Response Letter to Referee #1

The authors thank the reviewer for the careful review of our response and the revised manuscript and helpful comments. All the comments (in bold text) are addressed below point by point, with our response following in non-bold text and the corresponding revisions to the manuscript in blue. All updates of the original submission are tracked in the revised version.

In their manuscript "Volatility of aerosol particles from NO3 oxidation of various biogenic organic precursors", the authors present a revised discussion of volatility of observed products classified by molecular formula, comparing four volatility parameterizations and two volatility measurement approaches. This is a valuable contribution and is nearly ready for publication once an issue in the Daumit parameterization is addressed (see major comment 1).

I think the reviewers for their thoughtful responses and appreciate their detailed discussion of the C*-T_D relationship from FIGAERO, which I know has been the subject of a lot of work since I last dealt with it. I look forward to looking at their data to see what else we can learn.

We thank the reviewer for the positive assessment of our response and the revised manuscript.

Major comments:

(1) I am not convinced the implementation of the Daumit method is really correct. The assumption that the only source of DBE is carbonyl (and nitrate) is not necessarily correct, since rings add DBE and may be preserved in a-pinene and B-caryophyllene products. This is typical for the Daumit method, but the impact of rings should probably be mentioned explicitly, since a-pinene and B-cary products can very possibly have rings preserved. More importantly though, this issue can be dangerous given the equations as written. If there are other sources of DBE (e.g., rings), the number of carbonyls Eq. 6 will produce can actually return more carbonyls than there are functional groups. For example, the a-pinene product C10H14N2O8 (observed in this work as shown in Fig. AC3) is calculated to have 3 carbonyls (10-14/2-2/2+1 = 3), though in reality there are likely two only two non-nitrate other functional groups. (and probably a preserved ring). For other cases, for instance C7H9NO5 which GECKO-A predicts as a product, equation 6 estimates 3 carbonyls (7-9/2-1/2+1 = 3), again impossible as there are only two non-nitrate oxygens. Another example is C9H12O3, a GECKO-A predicted non-nitrate product that equation 6 estimates contains 5 carbonyls despite having only 3 oxygens. This issue probably applies to a minor fraction of formulas, but is probably present to some degree.

Part of the issue comes from the definition of n_carbonyl, which is defined here as DBE-n_NO3. For one thing, I don't think the double bond in the nitrate actually matters in terms of carbonyl groups because it doesn't come at the expense of two hydrogens on the arbon backbone like the carbonyl does (in other words, it is not giving us any information about double-bonded carbons, which is used to estimate carbonyl number). However, the

nitrate group itself does come at the expense of a hydrogen, so it is more accurately considered as n_carbonyl = DBE = n_C-(n_H+n_N)/2+1. The end equation is actually the same, so maybe it doesn't matter, but I'm not sure it is actually correct as written. More importantly, though, is the excess DBE problem. I think you have to write it as n_carbonyl = min(n_C-(n_H+n_N)/2+1 , n_O-3*n_N). Basically, you can't have more carbonyls than you have functional groups. This issue is inherent in this formulation of the Daumit method, which was originally developed to estimate carbon number from AMS data. I think it has to be implemented in the form log c* = log a + b_0 + b_C*n_C + b_OH*n_OH + b_=O*n_=O + b_NO3*n_NO3. I'm not sure where that leaves you with Eq. 8, but this approach would still allow the authors to tune the b_NO3 as done in Table 2.

This change probably won't have significant influence on your figures or conclusions, but should be implemented prior to publication.

The reviewer brings up interesting points. Indeed, the definition of DBE includes the contribution of double bonds as well as rings, i.e. defines the degree of carbon saturation. Hence, as pointed out by the reviewer, by using the Daumit method, which determines the number of carbonyl groups based on DBE, and by us modifying it to accommodate nitrate groups, the number of carbonyls may be overestimated. Whereas the Daumit method provides some information on molecular structure, it is still a method based on molecular composition, and thus cannot assign functional groups, e.g. rings, 100% correctly.

The reviewer brings up a few examples of compounds (based on GECKO-A), where the number of oxygen atoms available for carbonyl functional groups is less than the number of carbonyl groups predicted by the modified Daumit method. We have checked all identified molecular formulae in our experiments and find that this applies to 48 (out of 415), 85 (out of 425) and 117 (out of 366) of compounds (making up 2-3%, 29-45% and 35-41% of signal) for isoprene, α-pinene and β-caryophyllene, respectively. We however abstain from introducing a minimum condition in the parametrization, as introducing a condition for the maximum number of carbonyls never exceeding the total number of functional groups would improve the overestimation of carbonyl groups, but not entirely solve this issue. For instance, consider the compound $C_{20}H_{32}N_2O_8$ from the α-pinene + NO_3 system:
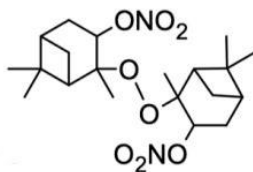
Based on the modified Daumit method as presented in the paper we would for $C_{20}H_{32}N_2O_8$ get four carbonyl groups that contain non-nitrate oxygen atoms. With n_carbonyl = nO-3*nN (i.e. limiting the number of carbonyl groups based on available non-nitrate oxygen), we would obtain two carbonyl groups. This would then equally not represent the actual structure of the molecule well, as neither the four rings, nor the peroxide group are represented correctly. We therefore feel like adding additional conditions would not improve the parametrization. Instead, we do see the

possibility of running chemical kinetic models to get more detailed structure information, potentially improve the application of DMT, and get a better estimation of the volatility. Such a rather comprehensive endeavor is, however, outside the scope of this study.

We added the following discussion about the impacts of rings to the revised manuscript:

"As MHR works better for the α-pinene + O_3 system and DMT works better for the α-pinene + NO_3 system, it is possible that the α-pinene + O_3 system has more -OOH and the α-pinene + NO_3 system has more -OH and =O. However, it is worth noting that as the definition of DBE includes double bonds and rings, and we cannot exclude contributions of oxidation products with rings retained in the α-pinene and β-caryophyllene systems, we note that n_carbonyl represents an upper limit."

The reviewer also brings up another issue: the treatment of the nitrate group in the calculation of DBE. Whereas we agree with the reviewer that the number of double bonds in the nitrate group does not give information about double-bonded carbon and with that the number of carbonyls in a molecule, the DBE formulation still includes all double bonds in all functional groups. As also pointed out by the reviewer, the subtraction of one double-bond equivalent per nitrate group from DBE yields the same number of carbonyls as treating a terminal nitrogen as a hydrogen or –OH. These are just different ways of thinking about a molecule's structure. We therefore keep the formulation as is. In order to make this clear to readers, we have added the following sentences in the manuscript:

"We note that including the nitrate group in the calculation of $n_{=O}$ can be critically discussed, as the nitrate group does not yield any information on double-bonded carbons. However, treating the N of the nitrate group as a hydrogen in the DBE formulation ($C + 1 - (\frac{H}{2} + \frac{N}{2})$), yields the same final formula for $n_{=O}$ (Eq. 6)."

(2) The results in figure AC3 are very interesting. As the authors note in their reply, the impact of structure is of course quite important (trying to quantify it was in fact the main goal of Isaacman-VanWertz and Aumont), so it is interesting to see here. In particular, the C10H16N2O6 desorption temperatures are very different between the systems. The structures are of course quite different, since the isoprene structure must be a dimer, but it is nevertheless fascinating to see such a large difference, since the functional groups are probably very similar, so it is probably an interaction term that will be hard to capture. I look forward to exploring the data once posted!

Thank you!

Technical comments:

Line 59 is still not correct. Should be "there are many fewer", not there are "much fewer" Accepted.

Line 154. Should be "Samples were" not "Samples was"

Accepted.

Line 363. I would clarify a little and say that "DMT leads to higher VFR than the observation *at long evaporation time*...", since until then it is basically on time of observations, more or less like MHR.

We revised the sentence to make it more clear:

"The calculated evaporation of SOA from α-pinene ozonolysis in the VTDMA (Fig. 4a) using MHR and DMT reproduces the evaporation well, while the other two parameterizations, Li and PRK, result in lower VFR compared to the measurements. The overall performance is comparable for the isothermal evaporation data (Fig. 4e), i.e., MHR reproduces the evaporation best, while Li and PRK underestimate VFR, however, DMT overestimate the evaporation over time."

Line 427-428. This point about the C-O non-ideality is a very good one I think I had missed before. It is probably the reason for the difference in the Li modification between using the coefficient change (as used here) and the algorithmic conversion of NO3 to OH (as used in Isaacman-VanWertz and Aumont). The NO3 oxygen should almost certainly be excluded from the non-ideality as in the MHR equations. I agree it was not done in the Isaacman-VanWertz and Aumont discussion of this approach, but I'm not sure that was actually correct (and, as I mentioned, the paper figures actually use the funcational group conversion approach) and should maybe be corrected in this present work. The author's response to my comment about re-working the equation does make sense though; in fact, it makes it easier to correct the issue with the non-ideality.

Thank you.

Line 459. Should be "either" instead of "neither"

We revised the sentence to make it more clear, and thereby removing "neither" all in all

"Since none of the bN values were able to reproduce the data from different precursors for MHR, DMT, or Li, it is clear that simply adjusting the bN value would not resolve the discrepancy we observed between the measured and simulated VFR based on the chemical composition."

Line 497. The authors state an intention to make the data public, so data access should be described in the Data Availability statement

The data will be available through the Bolin Centre data base for everyone to download, we have updated the data availability description in the manuscript accordingly.

"The datasets will be published in the open access data base of the Bolin centre for climate research, available at https://bolin.su.se/data/."

References

Daumit, K. E., Kessler, S. H., and Kroll, J. H.: Average chemical properties and potential formation pathways of highly oxidized organic aerosol, Faraday Discussions, 165, 181-202, 10.1039/C3FD00045A, 2013.

Murray, K.K., Boyd, R.K, Eberlin, M.N., Langley, G.J., Li, L., and Naito, Y. Definitions of terms relating to mass spectrometry (IUPAC Recommendations 2013), Pure Appl. Chem., Vol 85, No. 7, pp. 1515-1609, 2013