The Effect of Ice Particles on the Tropospheric Ozone Budget via Heterogeneous Conversion processes

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ABSTRACT: Cirrus particles are ubiquitous throughout the mid- to upper troposphere and provide reactive surfaces onto which trace gas species may become either attached or chemically processed, thus modifying the chemical cycles active at high altitudes. Here we introduce two simple parameterizations for the description of the micro-physical properties of ice particle fields into a global 3D Chemistry Transport Model. We subsequently investigate the influence that the reversible loss of HNO_3 from the gas phase has on the tropospheric ozone budget. In contrast to previous studies there is a modest increase in the global tropospheric ozone burden, where there are stark hemispheric differences. By applying the EU-QUANTIFY 2050 aircraft emission scenarios using fixed meteorology for 2006 we show that the influence of heterogeneous scavenging becomes less important unless the available surface area upon which scavenging can occur would increase in the future.

1 INTRODUCTION

Ice particles form readily throughout the troposphere and may grow to significant sizes depending on both the ambient temperature and the partial pressure of water vapour. Once present they introduce both perturbations to the radiation budget and reactive surfaces upon which trace gas species may become either reversibly or irreversibly attached, depending on the chemical structure of the chemical species and their characteristic affinity for the ice surface. One such trace gas species which has a high affinity for being scavenged on ice is nitric acid (HNO_3). In the upper troposphere HNO_3 acts as an abundant reservoir species for reactive nitrogen, which, once oxidised, helps determine the *in-situ* formation of tropospheric ozone (O_3). By scavenging HNO_3 out of the gas-phase, a fraction of this reactive nitrogen is essentially removed (sequestered) from the gas phase, which has the potential to lower *in-situ* O_3 formation. Laboratory studies have determined the kinetic parameters needed to describe this reversible uptake and have found that saturation of the ice surface maybe accounted for by using a parameter to describe the maximum number of reactive sites available per cm^2 of ice surface (Cox et al, 2005). This uptake parameter is commonly known as the Langmuir uptake co-efficient. Here we introduce parameterizations into the global Chemistry Transport Model (CTM) TM4 for the calculation of the available reactive surface area utilizing the Ice Water Content (IWC) available from ECMWF meteorological data and investigate the effects of reversible scavenging of HNO_3 out of the gas phase.

2 DESCRIPTION OF THE CTM

The version of TM4 used in this study is similar to TM4_AMMA described in Williams et al (2009) apart from the application of updated heterogeneous uptake data for (e.g.) the scavenging of HCHO into cloud droplets. The gas phase conversion of N_2O_5 into HNO_3 involving water vapour is also included in the modified CBM4 scheme using the latest recommendations (Williams and Van Noije, 2008). For the present day simulations (denoted BASE and HNO3_UP) the emissions are taken from the RETRO database (http://retro.enes.org) for anthropogenic and biogenic emissions and the GFEDv2 database (van der Werf et al, 2006) for biomass burning emissions. An injection

height of 2km is used in the tropics (20°N-20°S), which is typical of the injection heights seen in recent measurements (Labonne et al, 2007). Moreover, a daily cycle is imposed on the biomass burning cycle, which peaks at 2pm local time as has been determined by analysing satellite data with staggered overpass times (Boersma et al (2008)) and geostationary platforms (Roberts et al, 2009). For the future simulations (denoted 2050 and 2050_HNO3_UP) aircraft emissions for the year 2050 are applied as taken from the QUANTIFY emission database. The model uses a vertical resolution of 34 layers and a horizontal resolution of 3° x 2°, where ECMWF meteorological data is applied using an update frequency of 6 hours. A spin-up period of 6 months was used for each individual simulation.

3   RESULTS

3.1 *The zonal distribution of ice particle*

For the description of ice particles we introduce the parameterization of Heymsfield and McFarquar (1996) for the derivation of the Surface Area Density (SAD), and we use the resulting cross-sectional area (A_c) in the parameterization of Fu (1996) for the calculation the effective radii (R_{eff}). Both parameterizations use the ECMWF IWC for the derivation of the respective micro-physical properties of the ice particles. A scaling ratio of 10 was used to convert A_c into SAD as suggested by Schmitt and Heymsfield (2005), which constitutes a correction for randomly shaped particles rather than spherical particles. This is higher than the values of 2-4, which are more representative of spherical particles, used in previous CTM studies (Lawrence and Crutzen, 1998; von Kuhlmann and Lawrence, 2005). Both parameterizations have been validated against a host of different in-situ measurements (e.g. Heymsfield, 2003). Figures 1a and b show the resulting zonal distribution of both the R_{eff} and SAD values for seasons DJF and JJA, respectively. The largest R_{eff} values occur in the upper troposphere (UT) in the tropics and the lower troposphere at the poles, where there is a zonal shift between the seasons. For the SAD the highest values tend to occur in the lower troposphere above 65° latitude, as determined by the frequency at which particles occur throughout the season. Analysing daily fields reveals that values of R_{eff} ranging between 50-100µm can occur (not shown), although such sizes do not show up in the seasonal means. Depending on the lifetime of the ice particles, gravitational settling can occur for the larger particles, which will re-distribute any scavenged trace species to lower altitudes.
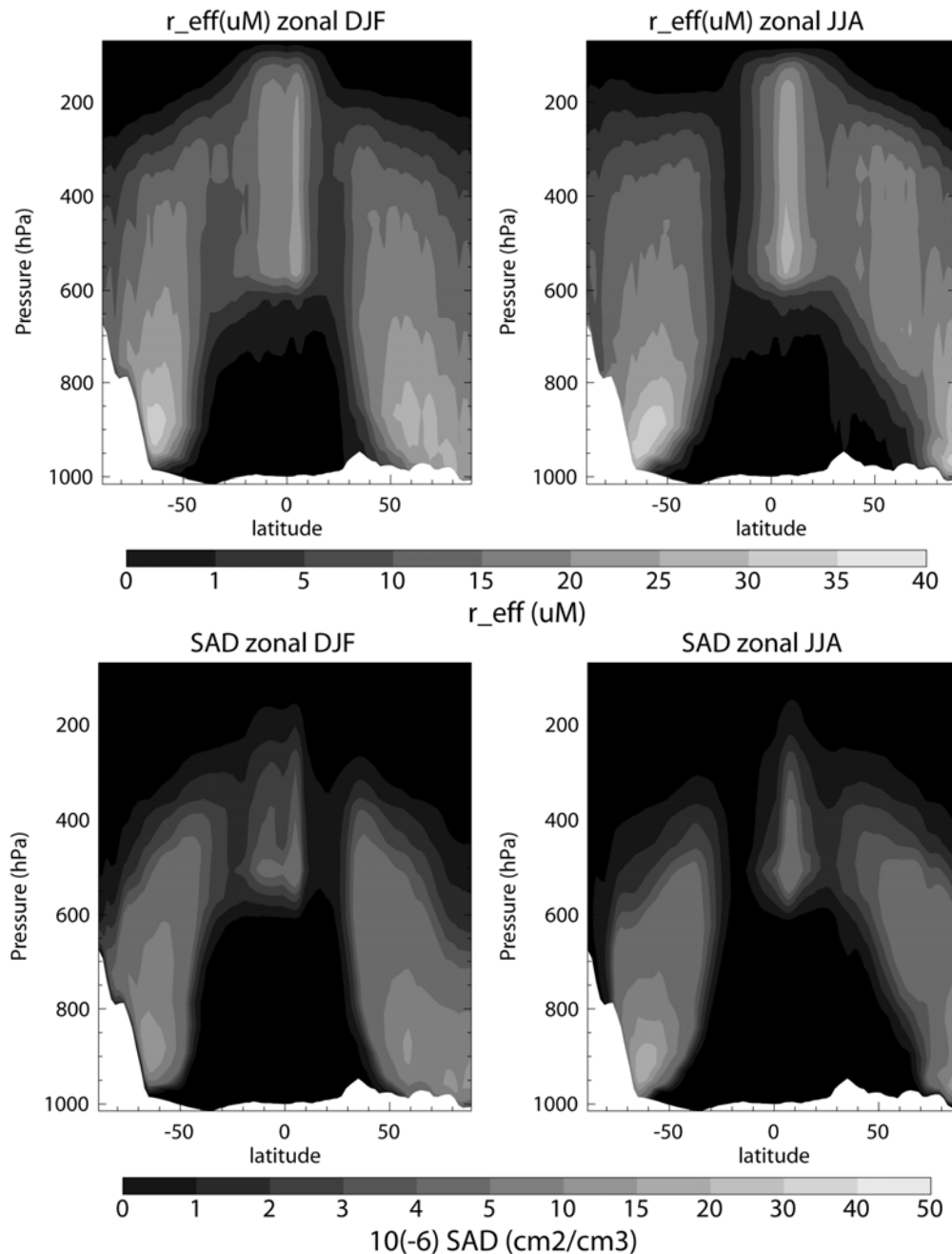
Figure 1: The zonal distribution of (top) R$_{eff}$ and (bottom) SAD for seasons DJF and JJA when applying the chosen parameterizations for calculating the microphysical properties of ice fields online in TM4.

3.2 *The effect of uptake of HNO3 on ice surfaces for present day emissions*

The uptake of HNO_3 on ice has been included in TM4 according to the latest recommendations given on the IUPAC website for chemical reaction data (www.iupac-kinetic.ch.cam.ac.uk), where the equilibrium rate is converted into a first-order absorption and desorption rate using the available SAD. It should be noted that trapping of HNO_3 by growing ice surfaces at low temperatures (<210°K) as recently proposed by Kärcher et al (2009) is not included. Figure 2 shows the zonally integrated annual differences introduced for O_3, NO_x, HO_x and the predominant nitrogen containing reservoir species. For the UT there are decreases in [HNO_3] of ~10%, with corresponding perturbations in [O_3] of ±2%. The differences in the lower troposphere are more moderate due to the higher temperatures which limit the available SAD. There is a clear difference in the simulated changes between the hemispheres as a result of higher [HNO_3] (and [NO_x]) in the NH UT that are due to aircraft emissions. This uptake and subsequent release of HNO_3 causes an increase in [NO_x] of between 2-5%, subsequently enhancing in-situ O_3 formation in the NH by a few percent. This is in contrast to previous studies, where decreases of between 40-60% have been simulated using NCEP meteorological data (von Kuhlmann and Lawrence, 2005). These authors did not provide in-

formation regarding the distribution of the available SAD, and no limit was placed on the number of reactive sites on the ice surface which can be occupied (*i.e.* saturation is ignored). Also a different uptake co-efficient was applied. In essence, the SAD values calculated here online in TM4 are low (20-50 $\mu m/cm^2$) compared to the range of values typically captured by in-situ measurements (20-500 $\mu m/cm^2$; Popp et al, 2004). This limits the amount of HNO_3 which can be scavenged out of the gas phase, where the low SAD is a result of the relatively large resolution adopted in the model and the ECMWF meterological dataset (typically 1km height in the UT). This could potentially be improved upon by introducing parameterizations of sub-grid processes (e.g.) for a more accurate description of aircraft contrails (which are currently ignored). Additional sensitivity tests including gravitational settling of large particles result in differences in NO_x of $\pm 1\%$ (not shown), due to the low fraction of HNO_3 removed from the gas phase. Inclusion of a fraction of irreversible loss ('Burial'), as proposed by Kärcher et al (2009), would enhance the effects presented here by providing a NO_x sink at high altitudes. Moreover, conversion of the NO_3 radical and irreversible loss of OH on the surface of ice particles were also tested and found to have relatively small effects on the composition of the UT.
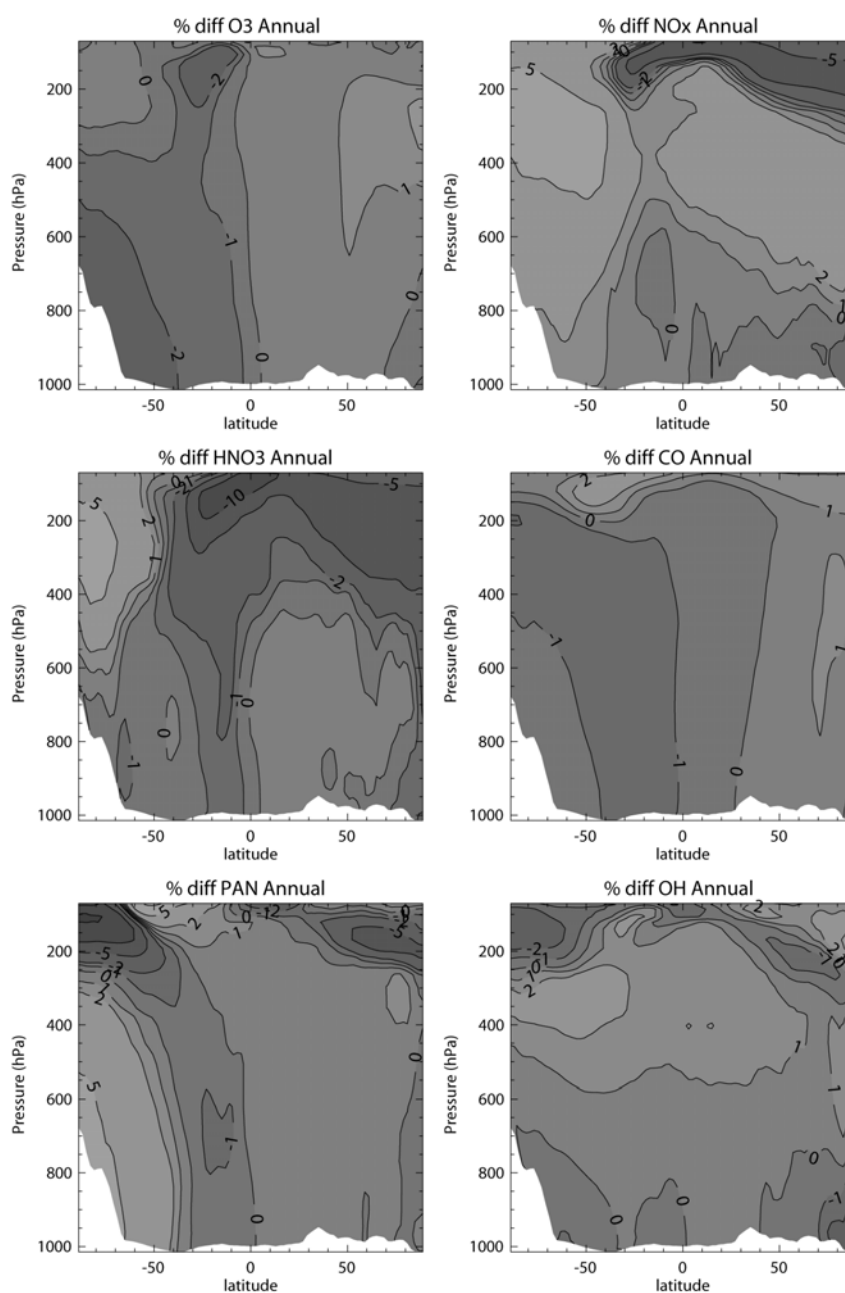

Figure 2: The zonally integrated annual differences in (a) O_3, (b) NO_x, (c) HNO_3, (d) CO, (e) PAN and (f) OH as a result of introducing heterogeneous uptake of HNO_3 on cirrus particles.

3.3 *The effect of future aircraft emissions for the year 2050*

The 2050 A1 future aircraft emissions as taken from the QUANTIFY project (www.pa.op.dlr.de/quantify) increase the annual global nitrogen budget by ~4.5Tg N, where the additional NO_X is predominantly injected between 200-600hPa in the NH. Here we apply the meteorology for 2006 in order to differentiate the influence of increasing the aircraft emissions towards the future estimates from possible meteorological differences in future years. Figure 3 shows the resulting increases in the zonally integrated annual means for O_3, NO_X and HNO_3. For [NO_X] increases of >200% occur between 200-400hPa, which increases the tropospheric burden of O_3 by ~10%. For HNO_3, there are corresponding increases of upto ~100%. Comparing Figs 1 and 3 shows that the largest increases in [HNO_3] generally occur above the altitude at which the ice particle field exhibits significant coverage.
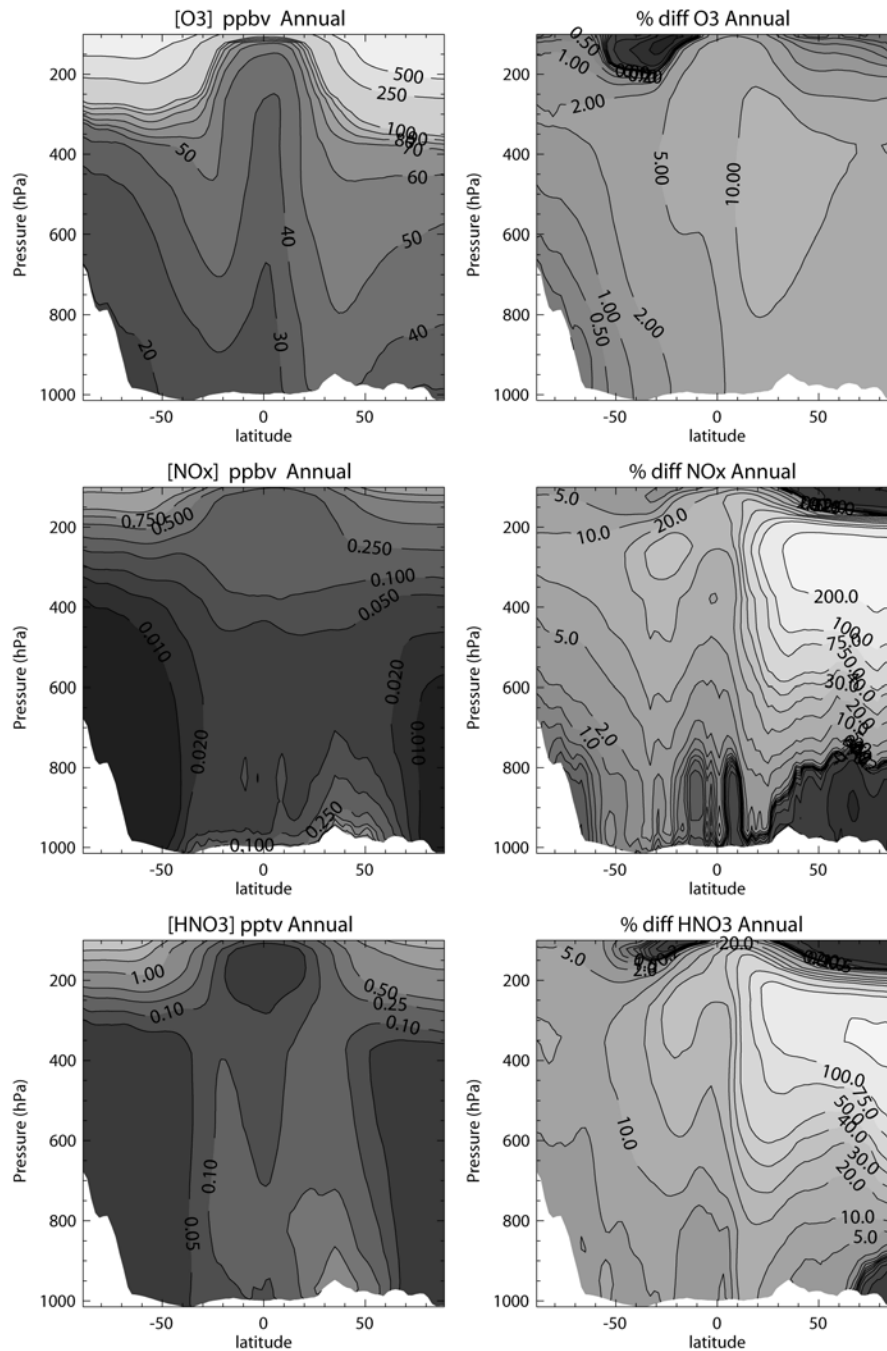

Figure 3: The zonally integrated annual means of (a) O_3, (b) NO_X and (c) HNO_3 in the BASE simulation and the resulting differences as compared to the BASE_2050 simulation using 2006 meteorology.

3.4 *The importance of heterogeneous scavenging with increased aircraft emissions*

For the 2050_HNO3_UP simulation the perturbation in the *in-situ* production of ozone becomes

less important. Table 1 provides the global tropospheric burdens for O_3, CO and HNO_3 for all of the simulations presented. Comparing the values for the BASE and 2050 simulations, it can be seen that the increase in $[O_3]$ substantially reduces the tropospheric burden of CO (although the corresponding future increase in CO emissions are not included in the simulation). For the solid $[HNO_3]$ the total integrated N scavenged onto ice surfaces increases +7% from 0.96 Tg yr^{-1} (present) to 1.03 Tg yr^{-1} (future). The percentage increase is less than that which occurs in the gas phase due to both saturation of the available ice surfaces and the differences in altitude between the SAD available and that where the largest increases in HNO_3 occur. The net effect on tropospheric O_3 is to reduce the observed increase which occurs in the present day scenario. In reality the changing climate could also impose an effect by modifying the SAD which is available, where increasing temperatures as a result of an increase in the radiative forcing from (e.g.) O_3 and a positive feedback due to enhanced evaporation (Dressler et al, 2008) would result in a decrease in the incidence of cirrus, thus diminishing the importance of such heterogeneous processes.

Table 1: The changes in the tropospheric burdens of O_3, CO and HNO_3 due to heterogeneous scavenging of HNO_3 onto cirrus particles. All numbers are globally integrated values for the year 2006, where the HNO3_UP and 2050_HNO3_UP values are given in paranthesis.

Trace Species	Present Tropo. Burden (Tg)	Future Tropo. Burden (Tg)
O_3	263.5 (275.5)	295.6 (294.6)
CO	305.7 (292.9)	274.3 (278.5)
HNO_3	0.645 (0.641)	0.649 (0.645)

4 CONCLUSIONS

In this study we have show that by incorporating simple parameterizations for calculating the micro-physical properties of cirrus particles in a global CTM, we can introduce seasonal and spatial variability in the ice particle fields as constrained by the meteorological input data available in the model. By introducing reversible scavenging of HNO_3 onto ice surfaces we have found that stark differences occur between the Northern and Southern Hemispheres with respect to the perturbation introduced to the in-situ formation of tropospheric O_3. This effect is more modest than that found in previous studies, in that our study gives an increase in the tropospheric O_3 burden as a result of an increase in the availability of reactive nitrogen. The limited amount of scavenging of HNO_3 out of the gas phase means that the effect of de-nitrification due to the gravitational settling of large particles can be neglected. For a more accurate assessment of the global effects, the fraction of HNO_3 lost irreversibly into ice particles needs to be included, along with sub-grid parameterizations to describe the high SAD of contrail cirrus. This should amplify the effects presented here leading the a net global decrease in tropospheric O_3. When adopting future aircraft emission estimates using fixed meteorology for 2006, we find that the fraction of HNO3 scavenged out of the gas phase is reduced due to saturation effects on the ice surface. Therefore, without a corresponding increase in SAD due to climate changes, which is not likely considering that temperature is likely to increase, the influence of heterogeneous scavenging will become less important.

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