Update on TexAQS II Findings

Presented by Mark Estes, TCEQ
mestes@tceq.state.tx.us
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Second TexAQS II data workshop held May 29-May 31, 2007

- Presentations can be found at TCEQ website: http://www.tceq.state.tx.us/implementation/air/airmod/texaqs-files/TexAQS_II.html#workshops
Preliminary emissions findings

- Large emissions of HRVOCs found by Solar Occultation Flux (SOF) measurements; the emissions observed appear to be much larger than the emissions reported in the 2004 EI. [Melqvist]
- Large temporal variability was observed by SOF. [Melqvist]
Solar occultation flux measurements are made by viewing the sun through the gas plume using a spectrophotometer. The gases in the plume will absorb part of the sunlight, depending upon their concentrations. The gases can be identified by which wavelengths they absorb; their concentrations can be inferred based upon the degree to which they absorb those wavelengths. Flux is estimated by multiplying the estimated cross-sectional of the plume by the concentrations and the wind speed.
Mt Belvieu Sep 25, ethene [Mellqvist]

Ethene, 566±35 kg/h
Mt Belvieu, Sep 25, propene [Mellqvist]

propene 646 kg/h
**HSC Sep 06,**
_Average emissions in kg/h [Mellqvist]_

<table>
<thead>
<tr>
<th>Species</th>
<th>Meas</th>
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<td>ethene</td>
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<td>propene</td>
<td>1500±500*</td>
<td>60</td>
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<td>alkanes</td>
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<td>372</td>
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<tr>
<td>NH3</td>
<td>190 ±20</td>
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<tr>
<td>NO2</td>
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<tr>
<td>SO2</td>
<td>5200 ±2400</td>
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</table>

* Uncertain due to large variability in the emissions
N-S Transect on Battleground road Aug 31. On Aug 31 & Sep 14 the measurements vary between 200-2000 kg/h) (upsets, flares?) [Mellqvist]

propene 2000 kg/h
“SOF box” of ethene around the HSC on Sep 19, 12-1400 [Mellqvist]
Here the colorcode correspond to the mass of ethylene measured in the solar light. The lines point towards the wind
Meteorological sites and North-south sectors into which the emissions data was divided into.
### VOC emissions in Sep 2006, with SOF [Mellqvist]

<table>
<thead>
<tr>
<th>Sector/Region</th>
<th>ethene</th>
<th>propene</th>
<th>alkanes</th>
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<tbody>
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<td>Allen Genoa Rd</td>
<td>96±15</td>
<td>1</td>
<td>1739 ± 759</td>
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<tr>
<td>Davison street</td>
<td>120±24</td>
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<td>Deer-Park</td>
<td>187±110</td>
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<td>Battleground road</td>
<td>92±47</td>
<td>380±390</td>
<td>1264 ± 343</td>
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<td>Miller cutoffroad</td>
<td>184±156</td>
<td>211±70</td>
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<td>Baytown</td>
<td>72 ± 24</td>
<td>260±95</td>
<td>976 ± 113</td>
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<td>Mt Belvieu</td>
<td>404±41</td>
<td>420±280</td>
<td>863</td>
</tr>
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<td>Bayport</td>
<td>170*</td>
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<td>Channelview</td>
<td>64±32</td>
<td></td>
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<tr>
<td>Chocolate-Bayou</td>
<td>136*</td>
<td>273.0*</td>
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<tr>
<td>Freeport</td>
<td>250±65</td>
<td>21</td>
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<tr>
<td>Sweeny</td>
<td>163±5</td>
<td>126±64</td>
<td>3633</td>
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<tr>
<td>Texas-City</td>
<td>83±12</td>
<td></td>
<td>2889 ± 399</td>
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Preliminary emissions findings

- Evidence for large underestimation of direct emissions of formaldehyde remains weak. Analyses so far cannot rule out primary point source HCHO emissions, but do not conclusively confirm them, either. More analysis is needed. [Herndon, de Gouw, Stutz, Rappenglück, Dasgupta]
Moody Tower Formaldehyde, PANs, H$_2$O$_2$

Formaldehyde max.: 23.4 ppbv

Daytime: Secondary formaldehyde coincides with PAN and PPN
H$_2$O$_2$ peaks in the late afternoon/early evening
Indications for primary formaldehyde emissions? Indications for formaldehyde production through reaction of \( \text{O}_3 \) with alkenes? Indications for turbulent mixing?
Occasionally, elevated formaldehyde levels coincide with SO₂ and PANs (less correlated with CO, NOₓ, O₃)
September 27 event  [Estes, Dasgupta]

HCHO spike coincides with large ozone and NO2 increases, and NO decrease. (Time is Local Standard Time (LST)).
HCHO vs. CO in Nighttime Urban Air [de Gouw]

Ron Brown: Herndon, Aerodyne

Nighttime:
\[ \frac{\Delta \text{HCHO}}{\Delta \text{CO}} = 2-3 \text{ ppt/ppb in urban outflow} \]

\[ \frac{\text{HCHO} - 0.8}{\text{CO} - 100} = 0.003 \]

or

\[ \text{HCHO/CO} = 3 \text{ pptv ppbv}^{-1} \]

Daytime: HCHO increased due to photochemistry

NOAA WP-3D: Fried, NCAR

Missed approach at Montgomery County airport (N of Houston)

\[ \Delta \text{HCHO/\Delta CO} = 1.8 \pm 0.3 \text{ ppt/ppb} \]
Diurnal Variation of HCHO [de Gouw]

- Alkenes highest at night: shallow BL, no chemistry
- HCHO highest during day: photochemical production

Ron Brown data from Barbour’s Cut
During the SO$_2$ plume at 9/3/06 4:00, a reversal of the HCHO profile, i.e. higher HCHO aloft, was observed. HCHO plumes correlated with SO$_2$ plumes were also observed during other times (not shown).
Preliminary emissions findings

- Ethene concentrations have decreased since 2000. Since other compounds display different trends, the evidence supports ethene emission decreases. HCHO concentrations have decreased by the same percentage as ethene concentrations, suggesting that the HCHO decrease may be related to the ethene decrease. [de Gouw]
Ethene Source Locations [de Gouw]

- Mont Belvieu
- Beaumont
- Texas City
- Freeport
- Chocolate Bayou
- Sweeney
- Bayport

- 7 point sources
- ⇒ most of the ethene plumes in Houston area

prevailing wind direction

2004 TCEQ Point Source Database
Barbour’s Cut versus La Porte airport [RH Brown vs La Porte]

Ethene at Barbour’s Cut (2006) 60% lower than at La Porte airport (2000) [de Gouw]
Relative Differences Between 2006 and 2000 [P3 aircraft]

- **Ethyne** -0%: urban tracer
- **CO** -17%: cleaner vehicles ⇒ expected = -6% year\(^{-1}\) [Parrish]
  observed = -3% year\(^{-1}\)
- **NO\(_y\)** -38%: power plant emissions lower [Ryerson et al.]
- **SO\(_2\)** +8%: increased shipping?
- **HCHO** -42%: reduced formation

Ethene -42% ⇒ *Weight of evidence suggests that emissions in 2006 were lower than in 2000*
Preliminary emissions findings

- NOx emissions from power plants have decreased, with Parish having the largest observed decrease. CEMS-based NOx EIs appear to be accurate. [Ryerson]
NO$_x$, SO$_2$, and CO emissions (Questions A, C, and D)

Rural electric utility power plants:

W.A. Parish

- 2000: four transects, avg. 1.25
- 2006: sixteen transects, avg. 0.25

Average decrease since 2000:
measured from aircraft: 80%
measured by CEMS: 79%

J. Peischl, NOAA ESRL
NO$_x$, SO$_2$, and CO emissions (Questions A, C, and D)

Rural electric utility power plants:

- NO$_x$ emissions have decreased by 25 to 80% since TexAQS 2000
- Annual SO$_2$ emissions appear to be largely unchanged since 2000
- discrepancy in CO reconciled by large increases in inventory CO emissions between 2000 and 2006 (revision to Finding D1)
- Emissions ratios from aircraft and hourly CEMS agree to $\pm$10% on average in 2006

J. Peischl, NOAA ESRL
Preliminary emissions findings

- More work is needed to reconcile the mobile source emissions inventory with observations. [Frost, Parrish]
- Large shipping vessel emission factors appear correct within about 25%. [Williams]
- Researchers have *not* observed ammonia leaking from NOx sources equipped with selective catalytic reduction units. [Ryerson]
- New land cover data yields lower biogenic emissions. Auto-GC data clearly shows diurnal and seasonal variations in isoprene consistent with biogenic emissions at most sites. [Estes]
Aircraft Observations of Mobile Source Emissions [Frost]

Example: NOAA P-3 Observations in Houston
Tuesday, 26 Sept 2006, 1258-1318 CDT, 400-500 m altitude

Slopes of Linear Fits
Units = mole/mole
(r = correlation coefficient)
CO/CO₂ = 0.0121 (r = 0.96)
NO₂/CO₂ = 0.00215 (r = 0.96)
CO/NO₂ = 5.32 (r = 0.95)

Ratios are an effective way to compare concentrations to emissions, if you’re careful.
Average Molar Emission Ratios
Weekdays Only

Bars = 2 standard deviations in tunnel ratios
Mobile Emission Estimates from Observations and Inventory [Frost]

Average Molar Emission Ratios
Weekdays Only

Bars = 2 standard deviations in tunnel ratios

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Average Molar Emission Ratios

Weekdays Only

Bars = 2 standard deviations in tunnel ratios
Preliminary findings--Frost

- Mobile source emission ratios in Houston and Dallas extracted from aircraft observations in 2000 and 2006
  - Houston and Dallas have similar mobile emission ratios
  - Small weekday variations between midday and late afternoon
    - Increase in CO due to higher proportion of gasoline vehicles during rush hour
  - No large changes seen between 2000 and 2006
- Compare 2000 Washburn Tunnel data to P-3 observations
  - Ratios with CO$_2$ somewhat higher in tunnel than in P-3 data
  - More variation between midday and late afternoon than in P-3 data
    - Rush hour increase in CO and decrease in NO$_x$
- Compare observations with 1999 emission inventory
  - Inventory CO higher than observations by factor of 2-4
  - Inventory NO$_x$ higher than observations by up to a factor of 2
  - No hourly variation in inventory
- More analysis of TexAQS 2006 P-3 data is needed
- Careful interpretation of P-3 data is crucial
- Information about absolute CO and NO$_x$ emissions obtained by analyzing ratios with CO$_2$, not just CO/NO$_x$ ratios

But NEI 99 has no diurnal variation, lower CO2 than a 2005/2006 EI. Higher CO2 in newer EI will decrease the CO/CO2 and NOy/CO2 ratios, bringing EI closer to obs [Kite].
NO\textsubscript{x}, SO\textsubscript{2}, and CO emissions (Questions A, C, and D)

Emissions from shipping:

Inventories of NO\textsubscript{x}, SO\textsubscript{2}, and CO large vessel emission factors are accurate to roughly ± 25%.

Ship NO\textsubscript{x} emission factors show no trend with vessel speed, consistent with literature data (revision to Finding D3).

Fractional contributions from ship NO\textsubscript{x} emissions are expected to increase over time.

_E. Williams, B. Lerner, and P. Murphy, NOAA ESRL_
Biogenic emissions for June 21, 2005, based upon Wiedinmyer et al. (2001) land use/land cover data:

4,241 tons VOC for the domain
Biogenic emissions for June 21, 2005, based upon UT-CSR land cover data:

2323 tons VOC for the domain

Decrease in Brazoria County biogenics; more consistent with P3 observations.
Frequency distribution for diurnal cycles, by month, for HRM3 2003-2005

Seasonal and diurnal cycles are consistent with biogenic emissions.
Seasonal cycle is consistent with biogenics (background?), but otherwise apparently dominated by plumes from anthropogenic source(s).
Eastern Harris County site shows biogenic signal with perhaps mobile influence during rush hours. 2006 appears to be representative of previous 9 years.

Two measurements >10 ppbv in September 2006 suggest anthropogenic isoprene plume.
Brazoria County site shows biogenic cycles, with concentrations often a bit lower than 3-yr median, and no apparent anthropogenic influence.
Preliminary met findings

- Temperatures in Houston were more typical than in 2000. [Sullivan]
- Wind speeds in Houston were higher than in 2000. [de Gouw]
- There were more N and SSE trajectories than an average year, and fewer short (~stagnant) trajectories. [Sullivan]
5 Clusters found in Aug./Sept. 1997-2006 trajectories [Sullivan]

5: north

Cluster 5 of 5 - 97_06
Backward trajectories
EDAS Meteorological Data

4: northeast

Cluster 4 of 5 - 97_06
Backward trajectories ending at various times
12 UTC 23 Sep - EDAS Forecast Initialization

3: south-southeast

Cluster 3 of 5 - 97_06
Backward trajectories ending at various times
17 UTC 25 Sep - EDAS Forecast Initialization

1: short fetch

Cluster 1 of 5 - 97_06
Backward trajectories ending at various times
17 UTC 26 Sep - EDAS Forecast Initialization

2: east-southeast

Cluster 2 of 5 - 97_06
Backward trajectories ending at various times
12 UTC 29 Sep - EDAS Forecast Initialization
Numerical summary of traj. factors & regional O₃ by year [Sullivan]

- Using 12 East Texas long-running sites, % of sites > 75ppb
- E.g., in 1999, on days w NE trajs, on avg 48% of sites > 75 ppb
- 2006 seems to have more “norths” than unusual

### Average pct of “high” sites by factor and year

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<th>year (Aug.-Sept.)</th>
<th>Avg by factor</th>
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<td>short</td>
<td>16.98</td>
<td>23.61</td>
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<td>E-SE</td>
<td>1.19</td>
<td>6.25</td>
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<td>Max</td>
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### Count of trajs by factor and year

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<td>59</td>
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Preliminary background ozone findings

- Regional ozone in eastern Texas was lower than the 10-year average. [Sullivan]
- Higher background ozone in Houston is associated with regional scale winds from the north, northeast, and east; lower background ozone is associated with winds from the Gulf. [Sullivan]
- Background ozone averaged about 50 ppb. [Sullivan, Hardesty]
Regional $O_3$ trend [Sullivan]

- Texas-85ppb trend shown; other graphs look similar.
- Wide year-to-year variability.
- Appears to have been a change after 2000.
- Classify 6 recent years as follows:
  - 2003, 2006, low;
  - 2001, 2005, moderate;
  - 2002, 2004, high;
  - Recall 2005 Katrina late-Aug., Rita mid/late-Sept.)
- 12 Texas sites:
  - 481830001 Longview C19
  - 480850005 Frisco C31/C680
  - 484392003 Keller C17
  - 482010024 Aldine C8
  - 482010051 Croquet C409
  - 483611001 W. Orange C9
  - 482450009 Beau.-Lamar C2
  - 484530014 Austin NW C3
  - 480290032 San Ant. NW C23
  - 484690003 Victoria C87
  - 483550025 CC West C4
  - 480610006 Brownsville C80

12 Texas Sites, Aug. & Sep. 85 ppb Exceedances

\[ y = -4.16x + 8366.3 \]
\[ R^2 = 0.30 \]
\[ F = 0.06 \]
2006 Back-trajectory points contoured kriging ("low" year) [Sullivan]
2004 Back-trajectory points contoured kriging (“high” year) [Sullivan]
Background Measurements: All days [Hardesty]

Caveat: Areas not uniformly sampled
Preliminary ozone chemistry findings

- OH-reactivity of VOCs remains high in the industrial areas of Houston. [Gilman, Brune]
- Radical budget measurements are intriguing, but much work remains to be done before solid conclusions can be drawn. [Brune, Rappenglück, Roberts, Lefer, Stutz, Herndon, et al.]
The unknown is the difference between the measurements and calculations using currently available data. Aromatics and large carbonyls are not included in the calculations yet and should be in the unknown.
Regional Distribution of VOC Reactivity [Gilman]

- Analysis of WAS data from the NOAA WP-3D
- Symbol size is total reactivity of the measured VOCs with OH
- Anthropogenic NMHCs = alkanes + alkenes + aromatics

Highest reactivity in the HSC, mostly from alkenes
Regional Distribution of VOC Reactivity [Gilman]

oxyVOCs = aldehydes + ketones + alcohols + acids

Lowest fraction in the HSC

Highest fraction away from sources

oxyVOCs / (oxyVOCs + Total NMHCs) (%)
Regional Distribution of VOC Reactivity [Gilman]

- Biogenic NMHCs = isoprene + monoterpenes

- Highest fraction NE of Houston
- Lowest fraction Over the HSC

Biogenic NMHCs / Total NMHCs (%)
Radical budget issues

- Photolysis rates
- Nighttime $\text{O}_3$+olefins
- Primary aldehyde emissions
- Daytime HONO formation
- Nighttime HONO, $\text{NO}_3$, $\text{N}_2\text{O}_5$ chemistry
- $\text{Cl}_2$ emissions and chemistry
- CINO$_2$
- Boundary layer dynamics, especially early morning
- Ability of chemical mechanisms, photochemical grid models to simulate radical budget
Preliminary long-range transport findings

- Satellite investigations have successfully traced Saharan dust across the Atlantic and Gulf into the Houston area, where it influenced PM concentrations. [Pierce, Garay]
- Satellite investigations of wildfires during TexAQS II suggest that Houston was influenced by wildfire emissions during TexAQS II. [Pierce]
CALISPO Backscatter profiles for August 17-28, 2006
Boundary Layer back trajectories from August 28 CALIPSO track shown in red
Dust from the Sahara Desert Reaches Houston, Texas

Observations from the Multi-angle Imaging SpectroRadiometer (MISR) Instrument on NASA’s EOS Terra Satellite
Miscellaneous preliminary findings

- Elemental mercury (Hg) observed by RH Brown in Houston Ship Channel cannot be attributed to any known Hg source. It may emanate from an ongoing Hg remediation effort.
Elemental mercury ($Hg^0$) emissions (Question E)

Elemental mercury data from R/V Brown show a persistent, narrow plume of $Hg^0$ in HSC (up to 250 ng/m$^3$).

$Hg^0$ was uncorrelated with all other chemical species measured on R/V Brown.

Not attributable to any known Hg source in current inventories.

Other, smaller $Hg^0$ plumes seen in BPA and elsewhere in HSC.

T. Fortin, NOAA ESRL
Elemental mercury ($Hg^0$) emissions (Question E)

$Hg^0$ observations are consistent with re-emission from soil, contaminated in the past, during soil remediation efforts occurring during the TexAQS 2006 study.

This site location is provisionally identified as Oxyvinyls Deer Park, which last reported substantial $Hg^0$ emissions in 2002.

This speculation is very preliminary and needs careful additional work to rule in or out.

T. Fortin, NOAA ESRL
Questions?