# A41I-2745: **Advantages of Hourly Resolved Formaldehyde (HCHO) Measurements in Identifying Impacts from Wildfire Emissions, a Case Study**.

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## 0. OBJECTIVE

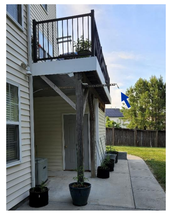
Data obtained from the Picarro G2307, a Cavity Ring Down Spectrometer (CRDS) for formaldehyde (HCHO) has previously demonstrated excellent overall correlation with data obtained via EPA Method TO-11A. Extensive intercomparison with trusted standards, and key opinion leader laboratory instruments, and a traceable calibration process has led to a revision of the instrument scaling that matches TO-11A methods very closely and consistently. To further improve performance, we introduced auto-zero functionality, allowing to track the instrument zero baseline in a highly resolved manner. We believe, by correcting for its drift over time, a lower detection limit and improved accuracy in different ambient outdoor and indoor air matrices are achievable.

## 1. MOTIVATION

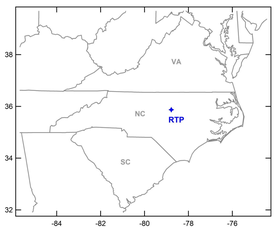
- **Toxic Carcinogen**
  - one of 188 hazardous APs listed by US EPA.
- **Primary Sources**
  - Industry (power plants)
  - Manufacturing
  - Incinerators
  - Biomass burning
- **Secondary Sources *via Oxidation of***
  - $CH_4$ + OH — *methane*
  - $CH_3OH$ + OH — *methanol*
  - $CH_3CHO$+OH — *acetaldehyde*
  - $C_5H_8$ + OH — *isoprene*
  - $C_4H_6$ + $O_3$ — *1,3-butadiene*
- **Indoor Exposure Risks**
  - Commercial and consumer products
- **NIOSH*:** workplace exposure < 16 $ppb_v$ over 10h, and < 100 $ppb_v$ over any 15 min period within.

**) REL adapted from OSHA' PEL for carcinogens in 29 CFR 1990*

## 2. MEASUREMENT LOCATION "RTP"



Residential neighborhood in Morrisville NC, ca. 7 km W from RDU, 4 km S from EPA campus.




Continuous HCHO measurements started on July 6th, 2022, and are ongoing.

## 3. INSTRUMENTATION

Picarro developed the G2307 HCHO instrument between 2017 and 2018 in response to a need for stable real-time measurements of HCHO in ambient settings where 8-24 hour average signals typically range from 0-10 ppb. The G2307 instrument was equipped with an adjacent $CH_4$ line to enable both real-time $CH_4$ measurements and an ability to determine laser and system health without needing to directly check/calibrate with HCHO.

**G2307 Instrument (near-IR CRDS)**

| G2307 Formaldehyde | Typical Performance** | Specifications*** |
|---|---|---|
| Lower Detection Limit (3σ, 300 sec) | 0.18 ppb | 0.3 ppb |
| Zero Drift (72 hrs)* *(peak-to-peak, 50-minute average)* | 0.33 ppb | 1.5 ppb |
| Precision (1σ, 2 sec)<br>Precision (1σ, 10 sec)<br>Precision (1σ, 300 sec) | 0.7 ppb + 0.1% of reading<br>0.31 ppb + 0.05% of reading<br>0.06 ppb + 0.02% of reading | 1.2 ppb + 0.1% of reading<br>0.6 ppb + 0.05% of reading<br>0.1 ppb + 0.02% of reading |
| Measurement Interval | <2 sec | <2 sec |
| Response Time (0–20 ppb) *(Rise/Fall Time 10–90% / 90–10%)* | <5 sec | <5 sec |
| Measurement Range | 0–30 ppm | 0–30 ppm |

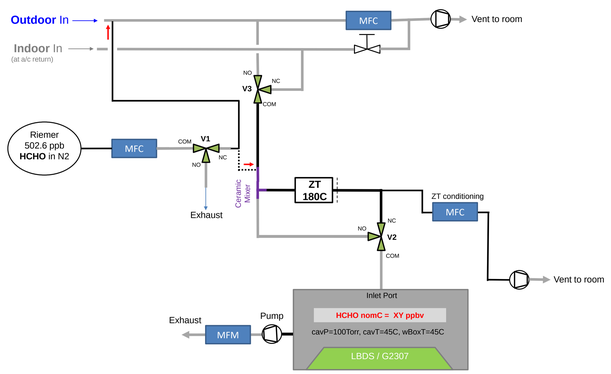
** Picarro analyzers do not require a zero reference gas or zero catridge to operate or meet specifications.*

*** Typical performance is defined as the median of testing results from ten sequentially built G2307 analyzers in 2019. Results available upon request.*

**** Specifications and an instrument-specific testing report (Certificate of Compliance) provided with every analyzer purchase.*

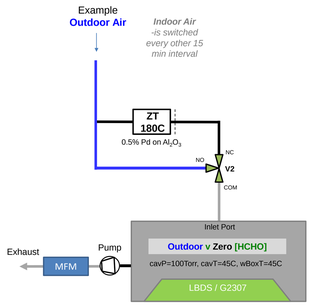
## 4. SETUP

**Goal:** Outdoor vs Indoor with frequent zeros and **standard additions** at either **Outdoor Inlet** to check transfer through sample line, or **Ceramic Mixer** to check air matrix effects.



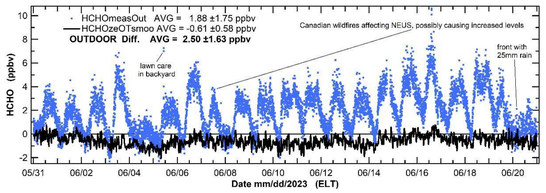

## 5. DATA QUALITY

### 5a. Instrument Baseline via Hot Catalyst (ZT)



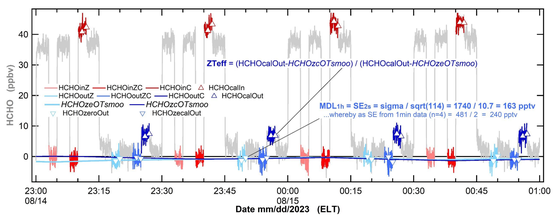

Picarro continued to work on options for auto-zero correction and identified the most effective and selective scrubbing medium least impacting the "Big 3" spectral absorbers ($H_2O$, $CO_2$, $CH_4$). HCHO absorption signal fitting algorithms have been developed with these Big 3 absorbers in mind. Thus, a material that selectively removes HCHO from the sample stream but transfers the Big 3 unaltered has been chosen. A catalyst containing 0.5% Pd on alumina pellets operated at 180C allows highly resolved, and baseline corrected HCHO measurements.

Tracking **instrument baseline** makes quality of reported data less sensitive to drift due to ambient interferences and surface degradation effects.




**Blue dots**: 1-min average of HCHO signal measuring outdoor air.
**Black line**: Smoothed (15-min running avg) interpolation of intermittent 1-min zero signals.
**Reported [HCHO]: Difference between blue dots and black line;** resulting negative values = 0.

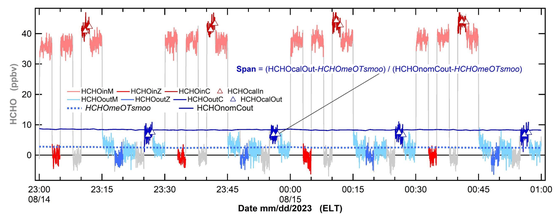
### 5b. Zero Trap Efficiency (ZTeff) and MDL




**ZTeff** determined from difference of cal signal with Zero vs loaded Zero smoothed baselines: **100 ±3%.**

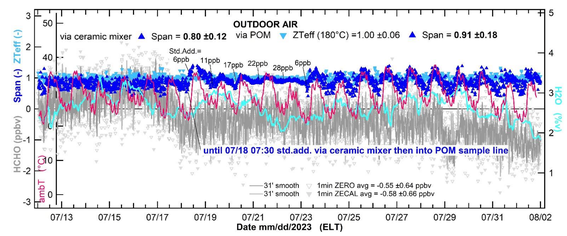
**Method Detection Limit (MDL)** from uncertainty in Zero expressed as standard error of high-resolution (2s) data available per hour (here n=114, STD=1740 pptv): **94 – 169 pptv.**

### 5c. Recovery (Span)



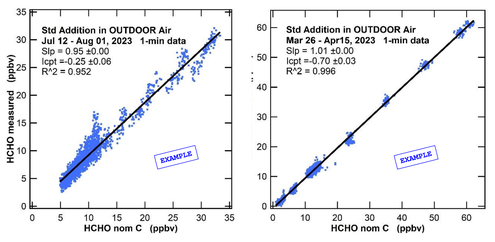

**Span** determined from standard addition signal response *HCHOcalOut* above outdoor air signal relative to expected delta signal increase from standard's dynamic dilution into outdoor air sample: **87 ±13%.**

### 5d. Transfer Thru Sample Line




Standard additions to **10m POM line** yields **91 ±18%** recovery. POM yields **~5% lower recovery than HDPE.**

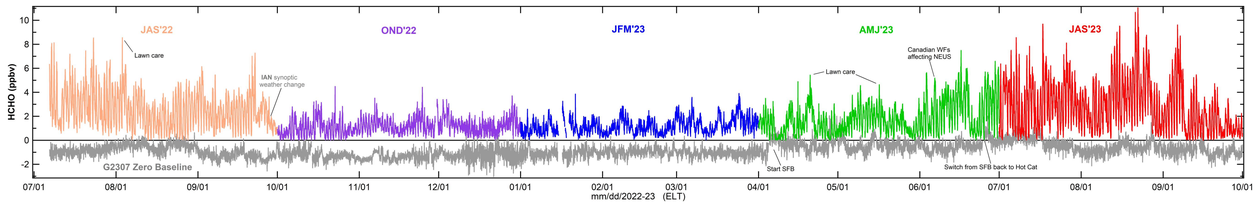
### 5e. Linearity and Precision



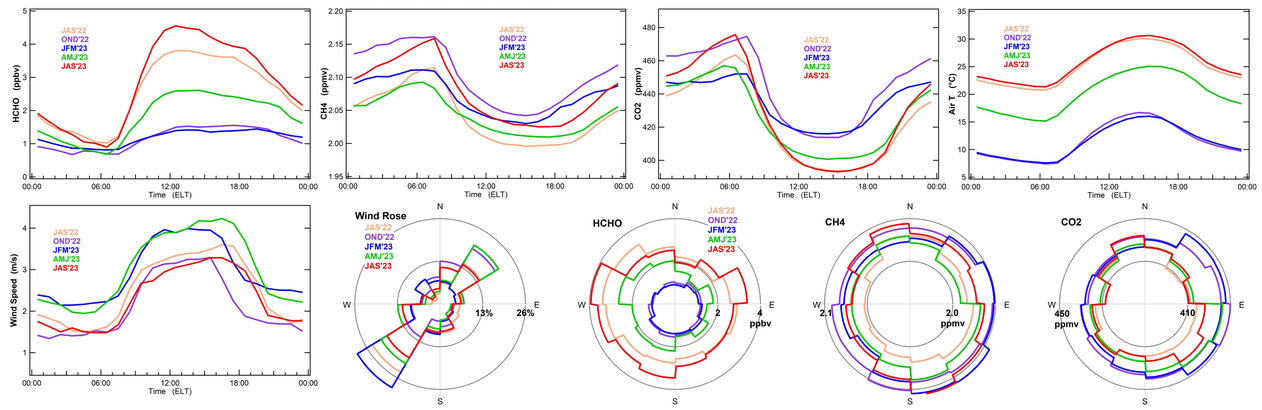

Linearity: A 1:1 linearity was maintained to **within 92%** or better across the 2 to 60 ppbv range.
Precision: The 1-sigma variability in hourly Recovery (Span checks) ranged between **3 - 18%.**

## 6. DATA SET

### 6a. Diurnal Features of HCHO and Supporting Parameters

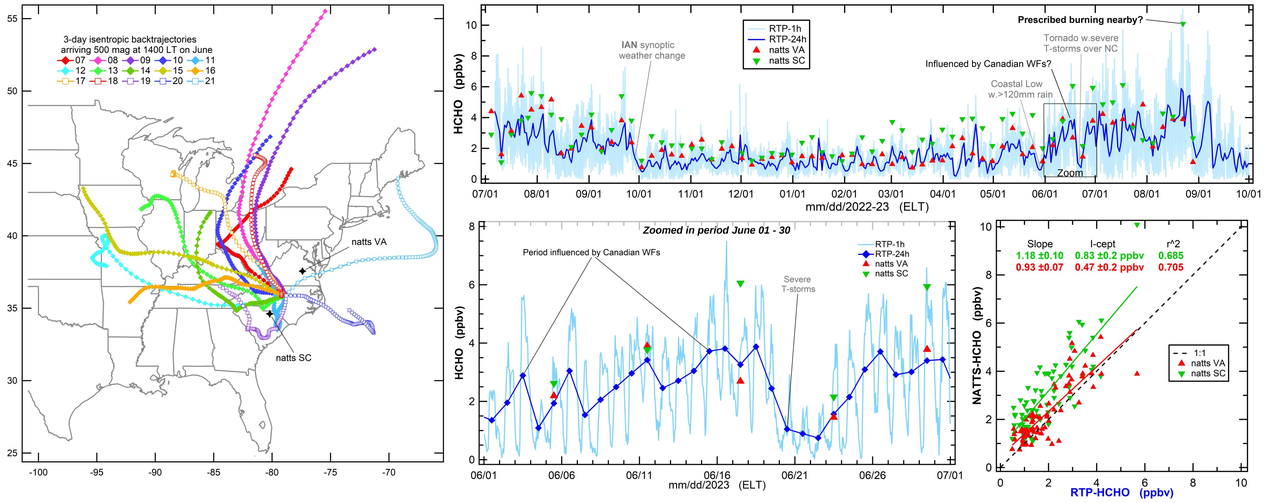



G2307 baseline levels vary hourly, while lower frequency drifts occur during 15-month period. Baseline-corrected HCHO (colored quarterly) show expected diurnal and seasonal variability due to known photochemical production / destruction mechanisms. Episodic atmospheric disturbances like TS Ian in Sep'22, cause prolonged drops in [HCHO]. Short-term spikes are due to local sources. CH4 and CO2 show elevated nighttime levels and afternoon minima due to BL dynamics.




Prevailing wind directions are SW and NE. Episodic NW winds occur in colder months. Westerly winds carried highest [HCHO] in summer and spring. Highest CH4 and CO2 were transported from easterly directions. Knowing the diurnal features, westerly flows occur during well-mixed daytimes allowing signatures from long-range transport, while easterlies carry signatures from local sources enhanced by compressed nocturnal boundary layer.

### 6b. Comparison with HCHO via EPA's TO-11A at Neighboring NATTS




Our hourly HCHO concentrations were further reduced to daily (24h) averages and compared with two of EPA's national air toxics trends sites (**NATTS**) closest to ours. NATTS collect HCHO with 2,4-dinitrophenylhydrazine coated cartridges that are subsequently analyzed by high-performance liquid chromatography, known as EPA compendium method TO-11A. The two NATTS are in VA and SC, equal distance from RTP to the NE and SW, respectively. Early June 2023, large wildfires burned in the Canadian provinces of Ontario and Quebec, inundating NY City and other large east-coast cities in smoke. The polluted air masses also reached the Carolinas with westerly trajectories, causing the westerly HCHO contributions in above **AMJ'23** rose. During this long-range plume transport event, our 24h-averaged data agreed well with the two data points from both NATTS. However, the entire 14-month period shows poor agreement indicated by the regression plot.

## 7. CONCLUSIONS

The Picarro G2307 has been demonstrated to generate high quality HCHO data at a minute-based resolution in a continuous monitoring setting. When compared to regional daily data from the EPA NATTS network, its high-resolution data provides valuable information about acute exposure risks during potentially harmful periods that are impacted by wildfire or other biomass burning emissions. Prescribed burning (PB) is a common land management tool employed in the SEUS, including SC. The monthly acres burned 2023 in SC are 328 (Jan), 800 (Feb), 2116 (Mar), 401 (Apr), 1059 (May), and 66 (Jun), potentially contributing to the systematically higher HCHO values seen at the SC site in those months. PB data for month of Aug'23 when SC site recorded 10 ppbv HCHO on 08/22, was not yet available. As shown above, the large wildfires raging early June in eastern Canada, impacted the Carolinas via long-range transport of those emissions. HCHO was "conserved" in this multi-day journey by i) more of it being formed from complex daytime (photochemical) oxidation of mainly isoprene and terminal alkenes, that are co-emitted significantly, and ii) multiphase regeneration involving dissolved $SO_2$ (sulfite) and Hydroxymethanesulfonate (HMS, $CH_2(OH)SO_3^-$) in aerosol. HMS is an important organosulfur compound, contributing to secondary aerosol formation. Complex aerosol condensation and drying mechanisms occurring over night and next morning could help HCHO partition into the gas-phase, explaining the observed elevated nighttime levels during these plume transport events. Comprehensive studies of the chemical evolution of such plumes are underway to better understand the complex multi-phase processes.

## 8. ACKNOWLEDGEMENTS

The authors gratefully acknowledge the NOAA Air Resources Laboratory (ARL) for the provision of the HYSPLIT transport and dispersion model and READY website (https://www.ready.noaa.gov) used in this presentation. We appreciate the provision of most recent NATTS data from the respective State agencies via Ms. Renee Madden (SC Dept. of Health & Environmental Control), and Ms. Namita Verma (VA Dept. of Environmental Quality), and of current fire data from Forest Protection Chief Darryl Jones (SC Forestry Commission). KB thanks Jan Wozniak for help with the 2s-binning of raw data.

PICARRO

SCAN ME

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