



Comment on acp-2021-230

Anonymous Referee #1

Referee comment on "Gas-particle partitioning of polyol tracers at a suburban site in Nanjing, east China: increased partitioning to the particle phase" by Chao Qin et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-230-RC1>, 2021

In this work, the author's present an in-depth look at the gas-particle partitioning of a handful of important, highly oxygenated compounds. Uncertainty in the partitioning of these compounds, and the potential of salting-in to describe observed discrepancies is an important unanswered question that is of interest to readers of this journal. Overall, this work is technically sounds and should be published. Some minor concerns and comments are described below:

General comments:

1. The approach to modeling partitioning nicely accounts for partitioning between phases, but a lot of the information to understand their approach is split between the SI and the main text. Some of the SI I think should maybe be brought into the main text (probably at least Eq. S1 and/or S2, and Figure S2)

2. A critical question in this work, I think, is what is the uncertainty on F%? Uncertainty on these measurements is not really discussed. This parameter is calculated as the ratio of two measurements, each of which likely have at least 10-15% uncertainty (typical of GC), so there is some uncertainty on F% for any given point (though that may decrease as you get to the extreme cases of being mostly in the particle phase as in this case). That doesn't account for the uncertainty on the breakthrough which is significant (e.g., methyltetrols breakthrough is $\sim 20 \pm 10\%$, so the correction factor for breakthrough is between a factor of roughly 1.1 and 1.3). Random error on each point should be reduced in the average (i.e., the average F% is known better than any one point), but the averages could be susceptible to systemic errors like uncertainty in breakthrough that could create bias. I do notice that during the periods of high particle concentrations for e.g., 2-MTs, F% does sometimes reach 100%, so perhaps bias is minimal, but it would be nice to get some estimates of uncertainties, or additional discussion and analysis of potential error. For instance, couldn't the divergence in Figure 2 of the isoprene tracers from the line be due to some bias like uncertainty in breakthrough?

3. Some of these results might be impacted by uncertainty in theoretical partitioning coefficients and by poorly constrained empirically determined coefficients. All of the tracers shown here have values close to 100%, so there is not much dynamic range in the data and it might be susceptible to biases. Calculation of partitioning coefficients in particular could be sensitive to uncertainties because of this (as you approach 100% in

one phase, small changes in partitioning might imply large changes in K). For this reason, I'm not sure the discussion of comparison between theoretical and measured K is always that meaningful. As an extreme example, levoglucosan looks like it is always at ~100% except for maybe one point. Under these conditions, how can any meaningful K be measured, since a partitioning coefficient of 10^3 and 10^{100} would both produce the same effect? On the other hand, there is substantial error in the theoretical values as well, with uncertainty in vapor pressure likely on the order of 1-2 orders of magnitude for most of these compounds (and some evidence that EPI has a tendency to overestimate compared, see Barley and McFiggans 2010). While I agree that the time-dependent comparisons between measured and expected K against things like sulfate (e.g., Figure 3) provide insight, comments like that on line 345 comparing measured to theoretical K quantitatively aren't that meaningful. Similarly, if you account for these sources of uncertainty, it's not clear to me that the lines in Figure 3 necessarily have a negative intercept as described. Some discussion of these uncertainties and biases might help clarify what we do know (e.g., these tracers are mostly particle phase, theoretical vapor pressures are wrong, and correlations with absorptive theory are poor), with the quantitative aspects we don't know as well (e.g., how wrong are the vapor pressures, how strong is the dependence on salt).

Specific comments:

Line 57: Typo, "Filed" should say "Field"

Line 85: Probably also worth mentioning that Yatavelli et al. (2014, 10.5194/acp-14-1527-2014) and Isaacman-VanWertz et al. (2016) also found good agreement with theory for alkanolic acids

Line 90: Typo, "every" should say "very"

Line 176: When quantifying the isoprene tracers using meso-erythritol, I assume the effect of fragmentation on the quant ion was accounted for, but that is not clear here or in the supplemental. In other words, while m/z 219 is used for the 2-MTs, something different, likely m/z 217, is used for meso-erythritol, and the fraction of total signal that is the quant ion could be different - if this was corrected for it should be stated at least in the SI, if not it should be justified.

Line 197: If gas-phase mass is being taken as Q_b plus PUF, what is the purpose of the Q_b measurement at all? Why not just do Q_f backed by a PUF?

Line 220-225: I'm not completely clear on the partitioning approach. The K_{ow} is used to partition the particle fraction between condensed phases - is this information then used in the gas-particle partitioning? For instance, is K_{OM} used for the organic component, and K_H used for the aqueous? I guess I'm just not clear on how K_{ow} fits into the scheme.

Line 297-298: Isaacman-VanWertz et al. (2016) also show hourly diurnal profiles with a daytime high, it is interesting to see in this work that the difference between daytime and nighttime values was not significant. As noted later in the manuscript, in the summer when there are actually strong concentrations of these compounds, there is a strong diurnal, so I'm not sure it really makes sense to claim here there is no diurnal.

Line 336: This is the first place $F\%$ is given any error or range, though I assume here the uncertainty is the standard deviation.

Line 370: This could also be due to some systematic bias in how EPI estimates vapor pressures. This might be reconciled by testing other vapor pressure estimation methods. For example EVAPORATION agrees with EPI on the vapor pressure of erythritol (log vp

(atm) = $\sim -8.2-8.5$) but EPI estimates mannose to be two orders of magnitude more volatile ($\log v_p$ (atm) = -9.5) than EVAPORATION estimates ($\log v_p$ (atm) = -11.5). This also highlights the uncertainty of using comparisons against theoretical K to draw conclusions.

Line 391: Here and throughout, why use $K_{H,e}$ and $K_{H,w}$ for measured and predicted, respectively, for Henry's law, but K_p^m and K_p^t or measured and predicted, respectively, for absorptive partitioning. I think the discussion would be more clear if notation were more consistent (e.g, K_H^m and K_H^t

Line 407: out of curiosity, why did the authors choose to switch to molality instead of molarity?