Photochemical and Lagrangian transport study of the Mexico City plume during the 2006 Megacities and their Impact on the Regional and Global Environment (MIRAGE) Period

National Center for Atmospheric Research

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MILAGRO Workshop May 15-18, 2007

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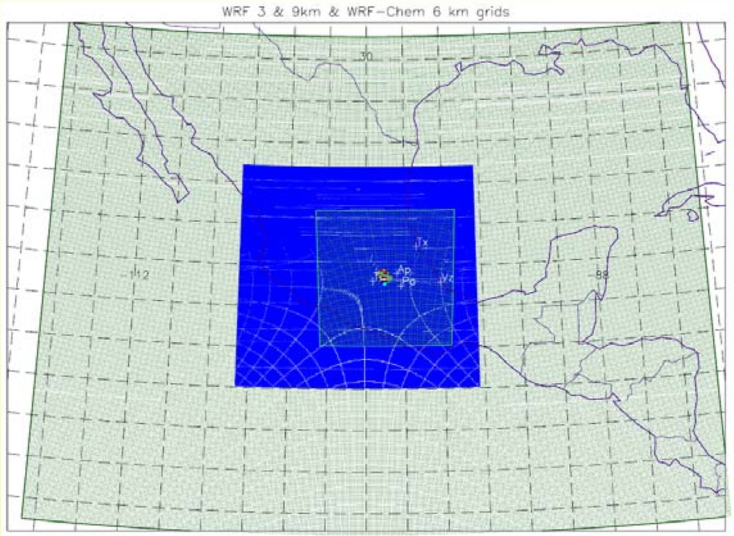
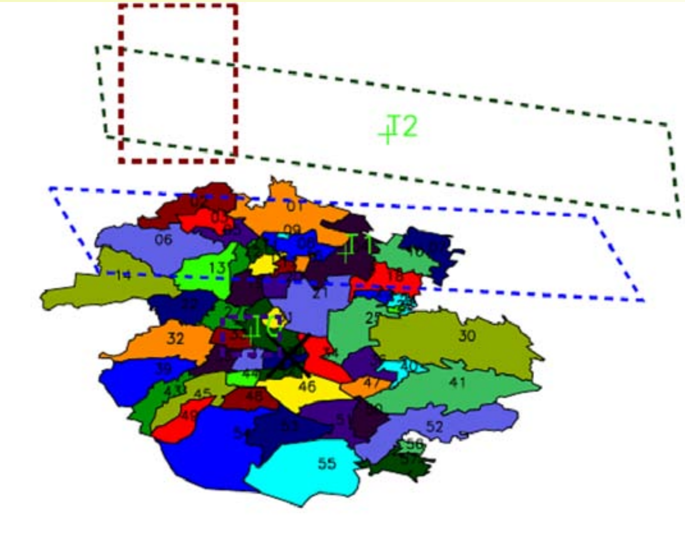
Data Types

- PANs CIMS
  - Frank Flocke
- NOx, NOy Chemiluminescence
  - Andy Wienheimer.
- Bottle Samples GC analysis
  - Don Blake, Nicola Blake & Elliot Atlas
- TOGA fast GC
  - Eric Apel & Dan Reimer
- SO2 CIMS
  - Paul Wennberg, John Crouse, C. Heizer, D. McCabe
- SO2 Flame Photoionization
  - John Holloway
- CIMS HO, H2SO4
  - Lee Mauldin
- WRF-chem Simulations
  - X.X. Tie
- WRF operational simulations
  - W.Skamarock

Trajectory Calculations

- Flexpart-WRF
  - Fast & Easter
- Wind Fields
  - Prepared by W. Skamarock
    - 9km & nested 3km grids
    - 1 hour wind updates @ 3km &
    - 6 hour wind updates @ 9km
      - (T+12-T+36).(T+12-T+36)

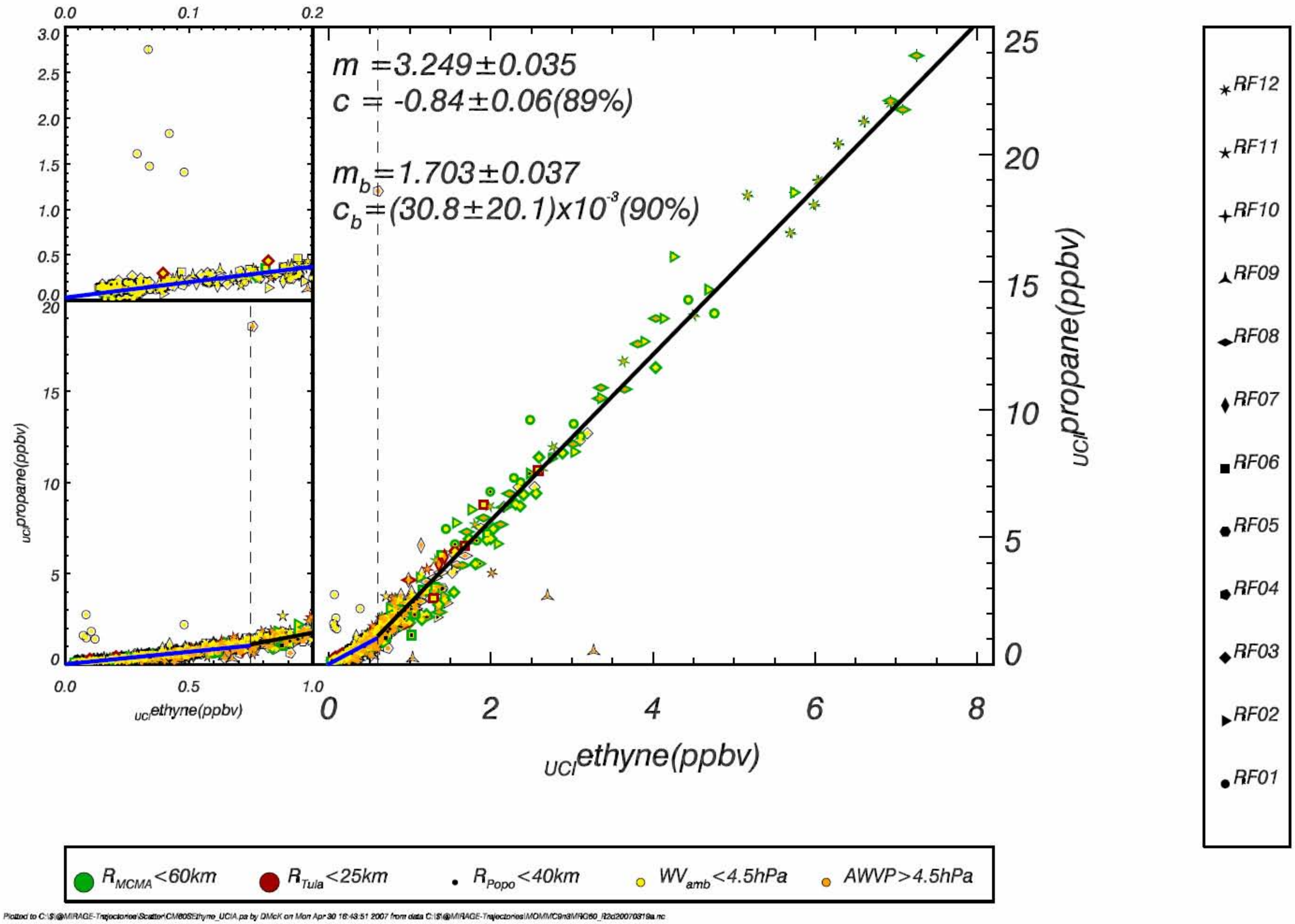


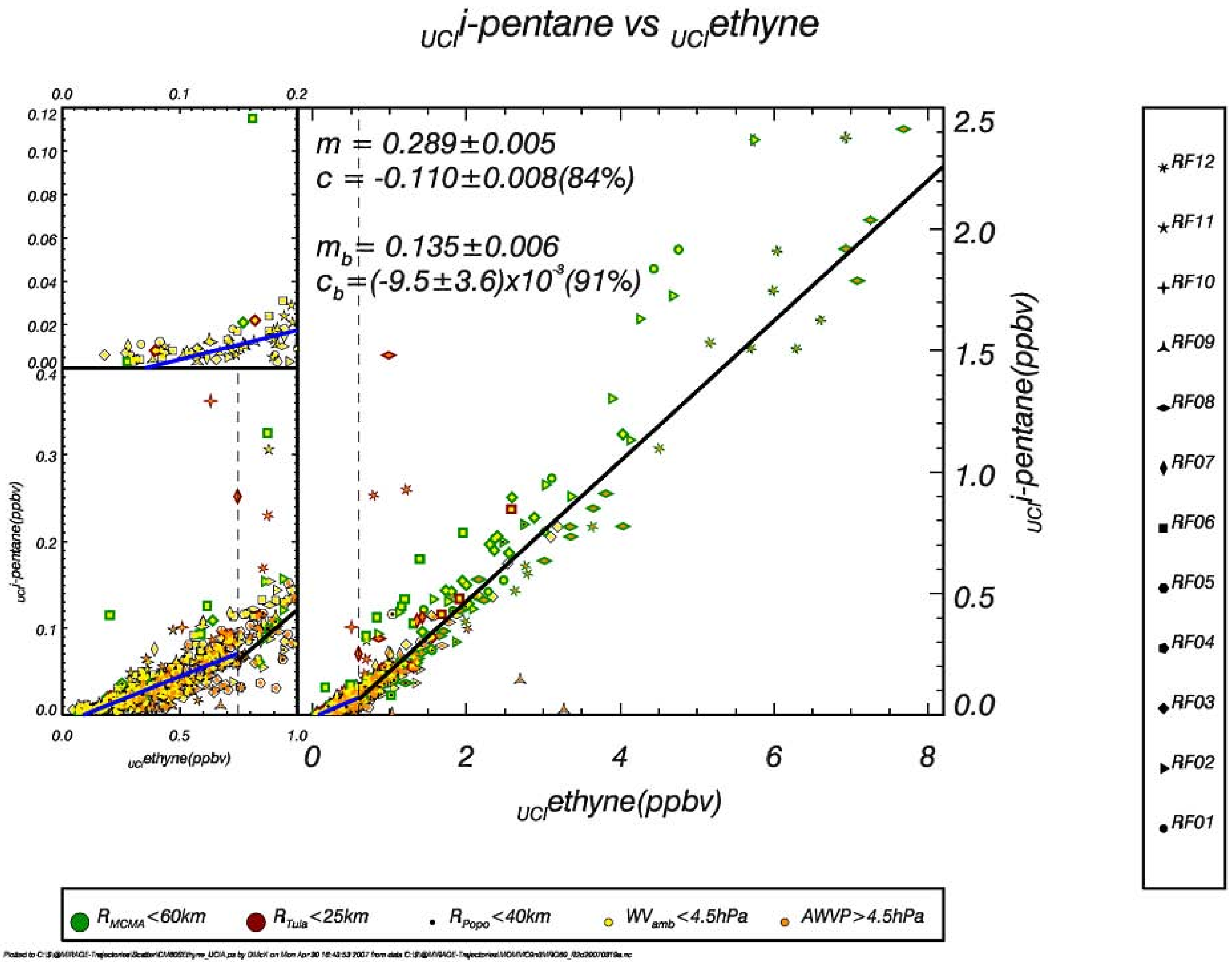


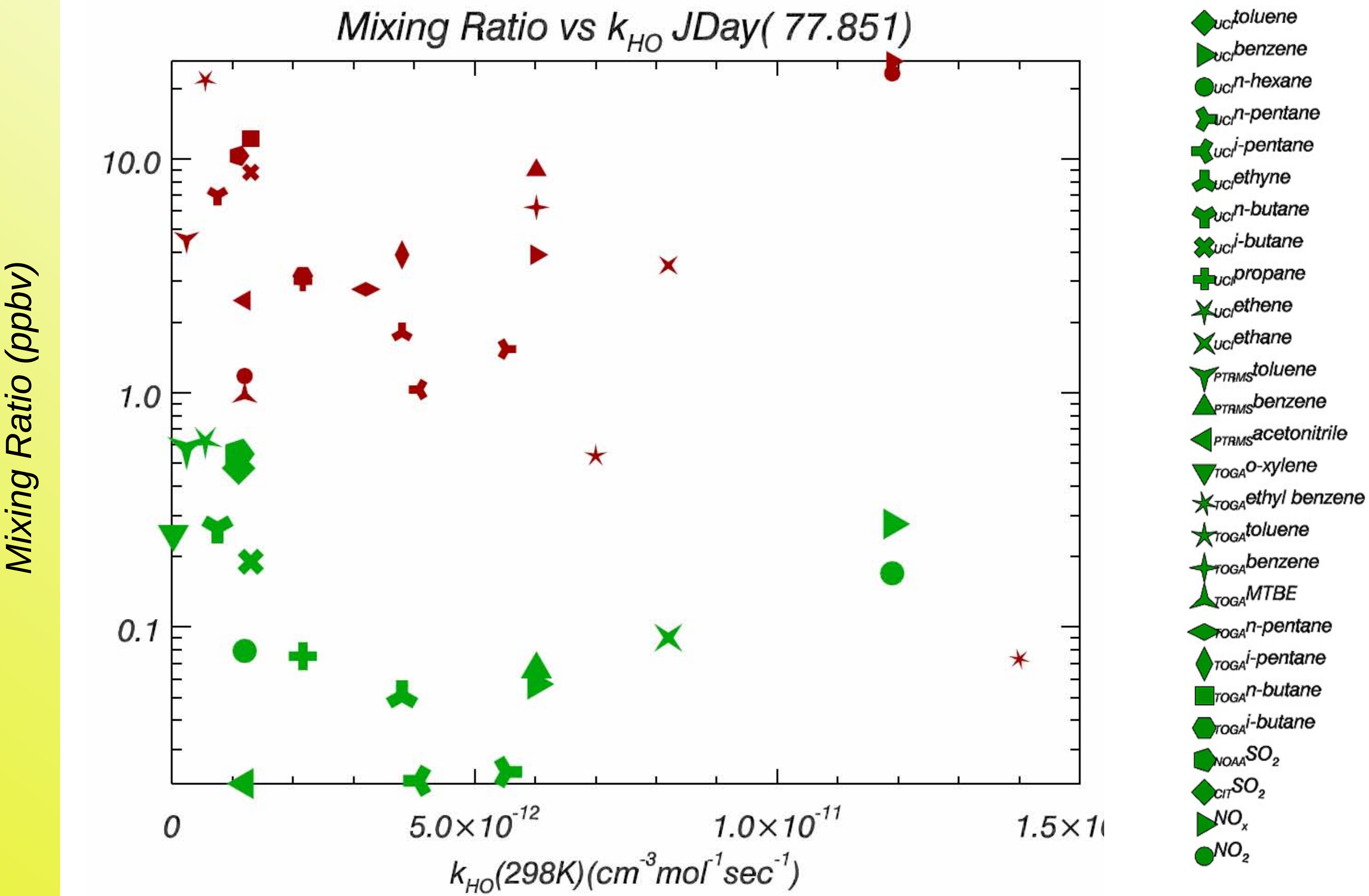
Determining Photochemical Age
Variations on a theme

- Filter out effects of dilution (intercept=0)
  - $Log_{10}(NOx/NOy)$ vs $k_{NO2??????}$
    - NOy is a proxy for NOx initial plus dilution
  - $Log_{10}(SO_2/(SO_2+H_2SO_4))$ vs $k_{SO2??????}$
    - $SO_2+H_2SO_4$ proxy for SO_2 initial
  - $Log_{10}(HC/HC_0)*(HC_0^{ref}/HC^{ref})$ vs $k_{HO}-k_{HO}^{ref}$
- Represent dilution effects (intercept≠0)
  - $Log_{10}(HC_1/HC_1^0)$ $-log(HC^0_2/HC_2)$ vs $k^1_{HO}-k^2_{HO}$
    - HC_1 = benzene; HC_2 = toluene, …UCI, TOGA,PTRMS
    - HC_1 = propane; HC_2 = n-butane …UCI

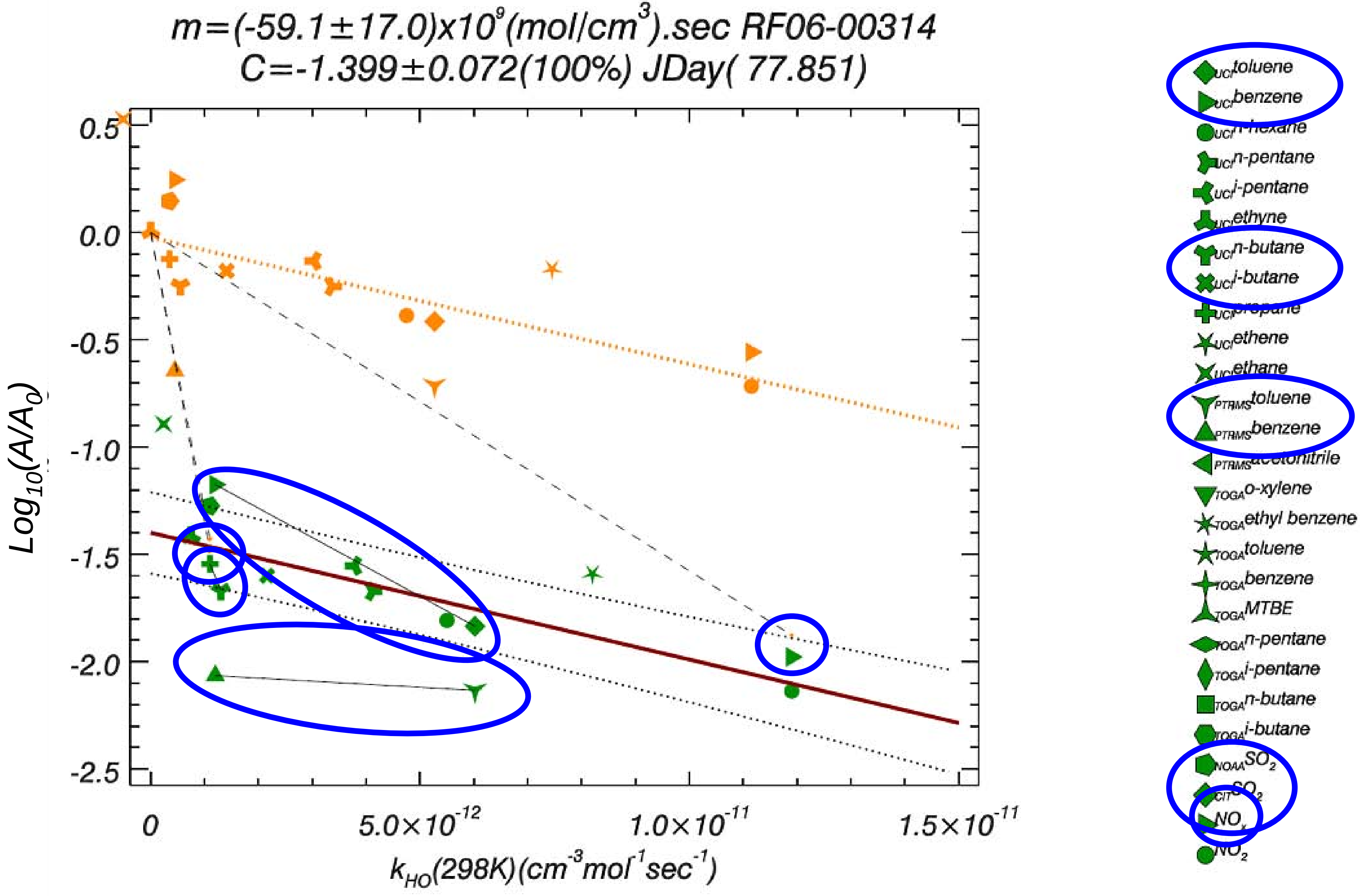
$_{UCI}$propane vs $_{UCI}$ethyne



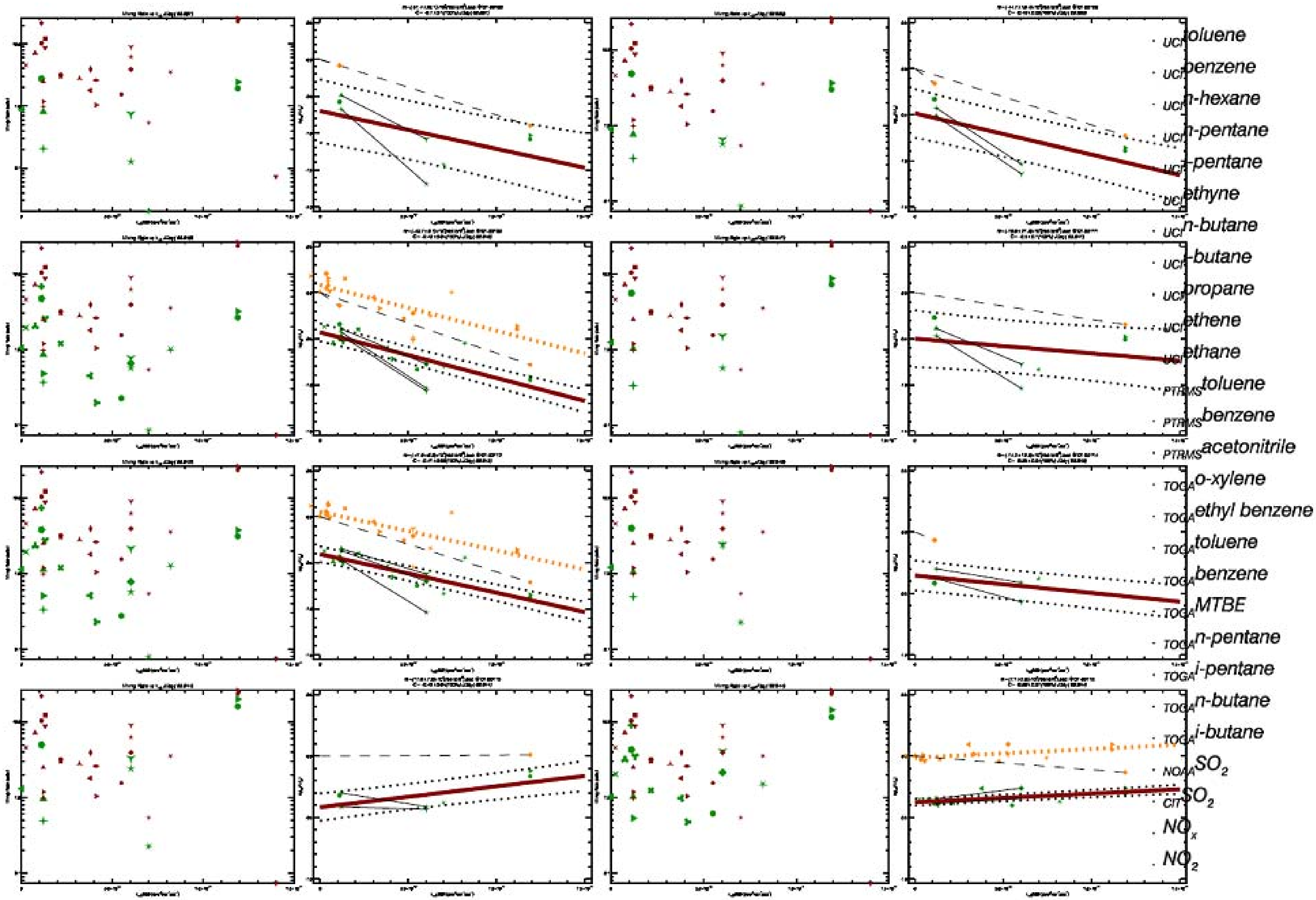

UCI i-pentane vs UCI ethyne
m = 0.289±0.005
c = -0.110±0.008(84%)
m_b = 0.135±0.006
c_b = (-9.5±3.6)x10^-3(91%)
UCI i-pentane(ppbv)
UCI ethyne(ppbv)
RF12
RF11
RF10
RF09
RF08
RF07
RF06
RF05
RF04
RF03
RF02
RF01
R_MCMA<60km
R_Tula<25km
R_Popo<40km
WV_amb<4.5hPa
AWVP>4.5hPa

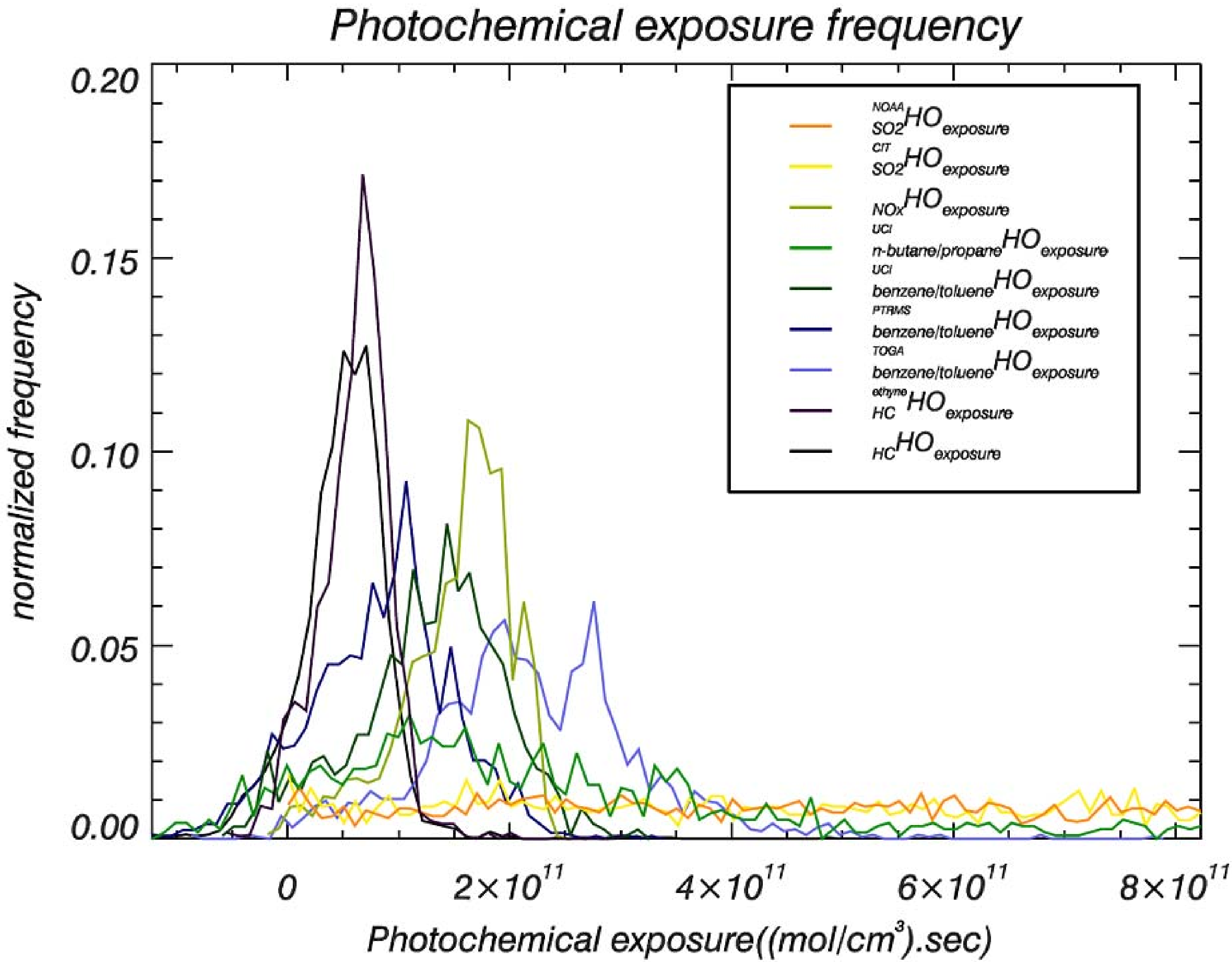


Mixing Ratio vs k_HO JDay(77.851)
Mixing Ratio (ppbv)
10.0
1.0
0.1
0
5.0×10^-12
1.0×10^-11
k_HO(298K)(cm^-3 mol^-1 sec^-1)
UCI toluene
UCI benzene
UCI n-hexane
UCI n-pentane
UCI i-pentane
UCI ethyne
UCI n-butane
UCI i-butane
UCI propane
UCI ethene
UCI ethane
PTRMS toluene
PTRMS benzene
PTRMS acetonitrile
TOGA o-xylene
TOGA ethyl benzene
TOGA toluene
TOGA benzene
TOGA MTBE
TOGA n-pentane
TOGA i-pentane
TOGA n-butane
TOGA i-butane
NOAA SO2
CIT SO2
NOx
NO2



m=(-59.1±17.0)x10^9(mol/cm^3).sec RF06-00314
C=-1.399±0.072(100%) JDay(77.851)
Log10(A/A0)
kHO(298K)(cm^-3mol^-1sec^-1)
0.5
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
0
5.0×10^-12
1.0×10^-11
1.5×10^-11
UCI toluene
UCI benzene
UCI n-hexane
UCI n-pentane
UCI i-pentane
UCI ethyne
UCI n-butane
UCI i-butane
UCI propane
UCI ethene
UCI ethane
PTRMS toluene
PTRMS benzene
PTRMS acetonitrile
TOGA o-xylene
TOGA ethyl benzene
TOGA toluene
TOGA benzene
TOGA MTBE
TOGA n-pentane
TOGA i-pentane
TOGA n-butane
TOGA i-butane
NOAA SO2
CIT SO2
NOx
NO2


UCI toluene
UCI benzene
UCI n-hexane
UCI n-pentane
UCI i-pentane
UCI ethyne
UCI n-butane
UCI i-butane
UCI propane
UCI ethene
UCI ethane
PTRMS toluene
PTRMS benzene
PTRMS acetonitrile
TOGA o-xylene
TOGA ethyl benzene
TOGA toluene
TOGA benzene
TOGA MTBE
TOGA n-pentane
TOGA i-pentane
TOGA n-butane
TOGA i-butane
NOAA SO2
CIT SO2
NOx
NO2



Photochemical exposure frequency
normalized frequency
0.20
0.15
0.10
0.05
0.00
0
2×10^11
4×10^11
6×10^11
8×10^11
Photochemical exposure((mol/cm³).sec)
NOAA SO2 HO exposure
CIT SO2 HO exposure
NOx HO exposure
UCI n-butane/propane HO exposure
UCI benzene/toluene HO exposure
PTRMS benzene/toluene HO exposure
TOGA benzene/toluene HO exposure
ethyne HC HO exposure
HC HO exposure
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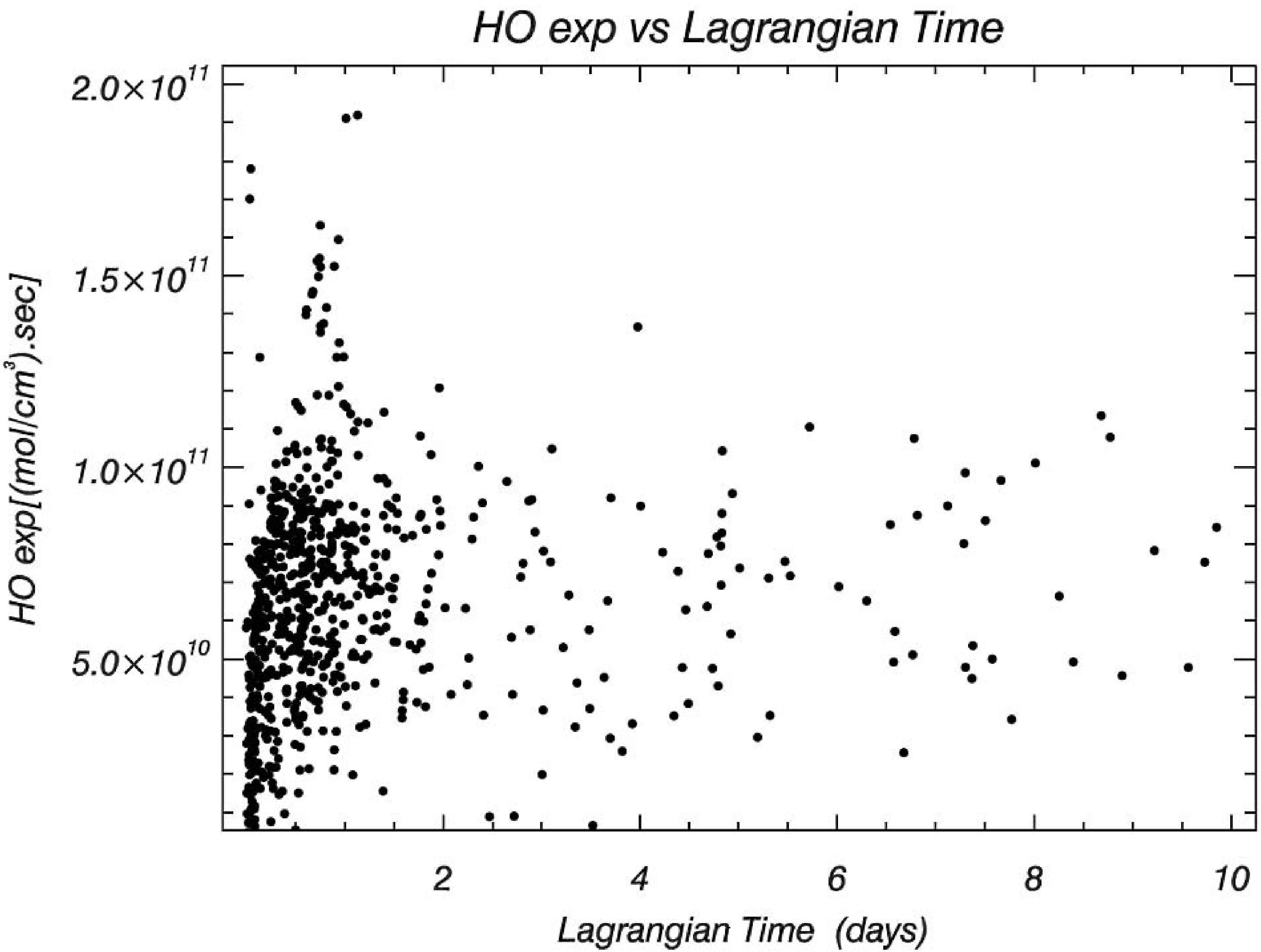

HO exp vs Lagrangian Time
2.0×10^11
1.5×10^11
1.0×10^11
5.0×10^10
HO exp[(mol/cm^3).sec]
2
4
6
8
10
Lagrangian Time (days)

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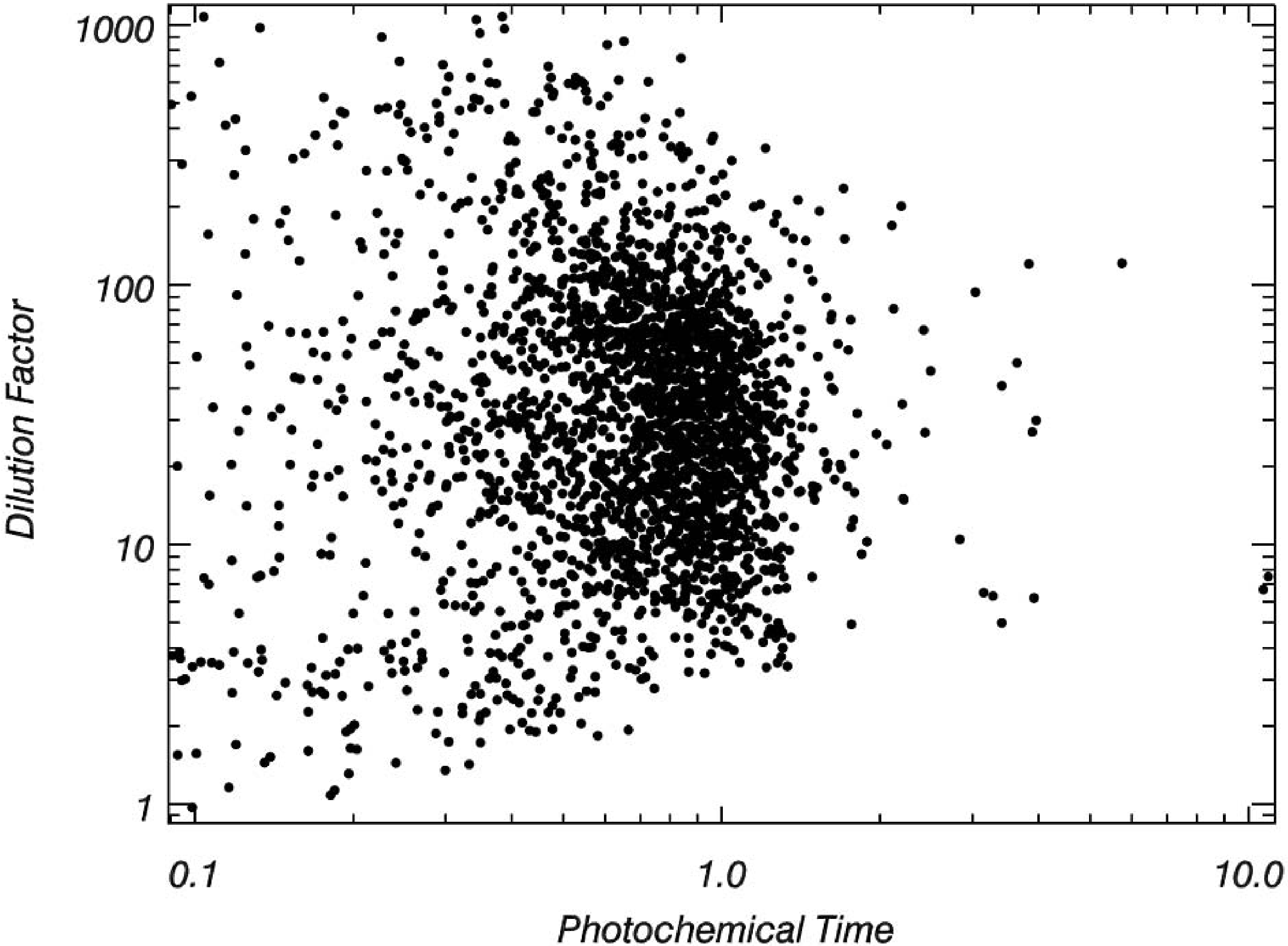
Dilution Factor vs Photochemical Time



Conclusions

- An ensemble approach using information from several hydrocarbons will likely yield a more reliable estimate of Total HO exposure or photochemical age.
- NO_x-> NO_y conversion by non-HO reaction ~twice as fast as NO_2+HO to HNO_3
- Median OH exposure ~ $6x10^{10}$ (mol/cm3).sec
  - Corresponding to HO concentrations of $1x10^6$ mol/cm3 for typical transport times
- Gas phase signatures of primary city pollution no longer clearly detectable in air ~2 days downwind of Mexico City.