Emissions of Radical Precursors and Related Species from Traffic in Houston, Texas – Implications for Air Quality Modeling

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Background

• The Houston region is in non-attainment for the 1-hr, 1997 and 2008 8-hr ozone standard

• This study focus on ozone precursors: HONO, HCHO, CO, NO/NO2/NOx

• Observational data is compared to modeling data (MOBILE6 and MOVES) on an urban highway junction in Houston
Daytime Photochemical Process

Termination by NO\textsubscript{x}

Photolysis of O\textsubscript{3}, RCHO, HONO, H\textsubscript{2}O\textsubscript{2}, CINO\textsubscript{2} + alkene ozonolysis

Termination by NO\textsubscript{x} + RO\textsubscript{x}

PAN’s

NO

HNO\textsubscript{3}

O\textsubscript{3} \rightarrow O\textsubscript{1}(D) \rightarrow OH* + H\textsubscript{2}O

RCH* \rightarrow RCH\textsubscript{2}O\textsubscript{2} + RCHO

RC(O)O\textsubscript{2} \rightarrow RCO* + HO\textsubscript{2} + H\textsubscript{2}O

RC(O)O* \rightarrow RCH\textsubscript{2}O* + +O\textsubscript{2}

RCH\textsubscript{2}O* \rightarrow H\textsubscript{2}O \rightarrow H\textsubscript{2}O + RCH\textsubscript{2}OOH

PAN

PPN (anthropogenic)

MPAN (biogenic)
CMAQ modeling of contributions of O3, HONO, HCHO and H2O2 to hourly OH formation in Houston TX

- HCHO contributes to OH formation on late morning hours
- HONO contributes to OH formation on early morning hours
Experimental Data

• Continuous ambient air measurements averaged to 10 min interval
Experimental Data

• The data was screened for:
  - weekdays
  - Rush hour time 4-8 am CST
  - Global radiation < 10 W/m²
  - PAN < 50 pptv
  - No precipitation
  - RH > 80%
• Very good agreement with Parrish study for rush hour times in selected cities.

Experimental Data

\[
y = 6.01(\pm 0.15)x + 95.5(\pm 7.2) \\
R^2 = 0.91
\]

September 28, 2009

\[
y = 5.76x + 114.7 \\
R^2 = 0.80
\]
Emission Modeling
Emission Modeling

• **MOBILE6**: hourly Harris county emission factors for on-road for NOx, CO, VOC, HCHO
  - Observed meteorology at the Galleria site for the model day: September 28, 2009
  - 2009 local registration distribution
  - 2009 local diesel fractions
  - 2009 local VMT per hour
  - Local inspection and maintenance program
  - Anti-tampering program
  - Reformulated gasoline
**Emission Modeling**

- **MOVES**: MOVES2010a was used to calculate EF for on-road and off-network for NOx, CO, VOC, HCHO, CO$_2$ (atm), NO, NO$_2$. MOVES2010b was used to calculate HONO.

- The county data manager was used to enter the local data:
  - Avgspeeddistribution
  - Dayvmtfraction
  - Fuelformulation
  - Fuelengfraction
  - Fuelsupply
  - Hourvmtfraction
  - Hpmvtypeyear
  - Imcoverage
  - Monthvmtfraction
  - Roadtypedistribution
  - Sourcetypeagedistribution
  - Sourcetypeyear
  - Zonemonthhour
Emission Modeling

Using the Texas Transportation Institute suite of programs:

- The EFs were adjusted for TxLED and the motorcycle rule
- The emissions were calculated multiplying the hourly adjusted emission factors (according to speed) by the hourly VMT per link, using the 2009 hourly VMT mix.
- The output is link-level emissions by vehicle type
Diurnal variation of VMT for the Galleria site study area September 28, 2009
Results

- For the morning rush hour, MOBILE6 overestimates the CO/NOx ratio by almost a factor of 2, while MOVES is 30% higher.
Results

- MOBILE6 largely underestimates HCHO/CO ratio
- MOVES calculates a very high ratio for very early morning due to heavy duty diesel off-road emissions (idling and starting trucks)

Equation for all data:
\[ y = 3.14(\pm 0.14)x + 0.69(\pm 0.07) \]
\[ R^2 = 0.68 \]

Equation for September 28, 2009:
\[ y = 2.69x + 0.54 \]
\[ R^2 = 0.68 \]
The differences in CO/NOx and HCHO/CO ratios are largely due to higher NOx and HCHO in MOVES (30% and 57% more than in MOBILE6) while CO emissions are about the same for both models.
Results

MOVES shows a constant HONO/NOx ratio from a tunnel study done more than 15 years ago. The observed HONO/NOx ratio is twice the modeled.
• As expected due to the underestimation of HONO/NOx, the MOVES also underestimates the HONO/CO ratio, except at very early morning hours.
Results

- Earlier studies showed a NO2/NOx ratio of 5%.
- MOVES shows a ratio 9.3% for rush hour time.
- The observation ratio is about twice.
• MOVES calculates 3 times higher CO/CO2 than observed.
• It seems that MOVES overestimates the CO/CO2 ratio from light duty gasoline vehicles.
Results

Light Duty Gasoline CO/CO2

Heavy Duty Diesel CO/CO2
Conclusions

• For CO/ NO\textsubscript{x} ratio of around 6.01 ppbv CO / 1 ppbv NO\textsubscript{x} (r\textsuperscript{2} = 0.91) in agreement with other studies. MOBILE6 and MOVES, overestimate the corresponding observed emission ratio. MOVES gets closer, but is 30% above the observed value.

• For HCHO/CO ratio of around 3.14±0.14 g HCHO / kg CO. While MOBILE6 largely underestimates this ratio, MOVES calculates higher ratios, but is lower than the observed ratio. MOVES shows high HCHO/CO ratios during the early morning hours due to heavy duty diesel off-road emissions (Potential reasons are idling and starting trucks).
Conclusions

• The differences of the modeled CO/NO\textsubscript{x} and HCHO/CO ratios are largely due to higher NO\textsubscript{x} emissions in MOVES (30% increased from MOBILE6) and higher HCHO emissions in MOVES (57% increased from MOBILE6); CO emissions were about the same in both models.

• The observed HONO/NO\textsubscript{x} emission ratio is around 0.016 kg HONO / kg NO\textsubscript{x} which is twice as high as in MOVES.

• The observed NO\textsubscript{2}/NO\textsubscript{x} emission ratio is around 0.18, which is twice than in MOVES.

• MOVES overestimates the CO/CO\textsubscript{2} emission ratio by a factor of 3 compared with the observations.

• The above findings indicate an overestimation of CO for light duty gasoline vehicles and an underestimation of HONO, HCHO, NO2 for heavy duty diesel vehicles in MOVES.