Atmos. Chem. Phys. Discuss., 2, S1081–S1088, 2002
www.atmos-chem-phys.org/acpd/2/S1081/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "A novel model to predict the physical state of atmospheric $H_2SO_4/NH_3/H_2O$ aerosol particles" *by* C. A. Colberg et al.

C. A. Colberg et al.

Received and published: 7 March 2003

S. Metzger's comments fall into two principal categories:

(i) There is some criticism on our method to compute the deliquescence/ efflorescence hysteresis since it is based on offline ASR fields. We will explain the reasons for that and evaluate this point with a sensitivity study using time-dependent ASR fields. In this context the novelty and usefulness of our method is questioned. In our opinion this is criticism is injustified - we say that to our present knowledge our study is indeed the first to take the deliquescence/efflorescence hysteresis as a process fully into account. Of course the data base used for this process treatment is not perfect - and never will be. We state that "The treatment of the $H_2SO_4/NH_3/H_2O$ system is a first step towards global aerosol physical state modeling, which allows an estimation of the occurrence of solid-containing particles in the atmosphere." and we think that this remains true.

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

(ii) We are asked to review our own results more critically and further sensitivity studies are suggested. Therefore we have performed more detailed sensitivity studies and we are now able to show that the main statement of this study remains unaffected, namely that significant amounts of mixed-phase ammoniated sulfate particles, and particularly of letovicite, are expected.

In the following we respond to S. Metzger's specific comments in his order of mention:

(1) Comparison to other aerosol models and offline ASR-values:

In order to show the benefits of our study we first want to give some introductory remarks, which we will state in the final manuscript as well:

To estimate the occurrence of solid-containing phases in the $H_2SO_4/NH_3/H_2O$ aerosol system it is insufficient to know the ambient RH and the ASR at a given point in time, but the time history of the investigated air parcel needs to be known in order to account for the deliquescence/efflorescence hysteresis effect.

Global aerosol modeling initially included only the sulfuric acid aerosol with extensions to multicomponent sulfate aerosol in recent models only (e.g. Adams et al., Jacobson, Metzger et al.). This is in the context of this study of highest interest. However, to our knowledge the complete efflorescence/deliquescence hysteresis has not been included in any of the existing global 3-D aerosol models so far. Jacobson assumes crystallization of a solid in a multicomponent solution once the RH drops below the DRH of the particular solid. Adams et al. model global concentrations of tropospheric $H_2SO_4/NH_3/HNO_3/H_2O$ aerosols in a GCM-study with prescribed chemistry fields. They do not assume solidification at all and consider all aerosols to be liquid droplets. Metzger et al. also model the $H_2SO_4/NH_3/HNO_3/H_2O$ system. They treat the semi volatile ammonium nitrate aerosol fraction fully dynamical, since they focus on the implications of gas/aerosol partitioning for global modeling. As Jacobson they assume the aerosols being liquid for RH above the DRH. In addition, they performed a pragmatic sensitivity study on the influence of hysteresis on the radiative effect. Al-

ACPD

2, S1081–S1088, 2002

though the global effect is rather small for the considered aerosol species hysteresis is important when aerosol particles are transported to dry regions, e.g. upward into the free troposphere. Especially at higher altitudes the RH is often so low that solid formation becomes important. The main focus of our current study is a microphysically consistent treatment of the hysteresis effect, not its implications for radiative forcing.

Since the history of the air parcel needs to be known in order to model hysteresis we decided to perform a Lagrangian trajectory study. Along ECMWF trajectories we use 6-hourly RH(x,y,z,t) data, also obtained from ECMWF reanalysis, and a fixed GCM ASR(x,y,z,t) climatology (Adams et al.) for July and January. We decided to include high resolution (in time and space) RH data rather than ASR data since the variability in RH is expected to have a larger influence on hysteresis (and therefore the physical state of $H_2SO_4/NH_3/H_2O$ aerosol particles) than ASR. This is based on microphysical reasons stemming from the structure of the phase diagram displayed in Figure 2. For ASR between 1 and 2 DRH and ERH are almost insensitive to ASR but very sensitive to RH. For ASR below 0.8 - 1.0 efflorescence cannot occur anyway. So, on an average, a variation in RH, e.g. 10 % in RH, results in a larger number of phase transitions than the comparable variation of 0.2 in ASR units.

Since the issue how ASR variability, on shorter timescales than one month, will influence the physical state of the aerosol, came up we performed a sensitivity study using time dependent ASR fields. Instead of using monthly ASR climatologies, we used 15 successive ASR(x,y,z,t) fields of that particular month and compared it to the original monthly mean results (compare to Table 1 and 2). For July we obtain an absolute/relative deviation of -2.0 % / -3.5 % (200-400 mbar), -1.7 % / -4.2 % (400-600 mbar) and -1.0 % / -4.0 % (600-800 mbar) in the global mean values of our solid number fraction. These differences are rather small and this justifies the use of monthly ASR climatologies.

At this stage of the study it is impossible to use online ASR values as they are simply not available. ECMWF, which we used for the trajectories and the RH values, does

ACPD

2, S1081–S1088, 2002

not provide ASR. Therefore we are dependent on ASR data from another source. We chose state of the art ASR fields from the aforementioned GCM-study by Adams et al.. However, nudging the GCM-model to ECMWF wind fields could be an option to solve this problem in the future.

We will add a statement of clarification in the final manuscript to emphasize the fact that we used offline ASR values and also give an explanation why we did so. We will also point out that a time series analysis did not provide any substantially different results and give the quantitative values.

(2) Sensitivity studies:

Up to now we have tested the importance of errors introduced by the various input parameters (DRH, ERH, ASR and RH) along trajectories in a rather qualitative manner.

Triggered by the referee's comment, we performed systematic sensitivity studies and analyzed them quantitatively. This is explained in the following paragraphs:

(i) DRH-/ERH-values:

The used microphysical input data (DRH-/ERH-values) are definitely the most accurate input parameters. This is due to the combination of our own laboratory measurements and the use of a state of the art thermodynamic model by Clegg et al.. The model is verified by numerous measurements as described in the manuscript. As a conservative error estimate we take an absolute deviation of +/- 2.5 % in ERH and performed a sensitivity study. In doing so we obtain for July an absolute/relative deviation in the global mean values of the solid number fraction of: 2.6 % / 2.6 % (200-400 mbar), 2.5 % / 5.8 % (400-600 mbar) and 1.5 % / 7.5 % (600-800 mbar) for the variation of + 2.5 % in ERH and -3.0 % / -5.3 % (200-400 mbar), -1.6 % / -6.7% (400-600 mbar) and -1.5 % / -7.8 % (600-800 mbar) for the variation of - 2.5% in ERH. Deviations resulting from a variation of the DRH-values will be even smaller, since the DRH-values are even more confident than the ERH values.

ACPD

2, S1081–S1088, 2002

(ii) RH:

As an error estimate we take +/- 10 % relative deviation in RH (Clark and Harwood). This is the estimate for the upper troposphere/lower stratosphere and is therefore a conservative assumption, since ECMWF RH values are more reliable in the lower troposphere. We obtain an absolute/relative deviation in the global mean values of the solid number fraction of: -4.6 % / -8 % (200-400 mbar), -3.4 % / -12 % (400-600 mbar) and -5.5 % / -14 % (600-800 mbar) for the variation of + 10 % in RH and 4.9 % / 8.7 % (200-400 mbar), 4.2 % / 10.9 % (400-600 mbar) and 3.2 % / 16.3 % (600-800 mbar) for the variation of - 10 % in RH.

(iii) ASR:

As an error estimate we take +/- 20 % relative deviation in ASR. Due to the lack of a quantitative assessment of the used ASR data we take this as a reasonable estimation. In doing so we obtain an absolute/relative deviation in the global mean values of the solid number fraction of: 4.8 % / 7.4 % (200-400 mbar), 8.3 % / 25 % (400-600 mbar) and 5.6 % / 28.5 % (600-800 mbar) for the variation of + 20 % in ASR and -6.6 % / -11.6 % (200-400 mbar), -6.8 % / -22 % (400-600 mbar) and -5.6 % / -27.8 % (600-800 mbar) for the variation of - 20 % in ASR.

We will assort the absolute and relative results in a table and add it to the final manuscript. The main statement of this study, namely the overall result that significant amounts of mixed-phase ammoniated sulfate particles, and particularly of letovicite, are expected remains unaffected.

Finally we want to point out that the objective of our study is the ternary $H_2SO_4/NH_3/H_2O$ and not the quaternary $H_2SO_4/NH_3/HNO_3/H_2O$ system. The quaternary system cannot be treated at the moment, because of the lack of reliable ERH data for this system, and hence represents a major task in the future for both ex-

ACPD

2, S1081–S1088, 2002

perimentalists and modelers. The restrictions of investigating a subclass system and neglecting - besides nitrate - sea salt, organic compounds and elemental carbon are already discussed in detail in the manuscript.

(3) Applicability to climate modeling

The applicability of our study to climate modeling is not subject of the current paper. We rather want to show with this study that it is possible to take full account of the deliquescence/efflorescence hysteresis as a process. However, we are thinking of extending our model in order to be able to perform calculations on the radiative effect of aerosol particles being allowed to undergo hysteresis. Currently with the given number fractions of solid containing particles and the global mean values first estimations of the hysteresis effect on climate forcing according to our results could be performed with a suitable model.

(4) Atmospheric relevance of letovicite

Our study clearly shows that letovicite is the dominant solid phase within the $H_2SO_4/NH_3/H_2O$ system. Therefore we suggest that letovicite has to be discussed with respect to its atmospheric relevance. With our study we want to give a thought-provoking impulse that letovicite might be of global importance. From our calculations it is obvious that if someone assumes ammonium sulfate to be of any atmospheric relevance, the same is true for. Apparently, there are many other constituents in a real atmosphere. However, if HNO_3 is added to the ternary system letovicite becomes even more important, since model results by Lin and Tabazadeh show that HNO_3 dissolution in ammoniated aerosol solutions can prevent the efflorescence of ammonium sulfate and ammonium bisulfate in favor of letovicite crystallization. If crystallization is inhibited at all in the aerosol, e.g. by organic constituents, letovicite would be evidently unimportant. But this has so far not been shown.

In order to meet the concern that it might be questionable to stress the global importance of letovicite at this preliminary stage we will moderate relevant statements in the

ACPD

2, S1081–S1088, 2002

Interactive Comment

revised manuscript. We will stress the fact that we want to give a thought-provoking impulse that letovicite might be of global importance and that from our calculations, it is obvious that if someone assumes ammonium sulfate to be of any atmospheric relevance, then letovicite is not less significant.

(5) Offline ASR-values:

This point has already been discussed in detail in section (1).

(6) Change of Title:

Since this study is not a sensitivity study of the physical state of $H_2SO_4/NH_3/H_2O$ aerosol particles but rather a model to predict the physical state of $H_2SO_4/NH_3/H_2O$ aerosol particles we prefer to keep our original title.

References:

Adams, P. J., Seinfeld, J. H., and Koch, D. M.: Global concentrations of tropospheric sulfate, nitrate, and ammonium aerosol simulated in a general circulation model, *Journal of Geophysical Research*, 104, 13 791-13 823, 1999.

Clark, H. L., and Harwood, R. S.: Upper-Tropospheric Humidity from MLS and ECMWF Reanalyses, *Monthly Weather Review*, 131, 542-555, 2002.

Clegg, S. L., Brimblecombe, P., and Wexler, A. S., A thermodynamic model of the system H+/NH4+/SO42-/NO3-/H2O at tropospheric temperatures, *Journal of Physical Chemistry A*, 102, 2137-2154.

Jacobson, M. Z.: Development and application of a new air pollution modeling system. 3. Aerosol-phase simulations, *Atmospheric Environment*, 31, 587-608, 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, *Geophysical*

ACPD

2, S1081–S1088, 2002

Research Letters, 10.1029/2002GL015251, 2002.

Metzger, S., Dentener, F., Krol, M., Jeuken, and A., Lelieveld, J.: Gas/aerosol partitioning - 2. Global modeling results, *Journal of Geophysical Research*, 107, 4313, 2002.

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 2449, 2002.