A climatological view of HNO₃ partitioning in cirrus clouds

M. Krämer,a* C. Schiller,a C. Voigt,b H. Schlagerb and P. J. Popp,c,d

a Institut für Chemie und Dynamik der Geosphäre, Forschungszentrum Jülich, Germany
b Institut für Physik der Atmosphäre, DLR Oberpfaffenhofen, Germany
c NOAA Earth System Research Laboratory, Boulder, Colorado, USA
d Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, USA

ABSTRACT: A new in situ climatology of cirrus ice water content (IWC) is used, together with observed molar ratios of HNO₃/H₂O in cirrus ice particles, to estimate the range of HNO₃ content in cirrus ice in the temperature interval 185 – 240 K. We find that nearly over the complete temperature range HNO₃ percentages in ice between 0.01 and 100% are possible in cirrus clouds and that IWC is a major parameter determining the content of HNO₃ in ice at given temperatures. Considering average conditions, the HNO₃ content increases with decreasing temperature from 1% to about 10% in the range 240 – 200 K. For colder ice clouds, the average HNO₃ content again decreases down to 6%. At higher temperatures, less efficient HNO₃ uptake limits the HNO₃ content in cirrus ice, while at low temperatures small IWCs permit only little HNO₃ in ice, thus causing the convex-shaped average HNO₃ content curve. The highest HNO₃ content is expected in tropical ice clouds with very large IWCs, especially at temperatures between 190 and 210 K. Thus, tropical cirrus clouds show the highest potential to vertically redistribute HNO₃.

Copyright © 2008 Royal Meteorological Society

1. Introduction

Vertical redistribution of nitric acid (HNO₃) by sedimenting cirrus ice crystals is discussed as a possible mechanism for lowering upper tropospheric ozone. A reduction of the greenhouse gas ozone would give negative feedback to climate. The temperature in the tropopause region is very sensitive to changes in ozone mixing ratio. For example, Forster and Joshi (2005) estimate, based on a narrowband fixed dynamical heating model, that the annual average temperature change at the tropical coldpoint tropopause for a 10% increase in ozone is 0.6 K. Forster and Joshi (2005) estimate, based on a narrowband fixed dynamical heating model, that the annual average temperature change at the tropical coldpoint tropopause for a 10% increase in ozone is 0.6 K. Meier and Hendricks (2002) report a maximum ozone reduction of about 14%, while recently von Kuhlmann and Lawrence (2006) estimated a lower maximum value of 5% by using a global-scale chemistry-transport model. However, the authors state that the largest uncertainty of this result is likely to be linked to the actual theory describing the HNO₃ uptake process on ice.

Dissociative Langmuir isotherms determining HNO₃ as equilibrium ice surface coverages have often been employed in models (e.g. by von Kuhlmann and Lawrence, 2006), but, as shown by Popp et al. (2004), could not satisfactorily fit atmospheric measurements. Kärcher (2005) and Krämer et al. (2006) show that adsorption of HNO₃ on the ice surfaces is not the only pathway for HNO₃ in ice, but that a substantial amount of HNO₃ may enter the ice via freezing of liquid ternary aerosol particles. Further, Kärcher (2005) demonstrates that another important pathway of HNO₃ in cirrus is trapping of HNO₃ by growing ice crystals.

Here, we derive parametrizations of the HNO₃ content in ice for use in global models from field measurements by using a new approach to describe the HNO₃ content of cirrus clouds for most atmospheric conditions. The first step is to compile a large database of HNO₃ content in cirrus for a broad range of atmospheric conditions. In the last decade, several field campaigns were performed where the amount of HNO₃ in cirrus ice (HNO₃,ice) - amongst other parameters - was measured in different geographical regions (Table I).

Voigt et al. (2006) summarised average values of most HNO₃,ice measurements and expressed them in terms of molar ratios, M_HNO₃, by dividing HNO₃,ice by the ice water content (IWC):

\[ M_{\text{HNO}_3} = \frac{\text{HNO}_3,\text{ice}}{\text{IWC}}. \]  

An increase of M_HNO₃, with decreasing temperature in the range 225 – 198 K and an increase of M_HNO₃, with increasing total HNO₃ (HNO₃,total = gas phase + parti – culate HNO₃) is found by Voigt et al. (2006).

Kärcher and Voigt (2006) expressed the same dataset as a fraction of HNO₃,ice in ice

\[ F_{\text{HNO}_3} = 100 \cdot \frac{\text{HNO}_3,\text{ice}}{\text{HNO}_3,\text{total}}. \]  

*Correspondence to: M. Krämer, ICG-1, FZ Jülich, Germany. E-mail: m.kraemer@fz-juelich.de

Copyright © 2008 Royal Meteorological Society
and proposed an increasing $F_{\text{HNO}_3}^\text{ice}$, with decreasing temperature for 240–195 K. Combining Equations (1) and 2 yields

$$F_{\text{HNO}_3}^\text{ice} = M_{\text{HNO}_3}^\text{ice} \cdot \frac{\text{IWC}}{\text{HNO}_3^\text{total}}. \quad (3)$$

We here develop a climatology of average $F_{\text{HNO}_3}^\text{ice}$ as well as the total range of HNO$_3$ content in cirrus ice in the temperature range 185–240 K. For that purpose, firstly the new in situ IWC climatology (Schiller et al., 2008), derived from ten field campaigns and covering the temperature range 182–250 K, is used (see section 2.1). Secondly, a new climatology for $M_{\text{HNO}_3}^\text{ice}$, is derived from the database of Voigt et al. (2006), extended by new observations down to temperatures of 185 K (section 2.2). The range of total available nitric acid HNO$_3^\text{total}$ is estimated based on observations, and the resulting $F_{\text{HNO}_3}^\text{ice}$ climatology is presented in section 3.1.

Based on the newly derived climatological average of molar ratios $M_{\text{HNO}_3}^\text{ice}$, the average content of HNO$_3$ in ice is presented for Arctic, midlatitude and tropical cirrus clouds in section 3.2. In section 3.3, the average vertical distribution of $F_{\text{HNO}_3}^\text{ice}$ is shown.

2. IWC and $M_{\text{HNO}_3}^\text{ice}$ climatologies

2.1. IWC of cirrus clouds

The IWC of cirrus clouds was observed during ten field experiments using the Lyman-α fluorescence Fast In situ Stratospheric Hygrometer (FISH; Schiller et al., 2008) with a forward-facing inlet sampling total water (= gas phase + particulate water). IWC was determined as the difference between total water and water vapour saturation with respect to ice. From the comprehensive dataset representing 27 hours flight time inside 52 Arctic, midlatitude and tropical cirrus clouds, Schiller et al. (2008) derived a new in situ climatology of IWC for the temperature range 182–250 K (Figure 1). The climatology encompasses the range of observed IWC by means of temperature-dependent functions (given in Table II) for the maximum (green), mean (red, without convective events) and minimum (orange) IWC. Schiller et al. (2008) also provide functions for mean IWC including convective events as well as median IWC. Here, the mean IWC is used because the properties derived from IWC depend on the ice volume (Equation (3)). The functions are derived as fits through values in 1 K temperature bins. Schiller et al. (2008) provide a detailed description of IWC observations, and the derivation of the climatology and uncertainties. However, it should be noted that the uncertainty of individual data points is 11–23% for the low IWC for 195–182 K and 8-11% for 250–195 K; hereby, a potential systematic error can be estimated by the accuracy of the FISH calibration of 6% (details in Schiller et al., 2008). These uncertainties are small compared to the wide range of IWC observed for a particular temperature bin.

From Figure 1 it can be seen that the IWC decreases with decreasing temperature while covering several orders of magnitude for each temperature. The dataset underlying the climatology includes cirrus clouds at various stages of development – from just formed very thin cirrus via fully developed to almost dissipated cirrus. The strong variation of IWC at certain temperatures is caused by varying cooling of raising air parcels that form ice clouds. The stronger the cooling of a vertically moving air parcel, the higher is the IWC of the developing cirrus ice cloud. This is caused by the increasing difference in ice saturation at the temperature of the initial air parcel and the temperature after cooling. Consequently, the decrease of the IWC band with decreasing temperature reflects the exponential decrease of the ice saturation value.

Also plotted in Figure 1 are mean IWC observed during selected field campaigns (i.e. POLSTAR, TROCCINOX, SCOUT-O$_3$ and CR-AVE). These data points will be discussed individually in section 3.1.

2.2. Molar ratio $M_{\text{HNO}_3}^\text{ice}$ in cirrus ice

HNO$_3$ in cirrus ice was measured in a series of field experiments by means of forward- and aft-facing inlets of total reactive nitrogen (NO$_y$) instruments, or mass spectrometers that measure HNO$_3$ specifically. For this

<table>
<thead>
<tr>
<th>Table I. Projects measuring HNO$_3$ in cirrus ice.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SUCCESS 1996</td>
</tr>
<tr>
<td>POLSTAR 1998</td>
</tr>
<tr>
<td>INCA 2000</td>
</tr>
<tr>
<td>SOLVE–TRESEO 2000</td>
</tr>
<tr>
<td>CRYSTAL–FACE 2002</td>
</tr>
<tr>
<td>TROCCINOX 2003</td>
</tr>
<tr>
<td>SCOUT–O$_3$ 2005</td>
</tr>
<tr>
<td>CR–AVE 2005</td>
</tr>
</tbody>
</table>

Copyright © 2008 Royal Meteorological Society

DOI: 10.1002/qj
work, we assume that condensed-phase reactive nitrogen measured by the NO$_3$ instruments is HNO$_3$. The publications listed in Table I provide a description of the measurements and techniques. An intercomparison of the different methods measuring HNO$_3$ in ice is not yet available. Therefore, the uncertainty of $M_{HNO_3}^{ice}$ is here estimated to be 20%, a range that covers possible differences between the methods.

Average values of the molar ratios $M_{HNO_3}^{ice}$ are shown in Figure 2 for all experiments. (For better differentiation, the term ‘average’ is used in combination with HNO$_3$, while ‘mean’ is used for H$_2$O quantities, though both denote the arithmetic mean value.) Most of the data points are taken from Voigt et al. (2006), reporting observations in the temperature range 195–240 K. Three new observations are added here, all representing averages of one cirrus penetration: one measurement is an extreme case of a very thin ice cloud, possibly in its formation stage (TROCCINOX 2005; Voigt et al., 2007) and two measurements are at very low temperatures (CR-AVE 2005 and SCOUT-O3 2005). The latter measurements are especially important as they allow extension of the temperature range to less than 195 K, which is of particular importance for tropical cirrus.

$M_{HNO_3}^{ice}$ generally increases with decreasing temperature, i.e. the concentration of HNO$_3$ in ice is higher at lower temperatures. Kärcher and Voigt (2006) attribute this behaviour to less efficient HNO$_3$ trapping at higher temperatures despite faster ice growth rates, caused by increasingly rapid escape of adsorbed HNO$_3$ into the gas phase. The broad range of $M_{HNO_3}^{ice}$ at a certain temperature is caused by a varying amount of HNO$_3^{total}$ and IWC, whereas increasing HNO$_3^{total}$ or decreasing IWC raises $M_{HNO_3}^{ice}$. As described for the IWC, the variation of $M_{HNO_3}^{ice}$ at a certain temperature also reflects different stages in the lifetime of cirrus, and the varying stages of the uptake process at which equilibrium of HNO$_3$ with the ice surfaces is reached.

We here derive temperature-dependent functions for minimum, average and maximum $M_{HNO_3}^{ice}$ (Figure 2; Table II). The average function for $M_{HNO_3}^{ice}$ is similar to that presented by Kärcher and Voigt (2006) by applying a trapping model for HNO$_3$ uptake into ice crystals (not shown here).

### 3. Partitioning of HNO$_3$ in cirrus clouds

#### 3.1. Overall HNO$_3$ partitioning

We transform Equation (1) for HNO$_3^{ice}$

$$\text{HNO}_3^{ice} = M_{HNO_3}^{ice} \cdot \text{IWC}$$

(4)

and insert the climatology of IWC (Figure 1) and $M_{HNO_3}^{ice}$ (Figure 2). The resulting potential range of the amount of HNO$_3$ taken up in cirrus clouds is displayed in Figure 3. The average curve (solid red) represents Equation (4) for the average $M_{HNO_3}^{ice}$ (solid line in Figure 2) and the mean IWC (red line in Figure 1). The maximum (dashed green) and minimum (dotted orange) amounts of HNO$_3$ in ice are derived similarly.

On average, the potential of cirrus ice to take up HNO$_3$ is about 1–10 pptv over the whole temperature range, but the total span ranges from 0.005 pptv at low IWC or molar ratios $M_{HNO_3}^{ice}$ up to about 35 ppbv in a situation where both IWC and $M_{HNO_3}^{ice}$ are high.

The fractions of HNO$_3^{total}$ taken up in cirrus ice ($F_{HNO_3}^{ice}$) are derived from the IWC and $M_{HNO_3}^{ice}$ functions under the assumption of minimum/average/maximum values of HNO$_3^{total}$ = 0.02/0.1/0.8 ppbv by means of Equation (3) and are plotted in Figure 4. (The average of 0.1 ppbv corresponds to $2 \times 10^{-3}$ hPa at 200 hPa given by Kärcher and Voigt (2006) as average over many field campaigns. The minimum/maximum values are chosen to describe a large range of atmospheric conditions. Smaller/larger HNO$_3^{total}$ values are possible in specific situations, but would not affect the result discussed here.) At a given temperature nearly every value of $F_{HNO_3}^{ice}$, between about 0.01 and 100% is possible in cirrus clouds over almost the total temperature range.

Table II. Temperature-dependent functions for ice water content, IWC, and molar ratio of HNO$_3$/H$_2$O, $M_{HNO_3}^{ice}$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Temperature (K)</th>
<th>Function exponent, $E$</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>($a_0 \cdot a_1^E + a_2$)</td>
<td>$a_0$</td>
</tr>
<tr>
<td>IWC$_{min}$</td>
<td>(ppmv)</td>
<td>185–240</td>
<td>($a_0 \cdot a_1^E + a_2$)</td>
<td>$-29.0184$</td>
</tr>
<tr>
<td>IWC$_{mean}$</td>
<td>(ppmv)</td>
<td>185–240</td>
<td>($a_0 \cdot a_1^E + a_2$)</td>
<td>$-1190.68$</td>
</tr>
<tr>
<td>IWC$_{max}$</td>
<td>(ppmv)</td>
<td>185–240</td>
<td>($a_0 \cdot a_1^E + a_2$)</td>
<td>$-4.72212 \times 10^{18}$</td>
</tr>
<tr>
<td>IWC$_{mean}$</td>
<td>(ppmv)</td>
<td>197–240</td>
<td>($a_0 \cdot a_1^E + a_2$)</td>
<td>$-8025.80$</td>
</tr>
<tr>
<td>IWC$_{mean,mid}$</td>
<td>(ppmv)</td>
<td>203–240</td>
<td>($a_0 + a_1^E$)</td>
<td>$-2.48507$</td>
</tr>
<tr>
<td>IWC$_{mean,tropics}$</td>
<td>(ppmv)</td>
<td>185–240</td>
<td>($a_0 \cdot a_1^E + a_2$)</td>
<td>$-21161.4$</td>
</tr>
<tr>
<td>$M_{HNO_3}^{ice}_{min}$</td>
<td>–</td>
<td>185–240</td>
<td>$[-(a_0 \cdot a_1^E + a_2) - 1.1]$</td>
<td>$-26.4641$</td>
</tr>
<tr>
<td>$M_{HNO_3}^{ice}_{avg}$</td>
<td>–</td>
<td>185–240</td>
<td>$[-(a_0 \cdot a_1^E + a_2)]$</td>
<td>$-26.4641$</td>
</tr>
<tr>
<td>$M_{HNO_3}^{ice}_{max}$</td>
<td>–</td>
<td>185–240</td>
<td>$[-(a_0 \cdot a_1^E + a_2) + 1.3]$</td>
<td>$-26.4641$</td>
</tr>
</tbody>
</table>

IWC from Schiller et al., 2008; Functions are $10^E$; noconvect = convective events are excluded from the climatology.
Figure 1. In situ climatology of maximum, mean (without convective events) and minimum ice water content (Schiller et al., 2008). Diamonds denote mean field observations; for colour code see Figure 2. This figure is available in colour online at www.interscience.wiley.com/qj.

Figure 2. Molar ratio ($\lambda_{\text{HNO}_3}^{\text{HNO}_3}$) of $\text{HNO}_3$ to IWC in cirrus ice. Lines show maximum, average, and minimum molar ratios, diamonds are average field observations, and data points except SCOUT-O3 and CR-AVE are adapted from Voigt et al. (2006, 2007). This figure is available in colour online at www.interscience.wiley.com/qj.

Figure 3. Maximum, average and minimum potential of $\text{HNO}_3$ uptake in cirrus ice. $\text{HNO}_3$ is derived from Equation (1). This figure is available in colour online at www.interscience.wiley.com/qj.
Figure 4. Fraction of HNO$_{3\text{tot}}$ in cirrus ice ($F_{\text{HNO}_3}^{\text{ice}}$), derived from Equation (3); minimum (dotted), average (solid) and maximum (dashed) for IWC minimum (orange), mean (red) and maximum (green). The respective HNO$_{3\text{tot}}$ are indicated in the legend. Diamonds are field observations; data points except TROCCINOX, SCOUT-O3 and CR-AVE 2005 are from Kärcher and Voigt (2006). For colour code see Figure 2. This figure is available in colour online at www.interscience.wiley.com/qj

Figure 4 illuminates the mechanisms leading to this wide spread of $F_{\text{HNO}_3}^{\text{ice}}$. The solid red line represents the average $F_{\text{HNO}_3}^{\text{ice}}$ in cirrus ice (derived from mean IWC, average $M_{\text{HNO}_3}^{\text{ice}}$ and average HNO$_{3\text{tot}}$). $F_{\text{HNO}_3}^{\text{ice}}$ shows a slight convex form, increasing from about 1% to 10% when the temperature decreases from 240 K to about 200 K. For temperatures lower than 200 K, $F_{\text{HNO}_3}^{\text{ice}}$ drops again to 6% at 185 K. The dotted (dashed) red curves encompassing the average $F_{\text{HNO}_3}^{\text{ice}}$ represent mean IWC by using minimum (maximum) $M_{\text{HNO}_3}^{\text{ice}}$, and minimum (maximum) HNO$_{3\text{tot}}$. Note here that the $F_{\text{HNO}_3}^{\text{ice}}$ curves vary by only $\pm 0.05$–5% when assuming the IWC and $M_{\text{HNO}_3}^{\text{ice}}$ uncertainties shown in sections 2.1 and 2.2. An important result is that the large scatter in $M_{\text{HNO}_3}^{\text{ice}}$ (Figure 2) and HNO$_{3\text{tot}}$ causes a variation of only several percent in $F_{\text{HNO}_3}^{\text{ice}}$.

The largest scatter in $F_{\text{HNO}_3}^{\text{ice}}$ is caused by IWC. The orange curves represent the low range of 0.03 to 1% $F_{\text{HNO}_3}^{\text{ice}}$ of thin cirrus clouds while the green curves represent cirrus clouds with a very high ice water mass; due to the high IWC, these clouds have the highest potential to efficiently scavenge the available HNO$_3$. For temperatures larger than 220 K, the maximum IWC is nearly constant (Figure 1), but $M_{\text{HNO}_3}^{\text{ice}}$ is so small (Figure 2) that the HNO$_3$ could not be completely scavenged by the ice. Nevertheless, even here 4–100% HNO$_3$ could be taken up by cirrus. At 220–200 K, the steadily high maximum IWC, in combination with increasing $M_{\text{HNO}_3}^{\text{ice}}$, results in a complete uptake of HNO$_3$ in cirrus ice at maximum IWC. In the range 200–185 K, the maximum IWC decreases but, combined with the continuously increasing $M_{\text{HNO}_3}^{\text{ice}}$, all available HNO$_3$ could still be scavenged by the ice. Below 185 K, the maximum IWC becomes so small that $F_{\text{HNO}_3}^{\text{ice}}$ drops again despite the increasing $M_{\text{HNO}_3}^{\text{ice}}$.

Obviously, IWC is the parameter mainly determining the content of HNO$_3$ in cirrus clouds at given temperatures. Thin cirrus clouds are not able to efficiently scavenge HNO$_3$, while thick cirrus can contain all available HNO$_3$. However, at higher temperatures the low $M_{\text{HNO}_3}^{\text{ice}}$ molar ratio (caused by less efficient HNO$_3$ trapping; Kärcher and Voigt, 2006), and at low temperatures the low IWC, limits HNO$_3$ uptake in cirrus ice, thus causing the convex-shaped broad range describing the fraction of HNO$_3$ in cirrus ice clouds.

Also plotted in Figure 4 are observed average percentages of HNO$_{3\text{tot}}$ in ice, $F_{\text{HNO}_3}^{\text{ice}}$, from the field campaigns shown in Figure 2. (The data points represent different kinds of averages: INCA, SOLVE-THESEO, CRYSTAL FACE, EUPLEX have averages over temperature intervals, whereas SUCCESS, POLSTAR, TROCCINOX, SCOUT-O3, CR-AVE have averages over single events; data points, except TROCCINOX, SCOUT-O3 and CR-AVE 2005, are taken from Kärcher and Voigt, 2006.) Most of the data points group well around the presented average range of $F_{\text{HNO}_3}^{\text{ice}}$. A closer look at some of the data lying outside (CR-AVE 2005, TROCCINOX 2005) shows that the high $F_{\text{HNO}_3}^{\text{ice}}$ of CR-AVE 2005 could be caused by an IWC higher than the mean value (Figure 1). The low $F_{\text{HNO}_3}^{\text{ice}}$ of TROCCINOX 2005 stems from the very low corresponding IWC. Data points showing typical IWCs and $M_{\text{HNO}_3}^{\text{ice}}$ like POLSTAR 1998 and SCOUT-O3 2005, are very close to the average $F_{\text{HNO}_3}^{\text{ice}}$ curve.

Kärcher and Voigt (2006) derived the dependence on temperature of the average fraction of HNO$_3$ ($F_{\text{HNO}_3,\text{avg}}^{\text{ice}}$) by applying a trapping model for HNO$_3$ uptake into ice crystals. Figure 5(b) shows a comparison of the modelled and our climatologically derived curve. Very good agreement between the model result and the climatology is seen in the temperature range 210–240 K. However, at lower temperatures, the simulated $F_{\text{HNO}_3,\text{avg}}^{\text{ice}}$ steadily increases with decreasing temperature, while $F_{\text{HNO}_3,\text{avg}}^{\text{ice}}$ from the climatology reported here shows the slight convex form discussed above.

This difference can be traced back to the climatology of IWC. The IWC used by Kärcher and Voigt (2006) is provided by Wang and Sassen (2002) from remote-sensing
observations in midlatitude clouds in the temperature range 203–240 K and extrapolated down to 195 K by Kärcher and Voigt (2006) (Figure 5(a), dotted line). Compared to the IWC used here (Figure 5(a), solid line), the Wang and Sassen (2002) IWC is very similar for temperatures higher than about 210 K, but for lower temperatures (i.e. the extrapolated range) the IWC of the new in situ climatology (Schiller et al., 2008) strongly decreases. A higher IWC leads to the higher HNO₃ fractions in ice with decreasing temperature reported by Kärcher and Voigt (2006), compared with the convex-shaped $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$ curve presented here.

### 3.2. Average HNO₃ in Arctic, midlatitude and tropical cirrus

Based on climatologies of mean IWC for Arctic, midlatitude and tropical cirrus (Figure 6(a); Schiller et al., 2008), we derived the average HNO₃ fraction in ice, $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$ (Figure 6(b)), from IWC with average $M_{\text{HNO}_3}^{\text{ice}}$ and HNO₃ as described in the previous section.

**Arctic cirrus** (blue line). The temperature of Arctic cirrus is found to range between 196 and 240 K. $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$ shows a convex shape similar to the overall average discussed in the previous section and here plotted for comparison (black line). The derivations of the Arctic mean IWC from the overall mean propagates to $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$. The maximum $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$ of 10% is found between 210 and 215 K, with smaller values at lower and higher temperatures.

**Midlatitude cirrus** (green line) are observed in the temperature range 203–240 K. The decrease of the mean IWC with temperature is low in midlatitude cirrus and does not show a convex shape. Thus, $M_{\text{HNO}_3}^{\text{ice}}$ determines $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$, resulting in a strong increase of HNO₃ fractional uptake in ice with decreasing temperature that reaches 20% at the lowest midlatitude cirrus temperature of 203 K. The temperature dependence of the midlatitude $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$ is of the type proposed by Kärcher and Voigt (2006) (Figure 5(b), dotted curve).

**Tropical cirrus** (red line) cover the broadest temperature (185–240 K) and IWC range. $F_{\text{HNO}_3}^{\text{ice},\text{avg}}$ shows a
strong curvature, caused by the mechanisms explained in the previous section.

Apart from the varying temperature ranges, the differences in the mean IWC climatologies and HNO₃ partitioning in cirrus between the different geographical regions are moderate. Thus, we recommend considering the Arctic, midlatitude or tropical temperature ranges when using the climatologies for model simulations.

3.3. Vertical distribution of HNO₃ in cirrus

In section 3.1 we have shown that IWC mainly determines the HNO₃ content of cirrus clouds at a given temperature. Thus, we use the average function for $M_{\text{ice}}^{\text{HNO}_3}$ (Table II) and the average HNO₃ to convert single IWC data points taken at 1 Hz in Arctic, midlatitude and tropical field experiments to average HNO₃ fractions $F_{\text{ice}}^{\text{HNO}_3,\text{avg}}$. The IWC data points are plotted in Figure 7(a) versus potential temperature $\theta$. Note that the actual HNO₃ fraction data points may scatter only a little around the average as shown in Figure 4 since the influence of changes in HNO₃ total and $M_{\text{ice}}^{\text{HNO}_3}$ is small compared to the influence of varying IWC. In Figure 7(b) the resulting $F_{\text{ice}}^{\text{HNO}_3,\text{avg}}$ from 52 observed cirrus events, corresponding to 27 hours inside clouds, are plotted versus $\theta$.

As shown in Figure 7(a), the upper IWC envelope of Arctic and midlatitude cirrus reaches values up to a few hundreds of ppmv H₂O throughout the observed $\theta$ range of 300–340 K. The tropical cirrus, found at higher $\theta$ levels, show a pronounced vertical structure: between 340 and 360 K, IWC reaches its maximum values of up to 1000 ppmv of condensed H₂O, then decreases to about 380 K, where the tropical tropopause is located. The highest IWCs at $\theta$ 340–360 K, i.e. higher then 100–10 ppmv, are identified as deep convection events (Schiller et al., 2008). Likewise, the high IWCs detected above 380 K are attributed to deep convection events. Here, IWC up to about 50 ppmv H₂O are found to be transported from the stratosphere to the top of the tropical tropopause layer at 410–420 K.

The corresponding $F_{\text{ice}}^{\text{HNO}_3,\text{avg}}$ (Figure 7(b)) show that in Arctic and midlatitude cirrus the upper envelope of HNO₃ content in ice increases from about 20% at 300 K to about 80% at 330 K. Tropical cirrus have the potential to take up all available HNO₃ between 350 and 370 K. Farther up at 380 K, where the cold-point tropopause is located, the maximum reaches only about 10%. In overshooting events above the tropopause, again high uptake of HNO₃ in cirrus up to 100% can be expected.

In summary, tropical cirrus clouds show the highest potential to vertically redistribute HNO₃. However, midlatitude cirrus at lower altitudes can also transport substantial amounts of HNO₃. Thus, below the tropopause a downward transport of HNO₃ by large ice crystals can occur. In addition, HNO₃ can be transported to the top of the tropical tropopause layer by overshooting deep convection events.

4. Summary and conclusions

We have provided a climatological view of the partitioning of HNO₃ in cirrus clouds in dependence on temperature. The analysis is based on a new in situ climatology of cirrus clouds IWC (Schiller et al., 2008), and a survey of molar ratios of HNO₃/H₂O in ice crystals, $M_{\text{ice}}^{\text{HNO}_3}$. The major results are:

- The dataset of observed $M_{\text{ice}}^{\text{HNO}_3}$ (Voigt et al., 2006) is extended by new observations down to temperatures of 185 K and covers now the temperature range 185–240 K.
• Functional relations for the temperature dependence of $M_{\text{HNO}_3}$ and the HNO$_3$ percentages in cirrus ice, $F_{\text{HNO}_3}$, are provided for the temperature range 185–240 K. In addition, regional averages of HNO$_3$ content in cirrus are provided for Arctic, midlatitude and tropical cirrus clouds (Table II; Equation (3)). These functions can be used in global climate models to constrain the impact of the HNO$_3$ content of ice particles on the upper tropospheric concentrations of ozone.

- From the HNO$_3$ climatology, IWC is identified as an important parameter determining the HNO$_3$ content in ice at given temperatures. The highest HNO$_3$ content of up to 100% is expected in thick tropical cirrus clouds, while very thin ice clouds carry maximally only 1% of the HNO$_3$.

The average HNO$_3$ content in ice versus temperature is convex shaped: a maximum of about 10% HNO$_3$ is found in the range 200–210 K at higher and lower temperatures the HNO$_3$ content is smaller. At higher temperatures, low $M_{\text{HNO}_3}$ causes this decrease, while at lower temperatures the strong decrease of IWC is responsible for the low HNO$_3$ content in ice.

The overall range of HNO$_3$ percentages in cirrus ice is estimated to 0.01 and 100% at given temperatures over nearly the whole temperature range. This reflects the variability of atmospheric conditions determining the HNO$_3$ content, which are cloud age and corresponding IWC, total available HNO$_3$, and the stage of the HNO$_3$ uptake process in relation to equilibrium.

- An average vertical distribution of the HNO$_3$ content of ice clouds is derived, showing that tropical convective cirrus clouds have, due to their high IWC, the highest potential to vertically redistribute HNO$_3$ by sedimenting ice crystals. Equally, HNO$_3$ may be uplifted by ice crystals to the top of the tropical tropopause layer in overshooting deep convection events.

The extent to which the upper tropospheric (and maybe lower stratospheric) chemistry can be disturbed by transport of HNO$_3$ through the tropical tropopause layer is an important issue for future investigations.

Acknowledgements

The authors thank the coordinators and all teams contributing to the field experiments compiled in the study presented here. Progress in the challenging task of providing an estimate of the nitric acid content of ice for most atmospheric conditions is only possible due to the large effort flowing into all the experiments.

Funding from various agencies for the different projects is acknowledged, in particular for SCOUT-O3 which is funded by the EC within FP6 under contract GOCE-CT-2004-505390. C. Voigt appreciates funding by the Helmholtz Young Investigators Fund and the SPF-641 TROP-ICE. The authors also would like to thank Bernd Kärcher for stimulating discussions. As always, Rolf P. Müller is gratefully acknowledged.

References


