This study presents the results of simultaneous gas- and particle-phase measurements of oxygenated organic compounds in Nanjing, China. Due to some potential measurement artifacts with some compounds, the results focus on C5-alkene triols, 2-methyltetrols, and levoglucosan. The major finding is that the particle-phase fraction of these compounds were on average orders of magnitude higher than can be explained by either absorptive partitioning theory or Henry's law. There is moderate evidence that sulfate caused a "salting in" effect, though more discussion and/or data are needed to support this point (comment detailed below). The writing and organization are generally good, and the topic is of interest to a broad audience. I recommend the manuscript for publication after the following comments are addressed.

Response:

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

Specific Comments

1. How much does measurement uncertainty affect the partitioning coefficients? The stated acceptable threshold for breakthrough (< 33%) seems relatively high. How do the observed levels of breakthrough contribute to the uncertainty in the partitioning coefficients? Further, did breakthrough vary as a function of ambient temperature, OA loading, etc? Discussion of these points is needed.

Response:

The estimation of measurement uncertainties and their influences on partitioning coefficients were added in the revised manuscript. In general, measurement uncertainties of polyol tracers in filter samples were estimated from averages and ranges of their recoveries and method detection limits. Breakthrough of gaseous sampling was additionally considered for measurement uncertainties of PUF samples. Uncertainties associated with the calculations of particle-phase fractions and partitioning coefficients were estimated using a simplified root sum of squares (RSS) method by propagating measurement uncertainties of gas- and particle-phase concentrations. Details of the method were provided in Text S5 in supplementary information and mentioned in the main text.

Text S5 in supplementary information:

"***Text S5. Uncertainty estimation methods***

In this work, the measurement results of some polyol tracers in filter and PUF samples are subject to substantial uncertainties due to their low and variable recoveries (Table S2) and excessive breakthrough (Figure S2). A general equation was derived to estimate measurement uncertainties of individual polyols in filter and PUF samples

$$\Delta C = \sqrt{(\text{error fraction} \times \text{concentration})^2 + (0.5 \times \text{detection limit})^2} \qquad (5)$$

where ΔC is the uncertainty of target species in filter (ΔQ_f and ΔQ_b, ng m^{-3}) or PUF (ΔPUF, ng m^{-3}) samples. The error fraction (%) of filter sample analysis was defined as half of the difference between maximum and minimum recoveries scaled by the average (Table S2), which was divided by (1 - average breakthrough) for PUF analysis (Figure S2). The average breakthrough of meso-erythritol (23.8%), mannose (38.1%), xylitol (36.4%), and arabitol (36.4%) were set as those of C5-alkene triols, glucose, and mannitol, respectively. According to the gas-particle separation method in this work, ΔQ_f was used to represent the uncertainty of particle-phase concentration (ΔF, ng m^{-3}), and the uncertainty of gas-phase concentration (ΔA, ng m^{-3}) was propagated by

$$\Delta A = \sqrt{\Delta Q_b{}^2 + \Delta \mathrm{PUF}^2} \qquad (6)$$

Then the uncertainty of total concentration (ΔS, ng m^{-3}) was calculated as

$$\Delta S = \sqrt{\Delta F^2 + \Delta A^2} \qquad (7)$$

The uncertainties of particle-phase fractions (ΔF%) and partitioning coefficients ($K^{m}_{p,OM}$ and $K^{m}_{p,WIOM}$, m^3 ug^{-1}; $K^{m}_{H,e}$, mol m^{-3} atm^{-1}) were estimated by propagating ΔF, ΔS, and ΔA using a simplified root sum of squares (RSS) method (Dutton et al., 2009)

$$\Delta F\% = \sqrt{\left(\frac{\partial F\%}{\partial F}\Delta F\right)^2 + \left(\frac{\partial F\%}{\partial S}\Delta S\right)^2} \times 100\% \qquad (8)$$

$$\Delta K = \sqrt{\left(\frac{\partial K}{\partial F'}\Delta F'\right)^2 + \left(\frac{\partial K}{\partial A}\Delta A\right)^2} \qquad (9)$$

where ΔK is the uncertainty of $K^{m}_{p,OM}$, $K^{m}_{p,WIOM}$, or $K^{m}_{H,e}$; F' could be F, concentrations of polyols in WIOM (F_{WIOM}) or aqueous (F_w) phases, depending on the partitioning scheme (*Cases 1–3*) and partitioning coefficient for calculation. ΔF was split into ΔFw and ΔF_{WIOM} (or ΔF_{OM}) based on their ratios in eq. 4 of the main text. In Table S5, the estimated uncertainties are summarized and expressed in average ratios. As $K^{m}_{p,OM}$ and $K^{m}_{H,e}$ are all directly related to the ratio of particle- (F, ng m^{-3}) and gas-phase (A, ng m^{-3}) concentrations (eqs. 2, 4, 5, and 6 in the main text), their average $\Delta K/K$ values are the same (Table S5). "

Page 13, lines 296 – 303 of the main text:

"***Uncertainty estimation.*** To obtain the uncertainty associated with the calculation of F% and partitioning coefficients ($K^{m}_{p,OM}$ and $K^{m}_{H,e}$), measurement uncertainties of polyol tracers in filter and PUF samples were estimated from their recoveries and breakthrough for gaseous sampling. The root sum of squares (RSS) method was applied to propagate uncertainties of gas and particle-phase concentrations for F%, $K^{m}_{p,OM}$, and $K^{m}_{H,e}$ calculations. Details of the uncertainty estimation and propagation methods were provided in Text S5, and the average relative uncertainties were summarized in Table S5."

According to the equation for breakthrough calculation, a value of 33% means that the amount of a certain compound in backup PUF samples is half of that in front PUF samples. It was used as an indicator of excessive breakthrough in several previous studies (Peters et al., 2000; Ahrens et al., 2011; Xie et al., 2014a, b). However, the breakthrough value was rarely used to correct measurement results.

In the revised manuscript, the breakthrough of gaseous sampling was included for the estimation of measurement uncertainties and their influences on partitioning coefficients, but its individual contributions cannot be separated. In Table S5 (shown below), uncertainties of gas- and particle-phase concentrations, particle-phase fractions, and partitioning coefficients are expressed in average relative abundance.

Due to the limit in sample number for breakthrough tests and low detection rates, we can hardly evaluate the dependence of breakthrough on ambient temperature or OA loadings. The breakthrough of an ideal sampling method is expected to be extremely low (e.g., <10%) and have no dependence on ambient temperature or OA loadings. These statements were added in the revised manuscript (Pages 14-15, 337–341).

Table S5. Average relative uncertainties of measurements and calculated parameters.

Species	Δ*F*/*F*[a]	Δ*A*/*A*[b]	Δ*S*/*S*[c]	Δ*F*%/*F*%[d]	Δ*K*/*K*[e]
Isoprene SOA tracers					
C5-alkene triol 1	0.028	0.032	0.027	0.037	0.043
C5-alkene triol 2	0.028	0.054	0.033	0.036	0.059
C5-alkene triol 3	0.028	0.077	0.034	0.038	0.084
2-Methylthreitol	0.028	0.051	0.028	0.033	0.059
2-Methylerythritol	0.028	0.066	0.030	0.035	0.072
Biomass burning tracer					
Levoglucosan	0.051	0.16	0.054	0.072	0.17
Sugars ang sugar alcohols					
Meso-erythritol	0.028	0.11	0.028	0.040	0.12
Fructose	0.23	0.27	0.26	0.31	0.36
Mannose	0.045	0.27	0.049	0.062	0.28
Glucose	0.094	0.28	0.10	0.18	0.31
Xylitol	0.10	0.12	0.10	0.14	0.16
Arabitol	0.097	0.26	0.099	0.14	0.28
Mannitol	0.21	0.42	0.21	0.29	0.47

[a] Particle-phase concentration; [b] gas-phase concentration; [c] total concentration; [d] particle-phase fraction; [e] partitioning coefficients of gas vs. organic and aqueous phases.

2. The assumption of LLPS should be discussed. Other studies, for example Pye et al. (2018), could be included in this discussion.

Response:

Thanks. We discussed the assumption of LLPS by citing two existing studies (Zuend and Seinfeld, 2012; Pye et al., 2018) in the revised manuscript. Pye et al. (2018) was included in discussions on the agreement between measurement-based and predicted partitioning coefficients.

Page 11, lines 258-262

"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."

Pages 19-20, lines 444-464

"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 $K^{m}_{p,OM}$ of the above mentioned compounds became much closer to or even lay within the range (e.g., 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. 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."

Page 21, lines 487-490

"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⩾0.6; e.g., isoprene SOA tracers and levoglucosan) into the particle phase (Pye et al., 2018)."

3. I think that the title is somewhat misleading because the answer to the question is actually "neither" for most of the organic markers investigated. I suggest revising the title to reflect this.

Response:

In the revised manuscript, it was shown that the solubility of polyol tracers in aerosol liquid water should not be ignored. Comparisons of measurement-based effective Henry's law constants versus predicted values in pure water indicated increased partitioning toward the particle phase.

Then the title has been changed into

"Gas-particle partitioning of polyol tracers at a suburban site in Nanjing, east China: Increased partitioning to the particle phase"

4. The comparisons to Denver, CO seem completely random given that meteorology, OA loadings, inorganic composition, and ALWC are quite different between the two locations. I understand that this research group made measurements in both locations, but some additional discussion is warranted to better connect the two locations.

Response:

The observation study in Denver, CO (Xie et al., 2014b) did not measure inorganic composition or estimate ALWC. In that study, evidences showing that gas-particle partitioning of 2-methyltetrol and levoglucosan depended on variations in ambient temperature and absorbing OM mass. Then the influence of aerosol liquid water on partitioning coefficients could not be compared between these two studies. Thus, in the revised manuscript, we only kept the comparisons of measured gas- and particle-phase concentrations. The partitioning coefficients obtained here were discussed by referring to other studies (e.g., Isaacman-VanWertz et al., 2016; Pye et al., 2018)

Pages 19-20, lines 444-464

"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 $K^{m}_{p,OM}$ of the above mentioned compounds became much closer to or even lay within the range (e.g., levoglucosan) of log $K^{t}_{p,OM}$ (Table 1). These results indicated that the aerosol liquid water (21.3 ± 24.2 $\mu g\ m^{-3}$; 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 $K^{m}_{p,OM}$. 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."

5. Several points in the manuscript, including in the 1st sentence of the abstract, the discussion links gas-particle partitioning to source apportionment. However, gas-particle partitioning has importance in the atmosphere that extends way beyond source apportionment (e.g., it affects the PM mass concentration, the lifetime and distribution of organics in the atmosphere, among others). The study thus has broader relevance than is discussed in the manuscript.

Response:

Gas/particle partitioning is important in predicting the formation, transport, and life time of organic aerosols in the atmosphere, which are mostly involved in atmospheric transport models (e.g., CMAQ).

Tracer-based source apportionment is a different research method highly dependent on the identification of source-specific tracers. As mentioned in the introduction, the target polyols in this work are firstly known as tracers liked with specific emission sources. But their gas-particle partitioning was poorly characterized. Several measurement studies on gas-particle partitioning of polar organic tracers also emphasized its importance in both modeling and tracer-based source apportionment of organic aerosols (e.g., Zhao et al., 2013; Isaacman-VanWertz et al., 2016). That's the reason gas-particle partitioning of polyol tracers was also linked to source apportionment in some places of the manuscript.

In the abstract, the first sentence has been changed into

"Gas-particle partitioning of water-soluble organic compounds plays a significant role in influencing the formation, transport, and lifetime of organic aerosols in the atmosphere, but is poorly characterized." (Page 2, lines 31-33)

Technical Corrections

(1) Line 55: “documented” is not the right word here

Response:

Here, “documented for” was replaced by “in”. (Page 4, line 78)

(2) Line 65-66: include “GC-MS” in parentheses after introducing the terms

Response:

It was revised as suggested. (Page 4, line 89)

(3) Line 80-83: I do not follow the logic of this sentence, please clarify

Response:

The original expression has been changed 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).” (Page 5, 104-108)

(4) Line 90: typo in this line

Response:

Thanks, “every” should be “very”. (Page 5, line 117)

(5) Line 93: suggest changing “depict” to “describe”

Response:

It has been changed as suggested. (Page 5, line 120)

(6) Line 101: delete “termed”

Response:

It was deleted as suggested.

(7) Line 116: “unveils” is not the right word here

Response:

It was replaced by “tends to explain”. (Page 6, line 145)

(8) Line 118-120: suggest deleting this sentence

Response:

It was deleted as suggested.

(9) Line 134: change “was” to “were”

Response:

It was changed as suggested. (Page 7, line 163)

(10) Line 153: change “involving” to “using” or similar

Response:

Here, “involving” was replaced by “using”. (Page 7, line 179)

(11) Line 221-222: specify that this is theoretical

Response:

The whole sentence has been deleted in the revised manuscript.

(12) Line 244: edit sentence for grammar

Response:

The original expression has been changed into

“It is therefore suitable to collect gaseous 2-methylterols and levoglucosan using PUF materials only.” (Page 13, lines 312-313)

(13) Line 317: edit sentence for grammar

Response:

The original expression has been changed into

“………which might be attributed to high levels of vegetation during growing seasons and autumn decomposition (Burshtein et al., 2011).” (Page 17, lines 390-491)

(14) Line 331: delete “data”

Response:

It was deleted and the whole paragraph has been rewritten. (Pages 17-18, lines 397-419)

(15) Line 333: suggest deleting “majorly” and revising the sentence accordingly

Response:

The sentence has been changed into

"Gas-phase C5-alkene triols and 2-methyltetrols had maximum concentrations in summer and significant ($p < 0.05$) day-night variations (Figure S4)…………." (Pages 17, lines 402-403)

(16) Line 360: "prediction" should be plural

Response:

It was changed as suggested. (Page 19, line 451)

(17) Line 380: change "less stable" to "lower"

Response:

We added "lower and" in that sentence. (Page 20, line 478)

(18) Line 386-388: it is quite difficult to follow the discussion here

Response:

Here, the comparisons were reorganized and most of the discussions on $K_{\mathrm{p,OM}}$ were rewritten.

"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 μg m^{-3}; Table S1) is also an important absorbing phase of ambient polyol tracers in Nanjing." (Page 19, lines 444-450)

(19) Line 412: efflorescence RH is more relevant than DRH in this scenario

Response:

Here, we deleted the original explanation, and changed the original expression into

"The log ($K^{\mathrm{t}}_{\mathrm{H,w}}/K^{\mathrm{m}}_{\mathrm{H,e}}$) 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}." (Pages 22, lines 521-525)

(20) Line 462-463: delete "barely" and revise sentence accordingly

Response:

The original expression was changed into

"Then gas-particle partitioning of polyol tracers should have little influence on source apportionment based on particle-phase data in Nanjing." (Page 24, lines 564-566)

(21) Line 465: not sure what exactly is a "concern"? clarification needed

Response:

The whole sentence was deleted.

(22) Line 478: delete "pre-"

Response:

It was deleted as suggested. (Page 25, line 579)

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