Observational insights into N$_2$O$_5$ heterogeneous chemistry:
Influencing factors and its contribution to wintertime air pollution

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AGU Fall Meeting, Dec. 15, 2017
The Fate of $\text{N}_2\text{O}_5$...Important to Wintertime Air Quality

$\text{O}_3$ $\rightarrow$ \text{NO} $\rightarrow$ $\text{NO}_2$ $+$ $\text{O}_3$ $\rightarrow$ $\text{NO}_3$ $\leftrightarrow$ $\text{N}_2\text{O}_5$

**Introduction**

- $\text{N}_2\text{O}_5$ Het. Chem.
- Key Parameters

**Method**

- Campaigns
- Box Model

**Results**

- Model Treatment Assessment
- Air Quality Impact
The Fate of $\text{N}_2\text{O}_5$...Important to Wintertime Air Quality

$\text{NO}_x$ Emissions $\rightarrow$ NO $\rightarrow$ NO$_2$ + O$_3$ $\rightarrow$ NO$_3$ $\leftrightarrow$ N$_2$O$_5$ $\rightarrow$ O$_3$, NO$_2$ Source

$\text{O}_3$, Sunlight

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$\text{N}_2\text{O}_5 + \text{O}_3 + \text{NO}_2 + \text{O}_3 \rightarrow \text{N}_2\text{O}_5 + \text{Aerosol}$

- **Key Parameters**
  - Campaigns
  - Box Model
  - Model Treatment Assessment
  - Air Quality Impact

- **Particulate Matter (PM) Source**
  - $\text{HNO}_3 + \text{NH}_3 \rightarrow \text{PM}$

- **O$_3$, NO$_2$ Source**

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The Fate of N\textsubscript{2}O\textsubscript{5}...Important to Wintertime Air Quality

\textbf{Introduction}

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\textbf{Particulate Matter (PM) Source}

\textbf{O_3, NO_2, Cl Source}

\textbf{O_3, NO_2, PM} = U.S. Criteria Pollutants

\textbf{NO_x Emissions}

\textbf{NO, NO_2 + O_3 \rightarrow NO_3 \rightarrow N_2O_5 \rightarrow Aerosol}

\textbf{HNO_3 + NH_3 \rightarrow PM}

\textbf{CINO_2}

\textbf{Sunlight}

NO\textsubscript{2}, O\textsubscript{3}, PM\textsubscript{2.5} = U.S. Criteria Pollutants

\textbf{N_2O_5 Het. Chem. • Key Parameters}

\textbf{Campaigns • Box Model}

\textbf{Model Treatment Assessment • Air Quality Impact}
The Fate of N$_2$O$_5$...Important to Wintertime Air Quality

\[ \text{NO}_x \xrightarrow{\text{Emissions}} \text{NO} \xrightarrow{\text{Sunlight}} \text{NO}_2 + \text{O}_3 \xrightarrow{\text{O}_3} \text{NO}_3 \xrightarrow{\text{Aerosol}} \text{N}_2\text{O}_5 \]

Particulate Matter (PM) Source

\[ \text{HNO}_3 + \text{NH}_3 \xrightarrow{\gamma} \text{PM} \]

\[ \text{O}_3, \text{NO}_2, \text{Cl} \text{ Source} \]

\[ \text{O}_3, \text{NO}_2, \text{PM}_{2.5} = \text{U.S. Criteria Pollutants} \]

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Derived Parameters $\gamma(N_2O_5)$ and $\varphi(\text{ClNO}_2)$

**$\gamma(N_2O_5)$**
- Reactive Uptake Coefficient

$\gamma(N_2O_5)$ = $\frac{1}{4} \times \bar{c} \times S_A \times \gamma(N_2O_5)$

- 1st order loss rate coefficient for $N_2O_5$
- Mean molecular speed
- Aerosol Surface Area

Field-Derived Range $\gamma(N_2O_5)$: $10^{-4}$ – 0.1

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Derived Parameters $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$

**$\gamma(N_2O_5)$**

Reactive Uptake Coefficient

Field-Derived Range $\gamma(N_2O_5)$:

$10^{-4}$ – 0.1

**$\varphi(ClNO_2)$**

Production Yield

Field-Derived Range $\varphi(ClNO_2)$:

0 – 1

$k(N_2O_5) = \frac{1}{4} \times \bar{c} \times S_A \times \gamma(N_2O_5)$

1st order loss rate coefficient for $N_2O_5$

Mean molecular speed

Aerosol Surface Area
Derived Parameters $\gamma(N_2O_5)$ and $\varphi(ClNO_2)$

Understanding of uptake ($\gamma$) and yield ($\varphi$) during winter → limited by lack of wintertime field data!
Wintertime Aircraft Campaigns

**WINTER – 2015**
U.S. East Coast

**UWFPS – 2017**
Northern Utah

**Flights Hours**

~100 Hours (60% nocturnal) vs. ~60 Hours (50% nocturnal)

**Approach**

Regional flights to survey variability vs. Repeated flights to gain statistics

**Analysis Goal**

Assess $N_2O_5$ model treatment vs. Assess $N_2O_5$ air quality impacts

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Model Principle:

- Simulate chemical evolution of air from sunset until measurement time
- Iterate uptake ($\gamma$) and yield ($\phi$) to fit observed $N_2O_5$ and ClNO$_2$

Model Chemical Mechanism

Example: Iterate $\gamma$ to fit $N_2O_5$
Campaign Results #1: WINTER

U.S. East Coast – Winter 2015

\( \gamma \): \( \text{N}_2\text{O}_5 \) Uptake

\( \phi \): \( \text{ClNO}_2 \) Yield

\( \text{Campaign Median: 0.17} \)

\( \text{Most Frequent: 0.02} \)

\( \text{N = 3116} \)

\( \text{Campaign Median: 0.014} \)

\( \text{Most Frequent: 0.016} \)

\( \text{N = 2876} \)

\( \text{Campaign Median: 0.17} \)

\( \text{Most Frequent: 0.02} \)

\( \text{N = 3116} \)

\begin{tabular}{|l|l|}
\hline
Introduction & Method & Results \\
\hline
\text{N}_2\text{O}_5 \text{ Het. Chem.} \& \text{Key Parameters} & \text{Campaigns} \& \text{Box Model} & \text{Model Treatment Assessment} \& \text{Air Quality Impact} \\
\hline
\end{tabular}
Campaign Results #1: WINTER

U.S. East Coast – Winter 2015

N$_2$O$_5$ Uptake ($\gamma$)

ClNO$_2$ Yield ($\varphi$)

**N$_2$O$_5$ Uptake ($\gamma$)**

- Campaign Median: 0.014
- Most Frequent: 0.016
- N = 2876

**ClNO$_2$ Yield ($\varphi$)**

- Campaign Median: 0.17
- Most Frequent: 0.02
- N = 3116
Parameterization of Uptake ($\gamma$)

14 Parameterizations Tested
Parameterization of Uptake ($\gamma$)

Bertram and Thornton, ACP, 2009

Inorganic Only:

$$\frac{1}{\gamma} = \frac{4V}{cSA} \frac{1}{K_H k_{R3}} \left( 1 - \frac{k_{R5}[H_2O(l)]}{k_{R4}[NO_3^-]} \right) + \frac{1}{1 + \left( \frac{k_{R6}[Cl^-]}{k_{R4}[NO_3^-]} \right)}$$

$\gamma$ Increase w/ Water

$\gamma$ Decrease w/ Nitrate

$\gamma$ Increase w/ Chloride/Nitrate

Water

Nitrate

Cl-/NO$_3^-$

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Parameterization of Uptake ($\gamma$)

Best Agreement:

$$\frac{1}{\gamma} = \frac{4 V}{c SA} k_{H} k_{R3} \left( 1 - \frac{k_{R5} [H_2O(l)]}{k_{R4} [NO_3^{-}]} \right) + \frac{1}{1 + \left( \frac{k_{R6} [Cl^{-}]}{k_{R4} [NO_3^{-}]} \right)} + \frac{4RT \epsilon H_{aq} D_{aq} R_c}{c \ell R_p}$$

**Inorganic + Organic:**

- $\gamma$ Increase w/ Water
- $\gamma$ Decrease w/ Nitrate
- $\gamma$ Increase w/ Chloride/Nitrate
- $\gamma$ Decrease w/ Organics

**Water**

**Nitrate**

**Cl-/NO$_3$-**

**Organics**

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Bertram and Thornton, ACP, 2009

Riemer et al., JGR, 2009

Gaston et al., ACP, 2014
Parameterization of Uptake ($\gamma$)

Best Agreement:

Inorganic + Organic:

$$\frac{1}{\gamma} = \frac{4V}{cSA} k_H k_{R3} \left( 1 - \frac{k_{R5}[H_2O(l)]}{k_{R4}[NO_3^-]} \right) + 1 + \frac{k_{R6}[Cl^-]}{k_{R4}[NO_3^-]} + \frac{4RT \varepsilon H_{aq} D_{aq} R_c}{c\ell R_p}$$

Conclusions:

- Lowest values not captured by observed variables; likely aerosol phase (solid or glass) or morphology (core-shell)
- 11 of 14 parameterizations reproduced WINTER median
Campaign Results #1: WINTER

U.S. East Coast – Winter 2015

N$_2$O$_5$ Uptake ($\gamma$)

ClNO$_2$ Yield ($\phi$)

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Parameterization of ClNO$_2$ Yield ($\varphi$)

$$
\varphi = \left(1 + \frac{k_3[H_2O]}{k_4[Cl^-]}\right)^{-1}
$$

Increase w/ aerosol chloride

Behnke et al., JGR, 1997
Roberts et al., GRL, 2009
Bertram and Thornton, ACP, 2009
Parameterization of ClNO$_2$ Yield ($\varphi$)

$\varphi = \left(1 + \frac{k_3[H_2O]}{k_4[Cl^-]}\right)^{-1}$

Increase w/ aerosol chloride

Conclusions:
• Box Model $\varphi < $ Parameterizations  
• Models may over-predict ClNO$_2$ production
Campaign Results #2: UWFPS

N$_2$O$_5$ Uptake ($\gamma$)

Northern Utah– Winter 2017

CINO$_2$ Yield ($\phi$)

- Campaign Median: 0.05 (5x > WINTER)
- Most Frequent: 0.08

- Campaign Median: 0.21
- Most Frequent: 0.05

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Campaign Results #2: UWFPS

N$_2$O$_5$ Uptake ($\gamma$)

Northern Utah – Winter 2017

CLNO$_2$ Yield ($\phi$)

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<th>Frequency (%)</th>
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<tr>
<td>10^-4</td>
<td>0.0</td>
</tr>
<tr>
<td>10^-3</td>
<td>1.0</td>
</tr>
<tr>
<td>10^-2</td>
<td>2.0</td>
</tr>
<tr>
<td>10^-1</td>
<td>3.0</td>
</tr>
<tr>
<td>10^0</td>
<td>4.0</td>
</tr>
<tr>
<td>10^1</td>
<td>5.0</td>
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Campaign Median: 0.05 (5x > WINTER)
Most Frequent: 0.08

Campaign Median: 0.21
Most Frequent: 0.05
N₂O₅ Chemistry and Utah Air Quality

Average Mass Fraction

- Org.
- NO₃
- NH₄

Average Total Mass: 80 μg/m³

Salt Lake City – Jan. 30th, 2017

HNO₃ + NH₃ → PM

Limiting Reagent

Contribution from Nocturnal N₂O₅ Chemistry?

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N$_2$O$_5$ Chemistry $\rightarrow$ Major Source of Total Nitrate

$\gamma = 0.05$

$\varphi = 21\%$

Example Simulation over Salt Lake City ($\gamma = 0.05$)

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$\text{N}_2\text{O}_5$ Chemistry $\rightarrow$ Major Source of Total Nitrate

\[ \gamma = 0.05 \quad \varphi = 21\% \]

Example Simulation over Salt Lake City ($\gamma = 0.05$)

- Time of Measurement
- 60% contribution from $\text{N}_2\text{O}_5$ chemistry by sunrise
- Salt Lake City Average: $68\% \pm 23\%$

### Results
- Air Quality Impact

### Introduction
- $\text{N}_2\text{O}_5$ Hetr. Chem. • Key Parameters

### Method
- Campaigns • Box Model

### Model Treatment Assessment
- Model Treatment Assessment • Air Quality Impact
Results & Summary

- $\text{N}_2\text{O}_5$ Uptake ($\gamma$) and ClNO$_2$ Yield ($\phi$) describe nocturnal $\text{N}_2\text{O}_5$ fate and air quality importance.

- Box modeling of recent aircraft campaigns provide some of the newest uptake ($\gamma$) and yield ($\phi$) determinations.

- Parameterizations can reproduce WINTER median uptake ($\gamma$), but not lowest values.

- WINTER yields ($\phi$) do not agree with parameterizations.

- Utah study showed $\text{N}_2\text{O}_5$ chemistry can contribute to the majority of observed nitrate, impacting local air quality.