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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Strong atmospheric new particle formation in winter, urban Shanghai, China" *by* S. Xiao et al.

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"Strong Atmospheric New Particle Formation in Winter, Urban Shanghai, China" (acp-2014-719) by Shan XIAO, Mingyi WANG, Lei YAO, Markku Kulmala, Bin ZHOU, Xin YANG, Jianmin CHEN, Dongfang WANG, Qingyan FU, Douglas R. Worsnop, and Lin WANG

We are grateful to the helpful comments from the anonymous referees, and have carefully revised our manuscript accordingly. A point-to-point response to the reviewers' comments, which are repeated in italic, is given below.

Anonymous Referee #1

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Interactive Discussion

Discussion Paper

This paper reports on field measurements of new particle formation in the urban atmosphere of Shanghai. The concentrations of clusters and nanoparticles along with concentrations of potential nucleation precursors obtained during the field campaign are used to derive the nucleation and growth rates. Conclusions are made regarding the different factors that govern the nucleation and growth mechanisms. This study provides substantial data that will help to understand mechanistic details and identify the sources of secondary aerosols in China, where aerosol pollution is severe but its causes are not understood. A major deficiency of this paper is that presented data do not always substantiate the conclusions and interpretations; also, some crucial statistical information is missing. These deficiencies need to be addressed before the manuscript can be considered for publication.

Major points:

1. As presented, the paper lacks clear focus. It will be beneficial to list scientific questions that were to be addressed by the field campaign.

Reply: A new paragraph has been added to clearly present the scientific goals of this field campaign, which reads (L93-106),

Direct measurements of atmospheric nucleation rates down to 1.5 ± 0.4 nm provide a better and more accurate characterization of atmospheric nucleation, since the indirect calculation of atmospheric nucleation rates from the formation rates of 3 nm particles leads to substantial uncertainty due to our incomplete understanding of condensational growth and coagulation scavenging of particles in the 1.5 to 3 nm range (Anttila et al., 2010; Korhonen et al., 2011). With the growing number of reports of real nucleation rates in clean atmosphere (e.g., Kulmala et al., 2012; Yu et al., 2014), it is ideal to measure nucleation rates in a polluted urban atmosphere to find out how atmospheric nucleation rates vary under different atmospheric conditions. In addition, the nucleation mechanism in a polluted urban atmosphere that is vital to understand atmospheric nucleation at a global scale and for atmospheric model development can be preliminarily

ACPD
14, C10740–C10751, 2015

investigated by examining the relationship between the measured atmospheric nucleation rates and the well-accepted precursor gases that exist in high concentrations.

In addition, we have revised the abstract to present the main scientific findings of this study (L30-31).

2. Based on the slope (L359-367), authors conclude that the nucleation of new particles can be explained by the activation theory. However, no standard deviation of the slope is given anywhere in the article. In fact, Figure 4 shows very poor correlation between the nucleation rate and sulfuric acid concentration, so the reported value of 0.64 could be significantly higher or lower. This needs to be addressed. Similarly, the standard deviation must be provided for the slope obtained from Figure 5 for ammonia. What is the uncertainty in the calculation of proxy sulfuric acid concentration? Is daytime average sulfuric acid proxy a good metric for producing Figure 4? Maybe better use the peak concentration?

Reply: According to Mikkonen et al. study (2011), the uncertainty for the calculation of sulfuric acid proxy is 42%. We have now added the error bars of the sulfuric acid proxy in Figure 4, and clearly stated in our experimental session that (L231-233) "The relative error between calculated sulfuric acid proxy and measured sulfuric acid concentration is estimated to be 42% (Mikkonen et al., 2011)."

Following Anonymous Referee #1's advice, the peak concentration of sulfuric acid proxy instead of daytime average of sulfuric acid proxy is now used in Figure 4, which gives of a power exponent of 0.65 ± 0.28. To address the correlation between the nucleation rate and sulfuric acid proxy, we have now stated that (L406-414) "Our P of 0.65 ± 0.28 is of a significant uncertainty, which could come from the uncertainty during the calculation of sulfuric acid proxy and the scarcity of our data points. The upper limit of our P indicates that nucleation occurs after activation of clusters containing one molecule of sulfuric acid, with subsequent growth involving other species (Kulmala et al., 2006). The lower limit, on the other hand, suggests that a less important role of

ACPD
14, C10740–C10751, 2015

sulfuric acid in the critical nucleus during our campaign, which is unlikely to be true according to numerous previous studies (Weber et al., 1996; Sipila et al., 2010; Yu and Hallar, 2014)."

In addition, since the diurnal profile of ammonia was irregular, there was no peak concentration for ammonia. In this case, daytime average concentration of ammonia is used to investigate the relation between the nucleation rate and ammonia. In figure 5, the error bar of the ammonia concentration represent the standard deviation of daytime average concentration of ammonia, and a power exponent of 0.57±0.17 was obtained.

3. Figure 8 shows no clear correlation between GR and PM2.5. What are the corresponding correlation coefficient and standard deviation for the slopes? Would aerosol surface provide a better correlation? If not, in my opinion, this fragment and Figure 8 should be removed.

Reply: The correlations coefficient and standard deviation for the slopes are -0.019± 0.022, -0.041±0.071, 0.135±0.054 for GR 1.35∼2.39, GR2.39∼7 and GR7∼20 with PM2.5, respectively.

We have tested the correlation between GR and aerosol surface, which does not give a better correlation. Hence, as suggested by Anonymous Referee #1 and #2, Figure 8 and corresponding texts have been removed in the revised manuscript.

4. The abstract gives an excessively detailed description of some of the obtained results, e.g., growth rates binned for many size ranges are given with standard deviations. On the other hand, no standard deviation is provided for the power exponent of the sulfuric acid, although the latter is used to make an important conclusion regarding the nucleation mechanism.

Reply: The standard deviation for the correlation between the nucleation rate and sulfuric acid proxy is elaborated in the revised manuscript. We have now stated that (L28-31) that "Correlation between nucleation rate (J1.34) and sulfuric acid proxy in-

ACPD
14, C10740–C10751, 2015

dicates that nucleation rate J1.34 was proportional to a 0.65±0.28 power of sulfuric acid proxy, indicating that the nucleation of particles can be explained by the activation theory".

5. I suggest adding a scatter plot showing the concentration of 1.34-10 nm nanoparticles as a function of the aerosol surface area obtained from SMPS measurements (L439- 452). The scatter plot may show a better dependence. Also, the surface area may be a better parameter than PM2.5.

Reply: As suggested by Anonymous Referee #1, the PM2.5 mass plot has been replaced with the surface area plot in Figure 7. It is evident that NPF events in urban Shanghai occurred with low levels of aerosol surface area and that high sulfuric acid favored NPF events when aerosol surface area was low. The text in Section 3.4 has been revised accordingly.

Minor comments and corrections:

6. L68: add comma after 'air pollution'

Reply: A comma has been added.

7. L93,99: replace 'have been' with 'are'

Reply: As suggested by Anonymous Referee #1, the sentence at L110 has been revised. As suggested by Anonymous Referee #2 (comments #14), the sentence at L99 has been removed in the revised manuscript.

8. L119: A flow rate of 153 CFM corresponds to more than 4 m3/min. This does not appear to be a 'low-volume blower'.

Reply: We have now stated that "Ambient air was drawn into a stainless steel manifold of 5.0 m length and 4 inch inner diameter at a flow rate of 153 CFM using a blower (Model DJT10U- 25M, NUSSUN, China)" (L133-135).

9. L127: replace 'silica' with 'silicon'

ACPD
14, C10740–C10751, 2015

Reply: We replaced “silica” with “silicon” (L142).

10. L136: replace ‘grow’ with ‘grows’

Reply: We replaced “grow” with “grows” (L152).

11. L170: ‘aerosol cutter’ is not a good term

Reply: This sentence has been removed in the revised manuscript because the mass concentrations of PM2.5 are not presented in the revised manuscript.

12. L176: must be ‘Data Processing’

Reply: We replaced “Date Processing” with “Data Processing” (L190).

13. L182: perhaps a better term can be used instead of ‘growth losses’. Unlike coagulation, growth does not reduce the particle number concentration.

Reply: We used the term “condensational growth out of the considered size range”, instead (L196).

14. L229: rho_d is not defined. Also, is it not necessary to account for the uptake of water by sulfuric acid, e.g., by assuming that sulfuric acid is instantaneously equilibrated with gas-phase water?

Reply: The definition of rho has been added as a correction factor according to (Nieminen et al., 2010) (L243).

We agree with Anonymous Referee #1 that the particle growth due to the hydration of H2SO4 should be taken into account. We have now stated that (L248-253) “The particle growth due to the hydration of H2SO4 is taken into account by assuming that sulfuric acid is instantaneously equilibrated with gas-phase water. During our campaign, daily average RH varied between 28.7%∼60.0%. Hence, using the H2SO4-hydrate distribution data given by Kurte ÌĄn et al.(2007) , the density and mass of the average hydrated H2SO4 molecule at 50% relative humidity is calculated and further used in

ACPD
14, C10740–C10751, 2015

equation (6)".

15. L238-242: 'In this study, ...event' – this sentence is very heavy. Consider rewriting.

Reply: We have now stated that (L264-268) "In this study, we define an observation day with appearances of sub-3 nm clusters/particles over a time span of hours and subsequent growth to larger sizes for a few hours as a NPF event day. In this case, a NPF day will present a banana-shaped contour plot of particle size distributions obtained from SMPS (Dal Maso et al., 2005). We focus on characteristics and potential mechanisms of these events".

16. L273-276: Elaborate explicitly on why similar size distributions 'suggest' that photochemical products contribute to the formation of smallest particles. It is not clear as written.

Reply: We have now stated that (L296-302) "On the NPF day, 1.34-3 nm particles appeared as early as 7 am in the morning that was right after sunrise (6:42 am on Dec. 11th, 2013), reached its maximum just before noontime, and spanned for almost the whole daytime (sunset at 4:52 pm, Dec. 11th, 2013), suggesting that photochemistry products likely contribute to formation of smallest particles. This size distribution of atmospheric neutral and charged clusters/particles by a scanning PSM is identical to that measured at Hyytiälä, Finland (Kulmala et al., 2013)".

17. Section 3.2 and Table 1: It would be beneficial to add and discuss the data obtained in other sulfur-rich locations, e.g., Atlanta

Reply: Results from two Atlanta studies (Stolzenburg et al., 2005; Kuang et al., 2012) have been added into Table 1 and texts of session 3.2. We have now stated that (L354-360) " GR1.35∼2.39, GR2.39∼7, and GR7∼20 were in the range of 0.49-8.1, 3.1-35.7, 4.5-38.3 nm h-1, respectively. The arithmetic average values of GR1.35∼2.39, GR2.39∼7, and GR7∼20 were 2.0±2.7 (one standard deviation), 10.9±9.8 and

ACPD
14, C10740–C10751, 2015

11.4±9.7 nm h-1, respectively, which are comparable to 3-20 nm h-1 for nucleation mode particles in another sulfur-rich city, Atlanta, GA (Stolzenburg et al., 2005). In addition, at Shanghai is smaller than the growth rates (5.5-7.6 nm h-1) for particles in 1∼3 nm geometric diameter range in Atlanta (Kuang et al., 2012)."

18. L331-336: This sentence is very heavy. Consider adding a small table and revising the sentence.

Reply: We have now stated that (L360-366): "A closer examination of growth rates was performed by dividing GR1.35∼2.39 into growth of clusters/particles from one bin to another, i.e., GR1.35∼1.39 (1.6±1.0 nm h-1 from the bin of 1.34-1.37 nm to the bin of 1.37-1.41 nm), GR1.39∼1.46 (1.4±2.2 nm h-1 from 1.37-1.41 nm to 1.41-1.52 nm), GR1.46∼1.70 (7.2±7.1 nm h-1 from 1.41-1.52 nm to 1.52-1.89 nm), and GR1.70∼2.39 (9.0±11.4 nm h-1 from 1.52-1.89 nm to 1.89-3.0 nm). These growth rates show a clear size-dependent particle growth (Fig.3), owing to. . .".

19. L336: Replace 'size depend' with 'size-dependent'

Reply: We replaced "size-depend" with "size-dependent" (L366).

20. L336: Elaborate explicitly why size-dependent growth owes to nano-Kohler activation. What about size-dependence of the accommodation coefficient of sulfuric acid on clusters/nanoparticles? Isn't it supposed to decrease for with decreasing size?

Reply: We meant to suggest that "size-dependent growth owes to the combined effect of nano-Köhler activation, Kelvin effect and surface or volume-controlled reaction corrected for the Kelvin effect on surface or volume concentrations, not only owes to nano-Köhler activation". According to the nano-Köhler activation theory, inorganic stable nano-clusters will be activated into aerosol particles in a supersaturated organic vapor which initiates spontaneous and rapid growth of clusters. After activation, nanoparticles are expected to grow faster due to a decreasing Kelvin effect and, thus, an enhanced condensation flux. We have now stated that (L365-370) "These growth rates show a

ACPD
14, C10740–C10751, 2015

clear size-dependent particle growth (Fig.3), owing to the nano-Köhler activation that suggests a faster growth for activated nanoparticles due to a decreasing Kelvin effect and, thus, an enhanced condensation flux (Kulmala et al., 2004), Kelvin effect, and surface or volume-controlled reaction corrected for the Kelvin effect on surface or volume concentrations (Kuang et al., 2012)".

On the other hand, mass accommodation coefficient is the probability that a molecule that strikes the liquid/solid surface and then enters the bulk. The value of the mass accommodation coefficient depends on the system parameters and can either increase or decrease with a reduction in the nanoparticle size (Levdansky, 2012).

21. L344: 'was intense' – consider rewording

Reply: We have now stated that (L375-376) "indicating that high concentrations of condensable vapors existed".

22. L346: replace 'will grow' with 'would grow'

Reply: We replaced "will grow" with "would grow" (L377).

23. L360,362: replace 'have been' with 'were'

Reply: We replaced "have been" with "were" and "was", respectively (L391,393).

24. L362: replace 'the data points on both figures are' with 'the number of data points on both figures is'

Reply: We replaced "the data points on both figures are' with 'the number of data points on both figures was" (L393).

25. L363-364: why proxy for ammonia? Was it not measured directly?

Reply: The concentration of ammonia was measured directly. We have now stated that (L394-396) "Daily peak concentration of sulfuric acid proxy and daytime (6 am – 6 pm) averages of ammonia were used as approximations for their effective concentrations

ACPD
14, C10740–C10751, 2015

on a NPF day since there was no peak concentration for ammonia".

26. L391: elaborate explicitly on the 'co-occurring sulfuric acid concentration'

Reply: "Co-occurring sulfuric acid concentration" means when both sulfuric acid and ammonia concentration was high enough, new particle formation occurs with ternary nucleation. We have now used the term "co-existing" instead (L426).

Reference:

Anttila, T., Kerminen, V.-M., and Lehtinen, K. E. J.: Parameterizing the formation rate of new particles: The effect of nuclei self-coagulation, Journal of Aerosol Science, 41, 621-636, 10.1016/j.jaerosci.2010.04.008, 2010.

Dal Maso, M. D., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P., and Lehtinen, K. E.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, Boreal Environment Research, 10, 323-336, 2005.

Korhonen, H., Sihto, S. L., Kerminen, V. M., and Lehtinen, K. E. J.: Evaluation of the accuracy of analysis tools for atmospheric new particle formation, Atmospheric Chemistry and Physics, 11, 3051-3066, 10.5194/acp-11-3051-2011, 2011.

Kuang, C., Chen, M., Zhao, J., Smith, J., McMurry, P. H., and Wang, J.: Size and time-resolved growth rate measurements of 1 to 5 nm freshly formed atmospheric nuclei, Atmospheric Chemistry and Physics, 12, 3573-3589, 10.5194/acp-12-3573-2012, 2012.

Kulmala, M., Petäjä, T., Nieminen, T., Sipilä, M., Manninen, H. E., Lehtipalo, K., Dal Maso, M., Aalto, P. P., Junninen, H., Paasonen, P., Riipinen, I., Lehtinen, K. E. J., Laaksonen, A., and Kerminen, V.-M.: Measurement of the nucleation of atmospheric aerosol particles, Nature Protocols, 7, 1651-1667, 10.1038/nprot.2012.091, 2012.

Kurtén, T., Noppel, M., Vehkamaeki, H., Salonen, M., and Kulmala, M.: Quantum

ACPD

14, C10740–C10751, 2015

chemical studies of hydrate formation of H2SO4 and HSO4-, Boreal Environment Research, 12, 431-453, 2007.

Levdansky, V. V.: Mass Accomodation Coefficient for Nanoscale Aerosol Particles, in, edited by: Ždímal, V., Moravec, P., and Smolík, J., VÃ¡roční konference České aerosolové společnosti /13./, Ústav chemickÃ¡ch procesů, Rozvojová 135, 165 02 Praha 6, http://www.icpf.cas.cz/, 2012.

Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, Atmospheric Chemistry and Physics, 10, 9773-9779, 10.5194/acp-10-9773-2010, 2010.

Sipila, M., Berndt, T., Petaja, T., Brus, D., Vanhanen, J., Stratmann, F., Patokoski, J., Mauldin, R. L., Hyvarinen, A. P., Lihavainen, H., and Kulmala, M.: The Role of Sulfuric Acid in Atmospheric Nucleation, Science, 327, 1243-1246, 10.1126/science.1180315, 2010.

Stolzenburg, M. R., McMurry, P. H., Sakurai, H., Smith, J. N., Mauldin, R. L., Eisele, F. L., and Clement, C. F.: Growth rates of freshly nucleated atmospheric particles in Atlanta, Journal of Geophysical Research, 110, 10.1029/2005jd005935, 2005.

Weber, R., Marti, J., McMurry, P., Eisele, F., Tanner, D., and Jefferson, A.: Measured atmospheric new particle formation rates: Implications for nucleation mechanisms, Chemical Engineering Communications, 151, 53-64, 1996.

Yu, F. Q., and Hallar, A. G.: Difference in particle formation at a mountaintop location during spring and summer: Implications for the role of sulfuric acid and organics in nucleation, Journal of Geophysical Research-Atmospheres, 119, 12246-12255, 2014.

Yu, H., Gannet Hallar, A., You, Y., Sedlacek, A., Springston, S., Kanawade, V. P., Lee, Y. N., Wang, J., Kuang, C., and McGraw, R. L.: Sub-3 nm particles observed at the coastal and continental sites in the United States, Journal of Geophysical Research: Atmospheres, 119, 860-879, doi: 10.1002/2013JD020841, 2014.

ACPD

14, C10740–C10751, 2015

Zheng, J., Hu, M., Zhang, R., Yue, D., Wang, Z., Guo, S., Li, X., Bohn, B., Shao, M., and He, L.: Measurements of gaseous H2SO4 by AP-ID-CIMS during CAREBeijing 2008 campaign, Atmospheric Chemistry and Physics, 11, 7755-7765, 2011.

Zheng, J., Ma, Y., Chen, M., Zhang, Q., Wang, L., Khalizov, A. F., Yao, L., Wang, Z., Wang, X., and Chen, L.: Measurement of atmospheric amines and ammonia using the high resolution time-of-flight chemical ionization mass spectrometry, Atmospheric Environment, 102, 249-259, 10.1016/j.atmosenv.2014.12.002, 2015.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C10740/2015/acpd-14-C10740-2015-supplement.pdf

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