Preliminary results of formaldehyde measurements during TexAQS 2006

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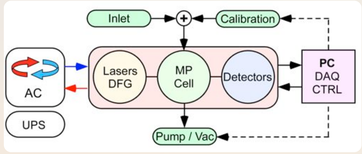
Abstract

Airborne, 1s measurements of formaldehyde were performed using a tunable mid-IR difference frequency generation (DFG) laser spectrometer. The average detection limit (S/N=1) for all flights was 117 pptv (1 s) and 21 pptv (60 s), respectively. For most flights, the instrument was operated semi-autonomously with a duty cycle of 70% (60 s sample / 30 s background, incl. flushing) affording good spatial coverage and precision. The instrument worked with the quoted performance for over 94 % of research flight time. Using an advanced DFG laser source, the present instrument performed with 2x better sensitivity, longer sampling times (60 s), and increased duty cycle of 70%, compared to the liquid nitrogen cooled tunable lead-salt diode laser absorption spectrometer (TDLAS) employed during the TexAQS 2000 study.
Compared to the study in 2000 (TexAQS 2000), the median concentrations in the vertical distributions are significantly lower (50 %) and this may be due to different ambient sampling / photochemistry conditions (Sep./Oct. 2006 vs. Aug./Sep. 2000) during TexAQS 2006. Downwind plumes from power plants, the Houston shipping channel and selected refineries have been intercepted and show a clear signature and correlation with O_3 and NO_y. Significant direct sources of formaldehyde have not yet been identified during the preliminary analysis of the CH_2O dataset.

Instrument design

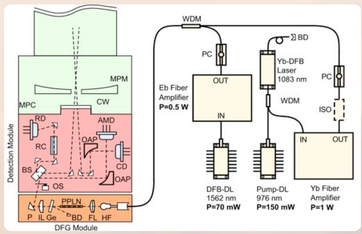
System Overview and WP-3 Installation



- Two FAA certified HIAPER racks (22 x 26.5 x 49) inch
- Temperature controlled inlet
- Total weight: 570 lbs (incl.racks)

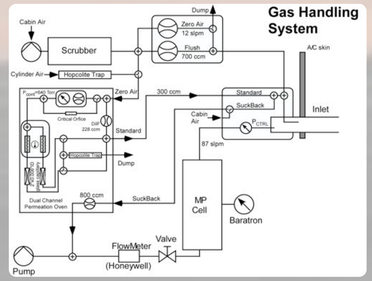
Laser spectrometer

- Tunable optical fiber pumped Difference Frequency Generation (DFG) source
- Detection Principle: 2-f, long-path absorption spectroscopy (100 m multi-pass absorption Cell), and amplitude noise subtraction.
- Wavelength: 2831 cm^{-1}
- Optical Power: 0.1 - 1 mW (adj.)



Inlet & calibration system

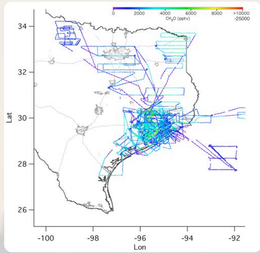
- Heated and pressure controlled teflon tube inlet
- Dual permeation oven for high and low calibration standard addition
- Heated Pd/Al_2O_3 catalyst for background subtraction

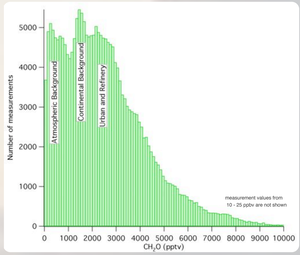


Instrument performance

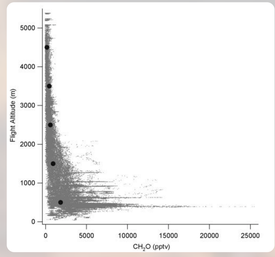
- Detection Limits (all flights where CH_2O <500 pptv and SDEV <400 pptv (atmospheric background air):
  1 second : 100 pptv (detectable absorbance = $3x10^{-6}$)
  60 seconds: 21 pptv (detectable absorbance = $7x10^{-7}$)
- Duty Cycle = 70 %
- Coverage = 94 % (missed flight on 09/27/2006 due to computer problems)
- Semi-autonomous operation (start-up / shut-down / in-flight calibration)
- Number of 1 s measurements: 233,753

Overview of research flights (8/31 - 10/13)





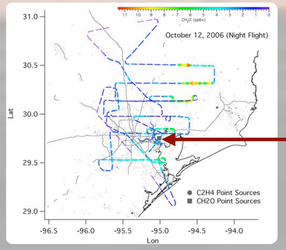
Vertical distribution for CH_2O [1]



Flight Altitude Range (m)	TexAQS 2000 Median CH_2O (ppbv)	TexAQS 2006 Median CH_2O (ppbv)	Difference (pptv)
0 - 1000	3.3	1.84	1.46
1000 - 2000	2.7	0.93	1.77
2000 - 3000	1.0	0.58	0.42
3000 - 4000	0.26	0.45	-0.19
4000 - 5000	0.21	0.17	0.04

· Does not take into account differences in flight path coverage, average wind speeds, and ambient photochemistry conditions

Night flight 10/12

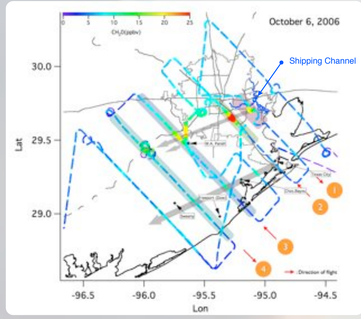


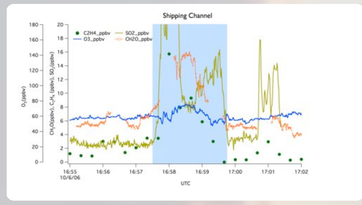
- No obvious major direct CH_2O sources evident (preliminary)
- Residual CH_2O from daytime oxidation of precursors
- Persistent progression of plume indicates in-situ production of CH_2O.

Houston Ship Channel

Highlight: Research flight 10/06/2006

- Clear separation & signatures of Ship Channel, W.A. Parish power plant, and Choc.Bayou / Texas City
- Highest level of CH_2O measured during TexAQS (25 ppbv)





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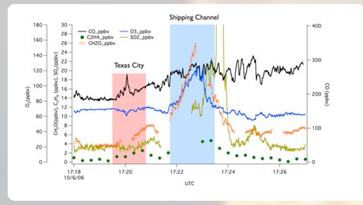

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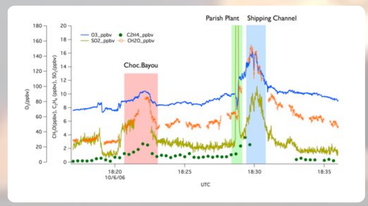

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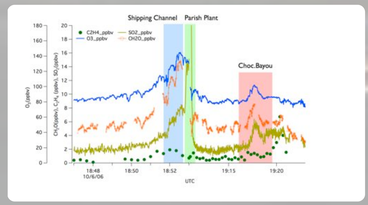

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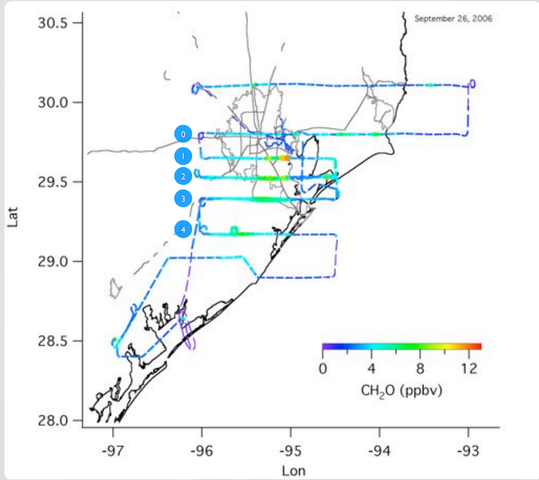
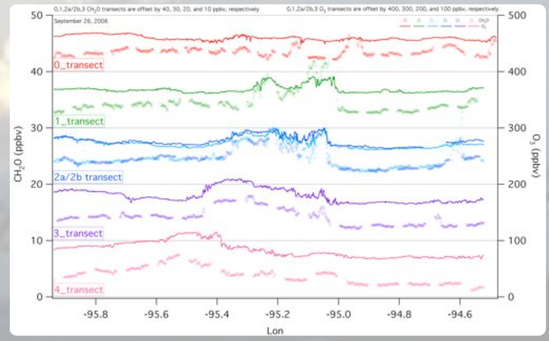
Highlight: Research flight 09/26/2006

- Good separation of urban and industrial plumes
- High degree of measurement precision for two consecutive transects at Lat 29.4 deg. (2a/b)





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[2] D. Richter and P. Weibring, "Ultra-high precision mid-IR spectrometer I: Design and analysis of an optical fiber pumped difference-frequency generation source," Applied Physics B: Lasers and Optics 82, 479-486, March 2006
[3] P. Weibring, D. Richter, A. Fried, J.G. Walega and C. Dyroff, "Ultra-high precision mid-IR spectrometer II: System description and Spectroscopic Performance," Applied Physics B: Lasers and Optics 85, 207-218, November 2006
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The National Center for Atmospheric Research is sponsored by the National Science Foundation

This research was funded in part by NOAA

Credits: Background photo by W. Daube :: Data PI's: Ethylene: Joost de Gouw, Carsten Warnecke; SO_2,CO: John Holloway; O_3, Thomas Ryerson