Chlorine Emissions from Activated Sea-Salt Aerosols and Their Potential Impact on Ozone

Donald Dabdub
University of California, Irvine

Chairman's Air Pollution Seminar
California Air Resources Board
July 22, 2002
The Measurements

Unexpected high concentration of molecular chlorine in coastal air

Spicer et al.
Cl\textsubscript{2} Signals at a Coastal Site
Long Island, N.Y., June 7/8, 1996

Spicer et al.,
Important Questions

- Is there any evidence for chlorine and bromine atom sources in the lower atmosphere?

- If “yes”, what is the chemistry forming these sources?

  “The mechanism for Cl atom precursors from the sea salt aerosol is unclear”

  (D. J. Jacob, Heterogeneous chemistry and tropospheric ozone, Atm Env 2000)

- Is there some “new” chemistry? If so, how does it affect air quality in California?
The Experiments

- Add NaCl particles to aerosol chamber
- Add humid air to a relative humidity above the deliquescence point
- Add ozone
- Photolyze at 254 nm (generate OH radicals)
- Measure gaseous reactants and products using FTIR, DOAS, and API-MS
Formation of Hydroxyl Radicals

Ozone: $O_3$

Molecular Oxygen: $O_2$

Excited Oxygen Atom: $O(1D)$

Water Vapor: $H_2O$

Hydroxyl Radical: $OH$

Hydroxyl Radical: $OH$
Aerosol Chamber
(Top View)

- FTIR
- Atmospheric Pressure Ionization Mass Spec (API-MS)
- 560L Stainless Steel and Aluminum Chamber
- Photolysis lamps
- Gas inlet
- Water regulated temperature control
- Differential Optical Absorption Spectroscopy (DOAS)
- Aerosol Generation and Measurement
- Xe lamp
- Spectrometer
- MCT
- CPC
- DMA
Typical Experiment: Cl₂ Production

![Graph showing Cl₂ (10^{12} molecule cm^{-3}) and Ozone (10^{14} molecule cm^{-3}) production over photolysis time (min)].

- Cl₂ (10^{12} molecule cm^{-3})
- Ozone (10^{14} molecule cm^{-3})

Photolysis Time (min)
Experiments Varying Initial O$_3$ Concentration

Initial Ozone
- 14 ppm
- 10 ppm
- 2.6 ppm

Photolysis Time (min)

$\text{Cl}_2(10^{12} \text{ molecule cm}^{-3})$
Physical and Chemical Processes of MAGIC

**Aqueous Phase Chemistry**

$O_3, H_2O_2 \rightarrow OH$

$OH + Cl^- \rightarrow Known Aqueous Phase Chemistry$

$O_3, H_2O_2 \rightarrow Cl_2$

Model of Aerosol, Gas and Interfacial Chemistry

**Equilibrium**

**Transport**

**Chemical Reaction**

**Diffusion**
Schwartz 1986 Mass Transfer Method

**Mass transfer coefficient:**
\[
k_{mt} = \left[ \frac{R_p^2}{3D_g} + \frac{4R_p}{3c\alpha} \right]^{-1}
\]

**Aqueous-phase diffusion:**
\[
\left\langle C_j \right\rangle = QC_j^* + (1 - Q) \frac{P_j}{k_{L,j}}
\]

**Activity coefficients:**
Pitzer ion-interaction approach

**Kinetic salt effect:**
\[
\log k = \log k^o + \frac{A\Delta z^2 \sqrt{I}}{1 + \sqrt{I}}
\]

Debye-Hückel-Bronsted equation
Governing Equations of Gas- and Aqueous-Phase Chemistry/Mass Transport Model

**Gas Phase:** \[ \frac{dC_g}{dt} = -k_{mt} w_L C_g + \frac{k_{mt}}{H_A RT} C_{aq} w_L + R_g + R_{int} \]

**Aqueous Phase:** \[ \frac{dC_{aq}}{dt} = k_{mt} C_g - \frac{k_{mt}}{H_A RT} C_{aq} + \langle R_{aq} \rangle + R_{int} \]
Potential Mechanism for Cl₂ Production

Based on Known Aqueous-Phase Chemistry

Eigen and Kustin, 1962; Jayson et al., 1973; Nagararan and Fessedon, 1985; Neta et al., 1988 and references therein
Description of Chamber Model Chemistry

• **Gas Phase:**
  - 15 Species
  - 52 Reactions

• **Aqueous Phase:**
  - 32 Species
  - 99 Reactions
    » 48 - Chlorine chemistry
    » 37 - Oxygen-Hydrogen chemistry
    » 14 - Carbonate chemistry
  - 8 Aqueous acid/base equilibria
  - 10 Mass transfers between gas and aqueous phases
  - Aqueous phase diffusion treatment for transported species
  - Activity coefficient evaluation: Pitzer method

† Gas-phase and aqueous-phase organic, nitrogen and sulfur chemistry included during model evaluations of the marine boundary layer
Base Case and Constant pH Modeling Scenarios

Using Known Gas- and Aqueous-Phase Chemistry and Mass Transfer
Potential Mechanism for Cl$_2$ Production

Based on Known Aqueous-Phase Chemistry

Eigen and Kustin, 1962; Jayson et al., 1973; Nagaran and Fessedon, 1985; Neta et al., 1988 and references therein
Base Case and Constant pH Modeling Scenarios
Using Known Gas- and Aqueous-Phase Chemistry and Mass Transfer

![Graph showing the concentration of Cl₂ over time for different pH levels.]

- **Cl₂ (Base Case)**
- **Cl₂ pH = 3.5**
- **Cl₂ pH = 4.0**

**Time (min)**

**Cl₂ (10⁻¹² molecules cm⁻³)**
Proposed Mechanism for Cl\textsubscript{2} Production

\[ \text{O}_3, \text{H}_2\text{O}_2 \xrightarrow{\text{OH}} \text{OH} \]

Known Aqueous Phase Chemistry

\[ \text{OH} + \text{Cl}^- \xrightarrow{\text{Cl}_2} \text{Cl}_2 \]

Potential Surface Reactions

\[ \text{Cl}_2 \xrightarrow{\text{OH} \cdot \text{Cl}^-} \text{OH} \cdot \text{Cl}^- \]

\[ \text{OH} \cdot \text{Cl}^- + \text{OH} \cdot \text{Cl}^- \xrightarrow{\text{2 OH}^-} \text{2 OH}^- \]
Chlorine Gas
Hydroxide Ion
Chloride Ion
Hydroxyl Radical
Wet Sea-Salt Particle
Particle Interface
Chloride Ion
Hydroxide Ion
Questions to be examined

• Are chloride ions available at the interface?

• If all is correct, what is the impact of Cl in the overall chemistry of the atmosphere?

• What is the role of other halogen compounds?
Molecular Dynamics Simulations of NaCl / H₂O

Snapshot of the open surface of an infinite “slab” consisting of 96 NaCl and 864 water molecules per unit cell.

Model predicted surface coverage:
- 11.9% Cl⁻
- <0.2% Na⁺
$\text{NA}^{+}_{96}\text{Cl}^{-}_{96}(\text{H}_2\text{O})_{864}$ slab

DENSITY PROFILES ALONG Z-AXIS

\[ g_z (\text{arb. units}) \]

\[ r (\text{A}) \]

\[ \text{Cl}^{-} \]
\[ \text{Na}^{+} \]
\[ \text{O} \]
Accessible Surface Exposure: Cl\(^-\) and Na\(^+\)
How Does Sea-Salt Aerosol Affect Coastal Urban Ozone?
How does chlorine affect the atmosphere?

\[
\text{Cl} + \text{O}_3 \rightarrow \text{Ozone destruction}
\]

\[
\text{Cl} + \text{organics} \rightarrow \text{Ozone production}
\]

\[
\text{Oxides of Nitrogen}
\]
Ozone generation

\[ \text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5 \]

Alkyl radical and \( \text{O}_2 \) forms peroxo alkyl radical (\( \text{RO}_2 \))

\[ \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \]

Photolysis of \( \text{NO}_2 \) generates ozone

\[ \text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^{(3P)} \]

\[ \text{O}^{(3P)} + \text{O}_2 \rightarrow \text{O}_3 \]
The Modeling

- 133 Gas Species
- 280 Aerosols: 35 species, 8 sizes
- 361 Reactions

80 Cells
Each Cell: 5 x 5 km²
South Coast Air Basin Model Domain
# Available Parallel Machines

<table>
<thead>
<tr>
<th></th>
<th>CRAY T3E SDSC</th>
<th>CRAY T3E UTejas</th>
<th>IBM SP SDSC</th>
<th>SUN HPC SDSC</th>
<th>IBM SP UMichigan</th>
<th>HP Exemplar Caltech</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number of Processors</strong></td>
<td>272</td>
<td>88</td>
<td>128</td>
<td>64</td>
<td>64</td>
<td>256</td>
</tr>
<tr>
<td><strong>Processor Type</strong></td>
<td>DEC Alpha 21164</td>
<td>DEC Alpha 21164</td>
<td>IBM 160 Mhz Power2 Thin Nodes</td>
<td>UltraSparc II</td>
<td>IBM 160 Mhz Power2 Thin Nodes</td>
<td>PA-8000 180MHz</td>
</tr>
<tr>
<td><strong>Memory per Processor</strong></td>
<td>128 MB</td>
<td>128 MB</td>
<td>256 MB</td>
<td>64 GB (Total)</td>
<td>1 GB</td>
<td>256 MB</td>
</tr>
<tr>
<td><strong>Peak Performance</strong></td>
<td>154 Gflops</td>
<td>34 Gflops</td>
<td>62 Gflops</td>
<td>51 Gflops</td>
<td>31 Gflops</td>
<td>184 Gflops</td>
</tr>
<tr>
<td><strong>Largest Available Filesystem</strong></td>
<td>100 GB</td>
<td>34 GB</td>
<td>71 GB</td>
<td>140 GB</td>
<td>1.5 TB</td>
<td>64 GB</td>
</tr>
<tr>
<td><strong>Operating System</strong></td>
<td>Unicos/mk 2.0.3</td>
<td>Unicos/mk 2.0.4</td>
<td>AIX 4.2</td>
<td>Solaris 7.0</td>
<td>AIX 4.1/4.2.1</td>
<td>HP-UX 10.20</td>
</tr>
</tbody>
</table>
UC Irvine professors Herbert Hamber, left, and Donald Daboub use the Linux operating system to link their computers to create a...
On February 2001, SDSC dedicated Blue Horizon, the newest addition to the NPACI complement of high-performance computers. Blue Horizon, a 1,152-processor IBM RS/6000 SP capable of 1.02 teraflops, is the most powerful computer available to the U.S. academic community and the world's tenth most powerful computer.
New Chlorine Chemistry

- New Cl Chemistry:
  - 12 additional gas-phase species
  - 83 additional gas-phase reactions
    » Includes oxidation of VOC’s by Cl⁻

- Heterogeneous reactions:
  » \( \text{OH}^- + \text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + \text{OH}^- \)
  » \( \text{N}_2\text{O}_5 + \text{Cl}^- \rightarrow \text{ClNO}_2 + \text{NO}_3^- \)
  » \( \text{ClONO}_2 + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{NO}_3^- \)
  » \( (\text{NO}_3^- + \text{Cl}^- \rightarrow \frac{1}{2} \text{Cl}_2 + \text{NO}_3^-) \)

- JPL & IUPAC recommendations were considered. However, results from uptake studies on solid salts, salt powders and fresh synthetic sea-salt aerosol are not easily transferable to urban airshed models.

- New model for sea-salt aerosol emission at coastal surf zone
  » de Leeuw and coworkers
Source Functions for Sea-Salt Aerosol

• **Monaham et al., 1986 open ocean source function.**
  - Used in global models, e.g. Gong et al., 1997 and Erickson et al., 1999.

• **De Leeuw et al., 2001 surf zone source function.**
  
  \[
  \frac{dF_{N-Surf}}{dD_0} = 1.1 \times 10^7 \times e^{0.23U_{10}} \times D_0^{-1.65}
  \]
  
  - Developed from measurements in La Jolla, CA and Monterey, CA.
  - Assuming 231 km of coast and 100m wide surf zone.

• **Source function defined for particle diameter at formation.**
  
  - \( D_0 = 2D_{80} = 4D_{\text{dry}} \)
  - A 10 micron particle will settle from the TOP of the lower model layer (12.98m) in ~ 1 hr.
24-hr Average PM Contours: Friday, September 9, 1993

PM$_{1.0}$ 24hr Avg: Case Cl Chem

PM$_{2.5}$ 24hr Avg: Case Cl Chem

Cl$^-$ (PM$_{1.0}$) 24hr Avg: Case Cl Chem

Cl$^-$ (PM$_{2.5}$) 24hr Avg: Case Cl Chem

all units in µg/ m$^3$
Chloride deficits are predicted due to hydrochloric acid displacement.

Most sea-salt particles settle quickly and do not reach inland regions.
## Comparison of 24-hr Average Sodium Concentrations
**Friday, September 9, 1993**

<table>
<thead>
<tr>
<th></th>
<th>Long Beach</th>
<th>Claremont</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM\textsubscript{2.5}-sodium</td>
<td>TSP\textsubscript{-sodium}</td>
</tr>
<tr>
<td><strong>Observed</strong></td>
<td>0.50</td>
<td>3.11</td>
</tr>
<tr>
<td></td>
<td><em>PM\textsubscript{10}-sodium</em></td>
<td></td>
</tr>
<tr>
<td><strong>Modeled</strong></td>
<td>0.91</td>
<td>2.65</td>
</tr>
</tbody>
</table>

(all units in $\mu g/m^3$)
Cl$_2$ levels reach up to 12 ppt - a thirty fold improvement over the simulations of Spicer et al., albeit an order of magnitude below observations.

all units in ppt
ΔO₃ Contours: Friday, September 9, 1993

all units in ppb
$\text{Cl}_2$ contours: Friday September 9, 1993

adding nighttime chlorine production

$\text{Cl}_2$ concentrations are on the order observed by Spicer et al. and Keene et al. ...

all units in ppt
... however, photolysis of NO$_3$ and Cl$_2$ at dawn cause Cl$_2$ concentrations to drop rapidly.

Cl concentrations similar to the Case Cl Chem simulation are predicted and $\Delta$[O$_3$] are only slightly different than in previous slides.

all units in ppt
O₃ Contour Slices along “The Strip”

Ozone Slice on Sep 8 700

- Base Case
- [Cl₂] = 150 ppt
- [Cl₂] = 1500 ppt

Ozone Slice on Sep 8 1200

Ozone Slice on Sep 8 1500

Ozone Slice on Sep 8 1000

Location (CIT Cell Number = 500 + x) along The Strip

Ozone Concentration (ppb)
Conclusions

• Modeling results adequately reproduce regional sea-salt particle concentration

• Chlorine levels in the model are predicted an order of magnitude below observed values, albeit 30 times better than previous studies.

• Inclusion of sea-salt derived chlorine chemistry may increase:
  – morning ozone predictions by as much as ~12 ppb in coastal regions
  – peak domain ozone by ~ 4 ppb in the afternoon

• Most monitoring sites experience an increase:
  – in peak ozone concentration of 2-4 ppb
  – even higher ozone increases, up to 7 ppb, at times not coinciding with the peak

• These particular heterogeneous/multiphase chemical reactions do not affect the rate of hydrochloric acid displacement nor do they enhance aerosol nitrate formation
Aerosol Processes

- condensation
- evaporation
- surface chemistry
- coagulation
- water uptake
- oxidation
- precursor emissions
- activation
- subcloud scavenging
- dry deposition
- nucleation
- aqueous chemistry
- resuspension
- primary emissions
Acknowledgements

• **Financial Support**
  Air Resources Board of California
  U.S. National Science Foundation
  U.S. Environmental Protection Agency
  Organization of American States

**Helpful Discussions, Collaborators, Graduate Students**

- James Pitts, Jr.
- Robert Huie
- Barbara Finlayson-Pitts
- Paul Davidovits
- Elaine Chapman
- Carl Berkowitz
- Chet Spicer
- John Seinfeld

**Eladio Knipping**

- Khoi Nguyen
- Rolf Sander
- Stephen Schwartz