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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Insight into winter haze formation mechanisms based on aerosol hygroscopicity and effective density measurements" *by* Yuanyuan Xie et al.

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Anonymous Referee #2 Received and published: 28 February 2017 In this study, aerosol measurements were performed over about three weeks during winter to understand the causes of severe haze pollution in Shanghai. The measured aerosol properties include particle size distributions, hygroscopicity, effective density, and chemical composition. From the analysis of aerosols, trace gases, and meteorological data, it is concluded that the particle pollution events are caused by the accumulation of local emissions under stagnant meteorological conditions and exacerbated by rapid particle growth via secondary processes. Overall, the study is well executed, data analysis is mostly appropriate, and the paper is reasonably well written. I believe that it would

be beneficial to extend the analysis to include several other effects, as detailed below. Also, a number of minor issues need to be addressed before the paper can be accepted for publication. A recent publication by Wang, G., et al. (Persistent sulfate formation from London Fog to Chinese haze. Proc. Natl. Acad. Sci. USA 2016, 113 (48), 13630-13635) has shown that in two other major Chinese cities the aqueous oxidation of SO2 by NO2 in the absence of light can lead to efficient sulfate formation on fine aerosols. The process requires high relative humidity and the presence of NH3. It is suggested that in heavily polluted environments, this heterogeneous process can form large amounts of particulate sulfate and nitrate in aqueous particles. Do you have photoactinic light intensity measurements to evaluate the relative contributions from photochemical and dark reactions leading to the particle growth? Were ammonia measurements available for the study period? Can you use particle hygroscopicity measurements reported in your study to derive aerosol state (aqueous/dry) and relate with the particle growth rates? Doing so would bring this study to an entirely new level.

Answer: We sincerely thanks you for your pertinent comments and valuable suggestions. The publication by Wang et al (2016) provided a new insight into night formation mechanisms of PM2.5 and pointed out us the research direction in the future. However, the correlation between particle growth rate and aerosol water content cannot be obtained in this study, because RH-dependent hygroscopic growth was not measured in the observation.

The authors should at least attempt to explain the 5-day cycle. Was it related to the workweek/weekend cycle or something else?

Answer: The periodic PM episodes are really unrelated to weekend cycles. Detailed description has been added: During the end of each PM episode, the change in weather conditions played a key role in the decrease of particle concentration. As shown in Figure S1, the prevailing winds on haze days were from the northwest. The prevailing winds during two clean periods (December 25-27 and January 12-14) were northeasterly, which bring clean air mass from East China Sea. Two cold fronts from

the north swept Shanghai on December 31 and January 6, bringing gale and lower temperature, which favored the dispersion of atmospheric pollutants.

Minor comments: L11: Particulate matter (PM) and haze are not synonymous, strictly speaking. The former term is typically used to describe aqueous aerosol particles (deliquesced, but not cloud droplets). These two terms cannot be interchanged; such use creates confusion. I suggest revising the use of haze and PM in the abstract and throughout entire manuscript.

Answer: I agree with you that particulate matter and haze are not the same. Particulate matter (PM) are microscopic solid or liquid matter suspended in the atmosphere (https://en.wikipedia.org/wiki/Particulates). Generally, haze pollution in china is defined as visibility decrease caused by the increase of fine particulate matter. To avoid confusion, the term “haze episode” was replaced by “haze event” in the revised manuscript.

L15: This sentence may become clearer if re-written as follows: “The mass ratio of SNA/PM1.0 (sulfate, nitrate, and ammonium) fluctuated only slightly around 0.28, suggesting that both secondary inorganic compounds and carbonaceous aerosols contributed substantially to the haze formation, regardless of pollution level.” Also, the original sentence implies that all of the non-SNA material is carbonaceous. Perhaps this must be stated explicitly.

Answer: This sentence has been revised following your suggestions.

L77: This statement implies that all traffic particles are soot aggregates, which is not correct

Answer: The nascent larger traffic particles are aggregates of primary particles with varying content of semi-volatile material. To avoid confusion, the sentence has been revised as “The effective density of nascent traffic particles varies from approximately 0.9 g cm-3 to below 0.4 g cm-3, decreasing with the increase of particle size, because there are more voids between primary particles in relatively larger aggregates

(Momenimovahed and Olfert, 2015).”

L78: Do the authors refer to material density or effective density?

Answer: Effective density. Revised.

L85: Must be ‘cascade impactor’ here and throughout the rest of the manuscript

Answer: All of them has been revised following your suggestions.

L87: Mass spectrometry is used to measure the particle composition, which is used to infer the particle hygroscopicity and density.

Answer: We have not determined the particle hygroscopicity and density by method of chemical closure in this study. Information on particle composition measured in this study can provide some explanation to the variations of particle hygroscopicity and density. The statement has been revised as “cascade impactor samples were collected and temporal variations of particle composition were determined by a single particle mass spectrometry, which provided further insight into the hygroscopicity and density variations.”

L112: HTDMA does not measure the particle number size distribution

Answer: Our HTDMA has the function of SMPS. Detail information on this HTDMA can see Ye et al., A multifunctional HTDMA system with a robust temperature control, Advances in Atmospheric Sciences, 26 (2009)1235-1240.

L132: ‘. . .Mass SpectrometER’

Answer: The official name is Single Particle Aerosol Mass Spectrometry.

L166: these values must be rounded off, e.g., 57 +/- 37

Answer: Thanks for your suggestions, the sentence has been revised as “The average concentrations of PM1.0, PM2.5, and PM10 were 57 ïĆś 37, 87 ïĆś 67, and 129 ïĆś78 ïĄg m-3, respectively.”

L175: what does ‘late’ refer to?

Answer: The statement has been revised as “During the end of each episode”.

L188: This sentence is confusing because it compares the contribution from a chemical (NOx) with that from a source of a chemical (presumably SO2) – coal-fired power plants. Also, doesn’t coal combustion release NOx as well? The authors must provide data showing that traffic contributes more to the NOx burden than the power plants and other industrial sources that utilize coal.

Answer: Indeed, coal combustion release NOx, although NOx emission decreased significantly due to the full implement of flue gas deNOx in power plants. To avoid confusion, the statement has been revised as “This indicated that NOx contributed more to haze formation in Shanghai compared to SO2.”

L194: what does ‘their’ refer to?

Answer: The statement has been revised as “due to different atmospheric lifetimes among SO2, NOx, and VOCs”.

L195: Isn’t sulfate also of secondary origin?

Answer: Sulfate is certainly of secondary origin. However, regional transport is a big source of SO2. So, sulfate is excluded from secondary transformation of local emissions.

L209: The meaning of this sentence is unclear. Why was hygroscopicity limited to smaller sizes? Do you mean ‘measurements were limited to sizes smaller than 250 nm’?

Answer: The statements has been revised as “Generally, HTDMAs measure dry particles smaller than 300 nm due to technical limitations, and it is common that particle hygroscopicity increases with increase of particle size (Liu et al., 2014;Swietlicki et al., 2008).”

L226: replace ‘contradictory’ with ‘opposite’

Answer: Revised.

L240: Insert a reference to Figure 2 early on in this paragraph

Answer: Revised as “As shown in Figure 2”.

L282: Not all VOCs react with ozone. Can you provide data on the concentration of unsaturated organics?

Answer: The concentration of unsaturated organics is not available in this studies.

L286: ‘. . .were less- and some that were more’ - what?

Answer: The statement has been revised as ”the nearly-hydrophobic particles were externally mixed with some hygroscopic particles”.

L304 and several other instances: ‘less-massive’ – did you mean ‘lower density’?

Answer: the term ‘lower density’ is replaced by ‘less-massive’ in the revised manuscript.

L381: ‘. . .contributed substantially. . .because the . . .ratio was almost constant. . .’ – this is an invalid argument. The second part does not follow from the first part.

Answer: The statement has been revised as “Both secondary inorganic salts and carbonaceous aerosols contributed substantially to haze formation, because the mass ratio of SNA/PM1.0 fluctuated slightly around 0.28 during the observation period.”

Figure 2: explain in figure caption the meaning of the dashed line

Answer: Revised.

Figure 3: What is ‘SIA’ in figure legend. Use a secondary Y-axis for the SIA/PM ratio

Answer: Revised following your suggestions.

Reference: Liu, H. J., Zhao, C. S., Nekat, B., Ma, N., Wiedensohler, A., van Pinxteren, D., Spindler, G., Müller, K., and Herrmann, H.: Aerosol hygroscopicity derived from size-segregated chemical composition and its parameterization in the North China Plain, Atmospheric Chemistry and Physics, 14, 2525-2539, 10.5194/acp-14-2525-2014, 2014. Momenimovahed, A., and Olfert, J. S.: Effective density and volatility of particles emitted from gasoline direct injection vehicles and implications for particle mass measurement, Aerosol Sci. Technol., 49, 1051-1062, 10.1080/02786826.2015.1094181, 2015. Swietlicki, E., Hansson, H. C., Hameri, K., Svenningsson, B., Massling, A., McFiggans, G., McMurry, P. H., Petaja, T., Tunved, P., Gysel, M., Topping, D., Weingartner, E., Baltensperger, U., Rissler, J., Wiedensohler, A., and Kulmala, M.: Hygroscopic properties of submicrometer atmospheric aerosol particles measured with H-TDMA instruments in various environments - a review, Tellus Ser. B-Chem. Phys. Meteorol., 60, 432-469, 10.1111/j.1600-0889.2008.00350.x, 2008.

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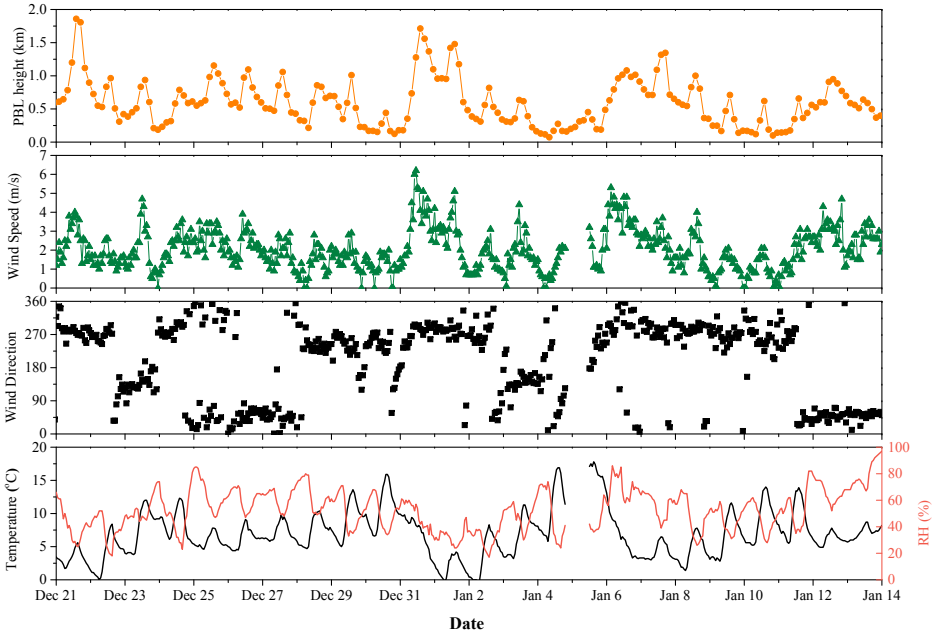

Fig. 1. Figure S1