The Implications of Uncertain NO2 + OH for Ozone and Precursors

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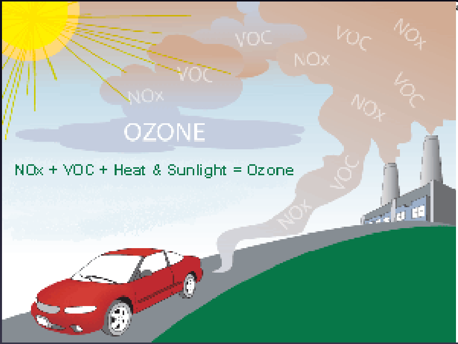
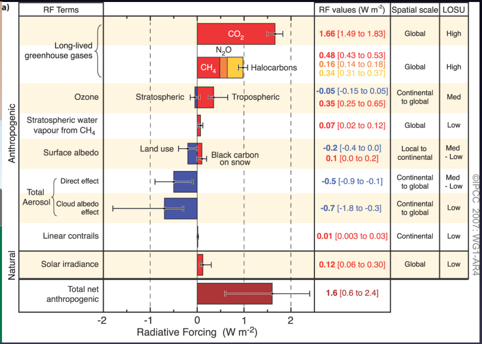
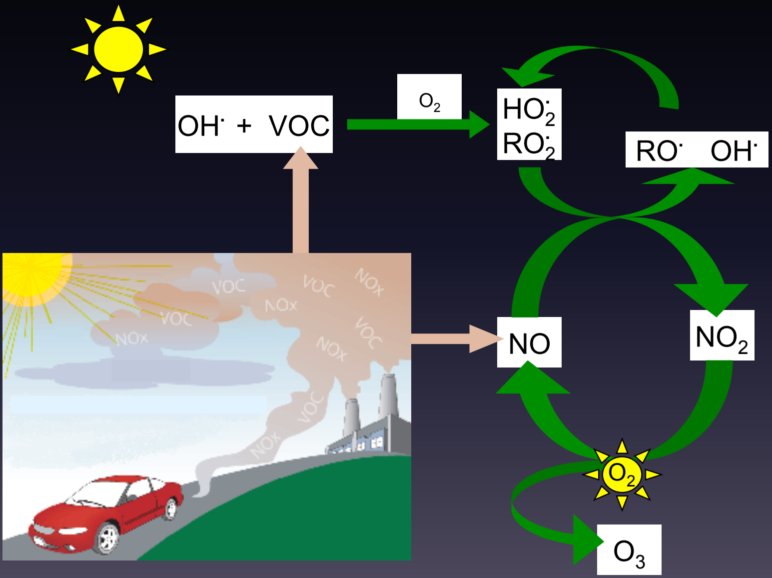
Ozone Overview

- Secondary chemical: not emitted, but formed
- National Ambient Air Quality Standard criteria pollutant
- Third largest positive short-lived climate forcer





Ozone Chemical Formation Primer



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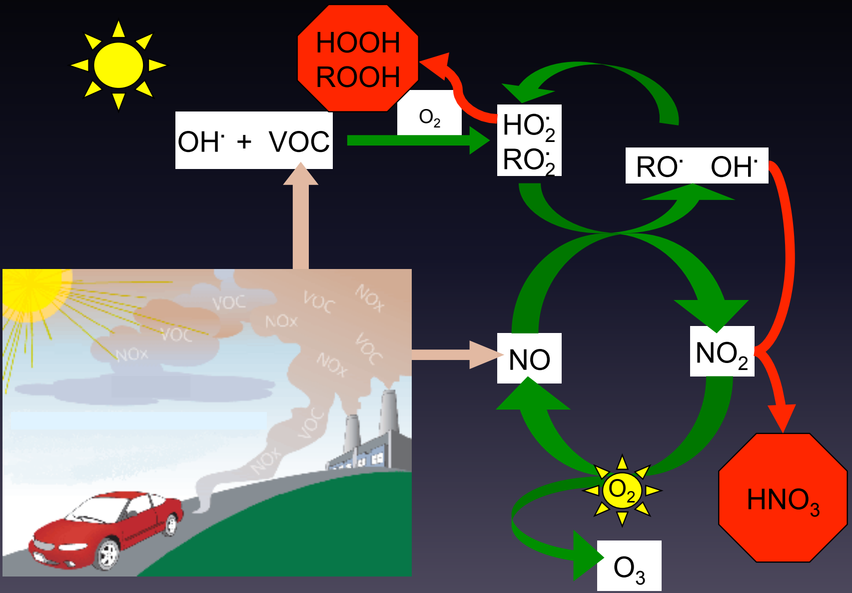
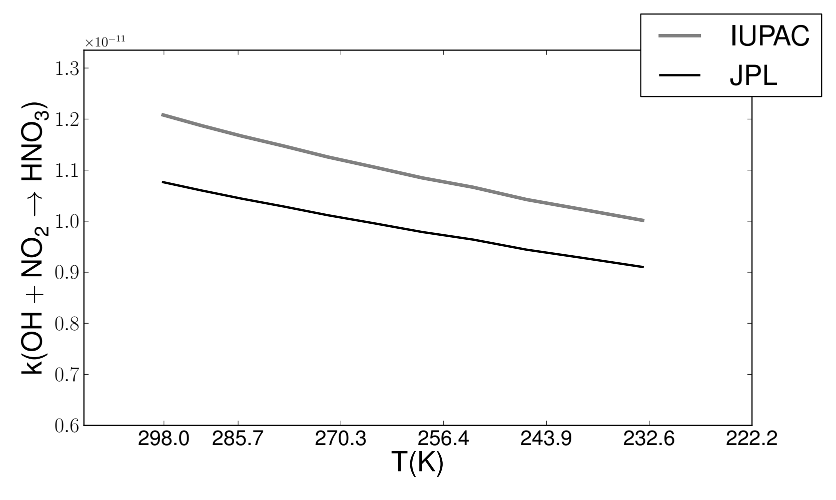


$NO_2 + HO^{\cdot} \rightarrow HNO_3$: Important, Uncertain



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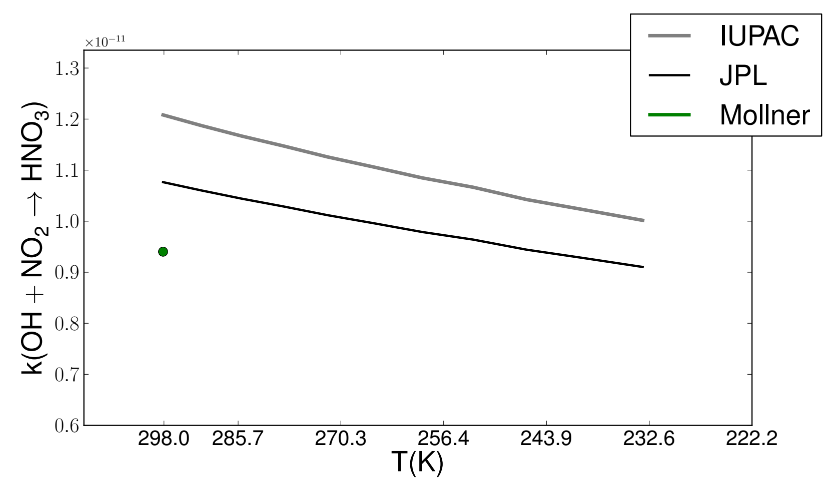

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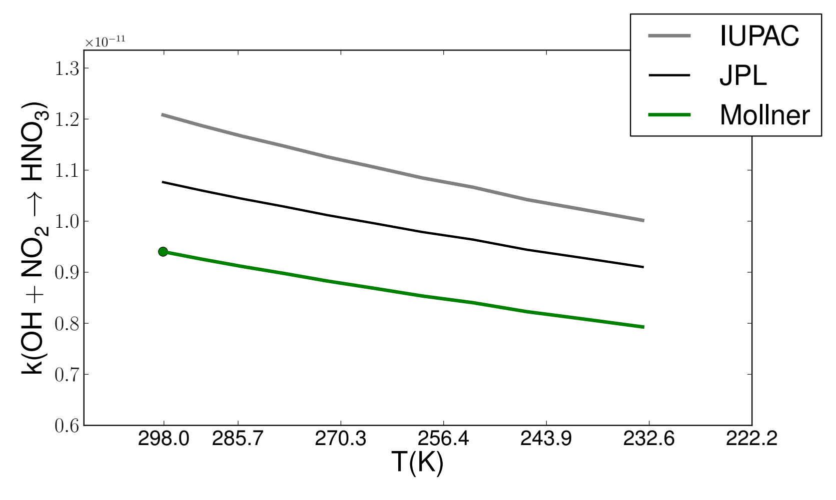

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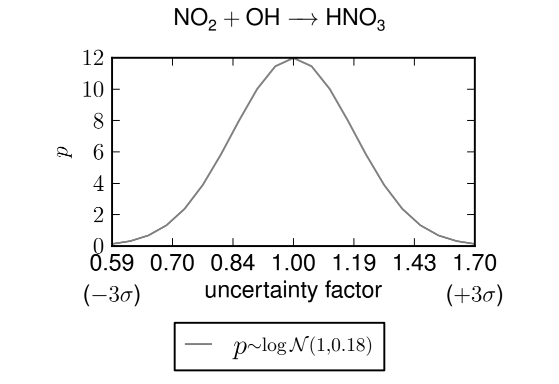
Modeling framework

- Simulates air parcels post-convection event, identified by NO_x/HNO_3
  - Initial conditions from aircraft measurements
  - Stochastic model of subsidence following convection
  - Mixing with background air
  - ISORROPIA for aerosol partitioning
  - Heterogeneous reactions for N2O5, HO2, NO2, etc.
  - Gas-phase chemistry: **GEOS-Chem** and Carbon Bond ’05
- Results: under-predicts NO_2 and over-predicts oxidation rate

Henderson et al., ACP 2011

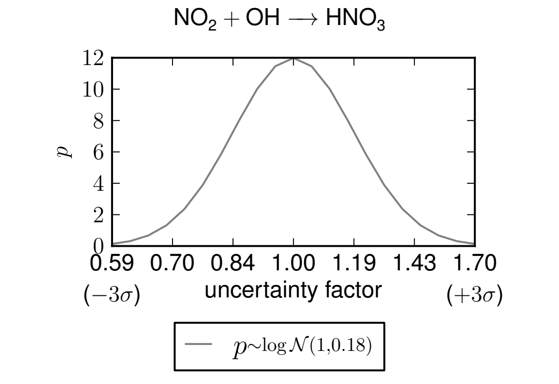
Constraining $K(\mathrm{NO_2} + \mathrm{OH})$ from observations

- Uncertainty range from Jet Propulsion Laboratory Kinetic Data Evaluation 2011



Constraining $K(\mathrm{NO_2} + \mathrm{OH})$ from observations

- $\mathbf{p} = p(K_{-3\sigma}), ..., p(K_{3\sigma})$



Constraining $K(\mathrm{NO_2} + \mathrm{OH})$ from observations

- $\mathbf{p} = p(K_{-3\sigma}), ..., p(K_{3\sigma})$
- Using model results, we calculate the likelihood of the observations given each possible rate ($L(O|K)$)

$$\mathbf{L} = \prod_i \hat{f}_{-3\sigma}(o_i), ..., \prod_i \hat{f}_{3\sigma}(o_i)$$

Constraining $K(\mathrm{NO_2 + OH})$ from observations

- $\mathbf{p} = p(K_{-3\sigma}), ..., p(K_{3\sigma})$
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- Bayes Theorem

$$\mathbf{P} = \frac{\mathbf{pL}}{\sum_i \mathbf{pL}}$$

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- $\mathbf{p} = p(K_{-3\sigma}), ..., p(K_{3\sigma})$
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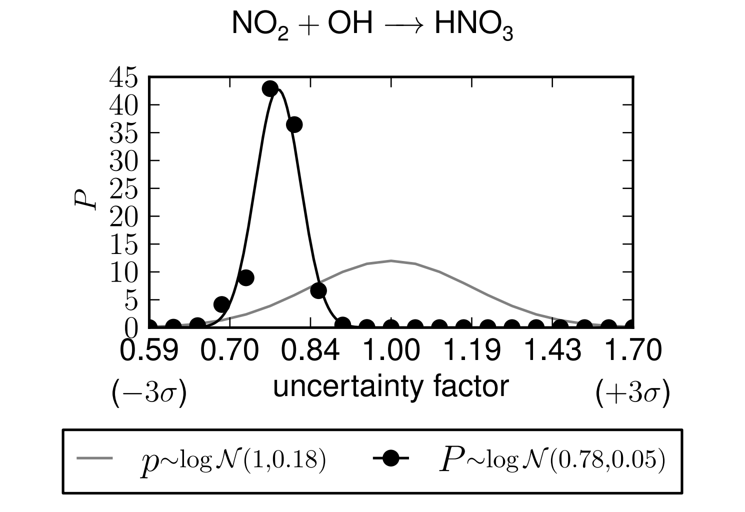
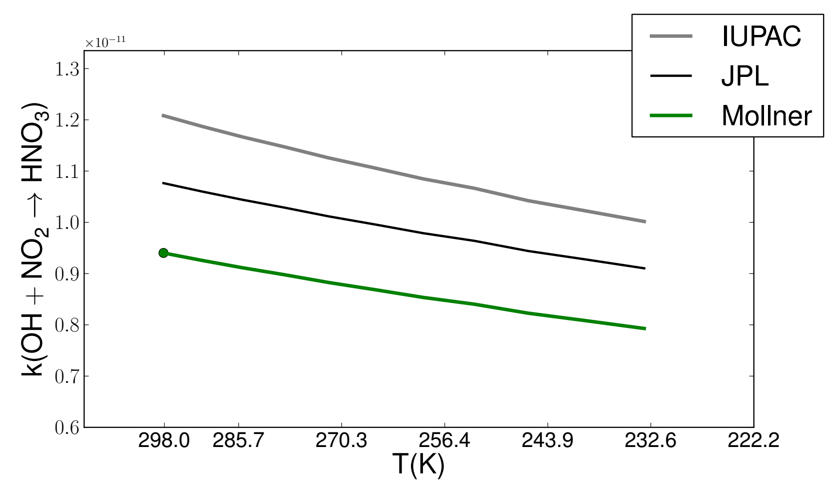
- Bayes Theorem
- More details at Henderson et al., ACPD 2011

Constrained Reaction Rate



Uncertainty in $NO_2 + HO^{\cdot} \rightarrow HNO_3$



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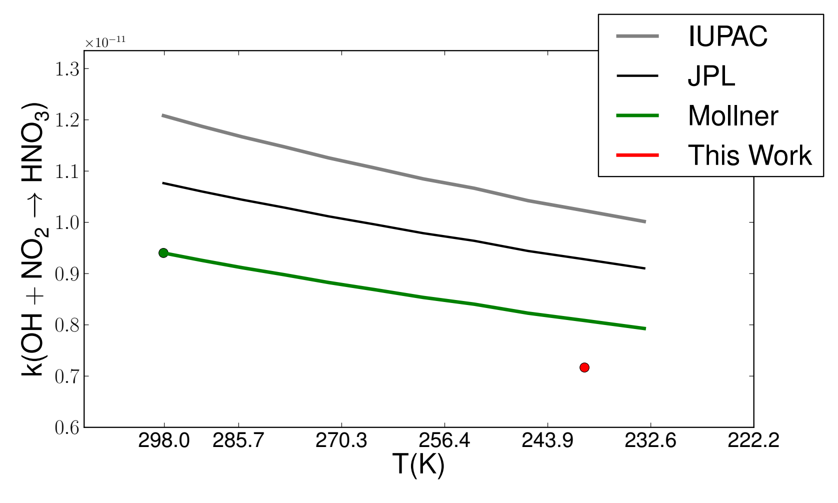

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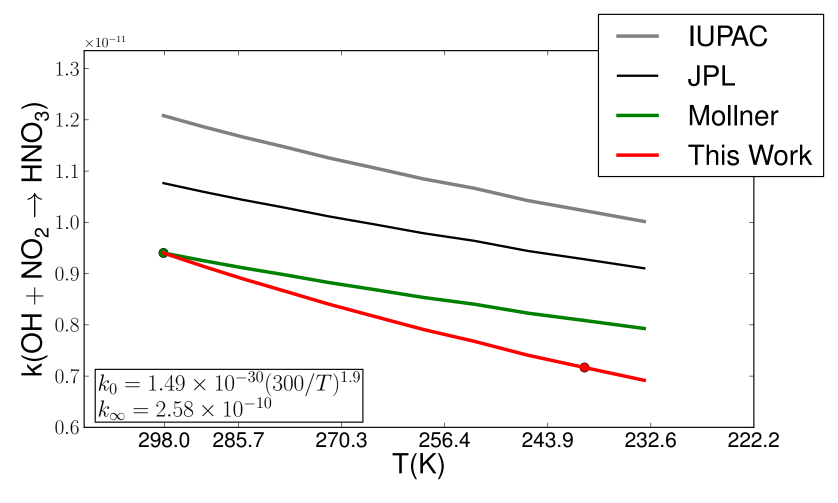
Uncertainty in $NO_2 + HO^{\cdot} \rightarrow HNO_3$



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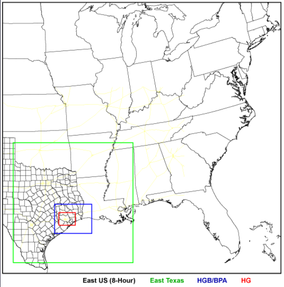
Implications depend on scale of interest

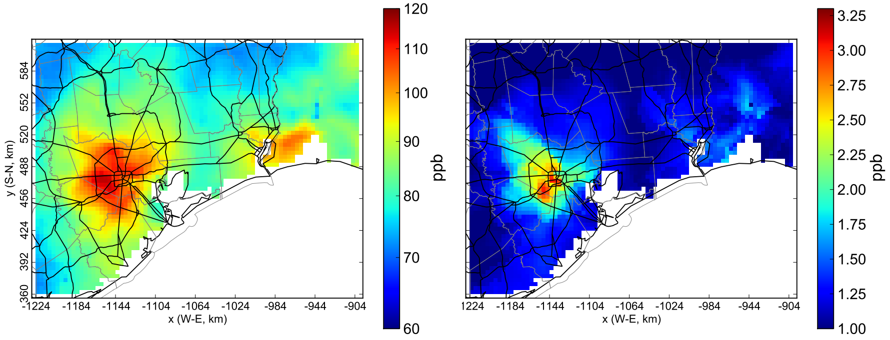
Urban, Regional, Continental: CAMx

- TCEQ SIP Modeling for Houston
- Episode: July 26-Aug 8 2005
- Domains: 36k-Eastern US; 12k-Texas; 4k-Harris County; 2k-Houston
- Focus
  - Max daily 8h average (MDA8)
  - Responsiveness to 20% NOx emission change



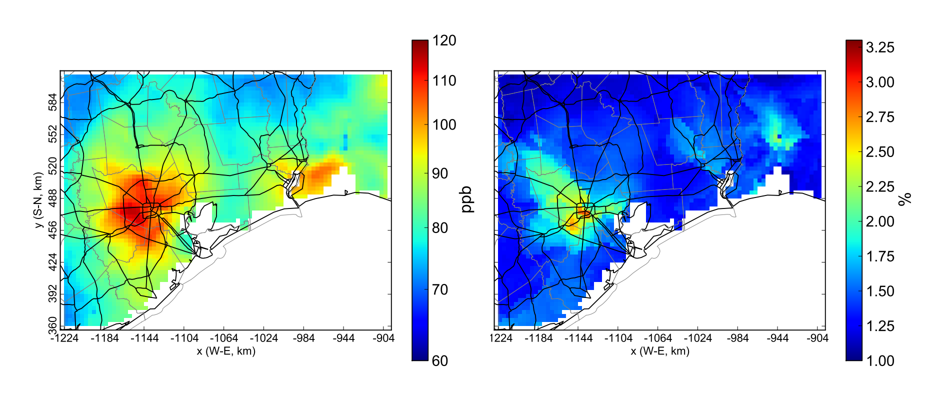
Urban scale (4k - Harris Cnty): Top 4 MDA8

Mixing Ratio / Difference (New - Std)



Urban scale (4k - Harris Cnty): Top 4 MDA8

Mixing Ratio — Percent (Diff / Std * 100)

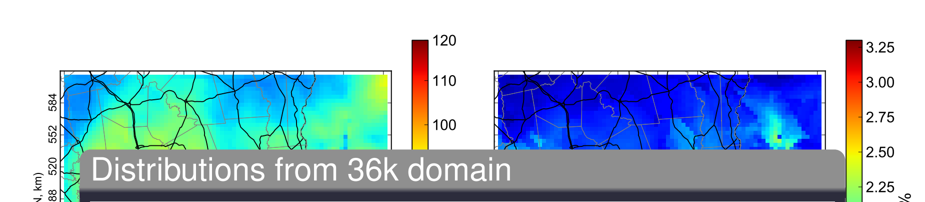


- Sensitivity consistent with Cohan et al., 2010 (AE)

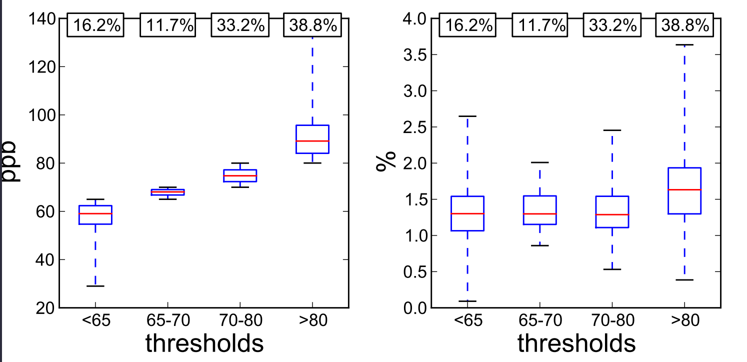
Urban scale (4k - Harris Cnty): Top 4 MDA8

Mixing Ratio

Percent (Diff / Std * 100)



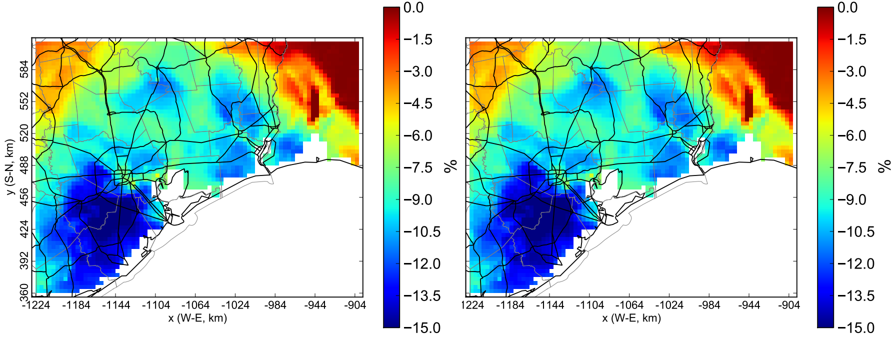
Distributions from 36k domain



- Se

4km - Harris County): $\Delta O_3 @80\% E(NO_x)$

Standard Response | With Updated Rate



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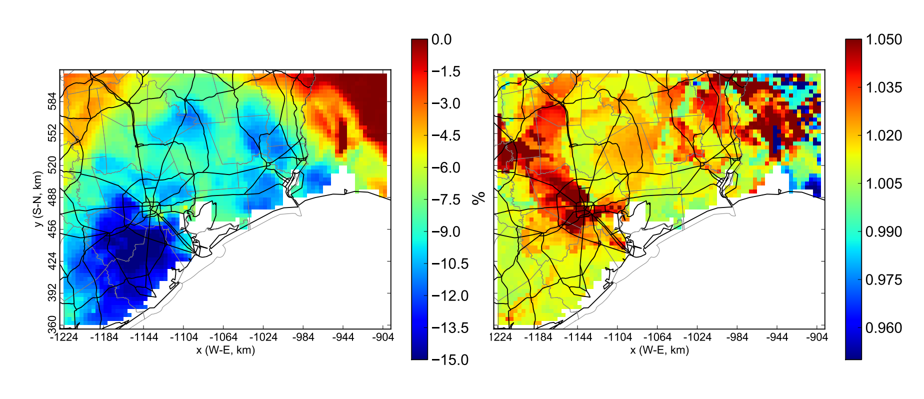
Standard Response | Ratio (New/Std)



- Second order sensitivity lower than Cohan et al., 2010 (AE), most likely because of non-linearity of local-sensitivity

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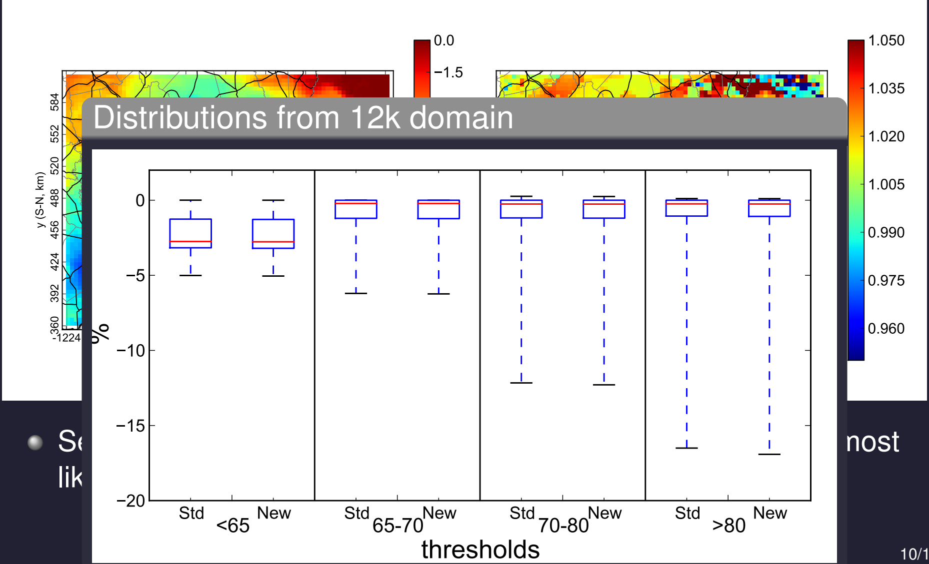
Standard Response | Ratio (New/Std)



- Se... most lik...

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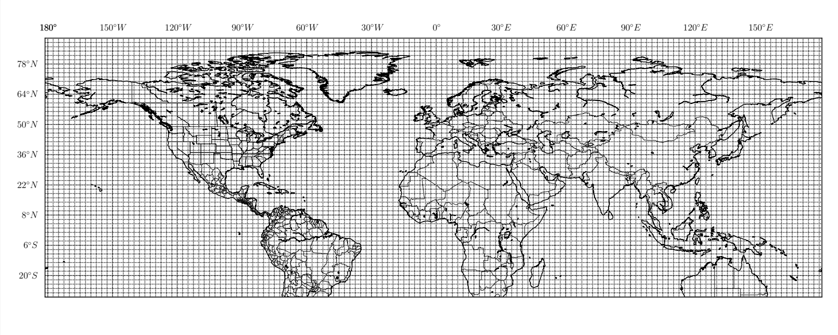
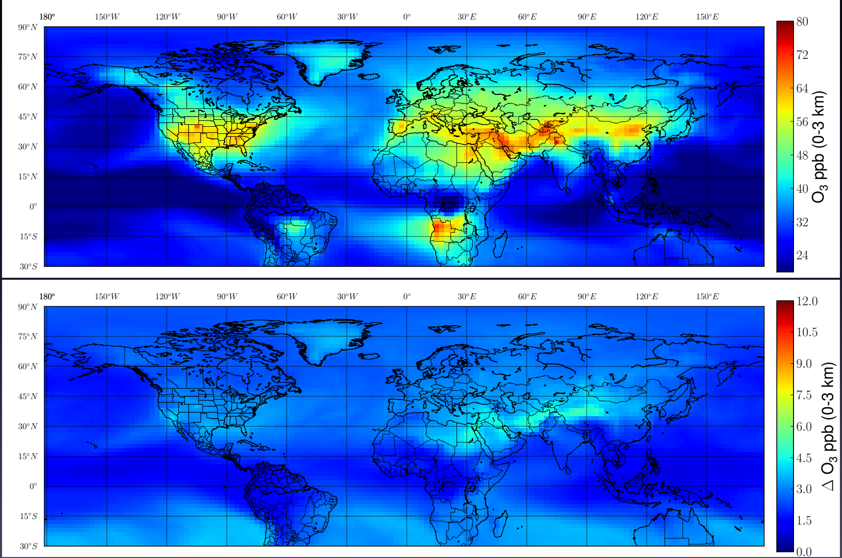
Global: GEOS-Chem

- INTEX-NA 2004 campaign
- $2^\circ \times 2.5^\circ$ with GEOS-5 meteorology
- 1 year spin-up
- Emissions following Hudman JGR 2007
- Focus: Mean ozone change; responsiveness to emissions



Low Trop Ozone: Influences West Coast



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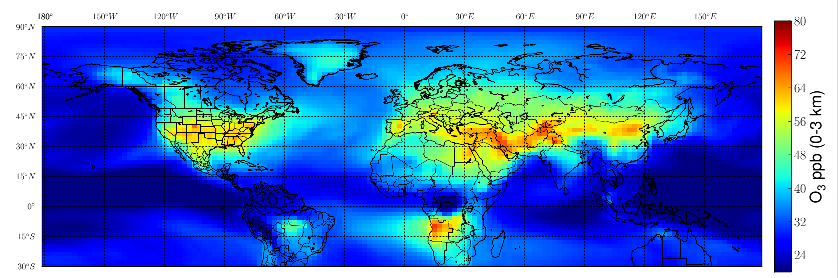
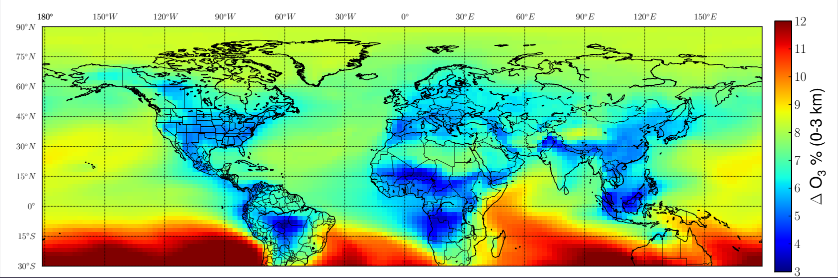
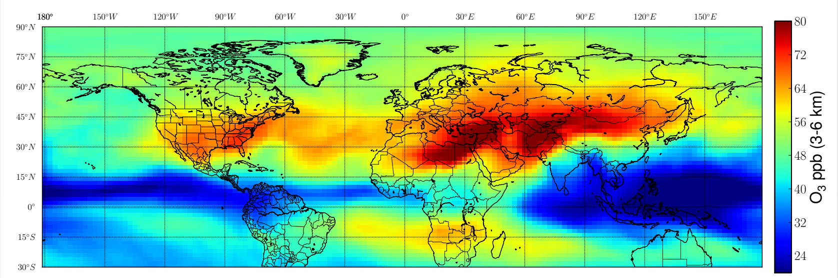
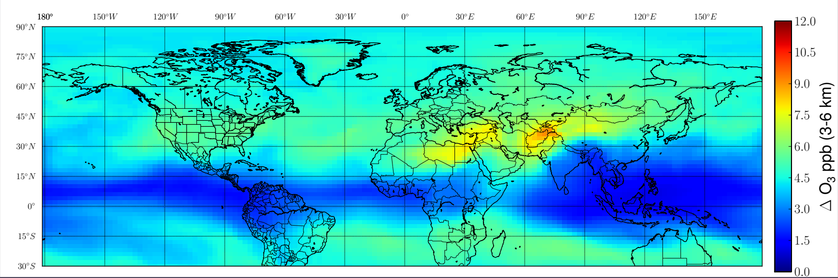




Mid Trop Ozone: Influences Interior US





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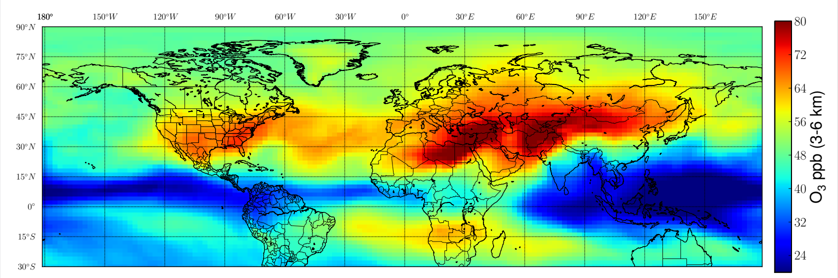
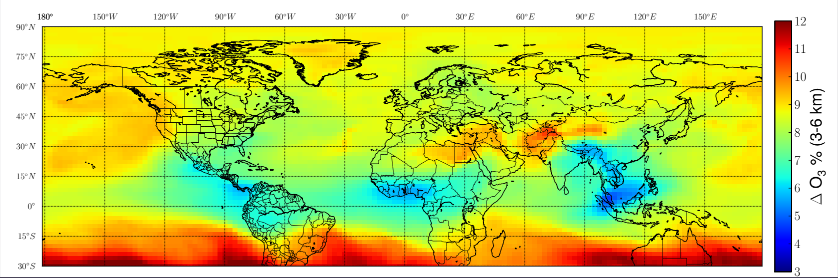
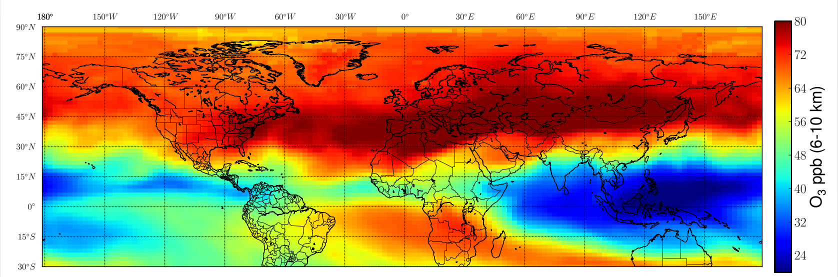
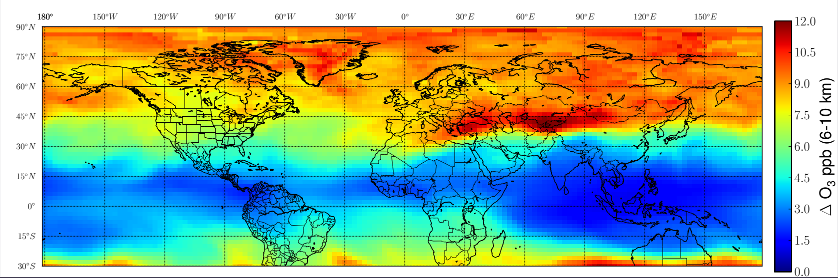




Upper Trop Ozone: Climate Forcing





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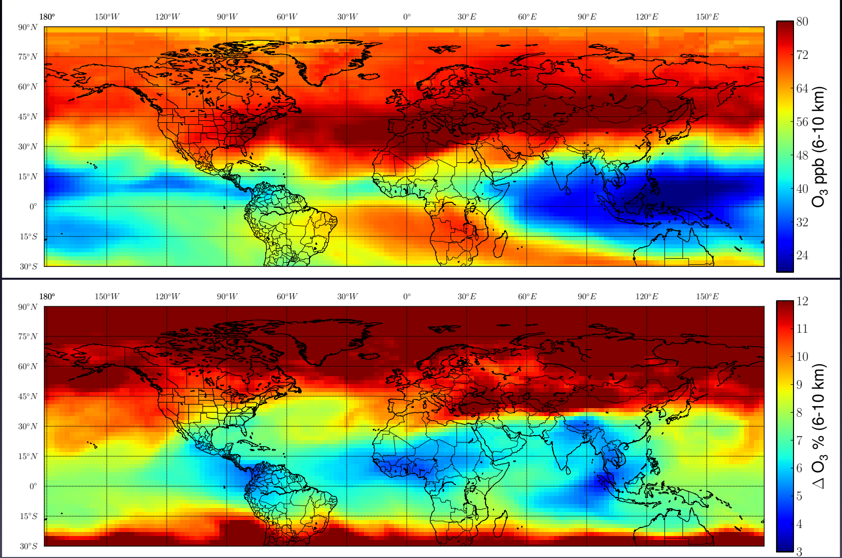

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- maximum daily 8 hour average results do not account for increased boundary conditions
- Using the model in a relative sense is largely unaffected

Acknowledgments

Co-authors on framework and inference papers:

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A. Fahr, Howard	Golam Sarwar US EPA
Bill Hutzell, US EPA	Rohit Mathur, US EPA
Ann Marie Carlton, Rutgers	Havala O.T. Pye, US EPA
Farhan Akhtar, US EPA	

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Gao Chen, NASA	Kinetic Pre-Processor
MAQLAB, UNC Chapel Hill	

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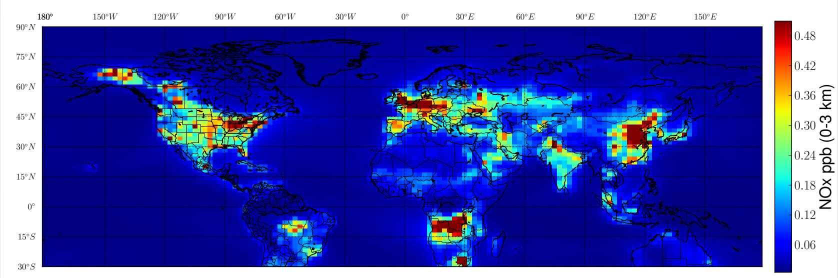
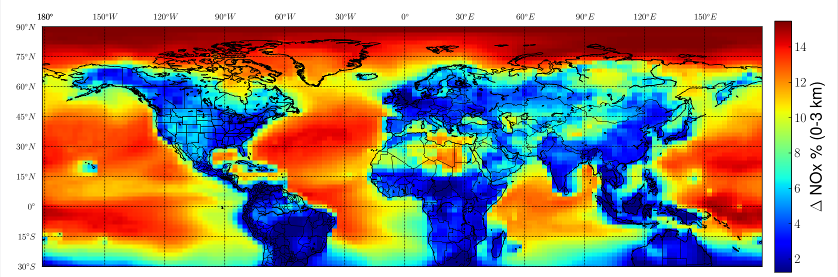
NO_x: Lower

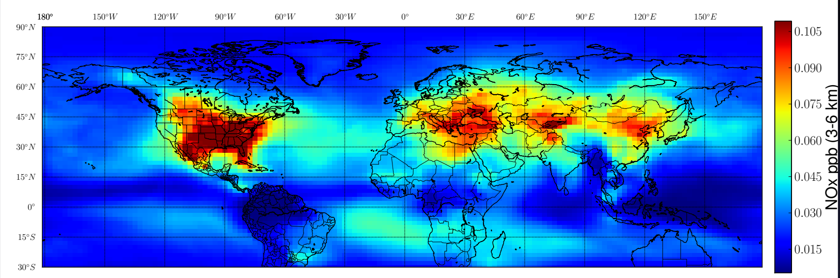


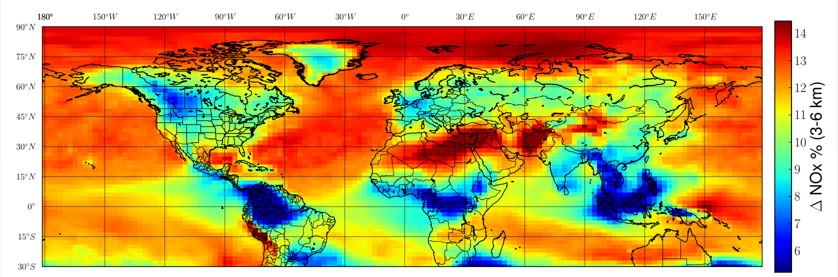
180°
150°W
120°W
90°W
60°W
30°W
0°
30°E
60°E
90°E
120°E
150°E
90°N
75°N
60°N
45°N
30°N
15°N
0°
15°S
30°S
0.48
0.42
0.36
0.30
0.24
0.18
0.12
0.06
NOx ppb (0-3 km)



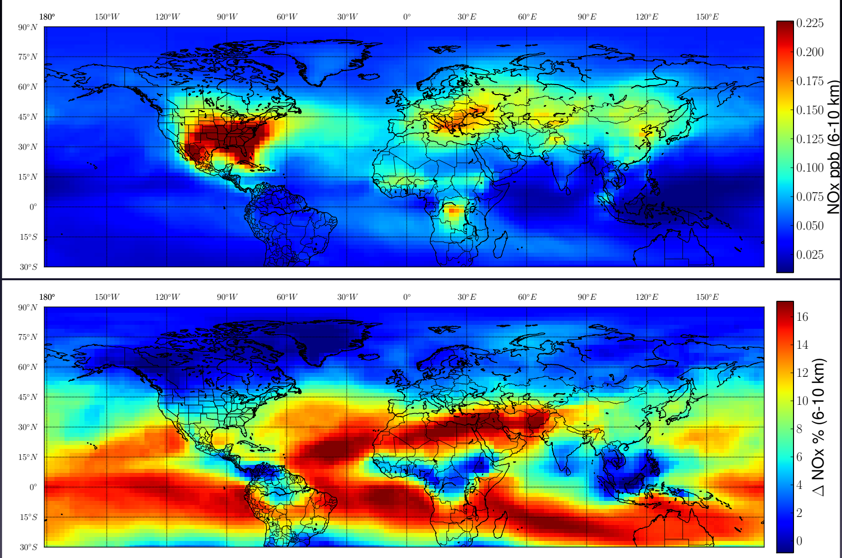
180°
150°W
120°W
90°W
60°W
30°W
0°
30°E
60°E
90°E
120°E
150°E
90°N
75°N
60°N
45°N
30°N
15°N
0°
15°S
30°S
14
12
10
8
6
4
2
Δ NOx % (0-3 km)

NO_x: Middle

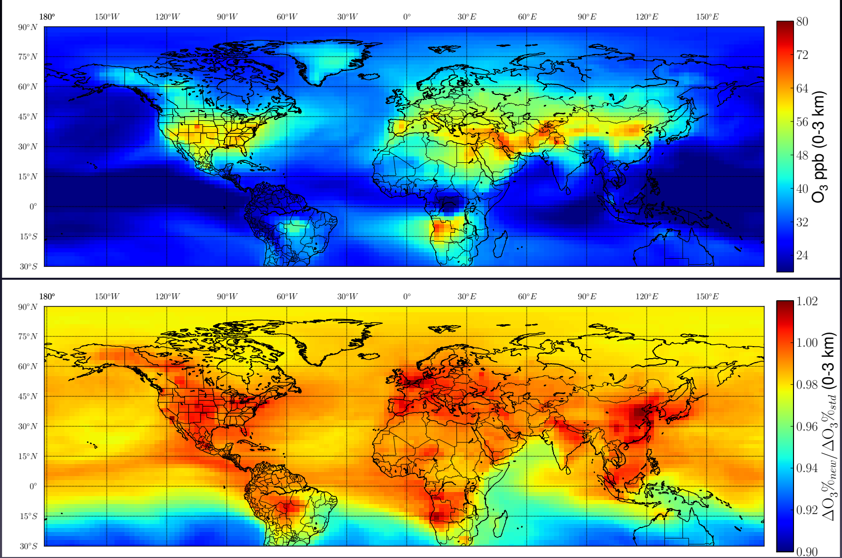

180°
150°W
120°W
90°W
60°W
30°W
0°
30°E
60°E
90°E
120°E
150°E
90°N
75°N
60°N
45°N
30°N
15°N
0°
15°S
30°S
0.105
0.090
0.075
0.060
0.045
0.030
0.015
NOx ppb (3-6 km)


180°
150°W
120°W
90°W
60°W
30°W
0°
30°E
60°E
90°E
120°E
150°E
90°N
75°N
60°N
45°N
30°N
15°N
0°
15°S
30°S
14
13
12
11
10
9
8
7
6
Δ NOx % (3-6 km)

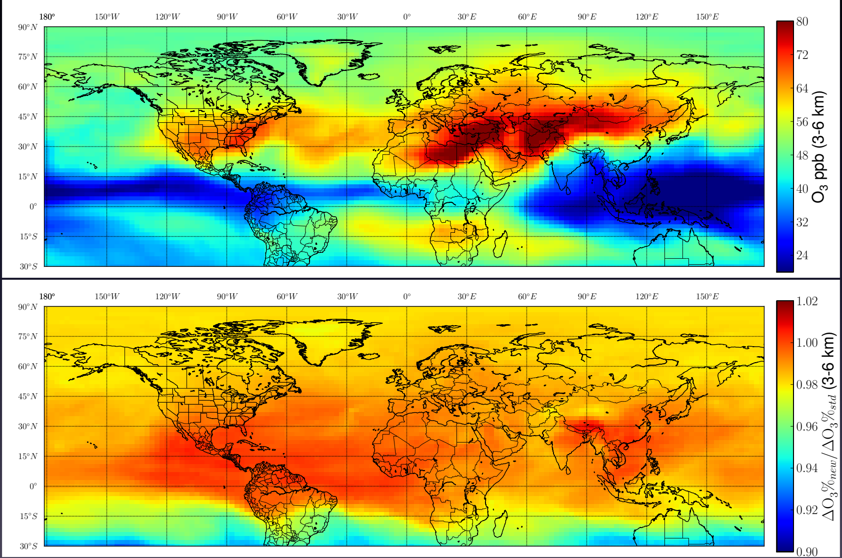
NO_x: Upper


180°
150°W
120°W
90°W
60°W
30°W
0°
30°E
60°E
90°E
120°E
150°E
90°N
75°N
60°N
45°N
30°N
15°N
0°
15°S
30°S
0.225
0.200
0.175
0.150
0.125
0.100
0.075
0.050
0.025
NOx ppb (6-10 km)
16
14
12
10
8
6
4
2
0
Δ NOx % (6-10 km)

Spatial NO_x Sensitivity: Lower



Spatial NO_x Sensitivity: Middle



Spatial NO_x Sensitivity: Upper