Biogenic and Urban Emissions of Atmospheric VOCs and Comparison with Inventories

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Outline:

1. Comparison of Observations with Biogenic Emission Inventory
2. Determination of Urban VOC Emission Ratios
3. Comparison to Industrial Sources

Measurements and Inventories

VOC Measurements:

NOAA WP-3 Aircraft: regional coverage

- PTR-MS: Fast time response (J.A. de Gouw, L. Del Negro)
- Canister samples (E. Atlas)

NOAA Ron Brown:

- GC-MS (J. Gilman, B. Kuster, P. Goldan)

VOC emissions inventories:

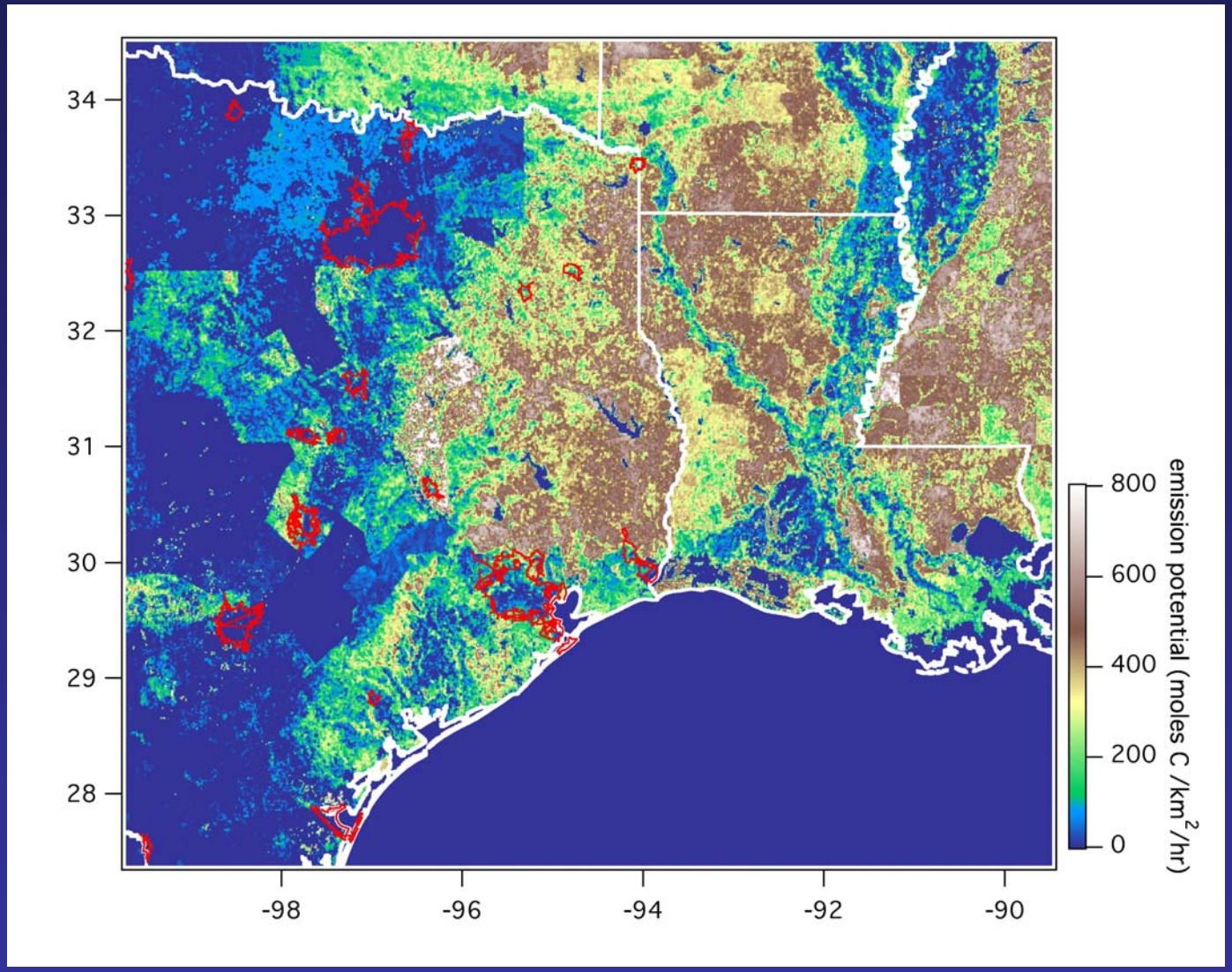
EPA databases

- BEIS3 emissions inventory for biogenics (S. McKeen)
- NEI99 based emissions inventory for anthropogenics (S. McKeen)

Model Calculations:

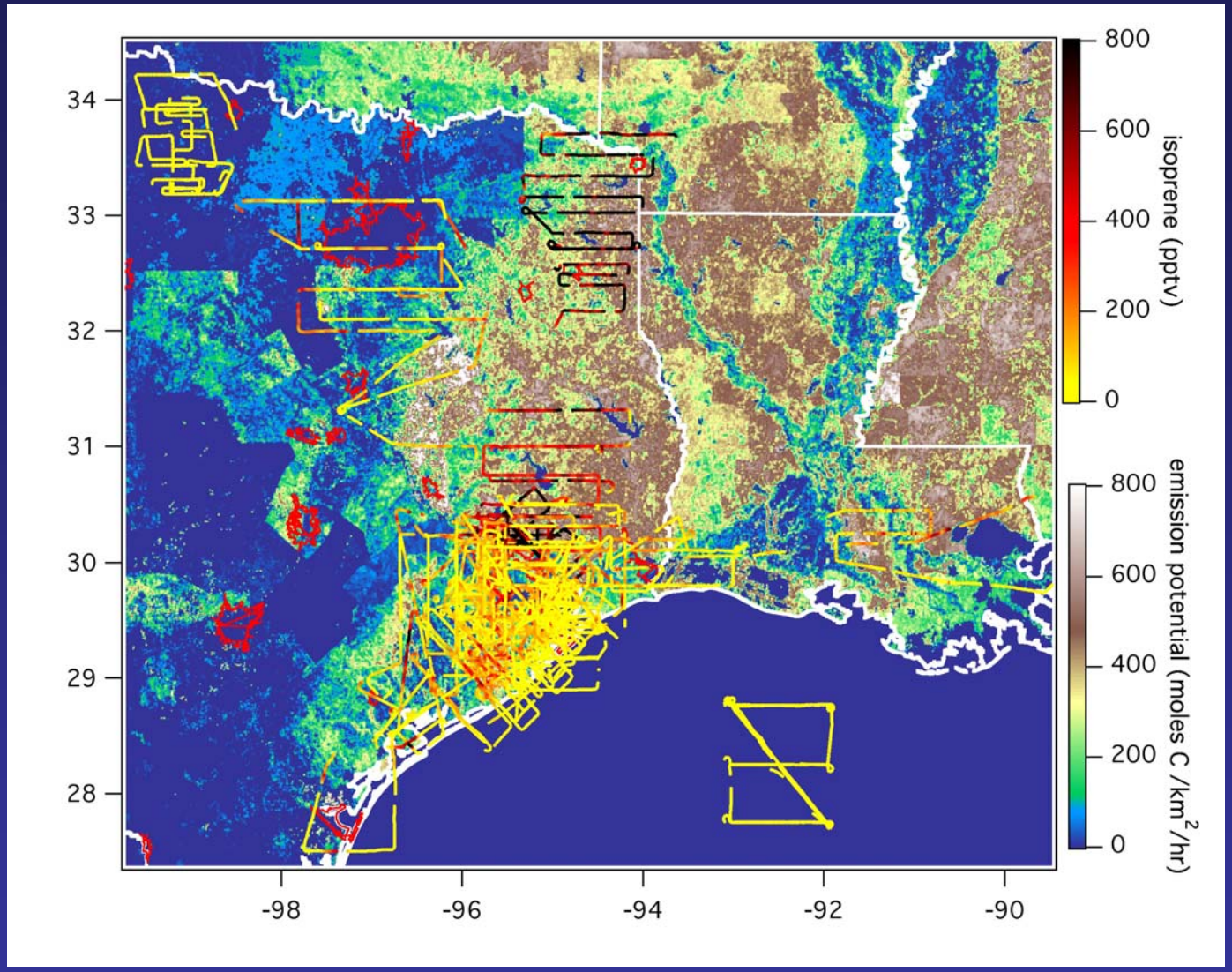
FLEXPART (J. Brioude)

Biogenic VOCs



- EPA BEIS-3 emissions inventory

Biogenic VOCs



- EPA BEIS-3 emissions inventory
- Isoprene measurements (boundary layer only)

Quantitative Comparison of Measurements with Emissions Inventory (EPA BEIS3)

Method 1:

Estimate emissions from mixing ratios:

- Chemistry: lifetime due to OH
- Boundary layer height
- Temperature and light dependence
- Transport (omitted)

Method 2:

Use FLEXPART transport model

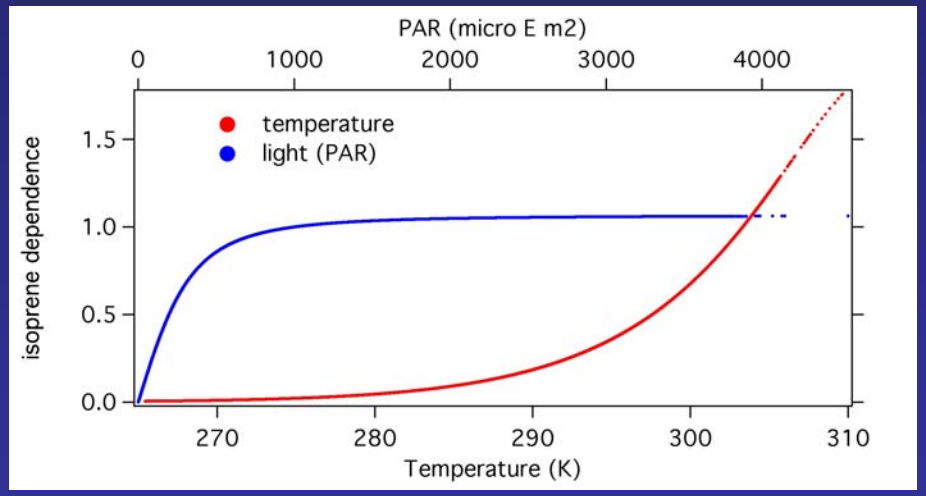
- BEIS3 emissions incorporated
- Emissions within 1h of transport
- Chemistry (omitted)

Mixed Boundary Layer Method

Method 1: Mixed Boundary Layer Method

$$\text{emission} = \text{isoprene} * OH * k_{OH} * BL_{height}$$

- OH from Ehhalt et al. OH parameterized with j_{Ozone}, j_{NO2}, NO_2
- Boundary layer height (average height per flight)
- Temperature and light dependence from aircraft data (Guenther et al algorithm)



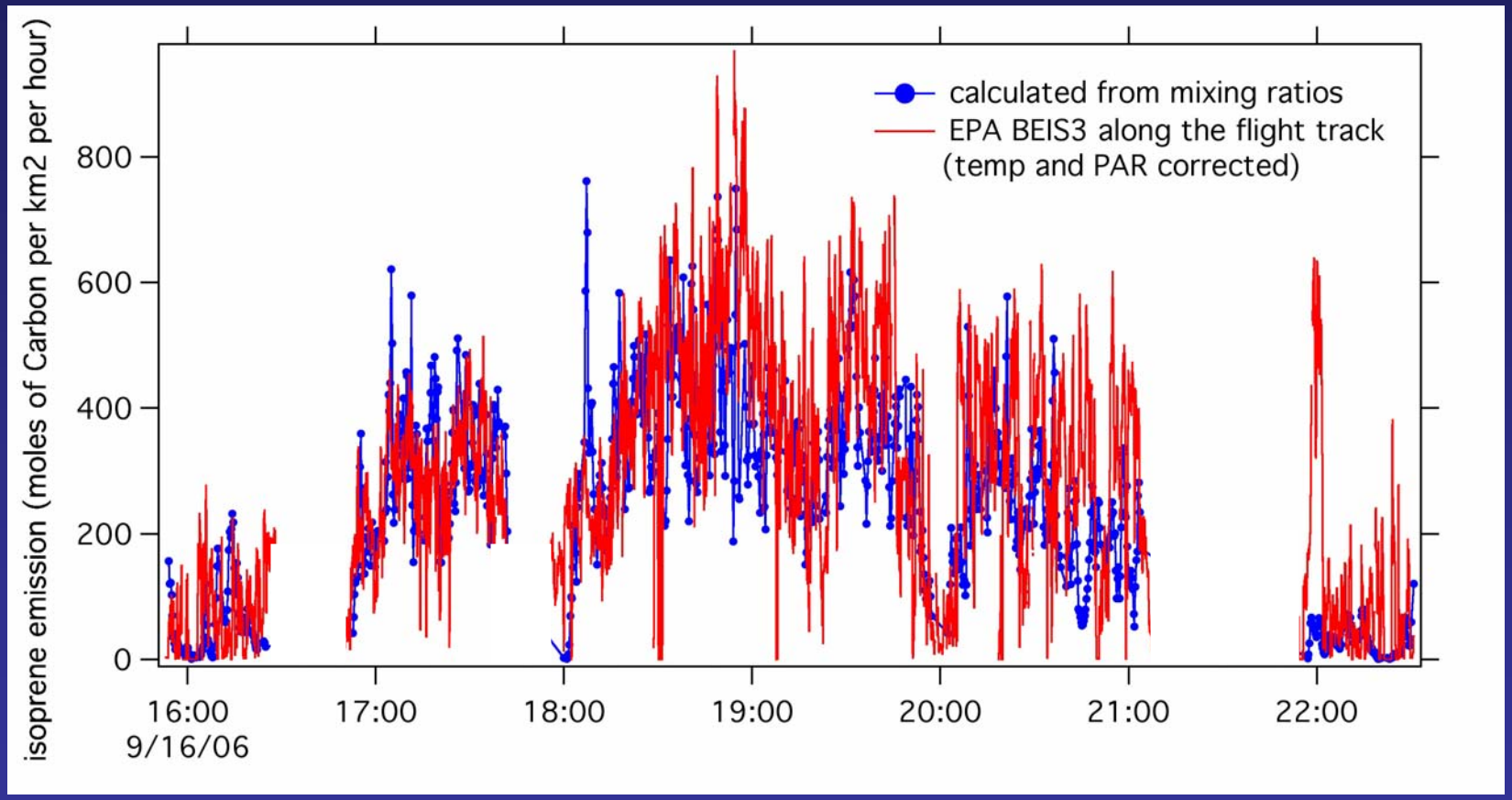
Potential problems:

- isoprene gradient in the BL
- horizontal transport
- T, PAR at aircraft different from ground
- OH not very accurate

Mixed Boundary Layer Method

Method 1: emission = isoprene * OH * k_{OH} * BL_{height}

Example: Flight 09/16/2006 NE Texas



Summary Method 1:

- Each flight agrees within ± 50%
- Overall fairly good agreement (within 50%)

Biogenic Emissions in FLEXPART

Method 2: EPA BEIS3.11 in FLEXPART

- Transport model using ECMWF meteorology
- Release of 40000 trajectories along many points of the flight track
- Mixing ratios: trajectories in the boundary layer * emissions data
- 0.15^0 x 0.15^0 resolution of BEIS3.11 emissions
- Temperature and light dependence from ECMWF

- Isoprene along the flight track
- Emissions within 1h

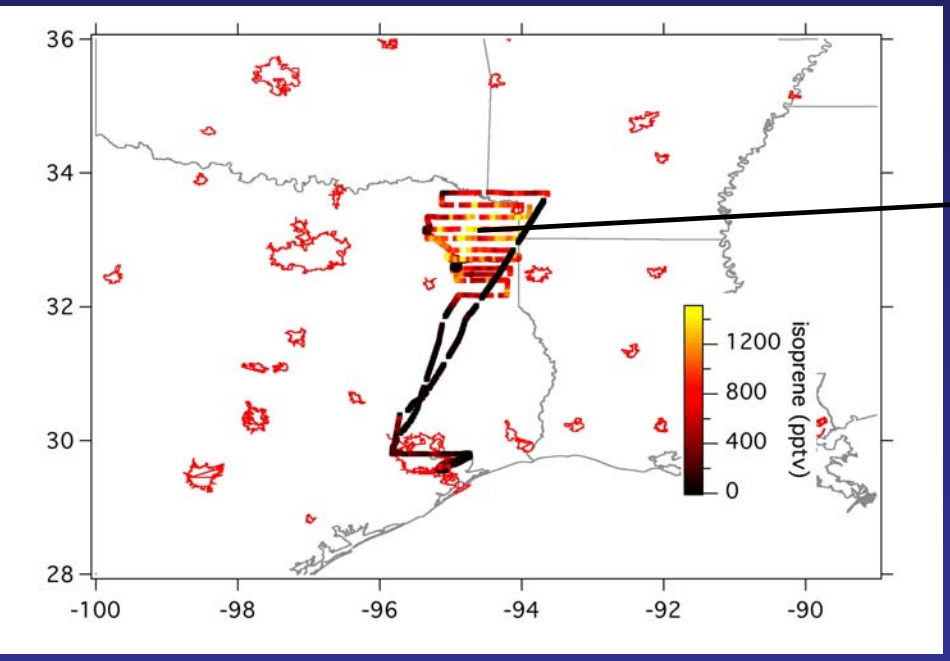
Potential problems:

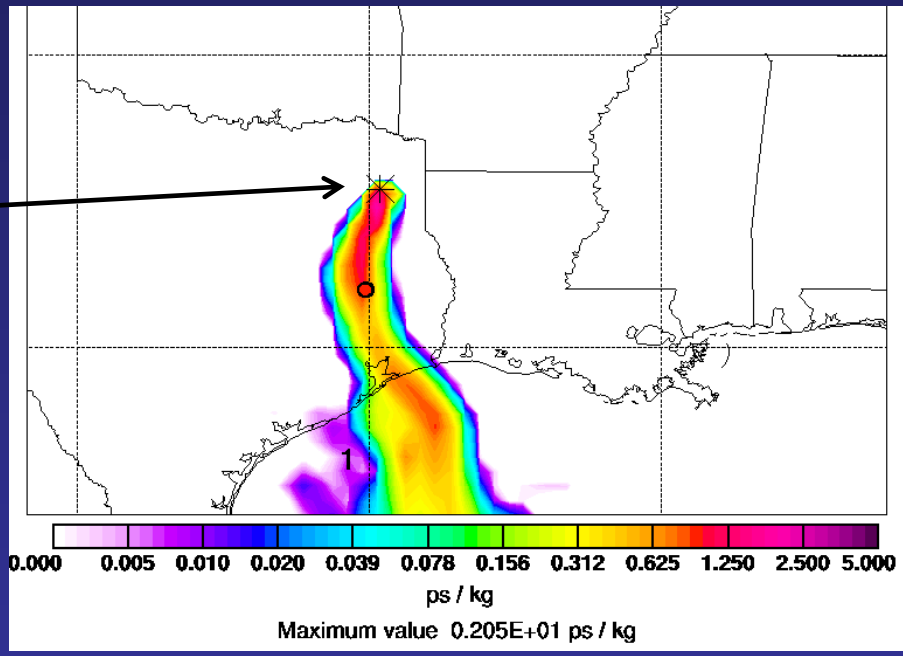
- No chemistry
- Model resolution
- ECMWF instead of aircraft data for temperature and light

Biogenic Emissions in FLEXPART

Method 2: FLEXPART footprint

Example: Flight 09/16/2006 NE Texas



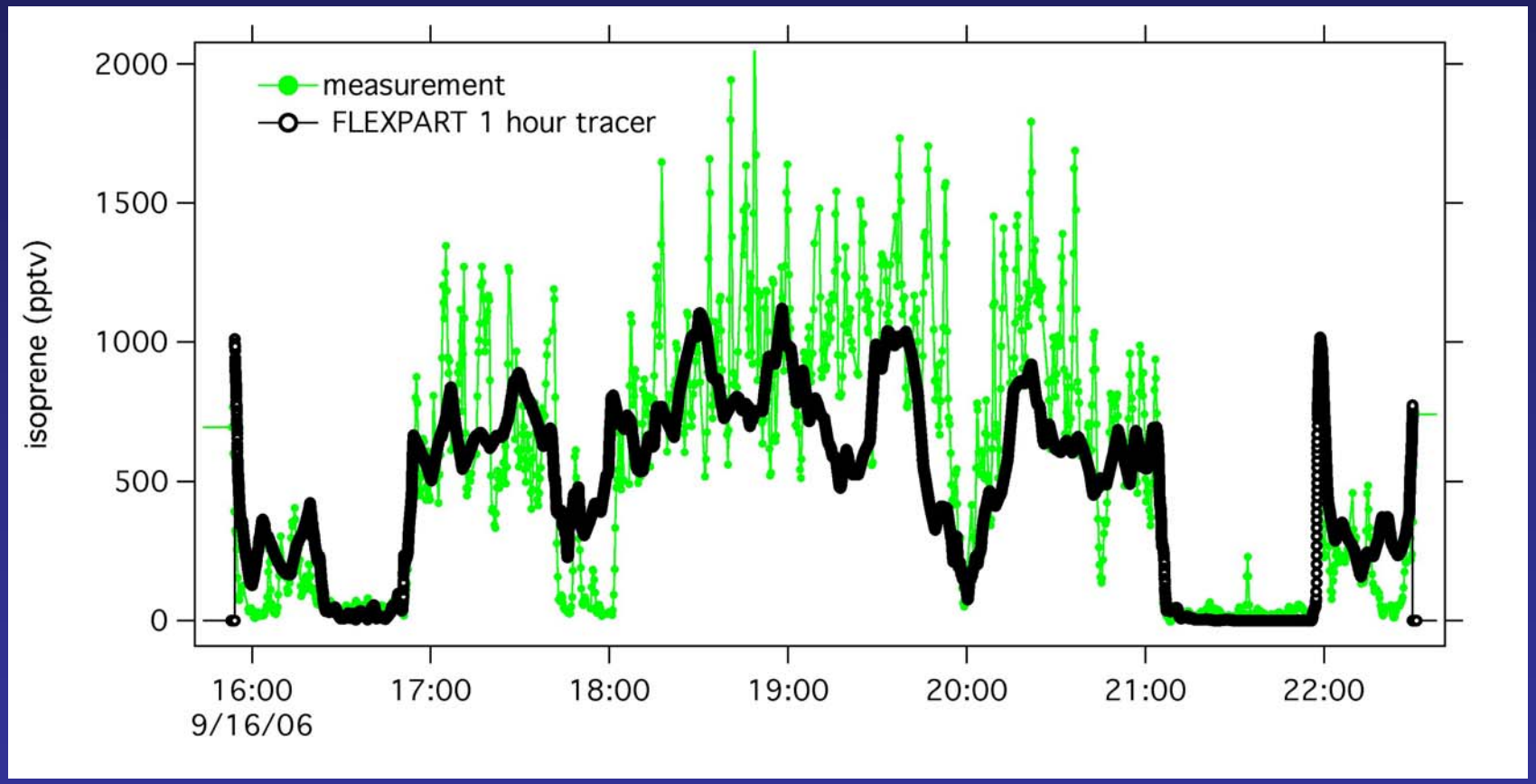


- emissions along the footprint within 1h
- note logarithmic scale

Biogenic Emissions in FLEXPART

Method 2: Isoprene emissions within 1 hour of transport from FLEXPART

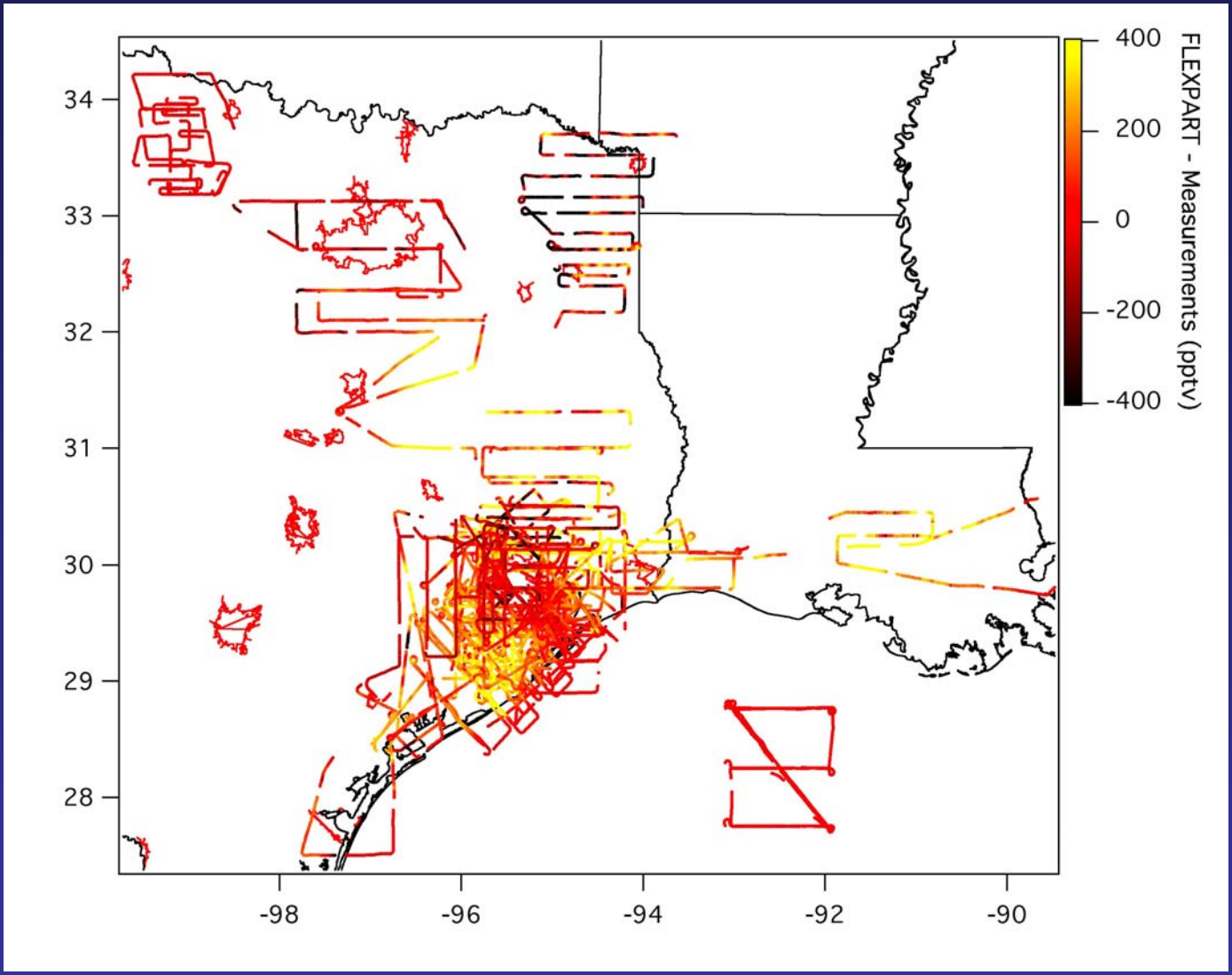
Example: Flight 09/16/2006 NE Texas



Summary Method 2:

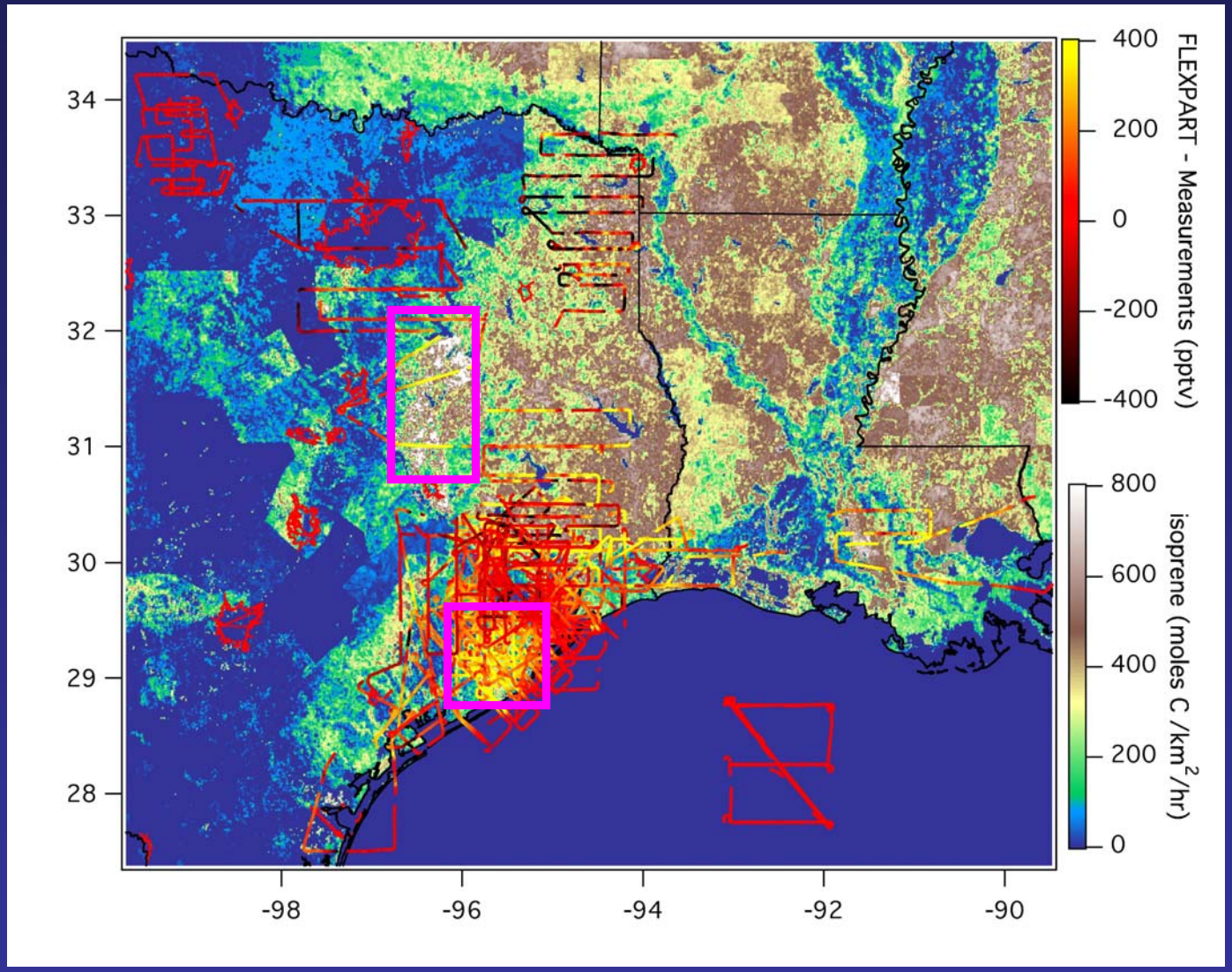
- Each flight agrees within ± 50%
- Overall a little better than Method 1

Differences by Location



- Reasonable agreement in NE Texas and around Houston

Differences by Location



- Reasonable agreement in NE Texas and around Houston
- BEIS3 too high between Houston and Dallas and SW of Houston

Summary Quantitative Comparison of Biogenic Emissions

Comparison of observations with BEIS3 inventory good within 50%

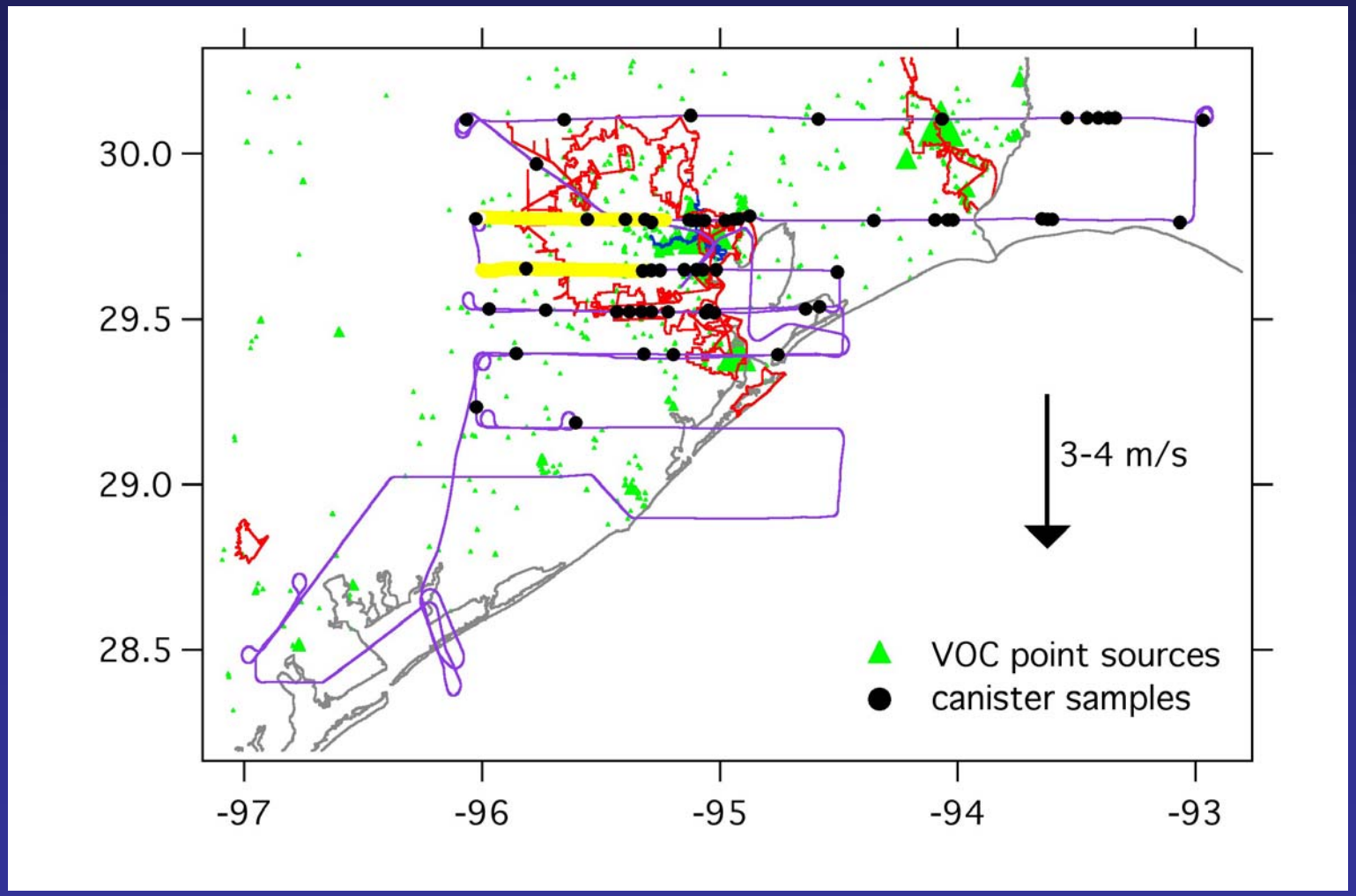
Other work:

- Air quality forecast models (Stu McKeen)
- MEGAN Emission inventory (Guenther et al)
- Why are there differences in certain locations (2000 vs. 2006)

  Different land cover datasets (Mike Feldman poster)

Determination of Urban Emission Ratios

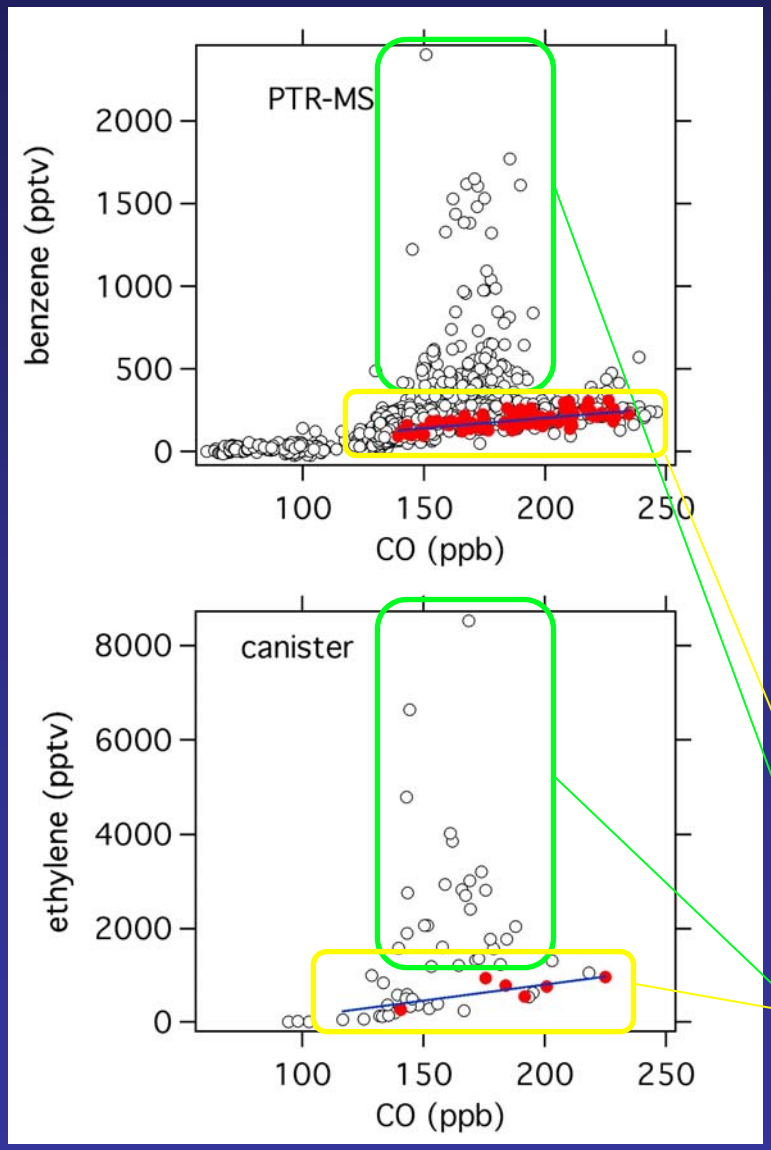
Example: Flight 09/26/2006



- Section of flight over Houston w/o industrial influence
- only few occasions, only few canister samples

Determination of Urban Emission Ratios

Example: Flight 09/26/2006



VOC emission ratio is the slope with CO

- small CO emissions from industrial sources

⇒ CO urban tracer

- relatively small benzene emissions from urban areas and long lifetime

⇒ benzene industrial tracer

Urban emissions

Industrial emissions

Urban Emission Ratios of all Measured VOCs

Correlation plots done for all VOCs and all opportunities

↓

Emission ratios for all measured VOCs

↓

Comparison with measurements of other US cities (New York City) (Warneke et al 2007)

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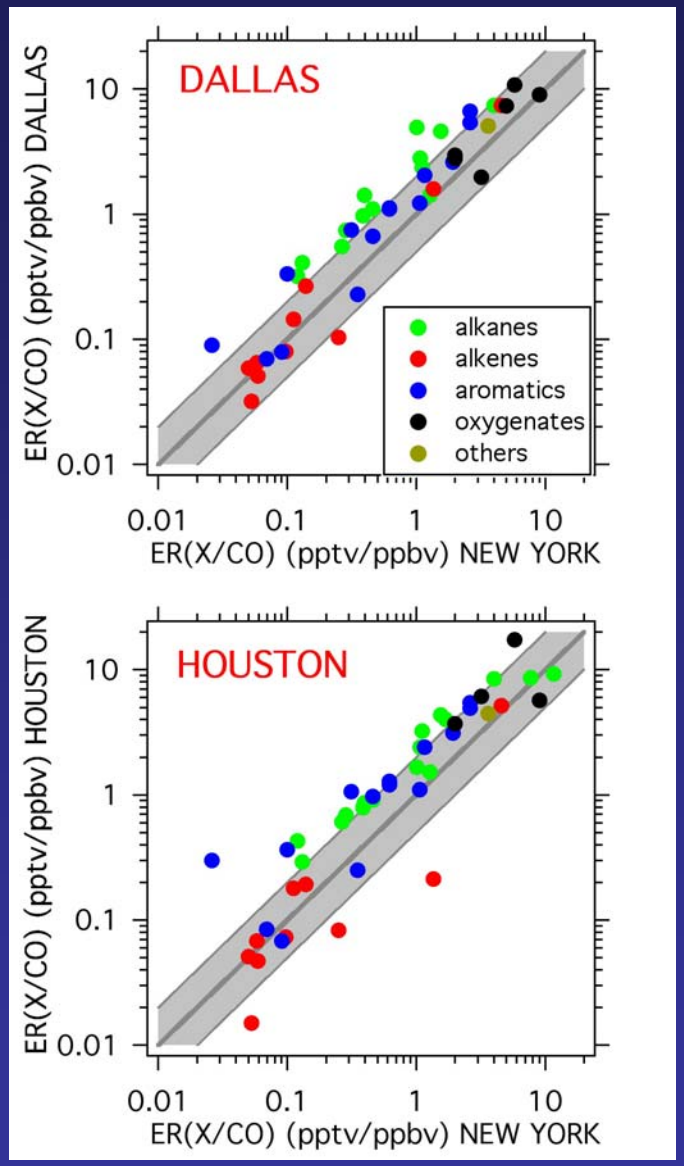


Includes:

alkanes
alkenes
aromatics
oxygenates

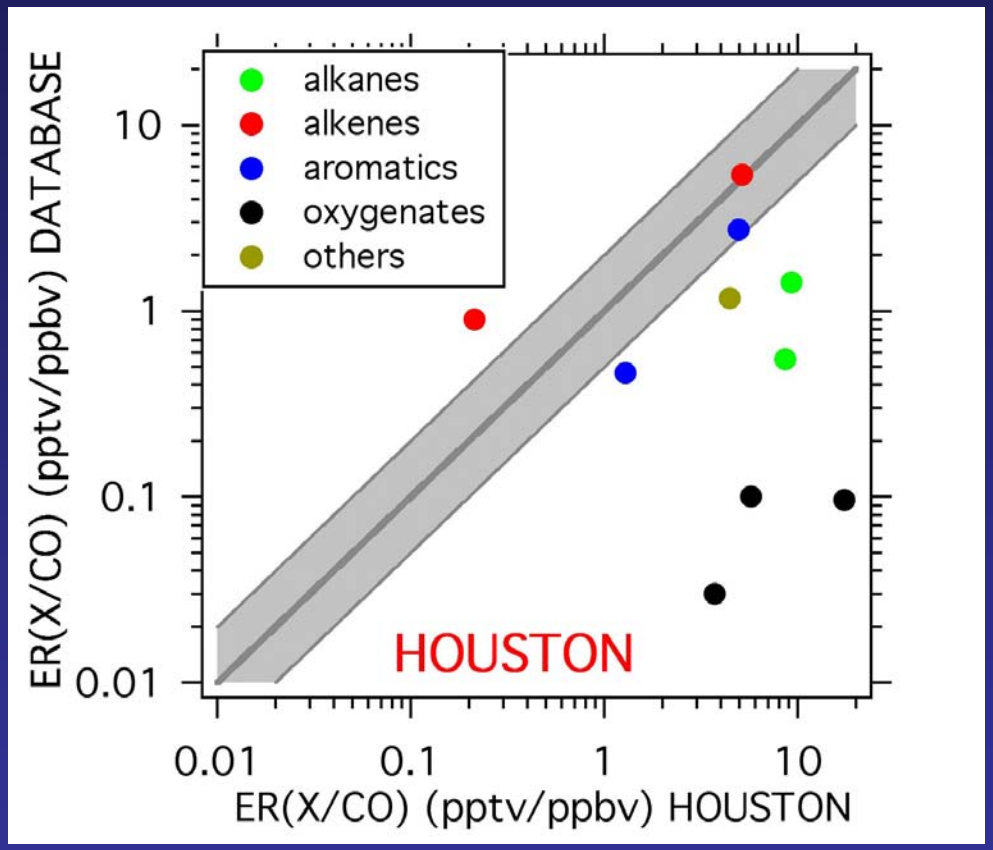
Measurements:

Houston/Dallas VOC emission ratios similar to other US cities

Urban VOC Emission Ratios Inventory

Inventory:

- based on EPA NEI-99 Ver. 3
- made for photochem. models
- on-road, non-road, area, point sources
- box around Houston
- ratio with CO (point sources excluded)



Inventory:

Houston (and other US cities) Urban VOC emission ratios do not compare well with inventory

Urban VOC Emission Ratios Inventory

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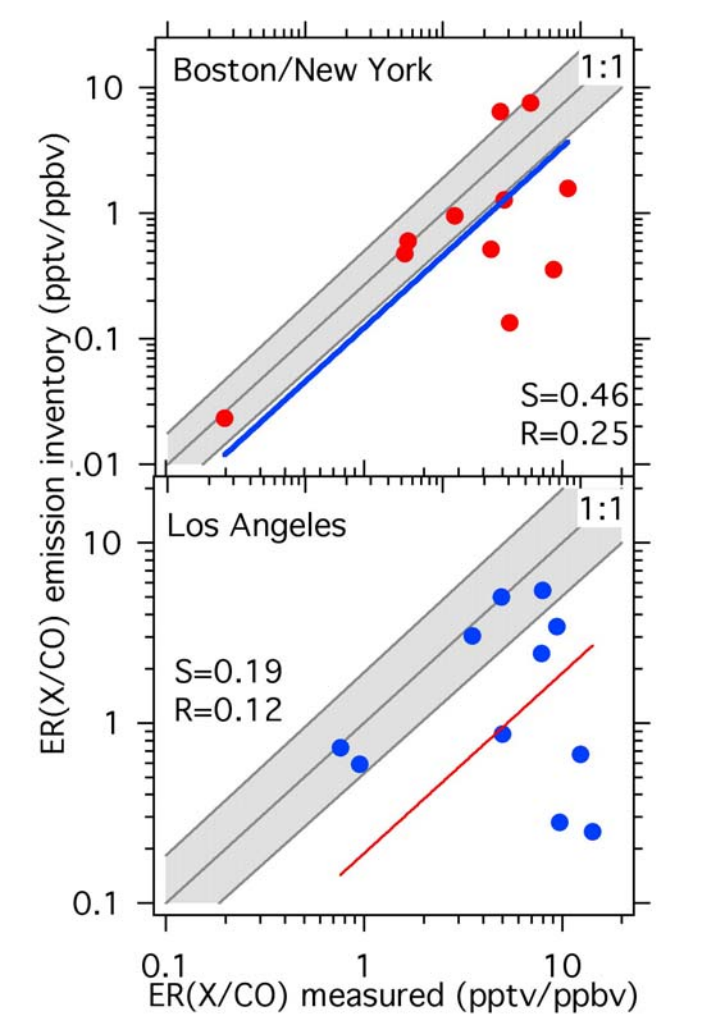
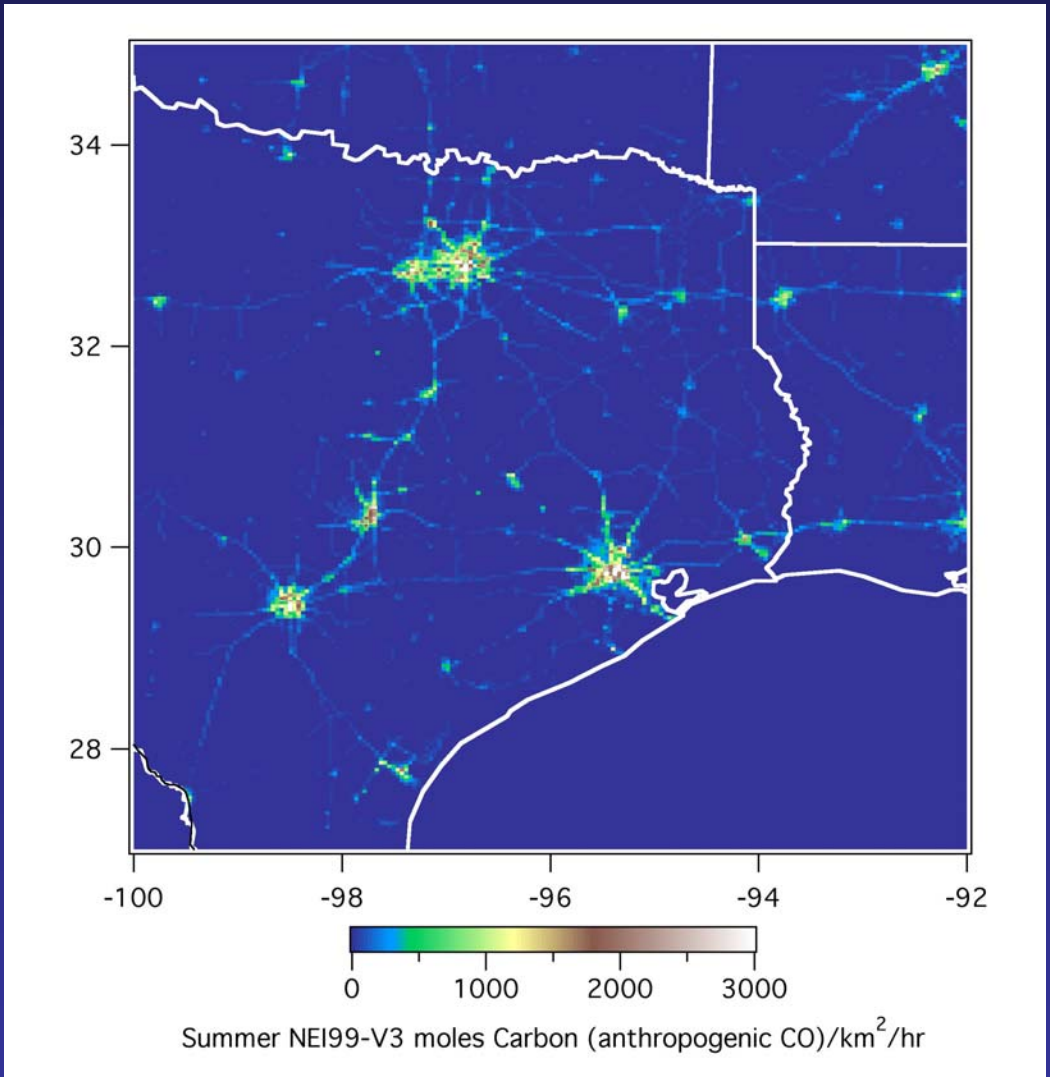


Warneke et al 2007

Inventory:

Houston (and other US cities) Urban VOC emission ratios do not compare well with inventory

CO/VOC Emissions Inventory



- assume CO emissions are accurate (see G. Frost talk)
- VOC emissions from VOC/CO ratios

Summary Urban VOC Emissions

Urban area of Houston has comparable VOC emission ratios as measured in other US cities

Houston (and other cities) urban VOC emission ratios do not compare well with a commonly used inventory

Reactivity of Urban VOCs

Reactivity or $OH_{loss\ rate}$: important for possible ozone production

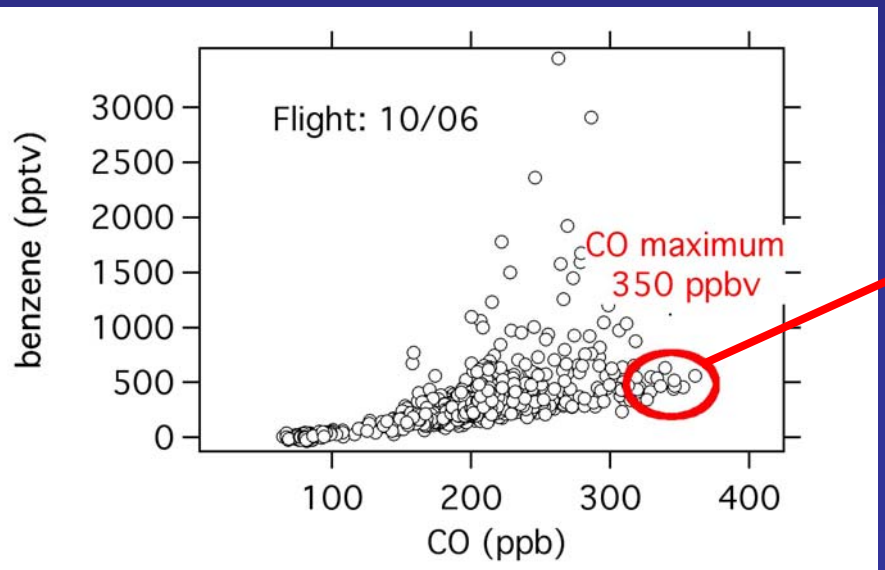
$$OH_{loss\ rate} = VOC * k_{OH}$$

Urban VOC reactivity

CO is an urban tracer (assume industrial CO emissions small)

VOC Emission ratios with CO in Houston

$$\text{urban } OH_{loss\ rate} = (CO - CO_{bg}) * ER_{VOC\text{-}CO} * k_{OH(VOC)}$$

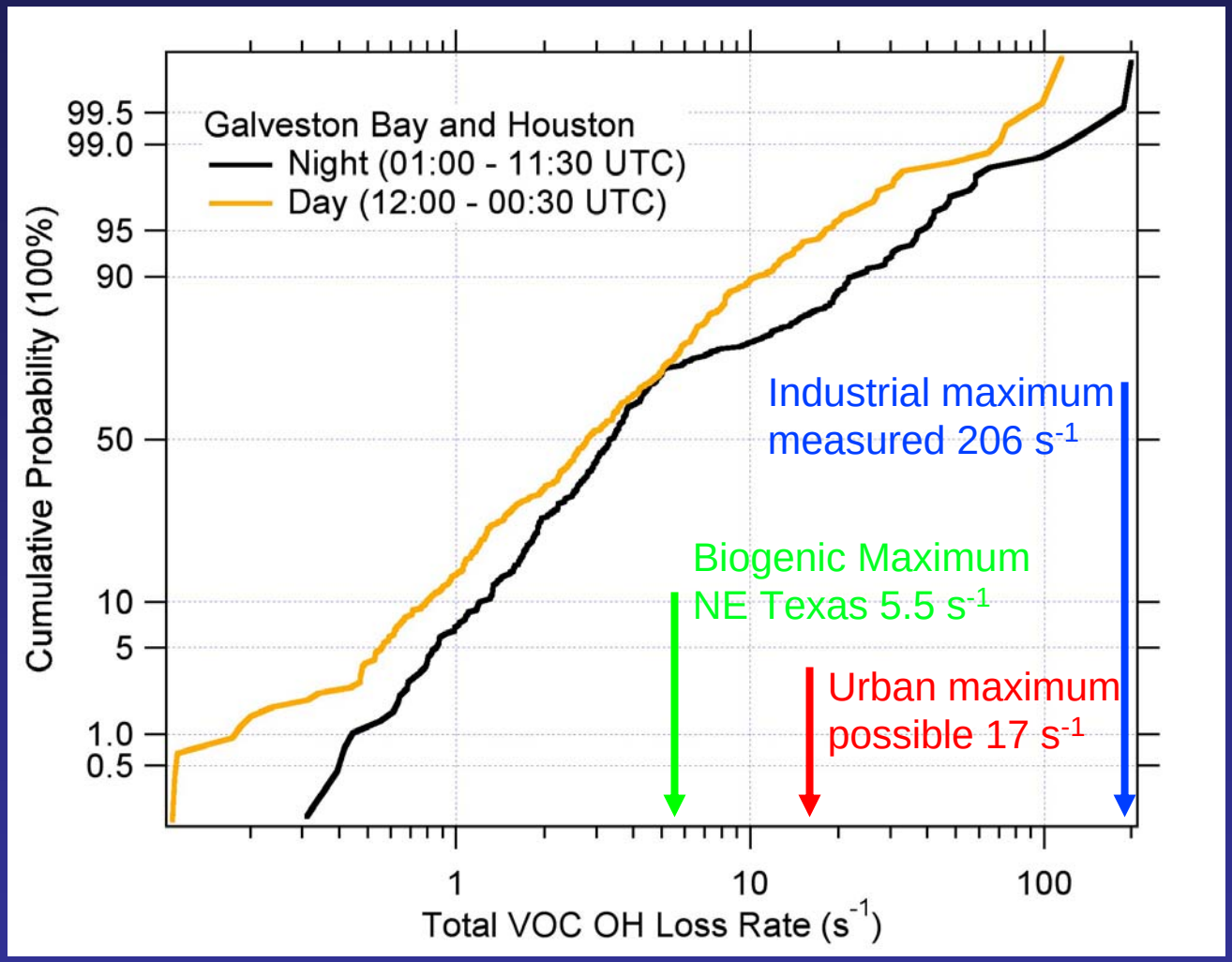


Maximum urban CO for all flights

$\Rightarrow$

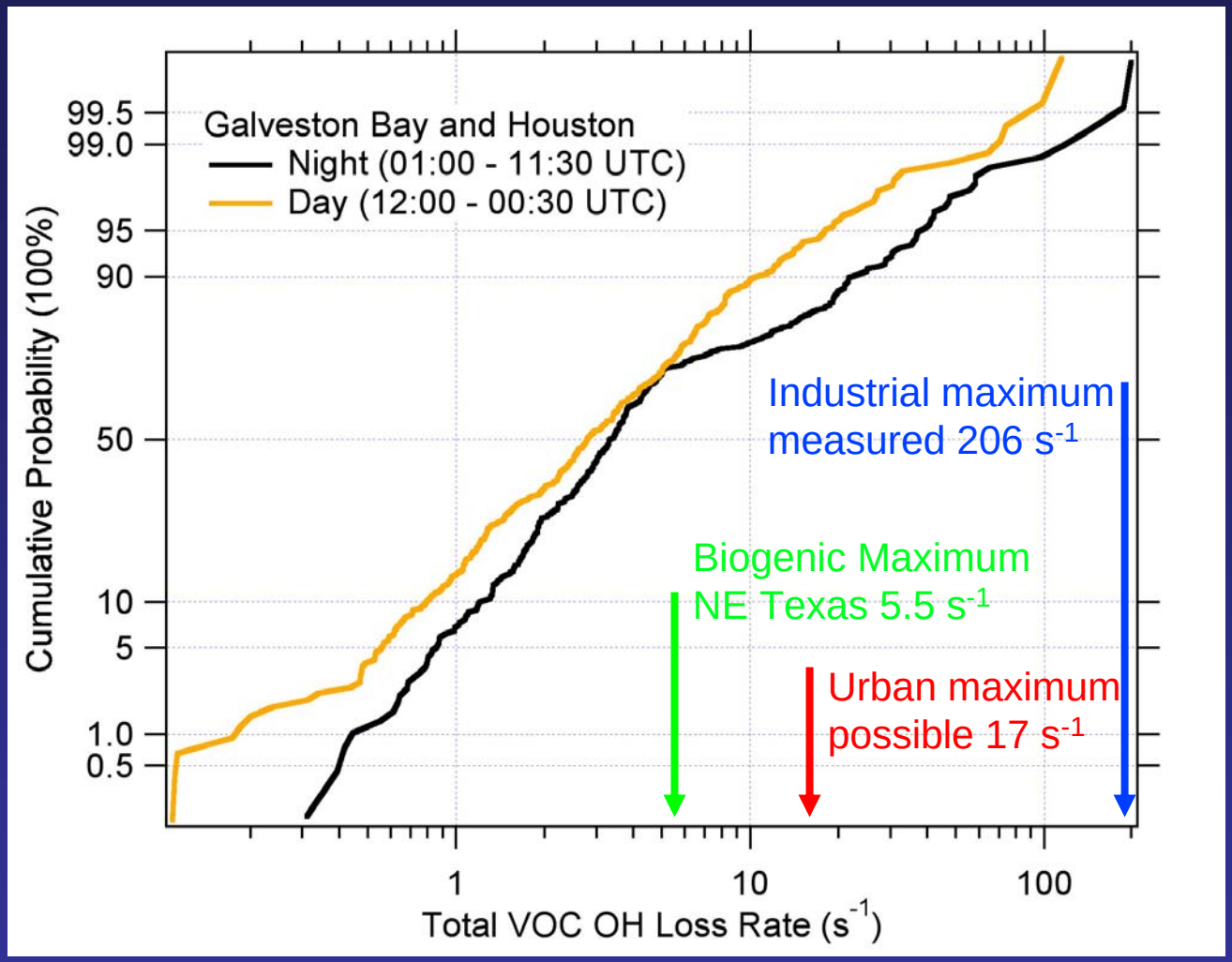
Maximum urban $OH_{loss\ rate}$

Comparison with Industrial Reactivity



- reactivity probability plot from NOAA Ronald H. Brown measurements
- using highest measured CO and emission ratios ⇒ urban maximum
- maximum measured biogenic reactivity: NE Texas

Comparison with Industrial Reactivity



Industrial emissions can cause at least 10 times larger VOC reactivity than urban or biogenic emissions

Summary

- Biogenic VOC emissions compare reasonably well with BEIS3 inventory
- Urban VOC emissions ratios from Houston and Dallas are similar to other US cities
- Urban VOC emission ratios do not compare very well with inventory
- Industrial VOC emissions result in much larger reactivities than possible from biogenic and urban emissions

Thanks to

- Joost de Gouw, Lori Del Negro: PTR-MS, LPAS
- Elliot Atlas: WAS
- Stu McKeen: BEIS and NEI
- Jerome Brioude: FLEXPART
- Greg Frost: point sources emissions
- John Holloway: CO
- Harald Stark: j values, PAR
- Tom Ryerson: NO_2
- Jessica Gilman, Bill Kuster, Dan Welsh-Bon, Paul Goldan: RHB VOC data
- Fred Fehsenfeld, Michael Trainer, Jim Meagher, Ravishankara