

***Interactive comment on “Technical note: Vapor pressure estimation methods applied to secondary organic aerosol constituents from  $\alpha$ -pinene oxidation: an intercomparison study” by S. Compernelle et al.***

**Anonymous Referee #1**

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General Comments

This reviewer believes that this article is suitable for publication in Atmospheric Physics and Chemistry after minor modification. This technical note describes the application of several vapour pressure estimation methods to generate vapour pressure values for compounds formed during the oxidation of  $\alpha$ -pinene as described by the BOREAM model. The authors highlight the differences between the estimation methods, their extension to include new group contributions for atmospherically important functional groups, and the problems with one estimation method when applied to certain multi-

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functional compounds. A major issue with many vapour pressure estimation methods is the lack parameters for some functional groups; hence the provision of new parameters for atmospherically important chemical groups is a particularly valuable contribution. Most of the specific points listed below are aimed at improving the author's description of how these parameters were derived.

Specific Comments

- 1) The authors seem confused about some of the available vapour pressure data for hydroperoxides, peroxyacids and peroxyacetyl nitrate. Egerton et al (1951) have published correlations of experimental vapour pressure data for three hydroperoxides and three peracids. With the exception of methyl hydroperoxide all these correlations go up to at least 90°C, and for three of the compounds up to 120°C, with boiling points obtained by extrapolation. Hence it is a bit misleading to refer to these data as "room temperature vapor pressure data" (line 133). The authors are correct to avoid calling the boiling points provided by Egerton et al "experimental" although as they are obtained with a relatively short extrapolation (< 20K for 5 out of the 6 compounds) they should be good estimates if the underlying data is of good quality. However for peroxyacetyl nitrate the source quoted by the authors (Bruckmann and Willner, 1983) provides a correlation for the temperature range -50 to +18°C and a boiling point value. There is no explanation about how the boiling point value is obtained and there is certainly no claim that it is experimental. From the context it has to be assumed that it was obtained by extrapolation (and a long extrapolation at that - almost 90°C). Hence the authors of this paper are wrong to refer to the boiling point provided by Bruckner and Willner as "experimental" (line 135).
- 2) The authors appear to be unaware of a second set of data relevant to the vapor pressure and boiling point of peroxyacetyl nitrate. Kacmarek et al (1978) provide 8 vapour pressure points and an extrapolated boiling point in good agreement

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(103°C vs 106°C) with that of Bruckner and Willner. The extrapolation to the boiling point for this dataset is considerably shorter than that for the Bruckner and Willner dataset.

- 3) The authors use the boiling point value of Bruckmann and Willner to directly obtain a boiling point increment for the PAN group (line 66-67) but do not use the boiling points provided by Egerton for the hydroperoxides and peracids to provide similar group contributions for these groups despite the extrapolation to obtain the boiling point for peroxyacetyl nitrate being so much greater than that required to obtain the boiling points for the hydroperoxides and peroxyacids. The authors need to describe in more detail why they felt the Egerton et al. boiling points were unsuitable for this work and why the method they used (extrapolation of "reduced boiling points found in the work of Sanchez and Myers (2000) by the Newton-Hass method (Hass, 1936), with the entropy estimated following Myrdal et al. (1996)"....lines 67-70) was better, particularly as they return to the data of Egerton et al. to obtain estimates of the dB parameter for these two groups. The data provided by Sanchez and Myers are single point vapour pressure values (or reduced boiling points) for 19 hydroperoxides of diverse structure and 5 peroxyacids. The authors should describe in more detail which hydroperoxides and peroxyacids were used (perhaps as a footnote to Table 2) to obtain extrapolated normal boiling points ( $T_b$ ) using the method they describe and how an average  $T_b$  increment for the hydroperoxide and peroxyacid groups were obtained from these results.
- 4) Section 2.1:- For the boiling point method of Joback and Reid the authors use a group additivity approach to obtain increments for hydroperoxides and peroxyacids. However for the Nannoolal method they go to considerable trouble to obtain boiling point values for some unspecified hydroperoxides and peroxyacids (point 3 above) which could then have been used to obtain  $T_b$  increments for the Joback method. This provides a needless inconsistency between the two

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methods for estimating  $T_b$ . If the authors believe that the group additivity approach would give better results than fitting to calculated  $T_b$  values for selected hydroperoxides and peroxyacids then they should have used this method for the Nannoolal  $T_b$  increments. The authors need to provide a better explanation for why they used a different method for the Joback and Reid increments and the Nannoolal method and note that this difference could confuse comparisons between the two  $T_b$  estimation methods.

- 5) Lines 132-137:- Can the authors please be a bit more explicit about the methods used to obtain the dB parameters given in Table 2. The increments (dB) for the Nannoolal vapour pressure equation could be obtained from the authors calculated  $T_b$  values for the three hydroperoxides and three peroxyacids (assuming these compounds were used in the calculations commented upon in point 3 above) by adjusting the dB parameter for the hydroperoxide or peroxyacid group until a good fit was obtained between the vapour pressure correlations provided by Egerton et al. and the values predicted by the Nannoolal method. Is this the method used by the authors?
- 6) Line 72 and lines 136-138. Group interaction parameters are set to zero because of the lack of data. The authors should discuss this issue in more detail. They have already identified hydroperoxide and peroxyacids as hydrogen bonding groups when using the vapour pressure method of Myrdal and Yalkowsky (Section 2.6). It is clear that hydrogen bonding makes a major contribution to interactions between molecules containing these groups, otherwise the vapour pressures provided by Egerton et al. would be much higher. Hence there is an argument that these groups should take on the group interactions of a closely related group for which interactions are known - namely alcohols for the hydroperoxide group and carboxylic acids for the peroxyacids. The authors should recognise that there is an alternative approach and explain why their approach (the assumption of zero interactions for these groups) is to be preferred.

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- 7) Line 81-82 "...In this work, we chose the method of Marrero and Gani(2001) to estimate this hydrocarbon part." Is this sentence superfluous given that the previous sentence states that "the method of Marrero and Gani(2001) was used to provide  $T_b$ , critical temperature and critical pressure, which were then converted to" hydrocarbon vapour pressures "by the method of Ambrose and Walton (1989).
- 8) Line 81. The method of Ambrose and Walton(1989) appears to be specific to normal alkanes. Could the authors please explain how they adapted the method to calculate the vapour pressures of cyclic and branched hydrocarbons required to use the CM method on the products of  $\alpha$  pinene oxidation.
- 9) Section 2.3- group contributions for ether, peroxide and ester groups for use in the CM method. The authors need to provide more information (perhaps as a note to Table 3) about these group contributions- specifically- line 96:- which simple molecules were used and what was the source of the vapour pressure data used in the fitting?
- 10) Line 269. "...for hydroperoxides and peroxyacids..."no boiling points are available as they decompose upon heating". Boiling point values are available- but not experimental values; and the problem is that the compounds decompose at temperatures below the normal boiling point- (see point 2 below) rather than they decompose on heating

Minor comments

- 1) Line 54 "subdivided" rather than "subdivised".
- 2) Lines 63-64 ..."It is known that hydroperoxides and peracids decompose before the boiling point is reached"... could the authors please provide a reference for this statement.

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- 3) Line 64- insert "group" after peroxy acyl nitrate.
- 4) In line 69 the authors use entropy when they should use entropy of vaporization.
- 5) Line 76 "This vapor pressure..." not quite clear which vapour pressure is being referred to. Suggest insert "hydrocarbon" after "this" to improve clarity.
- 6) Line 78- "were" rather than "was".
- 7) Lines 172-174- introduction of mean deviation and mean absolute deviation. The authors introduce these terms before they are defined (with specific reference to the CM method) in equations 11 and 12. Suggest it might be better to reference previous papers where these terms have been defined in a general sense at this point and leave equations 11 and 12 to define  $\Delta$  and  $\sigma$  as specifically the mean deviation and the mean absolute deviation from the CM model.
- 8) Line 208 "systematic difference in  $\log_{10}(P)$ ", is this the same as mean deviation?
- 9) Lines 212-214:- need to reword. Suggest "we note in this respect that Barley and McFiggans(2010) devised a simplified version of the method of Nannoolal et al.(2008), with fewer parameters and without group interactions, and found that this method performed almost as well as the original method when tested against their experimental vapour pressures."
- 10) Line 227:- "t" dropped from "not".
- 11) Line 260 "volatility" rather than "volatile".
- 12) Line 263 insert "for atmospheric modelling" after "probably less appropriate". Vapour pressure estimation methods using critical data are appropriate

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for volatile fluids, particularly if experimentally measured critical parameters are available.

- 13) Line 377:- remove extra "doi".
- 14) Line 398:- Sanchez and Myers. The authors should include in this reference that this is an article in Kirk-Othmer Encyclopedia of Chemical Technology (which edition?).
- 15) Table 4- footnote a- should read "3-methyl-1,2,3-butane tricarboxylic acid"

Kacmarek, A. J. and Solomon, I. J. and Lustig, M.: Preparation and Properties of Peroxyacetyl Nitrate, *Journal of Inorganic and Nuclear Chemistry*, 40, 574-576, 1978.

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