

# Sensitivity of Arctic ozone loss to stratospheric H<sub>2</sub>O

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[1] Likely causes of a future increase in stratospheric H<sub>2</sub>O are a rise in tropospheric CH<sub>4</sub> and H<sub>2</sub> leakages from an increased integration of hydrogen into the energy supply system. Here we evaluate the impact of potential future stratospheric H<sub>2</sub>O increases on Arctic ozone loss by comparing ozone loss proxies based on two different mechanisms of chlorine activation. In particular, the H<sub>2</sub>O dependence of the volume of air is analyzed where temperatures are low enough to form nitric acid trihydrate, denoted as V<sub>PSC</sub>, and for Cl activation on liquid sulfate aerosols, denoted as V<sub>ACI</sub>. We show that V<sub>ACI</sub> increases faster than V<sub>PSC</sub> with increasing H<sub>2</sub>O mixing ratios in the altitude range of 400 K to 550 K potential temperature. As a consequence, the additional ozone column loss is expected to be most pronounced for cold winters and large H<sub>2</sub>O increases and to be significantly higher when V<sub>ACI</sub> is used as a proxy. **Citation:** Feck, T., J.-U. Groöb, and M. Riese (2008), Sensitivity of Arctic ozone loss to stratospheric H<sub>2</sub>O, *Geophys. Res. Lett.*, 35, L01803, doi:10.1029/2007GL031334.

## 1. Introduction

[2] Polar stratospheric ozone depletion is driven by temperature-dependent processes that lead to the release of active chlorine (Cl, ClO, Cl<sub>2</sub>O<sub>2</sub>, Cl<sub>2</sub>) from its reservoir species (HCl, ClONO<sub>2</sub>). Hence, the understanding of the relationship between temperature and ozone loss is one of the key parameters for the estimation of future ozone depletion. Today it is assumed that chlorine activation is connected with the existence of polar stratospheric clouds (PSCs) that consist either of nitric acid trihydrate (NAT) or supercooled ternary solutions (STS). PSCs are present in the winter atmosphere below the NAT threshold temperature T<sub>NAT</sub> at about 195 K [Hanson and Mauersberger, 1988]. Because it is generally accepted that chlorine activation also occurs at about 195 K, the formation of NAT is commonly regarded as the dominant process in the activation of chlorine [e.g., World Meteorological Organization (WMO), 2003].

[3] Rex *et al.* [2004] found an empirical relationship between the Arctic ozone column loss and the total volume of air exposed to temperatures below T<sub>NAT</sub>, denoted by them as V<sub>PSC</sub>, which was confirmed by Tilmes *et al.* [2004] in an independent study. Interestingly, ozone column loss and V<sub>PSC</sub> show a compact linear correlation. Therefore, V<sub>PSC</sub> seems to be a convenient proxy for ozone loss. Rex *et al.* [2004] noted that their findings were quite surprising since other factors like the degree of denitrification in the Arctic

vortex, the timing of the PSC periods during winter, the location of PSCs within the Arctic vortex and the stratospheric sulfate aerosol loading should also influence the ozone loss.

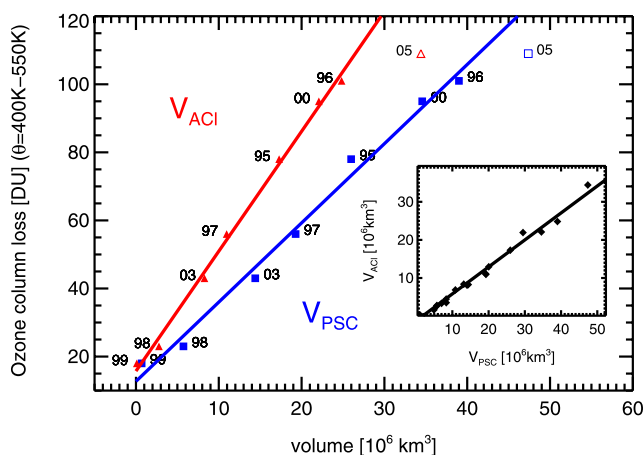
[4] A recent study (K. Drdla, Temperature thresholds for polar stratospheric ozone loss, submitted to *Science*, 2007, hereinafter referred to as Drdla, submitted manuscript, 2007; see auxiliary materials) investigated Cl activation on liquid sulfate aerosols and solid aerosols in a more comprehensive way. Drdla showed that Cl activation is sufficiently fast on liquid sulfate aerosols and that the threshold temperature for Cl activation T<sub>ACI</sub> (≈195 K) depends only on the potential temperature, the sulfate aerosol surface area density (SAD) and the H<sub>2</sub>O mixing ratio. Therefore Drdla concluded that Cl activation is solely controlled by liquid sulfate aerosols. Drdla also demonstrated that T<sub>NAT</sub> roughly coincides with T<sub>ACI</sub> under current atmospheric conditions and concluded that T<sub>NAT</sub> only fortuitously describes both PSC formation and Cl activation. Because atmospheric conditions are likely to change in future it is important to know whether either liquid sulfate or solid aerosols dominate Cl activation since this could lead to significant differences in the prediction of future polar ozone loss.

[5] Stratospheric H<sub>2</sub>O, for instance, is predicted to increase as a result of increased tropospheric CH<sub>4</sub> levels [Röckmann *et al.*, 2004] and H<sub>2</sub> leakages from an increased integration of hydrogen into the energy supply system [Schultz *et al.*, 2003; Tromp *et al.*, 2003; Warwick *et al.*, 2004]. There are also variations in the stratospheric H<sub>2</sub>O mixing ratio that might be due to changes in the tropopause temperature or the tropical upwelling circulation [Randel *et al.*, 2006]. Box model calculations by Röckmann *et al.* [2004] indicate that the projected increase of tropospheric methane by WMO scenarios will lead to an increase of the upper stratospheric H<sub>2</sub>O mixing ratio of about 0.4 ppmv by 2050. A similar increase was proposed by Riese *et al.* [2006] as a realistic upper limit of the impact of a H<sub>2</sub> economy.

## 2. Impact of Future H<sub>2</sub>O Levels

[6] Here we analyze the impact of stratospheric H<sub>2</sub>O increases on two different mechanisms of chlorine activation and the consequences for the prediction of Arctic ozone loss on the basis of ECMWF operational analysis of the past two decades. Instead of performing simulations with a global 3-D model, which tends to have difficulty in reproducing polar ozone loss [e.g., Austin *et al.*, 2003], we use proxy-ozone column loss correlations as, for example, given by Rex *et al.* [2004]. Therefore we investigate the impact of H<sub>2</sub>O increases on the evolution of the total volume of air exposed to temperatures below T<sub>NAT</sub> (V<sub>PSC</sub>) and T<sub>ACI</sub> (V<sub>ACI</sub>). Both V<sub>PSC</sub> and V<sub>ACI</sub> are used as proxies to estimate

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**Figure 1.** Relation of averaged ozone column loss in Dobson units (DU) versus  $V_{ACI}$  and  $V_{PSC}$  for the Arctic winters 1995 to 2000, 2003 and 2005. Blue and red solid lines represent the corresponding linear fits for all winters except 2005. According to *Rex et al.* [2006] this winter is characterized by an unusual meteorology, which caused significant ozone depletion below 400 K potential temperature. The small inset shows a linear and compact correlation for  $V_{PSC}$  and  $V_{ACI}$  for all Arctic winters between 1984 and 2005.

possible additional Arctic ozone column losses in the altitude range of 400 K to 550 K potential temperature due to a H<sub>2</sub>O increase. Ozone column loss values are taken from *Rex et al.* [2006] and were derived by the so-called vortex average method. Hydrogen leakage scenarios of a future H<sub>2</sub> economy served as the basis for simulations of potential future stratospheric H<sub>2</sub>O increases due to an increase of tropospheric H<sub>2</sub> [*Schultz et al.*, 2003; *Tromp et al.*, 2003; *Warwick et al.*, 2004].

[7] Because in this study we consciously concentrate on a single effect of a complex problem it should be pointed out that our study has certain limitations. It does not account for dynamical feedbacks of a potential H<sub>2</sub>O increase. Moreover, neither the emission trade-offs that would be associated with the H<sub>2</sub> economy (e.g. decline of CO<sub>2</sub> and CH<sub>4</sub> emissions) nor the declining levels of anthropogenic halogens that would eventually reduce chemical ozone loss are considered. Furthermore, it should be noted that it is generally assumed that a global H<sub>2</sub> economy is unlikely to be put in place while stratospheric chlorine mixing ratios are high. This certainly has an impact on the proxy/O<sub>3</sub>-loss correlations that are presented here.

## 2.1. $V_{PSC}$ and $V_{ACI}$ Under Current Conditions

[8] We computed  $V_{PSC}$  and  $V_{ACI}$  from ECMWF operational analysis for the period 1984 to 2005. Both  $V_{PSC}$  and  $V_{ACI}$  are calculated between 400 K and 550 K potential temperature and averaged over the period from mid-December to the end of March using the NAT equilibrium temperature  $T_{NAT}$  [*Hanson and Mauersberger*, 1988] and the Cl activation threshold  $T_{ACI}$  (*Drdla*, submitted manuscript, 2007), respectively. In both cases, we apply the same Arctic winter H<sub>2</sub>O profiles to our calculations. These are based on the H<sub>2</sub>O climatology compiled by *Groß* and

*Russell* [2005] from a data analysis of the Halogen Occultation Experiment (HALOE) and averaged over equivalent latitudes  $\geq 65^\circ\text{N}$ . According to the method used by *Rex et al.* [2004] for the calculation of  $T_{NAT}$ , we select an Arctic vortex average HNO<sub>3</sub> winter profile derived from a simulation without denitrification [*Groß et al.*, 2005].

[9] Because no observation dataset is available that provides a detailed SAD climatology for the Arctic polar vortex, we use an average stratospheric SAD background value of  $0.5 \mu\text{m}^2 \text{cm}^{-3}$  for the calculation of  $T_{ACI}$ . This value is extracted from a dataset provided by D. B. Considine [*Stratospheric Process and Their Role in Climate*, 2006]. Higher SAD values are not considered here due to the unpredictability of future volcanic eruptions. For current H<sub>2</sub>O mixing ratios and background SAD, the quantities of  $V_{PSC}$  and  $V_{ACI}$  derived in this way show a linear and compact correlation (see Figure 1, inset). The slope of a linear fit is  $0.71 \pm 0.02 \cdot 10^6 \text{ km}^3 V_{ACI}$  per  $10^6 \text{ km}^3 V_{PSC}$  with a correlation coefficient ( $r$ ) of 0.994.

## 2.2. Arctic O<sub>3</sub> Loss Versus $V_{PSC}$ and $V_{ACI}$

[10] In accordance with the empirical method used by *Rex et al.* [2004], we plotted Arctic ozone column loss data derived by *Rex et al.* [2006] on the basis of the vortex average method against  $V_{PSC}$  and  $V_{ACI}$ . Figure 1 shows the corresponding correlation for the years 1995 to 2000, 2003 and 2005. Data points for 1992 to 1994 are not shown in Figure 1 as the Mount Pinatubo eruption in 1991 caused significantly higher stratospheric SAD values. Data points for 2001 and 2002 are omitted since these winters were characterized by a weak vortex and high temperatures and therefore the ozone loss was low. The winter 2005 is shown in Figure 1, but has not been considered for the linear interpolation since this winter was characterized by an unusual meteorology, which caused significant ozone depletion below 400 K potential temperature [*Rex et al.*, 2006]. For all other winters ozone column loss shows a good linear correlation with both proxies  $V_{PSC}$  and  $V_{ACI}$ , but with different slopes due to the differently defined temperature thresholds (see Figure S1 of the auxiliary materials).<sup>1</sup> The slope of a linear fit in the first case ( $V_{ACI}$ , red solid line) is  $3.52 \pm 0.10 \text{ DU per } 10^6 \text{ km}^3 V_{ACI}$  ( $r = 0.998$ ), whereas the linear fit in the second case ( $V_{PSC}$ , blue solid line) is  $2.33 \pm 0.11 \text{ DU per } 10^6 \text{ km}^3 V_{PSC}$  ( $r = 0.995$ ). This difference would become important if a stratospheric H<sub>2</sub>O increase were to lead to a decoupled evolution of  $V_{PSC}$  and  $V_{ACI}$  and, consequently, to a divergence of the compact correlation described in subsection 2.1.

## 2.3. Stratospheric H<sub>2</sub> and H<sub>2</sub>O Scenarios

[11] We selected four H<sub>2</sub> scenarios that reflect the ongoing discussion about the potential increase of atmospheric H<sub>2</sub> due to leakages caused by a future hydrogen economy [*Schultz et al.*, 2003; *Tromp et al.*, 2003; *Warwick et al.*, 2004]. These scenarios are listed in Table 1, whereby S1–S3 are assumed to be the realistic lower (S1) and upper limits (S2 and S3) of a H<sub>2</sub> economy, respectively. It has been asserted that S4 is unrealistic due to the high leakage rate assumption [*Prather*, 2003]. However, as an extreme assumption we also take the latter scenario into account.

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2007GL031334.

**Table 1.** Box Model Initial Values for Hydrogen at 15°N and 100 hPa for All H<sub>2</sub> Scenarios and the Corresponding Simulation Results of the Absolute and Relative Arctic H<sub>2</sub>O Increase Averaged Over Equivalent Latitudes ≥65°N, From 400 K to 550 K Potential Temperature and From December to March<sup>a</sup>

Scenario	Reference	H <sub>2</sub> , ppmv	$\Delta$ H <sub>2</sub> O	
			ppmv	%
Reference case		0.56	0.	0.
S1	<i>Schultz et al.</i> [2003]	0.65	0.03	0.6
S2	<i>Schultz et al.</i> [2003]	1.10	0.18	3.6
S3	<i>Warwick et al.</i> [2004]	1.40	0.27	5.6
S4	<i>Tromp et al.</i> [2003]	2.30	0.58	11.8

<sup>a</sup>Hydrogen, H<sub>2</sub>; Arctic H<sub>2</sub>O increase,  $\Delta$ H<sub>2</sub>O.

[12] The relative importance of increased H<sub>2</sub> levels for a potential increase in stratospheric H<sub>2</sub>O is analyzed using a box model, which consists of the chemistry module of the Chemical Lagrangian Model of the Stratosphere (CLaMS) [McKenna *et al.*, 2002]. In our analysis we follow the procedure suggested by Röckmann *et al.* [2004]. According to this procedure, we carried out CLaMS box simulations with a single air parcel that ascends from the tropical stratosphere (15°N, 100 hPa) to 1 hPa along an idealized trajectory over a period of 4 years, in accordance with the so-called tape recorder effect noted by Mote *et al.* [1996].

[13] The air parcel was initialized by applying a typical chemical composition of air masses near the tropical tropopause based on HALOE data for H<sub>2</sub>O and CH<sub>4</sub> [Groß and Russell, 2005] and simulations of the Mainz 2-D model [Groß, 1996]. Table 1 shows the averaged ( $\Theta = 400$ –550 K, Dec.–Mar.) Arctic H<sub>2</sub>O increase ( $\Delta$ H<sub>2</sub>O) for the different hydrogen scenarios. We translate the results of this tropical box model simulation to polar latitudes by the following assumptions. Air masses with equal CH<sub>4</sub> mixing ratios encounter a comparable state of hydrogen oxidation regardless of whether they were transported poleward by the global-scale mean circulation or whether they stayed in the tropics. At Arctic altitudes where chemical ozone depletion occurs ( $\Theta \approx 400$ –550 K) we find typical CH<sub>4</sub> mixing ratios from 0.67 to 1.26 ppmv in the HALOE climatology. This corresponds to an altitude range from 2.7 to 5.8 hPa in the tropical simulation. The simulations with different H<sub>2</sub> mixing ratios indicate that in this altitude range 21% to 52% of H<sub>2</sub> has been converted to H<sub>2</sub>O. The applicability of this method was confirmed by comparing CH<sub>4</sub>-H<sub>2</sub>-H<sub>2</sub>O correlations for different trajectories. The results show that the pathway of an air parcel and the H<sub>2</sub> initial value have only a minor impact ( $\leq 1\%$ ) on the correlations.

#### 2.4. Impact of H<sub>2</sub>O Increase on V<sub>PSC</sub> and V<sub>ACI</sub>

[14] Based on these assumptions, we modify Arctic HALOE H<sub>2</sub>O profiles to account for the effects of air masses with increased tropical H<sub>2</sub> mixing ratios that enter the stratosphere through the tropical tropopause. These profiles are used to recalculate the corresponding average V<sub>PSC</sub> and V<sub>ACI</sub> values for all hydrogen scenarios as listed in Table 1. Figure 2 shows the corresponding absolute (Figure 2, left) and relative increase (Figure 2, right) of V<sub>PSC</sub> and V<sub>ACI</sub> versus the average  $\Delta$ H<sub>2</sub>O increase for three winters that reflect the full spectrum of Arctic stratospheric winter conditions during the past two decades (1999: warm, 1997: medium, 1996: cold). The dotted lines in Figure 2

indicate a polynomial fit to the data points. The absolute increase of V<sub>PSC</sub> and V<sub>ACI</sub> with increasing H<sub>2</sub>O is very similar except for the warm winter. However, in all cases the relative increase of V<sub>ACI</sub> with increasing H<sub>2</sub>O is larger than V<sub>PSC</sub>. For a H<sub>2</sub>O increase of 0.58 ppmv (S4) and medium to cold winters, the relative volume increase is almost a factor of 2 larger for V<sub>ACI</sub> than for V<sub>PSC</sub>.

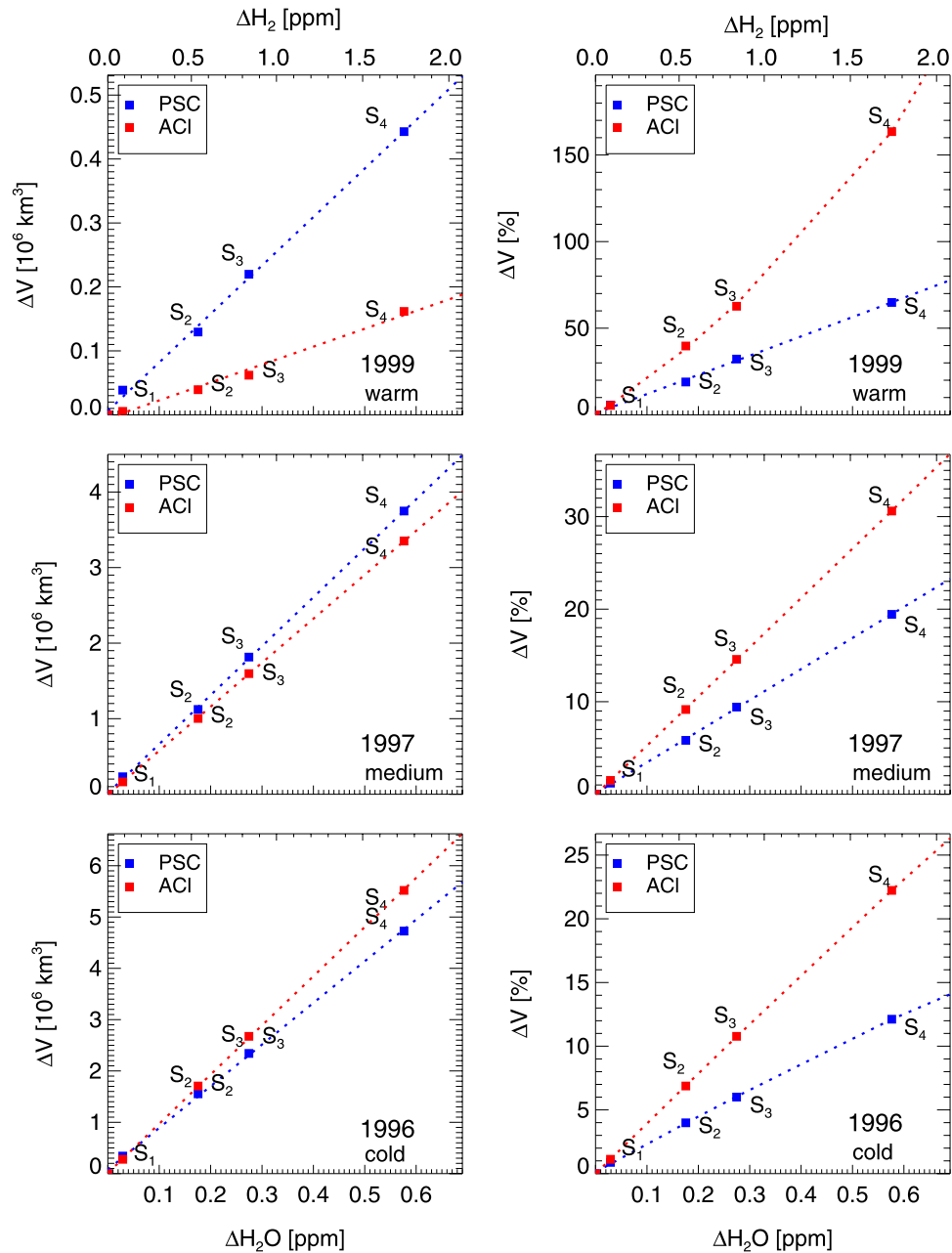
[15] We also estimated the radiative feedback of a H<sub>2</sub>O increase on V<sub>PSC</sub> and V<sub>ACI</sub> using the relation between stratospheric H<sub>2</sub>O increase and temperature response as given by Forster and Shine [2002]. Accordingly, a H<sub>2</sub>O increase of 3.6% or 0.18 ppmv (Table 1, S2) will cool the Arctic vortex by  $\approx 0.13$  K. Based on this assumption, we recalculated the V<sub>PSC</sub> and V<sub>ACI</sub> values for the lower temperatures. Our results show that in the case of V<sub>ACI</sub> (V<sub>PSC</sub>) radiative forcing would increase  $\Delta$ V<sub>ACI</sub> ( $\Delta$ V<sub>PSC</sub>) further by 4% (3%) during a cold winter like 1996. Thus, the radiative feedback due to a H<sub>2</sub>O increase is somewhat smaller than the direct impact of H<sub>2</sub>O on V<sub>ACI</sub> and V<sub>PSC</sub> (Figure 2, S2), but is of a similar order of magnitude. However, the indirect impact due to H<sub>2</sub>O radiative forcing has a stronger effect on V<sub>ACI</sub>. Both direct and indirect effects of a H<sub>2</sub>O increase indicate a larger impact on ozone loss when V<sub>ACI</sub> is used as a proxy.

#### 2.5. Estimation of Future Arctic Ozone Losses

[16] Since Rex *et al.* [2006] showed that the linear correlation between V<sub>PSC</sub> and ozone column loss for the coldest winter so far (2004/2005), which is characterized by a 37% larger V<sub>PSC</sub> compared to the winter 1995/1996, still seems to be valid we assume that a reasonable extrapolation of the correlations shown in Figure 1 by 9% in the case of V<sub>PSC</sub> and 16% in the case of V<sub>ACI</sub> is justified. Hence, we estimate the direct effect of a H<sub>2</sub>O increase (without considering radiative feedbacks) on additional Arctic ozone losses by applying the linear fits shown in Figure 1 to  $\Delta$ V<sub>PSC</sub> and  $\Delta$ V<sub>ACI</sub> for all H<sub>2</sub>O scenarios (Table 1) and for all Arctic winters between 1984 and 2005.

[17] A comparison of the diagrams in Figure 3 shows that in both cases the estimated additional ozone loss is small for small H<sub>2</sub>O increases ( $\leq 0.15$  ppmv) even during cold winters. Similar conclusions apply for warm winter conditions (e.g. 1999) where a H<sub>2</sub>O increase of as much as 1 ppmv is expected to have no significant impact on the additional ozone loss ( $\Delta$ O<sub>3</sub>). However, for cold Arctic winter conditions and for a  $\Delta$ H<sub>2</sub>O between 0.18 and 0.27 ppmv (S2 and S3, Table 1) we estimated an additional ozone loss of up to 5 DU in the case of V<sub>PSC</sub> compared to 8 DU in the case of V<sub>ACI</sub>. For higher H<sub>2</sub> mixing ratios (S4, Table 1), a maximum additional ozone column loss of 11 DU in the case of V<sub>PSC</sub> and 20 DU using V<sub>ACI</sub> as a proxy is calculated. It should be noted that such high leakage rates are very unlikely to occur in a future global H<sub>2</sub> economy simply for economic reasons. It is more likely that significantly lower H<sub>2</sub> emissions rates (3% – 10%) will be achieved, which are comparable to the assumptions used here in scenarios S1 and S2 [Schultz *et al.*, 2003]. Assuming that liquid sulfate aerosols dominate the process of chlorine activation as suggested by Drdla (submitted manuscript, 2007) and an average undisturbed Arctic ozone column of 400 DU, a H<sub>2</sub> economy would increase the ozone column loss in this region by about 0.4% (S1) to 2% (S2). In the





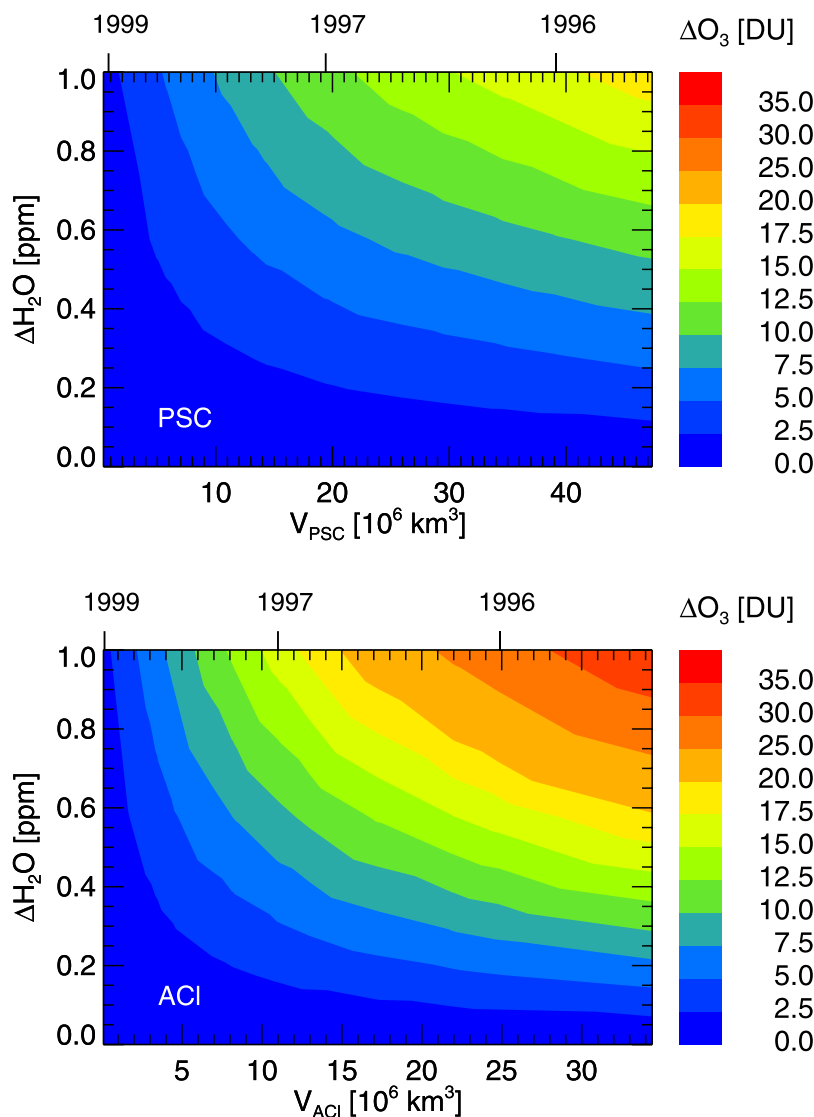
**Figure 2.** Absolute and relative change of  $V_{\text{PSC}}$  (blue dashed lines) and  $V_{\text{ACI}}$  (red dashed lines) due to an increase of stratospheric H<sub>2</sub>O for a selection of Arctic winters (1999: warm, 1997: medium, and 1996: cold). Data points are fitted with a third-order polynomial. In addition, the corresponding hydrogen increase ( $\Delta\text{H}_2$ ) is displayed on the upper abscissa.

very unlikely event that stratospheric H<sub>2</sub> levels were to increase as much as assumed in scenario S4 [Tromp *et al.*, 2003] and an increase of the tropospheric methane level were to occur as predicted by WMO scenarios [WMO, 2003], a monotonic H<sub>2</sub>O increase of as much as 1 ppmv would be possible. In this case, our calculations show an additional Arctic ozone loss during cold Arctic winters of up to 34 DU (9%) using  $V_{\text{ACI}}$  and 19 DU (5%) using  $V_{\text{PSC}}$  as a proxy.

### 3. Summary and Conclusions

[18] According to the methodology applied here, we calculated  $V_{\text{PSC}}$  and  $V_{\text{ACI}}$  utilizing ECMWF operational

analysis for 22 different Arctic winters and different Arctic H<sub>2</sub>O profiles motivated by a potential stratospheric H<sub>2</sub>O increase due to a future H<sub>2</sub> economy. The comparison of the H<sub>2</sub>O sensitivity of the two proxies indicates a stronger relative increase of  $V_{\text{ACI}}$  by almost a factor of 2 for a H<sub>2</sub>O increase of 0.58 ppmv in medium to cold winters. This effect is increased further if radiative feedbacks due to a stratospheric H<sub>2</sub>O increase are taken into account. The linear correlation of the proxies with ozone loss was used to provide estimates of the H<sub>2</sub>O dependence of polar ozone loss. Under current stratospheric conditions,  $V_{\text{ACI}}$  and  $V_{\text{PSC}}$  are equally valid proxies for ozone depletion. However, the impact of a stratospheric H<sub>2</sub>O increase on Arctic ozone loss for both proxies is different. If liquid sulfate aerosols



**Figure 3.** Contour plots of the additional Arctic ozone losses ( $\Delta O_3$ ) in Dobson units (DU) due to an increase of the stratospheric H<sub>2</sub>O mixing ratio ( $\Delta H_2O$ ) as calculated for all Arctic winters between 1984 and 2005. (top) The impact of increased H<sub>2</sub>O on solid aerosols, and (bottom) that on liquid aerosols for different Arctic winter conditions represented here by the proxies  $V_{PSC}$  and  $V_{AC1}$ .

dominate the process as suggested by Drdla, it is likely that  $V_{AC1}$  better describes chlorine activation and polar ozone loss under changing stratospheric H<sub>2</sub>O conditions. This also becomes important for predicted increases of stratospheric H<sub>2</sub>O mixing ratios due to increased stratospheric methane levels [Röckmann *et al.*, 2004] and decreases of stratospheric temperatures as expected due to future increases in greenhouse gases [Rex *et al.*, 2006].

[19] Using  $V_{AC1}$  as a proxy indicates that a realistic upper limit of 0.54 ppmv (S2) for a tropospheric H<sub>2</sub> increase is expected to have no significant impact ( $\leq 2\%$ ) on Arctic ozone loss. Higher H<sub>2</sub> emission scenarios (S4) combined with a projected increase of tropospheric methane levels [Röckmann *et al.*, 2004] suggest a possible stratospheric H<sub>2</sub>O increase of 1 ppmv. This is estimated to cause an additional Arctic ozone loss of up to 9%. However, it is generally assumed that scenario S4 is far from being realistic [e.g., Prather, 2003]. Consequently, on the basis

of our results and the predicted future decline of stratospheric chlorine loading by 2050 we do not expect any substantial impact of a future H<sub>2</sub> economy on Arctic ozone loss, nor is the H<sub>2</sub> economy projected to reach a global dimension before the middle of this century.

[20] **Acknowledgment.** The authors would like to thank Katja Drdla for providing the formula to calculate the temperature threshold for liquid sulfate aerosols prior to its publication.

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