

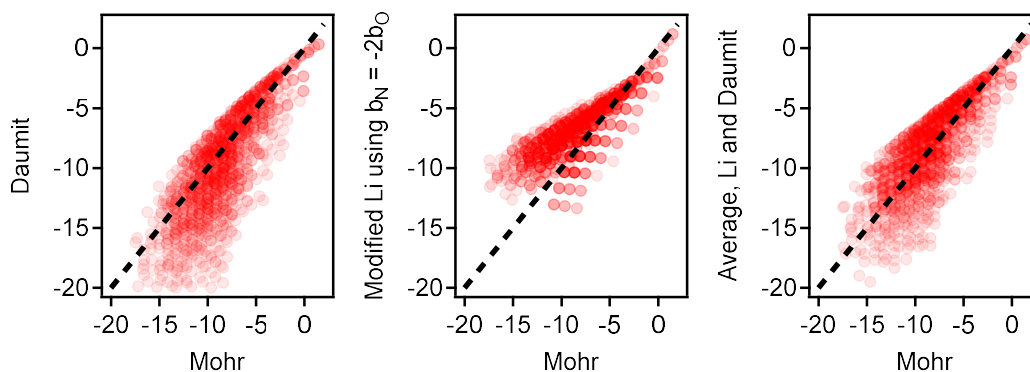
In their work, “Volatility of aerosol particles from NO<sub>3</sub> oxidation of various biogenic organic precursors,” the authors present a detailed examination of the volatility distributions of SOA formed through BVOC+NO<sub>3</sub> reactions. Several different experimental methods are coupled with multiple formula-based parameterizations to generate a full picture of the distribution. In general, it is a very thorough and nice work, with cohesive conclusions and well-written presentation. NO<sub>3</sub> chemistry is an important and understudied topic, and there are some very interesting results here.

The formula-based vapor pressure parameterization approach used in this work is a topic with which I have some very specific expertise and interest, and I believe there are some specific major aspects that need to be re-examined, as discussed below. I do not think they will be hard to incorporate, but they will require some major revisions. I would be very happy to work with the authors directly and to answer any questions or clarifications, please do not hesitate to contact me at [ivw@vt.edu](mailto:ivw@vt.edu).

--Gabriel Isaacman-VanWertz.

- (1) I don't think that the parameterization implemented in this work should be referred to as IvWA (also, I usually use an uppercase “V”). What is being implemented here is the Li et al. method, with modifications implemented as suggested by Isaacman-VanWertz and Aumont. The distinction being that we did not develop the coefficients or approach being used. Based on the best available structure-based estimation techniques, our proposed parameterization was actually to use the average of the modified Li method with the Daumit method, which is not included in the present work but relies heavily on SIMPOL like the Donahue and subsequent Mohr methods do. Modified Li et al. alone was shown to be higher volatility than the best structure-based estimation techniques, while Daumit (SIMPOL) tends to be lower. The average method is what is recommended by the PEACH scripts published as part of Isaacman-VanWertz and Aumont. I have actually updated PEACH to include the Mohr formulation am happy to send it along; I will update the git repository as soon as I get a chance, sorry it was not included in the first version.
- (2) I would recommend trying the combined Li-Daumit method (which I would not object to being cited as IVWA, as it is a somewhat different approach than either alone). As noted above, it does the best job of mapping structure-based vapor pressure estimates onto formulas. This of course does not provide any information about how accurate the actual estimates are, which is a nice aspect of the present work, but it would still probably be the best parameterization to use for formulas. Below I have included comparison figures of the Mohr method with the modified Li method (essentially, the IvWA method in this work, though see comment 3 below), the Daumit method, and the Li-Daumit average recommended by Isaacman-VanWertz and Aumont. For comparison, the ~1200 formulas generated in Isaacman-VanWertz and Aumont are used, values are vapor pressure in units of atm (to convert to C\* easily, just add roughly 9.5 orders of magnitude).

All formulas from Isaacman-VanWertz and Aumont ( $vp$  in atm)



Only formulas containing  $\text{NO}_3$  ( $vp$  in atm)

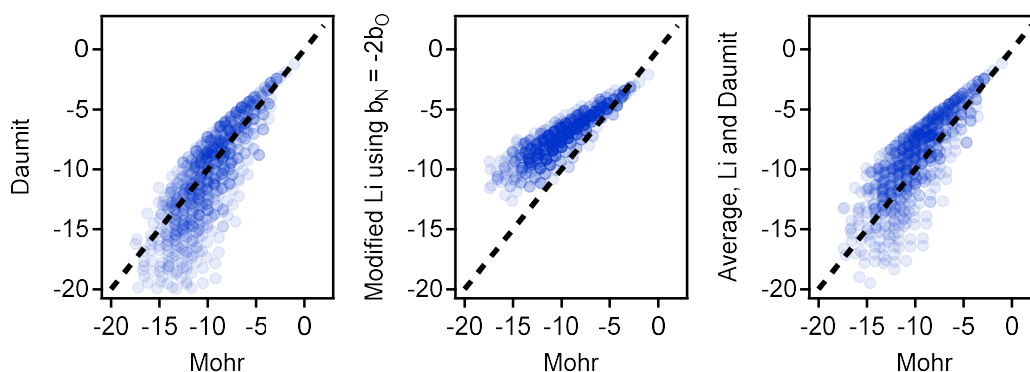


Figure RC1. Comparison of vapor pressures estimated for 1200 formulas using four parameterizations: Mohr et al. ("MHR" in manuscript), Modified Li et al. ("lvWA" in manuscript), Daumit et al., and average Li-Daumit (recommended by Isaacman-VanWertz and Aumont, using other Li modification, see comment 3). Values are in units of atm.

Generally, the Daumit method, which is based in part on SIMPOL coefficients like the Mohr method, is broadly near agreement with the Mohr method, while the modified Li method tends to predict higher vapor pressures because it is tuned to values from the EPI suite vapor pressure estimator, which tends to be higher than other methods. These features of the methods are consistent with the observations in the present work. lvWA is found to be generally too volatile, consistent with the known high-volatility tendency of the Li method, and the Mohr method is often found to be a bit too low volatility, consistent with the Daumit method that is similarly based on SIMPOL (and the tendency of SIMPOL to predict lower volatilities than other methods).

The average Li-Daumit method is somewhat in between of course. Given that this method best captures structure-based estimates and might correct for some of the other methods in the present work, I would strongly suggest considering including it in the comparisons. As currently written, a lot of the results can be explained by the estimation methods, not inherently by the fact that the formula-based approaches implicitly ignore structure or by errors in the best available estimation methods. If Li-Daumit still fails (and it will, I'm sure, we're just not that good at these estimations

yet), we could better probe our capabilities of estimating these properties (Do we need structure? Or is even our structure-based estimation not good enough? See comment 5).

- (3) I have a few minor concerns about how the modifications to Li et al. suggested by Isaacman-VanWertz and Aumont are actually presented, particularly in the discussion of the treatment of  $\text{NO}_3$ .

I find the formulation and discussion of Equation 4 a little confusing. What we originally proposed was  $b_N = -2b_O$ , with a different formulation of the actual equation (i.e., no subtraction term in the oxygen count). Using Equation 4 as written with  $b_N = b_O$  is mathematically equivalent, but it is somewhat confusing because a reader may not realize the difference in the equation and may be confused by the two different equivalencies of  $b_N$ , especially given that you cite our work directly after stating  $b_N = b_O$ . I think it would be less confusing to keep the original Li formula and use  $b_N = -2b_O$ .

Similarly, I don't really agree with citing our work after the statement on line 194 that  $\text{NO}_3$  "thus reduces a compound's vapor pressure by 0.7732 orders of magnitude" – our work was agnostic to the magnitude of the decrease in vapor pressure, we simply noted that an  $\text{NO}_3$  group is equivalent to an OH group in SIMPOL so should be able to be treated as such, as is down in the Mohr method. The magnitude of the effect, i.e., the coefficients, is defined by the model treatment of O in Li et al. (which is generally higher volatility as noted above). A similar issue arises on line 399, though if you referenced the method as a modified Li method I would not object to the characterization.

Note also, we actually proposed two different possible treatments of  $\text{NO}_3$  – either directly setting  $b_N = -2b_O$  as implemented in this work, or programmatically changing each  $\text{NO}_3$  unit within the formula to an OH unit. In Isaacman-VanWertz and Aumont, we could not clearly establish either as better than the other and they both removed the apparent bias and are based on the same idea ( $b_{\text{NO}_3} = b_{\text{OH}}$ ). However, there is interestingly some difference, with the coefficient approach being used here yielding slightly higher vapor pressures than the conversion approach, see figure below of the 1200 formulas used in Isaacman-VanWertz and Aumont. I have included both approaches in the updated PEACH scripts that will be uploaded shortly.

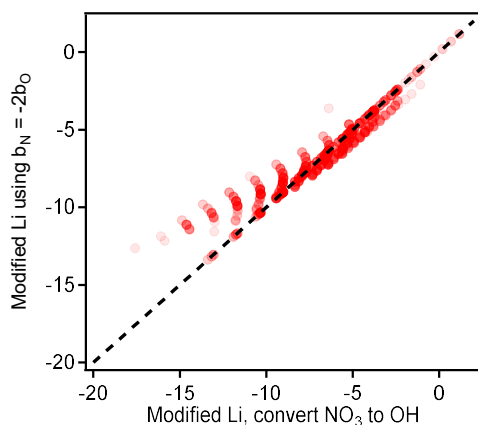


Figure RC2. Comparison of vapor pressures estimated for 1200 formulas using two modifications to Li et al., one based on modified coefficients ("IvWA" in manuscript) and one changing  $\text{NO}_3$  units to OH (used by PEACH in average Li-Daumit method). Values are in units of atm.

- (4) In Figure 3, the three parameterizations are compared. It would be nice to see how these compare the VBS derived from the FIGAERO-CIMS distribution. In later figures, the parameterizations are compared to the TD and isothermal results, but there is no real comparison to the FIGAERO results, which could maybe be used as a sort of “truth”. It would actually be interesting to try to tune a Li-like method that uses all the FIGAERO-CIMS thermograms to actually tune the coefficients. This thought is implicit in the efforts to tune  $b_N$  by precursor (around line 420) - no single value works, but maybe there is a value that considers the CO interaction and maybe even some additional term.
- (5) Line 402 is an interesting point, that the strengths of these methods depend on their tuning. PRK is tuned for this, so of course it works. The others are tuned more generally, so they are more widely applicable, but maybe less accurate. See comment 4 above that maybe we can find a more universal tuning.

With that in mind, it would have been nice to see a little more in-depth dive into why these parameterizations do or don't capture different systems. Implicit in parameterizations is that each atom is associated with specific functional groups, so is this telling us something about differences in functionalities between systems? Do you see some formulas that desorb from FIGAERO at very different temperatures in each system? If so, that implies it is differences in structure that cannot be captured by formula alone. Or is it rather that formulas of some systems are being well represented and captured but other systems the formulas are different and are not being captured. For example, why do the parameterizations invert the volatility of the O3 and NO3 systems, is it just the volatility of NO<sub>3</sub> groups or are there other functionality differences contributing (e.g., do the distributions of their non-NO<sub>3</sub> components show the same inversion, or are they captured reasonably?)? These different possible outcomes would help answer the question of whether the issue in our vapor pressure estimation is that structural information is necessary (and inherently unavailable in MS data) or that our actual structure-based estimation methods are still not correct.

All of this is related to comment 4 above, using the FIGAERO data to probe what these parameterizations are actually telling us. If the authors are not interested in this problem, let me know, I would be happy to play with it if they would share the data. In general, I think the present data provide a great opportunity to understand and improve these parameterizations, but I'm not sure it is being done in this work or if the authors intend to examine this in the future.

All these comments above will have effects on discussion and figures throughout Sections 3.3 and 3.4, so I have not provided too much additional discussion or comments on these sections here.

Technical comments.

Overall, the paper is very nicely written, I have very few detailed technical comments.

Line 57: “number of studies...are much fewer” is not grammatically odd. Should be “number of studies...is lower” or “there are many fewer studies”

Line 70: I'm not sure the connection between the low-volatility of ON-containing HOMs and the 2.5 order drop from NO<sub>3</sub> follow from one another. I understand the connection the authors are pointing towards, but that same drop is true of OH groups, and there are plenty of SVOC and high volatility

alcohols. Assuming the 2.5 orders is correct, it takes a combination of functional groups to get to (E)LVOC.

Line 106-108: Run-on sentence

Line 206: Needs a comma before "referred"

Line 260-262: A bit of a complicated/run-on sentence

Figure 2: a-Pinene data is pretty hard to see, maybe use a darker green

Line 374: How is thermal decomposition subtracted out? And is it not then added back in as the presumed undecomposed mass? If not, that would remove a lot of low-volatility mass from the model, I would think. That is discussed somewhat, but I'm not completely clear how it is quantitatively being handles.

Line 387: "approach" should be plural or some other correction needs to be made

SI: It would be very helpful for the authors to share their data directly. In particular, what are the formulas observed in each oxidation experiment or system? For example, for Figure RC1 above I wanted to make the figure with the actual formulas used in this work, but they were not available, so I had to use those from Isaacman-VanWertz and Aumont.