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Discussions

The effect of phase partitioning of semivolatile compounds on the measured CCN activity of aerosol particles

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Phase partitioning of semivolatile compounds in the CCN counter

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Abstract

The effect of inorganic semivolatile aerosol compounds on the CCN activity of aerosol particles was studied by using a computational model for a DMT-CCN counter, a cloud parcel model for condensation kinetics and experiments to quantify the modelled results. Concentrations of water vapour and semivolatiles as well as aerosol trajectories in the CCN column were calculated by a computational fluid dynamics model. These trajectories and vapour concentrations were then used as an input for the cloud parcel model to simulate mass transfer kinetics of water and semivolatiles between aerosol particles and the gas phase.

Two different questions were studied: (1) how big fraction of semivolatiles is evaporated from particles before activation in the CCN counter? (2) How much the CCN activity can be increased due to condensation of semivolatiles prior to the maximum water supersaturation in the case of high semivolatile concentration in the gas phase?

The results show that, to increase the CCN activity of aerosol particles, a very high gas phase concentration (as compared to typical ambient conditions) is needed. We used nitric acid as a test compound. A concentration of several ppb or higher is needed for measurable effect. In the case of particle evaporation, we used ammonium nitrate as a test compound and found that it partially evaporates before maximum supersaturation is reached in the CCN counter, thus causing an underestimation of CCN activity. The effect of evaporation is clearly visible in all supersaturations, leading to an underestimation of the critical dry diameter by 10 to 15 nanometres in the case of ammonium nitrate particles in different supersaturations. This result was also confirmed by measurements in supersaturations between 0.1 and 0.7 %.

1   Introduction

Atmospheric aerosol particles are composed of a large variety of chemical compounds. Some of these can be considered to be nonvolatile meaning their vapour pressure is so low that, in practice, they are always found from the particle phase. The other group of compounds found from particles is semivolatile. Depending on conditions such as temperature and relative humidity, these compounds may exist in a gas, liquid, or solid particle phase. In the case of aqueous droplets, the partitioning between phases depends on the effective Henry's law coefficient that can be determined from liquid phase thermodynamics.

According to Köhler theory, which describes how droplet equilibrium size changes as a function of water vapour saturation ratio, the ability of a single aerosol particle to form cloud droplet at some supersaturation is mainly dependent on the amount and type of soluble material present in the particle (Köhler, 1936). Later, the Köhler theory was modified to take into account the semivolatile gases present at trace-level concentrations in the atmosphere, and they have been found to affect the CCN activity of aerosol particles (Laaksonen et al., 1998; Kokkola et al., 2003a; Topping and McFiggans, 2012). Several modelling studies have shown that acidic gases, like nitric acid and hydrochloric acid, may increase the amount of solute in the liquid aerosol particles prior to cloud droplet formation and thus enhance their ability to form cloud droplets (Kulmala et al., 1993; Nenes et al., 2002; Xue and Feingold, 2004; Romakkaniemi et al., 2005). This effect is further enhanced by the presence of a base gas, like ammonia, that neutralizes the liquid solutions, allowing the uptake of both acid and base at a lower relative humidity (Hegg, 2000; Kokkola et al., 2003a; Romakkaniemi et al., 2005b). Although the ability of nitric acid to enhance activation has been theoretically shown (Laaksonen et al., 1998), and its potential to affect cloud droplet number concentrations on global scale has been also modelled (Makkonen et al., 2012; Xu and Penner, 2012), the effect is not yet quantitatively addressed by measurements. Some observational evidence exists that nitric acid can cause the formation of large droplets

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at subsaturated air (Ma et al., 2010; Henin et al., 2012), as postulated by Kulmala et al. (1997).

The CCN activity of atmospheric aerosols can be measured using the so-called CCN counters (CCNc), where aerosol particles are exposed to known water vapour supersaturation and the activated droplets grown to micrometre sizes are counted optically. Usually, with these instruments, it is assumed that only water is condensing on particles. In this study, we show that Droplet Measurement Technologies (DMT) CCN counters (Roberts and Nenes, 2005) can be used to assess the effect of nitric acid on aerosol CCN activity. Nitric acid was chosen as it is abundant in the atmosphere with concentrations up to several ppb, and its effect on cloud droplet formation is modelled in several publications (e.g. Kulmala et al., 1993; Laaksonen et al., 1998; Nenes et al., 2002, Romakkaniemi et al., 2005). HNO_3 has a Henry law coefficient of $2.1 \times 10^5\,mol\,kg^{-1}\,atm^{-1}$ at room temperature. After uptake, the acid is quickly dissociated in water to form hydrogen and nitrate ions. The degree of dissociation, which eventually controls the amount of acid dissolved in the aqueous phase, is influenced by other ions present. For this, the effect of nitric acid on cloud droplet formation is weaker for particles with acidic non-volatile compounds (e.g. sulphuric acid) than for more neutral particles (e.g. ammonium sulphate).

Beyond the enhancement in CCN activity due to the condensation of semivolatile compounds, we also studied how the possible evaporation of semivolatile compounds from droplets decreases their CCN activity. It has been shown that compounds like ammonium nitrate and ammonium chloride partly evaporate in the HTDMA-system, thus decreasing their apparent hygroscopicity (e.g. Hu et al., 2010). We expect similar evaporation to take place also in the CCN counter (seen already by Asa-Awuku et al., 2009), where the typical residence time before the maximum supersaturation is reached is between 2 to 4 s.

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2 Methods

In the atmosphere, the effect of semivolatile compounds on cloud droplet formation is dependent on the Henry's law coefficient of the condensable, number of particles present, and time available for condensation before the activation into cloud droplets.
⁵ In the Droplet Measurement Technologies (DMT) Continuous Flow Streamwise Thermal Gradient Chamber (CFSTGC, Roberts and Nenes, 2005), we also have to take account the wetted walls, which act not only as a source for water vapour but also as a sink for semivolatile compounds. To take account of this, we have updated the most recent version of the CFSTGC model (Raatikainen et al., 2012) to also include
¹⁰ semivolatile gases. With the augmented CCN counter-model, we are able to calculate trajectories for aerosol particles inside the CCN column, and these trajectories are used to drive the air parcel model to simulate the condensation/evaporation of different compounds on/off the particles. The air parcel model (Kokkola et al., 2003b; Romakkaniemi et al., 2009) contains an aqueous-phase thermodynamics module and can more ac-
¹⁵ curately simulate droplet activation compared to what exists in the CFSTGC model. In the following, the methods and models used are described in more detail.

2.1 Experiments

The operation principle of the DMT CFSTGC is presented here briefly and presented in detail by Roberts and Nenes (2005) and Lance et al. (2006). In the instrument sheath
²⁰ and aerosol sample flows are introduced into the top of a cylindrical vertical tube so that sample flow will stay close to the chamber centreline. In the direction of flow, the positive thermal gradient is maintained on the wetted walls; supersaturation is formed owing to the rapid diffusion of the water, compared to heat, on the centerline and particles having lower critical supersaturation will activate to form cloud droplets. The cloud
²⁵ droplets that form are counted at the exit of the chamber by an optical particle counter. The supersaturation in the column will determine the smallest particle size that can

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activate. Usually, this size is referred as critical (dry) particle size, and it depends on the composition of particle.

Our experimental setup consisted of an atomizer (TSI 3076), followed by a diffusion drier, Vienna type DMA (length 28 cm, inner radius 25.0 mm, and outer radius 33.0 mm) and the DMT-CCNc described above. Particles generated in the atomizer were dried, classified in the DMA (operating at a sheath:aerosol ratio of 10 : 1 with both sheath and excess flows set at 10 L min^{-1}). To minimize volatilization of the dried particles, the distance between DMA and CCN counter was kept as short as possible ($\sim$ 0.3 s). Critical dry size in different supersaturations was determined by changing the particle size with DMA and keeping the supersaturation constant in the CCN column. Activation curves were corrected to take into account multiple charging in the DMA, and the critical dry size was determined as a size where 50 % of particles activated (diameter commonly referred a D50). This was repeated for supersaturations between 0.1 and 0.8 %.

2.2 CCNc model

The CCN counter model calculates flow velocity fields and distributions of temperature, pressure, water vapour, and semivolatile gases in the CCN column using known boundary conditions such as sheath and sample flow rates, column top temperature, sample flow pressure, and calibrated maximum supersaturation. Aerosol trajectories are calculated from the velocity fields, and these, with related gas phase concentrations and temperature profiles, are saved to be used in the cloud parcel model. The current model version is based on the original instrument model of Lathem and Nenes (2011), later updated by Raatikainen et al. (2012). An additional section similar to that of water vapour was added to the model for the semivolatile gas, which is here either ammonia or nitric acid. The only sources for the semivolatile gases are sheath and sample flows at the inlet, and the wet chamber walls are a sink. For moderate semivolatile gas concentrations, the water flow rate at the chamber wall is large enough to absorb all the gas. Similarly, when using moderate aerosol concentrations ($<$ 3000 cm^{-3}), aerosols are a negligible sink or source for the semivolatile gases, as will be shown later. When

these two assumptions hold, droplet growth can be examined in the detailed cloud parcel model using aerosol trajectories, vapour concentrations, and temperature from the CCNc model.

2.3 Cloud parcel model

To simulate the uptake of water and semivolatile gases on aerosol particles, we are using the cloud parcel model. The model used has been described elsewhere (Kokkola et al., 2003b), and it has been used in several aerosol cloud interaction studies (e.g. Romakkaniemi et al., 2005a, 2011, 2012). Instead of running the model adiabatically, as is usually done, the ambient temperature and gas phase concentrations are fed to model as trajectories in a similar manner as done in Romakkaniemi et al. (2009), where the same model was used with trajectories from Large Eddy Model simulations. We assumed that the mass transfer between particles and gas is not affecting the gas phase concentration. It was also verified that this assumption is not affecting the results. In the model, the differential equations are solved using an ordinary differential equation solver DLSODE (www.netlib.org), which solves initial-value problems for stiff or non-stiff ordinary differential equations using backward differentiation formulae. The liquid phase thermodynamics needed for the calculation of equilibrium vapour pressures is based on a modified version of aerosol equilibrium code EQUISOLV II (Jacobson, 1999).

In the analysis of modelling results, we concentrate on two different applications of the model: the ability of nitric acid to condense on aerosol particles prior to activation into cloud droplets and the possibility of evaporation of semivolatile gases before the activation takes place. The simulations are carried in a way that the aerosol is equilibrated with respect to water in the inlet (no mass transfer of semivolatiles), and, as soon as the aerosol arrives in the CCN column and deliquescence RH is achieved, the mass transfer of semivolatiles and water vapour is allowed.

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3   Results

First, we study and compare the mass transfer timescales for HNO_3. In the CCN column, the supersaturation is usually reached within 2-3 seconds from entrance into the column. As the diffusion coefficient used for HNO_3 is $1.18 \times 10^{-5}\,m^2\,s^{-1}$, mass transfer to the walls is rapid compared to time needed for droplet activation. Figure 1 shows an example of HNO_3 concentration when the HNO_3 concentration is initially 10 ppb in both sample and sheath air. In the upper panel, the concentration is presented for the column half cross section and in the lower panel at the centreline, where the aerosol sample is assumed to stay. It can be seen that, before reaching supersaturation, more than 90 % of HNO_3 is already lost to the walls. Thus, it is clear that a high amount of HNO_3 is needed in the gas phase to see a notable increase in aerosol mass and CCN activity. On the other hand, fast depletion of semivolatiles from gas phase will also enhance the evaporation of these compounds from particles.

To evaluate our model performance, we studied how ammonium nitrate particles evaporate in the CCN column. Here, we assume that ammonia and nitric acid have an inlet concentration of 100 ppt, but, after that, both gases can diffuse to the column walls. The sample aerosol deliquesces soon after arriving to the CCN column, and both ammonia and nitric acid will start evaporating.

In Fig. 2, an example of particle evaporation is shown with particles composed initially of 90 mass % of ammonium nitrate and 10 mass % of ammonium sulphate. As can be expected, the evaporation of HNO_3 and NH_3 (and decrease in the effective dry size) is fastest after the introduction of particles into the column. Droplets are more diluted later in the column, and this decreases the evaporation. The mass fraction evaporated before the activation is dependent on the size of the original particle. In the example, the smallest particle has already lost 58 % of the initial dry volume before S reaches unity and 85 % before the maximum supersaturation. For the smallest size still activating, the corresponding values are 30 and 36 %. However, as can be seen from Fig. 2, the particles continue to lose matter even after the supersaturation is reached.

How much semivolatiles evaporate (and thus decrease the measured hygroscopicity) before the column maximum supersaturation is achieved depends on the time (location of the maximum supersaturation), size, concentration of particles, and gas phase concentration. We have studied this by doing simulations using 100 ppt concentration of both gases in the sample and sheath air, and changing the supersaturation. The 100 ppt is a reasonable concentration for background air, but the effect on evaporation rates is small because this concentration is well below the equilibrium value. We also performed laboratory experiments by using a DMT CCN counter (Roberts and Nenes, 2005; Lance et al., 2006). In the experiment, ammonium nitrate particles were created and their critical dry diameters were measured as a function of supersaturation. In the experiments, the aerosol concentration was $\sim 500\,cm^{-3}$ after the DMA. Figure 3 shows the experimental and simulated (with and without evaporation) critical particle dry sizes as a function of supersaturation. The red curve would give expected D50 if there were no evaporation of nitric acid and, in the case of the blue curve, the evaporation is taken into account. The simulation results show that the evaporation in the CCN column is leading to a 10 to 15 nm reduction in the effective dry size with particles having the initial size between 40 and 120 nm. Thus, it should be detectable for all supersaturations, but the effect is relatively stronger in high supersaturation where particle size is smaller. This happens mainly because small particles are able to follow their equilibrium size more closely than the larger ones, as their surface-to-volume ratio is higher, and thus they are losing ammonia and nitrate more quickly. The laboratory experiments are in good agreement with the simulations accounting for ammonium nitrate evaporation. The model overestimates the change in effective dry size due to evaporation on average by 1.9 nm, meaning a 16 % relative difference.

Next, we study with the model how the condensation of nitric acid from gas phase could enhance particle activation. In Fig. 4a, the change in critical dry diameter is presented as a function of HNO_3 concentration for nine different aerosol compositions. Both sample and sheath air are assumed to have the same gas phase concentration, and the maximum supersaturation in the counter is 0.2 %. Ammonia is also assumed

nonvolatile; this is justified by the large excess of HNO_3. Different red lines show how the ratio of soluble to insoluble matter affects the HNO_3 potential by considering ammonium sulphate as soluble with mass fractions of 1, 10, 50 and 100 %, with the rest being insoluble. As can be seen, the nitric acid effect is practically independent of the soluble mass fraction. Also, the effect becomes notable when the concentration in inlet is few ppb, but ~ 13 ppb concentration is needed to get over a 10 % reduction in critical dry diameter. To examine the HNO_3 effect on measured aerosol hygroscopicity, we can use the equation

$$\kappa = \frac{4\,A^3}{27\,D_c^3 \ln^2 S_c}, A = \frac{4\,\sigma_w M_w}{R\,T\,\rho_w}, \tag{1}$$

where D_c is the critical dry diameter, S_c is the supersaturation applied in the CCNc, σ_w is surface tension, M_w is mole mass, and ρ_w is water density (Petters and Kreidenweis, 2007). In the equation, critical dry diameter has a power of -3, and thus only a 3 % decrease in the critical dry diameter will lead to ~ 10 % overestimation in the hygroscopicity. As can be seen from Fig. 4b, only 3 ppb of HNO_3 is needed to produce such overestimation in the case of ammonium sulphate and 5 ppb in the case of ideal model aerosol that has no interaction with the condensed acid. For comparison, the theoretical calculation based on Laaksonen et al. (1998) gives a 35 % reduction in critical dry size of ammonium sulphate with 1 ppb of nitric acid, and compared to this the effect seen in CCN counter is much smaller.

Aerosol acidity and hygroscopicity are more important than the mass fraction of soluble compounds. The uptake of nitric acid is instantaneous after the deliquescence of neutral ammonium sulphate leading to a strong increase in measured aerosol hygroscopicity. In the case of more acidic aerosols such as ammonium bisulphate and sulphuric acid, the uptake of HNO_3 is postponed to a higher relative humidity. Also, the increase in measured aerosol hygroscopicity is smaller than in the case of ammonium sulphate. If there is no interaction between the condensed HNO_3 and particle's original components, condensed HNO_3 causes a smaller increase in the hygroscopicity than

for ammonium sulphate. We studied this in more detail by introducing an ideal-model aerosol and varying its hygroscopicity in terms of κ. As can be seen from Fig. 4b, the relative effect of HNO_3 condensation on measured hygroscopicity is not dependent on the original hygroscopicity. With other aerosol components, like NaCl, the Cl^- is re-placed by NO_3^- leading to evaporation of HCl (e.g. Gard et al., 1998). This could cause the measured hygroscopicity to be less than NaCl hygroscopicity. An even more com-plex situation could be with dust containing $CaCO_3$, where CO_3^{2-} could be replaced by $2NO_3^-$ leading to very hygroscopic $Ca(NO_3)$ (e.g. Goodmann et al., 2000).

In the simulations, we have assumed a quite low aerosol number concentration ($100\,cm^{-3}$), and the amount of HNO_3 in the single particle at the time of maximum supersaturation is between 0.05 and 0.15 % of the amount in the gas phase. In Fig. 5, the partitioning and change in the particle phase concentration is presented in more detail in the case of ammonium sulphate. It can be seen that the maximum HNO_3 concentration in the particles is actually achieved before the maximum supersaturation (3.5 and 4.3 s in Fig. 5) and, at that time, the amount of HNO_3 in the particles is only 4 % of total amount. Thus, the system is not sensitive to particle-number concentration with moderate concentrations. However, care must be taken if the results presented are used with high aerosol loading ($> 3000\,cm^{-3}$), and, to get reliable results in such conditions, a more accurate thermodynamic model should be coupled to the CFSTGC model directly. With a higher supersaturation, the fraction of semivolatiles partitioned to particles is even smaller as supersaturation is reached earlier in the column and particles are of smaller size. For example, with 0.8 % supersaturation, the amount of HNO_3 partitioned to a single particle is between 0.007 and 0.02 % of the amount in the gas phase depending on the particle's composition.

Another potential parameter affecting the increase in CCN potential due to semivolatiles is the water vapour supersaturation. This is shown in Fig. 6, where the change in aerosol hygroscopicity due to 10 ppb of HNO_3 is presented as a function of supersaturation for two different types of particles. It can be seen that the nitric acid effect is highest close to 0.2 % supersaturation, decreasing slightly towards higher

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supersaturations. The behaviour is same for both ideal model particles ($\kappa = 0.3$) and ammonium sulphate particles.

In the simulations presented, we have used nitric acid as an example of semivolatile compound that can partition from vapour phase to aerosol particles. The effect seen on particles' CCN activity is naturally dependent on the compounds, and, especially, the Henry's law coefficient. With a lower coefficient, the uptake is postponed and, thus, the enhancement in the CCN activity will get smaller. The opposite will happen when evaporation is considered, and CCN activity will be underestimated. Also, the diffusion coefficient will play some role, and, with larger molecules, the diffusion to walls is slower and thus semivolatiles have more time to condense on particles. However, smaller diffusion coefficient will slow condensation on the particles, and, thus, the total effect is minor compared to the Henry's law coefficient.

4   Conclusions

In this study, we have constructed a model that can be used to study how semivolatile water-soluble compounds, like nitric acid and ammonia, can affect the CCN potential of aerosol particles by condensing on or evaporating of the liquid particles/droplets in the CCN counter. The existing CCN model (designed for the Droplet Measurement Technologies CCN counter) was modified to include diffusion of semivolatile gases from sample flow to chamber walls. The CCN model was used to produce aerosol trajectories inside the CCN column, which were later used as an input for the air parcel model to simulate growth of aerosol particles to cloud droplet sizes.

It is shown that care must be taken when the results from CCN counter experiments are used to study the CCN potential of aerosol particles. The semivolatile concentrations needed to increase the CCN potential of aerosol particles are high but such that they are present in the atmosphere in highly polluted conditions, and inclusion of several other semivolatiles, many of them organics, could affect the results considerably (Topping and McFiggans, 2012; Topping et al., 2013). This is especially im-

portant in laboratory studies, where the concentrations used might be tenfold higher than those found in the atmosphere. However, typical conditions in the atmosphere are such that the concentrations of semivolatile gases are too low to considerably increase the CCN potential and thus affect the CCN studies. In addition, diffusional losses of semivolatile gases within the measurement system are likely to decrease concentrations before actual measurements. The more important effect comes from the evaporation of some semivolatiles before particles reach cloud droplet sizes. The ambient temperature might be clearly lower than the temperature inside the CCN column. High temperature increases volatility and the rate of mass transfer; thus, part of the semivolatiles might be evaporating before cloud droplet activation (e.g. Asa-Awuku et al., 2009). Also, in the CCN counter, semivolatiles are removed from the system and they are not participating in the cloud droplet formation as in the ambient conditions.

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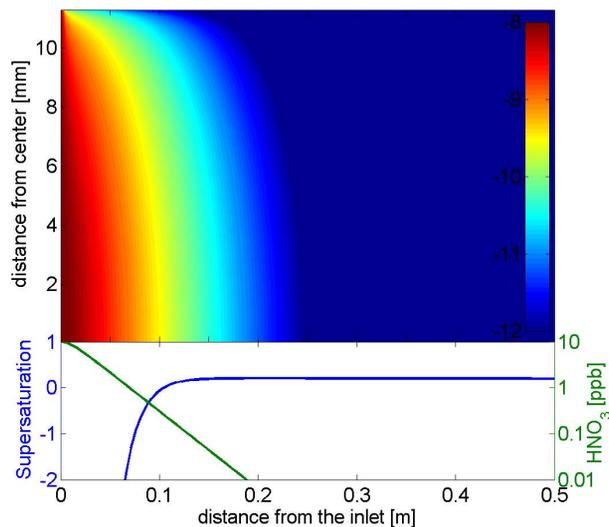
Fig. 1. Nitric acid concentration in the column. The air flow is from left to right and the sample flow is within 2.3 mm from the centre.
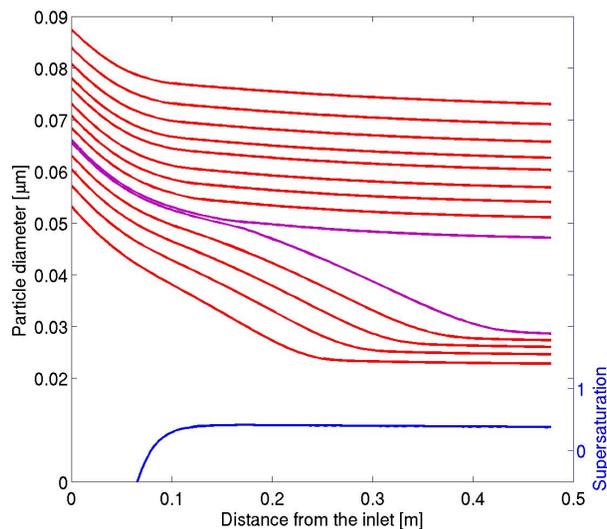
Fig. 2. Effective dry size of particles composed of 90 mass % of ammonium nitrate and 10 mass % of ammonium sulphate as a function of position in the CCN column. Particles closest to the activation size are marked with magenta. The supersaturation is represented by a blue line.
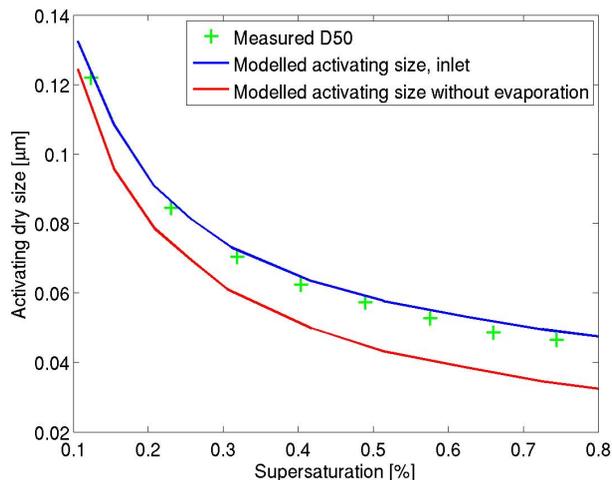
Fig. 3. Size of activating particles in different supersaturations when the evaporation of nitric acid and ammonia is not taken into account (red curve) and when the evaporation is taken into account in the model. The green crosses are measured critical particle dry sizes for ammonium nitrate in different supersaturations.
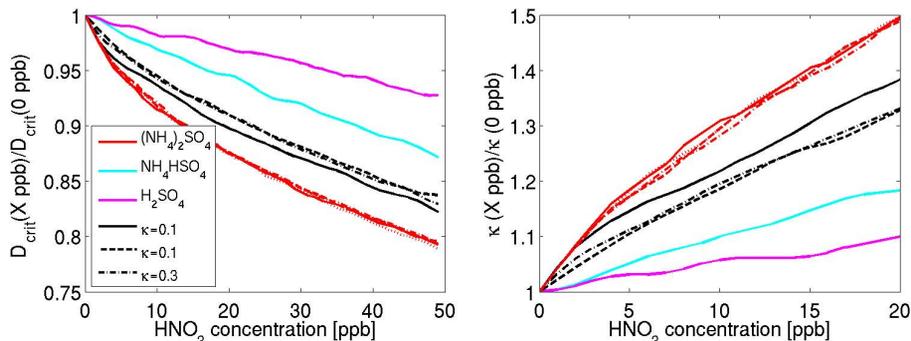
Fig. 4. (a) Relative change in the critical dry diameter (at the supersaturation of 0.2 %) as a function of nitric acid concentration for aerosol having nine different compositions. Critical dry diameters for the case modelled without nitric acid are 81, 106, 184, and 364 nm for the four different ammonium sulphate mass fractions and 80, 77, 148, 117, and 102 nm for the other species presented in the legend. **(b)** Relative change in estimated aerosol hygroscopicity.

Fig. 5. Partitioning of HNO_3 between the gas and particle phase (blue curve) and total HNO_3 concentration in the particles (scaled to give 1 as a maximum) in the case of 0.2 % supersaturation and ammonium sulphate aerosol.

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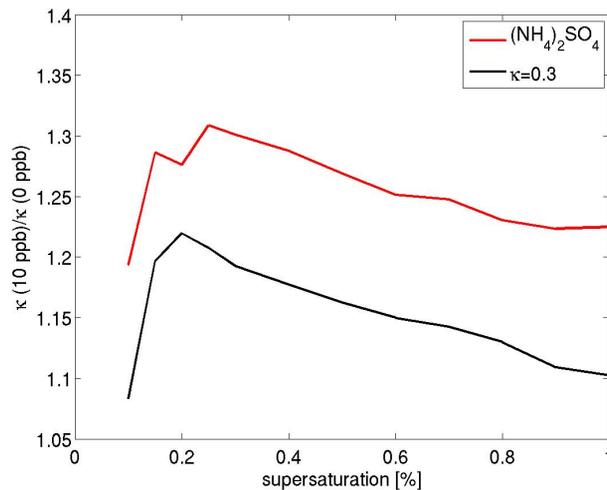
Fig. 6. Change in modelled aerosol hygroscopicity due to 10 ppb of HNO_3 as a function of supersaturation for aerosol composed of ammonium sulphate and model aerosol with the hygroscopicity κ of 0.3.