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

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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 seven 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 2015. We found that NPF took place 29% of the available days, undefined days were 26% and non-event days 45%. NPF is more frequent in April and May probably due to the biogenic activity and is less frequent in August and November. The NPF frequency increased during the measurement period, while particle growth rates showed a decreasing trend, indicating possible changes in the ambient sulfur dioxide concentrations in the area. Throughout the period under study, we frequently observed production of particles in the nucleation mode during night-time, a feature rarely observed in the ambient atmosphere. Nucleation mode particles had the highest concentration in winter, mainly because of the minimum sinks, and their average contribution to the total particle number concentration was 9%. 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 measurements differed from the corresponding classification based on mobility spectrometer measurements, 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.


## 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. 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 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 seven 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?

## 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 seven years, between June 2008 and June 2015. 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.

In order to monitor the NPF events from the early stages of nucleation, 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 consists 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

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calibrations. These measurements 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). 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 $1.3 \cdot 10^{-3}$ $cm^2\ V^{-1}\ s^{-1}$). 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. 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 were calculated as:

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

$\Delta N_{D_p}$ is the increase in nucleation mode particles' number concentration ($D_p$<25nm), CoagS is the coagulation of particles in this size range, 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. 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:

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

CS is the sulfuric acid sink caused by the preexisting aerosol population with unit $s^{-1}$.

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

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Atmospheric Chemistry and Physics
Discussions

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.

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

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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.

## 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 2008-2015 was 82 %, providing 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.

First, we calculated the total particle number concentration (median concentration was 2138 $cm^{-3}$) and corresponding number concentration in the nucleation mode ($d_p$<25nm, median 78 $cm^{-3}$), Aitken mode (25nm<$d_p$<100nm, median 992 $cm^{-3}$) and accumulation mode ($d_p$>100nm, median 878 $cm^{-3}$). We found that Aitken mode accounted for 46% and accumulation mode 41% of the total particle number concentration, while the nucleation mode accounted only for 3%. The standard deviation of the nucleation particle number concentration was 537 $cm^{-3}$, 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 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. 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 before 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 almost the same in all the seasons. This suggests that there is some new particle production mechanism at night 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. 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.

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 the major 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 or atmospheric chemical composition in this environment. Air mass back trajectories calculated using the HYSPLIT model showed no major 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 (27% against 24% of all days), followed by northwestern air masses that were more frequent than the average (21% against 17%) and northern directions (18% against 20%).

Next, we focused on determining the main characteristics of daytime NPF at Finokalia. Overall, 623 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 29% of the 2121 available measurement days whereas no event occurred on 45% of those days. It is worth noting that 26% of the days were 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 least frequent in August and November (Figure 4) probably due to high wind speeds occurring these months from NE and S/SW directions respectively (not shown). Nevertheless, NPF takes place throughout the year. One would expect NPF to be most frequent in winter when the highest concentrations of nucleation particles are observed, however this was not the case. A possible explanation for the high nucleation mode particle number concentrations in winter could be that the probability of a newly formed particle to survive is larger than in other times of the year. The survival probability of newly-formed particles is closely related to the ratio GR/CS (Kerminen and Kulmala, 2002; Kulmala et al., 2017). By looking at the seasonal variability of CS and GR (Figures 1b and 6b), the particle survival probability seems to be the highest in winter.

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 26% 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 1.1 ± 1.6 $cm^{-3}\,s^{-1}$ (median 0.5 $cm^{-3}\,s^{-1}$). 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 formation rates were observed in November and March. The spring maximum in the particle formation rate might be due to the enhanced biogenic activity and increasing photochemical activity. The November maximum might appear as a result of the initiation of the rain season at Crete and the subsequent rapid drop in CS, even though it is very 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 5.1±3.9 nm $hr^{-1}$ (median 4.1 nm $hr^{-1}$). We found that $GR_{9\text{-}25}$ is highest in summer 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). The average duration of the NPF in summer seems to be shorter as shown in Figure 2a and that may be explained by the higher growth rates observed.

### 3.3) NPF trends during the 2008-2015 period

By looking at the inter-annual evolution of the NPF monthly event frequency at Finokalia for the 85 available months, we observe a slight increase of about 1.5 % per year (Figure 8a). This trend is not statistically significant since p-value was found to be 0.07. This increase is a result of a notable increase of Class II NPF events despite a simultaneous decrease of Class I events from 2008 to 2015 (8b). During the measurement period under study, no trend in $J_9$ was observed, but the winters 2008-9 and 2012-13 had clearly higher values of $J_9$ than the rest of the time (Figure 8c).

When looking at the temporal variation of GR (Figure 8d), we observe a clear decreasing trend of about 0.3 nm $hr^{-1}$ $yr^{-1}$. This trend can be considered statistically significant, the no-trend hypothesis test returned a 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 can observe a clear decline in its concentration (Paraskevopoulou et al., 2015). We can therefore assume also a regional decrease in $SO_2$ emissions, since a major part of $SO_2$ at Finokalia can be attributed to transported pollution (Sciare et al., 2003). This would 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 observed 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. Taken together, we conclude that the observed decrease in the particle growth rate and frequency in the most pronounced NPF events in Finokalia could as well be due to decreased $SO_2$ concentrations. The reasons for the overall increase in the NPF frequency and little change in $J_9$ remain unclear, even though factors like meteorological conditions and organic vapor abundance have probably played some role in this respect.

### 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 (Figure 9).

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 data. 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 to the different measurement characteristics of the AIS and SMPS instruments. For example, 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 $JO^{1D}$ 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.

During the ‘’event week’’ the simulated formation of new particles successfully coincided with the observations, as shown in Figures 11a and 11b. The NPF levels 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. 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 $5\times10^{-16}$ $s^{-1}$ and increasing by a factor of 10 the α- and β-pinene concentrations. With these modifications the model results greatly improved and the aerosol number size distributions were well captured, as well as total number and volume concentration of aerosol particles (Figures 11c and d respectively). This was the first time that we were able to simulate in such detail NPF in the eastern Mediterranean. 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 $6.0 \times 10^{-13}$ $s^{-1}$.

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 well captured 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 more appropriate input data for Malte-box will become available (concurrent detailed measurements of gases and aerosol distributions) at Finokalia, new detailed simulations will further provide insight in NPF phenomena and the factors controlling them in the eastern Mediterranean atmosphere.

## 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 2121 days of aerosol number size distribution data from June 2008 until June 2015 and found that NPF took place 29% of the available days, more frequently in spring and less frequently in late summer and autumn. 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.

During the measurement period, the frequency of NPF occurrence increased by 1.5 % per year while the average GR decreased by 0.3 nm $hr^{-1}$ $yr^{-1}$, probably reflecting the decrease of ambient $SO_2$ concentrations due to the economic crisis. 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.

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 | 623 | 29.37 |
| Class I | 161 | 7.59 |
| Class II | 462 | 21.78 |
| | | |
| Undefined | 555 | 26.17 |
| Non-event | 943 | 44.46 |
| | | |
| Total days | 2121 | 100.00 |

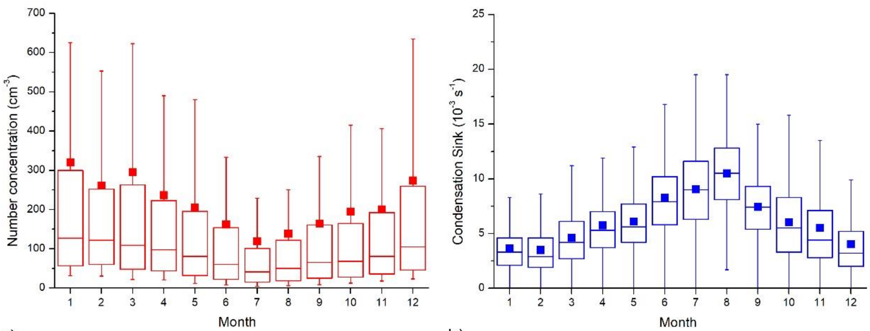
Table 1) Total available measurement days and percentage of NPF events observed at Finokalia during the period June 2008-June 2015

| | $J_9$ ($cm^{-3}$ $s^{-1}$) | | | $GR_{9\text{-}25}$ (nm $hr^{-1}$) | | | CS x $10^{-3}$ ($s^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Mean | Median | SD | Mean | Median | SD | Mean | Median | SD |
| Winter | 0.7 | 0.6 | 0.4 | 3.3 | 2.7 | 2.2 | 3.7 | 3.1 | 2.6 |
| Spring | 0.9 | 0.8 | 0.6 | 3.5 | 2.7 | 2.5 | 5.5 | 5.1 | 2.7 |
| Summer | 0.7 | 0.6 | 0.4 | 6.8 | 6.4 | 3.5 | 9.1 | 8.9 | 3.7 |
| Autumn | 1.0 | 0.9 | 0.9 | 5.0 | 4.4 | 2.9 | 6.3 | 5.8 | 3.6 |

Table 2) Formation rates for 9nm particles ($J_9$), growth rates in the size range 9-25 nm ($GR_{9\text{-}25}$) for NPF events observed at Finokalia and condensational sink for sulphuric acid (CS) on seasonal base during the period June 2008-June 2015 (mean, median and standard deviation).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 11 April 2018


8) Figures




a) b)

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 2015. 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.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
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Discussion started: 11 April 2018


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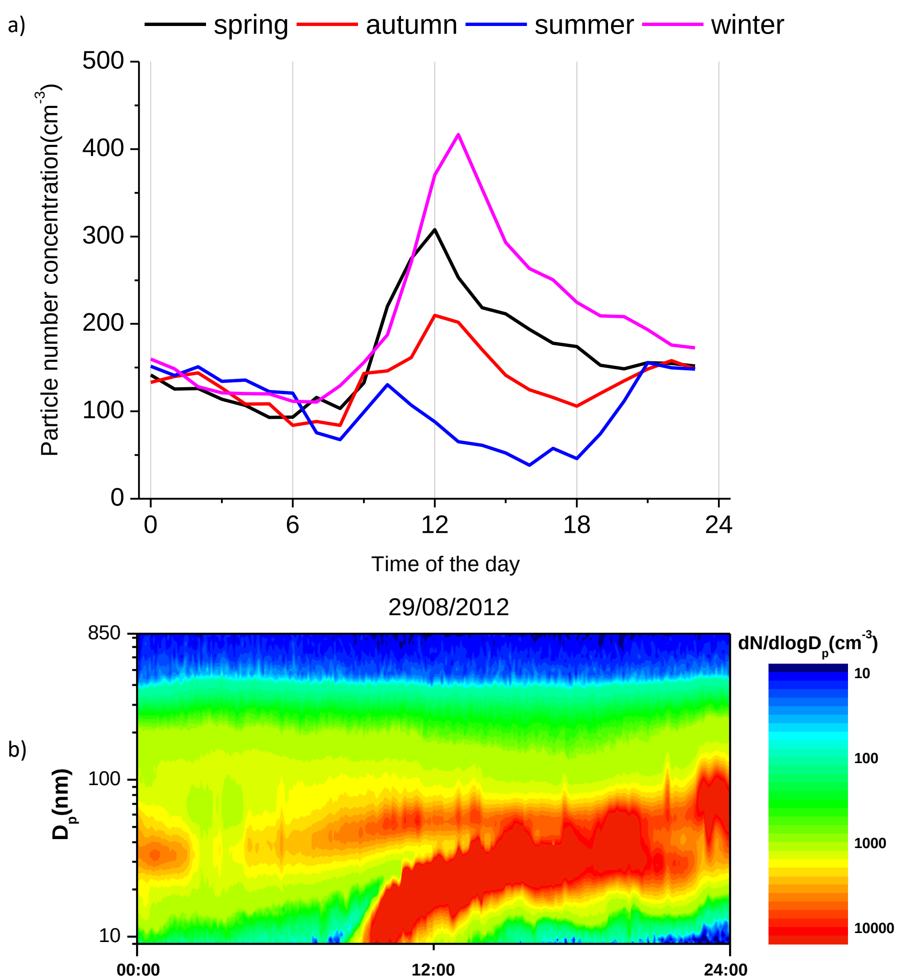
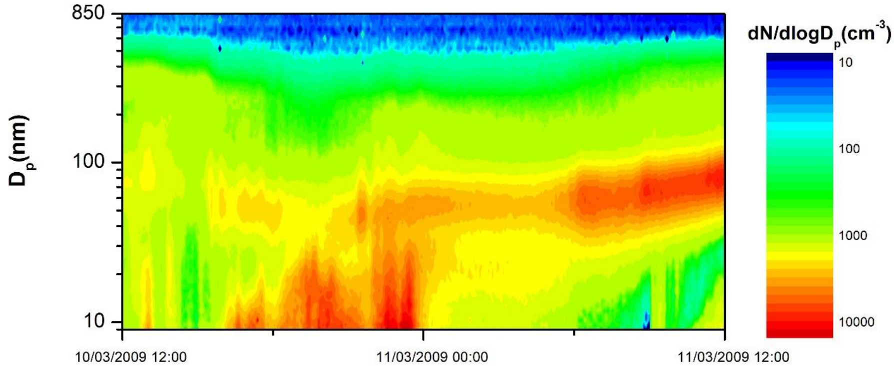
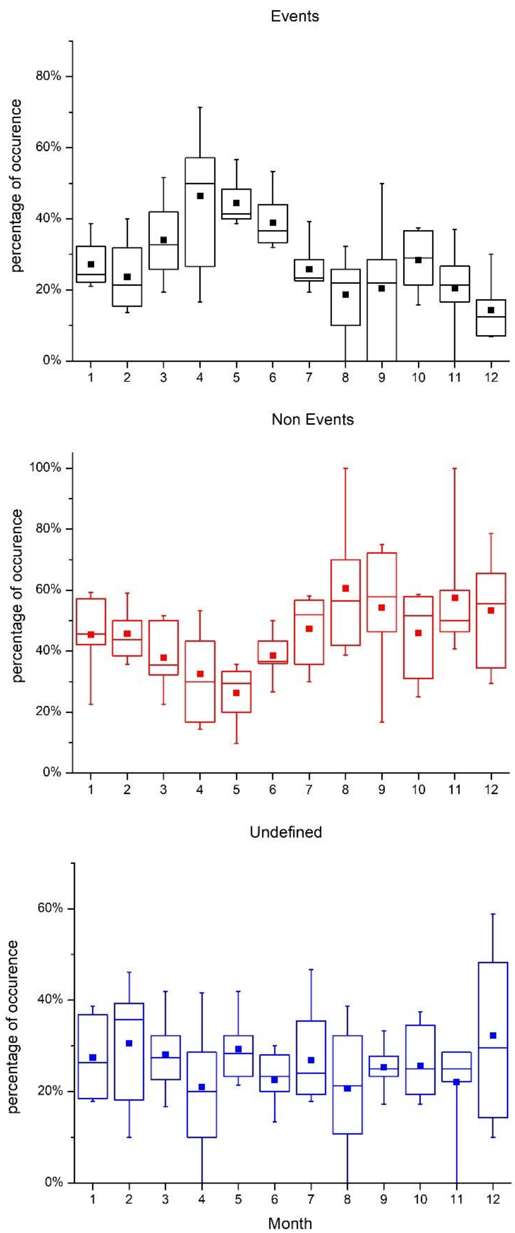



2) a) Average diurnal variation of nucleation mode particle number concentration (hourly values) at Finokalia over the period June 2008-June 2015 b) New particle formation event captured at Finokalia on 29/08/2012

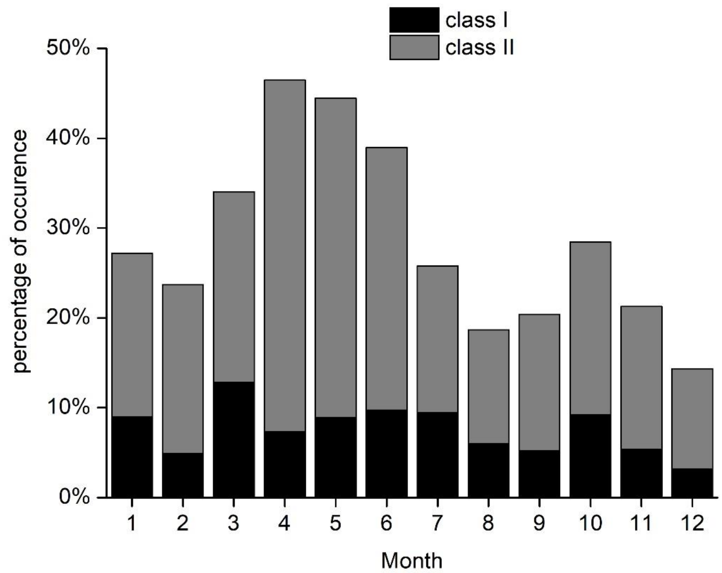
Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 11 April 2018


3) Example of appearance of nucleation mode particles during several hours as observed during the night of 10 to 11/09/2009.

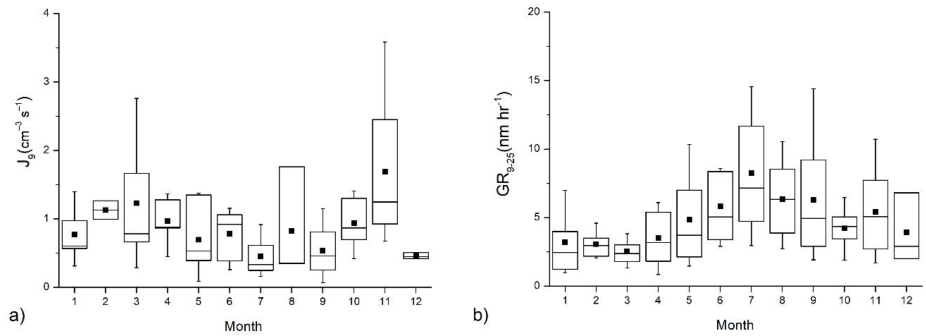



4) Seasonal variation of NPF percentage of occurrence of event, non-event and undefined days relatively to available measurement days at Finokalia for the period June 2008-June2015. Whiskers represent 10th and 90th percentiles, box edges are 75th and 25th percentiles, the line in the box is the median, square is mean.

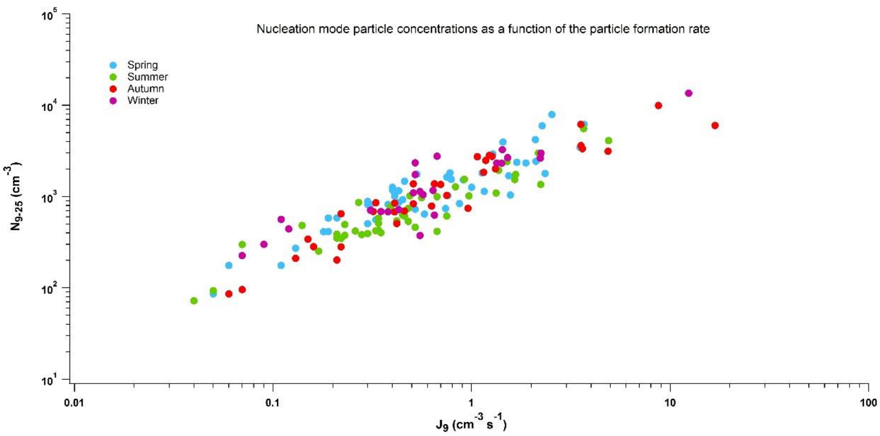



5) Seasonal variation of percentage of occurrence of NPF Class I & II events relatively to available measurement days at Finokalia in the eastern Mediterranean for the period June 2008-June2015.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 11 April 2018

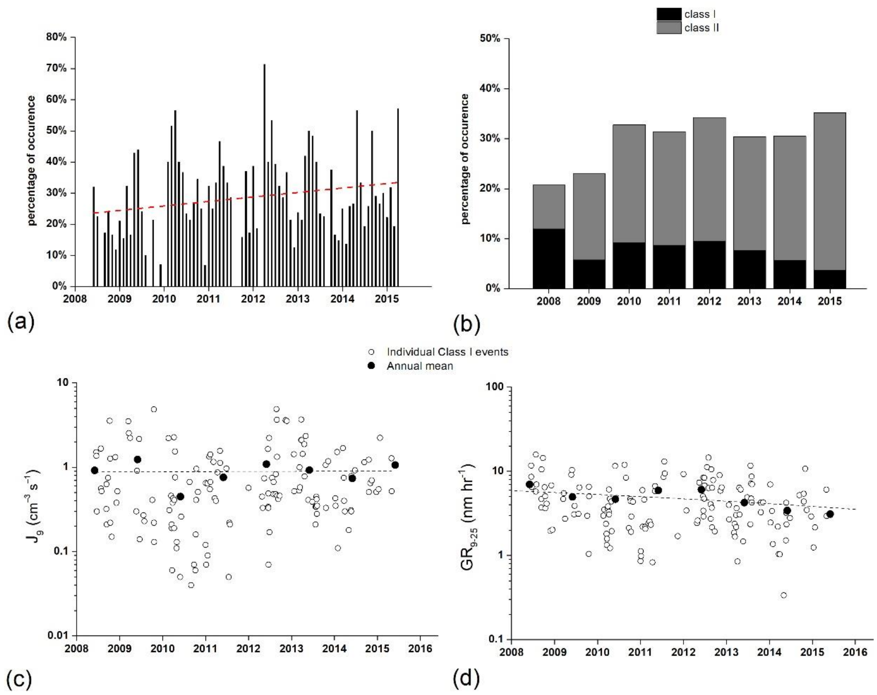




6) Seasonal variation of a) formation rate of 9nm particles ($J_9$) and b) growth rate in the size range 9-25nm ($GR_{9-25}$) as calculated during Class I NPF events at Finokalia for the period June 2008-June 2015. Whiskers represent 10th and 90th percentiles, box edges are 75th and 25th percentiles, the line in the box is the median and the solid square is the mean.

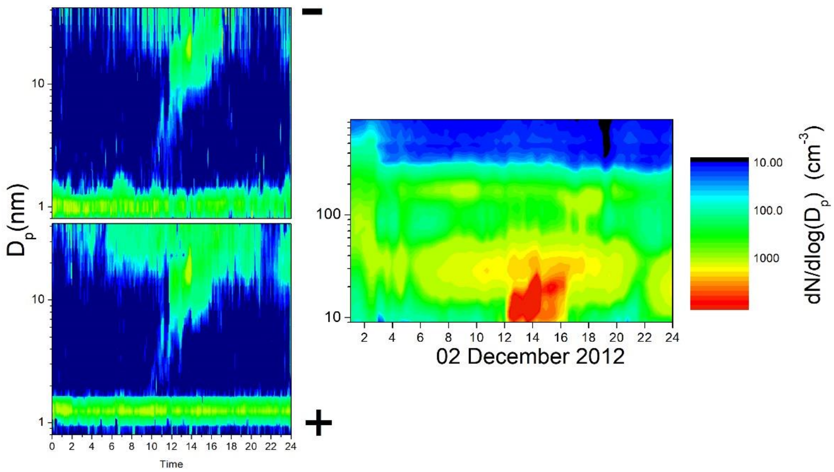



7) Scatter plot of formation rate of 9nm particles ($J_9$) versus the number concentration of nucleation mode particles ($N_{9-25}$) (hourly maximum value during the event) at Finokalia, for events that $J_9$ could be calculated with a good level of confidence (Class I events).

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 11 April 2018

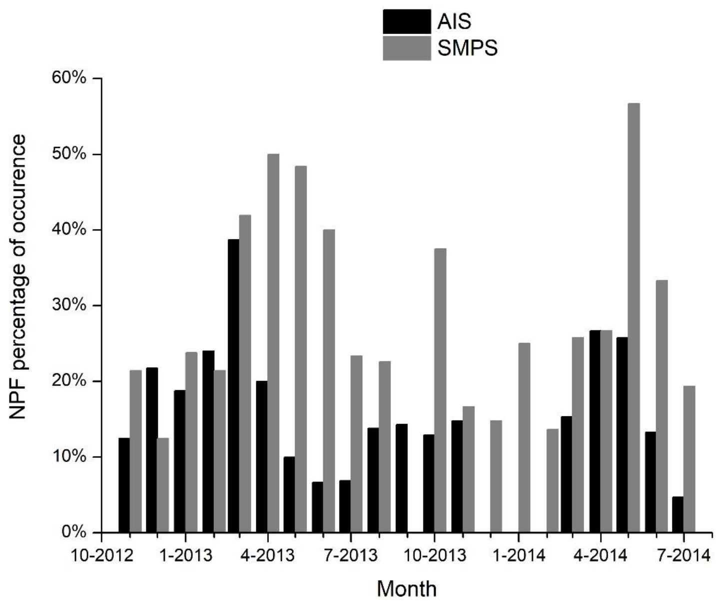




8) a) Time series of monthly NPF percentage of occurrence at Finokalia for the years 2008-2015. b) Annual NPF percentage of occurrence at Finokalia for the period June 2008-June 2015 for Class I&II events. Interannual variation of c) formation rates of 9nm particles ($J_9$) and d) growth rate in the 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).



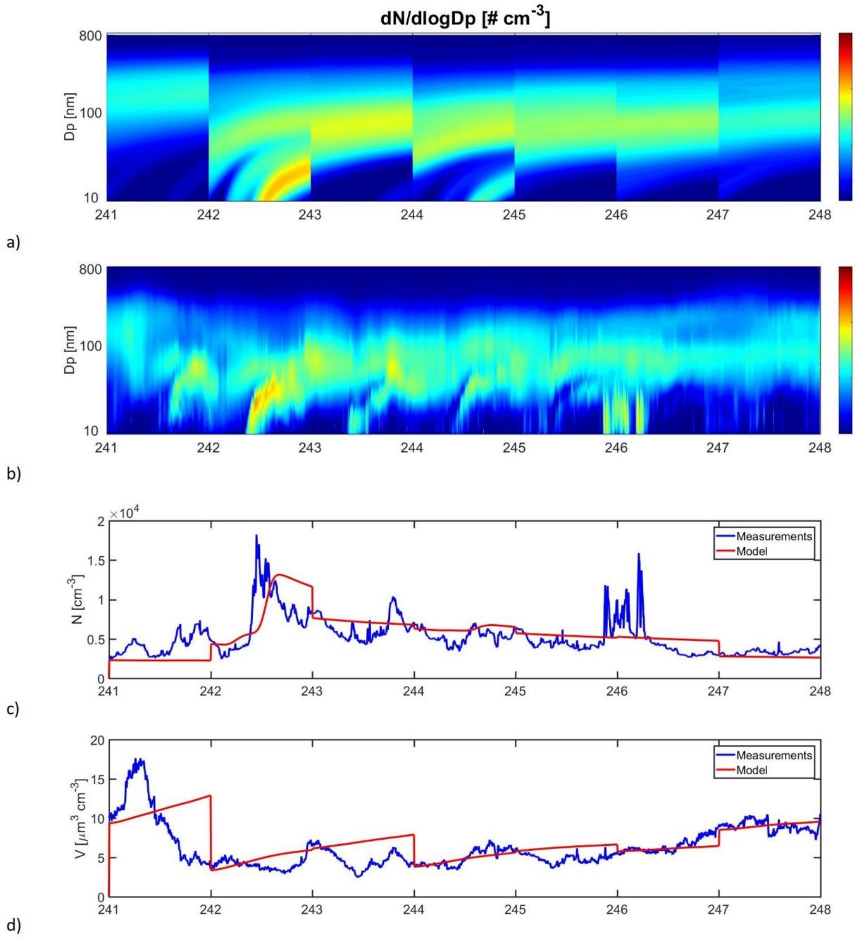

9) Nucleation event observed at Finokalia on 2 December 2012 as captured by AIS (left panels for negative (up) and positive (bottom) polarity) and SMPS (right panel)

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 11 April 2018

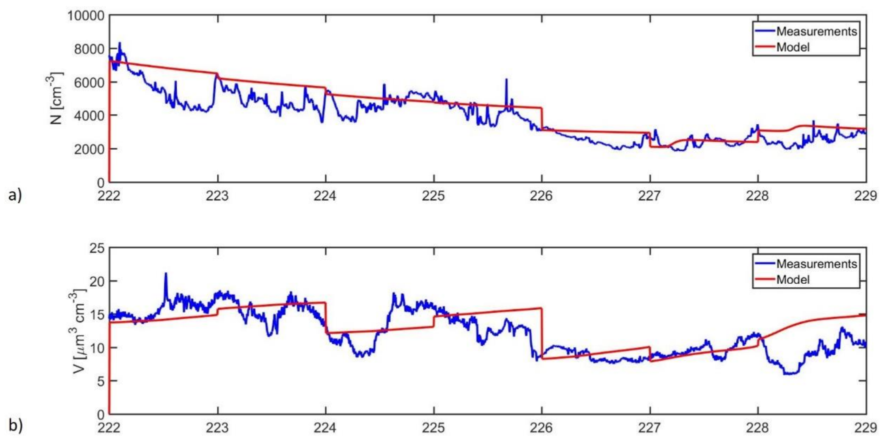




10) Monthly variability of NPF events' percentage of occurrence relatively to available measurement days at Finokalia as determined by analysis of AIS data during the FRONT experiment (Nov. 2012-July 2014). For a direct comparison, the monthly variability of NPF events as obtained from the SMPS measurements for the same period is included.

Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-229
Manuscript under review for journal Atmos. Chem. Phys.
Discussion started: 11 April 2018


11) Particle size distributions at Finokalia for the event week: a) simulations with the adjusted parameters for the sub-tropical environment The discontinuities observed every midnight in the model results are due to initialization of the model every midnight with measured number size distributions. b) observations of number size distributions (modified from Tzitzikalaki et al., 2017). Measured and modelled d) total number concentration and e) total volume concentration for the same period. The x-axis in all figures is Julian day of 2012.




12) Measured and modelled a) total number concentration and b) total volume concentration for a non-event week at Finokalia. The x-axis in both figures is Julian day of 2012.