It's a...

Four very short stories about NOy: the C-130 perspective

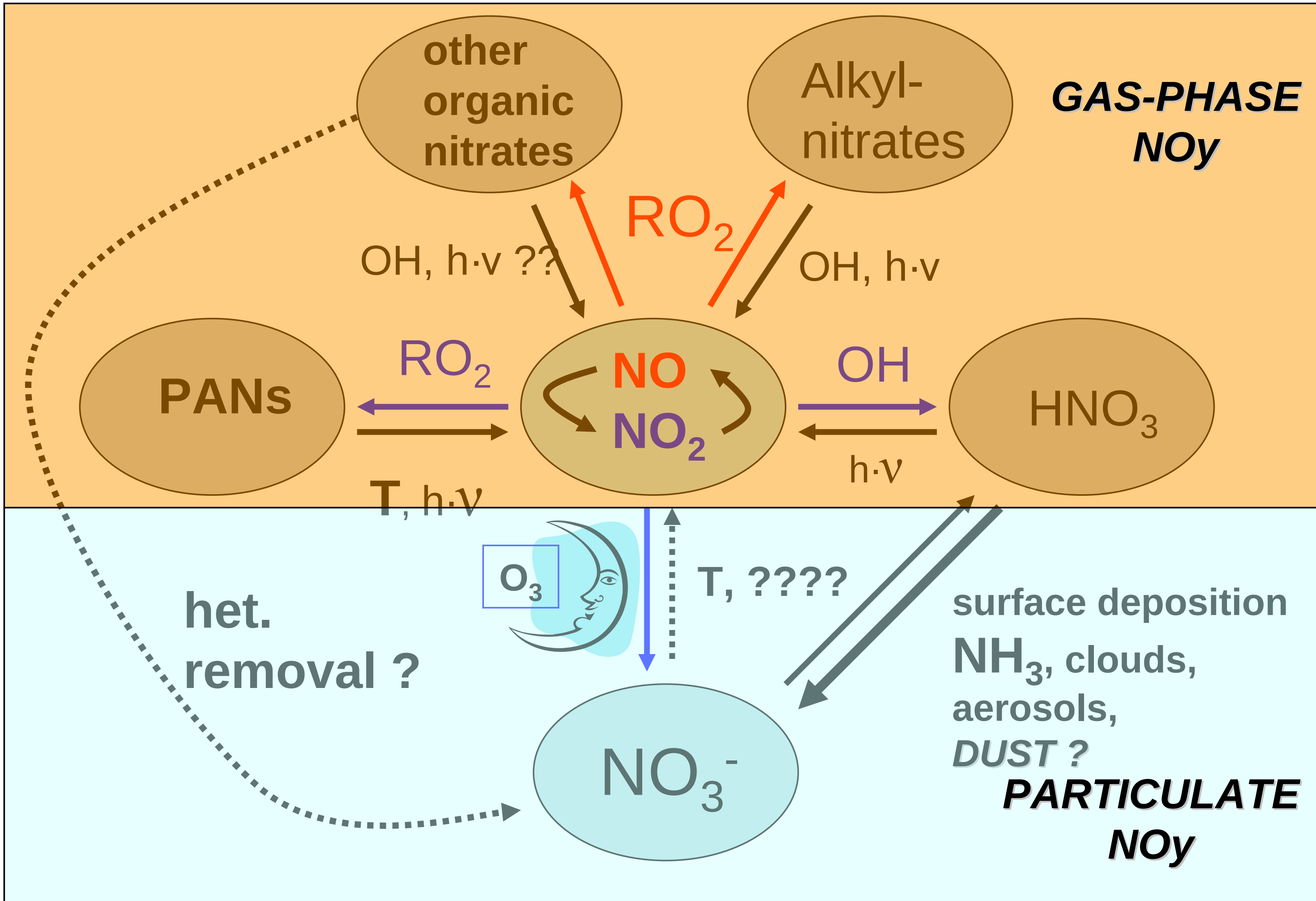
The C-130 science team,
Frank Flocke, Andy Weinheimer, Danny McKenna, and the NCAR CARI group, Tony Clarke and the HIGEAR team, the **DOE G-1 team,**
and Ron Cohen's group (UC Berkeley) at T-1
MILAGRO Met. forecasting team

Thanks to: Sasha Madronich
XueXi Tie, Louisa Emmons

NCAR/RAF, pilots, mechanics, project management
NCAR/EOL (JOSS)
NCAR logistics
Menzies (esp. Adolfo) and VER Airport personnel
SENEAM and Mexico City ATC
Mexican Air Force (particularly Capt. Jorge Hiucochea)

It's a...

NOy



other organic nitrates
Alkyl-nitrates
GAS-PHASE NOy
RO2
OH, h·v ??
OH, h·v
RO2
PANs
NO
NO2
OH
HNO3
h·ν
T, h·ν
O3
T, ????
het. removal ?
surface deposition
NH3, clouds, aerosols,
DUST ?
PARTICULATE NOy
NO3-

It's a...

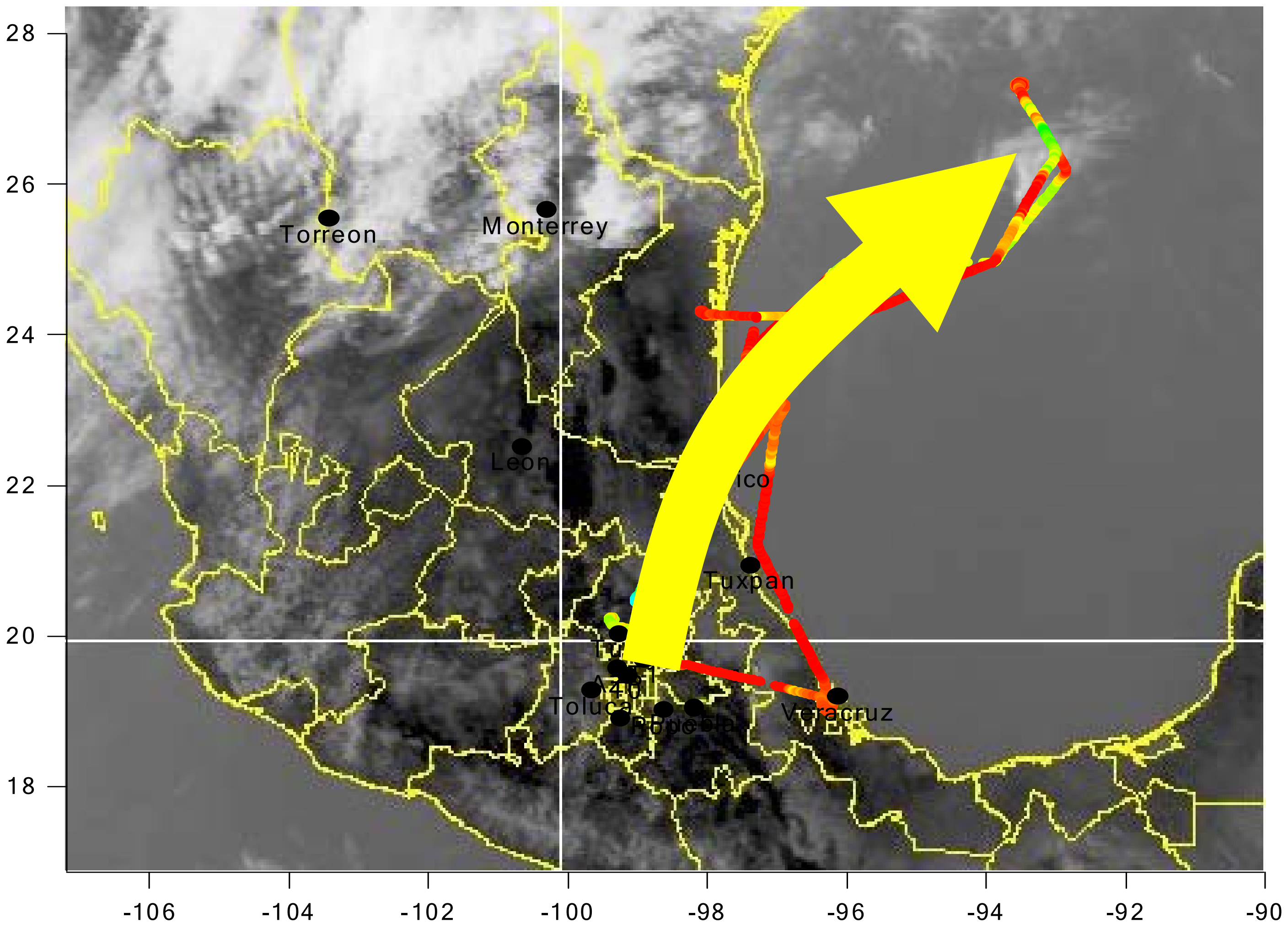
two scenarios:

• 3/19/2006 flight (fresh outflow, 1 day and 2 day old air sampled)
both the C-130 and the G-1 sampled MCMA outflow on the 18th

• all flights – samples where air mass passed over MCMA
previously – as derived from FLEXPART trajectories

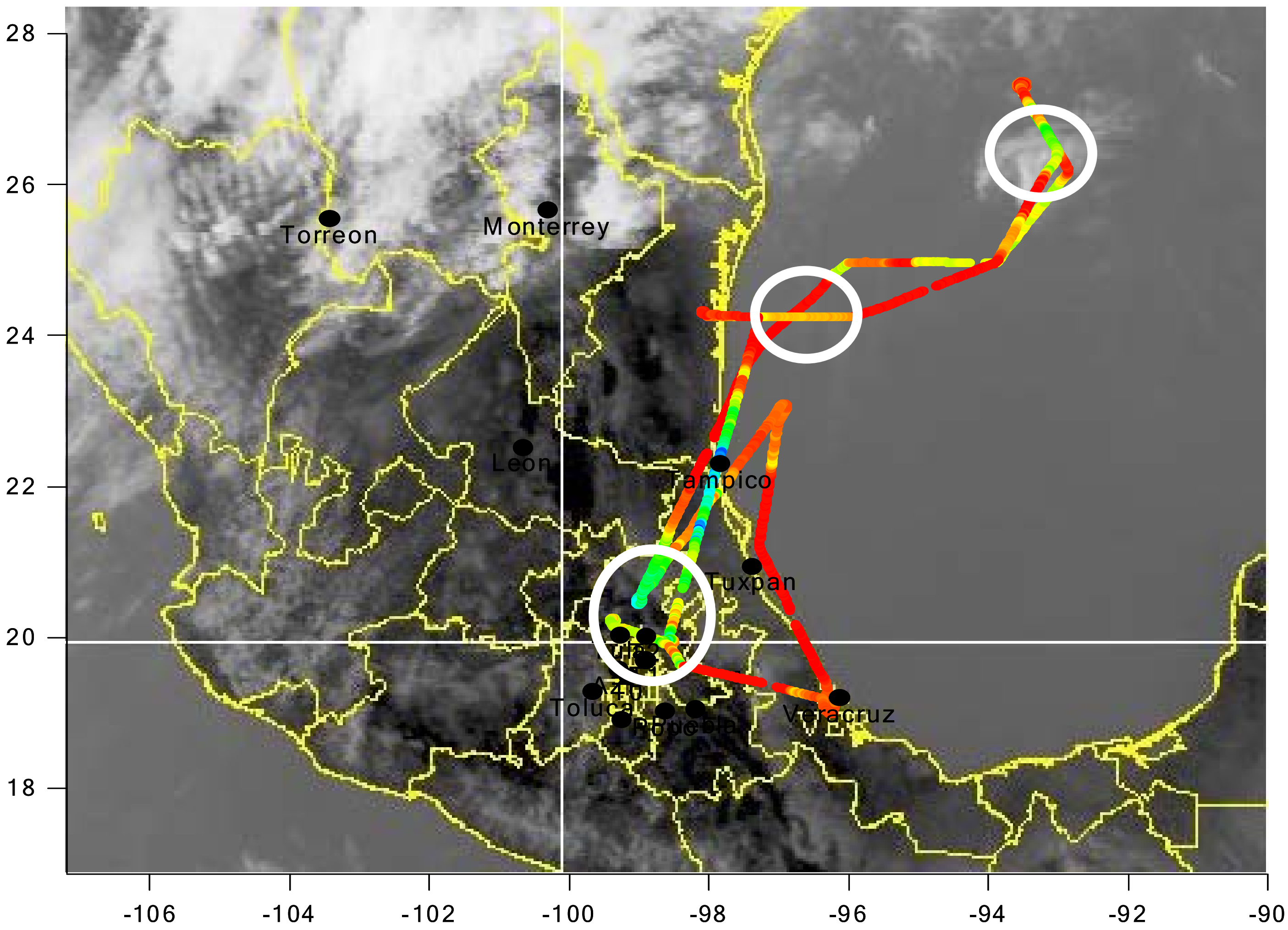
It's a...

C-130: 3/19 flight

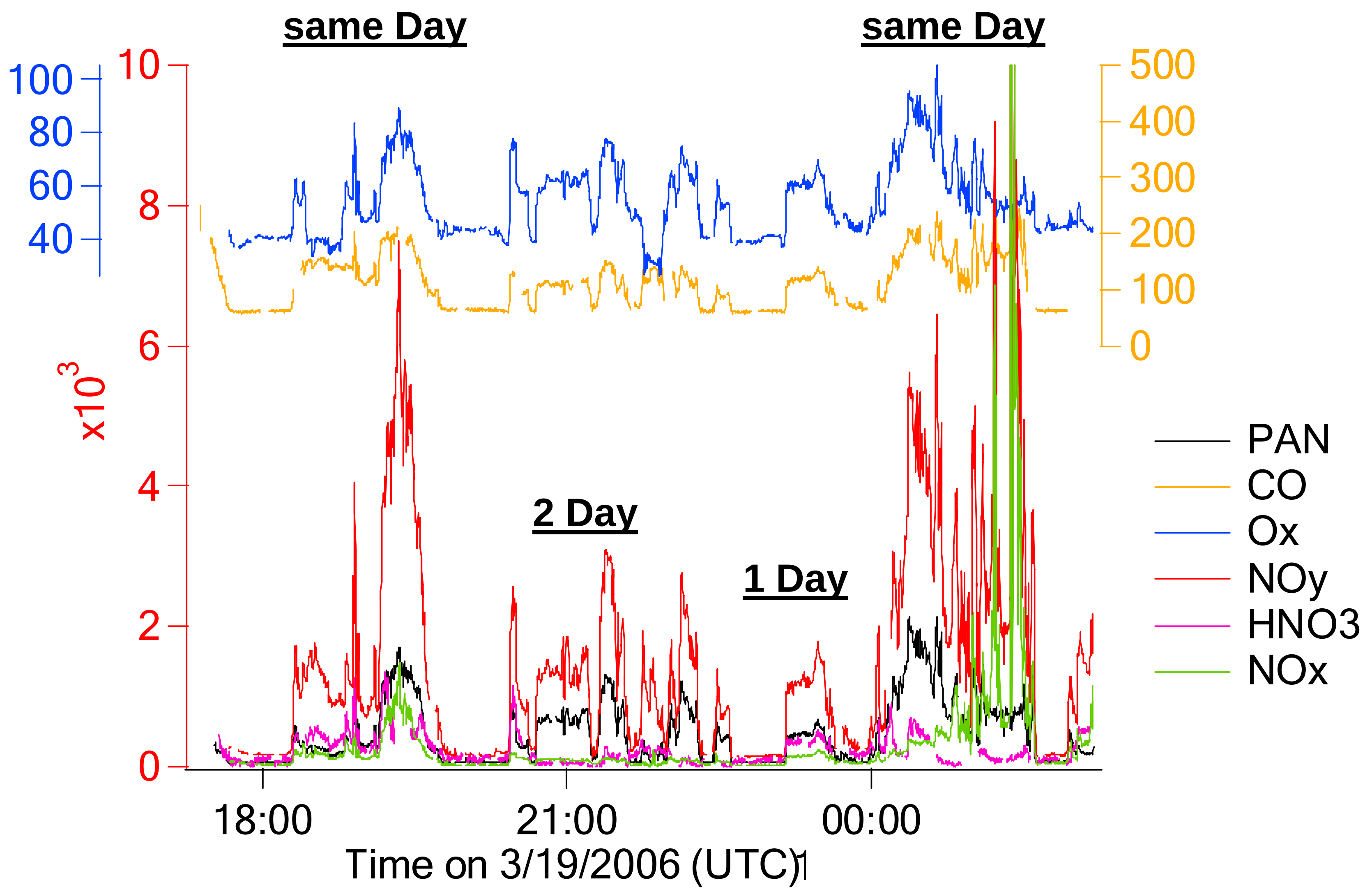


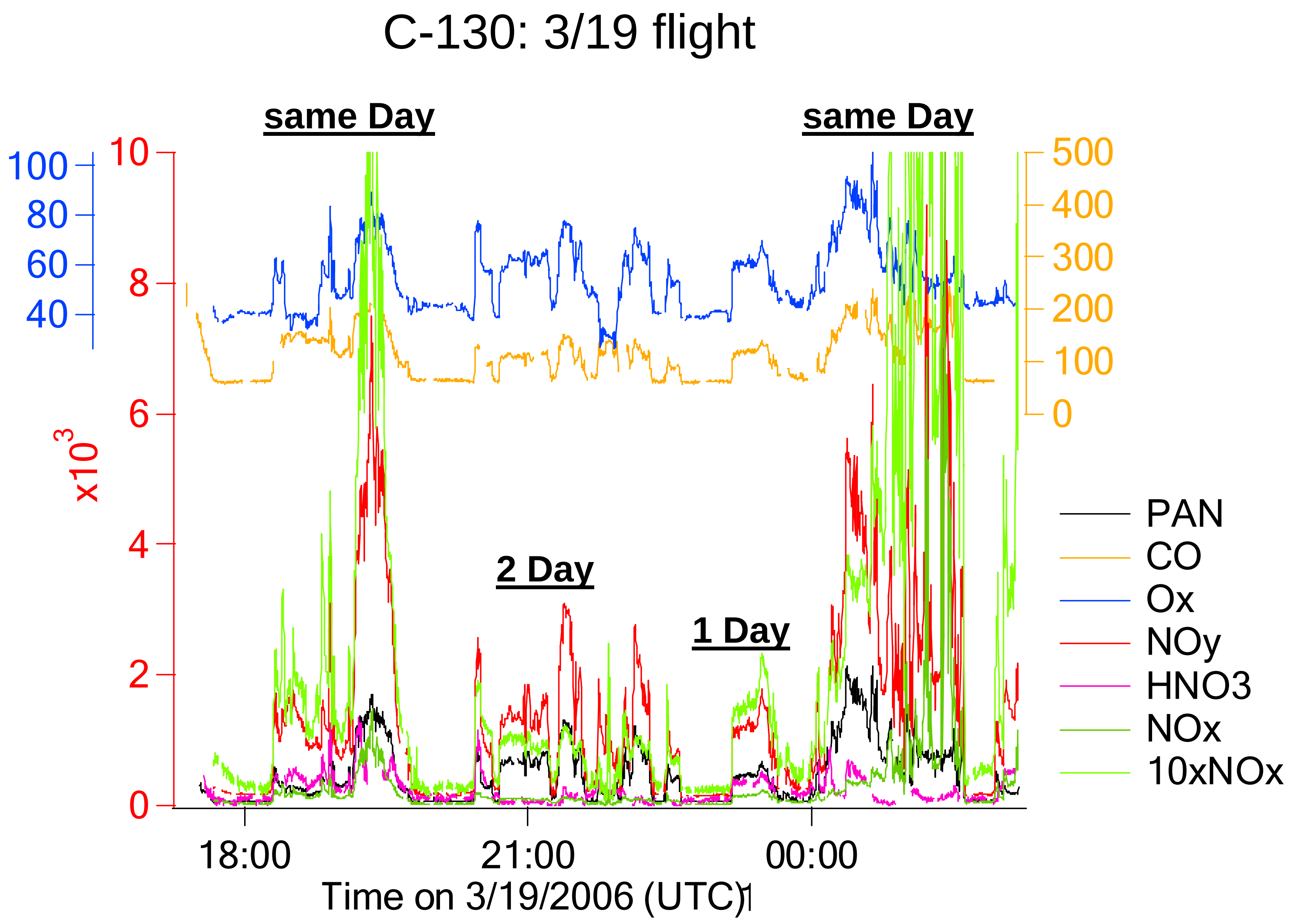
It's a...

C-130: 3/19 flight



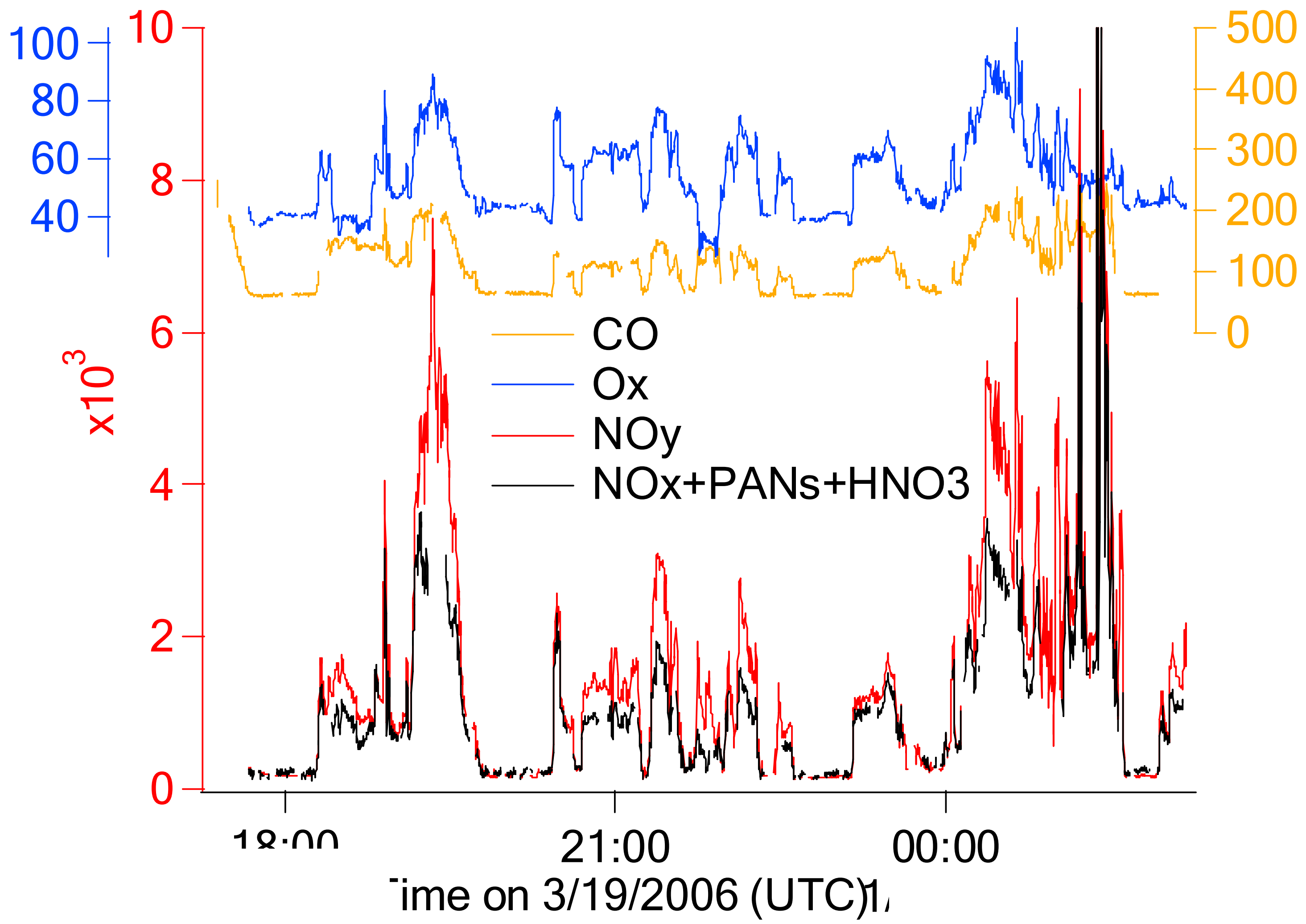
C-130: 3/19 flight





C-130: 3/19 flight
same Day
same Day
2 Day
1 Day
100
80
60
40
10
8
6
4
2
0
x10^3
500
400
300
200
100
0
PAN
CO
Ox
NOy
HNO3
NOx
10xNOx
18:00
21:00
00:00
Time on 3/19/2006 (UTC)

C-130: 3/19 flight

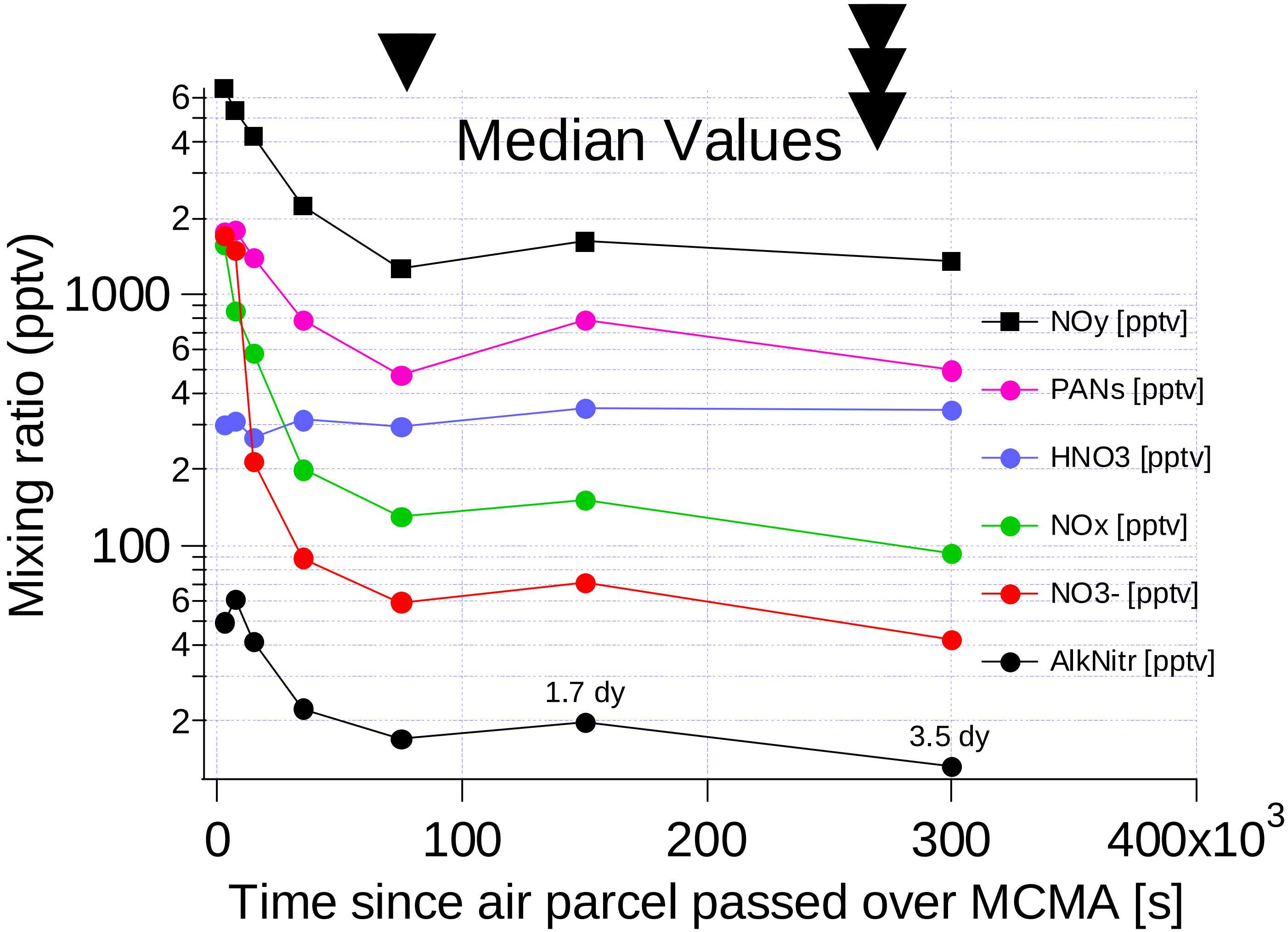


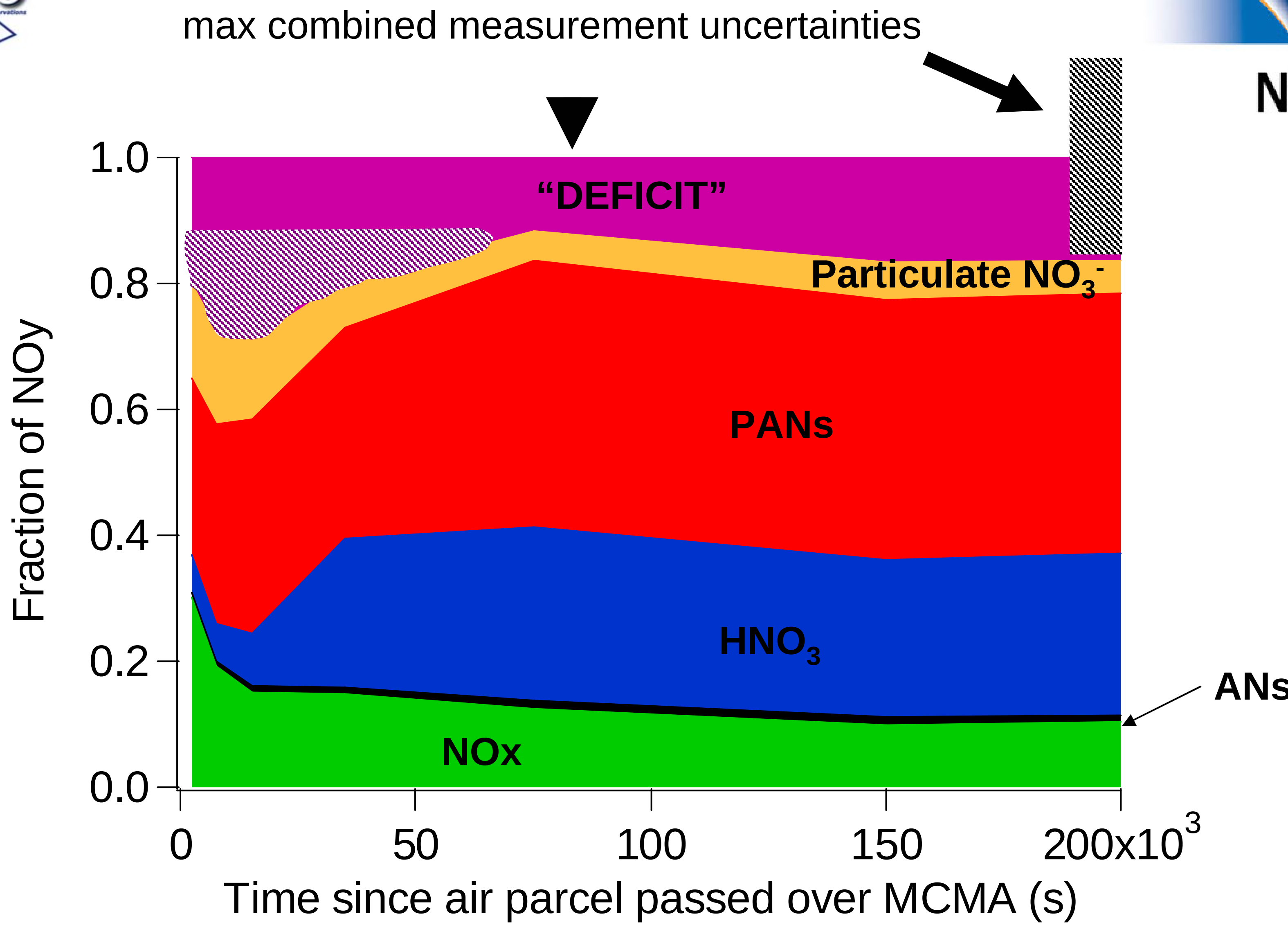
Is this March 18/19 outflow event typical
for all MCMA outflow events observed from the C-130 ?

NOy shortfall
NOx
Ozone

It's a...

NOy species mixing ratios downwind of MCMA – data from all flights where air was sampled which had previously passed over the city (D. McKenna)



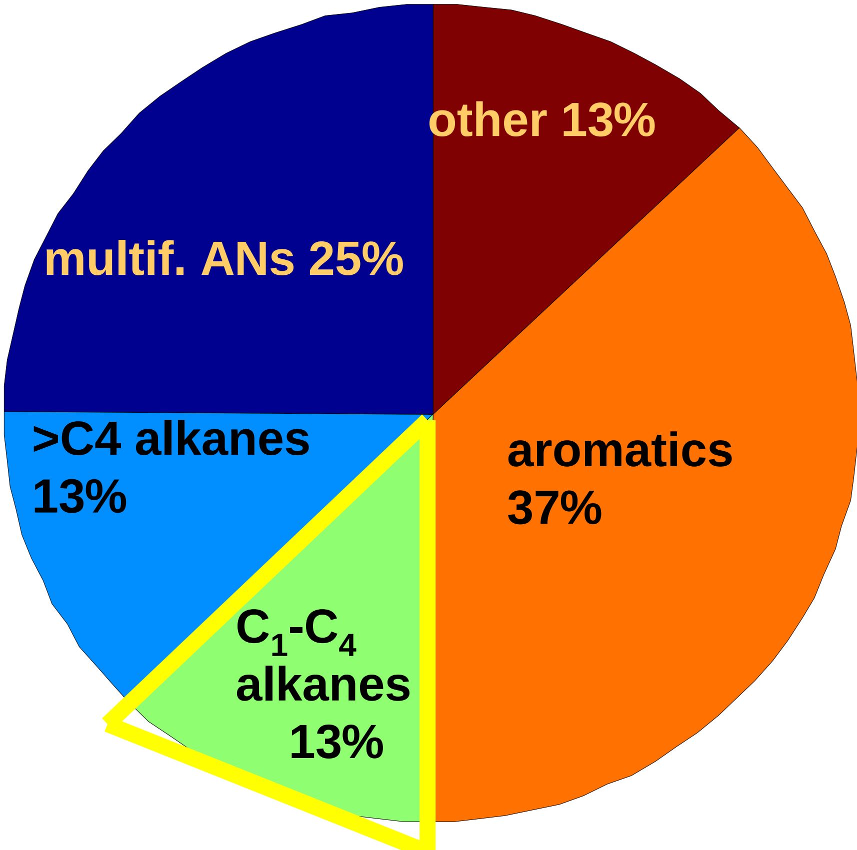


max combined measurement uncertainties
"DEFICIT"
Particulate NO_3^-
PANs
HNO_3
ANs
NOx
Fraction of NOy
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
$200x10^3$
Time since air parcel passed over MCMA (s)

Alkyl and Multifunctional nitrates at T1

The Berkeley model predicts a large fraction of complex organic nitrates formed from VOC emitted in the MCMA.

The small alkyl nitrates (measured on the aircraft) are calculated to represent only 13% of the total. Thus the contribution of ANs to NOy (close to the city) could be as large as 15%



12-18h, ANs precursor distribution

Ron Cohen et al., UC Berkeley

Observations:

- PANs are the dominant fraction of NOy
- persistent NOx far downwind
- HNO_3 as a fraction of NOy is small
- large NOy "deficit" close to MCMA, decreasing somewhat downwind. May be due to complex, but short-lived, ANs

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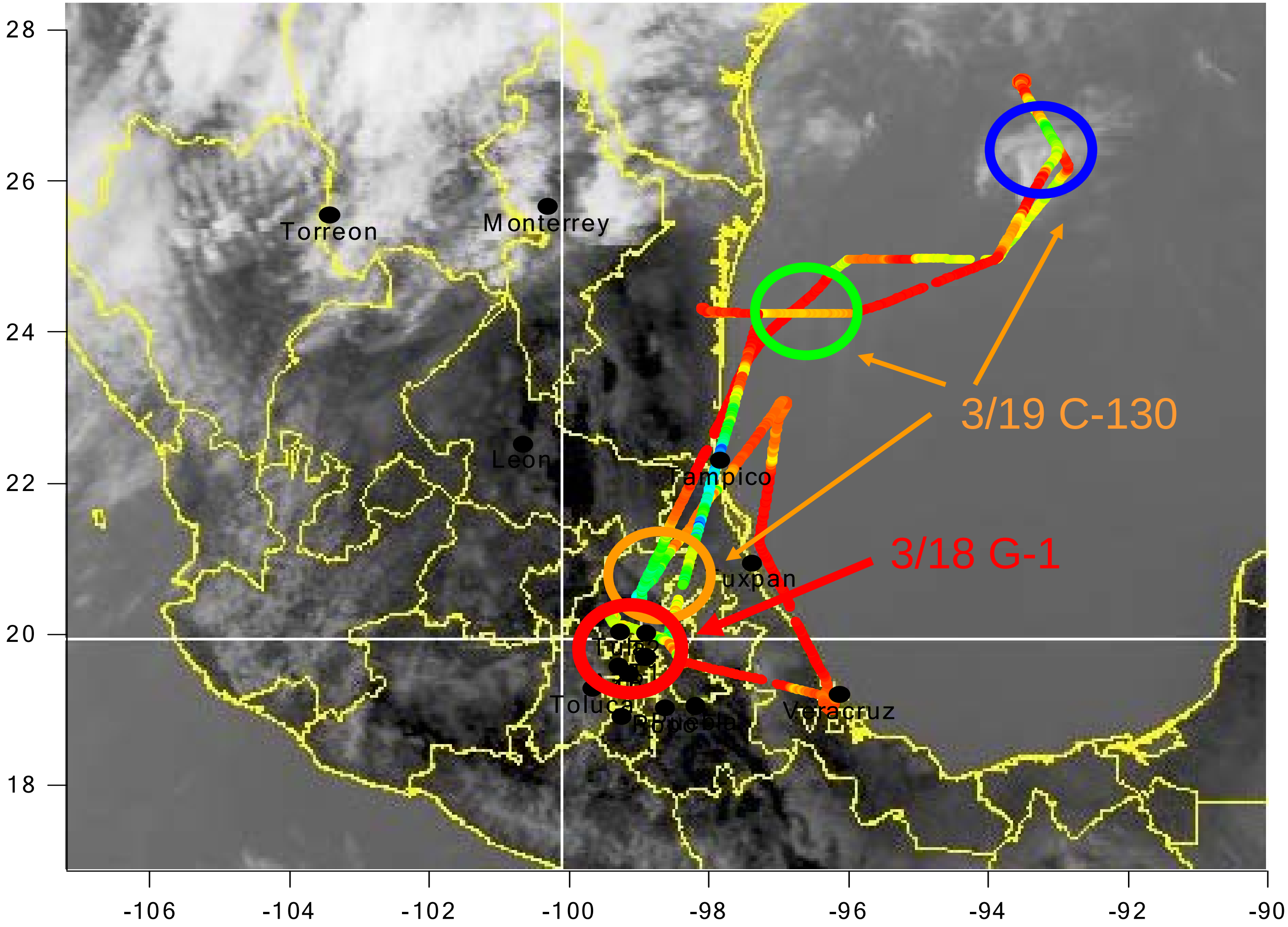
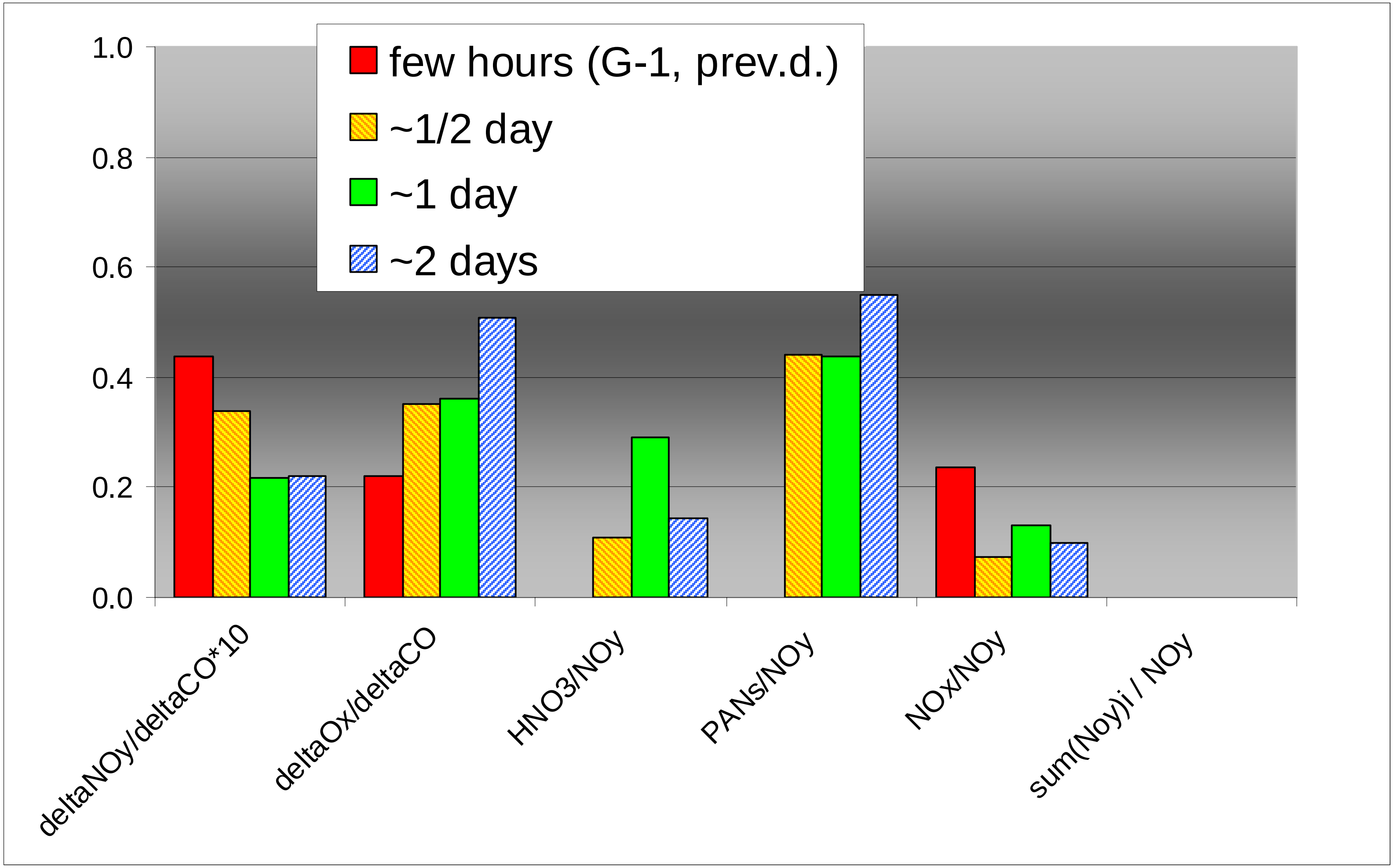
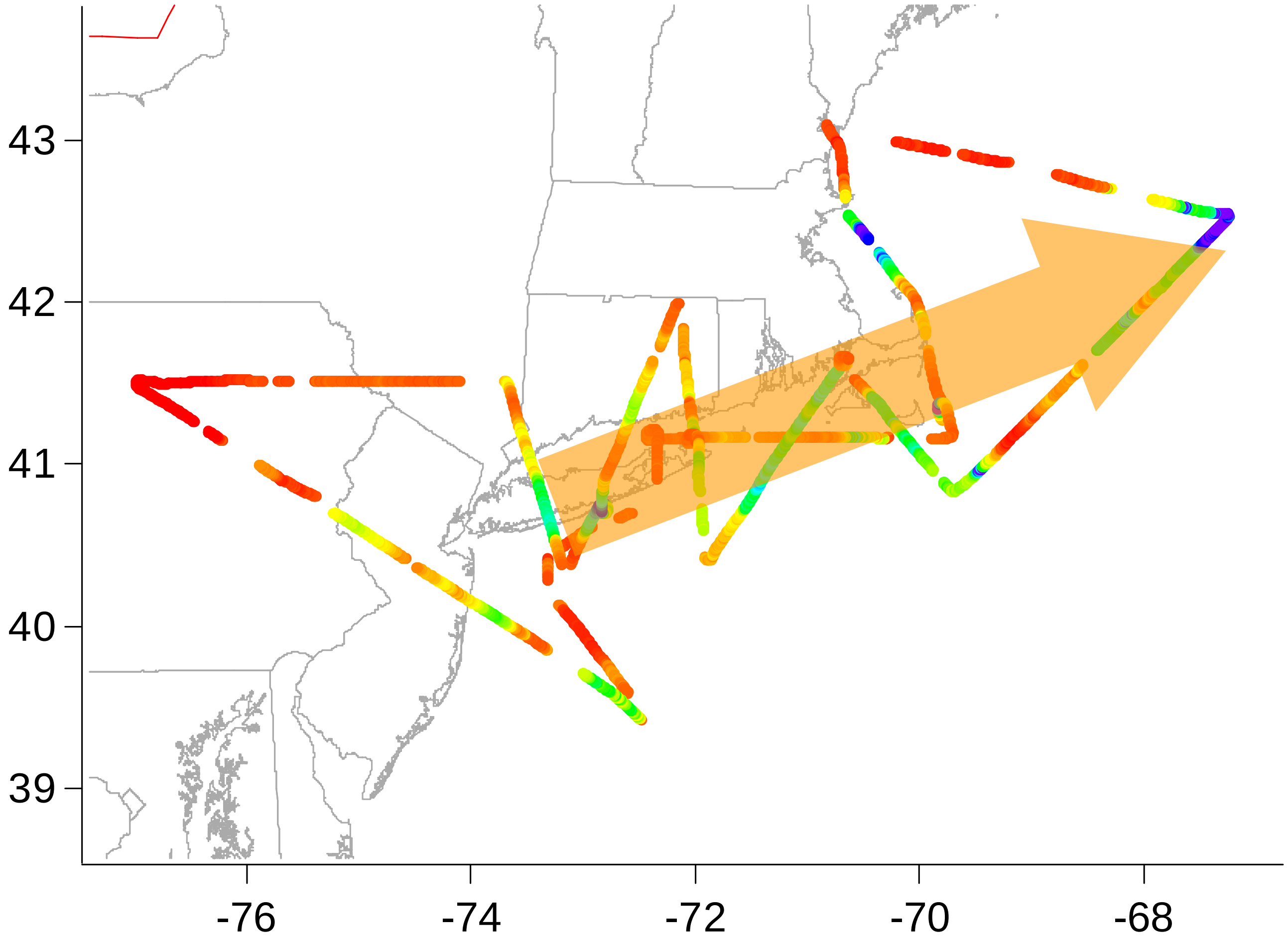

28
26
24
22
20
18
-106
-104
-102
-100
-98
-96
-94
-92
-90
Torreon
Monterrey
Leon
Tampico
Tuxpan
Toluca
Puebla
Veracruz
3/19 C-130
3/18 G-1

Mexico City

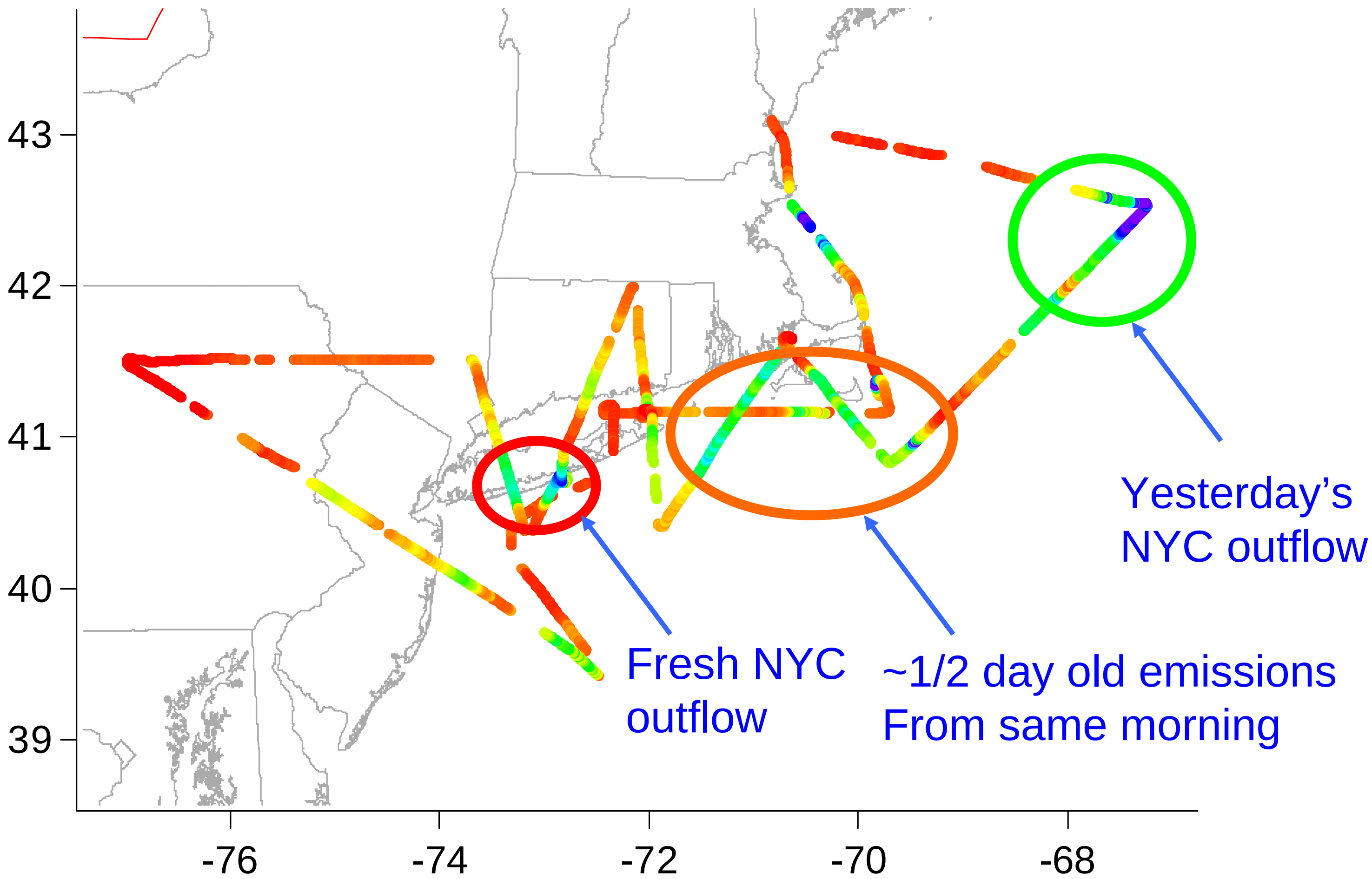


1.0
0.8
0.6
0.4
0.2
0.0
few hours (G-1, prev.d.)
~1/2 day
~1 day
~2 days
deltaNOy/deltaCO*10
deltaOx/deltaCO
HNO3/NOy
PANs/NOy
NOx/NOy
sum(Noy)i / NOy

NEAQS 2004 study, 7/20/2007
NYC outflow study (NOAA P3B)

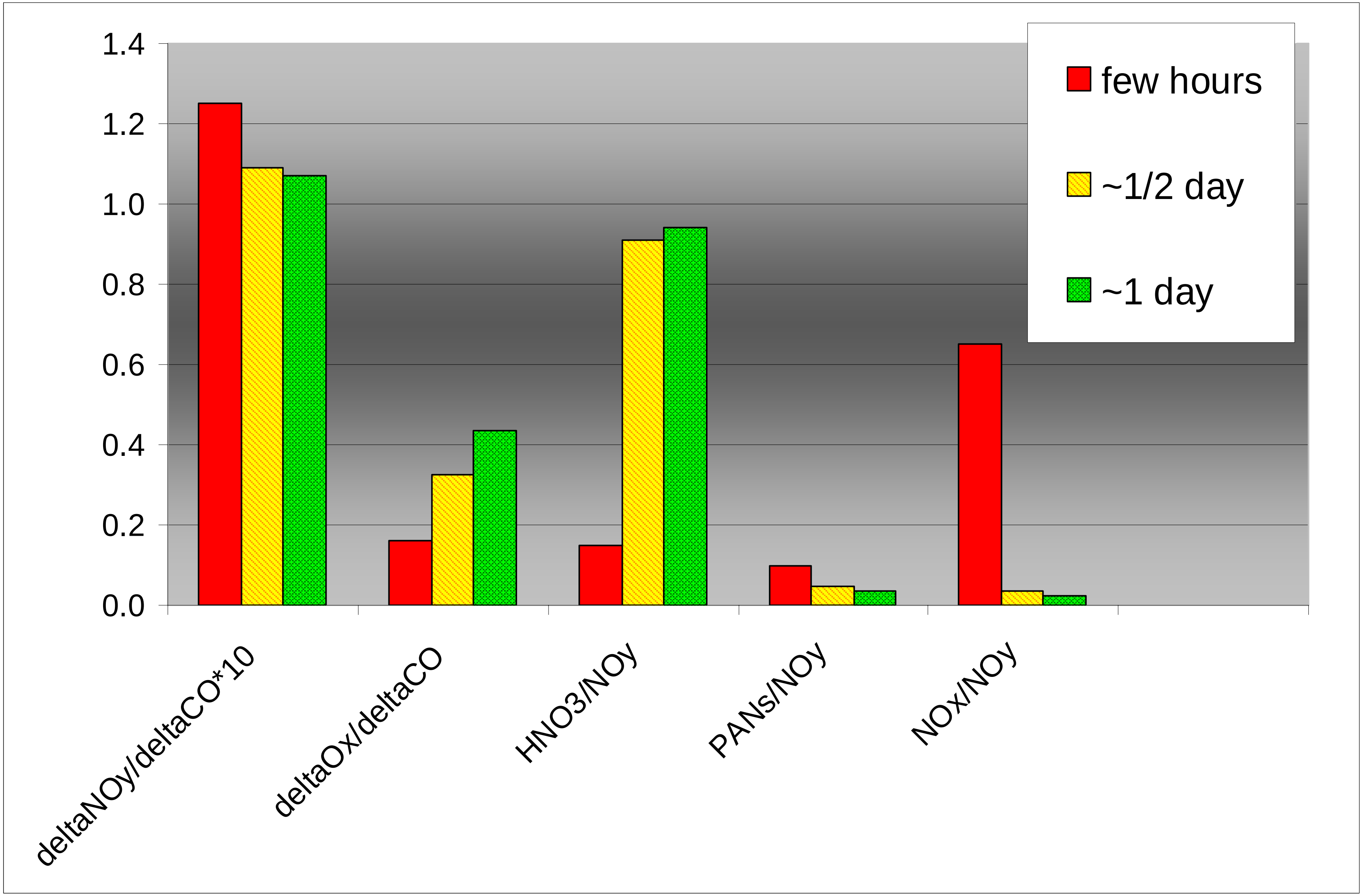


NEAQS 2004 study, 7/20/2007
NYC outflow study (NOAA P3B)



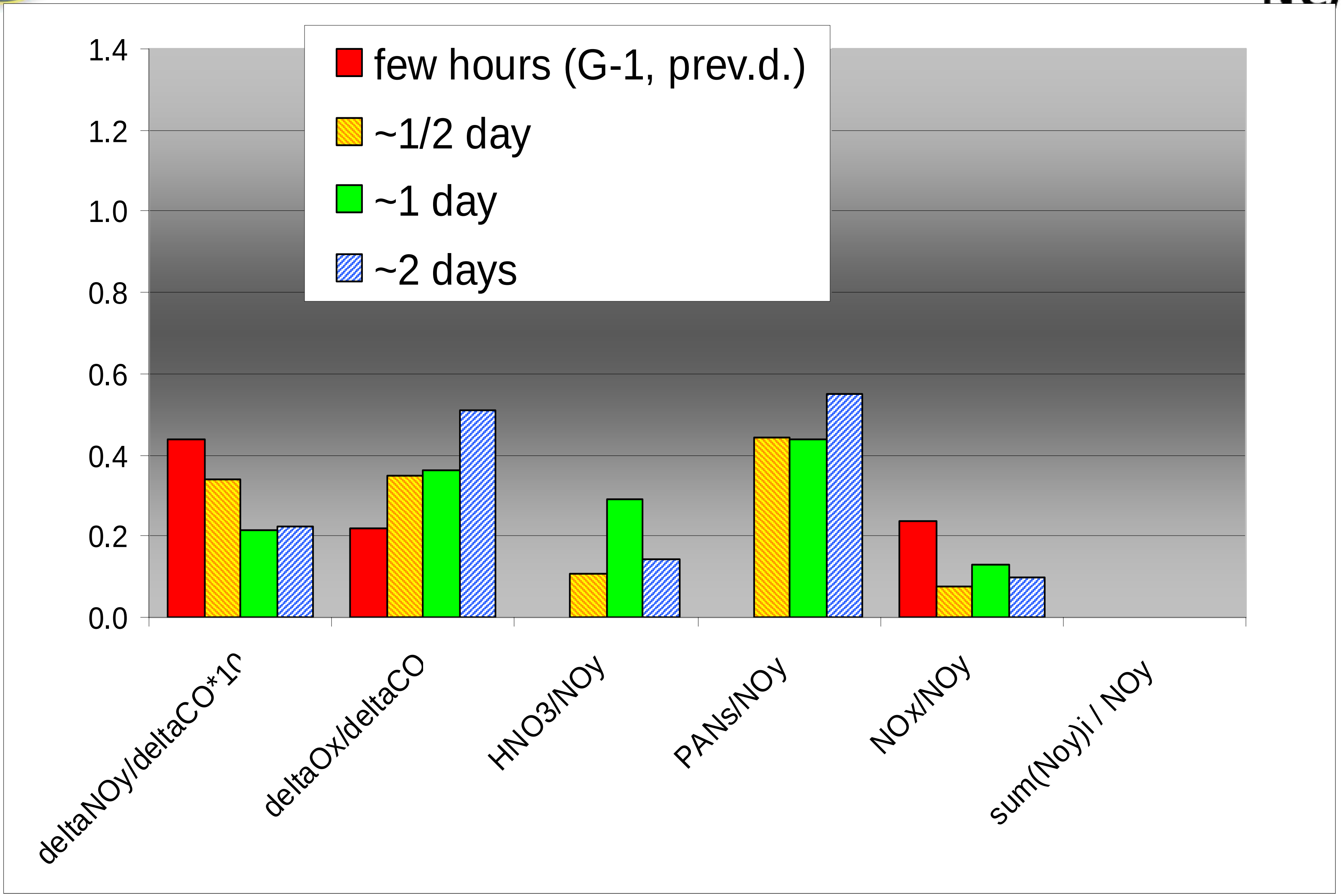
It's a...

New York City



It's a...

Mexico City



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MCMA - NYC

NCAR

• high VOX / NOx ratio.
• high altitude outflow at lower T.

• PANs dominate NOy, HNO_3 fraction is very small

•

•NOx release from PAN decomposition keeps NOx at moderate levels (few 100 pptv).

•Ozone production is slower but still very efficient even after 2 days.

•Ozone will be produced for an extended time further downwind as PANs are still ~1 ppbv in the 2 day old plume observed on the 19^{th} of March.

• evidence for HNO_3 removal process (dust?)

• low VOX / NOx ratio (because of lower VOC.
• low altitude outflow at higher T.

• PANs are very low, HNO_3 is >90% of NOy after ½ day.

•NOx release from PAN decomposition downwind is small.

•Ozone production is faster initially but tapers off after 1 day because of rapidly decreasing NOx.

•HNO_3 is not removed efficiently (air is shielded from ocean surface by MBL).

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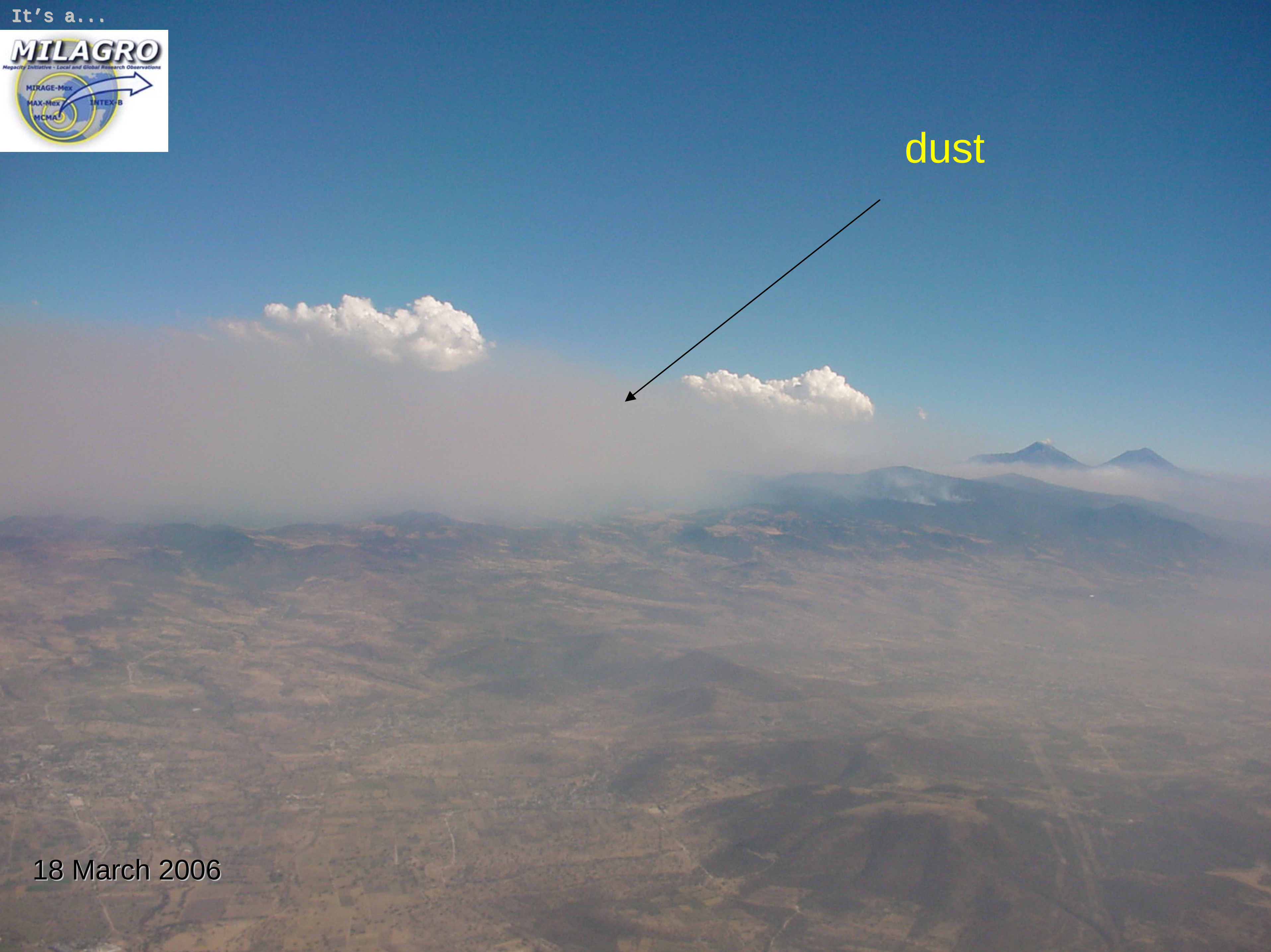
HNO3 uptake by mineral dust?

NCAR

Underwood et al, JGR v. *106* (2001): $\tau_{HNO3} \approx$ 10hrs (Asian dust)

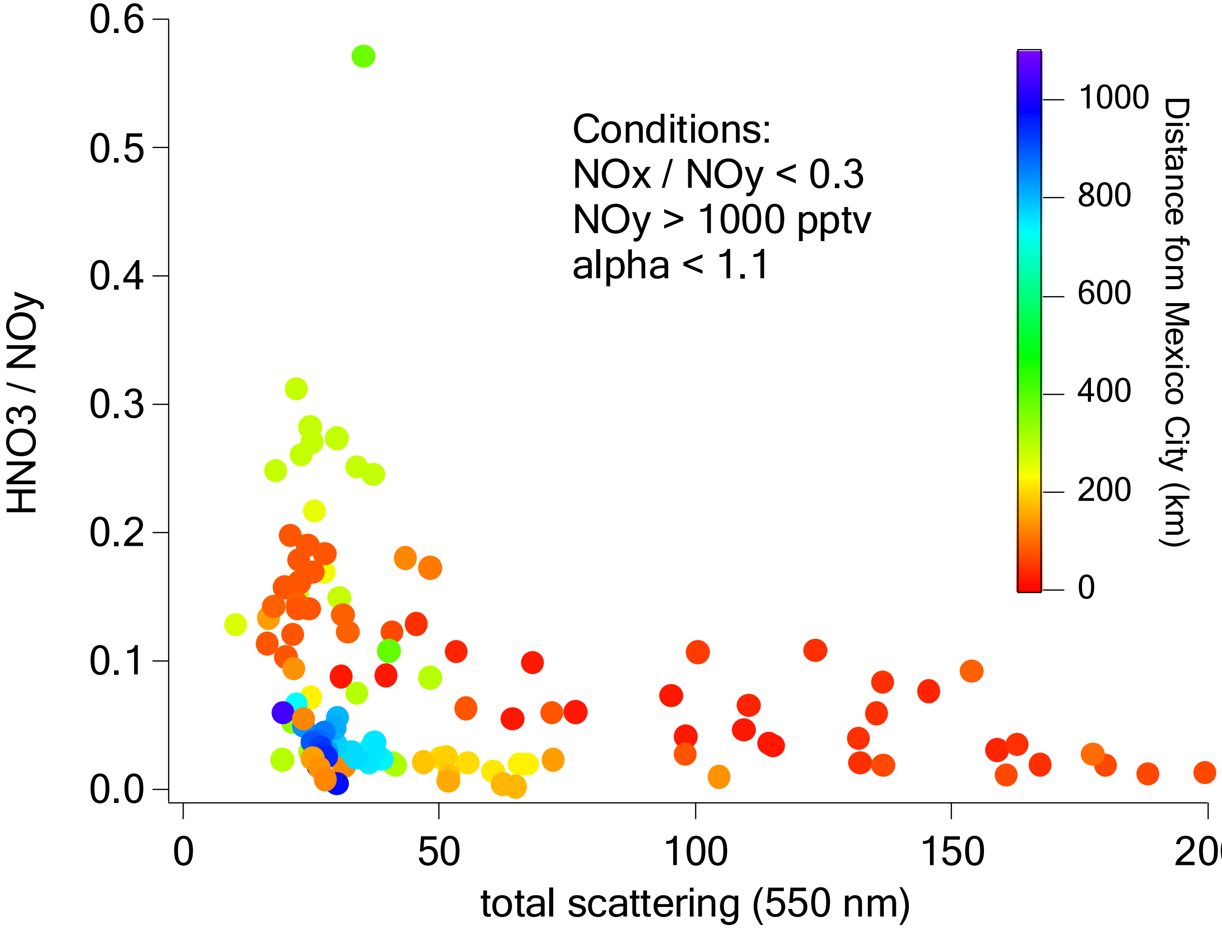
Dentener and Carmichael, Clarke, others (TRACE-P, ACE-Asia)

Mashburn et al., JGR, v.*111* (2006): "The factor of greatest uncertainty in current modeling studies of tropospheric O_3 is the heterogeneous uptake coefficient of HNO_3 on mineral aerosol surfaces"


It's a...
dust
18 March 2006

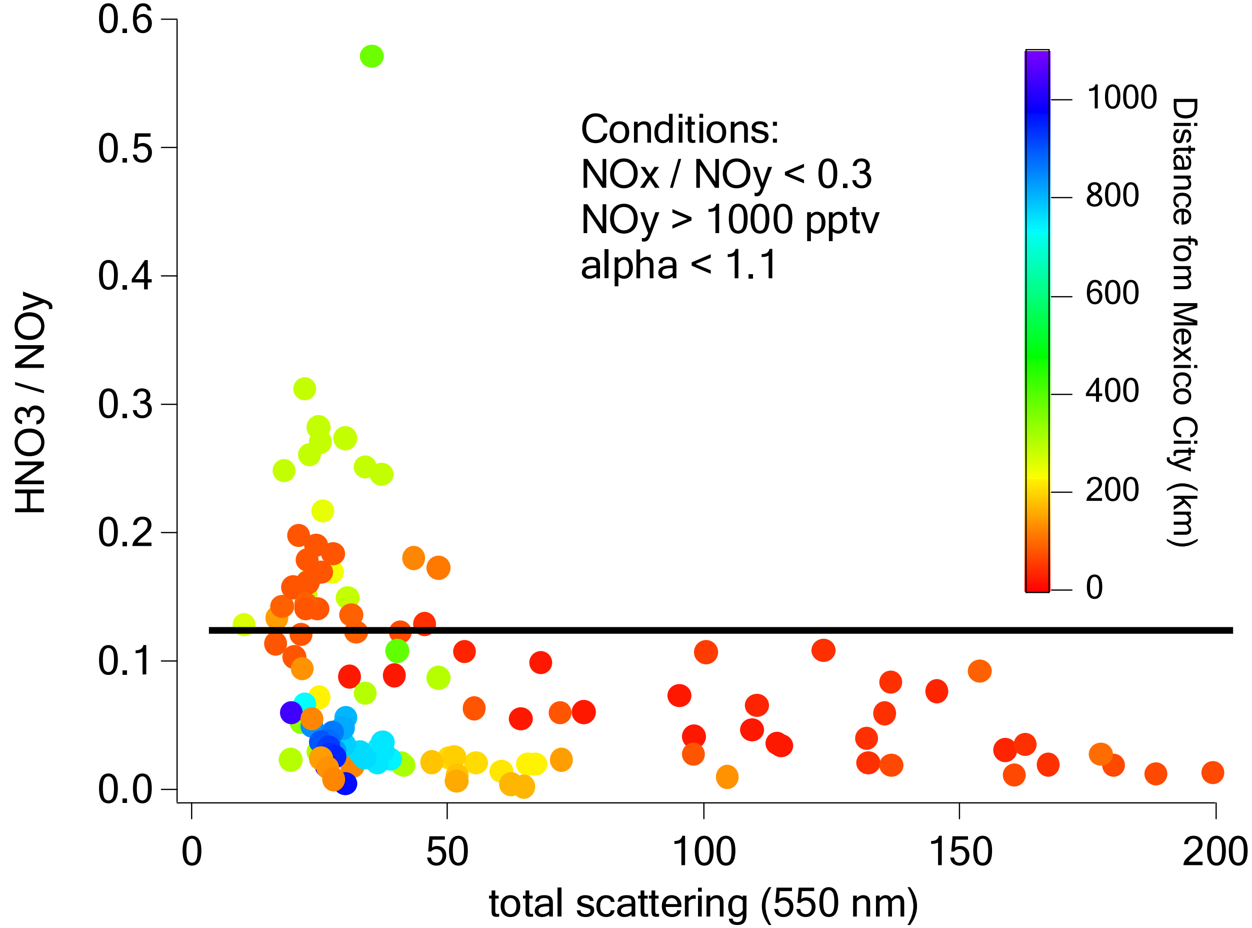
It's a...

HNO3 uptake by mineral dust?



It's a...

HNO3 uptake by mineral dust?



Conclusions

- Because of the large VOC/NOx ratio (despite MCMA probably being VOC-limited most of the time), combined with the high altitude outflow and resulting moderate to low temperatures
  - Ozone production is only moderately fast but
  - continues for several days downwind due to the
  - slow and steady supply of NOx from PANs decomposition

- MCMA outflow exhibits a larger than normal NOy deficit. This could be attributable to complex alkyl and other organic nitrates which were not measured on the aircraft

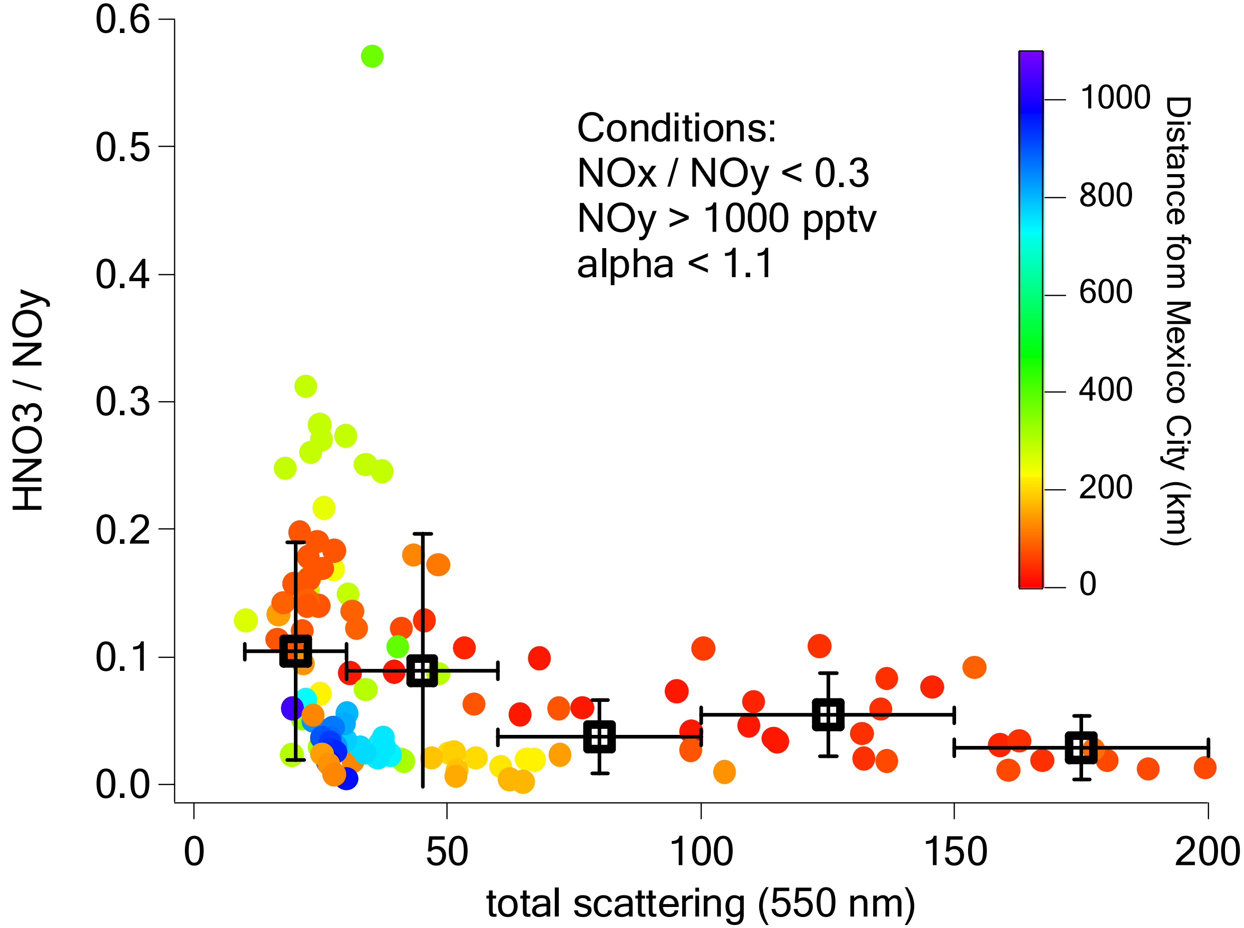
- There is evidence for HNO3 removal by deposition onto mineral dust

- Emissions from wild-fires around MCMA do not appear to contribute substantially to NOx/VOC photochemistry and ozone production in the MCMA outflow

extras

It's a...

HNO3 uptake by mineral dust?



Aerosol optical thickness:

$$\tau 1 = \beta \bullet \lambda_1^{-\alpha}$$

$$\tau 2 = \beta \bullet \lambda_2^{-\alpha}$$

with β = turbidity coeff., λ = wavelength, and α = Ångstrom exponent

α, β are independent of λ

→ for two different wavelengths:

$$\tau 1/(\lambda_1^{-\alpha}) = \tau 2/(\lambda_2^{-\alpha})$$

with:

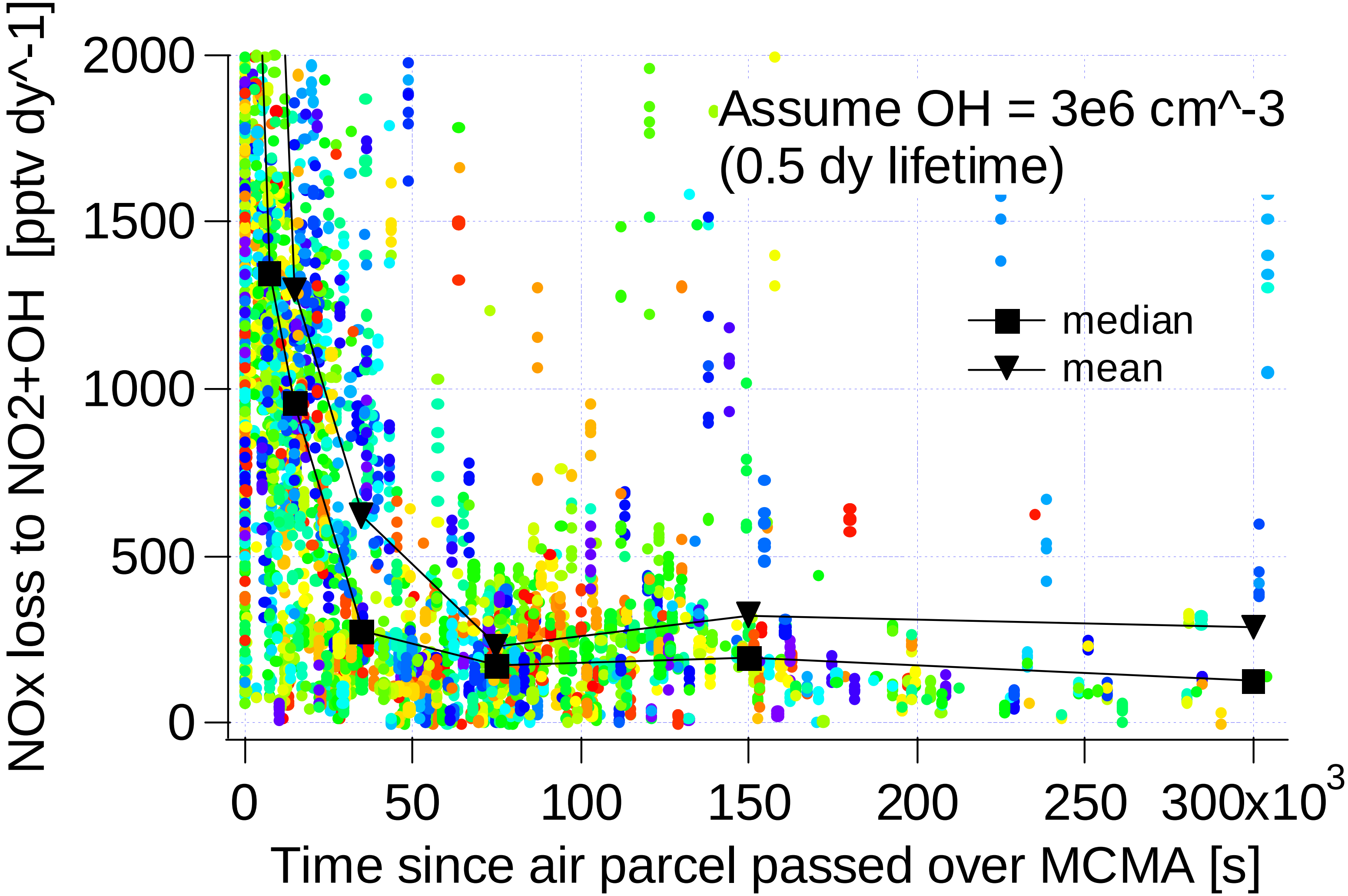
$$\alpha = \ln(\tau 1/\tau 2)/\ln(\lambda 2/\lambda 1)$$

It’s a...

- processing and fate of the NOx emitted from MCMA
- comparison to chemical processing downwind of NYC
- effects on photo-oxidant production (role of PAN)
- influence of mineral dust aerosol

- influence of forest and agricultural fires on MCMA photochemistry

It's a...



Assume OH = 3e6 cm^-3
(0.5 dy lifetime)
median
mean
NOx loss to NO2+OH [pptv dy^-1]
2000
1500
1000
500
0
0
50
100
150
200
250
300x10^3
Time since air parcel passed over MCMA [s]

It's a...

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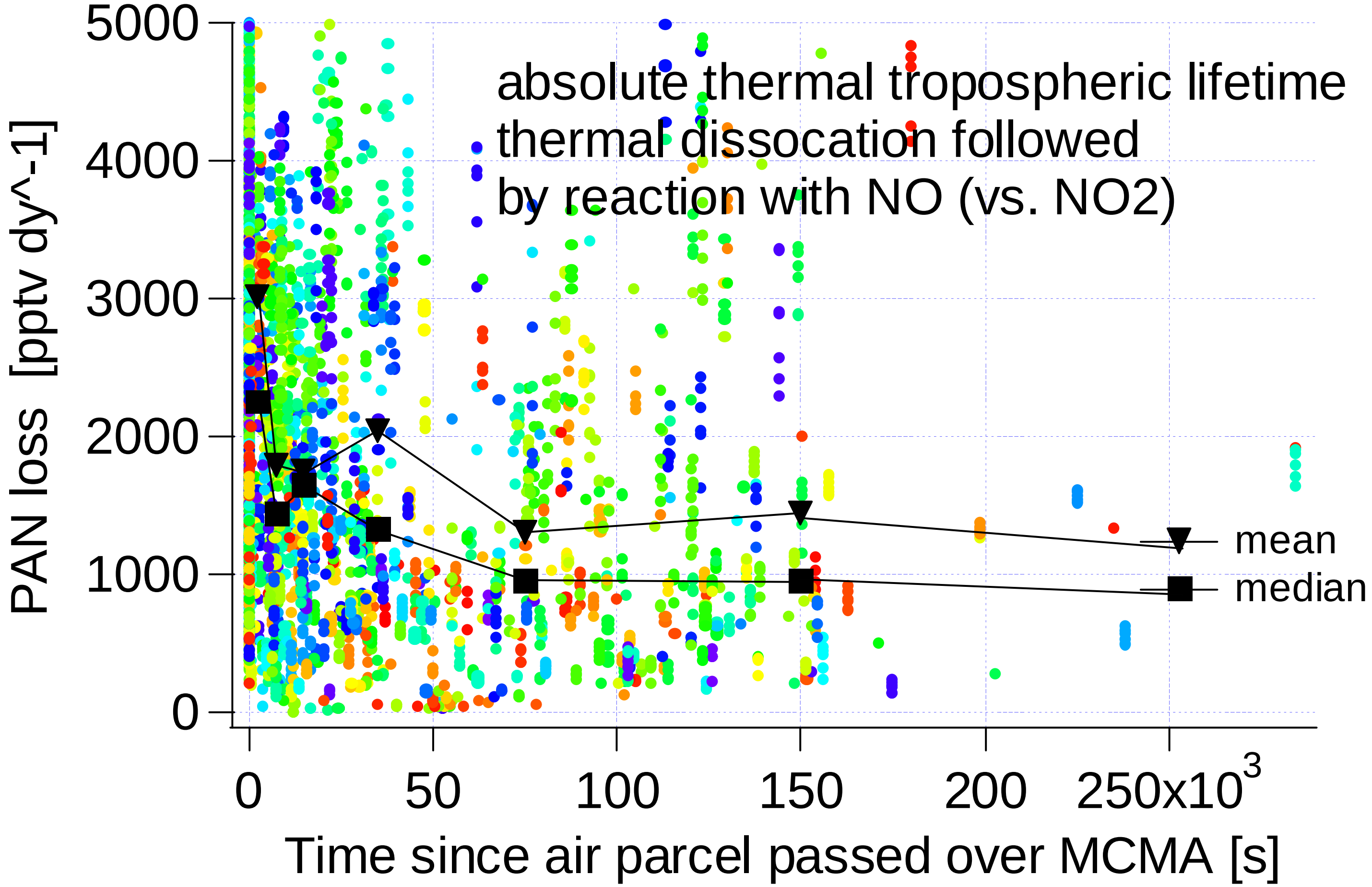
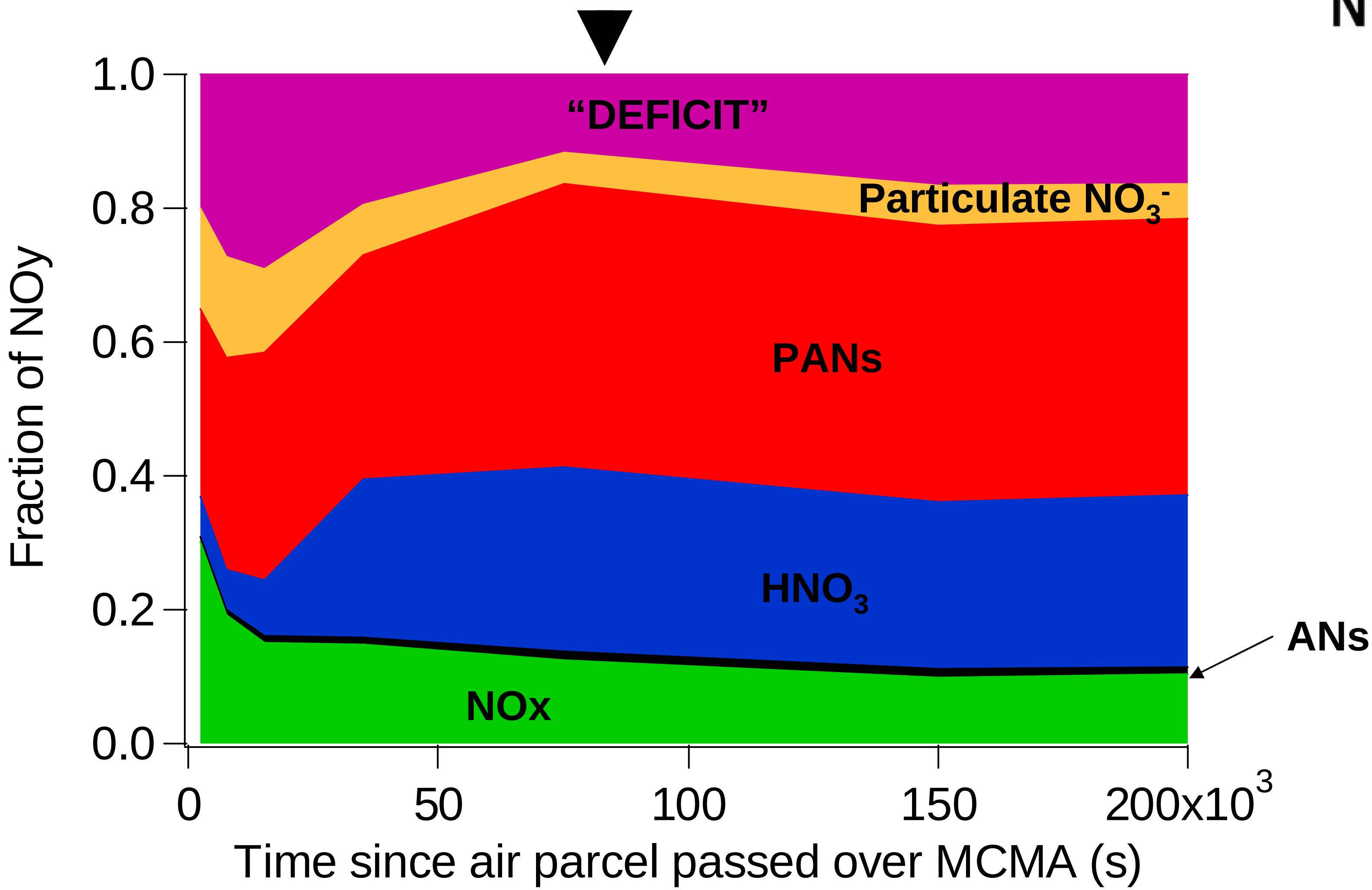
NCAR



NOy partitioning – median values



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Fires in the hills just south of México City

It's a...

It's a...

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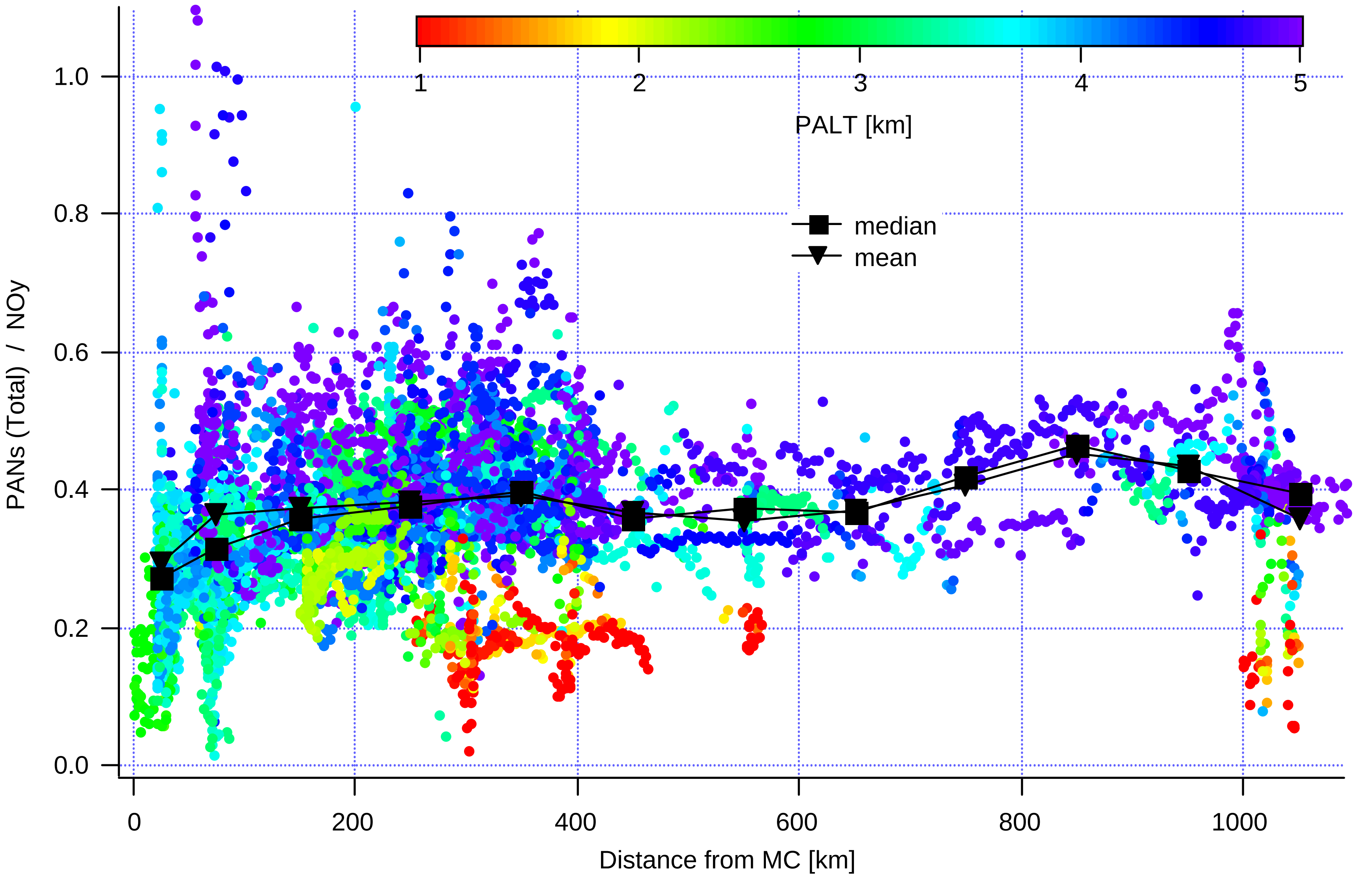
Megacity Initiative - Local and Global Research Observations

MIRAGE-Mex

MAX-Mex

INTEX-B

MCMA



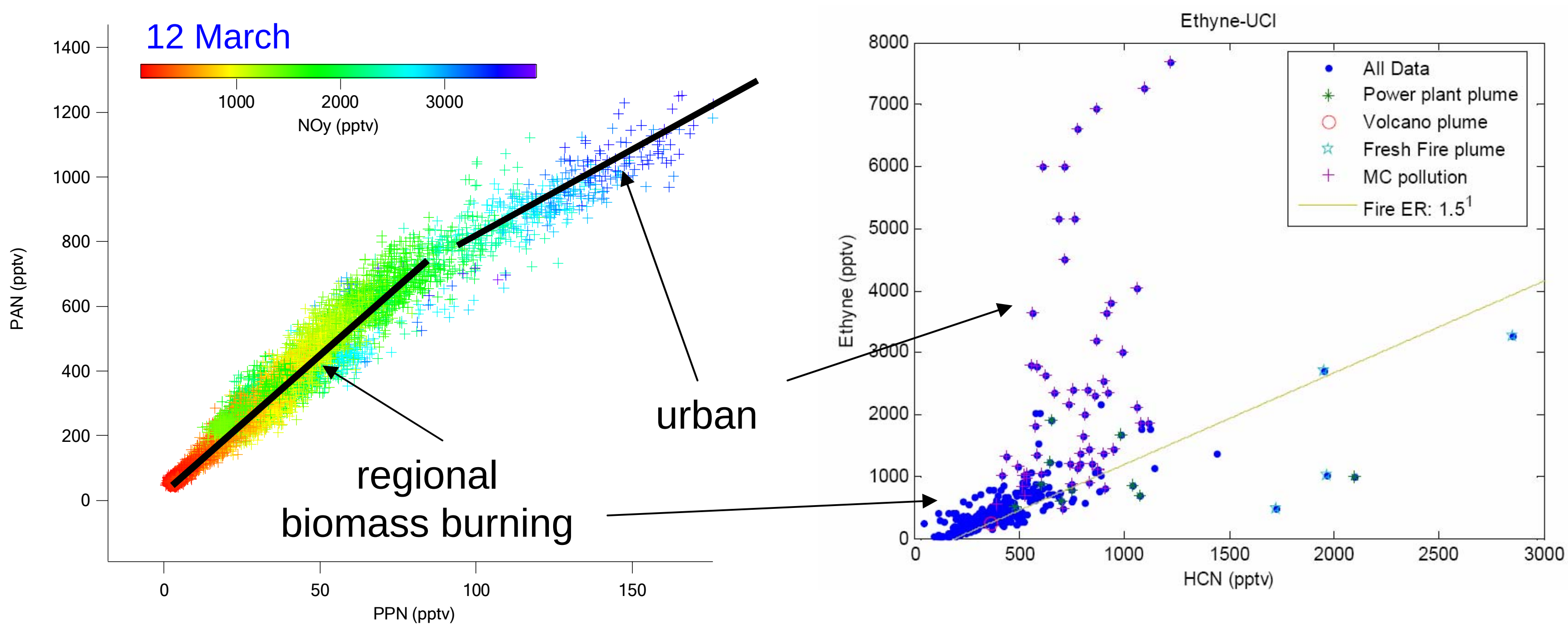
1.0
0.8
0.6
0.4
0.2
0.0
0
200
400
600
800
1000
Distance from MC [km]
PANs (Total) / NOy
1
2
3
4
5
PALT [km]
median
mean

On 20060319:

C130 sampled 2-day outflow near TX, sampled 1-day-old outflow on return toward MC (~0-day-old)

Convenient case for looking at the evolution of the chemistry over the 0-2 day time scale.

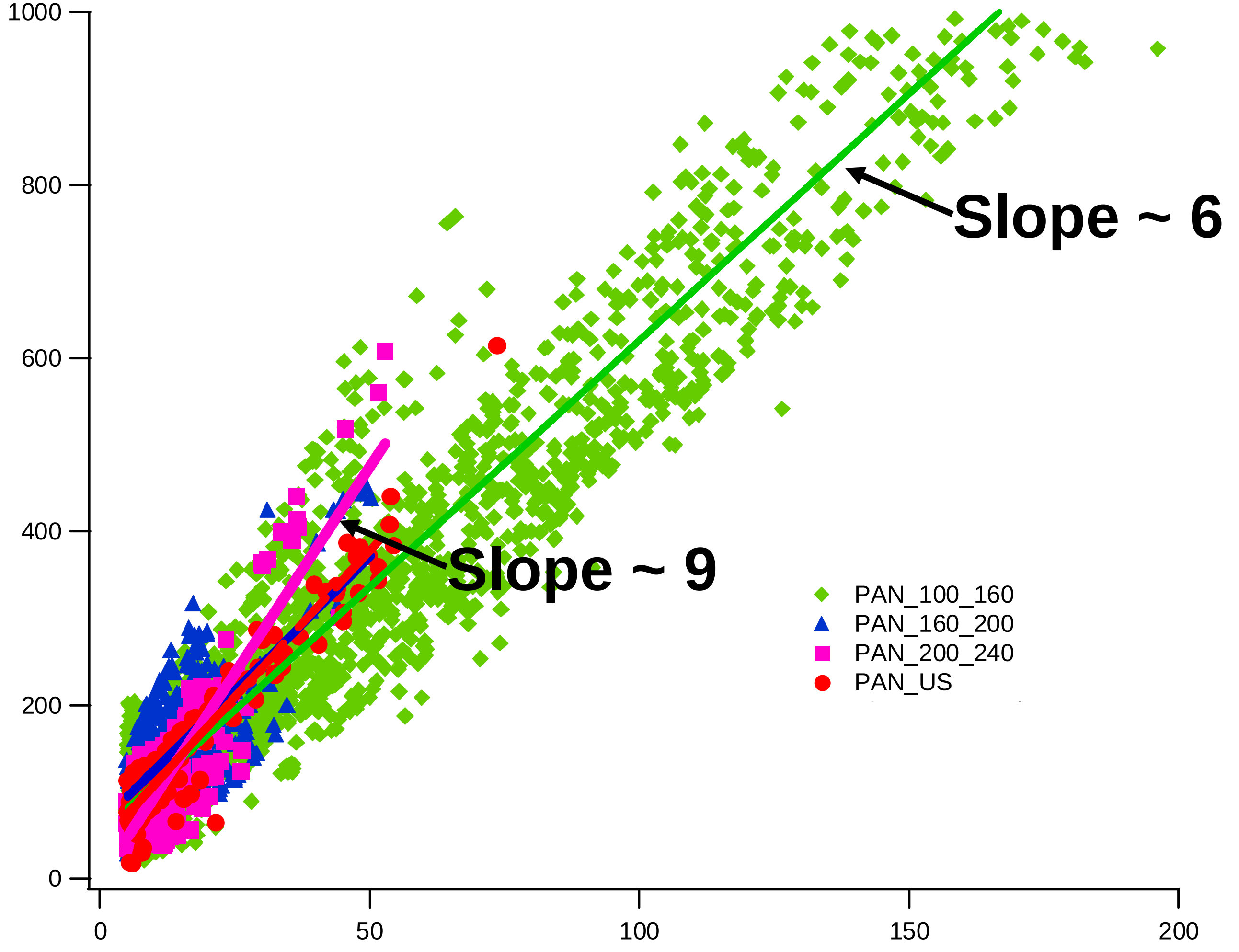
BIOMASS BURNING vs. URBAN



F. Flocke, W. Zheng

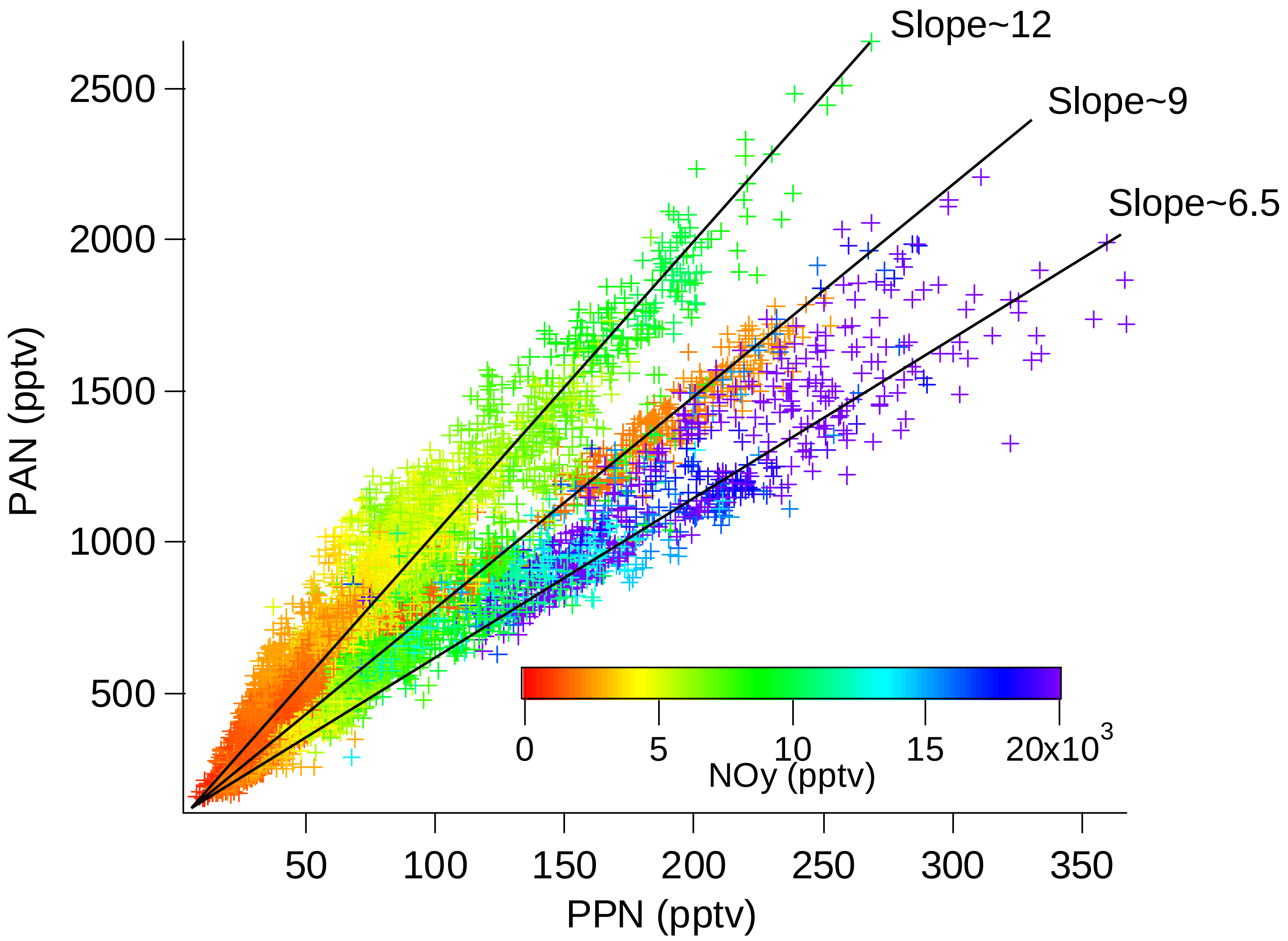
J. Crounse, D. McCabe, P. Wennberg, E. Atlas, D. Blake

PAN/PPN during TRACE-P



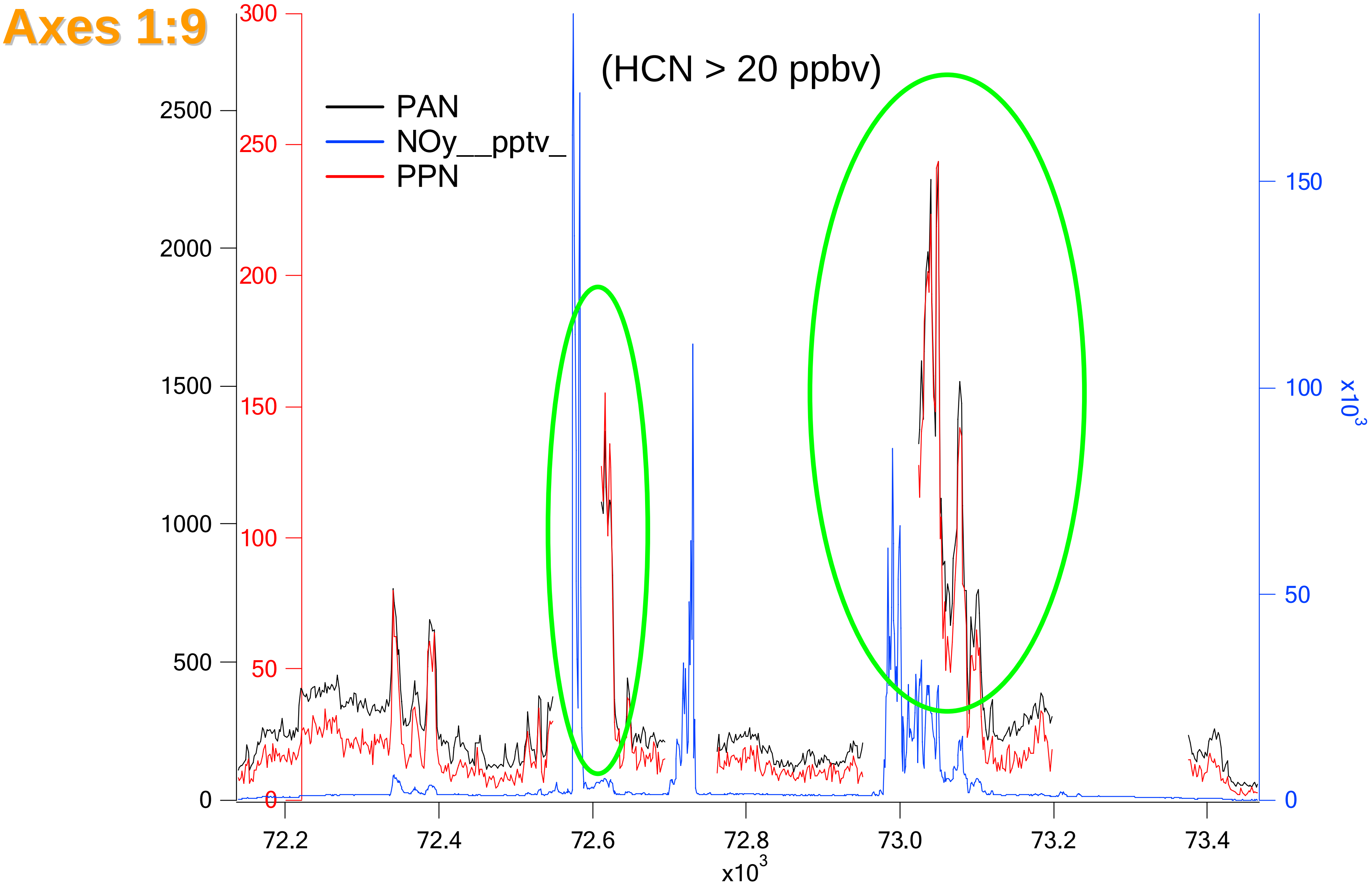
Similar slopes of PAN / PPN were obtained in Houston (TexAQS 2000), during TOPSE (Spring 2000) and in/over other urban areas

ICARTT flight 7/20/2004



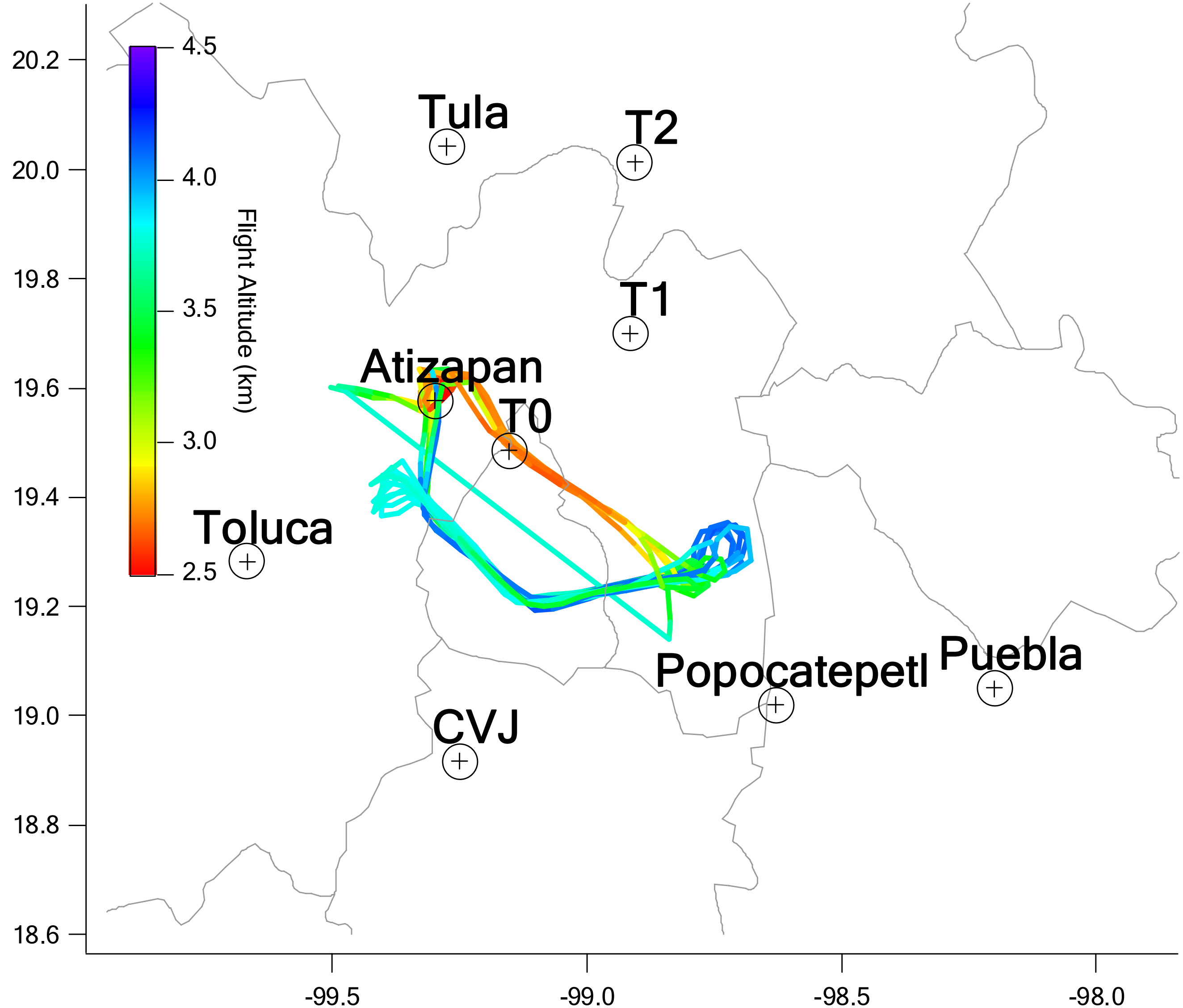
BB plume 3/23/2006 (Yucatan)

3/23/ Fire (Yucatan)

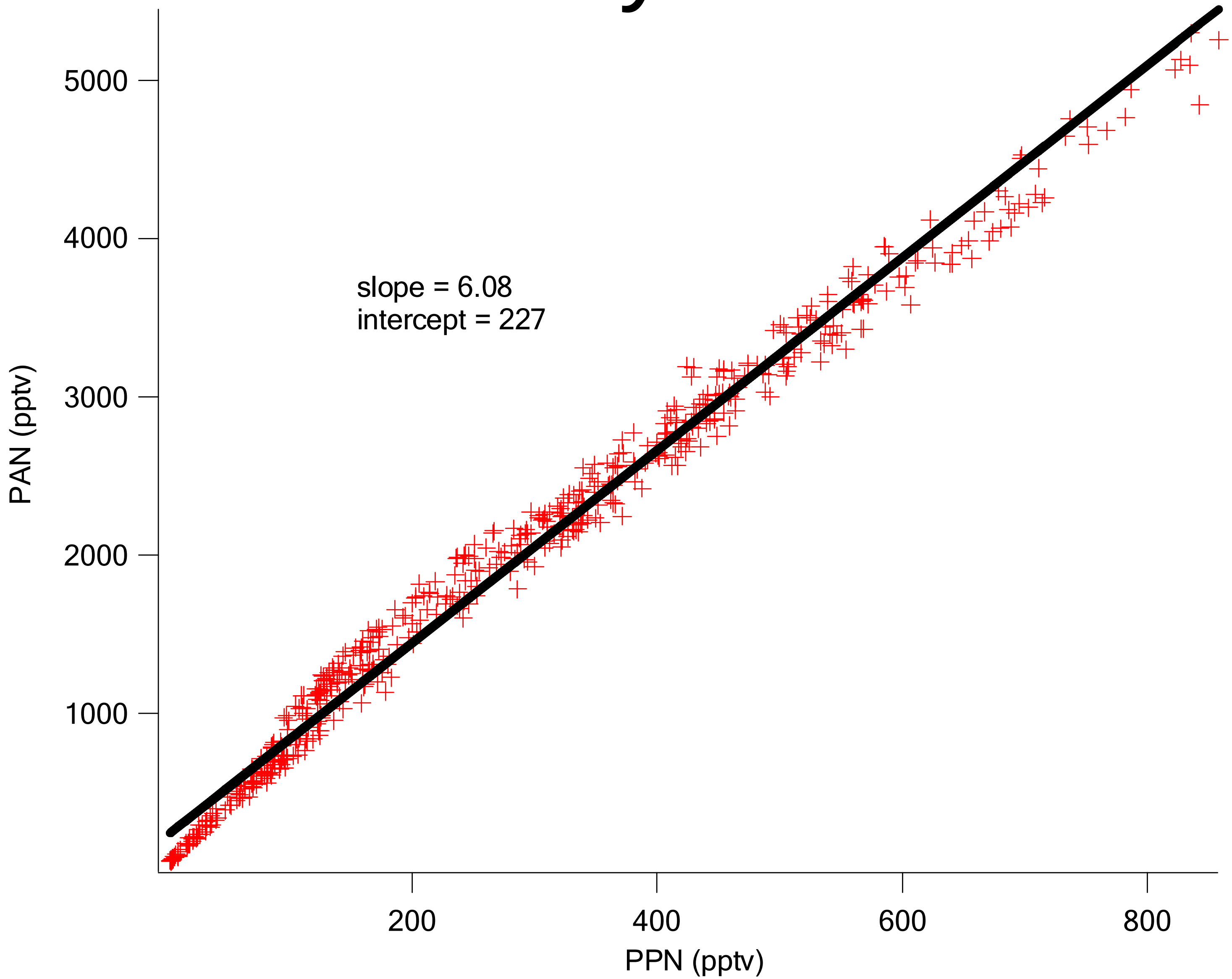


Mexico City PANs

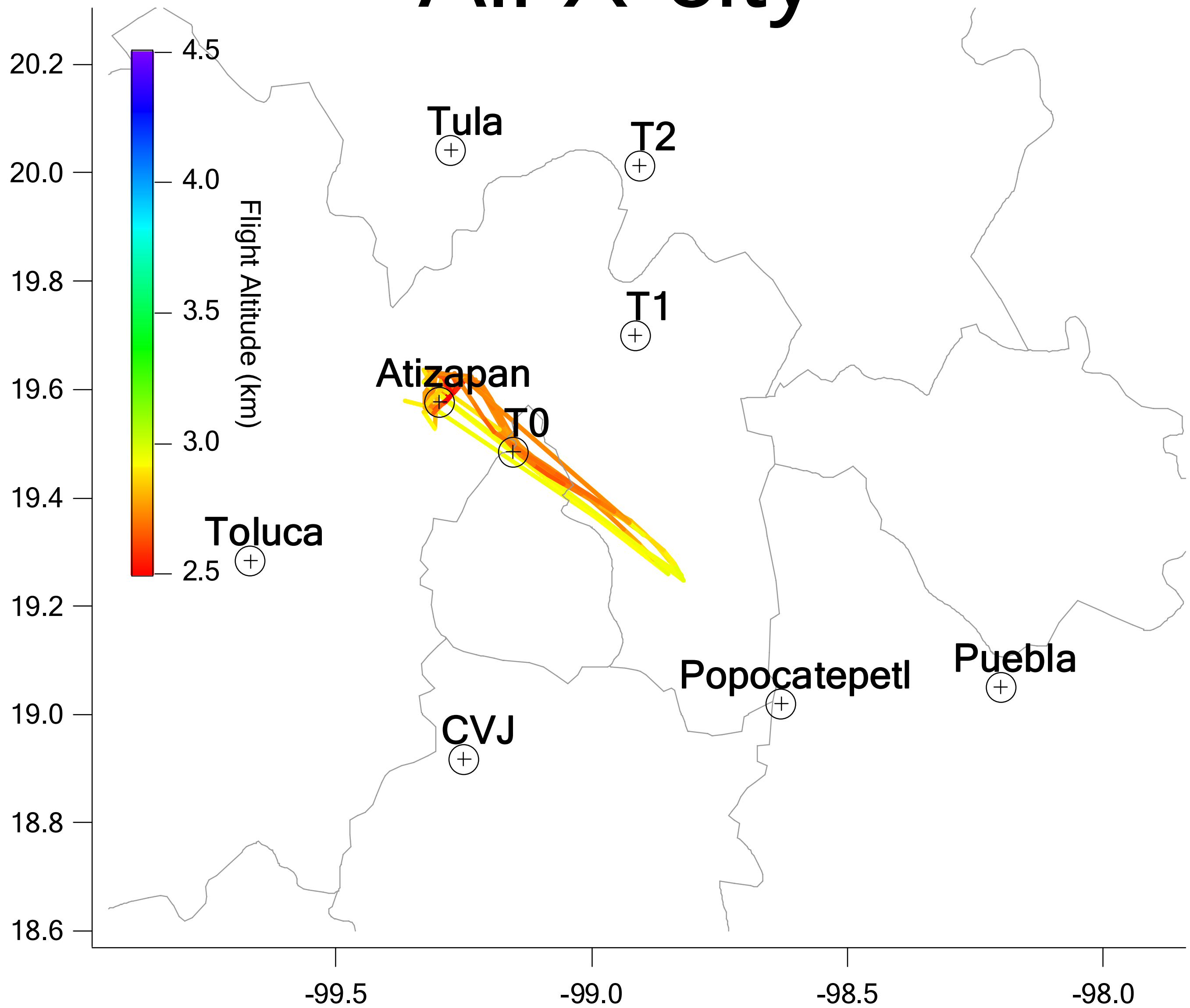
All city runs



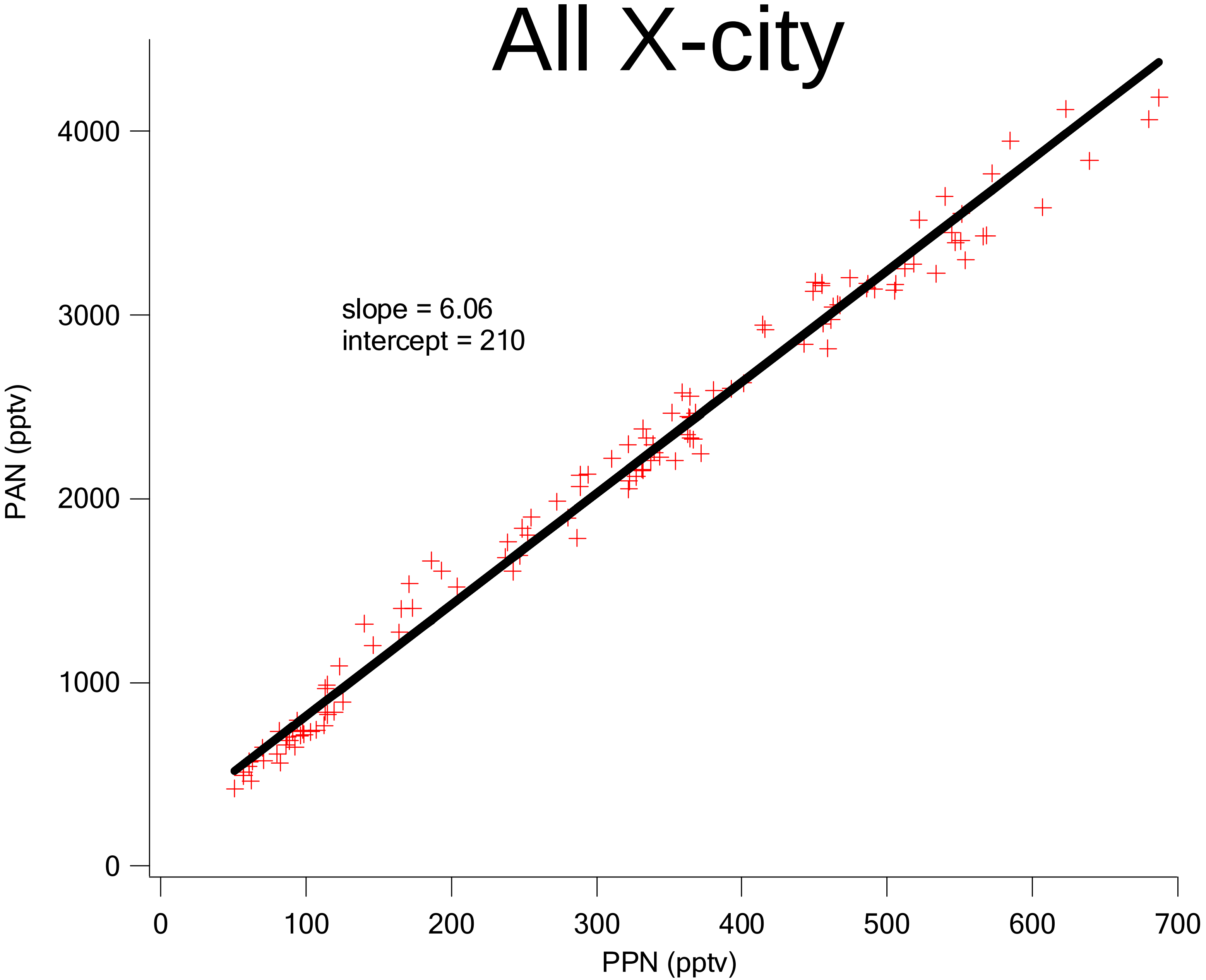
All city runs



All X-city

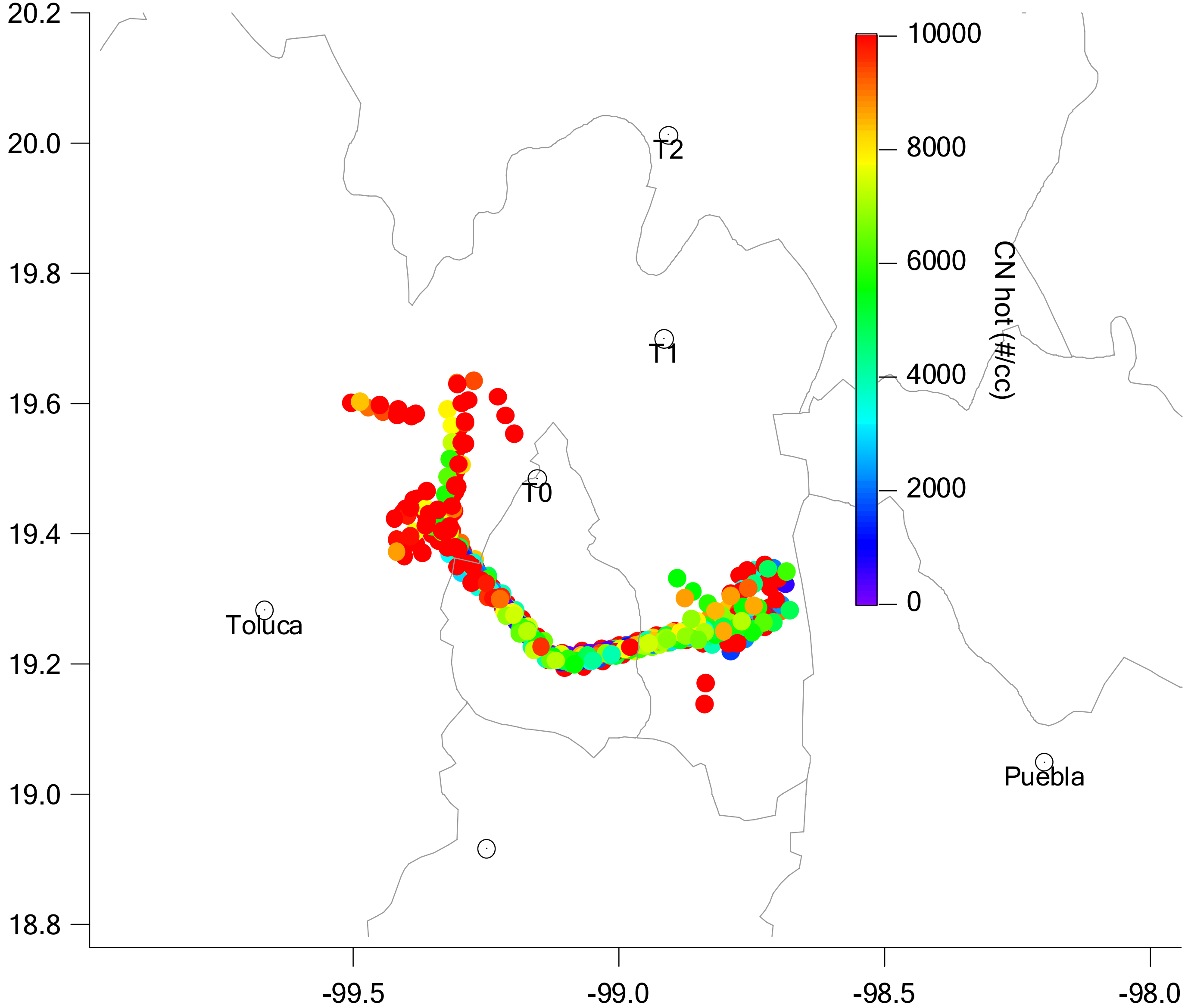


4.5
4.0
3.5
3.0
2.5
Flight Altitude (km)
20.2
20.0
19.8
19.6
19.4
19.2
19.0
18.8
18.6
-99.5
-99.0
-98.5
-98.0
Tula
T2
T1
Atizapan
T0
Toluca
Popocatepetl
Puebla
CVJ

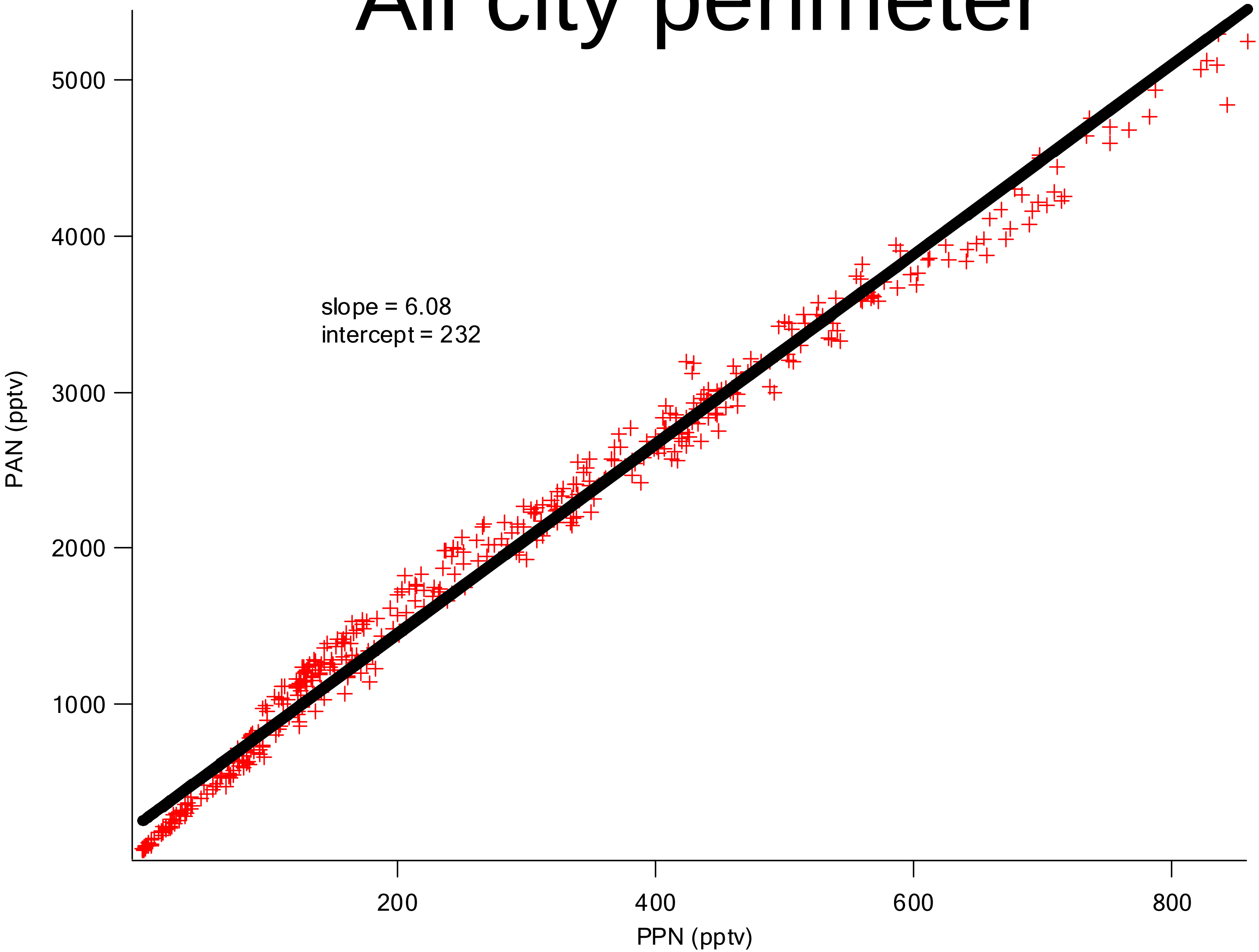


All X-city
slope = 6.06
intercept = 210
PAN (pptv)
0
1000
2000
3000
4000
PPN (pptv)
0
100
200
300
400
500
600
700

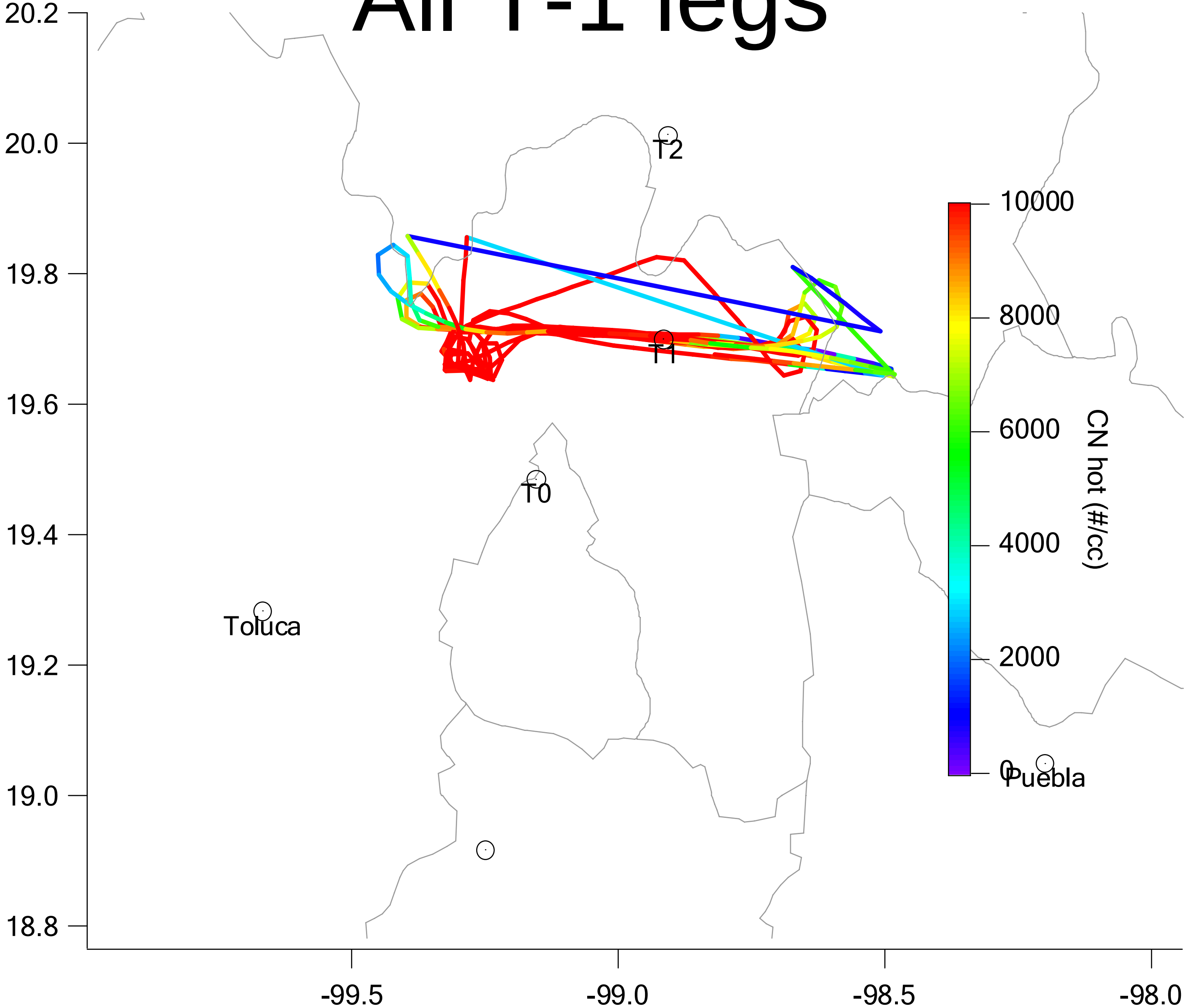
All city perimeter



All city perimeter

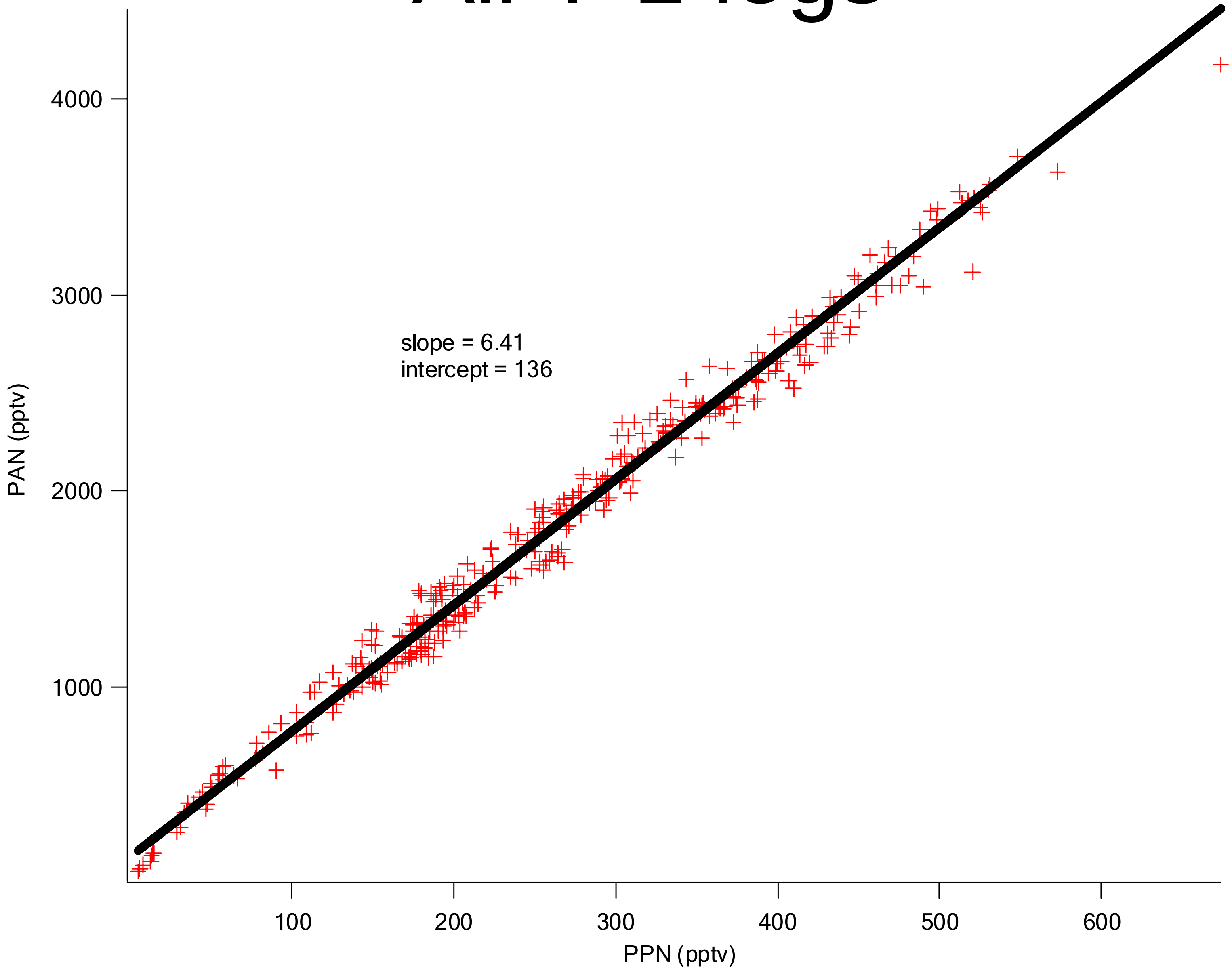


All T-1 legs



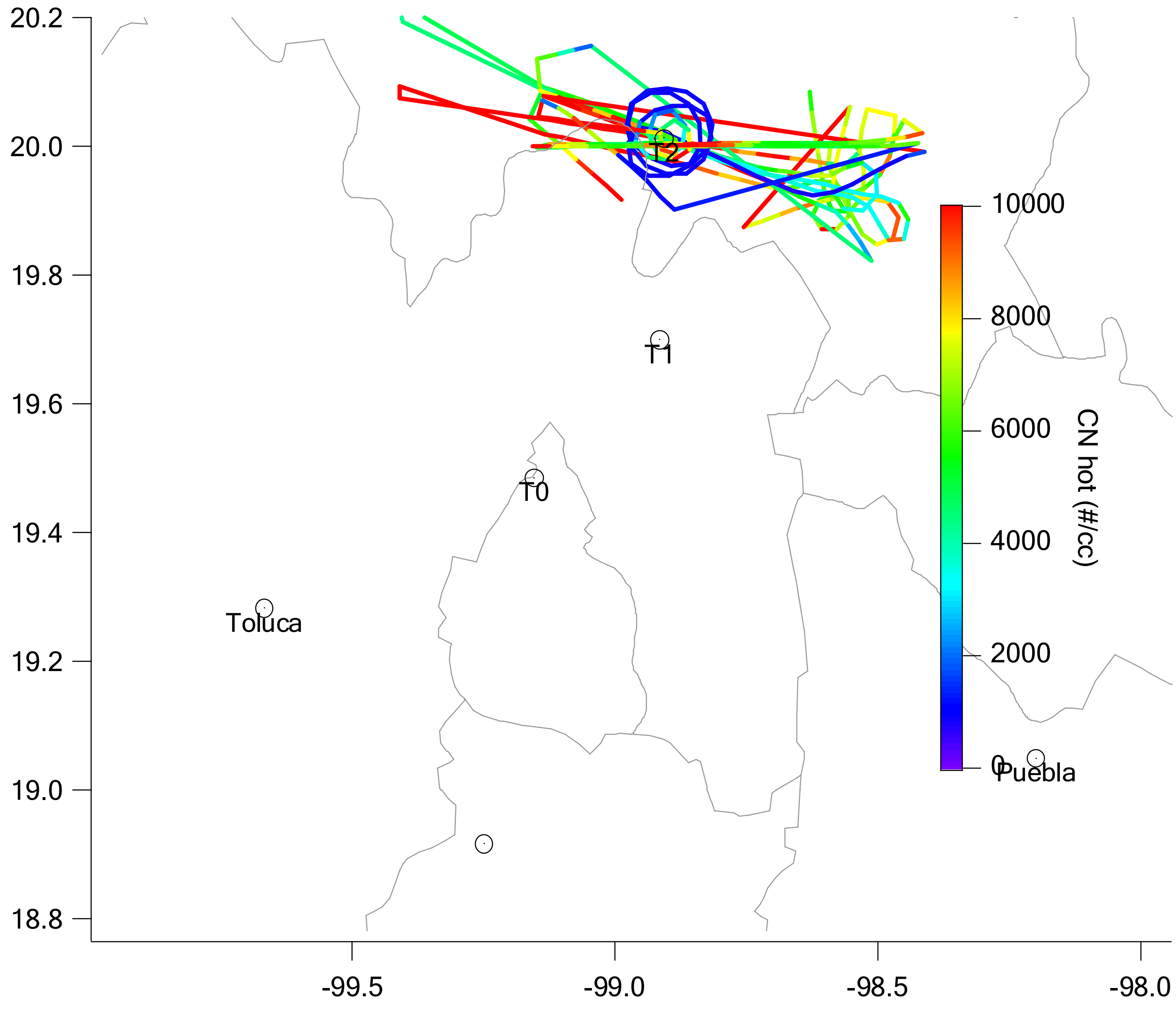
20.2
20.0
19.8
19.6
19.4
19.2
19.0
18.8
-99.5
-99.0
-98.5
-98.0
T2
T1
T0
Toluca
Puebla
10000
8000
6000
4000
2000
0
CN hot (#/cc)

All T-1 legs



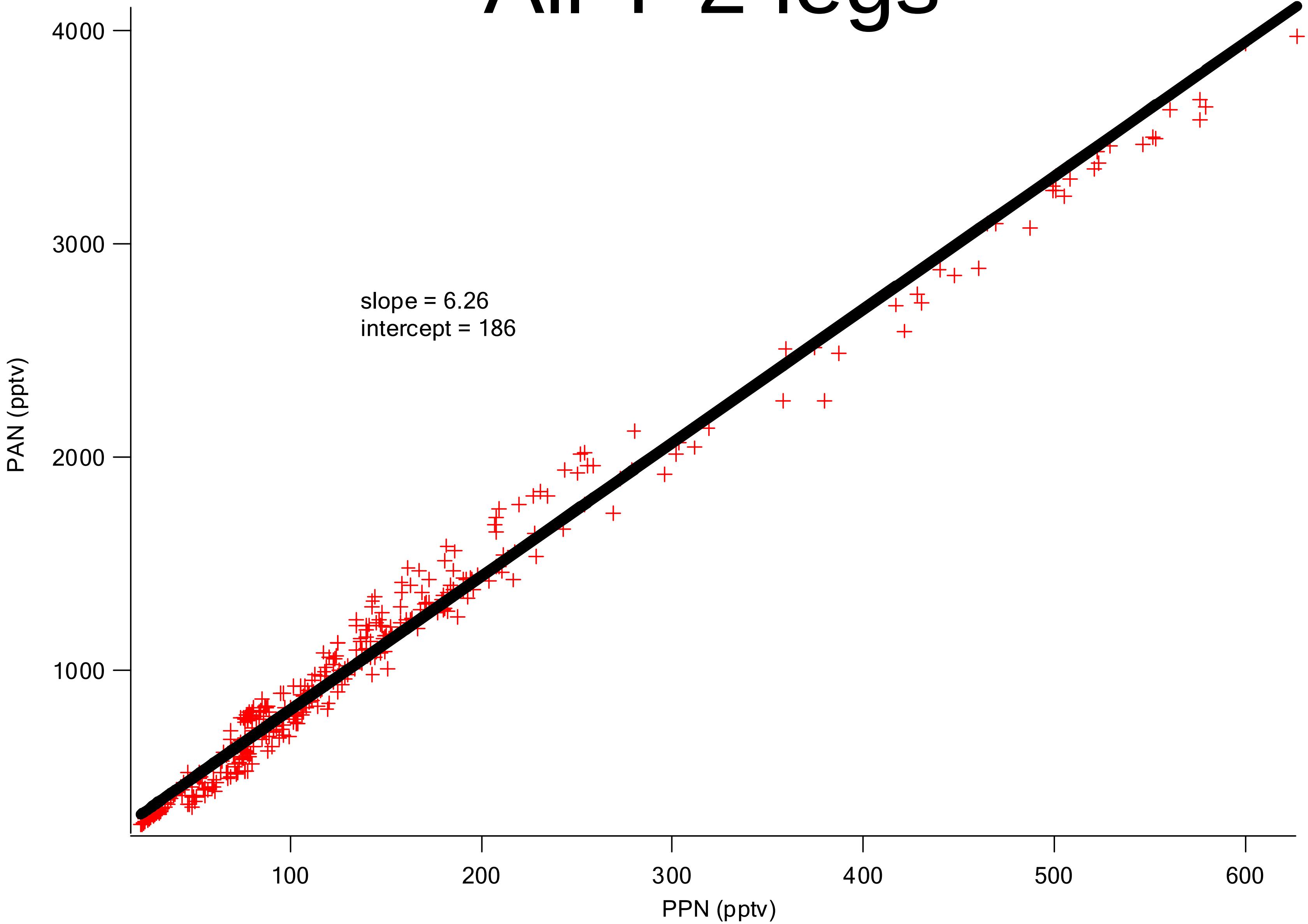
4000
3000
2000
1000
PAN (pptv)
slope = 6.41
intercept = 136
100
200
300
400
500
600
PPN (pptv)

All T-2 legs



20.2
20.0
19.8
19.6
19.4
19.2
19.0
18.8
-99.5
-99.0
-98.5
-98.0
T2
T1
T0
Toluca
Puebla
10000
8000
6000
4000
2000
0
CN hot (#/cc)

All T-2 legs



slope = 6.26
intercept = 186
PAN (pptv)
PPN (pptv)
1000
2000
3000
4000
100
200
300
400
500
600

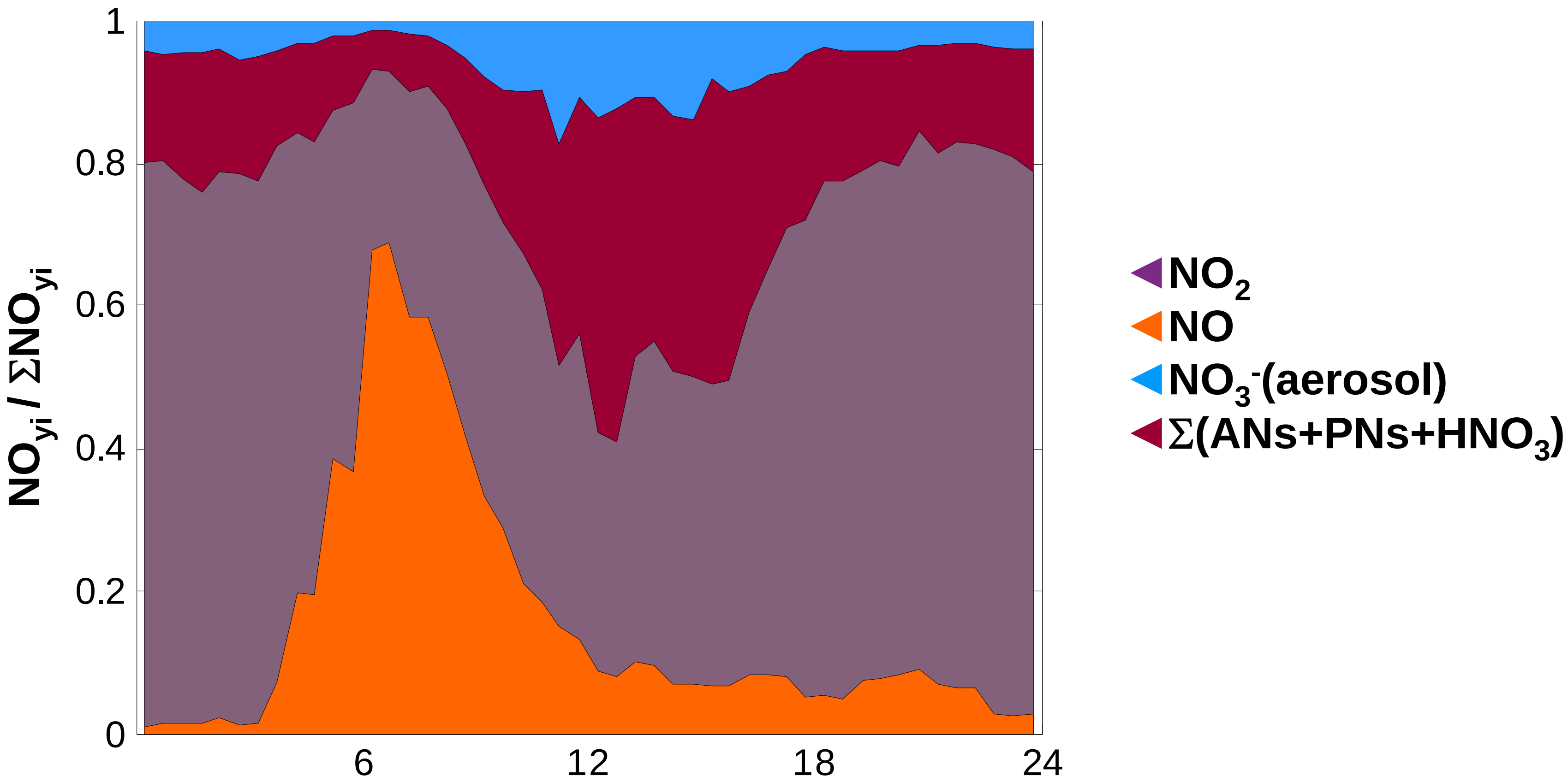
- low, “city-like” PAN / PPN ratio indicates that fire emissions do not contribute much to photochemisty over M/C

- 15% of the CO emissions from fires would be in line with that

- No indication of downwind fire influence

NO_y partitioning at T1

At midday on average 50% is represented by higher oxides consistent with being well downwind of the primary source.



It's a...

It’s a...

It's a...