Characterization of Background Ozone and Aerosols
(RSST Questions G & H)

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Rapid Science Synthesis Meeting
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Regional distribution of background $O_3$ in East Texas

Airborne lidar flights 08/01 – 09/13/2006
- Remove O₃ plume data from all flights
- Average remaining background O₃ data between 400 and 800 m ASL
- Segregate by region
Background ozone by region
(from airborne lidar 08/01 – 09/13/2006)

<table>
<thead>
<tr>
<th>Region</th>
<th>Background O₃, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gulf</td>
<td>39</td>
</tr>
<tr>
<td>Coast</td>
<td>46</td>
</tr>
<tr>
<td>SE TX</td>
<td>51</td>
</tr>
<tr>
<td>NE TX</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure G1. Six-year (1998-2003) average background ozone in various regions in eastern Texas. Curves are smoothed with a 31-point running mean filter. (Figure from Nielsen-Gammon et al., 2005). The blue and red line segments indicate 2006 background ozone as described in the text.
Background $O_3$ trend

From Nielsen-Gammon et al., January 2005
Top 3-6 Background Ozone Values

From John Nielsen-Gammon et al., January 2005
How does background $O_3$ in East Texas vary with different meteorological conditions & transport patterns?

Airborne lidar data: 08/01 – 09/13/2006
Under higher wind speed conditions low background $O_3$ values (close to 30 ppbv) are observed at SW flow (marine) conditions in coincidence with low level $O_3$ days in $O_3$ time series.
1. Formation of ClNO$_2$ during overnight transport of NO$_x$ pollution in the marine boundary layer over the Gulf of Mexico releases chlorine radicals during the morning hours and may affect O$_3$ production rates in coastal areas.

**Mechanism**

**Nocturnal formation of N$_2$O$_5$:**

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2
\]

\[
\text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5
\]

**Heterogeneous reaction of N$_2$O$_5$ with chloride containing aerosol (e.g. sea salt):**

\[
\text{N}_2\text{O}_5(\text{g}) + \text{Cl}^- (\text{aq}) \rightarrow \text{ClNO}_2(\text{g}) + \text{NO}_3^- (\text{aq})
\]

**Sunrise photolysis of ClNO$_2$:**

\[
\text{ClNO}_2 + h\nu \rightarrow \text{Cl} + \text{NO}_2
\]

Example of overnight transport of NOx sources over coastal regions on September 8, a night in which ClNO$_2$ was observed

From Steve Brown et al.
2. Heterogeneous hydrolysis of \( \text{N}_2\text{O}_5 \), measured in \( \text{NO}_x \) plumes from sources in Houston and continental areas of Texas, was generally inefficient. Because \( \text{N}_2\text{O}_5 \) was stable, it could serve as a reservoir for overnight transport of \( \text{NO}_x \) and \( \text{O}_3 \).

\[
\text{Nighttime P-3 Intercepts of Parish power plant on October 12}
\]

Nocturnal nitrogen oxide partitioning

\[
F(\text{NO}_x) = \frac{\text{NO}_3 + 2\text{N}_2\text{O}_5}{\text{NO}_2 + \text{NO}_3 + 2\text{N}_2\text{O}_5}
\]

From Steve Brown et al.
3. Reduced N₂O₅ hydrolysis made larger concentrations of NO₃ available to initiate nocturnal oxidation of highly reactive VOC, mainly higher alkenes (i.e., other than ethene).

\[ R_{VOC} = \sum k(\text{NO}_3 + VOC_i) \times [\text{NO}_3] \times VOC_i \]

VOC Loss Rates of 0.5 - 4 ppbv hr⁻¹ within plumes emitted from industrial sources

NO₃ reactivity by VOC type. Biogenic VOC includes isoprene, some of which arises from industrial sources. Oxygenates here are mainly aldehydes (e.g., acetaldehyde).

From Steve Brown et al.
Which sources contribute to background $O_3$ and precursors in East Texas?

Local: Stagnation, recirculation, stalled fronts

Regional: Emissions from Texas urban areas

Continental-scale:
- Long-range transport of ozone/precursors into TX from other parts of US or Mexico
- Agricultural/biomass burning in US & Mexico
- Forest fires in western US, Canada, Alaska
Increase in background $\text{O}_3$ during multi-day Houston stagnation episode

Background $\text{O}_3$ in Houston area
8/29 – 9/01/2000
Export of ozone from urban areas into East Texas
Horizontal ozone flux

- **Dallas**
- **Houston, TexAQS I**

Graph showing ozone flux over time for different dates.
### Results of flux calculations
(for transects with highest flux)

<table>
<thead>
<tr>
<th>Metro area</th>
<th>Date</th>
<th>Wind direction</th>
<th>Wind speed, m s⁻¹</th>
<th>Time, CST</th>
<th>Background O₃, ppbv</th>
<th>O₃ enhancement, ppbv</th>
<th>Flux, molec O₃ s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Houston</td>
<td>8/12/2006</td>
<td>S</td>
<td>7.3</td>
<td>16:57 - 17:34</td>
<td>29</td>
<td>39</td>
<td>5.0*10²⁶</td>
</tr>
<tr>
<td>Houston</td>
<td>8/14/2006</td>
<td>S</td>
<td>4.5</td>
<td>16:58 - 17:26</td>
<td>34</td>
<td>55</td>
<td>5.0*10²⁶</td>
</tr>
<tr>
<td>Houston</td>
<td>8/30/2006</td>
<td>N</td>
<td>3.8</td>
<td>17:10 - 17:43</td>
<td>59</td>
<td>52</td>
<td>3.2*10²⁶</td>
</tr>
<tr>
<td>Houston</td>
<td>8/28/2000</td>
<td>S</td>
<td>4.2</td>
<td>16:11 – 16:40</td>
<td>53</td>
<td>52</td>
<td>6.0*10²⁶</td>
</tr>
<tr>
<td>Houston</td>
<td>9/06/2000</td>
<td>NE</td>
<td>5.2</td>
<td>14:13 – 14:43</td>
<td>69</td>
<td>46</td>
<td>3.6*10²⁶</td>
</tr>
<tr>
<td>DFW</td>
<td>9/13/2006</td>
<td>N</td>
<td>4.6</td>
<td>15:49 - 16:34</td>
<td>57</td>
<td>18</td>
<td>1.7*10²⁶</td>
</tr>
</tbody>
</table>
• Above-background ozone flux produced in Houston metro area ranges from $3.2$ to $6.0 \times 10^{26}$ molec/s.

• A flux of $4.6 \times 10^{26}$ molec O$_3$ / s (average of all Houston cases) emitted over a day is equivalent to a 10-ppb increase in ozone over an approx. 10,000 square mile area, assuming a 2-km deep mixed layer.

• Export of ozone from DFW metro area is about a factor of 2 to 3 less than from Houston (based on 1 Dallas case only).
Flux Calculation Comparison

- Aircraft Lidar Data vs. Ground Monitoring Network Calculations
  - Since aircraft flights/Lidar data are infrequent; how reliable are other estimation techniques?
  - Can the surface monitors provide reasonable flux estimates?

<table>
<thead>
<tr>
<th>Metro area</th>
<th>Date</th>
<th>Ozone Flux (molec./s)</th>
<th>Ozone Flux (ground network) (molec./s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Houston</td>
<td>12-Aug</td>
<td>5.0*10E26</td>
<td>2.2*10E26</td>
</tr>
<tr>
<td>Houston</td>
<td>14-Aug</td>
<td>5.0*10E26</td>
<td>4.1*10E26</td>
</tr>
<tr>
<td>Houston</td>
<td>30-Aug</td>
<td>3.2*10E26</td>
<td>4.0*10E26</td>
</tr>
<tr>
<td>DFW</td>
<td>13-Sep</td>
<td>1.7*10E26</td>
<td>1.3*10E26</td>
</tr>
</tbody>
</table>

From Mariana Dionisio et al.
Intensive studies: TexAQS 2006

- chemical data illustrate transport of separate sulfate and benzene plumes

From Tom Ryerson et al.
Intensive studies: TexAQS 2006

NOAA WP-3D track
09/16/2006

- chemical data illustrate transport of separate sulfate and benzene plumes

From Tom Ryerson et al.
Intensive studies: TexAQS 2006

Clear example of coastal plumes affecting northeast TX, LA, AR, OK

From Tom Ryerson et al.
Alaskan fires (July ‘04) impact Houston ozone levels.

From Gary Morris et al.