In Situ Airborne Measurement of Formaldehyde with a New Laser Induced Fluorescence Instrument

Heather L. Arkinson[1] T. Hanisco[2] M. Cazorla[3] A. Fried[4] J. Walega[4] R. Dickerson[1] heather@atmos.umd.edu

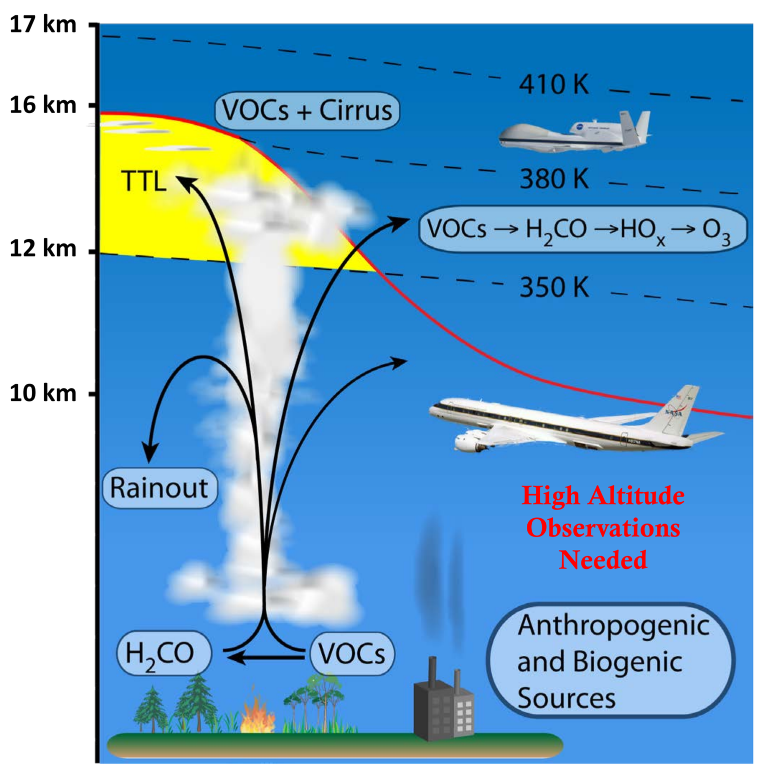
[1]University of Maryland, College Park, Maryland [2]NASA Goddard Space Flight Center, Greenbelt, Maryland [3]Universidad San Francisco de Quito, Quito, Ecuador [4]University of Colorado, Boulder, Colorado

Objective Obtain in situ measurements of formaldehyde (HCHO) in the upper troposphere and lower stratosphere with high resolution and accuracy to improve understanding of transport mechanisms and effects of lofted pollutants.

Approach Measure HCHO with a novel In Situ Airborne Formaldehyde (ISAF) instrument that employs Laser Induced Fluorescence (LIF) to achieve the high sensitivity and fast time response needed to detect low levels and capture fine structure.

Conclusion The ISAF instrument demonstrates precision and resolution of rapidly changing concentrations as required to detect HCHO in the upper troposphere and lower stratosphere and elucidate vertical transport of boundary layer pollutants.

Significance of Formaldehyde



Motivation for Airborne HCHO Measurements

Improve understanding of convective transport and ozone production

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Provide a tracer for boundary layer pollutants lofted to higher altitudes

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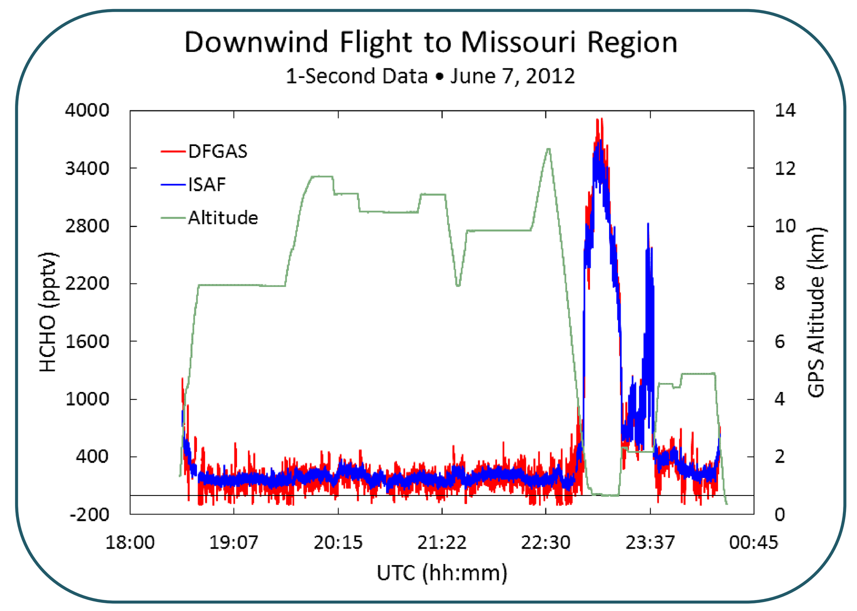
Validation of satellite and ground based remote sensing measurements

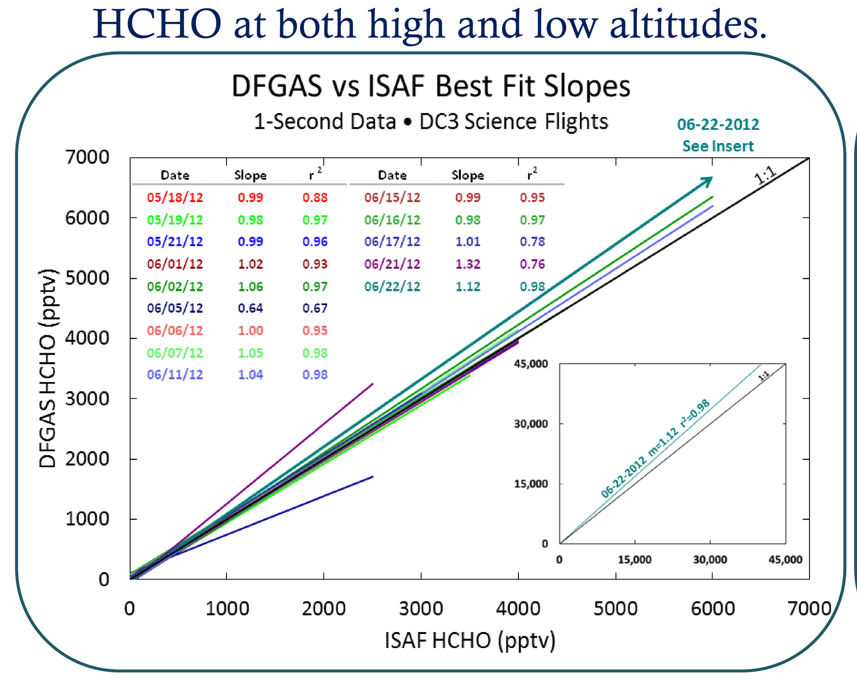
- HCHO is a highly reactive and ubiquitous compound in the atmosphere that originates from primary emissions and secondary formation by photochemical oxidation of anthropogenic and biogenic volatile organic compounds.
- HCHO contributes to the pool of atmospheric radicals and has a lifetime of hours to a day. Thus HCHO is an important precursor to the formation of ozone and an ideal tracer for the transport of boundary layer pollutants.
- In situ measurements of HCHO are needed to improve understanding of convective transport mechanisms and effects of lofted pollutants on ozone production and cloud microphysics in the upper troposphere.

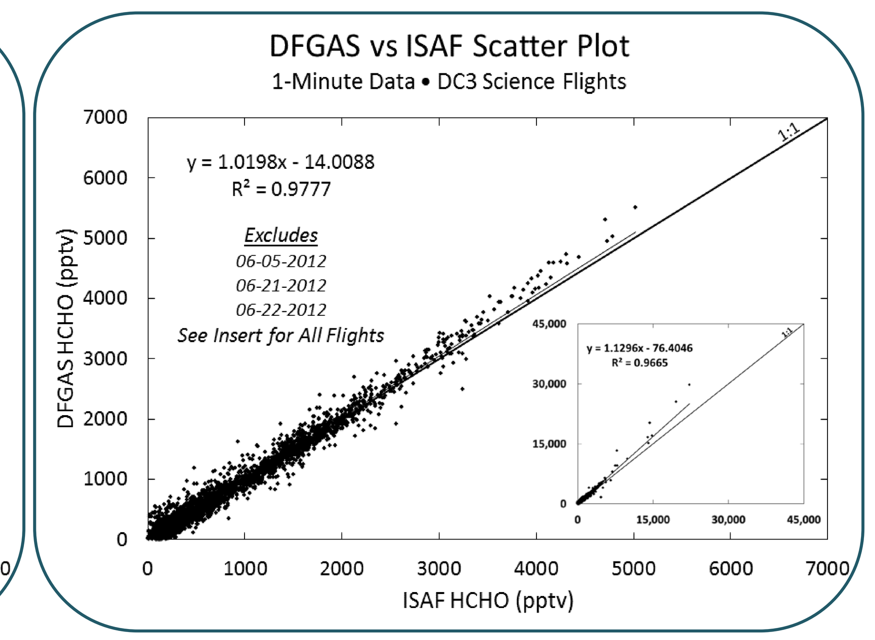
Formaldehyde Instrument Comparison



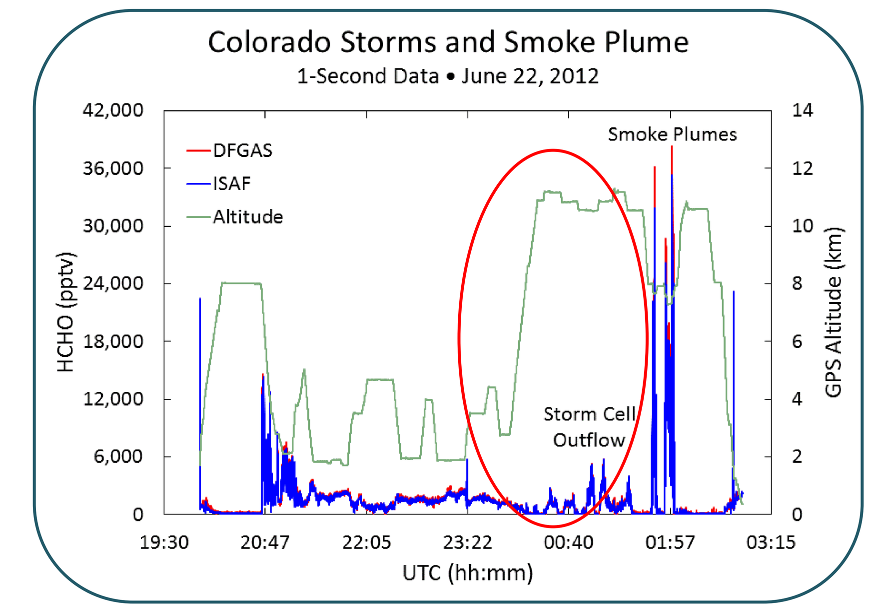
ISAF and DFGAS results track closely through frequent and abrupt changes in HCHO at both high and low altitudes.

- The ISAF and DFGAS were both deployed to measure HCHO from the DC8 during the DC3 field campaign.
- The ISAF detects HCHO via LIF, while the DFGAS detects HCHO via infrared absorption in a Herriott cell.
- Preliminary field data suggests that ISAF and DFGAS measurements agree to within 2.0±0.3% on average.
- A high degree of correlation between the measurements is evident for both 1-second and 1-minute data.



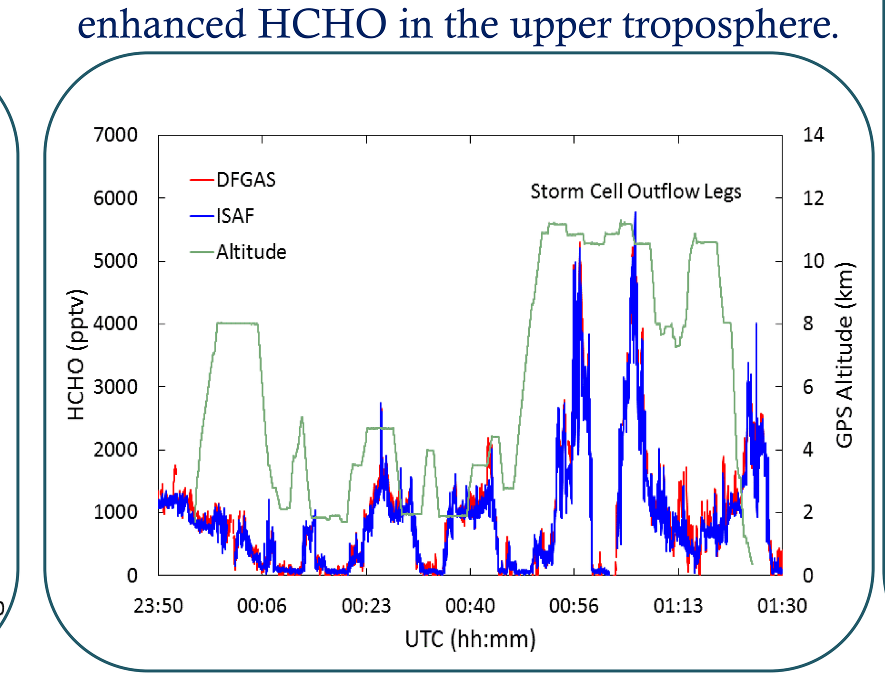


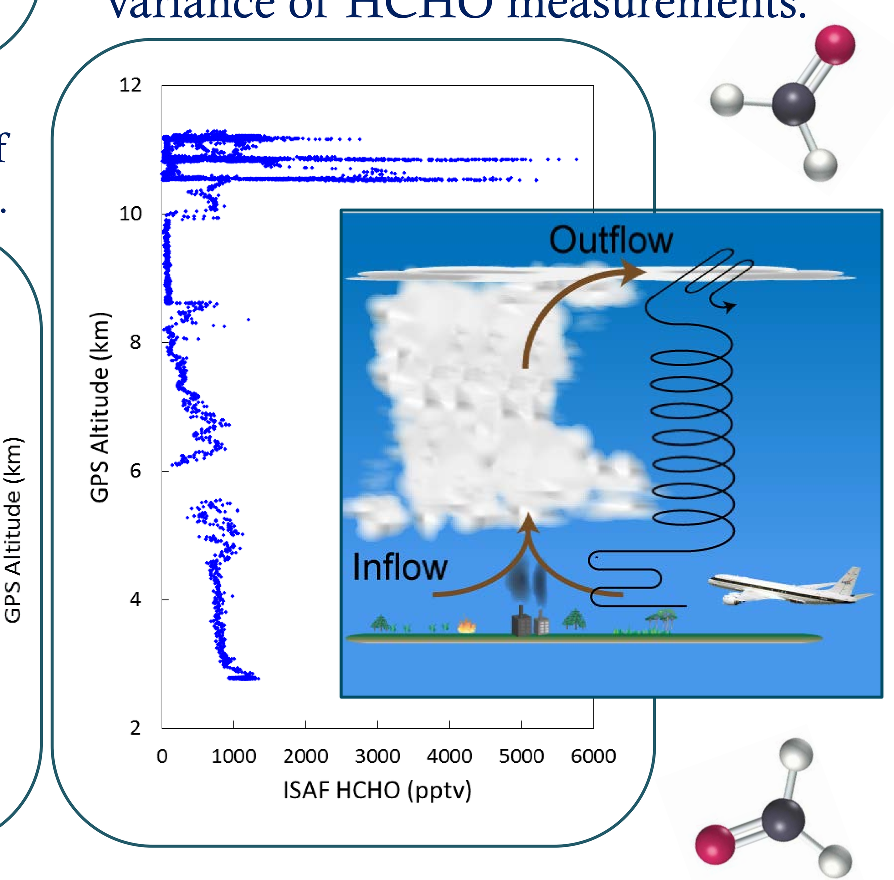
Convective Vertical Transport



A vertical profile plot of the spiral up to storm outflow provides striking evidence of enhanced HCHO in the upper troposphere.

- Multiple layers with elevated HCHO were captured in the Jun 22nd flight.
- HCHO rapidly jumped from 35 pptv in clean air to 35 ppbv in the plume.
- Vertical transport is indicated by the 6 ppbv in storm outflow at 35,000 ft.
- Flight is separated in correlation plots to accommodate the large range and variance of HCHO measurements.





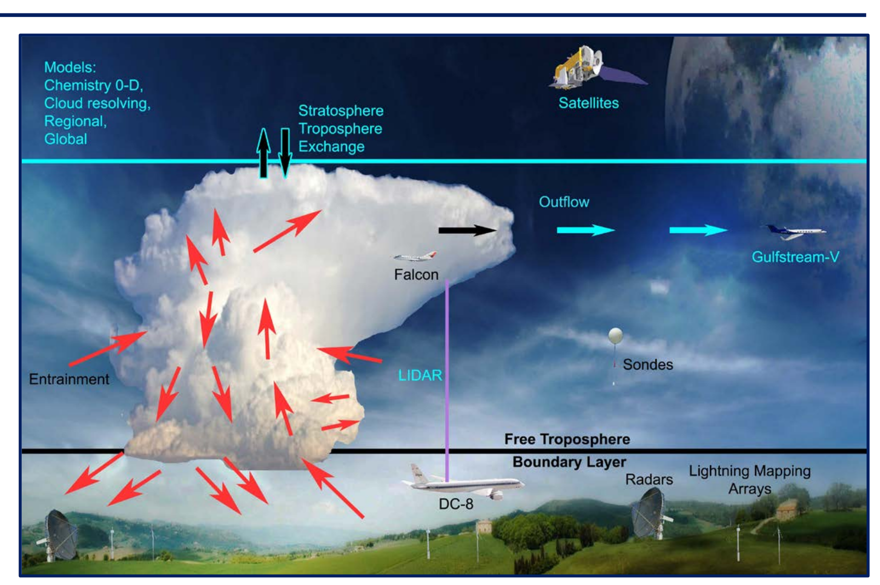
DC3 Field Campaign

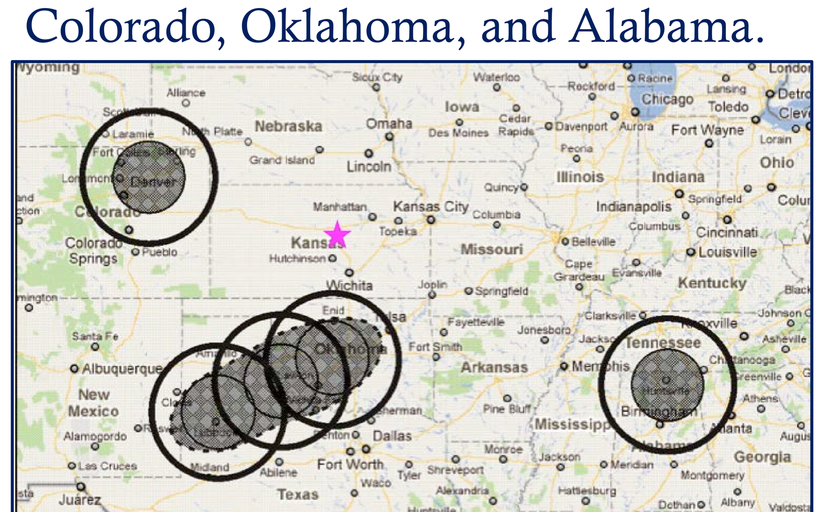
Deep Convective Clouds and Chemistry Project

Objective Explore the effects of deep midlatitude continental convection on chemistry and physics in the upper troposphere

Approach Investigate the vertical transport of fresh emissions and water to high altitudes and characterize changes in atmospheric composition

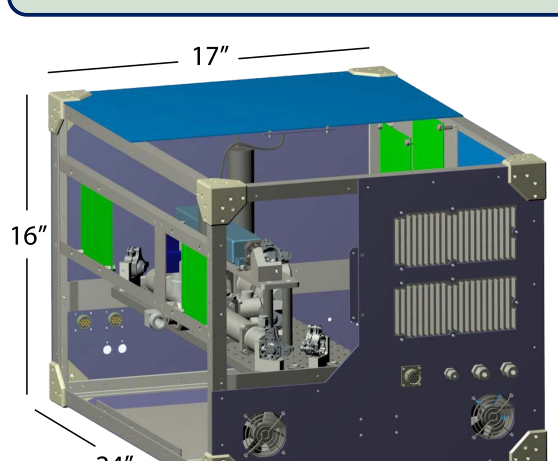
DC3 was conducted in May and June 2012. Coordinated observations were performed during the campaign from ground stations and aircraft including the NCAR GV, the NASA DC8, and the DLR Falcon. Flights to convective storms targeted regions centered over Colorado, Oklahoma, and Alabama.

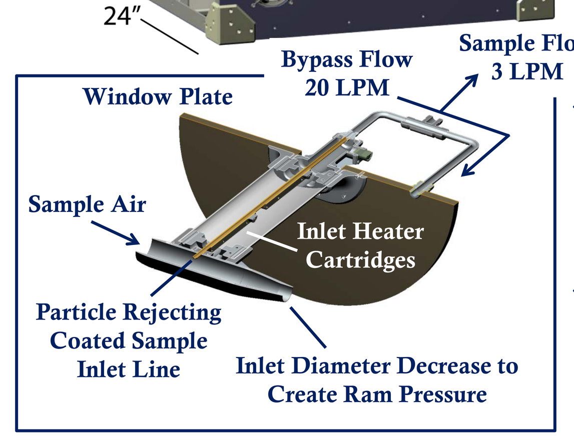




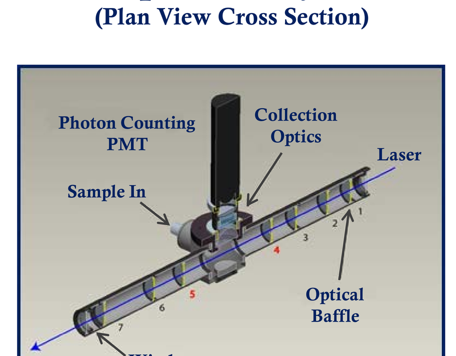
The DC8 payload included the ISAF and the Difference Frequency Generation Absorption Spectrometer (DFGAS) to measure HCHO from storm inflow and outflow, providing ample comparative opportunities for instrument validation.

ISAF Instrument Description





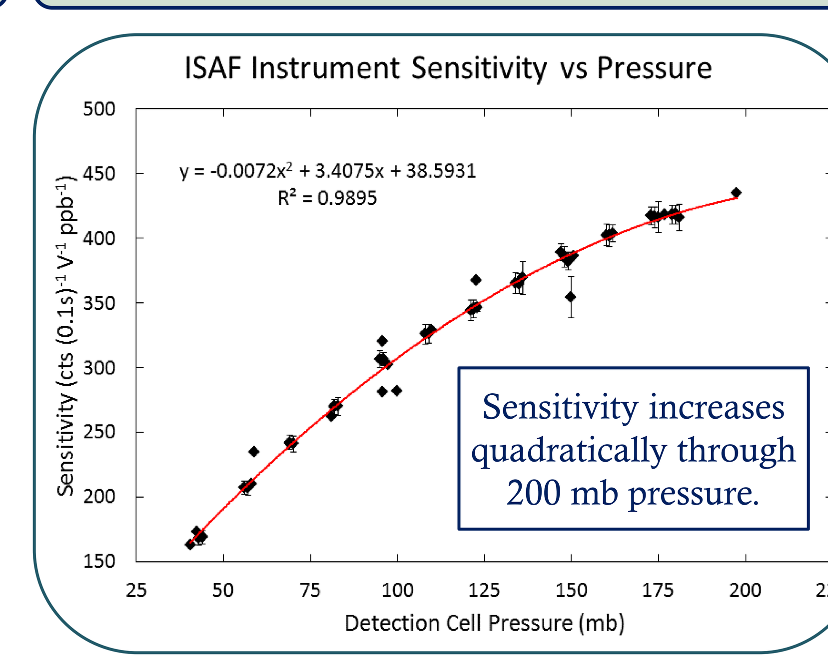
Sample Inlet System
(Plan View Cross Section)



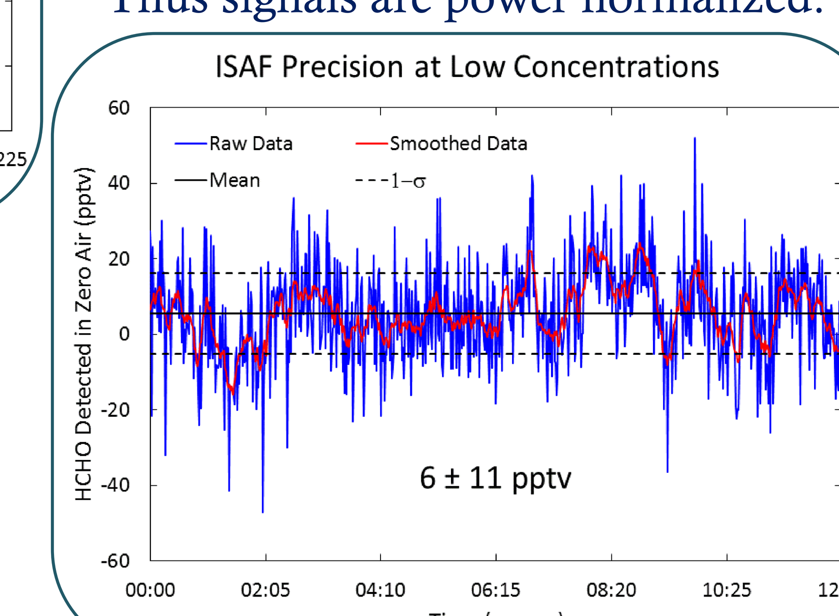
Detection Cell Schematic
(Side View Cross Section)

- ISAF employs a pulsed tunable fiber laser to detect HCHO via LIF with excitation of sample air at 353 nm and detection of resulting fluorescence with a photon counting photo multiplier tube (PMT).
- One pass detection cell is configured with the laser path, sample stream, and PMT in orthogonal planes and with carbon nanotube coated baffles in detection cell arms to reduce laser scatter.
- Laser is tuned on and off resonance with the single rotational feature of HCHO to achieve specificity in detection and remove interfering signals.
- HCHO concentration equals the difference between the online and offline signals normalized by laser power and scaled by a calibration factor.
- Reference cell with a permanent source of HCHO continuously tracks the specific excitation spectrum.
- Calibration is performed by standard addition of HCHO gas mixtures, and 2-σ uncertainty is ±10%.
- Time response is limited by flush time and reversible uptake of HCHO on surfaces.
- Sample inlet has a bypass flow and heated sample line with specialized coatings to improve response.

ISAF Instrument Sensitivity



- The ISAF is designed for use at high altitudes where background HCHO levels are on the order of 10 pptv.
- LIF sensitivity depends on laser power and detection cell pressure.
- Sensitivity increases with laser power. Thus signals are power normalized.



- Motorized optical mounts and a delay to the photon counting gate have been instituted since DC3 to improve instrument precision.
- With 7 mW laser power, 100 mb pressure, and 1-second integration, the 1-σ precision is just over 10 pptv.

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