Formaldehyde Measurements from R/V Brown during TexAQS II


Photos by Richard Marchbanks and Dan Welshbon
Formaldehyde (HCHO) Measurement Overview

FORMALDEHYDE TEXAQS-2006

RON BROWN SHIP TRACKS Leg 2
HOUSTON-GALVESTON
AUGUST 21 to SEPTEMBER 11

Houston
Galveston Bay
Outline

Introduction
   HCHO in the urban atmosphere
   Why HCHO emissions are important in Urban Air Quality

Analytical Approach
   Tunable Infrared Differential Absorption Spectroscopy
   Inlet Schematic, Characterization, Performance

Comparison with P3 overflight
Primary & Secondary HCHO
   Time Series Analysis
   Direct Emissions
HCHO in the Urban Atmosphere

\[
\begin{align*}
R-H (VOC) + O_2 &\rightarrow OH \\
\text{peroxy-radical} &\rightarrow ROO^* \\
\text{alkoxy-radical} &\rightarrow RO^* \\
\end{align*}
\]

\[
\begin{align*}
HCHO + OH &\rightarrow H_2O + HCO \\
+O_2 &\rightarrow HO_2 \\
HCHO + hv &\rightarrow H + HCO + 2O_2 \rightarrow 2HO_2 \\
&\rightarrow H_2 + CO \\
\end{align*}
\]
HCHO Emission and Influence on O₃

pre-sunrise HCHO acts as an efficient HOx source

Lerner et al.

diurnal, whole campaign (UTC)
Inlet Sampling Schematic

Ron Brown 2006 Tower Sample Box

Temperature Controlled (43 C) PFA Teflon

Pressure Drop
100-75 Torr
{4.9, 10.5, 11.2 alpm}

0.13 s

Siloxyl Coated Glass Orifice

1.08 slpm to Vacuum

204 sccm to Vacuum

155 sccm to Vacuum

0.24 s

Instrument Absorption
Cell @ 39-44 Torr
303 K (1/e 0.14 s)

Instrument in Deck Trailer
Tunable Infrared Laser-Differential Absorption Spectroscopy
Dual Quantum Cascade Lasers

Two Wavelength Regions contain 4 decent absorbers

LASER 1 (1765 cm⁻¹) LASER 2 (965 cm⁻¹)

HCHO HCOOH C₂H₄ NH₃
HCHO AVERAGED SPECTRUM in MBL

4 Hr AVERAGE SPECTRUM 0.5 ppb
ABORBANCE NOISE 2e-7 → 10 ppt

ALLAN PLOT
50 ppt @ 30s
Inlet Characterization Results

Permeation sources of HCHO and NH$_3$

HCHO: inlet transmission complete and quick
NH$_3$: inlet transmission ok but slow

At-Sea Inlet Characterization (5 mins. of each hour)
Even hours: Perm + Zero Air
Odd hours: Standard Addition

Advice from Osthoff, Roberts, Kuster
Alternate ambient O$_3$ and enhanced (120 ppbv) O$_3$
No change in measured HCHO in MBL with O$_3$ Addition

Additional Inlet Tests (at sea)

Total Flow Variations different residence times by factor of 5, saw no difference in diurnal MBL HCHO
Ron Brown comparison with P3 overflight

Below PBL raw difference is 7.5%

P3 HCHO - Richter, Fried et al.
Overflight comparison is short - spatial overlap - amounts to one point comparison
Acetaldehyde - North vs East

Airmass below PBL where HCHO was elevated also has high CH$_3$CHO

de Gouw, Warneke, Welshbon
1,3 Butadiene Plume

$\Delta \text{HCHO} \approx 0.6$
$\Delta \text{CO} \approx 8.5$

70 ppt ppb$^{-1}$

1,3 Butadiene Oxidation 1st Gen.

1, 3 Butadiene

1,3 Butadiene oxidation yields, Sprengnether et al. & Tuazon et al.

Lerner, Gilman, Kuster et al.
Primary, Secondary HCHO

‘Primary’ = directly emitted from various sources     HOx source
‘Secondary’ = produced in the atmosphere              costs an OH, O₃ et al.

Part 1: Time-series analysis
untangle directly emitted HCHO from atmospheric production

Houston/Galveston Bay Area
diurnal average & median
Tracer Pair Correlation, CO and O₃

Part 2: Exhaust Plume Analysis (w/source attribution)
Measure directly emitted HCHO, ratio by dilution tracer CO₂

Ship Channel Plume Encounters (Williams et al.)
Anchored Ship Emissions
Drilling Platform (gas-flare vs diesel generator)
Houston/Galveston Bay - Diurnal HCHO

Houston/Galveston Area (18.5 days)
Diurnal Median vs Average

\[ \frac{d[HCHO]}{dt} = p + \text{emis(Dilution)} - (\text{KOH [OH]} + j_{\text{HCHO}}) [HCHO]_{\text{measured}} \]

- **HCHO (ppbv)**
  - Average HCHO
  - Median HCHO

- **CO (ppbv)**
  - Average CO
  - Median CO

Diurnal, Houston/Galveston (UTC)
Simple HCHO vs CO correlation

How representative is median correlation plot of Houston Ensemble Emissions?
First Visit to Turning Basin 8/2

Turning Basin 8/2
Night-time/Early AM

\[
\frac{(\text{HCHO} - 0.8)}{(\text{CO} - 100)} = 0.003
\]
or
\[
\text{HCHO}/\text{CO} = 3 \text{ pptv ppbv}^{-1}
\]

Primary vs Secondary HCHO
30 minute segments in the turning basin analyzed for primary HCHO/CO plume content; 2 - 10 ppt/ppb

Primary vs Secondary HCHO
Primary vs Secondary HCHO

Friedfeld et al. - Tracer Pair (CO w/time lag; \(O_3\))
  Houston Area: **Primary HCHO 37%**
Possanzini et al. HCHO/Toluene
  Rome, Italy: Primary **less than 20%** in summer
Li et al. - Principal Component Analysis
  Vancouver: **Primary~ 20%**
Jimenez et al. Tracer Pair (NOx; \(O_3\))
  Grenoble, France: **Primary <20%**
Garcia et al. - Tracer Pair (CO; glyoxal & CO; \(O_3\))
  Mexico City Metro. Area: **Primary 40%**
  (allowing for ~20% as point source, or area bg.)
Return to Diurnal - CO, O₃

Scenario #1 \[ HCHO = 1.25 + 0.03 \times (CO - 120) + 0.06 \times (O₃ - 10) \]

Scenario #2 \[ HCHO = 1.25 + 0.008 \times (CO - 100) + 0.06 \times (O₃ - 10) \]
H$_2$CO Loadings by Combustion Sources

<table>
<thead>
<tr>
<th>Source</th>
<th>ppb H$_2$CO / ppm CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automobiles with functioning Catalytic Converter</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Gasoline “Engine Out”</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Diesel Heavy Duty</td>
<td>&lt;0.03-0.1</td>
</tr>
<tr>
<td>Compressed Natural Gas</td>
<td>~0.5</td>
</tr>
<tr>
<td>high bypass turbine engine (aircraft engines)</td>
<td>low throttle: 0.9-2.2</td>
</tr>
<tr>
<td></td>
<td>take-off: &lt;0.02</td>
</tr>
<tr>
<td>Ships in HSC</td>
<td>?</td>
</tr>
</tbody>
</table>

Primary HCHO Direct Measurement
Ship Emissions

Despite different inlets, and different computer times, plume attribution is possible ($\Delta t = 3.7s$)

Primary HCHO Direct Measurement

Williams and Lerner
Despite challenges, can limits be set for direct HCHO emissions?

Primary HCHO Direct Measurement

tentative anticorrelation with target speed
Two combustion sources
single platform
long time series
dithering wind

Primary HCHO Direct Measurement
Drilling Platform **Flare Fire** vs Diesel Generator

Dan Lack

Photoacoustic Black Carbon \( \Rightarrow \) ER(BC) flare \(~\frac{1}{2}\) diesel

Diesel Generator contained Fuel Sulfur Content \(~\frac{1}{2}\)%

Primary HCHO Direct Measurement

\[\text{HCHO/CO} = 12 \pm 1 \text{ (ppt ppb}^{-1}\text{)}\]

\[\text{HCHO (ppbv)}\]

\[\text{CO (ppbv)}\]

\[\text{NO, NO}^{-2} \text{ (ppbv)}\]

\[\text{O}_3 \text{ (ppbv)}\]

\[\text{CO}_2 \text{ (ppmv)}\]

\[\text{SO}_2 \text{ (ppbv)}\]

\[0.9 \text{ g HCHO kg}^{-1} \text{ CNG fuel}\]

\[\text{08/04/2006 03:16 UTC} \rightarrow \text{03:24 UTC}\]
<table>
<thead>
<tr>
<th>Combustion Sources</th>
<th>ppb H$_2$CO / ppm CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Automobiles</strong></td>
<td></td>
</tr>
<tr>
<td>with functioning Catalytic Converter</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Boston Fleet Traffic</td>
<td>0.03</td>
</tr>
<tr>
<td>Mexico City Fleet (2002)</td>
<td>0.14</td>
</tr>
<tr>
<td>Mexico City Fleet (2006)</td>
<td>0.11</td>
</tr>
<tr>
<td><strong>Gasoline “Engine Out”</strong></td>
<td>0.2-0.4</td>
</tr>
<tr>
<td><strong>Diesel Heavy Duty</strong></td>
<td>&lt;0.03-0.1</td>
</tr>
<tr>
<td><strong>Compressed Natural Gas</strong></td>
<td>~0.5</td>
</tr>
<tr>
<td>high bypass turbine engine (aircraft engines)</td>
<td></td>
</tr>
<tr>
<td>low throttle</td>
<td>0.9-2.2</td>
</tr>
<tr>
<td>take-off</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td><strong>Ships in HSC</strong></td>
<td></td>
</tr>
<tr>
<td>1 Flare in Gulf of Mexico</td>
<td>0.02-0.15</td>
</tr>
<tr>
<td>Prelim analysis</td>
<td>~ 0.6</td>
</tr>
</tbody>
</table>
Summary and Conclusions

Dual QCL TILDAS Performance
- HCHO 1s rms < 250 pptv; 2σ D.L. (1 minute) 75 pptv
- Systematic Error Est. 7% linestrength, 9% total
- No evidence of Inlet effects for marine BL HCHO
- Instrument also measured HCOOH, C₂H₄, sharp NH₃ plumes*

Analysis
- Diurnal time-series suggest substantial photochemical production
- Turning Basin ER (HCHO) 30 min dist. (2-10) 3 ppt ppb⁻¹ CO
  - CO, O₃ tracer pairs indicate upper limit for HCHO/CO
    ER (HCHO) 0.008; (8 ppt ppb⁻¹ CO)
    CO, O₃ do not capture HCHO temporal profile (poor pair)
- Direct HCHO EF from working ships in HSC/Galv. (g HCHO kg⁻¹ fuel)
- Ship EF is greater than anticipated, more like on-road category
  ‘diesel working hard’ -- EF < 0.05 * EF(CO)
Backup Slides
Tentative Inverse Correlation: HCHO with Target Speed

Primary HCHO Direct Measurement
Diurnal Day in Houston-Galveston Area

UTC RHB Leg 1 & 2

mid morning production of HCHO
afternoon production of HCOOH
conversion of O₃ to NO₂
HCHO and HCOOH Spectroscopic Purity

- Limit on cross talk; orthogonal retrievals; first figure of this type; only limit because no measure of HCOOH
Additional Inlet Tests (at sea)

Total Flow Variations
different residence times
by factor of 5, saw
no difference
in diurnal MBL HCHO

With O₃ Addition
Alternate ambient O₃
and enhanced O₃

No significant change
with 120 ppb of added O₃

Measured HCHO in MBL
is not due to O₃
inlet effects

Advice from Ostoff, Roberts, Kuster
Instrument Performance

- Allan plot and systematic error estimates

Detection limits:
- $10 \text{ s} = 360 \text{ pptv}$
- $200 \text{ s} = 66 \text{ pptv}$
HCHO in MBL

- Steady state model showing methane-only production in clean MBL represents measurement.
- Maybe figure or mention of the O3 spiking and other inlet tests to show inlet not producing HCHO.
- Distill next three slides to one.
Back Trajectories all from the South
Primary vs Secondary HCHO
Drilling Platform Flare Fire vs Diesel Generator

HCHO/CO = 13 ± 1 (ppt ppb⁻¹)
HCHO/CO₂ = 0.40 ± 0.03 (ppb ppm⁻¹)

Primary HCHO Direct Measurement