This study by Chao Qin et al. reports on filter-based measurements of the gas–particle partitioning of a selection of semi-volatile 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.

Response:

Thanks for the reviewer's comments, and we will reply these point by point in the reviewers' specific comments.

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).

Response:

In the revised manuscript, we defined three gas-particle partitioning cases. *Case 1* assumed that the particulate OM was the only absorbing material in aerosols based on the equilibrium absorptive partitioning theory. Solubility of polyol tracers in an aqueous phase was included in *Cases 2 and 3*, where water-soluble and water-insoluble OM partitioned into different liquid phases and a single OM phase, respectively. Moreover, measurement uncertainties and their influences on partitioning coefficients of gas versus organic/aqueous phases in aerosols were estimated. It was shown that the average relative uncertainties of measurements and calculated partitioning coefficients ranged from a few percent to ~50%, which corresponded to an uncertainty of less than ± 0.30 for their logarithm values. Although the variability of theoretical partitioning coefficients was large, we still obtained an improved agreement between measurement-based and predicted gas-organic partitioning coefficient ($K_{p,OM}$) for *Cases 2* and *3*. So, aerosol liquid water should have substantial influences on gas-particle partitioning of target polyol tracers in this work.

The interactions of organic and inorganic compounds in the aqueous phase were expected to increase the partitioning of highly water-soluble compounds into the condensed phase (Kroll et al., 2005; Ip et al., 2009; Kampf et al., 2013; Pye et al., 2018). Then the effective Henry's law constants ($K_{H,e}$, mol m^{-3} atm^{-1}) of target polyol compounds in aerosols should be greater than those in pure water ($K_{H,w}$). In the revised manuscript, predicted $K_{H,w}$ values from EPI and SPARC estimates varied by several orders of magnitude. Literature $K_{H,w}$ values were closer to those of 2-methyltetrols and levoglucosan estimated by EPI, while the predicted $K_{H,w}$ with SPARC was unreasonably larger than $K_{H,e}$. So, $K_{H,w}$ values based on EPI estimates were used for further data analysis. Because the "salting-in" effect is a known phenomenon that is not likely linked with a specific physical or chemical mechanism, we made some possible explanations (e.g., reactive uptake) for the enhanced uptake of polyol tracers in aerosol liquid water.

Pye et al. (2018) re-evaluated the measurement data of gas- and particle-phase oxygenated compounds in southeastern US using a thermodynamic equilibrium gas-particle partitioning model in two LLPS modes. The modeling work was based on the AIOMFAC model and programed inorganic-organic interactions and variations of activity coefficients as a function of liquid PM mixture composition. The resulting predictions captured both the average and diurnal variability of measured $F\%$ for polyol tracers, suggesting a necessity in obtaining time-resolved activity coefficients for the implementation of absorptive equilibrium partitioning model. In this study, partitioning coefficients of polyol tracers were calculated and predicted empirically assuming equilibrium between gas phase and organic/aqueous phases in aerosols. Moreover, particulate OM phase was presumed as an ideal solution in which the activity coefficient ζ_{OM} was equal to 1, and no organic-inorganic interactions were considered. So, the temporal variability of $K_{p,OM}$ was poorly predicted in this work, and the gap between $K_{H,e}$ and $K_{H,w}$ could not be explicitly interpreted. Details of the changes were provided in the revised manuscript and responses to specific comments below.

Specific comments

1. 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.

Response:

Thanks. Here we did not intend to state that the absorptive partitioning is an incorrect partitioning mechanism. The mismatch between measurement and prediction could be associated with inappropriate assumptions on absorbing phase (e.g., particulate OM only) and formation pathways (e.g., gas-phase oxidation).

To make it clear, we changed the original expression into

"In addition to absorptive partitioning to particulate OM after the formation of oxygenated organic compounds in gas phase, other formation pathways (e.g., reactive uptake) have been identified and are responsible for the large discrepancy between modeled and observed SOA loadings (Jang et al., 2002; Kroll et al., 2005; Perraud et al., 2012). Unlike non-polar species (e.g., *n*-alkanes, polycyclic aromatic hydrocarbons) and alkanoic acids that are well simulated (Simcik et al., 1998; Xie et al., 2014a; Yatavelli et al., 2014; Isaacman-VanWertz et al., 2016), particle-phase concentrations of carbonyls were underestimated by several orders of magnitude when particulate OM is presumed as the only absorbing phase in ideal condition (Healy et al., 2008; Kampf et al., 2013; Shen et al., 2018)." (Page 5, lines 104-114)

In the original manuscript, the absorptive partitioning means partitioning between gas phase and particulate OM in aerosols; Henry's law partitioning corresponds to the equilibrium between gas phase and aerosol liquid water. We have clarified this throughout the manuscript.

2. 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.

Response:

Zhao et al. (2013) stated that the aerosol water plays a role in the formation of particle-phase pinonaldehyde in the atmosphere. This might be related to the water uptake. So, here we replaced "favored" with "played a role in". (Page 5, lines 116)

3. 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.

Response:

The work by Volkamer et al. (2009) has been cited here.

"An effective Henry's law coefficient ($K_{\mathrm{H,e}}$, mol $\mathrm{m^{-3}}$ $\mathrm{atm^{-1}}$) can be used to account for the measured partitioning between the gas phase and aerosol liquid water (Volkamer et al., 2009)." (Page 5-6, lines 124-126).

Volkamer et al. (2009) focused on the effect of seed chemical composition and photochemistry on SOA yields. They found that the WSOC photochemical reactions can cause increased SOA yield. So, this work was also cited later in the manuscript.

"Moreover, log ($K^{\mathrm{t}}_{\mathrm{H,w}}/K^{\mathrm{m}}_{\mathrm{H,e}}$) values of polyol tracers also negatively correlated with the aqueous-phase concentrations of WSOC (c_{WSOC}, Figure S6), but not NH_4^+ or NO_3^-. This dependence might be associated with the "like-dissolves-like" rule, or indicate the importance of aqueous-phase heterogeneous reactions (Hennigan et al., 2009; Volkamer et al., 2009)." (Pages 23-24, lines 552-556)

4. 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 (Qf) 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.

Response:

Based on absorptive equilibrium partitioning theory, the partitioning coefficient of a certain compound between gas and particulate OM phases ($K_{\mathrm{p,OM}}$, $\mathrm{m^3}$ $\mathrm{ug^{-1}}$) is defined as

$$K_{\mathrm{p,OM}} = \frac{F/M_{\mathrm{OM}}}{A} \qquad (1)$$

where F and A are (ng $\mathrm{m^{-3}}$) are particle- and gas-phase concentrations, and M_{OM} (μg $\mathrm{m^{-3}}$) is the mass concentration of particulate OM. It is assumed that the quantity F/M_{OM} (ng $\mathrm{\mu g^{-1}}$) represents the equilibrium concentration in the particulate matter (Pankow and Bidleman, 1992; Liang et al., 1997).

In previous studies, $K_{p,OM}$ values based on offline measurements were typically obtained using sampling periods of many hours (e.g., 8, 12, or 24 h). When ambient concentrations (F, A, or M_{OM}) or temperature change within a sampling interval, the particulate OM initially collected on the filter will tend to re-equilibrate with the A value though evaporation or absorption. Then whether the accumulated aerosol mass will uptake or release gaseous organic compounds depends on how changes in F, A, M_{OM}, and ambient temperature take place. Measured values of F, A, and M_{OM} will be averages over the whole sampling period, not reflecting real-time atmospheric concentrations. Therefore, the situation raised in the comment seems not applicable to this study.

5. 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 (kappa) and the median or actual RH values to estimate the organic-contributed water content by the WSOC mass fraction in particles.

Response:

According to Isaacman-VanWertz et al. (2016), the water uptake by WSOC (W_O, μg m^{-3}) could be estimated as

$$W_O = \frac{V_{WSOC} \times [\kappa \times (O:C)]}{(\frac{100}{RH\%} - 1)} \qquad (2)$$

where V_{WSOC} represents WSOC volume, and is calculated as the organic mass (WSOC ×1.6) divided by its density (1.4 g cm^{-3}). The hygroscopicity parameter (κ) and oxygen to carbon ratio (O:C) of WSOC were assumed as 0.10 and 0.5, respectively, based on field and laboratory studies (Taylor et al., 2017; Cai et al., 2020). The resulting W_O had an average of 0.47 ± 1.14 μg m^{-3}, far below the amount caused by inorganic ions (21.3 ± 24.2 μg m^{-3}). Taylor et al. (2017) predicted a growth factor range of 1.00–1.20 with κ varying from 60 to ~100%, which lead to a comparable average W_O (0.42 ± 0.70 μg m^{-3}) in this work. Thus, the water content contributed by WSOC was not accounted for in this work.

We have clarified this in the revised manuscript and supplementary information. (Page 8, lines 180-182)

"The estimated water content contributed by hygroscopic WSOC was relatively small (< 1 μg m^{-3}) and not accounted for in this work (Text S1 of supplementary information)."

6. Line 209: I suggest adding these equations to the main text.

Response:

We have defined three partitioning cases and included these equations in the revised manuscript. (Pages 10 -13, lines 238-295)

"Here, we defined three partitioning cases to explore the influence of dissolution in aerosol liquid water on gas-particle partitioning of polyol tracers in the atmosphere. *Case 1* presumes instantaneous equilibrium between the gas phase and particulate OM based on the equilibrium absorptive partitioning theory. In this case, particulate OM is assumed to be the only absorbing phase and behave as an ideal solution. Then the absorptive gas-particle partitioning coefficients ($K_{\mathrm{p,OM}}$, m^3 μg^{-1}) were calculated from measurements ($K^{\mathrm{m}}_{\mathrm{p,OM}}$) and predicted theoretically ($K^{\mathrm{t}}_{\mathrm{p,OM}}$) as follows

$$K^{\mathrm{m}}_{\mathrm{p,OM}} = \frac{F/M_{\mathrm{OM}}}{A} \qquad (2)$$

$$K^{\mathrm{t}}_{\mathrm{p,OM}} = \frac{RT}{10^6 \overline{\mathrm{MW}}_{\mathrm{OM}} \zeta_{\mathrm{OM}} p^{\mathrm{o}}{}_{\mathrm{L}}} \qquad (3)$$

where M_{OM} denotes the mass concentration of absorptive organic matter (OM = OC × 1.6; Turpin and Lim, 2001); F (ng m^{-3}) and A (ng m^{-3}) are particulate and gaseous concentrations of individual polyols, respectively. In eq 2, R (m^3 atm K^{-1} mol^{-1}) and T (K) are the ideal gas constant and ambient temperature; $\overline{\mathrm{MW}}_{\mathrm{OM}}$, average molecular weight of absorptive OM, is set at 200 g mol^{-1} for all samples (Barsanti and Pankow, 2004; Williams et al., 2010); ζ_{OM} denotes the mole fraction scale activity coefficient, and is presumed to be unity for all species in each sample; $p^{\mathrm{o}}{}_{\mathrm{L}}$ (atm) is the vapor pressure of each pure compound, and is predicted with several estimation tools and adjusted for each sampling interval based on the average temperature (Text S3 and Table S4).

Due to the influence of mixing state and water content in aerosols, several studies modeled the gas-particle partitioning of oxygenated organic compounds by defining a liquid-liquid phase separation (LLPS) in the aerosol (Zuend and Seinfeld, 2012; Pye et al., 2018). The organic-inorganic interactions and changes of activity coefficients in aqueous mixtures were fully considered as well. In this study, we proposed a simplified LLPS partitioning mechanism (*Case 2*) in Figure 1. First, aerosol water and water-insoluble OM (WIOM = OM – WSOC × 1.6) exist in two separate liquid phases, and WSOC and inorganic ions are totally dissolved in the aqueous phase. The distribution of polyol tracers between aqueous (F_{W}, ng m^{-3}) and WIOM (F_{WIOM}, ng m^{-3}) phases is simply depicted by their octanol-water partition coefficients (K_{OW})

$$K_{\mathrm{OW}} = \frac{F_{\mathrm{WIOM}}/V_{\mathrm{WSIOM}}}{F_{\mathrm{W}}/V_{\mathrm{W}}} = \frac{c_{\mathrm{WIOM}}}{c_{\mathrm{W}}} \qquad (4)$$

where V_{WIOM} and V_{w} are volumes (m^3) of WIOM and water in aerosols per cubic meter air; c_{WIOM} and c_{w} are solution concentrations (ng m^{-3}) of polyols concentrations in organic and aqueous phases; log K_{OW} values of target polyols were estimated using the Estimation Programs Interface (EPI) Suite developed by the US Environmental Protection Agency and Syracuse Research Corporation (Table S4; US EPA, 2012). The density of organic matter and water (ρ_{w}) in aerosols are set at 1.4 and 1.0 g cm^{-3}, respectively (Isaacman-VanWertz et al., 2016; Taylor et al., 2017). Second, gas-phase polyol tracers are in equilibrium with hydrophobic OM and the aqueous phase, respectively

$$K^{\mathrm{m}}_{\mathrm{p,WIOM}} = \frac{F_{\mathrm{WIOM}}/M_{\mathrm{WIOM}}}{A} \qquad (5)$$

$$K^{\mathrm{m}}_{\mathrm{H,e}} = \frac{\frac{F_W}{M_i}}{\frac{A}{M_i} \times R \times T \times \frac{c_{\mathrm{ALW}}}{\rho_{\mathrm{W}}}} = \frac{\rho_{\mathrm{W}} \times F_W}{A \times R \times T \times c_{\mathrm{ALW}}} \qquad (6)$$

where $K^{\mathrm{m}}_{\mathrm{H,e}}$ (mol m^{-3} atm^{-1}) is the measurement-based effective Henry's law coefficient; M_{WIOM} represents the mass concentration (μg m^{-3}) of WIOM; M_i (g mol^{-1}) is the molecular weight of specific compound; c_{ALW} (μg m^{-3}) is the mass concentration of aerosol liquid water predicted using ISORROPIA II model. *Case 3* is generally the same as *Case 2*, and the only difference is that water-soluble OM (WSOM) and WIOM exist in a single organic phase. Here total particulate OM was used instead of WIOM to assess the distribution of polyol tracers between aqueous and organic phases, and calculate partitioning coefficients of gas vs. particulate organic ($K^{m}_{p,OM}$) and aqueous ($K^{m}_{H,e}$) phases. Note that the polarity of particulate OM phase in *Case 3* was expected to increase, then using K_{OW} to calculate the distribution of polyols between organic and aqueous phases might lead to underestimated $K^{m}_{p,OM}$ and overestimated $K^{m}_{H,e}$. For comparison purposes, the Henry's law coefficient in pure water at 25 °C ($K^{*}_{H,w}$) was estimated using EPI and SPARC (Hilal et al., 2008; http://archemcalc.com/sparc-web/calc), respectively (Table S4), and was adjusted for each sampling interval due to the changes in ambient temperature using van 't Hoff equation (Text S4)."

7. 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 KOW. 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).

Response:

As mentioned in responses to *Comment 5*, the estimated contribution of WSOC to aerosol liquid water is relatively small. In this study, gas-particle partitioning coefficients of polyol tracers were calculated and predicted empirically by assuming equilibrium between gas phase and organic/aqueous phases in aerosols, and the organic-inorganic interactions were not considered. This might be an important reason for the gap between measurement-based $K_{H,e}$ and predicted $K_{H,w}$. Pye et al. (2018) re-analyzed the measurement data from Isaacman-VanWertz et al. (2016) using a thermodynamic equilibrium gas-particle partitioning model in two LLPS modes, which involved inorganic-organic interactions and estimations of activity coefficients as a function of liquid PM mixture composition. The resulting predictions captured both the average and diurnal variations of measured *F*% for polyol tracers, suggesting a necessity in obtaining time-resolved activity coefficients for the implementation of absorptive equilibrium partitioning model. These discussions have been added in the revised manuscript. (Pages 19-20, lines 457-464)

As suggested by the reviewer, we defined a third partitioning case assuming all WIOM and WSOC organics partitioned to a single organic phase (*Case 3*, see responses to *Comment 6*). However, the measurement-based partitioning coefficients of polyol tracers in *Case 3* are very close to those in *Case 2*, where WIOM and WSOC were assumed to partition into separate liquid phases. In the revised manuscript, we defined three gas-particle partitioning cases and re-analyzed the difference between measured and predicted partitioning coefficients. (Pages 10-13, lines 238-295, see responses to *Comment 6*; Sections 3.4 and 3.5 in the revised manuscript, Tables 1 and 2 below).

Table 1. Comparisons of measurement-based log $K_{p,OM}$ (m^3 μg^{-1}) at three proposed cases and predicted values.

Species	No. of obs.	Log $K^{m}_{p,OM}$ [a]			Log $K^{t}_{p,OM}$ [b]			
		Case 1	Case 2	Case 3	EPI	EVAPORATION	SPARC	SIMPOL
Isoprene SOA tracers								
C5-alkene triol 1	53	0.33 ± 0.71	-0.79 ± 0.86	-0.82 ± 0.85	-3.09	-2.84	-1.19	-2.88
C5-alkene triol 2	63	0.15 ± 0.55	-1.02 ± 0.74	-1.05 ± 0.73	-3.62	-3.67	-4.14	-2.85
C5-alkene triol 3	83	0.35 ± 0.68	-0.83 ± 0.86	-0.86 ± 0.85	-2.90	-2.65	-1.00	-2.69
2-Methylthreitol	101	-0.12 ± 0.48	-2.09 ± 0.71	-2.09 ± 0.70	-1.87	-1.30	-1.18	-0.47
2-Methylerythritol	95	-0.011 ± 0.58	-1.96 ± 0.71	-1.96 ± 0.71	-1.90	-1.34	-1.22	-0.50
Biomass burning tracer								
Levoglucosan	65	2.23 ± 0.72	0.63 ± 0.90	0.62 ± 0.90	-0.04	-0.81	1.04	-0.76
Sugars ang sugar alcohols								
Meso-erythritol	31	0.87 ± 0.53	-1.43 ± 0.60	-1.43 ± 0.60	-0.65	-1.21	-0.45	
Fructose	85	0.65 ± 0.73	-1.20 ± 0.83	-1.20 ± 0.89	1.17	2.76	6.94	
Mannose	74	0.62 ± 0.71	-2.12 ± 0.95	-2.12 ± 0.95	1.28	2.13	4.77	
Glucose	88	0.42 ± 0.67	-2.77 ± 0.93	-2.77 ± 0.93	0.34	3.75	7.32	
Xylitol	22	0.24 ± 0.54	-2.61 ± 0.72	-2.61 ± 0.72	3.37	2.34	3.57	
Arabitol	30	1.46 ± 0.89	-1.35 ± 1.24	-1.35 ± 1.24	3.25	1.67	2.90	
Manitol	65	1.08 ± 0.63	-2.24 ± 0.95	-2.24 ± 0.95	2.33	4.16	6.68	

[a] Average ± standard deviation; [b] temperature range: -4~36 °C.

Table 2. Comparisons of measurement-based log $K_{H,e}$ (mol m^{-3} atm^{-1}) and predicted log $K_{H,w}$ of individual polyol tracers.

Species	No. of obs.	Log $K^{m}_{H,e}$ (Cases 2) [a]			Log $K^{t}_{H,w}$ [b]	
		Median	Average	Range	EPI	SPARC
Isoprene SOA tracers						
C5-alkene triol 1	53	14.0	13.9 ± 0.86	11.5 – 16.4	7.22	11.7
C5-alkene triol 2	63	13.7	13.6 ± 0.73	11.2 – 16.1	7.34	7.66
C5-alkene triol 3	83	13.9	13.8 ± 0.85	10.6 – 16.1	7.43	11.9
2-Methylthreitol	101	13.4	13.3 ± 0.70	10.9 – 14.8	10.0	14.1
2-Methylerythritol	95	13.5	13.5 ± 0.71	11.6 – 15.6	9.95	14.1
Biomass burning tracer						
Levoglucosan	65	15.7	15.7 ± 0.90	13.2 – 17.3	13.4	16.1
Sugars ang sugar alcohols						
Meso-erythritol	31	14.5	14.4 ± 0.60	12.8 – 15.6	9.65	13.8
Fructose	85	14.2	14.1 ± 0.89	11.9 – 16.5	14.7	19.9
Mannose	74	14.0	14.1 ± 0.94	12.1 – 16.8	10.9	18.8
Glucose	88	13.9	13.9 ± 0.93	11.3 – 16.3	14.7	20.9
Xylitol	22	13.8	13.7 ± 0.72	12.6 – 15.0	12.1	18.1
Arabitol	30	15.1	15.0 ± 1.23	13.0 – 18.2	11.3	17.4
Mannitol	65	14.6	14.5 ± 0.94	12.1 – 16.4	12.9	20.8

[a] Log $K^{m}_{H,e}$ values of *Case 3* had ignorable difference, and were not exhibited separately; [b] temperature range: -4~36 °C.

8. 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.

Response:

As we mentioned in responses to the general comment and specific comment 6, three partitioning cases were proposed in the revised manuscript. In the newly defined *Case 3* where WIOM and WSOC organics partitioned to a single organic phase, the solubility of polyol tracers in the organic phase was expected to increase, and using K_{OW} to calculate the distribution between organic and aqueous phases in aerosols would lead to an underestimation of $K_{p,OM}$, which might not be reasonably adjusted. This was acknowledged in the revised manuscript.

Pages 12-13, lines 288-291.

"Note that the polarity of particulate OM phase in *Case 3* was expected to increase, then using K_{OW} to calculate the distribution of polyols between organic and aqueous phases might lead to underestimated $K^{m}_{p,OM}$ and overestimated $K^{m}_{H,e}$."

9. 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 MWOMof 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.

Response:

Among the three proposed partitioning cases in the revised manuscript, *Case 1* assumed that the particulate OM was the only absorbing material in aerosols, ignoring the influence of aerosol liquid water. While in *Cases 2* and *3*, particulate OM and aerosol liquid water were assumed to exist in separate liquid phases, and there was no phase distribution of water. By comparing measurement-based and predicted partitioning coefficients for different cases, we inferred that the aerosol liquid water should play a significant role in influencing gas-particle partitioning of polyol tracers (Table 1, see responses to *Comment 7*). An enhanced uptake of polyol tracers was also identified, which should be closely associated with the organic-inorganic interactions.

In this study, the particulate organic phase was assumed to contain no water, and partitioning of gaseous polyols to organic and aqueous phases in aerosols were assessed separately. So, the influence of water content on molecular weight of particulate organic matter (MW_{OM}) was not considered.

10. 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.

Response:

Thanks. We also obtained Henry's law constants of polyols in pure water at 25 ^{o}C

($K^*_{H,w}$) from SPARC (Hilal et al., 2008; http://archemcalc.com/sparc-web/calc) estimates and literatures (Table S4).

Although the $K^*_{H,w}$ (mol m^{-3} atm^{-1}) from EPI and SPARC differed by several orders of magnitude, literature values of isoprene SOA and levoglucosan were closer to the estimates of EPI (Table S4). If SPARC $K^*_{H,w}$ values were used, the average log $K^m_{H,e}$ of most polyol tracers would be lower than predictions (log $K^t_{H,w}$, Table 2; see responses to *Comment 7*), indicating that the aqueous phase of ambient aerosol is less hospital to polyol tracers than pure water. This is in conflict with the fact that the interactions of organic compounds, water, and inorganic ions in aerosols will increase the partitioning of highly oxygenated compounds (O:C $\geqslant 0.6$; e.g., isoprene SOA tracers and levoglucosan) into the particle phase (Pye et al., 2018). Several studies identified a close relationship between salt concentrations of aerosol water and enhanced uptake of very polar compounds (Kroll et al., 2005; Ip et al., 2009; Kampf et al., 2013). Thus, log $K^t_{H,w}$ values of EPI estimates were used for further data analysis. (Pages 20-21, lines 482-494)

11. 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 at 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.

Response:

Thanks. The original Figure 2 (now Figure 3) and associated discussions was changed considering the uncertainties in measurements

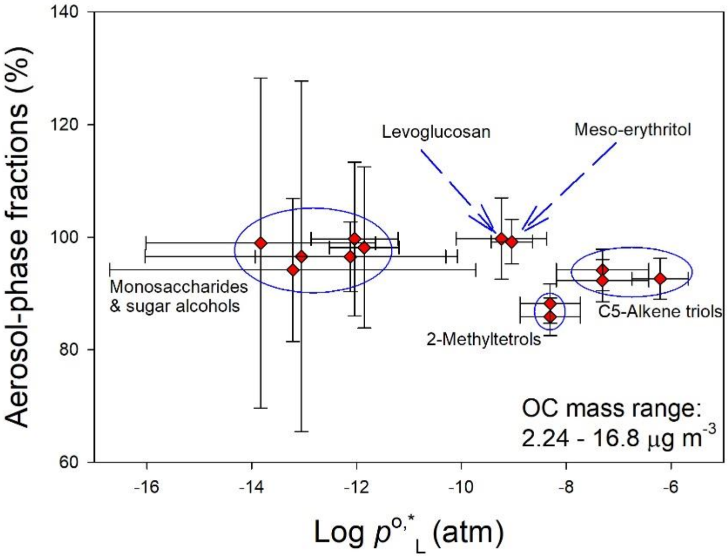


Figure 3. Average particle-phase fractions and log $p^{o,*}_L$ of individual polyol tracers. Whiskers represent uncertainties of *F*% and one standard deviation of log $p^{o,*}_L$ derived from different estimation tools.

Pages 17-18, lines 410-419

"In Figure 3, the average *F*% uncertainties (6.16–31.2%) of monosaccharides (e.g., fructose) and sugar alcohols (e.g., mannitol) were larger than those of isoprene SOA tracers and levoglucosan (3.33–7.24%) due to their low and variable recoveries (Table S2) and excessive breakthrough (Figure S2). However, the estimated uncertainties of *F*% for less volatile polyols ($p^{o,*}_L < \sim 10^{-10}$ atm) were not physically meaningful, as more than 95% of these compounds existed in the particle phase. Considering the uncertainties in *F*% and log $p^{o,*}_L$ and high average *F*% (> 85%) of target polyol tracers, a dependence of *F*% on the vapor pressure could not be determined, and the seasonality and day-night difference ($p > 0.05$) of *F*% were obscured."

12. 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.

Response:

The original expression has been changed. See responses to *Comment 11* (Pages 17-18, lines 410-419).

13. 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?

Response:

Thanks. Xie et al. (2014) found that the gas-particle partitioning of 2-methyltetrols and levoglucosan in urban Denver were dependent on the variations in ambient temperature and absorbing organic matter (M_{OM}). So, the original expression was changed into

"Thus, the changes in vapor pressures with the ambient temperature and/or particulate OM loadings might not be the main factors driving gas-particle partitioning of polyol tracers in Nanjing." (Page 17, lines 408-410)

14. 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.

Response:

When the dissolution of polyols in aerosol water was included, the agreement between measurement-based and predicted partitioning coefficients of gas vs organic phases ($K_{p,OM}$) were improved substantially. However, the variability of gas-particle partitioning was poorly predicted. The study by Pye et al. (2018) was cited and discussed to explain the discrepancy between measurements and predictions. (Pages 19-20, lines 450-464)

"Similarly, the measured average *F*% of isoprene SOA tracers in southeastern US and central Amazonia were higher than predictions by assuming instantaneous equilibrium between the gas phase and particulate OM only, and the agreement was improved when parameterization of solubility was included for predictions (Isaacman-VanWertz et al., 2016). But none of these two studies could reasonably predict the temporal variability of *F*% or log $K^{m}_{p,OM}$. One possible explanation is that the activity coefficients of isoprene SOA tracers and levoglucosan deviate from unity (0.42–2.04; Pye et al., 2018) and vary with PM composition. Pye et al. (2018) re-analyzed the measurement data from Isaacman-VanWertz et al. (2016) using a thermodynamic equilibrium gas-particle partitioning model in two LLPS modes, which involved organic-inorganic interactions and estimations of activity coefficients as a function of liquid PM mixture composition. The resulting predictions captured both the average and diurnal variations of measured *F*% for polyol tracers, suggesting a necessity in obtaining time-resolved activity coefficients for the implementation of absorptive equilibrium partitioning model."

15. 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.

Response:

Thanks. In the revised manuscript, the absorptive partitioning of gaseous polyols to organic and aqueous phases in aerosols were clearly distinguished, and uncertainties of measurements and predictions and their influences on the calculation of partitioning coefficients were estimated.

Through the comparisons of measurement-based and precited $K_{p,OM}$ before and after the inclusion of polyols dissolution in aerosol water, we inferred that the aerosol liquid water is also an important absorbing phase of ambient polyol tracers in Nanjing. The large gaps of $K^{m}_{H,e}$ versus $K^{t}_{H,w}$ could be partly parameterized using the equation defining "salting-in" effects. However, the "salting-in" effect is a known phenomenon that is not likely linked with a specific physical or chemical mechanism. According to existing studies, reactive uptake, aqueous phase reactions, and chemical similarity between partitioning species and the absorbing phase might be responsible for increasing the partitioning of polyol tracers into the condensed phase. In the revised manuscript, we have re-organized and re-written most of the discussions on comparisons between measured and predicted partitioning coefficients. (Sections 3.4

and 3.5, Pages 18-23, lines 420-560).

Here are some discussions on mechanisms related to the gap between $K^{m}_{H,e}$ and $K^{t}_{H,w}$. (Pages 23-24, lines 534-560)

"However, the "salting-in" effect is a known phenomenon that is not likely linked with a specific physical or chemical mechanism. Quantum chemical calculation results indicated negative Gibbs free energy of water displacement for interactions between SO_4^{2-} and glyoxal monohydrate (Waxman et al., 2015). The net "salting-in" effect of 1-nitro-2-naphthol in NaF solution was interpreted by postulating hydrogen bonding (Almeida et al., 1983). A direct binding of cations to ether oxygens was proposed to be responsible for the increased solubility of water-soluble polymers (Sadeghi and Jahani, 2012). Due to the moderate correlations and negative intercepts in Figures 4 and S5, the gap between $K^{t}_{H,e}$ and $K^{m}_{H,w}$ cannot be closed by the "salting-in" effect alone. Shen et al. (2018) also obtained negative intercepts when plotting log ($K^{t}_{H,w}/K^{m}_{H,e}$) over c_{sulfate} for glyoxal and methylglyoxal in ambient atmosphere, and attributed this to unknown gas-particle partitioning mechanisms. Evidences showing that the thermal degradation of less volatile oligomers and organosulfates can lead to an overestimation of 2-methyltetrols by 60–188% when using a conventional GC/EI-MS method (Cui et al., 2018). To fit the gas-particle distribution of 2-methyltetrols in southeastern US, 50% of particulate 2-methyltetrols was presumed to exist in chemical forms with much lower vapor pressures by Pye et al. (2018). So, the reactive uptake and aqueous phase chemistry could be explanations for the enhanced uptake of isoprene SOA tracers. Moreover, log ($K^{t}_{H,w}/K^{m}_{H,e}$) values of polyol tracers also negatively correlated with the aqueous-phase concentrations of WSOC (c_{WSOC}, Figure S6), but not NH_4^{+} or NO_3^{-}. This dependence might be associated with the "like-dissolves-like" rule, or indicate the importance of aqueous-phase heterogeneous reactions (Hennigan et al., 2009; Volkamer et al., 2009). Although several studies have estimated Henry's law constants for a variety of polar organic compounds in pure water (e.g., polyols and polyacids; Compernolle and Müller, 2014a, b), more work is warranted to decrease the estimation uncertainty and explain their increased partitioning toward aerosol liquid water explicitly."

16. 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 Kp 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.

Response:

Yes, the agreement between measurement-based and predicted $K_{p,OM}$ will be significantly improved when the "appropriate" absorbing organic phase is used.

To make it clear, we defined three partitioning cases in the revised manuscript. *Case 1* assumed that the particulate OM was the only absorbing material in aerosols based on the equilibrium absorptive partitioning theory. Solubility of polyol tracers in an aqueous phase was included in *Cases 2 and 3*, where water-soluble and water-insoluble OM partitioned into different liquid phases and a single OM phase, respectively. We found a much better agreement between measurement-based and precited $K_{p,OM}$ after considering polyols dissolution in aerosol liquid water, indicating that aerosol liquid water is also an important absorbing phase of ambient polyols in Nanjing.

Pages 18-19, lines 421-450

"To understand if particulate OM is the only absorbing phase in aerosols for polyol tracers in Nanjing, the absorptive partitioning coefficients of gas vs. organic phases were calculated based on measurement results ($K^{m}_{p,OM}$) for predefined *Cases 1-3* and predicted theoretically ($K^{t}_{p,OM}$) using eq. 3 and vapor pressures listed in Table S4. In Table 1, $K^{t}_{p,OM}$ ranges of isoprene SOA tracers, levoglucosan, and meso-erythritol are within two orders of magnitude, while those of monosaccharides and mannitol are larger (> 10^3).When particulate OM was assumed as the only absorbing phase (*Case 1*), the average $K^{m}_{p,OM}$ of isoprene SOA tracers, levolgucosan, and meso-erythritol were more than 10 times greater than most of their $K^{t}_{p,OM}$ (Table 1), and this difference was not likely susceptible to measurement uncertainties. As shown in Table S5, the average relative uncertainties of measurement-based partitioning coefficients are all <50%, leading to an uncertainty of log $K^{m}_{p,OM}$ less than ± 0.30.. ……………………………………………

When solubility in aerosol liquid water was considered by defining a LLPS in ambient aerosols, and whenever WSOM and WIOM partitioned into separate (*Case 2*) or single (*Case 3*) phases, the average log $K^{m}_{p,OM}$ of the above mentioned compounds became much closer to or even lay within the range (levoglucosan) of log $K^{t}_{p,OM}$ (Table 1). These results indicated that the aerosol liquid water (21.3 ± 24.2 μg m^{-3}; Table S1) is also an important absorbing phase of ambient polyol tracers in Nanjing."

17. 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.

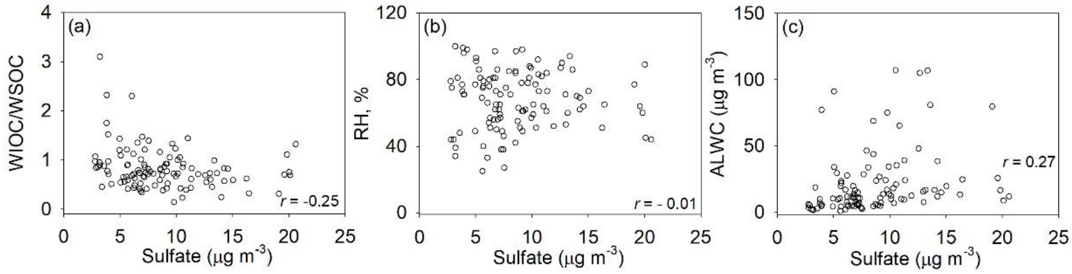
Response:

Although the "salting-in" effect has been known for a long time, it is poorly characterized at high salt concentrations and is not understood mechanistically. The "salting-in" effect could be considered as a phenomenon that is not specifically linked with a physical or chemical mechanism. So, the equation defining "salting-in" effects was only used to parameterize the enhanced uptake of polyols in aerosol liquid water. In the revised manuscript, we provided some guesses on mechanisms related to the "salting-in" effect from previous work and other explanations for increased partitioning to the particle phase.

Pages 23-24, lines 534-560

"However, the "salting-in" effect is a known phenomenon that is not likely linked with a specific physical or chemical mechanism. Quantum chemical calculation results indicated negative Gibbs free energy of water displacement for interactions between SO_4^{2-} and glyoxal monohydrate (Waxman et al., 2015). The net "salting-in" effect of 1-nitro-2-naphthol in NaF solution was interpreted by postulating hydrogen bonding (Almeida et al., 1983). A direct binding of cations to ether oxygens was proposed to be responsible for the increased solubility of water-soluble polymers (Sadeghi and Jahani, 2012). Due to the moderate correlations and negative intercepts in Figures 4 and S5, the gap between $K^{t}_{H,e}$ and $K^{m}_{H,w}$ cannot be closed by the "salting-in" effect alone. Shen et al. (2018) also obtained negative intercepts when plotting log ($K^{t}_{H,w}/K^{m}_{H,e}$) over $c_{sulfate}$ for glyoxal and methylglyoxal in ambient atmosphere, and attributed this to unknown gas-particle partitioning mechanisms. Evidences showing that the thermal degradation of less volatile oligomers and organosulfates can lead to an overestimation of 2-methyltetrols by 60–188% when using a conventional GC/EI-MS method (Cui et al., 2018). To fit the gas-particle distribution of 2-methyltetrols in southeastern US, 50% of particulate 2-methyltetrols was presumed to exist in chemical forms with much lower vapor pressures by Pye et al. (2018). So, the reactive uptake and aqueous phase chemistry could be explanations for the enhanced uptake of isoprene SOA tracers. Moreover, log ($K^{t}_{H,w}/K^{m}_{H,e}$) values of polyol tracers also negatively correlated with the aqueous-phase concentrations of WSOC (c_{WSOC}, Figure S6), but not NH_4^+ or NO_3^-. This dependence might be associated with the "like-dissolves-like" rule, or indicate the importance of aqueous-phase heterogeneous reactions (Hennigan et al., 2009; Volkamer et al., 2009). Although several studies have estimated Henry's law constants for a variety of polar organic compounds in pure water (e.g., polyols and polyacids; Compernolle and Müller, 2014a, b), more work is warranted to decrease the estimation uncertainty and explain their increased partitioning toward aerosol liquid water explicitly."

As shown in the Figure below, concentrations of sulfate do not correlate with WIOC/WSOC ratios, RH, or ALWC in this work, so the condition raised in the comment was not considered.



Marcolli and Krieger (2006) found that ammonium sulfate (AS) and NaCl are "salting-out" agent for alcohols with medium hydrophilicity, including glycerol, 1,4-butanediol, 1,2-hexanediol, and PEG400. But all the target polyols in this study are highly water soluble, and there is no evidence showing that AS is salting out agent for any of the polyols studied in this work. A number of studies identified a close relationship between salt concentrations of aerosol water and enhanced uptake of very polar compounds (Setschenow 1889; Almeida et al., 1983; Kroll et al., 2005; Ip et al., 2009; Kampf et al., 2013; Shen et al., 2018). The particle-phase interactions of organic compounds, water, and inorganic ions were found to increase partitioning of isoprene SOA tracers and levoglucosan into the condensed phase (Pye et al., 2018). Since none of the polyol compounds in Marcolli and Krieger (2006) was studied in this work, the moderate dependence of increased uptake on sulfate concentrations is not contrary to their findings, and we did not compare the study results between these two studies.

In the revised manuscript, we re-organized section 3.5 (*Partitioning coefficients of gas versus aqueous phases*) and rewrote most part of it.

18. Lines 445 – 448: related to the previous comment, here the authors state that the large gap between KH,e and KH,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.

Response:

Reactive uptake is very likely contributing to increased partitioning of polyols into the particle phase. In the revised manuscript, we have clarified that the "salting-in" effect is a is a known phenomenon that is not specifically linked with a physical or chemical mechanism (Pages 23-24, lines 534-560, See responses to *Comments 15 and 17*).

The equation defining "salting-in" effects was only used to parameterize the enhanced uptake of polyols in aerosol liquid water (Pages 22-23, lines 517-533).

"As sulfate has been identified as the major factor influencing the salting effect of carbonyl species (Kroll et al., 2005; Ip et al., 2009), Figure 4 shows modified Setschenow plots for C5-alkene triols, 2-methyltetrols, and levoglucosan, where log ($K^{t}_{H,w}/K^{m}_{H,e}$) values were regressed to the molality of sulfate ion in aerosol liquid water ($c_{sulfate}$, mol kg^{-1} ALWC). The log ($K^{t}_{H,w}/K^{m}_{H,e}$) data increased faster when $c_{sulfate}$ approached 0, and deviated from their expected behavior with increased $c_{sulfate}$. Kampf et al. (2013) selected a threshold $c_{sulfate}$ of 12 mol kg^{-1} ALWC to illustrate the deviation for chamber experiments, and attributed it to elevated viscosity and slow particle-phase reactions at high $c_{sulfate}$. In Figure 4, negative correlations ($p < 0.01$) are observed at $c_{sulfate} < 12$ mol kg^{-1} ALWC, and Figure S5 exhibits significant negative correlations ($p < 0.01$) between log ($K^{t}_{H,w}/K^{m}_{H,e}$) and $c_{sulfate}$ for individual polyols even without excluding the deviations at high $c_{sulfate}$. The K_s values of polyol tracers from Figures 4 and S5 (-0.17 – -0.037 kg mol^{-1}) are in a similar range as that of glyoxal (-0.24 – -0.04 kg mol^{-1}; Kampf et al., 2013; Shen et al., 2018; Waxman et al., 2015). These results indicated that the shifting of gas-particle equilibrium toward the condensed phase might be partly parameterized by the equation defining "salting-in" effects."

Moreover, we added some discussions about the influence of reactive uptake/aqueous chemistry on enhanced particle-phase concentrations. (Pages 23-24, lines 545-556)

"Evidences showing that the thermal degradation of less volatile oligomers and organosulfates can lead to an overestimation of 2-methyltetrols by 60–188% when using a conventional GC/EI-MS method (Cui et al., 2018). To fit the gas-particle distribution of 2-methyltetrols in southeastern US, 50% of particulate 2-methyltetrols was presumed to exist in chemical forms with much lower vapor pressures by Pye et al. (2018). So, the reactive uptake and aqueous phase chemistry could be explanations for the enhanced uptake of isoprene SOA tracers. Moreover, log ($K^{t}_{H,w}/K^{m}_{H,e}$) values of polyol tracers also negatively correlated with the aqueous-phase concentrations of WSOC (c_{WSOC}, Figure S6), but not NH_4^+ or NO_3^-. This dependence might be associated with the "like-dissolves-like" rule, or indicate the importance of aqueous-phase heterogeneous reactions (Hennigan et al., 2009; Volkamer et al., 2009)."

19. 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.

Response:

Unites and temperatures were added in all related Tables as suggested (See responses to *Comment 7*).

20. Figure 2: Assuming a form of absorptive vapor–liquid equilibrium partitioning, the fraction in the particle phase of a semi-volatile 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.

Response:

In this work, mass concentrations of OC were directly obtained from measurements, and were used for the calculation of $K_{p,OM}$. The concentration range of OC (2.24 – 16.8 μg m^{-3}) was added as suggested (now Figure 3, See responses to *Comment 11*).

Supplementary Information (SI):

21. 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.

Response:

In this work, the organic phase in aerosols was assumed to behave as ideal solution, and the variability of activity coefficient as a function of PM composition was not considered. This should be one reason the variations of measurement-based $K_{p,OM}$ were poorly characterized in this work. Mean activity coefficients of isoprene SOA tracers and levoglucosan in organic-rich phases had a range of 0.42 to 2.04 based on AIOMFAC predictions (Pye et al., 2018), then assuming the activity coefficient to be unity will contribute an uncertainty far less than an order of magnitude.

We added some discussions to state the influence of variability in activity coefficients in the revised manuscript.

Pages 19-20, lines 450-464.

"Similarly, the measured average F% of isoprene SOA tracers in southeastern US and central Amazonia were higher than predictions by assuming instantaneous equilibrium between the gas phase and particulate OM only, and the agreement was improved when parameterization of solubility was included for predictions (Isaacman-VanWertz et al., 2016). But none of these two studies could reasonably predict the temporal variability of F% or log $K^{m}_{p,OM}$. One possible explanation is that the activity coefficients of isoprene SOA tracers and levoglucosan deviate from unity (0.42–2.04; Pye et al., 2018) and vary with PM composition. Pye et al. (2018) re-analyzed the measurement data from Isaacman-VanWertz et al. (2016) using a thermodynamic equilibrium gas-particle partitioning model in two LLPS modes, which involved organic-inorganic interactions and estimations of activity coefficients as a function of liquid PM mixture composition. The resulting predictions captured both the average and diurnal variations of measured F% for polyol tracers, suggesting a necessity in obtaining time-resolved activity coefficients for the implementation of absorptive equilibrium partitioning model."

22. 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.

Response:

The term "subcooled liquid vapor pressure" has been changed into "liquid-state vapor pressure".

23. 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 Kp estimates.

Response:

Thanks. Pure-compound vapor pressures were estimated using a variety estimation tools (EPI, Evaporation, SPARC, and SIMPOL; Table S4), and the resulting $K_{\mathrm{p,OM}}$ predictions were compared with measurement-based values in Table 1 of the revised manuscript (See responses to *Comments 7*). Descriptions of the results and associated discussions were rewritten (Section 3.4).

Pages 18-19, lines 420-464

"To understand if particulate OM is the only absorbing phase in aerosols for polyol tracers in Nanjing, the absorptive partitioning coefficients of gas vs. organic phases were calculated based on measurement results ($K^{\mathrm{m}}_{\mathrm{p,OM}}$) for predefined *Cases 1-3* and predicted theoretically ($K^{\mathrm{t}}_{\mathrm{p,OM}}$) using eq. 3 and vapor pressures listed in Table S4. In Table 1, $K^{\mathrm{t}}_{\mathrm{p,OM}}$ ranges of isoprene SOA tracers, levoglucosan, and meso-erythritol are within two orders of magnitude, while those of monosaccharides and mannitol are larger (> 10^3).When particulate OM was assumed as the only absorbing phase (*Case 1*), the average $K^{\mathrm{m}}_{\mathrm{p,OM}}$ of isoprene SOA tracers, levolgucosan, and meso-erythritol were more than 10 times greater than most of their $K^{\mathrm{t}}_{\mathrm{p,OM}}$ (Table 1), and this difference was not likely susceptible to measurement uncertainties. As shown in Table S5, the average relative uncertainties of measurement-based partitioning coefficients are all <50%, leading to an uncertainty of log $K^{\mathrm{m}}_{\mathrm{p,OM}}$ less than ± 0.30. Comparable or even greater (up to 10^5) gap between $K^{\mathrm{m}}_{\mathrm{p,OM}}$ and $K^{\mathrm{t}}_{\mathrm{p,OM}}$ has been observed for carbonyls in a number of laboratory and field studies (Healy et al., 2008; Zhao et al., 2013; Shen et al., 2018), which could be ascribed to reactive uptake (e.g., hydration, oligomerization, and esterification) of organic gases onto condensed phase (Galloway et al., 2009). Oligomers, sulfate and nitrate esters of 2-methyltetrols can be formed in the aerosol phase (Surratt et al., 2010; Lin et al., 2014), and their decomposition and hydrolysis during filter analysis will lead to an overestimation of particle-phase concentrations (Lin et al., 2013; Cui et al., 2018). However, the occurrence of oligomers, sulfate or nitrate esters of levoglucosan was not ever reported in ambient aerosols, although it can be readily oxidized by •OH in the aqueous phase of atmospheric particles (Hennigan et al., 2010; Hoffmann et al., 2010).

When solubility in aerosol liquid water was considered by assuming a LLPS in ambient aerosols, and whenever WSOM and WIOM partitioned into separate (*Case 2*) or single (*Case 3*) liquid phases, the average log $K^{\mathrm{m}}_{\mathrm{p,OM}}$ of the above mentioned compounds became much closer to or even lay within the range (e.g., levoglucosan) of log $K^{\mathrm{t}}_{\mathrm{p,OM}}$ (Table 1). These results indicated that the aerosol liquid water (21.3 ± 24.2 $\mu\mathrm{g\ m^{-3}}$; Table S1) is also an important absorbing phase of ambient polyol tracers in Nanjing. Similarly, the measured average *F*% of isoprene SOA tracers in southeastern US and central Amazonia were higher than predictions by assuming instantaneous equilibrium between the gas phase and particulate OM only, and the agreement was improved when parameterization of solubility was included for predictions (Isaacman-VanWertz et al., 2016). But none of these two studies could reasonably predict the temporal variability of *F*% or log $K^{\mathrm{m}}_{\mathrm{p,OM}}$. One possible explanation is that the activity coefficients of isoprene SOA tracers and levoglucosan deviate from unity (0.42–2.04; Pye et al., 2018) and vary with PM composition. Pye et al. (2018) re-analyzed the measurement data from Isaacman-VanWertz et al. (2016) using a thermodynamic equilibrium gas-particle partitioning model in two LLPS modes, which involved organic-inorganic interactions and estimations of activity coefficients as a function of liquid PM mixture composition. The resulting predictions captured both the average and diurnal variations of measured *F*% for polyol tracers, suggesting a necessity in obtaining time-resolved activity coefficients for the implementation of absorptive equilibrium partitioning model."

24. Figure S5: Please state the vapor pressure units and reference temperature used for the stated Log (p0L) values (one should not have to go back to the text to search for these).

Response:

The vapor pressure unit (atm) and reference temperature (25^{o}C) were added in the figure caption of Figure S5 (now Figure S4).

"Figure S4. Temporal variations of gas-phase concentrations and particle-phase fractions (*F*%) of polyol tracers. $p^{o,*}{}_{L}$: Liquid-state vapor pressure (atm, EPI estimates) at 25 ^{o}C."

References

Almeida, M. B., Alvarez, A. M., Miguel, E. M. D., and Hoyo, E. S. D.: Setchenow coefficients for naphthols by distribution method, Can. J. Chem., 61, 244-248, 10.1139/v83-043, 1983.

Cai, J., Zeng, X., Zhi, G., Gligorovski, S., Sheng, G., Yu, Z., Wang, X., and Peng, P.: Molecular composition and photochemical evolution of water-soluble organic carbon (WSOC) extracted from field biomass burning aerosols using high-resolution mass spectrometry, Atmos. Chem. Phys., 20, 6115-6128, 10.5194/acp-20-6115-2020, 2020.

Hilal, S. H., Ayyampalayam, S. N., and Carreira, L. A.: Air−liquid partition coefficient for a diverse set of organic compounds: Henry's law constant in water and hexadecane, Environ. Sci. Technol., 42, 9231-9236, 10.1021/es8005783, 2008.

Ip, H. S. S., Huang, X. H. H., and Yu, J. Z.: Effective Henry's law constants of glyoxal, glyoxylic acid, and glycolic acid, Geophys. Res. Lett., 36, L01802, https://doi.org/10.1029/2008GL036212, 2009.

Isaacman-VanWertz, G., Yee, L. D., Kreisberg, N. M., Wernis, R., Moss, J. A., Hering, S. V., de Sá, S. S., Martin, S. T., Alexander, M. L., Palm, B. B., Hu, W., Campuzano-Jost, P., Day, D. A., Jimenez, J. L., Riva, M., Surratt, J. D., Viegas, J., Manzi, A., Edgerton, E., Baumann, K., Souza, R., Artaxo, P., and Goldstein, A. H.: Ambient gas-particle partitioning of tracers for biogenic oxidation, Environ. Sci. Technol., 50, 9952-9962, 10.1021/acs.est.6b01674, 2016.

Kampf, C. J., Waxman, E. M., Slowik, J. G., Dommen, J., Pfaffenberger, L., Praplan, A. P., Prévôt, A. S. H., Baltensperger, U., Hoffmann, T., and Volkamer, R.: Effective Henry's law partitioning and the salting constant of glyoxal in aerosols containing sulfate, Environ. Sci. Technol., 47, 4236-4244, 10.1021/es400083d, 2013.

Kroll, J. H., Ng, N. L., Murphy, S. M., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds, J. Geophys. Res. Atmos., 110, D23207, https://doi.org/10.1029/2005JD006004, 2005.

Liang, C., Pankow, J. F., Odum, J. R., and Seinfeld, J. H.: Gas/particle partitioning of semivolatile organic compounds to model inorganic, organic, and ambient smog aerosols, Environ. Sci. Technol., 31, 3086-3092, 10.1021/es9702529, 1997.

Marcolli, C., and Krieger, U. K.: Phase changes during hygroscopic cycles of mixed organic/inorganic model systems of tropospheric aerosols, J. Phys. Chem. A, 110, 1881-1893, 10.1021/jp0556759, 2006.

Pankow, J. F., and Bidleman, T. F.: Interdependence of the slopes and intercepts from log-log correlations of measured gas-particle paritioning and vapor pressure—I. theory and analysis of available data, Atmos. Environ. Part A. General Topics, 26, 1071-1080, 10.1016/0960-1686(92)90039-n, 1992.

Pye, H. O. T., Zuend, A., Fry, J. L., Isaacman-VanWertz, G., Capps, S. L., Appel, K. W., Foroutan, H., Xu, L., Ng, N. L., and Goldstein, A. H.: Coupling of organic and inorganic aerosol systems and the effect on gas–particle partitioning in the southeastern US, Atmos. Chem. Phys., 18, 357-370, 10.5194/acp-18-357-2018, 2018.

Setschenow, J.: Über die Konstitution der Salzlösungen auf Grund ihres Verhaltens zu Kohlensäure, Z. Phys. Chem., 4U, 117-125, https://doi.org/10.1515/zpch-1889-0409, 1889.

Shen, H., Chen, Z., Li, H., Qian, X., Qin, X., and Shi, W.: Gas-particle partitioning of carbonyl compounds in the ambient atmosphere, Environ. Sci. Technol., 52, 10997-11006, 10.1021/acs.est.8b01882, 2018.

Taylor, N. F., Collins, D. R., Lowenthal, D. H., McCubbin, I. B., Hallar, A. G., Samburova, V., Zielinska, B., Kumar, N., and Mazzoleni, L. R.: Hygroscopic growth of water soluble organic carbon isolated from atmospheric aerosol collected at US national parks and Storm Peak Laboratory, Atmos. Chem. Phys., 17, 2555-2571, 10.5194/acp-17-2555-2017, 2017.

Zhao, Y., Kreisberg, N. M., Worton, D. R., Isaacman, G., Weber, R. J., Liu, S., Day, D. A., Russell, L. M., Markovic, M. Z., VandenBoer, T. C., Murphy, J. G., Hering, S. V., and Goldstein, A. H.: Insights into secondary organic aerosol formation mechanisms from measured gas/particle partitioning of specific organic tracer compounds, Environ. Sci. Technol., 47, 3781-3787, 10.1021/es304587x, 2013.