



Interactive comment on “Description of EQSAM4: gas-liquid-solid partitioning model for global simulations” by S. Metzger et al.

R. Lescroart (Referee)

ralph.lescroart@hebp.be

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A key problem with this paper is lack of clarity. The entire subject, often described in a confusing way, is scattered in at least three main papers¹, with references to even more papers for important aspects. I could accept this if these papers actually worked so that they complement each other in a clear way, but I do not have the impression that it is the case: I often ended up unable to clarify the origin of the model equations by following these references. This makes efficient reviewing very difficult: one has to transcribe formulas, compare interpretations, track contradictions, control references, To make up one's confidence in the model presented here, one has to take

¹ML07, M2011, and an unpublished paper cited in M2011 about functions called A and B; see appendix 2 of this review for further information.

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into account a long history of papers that are at the basis of the present one, but were already criticized and do not always clearly support the statements in the present paper. I provide important examples of such problems below. However, there are so much developments that look strange, or at least very unclear, that I do not think that I could list all of the anomalies to be found in this paper. The idea of developing a simple and efficient model is of course attractive, but I do not think that it is well implemented here.

As a consequence of the general lack of clarity, it is very difficult to understand why and to what extent EQSAM4 is an improvement over earlier versions. In the description of EQSAM3, it was claimed that the representation of water activity had a physical basis; now, it appears to be presented as a parameterization on an empirical basis (the “ ν_i ” theory), but still it is written that “the overall analytical structure is largely unchanged”. What are the changes?

Examples of unclear statements and expressions that do not appear clearly supported by the provided references:

- Section 2.2.1, equations (1) and (2):

This equation probably traces back to equation (21) in Metzger and Lelieveld (2007, hereafter ML07). As I've shown in my comments on Xu et al. (2009), ML07 is heavily flawed. Equation (21) has never been introduced correctly. It came from nowhere. Equation (1) here can be equated to equation (21) in ML07 if (a) we neglect B98, the origin of which we know nothing yet, and (b) we assume $\nu_i = \nu_e/\nu_w$ the latter two parameters being ill-defined as I showed in my earlier comments. For NaCl, Table 1 here shows $\nu_i = 1,385$ and calculations with values from Table 1 in ML07 provide $\nu_e/\nu_w = 1,405$. As mentioned above, these numbers were previously assumed to have a physical basis, now they are just empirical parameters. However, the reference for

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equation (1) is the new paper M2011, while ML07 is used to justify equation (2) – this is at least very confusing. Equation (2) suggests that the authors implicitly use the hypothesis that I made above, ie. $B98 = 0$ and $\nu_i = \nu_e/\nu_w$, and once again, this would not explain where the formula itself comes from.

- Section 2.2.2 (Determination of ν_i) is very confusing:

1. If RHD values are available then ν_i is calculated by solving (16b) from Metzger et al. (2011, hereafter M2011), with a bisection method. I have shown in my comment about M2011 that there are reasons to suspect that the method presented to find ν_i involves problems (will the method always converge to a unique solution? See my comment on M2011 in ACPD, summarized here in appendix 1).
2. If RHD values are not available, then " ν_i is obtained from the solute's mass fraction solubility, w_s , following Metzger and Lelieveld (2007), by using Eq. (3) with $x=1$ ". This raises a number of questions:
 - (a) the authors should explain what exactly follows from ML07 and why, because (i) there is no trace of ν_i in ML07, (ii) w_s is a well defined constant (so ML07 is not needed regarding it), and (iii) there is nothing comparable in ML07 that links w_s to ν_i , even if we accept the assumption $\nu_i = \nu_e/\nu_w$ (see above comment on section 2.2.1).
 - (b) "with $x = 1$ ": if we look at examples with RHD available in tables 1, then setting $x = 1$ in other cases doesn't look an obvious option. Further, in eqn. (3), " x " was said to be "an arbitrary variable"; how could it be set to 1 here, and what does this mean?
 - (c) "pre-calculated B98 and ν_i "; the authors should specify how they pre-calculate: with $x = 1$ and knowing w_s , equation (3) yields B98 and ν_i ,
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but what are the "required thermodynamic data shown in table 1" that are needed†? (Or is the assumption $\nu_i = \nu_e/\nu_w$ †used?)

- Section 2.2.4 – page 2803 line 9-11:

"an empirical relation between the solute molality m_s and activity coefficient γ_s is assumed as a function of RH and ν_i , following Metzger et al. (2002a) and Metzger and Lelieveld (2007)". Where does this come from? I did not find this equation in ML07. Furthermore, in Metzger (2002a), ν_i was defined as a stoichiometric coefficient, while it is now a parameter - this needs to be clarified. What are the differences with the model version presented in Metzger et al. (2002) ?

- Section 2.4 – page 2809, line 20-24:

While most of this paper assumes $RH < 98\%$, here supersaturation cases are considered, hence the A and B functions defined in M2011 need to be calculated. The description of these functions is not given in M2011, were it is said to be "outside of the scope of the paper". And how can we know that it is satisfying outside the two solutes tested in M2011 (page 2800 line 12 suggests that we cannot) ?

- Section 4 (Conclusions)

"The key equations on which EQSAM4 builds are detailed in M2011 (companion paper) and based on a solute specific coefficient ν_i ". As M2011 itself refers to another paper, of which we know nothing, to describe substantial parts of the parameterization (the "functions" A and B), and remains unclear on others ("B98"), this sentence summarizes the kind of confusion created by citations in this paper – ultimately some elements appear to be missing.

Other specific comments:

- Title: why "global" simulations†?
- (line 10, p. 2792): multi-component: here it only means a juxtaposition of components without interaction (ZSR, volume additivity). It should be made clear from the start that this approximation is a key basis of the model, and its applicability and limitations should be summarized.
- (lines 14 to 15, p. 2794): A thorough analysis of "the more detailed description of the parameterization" shows that it is necessary to assume beforehand that ν_i is a constant (see Appendix 1). This is a strong assumption; with the very limited information that we have on the parametrisation, it looks almost miraculous that it can work, for many components, with ν_i defined as a constants over the entire range of RH.
- (lines 16 to 17, p. 2795): Solute molality μ_s is moles of solute per kilograms of water, so its value should depend on the water content of the solution – by definition, so the sentence is at least poorly written. But if $\nu_i(T)$ of the compound is easily computable (as M2011 claims it is), then from 16(a) in M2011, μ_s for single solutes could be calculated for every RH. Provided that 16(a) can be applied to all relevant components, a solution for multi-component solutions could be obtained with the ZSR approximation.
- (lines 17 to 21, p. 2795): This is a logical conclusion from the above. But actually, a multi-component solution is a complex problem where the behaviour of one component should depend on that of all the others. One of the properties to look for in order to recognize a complex problem, is that its "solution" needs iterations to be found. The complexity of the mixed solutions is bypassed (see above comment on line 10, p. 2792).

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- (line 21, p. 2795): What is meant by the "internal compound loops"†?
- (lines 21 to 22, p. 2795): There should be electro-neutrality (line 26, and line 28, p. 2797), hence as much positive charges as negative. So, if some anion (cation) is lacking, it suggests that somewhere – in the neutralization loops another anion (cation) will be supernumerary? The authors should detail cases where this may happen without putting the ZSR rule into danger. Would this sentence simply means that if a given cation or anion is not present at all (neutralized or not) in the atmospheric model at a given place, no calculations are done about it ?
- (lines 1 to 7, p. 2798): The authors should mention that the staged neutralization order is only an image and that the real processes are much more intricate: e.g. the "first anion-cation pair" hasn't disappeared completely before the second one already starts neutralizing.
- (line 7 to 13, p. 2799): In my opinion, the two statements about RHE do not correspond.
- (line 22, p. 2799): The authors should show why they set $A = 1$ and $B = B98$ †?
- (line 5, p. 2800): Equation (3): how did the authors come to it and how does it behave in comparison with the general formula (19) in Metzger et al. 2011†? The authors should show how B and B98 overlap or connect for the critical values (for RH from 95 at 98%†?). This is not explained in M2011 either. According to it, if $B98 = 0$ then $\nu_i = 0^-$ which is not acceptable, but we have seen above that to make some equations comparable to their ML07 versions, we would need to have $B98 = 0$, so what should we conclude?
- (line 7-10, p. 2800): It would be useful if the authors could recall what they mean by "without iterations". In addition, if the advantage of analytical solution is available only when $A = 1$ and $B = B98$, and these values are validated only for

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two components anyway, shouldn't we conclude that the model may be efficient but far from accurate when RH > 98%? (as suggested by the results in M2011)

Being able to calculate directly and quickly the expected water content of an aerosol knowing the possible (present pollution) solutes and the RH of the surrounding air looks nice. But looking at what goes on inside droplets, I see much place for complex interactions and hence for non-linear behaviour. This means that a straight analytical calculation cannot be accurate, so how close to accuracy can we go with simplifications such as the ZSR approximation? Nevertheless, the authors may have discovered a fit (*how†?*) featuring a parameter that works (*for good reasons?*) but that, in my opinion, doesn't rest on stable scientific grounds. I further think that the applicability of the method is still too narrow to allow for a publication. Even more annoying, the explanations of the authors are often confused and confusing, and I'm afraid there are some loopholes in their development.

I therefore recommend the paper to be rejected at least until a very profound revision (form and consistency) has taken place and all the necessary material to understand it thoroughly has been added.

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Appendix 1 : Summary of comments on the related paper M2011 (ACPD)

See Atmos. Chem. Phys. Discuss., 11, C11027–C11031, 2011

The authors want to introduce a new and simpler parameterization for the water activity in function of the solute molality. The problem is that this relation depends on n_i and two other functions (or best fittings (line 13 p 24827) A and B (equations (18 to (20)) themselves depending on n_i . Due to the complexity of the equations, a numerical method is required, but we do not know if it will always converge, and if it does, how long it will take and if the solution is unique.

A deeper look could also yield following conclusion:

- A and B are functions of ν_i and μ_s only, saturation or not,
- (16a) is an expression between three variables: RH, μ_s and ν_i , with 2 (unexplained) expressions A and B, (computed for saturation or not),
- (16b) is (16a) computed for saturation only, and leaving (RH= RHD known, $\mu_s = \mu_{s,sat}$ known) only one variable ν_i with A and B,
- replacing A and B into (16b) makes it an expression with only one variable, ν_i , but valid for saturation only,
- so the value of ν_i , one is calculating with (16b) is for saturation only,
- therefore it is essential to make the assumption that $\nu_i = \text{constant}$ for the whole domain.

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Appendix 2 : Annotated references

While it is normal to cite earlier works when developing a new model, in the present case I think that many of these references are actually leading to papers that either involve serious problems that make them inappropriate for further use, or do not actually have a content that clearly supports the current paper. This is why notes are added.

1. (Metzger et al. 2002a) Metzger, S., Dentener, F., Pandis, S. N., & Lelieveld, J. (2002). Gas/aerosol partitioning: 1. A computationally efficient model. *Journal of Geophysical Research*, 107(D16), 1-24. doi:10.1029/2001JD001102
I have no comment on this paper, but it is used here in an unclear manner due to changes in equations (see main text of this review)
2. (ML07) Metzger, S. and Lelieveld, J.: Reformulating atmospheric aerosol thermodynamics and hygroscopic growth into fog, haze and clouds, *Atmos. Chem. Phys.*, 7, 3163–3193, 20 doi:10.5194/acp-7-3163-2007, 2007.
I have heavily critiqued this paper, already published when I was commenting Xu et al. 2009. I think that this paper should not have passed peer review.
3. (Metzger et al. 2010) Metzger, S., Steil, B., Penner, J. E., Xu, L., and Lelieveld, J.: Derivation of the stoichiometric coefficient of water (ν_w) to account for water uptake by atmospheric aerosols, *Atmos. Chem. Phys. Discuss.*, 10, 8165–8188, doi:10.5194/acpd-10-8165-2010, 2010.
I reviewed a revised version of the paper and proposed to reject it (Atmos. Chem. Phys. Discuss., 10, C1–C15, 2010).
4. (M2011) Metzger, S., Steil, B., Xu, L., Penner, J. E., and Lelieveld, J.: Aerosol hygroscopic growth parameterization based on a solute specific coefficient, *Atmos. Chem. Phys. Discuss.*, 11, 24813–24855, doi:10.5194/acpd-11-24813-2011, 2011.

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I have commented (Atmos. Chem. Phys. Discuss., 11, C11027–C11031, 2011) this paper and my overall conclusions have been quite negative. Especially the way ν_i is calculated.

5. (Xu et al. 2009) Xu, L., Penner, J. E., Metzger, S., and Lelieveld, J.: A comparison of water uptake by aerosols using two thermodynamic models, *Atmos. Chem. Phys. Discuss.*, 9, 9551–9595, doi:10.5194/acpd-9-9551-2009, 2009.
I have commented this paper. Atmos. Chem. Phys. Discuss., 9, C1712–C1715, 2009. It has been rejected: Atmos. Chem. Phys. Discuss., 9, C4208–C4209, 2009.
6. (Xu et al. 2011) (line 22, page 2792)
Not referenced and not available detailed model inter-comparison of EQSAM4 and EQUISOLV†II. Revision of (Xu et al. 2009)†?
7. (Metzger et al. 2011) Metzger, S., Steil, B., Xu, L., Penner, J. E., and Lelieveld, J.: Description of EQSAM4: gas-liquid-solid partitioning model for global simulations, *Geosci. Model Dev. Discuss.*, 4, 2791–2847, doi:10.5194/gmdd-4-2971-2011, 2011.
The present paper under discussion.

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