Continuous measurements of $O_3$ and $NO_2$ at two heights in Houston, TX

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Background

- Monthly reports of the five H-NET sites include comparisons of 1:00 pm hourly O₃ to nearby CAMS
- Moody Tower comparison shows good correlation with nearby sites but often is higher than nearby CAMS (slope ±10-15%)
- Possibilities for the observed differences included calibration issues, O₃ titration, O₃ deposition, or differences in O₃ production
- In 2011 & 2012 TCEQ funded additional measurements of NO & NO₂ at the Moody Tower and O₃, CO, NO, and NO₂ at a surface site on the UH campus with the goal of examining Oₓ (O₃ + NO₂) differences between the two heights
Site descriptions

- Moody Tower – Roof of 18-story dorm, sample height ~70m, daily zero/span, biweekly multipoint checks
  - Ozone – TEI 49C (± 3%)
  - CO – TEI 48i-TLE, hourly autozero (± 4%)
  - NO/NO\textsubscript{x} – TEI 42i-TL with AQD blue light photolytic converter (± 5%)

- Launch Trailer – converted truck trailer, sample height ~5m, daily zero/span, weekly multipoint checks, \textit{jNO}_2, PBL lidar
  - Ozone – TEI 49C (± 3%)
  - CO – TEI 48i-TLE, hourly autozero (± 4%)
  - NO – TEI 42c, hourly autozero (± 5%)
  - NO\textsubscript{x} – TEI 42c-TL with AQD blue light photolytic converter, hourly autozero (± 5%)
Measurement period

- Data examined was collected between 10/7-12/12/2011 (66 days) and 9/17-11/13/2012 (57 days).
- Both periods were dominated by southeasterly winds however 2012 saw more northeasterly winds than in 2011.
2012 1:00 pm O$_3$ at UH

- Moody Tower and Launch Trailer 1:00 pm hourly O$_3$ during the 2012 period examined agrees very well, 2011 yielded similar results.

- Sites are close together and daytime vertical mixing minimizes the afternoon differences.

![Graph showing correlation between Moody Tower 1 pm O$_3$ and Launch Trailer 1 pm O$_3$.]
O₃ vs. Oₓ

• Site to site variability in O₃ may be due in part to localized titration, however Oₓ (O₃ + NO₂) is more likely to be preserved and allows for better comparability.
\( l \) = length of light path
\( C \) = concentration of trace gases
O$_3$ and O$_x$

- Long-path DOAS measurements by UCLA between Moody Tower and Downtown (~4-5 km) at three heights show good agreement in O$_x$ during 2006 & 2009.
High/Low O₃ days in 2012

High days 1h O₃ > 70 ppbv (8 days)  
Low days 1h O₃ < 40 ppbv (7 days)

Agreement during midday but significant differences during the overnight hours, up to 20 ppbv on high O₃ days.

Titration of O₃ by NO from surface emissions causes higher NO₂ at the surface when vertical mixing is weak.

Nighttime differences in Oₓ on high O₃ days are reduced by ~50% compared to differences in O₃. Agreement is good throughout low O₃ days.
Overnight differences in $O_x$ tend to occur on nights when boundary layer heights approach the height of the Moody Tower, indicating that $O_3$ from the residual layer may be sampled.

Differences in $O_x$ on some mornings seem to be driven by a loss of NO$_2$ at the Launch Trailer which occurs with strong plumes from the northeast before sunrise, possibly from mobile sources ($CO/NO_x \sim 5.3 \pm 0.05$). (Parrish, D. D. (2006), Critical evaluation of US on-road vehicle emission inventories, *Atmospheric Environment*, 40(13), 2288-2300.)
MT vs. other CAMS fall 2011

- Left graph: $R^2 = 0.87$
  - Offset: $-0.65 \pm 1.8$
  - Slope: $0.83 \pm 0.04$

- Middle graph: $R^2 = 0.81$
  - Offset: $-5.1 \pm 2.5$
  - Slope: $0.87 \pm 0.05$

- Right graph: $R^2 = 0.83$
  - Offset: $-2.2 \pm 2.8$
  - Slope: $1.03 \pm 0.06$
There are times when we would not expect $O_3$ to agree between sites, especially at high $O_3$.

In general Moody Tower agreement is better with most urban Houston sites where we saw larger differences before.
Conclusions

• Differences in measured O$_3$ and O$_x$ are smallest during the day when vertical mixing is strongest, largest at night and early AM.

• Titration of O$_3$ to NO$_2$ accounts for ~50% of the nighttime difference between O$_3$ measured at 5 and 70m on the UH campus.

• O$_3$ dry deposition is a likely candidate for remainder of nighttime O$_x$ difference.

• Long-path DOAS data show that O$_x$ is conserved over a broader area and range of altitudes.

• Significant differences seen between Moody Tower and some Houston area O$_3$ monitors during 2010 and 2011. Improved agreement with troublesome monitors observed in 2012.

Future Work

• Preparing to measure through the whole O$_3$ season in 2013 and add NO$_y$ measurements to both heights.

• Calculate O$_x$ at nearby CAMS sites and compare to results from UH campus.

• Measure/calculate O$_3$ dry deposition near surface.
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