

Interactive comment on “Parameterization of the nitric acid effect on CCN activation” by S. Romakkaniemi et al.

S. Romakkaniemi et al.

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We thank Referee # 1 for the comments.

The parameterization is relatively complex and not intuitively understandable, and I am curious how it was derived. The authors refer to a previous paper, Laaksonen et al., 1998. Note: this did not appear in J. Atmos. Sci. as stated in the references but in J. Aeros. Sci. instead! Unfortunately this is not available at my institute. I assume this applies to more readers as well. Therefore the authors should definitely elaborate on this.

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We apologize for the wrong reference and we will correct that. We agree that the parameterization is quite complex. The basic form of parameterization is adopted from Laaksonen et al. (1998) paper. They stated that $F = 1 + (F_0 - 1)\exp(-0.5x^{0.6}F_0^2)$, where x is HNO_3 concentration. Our equation (11) is of same form. The origin of the mathematical form is in notion that the F_x vs. F_0 -curves qualitatively resemble vapor-liquid equilibrium curves in some binary systems. The simple yet flexible Van Laar equations can be used to represent the VLE data, and we figured that the same mathematical form could be useful for parameterizing the nitric acid effect.

The parameterization contains a parameter B_c which depends on the composition and has values of 0, 1, and 2 for ammonium sulfate, ammonium bisulfate and sulfuric acid (Table 1). These values do not appear to be related to ion yield, molar weight or density. They could be related with the number of H^+ released, but my guess is that this does not influence the dissolution of strong acids as HNO_3 very much, while the fact that NH_4^+ releases additional H^+ after dissociation is not considered. So, I am curious to see the meaning of B_c . Does this also mean the aerosol has to be externally mixed, i.e., no internal mixtures?

B_c is related to the number of H^+ released and it does influence the dissolution of HNO_3 . Most important this becomes in situations, where the haze mode composed of sea salt exists. The higher the pH of the particles is, the lower is the RH at which HNO_3 starts to condense. So the pH of the pre-existing aerosol particles is important when the partitioning of HNO_3 between different drops is considered. pH is also important if the number of aerosol particles is small. In case of acidic particles, the condensation on drops begins at RH close to 100%, and, if the updraft velocity is not very low, there is not enough time for all the HNO_3 condense before activation occurs.

Naturally if we would like to take everything into account, molar weight and density

would have some bearing, but we found that the number of H⁺ released is more important.

Different modes can have different compositions, so in this sense the aerosol can be externally mixed. Within individual modes the mixing has to be internal.

The parameterization predicts the activated fraction of aerosol particles F . What is this exactly: the fraction of CCN (e.g. at 1%) or fraction of the total aerosol population represented in the parcel model? This is an important difference, but it is not explained. If the latter is the case then it seems that the parameterization reflects specific model characteristics. Example: suppose 200 aerosols from a population of 500 activate, then the fraction is 0.4, and it may be enhanced to 0.5 (250 drops) with a certain amount of HNO₃. $F_x - F_0$ is then 0.1. The total aerosol particle concentration in a cloud parcel model is mainly determined by the smallest aerosol size considered. Decreasing this lower limit means automatically that a larger number of aerosol particles is present, say 800. For simulation of the same cloud, the eventual drop concentration does not change because the smallest aerosol do not activate anyway, but the fraction of activated aerosols is now smaller, $200/800=0.25$, and with HNO₃: $250/800=0.31$. Now, $F_x - F_0$ is 0.06. So this would make the parameterization highly specific and not general applicable. Am I wrong in this interpretation?

The activated fraction means the fraction of the total aerosol population represented in the parcel model. It is true that in the above example, the difference between F_x and F_0 changes but it does not change the fact that 50 more aerosol particles activate. If you look at the shapes of the F_x vs. F_0 -curves (e.g. Fig. 1), the difference $F_x - F_0$ has a maximum close to $F_0 = 0.5$, so in this sense the parametrization has the above effect qualitatively correct: the difference should decrease when F_0 decreases from 0.4. It should also be remembered that we rely on lognormal aerosol modes, thus, if you

increase the number of small particles within a mode, the number of larger particles has to increase in proportion. Of course, one could envision a situation in which no particles from the smaller mode activate, and increasing the number of particles in the smaller mode would then produce the effect described in the example above.

Actually, if the radius of “small added” mode is much smaller than the activating mode, the parameterization underpredicts the activated number. This can be corrected by modifying Eq. (9) in Table 1

$$B_3 = 0.23 \left(\frac{r_{g2} - r_{g1}}{r_{g1}} \right)^{1.05} \left(\frac{N_2 N_1}{N^2} \right)^{0.13} \left(\frac{F_0 N}{N_2} \right) \left(\frac{r_{g2} - r_{g1}}{r_{g1}} \right) \left(\frac{N_2}{N_1} \right)^{1.3}, \quad F_0 < N_2/N$$

This correction improves agreement between model and parameterization in situations envisioned by the referee. It will not change the parameterization in unimodal or marine cases, in which the number of activated drops is usually higher than the number of haze mode drops. We will revise the manuscript accordingly.

With our cloud parcel model we carried out a few experiments on the influence of HNO₃ on activation. The results indicate that the magnitude of the enhancement also depends on the initial relative humidity of the parcel, with which the initial wet aerosol sizes are assumed to be in equilibrium. The relative growth of especially the large aerosols is not fast enough to maintain the equilibrium size during parcel ascent. So the initial RH influences the distribution of initial water over the aerosol and this affects the dissolution of HNO₃ over the aerosol population. Again, do I see this wrong? How is the parcel model initialized and how important is this for the results?

In this study we have equilibrated both water and nitric acid in the beginning of model run. In doing so we have supposed the system to be closed. The initial RH is chosen

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to be so low, that there is no difference in activated number whether the system is equilibrated or not. At temperatures above about 260K it suffices that the equilibration RH is 95 %.

The aerosol matter is ammonium (bi) sulfate or sulfuric acid. In present day aerosol-climate models sometimes more aerosol species are considered (seasalt, organics, dust). Would the parameterization still be applicable here; would it be easy to adapt for such models?

Seasalt is included in the parameterization and dust as well as water-insoluble organics can be represented using the insoluble fraction of aerosol particles which is included in the parametrization. Water soluble organics are much more complicated. At the moment there is no publications about the simultaneous effect of nitric acid and organics on aerosol activation and so it would be somewhat speculative to give statements about the applicability of our new parameterization with water soluble organics.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 7859, 2004.

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