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## Comment on acp-2021-1006

Anonymous Referee #3

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Referee comment on "Volatility parameterization of ambient organic aerosols at a rural site of the North China Plain" by Siman Ren et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-1006-RC3>, 2022

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In the manuscript "Volatility Parameterization of Ambient Organic Aerosols at a rural site of the Northern China Plain", Ren et al. report on the results of thermal desorption mass spectrometry measurements of the organic aerosol component of filter-collected ambient aerosol. The work also features a convincing effort in carefully "calibrating" the desorption method so that effective volatilities (or vapor pressures, saturation concentrations  $C^*$ ) can be inferred for individual organic compositions. The calibration experiments did not turn out as good as they maybe could have, and much of the ambient data (section 3.2) at least appears to have been discarded in favor of focusing on easier-to-analyze signals. An additional data selection criteria, however, was the continued prevalence of the respective compositions, which makes the selection particularly useful despite its potential narrowness. Importantly, the calibrations allow a thorough analysis of the observations. The authors explore how the resulting  $C^*$  values could be parameterized based on compositions. They compare their findings to previous attempts in the literature, but which have to a large part been relying on calculations using group contribution theory to extrapolate to compositions observed in organic aerosol. Thereby, this study's analysis of thermal desorption mass spec data goes deeper than what is often provided by other studies using similar datasets.

For these reasons, I believe the manuscript is of considerable interest and deserves publication in Atmospheric Chemistry & Physics, although I do suggest substantial "polishing" before that, considering my comments below.

I also stumbled upon an apparent contradiction in the analysis, e.g. when comparing Figs. 3-4 with Fig. 5. I am elaborating on that in my comments as well. Some clarification is at least warranted, or possibly some semi-major revision.

### General notes:

I noted that only one week's worth of ambient was being used in this study. Was there particular reasons for that?

An additional result that might be worth looking into, similar to the analysis using retrieved  $T_{\max}$  values, would be the **widths** of the fitted peaks, which I understand were largely unconstrained.

For example, could those widths tend to change with increasing/decreasing molecular weights, O/C or  $T_{\max}$ ? And most importantly: could they help identifying decomposition processes?

### **Technical comments:**

Check that peer-reviewed papers are being cited rather than their discussions papers (e.g. ACPD and AMTD), where available.

There are many (individually minor) grammatical and semantical mistakes here and there. The manuscript is readable overall, but they do impede comprehensive reading at some places. Some of the semantical mistakes at least will also confuse readers, in particular if not familiar with the used methodology. I suggest appropriate proof-reading/language checks.

### **Major specific comments:**

Lines 367-369: I am not following here. Aren't the compounds used for the "Eq. (4-1)" parametrization by definition containing (exclusively) OOA species?

In any case, however, the fair agreement with SIMPOL predictions is remarkable (even though only shown for 15 selected compounds) and worth pointing it, as it follows directly from calibrations and measurements, without using SIMPOL calculations. Whereas, if I remember correctly, the other cited works (Li, Tröstl, Stolzenburg) indeed *based* their parametrizations on SIMPOL calculations (so their agreement is expected).

Beyond Fig. 5a, however, it would be interesting to see how the authors' parametrization, i.e., Eq. (4-1), worked out for the other compounds in this group? I.e., do measurement-derived  $C^*$  agree with SIMPOL also for other compositions in the high-O/C group, besides the 15 examples shown? That would however require making assumptions on molecular structures and new SIMPOL calculations. But the authors did that for members of the low-O/C group (Fig. 5b), so my suggestion might be relatively straight forward to implement. (But not sure which compounds were used in Fig. 5b see comment below also ("Moreover,....").)

Lines 391-399: I am lost a bit again. I had to read the first sentence (lines 390-393) several times, as I failed to understand for a while which 42 compounds were being referred to.

More generally, the paragraph here spends a lot of time arguing why the "Eq. (4-2)" parametrization agrees poorly with NIST data, whereas SIMPOL-based parametrizations

perform better (Fig. S9). The point raised about this study's parametrization being based on observations of compounds with generally lower volatility (at least as inferred by  $T_{\max}$ ) may be part of the reason. But the main point, which may be lost, is that the agreement with SIMPOL is also poor for the other 132 (=observed?) compounds (Fig. 5b). The questions I would then have are: (1) is there a reason for SIMPOL to be less accurate for compounds with lower O/C? or (2) is there a reason for the "Eq. 4-2" parametrization to be less accurate, i.e., for the inference of  $C^*$  based on  $T_{\max}$  to be not or less valid? In other words, the results shown in Fig. S9, although interesting, may distract/confuse the more important points of discussion in the main text.

Moreover, it remains unclear which those 132 selected compounds for Fig. 5b are. Is there substantial overlap with observed compositions, or possibly even hardly any? And a key message of Fig. 5b is that parametrization Eq4-2 gives TOO LOW  $C^*$  values (compared to SIMPOL). On the other hand, Figs. 3 and 4 suggest that parametrization Eq4-2 would yield overall HIGHER  $C^*$  values than parametrization Eq4-1 (which agrees well with SIMPOL, Fig. 5a).  
What am I missing?

As a consequence, I would be more careful in the final summary of atmospheric implications (lines 410+). I agree that Eq. 4-1 is doing quite well (for higher-O/C lower-MW compounds), but I am not convinced about Eq. 4-2 (for lower-O/C higher-MW compounds). At least I would not go as far as to claim that it is "more accurate" (and more than what?) for ambient aerosol. The authors hypothesize that interactions with inorganic aerosol components play a more important role for low-O/C compounds, thus lowering their effective  $C^*$ . That hypothesis is plausible in principle, and I agree that those interactions are insufficiently studied. But here, it remains rather poorly supported by some discrepancies during calibration. (In the minor comments below, I also suggest an alternative hypothesis for those discrepancies.) Alternative hypotheses would be warranted too. For example, could those higher-MW compounds be structurally different in some fundamental difference for SIMPOL to stop working? Is there a possibility for the FIGAERO method to be less reliable for those compounds?

And besides that, I still don't quite understand the discrepancy between the following (see also comment above, "Moreover,..."):

- Eq. 4-2 gives LOWER  $C^*$  than expected e.g. using Li et al. (2016)
- Eq. 4-1 gives  $C^*$  about as expected by Li et al. (2016)
- Compounds used for establishing Eq. 4-2 have HIGHER  $C^*$  than expected from the  $C^*$  of the compounds used for establishing Eq. 4-1.

### **Minor specific comments:**

Abstract:

I suggest making clearer that grouping into two different O/C regimes was also supported

by systematically different thermal desorption behavior (Figs. 3-4).  
Indeed, I believe this is also a key result that is missing (or unclear) in the abstract.

Main text:

General: should briefly go into the difference between a compound's saturation vapor pressure and a compound's effective saturation vapor pressure (or concentration) in regards to partitioning in/out of aerosol particles.

Lines 56-60 ... If I remember correctly, Tröstl et al. did not *know* the molecular structures of the observed compositions classified as HOM, nor their saturation concentrations, but guessed the former and correspondingly modeled (using SIMPOL?) the latter.  
(Subsequently, it also remains unclear here what Stolzenburg et al. were "fitting" to.)

Lines 71-74: An important missing piece of information on the FIGAERO procedure is that the desorption temperature is ramped up linearly.

Lines 77-80: A weakness of the "second method" is potential measurement artifacts that obscure the true composition of detected species, which thermal desorption methods are prone to. But I would not conclude that the "third method" is generally and necessarily superior, as these lines now seem to suggest.

Lines 94-95: I believe some text is redundant here (explained twice what volatility is important for).

Line 100: I would explicitly mention how (by which of the 3 methods) was "C\* measured".

Line 110: Unclear how thermal desorption was performed. There was a flow of 2.3 lpm and one of 1.0 lpm. If only 1.0 lpm went through the filter and into the IMR, what happened to the remainder 1.3 lpm flow, and what was it for?

I would also clarify in this paragraph how the filter was heated -- or rather that (presumably) it was the UHP N<sub>2</sub> that would pass through the filter that was heated. In this regard: where and how was the nominal desorption temperature measured?

Lines 113-115: Why was 134 °C chosen as the highest temperature? Typically, FIGAERO

is operated using desorption temperatures up to 200 °C. A shorter ramp could make sense if going primarily for  $T_{\max}$ , as most "nice" peaks would probably occur before 134 °C. On the other hand, I would be worried about accumulating organic material on the filter, which might cause measurement artifacts...

Line 116: How was the "blank filter" used for obtaining backgrounds?

Also: What desorption temperature ramp rate was used? Thornton et al. (2020) and Ylisirniö et al. (2021), e.g., have suggested that that ramp rate may affect the thermograms and hence  $T_{\max}$ .

Section 2.2: Was the desorption procedure (as described in 2.1) for the calibration experiments the same as for the field measurements?

Fig. 1: I believe the caption could be considerably shortened, using reference to Table 1. Table 1 plus the legend of Fig. 1 contain most of the information given in the caption.

Lines 224-228: I would opt to disagree with the conclusion that the reason that  $T_{\max}$  for calibration set #5 were higher than for set #4 was due to the ammonium sulfate. I would instead rather argue the effect was due to increased filter loading: 1000 ng for set #5 vs. 200 ng for set #4. 1000 ng is clearly in the range of filter loadings that previous studies have seen increased  $T_{\max}$  for that were argued to arise from matrix effects, specifically, I believe, loss of relative surface area available for desorption (Huang et al. 2018; Thornton et al., 2020).

Both effects might play a role, but I do not think they can be separated here.

Oh, reading on, I see that this reason is in fact brought up towards the end of the paragraph. I would consider reformulating or restructuring the paragraph to improve clarity.

However, I still disagree with the wording in Line 232 ("In other words,..."). Enhanced interactions between aerosol components could lower the *effective*  $C^*$  also without increasing viscosity. Again, reading on, I believe the authors would agree with that, but the way viscosity is brought up may be confusing...

Lines 244-247: I am not sure I am following. Also, judging from Ylisirniö et al. (2021), more information on the calibration procedure used by Nah et al. (2019b) would be needed to ascertain that the the cyan dash-dot and solid black lines in Fig. 1 should actually be compared.

Lines 254-261 (last paragraph in 3.1): I think the argument for using calibration #5 for the analyzing the ambient measurements is sound, in principle, and would deliver the most accurate estimates for  $C^*$  here.

However, it could not be only the deposited mass on the filter that affects  $T_{\max}$ , but also

the particle (mass) size distribution of the deposited aerosol. I wonder therefore also how those distributions compared between calibration experiments and ambient samples?

Lines 274-276: For clarity, I would re-iterate, which peak was chosen for obtaining  $T_{\max}$  in cases where there was more than one fitted peak. I.e., was it *a/ways* the cooler one, as indicated in Section 2? (Fig. S5d shows an interesting example where of a wide lower cooler peak, and a sharper higher hotter peak. Was it still the cooler one that was chosen, despite being lower?)

Oh, peaking forward, I see that  $T_{\max}$  of both or all peaks were actually considered, at least at first. So this comment may be moot. Still, these lines could already be clearer in respect to how (and which)  $T_{\max}$  were obtained and used for further analysis.

Line 307 (and in general): It seems to be suggested, as also suggested in previous instances in the text, that the higher  $T_{\max}$  obtained from thermograms exhibiting double peaks have rigorously been attributed to arising thermal decomposition, rendering them unusable for further analysis for assessing  $C^*$ . That may be correct reasoning in many instances, but conceivably not always (e.g., for the case of isomers with substantially, but not necessarily unreasonably, different  $C^*$ ). It may be of interest to at least initially keep those hotter peaks "in the game", and discard them at a later point, as the authors' further analysis would probably be able to make a much stronger argument pro/contra decomposition being involved.

Fig. 4: I would clarify in the caption: Are the whiskers ultimately due to variability in the measured  $T_{\max}$  (and hence variability in derived  $C^*$ )?

Line 328-329: Please clarify, are those correlations for the two given compounds average correlations (plus standard deviations), while averaging over the individual correlations with each compound in the respective groups? That's how I understood it, but I could see how I could also be misunderstanding...

Line 338: Please remind the reader on which volatility range the fits/parametrizations in Mohr et al. are based on?

Table 2: Please include also values that have been used in/suggested by the cited literature!

Line 353: Was there any specific kind of OOA that Donahue et al. (2011) referred to corresponding to the yellow-dashed box in Fig. S7?

Line 362: "accuracy" in which respect? Please clarify.

Line 366: What is "therefore" referring to?