# Understanding the Relation between V<sub>PSC</sub> and Arctic Ozone Loss

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SPARC 4<sup>th</sup> General Assembly, Bologna 3<sup>rd</sup> September 2008





# Outline

- 1. Introduction
- 2. Approach and previous results
- 3. Updated results
- 4. Idealised photochemical model study
  - a) Ozone loss on a single layer
  - b) Three dimensional aspects
- 5. Simple model of vortex average ozone loss
- 6. Summary

#### Acknowledgements:

- Many, many ozonesonde personnel; ECMWF; FU Berlin; Univ. Leeds
- European Commission, BMBF
- G. Bodeker & P. Huck (NIWA)







## Polar ozone loss processes



#### **Complicating factors:**

- meteorological variations
- denitrification
- solar exposure
- initial chemical fields

- descent rates
- in-mixing
- vortex inhomogeneities
- vertical extent



Left panel: Daily averages of CIO (red dots) and HCI (green dots) observed by Aura MLS, and CIONO<sub>2</sub> (cyan triangles) observed by ACE-FTS at 490 K (~20 km) during the 2005 Antarctic winter/spring, calculated for 70°-75° equivalent latitude using the Global Modeling and Assimilation Office GEOS-4 temperatures and potential vorticity. Only daytime measurements are included in the averages for CIO; CIO data appear sparser because measurements in sunlight are not always available at high equivalent latitudes, especially in early winter. The sampling of ACE-FTS does not provide coverage of this equivalent latitude band at all times throughout the winter.

Right panel: As in the left panel, for the 2004/2005 Arctic winter/spring.

#### WMO, 2007

# **APPROACH**

**Ozone loss** is calculated on descending potential temperature surfaces with heating rates from SLIMCAT and ozone measurements from the Arctic ozonesonde network ("vortex average")

 $\mathbf{V}_{\text{PSC}}$  is calculated from ECMWF temperature fields and  $\mathsf{T}_{\mathsf{NAT}}$ 

Both seasonal integrals/averages.



(a) VPSC (black columns) and DO3 (red columns). DO3 was estimated from the data shown in Figure 1 between day 15 and day 85 of each year. Days 25 and 75 were chosen as start or end date of the integration for years when the well isolated vortex established late (1994, 1999) or broke up early (1992, 1998, 2003). In these cases ozone loss is not expected during the omitted ten days.

#### Rex et al., GRL, 2004

# **Ozone loss versus PSC formation potential (V<sub>PSC</sub>)**

V<sub>PSC</sub>: winter average volume of air cold enough for the formation of PSCs (e.g. -78°C in 18 km Altitude)



- climate sensitivity of ozone loss: 15 DU / 1°C cooling
- good test of model

Rex et al., GRL 2006; WMO 2007

# Long term evolution of $V_{PSC}$



- Long term increase in the maximum values reached during the cold winters
- This change in climate conditions in the Arctic stratosphere contributed to large ozone losses since the middle nineties.

Rex et al., GRL 2006; WMO 2007

# **Ozone loss versus PSC formation potential (V<sub>PSC</sub>)**

 $V_{PSC}$ : winter average volume of air cold enough for the formation of PSCs



1991/92 - 2007/08

update of Rex et al., GRL 2006; WMO 2007



#### Moving to 3D



Intercept	1.429
slope	0.334
R2	0.795



Intercept	1.520
slope	0.633
R2	0.874





### **Activation**

AWI chemical box model,  $CI_v = 3ppb$ 

sinusoidal 6 day cycle between 60 & 80° N at 50hPa (equiv to 20° offset vortex) **Persistent** PSCs

80..60 N; T = 194 K





### **Activation**

AWI chemical box model,  $CI_v = 3ppb$ 

sinusoidal 6 day cycle between 60 & 80° N at 50hPa (equiv to 20° offset vortex) Intermittent PSCs

80..60 N; one-day periods of 194 K (near 80 N)



# **Ozone loss vs de-activation**

Both, ozone loss and chlorine deactivation are driven by sunlight: Ozone loss:

$$C|OOC| + \frac{hv}{V} \rightarrow C|OO + C|$$

Chlorine deactivation:

 $HNO_3 + hv \rightarrow NO_2 + OH$  followed by  $NO_2 + CIO \rightarrow CIONO_2$ 



- Both cross sections fall off steeply between UV and vis
- HNO<sub>3</sub> fall off somewhat steeper



## **Ozone loss vs de-activation**

Both, ozone loss and chlorine deactivation are driven by sunlight: Ozone loss:

$$\mathsf{C}|\mathsf{OOC}| + \mathsf{hv} \to \mathsf{C}|\mathsf{OO} + \mathsf{C}|$$

Chlorine deactivation:

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As SZA increases:

- both Js increase
  - ⇒ ozone loss rate ↑
  - $\Rightarrow$  ozone loss rate period  $\downarrow$
- $J_{HNO3}$  increases more
- Deactivation > loss



### **Ozone loss vs de-activation**



- A PSC event that activates 3 ppbv ClO<sub>x</sub> will result in ~1.1 ppmv loss of ozone, no matter when the PSCs occur (assuming stable vortex)
- Later activation: initially faster, but slightly less overall



## Moving to 3D - offsetting CIO<sub>x</sub> factors

 $O_3$  loss close to linear with  $CIO_x$  (not close to quadratic)

- though (+)ve non-linearity partly offsets (-)ve non-linearity in activation



## Moving to 3D - offsetting CIO<sub>x</sub> factors

 $O_3$  loss depends on initial  $CIO_x$  at different altitudes more loss at lower altitudes for given  $CIO_x$  $CI_v$  vertical profile provides upper limit to  $O_3$  loss and vertical variation

Limit to effect of PSC altitude variations on  $O_3$  loss



#### Moving to 3D - denitrification



#### Moving to 3D - denitrification

#### Seen in 2000??



e	0.334
	0.795

R2



/ 5
39
42



Incorcope	1.020
slope	0.633
R2	0.874



Intercept	0.698
slope	0.276
R2	0.432

# Simple model of Arctic vortex average ozone loss - I

Activation:

initial: FAP × CIONO<sub>2</sub> further supply through J(HNO<sub>3</sub>), i.e. FAS-dependent calculate instantaneous activation rate i.e. CIONO<sub>2</sub>, HCl and CIO<sub>x</sub> evolution through winter

Ozone loss:

 $O_3 \text{ loss} \propto \text{ClO}_x \times \text{FAS}$ 

**Deactivation:** 

depends mainly on HNO<sub>3</sub>, CIO<sub>x</sub> & FAS (Arctic)

Method:

- Solve 4 coupled differential equations
- Initial Cl<sub>y</sub> and ClONO<sub>2</sub>/HCl
- Meteorological fields (vortex fraction (a) with PSCs (FAP) & (b) sunlit (FAS))
- Chemical rates by training on CIONO<sub>2</sub> (ACE) and CIO & HNO<sub>3</sub> (MLS)

Poster by Petra Huck on similar model for Antarctic [Session C ; P37; Thurs 1730]



# Simple model of Arctic vortex average ozone loss - II



Large interannual variability in HCl,  $CIONO_2$ and  $CIO_x$  evolution (c.f. Santee et al., JGR, 2008)

Effect of interplay between PSC and sunlit exposure

Currently realistic, but preliminary

Rex et al., in preparation



# Simple model of Arctic vortex average ozone loss - II



Rex et al., in preparation

# **Implications for CCMs**

Critical parameters for calculating Arctic vortex ozone loss

- Cl<sub>v</sub>, NO<sub>v</sub>, meteorological fields as input
- T -> activation (FAP) (PSC scheme?)
- Photolysis rates (ClOOCI, HNO<sub>3</sub>) in 300-380nm -> deactivation
- Vortex position & extent -> solar exposure (FAS)

→ Development of simple algorithm for use in climate models?



# Summary

Relation updated - it still holds

Activation:

linearity:  $J(HNO_3)$  limits  $CIONO_2 \& CIO_x$  formation *(if PSCs present)* spatial/temporal averaging smooths idealised relation

Competition between  $O_3$  loss and deactivation ~0.4 ppm of  $O_3$  loss / 1ppb  $ClO_x$  $J(Cl_2O_2)$  vs  $J(HNO_3)$  cancels out effects on  $O_3$  loss Vertical offsets

vertical profile of Cly denitrification / renitrification

Simple model

surprisingly good description - needs comparison with chemical fields

All these processes in CTMs and CCMs show linear, compact behaviour No new processes involved



# **Thank You!**



#### CALIPSO PSC Volume versus T<T<sub>NAT</sub> Volume Arctic Only



**Compactness of ozone loss vs. V<sub>PSC</sub> relation** Quantitative work in progress about:

• Cancelling effect of denitrification on column loss:

denitrification at one level <=> renitrification at level below larger loss less loss

• Cancelling effect of baroclinicity on chlorine activation/denitrification:

PSCs in vortex corecold region displacedless air processed<=>more air processedmore denitrificationless denitrification

Cancelling effect of solar illumination on ozone loss rates and chlorine deactivation:

early PSCs late PSCs slow ozone loss<=> rapid ozone loss slow recovery / long loss periodrapid recovery / short loss period

> work in progress Harris, Rex, Lehmann



#### **Activation**

6

#### **SLIMCAT** overestimates activation



**Figure 2.** Time series over the 2004/2005 Arctic winter as a function of equivalent latitude (EqL) at 490 K. (Top row) ClO and HCl data from MLS and ClONO<sub>2</sub> data from ACE-FTS. Only daytime (ascending) data are shown for ClO; the individual measurements contributing to the daily averages have been adjusted to correct for a known negative bias in the MLS ClO data as discussed in section 2.1. Small gaps in the data have been filled using a Kalman smoother as in Figure 1. The  $1.6 \times 10^{-4}$  s<sup>-1</sup> contour of sPV is overlaid in black to demark the approximate edge of the polar vortex. (Bottom row) Corresponding SLIMCAT model results, sampled at the MLS measurement locations and times.

#### **Basic requirements**

Cold - PSCs - active chlorine - sunlight - isolation

#### **Complicating factors:**

- meteorological variations
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Figure 6. Time series of APSC for December to March of winter 2000 (blue) and 2005 (red) at the  $\Theta$  = 380, 400, 475 and 550 K levels. Grey shading indicates the range of APSC between 1992 and 2004 (excluding the winter of 2000). Here, APSC denotes the daily horizontal extent of temperatures low enough for PSCs to exist



#### **Activation**

AWI chemical box model,  $CI_y = 3ppb$ sinusoidal 6 day cycle between 60 & 80° N at 50hPa (equiv to 10° offset vortex)



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