Response to comments by anonymous referee #1:

Wang et al investigated the effect of mixing structure on the water uptake of mixtures of ammonium sulfate and phthalic acid particles by taking homogeneously internal mixture and core-shell structure into account. The aerosol water uptake is an important factor to determine many atmospheric processes, such as multiphase reactions and visibility reduction. The hygroscopicity of inorganic and organic mixtures is not well understood. The authors emphasized the importance of the particle morphology and mixing structure for inorganic-organic mixture water uptake. I would like to recommendit to publish to ACP after some minor revisions.

Response: We are grateful to referee #1 for comments and suggestions to improve our manuscript. We have implemented changes based on these comments in the revised manuscript. We repeat the specific points raised by the reviewer in italic font, followed by our response. The page numbers and lines mentioned are referring to the Atmospheric Chemistry and Physics Discussions (ACPD) version.

Comments:

1. Regarding the core-shell structure, the particle morphology may change when the particles are exposed to a high relative humidity condition. This could attribute to both core and shell take up enough water and get mixed together. Thus, the core-shell structure could be ambiguous.

Response: Thanks. The reviewer is right, it is difficult to directly determine the morphology and the mixing state of aerosol particles at the high relative humidity (RH) when both core and shell components adsorb water. We tried to use several possible approaches for characterizing the morphology and mixing state of ammonium sulfate (AS) with phthalic acid (PA) in the RH range from 5 to 90 %: (1) utilize observational techniques such as optical microscopy and TEM; (2) assess the possibility of the presence of a non-well-mixed state utilizing a simplified model of the prevalence of liquid-liquid phase separation as a function of O:C ratio of the organic component and RH such as that described by You et al. (2013); (3) perform thermodynamic equilibrium calculations to model phase state as a function of water content (e.g., Song et al., 2012; Zuend and Seinfeld, 2013; Hodas et al., 2015). The detailed information has been described as follows:

(1) Although optical microscopy provides information on the morphology and the mixing state of particles, optical microscopy is applicable to micron-sized particles. Electron microscopy

technique (e.g., scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) can characterize the morphology and the mixing state of sub-micron particles (Tang et al., 2019). However, the limitation of this technique is the vacuum condition, which is difficult to apply to measure the particle morphology and the mixing state at high RH. When collected core-shell particles at the high RH are exposed to the vacuum condition, it may affect their original physical state and mixing state (Tang et al., 2019).

(2) You et al. (2013) suggested that the liquid-liquid phase separation in particles containing organics and inorganic salts may occur when the O:C ratio of organic components is within 0.5 < O:C < 0.8 based on their observations. In our study, the ratio of O:C in the phthalic acid components in the AS/PA mixtures is ~ 0.5, which is possible to occur LLPS during humidification processes.

(3) Zuend group (Zuend and Seinfeld, 2013) has carried out the Aerosol Inorganic-Organic Mixtures Functional groups Activity Coefficients (AIOMFAC) gas-particle equilibrium calculations for core-shell AS/PA system. In the case of core-shell 200 nm AS coated by 50 nm PA aerosol particles, AIOMFAC model predicts that PA is assumed to be phase separated from AS all the time. Figure R1 shows that the AIOMFAC predictions are not in good agreement with the core-shell particles with 46 wt % PA when AS is completely deliquesced at RH above 80 %. This suggests that the morphology of core-shell aerosol particles may change due to both of AS and PA uptake water at RH above 80 %. Therefore, the morphology/mixing state in the humidification process, especially at high RH is still to be investigated.
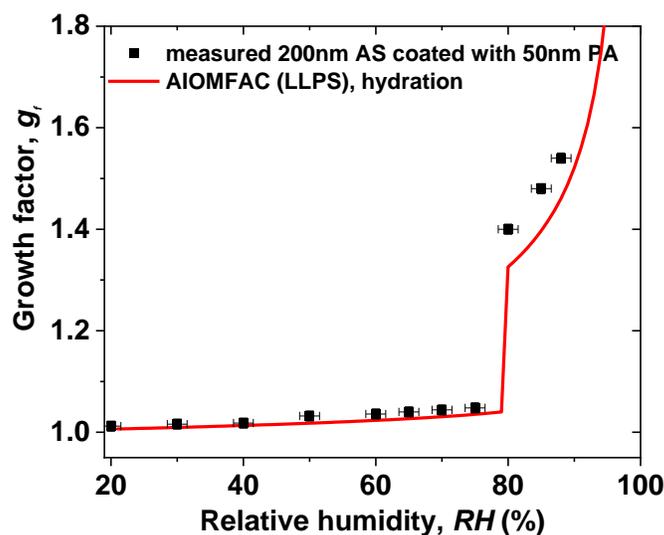
Figure R1. Hygroscopic growth factor for core-shell for 200nm ammonium sulfate (AS) core with coating 50nm phthalic acid (PA) (black square). In comparison, the AIOMFAC prediction for growth factor of core-shell AS/PA aerosol particles with considering liquid-liquid phase separation (LLPS) (red line).

2. The kinetic limitation has been referred for explaining the effect of core-shell structure on particle water uptake. In HTDMA system, the residence time of particles passing through the conditioned part may be short and lead to a kinetic limitation. This could not be the case when RH exceeds the DRH and particles are liquefied. We should also note that the particles with core-shell structure may have enough time to eliminate such kinetic limitation in the real atmosphere, different from the situation in the HTDMA system.

Response: Thanks for the comment. The reviewer is right, the equilibrium time may be inadequate for equilibrium particle growth/shrink such as those coated with organic layers, which results in kinetic limitation. The transportation of water molecules into the bulk of particles and droplets can be kinetically limited by surface processes (e.g., surface accommodation and surface-bulk transfer) or by diffusion in the particle bulk (Seinfeld and Pandis, 2006; Taraniuk et al., 2007; Pöschl et al., 2007). For example, in case of the highly viscous substances, water absorption is likely to be restricted by bulk diffusion, leading to kinetically limited and gradual deliquescence transitions (Chan and Chan, 2005; Mikhailov et al., 2009). Also, organic coating can act as a physical barrier to prevent the water condensation/evaporation rate on droplet surfaces (Gill et al., 1983; Barnes, 1986) and can lower the accommodation coefficient (Pandis et al., 1995). Chuang (2003) suggested that these atmospheric particles exhibit longer equilibrium times for particles with a coating of an organic film with an approximate accommodation coefficient in the range of 1×10^{-5} to 4×10^{-5}. Therefore, next, potential kinetic limitations in the HTDMA-measured hygroscopicity of core-shell aerosol particles is to be investigated in both humidification and dehumidification conditions.

The atmospheric aerosol particles are more likely internally mixed with organic fractions (e.g., well-mixed, core-shell mixing state), which are in equilibrium with surrounding conditions (e.g., temperature, RH, and reactive species (Bones et al., 2012; lei et al., 2014). Due to the complex physical chemistry of aerosol particles, e.g., amorphous aerosol particles refer to the rubber, gel, glassy, and viscous liquid, it is difficult and impossible to equilibrate water vapor in a short time (Chan and Chan, 2005: Mikhailov et al., 2009; Bones et al., 2012). For example, Bones et al. (2012) observed secondary organic compounds in the glassy state have mass transfer limitation in

equilibrium with surrounding water vapor. They further found that the timescale can be »10^3 for water equilibration with particles containing sucrose/sodium chloride/aqueous droplets as a proxy for multicomponent ambient aerosol. Also, due to complex atmospheric condition (i.e., wind, reaction, RH, T affect particle mixing state), their mixing state may change as aerosol particles are exposed to the real atmosphere (Riemer et al., 2019). Therefore, we need to comprehensively understand the kinetic limitations that may control water partitioning in ambient particles, especially for the amorphous aerosol particles.

3. In addition, if the phthalic acid is surface active? The reduction in surface tension may be closely related to the hygroscopicity of core-shell particles.

Response: Thanks for the comment. The phthalic acid is not surface active according to the previous reference (Padró et al., 2007). For the aerosol particles containing organic with surface active system, the hygroscopicity of aerosol particles may be enhanced by surface-active components. Ruehl et al. (2012) studied on droplet surface tension of mixed organic-inorganic particles at high RH (99.3–99.9 %). They found that there is 50-75 % reduction for the surface tension of droplets containing NaCl and a-pinene ozonolysis products, but only when enough organic material was present to coat on the droplet surface at least 0.8 nm thickness. They suggest that if surface-active particles account up more than 80 % in the atmosphere, their effect on cloud properties and thus climate could be enhanced (Padró et al., 2007):

4. There are numerous English grammar errors, especially in the summary and conclusion section (Line 354-360).

Response: Thanks for the comment. We have carefully revised the whole manuscript regarding language issues, including grammar, wording, and sentence structure, following the reviewer's suggestions, we have rewritten Sect. 4 (Summary and conclusion) they now reads as:

Page 16 line 345-Page 18 line 381: "In this study, we focused on PA to represent common organic compounds produced by various sources (e.g., vehicles, biomass burning, photo-oxidation). It is found that PA aerosol particles uptake water continuously as RH increases. We further investigated the effect of PA coating on the hygroscopicity of core-shell-generated aerosol particles. As PA coating thickness increases, the hygroscopic growth factor of AS/PA core-shell-generated particles increases prior to the deliquescence of AS, but the water uptake decreases at RH above 80 %. Furthermore, we compared the hygroscopic behavior of AS/PA core-shell-generated particles with

that of AS/PA initially well-mixed particles. Due to mixing state effects, higher hygroscopic growth factors of AS/PA core-shell-generated particles, compared to that of initially well-mixed particles, were observed in this study at RH above 80 %. In addition, the ZSR relation prediction is in good agreement with measured results of AS/PA initially well-mixed particles, but leads to the underestimation of the hygroscopic growth factor of AS/PA core-shell-generated particles at RH above 80 %. We attribute these discrepancies to the morphology effect when AS deliquesces in the core-shell-generated particles.

There are a vast number of internally mixed organic-inorganic aerosol particles existing in the atmosphere. The hygroscopicity behavior of mixture particles exhibits variability during RH cycles depending on the chemical composition, size, and mixing state. Humidity cycles may lead to liquid-liquid phase separation, e.g., in the form of core-shell aerosol particles, including at higher RH or in the salt-supersaturated concentration range. Also, due to the different physicochemical properties of organic compounds (e.g., viscosity, solubility, physical state, and morphology), the equilibrium time varies for these organic coated with inorganic aerosol particles. Therefore, potential kinetic limitations in the HTDMA-measured hygroscopicity of core-shell aerosol particles is to be investigated in both humidification and dehumidification conditions."

Related changes included in the revised manuscript:
In this study, we have systematically investigated the hygroscopicity of AS/PA aerosol particles with different mass fractions of PA in the different mixing states in terms of initial particle generation. Therefore, we revised "well mixed" as "initially well-mixed" in the response to referee files and the whole paper, including figures. Also, we added the explanation for the term "initially well-mixed aerosol particles". To further avoid the misleading terminality "core-shell", we revised "core-shell" as "core-shell-generated" in response to referee files and the whole paper, including figures.

Page 3 line 58-61: "Most of the previous studies on the hygroscopic behavior of multi-components aerosol focus on the well-mixed particles generated from initially well-mixed solutions (Miñambres et al., 2010; Shi et al., 2014; Gupta et al., 2015; Jing et al., 2016; Lei et al., 2014; 2018).

Page 7 line 141: "2.1.1 Initially well-mixed AS/PA Aerosol particles"

Page 7 line 154: "2.1.2 Core-shell-generated AS/PA aerosol particles"

Page 9 line 188: "3.1 Hygroscopic growth of initially well-mixed aerosol particles"

Page 13 line 281-282: "3.3 Comparison of core-shell-generated and initially well-mixed AS/PA aerosol particles"

Page 14 line 291-293: "At 75 % RH, the measured growth factor value of core-shell-generated particles is lower than that of initially well-mixed mixtures in the PA mass fraction range from 68 to 46 wt % due to the mass transfer limitations of water vapor transport to the AS core in the core-shell particles."

Page 2 line 29-30: "For the AS/PA initially well-mixed particles, a shift of deliquescence relative humidity (DRH) of AS (~80 %, Tang and Munkelwitz (1994)) to lower relative humidity (RH) is observed due to the presence of PA in the initially well-mixed particles."

Page 3 line 61-64: "For example, Choi and Chan (2002) studied on the effects of glycerol, succinic acid, malonic acid, citric acid, and glutaric acid on the hygroscopic properties of sodium chloride and AS in the initially well-mixed aerosol particles, respectively, using an electrodynamic balance."

Page 14 line 288-290: "However, compared to Fig 5a-b, Fig. 5c shows the hygroscopic growth factors of initially well-mixed AS/PA is slightly higher than that of AS/PA core-shell-generated particles with 46 wt % PA."

Page 14 line 293-294: "For the initially well-mixed AS/PA particles, however, partial dissolution of AS into the liquid AP phase may lead to more water uptake by initially well-mixed particles."

Page 31 line 660-662: "In comparison, the E-AIM model, the fitted expression Eq. (1), and the ZSR relation predicted growth factors of ammonium sulfate (AS), PA, and initially well-mixed particles with different mass fractions of PA, respectively."

Page 34 line 694-697: "In comparison, the E-AIM model, the fitted expression Eq. (1), and the ZSR relation predicted growth factors of ammonium sulfate (AS), PA, and initially well-mixed particles with different mass fractions of PA, respectively."

Page 3 line 54-58: We revised as "The initially well-mixed aerosol particles may be divided into homogeneous and heterogeneous internally mixed aerosol particles (Lang-Yona et al., 2009), which could, in turn, strongly influence the water uptake, optical properties, and the cloud condensation nuclei (CCN) ability of the particles (Lesins et al., 2002; Falkovich et al., 2004; Zhang et al., 2005; Schwarz et al., 2006; Su et al., 2010)."

Page 4 line 69-72: We revised as "However, to date, few laboratory studies have been investigated on the influence of organic coatings on the hygroscopic behavior of core-shell particles and the difference of mixing state effects on the hygroscopicity of aerosol particles (Zhang et al., 2008; Pagels et al., 2009; Xue et al., 2009; Lang-Yona et al., 2010; Ditas et al., 2018)."

Page 4 line 76-77: We revised as "They suggest that different organic coatings lead to changes in the hygroscopic properties of core-shell-generated particles."

Page 5 line 92-94: We revised as "The organic PA can have a profound effect on light scattering, hygroscopicity, and phase transition properties of multicomponent atmospheric aerosols."

Page 8 line 161: We added "The temperature required for vaporizing PA is between ~100 and ~130°C, which corresponds to coating thickness between 10 and 50 nm."

Page 8 line 166-167: We revised as "After core-shell-generated particle-sizing, aerosols were pre-humidified in a Nafion tube and flowed into the second Nafion humidifier at the set RH2 to reach equilibrium for growth of aerosol particles."

Page 8 line 167-168: We revised as "Finally, the humidified core-shell-generated particles were detected by a DMA3 and a CPC at ambient temperature."

Page 10 line 209-212: We revised as "For example, in the case of 1:3 mixtures of AS:PA (by mass), 75 wt % PA in the initially well-mixed particles suppresses the deliquescence of AS, i.e., AS in the initially well-mixed particles slowly dissolves into the liquid phase due to continuous water uptake of PA prior to DRH of AS (80 % RH)."

Page 8 line 156-158: We revised as "After a passage through a silica gel diffusion dryer and a neutralizer, the AS core aerosol particles with a certain diameter (100, 150, and 200 nm, respectively) were firstly selected by a DMA1 and then exposed to organic vapors in a coating system."

Page 9 line 193-195: We revised as "However, an abrupt increase in the hygroscopic growth factor is observed at 75 % RH for initially well-mixed particles containing 50 and 75 wt % PA, of which the growth factor is higher than that of pure PA aerosol particles (1.09 ± 0.01 nm from measurements shown in Fig. 2) at the same RH."

Page 10 line 201-204: We revised as "For example, the measured growth factors for initially well-mixed containing 25, 50, and 75 wt % PA are 1.36, 1.28, and 1.19 at 80 % RH, respectively, lower than the growth factor of 1.45 for pure deliquesced AS particles (value from measurements shown in Fig. 2) at the same RH."

Page 11 line 230-231: We revised as "Here, we investigated the hygroscopic behavior of samples of various AS core particle sizes (AS particle dry diameter of 100, 150, and 200 nm) and coating (PA coating of 10, 20, 30, and 50 nm), respectively."

Page 11 line 237-239: We revised as "For example, the measured growth factor value at 80 % RH is 1.45, 1.40, 1.32, and 1.28 for core-shell-generated particles containing 100 nm AS and 10, 20, 30, and 50 nm coating PA shell, respectively."

Page 12 line 265-Page 13 line 268: We revised as "In the case of 50-nm PA shell coated with a certain size of the AS core (100, 150, and 200 nm) with respect to 68, 55, and 46 wt % PA in the core-shell-generated particles, it exhibits an increase in hygroscopic growth factor of core-shell-generated particles at RH below 80 % as the size of AS core decreases."

Page 12 line 246-247: We revised as "The underprediction of the ZSR relation was also observed in the literature (Chan et al., 2006; Sjogren et al., 2007)."

Page 12 line 246-247: We revised as "Sjogren et al. (2006) observed an enhanced water uptake of mixtures consisting of AS and adipic acid with different mass ratios (1:2, 1:3, and 1:4) at RH above 80 % compared with ZSR relation in the hydration condition."

Page 13 line 276-278: We revised as "For ZSR prediction, it is assumed that volume fraction of AS components is constant according to the ratio of the volume of AS core in the sphere to the volume of a core-shell sphere based on Eq. (3)."

Page 14 line 288-290: We revised as "However, compared to Fig 5a-b, Fig. 5c shows the hygroscopic growth factors of initially well-mixed AS/PA are slightly higher than that of AS/PA core-shell-generated particles with 46 wt % PA."

Page 14 line 293-294: We revised as "For the initially well mixed AS/PA particles, however, partial dissolution of AS into the liquid PA phase may lead to more water uptake by initially well-mixed particles."

Page 14 line 293-294: We revised "Core-shell-generated particle morphology may experience the restructuring and associate size change of particles." as

"Accordingly, at high RH, the occurrence of microscopic restructuring of core-shell-generated particles may affect their size."

Page 14 line 301-304: We revised as "Chan et al. (2006) investigated hygroscopicity of 49 wt % glutaric acid coated on AS core during two continuous hydration cycles. They observed that the experimental growth factor of the fresh core-shell of AS and glutaric acid in the first hydration cycle is slightly higher than those in the second hydration cycle with the same mass fractions of glutaric acid."

Page 14 line 309-Page 15 line 310: We revised as "However, a contrasting phenomenon was observed in the previous study (Maskey et al., 2014)."

Page 14 line 332-334: We revised as "they found that the slightly higher growth factors of initially well-mixed particles are than that of core-shell-generated aerosol particles (12-nm levoglucosan coated 88-nm AS)."

Page 16 line 338-342: We revised as "In addition, for the AS/PA mixture aerosol particles containing 46-68 wt % PA, the measured growth factors of initially well-mixed AS/PA particles are in good agreement with the ZSR relation prediction comparing with that of core-shell-generated AS/PA particles."

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