Urban Emissions and Chemistry of Gas-Phase and Particulate Organic Carbon in the Atmosphere

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Outline:
1. Northeastern U.S.:
   Urban emissions of VOCs and organic aerosol Chemistry in urban plumes
2. Not every city is the same:
   Houston, Texas
Our Measurements in North America

2006: TexAQS
WP-3D
Ron Brown

2006: Milagro

2002: ITCT

2002: NEAQS

2004: ICARTT

Legend:
- red: aircraft
- blue: ship
- green diamond: ground
### Organic Carbon Measurements Used

<table>
<thead>
<tr>
<th>WP-3D</th>
<th>Ron Brown</th>
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<td><strong>Gas Phase:</strong></td>
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<td>PTR-MS</td>
<td>GC-MS</td>
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<tr>
<td>de Gouw</td>
<td>Goldan</td>
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<td>WAS</td>
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<td>Atlas</td>
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AMS: organic mass (OM)
OC/EC: organic carbon (OC)
PILS: water-soluble OC (WSOC)

OM > OC > WSOC
PTR-MS Development

GC-PTR-MS

Ion Trap PTR-MS

Inter-comparisons

De Gouw and Warneke (2007)
Urban Emissions of Organic Carbon in New England

Ron Brown data from 2002 and 2004
Urban Emissions of VOCs

Photochemical age from measured benzene/toluene ratios:

\[
\frac{[\text{benzene}]}{[\text{toluene}]} = \frac{[\text{benzene}]}{[\text{toluene}]}_{t=0} \exp\left(-(k_{\text{benzene}} - k_{\text{toluene}})[\text{OH}]\Delta t\right)
\]

GC-MS data: Paul Goldan
Urban Emissions of VOCs

- $k_{\text{benzene}+\text{OH}} \approx k_{\text{acetylene}+\text{OH}}$
- $k_{\text{ethyl benzene}+\text{OH}} > k_{\text{acetylene}+\text{OH}}$

⇒ ratio constant with age
⇒ ratio decreases with age

- Intercepts give the emission ratios
Good agreement between data from 2002 and 2004
Good agreement with tunnel studies except small alkanes
Good agreement with results from Blake group
Agreement with inventories is poor!

[Warneke et al., JGR accepted]
Urban Emissions of Oxygenated VOCs

Harder to determine:
biogenic sources + secondary formation

Urban emissions of oxygenated VOCs >> emissions from automobiles

What are the sources?

Note the logarithmic scale!

Tunnel studies:
- Harley et al., ES&T 1992
- Kristensson et al., AE 2004
Urban Emissions of Organic Aerosol

AMS data from NEAQS 2002 (Ann Middlebrook)

- Minor enhancements close to urban sources

- AMS data from NEAQS 2002 (Ann Middlebrook)
- Minor enhancements close to urban sources
Urban Emissions of Organic Aerosol

**POM emissions from vehicles**

\[ \Delta \text{POC}/\Delta \text{CO} = 2.1 \ \mu g \ m^{-3} \ \text{ppmv}^{-1} \]
(Kirchstetter, AE 1999)

\[ \Delta \text{toluene}/\Delta \text{CO} = 4.2 \ \text{ppbv} \ \text{ppmv}^{-1} \]
(Warneke, JGR in press)

\[ \Delta \text{POM}/\Delta \text{POC} = 1.78 \]
(de Gouw, JGR 2005)

From which follows:

\[ \Delta \text{POM}/\Delta \text{toluene} = 0.9 \ \mu g \ m^{-3} \ \text{ppbv}^{-1} \]

\[ \Delta \text{toluene} = 0.6 \ \text{ppbv} \Rightarrow \Delta \text{POM} = 0.5 \ \mu g \ m^{-3} \]
At time of emission:

- Dominated by vehicle emissions
- Significant contribution from oxygenated VOCs

What happens to this mix of emissions?
Chemistry of Organic Carbon in Urban Plumes

NOAA WP-3D data from 2004
Example of Young Urban Plume: July 20

CO data: John Holloway

CO data: John Holloway

New York City

Mixing ratio (ppbv)

Benzene
Toluene

Mixing ratio (ppbv)

Acetaldehyde
Acetone

CO (ppbv)
Enhancement Ratios

\[ \frac{\Delta \text{VOC}}{\Delta \text{CO}} = \text{Slopes of the scatter plots} \]

This work: describe \( \frac{\Delta \text{VOC}}{\Delta \text{CO}} \) vs. transport time for 59 urban plumes sampled from the WP-3D
Example of Aged Urban Plume: July 22

- Map showing the movement of aged urban plumes from areas like New Brunswick, Maine, and Nova Scotia.
- Graphs showing mixing ratios of various compounds like CO, Benzene, Toluene, Acetone, and Acetaldehyde.

**Graph Details**

- **CO (ppbv)**
  - 100
  - 200
  - 300
  - 400

- **Mixing ratio (pptv)**
  - Benzene
  - Toluene
  - Acetone
  - Acetaldehyde

**Legend**

- Black dots for Benzene
- Red dots for Toluene
- Blue dots for Acetone
- Red dots for Acetaldehyde
FLEXPART = Lagrangian transport model:
BL residence time of 40000 particle back trajectories

[Stohl et al., JGR 2003]
Air Mass Origin: FLEXPART Model

CO source contribution = BL residence time × emissions inventory

Location of the NOAA WP-3D
Source region is centered around New York City

[Stohl et al., JGR 2003]
All plumes observed at low altitudes (200-2000 m)
Evolution of Aromatic VOCs

- Toluene more reactive than benzene
- Toluene high near New York and Boston
- Benzene more widespread
Evolution of Oxygenated VOCs

- Acetone produced after 2-3 days
- Acetaldehyde very reactive, yet fairly widespread
  ⇒ efficient secondary production
Evolution of Oxygenated VOCs in Urban Air

Reasons for the scatter:
- Day-night differences
- Emission ratios vary
- Biogenic sources
- Wet deposition

ICARTT 2004  NEAQS 2002  Direct emissions
MCM Modeling of Urban Plumes
Leeds Master Chemical Mechanism

Input data:

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(ΔVOC/ACO) (ppbv ppmv⁻¹)
MCM Modeling of Urban Plumes

- MCM has diurnal OH plus nighttime chemistry ⇒ irregular curves
- Trends reasonably described for methanol, acetaldehyde and acetone
- MCM produces hardly any acetic acid

Thanks to: Roberto Sommariva
SOA Growth in NYC plume

WP-3D data from ICARTT

$\Delta WSO/C/\Delta CO:$

8.9 $\mu g \cdot m^{-3}$ ppmv$^{-1}$ (July 20)

23 $\mu g \cdot m^{-3}$ ppmv$^{-1}$ (July 21)

N.B. $\Delta OC/\Delta CO$: 2.1 $\mu g \cdot m^{-3}$ ppmv$^{-1}$ (tunnel study)
SOA Growth in Urban Plumes

WSOC data: Weber et al.
Graph: Chuck Brock

- Transport age from Flexpart, chemical age from VOC ratios
- WSOC increase ≠ formation calculated from known precursors
Secondary Formation from Measured VOCs

- Sums up to \(\sim 3.7 \, \mu g \, m^{-3} \, ppmv^{-1}\)
- Measurements show >30 \(\mu g \, m^{-3} \, ppmv^{-1}\)
Why is the SOA Formation Much Higher Than Expected?

1. **Formation from higher-mass, lesser-volatile VOCs?**
   - Only few measurements. Enough mass available?

2. **Formation more efficient than observed in smog chambers?**
   - New studies give higher yields, but not 10x higher
   - 20% yield for all VOCs explains data

3. **Formation from biogenic VOCs more efficient in urban air?**
   - Would explain correlation with pollutants and C14 data
   - But similar observations in cities with low biogenics
     - Mexico City (Volkamer, *GRL* 2006)
     - Tokyo (Takegawa, *GRL* 2006)
   - Biogenic precursors ≠ naturally occurring POM

Probably a combination of all 3!
After 2 days of processing:

- The composition has changed
- SOA >> POA
- The pie has shrunk:
  oxidation into non-measured species & deposition
Not Every City is the Same: Houston, Texas

NOAA WP-3D data from 2006

Photo: Dan Welsh-Bon
VOCs from Industrial Sources

TexAQS 2006: What are the emissions and effects of VOCs from petrochemical sources?

Example: Flight from September 25
VOCs from Industrial Sources

- \( \Delta \text{benzene}/\Delta \text{CO} \) is different in the Houston Ship Channel
VOCs from Industrial Sources

- Δbenzene/ΔCO is different in the Houston Ship Channel
VOCs from Industrial Sources

- $\Delta$benzene/$\Delta$CO is different in the Houston Ship Channel
Importance of Alkenes in Houston

- Petrochemical industry is a large source of alkenes.
- Of all VOCs, alkenes dominate the OH reactivity.

Ryerson et al., JGR 2003

- Petrochemical industry is a large source of alkenes.
- Of all VOCs, alkenes dominate the OH reactivity.
Laser Photo-Acoustic Spectroscopy (LPAS)  
Measurements of Ethene

**Principle of Operation**
1. CO$_2$ laser excites ethene
2. Ethene is de-excited in collisions
3. Heating leads to pressure gradient (=sound)
4. Signal measured with a microphone

**In Practice**
1. Laser intensity is modulated at ~1600 Hz
2. That frequency resonates in acoustic cavity
3. Acoustic signal detected with lock-in amplifier

Built by Sensor Sense in the Netherlands

**Thanks to:**  
Sacco te Lintel Hekkert  
Sensor Sense  
Frans Harren  
Univ. Nijmegen
Laser Photo-Acoustic Spectroscopy (LPAS)
PTRMS-LPAS Instrument Onboard the WP-3D
Comparison Between LPAS and Whole Air Sampler (WAS)

- **Graph 1:**
  - Y-axis: Ethene (ppbv)
  - X-axis: Time (4:00 PM to 7:00 PM on 10/13/06 UTC)
  - Data points for LPAS 5-sec, LPAS 20-sec, and WAS

- **Graph 2:**
  - Scatter plot of LPAS vs. WAS (ppbv)
  - Line of best fit:
    - Intercept: 0.05 ppbv
    - Slope: 0.85
    - $r^2$: 0.765
  - 1:1 line

- **Graph 3:**
  - Histogram of residuals (ppbv)
  - Gaussian distribution
  - $1\sigma$: 0.34 ppbv
Plumes of Ethene from the Houston Ship Channel

- Locate and quantify ethene sources
- Follow ozone chemistry in the plumes
Ethene in 2006 versus 2000

- Ethene was lower in 2006 compared with 2000
- Formaldehyde (formed from ethene) also lower
- Emissions lower or meteorology different?
Ethene in 2006 versus 2000

2006:
- higher wind speed
- more dilution of emissions
- lower temperature
- lower fugitive losses?

Reduction in emissions hard to prove from WP-3D data only
Summary

1. Quantified urban VOC and OA emissions
   - VOC emission inventories need improvement
   - Emission sources of oxygenated VOCs are unknown

2. Studied chemistry in urban plumes
   - Formation of carbonyls explained by MCM
   - Formation of organic acids and SOA >> expected

3. Characterized industrial emissions in Houston, TX
   - Opportunity for studying VOC and SOA formation in plumes with different VOC fingerprint
## Acknowledgments

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<thead>
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<th>Technique</th>
<th>Authors</th>
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<td>Carsten Warneke, Lori Delnegro</td>
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<td>Andreas Stohl</td>
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<td>Eric Williams, Brian Lerner</td>
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Chuck Brock, Owen Cooper, Fred Fehsenfeld, Jessica Gilman, Gerd Huebler, Shuji Kato, Jim Meagher, David Parrish, Tom Ryerson, Michael Trainer, Patrick Veres, Dan Welsh-Bon