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 will add 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 will be provided in the revised "Introduction" section.

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:

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

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

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) is applied to numerically solve for the concentrations of each compound, including sulphuric acid vapour. To make it clearer, we will add more relevant descriptions in Section 2.2.1.

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 will add detailed information in the revised manuscript.

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: It will be corrected to 10,000 # cm^{-3} in the revised manuscript.

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 will add the contribution of sulphuric acid vapour to the particle initial growth in a new figure and give 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 < $7x10^4$ ppm^{-1} min^{-1}, OLE2—alkenes with kOH > $7x10^4$ 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 < $2x10^4$ ppm^{-1} min^{-1} and ARO2—aromatics with kOH > $2x10^4$ 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 will be discussed separately in Section 3.2.1.

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.*

<u>Response</u>: 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 let's 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.

<u>Response</u>: We will add more explanations and discussions in the revised manuscript.

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.

<u>Response</u>: 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 ^{o}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 will add a new figure, 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 $J=6.0\times10^{-13}\times[H_2SO_4]^{2.0}$ will be added for reference. 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 will be 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 will highlight 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 rate 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.

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 will be shown in a newly-added figure.

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 will rephrase this sentence in the revised manuscript.

Minor comments:

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

Response: Accepted. We will change the title to "Comprehensive modelling study on observed new particle formation at the SORPES station in Nanjing, China". Diurnal variation of CS will be 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.

Response: We will check it. Y-Scales for all subplots will be added in the revised Fig. 3.

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

Response: Accepted. We will explain them in the caption of Fig.4.

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

Response: Checked. The unit should be "# cm^{-3}" and we will replott Fig. 5.

References

Carter, W. P. L.: Documentation of the SAPRC-99 Chemical Mechanism for VOC Reactivity Assessment, open file rep., University of California, Riverside, CA, USA, 446 pp., 1999.

Geng, F., Tie, X., Guenther, A., Li, G., Cao, J., and Harley, P.: Effect of isoprene emissions from major forests on ozone formation in the city of Shanghai, China, Atmospheric Chemistry Physics, 11, 10449-10459, 2011.

Guenther A B, Zimmerman P R, Harley P C, et al. Isoprene and monoterpene emission rate variability: model evaluations and sensitivity analyses. Journal of Geophysical Research: Atmospheres, 1993, 98(D7): 12609-12617.

Hinds, W C., Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles (Second Edition), 1998

Kulmala et al.: On the formation, growth and composition of nucleation mode particles, Tellus, 479-490, 2001

Li, M., Huang, X., Li, J., and Song, Y.: Estimation of biogenic volatile organic compound (BVOC) emissions from the terrestrial ecosystem in China using real-time remote sensing data, Atmospheric Chemistry and Physics Discussions, 12, 6551-6592, 2012.

McGrath M J, Olenius T, Ortega I K, et al. Atmospheric Cluster Dynamics Code: a flexible method for solution of the birth-death equations. Atmospheric Chemistry and Physics, 2012, 12(5): 2345-2355.