CESM Tutorial: Stratospheric Aerosols and Chemistry

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August 15, 2017
The Antarctic Ozone Hole

From https://svs.gsfc.nasa.gov/30602
Ozone Hole Recipe

- chlorofluorocarbons
- cold temperatures
- Polar stratospheric clouds
- sunlight
Overview of stratospheric heterogeneous chemistry in WACCM

• Aerosol types
  • Liquid binary sulfates (LBS)
  • Supercooled ternary solutions (STS, liquid)
  • Nitric acid trihydrate (NAT, solid)
  • Water-ice (solid)
• Denitrification and dehydration: aerosols sediment, removing nitrogen and water species that inhibit halogen ozone loss
• Heterogeneous reaction approach
  • Chemical reactions (17 total)
  • Rate constant derivation
    • Reactivity of PSC types
    • Surface area density (SAD)
• Halogen activation and ozone depletion
• Total column ozone
• Ozone recovery and volcanic influences
PSC Parameterization in WACCM

References
Considine et al., JGR, 2000.
Kinnison et al., JGR, 2007.
Wegner et al., JGR, 2013.

LBS = Liquid Binary Sulfate
NAT = Nitric Acid Trihydrate (Solid); Responsible for denitrification.
STS = Supercooled Ternary Solution (Sulfate); Swell by uptake of HNO₃ and H₂O.
ICE = Water-ICE; Responsible for Dehydration.

CALIOP Obs (Pitts et al., 2009) Showed liquid and solid PSC coexisted throughout the winter.

From MAM, volcanic and non-volcanic sources

LBS
NAT (T<Tsat)

HNO₃ → De-NOY

STS (APCM)

HNO₃ → De-NOY

Water-ICE

De-H₂O

Prognostic H₂O done in CAM4 Physics.
De-Nitrification

Temperature (K)

Aura MLS

CESM2 (WACCM)

Pressure, hPa

0.1

1.0

10.0

100.0

0

60

120

180

240

300

360

HNO$_3$ (ppbv)

Aura MLS

CESM2 (WACCM)

Pressure, hPa

0.1

1.0

10.0

100.0

0

60

120

180

240

300

360

Aura MLS binned up by Chuck Bardeen, NCAR
De-Hydration

Temperature (K)

Aura MLS

CESM2 (WACCM)

Pressure, hPa

Aura MLS

CESM2 (WACCM)

Pressure, hPa

H₂O (ppmv)

Aura MLS

CESM2 (WACCM)

H₂O (ppmv)

Aura MLS binned up by Chuck Bardeen, NCAR
17 Heterogeneous Reactions Included in WACCM

Table 1. Heterogeneous Reaction Probabilities Used in WACCM

<table>
<thead>
<tr>
<th>Reactions</th>
<th>NAT(^a)</th>
<th>ICE(^a)</th>
<th>Liquid Aerosols</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2\text{O}_5 + \text{H}_2\text{O})</td>
<td>0.0004</td>
<td>0.02</td>
<td>(~0.1)</td>
</tr>
<tr>
<td>(\text{ClONO}_2 + \text{H}_2\text{O})</td>
<td>0.004</td>
<td>0.3</td>
<td>(\text{Shi et al. (2001)})</td>
</tr>
<tr>
<td>(\text{ClONO}_2 + \text{HCl})</td>
<td>0.2</td>
<td>0.3</td>
<td>(\text{Shi et al. (2001)})</td>
</tr>
<tr>
<td>(\text{HOCl} + \text{HCl})</td>
<td>0.1</td>
<td>0.2</td>
<td>(\text{Shi et al. (2001)})</td>
</tr>
<tr>
<td>(\text{BrONO}_2 + \text{H}_2\text{O})</td>
<td>0.006(^b)</td>
<td>0.3(^c)</td>
<td>(\text{Hanson et al. (1996)})</td>
</tr>
<tr>
<td>(\text{HOBr} + \text{HCl})</td>
<td>–</td>
<td>0.3</td>
<td>(\text{Hanson (2003)})</td>
</tr>
</tbody>
</table>

\(^a\) Consistent with JPL10-6 except where noted.
\(^b\) Davies et al. [2002].
\(^c\) Listed as \(>0.2\) in JPL10-6.

Solomon et al., JGR, 2015.

Rate Constant \(\sim \frac{1}{4} \times V \times \text{SAD} \times \gamma\) (units: sec\(^{-1}\))

\(V\) = mean speed (units: cm sec\(^{-1}\))

\(\text{SAD}\) = Surface Area Density (units: cm\(^2\) aerosol/cm\(^3\) atm)

\(\gamma\) = Reaction Probability (unitless, 0-1); For NAT and ICE the gamma’s are listed above. For liquid aerosols see next slide.
At temperatures <200K, the reaction probability approaches one for several important heterogeneous reactions.

Gas-phase sulfur chemistry

- \( H_2SO_4 \) (aer)
  - \( H_2O \) (aer)
- \( H_2SO_4 \) (gas)
  - \( H_2O \)
  - \( h\nu \)
- \( SO_3 \)
  - \( h\nu \)
  - \( OH (M) \)
- \( SO \)
  - \( O_2, O_3 \)
  - \( OH \)
  - \( h\nu \)
- \( SO_2 \)
  - \( O \)
  - \( OH \)
  - \( OH, NO_3 \)
- \( S \)
  - \( OH \)
- \( OCS \)
  - \( emissions \)
- \( DMS \)
  - \( OCS \)
  - \( DMS \)
WACCM SO$_2$ compares well to in situ observations

While the MIPAS single-radiance retrievals provide global daily coverage, the precision of these data at low SO$_2$ mixing ratios is 70–100 pptv, necessitating significant averaging to quantify background SO$_2$ in the UT/LS. To compare the satellite retrievals with our in situ measurements we use zonally averaged satellite profiles from 10 to 25°N during the periods when enhancements due to significant volcanic activity appear to be minor as described in Höpfner et al. [2013].

For the profiles in Figure 3, we show the median and interquartile range of the individual ACE-FTS retrievals and of the MIPAS monthly means to provide a measure of the variability of the retrieved SO$_2$ mixing ratios.

3. Discussion

The temperature and ozone structure observed during the VIRGAS flights indicates that air sampled south of 25°N during VIRGAS is representative of tropical air masses (Figure 2). Therefore, we use measurements south of 25°N to characterize the tropical SO$_2$ field. Figure 3 shows statistics of the SO$_2$ measurements made from the aircraft in the tropical UT/LS region and compares these with the model calculations (Figure 3a) and satellite retrievals (Figure 3b). We show the median and interquartile range for the 1 min averaged in situ SO$_2$ measurements (blue markers and shading). In the lower stratosphere (18 km and above) a narrow distribution centered near 3 pptv was observed and values above 10 pptv were rare. In the tropopause region (~17 km), a broader distribution was observed with a median value of 10.8 pptv. In the upper troposphere (14–17 km) only a minor vertical gradient is observed, likely evidence of vertical mixing related to the extensive convection in this region.

Figure 3a presents two profiles produced by using both the WACCM and GEOS-5 models. For each model an average SO$_2$ profile is derived by sampling the model along aircraft flight tracks (Figure 3a solid lines). In addition, an annual zonal mean profile from each model for 2015 is calculated to estimate typical tropopause SO$_2$ levels (Figures 3a and 3b, dashed lines). Because the models include all known volcanoes globally, the zonal average model profiles estimate the effects of volcanoes outside of the sampling region. At the tropopause (~17 km), the flight-track sampled models show SO$_2$ values that are lower than the aircraft observations of 10.8 pptv by 25% (WACCM, 8.1 pptv) and 31% (GEOS-5, 7.5 pptv), although both models are well within the range of the observations (5.4–19.5 pptv). The tropopause zonal mean values from both WACCM and GEOS-5 are shown in Figure 3b.

Observations from VIRGAS experiment, October 2015. Figure from Rollins et al. (2017).
Stratospheric sulfur burdens: volcanic and non-volcanic

Mills et al. (JGR, 2016)
Liquid Binary Sulfate Surface Area Density

Volcanic SAD
July 1991-December 1996

Non-volcanic SAD
1997-2005

Sampled on balloon flight dates

Mills et al. (JGR, 2016)
Figure 1. Schematic diagram of key chemical processes involved in polar ozone depletion. Unreactive chlorine is converted to active chlorine by heterogeneous processes on PSC surfaces denoted by green arrows. It is deactivated by processes and species denoted in blue. A yellow dashed line marks the distinction between unreactive and reactive chlorine.
Comment: Exceptional model/MLS agreement of HCl, ClONO$_2$, and O$_3$.

Solid lines = WACCM; Symbols = Observations
Total Column Ozone (TOZ), SD configuration

Slide courtesy of D. Kinnison.
Slide Courtesy of D. Kinnison, NCAR

Total Column Ozone (TOZ), multiple WACCM configuration

TOZ [63S-90S] - October

- REFC1: [data ocean]
- REFC2: [interactive ocean]
- REFC1SD: [MERRA]
- Observations

Thin black line ~1980 TOZ
Symbols are individual realizations
3-point smoothing for solid lines

Year
1850 1900 1950 2000 2050 2100
Total Column Ozone (DU)
150 200 250 300 350 400 450
Emergence of healing in the Antarctic ozone layer

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Science (2016)

Abstract

Industrial chlorofluorocarbons that cause ozone depletion have been phased out under the Montreal Protocol. A chemically driven increase in polar ozone (or “healing”) is expected in response to this historic agreement. Observations and model calculations together indicate that healing of the Antarctic ozone layer has now begun to occur during the month of September. Fingerprints of September healing since 2000 include (i) increases in ozone column amounts, (ii) changes in the vertical profile of ozone concentration, and (iii) decreases in the areal extent of the ozone hole.

Along with chemistry, dynamical and temperature changes have contributed to the healing but could represent feedbacks to chemistry. Volcanic eruptions have episodically interfered with healing, particularly during 2015, when a record October ozone hole occurred after the Calbuco eruption.
Solomon et al. (Science, 2016) use WACCM to attribute variability in Antarctic ozone recovery to volcanic eruptions.


Calbuco significantly increased the size of 2015’s record ozone hole.
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  - Comparison of WACCM to Aura MLS
- Heterogeneous Reaction Approach
  - Chemical Reactions (17 total)
  - Rate constant derivation
    - Reactivity of PSC types.
    - Surface Area Density
- Halogen Activation and Ozone Depletion
  - Comparison of WACCM to Aura MLS
- Total Column Ozone
  - Comparison of WACCM to OMI and SBUV observations.