Response to Referee #1

This manuscript "First comprehensive modeling study on observed new particle formation at the SORPES station in Nanjing, China" presents measurements and modeling of new particle formation (NPF) events with the intention to investigate the contribution of different chemical compounds and aerosol properties on the formation and growth to 6 nm aerosol particles. It is fairly well written and the modeling tools used in the study are of good quality. However, some of the details of the methods are missing. It is also unclear, what is the main outcome of this study and how the scientific community would benefit from it. This should be clarified by the authors. In addition, Abstract and Conclusions do not include any quantification of the results. For example, it is said that "simulated NPF events were generally in good agreement with the corresponding measurements" but it is not explained which parameters are in good agreement and what qualifies as "good agreement".

Response: We would like to thank the referee for providing the insightful suggestions, which indeed help us reconsider and further explore the underlying problems in these NPF events and their simulations. In the revised manuscript, we have added more descriptions on the method of measurement and modeling, as well as in-depth discussions concerning model performance.

Major comments:

- *It is unclear how the nucleation coefficient k1 is determined for Equation (1). On Page 27506 it is said they were chosen "after comparing the simulations and DMPS measurements". This should be explained better. If the nucleation coefficient is tuned to match the model to measurements, wouldn't it be obvious that the model is in good agreement with the measurements? In addition to my previous point, the values of k1 are extremely low. For example, Pietikäinen et al. 2014, use k1 = 1.4×10^{15} and that is for the formation rate of 3 nm particles. For 1.5 nm particles it would be even higher. Could these extremely low values of k1 explain why the nucleation events start too late in the model?*

Response: Here we have to state that it is important to have reviewers who read the manuscript very carefully and find mistakes, which should normally not happen. After checking the numbers in the model again we realized that the units of k1 used here are m^3/# and not as mentioned in other publications like e.g. Boy et al., 2008 (Atmos. Chem. Phys., 8, 1577–1590, 2008) cm^3/#. Taking this into account we end up with values of $6x10^{-13}$ cm^3/# for 10 of July and 22 of August and $2.2x10^{-10}$ cm^3/# for 22 of June. How could this happen? UHMA the aerosol dynamic code used in MALTE-BOX was developed more than 10 years ago at the University of Helsinki and was written in SI units, so it uses for gases and particles #/m^3 and not #/cm^3 as we do in the other MALTE-

BOX code. Normally we change all the units when they are transferred to UHMA but the nucleation coefficients are set direct in UHMA and this caused the problem. So in practice the values were not wrong but compared to earlier values with different units.

The new or related to the units corrected values are now in full agreement with values published in Boy et al., 2008 for Hyytiälä with 5.7x10^{-13} cm^3/# to 5.5x10^{-14} cm^3/# or Heidelberg, Germany (more polluted) with 2.3x10^{-11} cm^3/#. Obviously, the most polluted day the 22 of June requires a higher (about 400 times higher compared to the other two days) kinetic nucleation coefficient, which could be related to more anthropogenic compounds in the nucleation mechanism similar to the comparison of Hyytiälä and Heidelberg.

Concerning the first statement of the referee how we achieved the values of the kinetic nucleation coefficient this was done similar as in other manuscripts like Boy et al., 2008 by running the model with different values until the best fit between measured and modeled number concentrations in the lowest available bins were achieved. We agree with the referee that this could be seen as tuned but it also provides us input how important sulfuric acid or other unidentified molecules are when comparing the required kinetic nucleation coefficient. And by comparing the values of these values with different stations it gives us some idea how important sulfuric acid is in the nucleation compared to other unidentified compounds

We have added all this information in the final version of the manuscript (Section 2.2.1) and of course correct the k1 values with units.

- *Since only three NPF events are investigated, it is unclear how well the model configuration reproduces observed NPF events in general. For example, has it been tested if the modeled frequency of NPF events is similar to observations?*

Response: 2-year DMPS measurements at the SORPES site have detected over 200 NPF events (Qi et al. 2015). It is time consuming and computationally demanding to simulate all these events using this comprehensive modeling method. Thus, the modeling of NPF frequency has not been tested yet. It will be addressed in our future work, but cannot be accommodated in this study. In this paper, we mainly focus on analysis and numerical simulation of the several typical NPF events, which were identified by the distinctions in the potential source regions of air masses.

- *One of the main results of the study is that biogenic organic compounds play an essential role in condensational growth of newly formed clusters. Model results supporting this finding are missing. Have you, for example, investigated the modeled fraction of these biogenic organics in 6 nm particles? If the fraction is significantly high in these particles, it would strengthen your case.*

Response: Accepted. To support the importance of biogenic organic compounds in condensational growth of newly formed clusters, we have added a new figure (Fig. 7) to show contributions from different kinds of condensing vapors to initial particle growth (particles with diameter less than 10 nm) in the revised manuscript.

- *Page 27516: It is said that the better correlation of using organic nucleation scheme is evidence for the involvement of ELVOC in NPF. Visual inspection of this data suggest that this increase in the correlation comes only from the fact that [H2SO4]2 has smaller variability than* $[H2SO4]^{1.0}[ELVOC]^{0.8}$*. Based on this approach activation type nucleation mechanism might have even higher correlation coefficient. In addition, the correlation coefficient seems to be calculated from the actual values while the x-data varies over 8 orders of magnitude, so it would have been more appropriate to calculate the correlation coefficients for the logarithm of the values. Please see the Referee #2 comments to improve this analysis.*

Response: Dashed lines showing $J=2.2\times10^{-10}\times[H_2SO_4]^{2.0}$ and $J=6.0\times10^{-13}\times[H_2SO_4]^{2.0}$ were added for reference in Fig.8 (b). The reason why we included this figure is to provide some hints if ELVOCs are crucial in the formation and growth of particles up to 6 nm. There was no aim from us to state that ELVOCs are important in the formation of clusters which is still open (see discussions on Referee #2's comments).

Minor comments:

- *Please check the grammar.*

Response: The grammar have been thoroughly checked and corrected.

- *How do you determine the OH radical concentration?*

Response: In the MALTE-BOX model, the chemical mechanism scheme is produced by selecting chemical reactions primarily from the Master Chemical Mechanism (MCM). The kinetic preprocessor (KPP) was applied to numerically solve for the concentrations of each compound, including OH radical. To make it clearer, we have added more relevant descriptions and references in Page 6, Line 10-16.

- *Photochemistry can also play a significant role in NPF and the model's cloud cover can affect that significantly. How well does WRF-Chem reproduce the cloud cover during these event days?*

Response: As mentioned, cloud cover exerts significant impacts on photochemistry and also NPF processes in the atmosphere. Comparison between WRF-Chem reproduced cloud fraction and corresponding satellite detections from OMI instrument on AQUA is shown in the following figure (Fig. R1). WRF-Chem model displayed similar spatial patterns to OMI observations on the NPF days. On 22 June, dense cloud covered Shandong and Zhejiang province. During the second case, little cloud was found in areas south of the Yangtze River Delta according to both observation and simulation. While on 22 August, most parts of South China were covered by thick clouds.

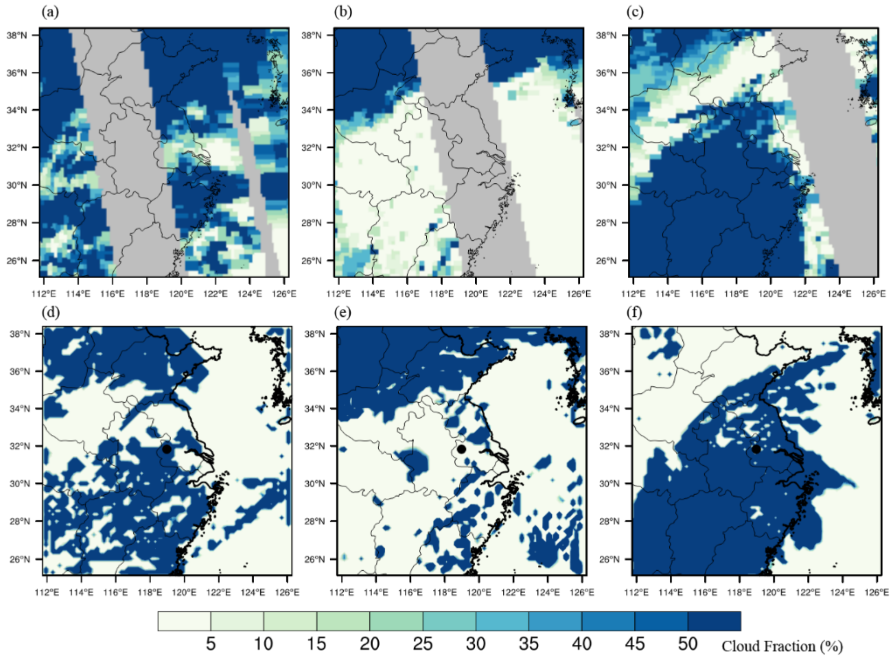

Fig. R1 Comparison of satellite-retrieved and model predicted cloud fraction during these three NPF days. (a-c) are OMI detected cloud fraction for 22 June, 10 July and 22 August, respectively. Corresponding simulations are displayed in (d-f).

- *The formation rate of 6 nm particles is not nucleation rate. A preferred term would be "new particle formation rate". Please correct this on Page 27515, Line 24, 25, and in the caption for Fig 7*

Response: Corrected. The term "nucleation rate" for 6 nm particle have been replaced with "new particle formation rate" throughout this manuscript.

- *Page 27506, Line 10: What do you mean by "good"?*

Response: Thanks. Here the words "good cluster formation rate" was unclear for readers. We rewrited this sentence as "Kinetic nucleation theory has been shown to have good performance in simulating cluster formation in various environments…" in the revised manuscript.

- *Page 27508, Line 20: Have you checked if this distribution is equal also in observations?*

Response: The distribution was not compared with observations. During the summer of 2014, GC-MS-FID (Gas Chromatography-Mass Spectrometry- Flame Ionization Detector) was used to measure concentrations of VOCs at the SORPES station. Technically, all the kinds of biogenic VOCs that listed in Table 1 can be measured. However, during the calibration, retention times were determined for a limited number of compounds. Among species in Table 1, only isoprene was included to generate the calibration curve. Thus, it is infeasible to get the profile of biogenic VOC distribution and compare it with model results in this work. We plan to include more VOC species, particularly biogenic ones, in future VOC measurements.

- *Page 27513, Line 18: This wording "succeeds, on average, to generally reproduce" is very ambiguous. Please rephrase this.*

Response: This sentence have been rephrased in the revised manuscript. Please see Page 12, Line 3-5.

Page 27507, Line 25: What does "for further analysis and box modeling" mean in this context?

Response: In this context, by "further analysis and box modeling", we mean that only the last 48-h simulation results of WRF-Chem were used to provide input to the box model and also data for some figures shown by us. It might be not so clear to use the word "further" and we have changed it to "following" in the revision (Page 7, Line 11).

- *Page 27510, Line 18: 500 000 #cm3 cannot be the correct value as it is extremely high.*

Response: It has been corrected to 10,000 # cm^{-3} in the revised manuscript, see Page 9, Line16.

- *Page 27512, Lines 17-18: It is said, that "On one hand, humid air mass transported from the ocean might have favored the particle growth". Please explain the reasoning behind this sentence.*

Response: Accepted. We have added some explanations in Section 3.1.

- *Page 27514, Line 17: The word "concentration" is missing?*

Response: The word "concentration" has been added (Page 13, Line 23).

- *Figure 5: Having different y-scales in the right column plots make the comparison of* *the events difficult.*

<u>Response</u>: The y-scales of the right subplots have been unified in the revised Fig. 5.

Reference

Qi, X. M., Ding, A. J., Nie, W., Petäjä, T., Kerminen, V.-M., Herrmann, E., Xie, Y. N., Zheng, L. F., Manninen, H., Aalto, P., Sun, J. N., Xu, Z. N., Chi, X. G., Huang, X., Boy, M., Virkkula, A., Yang, X.-Q., Fu, C. B., and Kulmala, M.: Aerosol size distribution and new particle formation in the western Yangtze River Delta of China: 2 years of measurements at the SORPES station, Atmos. Chem. Phys., 15, 12445-12464, doi:10.5194/acp-15-12445-2015, 2015.

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Zhou, L. X., Nieminen, T., Mogensen, D., Smolander, S., Rusanen, A., Kulmala, M., and Boy, M.: SOSAA - a new model to simulate the concentrations of organic vapours, sulphuric acid and aerosols inside the ABL - Part 2: Aerosol dynamics and one case study at a boreal forest site, Boreal Environ. Res., 19, 237-256, 2014.

Response to Referee #2

New particle formation (NPF) in the atmosphere is a hot topic in recent years. Although there are some studies conducted in China, no studies are reported in Nanjing, the capital of Jiangsu province in Yangtze River Delta region. In particular, this is the first study in China to understand the NPF mechanism using a number of models. In detail, this study utilized a comprehensive modeling system, combining WRF-Chem and MALTE-BOX model to investigate the complex processes of the NPF and subsequent growth in the Yangtze River Delta region. Three typical NPF events, which were probably influenced by distinguished emission sources, were selected for mechanism study. Two kinetic-type nucleation mechanisms including homogenous homo-molecular sulphuric acid vapours and hetero-molecular nucleation involving organic vapours were tested. The simulated NPF events were generally in good agreement with the field measurements, providing a possibility to better understand the NPF processes in this region. The paper is well organized and well written. It is worth to be published and will definitely add values to the literature. Nevertheless, more in-depth model simulations and discussion can contribute more to the literature. Hence, this paper can be further strengthened by more comprehensive discussion of the simulated results. The specific comments are shown as follows.

Response: We would like to greatly appreciate the referees for providing the insightful comments, which indeed help us reconsider and further explore these NPF events and their simulations. In the revised manuscript, we have added more descriptions on the method of measurement and modelling, as well as in-depth discussion concerning model performance.

Major comments:

In "Introduction" section, the information about the MALTE -BOX modelling studies on the aerosol formation in recent years should be provided.

Response: Accepted. Information on the MALTE modelling studies in recent years has been provided in the revised "Introduction" section. Please see Page 3, Line 14-21.

In "Data and methodology" section 2.1, has the diffusion loss been considered when sampling the ultrafine particles by DMPS, have you corrected the number concentration of nucleation mode particles (<10 nm) measured by DMPS due to the large diffusion loss of nanoparticles?

Response: The diffusion loss in the sampling line of DMPS has been considered during the data analysis. The method, that was used to correct raw data was described by Hinds et al. (1998). The penetration through a tube (P) can be expressed as:

$$P = \frac{n_{out}}{n_{in}} = 1 - 5.50\mu^{\frac{2}{3}} + 3.77\mu \text{ (for } \mu < 0.009)$$

$$P = 0.819 \exp(-11.5\mu) + 0.0975 \exp(-70.1\mu) \; (for\ \mu \geq 0.009)$$

where μ is a function of the dimensionless deposition parameter ($\mu = \frac{DL}{Q}$, where D is the diffusion coefficient of the particles, L is the length of the tube and Q is the volume flow rate through the tube). In addition, the diffusion loss in CPC was calculated by the calibration of the instrument.

In section 2.2.1, the calculation method or equation of sulphuric acid vapour concentration should be provided.

Response: In the MALTE-BOX model the chemical mechanism scheme is produced by selecting chemical reactions primarily from the Master Chemical Mechanism (MCM). The Kinetic PreProcessor (KPP) was applied to numerically solve for the concentrations of each compound, including sulphuric acid vapour. To make it clearer, we added more relevant descriptions in Page6, Line10-16.

Twenty ELVOCs and seven SVOCs were selected as condensable vapours. Why did you choose these compounds not others? What are the precursors of these condensable organic vapours? More detailed information should be provided.

Response: The chemistry scheme includes the full MCM chemical paths for the following parent molecules: methane, methanol, formaldehyde, acetone, acetaldehyde, 2-methyl-3-buten-2-ol (MBO), isoprene, alpha-pinene, beta-pinene, limonene and beta-caryophyllene. About twenty low-volatility organic compounds (ELVOCs) and seven selected semi-volatile organic compounds (SVOCs) are regarded as condensing vapours. Specifically, seven representative SVOCs with vapour pressures estimated to range from 10^4 to 10^6 molecules cm^{-3} and recently detected ELVOCs with vapour pressures between 10 and 10^3 molecules cm^{-3} are introduced in the model. The specific names of these twenty ELVOCs and seven SVOCs are listed in the Section 2.2.1. They are reaction productions of OH, O_3 and NO_3 oxidation of aforementioned VOCs based on MCM chemistry, which is available at http://mcm.leeds.ac.uk/MCMv3.1. We have added detailed information in Section 2.2.1

In section 3.1 lines17-18, the number concentration of 500 000 # cm-3 is extremely higher than other studies. Double check if the number concentration of particles here is in unit particles/cm3 not in the unit dN/dLogDp.

Response: Checked. It has been corrected to 10,000 # cm^{-3} in the revised manuscript (Page 9,Line 16).

Page 27511 lines 8-9, the contribution of sulphuric acid vapour to the particle growth can be calculated, and also this sentence is not very clear, please rewritten.

Response: We added the contribution of sulphuric acid vapour to the particle initial growth in Fig. 7 and gave more discussions in Section 3.2.2.

In section 3.2.1 line 17 what are the major species of alkenes and aromatic compounds simulated by WRF-Chem? (e.g. were only biogenic terpenes included in the alkenes group?)

Response: We used SAPRC scheme to describe gas-phase chemistry in WRF-Chem simulation, as mentioned in Line 15 on Page 27508. Alkenes include ETHE—ethene, OLE1—alkenes (other than ethene) with kOH < $7\text{x}10^4$ ppm^{-1} min^{-1}, OLE2—alkenes with kOH > $7\text{x}10^4$ ppm^{-1} min^{-1}, biogenic terpenes and isoprene. As for aromatics, they are divided into two lumped groups for both emission and photochemistry procedure: ARO1—aromatics with kOH < $2\text{x}10^4$ ppm^{-1} min^{-1} and ARO2—aromatics with kOH > $2\text{x}10^4$ ppm^{-1} min^{-1}. Detailed descriptions on SAPRC scheme can be found in the cited reference Carter (1999).

Lines 17-19, based on the normalized mean bias, the simulated results of alkenes, aromatic and isoprene concentration should be evaluated separately, such as, which one showed better agreement and why?

Response: Accepted. Model's performances on simulation of alkene, aromatic and isoprene concentration are discussed separately in Section 3.2.1. Please see Page 12, Line 3-16.

Lines 21-26, the simulated varied spatial patterns of biogenic terpenes during the three NPF days could not be explained by the dominant wind directions. Since biogenic emissions are closely related to the weather temperature, as shown in Fig.3, the higher temperature during the second NPF case was observed than that in the other two cases. That would be one important reason causing high biogenic terpenes emission simulated by WRF-chem.

Response: Yes, we agree that the spatial pattern are mainly due to the distribution of air temperature and land cover. Here we highlight the wind-direction is just to show how the transport of biogenic terpenes could influence the SORPES station under specific weather (wind) condition.

In section 3.2.2, this part should be further improved with more model test and in-depth discussion.

Two kinetic nucleation mechanisms were introduced in this section. However, only homogenous nucleation mechanism of sulfuric acid vapours was tested by the box model. The nucleation mechanism involving organic vapours was only investigated by the relationship of $[H2SO4]^{1.0}[NucOrg]^{0.8}$ *and J6, and not applied into the model to evaluate whether it improved the simulation results or not.*

Response: The aim of this manuscript was not to test all available nucleation theories, which are listed in scientific manuscripts like e.g. Paasonen et al., 2010. Up to our knowledge there is still a quite strong discussion in the scientific community what molecules are really participating in the nucleation or lets say better in the formation of clusters, which are stable enough to grow to detectable sizes. If ELVOCs are really part of this mechanism is still unclear and needs to be further investigated in chamber experiments and detailed chamber model simulations but was not the main aim of this manuscript. For this reason we used in the model runs here only the most widely spread kinetic cluster formation mechanism of sulphuric acid to compare the achieved values with other stations.

As shown in Fig.5, in Cases 2 and 3, simulated nucleation mode particle number concentrations were higher than observed values, while in case 1 it was opposite. Also, the simulated results were the highest in case 3, followed by cases 2 and 1. These findings need more explanations and discussions in order to explore the major factors influencing the results during the each event. For example, in case 3, the RH was very high, while the wet deposition was not included in the MALTE model; hence the weather condition may partly influence the modelled results causing a higher simulated result than the observed one. As described in the paper, the highest condensation sink (CS) and biogenic VOCs concentration were observed or simulated during the first and second events, while the lowest condensation sink and higher sulphuric acid production were found during the third event. These three events provide a good opportunity to investigate the relative role and sensitivity of CS, BVOCs and sulphuric acid vapour concentrations in the new particle formation and to the growth, respectively.

Response: We added more explanations and discussions in the Section 3.2.2 (Page 13-14).

For Case 1, the event occurred even under the high level of condensation sink. How high CS would finally inhibit the event on this day? And also how low sulphuric acid vapour concentration could still trigger the nucleation under such high CS? Their contributions and sensitivity tests on new particle formation rate and growth rate can be conducted by increasing the CS value or decreasing the calculated sulphuric acid vapour concentration gradually for box model runs.

Response: The sensitivity runs suggested by the referee would only be valid for this special day and in our opinion provide no information for any other set of values because the formation and growth of particles is a complex mechanism. Many parameters like CS, RH, OH, H_2SO_4, ELVOC, SVOC, … will influence the occurrence of new-formed particles in a non-linear manner. So just increasing the CS values on one special day and investigating when new-particle formation is damped could not be used for other days and would not provide further interesting outcome for the scientific community. For this reason we see no reason to perform this simulations without any further reason why they should be useful for other studies.

Similarly, for Case 3 (actually, it is not a suitable day identified as a NPF event occurred under the low level of condensation sink since it was a rainy or cloudy day, and the RH was very high on this day which enhanced the condensation sink), it would be better to select a sunny NPF day when condensation sink was very low. If not, at least you could investigate the lowest level of sulphuric acid vapour, which would induce the initial nucleation during this event.

Response: Also here the authors as explained above see no reason what is the scientific outcome of sensitivity runs with decreasing sulphuric acid concentration. It is obvious that the complex mechanism in the particle formation process could not provide more information useful for other readers than one value of sulphuric acid concentration at this specific location and this specific set up of all other parameters where no more particles are formed.

Concerning the comment of the referee related to the high RH. The solar radiation input measured at the SORPES station should a clear daily pattern with values up to 500 W/m^2 and the temperature reached 32 °C. Although the RH especially in the morning was very high on this day we selected it because of the air mass origin and the availability of measurements at the SORPES station required for input in MALTE-BOX. If other nucleation days with the same requirements would have been available we definitely would have selected a different one.

For Case 2, organic vapours were showing more important role in the particle formation than the other two cases, and the authors also tried to use a hetero-molecular nucleation theory involving organic vapours to better explain the observed particle formation rate. However, the focus was lost by combination of all data during the three events as shown in Fig. 7. Based on the distinguished characteristics of these three events, sulphuric acid vapours and organic vapours may play different roles in the formation process, and only using one relationship ($[H2SO4]^{1.0}$ $[NucOrg]^{0.8}$) *of sulphuric acid and organic vapours for the simulation of three events is not scientific. According to the observation, sulphuric acid vapours seem to involve more significantly into nucleation process during the Case 1 and Case 3 than during Case 2. Here, the importance of sulphuric acid and organic vapours in each event should be investigated individually.*

Response: As already mentioned above in our opinion it is very open until now if ELVOCs are really participating in the formation for clusters, which are able to grow to detectable sizes. Currently we are including in MALTE-BOX a new particle or cluster formation model, which is based on the ACDC code (Atmospheric Cluster Dynamics Code; McGrath et al., 2012) developed in the group of Prof Hanna Vehkamäki at the University of Helsinki. This code predicts the surviving probability of clusters containing sulphuric acid and other organic molecules based on quantum chemical calculations. This new code will provide us for the first time the chance to simulate the concentrations of particles or clusters from sulphuric acid and organic compounds. However, this process is still in progress and not ready for this manuscript.

Coming back to the referee suggestion by testing the ELVOC or sulphuric acid contribution for the formation during the three events. We have added figure 7, which shows the contribution of the single compounds to the growth of the particles, however a test of the different formation mechanisms in the model would not provide further outcome because the only mechanism used quite often in the literature is the kinetic formation of sulphuric acid. This results could be compared with data from other stations and so provide us some hints about the impact of sulphuric acid at this station.

In our opinion already the results of table 2 gives a clear understanding how important other molecules – most probably for the growth – are on day number 3, when the air mass originated partly over the Shanghai area. The model underpredicts the growth rate nearly by a factor of 7 and overestimates the formation rate by 3. This means that most probably other anthropogenic compounds not included in the model until now are contributing strongly to the growth and decrease the surviving probability of the clusters formed in the model. This is completely opposite on the second day, when the air mass originated not from strong anthropogenic influenced areas. Here the model outcome is surprisingly in good agreement with the measurements. In our opinion these results show that in heavy anthropogenic polluted areas other mechanism for both formation and growth of particles have to be investigated.

As mentioned above, in Fig.7 (b) and (c) the relationship of sulfuric acid and organic vapours with particle formation rate should be separately investigated during each event. In Fig.7 (b), two lines should be drawn based on the equations provided in the manuscript, i.e., $J = 6.0*10^{-19}*[H2SO4]^{2.0}$ *for 10 July (Case 2) and 22 August (Case3), and* $J = 2.2*10^{-16}* [H2SO4]^{2.0}$ *for 22 June (Case 1). In Fig.7 (c), a line based on the equation* $J1.5 = 7.2\pm1.4*10^{-13}* [H2SO4]^{1.0} [NucOrg]^{0.8}$ *should be drawn. It is very noteworthy that J6 in Fig. 7(c) should be J1.5 which is significantly larger than J6, and can be calculated based on J6. Then the correlation coefficients of sulfuric acid and organic vapours with particle formation rate during each event in Fig.7 (b) and (c) can be calculated, respectively, by linear regression analysis. According to these correlation coefficients, you can find out which line fit well with which event and explore the potential formation mechanisms during each NPF event.*

Response: Dashed lines showing $J=2.2\times10^{-10}\times[H_2SO_4]^{2.0}$ and $J=6.0\times10^{-13}\times[H_2SO_4]^{2.0}$ have been added for reference in Fig.8 (b). In our opinion it would make no sense to compare to J1.5 values because these measurements are not available by the DMPS-system and would only include another uncertainty when using a parameterisation for scaling in down. The reason why we included this figure is to provide some hints if ELVOCs are crucial in the formation and growth of particles up to 6 nm. There was no aim from us to state that ELVOCs are important in the formation of clusters which is still open (see discussion above).

Page 27508, section "data analysis". What is the difference between coagulation loss and condensation sink. CS was not included in equation (2).

Response: Condensation sink describes the speed at which condensable vapour molecules condense onto the existing aerosol while coagulation loss (coagulation sink) describes the aerosol particles collide and stick to each other. Generally, the coagulation sink has positive correlation with condensation sink (Kulmala et al., 2001). Formation rate was not the function of condensation sink but coagulation sink.

Page 27511, section 3.1 "Observations and data analysis". "Along with the active photochemistry and high concentration of O3, rapid oxidation of SO2 and accumulation of gaseous sulphuric acid are expected". The authors should briefly introduce the mechanism of SO2 oxidation by O3 or OH.

Response: Accepted. Brief introduction of gaseous oxidation of SO_2 by OH radical was added in the section 3.1.

Page 27514, the explanation of third NPF case (22 August) was not convincing enough. The concentrations of SO2, sulphuric acid, SVOCs and ELVOCs were all pretty lower than those in the other two cases. However, the concentration of OH was remarkably higher. The explanation of "little condensational loss" was a factor causing the third NPF. However, it maybe not enough, the authors need dig depth for better explanations.

Response: Accepted. We highlighted the importance of increased OH concentrations in H_2SO_4 accumulation during the third NPF case.

Page 27515-27516. Can the equation of nucleation rate of 1.5 nm cluster (equation (5)) be directly applied to J6?

Response: Indeed, nucleation rates for 1.5 nm is quite different from those for 6 nm. The latter was influenced by growth processes to a greater extent. That is, the measured J_6 in this work contains more information on growth processes when compared with $J_{1.5}$ in Metzger et al. (2010). Ideally, $J_{1.5}$ makes more sense to analyse the role of biogenic VOC in NPF. However, the detection limit of existing DMPS measurements at the SORPES station is 6 nm, and thus what we can direct measure is J6. In addition, as disscussed before, the reason why we included this figure is to provide some hints if

ELVOCs are crucial in the formation and growth of particles up to 6 nm. The reason why we included this figure is to provide some hints if ELVOCs are crucial in the formation and growth of particles up to 6 nm. There was no aim from us to state that ELVOCs are important in the formation of clusters which is still open.

Page 27515, lines 14-16, as the production of ELVOCs and SVOCs was mainly initialized by the reactions between monoterpene and ozone, the contribution of monoterpene oxidation to the production of ELVOCs and SVOCs should be evaluated by models and provided here.

Response: This is an interesting aspect and is shown in newly-added figure 7.

Page 27516 lines 15-21, for the particle growth, the contributions of the OH and O3 oxidation mechanism on the volume concentration of small particles can be further investigated to find out the dominant precursors and their oxidations involving in the particle growth in these studied events.

Response: Yes this would be interesting to identify the strength of OH compared to O_3 oxidation products contributing to the growth of particles. However, it is not so easy forward by using the MCM chemistry with thousands of reactions. Of course we could only set Ozone or OH to zero but this would influence the chemistry strongly because we are not only taking the first reactions into account but a whole reaction chain with Ozone and OH being reaction partners many times. We are currently working on a plausible way to investigate the contribution of this two or if we take NO_3 also into account on the three main oxidants. This is in progress and will take some time but could not be offered in this manuscript.

P27517 lines 2-5, the sentences "According to the simulation, ... at the experimental site." are difficult to be understood.

Response: We have rephrased this sentence in the revised manuscript (Page 15, Line 20).

Minor comments:

It may be inappropriate to use "first" in the title. In Fig. 3, draw diurnal variation of CS.

Response: Accepted. We have changed the title to "Comprehensive modelling study on observed new particle formation at the SORPES station in Nanjing, China". Diurnal variation of CS was plotted in Fig. 3.

In Fig. 3, check if the diurnal variation of particle size distribution during the first event is in the same value scale range as other two events.

<u>Response</u>: Checked. Y-Scales for all subplots have been added in the revised Fig. 3.

In Fig. 4 (a), (b) and (c), the meanings of the dashed lines should be provided.

<u>Response</u>: Accepted. Please see the caption of Fig.4.

In Fig.5, check if the unit of particle number concentration is not "dN/dLogDp" in right panel.

<u>Response</u>: Checked. The unit should be "# cm^{-3}" and we replotted Fig. 5.

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Comprehensive modelling study on observed new particle formation at the SORPES station in Nanjing, China

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Abstract

New particle formation (NPF) has been investigated intensively during the last two decades because of its influence on aerosol population and the possible contribution to cloud condensation nuclei. However, intensive measurements and modelling activities on this topic in urban metropolitans in China with frequently high pollution episodes are still very limited. This study provides results from a comprehensive modelling study on the occurrence of new particle formation events in the western part of the Yangtze River Delta region (YRD), China. The comprehensive modelling system, which combines regional chemical transport model WRF-Chem (the Weather Research and Forecasting model coupled with Chemistry) and the sectional box model MALTE-BOX (the model to predict new aerosol formation in the lower troposphere), was shown to be capable of simulating atmospheric nucleation and subsequent growth. Here we present a detailed discussion of three typical NPF days, during which the measured air masses were notably influenced by either anthropogenic activities, biogenic emissions, or mixed ocean and continental sources. Overall, simulated NPF events were generally in good agreement with the corresponding measurements, enabling us to get further insights into NPF processes in the YRD region. Based on the simulations, we conclude that biogenic organic compounds, particularly monoterpenes, play an essential role in the initial condensational growth of newly formed clusters through their low volatile oxidation products. Although some uncertainties remain in this modelling system, this method provides a possibility to better understand particle formation and growth processes.

1 Introduction

Ambient aerosols affect human health adversely, degrade visibility, and play an important role in climate change through directly scattering/absorbing solar radiation or indirectly modifying microphysical properties of clouds (Eidels-Dubovoi, 2002; Davidson et al., 2005; Lohmann and Feichter, 2005; Myhre et al., 2013). Atmospheric new particle formation (NPF), characterized by a sharp increase in number concentration of nucleation-mode aerosol, has been observed under a wide variety of circumstances and has been shown as a significant source of atmospheric fine particles (O'Dowd et al., 2002; Kulmala and Kerminen, 2008; Gao et al., 2011; Guo et al., 2012; Guo et al., 2014; Wang et al., 2014). As the newly formed particles and their following growth may lead several-fold increases in aerosol number concentrations, atmospheric NPF could substantially contribute to the global CCN (Cloud condensation nuclei) budget and its subsequent cooling effect (Lihavainen et al., 2003; Merikanto et al., 2009; Yu and Luo, 2009; Wang and Penner, 2009; Kerminen et al., 2012; Makkonen et al., 2012; Scott et al., 2015).

NPF has been extensively and intensively studied globally during the last two decades. It is well known that particle formation in the atmosphere is strongly dependent on the abundance of sulphuric acid (Weber et al., 1999; Kulmala et al., 2004b; Sipila et al., 2010). Meanwhile, other compounds in the atmosphere may be responsible for NPF occurrence in different environments. Iodine-containing vapours were identified as the precursors for marine new particle formation (O'Dowd et al., 2002). Observations in Pittsburgh imply that ammonia could considerably enhance the atmospheric particle formation (Q. Zhang et al., 2004). In the boreal forest, oxidation products of monoterpenes together with sulphuric acid were very likely to lead to NPF (Schobesberger et al., 2013) and new findings indicate that organic amines (e.g. dimethylamine) can enhance water-sulphuric acid particle formation rates more than 1000-fold compared to ammonia (Almeida et al., 2013). In addition to direct in-situ observations of NPF events, model simulation has been serving as a useful tool for analysing NPF dynamics since 1990s (Kulmala et al. 1995; Kerminen and Wexler, 1996; Korhonen et al., 1999). In recent years, MALTE model has been successfully utilized in NPF analysis, for instance, reproducing OH radical and gaseous sulphuric acid levels (Petaja et al., 2009), validating various plausible nucleation mechanisms and particle growth (Boy et al., 2007; Wang et al., 2013b), and identifying important factors influencing NPF occurrence (Boy et al., 2006, 2008; Ortega et al., 2012).

As one of the most economically invigorating and densely populated countries, China features simultaneous high aerosol loadings and NPF rates (S. Liu et al., 2008; Gao et al., 2011; Guo et al., 2012). Moreover, the condensational growth of nucleation-mode particles has been indicated as a plausible cause of regional haze events (Guo et al., 2014). Since 2000s, several field campaigns as well as long-term measurements have been conducted in several regions such as Beijing, the Pearl River Delta as well as the Yangtze River Delta, showing high occurrence frequencies and formation rates across China (S. Liu et al., 2008; Gao et al., 2009; Yue et al., 2010; Herrmann et al., 2014; Qi et al., 2015; Xiao et al., 2015). However, modelling studies that provide a further insight into the processes of atmospheric aerosol formation, are still very limited in China. Numerical simulations of formation and growth processes usually require detailed and high time-resolving measurements of the relevant compounds, however, hardly can any field campaign or in-situ measurement station in China meet this requirement. The novel combination of a regional chemical transport model and a zero-dimensional box model with detailed aerosol dynamics makes it possible to accomplish NPF studies without direct measurements of all specific chemical species. Here, we present a comprehensive modelling study targeting at reproducing observed NPF events under distinct conditions at the Station for Observing Regional Processes of the Earth System (SORPES) at Nanjing University in Nanjing, China (Ding et al., 2013a). This is the first attempt to integrate the regional model, box model and in-situ measurements to investigate NPF events in China, enabling us to gain more insights into NPF mechanism in the YRD region.

2 Data and Methodology

2.1 In-situ measurements

The SORPES site is located in the Xianlin campus of Nanjing University in the suburban area northeast of Nanjing, which is about 20 km east from the downtown area (118°57’10’’ E, 32°7’14’’N, 40 m a.s.l. as shown in Fig. 1 in Ding et al., 2013a). This site, with few local emission sources around it, is generally upwind of downtown Nanjing and also downwind of the city clusters of the Yangtze River Delta. Hence it can be regarded as a regional background station (Ding et al., 2013a).

On-line and high time-resolving measurements of trace gases, aerosol characteristics, and relevant meteorological parameters have been conducted since the summer of 2011. Ozone (O_3), sulphur dioxide (SO_2), nitrogen monoxide (NO), nitrogen dioxide (NO_2), total reactive nitrogen (NO_y), carbon monoxide (CO) and $PM_{2.5}$ (fine particulates less than 2.5 microns in aerodynamic diameter) are routinely measured by Thermo Instruments (TEI 49i, 43i, 42i, 42iY and 48i) and MARGA (Monitor for Aerosols & Gases in Ambient Air) (Ding et al., 2013a,b). The Differential Mobility Particle Sizer (DMPS) coupling a differential mobility analyzer with two different flow rates and a condensation particle counter are used to measure number distributions of atmospheric particles from 6 to 800 nm (Herrmann et al., 2014, Qi et al., 2015). More thorough information on the instruments at the SORPES site is elaborated in detail in Ding et al. (2013a,b).

2.2 Model description

2.2.1 MALTE-BOX model

MALTE is a one-dimension model comprising of boundary layer meteorology, biogenic emission of volatile organic compounds, gas-phase chemistry and aerosol dynamics in order to predict particle formation and growth processes under atmospheric conditions (Boy et al., 2006). Here, we apply the zero-dimensional version, namely, MALTE-BOX model, to simulate NPF events at the SORPES station. In the MALTE-BOX model, boundary layer meteorology and biogenic emission modules are switched off; instead, the biogenic and anthropogenic VOC emissions and their following transport and dispersion are calculated by the regional chemical transport model WRF-Chem. Concentration of various organic compounds at the SORPES station predicted by WRF-Chem model are inputted into MALTE-BOX model every 10 minutes (Table 1 provides the compounds calculated by WRF-Chem as input to MALTE-BOX). Likewise, measured concentrations of trace gases including CO, SO_2, NO, NO_2 and O_3, with the same temporal resolution, are also included as input fields. In addition to gas phase precursors, the inputs also include an initial particle number size distribution at 0:00 LT on each day, ambient temperature, relative humidity and the condensation sink of sulphuric acid (as defined in Sect. 2.3).

In the MALTE-BOX model, particles are assumed to be spherical. Fixed sectional approach with 40 size bins ranging from 1.4 to 2000 nm in diameter is used in the present study. The aerosol dynamics has all basic aerosol processes, including nucleation, condensation, coagulation, and deposition. The new particle formation rates of newly formed clusters are estimated by the kinetic nucleation theory of sulphuric acid (Sihto et al., 2006), which is related to the sulphuric acid concentration as follows:

$$J = k_1 \times [H_2SO_4]^2 \qquad \text{Eq. 1}$$

where k_1 is the kinetic coefficient that includes both the collision frequency and the probability of forming a stable cluster after the collision. Kinetic nucleation theory has been shown to have good performance in simulating cluster formation in various environments including both clean continental area and polluted urban site (Wang et al., 2013b; Zhou et al., 2014). The nucleated particles were added to the first size bin in the model.

We conducted a set of sensitivity simulations to establish a suitable value for the nucleation coefficient k_1. After comparing the simulations and DMPS measurements, k_1 was set to

6.0×10^{-13} cm^3/# for 10 July and 22 August, and 2.2×10^{-10} cm^3/# for 22 June, respectively. These values were similar than those we commonly used in the simulations for NPF at other stations (Boy et al., 2008a, Paasonen et al., 2010; Zhou et al., 2014). The high value on the 22 June might imply that other low volatile vapours - most probably from anthropogenic origin - are involved and play a crucial role in the particle formation process at this urban site. Moreover, being limited by the detectable size of the DMPS (what we can monitor are the particles larger than 6 nm in diameter), means that the observed formation process could be steered by the condensational growth of the smallest clusters to the detection limit.

We included relevant chemical reactions of the MCM (Master Chemical Mechanism) in this model, as described in Boy et al (2013). The chemistry scheme included the full MCM chemical paths for the following parent molecules: methane, methanol, formaldehyde, acetone, acetaldehyde, 2-methyl-3-buten-2-ol (MBO), isoprene, alpha-pinene, beta-pinene, limonene and beta-caryophyllene. The Kinetic PreProcessor (KPP) was applied to numerically solve for the concentrations of each individual compound (Damian et al., 2002), except for those species whose concentrations were manually inputted from direct measurements and WRF-Chem model. Apart from sulphuric acid, about twenty low-volatility organic compounds (ELVOCs) and seven selected semi-volatile organic compounds (SVOCs) are regarded as condensing vapours, following the simplified chemical mechanism presented by Ehn et al. (2014). Specifically, seven representative SVOCs (MCM-nomenclature: C719OOH, LIMALOOH, C924OOH, NORLIMOOH, C811OOH, C818OOH and C819OOH) with vapour pressures estimated to range from 10^4 to 10^6 molecules cm^{-3} (using the group contribution method described by Nannoolal et al. (2008)) and recently detected ELVOCs ($C_{10}O_{5-12}H_x$, $C_{10}NO_{5-13}H_x$ and $C_{20}O_{8-16}H_x$) with vapour pressures between 10 and 10^3 molecules cm^{-3} are included as condensing vapours in the model.

2.2.2 WRF-Chem

The WRF-Chem version 3.6 was used here to estimate concentrations of various organic vapours from anthropogenic and biogenic emissions as there was no VOCs measurement at the SORPES site during the study period. WRF-Chem is an online three-dimensional, Eulerian chemical transport model that considers the complex physical and chemical processes, such as emission and deposition of pollutants, advection and diffusion, gaseous and aqueous chemical transformation, aerosol chemistry and dynamics (Grell et al., 2005). It is capable of simulating atmospheric chemistry on a regional scale and has been successfully applied in several of our previous studies (Huang et al., 2014, 2015). In this study, the model domain covered East China and its surrounding area, centring at 32.0°N, 119.0°E with a 20×20 km grid resolution, as demonstrated in Fig. 1. There are 24 vertical layers from the ground level to the top pressure of 50 hPa, in which 10 layers are placed under 1 km to better resolve the boundary layer process. The 6 hourly Final operational global analysis (FNL) data with a 1°× 1° spatial resolution produced by the National Centres for Environmental Prediction (NCEP) was used as initial and boundary conditions of meteorological fields. The simulations were conducted for June to August 2013 when NPF events were frequently detected (Qi et al., 2015). During the simulation period, each run covered 60 hours, in which the first 12 hours were just for model spin-up and the last 48-hour results were adopted for following analysis and box modelling. The outputs of compound concentrations from the preceding run were treated as the initial conditions for the next run. Key physical parameterization options for the WRF-Chem modelling are the Noah land surface scheme to describe the land-atmosphere interactions (Ek et al., 2003), the Lin microphysics scheme (Lin et al., 1983) with the Grell cumulus parameterization to reproduce the cloud and precipitation processes (Grell and Devenyi, 2002), the YSU boundary layer scheme (Hong, 2010), and the RRTMG short- and long-wave radiation scheme (Mlawer et al., 1997).

Anthropogenic emissions from power plants, residential combustion, industrial processes, on-road mobile sources and agricultural activities were derived from the MEIC database (Multi-resolution Emission Inventory for China, see www.meicmodel.org). Emissions of major pollutants, such as carbon monoxide, sulphur dioxide, nitrogen oxides, ammonia and speciated VOCs are all included in this emission inventory database. MEGAN (Model of Emissions of Gases and Aerosols from Nature, version 2) module embedded in WRF-Chem is used to calculate biogenic emissions online (Guenther et al., 2006). It estimates the net emission rates of isoprene, monoterpene and other biogenic VOCs from terrestrial ecosystems into the above-canopy atmosphere. Gas-phase chemistry is explicitly represented by the model through the SAPRC photochemistry scheme (Carter, 1999), which includes 225 gas-phase reactions among 81 chemical species in the model. We mapped some predicted organic species in WRF-Chem to the MALTE-BOX following the correspondence denoted in Table 1. Regarding the monoterpenes (alpha-pinene, beta-pinene, camphene, myrcene, carene and limonene) used in MALTE-BOX chemistry (details in Boy et al., 2013), the distribution was performed equally because no VOC-measurement were available at the SORPES station.

2.3 Data analysis

The calculations of particle growth and formation rates are conducted following the procedures outlined by Kulmala et al. (2012). The formation rate is obtained from the following equation:

$$J_{dp} = \frac{dN_{dp}}{dt} + CoagS_{dp} \times N_{dp} + \frac{GR}{\Delta dp} \times N_{dp} + S_{losses} \quad \text{Eq. 2}$$

where J_{dp} refers to the particle formation rate of diameter *dp*, the first term on the right side is the time evolution of the particle number concentration with size ranging from *dp* to $dp+\Delta dp$. The second term derives the coagulation loss by the product of coagulation sink ($CoagS_{dp}$) and the number concentration in the size range [$dp, dp+\Delta dp$]. The third term is the growth out of the considered size range, in which *GR* means measured growth rate. The last term S_{losses} represents additional losses, which were not considered in this study.

The growth rate of particles during the NPF events can be expressed as

$$GR_{dp} = \frac{d_{p1} - d_{p2}}{t_1 - t_2} \quad \text{Eq. 3}$$

where d_{p1} and d_{p2} are the representative of the diameter of nucleated particles at the times t_1 and t_2, respectively. For calculation, d_{p1} and d_{p2} is then defined as the central size of each bin and t_1 and t_2 are the moments when the concentration of this size bin peaks.

The condensation sink determines how rapidly condensable vapour molecules will condense onto pre-existing aerosols. It can be derived by DMPS-measured particle number size distribution according to the following method (Kulmala et al., 2001).

$$CS = 4\pi D \sum_{dp'} \beta_{m,dp'} dp' N_{dp'} \quad \text{Eq. 4}$$

where D is the diffusion coefficient of the condensing vapour, β_m is a transition-regime correction, dp' is the discrete diameter and $N_{dp'}$ is the particle number concentration in respective size bin.

3 Results and discussions

This chapter is divided into two parts. The first subsection provides discussion of measured particle size distributions on three typical NPF days. Air mass transport pathways and parameters that favour the formation of new particles at the SORPES site will be investigated. The second subsection focuses on the numerical simulation of observed NPF events. A further detailed analysis of particle formation and following growth will be presented.

3.1 Observations and data analysis

Summer marks the season with frequent NPF events at the SORPES site, especially in the year of 2013 (Qi et al., 2015). From June to August 2013, 50 NPF events were detected during the 76-day measurement period when DMPS functioned normally, resulting in the particle formation probability of 66%. Among the observed NPF events, three representative cases were identified according to the retroplumes calculated based on Lagrangian dispersion model HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) following the method developed by Ding et al., (2013c). These selected NPF days are 22 June, 10 July and 22 August 2013, when the site was dominantly influenced by air masses from the YRD region, South China, and mixed ocean and continental areas, respectively (Fig. 2).

On 22 June 2013, a clear banana-shaped particle size distribution was captured by the DMPS in the morning (9:00-11:00 LT, Fig. 3). According to the DMPS observations, the number concentration of particles with diameter ranging from 6 to 30 nm reached up to 10,000 # cm^{-3} around 10:00 LT. The formation rate of 6 nm particles, namely J_6 calculated following Eq. 2, was 7.6 cm^{-3} s^{-1}. It was generally comparable to those typically observed elsewhere in China, for instance, 0.97-10.2 cm^{-3} s^{-1} in Hong Kong ($J_{5.5}$) (Guo et al., 2012). The diurnal variations of measured number size distribution and relevant trace gases are demonstrated in Fig. 3. This NPF event featured a large background particle loading with $PM_{2.5}$ mass concentration exceeding 50 μg m^{-3} because the air mass was lingering over city clusters in the YRD region before approaching the SORPES station, as shown in Fig. 2(a). Dense particle emissions from the rapidly urbanized and industrialized YRD region (Fig. 2(e)) corresponded to a high condensation sink of 4.2×10^{-2} s^{-1}, close to those typically observed in other urban areas in China (Gao et al., 2012; Xiao et al., 2015). For the same reason, influenced by the emissions in the YRD region (Fig. 2(d)), SO_2 concentration was observed to be 20–30 ppb, considerably higher than the normally observed level at the site, which is less than 10 ppb during summertime (Ding et al., 2013a). High-concentration of O_3 and increasing radiation intensity were indicative of active ozone photolysis and production of OH radicals, rapid gas-phase oxidation of SO_2 by OH radical and accumulation of gaseous sulphuric acid are expected, leading to the onset of NPF despite the high level of condensation sink. The subsequent growth was fast, with a GR_{6-30} (growth rate from 6 to 30nm) of 12.6 nm h^{-1}. Accumulating sulphuric acid with increasing ozone concentration might be one contributor. In addition, the presence of aromatic-related oxidation products from residential and industrial combustion in the YRD region could also substantially enhance particle formation and subsequent growth by absorption or heterogeneous reactions (R. Y. Zhang et al., 2004; Y. Liu, et al., 2008).

On 10 July when the air masses mostly came from the densely wooded area in South China, NPF showed much lower new particle formation rates than on 22 June, yet a slightly faster particle growth rate (Table 2). Previous investigations have revealed that overall GR is correlated with the rate of terpenes reactions with atmospheric photochemical oxidants, highlighting the importance of biogenic VOCs in the particle growth process (e.g. Boy et al., 2003; Kulmala et al., 2004a). During the QUEST (Quantification of Aerosol Nucleation in the European Boundary Layer) field campaign in Hyytiälä, Finland, recorded particle growth rates during NPF events correlated notably with gas-phase monoterpene concentrations, indicating that the oxidation products from biogenic VOCs may dominate particle growth (Laaksonen et al., 2008; Yli-Juuti et al., 2011). The positive correlation between freshly formed particle growth rates and monoterpenes and their oxidation rates by ozone was also verified in Hong Kong, China (Guo et al., 2012). Fig. 2(f) presents the spatial distribution of monoterpene emission rates during summertime across China calculated by the MEGAN model (Li et al., 2012). It is obvious that monoterpene emission is overwhelmingly intensive in South China, which is covered by large areas of broadleaf forests and shrubs. It is plausible that air masses passed over biogenic VOC-rich regions were saturated with sufficiently low volatile oxidation products, which enhanced the observed particle growth. The simulation results from the WRF-Chem model supported this view. Modelled isoprene and terpenes concentrations were 1.2 and 0.15 ppb at the SORPES site during NPF on 10 July, 150% and 50% higher than the corresponding values on 22 June. Besides, lower pre-existing particle loading is another cause of faster growth due to less particle surface area for vapours condensation.

Another NPF event, characterized by mixed marine and continental source regions, occurred on 22 August. Because of relatively clean air from the ocean and high wind speed of around 8 m s^{-1}, $PM_{2.5}$ and SO_2 concentrations were unusually low, only 11.0 μg m^{-3} and 2.8 ppb when NPF event took place. Accordingly, the condensation sink fell down to 1.9×10^{-2} s^{-1}. Existing measurements and analysis concluded that the main obstacle for the initial onset of new particle formation at the SORPES site is condensation sink, since SO_2 concentration is always high and there tends to be enough solar radiation as well (Herrmann et al., 2014). So, even though the SO_2 concentration was pretty low during that day, a fairly small condensation sink could trigger the onset of this NPF event. The nuclei growth rate, $GR_{6\text{-}30}$, was estimated to be 15.7 nm h^{-1}. On one hand, humid air mass transported from the ocean might have favoured the particle growth due to that high humidity could enhance the uptake and oxidation of SO_2 and also facilitate the transformation of gaseous nitric acid to particulate ammonium nitrate (Hildemann et al., 1984; Rattigan et al., 2000). As displayed in Fig. 3, the measured relative humidity (RH) was over 80% when the NPF began. On the other hand, the sampling site was also partly influenced by the air masses from the YRD region (Fig. 2(c)), which means that anthropogenic VOCs and oxidation products with low volatility might also exert a notable impact on particle growth.

3.2 Simulations of NPF events

To shed further light on NPF processes at the SORPES station, comprehensive simulations were performed by combining WRF-Chem regional atmospheric transport model and the MALTE-BOX model. Measurements of meteorological fields, trace gases and aerosol characteristics from the SORPES station are input to the box model. In the meantime, input also includes the concentrations of gaseous organic compounds from the WRF-Chem regional model (see Table 1). The simulations were conducted for the aforementioned three NPF days.

3.2.1 Evaluation of simulations by WRF-Chem model

Meteorological conditions play an important part in transport, diffusion, and chemical reactions in the atmosphere. Simulated hourly 2-m temperature and 10-m wind speed were evaluated using hourly temperature and relative humidity observations at the SORPES station. Statistical analysis of model performance for the three NPF days are listed in Table 3, including mean bias (MB) and root mean square error (RMSE). Generally, the model reproduced the observed 2-m temperature and 10-m wind. As mentioned, modelled VOC concentrations, which are vital for NPF simulation, are included as an input field in the MALTE-BOX model. Although there was no VOC measurement during the summer of 2013, the SORPES site and the Environmental Monitoring Centre of Jiangsu Province (118°47’E, 32°4’N) were equipped with GC/MS (gas chromatography/mass spectrometry) in the summer of 2014. In order to evaluate model’s performance in simulating VOC concentrations, we conducted another WRF-Chem run for the August of 2014 and then compared the model results with corresponding observations. The comparison of alkene, aromatic and isoprene concentrations in Fig. 4(a-c) illustrates that WRF-Chem is capable of reproducing the magnitude and temporal variations of VOC concentration originating from both anthropogenic and biogenic sources. Specifically, modelled results tend to underestimate alkene concentration but over predict aromatic level with normalized mean bias of -11% and 20%, similar to previous simulations for Shanghai (Tie et al., 2013). There still exist substantial uncertainties in China's anthropogenic VOC emission inventory, particularly speciated estimations, which was ascribed to uncertainties in the activity data, limited direct experiments on emission factors and source profiles (Wei et al., 2008; Zheng et al., 2009). Large biases in model-predicted aromatic level are expectable since it mainly emitted from petrochemical plants, gasoline vehicle and biomass burning with greater uncertainties in activity level estimation (Liu et al., 2008). In term of biogenic VOC, simplification in vegetation classification and numerical descriptions, limited understanding of controlling factors could introduce biases in modelled levels of BVOCs (Guenther et al., 2013). Given these uncertainties, the gaps between simulation and observations in Fig. 4(a-c) are acceptable. As for simulated biogenic terpenes, whose oxidation products have low vapour pressures similar to sulphuric acid and condense onto aerosol surfaces, the spatial patterns in the morning of the aforementioned three NPF days showed great differences (Fig. 4(d-f)). During the first and third NPF cases, prevailing easterly winds did not bring much biogenic VOC since biogenic emissions are most intensive in the southern part of China. By contrast, on 10 July when the air temperature was getting higher and southwesterly winds dominated, enhanced biogenic emissions and the shift in wind direction caused that the modelled terpene concentrations at the SORPES station were almost two times those in the other two NPF days.

3.2.2 MALTE-BOX simulations

Fig. 5 shows the variations of modelled particle number size distributions during the three NPF days. The model system does reproduce the occurrence of these three NPF events although they were under distinct meteorological conditions and affected by entirely different potential source regions. On 22 June when measured air masses originated from the urbanized YRD region, the calculated onset of activation of freshly formed cluster to grow above the 6 nm line appeared around 08:30 LT. According to the diurnal pattern of simulated concentrations of gaseous compounds illustrated in Fig. 6, the OH radical level increased rapidly from 1×10^5 to 3×10^6 # cm^{-3} just after sunrise, promoting the gaseous oxidation of SO_2 in the atmosphere and subsequent accumulation of sulphuric acid from nealy zero to around 5×10^6 # cm^{-3}. Simultaneously, the pre-existing particle concentration dropped down due to the boundary layer evolution (Fig. 3). The continuously growing sulphuric acid concentration and decreasing condensation sink jointly led to this fast NPF event. Simulated J_6 was 9.3 cm^{-3} s^{-1}, slightly higher than the observed value of 7.6 cm^{-3} s^{-1}. Among different kinds of condensing vapours, sulphuric acid contributed most to the growth of newly formed particles. As demonstrated in Fig. 7, while considering the growth of particles less than 10 nm in diameter, sulphuric acid's contribution accounted for more than 50%. The reason is that, influenced by air mass from the emission-intensive YRD region, SO_2 was reaching up to 20 ppb and the contribution of sulphuric acid on this day was much higher compared with the other two days and those published in earlier studies (Boy et al., 2003 and 2008b). GR_{6-30} was simulated to be 6.9 nm h^{-1}, about half of that derived from measurements. Overestimated newly formed clusters might be one reason for smaller simulated GR_{6-30}. Another, as described before, condensing vapours in the box model only included biogenic low volatile compounds. However, aromatic-related oxidation products have been suspected to be contributing to particle growth, especially in polluted area like China (Zhang et al., 2004; Yue et al., 2010). Failing to characterize condensing vapour originating from anthropogenic organic compounds might be another cause for under-predicted growth rate.

During the second NPF case, the OH radical concentration was mostly less than 1×10^6 # cm^{-3}. The production of sulphuric acid was expected to be relatively slow due to the simultaneous lower concentrations of both SO_2 and OH radical. As demonstrated in Fig. 6, the concentration of sulphuric acid was approximately 3×10^5 # cm^{-3} just when the NPF started, about one-tenth and one-seventh of the corresponding values on 22 June and 22 August, respectively. Nonetheless, prevailing south-westerly winds brought along terpenes-rich air masses. Some of the terpenes, such as alpha-pinene and limonene, feature significantly high yields of ELVOCs as well as SVOCs while reacting with ozone or OH radicals (Ehn et al., 2014; Jokinen et al., 2015). Such dense low volatile oxidation products substantially enhanced condensational growth of newly formed particles. The individual contributions from sulphuric acid, SVOCs, ELVOCs to growth of newly formed particles were quantified in Fig. 7, which indicated that biogenic low volatile compounds overwhelmingly dominated in the very initial stage of cluster growth with contribution as high as 95%, demonstrating a vital role of ELVOCs and SVOCs in this NPF event (Ehn et al., 2014). During this event, SVOCsinduced condensational growth of small clusters was especially higher, which might be attributed to the fact that modelled SVOC concentrations increased dramatically shortly after the nucleation started and was almost ten times higher than those during the other two events.

Unlike during the first two NPF cases, the level of pre-existing particles was unusually low during the third event because a strong wind from the ocean swept over East China. The clean air mass reduced the condensation sink (see Table 2), much lower than the values typically observed at the SORPES site before (Herrmann et al., 2014). Even though SO_2 concentrations were pretty low, sulphuric acid accumulated remarkably and probably initiated this NPF event. As listed in Table 2, during Case 3 when the air mass originated partly over the Shanghai and surrounding city clusters, the model underpredicted the growth rate nearly by a factor of 7 and overestimates the particle formation rate by 3 times. This means that most probably anthropogenic low volatile compounds not included in the model were contributing to the growth and decreased the surviving probability of the newly formed clusters in the model. It is completely opposite for Case 2 when the air mass originated not from strong anthropogenic influenced areas and the model outcome was in good agreement with the measurements.

3.2.3 Discussions and uncertainties

Though the model succeeded in the prediction of DMPS-measured NPF occurrence, the simulated activation of NPF was about one hour later than the observations. Considering the number concentration in the size range 6-10 nm (N_{6-10}) as the newly formed particles, model shows a distinct underestimation at the beginning of the NPF events (Fig. 5). As mentioned in Sect. 2, we assumed the kinetic mechanism in the MALTE-BOX. Nonetheless, chamber and in-situ experiments speculated that monoterpene oxidation products could cluster directly with a single sulphuric acid molecule under ambient conditions and that the interaction between organic and sulphuric acids likely leads to a reduced nucleation barrier (R. Y. Zhang et al., 2004b; Schobesberger et al., 2013). Furthermore, according to the simulation, the production of ELVOCs and SVOCs was mainly initialized by the reactions between monoterpene and ozone. It has been recognized that NPF events tend to be strongly associated with the monoterpene oxidation products by ozone in both remote and urban environments (Laaksonen et al., 2008; Guo et al., 2012). Thus, there was a good chance that the ELVOCs played an important part in the NPF processes considered here. As presented in Fig. 6, a considerable amount of ELVOCs accumulated before modelled NPF occurred and during the observed NPF events. The time shifts of the starting times is consistent with the hypothesis that organic vapours may play a key role in the particle formation process (Paasonen et al., 2009; Metzger et al., 2010). Fig. 8(a) shows the dependence of measurement-derived J_6 on modelled gaseous sulphuric acid and ELVOC concentrations. 6 nm new particle formation rates, even under the same sulphuric acid concentration, were substantially enhanced by the presence of ELVOCs. It is noteworthy that formation rates of 6 nm particles, not nucleation rates, are available here due to the limitation of instruments. It is hard to identify which process is mostly promoted by ELVOCs, either the particle formation or the early condensational growth. Metzger et al. (2010) attempted to disentangle the influence of organic oxidation products in particle formation and suggested an overall dependency on the formation rate of H_2SO_4 and organic oxidation products with the lowest volatility (NucOrg) as listed below.

$$J_{1.5} = k \times [H_2SO_4]^{1.0}[\mathrm{NucOrg}]^{0.8} \qquad \text{Eq. 5}$$

where, $J_{1.5}$ is new particle formation rate of 1.5 nm cluster; k represents pre-factor which recommended to be $7.2 \pm 1.4 \times 10^{-13}$ cm^3 s^{-1} in Metzger et al. (2010); [H_2SO_4] and [NucOrg] refer to the concentration of sulphuric acid and low volatile organic oxidation products that can participate in the particle formation process, respectively. By assuming that NucOrg is part of the ELVOCs in the present work, we examined the relationships between measured particle formation rate with $[H_2SO_4]^{1.0}[\mathrm{ELVOCs}]^{0.8}$ and compared it with $[H_2SO_4]^2$ in Fig. 8(b-c). The better representation and correlation of the latter provides further evidence for an involvement of ELVOCs in the formation and condensational growth of particles up to 6 nm.

In terms of the condensational growth of freshly-formed particles, ambient low-volatility compounds are predominant contributors, in particular, semi-volatile and possibly non-volatile organic matters generating from a complex series of photochemical reactions (Kroll and Seinfeld, 2008). In the present work, the model notably underestimates the nuclei condensational growth ($GR_{6\text{-}30}$) for Case 1 and Case 3 compared with the corresponding observations, whereas the observation and simulation were comparable for the Case 2 (Table 2). These differences could partly be due to the fact that here we only took oxidation products for certain selected organic compounds into account as sources of condensable vapours. When the experimental site was substantially influenced by intensive industrial activities and vehicle emissions from the YRD region in Case 1 and Case 3, reactive uptake and condensable secondary organic products from anthropogenic VOCs, which can accelerate particle growth (R. Y. Zhang et al., 2004b; Kroll et al., 2005; Volkamer et al., 2006), were partly missing in the present model. Regarding the impacts of biogenic VOCs, we found that ELVOCs and SVOCs remarkably contributed to particle condensational growth. Modelled contributions from ELVOCs, SVOCs and sulphuric acid demonstrated that, during these three NPF days, condensation of ELVOCs and SVOCs played an important role in the initial growth of particles less than 10 nm. In particular, the contribution increased to over 90% on 10 July when the terpenes-rich air mass influenced the SORPES site.

The comprehensive modelling study on the observed new particle formation makes it possible to better understand NPF processes at the SORPES station. However, there still lie many uncertainties in this modelling system, which need to be improved in future work. Given the expensive computational cost, reactions of VOCs are represented by the lumped mechanism in the regional-scale WRF-Chem model. Relevant parameters cannot be precisely determined for one lumped class, while the MALTE-BOX model provides accurate information for each specific organic compound. The gaps between the two models concerning VOC classification would introduce uncertainties. Moreover, in the MALTE-BOX model, sulphuric acid tends to be under-predicted, which was demonstrated in both polluted urban environment and clean rural environment (Wang et al., 2013a; Zhou et al., 2014; Zhou et al., 2015). There are multiple reasons behind the systematic underestimation. It has been shown by field measurements, laboratory experiments and numeric simulation that Crigee Intermediates (CIs) or other derivatives are capable of accelerating the oxidation of SO_2 into SO_3 (Hatakeyama and Akimoto, 1994; Kurten et al., 2011; Boy et al., 2013). These reactions have been incorporated in the MALTE-BOX model but would need further investigations concerning the reactions rates and other important reaction parameters (e.g. thermal lifetimes of CIs, pressure dependency, etc.). In addition, owing to the far incomplete knowledge of HONO sources, in particular during daytime, it was not yet possible to simulate realistic HONO levels using current models (Elshorbany et al., 2014; Czader et al., 2015). The lack of HONO measurement input to the model might also result in an underestimation of sulphuric acid, especially with dramatically increasing traffic emissions during the rush hours (Wang et al., 2013b). For instance, in the first case, the air masses were carrying on more characteristic from the emissions-intensive YRD region, the sulphuric acid concentrations and particle formation rates are more likely to be under-predicted. Last but not least, we adopted a mandatory value for the kinetic coefficient, which includes the probability that a collision of two molecules results in the formation of a stable critical cluster, as well as all other important details concerning the particle formation process such as temperature and humidity. This condition-dependent coefficient needs to be resolved in further modelling work on the basis of more in-situ and laboratory experiments.

4 Conclusions

This study combines the regional chemical transport model and box model to investigate atmospheric new particle formation and its subsequent nuclei condensational growth at the SORPES site in Nanjing, China. This combination makes it possible to simulate chemical and aerosol dynamical processes. Three NPF cases, during which entirely different potential source regions influenced the experimental site, were successfully reproduced by the modelling system. When the site was predominately influenced by air masses from city clusters in the YRD region on 22 June, 2013, despite a high condensation sink, the NPF event featured fast new particle formation rate due to the continuously accumulating sulphuric acid. Under the circumstance that biogenic VOC-rich air masses dominated, rapid growth of freshly formed particle was detected on 10 July, 2013, which was predominately attributed to the low-volatility oxidation products of terpenes. Air masses from marine origin could lead to the relatively low condensation sink on 22 August, 2013, thereby facilitating the occurrence of NPF event. On the basis of measurements and the corresponding modelling, we infer the controlling factors of the selected three NPF events, and these were mostly associated with sulphuric acid accumulation and low condensation sink. The comparison with the observations suggested that low-volatility organic compounds, including both SVOCs and ELVOCs, played a substantial role in the initial condensational growth of newly formed particles, particularly when the station was influenced by air masses originated from the South China. In addition, anthropogenic VOCs and the following photochemical oxidation produce a considerable amount of condensable compounds, exerting a significant impact on particle growth in the emission-intensive YRD region. Although some inadequacies still remain, such as the inclusion of anthropogenic non-volatile organic compounds as condensable vapours, the comprehensive modelling work provides a better insight of NPF processes.

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Table 1. Chemical species from WRF-Chem inputted to MALTE-BOX

WRF-Chem	MALTE-BOX
Acetaldehyde (CCHO)	CH3CHO
Acetone (ACET)	CH3COCH3
Methanol (MEOH)	CH3OH
Methyl Vinyl Ketone (MVK)	MVK
Isoprene (ISOPRENE)	C5H8
Terpenes (TERP)	alpha-pinene
	beta-pinene
	camphene
	myrcene
	carene
	limonene

Table 2. Formation rate of 6-nm particles (J_6), and particle growth rates from 6 to 30 nm (GR_{6-30}) of 3 NPF events based on DMPS measurements and numeric modelling[a].

	Date	J_6 (cm^{-3} s^{-1})	GR_{6-30} (nm h^{-1})	CS (10^{-2} s^{-1})
Case1	20130622	7.6(9.3)	12.6(6.9)	4.2
Case2	20130710	1.2(1.6)	13.5(10.7)	3.2
Case3	20130822	3.4(10.0)	15.7(2.3)	1.9

[a] values out of the parentheses are observations and those in the parentheses represent the corresponding model results.

Table 3. Statistical analysis of the simulated hourly 2-m temperature and 10-m wind speed versus the ground observations at the SORPES station

Date	Index[a]	2-m temperature (℃)	10-m wind speed (m/s)
22 June	MB	-0.33	0.80
	RMSE	1.29	1.63
10 July	MB	-1.07	-0.77
	RMSE	1.34	1.18
22 August	MB	0.19	0.17
	RMSE	1.38	1.27

[a] MB and RMSE refer to mean bias and root mean square error respectively.

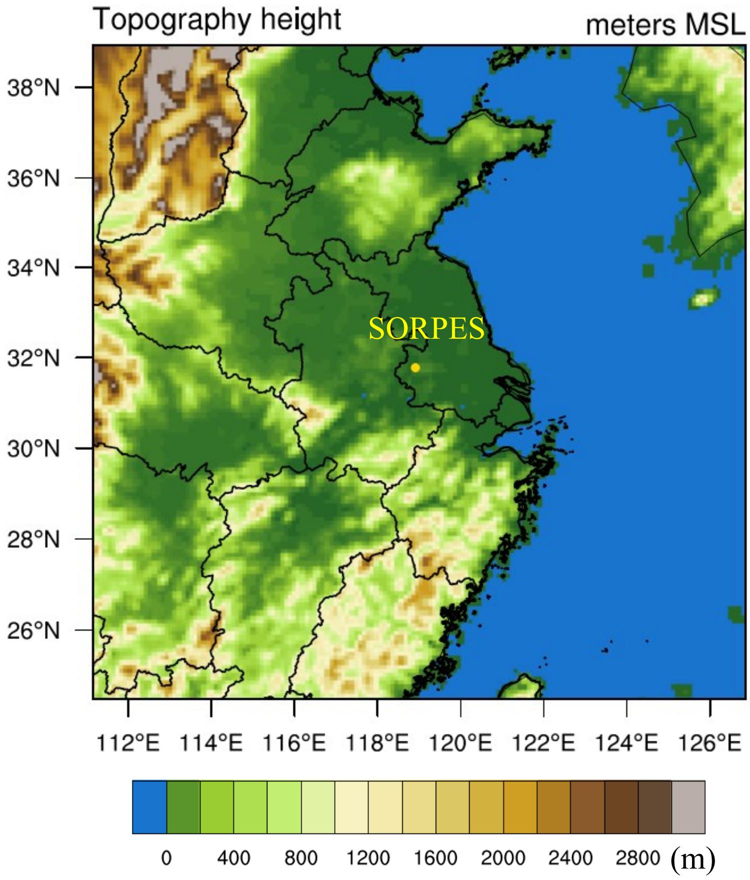

Figure 1. WRF-Chem model domain and topographic field (meter). The yellow dot marks the location of the SORPESstation.

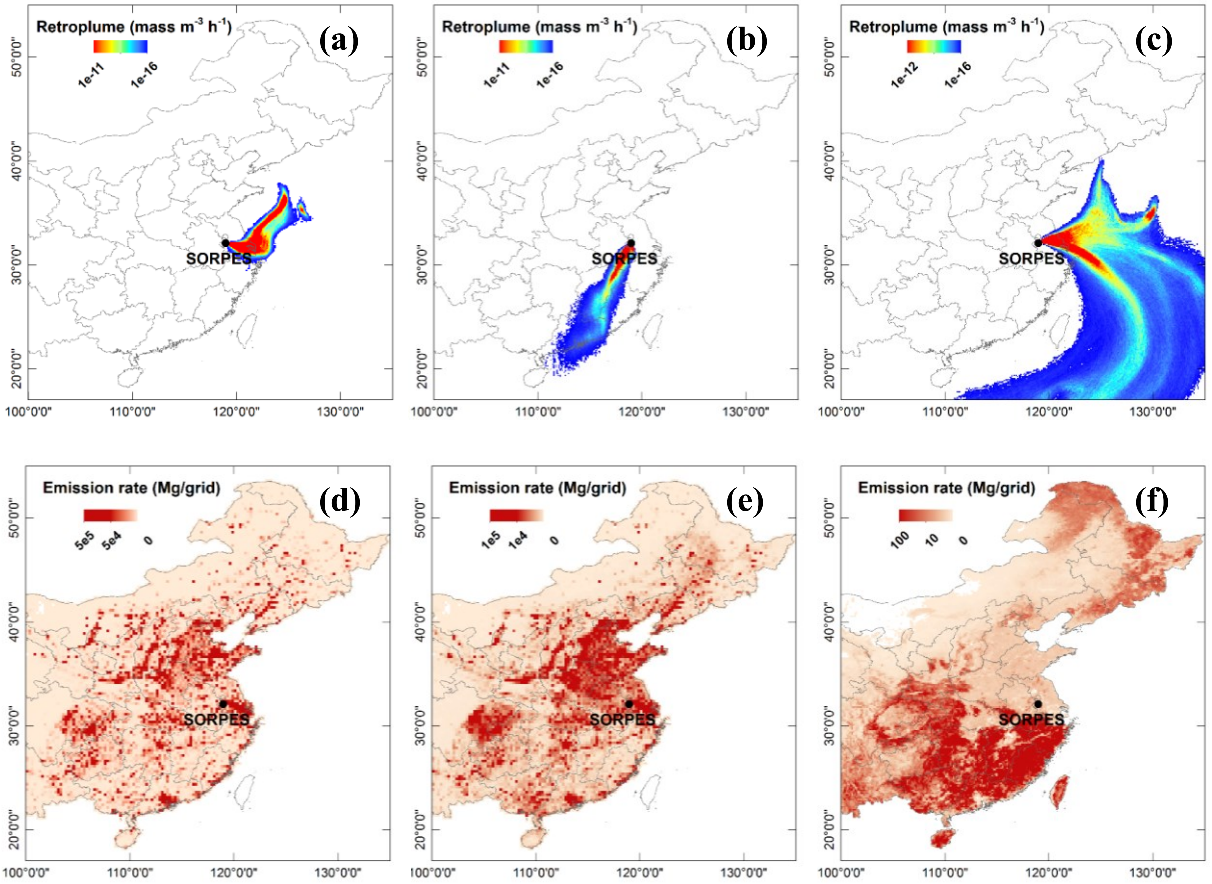

Figure 2. Retroplume (footprint residence time) showing transport pathways of air masses measured at the SORPES site for 22 June (a), 10 July (b) and 22 August(c). Spatial distributions of anthropogenic SO_2 (d), primary $PM_{2.5}$ (e) and biogenic monoterpene (f) emission rates.

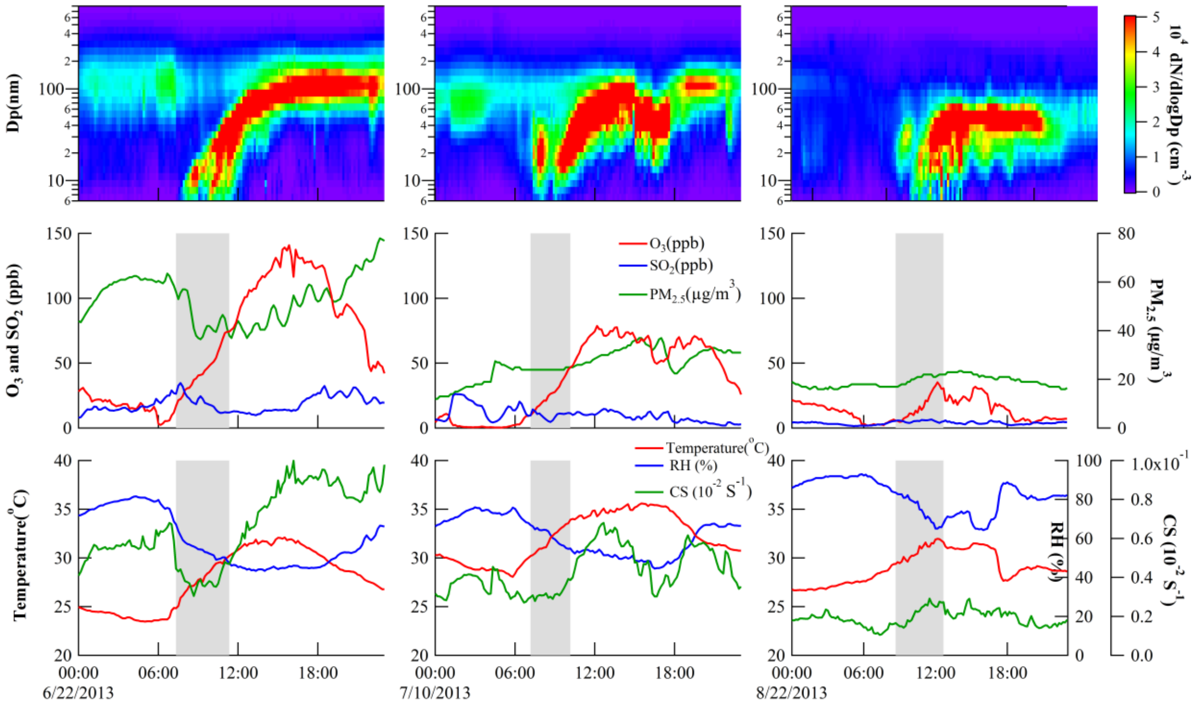

Figure 3. Measured diurnal variations of particle size distributions (upper panel), concentrations of SO$_2$, O$_3$ and PM$_{2.5}$ (middle panel), and meteorological conditions (bottom panel) during the three NPF days. Grey boxes show the time span of NPF events.

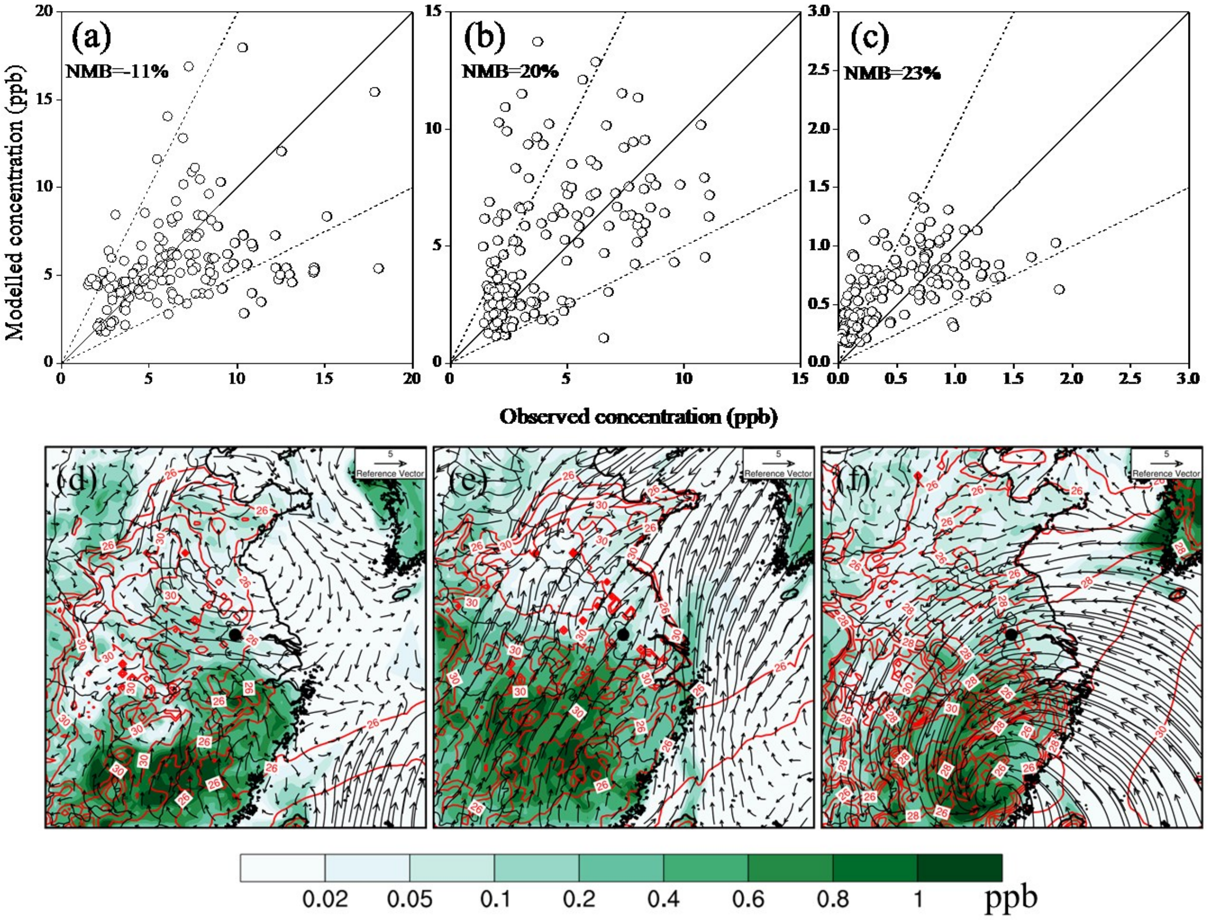

Figure 4. Scatter plots of observed and simulated alkene (a) aromatic (b) and isoprene (c) concentrations (NMB represents the normalized mean bias) in August 2014. The solid 1:1 lines and dashed 1:2 and 2:1 lines are shown for reference. Spatial distributions of terpene concentrations at 9:00 LT on 22 June (d), 10 July (e), and 22 August (f), 2013. 2-meter temperature are marked in red lines.The black dot marks the location of the SORPES station.

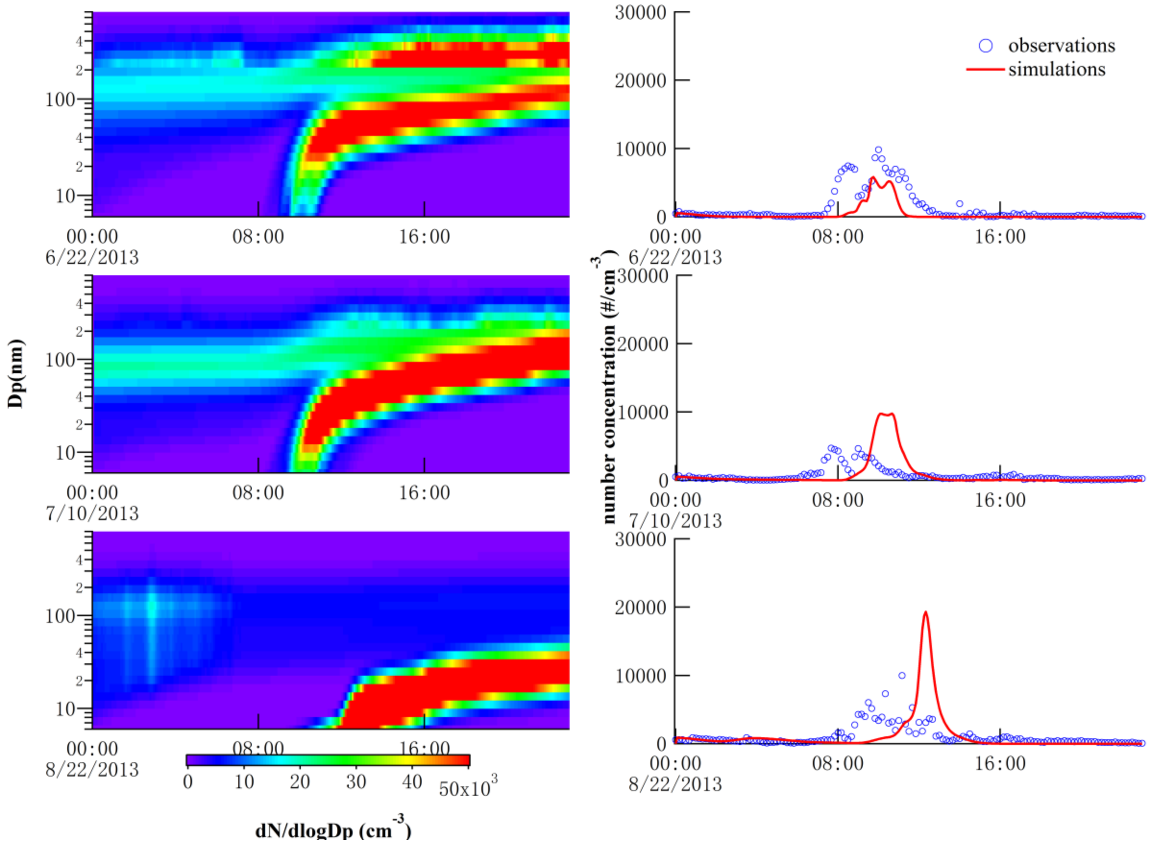

Figure 5. Modelled pattern of particle size distributions (left panel) and number concentrations of particles ranging from 6 to 10 nm during these 3 NPF days (right panel).

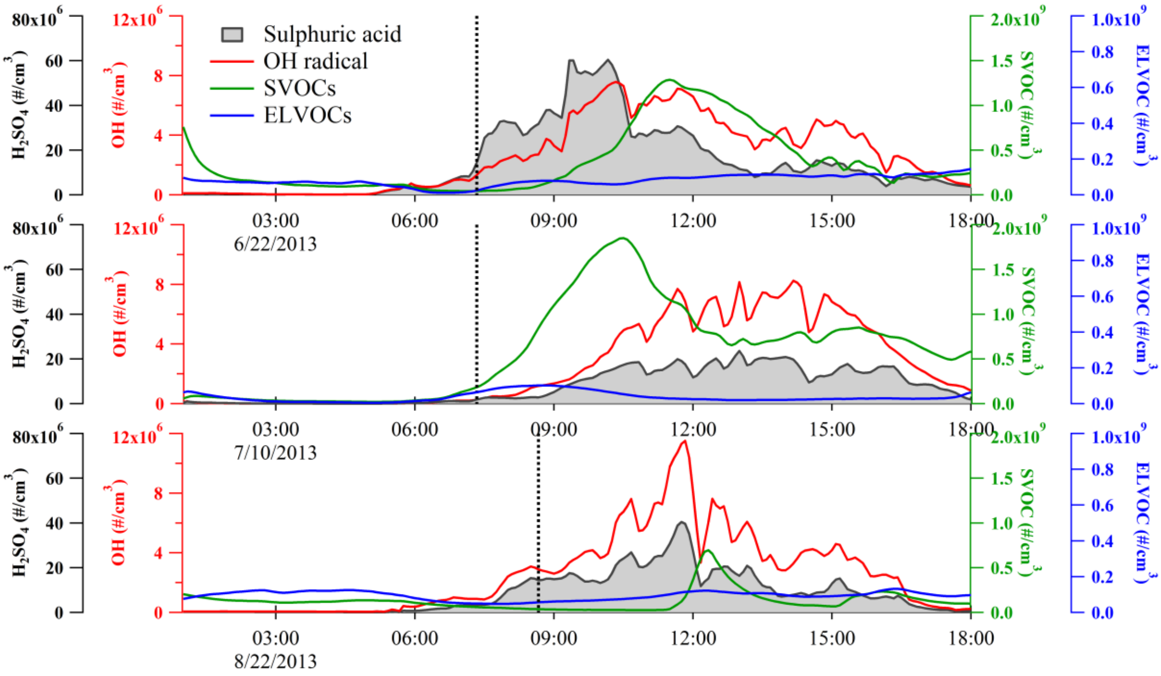

Figure 6. Time series of several gas concentrations (# cm^{-3}) during the three selected NPF days. Sulphuric acid, OH radical, SVOCs and ELVOCs are marked in grey area, red, green and blue lines, respectively. Dashed lines show the onset time of NPF according to DMPS measurements for reference.

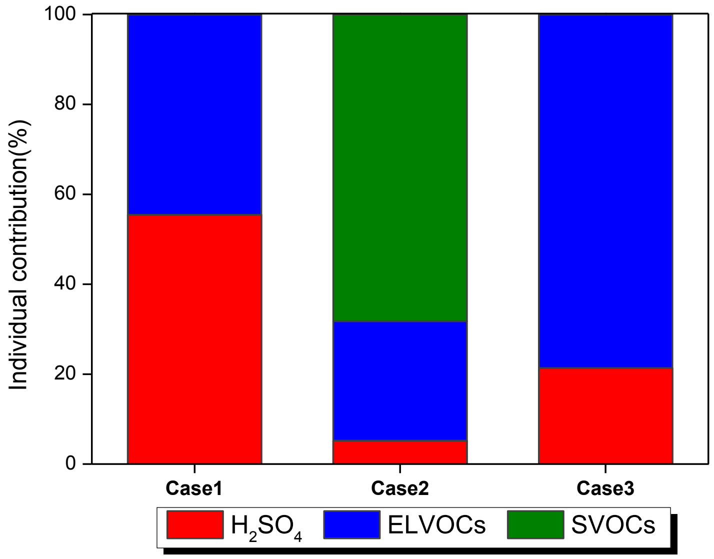

Figure 7. Contributions from three kinds of condensing vapours to growth of particle less than 10 nm during NPF events on 22 June (Case1), 10 July (Case2), and 22 August (Case3). Sulphuric acid, SVOCs and ELVOCs are marked in red, green and blue bars, respectively.

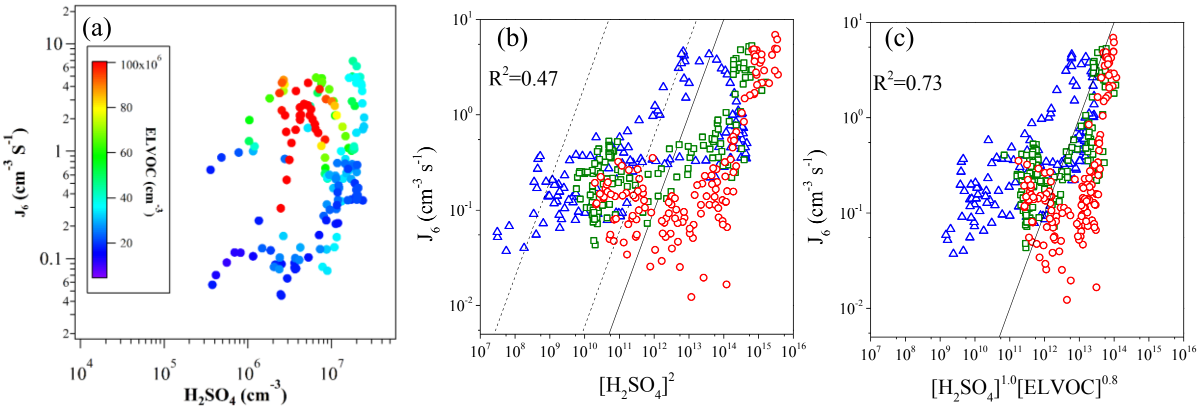

Figure 8. Correlations of estimated new particle formation rates (J_6) from DMPS measurements with modelled gaseous sulphuric acid and ELVOC concentrations for event days between 06:00 and 16:00 (a). Scatter plots of new particle formation rate J_6 estimated from measurements with modelled sulphuric acid and ELVOC concentrations (b-c), in which red, blue and green markers refer to June 22, 10 July and 22 August, respectively. The square of correlation coefficients (R^2) are labelled in (b) and (c). Black soild lines denote $y=10^{-13}x$. Dashed lines show $y=2.2\times10^{-10}$ x (left) and $y=6.0\times10^{-13}x$ (right) for reference in (b).