Texas - Regional transport Experiment (T-REX)
Houston 2013

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Where is ozone a problem?

Counties with Monitors Violating the 1997 8-Hour Ozone Standard of 0.08 parts per million (ppm)
(based on 2004-2006 Air Quality Data)

Source: EPA
Where is ozone a problem?

Counties with Monitors Violating the 2008 8-Hour Ozone Standard of 0.075 parts per million (ppm)

(based on 2004-2006 Air Quality Data)

Source: EPA
Where is ozone a problem in Texas?

Source: TCEQ
Texas – Regional transport Experiment (T-REX)

I. Ozone Trends

II. Results from previous studies

III. UH Measurement Platforms

8-Hour Ozone Exceedance Days in Texas from 1990 to 2005

TCEQ Data Analysis, 2006
Median Ozone Season NO\textsubscript{X} levels

Source: TCEQ
Daily Peak TNMHC levels

Source: TCEQ
Large pulses of HCHO > 25 ppb (Insitu aircraft, HSC, Moody Tower, LP-DOAS)
Portion of HCHO is “primary” associated with excess CO.
HONO in Houston can exceed 2 ppbv close to sunrise then remain at hundreds of pptv during day.
Strong vertical gradients indicate ground-level source of HONO (e.g. traffic)
Possible new heterogeneous mechanism: $\text{HNO}_3 \rightarrow \text{HONO}$ on HOA
CINO$_2$ present at ppbv levels in GOM, formed via $\text{N}_2\text{O}_5$ and HCl$(_g)$
Ozone production often greater than 40 ppbv/hr between 0800-1200 LT.
$\text{O}_3$ production is both NOx and VOC sensitive (NOx sensitive for 7 hrs).
Enhanced photochemistry in early AM due to high RVOC abundances.
SHARP 2009 (15 April – 31 May 2009)

B. L. Lefer
B. Rappenglueck
E. P. Olaguer
W. Brune
J. Stutz
J. E. Dibb
X. Ren
S. C. Herndon
B.T. Jobson

L. G. Huey, S. Dasgupta, R. Zhang, S. North, D. Collins, G. Morris,
J. L. Jimenez, J. Melqvist
1) Investigate the contribution of direct emissions of OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources and mobile sources.

2) Analyze the impact of soot (fresh and coated) on chemistry, radiation (photochemistry and climate), and dynamics.

3) Quantify ambient levels of ClNO₂ in Houston and determine potential as a radical source.

4) Host intercomparison of ambient HONO measurement techniques in urban atmosphere.

5) Identify the springtime ozone formation mechanisms in Houston.

Reducing uncertainties surrounding these processes will improve our ability to model radicals and ozone formation.
Moody Tower
Houston Network of Environmental Towers (H-NET)
TCEQ Monitoring Sites

Ozone Levels for Saturday May 30, 2009 14-15:00 CDT
# Moody Tower SHARP Measurements

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Instrument</th>
<th>PI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Meteorology (T, RH, P, ws, wdir, rain, cloud camera)</td>
<td>Campbell Research met system</td>
<td>Lefer (UH)</td>
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<tr>
<td>Basic Trace Gases (O₃, CO, SO₂, NO, NO₂, NOₓ)</td>
<td>Modified TECO Systems</td>
<td>Lefer (UH)</td>
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<tr>
<td>Photolysis Rates (jO₃, jNO₂, jHONO, jHCHO, etc)</td>
<td>Scanning actinic flux spectroradiometer (NCAR)</td>
<td>Lefer (UH)</td>
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<tr>
<td>Ozone Column, UV/VIS AOD</td>
<td>Brewer, CIMEL, UV-MFR</td>
<td>Lefer (UH)</td>
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<td>Mixed Layer Height</td>
<td>Vaisala CL-31 LIDAR</td>
<td>Lefer (UH)</td>
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<td>Vertical Profiles - O₃, T, P, RH, ws, wdir</td>
<td>Radiosonde/Ozonesonde Balloon</td>
<td>Morris (Valpo)/Lefer (UH)</td>
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<td>VOCs (C2-C10 NMHCs)</td>
<td>Realtime GC-FID (Perkin-Elmer)</td>
<td>Rappenglückeck (UH)</td>
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<td>HOOH, HONO</td>
<td>Aerolaser/QUMA-LOPAP</td>
<td>Rappenglückeck (UH)</td>
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<tr>
<td>Speciated PANs</td>
<td>Metcon GC-ECD</td>
<td>Rappenglückeck (UH)</td>
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<tr>
<td>HNO₃, HONO, HCl</td>
<td>Mist Chamber/IC</td>
<td>Dibb (UNH)</td>
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<td>OH, HO₂, RO₂, OH Reactivity</td>
<td>Laser Induced Fluoresence</td>
<td>Brune (Penn State)</td>
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<td>Oxy-VOCs, HCHO</td>
<td>PTr-MS</td>
<td>Jobson (WSU)</td>
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## Moody Tower SHARP Measurements

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<tr>
<td>ClNO₂, N₂O₅, PAN, PPN, APAN</td>
<td>CIMS</td>
<td>Huey (Ga Tech)</td>
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<tr>
<td>Aerosol Composition</td>
<td>Aerosol Mass Spectrometer (AMS)</td>
<td>Herndon (Aerodyne)</td>
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<td>HONO, HONO Flux, HONO Calibration Source</td>
<td>LOPAP</td>
<td>Ren (U. Miami)</td>
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<td>Water Soluble Aerosol Composition</td>
<td>PILS/IC</td>
<td>Griffin (Rice)</td>
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<td>Aerosol Size Distribution</td>
<td>DMA</td>
<td>Griffin (Rice)</td>
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<td>Ozone Production Rate</td>
<td>MOPS</td>
<td>Brune (Penn State)</td>
</tr>
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<td>Nitrophenols</td>
<td>IC coupled to ESI Tandem MS</td>
<td>Dasqupta (UT-Arlington)</td>
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<td>Aerosol Elemental and Organic Carbon</td>
<td>Sunset Labs EC/OC</td>
<td>Yu (PNNL)</td>
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<td>Aerosol morphology, size, mixing state</td>
<td>TRAC-SEM</td>
<td>Yu (PNNL)</td>
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<td>Potential Aerosol Mass</td>
<td>AMS with pre-reactor</td>
<td>Jimenez (Colorado)</td>
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<td>3 Levels Profiles (40m, 150m, 300m) of O₃, NO₂, SO₂, HCHO, HONO, NO₃</td>
<td>Long-Path DOAS</td>
<td>Stutz (UCLA)</td>
</tr>
</tbody>
</table>
Meteorological Conditions
Ozone

- 4 May
- 29 May
- 30 May

Ozone (ppbv)

- 1-hr
- 8-hr

Dates:
- 4 May
- 29 May
- 30 May

Dates:
- 4/17/09
- 4/24/09
- 5/1/09
- 5/8/09
- 5/15/09
- 5/22/09
- 5/29/09
Ozone Diurnal (10 min data)
CO Diurnal
NO₂ Diurnal (10 min data)
HCHO Diurnal - TRAMP

The graph shows the variation of HCHO concentration over a 24-hour period, with data points indicating the concentration at different times of day. The concentration is measured in parts per billion (ppbv) at 10 meters (m) height. The data is plotted with error bars, indicating the variability of the measurements.
SO$_2$ time series (wdir)
Long Path DOAS (UCLA)

![Graph showing concentration changes over time for various pollutants: 
- NO₃ (ppb)
- SO₂ (ppb)
- O₃ (ppb)
- HCHO (ppb)
- HONO (ppb)
- NO₂ (ppb)

Data for the dates 4/20/2009 18:30 and 4/21/2009 06:30 and 18:30]
Ozone Production Sensor (PSU)

Direct measurement of ozone production in Houston and correlation with ambient NO. May 4, 2009. Measured P(O3) will be compared with modeled P(O3) to test mechanisms. Measured P(O3) also can be compared with calculated P(O3) from peroxy radicals and NO. Cazorla, M. and Brune, W.
SHARP Related Projects

Moody Tower SHARP Intensive UH & many other groups
HONO Intercomparison Study (HINT) UH, UNH, UCLA, UMiami, Aerodyne, TAMU

Surface-induced Oxidation of Organics in the Troposphere (SOOT) TAMU
Traffic Related Emissions of HONO and HCHO (TRENF) UH
Study of HONO Surface Fluxes (HONO-FLUX) UH
Houston Urban Boundary Layer Study UH
Measurements of HCHO, PAN, and CO in Houston Ship Channel (HSC) UH
Nitrylphenols in Houston Atmosphere UT-Arlington
Formaldehyde and Olefins from Large Industrial Releases (FLAIR)
  Dual MAX-DOAS WSU & UCLA
  Imaging-DOAS UCLA
  Solar Occultation Flux (SOF) Chalmers University & UH
Aztec SHARP Flights UH
Aerodyne Mobile Lab Aerodyne
Plume Inversion Modeling Aerodyne
On-road emission factors

<table>
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<th></th>
<th>Houston 2000 (McGaughey et al., 2002)</th>
<th>Houston 2009 This study</th>
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<tr>
<td>FL (gas diesel)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO (g/kg fuel)</td>
<td>6.5</td>
<td></td>
</tr>
<tr>
<td>NOx</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2H4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle number (#/kg fuel)</td>
<td></td>
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</tbody>
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Overview of industrial emissions

- **Mont Belvieu**
  - Ethene, Propene
  - HCHO, butene, CH3CHO

- **Ship Channel**
  - Aromatics, butene, 1,3-butadiene, SO2, HCHO

- **Texas City**
  - Benzene, xylene...
  - Ethene, SO2, HCHO, SO4^2-
UH Aerosol LIDAR for Boundary Layer Height Measurements

University of Houston $\log_{10}$ of negative gradient on 19.+20.05.2009 in $10^{-9}$ m$^{-1}$ sr$^{-1}$

Height in m (240 m mean, tilted by 1°)

Time on 19.+20.05.2009 (1200 s mean)
SHARP Conclusions

1) The contribution of direct emissions of OH radical precursors HCHO and HONO from flares, smoke stacks, and other point sources and mobile sources.

Yes. Some “pseudo-primary” HCHO observed from some flares.

Maybe. HCHO and HONO in automobile exhaust plumes.
2) The ambient levels of ClNO$_2$ (and other halogens) in Houston and potential as a radical source.

Yes. GaTech found significant levels of ClNO$_2$ several nights. TAMU measured N$_2$O$_5$. UNH observed significant HCl levels, correlated with HNO$_3$.

3) Intercomparison of ambient HONO measurement techniques in urban atmosphere. Various instruments all measuring “HONO”, calibration/interference issues found.

4) Relative importance of springtime ozone formation mechanisms in Houston. Same mechanisms that produce ozone in Fall are active in the Spring. Post-frontal conditions, transport from North, re-circulation, entrainment of residual layer, etc.
UH Air Quality Measurement Aircraft
Local to Regional Scale Measurements

Houston urban plume advected over Waco, Texas
Baylor Institute for Air Science - Cessna 172 aircraft
(September 17, 2007 - 12:28 to 9:44 pm CST)

- Houston urban plume was transported approximately 163 miles.

(Map data courtesy of Greg Frost, NOAA)
Ozonesonde 2010 MARCH 04

The image shows a line graph with the following axes:

- X-axis: Ozone (ppbv) and RH (%)
- Y-axis: Altitude (km)

The graph includes data points for O3_ppbv (blue dots), RH_% (red dots), and Temp (green dots). The data appears to show a decrease in ozone concentration and an increase in temperature and humidity with increasing altitude.
Future Work

Dallas Measurements 2011
Regional Ozonesonde Network
Texas Regional transport Experiment (T-REX)
DISCOVER-AQ 2013