**Atmospheric
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The impact of ice uptake of nitric acid on atmospheric chemistry

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Abstract. The potential impact of the uptake of HNO_3 on ice on the distribution of NO_y species, ozone and OH has been assessed using the global scale chemistry-transport model MATCH-MPIC. Assuming equilibrium uptake according to dissociative Langmuir theory results in significant reductions of gas phase HNO_3. Comparison to a large set of observations provides support that significant uptake of HNO_3 on ice is occurring, but the degree of the uptake cannot be inferred from this comparison alone. Sensitivity simulations show that the uncertainties in the total amount of ice formation in the atmosphere and the actual expression of the settling velocity of ice particles only result in small changes in our results. The largest uncertainty is likely to be linked to the actual theory describing the uptake process and the value of the initial uptake coefficient. The inclusion of non-methane hydrocarbon chemistry partially compensates for the absence of HNO_3 uptake on ice when this is neglected in the model. The calculated overall effect on upper tropospheric ozone concentrations and the tropospheric methane lifetime are moderate to low. These results support a shift in the motivation for future experimental and theoretical studies of HNO_3-ice interaction towards the role of HNO_3 in hydrometeor surface physics.

1 Introduction

A large fraction of the loss of reactive nitrogen (NO_y) in the atmosphere occurs via scavenging of nitric acid (HNO_3) by clouds. Nitrogen oxides (NO_x=NO+NO_2), important precursors of ozone (O_3) and the hydroxyl radical (OH), can therefore be strongly affected by this process. HNO_3 has also recently been found to influence the growth of aerosols and cloud droplets (Nenes et al., 2002), and has been hypothe-

sized to affect ice crystals (Gao et al., 2004). Besides PAN, HNO_3 is an important reservoir species of NO_y (e.g. Neuman et al., 2001; Staudt et al., 2003), thus capable of transporting odd nitrogen into remote regions. A small direct radiative effect of HNO_3 has also been calculated (Evans and Puckrin, 2001); however, this is probably only of significance in highly polluted areas (up to $0.2\,W/m^2$ under those conditions).

During the last few years a large number of laboratory studies (Zondlo et al., 1997; Abbatt, 1997; Arora et al., 1999; Hudson et al., 2002; Hynes et al., 2002; Ullerstam et al., 2005; Ullerstam and Abbatt, 2005) and field observations (e.g. Weinheimer et al., 1998; Meilinger et al., 1999; Kondo et al., 2003; Popp et al., 2004; Ziereis et al., 2004) have investigated the uptake of HNO_3 on ice particles and have led to significant advances in the understanding of this process. However, until recently laboratory conditions were mostly different from those typically found in the atmosphere, and, combined with experimental uncertainties and natural variability, still render our knowledge of a generally applicable theory of the uptake process and its global importance incomplete. Also, different pathways of ice formation in the atmosphere – riming and diffusional growth – and the particle growth history in the dynamically changing environment (Kärcher and Basko, 2004; Ullerstam and Abbatt, 2005) complicate the situation.

Assuming efficient uptake rates on ice, Lawrence and Crutzen (1998) found a significant redistribution of HNO_3 by gravitational settling of ice particles resulting in reduced mixing ratios in the upper troposphere (UT). Tabazadeh et al. (1999) proposed applying dissociative Langmuir theory to the uptake process and suggested that the assumptions used in Lawrence and Crutzen (1998) probably resulted in too efficient uptake.

Using the formulation of Tabazadeh et al. (1999) in a box model, Meier and Hendricks (2002) assessed the chemical effects in the UT and instead found significant impacts for

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Table 1. Short descriptions and acronyms of the sensitivity simulations.

Experiment	Description
NOUP	No uptake of HNO$_3$ on ice surfaces.
HIGHUP	Efficient uptake of HNO$_3$ on ice as in von Kuhlmann et al. (2003a).
LANGM	Dissoc. Langmuir uptake, $\Delta H_{ads}=-44$ kJ/mol
LANGM2	As LANGM, but $\Delta H_{ads}=-59.4$ kJ/mol (Tabazadeh et al., 1999)
VHEYMS	As LANGM, but using an expression of ice settling velocity from Heymsfield (2003).
LESSICE	As LANGM, but $\approx 1/3$ IWC (Rasch and Kristjánsson, 1998).
CH4NOUP	As NOUP, but not including NMHC chemistry.
CH4HIGH	As HIGHUP, but not including NMHC chemistry.

some scenarios. Both studies, however, emphasize that the potential effects on a larger scale still have to be assessed with a 3-D model, which is the aim of this study.

Thus far, Liao et al. (2003) have incorporated an 0.3 monolayer uptake of HNO$_3$ on ice particles in their general circulation model and report an increase in zonal mean gas-phase HNO$_3$ of up to a factor of 2 when leaving out this process. Effects on other species, however, where not reported. Lawrence and Crutzen (1998) specifically focused on the effects of gravitational settling using simple assumptions about HNO$_3$ uptake. Here, we take a broader perspective and investigate the general effect of ice uptake on atmospheric chemistry using more elaborate uptake formulations, an extended chemistry scheme and a larger suite of observations. The influence of non-methane hydrocarbon (NMHC) chemistry on the calculated effects, which was neglected in Lawrence and Crutzen (1998), will also be investigated.

2 Model setup

We employ the global chemistry-transport model MATCH-MPIC (Model of Atmospheric Transport and Chemistry, Max-Planck-Institute for Chemistry version) (Rasch et al., 1997; Lawrence et al., 1999; von Kuhlmann et al., 2003a, and references therein) at a resolution of about 5.6°×5.6° (T21), with 28 vertical levels and a time step of 0.5 h. The model is driven by NCEP/NCAR reanalysis data (Kalnay et al., 1996). The model treats grid-scale advective transport, convection, vertical mixing, settling of ice particles, wet and dry deposition and chemical transformations of ozone and 55 related species, including non-methane hydrocarbons ($\leq$C4 and isoprene) through 144 reactions. Heterogeneous chemistry is only included in the case of hydrolysis of N$_2$O$_5$ on aerosols

and cloud droplets to form HNO$_3$ (Dentener and Crutzen, 1993).

As part of continuing model development we have updated the reaction rates (mainly to Sander et al., 2003) and the chemical mechanism. A detailed listing of all reactions is given in the supplementary material (http://www.atmos-chem-phys.org/acp/6/225/acp-6-225-sp.pdf). For example, photolysis channels of HNO$_4$ in the near-IR have been included according to Roehl et al. (2002). The global lightning source strength used here is about 2 Tg-N/yr and is distributed in the vertical according to Pickering et al. (1998). Other sources are implemented as described in von Kuhlmann et al. (2003a). Recent thorough comparisons of the model to observations of a large suite of trace gases have been presented by von Kuhlmann et al. (2003a,b); Lawrence et al. (2003) and Labrador et al. (2005). The version used here displays very similar characteristics as presented in these studies. While the distributions of O$_3$ and CO were generally well captured by the model, larger deviations were found in some nitrogen species. PAN was often overestimated in the remote UT, HNO$_3$ often underestimated at all altitudes compared to measurements. The regions where the underestimate of HNO$_3$ occur are often far away from direct surface sources (e.g., in the tropical Pacific), thus pointing towards too efficient washout in the model.

A number of sensitivity runs, listed in Table 1, were performed. For each case a simulation was run through 16 months (1 September 1995–31 December 1996) initialized with a September distribution from an earlier model run, and only the results for 1996 were used.

The case HIGHUP follows the approach previously used in MATCH-MPIC (von Kuhlmann et al., 2003a) which describes the uptake of HNO$_3$ analogous to Henry's Law, thus implicitly allowing for bulk uptake.

In the other experiments a dissociative Langmuir model as in Tabazadeh et al. (1999) is applied. Thus, we iteratively include the effect of HNO$_3$ depletion on the coverage and also allow only a maximum coverage of $0.27 \cdot 10^{15}$ molec/cm^2 to better match the data of Abbatt (1997).

Different from previous studies, calculation of the equilibrium constant is done using a reference laboratory value from Hynes et al. (2002) in order to avoid large uncertainties in the pre-exponential factors in the adsorption rate. It is assumed that equilibrium is reached in each time step, computed as

$$K_{eq} = K_{ref} \cdot \exp\left[\frac{-\Delta H_{ads}}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right], \quad (1)$$

where $K_{ref}=6.77 \cdot 10^4$ Torr^{-1}, $T_{ref}=228$ K and $\Delta H_{ads}=-44$ kJ/mol (Bartels-Rausch et al., 2002) (R is the universal gas constant). The value of ΔH_{ads} determined by Bartels-Rausch et al. (2002) is used here because their determination did not rely on a particular theory of the uptake process. In good agreement to this, Popp et al. (2004) empirically derive from field observations
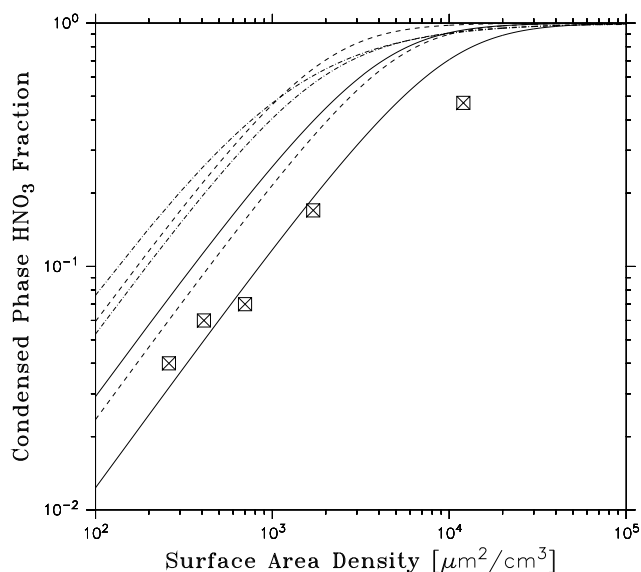
Fig. 1. Fraction of total HNO_3 predicted by the model formulation to be in the condensed phase. Three pairs of one thick and thin line are shown, corresponding to 100 pmol/mol and 500 pmol/mol of total HNO_3, respectively. Solid lines are for dissociative Langmuir theory using Eq. (1) at 214 K, dashed lines the same but for 200 K. The dash-dotted lines represent non-dissociative Langmuir theory and K_{eq} at 214 K according to Ullerstam et al. (2005). Symbols indicate quintiles of the data of Popp et al. (2004).

Table 2. Integrated annual mean tropospheric and upper tropospheric (p<500 hPa) tracer masses using the monthly mean diagnosed tropopause and monthly mean tracer fields. Absolute values are in Tg(O₃) for ozone and Gg(N) otherwise. Percent changes of CH4HIGH are with respect to the CH4NOUP scenario, otherwise changes are with respect to the NOUP simulation.

	HNO₃	NOₓ	PAN	O₃
	Troposphere			
NOUP	173	141	362	339
HIGHUP	−37%	−6.3%	−2.6%	−3.9%
LANGM	−24%	−4.4%	−1.7%	−2.7%
LANGM2	−23%	−4.5%	−1.6%	−2.7%
VHEYMS	−24%	−4.5%	−1.7%	−2.8%
LESSICE	−13%	−5.6%	−6.1%	−4.2%
CH4NOUP	215	146	–	296
CH4HIGH	−49%	−13%	–	−7.1%
	Upper Troposphere			
NOUP	69	66	196	180
HIGHUP	−70%	−15.6%	−4.3%	−4.9%
LANGM	−49%	−11.8%	−3.3%	−3.5%
LANGM2	−47%	−11.9%	−3.2%	−3.5%
VHEYMS	−49%	−12.0%	−3.3%	−3.6%
LESSICE	−36%	−11.1%	−7.7%	−4.8%
CH4NOUP	111	78	–	165
CH4HIGH	−76%	−25%	–	−7.6%

(CRYSTAL-FACE) a value of 46 kJ/mol for the adsorbtion enthalpy. They note, however, that this cannot to be taken as a fundamental thermodynamic parameter. However, because we calculate K_{eq} based on the measurements by Hynes et al. (2002) (at 228 K) our values for K_{eq} and thus for the uptake are on average higher than observed by Popp et al. (2004) (see Fig. 1). Popp et al. (2004) also tested the multi-layer Frenkel-Halsey-Hill (FHH) model as proposed by Hudson et al. (2002), but found less good agreement for temperatures below 205 K, where the FHH model overestimated the coverage compared to the measurements, though large scatter of a factor of 5 was also found in the observations.

Recently, Ullerstam et al. (2005) performed laboratory measurements under nitric acid partial pressures found in the upper troposphere. They found that a non-dissociative uptake law described their data better and provide an expression for K_{eq} between 214 and 239 K. Using this expression, however, would lead to a larger overstimate of the fractional HNO_3 coverage compared to the data of Popp et al. (2004) (see dash-dotted lines in Fig. 1).

The surface area density (SAD) of ice clouds and their mean settling velocity are parameterized based on the calculated ice water content (IWC) as in Lawrence and Crutzen (1998) based on measurements during the Central Equatorial Pacific Experiment (CEPEX).

$$SAD[cm^2/cm^3] = 2 \cdot 10^{-4} \times IWC[g/m^3]^{0.9}, \qquad (2)$$

where SAD is in cm²/cm³ and IWC is in g/m³. Thus, we assume a conservative value of 2 for the conversion factor from cross sectional area to surface area. It is noted that Popp et al. (2004) have found significantly higher surface area densities for a given IWC (see their Fig. 9b). The impact of this difference is further discussed in Sect. 3.3.

A maximum value for the settling velocity of 100 cm/s is applied to avoid unreasonably large values for very large IWCs (Lawrence and Crutzen, 1998).

The main differences between the model used by Liao et al. (2003) and MATCH is that Liao et al. (2003) include more aerosol/gas interactions (in MATCH only hydrolysis of N_2O_5 on sulphate aerosols is included), whereas this study treats HNO_3-ice interactions in a more sophisticated way.

3 Results and discussion

3.1 Effects on HNO₃

The general effect of the globally integrated tracer masses of HNO_3, O_3, NO_x and PAN is summarized in Table 2. Since the largest differences occur in the upper troposphere, total masses and changes for this region are also calculated. In the standard dissociative Langmuir uptake simulation (LANGM) a strong depletion of HNO_3 in the UT is calculated (Fig. 2).
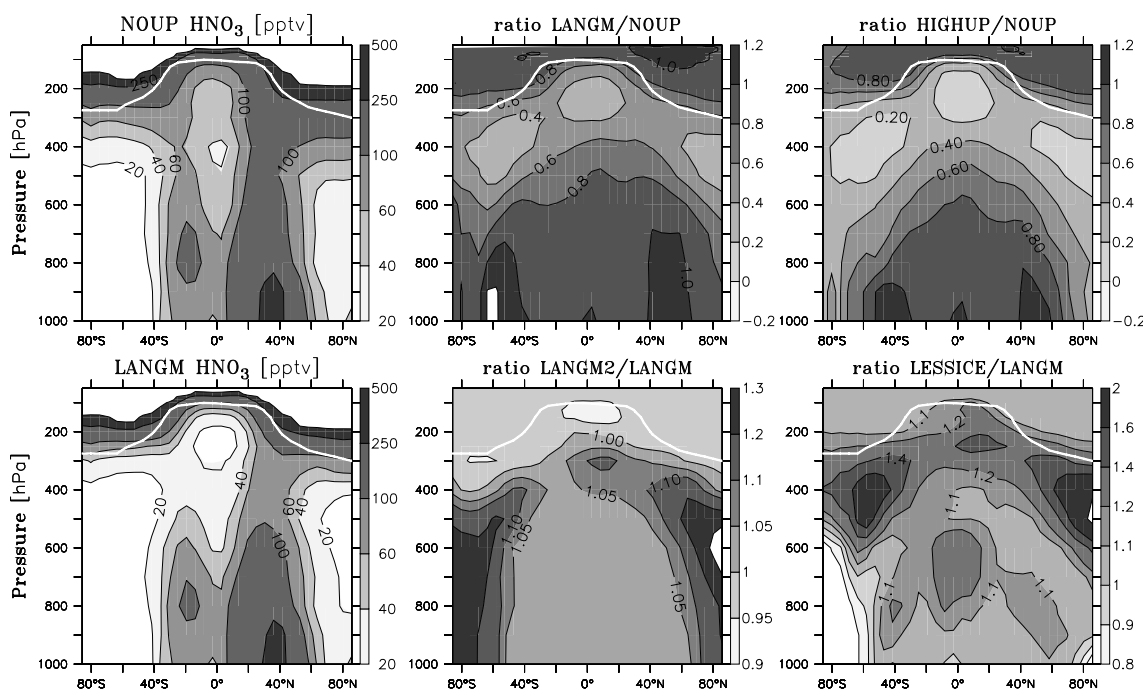
Fig. 2. Annual zonal mean HNO₃ from the NOUP and LANGM runs (left) and ratios of the LANGM and HIGHUP simulation to the run without uptake on ice (first row). Scenarios LANGM2 and LESSICE are compared to the LANGM run in the second row. The white line indicates the model tropopause.

The maximum effect (HIGHUP/NOUP) is also shown in Fig. 2. It is found that in the Langmuir uptake scenario already about 2/3 of the maximum effect is calculated. This is also reflected in integrated HNO₃ tracer masses in Table 2: The LANGM scenario results in 49% less HNO₃ in the upper troposphere on the annual average and in 70% less HNO₃ in the HIGHUP case compared to a simulation where uptake on ice is neglected (NOUP). The effects on tropospheric HNO₃ masses are still −24% and −37% for the LANGM and HIGHUP scenarios, respectively.

These results are different than the small effect expected by Tabazadeh et al. (1999) based on simple consideration for monodisperse ice clouds. A likely reason lies in their assumptions of a monodisperse size distribution and a constant IWC (=25 mg/m³). These assumptions combined actually reverse the positive correlation of SAD with mean settling velocity implicit in the observed positive correlation of IWC with SAD (Heymsfield and McFarquhar, 1996) and of IWC with the mean settling velocity (e.g. Heymsfield, 2003). Meier and Hendricks (2002) have also calculated significant reductions in their box-model scenarios, though using higher initial HNO₃ mixing ratios than generally found in MATCH-MPIC.

The calculated IWC contents were evaluated by Lawrence and Crutzen (1998) and found to be in good agreement with observations of Heymsfield and McFarquhar (1996). However, in view of the large scatter in the observations,

a sensitivity simulation (LESSICE) has been performed in which the globally averaged ice water path has been reduced from 57 to 19 g/m² (LESSICE) as in Rasch and Kristjánsson (1998). In the LESSICE simulation the overall reduction of HNO₃ is smaller, resulting in a larger tropospheric mass of 44 Gg(N) compared to 35 in the LANGM case, but the reduction of zonal mean HNO₃ still reaches 60% or more compared to the NOUP run. Compared to the LANGM run HNO₃ levels are higher especially in the upper troposphere by about 20%–60% (Fig. 2, lower right panel). The strong relative effect seen in polar regions is from cold temperatures and small overall HNO₃ levels there.

To test the sensitivity to the chosen temperature dependence in our formulation of the uptake a simulation using $\Delta H_{ads}=-59$ kJ/mol from Tabazadeh et al. (1999) is performed (LANGM2). In the zonal means moderate changes can be found (e.g. from about −5% to +10% in tropical and subtropical regions, see Fig. 2, lower middle panel). As expected, in the cold uppermost tropical troposphere a decrease of HNO₃ is found in the LANGM2 simulation as the larger value of ΔH_{ads} leads to more efficient uptake at lower temperatures, but to less efficient uptake at higher temperatures. However, the integrated effects on HNO₃ are very small (Table 2). Comparison of in-situ observations (e.g. Popp et al., 2004) allow a larger range of K_{eq} and thus this test is not intended to cover the full range of uncertainty in the uptake. This larger range in the observations also indicates that a

large uncertainty lies in the formulation of the theoretical model actually appropriate to describe the uptake process and possibly points towards a significant role for dynamic growth effects (Kärcher and Basko, 2004; Ullerstam and Abbatt, 2005).

Another uncertainty lies in the vertical settling process. A new parameterization for the mean terminal fall velocity (V_s in cm/s) of ice crystals has been derived by Heymsfield (2003):

$$V_s = 165 \cdot \text{IWC}^{0.24} - 10, \tag{3}$$

where IWC is in g/m³. The expression applies to all latitudes. The last term is to account for a difference between the mass and (cross sectional) area weighted mean fall velocity which may be more appropriate here and is only applied for IWC>0.01 g/m³. The maximum value allowed was increased to 140 cm/s (Heymsfield, 2003, see their Fig. 11c) for this simulation (VHEYMS). This expression yields larger values for larger IWC compared to the expression used by Lawrence and Crutzen (1998) (e.g., +28 cm/s or +30% for an IWC of 0.4 g/cm³). However, a test simulation using this relation only results in a few percent change in zonal mean HNO₃ compared to the LANGM case. The biggest change is found in the uppermost tropical troposphere, where up to 8% less HNO₃ (stronger denitrification) is found in the VHEYMS simulation due to faster fall velocities. Below this region a small (<3%) increase in HNO₃ is calculated (not shown). This result also implies that the small difference between mass and (cross sectional) area weighted mean fall velocities is probably of minor importance in redistributing HNO₃. However, the larger effects found for the LESSICE simulation suggests that this may be because the LANGM case is already largely depleted in HNO₃. Therefore, despite the small difference found here, the expression above is recommended for future studies due to the larger underlying database.

As can be seen in Table 2, all three sensitivity simulations to the standard Langmuir model (LANGM) result in only small changes in globally integrated masses of HNO₃ and other key species.

3.2 Effects on other species

The maximum effects on NO$_y$ species other than HNO₃ are also noticable but smaller (Table 2). Zonal mean mixing ratios of NO$_x$ and PAN are decreased by up to 20% and 5%, respectively, in HIGHUP compared to the NOUP case (−15.6% and −4.3% in terms of integrated UT masses). As expected the effect maximizes above 300 hPa in the tropics. For the tropical pacific region Staudt et al. (2003) also performed a sensitivity simulation assuming 100% scavenging by ice clouds and compared their results to data from the PEM-Tropics A and B campaigns also included in our comparison. The effects of switching from inefficient to effective scavenging in their study is somewhat less pronounced for

HNO₃ and NO$_x$ than found here. Possibly this is related to the fact that gravitational settling of non-precipitating cloud particles was not included in that study. In the upper troposphere of the Pacific warm pool region the relative effects for HNO₃ are strongest, up to a factor of 10 reduction (see e.g. Fig. 6, PEM-West-A: Phillipine-Sea region). Thus, if an influence of HNO₃ on surface hydrometeor physics (as e.g. in Gao et al. (2004)) can be established, the overall degree of uptake into the condensed phases would be very important for these processes.

On the other hand, we calculate that two important aspects of atmospheric chemistry and climate interactions, namely ozone in the UT as a greenhouse gas and the oxidizing efficiency of the atmosphere, are only weakly perturbed by uptake of HNO₃ on ice. In particular, zonal mean ozone concentrations are reduced by less than 7% when efficient uptake (HIGHUP) is switched on (Fig. 3). The differences between the other scenarios are even smaller (e.g., −4% for the LANGM scenario). The tropospheric mean methane lifetime (as a measure of the oxidizing efficiency) changes only by 3% between the HIGHUP and NOUP scenarios, since the largest changes are in the UT where the reaction rate for methane oxidation is slower.

3.3 Discussion of uncertainties

There are several aspects of the model formulation and experimental uncertainties which could affect these estimates. We assume that equilibrium between gas and condensed phase is reached during each 30 min timestep. While this propably leads to some overstimation of the uptake, implementing a kinetic limitation would result in an underestimation because all HNO₃ is transferred back into the gas phase for the computation of advection.

To gauge the severity of this overestimate we have calculated the HNO₃ lifetime for typical particle size discribtions (PSD) based on parameterizations derived by Heymsfield (2003, see their Fig. 3). In the calculation, limitations due to the diffusion to the particle, as well as the interfacial transport, expressed by the uptake coefficient γ, are taken into account. A spherical geometry is assumed for the ice particles. For typical ice clouds (at 218 K and 150 hPa) with IWCs of 50 mg/m³ and 15 mg/m³, and a SAD of 1900 and 600 μm²/cm³, respectively, HNO₃ lifetimes of 7 and 19 minutes are calculated. The diffusion limitation contributes about one third to these lifetimes. If γ=0.01 is assumed, the lifetimes for these cases increase to 20 min and about 1 h, respectively. Assuming γ=0.001 yields about 2 and 6 h, respectively.

There is considerable disagreement concerning the initial uptake coefficient of HNO₃ on ice surfaces. Uptake is generally found efficient ($\gamma \geq 0.1$) for temperatures below about 200 K, but for higher temperatures several authors report values between 0.001 and 0.01, in disagreement to Ullerstam et al. (2005) who recently reported $\gamma \geq 0.1$ for temperatures
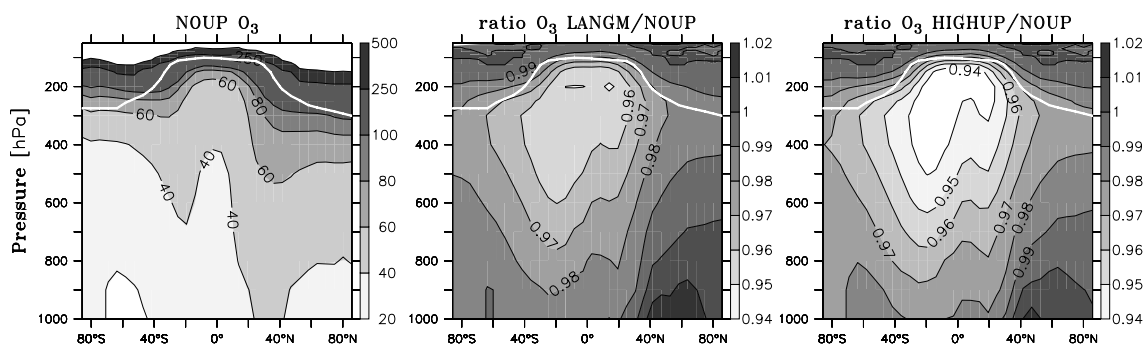
Fig. 3. Annual zonal mean O$_3$ from the NOUP run and ratios of the LANGM and HIGHUP simulation to the run without uptake on ice. The white line indicates the model tropopause.

as high as 239 K. The calculations above show that for $\gamma > 0.01$ the equilibrium approach leads only to significant overstimated uptake of HNO$_3$ for thin ice clouds which, however, do not lead to strong vertical redistribution through settling. If most ice clouds typically persist for several hours the overestimate in our approach should be small. This, however, assumes that the individual ice particle lifetime and the cirrus lifetime are comparable, which may not be the case (Barth et al., 2003). If, however, $\gamma \approx 0.001$, the equilibrium approach would lead to significantly overestimated effects of ice clouds on HNO$_3$ even for clouds with high SAD. Further studies to improve the experimental determination of this parameter are therefore necessary.

Another aspect to keep in mind is that ice particle mass is not only created via diffusional growth of small initial particles, but also through contact freezing of supercooled liquid droplets (riming), mainly in the upper part of convective clouds. Experimental and theoretical studies by Iribarne and Pyshnov (1990) and Stuart and Jacobson (2003) have suggested that most HNO$_3$ is probably retained during the freezing process. Neglecting to differentiate these pathways should therefore tend to underestimate the overall uptake of HNO$_3$ on ice particles. However, a global quantification of the relative importance of these ice formation pathways has not been attempted yet, and the effects on HNO$_3$ can therefore not be quantified easily.

The adsorption of HNO$_3$, as well as other gases, in the atmosphere takes place in a dynamic environment. The effect of burial of trace gases during growth of the ice crystals was theoretically described by Kärcher and Basko (2004). They calculate that trapping of HNO$_3$ could take place even at low ice supersaturations. Recently, Ullerstam and Abbatt (2005) found significantly enhanced uptake of HNO$_3$ in laboratory experiments under ice growth conditions compared to ice surfaces at equilibrium (i.e. 100% relative humidity). However, Ullerstam and Abbatt (2005) state that in light of discrepancies between their findings and the current model formulation by Kärcher and Basko (2004) and also because fundamental parameters are not well constrained, the knowl-

edge of this process is still incomplete. Furthermore, including such dynamic growth effects in a 3-D modelling framework is not straightforward, as unknown assumptions about different formation conditions of ice particles and the associated fluctuations in temperature and water vapour would have to be made. Therefore, these effects should be further studied in box models before a global extrapolation is attempted. However, neglecting this enhanced uptake in our simulations may lead to an underestimated trace gas uptake in our simulations.

Uncertainties also exist in the simulated ice amounts and in the calculated surface areas. As noted in Sect. 2, Popp et al. (2004) during the CRYSTAL-FACE campaign have found up to a factor of 10 higher SADs for a given IWC than calculated by Eq. (2). It is unclear if this difference reflects the large natural variability or if experimental issues or additional assumptions are different. A part of the difference may be explained by a larger ratio between cross sectional and surface area of the particles used by Lawrence and Crutzen (1998). For small ice crystals, which dominate the surface area, a spherical shape is a good approximation (see e.g. Heymsfield et al., 2002). The ratio of surface to cross-section for spheres is only a factor of 2 larger than the one used by Lawrence and Crutzen (1998) (4 versus 2). Therefore, this can likely only explain part of the difference. We have recalculated the SAD-to-IWC relation assuming a spherical shape by integrating over typical PSDs from Heymsfield (2003) and could reproduce within a factor of 2 the relationship in Eq. (2) used here. Although we cannot resolve this issue at present, it demonstrates the need for more data on ice cloud PSDs.

The range of effects tested in this study – from no uptake to quasi-Henry's Law bulk uptake (NOUP, HIGHUP) – should, nevertheless, bracket these uncertainties, with the exception of uncertainties in global SADs,

3.4 Comparison to observations

In search of observational evidence concering the interaction of HNO$_3$ and ice clouds, the model results have been
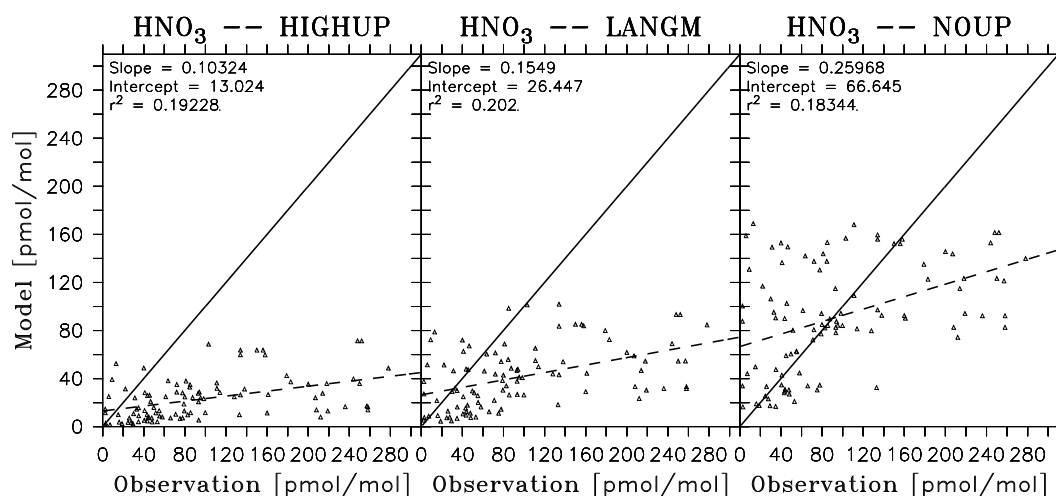
Fig. 4. Scatter plot of simulated monthly means versus regionally merged campaign profiles from Emmons et al. (2000) using all data above 8 km altitude for the HIGHUP, LANGM and NOUP runs. The dashed line is the linear regression line through the data.

compared to a large suite of campaign data taken mainly from Emmons et al. (2000), but also including more recent campaigns (TRACE-P, TOPSE, PEM-Tropics B). Monthly mean model data are compared to regionally merged profile data collected in different years. Comparison of large scale model data with point measurements have some inherent problems which need to be acknowledged. This is especially the case for HNO₃, for which a major loss process (wet deposition) is expected to be strongly heterogeneously distributed on the sub-grid scale. Therefore, we focus on main features that appear in the comparison and not on individual campaign results, and particularly on a statistical analysis.

51 regional profiles with 1 km vertical resolution merged from campaign data (Emmons et al., 2000) have been compared to the monthly mean modeled profiles in the same regions. Figure 4 shows scatter plots of the mean modeled values for each height interval above 8 km in each case versus the observed values. Only data above 8 km, where the largest effect would be expected, are plotted. Examples of individual profiles are discussed below and the full set of profile plots is provided in the supplement (http://www.atmos-chem-phys. org/acp/6/225/acp-6-225-sp.pdf). A general underestimate of modelled HNO₃ is found in the scenario with efficient uptake, consistent with von Kuhlmann et al. (2003b). If uptake on ice is switched off a large number of cases where the model strongly overestimates the observations is seen, yet some high mixing ratios are still underestimated. It can also be seen that the simulation applying Langmuir uptake is already very effectively reducing HNO₃. The same scatter plot is shown for the mid-troposphere (4–8 km) in Fig. 5. Again, a tendency of the model to underestimate large measured values can be seen. In the mid-troposphere the simulation without any uptake of HNO₃ appears to produce the smallest bias compared to observations. However, this is likely

due to compensating effects. As found in von Kuhlmann et al. (2003b), MATCH-MPIC generally tends to underestimate HNO₃ in the lower and mid-troposphere. Since this region is not expected to be strongly influenced by ice cloud, this is likely due to reasons not related to the treatement of ice-uptake. Scavenging by liquid cloud particles, unknown chemistry or underestimated sources are possible explanations.

As mentioned above, not too much weight should be given to each individual campaign comparison, due to the methodology of our comparison (using monthly means of one particular year). On the other hand, in comparisons with single or few measurement campaigns using the actual meteorological situation, correct (sub-grid) spatial sampling is still an issue and the results are more prone to errors in the representation of the meteorology during the campaign. Ideally, a statistical analysis of many campaigns using the spatially and temporaly interpolated model values should be performed (Brunner et al., 2003). However, performing several (multi-year) sensitivity simulations with this setup goes beyond the scope of this study. Nevertheless, inspecting the full ensemble of 51 regional comparisons (see the supporting online material: http://www.atmos-chem-phys.org/acp/6/225/acp-6-225-sp.pdf) can bring some insight.

The fact that in many cases, especially in remote regions with aged airmasses, there often is a general underestimation by the model, suggests that this might be due to other factors not related to ice affecting HNO₃ in the mid and lower troposphere, likely (liquid) precipitation scavenging (Velders and Granier, 2001). The formulation of wet scavenging used here is based on Henry's Law equilibrium which is assumed to be reached each time-step. This neglect of kinetic limitations in the gas uptake could lead to a general overestimation of scavenging of highly soluble gases.
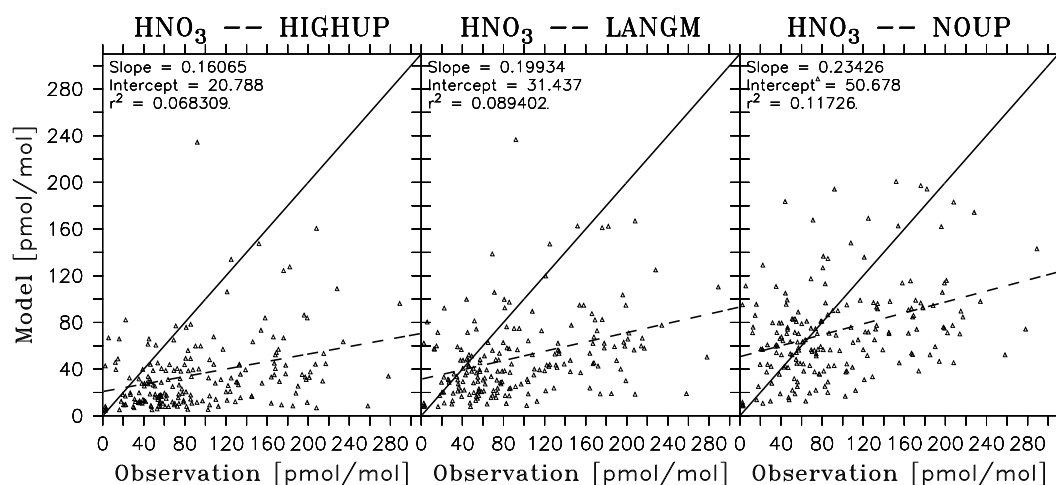
Fig. 5. Same as Fig. 4, but for the measurement and model in the height interval 4–8 km.

The general picture of the regional comparison is illustrated by a few example profile comparisons in Fig. 6. Often, when the model underestimates HNO$_3$ throughout the troposphere, not allowing for uptake on ice improves the comparison in the UT (left panel), while in many cases HNO$_3$ is not underestimated significantly, and in these cases the NOUP scenario often overestimates observations in the UT (right panel). Generally these individual profiles also show that a straightforward interpretation is not possible due to large scatter in the data and without analyzing the model representation of the meteorology for each campaign. An intermediate scenario, like the Langmuir uptake run (LANGM), would be expected to compare best. However, this is not apparant from the calculated statistics of the comparison (e.g., r^2=0.20 for LANGM).

It is noted that a tendency to underestimate high values is typical of this kind of comparison since a 3-D model is more averaged, both spatially and temporally, than the campaign data (von Kuhlmann et al., 2003b) and often campaign flights are targetting pollution plumes. Also, it cannot be ruled out that other factors such as gas/aerosol partitioning (Liao et al., 2003) have a strong influence on gas phase nitric acid concentrations. Thus, although there are many clear overestimates in the NOUP case none of the Langmuir uptake scenarios can be judged best based on this comparison. More measurements, in particular in the tropical UT, would be valuable to reach firmer conclusions.

3.5 Effects of non-methane hydrocarbons

How strongly are the results shown so far influenced by the inclusion of NMHCs, not present in Lawrence and Crutzen (1998)? To answer this the two extreme cases (without and including efficient uptake) have been repeated without NMHC chemistry (CH4NOUP and CH4HIGH). These are representative of the BASE and STDFALL runs in Lawrence

and Crutzen (1998). In Table 2 it can be seen that the relative effect of the uptake is stronger in the simulations without NMHCs. This is mainly due to the additional important NO$_y$ reservoir species peroxy acetylnitrate (PAN) which results from NMHC oxidation and reduces the availability of HNO$_3$ in the UT (compare HNO$_3$/NO$_x$ ratios in NOUP and CH4NOUP), and thus its additional loss through vertical redistribution. The supply of NO$_x$ through long-range transport of PAN and its thermal decomposition provides an alternative pathway to NO$_x$ and subsequently HNO$_3$ in the remote troposphere. This more direct link from a decrease in HNO$_3$ to a decrease in NO$_x$ causes the 25%-reduction of NO$_x$ in CH4HIGH simulation compared to its baseline, whereas in the HIGHUP run the reduction is only 16%. Therefore, also the effects on ozone are more pronounced in the CH4 runs (7.6% change in the global tropospheric burden). Thus, the effects of a more realistic Langmuir uptake scenario in this study should be less pronounced than if it were tested using the model-setup of Lawrence and Crutzen (1998).

4   Conclusions

We have assessed the potential impact of the uptake of HNO$_3$ on ice particles on the tropospheric concentrations of NO$_y$ species, ozone and OH using the global model MATCH-MPIC. Using a dissociative Langmuir equilibrium model for the uptake and through sensitivity simulations the following main points are brought out:

– Dissociative Langmuir theory for the uptake process results in a significant reduction of HNO$_3$ in the upper troposphere, in contrast with Tabazadeh et al. (1999) but in basic agreement with Meier and Hendricks (2002).

– Neglecting the uptake results in a large number of striking overestimates of HNO$_3$ compared to observations
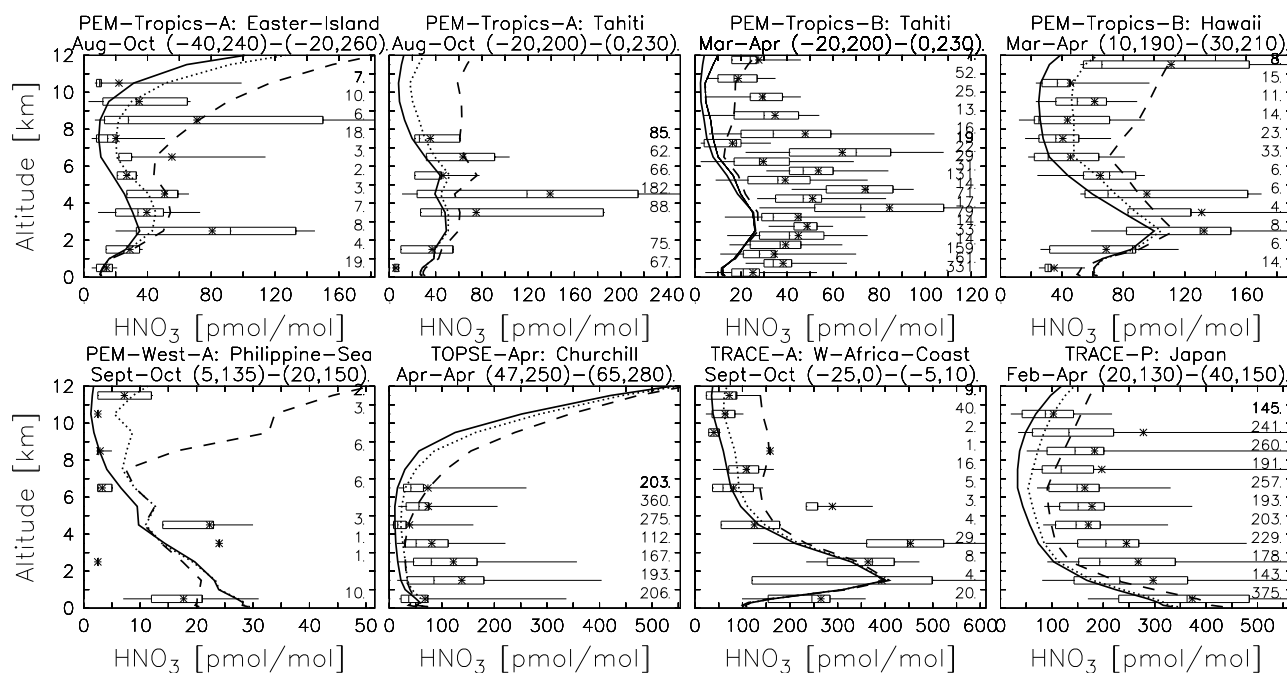
Fig. 6. Comparison of regional vertical profiles of HNO₃ to model output. Solid, dotted and dashed lines are for the HIGHUP, LANGM, and NOUP simulations, respectively. Boxes, whiskers, horizontal line and asterix mark the central 50 and 90%, median and mean of the observations, respectively. The number of observations at each altitude interval is given to the right. In region "Tahiti" (PEM-Tropics B) measurements from two platforms (DC8 and P3) are shown in the upper and lower parts of the 1 km intervals.

despite a general tendency of the model to underestimate HNO₃.

– However, due to large scatter and other uncertain factors in the comparison, no best uptake rate can be deduced based on this comparison.

– More measurements of ice water content and surface area densities are needed to better constrain the model fields.

– Clarification of the value of the initial uptake coefficient at temperatures above 200 K is necessary as it could make uptake of HNO₃ inefficient for short-lived ice clouds or if individual particle lifetimes are less than about a few hours.

– NMHC chemistry buffers the effect on HNO₃ and on other gases, by providing PAN as an alternative NOᵧ reservoir species.

– While local effects on HNO₃ can be strong, they only translate into moderate to small overall effects on global tropospheric O₃ and the oxidation efficiency of the troposphere. However, the effects of HNO₃ taken up by hydrometeors or aerosols on surface physics may be much more important.

While inclusion of a best guess of the uptake effects based on current knowledge is nevertheless recommended for inclusion in atmospheric chemistry models, the effect of remaining uncertainties on ozone and the oxidation efficiency are probably small compared to other issues.

An untested chemical issue remains the possibility of reactions on the ice surface, such as the photolysis of the nitrate radical (e.g. Honrath et al., 1999, 2000; Zhou et al., 2003). Although a recent study by Chu and Anastasio (2003) have judged the latter process to be of minor importance, further evidence is needed. Moreover, these points suggest that a stronger emphasis should be placed on investigations of the impact of HNO₃ on surface hydrometeor physics (e.g. Gao et al., 2004), which could have a significant influence on cirrus formation, lifetime and albedo, and thus on the radiative effects of cirrus clouds.

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