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Atmospheric
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Discussions

# *Interactive comment on* "A comparison of water uptake by aerosols using two thermodynamic models" *by* L. Xu et al.

**Anonymous Referee #1**

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The authors present comparisons between two thermodynamic models with reference to total particulate matter, particulate nitrate, ammonium, chloride, pH and water uptake.

The two models in question are often chosen for their computational efficiency and open ended architecture, whilst known to compromise some accuracy in reference to more detailed models such as E-AIM. However the ability to include further compounds and reduce complexity within representations of detailed processes can be the overriding factor.

Before some minor comments are given, I have some broad questions would I would like addressing.

I think the title is a little bit confusing. In a sense it seems to convey a subset of your work which includes particulate mass loading, chemical speciation and of course, water uptake. Whilst the ability to predict water uptake relies on all factors, the two models which you are comparing have subtle differences which, of course, you have explored in various levels of detail. I would suggest maybe changing the title to reflect comparison between two thermodynamic equilibrium models as referenced to your chosen metrics.

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Model versus model comparisons, whilst informative, are slightly limited in scope, particularly without benchmark comparisons. I understand the need to appreciate model skill when applied to various environments. However, without reference to model evaluations against benchmark models, or even experimental data, for your chosen metrics, it is difficult to ascertain why models do not capture results from ambient studies. For example, both EQUISOLV II and EQSAM3 rely on underlying routines with different theoretical frameworks, thus have different abilities to reproduce activity coefficients in moderate to concentrated solutions. Without comparisons against models such as E-AIM it is difficult to ascertain which is correct, if any. On page 9554, lines 18 onwards you present rationale for the comparison presented. I would like to see a brief discussion or statement as to why you have not conducted benchmark analysis for water uptake and activity coefficients. These comparisons would be of great use to the community if it becomes clear that regions of model discrepancy when compared with ambient data are caused by a basic inability to capture fundamental properties.

The model comparisons are for inorganic solutes. I agree it is still necessary to inform the community of how capable inorganic schemes are. However, we also have the ability to perform extensive comparisons with extremely accurate inorganic modules as raised in my point above.

Whilst it is difficult to include organic components it would be nice to reference the extent to which predictions of solid precipitation for inorganic systems are of any use. Multiple experimental, theoretical and ambient studies on water uptake have indentified that aerosol particles remain aqueous and/or amorphous even at low RH. In any case, the ability to include predictions of solid precipitation is restricted to only a very small subset of organic functionality in mixed inorganic/organic systems.

Sections 3.1- 3.7 all discuss comparisons between key aspects of the two chosen models whilst no reference to any broad results are ascertained by the reader within the abstract. In some respect this makes it hard to follow and slightly turgid. It would be nice to broader the scope of the abstract

## 1 Minor comments:

Section 2, page 9556, lines 15-18. To the best of my knowledge, Bromley's mixing rule cannot be relied upon to accurately reproduce activity coefficients in moderate to concentrated solutions. Can you provide reference to studies which suggest this is or isnt the case?

Section 2. The ability of ZSR to reproduce water content and growth factors in moderate to highly acidic solutions depends largely on how the partitioning of ions to relevant solutes is treated ($H_2SO_4$, $(NH_4)_2SO_4$, $NH_4HSO_4$, $(NH_4)_3H(SO_4)_2$). For example, Zaveri et al (2005) present a parameterised scheme which accounts for any partial dissociation on the stability of appropriate solutes. Can you comment at this stage on how the ZSR method is used in EQUISOLV II?

Section 2, page 9558, lines 15-21. Has the ability of models to prescribe crystallization relative humidity (CRH) been tested against experimental data?

Section 2, page 9558, line 24. 'Since the RH fixes the water activity of atmospheric aerosols in equilibrium with the ambient air..' This is true only when there is a negligible Kelvin effect. Please add comment accordingly.

Section 3, page 9559, lines 10-20. In this section you refer to chosen compositions for which you perform model comparisons. Are these compositions representative of

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certain environments?

Section 3.1 Aerosol water.
A difference in water content by a factor of two between EQSAM3 and EQUISOLV II is a tad worrying, specifically in reference to sulphate rich regimes in which the assumption employed within EQSAM3 may not hold. If EQUISOLV II is to be regarded as the benchmark code in this study, as indicated by comments such as 'EQSAM3 under/overestimated..' then I think a clear description of the ZSR scheme in EQUISOLV II, or at least an adequate reference, is required in line with my previous comments.

Section 3.3, page 9564, line 25. The statement 'coupling with an aqueous phase chemistry module is foreseen instead' is very vague. What exactly does this mean?

Section 3.6. Compared with all previous sections, this section is particularly small. The opening statement 'there is a larger discrepancy between predictions of potential of hydrogen (pH) in the solution system between these two models for the sulphate rich and neutral regimes.' seems a touch out of context and jumps into a particularly discussion too soon. Wouldn't we expect a large discrepancy between predicted pH in sulphate rich regimes? I would like to see some more statistics in this section.

Section 3.8 Growth Factor. In this section you present a derivation for hygroscopic growth factor. However this equation seems to be incorrect. If you derive the ratio of wet to dry radius then the density ratio should be that of the solution over the dry particle, not solution density over that of water. Can you check this and reference where you found this equation if possible. The sensitivity of growth factor to assumed stable salt, thus dry density, has been probed by numerous researchers and would change the conclusions significantly.

Section 4 page 9571. I think the inability of both models to capture nitrate mass loadings, particularly for EQSAM3 needs to be portrayed in the abstract. This would have impacts for future scenarios with reduced sulphate emissions.

Section 5, page 9574, line 14. Again, please elucidate on the comment '..coupling with an aqueous phase chemistry module is foreseen instead'.