

Interactive
Comment

Interactive comment on “UManSysProp: an online facility for molecular property prediction and atmospheric aerosol calculations” by D. Topping et al.

D. Topping et al.

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We would like to thank the reviewer for comments provided which we feel has improved the submitted manuscript. In the following text we respond to all comments made and highlight where changes have been made in the next version of the manuscript.

Referee comment *My main concern is that neither the manuscript nor the website clearly describes the basic conditions and assumptions of the models used for calculating the different properties, which puts the otherwise great tool in danger of becoming a completely black box. I appreciate that the authors refer to previous papers describing model development and validation and that validation against data*

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and other predictive tools is outside the scope of the present paper. But I would as a minimum prefer to have a short list of the most fundamental assumptions behind each model and a brief mentioning of cases where other existing models yield significantly different predictions for the same properties.

Response: With regards to the first point, we apologise for this perceived lack of clarity. To counteract this we have placed an extra paragraph at the header of every page to more clearly define conditions covered in the simulations, that are not explicitly covered by the maximum/minimum range of conditions allowed. For all pure component predictions we have added the following: *All group contribution techniques parse the entered compound, represented by a SMILES string, into specific functional groups according to a SMARTS library. These functional groups combinations are then combined with 'interaction' parameters and/or physical parameters to arrive at a given property estimate according to the underlying equations.*

For all activity coefficient predictions we have added the following: *Activity coefficients are predicted assuming a homogeneous bulk representation, allowing all compounds to interact according to the technique applied. No partitioning between the liquid and another phase is accounted for.*

For all absorptive partitioning simulations we have added the following: *'Absorptive partitioning simulations do not account for any gas phase reactions or gas phase non-ideality, the former not expected to occur under ambient conditions. It is assumed the SMILES strings and abundances uploaded represent a given point in time of interest to the user.*

Referee comment *For example, how is ideality defined, what does it cover? Are all components always assumed either ideal or non-ideal (to whatever degree that may be)?*

Response: For non-ideal simulations, all compounds are accounted for in the calculations. Similarly, for ideal simulations all compounds are ideal.

Referee comment *What are the dimensions of output variables?*

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Response: For activity coefficients these are dimensionless variables. Nonetheless, we have re-iterated on the header for that page that these calculations refer to the liquid state.

Referee comment *Are there any limits on applicability ranges of mixtures?*

Response: There are two aspects to this. Firstly, as we state in the manuscript, aside from referencing detailed evaluation studies in the literature, the purpose of this facility is to enable such investigations. Secondly however, the guarantee of functional group specificity is dependent on evaluating how the SMARTS libraries perform for a range of compound structures. As in response to referee Takahama, and to now clarify this for all users, we will add a new section on the ‘provenance’ page of our site: *Property prediction specificity: Checks of specificity for any given property predictive technique were carried out by hand for atmospheric chemical mechanisms. Whilst the current facilities check for under or over counting of atoms for any given set of functional groups, a future development would need an automatic method of checking specificity for compounds falling outside of this subset such as those proposed by Ruggeri Takahama (2015). More detail on the quality checks in place for ensuring structural features are captured are described in our paper.*

Referee comment *Which components are assumed to interact and what are the assumptions regarding these interactions? For example, are some components in the mixtures always ideal or always inert? What is assumed regarding the gas-phase ideality?*

Response: Only condensed phase components interact and we assume gas phase ideality (i.e. fugacity = mole fraction) and have now indicated this in new page headers, as detailed above.

Referee comment *What are the most basic assumptions behind calculations of pure component vapor pressures?*

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Response: The definition of a pure component equilibrium vapour pressure is the pressure exerted by a vapour in thermodynamic equilibrium with its condensed phases at a given temperature in a closed system, and we work to this definition. We rely on the group contribution concept in all current estimation techniques. As noted in the paper, and now added to each page header for such techniques, *'All group contribution techniques parse the entered compound, represented by a SMILES string, into specific functional groups according to a SMARTS library. These functional groups combinations are then combined with 'interaction' parameters and/or physical parameters to arrive at a given property estimate according to the underlying equations.'*

Referee comment *Exactly what type of vapor pressures are yielded for e.g. organics over aqueous mixtures, e.g. are they equilibrium partial pressures? This would allow the user to more readily gauge the applicability of the present predictions for their own purposes. It would also prevent obscuring the great complexity and many remaining unresolved aspects and mutual model inconsistencies behind the smooth delivery of variables with the present online tool, in particular for new users who do not have extensive experience with aerosol and liquid phase thermodynamic calculations.*

Response: Yes this is correct. Where vapour pressures are calculated over mixtures, they are specifically noted as equilibrium vapour pressures above the solution.

Referee comment *It would be helpful to specify very clearly when a "liquid phase" is an organic mixture or an aqueous phase comprising organics, e.g. p. 9676 l. 7. Or if both options are possible in all cases. In general, the conditions for how water is accounted for would be crucial to specify explicitly, see above.*

Response: We can clarify this presuming the question is directed for any simulations that calculated non-ideality in solution. For each of these simulations, we have added the following text to relevant pages: *As requested, water is included as a separate*

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variable within the 'organic' lists. We do not require you to specify whether the mixture is defined as 'organic' or 'aqueous', rather the predictions of activity coefficients rely solely on the relative concentrations of each component without need for defining a specific composition as reference state.

Referee comment *On a minor note, I was a bit puzzled by the use of the term "Kappa Kohler" values, C3392 e.g. p. 9681. Is this convention replacing the use of symbol K(kappa) and the term Köhler theory?*

Response: Whilst we have targeted, largely, the atmospheric community, there is a chance that users would be confused by simply providing the symbol K(kappa). Rather, we decided to fully reference the original papers from which the variable is defined. For clarity however, we have now replaced the above term with K(kappa) Köhler values.

Referee comment *The website requires very different input variable formats, e.g. concentrations scales are requested as molecules, grams, or micromoles per some volume. It could be helpful if it would be possible for the user to give these in a number of different preselected dimensions and then the online tool would make the appropriate conversions for the models.*

Response: This is a good suggestion. Whilst we have used standard units in all linked publications prior to this facility, we will judge user feedback as to whether this would be a useful component in a future release.

Specific comments

Referee comment *p. 9676 l. 10: XX species?*

Response: Apologies, this has now been corrected

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Referee comment In Sect. 3, it is unclear what it means that properties are limited to 5000 or 1000 compounds. Are these the total number of compounds possible to handle, or at a given time?

Response: Apologies, this has now been clarified. As is response to referee Epstein, we have limited the number of compounds for different predictions due to computational burden and delays on providing results. We have added the following text to page 9675, lines 21-23: ‘[...] at any one time via the web portal’.

Referee comment In Sect. 3.1, and Figs. 5 and 7, it is unclear what the dimension of vapor pressure is.

Response: This has now been corrected, the units are Log10 atmospheres.

Referee comment In Fig. 5, activity coefficients are given as unitless with no reference to concentration scale or reference state. The dimension is specified on the website, but this information should be clearly stated in the documentation.

Response: This has now been added to the figure caption.

Referee comment In Fig. 7, the dimension of mass increase is not specified.

Response: This has now been added to the figure caption.

Referee comment In Fig. 4, I suggest using units of $[g\ cm^{-3}]$ instead of $[g/cc]$.

Response: This has now been added to the figure caption.

Referee comment In Table 6, specify that “dry size” is diameter (if that is the case).

Response: This has now been added to the table caption.

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