

## ***Interactive comment on “A group contribution method for estimating the vapour pressures of $\alpha$ -pinene oxidation products” by M. Capouet and J. F. Müller***

**Anonymous Referee #1**

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The topic is of relevance to the atmospheric chemistry/smog science/atmospheric aerosol community, where formation of organic aerosols is known to be critically dependant on vapour pressure, and many of the compounds of interest have no known vapour pressures. This paper is a valuable contribution to the methodologies currently in use for estimating vapour pressures and should be published in ACPD following revisions, the latter being outlined below.

Major points (e.g. places where the text needs clarification, methodological issues, etc.):

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Page 11255, line 6 (eqn 3): A comment on the impact of the accuracy of the fusion enthalpy change term is needed, here (see also later comments on this point). Later (page 11261, line 11), an average estimate of this term is used based on other compounds - what is the error associated with this estimate, based on using the two compounds of page 11261, line 11 as upper and lower limits? Note that its not completely true that the values in Figure 5 include “measured” values, since the latter in part are based on an estimate of the fusion enthalpy change.

Page 11256, line 16 (eqn 4) and discussion that follows, up to line 6 page 11256: It’s not always clear in this discussion on the extent to which the group contribution parameters are based on measured or group contribution estimated vapour pressures. This needs to be clarified. In the best case scenario, both pressure terms in (4) would be from measurements, not another estimation method. The text in its current form implies that the first pressure term is derived from a Lee-Kessler estimation - why were experimental measurements not used? Or were no experimental vapour pressure measurements available for these compounds (while experimental values of the critical parameters required by the LK method were available)? The sentence beginning “When no experimental value of the vapour pressure” seems to imply that this refers to the second, alkanolic, vapour pressure term in (4) from the way its used in the paragraph. I suspect that the authors intend it to refer to both vapour pressure terms in (4) since its much more likely that measured vapour pressures for the alkanolic compounds are available rather than for the substituted compounds. Another important point that must be clarified with regards to (4): for those instances in which the LK method is being used, are the critical properties always being estimated from the Marrero and Gani approach, or are there measurements of these critical properties sometimes being used. The authors should state how many of the substituted, and how many of the alkanolic species, made use of the LK method for vapour pressure estimation (and how many of those required estimated group contributions). The authors’ method as it currently stands is a fit to both experimental data and other group method estimates, and its not clear as to the relative impact of each of these sources

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of information. If, for example, 90% of the vapour pressures had to be estimated using other group methods, then the usefulness of the authors' method becomes less clear (i.e. one could use the original group methods on which it is based with presumably the same accuracy). If on the other hand only a small number of vapour pressures in (4) are based on group method estimates, then a much stronger case for the authors' work as being new can be made.

Page 11256, line 27. The work later (Table 2) seems to focus on primary, secondary and tertiary degrees of substitution, while the given line refers to alpha-carbon substitutions only. Do the authors mean that they only consider compounds that have multiple substitutions on the same carbon atom? This does not seem to be the case from the specific compounds listed under Figure 1. This needs to be clarified. Similarly, page 11257, lines 2 - 12 mentions an exception to the rule for primary versus secondary substitutions which is not easy to follow. Its not clear as to whether the degree of substitution is with reference to the substitution of C-H bonds for C-oxygenated group, or whether C-C is also to be included as "substitution". I suspect the latter, but this needs to be specified in the text. A few more examples along the lines of Figure 2 would probably help in this.

Page 11257, lines 11 to 13: What is the likely impact of this approximation for the secondary and tertiary dinitrates? E.g. if a similar approximation was made for monoalcohols, what would be the effect on the estimated vapour pressure?

Page 11257, lines 24 to 26: I suspect that the "pinic acid parent compound" of figure 2 is not correct. The structure displayed shows a carbon atom at the location of the uppermost OH group. The unsubstituted alkanolic parent should have the same number of carbon atoms as pinic acid (which has 9 - the parent compound displayed has 10). Hopefully a typo - but the authors should double check their parent alkanolic structures used in the formulation carefully, given that this one appeared as an example in the text.

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Page 11263, lines 25-28: This implies that the OH and OOH groups have interactions that may not be well estimated due to a lack of measurement data. Would the authors expect similar problems with other di-substitutions (e.g. nitrates and hydroxy, peroxy and nitrates, etc.?).

Minor points (typos, etc.)

Page 11252, line 6. Mathematical function - 'mathematical/physical' might be a better choice of words - the functions employed sometimes have a basis in thermodynamics and experimental results, in order to improve the fit.

Page 11259, lines 11-12: It would be worthwhile doing a few plots of the authors' method vs the UNIFAC method as a function of temperature, for some of the more substituted compounds. Is the temperature trend similar?

Page 11260, lines 22-28: It would be worth noting that these sigma values could be significantly improved if the J function was made more compound-class specific (i.e. do a separate J for monoalcohols, monoacids, etc).

Page 1262, line 3: Better to say 298.15K rather than "ambient" - some measurement networks correct values to "ambient" temperatures of 273.15K. Also need a reference for the statement of 90% of the total vapour pressure of acetic acid being due to the dimer.

Page 11262, line 13-14: Another figure with the structures of the two dimers would help in clarifying this point.

Page 11272, figure 2: The text makes mention of 2,3-dimethyl-propanediol as an example, but 3 possible compounds are shown on the plot. All the off-line compounds should have different symbols in order to make this more clear. The figure would also benefit from a separate key for the n-group compound lines rather than the current approach of labels on the plot itself.

Page 11273, figure 2: Pretty sure that the pinic acid parent compound has one more

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carbon atom than it should (see above).

Page 11276, Fig 5: to what extent would the pinic acid values vary based on the error in the fusion enthalpy term? Error bars on the “measurements”?

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 11249, 2005.

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