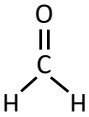
PICARRO

Quantification of formaldehyde by near-infrared cavity ring-down spectroscopy

D. Kim-Hak
Chris W. Rella , J. A. Hoffnagle

Picarro, Inc., Santa Clara, CA

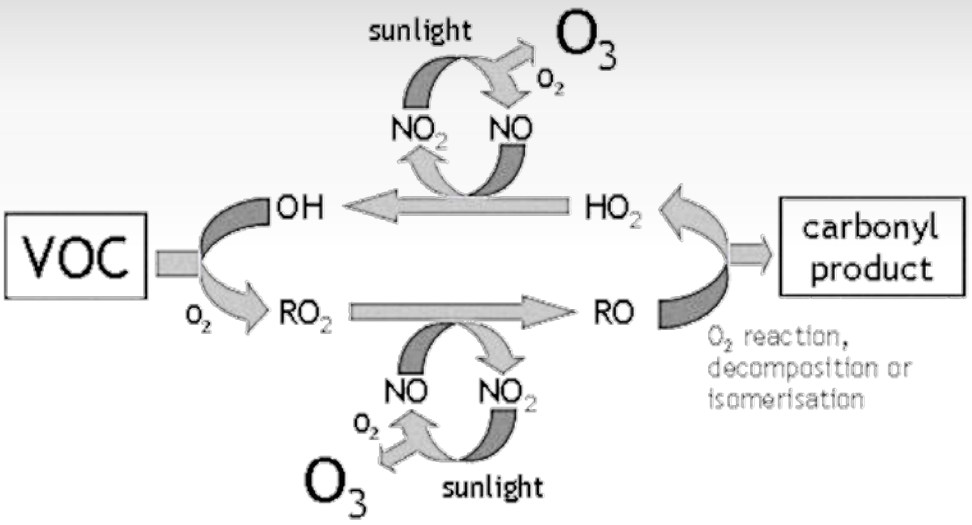
Why Measure Formaldehyde in the Atmosphere?



- HCHO is an important ozone precursor
  - It is an intermediate species in the photochemical oxidation of airborne VOCs (Volatile Organic Compounds)
- HCHO is involved in, and emitted from a variety of materials (composite wood product, carpets) and industrial processes
- HCHO is a respiratory irritant and a known carcinogen
  - NIOSH (National Institute for Occupational Safety and Health) Recommended Exposure Limit (REL) = **16 ppb**

PICARRO

HCHO in the Troposphere



HCHO

- HCHO in the troposphere is the result of direct anthropogenic emissions and indirect formation from VOC oxidation (photochemically driven)
- HCHO is scavenged from the atmospheric via similar oxidation pathways
- Lifetime of formaldehyde in the troposphere is typically on the scale of hours

- **In-situ formaldehyde observations inform photochemical models, improving understanding of ozone and secondary organic aerosol formation**

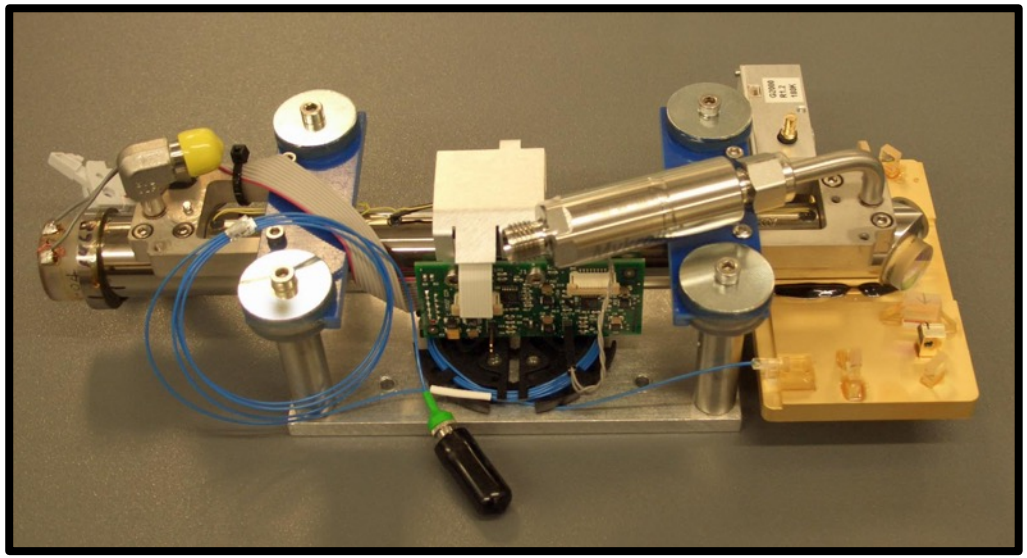
http://mcm.leeds.ac.uk/MCM/project.htt

Alternative Methods for Formaldehyde Detection (at ppb levels)

- DNPH cartridges + High Performance Liquid Chromatography
  - Sensitive, selective, well-benchmarked and tested, measures other aldehydes and ketones
  - Not real time, requires off-line analysis
- closed cell FTIR
  - Selective, measures other species
  - Not sufficiently sensitive without preconcentration (~ 10s ppb in 5 minutes)
- Laser Induced Fluorescence
  - very sensitive and selective, real time
  - Requires UV source, no commercially available options
- Tunable Laser Absorption Spectroscopy with a multi-pass cell
  - selective, marginal sensitivity
  - requires mid-infrared laser source
- DOAS (Differential Optical Absorption Spectroscopy)
  - Selective, complementary to point-source in-situ data, useful for column measurements or path integrals
  - difficult to calibrate, only available during clear sky daylight hours, not easy to deploy indoors
- Gas Chromatography
  - sensitive and selective, measures many other species
  - not real time, requires preconcentration and more advanced detectors for sub-ppb precision
- PTR-MS (Proton Transfer Reaction - Mass Spectrometry)
  - sensitive and selective, measures many other species
  - complicated, difficult to field deploy

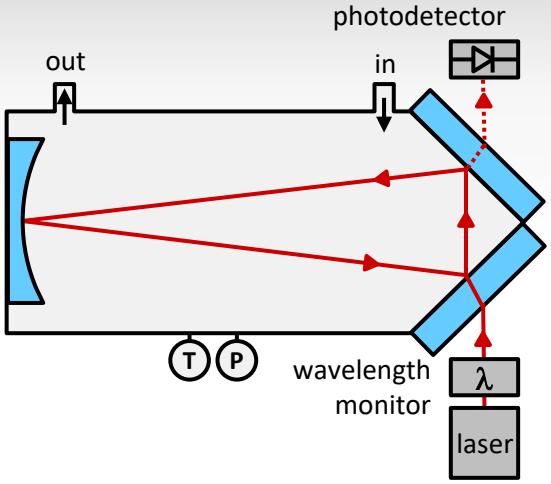
HCHO measurements in the near-infrared

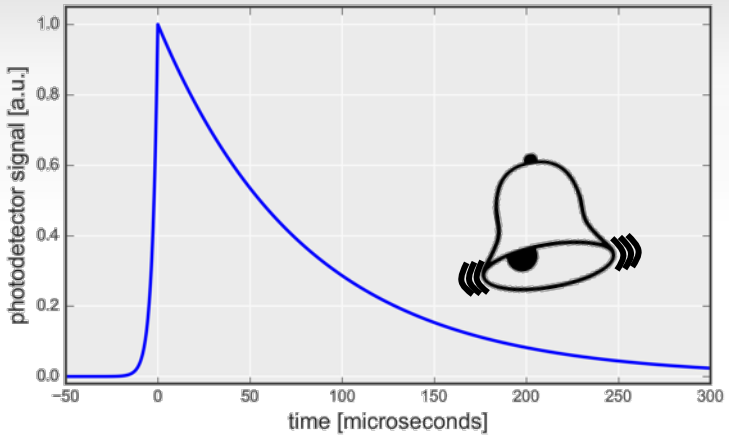
- **Sensitive:** (1-σ) precision 1 ppb in 1 sec, 0.1 ppb in 100 sec
- **Real-time:** responds in seconds to ppb-level changes in HCHO
- **Accurate:** only simple and infrequent calibration required
- **Selective:** measures HCHO accurately in the presence of other atmospheric species (H_2O, CO_2, CH_4, and other aldehydes and VOCs)
- ***In-situ:*** no sample prep or laboratory consumables; robust, easy to use; field deployable with no user intervention
- **Other Measurements:** CH_4 and H_2O



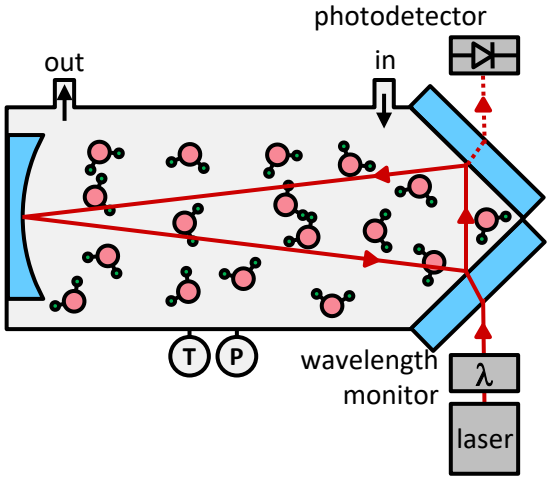
Picarro's Cavity Ring Down Spectrometer

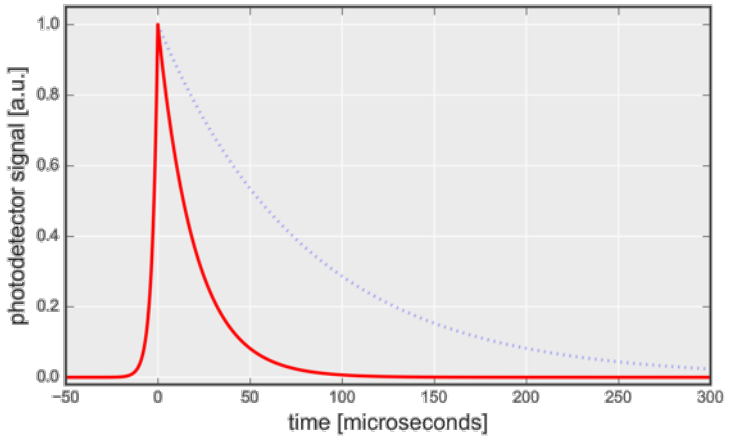
No gas molecules in cavity





Gas molecules in cavity

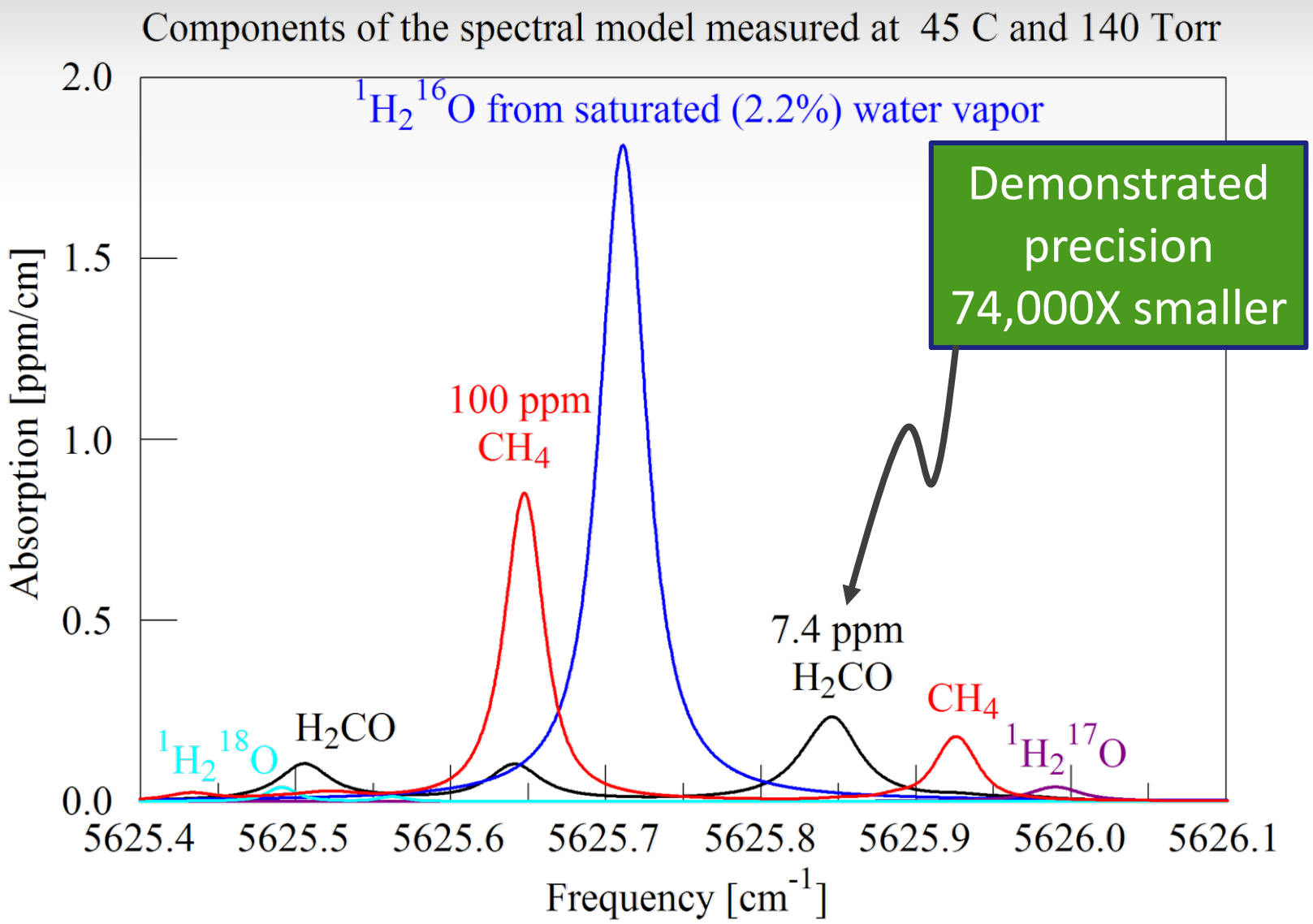




Time-based measurement means very high precision and accuracy

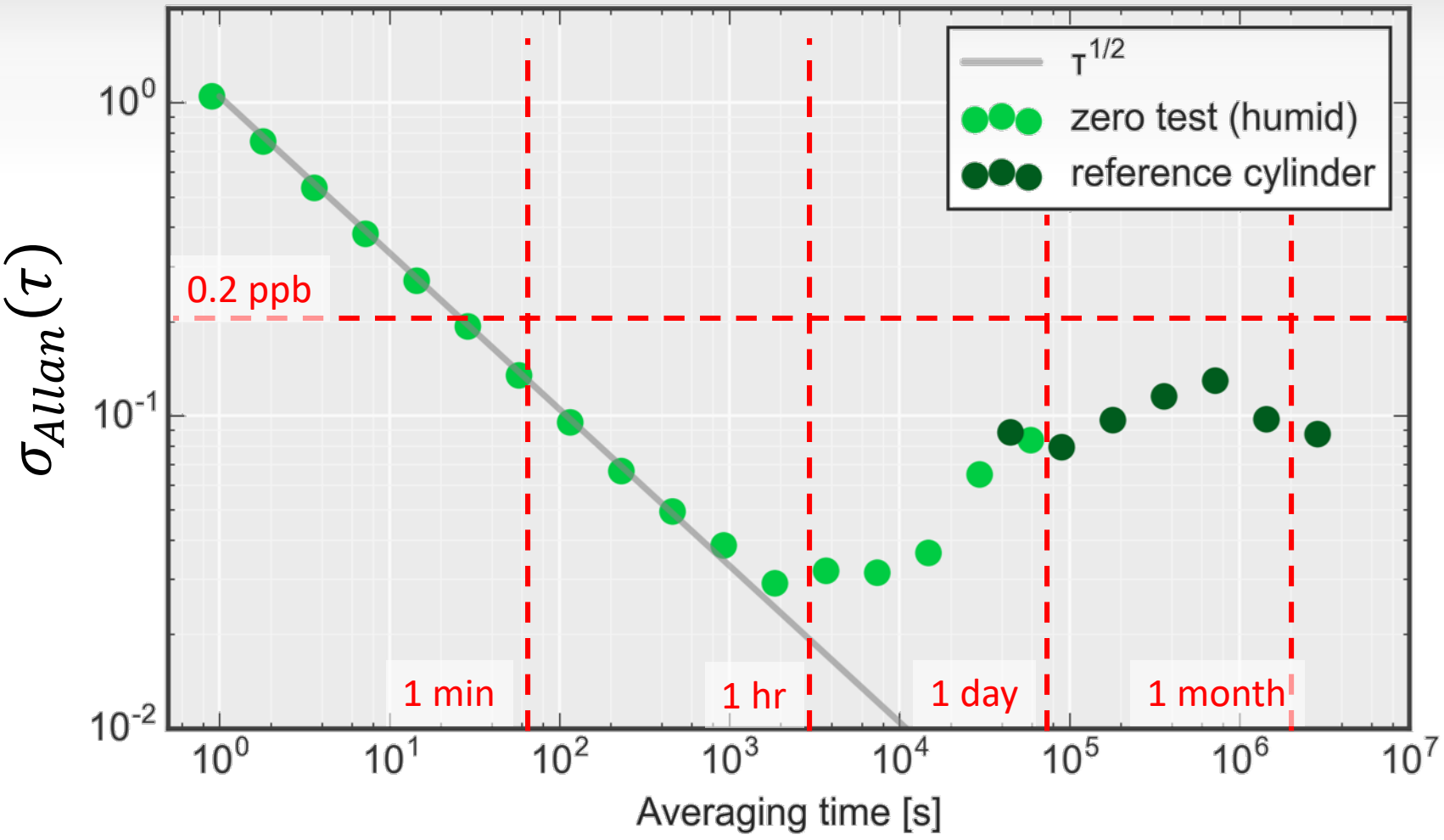
PICARRO

Near Infrared Spectrum of HCHO, CH_4, and H_2O



PICARRO

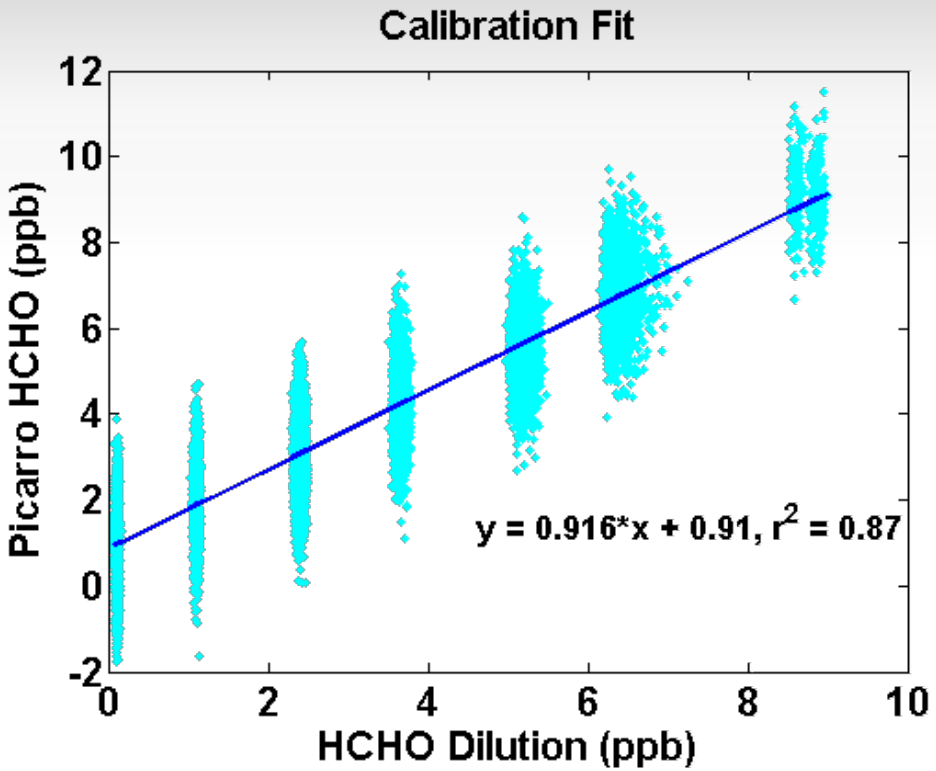
Allan Standard Deviation: Characterizing Precision and Drift at zero

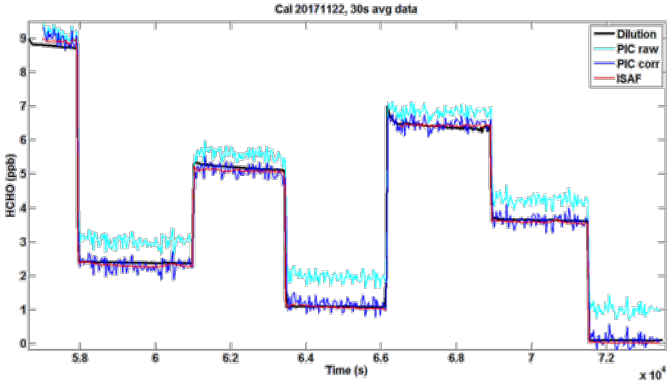


PICARRO

CRDS – Calibration and Linearity

- Initial calibration from literature (Saha et al. and Barry et al.)
- Calibration confirmed against a bottle of ~600 ppb HCHO in N_2
  - bottle value assigned via UV cross-section (Hanisco and Wolfe)
- Testing against well-characterized Laser-Induced Fluorescence (LIF) instrument shows excellent linearity





[1] Saha et al., *Molecular Physics* **107**, 797-805 (2007)
[2] Barry et al., *Phys. Chem. Chem. Phys.* **4,** 445 (2002).
[3] Wolfe, G and Hanisco, T., NASA GSFC, *personal communication (2018).*

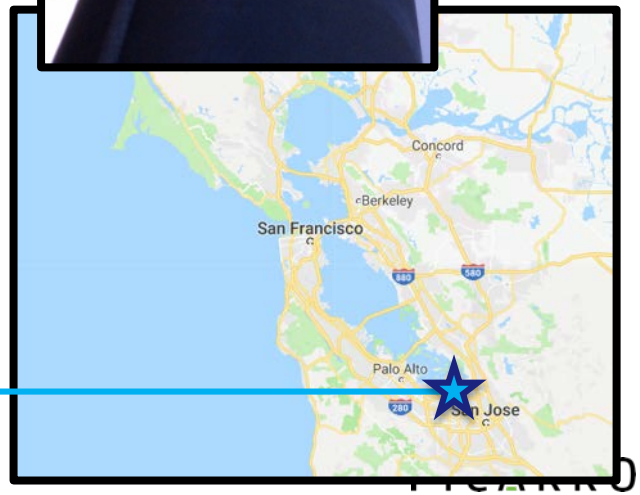
PICARRO

Ambient Measurements of HCHO

- Species Measured:
  - H_2CO
  - H_2O
  - CH_4

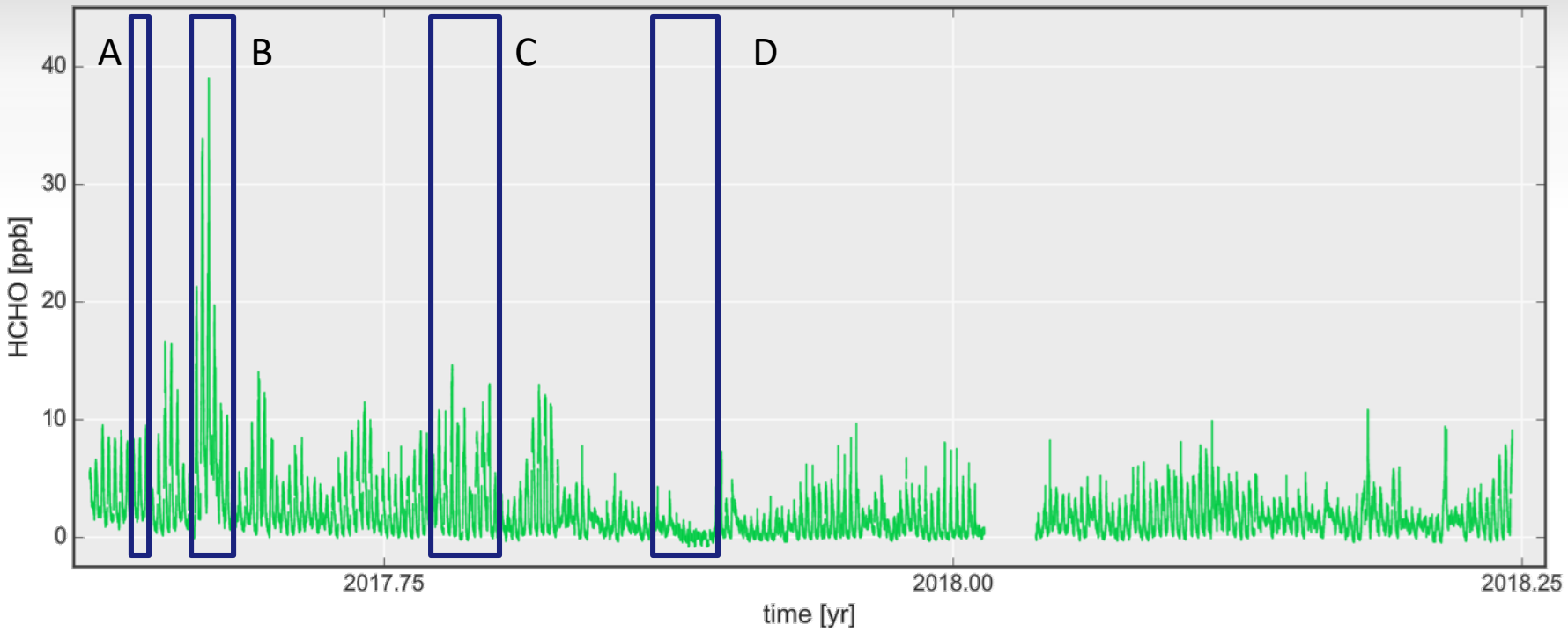
  G2307 Analyzer
  - CO
  - CO_2

  G1302: CO_2 and CO analyzer
- Measurements for about 200 days (and counting) at the Picarro 8 m “Urban Tower” (a.k.a., the flagpole outside our office)
- Gas stream not dried
- Transfer lines not heated
- Single bottle reference check for 10 minutes twice / day (02:00 and 14:00)



Picarro Urban Tower

Ambient HCHO Time Series (7 months)



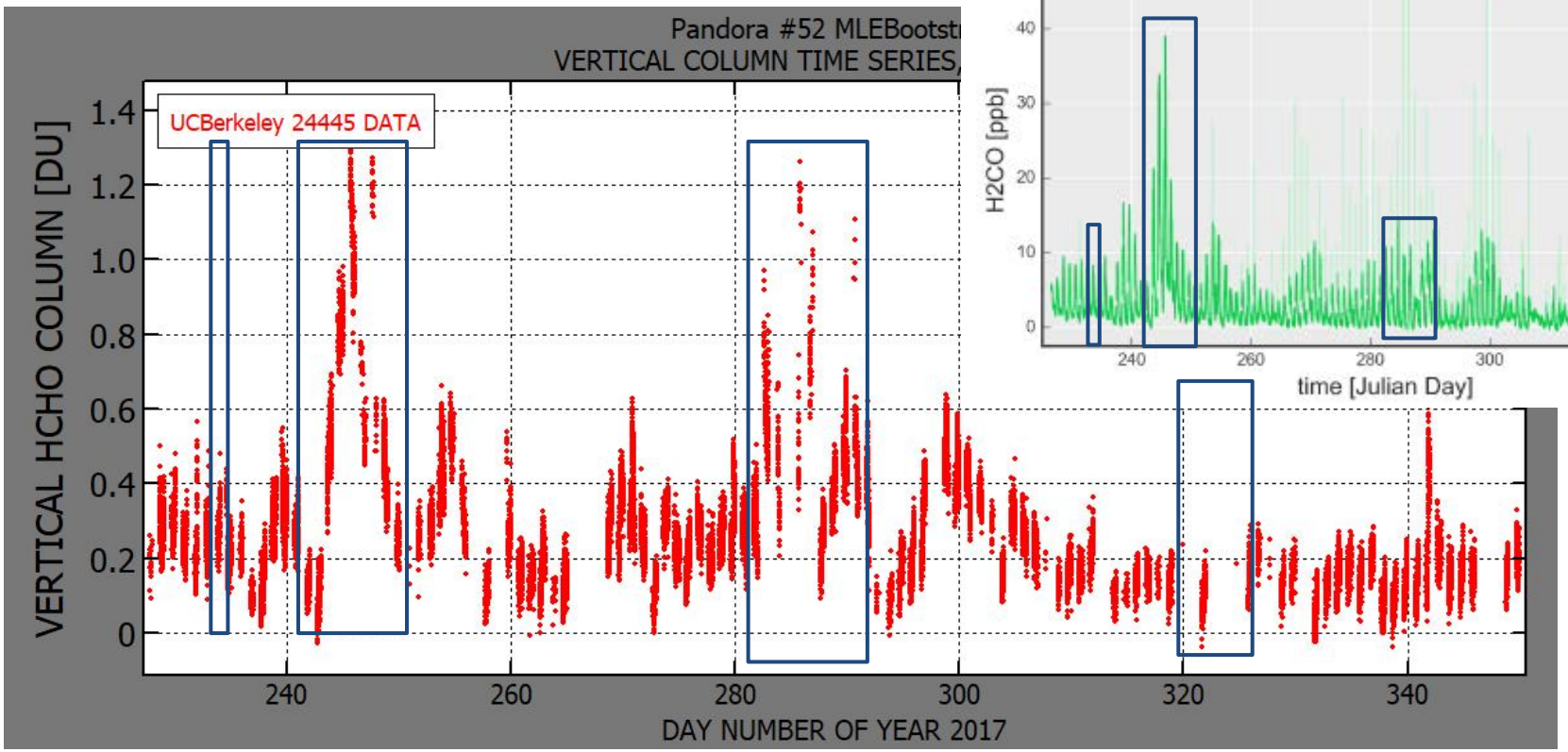
- A: Partial Eclipse
- B: Heat wave / ‘Spare The Air’ days
- C: Northern California Wildfires (100 – 150 km distant)
- D: Overcast / rainy (late fall)

(Data gap due to water intrusion in outdoor sampling line)

PICARRO

Comparison to Pandora Spectrometer @ UC Berkeley

- Pandora: total column measurement of HCHO, NO2, ozone and other species using UV-VIS solar spectroscopy



PANDORA data courtesy of :

Mueller, M and Tiefengraber, M., Luftblick Earth Observation Technologies, Kreith, Austria.

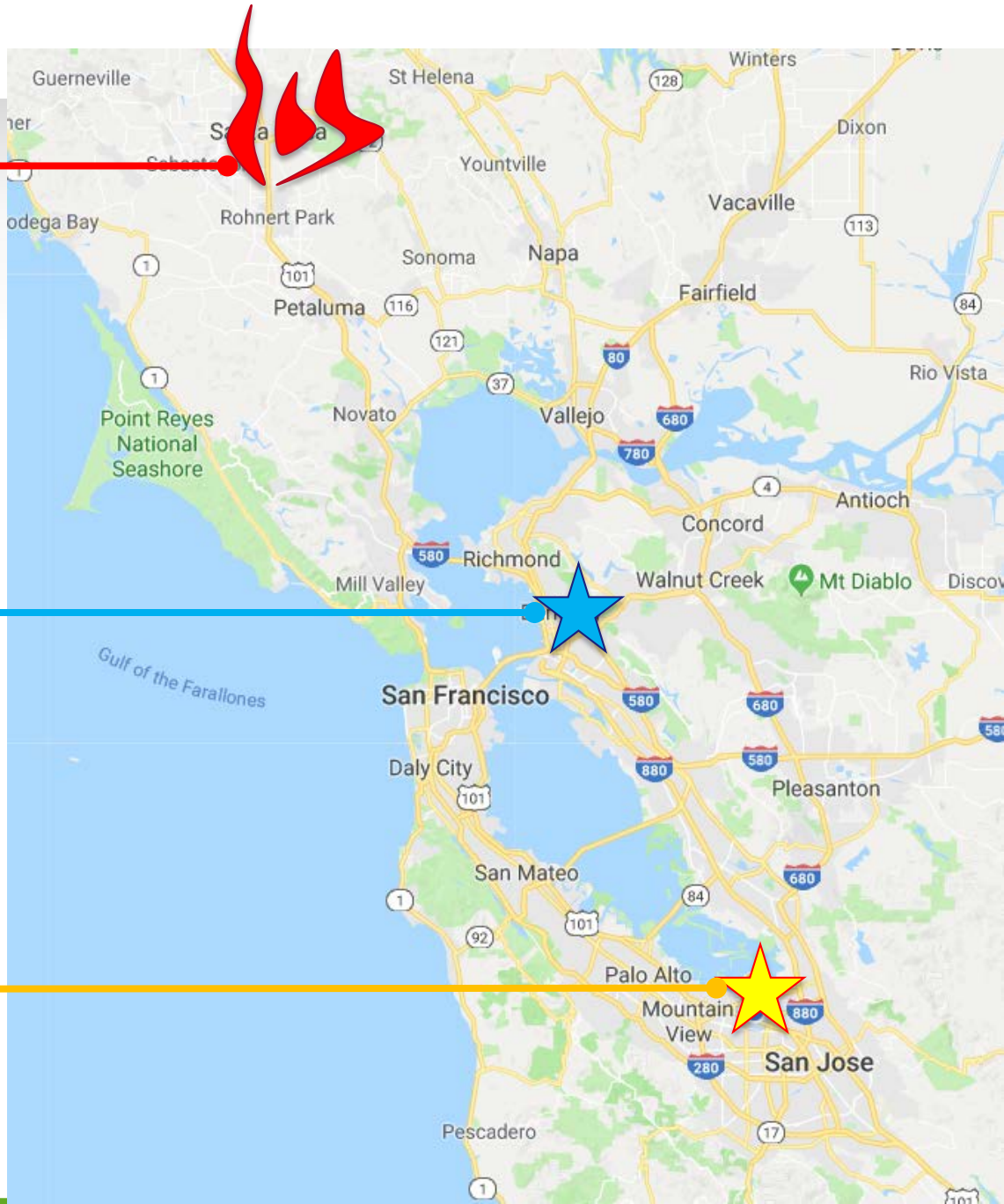
Wooldridge, P. and Cohen, R., U.C. Berkeley

PICARRO

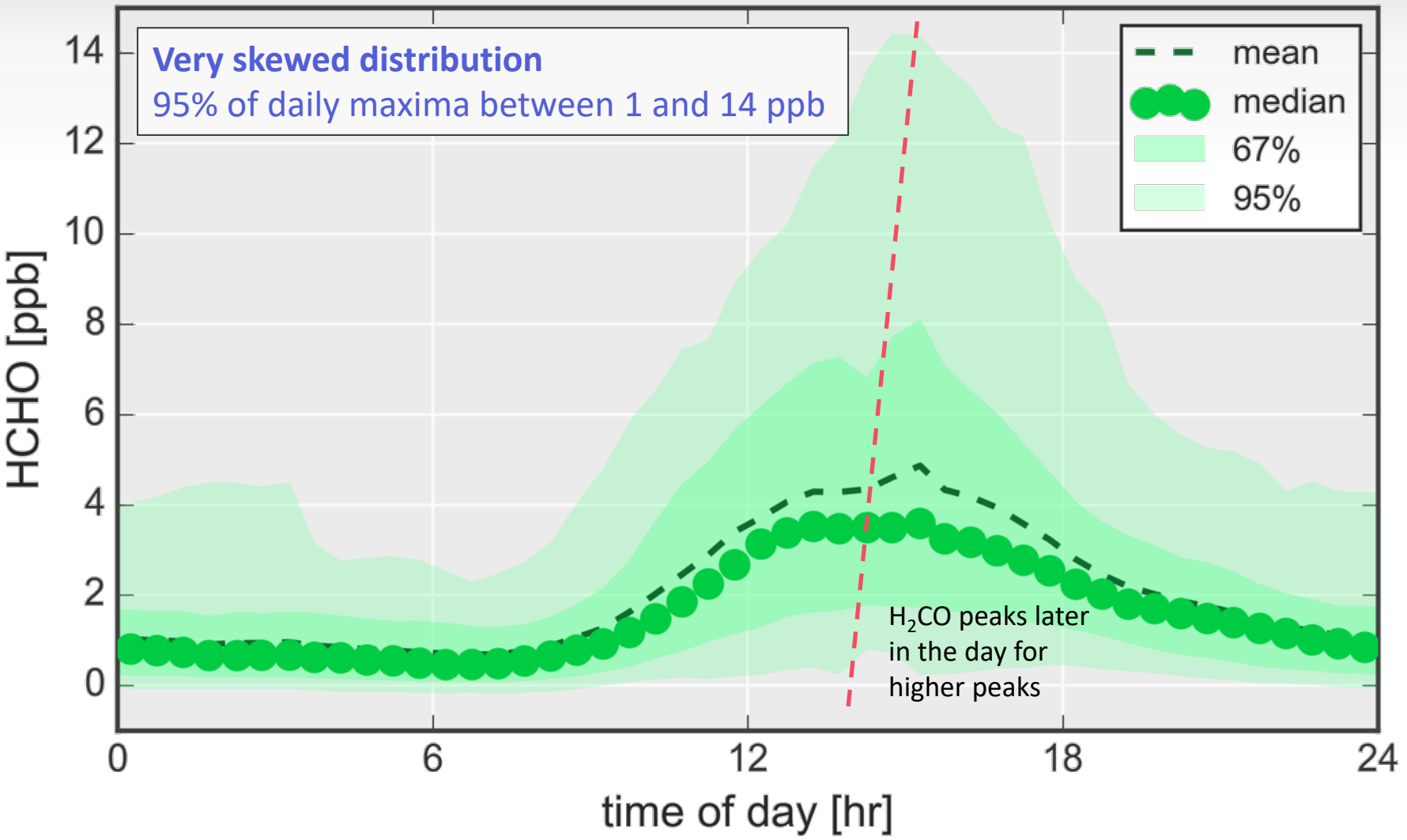
Northern CA Wildfires

UC Berkeley Pandora

Picarro CRDS



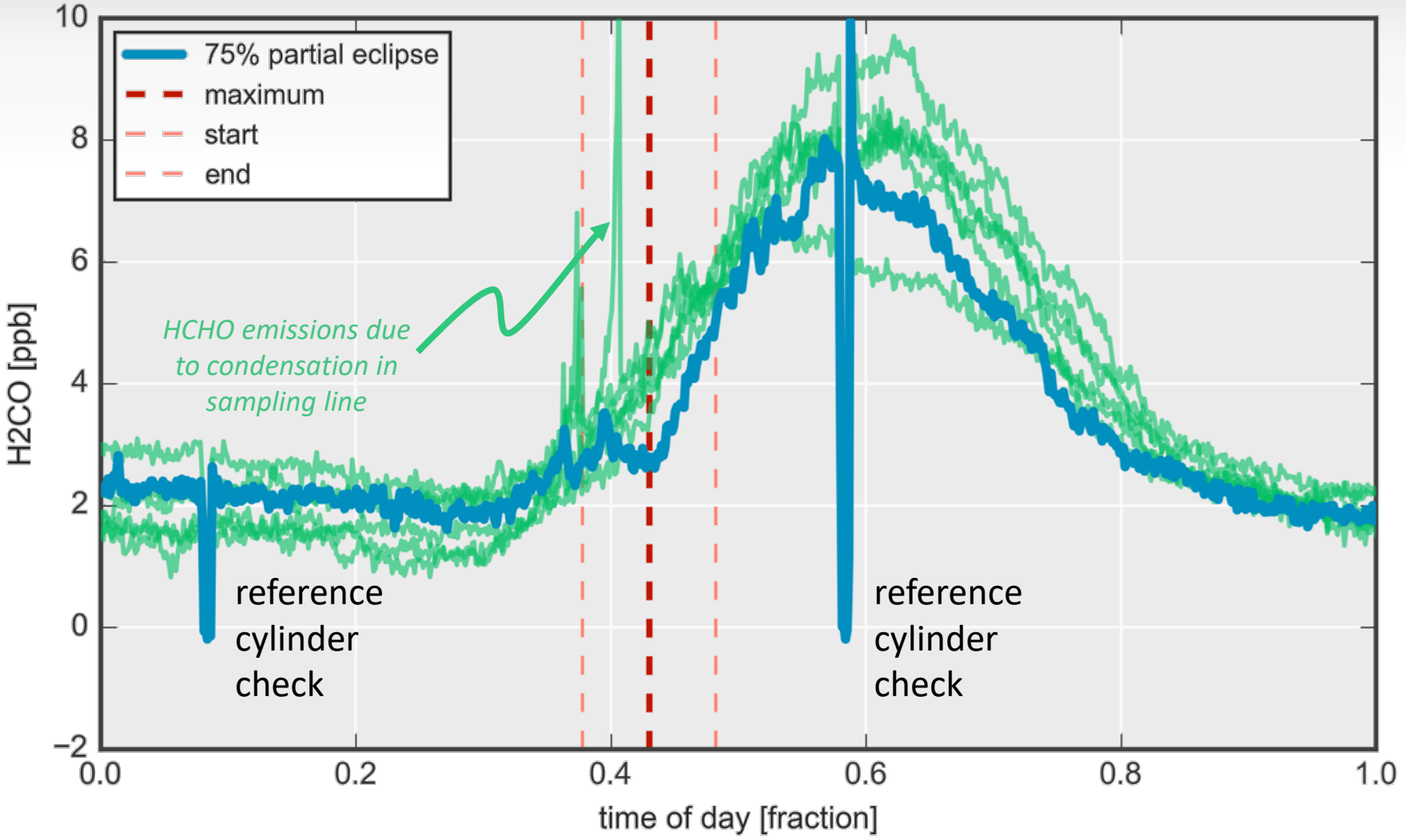
Diurnal Cycle – Formaldehyde (7-month test)



PICARRO

The 2017 American Eclipse on Aug 21st, 2017

Can We See The Partial Eclipse in the Formaldehyde Signal?



PICARRO

Thank you!

Thanks to E. Wahl, D. Fleck, T. Hanisco, L. Valin, G. Wolfe, M. Mueller, M. Tiefengraber, P. Wooldridge, L. Araci, J. Morerro, and R. Cohen

CRDS – Calibration

- Picarro Initial Calibration: literature values for our absorption line[1,2]

- Measurement of NASA-calibrated HCHO reference cylinder[3]
  - **Cylinder assigned Value: 580 ± 15 ppb in balance N_2**
    - assigned by NASA group via UV-cross-section
  - **Picarro measurement : 575.5 ppb ± 5 ppb**

    (difference of 0.8%)
    - after spectroscopic correction for N_2 vs air (+6.25%) was applied
    - well within uncertainty on cylinder assignment

[1] Saha et al., *Molecular Physics* **107**, 797-805 (2007)
[2] Barry et al., *Phys. Chem. Chem. Phys.* **4,** 445 (2002).
[3] Wolfe, G and Hanisco, T., NASA GSFC, *personal communication (2018).*