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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Formation and growth of atmospheric nanoparticles in the eastern Mediterranean: Results from long-term measurements and process simulations" *by* Nikos Kalivitis et al.

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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 changes 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 Dp (in this study Dp=9nm) were calculated..”

L25: “CoagS is the coagulation of particles in this size range” (should be CoagSDp): which (lowest) particle size was used to calculate CoagSDp? I would suggest a more

accurate formulation, such as “CoagSDp is the coagulation sink of XX nm particles on larger particles”;

-The sentence was modified as “CoagSDp 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 Kact.”

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 J9 and nucleation mode particle concentration (N9-25) can be considered as a strong support for NPF being the main source of nucleation particle, since according to Eq. (1) J9 calculation includes N9- 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 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 circle and the scatter plot of J9 and Nnuc.

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, SO2, 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 au-

thors 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 were performed, were parameters other than nucleation coefficient and monoterpenes concentration also tuned?

-In this revised version of the manuscript data from 2008 until 2008 were used and formation rates were found to be higher in winter rather than spring or summer possibly due to the low CS. This is now mentioned in the text. All the variations described refer to measurements performed at Finokalia and nor simulations.

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 finding 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 will further provide insight in the nucleation mechanisms, the growth process and the factors controlling NPF in the eastern Mediterranean atmosphere."

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