Determination of Urban VOC Emission Ratios and Comparison with Inventories

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Outline:
- Determination of emission ratios for urban VOCs
- Comparison of results with other years, cities & studies
- Comparison of results with NEI-99
Measurement Locations

Cities samples during recent NOAA missions in North America:

- Boston
- Dallas
- Denver
- Houston
- Los Angeles
- Mexico City
- New York City
- and many others…

This presentation summarizes the results from these missions.
Platforms and Instruments

**NOAA Ronald H. Brown**
- On-line GC-MS
- PIT-MS

  - Goldan
  - Warneke

**NOAA WP-3D**
- PTR-MS
- Whole Air Sampler

  - de Gouw
  - Atlas

**Inter-comparisons**
- PTR-MS vs. GC-MS
  - *de Gouw*, JGR 2003
- PTR-MS vs. WAS
  - *de Gouw*, JGR 2006
- PIT-MS vs. GC-MS
  - *Warneke*, ES&T 2005
Determination of Emission Ratios

How do you separate the effects of emissions and chemical removal?

1. Determine “photochemical age”, Δt, from measured ratios between toluene and benzene:

\[ Δt = \frac{1}{[OH](k_{\text{toluene}} - k_{\text{benzene}})} \times \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} \bigg|_{t=0} \right) - \ln \left( \frac{[\text{toluene}]}{[\text{benzene}]} \right) \]

2. Extrapolate hydrocarbon emission ratios to Δt=0

*de Gouw, JGR, 2005, Warneke, 2007*
Determination of Emission Ratios: Ron Brown Data

\[ k_{\text{benzene} + \text{OH}} \approx k_{\text{acetylene} + \text{OH}} \]
\[ k_{\text{ethyl benzene} + \text{OH}} > k_{\text{acetylene} + \text{OH}} \]

⇒ well correlated
⇒ ratio decreases with age
Determination of Emission Ratios: Ron Brown Data

Intercepts give the emission ratios:
Benzene / acetylene = 0.21  (2004: 0.17)
Ethyl benzene / acetylene = 0.11  (2004: 0.09)
Results from the Northeastern U.S.

Good agreement between the 2 years

de Gouw [JGR 2005]; Warneke [JGR 2007]
Results from the Northeastern U.S.

Good agreement between the 2 years
Comparison with other Cities: Los Angeles

We find very similar VOC patterns in different cities in the U.S. and elsewhere, including Mexico City and Beijing [Parrish, IGAC Newsletter, April 2008]

- One exception, Houston, is discussed later in this talk.
Baker [AE 2008] published summary of VOC observations from 28 U.S. cities, including emission ratios. Good agreement with our work.
Comparison with Emission Inventory

Inventory

- Based on EPA NEI-99 Version 3
- Made for photochemical models
- On-road, non-road, area and point sources
- Box around Boston, New York, Los Angeles, Houston and Dallas, etc. and sum up all emissions
- Ratio with CO (point sources excluded)

Acknowledgements: Greg Frost and Stu McKeen
Comparison with Emission Inventory

[Map of the area with the text "Emission inventory for this area" pointing to a specific region on the map.]
Comparison with Emission Inventory

- Small alkanes underestimated in inventory
- Similar to findings of Sive et al. in 2002
Comparison with Emission Inventory

- Inventory underestimates oxygenates
- Oxygenates are low in vehicle exhaust
- What are the primary urban sources?
Comparison with Emission Inventory

Emission inventory for this area

Inventory overestimates toluene by factor of ~2.5
Overestimate of toluene by the WRF-CHEM model consistent with overestimate in the emissions inventory
Not All Cities are Created Equal: Houston, Texas

- Houston has large petrochemical point sources along the Houston Ship Channel.

- Example: research flight from September 25.
ΔVOC/ΔCO is different in the Houston Ship Channel
Not All Cities are Created Equal: Houston, Texas

- $\Delta$VOC/$\Delta$CO is different in the Houston Ship Channel
Not All Cities are Created Equal: Houston, Texas

$\Delta$VOC/$\Delta$CO is different in the Houston Ship Channel
Separating the urban and industrial emissions of most VOCs is done using scatter plots versus CO.

Urban VOC emissions in Dallas and Houston are similar to the rest of the country.
Are Inventories for Urban VOCs Too Complicated?

- NEI-99: different cities have different VOC sources
- Measurements: different cities have remarkably similar VOC composition

*Parrish, IGAC Newsletter, April 2008*
Conclusions

- A method was developed to determine VOC emission ratios from urban areas.
- Emission ratios reproduced between different years and agreed with different studies.
- Emission ratios agreed more poorly with NEI-99 inventory.
- VOC emission ratios are remarkably similar for different cities in the U.S. (and elsewhere).
- Are there primary sources of oxygenates VOCs that are currently not accounted for?
Acknowledgements

Paul Goldan, Bill Kuster, Jessica Gilman  RHB GC-MS
Dan Welsh-Bon  PIT-MS
Elliot Atlas  WAS
Brian Lerner, Eric Williams  RHB CO
John Holloway  WP-3 CO
Greg Frost, Stu McKeen  WRF-CHEM
Andreas Stohl  Flexpart

Fred Fehsenfeld, Gerd Hübler, Jim, Meagher, Tom Ryerson, Michael Trainer