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Sensitivity of Polar Stratospheric Ozone Loss to Uncertainties in Chemical Reaction Kinetics

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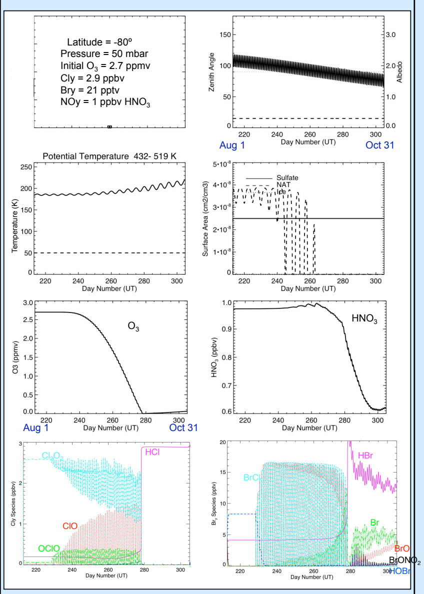
Introduction and Abstract

Several recent observational and laboratory studies of processes involved in polar stratospheric ozone loss have prompted a reexamination of aspects of our understanding for this key indicator of global change. To a large extent, our confidence in understanding and projecting changes in polar and global ozone is based on our ability to simulate these processes in numerical models of chemistry and transport. The fidelity of the models is assessed in comparison with a wide range of observations. These models depend on laboratory-measured kinetic reaction rates and photolysis cross sections to simulate molecular interactions. The rates of all of these reactions are subject to uncertainty, some substantial. In particular, recent lab measurements of the Cl_2O_2 photolysis cross sections [Pope et al., 2007] are significantly different (smaller) than those reported in the latest JPL rate compendium [Sander et al., 2006].

In this study we use a simple box-model scenario for Antarctic ozone to estimate the uncertainty in loss attributable to known reaction kinetic uncertainties. Following the method of earlier work [Stolarski et al., 1978; Stolarski and Douglass, 1986], rates and uncertainties from the latest laboratory evaluation are applied in random combinations. We determine the key reactions and rates contributing the largest potential errors and compare the results to observations to evaluate which combinations are consistent with atmospheric data. Implications for our theoretical and practical understanding of polar ozone loss are highlighted.

MODEL SCENARIO

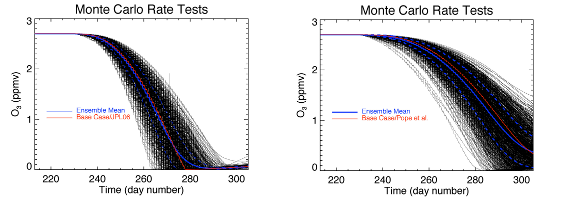


Kinetic Rate Uncertainties

- Basic Goddard stratospheric chemistry mechanism
  - 122 Kinetic reactions (gas-phase)
  - 37 Photolysis reactions
- 1000 Monte Carlo sets of rate coefficients each varying randomly within the distribution given by +/- 1σ errors from JPL'06
- 2 sets of Monte Carlo runs: standard JPL'06 and Pope et al. Cl_2O_2 cross sections
- Sensitivity runs varying each rate individually at 1 +/- 1σ

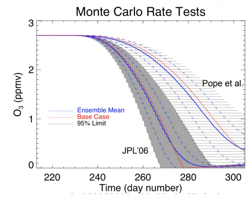
ANTARCTIC OZONE

Model Uncertainty Scenarios

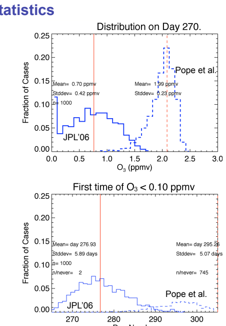


- Large range of calculated O_3 loss within JPL'06 error limits
- Significantly slower loss with Pope et al. Cl_2O_2 cross sections

Ozone Loss Statistics

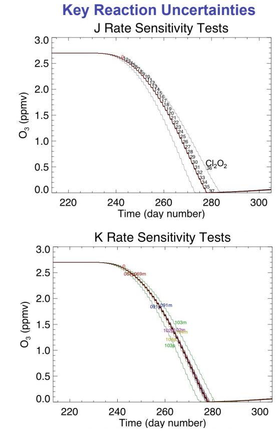


- Cl_2O_2 cross-section scenarios are distinct at the 95% confidence level.



RATE SENSITIVITY

Key Reaction Uncertainties



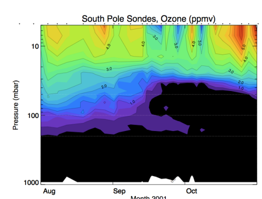
First O_3 < 0.1 ppmv (base case = day 276.7)

Rate File	+1σ	Δt (days)	-1σ
$BrO + ClO \rightarrow Br + ClOO$	-3.29		2.96
$BrO + ClO \rightarrow BrCl + O_2$	-0.875		0.75
$Br + O_3 \rightarrow BrO + O_2$	-0.33		0.917
$ClO + OH \rightarrow HCl + O_2$	0.71		-0.167
$BrO + ClO \rightarrow Br + OClO$	0.666		-0.167
$ClO + ClO + M \rightarrow Cl_2O_2 + M$	-0.125		0.125
$Br + H_2CO \rightarrow HBr + HCO$	0.5		-0.08

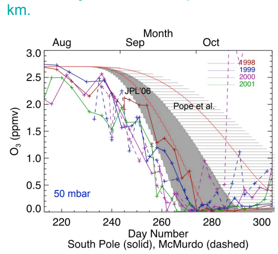
Sensitivity tests show that O_3 in this scenario is most sensitive to the Cl_2O_2 cross section and bromine-chlorine reaction uncertainties. These calculations may provide guidance for lab measurements to target key uncertainties.

COMPARISON WITH OBSERVATIONS

Ozone Sondes

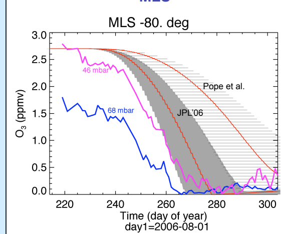


- Sonde O_3 near 0 in Spring from 14 to 21 km.

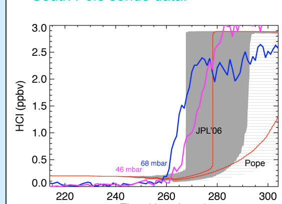


- Measured O_3 in each year favors JPL'06 scenario or even faster loss.

MLS



- MLS zonal mean O_3 similar to South Pole sonde data.



- MLS and model HCl increase consistent with respective O_3 loss

Summary

- Known uncertainties in kinetic reaction rate parameters from laboratory measurements produce significant uncertainty in Antarctic O_3 loss calculated in a simple, but representative, model.
- The impact of varying Cl_2O_2 cross sections between JPL'06 and Pope et al. is distinguishable at the 95% confidence level in a spring Antarctic O_3 loss scenario.
- Comparison to observations shows the ozone sonde and MLS data are consistent with JPL'06 rates but not Pope et al. within model uncertainty.
  - Both data sets suggest somewhat faster O_3 loss needed in the model relative to the base case
- Findings are consistent with previous work with earlier rate compilations at mid latitudes and in the Arctic (Fish and Burton [1997]; Rex et al.).

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