



Department of
Environmental
Conservation



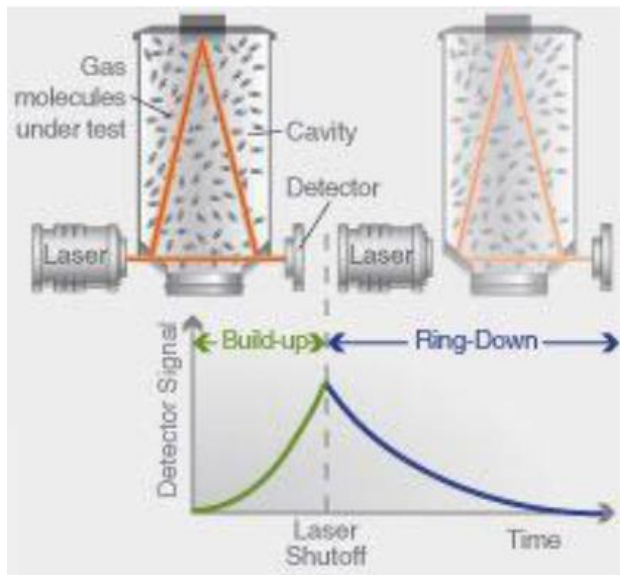
Draft Experiences with Picarro G2307 HCHO Analyzers

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Division of Air Resources
Bureau of Air Quality Surveillance

NACAA Monitoring Steering Committee
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Method – The Theory

Cavity Ring-Down Spectroscopy (CRDS)



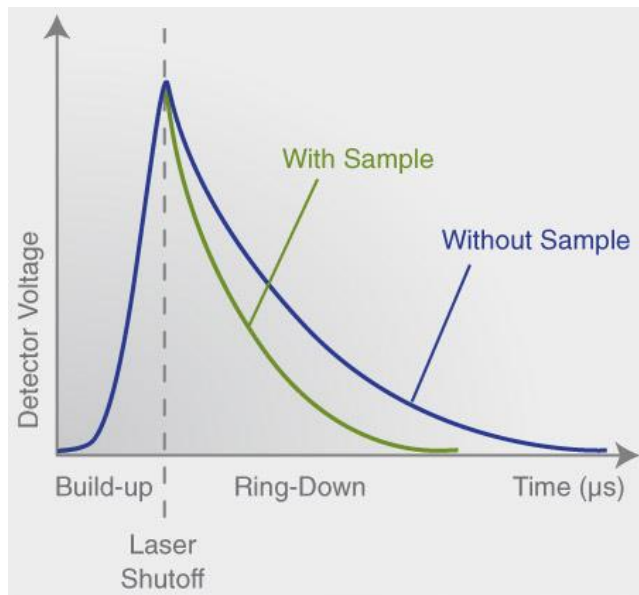
Light from a single frequency laser enters a cavity where three mirrors reflect the laser light (Left)

Then the laser is turned off (Right) and the intensity of the light reaching the detector decreases. The decay, or "ring-down," is measured in real time by the photodetector.

The light typically bounces between the mirrors 40,000 times in about 20msec, effective pathlength about 12 miles.

Method – The Theory

Ring down time difference
proportional to concentration



Key Concepts of CRDS

Under controlled temperature (45°C) and pressure (100 mTorr in cavity) near IR absorption bands are very narrow.

Tunable laser “lights” the cavity at a wavelength at which target molecules absorb. Ringdown time measured.

At a wavelength where the target molecule doesn’t absorb the cavity is relit. Ringdown time measured.

Because everything is known and the measurement is a differential, concentration can be directly determined.*

Method – The Reality: Formaldehyde

1. Zero Drift / Precision

Instr. Specifications: Zero Drift 1.5 ppb/day (Too much)
Drift was both positive and negative (not predictable)

2. Determination of Accuracy

Calibrations using Methane/HCHO blended and
HCHO only cylinders gave low responses

3. Data Access and Usability

Downloaded analyzer data were in uneven Hz intervals
unique to specific instruments ringdown frequency
(Files were hourly, MBs to GBs and tedious to
download and difficult to parse)

Drift / Precision - Resolution

Use 2-Min rolling average data output from Analyzer
Envidas Data Logger saves 1-Min data

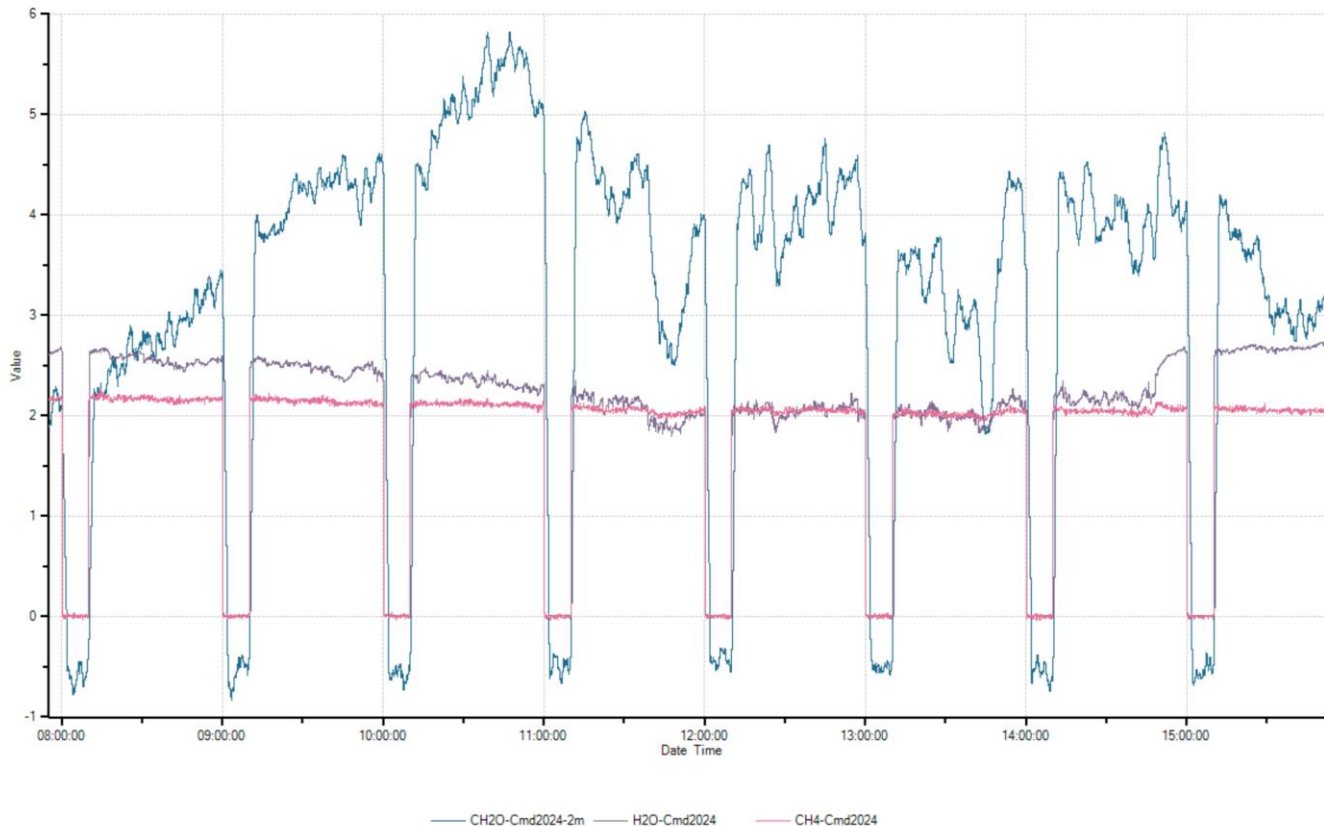
Auto-zero the analyzers for 10 min at the top of each hour
Envidas controlled solenoid, output from ZAG.
Solenoid – IPS 3 way, normally open, run closed to
keep hot – eliminates interferences

Subtract zero value (avg minutes 6-9) from the average of
the final 45 minutes of data in that hour.

Repeat every hour. Currently done off line with an Excel
macro. Goal is for Envidas to develop a calculated
channel to enable real time hourly data.

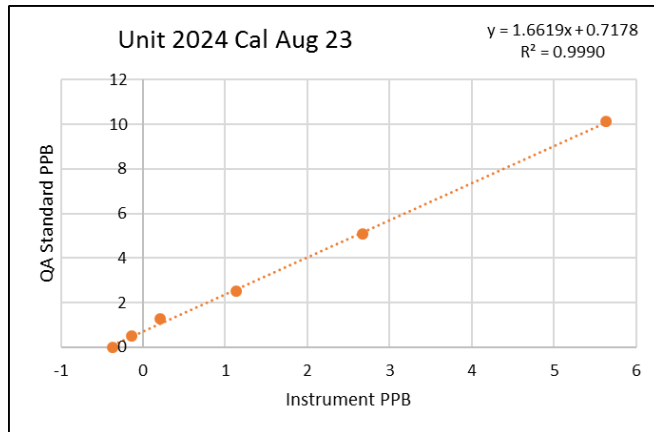
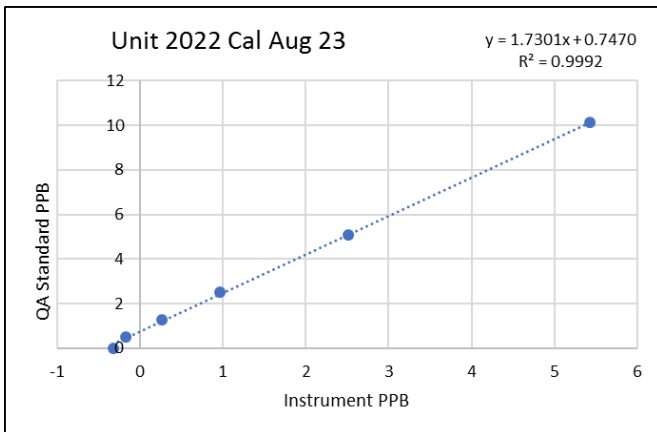


1-Min Data Shows Zero Cycle (1-Hr Data Valid)



Method Issues – Determination of Accuracy

The cal results using blended HCHO/Methane cylinders were abysmal. On the bright side, linearity was excellent



The experimentation began.....

Method Issues – Determination of Accuracy

At Picarro, the blended CH₄/HCHO cylinder was 50% low for formaldehyde. Even though Picarro maintains that CH₄ up to 25 ppm is compensated for, this is not what we found.

With a formaldehyde only cylinder and Floropel coated flow controllers the results from April through June were better but still not acceptable:

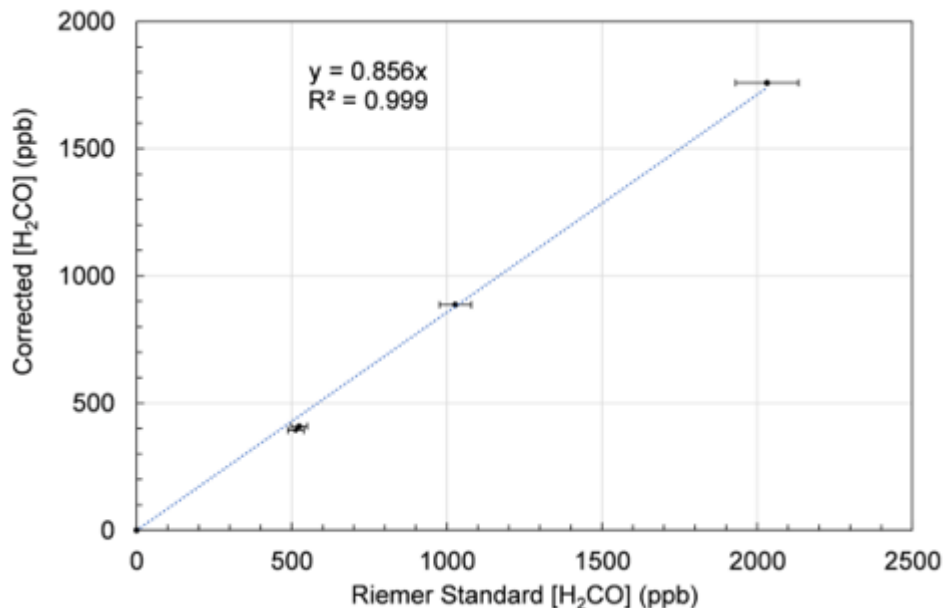
Slope: 0.76 – 0.88

Intercept: -0.83 to 0.16

R Squared: 0.999



Picarro Changed the Factory Span

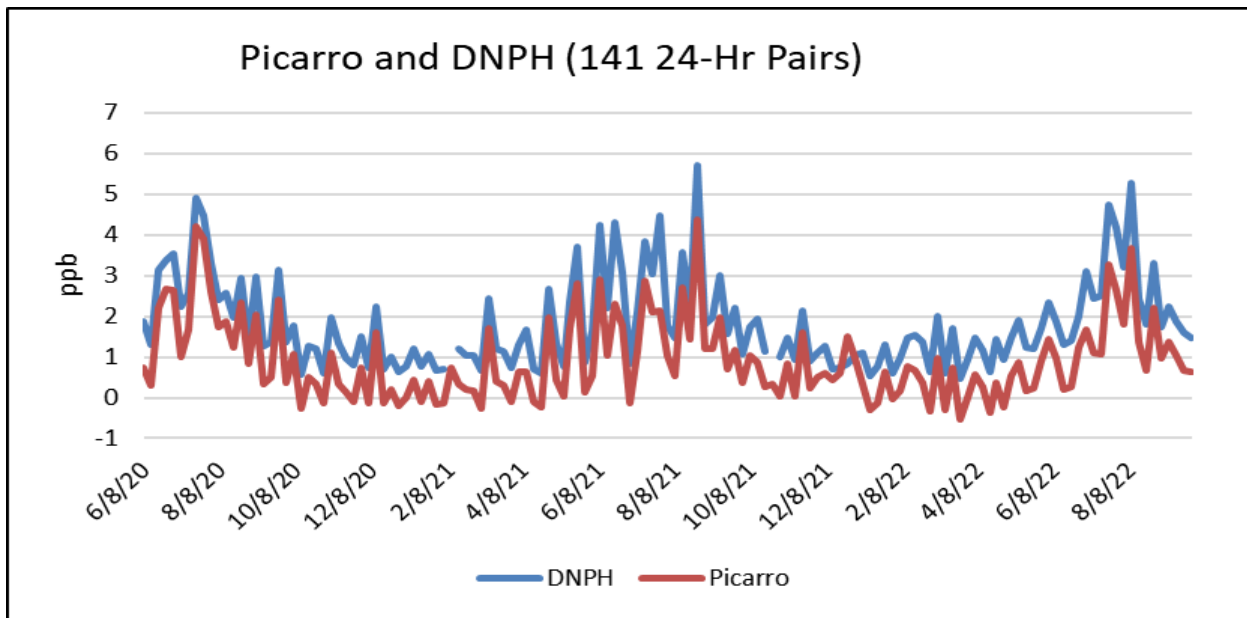


Direct connection to the cylinder and each point ran for 4 hrs

HCHO stds cannot be diluted in a calibrator and low conc stds are not stable

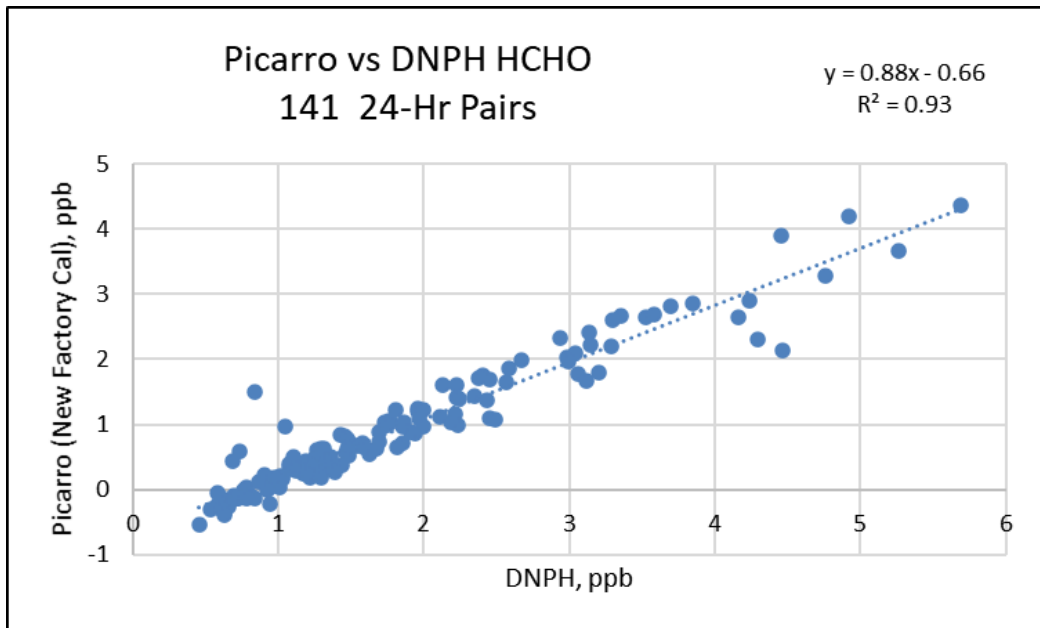
Method	Calibration Adjustment Factor
Direct Cylinder Calibration Relative to Original Scaling	1.168

Picarro with New Cal Compared to 24-Hr DNPH



The Picarro data have a negative offset which could be the Picarro's zero or a positive offset for DNPH

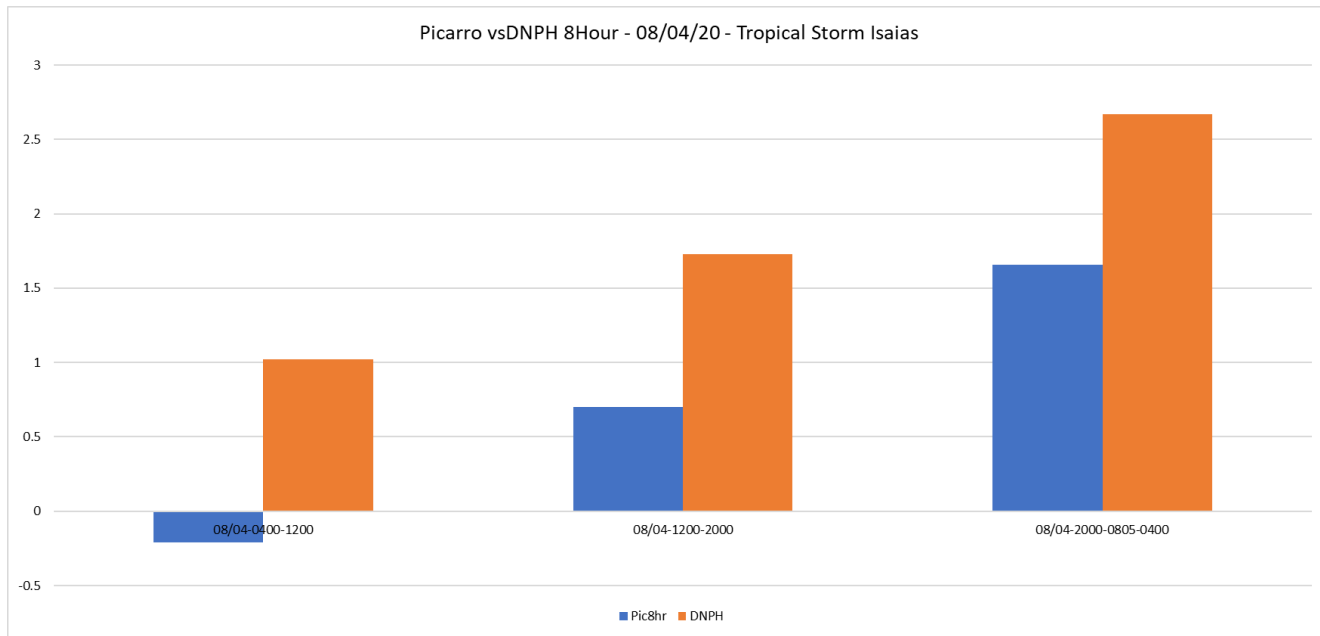
Picarro with New Cal Compared to 24-Hr DNPH



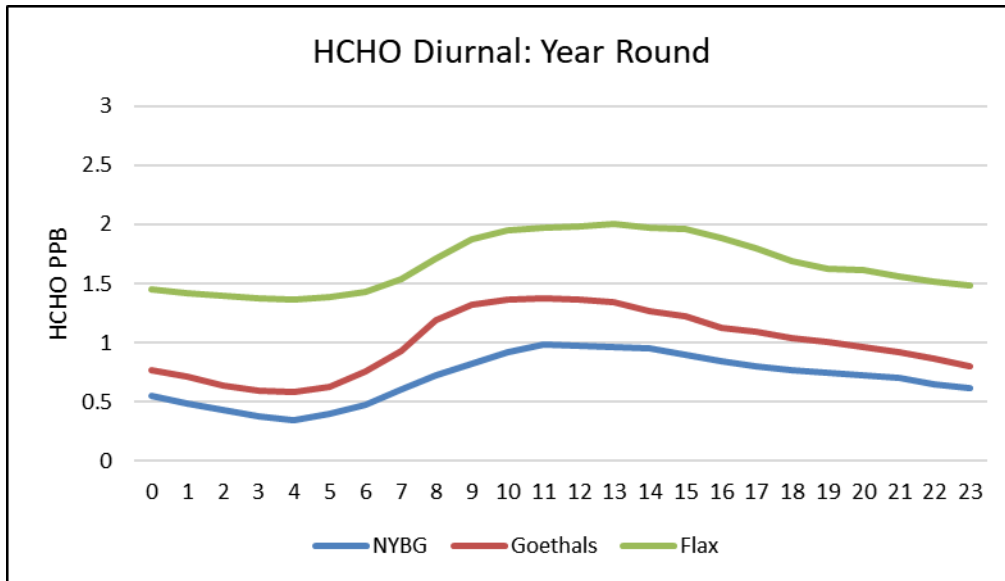
The Picarro data have a negative offset which could be the Picarro's zero or a positive offset for DNPH

Tropical Storm Isaias Comparison

Ambient Formaldehyde should go to zero during a heavy rain event. The Picarro is close to zero, DNPH does not drop below 1 ppb.

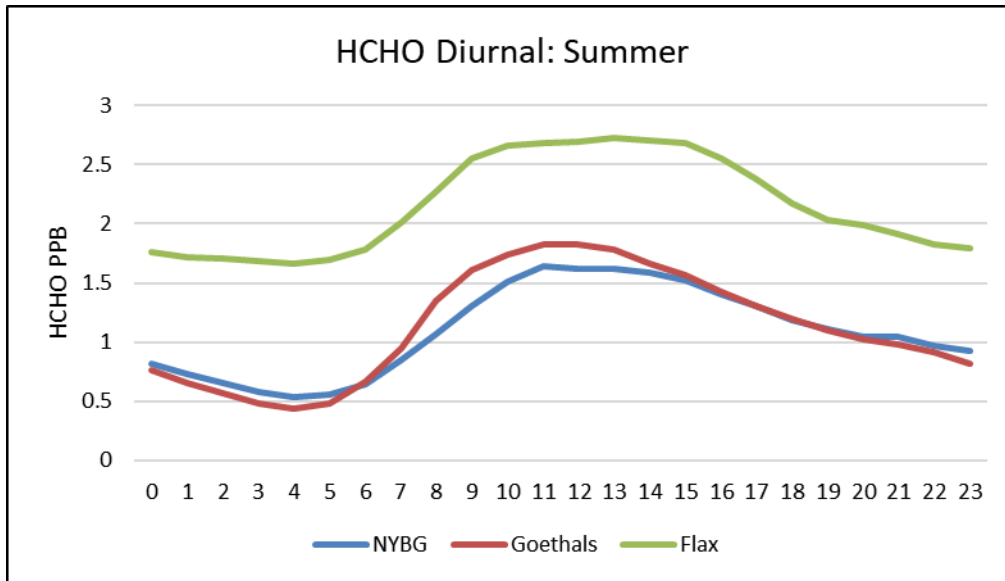


Picarro 1-Hr Data



Flax Pond is on the north-east coast of Long Island, Goethals is on Staten island downwind of Bayway Refinery, NYBG is a PAMS site in the Bronx

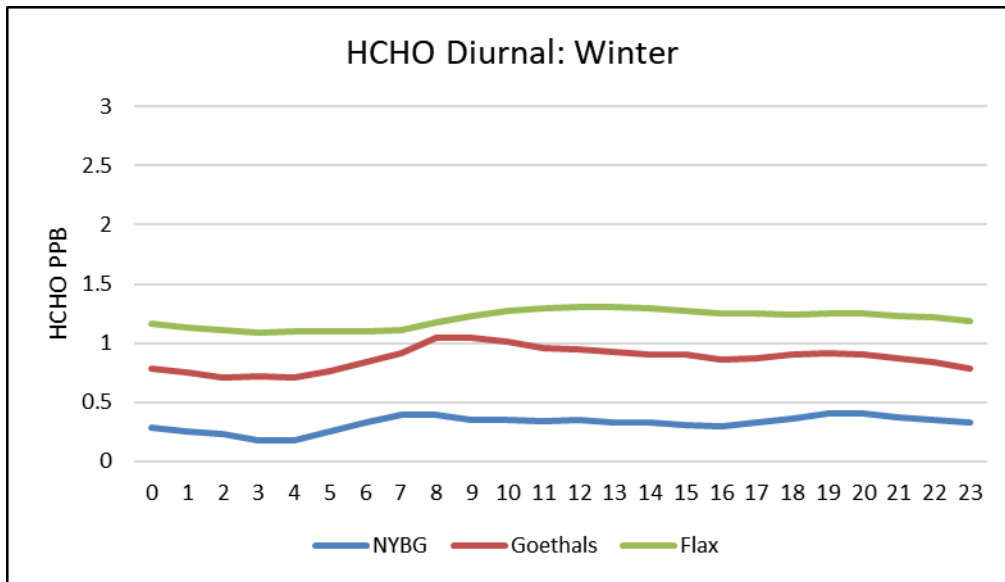
Picarro 1-Hr Data



Goethals seems to have more "chemical fuel" than the neighborhood scale sites

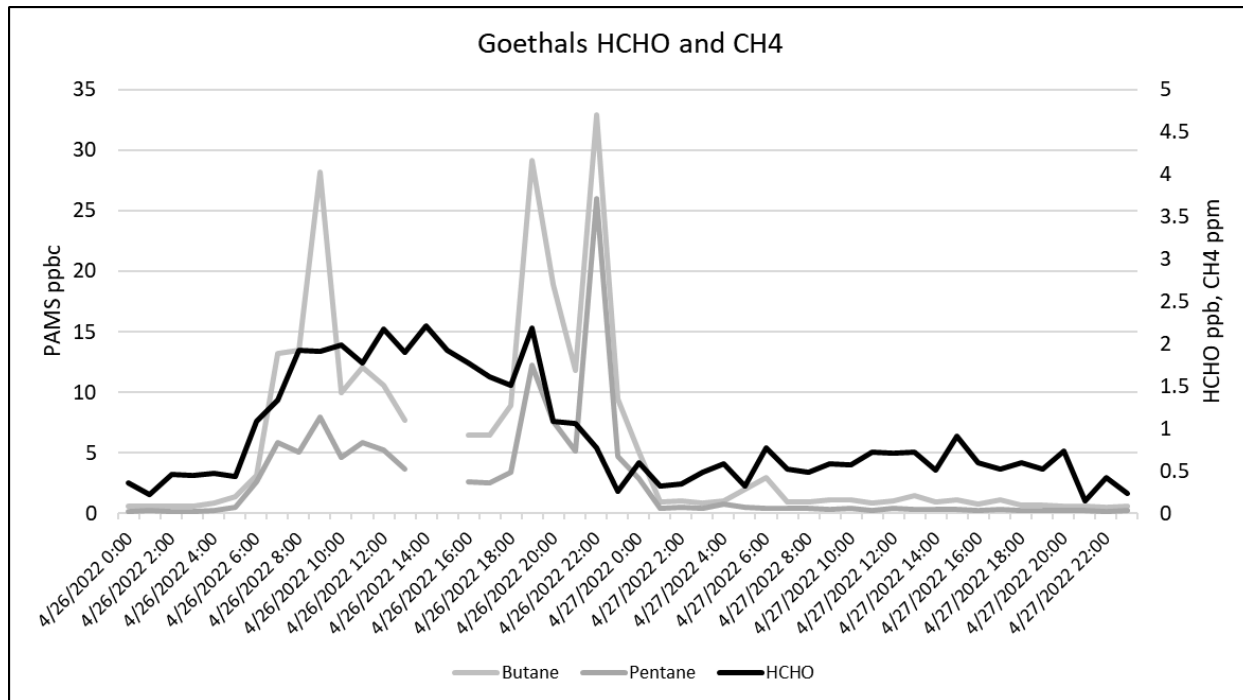
Flax Pond has the least scavenging

Picarro 1-Hr Data



In the winter, scavenging is overwhelming production

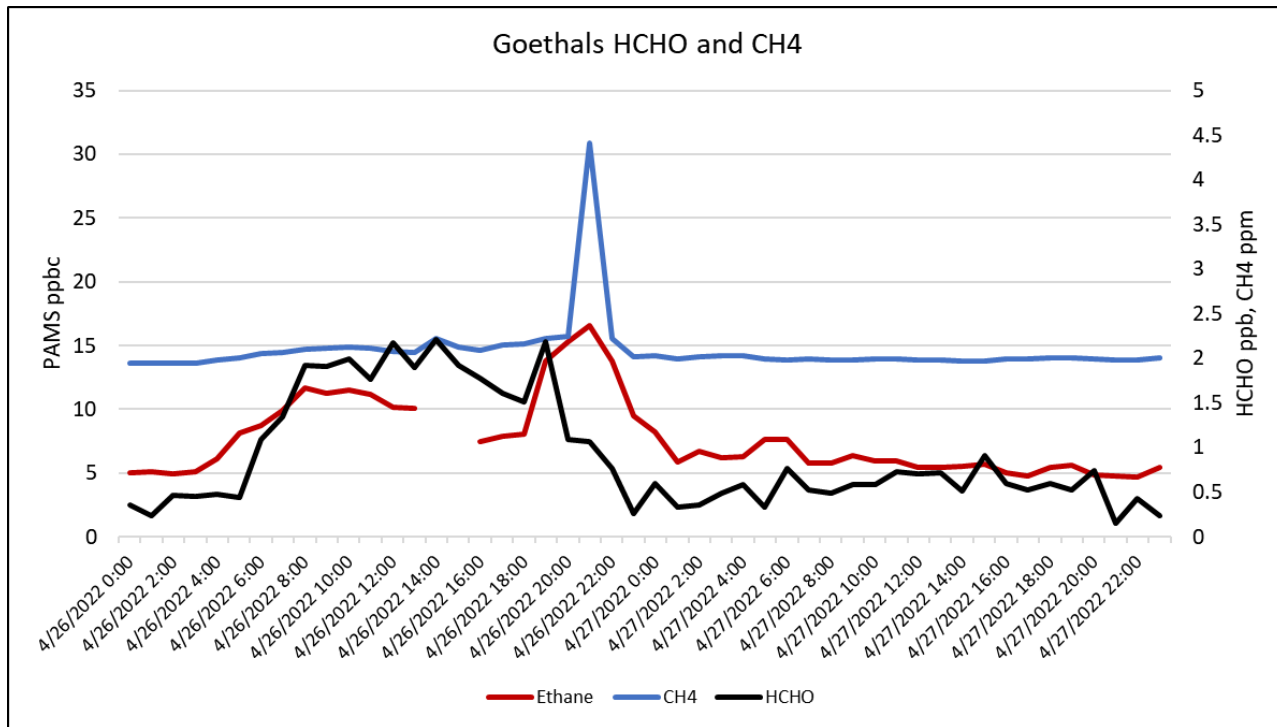
1-Hr Data (Daytime Episode)



HCHO increases with high VOCs from gasoline production

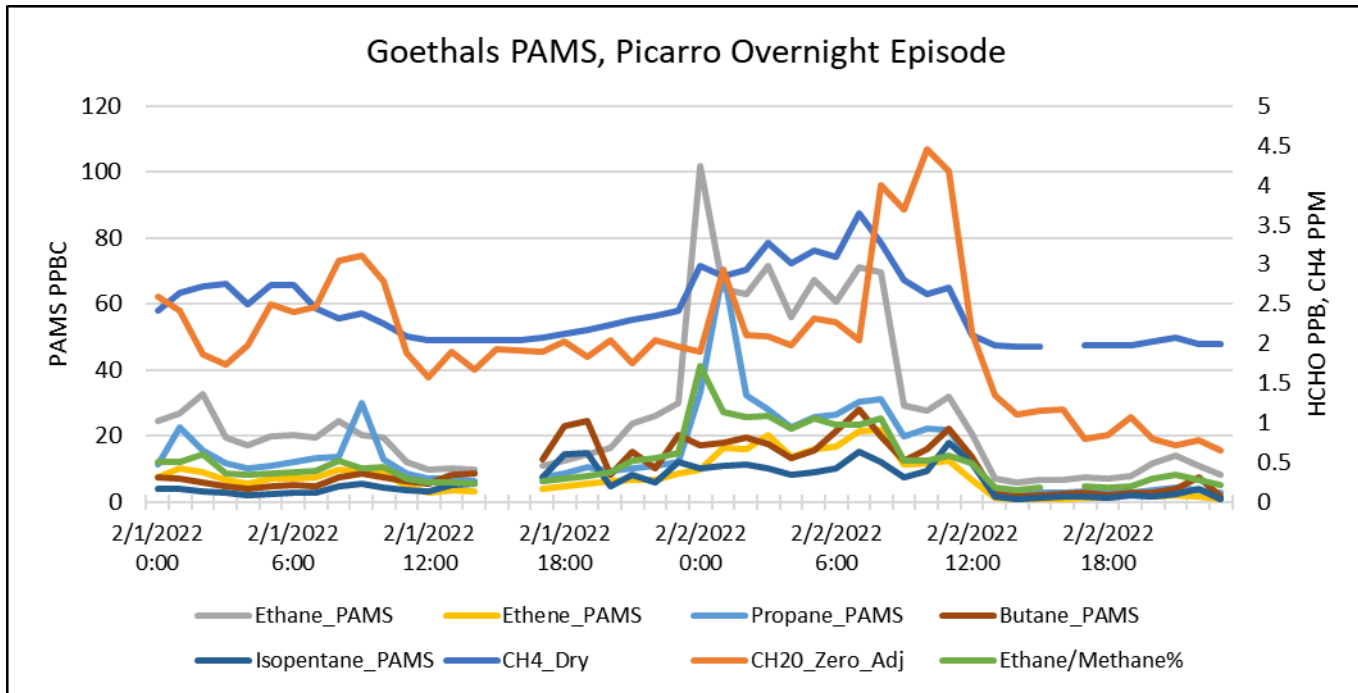


1-Hr Data (Daytime Episode)



CH4 increases along with Ethane

1-Hr Data (Night-time Episode)



VOCs high and Eth/Meth Ratio. HCHO incr. when the sun comes up (eth/meth poor combustion?)

Observations and Conclusions

- Hourly data provides insight into source and atmospheric interactions that are not possible with DNPH
- Third party instrument control/data management software(DrDas) nearly enables automation of hourly zero
- HCHO Accuracy: 10 – 12% low in comparison to DNPH, still has a <0 offset
- DNPH may be biased high
- Analyzer performance for methane is superb



Thanks and Acknowledgements

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Thank You

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