Measurements of Nonmethane Hydrocarbons in Several Urban Areas

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Objectives

- Evaluate the relative importance of the local formation of pollutants versus long range transport for areas with different meteorology and pollutant emission inventories.

- Investigate day/night contrasts in chemical and meteorological processes.

NMHC Measurements

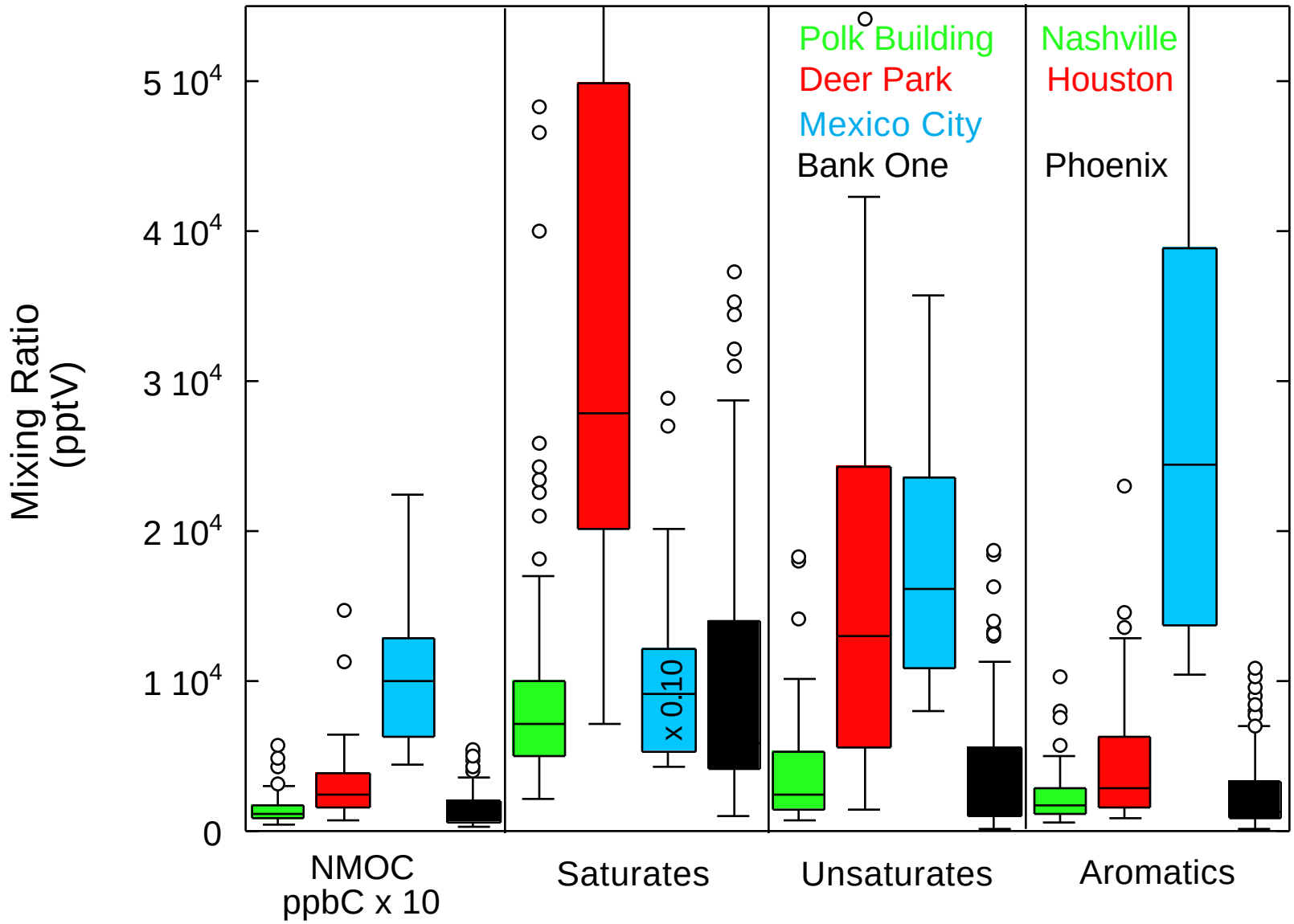
- Sites - IMP Laboratories, Mexico City, Feb. - March 1997
  Tahrir Square, Cairo, Egypt, June 1997
  Polk Building, Nashville (elevation 100 m), June - July 1999
  Williams Tower, Houston (elevation 253 m), August - Sept. 2000
  Deer Park, Houston
  University of Puerto Rico, San Juan, March 2001
  Bank One Building, Phoenix (139 m), June 2001

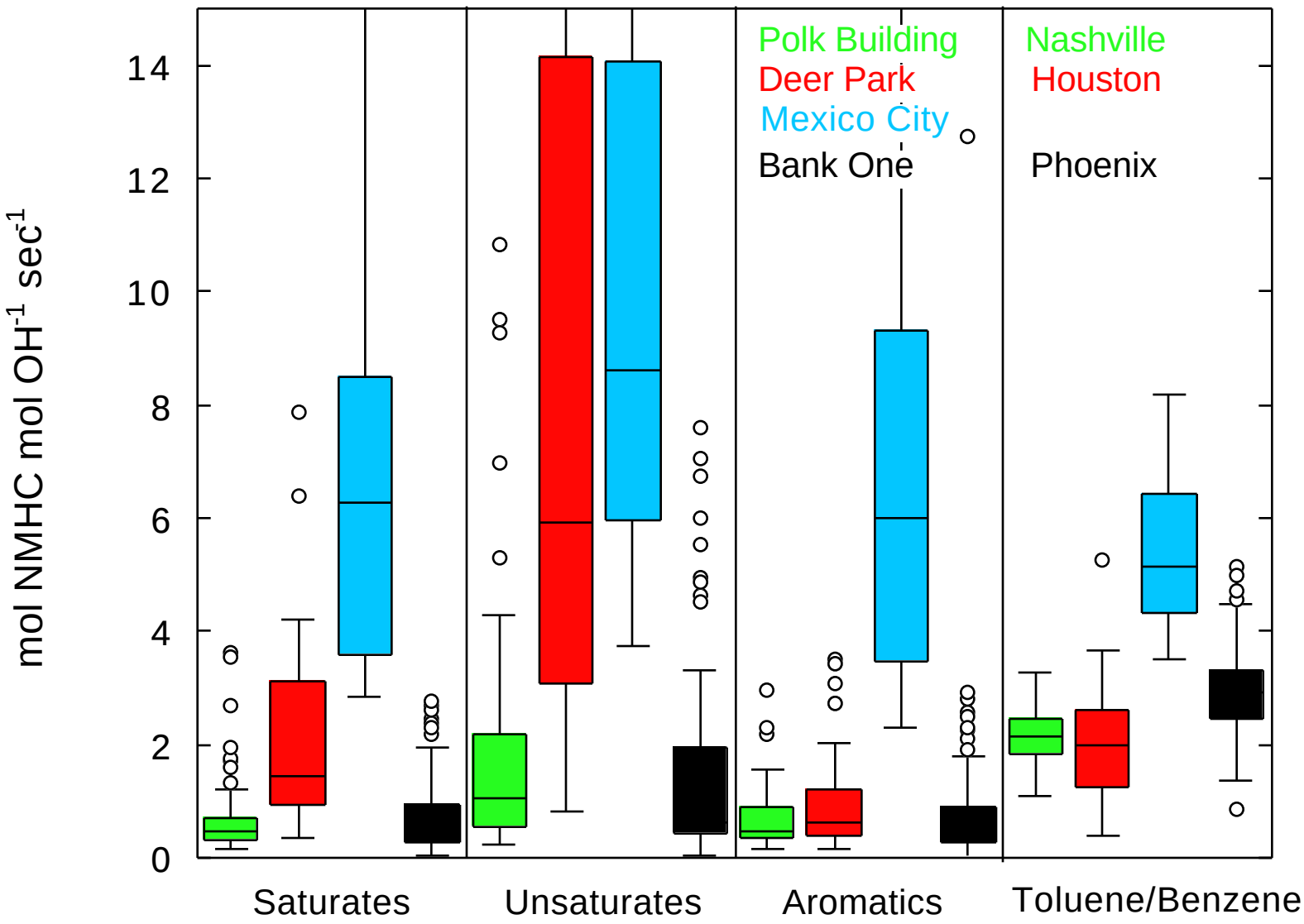
- Sample collection - Automated 10 canister sampler.

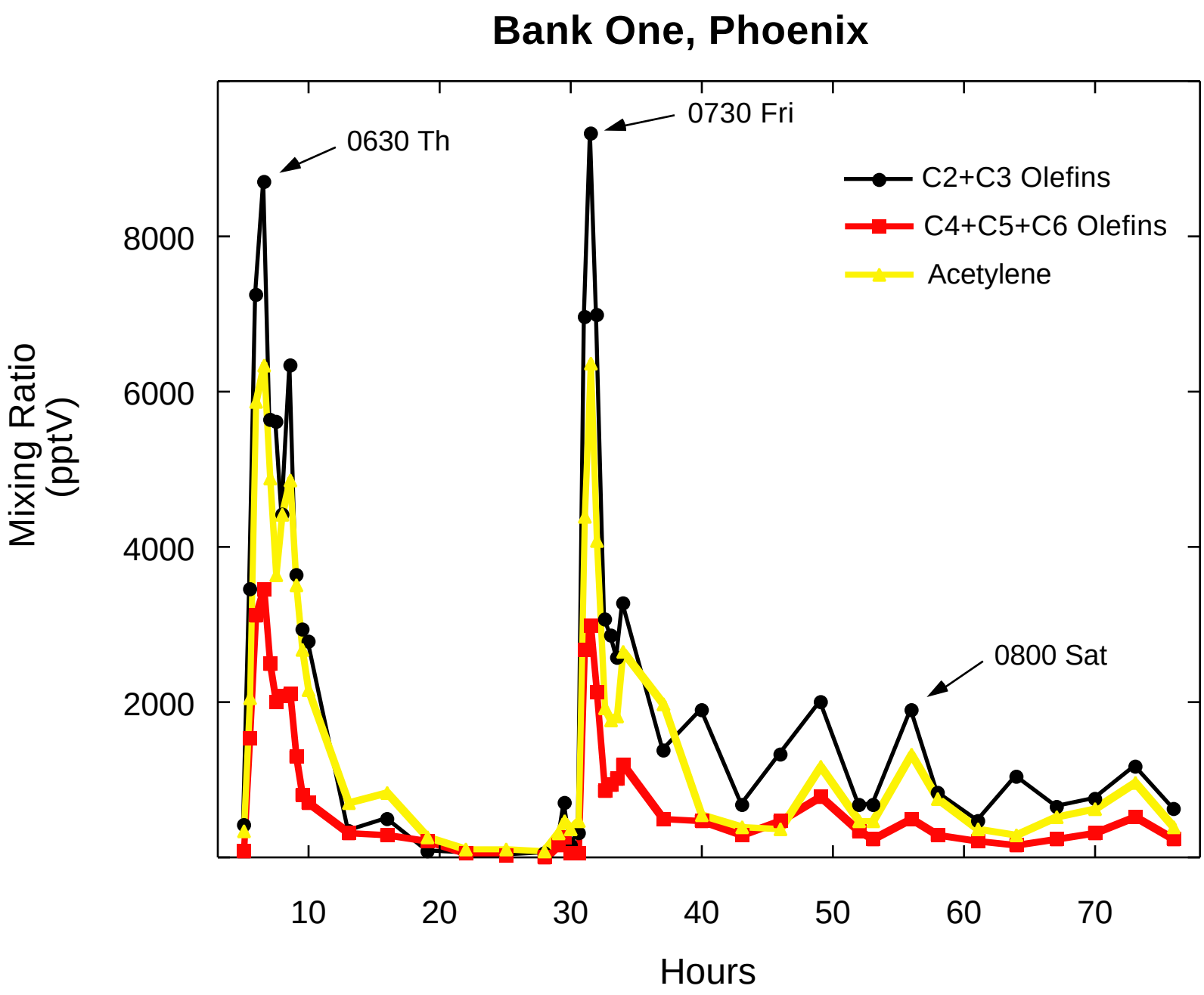
- Sampling Strategy and Frequency - 5 minute sample collected every two hours between 0700 and 1900 LT and every three hours between 1900 and 0700 LT.

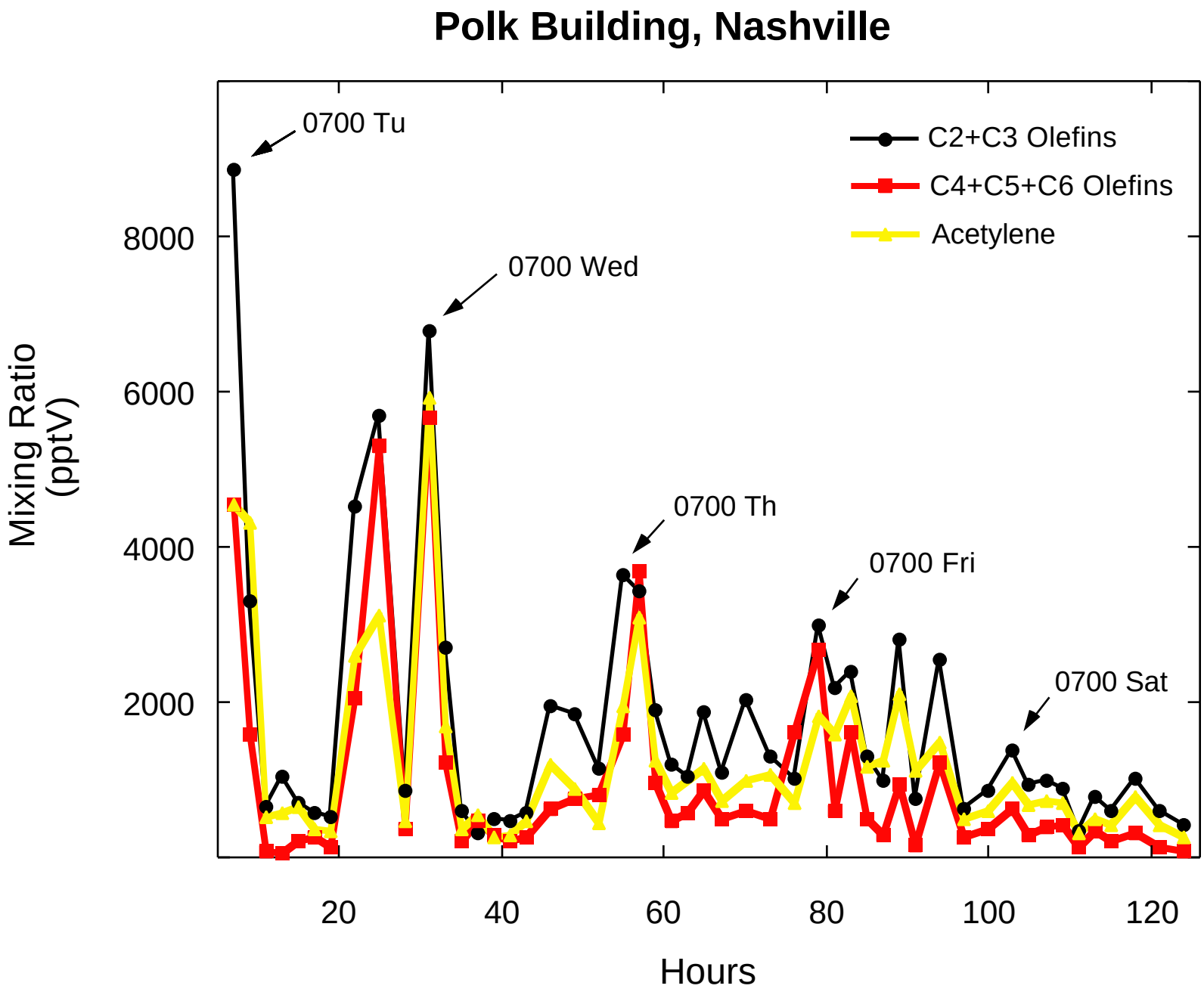
- Sample Analysis - In mobile laboratory by cryogenic preconcentration/high-resolution gas chromatography with flame ionization detection.

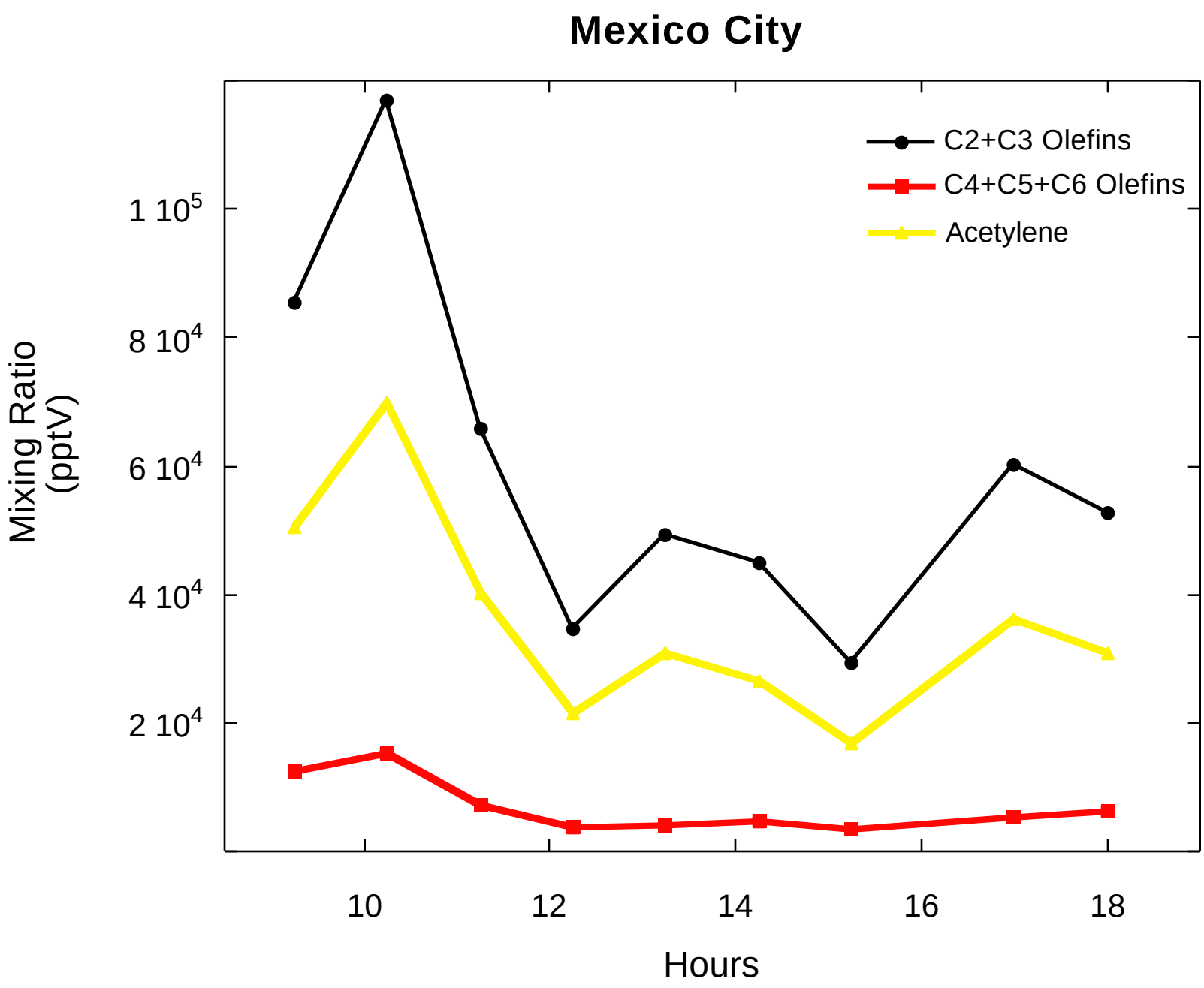
Molecule	OH Reaction Rate ($10^{12} \times k$)
Ethane	0.257
2-MeButane	3.9
3-MePentane	5.7
n-Octane	8.68
Ethene	8.52
Propene	26.3
2-MePropene	51.4
2-Me-2-Butene	86.9
Isoprene	101
Benzene	1.23
Toluene	5.96
m-Xylene	23.6
m-EtToluene	19.2
1,3,5-TriMeBenzene	57.5

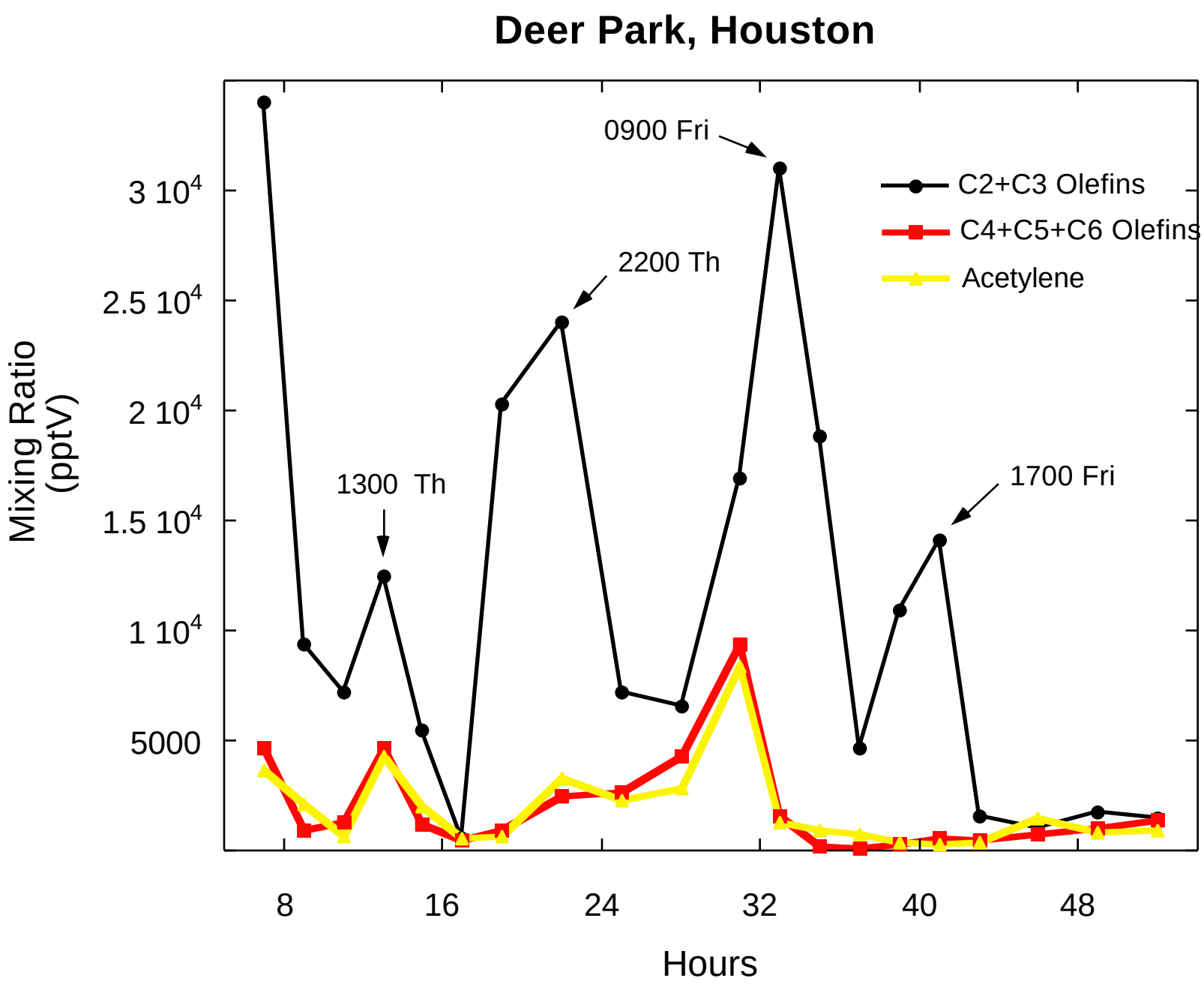

Mixing Ratio
(pptV)
5 10^4
4 10^4
3 10^4
2 10^4
1 10^4
0
Polk Building
Deer Park
Mexico City
Bank One
Nashville
Houston
Phoenix
x 0.10
NMOC
ppbC x 10
Saturates
Unsaturates
Aromatics

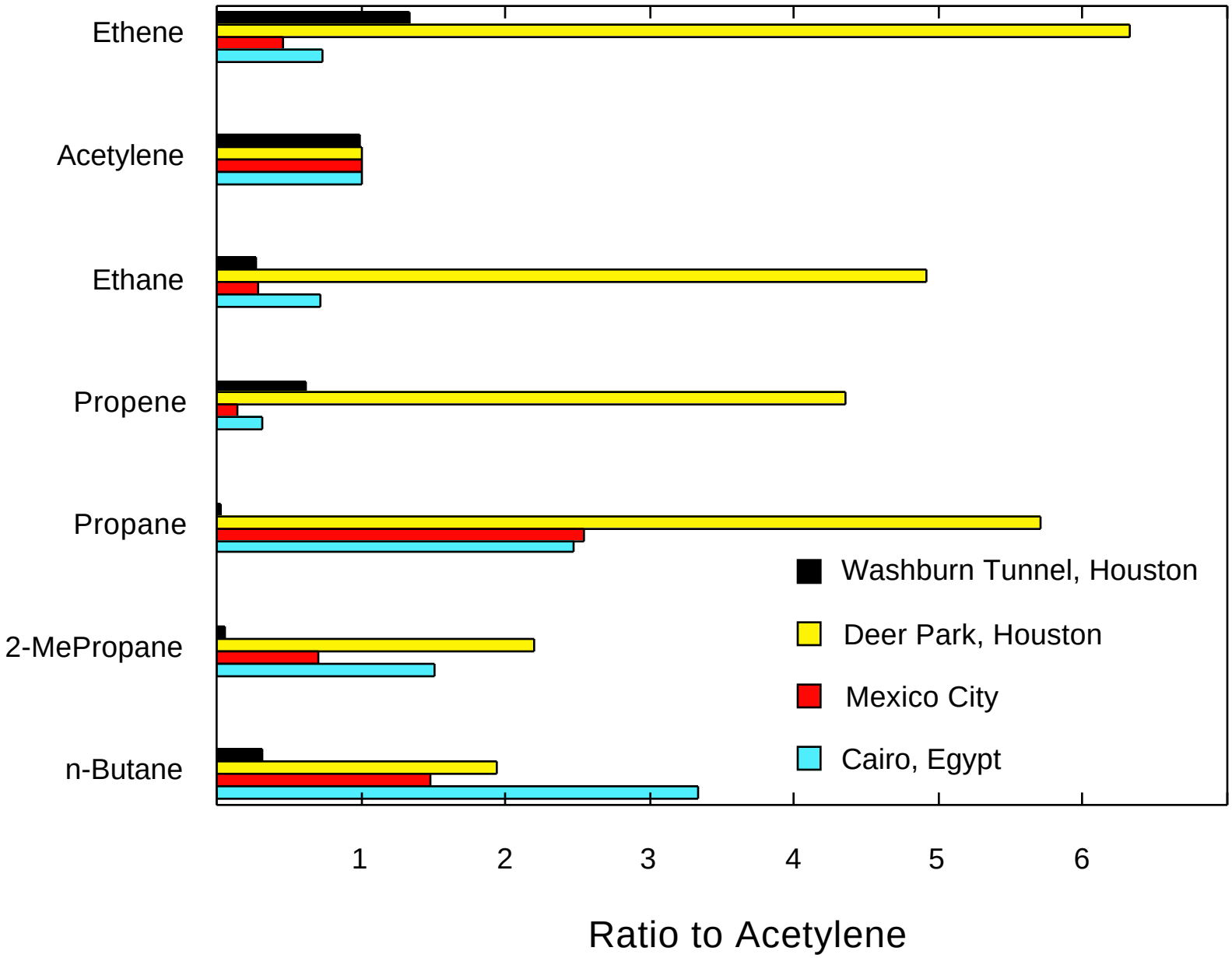

mol NMHC mol OH-1 sec-1
0
2
4
6
8
10
12
14
Polk Building
Deer Park
Mexico City
Bank One
Nashville
Houston
Phoenix
Saturates
Unsaturates
Aromatics
Toluene/Benzene

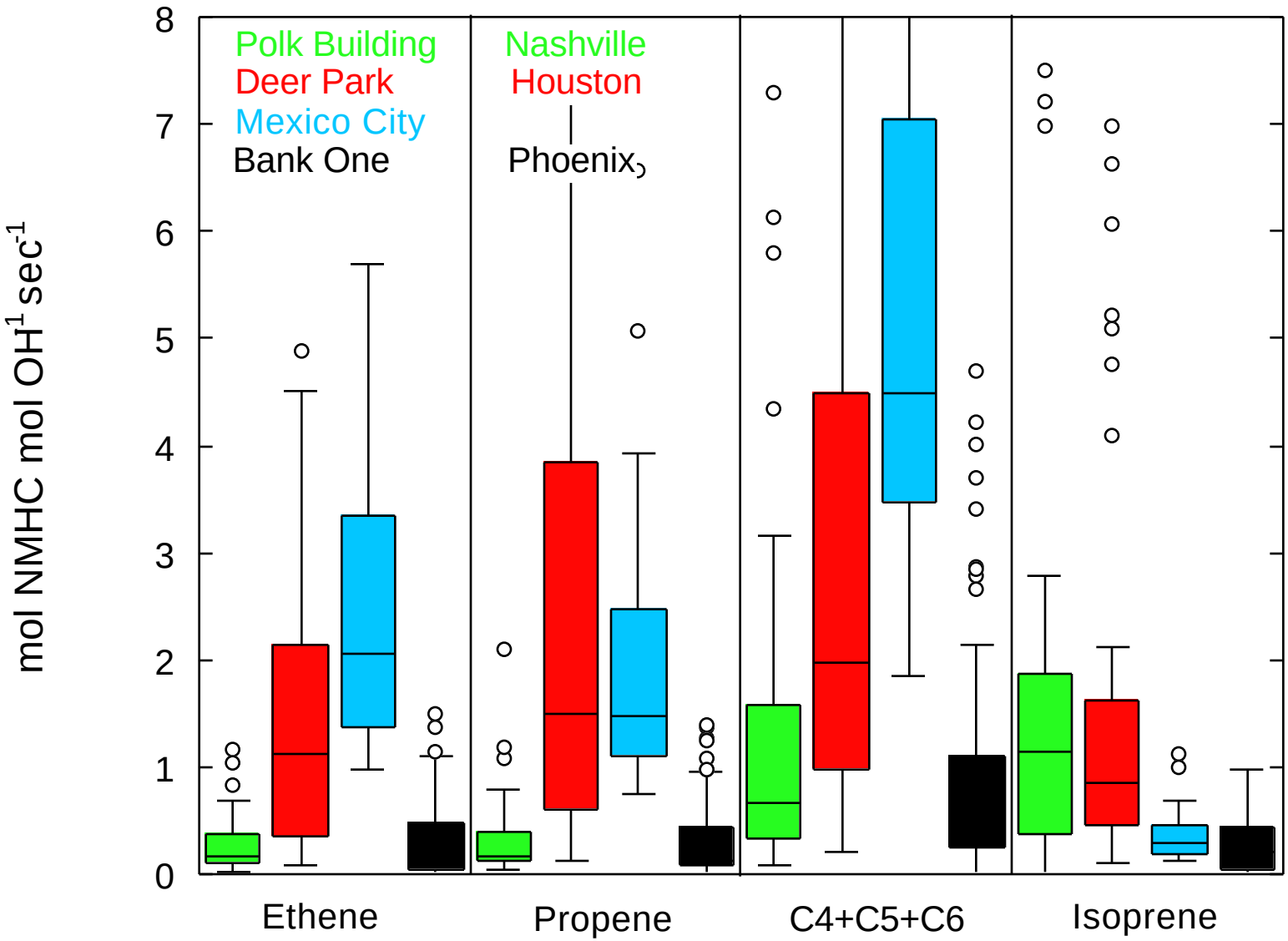

Bank One, Phoenix
0630 Th
0730 Fri
0800 Sat
C2+C3 Olefins
C4+C5+C6 Olefins
Acetylene
Mixing Ratio
(pptV)
8000
6000
4000
2000
10
20
30
40
50
60
70
Hours

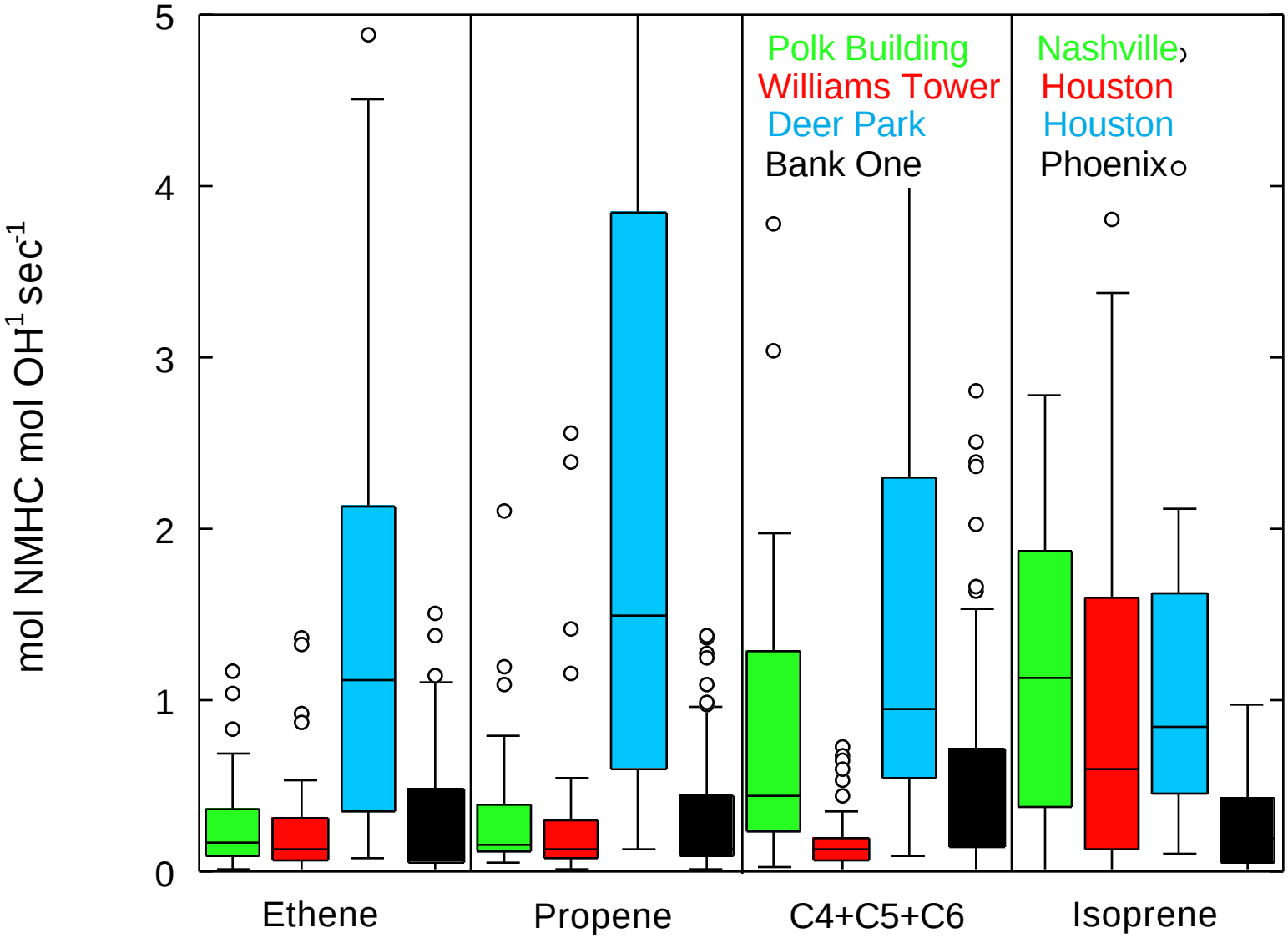

Polk Building, Nashville
0700 Tu
0700 Wed
0700 Th
0700 Fri
0700 Sat
C2+C3 Olefins
C4+C5+C6 Olefins
Acetylene
Mixing Ratio (pptV)
8000
6000
4000
2000
20
40
60
80
100
120
Hours

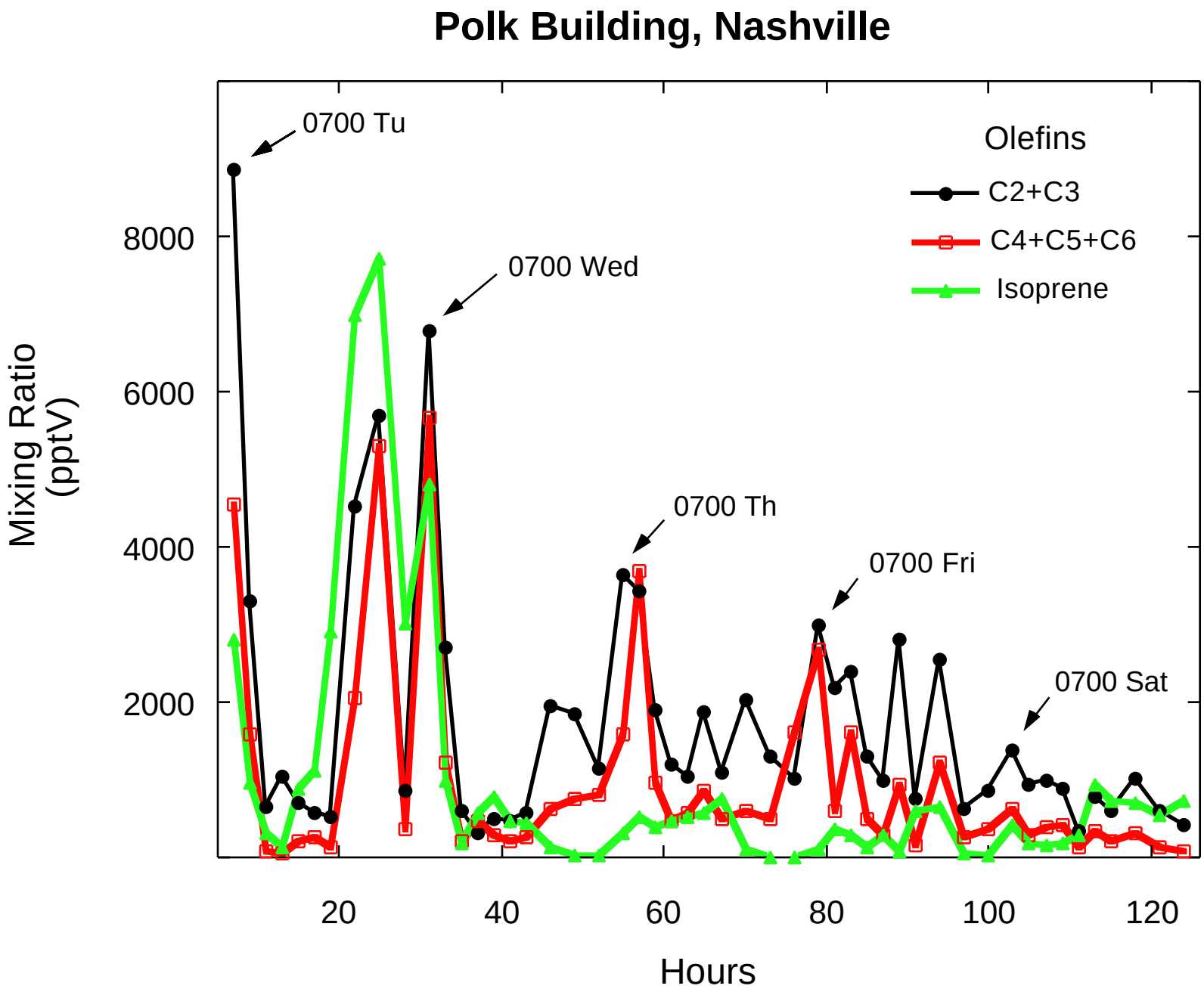

Mexico City
C2+C3 Olefins
C4+C5+C6 Olefins
Acetylene
Mixing Ratio
(pptV)
1 10^5
8 10^4
6 10^4
4 10^4
2 10^4
10
12
14
16
18
Hours

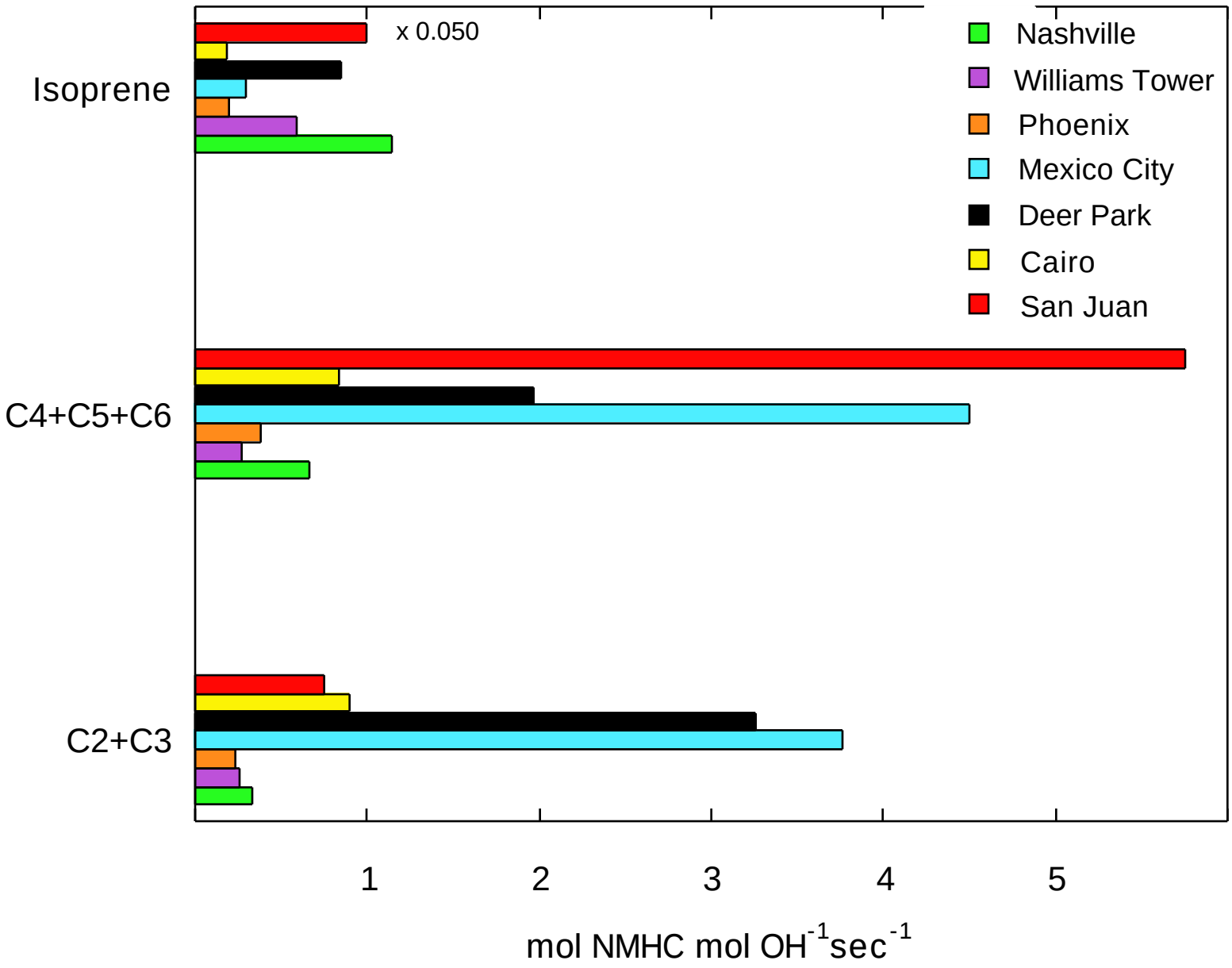

Deer Park, Houston
0900 Fri
2200 Th
1300 Th
1700 Fri
C2+C3 Olefins
C4+C5+C6 Olefins
Acetylene
Mixing Ratio (pptV)
3 10^4
2.5 10^4
2 10^4
1.5 10^4
1 10^4
5000
8
16
24
32
40
48
Hours


Ethene
Acetylene
Ethane
Propene
Propane
2-MePropane
n-Butane
Washburn Tunnel, Houston
Deer Park, Houston
Mexico City
Cairo, Egypt
1
2
3
4
5
6
Ratio to Acetylene


Polk Building
Deer Park
Mexico City
Bank One
Nashville
Houston
Phoenix
mol NMHC mol OH-1 sec-1
0
1
2
3
4
5
6
7
8
Ethene
Propene
C4+C5+C6
Isoprene


mol NMHC mol OH-1 sec-1
0
1
2
3
4
5
Ethene
Propene
C4+C5+C6
Isoprene
Polk Building
Williams Tower
Deer Park
Bank One
Nashville
Houston
Houston
Phoenix


Polk Building, Nashville
Olefins
C2+C3
C4+C5+C6
Isoprene
0700 Tu
0700 Wed
0700 Th
0700 Fri
0700 Sat
Mixing Ratio (pptV)
8000
6000
4000
2000
20
40
60
80
100
120
Hours


x 0.050
Isoprene
C4+C5+C6
C2+C3
Nashville
Williams Tower
Phoenix
Mexico City
Deer Park
Cairo
San Juan
1
2
3
4
5
mol NMHC mol OH-1sec-1

Conclusions

- NMHC distributions in downtown Nashville and Phoenix are characteristic of vehicle emissions.
- Isoprene can be transported from nearby rural areas into downtown Nashville and can attain ppbV levels in the nocturnal boundary layer.
- A 3-D model calculation using the ANL isoprene emission model and the CMAQ model was able to simulate this episode.
- NMHC distributions in Houston are dominated by C_2-C_4 hydrocarbons emitted by the many petrochemical industries in the metropolitan area.
- Sporadic emissions of C_2 and C_3 olefins from point sources in Houston can produce ambient levels of approximately 20 ppbV at nearby surface sites and may be responsible for the spatial and temporal variability in ozone levels in the metropolitan area.
- Isoprene transported from nearby rural areas into the Houston metropolitan area may also play a role in ozone production.

Conclusions

- NMHC distributions in Cairo and Mexico City are dominated by C_3 and C_4 hydrocarbons originating from the use of liquefied petroleum gas. However, reactive olefins contributed from mobile sources in both urban areas are the greatest source of potential reactivity.

- Mobile source emissions of reactive olefins in Mexico City produce a somewhat uniform distribution of ozone throughout the metropolitan area in contrast to Houston where sporadic emissions of C_2 and C_3 olefins from point sources may be responsible for greater spatial and temporal variability in ozone levels.

- Levels of reactive olefins in a sample collected in San Juan exceeded the concentrations observed in Mexico City and Houston. The isoprene concentrations were also high and may be a major source of potential reactivity.

Acknowledgments

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