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Discussions

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Interactive comment on "Improvement and further development in CESM/CAM5: gas-phase chemistry and inorganic aerosol treatments" *by* J. He and Y. Zhang

Anonymous Referee #3

General Comments:

The authors have implemented the gas-phase photochemical mechanism (CB05-GE), an ion-mediated nucleation parameterization, and an inorganic aerosol equilibrium module (ISORROPIA) to the existing framework of CESM/CAM5.1-MAM7 model. The performance of the updated CAM5.1 model is evaluated for the full year of 2001. Since one of the objectives of this work is to improve the global predictions of inorganic aerosols, it is critical that this is done correctly. Unfortunately, there are several significant technical and scientific issues regarding the implementation of the inorganic aerosol equilibrium module as outlined below in specific comments. These issues

must be clearly addressed before the present work can be considered an improvement to the existing CAM5.1 model. In my opinion this will require major changes to the existing implementation of the inorganic aerosol partitioning calculations as well as model evaluation. I therefore recommend that the manuscript be rejected in the present form.

Specific Comments:

1. The authors have implemented thermodynamic equilibrium for the fine aerosol modes (sub-micron) only, while the coarse sea-salt and dust aerosol modes have been completely ignored. The reason given for this is oversimplification is that the coarse modes are typically not at equilibrium and that dynamically solving the coarse mode non-equilibrium system (together with fine modes) is computationally expensive. There have been a number of studies, including Hu et al. (2008) (on which the corresponding author Y. Zhang was a co-author) that have shown that equilibrium approach (and even the hybrid method)fails to predict the distribution of semi-volatile species (NH4, NO3, and Cl) because of the equilibrium and internal mixture assumptions. Thus, simply ignoring the problem because it is difficult to solve is not an acceptable solution, especially since there are a few computationally efficient methods in the literature that can overcome this difficulty with varying degrees of efficiency and accuracy – for example see Jacobson (2005), Zhang and Wexler (2006), and Zaveri et al. (2008). Therefore, the present implementation of ISORROPIA in CAM5.1 cannot really be considered as an improvement. To the contrary, it is erroneous and will lead to meaningless results even though they may fortuitously appear to compare well with observations.

2. It is well known that, under stable conditions, inorganic aerosols can exist as completely solid (at low relative humidity), mixed solid and liquid phases (at moderate RH) and completely liquid (at high RH), depending on the mutual deliquescence relative humidity of a given multicomponent aerosol. They can also exist in com-

pletely liquid metastable state depending on the aerosol processing history and hysteresis effects. However, it is not clear how the phase state of the inorganic aerosols is treated in the present implementation of ISORROPIA. The only place I found a mention of this process in the entire manuscript is in Table 1, where it is simply stated that ISORROPIA aerosol thermodynamics was evaluated under metastable conditions. It therefore appears that phase transitions and hysteresis effects were not even considered in the present study. This is again a significant shortcoming in a global simulation where aerosols may encounter the full spectrum of relative humidity and processing histories depending on the geographyical location and meteorological conditions. Simply assuming metastable conditions under all relative humidity conditions at all the time is a gross oversimplification and cannot be considered an improvement (as several other global models have done this or are already doing something similar). The authors should therefore implement a treatment for hysteresis to allow proper investigation of the effects of phase transitions on inorganic aerosol partitioning.

3. The treatment of phase transition calculations in ISORROPIA is also somewhat problematic. It is my understanding that ISORROPIA does not rigorously solve solid-liquid equilibria, but rather tries to approximate it using an ad-hoc approach. For instance, Ansari and Pandis (1999) clearly showed that ISORROPIA has difficulty in reproducing the complex multistage deliquescence behavior and the associated water content in stable multicomponent aerosols due to many of the simplifying assumptions. More recently, Zaveri et al (2008) also showed that ISORROPIA predictions (stable solutions) had large errors compared to the benchmark thermodynamic model AIM (Wexler and Clegg, 2002) under low and moderate relative humidity conditions. Thus, even if the authors implement hysteresis in CAM5.1, ISORROPIA may still not be able to correctly capture the phase transitions themselves and hence their effects on dynamic gas-particle partitioning to size distributed aerosols.

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4. In section 2.2.4, line 25, the authors list a set of values for mass accommodation coefficients for H2SO4, NH3, HNO3, and HCl. This is very puzzling, because the mass accommodation coefficients are only needed if the gas-particle partitioning is done dynamically (kinetically) as opposed to the equilibrium assumption used in the present work. If the equilibrium assumption is enforced then the effects of differences in mass accommodation coefficients on the distribution of semi-volatile species among different size particles will vanish by definition. Trying to somehow capture the kinetic effects with a purely equilibrium model violates the basic concept of thermodynamic equilibrium for semi-volatile species.

5. The values of the mass accommodation coefficients used are also very surprising. Some of them appear to be way too low (they are 0.02, 0.097, 0.0024, and 0.005 for H2SO4, NH3, HNO3, HCl, respectively). I checked the Sander et al. (2002) reference cited in the paper and found that the values used in this study are actually the lower limits reported for H2SO4, HNO3, and HCl condensing on highly concentrated sulfuric acid solution while the value for NH3 is the lower limit for it condensing on pure water. The authors need to explain the rationale and atmospheric relevance for these choices (assuming that accommodation coefficients for semi-volatile species are somehow needed in an equilibrium calculation, in the first place).

6. Please provide details on which new reactions and species are included in cloud (aqueous) phase chemistry. What numerical solver is used to integrate aqueous phase chemistry?

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