Emissions and Photochemistry of Oxygenated VOCs in the Outflow from Urban Centers in the Northeastern U.S.

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Per October 1st 2005
This talk: focus on evolution of VOCs in urban plumes
VOC Measurements

PTR-MS = proton-transfer-reaction mass spectrometry

14 VOC species

1 Data point every 17 s

Detection limit ~20-100 pptv

Inter-compared during ICARTT with WAS & NASA DC-8

[de Gouw et al., JGR 2003]
Example of Young Urban Plume: July 20
Enhancement Ratios

= \frac{\Delta \text{VOC}}{\Delta \text{CO}}

= 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 P3
Example of Aged Urban Plume: July 22

- Benzene
- Toluene
- CO
- Acetone
- Acetaldehyde
Air Mass Origin: FLEXPART Model

FLEXPART = Lagrangian transport model:
column residence time of 40000 particle back trajectories

Location of the
NOAA WP-3

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

Footprint = BL residence time of particle back trajectories

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Footprint = BL residence time of particle back trajectories [Stohl et al., JGR 2003]
Air Mass Origin: FLEXPART Model

CO source contribution = footprint × emissions inventory

Source region is centered around New York City

[Stohl et al., JGR 2003]
Locations of the Urban Plumes

- All plumes observed at low altitudes (200-2000 m)

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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 production
Evolution of Oxygenated VOCs in Urban Air

- Average description of data from NEAQS 2002
- Transport time estimated from hydrocarbon ratios and an average $[\text{OH}]$

[de Gouw et al., JGR 2005]

Does this description hold up for the urban plumes observed in this work?
Evolution of Oxygenated VOCs in Urban Air

- Benzene
- Toluene
- Acetone
- Acetaldehyde

- ICARTT 2004
- NEAQS 2002
- Direct emissions

Transport time (days)
Evolution of Oxygenated VOCs in Urban Air

- Methanol
- Acetic Acid
- Methyl Ethyl Ketone

Transport time (days)

Data sources:
- ICARTT 2004
- NEAQS 2002
- Direct emissions
Reasons for the Scatter in the Data
- Transport time ≠ photochemical age (OH is not constant!)
- In-homogeneity of emission ratios
- Biogenic sources of oxygenated VOCs

Further Complicating Factors
- Ocean uptake of oxygenated VOCs?

Sharp decreases of acetone below 400 m
Urban emissions of oxygenated VOCs are much larger than emissions from automobiles.

What are the sources?

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What are the sources?
Conclusions

- Described the evolution of VOCs in urban plumes from the northeastern U.S.

- Empirical equations from NEAQS 2002 describe significant part of the variability observed in 2004

- Urban emissions of oxygenated VOCs are large, but do not come from automobiles

- Observed evidence for an ocean sink of oxygenated VOCs
Acknowledgements:

John Holloway  
Andreas Stohl  
Andy Neuman  
Fred Fehsenfeld, Gerd Hübler, Tom Ryerson, Donna Sueper, Michael Trainer  
Plus everybody else who collaborated!