An Assessment of Nitryl Chloride Formation Chemistry and its Importance in Ozone Nonattainment areas in Texas

AQRP Project 10-015

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Acknowledgement

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Purpose of AQRP Study

- A number of recent studies, including the 2006 TexAQS II, have shown that nighttime reactions between ozone (O₃), nitrogen oxides (NOₓ), hydrochloric acid (HCl) and particulate matter (PM) produce nitryl chloride (ClNO₂).

- Also, ClNO₂ photolyzes rapidly in the early morning producing NO₂ and chloride radical (Cl*):
  - NO₂ will photolyze generating O₃ and
  - Cl* will react with VOCs, similar to OH, to produce peroxide radicals.
  - The peroxide radicals, in turn, will convert NO to NO₂.

- This new NO₂ photolyzes producing O₃.
Scope of AQRP Study

- Using existing ambient air quality field study data sets for urban areas, develop nitryl chloride (CINO$_2$) formation chemistry

- Implement the CINO$_2$ chemistry in photochemical grid models to improve model performance, including rapid ozone production monitored during the morning hours on some days and the sensitivity of ozone to nitrogen oxides (i.e., NO$_X$)
Objectives of AQRP Study

- Analyze the ambient air quality data sets collected during the 2006 TexAQS II, SHARP 2009, and CalNex 2010 field studies
- Formulate and parameterize the chemistry producing ClNO$_2$
- Incorporate the parameterization in the CB05 chemical mechanism
- Quantify emissions sources of reactive chloride, including sea salt acidification
- Test the mechanism in CAMx by modeling the EPA July 2006 episode
Analysis of Ambient Air Quality

- Identify the series of chemical reactions that convert NO and O₃ to ClNO₂ and HNO₃
- Use simple chemistry reaction box model and the ambient air quality data sets to estimate the value of key parameters necessary to develop a chemical mechanism:
  - N₂O₅ uptake coefficient, C_N₂O₅
  - ClNO₂ conversion efficiency, C_ClNO₂
Nighttime Chemistry of NO\textsubscript{x}, O\textsubscript{3}, HCl and PM

- \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \)
- \( \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \)
- \( \text{NO}_3 + \text{NO} \rightarrow 2\text{NO}_2 \)
- \( \text{NO}_3 + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_5 \)
- \( \text{NO}_3 + \text{VOC} \rightarrow \text{Organic Nitrate Products} \)
- \( \text{N}_2\text{O}_5 + \text{AER:} \text{H}_2\text{O} \, \text{(het)} \rightarrow 2\text{HNO}_3 \, \text{(aq)} \)
- \( \text{N}_2\text{O}_5 + \text{AER:} \text{HCl} \, \text{(het)} \rightarrow \text{HNO}_3 \, \text{(aq)} + \text{ClNO}_2 \, \text{(q)} \)
N₂O₅ Uptake Coefficient and the ClNO₂ Conversion Efficiency

- N₂O₅ loss rate (i.e., total N₂O₅ uptake from reactions with AER:H₂O and AER:HCl):
  - \(-\frac{d}{dt}[N₂O₅] = K_{het}*[N₂O₅] = C_{N₂O₅}*S_a*v/4\)
    - \(K_{het}\) is the rate constant
    - \(C_{N₂O₅}\) is the uptake coefficient
    - \(S_a\) is the total aerosol surface area
    - \(v\) is the average N₂O₅ molecular speed
  - \(C_{N₂O₅} = 4* K_{het}*[N₂O₅] / (S_a*v)\)
  - ambient data indicates \(C_{N₂O₅}\) is dependant on the relative humidity (RH) and the aerosol organic composition

- ClNO₂ conversion efficiency (i.e., the fraction of the N₂O₅ loss rate yielding ClNO₂):
  - \(-\frac{d}{dt}[N₂O₅] = K_{ClNO₂}*[N₂O₅]\)
    - \(K_{ClNO₂}\) is the rate constant for the reaction with AER:HCl
  - \(C_{ClNO₂} = K_{ClNO₂}/K_{het}\)
    - \(C_{ClNO₂}\) is the ClNO₂ conversion efficiency
Box Modeling CalNex

Two episodes selected from the CalNex dataset:

- **5/30/2010; 23:37 PST**
  - High N$_2$O$_5$ (3.2 ppb)
  - low RH (30%)
  - high aerosol organic composition (80%)

- **6/3/2010; 04:17 PST**
  - High ClNO$_2$ (2.5 ppb)
  - high RH (90%)
  - low aerosol organic composition (25%)
Selected Episodes for Box Model
Selected Episodes for Box Model
Two episodes selected from the SHARP dataset:

- **5/19/2009; 22:30 CST**
  - high N$_2$O$_5$ and ClNO$_2$ (0.24 and 0.13 ppb, respectively)
  - relatively constant NO$_2$ (13 ppb)
  - steady wind direction from the east-southeast

- **5/30/2009; 04:17 CST**
  - high N$_2$O$_5$ and ClNO$_2$ (0.30 and 0.10 ppb, respectively)
  - variable NO$_2$ (15 to 25 ppb)
  - transitioning wind direction from west-southwest to south

- For both episodes, a continuous source of NO$_2$ (4 ppbv/hr) was added to the box model in order to maintain the ambient NO$_2$ concentrations
Selected Episodes for Box Model

Selected period: 10:30 pm (2230 hrs) 5/19/2009
High $N_2O_5 \sim 220$ pptv and ClNO2 $\sim 100$ pptv,
at constant NO2 $\sim 13$ ppbv, O3 $\sim 50$ ppbv &
WD $\sim 115$ (ESE)

Box Modeling w/o NO2 source from sunset
(1910 hrs, CST) to selected period (2230 hrs, CST), 3:20 hh:mm,
ClNO2 $\sim 0.11$ ppbv,
$N_2O_5 \sim 0.25$ ppbv, O3 $\sim 50$ ppbv & NO2 $\sim 4$ ppbv
$C_{N_2O_5} = 52E-3$ and $C_{ClNO2} = 3\%$

Box Modeling w/ NO2 source from sunset
(1910 hrs, CST) to selected period (2230 hrs, CST), 3:20 hh:mm,
$N_2O_5 \sim 0.25$ ppbv, O3 $\sim 50$ ppbv & NO2 $\sim 9$ ppbv
$C_{N_2O_5} = 100E-3$ and $C_{ClNO2} = 2\%$
Selected Episodes for Box Model

Selected period: 4:15 am (0415hrs CST) 5/30/2009
High N$_2$O$_5$ ~ 220 pptv and ClNO$_2$ ~ 80 pptv,
at variable NO$_2$ ~ 20 - 50 ppbv, O$_3$ ~ 20 - 40 ppbv &
WD ~ 145 (WSW) to 185 (S)

Box Modeling w/o NO$_2$ source from sunset
(1915 hrs, CST, 5/29/2009) to selected period
(0415 hrs, CST, 5/30/2009), 8:00 hh:mm,
ClNO$_2$ ~ 0.16 ppbv, N$_2$O$_5$ ~ 0.27 ppbv,
O$_3$ ~ 38 ppbv & NO$_2$ ~ 5 ppbv
C$_{N2O5}$ = 40E-3 and C$_{ClNO2}$ = 0.5%

Box Modeling w/ NO$_2$ source from sunset
(1915 hrs, CST, 5/29/2009) to Selected period
(0415 hrs, CST, 5/30/2009), 8:00 hh:mm
ClNO$_2$ ~ 0.10 ppbv, N$_2$O$_5$ ~ 0.35 ppbv,
O$_3$ ~ 30 ppbv & NO$_2$ ~ 20 ppbv
C$_{N2O5}$ = 100E-3 and C$_{ClNO2}$ = 1%
### Box Modeling Results

#### Summary of $C_{N2O5}$ and $C_{CINO2}$

<table>
<thead>
<tr>
<th>Modeled Event</th>
<th>$N_2O_5$ Uptake $C_{N2O5}$</th>
<th>$CINO_2$ Conversion Efficiency $C_{CINO2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CalNex: low RH &amp; High OC</td>
<td>4.40 E-03</td>
<td>6%</td>
</tr>
<tr>
<td>CalNex: High RH &amp; low OC</td>
<td>28.0 E-03</td>
<td>44%</td>
</tr>
<tr>
<td>SHARP: 5/19/09, w/o NO$_2$</td>
<td>52.0 E-03</td>
<td>3%</td>
</tr>
<tr>
<td>SHARP: 5/19/09, w/ NO$_2$</td>
<td>100.0 E-03</td>
<td>2%</td>
</tr>
<tr>
<td>SHARP: 5/29/09, w/o NO$_2$</td>
<td>40.0 E-03</td>
<td>0.5%</td>
</tr>
<tr>
<td>SHARP: 5/29/09, w/ NO$_2$</td>
<td>100.0 E-03</td>
<td>1%</td>
</tr>
</tbody>
</table>
Box Modeling Results

![Diagram showing box modeling results with various N₂O₅ uptake coefficients across different temperatures and relative humidities.](image)

- **N₂O₅ uptake coeff.** vs. **Relative Humidity (%)**
- Temperature markers: 291K, 298K, 308K
- Water (298K) point indicated.
CB05 Parameterization

- The CB05 chemistry mechanism was updated with N$_2$O$_5$ chemistry based on the parameterization by Bertram and Thornton (2009).

- N$_2$O$_5$ chemistry is parameterized by adding the pseudo heterogeneous gas-phase reactions:
  - N$_2$O$_5$ (g) + AER:H$_2$O(aq) $\rightarrow$ 2HNO$_3$(g);
  - N$_2$O$_5$ (g) + AER:HCl(aq) $\rightarrow$ HNO$_3$(g) + ClNO$_2$(g); and
  - the reaction coefficients (i.e., $K_{het}$ and $K_{ClNO2}$) are based on the values of C$_{N2O5}$ and C$_{ClNO2}$ which in turn are functions of H$_2$O(aq), Cl$^-$ (aq) and NO$_3^-$ (aq).

- The gas-particulate thermodynamic equilibrium model, ISORROPIA, is used to partition H$_2$O, chloride (Cl) and nitrate (NO$_3$) species between the gas and aqueous phases.
Modeling Emissions

The basic 2006 modeling emissions for gases and aerosols were developed by EPA for the national 12 km gridded domain covering the contiguous United States (US) with 26 vertical layers.

- **Case S1.** Added to the basic 2006 modeling emissions, chlorine (Cl\(_2\)) and hydrochloric acid (HCl) from the EPA 2006 hazardous air pollutant (HAP) inventory, and sea-salt aerosol emissions estimated from flux equations for breaking waves in the open ocean and surf zone.

- **Case S2.** Added to Case S1, Cl\(_2\) and hypochlorous acid (HOCl) emissions from swimming pools for a typical summer day based on the EPA 1999 NEI for all counties in the US, except Los Angeles and Harris counties, for which swimming pool emissions were estimated from GIS data for public and residential pools and typical emission factors (kg-Cl/pool/day).

- **Case S3.** Added to Case S2, particulate chloride (PCI) emissions from the EPA NEI for primary PM\(_{2.5}\), as well as typical PCI emissions from wildfires.
# Modeling Emissions Summary

| Region/Specie | S1 case | | S2 case | | S3 case | |
|---------------|---------|---------|---------|---------|---------|
| | Area | Point | Pool | Area | Point | Fire |
| **SCOS** | | | | | | |
| Cl₂ | 0.85 | 1.5 | 0.025 | 1.4 | 2.1 | 65 | 0.65 | 0.064 | 4.3 |
| HCl | | | | | | |
| HOCl | | | | | | |
| PCl | 65 | | 2.1 | | | |
| **HGB** | | | | | | |
| Cl₂ | 0.34 | 1.0 | 0.97 | 15 | 0.65 | 15 | 1.8 | 1.1 | 0.014 |
| HCl | | | | | | |
| HOCl | | | | | | |
| PCl | 15 | | 0.65 | | | |
| Contiguous US | | | | | | |
| Cl₂ | 4.8 | 84 | 8.6 | 1,168 | 31 | 31 | 127 | 21 | 241 |
| HCl | | | | | | |
| HOCl | | | | | | |
| PCl | 5,359 | | | | | |

Emissions are in tpd and represent the amount added for each case
Modeling Emissions for SCOS and HGB

![Bar chart for SCOS and HGB emissions]

- S3 (PCI from anthropogenic sources and wildfires)
- S2 (Cl2 & HOCl from swimming pool)
- S1 (Cl2 & HCl anthropogenic sources; PCI from sea salt)
CAMx Modeling

• Modeling period (July 2006) not the same period as ambient measurements
  – CalNex (Pasadena, CA) May 15 to June 15, 2010
  – SHARP (Houston, TX) April 15 to May 31, 2009

• Compared diurnal profiles of modeled and monitored values
  – Pasadena ground level monitoring site
  – Moody Tower elevated (~70 meters) monitoring site

• TexAQS II ambient ClNO$_2$ and N$_2$O$_5$ measurements at Barbour’s Cut, Houston Ship Channel, taken from the Ron Brown research vessel
Pasadena

(a) 04:00 – 12:00 PST

(b) 20:00 – 04:00 PST
Moody Tower

(a) 04:00 – 12:00 CST

(b) 20:00 – 04:00 CST
Barbour’s Cut

Graph showing nitryl chloride and nitrate concentrations over time at Barbour’s Cut.

- Nitryl Chloride, ppbv
- N₂O₅, ppbv

Time, UTC:
- 8:30 AM 9/2/06
- 8:40 AM
- 8:50 AM
- 9:00 AM
- 9:10 AM
- 9:20 AM
- 9:30 AM
- 9:40 AM

Concentrations:
- Nitryl Chloride: 0, 200, 400, 600, 800, 1000, 1200 ppbv
- N₂O₅: 0, 200, 400, 600, 800 ppbv
Modeled and Monitored Reconciliation

The under-prediction of ClNO$_2$, especially at the Pasadena monitor, suggests that sources of additional Cl$_2$, HCl and/or HOCl emissions are missing. The following sensitivities were run focusing on Pasadena:

- Ten-fold domain-wide emission increase;
- HNO$_3$ deposition releasing HCl from presumed sea salt coated surfaces (HNO$_3$ + NaCl $\rightarrow$ HCl + NaNO$_3$);
- Reduced dry deposition velocity for HCl by removing zero surface resistance constraint; and
- Include acidification of coarse-sized sea salt particulate (PM > 2.5 um), which is typically treated as inert.
Ten-fold Emissions Increase

Episode mean hourly ClNO\textsubscript{2} concentration at the Pasadena monitor with a ten-fold increase in Cl\textsubscript{2}, HCl and HOCl emissions
Episode mean hourly ClNO$_2$ concentration at the Pasadena monitor with increase in HCl emissions from acidification of sea-salt coated surfaces
Episode mean hourly ClNO₂ concentration at the Pasadena monitor with increase in HCl due to reduced deposition velocity.
Acidification of Coarse-Sized Sea Salt

Episode mean hourly ClNO₂ concentration at the Pasadena monitor with increase in HCl due to acidification of coarse-sized sea-salt
Conclusions

- The parameterized mechanism implemented in CAMx was able to simulate the formation of ClNO$_2$.
- Sea salt aerosols were likely underrepresented in the model leading to the significant under prediction of ClNO$_2$ due to under prediction of HCl and PCI.
- A combination of reducing the HCl dry deposition velocity and acidifying a fraction of the coarse-sized sea salt would likely yield better model performance.
- Additional work is needed to improve the ClNO$_2$ formation chemistry, including more monitoring of gas-phase and particle-phase chloride species and improving emission estimates.