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Atmospheric Chemistry and Physics
Discussions

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

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Reply to Reviewer 3's 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.

Reply:

We thank the reviewer for constructive comments. However, it appears to us that the reviewer may have misunderstood our implementation of ISORROPIA II into CAM5 and several related issues. We respectfully disagree with the suggested major changes to the existing implementation and the rejection of our paper suggested by the reviewer, as they are based on misunderstanding or somewhat incomplete understanding of our work. Below we clarify those issues.

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.

Reply:

We respectfully disagree with the reviewer's statements regarding our implementation of ISORROPIA II.

As indicated by one of the reviewers (i.e., Dr. Shaocai Yu of the US EPA), "The incorporation of ISORROPIA II into CAM5.1 significantly advances aerosol treatments in current global and Earth system models." Note that CAM5.1 only treats aerosol thermodynamics that involves sulfate and ammonium and does not treat those for nitrate and cloride. Considering aerosol thermodynamic treatments for all volatile species using ISORROPIA represents a significant improvement. To our best knowledge, our model is the only global climate/Earth system model that includes ISORROPIA II, although several other global models include ISORROPIA, which is an older version of ISORROPIA II. The main differences between the two versions lie in that ISORROPIA II accounts for the impact of crustal species on aerosol thermodynamics, which is not accounted for in ISORROPIA.

Hu et al. (2008) indeed showed that bulk equilibrium approaches fail to predict the distribution of semivolatile species (e.g., NH4+, Cl-, andNO3-) due to equilibrium and internal mixture assumptions. However, this was only true for two test cases (Hong Kong and Tampa Bay) shown in their paper, both cases occurred in the coastal areas where seasalt and nitrate concentrations in the coarse mode are relatively high, which may not represent the vast areas of the whole global domain. In CAM5, by default, it does not use the equilibrium approach for gas-to-particle mass transfer. Instead, it uses a kinetic approach to simulate condensation of several species on the surface of fine and coarse particles and inorganic aerosol thermodynamics of sulfate and ammonium for fine-mode particles.

As also indicated by Dr. Yu, nearly all regional and global models only consider thermodynamics for fine particles and neglect that for coarse particles. Not until recently, kinetic approach was considered for coarse particles in a regional model, i.e., CMAQ 4.7 and newer versions. This is supported by the well-accepted assumption that gas-to-particle mass transfer can reach thermodynamic equilibrium with a short time scale under most ambient conditions. Further, more than 90% of current regional/global models treat aerosols as internal mixtures. While the kinetic approach for both fine and coarse-mode particles is desirable, it is computationally much more expensive than equilibrium approach (by factors of 2-4 based on Hu et al. (2008)), thus the kinetic approach is appropriate for short-term model applications over regions with significant coarse particles when computational resources are permitted. Earth system models, on the other hands, are designed to run for multiple decades and a trade-off must be considered between accuracy and computational efficiency, the latter is critical for application of such models on an order of 30-50 years or longer. While a few computationally-efficient methods for kinetic gas-to-particle mass transfer do exist, none of those have been applied for multi-decadal climate/Earth system applications. Their appropriateness for multi-decadal applications needs to be examined before they can be considered for implementation into global/Earth system models for such long-term model applications.

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 completely 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 geographical 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.

Reply:

For applications of nearly all regional and global models such as CMAQ and GEOS-Chem, the metastable condition is a commonly-accepted assumption. This is supported by the fact that most ambient conditions are in metastable conditions and the metastable condition assumption represents the best compromise between accuracy and computational efficiency, the latter is an important factor for large scale, long-term applications. ISORROPIA II does offer an option (i.e., stable conditions) to simulate phase transitions and hysteresis effects, which may be important under some conditions (e.g., RH < 50% for nitrate, Fountoukis et al., 2009). However, based on the global annual mean RH values for the 2001 simulation, most regions have RH values > 60-70% (exceptions are over desert/arid regions such as Australia, the northern Africa, Arabian Desert, northwestern China, and western U.S.). We chose metastable conditions for the aforementioned reasons, which are particularly true for multi-decadal applications of CESM/CAM5.

To address the reviewer's comment, we have performed an additional 2001 simulation with ISORROPIA II under stable conditions and compare the results with those under metastable conditions, see Table 4 and Figure 8 in the revised paper. These results showed that on a global scale, the differences in results between stable and metastable conditions are overall insignificant (4.2%, 12.8%, -0.013%, and 2.0% for SO42-, NH4+, NO3-, and Cl-, respectively). Such a comparison further justifies our choice of metastable conditions for global scale long-term applications.

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.

Reply:

ISORROPIA II has been implemented in GEOS-chem, and is proven to be capable of predicting observed gas-aerosol partitioning (Fountoukis and Nenes, 2007). Our evaluation results using observations also showed that ISORROPIA II is capable of simulating gas-particle partitioning in the Earth system model.

To address the reviewer's comment, we have run ISORROPIA version 1.7 (which is very similar to the version used in Zaveri et al., 2008) and ISORROPIA II box model under four conditions tested in Zaveri et al. (2008), i.e., Cases 1, 2, 8, and 9. The RH value used in Cases 1 and 2 is 30%, and those used in Cases 8 and 9 are 55% and 52%, respectively. Those results are compared with AIM results from Zaveri et al. (2008) in Table 1 in the supplementary material to this reply.

We compared the above model results with AIM and ISORROPIA shown in Figures 1 and 3 in Zaveri et al. (2008). As shown in Figure 1, for Case 1, the predictions from ISORROPIA II and ISORROPIA are very close to those from AIM for all species except for NH4NO3(s), for which ISORROPIA II and ISORROPIA give a lower value than AIM (~28.8 nmol m-3 vs. 50 nmol m-3). For Case 2, gaseous species such as NH3, HNO3, and HCl predictions from ISORROPIA II are closer to those from AIM compared with ISORROPIA, although HNO3 predicted by ISORRPIA II is about 37% higher than AIM. While predictions of NaNO3(s) and Na2SO4(s) from ISORROPIA and ISORROPIA II agree well with those from AIM, that of NH4NO3(s) is ~21% lower than that of AIM. Compared to AIM, ISORROPIA II gives closer agreement to AIM except for Na2SO4(s). For Case 8, ISORROPIA II gives much closer agreement to AIM HNO3 prediction (140 nmol m-3) than ISORRPIA (163.7 vs. 236.0 nmol m-3, respectively). Compared with ISORROPIA, ISORROPIA II also gives closer agreement with AIM predictions for NH3, H2O, NH4+, NO3-, Cl-, and NH4Cl(s). For Case 9, compared to ISORROPIA, ISORROPIA II gives closer agreement to AIM prediction for all species expect for (NH4)2SO4(s), NH4NO3(s), and Na2SO4(s). These comparisons indicate that ISORROPIA used in Zaveri et al. (2008) may contain some bugs/inaccuracies. The latest version, i.e., ISORROPIA II, is more capable of predicting aerosol phase transition than ISORROPIA.

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 semivolatile 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.

Reply:

The reviewer may have misunderstood the model treatment for gas-to-particle mass transfer in CAM5. It is not based on the equilibrium approach. Instead, it is based on a kinetic approach using the gas-to-particle mass transfer expressions of Seinfeld and

Pandis (1998), although the non-equilibrium process is not treated for coarse particles. The condensation of species on the surface of fine and coarse mode particles is simulated by using a set of values for species-dependent mass accommodation coefficients for H2SO4, NH3, HNO3, and HCl, although such a condensation is assumed to be an irreversible process by default in CMA5.

This has been clarified in the revised paper.

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).

Reply:

The mass accommodation coefficient, by definition, indicates the mass fluxes of the condensable species from gas-phase to liquid/solid phases. However, some amounts of species may be evaporated back from liquid/solid phases to the gas-phase. Since by default the model treats the condensation of inorganic volatile gas species as irreversible process (no evaporation), the lower limit values of mass accommodation coefficients are used for these species to represent their net fluxes from the gas-phase to the liquid/solid phases. Such lower limit values correspond to uptake coefficients, which indicate the net fluxes and are smaller than mass accommodation coefficients.

To address the reviewer's comments, we have provided the rationale for the use of such lower limit values in the revised paper.

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?

Reply:

The default aqueous-phase chemistry is based on Barth et al. (2000). Dissolution and dissociation of HNO3 and HCl to produce NO3- and Cl- in cloud water are added in the model based on Schwartz (1984), Marsh and McElroy (1985), and Seinfeld and Pandis (2006).

The concentration of H+ (thus the pH value of the solution) is obtained by solving the electro-neutrality equation using the bisection method. The aqueous-phase chemistry of Barth et al. (2000) along with added aqueous dissolution and dissociation of HNO3 and HCl is solved analytically.

This information has been added in the revised paper.

Reference cited:

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Seinfeld, J. H. and S. N. Pandis, Atmospheric Chemistry and Physics: From Air Pollution to Climate Change. Hoboken, N. J, John Wiley, 1998.

Zaveri, R. A., R. C. Easter, J. D. Fast, and L. K. Peters, Model for Simulating Aerosol Interactions and Chemistry (MOSAIC), J. Geophys. Res., 113, D13204, doi:10.1029/2007JD008782, 2008.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/13/C13051/2014/acpd-13-C13051-2014-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 27717, 2013.