

We are grateful to the editor and referees for their careful reading and constructive suggestions that substantially help to raise the quality of our manuscript. Below we address each of the comments listed in blue font. Our answer is listed in black font and revised text is listed in green font. The number of lines in our answers is based on the revised manuscript, and the amendments were marked with a highlight in the revised version.

Referee #1:

This work describes measurements done in Beijing to understand phase transition during haze events using particle rebound and poke flow bulk viscosity measurements. The findings indicate that increased RH during haze events leads to particle phase transition from a semi-solid or solid to liquid phase state. This is shown to be due to increased inorganic fractions as well as uptake of more hygroscopic organics at elevated RH, both of which are promoted by uninhibited bulk diffusion in the liquid phase state. Overall, the level of detail and explanations of the results in this work are great and the limitations of interpretations of the results are clear. This work fits well within the scope of ACP and I would recommend it for publication once a few comments are addressed.

We appreciate the referee's review and very positive evaluation of our work. The comments were responded point-by-point in the following contents, and the manuscript was revised. We have made direct responses and substantial revisions which we believe properly address the referee's concerns.

General comments:

1. A limitation of using particle rebound fractions for ambient samples seems to be that a rebound fraction of 0.5 could indicate all your particles are semi-solid or 50% are solid and 50% are liquid and thus depends heavily on the mixing state of those ambient particles. Is there a way to validate that the particles sampled were internally mixed? Do the bulk viscosity measurements help to address this limitation?

We thank the referee for this comment.

We agree that using particle rebound measurement has such limitations on ambient samples since their mixing state may have impact on the number fractions of particle rebound. Therefore, to minimize this influence, we selected 300 nm mono-disperse particles by a Differential Mobility Analyzer for this measurement. As mentioned in Section 2.1 and 3.2, the measured f was representative of accumulation mode particles that dominated the mass concentration of submicron particles. In fact, validating the internally mixed state, even for mono-disperse particles, is challenging since the size-resolved chemical information is normally be inaccessible. However, the aerosols are supposed to be externally mixed during the clean period but turned to be internally

mixed during haze events as summarized by Peng et al (2021). Thus, the particle rebound measurement in this study fitted the aim furthest to show the phase state variation during the haze formation. The bulk viscosity measurement captured the phase information for water soluble components in PM_{2.5} filter samples, so that internally mixed chemical composition was established. However, this approach cannot validate the mixing state of the measured mono-disperse particles. It should be noted that we achieved good agreement between the online measurement of particle rebound and offline viscosity results obtained by poke and flow technique, demonstrating the feasibility of this approach. We have now established a new measurement approach based on particle rebound for ambient particles and conducted a field campaign, incorporating synchronous Hygroscopic Tandem Differential Mobility Analyzer (HTDMA) measurements to obtain hygroscopic mode information of specific mono-disperse particles. We aim to elucidate these influences in our subsequent studies.

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2. It is repeatedly suggested that multiphase chemistry is responsible for the increased oxidation of organics and the increased fraction of inorganics in particles at increased RH during haze events. However, could increased partitioning of these species due to higher aerosol-associated water not also explain these observations without any actual chemistry?

We thank the referee for this comment. Currently, delineating the contributions of different pathways to the secondary aerosol formation remains a significant challenge in high-resolution field measurements. Feng et al., (2023) utilized the isotopes measurement method to explore the formation pathways and contributions of nitrates. It was found that both gas-particle partitioning processes and heterogeneous reactions are enhanced during pollution episodes. In studies of secondary organic aerosols, the presence of abundant liquid water was suggested to facilitate the transfer of glyoxal from the gas phase to the particle phase, including both the partitioning process and the reactive uptake process, thereby increasing the mass concentration of organic aerosols or even the oxidation state (Volkamer et al., 2007; Hodas et al., 2014). In addition to liquid water, several other factors, such as temperature, oxidant levels, ionic strength, etc., also influence the formation pathways of these secondary products, adding considerable complexity to the research. Therefore, in our study, we have taken a cautious approach in interpreting the observed increase in ALW and its association with enhanced secondary aerosol formation rates via phase transition, and to focus on understanding the potential impact of phase state variations on secondary aerosol

formation. We agree that an increase in gas to particle partitioning of water-soluble compounds could also enhance the contribution of inorganics in particles or the oxidation state of organics. Therefore, we have discussed the potential influence on such pathway in the Section 3.3 and Section 3.4. We have noticed that this possibility was inadvertently omitted in the abstract, and it has now been rephrased in the revised manuscript:

Line 27-35:

“The presence of abundant ALW, favored by elevated RH and higher proportion of SIA, facilitates the partitioning of water-soluble compounds from gas to particle phase, as well as heterogeneous and aqueous processes in liquid particles. This leads to a substantial increase in the formation of secondary organic aerosols and elevated aerosol oxidation.”

Feng, X., Chen, Y., Chen, S., Peng, Y., Liu, Z., Jiang, M., Feng, Y., Wang, L., Li, L., and Chen, J.: Dominant Contribution of NO₃ Radical to NO₃⁻ Formation during Heavy Haze Episodes: Insights from High-Time Resolution of Dual Isotopes $\Delta^{17}\text{O}$ and $\delta^{18}\text{O}$, *Environmental Science & Technology*, 57, 20726-20735, 10.1021/acs.est.3c07590, 2023.

Volkamer, R., F. San Martini, L. T. Molina, D. Salcedo, J. L. Jimenez, and M. J. Molina (2007), A missing sink for gas-phase glyoxal in Mexico City: Formation of secondary organic aerosol, *Geophys. Res. Lett.*, 34, L19807, doi:10.1029/2007GL030752.

Angell, C. A.: Relaxation in Liquids, Polymers and Plastic Crystals - Strong Fragile Patterns and Problems, *J Non-Cryst Solids*, 131, 13-31, 1991.

Hodas, N., Sullivan, A. P., Skog, K., Keutsch, F. N., Collett, J. L., Decesari, S., Facchini, M. C., Carlton, A. G., Laaksonen, A., and Turpin, B. J.: Aerosol Liquid Water Driven by Anthropogenic Nitrate: Implications for Lifetimes of Water-Soluble Organic Gases and Potential for Secondary Organic Aerosol Formation, *Environmental Science & Technology*, 48, 11127-11136, 10.1021/es5025096, 2014.

3. This work shows more oxidized SOA in liquid particles with higher ALW. Can the authors comment on how this might affect the efficacy of commonly used parameterizations for OA viscosity, particularly those in Shiraiwa et al (2017) and DeRieux et al (2018) that would predict higher viscosities with higher levels of organic oxidation? Are these parameterizations still consistent with the results shown here if a composition dependent hygroscopicity parameter is used when calculating total aerosol viscosity?

We thank the insightful comments made by the referee.

Tg parameterizations are commonly used to predict the OA viscosity with considering the mixture of organics and organics-associated water. However, ambient aerosols

usually comprise high levels of inorganic and organic components. In our study, inorganics accounted for about 88% of the total ALW mass during the observation (with fixed k_{org}), implying that inorganics play a more significant role in driving the moisture-induced phase transition. It is a great point to consider the composition-dependent hygroscopicity parameter when calculating the viscosity of ambient organic aerosols through T_g parameterizations. We followed your suggestion and employed the overall particle hygroscopicity, including both inorganics- and organics- associated water, rather than focusing solely on organics for calculating the T_g of OA components under ambient conditions. The parameterization method proposed by Shiraiwa et al (2017) was employed. Unfortunately, we are unable to utilize the other two T_g parameterizations based on the volatility and elemental composition of organics, because of the lack of necessary input data. The common goal of viscosity studies is to accurately simulate and predict the evolution of viscosity in models. At the same time, concise and elegant parameterizations are also the pursuit of scientific researchers. We found that the characteristic of T_g/T versus ALW/NR-PM1 agrees well with our field observations with the incorporation of overall particle hygroscopicity into T_g calculation for ambient OA. This finding suggests that a composition-dependent hygroscopicity parameter may be considered in regions characterized by higher mass concentrations of inorganics, particularly under humid conditions.

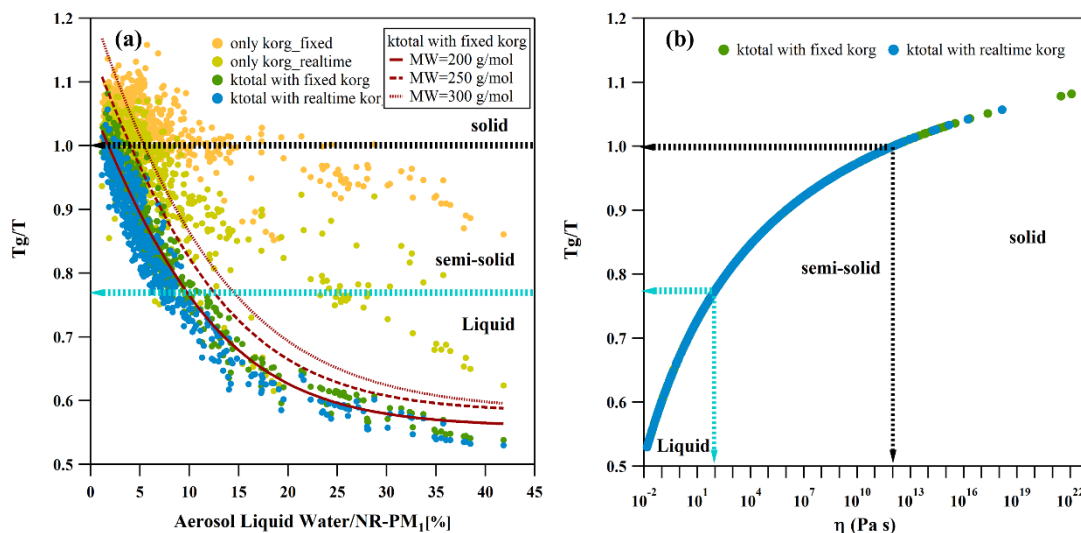
Combining the comments of the two referees, we chose to be cautious in comparing the calculation parts to our observation results, and to focus on the driving factors of the phase transition behaviors of these ambient particles observed in our study. This section was thoroughly rephrased in the revised manuscript and in the supplement:

Revised parts in Section 3.2:

“In addition to RH and aerosol compositions, environmental temperature also plays a significant role in determining the phase state (Koop et al., 2011; Shiraiwa et al., 2017; Petters et al., 2019). A reduction in temperature results in higher viscosity, whereas a rise in RH leads to a decrease in viscosity, attributed to the plasticizing effect of water (Koop et al., 2011). Although the relationship between f and temperature is not strongly evident as that of RH in this study (Figure S13), it's observed that a greater number of data points exhibited near 0.9 under low RH conditions (<30%), suggesting higher viscosity at colder temperatures (< -10 °C) than warmer scenarios. The glass transition temperature (T_g) is a key metric for the non-equilibrium phase transition from a glassy solid to a semi-solid state as temperature rises (Koop et al., 2011). Particles act as solid when the temperature falls below T_g ($T_g/T > 1$), and transition to semi-solid or liquid at temperature exceeding T_g . An increase in compound molecular weight, O: C ratio, and functional group composition are identified as key factors affecting the T_g of

OA (Saukko et al., 2012; Dette et al., 2014; Rothfuss and Petters, 2017; Shiraiwa et al., 2017). Shiraiwa et al (2017) proposed that T_g/T is an indicator for the semi-solid to liquid phase transition of OA, with a threshold of $T_g/T \approx 0.8$. In this study, we employed a T_g parameterization method for OA viscosity based on their molecular weight and O:C ratio to assess the combined effects of aerosol composition, RH and temperature on particle phase state (Shiraiwa et al., 2017). Considering the significant contribution of inorganics in total ALW mass of ambient aerosols, we adopted an overall particle hygroscopicity (k_{total}) approach. This method accounts for water associated with both inorganics and organics, rather than focusing solely on organics, to calculate T_g of ambient OA, as elaborated in Text S6.

Figure 3a displays the characteristic relations between T_g/T and ALW/NR-PM₁ with different approach for T_g calculations of ambient OA. Different phase state intervals are characterized by T_g/T based on predicted viscosity η as shown in Figure 3b, and are illustrated using dashed lines with arrows. The predicted viscosity η of OA was calculated by applying the Vogel–Tammann–Fulcher (VTF) equation (Angell, 1991) with a fragility parameter of 10 (DeRieux et al., 2018). Clearly, after calculating T_g in conjunction with k_{total} , there is a strong consistency in the characteristic relationship between the estimated T_g/T and ALW/NR-PM₁ with both fixed and variable k_{org} . This consistency aligns well with the phase state changes of atmospheric aerosols discussed earlier in this study. In contrast, even when accounting for variations in hygroscopicity due to different oxidation degrees of OA, the majority of these estimated T_g/T values fall within the semi-solid and solid range at higher ALW/NR-PM₁, significantly deviating from the field observations. This highlights the significant impact of environmental RH and chemical composition on the moisture-induced phase transition of atmospheric particles in the near-surface atmosphere. In particular, inorganic salts play a dominant role, contributing more significantly to the mass fraction of ALW in total particulate matter. The estimated T_g/T for ambient OA with k_{total} transitioned to a liquid state at ALW/NR-PM₁ > 10%, which is slightly lower than the transition threshold of 15% proposed in this study. It should be noted that the estimated T_g of OA adopted an average molecular weight (MW) of 200 g mol⁻¹, as used in previous studies (Williams et al., 2010; Shen et al., 2018). However, the average MW of ambient OA is likely variable due to the atmospheric aging process. Increasing the value of MW can shift the characteristic curve of T_g/T versus ALW/NR-PM₁ to the right, thereby aligning the semi-solid to liquid transition threshold more closely with the results observed in this study. This further suggests that incorporating of k_{total} into T_g calculation may potentially enhance the simulation results, especially in regions with a high proportion of inorganic salts under humid conditions. It should be noted that this aspect warrants further exploration in subsequent research.”



Added Figure 3. Characteristic relations between T_g/T and ALW/NR-PM₁ (a) and T_g/T as a function of predicted viscosity η (b) of organic aerosols under ambient conditions. In panel (a), the red curves, which employ sigmoid fitting, represent variations in average molecular weights of OA used for T_g calculation in consideration of the total hygroscopicity of the particles. The characteristics of the particle-phase state are delineated by arrows and dashed lines.

Added parts in Section 4:

“With the incorporation of k_{total} into T_g calculation for ambient OA, we found that the characteristic of T_g/T versus ALW/NR-PM₁ agrees well with our field observations. This finding offers insights into the effectiveness of ALW/NR-PM₁ as an indicator for quantifying the moisture-induced phase transition capacity of atmospheric particles. Furthermore, incorporating overall particle hygroscopicity into the T_g calculation may potentially enhance OA viscosity simulations, especially in regions with a high proportion of inorganic salts under humid conditions.”

Added TexS6 in the supplement:

“The glass transition temperatures of organic aerosols under dry conditions ($T_{g,org}$) are calculated by the parametrization based on their molecular weight (M) and O:C ratio as below (Shiraiwa et al., 2017):

$$T_g = A + BM + CM^2 + D(O:C) + EM(O:C), \quad (S1)$$

Where $A=-21.57$ K, $B=1.51$ K mol g⁻¹, $C=-1.7 \times 10^{-3}$ K mol² g⁻², $D=131.4$ K and $E=-0.25$ K mol g⁻¹, respectively. Here, we adopted an average molecular weight of 200 g mol⁻¹, as used in previous studies (Williams et al., 2010; Shen et al., 2018). O:C ratio was calculated by the parametrization of $O:C=0.079+4.31 \times f_{44}$ (Canagaratna et al., 2015).

The glass transition temperatures of organic-water mixtures (indicate the organic

aerosols under ambient conditions) can be simulated based on the Gordon-Taylor equation (Gordon and Taylor, 1952):

$$T_g(w_{org}) = \frac{(1 - w_{org})T_{g,w} + \frac{1}{k_{GT}}w_{org}T_{g,org}}{(1 - w_{org}) + \frac{1}{k_{GT}}w_{org}}, \quad (S2)$$

where w_{org} is the mass fraction of OA in the organic-water mixture, $T_{g,w}$ is the glass transition temperature of pure water (136 K), $T_{g,org}$ is the glass transition temperature of OA under dry conditions, and k_{GT} is the Gordon-Taylor constant which is assumed to be 2.5 (Koop et al., 2011). The mass concentration of water in the organic-water mixture is commonly treated as organics-associated water, assuming an externally mixed phase of ambient particles (Shiraiwa et al., 2017; DeRieux et al., 2018; Li et al., 2020). Considering the significant contribution of inorganics to the total ALW mass of ambient aerosols, and the optically undetected liquid-liquid phase separation under staged dehydration of filter-based Beijing PM_{2.5} droplets (Song et al., 2022), we assume in this study that OA particles are internally mixed with inorganic compounds such as sulfate and nitrate. Therefore, we adopted an overall particle hygroscopicity approach to calculate the total ALW mass in the organic-water mixture with the consideration of fixed k_{org} and variable k_{org} . The mass concentration of water of ambient aerosols are calculated, as detailed in Section 2.2.

Then, the viscosity η of ambient OA can be estimated by applying the Vogel–Tammann–Fulcher (VTF) equation (Angell, 1991):

$$\eta = \eta_{\infty} e^{\frac{T_0 D}{T - T_0}}, \quad (S3)$$

where η_{∞} is the viscosity at infinite temperature (10^{-5} Pa s; Angell, 1991), D is the fragility parameter, which is assumed to be 10 (DeRieux et al., 2018), and T_0 is the Vogel temperature calculated as $T_0 = \frac{39.17T_g}{D+39.17}$.

Specific comments:

1. A fixed k_{org} was used in this study and the supplement shows how a real-time k_{org} greatly impacts the organic-associated water content. Were any sensitivity studies done on the fixed k_{org} to see how the specific value of the fixed k_{org} affects the results?

We thank the referee for this comment.

Calculations of ALW have predominantly considered the contribution of inorganic salts in numerous studies. However, the calculations demonstrate that the organics-associated ALW cannot be ignored regardless of whether k_{org} remains fixed or varies with the degree of oxidation. In this study, we highlight the significant role of aerosol chemical composition and ambient RH in the evolution of particle-phase state during haze development. Acknowledging the plasticizing effect of water in particle-phase transition, we take the organics-associated ALW into account.

Our findings reveal that using only the content of ALW as a parameter does not adequately represent particle phase transitions. Instead, the proportion of liquid water in dry NR-PM₁ plays a more significant role. Therefore, although the contribution of organics to the overall ALW mass may be affected by variations in its hygroscopicity, its impact on ALW/NR-PM₁ is minor (see Figure S11).

Additionally, the relationship established in this study between ALW/NR-PM₁ and phase transitions from non-liquid to liquid has shown good performance. We also observe that the contribution of inorganic salts to the overall ALW is significantly higher than that of organic matter, indicating that inorganic salts remain the primary factor driving phase transition as RH increases during pollution events. Thus, we evaluate the frequency distribution of the three rebound fraction intervals in each ALW/NR-PM₁ bins for different ALW calculations by only inorganics, fixed k_{org} , and real-time k_{org} . As expected, the frequency distribution showed no obvious change among these three situations. The choice of a fixed k_{org} in this study does not affect our conclusions, and a lower value of 0.06 is acceptable.

We strongly concur with the opinions of the two reviewers and have incorporated a sensitivity analysis in the corresponding sections of the revised manuscript as well as in the supplement:

Manuscript (L169-172):

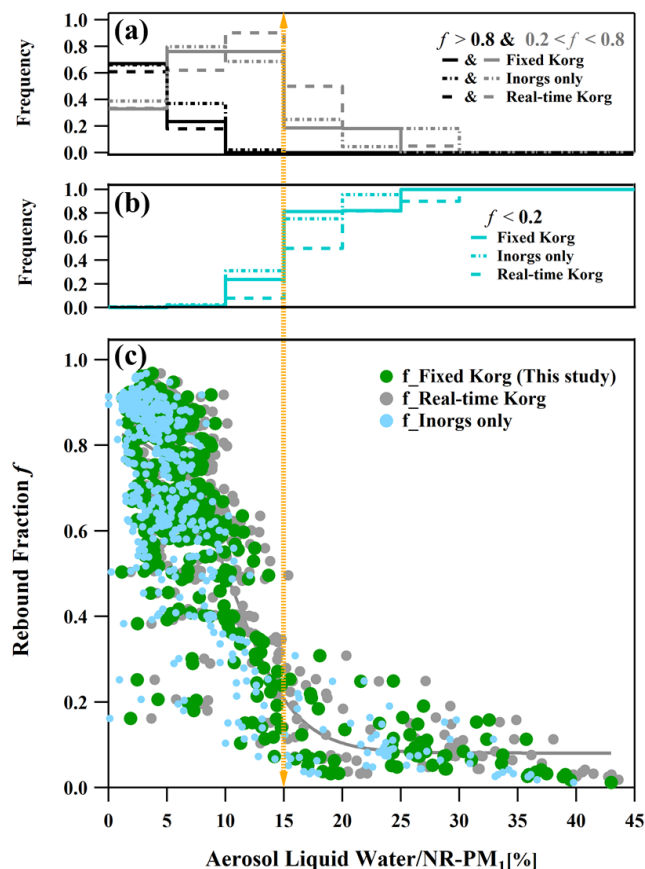
“In recognition of ALW's plasticizing effect on particle-phase state, the potential impacts of whether the hygroscopicity value of organics is fixed or varies in real-time on phase transition has been discussed in Section 3.2.”

Manuscript (L269-285):

“It should be noted that calculations of ALW in this study have considered inorganic salts and organics. Acknowledging that the hygroscopicity of organics, characterized by either a fixed k_{org} or varying in real-time, affects the calculation of ALW mass, a sensitivity analysis examining its impact on the phase transition threshold (ALW/NR-PM₁) is presented in Figure S11. There is no denying that the contribution of inorganic salts to ALW remains predominant, with their contribution to ALW being ~88% (a fixed k_{org} of 0.06) and ~73.5% (real-time k_{org}) on average during the observation (Figure S4), indicating that the impact of different ALW calculations on ALW/NR-PM₁ values was not significant. As expected, the frequency distribution of these three f intervals showed no obvious change for ALW calculations by inorganics, fixed k_{org} , and real-time k_{org} at the whole ALW/NR-PM₁ range. Although the frequency of $f < 0.2$ changed from ~0.8 to 0.5 at ALW/NR-PM₁ = 15-20% when shifting to real-time k_{org} , the frequency remained higher than 0.5 and approached 1.0 with larger ALW/NR-PM₁

values. This indicates that while the varying k_{org} impacts the number of data points within ALW/NR-PM₁ bins of 15-20%, it does not affect the overall transition trend. As a result, the impacts of different ALW calculation on ALW/NR-PM₁ were not significant, and the phase transition threshold of 15% remains valid.”

Supplement (Figure S11):



Added Figure S11. The frequency distribution of three f intervals ($f > 0.8$ and $0.2 < f < 0.8$ and $f < 0.2$) in each ALW/NR-PM₁ bins (a and b) and f as a function of ALW/NR-PM₁ using three different methods of ALW calculation (c).

2. Line 364: At this point it’s been awhile since k_{total} was introduced and it may be helpful to remind readers what it is here.

We followed the comment and modified the sentence:

“In Figure 5a, the relationship between the overall particle hygroscopicity (k_{total}) and RH is displayed.”

3. Fig 5c: Why does k_{inorg} level off at high RH, while k_{org} continues to increase?

We thank the referee for this comment.

Considering the variability in the composition of inorganics and organics, we used either real-time k_{org} characterized by the parametrization of $k_{org} = 1.04 \times f_{44} -$

0.02 and varied kinorg characterized by weighted volume fractions in inorganics as detailed in Section 2.2. The increasing trend of korg was attributed to the elevated oxidation degree of organics at higher RH conditions during the haze events. This was attributed to a clear increasing trend in f_{44} observed after phase transition and at higher ALW mass conditions. kinorg was determined by changing volume fraction of inorganic species ($k_{\text{NH}_4\text{NO}_3}=0.58$ and $k_{(\text{NH}_4)_2\text{SO}_4}=0.48$). With increasing RH, kinorg showed an upward trend due to increased nitrate contribution in total inorganics during the haze periods. However, nitrate contribution remained stable at $\text{RH}>60\%$ as well as higher particulate mass concentrations (see Figure. S5). This explains the leveling off of kinorg at higher RH values.

4. Fig S4 does not have a legend

We followed the comment and modified the figure as shown below:

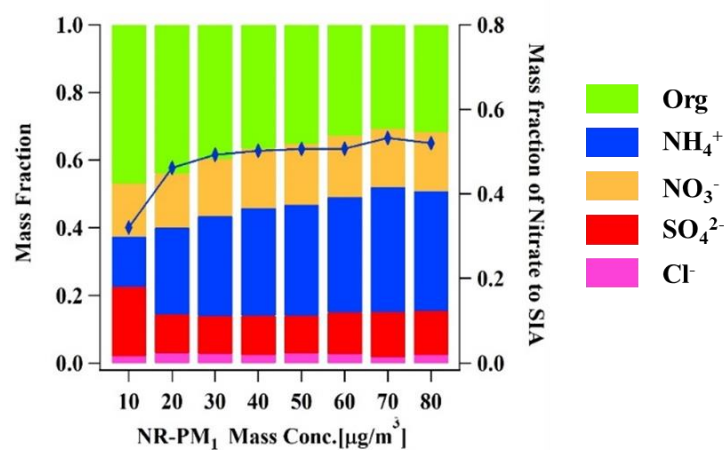


Figure S4. Modified Figure. S5

References:

DeRieux, W.-S. W., Li, Y., Lin, P., Laskin, J., Laskin, A., Bertram, A. K., Nizkorodov, S. A., and Shiraiwa, M.: Predicting the glass transition temperature and viscosity of secondary organic material using molecular composition, *Atmos. Chem. Phys.*, 18, 6331–6351, <https://doi.org/10.5194/acp-18-6331-2018>, 2018.

Shiraiwa, M., Li, Y., Tsimpidi, A. P., Karydis, V. A., Berkemeier, T., Pandis, S. N., Lelieveld, J., Koop, T., and Pöschl, U.: Global distribution of particle phase state in atmospheric secondary organic aerosols, *Nat. Commun.*, 8, 15002, <https://doi.org/10.1038/ncomms15002>, 2017.