

Determination of Urban VOC Emission Ratios and Comparison with Inventories

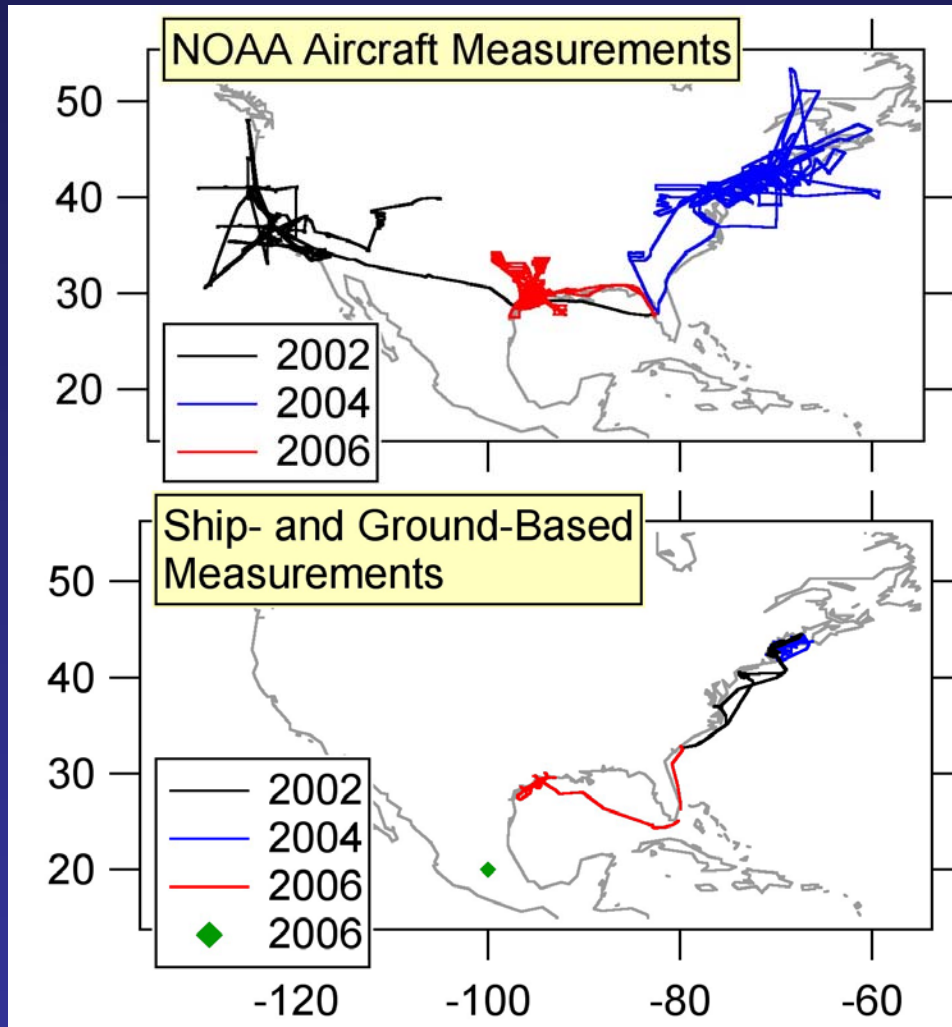
Carsten Warneke and Joost de Gouw

*NOAA Earth System Research Laboratory
and
CIRES, University of Colorado, Boulder, Colorado*

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

PTR-MS vs. WAS

PIT-MS vs. GC-MS

de Gouw, JGR 2003

de Gouw, JGR 2006

Warneke, ES&T 2005

Determination of Emission Ratios

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

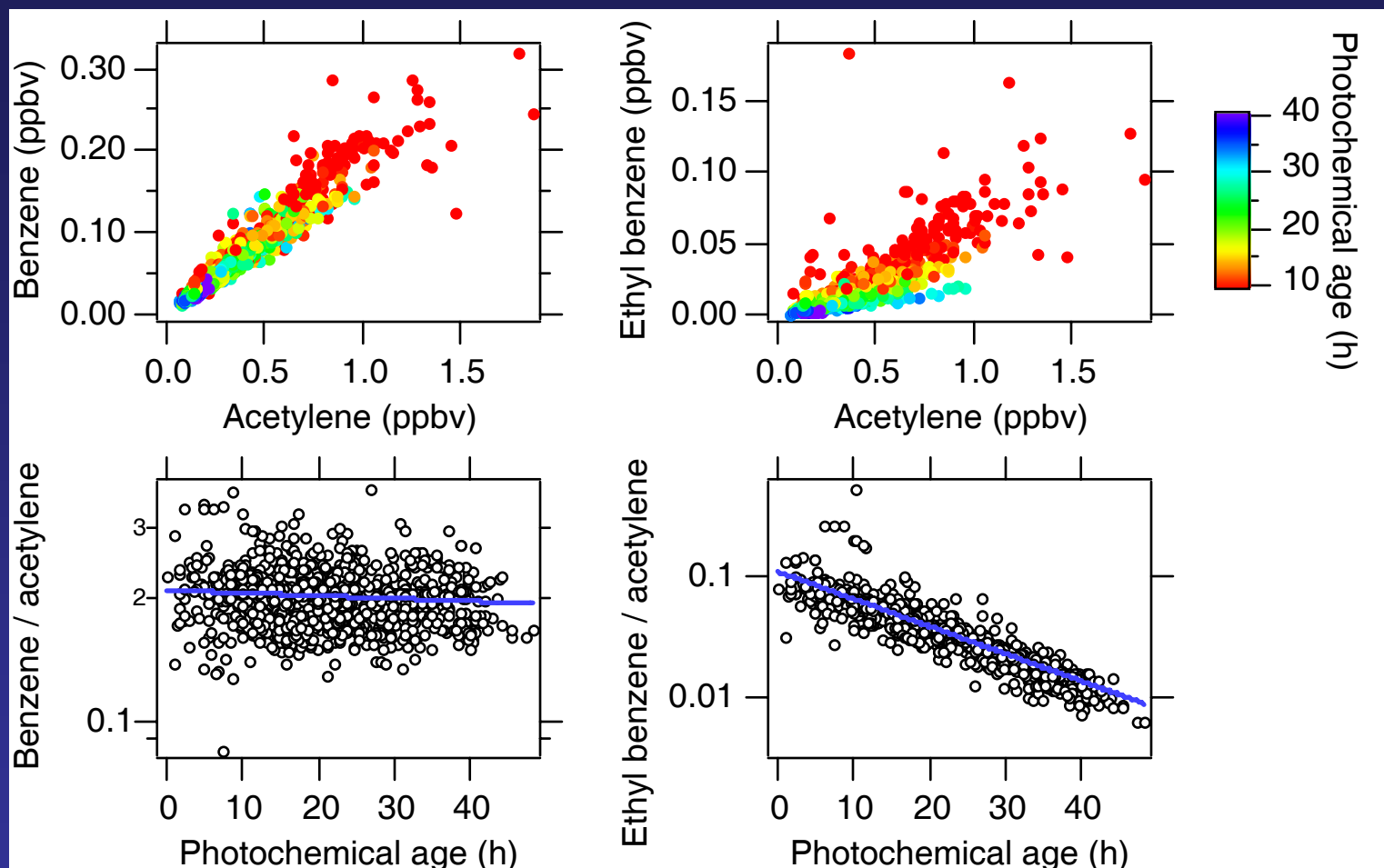
1. Determine “photochemical age”, Δt , from measured ratios between toluene and benzene:

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

2. Extrapolate hydrocarbon emission ratios to $\Delta t=0$

de Gouw, JGR, 2005, Warneke, 2007

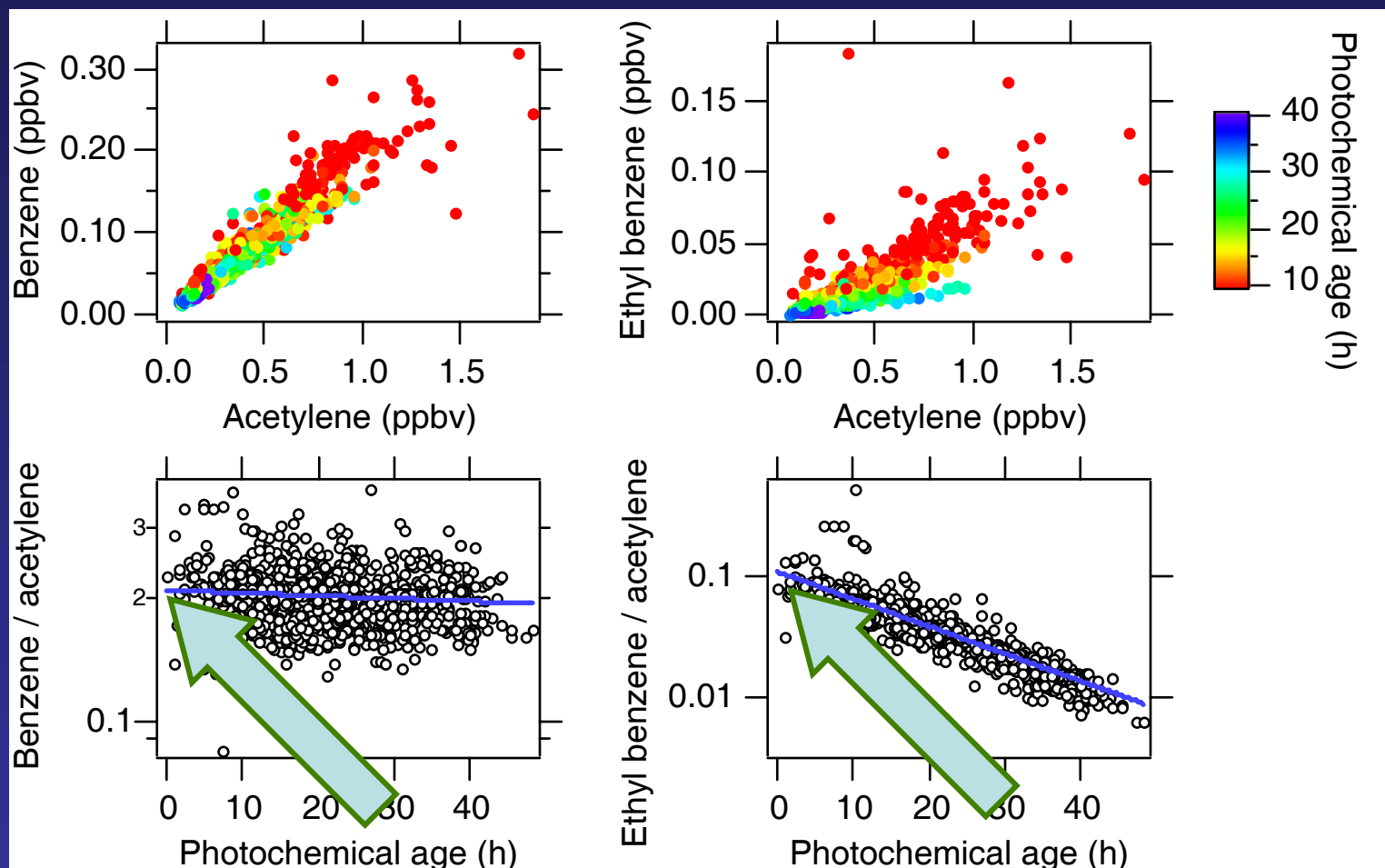
Determination of Emission Ratios: Ron Brown Data



$k_{\text{benzene}+\text{OH}} \approx k_{\text{acetylene}+\text{OH}} \Rightarrow$ well correlated

$k_{\text{ethyl benzene}+\text{OH}} > k_{\text{acetylene}+\text{OH}} \Rightarrow$ ratio decreases with age

Determination of Emission Ratios: Ron Brown Data



Intercepts give the emission ratios:

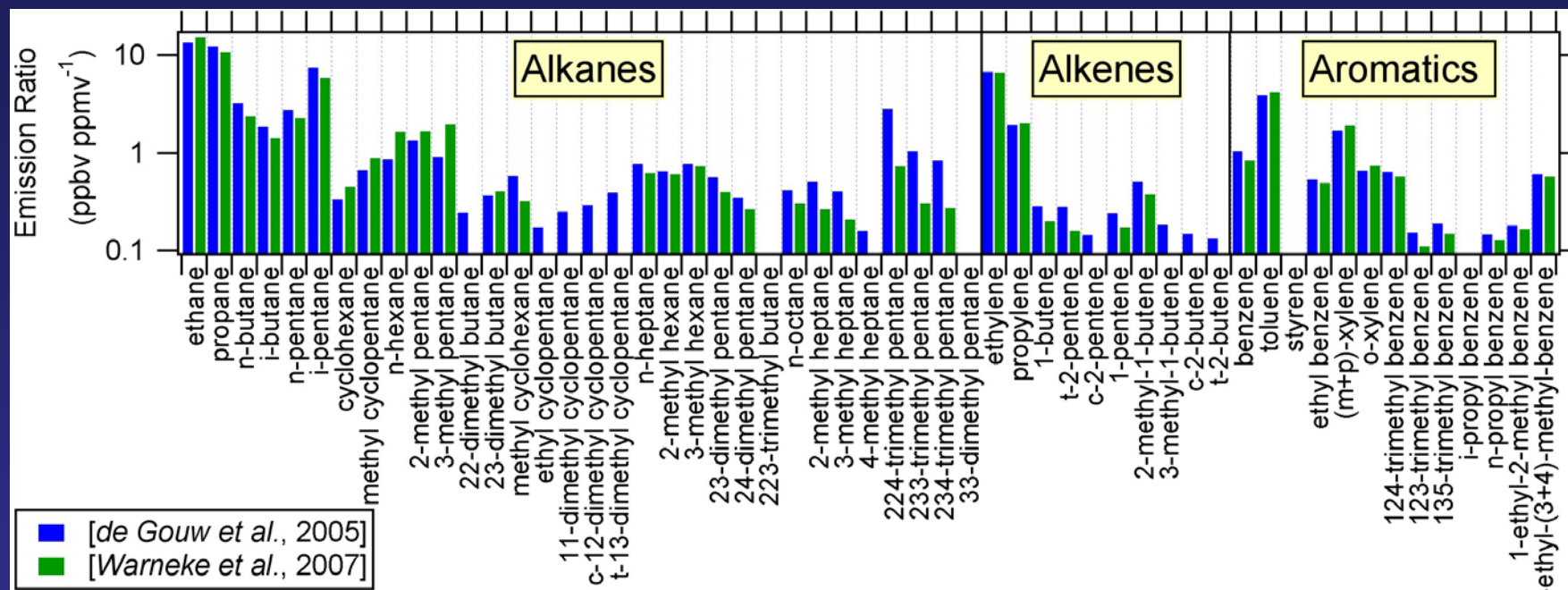
Benzene / acetylene = 0.21

(2004: 0.17)

Ethyl benzene / acetylene = 0.11

(2004: 0.09)

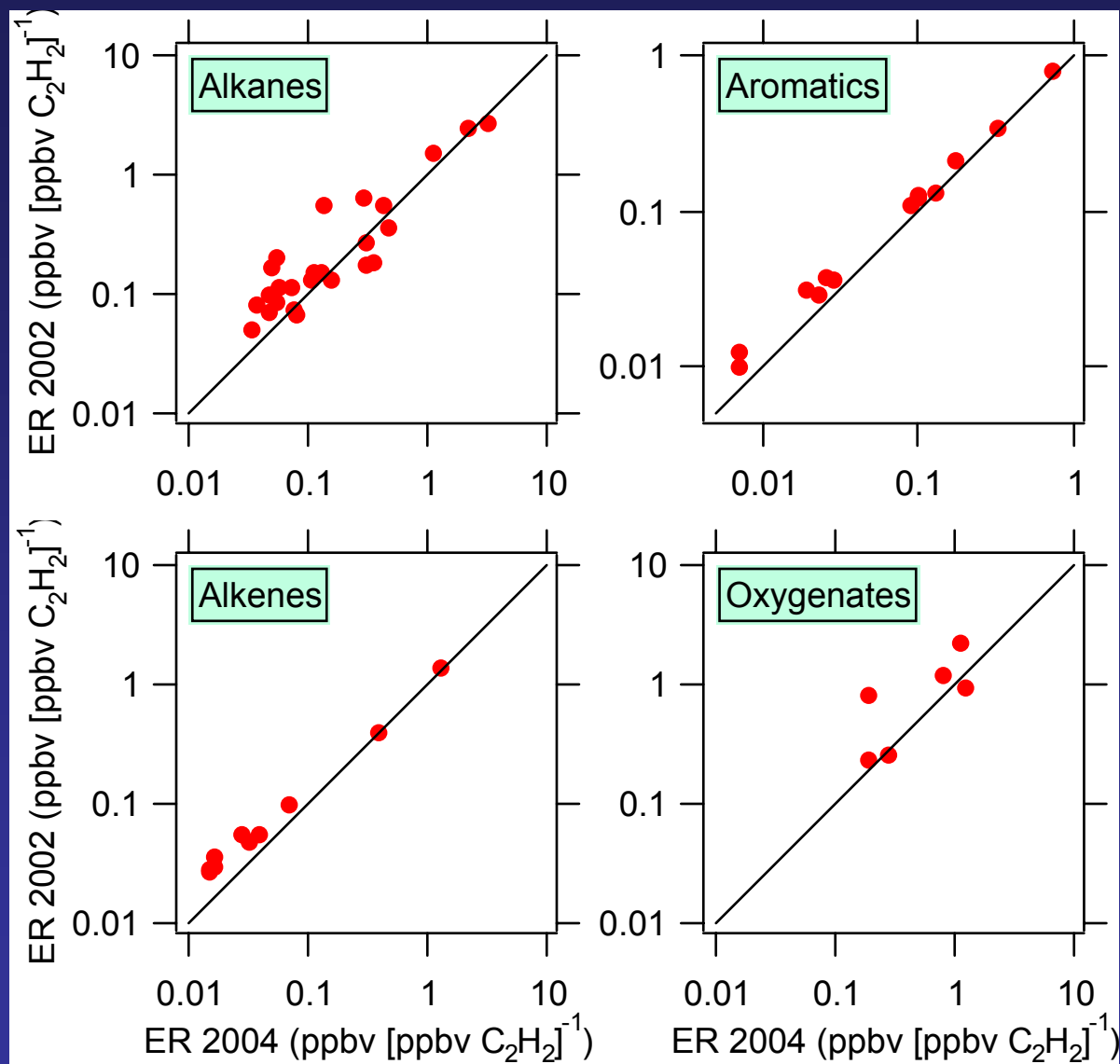
Results from the Northeastern U.S.



de Gouw [JGR 2005]; Warneke [JGR 2007]

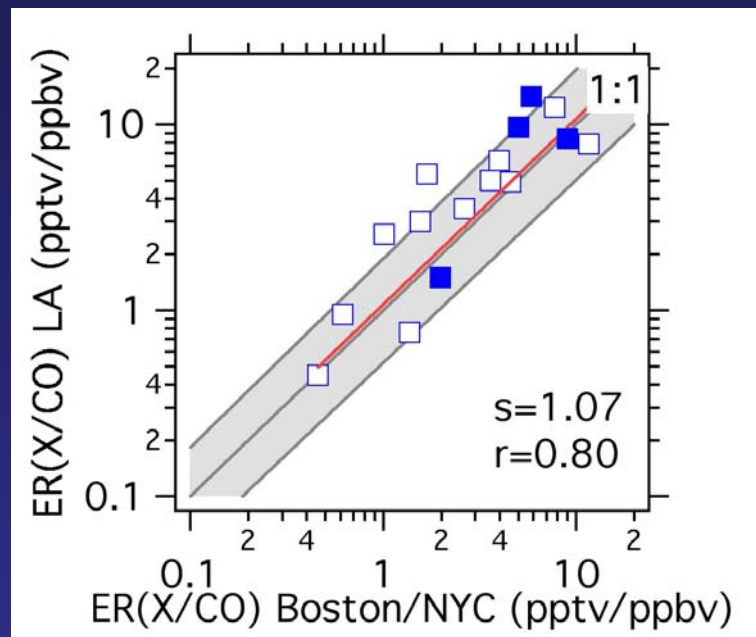
Good agreement between the 2 years

Results from the Northeastern U.S.



Good agreement between the 2 years

Comparison with other Cities: Los Angeles

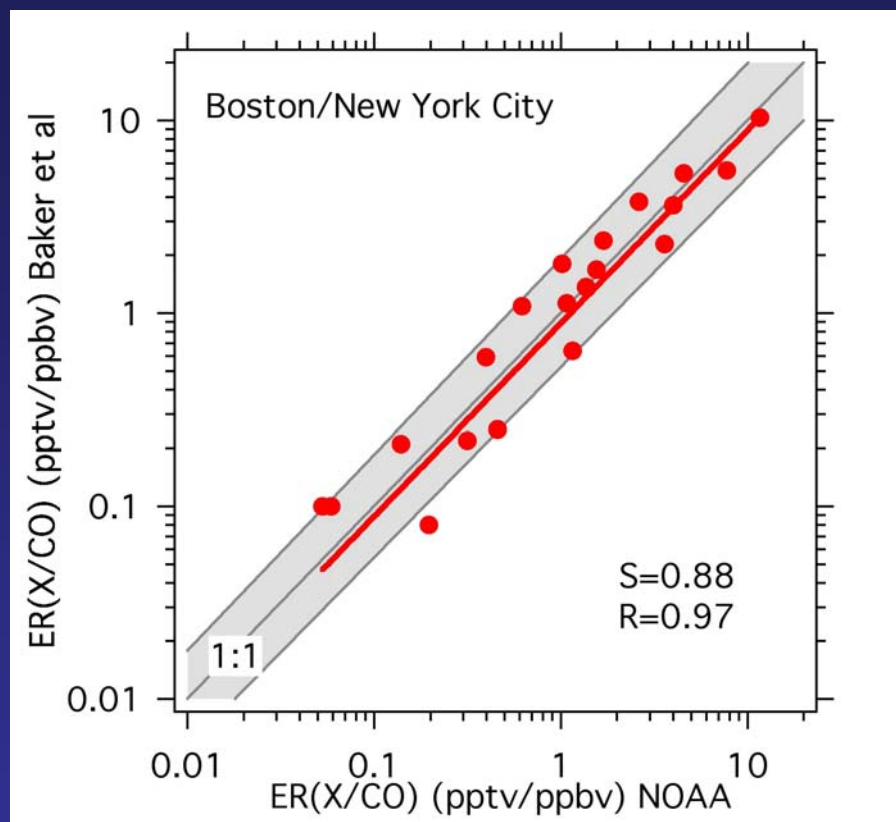


solid squares: oxygenates

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

Comparison with Other Studies



- *Baker* [AE 2008] published summary of VOC observations from 28 U.S. cities, including emission ratios
- Good agreement with our work

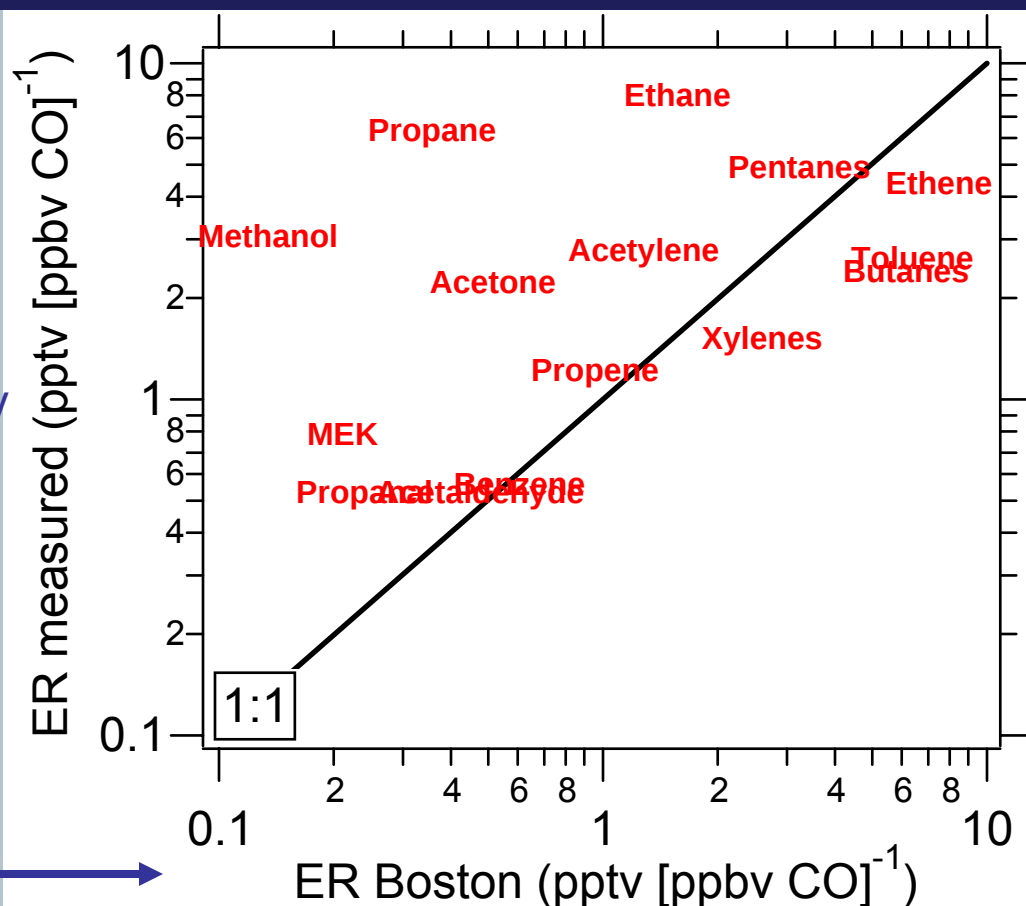
Comparison with Emission Inventory

Inventory

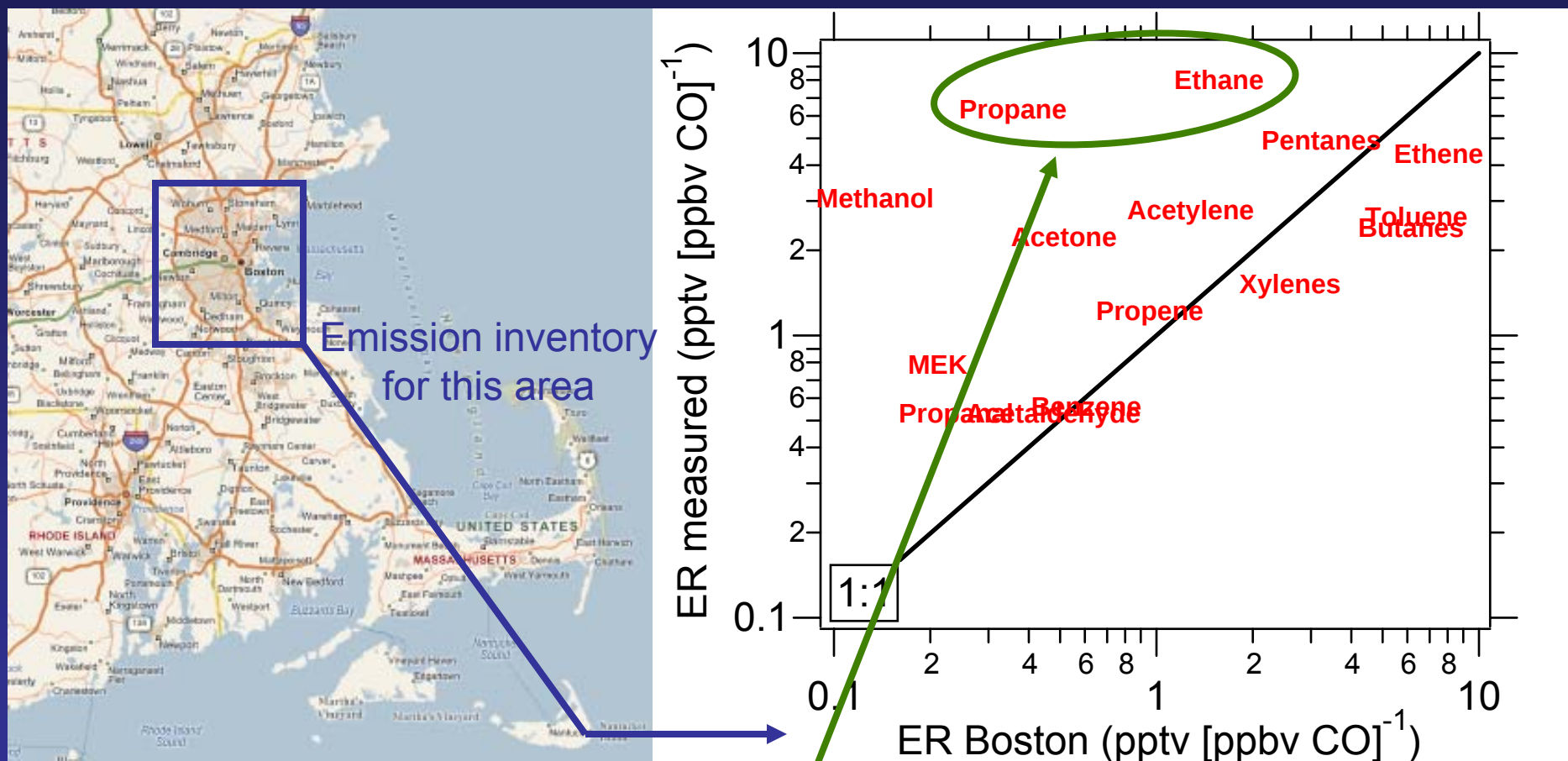
- Based on EPA NEI-99 Version 3
- Made for photochemical models
- On-road, non-road, area and point sources
- Box around Boston, New York, Los Angeles, Houston and Dallas, etc. and sum up all emissions
- Ratio with CO (point sources excluded)

Acknowledgements: Greg Frost and Stu McKeen

Comparison with Emission Inventory

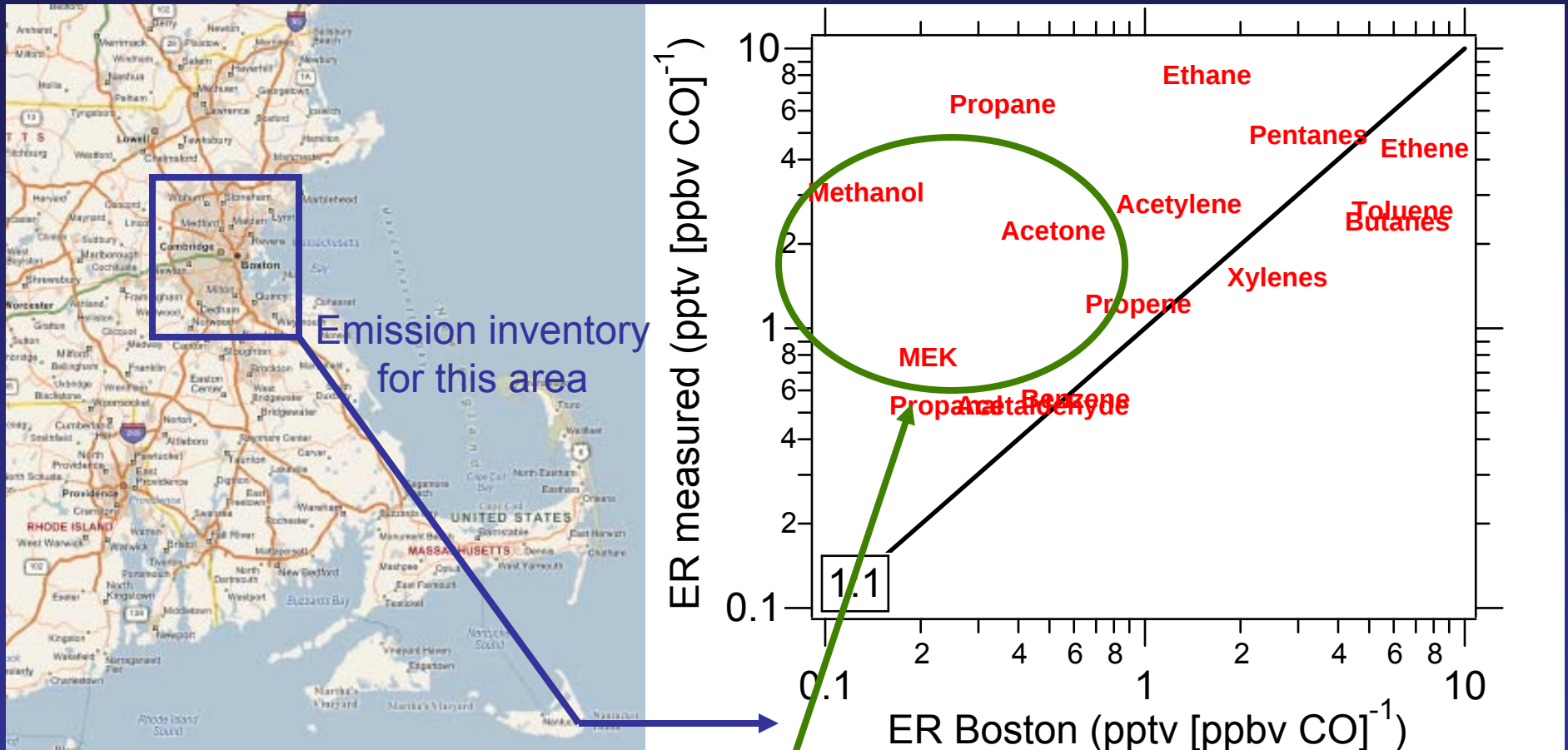


Comparison with Emission Inventory



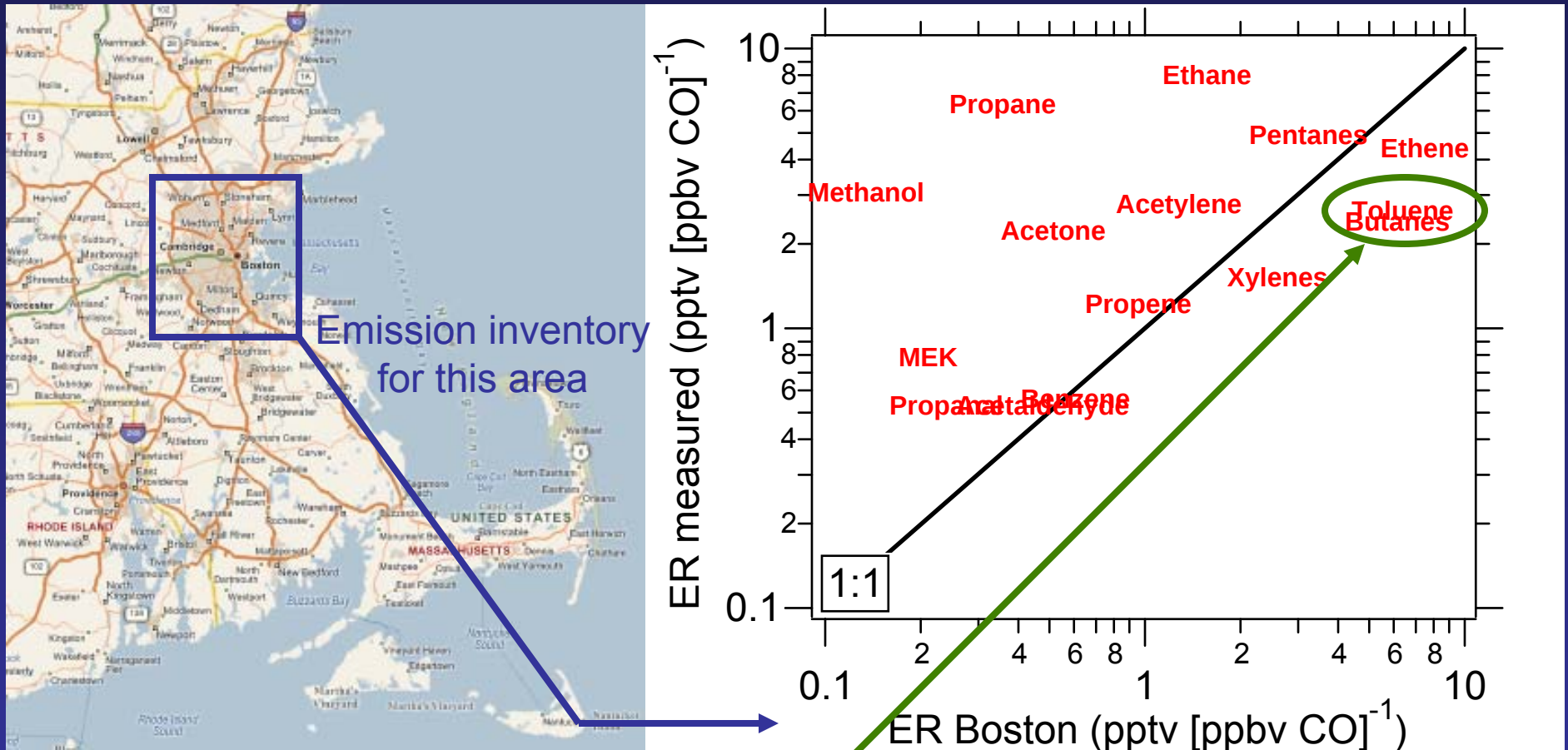
- Small alkanes underestimated in inventory
- Similar to findings of Sive et al. in 2002

Comparison with Emission Inventory



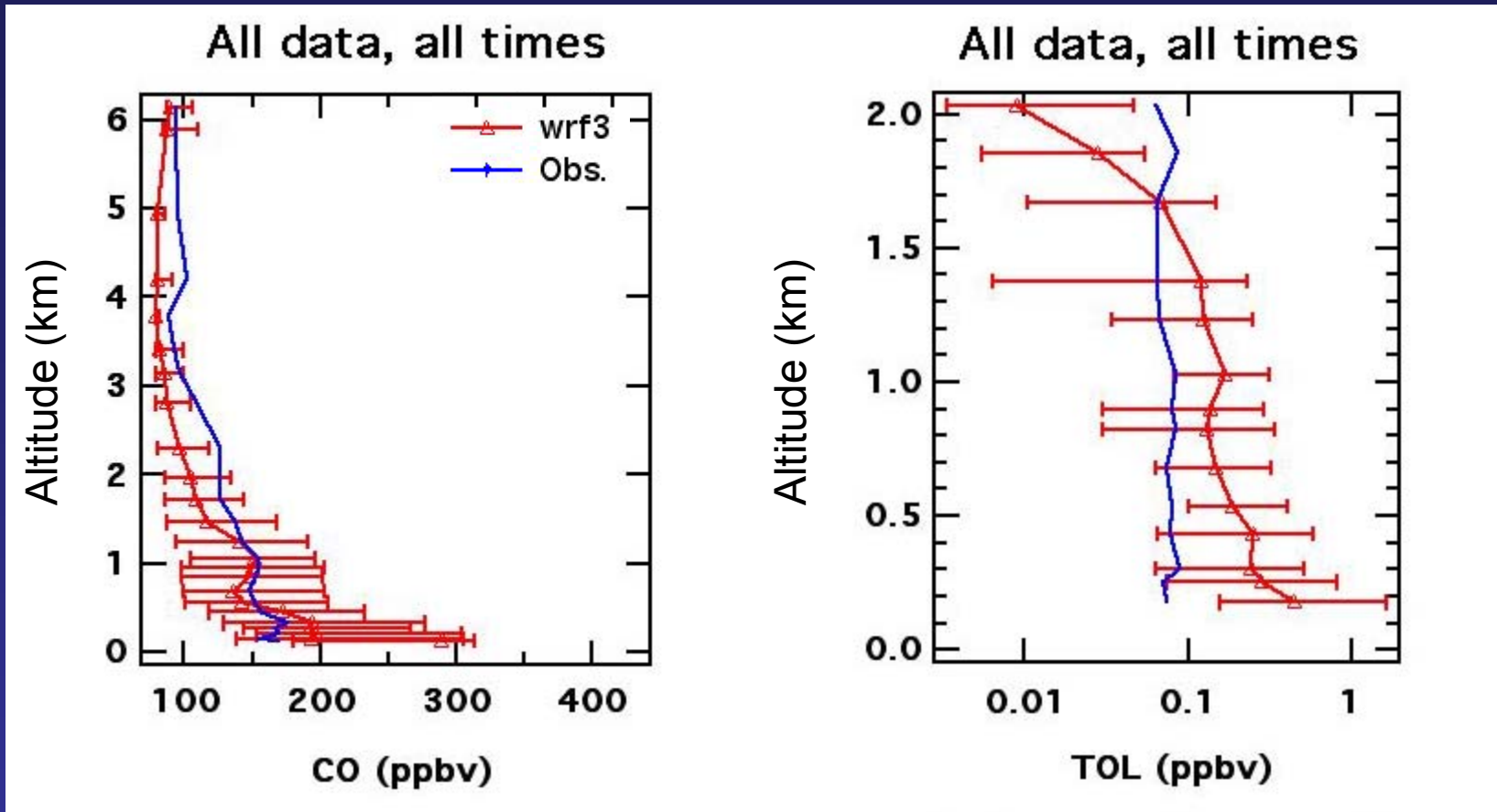
- Inventory underestimates oxygenates
- Oxygenates are low in vehicle exhaust
- What are the primary urban sources?

Comparison with Emission Inventory



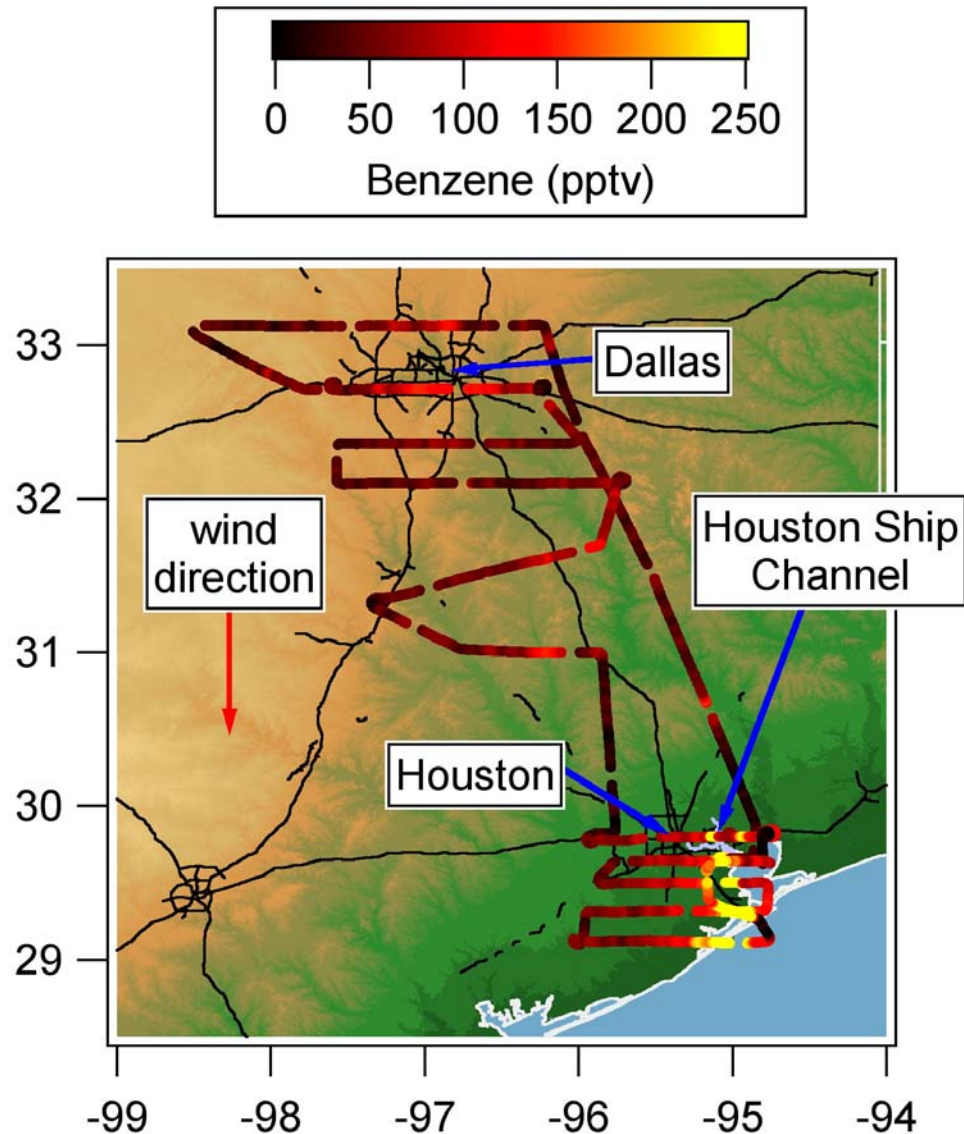
Inventory overestimates toluene by factor of ~2.5

Toluene: WRF-CHEM Model vs. Measurements



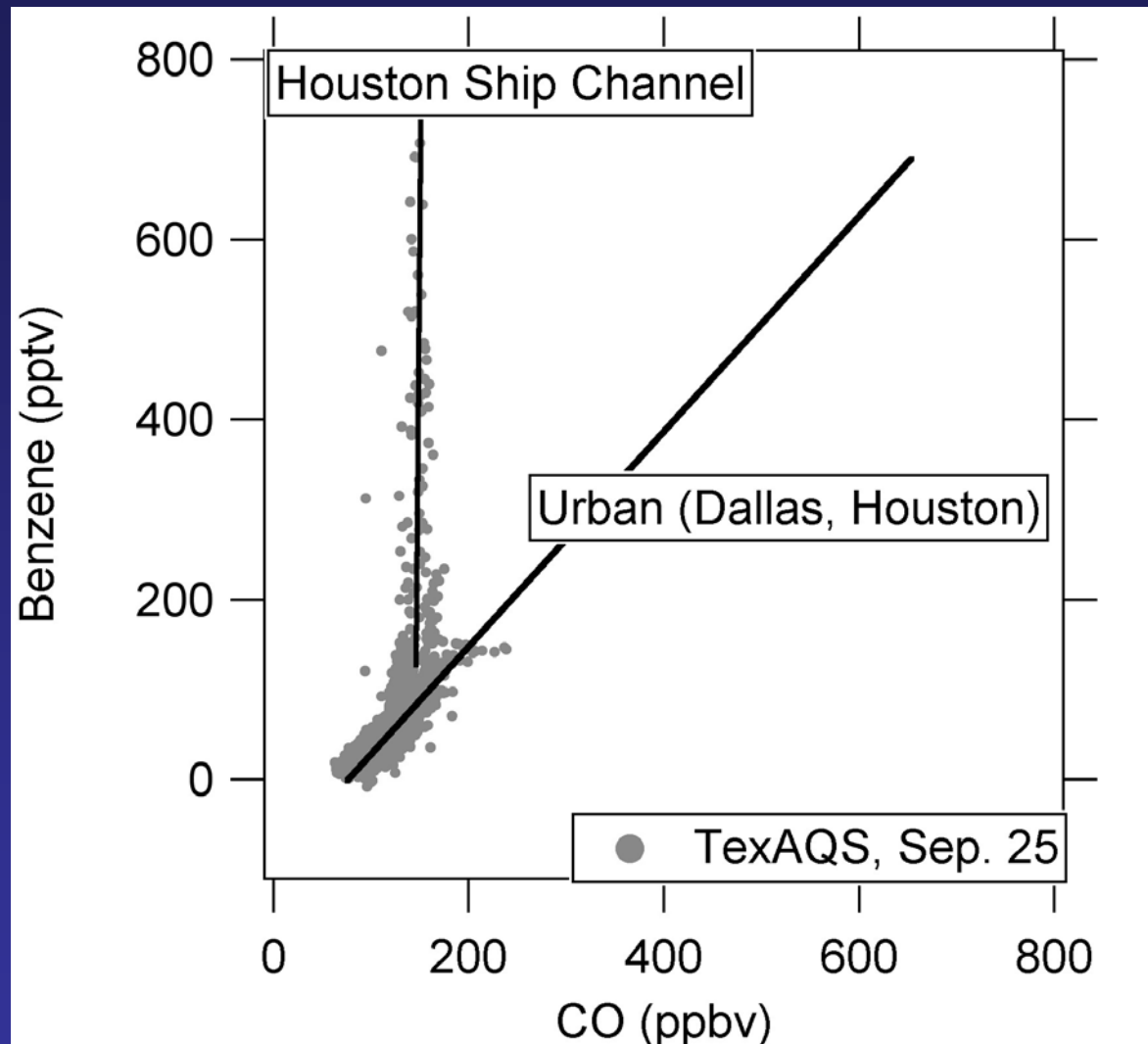
- Overestimate of toluene by the WRF-CHEM model consistent with overestimate in the emissions inventory

Not All Cities are Created Equal: Houston, Texas



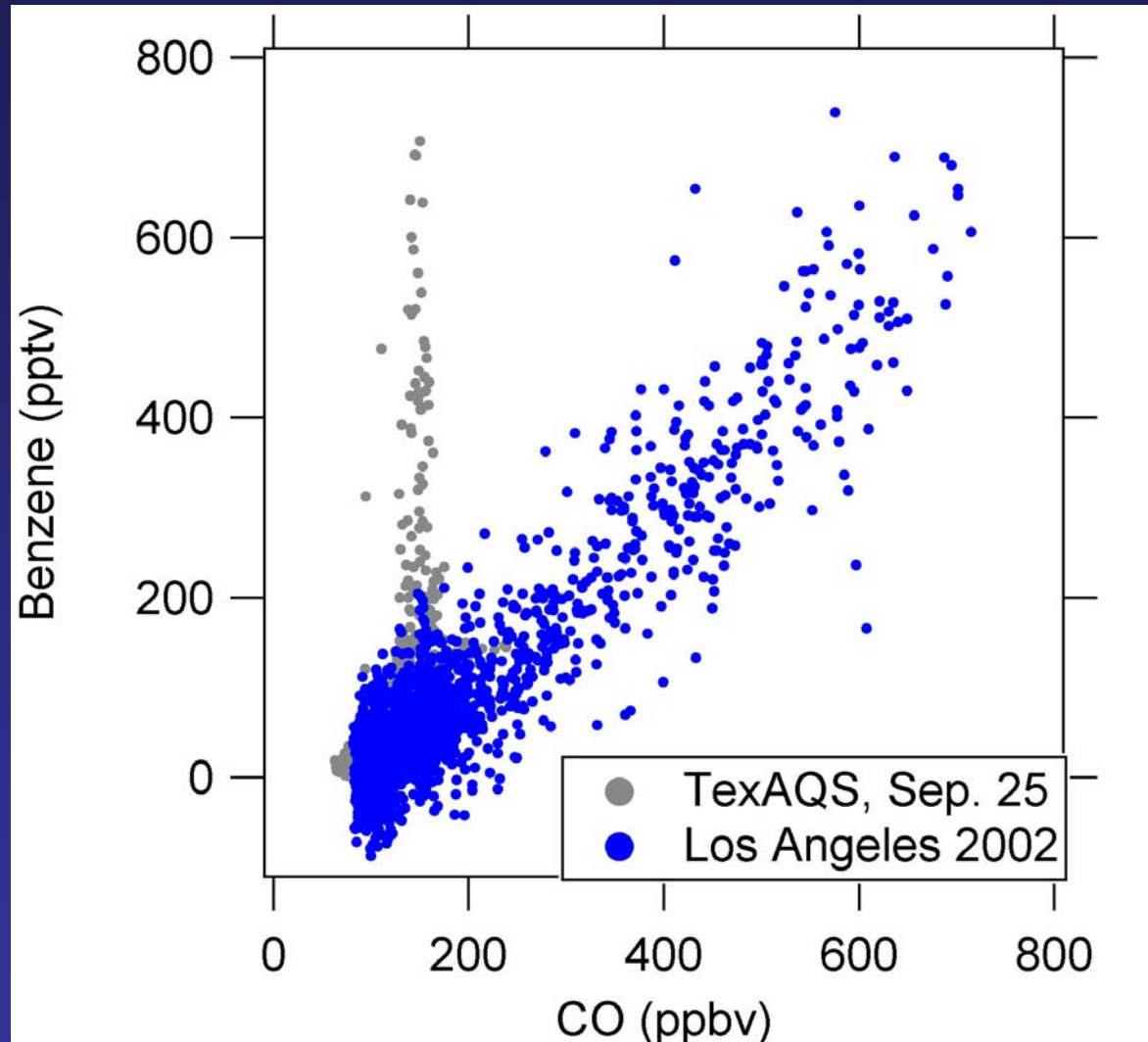
- Houston has large petrochemical point sources along the Houston Ship Channel
- Example: research flight from September 25

Not All Cities are Created Equal: Houston, Texas



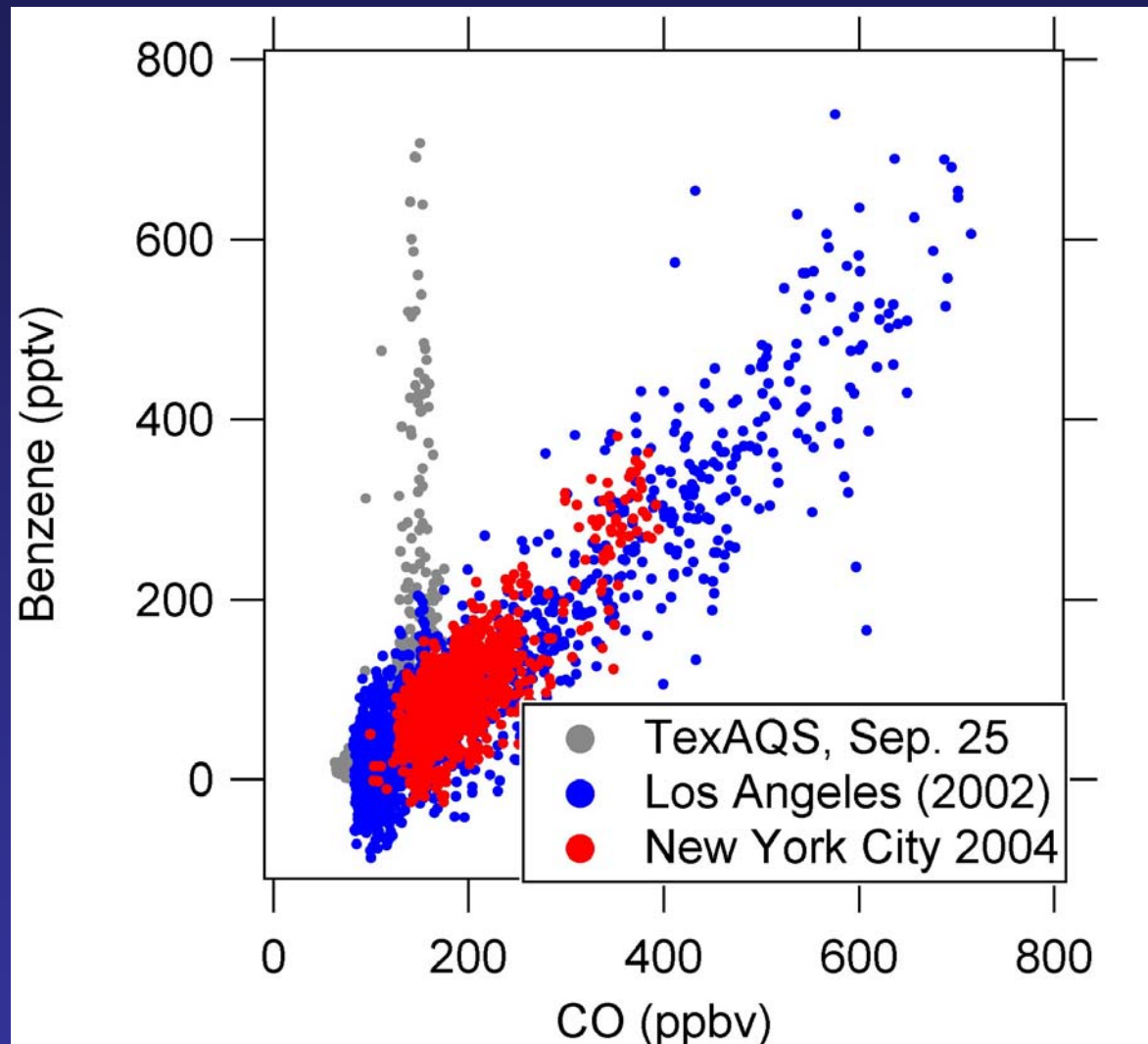
➤ $\Delta\text{VOC}/\Delta\text{CO}$ is different in the Houston Ship Channel

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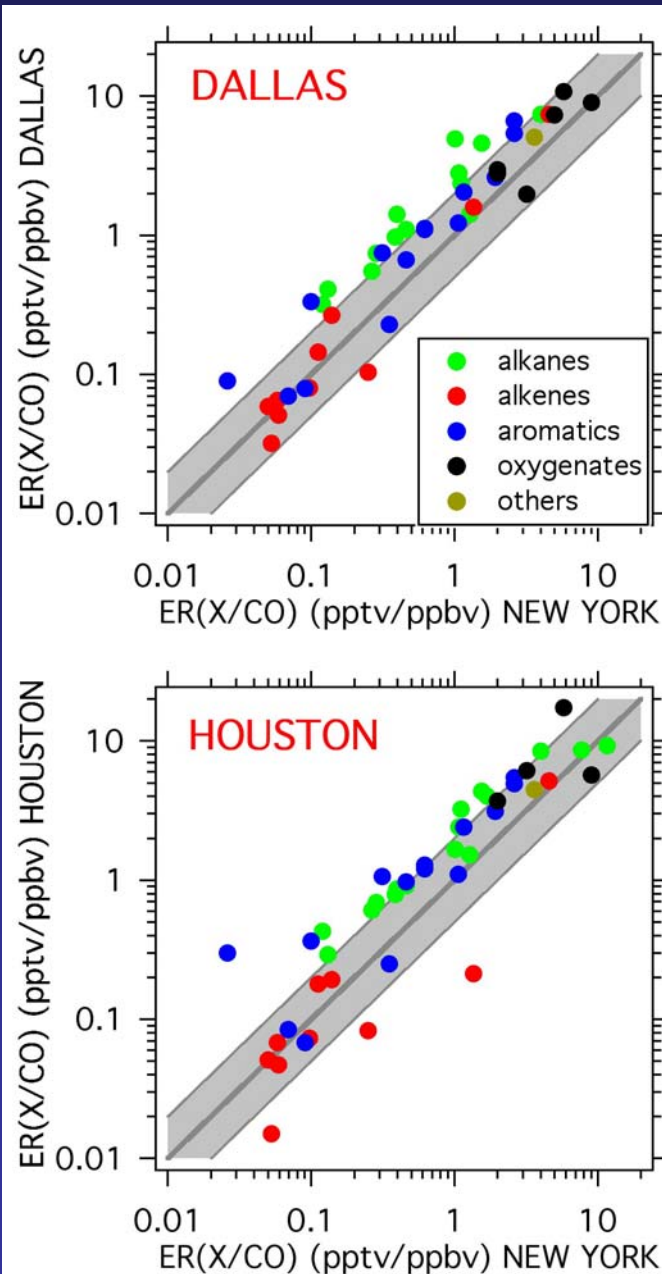
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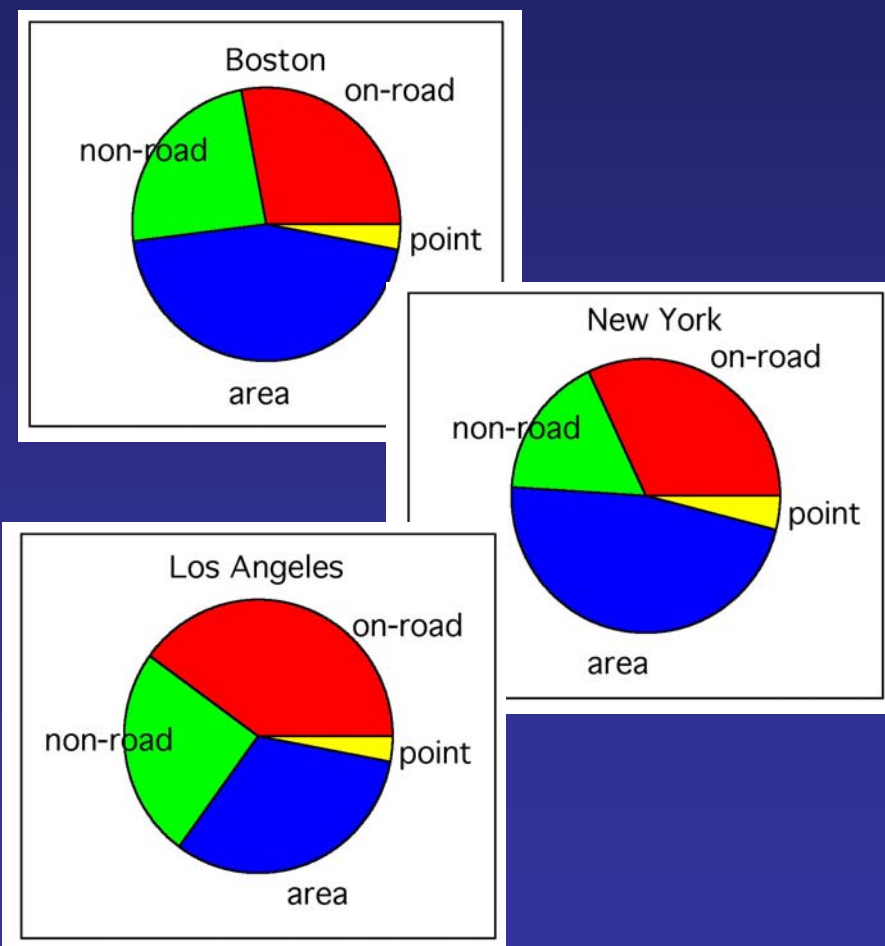
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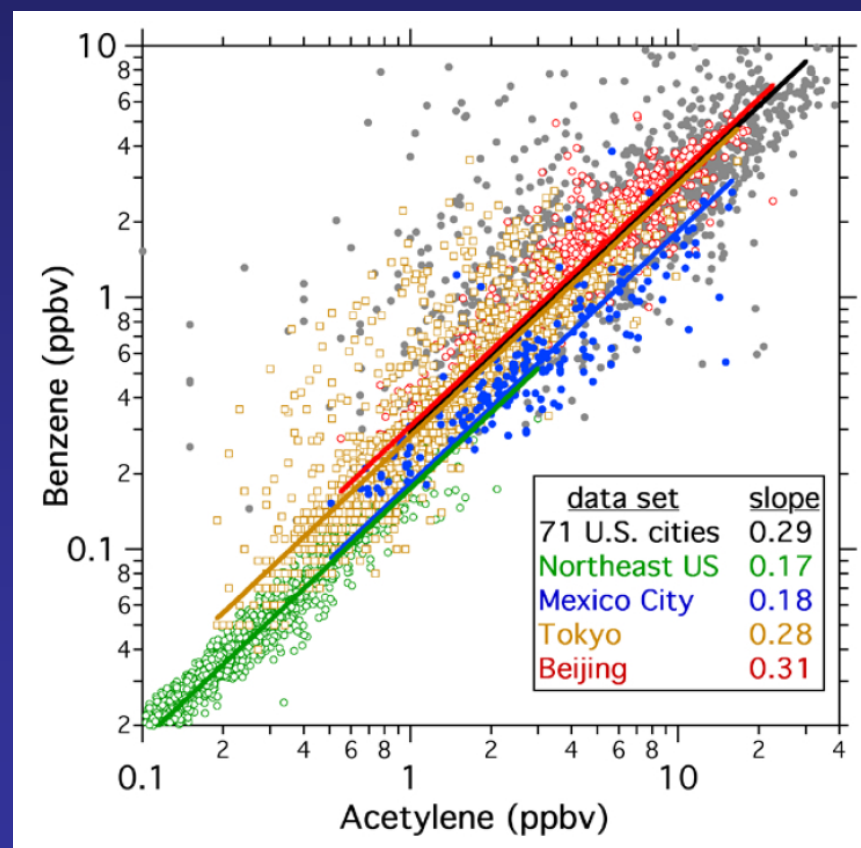
- Separating the urban and industrial emissions of most VOCs is done using scatter plots versus CO
- Urban VOC emissions in Dallas and Houston are similar to the rest of the country

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

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RHB GC-MS

PIT-MS

WAS

RHB CO

WP-3 CO

WRF-CHEM

Flexpart

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