AQRP Project 12-028

Implementation and evaluation of new HONO mechanisms in a 3-D Chemical Transport Model for Spring 2009 in Houston

Barry Lefer[1], Prakash Karamchandani[2], Chris Emery[2], Jochen Stutz[3], Evan Couzo[4], William Vizuete[4], and Greg Yarwood[2]

[1]University of Houston, Houston, TX
[2]ENVIRON International Corporation, Novato, CA
[3]University of California at Los Angeles, CA
[4]University of North Carolina, Chapel Hill, NC

ENVIRON

UCLA

THE UNIVERSITY of NORTH CAROLINA at CHAPEL HILL

HONO is an important OH Source

R1. HONO + $h\nu \rightarrow$ OH + NO (λ<400 nm)

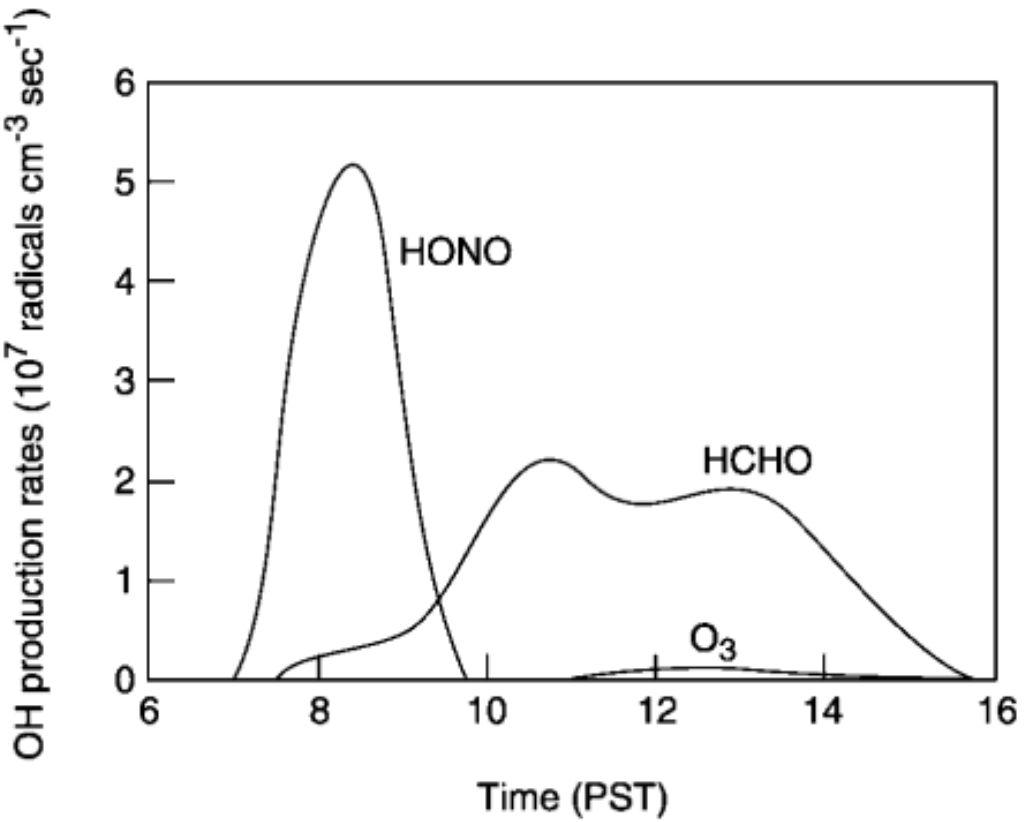


FIGURE 7.8 Calculated rates of formation of OH radical from photolysis of HONO, O_3, and HCHO at Long Beach, California, on December 10, 1987 (adapted from Winer and Biermann, 1994).

B.J. Finlayson-Pitts and J.N. Pitts, "Chemistry of the upper and lower atmosphere: theory, experiments, and applications", Academic Press, 969 p., 2000

Basic HONO Formation and Loss Reactions

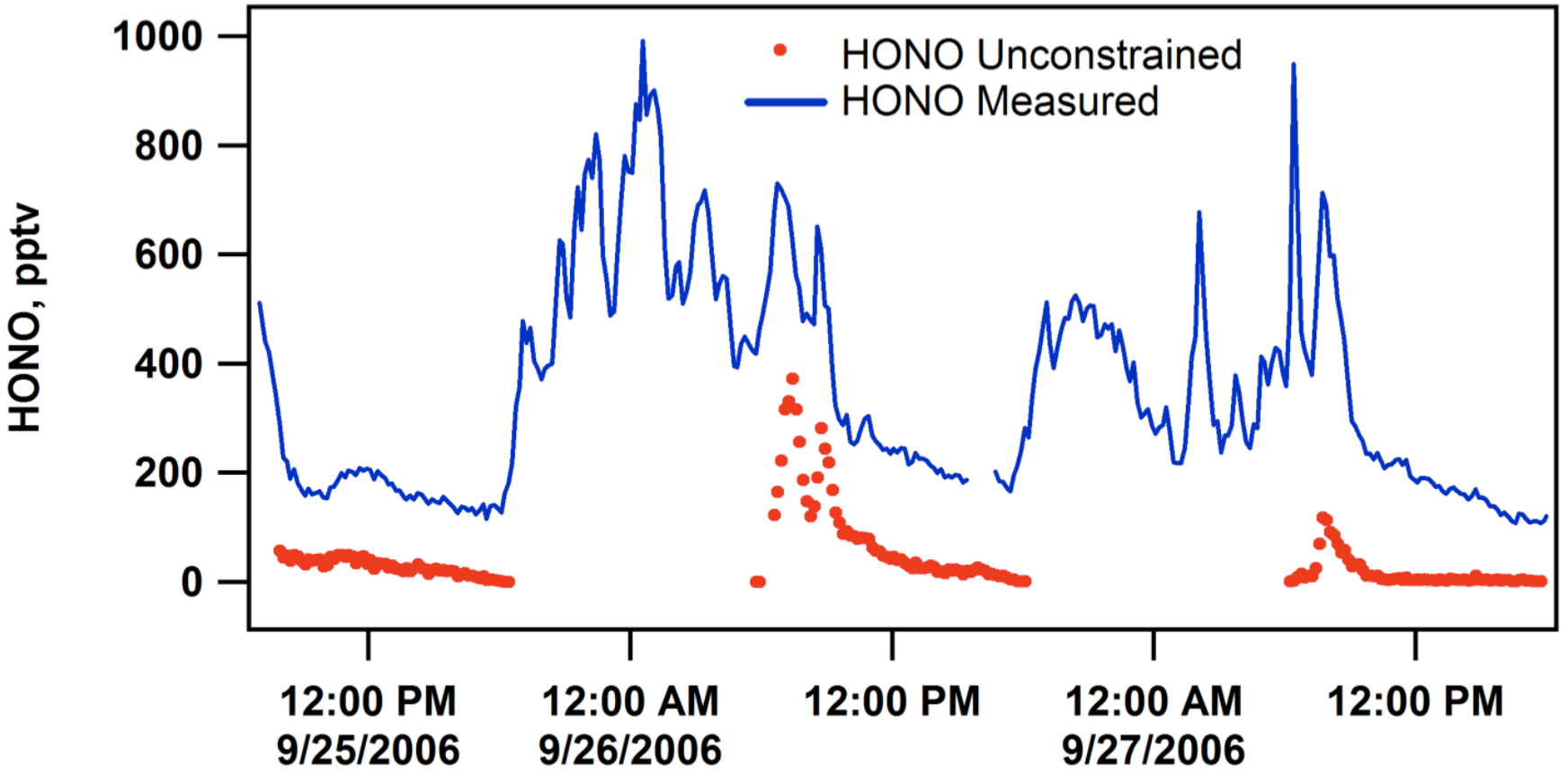
R1. $HONO + h\nu \rightarrow OH + NO$ ($\lambda < 400$ nm)

R2. $NO + OH \rightarrow HONO$

R3. $HONO + OH \rightarrow NO_2 + H_2O$

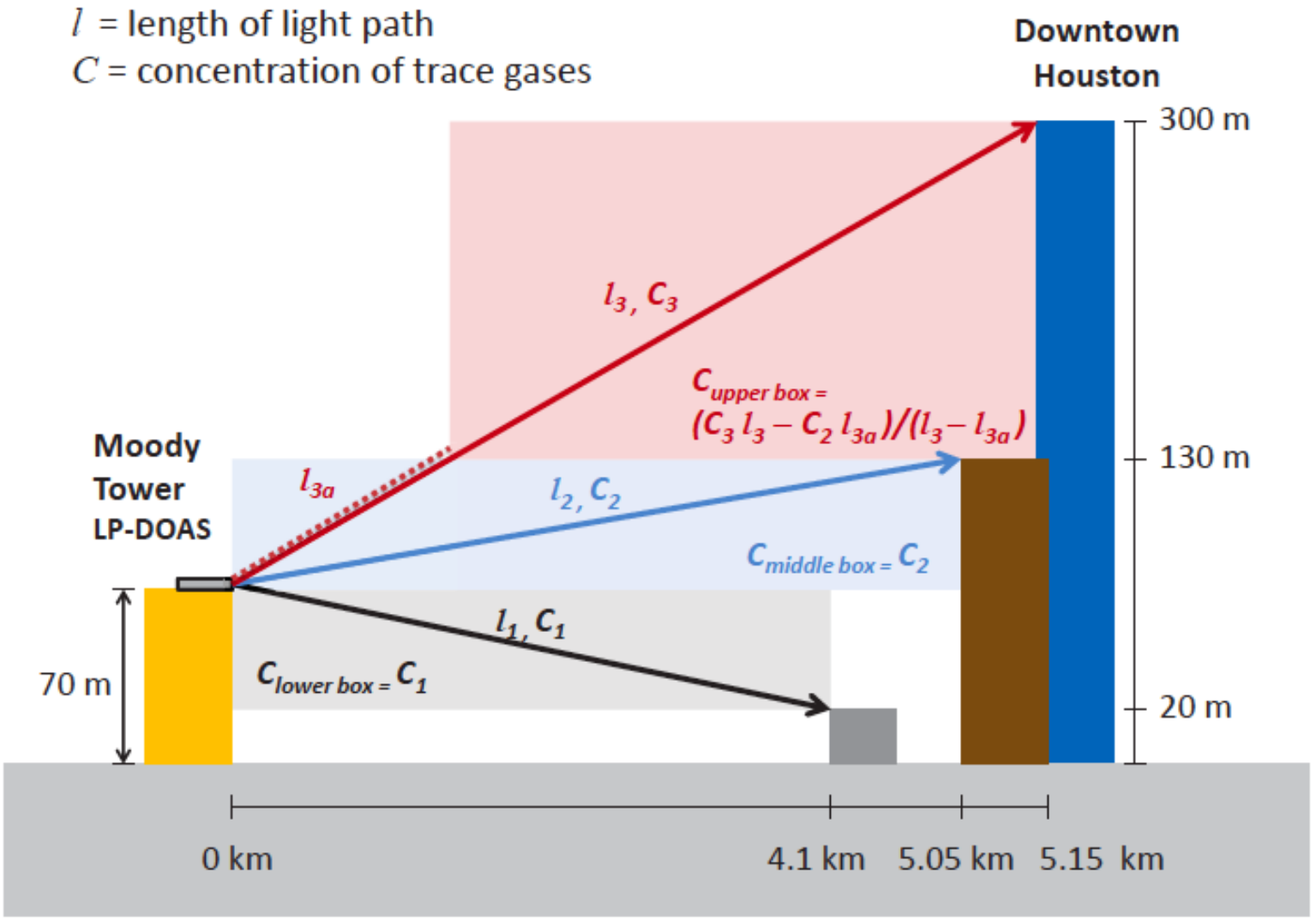
$$[HONO]_{ss} = \frac{k_2[NO][OH]}{J_{HONO} + k_3[OH]}$$

HONO in Houston - 2006



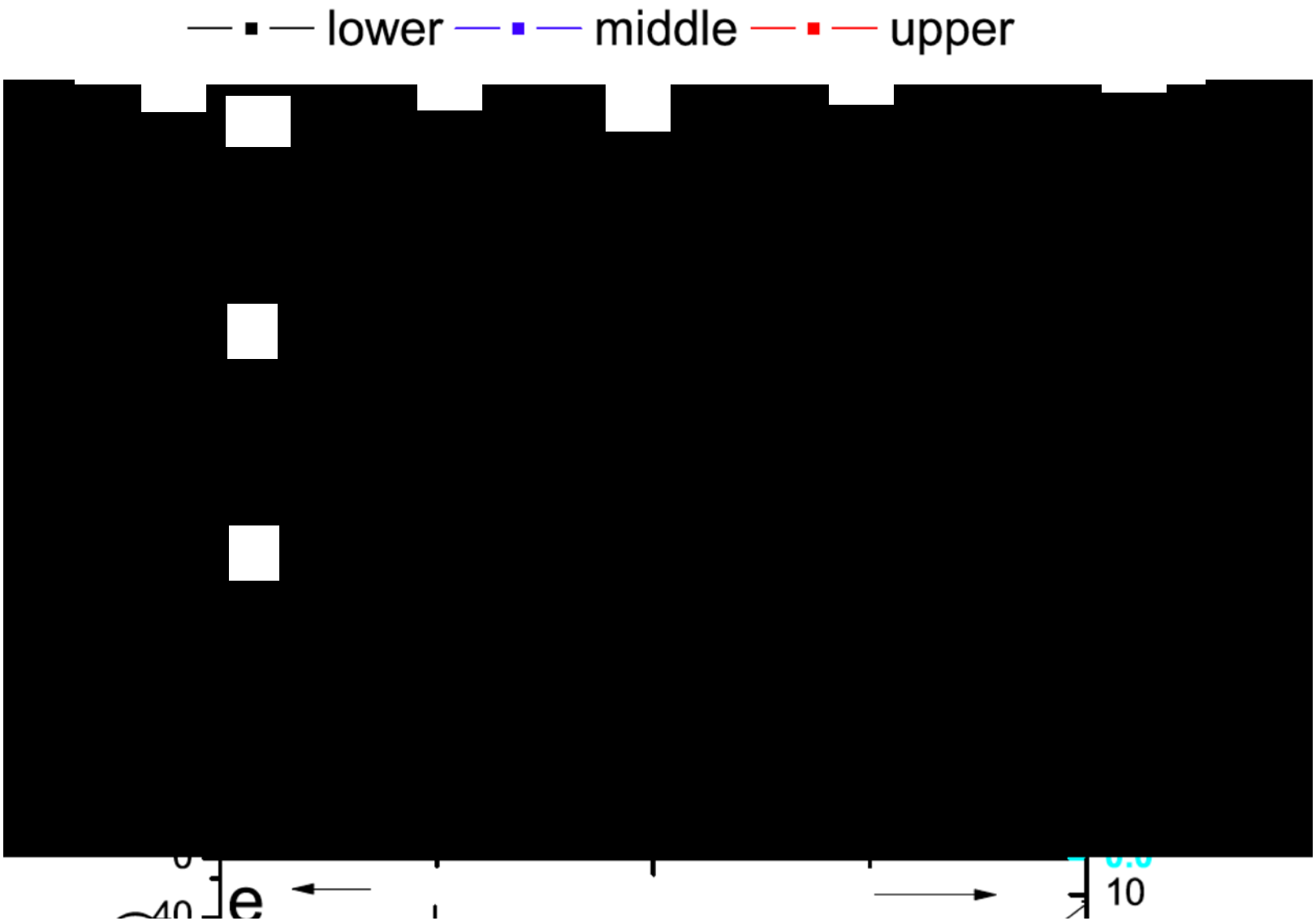
James Flynn (2009)

HONO via DOAS – Spring 2009



Wong, KW., C. Tsai, B. Lefer, C. Haman, N. Grossberg, W.H. Brune, X. Ren, W. Luke, and J. Stutz: Daytime HONO vertical gradients during SHARP2009 in Houston, TX, Atmos. Chem. Phys., 12, 635-652, doi:10.5194/acp-12-635-2012, 2012.

HONO Vertical Gradients – Spring 2009



Wong, KW., C. Tsai, B. Lefer, C. Haman, N. Grossberg, W.H. Brune, X. Ren, W. Luke, and J. Stutz: Daytime HONO vertical gradients during SHARP2009 in Houston, TX, Atmos. Chem. Phys., 12, 635-652, doi:10.5194/acp-12-635-2012, 2012.

HONO as a HOx source in Houston – Spring 2009

P(HOx) SHARP:

- HONO+hv in early morning
- $O(^1D) + H_2O$ during daytime
- O_3+ alkene reactions at night

Contributions on a 24-hr basis:

O_3 photolysis: 30%

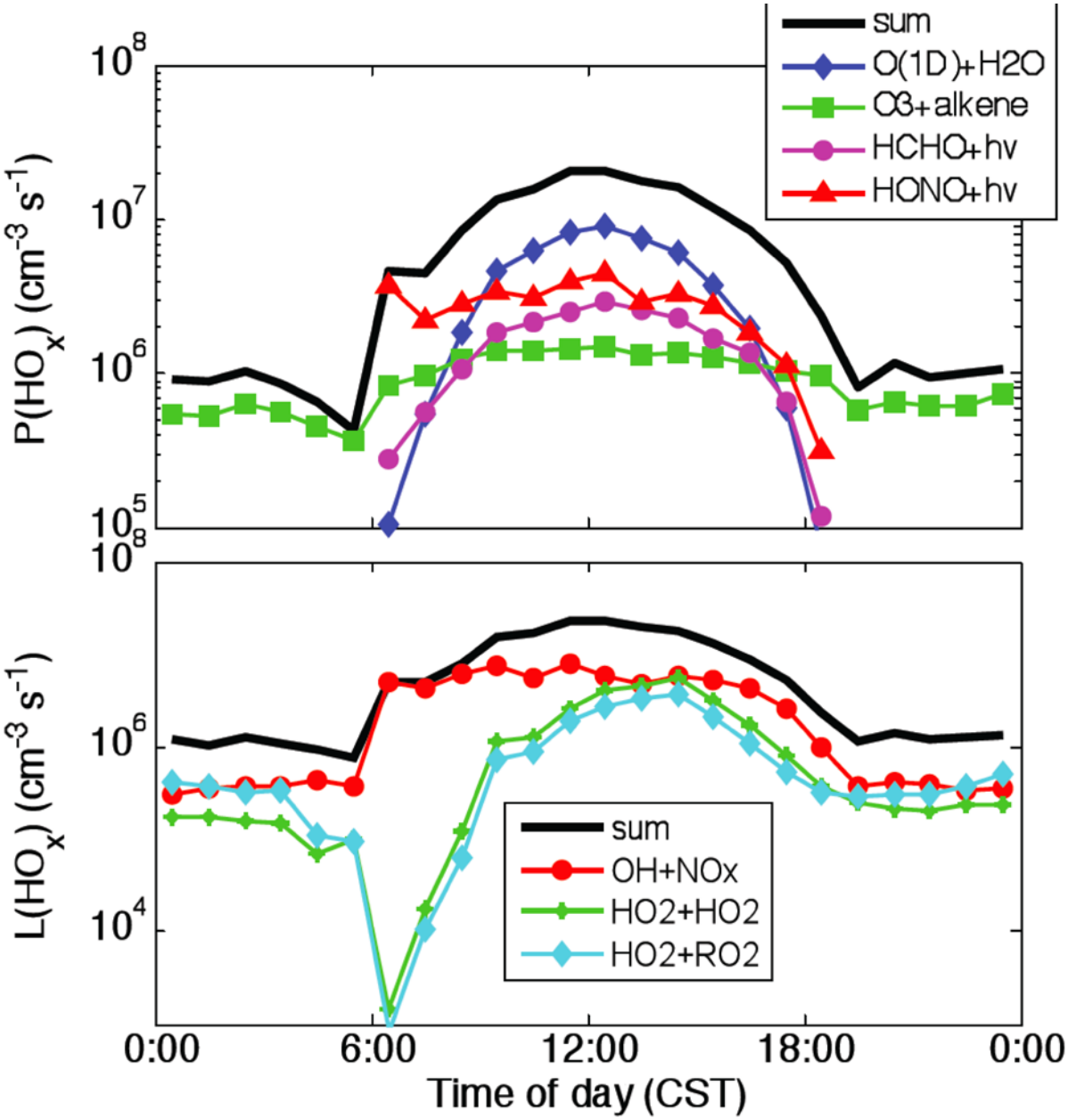
HONO photolysis: 22%

HCHO photolysis: 13%

O_3+alkenes: 13%

L(HOx) SHARP:

- dominant loss: OH + NO_2



Xinrong Ren and Bill Brune (2011)

Heterogeneous HONO formation not understood

R4. $2NO_2 + H_2O + surface \rightarrow HONO + HNO_3$

R5. $NO_2 + H_2O + surface\ reduced\ site \rightarrow HONO + surface\ oxidized\ site + OH^-$

R6. $NO + NO_2 + H_2O + surface \rightarrow 2HONO$

R7. $HNO_3 + NO + glass\ surface \rightarrow HONO + NO_2$

R8. $HNO_3 + HOA\ sfc \rightarrow HONO$

Note: Dark rxns appear to be SLOW.

Finlayson-Pitts, B.J., Wingen, L.M., Sumner, A.L., Syomin, D., Ramazan, K.A., "The heterogeneous hydrolysis of NO2 in laboratory systems and in outdoor and indoor atmospheres: an integrated mechanism" Physical Chemistry Chemical Physics 5 (2), 223–242, 2003.

Ziemba, L., Dibb, J., Griffin, R., Anderson, C., Whitlow, S., Lefer, B., Rappenglueck, B., and Flynn, J. "Heterogeneous conversion of nitric acid to nitrous acid on the surface of primary organic aerosol in an urban atmosphere", Atmos.

Other HONO formation rxns via photochemistry

R9. $NO_2^* + H_2O \rightarrow OH + HONO$

R10. $NO_2 + h\nu + \text{humic acid} \rightarrow HONO$

R11. $NO_2 + h\nu + \textit{phenol (surface)} + H_2O \rightarrow HONO$

R12. $HNO_{3(\text{glass or leaf surfaces})} + h\nu \rightarrow HONO$

R13. *ortho*-Nitrophenols + hv $\rightarrow$ HONO

R9. Li, S., Matthews, J., and Sinha, A.: Atmospheric hydroxyl radical production from electronically excited NO_2 and H_2O, Science, 319, 1657–1660, doi:10.1126/science.1151443, 2008.

R10. Stemmler, K., Ammann, M., Donders, C., Kleffmann, J., and George, C.: Photosensitized reduction of nitrogen dioxide on humic acid as a source of nitrous acid, Nature, 440, 195–198, doi:10.1038/nature04603, 2006.

R11. George, C., Strekowski, R., Kleffmann, J., Stemmler, K., and Ammann, M.: Photoenhanced uptake of gaseous NO_2 on solidorganic compounds: a photochemical source of HONO?, Faraday Discuss., 130, 195–210, doi:10.1039 b417888m, 2005.

R12a. Zhou, X., He, Y., Huang, G., Thornberry, T., Carroll, M., and Bertman, S.: Photochemical production of nitrous acid on glass sample manifold surface, Geophys. Res. Lett., 29, 1681, doi:10.1029/2002GL015080, 2002.

R12b. Zhou, X., Zhang, N., TerAvest, M., Tang, D., Hou, J., Bertman, S., Alaghmand, M., Shepson, P., Carroll, M., Griffith, S., Dusanter, S., and Stevens, P.: Nitric acid photolysis on forest canopy surface as a source for tropospheric nitrous acid, Nat. Geosci., 4, 440–443, doi:10.1038/NGEO1164, 2011.

R13. Bejan, I., Abd El Aal, Y., Barnes, I., Benter, T., Bohn, B., Wiesen, P., and Kleffmann, J.: The photolysis of ortho-nitrophenols: anew gas phase source of HONO, Phys. Chem. Chem. Phys., 8, 2028–2035, doi:10.1039/b516590c, 2006.

Examples of Recent Related Modeling Studies

- CMAQ
  - Sarwar et al. (2008); Eastern US
  - Czader et al. (2012); Houston
  - Zhang et al. (2012); PRD Region; China
- WRF-Chem
  - Li et al. (2010); Mexico City
  - Li et al. (2011); China
- Parameterizations based on various combinations:
  - Heterogeneous reactions on ground and aerosol surfaces
  - Surface photolysis reaction for HNO_3
  - Surface photolysis reaction for NO_2
  - Reaction of photo-excited NO_2 with water
  - Direct HONO emissions
- Improvement in performance for HONO although the models still under-predicted HONO concentrations in some cases

Scope of AQRP Study

- Identify missing HONO formation pathways and recommend parameterizations based on analysis of SHARP 2009 data (UCLA and UH)
- Extend CAMx surface model to include surface processes for core model species (ENVIRON)
- CAMx modeling of SHARP 2009 period and process analysis (UNC)
- Refinement of surface model parameters based on comparisons of model predictions and SHARP measurements (All team members)

Simplified new/missing HONO sources

Primary emissions (0.8% of NOx emissions) RUN B

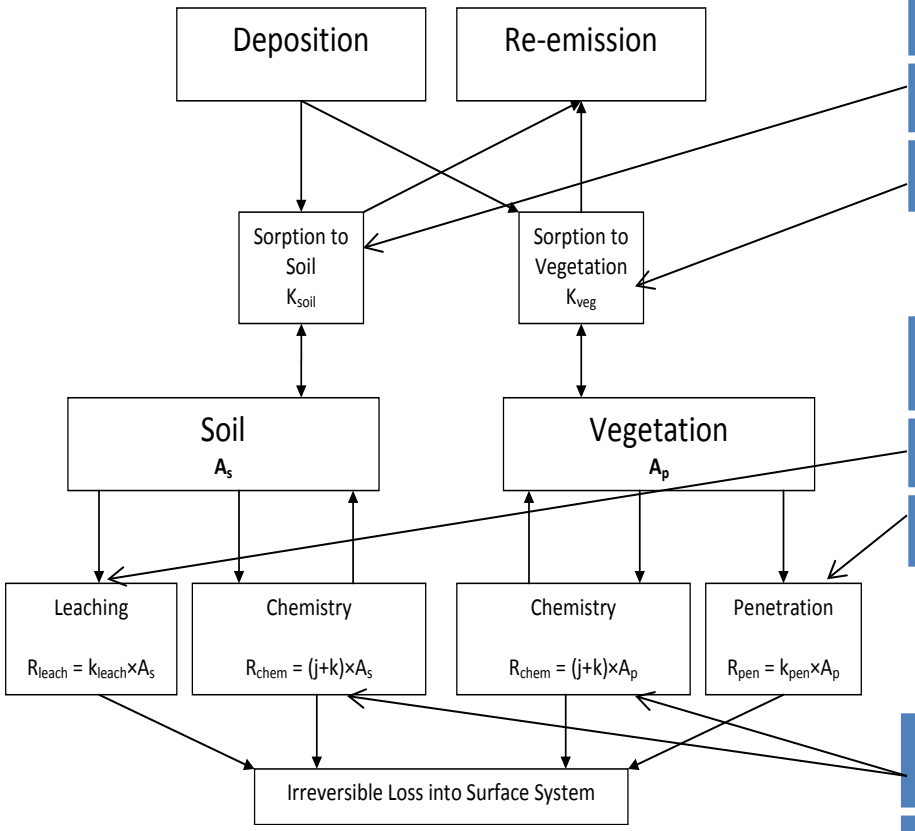
$NO_{2\ (on\ surface)} + (H_2O) \rightarrow HONO$

$NO_{2\ (on\ surface)} + hv \rightarrow HONO$

$HNO_{3\ (on\ surface)} + h\nu \rightarrow HONO$

RUN H

CAMx Surface Model and Key Parameters



Surface-Air Partitioning Coefficients

Parameter	Definition
K_{soil}	Soil-air partitioning coefficient
K_{veg}	Vegetation-air partitioning coefficient

Surface Removal Rates

Parameter	Definition
k_{leach}, min^{-1}	Soil leaching rate
k_{pen}, min^{-1}	Leaf penetration rate

Surface Reaction Rates

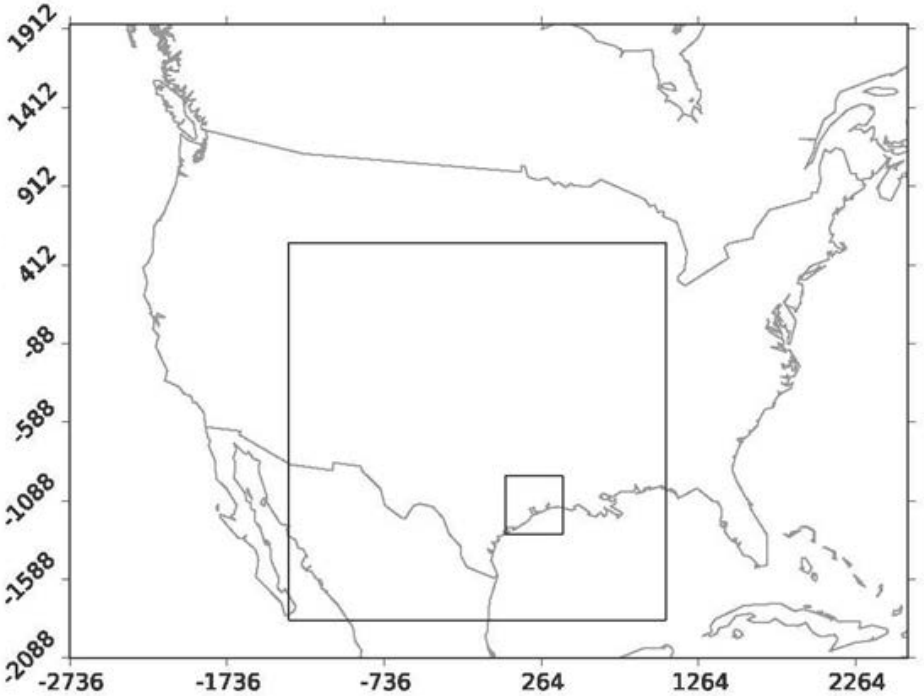
Parameter	Definition
k, min^{-1}	Thermal rate for NO_2
J, min^{-1}	Photolysis rate for HNO_3 & NO_2

Selection/Refinement of Model Parameters

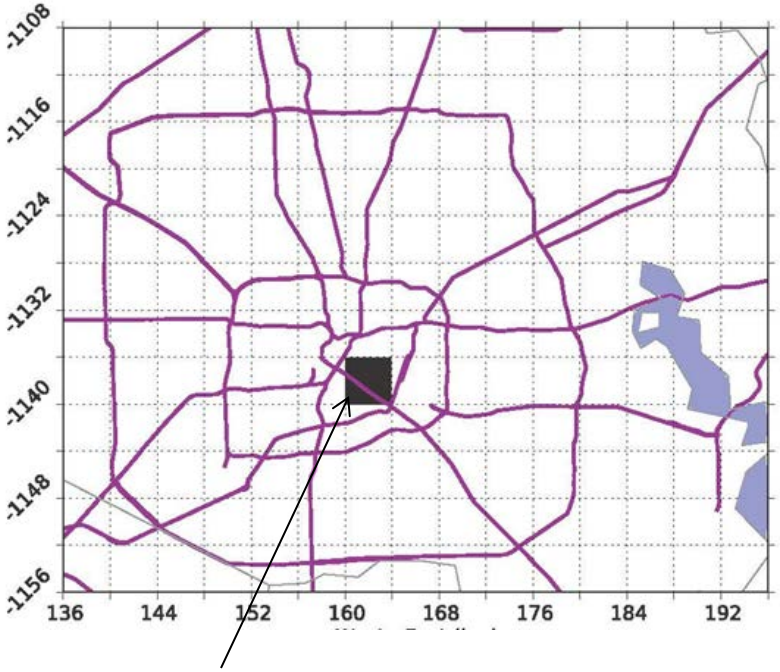
- Based on consideration of the physical and chemical attributes of the relevant species (NO_2, HNO_3, HONO)
- Sensitivity studies varying parameters within range of plausible values
- Evaluation of results, analysis and discussion among team members
- Focus on HONO:NO_2 ratios at night rather than absolute HONO values due to large NO_2 over-predictions on some days

CAMx Modeling Domain and Simulations

Nested 36/12/4 km grid



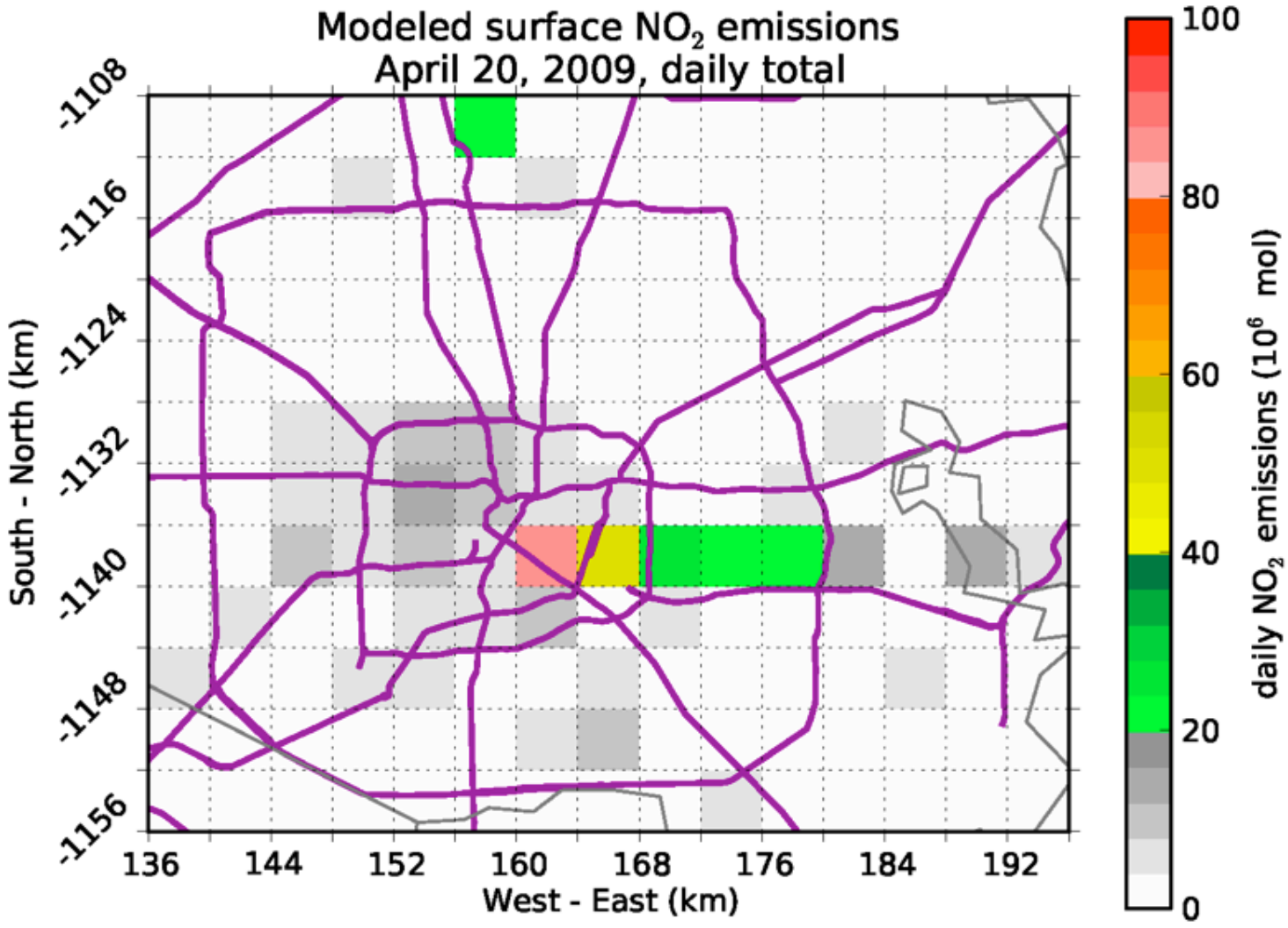
Houston area subdomain



Grid cell containing Moody Tower

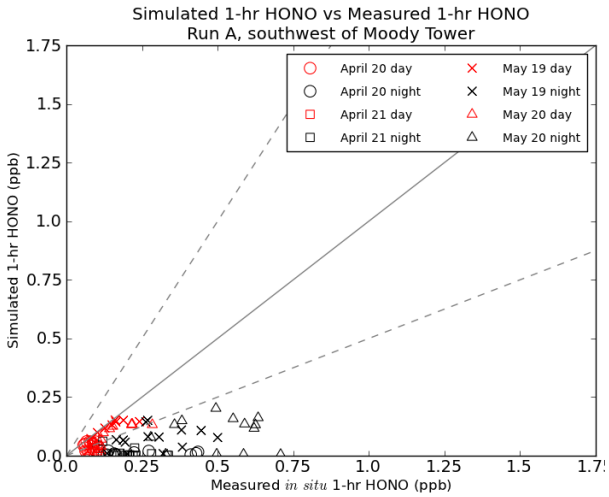
- CAMx 6.1, CB6, WRF-AWR
- Base model (no surface model; no HONO emissions): Run A
- Base model with HONO emissions = 0.8% of surface NO_x emissions: Run B
- Sensitivity studies with different parameter values: Runs C to H
- Analysis for 4 clear days with high O_3 concentrations and some of the highest recorded HONO concentrations during SHARP campaign

NO_2 Emissions



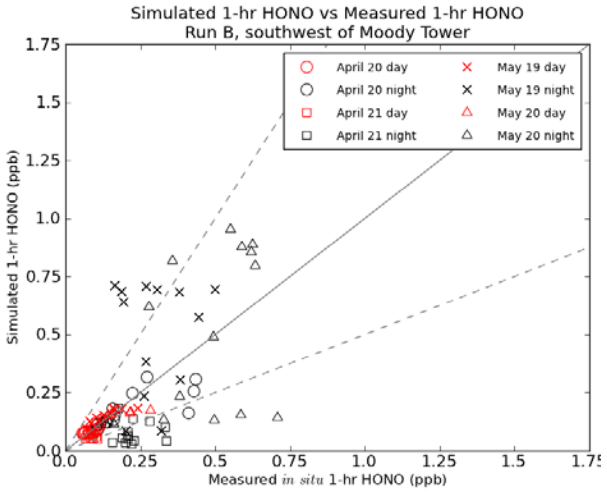
HONO Concentrations

Run A



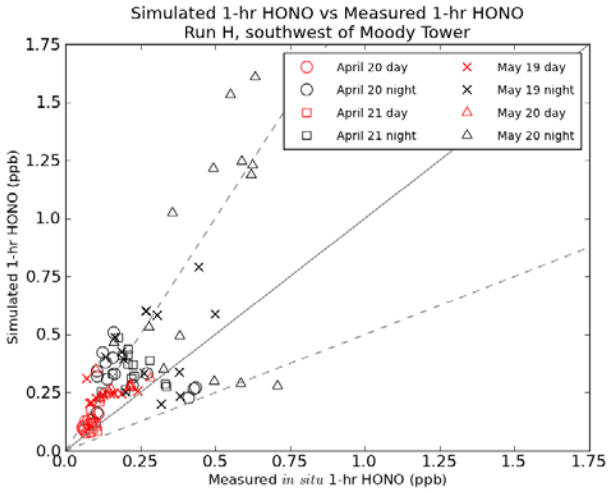
Gas-phase HONO Formation Only

Run B



Gas-phase Chemistry + Direct HONO Emissions

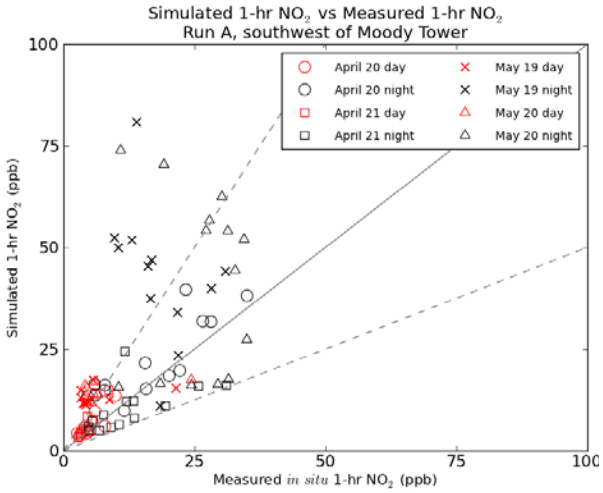
Run H



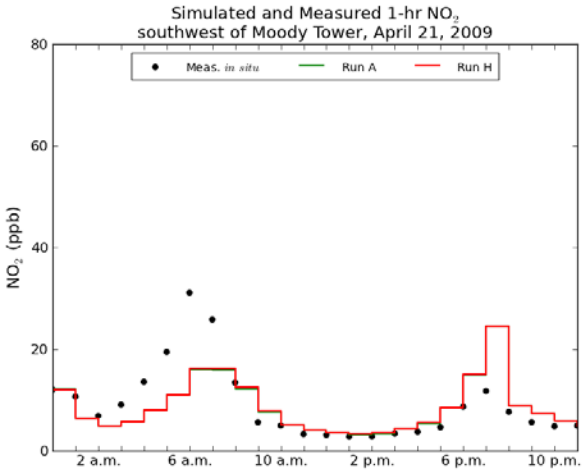
Gas-phase Chemistry + Surface Model

NO_2 Concentrations

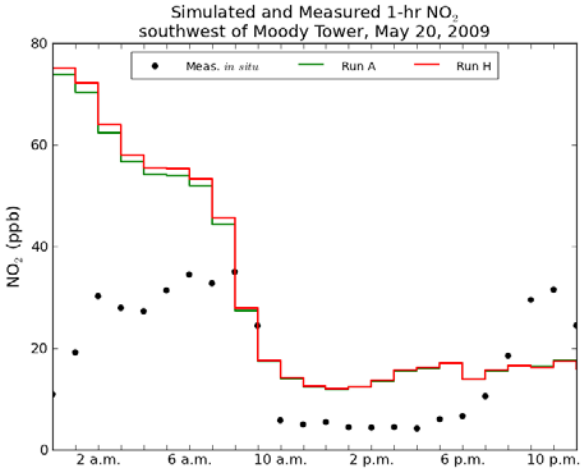
All days



April 21, 2009

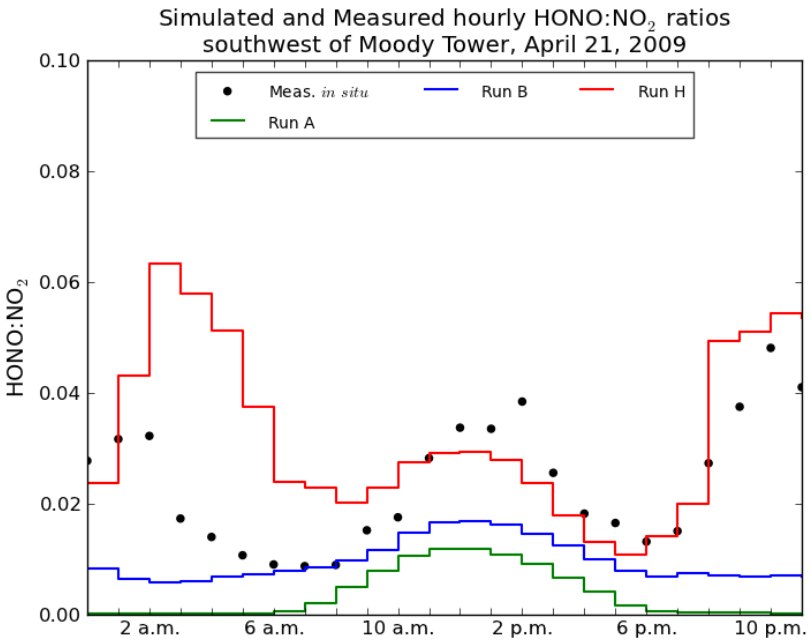


May 20, 2009



HONO:NO_2 Ratios

April 21, 2009



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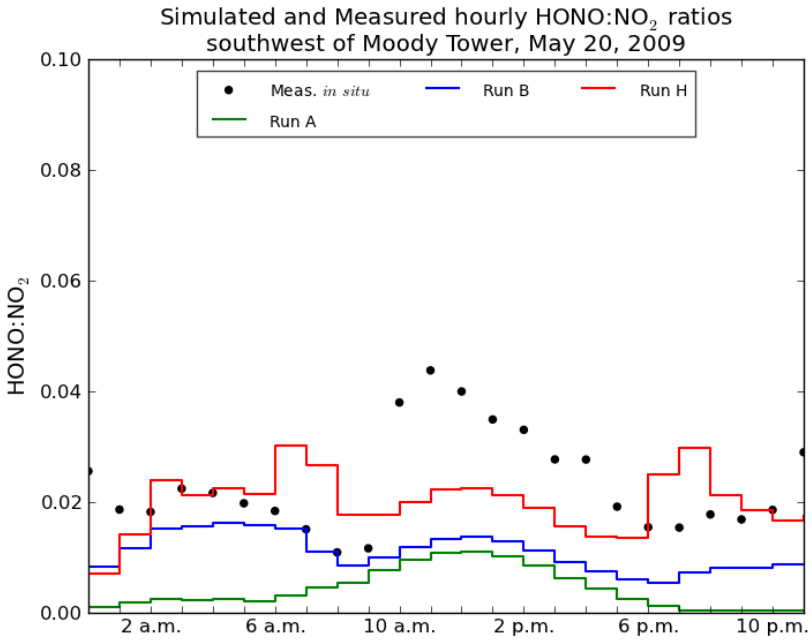
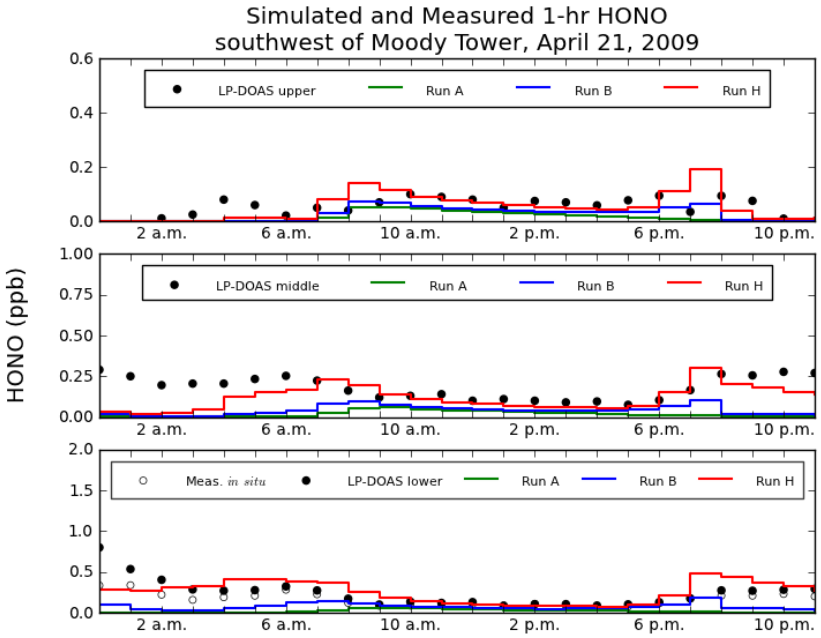
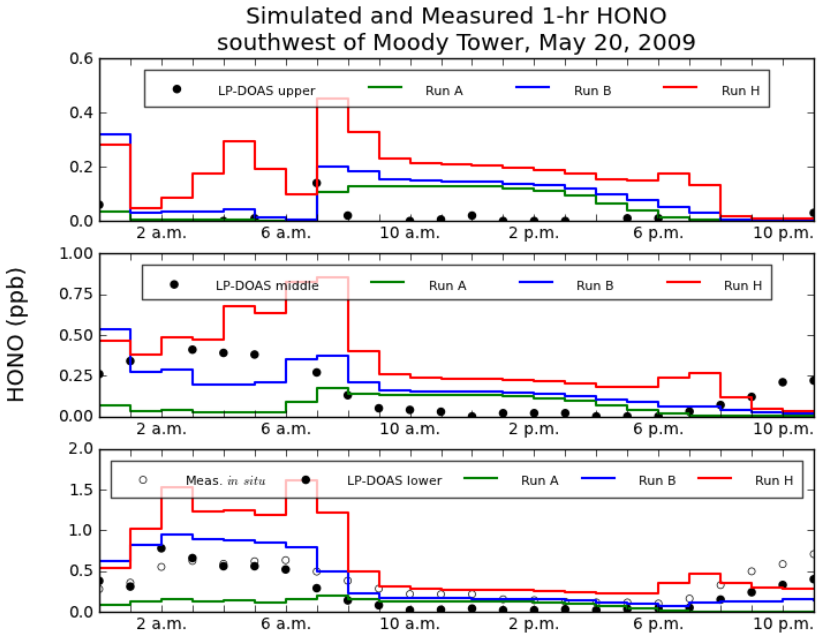


Time Series of HONO Concentrations

April 21, 2009



May 20, 2009



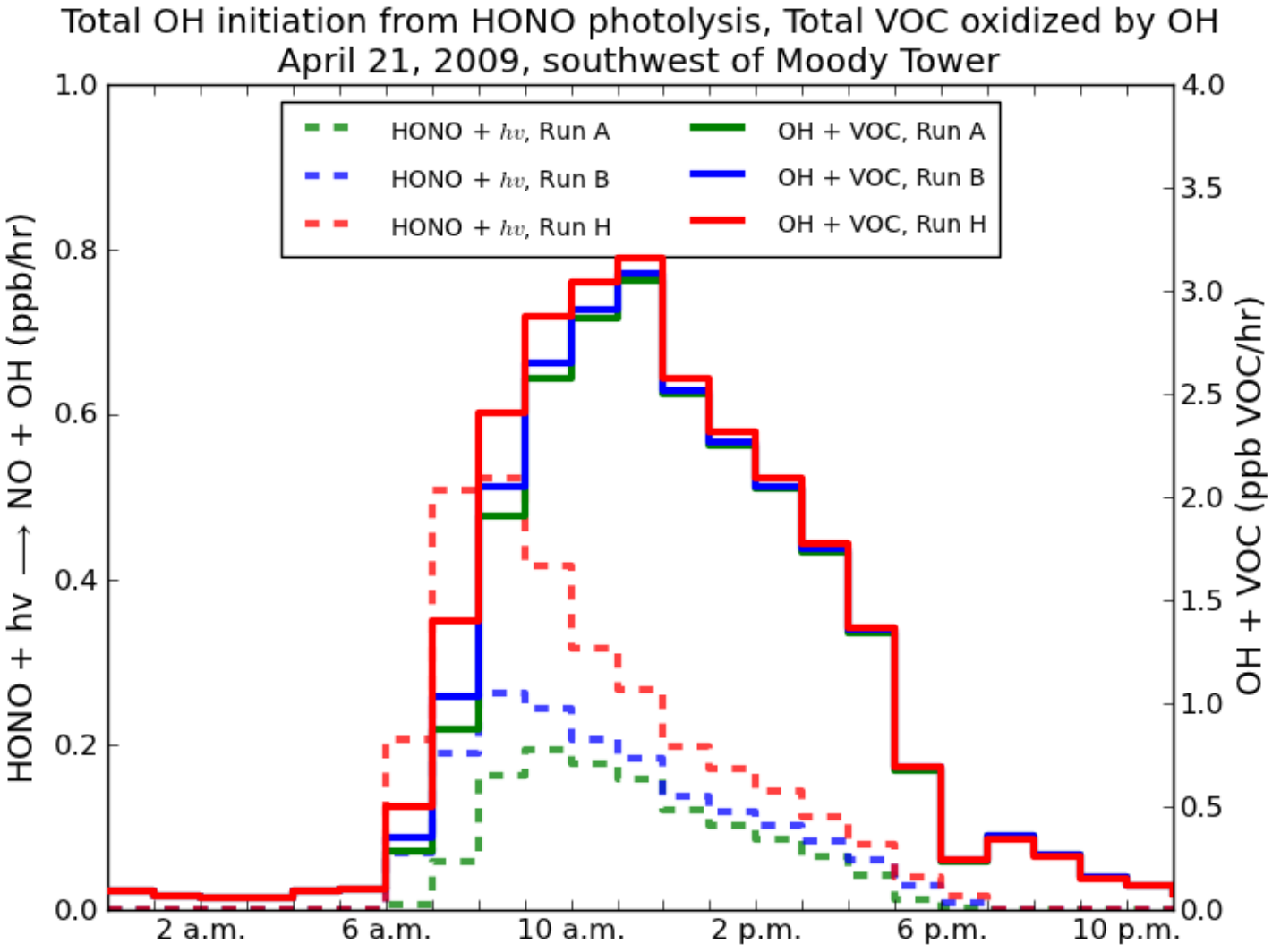
Comparison of HONO Surface Emissions

Date	Run B		Run H	
	µmole/day	ppbv/day	µmole/day	ppbv/day
April 20, 2009	1.07	25.8	2.52	60.3
April 21, 2009	1.06	25.8	2.87	69.9
May 19, 2009	1.09	26.3	4.84	116.9
May 20, 2009	1.08	26.4	6.45	156.9

Model Performance All Days (15 April – 30 May, 2009)

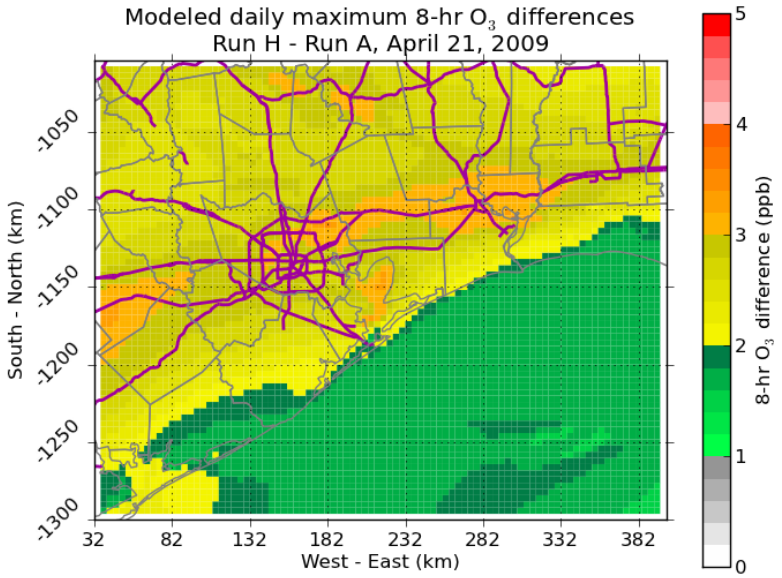
Model Run (Day/Night)	Normalized Mean Bias				
	HONO	NO_2	HNO_3	$HONO:NO_2$	$HONO:HNO_3$
Run A (Day)	-59	70	58	-76	-89
Run A (Night)	-83	83	80	-95	-93
Run B (Day)	-23	69	59	-59	-68
Run B (Night)	-1.5	83	82	-63	-52
Run H (Day)	20	71	72	-29	-63
Run H (Night)	50	86	96	-29	-44

Effect on OH Concentrations

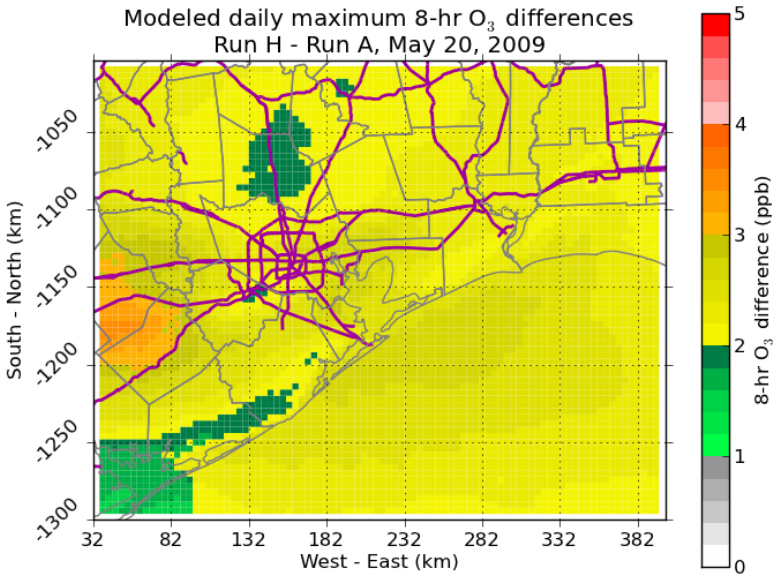


Effect on Daily Max 8-hour Average Ozone Concentrations

April 21, 2009



May 20, 2009



Summary

- New approach to modeling surface HONO formation implemented in CAMx
  - Deposition is not simply a removal process, but a dynamic process that makes deposited mass available for further chemical processing
  - Surface model will be part of core CAMx in future releases
- This AQRP study leveraged SHARP 2009 measurements to refine surface model parameterizations
- Surface model captures many of the observed features in SHARP HONO measurements
- Direct HONO emissions constitute less than 1% of NOx emissions for typical combustion sources and do not explain observed HONO levels and HONO:NO_2 ratios consistently
- HONO produced with the surface model has a substantial impact on morning OH levels, but only minor impacts on daytime OH and daily maximum 8-hour average O_3 concentrations

Acknowledgement

- This research was supported by the State of Texas through the Air Quality Research Program (AQRP) administered by The University of Texas at Austin by means of a grant from the Texas Commission on Environmental Quality (TCEQ), AQRP Project 12-028

- TCEQ has not yet reviewed the final project report and has not fully reviewed the findings presented here

- Alpine Geophysics