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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol" *by* M. H. Barley and G. McFiggans

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The authors would like to thank the reviewer for their careful consideration of the manuscript and wish to take this opportunity to make several suggested improvements to the paper in response to these comments. The reviewer had two main comments which we will address first before moving on to the section labled "other comments".

- *1) The authors correctly identify a problem with the method of Moller et al... This is unfortunate, as the former (i.e. Moller method) is supposed to be better optimised for the prediction of very low vapour pressures- the main requirement of atmospheric scientists... I suggest that the authors of this ms (sic) carry out at*

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least some tests with the corrected Moller et al. method, rather than reject it...

Following the correction of the method of Moller et al. and clarification from Bruce Moller this method has been successfully implemented and compared against the database of experimental vapour pressure data. A brief description of the method will be added to the text and an extra figure showing a direct comparison against the vapour pressure correlation of Nannoolal et al. will be included in the paper (see below). The conclusion is that the vapour pressure equation of Moller et al. gives similar results to that of Nannoolal et al.

In the amended paper the second paragraph on p18385(lines 14-21) will be deleted, and the first paragraph on this page (lines 3-13) will be moved to after item G) on p18386-line 4. The sentence "This work will also consider some variants on the Nannoolal method, a corresponding states method (Lee-Kesler), and two methods that don't require a boiling point. " will be inserted at p18386-line 5. The text will continue "...The accuracy of these methods will be compared to the accuracy of the best combined methods once these have been found using Test Set 2". This will then be followed by the description of the N-Sim method (presently p18385-lines 3-13), then a description of the method of Moller et al. followed by a description of the Lee-Kesler method (see response to Reviewer 2), and then the text presently at p18386 line 7 (starting "The Simpol.1 method of Pankow and Asher. . .") through to p18387- line 3. The new text describing the method of Moller et al. will be:-

The method of Moller et al. (2008) (will be referred to as the M-VP method) is an improvement of the Nannoolal et al. (2008) method. It features an additional term to improve predictions for aliphatic alcohols and carboxylic acids; new size dependent groups to improve predictions for several functional groups, and new hydrocarbon groups. Re-writing equation (9) and adding the extra term gives;

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$$\log_{10}(P_i^0) = B'\frac{T - T_b}{T - C(T_b)} + D'\ln\left(\frac{T}{T_b}\right) \qquad (1)$$

where the second term is the the new term for carboxylic acids and alcohols and D’ is set to zero when they are not present. In the Nannoolal et al. (2008) method, C = T_b/8, but this is replaced with the following term:

$$C(T_b) = -2.65 + \frac{T_b^{1.485}}{135} \qquad (2)$$

and B’ and D’ are obtained by the summation of the appropriated group contributions, including size dependant groups and group interactions. All group contributions were refitted to the above equations.

- *2) Although the authors searched for measured vapour pressures that are very low, it is still the case that they are not entirely within the range for atmospheric SOA. It would be very helpful if the authors provided a plot that shows, in some way, the errors in the predictions of the various models as a function of the measured vapour pressure... It would be worthwhile because some trend might emerge... that would give at least a rough impression of what kind of errors might be expected at lower vapour pressures than those of the test compounds.*

  A new figure 1 will be constructed which in four panels shows plots of P_{est} vs. P_{exp} for each of the vapour pressure equations (Nannoolal(N-VP), Myrdal and Yalkowsky(MY), Baum/Vetere(BV) and Baum/Fishtine factor(BK)) with the different T_b models (Nannoolal (N-Tb), Stein and Brown(SB), and Joback(JR)) indicated by the colour/shape of the symbol. Hence the MY panel will show points for T_b by the N-Tb, SB and JR methods in different colours with a regression line for each T_b model. The old figure 1 will become the new figure 2. A comment on the trends uncovered will be added to the discussion and conclusions. In addition the present figure 2 will be deleted and replaced with two figures (new figures 3

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and 4)- the first will be a two panel figure showing, in the left panel, P_{est} vs. P_{exp} for the 36 compounds that could be used with SIMPOL.1 while the right panel will show P_{est} vs. P_{exp} for the 9 compounds that can be used with the Capouet and Muller(CM) method. In each panel the models used will be N-Tb/N-VP, N-Tb/M-VP, J/MY and either SIMPOL.1 or CM. The second figure compares some extra vapour pressure method using the best available boiling point estimation method (identified as N-Tb in the text) for the full set of 45 compounds. In the first of two panels the N-Tb/N-VP and N-Tb/M-VP methods are compared. In the second panel the N-Tb/N-Sim method is compared to the N-Tb/LKA method (where N-Sim refers to the simplified Nannoolal vapour pressure equation and LKA stands for the Lee-Kesler method using critical properties calculated from the normal boiling point using the Ambrose method- see Response to reviewer 2). An additional table (Table 6) giving the regression coefficients and R^2 values for all the methods shown in these new figures will also be included in the paper.

Other Comments:-

- *The vapour pressure prediction methods available on the E-AIM website will, over the next several days, be revised to include both the corrected Moller et al. method and the method of Nannoolal et al. that the authors are currently recommending. Some changes are needed in the ms(sic)to reflect this. E-AIM needs to be cited, giving both its full name (the Extended Aerosol Inorganic Model) and the URL.*

In addition to the modifications outlined above about including the method of Moller et al. the sentence beginning p18379-line 18 will be changed to... E_AIM provides vapour pressure data either using T_b by Stein and Brown (1994) combined with the vapour pressure equation of Myrdal and Yalkowsky(1997); or with T_b estimated by Nannoolal et al (2004) coupled with either the vapour pressure equation of Nannoolal et al (2008); or that of Moller et al (2008), The following sentence (p18379-line 22) starting "Recently the E-AIM vapour pressure equation has been changed..." will be deleted. The citation for E-AIM included at the first mention of E-AIM (p18379-line14)... (used in E-AIM:-Extended Aerosol Inorganics Model, http://www.aim.env.uea.ac.uk/aim/aim.php- see Wexler and Clegg, 2002); and the older group contribution method...

- *...but I disagree with the last sentence of the first paragraph of the introduction. I think successful models of OA formation in the atmosphere will always be semi-empirical and are unlikely to be based on accurate vapour pressures of any but a small fraction of the compounds present.*

  We agree with the reviewer that the models will always be semi-empirical, and by using the term "accurate" we do not mean to imply "experimental" but rather a "good estimate". We recognise that we will probably never be able to identify the majority of the condensed components in OA and hence will not be able to identify important individual compounds to assign predicted vapour pressures. However we show in this paper that the amount of SOA can be very sensitive to the accuracy of the vapour pressures used. We believe that the accuracy of vapour pressures required to consistently predict an amount of SOA to within +/- 10% is far more demanding than researchers presently recognise. We hope to be able to put a figure on this sensitivity in a future paper. To make this clearer we propose to change this sentence to:- "Whether the goal is to model OA composition using explicit methods (e.g. Aumont et al., 2005; Bloss et al., 2005), or by the non-arbitary selection of model compounds, accurate estimates of the vapour pressures for all the thousands of organic compounds at ambient temperatures will be required..."

References

1. Wexler, A.S. and S.L. Clegg, Atmospheric aerosol models for systems including the ions H^+, NH_4^+, Na^+, SO_4^{2-}, NO_3^-, Cl^-, Br^-, and H_2O. Journal of Geophysical Research-Atmospheres, 107(D14): p. 4207, 2002.

2. Aumont, B., Szopa, S., and Madronich, S., Modelling the evolution of organic carbon during its gas-phase tropospheric oxidation: Development of an explicit model based on a self generating approach, Atmospheric Chemistry and Physics, 5, 2497-2517, 2005.

3. Bloss, C., Wagner, V., Jenkin, M. E., Volkamer, R., Bloss, W. J., Lee, J. D., Heard, D. E., Wirtz, K., Martin-Reviejo, M., Rea, G., Wenger, J. C., and Pilling, M. J.: Development of a detailed chemical mechanism (MCM v3.1) for the atmospheric oxidation of aromatic hydrocarbons, Atmospheric Chemistry and Physics, 5, 641-664, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 18375, 2009.