Reviewer 1

I thank the authors for their more detailed examination of error and uncertainty, as well as their more careful consideration of uncertainty in theoretical partitioning values. These revisions significantly improve the manuscript, and the authors have reasonably tempered some of their original claims based on these new insights.

I highlight a few specific remaining concerns below, the first of which absolutely needs to be addressed prior to publication while the others are suggestions to add clarity.

1. Equation S1 used by the authors to calculate "organic water" is not correct as written. Instead of kappa*O:C, the equation should estimate kappa from O:C, e.g., as 0.29*O:C, based on the work by Massoli et al. correlating kappa to O:C (https://doi.org/10.1029/2010GL045258). This change will roughly triple the calculated W_o, which will not significantly alter the conclusion that organic water is a minor component, but it needs to be corrected before publication.

Response:

Thanks. Here Eq. S1 was corrected into

$$W_{\mathrm{O}} = \frac{V_{\mathrm{WSOC}} \times \kappa}{(\frac{100}{\mathrm{RH\%}} - 1)} \quad (1)$$

where V_{WSOC} represents WSOC volume, and is calculated as the organic mass (WSOC ×1.6) divided by its density (1.4 g $\mathrm{cm^{-3}}$). The hygroscopicity parameter (κ) of secondary organic aerosol (SOA) was observed to increase as a function of its oxygen to carbon ratio (O:C; Massoli et al., 2010). Isaacman-VanWertz et al. (2016) estimated κ of hygroscopic organic matter by assuming a linear regression slope of 0.29 between κ and O:C. In previous field and laboratory studies, κ values of hygroscopic organic matter typically varied from 0.05 to 0.25 with a O:C range of 0.3–1.0 (Chang et al., 2010; Massoli et al., 2010; Taylor et al., 2017), and the corresponding average W_{O} based on Eq. S1 in this work ranged from 0.47 ± 1.14 to 2.34 ± 4.03 μg $\mathrm{m^{-3}}$, far below the amount caused by inorganic ions (21.3 ± 24.2 μg $\mathrm{m^{-3}}$, Table S1). Taylor et al. (2017) predicted a hygroscopic growth factor range of 1.00–1.20 with RH varying from 60 to ~100%, which lead to an average W_{O} of 0.42 ± 0.70 μg $\mathrm{m^{-3}}$ for this study. Thus, the water content contributed by WSOC was not accounted for in this work.

In Text S1 of supplementary information, the original expression was changed accordingly.

2. It's not clear to me why the authors use "S", "F", and "A" for total, particle, and gas concentrations, respectively, in units of mass per volume air. They also use M_OM for total organic mass per volume air. All of these are mass concentrations, and it seems to me they should use unified notation (e.g., M_i,tot, M_i,p , and M_i,g). In the end, that is a style choice, but as written does not follow typical chemistry notation guidance (e.g., IUPAC).

Response:

In previous studies where the gas-particle partitioning coefficient (K_p) was defined and calculated (e.g., Pankow, 1994a, b; Liang and Pankow, 1996; Liang et al., 1997; Mader and Pankow, 2002), "F" and "A" were always used to represent particle- and gas-phase concentrations, respectively, in units of mass per volume air. "S" was used to denote the sum of F and A in our previous work (Xie et al., 2013, 2014), where the influence of gas-particle partitioning on receptor-based source apportionment of organic aerosols was evaluated. To keep consistent with existing studies, "S", "F", and "A" were used for total, particle, and gas concentrations, respectively. Since all abbreviations have been clearly defined, the usage of "S", "F", and "A" will not introduce any ambiguity.

In the revised manuscript and supplementary information, we added some references for the definition of K_p (Page 11, lines 245-246) and "S" (or "ΔS"; Text S5 in supplementary information)

3. Line 545-548 has odd grammar, should be corrected.

Response:

Thanks, the original expression was changed into

"There is evidence showing that conventional GC/EI-MS analysis overestimates particle-phase 2-methyltetrols by 60-188% due (in part) to the thermal degradation of less volatile oligomers and organosulfates (Cui et al., 2018)". (Page 23, lines 546-549)

Reviewer 2

The authors have responded to the comments by referees and have made substantial changes and additions, which have clarified and improved this manuscript. The revisions are well done.
I appreciate the extra work put into quantifying uncertainties and the evaluation of gas-particle partitioning data based on three different cases. I have only a few minor comments below. I recommend this manuscript for publication in ACP.

Specific comments:
1) In the response/changed text the authors write "… 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)."
- Perhaps rephrase "in ideal condition" to "assuming ideal mixing conditions"

Response:

Thanks, the original expression was changed into
"…..particle-phase concentrations of carbonyls were underestimated by several orders of magnitude when particulate OM is presumed as the only absorbing phase assuming ideal mixing condition (Healy et al., 2008; Kampf et al., 2013; Shen et al., 2018)." (Page 5, line 113)

7) Tables 1,2: Good to have these comparisons in the manuscript. Make sure to indicate whether Log is base-10 log or natural log.

Response:

We stated that the logarithm values were using a base of 10 in the footnotes of Tables 1 and 2.

17) I consider glycerol to be among the group of highly water-soluble compounds (it is miscible in all proportions with water, i.e. infinitely soluble); therefore, it may be similar to the solubility of some of the "highly soluble" polyols studied in the present work. I agree that the weak correlation of polyol uptake with sulfate may not be in contradiction to the work by Marcolli and Krieger (2006), but only if salting-in by ammonium sulfate is not proposed to be the dominant mechanism (otherwise it would seem contradictory).

Response:

Although the ammonium sulfate (AS) is a "salting-out" agent for glycerol in water solution, it might not be appropriate to infer that AS is a "salting-out" agent for other water-soluble polyols in aerosol liquid water. The interactions of inorganic ions and organic compounds in the aqueous phase of aerosols might increase the partitioning of highly oxygenated compounds into the particle phase through reactive uptake and aqueous phase chemistry, but not the changes in water-solubility. That's why we consider the "salting-in" effect to be a phenomenon, but not a specific physical or chemical mechanism in this version of the manuscript (Page 23, lines 535-536).

"However, the "salting-in" effect is a known phenomenon that is not likely linked with a specific physical or chemical mechanism."

The definition equation for "salting-in" effect was only used to parameterize the increased partitioning of gas-phase polyols to the aqueous phase in aerosols (Page 23, lines 532-534), of which the potential underlying mechanisms were discussed separately (Pages 23-24, lines 546-557).

"There is evidence showing that conventional GC/EI-MS analysis overestimates particle-phase 2-methyltetrols by 60-188% due (in part) to the thermal degradation of less volatile oligomers and organosulfates (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)."

In both the abstract and conclusions, we stated that the enhanced uptake of polyol tracers in aerosol liquid water might be ascribed to mechanisms of reactive uptake, aqueous phase reaction, "like-dissolves-like" principle, etc. (Pages 2-3, lines 52-55; Page 24, lines 572-574) "Salting-in" by ammonium sulfate was not proposed to be the dominant mechanism for increasing the partitioning of polyol tracers into the condensed phase.

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

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Abstract

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. In this work, gas- and particle-phase concentrations of isoprene oxidation products (C5-alkene triols and 2-methylterols), levoglucosan, and sugar polyols were measured simultaneously at a suburban site of the western Yangtze River Delta in east China. All target polyols were primarily distributed into the particle phase (85.9–99.8%). Given the uncertainties in measurements and vapor pressure predictions, a dependence of particle-phase fractions on vapor pressures cannot be determined. To explore the impact of aerosol liquid water on gas-particle partitioning of polyol tracers, three partitioning schemes (*Cases 1-3*) were proposed based on equilibriums of gas versus organic and aqueous phases in aerosols. If particulate organic matter (OM) is presumed as the only absorbing phase (*Case 1*), the measurement-based absorptive partitioning coefficients ($K^{m}_{p,OM}$) of isoprene oxidation products and levoglucosan were more than 10 times greater than predicted values ($K^{t}_{p,OM}$). The agreement between $K^{m}_{p,OM}$ and $K^{t}_{p,OM}$ was substantially improved when solubility in a separate aqueous phase was included, whenever water-soluble and water-insoluble OM partitioned into separate (*Case 2*) or single (*Case 3*) liquid phases, suggesting that the partitioning of polyol tracers into the aqueous phase in aerosols should not be ignored. The measurement-based effective Henry's law coefficients ($K^{m}_{H,e}$) of polyol tracers were orders of magnitude higher than their predicted values in pure water ($K^{t}_{H,w}$). Due to the moderate correlations between log ($K^{m}_{H,e}/K^{t}_{H,w}$) and molality of sulfate ions, the gap between $K^{m}_{H,e}$ and $K^{t}_{H,w}$ of polyol tracers could not be fully parameterized by the equation defining

“salting-in” effects, and might be ascribed to mechanisms of reactive uptake, aqueous phase reaction, “like-dissolves-like” principle, etc. These study results also partly reveals the discrepancy between observation and modeling of organic aerosols.

1 Introduction

The water-soluble organic carbon (WSOC) in ambient aerosols can account for 20-80% of particulate organic matter (OM) based on carbon mass (Saxena and Hildemann, 1996; Kondo et al., 2007). Field studies on the hygroscopic growth and cloud condensation nucleus (CCN) activity of aerosol extracts indicated that WSOC contributed significantly to aerosol hygroscopicity, and modified the hydration behavior of inorganic species (e.g., sulfate, nitrate, and ammonium; Hallar et al., 2013; Taylor et al., 2017). Thus, WSOC plays an important role in changing radiative and cloud nucleating properties of atmospheric particles. Particulate WSOC is a complex mixture of polar organic compounds containing oxygenated functional groups (e.g., hydroxyl, carboxyl, and carbonyl groups), among which a list of organic compounds with multiple hydroxyl (polyols) groups have been identified using gas chromatography -mass spectrometry (GC-MS) and linked with specific emission sources. For example, C5-alkene triols and 2-methyltetrols are isoprene oxidation products (Claeys et al., 2004; Wang et al., 2005; Surratt et al., 2006); levoglucosan is a typical pyrolysis product of cellulose (Simoneit et al., 1999); primary saccharides (e.g., fructose and glucose) and saccharide polyols (e.g., arabitol and mannitol) are commonly associated with soil microbiota and fungal spores, respectively (Simoneit et al., 2004; Bauer et al., 2008).

To quantify the sources contributing to WSOC, concentrations of individual organic tracers are often used as inputs for receptor-based modeling (Zhang et al., 2009; Hu et al., 2010). Due to the influences of gas-particle partitioning on source apportionment, Xie et al. (2013, 2014c) suggested the involvement of gas-phase concentrations of organic makers through theoretical prediction or field measurements.

The equilibrium absorptive partitioning theory outlined by Pankow (1994a, b) and laboratory measurements of secondary organic aerosol (SOA) yields (Odum et al., 1996) have been widely applied to predict SOA formation in traditional modeling studies (Heald et al., 2005; Volkamer et al., 2006; Hodzic et al., 2010). 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~~ assuming ideal mixing condition (Healy et al., 2008; Kampf et al., 2013; Shen et al., 2018). Zhao et al. (2013) observed a positive dependence of particle-phase pinonaldehyde on relative humidity (RH, %), and inferred that aerosol water played a role in the formation of pinonaldehyde in the atmosphere. However, very few studies have been performed on the measurement of gaseous polyols (Xie et al., 2014b; Isaacman-VanWertz et al., 2016), and their gas-particle partitioning were poorly understood.

Henry's law can describe the uptake of a compound into a liquid, highly dilute solution (e.g., cloud droplets) in the atmosphere (Ip et al., 2009; Compernolle and Müller, 2014a). Aerosol water is also a major component of atmospheric particles, and accounts for 40% by volume at 50% RH in Europe (Tsyro, 2005). But the bulk aerosol solution is highly concentrated with inorganic ions and WSOC. An effective

Henry's law coefficient ($K_{H,e}$, mol m^{-3} atm^{-1}) can be used to account for the measured partitioning between the gas phase and aerosol liquid water (Volkamer et al., 2009). Both laboratory and field studies observed enhanced $K_{H,e}$ of carbonyl compounds with inorganic salt concentrations (in mol kg^{-1} aerosol liquid water content, ALWC; Kampf et al., 2013; Waxman et al., 2015; Shen et al., 2018). This "salting-in" effect (Setschenow, 1889) is not mechanistically understood, and might be linked with the hydrophilic interactions (e.g., hydrogen bonding) between polar organic compounds and inorganic ions leading to an increase of entropy or decrease of Gibbs free energy (Almeida et al., 1983; Waxman et al., 2015). Polyol tracers are highly water-soluble and their gas-particle partitioning is very likely driven by the aqueous phase containing substantial ionic species in ambient aerosols. In the Southeastern US, the particle-phase fraction (*F*%) of WSOC is highly dependent on RH and ALWC (Hennigan et al., 2009).

In the present study, polyols related to specific emission sources in gaseous and particle phases were measured concurrently in northern Nanjing, China. The sampling and chemical analysis were performed in a similar manner as Xie et al. (2014b), while an additional step was added prior to GC-MS analysis to clean the extracts of gaseous samples. To explore the roles of aerosol liquid water on gas-particle partitioning of polyol tracers, three modes (*Cases 1-3*) were proposed based on equilibriums between gas and liquid aerosol phases, and the measurement-based and predicted partitioning coefficients were compared across individual cases. This work tends to explain the gas-particle partitioning of polyols at a suburban site in eastern China, where the estimated average mass concentration of aerosol liquid water is close to 20 μg m^{-3} (Yang et al., 2021).

2 Methods

2.1 Field Sampling

Details of the sampling information were provided in Yang et al. (2021). Briefly, ambient air was sampled on the rooftop of a seven-story library building located in Nanjing University of Information Science and Technology (NUIST 32.21 °N, 118.71 °E), a suburban site in the western Yangtze River Delta of east China. A medium volume sampler (PM-PUF-300, Mingye Environmental, Gugangzhou, China) equipped with a 2.5 μm cut impactor was configured to collect particulate matter with aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) and gaseous organic compounds at a flow rate of 300 L min^{-1}. After the impactor, the sampled air flowed through a filter pack containing two stacked pre-baked (550 °C, 4 h) quartz filters (20.3 cm × 12.6 cm, Munktell Filter AB, Sweden) and a polyurethane foam (PUF, 65 mm diameter × 37.5 mm length) cartridge in series. The top quartz filter (Q_f) in the filter pack was loaded with $PM_{2.5}$; gaseous organic compounds adsorbed on the backup quartz filter (Q_b) were determined to evaluate sampling artifacts; and the PUF cartridge was used for the sampling of gaseous polyols. Filter and PUF samples were collected every sixth day during daytime (8:00 AM – 7:00 PM) and night time (7:00 PM – 7:00 AM next day), respectively, from 09/28/2018 to 09/28/2019. Collection efficiency of gaseous polyols were examined by performing breakthrough experiments using two PUF plugs during nine sampling intervals. Prior to sampling, PUF adsorbents were cleaned and dried in the same way as Xie et al. (2014b). Field blank filter and PUF materials were collected every 10th sample for contamination adjustment. Filter and PUF samples were sealed in prebaked aluminum foil and glass jars, respectively, at – 20 °C until analysis.

2.2 Chemical Analysis

Bulk speciation. The accumulated $PM_{2.5}$ mass and bulk components including water soluble ions (NH_4^+, SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+}, and K^+), organic (OC) and elemental carbon (EC), and WSOC were measured for each filter sample. Their final concentrations were determined by subtracting measurement results of Q_b from those of Q_f. Concentrations of aerosol liquid water were predicted by ISORROPIA II model using ambient temperature, RH, and concentration data of NH_4^+, SO_4^{2-}, and NO_3^- under the metastable state. 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). Table S1 lists averages and ranges of ambient temperature, RH, measured $PM_{2.5}$ components, and predicted aerosol liquid water from Yang et al. (2021).

Polyols analysis. Details of the analysis method for gaseous and particulate polyols were provided in supplementary information (Text S2). Briefly, 1/8 of each filter sample was pre-spiked with deuterated internal standard and extracted ultrasonically twice for 15 min in 10–15 mL of methanol and methylene chloride mixture (1:1, v/v). After filtration, rotary evaporation, N_2 blown down to dryness, and reaction with 50 μL of N, O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) containing 1% trimethylchlorosilane (TMCS) and 10 μL of pyridine, the derivatives of polyols were diluted to 400 μL using pure hexane for GC-MS analysis. Pre-spiked PUF samples were Soxhlet extracted using a mixture of 225 mL of methylene chloride and 25 mL of methanol, followed by the same procedures of filter sample pretreatment. Prior to GC-MS analysis, 50 μL of pure water was added to precipitate PUF impurities from the final extract. As shown in Figure S1e, all PUF residues are kept in aqueous phase at the bottom of the vial, while the derivatives of polyol tracers are supposed to be retained in the top clear hexane solution. An aliquot of 2 μL of the supernatant was injected for GC-MS analysis under splitless mode, and an internal standard method with a six-point calibration curve (0.05–5 ng μL^{-1}) was performed to quantify polyols concentrations. In this work, isoprene SOA products, including three C5-alkene triols (cis-2-methyl-1,3,4-trihydroxy-1-butene, 3-methyl-2,3,4-trihydroxy-1-butene, and trans-2-methyl-1,3,4-trihydroxy-1-butene; abbreviated as C5-alkene 1, 2, and 3) and two 2-methyltetrols (2-methylthreitol and 2-methylerythritol), were quantified using meso-erythritol; other polyols were determined using authentic standards.

Analytical recoveries of target polyols were obtained by adding known amounts of standards to blank sampling materials (quartz filter and PUF), followed by extraction and instrumental analysis identically as ambient samples. Method detection limits (MDL) of individual species were estimated as three times the standard deviation of their concentrations determined from six injections of the lowest calibration standard. Table S2 lists recovery and MDL values of authentic standard compounds. Concentrations of polyols in field blank samples were measured and subtracted from air samples if necessary. To obtain appropriate gas-particle distribution of polyol tracers, their field-blank corrected concentrations in filter and PUF samples were adjusted by recoveries. Final concentrations of individual polyols in Q_f, Q_b, and PUF samples are summarized in Table S3.

2.3 Data analysis

Gas-particle separation and breakthrough calculation. Polyol tracers detected in Q_b samples are contributed by both gaseous adsorption (“positive artifact”) and particle-phase evaporation from Q_f samples (“negative artifact”), but their relative contributions are unknown. Xie et al. (2014b) adjusted particle- and gas-phase concentrations of levoglucosan and 2-methyltetrol based on Q_b measurements in two different ways. One assumed that Q_b values were completely attributed to gaseous adsorption; the other presumed equal contributions from gaseous adsorption and Q_f evaporation. However, negligible difference in gas-particle distribution was observed due to the small Q_b values. In Table S3, concentrations of polyol tracers on Q_b are far below those on Q_f, and it would be safe to presume equal positive and negative artifacts. In this study, particle-phase concentrations of polyols were represented by Q_f values, and the gas phase was calculated as the sum of Q_b and PUF measurements.

The sampling efficiency of target polyols were evaluated by collecting and analyzing tandemly installed PUF plugs during nine sampling intervals. The breakthrough of each polyol was calculated as

$$B = \frac{[\text{PUF}]_{\text{back}}}{[\text{PUF}]_{\text{front}} + [\text{PUF}]_{\text{backup}}} \times 100\% \qquad (1)$$

where B is the breakthrough of gaseous sampling, and [PUF] represents the concentration of specific compound in front or backup PUF sample. A value of 33% was typically used to indicate excessive breakthrough (Peters et al., 2000; Ahrens et al., 2011).

Calculations of partitioning coefficients. 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 ($K_{\text{p,OM}}$, $\text{m}^3\ \mu\text{g}^{-1}$) were calculated from measurements ($K^{\text{m}}_{\text{p,OM}}$)

and predicted theoretically ($K^{t}_{p,OM}$) as follows (Pankow, 1994a, b; Liang and Pankow, 1996; Liang et al., 1997; Mader and Pankow, 2002)

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

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

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 3, R (m^{3} atm K^{-1} mol^{-1}) and T (K) are the ideal gas constant and ambient temperature; $\overline{MW}_{OM}$, 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; $p^{o}{}_{L}$ (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 ($K^{\mathrm{m}}_{\mathrm{p,OM}}$) and aqueous ($K^{\mathrm{m}}_{\mathrm{H,e}}$) 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).

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.

3 Results and discussion

3.1 Method evaluation

In our previous study, PUF/XAD-4 resin/PUF and PUF/XAD-7 resin/PUF adsorbent sandwiches were tested for sampling gaseous 2-methyltetrols and levoglucosan (Xie et al., 2014b). The results of breakthrough experiments suggested that both the two sandwiched composites had high sampling efficiency (close to 100%). Moreover, individual parts of the two types of composites (top PUF, middle XAD-4/XAD-7 resin, and backup PUF) were analyzed for 7 samples, and target compounds were only detected in top PUF. It is therefore suitable to collect gaseous 2-methylterols and levoglucosan using PUF materials only.

Although PUF materials were pre-cleaned prior to sampling, a few short-chain polyurethanes or impurities could be dissolved during Soxhlet extraction of target compounds using the mixture of methanol and methylene chloride. These substances precipitated when sample extracts were concentrated (Figure S1a, b), and re-dissolved in BSTFA:TMCS/pyridine and hexane after the derivatization step (Figure S1c, d). In Xie et al. (2014b), an aliquot of 2 μL of the sample extract as shown in Figure S1d was injected for GC-MS analysis. Since the dissolved PUF materials did not vaporize at ~300 ^{o}C, the GC inlet liner had to be changed for cleaning every few samples. In this work, 50 μL of pure water was added to separate PUF materials from polyol derivatives in hexane solution. As shown in Figure S1e, all PUF residues were retained in the aqueous solution after phase separation. This pretreatment step was added for the analysis of gaseous samples to save time for changing and cleaning GC inlet liners. However, the revised method did not improve the recoveries of meso-erythritol and levoglucosan in PUF samples (Table S2) compared to those in Xie et al. (2014b). This is because the dissolved PUF materials should have an impact on the derivatization efficiency of polyol species, and future work is warranted to remove dissolved PUF materials in sample extracts before the derivatization step.

Measurement results of breakthrough samples and the resulting *B* values were shown in Figure S2. C5-alkene triols and 2-methyltetrols were mainly observed in summertime, and levoglucosan was only detected in three pairs of breakthrough samples. Their average *B* values (< 33%) indicated no excessive breakthrough (Figure S2a-c), but were higher than those reported by Xie et al. (2014b). This might be ascribed to the greater face velocity (1.5 cm s^{-1}) for sampling gaseous polyols than that (0.61 cm s^{-1}) in our previous study. Due to the limit in sample number for breakthrough tests and low detection rates, the dependence of breakthrough on ambient temperature or OM loadings cannot be evaluated. The breakthrough of an ideal sampling method is expected to be extremely low (e.g., <10%) and have no dependence on ambient temperature, OM loadings, etc. Unlike fructose which had low breakthrough (Figure S2d), glucose and mannitol had comparable concentrations between front and backup PUF samples for several breakthrough experiments (Figure S2e, f), indicating that PUF materials are not suitable for sampling gaseous glucose and mannitol. Mannose and arabitol were not detected or had BDL values for breakthrough samples, and their breakthrough was not provided. In the current work, concentrations of polyol tracers in filter and PUF samples were all reported, but the data of mannose, glucose, arabitol, and mannitol in PUF samples should be treated with caution due to high breakthrough or the lack of valid breakthrough results.

3.2 General description of measurement results

Total ambient concentrations (Q_f + Q_b + PUF) of individual polyols are depicted using boxplots in Figure 2. Figure S3 presents temporal variations of total and Q_f concentrations of individual polyols with daytime and night-time measurements distinguished. In general, polyol tracers were predominantly observed on Q_f with averages 1-3 orders of magnitude higher than those on Q_b and PUF (Table S3). Levoglucosan had the highest average total concentration (66.1 ± 71.1 ng m^{-3}), followed by fructose (15.0 ± 62.9 ng m^{-3}) and mannose (14.3 ± 31.3 ng m^{-3}). C5-alkene triols and 2-methyltetrols are formed from isoprene epoxydiols (IEPOX) under low NO_X conditions (Surratt et al., 2010). All the five species on Q_b were more frequently detected and had average concentrations 2-20 times higher than those in PUF samples. While in Xie et al. (2014b), the sum of 2-methyltetrols in Q_b and adsorbent samples were up to 2.7 times higher than those on Q_f in summer Denver, so isoprene products are not similarly distributed between gas and aerosol phases across different regions. Moreover, isoprene-derived polyols exhibited prominent elevations in summer (Figure S3a-e), and their daytime concentrations (2.02 ± 3.73 – 10.5 ± 29.3 ng m^{-3}) were only slightly higher than those during night-time (1.63 ± 4.40 – 9.65 ± 32.7 ng m^{-3}). Previous field studies observed strong diurnal variations of isoprene SOA tracers with peak concentrations from afternoon till midnight (Fu and Kawamura, 2011; Isaacman-VanWertz et al., 2016). Although no IEPOX will be generated from the oxidation of isoprene by •OH and HO_2• after sunset, the formations of C5-alkene triols and 2-methyltetrols might continue until pre-existing IEPOX is exhausted. In this work, neither the daytime (8:00 AM–7:00 PM) or night-time (7:00 AM–7:00 AM next day) sample covered the whole period when isoprene SOA tracers had peak concentrations, and the strong diurnal variations of C5-alkene triols and 2-methyltetrols were not captured.

Levoglucosan was more frequently detected but far less concentrated in PUF than in Q_b samples. Its total concentrations were comparable to those in urban Denver (average 65.3 ± 96.8 ng m^{-3}, range 2.48 – 478 ng m^{-3}), where an average of ~20% partitioned into the gas phase (Xie et al., 2014b). Due to the enhanced biomass burning activities in cold periods for domestic heating at night, levoglucosan showed a clear seasonal pattern (winter maxima and summer minima) and significant (p = 0.03) higher concentrations during night-time (Figure S3f). Sugars and sugar alcohols are commonly linked with soil/dust resuspension and associated microbial activities (Simoneit et al., 2004). They were frequently detected in Q_b samples with comparable averages and ranges as those in PUF samples (Table S3). Total concentrations of fructose and glucose were strongly (r = 0.98) correlated peaking in middle spring (April 2019, Figure S3h, j), when Ca^{2+} on Q_f also reached its maxima of the year (Yang et al., 2021), indicating an influence from soil/dust resuspension. Arabitol and mannitol had identical seasonal pattern (r = 0.89) with elevated total concentrations from May to October (Figure S3i, m), which might be attributed to high levels of vegetation during growing seasons and autumn decomposition (Burshtein et al., 2011). Multiple peaks of mannose concentrations were observed from spring to autumn, suggesting a variety of contributing sources (e.g., microbial activity, vegetation). Xylitol is likely derived from biomass burning in northern Nanjing due to its strong correlation (r = 0.89) with levoglucosan.

3.3 Gas- and particle-phase distributions

As mentioned in sections 2.3, concentrations of particulate polyols were obtained directly from Q_f measurements, and the gas phase was calculated as the sum of Q_b and PUF values. Figure S4 shows the time series of gas-phase concentrations and particle-phase fractions (F%) of individual polyol tracers. The average F% values of measured species are plotted against the logarithms of their liquid-state vapor pressures at 25 °C ($p^{o,*}_L$) in Figure 3. Gas-phase C5-alkene triols and 2-methyltetrols had maximum concentrations in summer and significant ($p < 0.05$) day-night variations (Figure S4), while other polyols had extremely low concentrations in the gas phase with F% (average ± standard deviation) ranging from 94.2 ± 8.02 – 99.8 ± 1.21%. The average F% values of 2-methyltetrols (87.5 ± 10.6%) and levoglucosan (99.8 ± 1.21%) were greater than those in urban Denver (50–80%; Xie et al., 2014b), where the average sampling temperature (12.5 ± 10.1 °C) was much lower. 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. 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 ($p^{o,*}_{L}$ < ~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.

3.4 Partitioning coefficients of gas versus organic phases

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. Comparable or even greater (up to 10^5) gap between $K^{m}_{p,OM}$ and $K^{t}_{p,OM}$ 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 $K^{m}_{p,OM}$ 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.

Unlike isoprene SOA tracers and levoglucosan, the average $K^{t}_{p,OM}$ values of monosaccharides (fructose, mannose, and glucose) and sugar alcohols (xylitol, arabitol, and mannitol) were orders of magnitude larger than their $K^{m}_{p,OM}$ for *Cases 2 and 3* (Table 1). This is probably caused by the overestimation of gas-phase concentrations of sugar polyols. The organic matter on Q_b is mainly composed of volatile and semi-volatile organic compounds. If the concentrations of organic compounds on Q_b were comparable or higher than those on Q_f, their Q_f values should be dominated by positive artifact. As the vapor pressure decreases, the evaporation loss from Q_f samples becomes non-negligible. Note that the magnitude of negative artifacts is unknown and very difficult to assess, and the vapor pressures of monosaccharides and sugar alcohols are far below 10^{-10} atm (Table S4), their concentrations in Q_b and even PUF samples might contain more contributions from negative artifacts than isoprene SOA tracers and levoglucosan. As low-volatile sugar polyols had lower and less stable recoveries (Table S2) and greater breakthrough (Figure S2e, f), caution is warranted in analyzing their $K^{m}_{p,OM}$ values obtained in this study.

3.5 Partitioning coefficients of gas versus aqueous phases

The predicted Henery's law coefficients in pure water ($K^{t}_{H,w}$, mol m^{-3} atm^{-1}) from EPI and SPARC estimates differed by several orders of magnitude, but literature values of isoprene SOA and levoglucosan were closer to EPI estimates (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 their average log $K^{t}_{H,w}$ (Table 2), 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 (Almeida et al., 1983; Kroll et al., 2005; Ip et al., 2009; Kampf et al., 2013; Shen et al., 2018). Thus, log $K^{t}_{H,w}$ values of EPI estimates were used for further data analysis.

In Table 2, the $K^{t}_{H,w}$ values of isoprene SOA tracers, levoglucosan, and meso-erythritols based on EPI estimations were 10^{2} to 10^{6} lower than their corresponding $K^{m}_{H,e}$. Log $K^{m}_{H,e}$ values of *Cases 2* and *3* had ignorable difference and were not presented separately. Other polyol compounds exhibited less difference between log $K^{m}_{H,e}$ and log $K^{t}_{H,w}$, which was very likely caused by the overestimation of their gas-phase concentrations. The average $K^{m}_{H,e}$ values of polyol tracers (10^{13}–10^{15} mol m^{-3} atm^{-1}) in this study were several orders of magnitude larger than those of carbonyls derived from ambient measurements (10^{10}–10^{12} mol m^{-3} atm^{-1}; Shen et al., 2018) and chamber simulations (~10^{11} mol m^{-3} atm^{-1}; Kroll et al., 2005; Volkamer et al., 2006; Galloway et al., 2009). This is because low molecular weight carbonyls (e.g., glyoxal) are much more volatile ($p^{o,*}_{L}$ > 10^{-2} atm) than our target polyols (Table S4).

According to existing studies, the minimum concentrations of gas-phase glyoxal and methylglyoxal in Chinese cities (~0.1 μg m^{-3}) are magnitudes higher than the averages of polyol tracers in this work, while their particle-phase concentrations are of the same magnitude (Shen et al., 2018; Liu et al., 2020).

A number of previous studies observed enhanced $K_{\mathrm{H,e}}$ of carbonyls with salt concentrations in aqueous solution (Ip et al., 2009; Kampf et al., 2013; Waxman et al., 2015; Shen et al., 2018), and described this "salting-in" effect using

$$\mathrm{Log}\left(\frac{K_{\mathrm{H,w}}}{K_{\mathrm{H,e}}}\right) = K_{\mathrm{s}} c_{\mathrm{salt}} \qquad (7)$$

where K_{s} (kg mol^{-1}) is the salting constant, and c_{salt} is the aqueous-phase concentration of salt in mol kg^{-1} ALWC. This equation is originally defined in Setschenow (1889) by plotting log ($K_{\mathrm{H,w}}/K_{\mathrm{H,e}}$) versus the total salt concentration (mol L^{-1}).

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 ($K^{\mathrm{t}}_{\mathrm{H,w}}/K^{\mathrm{m}}_{\mathrm{H,e}}$) values were regressed to the molality of sulfate ion in aerosol liquid water (c_{sulfate}, mol kg^{-1} ALWC). 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}. In Figure 4, negative correlations ($p < 0.01$) are observed at $c_{\mathrm{sulfate}} < 12$ mol kg^{-1} ALWC, and Figure S5 exhibits significant negative correlations ($p < 0.01$) between log ($K^{\mathrm{t}}_{\mathrm{H,w}}/K^{\mathrm{m}}_{\mathrm{H,e}}$) 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.

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 $K^{\mathrm{t}}_{\mathrm{H,e}}$ and $K^{\mathrm{m}}_{\mathrm{H,w}}$ cannot be closed by the “salting-in” effect alone. Shen et al. (2018) also obtained negative intercepts when plotting log ($K^{\mathrm{t}}_{\mathrm{H,w}}/K^{\mathrm{m}}_{\mathrm{H,e}}$) over c_{sulfate} for glyoxal and methylglyoxal in ambient atmosphere, and attributed this to unknown gas-particle partitioning mechanisms. There is e~~E~~vidence~~s~~ showing that conventional GC/EI-MS analysis overestimates ~~–~~particle-phase 2-methyltetrols by 60-188% due (in part) to the thermal degradation of less volatile oligomers and organosulfates (Cui et al., 2018)~~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.

4 Implications and conclusions

In this work, concentrations of gas- and particle-phase polyol tracers were measured simultaneously in northern Nanjing. The temporal variations of individual compounds were dominated by their particle-phase concentrations. Then gas-particle partitioning of polyol tracers should have little influence on source apportionment based on particle-phase data in Nanjing. An improved agreement between measurement-based and predicted $K_{p,OM}$ of polyol tracers was observed when the solubility in aerosol liquid water was considered, indicating that the aqueous solution in aerosols is also an important absorbing phase. The large gaps of $K^{m}_{H,e}$ versus $K^{t}_{H,w}$ could be partly parameterized using the equation defining “salting-in” effects. 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. So, the results of this study have important implications on the prediction of gas-particle partitioning of water-soluble organics, and further studies are required to explain their enhanced aqueous-phase uptake mechanistically. Due to the hygroscopic properties of highly oxidized organic aerosols, this study also partly reveals the discrepancy between modeled and observed SOA in previous studies. However, several assumptions (e.g., LLPS) were made for proposed gas-particle partitioning schemes in this work, more laboratory research is needed to understand the mixing state of inorganic salts, organic components, and aerosol liquid water in atmospheric particles.

Data availability

Data used in the writing of this paper is available at the Harvard Dataverse (https://doi.org/10.7910/DVN/U3IGQR, Qin et al., 2021)

Author contributions

MX designed the research. CQ and YG performed the sampling and chemical analysis. CQ, YM, and MX analyzed the data. CQ and MX wrote the paper with significant contributions from YW, HL, and QW.

Competing interests

The authors declare that they have no conflict of interest.

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Table 1. Comparisons of measurement-based log $K_{p,OM}$ ($m^3\ \mu g^{-1}$) 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] Logarithms with base 10, a~~A~~verage ± 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] Logarithms with base 10 (~~Log~~ log $K^{m}_{H,e}$ values of *Case 3* had ignorable difference, and were not exhibited separately); [b] temperature range: -4~36 °C.

Figure 1

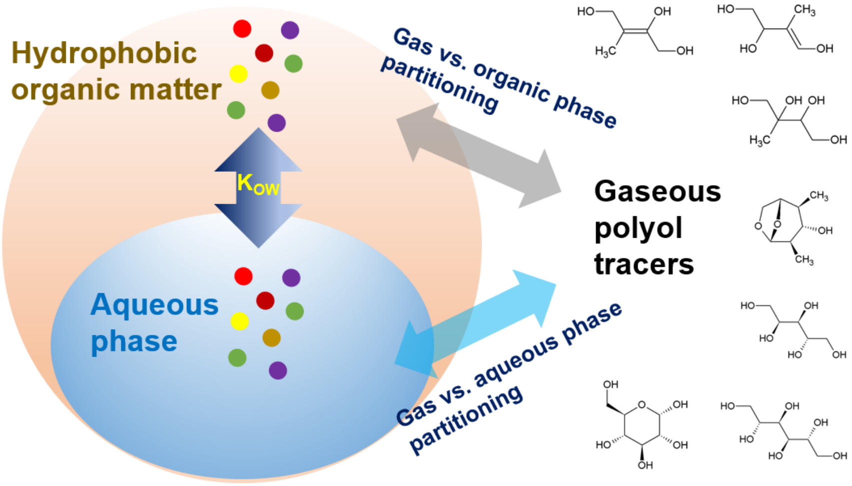

Figure 1. Proposed scheme for gas-particle partitioning of polyol tracers.

Figure 2

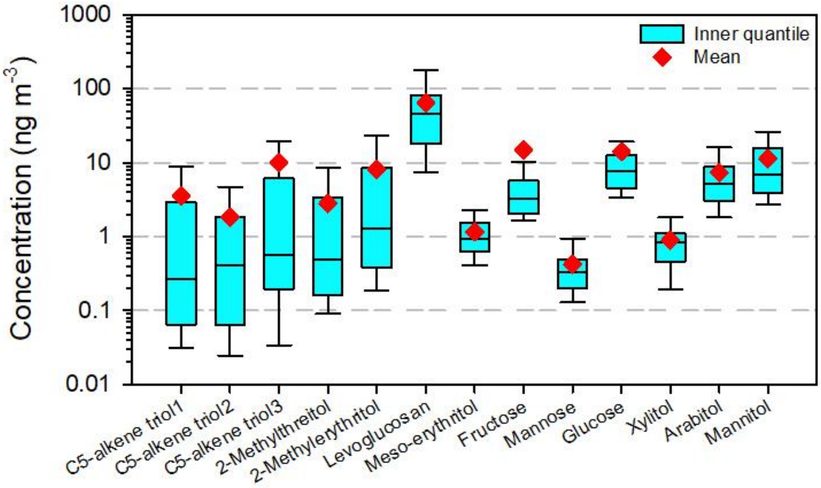

Figure 2. Total concentrations of individual polyols (Q_f + Q_b + PUF) in the ambient atmosphere of northern Nanjing. The boxes depict the median (dark line), inner quantile range (box), 10th and 90th percentiles (whiskers), and the mean (red diamond).

Figure 3

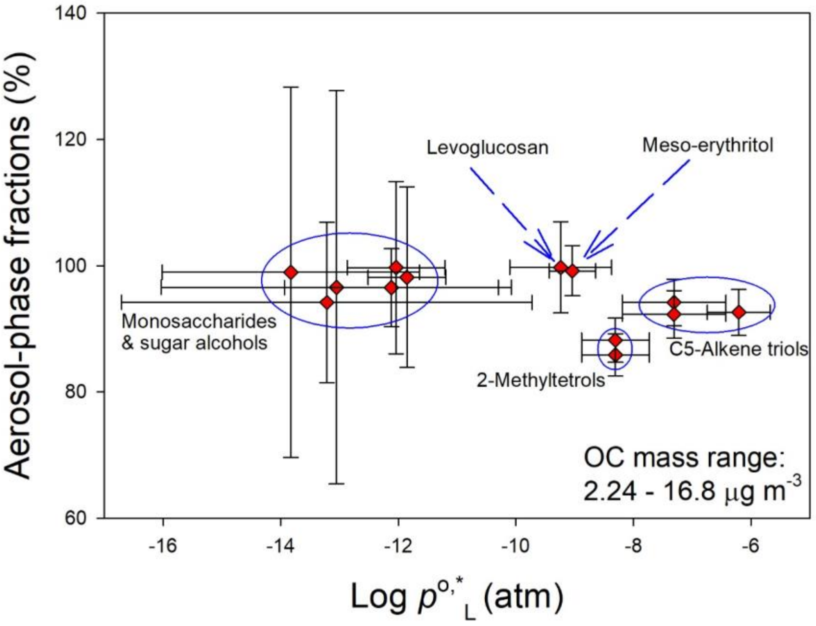

Figure 3. Average particle-phase fractions and log $p^{o,*}{}_{L}$ of individual polyol tracers. Whiskers represent uncertainties of *F*% and one standard deviation of log $p^{o,*}{}_{L}$ derived from different estimation tools.

Figure 4

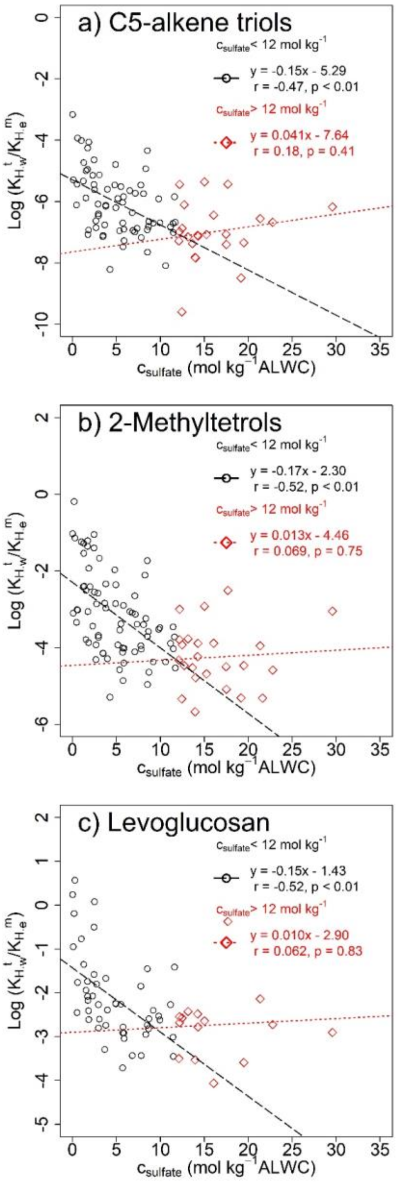

Figure 4. Modified Setschenow plots of log ($K^{t}_{H,w}/K^{m}_{H,e}$) versus $c_{sulfate}$ for (a) C5-alkene triols, (b) 2-methyltetrols, and (c) levoglucosan.