Survey of Trace Organic Gas Analyzer (TOGA) Measurements (and others) of VOCs During MIRAGE

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Outline

•Prominent VOCs measured on C-130 (abundance and reactivity)

•Determination of emission ratios
what do these tell us – contrast with NA, T1, ARI

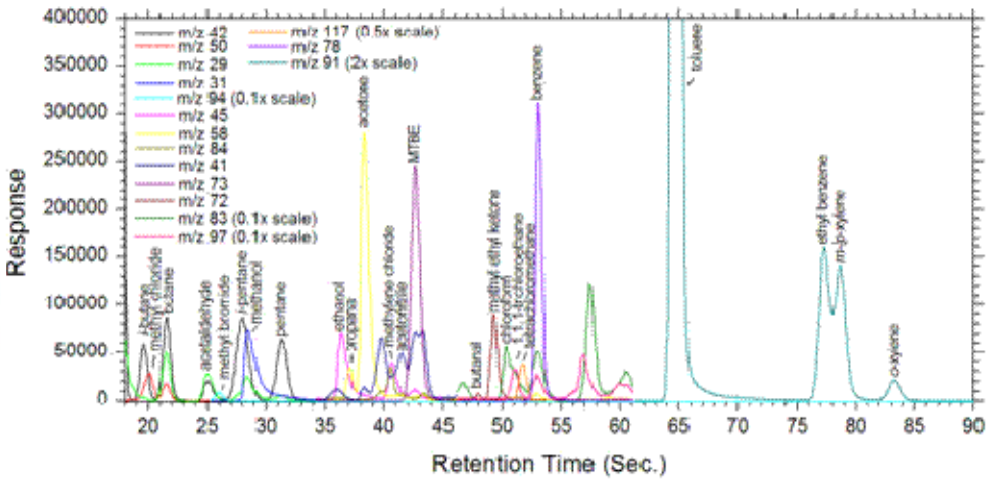
•Use ERs to look more closely at plume make-up and overall MCMA characteristics

TOGA – trace organics analyzer
MIRAGE/IMPEX

- GC-MS – Based System - ~35 compounds HCs, CFCs, OVOCs,
- e.g, methanol, toluene, benzene, toluene, mtbe, acetonitrile, etc.

- Chromatographically separated – mass selected

- All species collected simultaneously



MILAGRO
Megacity Initiative - Local and Global Research Observations
MIRAGE-Mex
MAX-Mex
INTEX-B
MCMA

INTERCONTINENTAL CHEMICAL TRANSPORT EXPERIMENT
INTEX-B
NASA
SPRING 2006

Mexico City VOCs

Primary Sources (Direct Emission)	
Biomass Burning	NMHCs, OVOCs
Vegetation	Isoprene, methanol, etc
Auto Emissions	NMHCs, OVOCs
Industrial Emissions	Toluene, MEK, etc
Non-industrial	???? – LPG, Household fires, etc.

Secondary Sources:

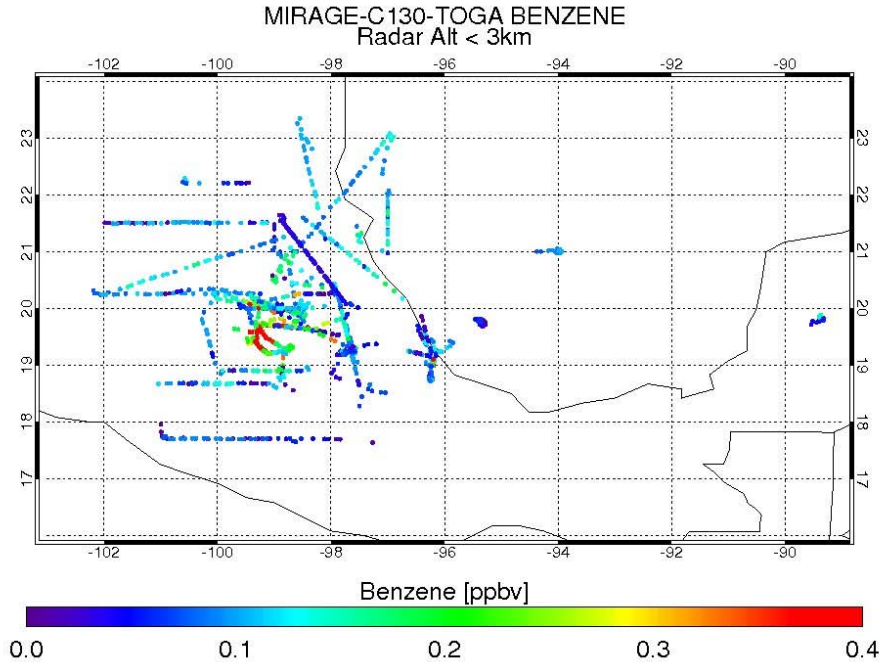
Chemical formation – via OH, O_3, NO_3

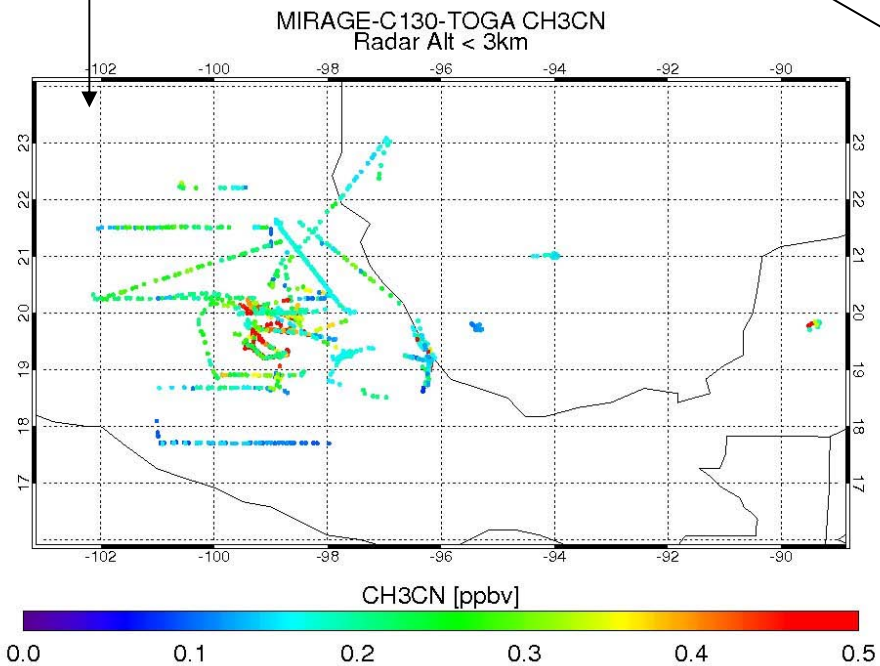
C-130: Measurement of various Species along flight tracks

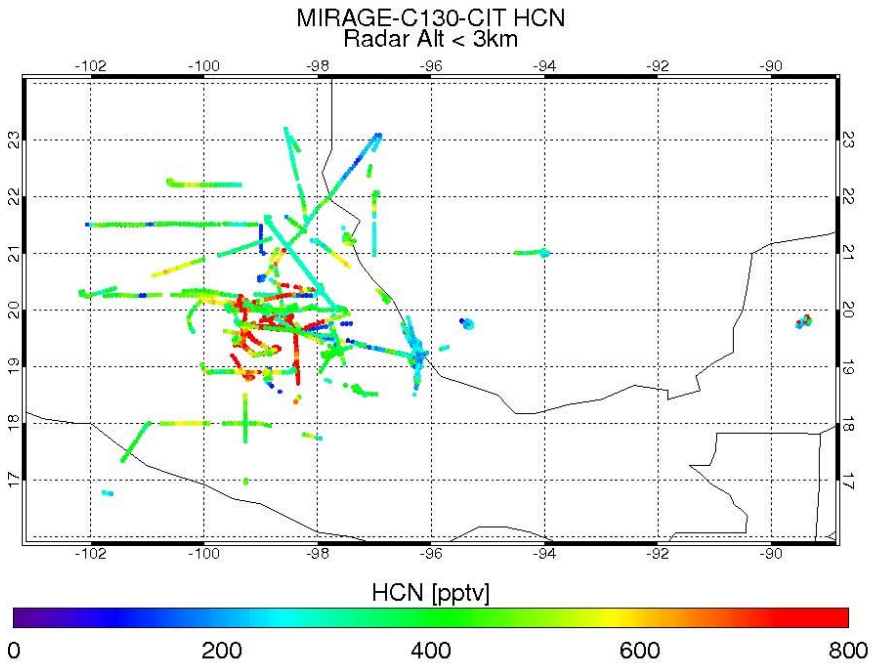
Benzene

Acetonitrile

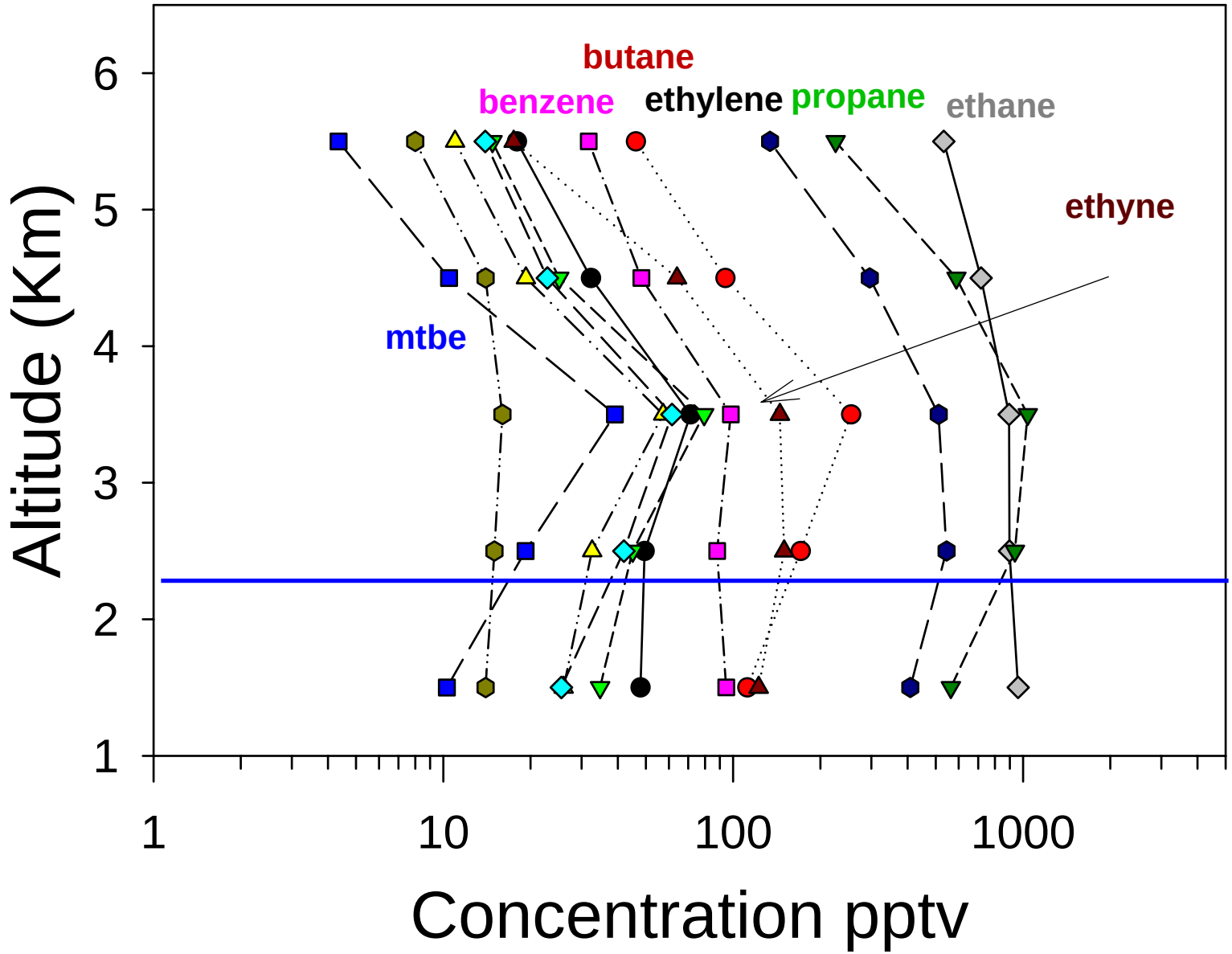
HCN (Caltech)

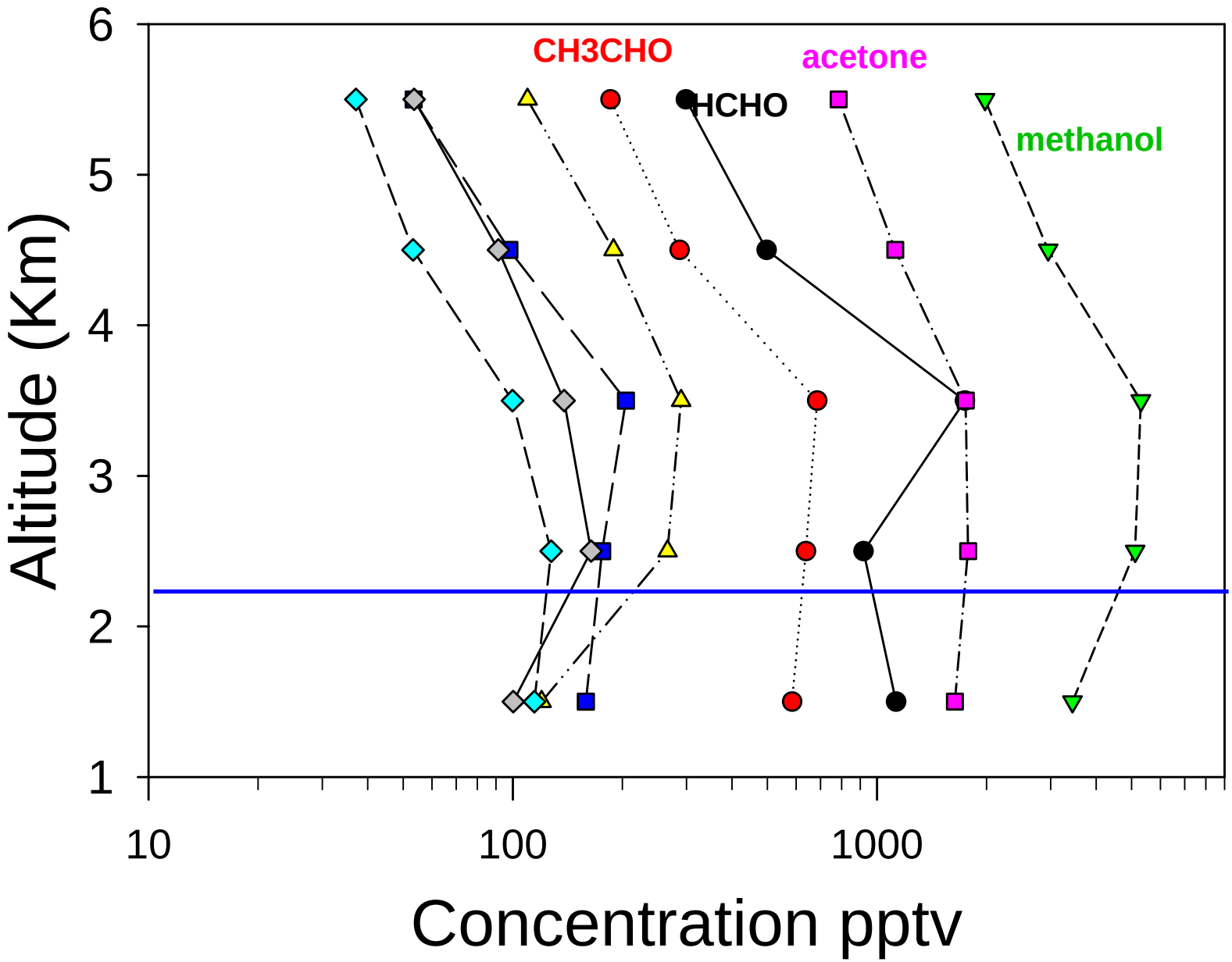




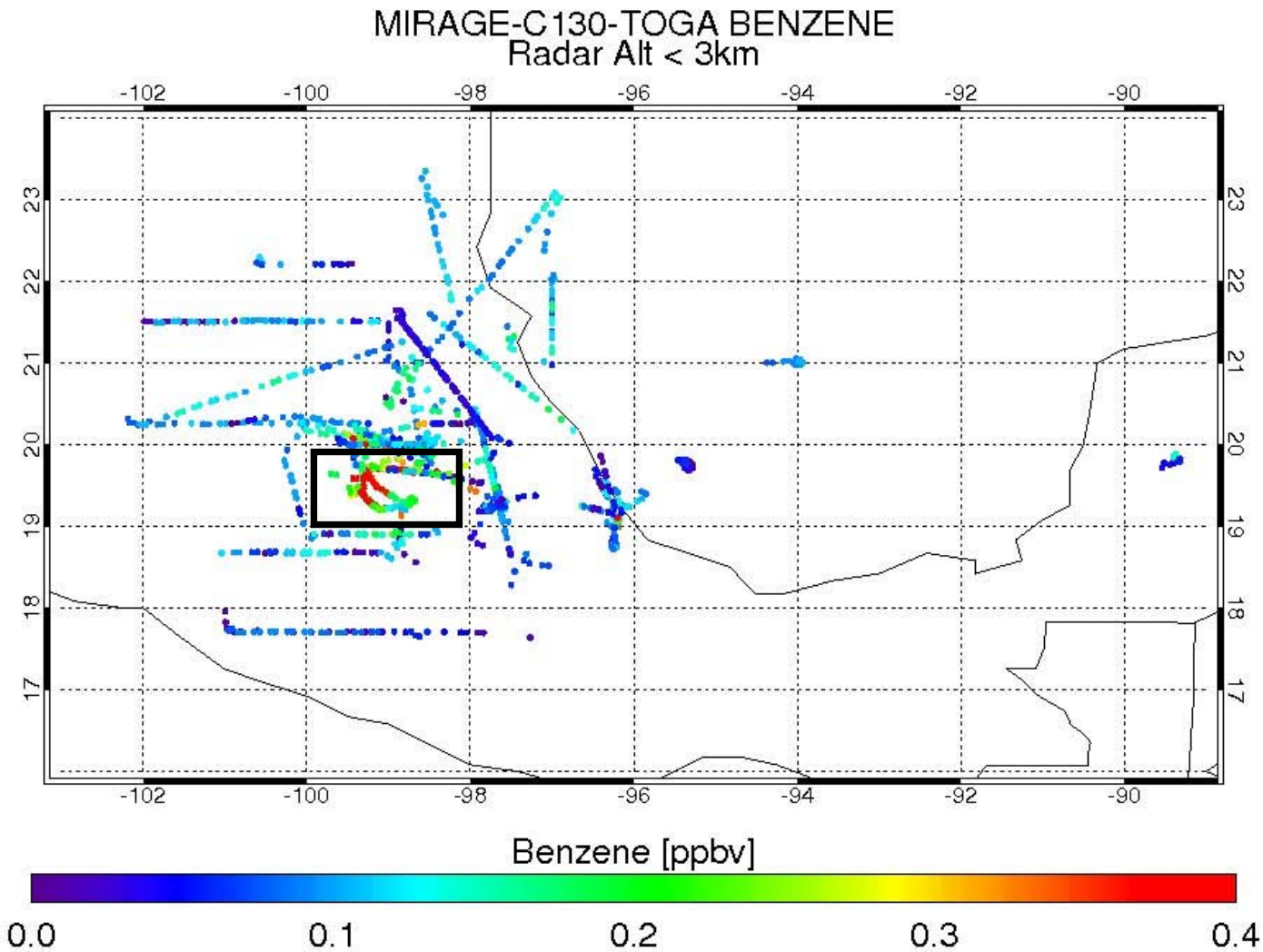


Median Concentrations NMHCs – Whole Study
TOGA + UCI measurements

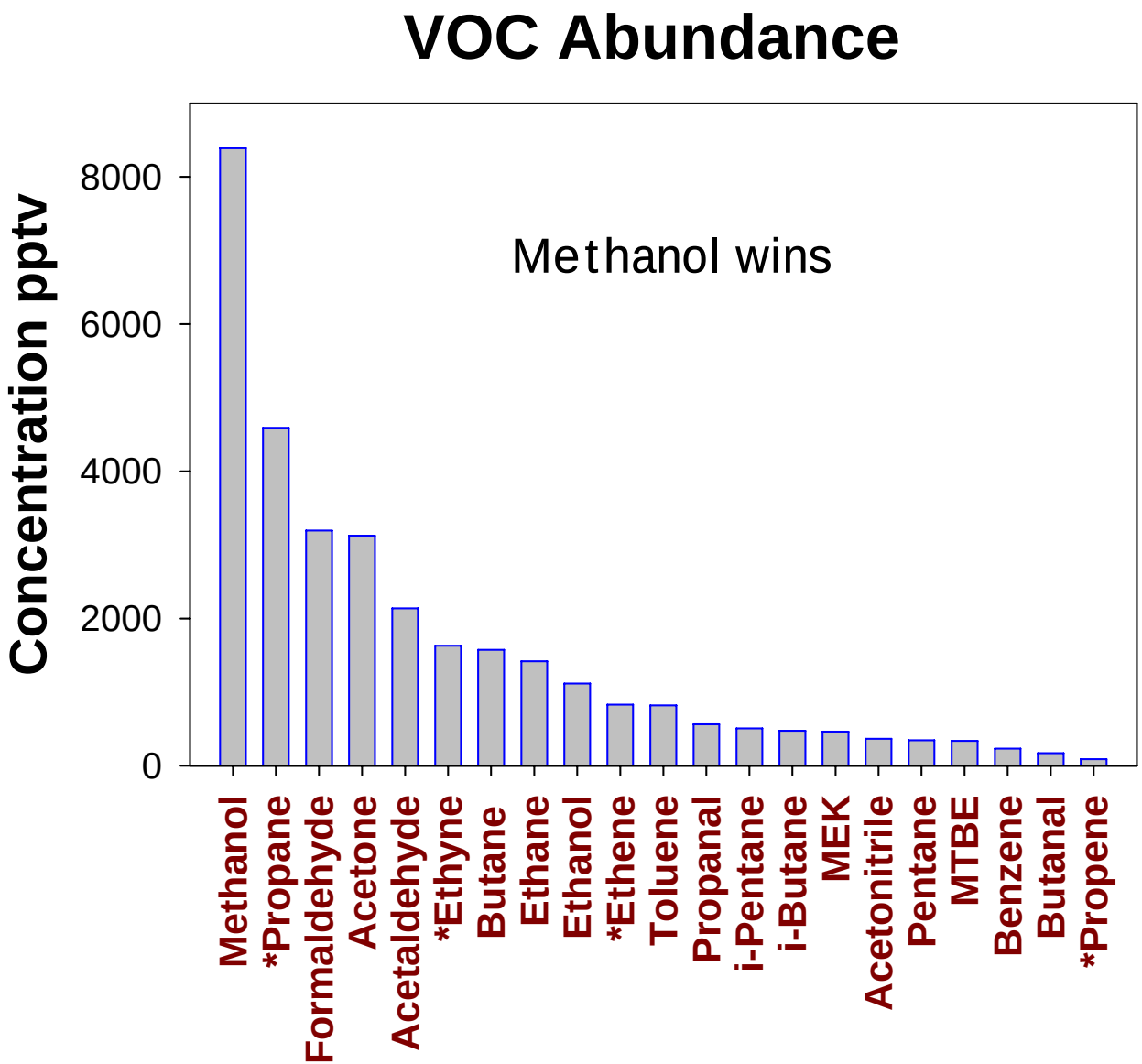



Median Concentrations OVOCs – Whole Study
TOGA + Fried (HCHO)
CH3CHO
acetone
HCHO
methanol
Altitude (Km)
6
5
4
3
2
1
10
100
1000
Concentration pptv

Define Mexico City "Box"



VOC abundance in Mexico City “box”

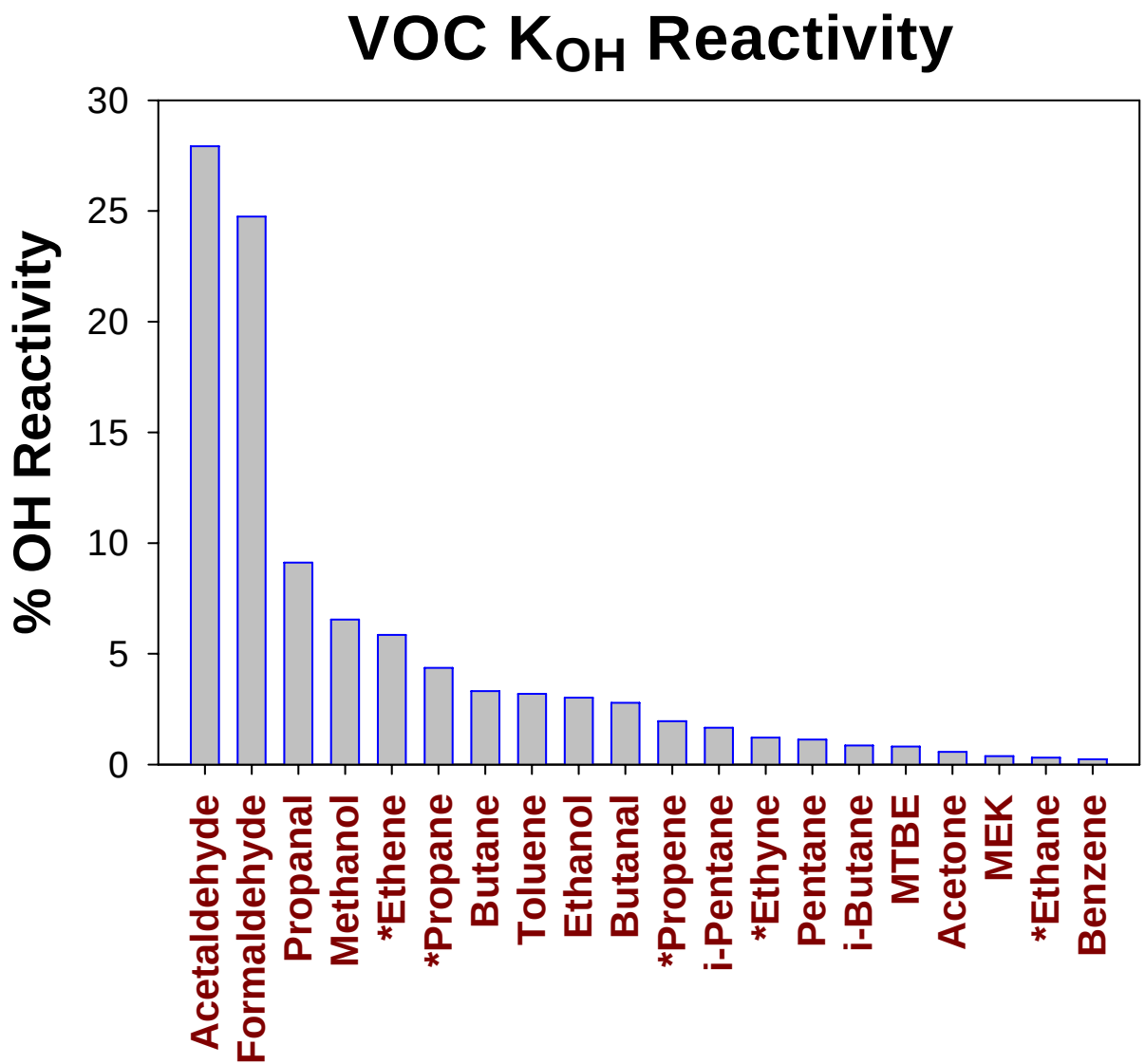


VOC Reactivity in box:

C-130 Measurements

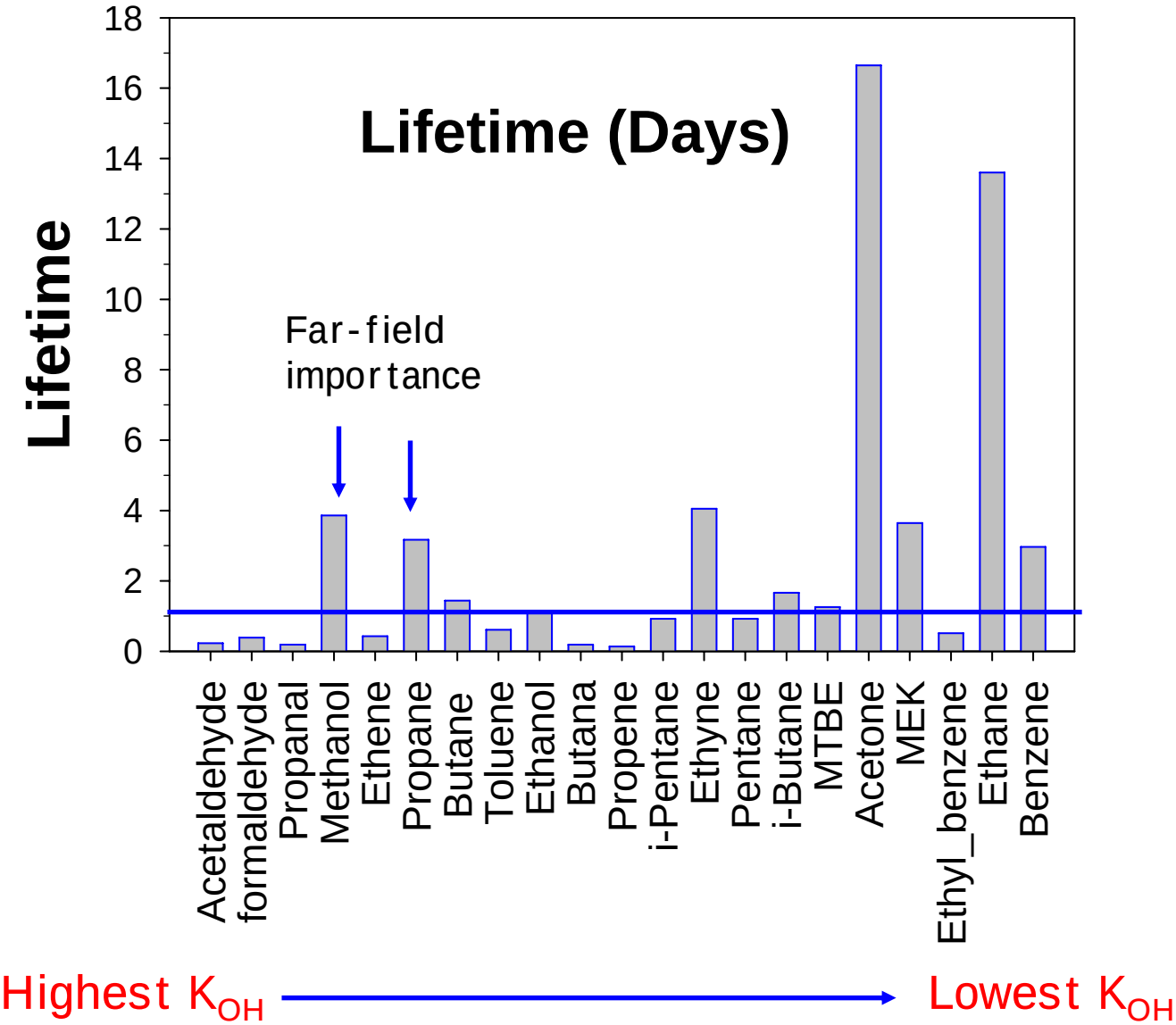
1) Acetaldehyde
2) Formaldehyde*
3) Propanal
4) Methanol
5) Ethene**
6) Propane
7) Butane
8) Toluene
9) Ethanol
10) Butanal
11) Propene**

* Fried, Weibring
** Blake



- Ignore photolysis

- Most VOC reactivity (> 80%) from species with lifetime < 1 day

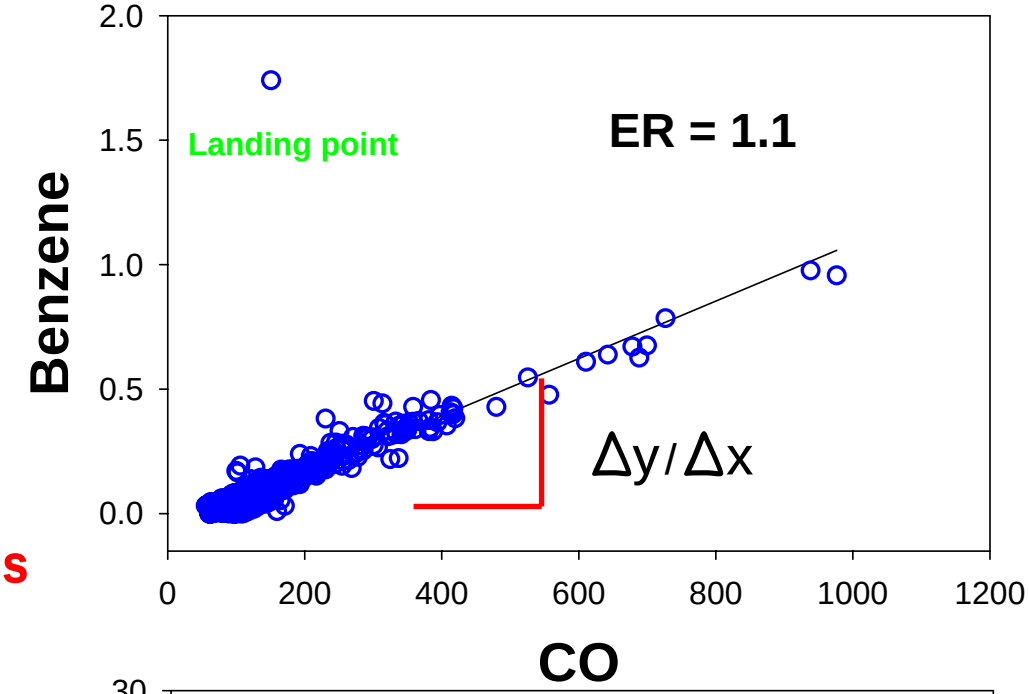


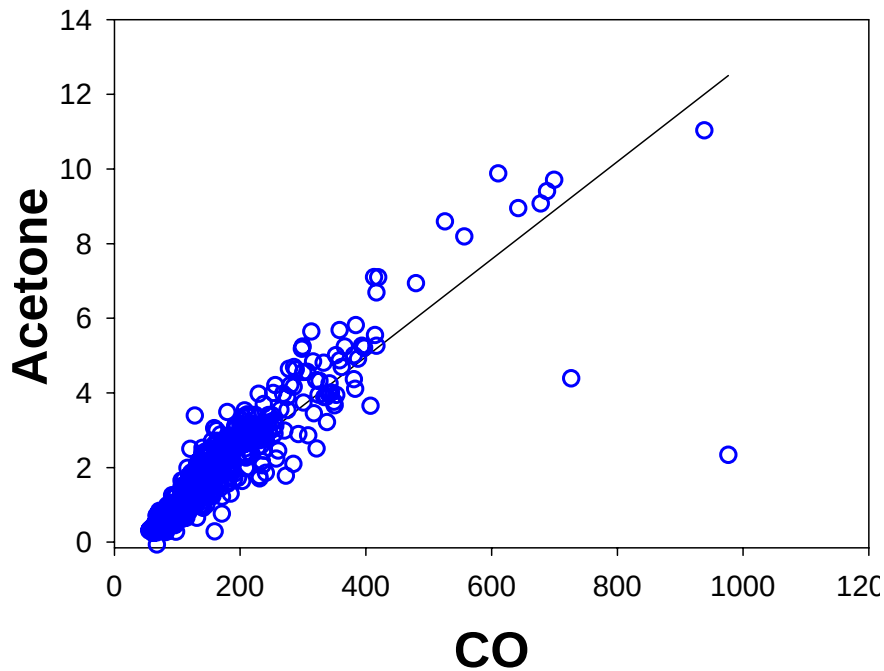
Photochemical lifetime calculation based on [OH] = $4X10^6$ (daytime = 12 hours)

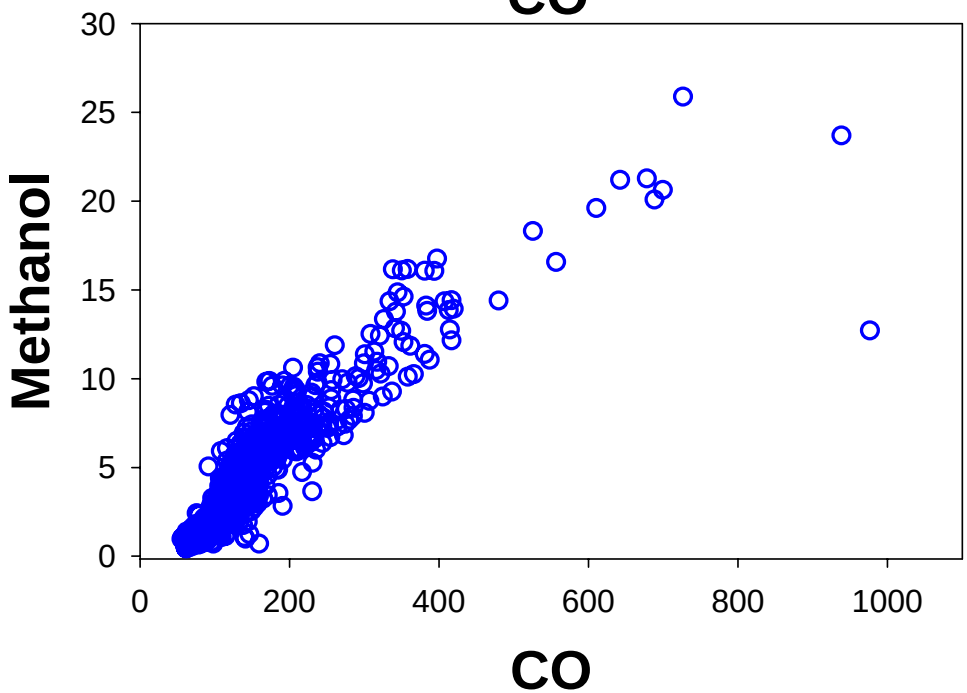
TOGA Data – determination of emission ratios

pptv/ppbv

For shorter lived species – mtbe filter fro fresh emissions







Urban Emission ratios:

ΔVOC/ΔCO (ppt/ppb)

Compare MCMA urban emission ratios w/ recent measurements in NA*

In general: oxygenates higher, low MW HCs higher, MCMA more like LA than NE

Possible reasons:

1) Combustion efficiency?

2) LPG – clear signature

* *Warneke et al., JGR, accepted*

	C-130	Warneke et al.*	
Compound	**Urban**	**2004 NE**	**LA**
HCN	0.6		
Formaldehyde	16.0		
Acetaldehyde	15.5	0.7	9.7
Methanol	31.0	4.0	8.4
i-Butane	4.9	1.0	2.6
Butane	14.9	1.7	5.4
i-Pentane	4.5	4.0	6.3
Pentane	3.3	1.6	3.0
Ethanol	10.5	5.8	
Propanal	3.6	0.7	
Acetone	12.8	2.9	14.2
Acetonitrile	0.3		
Butanal	1.3		
MEK	4.3	0.8	1.5
MTBE	3.2		
Benzene	1.2	0.6	1.1
Toluene	6.2	2.6	3.5
Ethyl_benzene	1.2	0.3	

Urban and Fire Emission Ratios

ΔVOC/ΔCO (ppt/ppb)

Compare urban emission ratios to fire emission ratios + literature*

Some species have very different ratios for urban vs. fire

e.g., pentanes

[1]*Friedli et al., 1999*
[2] *Andreae and Merlet, 2001*

	C-130	Warneke et al.[3]		C-130		
Compound	**Urban**	**2004 NE**	**LA**	**Fire**	**lit[1]**	**lit[2]**
HCN	0.6			12		8
Formaldehyde	16.0					17.45
i-Butane	4.9	1.0	2.6	0.03	0.13	0.09
Butane	14.9	1.7	5.0	0.15	0.46	0.32
i-Pentane	4.5	4.0	6.3	0.01	0.09	0.07
Pentane	3.4	1.6	3.0	0.07	0.21	0.18
Acetaldehyde	15.5	0.7	9.7	7.80	2.70	3.57
Methanol	31.0	4.0	8.4	12.22	2.40	16.36
Ethanol	10.5	5.8	0.0	0.24		0.10
Propanal	3.6	0.7	0.0	1.04	0.12	0.45
Acetone	12.8	2.9	14.0	2.05	2.05	2.26
Acetonitrile	0.3			1.40		1.21
Butanal	1.3					0.73
MEK	4.3	4.0	8.0	0.16	2.60	1.45
Benzene	1.2	0.6	1.1	1.09	1.35	1.68
Toluene	6.2	2.6	3.5	0.30	1.32	1.15
Ethyl_benzene	1.2	0.3	0.0	0.03	0.12	0.10

Fire ERs only

C-130

Compound	Fire	lit[1]	lit[2]
HCN	12.00		5-8
Acetonitrile	1.40		1.21
Acetaldehyde	7.80	2.70	3.57
Methanol	12.22	2.40	16.36
i-Butane	0.03	0.13	0.09
Butane	0.15	0.46	0.32
i-Pentane	0.01	0.09	0.07
Pentane	0.07	0.21	0.18
Ethanol	0.24		0.10
Propanal	1.04	0.12	0.45
Acetone	2.05	2.05	2.26
Butanal			0.73
MEK	0.16	2.60	1.45
MTBE			
Benzene	1.09	1.35	1.68
Toluene	0.30	1.32	1.15

Compare to ground measurements

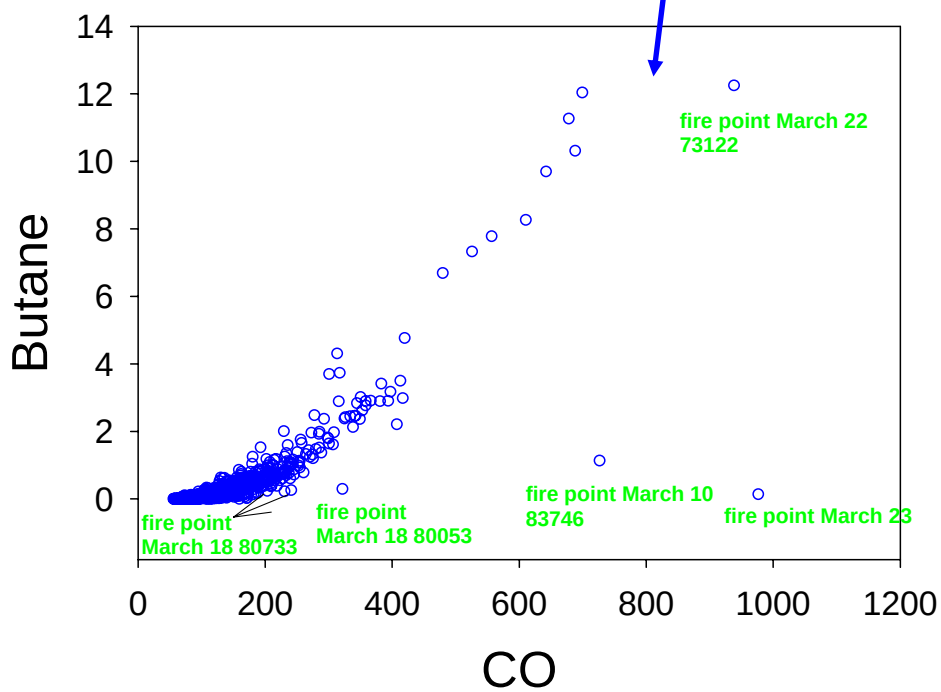
Butane/isobutane 0.33 (Velasco)/0.36 (TOGA)

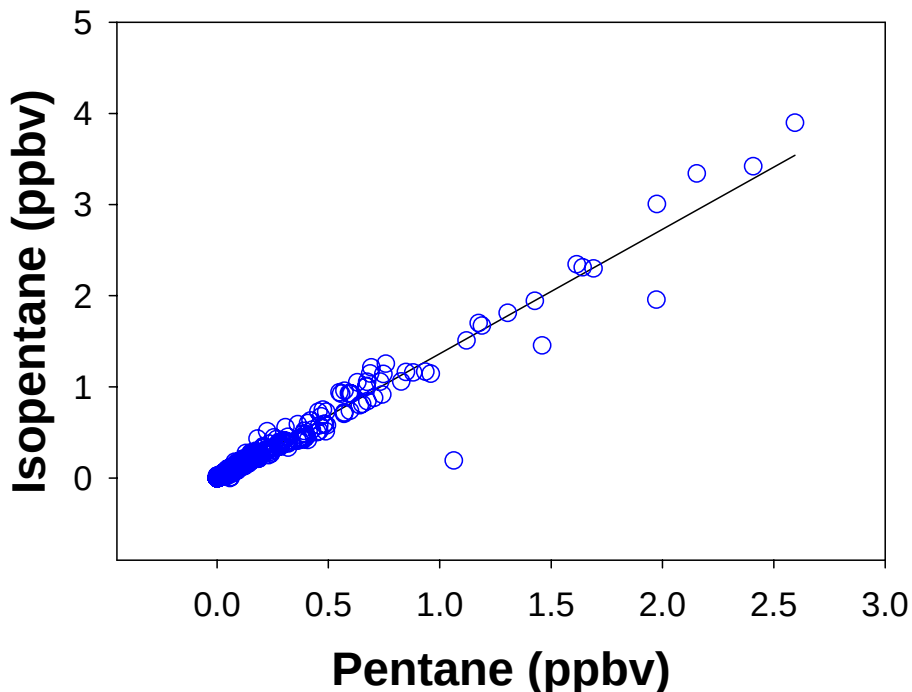
Isopentane/pentane 2.0 (Velasco)/1.4 (TOGA – bottom right)

Toluene/benzene (fresh): 5 (Velasco)/5(TOGA)

Using emission ratios to look at some data

Major fire points fall off trendline – very different ERs





Discussion vis a vis measurements shown at this meeting, etc.

Urban ppt VOC/ppb CO

Species	**C130**	**T1**	**ARI**
HCN	0.6		~ 0.5
CH_3CN	0.2-0.3	0.2	~ 0.15

Discussion: Are these emission ratios different than in US and elsewhere?

If so, what is the reason for the difference? Catalytic converter, no catalyst?

Further discussion points:

Emission ratios from other species derived from different sites/measurements

How well do they compare? Need to look at it more closely

If there are discrepancies, can we resolve them?

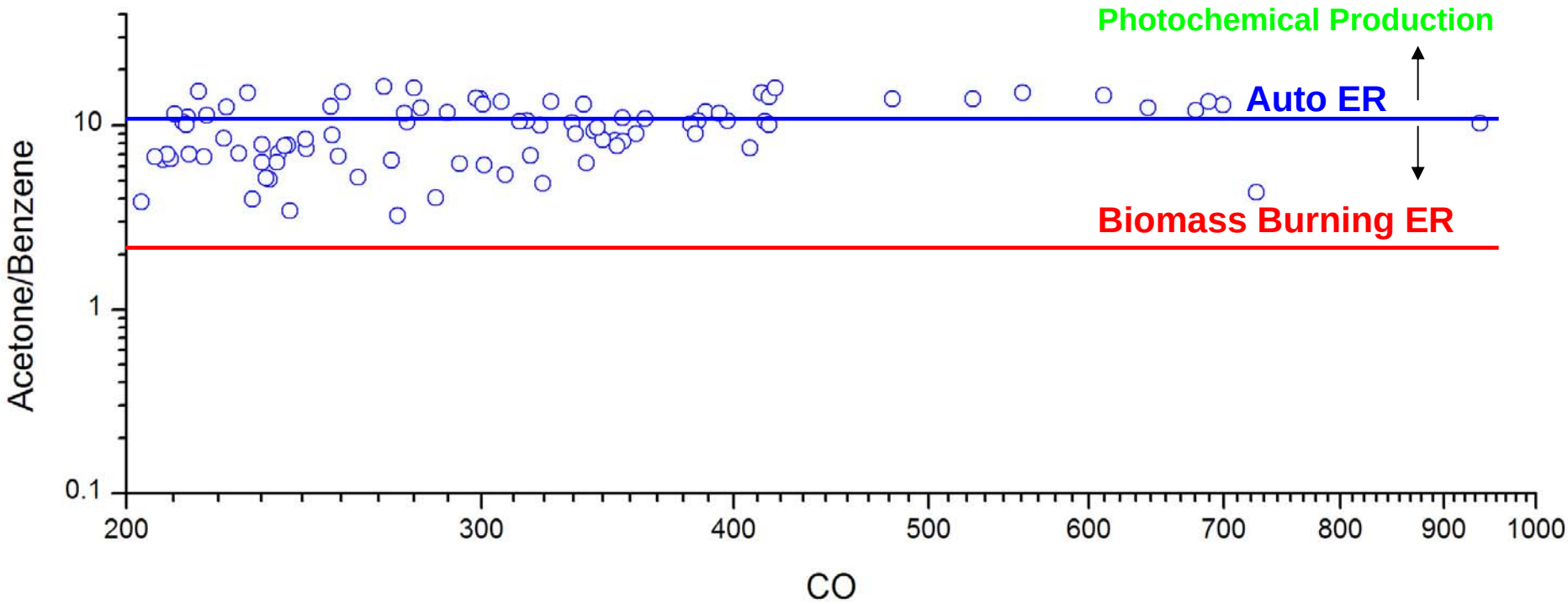
Data that needs a closer look based on talks, my look at posters:

- Acetone/propane C-130, T1, ARI, etc. - does the ratio make sense?

- Methanol – does not seem to make complete sense T1 vs. C130

Using ERs to look at urban vs.BB

Data from Mexico City Basin Showing BB Influence

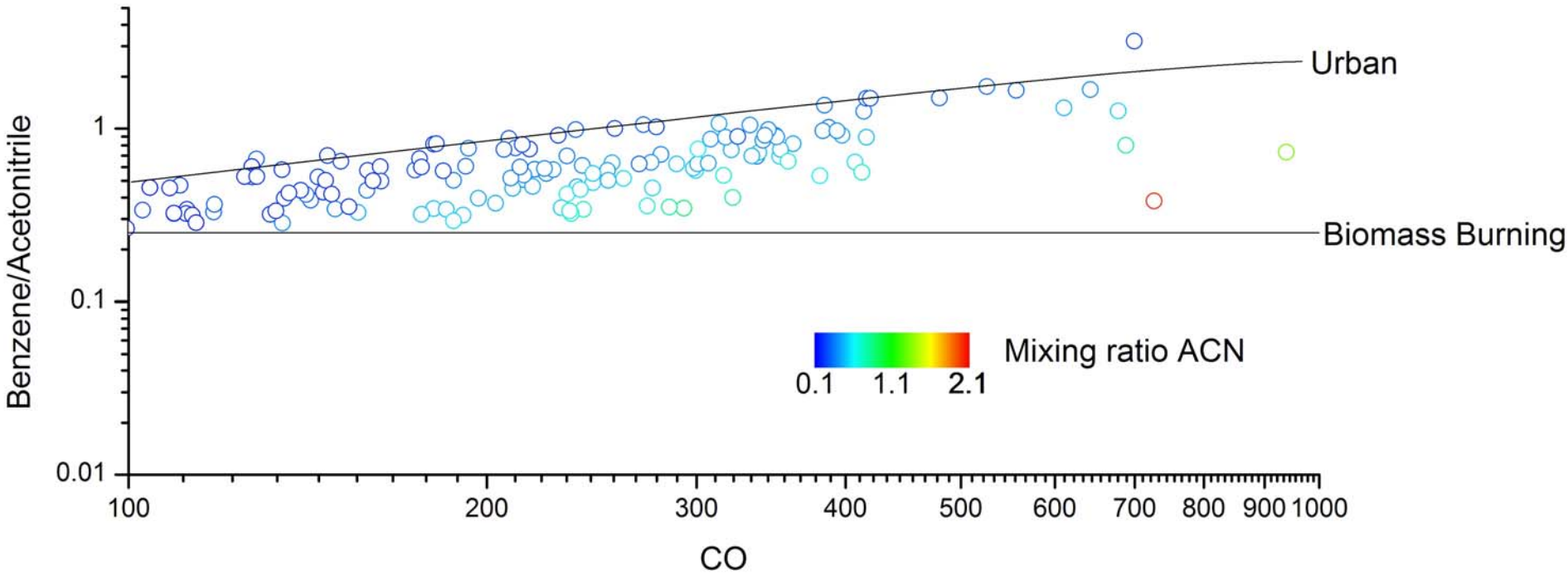


Crounse and Wennberg: Analysis using acetylene/benzene shows significant BB influence in MC basin, Louisa Emmons (modeling)

Conclusions/Hypotheses

- Most reactive measured VOCs are low MW NMHC and OVOCs
- Ethene → $HCHO + HO_2$
- Propene → $CH_3CHO + HO_2$
- HCHO →
- CH_3CHO →
- Methanol more "important" than propane (C-130, Blake and Rowland, 1995) – each more important in "far field"
- Lifetimes < day - each day chemically "separate" from next in MCMA
- Relatively high oxygenated content in VOC mixture (ERs) – implications for aerosols, etc.
- BB plays some role in MC air pollution (DeCarlo, Jimenez, de Gouw, Wennberg and Crounse, TOGA – many others – corroborated by TOGA data – how important?

Benzene/Acetontrile ratios in the “box”



Crounse and Wennberg: Analysis using acetylene/benzene shows significant BB influence in MC basin, Louisa Emmons (modeling)

Enhancement Ratios: ΔVOC/ΔCO (pptv/ppbv)

Calculate in a number of ways:

1) Fresh emissions; 2) slope; 3) ΔVOC/ ΔC_2H_2 vs. Photochemical age*:

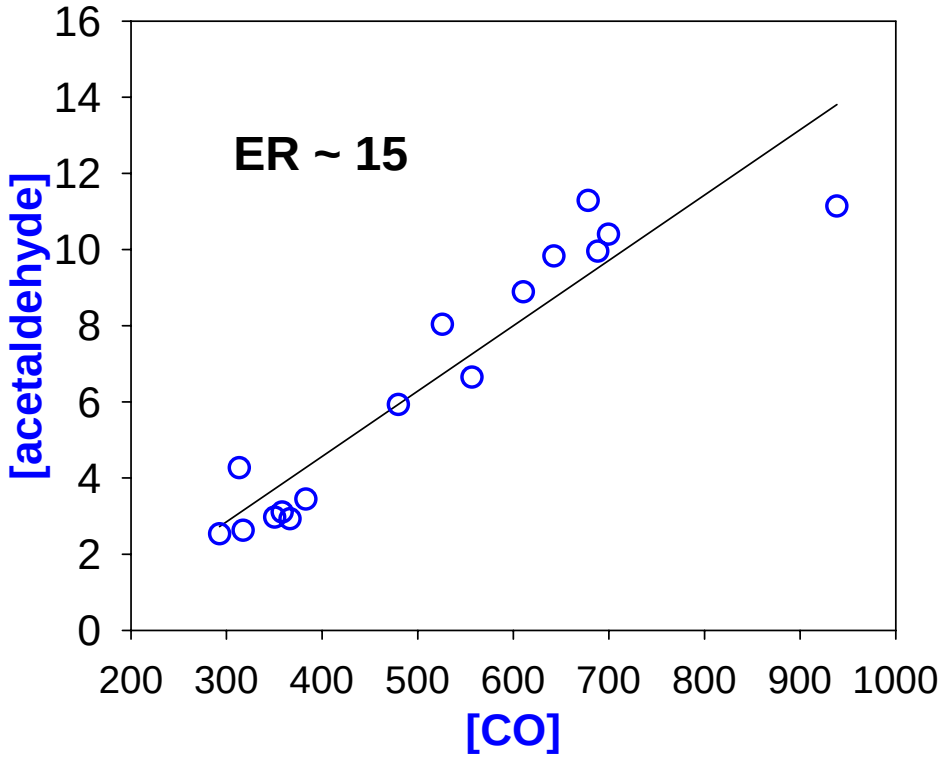
**Warneke et al. JGR, accepted*

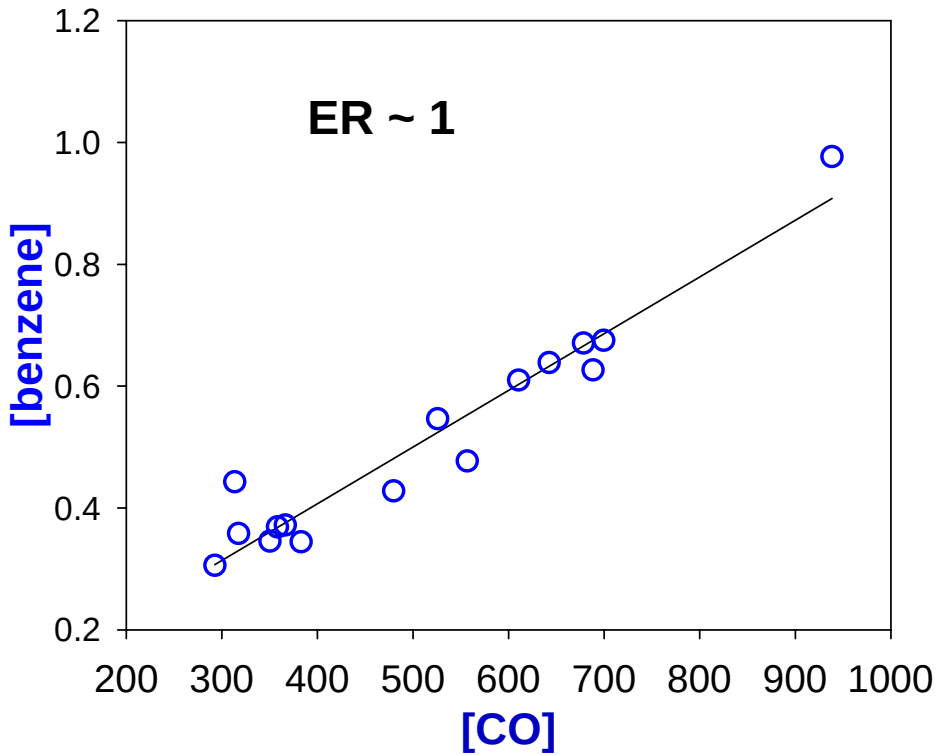
Used to:

- Compare to previous data
- Input into models – emissions data
- Disentangle observed data in terms of emissions

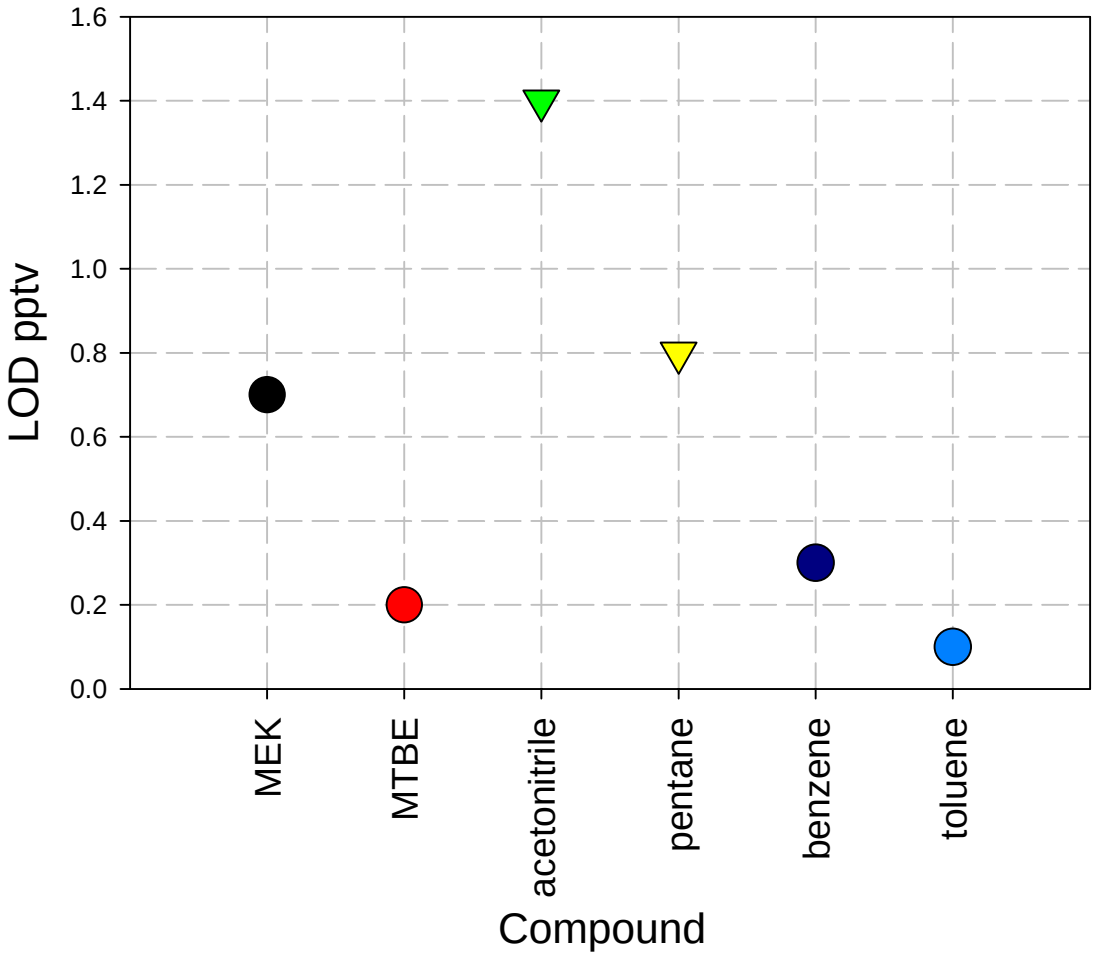
Apply filter for fresh emissions

mtbe> 0.9, toluene/benzene = 5





TOGA – example of detection limits



Mexico City VOCs

Previous studies – numerous

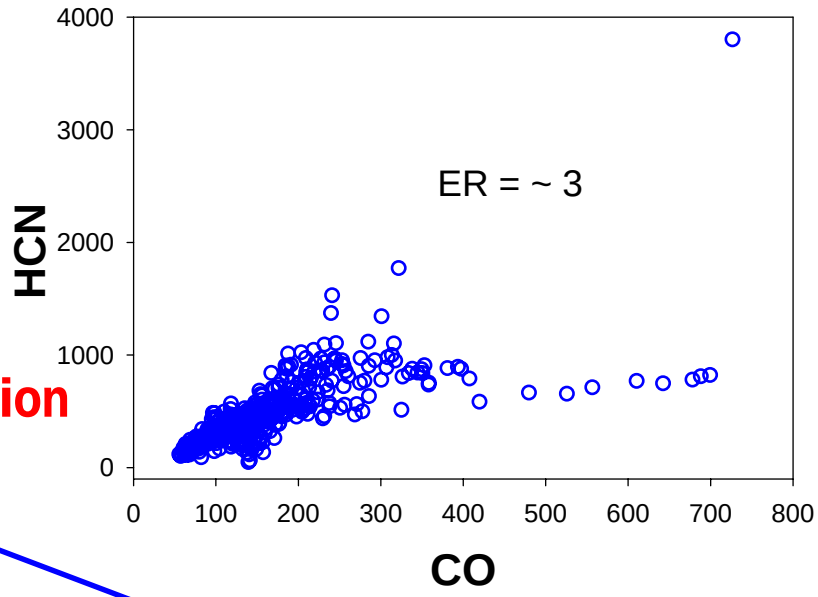
Recently: MCMA 2002 and 2003 campaigns Velasco et al. Atmos. Chem. Phys. Discus., 6, 7563, 2006.

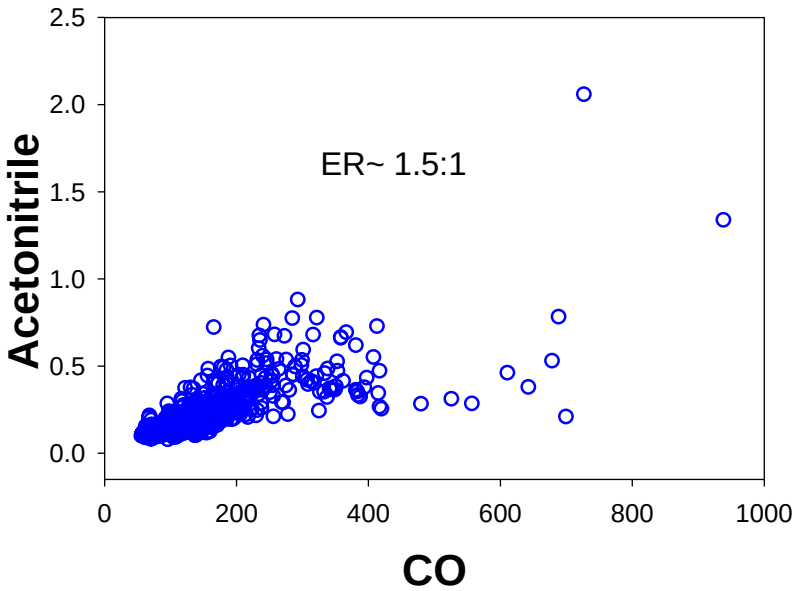
Example of Data:

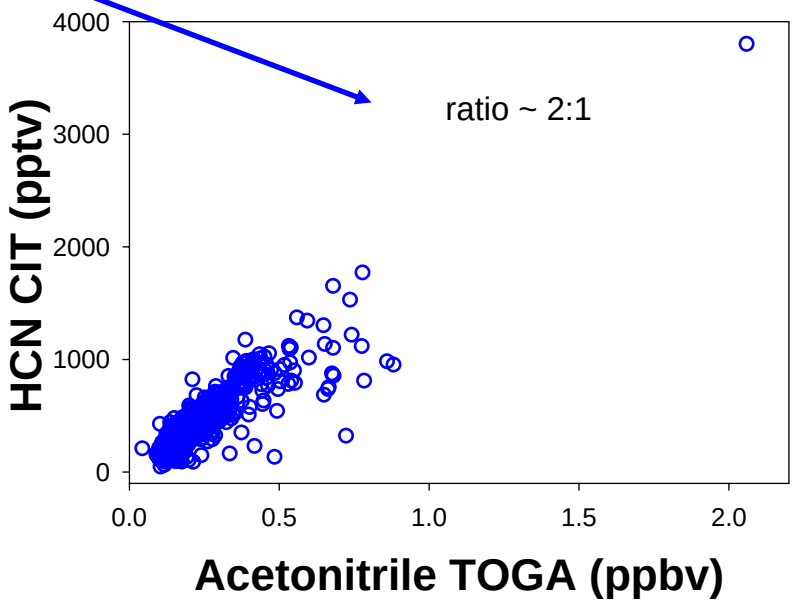
Fire Tracers

Acetonitrile (TOGA)

HCN (Caltech) excellent correlation





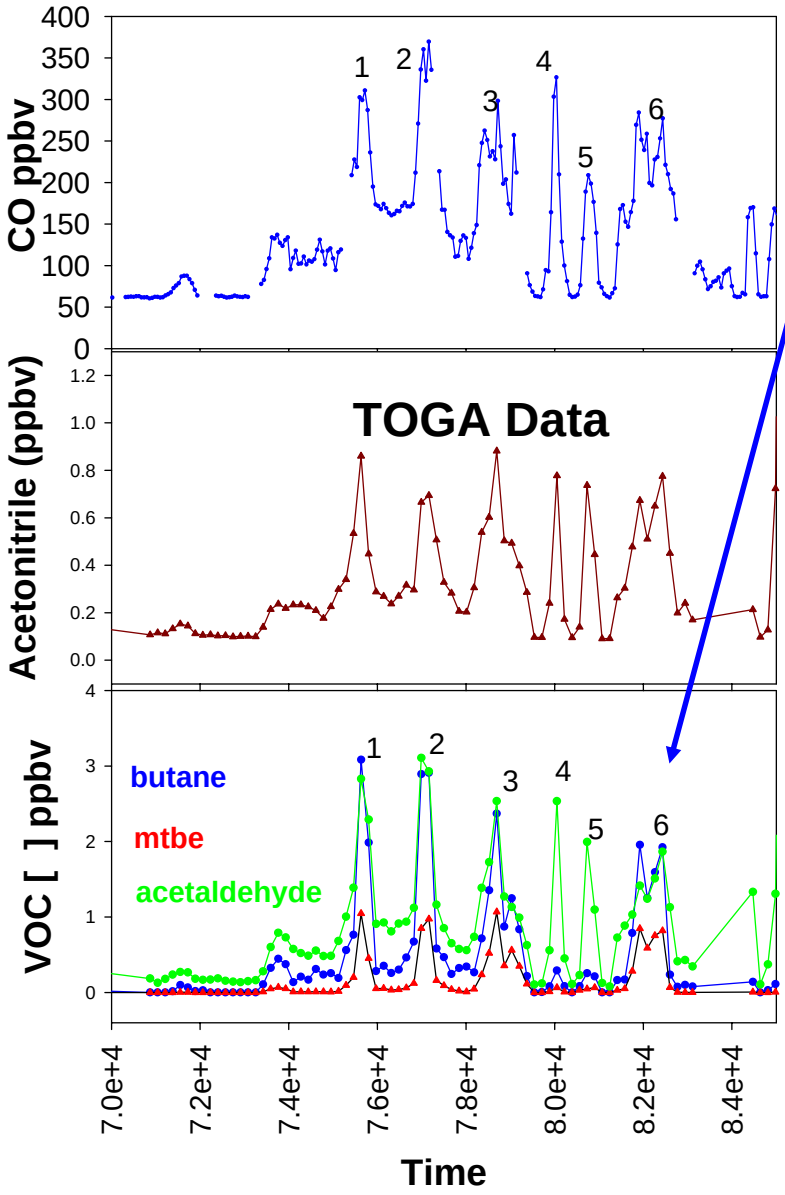


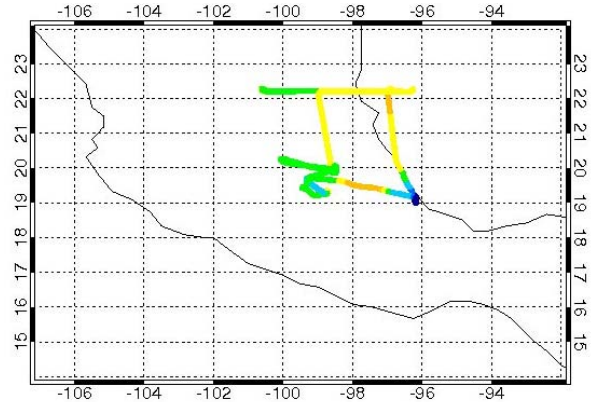
March 18

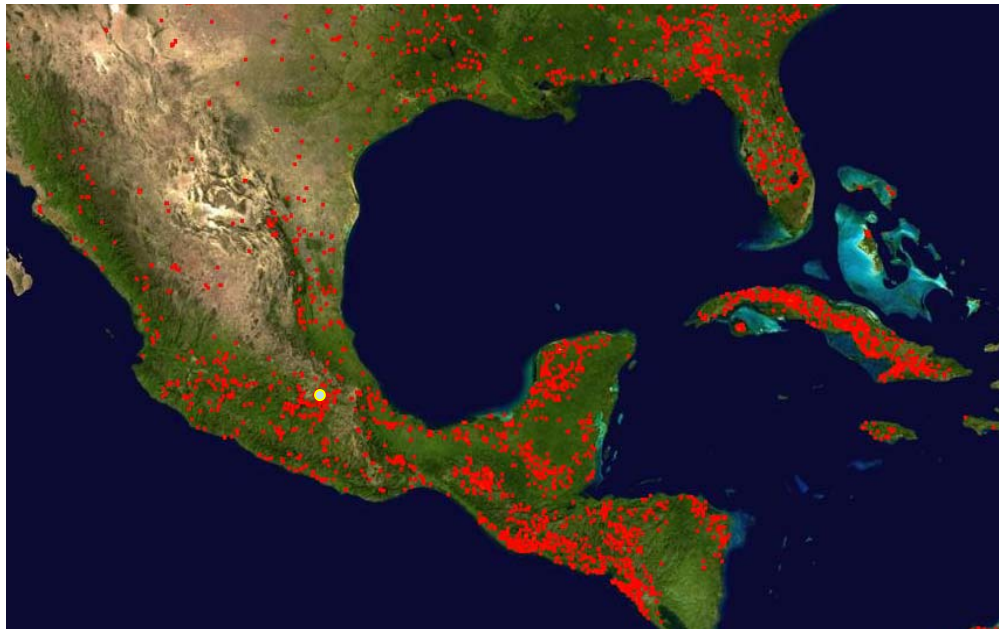
6 plumes: 1-6 – captured by Measurements and model

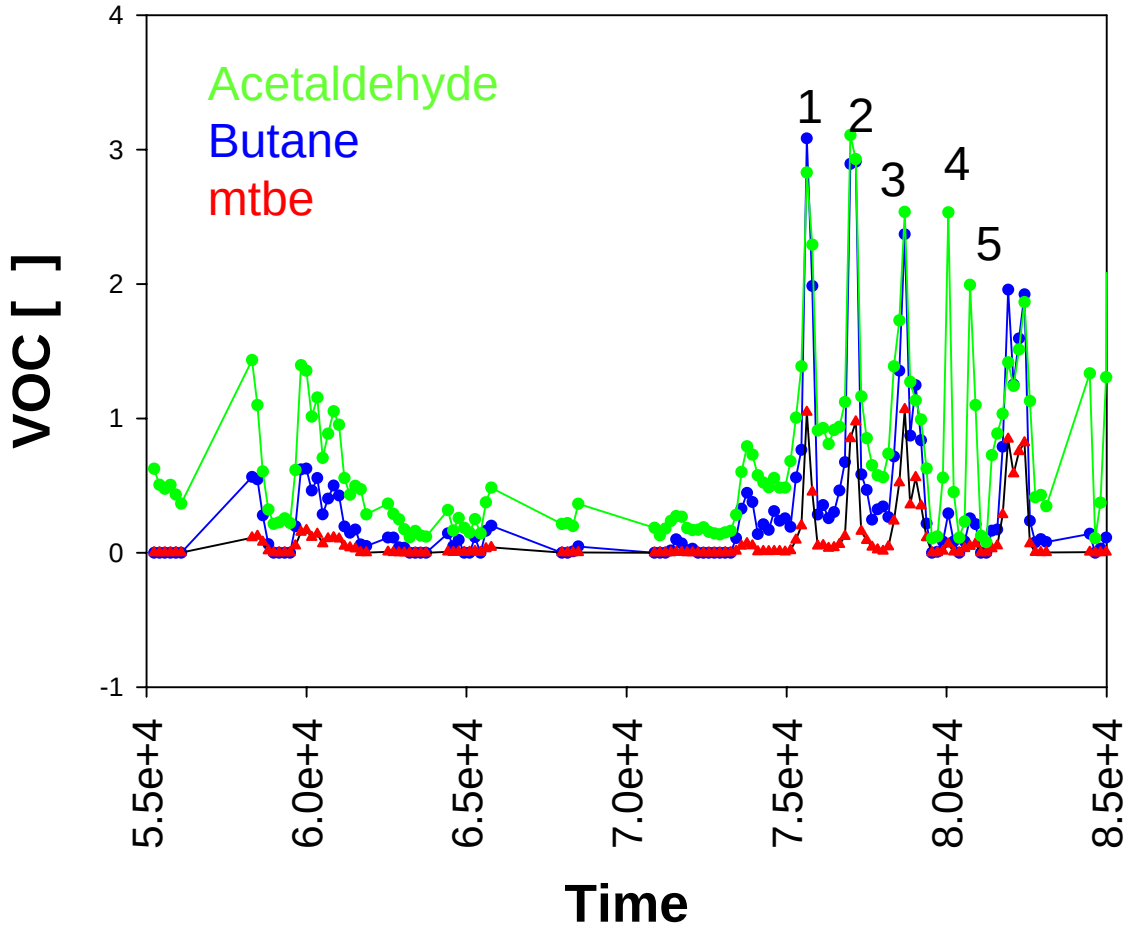
Use TOGA to apportion sources and compare with model

e.g. BB vs. Urban








Acetaldehyde
Butane
mtbe
1
2
3
4
5
VOC [ ]
4
3
2
1
0
-1
5.5e+4
6.0e+4
6.5e+4
7.0e+4
7.5e+4
8.0e+4
8.5e+4
Time