The Challenge of Modeling the Chemistry of Ozone

Greg Yarwood
gyarwood@ramboll.com
Topics

Chemical life cycle of nitrogen oxide (NO\textsubscript{x}) emission
Chemical controls over NO\textsubscript{x} removal and potential for NO\textsubscript{x} recycling
NO\textsubscript{x} influence on distributions of ozone concentration
Organic nitrate (ON) removal by condensed-phase hydrolysis
Nitrate radical + terpene reactions
Chemical life cycle of NOx emission

- NO
- NO2
- NO3
- N2O5
- O3
- PAN
- HONO
- HNO3
- pNO3
- SOA
- aerosol

Reactions:
- NOx recycling
- ON hydrolysis
- NO3 + terpene
Daytime NO\textsubscript{x} chemical removal: Urban/rural differences

Removing NO\textsubscript{x} stops it from participating in ozone formation

Urban (higher NO\textsubscript{x}): three pathways all active

Rural (low NO\textsubscript{x}): organic nitrate (ON) pathway becomes dominant
**NO$_x$ recycling: Distributing NO$_x$ to rural areas**

Chemical reactions of ON, HNO$_3$ and PAN can release NO$_x$: termed “NO$_x$ recycling”

Uncertain magnitude of NO$_x$ recycling from ON:
- Extent of ON partitioning to aerosol
- Rate of ON hydrolysis within aerosol

NO$_x$ recycling from PAN mediated by PAN decomposition: $T_{1/2}$ of 40 mins @ 298K vs. 40 hours at 273K
Modeling H4MDA8 Ozone variation with NO\textsubscript{X} and VOC

- Nationwide photochemical modeling (WRF/CAMx)
- Quantify emission reductions from 2006 to attain various potential National Ambient Air Quality Standards (NAAQS)
- Novel application of ozone sensitivity (DDM) allows continuous and independent variation

$$\Delta O_3 = \Delta N^1_N + \frac{1}{2} \Delta N^2_N + \Delta V^1_V + \frac{1}{2} \Delta V^2_V + \Delta N \Delta V^2_N,$$

where

- $S_N^1 = \partial O_3 / \partial NO_x$
- $S_N^V = \partial O_3 / \partial VOC$
- $S_N^{2N} = \partial^2 O_3 / \partial NO_x^2$
- $S_V^2 = \partial^2 O_3 / \partial VOC^2$
- $S_{NV}^{2V} = \partial^2 O_3 / \partial NO_x \partial VOC$

- Provides long (annual, ozone season) simulated ozone time-series at adjustable NO\textsubscript{X} & VOC emission level

H4MDA8 = annual fourth highest maximum daily 8-hour average

Emission reductions and urban ozone responses under more stringent US standards

Nicole Downey \textsuperscript{a, b}, Chris Emery \textsuperscript{b}, Jaegun Jung \textsuperscript{b}, Tanarit Sakulyanontvittaya \textsuperscript{b}, Laura Hebert \textsuperscript{c}, Doug Blewitt \textsuperscript{c}, Greg Yarwood \textsuperscript{c}
Reducing NO\textsubscript{x} changes the ozone distribution

- Emission reductions truncate the high tail of maximum daily 8-hour (MDA8) and hourly ozone
- Emission reductions also can truncate a low tail of suppressed ozone
  - Especially “downtown”
  - More pronounced for hourly than MDA8 ozone
  - More impact for full year than ozone season (not shown)
- As anthropogenic emissions -> zero the distribution of background ozone appears
Ozone exposure (ppb hours) recalcitrant to reducing emissions

![Graphs showing Ozone exposure](image)
ON formation and examples

**Precursor**
- n-octane
- 1-butene
- toluene

**Organic Nitrate**

From the Master Chemical Mechanism (MCM) version 3.3.1
Organic nitrates removed by condensed-phase hydrolysis

alpha-pinene derived nitrate (APN)

J. D. Rindelaub et al., 2016

Table 2. The hydrolysis lifetimes of isopropyl nitrate (IPN), isobutyl nitrate (IBN), and the \( \alpha \)-pinene-derived nitrate (APN) at varying pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>IPN</th>
<th>IBN</th>
<th>APN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>28 h</td>
<td>23 h</td>
<td>8.3 min</td>
</tr>
<tr>
<td>1.0</td>
<td>33 days</td>
<td>33 days</td>
<td>44 min</td>
</tr>
<tr>
<td>1.7</td>
<td>35 days</td>
<td>33 days</td>
<td>−</td>
</tr>
<tr>
<td>2.5</td>
<td>33 days</td>
<td>33 days</td>
<td>33 min</td>
</tr>
<tr>
<td>4.0</td>
<td>30 days</td>
<td>28 days</td>
<td>1.3 h</td>
</tr>
<tr>
<td>6.9</td>
<td>&gt; 8 months</td>
<td>&gt; 8 months</td>
<td>8.8 h</td>
</tr>
</tbody>
</table>

Figure 6. The proposed acid-catalyzed hydrolysis mechanism of an \( \alpha \)-pinene-derived nitrate.
Nitrate radical + terpenes: Remove NO\textsubscript{x} and form secondary organic aerosol (SOA)

- Terpenes dominate NO\textsubscript{3} radical loss at night and are important during the day
- Inferred molar yield of aerosol-phase monoterpane ON of 23–44 %
- ON comprised 30–45% of the total reactive nitrogen (NO\textsubscript{y}) budget during Southern Oxidant and Aerosol Study (SOAS)

Figure 4. Average diurnal profile of NO\textsubscript{3}/N\textsubscript{2}O\textsubscript{5} losses 1 June–
Thank You

Reminders:

• NO$_x$ recycling: Distributing NO$_x$ to rural areas
• Ozone *exposure* recalcitrant to reducing NO$_x$ emissions
• Organic nitrates removed by condensed-phase hydrolysis
• Nitrate radical + terpenes: Removing NO$_x$ and forming SOA