Chemical process analysis for Houston photochemical grid modeling

Southeast Texas Photochemical Modeling Technical Committee Meeting

August 19, 2009

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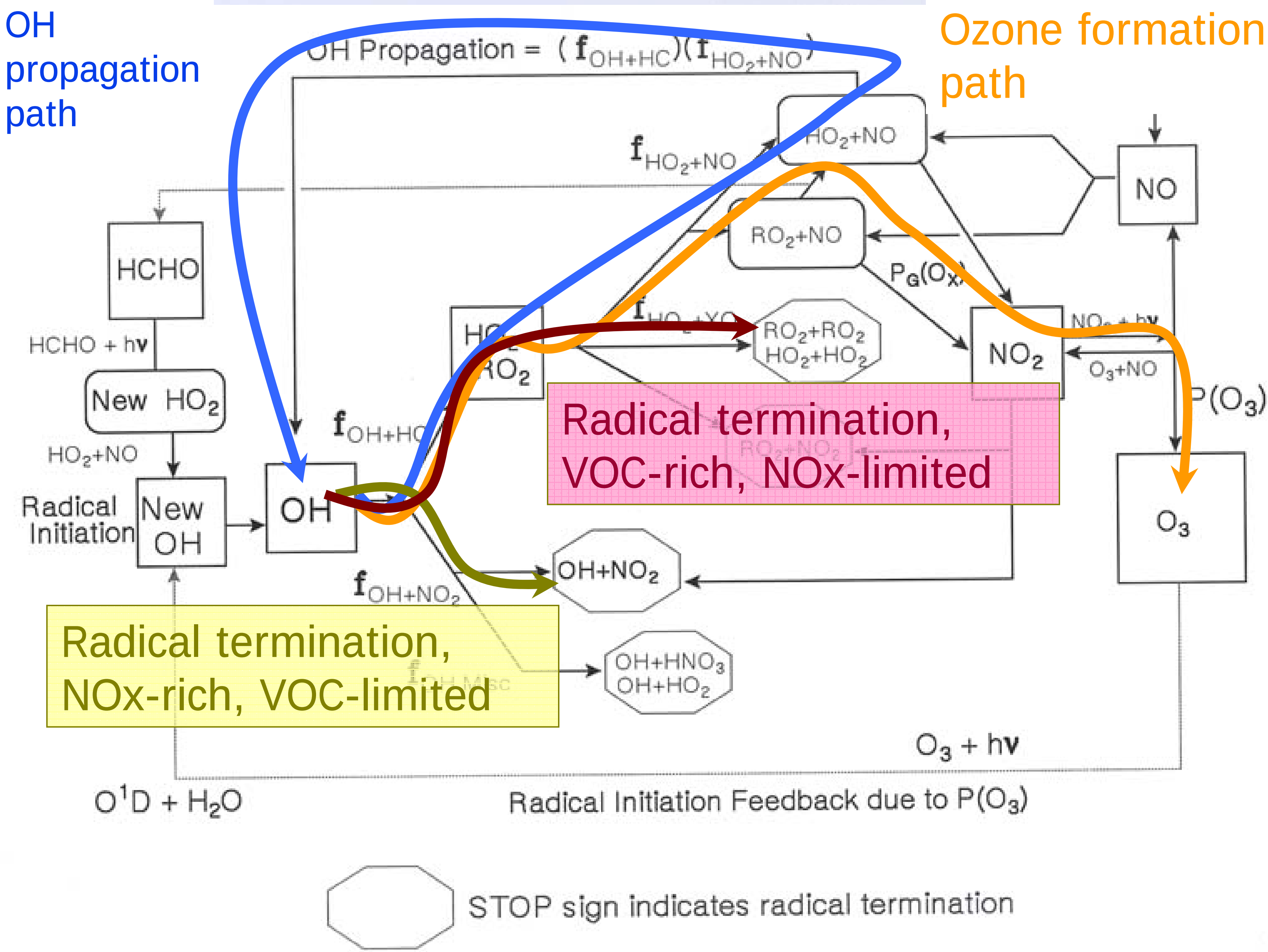
Air Modeling and Data Analysis Section
TCEQ

Chemical process analysis for Houston

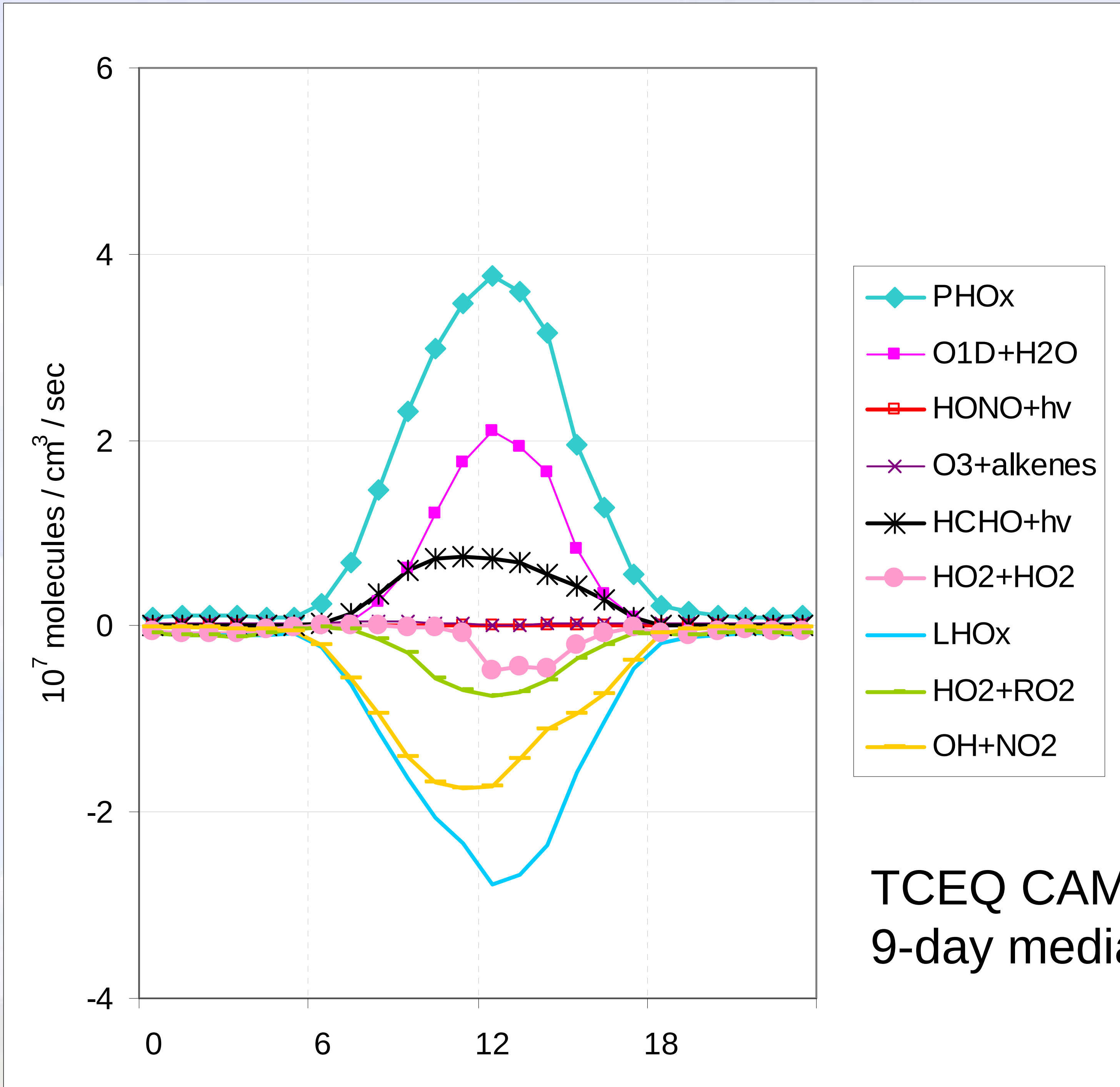
- Review of the chemistry of ozone formation
- Radical budgets: Measurements from TexAQS II, and TCEQ process analysis results
- Radical budgets: Testing different chemical mechanisms for the TexAQS II period
- Effect of industrial plumes on ozone production



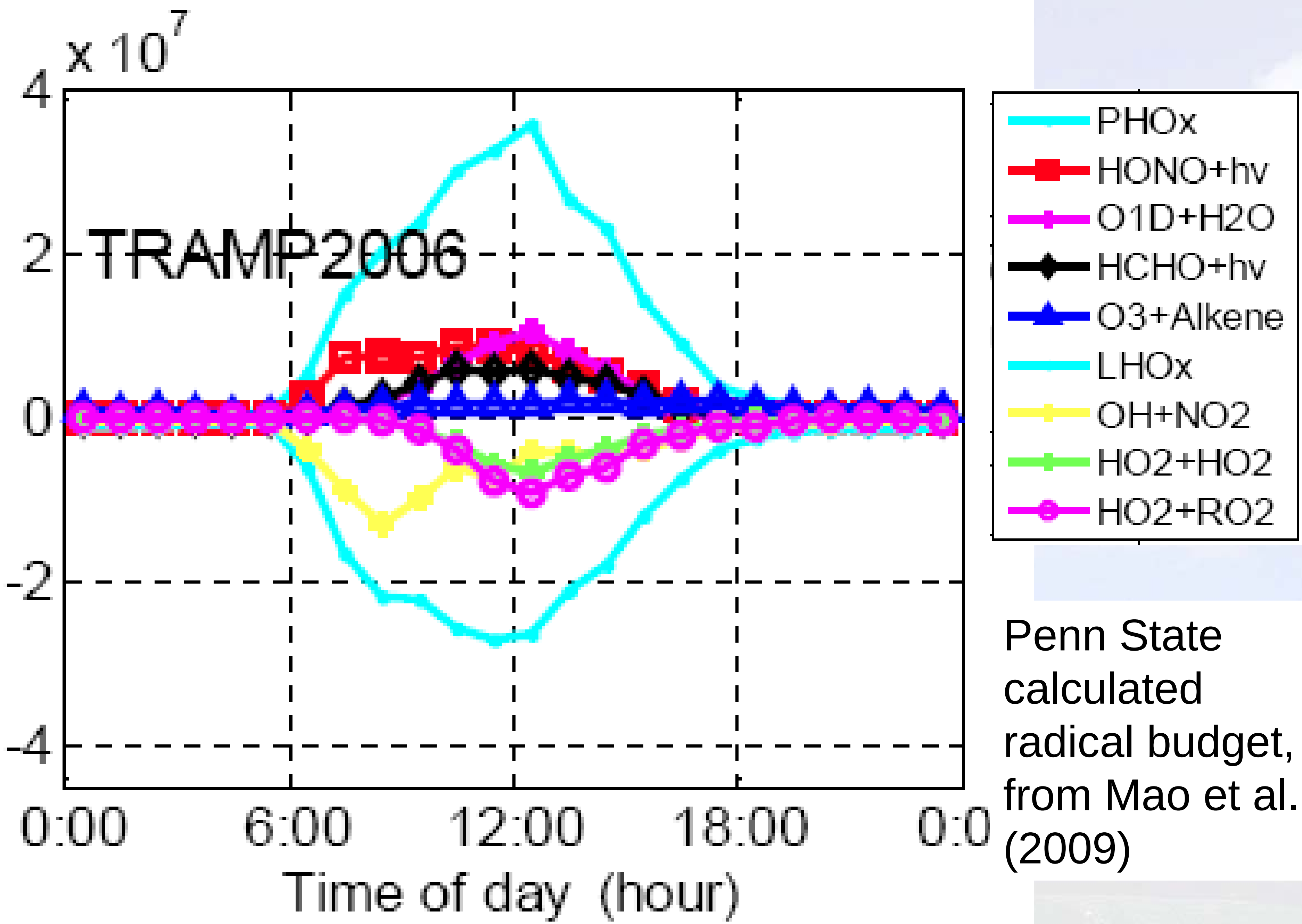
From Tonnesen, UC-Riverside

Mao et al. (2009) Radical budget study during TexAQS II

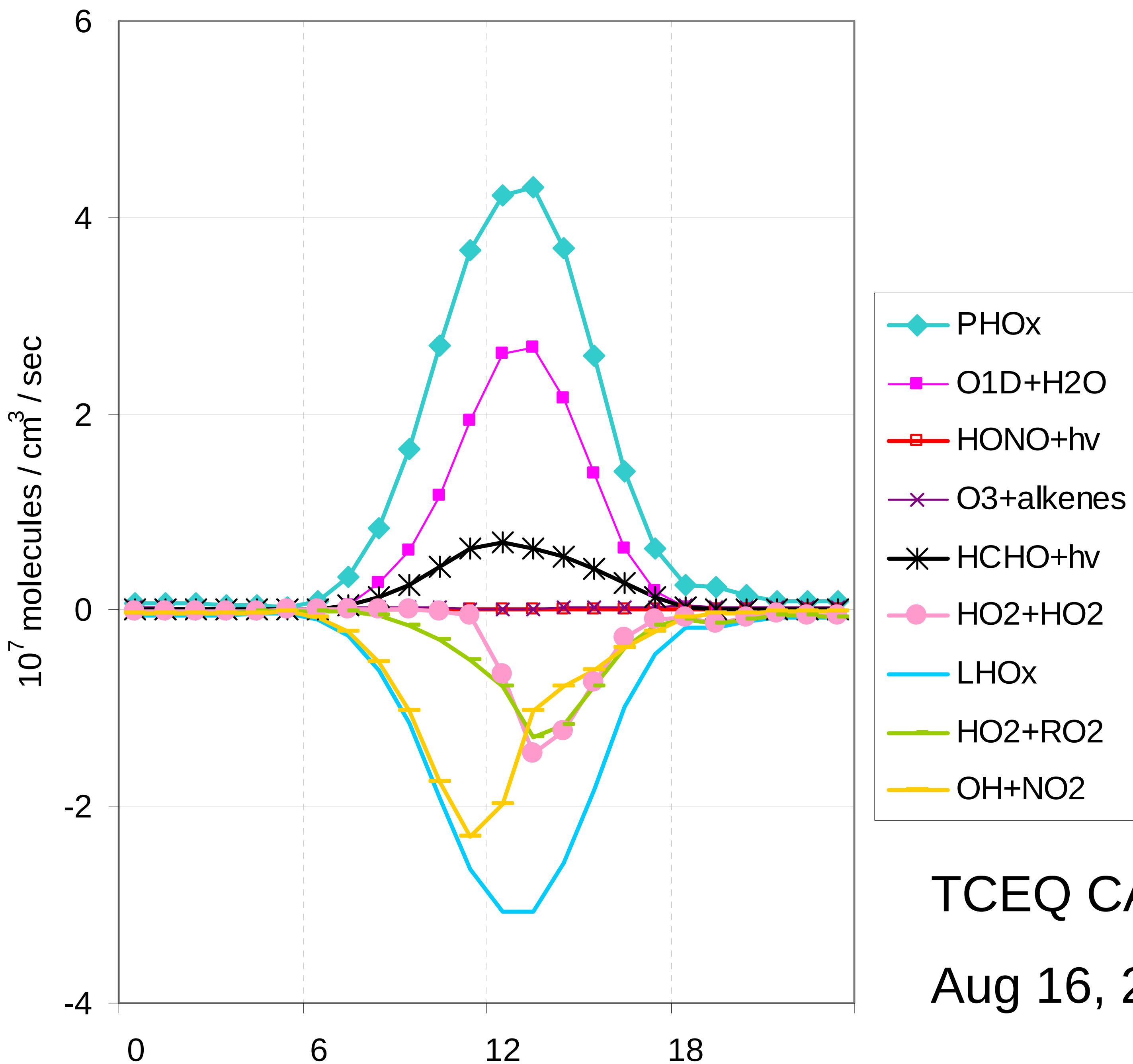
- Penn State researchers measured OH and HO2 radicals at the Moody Tower on the UH campus.
- Using their radical measurements, plus all other chemical measurements at Moody Tower and reaction rate constants from the literature, they calculated radical formation and loss rates.
- TCEQ used chemical process analysis to derive the same reaction rates from the CAMx modeling.



TCEQ CAMx
9-day median

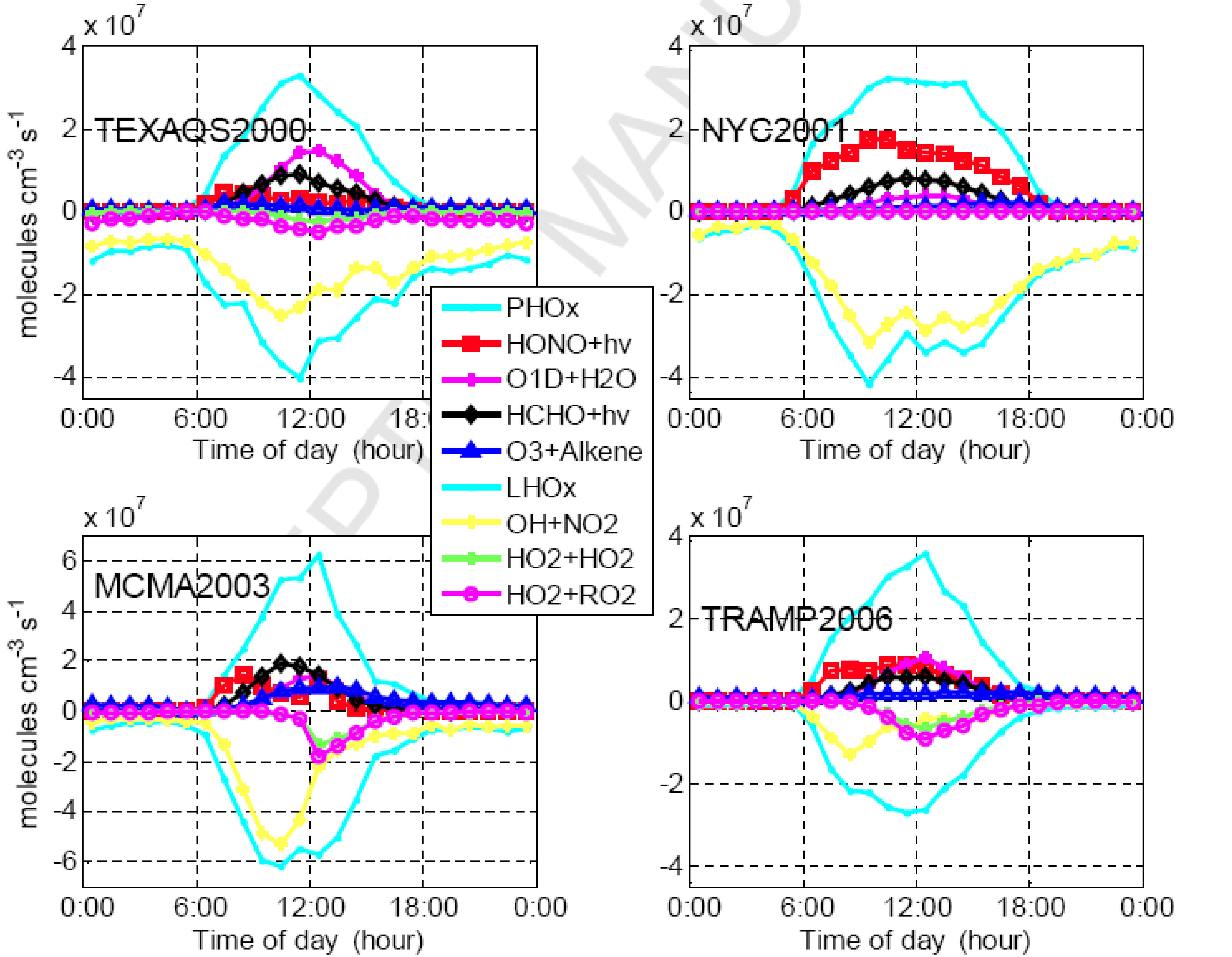


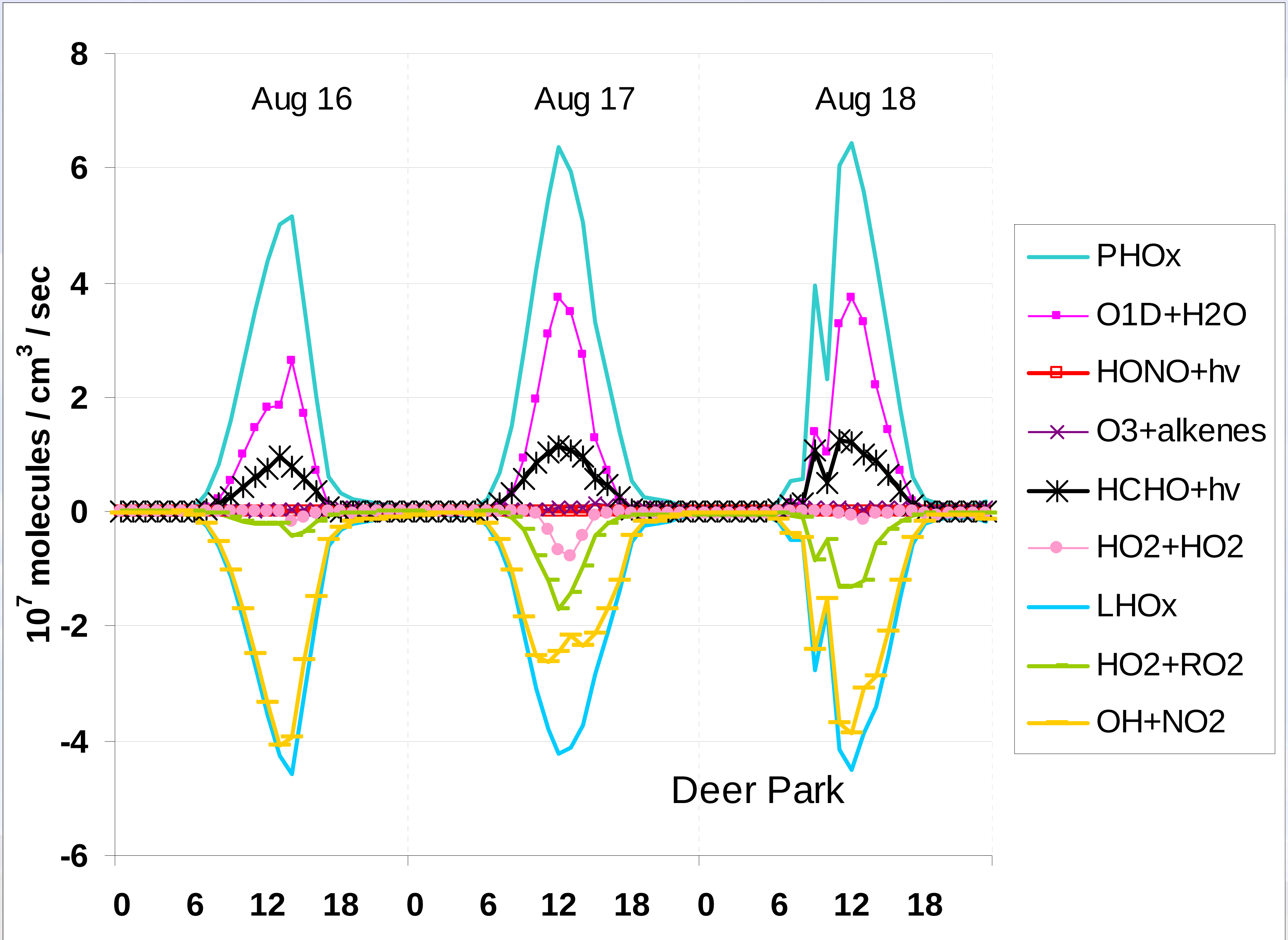
Penn State calculated radical budget, from Mao et al. (2009)

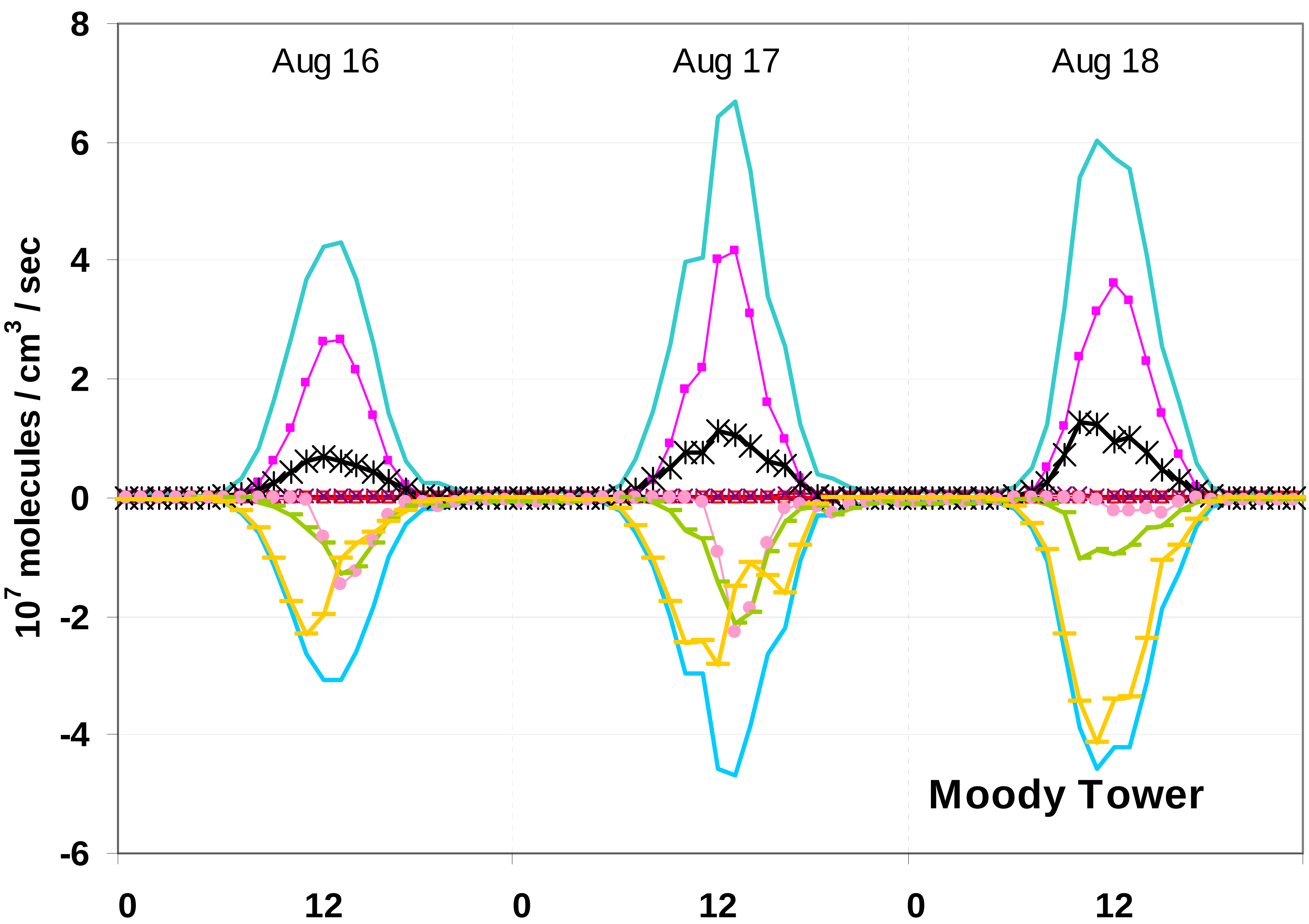


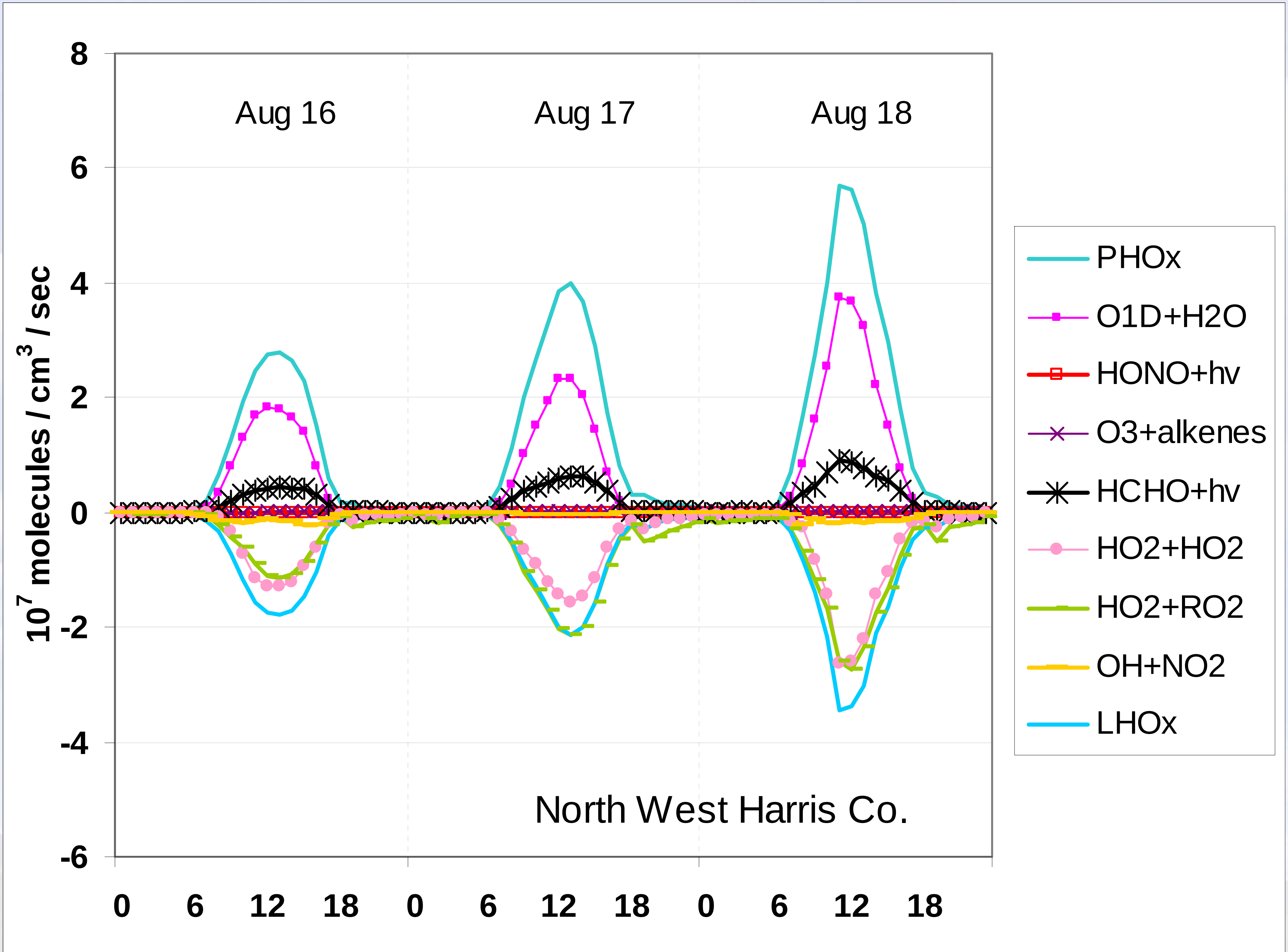
TCEQ CAMx

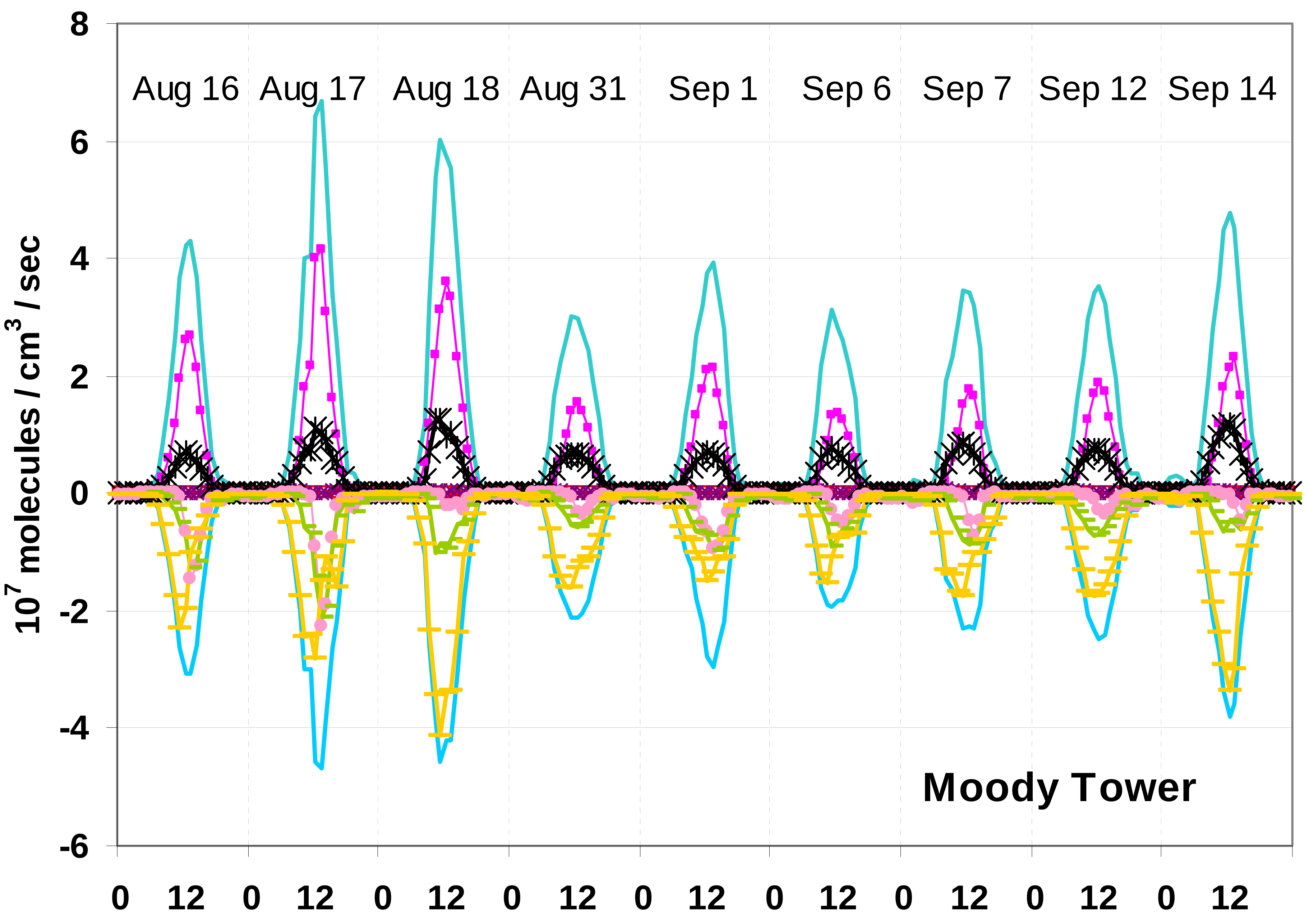
Aug 16, 2006

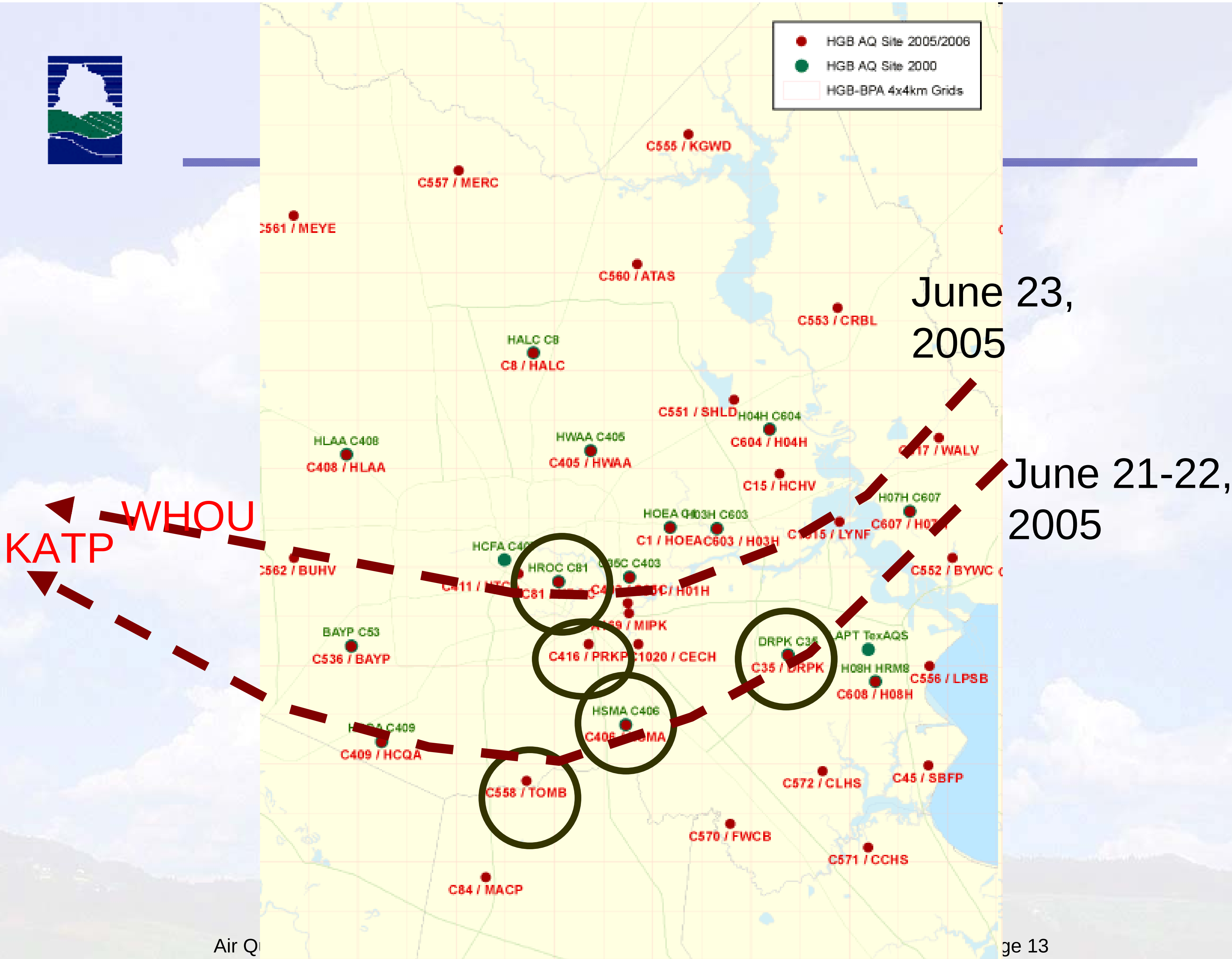

x 10^7
TEXAQS2000
NYC2001
MCMA2003
TRAMP2006
molecules cm^-3 s^-1
Time of day (hour)
0:00
6:00
12:00
18:00
PHOx
HONO+hv
O1D+H2O
HCHO+hv
O3+Alkene
LHOx
OH+NO2
HO2+HO2
HO2+RO2


Aug 16
Aug 17
Aug 18
Deer Park
10^7 molecules / cm^3 / sec
8
6
4
2
0
-2
-4
-6
0
6
12
18
0
6
12
18
0
6
12
18
PHOx
O1D+H2O
HONO+hv
O3+alkenes
HCHO+hv
HO2+HO2
LHOx
HO2+RO2
OH+NO2

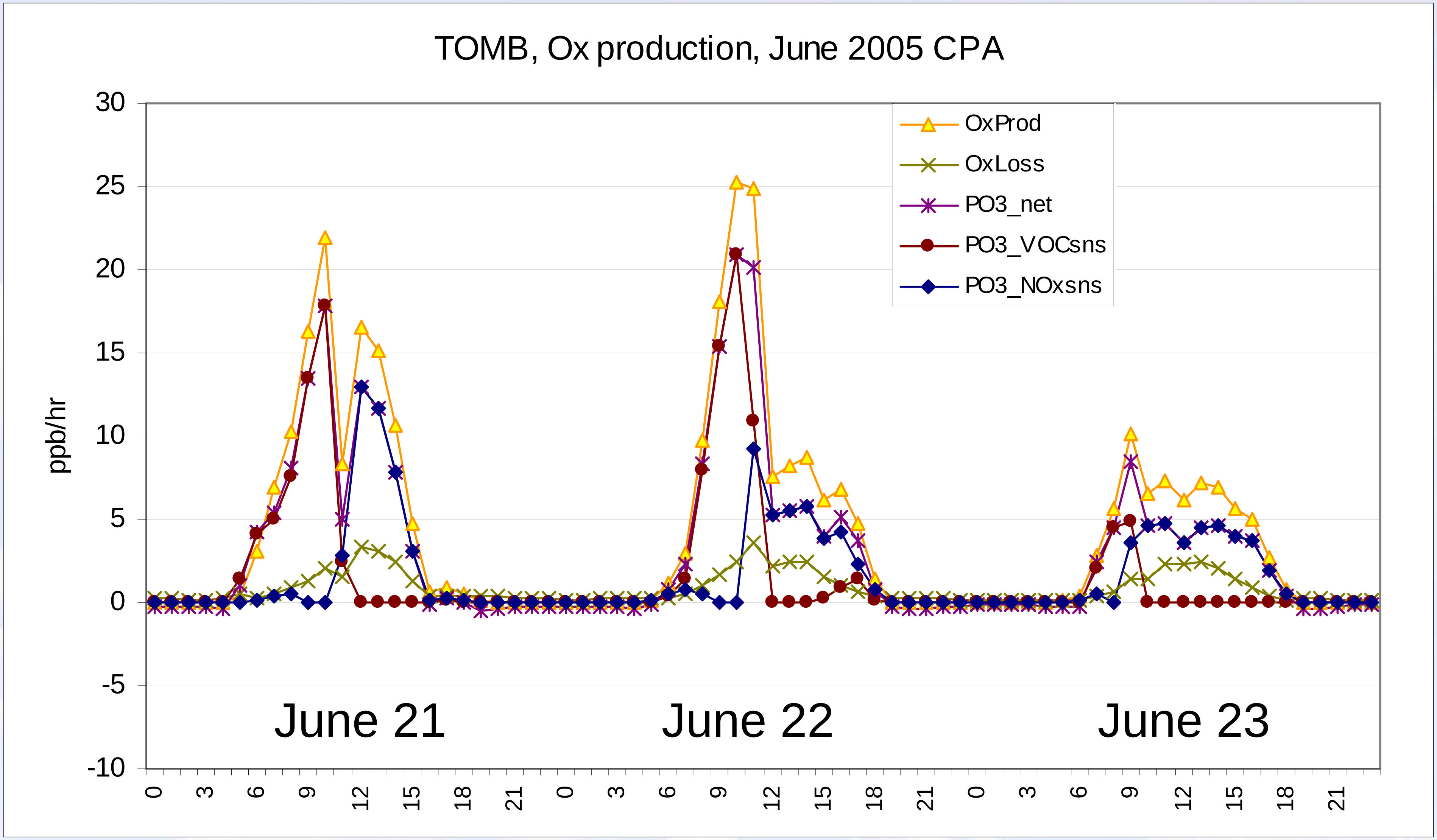

Aug 16
Aug 17
Aug 18
8
6
4
2
0
-2
-4
-6
10^7 molecules / cm^3 / sec
0
12
0
12
0
12
Moody Tower

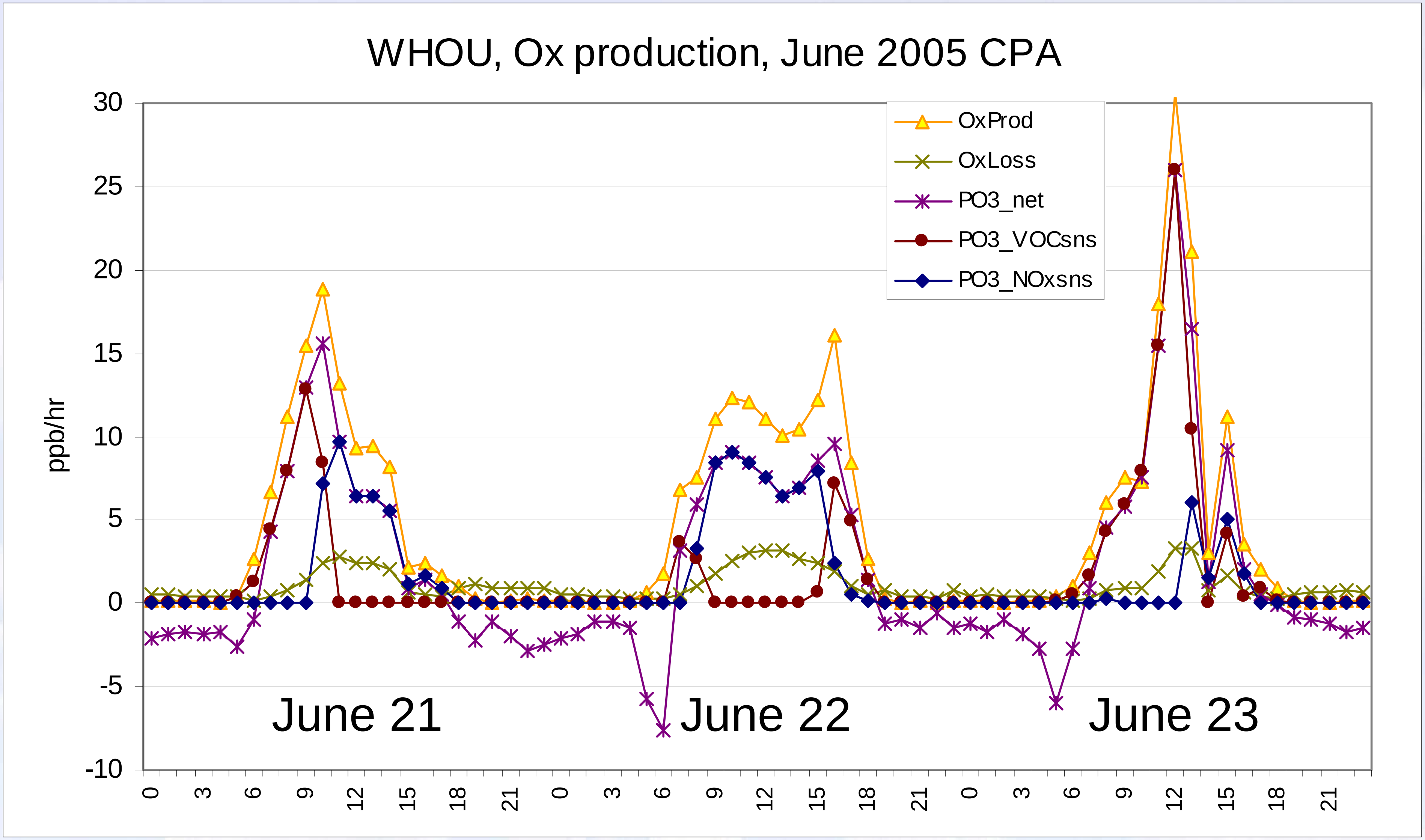

Aug 16
Aug 17
Aug 18
8
6
4
2
0
-2
-4
-6
10^7 molecules / cm^3 / sec
0
6
12
18
0
6
12
18
0
6
12
18
PHOx
O1D+H2O
HONO+hv
O3+alkenes
HCHO+hv
HO2+HO2
HO2+RO2
OH+NO2
LHOx
North West Harris Co.


8
6
4
2
0
-2
-4
-6
10^7 molecules / cm^3 / sec
Aug 16
Aug 17
Aug 18
Aug 31
Sep 1
Sep 6
Sep 7
Sep 12
Sep 14
Moody Tower
0
12
0
12
0
12
0
12
0
12
0
12
0
12
0
12
0
12



HGB AQ Site 2005/2006
HGB AQ Site 2000
HGB-BPA 4x4km Grids
C555 / KGWD
C557 / MERC
C561 / MEYE
C560 / ATAS
C553 / CRBL
HALC C8
C8 / HALC
C551 / SHLD
H04H C604
C604 / H04H
HLAA C408
C408 / HLAA
HWAA C405
C405 / HWAA
C15 / HCHV
H07H C607
C607 / H07H
HOEA C1
H03H C603
C1 / HOEA
C603 / H03H
HCFA C40
HROC C81
C562 / BUHV
C552 / BYWC
C416 / PRKP
C1020 / CECH
BAYP C53
C536 / BAYP
DRPK C35
C35 / DRPK
APT TexAQS
H08H HRM8
C608 / H08H
C556 / LPSB
HSMA C406
C409 / HCQA
C558 / TOMB
C572 / CLHS
C45 / SBFP
C570 / FWCB
C571 / CCHS
C84 / MACP
June 23, 2005
June 21-22, 2005
WHOU
KATP


TOMB, Ox production, June 2005 CPA
30
25
20
15
10
5
0
-5
-10
ppb/hr
OxProd
OxLoss
PO3_net
PO3_VOCsns
PO3_NOxsns
June 21
June 22
June 23
0
3
6
9
12
15
18
21


WHOU, Ox production, June 2005 CPA
ppb/hr
30
25
20
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10
5
0
-5
-10
OxProd
OxLoss
PO3_net
PO3_VOCsns
PO3_NOxsns
June 21
June 22
June 23
0
3
6
9
12
15
18
21

Chen et al. (2009): Box modeling with Moody Tower data

- Constrained photochemical steady-state box modeling, using Moody Tower observations as constraining variables
- Six different chemical mechanisms used: CB05, SAPRC99, SAPRC07, LaRC, RACM, Master Chemical Mechanism v.3.1

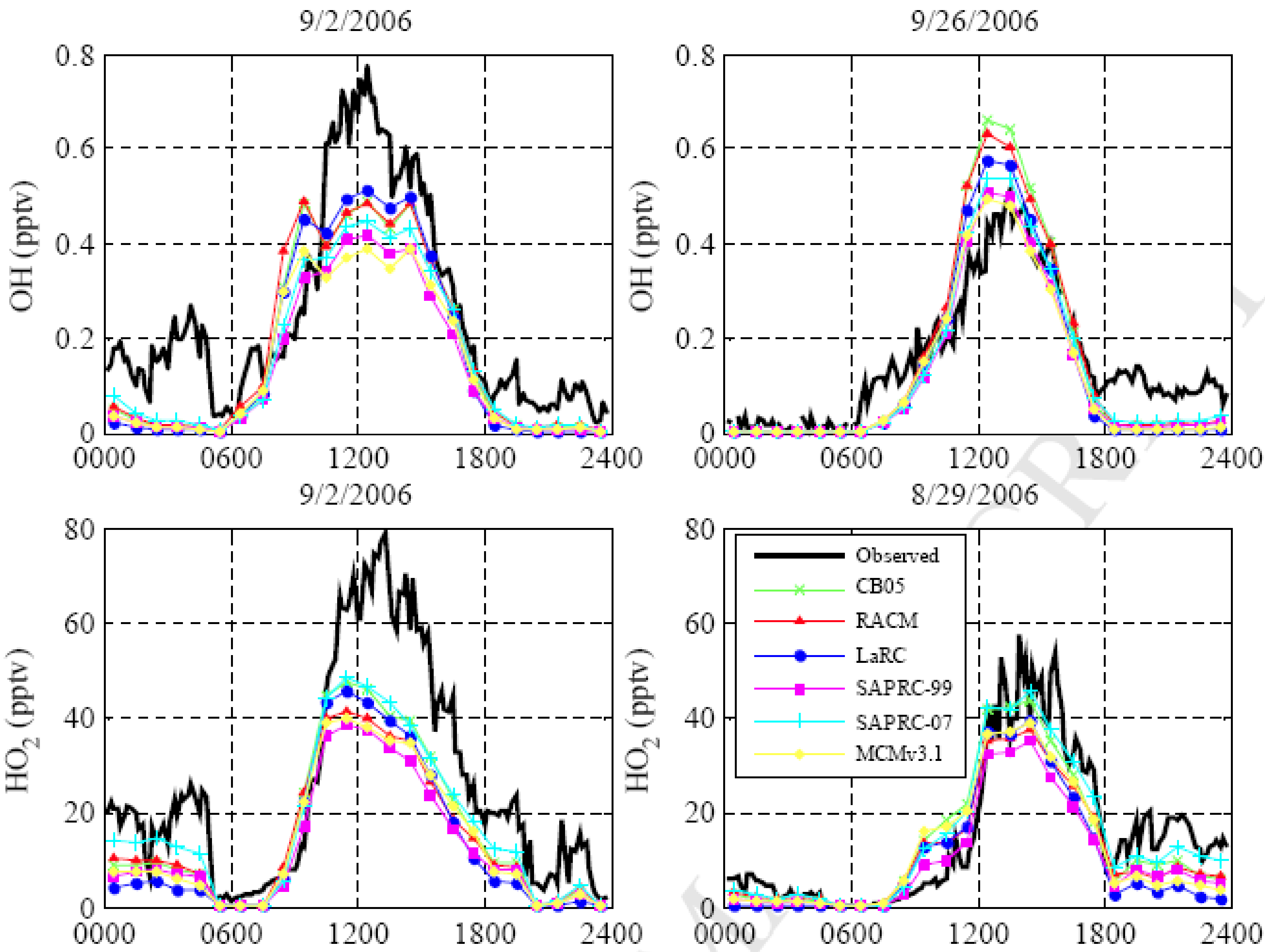
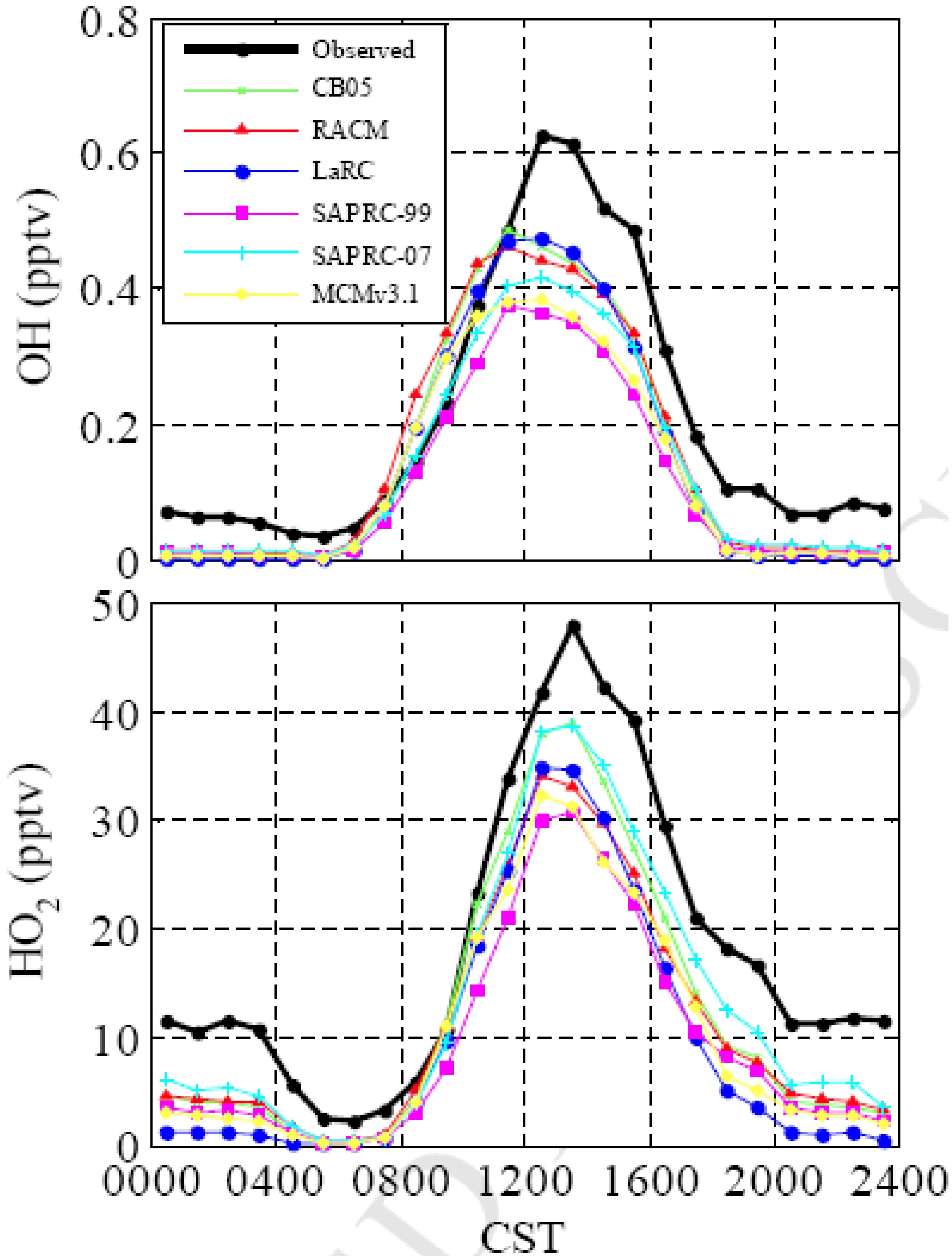


Fig. 1 Model-measurement comparison for OH (2 and 26 September) and HO_2 (29 August and 2 September). The OH mixing ratio of 0.6 pptv is equivalent to an OH concentration of about 1.4×10^7 cm^{-3}.

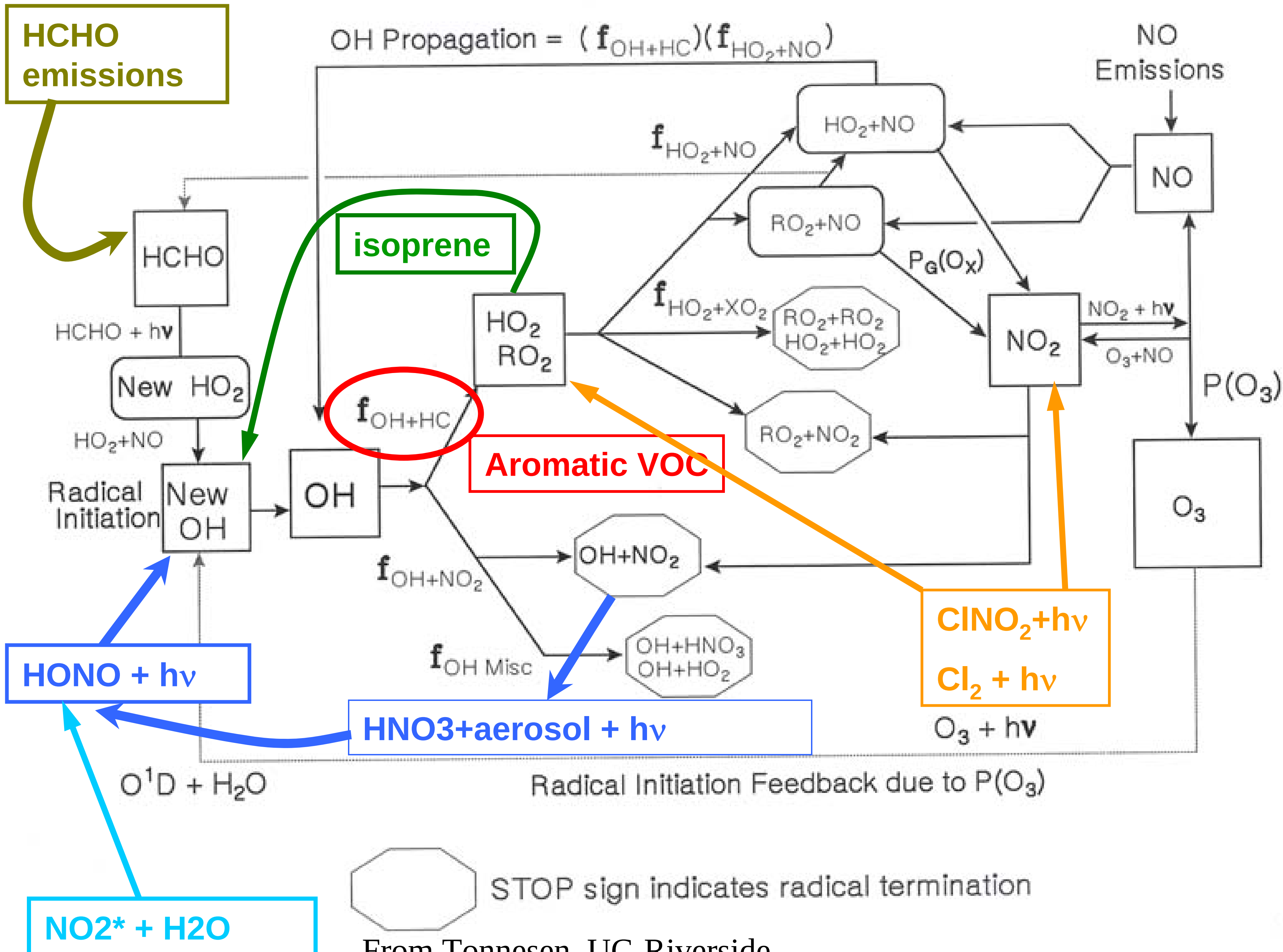
From Chen et al. (2009)



Median diurnal variation in OH and HO2 concentrations.

All mechanisms underestimate radical production.

From Chen et al. (2009).



From Tonnesen, UC-Riverside

Conclusions

- Both VOC-sensitive ozone formation and NOX-sensitive ozone formation occur in Houston every day, with VOC-sensitivity tending to occur in the morning and NOX-sensitivity in the afternoon. The radical data collected at the Moody Tower during TexAQS II indicate that **the ozone formation behavior modeled in CAMx is actually occurring in Houston.**
- VOC-sensitive conditions occur more often and more strongly in the industrial and urban core plumes.

Conclusions

- **The modeled shortfall in OH radical production is apparently common to more than one chemical mechanism, not just Carbon Bond 05.** The shortfall in radical production may be related to the underestimation in peak modeled eight-hour ozone concentrations.
- Hypotheses for the shortfall in radical formation include additional HONO production from photolysis of adsorbed HNO3 on aerosols (Ziemba et al., 2009), isoprene production of hydroxyl radical (OH) (Paulot et al., 2009; Lelieveld et al., 2008; North and Ghosh, 2009); formation and decomposition of electronically excited nitrogen dioxide (NO2*) (Li et al., 2008); nitryl chloride (ClNO2) chemistry (Osthoff et al., 2008; Simon et al., 2008); revised aromatic chemistry (Faraji et al., 2008; Hu et al., 2007); and molecular chlorine reactions (Chang et al., 2002; Tanaka et al., 2003; Chang and Allen, 2006; Sarwar and Bhave, 2007). **Total # hypotheses = 7**

Conclusions

- Due to the multitude of hypotheses for the radical production shortfall, TCEQ has not utilized any of the proposed corrections for radical production in this round of modeling. TCEQ is working with the developers of CB05 to add new isoprene and toluene chemistry to the mechanism.
- Radical production from photolysis of HONO is very low in the CAMx modeling, but not in the observations. The current chemical mechanisms do not have a path for producing the observed quantities of HONO during the daylight hours. The shortage of HONO could be one of the missing radical sources needed to improve the OH radical budget, but further studies are needed to describe the missing HONO formation pathway.