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# *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 #3**

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General Comments:

The authors propose a new group contribution based method for estimating vapor pressures of alpha-pinene oxidation products. Better estimates of the vapor pressures of these compounds would indeed be very welcome to model gas/particle partitioning more accurately. While the UNIFAC method proposed by Asher et al. (2002) is generally applicable and operates with a limited number of functional groups, the proposed method relies on very specific organic structures, namely complex hydrocarbons and functional groups that depend on the degree of substitution of the carbon atom that they are connected to. Taking these differences into account, it is rather disappointing that the proposed method does not perform considerably better than the one by Asher et al. As the authors state, it still fails to predict the vapor pressures of tri-O-acids.

One critical factor to obtain a good parameterization is the available experimental data. To parameterize the specific chemical groups as proposed in this paper, a large data set and a careful evaluation of the quality of the experimental data are needed. However, a comparison of data sets from different sources is not present in the paper. Moreover, some data sets that could have helped to extend the data base do not seem to have been considered (such as Yaws, Handbook of Vapor Pressure. Gulf Publishing Company, Houston; Howard and Meylan, Handbook of Physical Properties of Organic Chemicals, Lewis Publishers, 1997). Before publication in ACP, the authors should therefore reassess their experimental vapor pressure data and complement it at least with the compilation by Yaws. They should also elaborate better the strength and advantages of their new method, e.g. by presenting in one or two Figures examples of differently substituted substances whose vapor pressures are accurately predicted by the new method while other methods fail.

Specific comments:

At several instances in the manuscript, the authors use the phrase “alkanoic compounds”, (e.g. page 11251, line 14). While “alkanoic acid” is quite commonly used synonymously with “carboxylic acid”, “alkanoic compound” is not familiar to me. The authors should either define what they mean by “alkanoic compound” or exchange this phrase against more common terminology.

The phrase “1,n-dicarboxylic acid” should be replaced by “alpha,omega-dicarboxylic acid”. The use of “1,n” to describe an alpha,omega substitution in general is rather misleading since e.g. 1,n-butanediol can also be taken for 1,2-butanediol, 1,3-butanediol and 1,4-butanediol. It therefore seems clearer to use alpha,omega also for the diols and the other substance classes.

Page 11255, line 24: should it read pL,hc0(T) instead of pL,i0(T)?

Page 11256, lines 11-12: replace “butane-diol-1,2” by “1,2-butanediol” and “2-methyl propane-diol-1,2” by “2-methyl-1,2-propanediol”.

Page 11257, lines 16-19 and Figure 1: On page 11255, lines 3-8, it is written that the vapor pressures of the crystals are converted into the ones of the supercooled liquids. In this case, the vapor pressures of the even carbon number dicarboxylic acids should be comparable with the odd carbon number ones. Does Figure 1 show the converted vapor pressures for the supercooled dicarboxylic acids? If yes, the rather low values of the even carbon number dicarboxylic acids might still be within the experimental error. Comparison with other literature data for these substances might help to answer this question. Yaws, for example, gives vapor pressure values of dicarboxylic acids above their melting points.

Page 11262, lines 2-17, abstract and conclusion: the degree of dimerization of an acid in the gas phase depends on its gas phase concentration. Under ambient conditions this concentration is much higher for acetic acid than for pinic acid vapors in equilibrium with the condensed phase. The authors should take this difference into account and base their conclusions concerning the degree of polymerization of pinic acid on dimerization constants of pinic acid (if available) or similar compounds.

Fig. 1: The Figure caption as well as the text of the manuscript do not explicitly state whether experimental or calculated data is presented in this Figure.

Fig. 2: the pinic acid parent compound contains ten carbon atoms. This seems to be one too many compared with pinic acid: the methyl group on top seems to be wrong and should be removed.

Fig. 5: the comparisons shown in this Figure do not seem to be very conclusive: There are considerable differences between the vapor pressures predicted by the different methods: does this mean that there is still a large uncertainty or that with the new

method we are much closer to the correct result?

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