

Response to anonymous referee #1

General comments:

Aerosol hygroscopicity is closely related to cloud formation, visibility, and radiative forcing of aerosols. Although the hygroscopic properties of aerosols can be measured in detail using instruments, such as Hygroscopic Tandem Differential Mobility Analyzers (H-TDMA), parameterization methods are highly needed in view of the large spatio-temporal variability of aerosol hygroscopicity and the technical limitations in observations. The authors of this paper present aerosol hygroscopicity data derived from size-segregated chemical components obtained during the HaChi campaign in the North China Plain (NCP). Applying the κ -Köhler theory and the ZSR mixing rule, they have developed an iterative algorithm for calculating the hygroscopicity parameter (κ) from in-situ measurements and laboratory data. The values are obtained for 8 size ranges (0.03–8 μ m) and well consistent with those derived from the in-situ HH-TDMA measurements (0.05–0.25 μ m). Furthermore, the authors show an empirical relationship between and mass fractions of NH_4^+ , SO_4^{2-} , NO_3^- , and WSOC. An evaluation using data also from other Chinese sites suggests that this relationship may be used for parameterization. The topic of this paper is within the scope of ACP. The methods used in this paper are sound and novel. Assumptions made are valid. The results are of interest and valuable. The paper is well structured and written, and cites properly the related literature. I recommend publication of this paper in ACP after minor revisions.

Response: Thanks for the referee's comments. We have improved our work according to the referee's comments and suggestions.

Specific comments:

Comment:

1. P20898, L23-24, and P20905, L22-23, you show " NH_4NO_3 , H_2SO_4 , NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ " as if these compounds always co-exist. What is the real situation? Can H_2SO_4 exist at significant concentrations under summer conditions at the NCP rural site (higher NH_3 and lower SO_2 levels)? I strongly suggest that you make ion balance calculations to figure out the main co-existing ammonium salts since is different for different salts.

Response:

H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ can't coexist in the ambient particles as H_2SO_4 and SO_4^{2-} would react and produce HSO_4^- . We highlighted these four species in the manuscript because of their significant contribution to the particle hygroscopicity, while other inorganic salts have little contributions, which can be inferred from Fig. 6b of the manuscript.

Low concentration of SO_2 isn't equivalent to low concentration of SO_4^{2-} in the particulate matter. The concentration of SO_2 is relatively low in the summer (Xu, et al., 2011), while the concentration of SO_4^{2-} is very high according to our measurement. Other campaign studies report the similar results. (eg. Fig. 6 from Achtert et al., 2009) SO_2 is converted into SO_4^{2-} with the aid of OH radical, which is the most effective in

summer compared to in other seasons. Also, the high humidity condition in the summer facilitates the conversion of SO_2 through heterogeneous reactions.

We made the ion balance calculations according to the referee's suggestion (Fig. 1). If particles are acid, H_2SO_4 and NH_4HSO_4 exist in the particles. If particles are alkaline, $(\text{NH}_4)_2\text{SO}_4$ exists and no H_2SO_4 exists in the particles. We can see that particles are acid most of the time during the campaign, so H_2SO_4 can exist at a high concentration in the summer.

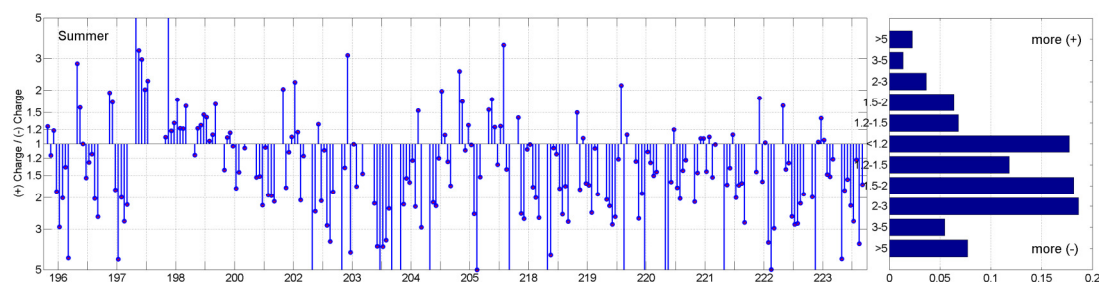


Figure 1 The ratio of positive charges to negative charges. If points are above the 1-to-1 line, particles are alkaline; if points are below the 1-to-1 line, particles are acid.

Reference:

Achtert, P., Birmili, W., Nowak, A., Wehner, B., Wiedensohler, A., Takegawa, N., Kondo, Y., Miyazaki, Y., Hu, M., and Zhu, T.: Hygroscopic growth of tropospheric particle number size distributions over the North China Plain, *J. Geophys. Res.-Atmos.*, 114, 2009.

Xu, W. Y., Zhao, C. S., Ran, L., Deng, Z. Z., Liu, P. F., Ma, N., Lin, W. L., Xu, X. B., Yan, P., He, X., Yu, J., Liang, W. D., and Chen, L. L.: Characteristics of pollutants and their correlation to meteorological conditions at a suburban site in the North China Plain, *Atmospheric Chemistry and Physics*, 11, 4353-4369, 10.5194/acp-11-4353-2011, 2011.

Comment:

2. P20890, L27, add diameter range after “stage 2-9”.

Response:

Thanks for your comment. We have added the diameter range “30nm-4 μm ” after “stage 2-9” following your comment and revised the manuscript.

Comment:

3. P20891, L21, please point out that S is equivalent to RH because you use RH instead of S in the description of iteration calculations (P20895).

Response:

Thanks. We have explicitly pointed out the equivalence of S and RH following your comment and revised the manuscript.

Comment:

4. P20891, L23, change “ T is the temperature” to “ T is the absolute temperature”.

Response:

Thanks. We have revised the manuscript following your suggestion.

Comment:

5. P20897, L3-8, the size distribution of OM seems to be very different from that found in Beijing (see, Sun et al., 2010). Any explanation?

Response:

Thanks for your comment. We've looked through the work by Sun et al. (2010) and found that the size distribution of OM in their work is similar to ours.

In P20897, L3-8 of our manuscript, we're talking about the mass fraction of OM. For fine particles, the mass fraction of OM is high. With increasing particle size, the fraction of OM decreases. But the shape of OM mass concentration is totally different from the shape of OM mass fraction. We draw a new figure here to compare our result with the result of Sun et al. (2010). Fig. 2 shows the distribution of mass concentration of four species in our work. All species including OM (green line) peak between 500-1000nm. In Fig. 3 (Fig. 6 from Sun et al., 2010), all species peak around 600nm. As the units for two y-axes are different, the absolute heights of the size distributions are not comparable. Taking the low size resolution of Berner Impactor into account, we consider the size distribution of OM in our work is similar to that in Sun et al. (2010).

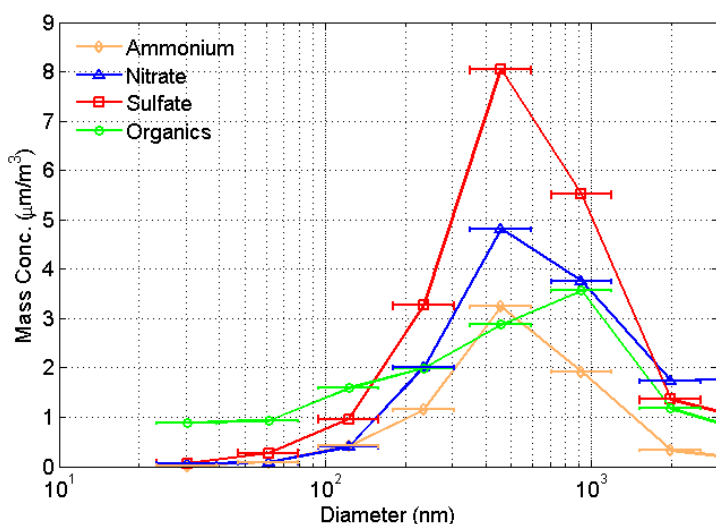


Figure 2 Size distributions of mass concentrations during “HaChi” Campaign. The error bar in horizontal orientation indicates the size range of each stage.

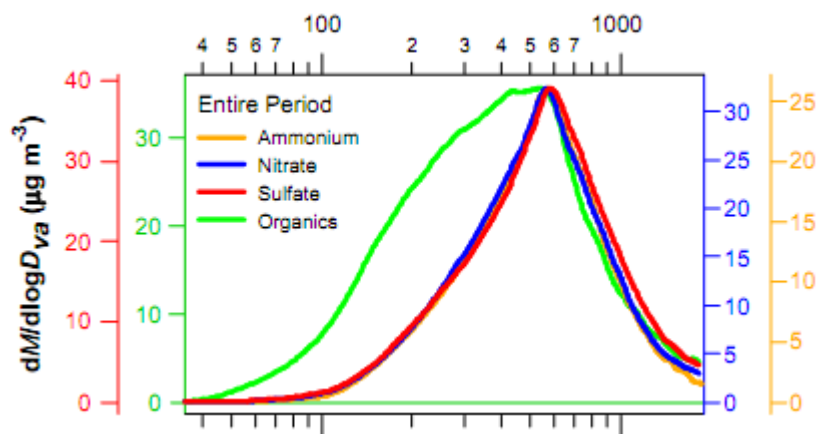


Figure 3 Size distributions of mass concentrations in July, 2006 in Beijing (Fig. 6 in Sun et al., 2010).

Reference:

Sun, J., Zhang, Q., Canagaratna, M. R., Zhang, Y., Ng, N. L., Sun, Y., Jayne, J. T., Zhang, X., Zhang, X., and Worsnop, D. R.: Highly time- and size-resolved characterization of submicron aerosol particles in Beijing using an Aerodyne Aerosol Mass Spectrometer, *Atmos. Environ.*, 44, 131-140, 2010.

Comment:

6. *P20899, L3-4, references are needed here.*

Response:

Thanks for your comment. We've explicitly indicated the origin of the value from Mader et al. (2004) in the manuscript.

Reference:

Mader, B. T., Yu, J. Z., Xu, J. H., Li, Q. F., Wu, W. S., Flagan, R. C., and Seinfeld, J. H.: Molecular composition of the water-soluble fraction of atmospheric carbonaceous aerosols collected during ACE-Asia, *J. Geophys. Res. -Atmos.*, 109, 2004.

Comment:

7. *A recent paper (Xing et al., 2013) can be cited regarding the OC to OM conversion.*

Response:

Thanks for your comment. Xing et al. (2013) calculated the OM/OC mass ratios with two different methods and reported the value of 1.59 and 1.68 in summertime Tianjin, which is close to the value of 1.6 used in our study. We have added this paper as a new reference to support our work and revised our manuscript.

Comment:

8. *Fig. 3, show also the "others" mass fraction on the bottom graph.*

Response:

Thanks. We accept your suggestion and redraw Fig. 4b in the manuscript (Fig. 3b in the discussion paper). The new figure is displayed below.

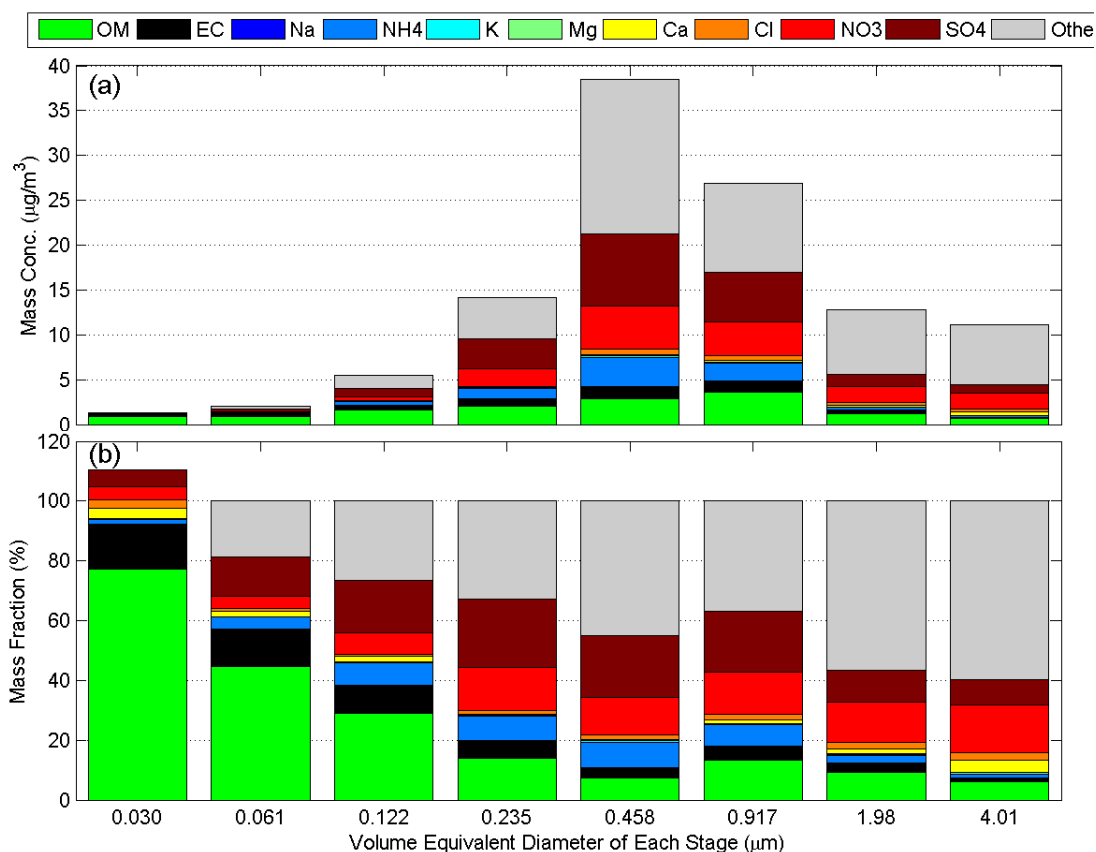


Figure 4 (Fig. 4 in the manuscript) The average size distributions of the particulate mass and the chemical composition during the HaChi campaign.

Comment:

9. Fig. 4, are the HGF-derived and Chemistry-derived values exactly from the same time period? Please make it clear.

Response:

Thanks for your comment. As BLPI and HH-TDMA didn't work continuously during the campaign, the two sets of values are not exactly from the same period. Fig. 5 shows the time series of valid measurements for two systems. Still, we consider the average values of the two sets are comparable.

The chemistry-derived values are from Berner Impactor with time resolution of 6 hours. The measurements distribute at the first 10 days and the last week of the campaign (Fig. 5) and covered half of the campaign period. The HGF-derived values are from HH-TDMA with time resolution of about 5 minutes. Measurements with HH-TDMA last for the entire campaign (Fig. 5). The mean values of both data sets can represent the average conditions in the summer and are comparable.

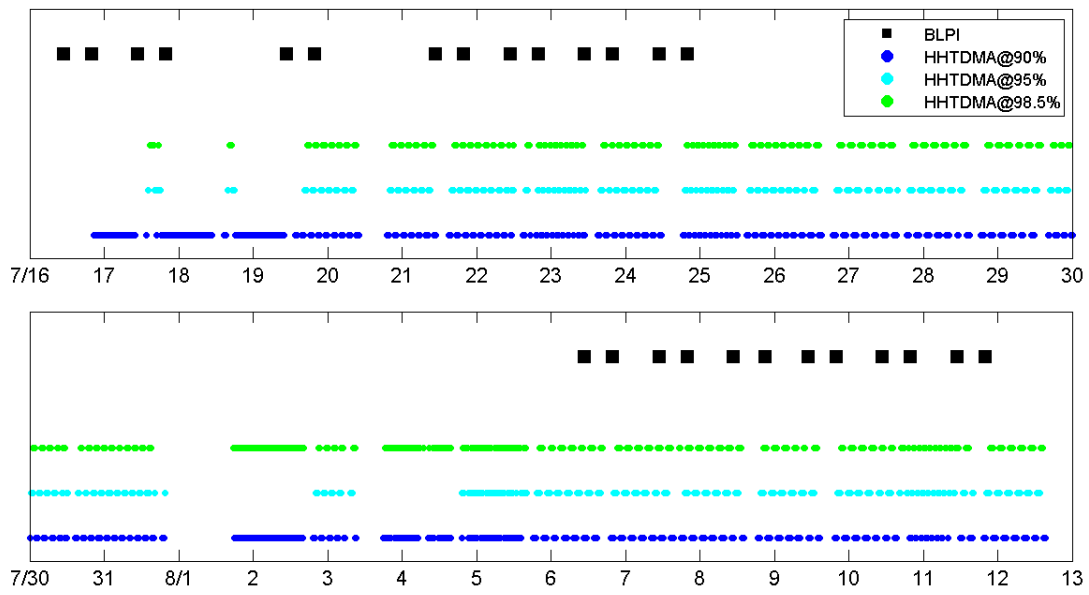


Figure 5 Time distribution of valid measurement for BLPI and HH-TDMA. Each point represents a set of data.

Comment:

10. Fig. 6, error bars should be included. In addition, significance tests should be made for the daytime-nighttime differences and included in the related discussions.

Response:

Thanks for your valuable comment. We have redrawn Fig. 7 in the manuscript (Fig. 6 in the discussion paper) with error bars included. Besides, we revised the discussions in Sect. 4.4 about the daytime-nighttime discrepancy with the help of the error bars.