Atmos. Chem. Phys. Discuss., 14, C10752–C10761, 2015
www.atmos-chem-phys-discuss.net/14/C10752/2015/

Atmospheric Chemistry and Physics
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Discussions

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

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Received and published: 4 January 2015

"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 #2

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The paper by Xiao et al. reports field observations of new particle formation events in a polluted environment and is trying to discern potential formation mechanisms. The paper is presented fairly well but lacks clear focus, good articulation of goals and more in-depth analysis of data, especially when it comes to unexpected findings. The paper may become suitable for publication pending consideration of comments and appropriate revisions.

Major Comments:

1. The goals of the study are presented poorly and it looks like a repetition of other similar studies in just a different area. The whole paper is presented like a report, seeking similarity with other studies. Why nucleation would be different at a Chinese location as is implied in line 14, P26658? At the moment I don't see one unique finding enhancing the understanding of new particle formation.

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

Regarding the Nucleation mechanisms in China, we have now stated that (L88-91) “where concentrations of sulfuric acid and basic gases including ammonia and amines are high (Zheng et al., 2011; Zheng et al., 2015) but concentrations of extremely low volatility organic compounds formed from biogenic emissions are yet to be determined.”.

2. The relationship between J1.34 nucleation rate and sulphuric acid proxy is poorly investigated and the conclusions poorly supported. The correlation between the two parameters is poor and above all not statistically significant. Note that R2 is not a correlation, but the variance. R2=0.23 suggests that only 23% of the total covariance can be explained by the relationship and owing the number of points (8) is not statistically significant even at P<0.05 level (r=0.71 at P<0.05 or r=0.83 at P<0.01 is required instead of obtained r=0.48). That is suggesting that either sulphuric acid plays insignificant role or the scarcity of data prevent statistical robustness. By contrast correlation with ammonia is much stronger and statistically significant, but it is played down to secondary role. What about considering organic species in forming new particles, like amines? The power of sulphuric acid proxy is also presented without error bars or standard deviation and considering the above is highly questionable. At the questionable. At the end there a big question mark whether sulphuric acid proxy was adequately derived.

Reply: We agree that the correlation between the two parameters is not quite satisfactory. A better R2 for ammonia and J1.34 than that for sulfuric acid and J1.34 does not necessarily mean that sulfuric acid plays a secondary role, since (1) sulfuric acid proxy was calculated with a 42% uncertainty whereas ammonia was directly measured with more confidence; (2) the daily peak concentration of sulfuric acid proxy was used whereas daily average of ammonia was used; and (3) the scarcity of data prevent statistical robustness. We have now stated that (L405-407) “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”.

At the moment, we cannot rule out potential contributions from organic species in-

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cluding amines. A recent measurement of ammonia and amines at Nanjing, China by Zheng J. et al (2015) observed good correlations between NH3 and amines, indicating similar emission sources. We have now stated that (L428-430) “A recent CIMS study (Zheng et al., 2015) observed good correlations between NH3 and amines at an urban site of Nanjing, China. Hence, it is plausible that amines may contribute to nucleation in our site at Shanghai, too”.

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

3. The relationship with PM2.5 concentration is not appropriate because new particle formation is unrelated to particle mass, but rather its surface. PM2.5 mass is a qualifier of air quality and only remotely linked to condensation sink. Why not to correlate to particle surface and also to examine any relationship between surface and mass?

Reply: As suggested, 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.

4. In a highly dynamic and polluted environment such as urban one should be very careful when it comes to averages. Strictly speaking average only applies to normally distributed values while generally aerosol parameters are log-normally distributed and, consequently, geometric average (median) and ranges should be used instead. Even more so that the authors presented parameters varying by more than one order of

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magnitude.

Reply: In this manuscript, arithmetic average of the number concentration of 55∼63nm particles and arithmetic average of size-dependent growth rates have been included.

The arithmetic averages of number concentration of 55∼63nm particles are averages of those simultaneously measured by a long-SMPS and a nano-SMPS, respectively. The purpose of this averaging is to have a better match for the results between the two instruments. The difference between the geometric mean and the arithmetic mean of 55∼63nm particles number concentrations was 0.83±4.55%. Hence, we conclude that there is no significant difference between the geometric mean and the arithmetic mean of 55∼63nm particles number concentrations.

The arithmetic averages of size-dependent growth rates are not averages of the growth rates over a number of particle size bins, but averages of the growth rate for a certain particle size bin over a number of NPF event days. We don't believe that growth rates for a certain size bin on different NPF event days were normally or log-normally distributed. Hence, the arithmetic averages have been used.

Minor comments:

5. Please tidy up numbers throughout the paper: report particle sizes to three digits consistently;

Reply: We have reported particle sizes to three digits consistently throughout the manuscript.

6. remove technical information about size bins in the abstract;

Reply: We have removed technical information about size bins in the abstract.

7. growth rates present with one number in the subscript;

Reply: Growth rates with one number in the subscript is not enough to elaborate explicitly on those of, for example, particles from 1.35nm to 1.39nm (GR1.35∼1.39). Hence, growth rates with three numbers is used in the subscript.

8. Present error bar for sulphuric acid proxy power.

Reply: According to Mikkonen et al. study (2011), the uncertainty for the calculation of sulfuric acid proxy is estimated to be 42%. We have now added the error bars of the sulfuric acid proxy in Figure 4.

9. Revise abstract according to major comments.

Reply: We have revised the abstract according to major comments.

10. P26657, Line 17. “Very recently progress has been made by the use of PSM, etc: : :”

Reply: We have now stated that (L59-61) “Very recently progress has been made by the use of Particle Size Magnifier (PSM) and Chemical Ionization Atmospheric Pressure interface Time-of-Flight (CI-APi-ToF) mass spectrometer”.

11. P26658, line 2. Populated region, not area.

Reply: We have replaced “area” with “region” (L76).

12. Line 13. “the use” not “employment”.

Reply: We have replaced “employment” with “use”(L85).

13. Line 13. Measurement down to the certain size is not the measurement of the nucleation which has to be worked out from data.

Reply: We have replaced “measure atmospheric nucleation” with “study atmospheric nucleation” (L86).

14. Line 24. Competition between available surface and condensable vapour is a fundamental process and is very well known.

Reply: This sentence has been removed in the revised manuscript.

15. The sampling manifold was poorly designed. First, the flow in the main duct was highly turbulent. Second, various instruments were non-isokinetically subsampling as the air velocity in the duct was 9.1m/s versus subsampling velocity is 0.75m/s. That created a two-fold problem. Particles of different sizes were not sampled at the same efficiency leading to under-sampling of small particles and over-sampling of larger ones (it was like in a virtual impactor). While under-sampling was probably a minor problem, oversampling was rather detrimental leading to overestimated condensation sink. Was the diffusion loss taken into account when processing data?

Reply: The diffusion loss of sampling lines for particles at each size was taken into account during data processing, which gives a “true” number of particles at each size. We have now stated that (L145-147) “The calculated diffusion loss is up to 29% for 1.35 nm particles with the above setup, and has been taken into account in the entire size range during the data processing”.

16. Please report time resolution of SO2 measurements as it is important in drawing some of the key conclusions.

Reply: The time resolution of SO2 measurements was 5 min. Since the time resolution of temperature and relative humidity was 1 hour, the time resolution of sulfuric acid proxy is 1 hour.

We have now stated that (L175-177) “At the same site, sulfur dioxide (SO2) was measured by an SO2 analyzer with pulsed UV fluorescence technique (Model 43i, Thermo, USA) with a time resolution of 5 min”, and that (L234-235) “The time resolution of calculated sulfuric acid proxy was 1 hour since those of temperature and relative humidity was 1 hour”.

17. P26661, line 8. PM2.5 aerosol inlet, not cutter.

Reply: This sentence has been removed in the revised manuscript because aerosol surface area instead of PM2.5 is used.

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18. P26665, line 15. Reduction of particles, not loss.

Reply: We have replaced the “loss” with “reduction” (L307).

19. P26668. More thorough study is required about sulphuric acid proxy. Present and study not only average concentrations. But also 25/75 percentiles and perhaps min/max too.

Reply: According to Mikkonen et al. study (2011), the uncertainty for the calculation of sulfuric acid proxy is estimated to be 42%. We have now added the error bars of the sulfuric acid proxy in Figure 4. In addition, 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.

20. Remove Figure 8 as it is conceptually wrong and the graph explains nothing.

Reply: As suggested by Anonymous Referee #1 and #2, Figure 8 and corresponding texts have been removed in the revised manuscript. âĂČ

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Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/14/C10752/2015/acpd-14-C10752-2015-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 26655, 2014.