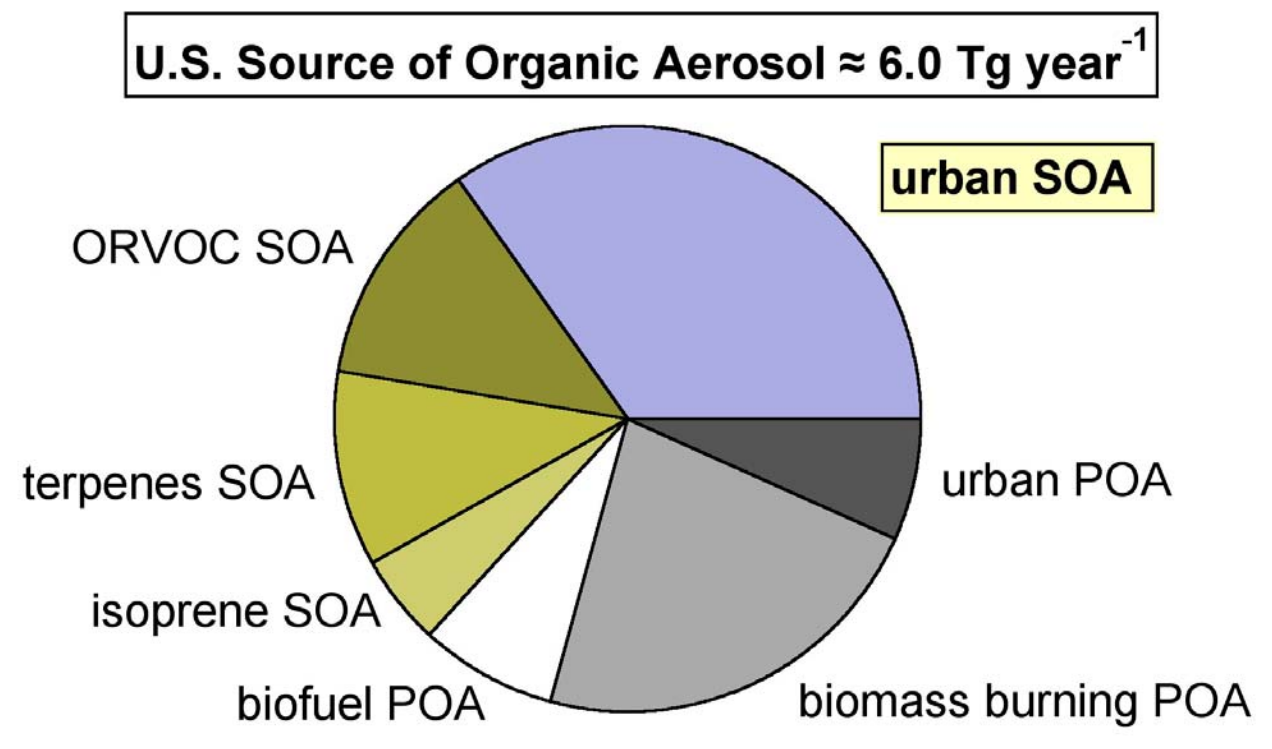
Secondary Organic Aerosol (SOA) in Polluted Atmospheres: Large Underestimates by Current Models

Joost de Gouw



Outline:

Urban SOA is underestimated
Potential explanations
Future directions: organic acids

Particulate Matter (PM) and Air Quality

1. Health impacts
2. Impairment of visibility

Why study chemical composition?

- Impacts visibility and maybe health
- Source attribution

  Direct emissions versus secondary formation

  What are the precursors?

What are the goals of the research?

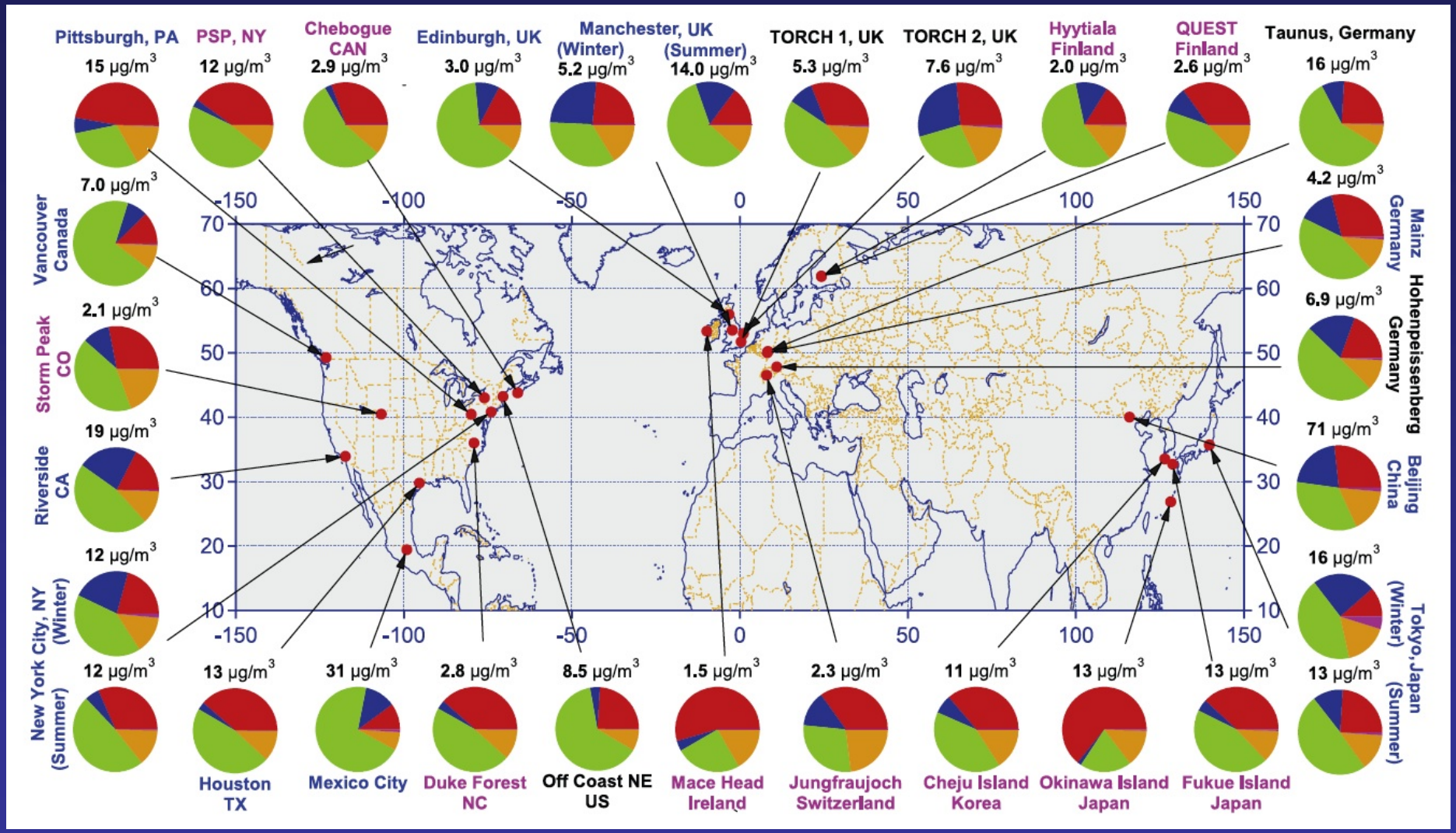
- Provide input for improved PM models / forecasts

  Emissions verification of primary PM

  Formation mechanisms of secondary PM

- Predict the effects of changes in (precursor) emissions

Aerosol Chemical Composition [*Zhang et al.*, GRL 2007]



Sulfate
Nitrate
Organics
Ammonium

A large fraction of aerosol consists of organic material

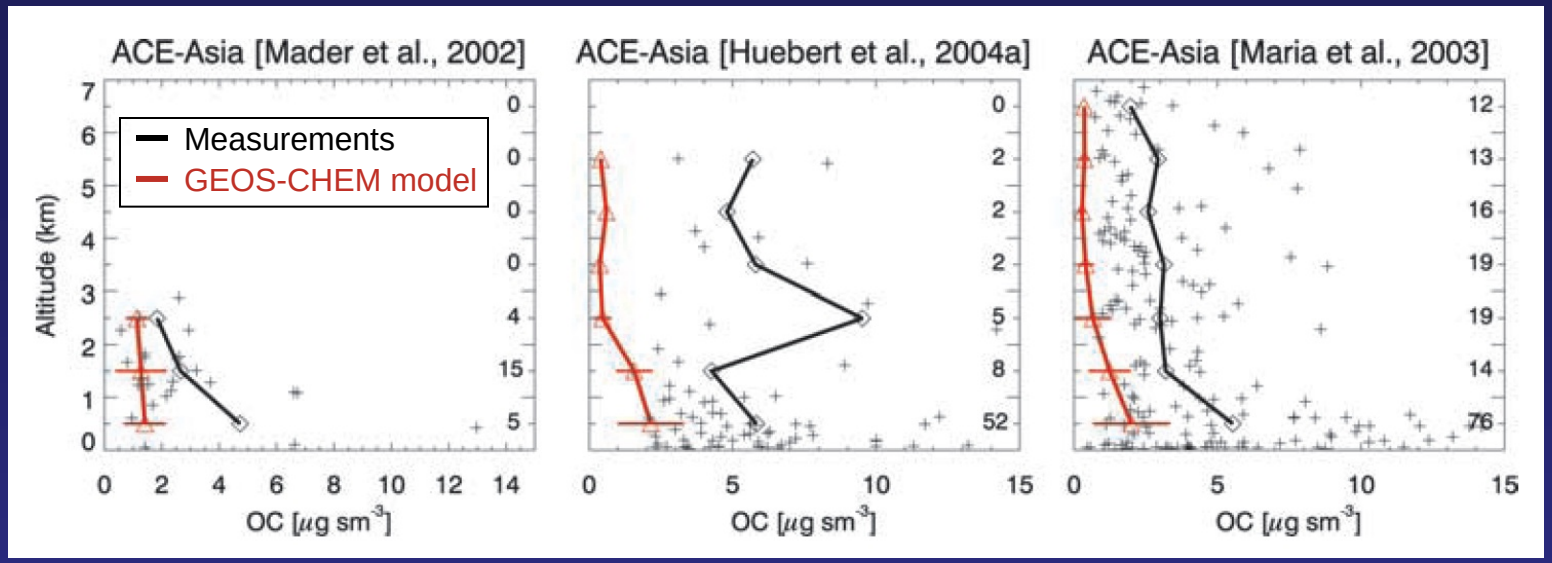
Bottom-Up Estimates of U.S. Organic Aerosol Sources

Direct or Primary Emissions:		
Biomass burning	1.7 Tg y^{-1}	2.1 Tg y^{-1}
Fossil fuel combustion	0.4 Tg y^{-1}	
Secondary Formation from:		
Monoterpenes	0.6 Tg y^{-1}	1.7 Tg y^{-1}
Other Reactive VOCs (sesquiterpenes, etc.)	0.8 Tg y^{-1}	
Isoprene	0.3 Tg y^{-1}	
Aromatics	small	

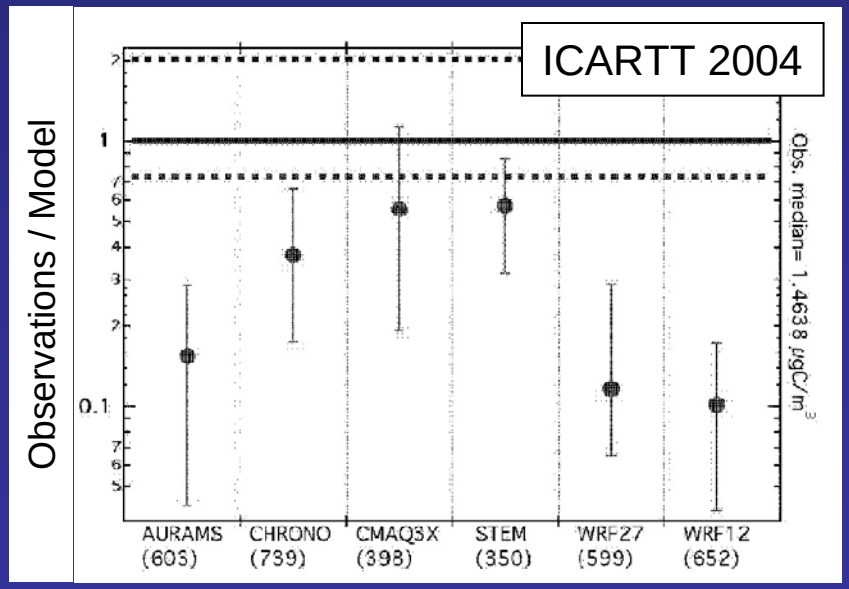
Bond [JGR 2004]; *Kanakidou* [ACP 2005]; *Henze & Seinfeld* [GRL 2006]

Outside fire episodes, biogenic SOA dominates
Urban sources of OA are minor and mostly primary

Model Performance for Organic Aerosol



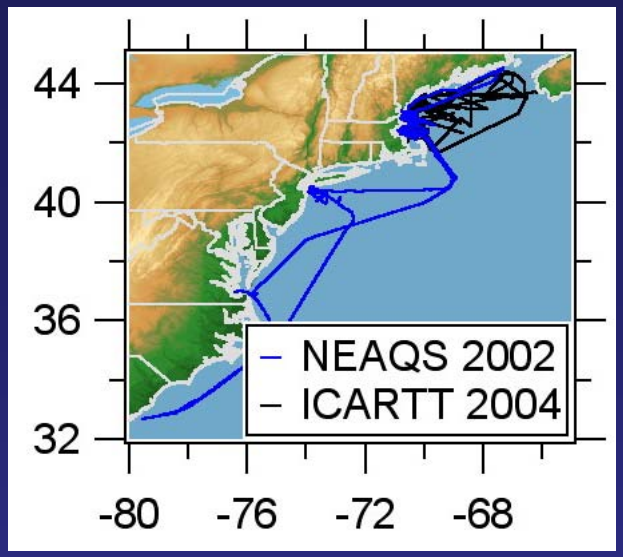
Heald et al. [GRL 2005]



McKeen et al. [JGR 2007]

Models typically underestimate organic aerosol by a factor 2-10

NOAA Field Studies in the Northeastern U.S.

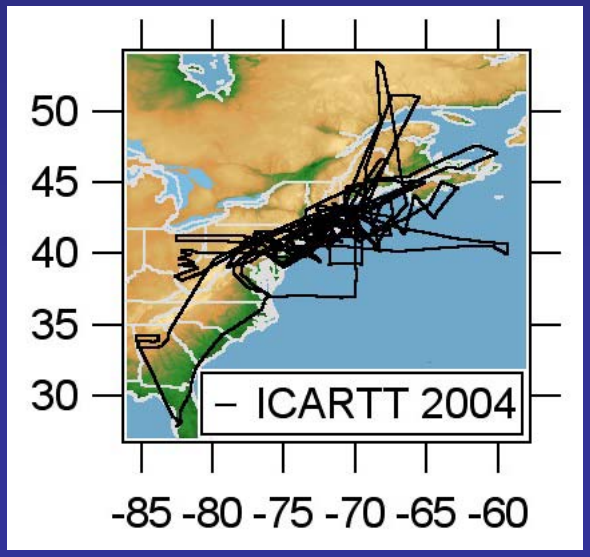


Ronald H. Brown:
NEAQS, Jul-Aug `02
ICARTT, Jul-Aug `04

AMS *Middlebrook, Bates, Quinn, Onasch*
WSOC *Bates, Quinn*
OC/EC *Bates, Quinn*

NOAA WP-3D:
ICARTT, Jul-Aug `04

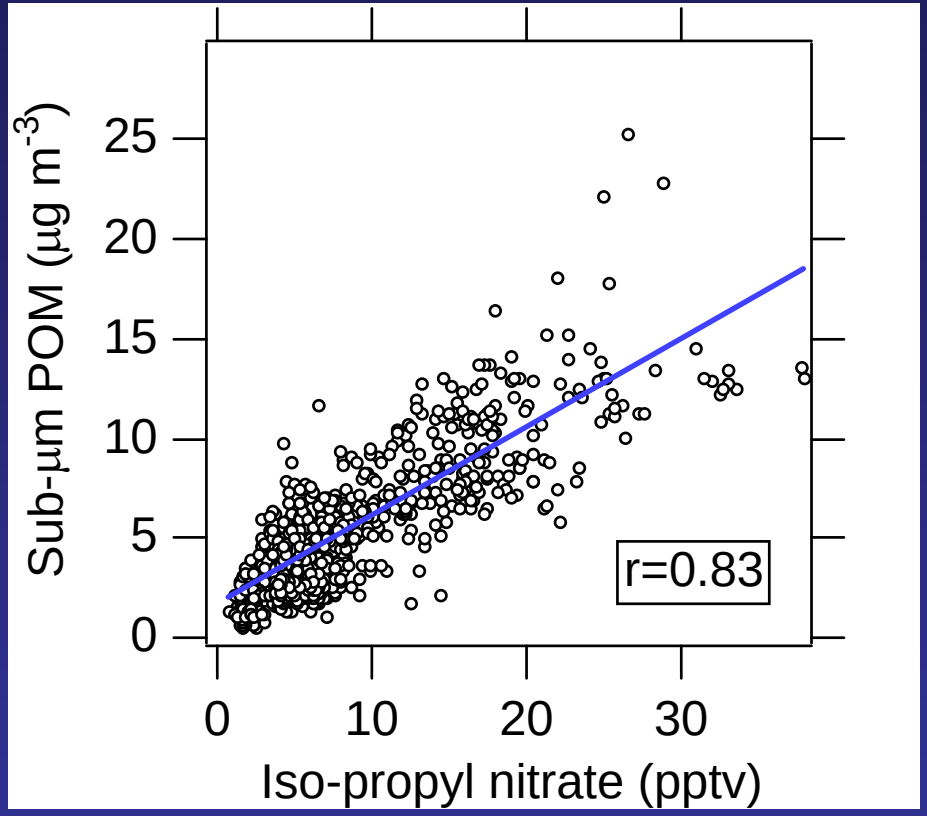
AMS *Middlebrook*
WSOC *Weber*



Extensive data set of organic aerosol and its precursors

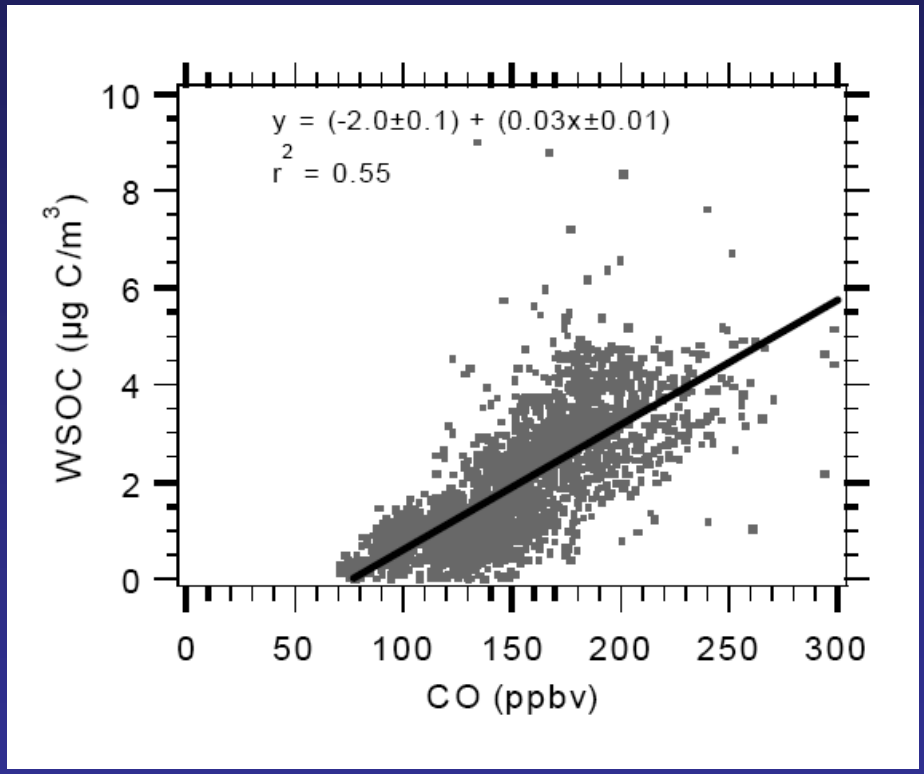
Correlation Between Organic Aerosol and Urban Tracers

NEAQS 2002 (Ron Brown):



de Gouw et al. [JGR 2005]

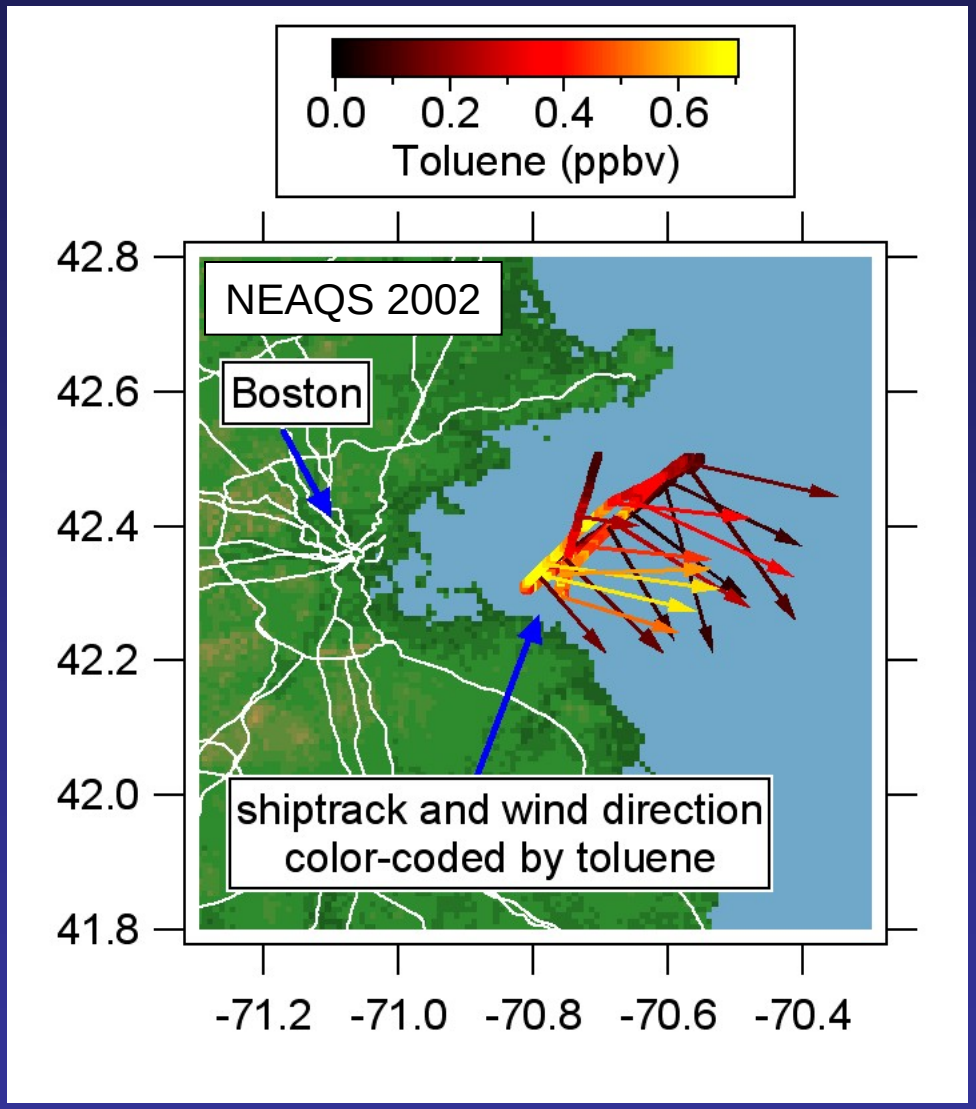
ICARTT 2004 (WP-3D):

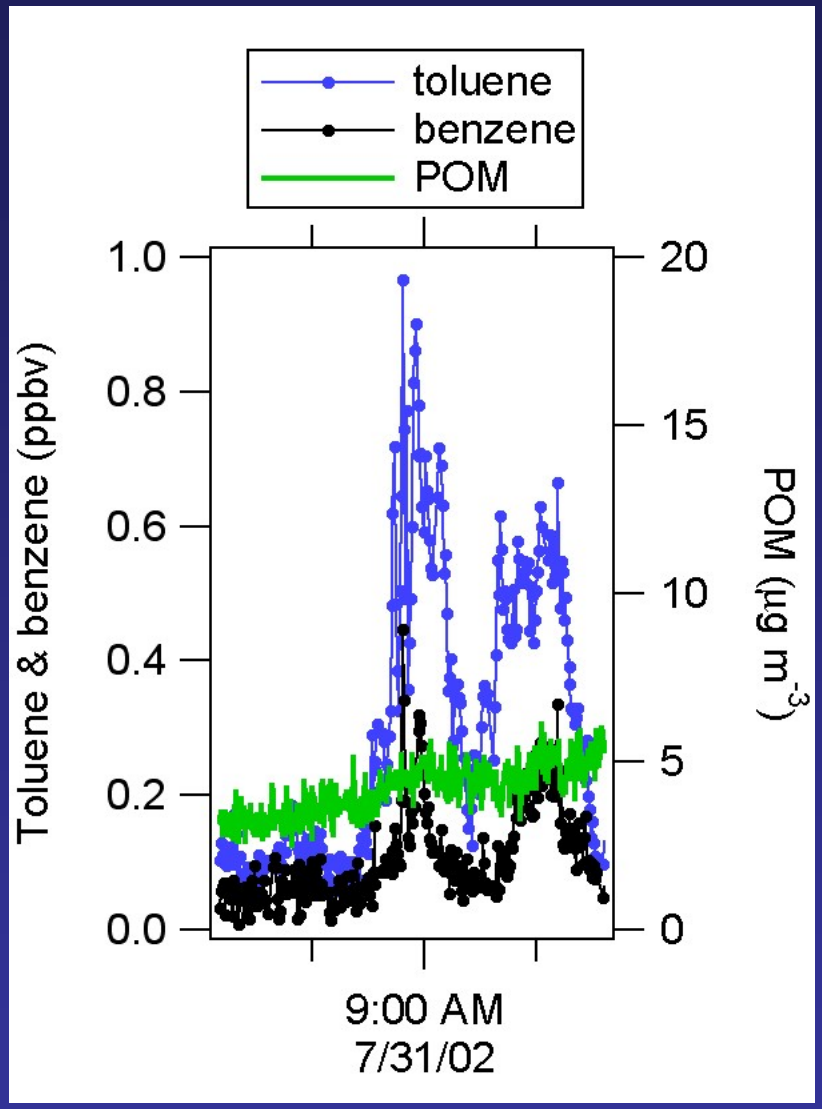


BB plumes removed using CH_3CN
Sullivan et al. [JGR 2006]

Organic aerosol in the northeastern U.S. correlates well with urban tracers (alkyl nitrates, CO)

Direct, Urban Emissions of Organic Aerosol

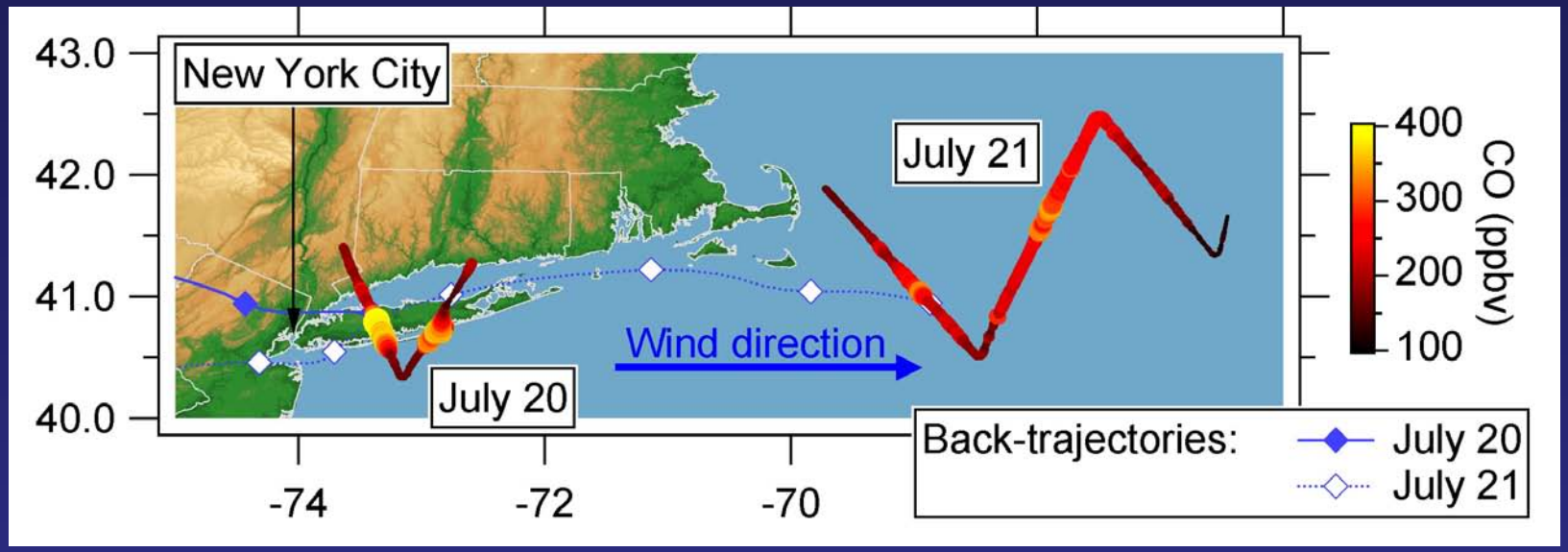




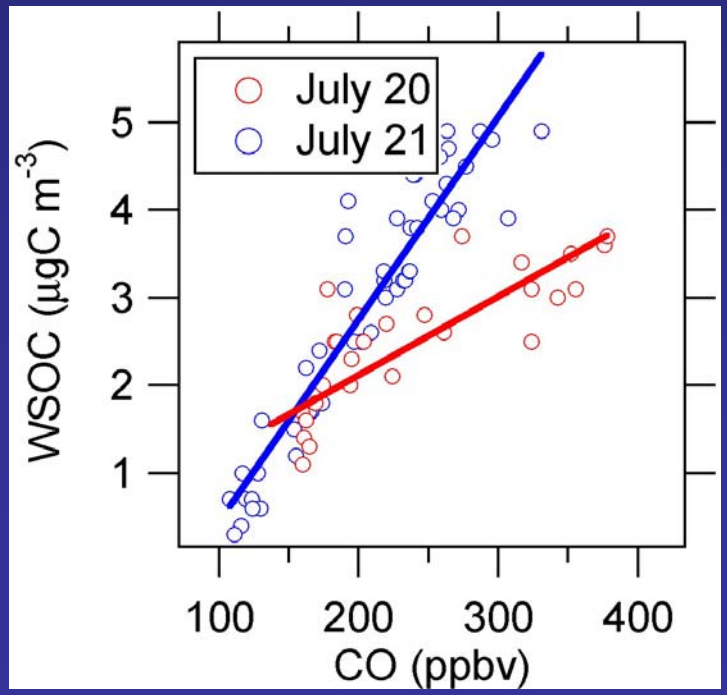
de Gouw et al. [JGR 2005]

- No large enhancement in non-processed urban plumes
- VOC-aerosol composition similar to tunnel studies

Airborne Study of SOA Formation During ICARTT



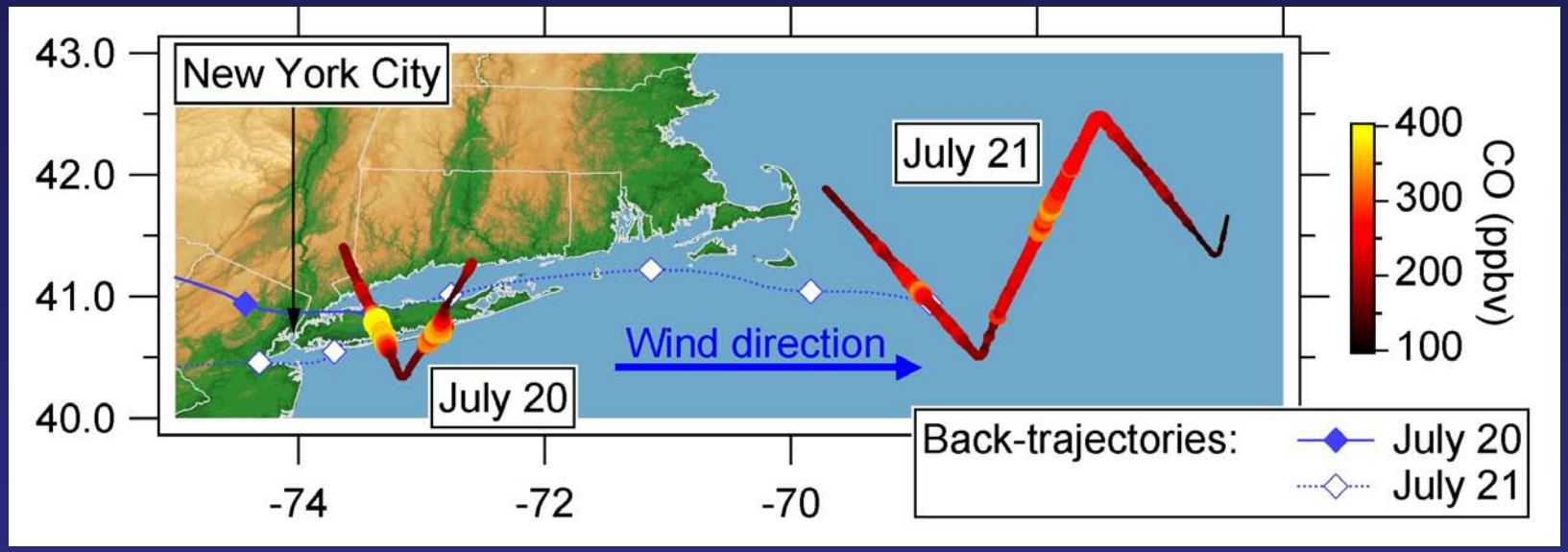
de Gouw et al. [JGR accepted]



- WSOC is higher on 2nd day (July 21)
- Observed increase:

  $9 \rightarrow 23$ µgC m^{-3} $ppmv^{-1}$

Airborne Study of SOA Formation During ICARTT



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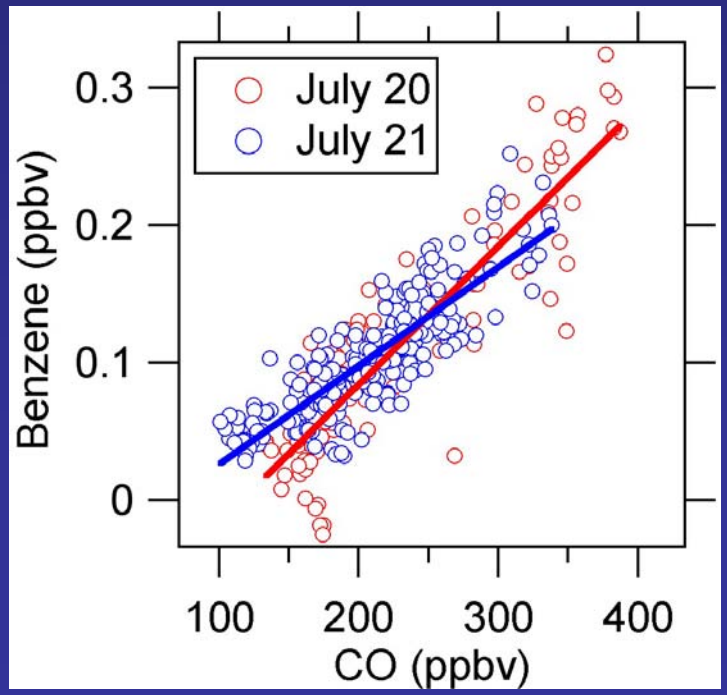
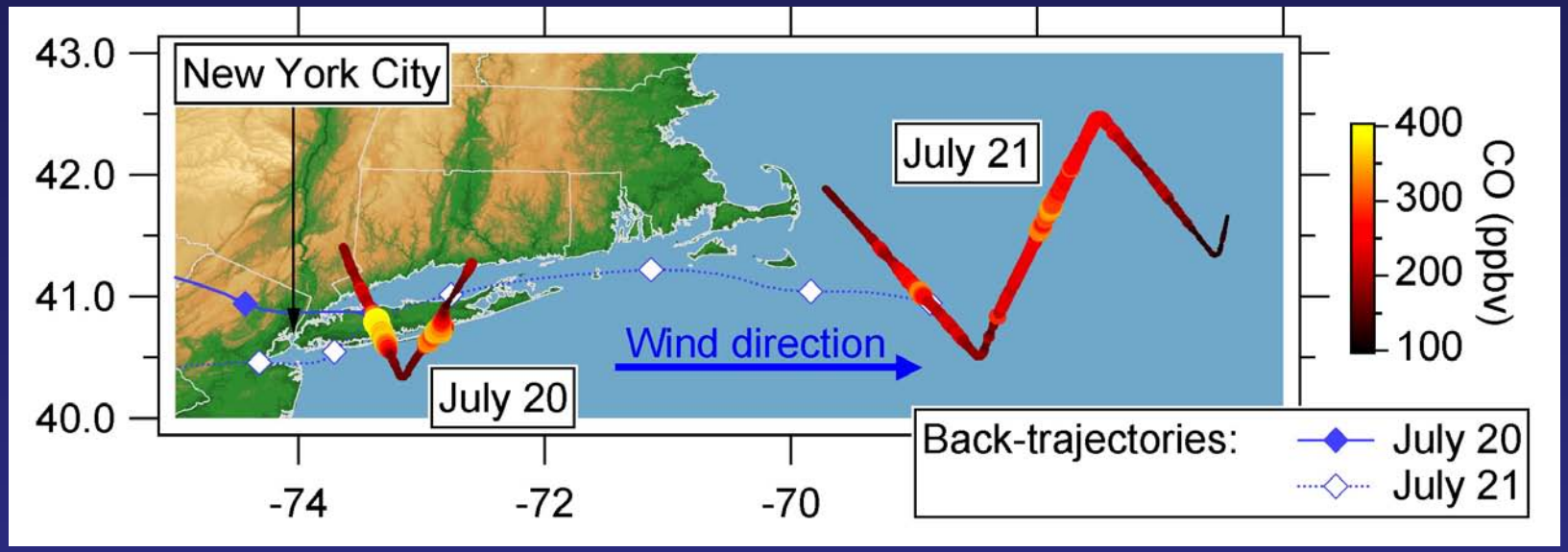
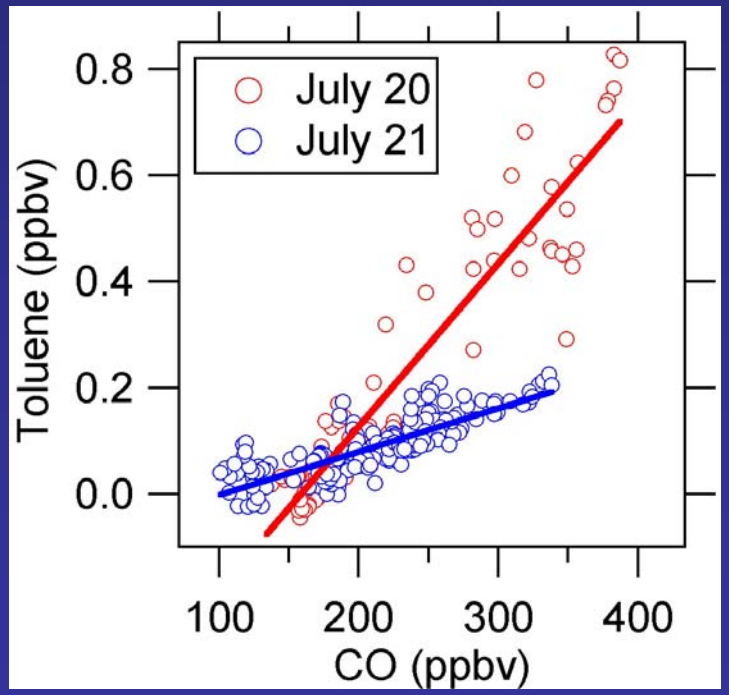


- Benzene is relatively inert
- Similar ratio observed on both days (July 20 and 21)

Airborne Study of SOA Formation During ICARTT



de Gouw et al. [JGR accepted]



- Toluene is more reactive
- Much smaller ratio observed on 2nd day (July 21)

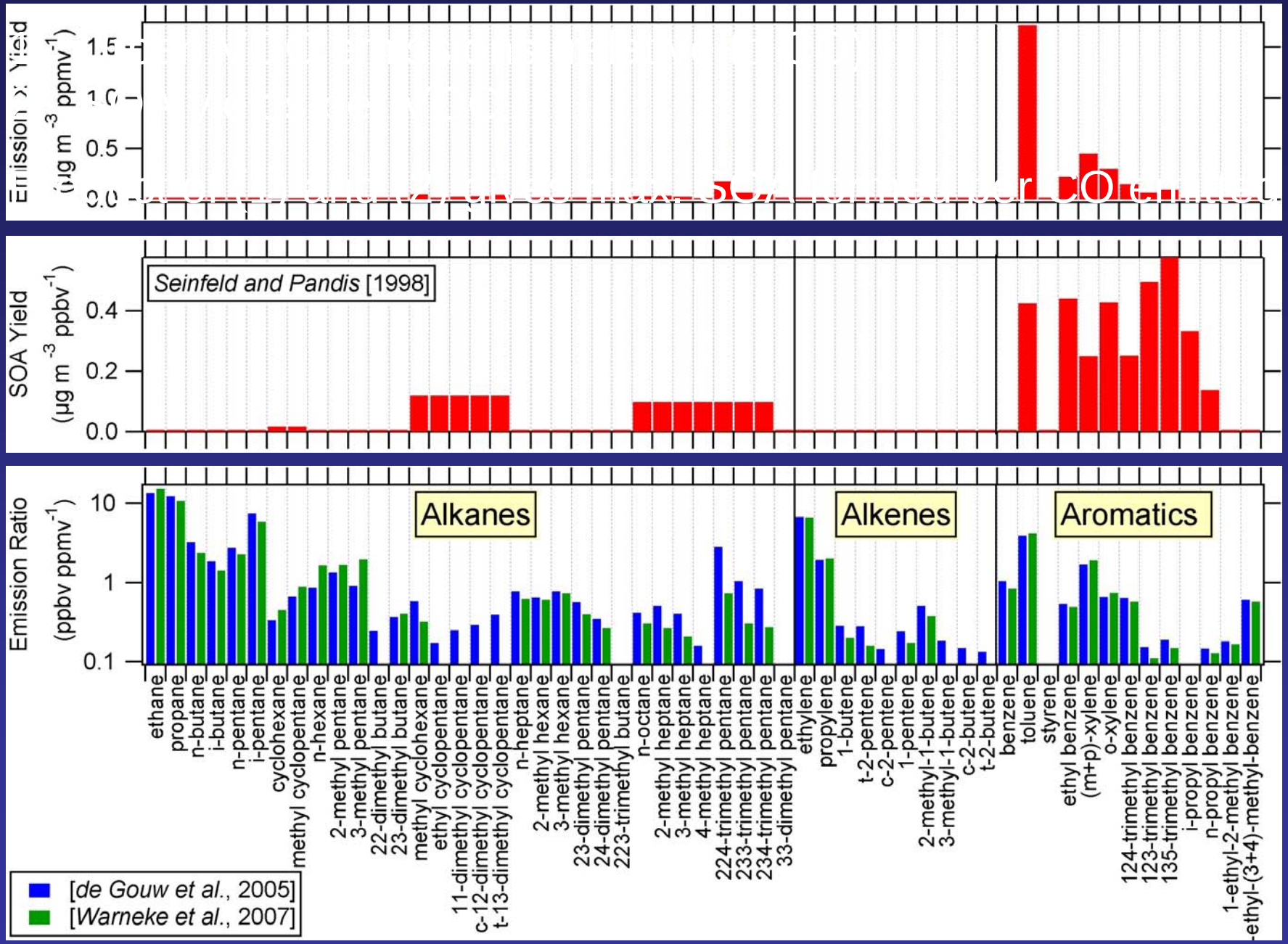
VOCs removed as expected.
Organic aerosol increases strongly in urban plumes

How Much SOA is Expected in Urban Plumes?

1. Urban VOC emissions (relative to CO)
2. SOA yields per VOC

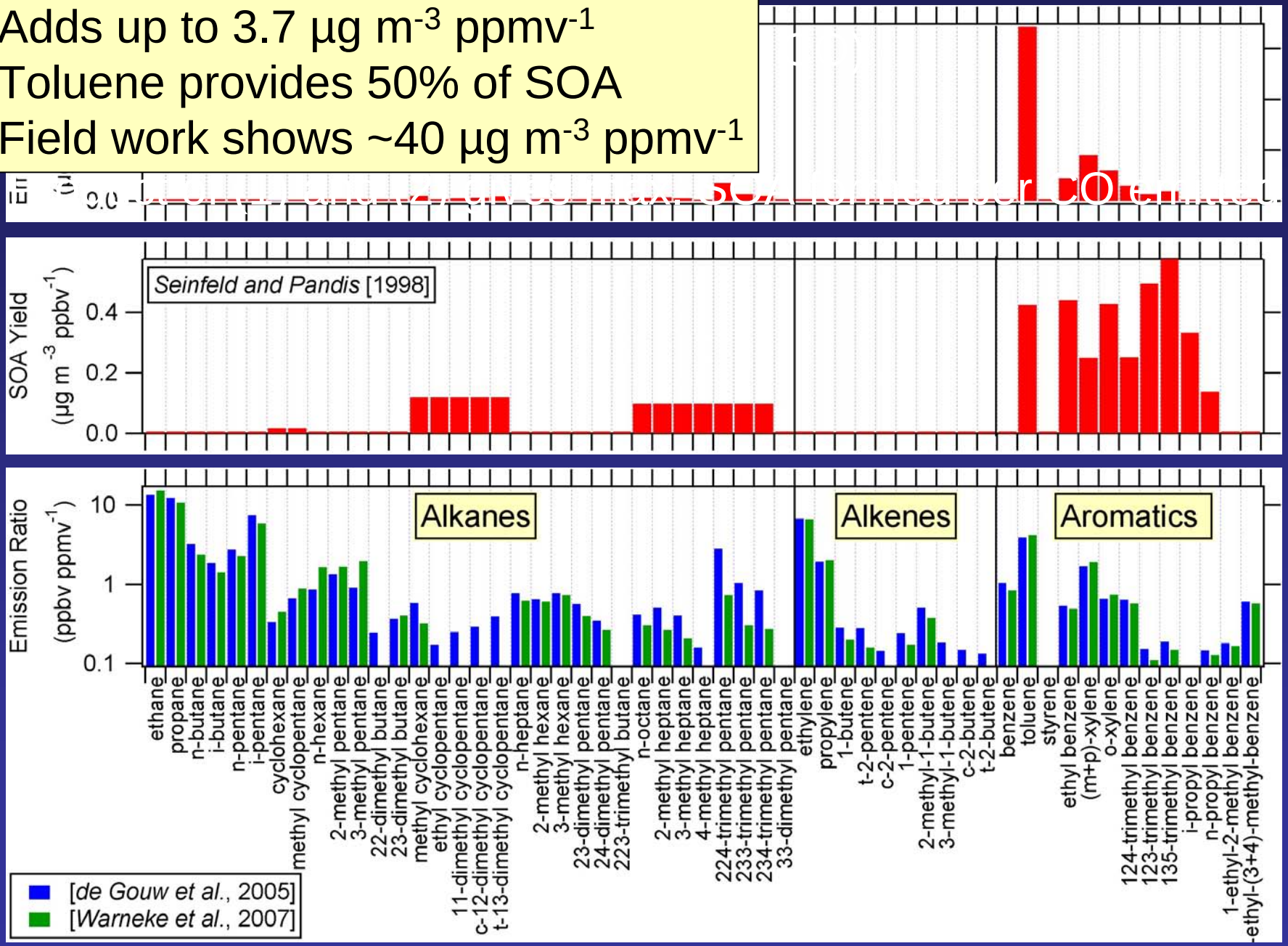
Product of (1) and (2) gives max. SOA formed per CO emitted

How Much SOA is Expected in Urban Plumes?

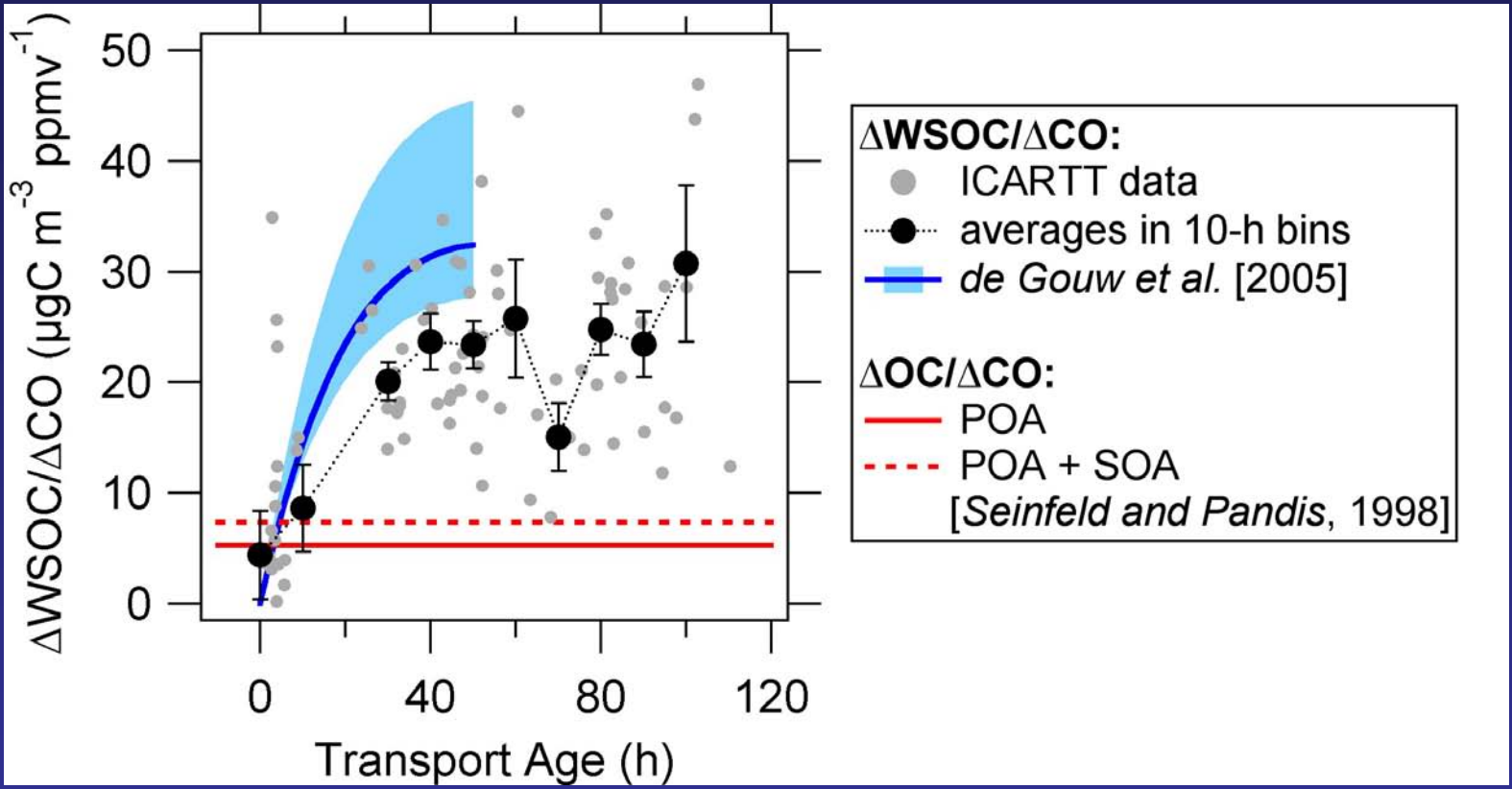


How Much SOA is Expected in Urban Plumes?

Adds up to 3.7 μg m^{-3} $ppmv^{-1}$
Toluene provides 50% of SOA
Field work shows ~40 μg m^{-3} $ppmv^{-1}$



Growth of WSOC in Urban Plumes During ICARTT



de Gouw et al. [JGR accepted]

- Large increase of WSOC in urban plumes, consistent between NEAQS 2002 and ICARTT
- SOA > POA after only few hours of processing

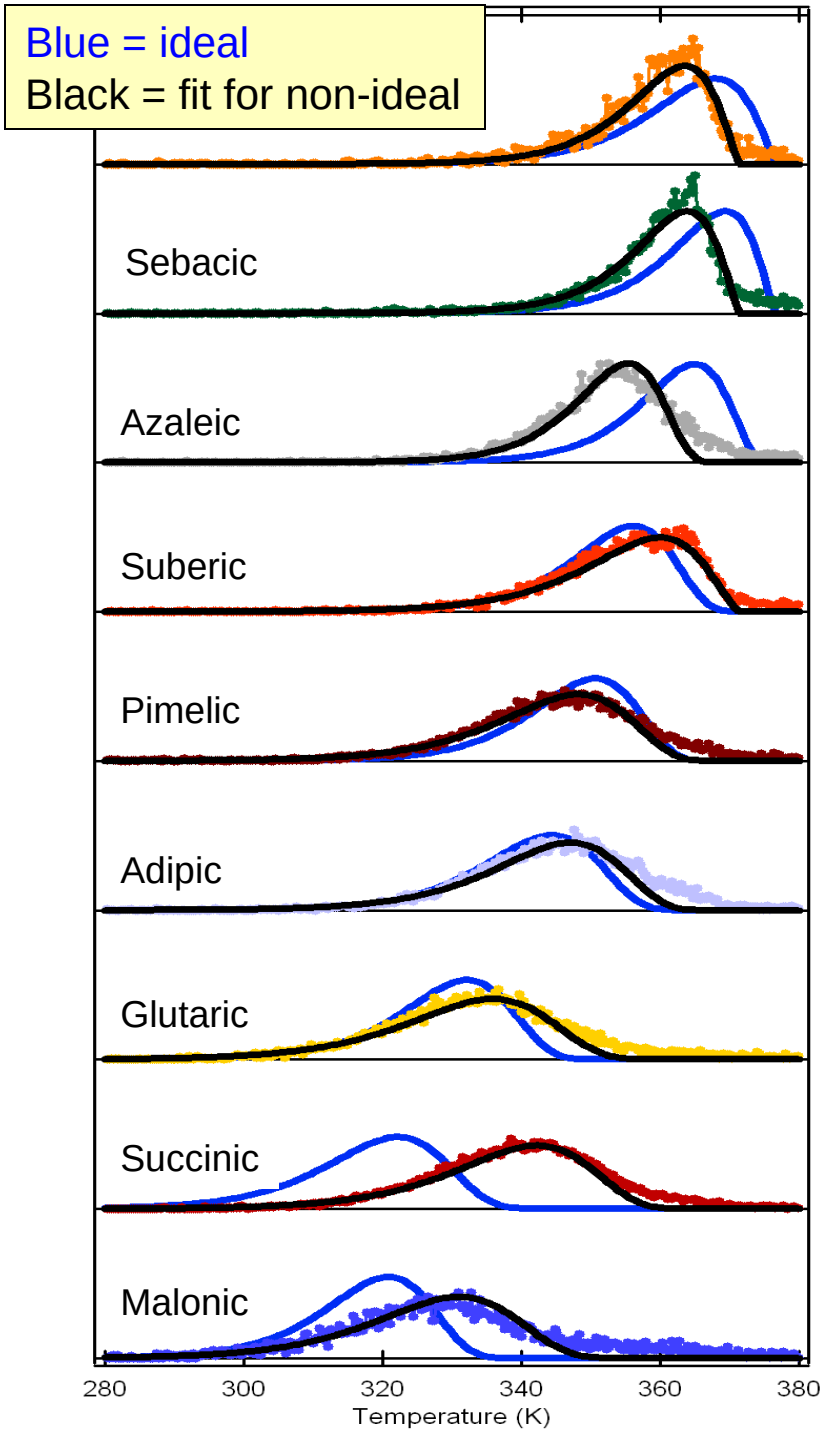
Why is Urban SOA Higher than Expected?

Also reported by: *Volkamer et al.* [2006], *Johnson et al.* [2006], *Takegawa et al.* [2006], *Kleinman et al.* [2007]

1. SOA yields are too low
   - *Ng et al.* [2007]: aromatic yields factor 3 higher in low-NOx
   - *Cappa et al.* [submitted]: VOC vapor pressures of mixtures
   - *and others…*

2. SOA is formed from other VOCs
   - *Lewis et al.* [2000]: 2-D GC shows many more species
   - *Robinson et al.* [2007]: semi-volatiles in Diesel exhaust

3. SOA from biogenic VOCs is more efficient in urban plumes
   - C-14 analyses show high fraction of modern carbon
   - Not easily seen in NOAA data from NE U.S.



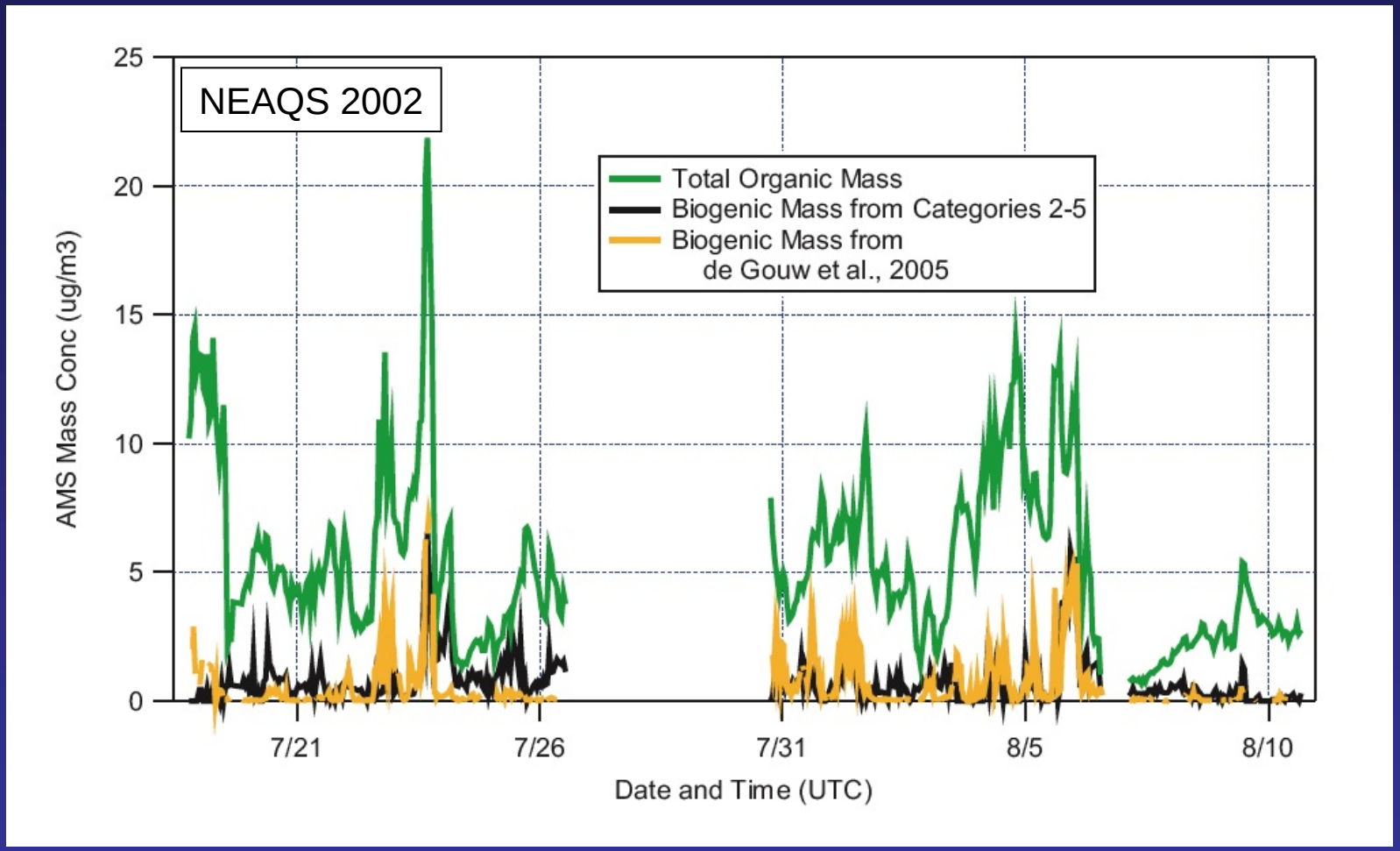
Vapor Pressures of Mixtures of Acids

- Measured evaporation rates as a function of temperature
- Pure compounds and mixtures
- Deduced vapor pressures

1. The vapor pressures are different than those above pure substances
2. Mixtures of >4 acids act like a liquid although individual components are solids!
3. Larger aerosol partitioning for lighter acids: explanation for larger SOA?

Cappa et al. [submitted]

Importance of Biogenic SOA



Marcolli et al. [ACP 2006]

Biogenic SOA estimated from:

1. Correlation with biogenic VOCs
2. Mass spectra from the AMS

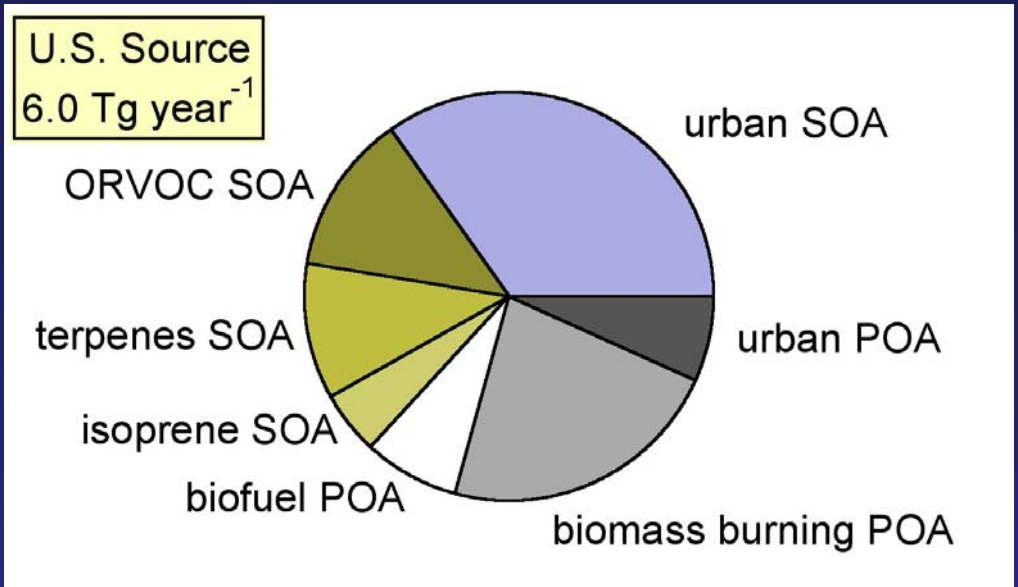
Both methods agree: biogenic SOA was 12-17% of the total OA

Importance of Urban SOA

Multiple field studies:
$\Delta SOA/\Delta CO \approx 40\ \mu g\ m^{-3}\ ppmv^{-1}$

U.S. fossil-fuel CO (EDGAR) = 63 Tg y^{-1}

$\Rightarrow$ Urban SOA in the U.S. = 2.0 Tg y^{-1}



de Gouw et al. [JGR accepted]
With estimates from: *Bond et al.* [2004], *Kanakidou et al.* [2005], *Henze and Seinfeld* [2006]

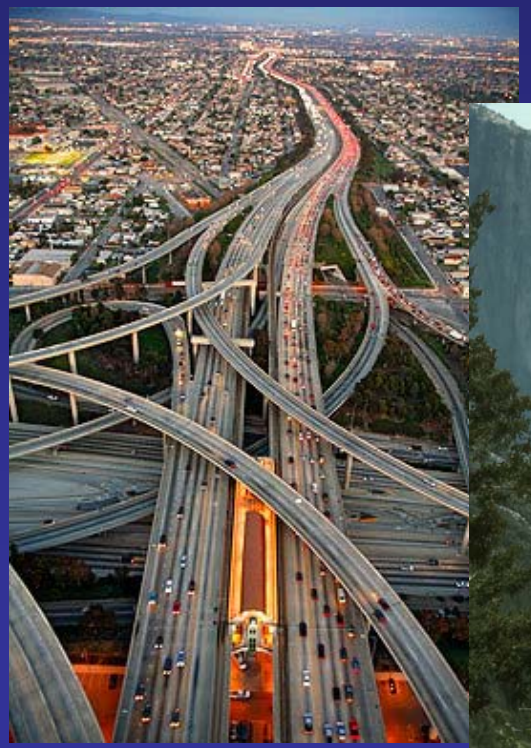
Urban SOA is ~35% of the total OA source in the U.S.

Fraction is higher in polluted regions (NEAQS: 57%)

Future Directions

Field Work:

- California 2010: air quality-climate interactions
- Contrast between LA and the Sierra Nevada



Organic Acid Measurements:

- Large fraction of SOA consists of organic acids
- Formation of gas-phase organic acids is also poorly understood
- Aerosol measurements using Particle-In-Liquid Sampling (PILS)
- Gas-phase measurements using chemical-ionization mass spectrometry (CIMS) [*Veres et al.*, IJMS submitted]

Summary and Implications

- Urban SOA is a major source of aerosol in most metropolitan (and many rural) areas in the U.S.
- The formation mechanism is poorly understood and not accurately represented in air quality models
- The effects of changes in precursor emissions, due to new policies and/or climate change, cannot be predicted with any confidence

Acknowledgements

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