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Modelling the effect of denitrification on polar ozone depletion for Arctic winter 2004/2005

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Abstract. A three-dimensional (3-D) chemical transport model (CTM), SLIMCAT, has been used to quantify the effect of denitrification on ozone loss for the Arctic winter 2004/2005. The simulated HNO_3 is found to be highly sensitive to the polar stratospheric cloud (PSC) scheme used in the model. Here the standard SLIMCAT full chemistry model, which uses a thermodynamic equilibrium PSC scheme, overpredicts the ozone loss for Arctic winter 2004/2005 due to the overestimation of denitrification and stronger chlorine activation than observed. A model run with a coupled detailed microphysical denitrification scheme, DLAPSE (Denitrification by Lagrangian Particle Sedimentation), is less denitrified than the standard model run and better reproduces the observed HNO_3 as measured by Airborne SUbmillimeter Radiometer (ASUR) and Aura Microwave Limb Sounder (MLS) instruments. Overall, denitrification is responsible for a ∼30 % enhancement in O_3 depletion compared with simulations without denitrification for Arctic winter 2004/2005, which is slightly larger than the inferred impact of denitrification on Arctic ozone loss for previous winters from different CTMs simulations. The overestimated denitrification from standard SLIMCAT simulation causes ∼5–10 % more ozone loss at ∼17 km compared with the simulation using the DLAPSE PSC scheme for Arctic winter 2004/2005. The calculated partial column ozone loss from SLIMCAT using the DLAPSE scheme is about 130 DU by mid-March 2005, which compares well with the inferred column ozone loss from ozonesondes and satellite data (127±21 DU).

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1 Introduction

Significant progress has been made in understanding the processes controlling the observed polar stratospheric ozone depletion during the recent decades through measurements, laboratory work and modelling studies (e.g., Solomon, 1999; Chipperfield et al., 2005). Previous extensive studies have shown that successfully understanding polar stratospheric ozone depletion depends crucially on the processes of polar stratospheric clouds (PSCs) in activating chlorine and denitrifying the stratosphere (e.g., Tabazadeh et al., 2000; WMO, 2006). Although the main processes that lead to ozone depletion are generally well understood, there remain open questions such as the duration of chlorine activation and its dependence on the abundance of nitrogen oxides (Kühl et al., 2004).

Reactive nitrogen (NO_y) species play an important role in the chemistry of stratospheric O_3, both directly through rapid catalytic cycles involving NO_x and indirectly through their interaction with e.g. halogen species. As stratospheric halogen levels decline, the role of NO_y species may become more important. However, over the past few years there have been a number of updates to laboratory data related to NO_y chemistry (e.g., Sander et al., 2006). In addition, studies using photochemical models have indicated problems in reproducing the observed abundance of NO_y and its partitioning into its components (e.g., Sen et al., 1998; Dufour et al., 2005). Denitrification is defined as the permanent removal of NO_y from a stratospheric air mass by the sedimentation of HNO_3-containing particles (e.g., Fahey et al., 1990; WMO, 2010). Significant denitrification leads to an increase in the lifetime of ozone-depleting chlorine species (ClO_x)

and therefore leads to an increase in the duration and extent of springtime polar ozone loss (e.g., Waibel et al., 1999; Esler and Waugh, 2002; Davies et al., 2002).

The Arctic winter 2004/2005 was one of the coldest winters ever recorded in the stratosphere, and has been studied extensively (e.g., Manney et al., 2006; Rex et al., 2006; von Hobe et al., 2006; Feng et al., 2007a; Singleton et al., 2007; Rosevall et al., 2008). Feng et al. (2007a) found that an updated version of the SLIMCAT 3-D chemical transport model (CTM) (Chipperfield, 2006) overestimated the observed ozone loss in the cold Arctic winter of 2004/2005. Therefore, further investigations of the processes which lead to Arctic ozone depletion are required to better understand the discrepancies between models and observed ozone loss. Previously models had systematically underestimated Arctic ozone loss in cold winters (e.g., Becker et al., 1998; Rex et al., 2004; Feng et al., 2005a; Chipperfield et al., 2005 and Singleton et al., 2005). More details of the updated SLIMCAT version can be found in Feng et al. (2005a, 2007b), Chipperfield et al. (2005) and Chipperfield (2006).

In this paper, we investigate the impact of using different model PSC schemes, including effect of denitrification on the ozone loss for the Arctic winter 2004/2005. We use airborne and satellite remote sensing observations from the Airborne Submillimeter Radiometer (ASUR) and Aura Microwave Limb Sounder (MLS) instruments to test the denitrification simulated by the model for the different PSC schemes.

2 ASUR and Aura MLS measurements

The ASUR (Küllmann et al., 1999; Kleinböhl, 2004) is an airborne radiometer measuring the thermal emission of trace gases in the stratosphere. The profile retrieval is performed on equidistant altitude levels of 2 km spacing (Kleinböhl, 2004). The instrument was successfully operated on board the NASA DC-8 research aircraft in the Polar Aura Validation Experiment (PAVE) over the period of 24 January to 9 February 2005 remotely measuring the trace gases HCl, O_3, ClO, N_2O and HNO_3 in the altitude range 14 to 40 km (Kleinböhl et al., 2005; Kuttippurath et al., 2004). The vertical resolution of these measurements is given by the width of the averaging kernels (∼6–20 km), decreasing with altitude from the lower to upper stratosphere (e.g., Kleinböhl, 2004; Kuttippurath et al., 2011). The total typical retrieval error is ∼ 20 % for HCl, ∼10 % for ClO, and less than 15 % for N_2O and 12 % for O_3 (e.g., von König, 2002; Bremer et al., 2002; Kleinböhl, 2004; Kuttipurath et al., 2007).

The Earth Observing System (EOS) MLS is an instrument on the NASA Aura satellite, launched on 15 July 2004. It observes a large suite of atmospheric parameters by measuring millimetre and submillimetre wavelength thermal emission from the Earth's limb viewing forward along the Aura spacecraft flight track. Vertical profiles of O_3, HNO_3, ClO, HCl, N_2O, H_2O, CO and other chemical compounds are retrieved. The horizontal and vertical resolution of the MLS retrievals, given below for each species of relevance, are obtained from the MLS averaging kernels (for details see the Aura MLS v3 Data Quality Document, Livesey et al., 2011). Aura MLS has better spatial resolution and coverage than the predecessor UARS MLS instrument with measurement made globally on daily basis. A feature of the MLS and ASUR technique is that its measurements can be obtained in the presence of ice clouds and aerosol, that prevent measurements by shorter-wavelength infrared, visible and ultraviolet techniques (for more information about MLS, see Schoeberl et al., 2006; Livesey et al., 2006; Waters et al., 2006; Santee et al., 2007; Santee et al., 2008). The MLS data used in this paper is version 3.3 (MLS v3.3) which has been released in 2011 (Livesey et al., 2011). The Aura MLS data for the 2004/2005 Arctic winter has been described in detail by Schoeberl et al. (2006) and Santee et al. (2008). The MLS v3.3 data has different recommended vertical range, i.e., 147–1.0 hPa for ClO, 100–0.32 hPa for HCl, 215–1.5 hPa for HNO_3, 100–0.46 hPa for N_2O and 261–0.02 hPa for O_3. The vertical resolution for ClO is 3–4.5 km and the uncertainty is about 5–20 %. HCl has 3 km vertical resolution and the uncertainty is about 10 % above 20 hPa with a large variable uncertainty with latitude and season in the lower stratosphere, due to the variability in HCl. The vertical resolution of the HNO_3 data is 3–4 km through most of the useful range, degrading to about 5 km at 22 hPa. The uncertainty of HNO_3 is 5–10 % between 100–6.8 hPa. O_3 data has about 2.5 km vertical resolution and 5–10 % uncertainty in the uppermost troposphere and stratosphere. The MLS v3.3 N_2O has coarse vertical resolution (4–6 km) over most of the useful range of the retrievals and the uncertainty varies with height from 9–25 %. For detailed MLS v3.3 information see http://mls.jpl.nasa.gov/data/v3-3_data_quality_document.pdf.

The ASUR and MLS data are very useful for understanding stratospheric ozone depletion and for validating atmospheric chemical transport models. Here we concentrate on the chemical species HNO_3, HCl, ClO, O_3 and N_2O. The observations of HNO_3 during the polar winter allow the quantification of denitrification. The ASUR HNO_3 observations have been successfully used to quantify denitrification in the Arctic winters 2000 and 2005 (e.g., Kleinböhl et al., 2002, 2005). The chlorine compounds HCl and ClO permit a testing of chlorine activation and other related chemical processes (e.g., Santee et al., 2008). N_2O will be used to determine changes due to atmospheric dynamics in the polar region (i.e., diabatic descent of air masses in the atmosphere) and validate the model transport. O_3 data will be used to estimate the polar ozone depletion.

3 Model and experiments

SLIMCAT is an off-line 3-D CTM described in detail by Chipperfield (1999, 2006) which now uses a hybrid σ-θ as vertical coordinate and includes the atmosphere from the surface up to ∼60 km. The model has been widely used to study transport and chemistry in the upper troposphere and lower stratosphere (UTLS) (e.g., Feng et al., 2005a, b; Chipperfield, 2006; Feng, 2006; Feng et al., 2007a, b). Horizontal winds and temperatures are specified using meteorological analyses. Vertical advection is calculated from diabatic heating rates using a NCAR chemistry climate model (CCM) radiation scheme (Briegleb, 1992) which gives a better representation of vertical transport in the model (see Feng et al., 2005a). Chemical tracers in SLIMCAT are advected using the scheme of Prather (1986) which conserves second-order moments and performs well in maintaining strong gradients. The model contains the principal stratospheric chemical species in the O_x, HO_x, NO_y, Cl_y, Br_y families as well as source gases (i.e., N_2O, CH_4, $CFCl_3$, CF_2Cl_2, CH_3Br) and a treatment of CH_4 oxidation. The photochemical data is based on the JPL recommendation (Sander et al., 2006) with the exception of the absorption cross sections of Cl_2O_2 which is taken from Burkholder et al. (1990) extrapolated to 450 nm. The Burkholder et al. (1990) cross-section (updated by Papanastasiou et al., 2009) are larger than other laboratory measurements, and have been found to reproduce the observed Arctic ozone loss rate (see SPARC, 2009). The model contains a detailed gas-phase stratospheric chemistry scheme and also a treatment of heterogeneous reactions on liquid aerosols, nitric acid trihydrate (NAT) and ice (see Chipperfield, 1999).

The standard SLIMCAT model uses a simplified PSC scheme for the simulation of heterogeneous chemistry and denitrification. This scheme is based on the assumption of thermodynamic equilibrium between the particles formed (whether liquid aerosol, NAT or ice) and the gas phase (e.g., Davies et al., 2002; Davies, 2003; Feng et al., 2005a, 2007a, b; Chipperfield et al., 2005). The equilibrium model assumes NAT forms in two modes (radius 0.5 and 6.5 µm), which is the same as the scheme described by Davies et al. (2002) and tested for the cold Arctic winter of 1999/2000 (Feng et al., 2005a). In this scheme NAT particles are sedimented from the model with fall velocities of 1 and 1100 m/day appropriate for particles of radius 0.5 and 6.5 µm, respectively. Ice particles with an assumed radius of 10 µm are sedimented at a rate of 1500 m/day.

However, a full microphysical PSC scheme is required for a detailed simulation of Arctic denitrification. Previous studies (e.g., Davies et al., 2002, 2006; Davies, 2003; Mann et al., 2002, 2003, 2005) used the separate microphysical Denitrification by Lagrangian Particle Sedimentation (DLAPSE) model to investigate denitrification effect in Arctic winters, but only Davies et al. (2006) combined this with the full SLIMCAT chemistry. These studies advected gas phase HNO_3 in SLIMCAT, interpolated to the Lagrangian particle positions, then ran the DLAPSE model to calculate the growth and sedimentation of several hundred thousand particles (more details can be found in Davies, 2003). In Davies et al. (2006), they were running two independent models (DLAPSE and SLIMCAT) and passing information between these two models. For this work, we have fully incorporated the Lagrangian particle denitrification model (DLAPSE) into the SLIMCAT model to extend the options of PSC scheme in the model. The coupled DLAPSE model uses the Lagrangian trajectory scheme contained in the SLIMCAT model (see Monge-Sanz et al., 2007). This is an improvement over the standard model because it calculates the growth and sedimentation of individual particles and is suitable for the simultaneous simulation of several hundred thousand particles (Carslaw et al., 2002). Despite the microphysical detail, the coupled DLAPSE model is computationally efficient as it only performs calculations when NAT particles are present and does not add any additional 3-D tracers in the model.

Table 1. SLIMCAT model experiments.

Runs	Denitrification scheme	Reference
EXP_A	Thermodynamical equilibrium	Feng et al. (2007a)
EXP_B	Microphysical DLAPSE	Davies et al. (2006)
EXP_C	No Denitrification	

Three model experiments with different treatment of PSCs were run for the Arctic winter of 2004/2005. Table 1 lists the different denitrification schemes used in SLIMCAT. Experiment A (EXP_A) is the standard SLIMCAT full chemistry run as described in Feng et al. (2007a), Experiment B (EXP_B) is the full chemistry run using the microphysical DLAPSE scheme. Here we used a constant volume average NAT nucleation rate (8.1×10^{-10} particles cm^{-3} s^{-1}). NAT particles are initialised with a radius of 0.1 µm. Finally, Experiment C (EXP_C) had denitrification switched off (no sedimentation). All of these model experiments used 24 vertical levels extending from the surface to ∼60 km and a horizontal resolution of 2.8° × 2.8°. The model was forced by 6-hourly European Centre for Medium-Range Weather Forecasts (ECMWF) operational analyses.

4 Results

Kleinböhl et al. (2005) reported that the NASA DC-8 research aircraft sampled air from the Arctic polar vortex on 31 January and 5 February 2005. Schoeberl et al. (2006) also investigated the process of filament formation and estimated the vortex denitrification using the measurements from aircraft and Aura MLS satellite observed on 31 January 2005. Figure 1 shows profiles of HNO_3, HCl, ClO, O_3 and N_2O

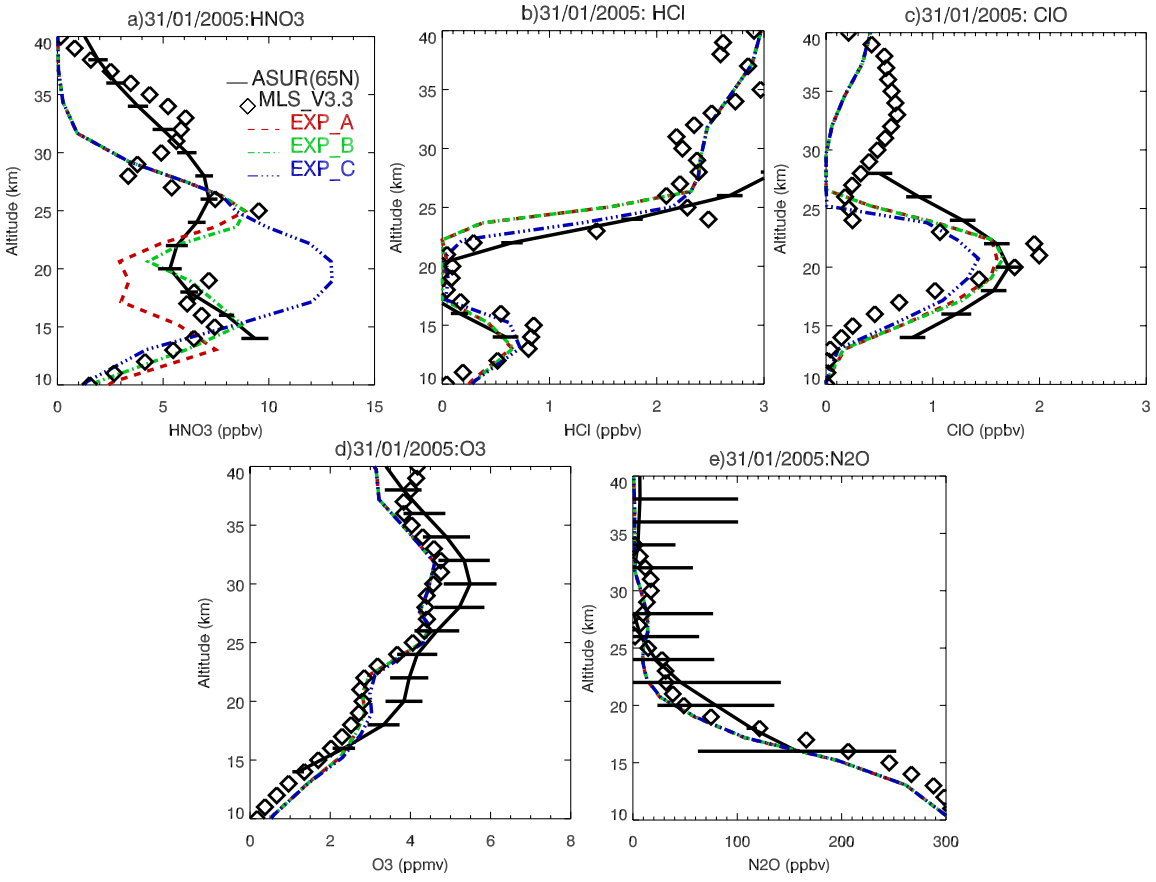

Fig. 1. Profiles of HNO_3, HCl, ClO, O_3 and N_2O from ASUR and MLS observations and model simulations using the equilibrium (EXP_A), DLAPSE (EXP_B) PSC schemes and without denitrification (EXP_C) for 31 January 2005.

from ASUR, MLS and the three SLIMCAT simulations for 31 January 2005. Figure 2 is similar to Fig. 1 but for 5 February 2005. The observed HNO_3 decreases with increasing altitude from ∼13 to ∼22 km, increases with altitude to ∼26 km and then decreases again in the middle and upper stratosphere. Obviously, there is a significant denitrification occurred in the lower stratosphere. MLS HNO_3 has a very similar profile below 20 km and above 25 km with ASUR. However, there is a large HNO_3 value between 22–24 km for 31 January 2005 compared with ASUR measurement (the MLS data is not shown between 22–24 km here). Overall, the model simulation EXP_A captures the observed profile well, but some differences exist. For example, EXP_A underestimates HNO_3 at 14 km (2–3 ppbv) and overestimates it around 24 km compared with ASUR, but matches better with MLS data. Please note the differences between ASUR and the model in HNO_3 around 24 km are likely related to the limited resolution of the ASUR HNO_3 measurement (Kleinböhl, 2011). By contrast, EXP_B using the microphysics DLAPSE denitrification scheme captures the MLS profile remarkably well. The model with the thermodynamic equilibrium PSC scheme overestimates denitrification of the lower stratosphere, while the simulation using the more detailed microphysical denitrification scheme is in excellent agreement with observed HNO_3 from ASUR measurements from 15 to 20 km, where the PSCs dominate and play important role in denitrification.

The MLS and ASUR measurements detected evidence for Cl activation from ClO and the absence of HCl between 16 and 22 km on the flights of 31 January and 5 February (the negative ASUR HCl values at 18 and 20 km and ClO profile comparison for 5 February are not shown here). The negative values in the ASUR HCl measurement are likely caused by the retrieval not quite being able to follow the steep slope from high values in the middle stratosphere to zero HCl in the lower stratosphere (Kleinböhl, 2011). The vertical distributions of modelled HCl and ClO in the SLIMCAT (EXP_A and EXP_B) compare quite well to ASUR and MLS below 25 km. The modelled ozone values in the lower stratosphere at 16–18 km are very close to the MLS and ASUR data. However, the model underestimates ASUR observed O_3 above 28 km but this is not the relevant region for polar stratospheric ozone depletion and agreement with MLS is better. There is still some O_3 difference between EXP_A

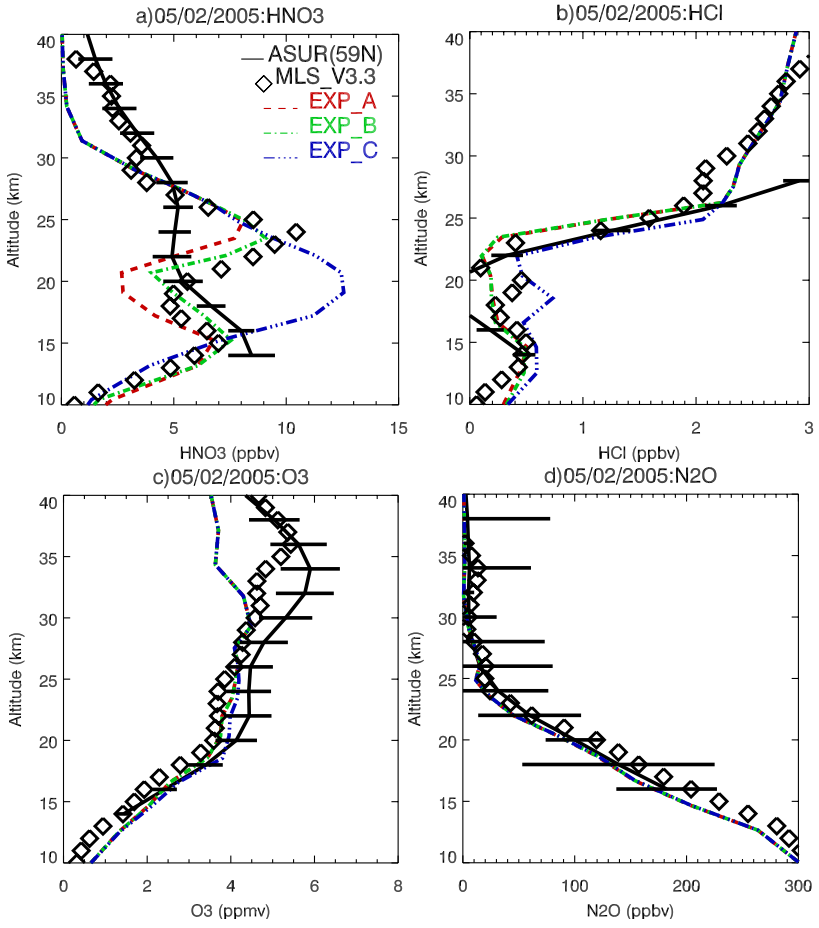

Fig. 2. HNO_3, HCl, O_3 and N_2O from ASUR observations and model simulations using equilibrium (EXP_A), DLAPSE (EXP_B) PSC schemes and without denitrification (EXP_C) for 5 February 2005.

and EXP_C (though it is small) at ∼17 km due to the effect of denitrification on O_3 loss at this time of the year. Profiles of the long-lived species N_2O can be used to verify modelled tracer transport (Feng et al., 2005a). The model has too strong descent in the lower stratosphere when compared with MLS and ASUR data for the flight on 31 January and also for the flight on 5 February.

Figure 3 shows the relative difference of profiles of HNO_3 and O_3 from ASUR, model simulations using two different PSC schemes (EXP_A, EXP_B) and the model run without denitrification (EXP_C) for 31 January and 5 February 2005. Again, the SLIMCAT simulation using the thermodynamic equilibrium has larger denitrification (relative difference is about 20–50 % at 15–20 km) than using the microphysical DLAPSE scheme (less than 10 %) which is much close to the ASUR observations. The relative O_3 differences between EXP_A, EXP_B and EXP_C are quite small (less than 10 %) in the lower stratosphere though there are larger relative percent differences with observations in the lowermost and middle stratosphere.

Figure 4 shows the time series of averaged HNO_3, HCl, ClO, N_2O and O_3 inside the vortex on the 456 K isentropic level (∼17 km) from MLS measurements and SLIMCAT simulations using the two PSC schemes (EXP_A and EXP_B) and no denitrification (EXP_C). Here the vortex is defined as the area enclosed by the 65° N equivalent latitude (EL) contour. Again, EXP_B, the SLIMCAT simulation with the detailed DLAPSE denitrification scheme, gives excellent agreement with observed HNO_3, where the equilibrium scheme overpredicts denitrification at 456 K. The model captures the temporal evolution of observed HCl and ClO, but the model with full chemistry (EXP_A and EXP_B) seems to have too much chlorine activation from late February to mid-March 2005 which is also confirmed by Santee et al. (2008). Even though the modelled HNO_3 field is significantly improved when using the DLAPSE microphysical scheme (EXP_B), the differences of the simulated O_3 at 456 K from the SLIMCAT full chemistry experiments (EXP_A and EXP_B) are not significant, possibly because the same surface area of the liquid aerosol are used for the chlorine

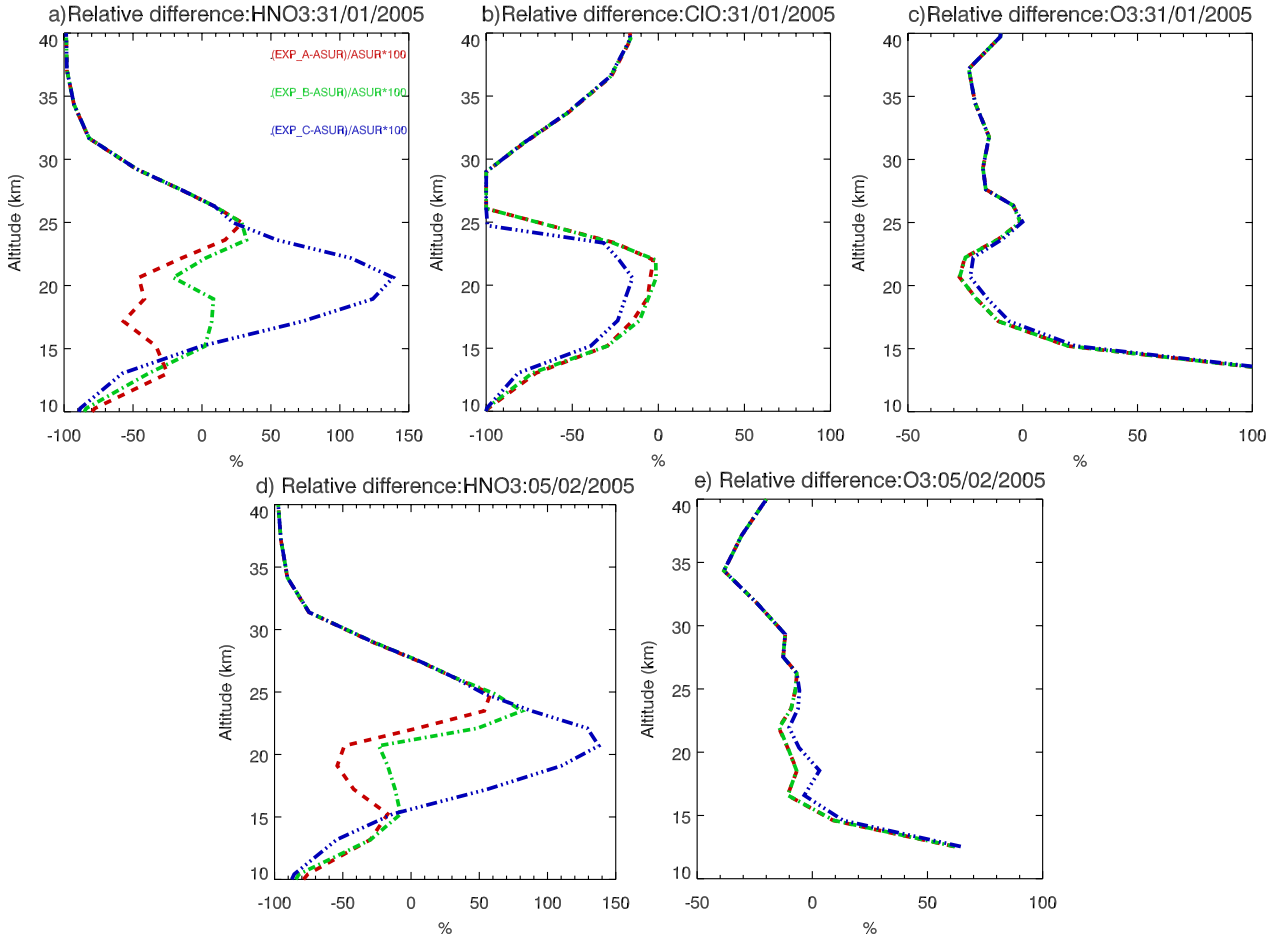

Fig. 3. The relative difference (%) of HNO_3, ClO and O_3 between ASUR measurements and SLIMCAT full chemistry simulations using the equilibrium (EXP_A) and DLAPSE (EXP_B) PSC schemes and without denitrification (EXP_C) for 31 January and 5 February 2005.

activation in these two experiments (EXP_A and EXP_B). This requires further detailed investigation. Obviously, the modelled ozone overestimates the observations if denitrification is not considered in the model (EXP_C). The observed N_2O values inside the vortex decreased rapidly in early December, increased in late December, then decreased again until mid January. The model captures many features of observed N_2O evolution, but overall, model has more diabatic descent than MLS observations.

Figure 5 shows the vortex-averaged modelled NO_y and ClO_x ($= Cl + ClO + 2 \times Cl_2O_2$) as a function of time and potential temperature for Arctic winter 2004/2005 from the three simulations. The NO_y has values larger than 10 ppbv above 450 K in early December but these decrease rapidly after mid December. Denitrification is predicted to have started in December and the very low ambient temperatures produce lower NO_y values due to PSC formation and denitrification between 400 and 530 K (∼14 to 22 km). NO_y in EXP_A, using the thermodynamic equilibrium scheme, is as low as 3 ppbv by late January, indicating that extensive denitrification has occurred. As shown in Mann et al. (2002, 2003) when the cold pool is offset from the centre of rotation of the vortex, denitrification is weak due to short particle lifetimes. EXP_B, using DLAPSE scheme, captures this behaviour, but the standard SLIMCAT model based on the equilibrium scheme (EXP_A) continues to predict denitrification.

Chlorine activation on PSCs occurred at high altitudes from early December and activation gradually extended downwards even to the lowermost stratosphere (below 400 K) which consistent with corresponding low temperatures and descent of air and potential PSC extent. Maximum ClO_x exceeded 2.7 ppbv from late December until early February. Modelled chlorine activation is reduced if denitrification is not considered in the model (EXP_C) as chlorine deactivation mainly occurs by the reaction of $ClO + NO_2 + M \rightarrow ClONO_2 + M$ and the time for stratospheric chlorine deactivation depends on the degree of denitrification in the Arctic.

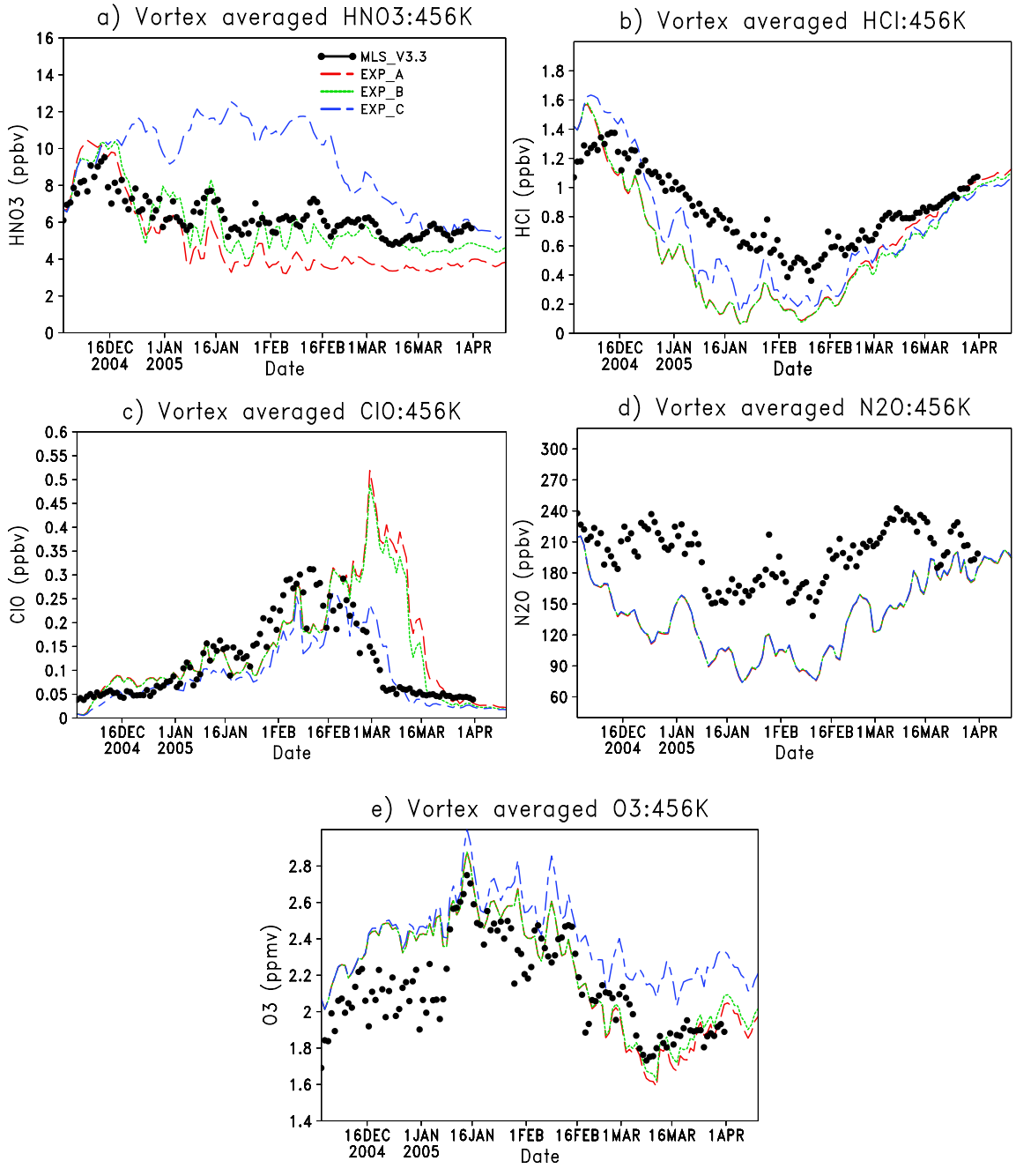

Fig. 4. Time evolution of HNO_3, HCl, ClO, N_2O and O_3 from MLS measurements and SLIMCAT simulations using the equilibrium (EXP_A) and DLAPSE (EXP_B) PSC schemes as well as the simulation without denitrification (EXP_C) at 456 K (∼17 km).

If NO_2 decreases due to the removal of nitrogen reservoirs by denitrification process, chlorine deactivation will be delayed. EXP_A using the equilibrium PSC scheme has stronger denitrification than EXP_B and has a longer deactivation time and prolonged Arctic ozone loss. The deactivation is even faster if no denitrification is included in the model. The DLAPSE denitrification scheme (EXP_B) has realistic denitrification, therefore, slowing down chemical ozone depletion compared to the thermodynamical equilibrium scheme (EXP_A).

Figure 6 is the absolute difference of vortex-averaged modelled NO_y and ClO_x between the full chemistry simulations (EXP_A, EXP_B) and the SLIMCAT simulation without denitrification (EXP_C). Overall, the patterns of NO_y and ClO_x differences are very similar. Again, more extensive

Table 2. Inferred maximum ozone loss for Arctic winter 2004/2005.

Reference	*Model*/Measurement	Ozone loss	Altitude	Period
Manney et al. (2006)	EOS MLS	1.2–1.5 ppmv (vortex)	450–500 K	Jan–mid-Mar
		2 ppmv (vortex edge)	500 K	Jan–mid-Mar
Rösevall et al. (2008)	Aura MLS	0.9–1.3 ppmv	450 K	1 Jan–mid-Mar
Rösevall et al. (2008)	Odin SMR	0.6–1.3 ppmv	450 K	1 Jan–mid-Mar
Jin et al. (2006)	ACE-FTS	1.8–2.6 ppmv	475–500 K	Jan–mid-Mar
		108-139 DU	Total column	Jan–mid-Mar
Rex et al. (2006)	Ozonesondes/SAGE III/POAM III	1.2–1.8 ppmv	400–450 K	5 Jan–25 Mar
		(121/110/113)127±21 DU	380–550 K	5 Jan–25 Mar
von Hobe et al. (2006)	M55 Geophysica aircraft	2.1–2.3 ppmv	380–470 K	Jan–7 Mar
		75–103 DU	Total column	Jan–7 Mar
Tsvetkova et al. (2007)	SAGE III	1.7 ppmv	450–475 K	1 Jan–25 Mar
		116–128±10 DU	Total column	1 Jan–25 Mar
Rösevall et al. (2008)	*DIAMOND*+Odin SMR	*1.0–1.1* ppmv	430–460 K	1 Jan–mid-Mar
Rösevall et al. (2008)	*DIAMOND*+Aura MLS	*0.7–0.9* ppmv	430–460 K	1 Jan–mid-Mar
Jackson and Orsolini (2008)	*Met Office*+EOS MLS/SBUV	*0.8–1.2* ppmv	450 K	Jan–early Mar
El Amraoui et al. (2008)	*MOCAGE*+Aura MLS	*1.5* ppmv	425 K	10 Jan–10 Mar
Singleton et al. (2007)	*SLIMCAT*/EOS MLS/POAM III			
	/SAGE III/ACE-FTS/MAESTRO	*2–2.3* ppmv	450 K	Dec–mid-Mar
Kuttippurath et al. (2010)	*Mimosa-Chim*/Aura MLS	*1.5–1.7* ppmv	475 K	Dec–Mar
		109 DU	350–550 K	Dec–Mar
Grooß and Müller (2007)	*CLaMS*	*1.08–1.66* ppmv	475 K	Jan–Mar
		69±21 DU	380–550 K	Jan–Mar
Feng et al. (2007a)	*SLIMCAT*:EXP_A	*2–2.3* ppmv	456 K	Dec–Mar
		140 DU	380–550 K	Dec–Mar
This work	*SLIMCAT*:EXP_B	*2–2.13* ppmv	456 K	Dec–Mar
		130 DU	380–550 K	Dec–Mar
This work	*SLIMCAT*:EXP_C	*0.6–0.8* ppmv	456 K	Dec–Mar
		90 DU	380–550 K	Dec–Mar

denitrification has occurred in the model with the thermodynamic equilibrium scheme (EXP_A) than with a detailed microphysical denitrification scheme DLAPSE (EXP_B). There are large ClO_x differences above 500 K (∼21 km) before mid-February and in the lower stratosphere in late February/early March. However, the difference in ClO_x is still small between EXP_A and EXP_B.

The ozone loss for Arctic winter 2004/2005 has been estimated through various methods by researchers using different measurements and/or models (e.g., Manney et al., 2006; Jin et al., 2006; Rex et al., 2006; von Hobe et al., 2006; Singleton et al., 2007; Grooß and Müller, 2007; Feng et al., 2007a; Tsvetkova et al., 2007; Rösevall et al., 2008; Jackson and Orsolini, 2008; Kuttippurath et al., 2010). However, there are large differences in the inferred maximum ozone loss. Table 2 gives the estimated/calculated Arctic ozone loss from the various measurements and/or model simulations for Arctic winter 2004/2005. For Arctic winter 2004/2005, the ozone loss inferred from Odin satellite SMR (Sub-Millimetre Radiometer) is 0.6–1.3 ppmv (Rösevall et al., 2008), which is lower than from other measurements, while the inferred ozone loss (2.1–2.3 ppmv) from M55 Geophysica aircraft data (von Hobe et al., 2006) and about 1.8–2.6 ppmv from ACE-FTS (Atmospheric Chemistry Experiment-Fourier Transform Spectrometer) measurement (Jin et al., 2006) is higher. The calculated ozone loss is 0.8–1.2 ppmv from the assimilation of measurement data into the models (Jackson and Orsolini, 2008; Rösevall et al., 2008). El Amraoui et al. (2008) also assimilated Aura MLS O_3 and N_2O data into the MOCAGE CTM model and they showed a maximum of 1.5 ppmv ozone loss at 425 K. Singleton et al. (2007) estimated 2.0–2.3 ppmv ozone loss using data from different satellite instruments and the SLIMCAT model which is similar to the estimate from Feng et al. (2007a). The calculated ozone loss is 1.08–1.66 ppmv from the 3-D CTM CLaMS (Chemical Lagrangian Model of the Stratosphere) (Grooß and Müller, 2007). The full chemistry of SLIMCAT with the simple thermodynamical equilibrium PSC scheme (EXP_A) gives 2–2.3 ppmv ozone loss while it is slightly lower when the DLAPSE denitrification scheme used (EXP_B). Clearly, SLIMCAT without denitrification (EXP_C) has less ozone loss (0.6–0.8 ppmv) as expected.

Figure 7 shows time series of vortex-averaged ozone loss and maximum local ozone loss at 456 K and partial column ozone loss (380–550 K) from the three simulations (EXP_A,

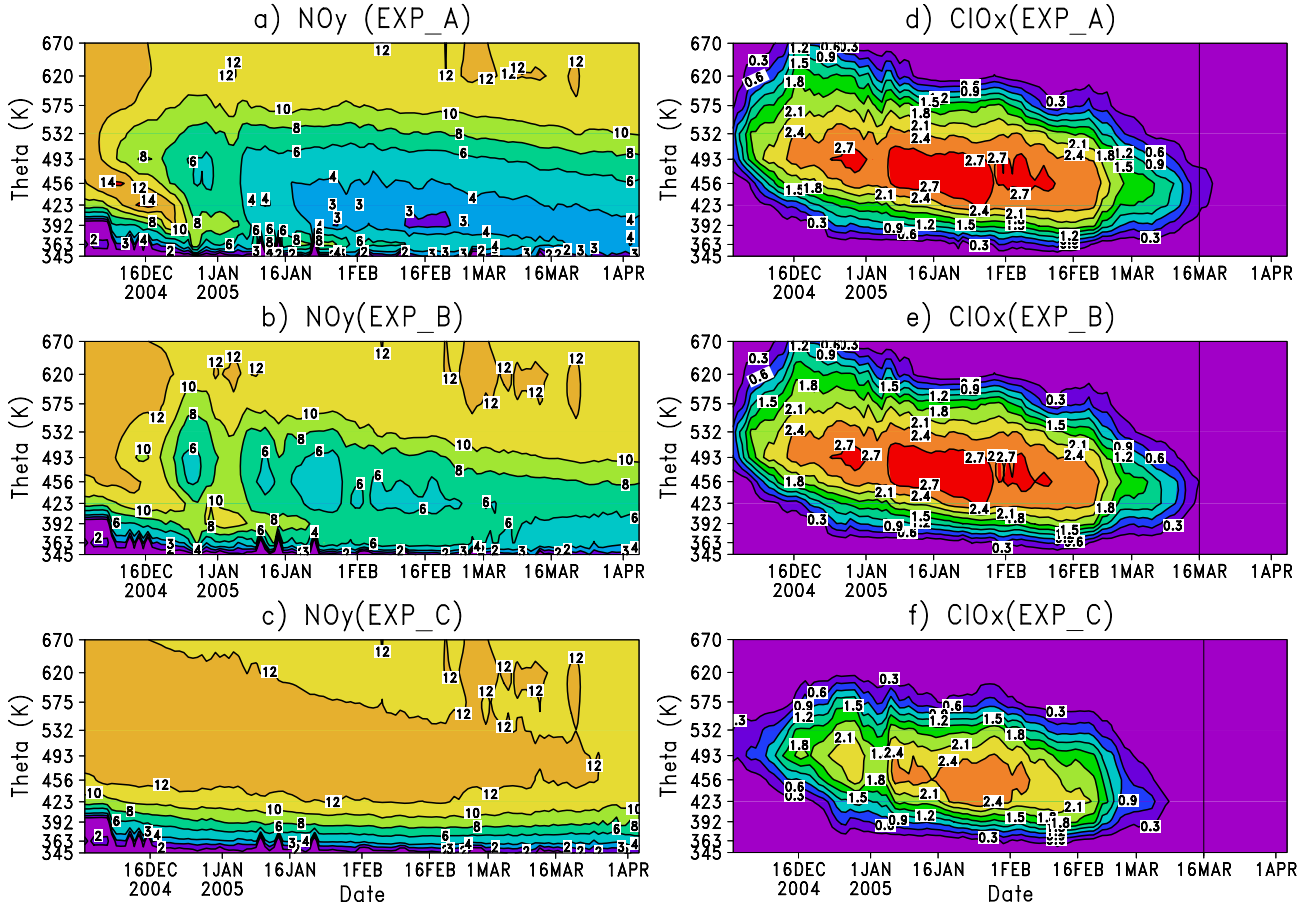

Fig. 5. Vortex-averaged NO_y and ClO_x (ppbv) as a function of time and potential temperature for SLIMCAT simulations using the equilibrium (EXP_A) and DLAPSE (EXP_B) PSC schemes and the simulation without denitrification (EXP_C) for Arctic winter 2004/2005.

EXP_B and EXP_C). Arctic polar ozone depletion began in December 2004 in the cold polar vortex and strong chlorine activation regions and the maximum ozone loss was reached in mid March 2005, followed by a decrease due to the vortex break-up and increased temperatures. The SLIMCAT full chemistry simulations have a similar ozone loss signal, but using the equilibrium scheme (EXP_A) has slightly higher ozone loss than EXP_B, while the ozone loss is much less for EXP_C, when denitrification is switched off. The lower stratospheric partial column ozone losses show very similar patterns. There is ∼90 DU partial column ozone loss between 380–550 K from the model without denitrification (EXP_C), much lower than the observed 127±21 DU by Rex et al. (2006) and inferred 109 DU ozone loss derived from Mimosa-Chim CTM and Aura MLS by Kuttippurath et al. (2010). The estimated partial column ozone from CLaMS is 69±21 DU, which is still unclear and needs further investigation (Grooß and Müller, 2007). The diagnosed partial column ozone loss from the model with the full microphysical DLAPSE scheme (EXP_B) is about 130 DU which better matches the observations (Rex et al., 2006), while the standard model based on a simple thermodynamic equilibrium PSC scheme (EXP_A) is about 140 DU, which slightly overestimates the observations (e.g., Jin et al., 2006; Rex et al., 2006; von Hobe et al., 2006; Tsvetkova et al., 2007). Figure 8 shows time series of differences in vortex-averaged ozone loss at 456 K and partial column ozone loss (380–550 K) between model sensitivity experiments (EXP_B, EXP_C) and standard SLIMCAT simulation (EXP_A) for Arctic winter 2004/2005. There are less ozone loss using a full microphysical DLAPSE denitrification scheme (EXP_B) than using a simple thermodynamic equilibrium PSC scheme (EXP_A) in SLIMCAT. The vortex-averaged ozone loss is small (less than 0.2 ppmv) between the full chemistry SLIMCAT (EXP_A and EXP_B), The partial column ozone difference is ∼10 DU in late winter/early spring 2004/2005. However, there are larger ozone loss differences (1.2–1.6 ppmv at 456 K, 40–60 DU partial column

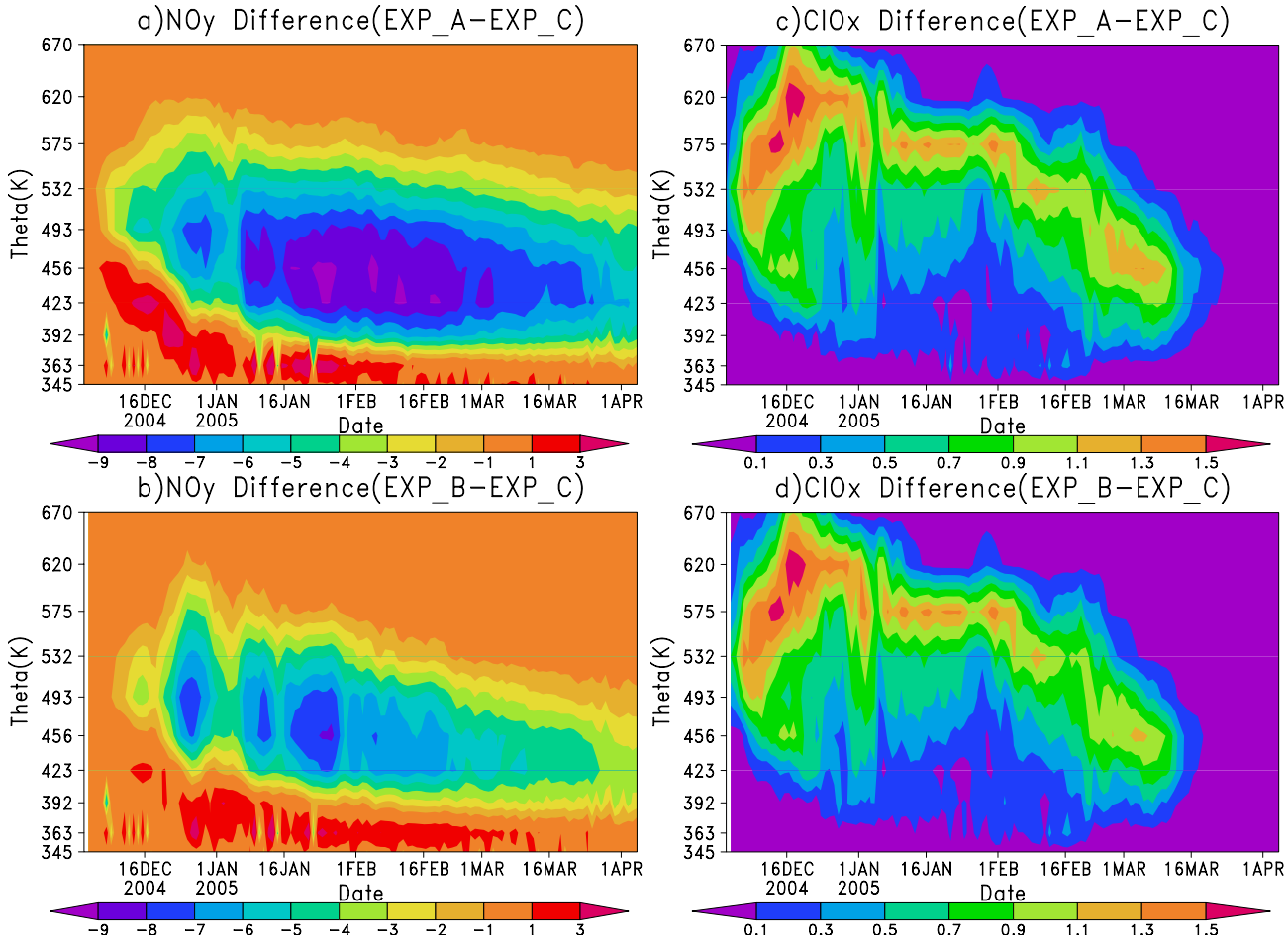

Fig. 6. Difference in vortex-averaged NO_y and ClO_x (ppbv) as a function of time and potential temperature for SLIMCAT full chemistry simulations using the equilibrium (EXP_A) and DLAPSE (EXP_B) PSC schemes with respect to the SLIMCAT simulation without denitrification (EXP_C) for Arctic winter 2004/2005.

ozone loss between 380–550 K) if denitrification is not considered in the model. This clearly shows the importance of considering denitrification in the model and emphasises the importance of denitrification for Arctic ozone depletion.

5 Conclusions

We have used a three-dimensional (3-D) chemical transport model SLIMCAT to quantify the effect of denitrification on ozone loss for the Arctic winter 2004/2005. This is an extension of work from Feng et al. (2007a). The standard SLIMCAT full chemistry model, when using a thermodynamic equilibrium PSC scheme, overestimates Arctic ozone loss for winter 2004/2005 due to too strong chlorine activation and the overestimation of denitrification. The model simulation using the microphysical denitrification scheme DLAPSE successfully reproduces the observed HNO_3 as measured by the ASUR and Aura MLS instruments. Kleinböhl et al. (2005) and Schoeberl et al. (2006) also used ASUR and MLS measurements to study the denitrification for Arctic winter 2004/2005. Kleinböhl et al.(2005) showed that the observed HNO_3 deficit from ASUR measurement in January/February 2005 is about 6 ppbv at 475 K. Schoeberl et al. (2006) also confirmed that there is large HNO_3 decrease in late January 2005 and the net HNO_3 changes are roughly corresponding with the coldest temperature based on Aura MLS measurements. Manney et al. (2003), Goutail et al. (2005) and Feng et al. (2007a) have shown large year-to-year variations of polar Arctic ozone loss due to different meteorological conditions. There have been extensive studies about denitrification for cold Arctic winters (e.g., Carslaw et al., 2002; Davies et al., 2002; Grooß et al., 2002; Kleinböhl, 2004; Kleinböhl et al., 2005; Jin et al., 2006; Davies et al., 2006; Schoeberl et al., 2006). Some of these studies also included the SLIMCAT model run with the equilibrium denitrification

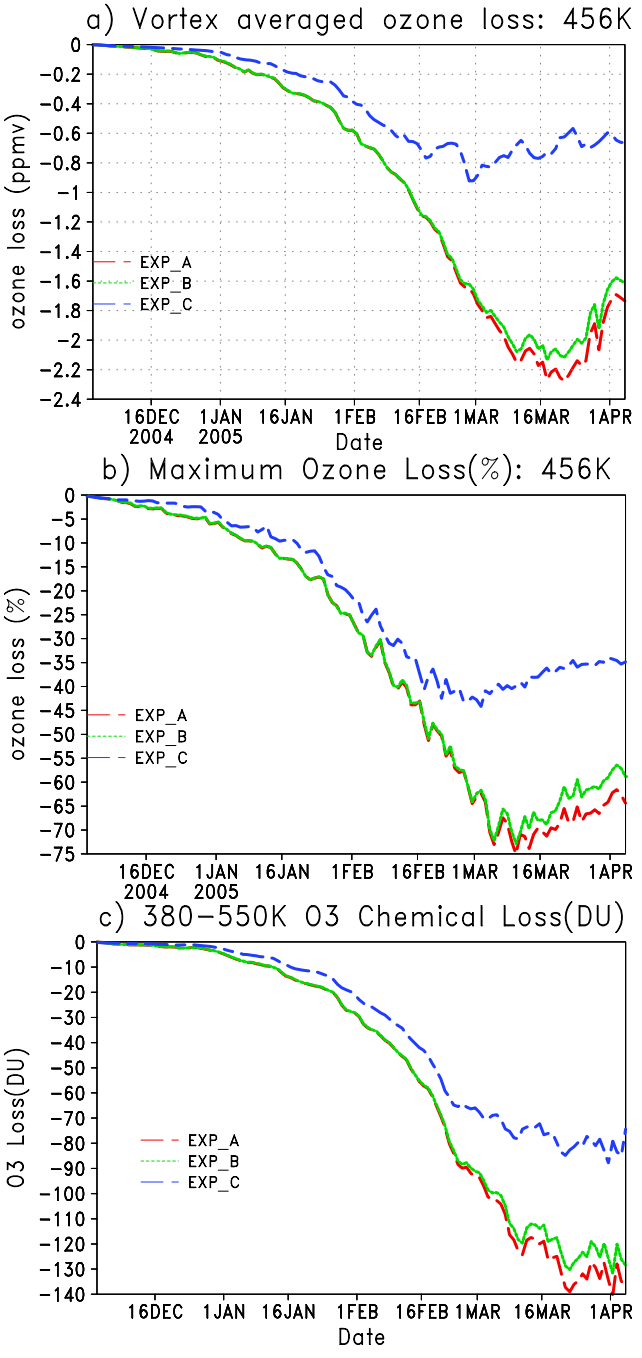

Fig. 7. Time series of **(a)** vortex-averaged ozone loss, **(b)** maximum local ozone loss at 456 K (∼17 km) and **(c)** partial column ozone loss between 380–550 K (∼13–23 km) from simulations EXP_A and EXP_B and EXP_C for Arctic winter 2004/2005.

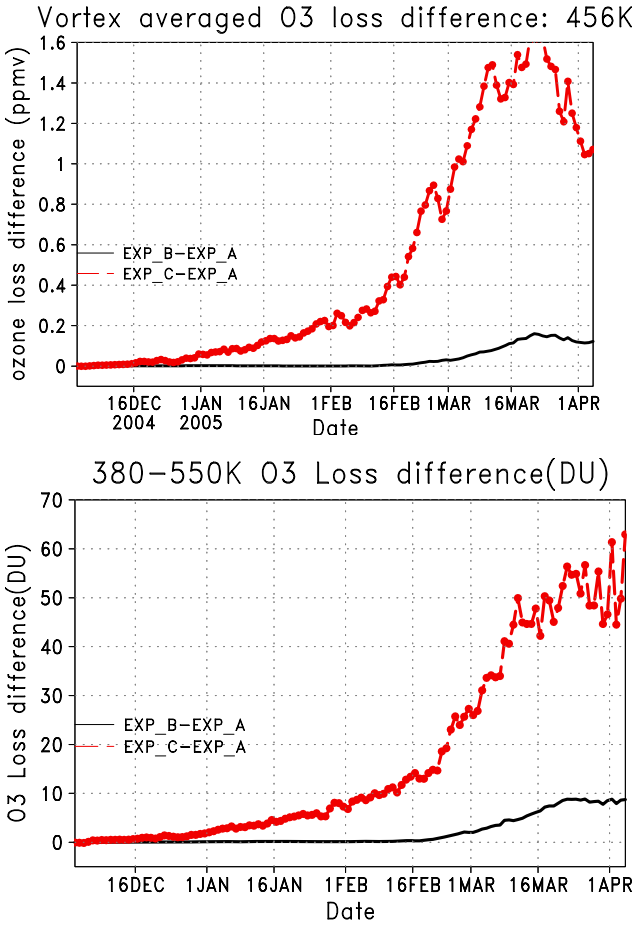

Fig. 8. Time series of differences in **(a)** vortex-averaged ozone loss ozone loss at 456 K (∼17 km) and **(b)** partial column ozone loss between 380–550 K (∼13–23 km) between model sensitivity experiments (EXP_B, EXP_C) and standard SLIMCAT simulation (EXP_A) for Arctic winter 2004/2005.

scheme or DLAPSE schemes. The results showed that the model using the DLAPSE microphysical denitrification scheme is able to produce denitrification and in good agreement with observations for the previous Arctic winters (e.g., 1999/2000, 2003/04). The simulation from the model run without denitrification process (EXP_C) underestimates the Arctic polar ozone depletion by ∼30 %, i.e. 40–60 DU partial column ozone loss for Arctic winter 2004/2005, which is slightly larger than the inferred contribution of denitrification of polar ozone loss for previous Arctic winters. For example, Davies et al. (2002) showed that denitrification induced extra 21–30 % maximum ozone loss at 460 K for Arctic winter 1999/2000 using SLIMCAT model. Grooß et al. (2002) also used the Lagrangian CTM model CLaMS to study the ozone depletion in spring 2000 and they showed that the denitrification had strong chlorine deactivation and ozone depletion starting in March 2000. The enhanced ozone loss due to the denitrification was 0.3 ppmv (about 18 %) at 450 K from 10 Feburary to 20 March 2000. Tripathi et al. (2010) estimated the contributions of denitrification on Arctic ozone loss were about 23 % for Arctic winter 1999/2000 and 17 % for Arctic winter 2002/2003 using the high resolution CTM MIMOSA-CHIM model.

The time taken for stratospheric chlorine deactivation depends crucially on the degree of denitrification. Therefore, accurately simulating the impact of denitrification on Arctic ozone depletion requires a detailed microphysical PSC scheme in the model. The simulations are quite sensitive to the PSC schemes used in the model, with about ∼5–10 % at ∼17 km effect on Arctic ozone loss when using the simple equilibrium or the microphysical PSC scheme.

Atmospheric chemistry models, i.e., chemistry climate models (CCMs) and chemical transport models (CTMs), are now widely used to predict future stratospheric ozone change. However, most CCMs and CTMs are still using simple thermodynamic equilibrium PSC schemes for the determination of heterogeneous chemistry and denitrification (e.g., SPARC CCMval., 2010). Many studies have shown that an increased severity of denitrification may delay the recovery of polar ozone in spring (e.g., Rex et al., 1997; Waibel et al., 1999; Esler and Waugh, 2002; Davies et al., 2002). In this paper, we have shown that using the microphysical denitrification scheme in SLIMCAT improves the HNO_3 simulation and partial column ozone depletion compared with measurements. Therefore, it would be very important to consider a full microphysical denitrification process in CCMs and CTMs for better simulations or predictions of current/future polar ozone trends in Arctic polar region.

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