HO_x Behavior as Observed Aboard the C-130 during MILAGRO

Chris Cantrell - NCAR

Rebecca Anderson, Lee Mauldin, Ed Kociuch, Jeff McCoy, Fred Eisele, Eric Apel, Dan Reimer, Alan Hills, Thomas Karl, David Knapp, DeeDee Montzka, Alan Fried, Petter Weibring, James Walega, Dirk Richter, Frank Flocke, Wengang Zheng, Louisa Emmons, James Crawford, Jennifer Olson, Gao Chen, Don Blake, Elliot Atlas, Teresa Campos, Jose Jimenez, Ed Dunlea, Peter DeCarlo, Tony Clarke, Steve Howell, Ron Cohen, Rick Shetter, Sam Hall, Lynn Russell, Greg Kok, Rodney Weber, Sasha Madronich, Paul Wennberg, John Crounse, David McCabe, John Holloway

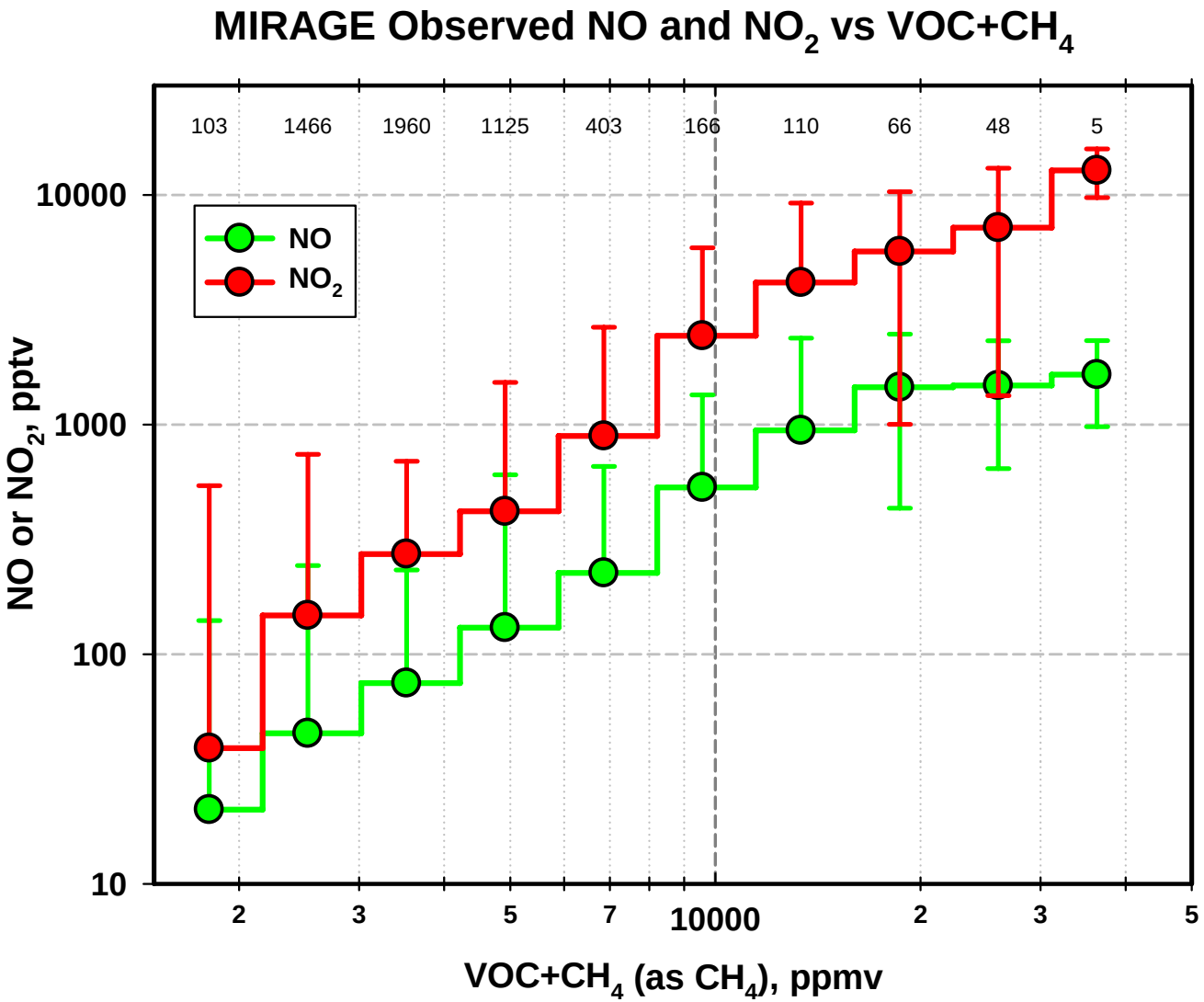
Observations

- HO_2+RO_2, HO_2, 1 minute
- OH, 30 seconds
  - H_2SO_4, 15 seconds
- Also:
  - HNO_3, 10 seconds
  - NH_3, about 1 minute

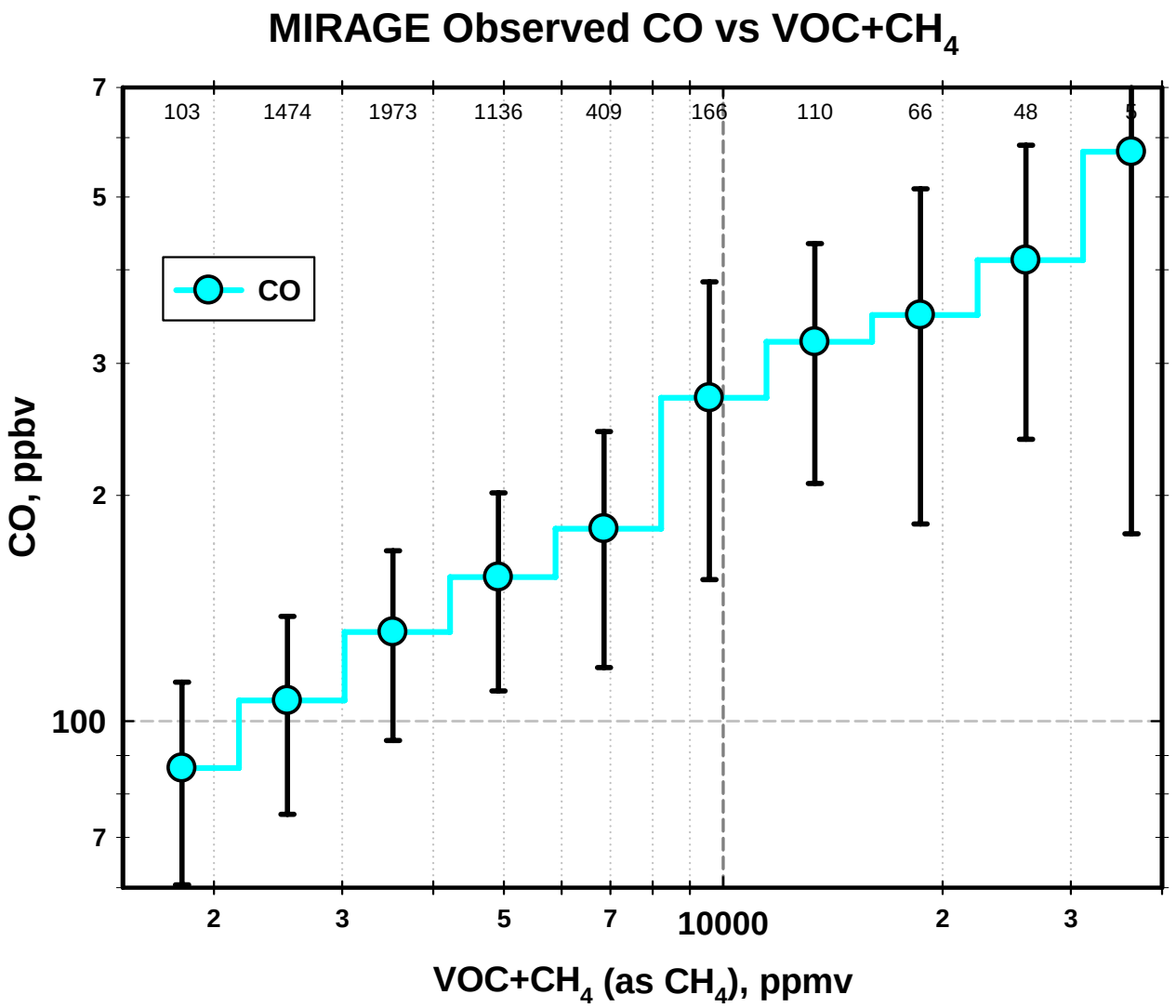
Constrained box models

- NCAR steady state model
- NASA diurnal steady state model
- Use observations of
  - NO, NO_2, CO, *j*-values, CH_2O, VOCs, OVOCs, H_2O_2, CH_3OOH, O_3, H_2O vapor, T, P, aerosol properties
  - Aircraft state parameters
  - Current kinetic and spectroscopy

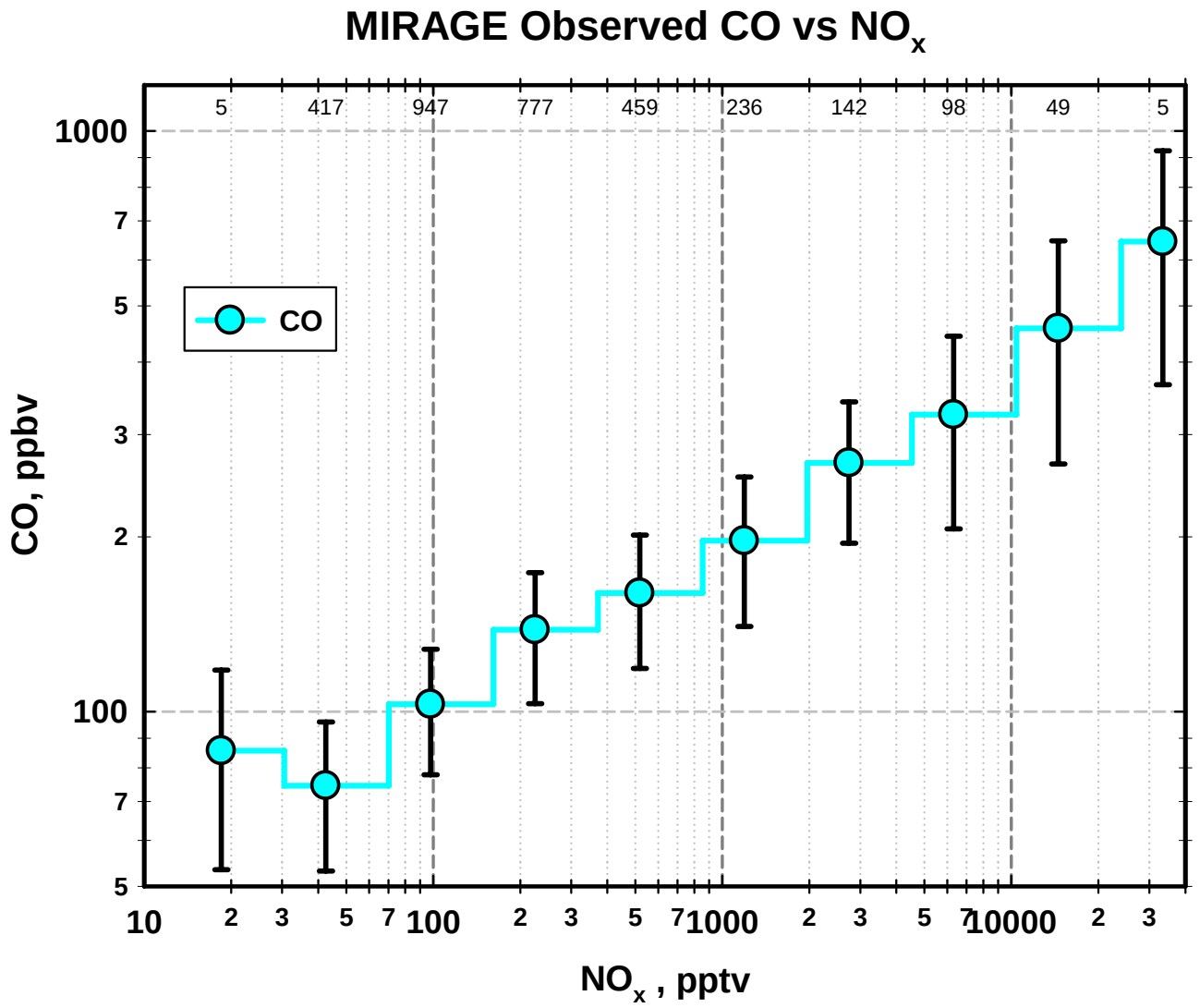
Average NO & NO_2 vs VOC+CH_4



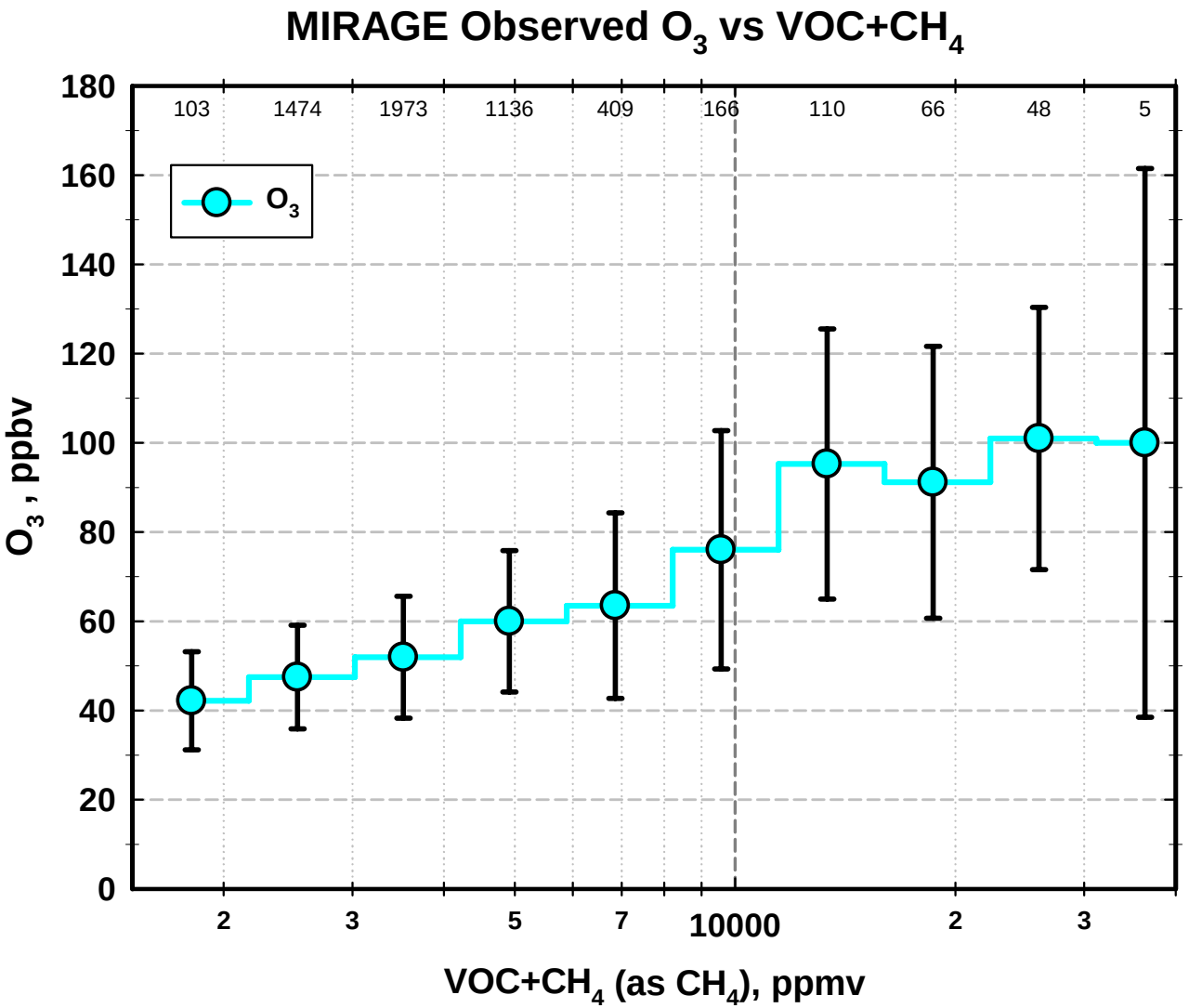
CO vs VOC+CH$_4$


MIRAGE Observed CO vs VOC+CH4
103
1474
1973
1136
409
166
110
66
48
5
CO
CO, ppbv
7
5
3
2
100
7
2
3
5
7
10000
2
3
VOC+CH4 (as CH4), ppmv

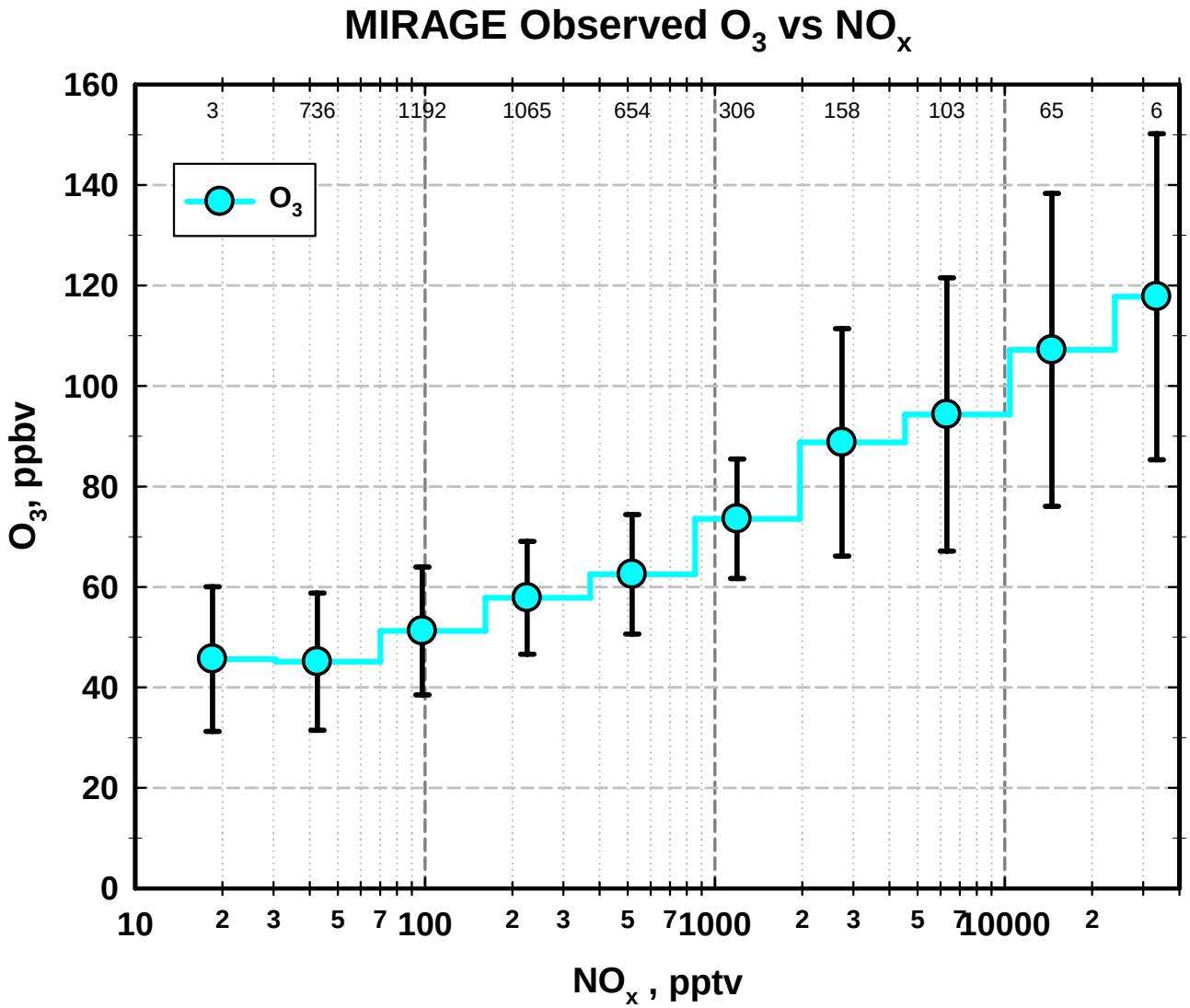
CO vs NO_x


MIRAGE Observed CO vs NOx
5
417
947
777
459
236
142
98
49
5
1000
7
5
3
2
100
7
5
CO
CO, ppbv
10
2
3
5
7
100
2
3
5
7
1000
2
3
5
7
10000
2
3
NOx , pptv

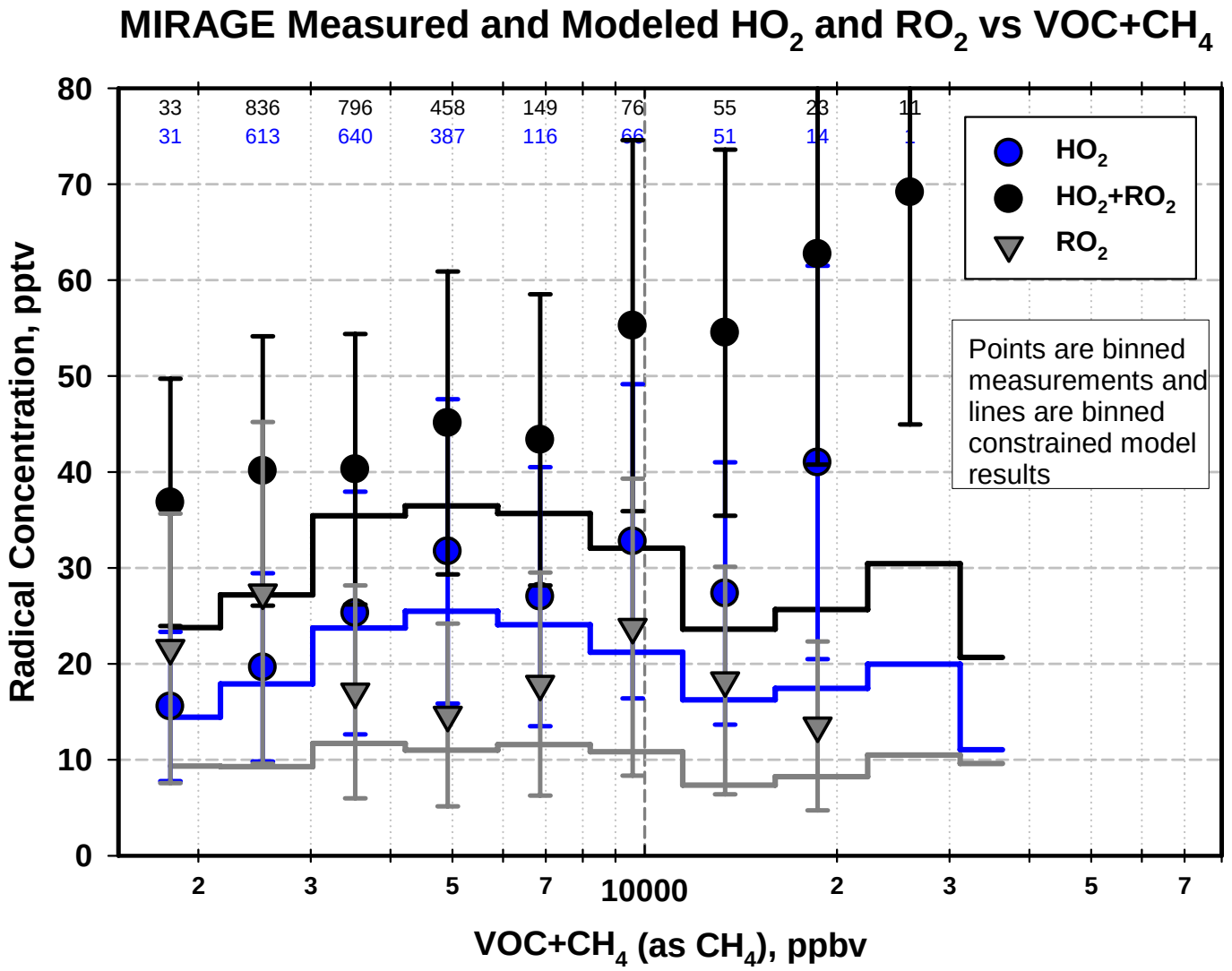
O_3 vs $VOC+CH_4$


MIRAGE Observed O3 vs VOC+CH4
103
1474
1973
1136
409
166
110
66
48
5
O3
180
160
140
120
100
80
60
40
20
0
O3 , ppbv
2
3
5
7
10000
2
3
VOC+CH4 (as CH4), ppmv

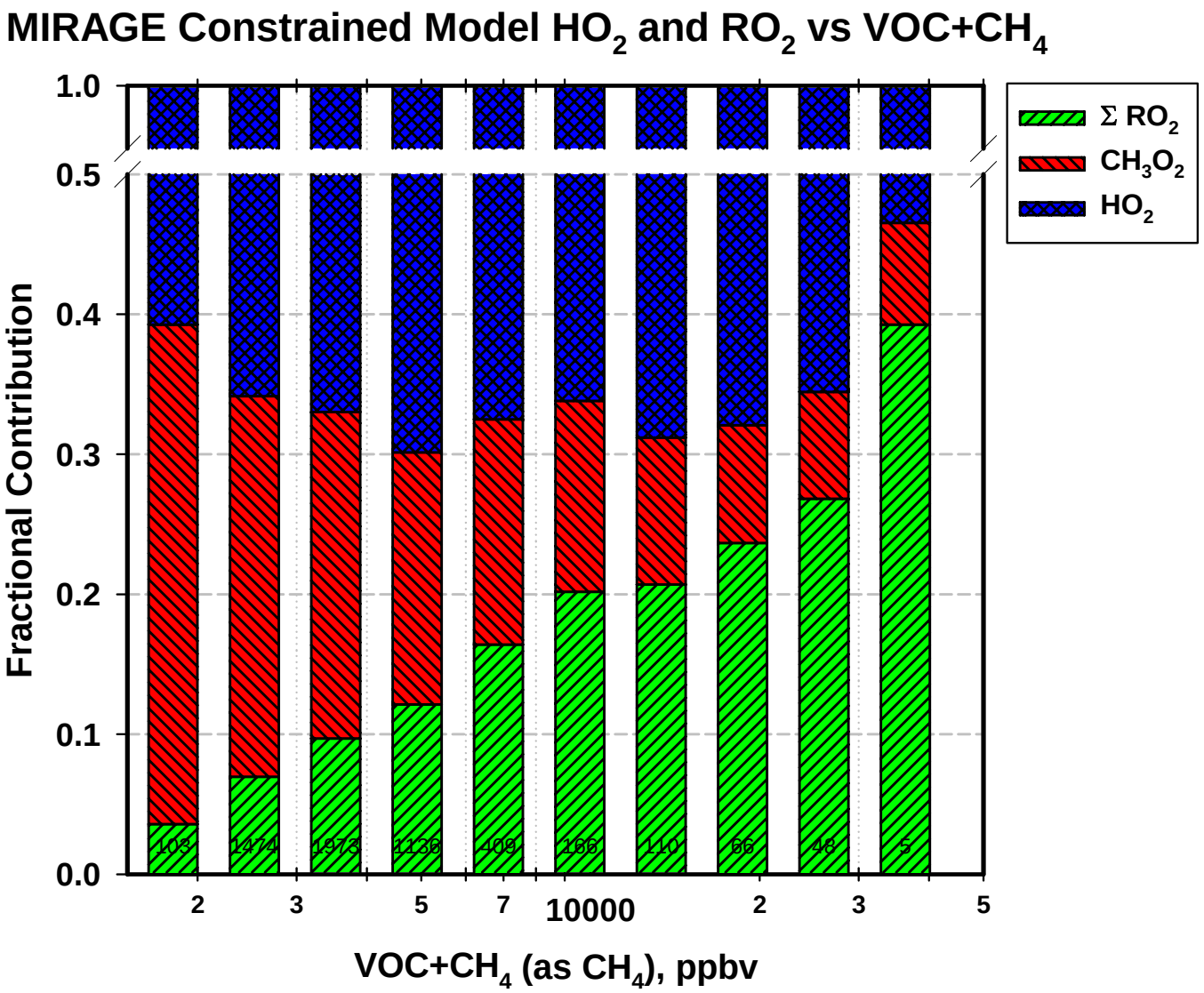
O_3 vs NO_x


MIRAGE Observed O3 vs NOx
3
736
1192
1065
654
306
158
103
65
6
O3
160
140
120
100
80
60
40
20
0
O3, ppbv
10
2
3
5
7
100
2
3
5
7
1000
2
3
5
7
10000
2
NOx , pptv

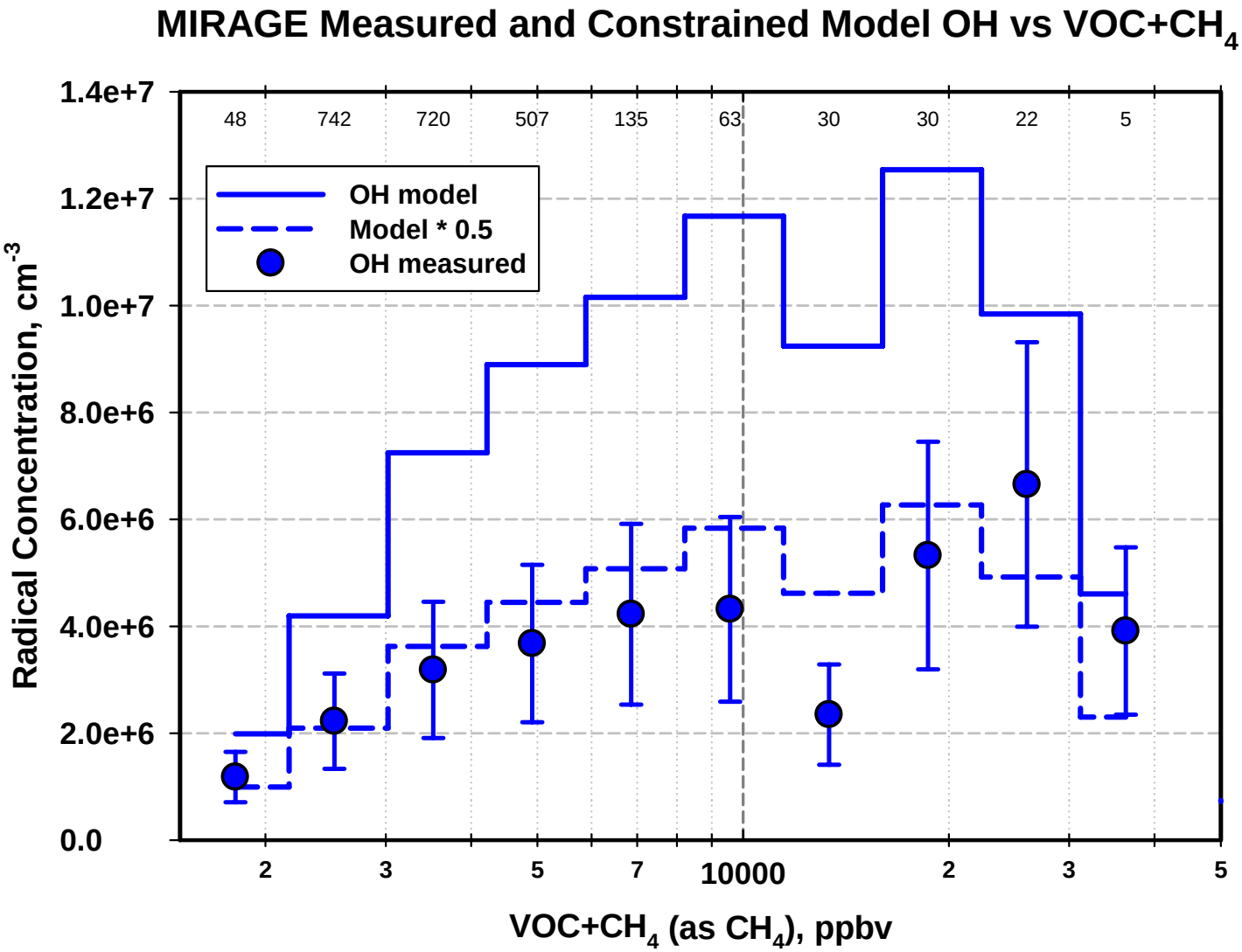
Peroxy Radicals vs VOC+CH_4



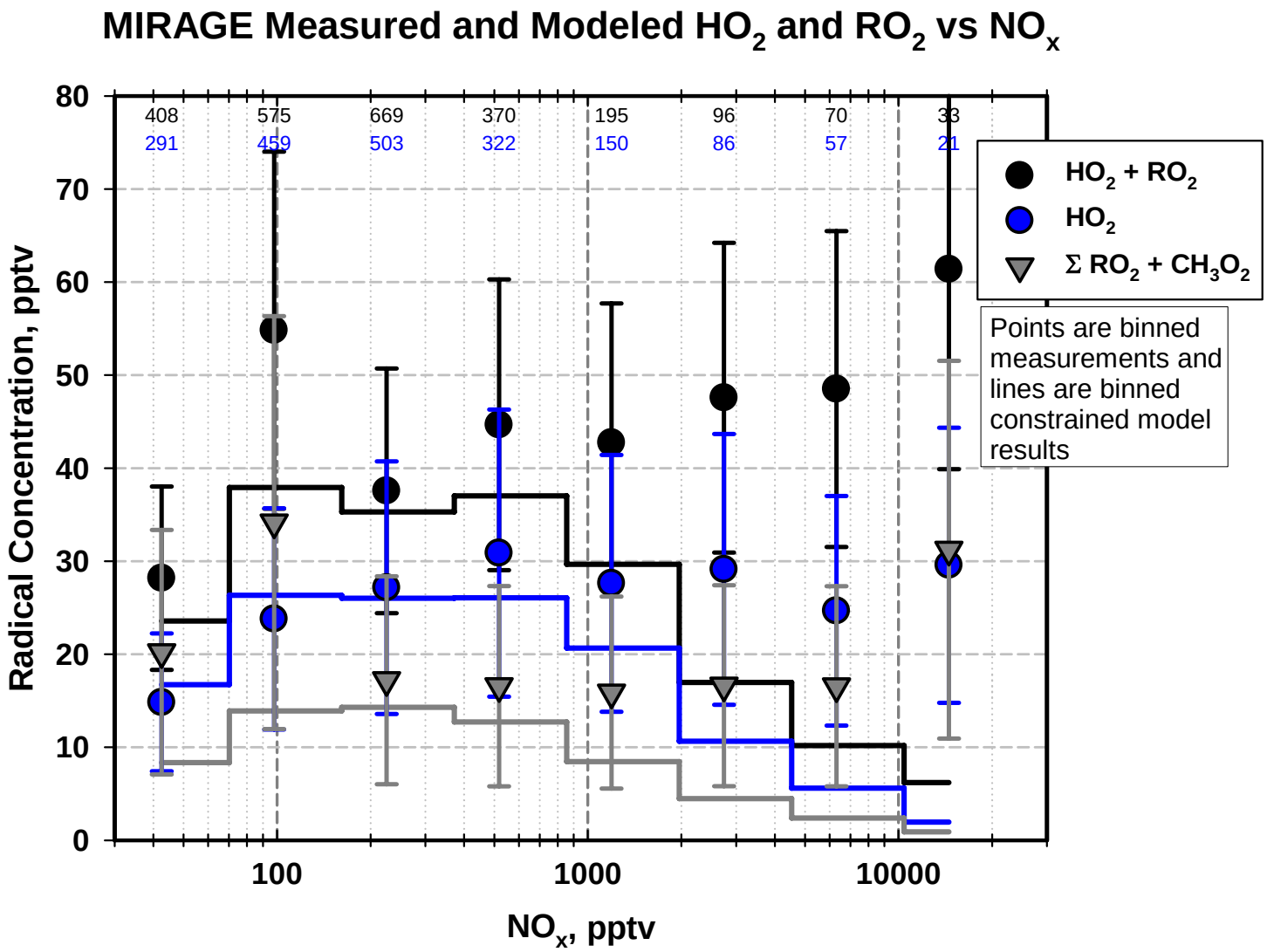
Fractional HO_2 & RO_2 vs $VOC+CH_4$



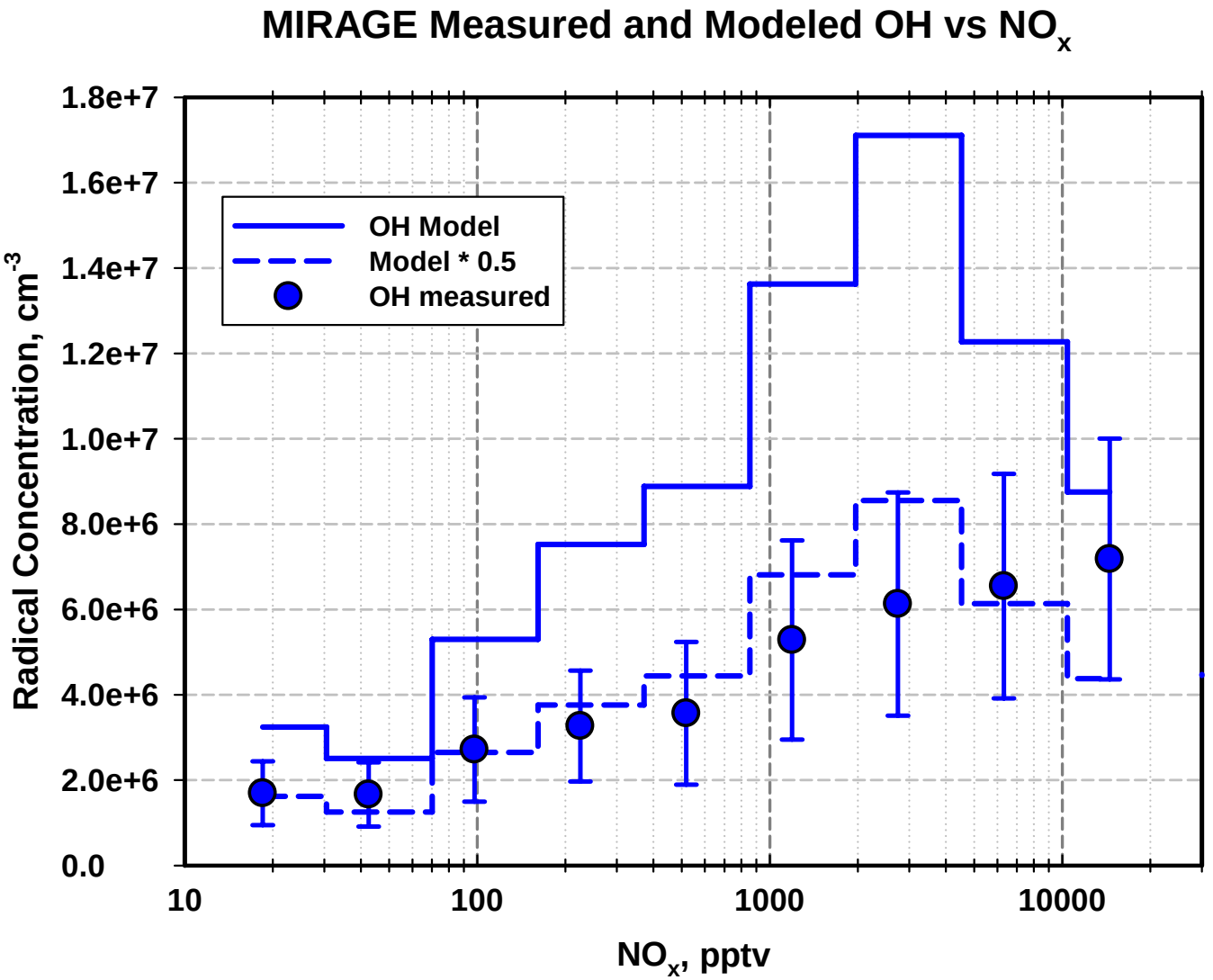
OH vs VOC+CH_4


MIRAGE Measured and Constrained Model OH vs VOC+CH4
48
742
720
507
135
63
30
30
22
5
OH model
Model * 0.5
OH measured
1.4e+7
1.2e+7
1.0e+7
8.0e+6
6.0e+6
4.0e+6
2.0e+6
0.0
Radical Concentration, cm-3
2
3
5
7
10000
2
3
5
VOC+CH4 (as CH4), ppbv

Peroxy Radicals vs NO_x



OH vs NO_x

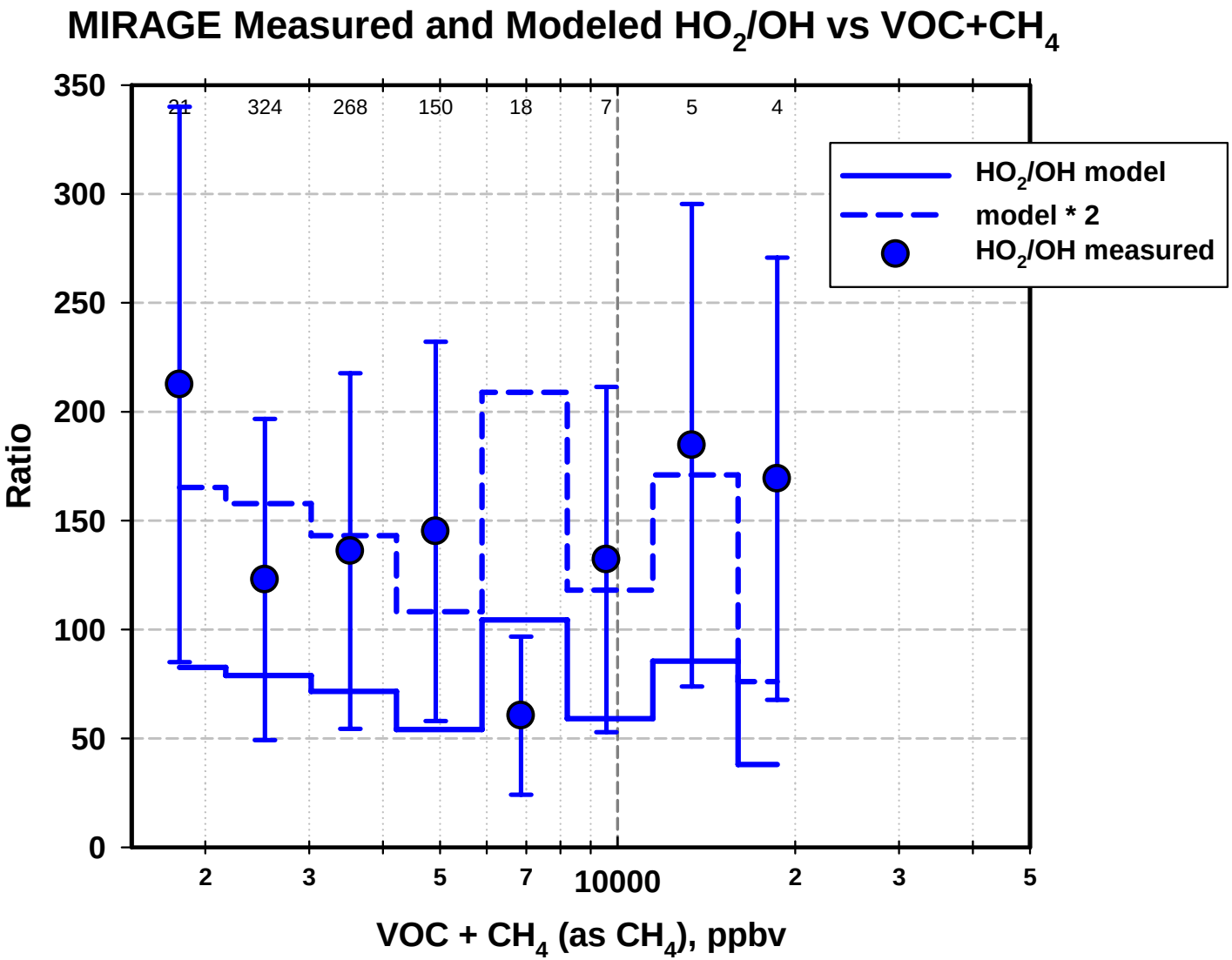

MIRAGE Measured and Modeled OH vs NOx
Radical Concentration, cm-3
1.8e+7
1.6e+7
1.4e+7
1.2e+7
1.0e+7
8.0e+6
6.0e+6
4.0e+6
2.0e+6
0.0
OH Model
Model * 0.5
OH measured
10
100
1000
10000
NOx, pptv

HO_2 / OH Ratio

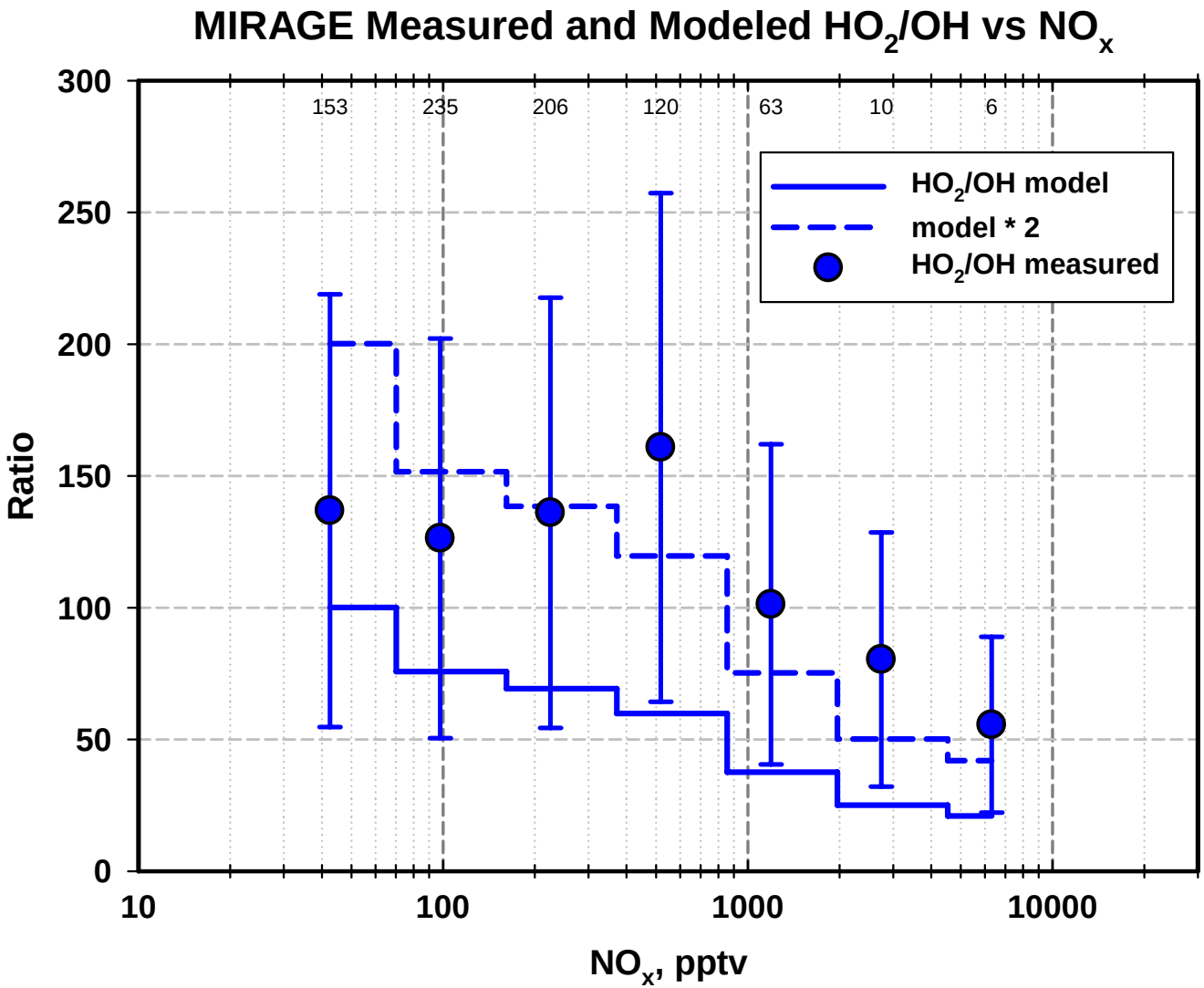
- Rapid Interconversion chemistry
  - HO_2 + NO, HO_2 + O_3
  - OH + CO, OH + VOCs, OH + O_3

$$\frac{[HO_2]}{[OH]} = \frac{k[CO] + \sum k[VOC] + k[O_3]}{k[NO] + k[O_3]}$$

HO_2/OH Ratio vs $VOC+CH_4$



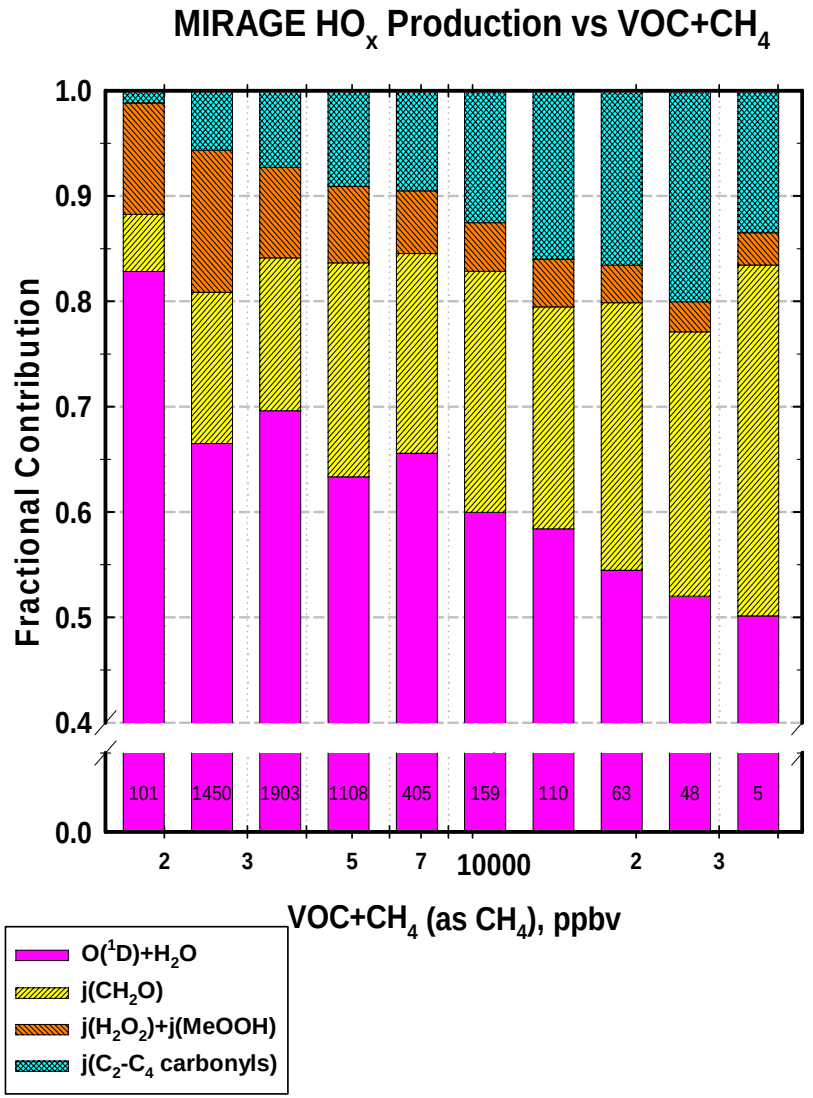
HO_2/OH Ratio vs NO_x

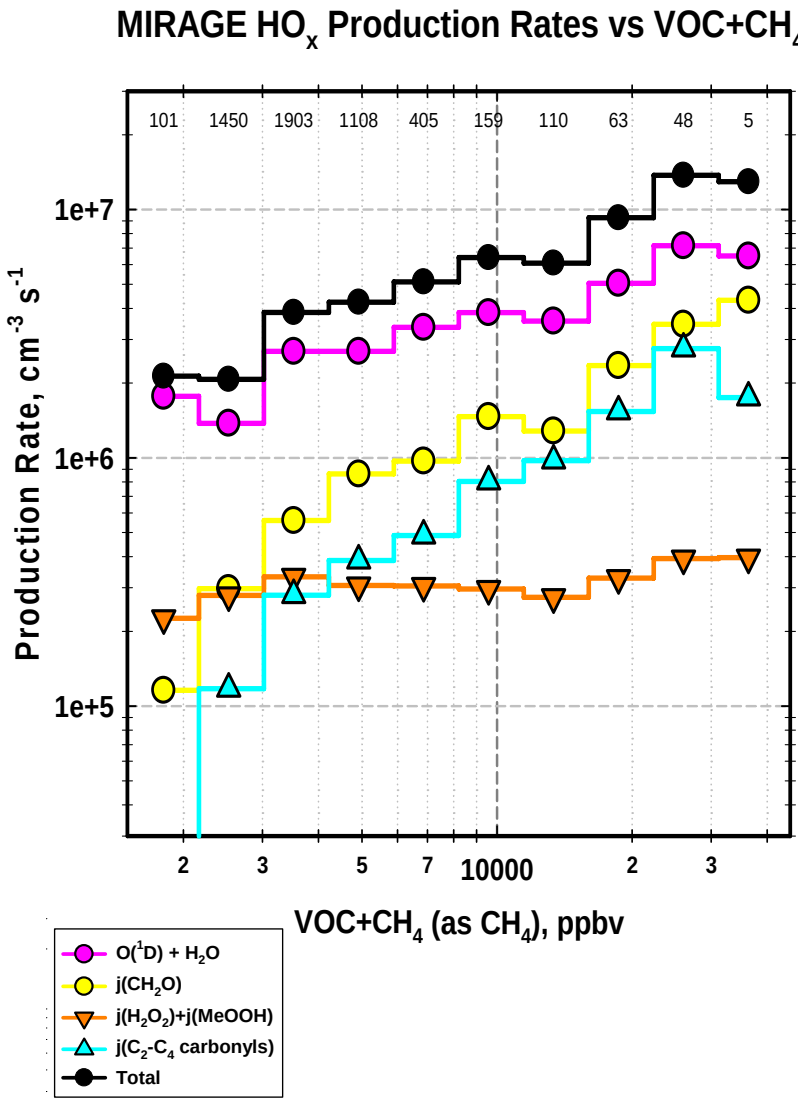


HO_x Production

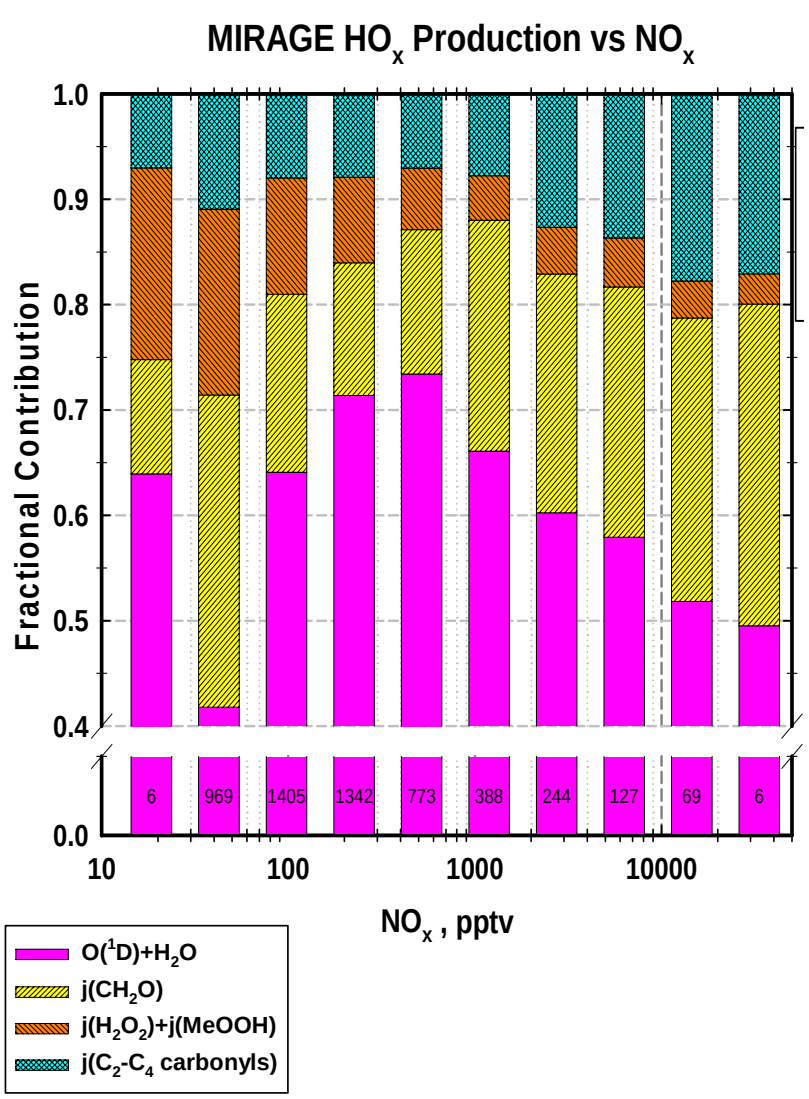
- $O_3 + h\nu \rightarrow O_2 + O(^1D)$
  - $O(^1D) + M \rightarrow O(^3P) + M$
  - $O(^1D) + H_2O \rightarrow 2\ OH$
- $CH_2O + h\nu \rightarrow H + HCO$
  - $H + O_2 + M \rightarrow HO_2 + M$
  - $HCO + O_2 \rightarrow HO_2 + CO$
- $H_2O_2 + h\nu \rightarrow 2\ OH$
- $ROOH + h\nu \rightarrow RO + OH$
  - $RO + O_2 \rightarrow HO_2 + R'CHO$
- $R_1R_2CO + h\nu \rightarrow R_1CO + R_2$
  - $R_1CO + O_2 + M \rightarrow R_1C(O)O_2 + M$
  - $R_2 + O_2 + M \rightarrow R_2O_2 + M$

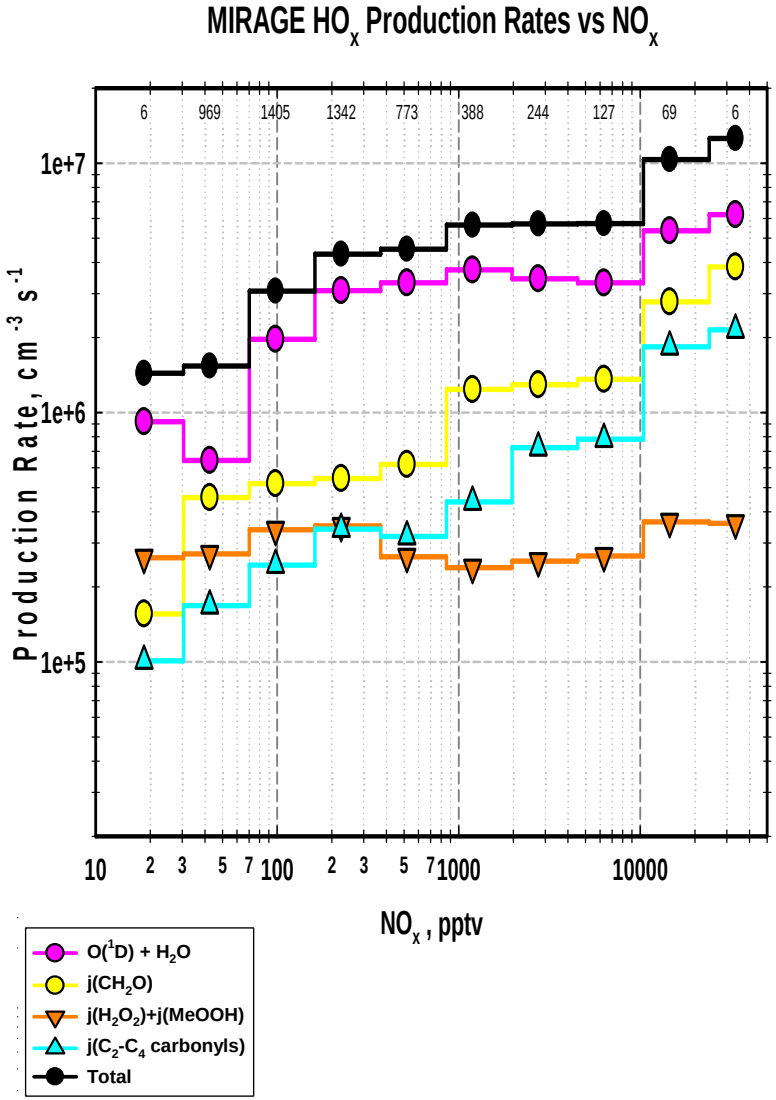
Fractional P_{HOx} vs VOC+CH_4



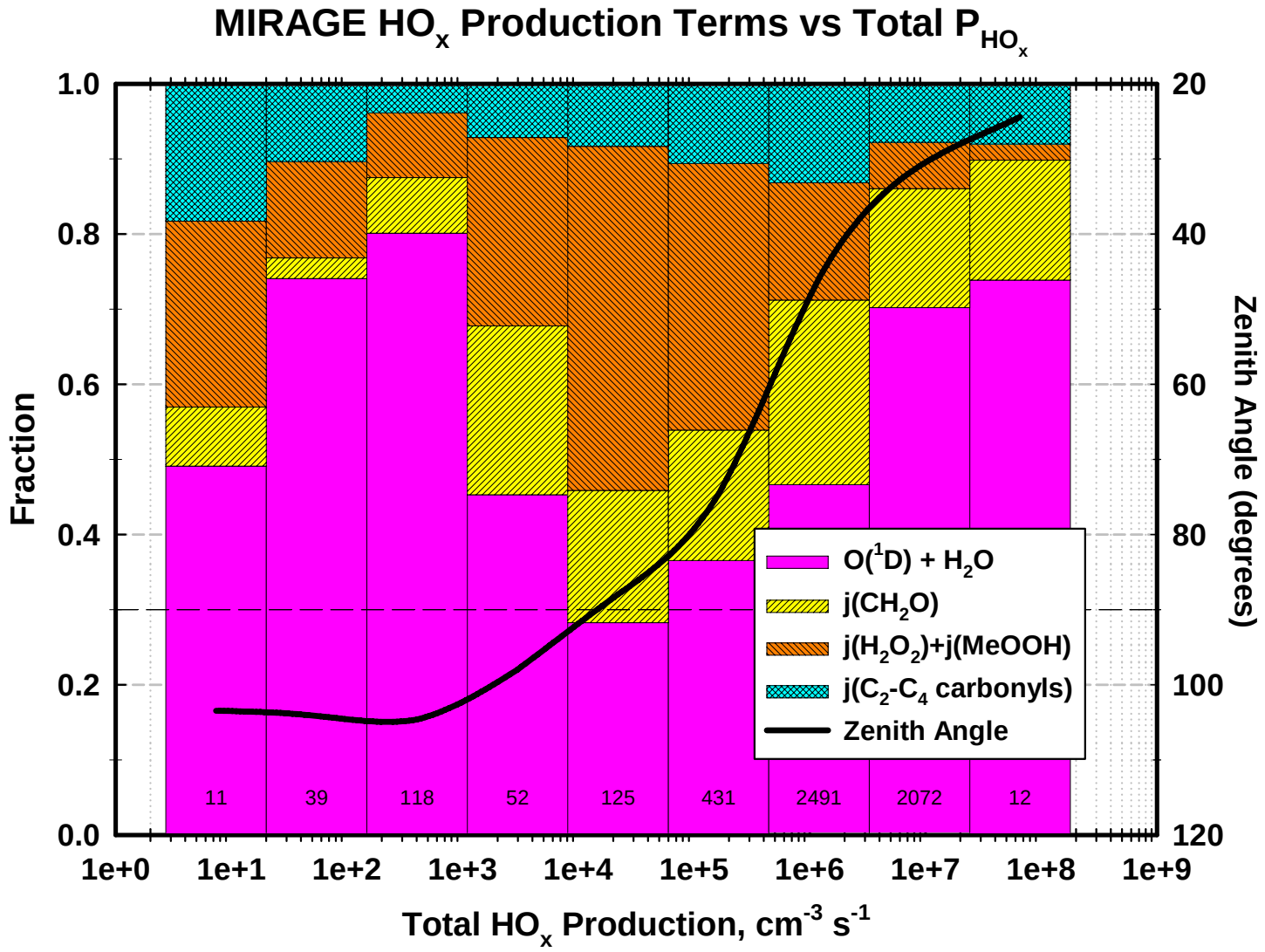


Fractional P_{HOx} vs NO_x

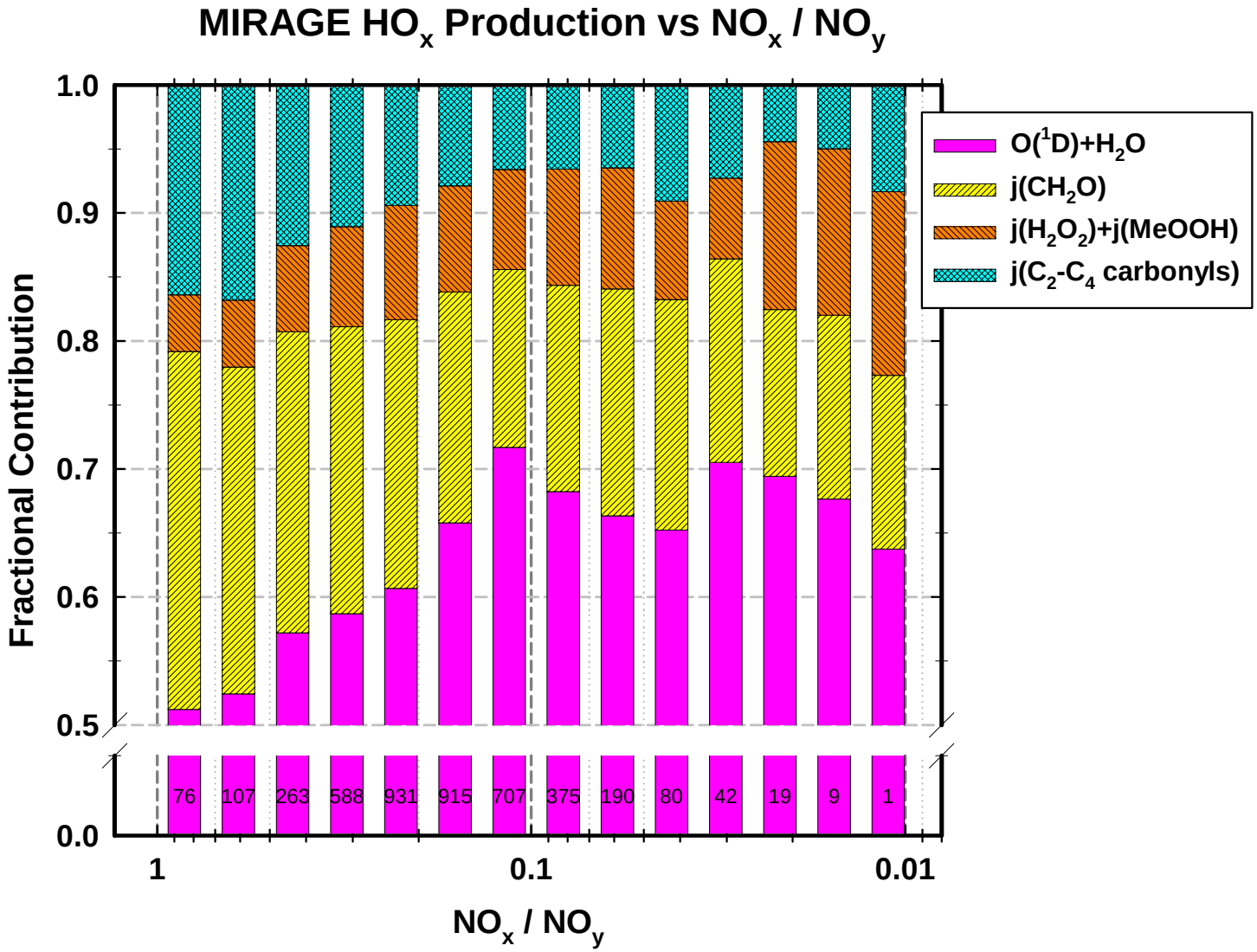




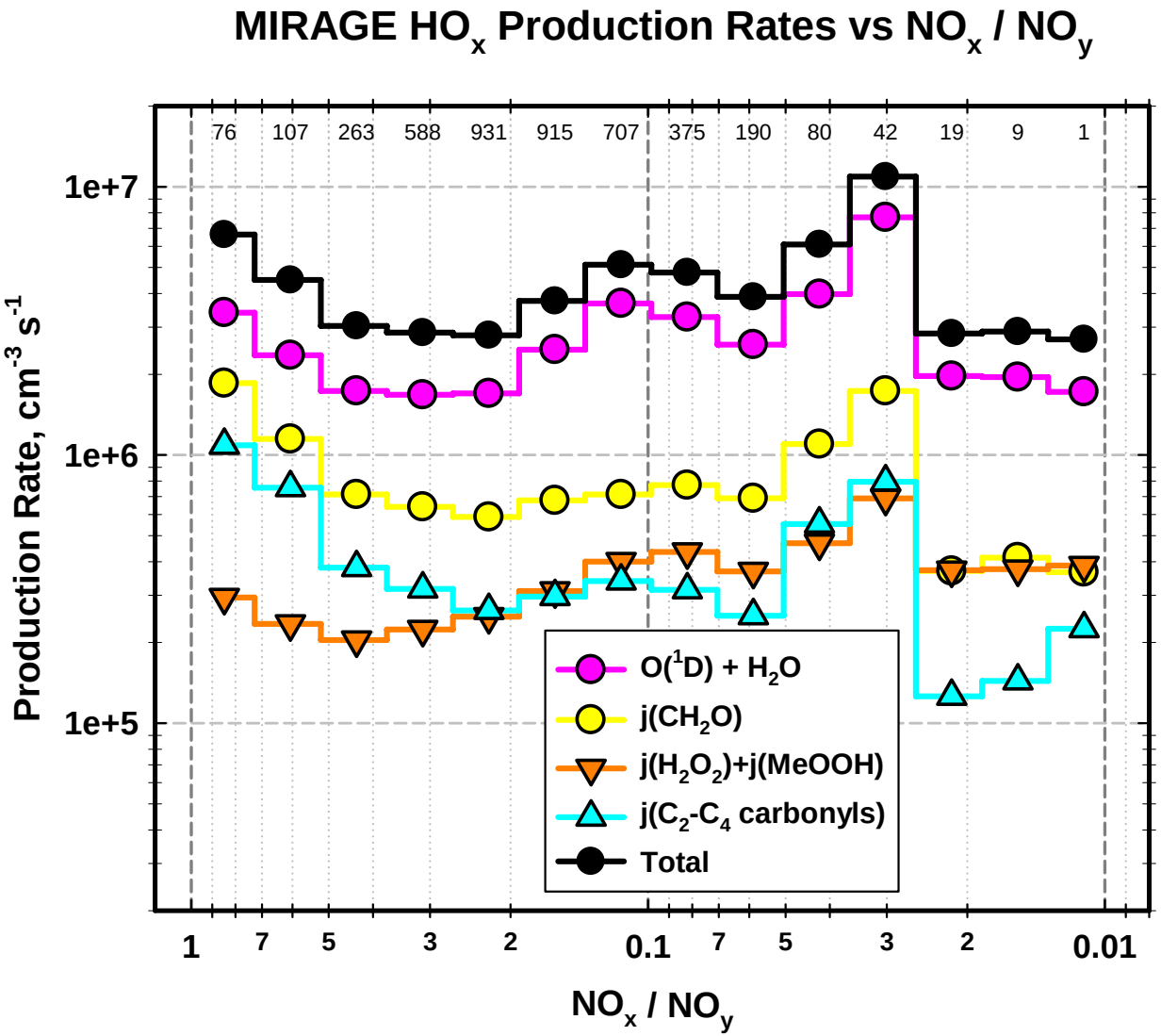
Fractional P_{HOx} vs Total P_{HOx}



Fractional P_{HOx} vs NO_x/NO_y



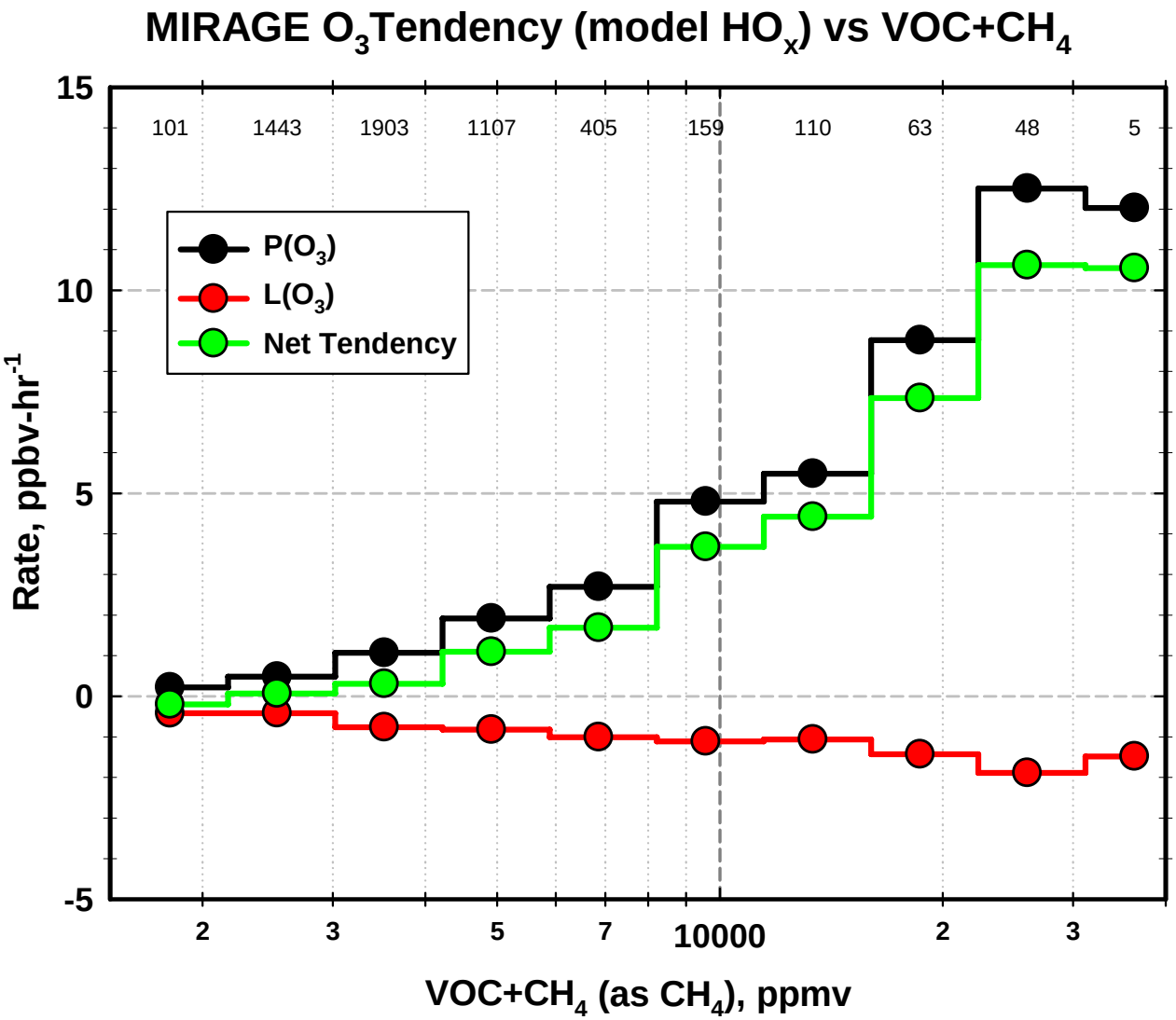
P_{HOx} vs NO_x / NO_y



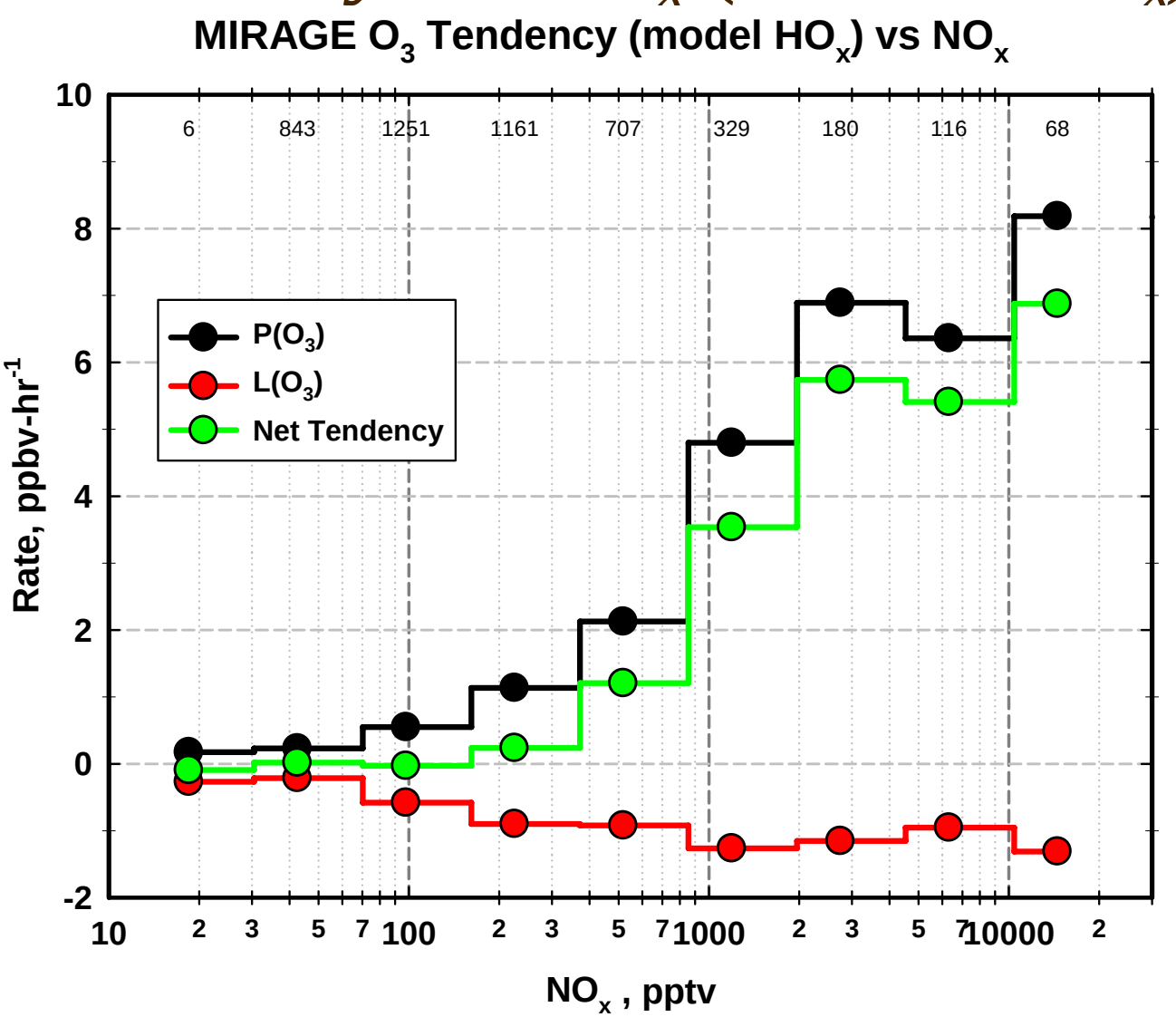
O_3 Tendency

- Production
  - HO_2 or $RO_2 + NO \rightarrow NO_2$
- Loss
  - $HO_2 + O_3$, $OH + O_3$, $O(^1D) + H_2O$
- Net Tendency
  - P - L

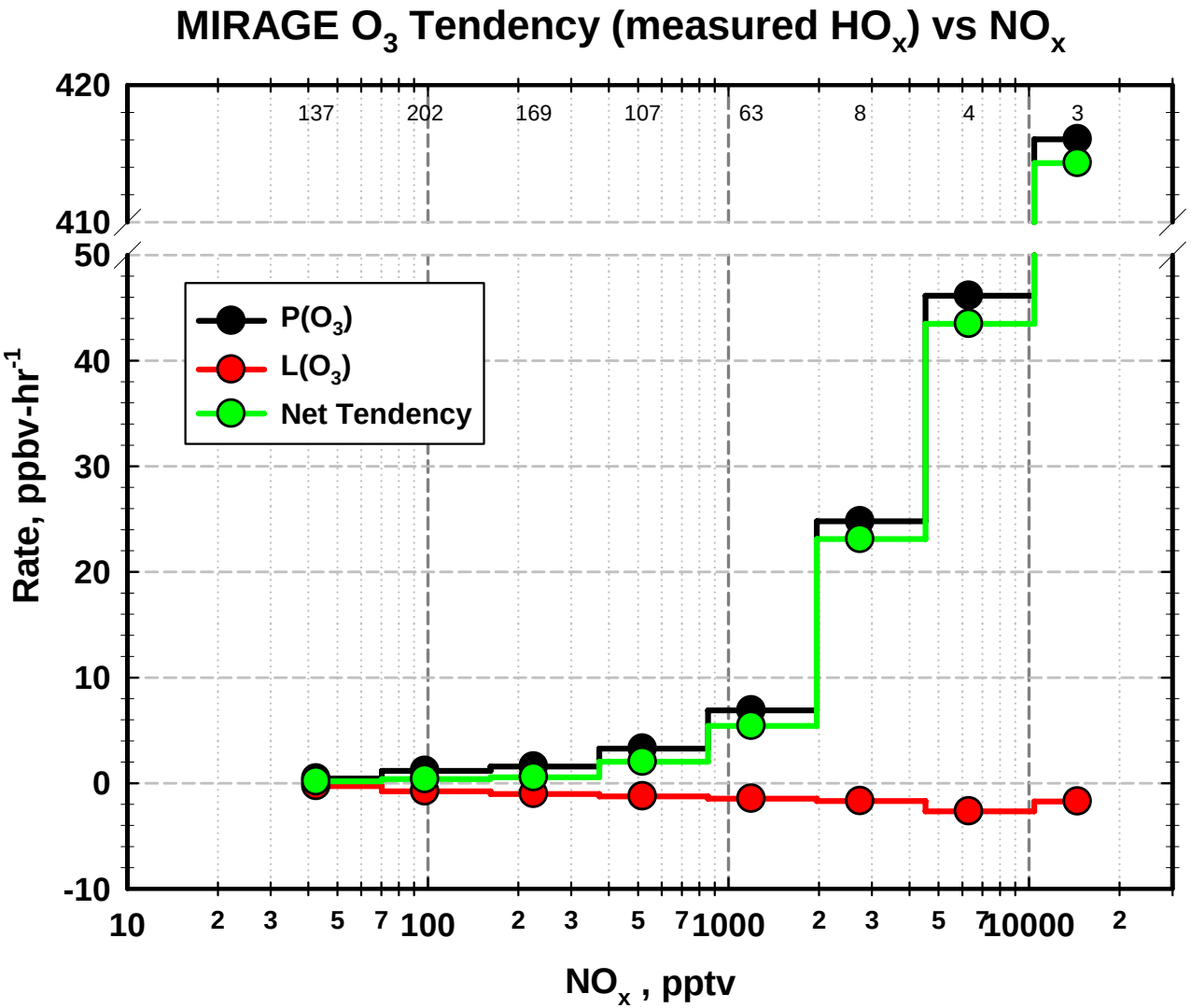
O_3 Tendency vs VOC+CH_4



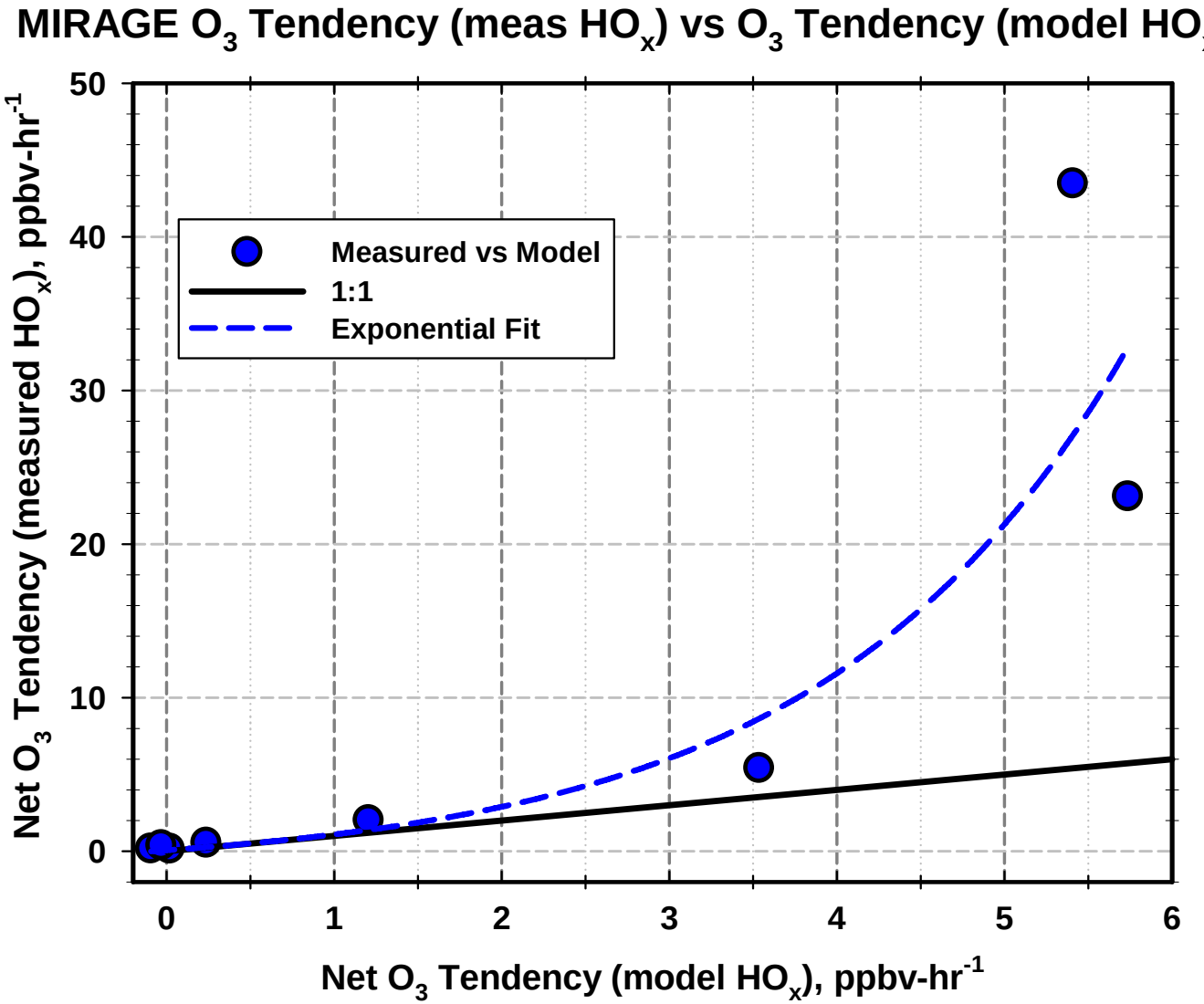
O_3 Tendency vs NO_x (model HO_x)



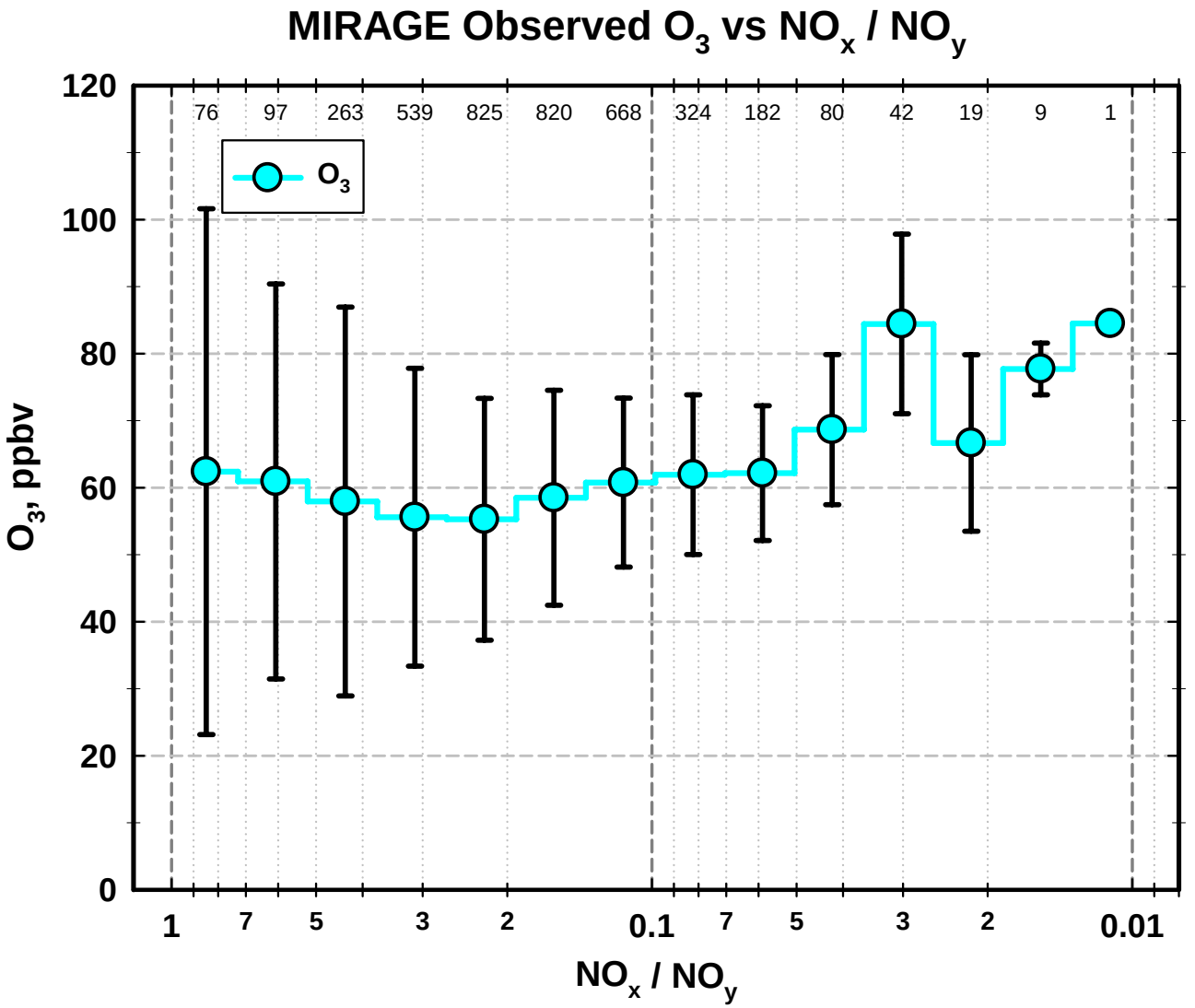
O_3 Tendency vs NO_x (meas HO_x)



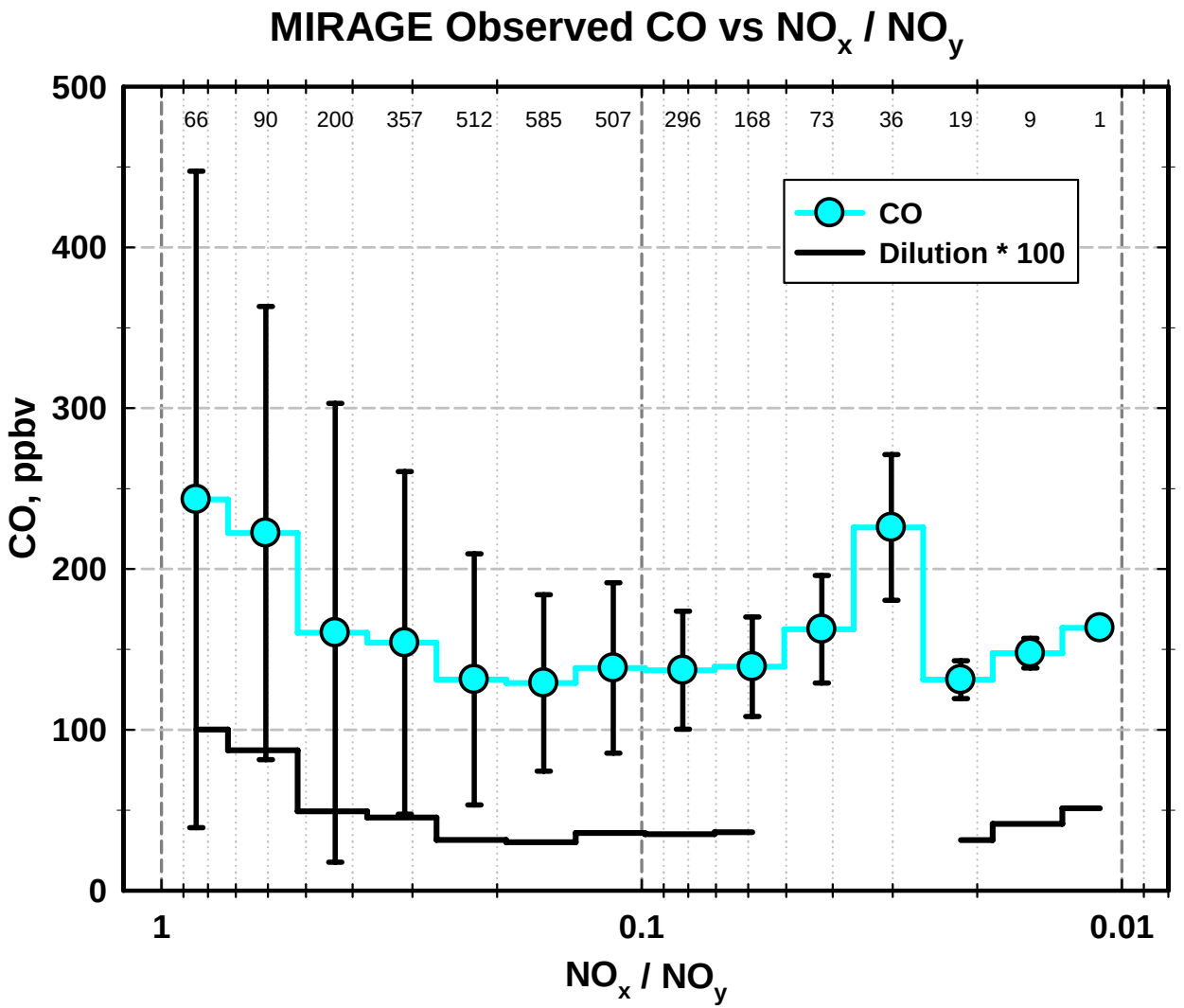
O_3 Tendency for Meas vs Model HO_x



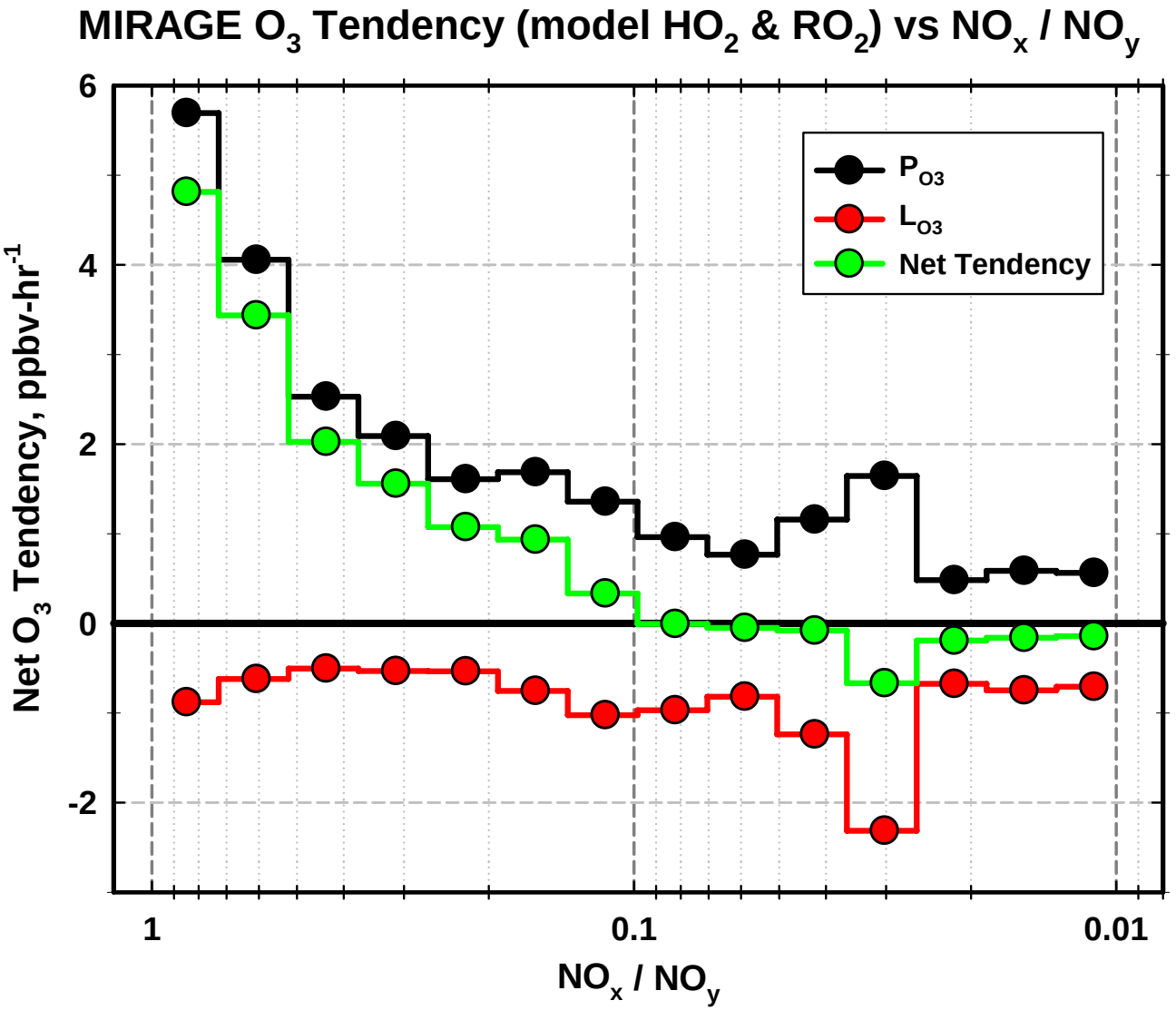
O_3 vs NO_x / NO_y


MIRAGE Observed O3 vs NOx / NOy
76
97
263
539
825
820
668
324
182
80
42
19
9
1
O3
120
100
80
60
40
20
0
O3, ppbv
1
7
5
3
2
0.1
7
5
3
2
0.01
NOx / NOy

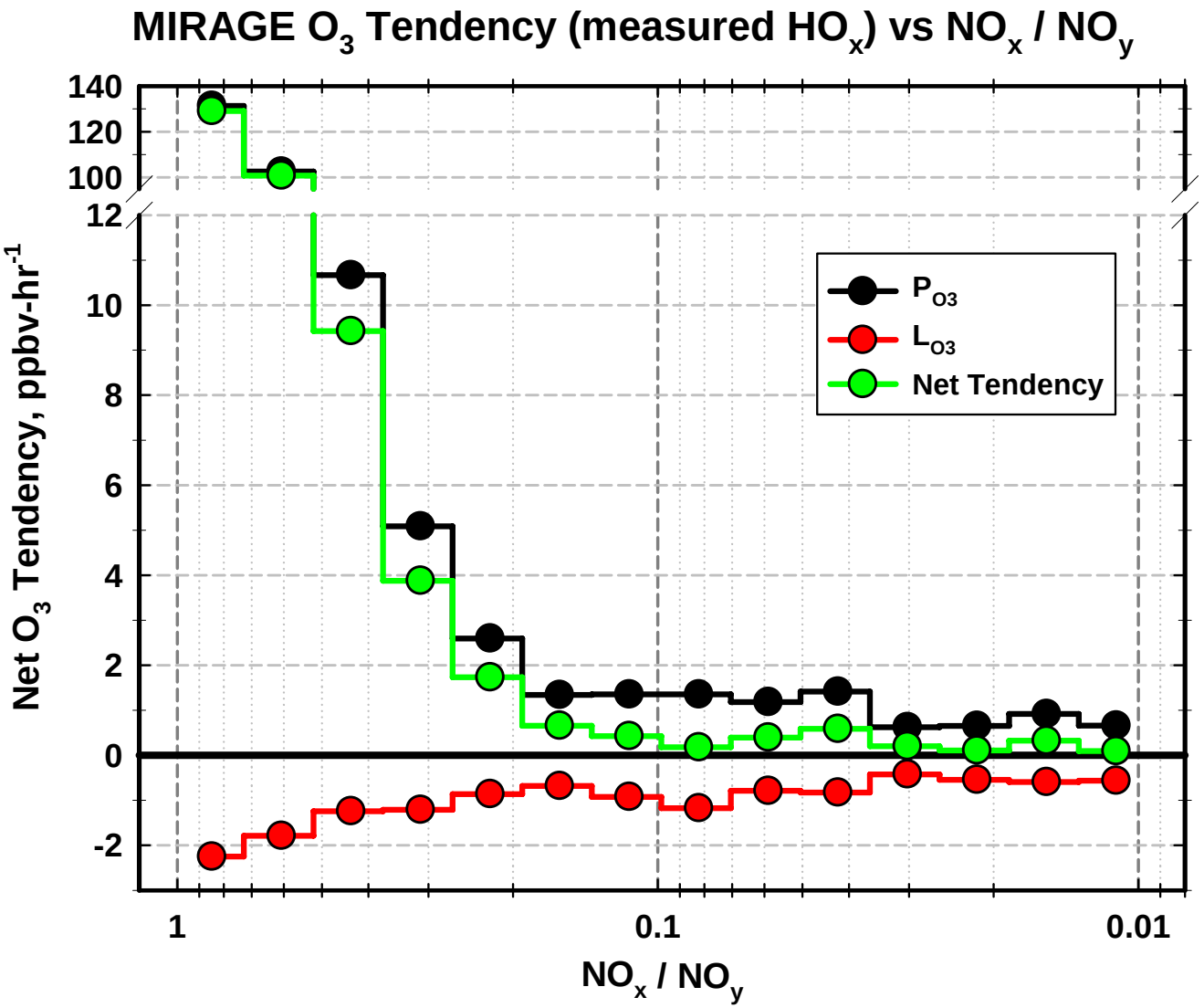
CO vs NO_x/NO_y


MIRAGE Observed CO vs NOx / NOy
66
90
200
357
512
585
507
296
168
73
36
19
9
1
CO
Dilution * 100
500
400
300
200
100
0
CO, ppbv
1
0.1
0.01
NOx / NOy

O_3 Tendency vs NO_x/NO_y (model HO_x)



O_3 Tendency vs NO_x/NO_y (meas HO_x)



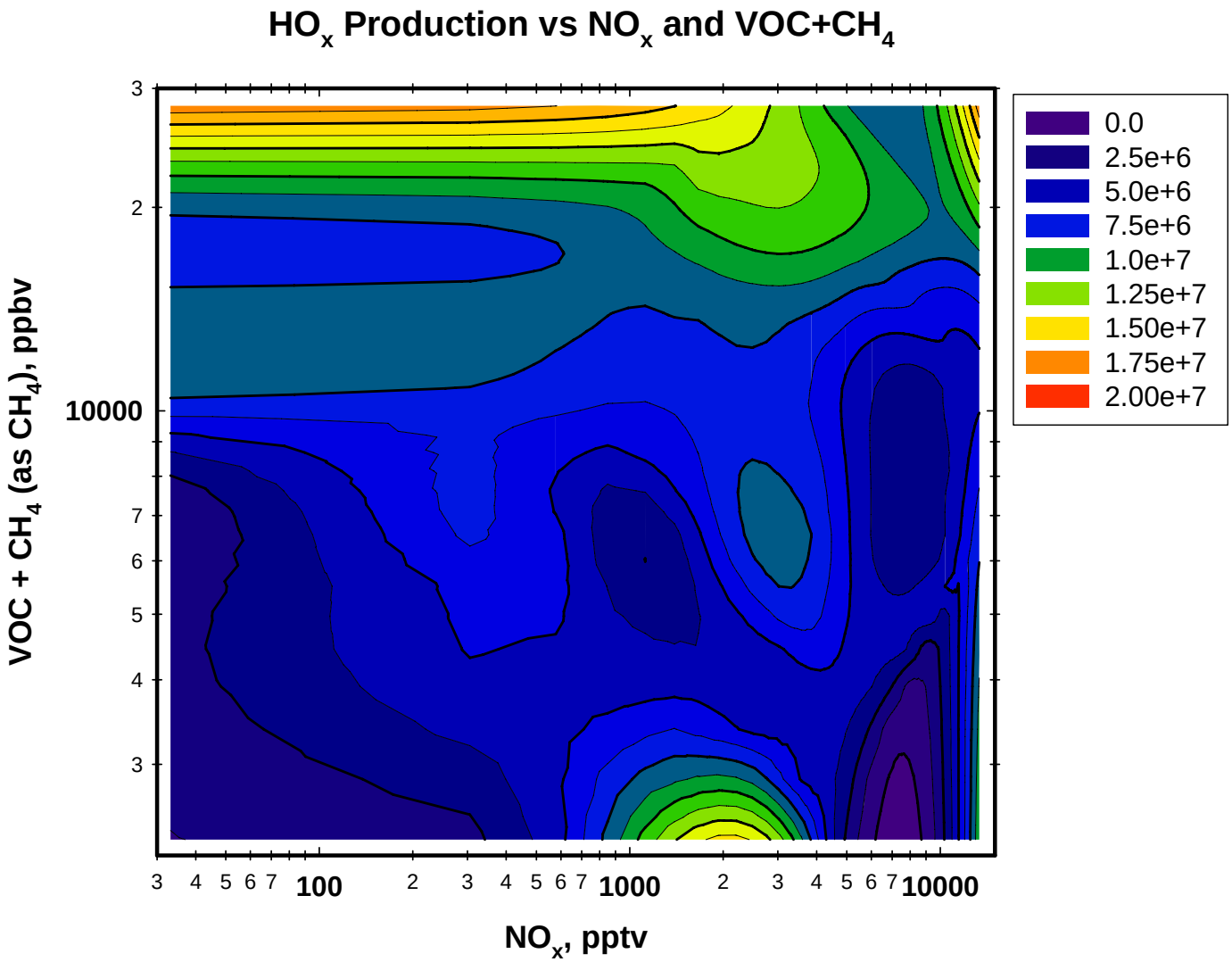
Summary

- Reasonable agreement between measured & modeled HO_2 & HO_2+RO_2 except at highest NO_x & VOC reactivity
- Model underestimates OH most of the time
  missing reactants?
- Rapid photochemistry in fresh emissions quickly slows as air mass ages & dilutes
- More work remains to fully understand the evolution of HO_x photochemistry

The End

Extra Slides

P_{HOx} vs NO_x & $VOC+CH_4$



O_3 vs NO_x & VOC+CH_4