Simulation of Polar Ozone Depletion: An Update

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While activation may take place during dark polar winter, substantial ozone losses require that sunlight as well as activated chlorine (and bromine) be present to catalytically destroy ozone.
Antarctic Vortex, 3-year Mean area coverage.

<= Supercooled Ternary Solution (STS), with some solid mixtures

STS is forming in early winter (~60%) at 20km.

<= Water-Ice (and STS)

<= STS-NAT clouds (low NAT #density)

<= STS-NAT clouds (high NAT #density)
Modifications to PSC Parameterization: 80/20 partitioning

Equilibrium Approach for WACCM...

- Considine et al., JGR, 2000.
  - Settling Velocity
- Kinnison et al., JGR, 2007.
- Empirically, the partitioning of 80% total HNO₃ into STS and 20% into NAT best represents the evolution of HNO₃(g) in WACCM.
- CALIOP measurements show PSCs Fractional area is >60% in early winter (Pitts et al., 2009).
- Wegner et al., JGR, 2013.
The model shows significantly less scatter than the satellite observation due to the simplification that all PSCs form instantaneously with a prescribed size distribution.
There is no temporal offset in gas-phase HNO₃ between model and Obs.

Mixture of NAT and STS forms in late May / early June.

Model DeNOy occurs throughout the winter / spring period.

Model overestimates HNO₃ (g) - larger NAT radius needed?
We have updated the PSC representation in WACCM using Aura MLS and CALIOP data as constraints (Wegner et al., JGR 2013).

The model now has a mixed phase of STS and NAT in early winter that is more consistent with CALIOP data.

The evolution of gas-phase HNO$_3$ also is in better agreement with Aura MLS.

We also updated (not shown) the dehydration threshold for polar stratospheric H$_2$O. We were dehydrating at 80% saturation of water over ICE. We are now dehydrating at 100%.
## Examine PSC Assumptions on Ozone Depletion

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Temperature</th>
<th>PSCS</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Het</td>
<td>-</td>
<td>NONE</td>
<td>Zeroed halogen het. rates.</td>
</tr>
<tr>
<td>Reference</td>
<td>-</td>
<td>ALL TYPES</td>
<td>CCMI Version</td>
</tr>
<tr>
<td>2Kbias</td>
<td>-2K applied</td>
<td>ALL TYPES</td>
<td>Only to the Het Module.</td>
</tr>
<tr>
<td>3xSAD</td>
<td>-</td>
<td>ALL TYPES</td>
<td>Show the sensitivity to sulfate SAD in polar region only.</td>
</tr>
<tr>
<td>REFnat</td>
<td>-</td>
<td>ALL TYPES</td>
<td>2-NAT MODES (0.0001, 5 particles cm⁻³)</td>
</tr>
<tr>
<td>SOLID</td>
<td>-</td>
<td>NAT, ICE</td>
<td>Liquid PSCs reactivity zeroed.</td>
</tr>
<tr>
<td>LIQUID#1</td>
<td>T≥195K</td>
<td>LBS</td>
<td>Test Drdlia+Muller 2012 result.</td>
</tr>
<tr>
<td>LIQUID#2</td>
<td>T≥192K</td>
<td>LBS, ~STS</td>
<td>STS starts to form.</td>
</tr>
<tr>
<td>LIQUID#3</td>
<td>-</td>
<td>LBS, STS</td>
<td></td>
</tr>
</tbody>
</table>
TOZ (DU) *** 82° S *** Zonal Mean *** 2011

OMI = △

- NoHET [Excluding N$_2$O$_5$+H$_2$O]
- REF [Standard CCM1 REFClSD]
- REF -2K [Applied to Het. Module]
- REF 3xSAD [Applied to CCM1 Sulfate SAD]

Dobson Units (DU)

Day-of-Year

~160DU
TOZ (DU) *** 82° S *** Zonal Mean *** 2011

OMI = △

NoHET [Excluding N₂O₅ + H₂O]
REF [Standard CCM, REFC1SD]
REF -2K [Applied to Het. Module]
REF 3xSAD [Applied to CCM, Sulfate SAD]
SOLID [ICE and NAT PSCs Only]
TOZ (DU) *** 82° S *** Zonal Mean *** 2011

- OMI = △
- Dobson Units (DU)
- NoHET [Excluding N$_2$O$_5$+H$_2$O]
- REF [Standard CCM1 REFC1SD]
- REF -2K [Applied to Het. Module]
- REF 3xSAD [Applied to CCM1 Sulfate SAD]
- SOLID [ICE and NAT PSCs Only]
- LIQUID#1 [T $\geq$ 195K; w/DeNOY at all T]
- LIQUID#2 [T $\geq$ 192K; w/DeNOY at all T]
- LIQUID#3 [T no limit; w/DeNOY at all T]
NOTE: A different Solid/Liquid approach gives similar TOZ.
April 3, 2011

SD-WACCM No HET Sim

REF - NoHET
-57 DU

-2Kbias - NoHET
-96 DU

3xSAD - NoHET
-75 DU

-2Kbias & 3xSAD - NoHET
-118 DU
TOZ Summary

• In the SH, the REF case underestimates the observed TOZ (OMI) by approximately 25DU.

• In the SH, adding a -2K bias to the heterogeneous module overestimates the depletion.

• In the SH, adding a 3xSAD to the input CCM sulfate SAD (which is consistent with small volcanic eruptions) shows very good agreement with OMI TOZ.

• The model has difficulty representing the observed TOZ in the NH. Only when the -2K bias and 3xSAD is applied does the model come close to the observed decrease. More work is needed to understand this model/observed difference.

• The depletion due to LIQUIDS and SOLIDS is not additive.
  • REF ≠ SOLID only + LIQUID#3
Activation vs Deactivation: 74° S, 61hPa

**Chlorine Activation:** Sum of all het. Rates that produce chlorine.

**Chlorine Deactivation:** Sum of the rate that produce NO\(_2\) (J HNO\(_3\), HNO\(_3\)+OH) and Cl+CH\(_4\) => HCl

Both liquid PSCs and water-ICE are important for chlorine activation at this location in the reference cases.

Overall – a very good representation of O\(_3\) depletion.

HNO\(_3\)(g), H\(_2\)O(g) and T in good agreement with MLS =>
LIQUI D#2 shuts off ozone loss process by converting a great deal of active chlorine back into the reservoir species (ClONO₂).

If deactivation into ClONO₂ occurs too early, related chemical indicator is a reduced rate of formation of HCl at later times.
Activation vs Deactivation: 74°S, 61hPa

[Graphs showing the dynamics of Total Cl and Chlorine activation at different levels: REF, LIQ#2 T≥192K, and SOLID.]

Species (ppbv)
HCl Rate Change as an Indicator of Heterogeneous Processing.

Vortex Core, 52hPa

\[
\frac{d[HCl]}{dt} = -k \cdot [Cl] \cdot [O_3] + k' \cdot [Cl] \cdot [CH_4]
\]

Douglass et al., 1995

Production and loss chemistry of ClONO2 is key.

Vortex Edge, 52hPa

\[
\frac{d[HCl]}{dt} = -k \cdot [Cl] \cdot [O_3] + k' \cdot [Cl] \cdot [CH_4]
\]

Cl + O_3 \rightarrow ClO + O_2

Cl + CH_4 \rightarrow HCl + CH_3,

Douglass et al., 1995
HCl Rate Change as an Indicator Het. Processing.

2011 HCl, CIONO2 Tendencies at 32.0 hPa -75 to -65
Summary

- We find that the occurrence of cold temperatures and PSC chemistry at $T<192$K is essential to produce substantial ozone loss (O3L).

- This conclusion is bolstered by broad agreement of the temporal behavior of computed ozone and related species (HNO$_3$, H$_2$O, HCl) compared to Aura MLS.

- The magnitude of the calculated TOZ in both polar regions is sensitive to small differences in temperature and sulfate surface area density (~10-40DU).
  - These sensitivities are important in quantifying ozone recover due to halogens.

- These results confirm earlier studies suggesting that liquid PSCs particles are sufficient to simulation nearly all of the O3L using current model chemistry.
  - However, solid PSCs do play an important role in de-NOY and de-H2O. They also add to the O3L for altitudes >18km.
  - We have shown that the results for O3L from each particle type are not additive.

- We’ve shown that the rate of change of HCl can be used as a key indicator of ozone depletion chemistry, primarily outside of the vortex core.