

Anonymous Referee #1

Comment:

This paper examines the relationship between $f(\text{RH})$ determined from RH-controlled nephelometer measurements and attempts to relate these to aerosol chemical composition and transport pathways.

"Hygroscopic growth factors" are referred to in the title and various places in the paper. Hygroscopic growth factors $[D(\text{rh})/D(\text{dry})]$ were not measured. What was measured is $f(\text{RH}) - [B_{\text{sp}}(\text{rh})/B_{\text{sp}}(\text{dry})]$. References to hygroscopic growth factors should be removed and replaced with $f(\text{RH})$, which is enhancement of B_{sp} due to hygroscopic growth.

There is also a reference to deliquescence RH on p. 5095. There is no clear evidence for deliquescence in Fig. 4 and the conclusions state that $f(\text{RH})$ varied smoothly and monotonically.

There is a fundamental deficiency in the experimental design in that the nephelometers measured TSP while the chemistry presented represents PM_{2.1}. Table 5 shows that the PM_{2.1}/PM₁₁ ratio was 50% or less. Thus, the $f(\text{RH})$ must be depressed by the presence of a significant mass of large particles. The results are thus inconsistent with those of Day and Malm, for example, who used nephelometers preceded by size selective inlets.

It is difficult for the authors to obtain quantitative light scattering closure based on measured $f(\text{RH})$ and PM_{2.1} chemical composition. Because of the large coarse composition, the relationship between $f(\text{RH})$ and chemistry is more qualitative than quantitative. I suggest that the authors attempt to do some closure calculations to make the results more quantitative. They could use dry scattering efficiencies used in the IMPROVE equation, i.e., 3 m²/g for ammonium sulfate and ammonium nitrate, 4 for organic carbon mass, 1 m²/g for fine dust, and 0.6 m²/g for coarse material > 2.1 μm. The authors routinely use a factor of 1.4 to convert OC to OMC. This may be appropriate for fresh urban emissions but aged OMC should display a higher ratio, e.g., 1.8 (Pitchford et al., 2007, AWMA, 57, 1326-1336). Closure could be obtained if particles larger than 2.1 μm are composed of non-hygroscopic dust with $f(\text{RH}) = 1$. The case would be difficult for periods where there was a high proportion of coarse sea salt, which is very hygroscopic. The authors would have had a much better opportunity to explain $f(\text{RH})$ in terms of chemical composition had they used a size-selective inlet with their nephelometers.

The authors attempt to relate some cases of high $f(\text{RH}) > 2$ with high proportions of aged OMC. While authors such as Dinar et al. and Gysel et al. have shown that ambient organics are

hygroscopic, the measured growth factors were never high enough to produce an $f(\text{RH}) > 2$.

The authors thank you for your precious contribution for the paper improvement. Your comments could be divided into four parts, As follows:

Part 1:

"Hygroscopic growth factors" are referred to in the title and various places in the paper. Hygroscopic growth factors $[D(\text{rh})/D(\text{dry})]$ were not measured. What was measured is $f(\text{RH}) = [B_{\text{sp}}(\text{rh})/B_{\text{sp}}(\text{dry})]$. References to hygroscopic growth factors should be removed and replaced with $f(\text{RH})$, which is enhancement of B_{sp} due to hygroscopic growth.

Replay:

We greatly thank you for this important remark. We recognized the difference between the "Hygroscopic growth factors" $g(\text{RH}) = [D(\text{rh})/D(\text{dry})]$ and $f(\text{RH}) = [B_{\text{sp}}(\text{rh})/B_{\text{sp}}(\text{dry})]$, and have replaced the term "hygroscopic growth factors" by hygroscopic growth factor of aerosol scattering coefficient $f(\text{RH})$ in the latest revised manuscript accordingly.

Part 2:

There is also a reference to deliquescence RH on p.5095. There is no clear evidence for deliquescence in Fig. 4 and the conclusions state that $f(\text{RH})$ varied smoothly and monotonically.

Replay:

As the referee pointed out, it was inappropriate to use the word "deliquescent RH" because the fitting $f(\text{RH})$ curves did not show clear "leap feature" behavior during aerosols growth, this has been corrected in the revised manuscript.

Part 3:

There is a fundamental deficiency in the experimental design in that the nephelometers measured TSP while the chemistry presented represents PM_{2.1}. Table 5 shows that the PM_{2.1}/PM₁₁ ratio was 50% or less. Thus, the $f(\text{RH})$ must be depressed by the presence of a significant mass of large particles. The results are thus inconsistent with those of Day and Malm. I suggest that the authors attempt to do some closure calculations to make the results more quantitative. Closure could be obtained if particles larger than 2.1 μm are composed of non-hygroscopic dust with $f(\text{RH}) = 1$. The case would be difficult for periods where there was a

high proportion of coarse sea salt, which is very hygroscopic.

Replay:

We agree to the referee that relationship between $f(\text{RH})$ of TSP and PM_{2.1} chemical composition is more qualitative than quantitative in the presence of large portion of coarse composition. According to your suggestion, we performed scattering closure calculations using both IMPROVE equation and Mie scattering theory coupled with size-segregated aerosol chemical compositions. Furthermore, according to calculations, we found that the influence of sea salt was weak. This confirmed your viewpoint. The results will be added into the manuscript.

Part 4:

The authors attempt to relate some cases of high $f(\text{RH}) > 2$ with high proportions of aged OMC. While authors such as Dinar et al. and Gysel et al. have shown that ambient organics are hygroscopic, the measured growth factors were never high enough to produce an $f(\text{RH}) > 2$.

Replay:

Thank you so much for this remark. For proper design control during the experiment, we have applied strictly the quality control procedure (SOP) to the operation of the instrument. The zero check was done automatically by pumping in particle-free air once each day, and weekly span check was performed manually using pure HFC-134a gas. The results of the zero/span check indicated that the bias for zero check was less than 2 Mm⁻¹, and less than 5% for span check. There was no evidence indicating that the nephelometer doesn't work well on this day (May 15th). In addition, the mean $f(\text{RH} < 40\%)$ for these days was around 0.99 ~ 1.01, and the constructed scattering coefficient based on aerosol compositions could account for about 88% of measured ones for May 15th. All indicated the two nephelometers were in good conditions and the results were reliable.

Therefore, we agree that it's difficult to explain such high hygroscopic properties of aerosol in terms of the fraction of aged organic matters. Nevertheless, such a phenomenon was also found in previous works (Day et al., 2000; Kotchenruther et al., 1999), and seemed to be due to mixing aerosols process(Choi et al., 2002; Cruz et al., 2000; Hameri et al., 2002; Huang et al., 2005; Saxena et al., 1995), further discussions about this strong hygroscopicity will be conducted in the revised manuscript.

Reference:

Choi M Y and Chan C K 2002.The effects of organic species on the hygroscopic behaviors of inorganic aerosols. Environ. Sci. Technol.[J] 36(11): 2422-2428.

Cruz C N and Pandis S N 2000.Deliquescence and Hygroscopic Growth of Mixed Inorganic? Organic Atmospheric Aerosol. Environ. Sci. Technol.[J] 34(20): 4313-4319.

Day D E, Malm W C and Kreidenweis S M 2000.Aerosol light scattering measurements as a function of relative humidity. J Air Waste Manag Assoc.[J] 50(5): 710-6.

Hameri K, Charlson R and Hansson H C 2002.Hygroscopic properties of mixed ammonium sulfate and carboxylic acids particles. AIChE Journal.[J] 48(6).

Huang X F, Hu M, He L Y, et al. 2005.Chemical characterization of water-soluble organic acids in PM_{2.5} in Beijing, China. Atmospheric Environment.[J] 39(16): 2819-2827.

Kotchenruther R A, Hobbs P V and Hegg D A 1999.Humidification factors for atmospheric aerosols off the mid-Atlantic coast of the United States. Journal of Geophysical Research.[J] 104(D2): 2239-2252.

Saxena P, Hildemann L M, McMurry P H, et al. 1995.Organics alter hygroscopic behavior of atmospheric particles. Journal of Geophysical Research-Atmospheres.[J] 100(D9).

Anonymous Referee #2

Comment:

The work published by Pan et al. reports observational results from the hygroscopic behaviors of atmospheric aerosol in the vicinity of Beijing mega-city. The dependence of the aerosol scattering coefficient on relative humidity is investigated, and potential links to the aerosol source region and to aerosol chemical composition are studied. The impact of aerosol chemistry and the resulting hygroscopic behaviors and particle optical properties still requires a broadening of the experimental data base although research started in the early 1970s and 1980s (Covert et al., 1972; Fenn et al., 1981).

The paper reports results from multi-stage impactor analyses on particle chemical composition restricted to a particle size range PM 2.1. Aerosol scattering properties are reported from a humidified nephelometer operated at RH = 80%. The nephelometer sampled from the total aerosol (PM 11). The authors used the term aerosol hygroscopic growth factors although they analyzed modifications of the aerosol scattering coefficient with humidity. A more precise terminology is required here. Furthermore, a more detailed description of the experimental procedure is needed.

Aerosol humidification function values for the aerosol scattering coefficient vary from values reported in the literature. The authors identified this deviation without giving potential explanations. In particular, high values of the order of 2.2 were found for two episodes which are assumed to have a strong urban aerosol impact, however without showing higher ratios of organic matter to ammonium sulfate. Such high humidity growth function values at RH = 80% are neither found in laboratory and field studies on aerosol hygroscopic growth (McFiggans et al., 2006; Gysel et al., 2007; Massling et al., 2007), nor in a recent numerical analysis of humidification effects on aerosol optical properties in the Pearl River delta in China (Cheng et al., 2008). The authors should revisit this discrepancy.

A general difficulty concerning this publication is the fact, that chemical composition and aerosol scattering coefficients are reported for completely different size ranges which makes a consistent data interpretation almost impossible. Following Table 1, mass concentrations between PM 2.1 and PM 11 varied by a

factor of 2.6 on average, and by a factor of 3.9 at maximum.

In Table 5, the authors expand the relationship between chemical composition and aerosol light scattering. This table requires further explanation because in particular the column on PM 2.1 / PM 11 is found confusing. In general, no significant correlation is found between composition and optical properties modification by humidity growth.

In its current form, the results presented in the paper are not very valuable. The major limitation arises from the fact that chemical composition and aerosol optical properties are reported for different particle size ranges. Furthermore, no particle size distribution information is reported although it should be available from the impactor data. Having at least the mass size distribution available for different chemical species should allow performing model calculations on the expected variation of aerosol scattering with relative humidity based on the chemical composition. The authors are encouraged to conduct this step of theoretical interpretation of observational data in order to make their case stronger.

The authors thank you for your precious contribution for the paper improvement. Your comments could be divided into four parts, As follows:

Part 1:

A more precise terminology is required here, and a more detailed description of the experimental procedure is needed.

Replay:

Great thanks for your precious advises. As you suggested, more precise terminological expression of aerosol hygroscopic growth should be used, for instance, the “hygroscopic growth factor of aerosol scattering coefficient $f(RH)$ ” will be utilized instead of hygroscopic growth factor in order to avoid confusing $f(RH)$ and $g(RH)$. In some previous papers, the light wavelength information was also involved in the hygroscopic growth factor of scattering, as $f(80\%, 525\text{nm})$, this will be corrected in the manuscript. And detailed descriptions of experimental procedures are added in the manuscript.

Part 2:

Aerosol humidification function values for the aerosol scattering coefficient vary from values reported in the literature. The authors identified this deviation without giving potential explanations.

Replay:

Yes, you are right. In the revised manuscript, we have compared our findings with many previous works in order to make insights into aerosols scattering humidification function variations.

Part 3:

In particular, high values of the order of 2.2 were found for two episodes which are assumed to have a strong urban aerosol impact, however without showing higher ratios of organic matter to ammonium sulfate. Such high humidity growth function values at RH = 80% are neither found in laboratory and field studies on aerosol hygroscopic growth (McFiggans et al., 2006; Gysel et al., 2007; Massling et al., 2007), nor in a recent numerical analysis of humidification effects on aerosol optical properties in the Pearl River delta in China (Cheng et al., 2008). The authors should revisit this discrepancy.

Replay:

Thank you so much for this remark. During the experiment, we have applied strictly the quality control procedure (SOP) to the operation of the instrument. The zero check was done automatically by pumping in particle-free air once each day, and weekly span check was performed manually using pure HFC-134a gas. The results of the zero/span check indicated that the bias for zero check was less than 2 Mm⁻¹, and less than 5% for span check. There was no evidence indicating that the nephelometer doesn't work well on this day (May 15th). In addition, the mean $f(RH < 40\%)$ for these days was around 0.99 ~ 1.01, and the constructed scattering coefficient based on aerosol compositions could account for about 88% of measured ones for May 15th. All indicated the two nephelometers were in good conditions and the results were reliable.

Therefore, we agree that it's difficult to explain such high hygroscopic properties of aerosol in terms of the fraction of aged organic matters, as mentioned in the

previous manuscript. Nevertheless, such a phenomenon was also found in previous works (Day et al., 2000; Kotchenruther et al., 1999), and seemed to be due to mixing aerosols process (Choi et al., 2002; Cruz et al., 2000; Hameri et al., 2002; Huang et al., 2005; Saxena et al., 1995), further discussions about this strong hygroscopicity will be conducted in the revised manuscript.

Part 4:

Chemical composition and aerosol scattering coefficients are reported for completely different size ranges which makes a consistent data interpretation almost impossible. The major limitation arises from the fact that chemical composition and aerosol optical properties are reported for different particle size ranges. Furthermore, no particle size distribution information is reported although it should be available from the impactor data. Having at least the mass size distribution available for different chemical species should allow performing model calculations on the expected variation of aerosol scattering with relative humidity based on the chemical composition.

Replay:

We agree with you. In the preview manuscript, we did not provide complete information concerning aerosols chemical composition and scattering coefficients for data consistent interpretation. This has been corrected in the revised paper, and we provide information about particles size distribution and model results. We performed modeling experiment by using **IMPROVE equation and Mie theory**.

Reference:

- Choi M Y and Chan C K 2002.The effects of organic species on the hygroscopic behaviors of inorganic aerosols. Environ. Sci. Technol.[J] 36(11): 2422-2428.
- Cruz C N and Pandis S N 2000.Deliquescence and Hygroscopic Growth of Mixed Inorganic? Organic Atmospheric Aerosol. Environ. Sci. Technol.[J] 34(20): 4313-4319.
- Day D E, Malm W C and Kreidenweis S M 2000.Aerosol light scattering measurements as a function of relative humidity. J Air Waste Manag Assoc.[J] 50(5): 710-6.

- Hameri K, Charlson R and Hansson H C 2002. Hygroscopic properties of mixed ammonium sulfate and carboxylic acids particles. *AIChE Journal*. [J] 48(6).
- Huang X F, Hu M, He L Y, et al. 2005. Chemical characterization of water-soluble organic acids in PM_{2.5} in Beijing, China. *Atmospheric Environment*. [J] 39(16): 2819-2827.
- Kotchenruther R A, Hobbs P V and Hegg D A 1999. Humidification factors for atmospheric aerosols off the mid-Atlantic coast of the United States. *Journal of Geophysical Research*. [J] 104(D2): 2239-2252.
- Saxena P, Hildemann L M, McMurry P H, et al. 1995. Organics alter hygroscopic behavior of atmospheric particles. *Journal of Geophysical Research-Atmospheres*. [J] 100(D9).