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

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Outline

- What was measured

- Comparison with ground measurements

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

- Determination of emission ratios
  what do these tell us – contrast with NA

- Use ERs to look more closely at plume make-up

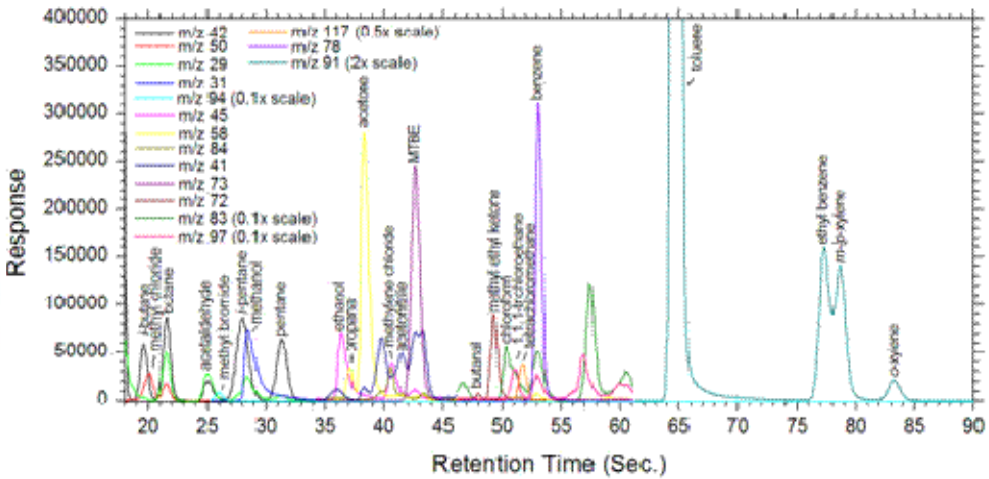
- Future directions

TOGA – trace organics analyzer
MIRAGE/IMPEX

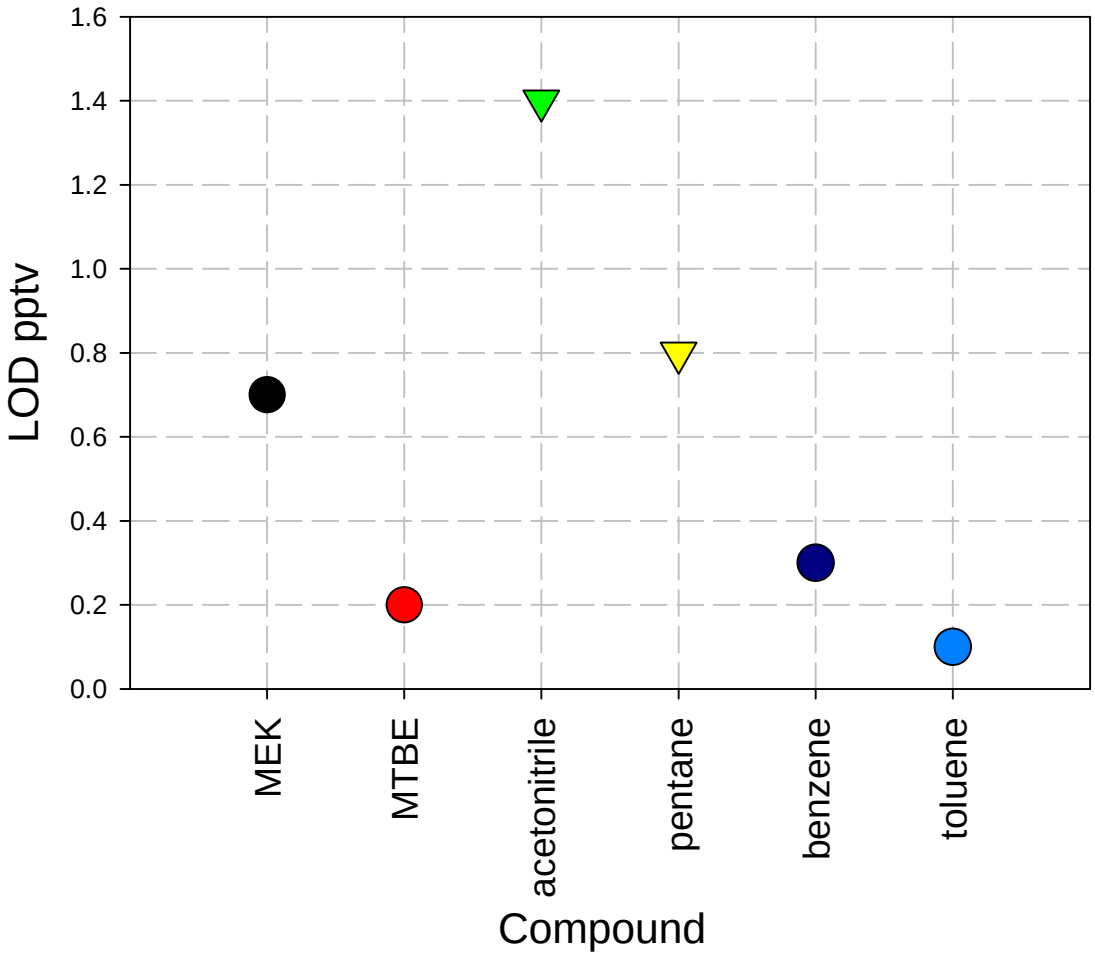
- GC-MS – Based System - ~35 compounds HCs, CFCs, OVOCs,
- e.g, methanol, toluene, benzene, toluene, mtbe, acetonitrile, etc.

- Chromatographically separated – mass selected

- All species collected simultaneously



TOGA – example of detection limits



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

Mexico City VOCs

Previous studies – numerous

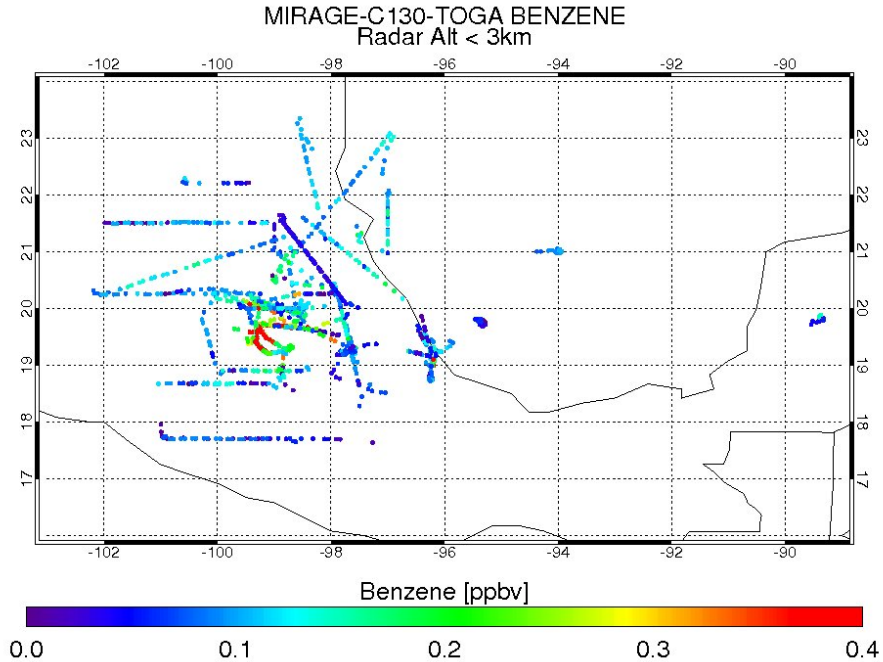
Recently: MCMA 2002 and 2003 campaigns Velasco et al. Atmos. Chem. Phys. Discus., 6, 7563, 2006.

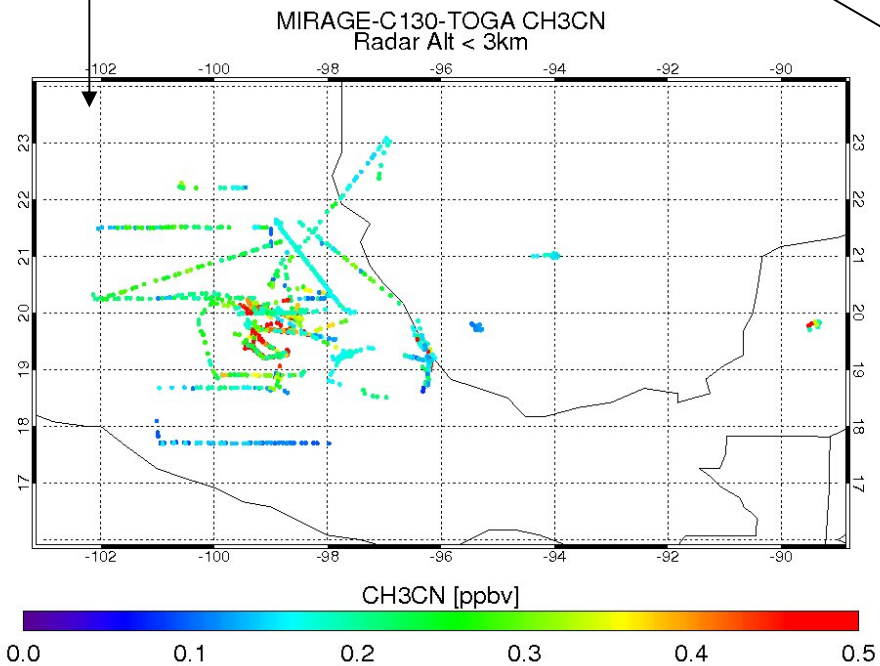
C-130: Measurement of various Species along flight tracks

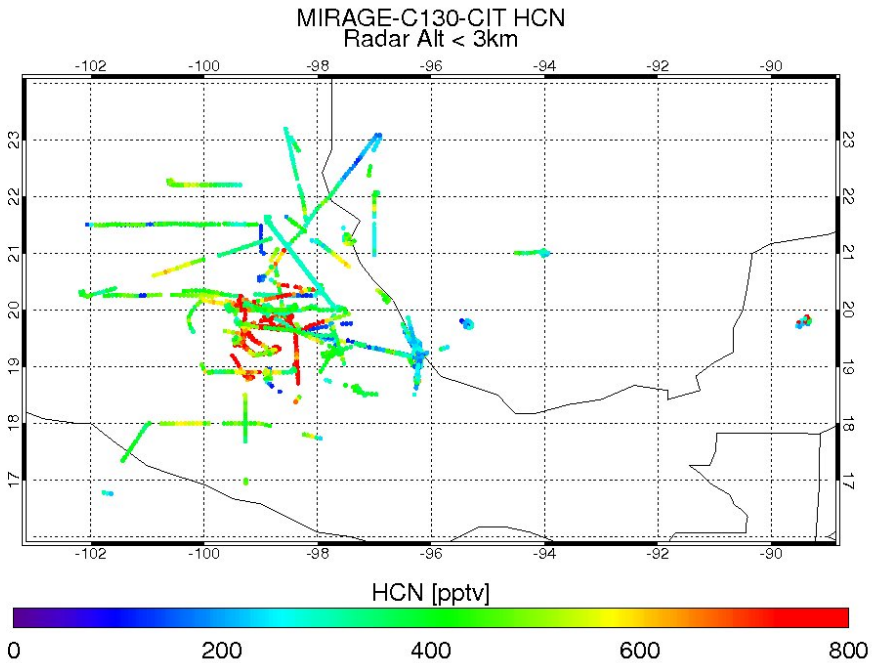
Benzene

Acetonitrile

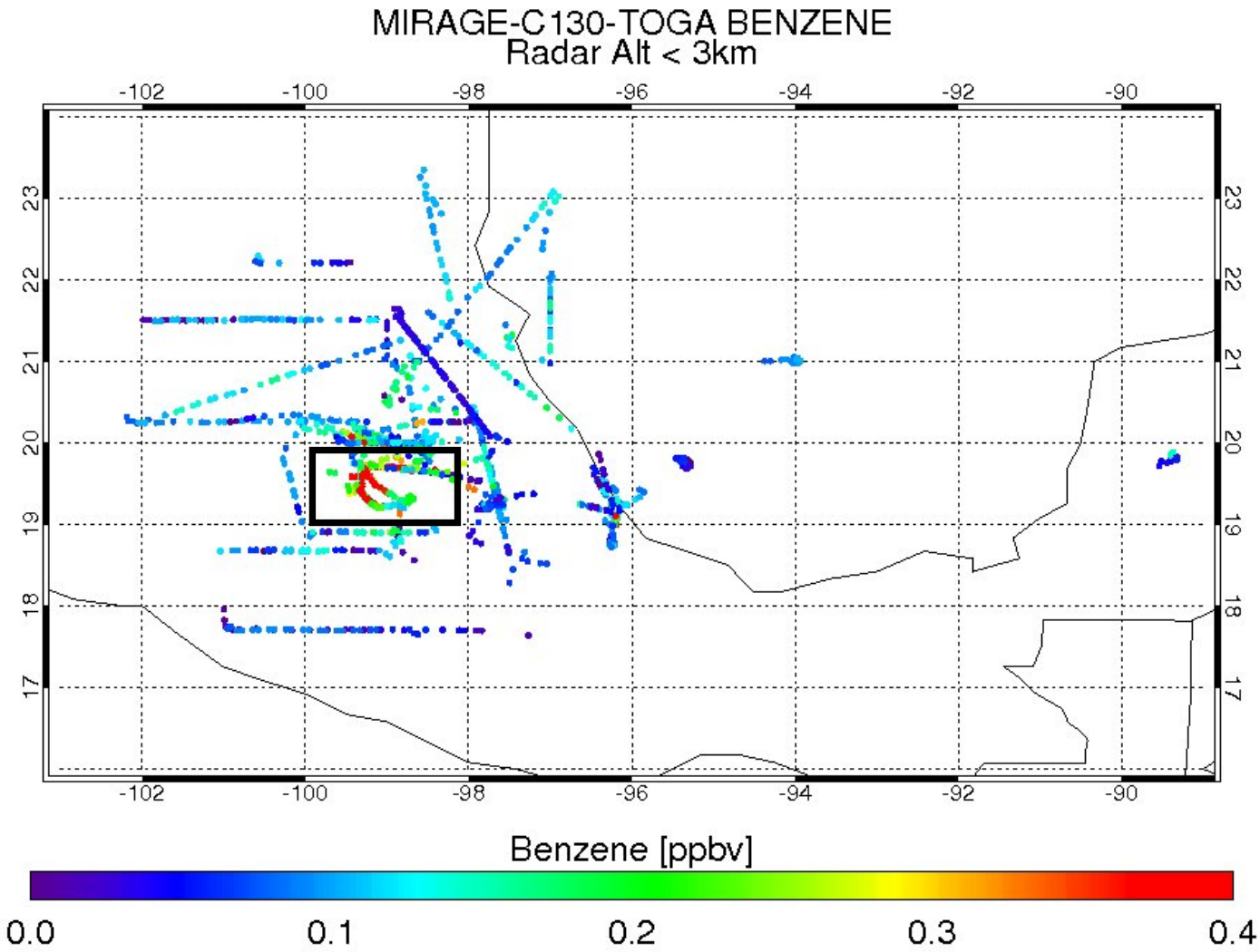
HCN (Caltech)







Define Mexico City "Box"



Enhancement Ratios: ΔVOC/ΔCO

Calculate in a number of ways:

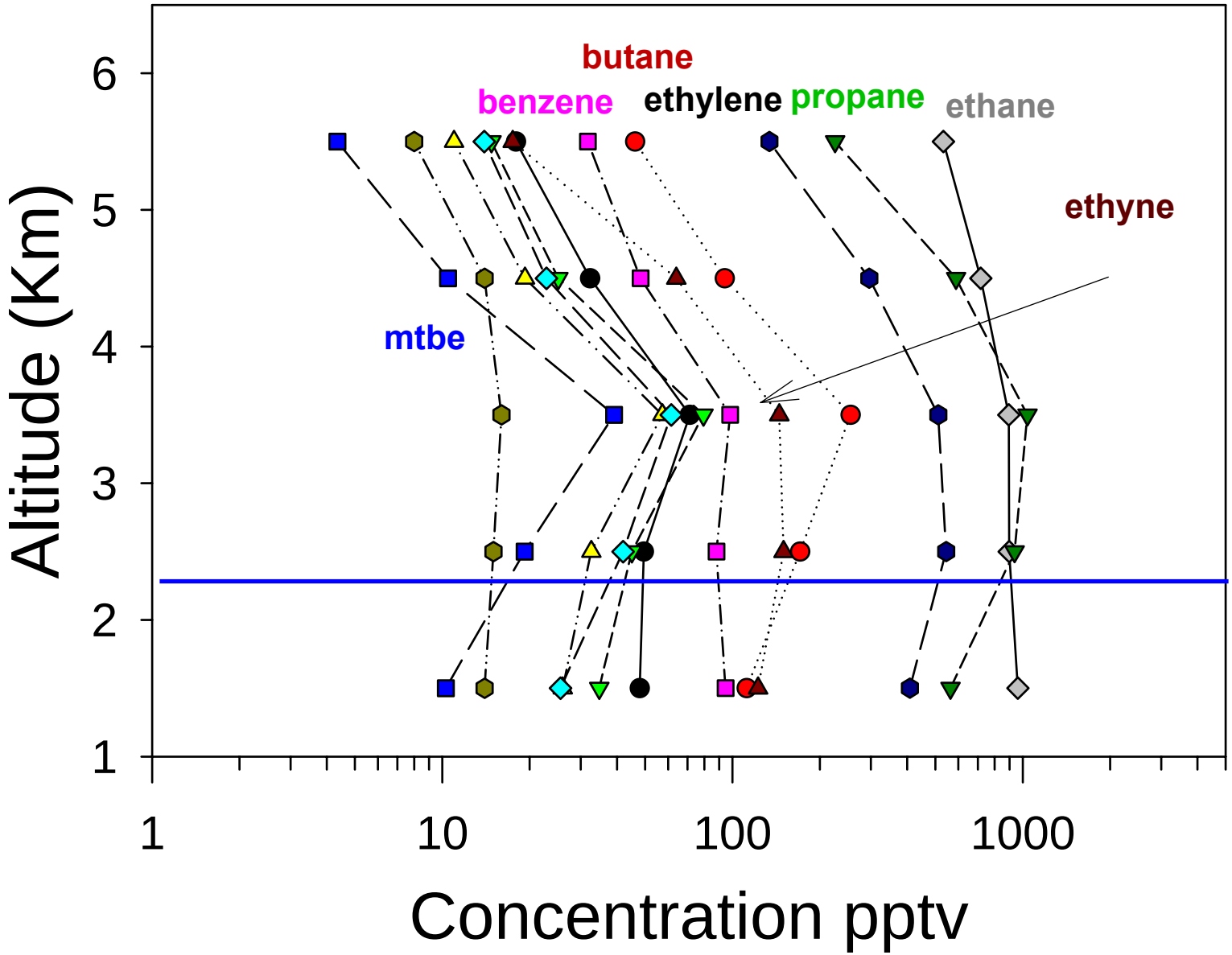
1) Fresh emissions; 2) slope; 3) ΔVOC/ ΔC_2H_2 vs. Photochemical age:

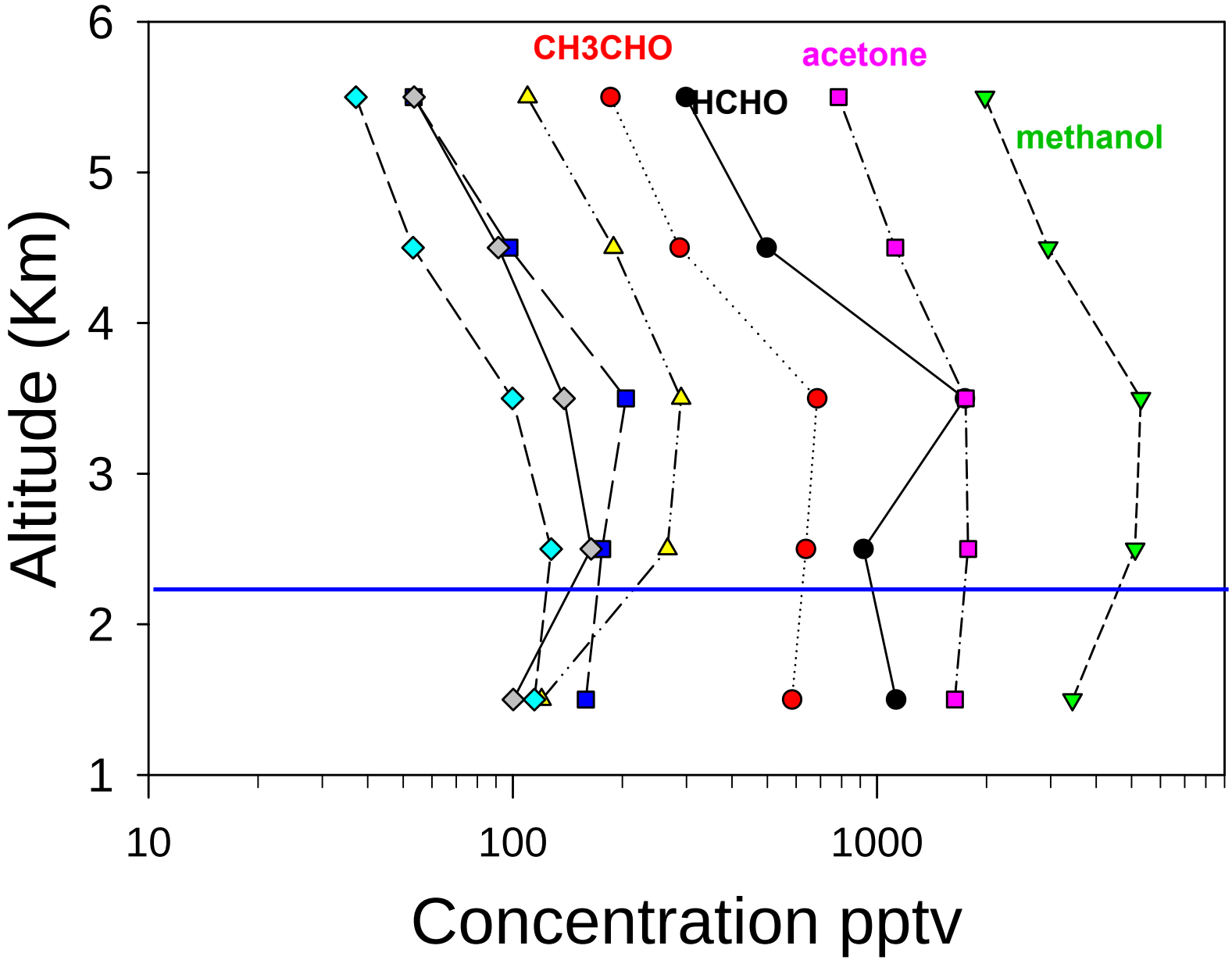
Warneke et al. JGR, accepted

Used to:

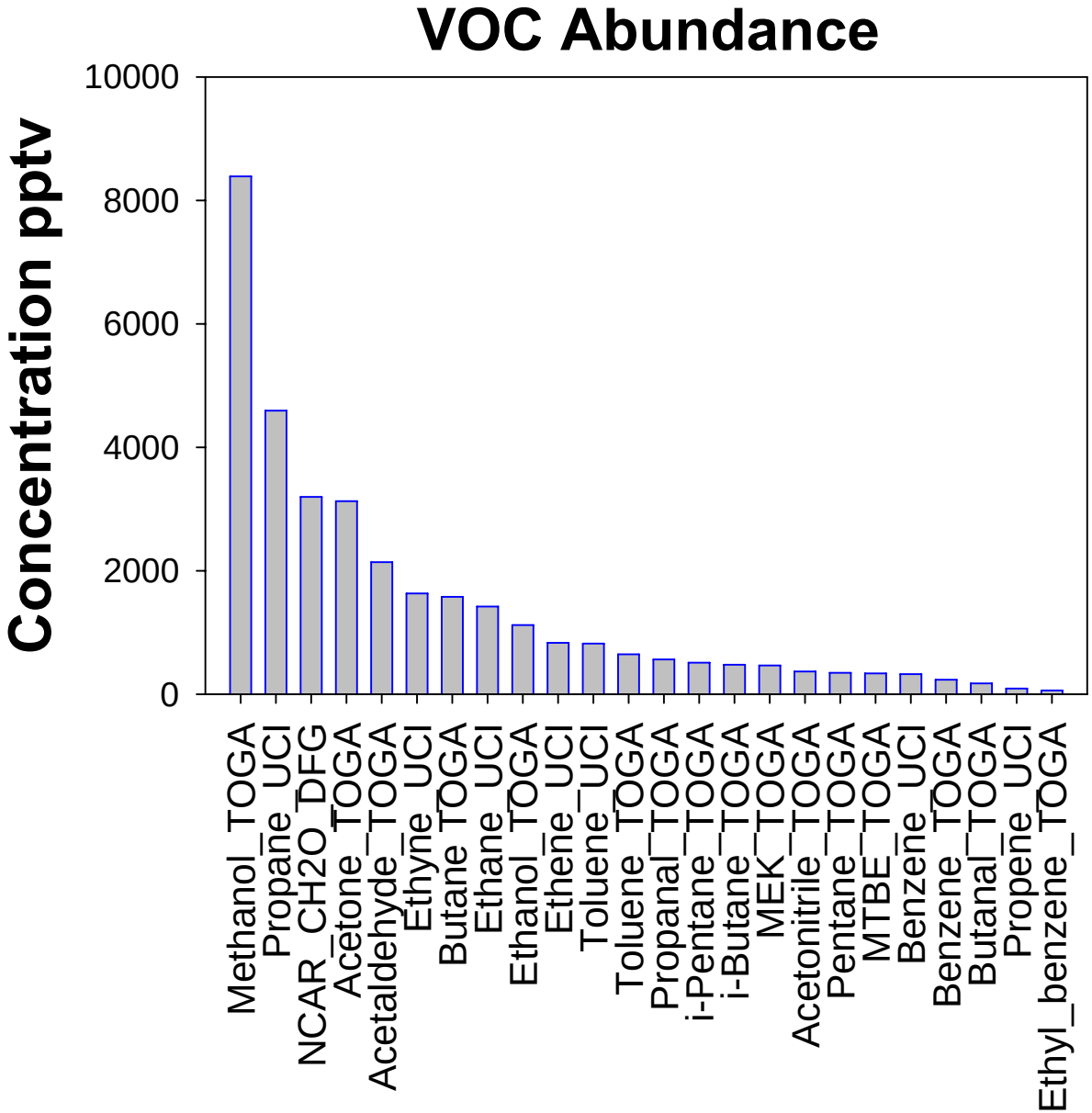
- Compare to previous data
- Input into models – emissions data
- Disentangle observed data in terms of emissions

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

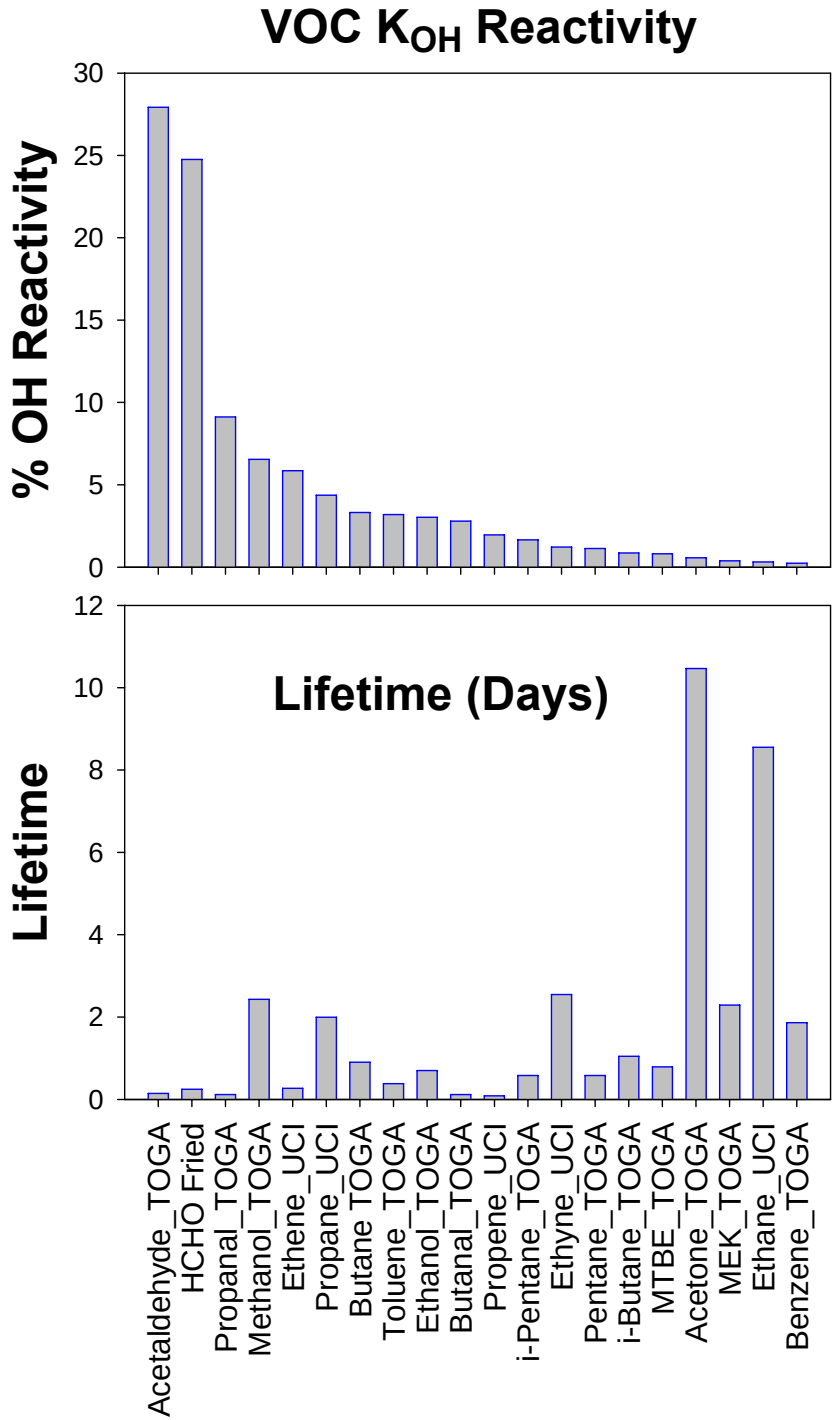
VOC abundance in Mexico City "box"



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

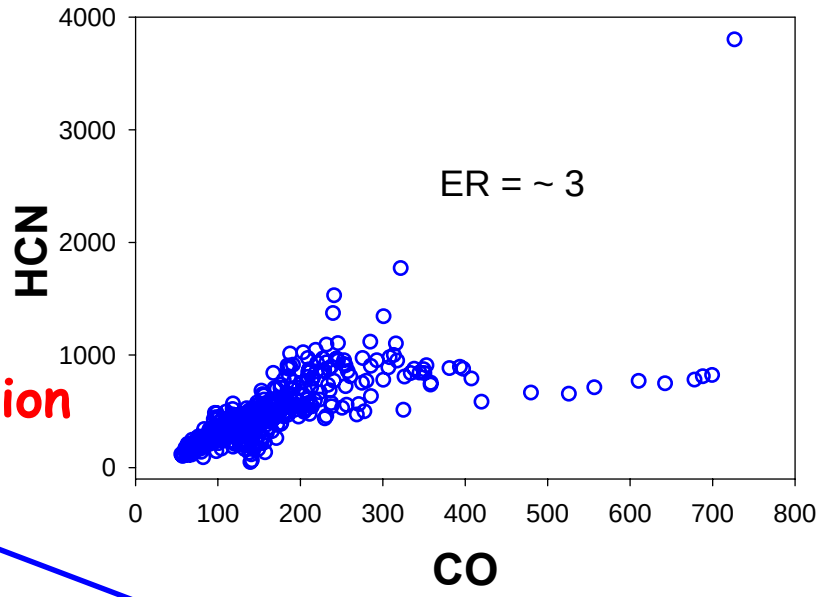


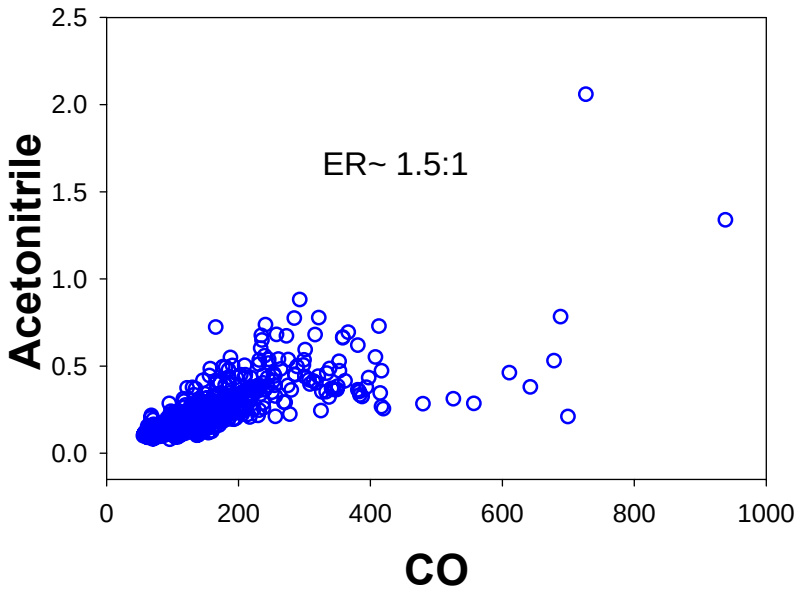
Example of Data:

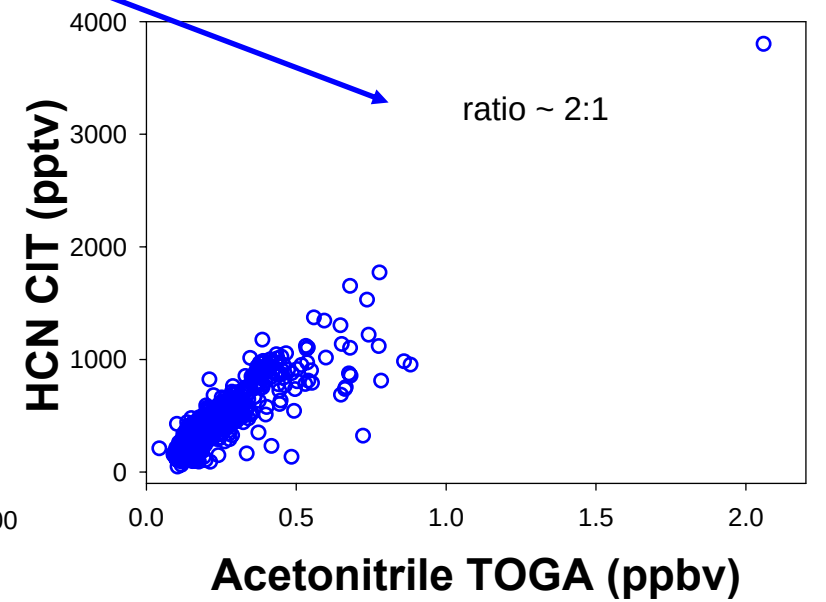
Fire Tracers

Acetonitrile (TOGA)

HCN (Caltech) excellent correlation

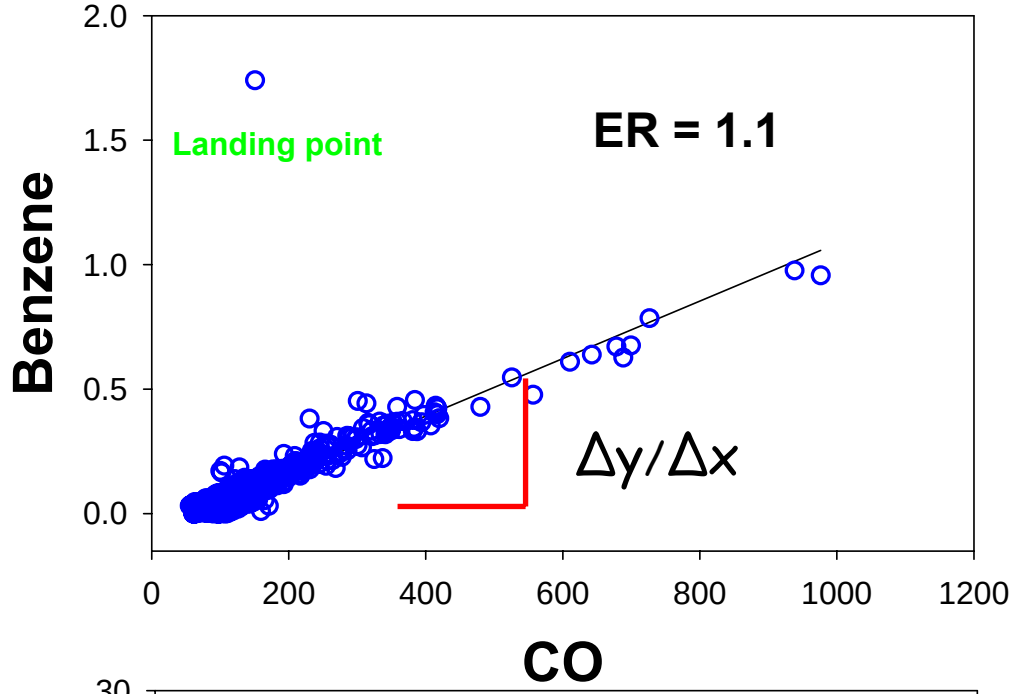


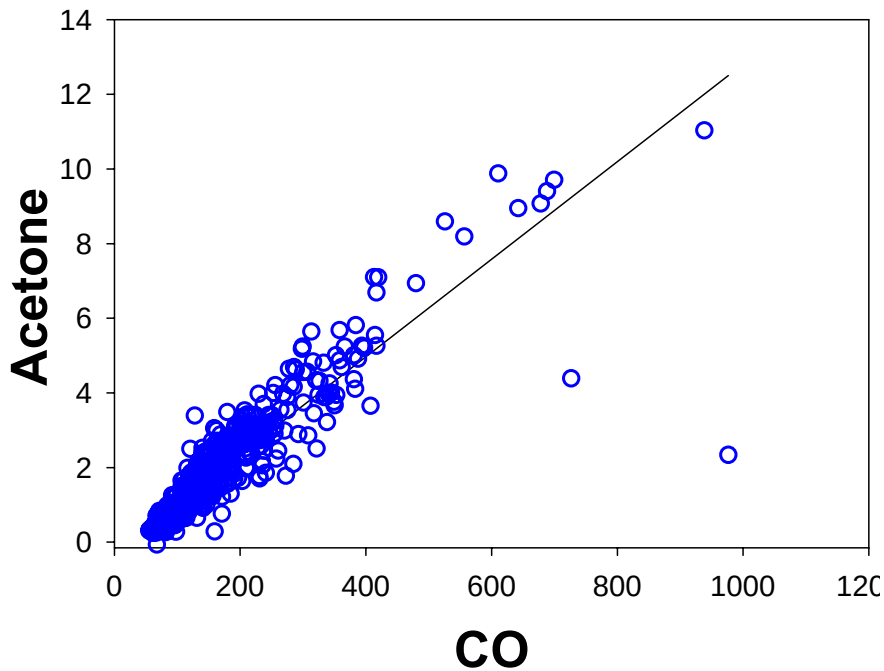


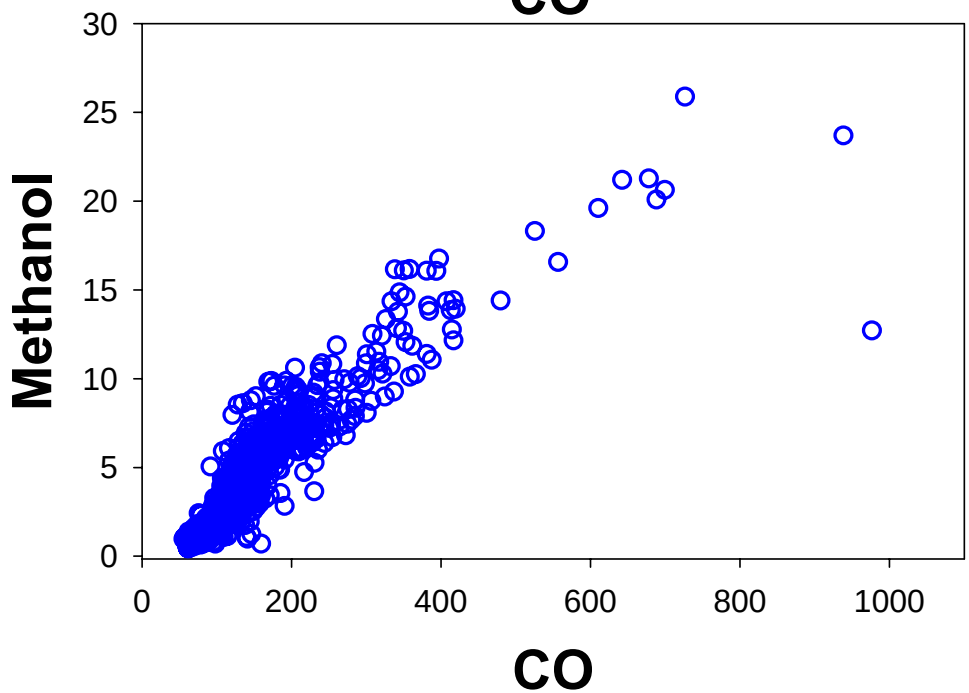


TOGA Data – determination of emission ratios

pptv/ppbv

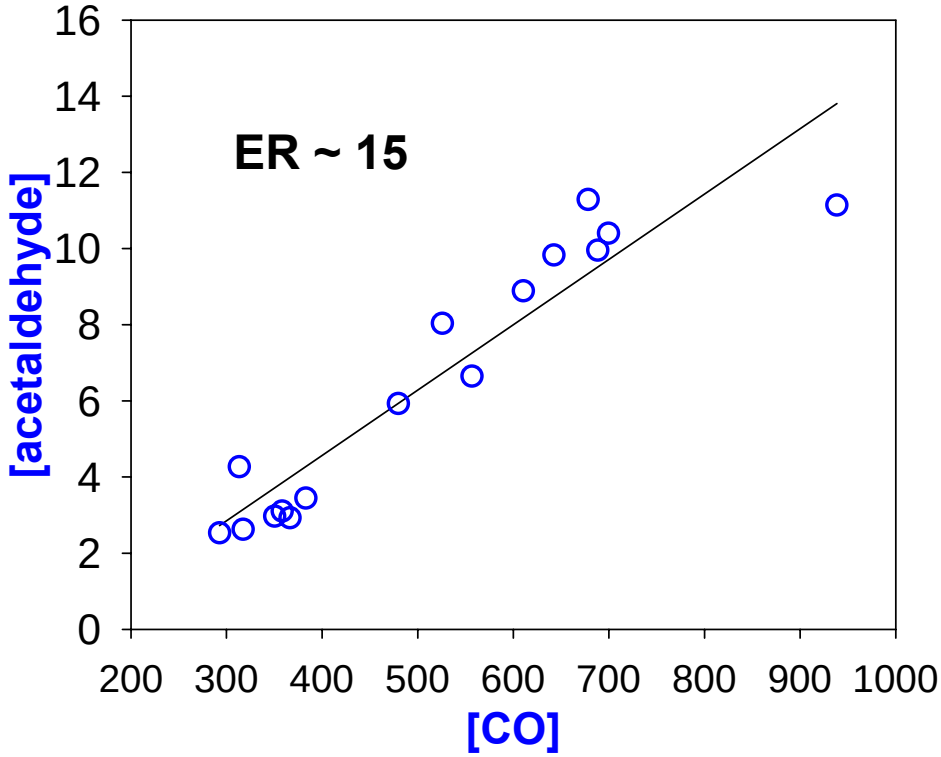


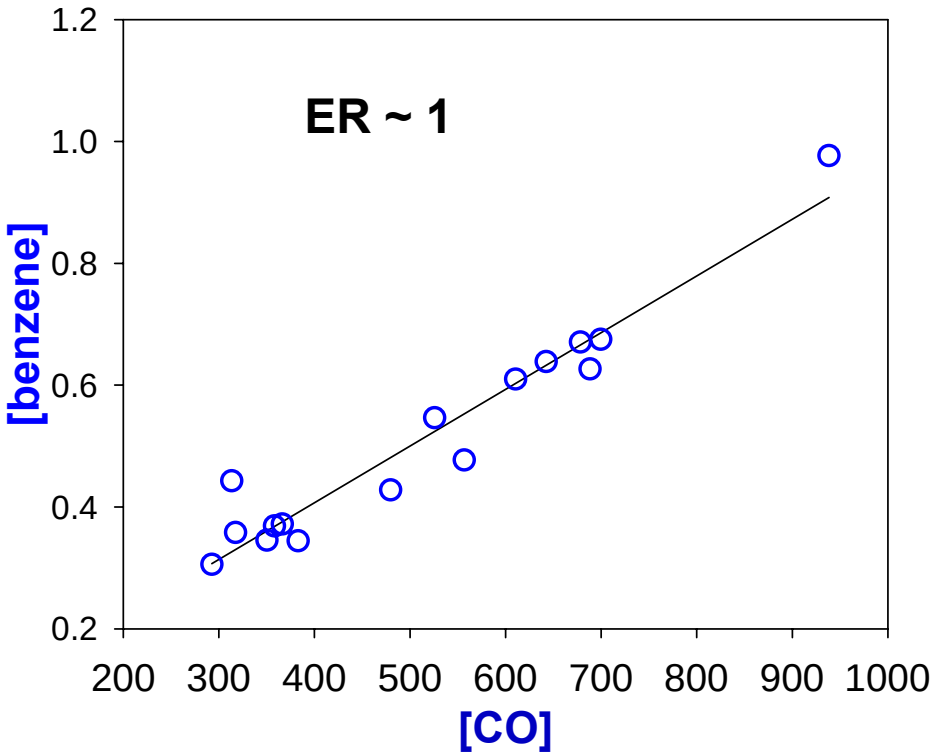




Apply filter for fresh emissions

mtbe> 0.9, toluene/benzene = 5





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

Possible reasons:

1) Combustion efficiency

2) LPG

Compound	C-130 Urban	Joost and Carsten 2004 NE	Joost and Carsten LA
HCN	0.8		
Formaldehyde	16.0		
i-Butane	4.3	1.0	2.6
Butane	16.3	1.7	5.0
Acetaldehyde	15.5	0.7	9.7
i-Pentane	4.4	4.0	6.3
Methanol	31.0	4.0	8.4
Pentane	3.4	1.6	3.0
Ethanol	10.5	5.8	0.0
Propanal	3.6	0.7	0.0
Acetone	12.8	2.9	14.0
Acetonitrile	0.3		
Butanal	1.3		
MEK	4.3	4.0	8.0
Benzene	1.2	0.6	1.1
Toluene	6.2	2.6	3.5
Ethyl_benzene	1.2	0.3	0.0

** Warneke et al., JGR, accepted*

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

* *Literature values*

Compound	C-130 Urban	C-130 Fire	Fire lit
HCN	0.8	8.6	5-18
Formaldehyde	16.0		
i-Butane	4.3	0.0	0.1
Butane	16.3	0.2	0.5
Acetaldehyde	15.5	7.8	2.5
i-Pentane	4.4	0.0	0.1
Methanol	31.0	12.2	20*
Pentane	3.4	0.1	0.2
Ethanol	10.5	0.2	0.0
Propanal	3.6	1.0	0.1
Acetone	12.8	2.1	2.1
Acetonitrile	0.3	1.4	1-2.5
MEK	4.3	0.2	0.3
Benzene	1.2	1.1	0.1
Toluene	6.2	0.3	0.1
Ethyl_benzene	1.2	0.0	0.0

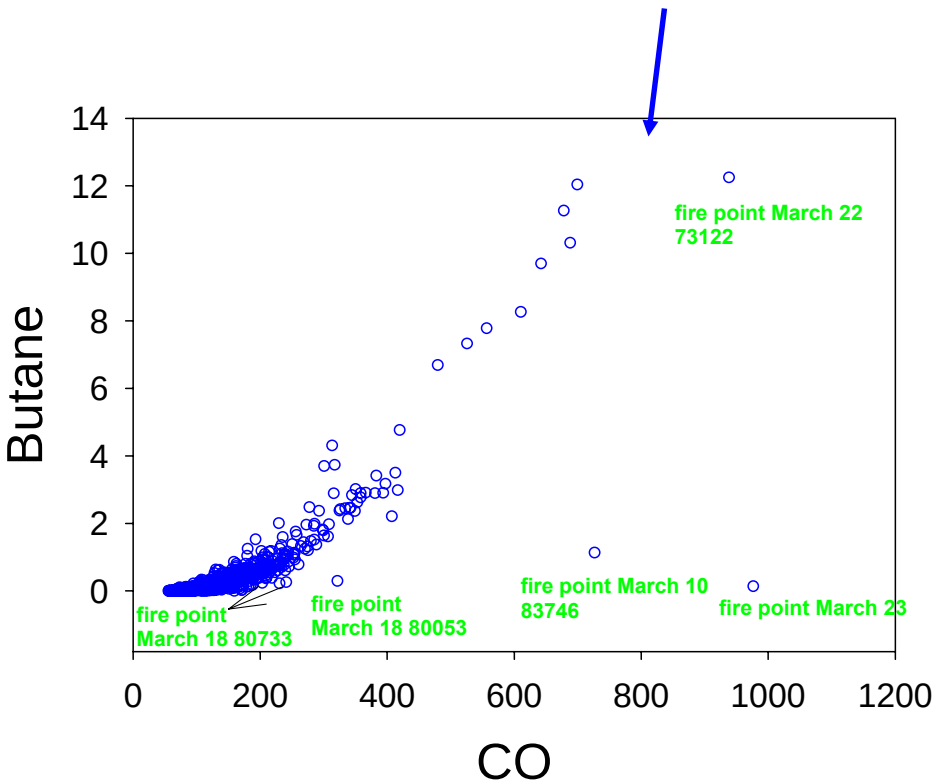
Compare to ground measurements

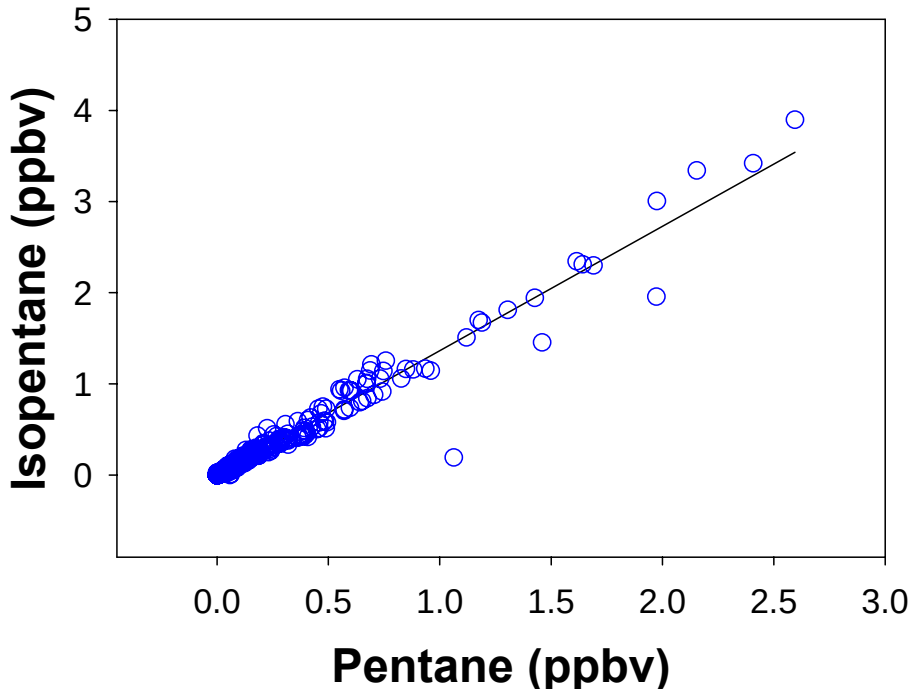
Butane/isobutane 0.33 (Velasco)/0.36 (TOGA)

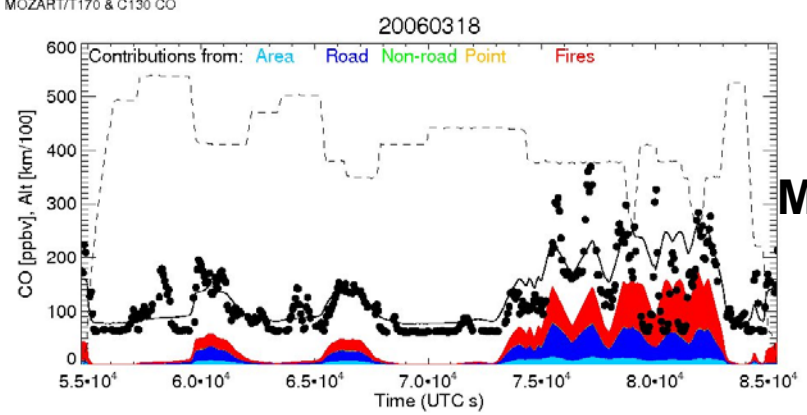
Isopentane/pentane 3.0/1.5 (TOGA – bottom right)

Toluene/benzene (fresh): 6/5

Major fire points fall off trendline – very different ERs







March 18

MOZART Model

Fire

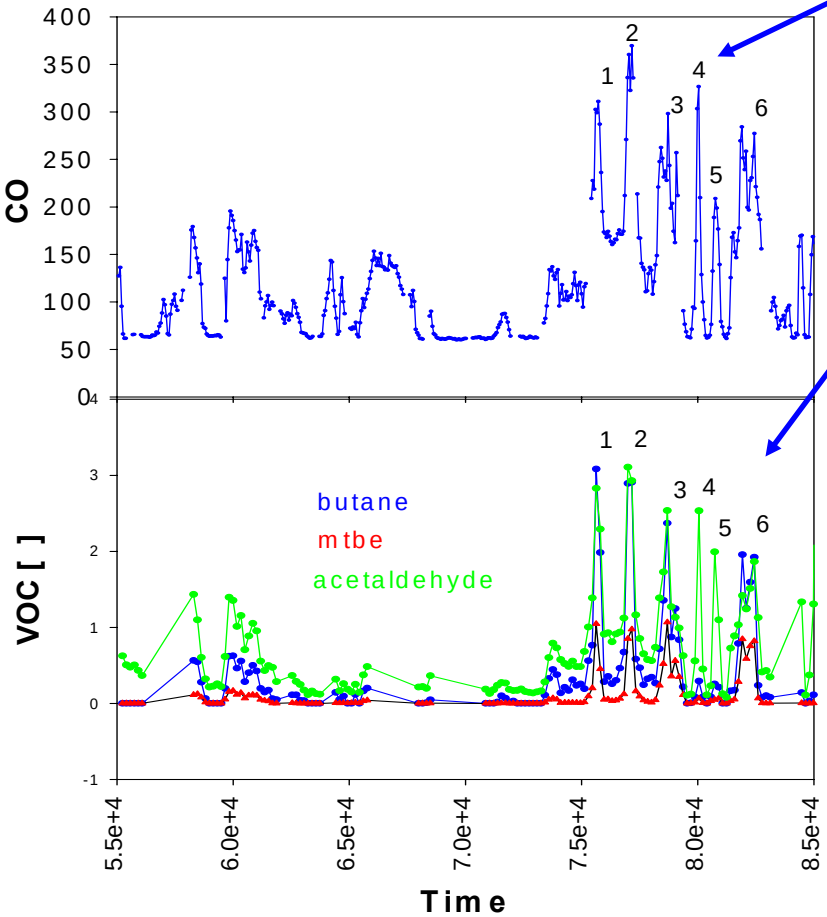
Road

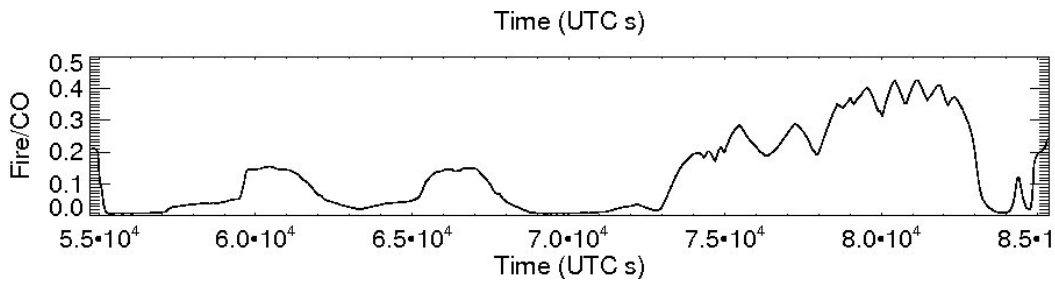
Area

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

Use TOGA to apportion sources and compare with model

e.g. BB vs. Urban





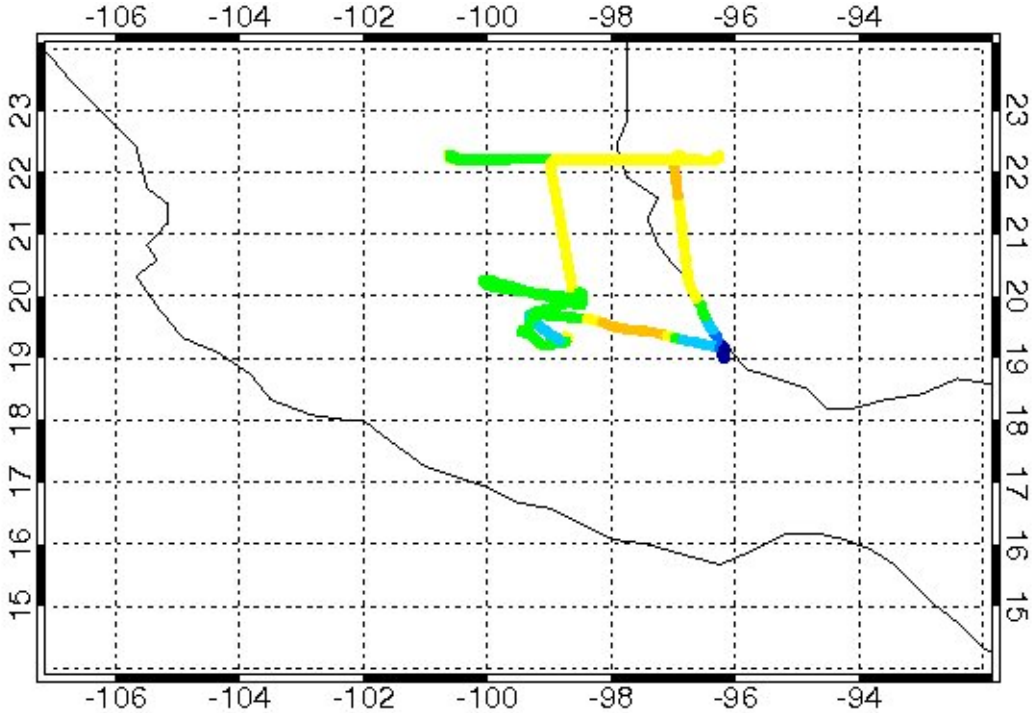
a Biofuel: resid heating/cooking
Non-road: vehicles
Point: factories

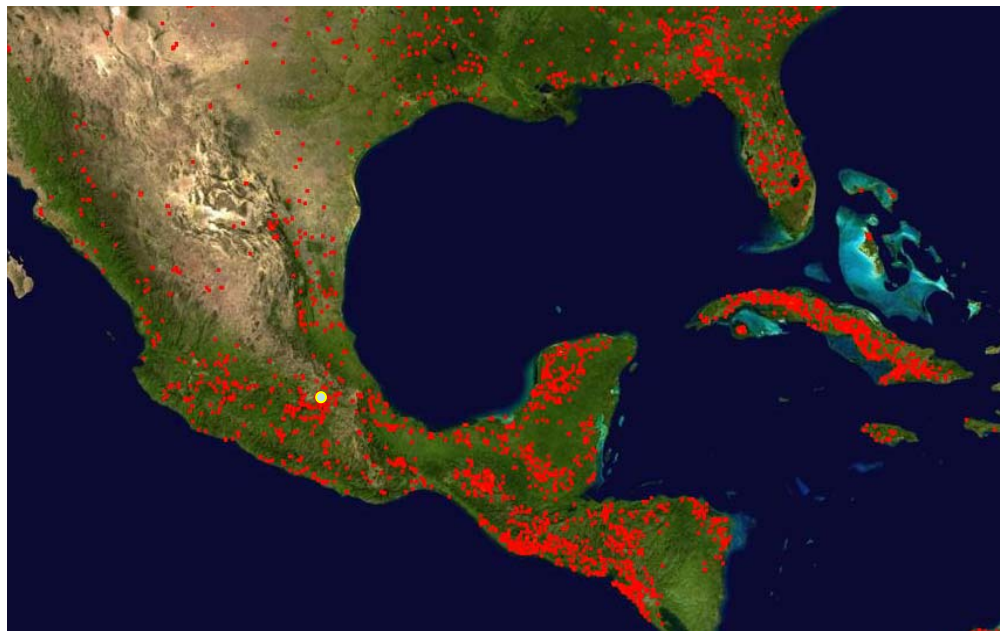
March 18 Flight:

6 Plumes intercepted

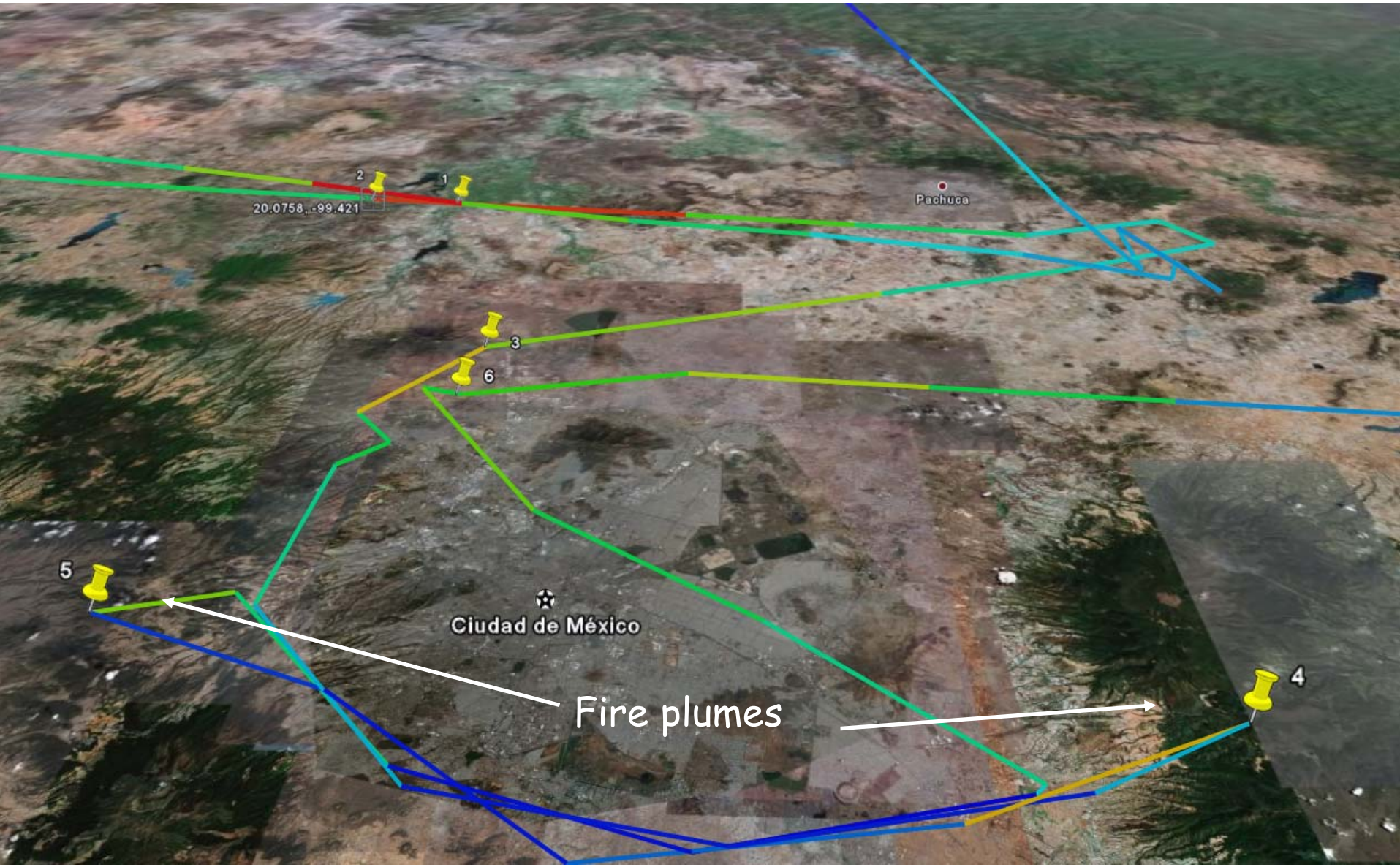
Urban emissions

BB emissions





March 18 plume interception

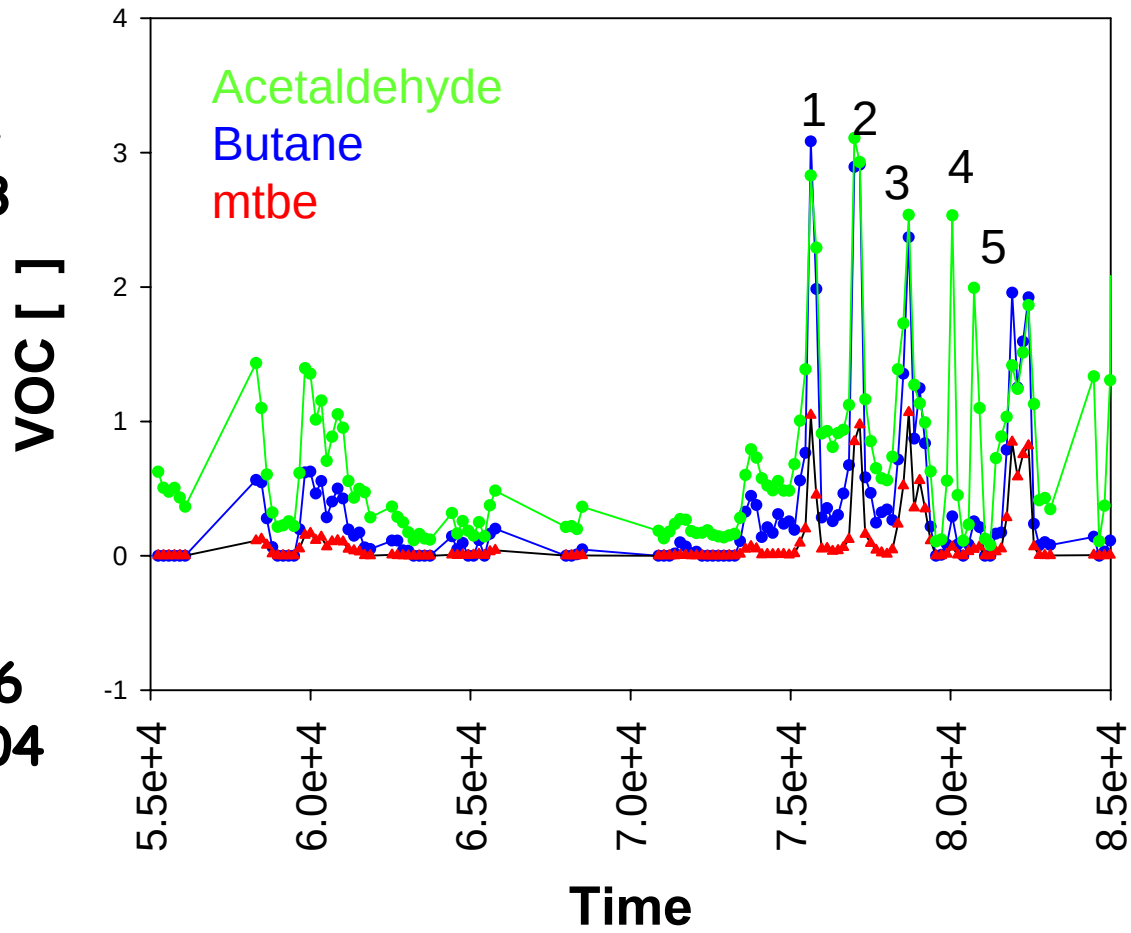


Peaks 1-3

mtbe
PAN/PPN ~ 6
Benzene/Toluene ~0.4
Isopentane/CO: 0.003

Peaks 4-5

PAN/PPN ~ 8-9
Benzene/Toluene ~ 1.6
Isopentane/CO: 0.0004
mtbe, acetaldehyde…



Conclude: Peaks 1-3 anthro>90%
Peaks 4-5 BB > 80% - South end of basin – fires present apparently

Conclusions/Hypotheses

- Most reactive measured VOCs are low MW NMHC and OVOCs
- Ethene → HCHO + HO2
- Propene → CH3CHO + HO2
- HCHO →
- CH3CHO →
- Lifetimes < day - each day chemically "separate" from next
- Relatively high oxygenated content in VOC mixture (ERs) – implications for aerosols, etc