

## Review of

### **“Description of EQSAM4: gas-liquid-solid partitioning model for global simulations”**

**By Metzger et al.**

In the series of EQSAM papers (and rebuttals), the authors have repeatedly claimed that their model can solve the multicomponent aerosol gas-liquid-solid equilibria accurately and in a computationally efficient manner. However, despite several attempts, they have been unsuccessful in clearly describing their method and have repeatedly failed to prove these rather fantastic claims. Unfortunately, the present manuscript is no exception. The material presented here under the guise of a newer version of EQSAM appears to be a confusing rehash of the previously submitted concepts, which have been questioned and rejected several times in ACPD. No new information or clarifying explanations are given here on how the multicomponent gas-solid-liquid equilibria are actually solved and how accurate and efficient the solutions really are. The manuscript is poorly written and the quality of the figures is also poor.

As I point out in “Specific Comments” below, the results shown in this manuscript are essentially meaningless, misleading, and do not prove any of the several substantial claims made by the authors. I am especially disappointed by this manuscript, because the authors have failed to respond to reviewers’ past criticisms and repeated requests to explain and prove their methodology clearly despite being given several opportunities to do so. The overall EQSAM concept, including the newest version EQSAM4 (this manuscript), still remains as confusing and cryptic as before, and I have to therefore strongly recommend that this manuscript be rejected from being published in GMD.

### **Specific Comments**

- 1) The authors had originally claimed that the compound specific coefficient  $v_i$  for calculating aerosol water content was based on thermodynamics principles. This claim was criticized and rejected by several referees in previous ACPD reviews. The authors have now repackaged the same concept as a “parameterization” instead of a thermodynamic model. While this may be acceptable, the main question is what is the real benefit of this new parameterization for calculating the equilibrium water content of aerosols when the available ZSR parameterizations (based on polynomial fits or tabulated values of single electrolyte molality as a function of water activity) in the literature are already quite accurate and efficient? Since EQSAM4 anyway uses look-up tables for solute molality as a function of RH, why not simply create the look-up tables using the most accurate sources of molality data in the first place (e.g., the AIM model or observations where available)? Why bother fitting the most accurate data with this single parameter  $v_i$  parameterization (which introduces errors) and then generate look-up tables?

In any case, the whole argument about the usefulness of the  $v_i$  parameterization for calculating single electrolyte molality as a function of water activity (or RH) is quite trivial and has proved to be a distraction from addressing the bigger issues in EQSAM with regard to solving the multicomponent gas-solid-liquid equilibria.

- 2) The origin of equation (8) for calculating activity coefficients of semi-volatile species  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  is unclear. Line 11 on page 2803 suggests that equation (8) follows from Metzger et al. (2002a) and Metzger and Lelieveld (2007), but I couldn't find this equation in those papers. To be clear, those two papers do have equations for activity coefficients, but their form looks different than equation (8).
- 3) The origin and basis for equation (14) for calculating activity coefficients of  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  in mixed solutions is not given. The accuracy of this new parameterization is also not clearly shown by comparing it against a benchmark model such as AIM.
- 4) It is not at all clear how exactly the equilibrium gas-phase  $\text{NH}_3$ ,  $\text{HNO}_3$ , and  $\text{HCl}$  concentrations over multicomponent particles are calculated using equation (14). The text following this equation on page 2806 and 2807 and repeated again in bullet (m) on page 2812 doesn't provide any information on how exactly the equilibrium gas-phase concentrations are calculated. All the pertinent gas-liquid-solid equilibrium reactions and the associated numerical solution procedure should be clearly shown to convince the reader that these calculations are done correctly. Just stating that they are solved is NOT enough. It should be noted that NONE of the previous papers describing earlier versions of EQSAM clearly show how the multicomponent gas-liquid-solid equilibria are solved accurately with analytical techniques. The technique and its accuracy have always remained a mystery. This is one of the main reasons why I strongly recommend rejecting this manuscript. Any future manuscripts on EQSAM should also be rejected upfront until the authors are able to CLEARLY describe their solution technique and quantify its accuracy by evaluating its performance against AIM for several of well-defined multicomponent systems in a meaningful manner.
- 5) Again, equation (12) is offered without any systematic evaluation of its performance. MRHD values for several Na-NH<sub>4</sub>-SO<sub>4</sub>-NO<sub>3</sub>-Cl salt mixtures at 298 K are known or can be computed using AIM, and the accuracy of equation (12) can be quite easily evaluated. Instead, they immediately decide to abandon equation (12) (see line 16 on page 2805) and adopt the MRHD values used in ISORROPIA. If this is what they were going to do anyway, then why even bother to show and discuss equation (12).
- 6) RHE calculation also seems to be seriously flawed. For example, Table 4 shows RHE value of 0.7636 for  $\text{MgNO}_3$  whereas its RHD value is 0.5401 in Table 3. Similarly RHE of  $\text{NaCl}$  is 0.8410 while RHD is 0.7528. How can RHE be greater than RHD?? It looks

like the authors have not even bothered to check their results to make sure they make any sense!

- 7) How is the complex multistage growth computed in the mixed-phase region that exists between the MRHD and the RH at which complete deliquescence occurs without using some sort of an iterative numerical solver. Does EQSAM4 simply assume that no solid phase exists for any RH above MDRH? If so, then this should be clearly stated. This is an oversimplification that can introduce errors in the calculated aerosol water content for mixed-phase particles. In any case, this certainly should not be viewed as some novel approach to increase model efficiency; any model can make this assumption and become more efficient, but at the cost of accuracy.
- 8) The whole discussion about domains and regimes in Tables 5 and 6 seems ad hoc and quite confusing. What is the difference between a domain and a regime in this context? How can one have a negative threshold for a ratio of two positive numbers?
- 9) Plots in Figures 1 and 2 show the performance of the molality and activity coefficient fits for single solute solutions using EQSAM, ISORROPIA, and EQUISOLV2. This is an absolutely trivial exercise and should not be counted as proof of good performance of EQSAM.
- 10) Figures 4 (a) through (f) are also trivial as they show evaluations of aerosol water content predictions for single solute systems, with RHD values adopted from ISORROPIA.
- 11) Only two examples of mixed salt systems are shown (Figures 4g and h), but interestingly the systems chosen do not really shed much light on the performance of EQSAM in the mixed-phase region (i.e., between MRHD and complete deliquescence RH).
- 12) In all cases in Figure 4, concentration of each solute was fixed to 1  $\mu\text{mol}/\text{m}^3(\text{air})$ . However, it is not clear if the semi-volatile solutes were allowed to partition between the gas and particle phases or were they restricted to particle phase only. Also, only one mixed salt system case included a semi-volatile species, and that too  $\text{NH}_4\text{Cl}$  (Fig 4h). Why not show a simple but more relevant case of  $(\text{NH}_4)_2\text{SO}_4 + \text{NH}_4\text{NO}_3$  in which  $\text{HNO}_3$  and  $\text{NH}_3$  are allowed to partition between the gas and particle phases as a function of RH? Also vary  $(\text{NH}_4)_2\text{SO}_4 : \text{NH}_4\text{NO}_3$  molar ratio from 0.1 to 10 so that the performance of the model can be clearly seen over the whole range.
- 13) Evaluation of the EQSAM4 performance using highly complex MINOS field observations (Figure 5) is also not at all meaningful and convincing when the model

is not even properly evaluated using simple but well-defined cases of relevant mixed salt systems.

- 14) Figures 5a, b, and c do not have any observations, so it is not possible to tell if the any of the models were performing well or not for aerosol water, total PM ( $\mu\text{g}/\text{m}^3$ ), and solid PM predictions.
- 15) Figure 5b and 5d are plots of total PM in  $\mu\text{g}/\text{m}^3$  and  $\mu\text{mol}/\text{m}^3$ , respectively, and therefore essentially the same. Then why does EQSAM4 agree well with ISORROPIA in Figure 5b but not in 5d? I can see a lot more green squares that are not coincident with red pluses in 5d than in 5b! Also, I can see some negative values for ISORROPIA in 5d. How is that even possible?
- 16) Figure 5e shows that there are errors of factor of 2 to 4 in  $\text{NH}_4^+(\text{aq})$  predictions by both EQSAM4 and ISORROPIA with respect to observations. This is not a sign of good performance.
- 17) Figures 5f, g, h, i, and j are completely trivial and meaningless as they are simply showing the comparisons of non-volatile species. These species are constrained by the observations, so it is not at all surprising if they agree right on with the observations!!
- 18) Figure 5l shows that EQSAM4  $\text{NO}_3^-(\text{aq})$  seems to agree well with observations in the fine mode. But since  $\text{NH}_4^+(\text{aq})$  predictions had errors of factor 2 to 4, the  $\text{NO}_3^-(\text{aq})$  is mostly “associated” with non-volatile cations such as  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  as opposed to being “associated” with  $\text{NH}_4^+$ . Again, it is trivial to get the former right and the question remains open whether EQSAM4 has any skill in predicting  $\text{NH}_4\text{NO}_3$  and  $\text{NH}_4\text{Cl}$  in multicomponent aerosols. The answer would be no if one looks at the EQSAM4’s performance for  $\text{NH}_4^+$ .
- 19) Is there any reason to even show the performances of different models for temperature and RH (Figures 6g and h)?