Responses to the reviewers

We appreciate the reviewers for their careful reading and constructive comments! We've made every effort to respond to reviewers' questions point to point, and revised our manuscript and the Supplementary Information (SI) according to their comments. For clarity, reviewers' comments are shown in *black italic font*. The response is shown in black normal font. The revised text in the manuscript and/or the SI is shown in **bold blue font**.

Reviewer: 2

General comments:

This study investigates individual particles from an urban environment using single-particle X-ray microscopy/spectroscopy techniques (STXM/NEXAFS). The authors utilize an environmental cell to explore water uptake potential and report that a significant fraction of the particles are internally mixed with organic and inorganic components and less than half of total particles took up water at 86% relative humidity. Major fractions of these particles exhibit core-shell morphology under both dry and humidified conditions. This is an interesting study, and the use of an environmental cell for water uptake analysis provides critical data for understanding how particle composition influences hygroscopic behavior at the functional group level. I have a few suggestions and questions that may help improve the clarity and impact of the manuscript.

Specific Comments:

1. Why were the water uptake experiments performed only up to 86% relative humidity? Was this due to instrumental or operational limitations?

[Response]: Thanks for your questions! The relative humidity (RH) range of STXM environmental cell at SLS used in this study is up to more than 90% (Huthwelker et al., 2010). One of the reasons why we chose 86%RH as humid conditions is that the deliquescence relative humidity (DRH) of commonly presented inorganics is less than 86% (for example, 78-82% for ammonium sulfate, 73-77% for sodium chloride, and 60-66% for ammonium nitrate; Peng et al., 2022). The other reason is for comparing our results with the published work under similar experimental conditions (Pöhlker et al., 2014; Piens et al., 2016).

2. From the images, it appears that OC particles did not uptake water at 86% RH, whereas in some cases, the IN component of OCIN mixed particles exhibited morphological changes. Can the authors expand the discussion on this observation?

[Response]: Thanks for your valuable question! To quantitatively explain the reason why some individual particles took up water while some did not, we tried to take the kappa (κ)-Köhler theory into account to reproduce the observation results. The κ-Köhler equation is as follows (Petters and Kreidenweis, 2007),

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} \exp\left(\frac{4\sigma_{s/a}M_w}{RT\rho_w D}\right) \quad \text{Eq. R1}$$

where S is the saturation ratio over an aqueous solution droplet, D is the diameter of the droplet, D_d is the dry diameter, κ is a single hygroscopicity parameter, $\sigma_{s/a}$ is the surface tension of the solution/air interface, M_w is the molecular weight of water, R is the universal gas constant, T is the temperature, and ρ_w is the density of water.

For gaining the value of the single hygroscopicity parameter (κ), the simple mixing rule based on the Zdanovskii-Stokes-Robinson (ZSR) assumption is used as follows (Stokes and Robinson, 1966):

$$\kappa = \sum_i \varepsilon_i \kappa_i \quad \text{Eq. R2}$$

$$\varepsilon_i = \frac{V_{si}}{V_s} \quad \text{Eq. R3}$$

where i is a component in a multicomponent system (multiple solutes + water), ε_i is the dry volume fraction for each component, κ_i is the hygroscopicity parameter of each component, V_{si} is the volume of each component within a dry particle, and V_s is the total volume of a dry particle.

However, we acknowledge the inherent challenges in obtaining three-dimensional volume information for each component within individual particles using two-dimensional STXM techniques. This limitation results in a lack of detailed hygroscopicity parameter information for each of the individual particles.

Although we cannot get the κ value for each individual particle, we speculate that the reason why organic carbon (OC) particles didn't take up water under humid conditions while some internally mixed particles composed of organic carbon and inorganic matter (OCIn) did is that the hygroscopic capacity of different components varies. As we mentioned in the manuscript, the κ of ammonium nitrate, ammonium sulfate, ammonium hydrogen sulfate, POA, and SOA is 0.58, 0.48, 0.56, 0, and 0.1, respectively (Wu et al., 2016). Therefore, inorganic matter tend to contribute to water uptake and the morphological change of individual particles.

3. I suggest reorganizing Figures 2 and 3. Instead of displaying particles under dry and humid conditions in separate figures, consider presenting side-by-side comparisons of the same particles before and after humidification. This would help readers more clearly visualize the morphological changes due to water uptake.

[Response]: Thanks for your suggestion! Due to the framework of our manuscript, we chose to display individual particle maps separately under dry and humid conditions. We also take your suggestion into consideration. For comparison, we put together the particle chemical maps of the same region of interest under dry and humid conditions. Please see as follows.

[Revise]: Line 319-320 in the manuscript: “For comparison, the one-to-one particle chemical maps of the same region of interest under both dry and humid conditions can be found in Fig. S9.”

Line 140-144 in the SI:

“

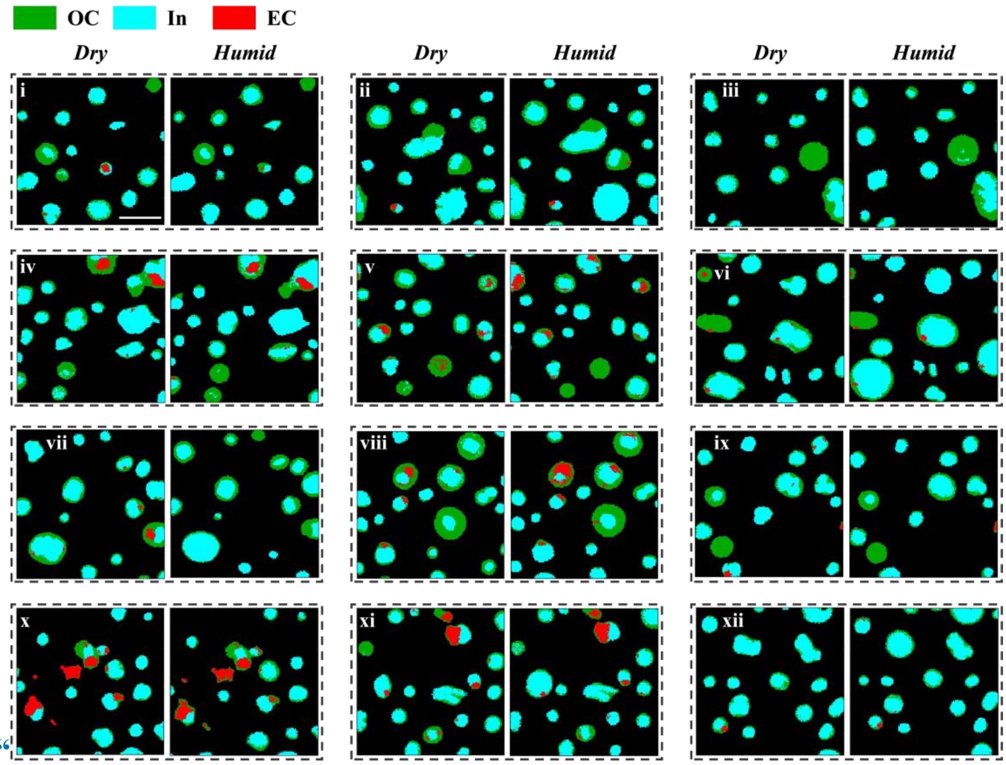

Fig. S9: Chemical maps of individual particles in 12 regions of interest under dry and humid conditions. Green, cyan, and red color represent dominant components of organic carbon (OC), inorganic matter (In), and elemental carbon (EC), respectively. The scale bar in the upper left image represents 2 μm and applies to all images.”

4. The study would benefit from an analysis of the mass growth of individual particles. Did the authors attempt to estimate the mass growth factor using oxygen maps data?

[Response]: Thanks for your valuable suggestion! We also thought about quantifying water uptake of individual particles. Based on the method described in Piens et al. (2016), for calculating the particle mass growth factor, we need to obtain the dry total mass of individual particles and the condensed water mass. The atomic fractions of elements within individual particles are necessary for estimating the dry total mass of particles. However, there is a lack of information regarding atomic fractions obtained using SEM/EDX in our study. Therefore, we failed to get the mass growth factor of particles. We will take it into account in our future research.

5. The conclusion section could be strengthened. For example, what are the implications of observing core-shell morphology under dry conditions? Similarly, how might the presence of such morphologies at 86% RH affect atmospheric processes?

[Response]: Thanks for your comment! We further organized and improved the Conclusions and Implications section. The content is as follows.

[Revise]: Line 428-438 in the manuscript: "This study directly displays the dominant chemical morphology (i.e., core-shell structure) and hygroscopic behavior of individual submicron urban aerosol particles at the microscale. The uptake coefficient onto aerosol particles with different phase states exhibit different patterns as the relative humidity changes (Wang and Lu, 2016). For aqueous particles, the uptake coefficient is closely related to RH (Wang and Lu, 2016). Specifically, when RH is lower than the DRH of the inorganic component, the uptake coefficient increased with the increasing RH. When RH is higher than DRH, the uptake coefficient remains constant. For solid particles, the relationship between the uptake coefficient and RH usually depends on particle species (Wang and Lu, 2016). Results highlight the importance of taking the core-shell structure into consideration for estimating the uptake coefficient and investigating heterogeneous reactions at different humidities, which can improve our comprehension of atmospheric processes of secondary aerosols in typical urban pollution atmospheres."

References

Huthwelker, T., Zelenay, V., Birrer, M., Krepelova, A., Raabe, J., Tzvetkov, G., Vernooij, M. G. C., and Ammann, M.: An in situ cell to study phase transitions in individual aerosol particles on a substrate using scanning transmission x-ray microspectroscopy, Rev. Sci. Instrum., 81, 113706, DOI: 10.1063/1.3494604, 2010.

Peng, C., Chen, L. X. D., and Tang, M. J.: A database for deliquescence and efflorescence relative humidities of compounds with atmospheric relevance, Fundam. Res., 2, 578–587, DOI: 10.1016/j.fmre.2021.11.021, 2022.

Petters, M. D. and Kreidenweis, S. M.: A single parameter representation of hygroscopic growth and cloud condensation nucleus activity, Atmos. Chem. Phys., 7, 1961–1971, DOI:10.5194/acp-7-1961-2007, 2007.

Piens, D. S., Kelly, S. T., Harder, T. H., Petters, M. D., O'Brien, R. E., Wang, B. B., Teske, K., Dowell, P., Laskin, A., and Gilles, M. K.: Measuring Mass-Based Hygroscopicity of Atmospheric Particles through in Situ Imaging, Environ. Sci. Technol., 50, 5172–5180, DOI: 10.1021/acs.est.6b00793, 2016.

Pöhlker, C., Saturno, J., Krüger, M. L., Förster, J. D., Weigand, M., Wiedemann, K. T., Bechtel, M., Artaxo, P., and Andreae, M. O.: Efflorescence upon humidification? X-ray microspectroscopic in situ observation of changes in aerosol microstructure and phase state upon hydration, Geophys. Res. Lett., 41, 3681–3689, DOI: 10.1002/2014gl059409, 2014.

Stokes, R. H. and Robinson, R. A.: Interactions in aqueous nonelectrolyte solutions. I. Solute-solvent equilibria, J. Phys. Chem., 70, 2126–2131, DOI: 10.1021/j100879a010, 1966.

Wu, Z. J., Zheng, J., Shang, D. J., Du, Z. F., Wu, Y. S., Zeng, L. M., Wiedensohler, A., and Hu, M: Particle hygroscopicity and its link to chemical composition in the urban atmosphere of Beijing, China, during summertime, Atmos. Chem. Phys., 16, 1123–1138, DOI: 10.5194/acp-16-1123-2016, 2016.