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Atmospheric
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Discussions

Interactive comment on "Modelling of nitrate particles: importance of sea salt" *by* G. Myhre and A. Grini

G. Myhre and A. Grini

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General The paper describes an interesting experiment on nitrate formation on the global scale. Altough the subject is of general interest for ACP readers, there are a number of issues that need significant improvement. My main comments are associated with validation, the influence of kinetics (vs thermodynamics) and the influence of the model resolution on the results. Further, I would encourage the authors to let a native speaker check the paper on English language.

Comments The validation of the model results is very limited and not presented in a quantitative way. To supply the reader with a sense to which extend reality is reproduced by the model, a comparison of modelled (total) nitrate, (total) ammonium and sulphate concentrations to the data from the network in the US and Europe should be given and discussed. The comparison should be given for both the simulation with and

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without sea salt to see the (large) influence of sea salt in comparison to observations. For Europe, a host of valuable data are available for total nitrate and total ammonium in the EMEP network.

Response: We thank for the constructive and useful comments that we feel have improved the manuscript. A new figure (Fig 4) with comparison of modeled and observed surface concentration of nitrate (with and without sea salt) and ammonium is included.

The authors use the EQSAM module for thermodynamic calculations. This module describes the thermodynamics in an appropriate way and the choice for this fast scheme does not affect the results much as it is very close to other schemes like Isorropia. The introduction of two size ranges (sulphate and sea salt dominated) for the calculation of fine and coarse mode nitrate is not perfect but appropriate as fine and coarse mode particles are by definition externally mixed. The authors indicate that mass transfer is important but do not implement it. The issue of mass transfer (kinetics) is probably most important in coastal areas where fine and coarse mode nitrate co-exist. The chosen approach to apply the equilibrium module to the coarse mode using the excess nitric acid, effectively transfers the excess nitric acid to the coarse mode. Hence, the equilibrium assumption causes the “kinetics” to be a function of the time step used in the study as each time step the available ammonium nitrate supplies the nitric acid in the gas phase which is than effectively transferred to the coarse mode (in the presence of enough sea salt). To my opinion the inclusion of kinetics for the coarse mode should be discussed. As there is a large discussion in literature whether or not the quenching of nitric acid by sea salt has a limit (kinetically) it would be interesting to learn the authors opinion about the time scale involved and how it would influence the nitrate partitioning in coastal areas?

Response: The following text is added as a response to this comment

The source of HNO3 is the photochemistry. Meng and Seinfeld (1996) (just after his equation 8) showed that the time scale to reach overall equilibrium in the gas phase

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is decided by the particles for which the transport time is smalles (i.e. the smallest aerosols). Further he defined a timescale for the overall system to reach equilibrium. This timescale is longer since it involves equilibration of the larger aerosols with the gas phase.

In our formulation we first let the fine mode equilibrate with gas, and thus let the smallest mode drive the gas phase to equilibrium before the coarse mode is allowed to “see” the new gas. This would happen within the 15 minute timescale of the chemistry/equilibrium timestep for most conditions. We chose to also let the coarse mode reach equilibrium (however only AFTER the fine mode). This choice is questionable since the timescale for the coarse mode aerosols to reach equilibrium can be order of hours which is longer than the time step of the model.

Therefore it is probable that the coarse mode is influencing the gas phase too rapidly when it in turn is allowed to equilibrate. In his simulations, Meng and Seinfeld (1996) found that on longer time scales, When NH3/HNO3 started to condense on the larger aerosols, the gas phase concentration decreased something which drove some of the condensed matter from the small aerosols back to the gas phase. This could happen already in the next timestep in our model if the coarse mode depletes HNO3 too much. In that sense, our results can be sensitive to the timestep when sufficient seasalt is present. This is in particular true in regions where there is both nitrate and seasalt present.

A fix to this problem would be to implement a kinetic formulation for the particles which have long equilibrium time scale. This was done by Capaldo et al. (2000). However we decided that implementing explicit kinetics in a global model would be too complex. The CPU time when calling the equilibrium module twice is already quite heavy. Our main goal of splitting into two modes is to avoid Na2SO4 formation which would have been predicted if all species had been treated together in one equilibrium calculation independent of size.

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The role of ammonia in this study does not receive a lot of attention, although the treatment of ammonia has a large influence on the results for nitrate. I agree with the authors that the seasonal cycle of ammonia should not be weighted with the sunlight hours to the power 4. In my opinion the power 4 relation by Adams et al was indeed tuning. Regional models use seasonal cycles which reflect to some extend a scaling with sunlight hours and are able to reproduce the amount and seasonal cycle of ammonium nitrate. Tests reveal that using different seasonal cycles may have large effects (up to a factor 2) on seasonal average nitrate levels. The background for the power 4 relation was probably the coarse model resolution, and associated underestimation of NH3 and NO3 formation in summer, used in the study by Adams et al (2001). The authors also use a coarse resolution model and may have similar problems (not clear in the paper). Hence, a discussion on the influence of the model resolution and the uncertain ammonia emissions and their influence on the results seems appropriate (see also next point).

Response: As responded above we have included a comparison with observations that shows reasonable agreement with the observations in Europe.

1463 26-29: These statements indicate that the authors feel that it is not appropriate to model nitrate distributions in a global model. As stated above the resolution effects and the validity of the resolution used should be discussed in the paper.

Response: Several global model estimates of nitrate already exist and it is important to quantify its abundance and radiative forcing on a global scale. However, nitrate is complicated to model due to its dependence of several aerosol precursors and thus non-linearity may become important. We have added more discussion of this issue in the discussion part and even briefly in the abstract. It can be noted that we have used 1x1 degree meteorological data in some new model simulations for a shorter period with in general similar results as with the coarse T42 (2.8 degree) resolution used in this work

1461 fine mode nitrate is also greatly influenced by relative humidity.

Response: We do not find a strong dependence of fine mode nitrate to the relative humidity but we have added it to the list

1461 the excess ammonium is an assumption in the thermodynamical module. Small amounts of nitric acid may dilute into the aerosol without excess ammonium.

Response: See improved description in section 2.

1463 line 5: the model represents rural areas. Hence, the gradients between rural and natural areas can be described, not the urban-rural ones. For rural to natural the statements are valid. For urban to rural a large number of studies show that the gradients of primary BC en OC are larger than for nitrate. The observation that nitrate is much higher in urban areas than in rural areas is probably biased due the locations of the sites in the Putaud et al publication and to my opinion not valid for European conditions.

Response: Some changes in the sentence to say ‘from urban and rural to natural’ to more directly indicate that this is about industrialized particles

1465 13 The definition of NP appears to me to be the fine mode nitrate concentration in molar units. Is that so? If so, defining NP does not make a lot of sense to me

Response: NP is not equal to NO3 in molar units. First, the definition in the text was wrong since the correct definition is excess NH4 divided by SO4. Second, we can get small amounts of aerosol nitrate even if the aerosol is not completely neutralized as described in new section 2.2

The definition has been corrected in addition we have added the following

Note that in this section we define the excess ammonium as what is left after sulphate has been completely neutralized to (NH4)2SO4. This is different from the definition of excess ammonium in section 2.2 where excess ammonium depends on aerosol acidity.

However, the definition here allows for a simpler diagnostic of the model, and although sulphate does not need to be completely neutralized to give aerosol nitrate, the aerosol nitrate will preferentially form in alkaline aerosols. Therefore, we believe this simpler definition is useful for understanding the limitations for formation of fine mode nitrate on the global scale.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 1455, 2006.

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