Evaluation of Continuous Formaldehyde Measurements in Air

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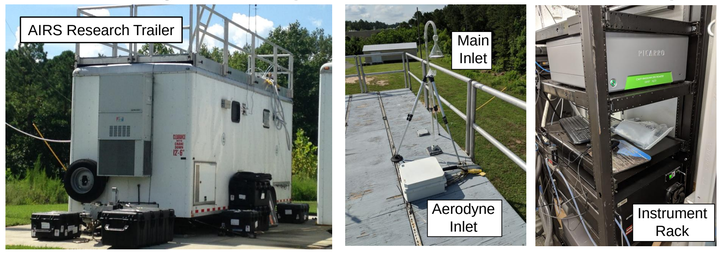
Introduction

Formaldehyde is an important hazardous air pollutant (HAP) that is a leading driver for HAP-related cancer risk in the United States. It is emitted directly by numerous anthropogenic and natural sources, and formed as a secondary product from volatile organic compounds (VOCs) photooxidation. Formaldehyde is a significant source of radicals in the atmosphere that result in ozone and particulate matter (PM) formation. Routine measurements of formaldehyde in regulatory networks rely on EPA Compendium Method TO-11A, which is based on HPLC analysis of derivatized, time-averaged cartridge samples.

The U.S. EPA Office of Research and Development has been involved in the continuing evaluation, analysis, and comparison of commercially available continuous formaldehyde measurements, as well as the promotion of novel technologies for ambient air and source emissions monitoring applications. We present results from our ongoing evaluation and intercomparison of newer formaldehyde measurement technologies in both controlled laboratory experiments and ambient air.

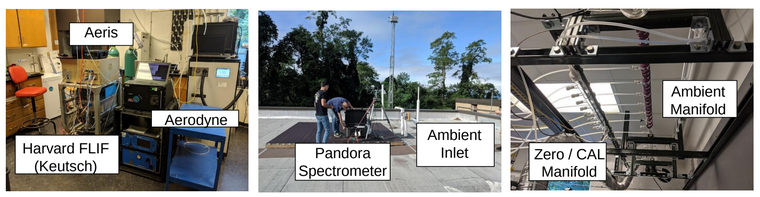
Instrument Evaluation Sites

Research Triangle Park, NC (Ambient Air Innovative Research Site)



Between June 2018 and July 2018, we ran the Aerodyne (for one week), Picarro, and Gasera formaldehyde monitors in a research trailer at the Ambient Air Innovative Research Site (AIRS) in Research Triangle Park, NC. We also ran collocated DNPH cartridges for several periods.

Flax Pond NY DEC (PAMS) Monitoring Site, Long Island, NY



Between September 2018 and October 2018, we ran the Aerodyne and Picarro instruments collocated at the Flax Pond Marine Laboratory in Old Field, NY as part of the Long Island Sound Tropospheric Ozone Study (LISTOS). Harvard University ran a fiber laser induced fluorescence instrument and Aeris formaldehyde monitor, SUNY Stony Brook ran a PTR-MS, and the New York DEC ran PAMS-style DNPH cartridges. The Gasera instrument was also run towards the end of the study.

Commercially Available CH_2O Instruments

Aerodyne Research, Inc.
Direct absorption instrument capable of high precision (research grade) CH_2O and formic acid measurements. High precision but large footprint

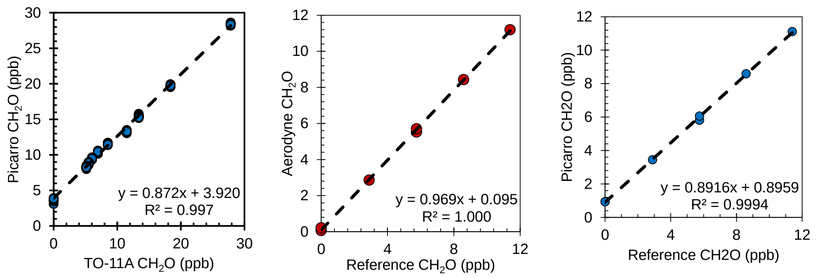
Picarro
Cavity ringdown spectroscopy measurements of CH_2O and CH_4, high stability.

Gasera
Photoacoustic spectroscopy measurements of formaldehyde.

Aeris Technologies, Inc.
Direct absorption formaldehyde measurements, lunchbox sized and portable, automated zeros (every 30 seconds) using a DNPH scrubber.

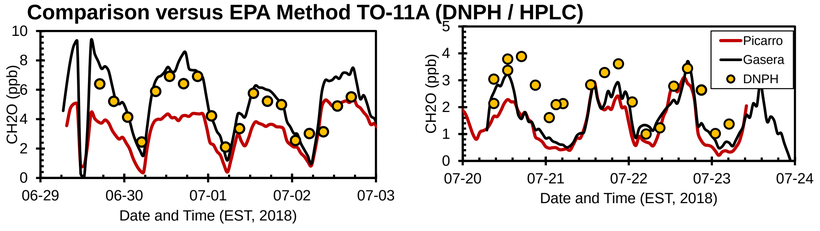
Comparisons Versus Reference Gas and TO-11A

Comparison versus Formaldehyde Reference Gas



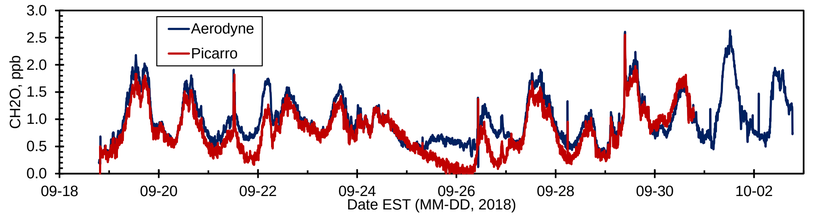
Picarro and Aerodyne compare well to reference formaldehyde from permeation tubes (left) and gas cylinders (center, right).

Comparison versus EPA Method TO-11A (DNPH / HPLC)

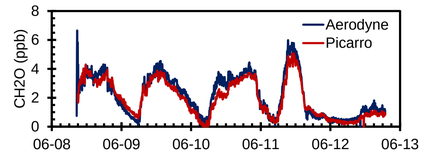


Comparison between spectroscopic measurements (Aerodyne, Gasera, and Picarro) and EPA Method TO-11A measurements do not always agree. Spectroscopic CH_2O was lower than TO-11A CH_2O during tests at both Research Triangle Park, NC and Flax Pond (New York, data not shown) sites. This source of these discrepancies in unclear and is currently under investigation.

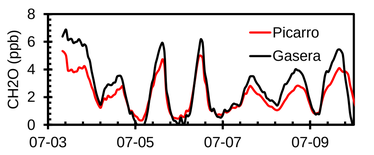
Ambient Air Comparisons



The Picarro and Aerodyne compare well during collocated ambient air measurements at Flax Pond. During the periods where discrepancies were observed, the Picarro generally read lower concentrations than the Aerodyne. These periods were generally associated with higher water vapor concentrations, suggesting an uncorrected water vapor interference in one or both methods.



The Picarro and Aerodyne compare well during a brief (5-day) collocation in Research Triangle Park.



Collocation between the Picarro and Gasera instruments suggest residual discrepancies exist.

Conclusions

Instruments capable of continuous spectroscopic measurements of formaldehyde in air are now commercially available and provide an opportunity to constrain formaldehyde emissions and secondary formaldehyde formation from VOCs, as well as better understand both population exposure and the impact of VOC emissions on ozone production. EPA recognizes the value of continuous formaldehyde measurements and allows for continuous (hourly) formaldehyde measurements in their Photochemical Assessment Monitoring Stations (PAMS) network. Our preliminary analysis of commercially available continuous formaldehyde monitors suggest significant promise. However, there remain minor discrepancies between instruments (mostly correlated with water vapor levels). In addition, discrepancies between the spectroscopic measurements and the EPA reference method (TO-11A) remain poorly understood. If deployed with proper validation and quality assurance checks, continuous formaldehyde monitors will provide high quality formaldehyde measurements for outdoor ambient, near-source, and indoor air measurements.

Acknowledgements

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