Response to Reviewer #1

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 ($N_{9\text{-}25}$) 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 $N_{9\text{-}25}$ 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."*

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-*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.*

Response to Reviewer #2

- ***Response to reviewer #2***

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.

"Formation and growth of atmospheric nanoparticles in the eastern Mediterranean: Results from long-term measurements and process simulations" reports long term data from a Station in South Europe. Whilst the data are of good quality and worth publication (long term smps data are scarce) the analysis is fair and does not add any new result. The increasing trend (and decreasing trend) or NPF and GR (respectively) may suffer from lack of data at the beginning of the period (2008-2012) relative to the last part of the period (2012-2015) - the trend may be a simple artifact.

-In order to address this issue we chose to expand our analysis until 2018 in order to have ten years of data. As you can see in the Picture 1 at the end of this response, indeed there were less data available at the beginning of period under study. Nevertheless, there was always at least 70% coverage of each year and total coverage 82%.

line 8 abstract : biogenic - marine or land or both? specify

-The terrestrial biogenic activity is expected to contribute more efficiently to NPF and this is now stated in the text.

line 11-13 Do not understand what the sentence means. please reprhase and specify simply you see NPF during night time (seen elasewhere too).

-The sentence was changed to "Throughout the period under study, nucleation was observed also during the night."

sentence 18-22 not very clear - maybe concomitant ion size distributions suggests

-We have rephrased the sentence to "Classification of NPF events based on ion spectrometer measurements differed from the corresponding classification based on a mobility spectrometer,.."

pg 3 perhaps report the study of Dall Osto et al (2018, Sci. Rep.) reported by same co-authors showing south Europe is different from Central and North Europe.

-We have added the sentence" It has been shown that the processes responsible for particle formation and growth differ substantially across the European continent (Dall' Osto et al., 2018)."

pg 8 line 16-20 I think this is not correct, likely the longest SMPS size distrubutions are likely in Barcelona and regional areas of Montsein (Dr. Querol s group).

-We changed the sentence to "one of the longest time series".

Increase NPF events and decreased GR - this is interesting, it makes sense if the CS is lower over time, there is likely more NPF events, and they likely grow less cause likely you have less condensing material.

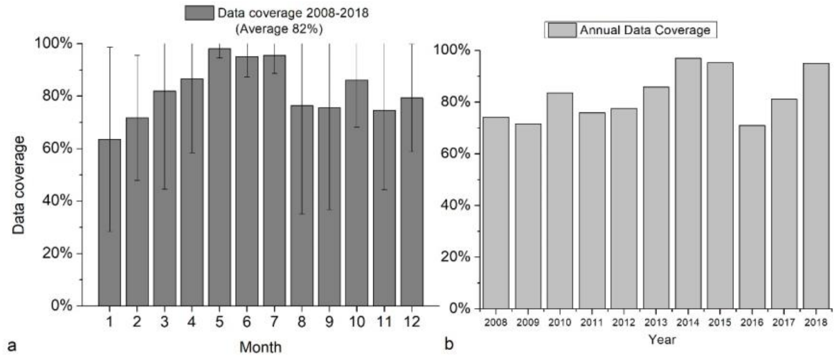
-As explained at the following comment this trend is not observed in the updated ten year analysis. However, we consider the observation for the period 2008-2015 important given the measurements availability.

Figure 8a. I think the whole conclusion may simply be noise. If looking at figure 8a, you see 2008-2010 you have less datapoints (perhaps in spring - summer) that causes the trend you may have. It looks if you remove the 2008-2009, the trend to me is not existing. I would be careful to say there is a trend (and so I would remove and change all abstract) - it is visually clear that years 2008-2010 have smaller data coverage that 2013-2015.

-The trends actually disappeared while including the additional years so that the time series covers form 2008 to 2018. If we remove the first two years as suggested, an opposite trend is revealed that it statistically significant and it is described in the manuscript, a clear decreasing trend in the period 2010-2018. The additional years added in the analysis showed that 1) we had a period of increased NPF frequency in 2010-2014, 2) there is a decreasing trend since 2010 until today 3) the decreasing trend of GR did not continue, however for the period 2008 - 2015 it was statistically significant. These are all now stated in the manuscript. Since however

they cannot be expanded for the whole timeseries they are removed from the abstract and the concluding marks as recommended.

Considering the above, I see this study does not add much additional novel results, although it is worth publication cause you clearly see a long SMPS time trend showing spring nucleations (different from typical summer ones).



Picture 1: Size distribution data availability at Finokalia, Greece during the period June 2008-June2018 on monthly basis (a) and interannualy (b)

List of Changes made

- **The abstract was changed according to suggestions**
- **All data presented have been expended for the period 2008-2018, so that data for the period 2015-2018 was added**
- **Changes in paragraphs 3.2 and 3.3 were made according to suggestions and new findings**
- **Tables were changed**
- **All figures except of 2 and 12 were updated or changed.**
- **Several minor edits across the manuscript**

Marked up manuscript version

Formation and growth of atmospheric nanoparticles in the eastern Mediterranean: Results from long-term measurements and process simulations

Nikos Kalivitis[1,2], Veli-Matti Kerminen[3], Giorgos Kouvarakis[1], Iasonas Stavroulas[1,4], Evaggelia Tzitzikalaki[1], Panayiotis Kalkavouras [1,5], Nikolaos Daskalakis[1,6], Stelios Myriokefalitakis[5,7], Aikaterini Bougiatioti[5], Hanna Elina Manninen[8], Pontus Roldin[9], Tuukka Petäjä[3], Michael Boy[3], Markku Kulmala[3], Maria Kanakidou[1], and Nikolaos Mihalopoulos[1,5]

1. Environmental Chemical Processes Laboratory, Chemistry Department, University of Crete, 70013, Heraklion, Greece

2. Institute for Astronomy, Astrophysics, Space Applications and Remote Sensing, National Observatory of Athens, I. Metaxa & Vas. Pavlou, 15236 Palea Penteli, Greece

3. Institute for Atmospheric and Earth System Research, Gustaf Hällströmin katu 2, P.O. Box 64, FI-00014 University of Helsinki

4. Energy, Environment and Water Research Center, The Cyprus Institute, Nicosia 2121, Cyprus

5. Institute for Environmental Research & Sustainable Development, National Observatory of Athens, I. Metaxa & Vas. Pavlou, 15236 Palea Penteli, Greece

6. Laboratory for Modeling and Observation of the Earth System (LAMOS), Institute of Environmental Physics (IUP), University of Bremen, Bremen, Germany,

7. Institute for Marine and Atmospheric Research (IMAU): Utrecht, Netherlands

8. Experimental Physics Department, CERN, 1211 Geneva, Switzerland

9. Lund University

Correspondence to: N. Kalivitis (nkalivitis@uoc.gr) and N. Mihalopoulos (nmihalo@noa.gr)

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Abstract

Atmospheric New Particle Formation (NPF) is a common phenomenon all over the world. In this study we present the longest time series of NPF records in the eastern Mediterranean region by analyzing ten years of aerosol number size distribution data obtained with a mobility particle sizer. The measurements were performed at the Finokalia environmental research station on Crete, Greece during the period June 2008-June 2018. We found that NPF took place 27% of the available days, undefined days were 23% and non-event days 50%. NPF is more frequent in April and May probably due to the terrestrial biogenic activity and is less frequent in August. Throughout the period under study, nucleation was observed also during the night. Nucleation mode particles had the highest concentration in winter and early spring, mainly because of the minimum sinks, and their average contribution to the total particle number concentration was 8%. Nucleation mode particle concentrations were low outside periods of active NPF and growth, so there are hardly any other local sources of sub-25 nm particles. Additional atmospheric ion size distribution data simultaneously collected for more than two years period were also analyzed. Classification of NPF events based on ion spectrometer measurements differed from the corresponding classification based on a mobility spectrometer, possibly indicating a different representation of local and regional NPF events between these two measurement data sets. We used MALTE-box model for a simulation case study of NPF in the eastern Mediterranean region. Monoterpenes contributing to NPF can explain a large fraction of the observed NPF events according to our model simulations. However the parametrization that resulted after sensitivity tests was significantly different from the one applied for the boreal environment.

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1) Introduction

Most of the atmospheric aerosol particles, and a substantial fraction of particles able to act as cloud condensation nuclei (CCN), have been estimated to originate from new particle formation (NPF) taking place in the atmosphere (Spracklen et al. 2006; Kerminen et al., 2012; Gordon et al., 2017). The exact mechanisms driving atmospheric NPF and subsequent particle growth processes are still not fully understood, nor are the roles of different vapors and ions in these processes (Kulmala et al., 2014; Lehtipalo et al., 2016; Tröstl et al., 2016). In order to understand how aerosol particles affect regional and global climate and air quality, it is necessary to quantify the factors that determine the occurrence of NPF and characterize the parameters that describe the strength of NPF, such as the new particle formation and growth rates, in various environments.

While NPF has been reported to take place worldwide (Kulmala et al., 2004a; Wang et al., 2017), observational studies on this subject are scarce in rural sub-tropical environments. It has been shown that the processes responsible for particle formation and growth differ substantially across the European continent (Dall' Osto et al., 2018).

Several studies have investigated NPF in eastern Mediterranean and found it to be a frequent phenomenon. Lazaridis et al. (2006) first reported NPF at the area and correlated these events to polluted air masses. Petäjä et al. (2007) presented NPF in Athens metropolitan area and showed that under the influence of urban pollution, condensing species leading to growth of the new particles are far more hygroscopic than under cleaner conditions. NPF events have also been reported to be frequent at the urban environment of Thessaloniki (Siakavaras et al., 2016). Kalivitis et al. (2008) showed that precursors and nucleation mode particles experience strong scavenging on Crete island during summer. Pikridas at al. (2012) suggested that nucleation events occurred only when accumulation mode particles were neutral, being consistent with the hypothesis that a lack of NH_3, during periods when particles are acidic, may limit nucleation in sulfate-rich environments such as the eastern Mediterranean. Additionally, based on ion observations, Pikridas et al. (2012) showed that NPF is more frequent in winter. By using the same data set from eastern Mediterranean, Kalivitis et al. (2012) reported night-time enhancements in ion concentrations with a plausible association with NPF, being among the very few locations where such observations have been made. Manninen et al. (2010) presented an analysis of a full year of observations of NPF with atmospheric ion spectrometers at various locations across Europe during the EUCAARI project and showed that NPF is less frequent in the eastern Mediterranean site than in other, mostly continental, European sites. On the other hand, Berland et al. (2017) showed that similar patterns are being observed throughout the Mediterranean when comparing observations from the island of Crete to a western Mediterranean site in terms of the frequency of occurrence, seasonality, and particle formation and growth rates. Kalivitis et al. (2015) studied for the first time the NPF-CCN link using observations of particle number size distributions, CCN and high-resolution aerosol chemical composition for the eastern Mediterranean atmosphere. From the hygroscopicity of the particles in different size fractions, it was concluded that smaller particles during active NPF periods tend to be less hygroscopic (and richer in organics) than larger ones. Finally, Kalkavouras et al. (2017) reported that NPF may result in higher CCN number concentrations, but the effect on cloud droplet number is limited by the prevailing meteorology.

In this work, we present results from the analysis of ten years of aerosol particles number size distributions and more than two years of atmospheric ion size distributions, representing the longest published NPF data set in the Mediterranean atmosphere. The main questions we wanted to address were: 1) How often does NPF take place in eastern Mediterranean, what are the characteristics of this phenomenon and to what extent has it changed over the period under study? 2) Are there features in NPF observed at the study area that are not common in other locations? and 3) How well can numerical models, used in different environmental conditions, represent NPF in this subtropical environment?

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2) Materials and methods

2.1) Measurements

Measurements presented in this work were carried out at the atmospheric observation station of the University of Crete at Finokalia, Crete, Greece (35˚20΄N, 25˚40΄E, 250m a.s.l) over ten years, between June 2008 and June 2018. The Finokalia station (http://finokalia.chemistry.uoc.gr/) is a European supersite for aerosol research, part of the ACTRIS (Aerosols, Clouds, and Trace gases Research Infrastructure) Network. The station is located at the top of a hill over the coastline, in the north east part of the island of Crete (Mihalopoulos et al., 1997). The station is representative for the marine background conditions of eastern Mediterranean (Lelieveld et al., 2002), with negligible influence by local anthropogenic sources. The nearest major urban center in the area is Heraklion with approximately 200 000 inhabitants, located about 50 km to the west of the station.

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In order to monitor the NPF events, a TROPOS type custom-built Scanning Mobility Particle Sizer (SMPS), similar to IFT-SMPS in Wiedensohler et al. (2012), was used at Finokalia. Particle number size distributions were measured in the diameter range of 9–848 nm every five minutes. The system was a closed-loop, with a 5:1 ratio between the aerosol and sheath flow and it consisted of a Kr-85 aerosol neutralizer (TSI 3077), a Hauke medium Differential Mobility Analyzer (DMA) and a TSI-3772 Condensation Particle Counter (CPC). The sampling was made through a PM_{10} sampling head and the sample humidity was regulated below the relative humidity of 40% with the use of Nafion® dryers in both the aerosol and sheath flow. The measured number size distributions were corrected for particle losses by diffusion on the various parts of the SMPS according to the methodology described in Wiedensohler et al. (2012). Three different types of calibration were performed for the SMPS, DMA voltage supply calibration, aerosol and sheath flows calibrations and size calibrations. These measurements

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have been performed at Finokalia on a continuous basis since 2008. The instrument used at Finokalia was audited on-site with good results in the framework of EUSAAR (European Supersites for Atmospheric Aerosol Research) project (http://www.wmo-gaw-wcc-aerosol-physics.org/audits.html) and has successfully passed twice laboratory intercomparison workshops (2013 and 2016, reports available at http://www.wmo-gaw-wcc-aerosol-physics.org/instrumental-workshops.html) in the framework of ACTRIS project. The instrument has been operated following the recommendations described in Wiedensohler et al. (2012). Additional information for newly formed particles were obtained with the use of an Air Ion Spectrometer (AIS- AIREL Ltd., Institute of Environmental Physics, University of Tartu, Estonia, Mirme et al., 2007). AIS is a cluster ion air spectrometer used to simultaneously measure electrical mobility distribution of positive and negative air ions (mobilities in the range of 2.4 to $1.3\cdot10^{-3}$ cm^2 V^{-1} s^{-1}). The mobility distributions were then transformed to size distributions in the size range 0.8-42 nm. The number counting threshold was approximately 10 cm^{-3} and the uncertainties of the AIS measurements were ~10% for negative and positive ion concentrations and ~0.5 nm in size (Manninen et al., 2010). The diameter of the AIS inlet tube was 35 mm and the sample flow rate was 60 L m^{-1}. The time step of the measurements was five minutes.

These measurements have been used to identify NPF for the whole period and provide a historical perspective for the frequency and the characteristics of NPF phenomena in the eastern Mediterranean. Calculations for formation rates of new particles (J), growth rates (GR) in various size ranges and condensation sink (CS) were made according to Kulmala et al. (2012). Formation rates of particles with diameter D_p (in this study D_p=9nm) were calculated as:

$$J_{Dp}=\frac{\Delta N_{D_p}}{\Delta t}+CoagS_{D_p}\cdot N_{D_p}+\frac{GR}{\Delta D_p}\cdot N_{D_p}+S_{losses} \quad (1)$$

ΔN_{D_p} is the increase in nucleation mode particles' number concentration (D_p<25nm), $CoagS_{Dp}$ is the coagulation of 9nm particles on larger particles, GR is the growth rate in the size range 9-25nm. S_{losses} takes into account additional losses and was neglected in this study. GR was calculated using the mode-fitting method (Dal Maso et al., 2005). The aerosol size distributions were fitted with lognormal distributions and the nucleation mode geometric mean diameter was plotted as a function of time. GR was calculated as the slope of the linear fit so that:

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$$GR = \frac{dD_p}{dt} \quad (2)$$

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

All important meteorological parameters were monitored every five minutes using an automated meteorological station, including the temperature, wind velocity and direction, relative humidity, solar irradiance and precipitation. Ozone concentrations were measured with a TEI 49C instrument and nitrogen oxides with a TEI 42CTL, both commercially available, with a time step of five minutes.

2.2) NPF simulations with the MALTE-Box model

The simulations of NPF events in the eastern Mediterranean atmosphere were here performed using the MALTE-box model of the University of Helsinki. This 0-d model able to simulate aerosol dynamics and chemical processes has successfully reproduced observations of aerosol formation and growth in the boreal environment (Boy et al., 2006) as well as in highly polluted areas (Huang et al., 2016). For the present study, chemical reactions relevant to the production of condensing species from the Master Chemical Mechanism were incorporated in the MALTE-box chemical mechanism, as described in Boy et al. (2013). These include the full MCM degradation scheme of the following volatile organic compounds (described in more detail in Tzitzikalaki et al., 2017): C_1-C_4 alkanes, C_2-C_3 alkenes, acetylene, isoprene, α- and β-pinene, aromatics, methanol, dimethyl sulfide, formaldehyde, formic and acetic acids, acetaldehyde, glycoaldehyde, glyoxal, methylglyoxal, acetone, hydroxyacetone, butanone and marine amines. The Kinetic PreProcessor (KPP) was used to produce the Fortran code for the calculations of the concentrations of each individual compound (Damian et al., 2002), except for those species whose concentrations were manually input from large scale model simulations.

The major aerosol dynamical processes for clear sky atmosphere were simulated by the size-segregated aerosol model UHMA (University Helsinki Multicomponent Aerosol Model, Korhonen et al., 2004) impended in the MALTE-Box model. Measured aerosol number size distributions were used to initialize UHMA daily, which simulates NPF, coagulation, growth and dry deposition of particles. 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}.

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Apart from sulfuric acid, about 20 extremely low-volatility organic compounds (ELVOCs) and 7 selected semi-volatile organic compounds (SVOCs) were treated as condensing vapors, following the simplified chemical mechanism presented in Huang et al. (2016). All condensing compounds were treated either as sulfuric acid or organic compounds and the condensation of organic vapors was determined by the nano-Kohler theory (Kulmala et al., 2004b).

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As input to the MALTE-Box model were used the observations at Finokalia station and when such observations were not available, the results from numerical simulations with the global 3-dimensional chemistry transport model (CTM) TM4-ECPL (Daskalakis et al., 2015, 2016; Myriokefalitakis et al., 2010, 2016) for Finokalia. Observational data include temperature, relative humidity, total radiation (meteorological input), ozone (O_3) and nitrogen oxides (NOx) concentrations as well as aerosol number size distributions. The aerosol number size distribution measured by the SMPS was used to calculate the condensation sink for H_2SO_4 vapors. Due to the lack of detailed measurements of VOC at Finokalia, as a first approximation, biogenic and anthropogenic concentrations of all the above mentioned VOCs resolved every 3 hours were taken from the TM4-ECPL model.

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The global TM4-ECPL model was run driven for this study by ECMWF (European Centre for Medium – Range Weather Forecasts) Interim re–analysis project (ERA – Interim) meteorology (Dee et al., 2011) of the year 2012 at an horizontal resolution of 3° in longitude x 2° in latitude with 34 vertical layers up to 0.1 hPa. The model used year-specific meteorology and emissions of trace gases and aerosols. For this study, that of the year 2012 was used, except for soil NOx and oceanic CO and VOCs emissions which were taken from POET inventory database for the year 2000 (Granier et al., 2005). TM4-ECPL simulations for this work were performed with a model time-step of 30 min, and the simulated VOC concentrations every 3-hours were used as input to MALTE box model; while SO_2 surface levels at Finokalia were taken from Monitoring Atmospheric Composition and Climate (MACC) data assimilation system (Inness et al., 2013).

For the calculations of the photo-dissociation rate coefficient by the MALTE-Box model, the solar actinic flux (AF) is needed. Unfortunately, AF was not measured at Finokalia in 2012, therefore AF levels were calculated by the Tropospheric Ultraviolet and visible Radiation Model (TUV, Madronich, 1993) version v.5 for cloud free conditions. The ability of TUV to calculate the AF at Finokalia was investigated by comparing observations of photo dissociation rates of O_3 (JO^1D) and NO_2 (JNO_2) and model calculations. The measurements of these photo dissociation rates were performed by filter radiometers (Meteorologie Consult, Germany).

The JO^1D was measured at wavelengths <325nm, while for JNO_2 wavelengths <420nm were used.

A series of sensitivity tests of AF to different input parameters was also performed to optimize the calculations. The model uses extra-terrestrial solar spectral irradiance (200-1000 nm by 0.01nm steps) and computes its propagation through the atmosphere taking into account multiple scattering and the absorption and scattering due to gases and particles. TUV inputs of interest were surface reflectivity (albedo), O_3 column, Aerosol Optical Depth at 500nm (AOD), Single Scattering Albedo of aerosol (SSA), NO_2 column, air density. Total O_3 column values were taken from Ozone Monitoring Instrument (OMI) on the Aura spacecraft of NASA (Levelt et al., 2006). Aerosol columnar optical properties were obtained from the Aerosol Robotic Network (AERONET). AOD data were measured at the FORTH_Crete station which is located 35 km west of Finokalia (Fotiadi et al., 2006). Data level 1.5 was used (cloud-screened). Total NO_2 column values were taken from GOME2 and OMI satellites. The calculations were carried out at wavelength from 280 to 650nm with a resolution of 5nm. Simulations using surface reflectivity of 0.075 and simulation using O_3 column taken from OMI had the best correlation with measurements. However, the TUV model still significantly overestimated JO^1D and JNO_2 data. Thus, a parameterisation took place following a simple empirical approach, according to Mogensen et al. (2015) and the ratios between the measured and modelled (from TUV) photolysis rate were calculated and used in the model.

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3) Results and discussion

3.1) Particle size distribution and its connection with NPF

We analyzed all available measurements of number size distributions of atmospheric aerosol particles measured at Finokalia in order to identify and analyze the NPF phenomenon in the eastern Mediterranean. The data coverage for the period 2008-2018 was 82 %, providing one of the longest time series of size distributions not only in this region but also in the southern Europe and a unique data base for aerosol physical properties.

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First, we calculated the total particle number concentration (median concentration was 2202 cm^{-3}, standard deviation (SD) 528 cm^{-3}) and corresponding number concentration in the nucleation mode (d_p<25nm, median 80 cm^{-3}, SD 528 cm^{-3}), Aitken mode (25nm<d_p<100nm, median 1028 cm^{-3}, SD 894 cm^{-3}) and accumulation mode (d_p>100nm, median 898 cm^{-3}, SD 605 cm^{-3}). We found that Aitken mode accounted for 50% and accumulation mode 42% of the total particle number concentration, while the nucleation mode accounted only for 8%. The

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standard deviation of the nucleation particle number concentration was 528 cm^{-3}, indicating that the abundance of these smallest particles is of episodic nature. The highest monthly average concentrations of nucleation mode particles were observed during winter and early spring and the lowest ones during summer (Figure 1a). Calculating the median diurnal variability of the nucleation mode, we can see that there is a clear pattern for all seasons of the year (Figure 2a) with a sudden burst in the number concentration around noon that is most pronounced in winter and least in summer. Such an observation suggests that the nucleation particle number concentration is controlled by NPF episodes rather than other sources such as combustion processes. As can be seen in Figure 2b where a typical “banana shaped“ pattern of an NPF event at Finokalia is presented, the sudden burst at noon is typical for a NPF event. In summer, nucleation mode particles have the highest concentrations during the night, yet another concentration relative maximum at noon can be attributed to NPF (Figure 2a). The shift in the average time of the daytime burst of nucleation mode particles can be attributed to the annual variation of the daylight length. Similar observations to ours have been reported in Cusack et al. (2013) for the western Mediterranean where the diurnal variation of nucleation mode particles presents a clear maximum at noon under both polluted and clean conditions.

It is worth noticing that during night-time the median nucleation mode particle number concentrations were similar in all the seasons. This suggests that there is some new particle production mechanism at night, especially in summer and autumn, that operates separately from daytime NPF. Frequently during the night-time, we observed a pronounced appearance of new nucleation mode particles over several hours as illustrated by Figure 3. While nocturnal NPF has been reported in the literature (see Salimi et al. (2017) and references therein), this phenomenon seems to be rare and it remains unclear what are the exact mechanisms leading to it. Given that we observed no or little growth during nighttime NPF, we may assume that the sources leading to the formation of new particles are local rather than regional and that the lack of photochemistry during night limits the abundance of condensable vapors driving particle growth. Observations of very localized NPF have been reported in Mace Head, Ireland, where intense NPF frequently takes place under low tide conditions when algae are exposed to the atmosphere (O’Dowd et al., 2002). Henceforth, we will exclude the nighttime NPF events from our further analysis. We refer the interested reader to Kalivitis et al. (2012) for a more detailed description of this phenomenon.

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Overall, we observed atmospheric NPF to take place during both day and night at Finokalia, but no sign of any other source of nucleation mode particles in measured air masses. We therefore hypothesize that atmospheric NPF is the dominant source of nucleation mode particles in this Mediterranean environment.

3.2) Characteristics of NPF in the eastern Mediterranean

We analyzed the dataset of aerosol size distributions following the approach of Dal Maso et al. (2005) in order to mark the available days as 1) NPF event days when a clear new nucleation mode and subsequent growth of newly-formed particles to larger diameters can be observed, 2) non-event days and 3) undefined days when either new particles appear into the Aitken mode or nucleation mode particles do not show a clear growth. The available days were manually inspected and classified.

We used the Statistica software package for Windows to carry out factor analyses, including meteorological parameters, ozone concentrations (as an important oxidant in the atmosphere) and PM_{10} mass concentration (as an index of particulate pollutant levels), in order to examine whether any of these factors were associated with the formation of new particles, represented by the nucleation mode number concentration. Furthermore, we divided our data to night and day time periods in order to separate daytime NPF from that taking place during nighttime. The only parameter that had some effect on the nucleation mode particle number concentration was the wind velocity: when strong winds were prevailing at Finokalia, it was more unlikely to observe nucleation particles. On the other hand, the lack of correlation to any other parameter may indicate that the NPF is not sensitive to local meteorological conditions, preexisting particulate matter and ozone levels in this environment. Air mass back trajectories calculated using the HYSPLIT model showed little difference during NPF events from air masses typical for the prevailing situation at Finokalia: air masses arriving at Finokalia from the northeast were the most frequent during NPF events (30% against 24% of all days), followed by northern directions (20% against 21%) and northwestern air masses that were more frequent than the average (19% against 17%).

Next, we focused on determining the main characteristics of daytime NPF at Finokalia. Overall, 837 NPF events were identified. This is the longest time series of the NPF phenomenon recorded in the Mediterranean atmosphere, providing a representative climatology of NPF events in this region. NPF took place 27% of the 3057 available measurement days whereas no event occurred on 50% of those days. It is worth noting that 23% of the days were

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characterized as undefined, which means that while no clear NPF event could be observed, there was some evidence of secondary particle formation although not at the immediate vicinity of the station (Table 1). We found that NPF is most frequent in April and May, probably due to the biogenic activity and the onset of intense photochemistry, and least frequent in August (Figure 4) probably due to high wind speeds occurring these month (not shown) and additionally the high Condensational Sink (Figure 1b). 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. NPF at Finokalia takes place throughout the year.

As a next step, we classified the NPF events into Class I or Class II events depending on whether the particle formation rate at 9 nm (J_9) and growth rates from 9 to 25 nm diameter ($GR_{9\text{-}25}$) could be calculated with a good confidence. Overall, Class I events corresponded to 8% of the available measuring days and 28% of the event days, and they were observed throughout the year, providing enough data for a statistical analysis of particle formation and growth rates during NPF events (Figure 5).

The average value of J_9 during the Class I NPF events in Finokalia was 0.9 cm^{-3} s^{-1} (median 0.5 cm^{-3} s^{-1}, SD 1.2 cm^{-3} s^{-1}). This is well in the range of values reported for J_{10} in other locations (Kulmala et al., 2004a), higher though than J_{16} reported by Berland et al. (2017) at the Finokalia site in 2013 (0.26 cm^{-3} s^{-1}), but substantially lower than the values found by Kopanakis et al. (2013) in western Crete (13.1 ± 9.9 cm^{-3} s^{-1}). The monthly variation of J_9 (Figure 6a) shows that the highest average formation rates were observed in December and January, probably as a result of the low CS values observed in winter, although it is difficult to say which factors determine the monthly variability of J_9 at Finokalia. Seasonal averages of J_9, $GR_{9\text{-}25}$ and CS are summarized in Table 2. Moreover, we found that J_9 and $N_{9\text{-}25}$ have a clear linear relation (Figure 7), which supports our earlier hypothesis that at Finokalia the main source of nucleation mode particles is their secondary formation in the atmosphere.

We calculated the average growth rate of the newly formed particles to be 5.4 nm hr^{-1} (median 4.5 nm hr^{-1}, SD 3.9 nm hr^{-1}). We found that $GR_{9\text{-}25}$ is highest in summer until September and lowest in winter and early spring, probably in line with the seasonal cycle of photochemical activity and biogenic emission patterns, producing condensable species that are driving the growth process (Figure 6b). Additionally, transported pollution in summer at Finokalia may contribute except of CS to GR as well, transported anthropogenic SO_2 may play a role in the growth process as a precursor for sulfuric acid.

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The survival probability of newly-formed particles is closely related to the ratio of CS to GR, at least for cluster sizes (Kerminen and Kulmala, 2002; Kulmala et al., 2017) and at Finokalia they present the same annual cycle. The survival probability for nucleation mode particles for Class I events was calculated based on the formula in Kulmala et al. (2017). It was found that on seasonal basis the median survival probability is higher in summer and winter, however varies between the seasons only within 5%. The concentrations of nucleation mode particles are lower during summer and the average duration of the NPF in summer seems to be shorter as shown in Figures 1 and 2a respectively. These observations may be explained by the higher CS and GR during summer. The CS (and hence CoagS) may directly affect the maximum concentrations observed. The slightly higher survival probability in summer explains perhaps that given the high CS, in order for new particles to survive the need to grow fast. On the other hand, one would expect NPF to be most frequent in winter when the highest concentrations of nucleation particles are observed and CS is the lowest, however this was not the case. A possible explanation for the high nucleation mode particle number concentrations in winter could be that the survival probability is higher than in spring or autumn.

3.3) NPF trends during the 2008-2018 period

During the period under study no statistically significant trends in NPF events were observed at Finokalia for the 120 available months. It should be noted though, that since 2010 a decreasing trend is observed, which is statistically significant with a p-value of 0.005. During the measurement period under study, no trend in J_9 was observed (Figure 8c). Although no statistically significant trend was observed for GR_{9-25} as well (Figure 8d), we observed a decreasing trend during the period 2008-2015 of about 0.3 nm hr^{-1} yr^{-1}. This trend can be considered statistically significant (p-value of 0.03). In order to explain this trend, we need to emphasize the regional characteristics of the observations at Finokalia, as this site is greatly affected by long-range transported pollutants of marine, desert dust and polluted continental origin (Lelieveld et al., 2002). Non-sea salt sulfate (nss-SO_4^{2-}) can be considered as an indicator of regional pollution from anthropogenic activities (SO_2 emissions), and since the beginning of the economic crisis in Europe, especially in Greece, we observed a clear decline in its concentration since 2008 (Paraskevopoulou et al., 2015) which however has stopped after 2015. We can therefore assume also a regional decrease in SO_2 emissions, since the main source of SO_2 at Finokalia is attributed to transported pollution (Sciare et al., 2003). This could

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result in a decrease in the availability of sulfuric acid, a major condensable species responsible for the particle growth (Bzdek et al., 2012).

Hamed et al. (2010) studied the effect of the reduction in anthropogenic SO_2 emissions in Germany between the years 1996-97 and 2003-06 as a result of the socio-economic changes in East Germany after the reunification. They observed a notable decrease in the NPF event frequency but an increase in the growth rate of nucleated particles. A decrease in the NPF frequency due to the reduction of anthropogenic SO_2 emissions in eastern Lapland was also reported by Kyrö et al. (2014), and this decrease was most pronounced for the Class I NPF events. Nieminen et al. (2014) analyzed the longest data set reported in literature from Finland and found that, despite major decreases in ambient SO_2 concentrations observed all over Europe as a result of overall air quality improvements, there was a slight upward trend in the particle formation and growth rates. This feature was attributed partly to increased biogenic emissions over the same period.

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In our case the reasons for the variations in the NPF frequency, J_9 and GR_{9-25} remain unclear, even though factors like meteorological conditions and organic vapor abundance have probably played some role in this respect.

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3.4) Atmospheric ion observations related to new particle formation

At the Finokalia station, atmospheric ion observations relevant to new particle formation were performed during two separate periods, 2008-2009 during the EUCAARI project (Manninen et al., 2010) and 2012-2014 during the FRONT (Formation and growth of atmospheric nanoparticles) project. Here we will focus only on FRONT data, since the EUCAARI dataset is discussed in detail in Manninen et al. (2010) and Pikridas et al., (2012). A typical nucleation event is presented in Fig. 9 as recorded by both the AIS and SMPS. AIS observations may provide information about the initial stages of new particle formation as particles can be observed emerging in the intermediate ion diameter range 1.6-7.4 nm. Intermediate ions appear only under certain circumstances, such as during precipitation, at high wind speeds, and when NPF is taking place (Hõrrak et al. 1998; Tammet et al., 2014; Leino et al., 2016; Chen et al., 2017). In the following we will focus on NPF and use only the observations from the negative polarity due to the better representation of NPF events in those data compared with corresponding positive ions in our dataset (Kalivitis et al., 2012).

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We classified all of the available AIS measurement days into event, non-event and undefined days, once again according to methods introduced by Dal Maso et al. (2005), and subsequently compared the findings from AIS data to those from the SMPS. In Figure 9 an NPF event is presented observed with both the AIS and the SMPS at Finokalia. Surprisingly, the two data sets for the same time period gave quite different results in terms of the NPF event frequency: in the AIS data the NPF event frequency peaked earlier during the year than in the SMPS data (Figure 10). This feature was evident in both periods of AIS measurements and is probably due and has been also reported at a rural site in Hungary (Yli-Juuti et al., 2009), probably because AIS detects only naturally charged particles while SMPS all particles. Additionally, it is possible that AIS data are more representative of local NPF events with limited particle growth, and such events may not be seen in the SMPS data. On the other hand, the SMPS measures neutral particles but has a much higher detection limit (9nm), so its data may be more representative of regional NPF that takes place over distances of hundreds of kilometers (Kalkavouras et al., 2017).

We calculated the growth rates at three different size ranges for the FRONT project similarly to Manninen et al. (2010) and Pikridas et al (2012) for the EUCAARI project data. The particle growth rates in the size ranges 1.5-3 nm, 3-7nm and 7-20 nm were 1.6 ±1.8 nm hr^{-1}, 5.4±4.9 nm hr^{-1} and 9.1±9.5 nm hr^{-1}, respectively. These values are lower than those in Pikridas et al. (2012) but comparable to those observed during the EUCAARI project for the first two size ranges, and higher than those observed during the EUCAARI project for the last size range (Manninen et al., 2010). Overall, we observed much faster growth of newly-formed charged particles in the eastern Mediterranean atmosphere after their first growth steps beyond 3 nm in diameter, reflecting probably the strong Kelvin effect at small particle sizes preventing condensation and hence growth, and the abundance of precursors leading to nucleation and condensing species contributing to each growth stage.

3.5) Simulations of NPF using the zero-dimensional model MALTE-box

In order to evaluate our understanding of the observed NPF events in the eastern Mediterranean we chose to simulate two distinct cases of one week duration each, during which NPF events have been observed (event week) or not (no event week). The selection was done from the summer of the year 2012, when $JO^{1}D$ and JNO_2 photodissociation measurements were also available at Finokalia. Two weeks in August 2012 were chosen, 28/08– 03/09 as event week and 09/08– 15/08 as non-event week. The "event week" was described in detail by Kalivitis et al. (2015). Applying the MALTE-Box model the aerosol size distribution and its evolution over the week has been simulated for these two cases.

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During the ‘‘event week’’ the simulated formation of new particles successfully coincided with the observations. The NPF events simulated using the nucleation rates as parameterized for the boreal environment overestimated the observations while the simulated growth of newly-formed particles was greatly underestimated as shown in Tzitzikalaki et al. (2017). The most likely reason for this is the very low concentration of monoterpenes, calculated by TM4-ECPL global model for the Finokalia model grid box, on which the ELVOC and SVOC chemistry was built on. Indeed, the TM4-ECPL model results for Finokalia were too low compared to monoterpenes observations in 2014 (not shown). Therefore, we performed a number of sensitivity tests to improve the simulations by adjusting the nucleation coefficient and the monoterpene concentrations until we simulated efficiently the nucleation and growth rates observed during the second day of the “event week” when the most pronounced NPF event was observed. The best agreement between model results and observations was reached by decreasing the nucleation coefficient from 10^{-11} s^{-1} (the value commonly used for the boreal environment) to 5×10^{-16} s^{-1} and increasing by a factor of 10 the α- and β-pinene concentrations. With these modifications the model results improved and the aerosol number size distributions were better simulated, as well as total number and volume concentration of aerosol particles (Figures 11a and b respectively). This was the first time that we were able to simulate NPF in the eastern Mediterranean environment. The almost five orders of magnitude lower nucleation coefficient used here for the sub-tropical set-up could be related to the contribution of still unknown compounds in the cluster-formation process. Huang et al. (2016) applied different kinetic nucleation coefficients at Nanjing, China, with the lowest value for a “China-clean” day of 6.0×10^{-13} s^{-1}. The higher monoterpene concentrations used are comparable to the findings at Finokalia but also to another location in eastern Mediterranean (Debevec et al., 2018).

Using the non-event week as our control case, we performed simulations of number size distributions at Finokalia station using the sub-tropical set-up and compared it to our measurements. For the “non-event week”, weak NPF were predicted by the model during the last two days that were not found in the measurements (Tzitzikalaki et al., 2017) but appear to be associated with the rapid drop of CS during day five of the simulations. Nevertheless, even if no NPF took place during the last two days, it was apparent in our measurements that some nucleation particles appeared (~200 cm^{-3}) and thus the general tendency was captured by the model. Both total number and volume concentrations were adequately simulated by the model (Figures 12 a, b). These results show the potential of MALTE-box model to simulate the NPF in the eastern Mediterranean and the importance of input data. Therefore, when

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more appropriate input data for Malte-box will become available (concurrent detailed measurements of gases and aerosol distributions) at Finokalia, 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.

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4) Conclusions

NPF in the atmosphere is a recurrent phenomenon in eastern Mediterranean. In this study, we presented the longest time series of NPF records in the region. We analyzed 3057 days of aerosol number size distribution data from June 2008 until June 2018 and found that NPF took place 27% of the available days, more frequently in spring and less frequently in late summer. Production of nucleation mode particles was common during night-time as well. Nucleation mode particle number concentrations were low outside periods of active NPF and subsequent particle growth indicating absence of local sources. Classification of NPF events based on atmospheric ion measurements differed from the corresponding classification based on mobility spectrometer measurements: the maximum frequency of NPF events was observed earlier in spring from AIS data than from SMPS data, possibly indicating a different representation of local and regional NPF events between these two data sets since SMPS measures new particles after they have grown to diameters larger than 9nm and hence records only regional events lasting for several hours.

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We used the MALTE-box model to simulate NPF observations in the eastern Mediterranean region. Using a “sub-tropical” environment parametrization, we were able to simulate with good agreement the selected time period. The parametrization used was significantly different than the one used for the boreal environment: nucleation rates were much lower, yet monoterpenes seemed to play a key role in the mechanisms governing NPF phenomena.

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From the results presented in this work it is evident that the Finokalia site is a unique location in the eastern Mediterranean for studying the processes leading to NPF in the marine environment. As a next step, a more detailed look to the precursors driving these processes is necessary, with special emphasis on VOCs, and the expansion of the available measurements at the site in order to eliminate the uncertainties introduced in our simulations from the use of model outputs instead of observations.

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7) Tables

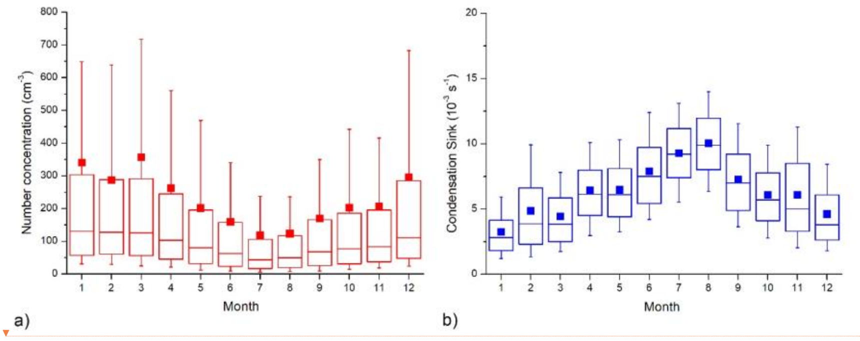
Day classification	Number of events	%
Total events	837	27.4
Class I	232	7.6
Class II	605	19.8
Undefined	687	22.5
Non-event	1533	50.1
Total days	3057	100.00

Table 1) Total available measurement days and percentage of NPF events observed at Finokalia during the period June 2008-June 2018

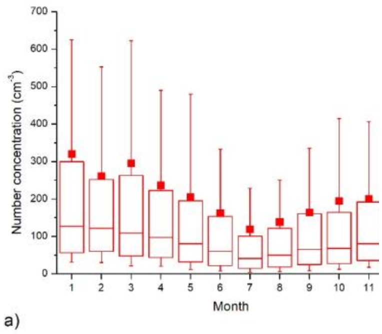
	J_9 (cm^{-3} s^{-1})			GR_{9-25} (nm hr^{-1})			CS x 10^{-3} (s^{-1})		
	Mean	Median	SD	Mean	Median	SD	Mean	Median	SD
Winter	0.9	0.6	1.4	3.3	2.6	2.4	4.3	3.5	2.9
Spring	1.0	0.6	1.0	4.2	3.3	3.1	5.8	5.5	3.0
Summer	0.7	0.5	0.9	7.3	6.8	3.9	9.1	9.0	3.1
Autumn	0.8	0.4	1.0	5.3	4.7	2.9	6.5	6.0	3.4

Table 2) Formation rates for 9nm particles (J_9), growth rates in the size range 9-25 nm (GR_{9-25}) for NPF events observed at Finokalia and condensational sink for sulfuric acid (CS) on seasonal base during the period June 2008-June 2018 (mean, median and standard deviation).

8) Figures



1) Monthly average variation of a) nucleation mode particle number concentration and b) sulfuric acid condensational sink (CS) at Finokalia station over the period June 2008-June 2018. Whiskers represent 10th and 90th percentiles, box edges are 75th and 25th percentiles, the line in the box is the median, the solid square is the mean.

Deleted: 

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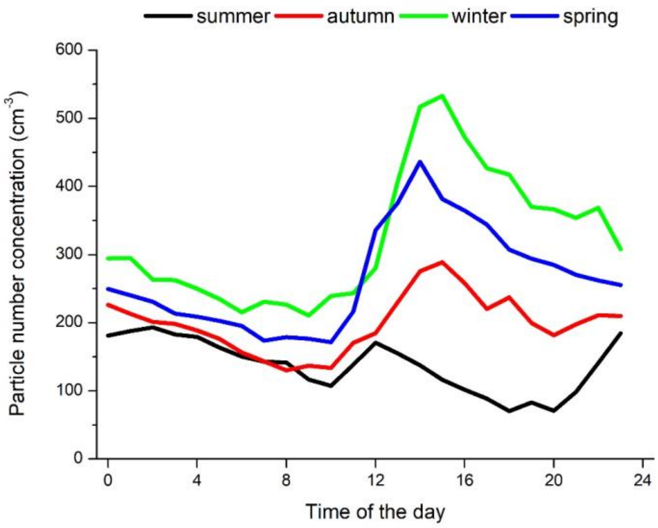

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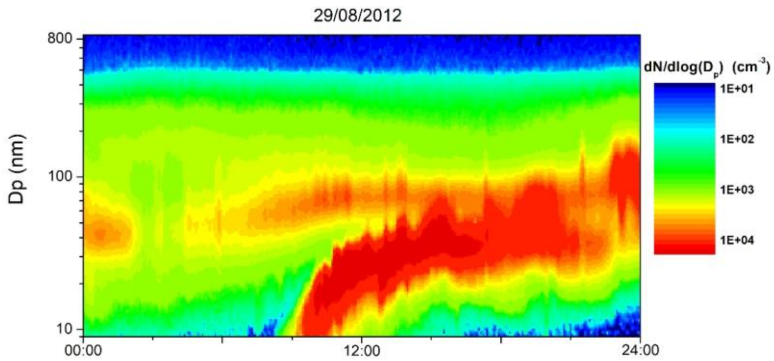

2) a) Average diurnal variation of nucleation mode particle number concentration (hourly values) at Finokalia over the period June 2008-June 2018 b) New particle formation event captured at Finokalia on 29/08/2012 (time in UTC+2).

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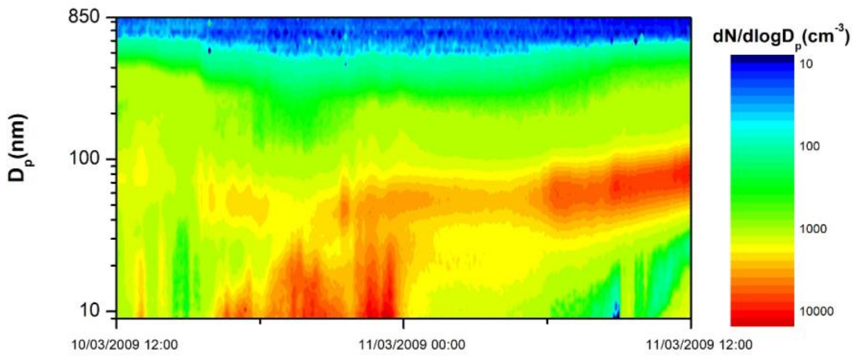

3) Example of appearance of nucleation mode particles during several hours as observed during the night of 10 to 11/03/2009 (time in UTC+2).

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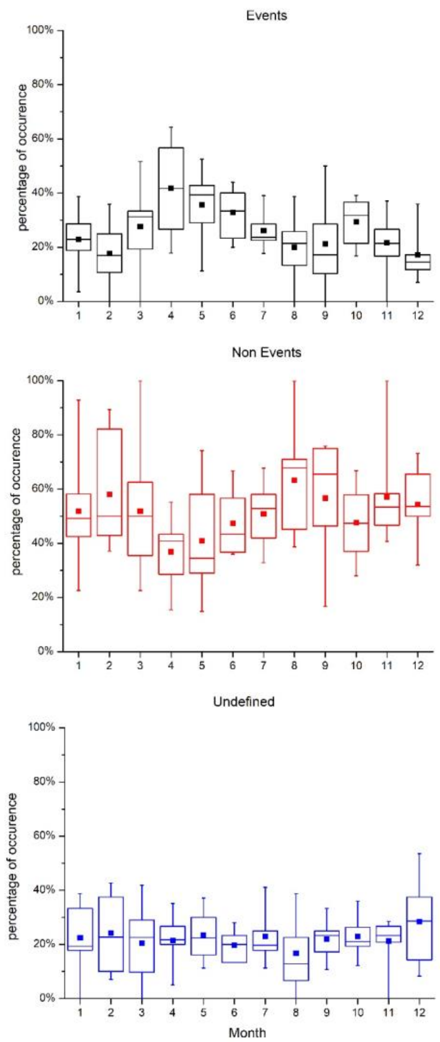

4) Seasonal variation of NPF percentage of occurrence of event, non-event and undefined days relatively to available measurement days at Finokalia for the period June 2008-June2018. Whiskers represent 10th and 90th percentiles, box edges are 75th and 25th percentiles, the line in the box is the median, square is mean.

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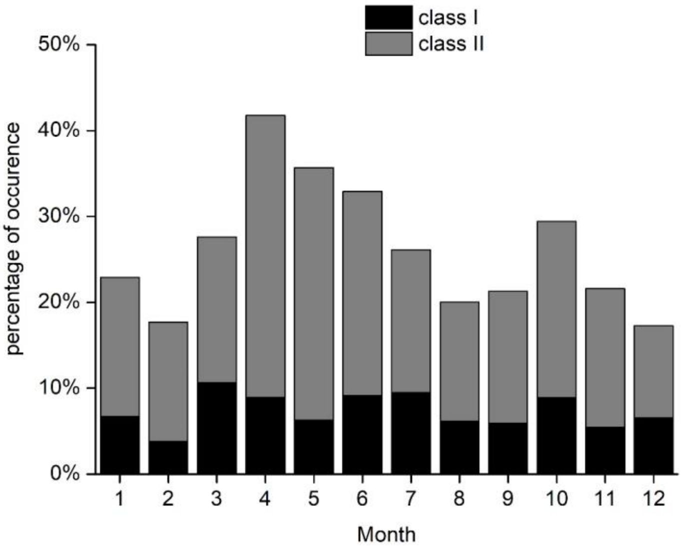

5) Seasonal variation of percentage of occurrence of NPF Class I & II events relatively to available measurement days at Finokalia in the eastern Mediterranean for the period June 2008-June2018.

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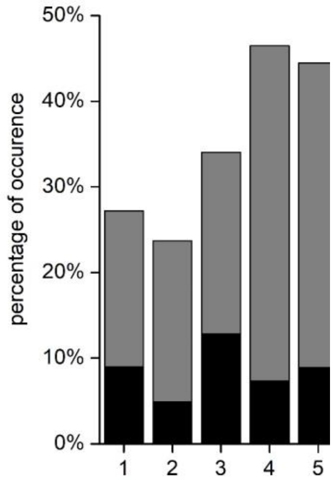

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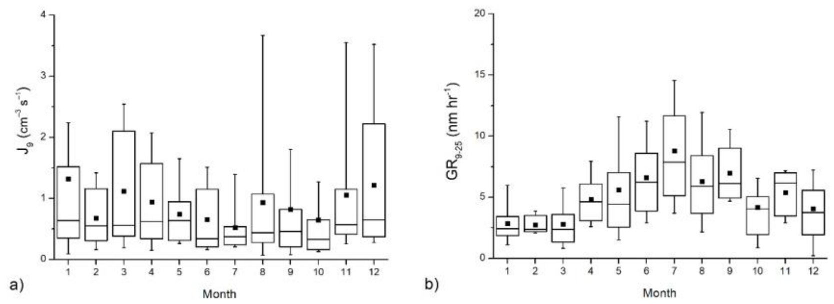

6) Seasonal variation of a) formation rate of 9nm particles (J_9) and b) growth rate in the size range 9-25nm (GR_{9-25}) as calculated during Class I NPF events at Finokalia for the period June 2008-June 2018. Whiskers represent 10th and 90th percentiles, box edges are 75th and 25th percentiles, the line in the box is the median and the solid square is the mean.

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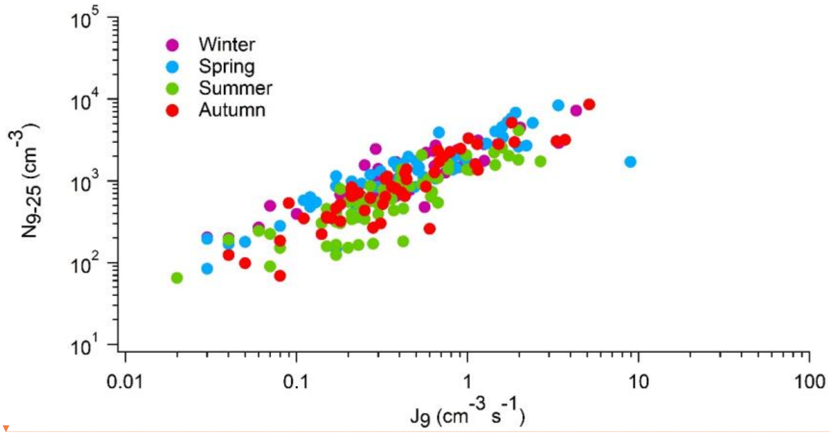

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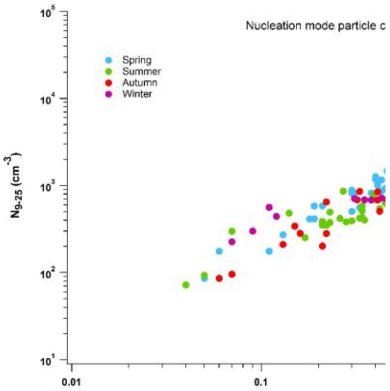
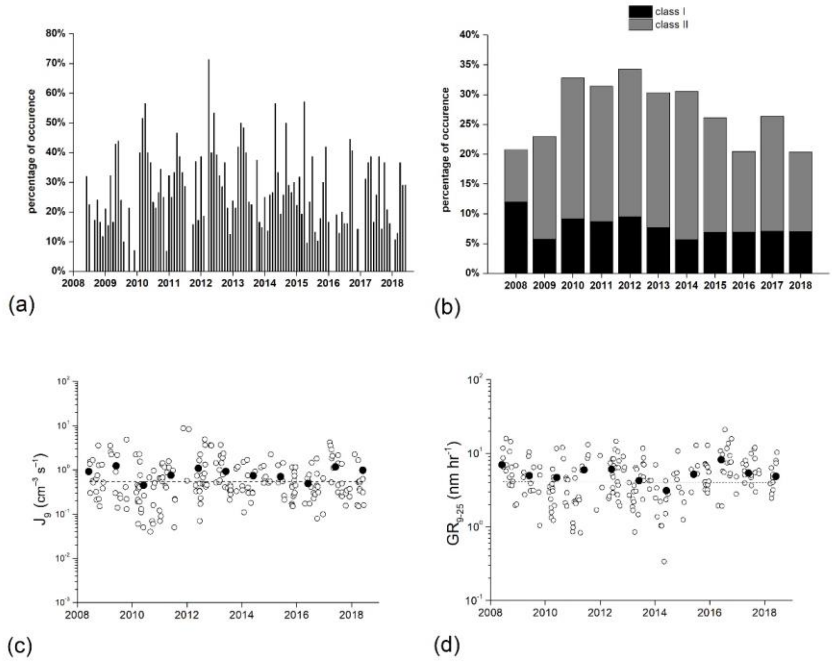


7) Scatter plot of formation rate of 9nm particles (J_9) versus the number concentration of nucleation mode particles ($N_{9\text{-}25}$) (hourly maximum value during the event) at Finokalia, for events that J_9 could be calculated with a good level of confidence (Class I events).



8) a) Time series of monthly NPF percentage of occurrence at Finokalia for the years 2008-2018. b) Annual NPF percentage of occurrence at Finokalia for the period June 2008-June 2018 for Class I&II events. Interannual variation of c) formation rates of 9nm particles (J_9) and d) growth rate in the size range 9-25nm (GR_{9-25}) during Class I NPF events at Finokalia for the period June 2008-June 2015 (solid circles represent annual averages).

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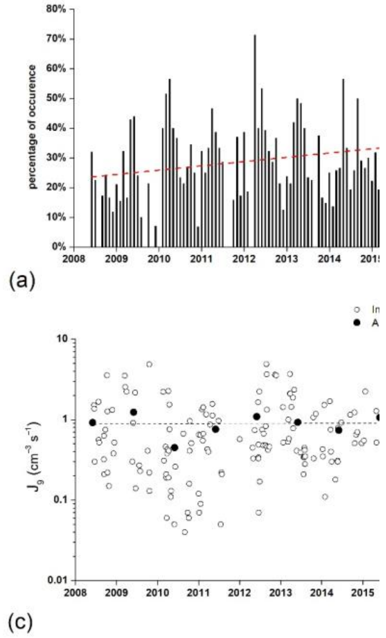

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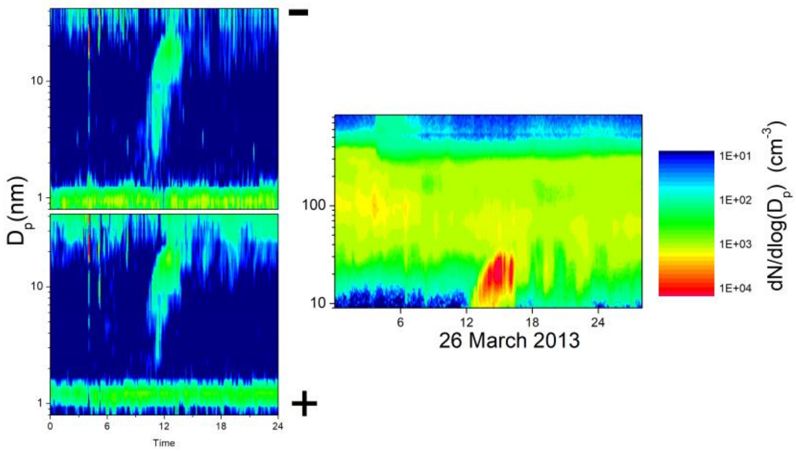

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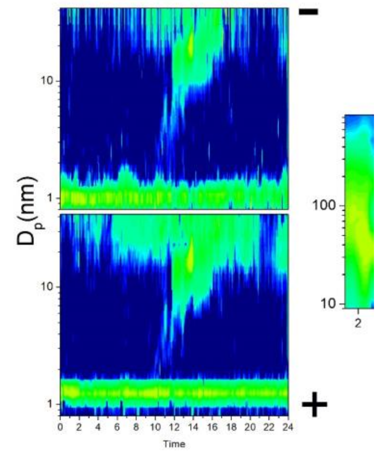

9) Nucleation event observed at Finokalia on 26 March 2013 as captured by AIS (left panels for negative (up) and positive (bottom) polarity) and SMPS (right panel) (time in UTC+2).

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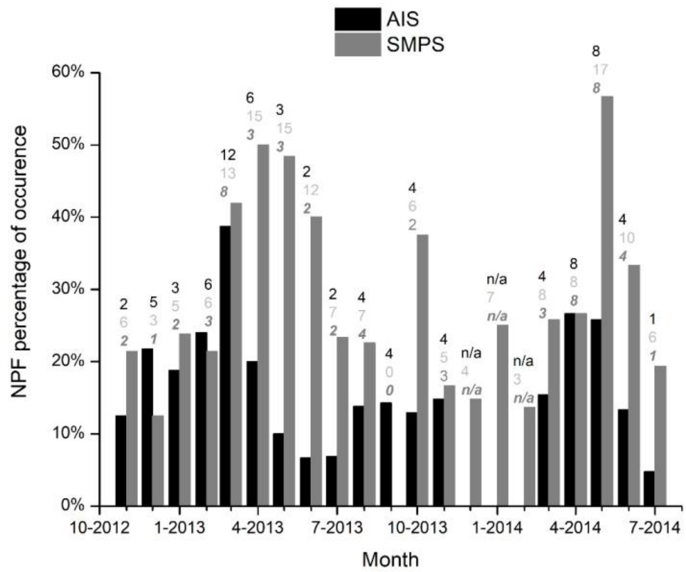
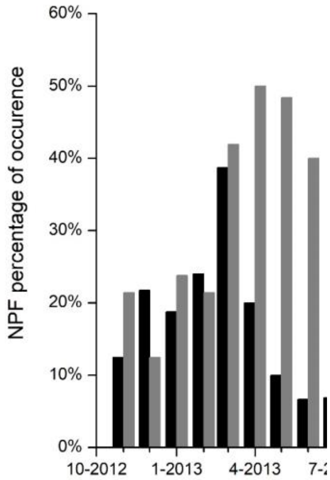


10) Monthly variability of NPF events' percentage of occurrence relatively to available measurement days at Finokalia as determined by analysis of AIS data during the FRONT experiment (Nov. 2012-July 2014). For a direct comparison, the monthly variability of NPF events as obtained from the SMPS measurements for the same period is included. On top of the columns, the NPF events observed for AIS (black), SMPS (grey) and the common events for both instruments (dark grey) for each month are presented.



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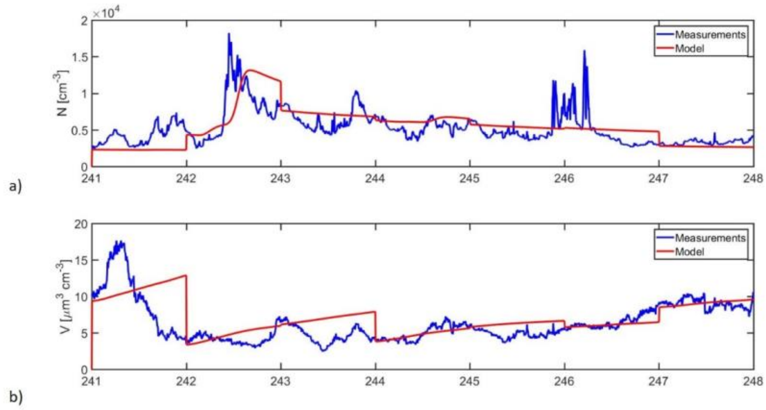

11) Simulations with the MALTE box with the adjusted parameters for the sub-tropical environment for the event week at Finokalia. Measured and modelled d) total number concentration and b) total volume concentration for the same period. The x-axis in both figures is Julian day of 2012.

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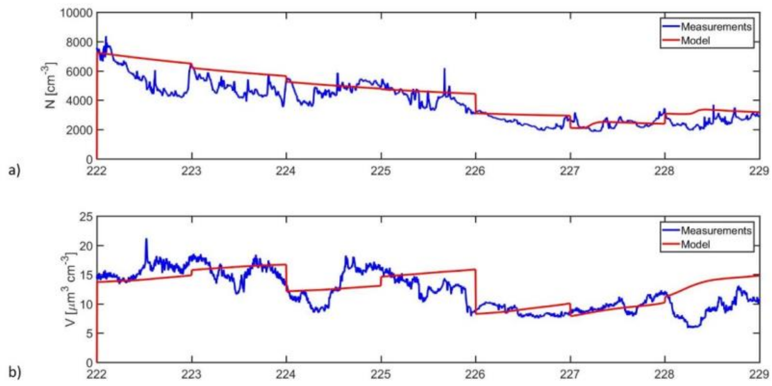

12) Simulations with the MALTE box with the adjusted parameters for the sub-tropical environment for the non-event week at Finokalia. Measured and modelled d) total number concentration and b) total volume concentration for the same period. The x-axis in both figures is Julian day of 2012.

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