Assessment of NOX & VOC in Urban Areas: Potential Implications for O$_3$ Planning

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Motivation

- Characterize the spatial and temporal variability in the relative mix of NO$_X$ and VOCs (surrogate for O$_3$ formation regime) in U.S. urban areas using readily available data.

- Can a photochemical model be used for this type of characterization, does it match limited observations?

- This type of evaluation also provides an assessment of how appropriately the modeling system may respond to changes in precursor emissions.
  - If predicted VOC:NO$_2$ ratios don’t match observed ratios, O$_3$ production regimes are likely not correctly characterized.

- Is VOC/NO$_X$ a useful indicator of the effectiveness of NO$_X$ and VOC reductions? Is model response directionally consistent with what is expected with the VOC/NOX ratio?

- Is this type of evaluation limited to areas dominated by production, i.e., won’t work on areas affected predominantly by transport?
Ozone Formation Regimes

**VOC limited**
- All urban centers (Milford et al, 1989; Milford et al, 1994)
- Los Angeles (Milford et al, 1989; Harley et al 1993)
- San Francisco (Steiner et al, 2006)
- Phoenix (Kleinman et al, 2005)
- New York City (Kleinman et al, 2000)

**NO\textsubscript{X} limited**
- Rural/suburban areas (Milford et al, 1989; Milford et al, 1994)
- Atlanta (Sillman, 1995; Daum et al, 1996)
- Nashville (Kleinman et al, 2005)
- Northeast corridor downwind of NYC (Cardelino and Chameides, 1995; Sillman et al, 1995)

**Both VOC and NO\textsubscript{X} limited**
- Houston (Daum et al, 2004)
- Philadelphia (Kleinmen et al, 2005)
Counties with O₃ Design Value > 70 ppb

Indicates a special monitoring/modeling campaign was published for this area
Counties with $O_3$ Design Value > 65 ppb

Indicates a special monitoring/modeling campaign was published for this area

Monday, October 11, 2010
Colocated VOC and NO$_x$ monitors in 2002
Methods: PAMS Observations

Ambient measurement data from the Photochemical Assessment Monitoring Stations (PAMS) network

Data obtained from EPA’s TTN website (www.epa.gov/ttn/airs/airsaqs/detaildata/downloadaqsdata.htm)

PAMS sites operated during ozone season & located in urban areas

2002, 2005 PAMS species: Total NMOC, isoprene, O₃, NO₂
Methods: Modeling System

- CMAQ v4.6.1i and CMAQ v4.7
- CB-05 gas phase chemical mechanism
- Annual 2002 & 2005 simulations:
  - 12 km Eastern U.S.
  - 12 km Western U.S.
- Annual 2020 simulation:
  - 12 km Eastern U.S.
- 14 vertical layers (15 km top)
- Boundary conditions from a 36 km CONUS CMAQ simulation
Results

- Operational performance assessment for $O_3$, $NO_2$, TNMOC (TNMOC=VOC for this presentation)
- $NO_2$ measurement uncertainty at PAMS monitors
- Spatial and temporal assessment of VOC:$NO_2$ ratios
- Model estimated TNMOC:$NO_2$ in 2002 compared to 2020
- How does the model respond to $NO_x$ and VOC reductions?
Focusing Evaluation on Elevated Ozone

- Examine VOC/NO$_2$ ratio and other precursors when observed ozone is elevated
- Modeling system tends to underestimate peak ozone formation events
- Operational evaluation most important for these events to better understand why peaks are missed
Observed 2002

Average TNMOC/NO$_2$ Ratio for Observed O$_3$ > 70 ppb

Model Predicted 2002

Avg TNMOC/(NO$_2$+PAN+HNO$_3$) Observed O$_3$ > 70 ppb

Model Predicted 2002

Avg TNMOC/NO$_2$ Ratio for Observed O$_3$ > 70 ppb

Circle indicates N >= 10
Triangle indicates N < 10
Average TNMOC/"NO\textsubscript{2}" Ratio when Observed O\textsubscript{3} > 70 ppb
Model estimates and observations are shown paired in time but not space.

Only shown are observations and model estimates where observed O₃ > 70 ppb.
Model estimates and observations are shown paired in time but not in space.

Only shown are observations and model estimates where observed $O_3 > 70$ ppb.
Model estimates and observations are shown paired in time but not in space.

Only shown are observations and model estimates where observed $O_3 > 70$ ppb.
Time series at 2 Chicago area monitors

OBSERVED O₃ (color indicates VOC/NO₂ ratio)

OBSERVED O₃ (color indicates VOC/NO₂ ratio)
Timeseries: North Chicago 2002

OBSERVED $O_3$ (color indicates VOC/NO$_2$ ratio)

MODELED $O_3$ (color indicates VOC/NO$_2$ ratio)
Timeseries: Los Angeles 2002

OBSERVED $O_3$ (color indicates VOC/NO2 ratio)

MODELED $O_3$ (color indicates VOC/NO2 ratio)
Average VOC/NO2 Ratio where observed O₃ in 2002 > 70 ppb

Model Predicted 2002

Model Predicted 2020
TNMOC/(NO2+PAN+HNO3) where Obs $O_3 > 70$

Modeled estimates at all ozone monitor locations
Modeled Change in Ozone
where predicted hourly ozone > 70 ppb

Hour of the Day (LST)

Day of the Week
• Comparing the model predicted change in $O_3$ (X axis) to the model predicted VOC/NO$_x$ ratio (Y axis); where observed $O_3 > 70$ ppb
Important Findings

- Observed VOC:NO$_2$ ratios vary from urban area to urban area; within urban areas; and sometimes from hour to hour

- CMAQ-predicted and PAMS-observed VOC:NO$_2$ ratios agree well in some parts of the country but not all
  - This suggests CMAQ may not be accurately capturing O$_3$ production regimes.
  - Emissions inventories may need improvement in some areas

- Current PAMS NO$_2$ measures NO$_2$ plus other nitrogen species which may confound interpretation

- Modeling system predicts urban areas will be more NO$_X$ limited in the future

- Model often responds to NO$_X$ and VOC reductions regardless of model estimated VOC/NO$_X$ ratio