

Impact of polar stratospheric cloud particle composition, number density, and lifetime on denitrification

Eric J. Jensen

NASA Ames Research Center, Moffett Field, California, USA

Owen B. Toon

Laboratory for Atmospheric and Space Physics, Department of Atmospheric and Oceanic Science, University of Colorado, Boulder, Colorado, USA

Azadeh Tabazadeh and K. Drdla

NASA Ames Research Center, Moffett Field, California, USA

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[1] One-dimensional simulations of polar stratospheric clouds (PSCs) composed of nitric acid trihydrate (NAT) and nitric acid dihydrate (NAD) particles are used to investigate vertical redistribution of nitric acid by clouds with these compositions. We find that for typical Arctic PSC lifetimes of a few days or less the net depletion of HNO_3 is well below 50%, regardless of the NAT or NAD particle number density. With cloud lifetimes of a week or longer, greater than 50% denitrification is possible even with relatively low NAT particle number densities (as low as $1 \times 10^{-3} \text{ cm}^{-3}$). Denitrification is most efficient with NAT particle number densities of about $3 \times 10^{-3} \text{ cm}^{-3}$ to 10^{-2} cm^{-3} . For a given temperature history the degree of denitrification by NAD clouds is much less severe than that by NAT clouds. The clouds also cause a local maximum in HNO_3 mixing ratios at the cloud base where the cloud particles sublimate. Our simulations suggest that repeated short-lived PSC events do not build up the denitrification beyond about 50%; however, the depth of the denitrified layer increases with each successive PSC event. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0320 Atmospheric Composition and Structure: Cloud physics and chemistry; *KEYWORDS:* denitrification

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1. Introduction

[2] The removal of nitric acid (denitrification) by polar stratospheric clouds involves condensation of nitric acid onto the cloud particles, sedimentation of the particles, and eventual release of the nitric acid at lower altitudes when the particles sublimate. Denitrification is believed to be an important factor controlling the magnitude of ozone loss in the polar winter. In particular, when sunlight returns to the polar region in spring, nitric acid photolysis releases NO_2 , resulting in rapid deactivation of chlorine and termination of ozone loss [Solomon, 1999]. If severe denitrification occurs, then ozone loss can continue into the sunlit springtime. Model results for the 1999/2000 Arctic winter indicate that as much as 30% of the net ozone loss at 20 km can be attributed to denitrification by PSCs [Drdla and Schoeberl, 2002].

[3] Both satellite and in situ measurements indicate severe denitrification occurs in the Antarctic winter strato-

sphere, accompanied by dehydration [Fahey *et al.*, 1990; Santee *et al.*, 1999]. Observations have suggested at least localized denitrification occurs in the Arctic [Fahey *et al.*, 1990; Waibel *et al.*, 1999; Dessler *et al.*, 1999; Kondo *et al.*, 2000]; however, satellite measurements generally do not indicate widespread, severe Arctic denitrification [Santee *et al.*, 1999]. Waibel *et al.* [1999] and Tabazadeh *et al.* [2000] suggested that widespread Arctic denitrification might occur in a colder, more humid future Arctic stratosphere, possibly enhancing future ozone loss. Predictions of future denitrification severity are uncertain due to both the challenge of predicting the future stratospheric environment and incomplete understanding of the conditions and processes required for denitrification to occur.

[4] In situ measurements [Fahey *et al.*, 1990] and satellite measurements [Tabazadeh *et al.*, 2000] have shown that denitrification can occur without significant dehydration. These measurements suggest the possibility that clouds composed of nitric acid hydrates might denitrify the air in regions where synoptic-scale temperatures do not drop below the ice frost point. Fahey *et al.* [2001] argued that large nitric acid-containing particles observed during the

SAGE III Ozone Loss and Validation Experiment (SOLVE) could be responsible for the significant denitrification observed [Popp *et al.*, 2001]. The large particles were frequently observed in regions much too warm for ice existence. Note that the satellite and in situ observations do not preclude the possibility that localized temperatures below the frost point are necessary for formation of the large nitric acid particles [Waibel *et al.*, 1999]; however, based on modeling of PSC formation during SOLVE, Drdla *et al.* [2002] argue that ice supersaturation is not necessary for NAT formation.

[5] Tabazadeh *et al.* [2000] used trajectory analysis and satellite data to show that the lengths of time periods cold enough for nitric acid hydrate clouds to form (i. e., the cloud lifetimes) may be a key factor determining the severity of denitrification. This suggestion is consistent with the modeling results presented by Toon *et al.* [1990], which showed that severe denitrification by nitric acid trihydrate (NAT) clouds is only possible if the cloud lifetimes were longer than about 1 week.

[6] The relatively large (10–20 μm diameter) nitric acid containing particles mentioned above were observed over large horizontal areas and over a large altitude range (16–21 km) during SOLVE [e.g., Fahey *et al.*, 2001]. The number densities of these large particles typically ranged from 10^{-6} to 10^{-3} cm^{-3} . Large particle detected with optical scattering probes in earlier Arctic aircraft campaigns were generally assumed to be ice crystals [Dye *et al.*, 1992]. The SOLVE measurements lead to the suggestion that denitrification may be caused by HNO_3 -containing PSCs with very low number densities [Fahey *et al.*, 2001; Drdla *et al.*, 2002].

[7] In this study, we use a one-dimensional (1-D) cloud model to investigate the potential denitrification due to NAT or nitric acid dihydrate (NAD) PSCs. We are focusing here on the vertical redistribution of nitric acid by the clouds. We examine the sensitivities of HNO_3 vertical redistribution to variables such as cloud particle composition, particle number density, and cloud lifetime. First, we describe the model and the setup of the simulations. Next, we present the model results and sensitivity analysis. Finally, we discuss the implications of the results for Arctic denitrification.

2. Model Description

[8] The key processes involved in HNO_3 vertical redistribution by PSCs are particle growth, sedimentation, and sublimation. To simulate these processes, we use the Community Aerosol and Radiation Model for Atmospheres (CARMA). This model has been used to simulate various types of clouds [e.g., Jensen *et al.*, 1998]. The piecewise parabolic method algorithm [Colela and Woodard, 1984] is used for sedimentation (advection in the vertical) and deposition growth (advection in particle diameter space). The calculation of NAT/NAD particle deposition growth rates and sedimentation rates follows the approach used by Toon *et al.* [1989]. We use the expressions for HNO_3 saturation vapor pressure over NAT and NAD given by Hanson and Mauersberger [1988] and Worsnop *et al.* [1993], respectively. The molecular diffusivity of HNO_3 in air is calculated using the measured value for H_2O and

scaling to adjust for the larger molecular weight and larger molecular diameter for HNO_3 than for H_2O [see Larsen, 1991].

[9] When the temperature drops below about 190–195 K, a large fraction of the gas-phase HNO_3 condenses on the ubiquitous $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aqueous aerosols. Since HNO_3 condensation occurs on all of the sulfate aerosols, they do not grow large enough to sediment substantially; however, since the nitric acid is mostly in the liquid aerosols, it is not immediately available for condensation on NAT/NAD particles. For calculation of the HNO_3 partitioning between gas-phase and ternary aerosols, we use the Aerosol Physical Chemistry Model (APCM) [Lin and Tabazadeh, 2001]. We assume a sulfate mixing ratio of 0.5 ppbv and a water vapor mixing ratio of 5 ppmv. At the beginning of each model time step, we first run the APCM code to calculate the gas-phase fraction of HNO_3 , and this value is used in calculations of HNO_3 saturation vapor pressure over NAT and NAD. After NAT or NAD particles form and deplete the gas-phase nitric acid, the HNO_3 in the liquid aerosols will be released to the gas-phase and be available for condensation of the HNO_3 hydrate particles. This exchange is handled properly in the model since time steps (10–20 min.) are much smaller than the typical particle growth times (hours-days), and the HNO_3 partitioning between aerosols and gas-phase is recalculated at each time step.

[10] The physical mechanisms and rates of NAT/NAD particle nucleation are not well understood [World Meteorological Organization (WMO), 1999]. In this study, we are focusing on the sensitivity of denitrification to cloud particle number density. Hence we use a simple scheme for nucleation which allows us to control the number densities of NAT/NAD particles nucleated. We assume the existence of NAT/NAD nuclei that are activated when the saturation ratio of HNO_3 over NAT or NAD exceeds a threshold value. We assume the NAT(NAD) nucleation rate on the nuclei is zero below a specific saturation threshold and 1 when the saturation exceeds this threshold. Effectively, this scheme acts as a switch such that all NAT(NAD) nuclei in a given spatial grid box are converted to NAT(NAD) rapidly when the saturation threshold is exceeded. The threshold HNO_3 saturation ratios used for NAT and NAD are 10 and 1.2, respectively. These saturation ratio thresholds are reached at temperatures about 3 K and 0.3 K below the NAT and NAD frost points, respectively. Once all the nuclei at a particular vertical level have been activated to NAT or NAD, nucleation ceases; Hence the number of cloud particles nucleated is directly controlled by the number of nuclei assumed to be present. These nuclei might be sulfate aerosols with an insoluble component allowing them to heterogeneously nucleate the HNO_3 hydrates. This scenario differs from the homogeneous nucleation scheme [Tabazadeh *et al.*, 2001] in which homogeneous NAT or NAD nucleation occurs in a small number of the ternary aerosols when exposed to temperatures of 190–192 K for long periods of time. In the homogeneous freezing scenario, the NAT/NAD particle number density is controlled by the ternary aerosol size distribution and the temperature history.

[11] We use a vertical domain of 10–30 km, with a vertical spacing of 100 m. A very small vertical diffusion

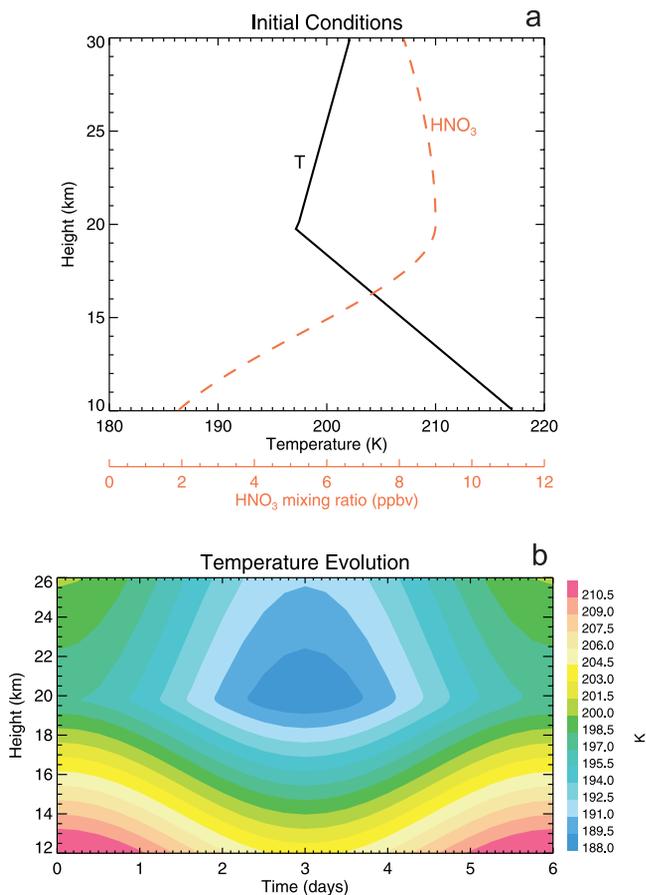


Figure 1. (a) The initial temperature and nitric acid mixing ratio are plotted versus height. (b) The prescribed evolution of temperature with time is shown for the 6-day period simulations.

coefficient is used ($10^2 \text{ cm}^2/\text{s}$), so diffusion has very little impact on the simulations. Since our advection scheme preserves strong vertical gradients and we are using relatively high vertical resolution, numerical diffusion should not be affecting the results. In fact, using higher vertical resolution had no significant effect on the results.

[12] Four particle types are included: NAT nuclei, NAD nuclei, NAT particles, and NAD particles. For each of the cloud particle types (NAD and NAT), 40 size bins are used spanning the diameter range of 0.02–40 μm . Given the lack of knowledge about the relative saturation thresholds for NAT and NAD nucleation, we only show simulations with either NAT or NAD formation, and we compare their impacts.

[13] The initial temperature and nitric acid mixing ratio profiles are shown in Figure 1, along with the assumed time evolution of temperature. The nitric acid mixing ratio has a maximum value of 9 ppbv at about 20 km, with mixing ratio decreasing below this altitude down to about 2 ppbv in the lowermost stratosphere. This profile is typical of the polar stratosphere in early winter [Gille *et al.*, 1996]. We assume a sinusoidal temperature evolution, with a minimum temperature of about 188 K at 20 km. The period of the temperature oscillation is varied in sensitivity studies described below. The temperature profile and oscillation amplitude

were based on the early to mid-January 2000 conditions [Newman and Harris, 2002].

3. Model Results

[14] To demonstrate the basic cloud evolution in these simulations, we will define a baseline simulation with 10^{-3} cm^{-3} NAT nuclei and a 6 day temperature oscillation. The model results are plotted versus height and time in Figure 2. The temperature decrease drives the NAT saturation ratio above 15. At temperatures below about 190 K, more than 75% of the nitric acid is condensed in the ternary aerosols. The HNO₃ uptake by ternary aerosols prevents the NAT saturation ratio from exceeding about 15. As described above, we allow rapid nucleation of NAT particles when the saturation ratio exceeds 10. NAT nucleation rapidly occurs on all available NAT nuclei beginning about 2 days into the simulation in the layer around 19–21 km where the saturation ratio is high enough. These NAT particles grow by deposition of HNO₃ and water vapor, such that by 4.5 days, the maximum HNO₃ condensed on NAT particles exceeds 5 ppbv. The gas-phase HNO₃ deficit caused by ternary aerosols and NAT growth is apparent at about 17–21.5 km.

[15] The condensed NAT mass (Figure 2c) shows that the NAT cloud actually has two layers. At the center of the temperature minimum (around 19–20 km), most of the nitric acid is in ternary aerosols, so NAT growth is inhibited; Hence the largest NAT mass accumulations occur just above and below the temperature minimum. These NAT mass maxima then descend with time due to particle sedimentation. The NAT particle area-weighted effective diameter exceeds 10 μm after 4 days, and sedimentation transports much of the condensed HNO₃ down to cloud base (16–17 km). After about 4.5–5 days, the temperature has increased enough to drive the NAT saturation ratio below 1, and the NAT particles begin to rapidly sublimate, releasing the HNO₃ back to the gas phase. The net result is a decrease in nitric acid mixing ratio at 20–21.5 km from 9 ppbv down to about 5.5 ppbv. There is a second layer with slight denitrification at about 17–18 km caused by the lower NAT cloud layer. Enhancements in HNO₃ mixing ratio due to release of nitric acid from each of the cloud layers are evident at about 18.7 and 16.2 km.

[16] In the simulations we have run, the NAT particles always grow to diameters of 10–20 μm in the mature clouds as long as the number density of NAT particles is limited to less than about 0.01 cm^{-3} . These particle sizes are consistent with the reported sizes of relatively large PSC particles observed during SOLVE [Fahey *et al.*, 2001]. The large particles are an inevitable result of the low nuclei number densities assumed here; Hence the nucleation process resulting in very few NAT particles is an important issue to resolve.

[17] The importance of condensed phase and cloud lifetime are shown in Figures 3 and 4. Figure 3 shows the evolution of nitric acid partitioning (analogous to Figure 2c), and Figure 4 shows the net impact of the clouds on the nitric acid vertical profile. Increasing the period of the temperature oscillation from 6 to 12 days (resulting in an increase in cloud lifetime from 3.5 to 7 days) has a dramatic impact on the nitric acid vertical redistribution. With the slower temperature oscillation, the NAT layer initiated below the

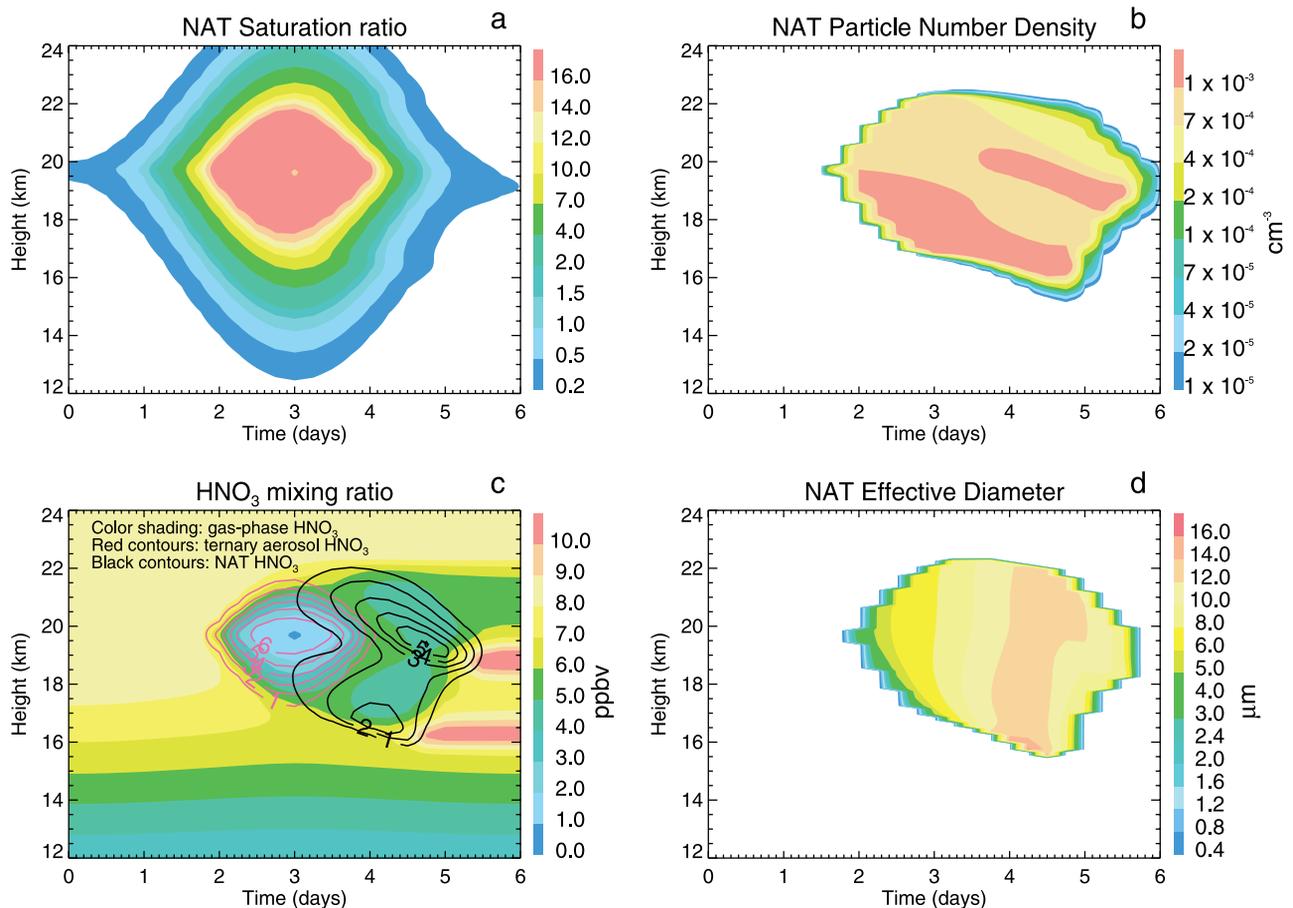


Figure 2. For the baseline simulation (with 10^{-3} cm^{-3} NAT nuclei), fields are plotted versus time and height: (a) HNO_3 saturation ratio with respect to NAT; (b) NAT particle number density; (c) gas-phase (color shading), ternary aerosol (red contours), and NAT (black contours) HNO_3 mixing ratio; (d) surface area weighted NAT particle effective diameter.

temperature minimum dominates over the upper layer, and both layers contribute to denitrification in the 18–22 km altitude range. The maximum HNO_3 depletion increases from about 35% to 65%, and the denitrification extends over a much broader vertical region. Hence, in agreement with earlier studies [Toon *et al.*, 1990; Tabazadeh *et al.*, 2000], these simulations support the requirement of long cloud lifetimes for severe denitrification. This sensitivity is expected since increasing the length of the cold time period gives the cloud particles more time to grow and more time to fall out before the temperature increases. Since the particles grow larger with longer duration cold periods, the cloud base and HNO_3 surplus occur at lower altitudes with the longer cloud lifetime.

[18] Another interesting point shown in Figure 3a is that the lifetime of individual NAT particles initially nucleated near 19.5 km is ultimately limited by their sedimentation through the NAT supersaturated region and sublimation in the subsaturated air below. Hence, for NAT clouds with long lifetimes, the maximum particle size and lifetime are ultimately limited by the depth of the NAT saturated layer. This conclusion is consistent with the Lagrangian particle calculations shown by Fahey *et al.* [2001] indicating that the largest particles observed must have fallen through several kilometers of NAT saturated air.

[19] The blue curve in Figure 4 shows that with the 6-day temperature oscillation, a NAD cloud has only a slight impact on the nitric acid vertical distribution. Our nucleation assumptions result in NAT and NAT particles forming at about the same time in the different simulations, but the saturation vapor pressure over NAD is much lower than that over NAT, so the NAD particles grow much more slowly. Even the 7-day lifetime NAD cloud causes less than 35% denitrification. As might be expected, decreasing the minimum temperature reached (by increasing the amplitude of the temperature oscillation) results in more severe denitrification by NAD clouds. Specifically, when we decrease the minimum temperature by 4 K in the NAD simulation with a 12-day oscillation period, the maximum denitrification increases from 35% to 60%. However, decreasing the temperature by 4 K results in a temperature minimum of 184 K. Such low temperatures were rarely reached during the SOLVE winter [Drdla *et al.*, 2002].

[20] We have run these simulations with NAT nuclei number densities ranging from 1×10^{-4} – $3 \times 10^{-2} \text{ cm}^{-3}$. As described above, since we are assuming nucleation occurs rapidly, the number of NAT particles nucleated is equal to the number of nuclei assumed. The impact of varying the NAT particle number density on the final HNO_3 mixing ratio profile is shown in Figure 5. As the NAT

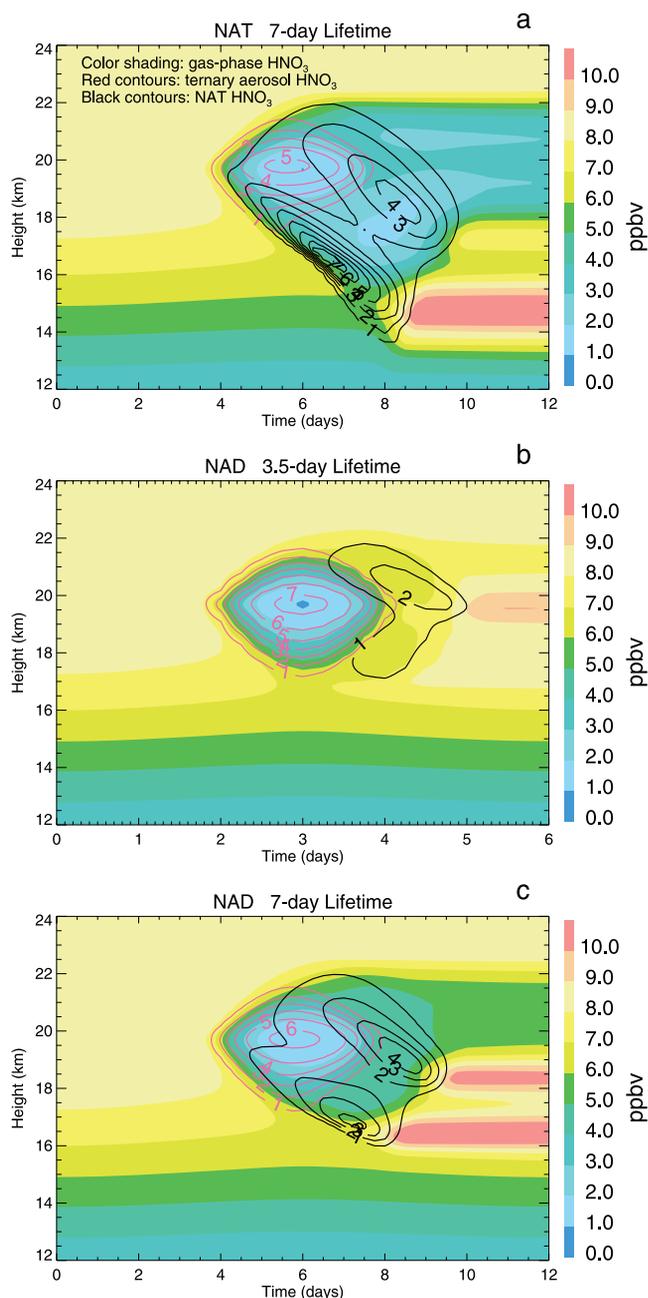


Figure 3. Same as Figure 2c, but for different simulations: (a) NAT cloud with 12-day temperature oscillation; (b) NAD cloud with 6-day temperature oscillation; (c) NAD cloud with 12-day temperature oscillation. See section 3 for discussion.

number density is increased from 1×10^{-4} to about $3 \times 10^{-3} \text{ cm}^{-3}$, the denitrification at 19–20 km increases simply because more nitric acid is condensed onto the NAT particles. Note that the amount of denitrification is extremely sensitive to NAT particle number density for number densities less than $1 \times 10^{-3} \text{ cm}^{-3}$. When the NAT number density is increased beyond about $3 \times 10^{-3} \text{ cm}^{-3}$, competition for HNO₃ vapor begins to limit the growth and sedimentation of the cloud particles. Hence, although most of the HNO₃ gets deposited on the NAT particles, they do not fall very far, and the HNO₃ is released

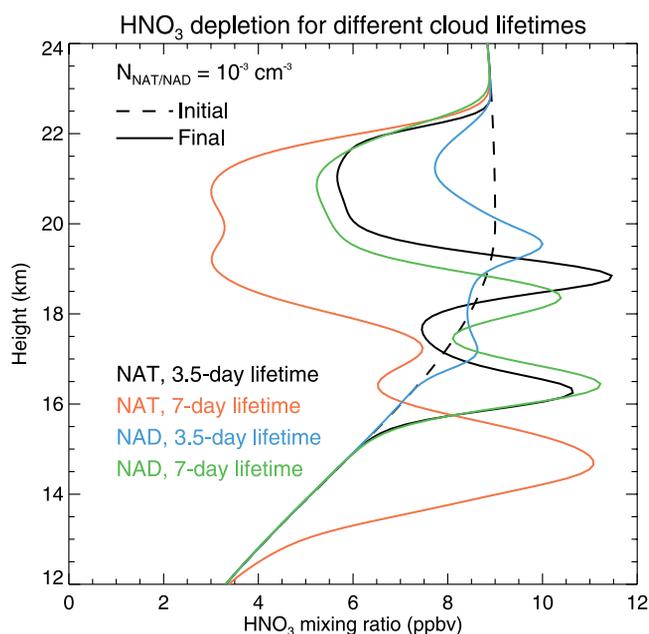


Figure 4. Height profiles of gas-phase HNO₃ mixing ratios are shown. The dashed curve is the initial profile. The solid profiles show the final HNO₃ mixing ratio profiles from four simulations. Black: NAT temperature oscillation (3.5-day cloud lifetime); red: NAT 12-day temperature oscillation (7-day cloud lifetime); blue: NAD 6-day temperature oscillation; green: NAD 12-day temperature oscillation.

at nearly the same altitude, resulting in limited irreversible denitrification.

[21] The sensitivity of denitrification to cloud particle number density is summarized in Figure 6. This figure

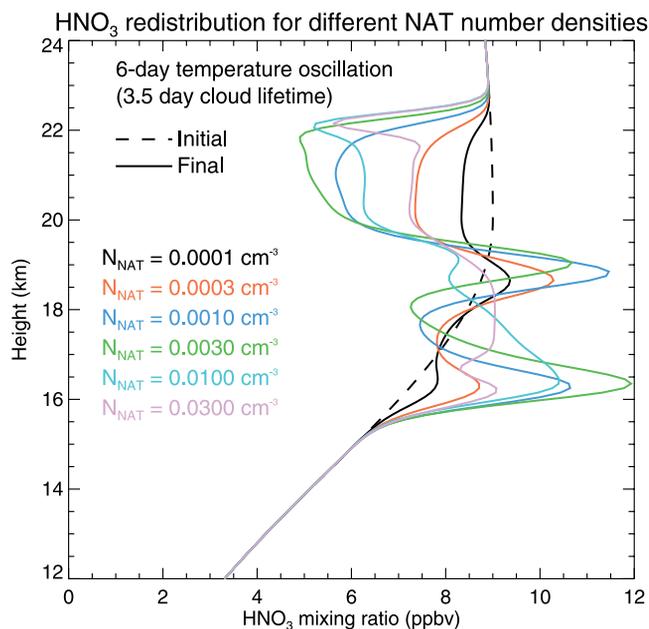


Figure 5. Same as Figure 4, except HNO₃ mixing ratio profiles are shown for the 6-day temperature oscillation and NAT clouds with a range of NAT nuclei number densities. The maximum denitrification occurs with NAT number densities of about $3 \times 10^{-3} \text{ cm}^{-3}$.

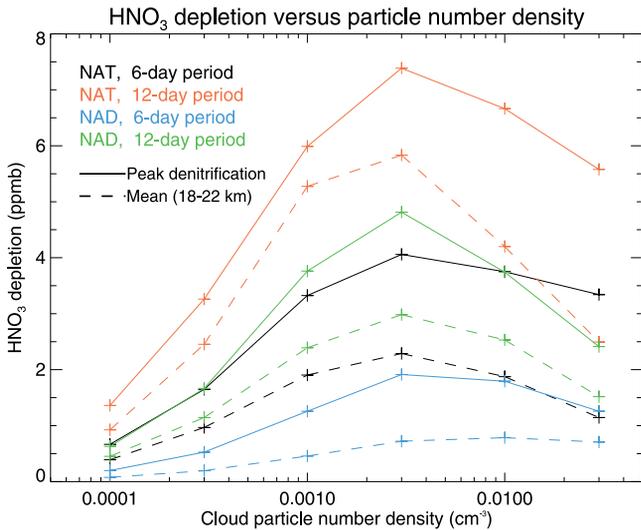


Figure 6. The potential for denitrification is plotted versus cloud particle number density. The solid curves show the change in nitric acid mixing ratio at the altitude where the denitrification was maximum, and the dashed curves show the average denitrification in the 18–22 km height range. Simulations are shown for NAT and NAD clouds with temperature oscillation periods of 6 and 12 days.

shows results from NAT and NAD cloud simulations with temperature oscillation periods of 6 and 12 days. Both the peak denitrification and the mean denitrification in the 18–22 km layer are shown. For most of these cases, the potential for denitrification is greatest if the cloud particle number density is near 3×10^{-3} . Figure 6 clearly shows the rapid decrease in denitrification with particle number density decreasing below $1 \times 10^{-3} \text{ cm}^{-3}$.

[22] Analysis of Arctic trajectories has shown that in a typical winter, air parcels make several passes through regions cold enough for PSC formation [Drdla et al., 2002; Tabazadeh et al., 2001]. One might expect that the denitrification would build up with each successive PSC formation event. Dessler et al. [1999] argued that multiple exposures to low temperatures were required to build up significant denitrification. To evaluate the potential accumulation of denitrification, we have run the baseline simulation with repeated temperature oscillations, resulting in repeated PSC formation. The cloud particles completely sublimate between events. Figure 7 shows vertical profiles of nitric acid after 1–5 cooling cycles with NAT and NAD clouds. Unexpectedly, in the NAT cloud simulation the minimum HNO_3 mixing ratio near 20 km does not decrease significantly with successive cloud events. However, the denitrified layer extends down to about 17.5 km after the second temperature cycle. Figure 8 shows that after the first PSC event, the subsequent clouds had very different vertical structure. Since the first PSC event denitrifies the 19–20 km region and scavenges the nuclei from this layer, little or no cloud forms above 19 km in the second temperature cycle. However, a NAT cloud forms below about 19 km where HNO_3 was enhanced by vertical redistribution in the first cloud event. This lower cloud denitrifies the 17.5–18.5 km layer.

[23] This behavior is partially an artifact of our assumption that NAT particles form on all available nuclei which are then scavenged by the first cloud event. Alternatively, if the NAT nuclei are formed by slow freezing of the abundant ternary aerosols, then each PSC event will remove only a very small fraction of the available aerosols, and subsequent PSCs will still have an ample supply of nuclei. We have run simulations with the NAT nuclei number density reset to its initial value after each PSC cycle, and in this case, the denitrification does continually build up with each successive cloud cycle; however, the incremental removal of

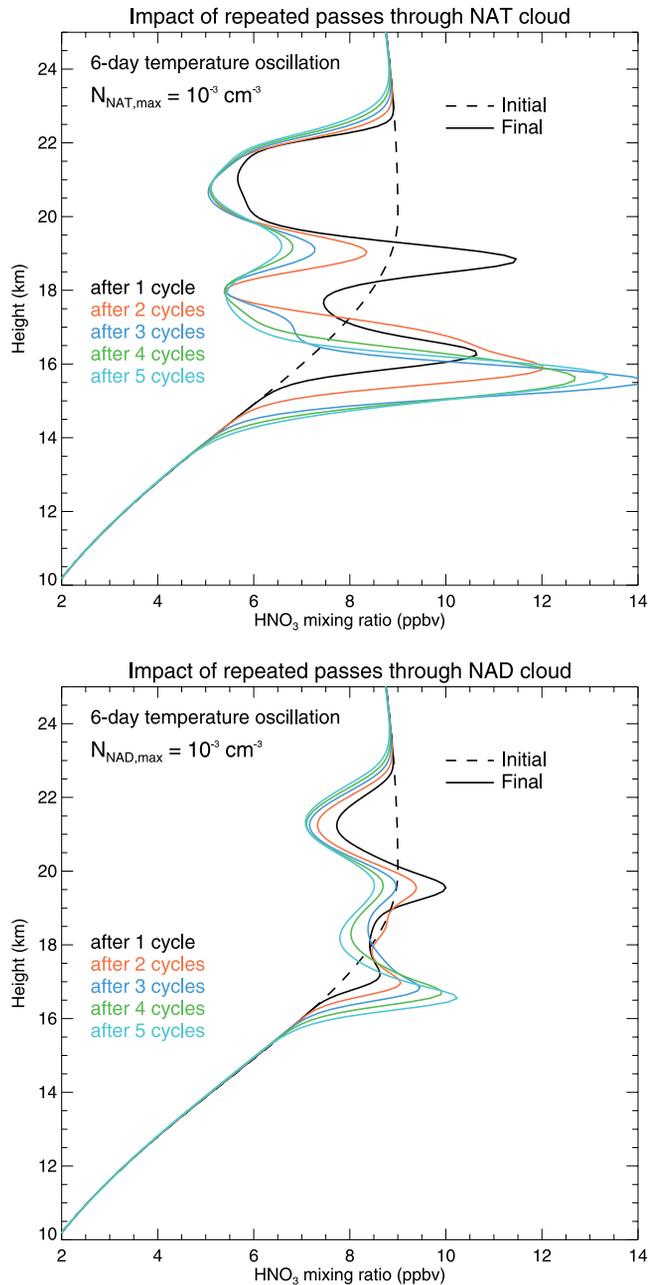


Figure 7. The impact of repeated PSC events on the vertical distribution of HNO_3 is shown. Height profiles of HNO_3 mixing ratio after each pass through the temperature minimum (each cloud cycle) are shown for (a) NAT clouds and (b) NAD clouds.

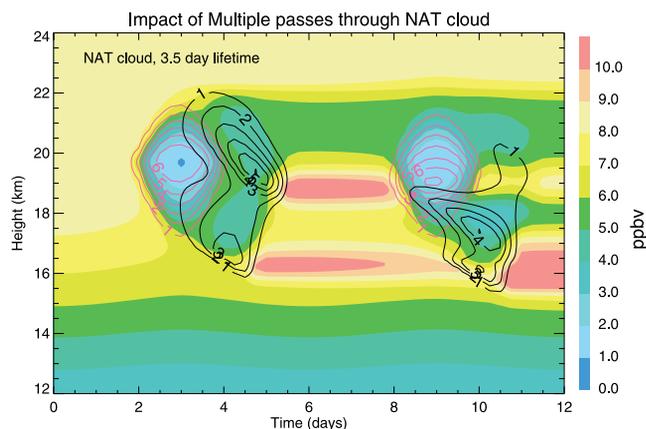


Figure 8. Time-height contour plot of HNO_3 mixing ratio through the first two temperature cycles in the 6-hour temperature period NAT simulation. Color shading: gas-phase HNO_3 ; red contours: ternary aerosol HNO_3 ; black contours: NAT HNO_3 . Since the first cloud cycle denitrifies the 19–21 km region, in the second cycle, the NAT cloud only forms below the temperature minimum. The second cloud event denitrifies the 17.5–18.5 km layer.

HNO_3 with each cloud event still decreases after each cycle due to denitrification of the 18–20 km region. The key result here is that a single PSC with a long lifetime is much more effective at removing nitric acid than several short PSC events.

[24] As shown in Figure 7b, the impact of repeated NAD cloud events is similar to that in the NAT cloud simulations. After the first cloud event, repeated cycles only moderately enhance the denitrification near 20 km, but denitrification at lower levels does significantly accumulate. Again, the denitrification in a single 7-day NAD PSC event is much larger than the denitrification caused by several cycles of 3.5-day cloud events.

4. Summary and Discussion

[25] We have used a 1-D cloud model to investigate the sensitivity of HNO_3 vertical redistribution to several variables. Based on these simulations, we make the following conclusions. (1) Severe (>50%) denitrification, as observed in SOLVE, is possible even with relatively low NAT particle number densities (as low as about $1 \times 10^{-3} \text{ cm}^{-3}$) if the cloud lifetime is greater than about 5 days. (2) The denitrification is largest with NAT number densities of about $3 \times 10^{-3} \text{ cm}^{-3}$. (3) With NAT number densities decreasing below 10^{-3} cm^{-3} , the degree of denitrification decreases rapidly. (4) Only moderate (<40%) denitrification is likely with NAD PSCs. (5) Repeated passes of an air column through short-lived (3–4 days) NAT or NAD clouds will build up the denitrification to only about 40–50%, but repeated cloud cycles increase the depth of the denitrified layer. (6) Denitrification is significantly limited by the uptake of nitric acid by ternary liquid aerosols.

[26] Our analysis suggests that cold events sufficient for NAT or NAD PSC existence must have long durations for severe denitrification. Tabazadeh et al. [2001] suggest that nucleation of sufficient numbers of NAT or NAD particles is

only possible if parcels spend at least a few days within a narrow temperature window (190–192 K). These results together emphasize the requirement of slow cooling and long-duration cold events for severe denitrification.

[27] Analysis of Arctic trajectories during the winter of 1999/2000 suggest that time periods with temperatures low enough to support NAT or NAD PSCs were longer than typical winters [Tabazadeh et al., 2001; Drdla et al., 2002], and SOLVE measurements indicate that the Arctic vortex was severely denitrified during January–March, 2000 [Popp et al., 2001]. These measurements are consistent with the theoretical prediction that long cloud lifetimes lead to significant denitrification.

[28] The SOLVE PSC measurements indicated a large fraction of the clouds had number densities of large (>10 μm diameter) particles less than 10^{-3} cm^{-3} [Fahey et al., 2001]. Based on the simulations presented here, this is precisely the number density range where denitrification is extremely sensitive to changes in particle number density. Hence it is important to understand what controls the number of large particles in PSCs. If the cloud particle number density is limited by the number of effective nuclei (as assumed in the simulations described here), then future changes in the stratospheric aerosol composition or number density would affect the degree of Arctic denitrification. Alternatively, if the PSC particle number density is controlled by the time air parcels spend in the 190–192 K temperature range (as suggested by homogeneous nucleation simulations) [Tabazadeh et al., 2001], then future changes in the Arctic thermal structure will be most important.

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K. Drdla, E. J. Jensen, and A. Tabazadeh, NASA Ames Research Center, MS 245-4, Moffett Field, CA 94035, USA. (katja@aerosol.arc.nasa.gov; jensen@sky.arc.nasa.gov; atabazadeh@mail.arc.nasa.gov)

O. B. Toon, Laboratory for Atmospheric and Space Physics, Department of Atmospheric and Oceanic Science, University of Colorado, Boulder, Colorado, USA.