



**HAL**  
open science

## Growth of upper tropospheric aerosols due to uptake of HNO<sub>3</sub>

S. Romakkaniemi, H. Kokkola, A. Petzold, A. Laaksonen

► **To cite this version:**

S. Romakkaniemi, H. Kokkola, A. Petzold, A. Laaksonen. Growth of upper tropospheric aerosols due to uptake of HNO<sub>3</sub>. Atmospheric Chemistry and Physics Discussions, 2004, 4 (1), pp.121-140. <hal-00300868>

**HAL Id: hal-00300868**

**<https://hal.science/hal-00300868v1>**

Submitted on 18 Jun 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

**Uptake of HNO<sub>3</sub> on  
UT aerosols**

S. Romakkaniemi et al.

# Growth of upper tropospheric aerosols due to uptake of HNO<sub>3</sub>

S. Romakkaniemi<sup>1</sup>, H. Kokkola<sup>1</sup>, A. Petzold<sup>2</sup>, and A. Laaksonen<sup>1</sup>

<sup>1</sup>University of Kuopio, Department of Applied Physics, Kuopio, Finland

<sup>2</sup>Deutsches Zentrum für Luft und Raumfahrt Oberpfaffenhofen, Institut für Physik der Atmosphäre, Wessling, Germany

Received: 24 October 2003 – Accepted: 16 December 2003 – Published: 7 January 2004

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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 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  $\text{HNO}_3$  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. This is mainly 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  $\text{HNO}_3$  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  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  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  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosols can effectively take up  $\text{HNO}_3$  and turn into supercooled ternary solutions before freezing homogeneously (Tabazadeh et al., 1994; Kärcher and Solomon, 1999). Uptake of  $\text{HNO}_3$  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.

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

## Uptake of $\text{HNO}_3$ on UT aerosols

S. Romakkaniemi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

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 HNO<sub>3</sub> 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 (NH<sub>4</sub>)<sub>3</sub>H(SO<sub>4</sub>)<sub>2</sub>. The DRH of letovicite is normally 87% at 210 K, but the presence of 2 ppb HNO<sub>3</sub> can decrease it down to 43%. The highest observed volume mixing ratios (VMR's) of HNO<sub>3</sub> 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 HNO<sub>3</sub> concentrations in the UT. In the future, increased air traffic and/or increased NO<sub>x</sub> 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.

In this study, 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 HNO<sub>3</sub> 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. We also calculate the HNO<sub>3</sub>-dependent DRH of letovicite. As a case study, equilibrium calculations are compared with the observations of Petzold et al. (2000).

**Uptake of HNO<sub>3</sub> on UT aerosols**

S. Romakkaniemi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

## 2. Theory

The equilibrium saturation ratio  $S_i$  of vapor  $i$  over a multicomponent droplet surface is obtained from

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

5 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  $i$ ,  $\sigma$  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 HNO<sub>3</sub>. At normal tropospheric conditions, Eq. (1) can be used for water as is, but the amount of HNO<sub>3</sub> 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 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 H<sub>2</sub>O and HNO<sub>3</sub> 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). Equations (2) are thus used to calculate the equilibrium size and the composition of aerosols in each size class as

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

## Uptake of HNO<sub>3</sub> on UT aerosols

S. Romakkaniemi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

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 HNO<sub>3</sub> in size class  $b$

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

Now we have two equilibrium equations for every size class, Eq. (1) for water and Eq. (4) for HNO<sub>3</sub>. These equations are iterated one size class at 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).

During the iteration we also calculate the saturation ratio of liquid phase 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 H<sub>2</sub>O and HNO<sub>3</sub> over the solution droplets and the saturation ratio of liquid phase 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 H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O-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 mode to consist of droplets larger than  $0.72 \mu\text{m}$  in diameter. Both  $\text{H}_2\text{SO}_4$  and  $\text{NH}_3$  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 that reported in the article of Petzold et al. (2000). The dry 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  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ -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. $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$

In Fig. 1a we present growth curves for distribution A at 3 different  $\text{HNO}_3$  VMR's as a function of saturation ratio. The growth due to  $\text{HNO}_3$  uptake is clear.

Figure 1b presents growth factors 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  $\text{H}_2\text{O}$  and  $\text{HNO}_3$  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).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

### 3.2. $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$

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 of  $S$  (black lines). It can be seen that with 1 ppb of  $\text{HNO}_3$  the DRH of letovicite is at 47.8%. At that point, the particles instantly take up  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  to maintain equilibrium. The GF due to pure deliquescence is approximately 1.15. The rest of the growth is caused by simultaneous uptake of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$ . The total GF at the DRH is 1.65.

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  $\text{HNO}_3$  content in the aqueous coating. Because of the Kelvin effect, the highest equilibrium concentration occurs on the biggest particles. Smaller particles with a lower  $\text{HNO}_3$  concentration in the liquid layer experience deliquescence at a higher RH.

### 4. Effect of increased $\text{HNO}_3$ and letovicite concentrations on the number of haze particles

From the examination above it is clear that both increased  $\text{HNO}_3$ , 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  $\text{HNO}_3$  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  $\text{HNO}_3$  is absorbed by the droplets to cause a substantial increase in  $N_{\text{haze}}$ . At 75% RH, only 0.1 ppb of nitric acid is needed for a similar effect. This is due to the lowered  $\text{HNO}_3$  vapour pressure over solution droplets and  $\text{HNO}_3$  dependent deliquescence of letovicite. With

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

increasing HNO<sub>3</sub> 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<sup>-3</sup>, but the amount of HNO<sub>3</sub> 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 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 H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O. It seems that an average of less than 1 ppb of HNO<sub>3</sub> is needed to explain the behaviour

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**Uptake of HNO<sub>3</sub> on  
UT aerosols**

S. Romakkaniemi et al.

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<sub>3</sub> but not nearly enough to explain the observations.

5 The increase in the number of haze mode particles is more problematic. It clearly cannot be explained without the influence of HNO<sub>3</sub>. However, even nitric acid is not able to explain all of the observations; with haze mode particles, more than 2 ppb of HNO<sub>3</sub> 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  
10 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.

[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  
15 Table 1) containing letovicite to their observations. The increase in haze mode particle concentration fits the measurements better than with distribution A. This is because with proper selection of HNO<sub>3</sub> concentration the DRH of letovicite can be adjusted to occur at  $S = 0.5$ . The amount of HNO<sub>3</sub> needed is close to 1 ppb. After deliquescence  
20 more HNO<sub>3</sub> is partitioned in droplets containing letovicite than in H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O droplets. That can be seen by comparing the growth of H<sub>2</sub>SO<sub>4</sub> 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  
25 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

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004

particles undergoing deliquescence to explain the observations, whereas for letovicite the growth factor is only 1.65.

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.

As reported by Krämer et al. (2003), the VMR of  $\text{HNO}_3$  during the POLSTAR 2 experiment was of the order of 1 ppb. The model results for the accumulation mode are in good agreement with the  $\text{HNO}_3$  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  $\text{HNO}_3$ .

---

**Uptake of  $\text{HNO}_3$  on  
UT aerosols**S. Romakkaniemi et al.

---

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

## 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  $\text{HNO}_3$  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  $\text{HNO}_3$  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  $\text{HNO}_3$  levels were on the order of 0.5–2 ppb.

*Acknowledgements.* We thank S. L. Clegg for providing us with a computer code of the AIM thermodynamic model. This study was supported by the Academy of Finland.

## References

- Carslaw, K. S., Peter, T., and Clegg, S. L.: Modeling the composition of liquid stratospheric aerosols, *Rev. Geophys.*, 35, 125–154, 1997. [126](#)
- 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. [125](#)
- Del Guasta, M., Morandi, M., Stefanutti, L., Balestri, S., Kyrö, E., Rummukainen, M., Kivi, R., Rizi, V., Stein, B., Wedekind, C., Mielke, B., Matthey, R., Mitev, V., and Douard, M.: Lidar observations of spherical particles in a  $-65^\circ$  cold cirrus observed above Sodankylä (Finland) during S.E.S.A.M.E, *J. Aerosol Sci.*, 29, 357–374, 1998. [123](#)
- Jacobson, M. Z.: *Fundamentals of Atmospheric Modeling*, Cam. Univ. Press, 1999. [125](#)
- 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. [122](#)

## Uptake of $\text{HNO}_3$ on UT aerosols

S. Romakkaniemi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

**Uptake of HNO<sub>3</sub> on  
UT aerosols**

S. Romakkaniemi et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Print Version

Interactive Discussion

© EGU 2004

- 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. [124](#)
- 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. [126](#)
- 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 synopsis based on field, laboratory and model studies, *Atmos. Chem. Phys. Discuss.*, 3, 413–443, 2003. [130](#)
- 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. [123](#)
- Lin, J. S. and Tabazadeh, A.: The effect of nitric acid uptake on the deliquescence end efflorescence of binary ammoniated salts in the upper troposphere, *Geophys. Res. Lett.*, 29, 1261–4, 2002. [123](#)
- Martin, E., George, C., and Mirabel, P.: Densities and surface tensions H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>/H<sub>2</sub>O solutions, *Geophys. Res. Lett.*, 27 197–200, 2000. [125](#)
- 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. [122](#)
- 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, 29387–29395, 2000. [122](#), [123](#), [126](#), [128](#), [129](#), [130](#), [139](#), [140](#)
- Sassen K., Arnott, W. P., Barnett, J. M., and Aulenbach, S.: Can cirrus clouds produce glories, *Appl. Opt.*, 37, 1427–1433, 1998. [123](#)
- 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. [122](#)
- 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. [122](#)
- 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. [122](#)

## Uptake of HNO<sub>3</sub> on UT aerosols

S. Romakkaniemi et al.

**Table 1.** Parameters for log-normal distributions used in the calculations. In dist B the mode 3 is composed of letovicite with sulfuric acid coating.

dist	property	mode 1	mode 2	mode 3
A	$N$ [cm <sup>-3</sup> ]	112.0	0.1	
	$D_{pg}$ [μm]	0.053	0.518	
	$\sigma_g$	1.70	1.35	
B	$N$ [cm <sup>-3</sup> ]	112.0	0.1	1.25
	$D_{pg}$ [μm]	0.050	0.518	0.270
	$\sigma_g$	1.70	1.35	1.30

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[I◀](#)
[▶I](#)
[◀](#)
[▶](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Print Version](#)
[Interactive Discussion](#)

## Uptake of HNO<sub>3</sub> on UT aerosols

S. Romakkaniemi et al.

**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 <sup>-3</sup> ]			$D_{pg}$ [μm]			$\sigma_g$		
	1	2	3	1	2	3	1	2	3
C <sub>1</sub>	99	-	1	0.05	-	0.27	1.7	-	1.3
C <sub>2</sub>	98	-	2	0.05	-	0.27	1.7	-	1.3
C <sub>3</sub>	97	-	3	0.05	-	0.27	1.7	-	1.3
C <sub>5</sub>	95	-	5	0.05	-	0.27	1.7	-	1.3
C <sub>10</sub>	90	-	10	0.05	-	0.27	1.7	-	1.3
D <sub>0</sub>	100	0.1	0	0.05	0.50	0.20	1.7	1.35	1.3
D <sub>1</sub>	99	0.1	1	0.05	0.50	0.20	1.7	1.35	1.3
D <sub>2</sub>	98	0.1	2	0.05	0.50	0.20	1.7	1.35	1.3
D <sub>3</sub>	97	0.1	3	0.05	0.50	0.20	1.7	1.35	1.3
D <sub>5</sub>	95	0.1	5	0.05	0.50	0.20	1.7	1.35	1.3
D <sub>10</sub>	90	0.1	10	0.05	0.50	0.20	1.7	1.35	1.3

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

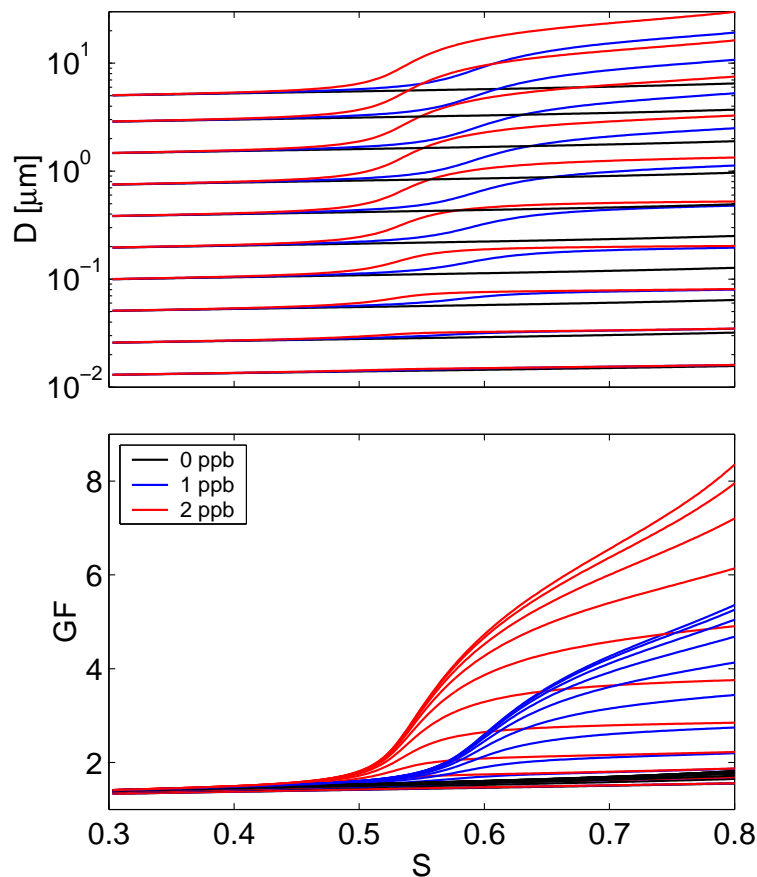
Full Screen / Esc

Print Version

Interactive Discussion

Uptake of  $\text{HNO}_3$  on  
UT aerosols

S. Romakkaniemi et al.



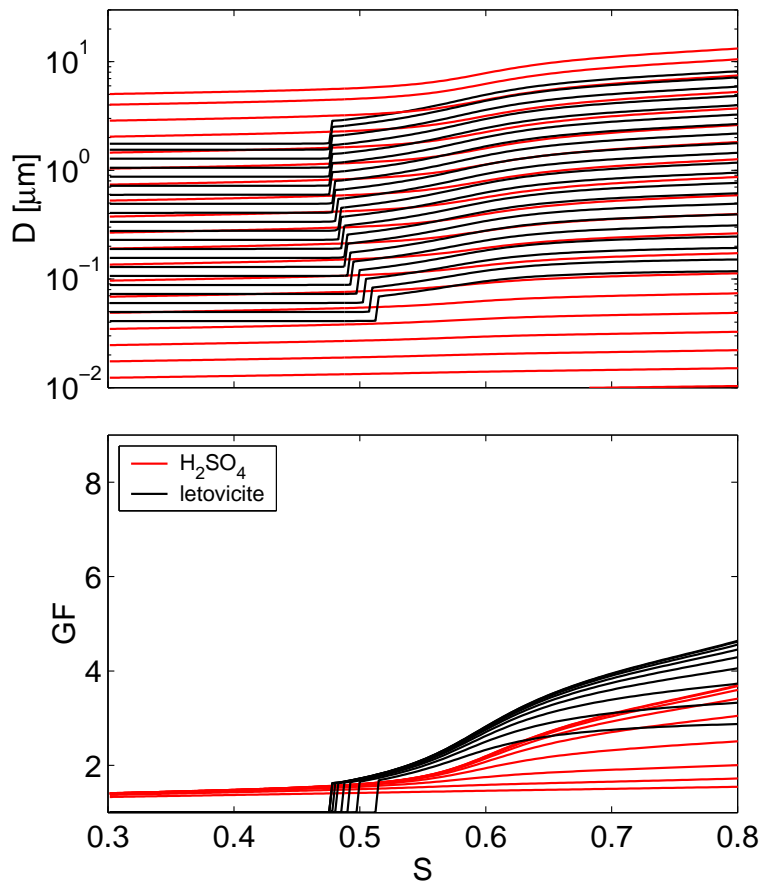
**Fig. 1.** (a) Growth curves for different size classes according to dist A in Table 1. (b) Growth factors for different size classes for the same distribution.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004

Uptake of  $\text{HNO}_3$  on  
UT aerosols

S. Romakkaniemi et al.



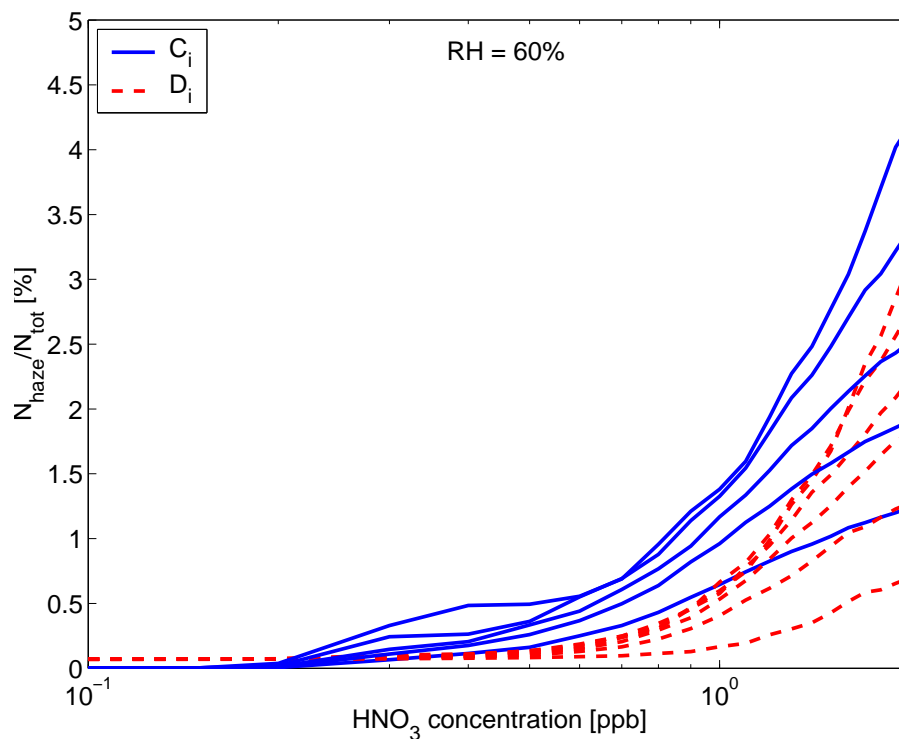
**Fig. 2.** (a) Growth curves and (b) growth factors for different size classes according to dist B in Table 1.  $\text{HNO}_3$  VMR is 1 ppb.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004

Uptake of  $\text{HNO}_3$  on  
UT aerosols

S. Romakkaniemi et al.



**Fig. 3.** Number concentration ratio  $N_{\text{haze}}/N_{\text{tot}}$  as a function of  $\text{HNO}_3$  concentration at 60% RH. 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.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004

Uptake of  $\text{HNO}_3$  on  
UT aerosols

S. Romakkaniemi et al.

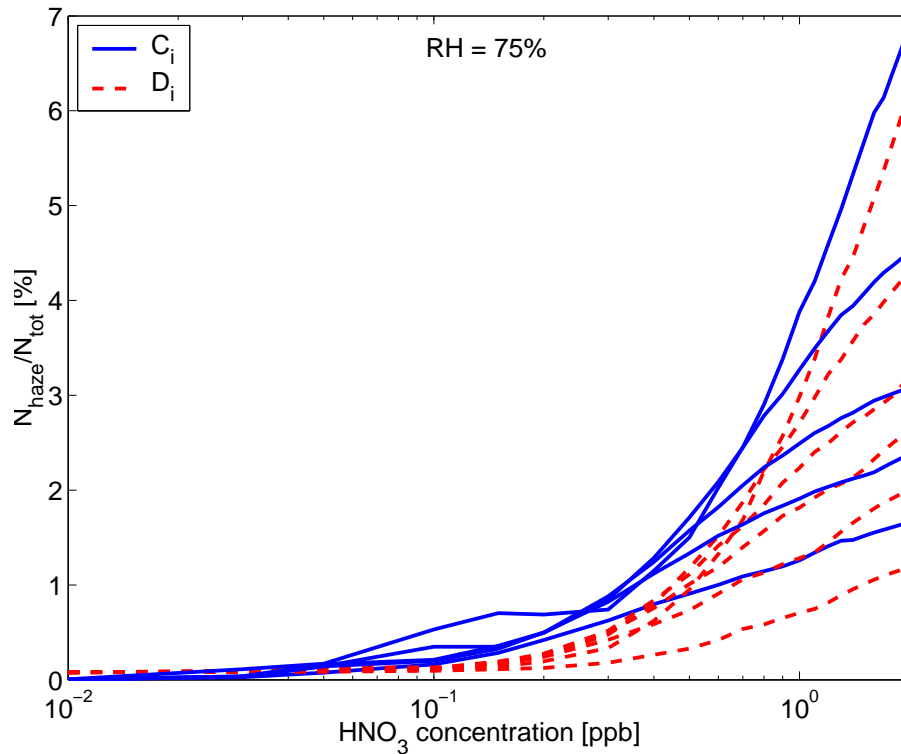


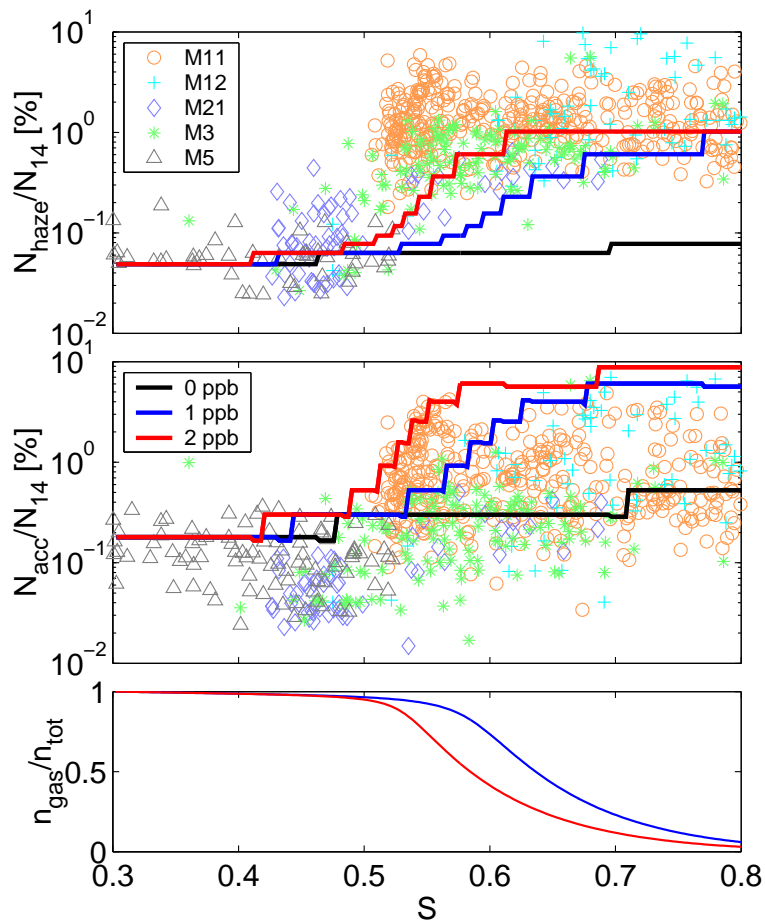
Fig. 4. Like Fig. 3 but RH is now 75%.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004

Uptake of  $\text{HNO}_3$  on  
UT aerosols

S. Romakkaniemi et al.



**Fig. 5.** Comparison to observations of [Petzold et al. \(2000\)](#) for distribution A at three different  $\text{HNO}_3$  VMR's. See [Petzold et al. \(2000\)](#) for explanations for different symbols representing the observations.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

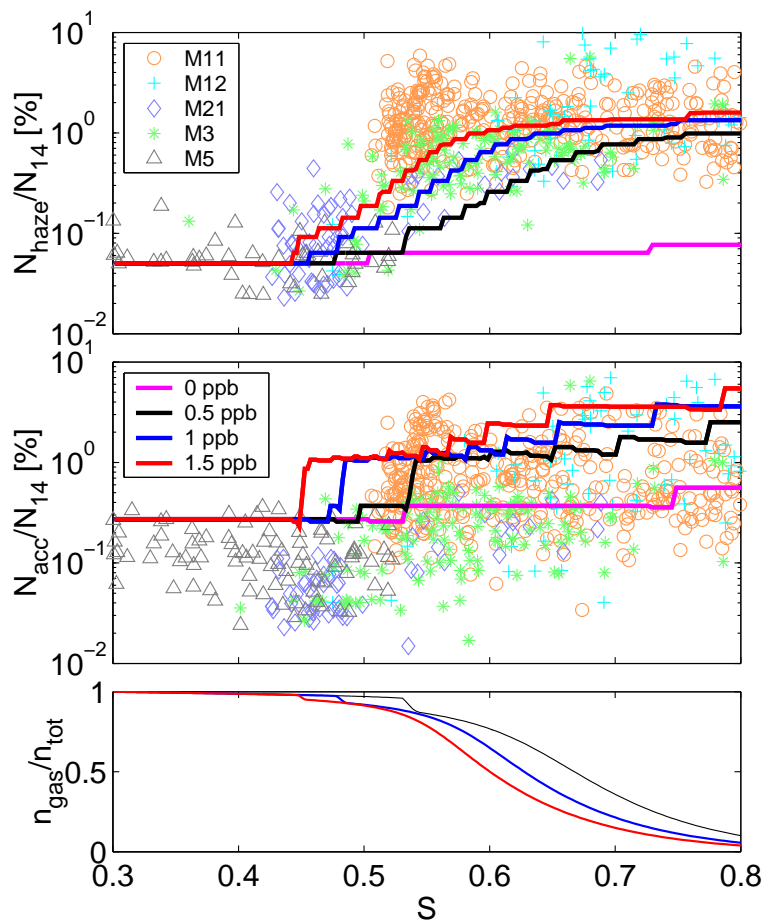
Print Version

Interactive Discussion

© EGU 2004

Uptake of  $\text{HNO}_3$  on  
UT aerosols

S. Romakkaniemi et al.



**Fig. 6.** Comparison to observations of Petzold et al. (2000) for distribution B with four different  $\text{HNO}_3$  concentrations.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)

© EGU 2004