JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 116, D05301, doi:10.1029/2010JD014234, 2011

Impact of stratospheric water vapor enhancements caused by CH_4 and H_2O increase on polar ozone loss

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Received 19 March 2010; revised 18 November 2010; accepted 23 November 2010; published 1 March 2011.

[1] Possible causes of a future increase in stratospheric H_2O are increasing tropospheric methane levels and a rise in tropospheric H_2 due to leakages from a possible increased integration of hydrogen into the energy supply system. Here we quantify the direct chemical impact of potential future stratospheric H_2O increases on Arctic ozone loss using the cold Arctic winter 2004/2005 as the basis for our study. We present simulations with the three-dimensional chemistry transport model CLaMS using enhanced stratospheric H_2O values. Previous studies emphasized that increasing H_2O concentrations cause stratospheric cooling, and some have suggested that this could significantly increase halogen-induced polar ozone loss. The impact of both increased stratospheric H_2O values and decreased temperatures on simulated ozone depletion is investigated. Assuming an average increase of water vapor in the lower polar stratosphere of ≈0.58 ppmv (averaged over equivalent latitudes ≥ 65°N, from 400–550 K potential temperature and from December to March) and in addition decreased temperatures (−0.2 K) yields at most 6.8 DU (≈11 %) more accumulated ozone loss in mid-March for the Arctic polar winter 2004/2005 compared to the ozone loss for undisturbed conditions. The assumed H_2O enhancement in future decades is in the range of current model predictions. Considering in addition the decrease of the future chlorine loading (−40 %) of enhanced H_2O values (see above) yields at most 3.4 DU (10 %) of accumulated ozone loss in springtime compared to current H_2O values. The impact of a potential future hydrogen economy alone (assuming an averaged increase of 0.18 ppmv H_2O in the lower stratosphere) on springtime accumulated ozone loss is found to be negligible (at most 2.5 DU (4 %)) in this study.

Citation: Vogel, B., T. Feck, and J.-U. Grooß (2011), Impact of stratospheric water vapor enhancements caused by CH_4 and H_2O increase on polar ozone loss, *J. Geophys. Res.*, *116*, D05301, doi:10.1029/2010JD014234.

1. Introduction

[2] Increasing anthropogenic emissions of the greenhouse gas methane raise stratospheric water vapor concentrations [e. g., *Röckmann et al.*, 2004; *Riese et al.*, 2006; *Rohs et al.*, 2006]. In addition, a possible future global hydrogen economy [e. g., *Schlapbach*, 2009] would also lead to increasing stratospheric water vapor concentrations [*LeTexier et al.*, 1988]. Some studies suggest that colder Arctic winters could occur in the future in a changing climate [*Rex et al.*, 2004] while others argue that a stronger stratospheric circulation which could lead to warmer Arctic winters is more likely [e. g., *Manney et al.*, 2005]. Low stratospheric polar temperatures cause the formation of polar stratospheric clouds (PSCs) and thereby trigger heterogeneous chlorine activation [e. g., *Solomon et al.*, 1986] and subsequent chlorine-induced polar ozone loss [e. g., *Solomon*, 1999]. Because stratospheric water vapor concentrations strongly impact the potential for PSC formation [e. g., *Kirk-Davidoff et al.*, 1999], in order to predict future ozone loss it is important to understand in detail the significance of enhanced stratospheric water vapor for cold Arctic winters.

[3] In general, an increase in stratospheric water vapor leads to an enhanced production of OH and enhances ozone depletion through the catalytic HO_x cycle [e. g., *Dvortsov and Solomon*, 2001]. The coupling of the HO_x cycle with the NO_x and Cl_x cycle leads to a less efficient NO_x cycle and enhances ozone loss by intensifying chlorine activation [e. g., *Dvortsov and Solomon*, 2001; *Shindell and Grewe*, 2002; *Stenke and Grewe*, 2005] resulting in a delay in the expected ozone recovery due to the decrease in the stratospheric halogen loading.

[4] In addition to the impact on gas-phase chemistry, *Kirk-Davidoff et al.* [1999] find that polar Arctic ozone loss depends critically on stratospheric water vapor variations because they determine both the critical temperature below which heterogeneous reactions become important and the temperature of the Arctic vortex itself. Thus, enhanced stratospheric water vapor would lead to a more frequent formation of PSCs [e. g., *Peter*, 1997; *Solomon*, 1999; *Lowe and MacKenzie*, 2008] and contribute significantly to the

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0148-0227/11/2010JD014234

observed cooling of the lower stratosphere [e. g., *Forster and Shine*, 2002; *Solomon et al.*, 2010, and references therein], which in addition would lead to enhanced formation of PSCs. In the polar Arctic vortex with temperatures near the threshold for chlorine activation, increases in water vapor may allow activation to occur when it otherwise would not. Therefore, enhanced water vapor would have the potential to delay the expected recovery of the stratospheric ozone layer [e. g., *Kirk-Davidoff et al.*, 1999; *Dvortsov and Solomon*, 2001; *Shindell and Grewe*, 2002].

[5] Further, enhanced stratospheric water vapor is an essential component for predicting future global surface climate change [e. g., *Wang et al.*, 1976; *Solomon et al.*, 2010]. In fact, in the midlatitude lower stratosphere, an apparent increase of water vapor of ≈0.05 ppmv/year was observed from 1980 to 2000 (in contrast to a decrease since 2000), which is too large to be attributed to methane oxidation alone [e. g., *Oltmans et al.*, 2000; *Rosenlof et al.*, 2001; *Randel et al.*, 2006; *Solomon et al.*, 2007].

[6] Most of the chemistry climate models (CCMs) (with the exception of one model) examined during the Chemistry Climate Model Validation Activity (CCMVal) for stratospheric processes show an increase in stratospheric water vapor most likely caused by warming of the tropical tropopause and by the increase of tropospheric methane concentrations [*Eyring et al.*, 2007]. Two out of eight CCMs show an increase of 0.9 ppmv and 1.45 ppmv, respectively, in stratospheric H_2O in the Arctic winter by 2049 [*Eyring et al.*, 2007]. All other models show an increase of less than approximately 0.55 ppmv. The reasons for these discrepancies are not evident. A recently published multimodel assessment of coupled CCMs shows that there is a wide spread in simulated water vapor from 2 to 6 ppmv just above the tropical tropopause layer (TTL), which is the entry point of the stratospheric tape recorder [*Gettelman et al.*, 2010]. This underlines the uncertainty of predicted water vapor increases inferred from CCMs. Current CCMs are limited in their representations of key processes that control the distribution and variability of water vapor within the stratosphere and do not consistently reproduce the recently observed changes in stratospheric water vapor [*Garcia et al.*, 2007; *Solomon et al.*, 2010; *Gettelman et al.*, 2010, and references therein].

[7] In recent years, the potential increase of stratospheric H_2O due to H_2 leakages caused by a possible future hydrogen economy has been discussed in several studies [*Schultz et al.*, 2003; *Tromp et al.*, 2003; *Warwick et al.*, 2004; *Feck et al.*, 2008]. *Tromp et al.* [2003] suggest that the mixing ratio of H_2 at the Earth's surface could increase from current levels of about 0.5 ppmv to 2.3 ppmv, while *Schultz et al.* [2003] suggest 1.1 ppmv. From these studies by *Tromp et al.* [2003] and *Schultz et al.* [2003], *Feck et al.* [2008] derived an average increase of 0.58 ppmv H_2O and 0.18 ppmv H_2O, respectively, in the lower polar stratosphere. The value of 2.3 ppmv H_2 at the Earth's surface suggested by *Tromp et al.* [2003] has been demonstrated [*Kammen and Lipman*, 2003; *Prather*, 2003; *Schultz et al.*, 2003; *Warwick et al.*, 2004; *Feck et al.*, 2008] to be unrealistic owing to the high leakage rate assumed, whereas the value of 1.1 ppmv H_2 suggested by *Schultz et al.* [2003] has been assessed as more realistic [*Feck et al.*, 2008].

[8] Previous model studies suggest that it is not expected that enhanced H_2O will cause a general increase in the polar ozone loss in the northern stratosphere [*Warwick et al.*, 2004; *Stenke and Grewe*, 2005]. In contrast, other studies found an impact of enhanced H_2O in the range of a few percent decrease of the total ozone column [*Tromp et al.*, 2003; *Feck et al.*, 2008] or even predicted an increase of ozone for Arctic winters [*Tian et al.*, 2009]. To assess all these model results the different stratospheric temperatures and the water vapor values used for the model simulations must be taken into account. However, it remains unclear what the impact of enhanced stratospheric H_2O will be on future polar ozone loss processes for cold Arctic winters.

[9] Therefore, the direct chemical effect and the impact of the radiative cooling of the stratosphere caused by enhanced stratospheric water vapor will be investigated here considering the case of the Arctic winter 2004/2005. This winter is the coldest Arctic winter on record since 1960 [*Rex et al.*, 2006]. The polar ozone loss in this winter was simulated with the Lagrangian three-dimensional chemistry transport model CLaMS [*McKenna et al.*, 2002a, 2002b; *Konopka et al.*, 2004] in agreement with satellite observations [*Grooß and Müller*, 2007]. Here, the simulation performed for undisturbed conditions by *Grooß and Müller* [2007] is used as a reference and is compared to model simulations using CLaMS with enhanced water vapor and reduced stratospheric temperatures. Because the direct chemical effect of the changing stratospheric halogen loading could be important, we also consider the decreasing chlorine burden in a future stratosphere and perform model simulations with reduced chlorine loading predicted for 2050–2060 conditions [*World Meteorological Organization* (*WMO*), 2007].

[10] Our study is partly motivated by the aim of assessing the impact of a possible future hydrogen economy on polar ozone loss. In addition, the influence of increased stratospheric water vapor concentrations on polar ozone caused by a potential increase of both CH_4 and H_2 is investigated. In the CLaMS simulations, we use enhanced stratospheric H_2O concentrations independent of the specific source of H_2O, which could be methane oxidation or a future H_2 economy. For our simulations, an average increase of 0.58 ppmv H_2O within the lower Arctic vortex is assumed, which is within the spread of the H_2O increase by 2049 predicted by CCMs [*Eyring et al.*, 2007]. In addition, this value constitutes an upper limit for a possible future H_2O increase caused solely by a future hydrogen economy. Further, we performed simulations with a lower stratospheric H_2O increase, which is also within the spread of the predicted H_2O increase by 2049, but which corresponds to a more realistic value caused by a possible future hydrogen economy alone [*Schultz et al.*, 2003; *Feck et al.*, 2008].

[11] Choosing the cold Arctic winter 2004/2005 as the basis for our study allows us to use a chemistry transport model (CTM), so that the dynamics and the temperature of the polar vortex can be accurately described. Further, the impact of enhanced stratospheric water vapor on Arctic polar ozone loss is strongest in cold Arctic winters [*Feck et al.*, 2008]. The three-dimensional CTM CLaMS is very well suited for this study because CLaMS has proven to excellently describe stratospheric transport processes, in particular in the presence of sharp tracer gradients as at the edge of the polar vortex, and is very well evaluated compared to high-

resolution measurements [e. g., *Vogel et al.*, 2003; *Konopka et al.*, 2004; *Grooß et al.*, 2005; *Grooß and Müller*, 2007; *Vogel et al.*, 2008].

[12] Theoretically, it is possible that changes in water vapor could not only cool the polar stratosphere, but due to H_2O-related cooling could also prolong the period over which the Arctic vortex remains stable in the spring season. Our model study using a three-dimensional CTM it is not suitable for addressing the question of a possible but uncertain prolongation of the vortex during spring.

[13] The goal of this paper is to investigate the impact of enhanced stratospheric H_2O on Arctic polar ozone using reasonable assumptions for a future stratospheric H_2O increase due to a rise in CH_4 and H_2 emissions and considering a future chlorine loading. Our model simulations show that increasing stratospheric H_2O concentrations have the potential to affect polar ozone loss processes during cold Arctic winters with a stable polar vortex under both current and future chlorine loading expected for the next few decades.

2. Model Simulations

[14] In our paper, a simulation with the Chemical Lagrangian Model of the Stratosphere (CLaMS) [*McKenna et al.*, 2002b, 2002a; *Konopka et al.*, 2004] for the Arctic winter 2004/2005 performed by *Grooß and Müller* [2007] is used as a reference (referred to as “ref run”). The simulations of this reference agree well with ozone measurements by the Fourier Transform Spectrometer (ACE-FTS) [*Walker et al.*, 2005]. The simulated vortex averaged column ozone loss between 380 and 550 K potential temperature is in approximate agreement with published estimates, but is significantly lower than other estimates which is most likely caused by the inhomogeneous ozone distribution within the vortex [*Grooß and Müller*, 2007]. The CLaMS simulation shows a strong chlorine activation at the beginning of March in agreement with observations [*von Hobe et al.*, 2006] that can only be explained if a significant denitrification (about 70%) is calculated in the model simulations.

[15] In addition, we present model simulations with enhanced stratospheric H_2O mixing ratios also considering the corresponding stratospheric cooling and deduce the induced additional amount of Arctic ozone loss. Taking into account the decreasing chlorine burden in the future stratosphere, we will also present simulations with a reduced amount of inorganic chlorine (Cl_y), which is expected to be present between 2050–2060 [*WMO*, 2007].

2.1. Description of the CLaMS Model

[16] Here, we present CLaMS simulations for the Northern hemisphere from 20 November 2004 until 31 March 2005 over an altitude range from 320 K to 900 K potential temperature (≈10–37 km). A horizontal resolution of 100 km (300 km) north (south) of 40°N and 32 levels corresponding to about 0.8 km vertical resolution was used for the simulations. The horizontal winds were taken from the meteorological analyses from the European Centre for Medium-Range Weather Forecasts (ECMWF). The vertical motion relative to potential temperature levels is determined from heating rates deduced from radiation calculations [*Morcrette*, 1991; *Zhong and Haigh*, 1995]. The mixing processes in CLaMS were parametrized using shear and deformation in large-scale winds to parametrize mixing processes [*Konopka et al.*, 2005]. Heterogeneous chemistry on water ice, nitric acid trihydrate (NAT), and liquid $H_2O/HNO_3/H_2SO_4$ ternary solution (STS) particles is included. The nucleation of NAT from STS requires a supersaturation of HNO_3 over NAT of 30 and is therefore strongly hindered. The four particle types may coexist in the steady state (for more details, see *McKenna et al.* [2002b]). Sedimentation of NAT particles was calculated as by *Grooß et al.* [2005] using a globally constant nucleation rate of 8×10^{-6} cm^{-3} h^{-1} in regions where temperatures are below the NAT equilibrium temperature T_{NAT}.

[17] The initialization of the chemical species on 20 November 2004 was derived from satellite data following *Grooß and Müller* [2007]. Ozone was derived from AURA-MLS [*Manney et al.*, 2006] and ACE-FTS data [*Walker et al.*, 2005] (for details, see *Grooß and Müller* [2007]). All other chemical tracers and families, CH_4, Cl_y, and Br_y were initialized using tracer correlations to AURA-MLS N_2O data.

2.2. Initialization of Enhanced H_2O

[18] To initialize the CLaMS simulations, a realistic spatial distribution of enhanced H_2O values in the stratosphere is required. The oxidation of H_2 and CH_4 in the stratosphere is very comparable [*Feck et al.*, 2008] which allows our study to be designed in such a way that the source of H_2O increase, CH_4 or H_2, is of minor importance. In contrast, an increase of stratospheric water vapor due to other sources such as enhanced transport from the troposphere (e. g., due to changes in the tropical tropopause temperature) or volcanoes results in a very different vertical profile of H_2O in the stratosphere.

[19] *Feck et al.* [2008] conducted box model studies for a single ascending air parcel in the tropical stratosphere to estimate the oxidation of CH_4 and H_2 in order to infer the additional H_2O production (ΔH_2O) from increased H_2 emissions. *Feck et al.* [2008] used different scenarios of increased H_2 emissions reflecting the ongoing discussion about the potential increase of atmospheric H_2 due to leakages caused by a possible future hydrogen economy [*Schultz et al.*, 2003; *Tromp et al.*, 2003; *Warwick et al.*, 2004]. We assume that air masses with equal CH_4 mixing ratios also encounter a comparable state of hydrogen oxidation regardless of whether they were transported poleward or whether they stayed in the tropics and regardless of the transport time of the air parcel from the tropics into the stratosphere (for more details, see *Feck et al.* [2008]). Therefore, for each methane level a ΔH_2O can be calculated using the results of *Feck et al.* [2008]

$$\Delta H_2O\ [\mathrm{ppmv}] = a + b \times CH_4\ [\mathrm{ppmv}] + c \times [CH_4\ [\mathrm{ppmv}]]^2 \quad (1)$$

where the parameters a, b, and c depend on the assumed H_2 emission rate (for details, cf. Table 1). The box model results by *Feck et al.* [2008] can be translated to other latitudes using this CH_4–ΔH_2O correlation to calculate the stratospheric water vapor contribution with

$$H_2O_{new} = H_2O_{ref} + \Delta H_2O \quad (2)$$

at each methane level, where H_2O_{ref} and H_2O_{new} are the water vapor mixing ratios of the reference run and a new

Table 1. Overview of All Model Simulations[a]

Run	H_2O	ΔT	Cl_y
Reference	current	current	current
Case A	enhanced [Tromp2003]	current	current
Case B	enhanced [Tromp2003]	cooling (−0.2 K)	current
Case C	enhanced [Schultz2003]	cooling (−0.1 K)	current
Case D	current	current	−40 %
Case E	enhanced [Tromp2003]	cooling (−0.2 K)	−40 %

[a] Assumptions used for initialization of the different CLaMS simulations are listed. Enhanced water vapor values are calculated according to equation (1) and (2) using $a = 1.62541$, $b = -1.13018$, and $c = 0.102556$ [*Tromp et al.*, 2003] or $a = 0.499985$, $b = -0.352470$, and $c = 0.0344476$ [*Schultz et al.*, 2003].

sensitivity run. With this method, transport processes, e. g., the descent of air masses within the Arctic vortex, are taken into account because ΔH_2O depends only on the CH_4 mixing ratio of the air masses considered. Thus, a realistic spatial distribution of enhanced stratospheric H_2O is available for the initialization of CLaMS.

2.2.1. H_2O Enhancement

[20] In our study, we used an additional amount of H_2O of on average 0.58 ppmv H_2O increase (averaged over equivalent latitudes ≥ 65°N, from 400–550 K potential temperature and from December to March) for typical Arctic winter conditions in altitudes where ozone loss usually occurred [*Tromp et al.*, 2003; *Feck et al.*, 2008], referred to in the following as “case A”.

[21] An average increase of 0.58 ppmv H_2O in the lower Arctic vortex is within the variation of predicted H_2O increase by 2049 [*Eyring et al.*, 2007] and thus represents a realistic assumption for future stratospheric water vapor increase. Considering only a future global hydrogen economy, the value of 0.58 ppmv water vapor increase represents an upper limit [*Feck et al.*, 2008]. Taking into account both the uncertainties of a predicted water increase and the impact of a possible future hydrogen economy, an average increase of 0.58 ppmv within the lower Arctic vortex is a reasonable assumption for a possible future H_2O increase for the next few decades.

[22] Further, it is evident that increased stratospheric water vapor contributes to stratospheric cooling [e. g., *Forster and Shine*, 2002, and references therein]. *Feck* [2009] deduced the expected decrease in stratospheric temperatures for the Arctic polar vortex assuming an increase of stratospheric water vapor according to “case A” using the fixed dynamical heating approximation [*Ramaswamy et al.*, 2001] implemented in the two-dimensional radiative transfer model RAD [*Shine*, 1991]. A mean temperature change of −0.2 K for the polar vortex region (380–550 K ≈ 16–26 km) was found. To estimate the impact of this temperature decrease we performed simulations with decreased stratospheric temperatures of −0.2 K, referred to as “case B”. A possible change in the vertical motion caused by changed water vapor values and changed temperatures is not considered here.

2.2.2. Moderate H_2O Enhancement

[23] To also consider a more realistic impact of enhanced H_2O on stratospheric polar ozone loss only caused by potential future H_2 emissions [*Feck et al.*, 2008], simulations were performed assuming that the mixing ratio of H_2 at the Earth’s surface is raised to 1.1 ppmv [*Schultz et al.*, 2003]. For this scenario, an average increase of 0.18 ppmv H_2O and a mean temperature change of −0.1 K for the polar vortex region was computed by *Feck et al.* [2008] and *Feck* [2009]. These values were used for the initialization of a CLaMS simulation, referred to as “case C”.

2.3. Chlorine Loading

[24] In our study, we investigate the direct chemical effect and the impact of the radiative cooling of the stratosphere caused by enhanced stratospheric water vapor. The amount of stratospheric chlorine is also important for determining the direct chemical effect of enhanced H_2O on polar ozone and thus for quantifying the impact of enhanced stratospheric water vapor in a changing climate. In our study, we used the current chlorine loading corresponding to an increase of factor 1.6 relative to the 1980 level. The effective stratospheric chlorine at the 1980 level is expected to be reached approximately between 2050 and 2060 [*WMO*, 2007], reduced by approximately 40 % compared to the Arctic winter 2004/2005. Therefore, we repeated our simulations with a total amount of inorganic chlorine Cl_y reduced by 40 % for the reference case and for “case B”; these simulations are referred to as “case D” and “case E”. An overview of all model simulations performed is given in Table 1.

3. Results

[25] In the following, the simulated ozone loss caused by enhanced water vapor is presented considering the case of the Arctic winter 2004/2005, which is the coldest Arctic winter since 1960 [*Rex et al.*, 2006]. The focus is on the Arctic polar vortex, which is approximately the region poleward of 65°N equivalent latitude from January until the end of March 2005 [*Grooß and Müller*, 2007]. The mean temperatures taken from ECMWF analyses for this region are shown in Figure 1.

[26] Figure 2 shows the estimated mean distribution of H_2O poleward of 65°N equivalent latitude for the “ref run” compared to “case A”. In “case A”, there is an increase of water vapor of 0.2–0.9 ppmv (4%–17%) compared to the reference case at altitudes where the greatest accumulated Arctic ozone loss occurred (380–550 K ≈ 16–26 km).

[27] Our simulations show that in “case A” and “case B”, compared to the reference, the formation of solid particles

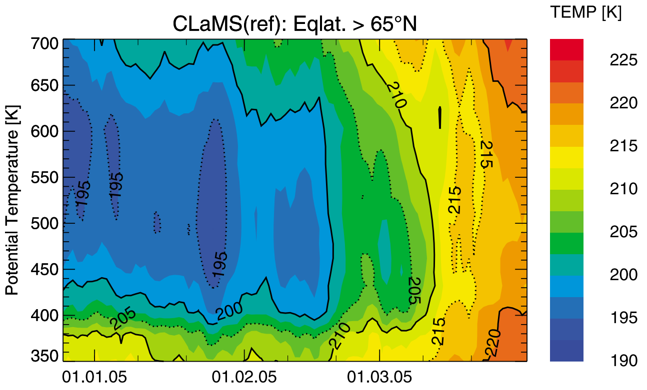

Figure 1. Mean distribution of temperature from January to March 2005 taken from ECMWF analyses, poleward of 65°N equivalent latitude, used for the reference run as a function of time and potential temperature (350–700 K ≈ 13–32 km).

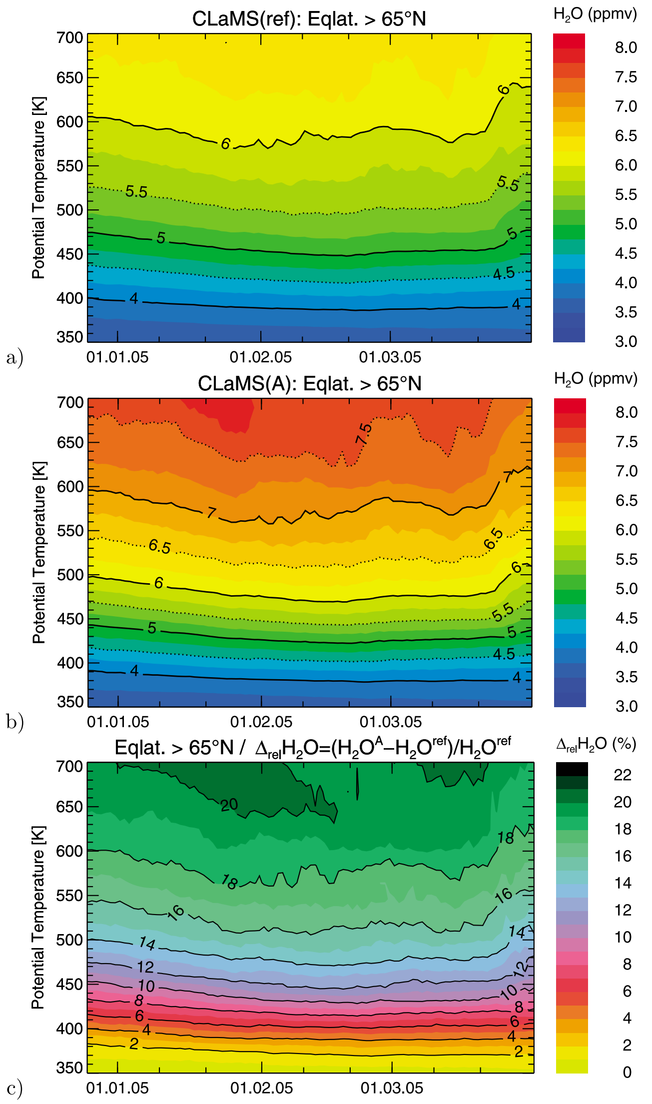

Figure 2. Mean distribution of water vapor, poleward of 65°N equivalent latitude, for (a) the reference, (b) “case A”, and (c) the percentage change between the reference and “case A” as a function of time and potential temperature (350–700 K ≈ 13–32 km).

(NAT and ice) is enhanced both in magnitude and in the time period over which they occurred. As expected, the strongest enhancement of NAT and ice particles occurred in “case B” as shown in Figures 3a–3d. The impact of liquid particles is more complex because liquid and solid particles interact (see Figures 3e and 3f).

[28] Denitrification is considered in our simulations via sedimentation of NAT particles calculated as by *Grooß et al.* [2005] using a globally constant nucleation rate of 8×10^{-6} cm^{-3} h^{-1} in regions where temperatures are below the NAT equilibrium temperature T_{NAT} (cf. section 2.1). In the reference run, a denitrification of 5–6 ppmv (up to 40 %) (see Figure 3e) was found during the cold periods between end of January and February 2005. In “case B”, up to 0.5–1.0 ppbv stronger denitrification was found between 500–600 K potential temperature compared to the reference (see Figure 3f).

[29] Dehydration via sedimentation from water ice particles is not considered in our model simulations. Dehydration has an impact on the formation of PSCs in late winter. However, in the Arctic intense denitrification is observed without intense dehydration [e. g., *Fahey et al.*, 1990; *Waibel et al.*, 1999]. Therefore, the impact of dehydration on Arctic polar ozone loss is not included in this study.

[30] In our simulations, enhanced PSC occurrence due to enhanced H_2O leads to an increased chlorine activation between 400 K and 600 K potential temperature mainly in January and February 2005 (see Figure 4). For “case A” and “case B”, an additional mean chlorine activation (ClO_x = ClO + 2 × Cl_2O_2) of 9% and 12 %, respectively, is found for the time between 1 January and 15 March 2005 between 380–550 K poleward of 65° equivalent latitude.

[31] Figure 5 shows the accumulated ozone loss versus time and potential temperature poleward of 65°N equivalent latitude. The accumulated ozone loss was determined as the difference between simulated ozone and a passively transported ozone tracer. This allows the quantification of the chemical contribution to ozone change during winter. The reference run (Figure 5a) yielded an accumulated ozone loss of up to about 1.2 ppmv at 475 K in mid-March, very close to that found in cases A (Figure 5b) and B (Figure 5c). Between 400 K and 550 K, differences between cases A and B and the reference run are less than 5 %.

[32] The chemical ozone loss above 550 K is caused by catalytic cycles involving NO_x similar to the observed for previous winters [*Grooß et al.*, 2005; *Konopka et al.*, 2007; *Vogel et al.*, 2008] and is not very sensitive to changes in H_2O or temperatures compared to halogen-driven polar ozone loss (see Figure 5).

[33] The impact of enhanced chlorine activation in “case A” and “case B” on simulated partial column ozone is shown in Figure 6, top, for a range of 380–550 K potential temperature (≈16–26 km). The column ozone is shown in red for the reference, in blue for “case A”, and in yellow for “case B”t. The corresponding accumulated column ozone loss in this altitude range calculated from the simulated O_3 values minus the passively transported ozone is shown in Figure 6, middle. Until the end of March, a column ozone loss of up to approximately 65 DU was simulated for the reference. Thereafter, the column ozone loss starts to decrease because the final warming has occurred [*Grooß and Müller*, 2007] resulting in the transport of midlatitude, ozone rich, air masses to the pole. In Figure 6, bottom, the ozone losses attributed to “case A” and “case B” are shown. These values are calculated from the difference between “case A” (blue) and “case B” (yellow), respectively, to the reference. Until mid-March the ozone loss attributable to “case A” rises to 5.9 DU (10 % of the accumulated ozone loss over the winter) and to 6.8 DU (11 % of the accumulated ozone loss over the winter) for “case B”.

[34] For “case A” and “case B”, different temperatures were used for the simulations. To compare the accumulated ozone loss between these two cases it is important to consider that using either fixed levels of potential temperature or fixed pressure levels to determine ozone loss leads to slightly different results. For the calculation of the ozone column in “case B”, it was assumed that the potential temperature levels between 380 K and 550 K are fixed and the corresponding pressure levels are shifted due to the lower

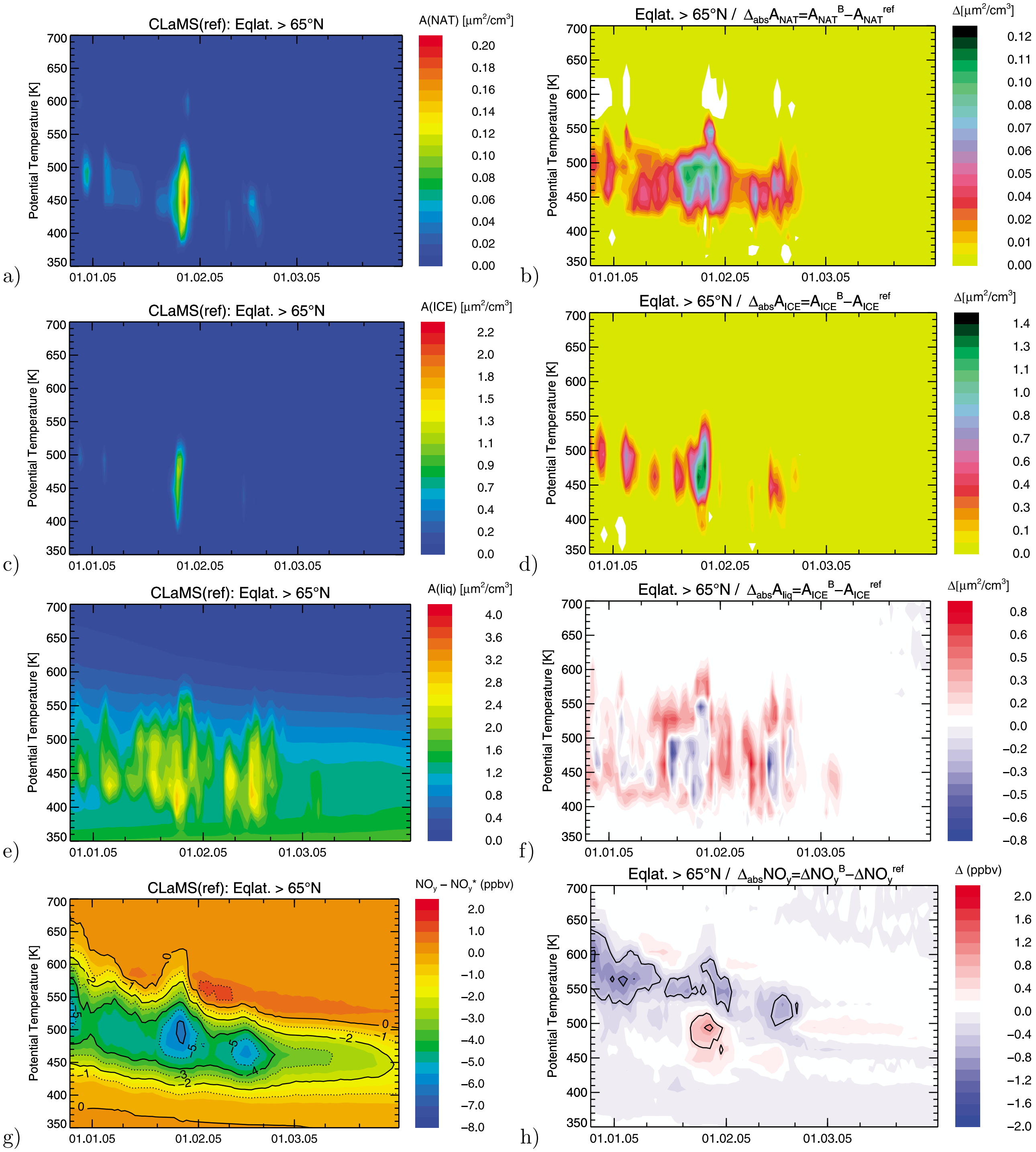

Figure 3. (left) Mean distribution of simulated surface areas of (a) NAT (A_{NAT}), (c) ice (A_{ICE}), (e) liquid (A_{liq}) particles, and (g) denitrification (NO_y - NO_y^*) for the reference as a function of time and potential temperature (350–700 K ≈ 13–32 km). (right) Absolute change of (b) A_{NAT}, (d) A_{ICE}, (f) A_{liq}, and (h) denitrification between reference and "case B".

temperature ($p = p_0 \times (T_{new}/\Theta)^{3.5}$ with p_0 = surface pressure, $T_{new} = T - 0.2$ K). For the case that the pressure levels are fixed and the corresponding levels of potential temperature are shifted according to lower temperatures, the ozone loss attributable to "case B" is about 0.5 % lower.

[35] In the vortex core poleward of 75°N equivalent latitude [*Grooß and Müller*, 2007], a column ozone loss of up to approximately 72 DU was simulated for the reference until the end of March. Here, the maximum additional partial column ozone loss caused by "case A" and "case B" rises to 7.3 DU (10 %) and 8.2 DU (12 %), respectively, of the accumulated ozone loss over the winter.

[36] Model simulation "case C" was performed to take into account a more realistic impact of enhanced H_2O on strato-

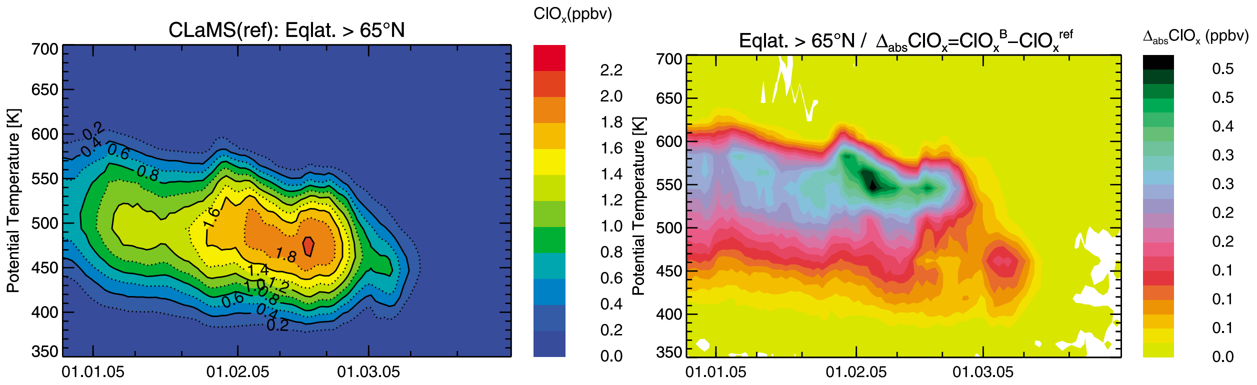

Figure 4. (left) Mean distribution of simulated activated chlorine ClO_x for the reference as a function of time and potential temperature (350–700 K ≈ 13–32 km). (right) Absolute change of ClO_x between reference and "case B".

spheric polar ozone loss caused only by potential future H_2 emissions [*Schultz et al.*, 2003; *Feck et al.*, 2008]. Here, the maximum partial column ozone loss is only 2.5 DU (4 % of the accumulated ozone loss over the winter) (as shown in Figure 5).

[37] To consider the decreasing chlorine burden in a future stratosphere, we reduced the total amount of inorganic chlorine Cl_y in our simulations by 40 % and repeated the reference case ("case D") and "case B" ("case E") using enhanced H_2O [*Tromp et al.*, 2003] and a stratospheric cooling of −0.2 K. As expected, for a chlorine loading at the 1980 level, a lower maximum ozone loss of 40 DU is simulated until the end of March (see Figure 7, "case D"), which is lower than the 65 DU ozone loss simulated for the reference. The maximum impact of enhanced water vapor and of stratospheric cooling under conditions of chlorine loading at the 1980 level is 10 % (3.4 DU) (see Figure 7, top). Thus, considering the reduced chlorine loading for the years 2050 and 2060, respectively, the polar ozone loss for a cold Arctic winter caused by enhanced water vapor would be still in the range of 10% of the accumulated ozone loss over the winter.

4. Discussion

[38] Both the possible increase in stratospheric H_2O caused by a possible future hydrogen economy [*Schultz et al.*, 2003; *Tromp et al.*, 2003; *Warwick et al.*, 2004] and that caused by increasing anthropogenic emissions of methane is investigated here. In previous studies, different types of atmospheric models and techniques at various levels of complexity ranging from ozone loss proxies [*Feck et al.*, 2008], two-dimensional models [*Tromp et al.*, 2003; *Warwick et al.*, 2004], or chemistry climate models [e. g., *Stenke and Grewe*, 2005; *Tian et al.*, 2009] have been used to determine the impact of enhanced stratospheric H_2O on polar ozone loss processes. In addition, model predictions of future stratospheric H_2O concentrations vary considerably from model to model and are thus rather uncertain [*Eyring et al.*, 2007]. In the following, the differences and similarities between our results and previous studies will be discussed.

4.1. Comparison to Results From Previous CCM Studies

[39] *Stenke and Grewe* [2005] performed CCM simulations with ECHAM4.L39(DLR)/CHEM (time slice simulations for year 2000 conditions) assuming an increase of strato-

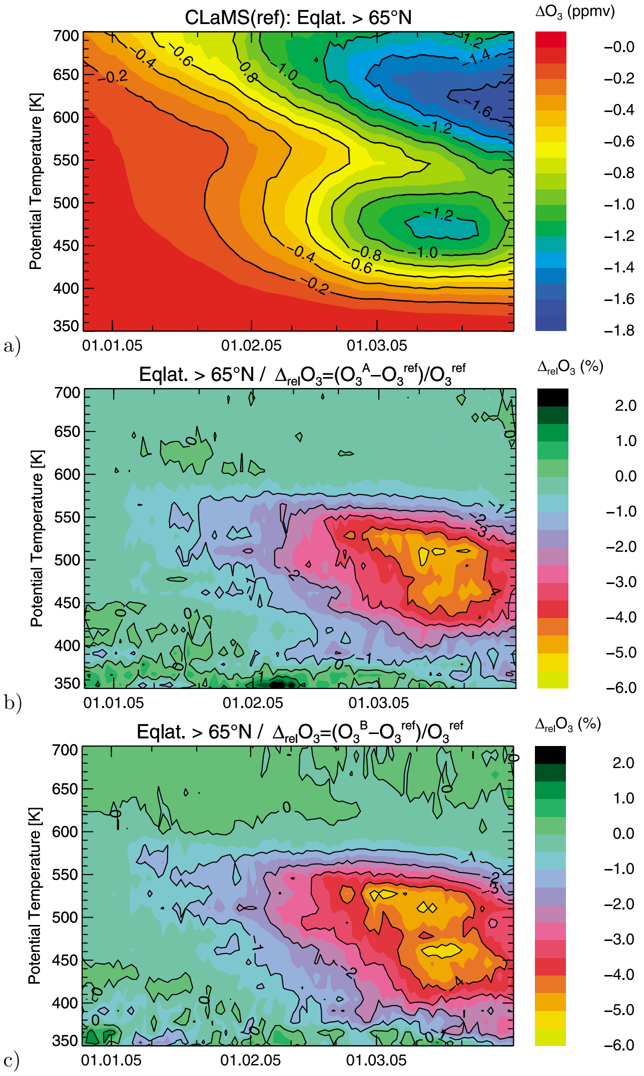

Figure 5. Mean distribution of accumulated chemical ozone change poleward of 65°N equivalent latitude, for (a) the reference and the percentage change to (b) "case A" and (c) "case B" as a function of time and potential temperature (350–700 K ≈ 13–32 km).

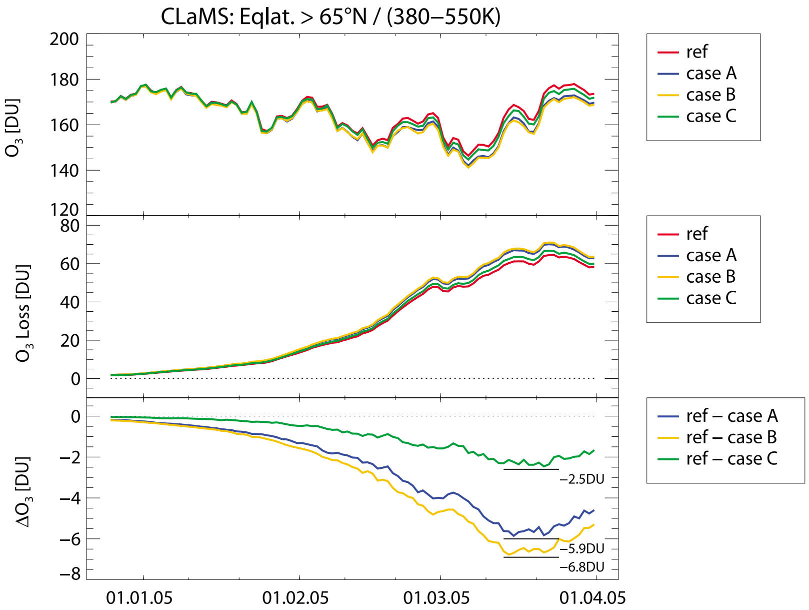

Figure 6. (top) Column ozone (in Dobson units) of the reference (red), with additionally increased H_2O ("case A", blue), "case A" with additional decreased temperatures ("case B", yellow), and with a moderate H_2O increase (including corresponding decreased temperatures, "case C", green) integrated over an altitude range from 380 K to 550 K (≈16–26 km) for equivalent latitudes poleward of 65°N. (middle) Ozone loss in DU for these model simulations. (bottom) ΔO_3 due to "case A" (blue), "case B" (yellow), and "case C" (green). A higher ozone loss of up to 5.9 DU (≈10 %), 6.8 DU (≈11 %), and 2.5 DU (4 %) is found in "case A", "case B", and "case C", respectively, compared to the reference.

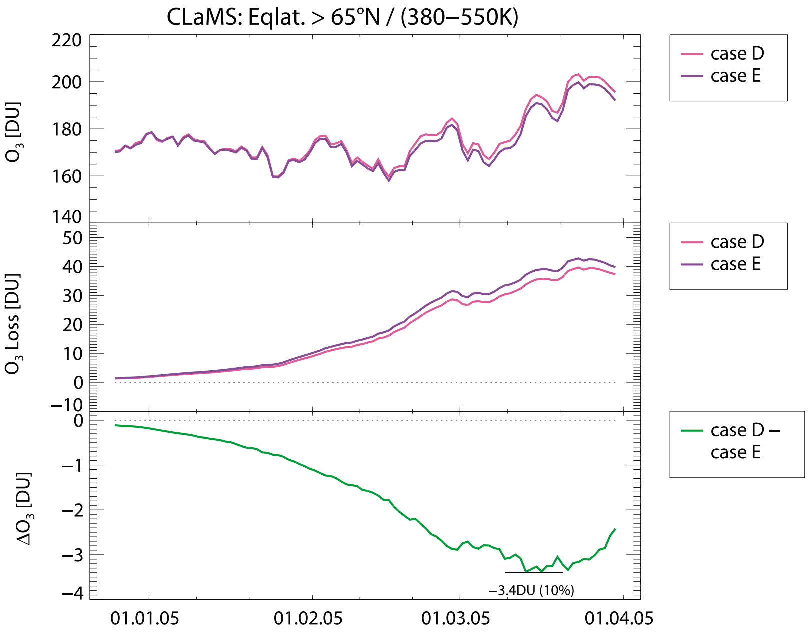

Figure 7. (top) Column ozone (in Dobson units) of the reference, but considering chlorine loading at the 1980 level ("case D", magenta) and a simulation with additionally increased H_2O and reduced stratospheric temperatures ("case E", purple) integrated over an altitude range from 380 K to 550 K (≈16–26 km) for equivalent latitudes poleward of 65°N. (middle) Ozone loss in DU for these model simulations. (bottom) ΔO_3 = "case D" – "case E" (green). A higher ozone loss of up to 3.4 DU (≈10%) is found in "case E" compared to "case D".

spheric water vapor in the range of ≈0.7 ppmv and ≈3.5 ppmv in the Arctic winter. Further, their model simulations do not include any water vapor effect on stratospheric temperatures (comparable to "case A" from our study). They conclude that the additional stratospheric water vapor content might affect the PSC activity in the Arctic polar vortex during single, very cold events, but the model results do not indicate a significant impact on PSC formation in general. This is in agreement with our simulations showing an enhanced PSC formation for periods with low temperatures. Our simulations show that in the Arctic winter 2004/2005 enhanced stratospheric H_2O has an impact on accumulated ozone loss in the range of 11 %. Because meteorological analyses are used for the CLaMS simulations, it is ensured that the temperatures used in our simulations are representative of cold Arctic winters.

[40] *Tian et al.* [2009] performed simulations with a fully coupled CCM model (Met Office Unified Model with SLIMCAT chemistry) assuming a water vapor increase of 2 ppmv in the entire stratosphere (from 150 hPa to 0.5 hPa). They performed idealized 10 year time slice runs and all model diagnostics by *Tian et al.* [2009] were 10 year averaged climatologies. In the Arctic, only in sufficiently cold winters does substantial polar ozone loss occur, therefore in 10 year averaged climatologies the impact of individual cold winters is hidden by averaging with warm winters without significant ozone loss. The analysis by *Tian et al.* [2009] considers Arctic winter conditions without significant ozone loss caused by PSC occurrence. In such warm winters, stratospheric ozone concentrations are solely determined by gas-phase chemistry.

[41] In our study, the impact of enhanced water vapor is investigated for an Arctic winter with sufficient chlorine-induced ozone loss depending on low temperatures. However, both the studies by *Stenke and Grewe* [2005] and by *Tian et al.* [2009] found enhanced heterogeneous ozone depletion during Antarctic spring where much lower temperatures occurred than in the Arctic spring. Our results show that also for sufficiently cold Arctic winters enhanced averaged H_2O of about 0.58 ppmv in the lower stratosphere has an impact in the range of 11 % on chlorine-induced springtime accumulated ozone loss. Therefore, our results provide useful and supplementary information to better understand the impact of enhanced water vapor on Arctic stratospheric ozone loss processes.

4.2. Comparison to Results Based on a Future Potential Hydrogen Economy

[42] In the following, we discuss our results on the assumption that the averaged enhanced water vapor values used are only based on H_2 emissions due to a future potential hydrogen economy. Compared to previous model studies, in our model simulations using enhanced water vapor caused by increased H_2 emissions proposed by *Tromp et al.* [2003] an increase of H_2O of up to ≈20 % (≈1.2–1.3 ppmv) at 700 K (≈32 km) is used according to *Feck et al.* [2008], although this percentage is significantly less than that suggested by *Tromp et al.* [2003]. This assumption is in agreement with *Warwick et al.* [2004], who also found that the H_2O concentrations in the stratosphere reported by *Tromp et al.* [2003] are too high. Since we use a three-dimensional chemistry transport model, there are no feedback effects caused by radiation in our model simulations. Therefore, we use a cooling of the lower Arctic stratosphere of −0.2 K in our simulations according to *Feck* [2009] and in agreement with *Warwick et al.* [2004], whereas *Tromp et al.* [2003] estimated a cooling of −0.5 K. In 2-D simulations, *Tromp et al.* [2003] found an O_3 depletion of about 5 to 8 % in boreal spring in the northern polar region. However, this study was based on both an overestimated stratospheric H_2O concentration and an overestimated stratospheric cooling. In contrast, *Warwick et al.* [2004] found in 2-D model simulations that an increase in H_2 emissions including the scenario proposed by *Tromp et al.* [2003] has likely no substantial impact on stratospheric ozone. A study by *Feck et al.* [2008] comparing ozone loss proxies based on two different mechanisms of chlorine activation (on PSCs or on liquid sulfate aerosols) found for H_2 emission rates proposed by *Tromp et al.* [2003] an additional Arctic ozone loss during cold Arctic winters of up to 11 DU (on PSCs) and 19 DU (on liquid sulfate aerosols), respectively. It should be noted that in calculating these values the radiative impact of H_2O is not taken into account and therefore these results should be compared with the results of "case A". Our findings ("case A", 5.9 DU) using a 3-D chemistry transport model yield much lower additional ozone loss caused by the H_2 emission rates proposed by *Tromp et al.* [2003] compared to *Feck et al.* [2008]. The reason for this is that the accumulated polar vortex average ozone loss in CLaMS is much lower than a time integration of the determined vortex average ozone loss rates as performed in the Match method [*Grooß et al.*, 2008] used to calculate the ozone loss proxies by *Feck et al.* [2008]. One reason for the difference between CLaMS-simulated and Match-deduced ozone loss is that the method of time integration of ozone loss rates in the Match method does not consider the transport of air masses across the vortex edge (for more details, see, *Grooß et al.* [2008]). Considering, in addition, the cooling of the stratosphere ("case B"), our findings show that an increase in H_2 emissions according to *Tromp et al.* [2003] has an impact in the range of 11 % on accumulated ozone loss during an Arctic winter as cold as the Arctic winter 2004/2005.

5. Conclusions

[43] The direct chemical impact of enhanced H_2O on polar stratospheric ozone processes was studied with the chemistry transport model CLaMS considering the case of the cold Arctic winter 2004/2005. Taking into account the fact that a possible future H_2 economy and a rise of anthropogenic methane emissions have the potential to increase stratospheric water vapor under a changing climate, model simulations were performed with enhanced water vapor and decreased temperatures. It should be noted that our model simulations do not include the fact that changes in water vapor could also prolong the period over which the Arctic vortex remains stable in the spring season.

[44] Using an average increase of 0.58 ppmv water vapor and an additional cooling of −0.2 K within the Arctic vortex in agreement with current model predictions an additional accumulated ozone loss of about 11 % was calculated compared to the reference. Our findings show that up to 5.5% more ozone is destroyed due to more extensive PSC formation and therefore higher chlorine activation. Our model results suggest that increasing stratospheric H_2O concentrations

have the potential to affect polar ozone loss processes during cold Arctic winters with a stable polar vortex. Our study suggests that the potential impact of enhanced water vapor caused only by a future global hydrogen economy is of minor importance for stratospheric ozone loss processes and will become even smaller as chlorine levels decline. Considering a chlorine loading at the 1980 levels and, in addition, an increase in stratospheric water vapor caused by the sum of a potential CH_4 increase and a future H_2 economy, our model suggests that enhanced stratospheric water vapor represents an additional variability in the existing variation of the ozone loss observed in cold Arctic winters for the next few decades.

[45] **Acknowledgments.** The authors thank Rolf Müller for very fruitful discussions and three anonymous reviewers for comments that resulted in significant improvements to the original manuscript. The study was funded by the European Commission as part of the project “A European Network for Atmospheric Hydrogen observations and studies (EUROHYDROS)” under contract 036916. Simulations were performed on the Jülich Multiprocessor (JUMP) and were supported by the John von Neumann Institute for Computing (NIC).

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