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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluation on the role of sulfuric acid in the mechanisms of new particle formation for Beijing case" *by* Z. B. Wang et al.

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We thank the reviewer for helpful comments and suggestions. Below we provide point to point response to each comment. The page number refer to the version published in ACPD.

1. Comment: Section 2.2.1. The recent analysis by Korhonen et al. (2011, ACP, pages 3051-3066) points out several problems that may arise when the cluster growth rate between 1.5 and 3 nm (GR) is estimated from the time delay between the increase in H2SO4 concentration and that of 3-6 nm particle concentration. The authors should discuss this issue further in section 2.2.1 by considering these findings. Most importantly, Korhonen et al. (2011) showed that a zero time delay, as observed in some of the cases here, may not necessarily indicate very fast growth of nucleated clusters.

Response: Thanks for your comment. The recent research showed the time delay method has its limitation as you pointed out. So in the revised manuscript, we discussed the possible problem in section 2.2.1 as below: "However the model simulation results indicated that the time delay method has its limitation, especially in the case of strong particle formation events (Korhonen et al., 2011). The previous formed nucleation mode particles could act as an extra coagulation sink for the small clusters that form later, which may cause the peak of N3-6 arised earlier than in the case of purely condensation controlled formation of these small particles. As a result, the time delay between N3-6 and sulfuric acid concentration may equal to zero or even negative in these cases." In addition, the new equation is used to calculate the J3 value to improve the accuracy in the section 2.2.2: "However, the recent studies (Vuollekoski et al., 2010;Korhonen et al., 2011) showed that there are potential problems in determining GR1.5-3. To improve the accuracy of J3 calculation the recommended Eq. (4) (shown in Fig.1)is used to simulate the J3 value in this study: The first and second terms on the right hand side of Eq. (4) are the same as Eq. (3). The differences between these two equations are: i) Here n6 is assumed roughly equal to N5-7/(7 nm–5 nm) and ii) the GR6 is assumed closer to the growth rate of the nucleation mode (GR3-7 estimated from particle number size distribution in this study) than GR1.5-3." However the simulation of J1.5 value could not avoid using this time delay method. In the revised manuscript, we pointed this issue out and discussed the uncertainty of J1.5 calculation : "However the simulation of nucleation rate J1.5 based on the Eq. (5) has great uncertainty. First the assumption of the constant growth rate in Eq. (5) is suspectable (Korhonen et al., 2011). The combined effect of various precursors could cause a strong deviation from the constant growth rate assumption. Second neglecting the intramodal coagulation in the nucleation mode in Eq. (5) may lead in theory to underestimation of J1.5. Third the time shift between the N3-6 and sulfuric acid concentration was not observed in most cases of this study. In these cases we have to assume the GR is equal to 9 nm/h (See Section 2.2.1), which may overestimate the real nucleation rate."

2. Comment: Page 24171, lines 13-16. I do not understand why the authors give specifically the exponent 3 here? Later on they provide exponents with broad range of values. Would it rather be better to say that exponents for J1.5 vs. H2SO4 clearly in excess of 2 are indicative some degree of thermodynamic influence on the nucleation process. I suggest that the authors replace "3" with "n>2.5" consistent with their analysis presented later in the paper.

Response: We agree. In the revised manuscript, the thermodynamic nucleation theory (with the exponent between J1.5 and H2SO4 large than 2.5) is defined as(shown in Fig.2): where T is the thermodynamic coefficient (in unit cm(3n-3) s-1).

3. Comment: Page 24172, lines 14-27. The authors conclude that it is the pre-existing aerosol concentration rather than gaseous sulphuric acid concentration determining the occurrence of NPF at the site. Is this a firm conclusion? I have a difficulty in following the reasoning of this conclusion.

Response: This point is very important. Actually, the NPF event is the product of the competition between source (here represented as H2SO4 concentration) and sink (CS). In the revised manuscript we added one figure which showed the relationship between the concentration of newly formed particles and the ratio of sulfuric acid concentration to condensation sink in Figure 2(in revised version). Meanwhile in the revised manuscript, we sharpened the conclusion as below: "The higher number concentration of newly formed particles was observed when the ratio of sulfuric acid concentration to condensation sink was larger, which is shown in Figure 2(b). The NPF event is the product of the competition between source (here represented as sulfuric acid concentration) and sink (CS). In the case of both higher source and sink values, the result of the competition between source and sink is more likely the key limiting factor to determine the observation of NPF events in the urban of Beijing."

4. Comment: Page 24174, lines 18-20. This is another conclusion I have a difficulty in understanding based on available data.

Response: Following your comment we changed the conclusion as below: "This results indicate that in the polluted urban environment of Beijing, the thermodynamic process seemed involved in the nucleation process, which could not simply explained by activation or kinetic nucleation theory as previous studies."

5. Comment: The recent analysis by Sihto et al. (2009, ACP, pages 2933-2947), Vuollekoski et al. (2010, Atmospheric Research 98, pages 229-236) and Korhonen et al. (2011) using aerosol dynamical model simulations challenge the interpretations that can be made based on the relation between the "nucleation exponent derived from atmospheric observations" and the "nucleation mechanism". Most importantly, these simulations show that 1) the connection between the "real" and "observed" nucleation exponent is more complicated than previously thought, and 2) on average, observed nucleation exponents tend to be on higher than the real ones, i.e. activation mechanism would typically produce "observed" exponents substantially larger than unity and kinetic mechanis would produce "observed" exponents typically larger than 2. The authors should carefull consider these results when discussing their findings in sections 3.2, 3.3, 3.4 and 4, as well as in abstract.

Response: Thanks for your comment. This point is very important. Considering that the method to calculate the nucleation rate could be problematic, so we pointed out the uncertainty and modified the equation in the revised manuscript (See response 1 and 7). Also the conclusions were discussed carefully in the abstract and following sections (Please see the details in the revised manuscript).

6. Comment: Section 2.1. Have the authors made any estimates on the accuracy of the gaseous H2SO4 measurements? If this information is available, please provide it here and give a possible citation to work in which such an estimate have been made.

Response: The previous manuscript gave the detailed description of the sulfuric acid measurements in the same campaign (Zheng et al., 2011). We cited this reference here to prove the accuracy of the gaseous H2SO4 measurement.

7. Comment: Page 24170, line 9. The assumption made here should read GR6=GR1.5-3. Since there are potential problems in determining GR1.5-3 (see my first major comment) and since GR1.5-3 may not be a good representative for GR6 due to size-dependencies in cluster growth rates, why did not the authors try to estimate GR6 from particle number size distribution measurements? I would think that the growth rate of the nucleation mode would be closer to GR6 than the highly inaccurate value of GR1.5-3.

Response: This point is very important. We modified the equation (3) as the previous studies (Vuollekoski et al., 2010;Korhonen et al., 2011) recommended to improve the accuracy of J3 calculation(shown in Fig. 1). Here we used the GR3-7 estimated from particle number size distribution to substitute the GR6. The detailed discussion of this equation could be seen in Response 1.

8. Comment: Page 24167, lines 16-17. Could the authors provide some examples of observations of NPF in urban polluted environments?

Response: In the revised manuscript, we provided the observations in urban polluted environments as below: "Although the NPF events were observed all over the world. The measurements of gaseous sulfuric acid are rare, especially in urban polluted environment. A few campaigns had been conducted in urban environments only provide the measurements of particle number size distributions (Dunn et al., 2004;Kulmala et al., 2005;Hamed et al., 2007;Smith et al., 2008;Salma et al., 2011)."

9. Comment: Page 24171, lines 2-3. Please add some reference for the kinetic cluster formation theory.

Response: We cited two references (McMurry and Friedlander, 1979;Lushnikov and Kulmala, 1998) in the revised manuscript.

10. Comment: Page 24172, lines 3-6. The authors are certainly correct but based solely on Figure 1, it is hard to see that N3-6 and H2SO4 have similar trends on NPF

days.

Response: Thank you for pointing this out. We revised it as: "It is evident that both the N3-6 and H2SO4 have the strong diurnal variations on NPF days (gray background)."

11. Comment: Section 3.4. The authors should mention that the nucleation coefficients A and K were derived for all the events regardless of which nucleation mechanisms obtained for that particular event.

Response: We appreciated the reviewer's comment and added the following sentences to make it clear: "In order to facilitate comparison with other studies, the nucleation coefficients A and K were calculated for all the events regardless of which nucleation mechanisms obtained for that particular event."

References

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$$J_3 = \frac{dN_{3-6}}{dt} + CoagS_4 \cdot N_{3-6} + \frac{1}{2nm} GR_6 \cdot N_{5-7}$$

Fig. 1. Eq. (4)

$$J_{1.5} = T[H_2SO_4]^n \qquad (n > 2.5)$$

Fig. 2. Eq. (8)