**Atmospheric
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Interactive comment on "Technical note: Vapor pressure estimation methods applied to secondary organic aerosol constituents from α-pinene oxidation: an intercomparison study" *by* S. Compernolle et al.

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Answer to the referees comments

28 June 2010

1   Answer to referee 1

We thank reviewer #1 for his helpful comments and suggestions.

1.1   General 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).

"room temperature" dropped.

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).

It is true that we assumed that the boiling point of peroxy acetyl nitrate of Bruckmann and Willner (1983) was experimental. We follow the reasoning of the reviewer that this assumption is probably incorrect and changed the text accordingly. The following sentences are added: "Bruckmann and Willner (1983) do not make explicit how this boiling point of 379.15 K is determined. As they evaluated the vapor pressure curve only up to 291.15 K, the reported boiling point of peroxy acetyl nitrate is probably obtained by extrapolation of their $p^0(T)$ correlation over almost 90 K."

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 ($103°C$ 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.

We thank the reviewer to bring the data of Kacmarek et al. (1978) to our attention, and hereby give us the opportunity to improve our group-contribution parameters for the PAN group. We use now this data and no longer Bruckmann and Willner (1983). Kacmarek et al. (1978) provide data points from 4 to $57°C$. However, the highest T, p point seems to be an outlier, and is probably also not used in deriving their vapor pressure equation. Therefore, we consider only the data points up to $42.8°C$, and - compared to the data of Bruckmann and Willner (1983)- the extrapolation interval is now reduced to a (still significant) $61°C$.

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 (Tb) using the method they describe and how an average Tb increment for the hydroperoxide and peroxyacid groups were obtained from these results.

As noted in point 1, we assumed, probably incorrectly, that the boiling point of peroxy acetyl nitrate reported by Bruckmann and Willner (1983) was experimental and not an extrapolation, which was the reason why we did use it directly, as opposed to the extrapolated boiling points of hydroperoxides and peracids provided by Egerton et al. (1951). We will assume now, however, that the boiling point of peroxy acetyl nitrate is an estimation, and hence in the revised manuscript, we treat peroxy acetyl nitrate on an equal footing as the hydroperoxides and the peroxyacids.

In using the same data source both for boiling point estimation on the one hand and dB parameter on the other hand we faced the following circularity problem:

- First, use Egerton's vapor pressure data to obtain extrapolated boiling points for

the three hydroperoxides and the three peroxy acids.

- Next, use this estimated boiling point to obtain the dB parameter for the OOH group and the C(=O)OOH group by fitting dB to exactly the same vapor pressure data.

In using different data sources (Sanchez and Myers (2000) to obtain the extrapolated boiling points, and Egerton et al. (1951) to obtain the dB parameter), we tried to circumvent this circularity problem to some extent. However, for the final parameters dB this approach did not make much of a difference compared to using Egerton's data for both T_b estimation and dB estimation. Also, as the referee indicates, we acknowledge that the procedure with the Hass-Newton method is quite complicated. Therefore, we will now adopt the simpler approach, for the peroxy acetyl nitrate, the hydroperoxides and the peroxy acids, in using Kacmarek's and Egerton's vapor pressure data both to obtain the extrapolated T_b and the dB parameter. Note that the boiling points obtained in this way can differ somewhat from the boiling points reported in the papers, especially in the case of ethyl hydroperoxide (374.25 K when solving the p^0, T correlation, vs. 368.15 K as cited by Egerton et al. (1951)).

We include now a table with extrapolated boiling points, and the temperature range of extrapolation. Regarding the data of Egerton et al. (1951), the following sentence is added: "For five out of six of them the extrapolation range is less than 20 K and hence the extrapolated boiling point should be a good estimate, provided the underlying data is of good quality". These boiling points are then used to obtain group contribution values for the boiling point methods of Joback and Reid (1987) and Nannoolal et al. (2004), by minimizing $\sum_i \left(T_{b,X,i} - T_{b,\exp,i}\right)^2$ with X the method considered (Joback-Reid or Nannoolal) and $T_{b,\exp,i}$ a boiling point based on experimental data (possibly extrapolated). Note that we now also derive group contribution values for the method of Joback and Reid (1987) (see point 4). The data of Sanchez and Myers (2000) on hydroperoxides and peracids are no longer used in deriving group contribution values

for the boiling point methods, but this has little impact on the precise value. Instead, we use the data of 9 hydroperoxides and 1 peracid, -not considered by Egerton et al. (1951)- to test the methods extended in this work.

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 Tb increments for the Joback method. This provides a needless inconsistency between the two methods for estimating Tb. If the authors believe that the group additivity approach would give better results than fitting to calculated Tb values for selected hydroperoxides and peroxyacids then they should have used this method for the Nannoolal Tb 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 Tb estimation methods.

We wanted to extend the boiling point method of Joback and Reid (1987) in a way compatible with the approach of Camredon and Aumont (2006). For the hydroperoxide group they assumed it could be considered as a sum of -O- + -OH, and we took a similar approach for the peracid. However, we acknowledge that this introduces an inconsistency between the JR and the Nannoolal methods. Therefore, we will now take the same approach as for Nannoolal et al. (2004). The newly derived group contribution values for the JR method are now included in the Table of group contributions (Table 2 in the discussion paper, Table 3 in the revised version). Note that our group contribution value for PAN differs slightly from Camredon and Aumont (2006), as we use now the data of Kacmarek et al. (1978) instead of Bruckmann and Willner (1983). Note also that for the JR method, we derive a group contribution for peroxides, based on the boiling points of 6 peroxides from the compilations of Sanchez and Myers (2000) and Balaban et al. (1992). We indicate the goodness-of-fit by including in the Table of group

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contributions the mean absolute deviation $\frac{1}{N}\sum_i |T_{b,X,i} - T_{b,\text{exp},i}|$.

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 Tb 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?

The T_b values, obtained by extrapolation, of the three hydroperoxides, the three peracids and the peroxy acetyl nitrate were used. The dB parameter was then obtained by a least square fitting to the correlations of Egerton et al. (1951) and the data points of Kacmarek et al. (1978). This has now been clarified in the text. The same approach is used to extend the method of Moller et al. (2008)

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.

Hydroperoxides and peracids are undoubtly hydrogen-bonding compounds. In the vapor pressure method of Myrdal and Yalkowsky (1997) hydrogen-bonding is a yes/no

feature (except for the weakly hydrogen bonding amines, which we do not consider), with the same parameter both for the OH and the C(=O)OH groups, notwithstanding the fact that the hydrogen bonding strength is quite different for both groups. It is therefore natural to also assign a "yes" to the OOH and C(=O)OOH groups.

On the other hand, in the vapor pressure methods of Nannoolal et al. (2008); Moller et al. (2008), the group interactions are a quantitative feature, different for alcohols and acids. Moreover, the magnitude of these group interaction parameters depends on the group contribution value of the functional group (mainly determined by mono-functional compounds) and these are different for OH and OOH, and for C(=O)OH and C(=O)OOH groups. For the method of Moller et al. (2008) the situation is even more complicated due to the presence of the parameter D for OH and C(=O)OH groups, obtained from the detailed behaviour of pressure-temperature behavior. No such parameter can be derived for the OOH and C(=O)OOH groups as we only have simple linear correlations for $\ln p^0$ vs. $1/T$ (from Egerton et al. (1951)), and the presence/absence of this parameter will also impact on the value of the GI parameters. Hence simply taking over the GI values of the OH and C(=O)OH for the OOH and C(=O)OOH group is probably not justified. On the other hand, neither is putting GI=0. We include therefore in the revised paper a sensitivity test where we do assume this analogy approach, taking over the GI values and (for the Moller method) the D parameter.

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 Tb, critical temperature and critical pressure, which were then converted to" hydrocarbon vapour pressures "by the method of Ambrose and Walton (1989).

The sentence is removed.

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 pinene oxidation.

We added the sentence:

"The vapor pressure is then calculated from these properties by the corresponding states method of Ambrose and Walton (1989) (Eq. (8) of their paper), with the acentric factor estimated with Eq. (2-3.3) of Poling et al. (2001).

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?

The molecules and data source have now been specified as a note to Table 3.

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

Sentence is changed into "no experimental boiling points are available as these compounds typically decompose below the normal boiling point".

1.2 Minor comments

1) Line 54 "subdivided" rather than "subdivised".

Correction applied.

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.

We made the statement less strong and added references. "Decomposition is a problem in for the direct determination of boiling points of hydroperoxides and peracids (Egerton et al., 1951; Kacmarek et al., 1978)".

3) Line 64- insert "group" after peroxy acyl nitrate.

Correction applied.

4) In line 69 the authors use entropy when they should use entropy of vaporization.

Correct. But as we do not use any more the approach with the Newton-Hass method in the revised version of the paper, this remark no longer applies.

5) Line 76 "This vapor pressure..." not quite clear which vapour pressure is being referred to. Suggest insert "hydrocarbon" after "this" to improve clarity.

"hydrocarbon" inserted.

6) Line 78- "were" rather than "was".

Correction applied

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 and as specifically the mean deviation and the mean absolute deviation from the CM model.

The definitions of mean deviation and mean absolute deviation are now put earlier in the text, and generalized as $\Delta_Y^X = \frac{1}{N} \sum_i \log_{10} \frac{p_{X,i}^0}{p_{Y,i}^0}$

$\sigma_Y^X = \frac{1}{N} \sum_i \left| \log_{10} \frac{p_{X,i}^0}{p_{Y,i}^0} \right|$ where X, Y refer to the methods employed, or to experiment.

8) Line 208 "systematic difference in log10(P) ", is this the same as mean deviation?

Indeed. At the place of definition of mean deviation, systematic difference is now included as a synonym.

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."

Sentence replaced.

10) Line 227:- "t" dropped from "not".

Corrected.

11) Line 260 "volatility" rather than "volatile".

Replacement done.

12) Line 263 insert "for atmospheric modelling" after "probably less appropriate". Vapour pressure estimation methods using critical data are appropriate for volatile fluids, particularly if experimentally measured critical parameters are available.

"for atmospheric modelling" inserted.

13) Line 377:- remove extra "doi".

I cannot find this 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?).

Information added.

15) Table 4- footnote a- should read "3-methyl-1,2,3-butane tricarboxylic acid"

Corrected.

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2 Answer to reviewer 2

We thank reviewer 2 for his comments and specifically for his information on the Moller et al. method.

2.1 General Comments

The method has meanwhile be overworked by Moller et al. based on this analysis and a correction will be published shortly.

Page 8501, line 14. The sentence "Note that this deficiency is known to the authors..." has been changed into: "Currently, the method has been reworked by Moller and coworkers based on this analysis, and a correction will be published shortly ."

Regarding the deficiency reported by Barley et al., which is also corrected in the reworked version, we change the text between the lines 19-23:

"This error is also corrected in the reworked version. As the BOREAM-molecules tested here do not include diacids with less than 10 atoms, it is unimportant for the present intercomparison exercise."

The drawback of this work and other comparable research lies in the very limited amount of basic experimental data in literature.

We agree with this statement. And as vapor pressure is an important property in SOA formation, this is a major limitation in this research field.

2.2 Specific Comments

1) 1 - Introduction, line 11-16 When discussing the use of corrections for non-additivity, the authors should remark that methods which lack such a feature are in principle

unable to correctly describe the vapor pressure of components with more than one hydrogen-bonding group. While this correction requires more parameters to be regressed, it is nevertheless important.

The text has been changed into: "... assume a linear dependence of $\ln\left(p_i^0\right)$ on the number of functional groups, but this approximation fails especially when multiple hydrogen bonding groups are present. To counter this deficiency, other methods introduce ...".

2) 2 – Description: : :, line 16-18 The Joback method should in principle only be applied to components within a certain boiling point range. Nevertheless, when used outside this range, a correction can be applied that can simply be derived from a plot of estimated vs. experimental normal boiling temperature for a sufficient number of components.

We added the comment of the reviewer in the text:

"The Joback method should in principle only be applied to components within a certain boiling point range. Outside this range, a correction has to be applied that can be derived e.g. from a plot of estimated vs. experimental normal boiling temperature for a sufficient number of components."

3) 2.2 Boiling : : :., line 13 blank missing: Data Bank hypenation: para-meter

Corrected.

4) 5 Conclusions, line 7ff It may seem a drawback to first estimate a normal boiling temperature and then calculate the vapor pressure value at a much lower temperature but this should also be viewed from the perspective of physical significance of the estimated properties. At the normal boiling temperature a certain ratio exists between the molecular interaction and the thermal energy while the entropy of vaporization only changes slightly and in a simple way with temperature. The normal boiling point correlates to some extend with the slope of the vapor pressure curve but this correlation

is not strict enough. Group contribution parameters that can describe the boiling temperature do not correlate well with those describing the slope. Generally estimation of vapor pressure at a given temperature is therefore much more difficult than estimation of a boiling temperature for a given pressure as it would require describing separate phenomena with one set of parameters.

We changed the sentence into:

"At first sight, it seems unnecessarily complicated to have to estimate a boiling point for molecules for which room-temperature vapor pressure data are available, while in the end one is only interested to estimate vapor pressures for ambient conditions. This is a drawback that direct estimation methods (Pankow and Asher, 2008; Capouet and Müller, 2006) do not have. On the other hand, direct estimation of vapor pressure at a given temperature is much more difficult than estimation of a boiling temperature for a given pressure (see discussion phase of this work). Hence the estimation of a normal boiling point is a convenient starting point to estimate a vapor pressure, even if this boiling point is far above the temperature of interest."

3   Other changes

- Section 3.2.4: Nan-Mol should be Mol-Nan.

- Figure 1: There was a sign mistake in the Δ for Nan-Nan vs. CM, which is corrected.

- Section 4.1 and Figure 1: For the hydrocarbon component of the CM vapor pressures accidentally the older Lee-Kesler corresponding states method was used instead of the Ambrose-Walton corresponding states method. This has only a tiny effect on the results (about 0.02 on $\log_{10} p^0$).

- Reference Ceulemans et al. (2010) updated.

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