

Atmos. Chem. Phys. Discuss., referee comment RC3
<https://doi.org/10.5194/acp-2021-230-RC3>, 2021
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Comment on acp-2021-230

Anonymous Referee #3

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-RC3>, 2021

This study by Chao Qin et al. reports on filter-based measurements of the gas–particle partitioning of a selection of semivolatile isoprene oxidation products, levoglucosan and polyols in Nanjing, China. Detailed simultaneous gas and particle phase measurements and assessments of the gas–particle partitioning and influence of aerosol liquid water are relatively scarce. Therefore, this manuscript and the measured data are certainly of interest to the atmospheric chemistry and physics community.

Overall, the manuscript is well written, of adequate lengths and with useful tables and figures. The field sampling and chemical quantification conducted over an extended time span are valuable. The comparison to different predictions by equilibrium gas–particle partitioning models/assumptions is of interest, but it also reveals several issues that need to be addressed.

My main concern is with the provided level of detail on the uncertainties of the measurements and the theoretical predictions, as outlined in the general and specific comments below. This manuscript should be (and can be) substantially improved by adding a better discussion and quantification of uncertainties and potential systematic biases as well as clarifications about partitioning mechanisms and involved assumptions. In the present manuscript, the partitioning model discussion is rather confusing, since the title and text suggest a fundamental difference between "absorptive partitioning" and Henry's law partitioning, not recognizing that Henry's law is a way of expressing equilibrium (absorptive) gas–liquid partitioning.

General comments

- The discussion of the presented mismatch between measured and predicted partitioning of several organic tracers in this manuscript would strongly benefit from a more thorough, quantitative uncertainty analysis of the filter measurements and of the assumptions made with the “theoretical” predictions of partitioning coefficients. This would likely lead to relatively wide error bounds on the median and average partitioning coefficients listed in the tables. At present, the study suggests that there is poor agreement with absorptive (Raoult’s law) partitioning as well as with solubility-based physical Henry’s law partitioning. However, there seem to be substantial uncertainties in the predictions applied and assumptions involved (see the specific comments below).
- A comparison to other studies involving the same or similar compounds should be included. The work by Pye et al. (2018) focuses on measurements and conditions in the southeastern United States and includes field measurements and equilibrium partitioning calculations for several polyols and organic acids in common with this study by Qin et al. Pye et al. (2018) also assessed partitioning of 2-methyltetrol, C5 alkene triol, levoglucosan, pinonic acid and other semivolatile compounds. The Pye et al. work includes predicted or assumed liquid–liquid phase separation cases that differ in phase composition from the assumptions made in this study. Importantly, their results show generally a much better agreement between predicted and measured particle phase fractions. Therefore, it is recommended that the authors compare their findings with those from the Pye et al. study and discuss potential reasons for discrepancies in the partitioning coefficients and their predictability (or that of particle phase fractions).

Specific comments

- Lines 83 – 87: It is stated that an absorptive partitioning model (which one?) underestimated particle-phase concentrations of carbonyls by several orders of magnitude. Is the argument made by the authors here (from the given phrasing) that absorptive partitioning is an incorrect partitioning mechanism? If so, should it be adsorptive partitioning or what kind? This statement requires further clarification/discussion.
For context, do you mean to say that (1) absorptive partitioning does not take place or (2) that the experiments are not measuring partitioning under equilibrium conditions or that (3) inadequate vapor pressures were used in the partitioning model or (4) something else? For example, could reactive uptake be at play (e.g. mentioned in the cited study by Healy et al., 2008). If the measurement/prediction mismatch is due to reactive uptake, it is questionable to blame absorptive partitioning for this, since that theory may still apply to the parent compound that is partitioning, but further reactions in the particle phase, like hydration of glyoxal, complex formation in presence of sulfate ions or reversible oligomerization may distort the understanding of what species and in what amount is partitioning. It may well be that absorptive equilibrium gas–particle partitioning applies to each of the individual species formed but cannot simply be assumed to be represented by the parent compound considered in the gas phase. Introducing an “effective” Henry’s law coefficient can be used to account for the measured partitioning; however, that formulation is then simply a parameterization and not directly elucidating a physical or chemical mechanism.
- Line 89: “favored the formation of pinonaldehyde”; do you mean “partitioning” instead of “formation”? The formation of pinonaldehyde (in the gas phase) is likely independent

from aerosol water content.

- Line 100: The work by Volkamer et al. (2009) on effective Henry's law partitioning and aqueous phase chemistry could also be cited here and perhaps discussed in context of the findings from this study later in the article.
- Line 133 – 135: From this description of the gas and aerosol measurements using filters in series, it is not clear how much the uptake of gaseous (semivolatile) organic compounds on accumulated aerosol mass loading of filter 1 (Q_f) will contribute to the total concentration on the particle filter. Based on absorptive equilibrium partitioning theory, the accumulated condensed-phase aerosol mass on the first filter may shift the actual gas-particle partitioning in the ambient air to favor additional partitioning from the gas phase to the condensed phase on the filter while the sampling flow passes through the filter, thus possibly leading to a systematic particle phase mass concentration bias. Given the long sampling times, this may constitute a substantial bias. Were such potential issues quantified in controlled experiments? Please discuss.
- Line 152 – 154: "Concentrations of aerosol liquid water were predicted by ISORROPIA II model"; this prediction will only account for water uptake by inorganic ions but neglect any water uptake by hygroscopic organic compounds (such as some WSOC), right? It may therefore lead to an underestimation of the WSOC effect on organic partitioning. The authors could use a simple estimation based on typical organic hygroscopicity parameters (κ) and the median or actual RH values to estimate the organic-contributed water content by the WSOC mass fraction in particles.
- Line 209: I suggest adding these equations to the main text.
- Line 212: If I understand your procedure, the ISORROPIA-derived aerosol water content is not accounting for water associated with WSOC, which could be substantial at high RH and when the WSOC represent a significant mass fraction of aerosol. Also, actual interactions among organics and ions within particle phases may affect the partitioning (both between liquid phases and gas/particle), which I assume is ignored in this work. Furthermore, WSOC, while water-extractable by definition, can be of relatively moderate polarity and may preferably partition to the WIOM organic-rich phase in presence of dissolved salts in an aqueous phase (see e.g. Zuend et al., 2012; You et al., 2014; Pye et al. 2018). Hence, it would be useful to estimate errors from such effects on the determined K_{OW} . It may also be adequate to consider other liquid-liquid phase separation scenarios, such as assuming that all WIOM and WSOC organics partitioned to one aqueous organic phase and all inorganic salts to a separate aqueous inorganic phase (compare to Fig. 3 of Pye et al., 2018).
- Lines 221 – 222: The rather low octanol-water partitioning coefficients indicate not only better solubility in water but also that the polyols of moderate to high polarity have low solubility in octanol; this is because octanol is a rather low polarity medium as choice for representing organic aerosol. SOA-rich phases may be of substantially higher polarity than octanol yet still form a separate phase from an aqueous salt-rich phase (e.g. You et al., 2014). This should be acknowledged, and consequences of partitioning assumptions considered in the uncertainty analysis.
- Line 224 and SI Eq. (2), Text S2: In the SI, it is stated that for the absorptive partitioning prediction an average organic molar mass MW_{OM} of 200 g/mol was used. This seems to be a common and reasonable assumption, but only for a water-free organic absorbing phase. However, for the partitioning of WSOC compounds when assumed to prefer the aqueous phase, one should account for the low molar mass of water present in substantial amounts in that phase, which would lower the weighted mean molar mass significantly (Liu et al., 2021; Gorkowski et al. 2019). Please consider this and, where applicable, correct the estimated partitioning coefficients.
- Line 233: Use of the EPI suite estimations should be considered uncertain by about one order of magnitude (or more in certain cases) for predictions involving multifunctional semivolatile compounds. A comparison to other estimation methods for physical Henry's law constants (and their estimated uncertainties) may provide some information on the reliability of this method.
- Line 328 – 332: Why was a linear regression/relationship used? Partitioning theory

would suggest that it should be a sigmoidal relationship (if applicable), e.g. O'Meara et al. (2014); Donahue et al. (2009). However, the partitioning of a specific compound will also depend on the condensed phase absorbing mass concentration (in organic or aqueous phase, as appropriate) and on non-ideality, such as presence of phase separation. Given that only particle phase fraction data above ~80% were determined from the measurements, the expected sigmoidal relationship is perhaps not clear from the data alone.

- Line 334: "their F% values did not show seasonality or day-night difference";
The range of particle phase fractions observed may not allow for such conclusions if the material is predominantly in the particle phase. Uncertainties in the measurements and temperature dependence of the vapor pressures may mask actual variations.
- Lines 339 – 340: "Thus, the changes in vapor pressures with the ambient temperature might not be the main factor driving gas-particle partitioning of polyol tracers in northern Nanjing."
What about variations in organic aerosol mass concentrations as additional influence?
- Line 360: The re-evaluation of the SV-TAG measurements by Isaacman-VanWertz et al. (2016) in the study by Pye et al. (2018) (see their Fig. 5) involving other models, considerations of vapor pressure adjustments and additional measurement comparisons, shows that higher and lower particle phase fractions were predicted, but that generally the agreement between models and observed F% were consistent across a selection of tracers and much better than the orders of magnitude differences reported in this manuscript.
- Lines 364 – 367: These statements are misleading and need to be rephrased. Henry's law partitioning is a form of absorptive partitioning (in contrast to adsorptive partitioning). In the case of SVOCs and LVOCs, the difference between vapor-liquid equilibrium and liquid-phase mixing described by using Raoult's law or Henry's law (when accounting for non-ideal mixing) is essentially a matter of choice of reference state (while for non-vapor gases only Henry's law can be applied).
The observed large differences between measurements and different predictions could be the result of a combination of issues and uncertainties associated with the measurements and the models used. If reactive uptake is considered to be the key difference between predictions and measurements, this should be clarified.
- Lines 387 – 389: The statements on these lines seem to support the conclusion that absorptive partitioning may be applicable to describing the partitioning of these isoprene SOA tracers, but only if one uses the "appropriate" absorbing organic phase mass in the estimation of the measured K_p values (and given the uncertainty in the vapor pressures and activity coefficients, this seems to be reasonable). The phrasing could be improved to make that point.
- Lines 415 – 421: The finding that the intercept in Fig. 3 of the linear regression does not go through 0.0 indicates that there are substantial uncertainties, making this comparison far less convincing. The scatter in the data is large, also hinting at salting-in as an effect alone does not seem to be a good explanation of the deviations between predicted and measurement-derived Henry's law partitioning. The authors also mention this on lines 445 – 448. There may be other confounding factors that happen to correlate with sulfate concentration; leading to a spurious conclusion of a causal salting-in effect that is not strongly supported by the provided evidence. For example, the ratio of WIOC to WSOC organic material may correlate with sulfate concentrations since sulfate and ammonia amounts will affect and respond to aerosol pH, which may also correlate with RH and absolute ALWC (Pye et al., 2020). Did the authors consider this? Furthermore, a salting-in of polyols by sulfate is a finding that would be contrary to other studies on liquid-liquid phase partitioning involving polyols and ammonium sulfate, e.g. see Table 1 of Marcolli and Krieger (2006). In the study by Marcolli and Krieger (2006), ammonium sulfate led to salting-out while ammonium nitrate was found to show a salting-in effect on polyols. However, the complexity of the samples from Nanjing, where perhaps acidity and other aerosol components affect uptake, may differ from those in laboratory experiments by Marcolli and Krieger. Please discuss your

findings of potential reasons for the model–measurement discrepancies and sulfate influence also in comparison to findings on salting-in/out from those studies.

- Lines 445 – 448: related to the previous comment, here the authors state that the large gap between $K_{H,e}$ and $K_{H,w}$ cannot be explained by salting-in by sulfate alone. This confirms my impression that the discussion about reasons of the substantial deviations is rather speculative. The presented analyses do not support a firm conclusion about absorptive or non-absorptive partitioning. Moreover, if the effective Henry's law coefficient obtained is due to reactive uptake and/or aqueous phase chemistry, such as oligomer formation, then enhanced particle-phase fractions would be a reasonable expectation. However, a key question would then be whether such chemistry would be reversible during the quantification of the filter material, such that an oligomerized species would appear as monomers, since otherwise it should not contribute to the parent species' particle phase amount. This reviewer would appreciate some discussion about this.
- Table 1. Units of $K_{p,OM}$ should be provided; also state the temperature range for the values shown. Same for Table 2 and other such table in the Supplementary Information document.
- Figure 2: Assuming a form of absorptive vapor–liquid equilibrium partitioning, the fraction in the particle phase of a semivolatile organic will not only depend on the pure component vapor pressure but also on the aerosol mass concentration of the absorbing phase (and its composition). Therefore, it would make sense to state the aerosol mass concentration range that was used from the measurements. This would also allow for better comparison to other field measurements.

Supplementary Information (SI):

- Text S2: activity coefficients were assumed to be unity for all species in each sample. Is that a justified assumption? Consider that activity coefficients could be far from unity for compounds that are moderately polar (between the polarity of water and that of hydrophobic organics) used for characterizing the two particle phases in this work. This might contribute an order of magnitude of uncertainty for some compounds, but little for others.
- Text S2, below Eq. (3): why is it the "subcooled" liquid vapor pressure? It would be sufficient to denote it as the liquid vapor pressure or liquid-state vapour pressure. Whether it is subcooled/supercooled at given temperature or just a "regular" liquid state does not matter.
Also, given the relatively large uncertainty associated with vapor pressure estimation methods (O'Meara et al., 2014), it may be advised to compare those values to predictions from other methods (e.g. using the UManSysProp online tools). Uncertainties in pure-component vapor pressures could contribute more than one order of magnitude of uncertainty to K_p estimates.
- S5: Please state the vapor pressure units and reference temperature used for the stated $\text{Log}(p^0_L)$ values (one should not have to go back to the text to search for these).

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