Heterogeneous HONO sources and ozone chemistry in Houston, Texas

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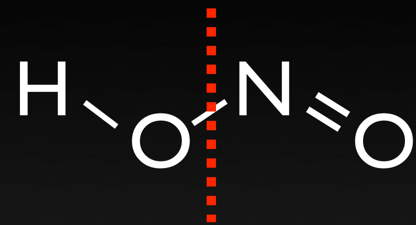
Nitrous acid is an important radical source.



- Early morning photolysis of HONO initiates radical formation before major sources of radicals (HCHO and O_3 photolysis) kicks in.

- Field campaigns and lab experiments point to new sources (direct emissions and heterogeneous chemistry).

- Regulatory models do not include these new HONO sources and under predict HONO concentrations.

- Measurements show a strong vertical HONO gradient with higher concentrations near the ground.

Heterogeneous chemistry is missing from models.

Homogeneous (gas phase only)

$NO + OH \longrightarrow HONO$

$NO + NO_2 + H_2O \longrightarrow HONO$

Heterogeneous (gas & surfaces)

$HNO_{3ads} + h\nu \longrightarrow NO_{2ads} + OH$

$2NO_{2ads} + H_2O_{ads} \longrightarrow HONO_{ads} + HNO_{3ads}$

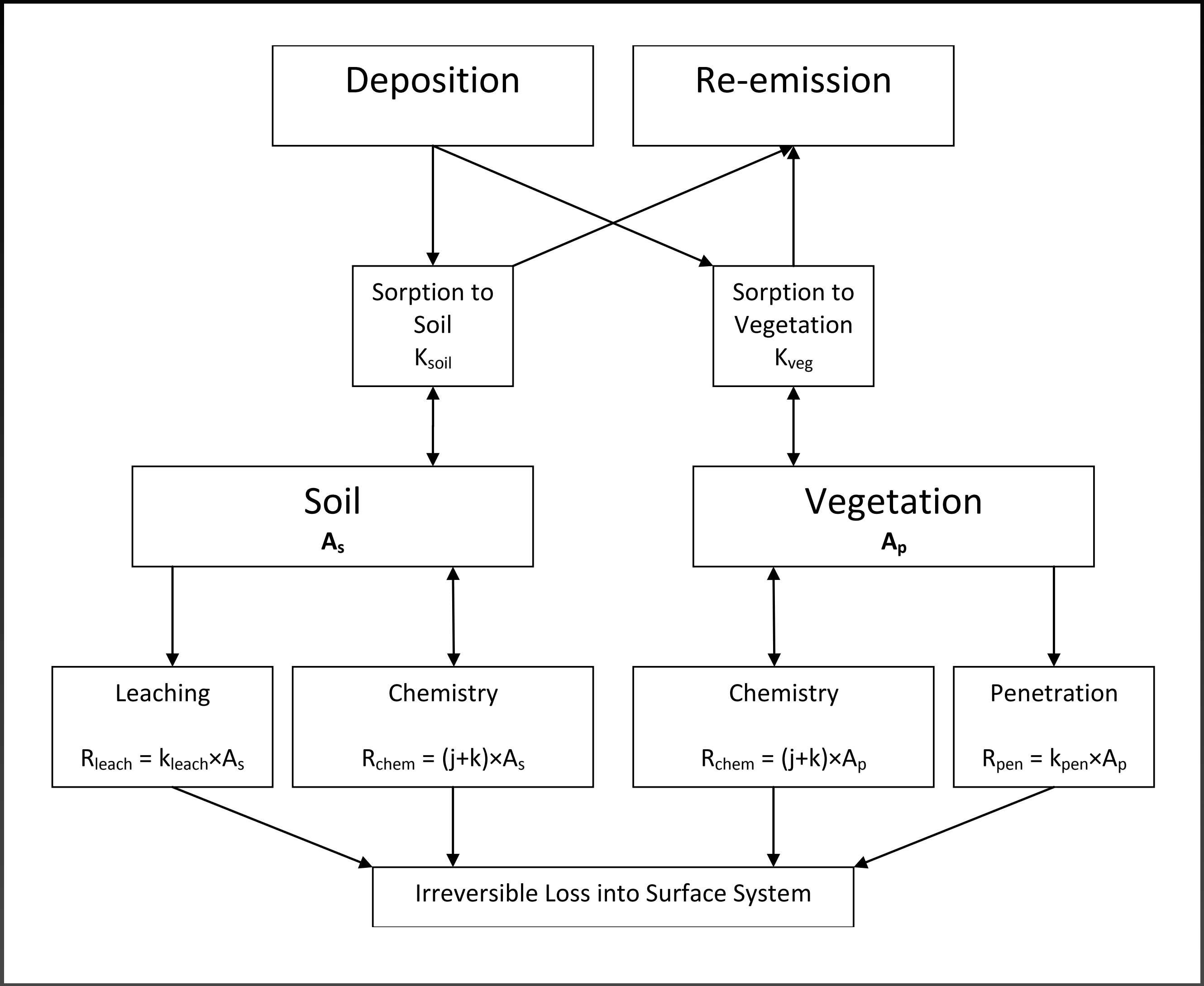
$HA + h\nu \longrightarrow A_{red} + X$

$A_{red} + X \longrightarrow A`$

$A_{red} + NO_2 \longrightarrow A`` + HONO$

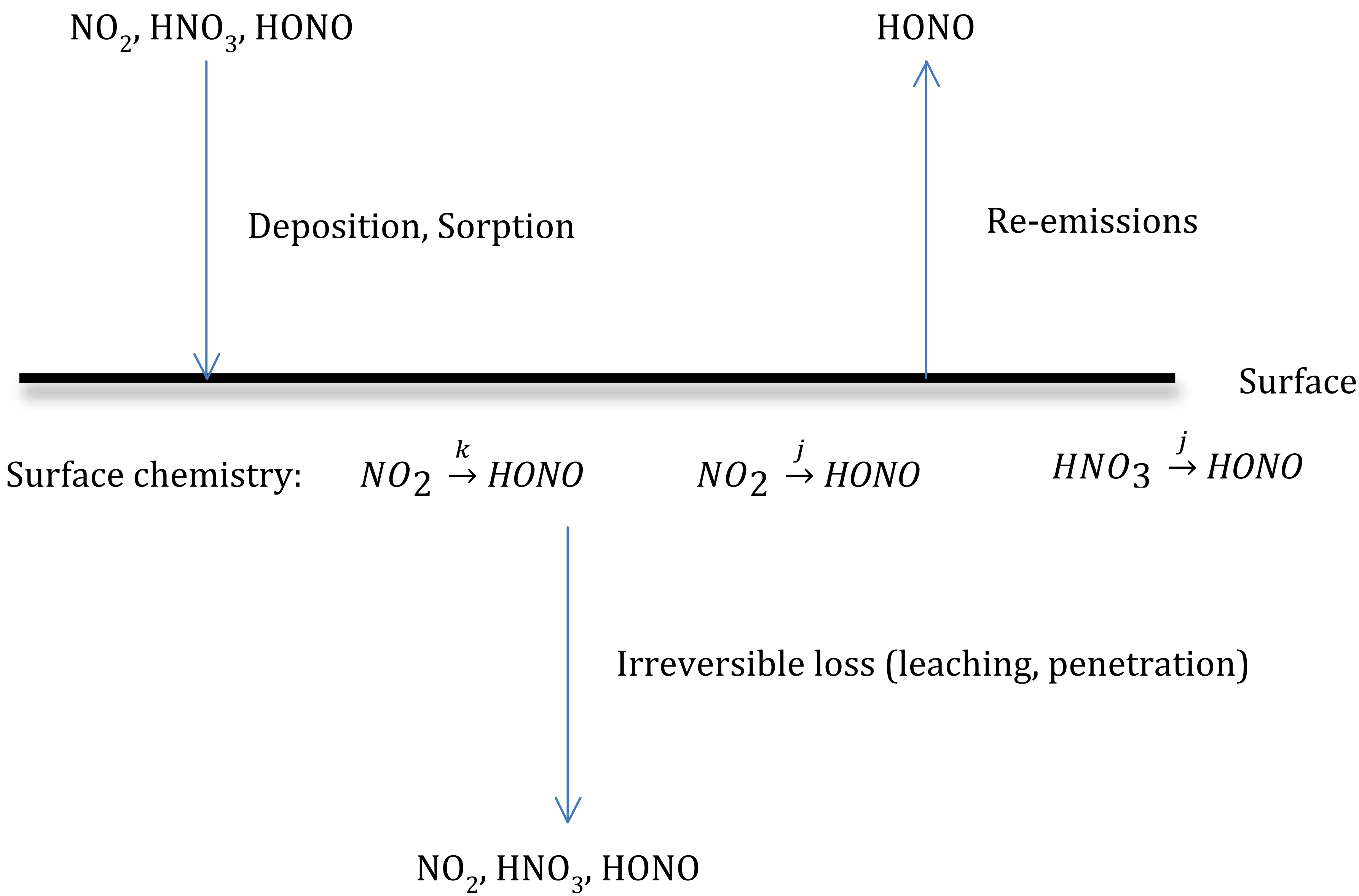
Heterogeneous chemistry has been parameterized using S/V with some success. But this is not a physically accurate description of the real environment.

A new surface sub-model chemically processes HNO_3 and NO_2.

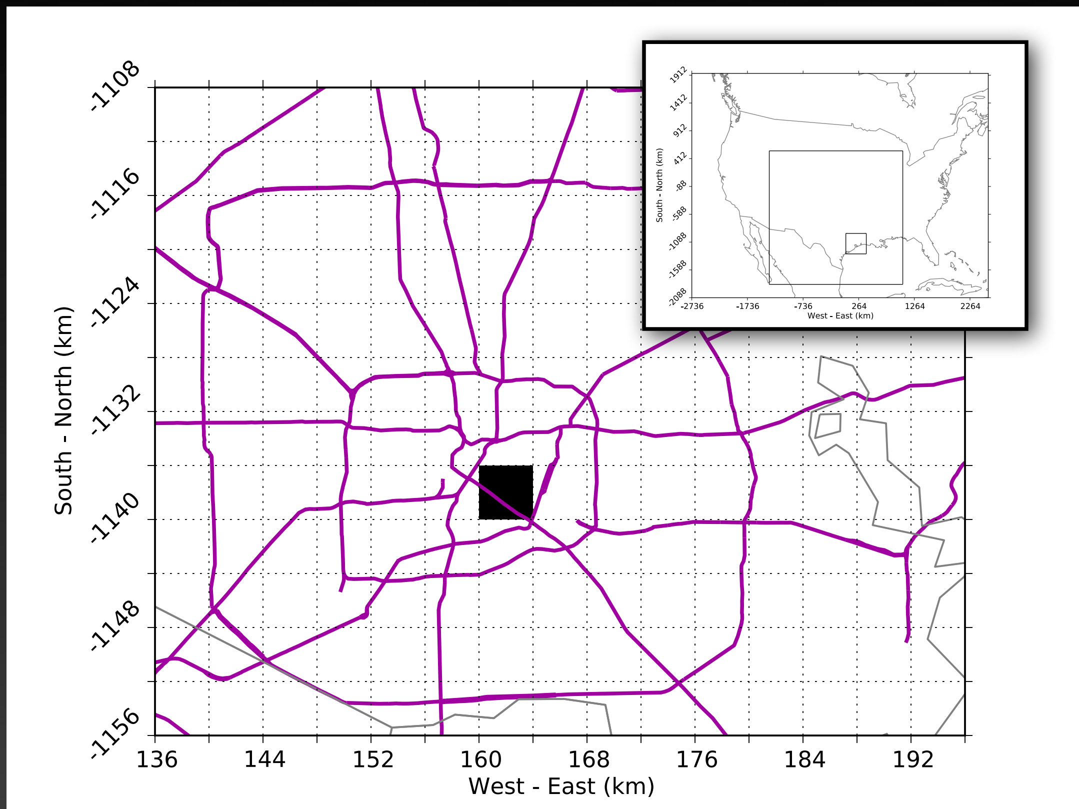


Dry deposition is no longer a total loss process. This is a totally new way of modeling heterogeneous chemistry in air quality models.

HONO Surface Model



New modeling episode aligns with SHARP measurements.



- Alpine Geophysics developed model inputs for 2009
- We are using an unreleased version of CAMx (6.1) with a surface model option
- Model resolution is 4 km over Houston

- Wide array of measurements taken at Moody Tower during SHARP.
- Our analysis focuses on Moody Tower grid cell on April 21, 2009.
- Greatest HONO and O_3 concentrations in April.
- Model data taken from 2nd vertical layer to match height of measurements.

Surface Model Parameters

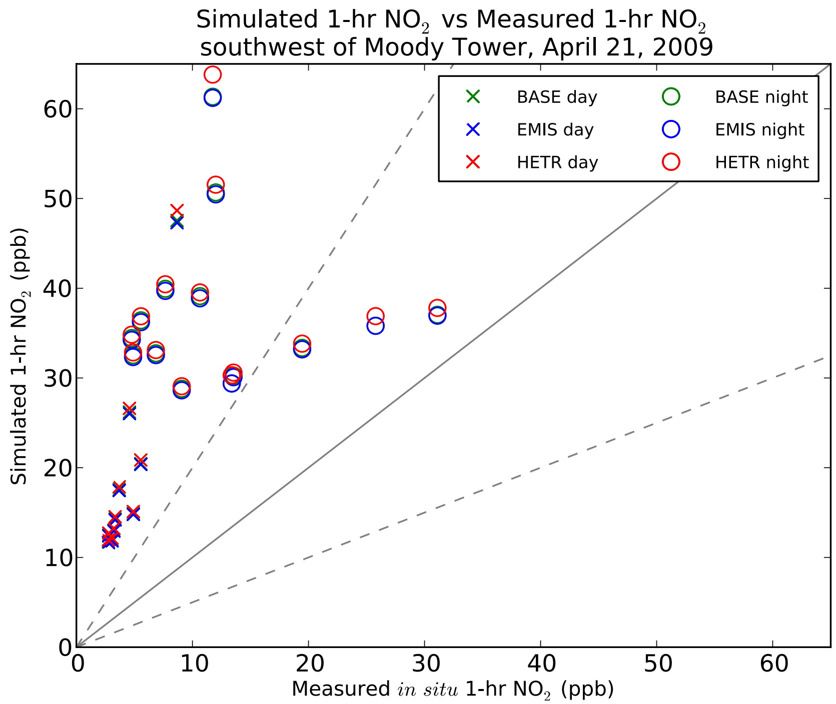
Parameter	Value		
	NO_2	HNO_3	HONO
K_{veg}, unit-less	1.00E+10	1.00E+10	1.00
K_{soil}, unit-less	1.00E+10	1.00E+10	1.00
k_{leach}, min^{-1}	0.01	2.4E-04	4.8E-04
k_{pen}, min^{-1}	0.01	0.01	4.8E-04

Rate Coefficient	Value	
	NO_2 --> HONO	HNO_3 --> HONO
Photolysis Rate Constant (J), min^{-1}	0.01	2.4E-03
Thermal Rate Constant (k), min^{-1}	0.002	0.00

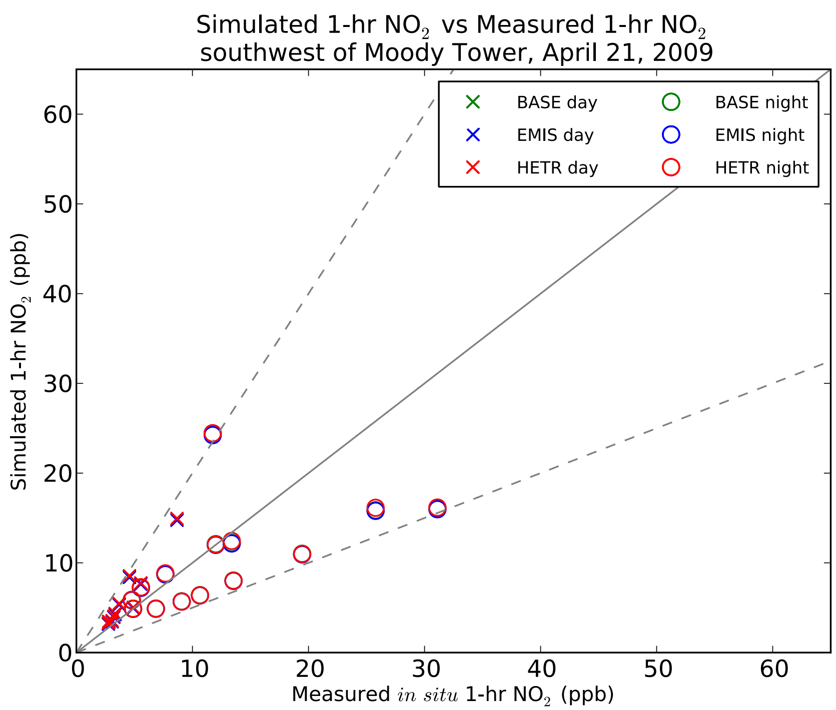
Three different model scenarios.

Scenario	Emission Inventory	Surface Model
BASE	base	no
EMIS	base + 0.8% HONO:NO	no
HETR	base	yes

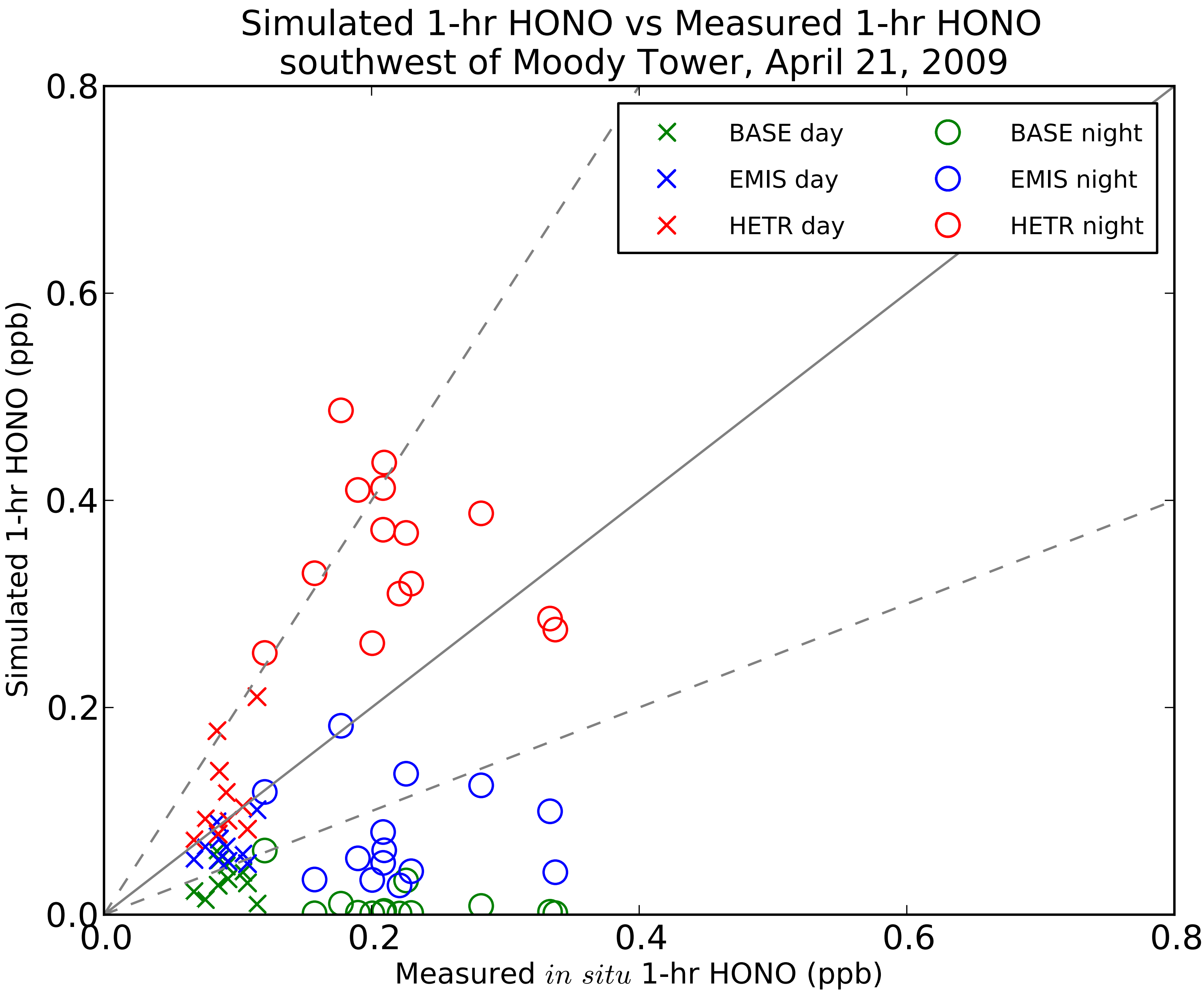
- Does additional HONO formation improve model performance?
- What is the effect on radical budgets and O_3 formation?



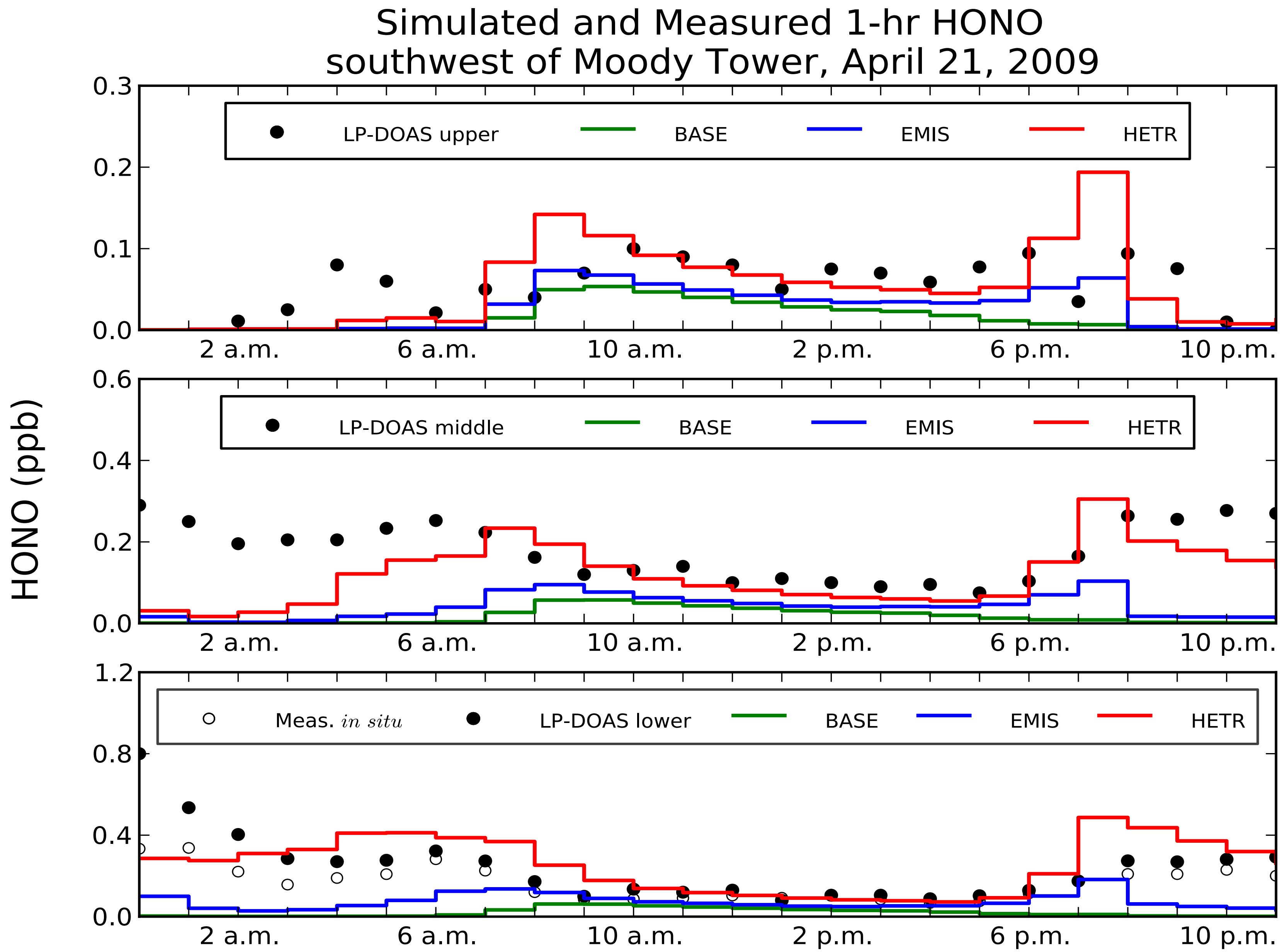
Simulated 1-hr NO2 vs Measured 1-hr NO2
southwest of Moody Tower, April 21, 2009
BASE day
EMIS day
HETR day
BASE night
EMIS night
HETR night
Simulated 1-hr NO2 (ppb)
Measured in situ 1-hr NO2 (ppb)
0
10
20
30
40
50
60

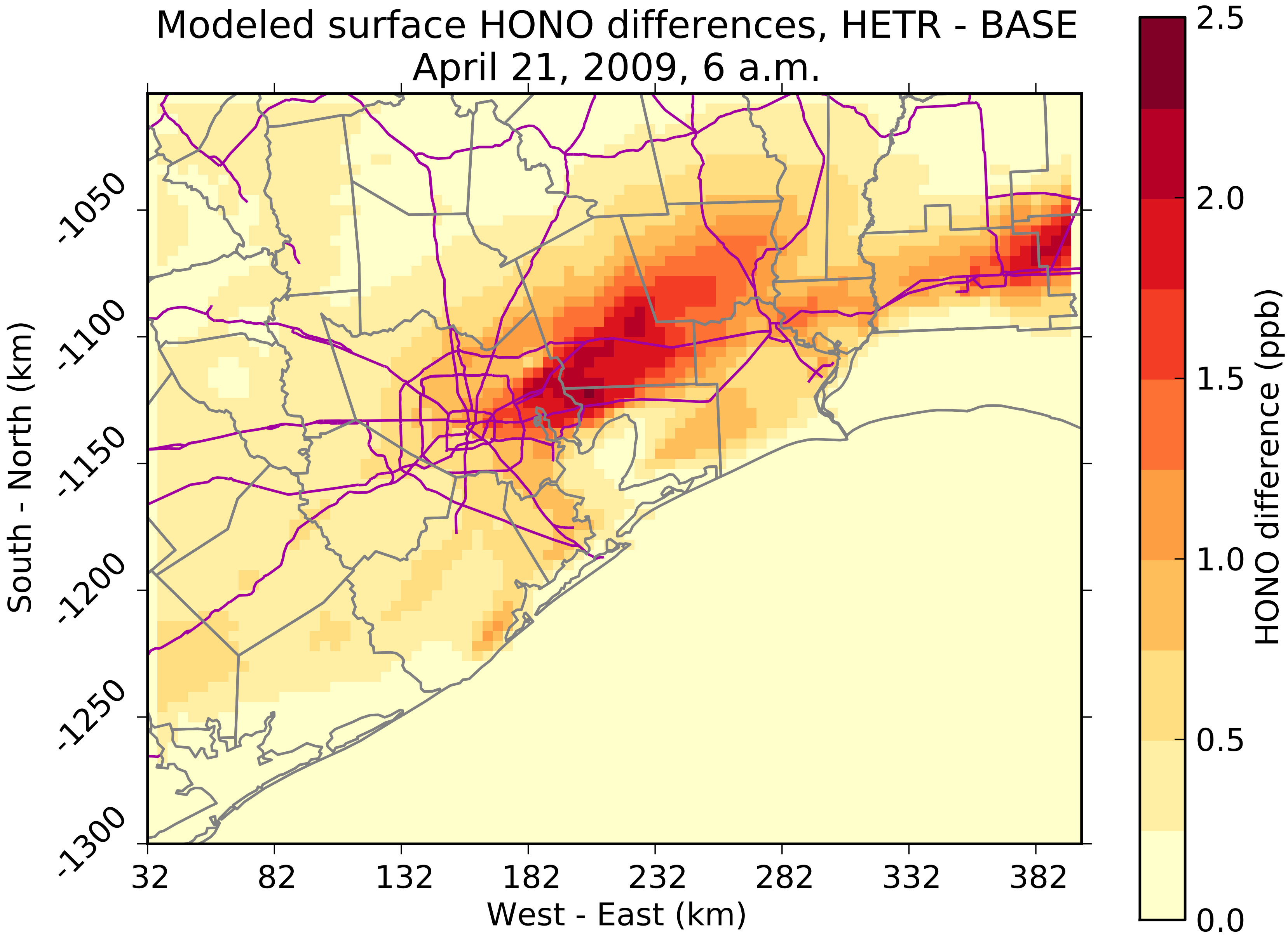


Simulated 1-hr NO2 vs Measured 1-hr NO2
southwest of Moody Tower, April 21, 2009
BASE day
EMIS day
HETR day
BASE night
EMIS night
HETR night
Simulated 1-hr NO2 (ppb)
Measured in situ 1-hr NO2 (ppb)
0
10
20
30
40
50
60

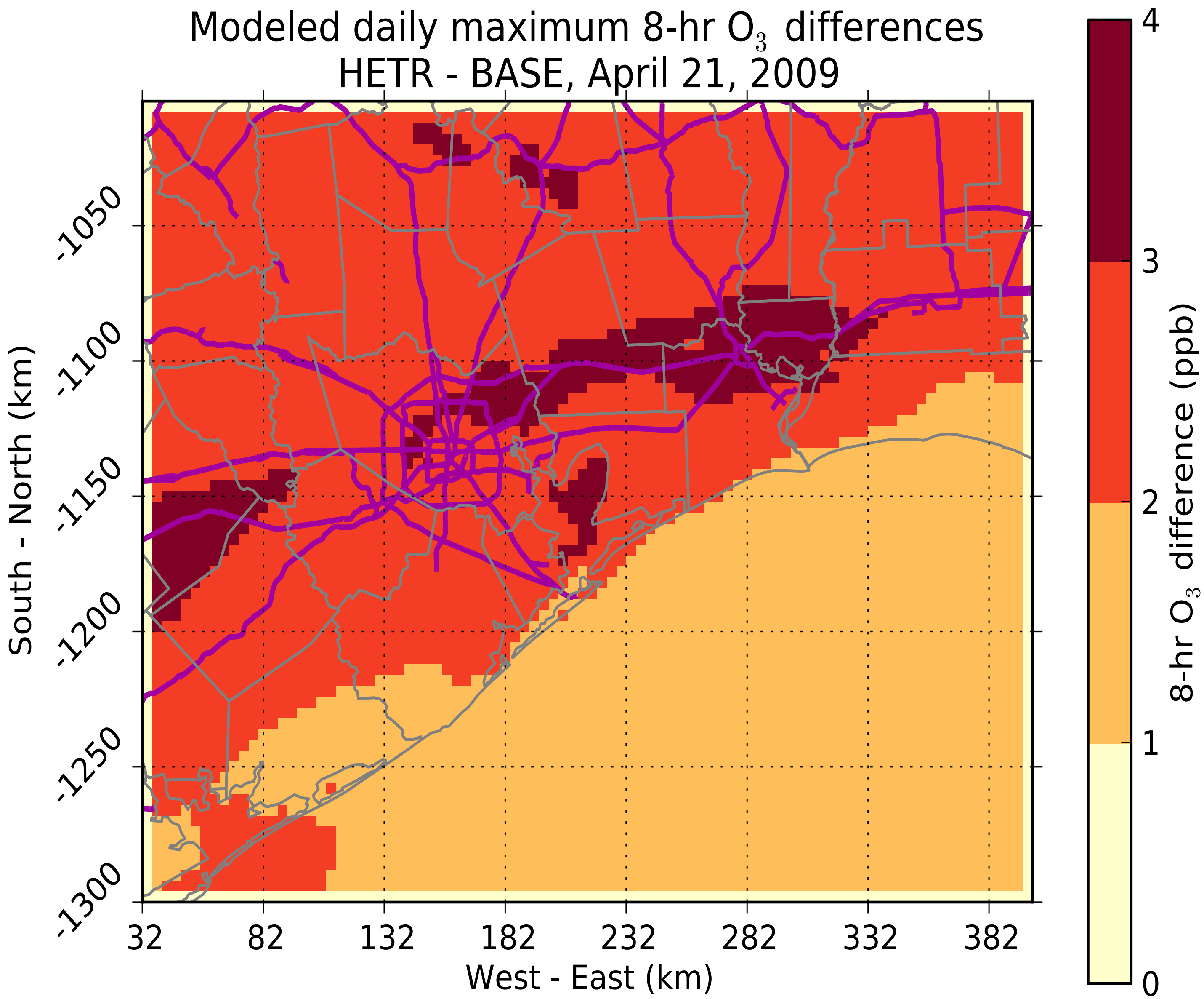


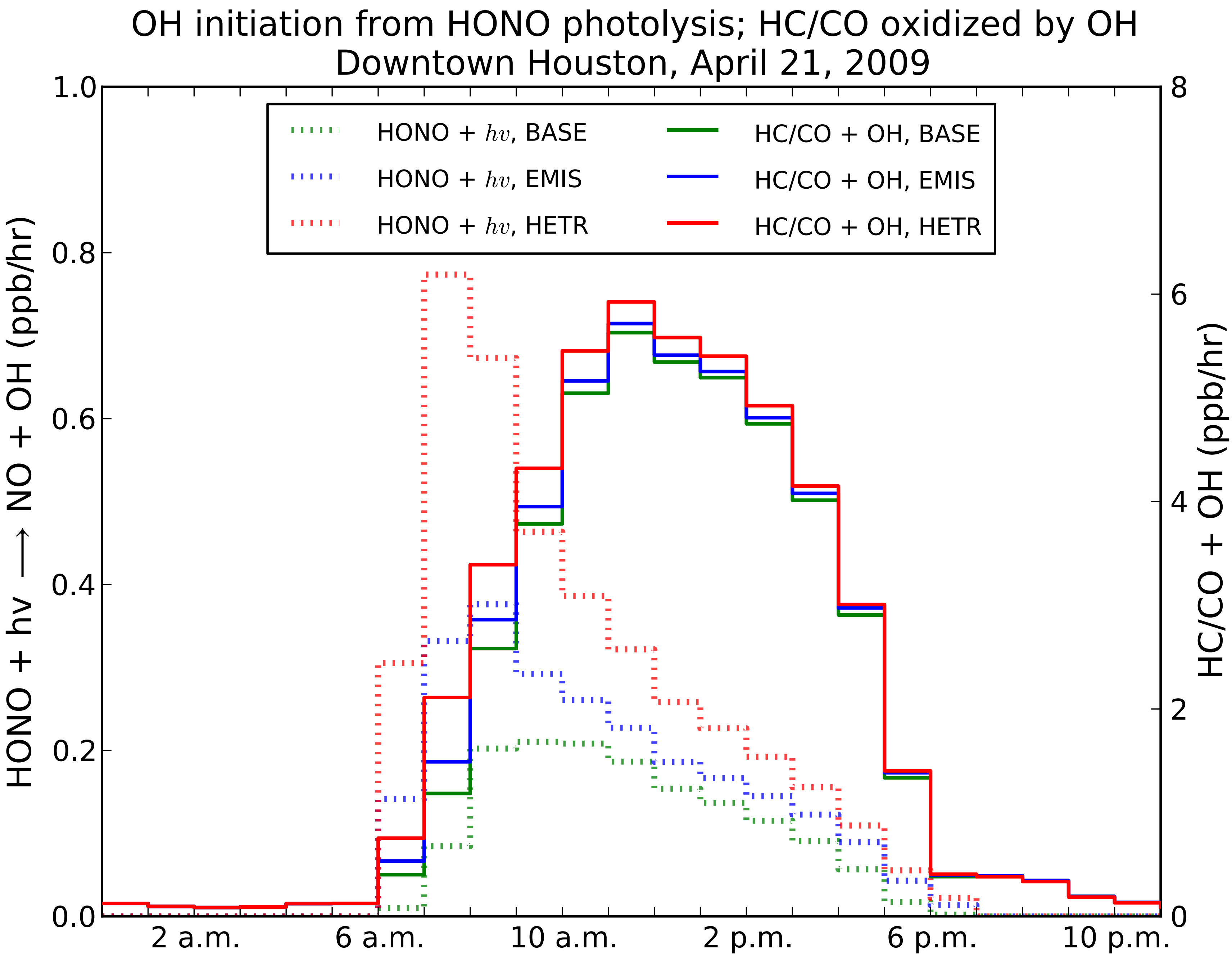
Simulated 1-hr HONO vs Measured 1-hr HONO
southwest of Moody Tower, April 21, 2009
BASE day
EMIS day
HETR day
BASE night
EMIS night
HETR night
Simulated 1-hr HONO (ppb)
Measured in situ 1-hr HONO (ppb)
0.0
0.2
0.4
0.6
0.8


Simulated and Measured 1-hr HONO
southwest of Moody Tower, April 21, 2009
HONO (ppb)
LP-DOAS upper
BASE
EMIS
HETR
LP-DOAS middle
Meas. in situ
LP-DOAS lower
0.0
0.1
0.2
0.3
0.4
0.6
0.8
1.2
2 a.m.
6 a.m.
10 a.m.
2 p.m.
6 p.m.
10 p.m.



Modeled surface HONO differences, HETR - BASE
April 21, 2009, 6 a.m.
South - North (km)
-1050
-1100
-1150
-1200
-1250
-1300
32
82
132
182
232
282
332
382
West - East (km)
HONO difference (ppb)
2.5
2.0
1.5
1.0
0.5
0.0


Modeled daily maximum 8-hr O_3 differences
HETR - BASE, April 21, 2009
South - North (km)
-1050
-1100
-1150
-1200
-1250
-1300
32
82
132
182
232
282
332
382
West - East (km)
8-hr O_3 difference (ppb)
0
1
2
3
4



OH initiation from HONO photolysis; HC/CO oxidized by OH
Downtown Houston, April 21, 2009
HONO + $h\nu$, BASE
HONO + $h\nu$, EMIS
HONO + $h\nu$, HETR
HC/CO + OH, BASE
HC/CO + OH, EMIS
HC/CO + OH, HETR
HONO + hv ⟶ NO + OH (ppb/hr)
HC/CO + OH (ppb/hr)
0.0
0.2
0.4
0.6
0.8
1.0
0
2
4
6
8
2 a.m.
6 a.m.
10 a.m.
2 p.m.
6 p.m.
10 p.m.

Conclusions

- Feasibility of a non-parameterized approach
- Heterogeneous production dominates
- Strong NO2 dependence
- Capture daytime HONO
- Night predictions a challenge

Thank You

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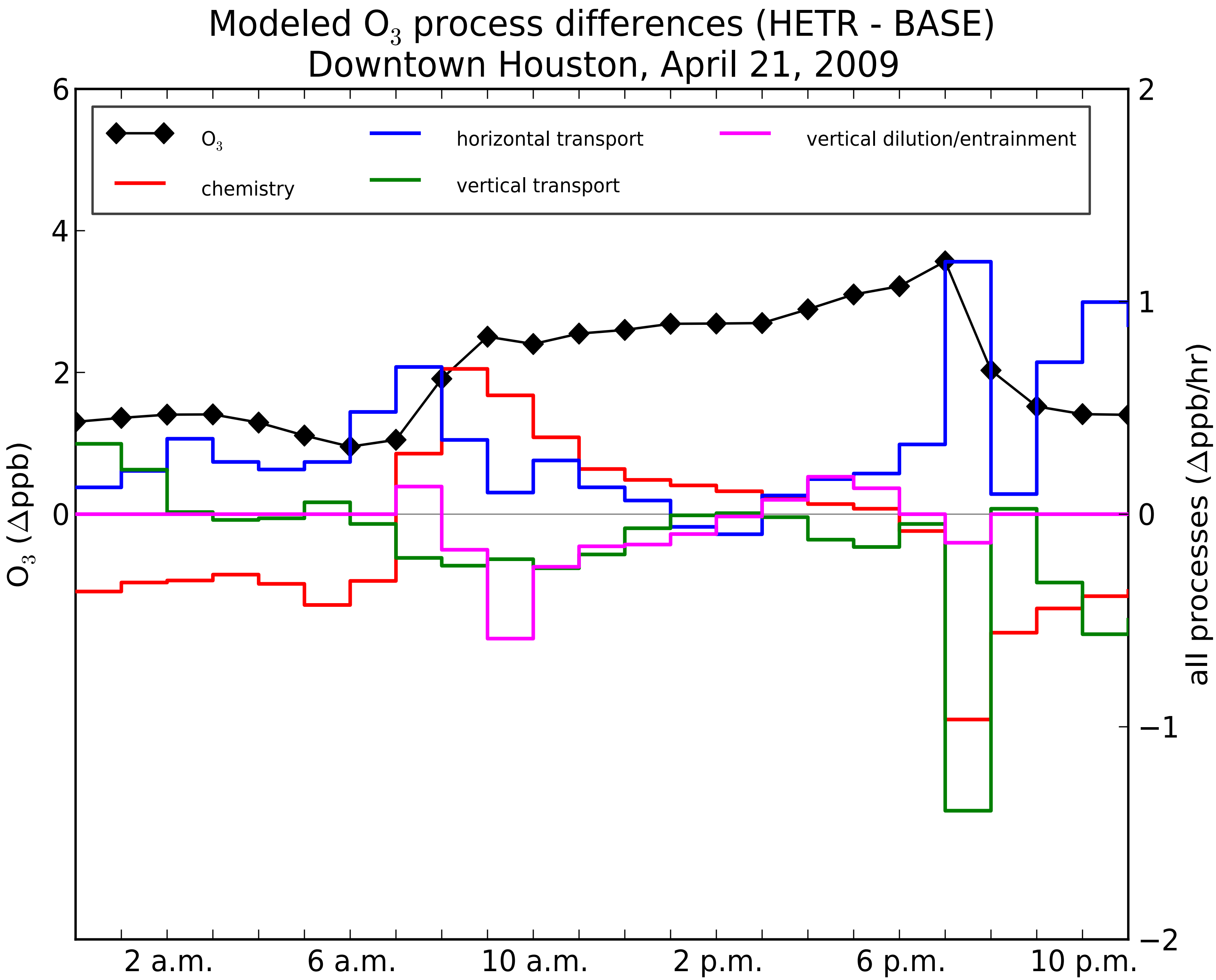
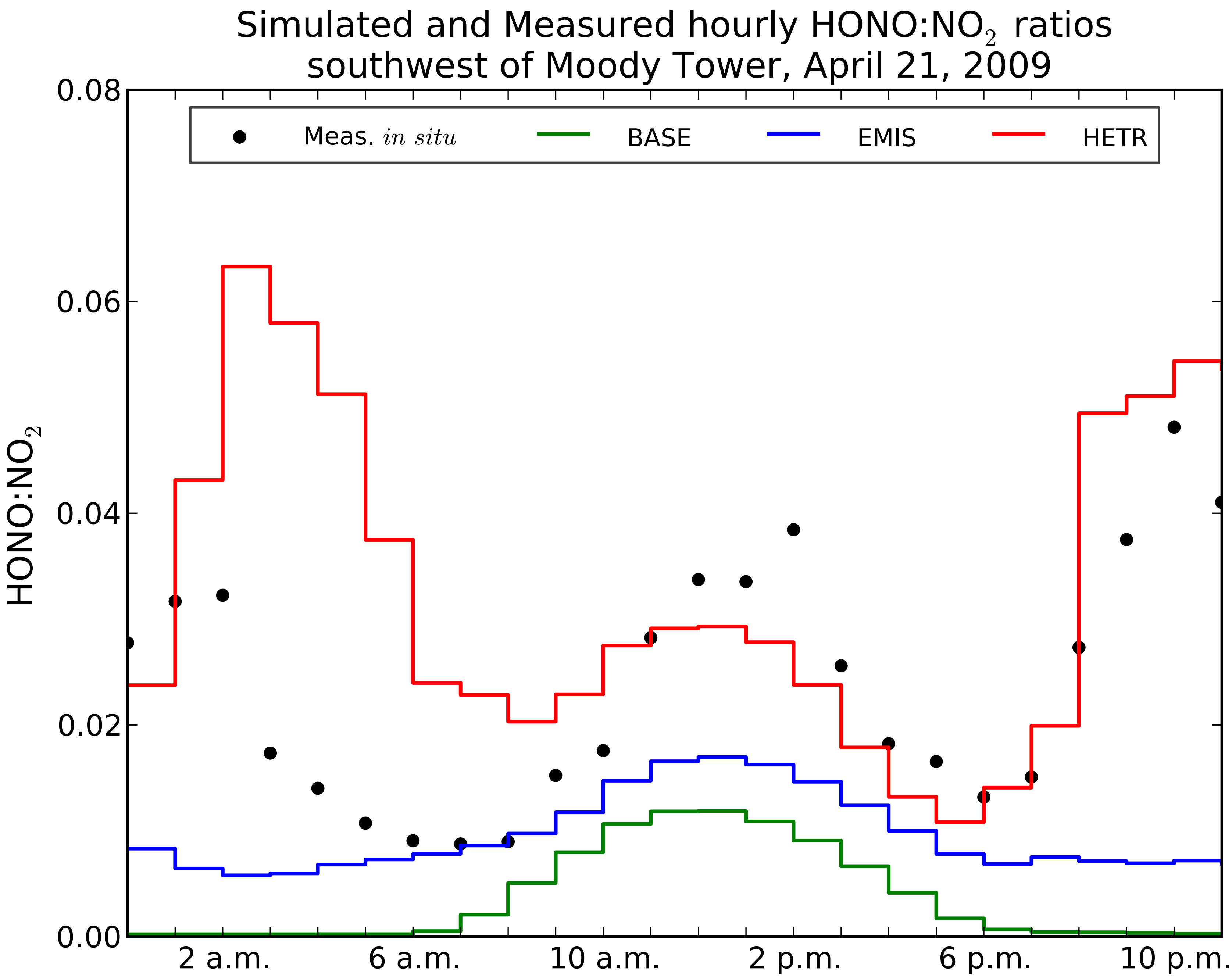
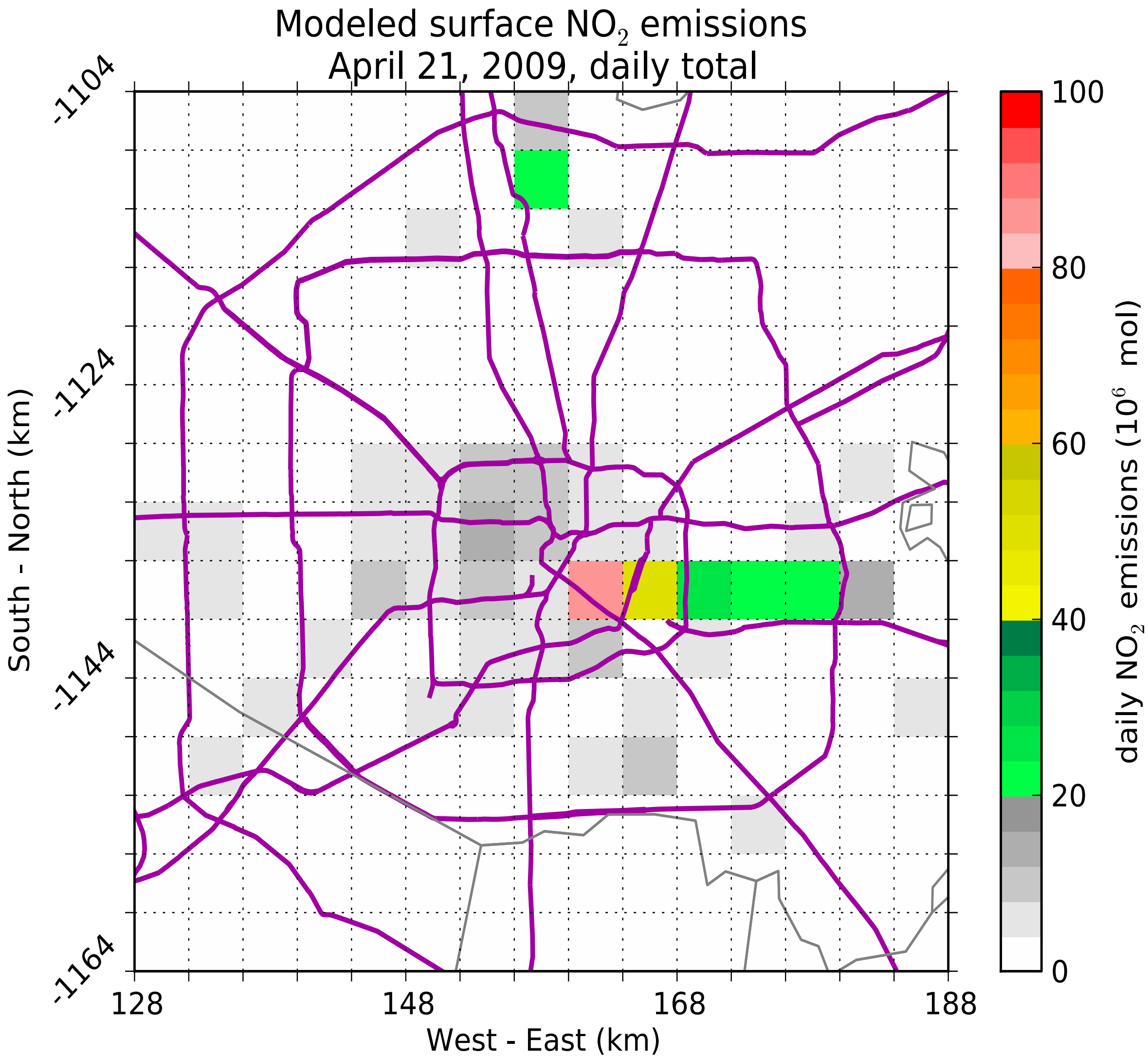


Modeled O_3 process differences (HETR - BASE)
Downtown Houston, April 21, 2009
O_3
horizontal transport
vertical dilution/entrainment
chemistry
vertical transport
6
4
2
0
2
1
0
−1
−2
O_3 (Δppb)
all processes (Δppb/hr)
2 a.m.
6 a.m.
10 a.m.
2 p.m.
6 p.m.
10 p.m.

	BASE	EMIS	HETR
Radical initiation			
OH	6.16	6.85	8.23
HO2	7.46	7.50	7.58
RO2	11.70	11.72	11.78
Radical Propagation			
OH	49.84	51.21	54.21
HO2	27.52	28.29	29.43
other HO2	2.58	2.64	2.91
RO2	9.00	9.17	9.62
Oxidation Reactions			
HC/CO + OH	44.36	45.84	48.60
NO + NO2	80.58	82.81	87.29
Ox production	84.25	86.64	91.30



Simulated and Measured hourly HONO:NO_2 ratios
southwest of Moody Tower, April 21, 2009
Meas. *in situ*
BASE
EMIS
HETR
HONO:NO_2
0.00
0.02
0.04
0.06
0.08
2 a.m.
6 a.m.
10 a.m.
2 p.m.
6 p.m.
10 p.m.



- NO_x over predictions are a concern at the Moody Tower grid cell.
- Large concentrations of NO_x are caused by large emission rates in the ship channel (~6 km to the east).