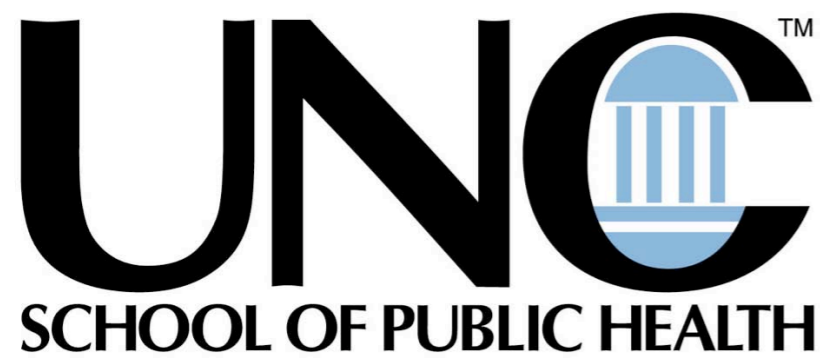


Analysis of
Modeling the TexAQS II
Intensive Period (H87UNC)

TERC SAC Feb 2007 Meeting

Harvey Jeffries and William Vizuetete, UNC-CH
February 21, 2008



Outline

- **The Problem:**
 - Understanding ozone formation in Houston, TX
- **Context:**
 - TCEQ CAMx Houston regulatory simulation for summer 2000 and UH CMAQ simulation for summer 2006
- **Methods:**
 - Comparison of PBLs, emissions, and magnitudes of physical and chemical processes of both models and radical source sensitivity runs
- **Results:**
 - Significant differences in vertical mixing and PBL evolution results in reduced NO_x concentrations in the 2006 episode
 - 2006 episode becomes NO_x limited whereas the 2000 episode was radical limited
 - 2006 episode ozone production is less sensitive to increases in radical sources
- **Conclusions:**
 - NO_x concentrations are the dominant influence on production of ozone
 - The reasons for ozone production have changed dramatically in 2006 and therefore will respond differently to control strategies

Source of Model Data

TCEQ CAMx Houston regulatory simulation

Met: uh1TCEQtke

EI: b1b.psito2n2

Episode: 8/18/2000 - 9/6/2000

UH CMAQ Houston simulation

Met: TMNS11n

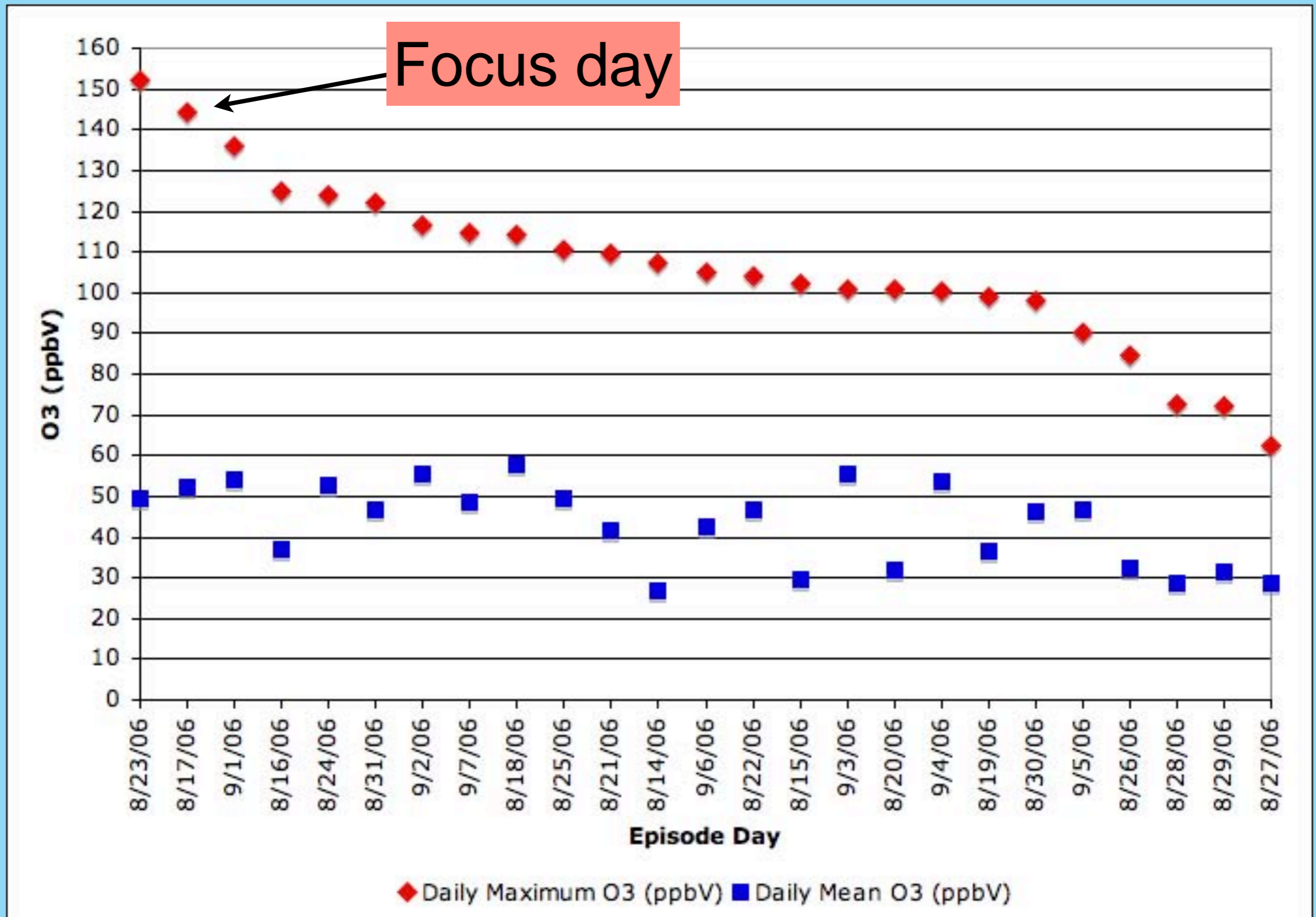
EI: F2A

Episode: 8/14/2006 - 9/7/2006

Received: 11/12/2007

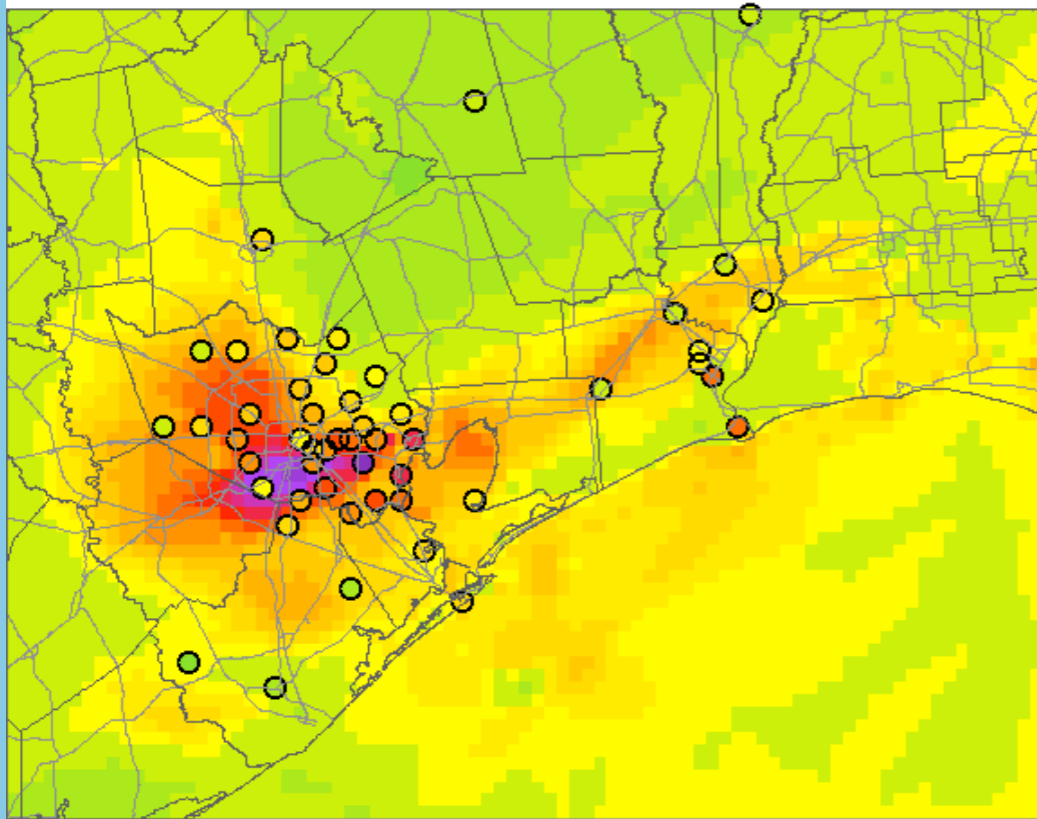
Component	AQF2 EI	BEMR 2006 EI
Texas Area area and nonroad	TEI 2000 TEI b5b-2000	b5b-2000 to 2007
Ex-Texas Area	NEI99	NEI2002
Mobile	M6 2000&2007 to 2003	M6 2000&2007 to 2005
Point Srcs	TEI 2000 to 2005	TPSI 2006 (AG&UH)
Imputed VOCs	TEI 2000	not used
Biogenic	TCEQ veg+MCIP Temp	TCEQ new GloBEIS

2006 Episode Modeled Max

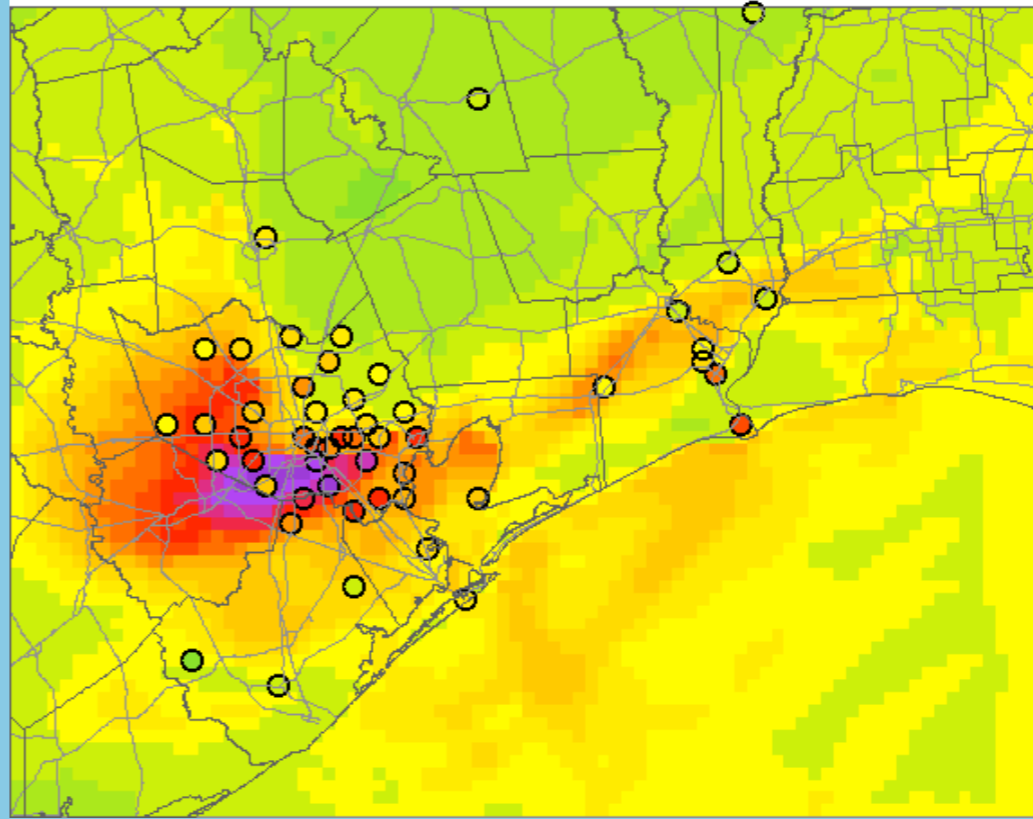


August 17, 2006

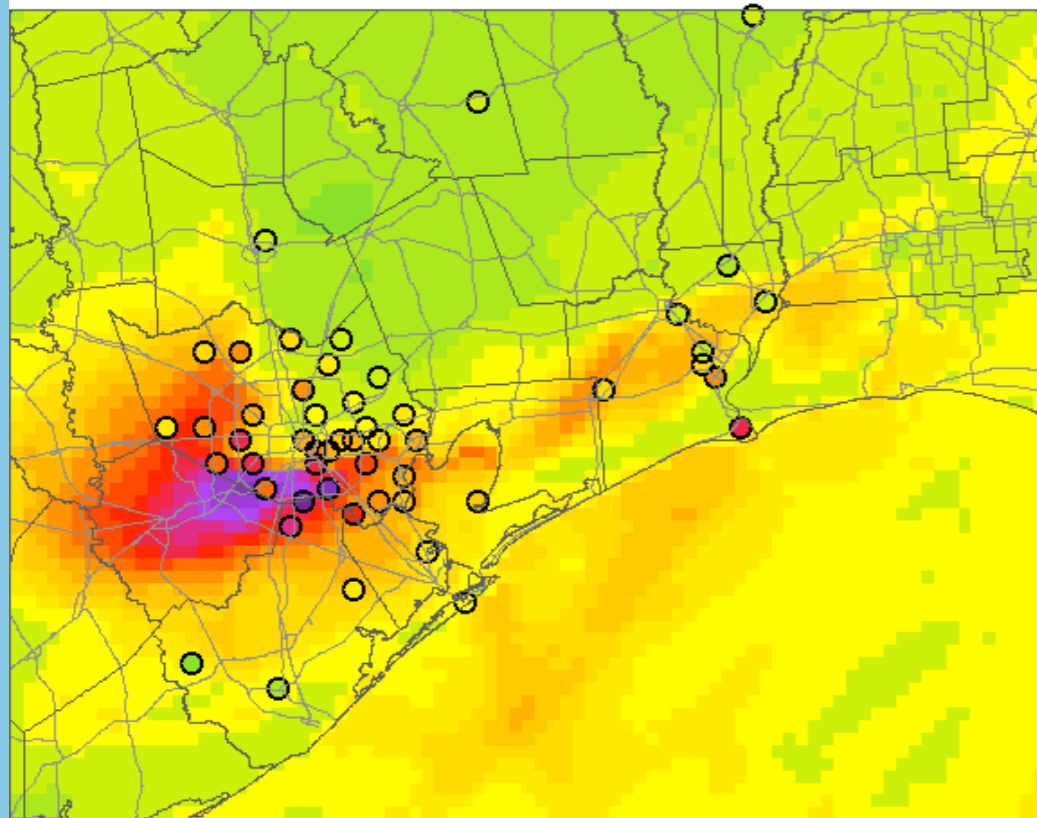
Ozone Conc. at 20060817:13cst [TMNS11n2]



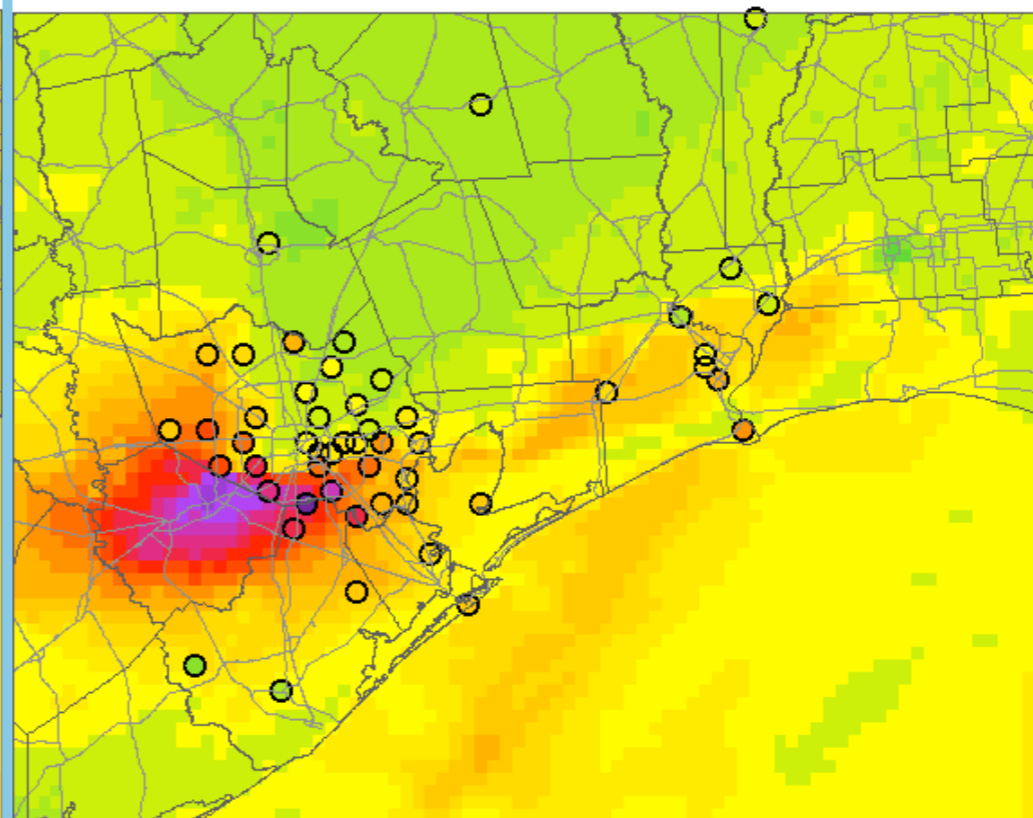
Ozone Conc. at 20060817:14cst [TMNS11n2]



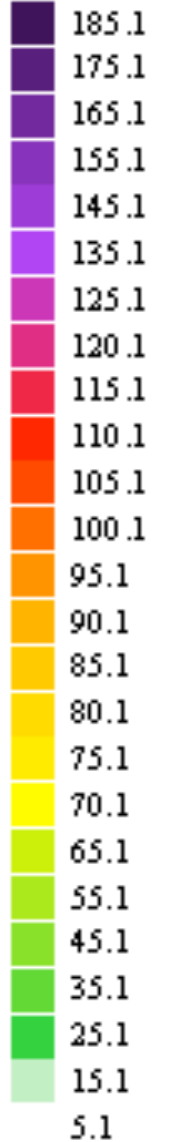
Ozone Conc. at 20060817:15cst [TMNS11n2]



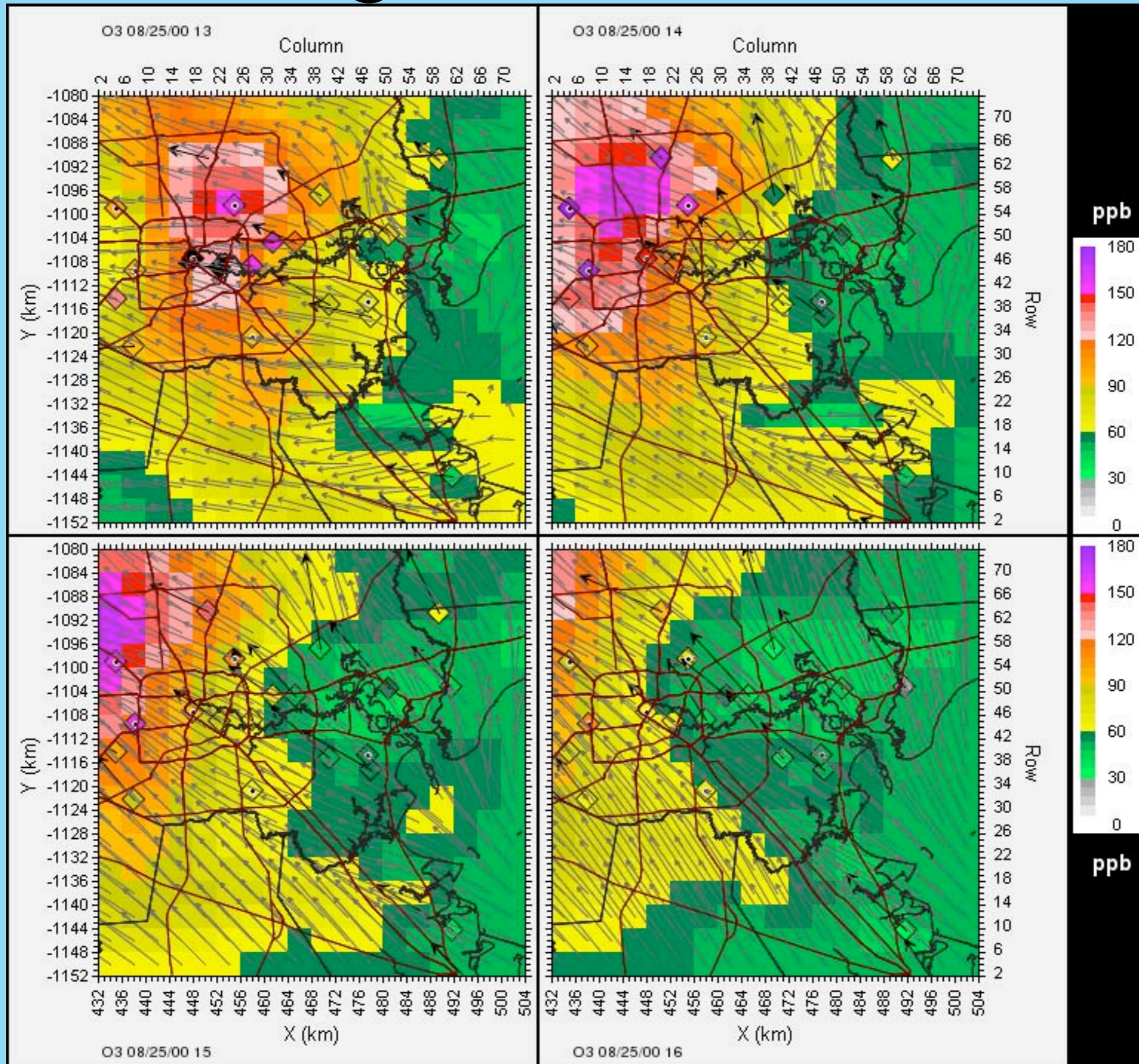
Ozone Conc. at 20060817:16cst [TMNS11n2]



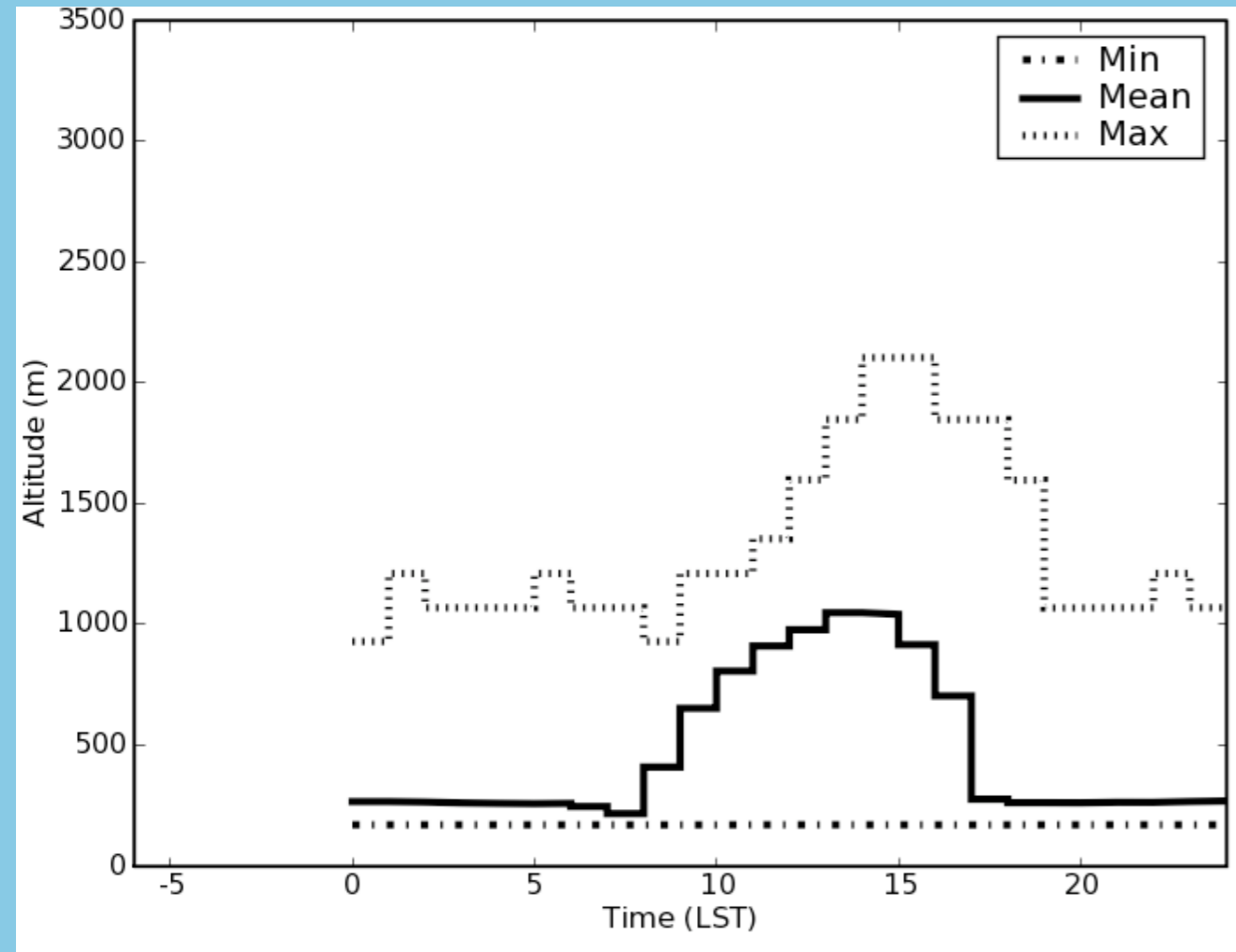
(ppb)



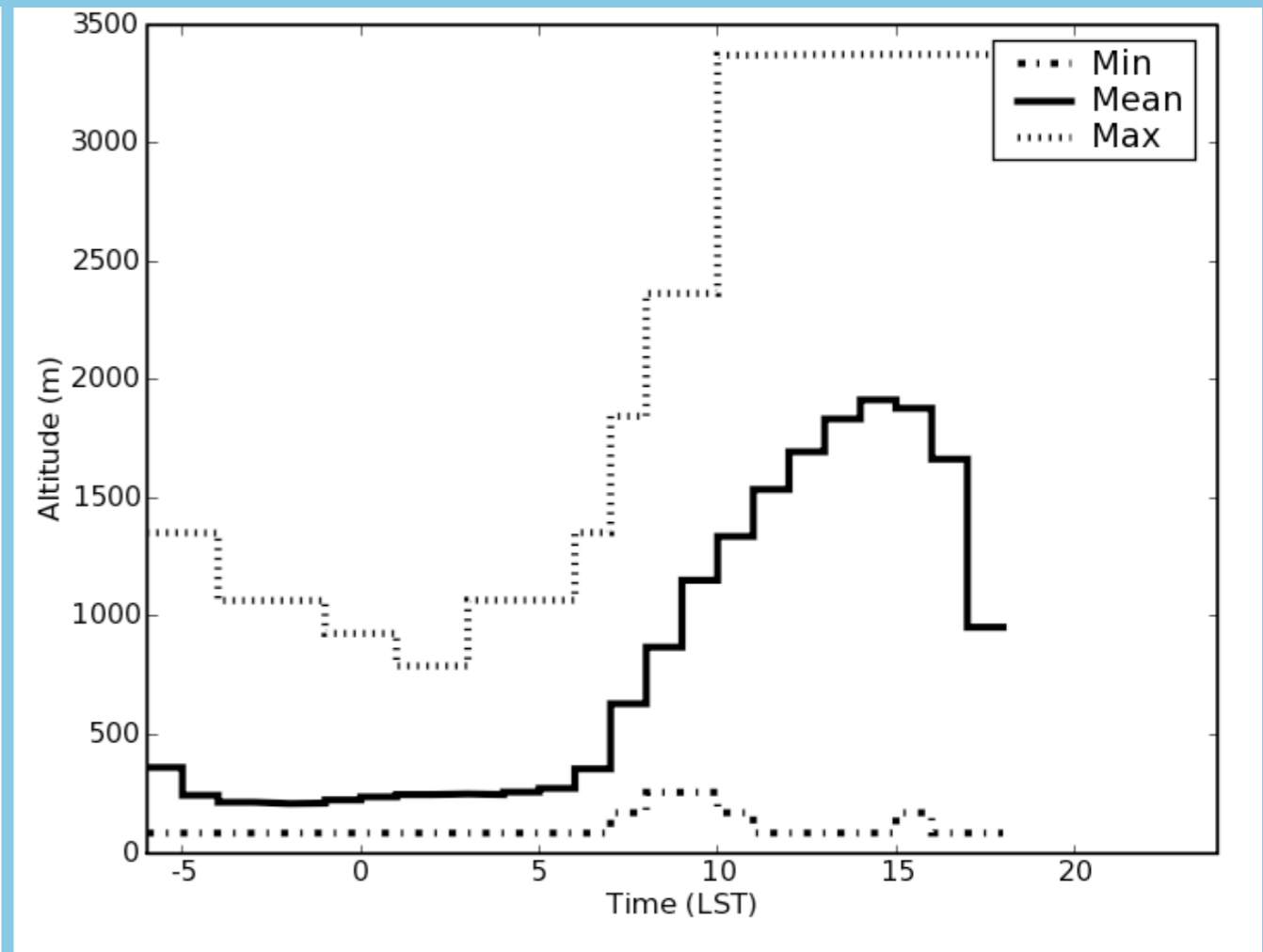
August 25, 2000



Domain-wide PBL



8/25/2000 CAMx

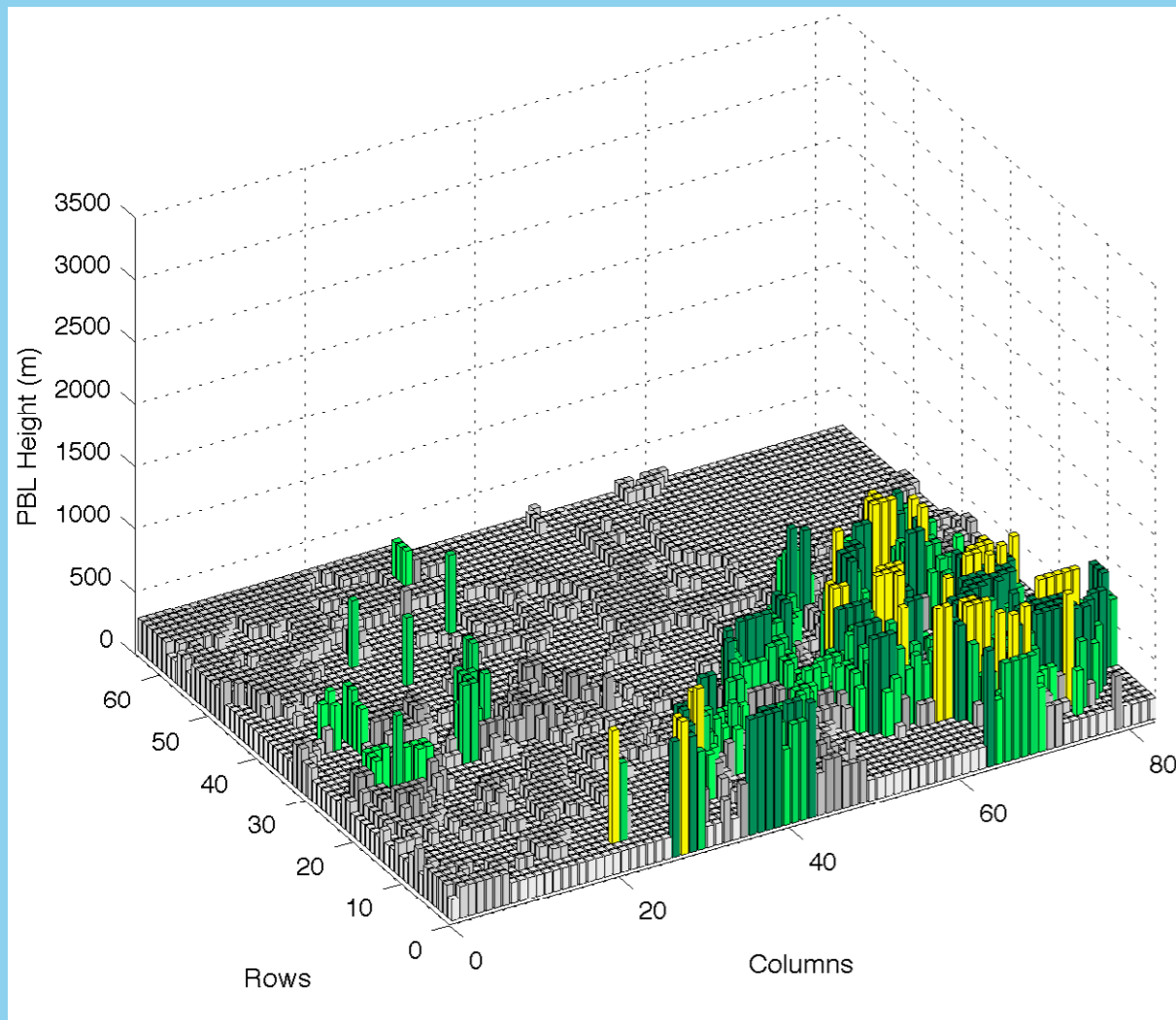


8/17/2006 CMAQ

- 4-km Domain-wide Max, Min, and Mean PBL
- 2006 episode higher peaks and faster rise

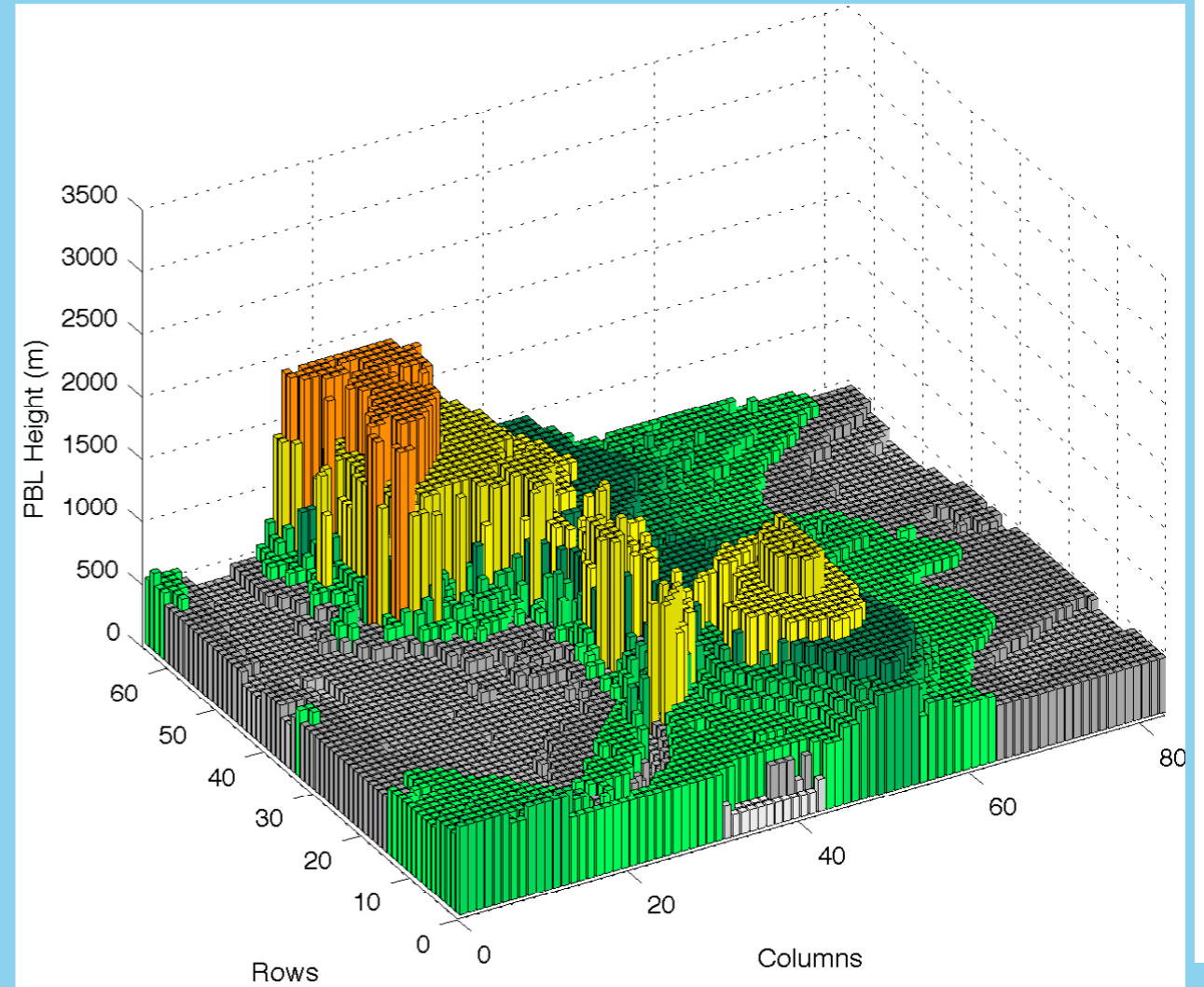
Domain-Wide PBL Heights

8/25/2000 CAMx



Hour 0800 LST

8/17/2006 CMAQ

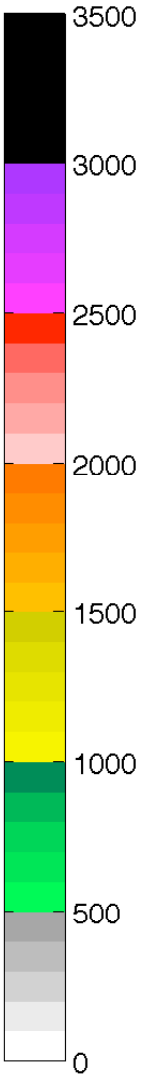
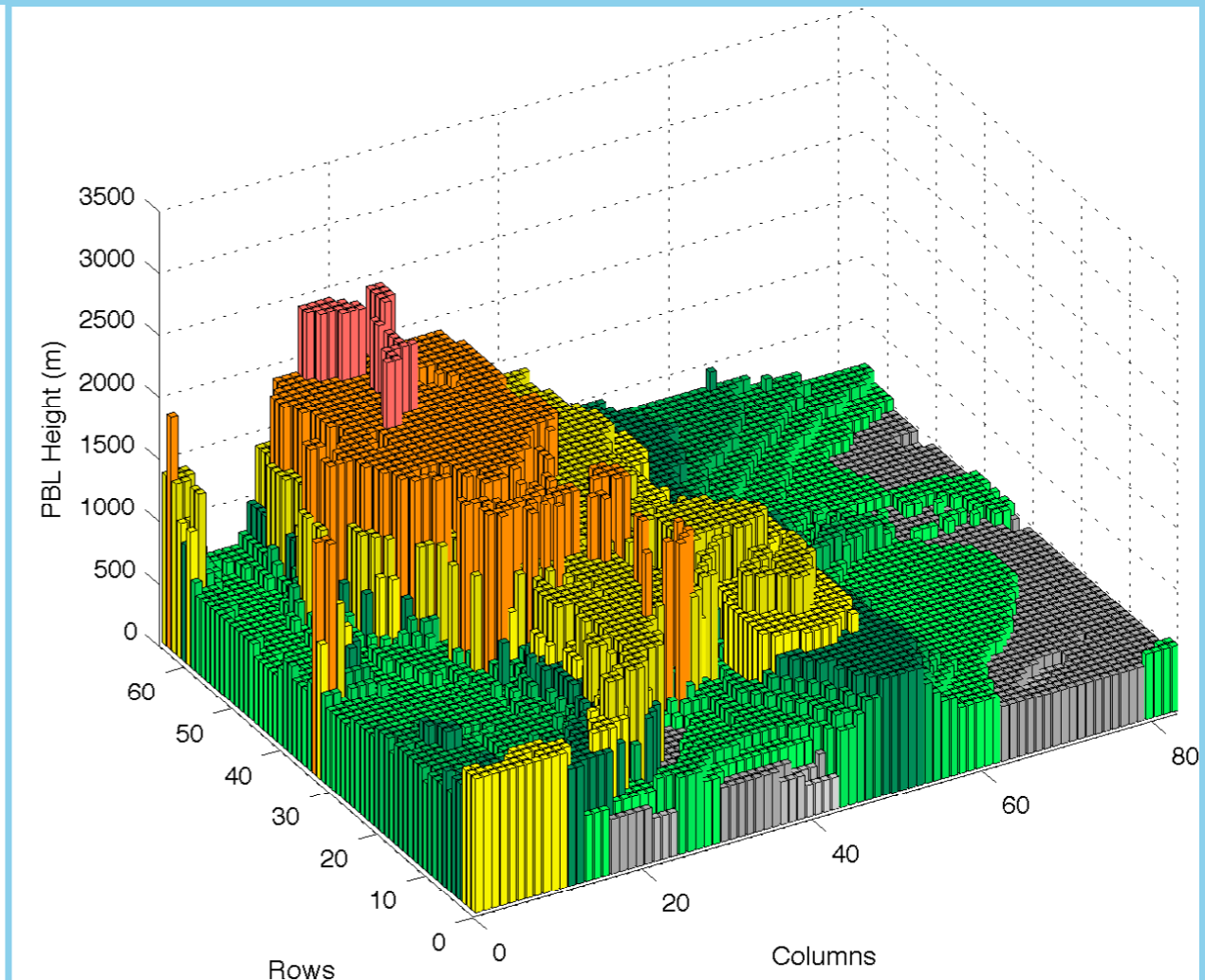
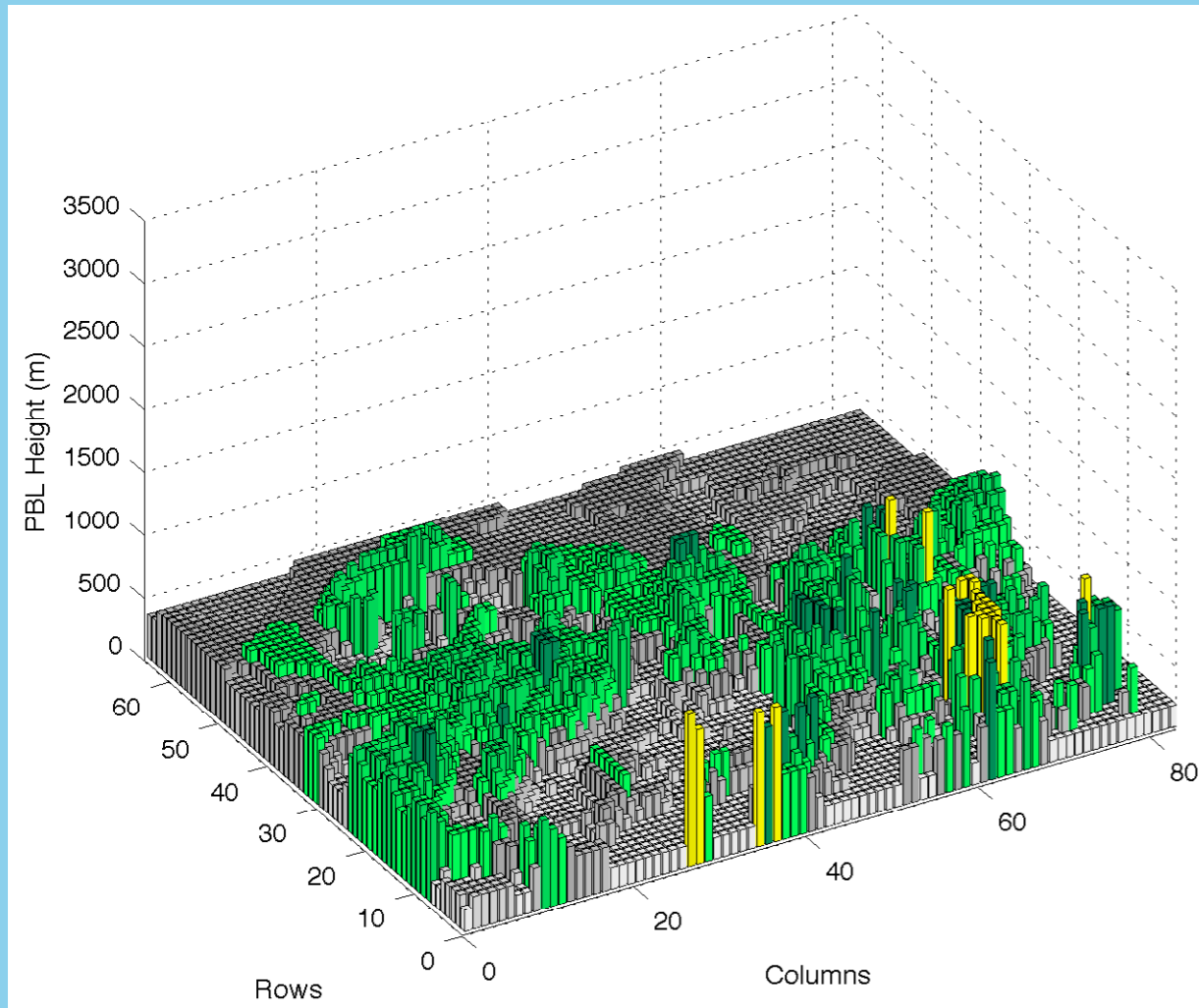


Hour 0800 LST

Domain-Wide PBL Heights

8/25/2000 CAMx

8/17/2006 CMAQ

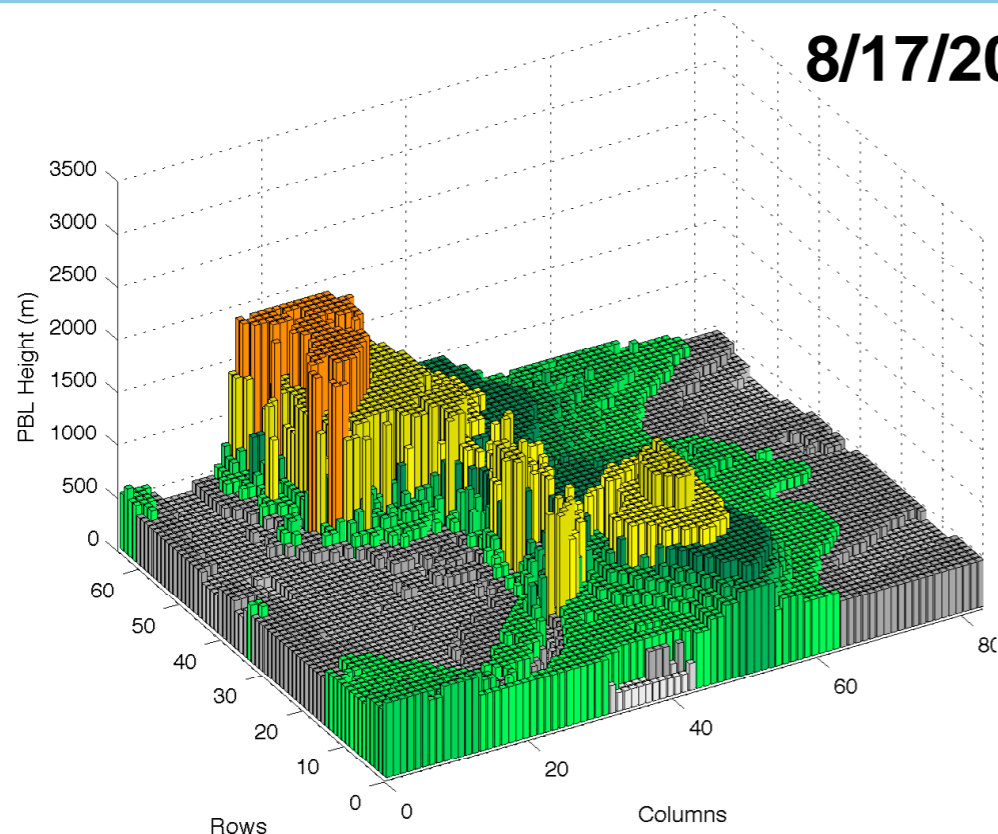


Hour 0900 LST

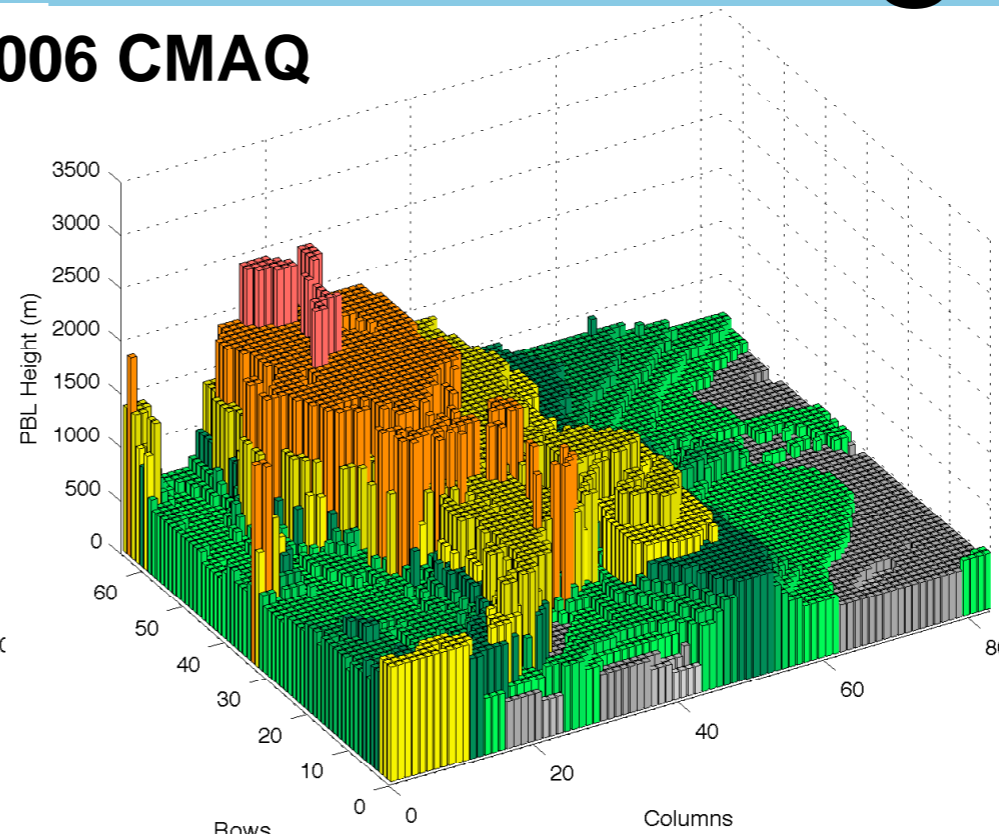
Hour 0900 LST

Domain-Wide PBL Heights

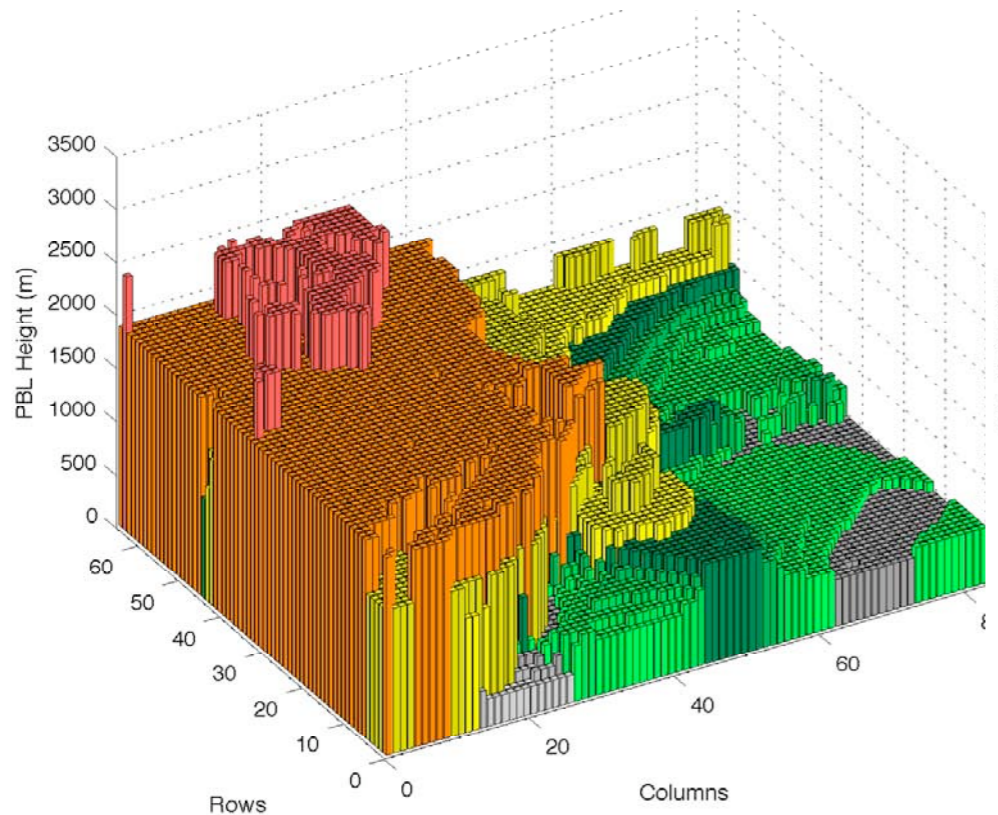
8/17/2006 CMAQ



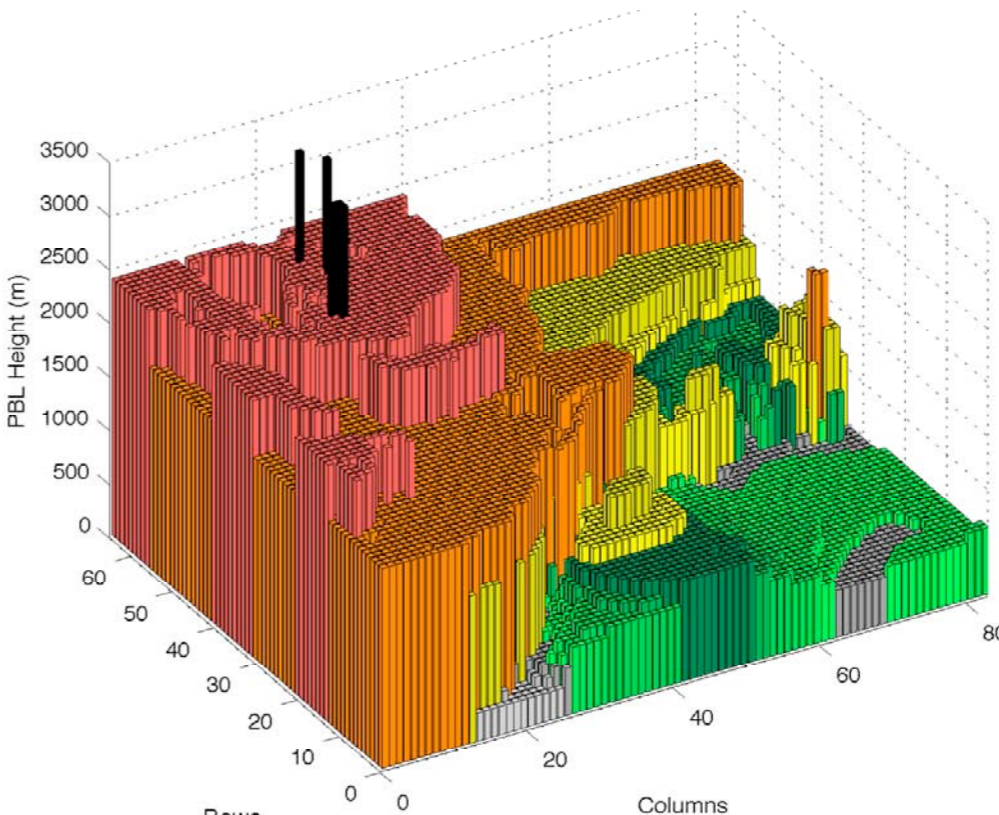
Hour 0800 LST



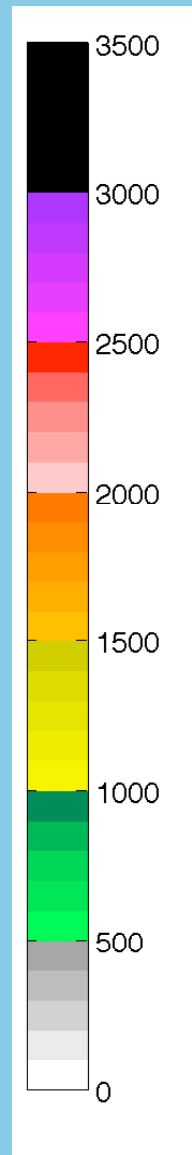
Hour 0900 LST



Hour 1000 LST

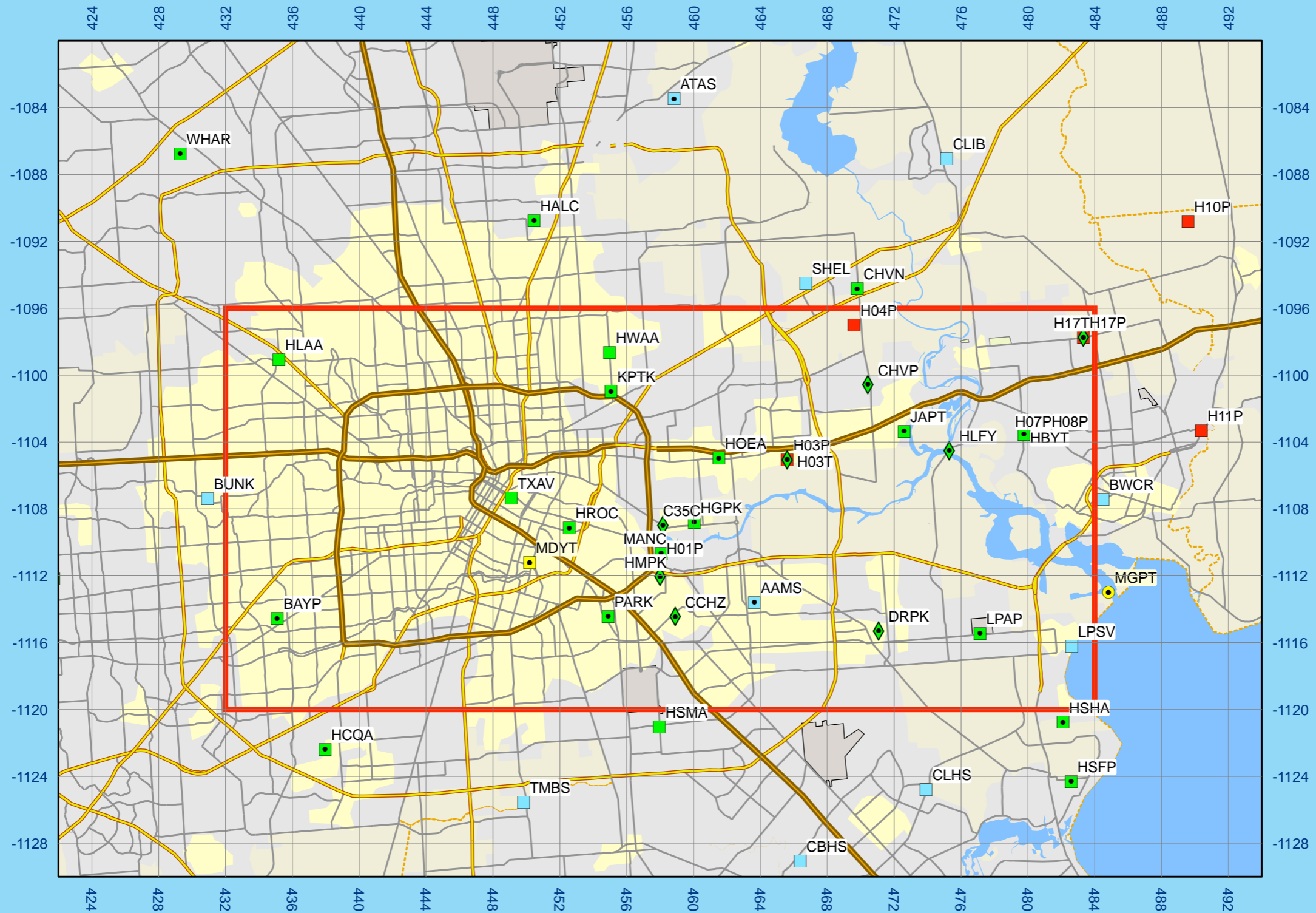


Hour 1100 LST

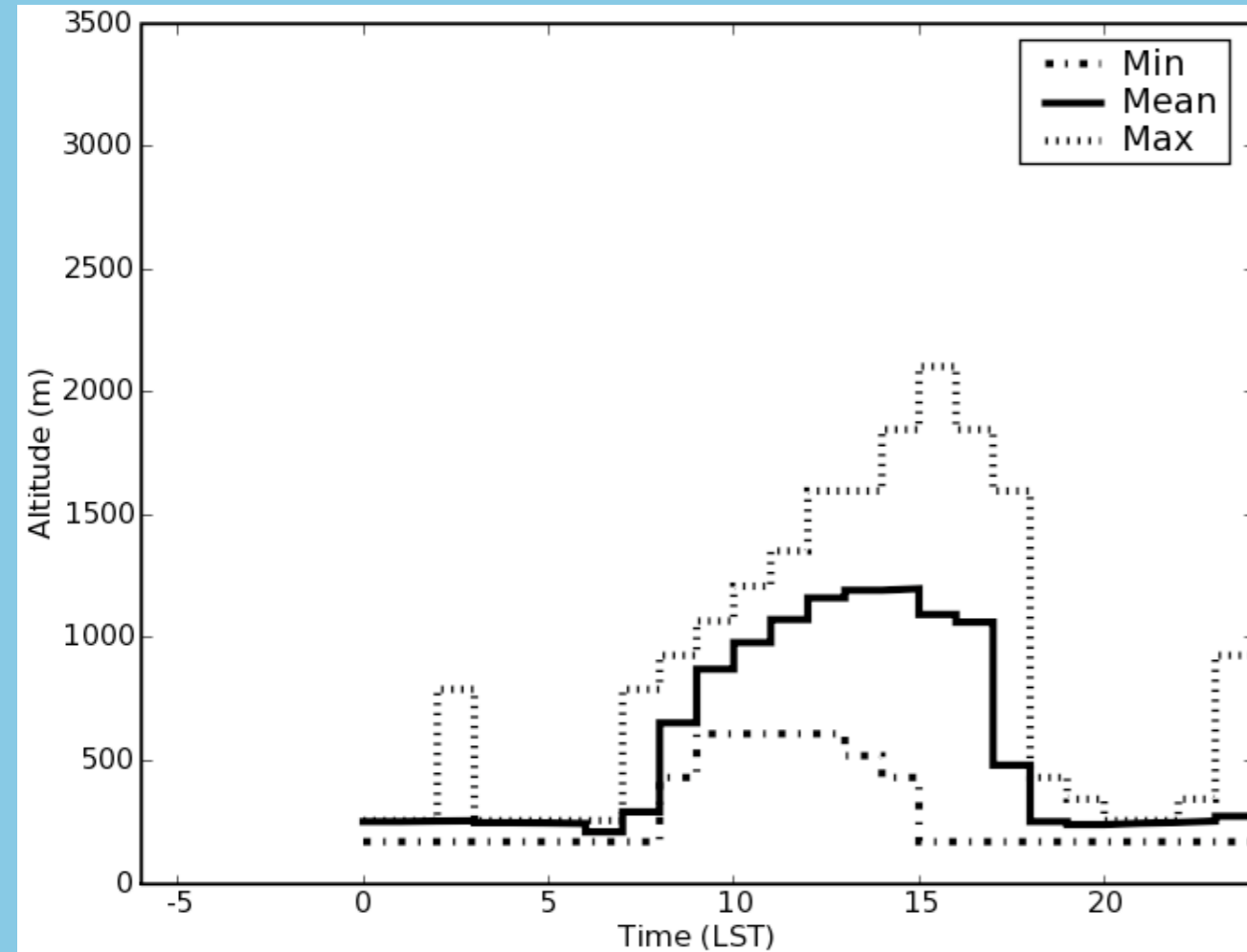


Process Analysis Domain

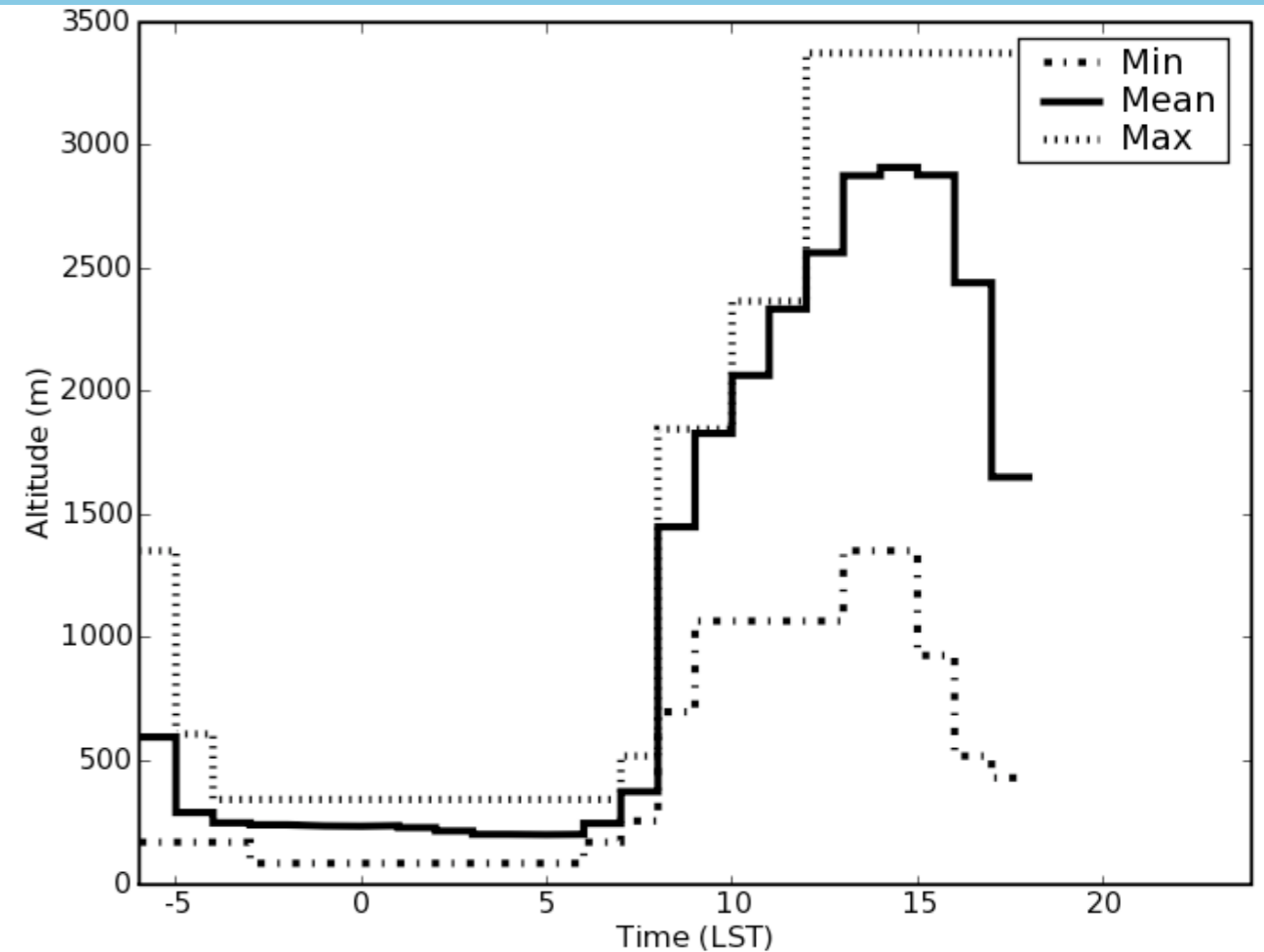
6 x 13 4-km cells, 1,250 km²



CHOU-wide PBL Heights



8/25/2000 CAMx

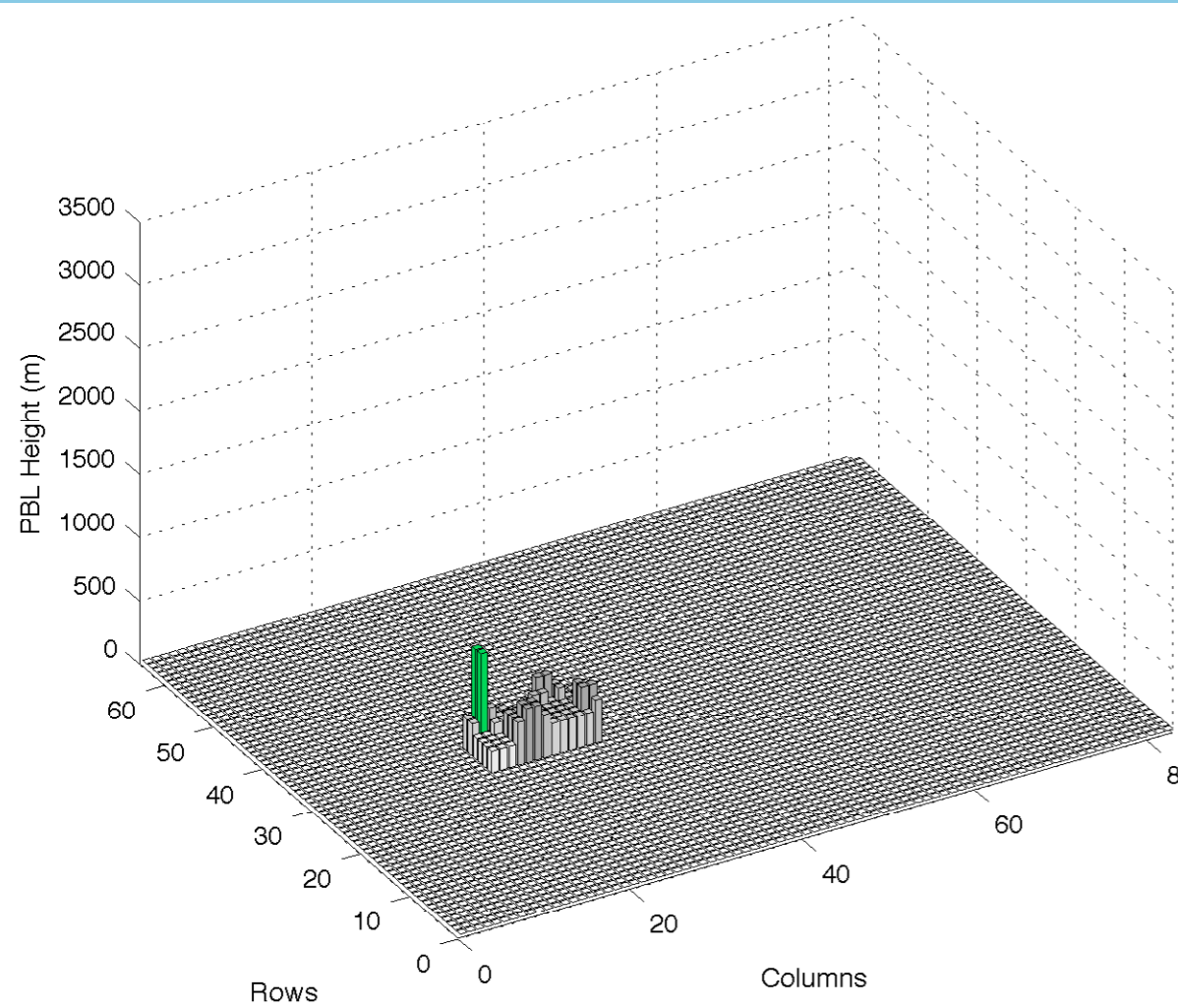


8/17/2006 CMAQ

- 4-km CHOU-wide Max, Min, and Mean PBL heights
- 2006 episode had a >1000 m rise in one hour

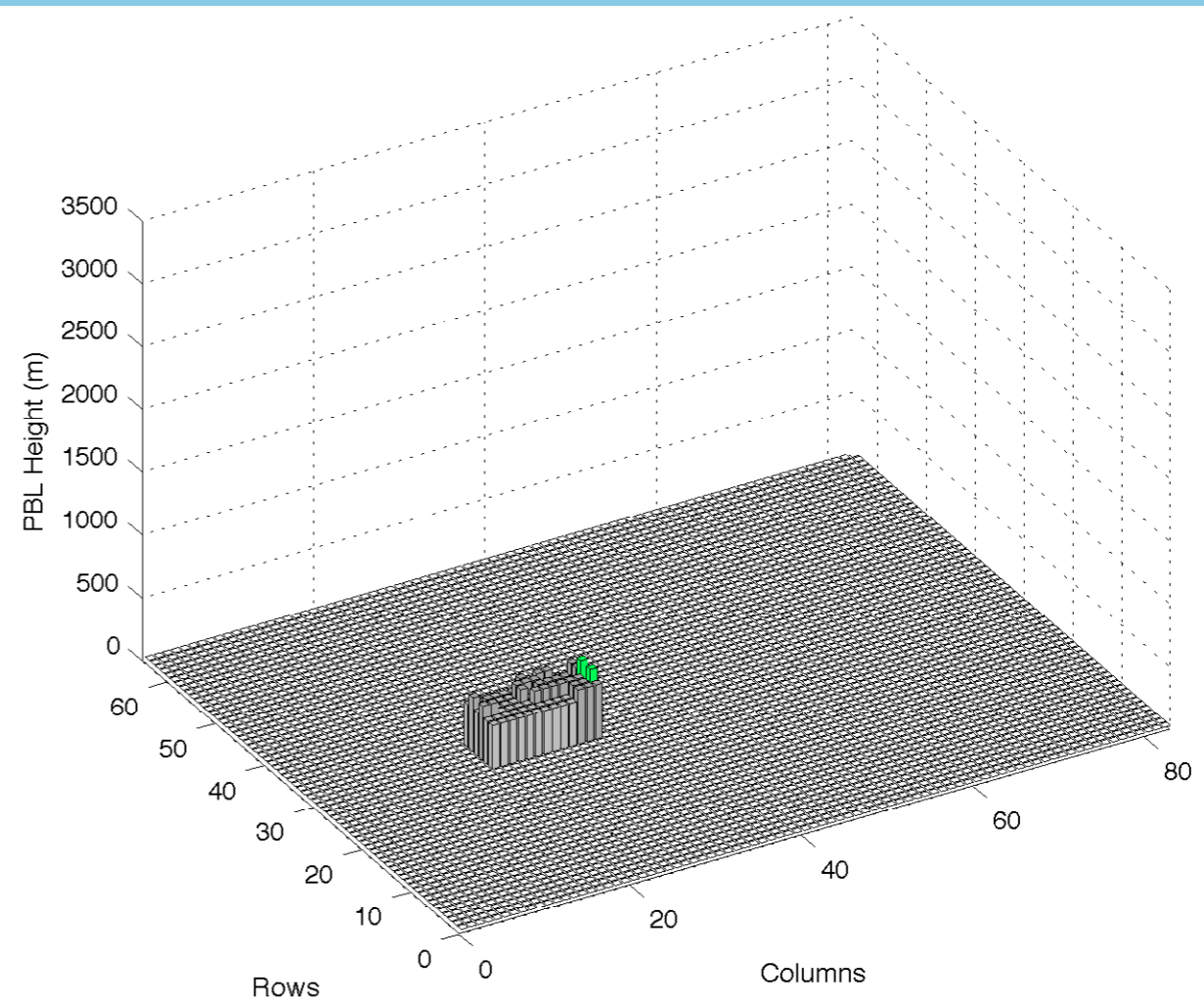
CHOU-wide PBL Heights

8/25/2000 CAMx

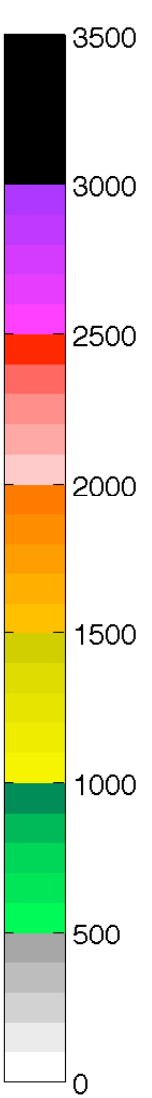


Hour 0800 LST

8/17/2006 CMAQ



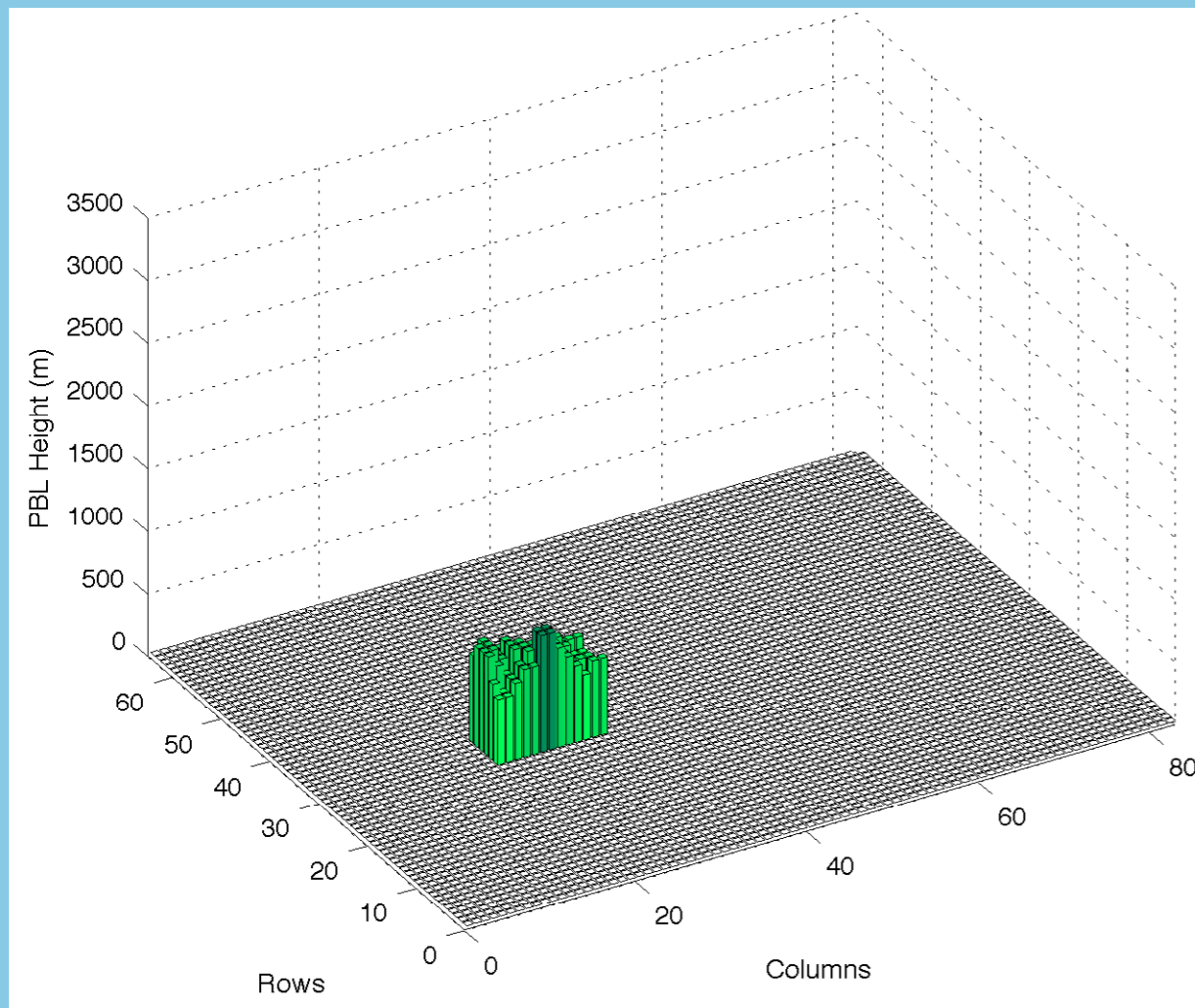
Hour 0800 LST



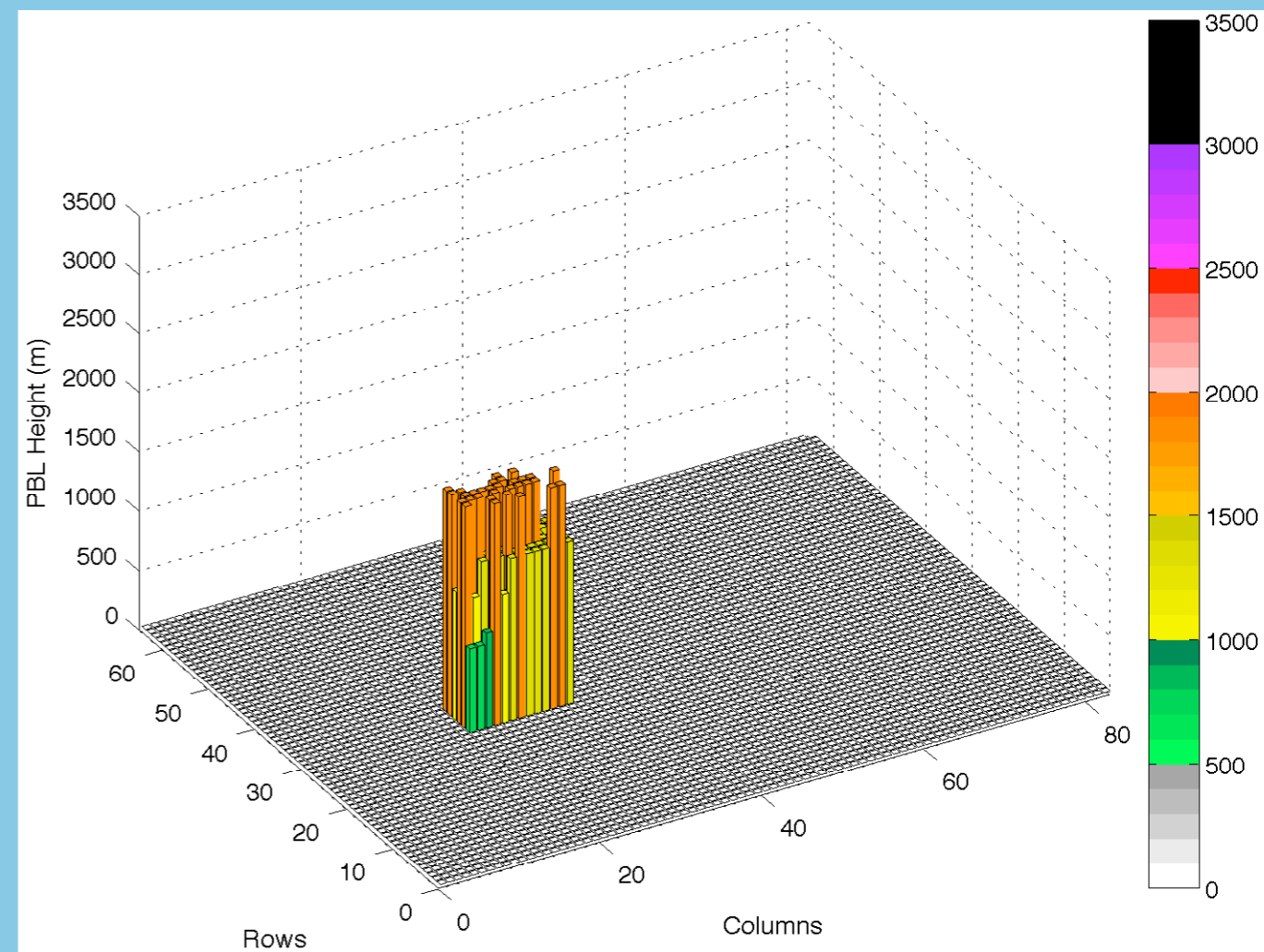
CHOU-wide PBL Heights

8/25/2000 CAMx

8/17/2006 CMAQ

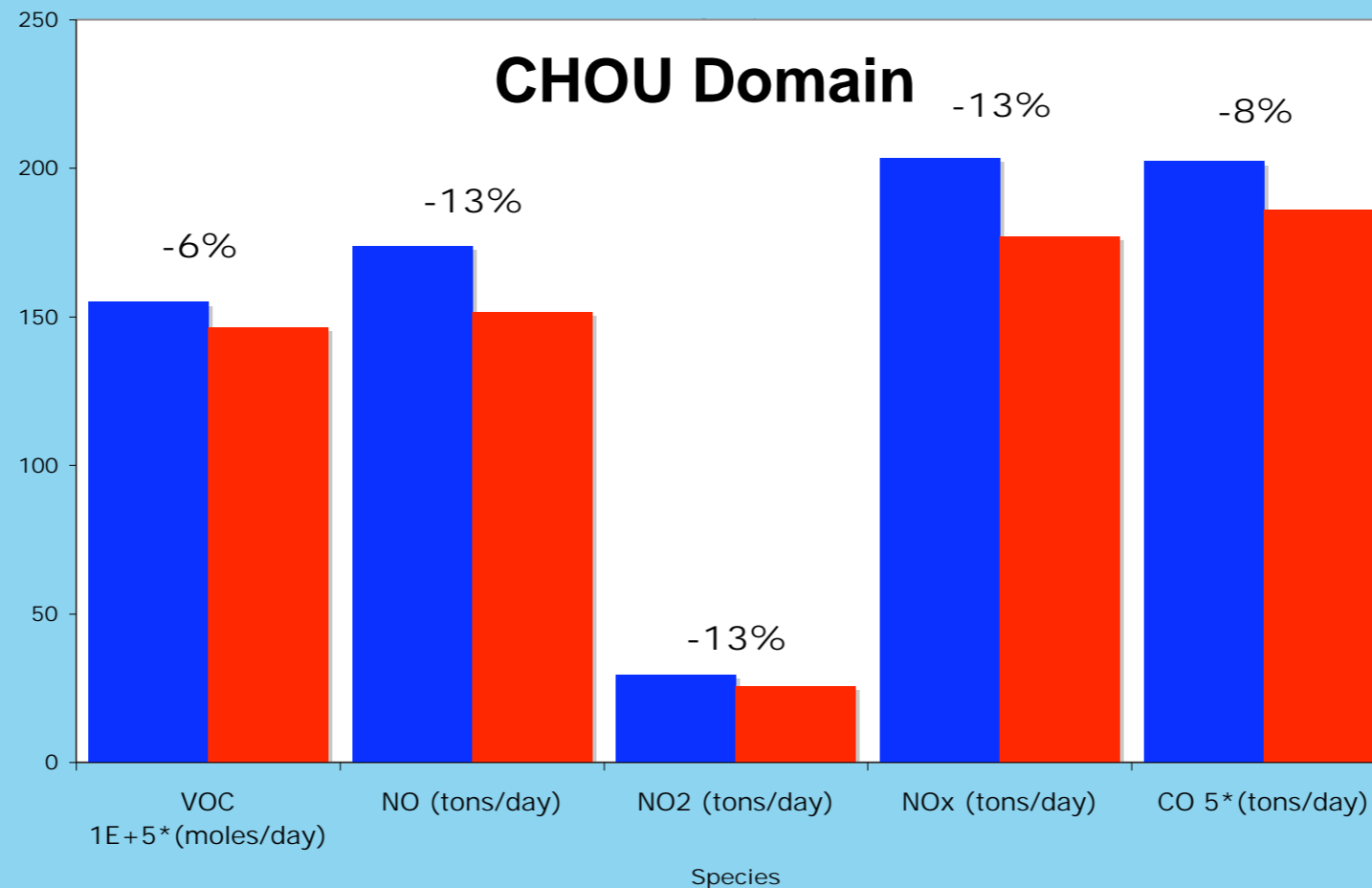
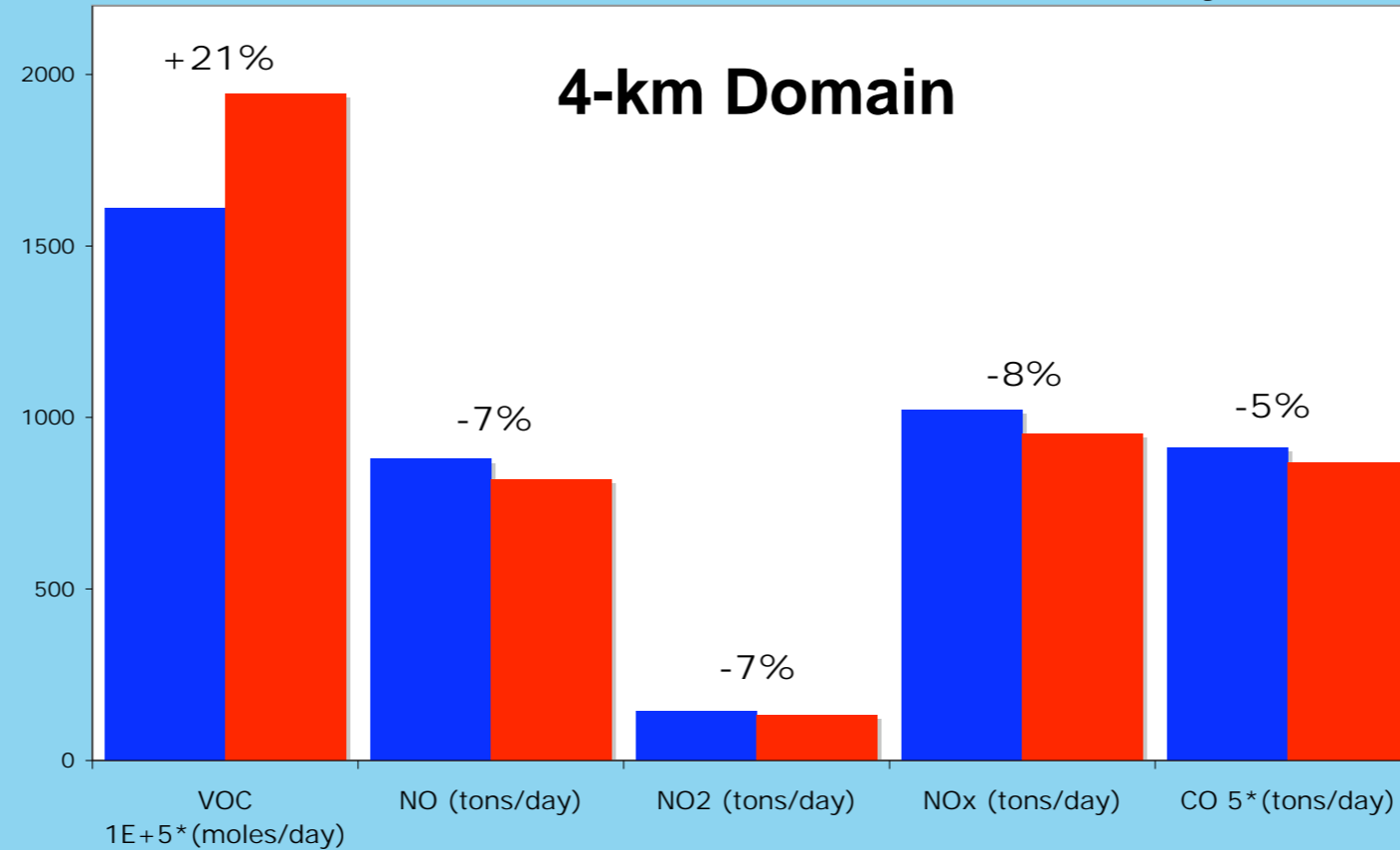


Hour 0900 LST



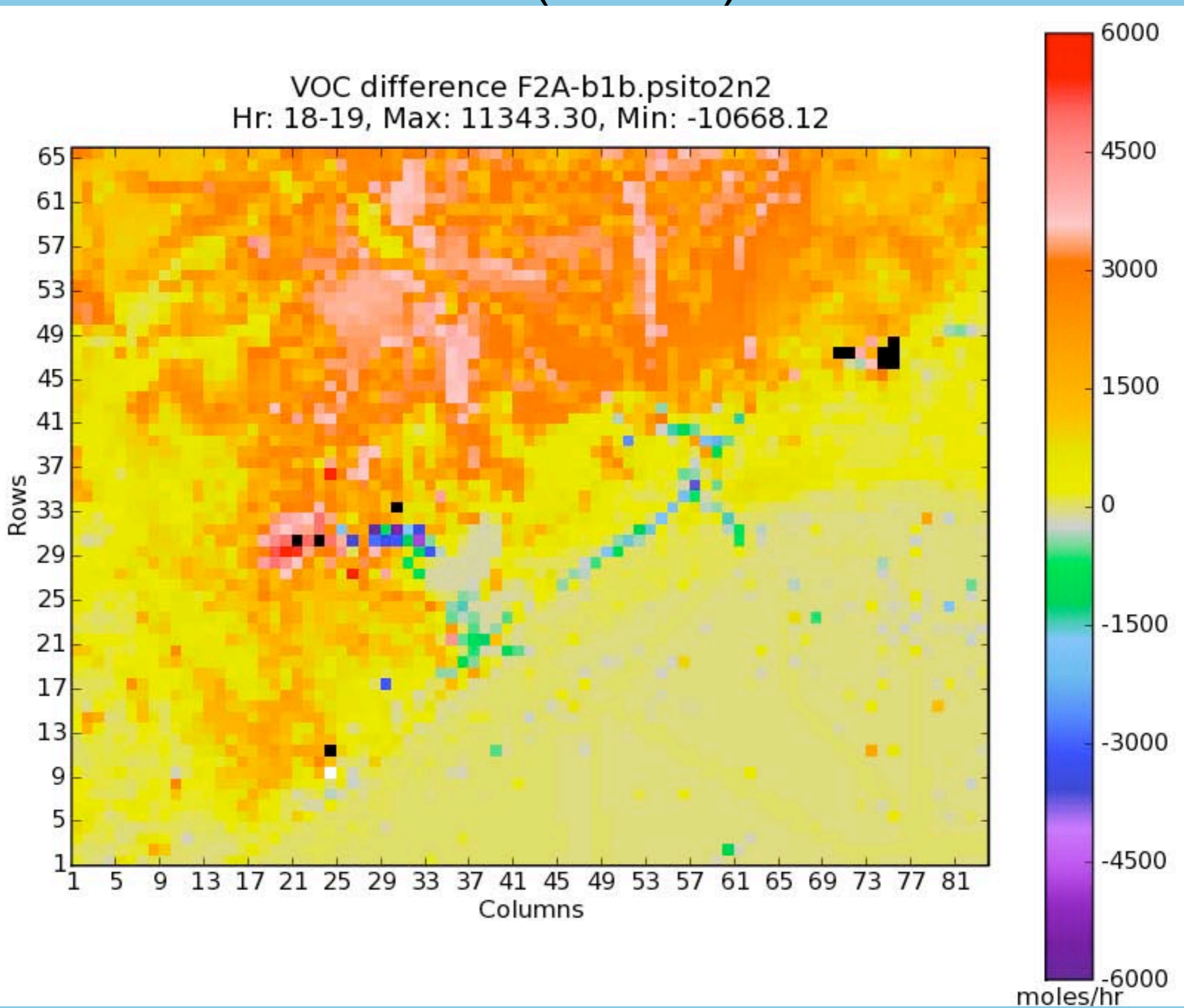
Hour 0900 LST

Emission Inventory

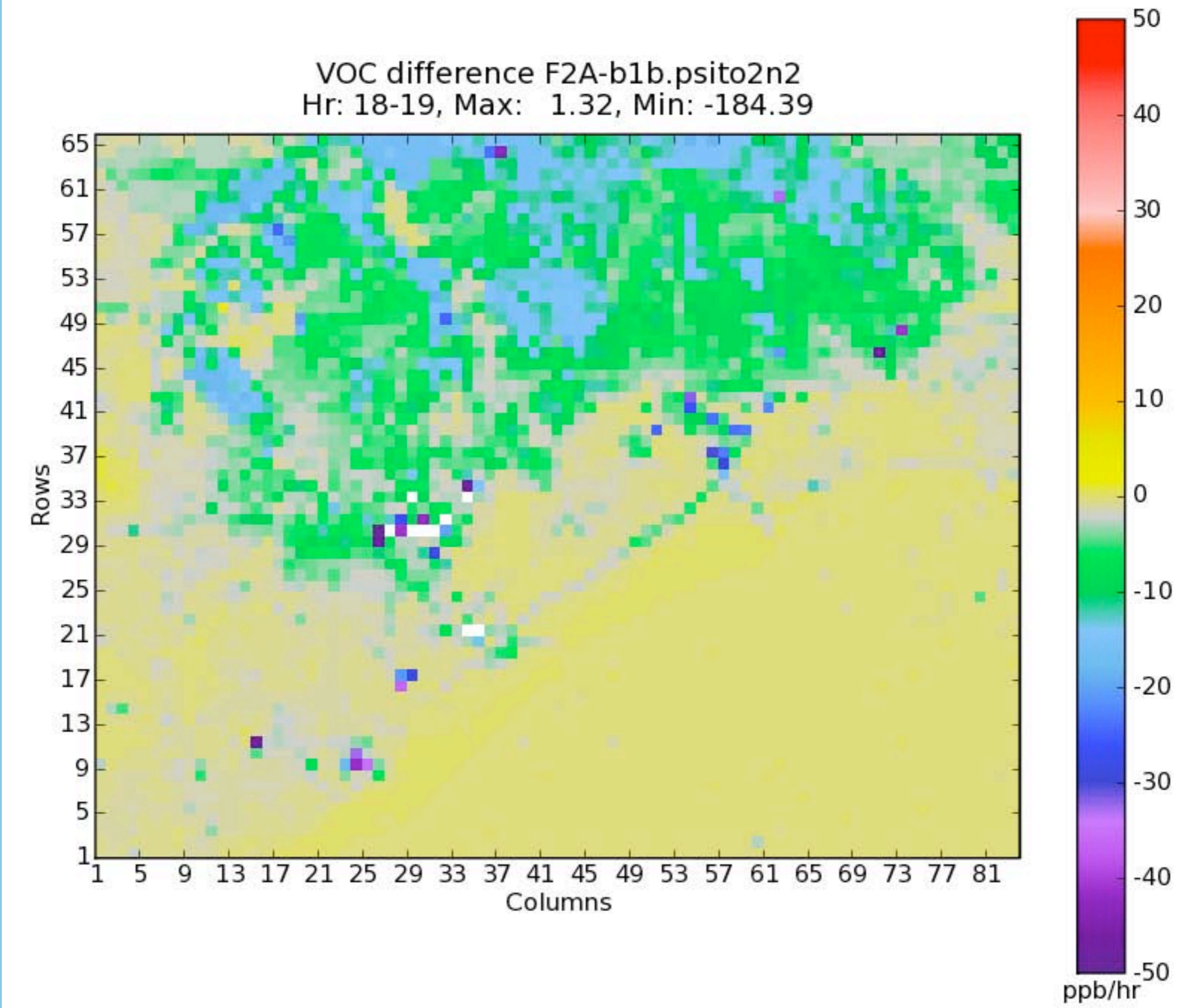


Species
■ August 25, 2000 ■ August 17, 2006

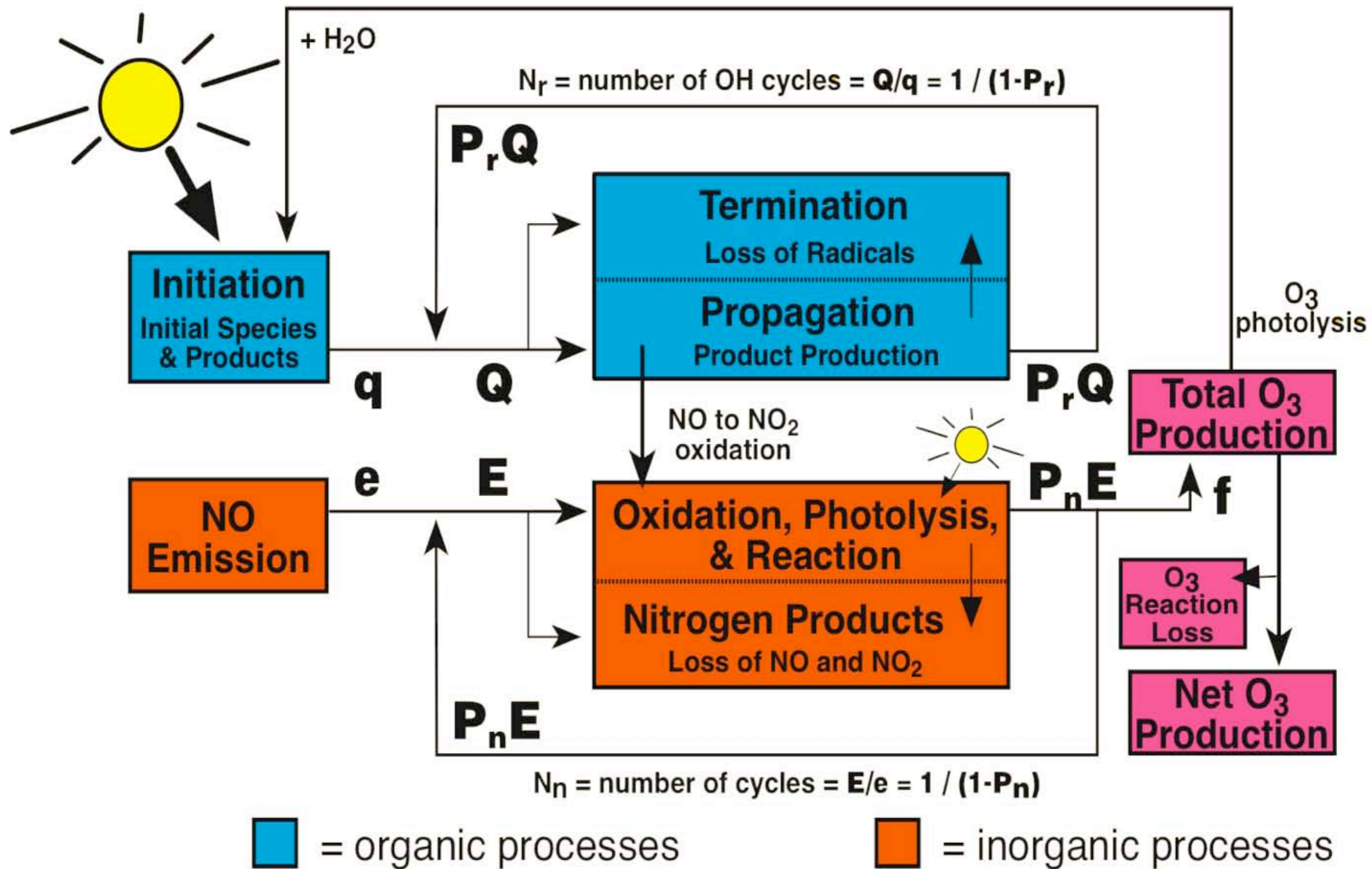
Emission Inventory VOC (mol/hr)



Emission Inventory VOC (ppb/hr)



Process Analysis, IRR

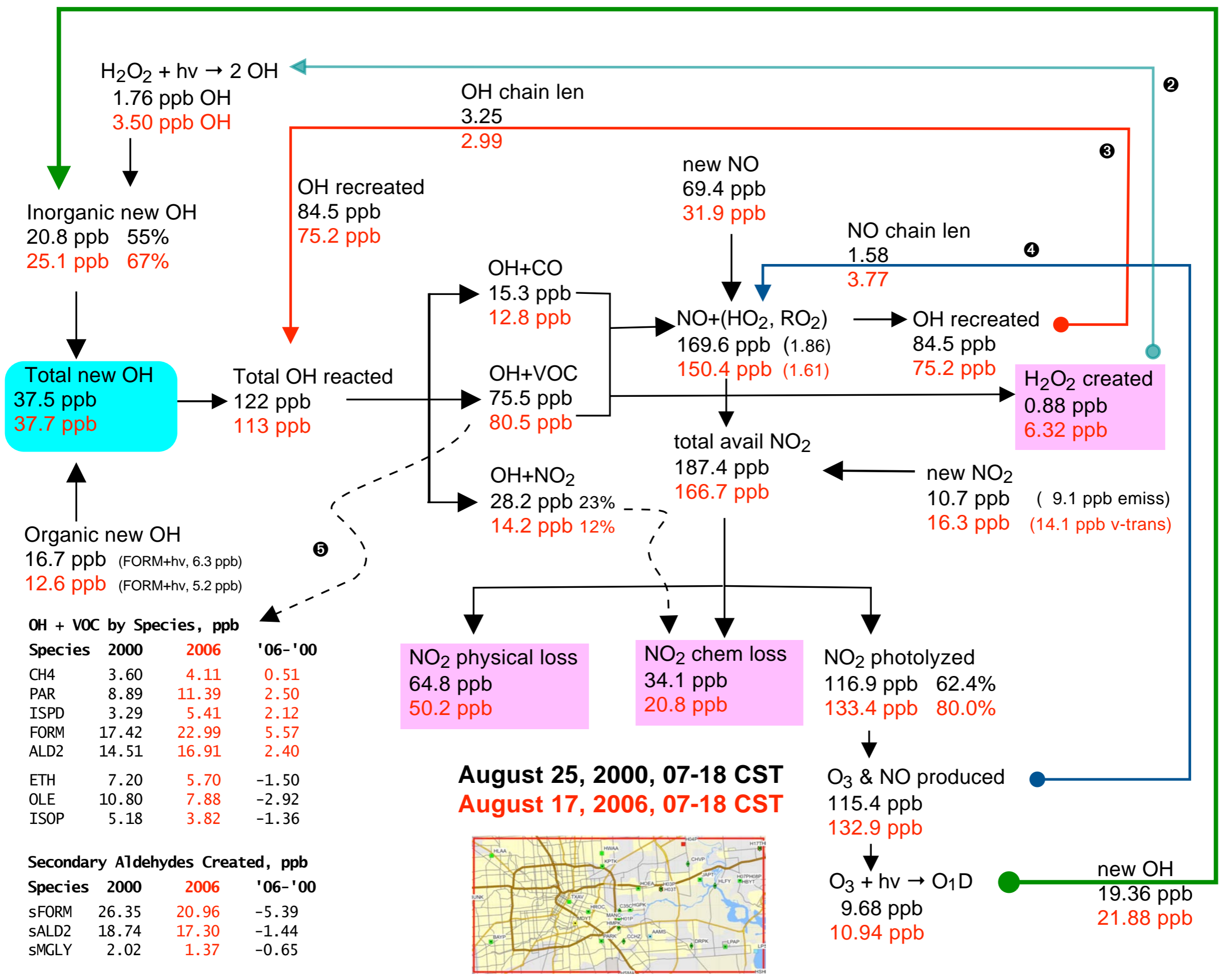


Critical PA Parameters: 2000 and 2006

Hours 7-18

Species	2000	2006
NOx	ppb	ppb
initial	47.3	52.8
emissions	73.8	16.5
average	16.1	6.6
final	13.5	4.0
NOy		
average	25.1	13.5
H transport	-43.5	-31.9
V transport	-23.9	15.3
pbl change	-24.5	-46.3
deposition	-13.7	-1.0
final	17.3	6.8
VOC, ppbV		
initial	156.1	159.4
emissions	174.3	29.6
average	67.2	62.1
H transport	-121.3	-11.2
V transport	-68.7	46.1
pbl change	-69.6	-117.9
deposition	-0.8	-0.2
final	37.3	68.1
VOC, ppbC		
average	85.3	73.5
final	48.5	80.0
VOCm/NOx		
emissions	2.4	1.8
average conc	4.2	9.4

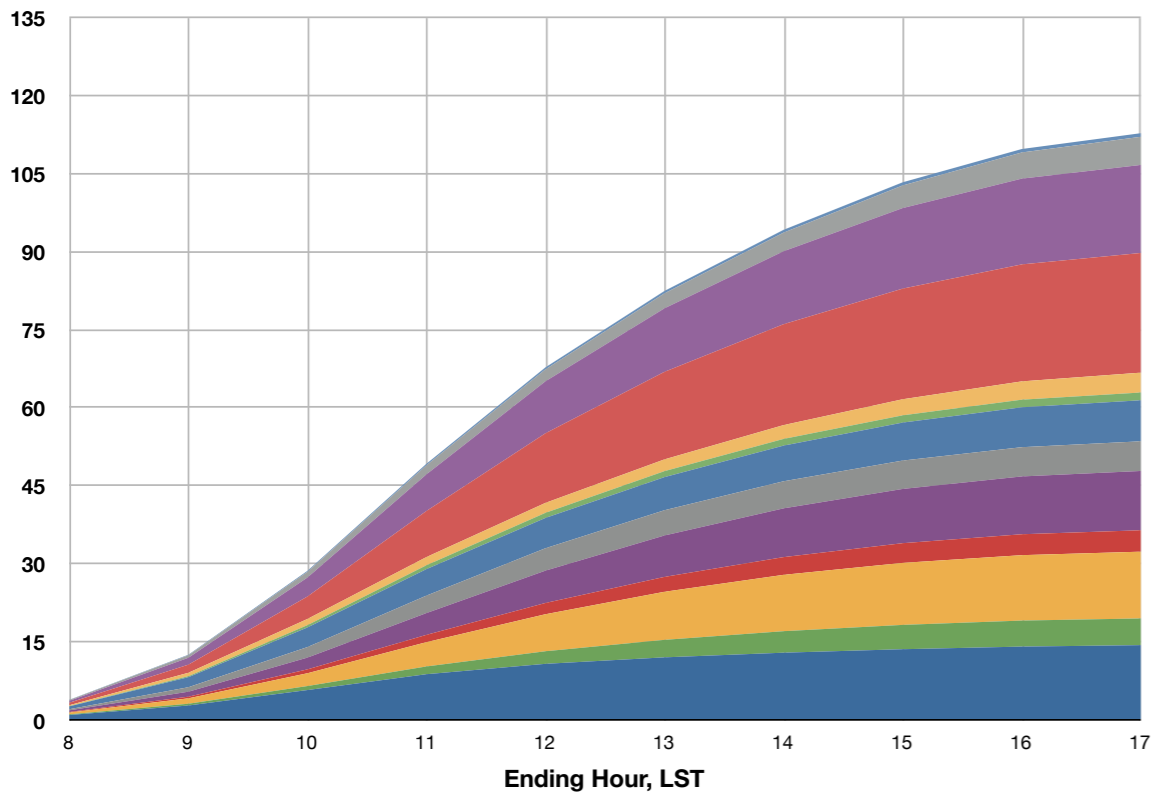
- All concentrations and concentration changes by process are based on total CHOU volume horizontally and vertically to the top of the PBL
- Nighttime PBL heights are similar, resulting in similar initial concentrations at Hour 07 for both models
- Significant differences in PBL volumes give very different contributions of emissions to box concentrations for both NOx and VOC
- Much of the VOC is blown out of box in 2000, much of the VOC is diluted into very large pbl volume in 2006
- VOC/NOx ratios based on emissions only and on average box concentrations are different within a model and between models. This reflects “carry-over” of VOC and loss of NOx from hour to hour. Between episode differences also reflect box ventilation rate (less in 2006). This has implications for observational based assessments or for “inverse modeling” of VOCs



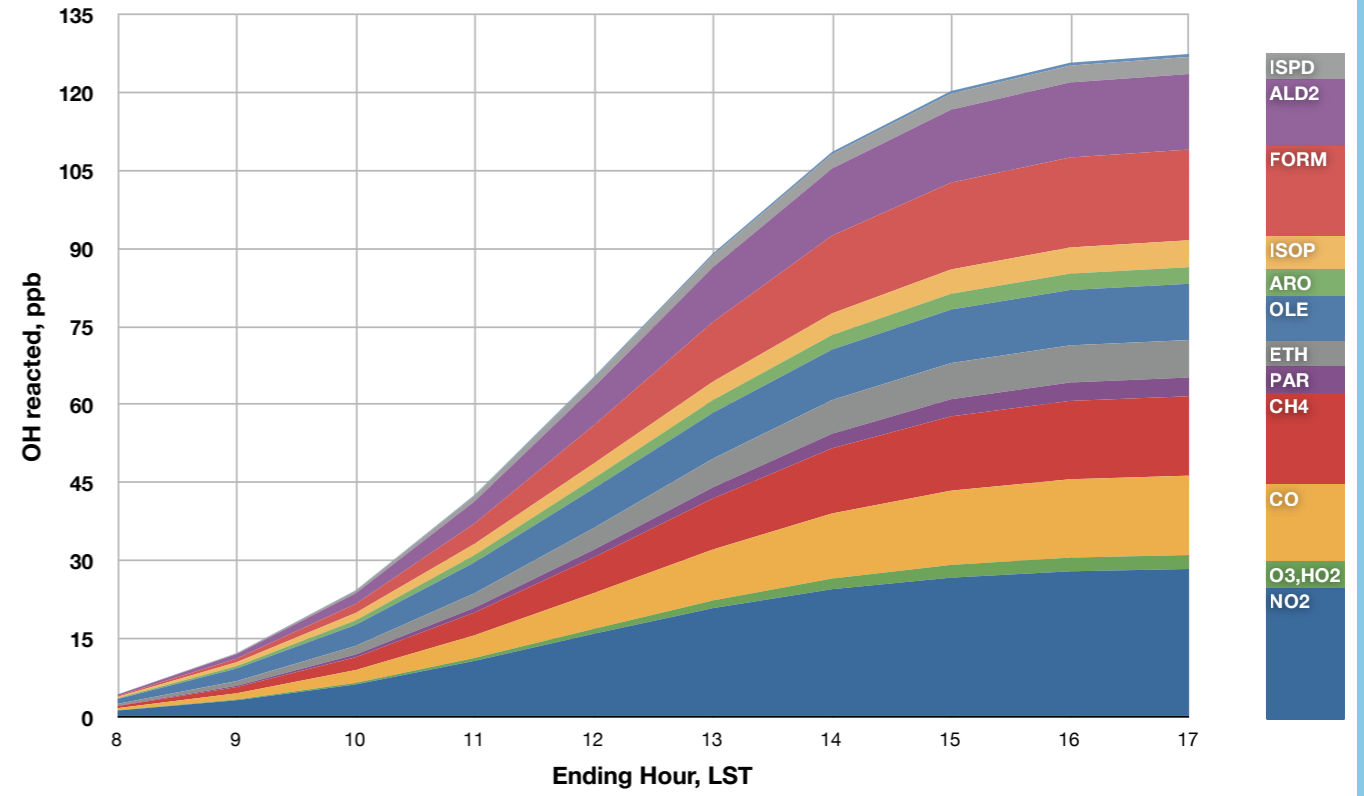
OH Reacted: 2000 and 2006

Hours 7-18

August 17, 2006, CHOU



August 25, 2000, CHOU



Process Analysis Results

- In 2006 reduced NO_x concentrations in morning resulted in higher ozone production making nearly 50% more new OH from photolysis of ozone before noon.
- In 2006 the model became NO_x limited in the afternoon resulting higher radical self-termination reactions (HO₂+HO₂;RO₂+RO₂) causing the 2000 episode to have higher cycling of OH in the afternoon; 2006 had higher cycling in morning
- UH H87 report stated: “TMNS11n2 simulation results show quite a good match of the spatial gradient of ozone concentrations compared to the observations although regional average ozone was over-predicted during daytime and in early morning hours.”
- In 2006 only 65% of HO₂ reacted with NO in afternoon versus 95% in 2000; H₂O₂ was formed in 2006; both evidence of NO_x limited environment in model. H₂O₂ obs data?

Process Analysis Results

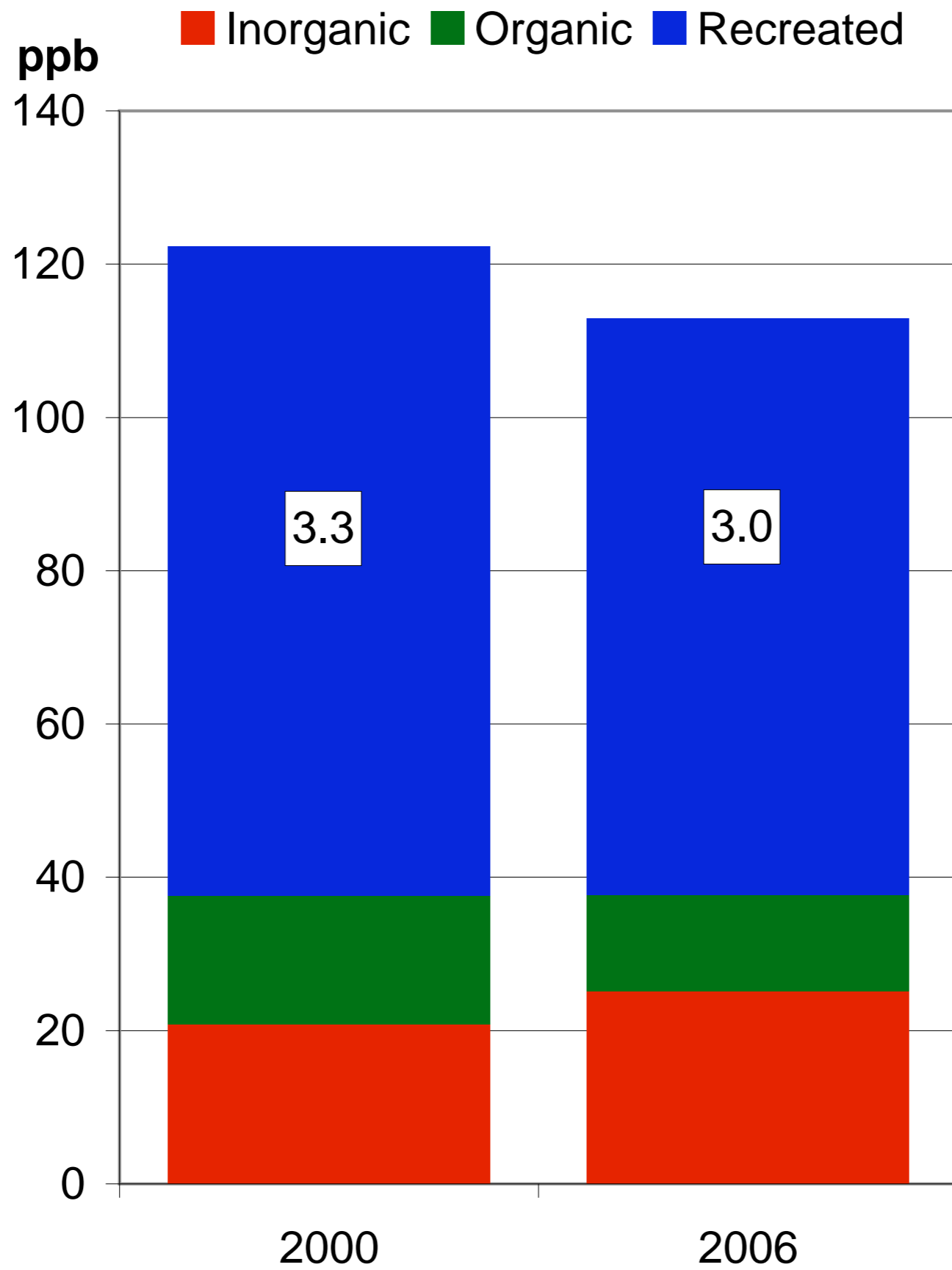
- NO_x Concentrations, not VOC concentrations, are the most influential factor in determining ozone production
- Changes in PBL and emission inventories resulted in lower early NO_x concentrations and shifted chemical environment from NO_x-inhibited to NO_x-limited condition
- 2006 reduced NO_x environment resulted in less nitric acid, less radical terminations, and increased propagation pathways
- 2006 had higher ozone production even with same amount of new OH radicals due to shift in termination/propagation pathways
- Sensitivity runs with increases in formaldehyde had less impact on ozone production rates in 2006; further evidence that the 2006 model is NO_x limited and not radical limited

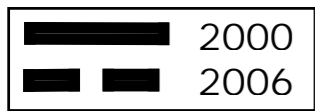
Summary

- Physical processes (PBL) cause significant change in ozone chemistry resulting in shift from radical limited to NO_x limited environment
- Each model would predict different responses to precursor reductions
- Meteorological processes require further evaluation
- Other days in episode need further evaluation

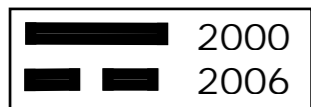
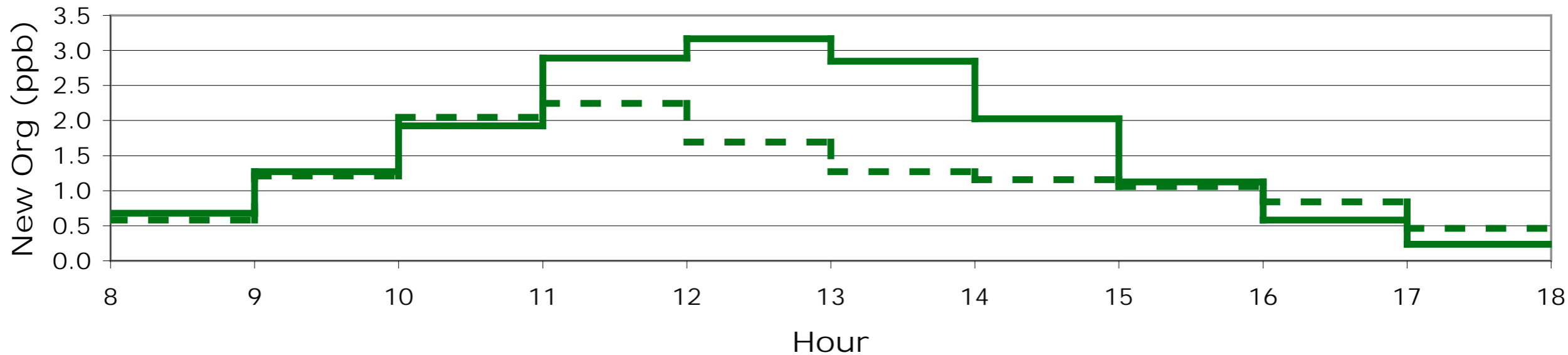
Appendix

OH Sources

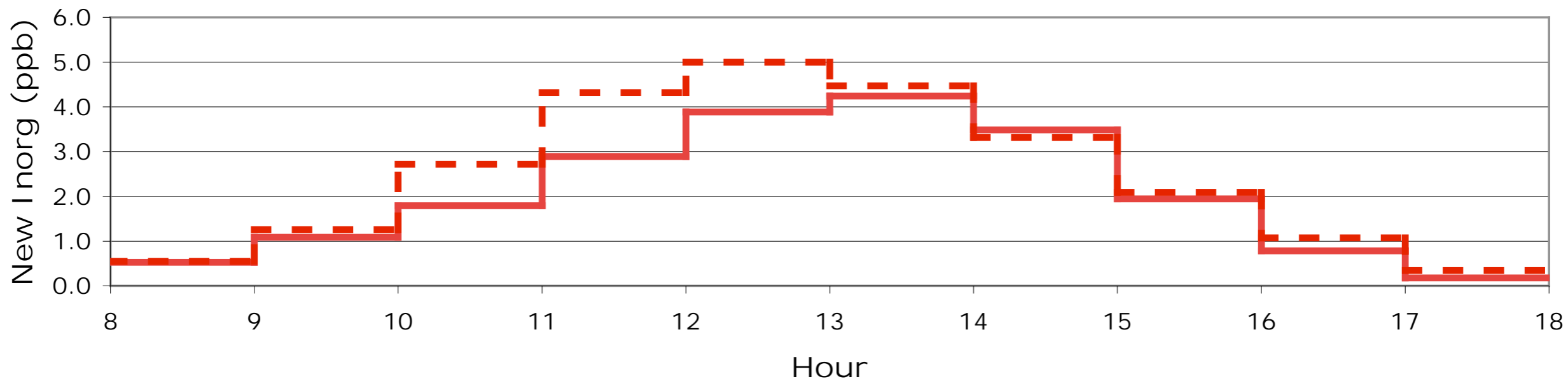


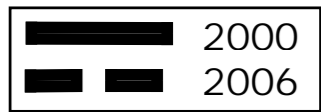


Hourly New OH Variation

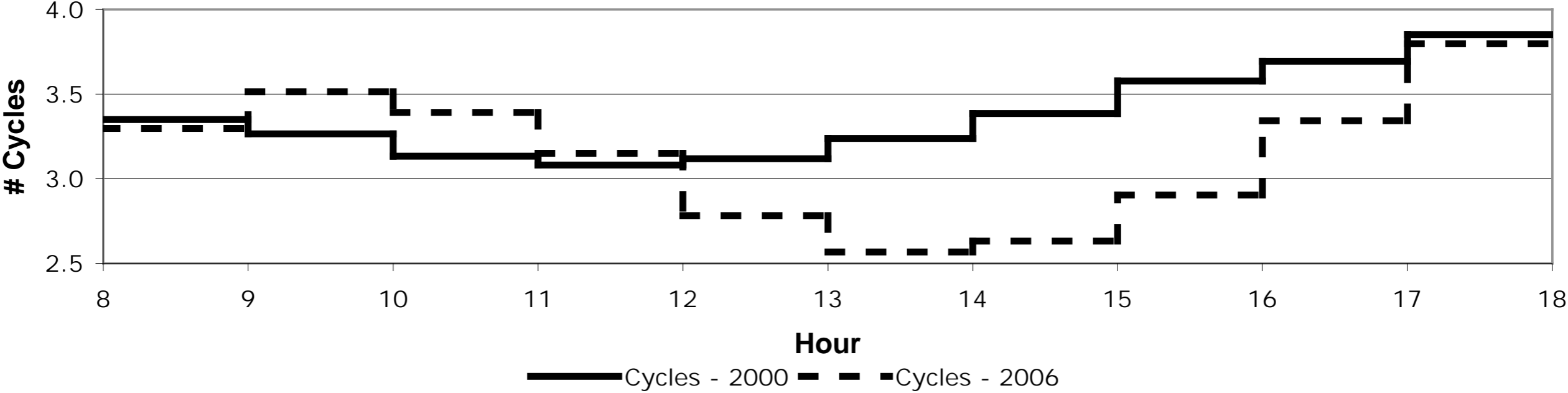


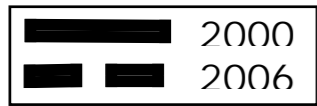
Hourly New OH Variation



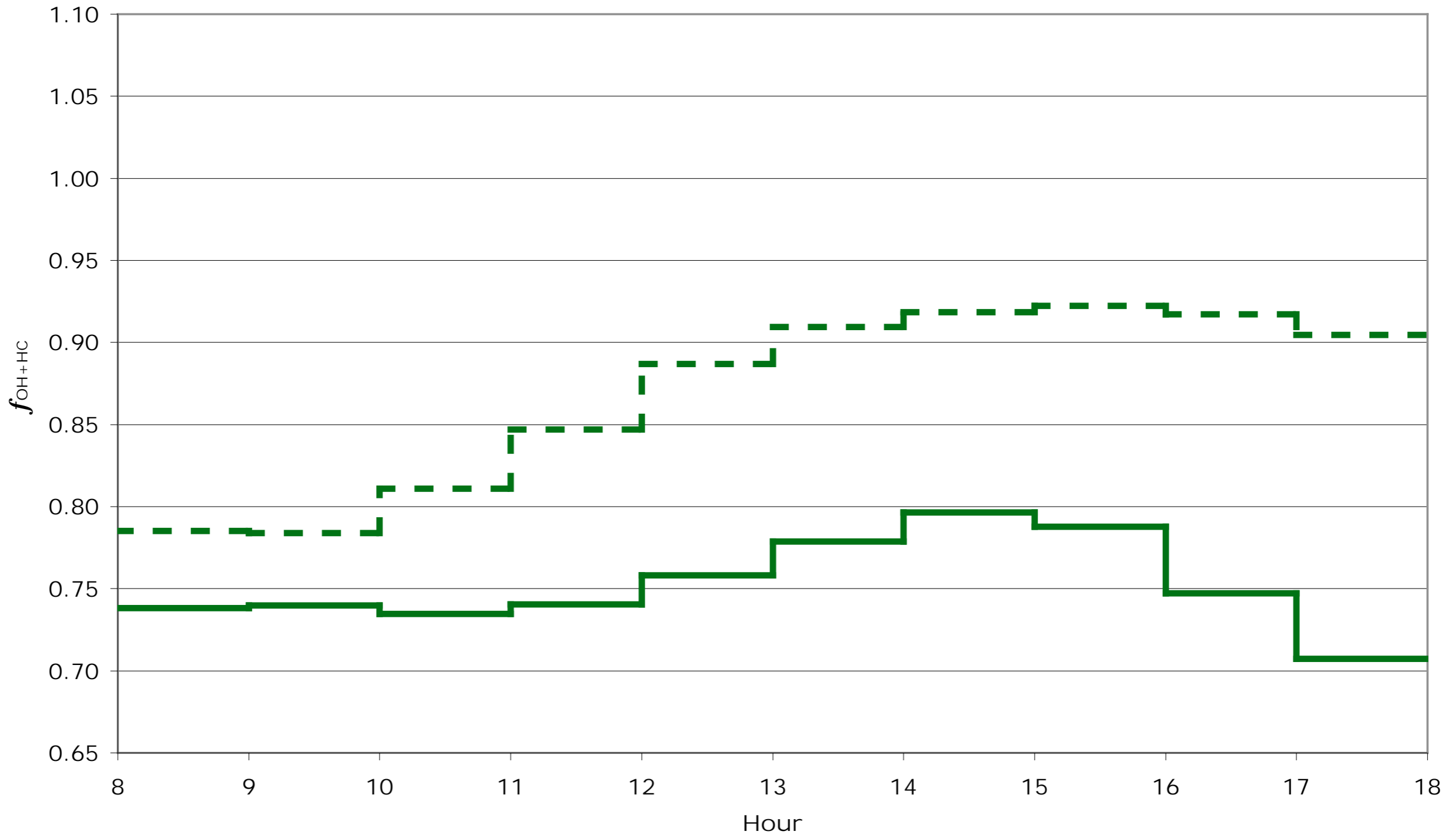


Cycles





Fraction of OH reacts with HC



Fraction of HO2 reacts with NO

