Response to reviewer #1

-The authors would like to thank the reviewer for the comments that helped to improve this manuscript. Please find below a point-by-point reply to all of the issues raised and the corresponding changes

The paper by Kalivitis et al. presents long term measurement of particle size distribution from Finokalia (eastern Mediterranean region). The main focus of the study is on nucleation mode particles and characteristics of new particle formation (NPF) events, including frequency of occurrence as well as particle formation and growth rates. The last part of the paper is dedicated to a simulation case study of NPF with the MALTE-box model.

I recommend the publication of this paper, as it is well written and describes a valuable dataset which allows for the investigation of NPF over 7 years, thus contributing to our understanding of the process.

I would however suggest some revisions before final publication of this study. In particular, some of the observations/conclusions reported throughout the manuscript should be slightly balanced.

-*We have tried to balance the conclusions throughout the manuscript.*

Also, I am not fully convinced by the modelling part in its current form: it is in my view missing a clear presentation of the strategy/sensitivity tests which lead to the final "good simulation", and it would also benefit from a quick discussion on the relevance of the values finally used for some of the key variables (e.g. monoterpenes concentration).

-*We have now added information in the modelling part regarding the simulation tests the led to the adequate agreement with the observations regarding the nucleation coefficient and the changes in the monoterpene concentrations.*

Moreover, it is not clear to me how the analysis reported in Section 3.5 of the present paper differs from that of Tzitzikalaki et al. (2017), as I cannot access this source.

-The Tzitzikalaki et al., 2017 publication refers to COMECAP 2016 conference proceedings where the contour plots of the simulations were presented and briefly described. The contour plot has been completely removed and only number and volume concentrations are now presented.

Detailed comments are listed below.

P3, L13-16 : I would suggest to clearly mention "only when accumulation mode particles were neutral", as with the current form of the sentence it is a bit confusing whether those particles are pre-existing particles or the newly formed ones.

-The sentence was changed according to suggestion.

P4, L21: I would suggest to remove "from the early stages of nucleation", since I think those cannot be investigated when measuring particles larger than 9 nm. Such statement would better suit to AIS measurements or to measurements conducted with instruments such as the particle size magnifier (PSM, Vanhanen et al., 2011), which allows for the detection of ~1-1.5 nm particles (charged + neutral).

-The sentence was changed according to suggestion as the SMPS operated at Finokalia can measure particles larger than 9 nm.

P5, L9-10: Please refer the reader to Mirme et al., (2007) for AIS measurements. Also, could the authors give more information about the uncertainties reported on L14-15 (calculation method or reference to a paper)?

-The reference Mirme et al., 2007 was added and for more information for the calibration and uncertainties of AIS we added the reference to Manninen et al, 2010.

P5, L22-31: Several short/minor comments about the description of the calculations:

L22: instead of "particles with diameter D" (should at least be Dp) and since the formation rate is not calculated for different particle diameters, I would clearly mention Dp = 9nm,

otherwise one has to wait until Section 3.2 to explicitly get this information (and it would also be more consistent with the description of the terms of Eq. (1));

-*We modified the sentence in Line 22 as "). Formation rates of particles with diameter D_p (in this study D_p=9nm) were calculated.."*

L25: "CoagS is the coagulation of particles in this size range" (should be $CoagS_{Dp}$): which (lowest) particle size was used to calculate $CoagS_{Dp}$? I would suggest a more accurate formulation, such as "$CoagS_{Dp}$ is the coagulation sink of XX nm particles on larger particles";

-*The sentence was modified as "$CoagS_{Dp}$ is the coagulation of 9nm particles on larger particles"*

- L27: Please refer the reader to Dal Maso et al. (2005) for the mode fitting method;

A reference to Dal Maso et al., 2005 was added

L31: For this first occurrence, instead of "the sulfuric acid sink", I would suggest to rather write something more explicit like "CS is the condensation sink caused by the pre-existing aerosol population and was calculated using the characteristics/properties of sulfuric acid".

-*We modified the sentence as "CS is the condensation sink caused by the pre-existing aerosol population and was calculated using the properties of sulfuric acid as condensing vapor."*

P6, L11: "relevant chemical reactions": I would recommend to add few words on the relevance of the reactions, at least mention they are related to sulfuric acid production.

-*We also used reactions for the production of organic compounds except of sulfuric acid so the sentence was changed as "For the present study, chemical reactions relevant to the production of condensing species from the Master Chemical Mechanism.."*

P6, L26-27: what is “free form nucleation”? I would suggest to briefly recall the parameterization which is used in the model and introduce the “nucleation coefficient”, later discussed in Section 3.5 (P16, L16 & L24-25).

-*We introduced the nucleation coefficient and changed the sentence as follow:” UHMA simulated new cluster formation using the activation nucleation parameterization, so that the nucleation rate has a linear relationship with sulfuric acid concentration, depending on the nucleation coefficient* $K_{act.}$*”*

P6, L29-30: “All these compounds were treated as sulfuric acid and organics”: what does this sentence mean? Also, on L27, if ELVOCs are considered please add “20 extremely low-volatility organic compounds”, otherwise change to “LVOCs.”

-*The word “extremely” was added since we actually refer to ELVOCs. All condensing species were treated either as sulfuric acid if inorganic or organic compounds and this is now made clear in the text “All condensing compounds were treated either as sulfuric acid or organic compounds and..”*

P7, L6-7: I am a bit confused with this sentence: only the particle size distributions are used to initialize the model (as reported on P6, L24-25), which then calculates a CS based on the simulated distributions, right? If the purpose of the abovementioned sentence is only to precise that SMPS data were used to calculate the CS, I would strongly recommend to move it to Section 2.1 (P5, L31), as Section 2.2 is dedicated to model description.

-*The sulfuric acid condensation sink is calculated based on measured size distributions and not the simulated, this is correctly stated in the text.*

P8, L11-13: I am a bit confused with the use of TUV: was the parameterisation used instead of TUV, or implemented in TUV?

-*The parametrization from Mogensen et al., 2015 was used which provides improvement to the calculation from TUV. We added “…and used in the model.” at the end of the sentence.*

P8, L21-27: I am somewhat sceptical about the values which are reported in this paragraph; I think they do not give much information since the shape of the particle size distribution is highly variable with respect to seasons, event vs non-event days, time of the day… I would thus suggest to either provide a more detailed description/comparison of the concentrations in the different modes and their contribution to total concentration, or at least provide quartiles/standard deviation for all reported values (not only for nucleation mode particle concentration).

-*We have added standard deviation to all reported mode concentrations.*

P8, L31: are the times local or UTC?

-*Thank you for pointing out that the time description is missing. All times are UTC+2 and this has been added to the captions of the Figures.*

P8, L32 - P9, L1: "Such an observation suggests that the nucleation particle number concentration is controlled by NPF episodes". Isn't it what we expect by definition? Which other sources would the authors expect for particles in this size range? This comment also refers to P2 L16-17, P9 L25, P11 L21-22, P15 L22-23. Moreover, concerning the statement P11 L20-22, I am not sure if the linear relation between J_9 and nucleation mode particle concentration (N_{9-25}) can be considered as a strong support for NPF being the main source of nucleation particle, since according to Eq. (1) J_9 calculation includes N_{9-25} in two of the three terms.

-*We refer to combustion sources of nucleation mode particles that may play significant role in polluted areas. At Finokalia we claim that there are no such sources and therefore all nucleation mode particles observed come from nucleation processes. We have added "rather than other sources such as local combustion processes" in the text to make it clear. If other sources than regional NPF contributed significantly that would be evident both in the diurnal cycle and the scatter plot of* J_9 *and* $N_{nuc.}$

P9, L10-23: I think that even if deep investigation of night time events is not in the scope of this paper, slightly more detailed description could be provided. In specific: - L10-12: Even if similar night time concentrations are observed during all seasons, they seem to result from different processes based on Fig. 2a. Indeed, there is an increase of the concentrations after 18:00 in summer and autumn, which may suggest evening time new particle formation, but during spring and winter the concentrations keep on decreasing until they reach the night time value, suggesting that evening events are not frequent during these seasons. I would thus

suggest to balance the sentence from L10-12, and maybe provide frequencies of occurrence of such events for each season, which will also help quantifying "Frequently" (L13).

-*We have modified the second sentence of this paragraph "This suggests that there is some new particle production mechanism at night, especially in summer and autumn,..". However, we prefer not to go into further detail as this is work in progress and these events lack the characteristics of regional NPF that are the focus of this study. There is a description of such events in Kalivitis et al., 2012 that is already cited here.*

L17-18: I would also add that on top of the "local" character of these events, which may partly explain the limited source of condensing vapours (and therefore particle growth), the absence of photochemistry during night time most likely strengthen the lack of vapours needed to sustain particle growth.

-*This is a very important remark and we appreciate this comment. We added at the end of the sentence "and that the lack of photochemistry during night limits the abundance of condensable vapors driving particle growth".*

P10, L3-18: I wouldn't say that ozone is "the major oxidant in the atmosphere", especially when focussing on daytime NPF events, during which OH is expected to play a significant (major?) role. Also, I don't think that based on the variables included in this factor analysis it is possible to state that NPF is not sensitive to "atmospheric chemical composition"; compounds other than ozone such as for e.g. NOx, SO_2, monoterpenes… would be needed to draw such conclusions.

-*We have rephrased the sentences so that "ozone concentrations (as an important oxidant in the atmosphere)" and with regard to the conclusions "…NPF is not sensitive to local meteorological conditions, preexisting particulate matter and ozone levels in this environment.*

P11, L3: "the particle survival probability seems to be the highest in winter": the authors have the data needed to actually test their hypothesis and provide a more robust conclusion, and even quantify the variations of the survival probability in different seasons.

-*We calculated the CS/GR ratio for all Class I events and we found it to be smaller in winter than spring and autumn but surprisingly larger than in summer. This was included in the text.*

P11: While they peak at slightly different times of the year, the maximum of the NPF frequency, particle formation and growth rates are all attributed to enhanced biogenic emissions and/or photochemistry
(P10 L27, P11 L16-17 and P11 L25-26, respectively). This hypothesis seems plausible as all maxima are observed during spring/summer, but could the authors comment on the different seasonal variations of the abovementioned variables? In contrast it can be seen from Fig. 1a and 6b that the GR and CS have similar seasonal patterns: is it then realistic to think that CS and the vapours involved in particle growth "share the same origin"?

-NPF frequency is maximum in mid –spring and early summer. The biogenic activity and the onset of intense photochemistry seem to play a key role in the formation of new particles. During summer however, despite the fact the GR is observed to be the highest for new particles, transported pollutants accumulating in the atmosphere due to the lack of precipitation result to the highest CS, suppressing the formation of new particles. Rain season in southeastern Europe in early autumn leads to gradual CS decrease, and as a result a local maximum in NPF frequency is observed in October. In the revised version of the manuscript that three more years of analysis have been included it was found that the average formation rates have higher values during December, January and March, when the CS is lower. This observation changes the above mentioned general remark that photochemical activity and biogenic emissions are the drivers for the formation rates-the preexisting particle population scavenging precursors is probably defining how fast the new particles form-the lowest formation rates are observed in summer until early autumn. The exact opposite is observed for GR, higher values are observed in summer and September and lowest in winter and March. Photochemistry and biogenic emission are probably driving the growth process. However, transported pollution may contribute except of CS to GR as well, transported anthropogenic SO_2 may play a role in the growth process as indicated later on when discussing trends. In any case, the minimum values of GR are observed in months that both biogenic and photochemical activity are lowest, and hence condensing vapors are scarce. These information are now included in the text.

P11, L27-28: It is true that based on Fig 2a the average duration of NPF in summer seems to be shorter compared to other seasons, but also the maximum of the concentration is lower. Since the CS (and consequently CoagS) is also higher during summer (Fig. 1a), I would think that both the CS (CoagS) and the GR are affecting the variation of nucleation mode particle concentration (should be checked by calculating the survival probability).

-The survival probability for nucleation mode particles for Class I events was calculated. It was found that on seasonal basis the median survival probability is higher in summer, however varies within 5% and therefore no safe conclusions can be made. On monthly basis the variability was within 13% with higher values observed in November. Nevertheless, we agree that the CS (and hence CoagS) may also affect the maximum concentrations observed. We hence modified the sentence as "The average duration of the NPF in summer seems to be shorter and the maximum concentrations of nucleation mode particles during the summer events are lower as shown in Figure 2a. These observations may be explained by the higher GR and CS during summer."

P12, L1, L5: I would slightly balance the statements ("notable increase", "clear decreasing") as in my opinion the reported observations are not as obvious as suggested.

- We have modified the whole paragraph since we included additional years in our analysis. In any case, we use modest expressions for our statements regarding the trends.

P12, L5-33: I am not fully convinced by the conclusion reported on L30, which suggests that decreased SO_2 concentrations related to the economic crisis in Europe may explain observed variations of GR and occurrence of class I NPF events. Main reasons for this are listed below:
The lack of SO_2 measurement in Finokalia prevents from any direct evaluation of the SO_2 concentration decrease at this site;
Based on previous studies mentioned in the present work it seems that decreasing SO_2 concentrations can lead to contrasting observations, thus pointing to the fact that robust conclusions cannot be inferred from the analysis of SO_2 alone;
While the important role of H_2SO_4 in early nucleation stage has been reported in different studies, the need for other species to explain observed GR has also been evidenced, and the present paper itself tends to emphasize the role of organic species in NPF at Finokalia. Indeed, maximum of NPF occurrence, J_9 and GR are all attributed to enhanced biogenic emissions, and best agreement between model simulation and observation is achieved when adjusting monoterpenes concentration in the model. I would thus think that SO_2 driving the observed variations of GR and NPF occurrence is not fully consistent with the aforementioned observations/results.

-*Given the objections of the reviewer, in the revised version of the manuscript we have rephrased the sentence, so that it simply provides to the reader the information that since the outbreak of the economic crisis we have observed changes in the atmospheric composition that could influence the vapors involved in NPF processes.*

P13, L12-14: Does this sentence mean that instrument malfunction was affecting measurement of positive ions? If not, it is fine to focus on negative ions only, but I wouldn't justify this choice based on their better ability to represent NPF events. Indeed, it is in my opinion complex to assess which polarity gives the "better representation of NPF events", as the different observations from the two DMAs may instead reflect the signature of the nucleation mechanism.

No, it does not indicate malfunction of the AIS instrument. The observation of NPF was more evident in the negative polarity and this has been reported in earlier work (Kalivitis et al., 2012) that was cited.

P13, L17-26: I would have expected the AIS-derived NPF frequencies to be more often higher (or at least equal) than SMPS-derived ones, while the opposite is shown on Fig. 10. Does it mean that the event day illustrated on Fig. 9 is only representative of a rather limited fraction of the events observed in Finokalia, while the majority of them is actually not visible from the AIS smallest diameters? In order to make the most of the FRONT dataset and provide more information on the nature of the events detected in Finokalia during this period, I would suggest to also report for each month (on Fig. 10 for instance) the number of events detected by each instrument and the number of event days they have in common. This will help assessing the fraction of events with very limited growth only visible in AIS data, the fraction of regional events detected by both instruments and that of events only visible in SMPS data..

-*We have modified the Figure 12 so that the event days are mentioned on top of each month that present NPF for AIS, SMPS and the common days. Indeed the NPF events are less in AIS than SMPS .This has been reported in the K-puszta station in Hungary (Yli-Juuti et al., 2009), probably because AIS detects only naturally charged particles while SMPS all particles. The reference was introduced in the manuscript.*

P14, L6-33: I have several comments/questions regarding model simulations:

L15: What does "NPF level" mean?

-*This was wrong expression ,we replaced it with "NPF events".*

L22-26: Could the authors briefly summarize the strategy they adopted to finally reach fair agreement between model simulation and observation? For instance, which sensitivity tests were performed, were parameters other than nucleation coefficient and monoterpenes concentration also tuned?

-*The approach was quite simplistic: to adjust the nucleation coefficient and the monoterpene concentrations so that we simulate efficiently the nucleation and growth rate observed during the second day of the "event week" when the most pronounced NPF event was observed. This is now also described in the manuscript.*

L25: are the levels of final simulated monoterpenes concentration realistic, are they for instance in agreement with observations from 2014?

-*Yes, the values are realistic and they compare well with the findings of Debevec et al., 2018 that measured monoterpenes during NPF events in eastern Mediterranean (Cyprus). This is now stated in the text.*

L27-29: I would slightly balance the conclusions ("well captured", "in such detail"), as if I agree with the fact that the reported results are very encouraging, one can observe some discrepancies between model and observation (e.g. NPF event from day 243 in not visible in model data);

-*We have tried to balance the conclusions by removing these expressions.*

L29-31: Do the authors also consider the possibility to test other nucleation mechanisms in

future simulations?

-*Yes, we plan to continue simulating NPF at Finokalia and introduce actual VOC measurements within 2019. We added at the last sentence ", new simulations and VOC measurements will further provide insight in the nucleation mechanisms, the growth process and the factors controlling NPF in the eastern Mediterranean atmosphere."*

References:

Mirme, A., E. Tamm, G. Mordas, M. Vana, J. Uin, S. Mirme, T. Bernotas, L. Laakso, A. Hirsikko, and M. Kulmala: A wide-range multi-channel Air Ion Spectrometer, Boreal Environ. Res., 12, 247–264, 2007.

Vanhanen, J., Mikkilä, J., Lehtipalo, K., Sipilä, M., Manninen, H. E., Siivola, E., Petäjä, T., and Kulmala, M.: Particle size magnifier for Nano-CN detection, Aerosol Sci. Tech., 45, 533–542, 2011.

-References

-Debevec, C., Sauvage, S., Gros, V., Sellegri, K., Sciare, J., Pikridas, M., Stavroulas, I., Leonardis, T., Gaudion, V., Depelchin, L., Fronval, I., Sarda-Esteve, R., Baisnée, D., Bonsang, B., Savvides, C., Vrekoussis, M., and Locoge, N.: Driving parameters of biogenic volatile organic compounds and consequences on new particle formation observed at an eastern Mediterranean background site, Atmos. Chem. Phys., 18, 14297-14325, https://doi.org/10.5194/acp-18-14297-2018, 2018.

-Yli-Juuti, T., Riipinen, I., Aalto, P. P., Nieminen, T., Maenhaut, W., Janssens, I. A., Claeys, M., Salma, I., Ocskay, R., Hoffer, A., Imre, K. and Kulmala, M.: Characteristics of new particle formation events and cluster ions at K-puszta, Hungary. Boreal Env. Res. 14: 683–698, 2009.