Reply to RC1

The manuscript "Significant contribution of organics to aerosol liquid water content in winter in Beijing, China" present a filed study in 2017 in Beijing China, focusing the aerosol liquid water content (ALWC). ALWC was derived from using the growth factor (GF) measured at 90% RH at three particle sizes in nucleation mode, Aiken and accumulation mode. ALWC was also calculated using ISORROPIA II model with the chemical composition characterized by AMS as input. It was found that generally $ALWC_{HTDMA}$ correlates with $ALWC_{ISORROPIA}$ at high RH, but not at RH<60%. Including $ALWC_{org}$, the ALWC contributed by organics, i.e., $ALWC_{ISORROPIA}$ + $ALWC_{org}$ improved the correlation with ALWC (HTDMA), especially at lower RH. The contribution of organic to total ALWC was 30+/-22%. ALWC correlated with mass concentration of sulfate, nitrate and SOA. Accumulation mode was found to contribute the largest portion to ALWC. In case study, ALWC contributed by organics may play an important role in the initial stage of haze event. The manuscript addresses ALWC, which an important parameter in atmospheric chemistry. The manuscript fits the scope of ACP. I have several comments which need to be addressed before the manuscript is considered to be published in ACP.

General comments

1. The manuscript emphasized the role of organics in total ALWC. The value fraction 30+/-22% has a large uncertainty, suggesting a large variation of the contribution and likely a much smaller contribution of organics total in some cases. Also, the conclusion is in contrast with Z. Wu et al., 2018, showing dominant role of inorganics in ALWC, as the authors also cited. The variations and the difference from the literature needs to be discussed in the manuscript.

Re: Good suggestion. This is likely related with the variation in mass fraction and hygroscopicity parameter of organics (κ_{Org}). To demonstrate this, we calculated the variation of the fraction of ALWCOrg in total ALWC (ALWCHTDMA) with the ambient relative humidity (RH) and presented in Fig. R1. It is seen that the contribution of organics to total ALWC varies strongly. The mass concentration of inorganics increases more than that of organics as RH increases, leading to a lower mass fraction of organics in the case of high ambient RH. Figure R1 also shows the $ALWC_{Org}$ fraction increases signficantly with the increase of κ_{org}. All these help explain a large variation in the $ALWC_{Org}$ contribution to total ALWC. Considering the distinct differences in ambient RH and κ_{org} between clean and polluted periods, we calculated respectively the fraction of $ALWC_{Org}$ during the two periods. There is a higher $ALWC_{Org}$ fraction (33% ± 23%) during clean periods than that during polluted periods (26% ± 11%). Yet, there is little variability of $ALWC_{Org}$ fraction during polluted periods. The larger variability in $ALWC_{Org}$ fraction during clean periods is likely caused by the highly variable κ_{Org} when the ambient RH is low. In summary, the mass fraction of organics and κ_{Org} are important contributors to total ALWC, which was not investigated in Z. Wu et al. (2018). Our results also suggest inorganics (nitrate and sulfate) play key roles in determining ALWC, which is similar to Z. Wu et al. (2018).

We have added the Figure R1 in the manuscript (Figure 4) and the discussion above in line 311-323.

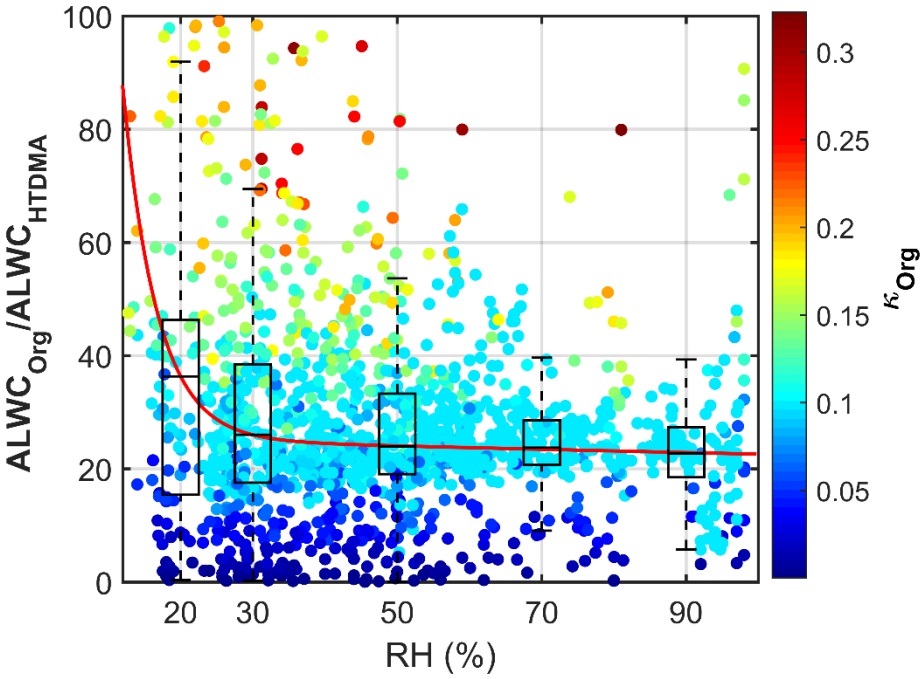

Figure R1. The variation of the fraction of $ALWC_{Org}$ in total ALWC ($ALWC_{HTDMA}$) with the ambient relative humidity (RH). The color of the dots denotes the hygroscopicity parameter of organics (κ_{Org}). The boxes show the fraction of $ALWC_{Org}$ with the 25th, 50th, and 75th percentiles. The extremities show the 5th and 95th percentiles. The red line shows the fitting curve with the function: $y = ae^{bx}$.

2. Some important details are lacking (see specific comments).

Specific comments

1. Line 77 "…its factors..." is confusing. Please specify.

Re: Good suggestion. The corresponding sentence was revised as "Overall, investigating the formation of SA and haze in North China requires an examination of ALWC and its factors including aerosol particle number size distribution (PNSD), aerosol chemical composition and ambient related humidity (RH) in this region" in line 77-78.

2. Line 156-159, at which three sizes the GF were measured?

Re: During this campaign, the H-TDMA was used to measure the GF at five particle sizes (40, 80, 110, 150, 200nm), which has been described in section 2.2. Then we follow the method of Chen et al. (2012) to calculate size-resolved GFs under different RHs, which is presented in section 3.1.

3. Line 162, the assumption of constant k in each mode may result in uncertainty in ALWC. It may be worthy discussing these lines 237-253.

Re: We assumed a constant κ in each mode based on the assumption that aerosols in a specific mode have common sources and experience similar aging processes, so κ in one mode should be the same due to the same chemical compositions (Chen et al., 2012). This may lead to a small uncertainty in size-resolved GFs at different RHs, resulting in a deviation in ALWC calculation. The following is added: "the assumption of constant κ in each mode may lead to a small uncertainty in size-resolved GFs at different RHs, resulting in small deviations in ALWC calculation. This may be another reason for the difference between $ALWC_{HTDMA}$ and $ALWC_{ISO}$." in the line 243-245.

4. Lines 237-253, for the chemical composition measured by AMS, do the authors use bulk composition or size resolved composition? This can also contribute to the ALWC derived by ISORROPIA.

Re: The bulk chemical composition measured by HR-AMS was used to simulate ALWC from ISOPPOPIA II model. Therefore, the simulated ALWC from ISOPPOPIA II denotes the total ALWC, which can't consider the contribution of organics on ALWC. The size resolved aerosol chemical composition data are hard to use in this model. We have added the sentence as "The bulk chemical composition was used in model." in line 188.

5. Lines 204-227, in deriving ALWCorg, among inorganics, only sulfuric acid, ammonium sulfate, ammonium hydrogen sulfate, and ammonium nitrate were considered. Actually, chloride is also present, as this study found. The can result in uncertainty in ALWCorg.

Re: The chloride detected by AMS may be from organics, and it is hard to be verified. So most previous papers didn't consider chloride when studying aerosol hygroscopicity (e.g., Gysel et al., 2007; Sjogren et al., 2008; Guo et al., 2015; Cerully et al., 2015). In addition, the mass concentration of chloride is always low in PM_1. Figure R2 show the time series of chloride mass concentration during the sample period. It shows the average mass fraction of chloride is only 6% ± 3%. We added the sentence as in line 223-224 as "The chloride was not taken into account in ion-pairing because its source is hard to determine. This may result in a minor uncertainty in κ calculation."

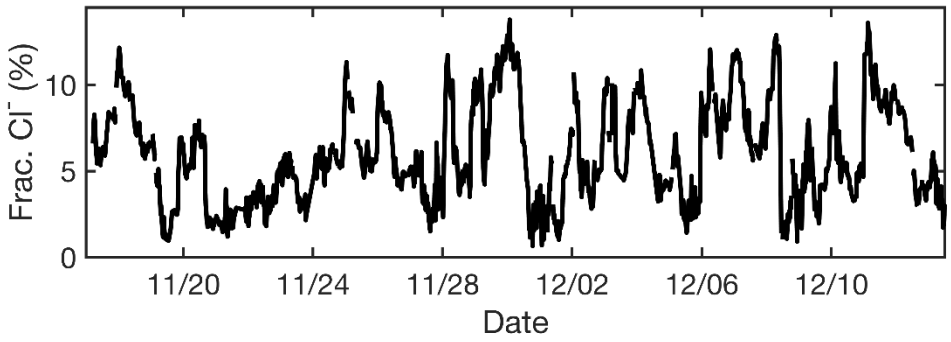

Figure R2. Time series of the mass fraction of chloride.

6. Line 281, how is b derived?

Re: b is derived by curve fitting through the data of $ALWC_{HTDMA}$ and RH using the fitting function $y = ae^{bx}$. This is clarified as "b is derived according to the relationship between $ALWC_{HTDMA}$ and RH that is fitted by the function $y = ae^{bx}$." in line 287-288.

7. Line 283, how are POA and SOA derived? Did the authors use PMF?

Re: The POA and SOA are derived using PMF. The sentence was added as "The positive matrix factorization (Paatero and Tapper, 1994) was applied on the organic aerosols (OA) spectral matrices to identify POA and SOA." in line 290-291.

8. Section 4.2.2, Fig. 4 does not provide new information to the discussion. The accumulation mode contributed dominant hygroscopic materials and ALWC to total ALWC. Naturally, the correlations are better.

Re: The analysis of the relationship between ALWC and the different modes under five different RH condition is for further evaluation of the impact of PNSD on the ALWC. Figure 4 shows the average contribution of different mode particles to $ALWC_{HTDMA}$ (f_{ALWC}) and the slope of the best linear regression. Figure 4 also shows that ALWC increases slightly as the volume concentration of accumulation mode particles increases under RH < 70 % conditions (slope < 0.001), but increases are stronger under higher RH conditions, especially under RH > 90 % conditions (slope = 0.0041). This suggests that there are more accumulation mode SA formed due to multiphase chemical reactions under high ambient RH conditions. Besides, Figure 4 also shows that the correlation between the Aitken mode particles and ALWC is enhanced significantly under RH > 90 % conditions, which

suggests that the Aitken mode can also absorb a significant amount of water when RH is higher than 90%. So, we think Fig. 4 is necessary to discuss the completeness of ALWC.

9. Line 323-325, such a statement is not necessarily true because many "processed" mineral particles are highly hygroscopic, such as Ca(NO3)2, or MgSO4, as shown by many field and laboratory studies.
Re: Agree, this statement is not accurate. Some mineral particles are hygroscopic and can impact ALWC. However, these particles are mainly in the coarse mode (Hussein et al., 2004; S. Liu et al., 2008). Bian et al. (2014) and Tan et al. (2017) found the ALWC contributed by coarse mode particles exists but not substantial. Because there were no APS data in this campaign, the coarse-mode particles with diameters greater than 1 μm are not considered in this study. The statement is revised as "Particles with diameters greater than 1 μm are not considered because some particles in the coarse mode are water soluble but their contribution on the ALWC is low (e.g., Hussein et al., 2004; S. Liu et al., 2008; Bian et al., 2014; Tan et al., 2017)." In line 342-345.

10. Line 321, why upper limit of Aitken mode is set at 110 nm?
Re: In general, aerosol particles are separated into four modes in the diameter lower than 1 μm according to their different origins (Whitby, 1978). And there are some different standards to separate them. Birmili et al. (2001) defined the particle modes based on a long-term observation data (Figure R3): "fresh" nucleation mode: 3-9 nm; "aged" nucleation mode: 9-30 nm; Aitken mode: 30-110 nm; accumulation mode (110-1000 nm). Bian et al. (2014) also set the diameter of Aitken mode between 30nm and 110nm when parameterizing the particle size distribution using a multiple lognormal fitting function. Therefore, it's thus reasonable to set the upper limit of Aitken mode at 110nm.

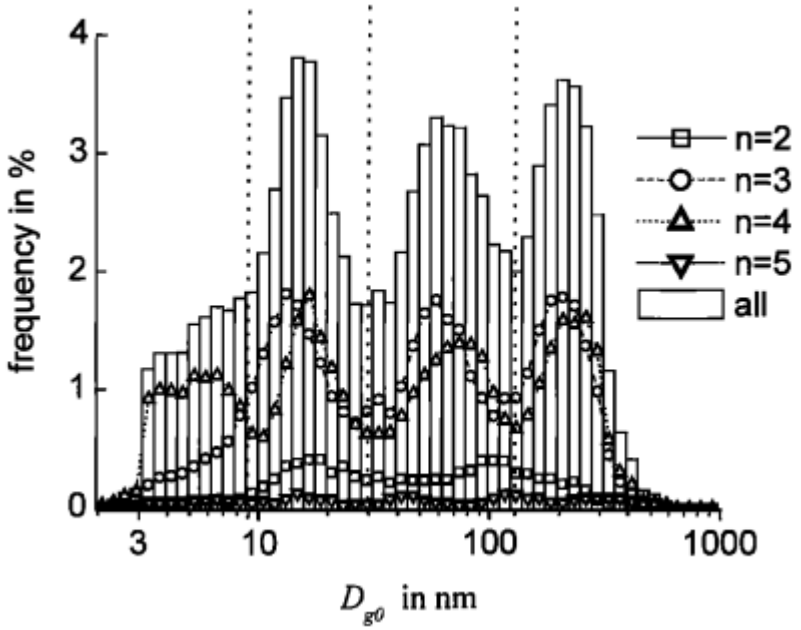

Figure R3. Frequency distribution of modal geometric mean diameters. Subsets of mode numbers 2-5 are included. The figure is from Birmili et al., (2001).

11. Line 320 (and 370), I am not sure whether using PNSD is proper here. The ALWC depends on the amount of hygroscopic materials, no matter which sizes they are present.
Re: The PNSD provides the information of the number concentration of particles at different sizes. ALWC not only depends on the number concentration of hygroscopicity particles but also depends on the particle size. Such as Aitken mode particles with small volume, because of the Kelvin effect, although the Aitken mode particles show a high hygroscopicity, they do not make a large contribution to ALWC. So, when Aitken mode particles and accumulation mode particles have the same

hygroscopicity and number concentration, the particles in the accumulation mode can contribute more to ALWC than that in Aitken mode because accumulation mode particles have larger volume. Furthermore, the particles in different sizes have different hygroscopicity because of their origins, which also affects the ALWC. So PNSD needs to be considered when studying ALWC. Bian et al. (2014) and Tan et al. (2017) also found that PNSD is an important factor of ALWC.

Reference:

Bian, Y. X., Zhao, C.S., Ma, N., Chen, J., Xu, W.Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, Atmos. Chem. Phys., 14 (12), 6417–6426, https://doi.org/10.5194/acp-14-6417-2014, 2014.

Birmili, W., Wiedensohler, A., Heintzenberg, J., and Lehmann, K.: Atmospheric particle number size distribution in central Europe: Statistical relations to air masses and meteorology, J. Geophys. Res.-Atmos., 106, 32005–32018, https://doi.org/10.1029/2000JD000220, 2001.

Cerully, K. M., Bougiatioti, A., Hite Jr., J. R., Guo, H., Xu, L., Ng, N. L., Weber, R., and Nenes, A.: On the link between hygroscopicity, volatility, and oxidation state of ambient and water-soluble aerosols in the southeastern United States, Atmos. Chem. Phys., 15, 8679-8694, https://doi.org/10.5194/acp-15-8679-2015, 2015.

Chen, J., Zhao, C. S., Ma, N., Liu, P. F., Göbel, T., Hallbauer, E., Deng, Z. Z., Ran, L., Xu, W. Y., Liang, Z., Liu, H. J., Yan, P., Zhou, X. J., and Wiedensohler, A.: A parameterization of low visibilities for hazy days in the North China Plain, Atmos. Chem. Phys., 12, 4935–4950, https://doi.org/10.5194/acp-12-4935-2012, 2012.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr., J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, https://doi.org/10.5194/acp-15-5211-2015, 2015.

Gysel, M., Grosier, J., Topping, D.O., Whitehead, J.D., Bower, J.N., Cubison, M.J., Williams, P.I., Flynn, M.J., McFiggans, G.B., Coe, H.: Closure study between chemical composition and hygroscopic growth of aerosol particles during TORCH2, Atmos. Chem. Phys., 7 (24), 6131–6144, https://doi.org/10.5194/acp-7-6131-2007, 2007.

Hussein, T., Puustinen, A., Aalto, P. P., Mäkelä, J. M., Hämeri, K., and Kulmala, M.: Urban aerosol number size distributions, Atmos, Chem. Phys., 4, 391–411, https://doi.org/10.5194/acp-4-391-2004, 2004.

Liu, S., Hu, M., Wu, Z., Wehner, B., Wiedensohler, A., and Cheng, Y.: Aerosol number size distribution and new particle formation at a rural/coastal site in Pearl River Delta (PRD) of China, Atmos. Environ., 42, 6275–6283, https://doi.org/10.1016/j.atmosenv.2008.01.063, 2008.

Paatero, P., & Tapper, U. (2010). Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. Environmetrics, 5(2), 111-126.

Sjogren, S., Gysel, M., Weingartner, E., Alfarra, M. R., Duplissy, J., Cozic, J., Crosier, J., Coe, H., and Baltensperger, U.: Hygroscopicity of the submicrometer aerosol at the high-alpine site Jungfraujoch, 3580 m a.s.l., Switzerland, Atmos. Chem. Phys., 8, 5715-5729, https://doi.org/10.5194/acp-8-5715-2008, 2008.

Tan, H., Cai, M., Fan, Q., Liu, L., Li, F., & Chan, P. W., et al.: An analysis of aerosol liquid water content and related impact factors in pearl river delta, Science of The Total Environment, 579, 1822-1830, https://doi.org/10.1016/j.scitotenv.2016.11.167, 2017.

Whitby, K. T.: The physical characteristics of sulfur aerosols, Atmos. Environ., 12, 135–159, https://doi.org/10.1016/j.atmosenv.2007.10.057, 1978.

Wu, Z., Wang, Y., Tan, T., Zhu, Y., Li, M., & Shang, D., et al.: Aerosol liquid water driven by anthropogenic inorganic salts: implying its key role in the haze formation over north china plain, Environ. Sci. Technol. Lett., 5(3), 160-166, https://doi.org/10.1021/acs.estlett.8b00021, 2018.

Reply to RC2

This study uses two methods (by measuring aerosol hygroscopic growth factor and particle number size distribution and by thermodynamic equilibrium modeling in combination of measured aerosol chemical species) to estimate the aerosol liquid water content ALWC from a field campaign in winter Beijing and argues that organics contribute significantly to the total ALWC and further that organics-ALWC plays a role in the formation of secondary aerosols through multiphase reactions at the initial haze stage.

Major comments

There could be inconsistency in phase states between the two methods of ALWC. Here, thermodynamic modeling assumes that the aerosol particles are in a stable thermodynamic state. But the measurements of hygroscopic growth factor increase the RH to 90% that effectively leads to a metastable thermodynamic state for the sampled aerosol particles. My question is: if the authors repeat ALWC calculations of thermodynamic models assuming a metastable state, whether the results would change? For example, whether the underestimates in ALWC by ISORROPIA would disappear? I feel that this point should be clarified in this study since it is one of the major arguments of this manuscript and since this point also affects the other argument made in this study: whether organics ALWC plays a role in the formation of secondary aerosols through multiphase reactions at the initial haze stage.

Re: Good suggestion. Bian et al. (2014) and Tan et al. (2017) both found the underestimation of ALWC simulated by ISOPPOPIA II model. Tan et al. (2017) used the ISOPPOPIA II model assuming the chemical species in the metastable state to simulate the ALWC, which also showed that the $ALWC_{ISO}$ was lower than $ALWC_{HTDMA}$ for RH below 70%. Their explanation is the lack of hygroscopicity of organic particles which was not taken into account in ISOPPOPIA II model. Here we repeat ALWC simulation using ISOPPOPIA II model assuming the chemical species in metastable state. As shown in Fig. R1a, the simulated ALWC in metastable state ($ALWC_{ISOmetastable}$) is similar with that in stable state ($R^2 = 0.99$), which is similar with the results in Song et al. (2018). They also showed that the simulated ALWC in metastable state is similar with that in stable state at low RH in Beijing. Figure R1b further compares the simulated ALWC in metastable state and calculated ALWC, showing $ALWC_{ISOmetastable}$ is still lower than $ALWC_{HTDMA}$. Moreover, regardless of the result of ISOPPOPIA II model, the average organic ALWC we inferred accounts for 30%. And for low RH and high organics hygroscopicity, the average organic ALWC accounts for up to 58%, suggesting the contribution of organics to ALWC cannot be ignored.

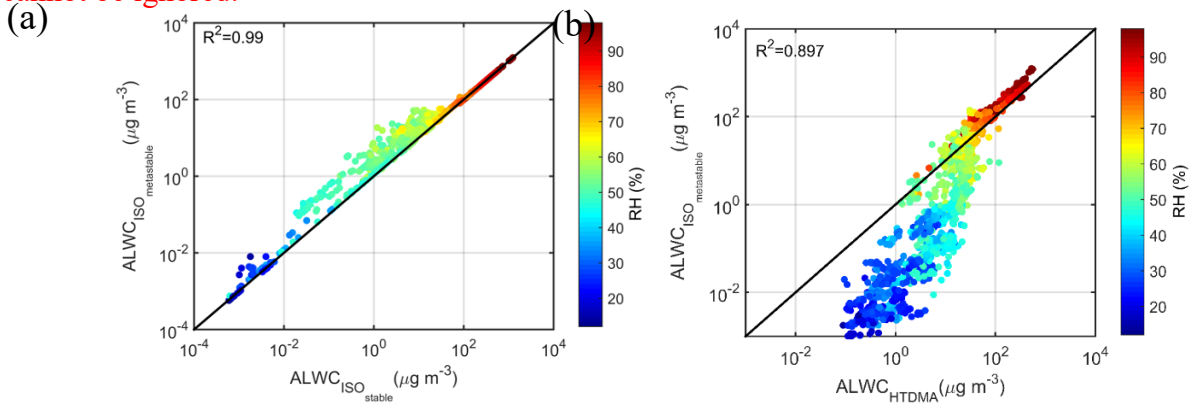

Figure R1. The correlation analysis between (a) $ALWC_{ISOstable}$ and $ALWC_{ISOmetastable}$ and (b) $ALWC_{HTDMA}$ and $ALWC_{ISO\ metastable}$. $ALWC_{HTDMA}$ refers to calculated ALWC based on the measured growth factor and PNSDs, $ALWC_{ISO\ stable}$ refers to simulated ALWC from the ISORROPIA II model assuming chemical species in the stable state. $ALWC_{ISO\ metastable}$ refers to simulated ALWC from the ISORROPIA II model assuming chemical species in the metastable state. The coefficient of determination R^2 is given in each panel. The color of the dots denotes the ambient RH; the black solid line denotes the 1:1 line.

Minor and grammatical comments:

Line 78: can the authors elaborate on what is the direct method to measured ALWC?
Re: To our knowledge, there are no techniques for measuring the ALWC directly (Kuang et al., 2018). The sentence has been revised as: "directly measuring real-time ALWC is not feasible yet because of technical limitations (Kuang et al., 2018)." in line 79.

Line 79: why the direct measurements of ALWC is especially difficult under high RH conditions? It seems to me that such measurements under low RH conditions are more difficult.
Re: Direct measurement of ALWC is not feasible at present, for any ambient RH conditions. A possible reason is that ALWC is sensitive to RH, but the RH of aerosol sample always changes inside any instrument.

Line 94: is should be was.
Re: Thanks, we have corrected it in the manuscript.

Line 160: show should be showed.
Re: Thanks, we have corrected it in the manuscript.

Line 215: I would be surprised if n_H2SO4 were larger than 0. Would it be? Eq. 8: where is n_NH4Cl?
Re: No, the calculated n_H_2SO_4 always equals to 0 in our campaign although the ion-pairing scheme (Gysel et al., 2007) used in this paper considers the contribution of H_2SO_4 to inorganics.

Figure R2 show the time series of the mass fraction of chloride during the campaign. The chloride detected by AMS may be from organics, and it is hard to be verified. So most previous papers didn't consider the contribution of chloride when studying aerosol hygroscopicity (e.g., Gysel et al., 2007; Sjogren et al., 2008; Guo et al., 2015; Cerully et al., 2015). In addition, the mass concentration of chloride is always low in PM_1. As shown in Figure R2, the average mass fraction of chloride is only 6% ± 3%. We added the sentence as in line 223-224 as "In this paper, the chloride was not taken into account in ion-pairing because its source is hard to determine. This may result in a minor uncertainty in κ calculation."

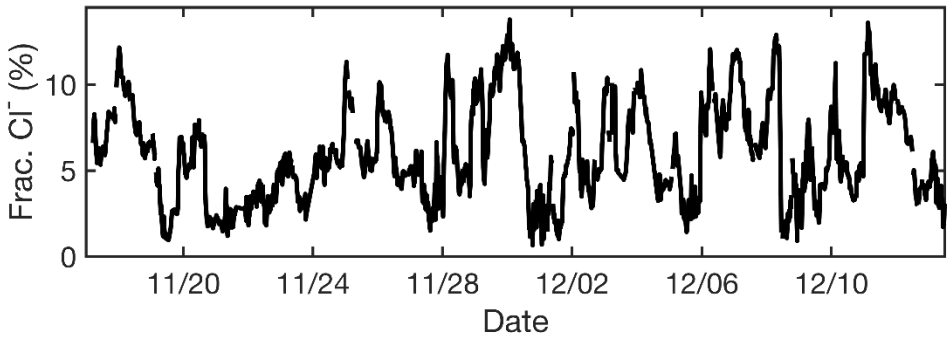

Figure R2. The time series of the mass fraction of chloride.

Line 295: ammonium is also an important component of secondary aerosols.
Re: Good suggestion, we have added the ammonium in the line 302.

Reference:

Bian, Y. X., Zhao, C.S., Ma, N., Chen, J., Xu, W.Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, Atmos. Chem. Phys., 14 (12), 6417–6426, https://doi.org/10.5194/acp-14-6417-2014, 2014.

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Kuang, Y., Zhao, C. S., Zhao, G., Tao, J. C., Xu, W., Ma, N., and Bian, Y. X.: A novel method for calculating ambient aerosol liquid water content based on measurements of a humidified nephelometer system, Atmos. Meas. Tech., 11, 2967–2982, https://doi.org/10.5194/amt-11-2967-2018, 2018.

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Tan, H., Cai, M., Fan, Q., Liu, L., Li, F., & Chan, P. W., et al.: An analysis of aerosol liquid water content and related impact factors in pearl river delta, Science of The Total Environment, 579, 1822-1830, https://doi.org/10.1016/j.scitotenv.2016.11.167, 2017.

Significant contribution of organics to aerosol liquid water content in winter in Beijing, China

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Abstract

The aerosol liquid water content (ALWC), an important component of atmospheric particles, has a significant effect on atmospheric optical properties, visibility and multiphase chemical reactions. In this study, ALWC is determined from aerosol hygroscopic growth factor and particle number size distribution (PNSD) measurements and also simulated by the ISORROPIA II thermodynamic model with measured aerosol chemical composition data at an urban site in Beijing from 8 November to 15 December 2017. Rich measurements made during the experiment concerning virtually all aerosol properties allow us not only to derive the ALWC but also to study the contributions by various species for which little has been done in this region. The simulated ALWC including the contribution of organics and the calculated ALWC are highly correlated (coefficient of determination R^2 = 0.92). The ALWC contributed by organics ($ALWC_{Org}$) accounts for 30 % ± 22 % of the total ALWC during the sampling period. These results suggest a significant contribution of organics to ALWC, which is rather different from previous studies that showed negligible contributions by organics. Our results also show that ALWC correlates well with the mass concentrations of sulfate, nitrate, and secondary organic aerosols (SOA) (R^2 = 0.66, 0.56, and 0.60, respectively). We further noted that accumulation mode particles play a key role in determining ALWC, dominating among all the aerosol modes. ALWC is an exponential function of ambient relative humidity (RH) whose strong diurnal variation influence the diurnal variation of ALWC. However, there is a three-hour lag between the extremes of ALWC and RH values, due to the diurnal variations in PNSD and aerosol chemical composition. Finally, a case study reveals that $ALWC_{Org}$ plays an important role in the formation of secondary aerosols through multiphase reactions at the initial stage of a heavy haze episode.

1. Introduction

China has experienced rapid economic developments during the past few decades, resulting in frequent heavy haze events. Severe air pollution may harm human health and affect the regional climate through aerosol direct and indirect radiation effects (Li et al., 2016; G. X. Wu et al., 2016). However, air pollution formation mechanisms and aerosol climate effects remain highly uncertain due to the complex physical and chemical processes involved (Tao et al., 2012; Y. Wang et al., 2014).

Aerosol liquid water (ALW), a component of atmospheric particles in the atmosphere, exists universally and plays an important role in many atmospheric physical and chemical processes (Nguyen et al., 2016). For example, ALW can influences aerosol optical properties, resulting in increased extinction coefficients, lowered atmospheric visibilities, enhanced aerosol optical depths (AODs), and changes in the direct climatic effect of aerosols (Dougle et al., 1996; Adams et al., 2001; Liao et al., 2005; Seinfeld and Pandis, 2006). Secondary aerosols (SA) are considered to be the main source of particulate pollution during heavy haze events in China (Huang et al., 2014). Many studies now highlight the significance of aerosol liquid water content (ALWC) in the formation of SA through chemical reactions (e.g., Arellanes et al., 2006; G. Wang et al., 2016; Cheng et al., 2016). This is because ALW can dilute the absolute concentration of solutes, adjust aerosol acidity, and serve as a reactant, resulting in increases in trace gas (e.g., N_2O_5 and HO_2) uptake coefficients (Wahner et al., 1998; Bertram et al., 2009; Abbatt et al., 2012). H. Wang et al. (2017) found that the uptake coefficient of N_2O_5 can be high, which is related to high ALWC in Beijing, thereby increasing the formation of nitrates. ALW can also speed up the aqueous phase chemical reaction by serving as a reactor for the transformation of SO_2 to sulfate (Zheng et al., 2015; G. Wang et al., 2016; Cheng et al., 2016). Some studies have found that ALWC can facilitate the formation of secondary organic aerosols (SOA) through aqueous-phase chemistry and photochemistry (Blando et al., 2001; Surratt et al., 2007; Hennigan et al., 2008; Song et al., 2019). Furthermore, observations in Beijing have shown that aqueous-phase processes play a dominant role in the additional formation of oxidized SOA (Xu et al.,

2017). Overall, investigating the formation of SA and haze in North China requires an examination of ALWC and its factors including aerosol particle number size distribution (PNSD), aerosol chemical composition and ambient related humidity (RH) in this region.

However, directly measuring real-time ALWC is not feasible yet because of technical limitations, ~~especially under high RH conditions~~ (Kuang et al., 2018). Four indirect methods have been proposed to calculate real-time ALWC: (1) the aerosol ~~particle number size distribution (~~PNSD~~)~~ under dry conditions and ambient ~~relative humidity (~~RH~~)~~ conditions are first measured, then ALWC is calculated as the difference between dry and ambient aerosol volumes (Stanier et al., 2004); (2) the increased aerosol volume due to water uptake (i.e., ALWC) is calculated according to the measured dry PNSD, size-dependent aerosol hygroscopicity, and ambient RH (Kitamori et al., 2009; Bian et al., 2014; Tan et al., 2017); (3) the dry and ambient aerosol volumes are first estimated using the measured aerosol optical enhancement and Ångström exponent, then ALWC is calculated as the difference between dry and ambient aerosol volumes (Kuang et al., 2018); and (4) ALWC is simulated using thermal equilibrium models such as the ISORROPIA thermodynamic model (Nenes et al., 1998), Aerosol Inorganics Model models (Wexler and Clegg, 2002), the Simulating Composition of Atmospheric Particles in Equilibrium model (Kim et al., 1993), and the Gibb's Free Energy Minimization model (Ansari et al., 1999) with aerosol chemical composition information as input.

ALWC mostly depends on aerosol PNSD, chemical composition, and ambient RH. Hodas et al. (2014) reported that ALWC in the Po Valley in Italy ~~is~~ was driven by locally formed anthropogenic nitrates. The implications for the lifetimes of water-soluble organic compounds and its potential influence on SOA formation were also discussed. Another study also revealed that ALWC in Beijing was driven by secondary inorganic aerosols (SIA; Z. Wu et al., 2018). Most previous studies have focused on the interaction between inorganic salts and ALWC, but the impact of organic species on ALWC been ignored to our knowledge (Blando et al., 2001; Surratt et al., 2007; Hennigan et al., 2008; Carlton et al., 2014). A thorough understanding of the association of ALWC with organic aerosols in

the atmosphere is lacking.

In this study, ALWC is calculated using the indirect method (2) and simulated using the ISORROPIA II model, i.e., indirect method (4), discussed previously. The effects of inorganic aerosols, organic aerosols, PNSD, and ambient RH on ALWC are then investigated separately. We demonstrate the significant contribution of organics to ALWC in Beijing and provide evidence that the ALW contributed by organics serves as a reactor for sulfate and SOA formation.

2. Data and measurements

2.1. Sampling site

The Air Pollution and Human Health (APHH) winter field campaign took place from 8 November to 15 December 2016 at the Chinese Academy of Sciences' Institute of Atmospheric Physics Tower Branch in Beijing. Beijing is located in the northwest part of the North China Plain, which has experienced rapid economic developments during the last few decades. A large amount of gaseous precursors and other air pollutants are emitted in this region every year, causing serious air pollution problems. The sampling site is located in the northwestern urban area of Beijing (39.97°N, 116.37°E), between the north third and fourth ring roads and surrounded by restaurants. Traffic and cooking emissions are thus the main pollutants at the site. Aerosols at this site can, therefore, well represent anthropogenic aerosols in highly polluted areas. Sun et al. (2013) and Y. Wang et al. (2017) provide more detailed descriptions of the sampling site.

2.2. Instrumentation

Sampling instruments used during the field campaign included a scanning mobility particle sizer (SMPS) equipped with a long differential mobility analyzer (DMA; model 3081A, TSI) and a condensation particle counter (CPC; model 3772, TSI). A custom-built hygroscopicity tandem differential mobility analyzer (H-TDMA) was installed in an air-conditioned mobile container at

ground level. The temperature inside the container was maintained at 20–25°C. A high-resolution aerosol mass spectrometer (HR-AMS) was set up in a sampling room located on a two-story roof, about 25 m north from the container. Sampled air went through a $PM_{2.5}$ cyclone inlet fixed on the top of the container before entering the instruments. The RH of the sampled air was dried to below 20 % by a dryer system consisting of a tube filled with silica gel and a Nafion dryer (model PD-70T-24ss, Perma Pure Inc., USA). Various meteorological parameters, including wind speed (WS), wind direction (WD), temperature (*T*), and RH, were measured from a 325-m meteorological tower located ~20 m west of the container. In this study, all times are reported in Beijing local time (UTC+8 h).

PNSDs with electrical-mobility diameters ranging from 10 to 600 nm were measured by a scanning mobility particle sizer (SMPS) at a 5-min time resolution. PNSDs were extended to diameters ranging from 0.6 to 1 μm by fitting the measured PNSDs with functions consisting of three-mode log-normal distributions (Hussein et al., 2005). Thus generated are PNSDs with a diameter range of 10 nm to 1 μm.

The H-TDMA system developed by the Guangzhou Institute of Tropical and Marine Meteorology measured the size-dependent aerosol hygroscopic growth factor (GF). The H-TDMA system mainly consists of four parts. The first part is a Nafion dryer to keep the RH of sampled air below 20 % and a bipolar neutralizer (soft X-ray, model 3088, TSI Inc.) to equilibrate the particle charge (Wiedensohler et al., 1988). Next, the sampled air passes through the first differential mobility analyzer (DMA1; model 3081L, TSI Inc.) to produce mono-dispersed particles. In this study, the diameters were set to 40, 80, 110, 150, and 200 nm. The sampled air then went through a Nafion humidifier (model PD-70T-24ss, Perma Pure Inc., USA) used to humidify the RH of sampled air to 90 %. The last part of the H-TDMA is the second DMA (same model as the DMA1) and a water-based condensation particle counter (model 3787, TSI Inc.), used to measure the number size distribution of humidified particles in the five selected diameters. Y. Wang et al. (2017) provide a detailed introduction to the H-TDMA system.

Size-resolved non-refractory sub-micron aerosol chemical species, including organics (Org), sulfate (SO_4^{2-}), nitrate (NO_3^-), ammonium (NH_4^+), and chloride (Cl^-), were measured by the HR-AMS. The sampled air dried by diffusion silica gel dryers was drawn into the HR-AMS through a $PM_{2.5}$ cyclone inlet to remove coarse particles larger than 2.5 μm. The HR-AMS was calibrated with pure ammonium nitrate following the procedures detailed in Jimenez et al. (2003). Sun et al. (2016b) provide operational details about the HR-AMS.

3. Method

3.1. ALWC calculation based on H-TDMA measurements

The ALWC is calculated based on measurements of the aerosol GF and particle number size distribution. Briefly, H-TDMA data are first used to derive the size-resolved particle GFs at various RHs. Then ALWC is calculated as the increased aerosol volume due to hygroscopic growth attributed to water uptake.

Chen et al. (2012) ~~show~~ showed how to calculate size-resolved particle GFs at different RHs. First, a three-mode log-normal distribution is applied to fit the measured PNSD to produce fitting parameters for each mode. The hygroscopicity parameter (κ) in any mode is assumed to be constant. The H-TDMA-derived size-dependent κ can then be used to deduce the corresponding κ for the nucleation mode, the Aitken mode, and the accumulation mode of PNSDs according to the following equation:

$$\kappa(D_P) = \frac{\sum_{i=1}^{3} \kappa_i \cdot N_i(D_p)}{\sum_{i=1}^{3} N_i(D_p)}, \quad (1)$$

where κ_i refers to the κ of the ith mode, and N_i (D_p) refers to the number concentration of particles in the ith mode. According to κ-Köhler theory (Petters and Kreidenweis, 2007), κ at a certain diameter (D_d) can be calculated as

$$\kappa(D_d) = (GF^3 - 1) \cdot \left[\frac{1}{RH} \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D_d GF}\right) - 1\right], \quad (2)$$

where RH is the control value by the humidifier in the H-TDMA system, T is the mean room

temperature of the container set to 293 K, $\sigma_{s/a}$ is the surface tension of the solution/air interface assumed to be the same as the surface tension coefficient between water and air (about 0.0728 N m^{-1} at 293 K), M_w is the molecular weight of water, R is the universal gas constant, ρ_w is the density of water, and D_d is the diameter of the dry particles. The GF at a given RH is defined as the ratio of the humidified diameter [D_p (RH)] to D_d:

$$\mathrm{GF} = D_p(\mathrm{RH})/D_d \ . \quad (3)$$

The known κ of each mode derives the size-resolved κ at 90 % RH using Eq. (1). Substituting the size-resolved κ into Eq. (2) results in size-resolved GFs at various RHs. Finally, the volume of ALWC at ambient RH is equal to the increased aerosol volume due to water uptake, i.e., ALWC can be calculated as

$$\mathrm{ALWC_{HTDMA}} = \left[\frac{1}{6}\sum_i n_i D_{p,i}^3 \left(GF\left(D_{p,i}, RH\right)^3 - 1\right)\right] \cdot \rho_w \ , \quad (4)$$

where n_i refers to the particle number concentration of dry particles for the corresponding particle size range in the ith mode, and $D_{p,i}$ refers to the particle diameter for the corresponding particle size range.

3.2. ALWC simulations based on the ISORROPIA II model

The thermodynamic equilibrium model ISORROPIA II developed by Fountoukis and Nenes (2007) using aerosol chemical composition information from the HR-AMS can simulate ALWC ($ALWC_{ISO}$). The bulk chemical composition was used in the model. However, the ISORROPIA II model only considers the contribution of inorganic species (Ca^{2+}, K^+, Mg^{2+}, NH^+, Na^+, SO_4^{2-}, NO_3^-, Cl^- and H_2O) on ALWC and neglects the contribution of organics. In this study, the phase state was assumed to be stable in the model calculation, and the model was set up to reverse mode due to the lack of measurements of gaseous ammonia.

According to the model assumptions that the aerosol curvature effect in Köhler theory is ignored, and the aerosol water uptake has no effect on ambient vapor pressure, the water activity (a_w) defined as the effective mole fraction of water is equal to the ambient RH in this model (Seinfeld and Pandis,

519 2006):

520 $$a_w = RH \quad (5)$$

521 The ALWC can be calculated using the Zdanovskii−Stokes−Robinson (ZSR) mixing rule (Stokes and
522 Robinson, 1966),

523 $$\mathrm{ALWC_{ISO}} = \sum_i \frac{M_i}{m_{0i}(a_w)}, \quad (6)$$

524 where M_i is the mole concentration of the ith species (mol m^{-3} in air), and m_{0i} (a_w) is the corresponding
525 molality of the binary solution of the ith species under the same a_w with complex solution. Finally,
526 with measured ambient RH and T values as input $ALWC_{ISO}$ values under different RH and T conditions
527 can be derived.

528 **3.3. Inferring the contribution of organics to ALWC**

529 According to the κ-Köhler theory and the ZSR mixing rule, κ can also be expressed as the sum of
530 the contributions of each aerosol component:

531 $$\kappa = \sum_i \varepsilon_i \kappa_i , \quad (7)$$

532 where ε_i and κ_i are the volume fraction and hygroscopicity of the ith species, respectively. Submicron
533 aerosols mainly consist of organic and inorganic species (Carbone et al., 2013; Zieger et al., 2017). As
534 mentioned in section 2.2, the HR-AMS measures the mass concentrations of organics and inorganics,
535 including SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-. The volume fraction of inorganic species can be calculated based
536 on the ion-pairing scheme given by the following equations (Gysel et al., 2007):

537 $$n_{\mathrm{NH_4NO_3}} = n_{\mathrm{NO_3^-}},$$

538 $$n_{\mathrm{NH_4HSO_4}} = \min\left(2n_{\mathrm{SO_4^{2-}}} - n_{\mathrm{NH_4^+}} + n_{\mathrm{NO_3^-}}, n_{\mathrm{NH_4^+}} - n_{\mathrm{NO_3^-}}\right),$$

539 $$n_{\mathrm{(NH_4)_2SO_4}} = \max\left(n_{\mathrm{NH_4^+}} - n_{\mathrm{NO_3^-}} - n_{\mathrm{SO_4^{2-}}}, 0\right),$$

540 $$n_{H_2SO_4} = \max\left(0, n_{\mathrm{SO_4^{2-}}} - n_{\mathrm{NH_4^+}} + n_{\mathrm{NO_3^-}}\right),$$

541 $$n_{\mathrm{HNO_3}} = 0, \quad (8)$$

where n represents the mole numbers, and "min" and "max" are minimum and maximum values, respectively. The κ values of the inorganic species sulfuric acid, ammonium sulfate, ammonium hydrogen sulfate, and ammonium nitrate are 1.19, 0.48, 0.56, and 0.58, respectively (Topping et al., 2005; Petters and Kreidenweis, 2007). So the ZSR model can be used to estimate the contribution of inorganic species to the κ value. In this paper, the chloride was not taken into account in ion-pairing because its source is hard to determine. This may result in a minor uncertainty in κ calculation. The hygroscopicity parameter of organics (κ_{Org}) can be calculated using the volume fraction of organics and the total κ value derived from the H-TDMA, according to Eq. (7). Finally, the ALWC contributed by organic species ($ALWC_{Org}$) can be calculated as (Petters and Kreidenweis, 2007)

$$ALWC_{Org} = \frac{m_{Org}\rho_W}{\rho_{Org}} \frac{\kappa_{Org}}{\left(\frac{1}{RH}-1\right)}, \quad (9)$$

where m_{Org} is the organic mass concentration from the AMS (Xu et al., 2015), and ρ_{Org} is the density of organics, taken as 1.4 g cm^{-3} (Moore et al., 2011; Lathem et al., 2013; Cerully et al., 2014).

4. Results and discussion

4.1. Comparison of calculated and simulated ALWC

The trends in ALWC calculated based on the hygroscopic growth factor and PNSD ($ALWC_{HTDMA}$) and simulated from ISOPPOPIA II model ($ALWC_{ISO}$) are generally consistent ~~(Fig. S1). However, the difference between $ALWC_{HTDMA}$ and $ALWC_{ISO}$ is large at low RH, especially at ultra-low RH (< 30 %).~~ Figure 1a shows that $ALWC_{HTDMA}$ and $ALWC_{ISO}$ agree well and that their coefficient of determination (R^2) is 0.89. The correlation is especially strong for RH over 90 %. However, for RH below 60 %, $ALWC_{ISO}$ is less than $ALWC_{HTDMA}$ and even close to 0 in some cases. Bian et al. (2014) and Tan et al. (2017) observed a similar phenomenon in northern and southern China. There are ~~two~~ three possible explanations for these results. H-TDMA samples were humidified to 90 % RH during the field campaign, thereby leading to the neglect of the deliquescence process in the $ALWC_{HTDMA}$ calculation. This may lead to overestimation of $ALWC_{HTDMA}$ for RH below the

deliquescence relative humidity (DRH). Second, the assumption of constant κ in each mode may lead to small uncertainty in size-resolved GFs at different RHs, resulting in small deviation in ALWC calculation. This may be another reason for the difference between $ALWC_{HTDMA}$ and $ALWC_{ISO}$. In addition, the ISORROPIA II model ignores the effect of aerosol shape and complex organic species on the DRH. Previous studies have suggested that the particle spherical assumption and simplified aerosol chemical species in this model can overestimate the DRH (Seinfeld and Pandis, 2006; Sjogren et al., 2007). So for RH below the simulated DRH (~60 %), particles may still be dry in the ISORROPIA II model, but may have been hydrated in the real atmosphere. Therefore, this model underestimates ALWC. The ambient aerosol deliquescent phenomenon is rare in the North China Plain (Kuang et al., 2016). In addition, the ISORROPIA II model cannot simulate water uptake by organics, which can lead to some bias between simulated and calculated ALWCs. As described in section 3.3, $ALWC_{Org}$ can be inferred and used to discuss differences between $ALWC_{ISO}$ and $ALWC_{HTDMA}$. Figure 1b shows that adding $ALWC_{Org}$ to $ALWC_{ISO}$ leads to a stronger correlation with $ALWC_{HTDMA}$ (R^2 = 0.92). The correlation improves significantly for RH below 60 %. This demonstrates that (1) organic species contribute significantly to ALWC, and (2) the underestimation of ALWC by the ISORROPIA II model is also related to the neglect of organic species in the model.

4.2. Impact of different factors on ALWC

4.2.1. Impact of aerosol chemical species on ALWC

Figure 2 shows the characteristics of seven heavy pollution events selected for examination. Figures 2a and 2c display the time series of WS, WD, and ambient RH. The prevailing wind during the haze episodes was a weak southerly wind that was favorable for bringing in pollutants from the highly populated and industrialized neighboring regions to the sampling site. This is beneficial to the formation and accumulation of SA (T. Wang et al., 2010; Y. Wang et al., 2017). However, the prevailing

winds during the clean events were strong northerly winds that always carried in a clean air mass, resulting in pollutants being quickly removed (Figure 2c). Note that the PM_1 mass concentration decreases somewhat in the evening during haze episodes, following the short-term change of WD from southerly to northerly. This is related to mountain-valley breezes in Beijing (Wehner et al., 2008; Gao et al., 2011; Y. Wang et al., 2017). These results demonstrate that heavy haze episodes have a strong correlation with local wind direction in Beijing.

Figures 2a and 2d show the time series of ambient RH and mass concentrations of aerosol chemical species in PM_1. These figures suggest that the increase in inorganic and organic aerosols is synchronous with the increase in ambient RH during the heavy pollution periods (P1-P7). This is likely because of a positive feedback mechanism driven by Henry's law and thermodynamic equilibrium (Z. Wu et al., 2018). Figure 2b also shows that ALWC continuously increases during the pollution accumulation period. On average, ALWC increases from 8 to 89 μg m^{-3} as ambient RH increases from 15 to 80 %, and the inorganic and organic aerosol mass concentrations increase from 15 to 120 μg m^{-3} and from 12 to 78 μg m^{-3}, respectively. These results imply that the increase in ambient RH and aerosol mass concentration are all important for the increase in ALWC.

Equation (4) also suggests that the absolute value of ALWC is dependent on the value of ambient RH and aerosol chemical composition (i.e., the GF value). To further investigate the impact of chemical composition on ALWC, the impact of RH on ALWC should be accounted for. Previous studies suggest there is an exponential relationship between ALWC and RH (e.g., Z. Wu et al., 2018). Here, we define the relative ALWC as the ratio of $ALWC_{HTDMA}$ and the function of ambient RH ($e^{b\mathrm{RH}}$). The b is derived according to the relationship between $ALWC_{HTDMA}$ and RH that is fitted by the function $y = ae^{bx}$. Figure 3a shows the relationship between relative ALWC and primary aerosols (PA) or SA mass concentrations. PA consists of primary organic aerosols (POA) and black carbon (BC), and SA consists of SOA, sulfate, and nitrate. The positive matrix factorization (Paatero and Tapper, 1994) was applied on the organic aerosols (OA) spectral matrices to identify POA and SOA.

615 The relative ALWC is highly correlated with SA mass concentrations (R^2 = 0.94) but poorly correlated
616 with PA mass concentrations (R^2 = 0.69). High relative ALWCs coincident with high SA mass
617 concentrations suggest that SA plays a key role in the increase in ALWC. This is likely because SA is
618 mainly generated from photochemical reactions in the daytime or reactions at night, making SA highly
619 aged with a hygroscopicity stronger than that of PA (Ervens et al., 2011; Sareen et al., 2017). SA can,
620 therefore, absorb more water vapor than PA in the atmosphere. The enhanced aerosol liquid water
621 induced by SA is further favorable for the formation of SA by speeding up the atmospheric chemical
622 reaction rate and serving as the medium for gas-particle heterogeneous reactions (G. Wang et al., 2016;
623 Cheng et al., 2016). This further increases the bulk aerosol hygroscopicity. This is also the reason why
624 inferred κ based on the ZSR model continuously increases during haze episodes (Figure 2c).

625 Secondary aerosols are mainly composed of nitrate, sulfate, ammonium and SOA. To determine
626 which species is the driver for ALWC in Beijing, Figure 3b shows the correlation analysis between
627 relative ALWC and the mass concentrations of different aerosol chemical species. Relative ALWC and
628 all SIA agree well [R^2 equal to 0.66 (sulfate) and 0.56 (nitrate)]. It has been reported that ALWC is
629 driven by inorganic salts with both nitrate and sulfate playing key roles in determining ALWC (Z. Wu
630 et al., 2018). ALWC also agrees well with SOA (R^2 = 0.60) in our study. This is unexpected because
631 the hygroscopicity of SOA is relatively lower than that of nitrate and sulfate. Some studies have also
632 suggested that the water uptake of aged organics accounts for only a few percent of the total aerosol
633 water uptake (e.g., Gysel et al., 2007; Engelhart et al., 2011). In our study, the contribution of $ALWC_{Org}$
634 to total ALWC is significant, accounting for 30 % ± 22 %. As shown in Figure 4, the contribution of
635 organics to total ALWC varies strongly. This is likely related with the variation in mass fraction and
636 hygroscopicity parameter of organics (κ_{org}). The mass concentration of inorganics increases more than
637 that of organics as RH increases, leading to a lower mass fraction of organics in the case of high
638 ambient RH. Figure 4 also shows $ALWC_{Org}$ fraction increases significantly with the increase of κ_{org}.
639 All these help explain a large variation in the $ALWC_{Org}$ contribution to total ALWC. Considering the

distinct ambient RH and κ_{org} between clean and polluted periods, we calculated respectively the fraction of $ALWC_{Org}$ during two periods. There is a higher $ALWC_{Org}$ fraction (33% ± 23%) during clean periods than that during polluted periods (26% ± 11%). Yet, there is little variability of $ALWC_{Org}$ fraction during polluted periods. The larger variability in $ALWC_{Org}$ fraction during clean periods is likely caused by the highly variable κ_{org} when the ambient RH is low. In summary, the contribution of organics in total ALWC varies with the variations of the mass fraction of organics and κ_{org}, and this contribution is significant during both clean and polluted periods. Studies of ALWC in Beijing, therefore, cannot neglect $ALWC_{Org}$. This is different from the studies in other regions such as in the Po Valley in Italy (Hodas et al., 2014) and the eastern U.S. (Carlton et al., 2013) where the ALWC was found to be only driven by nitrate and sulfate respectively.

An interesting phenomenon is frequently observed at the initial stage of heavy haze episodes (e.g., P4, P5, P6, and P7). $ALWC_{ISO}$ is almost close to 0, but both $ALWC_{HTDMA}$ and $ALWC_{Org}$ are always larger than 0, and the organic aerosol mass fraction is high at this stage. These observations reveal that at the initial stage of heavy haze episodes, the ALWC is mostly contributed by organic species. Meanwhile, κ is not very low and increases markedly as the PM_1 mass concentration increases, which is unexpected because of the lower hygroscopicity of organic aerosols compared to SIA. Therefore, some highly hygroscopic substance (i.e., SA) must be generated through multiphase chemical reaction at this stage. We propose that the liquid water contributed by organic species provides a reactor for the transformation of gaseous precursors to SA at the initial stages of heavy haze episodes, increasing the uptake of more liquid water by more SA and further accelerating the formation of heavy haze. Section 4.3 provides a case study to demonstrate this.

4.2.2. Impact of PNSD on ALWC

In addition to aerosol chemical composition, ALWC also depends on PNSD (Bian et al., 2014). As described in section 3.1, the nucleation mode (< 30 nm), the Aitken mode (30–110 nm), and the accumulation mode (110 nm to1 μm) (Whitby, 1978; Birmili et al., 2001) are considered in this study.

Particles with diameters greater than 1 μm are not considered because ~~most of these large particles are composed of hydrophobic species (e.g., dust or mineral substances) that contribute little to ALWC~~ some particles in the coarse mode are water soluble but their contribution on the ALWC is low (e.g., Hussein et al., 2004; S. Liu et al., 2008; Bian et al., 2014; Tan et al., 2017).

Figure 5~~S2~~ in the supplement shows that the contributions of nucleation mode, Aitken mode, and accumulation mode particles to ALWC are < 1.0 %, 18.0 %, and 82.0 %, respectively. Figure 6~~4~~ shows the correlations between $ALWC_{HTDMA}$ and the volume concentrations of different mode particles, and the average contribution of different mode particles to $ALWC_{HTDMA}$ (f_{ALWC}) under five different RH conditions. The R^2 and f_{ALWC} of the nucleation mode particles (left column in Figure 6~~4~~) are all less than 0.1 and 1 %, respectively, under all RH conditions. This is likely because the volume concentration of nucleation mode particles is very low, and most of these small particles are composed of hydrophobic chemical species such as BC and POA. Similarly, the number concentration of Aitken mode particles also shows weak correlations with $ALWC_{HTDMA}$ ($R^2 < 0.2$) under RH < 90 % conditions, but their correlation ($R^2 = 0.25$) is enhanced significantly under RH > 90 % conditions (middle column of Figure 6~~4~~). This is because there are more aged particles in the Aitken mode which can absorb much more water when the ambient RH is higher than 90 %. However, the contribution of the Aitken mode to ALWC ranges from 14 % to 21 % and decreases as RH increases. $ALWC_{HTDMA}$ is strongly correlated to the volume concentration of accumulation mode particles, with R^2 and f_{ALWC} greater than 0.6 and 75 %, respectively, under all RH conditions (right column of Figure 6~~4~~). Figure 6~~4~~ also shows that ALWC increases slightly as the volume concentration of accumulation mode particles increases under RH < 70 % conditions (slope < 0.001), but increases strongly under higher RH conditions, especially under RH > 90 % conditions (slope = 0.0041). This is likely because there are more accumulation mode SA formed due to multiphase chemical reactions under high ambient RH conditions. Swietlicki et al. (1999) have suggested that the contribution of accumulation mode particles to ALWC is largest for all-mode particles.

In summary, the contribution of nucleation mode particles to ALWC is very low. The contribution of Aitken mode particles is much higher than nucleation mode particles and decreases with increasing ambient RH. The contribution of accumulation mode particles to ALWC is largest under all RH conditions and increases with increasing ambient RH, thus playing a key role in determining ALWC.

4.2.3. Impact of RH on ALWC

As discussed in 4.2.1, the absolute value of ALWC has an exponential relationship with ambient RH. Figure 7~~5~~ shows the relationship between ALWC and RH for different PM_1 mass concentration ranges. ALWC increases slowly as RH increases under lower ambient RH conditions then sharply increases when RH exceeds a critical RH value. This critical RH value is different for different PM_1 mass concentrations. This is because the low RH conditions cannot provide enough water for aerosol particles, even though the PNSD is dominated by accumulation mode particles with higher hygroscopicity (Tan et al., 2016). This demonstrates the important influence of RH on ALWC. The lower critical RH value for higher PM_1 mass concentrations (~80 %) suggests that ALWC is easily formed under heavily polluted conditions. This is likely because there are more SA and accumulation mode particles during pollution periods (Sun et al., 2016a; Y. Wang et al., 2017).

Figure 8~~6~~a shows the diurnal variations of $ALWC_{HTDMA}$ and ambient RH during the sampling period. The extreme $ALWC_{HTDMA}$ values appear at night and during the day respectively, likely related to the diurnal variations of ambient RH. The elevated ambient RH at night not only increases ALWC through water uptake of particles directly, but also facilitates the formation of hydrophilic particulate nitrate through the speeding up of the uptake coefficient of N_2O_5 (Thornton et al., 2003; Bertram et al., 2009). This can further enhance ALWC. However, although the diurnal variations of $ALWC_{HTDMA}$ and ambient RH are similar, the peak and nadir of $ALWC_{HTDMA}$ (0300 LT and 1100 LT, respectively) appear three hours earlier than the peak and nadir of ambient RH (0600 LT and 1400 LT, respectively). This time difference is likely related to changes in PNSD. The diurnal variation of PNSD (Figure 8~~6~~b) shows that the number concentrations of Aitken and accumulation mode particles begin to decrease

quickly at 0300 LT. ALWC also begins to decrease, although the ambient RH increases slightly at that time. In the morning, ALWC decreases sharply following the ambient RH and PNSD changes due to the lifting planetary boundary layer height. ALWC decreases to its minimum value at ~1100 LT then begins to increase quickly. However, ambient RH still decreases at that time and reaches its minimum value at ~1400 LT. The increase in ALWC is likely associated with changes in aerosol chemical species and PNSD. Figure 8~~6~~b and 8~~6~~c show that there are many newly formed Aitken and accumulation mode particles and that the fraction of SA increases at noon, likely because of strong photochemical reactions. Y. Wang et al. (2017, 2018) have suggested that daytime photochemical reactions are efficient enough to enhance aerosol hygroscopicity and change the aerosol mixing state from external to internal in North China through the formation of hydrophilic chemical species. All this suggests that ambient RH is not the only determining factor for ALWC. PNSD and aerosol chemical composition are also important for ALWC.

4.3. A case study of the impact of $ALWC_{Org}$ on SA formation

As discussed in section 4.2.1, a hypothesis is proposed that $ALWC_{Org}$ maybe provide a reactor for the formation of secondary species. To verify this hypothesis, the P4 case shown in Figure2 is selected to further analyze the influence of $ALWC_{Org}$ on the formation of secondary aerosols (Figure 9~~7~~). Figure 9~~7~~a shows the time series of $ALWC_{HTDMA}$, $ALWC_{ISO}$, and $ALWC_{Org}$ during this case. On 27 November 2017, $ALWC_{ISO}$ was close to 0 all day long because of the low ambient RH, but both $ALWC_{HTDMA}$ and $ALWC_{Org}$ were always larger than 0, increasing with increasing PM_1 mass concentration (Figure 9~~7~~a). Figure 9a~~7a~~ also shows that the fraction of $ALWC_{Org}$ in $ALWC_{HTDMA}$ was high at the initial stage of this pollution case, but this fraction decreased as haze increased. This case was further divided into three periods (Figure 9~~7~~b). Organics were the most abundant chemical species during the first period (64 %), which explains the high fraction of $ALWC_{Org}$ in $ALWC_{HTDMA}$ at the initial stage of this haze case. The pie charts in Figure 9~~7~~b also show that both SOA and SIA (sulfate, nitrate, and ammonium) increases from the first to third periods but POA decreases, likely related to multiphase reactions (i.e.,

aqueous-phase reactions) due to the enhanced ALWC. Time series of f_{44} and the fraction of sulfate in total sulfur (F_{SO4}^{2-}) are also shown to further illustrate the influence of aqueous-phase reactions on aerosol chemical species. The *m*/*z* 44 signal intensity f_{44} (mostly contributed by the CO_2^+ ion) measured by the AMS can be used as an indicator of the oxidation level in organic species (Mei et al., 2013). The sulfur oxidation ratio F_{SO4}^{2-} (Sun et al., 2006) is defined as

$$F_{SO_4^{2-}} = \frac{n[SO_4^{2-}]}{n[SO_4^{2-}]+n[SO_2]}, \quad (10)$$

where $n[SO_4^{2-}]$ and $n[SO_2]$ refer to the molar concentrations of SO_4^{2-} and SO_2, respectively. Figure 9~~7~~b suggests that f_{44} and F_{SO4}^{2-} both increase gradually with increasing $ALWC_{HTDMA}$ and PM_1 mass concentration from 27 November to 30 November 2017. This is likely because the increase in ALWC is beneficial to the oxidation of organics and the transformation of SO_2 to SO_4^{2-}, implying the importance of aqueous-phase chemical reaction on haze formation in Beijing. The production of secondary organic and inorganic species can further enhance aerosol hygroscopicity, increasing ALWC in the atmosphere. This positive feedback is the reason behind the rapid formation of heavy haze events in Beijing (G. Wang et al., 2016). A rapid increase in f_{44} and F_{SO4}^{2-} was seen during the first period at night on 27 November (shown by green and red arrows in Fig. 9~~7~~) when organics contributed the most to ALWC. This suggests that ALWC contributed by organics may have played an important role in the formation of secondary species at the initial stage of the pollution event.

5. Conclusions

In this study, the aerosol liquid water content (ALWC) was calculated using the size-resolved aerosol hygroscopic growth factor and the particle number size distribution (PNSD) measured at a Beijing urban site during the APHH winter campaign (8 November to 15 December 2017). Also done were simulations using the ISORROPIA II model with measured aerosol chemical composition data

as input data. During the sampling period, seven heavy haze episodes were selected to investigate the influence of different factors (PNSD, ambient RH, and aerosol chemical composition) on ALWC.

The calculated and simulated ALWC ($ALWC_{HTDMA}$ and $ALWC_{ISO}$) agree well (correlation of determination R^2 equal to 0.89). However, $ALWC_{ISO}$ is much lower than $ALWC_{HTDMA}$ for RH below 60 %, even approaching zero many times. This deviation is in part attributed to the neglect of the contribution of organics to ALWC ($ALWC_{Org}$) in the ISORROPIA II model, contradicting with previous studies ignoring this contribution. The aerosol hygroscopicity of organics was also derived in this study for use in calculating $ALWC_{Org}$. The sum of $ALWC_{ISO}$ and $ALWC_{Org}$ has a higher correlation (R^2 = 0.92) with the calculated ALWC (i.e., $ALWC_{HTDMA}$), especially for RH below 60 %. This implies that organic aerosols are also an important contributor to ALWC.

PNSD, ambient RH, and aerosol chemical composition are all found to affect ALWC significantly. Nucleation mode and Aitken mode particles have little influence on ALWC. Accumulation mode particles play a key role in determining ALWC and dominate among all aerosol modes. ALWC is highly related to the relative humidity (RH) when RH exceeds a critical RH value that is different for different PM_1 mass concentrations. ALWC varies diurnally with its extreme values appearing at night and during the day respectively. The diurnal variation of ambient RH explains this. However, there is a three-hour difference between when the extreme ALWC and RH values occur, caused by the diurnal variations in PNSD and aerosol chemical composition.

On average, $ALWC_{Org}$ accounts for ~30 % ± 22 % of the total aerosol liquid water during the sampling period. This shows the significant contribution of organic species to ALWC. Our results suggest that ALWC is not only driven by inorganic salts but also driven by organics in Beijing. This is different from the results obtained in the Po Valley in Italy (Hodas et al., 2014) and the eastern U.S. (Carlton et al., 2013) where the ALWC is driven by nitrate and sulfate respectively. Finally, one case study was used to study the importance of $ALWC_{Org}$ on multiphase chemical reactions. $ALWC_{Org}$ was found to play an important role in the formation of secondary aerosols by speeding up aqueous-phase

reactions at the initial stage of heavy haze. Our study is important for investigating the contribution of organics to ALWC and its importance on haze formation in Beijing.

Data availability. Data used in the study are available from the first author upon request (201631490012@mali.bnu.edu.cn).

Author contributions. ZL and YW designed the experiment; YW, XJ, and WX carried it out and analyzed the data; other co-authors participated in science discussions and suggested additional analyses. XJ and YW prepared the paper with contributions from all co-authors.

Competing interests. The authors declare no competing interests.

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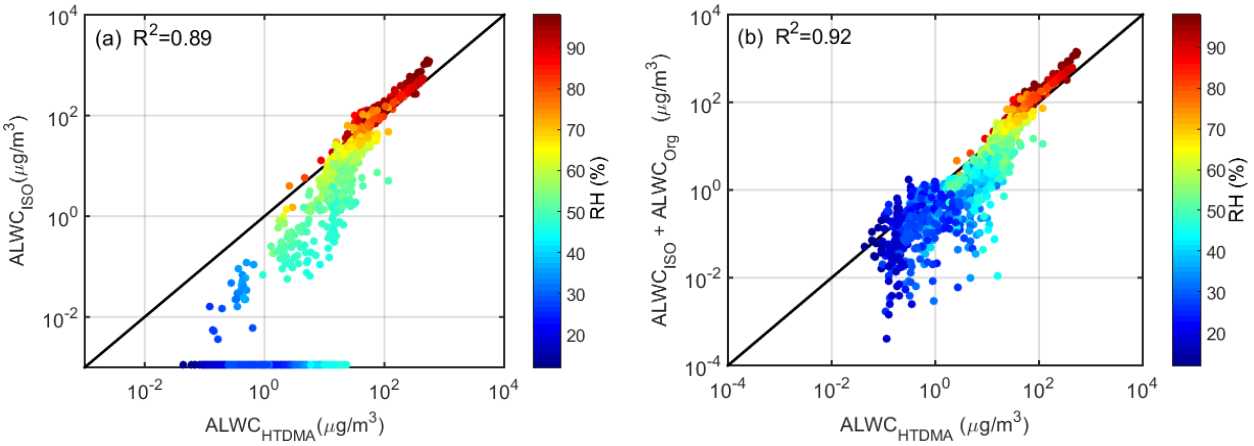

Figure 1. Comparison between $ALWC_{HTDMA}$ and (a) $ALWC_{ISO}$ and (b) the sum of $ALWC_{ISO}$ and $ALWC_{Org}$. $ALWC_{HTDMA}$ refers to calculated ALWC based on the measured growth factor and PNSDs, $ALWC_{ISO}$ refers to simulated ALWC from the ISORROPIA II model, and $ALWC_{Org}$ refers to the inferred ALWC contributed by organic species. The coefficient of determination R^2 is given in each panel. The color of the dots denotes the ambient RH; the solid line denotes the 1:1 line.

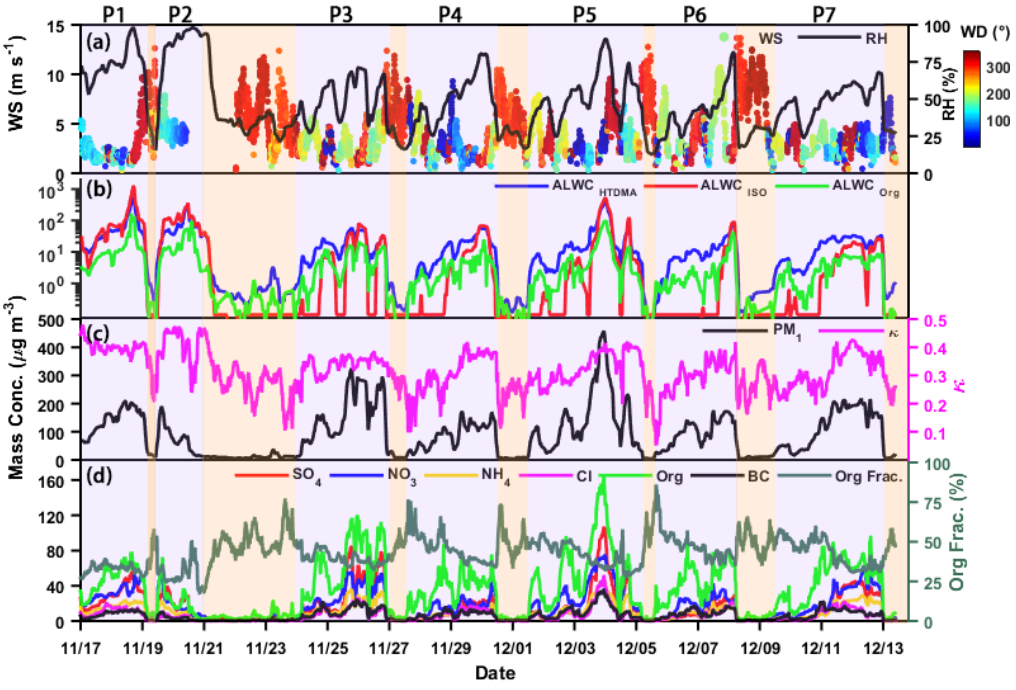

Figure 2. Time series of (a) wind speed (WS, left y-axis), ambient relative humidity (RH, right y-axis), and wind direction (WD, colored dots), (b) $ALWC_{HTDMA}$ (in blue), $ALWC_{ISO}$ (in red), and $ALWC_{Org}$ (in green), (c) PM_1 mass concentration (left y-axis) and hygroscopicity parameter (κ, right y-axis) calculated using the ZSR model described by Eq. (7), and (d) mass concentrations of aerosol species in PM_1 (left y-axis) and organic aerosol mass fraction

1059 **(right y-axis). Seven polluted episodes (segments of the time series with a purple background) are selected for**

1060 **examination.**

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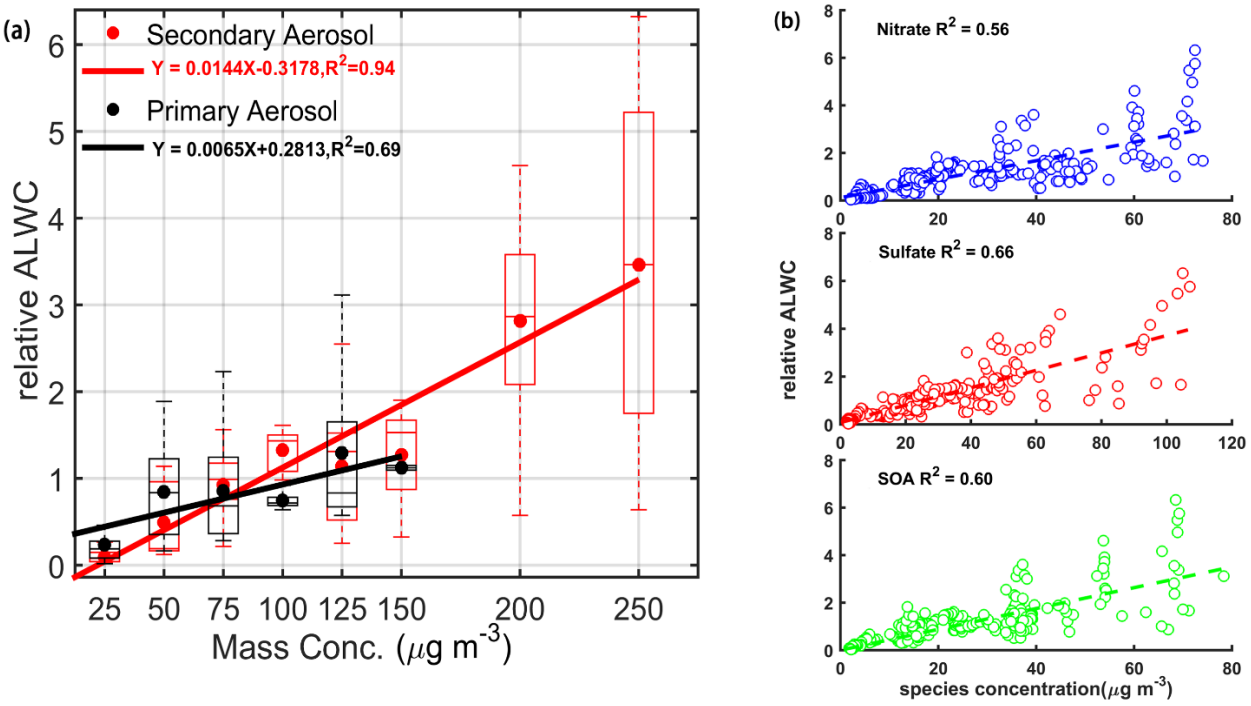

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1063 **Figure 3. The correlation analysis between relative ALWC and (a) primary (in black) and secondary (in red) aerosol**

1064 **mass concentrations, and (b) nitrate, sulfate, and secondary organic aerosol (SOA) mass concentrations. Panel (a)**

1065 **shows mean relative ALWCs (solid dots) with boxes showing the 25th, 50th, and 75th percentiles. The extremities**

1066 **show the 5th and 95th percentiles. The solid lines in (a) and the dashed lines in (b) both represent the corresponding**

1067 **best-fit lines from linear regression.**

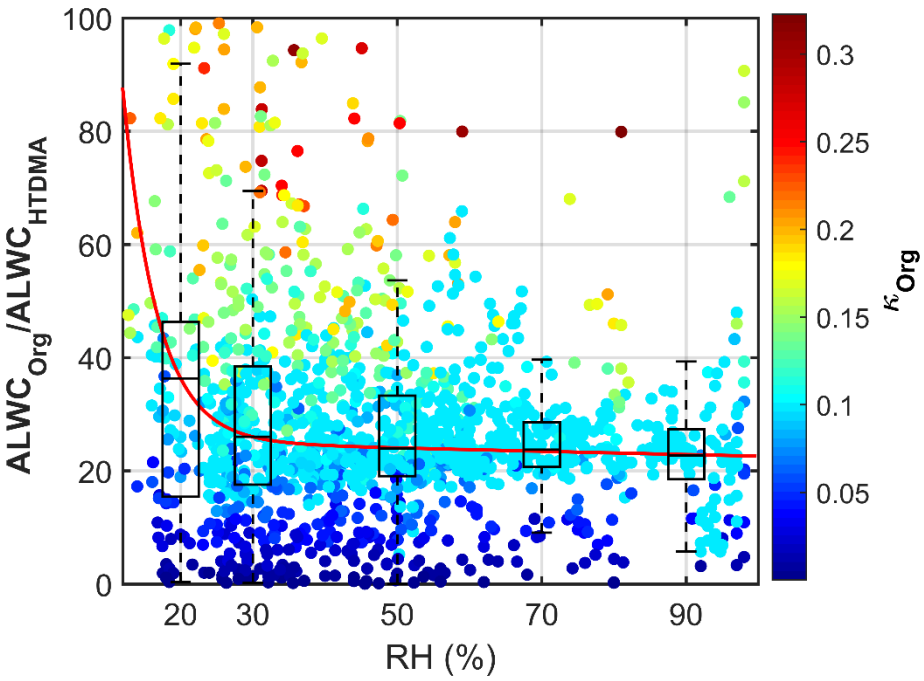

Figure 4. The variation of the fraction of $ALWC_{Org}$ in total ALWC ($ALWC_{HTDMA}$) with the ambient relative humidity (RH). The color of the dots denotes the hygroscopicity parameter of organics (κ_{Org}). The boxes show the fraction of $ALWC_{Org}$ with the 25th, 50th, and 75th percentiles. The extremities show the 5th and 95th percentiles. The red line shows the fitting curve with the function $y = ae^{bx}$.

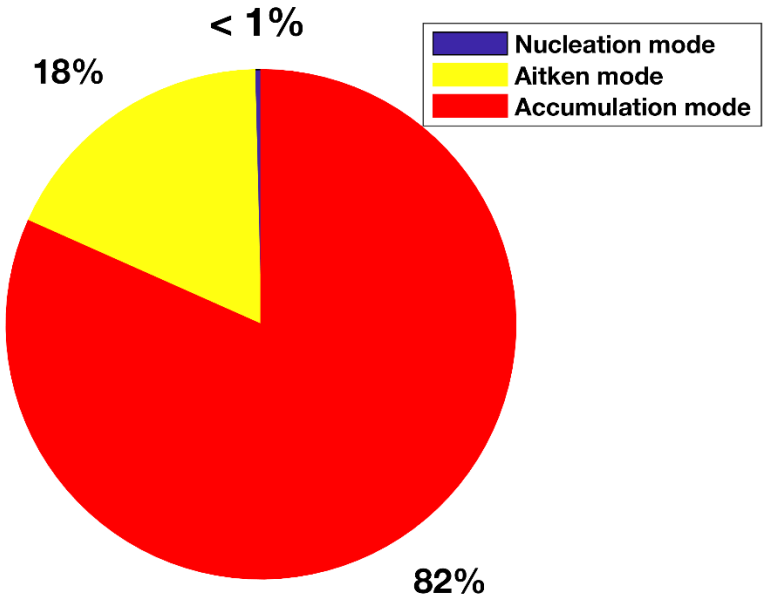

Figure 5. The contribution of particles different modes to $ALWC_{HTDMA}$

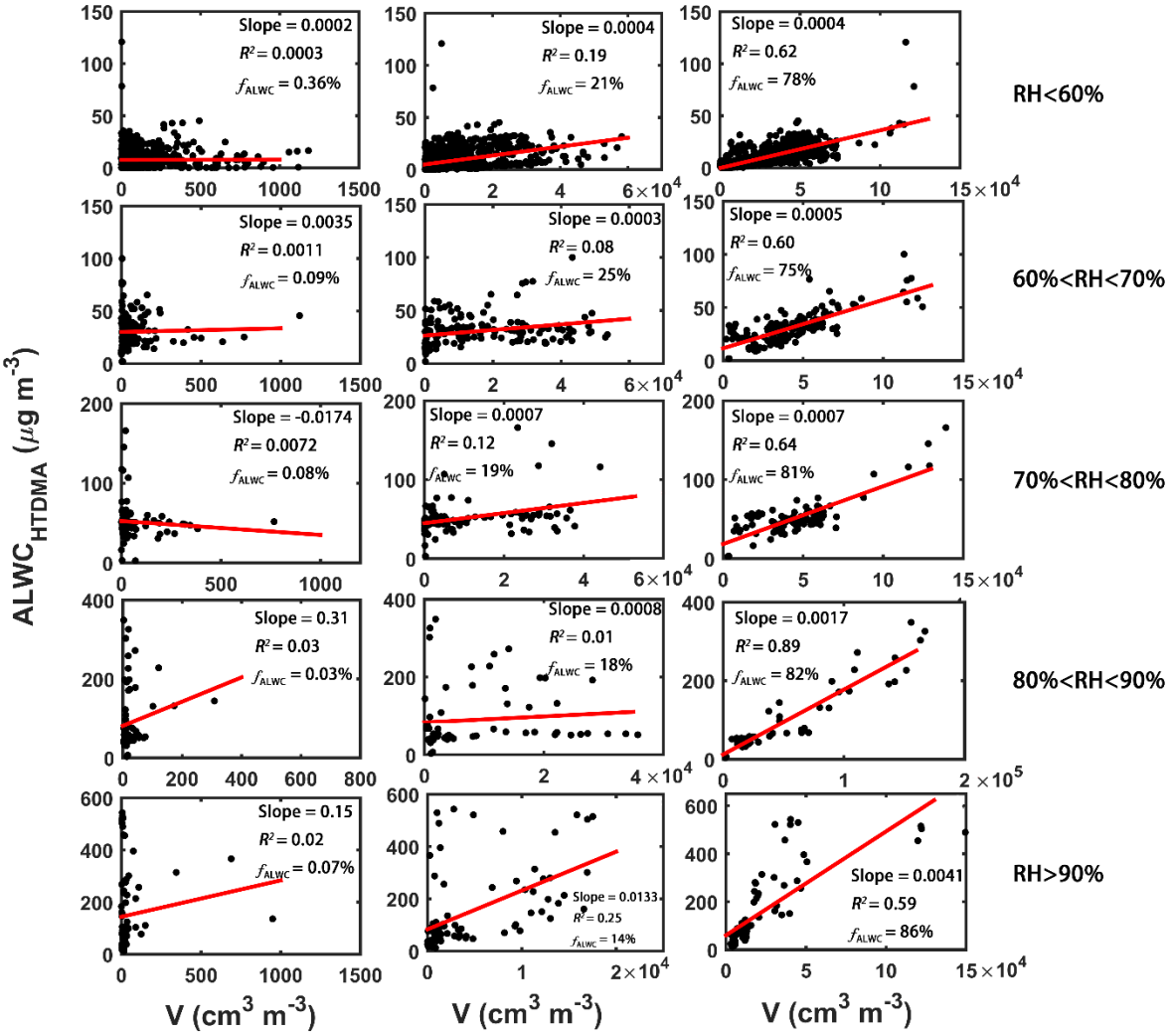

Figure 64. The correlation analysis between $ALWC_{HTDMA}$ and the volume concentration of nucleation mode (left column), Aitken mode (middle column), and accumulation mode (right column) particles under different ambient relative humidity (RH) conditions. The average contribution of each mode particles to ALWC under different ambient RH conditions is denoted by f_{ALWC}. The red lines represent the best-fit lines from linear regression.

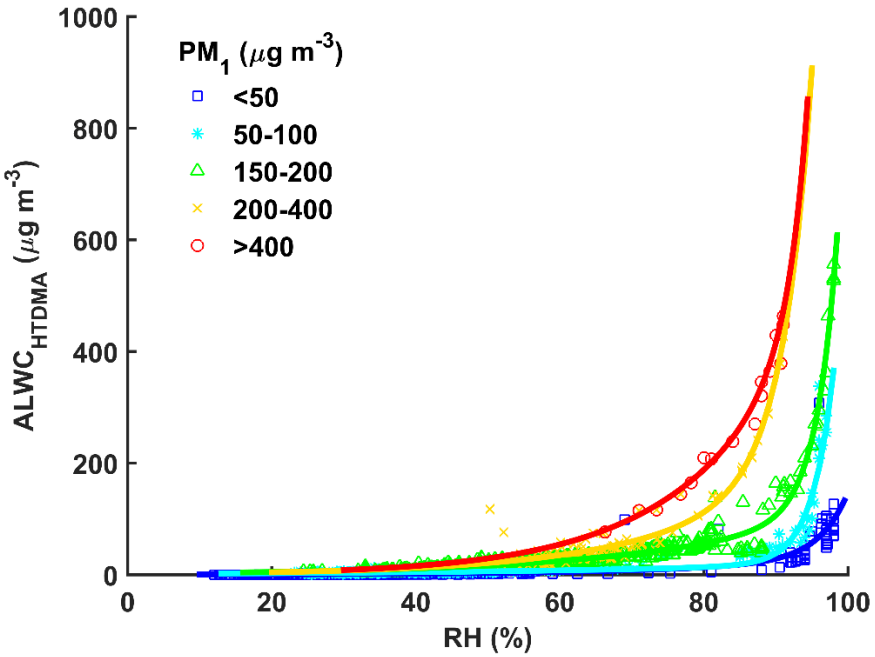

Figure 7~~5~~. The dots show how $ALWC_{HTDMA}$ varies with the ambient relative humidity (RH) for different PM_1 mass concentration ranges (colored symbols). The colored curves represent the best-fit lines through the data using the fitting function $y = ae^{bx}$.

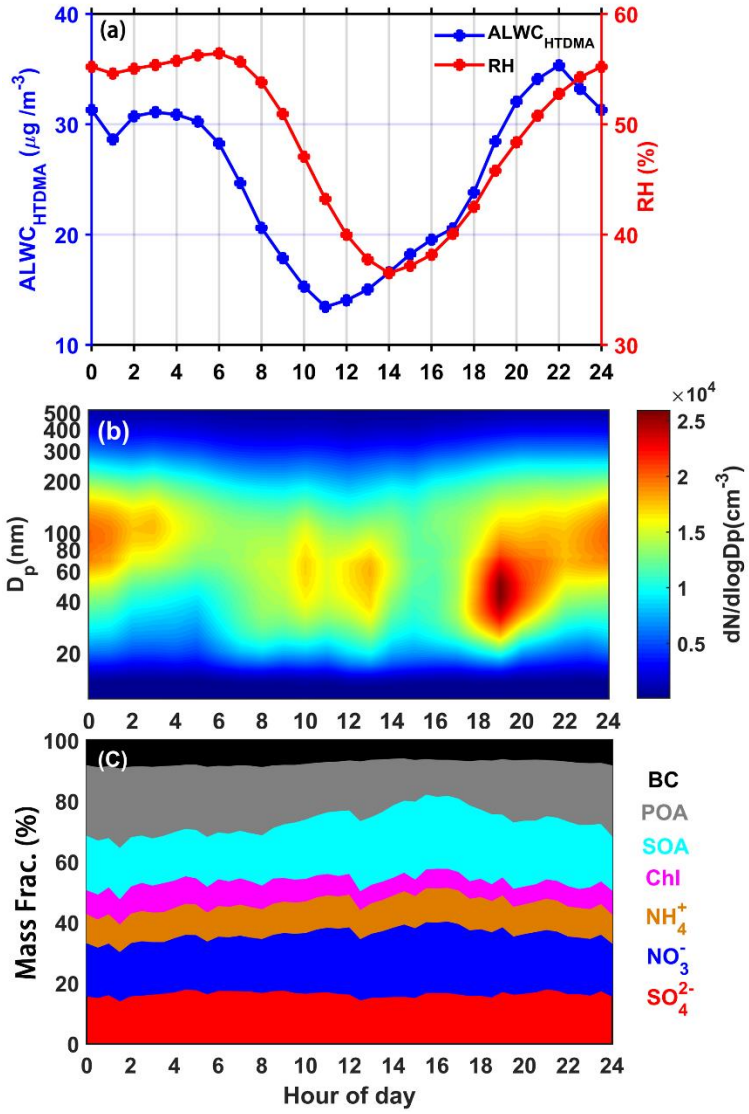

Figure 8~~6~~. Diurnal variations of (a) ALWC$_{HTDMA}$ (in blue) and ambient RH (in red), (b) particle number size distribution, and (c) the mass fraction of different chemical species. The time is in Beijing time.

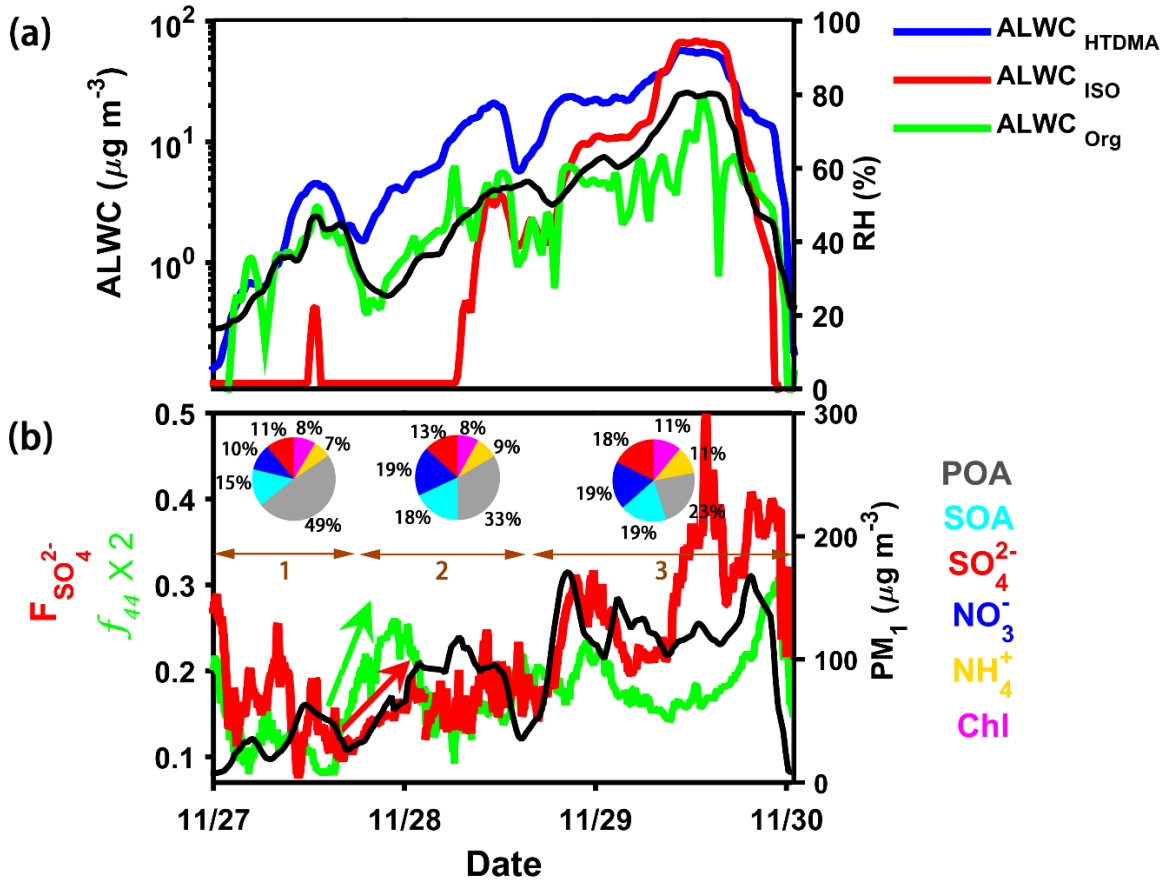

Figure 97. Time series of (a) $ALWC_{HTDMA}$ (in blue), $ALWC_{ISO}$ (in red), $ALWC_{Org}$ (in green), and RH (right y-axis), and (b) the sulfur oxidation ratio ($F_{SO4^{2-}}$), f_{44}, and PM_1 mass concentration (right y-axis) during the P4 case in Figure 2. The pie charts in (b) represent the average chemical compositions of PM_1 during three stages of the pollution event (denoted by brown horizontal lines). The red and green arrows in (b) indicate the rapid increase in $F_{SO4^{2-}}$ and f_{44} at the initial stage.