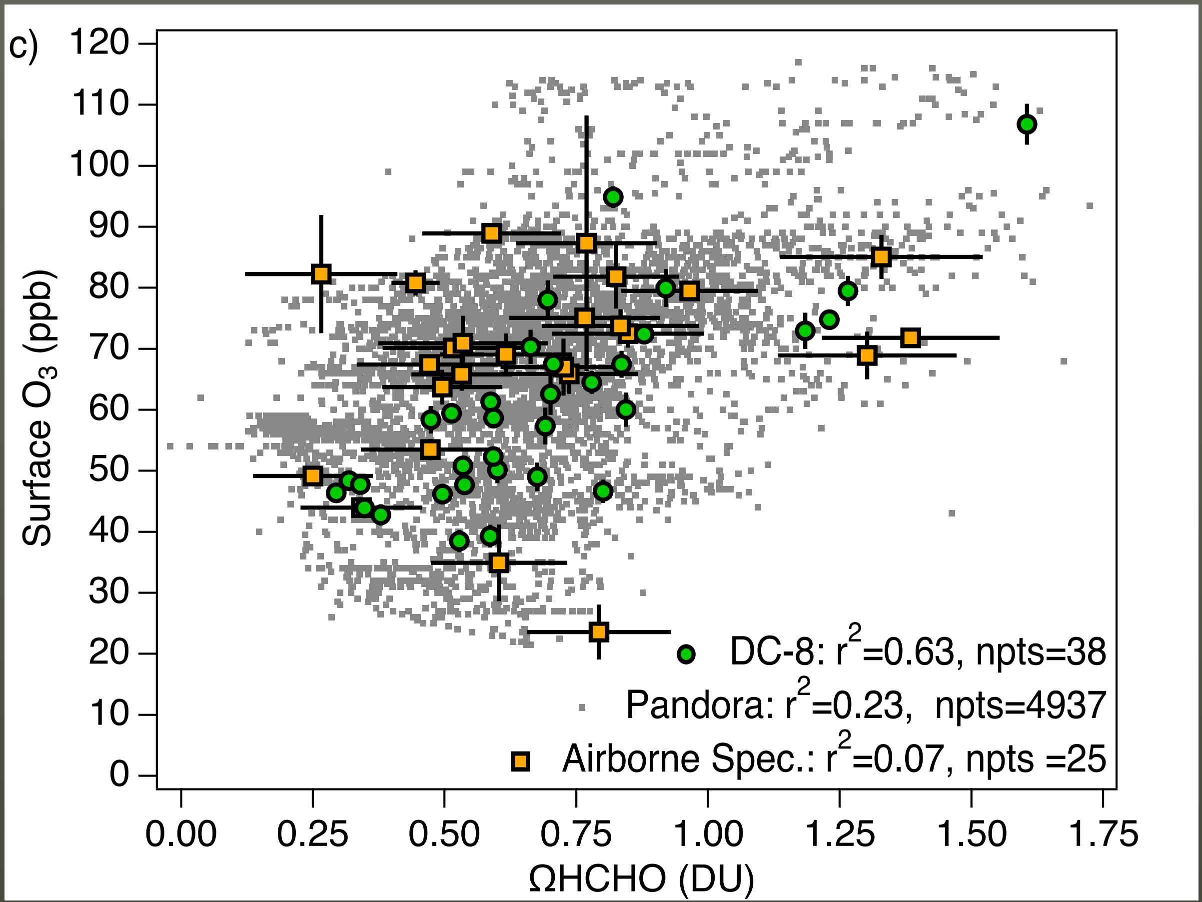


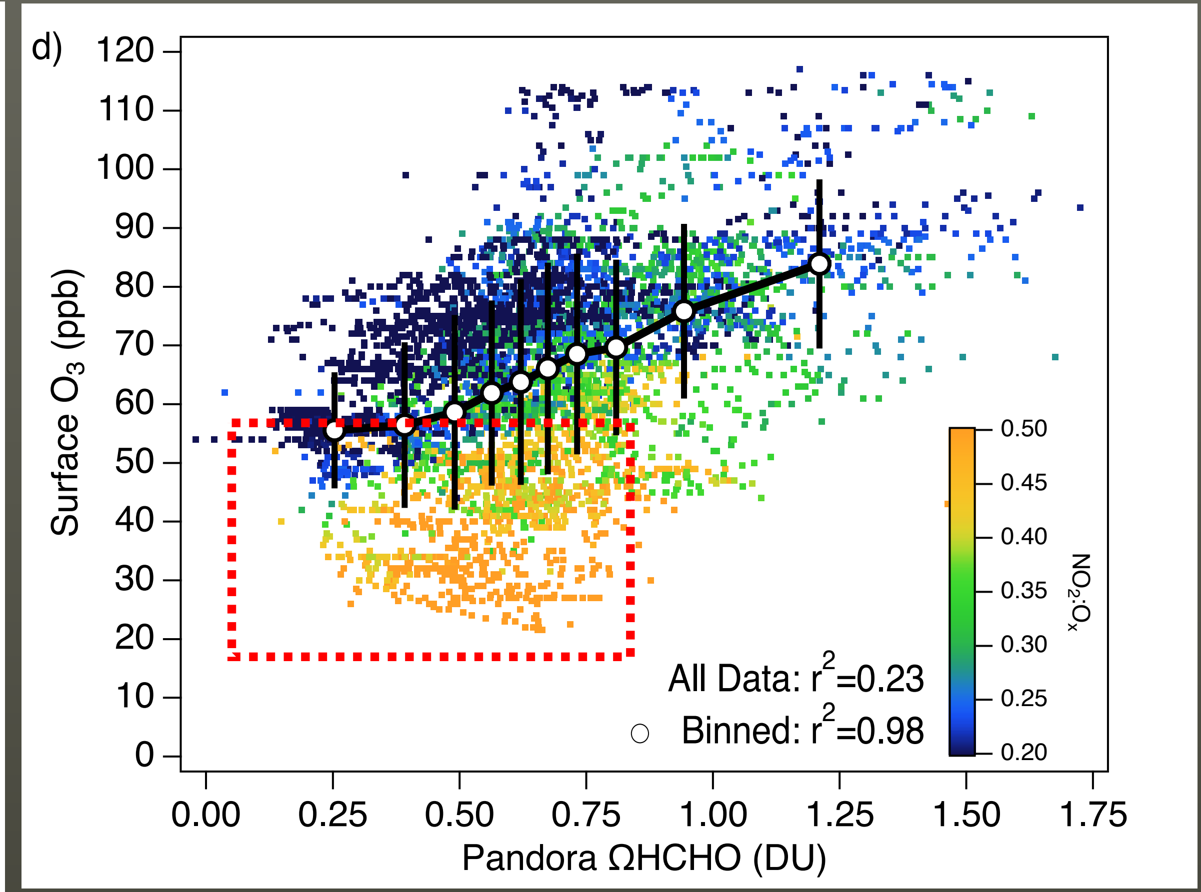
ΩHCHO from three instruments generally agree



- Airborne spectrometer is the most uncertain measurement due to the reliance on an a priori, but also had the fewest number of samples.
- For comparison to ozone:
  - Compare Pandora & airborne spectrometer ΩHCHO to ozone at Olympic Park only.
    - Airborne spectrometer data averaged ~1 km radius of Olympic Park.
  - DC-8 ΩHCHO are compared to the 7 Air Korea monitors along the lowest portion of the aircraft missed approach.
  - Surface monitors are averaged within $\pm$0.5 hour of the ΩHCHO coincidences with the exception of Pandora that is matched to the nearest surface measurement within 5 minutes.

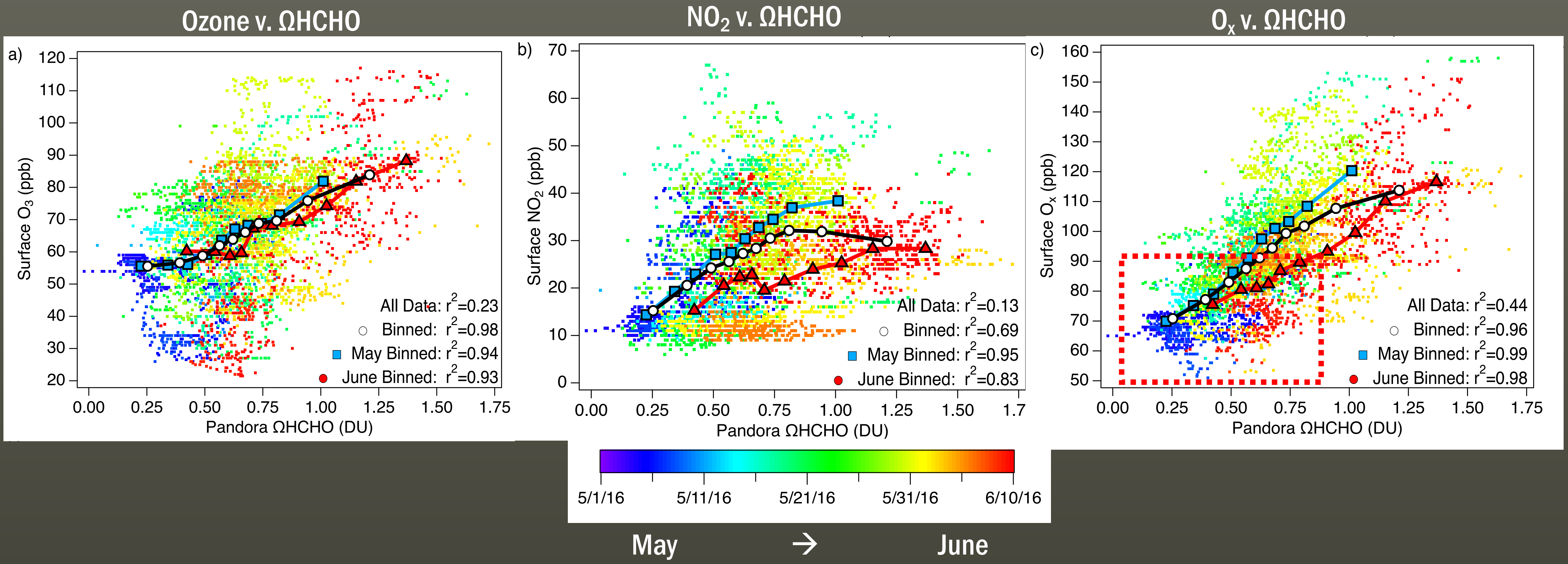
Strong relationship between ozone and ΩHCHO from Pandora and DC-8





- Airborne spectrometer does not correlate with surface ozone, which we attribute to the insufficient sampling (confirmed by subsetting Pandora data to only airborne spectrometer overpass times)
- Clear population of low ozone values that departs from the linear relationship that is high in NO_2 (ozone titration).

Comparing ΩHCHO-O_x results in less values that departed low in the relationship



- We see a shift in ΩHCHO-NO_2 from May to June, likely driven by greater oxidation of NO_2 to PAN, HNO_3 etc.

Conclusions/Next steps

1. Column formaldehyde (ΩHCHO) shows a significant spatial and temporal relationship with surface ozone during the LISTOS and KORUS-AQ field campaigns.

   This suggests that is could be a satellite indicator for poor surface air quality

2. ΩHCHO is better correlated with O_x (ozone + NO_2) indicating its utility for also understanding ozone production sensitivity and related photochemical oxidants.

   As NO_x emissions are reduced, ozone titration will no longer occur, and ozone production efficiency will increase.

3. With sufficient retrieval precision and data density, ΩHCHO could be used as an indicator of ozone and related photochemical oxidants useful for informing air quality monitoring strategies.

   The spatial range observed during LISTOS was only 0.12 DU. The required TEMPO reported precision is 0.37 DU. How far can this precision be improved upon by temporal averaging? TBD…

4. If this retrieval quality is met from satellites, ΩHCHO could be used in conjunction with models to evaluate this relationship with ozone pollution over diverse spatial and temporal domains. For now, deeper analysis will be explored with the expanding network of Pandora spectrometers.

Questions/ideas? → katherine.travis@nasa.gov or laura.m.judd@nasa.gov

Ideas for Future Steps w.r.t. TAQ data

Science objectives that deserve further exploration:

- **Further exploration on the temporal behavior of this relationship spanning from diurnal, to seasonal, to specific meteorological patterns**

Delrin-free Pandora spectrometers operating in summer 2021: White open circles

- LISTOS: EPA-NASA-States collaboration (9 sites?)
- TAQ at 4 sites:

TOLNet and HSRL-2 ozone lidar

+

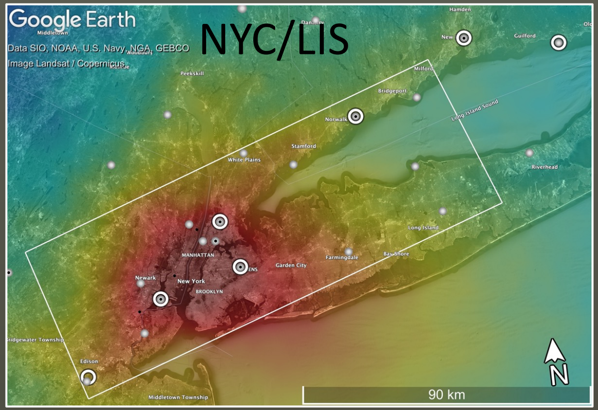
GCAS ΩHCHO

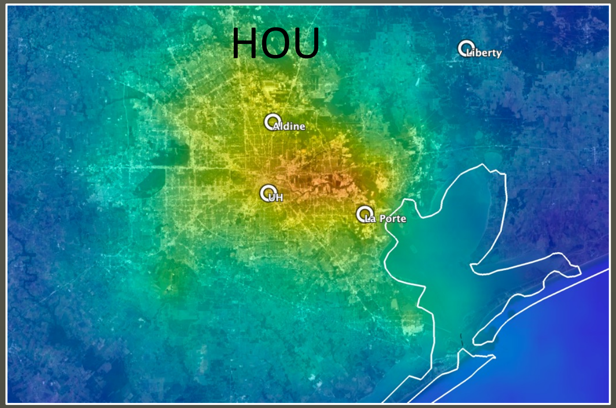
+

TCEQ Ozone network

+

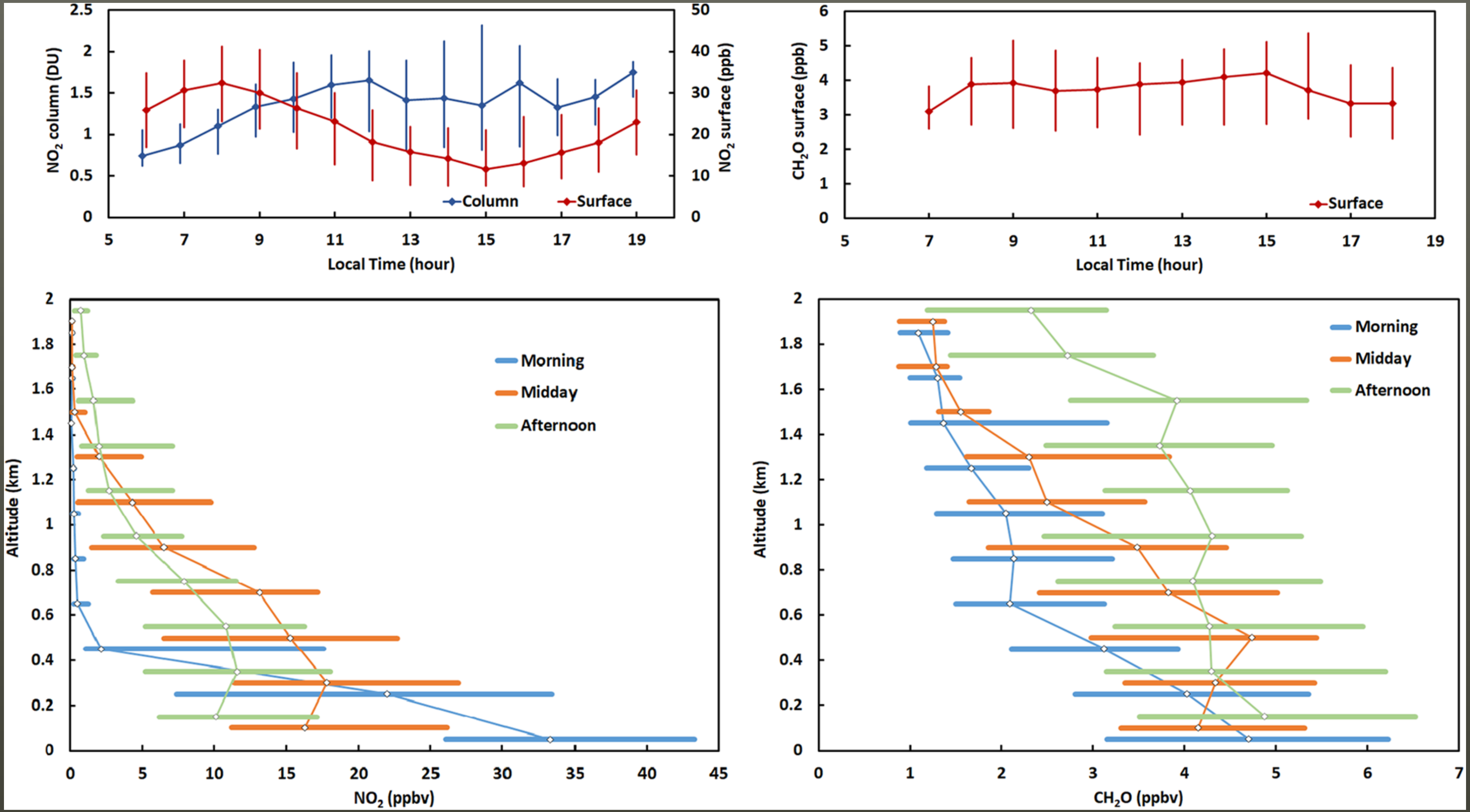
MAQL1 in situ observations?





- **Using chemical transport models to better understand the non-linearities ozone photochemistry in response to other photochemical oxidants**
- **Additionally motivated to use the MAX-DOAS profiles to communicate the tradeoffs in using column vs. in situ ratios of HCHO/NO2 for ozone production sensitivity regimes**
- **When available, assess the ability of TEMPO ΩHCHO**

NO_2 is less related to the surface



Crawford et al., 2021

KORUS-AQ PAN and HNO_3

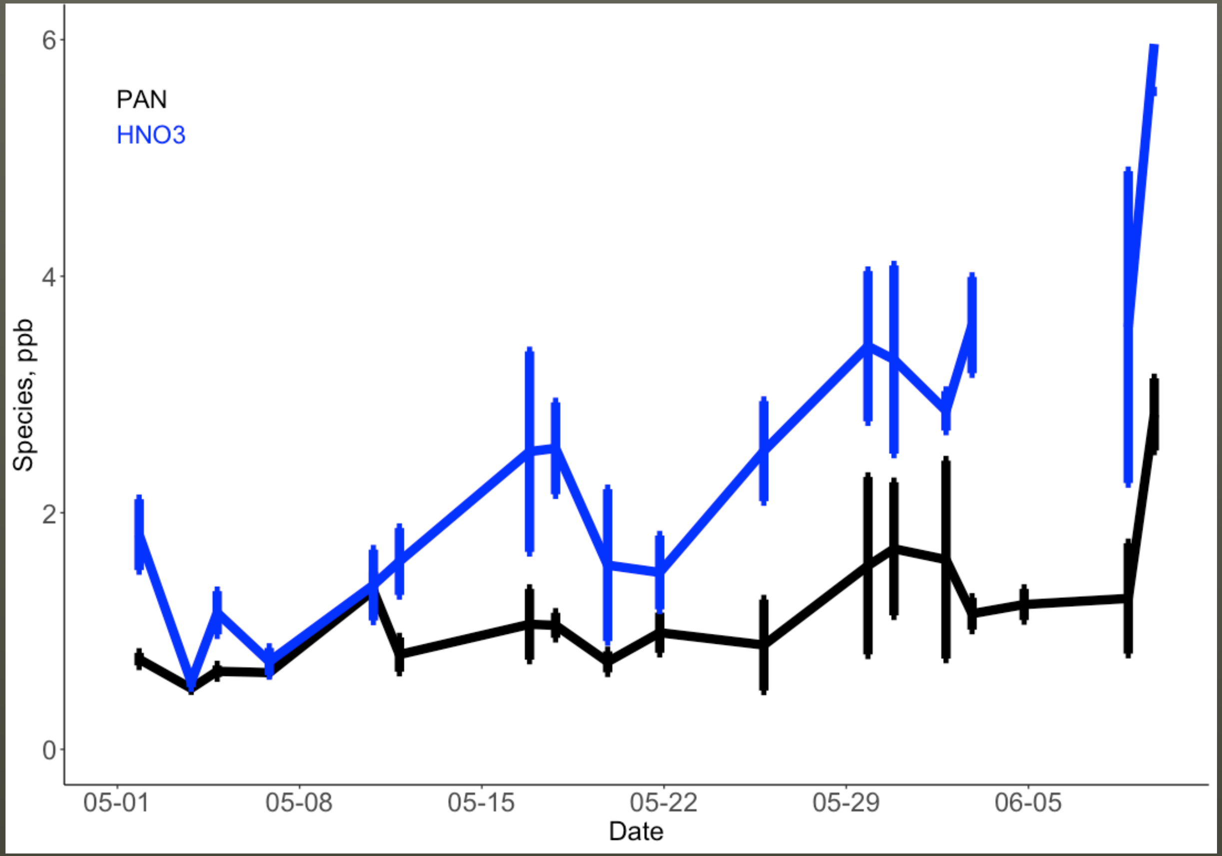


Figure S4. Average PAN and HNO_3 below 0.5 km between 10 to 16 KST from the DC-8 aircraft descents described in Section S2. The PAN measurement is from the Georgia Tech chemical ionization mass spectrometer (GT-CIMS) and the HNO_3 measurement is from the Caltech CIMS (CIT-ToF-CIMS).

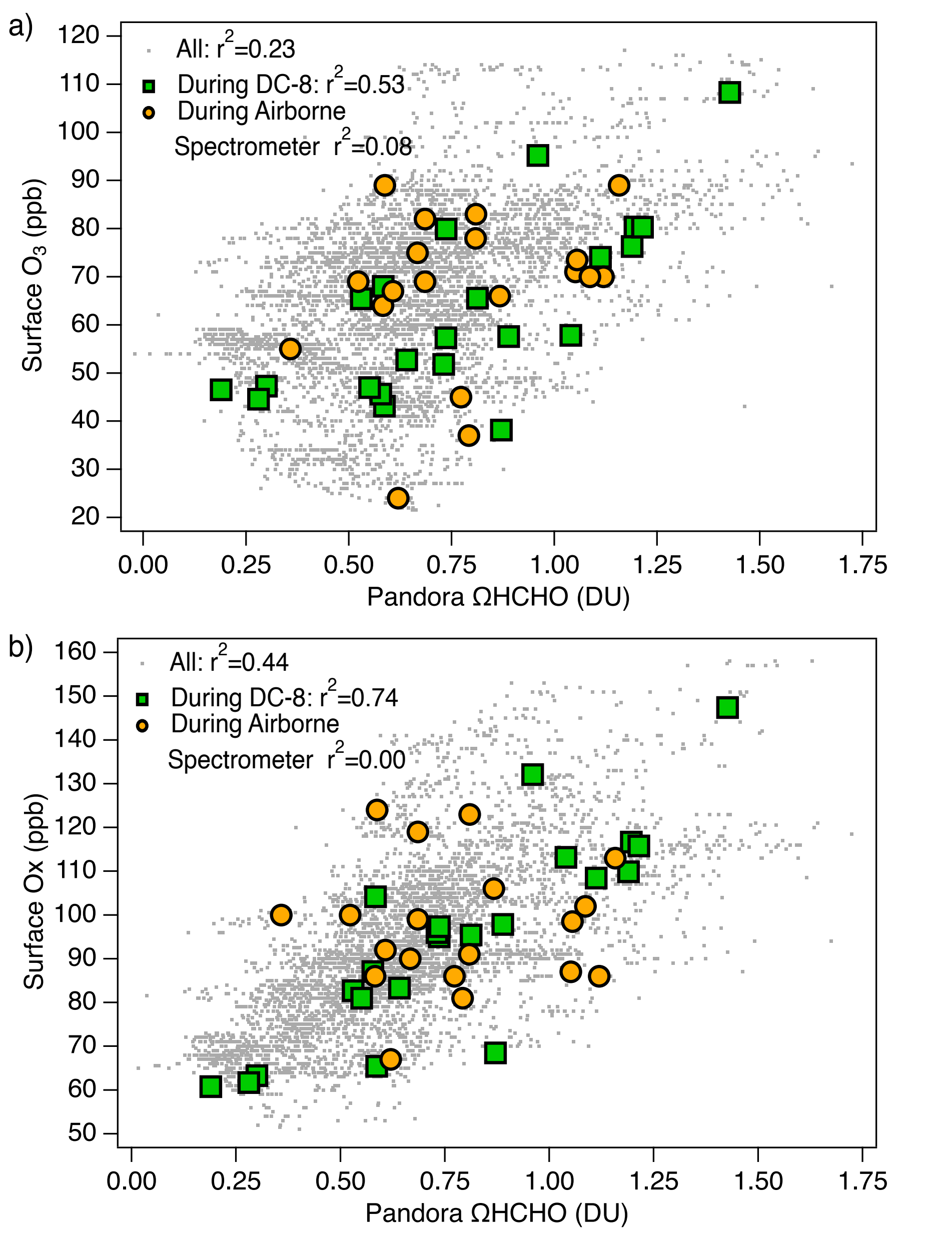


Figure S3. Surface ozone a) and O_x b) vs. WHCHO from all Pandora data, Pandora data during the DC-8 overpasses (green squares) and the airborne spectrometer overpasses (orange circles).