

## ***Anonymous Referee #2***

We thank this reviewer for helpful comments and suggestions. Below we provide a point-by-point response to this referee's comment. The page numbers refer to the original version published in ACPD.

### **1. Comment:**

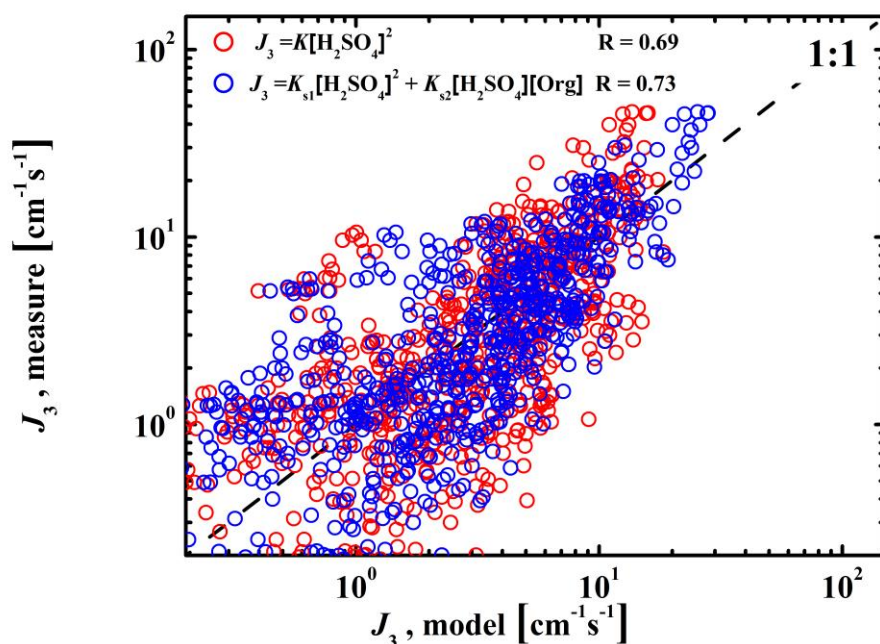
It has to be stated that the entire atmospheric data set of the 17 nucleation events has already been published and analyzed for H<sub>2</sub>SO<sub>4</sub> nucleation by Wang et al., ACP, 2011. The method to test the data for the contribution of low volatility oxidized organics to the nucleation rate has been described in detail and tested by Paasonen et al., ACP, 2010, where results of 36 nucleation events at four different sites in Europe were analyzed. Therefore, both the data sets as well as the method used for the additional analysis have been published before. Furthermore, it is a significant shortcoming that neither the precursor organics, nor the oxidizing agents, nor the low volatility organic oxidation products were directly measured. Instead, a daily average for the sum of the condensing organic species is derived in a very indirect way including many assumptions (role of O<sub>3</sub> and other oxidants neglected; OH is inferred from global radiation measurement; participation of inorganics such as ammonia for nucleation and growth is neglected, etc.). Altogether, the results, namely a range of correlation coefficients for the various nucleation mechanisms including organics, are a) all in a very similar range (0.67 – 0.73) and therefore no firm conclusion on the occurrence of any of the suggested nucleation mechanisms can be drawn; the results are all highly uncertain as admitted by the authors in Section 3.3 because of the many assumptions necessary to derive concentrations of organics (and differences between of nucleation mechanisms between R=0.66 and R=0.67 as mentioned in the conclusions (lines 10-12) are therefore meaningless); The studied data set is only a minor extension to the existing data set from Paasonen et al., 2010.

### **Response:**

In our earlier study (Wang et al., 2011), we investigated new particle formation in Beijing and analyzed the connection between sulfuric acid concentration and new particle formation rate. In that work, two kinds of NPF events were identified in Beijing: Case I, the exponent is between 1 and 2 in the correlation of the particle formation rates and sulfuric acid concentrations, which is similar with other observations in clean environments, implying that activation or kinetic nucleation represents the possible nucleation mechanism (Sihto et al., 2006; Riipinen et al., 2007;

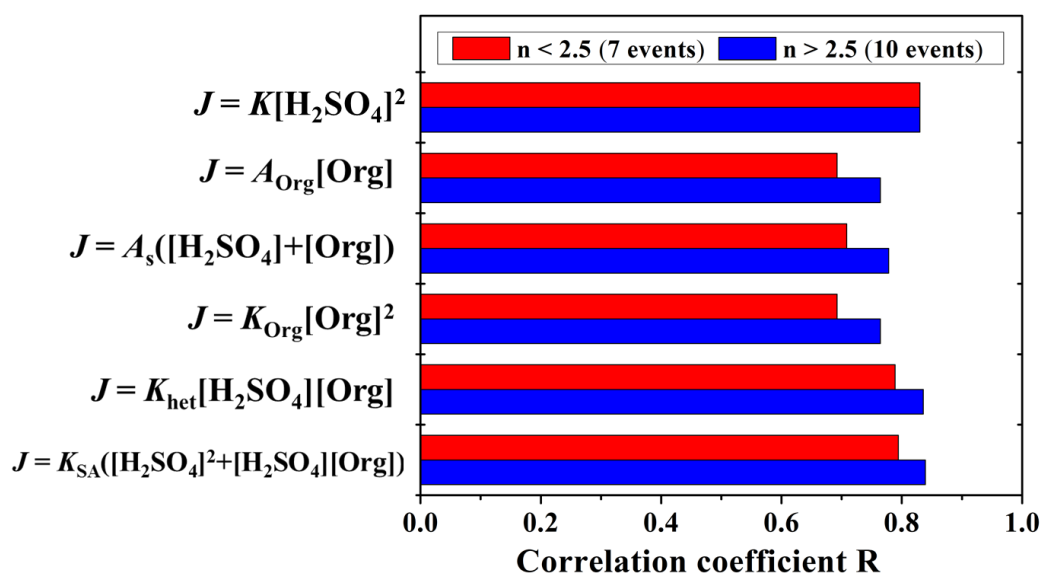
Kuang et al., 2008; Paasonen et al., 2009); For Case II, the exponent is larger than 2.5, which has been rarely observed previously in less polluted environments. However, more than half of the NPF events (58% in 17 investigated days) in Beijing belong to the second type, which is one of the reasons why the Beijing data needed to be studied further.

In the present work, we aim at elucidating the contributions of organics to new particle formation in Beijing. We have shown that, while Case I NPF in Beijing is similar to those commonly observed in clean environment (Sihto et al., 2006; Riipinen et al., 2007; Paasonen et al., 2009) and can be accounted for reasonably with the activation or kinetic nucleation. Case II NPF in Beijing is considerably different from any previous studies, including that reported by Paasonen et al. (2010). We have explained that the later case has been attributed to the unique extreme pollution conditions in Beijing. Followed the methods described by Paasonen et al. (2010), we have considered organic molecules (oxidation products of monoterpenes, MTOP) as one of the new particle formation precursors and evaluated several representations for the nucleation theories (Eqs. 7-14 in the MS) involving the organics. We have added one new figure to display the improvement in the present work. Figure 5 shows the comparisons between modelled and observed particle formation rates in our previous kinetic nucleation ( $J=K[\text{H}_2\text{SO}_4]^2$ ) and the homogenous homomolecular nucleation with separate nucleation coefficients in this study ( $J=K_{\text{SA1}}[\text{H}_2\text{SO}_4]^2+K_{\text{SA2}}[\text{H}_2\text{SO}_4][\text{Org}]$ ). The results show that a higher correlation coefficient ( $R=0.73$ ) compared with the traditional kinetic nucleation ( $R=0.69$ ).



**Fig.5** Comparison between observed particle formation rate and formation rate modelled with two different parametrizations. Red: kinetic sulphuric acid nucleation; Blue: kinetic nucleation of sulphuric acid alone and with organic vapours. The dash line presents the 1:1 line.

We have further demonstrated that the nucleation rate in the polluted case (II) is two times higher than that in the clean case (I) and concluded that the contribution by organics to NPF can be even larger than that in the clean case. To compare with our 2011 publication, Figure 6 has been modified to include the kinetic nucleation (i.e.,  $J=K[\text{H}_2\text{SO}_4]^2$ ). Our results suggest that the mean correlation coefficients in the kinetic nucleation expression are identical in the two types of NPF events, suggesting a similar role of sulfuric acid in all NPF events. However, the mean correlation coefficients in Case II are higher than those in Case I in all nucleation expressions considering the organic vapors. This phenomenon implies that the important role of organic vapors in the new particle formation process on polluted days.



**Fig. 6.** Comparisons of correlation coefficients in different nucleation mechanisms between two kinds of NPF events days. Red ones indicate days with the exponent smaller than 2.5, blue ones indicate the days with the exponent larger than 2.5.

For the concentrations of organic vapors, we have now clearly pointed that currently the identity of organic compounds contributing to new particle formation remains highly uncertainty (Zhang et al., 2012). Furthermore, we have pointed out that current analytical instruments to detect low volatile organic compounds are very limited. Hence, we believe that it is reasonable to follow the previous studies (Laaksonen et al., 2008; Paasonen et al., 2010; Lauros et al., 2011) and assumed that the organic vapours are the products of monoterpenes via OH radicals oxidation products (MTO). Meanwhile, all the assumptions made in this article are related to the

time-dependency of [org], but not to the daily level of [org], which is derived from GR. We have clarified it in the revised manuscript.

It is true that the studied dataset in our present work were previously analyzed in our publication in 2011 (Wang et al.) and the applied methods are similar to those described by Paasonen et al., (2010). However, our present work is the first to explore the roles of organics on atmospheric new particle formation in polluted urban environment like Beijing, indicating a larger role of organics in new particle formation than that in clean environments. We now recognize that in our initial submission the novelties of this present work were not clearly highlighted compared to the work of Wang et al. (2011). In revision, we have modified the manuscript to clearly reflect those above aspects in the abstract, main text, and conclusions.

## 2. Comment:

Minor comment: There are many instances where the text needs improvement in the use of English language and where inappropriate words or phrases have to be replaced.

### Response:

We appreciate the reviewer's comment and have checked the entire manuscript and corrected all identified errors.

## References

- Kuang, C., McMurry, P. H., McCormick, A. V., and Eisele, F. L.: Dependence of nucleation rates on sulfuric acid vapor concentration in diverse atmospheric locations, *J Geophys Res-Atmos*, 113, D10209, Doi 10.1029/2007jd009253, 2008.
- Laaksonen, A., Kulmala, M., O'Dowd, C. D., Joutsensaari, J., Vaattovaara, P., Mikkonen, S., Lehtinen, K. E. J., Sogacheva, L., Dal Maso, M., Aalto, P., Petäjä T., Sogachev, A., Yoon, Y. J., Lihavainen, H., Nilsson, D., Facchini, M. C., Cavalli, F., Fuzzi, S., Hoffmann, T., Arnold, F., Hanke, M., Sellegri, K., Umann, B., Junkermann, W., Coe, H., Allan, J. D., Alfarra, M. R., Worsnop, D. R., Riekkola, M.-L., Hyötyläinen, T., and Viisanen, Y.: The role of VOC oxidation products in continental new particle formation, *Atmos Chem Phys*, 8, 2657-2665, 2008.
- Lauros, J., Sogachev, A., Smolander, S., Vuollekoski, H., Sihto, S.-L., Mammarella, I., Laakso, L., Rannik, Ü., and Boy, M.: Particle concentration and flux dynamics in the atmospheric boundary layer as the indicator of formation mechanism, *Atmos. Chem. Phys.*, 11, 5591-5601, 10.5194/acp-11-5591-2011, 2011.
- Paasonen, P., Sihto, S.-L., Nieminen, T., Vuollekoski, H., Riipinen, I., Plass-Dülmer, C., Berresheim, H., Birmili, W., and Kulmala, M.: Connection between new particle formation and sulphuric acid at Hohenpeissenberg (Germany) including the influence of organic compounds, *Boreal Env. Res.*, 14, 616-629, 2009.
- Paasonen, P., Nieminen, T., Asmi, E., Manninen, H. E., Petäjä T., Plass-Dülmer, C., Flentje, H.,

Birmili, W., Wiedensohler, A., Hõrrak, U., Metzger, A., Hamed, A., Laaksonen, A., Facchini, M. C., Kerminen, V.-M., and Kulmala, M.: On the roles of sulphuric acid and low-volatility organic vapours in the initial steps of atmospheric new particle formation, *Atmos Chem Phys*, 10, 11223-11242, 10.5194/acp-10-11223-2010, 2010.

Riipinen, I., Sihto, S.-L., Kulmala, M., Arnold, F., Dal Maso, M., Birmili, W., Saarnio, K., Teinilä K., Kerminen, V.-M., Laaksonen, A., and Lehtinen, K. E. J.: Connections between atmospheric sulphuric acid and new particle formation during QUEST III-IV campaigns in Heidelberg and Hyytiälä *Atmos Chem Phys*, 7, 1899-1914, 2007.

Sihto, S.-L., Kulmala, M., Kerminen, V.-M., Dal Maso, M., Petäjä T., Riipinen, I., Korhonen, H., Arnold, F., Janson, R., Boy, M., Laaksonen, A., and Lehtinen, K. E. J.: Atmospheric sulphuric acid and aerosol formation: implications from atmospheric measurements for nucleation and early growth mechanisms, *Atmos Chem Phys*, 6, 4079-4091, 2006.

Wang, Z. B., Hu, M., Yue, D. L., Zheng, J., Zhang, R. Y., Wiedensohler, A., Wu, Z. J., Nieminen, T., and Boy, M.: Evaluation on the role of sulfuric acid in the mechanisms of new particle formation for Beijing case, *Atmos Chem Phys*, 11, 12663-12671, 10.5194/acp-11-12663-2011, 2011.

Zhang, R., Khalizov, A., Wang, L., Hu, M., and Xu, W.: Nucleation and Growth of Nanoparticles in the Atmosphere, *Chemical Reviews*, 112, 1957-2011, 10.1021/cr2001756, 2012.