

Interactive comment on "Distribution of gaseous and particulate organic composition during dark α -pinene ozonolysis" by M. Camredon et al.

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Steven Compernelle in a recent interactive comment on this paper has pointed out that the Joback-Reid (JR) group contribution method is known to provide boiling point values that are too high, and that these high boiling point values will in-turn give vapour pressure predictions that are too low. This will go a long way to explain why these authors get relatively good agreement between their predicted and experimentally found SOA mass while Jenkin et al. using a different vapour pressure estimation technique got very poor agreement.

I agree completely with Steven Compernelle's comments on this matter, and would like to make some additional points:-

- 1) The JR group contribution method provides reasonable estimates of the boiling point for relatively volatile compounds. Stein & Brown (SB) introduced their correction for boiling point values above 500K; below this value no correction was required. The calculated correction is quite small for boiling point values close to 500K but increases rapidly at higher temperatures. In Camredon and Aumont (2006) a good correlation is found between experimental boiling points and those estimated by the JR method. However in their figure 1 there are only a handful of points at experimental boiling points above 550K (where the correction is about 21 K) and none above 575K (where the correction is about 29K). Hence the correlation shown is dominated by experimental points where the correction is either not needed (<500K) or small relative to the scatter in the predicted values (500-575K). If experimental boiling points above 600K had been included in this figure the divergence from the line may have been much clearer.
- 2) In Barley and McFiggans (2009) we show that for a set of 45 multifunctional compounds with low experimental vapour pressure values the JR method predicts too high boiling points (and hence too low vapour pressures) for many of the compounds. Compounds of atmospheric importance that are likely to condense into SOA will probably be even less volatile than our test set and the errors introduced by the JR method correspondingly higher. This is emphasized in Figure 1 (included in the final version of Barley and McFiggans (2009)) which shows scatter plots of the 12 combined vapour pressure methods (all combinations of three boiling point estimation methods with four vapour pressure equations). The coefficients for the regression lines shown in these plots are summarised in Table 1. The regression lines for those methods using boiling point estimation by the JR method all have slopes above 1.5 consistent with the error introduced by the JR method increasing exponentially as vapour pressures are reduced. The Myrdal and Yalkowsky (MY) vapour pressure equation has a bias in the opposite direction and tends to over estimate vapour pressure values. This is shown in panel b) where the three methods using the MY vapour pressure equation are compared.

The two methods using the more reliable boiling point estimation methods:- the N-Tb method (Nannoolal et al., 2004), and the SB method; have regression lines above the X=Y line (slopes <1) and the gap between the JR line and X=Y is considerably reduced compared to the vapour pressure equations assessed in panels a):- the N-VP model (Nannoolal et al., 2008); and c):- the Baum equation using the equations of Vetere published in 1995:- the BV model, similar to the method used by Jenkin.

Also, while it is true that the JR/MY method may give better results than the N-Tb/N-VP for certain classes of compounds (eg. some dicarboxylic acids); the results shown here (and in Barley and McFiggans (2009)) for 45 multifunctional compounds with a wide range of structural features are a better test of the quality of the estimation methods. Models that give good results for a class of compounds by the cancellation of errors have no guarantee of accuracy when applied to a wider range of functional groups.

- 3) In Barley and McFiggans (2009) we show that the amount of SOA predicted using the partitioning model is very sensitive to the accuracy of the vapour pressure values used. It follows that the selection of components that condense into SOA using these models will be similarly sensitive to the vapour pressure values. The authors should include suitable caveats in their conclusion section reflecting this sensitivity.

Barley, M. H., and McFiggans, G.: The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol, *Atmos. Chem. Phys. Discuss.*, 9, 18375-18416, 2009.

Camredon, M., and Aumont, B.: Assessment of vapor pressure estimation methods for secondary organic aerosol modeling, *Atmospheric Environment*, 40, 2105-2116, 2006.

Nannoolal, Y., Rarey, J., Ramjugernath, D., and Cordes, W.: Estimation of pure component properties part 1. Estimation of the normal boiling point of non-electrolyte

organic compounds via group contributions and group interactions, *Fluid Phase Equilibria*, 226, 45-63, 2004.

Nannoolal, Y., Rarey, J., and Ramjugernath, D.: Estimation of pure component properties. Part 3. Estimation of the vapor pressure of non-electrolyte organic compounds via group contributions and group interactions, *Fluid Phase Equilibria*, 269, 117-133, 2008.

Table 1. The regression coefficients for the datasets

VP Estimation Method ^a	Regression Coeffs. ^b	R ²
Figure 1; n = 45		
N-Tb/N-VP	1.0316X + 0.1127	0.798
SB/N-VP	1.1018X + 0.1800	0.7153
JR/N-VP	1.8064X - 1.0682	0.6106
N-Tb/MY	0.8696X + 0.4419	0.7332
SB/MY	0.9462X + 0.5077	0.6614
JR/MY	1.5643X - 0.6367	0.5845
N-Tb/BV	0.9669X - 0.1209	0.5359
SB/BV	1.0566X - 0.0548	0.4633
JR/BV	1.7903X - 1.4472	0.4954
N-Tb/BK	0.8232X - 0.3287	0.5922
SB/BK	0.9018X + 0.3960	0.5351
JR/BK	1.5216X - 0.7733	0.5147

^a The first term is the key for the T_b estimation method (N-Tb= Nannoolal, SB=Stein and Brown, JR=Joback) and the letters after the slash are the key to the vapour pressure equation. N-VP= Nannoolal equation; BK= Baum equation with $\Delta S_{\text{vap}} = K_f R \ln(82.06 \cdot T_b)$; BV= Baum equation with Vetere equations; MY= the Myrdal and Yalkowsky equation.

^b Equation of line $\log_{10} P_{\text{est}} = A \log_{10} P_{\text{exp}} + B$, with X = $\log_{10} P_{\text{exp}}$ and A, B are the coefficients given in the table.

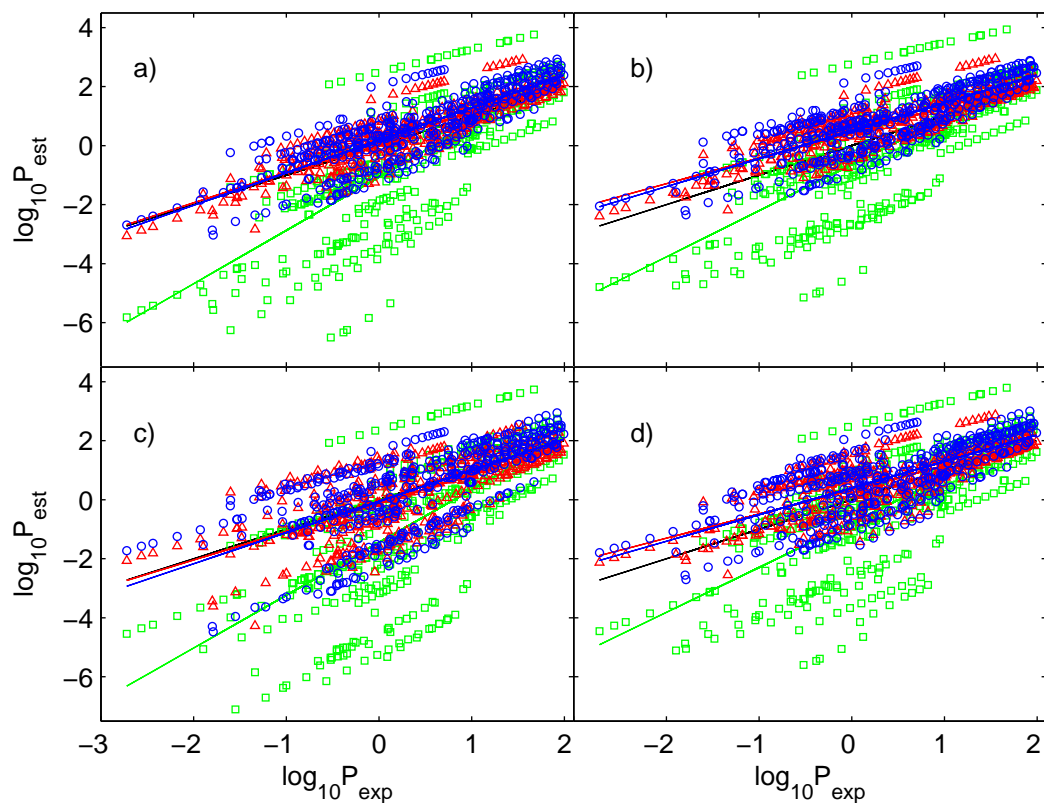


Fig. 1. P_{est} vs. P_{exp} plots for the 12 combined methods applied to Test Set 2. Each panel uses a different vapour pressure equation:- a) N-VP, b) MY, c) BV and d) BK with the symbols colour-coded according to the boiling point estimation method used:- Blue: N-Tb, Red: SB and Green: JR; where N-Tb= Nannoolal, SB= Stein and Brown, JR= Joback T_b estimation methods. The coloured lines are regression lines for each dataset (for coefficients see Table 1) and the black line is $X=Y$. The key to the vapour pressure equations is:- N-VP= Nannoolal equation, BK= Baum equation with $\Delta S_{\text{vap}} = K_f R \ln(82.06 \cdot T_b)$, BV= Baum equation with Vetere equations, and MY= the Myrdal and Yalkowsky equation.