The Implications of Uncertain NO2 + OH for Ozone and Precursors

Barron H. Henderson¹, Rob W. Pinder¹, James Crooks², Farhan Akhtar¹, Havala O.T. Pye¹, William Vizuete²

¹Atmospheric Modeling and Analysis Division, U.S. EPA
²Biostatistics and Bioinformatics Research Core, U.S. EPA
³Dept. of Environmental Science and Engineering UNC Chapel Hill

October 26, 2011

barronh@gmail.com
Ozone Overview

- Secondary chemical: not emitted, but formed
- National Ambient Air Quality Standard criteria pollutant
- Third largest positive short-lived climate forcer
The reaction $\text{NO}_2 + \text{HO} \cdot \rightarrow \text{HNO}_3$: Important, Uncertain

JPL's recommended rate is 11% below IUPAC's
NO₂ + HO· → HNO₃: Important, Uncertain

- JPL’s recommended rate is 11% below IUPAC’s
- rate from latest lab data (all at 298 K) is 13% below JPL
\[ \text{NO}_2 + \text{HO} \cdot \rightarrow \text{HNO}_3: \text{ Important, Uncertain} \]

- JPL’s recommended rate is 11% below IUPAC’s
- Rate from latest lab data (all at 298 K) is 13% below JPL
Modeling framework

- Simulates air parcels post-convection event, identified by $\text{NO}_x/\text{HNO}_3$
  - 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 $K(\text{NO}_2 + \text{OH})$ from observations

- Uncertainty range from Jet Propulsion Laboratory Kinetic Data Evaluation 2011

$$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$$

$p \sim \log N(1, 0.18)$

 Uncertainty factor

0.59 0.70 0.84 1.00 1.19 1.43 1.70

$(-3\sigma)$ $(+3\sigma)$
Constraining $K(\text{NO}_2 + \text{OH})$ from observations

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

Using model results, we calculate the likelihood of the observations given each possible rate ($L(O|K)$).

Bayes Theorem

More details at Henderson et al., ACPD 2011

\[
\begin{align*}
\text{NO}_2 + \text{OH} & \rightarrow \text{HNO}_3 \\
p & \sim \text{log } N(1,0.18)
\end{align*}
\]
Constraining $K(\text{NO}_2 + \text{OH})$ from observations

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

$$L = \prod_i \hat{f}_{-3\sigma}(o_i), \ldots, \prod_i \hat{f}_{3\sigma}(o_i)$$
Constraining $K(\text{NO}_2 + \text{OH})$ from observations

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

$$P = \frac{pL}{\sum_i pL}$$
Constraining $K(\text{NO}_2 + \text{OH})$ from observations

- $p = p(K_{-3\sigma}), ..., p(K_{3\sigma})$
- Using model results, we calculate the likelihood of the observations given each possible rate ($L(O|K)$)
- Bayes Theorem
- More details at Henderson et al., ACPD 2011
Constrained Reaction Rate

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]

\[ P \sim \log \mathcal{N}(0.78, 0.05) \]

\[ p \sim \log \mathcal{N}(1, 0.18) \]
Uncertainty in $\text{NO}_2 + \text{HO}^- \rightarrow \text{HNO}_3$

JPL’s recommended rate is 11% below IUPAC’s rate from latest lab data (all at 298 K) is 13% below JPL.
JPL’s recommended rate is 11% below IUPAC’s
rate from latest lab data (all at 298 K) is 13% below JPL
this work is 11% below rate from latest lab data at 241 K
Uncertainty in $\text{NO}_2 + \text{HO}^\cdot \rightarrow \text{HNO}_3$

JPL’s recommended rate is 11% below IUPAC’s
rate from latest lab data (all at 298 K) is 13% below JPL
this work is 11% below rate from latest lab data at 241 K
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)
Sensitivity consistent with Cohan et al., 2010 (AE)
Urban scale (4k - Harris Cnty): Top 4 MDA8

Mixing Ratio

Percent (Diff / Std * 100)

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

Distributions from 36k domain
4km - Harris County): $\Delta O_3@80\%E(\text{NO}_x)$

Standard Response

With Updated Rate
Second order sensitivity lower than Cohan et al., 2010 (AE), most likely because of non-linearity of local-sensitivity
4km - Harris County): $\Delta O_3 @ 80\% E(\text{NO}_x)$

Standard Response

Ratio (New/Std)

Distributions from 12k domain

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

Thresholds:


%
Implications depend on scale of interest

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
Low Trop Ozone: Influences West Coast
Mid Trop Ozone: Influences Interior US

O₃ ppb (3-6 km)

Δ O₃ ppb (3-6 km)
Mid Trop Ozone: Influences Interior US
Upper Trop Ozone: Climate Forcing
Upper Trop Ozone: Climate Forcing
Conclusions

- Created a new evaluation framework – published in ACP 2011
Conclusions

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature

Small (<4%) increases for the maximum daily 8-hour average
Medium (>6−12%) increases for US background concentrations
Effect increases with altitude

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

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature
- Implemented new rate in Global, Regional, and Urban scales
Conclusions

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature
- Implemented new rate in Global, Regional, and Urban scales
  - Small (< 4%) increases for the maximum daily 8 hour average
  - Medium (6−12%) increases for US background concentrations
  - Effect increases with altitude
  - Maximum daily 8 hour average results do not account for increased boundary conditions
  - Using the model in a relative sense is largely unaffected
Conclusions

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature
- Implemented new rate in Global, Regional, and Urban scales
  - Small (< 4%) increases for the maximum daily 8 hour average
  - Medium (> 6 – 12%) increases for US background concentrations

Effect increases with altitude; maximum daily 8 hour average results do not account for increased boundary conditions; using the model in a relative sense is largely unaffected.
Conclusions

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature
- Implemented new rate in Global, Regional, and Urban scales
  - Small (< 4%) increases for the maximum daily 8 hour average
  - Medium (> 6 – 12%) increases for US background concentrations
  - Effect increases with altitude
Conclusions

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature
- Implemented new rate in Global, Regional, and Urban scales
  - Small ($< 4\%$) increases for the maximum daily 8 hour average
  - Medium ($> 6 – 12\%$) increases for US background concentrations
  - Effect increases with altitude
- Maximum daily 8 hour average results do not account for increased boundary conditions
Conclusions

- Created a new evaluation framework – published in ACP 2011
- Bayesian inference – submitted to ACP in July 2011
  - Confirms laboratory based rate reduction
  - Recommends further reduction at low temperature
- Implemented new rate in Global, Regional, and Urban scales
  - Small (< 4%) increases for the maximum daily 8 hour average
  - Medium (> 6 – 12%) increases for US background concentrations
  - Effect increases with altitude
- 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:

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. Crooks</td>
<td>US EPA</td>
</tr>
<tr>
<td>Wendy Goliff</td>
<td>UC Riverside</td>
</tr>
<tr>
<td>A. Fahr</td>
<td>Howard</td>
</tr>
<tr>
<td>Bill Hutzell</td>
<td>US EPA</td>
</tr>
<tr>
<td>Ann Marie Carlton</td>
<td>Rutgers</td>
</tr>
<tr>
<td>Farhan Akhtar</td>
<td>US EPA</td>
</tr>
<tr>
<td>R. C. Cohen</td>
<td>UC Berkley</td>
</tr>
<tr>
<td>Bill Stockwell</td>
<td>Howard</td>
</tr>
<tr>
<td>Golam Sarwar</td>
<td>US EPA</td>
</tr>
<tr>
<td>Rohit Mathur</td>
<td>US EPA</td>
</tr>
<tr>
<td>Havala O.T. Pye</td>
<td>US EPA</td>
</tr>
</tbody>
</table>

Thanks to:

<table>
<thead>
<tr>
<th>Name</th>
<th>Institution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mat Evans</td>
<td>Univ. of LEEDS</td>
</tr>
<tr>
<td>Gao Chen</td>
<td>NASA</td>
</tr>
<tr>
<td>MAQLAB, UNC Chapel Hill</td>
<td>Kinetic Pre-Processor</td>
</tr>
<tr>
<td>Jingqiu Mao</td>
<td>Princeton</td>
</tr>
</tbody>
</table>
Acknowledgments (continued)

Special thanks for DC8 observational data to:
Melody Avery, Donald Blake, William Brune, Alan Fried, Brian Heikes, Greg Huey, Glen Sachse, Hanwant Singh, Paul Wennberg, and the INTEX team.

Support:
This research was supported in part by an appointment to the Research Participation Program at the National Exposure Research Laboratory, U.S. Environmental Protection Agency administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and EPA.

Thanks also to the TCEQ for their freely available model inputs.
The Implications of Uncertain NO2 + OH for Ozone and Precursors

Barron H. Henderson\textsuperscript{1}, Rob W. Pinder\textsuperscript{1}, James Crooks\textsuperscript{2}, Farhan Akhtar\textsuperscript{1}, Havala O.T. Pye\textsuperscript{1}, William Vizuete\textsuperscript{2}

\textsuperscript{1}Atmospheric Modeling and Analysis Division, U.S. EPA
\textsuperscript{2}Biostatistics and Bioinformatics Research Core, U.S. EPA
\textsuperscript{3}Dept. of Environmental Science and Engineering UNC Chapel Hill

October 26, 2011

barronh@gmail.com
NO$_x$: Middle
NO$_x$: Upper

![NO$_x$ ppb (6-10 km)](image)

![Δ NO$_x$ % (6-10 km)](image)
Spatial NO$_x$ Sensitivity: Lower
Spatial NO\textsubscript{x} Sensitivity: Middle
Spatial NO\textsubscript{x} Sensitivity: Upper

![Map of NO\textsubscript{x} sensitivity](image-url)