Mexico City Emissions: mixing and photochemistry in the first few hours of the urban plume

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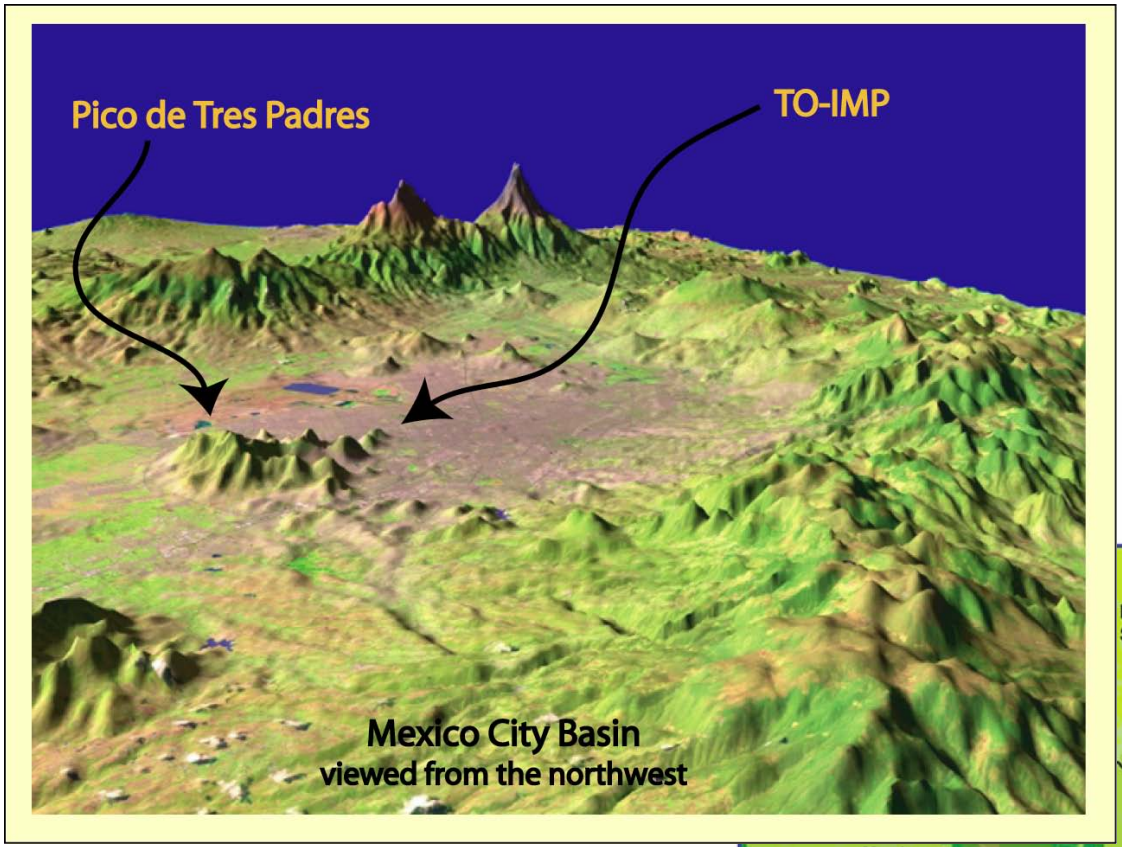
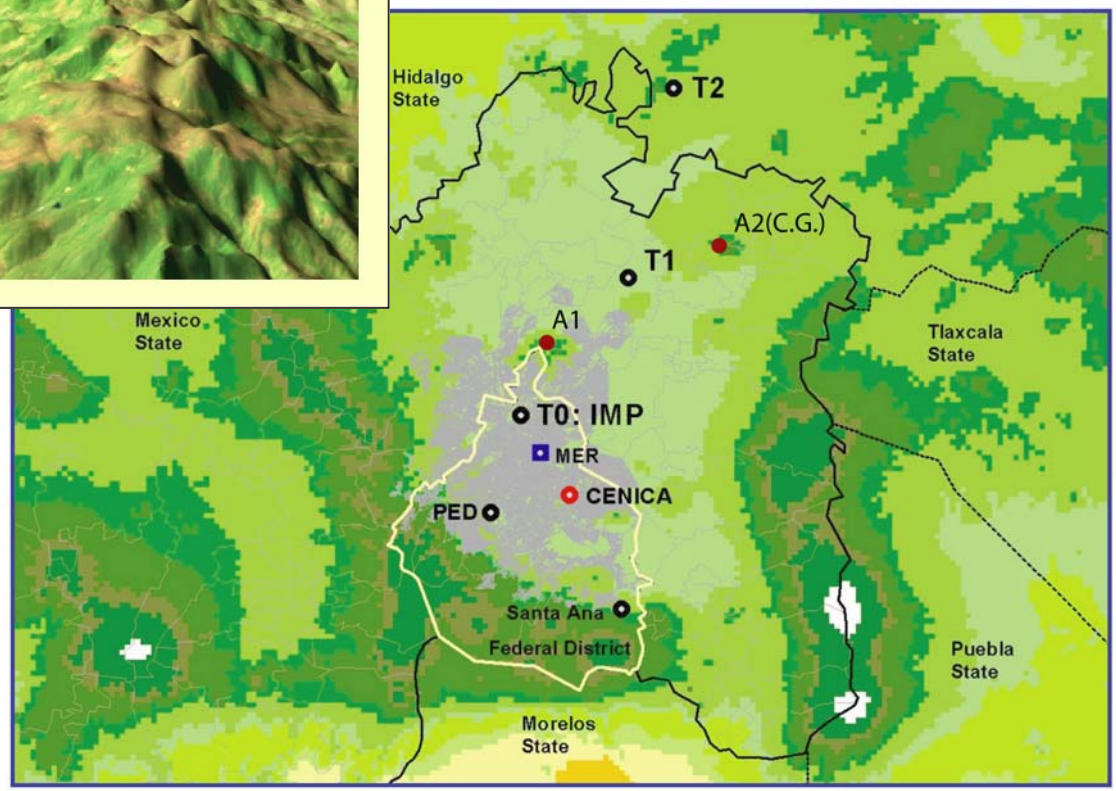
Topics

- Anatomy of a day : T0/PTP mixing height
- Photochemistry in action
  - VOC ratios (reactants and products)
- Secondary Aerosol
  - AMS Organic / CO and OOA, HOA and BBOA
- Observations



MCMA2006
Pico de Tres Padres
Site A1 or PTP

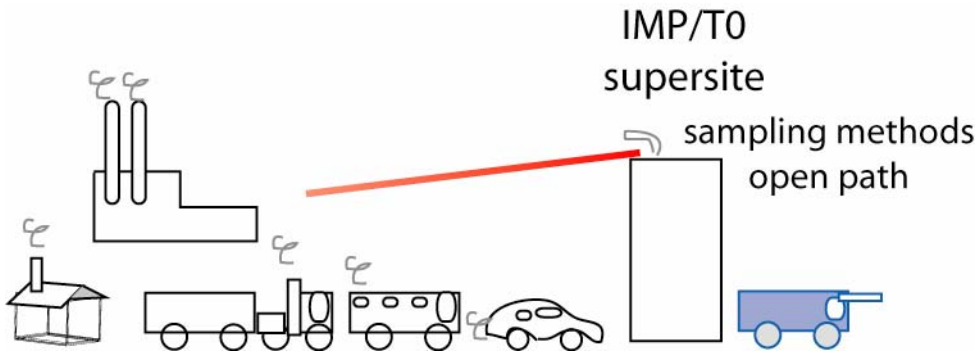
- few nearby emission sources
- ~mixed urban plume
- *clean* air at night

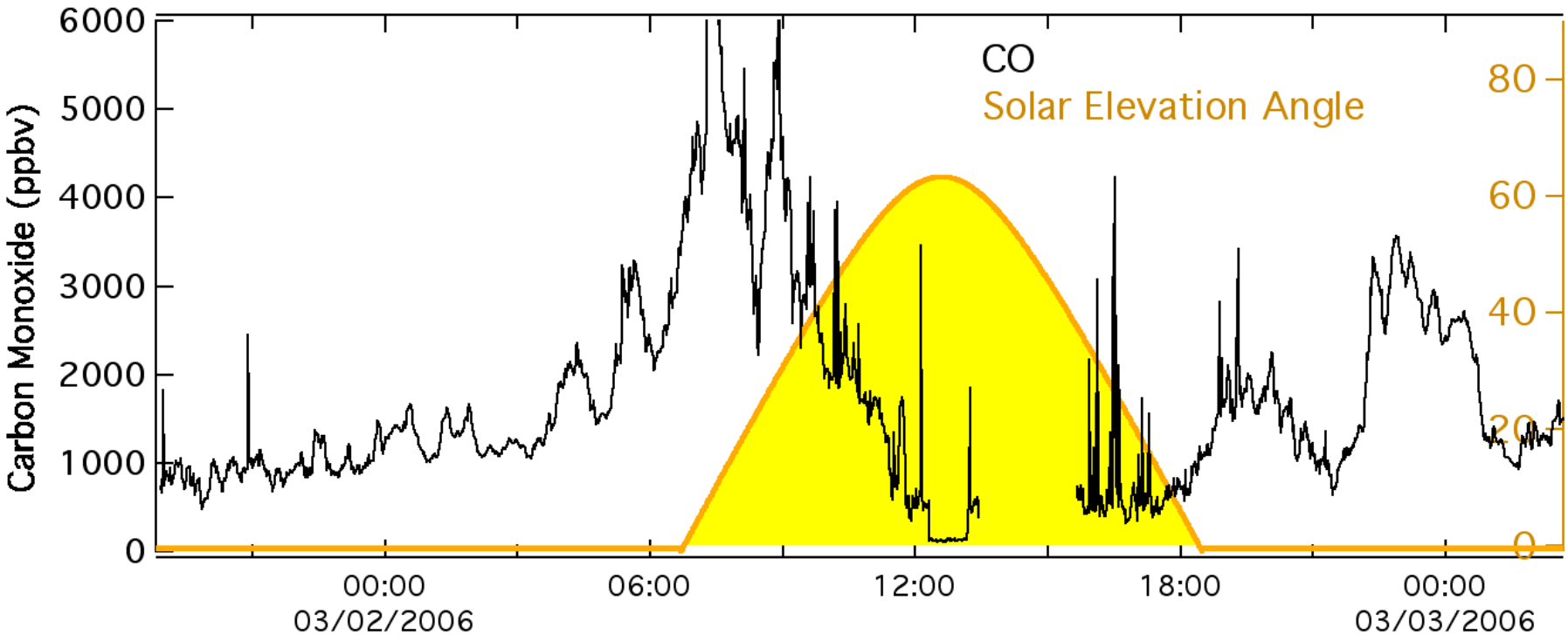


Aerodyne Mobile Laboratory Site Locations

Emissions and Boundary Layer Height: Influence on Mixing Ratios

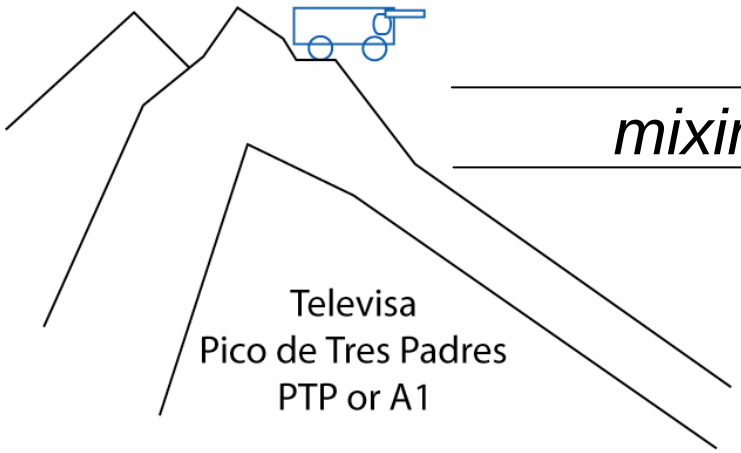
mixing layer height

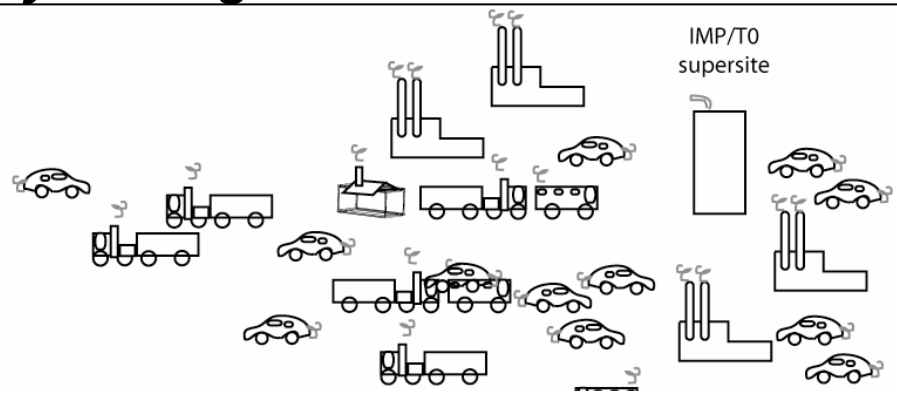


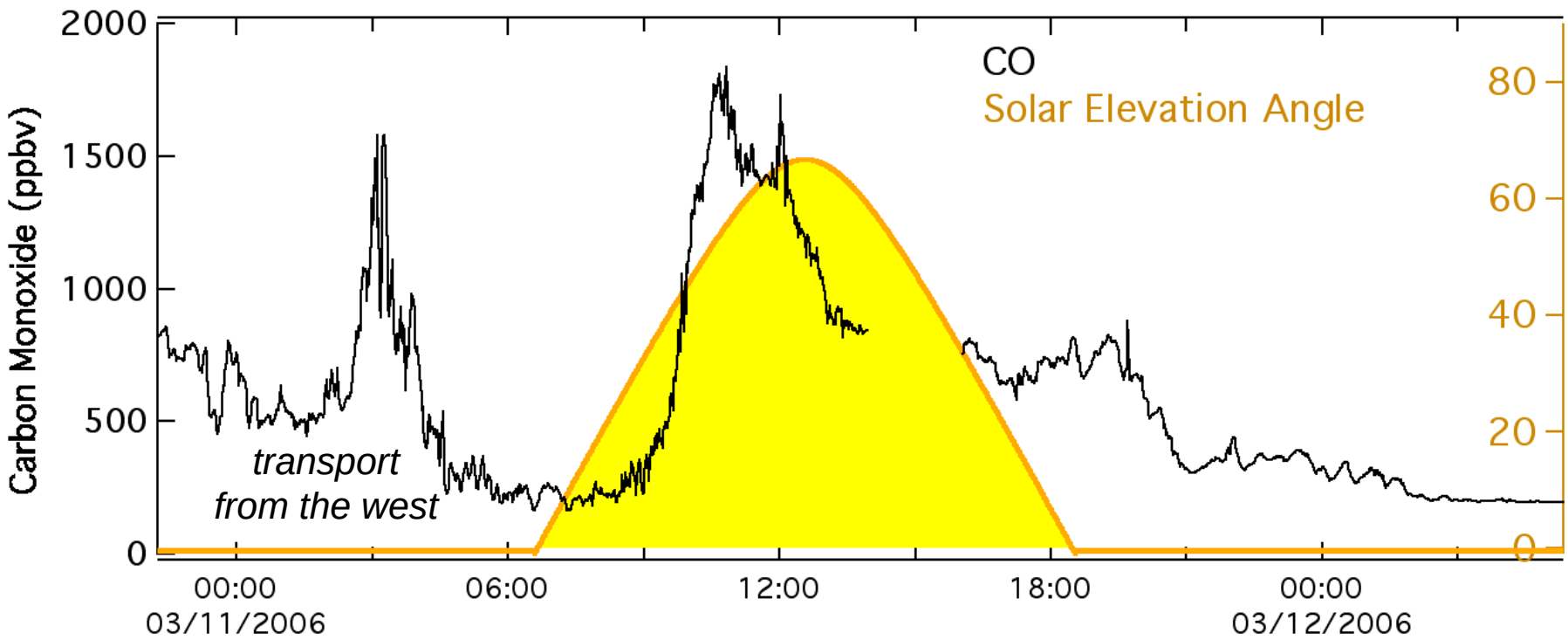


Emissions and Boundary Layer Height: Influence on Mixing Ratios

mixing layer height



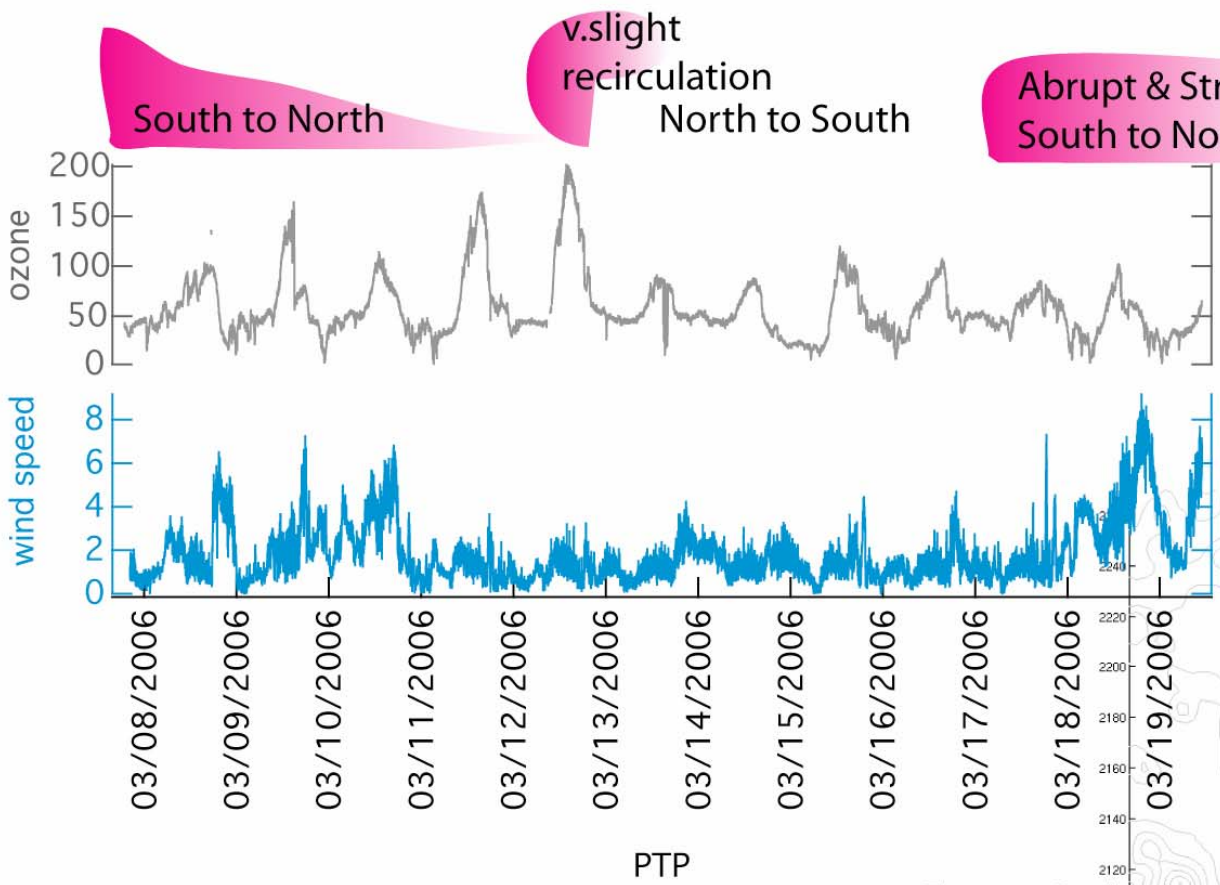


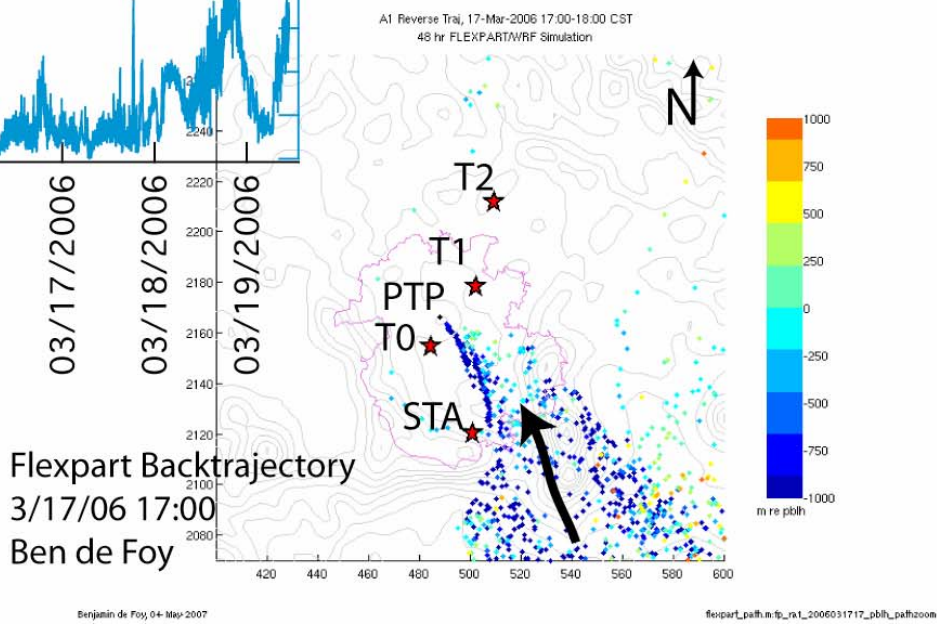


PTP Ozone and Transport Overview

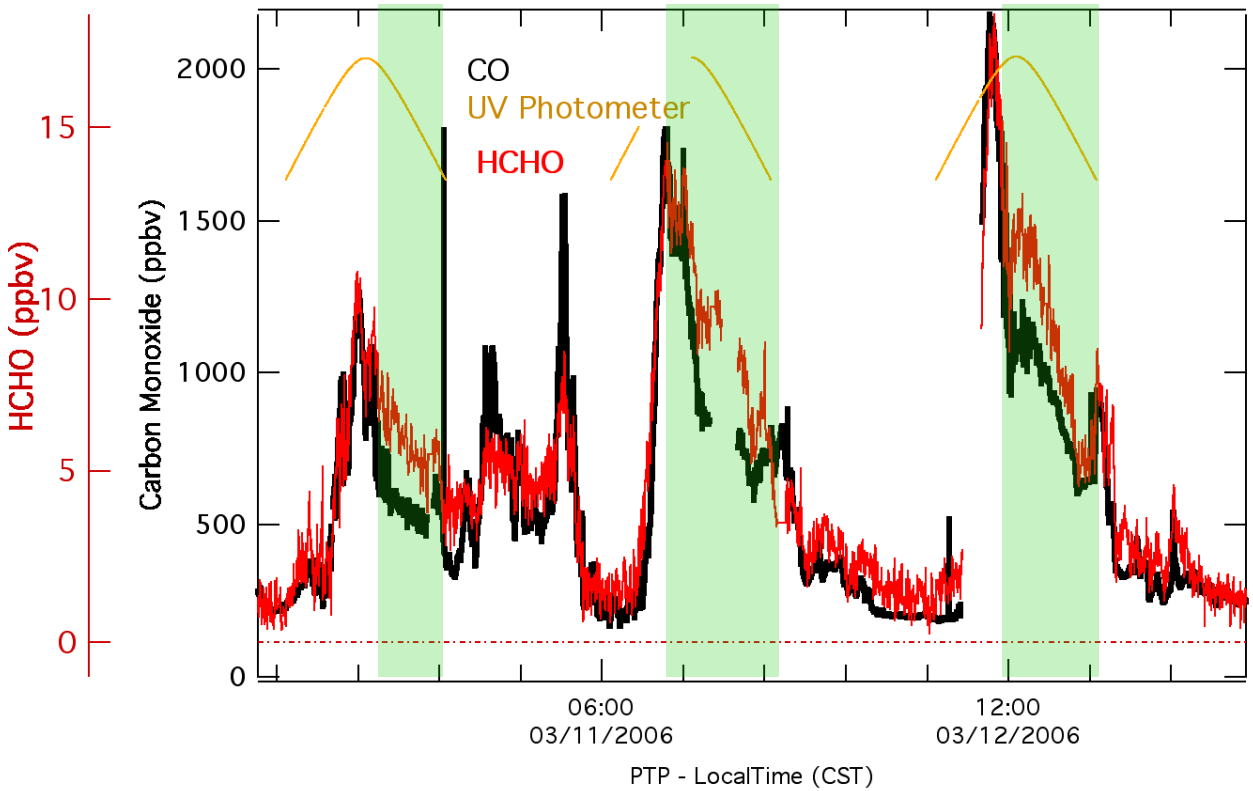
daytime transport of urban emissions: South & North

nighttime sampling trapped layers or urban burps

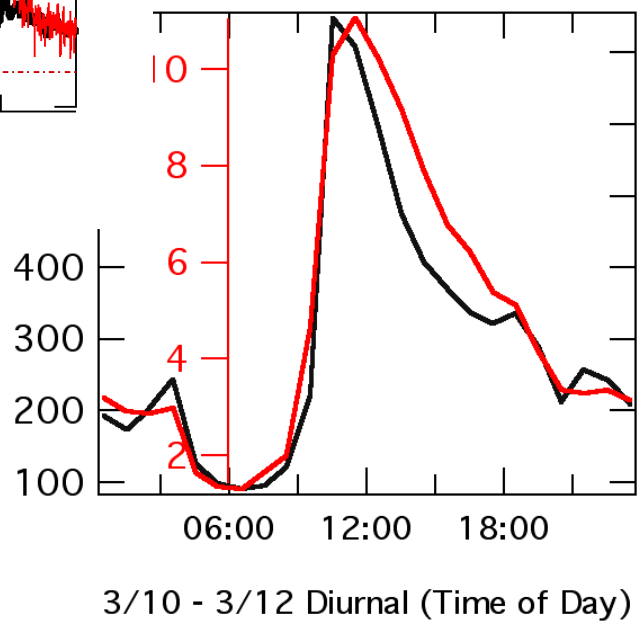




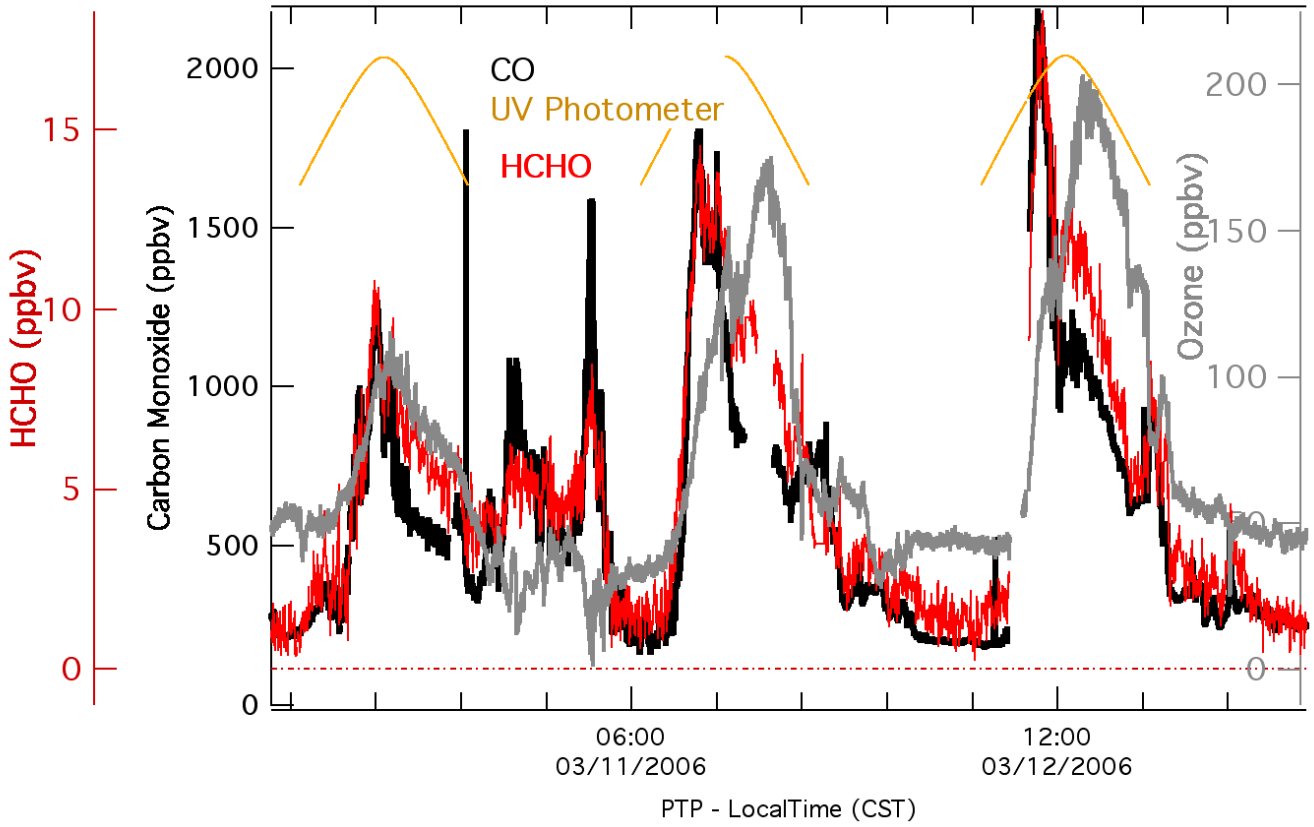
Pico de Tres Padres: 2nd HCHO



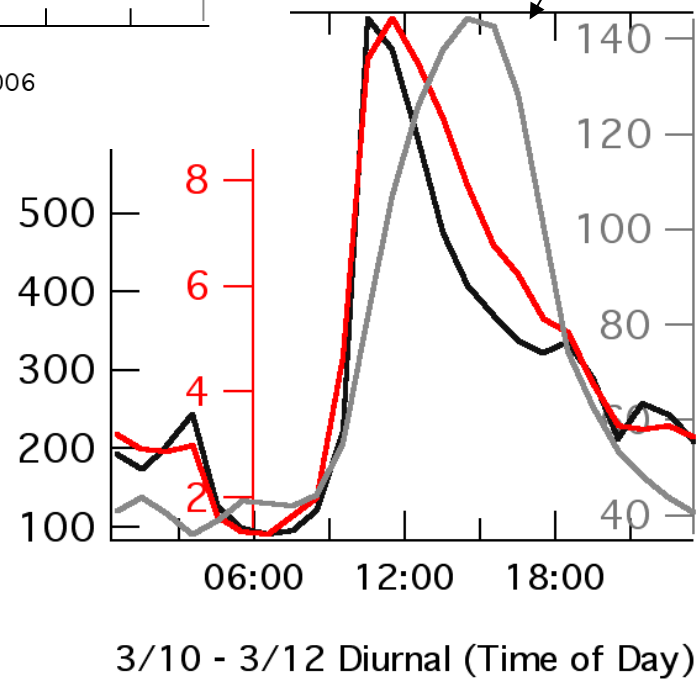
Photochemical production of HCHO, exhibited by increased HCHO/CO



PTP Ozone



O_3 peak later in the diurnal day

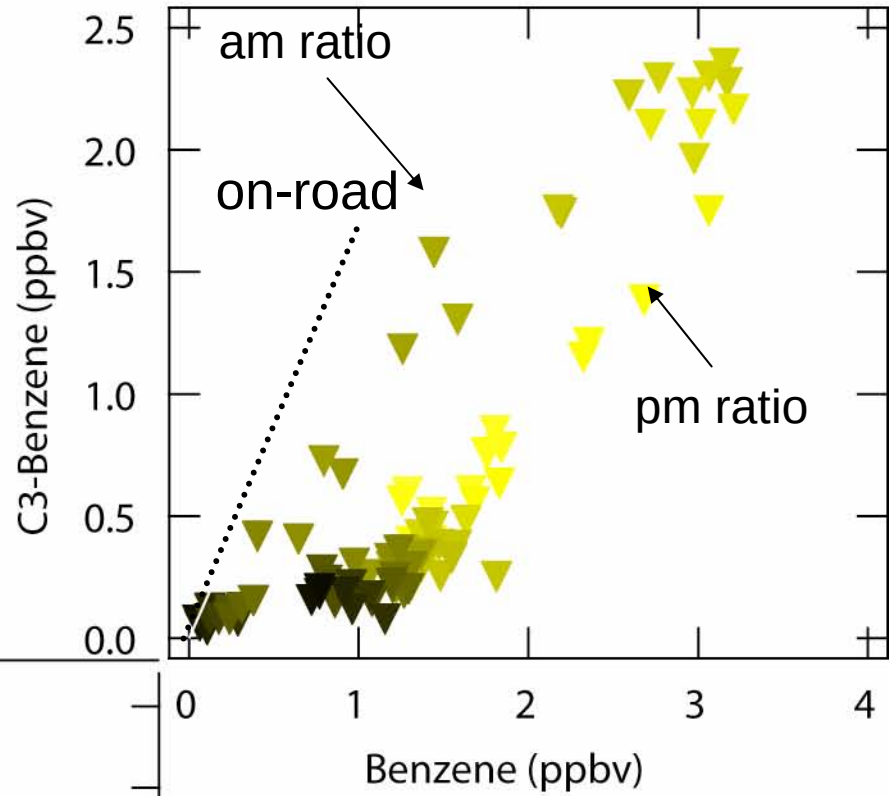


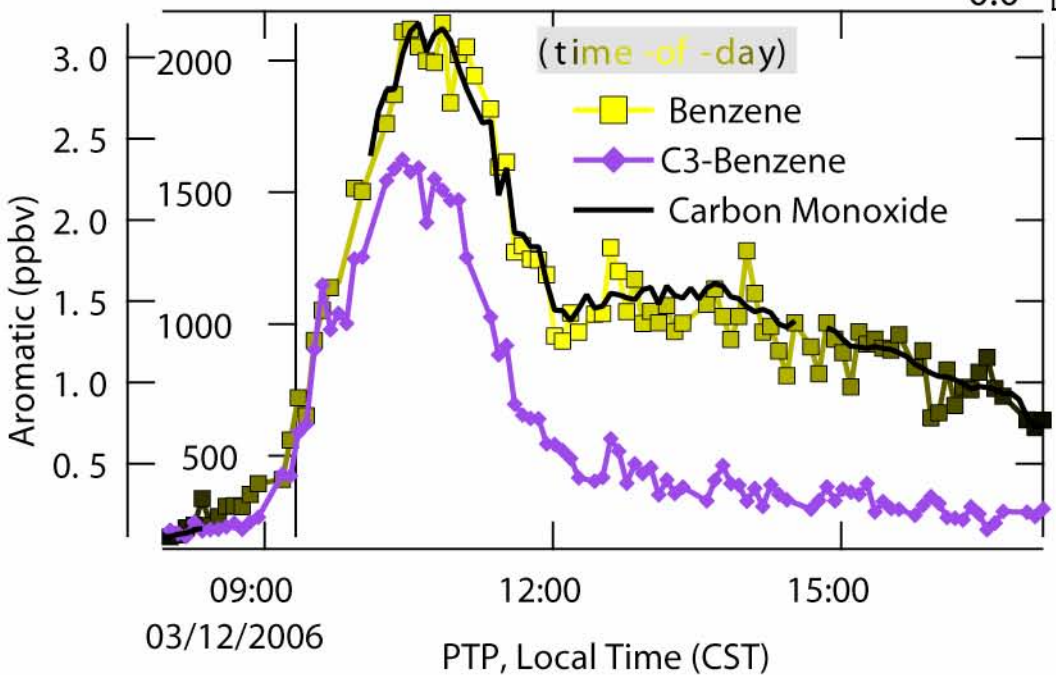
HOx and NOx cycling in the urban plume produces O_3

Photochemistry in action

Benzene

1,2-4-trimethylbenzene
1,3,5-trimethylbenzene
m-ethyltoluene
p-ethyltoluene
o-ethyltoluene
n-propylbenzene





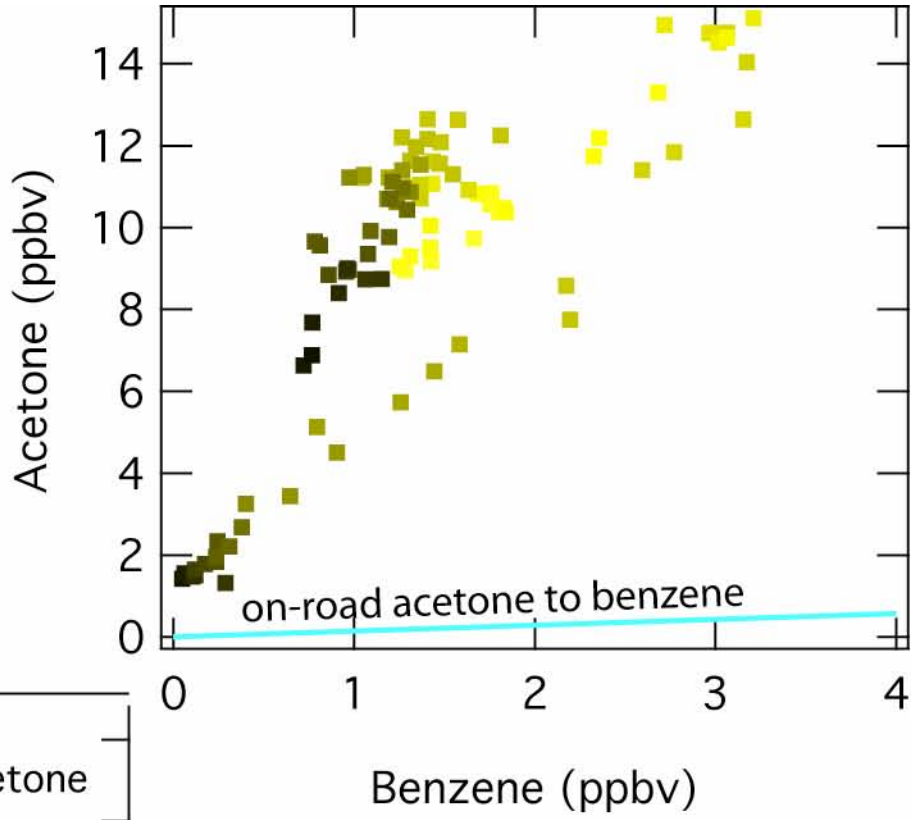
Benzene tracks CO

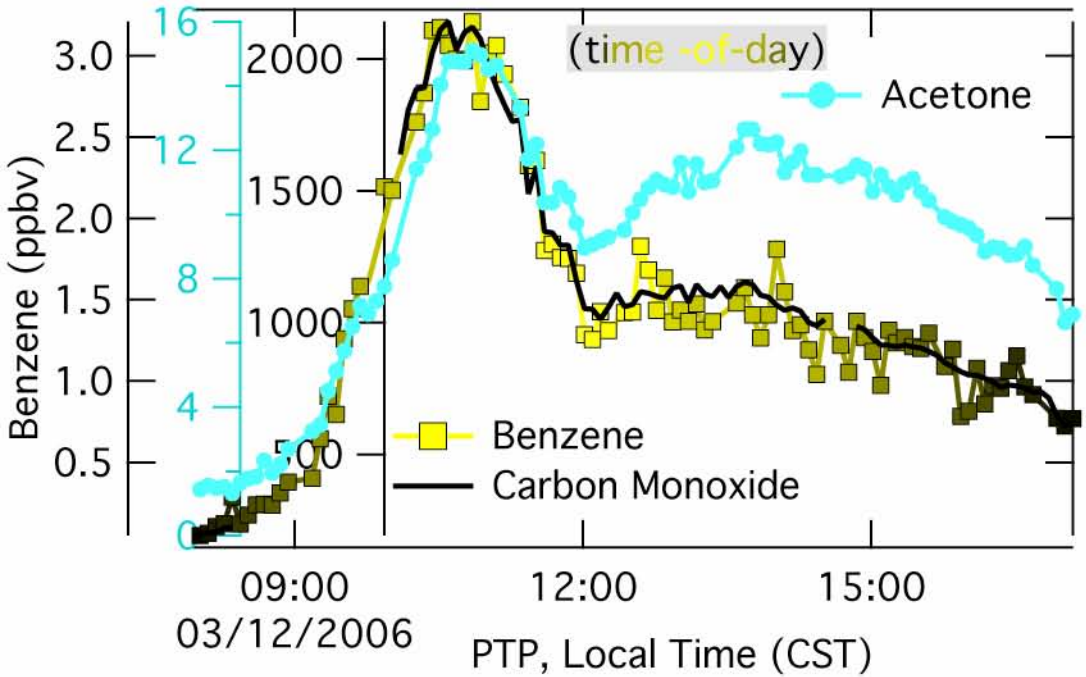
C3-Benzene/Benzene Ratio varies with time of day

Is a swift clock appropriate for timing oxidation at PTP site?

Photochemistry Products: Gas Phase

propane oxidation produces
Acetone + HO_2

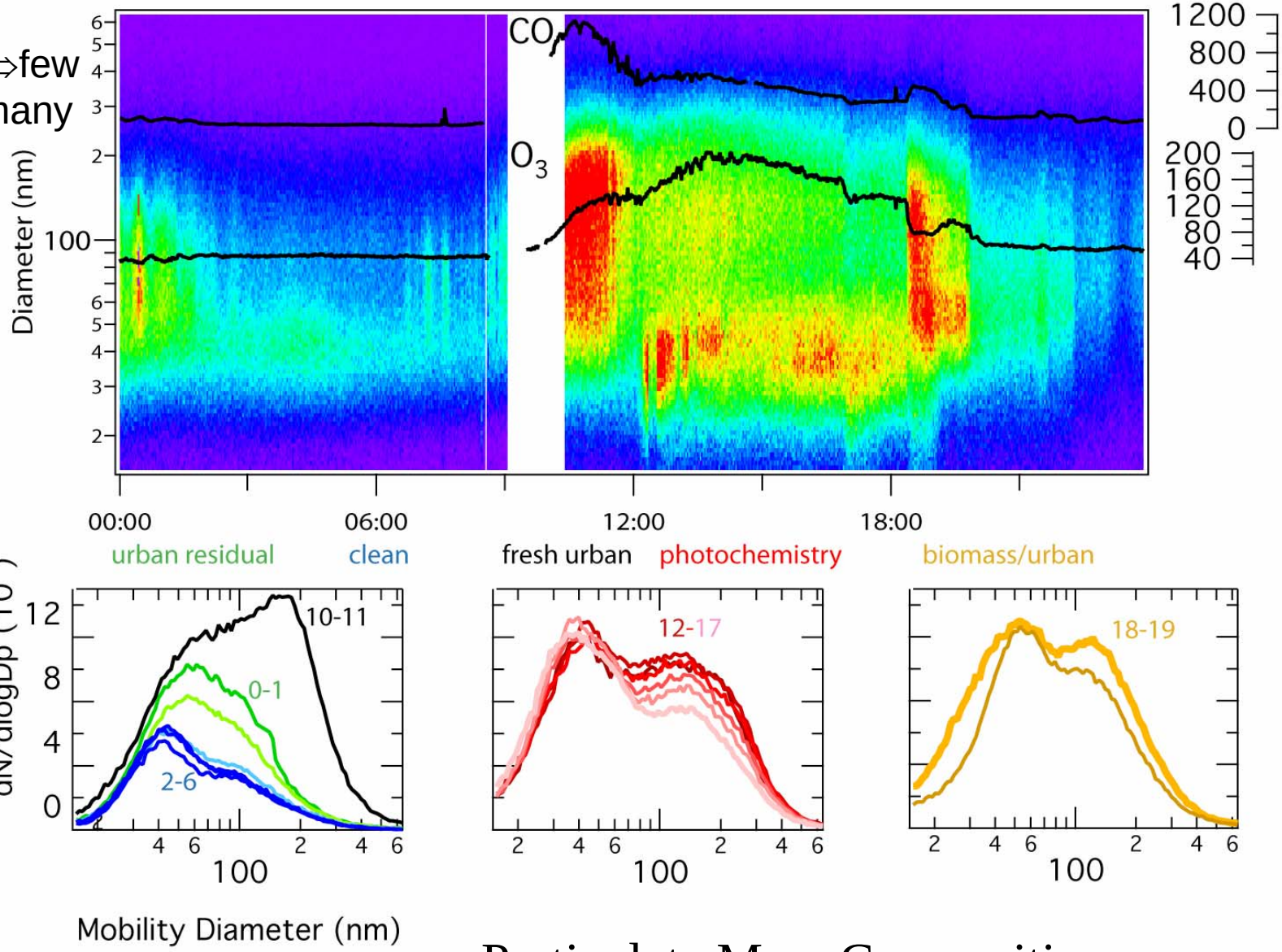




Similar in Acetaldehyde

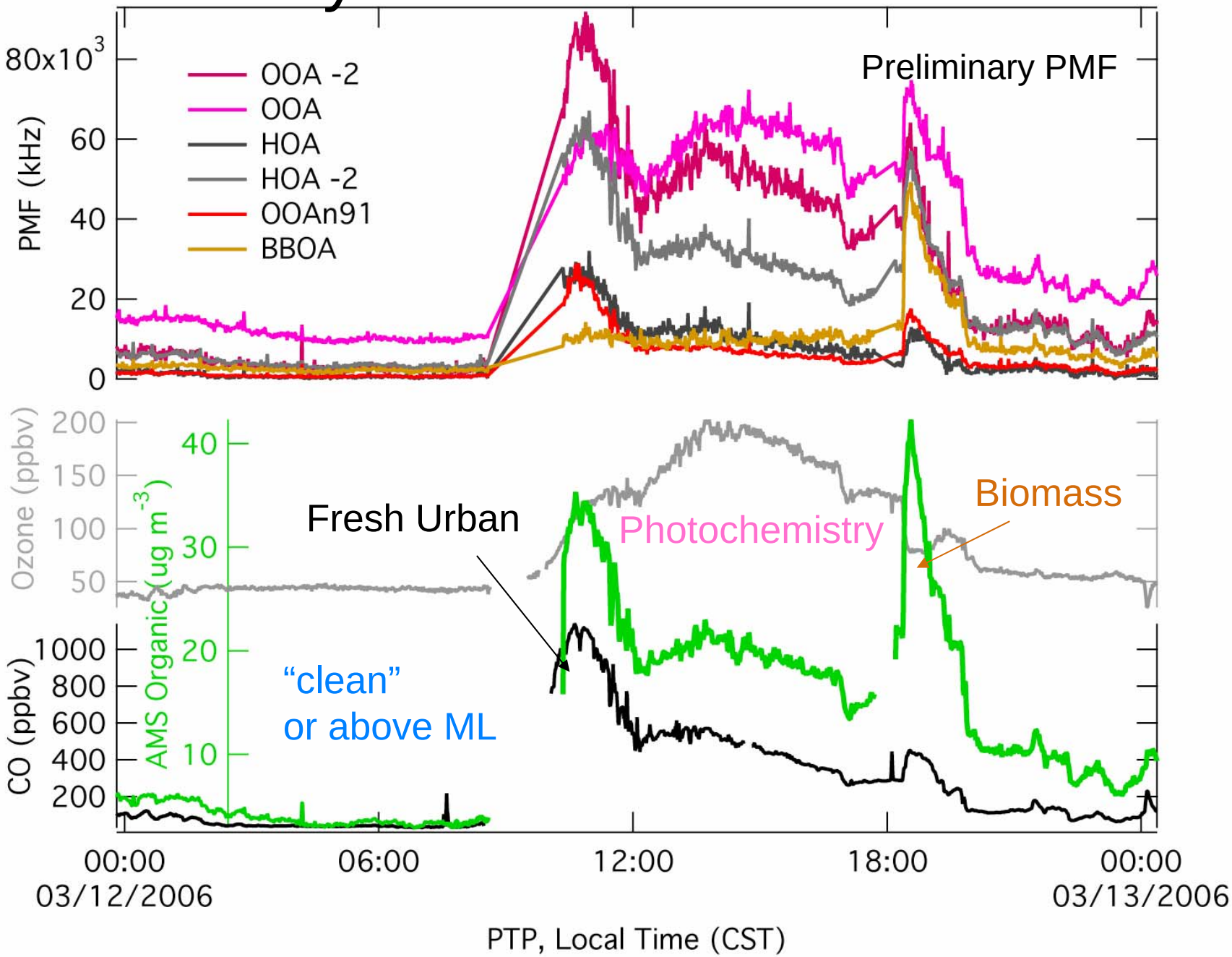
Photochemical Secondary Aerosol

SMPS
Purple ⇒few
Red ⇒many



Particulate Mass Composition…

Secondary Aerosol & Biomass Event

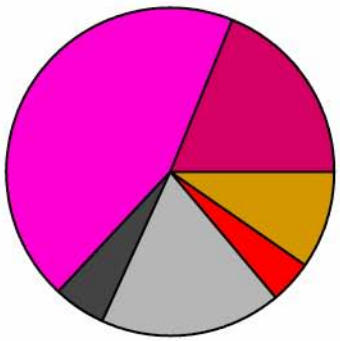


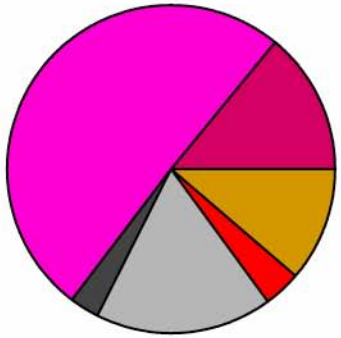
urban residual
00:00:00

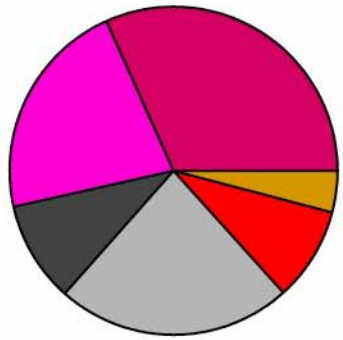
"clean"
05:00:00

fresh urban
10:00:00

OOA
OOA-2
BBOA
OOAn91
HOA-2
HOA







$$\frac{\text{AMS Organic}}{\text{CO}} = 50$$

$$\frac{\text{AMS Organic}}{\text{CO}} = 60\text{-}70$$

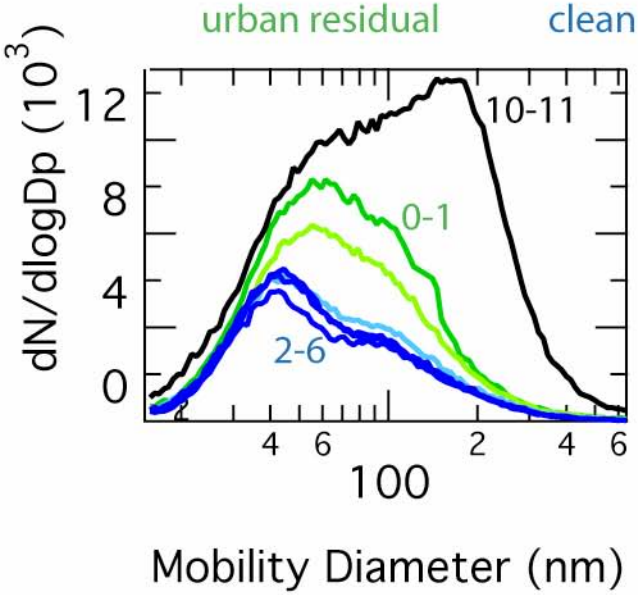
$$\frac{\text{AMS Organic}}{\text{CO}} = 31$$

$(\mu g\ m^{-3}\ ppm^{-1})$

00:00 urban residual

06:00 clean

12:00 fresh urban



"Fresh urban" at PTP is already 10+ times greater than observations of traffic at T0

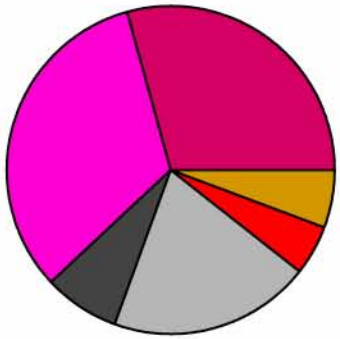
photochemistry
12:00:00

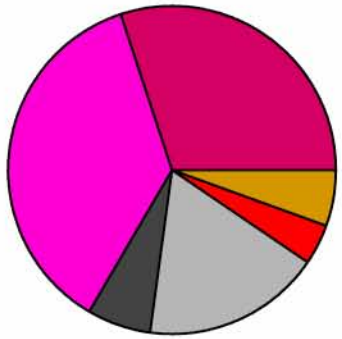
photochemistry
14:00:00

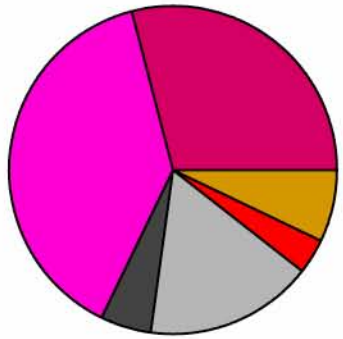
photochemistry
16:00:00

OOA
OOA-2
BBOA

OOAn91
HOA-2
HOA







$$\frac{\text{OOA}}{\text{OOA-2}} = 1.1$$

$$\frac{\text{OOA}}{\text{OOA-2}} = 1.2$$

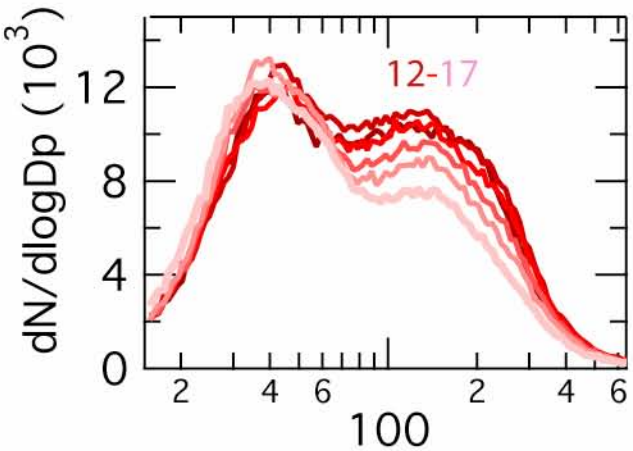
$$\frac{\text{OOA}}{\text{OOA-2}} = 1.4$$

$$\frac{\text{AMS Organic}}{\text{CO}} = 36$$

$$\frac{\text{AMS Organic}}{\text{CO}} = 42$$

$$\frac{\text{AMS Organic}}{\text{CO}} = 57$$

ug m^{-3} ppm^{-1}

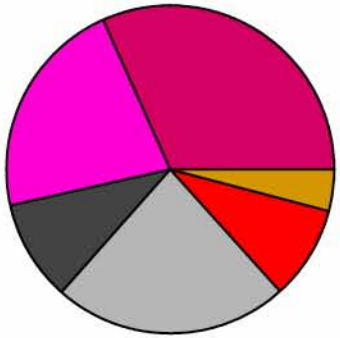


AMS Organic/CO increases 12-16 OOA to OOA-2

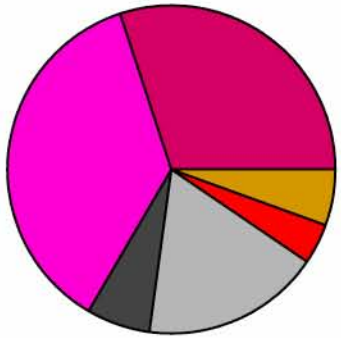
OOA
OOA-2
BBOA

OOAn91
HOA-2
HOA

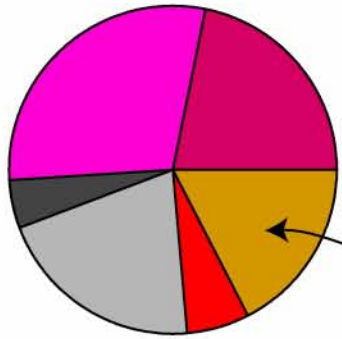
fresh urban
10:00:00



photochemistry
14:00:00



biomass/urban
18:00:00

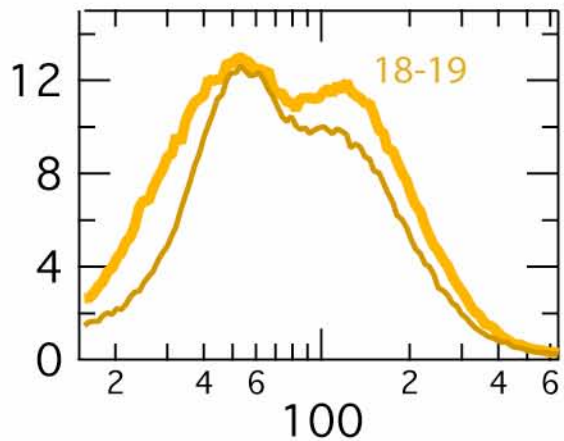


$$\frac{\text{AMS Organic}}{\text{CO}} = 31 \qquad \frac{\text{AMS Organic}}{\text{CO}} = 42 \qquad \frac{\text{AMS Organic}}{\text{CO}} = 107$$

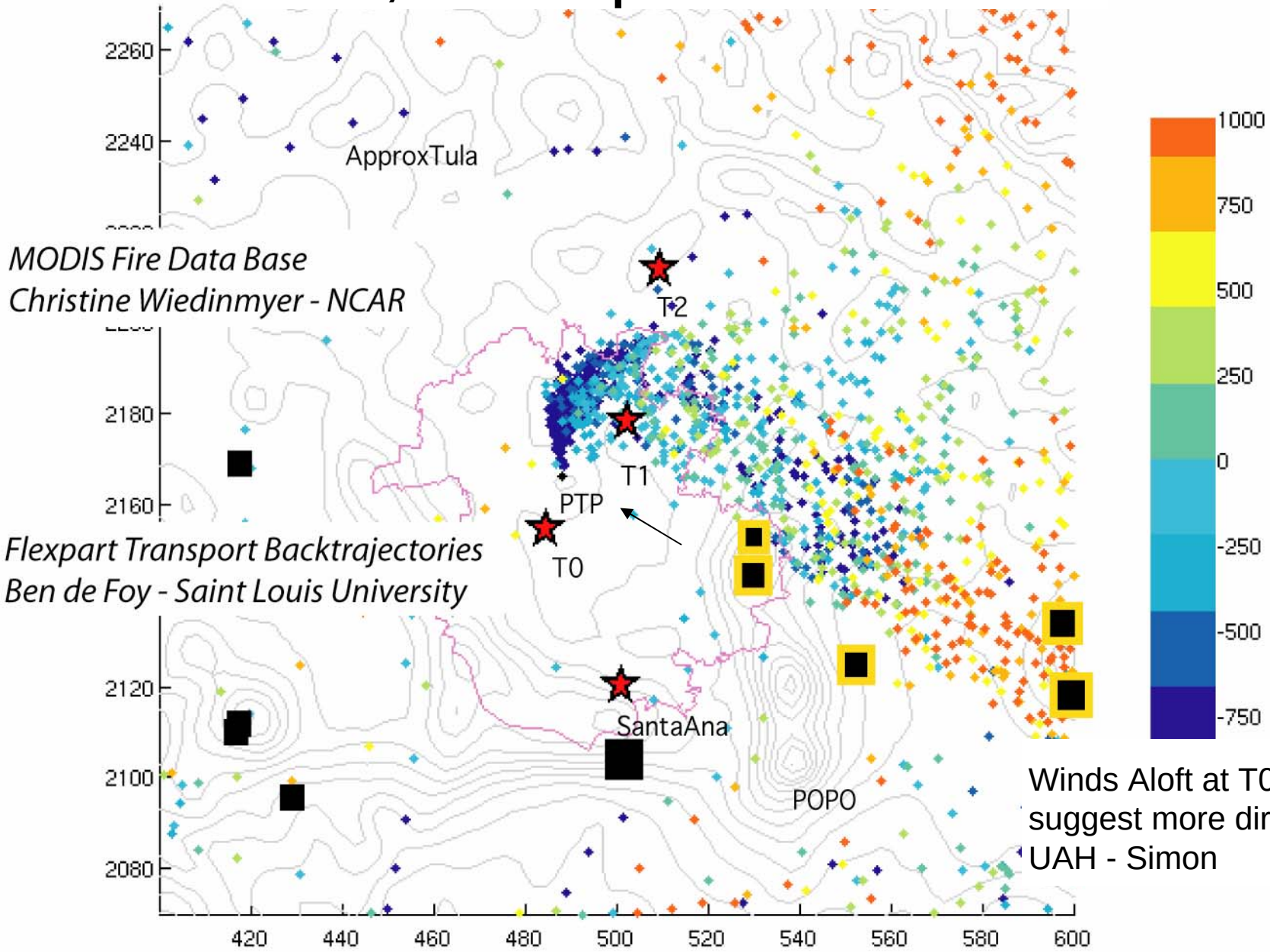
$\mu g\ m^{-3}\ ppm^{-1}$

Where did the fire plume come from?

18:00
biomass/urban



MODIS, Transport & Winds Aloft

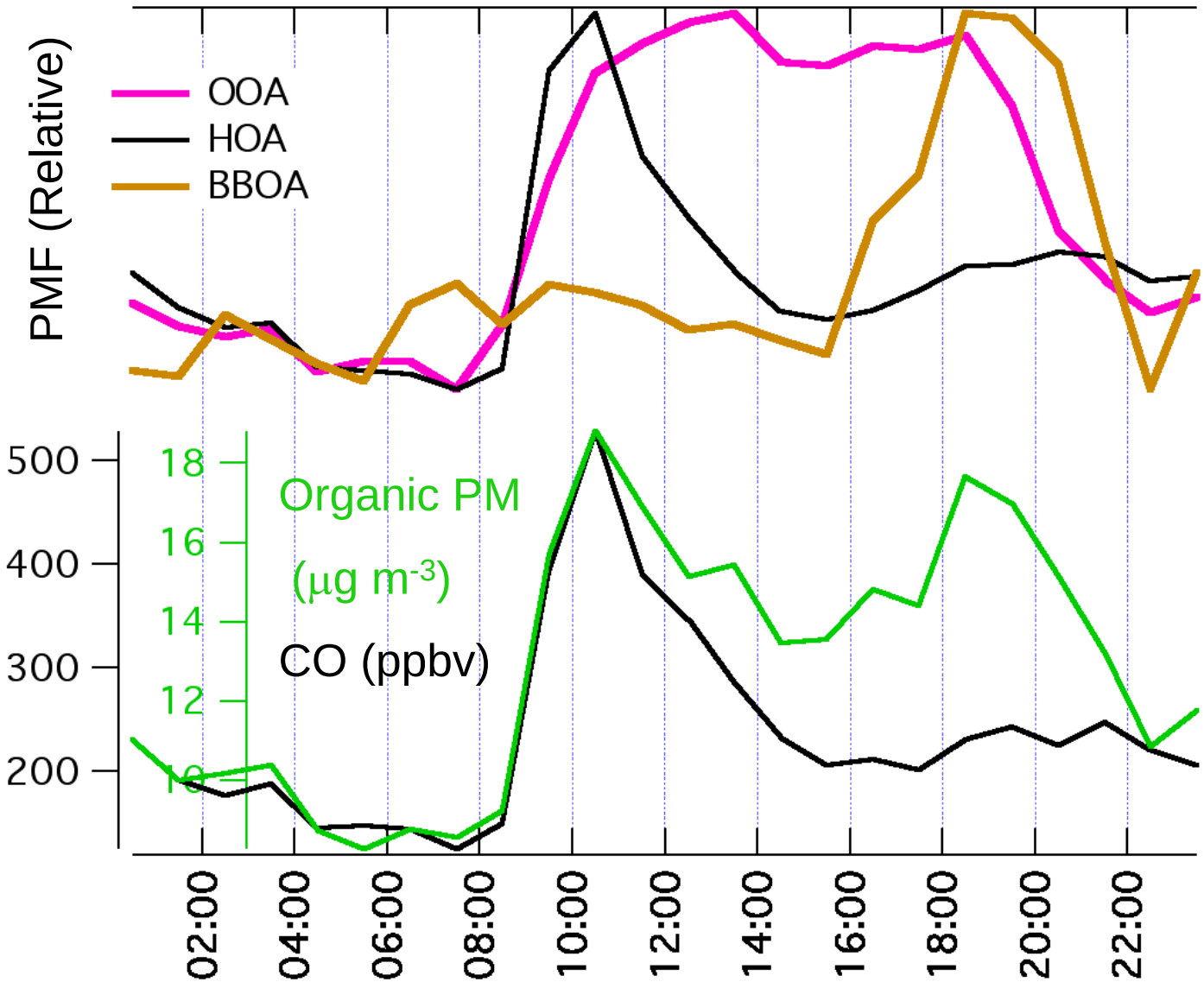


MODIS Fire Data Base
Christine Wiedinmyer - NCAR

Flexpart Transport Backtrajectories
Ben de Foy - Saint Louis University

Winds Aloft at T0
suggest more direct route
UAH - Simon

Secondary Aerosol



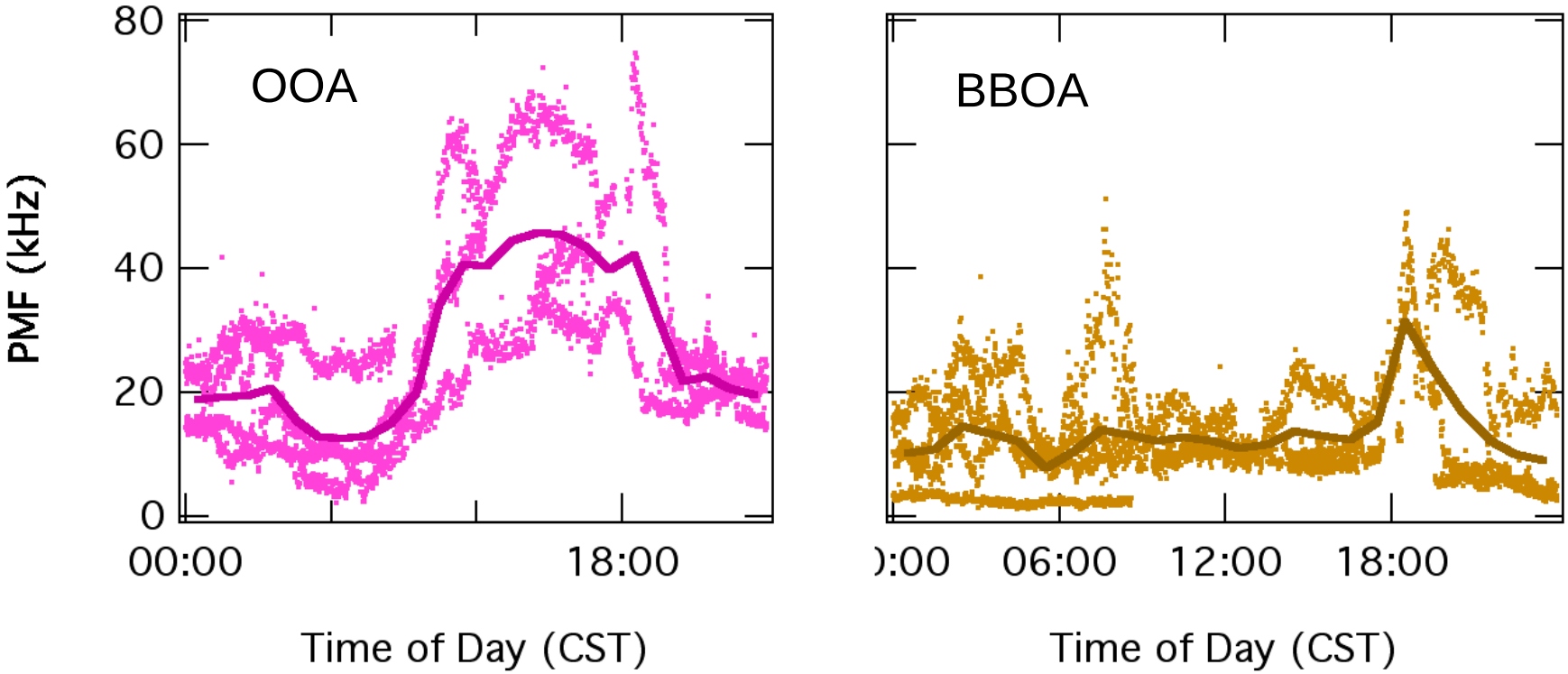
HOA correlates with am urban plume

OOA correlates with photochemical processing of urban plume

Fire events BBOA+ One such event - corroborated by transport and MOUDIS

all data PTP

OOA and BBOA Diurnal Profiles



OOA genuine “diurnal”

BBOA “events”

only “South to North” PTP

Observations

PTP site received mixed urban emission with some biomass each morning with mixing layer increase

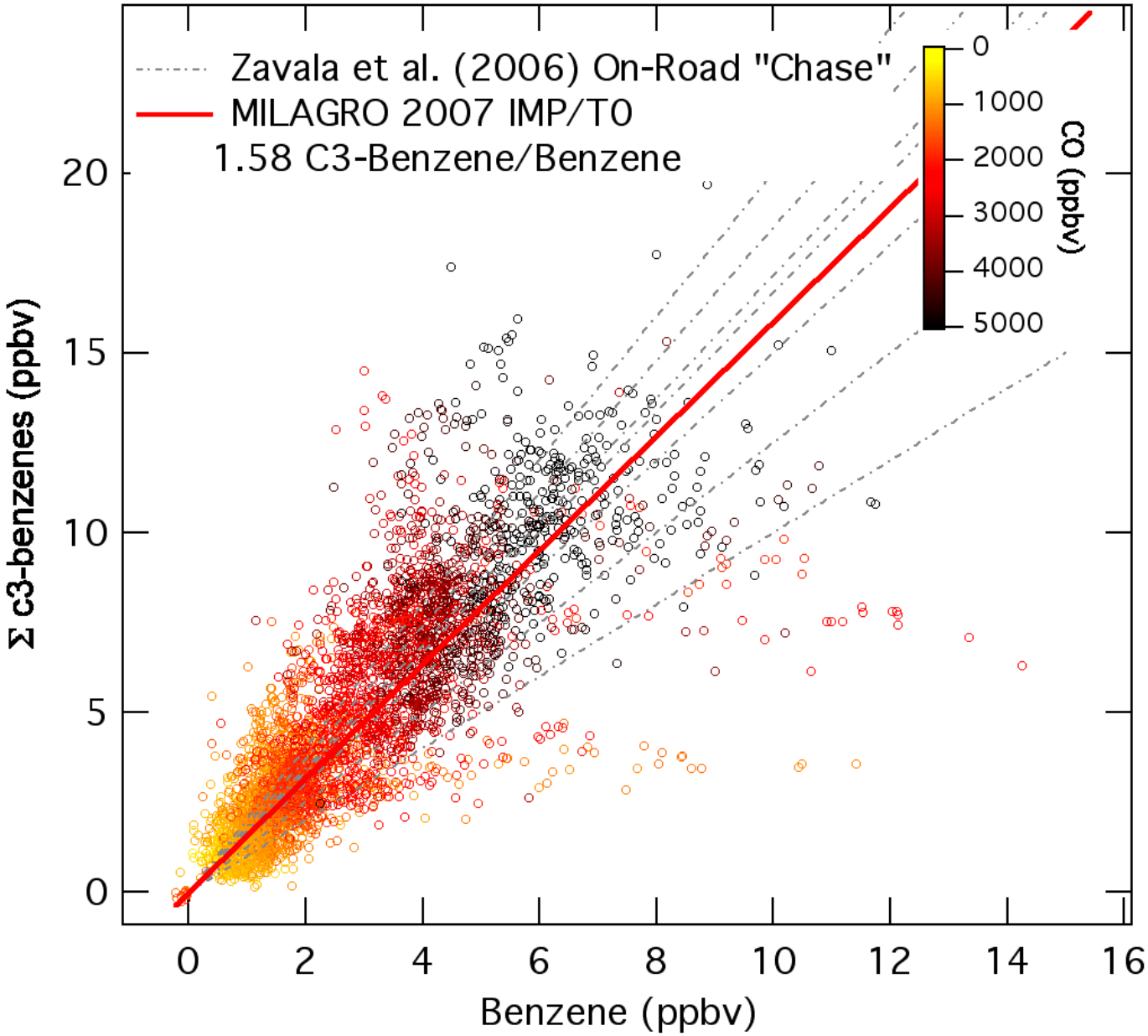
VOC ratios to CO or Benzene indicate airmass is semi-processed (2 hrs after sun-up)
VOC ratios suggest active photochemistry

Organic PM/CO ratio increased with photochemical processing -subdefined Organic OOA-2 (less ox) to OOA (more ox) shows oxidation

Air influenced by biomass burning is transported to PTP; sometimes in dramatic events.

Continue Analysis… transport and catalog events
Canister VOC results to further pinpoint age & signatures
Assess VOC photochemical clock times and starting ratios

On-Road Distribution Of Emission Ratios



Emissions

Combustion

gasoline
diesel*
Jet*
natural gas
liquefied petroleum
-=-=-=-=-=-=-
wood (fires)
coal*
natural gas
diesel*

$C_xH_y + O_2 \rightarrow H_2O + CO_2$

not always perfect...

C_xH_y unburned

$C_xH_y + O_2 \rightarrow C_{x-?}H_{y-?}O$ partial burn

$\rightarrow$ CO (carbon monoxide)

black carbon (soot)

comes from air
contains 80% N_2

$N_2 + O_2 \rightarrow NO, NO_2$

'zeldovich-green'

"NOx" = $NO + NO_2$

*may contain sulfur ->SO_2, H_2SO_4

Industrial

volatile organic compounds
myriad species
ethene, propene, butadiene
formaldehyde, acetaldehyde
ammonia (NH_3)

Agricultural

methane (CH_4)
NH_3, N_2O

Biogenic

isoprene
terpenes
NH_3
H_2S
DMS (marine)

subset of mobile lab measurements

"quartet+"

CO_2, CO, NO, NO_2, SO_2

Aromatics

benzene, toluene
xylene (C2-benzene)
trimethyl (C3-benzene)

Oxygenates

formaldehyde,
acetaldehyde
acetone, glyoxal
methanol

Other Species

ethene, propene
isoprene, methanol
NH_3; GC - VOCs

Particulate

Black Carbon PM
Organic, Sulfate
Ammonium, Nitrate
Chloride
Number count
Optical Dust

Emissions and Boundary Layer Height: Influence on Mixing Ratios

- mixing layer above PTP

- mixing layer below PTP