

Growth of upper tropospheric aerosols due to uptake of HNO₃

S. Romakkaniemi¹, H. Kokkola¹, A. Petzold², and A. Laaksonen¹

¹University of Kuopio, Department of Applied Physics, Kuopio, Finland

²Deutsches Zentrum für Luft und Raumfahrt Oberpfaffenhofen, Institut für Physik der Atmosphäre, Wessling, Germany

Received: 24 October 2003 – Published in Atmos. Chem. Phys. Discuss.: 7 January 2004

Revised: 1 March 2004 – Accepted: 24 March 2004 – Published: 30 March 2004

Abstract. The effect of nitric acid on the equilibrium size distributions of upper tropospheric aerosols is calculated as a function of relative humidity. It is shown that HNO₃ concentrations above a few tenths of a ppb can cause substantial increases in haze mode particle concentrations at relative humidities at about 60% and above. The effect can be strongly magnified when letovicite particles are present in addition to sulfuric acid aerosols. Letovicite particles are less acidic than the sulfuric acid particles and so more nitric acid can be absorbed. This effect can be seen even at RH below 50% due to the lowering of the deliquescence RH of letovicite in the presence of gaseous nitric acid at low temperatures. We have also compared equilibrium calculations of the HNO₃ effect with observations of increased haze mode concentrations at relative humidities above 50% (Petzold et al., 2000). Nitric acid mixing ratios on the order of 0.5–2 ppb may explain the observed increase of haze mode particles at least partially.

1 Introduction

Aerosols in the upper troposphere and stratosphere are mainly composed of H₂SO₄ and H₂O but also ammoniated sulfate and other components have been observed (Xu et al., 2001; Sheridan et al., 1994; Murphy et al., 1998). It has been shown that binary H₂SO₄/H₂O aerosols can effectively take up HNO₃ and turn into supercooled ternary solutions before freezing homogeneously (Tabazadeh et al., 1994; Kärcher and Solomon, 1999). Uptake of HNO₃ increases the hygroscopic mass of aerosols, causing further growth of the droplets due to absorption of water. This affects both the optical properties of the aerosols and the stratospheric heterophase chemistry.

Correspondence to: S. Romakkaniemi
(sami.romakkaniemi@uku.fi)

Recently, Petzold et al. (2000) made observations about the occurrence of haze-mode aerosols in the upper troposphere. The number of haze mode particles increased abruptly as the saturation ratio exceeded 0.5. It was argued that the particles were likely to be composed of ammoniated sulfates undergoing deliquescence transition forming liquid droplets (Petzold et al., 2000). There are also some other observations on large spherical particles in the upper troposphere (Sassen et al., 1998; Del Guasta et al., 1998). The sphericity of the particles indicates strongly that they are in fact liquid droplets.

Recent thermodynamic equilibrium model calculations have shown that HNO₃ can lower the deliquescence relative humidity (DRH) of ammoniated salts at upper tropospheric conditions (Lin and Tabazadeh, 2002). It was also shown that the most likely ammoniated salt to exist at temperatures near 200 K is letovicite (NH₄)₃H(SO₄)₂. The DRH of letovicite is normally 87% at 210 K, but the presence of 2 ppb HNO₃ can decrease it down to 43%. The highest observed volume mixing ratios (VMR's) of HNO₃ in the upper troposphere are as high as 3 ppb (Laaksonen et al., 1997). High nitric acid VMR's are possible in air masses with continental influence or near flight corridors. Also, sedimentation of nitric acid particles from the stratosphere can cause increased HNO₃ concentrations in the UT. In the future, increased air traffic and/or increased NO_x emissions on the ground may cause high upper tropospheric nitric acid concentrations to occur more frequently, which in turn, may influence the number concentrations of haze mode particles.

The role of ammoniated sulfates in UT aerosol has been discussed in previous studies (e.g. Kärcher and Solomon, 1999; Lin and Tabazadeh, 2002). It is clear, that ammonia neutralizes acidic solutions and so enhances the uptake of HNO₃. However, this effect has not been quantified so far for UT aerosols in terms of droplet diameter growth and enhancement of haze mode concentrations. Instead, Lin and Tabazadeh (2002) considered the effect of HNO₃ on

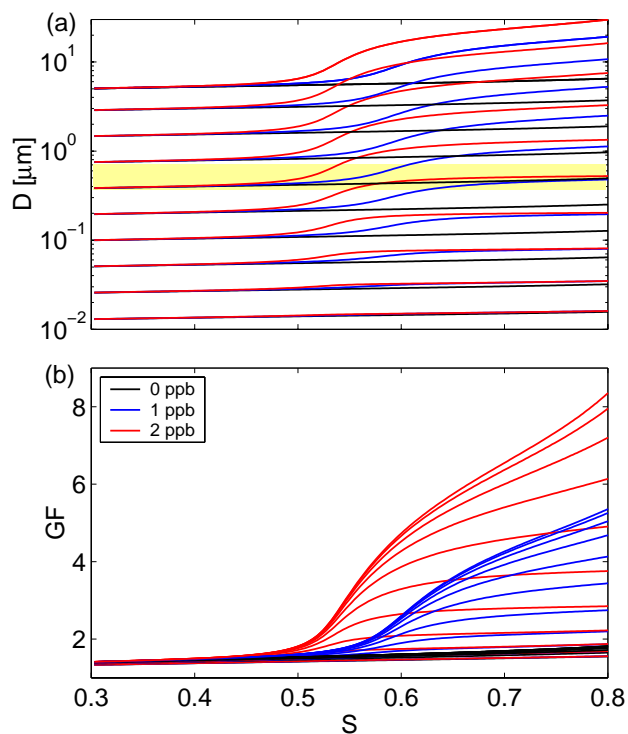


Fig. 1. (a) Growth curves for different size classes for three HNO₃ concentrations. Dry aerosol particle distribution is dist A from Table 1. The accumulation mode is illustrated with yellow colour. Particles bigger than that are in the haze mode. (b) Growth factors for different size classes for the same distribution. The highest growth factors are for the biggest particles and vice versa.

the deliquescence RH of letovicite particles, but not how much HNO₃ enhances hygroscopic growth, while Kärcher and Solomon (1999) calculated the effect of HNO₃ on sulfuric acid aerosol extinction coefficients as a function of temperature reduced by the local frost point, but did not give quantitative numbers on the effect of HNO₃ on ammoniated aerosols.

In the present work, equilibrium equations are used to model nitric acid and water partitioning between gas phase and different aerosol size classes in order to study the influence of HNO₃ on upper tropospheric particle growth at different relative humidities. Assuming that sulfuric acid and ammoniated sulfates can be considered completely involatile, the equilibrium requirements are that the saturated vapor pressures of water and nitric acid above the droplet surfaces have to equal the respective partial pressures in the gas. Due to the assumption, the sulfate to ammonium ratio is fixed and independent of RH. Based on the study of Lin and Tabazadeh (2002), we choose letovicite to be the only ammoniated salt studied. For letovicite we calculate the HNO₃-dependent DRH. As a case study, equilibrium calculations are compared with the observations of Petzold et al. (2000).

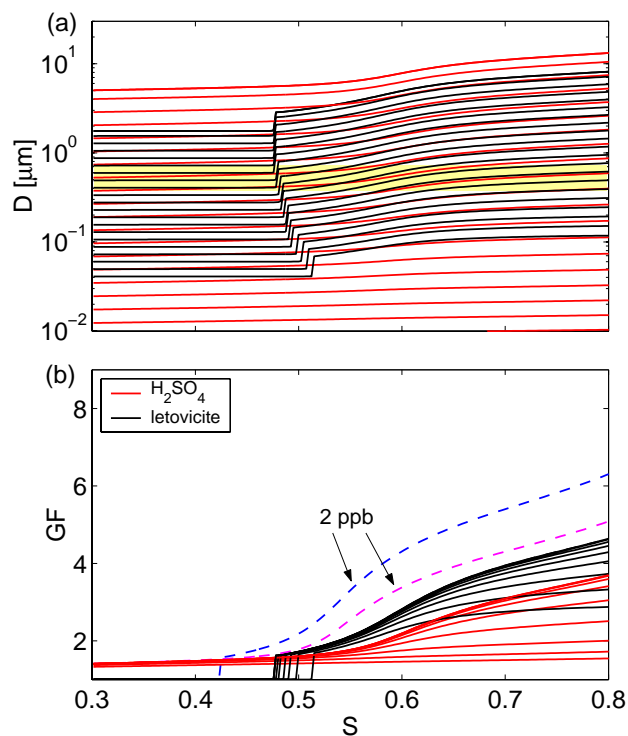


Fig. 2. (a) Growth curves and (b) growth factors for different size classes according to dist B in Table 1. In (a) the accumulation mode is illustrated with yellow colour. For clarity, size-dependent curves are presented only for 1 ppb of HNO₃. For 2 ppb of HNO₃ only the highest GF's for letovicite (blue) and for H₂SO₄ (magenta) are presented

2 Theory

The equilibrium saturation ratio S_i of vapor i over a multi-component droplet surface is obtained from

$$S_i = \frac{p_i}{p_{si}} = f_i X_i \exp\left(\frac{2\sigma v_i}{RT r}\right), \quad (1)$$

where p_i is the partial pressure, p_{si} is the saturation vapor pressure, X_i the mole fraction, f_i is the activity coefficient, v_i is the partial molar volume of species i , σ is the surface tension of the solution, R is the gas constant, T is the temperature, and r is the droplet radius.

To describe the equilibrium growth of aerosols we need to write separate equilibrium (Köhler) equations for every condensing vapor. In this study we have equations for water and HNO₃. At normal tropospheric conditions, Eq. (1) can be used for water as is, but the amount of HNO₃ in the air is small compared to water and we need to take into account the fact that condensation depletes the vapor phase. Using the ideal gas law ($pV = nRT$) we can write an equilibrium

Table 1. Parameters for log-normal distributions used in the calculations. In dist A all the modes are composed of sulfuric acid and in dist B modes 1 and 2 are composed of sulfuric acid and the mode 3 is composed of letovicite with thin sulfuric acid coating.

dist	property	mode 1	mode 2	mode 3
A	N [cm ⁻³]	112.0	0.1	
	D_{pg} [μm]	0.053	0.518	
	σ_g	1.70	1.35	
B	N [cm ⁻³]	112.0	0.1	1.25
	D_{pg} [μm]	0.050	0.518	0.270
	σ_g	1.70	1.35	1.30

equation that takes account of the mass balance of species i as

$$S_i = \frac{(n_{ti} - n_{di})CRT}{p_{si}} = X_i f_i \exp\left(\frac{2\sigma v_i}{RT r}\right), \quad (2)$$

where n_{ti} is the total amount of moles of substance i in the system per one droplet, n_{di} is the amount of moles of i in a droplet, and C is the concentration of droplets.

The droplet radius r and the number of moles n_{di} of condensable substances i (in our case water and nitric acid) can be calculated from Eqs. (2) for a monodisperse droplet population with an iterative method at a given temperature if the total concentrations of H₂O and HNO₃ are known. For the present calculations, the theory is expanded for a discrete particle size distribution including N size classes to obtain sufficient accuracy (see Kokkola et al., 2003, for more details). Equation (2) is thus used to calculate the equilibrium size and the composition of aerosols in each size class as a function of S_i in a closed system. In practice, this can be done with the following method. Equation (2) is modified so that n_{di} and C are replaced with $n_{di,k}$ and C_k where k denotes the number of size class. The number of moles per droplet n_{ti} in size class b under iteration can be expressed as

$$n_{ti,b} = \frac{n_{tot,i} - \sum_{k \neq b} n_{di,k} C_k}{C_b}, \quad (3)$$

where $n_{tot,i}$ is the total number of moles of substance i in the system (not per one droplet). By substituting Eq. (3) into Eq. (2) we get a new equation for HNO₃ in size class b

$$\frac{(n_{tot,n} - \sum_k n_{dn,k} C_k)RT}{p_{sn}} = X_n f_n \exp\left(\frac{2\sigma v_n}{RT r_b}\right) \quad (4)$$

Now we have two equilibrium equations for every size class, Eq. (1) for water and Eq. (4) for HNO₃. These equations are iterated one size class at a time until all size classes are in equilibrium with both condensing vapors. This method is similar to the mass flux iteration method (see e.g. Jacobson, 1999).

Table 2. Parameters for log-normal distributions used in the calculations. Modes 1 and 2 are composed of sulfuric acid and mode 3 is composed of letovicite.

dist	N [cm ⁻³]			D_{pg} [μm]			σ_g		
	1	2	3	1	2	3	1	2	3
C ₁	99	–	1	0.05	–	0.27	1.7	–	1.3
C ₂	98	–	2	0.05	–	0.27	1.7	–	1.3
C ₃	97	–	3	0.05	–	0.27	1.7	–	1.3
C ₅	95	–	5	0.05	–	0.27	1.7	–	1.3
C ₁₀	90	–	10	0.05	–	0.27	1.7	–	1.3
D ₀	100	0.1	0	0.05	0.50	0.20	1.7	1.35	1.3
D ₁	99	0.1	1	0.05	0.50	0.20	1.7	1.35	1.3
D ₂	98	0.1	2	0.05	0.50	0.20	1.7	1.35	1.3
D ₃	97	0.1	3	0.05	0.50	0.20	1.7	1.35	1.3
D ₅	95	0.1	5	0.05	0.50	0.20	1.7	1.35	1.3
D ₁₀	90	0.1	10	0.05	0.50	0.20	1.7	1.35	1.3

During the iteration we also calculate the saturation ratio of ammonium and sulfate ions with respect to letovicite. If the saturation ratio is over unity, letovicite is in the solid phase. As soon as the saturation ratio drops below unity, deliquescence occurs and letovicite is moved from the solid phase to the liquid phase.

In the present study, the vapor pressures of H₂O and HNO₃ over the solution droplets and the saturation ratio of liquid phase ammonium and sulfate ions with respect to letovicite are calculated using the thermodynamic electrolyte model of Clegg et al. (1998). Data for surface tensions and densities of multicomponent solutions composed of water, nitric acid, sulfuric acid and ammonia are not available, and some approximations are needed. The system is therefore simplified by excluding the effect of ammonia on surface tension and density of the solution, whereby those quantities can be calculated using the expression given by Martin et al. (2000), valid for H₂SO₄/HNO₃/H₂O-solutions.

3 Growth factors

In the following calculations concerning upper troposphere we assume (unless otherwise stated) that the total pressure $p=200$ mbar and the initial temperature and water vapor saturation ratio are $T_0=206$ K and $S_0=0.3$. In conformity with Petzold et al. (2000), we define the haze and the accumulation mode to consist of droplets larger than 0.72 μm in diameter and droplets with diameter between 0.37 μm and 0.72 μm, respectively. Both H₂SO₄ and NH₃ are assumed to remain in the droplets during the equilibrium growth in accordance with the original distribution. The size distributions are presented in Table 1. Distribution A is similar to those reported in the article of Petzold et al. (2000). The dry

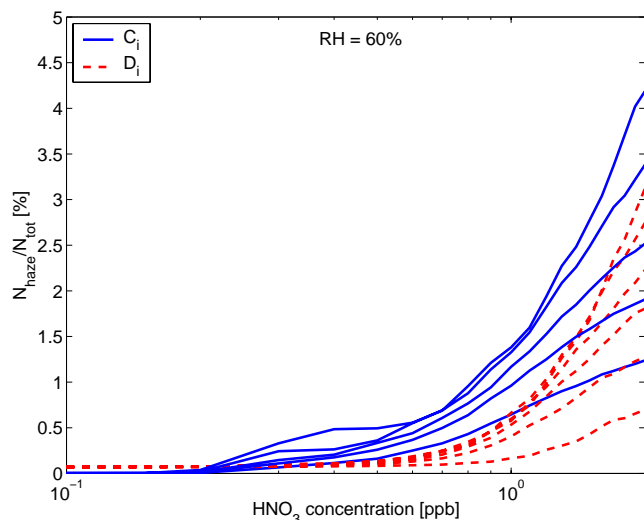


Fig. 3. Number concentration ratio $N_{\text{haze}}/N_{\text{tot}}$ as a function of HNO₃ concentration at 60% RH for size distributions presented in Table 2. The lowermost curves of C_i and D_i correspond to distributions C_1 and D_0 in Table 2 and the uppermost correspond to C_{10} and D_{10} , respectively.

radius is obtained by dividing values given at $S=0.38$ by a factor of 1.4, which is estimated to be the growth factor of H₂SO₄/H₂O-solution droplets at that saturation ratio.

With these initial values, homogeneous freezing would take place at $S \gtrsim 0.78$ ($T \sim 199$ K) depending on droplet size and timescale of the process (Koop et al., 2000).

3.1 H₂SO₄/HNO₃/H₂O

In Fig. 1a we present growth curves for different size classes for distribution A at 3 different HNO₃ VMR's as a function of saturation ratio. In the calculations the number of size classes was higher but for clarity only 10 are presented in the figure. In the Fig. 1a the accumulation mode is presented with yellow colour. The growth due to HNO₃ uptake is clear.

Figure 1b presents growth factors (=droplet diameter divided by the dry particle diameter) for the same distribution and reveals that the equilibrium growth factors are not size-independent. Because the Kelvin effect tends to increase the saturated vapor pressures, the concentrations of H₂O and HNO₃ have to decrease with decreasing droplet diameter in order to ensure equilibrium for all sizes. Previously, Carslaw et al. (1997) have noted that the equilibrium composition of stratospheric ternary droplets are size dependent (however, they did not calculate the effect on growth factors).

3.2 (NH₄)₃H(SO₄)₂

In Fig. 2, growth curves are presented for distribution B (see Table 1) containing an additional mode of letovicite. Figure 2 shows the growth of the letovicite mode as a function

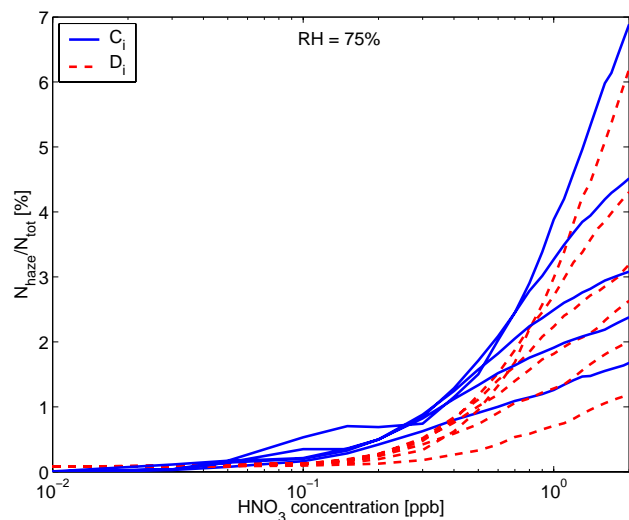


Fig. 4. Like Fig. 3 but RH is now 75%.

of S (black lines). It can be seen that with 1 ppb of HNO₃ the DRH of letovicite is at 47.8%. At that point, the particles instantly take up HNO₃ and H₂O to maintain equilibrium. The GF due to pure deliquescence is approximately 1.15. The rest of the growth is caused by simultaneous uptake of HNO₃ and H₂O. The total GF at the DRH is 1.65. An assumption of different ammonium to sulfate ratio than that of letovicite would change the deliquescence behaviour of particles (see Lin and Tabazadeh, 2002) and thus change the GF at the DRH. However, based on Lin and Tabazadeh (2002), letovicite will be formed in the solid phase also for nonstoichiometric ammonium to sulfate ratios and so there will be at least partial deliquescence at the DRH of letovicite.

It can also be seen that the DRH is size dependent. The smallest particles persist in the solid state to higher RH than do the bigger ones. The first particles to become deliquescent are those with the highest HNO₃ content in the aqueous coating. Because of the Kelvin effect, the highest equilibrium concentration occurs on the biggest particles. Smaller particles with a lower HNO₃ concentration in the liquid layer experience deliquescence at a higher RH.

From Figs. 1 and 2 we can see that the highest GF's for letovicite are indeed lower than for H₂SO₄ when the letovicite is absent. There are two reasons for that, the total volume of the distribution B is bigger than the volume of the distribution A and the GF of (NH₄)₃H(SO₄)₂-H₂O droplets is smaller than the GF of H₂SO₄-H₂O droplets. However, the equilibrium growth of letovicite particles is not as size-dependent as is the growth of H₂SO₄-particles and so the presence of letovicite particles increases the number of haze mode droplets.

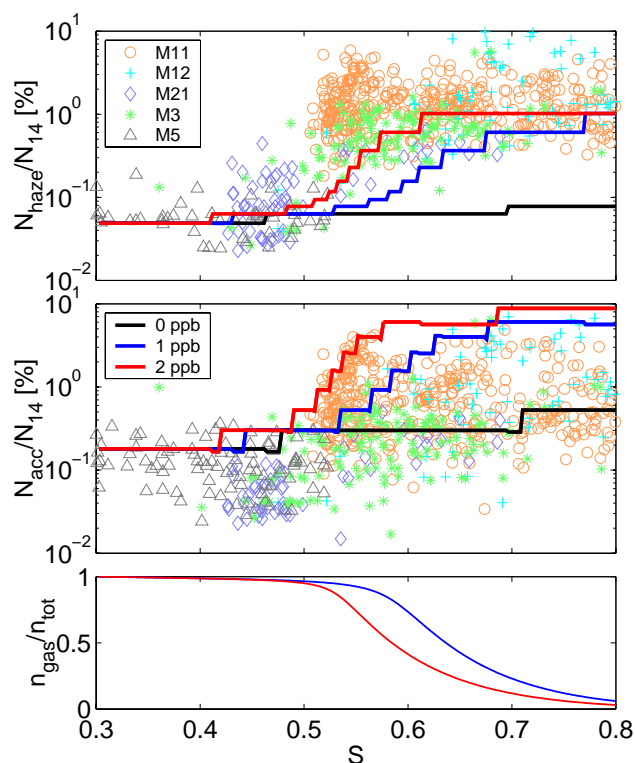


Fig. 5. Comparison to observations of Petzold et al. (2000) for distribution A (pure sulfuric acid droplets) at three different HNO₃ VMR's. Different symbols representing the observations (M11, M12, M21, M3, M5) refer to different POLSTAR II flights. For more information about measurements see Petzold et al. (2000). N_{haze}/N_{14} is the ratio of particles with diameter between 0.72 μm and 10 μm to particles with diameter bigger than 0.014 μm . N_{acc}/N_{14} is the ratio of particles with diameter between 0.37 μm and 0.72 μm to particles with diameter bigger than 0.014 μm . n_{gas}/n_{tot} is the ratio of gas phase HNO₃ to the total HNO₃ concentration.

4 Effect of increased HNO₃ and letovicite concentrations on the number of haze particles

From the examination above it is clear that both increased HNO₃, and increased letovicite concentrations lead to increased numbers of haze mode particles. This effect is further demonstrated in Figs. 3 and 4 presenting the ratio of haze mode particles to all particles as a function of HNO₃ concentration for 11 different aerosol particle distributions (Table 2) containing different amounts of sulfuric acid and letovicite. Figure 3 shows that at 60% relative humidity, nitric acid concentrations below about 0.2 ppb have little effect on the haze mode. However, above 0.2 ppb, enough of HNO₃ is absorbed by the droplets to cause a substantial increase in N_{haze} . At 75% RH, only 0.1 ppb of nitric acid is needed for a similar effect. This is due to the lowered HNO₃ vapour pressure over solution droplets and HNO₃ dependent

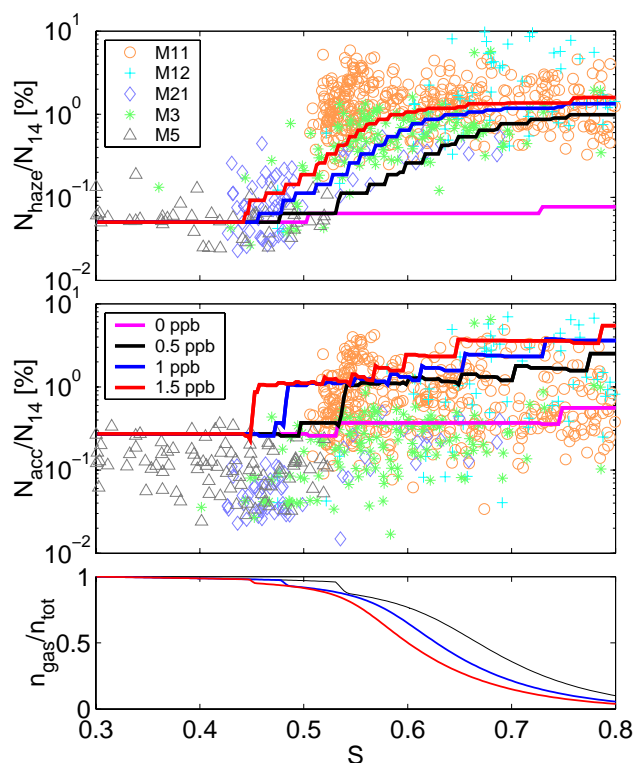


Fig. 6. Comparison to observations of Petzold et al. (2000) for distribution B containing letovicite with four different HNO₃ concentrations. Axes are same as in the Fig. 5.

deliquescence of letovicite. With increasing HNO₃ concentrations, the fraction of haze mode particles to all particles can increase to more than 5% depending on the amount and size of letovicite particles present.

Even without letovicite, the haze mode concentration can increase to more than 1 cm^{-3} , but the amount of HNO₃ needed is higher than in the presence of letovicite particles. Altogether, the variation in the haze mode concentrations for the different size distributions shown in Table 2 is close to an order of magnitude at both 60% and 75% relative humidities. Nitric acid causes a substantial enhancement of haze mode particles already when the aerosol distribution is composed of sulfuric acid alone, however, the presence of letovicite magnifies the effect greatly.

5 A case study

Petzold et al. (2000) observed pronounced increases of upper tropospheric haze mode particles at relative humidities above 50%. Here, we compare our calculations to the observation in order to examine whether nitric acid may have contributed to the haze mode concentrations. To be able to carry out the comparison, we define two modes with size limits 0.37 $\mu\text{m} < D < 0.72 \mu\text{m}$ (accumulation

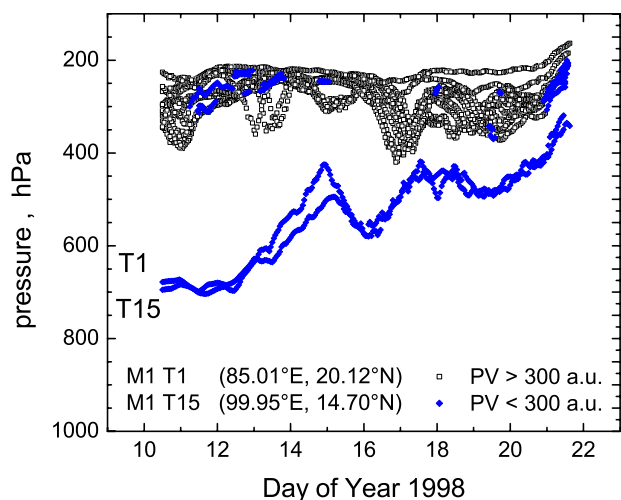


Fig. 7. History of air parcels encountered during mission flight 1 on 21 January 1998 given as pressure altitude vs. time. Blue symbols indicate air parcels of tropospheric origin (scaled potential vorticity < 300), while black symbols indicate air masses of stratospheric origin (scaled potential vorticity > 300). Starting points of tropospheric trajectories are labelled as T1 and T15

mode) and $0.72 \mu\text{m} < D < 10 \mu\text{m}$ (haze mode). Due to the measurement setup, the modes defined by Petzold et al. (2000) were $0.37 \mu\text{m} < D < 0.69$ and $0.75 \mu\text{m} < D < 10 \mu\text{m}$, but this difference should not influence our analysis too much. Figure 5 shows the concentration ratios N_{acc}/N_{14} and N_{haze}/N_{14} , where N_{14} is the concentration of all particles with $D > 0.014 \mu\text{m}$, as a function of the saturation ratio of water vapor at different nitric acid VMR's when the aerosol is composed of sulfuric acid and water (distribution A of Table 1). Also the partitioning of nitric acid between the gas and the liquid phases is shown. The data-points in Fig. 5 are the observations of Petzold et al. (2000).

The observed increase in the number of accumulation mode particles is consistent with the modeled increase caused by uptake of nitric acid on liquid $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$. It seems that an average of less than 1 ppb of HNO_3 is needed to explain the behaviour of the accumulation mode particle concentration, and VMR's above 2 ppb would lead to an overestimation of the increase in N_{acc}/N_{14} . A small increase in number of the accumulation mode particles can be seen even without HNO_3 but not nearly enough to explain the observations.

The increase in the number of haze mode particles is more problematic. It clearly cannot be explained without the influence of HNO_3 . However, even nitric acid is not able to explain all of the observations; with haze mode particles, more than 2 ppb of HNO_3 would be needed to explain a large part of the increase in the haze mode. By adjusting the initial size distribution, the model results could be made to match the observations somewhat better, i.e. a larger increase in haze

mode would be seen at a given nitric acid VMR. However, this would inevitably cause an increase also in the accumulation mode concentration, spoiling the agreement obtained with the size distribution A of Table 1, which is very similar to the distribution measured at $S=0.53$ (see Table 4 in Petzold et al., 2000). Only the number densities of different modes are slightly adjusted to get better agreement with observation data at low saturation ratios.

Petzold et al. (2000) proposed, that their observations could be explained with particles undergoing deliquescence. In Fig. 6 we compare our results for distribution B (see Table 1) containing letovicite to their observations. We have ammonia only in mode 3 because it is likely that the UT air considered here contains an external mixture of aerosol particles: sulfuric acid aerosols formed in situ in the UT, and letovicite containing particles originating from mixing of air that has had contact with the surface. Moreover, like already stated in the Petzold et al. (2000) paper, the accumulation mode particles behave as if they are $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ droplets. The increase in haze mode particle concentration fits the measurements better than with distribution A. This is because with proper selection of HNO_3 concentration the DRH of letovicite can be adjusted to occur at $S=0.5$. The amount of HNO_3 needed is close to 1 ppb. Without letovicite, 2 ppb of HNO_3 is needed to get as good agreement for the haze mode. After deliquescence, more HNO_3 is partitioned in droplets containing letovicite than in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ droplets. That can be seen by comparing the growth of H_2SO_4 droplets in Figs. 1 and 2.

It can be seen that our equilibrium model predicts too high accumulation mode concentration if we adjust the haze mode concentration behavior within observations. In order to make the letovicite particles to increase the haze mode enough, the letovicite distribution is such that the accumulation mode of distribution B has more particles than that of distribution A already at $S=0.3$ (see Table 1 and Figs. 2 and 4). Growth of the letovicite particles due to the deliquescence and nitric acid uptake from sizes below the accumulation mode is not strong enough to bring them directly to the haze mode as deliquescence takes place. Growth factors over 2 (up to 3) would be needed for particles undergoing deliquescence to explain the observations, whereas for letovicite the growth factor (including the uptake of HNO_3) is only 1.65 (see Fig. 2). The GF could be different if the ammonium to sulfate ratio was different from that of letovicite and thus the assumption of a fixed composition can produce some uncertainty into our analysis.

However, discussing the agreement between observations and modeling results should consider the random-type nature of the observations as presented by Petzold et al. (2000). The data were obtained by compiling all observations in the upper free troposphere during the POLSTAR 2 experiment. In the case of high ozone concentrations > 220 ppb and simultaneously observed low relative humidities $\leq 20\%$ data were identified as from the lower stratosphere and were excluded.

In total, 40% of the data originate from drier air masses with $S \leq 0.45$, 15% originate from air masses close to ice saturation with $S \sim 0.50$, and the remaining 45% originate from humid air masses above ice saturation with $S \geq 0.55$. Hence, the air masses close to ice saturation are not equally represented compared to more dry and more humid air masses, respectively. Additionally, no Lagrangian flights with the focus on particle formation and growth were performed during POLSTAR 2. The gap between the accumulation mode and the haze mode which occurs in the model results compared to the observations, is likely to be explainable by the missing information for air masses around ice saturation. The size distributions A and B used for the modeling studies are both likely to occur compared to the observed average number density of $\sim 1 \text{ cm}^{-3}$ for particles in the size range $0.37 \mu\text{m} < D < 0.72 \mu\text{m}$. Hence, the observations do not allow for an unambiguous preference for one of the selected size distributions.

In order to examine the likelihood that enhanced HNO₃ concentrations and ammoniated aerosols were actually present in the air masses encountered during the POLSTAR 2 flights, trajectory analysis was done. Measured data were sorted according to the related ozone level for separating tropospheric and stratospheric air masses. To obtain a similar separation for trajectory data, the potential vorticity scaled by atmospheric pressure was used. The analysed data suggest a clear separation of mainly tropospheric from mainly stratospheric air at a value of 300–400 scaled PV units. For all mission flights when haze mode events were observed, the trajectories indicate a lifting of tropospheric air parcels during the past 10 to 12 days prior to the measurement. The origin of these tropospheric air masses varies between 14 and 37 deg. N and 85 to 118° E, i.e. from the Eurasian continent. Figure 7 shows an example for mission flight 1. Blue symbols indicate $PV < 300$ a.u. while black symbols indicate $PV > 300$ a.u.. Summarising, the trajectory data analysis supports the assumption that air masses close to the polar tropopause can be influenced by boundary layer air masses from lower latitudes and can thus carry chemical species of continental origin.

As reported by Krämer et al. (2003), the VMR of HNO₃ during the POLSTAR 2 experiment was on the order of 0.5 ppb. During the flight M3 of POLSTAR 2, the VMR of HNO₃ varied between 0.2 and 0.9 ppb (green stars in our Figs. 5 and 6, see fig 1 of Krämer et al. (2003)). The model results for the accumulation mode are in good agreement with the HNO₃ observations. Without overrating the observations, they also support the model results which indicate a considerable growth of an upper tropospheric haze mode in the presence of sufficient HNO₃.

6 Conclusions

We have shown that uptake of nitric acid by upper tropospheric aerosols causes notable increases in haze mode particle concentrations at relative humidities above 50%. At a relative humidity of 75%, a few tenths of a ppb of HNO₃ is enough to have an effect when the aerosol is composed of pure sulfuric acid. The presence of letovicite can substantially enhance the nitric acid effect, decreasing the threshold to about 0.1 ppb, and causing a severalfold increase in the haze mode concentrations at a given HNO₃ concentration. Our equilibrium calculations indicate that uptake of nitric acid by sulfuric acid aerosol may at least partially explain the observed increases of upper tropospheric haze- and accumulation mode particles at relative humidities above 50%. A letovicite mode improved the agreement between calculations and observations somewhat. The required HNO₃ levels were on the order of 1–2 ppb with sulfuric acid particles and 0.5–1 ppb when the letovicite mode was present.

Acknowledgements. We thank S. L. Clegg for providing us with a computer code of the AIM thermodynamic model. The trajectory analysis within POLSTAR 2 was conducted by Raimond Alfier from Meteorologisches Institut der Freien Universitaet Berlin. This study was supported by the Academy of Finland.

Edited by: S. Martin

References

- Carslaw, K. S., Peter, T., and Clegg, S. L.: Modeling the composition of liquid stratospheric aerosols, *Rev. Geophys.*, 35, 125–154, 1997.
- Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: A thermodynamic model of the system at tropospheric temperatures, *J. Phys. Chem. A*, 102, 2137–2154, 1998.
- Del Guasta, M., Morandi, M., Stefanutti, L., Balestri, S., Kyrö, E., Rummukainen, M., Kivi, R., Rizzi, V., Stein, B., Wedekind, C., Mielke, B., Matthey, R., Mitev, V., and Douard, M.: Lidar observations of spherical particles in a -65° cold cirrus observed above Sodankylä (Finland) during S.E.S.A.M.E, *J. Aerosol Sci.*, 29, 357–374, 1998.
- Jacobson, M. Z.: *Fundamentals of Atmospheric Modeling*, Cam. Univ. Press, 1999.
- Kärcher, B. and Solomon, S.: On the composition and optical extinction of particles in the tropopause region, *J. Geophys. Res.*, 104, 27 441–27 459, 1999.
- Kokkola, H., Romakkaniemi S., and Laaksonen A.: Köhler theory for a polydisperse droplet population in the presence of a soluble trace gas, and an application to stratospheric STS droplet growth, *Atmos. Chem. Phys.*, 3, 2139–2146, 2003.
- Koop, T., Luo, B., Tsias, A., and Peter, T.: Water activity as the determinant for homogenous ice nucleation in aqueous solutions, *Nature*, 406, 611–614, 2000.
- Krämer, M., Beuermann, J., Schiller, C., Grimm, F., Arnold F., Peter, Th., Meilinger, S., Meier, A., Hendricks, J., Petzold, A., and Schlager, H.: Nitric acid partitioning in cirrus clouds: a syn-

- opsis based on field, laboratory and model studies, *Atmos. Chem. Phys. Discuss.*, 3, 413–443, 2003.
- Laaksonen, A., Hienola, J., Kulmala, M., and Arnold, F.: Supercooled cirrus cloud formation modified by nitric acid pollution of the upper troposphere, *Geophys. Res. Lett.*, 24, 3009–3012, 1997.
- Lin, J. S. and Tabazadeh, A.: The effect of nitric acid uptake on the deliquescence and efflorescence of binary ammoniated salts in the upper troposphere, *Geophys. Res. Lett.*, 29, 1261–4, 2002.
- Martin, E., George, C., and Mirabel, P.: Densities and surface tensions H₂SO₄/HNO₃/H₂O solutions, *Geophys. Res. Lett.*, 27, 197–200, 2000.
- Murphy D. M., Thomson, D. S., and Mahoney, M. J.: In situ measurements of organics, meteoritic material, mercury, and other elements in aerosols at 5 to 19 km, *Science*, 282, 1664–1669, 1998.
- Petzold, A., C. Hoell, C., Kärcher, B., Beuermann, J., Schiller, C., Ziereis, H., and Schlager, H.: In situ observations of aerosol properties above ice saturation in the polar tropopause region, *J. Geophys. Res.*, 105, 29 387–29 395, 2000.
- Sassen K., Arnott, W. P., Barnett, J. M., and Aulenbach, S.: Can cirrus clouds produce glories, *Appl. Opt.*, 37, 1427–1433, 1998.
- Sheridan, P. J., Brock, C. A., and Wilson, J. C.: Aerosol particles in the upper troposphere and lower stratosphere: elemental composition and morphology of individual particles in northern midlatitudes, *Geophys. Res. Lett.*, 21, 2587–2590, 1994.
- Tabazadeh, A., Turco, R. P., and Jacobson, M. Z.: A model for studying the composition and chemical effects of stratospheric aerosols, *J. Geophys. Res.*, 99, 12 897–12 914, 1994.
- Xu, L., Okada, K., Iwasaka, Y., Hara, K., Okuhara, Y., Tsutsumi, Y., and Shi, G.: The composition of individual aerosol particle in the troposphere and stratosphere over Xianghe (39.45° N, 117.0° E), *Atmos. Environ.*, 35, 3145–3153, 2001.